

**Synthesis and Characterization of Anionic and Cationic
Intercalation Compounds of WTe_2 , with Extensions to
Transition-Metal Chalcogenide–Halide Reactions and
Melamine-Based SHG-Active Compounds**

Dissertation

der Mathematisch-Naturwissenschaftlichen Fakultät

der Eberhard Karls Universität Tübingen

zur Erlangung des Grades eines

Doktors der Naturwissenschaften

(Dr. rer. nat.)

vorgelegt von

M.Sc. Patrick Michael Schmidt

aus Filderstadt

Tübingen

2026

Gedruckt mit Genehmigung der Mathematisch-Naturwissenschaftlichen Fakultät
der Eberhard Karls Universität Tübingen.

Tag der mündlichen Qualifikation:

28.07.2026

Dekan:

Prof. Dr. Thilo Stehle

1. Berichterstatter:

Prof. Dr. Hans-Jürgen Meyer

2. Berichterstatter:

Prof. Dr. Eberhard Schweda

3. Berichterstatter:

Prof. Dr. Martin Köckerling

Acknowledgements

First and foremost, I would like to express my sincere gratitude to Prof. Dr. H.-Jürgen Meyer for giving me the opportunity to carry out this research in his group, for his valuable guidance, for the many helpful discussions throughout this work, and for the considerable freedom he granted me in pursuing my research.

My special thanks go to Dr. Markus Ströbele, whose extensive knowledge, unwavering willingness to help, and constructive input greatly enriched this work. His insightful ideas, countless engaging discussions, and generous support have been of great importance throughout my doctoral journey. I have learned a great deal from him, for which I am truly grateful.

I would also like to thank Dr. Jochen Glaser for conducting the ICP-OES measurements and for the inspiring conversations that accompanied them.

Furthermore, I am grateful to Dr. Carl Romao for his contribution in carrying out the theoretical calculations that complemented this work.

I extend my sincere thanks to the entire research group for their continuous support and the collegial atmosphere, which made even the hottest days in the lab during summer both productive and enjoyable.

Finally, and most importantly, I thank the most important people in my life—my family, my friends, and especially my wife. Her unwavering support, encouragement, and understanding in all aspects of life have been a cornerstone of this journey.

Contents

List of Abbreviations	V
Summary	VII
Zusammenfassung	IX
List of Publications	XI
Scientific Contribution	XIII
1 Introduction	1
1.1 Transition-metal dichalcogenides (TMDCs)	1
1.2 Intercalation in layered materials and TMDCs	2
1.3 Halogen-Induced Decomposition and Cluster Formation in the <i>TM-Q-X</i> system	5
1.4 Melamine-based SHG materials	7
2 Objectives	10
3 Summary of the Main Results	11
3.1 Intercalation of Alkali Metal into WTe_2 , the Crystal Structure of $A_{0.5}\text{WTe}_2$ and Observation of a Metal-to-Semiconductor Transition (Publication 1)	11
3.2 Reversible Iodine Intercalation into Tungsten Ditelluride (Publication 2) . . .	16
3.3 Structural Evolution during Reversible Halogen Intercalation in WTe_2 : Com- mensurate–Incommensurate WTe_2I and Multistage WTe_2Br_x ($x = 0.5, 1.0$ and 1.25) (Publication 3)	20
3.4 A New Modification of TeI_4 Possessing the Crystal Structure Proposed for WI_4 (Publication 4)	29
3.5 Synthesis and Structural Characterization of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ (Publication 5) .	31
3.6 $\text{Ta}_4\text{SBr}_{11}$: A Cluster Mott Insulator with Corrugated, Van der Waals Layered Structure (Publication 6)	35
3.7 The family of tetranuclear $\text{Nb}_4\text{OI}_{12-x}$ clusters ($x = 0, 1, 2$): from the molecular $\text{Nb}_4\text{OI}_{12}$ cluster to extended chains and layers (Publication 7)	37
3.8 Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicentre Nb–Nb bonding (Publication 8)	40
3.9 Hydrothermal Synthesis and Characterization of the Melamine-Based Second- Harmonic Generation Material $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ (Publication 9)	44

3.10 Synthesis and SHG Properties of the Melamine-Based Zinc Halides (C ₃ N ₆ H ₇)ZnX ₃ (C ₃ N ₆ H ₆) ($X = \text{Cl, Br}$) (Publication 10)	49
3.11 A complete cathode recovery cycle of an exhausted and dismantled lithium battery material (Manuscript 1)	54
4 Conclusion	58
References	59
Appendix	69
5 Publications	70
Publication 1	70
Publication 2	95
Publication 3	113
Publication 4	162
Publication 5	172
Publication 6	181
Publication 7	202
Publication 8	214
Publication 9	226
Publication 10	240
6 Unpublished Manuscripts	257
Manuscript 1	257

List of Abbreviations

BBO	β -BaB ₂ O ₄
CVT	chemical vapor transport
DFT	density functional theory
DRIFT	diffuse reflectance infrared fourier transform
DRUV	diffuse reflectance ultraviolet–visible
DTG	differential thermo gravimetry
EDX	energy-dispersive X-ray
ELF	electron localization function
GGA	generalized gradient approximation
ICP-OES	inductively coupled plasma optical emission spectroscopy
IR	infrared
KTP	potassium titanyl phosphate
MAS-NMR	magic-angle spinning nuclear magnetic resonance
NIR	near-infrared
NLO	nonlinear optical
NMC	nickel-manganese-cobalt
NMR	nuclear magnetic resonance
PXRD	powder X-ray diffraction
SC-XRD	single-crystal X-ray diffraction
SEM	scanning electron microscopy
SHG	second-harmonic generation
SOJT	second-order Jahn-Teller
TG	thermogravimetry
THF	tetrahydrofuran
TMDC	transition-metal dichalcogenides
TXRF	total reflection X-ray fluorescence
UV-Vis	ultraviolet–visible
vdW	van der Waals

Summary

This work investigates the reactions and chemical modifications of WTe_2 and related solid-state systems, with a particular focus on intercalation chemistry, halogen-induced transformations, cluster formation, and structure–property relationships in inorganic and hybrid materials. Hereby WTe_2 is used as a chemically tunable layered host because its distorted T_d -type structure, weak van der Waals (vdW) gaps, and characteristic W–W zigzag chains make it highly responsive to changes in electron count and interlayer bonding.

A central part of the work is about the intercalation of cationic and anionic guest species into WTe_2 . Low-temperature solution reactions with alkali naphthalenides yielded the ordered intercalation compounds $A_{0.5}\text{WTe}_2$ ($A = \text{K}, \text{Rb}, \text{Cs}$). These phases retain the layered host structure, but show a systematic expansion of the van der Waals gap, ordered alkali-metal arrangements, and distortions of the tungsten chains, thereby directly affecting one of the key structural motifs responsible for the characteristic properties of WTe_2 . The resulting $A_{0.5}\text{WTe}_2$ phases ($A = \text{K}, \text{Rb}, \text{Cs}$) are consistently described by optical measurements, electrical transport data, and density functional theory calculations as narrow-gap semiconductors with band gaps of approximately 0.35–0.48 eV.

The oxidative intercalation chemistry of WTe_2 was extended from iodine to bromine. WTe_2I was confirmed as a reversible anionic intercalation compound and was structurally described in substantially greater detail. Instead of a simple average structure, it occurs in closely related commensurately and incommensurately modulated variants, both dominated by modulation of the iodine substructure. No phase transition was observed between 100 K and 270 K, showing that the modulation is an intrinsic structural feature. Bromine intercalation gave access to the multistage series WTe_2Br_x with $x = 0.5, 1.0$, and 1.25 . The compound $\text{WTe}_2\text{Br}_{0.5}$ contains bromine atoms in the van der Waals gap that form directional Te–Br contacts and exhibit pronounced positional disorder. At higher bromine content, $\text{WTe}_2\text{Br}_{1.25}$ adopts a staged bromine-rich structure with two different bromine interlayers, corresponding to 0.5 and 0.75 Br per WTe_2 formula unit. The differences in the interlayer distances reflect the different filling levels. These results show that halogen intercalation in WTe_2 combines reversible guest uptake, staging, modulation, and strong host–guest interactions.

At elevated temperature or higher halogen activity, the chemistry of WTe_2 shifts from topochemical intercalation to reconstructive halogenation. The previously reported assignment of WI_4 was corrected and shown to correspond to the new metastable polymorph $\zeta\text{-TeI}_4$. In addition, the iodination of WTe_2 at comparatively mild conditions yielded $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$, a tungsten iodide cluster compound composed of $[\text{W}_6\text{I}_{14}]^{2-}$ anions and $(\text{TeI}_3)^+$ cations. These

studies connect the intercalation chemistry of WTe_2 with follow-up reactions leading to tellurium iodides and metal-halide clusters.

Further contributions address transition-metal chalcogenide and oxyiodide cluster compounds. $\text{Ta}_4\text{SBr}_{11}$ was characterized as a corrugated van der Waals layered compound based on butterfly-shaped $[\text{Ta}_4\text{S}]$ clusters and was described as a likely cluster Mott insulator. The niobium oxyiodide family $\text{Nb}_4\text{OI}_{12-x}$ ($x = 0, 1, 2$) establishes a structural sequence from molecular clusters to one-dimensional chains and two-dimensional layers. The compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ further extend this chemistry from $[\text{Nb}_4\text{O}]$ and $[\text{Nb}_5\text{O}_4]$ motifs to larger $[\text{Nb}_7\text{O}_5]$ and $[\text{Nb}_8\text{O}_5]$ cluster cores with multicenter Nb–Nb bonding.

The work also includes melamine-based hybrid halides as SHG materials. $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ crystallizes in the polar space group $C2$ and combines a layered mercury chloride substructure with ordered melamine molecules, resulting in pronounced second-harmonic generation (SHG) activity. The related zinc halides $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnX}_3(\text{C}_3\text{N}_6\text{H}_6)$ ($X = \text{Cl}, \text{Br}$) show how changes in symmetry, hydrogen bonding, and polarizability influence nonlinear optical response.

Finally, a complete recovery cycle for spent graphitic Li-NMC battery material was developed, combining thermal treatment, leaching, impurity precipitation, copper electrolysis, and aqueous sol–gel synthesis to regenerate fresh Li-NMC cathode material.

Overall, the results show how targeted synthesis, careful structural characterization, and complementary physical measurements reveal direct links between composition, guest ordering, cluster connectivity, symmetry, and functional properties in complex inorganic and hybrid materials.

Zusammenfassung

Diese Arbeit untersucht Reaktionen und chemische Modifizierungen von WTe_2 und verwandten Festkörpersystemen, mit besonderem Fokus auf Interkalationschemie, halogeninduzierte Umwandlungen, Clusterbildung sowie Struktur-Eigenschafts-Beziehungen in anorganischen und hybriden Materialien. WTe_2 wurde als chemisch veränderbarer Schichtwirt eingesetzt, da seine verzerrte T_d -Struktur, schwach gebundene vdW-Lücken und charakteristische W–W-Zick-Zack-Ketten eine hohe Empfindlichkeit gegenüber Änderungen der Elektronenzahl und der Wechselwirkungen zwischen den Schichten bewirken.

Ein zentraler Teil der Arbeit behandelt die Interkalation kationischer und anionischer Gastspezies in WTe_2 . Durch Tieftemperaturreaktionen mit Alkalinaphthaleniden konnten die geordneten Interkalationsverbindungen $A_{0.5}\text{WTe}_2$ ($A = \text{K}, \text{Rb}, \text{Cs}$) erhalten werden. Diese Phasen behalten die schichtartige Wirtsstruktur bei, zeigen jedoch eine systematische Aufweitung der van-der-Waals-Lücke, geordnete Alkalimetallanordnungen und elektronenzahlbedingte Verzerrungen der Wolfram Zick-Zack-Ketten. Im Gegensatz zum semimetallischen WTe_2 werden diese Verbindungen durch optische Messungen, temperaturabhängige Leitfähigkeitsmessungen und Dichtefunktionaltheorie-Rechnungen übereinstimmend als schmalbandige Halbleiter mit Bandlücken von etwa 0.35–0.48 eV beschrieben.

Die oxidative Interkalationschemie von WTe_2 wurde von Iod auf Brom erweitert. WTe_2I wurde als reversible anionische Interkalationsverbindung bestätigt und strukturell deutlich detaillierter beschrieben. Anstelle einer einfachen mittleren Struktur liegen eng verwandte kommensurabel und inkommensurabel modulierte Varianten vor, deren Modulation hauptsächlich von der Iodteilstruktur ausgeht. Zwischen 100 K und 270 K wurde kein Phasenübergang beobachtet, sodass die Modulation als intrinsisches Strukturmerkmal angesehen werden kann. Die Brominterkalation führte zur mehrstufigen Reihe WTe_2Br_x mit $x = 0.5, 1.0$ und 1.25. In $\text{WTe}_2\text{Br}_{0.5}$ befinden sich Bromatome in der van-der-Waals-Lücke und bilden gerichtete Te–Br-Kontakte, wobei die Bromatome ungewöhnlich große Atomauslenkungsparameter zeigen. Bei höherem Bromgehalt bildet sich $\text{WTe}_2\text{Br}_{1.25}$ mit zwei unterschiedliche Bromzwischen-schichten, die 0.5 und 0.75 Br pro WTe_2 -Formeleinheit enthalten. Die verschiedenen Schichtabstände spiegeln diese unterschiedlichen Füllgrade wieder. Diese Ergebnisse zeigen, dass die Halogeninterkalation in WTe_2 durch reversible Gastaufnahme, stufenweise Einlagerung, Modulation und ausgeprägte Wirt–Gast-Wechselwirkungen geprägt ist.

Bei erhöhter Temperatur oder höherer Halogenaktivität verschiebt sich die Chemie von WTe_2 von topochemischer Interkalation zu rekonstruktiver Halogenierung. Die frühere Zuordnung eines Reaktionsproduktes als WI_4 wurde korrigiert und stattdessen als neue metastabile

bile Modifikation ζ - TeI_4 identifiziert. Darüber hinaus lieferte die Iodierung von WTe_2 unter vergleichsweise milden Bedingungen die Clusterverbindung $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$, die aus $[\text{W}_6\text{I}_{14}]^{2-}$ -Anionen und $(\text{TeI}_3)^+$ -Kationen aufgebaut ist. Diese Untersuchungen verknüpfen die Interkaltionschemie von WTe_2 mit Folgereaktionen zu Telluriodiden und Metallhalogenidclustern.

Weitere Beiträge betreffen Übergangsmetall-Chalkohalogenid- und Oxyiodidcluster. $\text{Ta}_4\text{SBr}_{11}$ wurde als gewellte van-der-Waals-Schichtverbindung auf Basis butterfly-artiger $[\text{Ta}_4\text{S}]$ -Cluster charakterisiert und als wahrscheinlicher Cluster-Mott-Isolator beschrieben. Die Nioboxyiodidreihe $\text{Nb}_4\text{OI}_{12-x}$ ($x = 0, 1, 2$) zeigt eine strukturelle Abfolge von molekularen Clustern über eindimensionale Ketten bis zu zweidimensionalen Schichten. Mit $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ und $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ wurde diese Chemie von $[\text{Nb}_4\text{O}]$ - und $[\text{Nb}_5\text{O}_4]$ -Motiven zu größeren $[\text{Nb}_7\text{O}_5]$ - und $[\text{Nb}_8\text{O}_5]$ -Clusterkernen mit multizentrischen Nb–Nb-Bindungen erweitert.

Außerdem wurden melaminbasierte Hybridhalogenide als Materialien für Second-Harmonic Generation untersucht. $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ kristallisiert in der polaren Raumgruppe $C2$ und kombiniert eine geschichtete Quecksilberchlorid-Teilstruktur mit geordneten Melaminmolekülen, woraus eine ausgeprägte SHG-Aktivität resultiert. Die verwandten Zinkhalogenide $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnX}_3(\text{C}_3\text{N}_6\text{H}_6)$ ($X = \text{Cl}, \text{Br}$) zeigen, wie Symmetrie, Wasserstoffbrückenbindungen und Halogenidpolarisierbarkeit die nichtlineare optische Eigenschaften beeinflussen.

Abschließend wurde ein vollständiger Rückgewinnungszyklus für graphithaltiges Li-NMC-Altbatteriematerial entwickelt, der thermische Behandlung, Laugung, Fällung von Verunreinigungen, Kupferelektrolyse und wässrige Sol–Gel-Synthese kombiniert, um frisches Li-NMC-Kathodenmaterial zu regenerieren.

Insgesamt zeigen die Ergebnisse, wie gezielte Synthese, sorgfältige Strukturanalyse und ergänzende physikalische Untersuchungen direkte Zusammenhänge zwischen Zusammensetzung, Gastordnung, Clusterverknüpfung, Symmetrie und funktionellen Eigenschaften komplexer anorganischer und hybrider Materialien sichtbar machen.

List of Publications

Publication 1:

Intercalation of Alkali Metal into WTe_2 , the Crystal Structure of $A_{0.5}WTe_2$ and Observation of a Metal-to-Semiconductor Transition

Patrick Schmidt, Fabian Strauß, Marcus Scheele, Carl P. Romao, H.-Jürgen Meyer

Dalton Trans., **2026**, 55, 3296-3309.

Publication 2:

Reversible Iodine Intercalation into Tungsten Ditelluride

Patrick Schmidt, Philipp Schneiderhan, Markus Ströbele, Carl P. Romao, H.-Jürgen Meyer

Inorg. Chem., **2021**, 60, 1411-1418.

Publication 3:

Structural Evolution during Reversible Halogen Intercalation in WTe_2 : Commensurate-Incommensurate WTe_2I and Multistage WTe_2Br_x ($x = 0.5, 1.0$ and 1.25)

Patrick Schmidt, Carl P. Romao, H.-Jürgen Meyer

Dalton Trans., **2026**, 55, 8228-8242.

Publication 4:

A New Modification of TeI_4 Possessing the Crystal Structure Proposed for WI_4

Philipp Schneiderhan, Patrick Schmidt, Markus Ströbele, Carl P. Romao, H.-Jürgen Meyer

Cryst. Growth Des., **2020**, 20, 3780-3784.

Publication 5:

Synthesis of $(TeI_3)_2[W_6I_{14}]$ via Iodination of WTe_2

Patrick Schmidt, Amira Siai, Philipp Schneiderhan, Markus Ströbele, H.-Jürgen Meyer

Eur. J. Inorg. Chem., **2020**, 8, 716-719.

Publication 6:

Ta_4SBr_{11} : A Cluster Mott Insulator with a Corrugated, Van der Waals Layered Structure

Fabian Grahlow, Fabian Strauß, Patrick Schmidt, Jaroslav Valenta, Markus Ströbele, Marcus

Scheele, Carl P. Romao, H.-Jürgen Meyer

Inorg. Chem., **2024**, 63, 19717-19727.

Publication 7:

The family of tetranuclear Nb_4OI_{12-x} clusters ($x = 0, 1, 2$): from the molecular Nb_4OI_{12} cluster to extended chains and layers

Jan Beitzlberger, Mario Martin, Marcus Scheele, Patrick Schmidt, Markus Ströbele, H.-Jürgen Meyer

Dalton Trans., **2025**, 54, 5486–5493.

Publication 8:

Niobium oxyiodide cluster compounds $Li_3Nb_7O_5I_{15}$ and $Nb_8O_5I_{17}(NbI_5)$ with expanding cluster architectures and multicentre Nb-Nb bonding

Jan Beitzlberger, Markus Ströbele, Patrick Schmidt, Carl P. Romao, H.-Jürgen Meyer

Dalton Trans., **2025**, 54, 14376–14383.

Publication 9:

Hydrothermal Synthesis of the Melamine-Based SHG Material $HgCl_2(C_3N_6H_6)$

Melena Groß, Patrick Schmidt, Carl P. Romao, David Enseling, Thomas Jüstel, Mykhailo Brytskyi, Scott Kroeker, H.-Jürgen Meyer

Eur. J. Inorg. Chem., **2025**, 28, e202500256.

Publication 10:

Synthesis and SHG Properties of the Melamine-Based Material $(C_3N_3H_7)ZnX_3(C_3N_3H_6)$ ($X = Cl, Br$)

Melena Groß, Catharina Darine Brand, Patrick Schmidt, Tim Parker, Dai Zhang, Carl P. Romao, H.-Jürgen Meyer

Dalton Trans., **2025**, 54, 17941–17949.

Manuscript 1:

A complete cathode recovery cycle of an exhausted and dismantled lithium battery material

Fabian Grahlow, Patrick Schmidt, H.-Jürgen Meyer

Scientific Contribution

Publication 1:

Intercalation of Alkali Metal into WTe_2 , the Crystal Structure of $A_{0.5}WTe_2$ and Observation of a Metal-to-Semiconductor Transition

I planned and conducted the experimental work and wrote the manuscript in collaboration with Prof. Dr. H.-J. Meyer. I performed the DRIFT measurements, prepared the samples for the analytical measurements, carried out all data evaluation, and solved/refined the structures. E. Nadler recorded the scanning electron microscopy (SEM) images and performed the energy-dispersive X-ray (EDX) measurements. Dr. J. Glaser and I conducted the ICP-OES measurements. Dr. F. Strauß performed the conductivity measurements; Dr. F. Strauß and Prof. Dr. M. Scheele reviewed and corrected the manuscript. Dr. C. P. Romao carried out the theoretical calculations and wrote the corresponding part of the manuscript.

Publication 2:

Reversible Iodine Intercalation into Tungsten Ditelluride

The manuscript was prepared in collaboration with Philipp Schneiderhan, Dr. Markus Ströbele, Dr. C. P. Romao and Prof. Dr. H.-Jürgen Meyer. I planned and carried out the synthesis, measured the SC-XRD/PXRD and performed thermal analysis. Dr. J. Glaser conducted the ICP-OES measurement. Dr. M. Ströbele carried out the structure refinement. Dr. C. P. Romao conducted the theoretical calculations and wrote the respective part of the manuscript.

Publication 3:

Structural Evolution during Reversible Halogen Intercalation in WTe_2 : Commensurate-Incommensurate WTe_2I and Multistage WTe_2Br_x ($x = 0.5, 1.0$ and 1.25)

I planned and conducted the experimental work and wrote the manuscript in collaboration with Prof. Dr. H.-J. Meyer. I performed the measurements, carried out all data evaluation, and solved/refined the structures. RNDr. Václav Petříček (The Czech Academy of Sciences) assisted with the structure solution of the modulated WTe_2I compounds. Dr. J. Glaser and I conducted the ICP-OES measurements. Dr. C. P. Romao carried out the theoretical calculations and wrote the corresponding part of the manuscript.

Publication 4:

A New Modification of TeI_4 Possessing the Crystal Structure Proposed for WI_4

The manuscript was prepared in collaboration with Philipp Schneiderhan, Dr. Markus Ströbele, Dr. C. P. Romao and Prof. Dr. H.-Jürgen Meyer. I synthesised the bulk material, crystals and performed thermal characterization. Dr. J. Glaser conducted the ICP-OES

measurement. The electron microprobe analysis was performed by Dr. Thomas Wenzel. E. Nadler recorded the scanning electron microscopy (SEM) images. Dr. M. Ströbele performed the SC-XRD measurements and carried out the structure refinement. Dr. C. P. Romao conducted the theoretical calculations and wrote the respective part of the manuscript.

Publication 5:*Synthesis of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ via Iodination of WTe_2*

The manuscript was prepared in collaboration with P. Schneiderhan, Dr. A. Siai, Dr. M. Ströbele and Prof. Dr. H.-J. Meyer. I designed and carried out the synthesis and performed the SC-XRD measurements. Dr. J. Glaser conducted the ICP-OES measurement. The electron microprobe analysis was performed by Dr. T. Wenzel. E. Nadler recorded the scanning electron microscopy (SEM) images. Dr. M. Ströbele carried out the structure refinement. Dr. A. Siai performed the UV-Vis-NIR spectroscopy and conducted the theoretical calculations and wrote the respective part of the manuscript.

Publication 6: *$\text{Ta}_4\text{SBr}_{11}$: A Cluster Mott Insulator with a Corrugated, Van der Waals Layered Structure*

The manuscript was written by F. Grahlow and Prof. Dr. H.-J. Meyer. F. Grahlow designed and carried out the synthesis, performed the SC-XRD measurements and performed the TXRF measurements. E. Nadler recorded the SEM images and performed EDX measurements. I assisted with the structural evaluation and transformations, carried out the diffuse reflectance infrared fourier transform (DRIFT) spectroscopy measurements, and wrote the corresponding section. The conductivity measurements were carried out by F. Grahlow together with Dr. F. Strauß, who also wrote that part in the manuscript. Prof. M. Scheele edited the manuscript. Dr. C. P. Romao performed the theoretical calculations and contributed the respective text. J. Valenta conducted the magnetic measurements and wrote that section. Dr. M. Ströbele was responsible for the structure refinement.

Publication 7:*The family of tetranuclear $\text{Nb}_4\text{OI}_{12-x}$ clusters ($x = 0, 1, 2$): from the molecular $\text{Nb}_4\text{OI}_{12}$ cluster to extended chains and layers*

The manuscript was written by J. Beitzberger and Prof. Dr. H.-J. Meyer. J. Beitzberger planned and carried out the synthesis. I and Dr. M. Ströbele solved the structures and did the refinements. The electronic conductivity measurements and the corresponding section of the manuscript was written by M. Martin in collaboration with Prof. Dr. M. Scheele.

Publication 8:

Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicentre Nb-Nb bonding

The manuscript was written by J. Beitzberger in collaboration with me and Prof. Dr. H.-J. Meyer. J. Beitzberger planned and carried out the synthesis. I and Dr. M. Ströbele solved the structures and did the refinements. The electronic band structure, the electron localization function calculations and the corresponding section was performed and written by Dr. C. P. Romao.

Publication 9:

Hydrothermal Synthesis of the Melamine-Based SHG Material $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$

The manuscript was prepared in collaboration with M. Groß, Dr. C. P. Romao and Prof. Dr. H.-J. Meyer. I and M. Groß planned the synthesis and M. Groß conducted the experiments. I performed the thermogravimetric analysis, the DRIFT analysis and the SC-XRD measurements and refinements. Dr. D. Ensling and Prof. Dr. T. Jüstel performed photoluminescence measurements. M. Brytskyi and Prof. Dr. S. Kroeker performed the MAS-NMR spectroscopy measurements. Dr. T. Parker carried out the SHG and P. Janoschek performed the DRUV measurements. Dr. C. P. Romao conducted the theoretical calculations and wrote the respective part of the manuscript.

Publication 10:

Synthesis and SHG Properties of the Melamine-Based Material $(\text{C}_3\text{N}_3\text{H}_7)\text{ZnX}_3(\text{C}_3\text{N}_3\text{H}_6)$ ($X = \text{Cl}, \text{Br}$)

The manuscript was prepared in collaboration with M. Groß, C. D. Brand, Dr. C. P. Romao and Prof. Dr. H.-J. Meyer. I planned the synthesis together with M. Groß and C. D. Brand. M. Groß and C. D. Brand conducted the experiments. I performed the thermogravimetric analysis, the DRIFT analysis and the SC-XRD measurements and refinements. Dr. T. Parker carried out the SHG and P. Janoschek performed the DRUV measurements. Dr. C. P. Romao conducted the theoretical calculations and wrote the respective part of the manuscript.

Manuscript 1:

A Complete Cathode Recovery Cycle of an Exhausted and Dismantled Lithium Battery Material

The manuscript was written in collaboration with F. Grahlow and Prof. Dr. H.-J. Meyer. F. Grahlow and I planned and performed all experimental procedures together.

1 Introduction

1.1 Transition-metal dichalcogenides (TMDCs)

Transition-metal dichalcogenides (TMDCs) form a versatile class of layered solids with the general composition MQ_2 (with M = transition metal and Q = S, Se, Te). Their structures are built from covalently bonded $Q-M-Q$ layers, while adjacent layers interact only weakly through van der Waals forces. This pronounced bonding anisotropy enables mechanical exfoliation down to the monolayer limit and allows many chemically and electronically distinct polytypes to exist, often with only small energetic differences.^[1–11] As a consequence, TMDCs provide a chemically flexible platform in which composition, stacking, strain, thickness, and external stimuli can be used to tune electronic structure and collective phenomena such as charge density waves or superconductivity.^[1,7,12–23] Among the telluride TMDCs, WTe_2 is particularly notable, because its low-symmetry structure is closely tied to unusual electronic and vibrational properties.^[13,15,24–45] In contrast to many hexagonal TMDCs, WTe_2 adopts a distorted $1T$ -derived structure (often denoted T_d), characterized by tungsten atoms displaced from ideal octahedral centers, forming zigzag W–W chains within the layers (see Fig. 1).

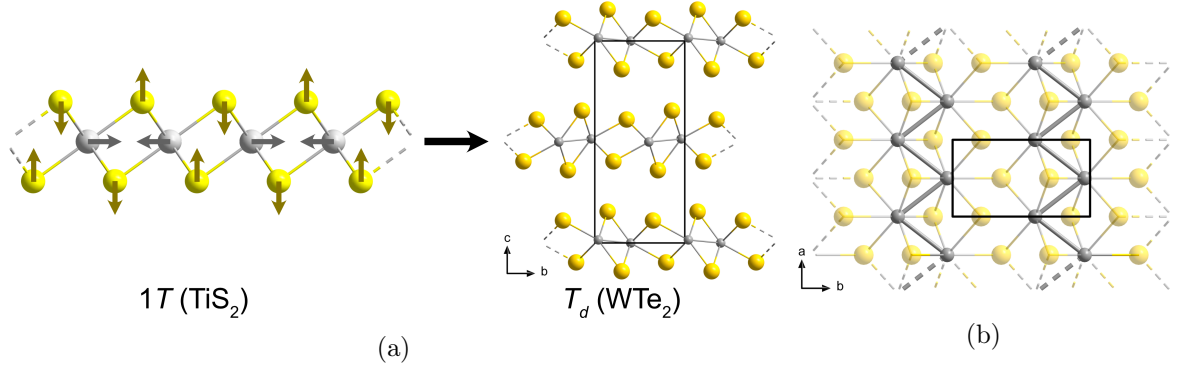


Figure 1: a) Sections of the crystal structures of TiS_2 (Ti:grey; S:yellow) and WTe_2 (W:grey; Te:orange; unit cell highlighted) viewed orthogonal to the layers. Arrows in TiS_2 indicate the distortion that leads to the WTe_2 -type structure. b) A single WTe_2 layer viewed along the c direction; tellurium is shown slightly transparent to highlight the W–W zigzag chains with unit cell highlighted.

This structural motif makes WTe_2 highly responsive to changes in electron count and interlayer interactions (e.g. strain/stress or Moiré effects/superlattices),^[25,29,39,43–46] motivating chemical approaches that deliberately perturb the van der Waals gap and/or the charge balance.^[10,42,47–52] Therefore, WTe_2 offers two intertwined pathways for modification: redox-driven changes in electron count and vdW gap perturbations (spacing, registry, guest ordering), which are typically coupled through concurrent charge transfer and structural relaxation.

1.2 Intercalation in layered materials and TMDCs

Intercalation describes the insertion of guest species into the van der Waals gap of a layered host without destroying its fundamental layer topology (see Fig. 3). Because the host framework remains largely intact (i.e., the process is topotactic), intercalation provides a particularly controlled route to tune lattice parameters, carrier concentration, and bonding interactions, often in a continuous and reversible fashion.^[7,53–56] A hallmark of many intercalation compounds is the emergence of ordered host–guest arrangements, frequently expressed as staging phenomena in which filled interlayers alternate with empty ones (see Fig. 2), as well as order–disorder behavior and symmetry changes as the guest content varies.^[54,57]

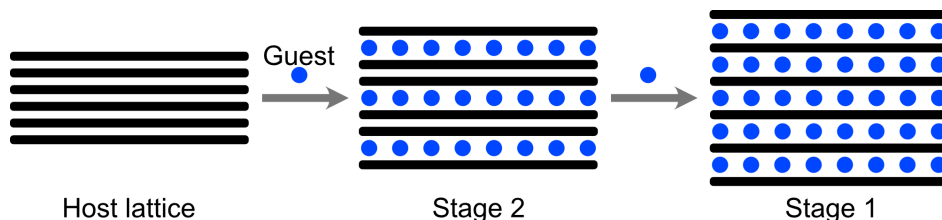


Figure 2: Schematic illustration of the intercalation mechanism (e.g. lithium; intercalant/guest: blue spheres) into the layered structure (e.g. graphite; black lines).

In layered transition-metal dichalcogenides (TMDCs), intercalation spans electron-donor cations (alkali, alkaline-earth metals or transition metals),^[58–65] neutral or weakly coordinating molecules,^[66–69] and redox-active guests.^[18,70,71] Depending on the degree of charge transfer and steric demand, it can trigger structural phase transitions, superstructures, and pronounced property changes, ranging from modified transport and magnetism to altered collective states.

Several complementary synthetic strategies are used to intercalate layered TMDCs, and the chosen route often determines whether the product represents a thermodynamic endpoint or a kinetically trapped intermediate. In *direct solid-state* or *vapor-phase* approaches, the host is exposed to a reactive guest source in sealed ampoules (or under controlled vapor pressures), which can favor well-defined staging and ordered interlayer motifs when diffusion and guest activity are sufficiently high.^[53,66,71–75] In contrast, *electrochemical intercalation* enables continuous control over the guest content and can access narrowly spaced compositions that may be difficult to isolate by bulk synthesis. *Solution-based redox routes* provide further flexibility: chemical reduction of the TMDC layers (followed by uptake of charge-compensating cations) can proceed rapidly and often induces strong layer expansion, which in turn facilitates

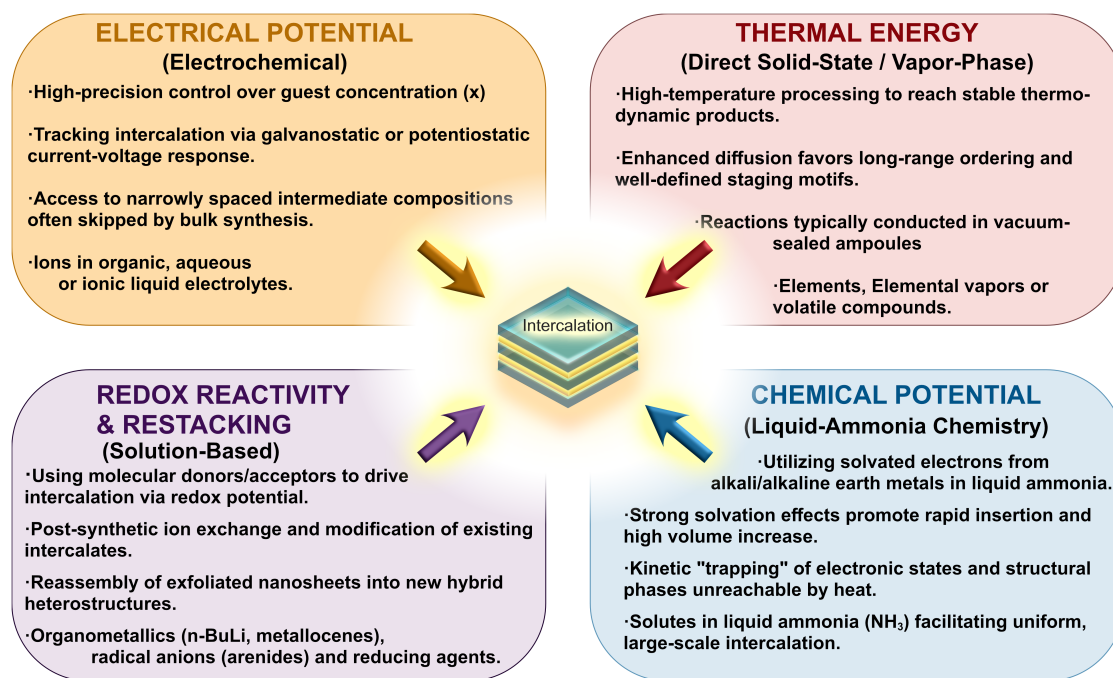


Figure 3: Principal synthetic routes for the intercalation of layered materials. The diagram categorizes strategies into four quadrants: electrical potential (electrochemical), thermal energy (vapor/solid-state), redox reactivity/restacking (solution-based), and chemical potential (liquid ammonia).

subsequent guest exchange or exfoliation. A particularly powerful variant is *liquid-ammonia chemistry*, where solvated electrons generated from alkali metals promote reduction and fast insertion of Li^+ , Na^+ , or related cations. Such conditions are well known to yield highly expanded intercalates and to open access to metastable structural/electronic states. In addition, *organometallic donors* (e.g., metallocenes) can act as charge-transfer reagents, and *post-synthetic ion exchange* allows conversion of readily accessible intercalates into compositions that are otherwise challenging to obtain. Finally, *bottom-up restacking routes* start from exfoliated (often chemically reduced) TMDC nanosheets and reassemble them from dispersion in the presence of selected guests, offering a complementary handle on interlayer spacing, stacking order, and metastable intercalate compositions.^[54,55,57,70,71]

Beyond serving as a versatile chemical strategy for tuning the properties of layered solids, intercalation is also the central working principle of modern rechargeable batteries (see Fig. 4). The archetypal Li-ion cell operates through reversible intercalation/deintercalation of Li^+ between two host electrodes: a layered or framework cathode (classically LiCoO_2) and a graphite anode that forms C_6Li_x ($x \leq 1$) upon charging.^[76,77] This conceptual link is valuable in the TMDC context because it highlights the importance of diffusion pathways, staging, and the delicate balance between structural stability and redox activity: sufficiently rigid host layers

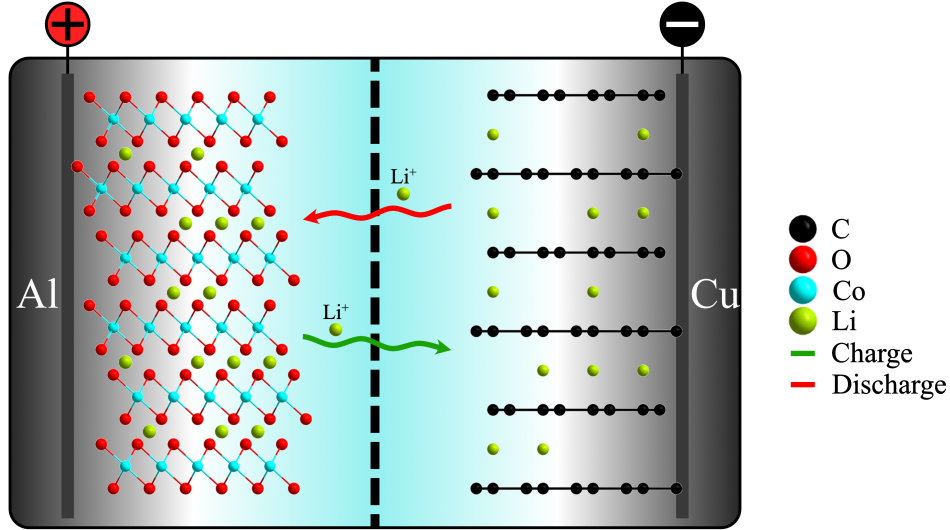


Figure 4: Illustration of a lithium-ion battery with a layered LiCoO_2 cathode and carbon anode. Li^+ ions shuttle between electrodes during charge (green) and discharge (red).

enable reversibility, while even subtle changes in stacking, coordination, or layer distortion can strongly influence kinetics and cycling stability. In practice, intercalation is also widely used as a chemical tool for exfoliation and the preparation of metastable compositions, where insertion-induced expansion and charge transfer weaken interlayer cohesion and can unlock phases not accessible by direct synthesis.

While cationic intercalation in TMDCs is well established, truly anionic intercalation is uncommon and often difficult to disentangle from low-level “anionic doping” or surface decoration. In many systems, halogens introduced under growth or transport conditions are later detected only in dilute, disordered environments that do not yield ordered intercalation phases or a substantial expansion of the host lattice; such cases are better described as halogen-doped or halogen-decorated TMDCs rather than stoichiometric intercalation compounds.^[78–91] In contrast, stoichiometric halogen intercalation—where an oxidizing guest forms an ordered interlayer motif and acts as a genuine structural component—represents a distinct and much rarer regime, because it combines strong redox chemistry with the requirement of preserving the layered host topology. This distinction between dilute anionic doping and structurally defined anionic intercalation is particularly relevant for WTe_2 , where halogen insertion can couple lattice expansion, staging/modulation, and controlled oxidation (hole doping) within a van der Waals solid.

1.3 Halogen-Induced Decomposition and Cluster Formation in the $TM-Q-X$ system

The interaction between halogens and layered transition-metal dichalcogenides (MQ_2) at elevated temperatures represents a complex chemical continuum, shifting from limited modification to true halogenation and structural oxidation.^[92,93] In this high-temperature regime, robust $M-Q$ bonds ($Q = S, Se, Te$) are cleaved, feeding equilibria that generate metal-halide species, while the chalcogen is converted into molecular chalcogen halides (e.g. S_2Cl_2 , $SeCl_2$ and TeI_4) that are generally volatile and therefore tend to sublime and redistribute into colder regions of the reaction container. While these chalcogen halides are transported in the gas phase, the metal component in the iodine case is often retained as non-volatile cluster residues or stabilized within ternary metal–chalcogenide–halide frameworks.^[92,94–98] These equilibria form the fundamental chemical basis of chemical vapor transport (CVT), where halogens act as transport agents by forming mobile halide intermediates in the hot zone and re-depositing material in the cold zone (e.g. Van Arkel–de Boer process, see Fig. 5).^[92,93,99] Importantly, high-temperature halogen chemistry often stalls at intermediate chalcogenide halide (chalcobalide) compositions where metal–metal bonded clusters or polymeric motifs are stabilized rather than preserving the original MQ_2 layer framework.^[100,101]

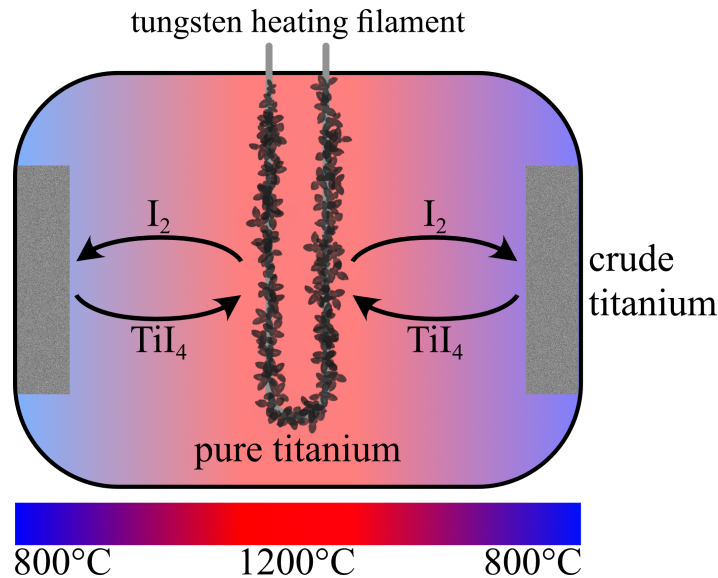


Figure 5: Schematic illustration of the van Arkel-de Boer process with typical pressure of 0.1 to 20 Pa.

Classic outcomes at moderate temperatures include ternary chalcogenide halides incorporating small metal fragments and mixed Q/X coordination. Representative motifs include the triangular $Mo_3Q_7X_4$ and $W_3Q_7X_4$ ($Q = S, Se, Te$; $X = Cl, Br, I$) families; for instance,

the $[\text{W}_3\text{Te}_7]$ core can be assembled at temperatures between 300–400 °C in halide-rich environments.^[97,100,102] These illustrate how partial halogenation can promote metal clustering and chalcogen-rich linking motifs instead of complete conversion into binary metal halides. Similarly, investigations into the niobium-halogen system established the existence of stable NbS_2Cl_2 and NbSe_2I_2 phases, characterized by cage-shaped $[\text{Nb}_2\text{Q}_4]$ units linked by halogen atoms into sheets. These materials exhibit diamagnetic and semiconducting behavior due to $\text{Nb}^{4+}\text{--Nb}^{4+}$ pairing within the units.^[103]

Reduced niobium and tantalum cluster compounds are commonly obtained by classical high-temperature solid-state syntheses from the elements or by comproportionation/metallothermic reactions, often assisted by alkali-halide fluxes or halide transport.^[104,105] Under such conditions, thermodynamically robust M_3 and M_6 motifs dominate, for example trigonal M_3 clusters in Nb_3SI_7 , Nb_3SBr_7 , and Ta_3SBr_7 , as well as octahedral M_6 clusters in Nb_6I_{11} .^[106–109] The introduction of heteroanions broadens this chemistry toward non-octahedral cluster types, especially M_4 motifs, for example planar Nb_4 units in $\text{CsNb}_4\text{Cl}_{11}/\text{CsNb}_4\text{Br}_{11}/\text{RbNb}_4\text{Cl}_{11}$, pnictide-capped butterfly clusters in $\text{Nb}_4\text{PnX}_{11}$ ($\text{Pn} = \text{N}, \text{P}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), and tetrahedral Nb_4/Ta_4 clusters in GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 .^[110–112] Access to less common or metastable architectures often requires milder, non-conventional reduction strategies: phosphorus-based reductions of tungsten halides afford phosphorus-centered or phosphinidene-capped clusters such as $\text{W}_4(\text{PCl})\text{Cl}_{10}$, $\text{W}_6\text{PCl}_{17}$, and $\text{W}_4(\text{PBr})\text{Br}_{10}$, whereas antimony or transition-metal reductants yield products such as $\text{W}_5\text{Br}_{12} \cdot \text{SbBr}_3$ and intermediate Fe--W--Cl phases.^[113–117] These examples illustrate how moving away from prolonged high-temperature equilibration toward softer heterogeneous reductions can redirect cluster condensation toward different nuclearities and connectivities.^[114,116–118]

Under more halogen-rich or higher-temperature conditions, larger hexanuclear cluster solids become accessible. A prominent family is provided by ternary chalcogenides with the formula $\text{Mo}_6\text{S}_6\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$), which are isotypic with the classic superconducting Chevrel phases ($M_x\text{Mo}_6\text{Q}_8$, where M can be metals such as Pb , Sn , Cu , or Ba). While the ternary $\text{Mo}_6\text{S}_6\text{X}_2$ series is thermodynamically stable at high temperatures, the binary parent phase Mo_6Q_8 is unstable under these conditions and cannot be synthesized directly.^[100] In this specific series, structural stability is achieved through the filling of metal–metal bonding orbitals ($\text{VEC} = 22$) and the location of two halogen atoms (X) close to each other on the threefold axis. For bromine and iodine, this proximity creates a van der Waals interaction that effectively fills the structural vacancy.^[100] Analogous tungsten clusters featuring octahedral $[\text{W}_6\text{Te}_8]$ cores have also been isolated, demonstrating the versatility of the group 6 transition metals in forming

stable chalcogenide frameworks.^[119,120]

A modern illustrative example of this behavior is $\text{Mo}_6\text{S}_3\text{Br}_6$, a layered van der Waals solid constructed from covalently linked superatomic building blocks.^[121] High-quality crystals of $\text{Mo}_6\text{S}_3\text{Br}_6$ exhibit a direct electronic bandgap of approximately 1.64 eV.^[122] Analogously, the cluster solid $\text{Re}_6\text{Se}_8\text{Cl}_2$ has become a widely cited prototype of a "superatomic" 2D semiconductor family. Early reports indicated a direct gap of approximately 1.4 eV,^[123] while recent studies exploit exfoliated crystals to probe coherent excitonic transport phenomena.^[124]

Because chemical vapor transport (CVT) and related halogen-mediated equilibria rely on reversible halide formation,^[80,85,93,125] they can also introduce halogen-derived species as intrinsic defects. Quantitative studies confirm that transport agents like I_2 , Br_2 , and TeCl_4 are incorporated as intercalates or substitutions, creating donor or acceptor levels with activation energies in the range of 20–90 meV.^[125] In selected hosts like HfS_2 or MoSe_2 , the presence of trapped molecular I_2 results in low-temperature bound-exciton photoluminescence, which exhibits narrow emission lines and phonon replicas at energies roughly 0.1 eV below the indirect bandgap of the host crystal.^[87,88]

1.4 Melamine-based SHG materials

Second-harmonic generation (SHG) is a prototypical second-order nonlinear optical (NLO) effect in which two photons are converted into a single photon of doubled frequency (halved wavelength), enabling processes such as frequency conversion and electro-optic modulation in optoelectronic applications (see Fig. 6).^[126,127] As a macroscopic second-order response, SHG is only symmetry-allowed in non-centrosymmetric solids.^[128]

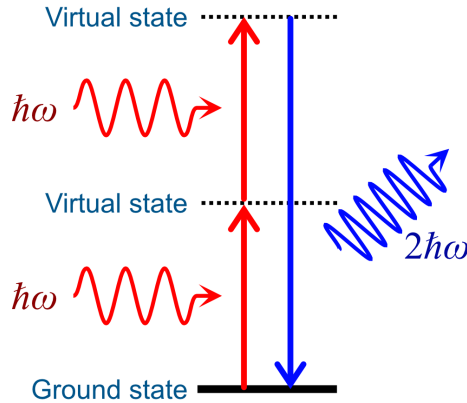


Figure 6: The principles of second-harmonic generation (SHG) illustrated as a two photon process.

While this symmetry requirement is conceptually simple, it is often difficult to realize in practice because many molecular and hybrid solids preferentially crystallize in centrosymmetric space groups—an issue frequently referred to as the “inversion symmetry trap”.^[129,130] Overcoming it commonly relies on introducing asymmetry at the building-block level and/or inducing symmetry breaking through targeted chemical modifications that enforce polar distortions or non-centrosymmetric packing.^[131,132]

A widely used crystal-chemical principle is to combine structurally and electronically polarizable units with packing motifs that promote polar alignment. Benchmark NLO crystals such as β -BaB₂O₄ (BBO) illustrate how planar, π -conjugated groups—often discussed in terms of (B₃O₆)³⁻ building units—can support sizeable optical nonlinearities when arranged in a non-centrosymmetric lattice. This design principle has motivated the exploration of other planar π -systems with delocalized electrons, which tend to enhance polarizability and can thus increase NLO responses (see Fig. 7).^[133,134] In this context, cyanurate-based systems built from (C₃N₃O₃)³⁻ units (e.g., Ca₃(C₃N₃O₃)₂ and Sr₃(C₃N₃O₃)₂) have been highlighted as promising inorganic platforms that translate planar π -conjugation into non-centrosymmetric crystal architectures.^[135–138]

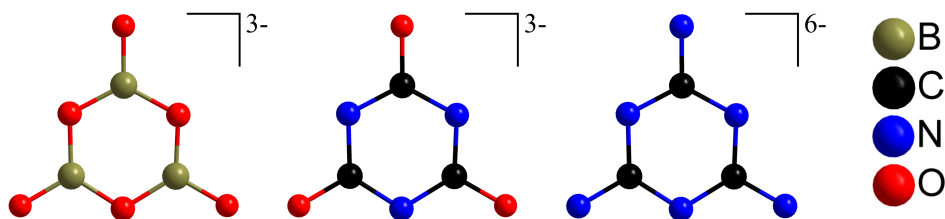


Figure 7: Different π -conjugated molecules ((B₃O₆)³⁻ (left), (C₃N₃O₃)³⁻ (middle) and (C₃N₆)⁶⁻ (right)).

Melamine (C₃N₆H₆) provides a closely related, π -rich building block: it offers a rigid triazine core, multiple nitrogen donors for coordination, and a strong propensity to form extended hydrogen-bond networks.^[139] In its monovalent cationic form (melaminium), melamine can additionally act as a structure-directing component in organic–inorganic systems, stabilizing arrangements of reduced symmetry through ionic templating and hydrogen-bond directionality.^[140] At the same time, melamine-rich solids often adopt highly symmetric packing motifs that suppress macroscopic polarity, so deliberate symmetry breaking is usually required to access SHG-active phases.^[141–144] Effective approaches include combining melamine/melaminium with suitably asymmetric, inorganic secondary building units, such as transition-metal halides, and exploiting soft, polarizable cations (especially period 6 elements and/or d¹⁰ metals) whose flexible coordination environments can support non-centrosymmetric arrange-

ments.^[145–148] In addition to highly polarizable heavy-metal systems, the same design principles motivate studies with less hazardous metal centers (e.g., zinc halides), which can offer a practical balance between structural flexibility, stability, and safety.

From a synthetic perspective, melamine-based hybrid halides are readily accessible via mild hydrothermal and solvothermal routes, as well as low-temperature solution growth. These methods enable the systematic screening of composition, protonation state, and polymorphism, which is critical for identifying non-centrosymmetric phases.^[145,146] Specifically, these low-energy synthetic regimes facilitate the stabilization of metastable NLO-active arrangements that might otherwise transform into centrosymmetric motifs under high-temperature conditions.

2 Objectives

The central objective of this dissertation is to establish WTe_2 as a chemically tunable layered host and to connect composition–structure relationships to reaction pathways across intercalation and follow-up chemistry. This includes developing reliable synthetic routes and handling concepts for moisture- and air-sensitive samples, determining crystal structures from powder and single-crystal diffraction data with particular emphasis on ordering phenomena, real-structure effects, and (in)commensurate modulation, and correlating these structural results with the observed physical and chemical properties. On this basis, the work aims to map systematic trends in reduced intercalation compounds $A_{0.5}\text{WTe}_2$ across the alkali series, to extend oxidative halogen intercalation from the established iodine intercalate WTe_2I to bromine-rich WTe_2Br_x phases exhibiting multi-stage behavior and pronounced kinetic lability, and to rationalize how increased temperature and halogen activity shift the system from topochemical intercalation to reconstructive transformations, including tellurium iodide formation (TeI_4 polymorphism) and tungsten iodide cluster products. The melamine-based SHG materials and the Nb/Ta oxyhalide cluster chemistry are included concisely as complementary examples of how targeted synthesis, symmetry, connectivity, and structure–property considerations intersect across different areas of solid-state inorganic chemistry.

3 Summary of the Main Results

The main results presented in this work originate from several thematically distinct studies, covering halogen-induced reactions, intercalation processes, cluster chemistry and the hydrothermal synthesis of melamine-based materials. The following sections summarize each publication separately, focusing on the structural findings and the resulting chemical and physical properties of the investigated compounds. At the same time, this overview shows how complementary analytical methods were required to characterize these complex chemical systems.

3.1 Intercalation of Alkali Metal into WTe_2 , the Crystal Structure of $A_{0.5}\text{WTe}_2$ and Observation of a Metal-to-Semiconductor Transition (Publication 1)

The cationic intercalation of tungsten ditelluride with alkali metals gives access to a chemically well-defined series of compounds with the composition $A_{0.5}\text{WTe}_2$ ($A = \text{K}, \text{Rb}, \text{Cs}$). A central result of the study is that these phases cannot be prepared reliably by classical direct routes. Reactions of WTe_2 with liquid alkali metals or alkali vapor led mainly to alkali tellurides, unreacted starting material, and only minor amounts of the desired intercalates. In addition, the intercalation compounds decompose slowly on heating above about 100 °C. Phase-pure products were therefore obtained only by low-temperature solution chemistry using alkali naphthalenides in tetrahydrofuran (THF). Under these conditions, powders formed at -50 °C within a few hours, whereas single crystals required several weeks at -80 °C. Even though single crystals could be intercalated, their extreme sensitivity toward moisture, air, and even mechanical handling prevented a reliable single-crystal diffraction study, so the structural characterization had to rely mainly on powder X-ray diffraction (PXRD).

The diffraction data show that $\text{K}_{0.5}\text{WTe}_2$, $\text{Rb}_{0.5}\text{WTe}_2$, and $\text{Cs}_{0.5}\text{WTe}_2$ are isotypic and crystallize in the monoclinic space group $P2_1/m$. An instructive aspect of the structure solution is that the first indexing of $\text{Rb}_{0.5}\text{WTe}_2$, based only on the strongest reflections, suggested a smaller monoclinic cell with apparently disordered rubidium positions of about half occupancy. Only after the weaker reflections were included did the correct cell with nearly doubled volume emerge, resolving the alkali positions in an ordered way. Compared with pristine WTe_2 in $Pmn2_1$, alkali intercalation leaves the basic WTe_2 layers largely intact, but causes a pronounced reorganization of their relative stacking and a slight distortion within the layers. The adjacent layers shift relative to one another along $[10\bar{1}]$, which aligns the tungsten zigzag chains along the b direction in the chosen setting (see Fig. 9). At the same

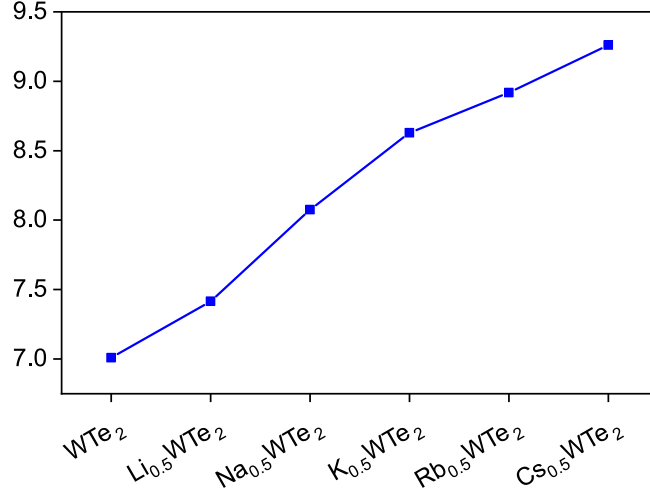


Figure 8: Interlayer spacing of pristine WTe_2 and its alkali-metal-intercalated derivatives, determined from PXRD via the (002) Bragg reflection.^[149]

time, the interlayer distance increases systematically with alkali-metal size, from 7.009 Å in WTe_2 to 8.6297 Å for $\text{K}_{0.5}\text{WTe}_2$, 8.9179 Å for $\text{Rb}_{0.5}\text{WTe}_2$, and 9.2606 Å for $\text{Cs}_{0.5}\text{WTe}_2$ (see Fig. 8). The systematic expansion of the interlayer distance illustrates that the van der Waals gap accommodates the alkali cations in an ordered fashion.

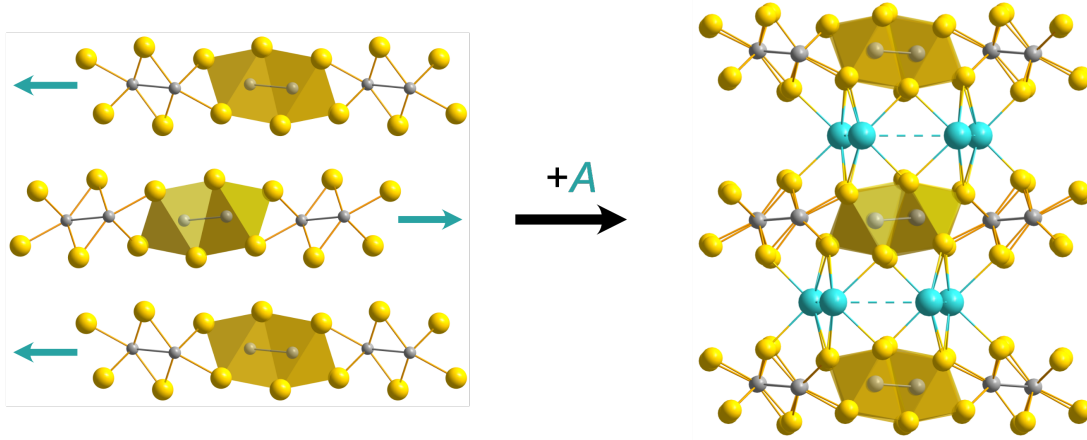


Figure 9: Structural transformation of WTe_2 (left) to $\text{A}_{0.5}\text{WTe}_2$ (right) induced by alkali intercalation. The adjacent WTe_2 layers experience a significant shift, highlighted by the tungsten telluride chains (W: grey, Te: yellow, A: turquoise).^[149]

A second important structural result concerns the arrangement of the intercalated alkali-metal atoms. In the refined models, the cations occupy two crystallographically distinct positions within the van der Waals gap and form an ordered honeycomb-like pattern perpendicular to the b direction (see Fig. 10). For $\text{Rb}_{0.5}\text{WTe}_2$, representative $\text{Rb} \cdots \text{Rb}$ separations lie between 3.7917(7) Å and 5.140(1) Å. Each alkali site is surrounded in a distorted cubic coordination environment by tellurium atoms, with $\text{Rb}-\text{Te}$ distances between 3.556(4) Å and 4.122(5) Å. Although the layer topology remains recognizable, the intercalation is not a purely

spacing effect. The symmetry lowering from $Pmn2_1$ to $P2_1/m$ is accompanied by subtle but significant distortions of the WTe_2 host layer itself. Chemical analysis by ICP-OES and EDX confirmed the expected stoichiometry, and SEM images showed the expected platelet-like morphology, consistent with the layered character of the structure. At the same time, time-resolved powder diffraction under non-hermetic conditions revealed rapid degradation under hydrolysis, showing that the structural integrity depends strongly on strict inert handling.

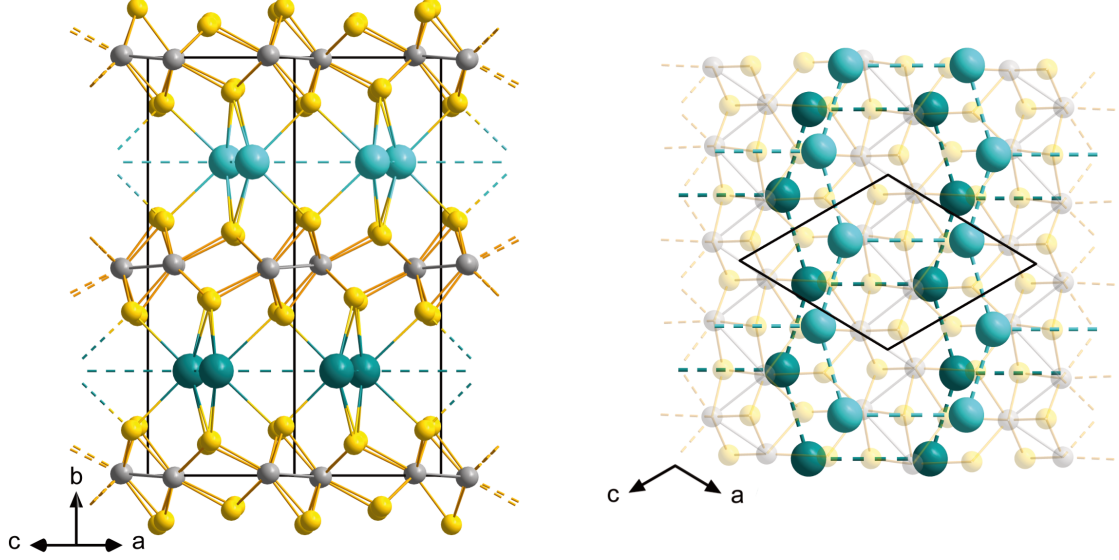


Figure 10: Section of the $\text{Rb}_{0.5}\text{WTe}_2$ crystal structure. View along the tungsten zigzag chains (left). View along the b -axis (right) showing the arrangements of Rb ions, shown turquoise, one of them semi-transparent (75% opacity), separated by one central WTe_2 layer (W: grey, Te: yellow).^[149]

Within the layers, the tungsten chains show the most striking structural response, becoming distinctly distorted upon intercalation. In pristine WTe_2 the W–W contacts are uniform, whereas in the intercalated compounds they split into shorter and longer distances, indicating clustering of the tungsten atoms. For $\text{Rb}_{0.5}\text{WTe}_2$ the W–W distances range from 2.794(3) Å to 3.146(3) Å, while the potassium and cesium analogues exhibit the same distortion motif with slightly different bond lengths. The distortion of the tungsten chains can be understood as a structural consequence of the formal reduction of the WTe_2 layers by half an electron per formula unit. In other words, electron donation from the alkali metal does not simply fill bands rigidly, but drives a structural response within the tungsten sublattice. The resulting distortion can be described in terms of rhombic W_4 units and shows, in a broader sense, parallels to electron-count-driven clustering phenomena observed in related dichalcogenides such as ReSe_2 and in halide cluster compounds such as $\text{CsNb}_4\text{Cl}_{11}$.^[110,150]

The electrical measurements show that this structural reorganization is accompanied by a clear change in electronic behavior (see Fig. 12). Temperature-dependent conductivity mea-

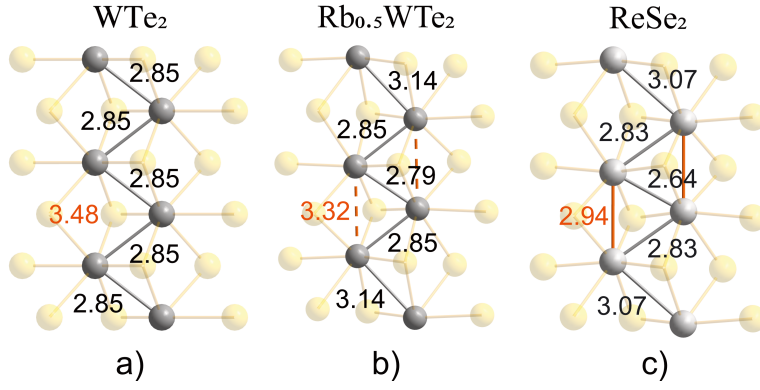


Figure 11: Section of the (a) WTe_2 (b) $\text{Rb}_{0.5}\text{WTe}_2$ and (c) ReSe_2 structure visualizing the distortion of the metal chain with metal-to-metal distances given in Å (tungsten/rhenium in grey, chalcogens in high opacity yellow).^[149]

Measurements on $\text{Rb}_{0.5}\text{WTe}_2$ single crystals reveal ohmic current-voltage characteristics between 75 K and 300 K, with a maximum conductivity of 24.3 mS m^{-1} at 300 K. The conductivity decreases with decreasing temperature, which is characteristic of a semiconductor. From the Arrhenius-like representation, an activation barrier of 0.476 eV was estimated for the range between room temperature and 150 K. Additional support for semiconducting behavior comes from the pronounced photoresponse under irradiation with a 779 nm laser. The initial fast rise is assigned to photogenerated charge carriers, whereas the slower second component is attributed to heating effects during illumination.

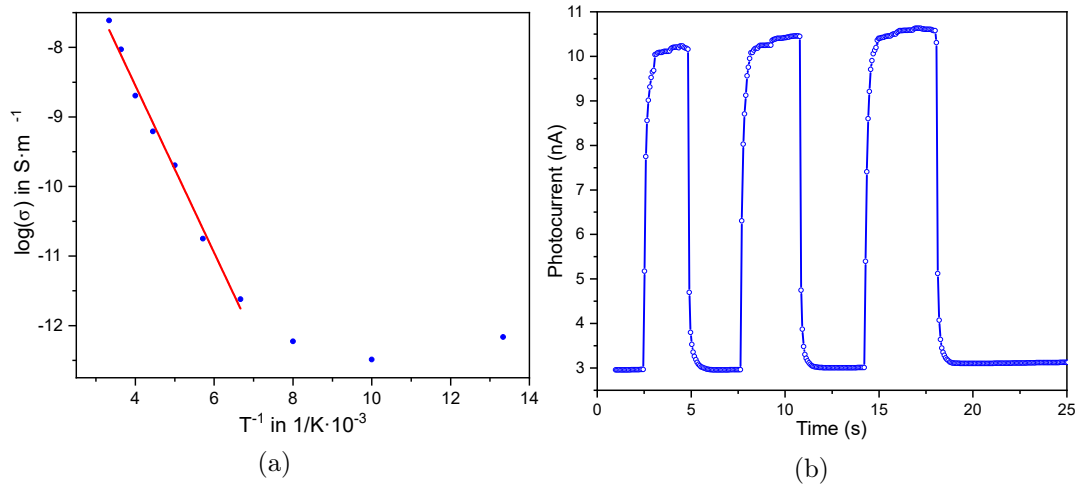


Figure 12: a) Arrhenius plot of the electrical conductivity of $\text{Rb}_{0.5}\text{WTe}_2$ at temperatures in the range of 75 K to 300 K. The red line is a linear fit for the range between 150 K and 300 K. b) Photoresponse of a $\text{Rb}_{0.5}\text{WTe}_2$ crystal toward a 779 nm laser at 250 K under a bias of 0.2 V.^[149]

The optical data further support a narrow-gap semiconducting description of the intercalation compounds. Although the absorption edge is rather broad and a conventional Tauc evaluation remains ambiguous, the Zanatta approach gives direct gap values of 0.431 eV for

$\text{K}_{0.5}\text{WTe}_2$, 0.448 eV for $\text{Rb}_{0.5}\text{WTe}_2$, and 0.440 eV for $\text{Cs}_{0.5}\text{WTe}_2$ (see Fig. 13a).^[151–157] Theoretical calculations are consistent with these observations and predict indirect band gaps of about 0.35–0.4 eV for all three compounds (see Fig. 13b). The states near the Fermi level are dominated mainly by W $5d$ and Te $5p$ orbitals, whereas the alkali-metal states lie far from the gap region and thus act primarily as electron donors and structure-directing species. Particularly important is the conclusion that the semiconducting state does not arise from charge transfer alone, but from the combination of electron donation and the accompanying lattice distortion. This interpretation is further supported by calculations on the same framework without cations, which show that charge alone would not be sufficient to account for the observed behavior. At the same time, the calculations indicate that this narrow-gap semiconducting state is delicate, since even moderate tensile or compressive strain along the interlayer direction is sufficient to reduce or even close the gap.

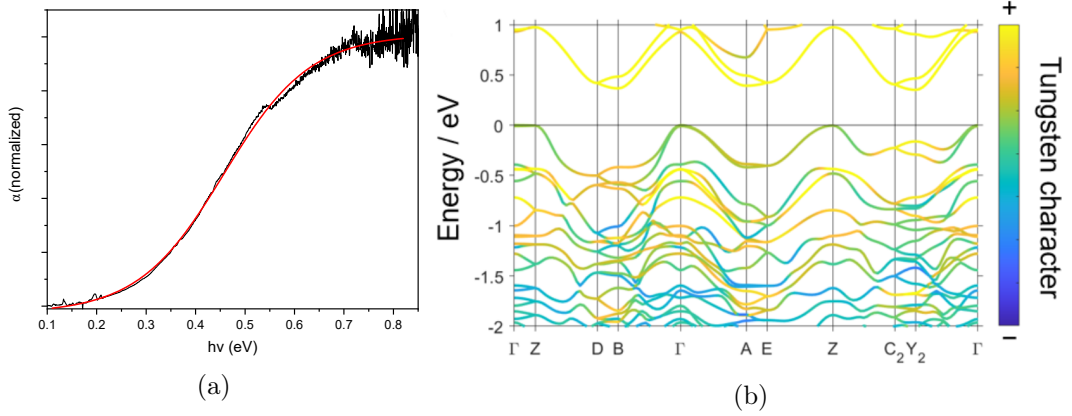


Figure 13: a) Optical absorption coefficient spectrum of $\text{K}_{0.5}\text{WTe}_2$ with the Boltzmann function ($R^2 = 0.997$, $\chi^2 = 4.00 \cdot 10^{-4}$) used to fit α (normalized). b) Calculated electronic band structures of $\text{K}_{0.5}\text{WTe}_2$ with bands colored by their tungsten character. Special points ($\Gamma = (0\ 0\ 0)$, $Z = (0\ 0.5\ 0)$, $D = (0\ 0.5\ 0.5)$, $B = (0\ 0\ 0.5)$, $A = (-0.5\ 0\ 0.5)$, $E = (-0.5\ 0.5\ 0.5)$, $C_2 = (-0.5\ 0.5\ 0)$, $Y_2 = (-0.5\ 0\ 0)$) in and paths through reciprocal space were chosen following the literature.^[149,158]

In summary, the results demonstrate that low-temperature alkali-metal intercalation transforms semimetallic WTe_2 into an ordered family of narrow-gap semiconductors while largely preserving the layered host structure. The key features are the regular occupation of the van der Waals gap by alkali ions, the systematic increase of the interlayer distance across the alkali series, and the electron-count-driven distortion of the tungsten substructure. The $\text{A}_{0.5}\text{WTe}_2$ compounds thus define a coherent structural series in which electronic behavior is directly coupled to the lattice response.

3.2 Reversible Iodine Intercalation into Tungsten Ditelluride (Publication 2)

Transition-metal dichalcogenides are a prominent class of layered solids in which weak van der Waals interactions between adjacent layers permit extensive intercalation chemistry and, with it, a targeted modification of electronic properties.^[4,70] Within this family, WTe_2 is particularly attractive because its distorted T_d structure combines a low-dimensional layered arrangement with pronounced W–W zigzag chains and an unusual electronic structure that has been associated with semimetallic transport, large magnetoresistance, charge-density-wave phenomena, and topological band features.^[15,16,26,35,159,160] Against this background, the low-temperature iodination of WTe_2 was investigated as a route toward an anionically intercalated derivative in which the host lattice might be retained while its electronic structure is substantially altered.

The reaction of WTe_2 with iodine in sealed silica ampules indeed yielded the new phase WTe_2I as the first identifiable product of the iodination sequence. Bulk material was obtained already under comparatively mild conditions, and chemical analysis confirmed a composition very close to the ideal 1:2:1 ratio. Powder diffraction showed that the new compound remains structurally related to the parent telluride and can be described in the orthorhombic space group $Pmmn$ as an average structure derived from the T_d host. In this sense, the work established that the reaction with iodine does not immediately destroy the WTe_2 layers, but first gives access to a genuine intercalation compound that represents the low-temperature entry point into the wider W–Te–I reaction chemistry.

The basic geometry of the WTe_2 layers is preserved to a remarkable extent (see Fig. 14). The intralayer W–W and W–Te distances remain close to those of pristine WTe_2 , whereas the stacking direction expands dramatically because iodine is inserted between every pair of adjacent layers. This expansion is not a minor perturbation. Rather, the distance between neighboring layers increases strongly, and the interlayer region is reorganized into nearly planar iodine nets. In the average structure, these iodine atoms form a rectangular arrangement with short I–I contacts that are far more condensed than would be expected for a purely space-filling interlayer species. The resulting geometry is noteworthy because it combines a largely intact WTe_2 host with a chemically distinct iodine substructure that dominates the van der Waals gap. In this respect, WTe_2I differs clearly from more common cation-intercalated dichalcogenides, for which the interlayer expansion is often much smaller.^[161–163] The pronounced structural response also explains the frequent occurrence of layer dislocations in the crystals.

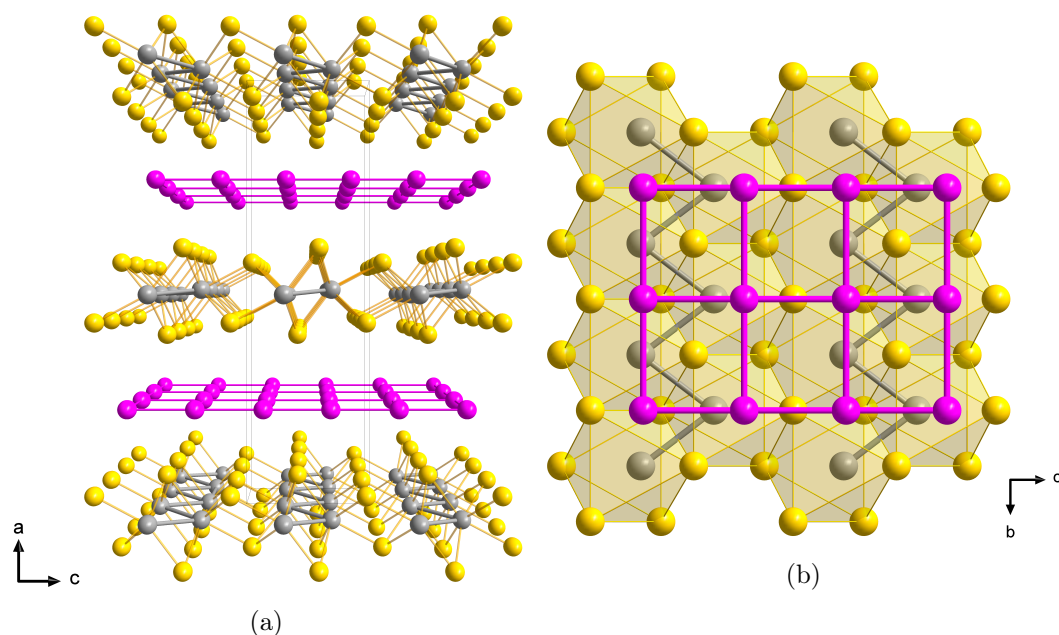


Figure 14: Sections of the WTe_2I crystal structure with tungsten atoms shown in gray, iodine atoms in violet, and tellurium atoms in yellow. a) Perspective projection viewed along the b -axis, illustrating the layered arrangement of the structure. b) View along the a -axis, showing the rectangular iodine net above a WTe_2 layer.^[47]

At the same time, the crystallographic model already showed that the iodine arrangement could not be fully described by a simple ordered average structure. The refined iodine positions exhibited unusually large anisotropic displacement parameters, and additional weak reflections in both powder and single-crystal diffraction indicated deviations from the periodicity of the basic lattice. Low-temperature powder diffraction did not remove this effect. The large displacement parameters therefore could not be dismissed as a merely thermal phenomenon but instead pointed to a more fundamental modulation of the iodine substructure. This is an important aspect because it shows that the first structural model of WTe_2I was already physically informative even where it was incomplete. The average $Pmmn$ description captured the general architecture of the intercalate, while the diffraction anomalies clearly signaled that the real iodine arrangement is modulated and more complex than the average structure suggests.

The reaction behavior further demonstrated that this iodine intercalation is reversible. Thermal analysis in an open system showed that iodine is released again above about 100°C , ultimately leading to complete deintercalation under the measurement conditions (see Fig. 15). Notably, the intercalation itself did not produce a distinct calorimetric event in the sealed-ampoule experiment, whereas deintercalation is readily followed in the open setup through the mass loss associated with iodine sublimation. This establishes WTe_2I not only as a well-

defined intercalation compound but also as a metastable intermediate whose existence depends on iodine chemical potential.

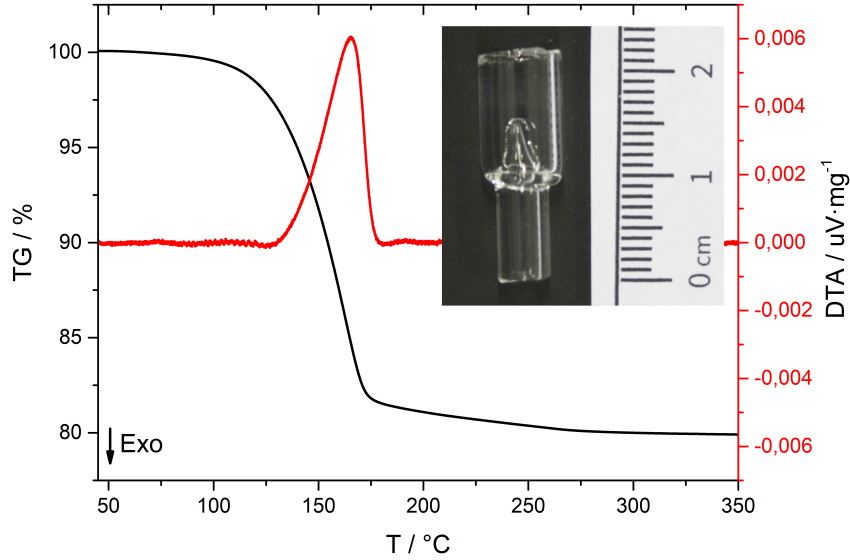


Figure 15: DTA/TG measurement of WTe_2I in an open SiO_2 container up to 350°C with complete iodine loss (DTA: red line, TG: black line).^[47]

The electronic structure calculations showed that the insertion of iodine changes the role of the van der Waals gap from a passive separation region into an electronically active part of the structure (see Fig. 16). Compared with pristine WTe_2 , the calculated density of states at the Fermi level increases markedly, such that the intercalated phase is no longer described as a semimetal but as a metal.^[26,35] This change is connected with a downward shift of the Fermi level and a partial transfer of electron density from the tungsten telluride layers to the interlayer iodine network. The calculations estimate this charge redistribution to be substantial, and they further show that the new states at the Fermi level are not distributed uniformly over the whole structure. Instead, steep and highly dispersive bands with strong iodine *p*-character appear, especially along reciprocal-space directions that probe the interlayer iodine subsystem. Electron-density analysis supports this interpretation by indicating direct I–I bonding contributions, especially along the direction of the shorter iodine contacts. Thus, the intercalated iodine is not merely a charge-balancing oxidant between WTe_2 layers. It forms an electronically relevant substructure of its own and decisively contributes to the metallic behavior of WTe_2I .

A particularly interesting consequence of this electronically active iodine network is its relation to the lattice instability of the compound. Phonon calculations for the average structure re-

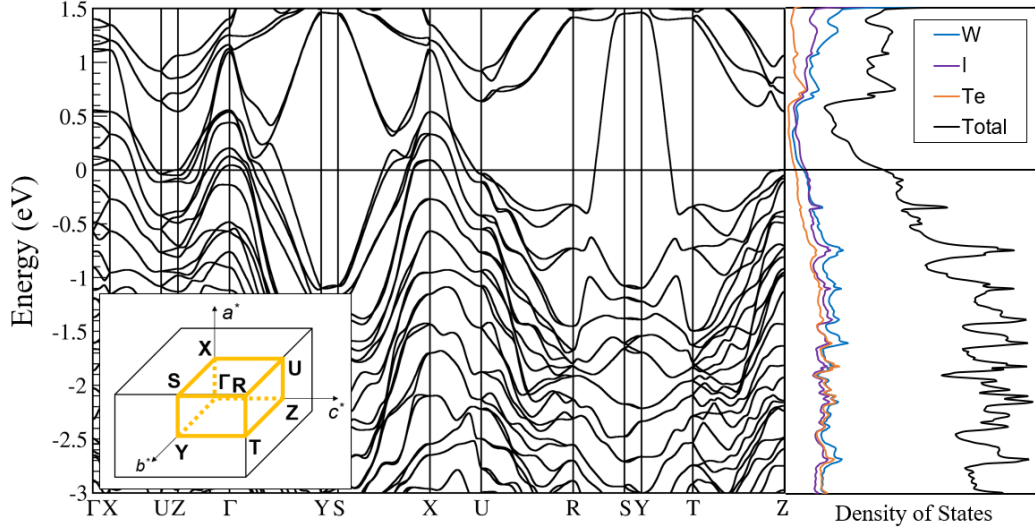


Figure 16: Electronic band structure and density of states of WTe_2I , calculated with spin-orbit coupling. The projected densities of states within the PAW spheres are shown as colored lines at right. Special points in the Brillouin zone are shown as an inset.^[47]

vealed several soft modes with imaginary frequencies, which were interpreted as Kohn anomalies and therefore as fingerprints of an instability toward charge-density-wave ordering.^[16,164] These results provide a natural explanation for the diffraction evidence of modulation. In other words, the disorder-like features of the iodine atoms in the average structure are better understood as the crystallographic signature of an incipient ordered distortion. Analysis of the corresponding eigenvectors showed that these soft modes are dominated by motions of individual iodine atoms, accompanied in part by rocking motions of the WTe_2 layers. The instability is therefore rooted primarily in the weakly bonded iodine substructure rather than in a rigid displacement of intact I_2 units. In this sense, the behavior of WTe_2I can be related conceptually to other iodine-rich solids with condensed iodine substructures.^[161]

Overall, this publication established WTe_2I as a reversible iodine intercalation product of WTe_2 in which the parent telluride layers remain largely intact while the interlayer region is fundamentally reconstructed. The study showed that anion-based intercalation can oxidize WTe_2 , strongly expand the layer separation, introduce a planar iodine substructure, and transform the electronic ground state from semimetallic to metallic. At the same time, the work already revealed that the average crystal structure is only an approximation and that the intercalated iodine layers are intrinsically unstable toward modulation. It therefore provided both the first structural description of WTe_2I and the essential conceptual basis for a more detailed understanding of halogen-intercalated WTe_2 phases in later work.

3.3 Structural Evolution during Reversible Halogen Intercalation in WTe_2 : Commensurate–Incommensurate WTe_2I and Multistage WTe_2Br_x ($x = 0.5, 1.0$ and 1.25) (Publication 3)

Halogen intercalation into WTe_2 gives access to an unusual series of anionically modified layered compounds in which the host framework is largely retained, while the van der Waals gap is reorganized in a halogen-specific manner. For iodine, the previously known compound WTe_2I could be described in substantially greater structural detail.^[47] Instead of a simple average arrangement, WTe_2I occurs in closely related incommensurately and commensurately modulated variants. Both are described in the superspace group $P2_1/m(\alpha 0 \gamma)00$, with the incommensurate phase characterized by the modulation vector $q = (0.4487, 0, 0.1617)$ and the commensurate polytype by the lock-in vector $q = (1/2, 0, 1/6)$. The latter can also be represented as a conventional three-dimensional supercell. No phase transition was observed between 100 K and 270 K, indicating that the modulation is an intrinsic structural feature of WTe_2I rather than a temperature-induced transformation.

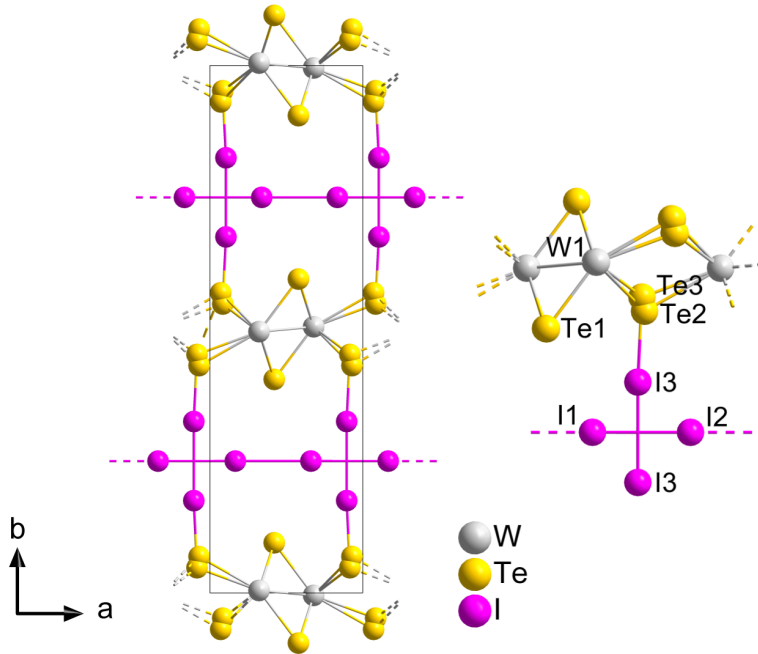


Figure 17: Section of the average incommensurate WTe_2I structure (left) and a smaller section with atom labels (right). Note, the zig-zag chains of tungsten atoms running parallel to the c -axis.^[165]

The modulation in WTe_2I is dominated by the iodine substructure (Fig. 17). The average structure is closely related to the previously reported model, but requires additional minor split positions, Te3 and I3, with occupancies of about 15.5 %. These sites describe a local defect motif in which an I_2 unit rotates by approximately 90° out of the iodine-net plane.

This rotation is coupled to a shift of the adjacent tellurium atom from Te2 to Te3, avoiding an unrealistically short Te–I contact and instead generating a Te3–I3 distance of about 2.77 Å. This value is consistent with a localized covalent interaction between the intercalated iodine and the WTe₂ host layer. The modulation is therefore not merely a crystallographic description of positional disorder, but reflects a chemically meaningful host–guest interaction that locally anchors the iodine substructure.

Within the iodine layer, the displacive modulation leads to a broad distribution of I–I distances and a strongly non-uniform iodine net (see Fig. 18). Over one modulation period, the contacts within the I1/I2 net span from 2.688(8) to 4.018(8) Å, while the I3–I3 distance remains comparatively long at about 3.272(2) Å. The interlayer can therefore no longer be described as a regular rectangular iodine sheet, but rather as a strongly distorted halogen substructure with alternating shorter and longer contacts. The displacement modulation is most pronounced in the *ac*-plane and is accompanied by an occupational modulation of the Te2/I2 and Te3/I3 split positions. This was described by crenel functions, which reflect the intermittent appearance of the I3 site and therefore the local out-of-plane rotation of an I₂ unit. In this way, the modulation combines two effects: a wave-like distortion of the iodine net and the periodic occurrence of a chemically distinct defect motif.

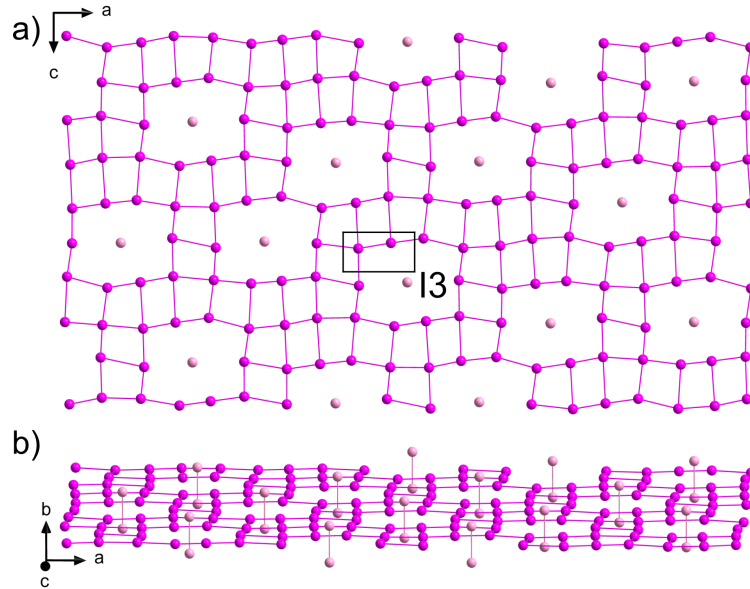


Figure 18: Section of the incommensurate WTe₂I structure a) only showing one iodine layer with I₂ dumbbells of I₃ being aligned along the *b*-axis, including the projected unit cell; and b) a corresponding view along the *c*-axis, emphasizing the I₂ dumbbells of I₃. I₁ and I₂ are displayed purple, and I₃ in lighter purple.^[165]

The WTe₂ layers are affected less strongly than the iodine substructure, but they are not completely rigid. The Te2/Te3 splitting induces subtle distortions in the host layer, and the

tungsten positions show a clearly resolved saw-tooth-like modulation (see Fig. 19 and Fig. 20). The average W–W distance is $2.86(1) \text{ \AA}$, with the shortest contact of $2.78(1) \text{ \AA}$ remaining close to the average, whereas the longest distance of $3.10(2) \text{ \AA}$ marks a periodic disruption of the tungsten chain. These elongated contacts occur after segments of roughly twelve tungsten atoms and are induced by the out-of-plane I3 dumbbells above and below the tungsten-chain plane. Apart from these local interruptions, the W–W distances vary only modestly by about $0.08 \text{ \AA}$, showing that the modulation is primarily rooted in the intercalated iodine layer and only secondarily transmitted into the WTe_2 framework. The commensurate supercell model is therefore useful because it translates this complex modulation into a periodic real-space motif and makes both the iodine-net distortion and the ordered occurrence of the I3 defect easier to visualize.

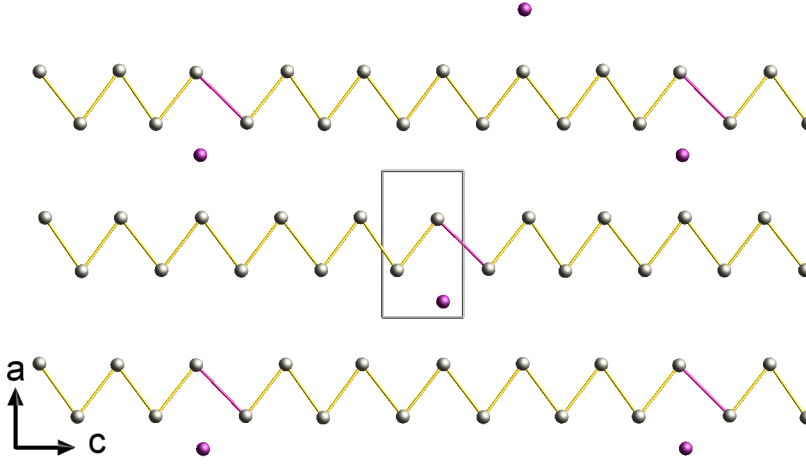


Figure 19: Section of the incommensurate WTe_2I structure viewed along the b direction with highlighted unit cell. For clarity, tellurium atoms are omitted and only one interlayer section in the ac -plane of the tungsten zigzag chains is shown, together with the I_2 dumbbells (I3 sites) aligned along b which are directly above and beyond of the ac -plane section. Elongated W–W contacts, indicating disruption of the tungsten chain are highlighted by violet bonds (W: grey; I: violet; $t = 0.62$).^[165]

The calculated electronic structure shows that the iodine substructure contributes directly to the states at the Fermi level. Commensurately modulated WTe_2I is metallic and contains flat iodine-derived bands at the Fermi level. The flatness of these bands indicates localized metallic states, while anticrossings with tungsten-derived bands show that the iodine and host-layer states are coupled. Compared with the previously discussed unmodulated average model,^[47] the modulated structure shows a much smaller shift of the Fermi level, suggesting that the oxidation of the WTe_2 layers is comparatively weak in the fully modulated description. The electronic structure is therefore governed not simply by charge transfer, but by the detailed organization of the iodine net and its interaction with the host lattice.

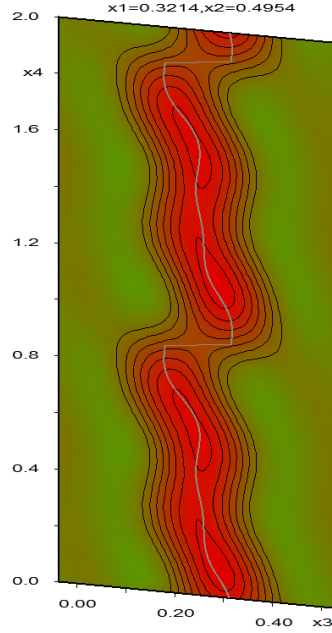


Figure 20: de Wolff sections (Fobs) of x3-x4 plane for W1 in WTe₂I. Refined atomic positions are indicated by a grey line. The electron density is visualized as a heat map (red = high, green = low).^[165]

Bromine intercalation leads to a more dynamic situation. In the WTe₂Br_{*x*} system, distinct composition regimes with $x = 0.5$, 1.0, and 1.25 are observed, but they are connected by rapid and reversible bromine uptake and release. This “breathing” behavior occurs already under mild conditions and is directly reflected in time-resolved PXRD experiments (see Fig. 21). The bromine content depends strongly on bromine activity and temperature. Bromine-rich material can be stabilized at lower temperature or under bromine-rich conditions, whereas bromine loss under argon flow leads toward the bromine-poor phase WTe₂Br_{0.5}. The intermediate composition WTe₂Br_{1.0} is supported by diffraction and thermal-analysis data, but could not be isolated as a phase-pure compound for complete structure determination. It is therefore best regarded as an intermediate stage within the reversible bromine-intercalation sequence.

The bromine-poor phase WTe₂Br_{0.5} crystallizes in the orthorhombic space group $Pm\bar{m}n$ with refined lattice parameters of $a = 16.7450(4)$ Å, $b = 3.67734(3)$ Å, and $c = 6.29678(8)$ Å. In this setting, the a -axis corresponds to the stacking direction, so that the enlarged lattice parameter directly reflects the expansion of the layer sequence by bromine incorporation. The WTe₂ layers remain intact, but the stacking arrangement generates enlarged interlayer voids for bromine incorporation (see Fig. 22). In contrast to the more continuous iodine layer

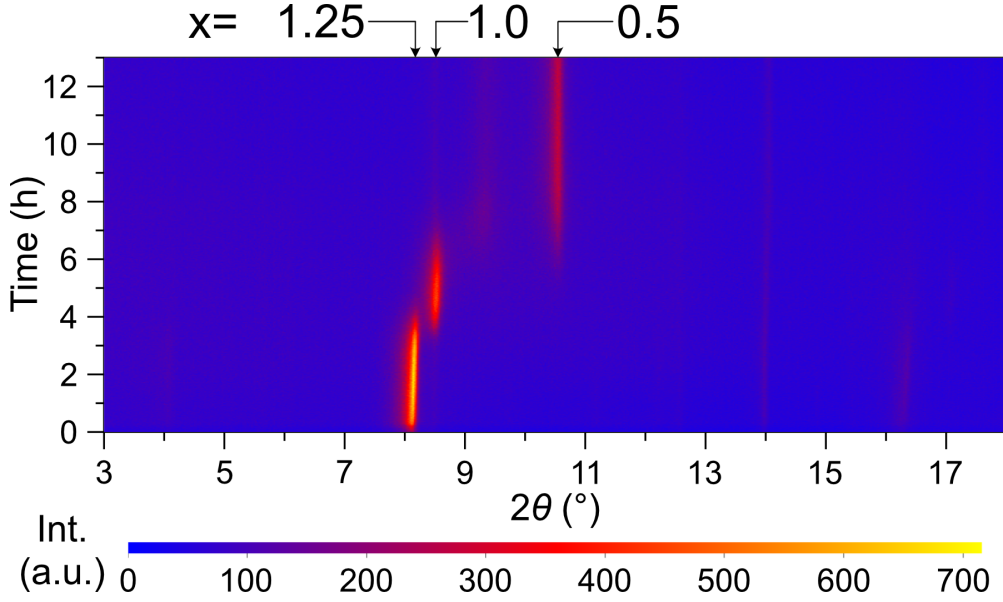


Figure 21: Time resolved PXR D analysis of WTe_2Br_x showing structural evolution during bromine deintercalation with discrete phases from $x = 1.25$ to 1.0 and 0.5.^[165]

in WTe_2I , only half as many halogen atoms are present. The bromine atoms are shifted toward one tellurium site and form short Te1-Br1 contacts of $2.946(2) \text{ \AA}$, thereby connecting adjacent WTe_2 layers through local Te-Br interactions. Direct Br-Br interactions are much less important, because the Br-Br separations are comparatively long. A defining feature of $\text{WTe}_2\text{Br}_{0.5}$ is the very large and anisotropic displacement of Br1 , which indicates pronounced positional disorder and/or dynamic motion in the van der Waals gap. This crystallographic observation is consistent with the rapid bromine mobility inferred from the reversible breathing behavior.

The electronic structure of $\text{WTe}_2\text{Br}_{0.5}$ differs from that of WTe_2I . Although $\text{WTe}_2\text{Br}_{0.5}$ is also metallic and also exhibits a flat band at the Fermi level, bromine does not contribute significantly to the states near the Fermi energy. The localized metallic states are instead mainly located within the WTe_2 layers. The stronger Fermi-level shift of about 0.35 eV indicates a more ionic interaction and a stronger oxidation of the host layers than in modulated WTe_2I . Phonon calculations show several soft modes involving both bromine and WTe_2 displacements, which explains the tendency toward disorder or subtle modulation even though no fully developed modulated structure analogous to WTe_2I was resolved.

At higher bromine content, $\text{WTe}_2\text{Br}_{1.25}$ adopts a substantially more complex orthorhombic structure in $Imm2$ (see Fig. 23), with lattice parameters of $a = 10.6218(4) \text{ \AA}$, $b = 43.038(3) \text{ \AA}$, and $c = 12.6285(9) \text{ \AA}$. The long b -axis corresponds to the stacking direction and contains the periodically alternating bromine interlayers, while the in-plane metric can be understood approximately as an expanded WTe_2 -type layer repeat, with a threefold repeat along the W -

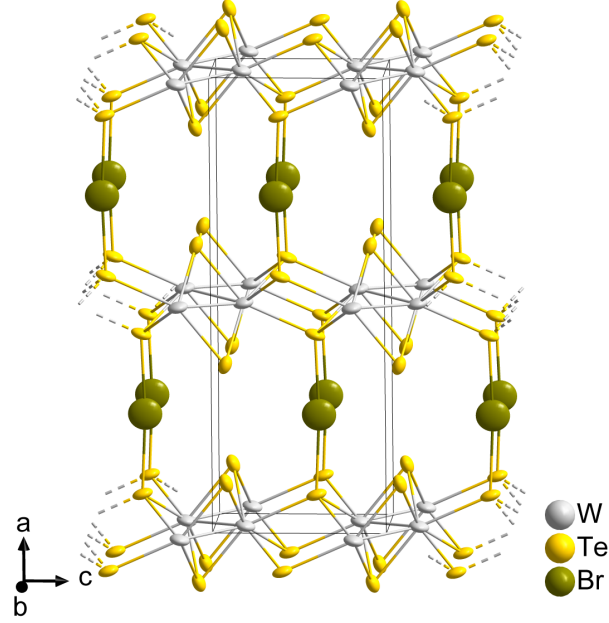


Figure 22: Section of the $\text{WTe}_2\text{Br}_{0.5}$ crystal structure highlighting the position of bromine atoms within the van der Waals gap, with their alignment toward Te1, thereby connecting adjacent WTe_2 layers. Atomic displacement parameters are shown as anisotropic displacement ellipsoids at the 50% probability level.^[165]

W chain direction and an approximately doubled repeat perpendicular to it. In contrast to $\text{WTe}_2\text{Br}_{0.5}$, where all van der Waals gaps are filled in the same way, $\text{WTe}_2\text{Br}_{1.25}$ contains two crystallographically distinct bromine interlayers. One interlayer contains 0.5 Br per WTe_2 formula unit and has an interlayer distance of $10.1573(2) \text{ \AA}$, whereas the second contains 0.75 Br per WTe_2 formula unit and is expanded to $11.3493(2) \text{ \AA}$. The structure is therefore best understood as a staged bromine-rich intercalation compound rather than a uniformly filled derivative.

The less bromine-rich interlayer contains an essentially planar bromine arrangement, but also includes out-of-plane Br_2 -like dumbbells aligned parallel to the b -axis (see Fig. 24). These dumbbells have a Br–Br distance of $3.13(4) \text{ \AA}$ and form short Te–Br contacts of $2.50(3) \text{ \AA}$ to the adjacent WTe_2 layers. Within the same interlayer, the bromine atoms form a rectangular network with Br–Br separations ranging from $2.51(4)$ to $4.42(6) \text{ \AA}$. The corresponding bromine sites show strongly anisotropic displacement parameters, extended mainly within the ac -plane, which indicates pronounced positional flexibility and possibly dynamic disorder.

The more bromine-rich interlayer contains a broader variety of motifs (see Fig. 25). Besides individual bromine atoms in close Te–Br contact with the host layer, with a shortest contact of about $2.48(3) \text{ \AA}$ (Br6 in Fig. 25, orange color), it also contains chain-like bromine arrangements (Fig. 25, green colored atoms) and more complex polybromide-like units located fully within

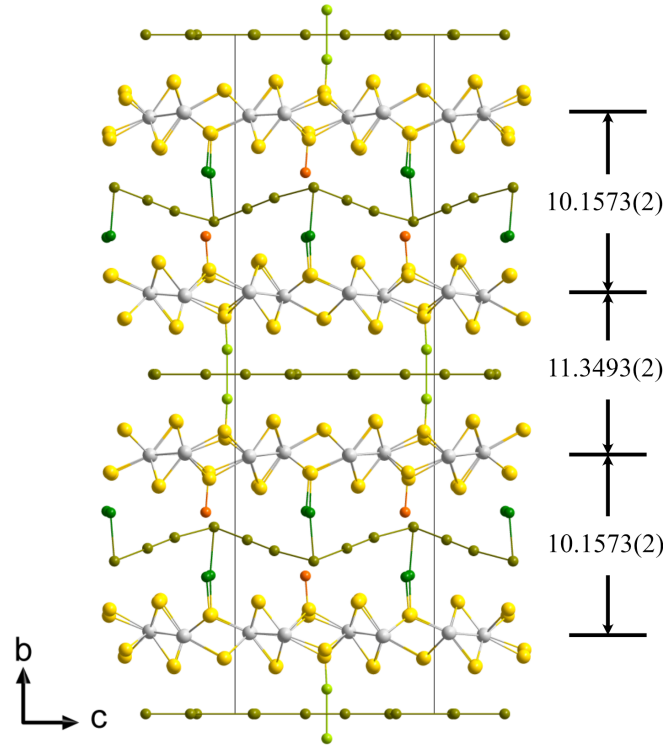


Figure 23: Section of the $\text{WTe}_2\text{Br}_{1.25}$ crystal structure viewed along the a -direction (W: grey, Te: yellow, Br: light green/green/olive/orange). Bromine atoms are shown in different colors to distinguish the individual bromine sites and to highlight the polybromide motifs.^[165]

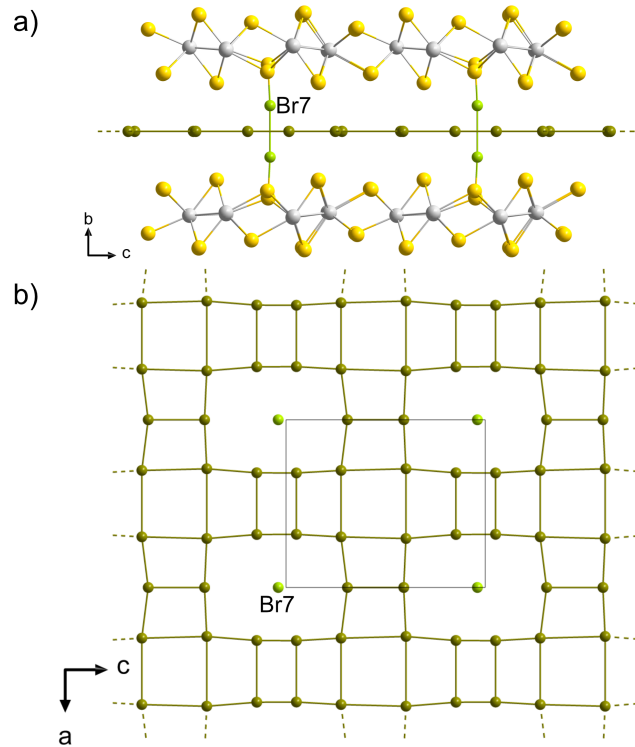


Figure 24: Section of the crystal structure of $\text{WTe}_2\text{Br}_{1.25}$ showing interlayer bromine atoms (0.5 Br per formula unit WTe_2) a) between adjacent WTe_2 layers along the a -axis and b) the same bromine net viewed along the b -direction. (W: grey, Te: yellow, Br: green/olive). The Br_2 dumbbells (Br7) connecting adjacent WTe_2 layers are aligned along the b -axis and highlighted green.^[165]

the interlayer space (Fig. 25, olive colored atoms). In these polybromide motifs, the Br–Br distances span 2.36(3) to 3.56(2) Å, consistent with polybromide bonding. Compared with the more flexible rectangular bromine net, the polybromide sites exhibit less pronounced anisotropic displacement parameters, although they remain slightly enlarged relative to the WTe₂ framework atoms.

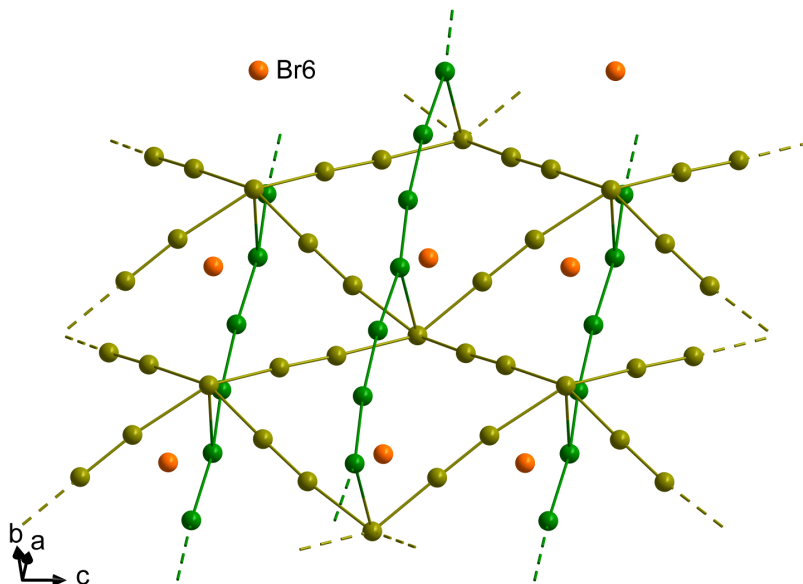


Figure 25: Section of the crystal structure of WTe₂Br_{1.25} showing interlayer bromine atoms (0.5 Br per formula unit WTe₂) a) between adjacent WTe₂ layers along the *a*-axis and b) the same bromine net viewed along the *b*-direction. (W: grey, Te: yellow, Br: green/olive). The Br₂ dumbbells (Br7) connecting adjacent WTe₂ layers are aligned along the *b*-axis and highlighted green.^[165]

The WTe₂ layers remain recognizable in WTe₂Br_{1.25}, but the W–W zigzag chains are much more strongly perturbed than in WTe₂Br_{0.5}. Five consecutive W–W contacts remain in the typical range of 2.771(9)–2.815(9) Å, followed by two distinctly elongated contacts of 2.925(9) and 2.954(9) Å. These longer contacts are associated with directional Te–Br interactions from the neighboring bromine interlayers and are therefore a direct structural response of the host layer to the more complex bromine substructure. This point is particularly well suited for illustration, because the elongated W–W contacts visually mark where the tungsten chain is disrupted by the adjacent bromine motifs (see Fig. 26).

In summary, iodine and bromine intercalation into WTe₂ preserve the layered host framework but generate very different interlayer architectures. WTe₂I is best described as an intrinsically modulated intercalation compound in which the iodine net is directly involved in the electronic structure and imposes a periodic distortion on the otherwise largely preserved WTe₂

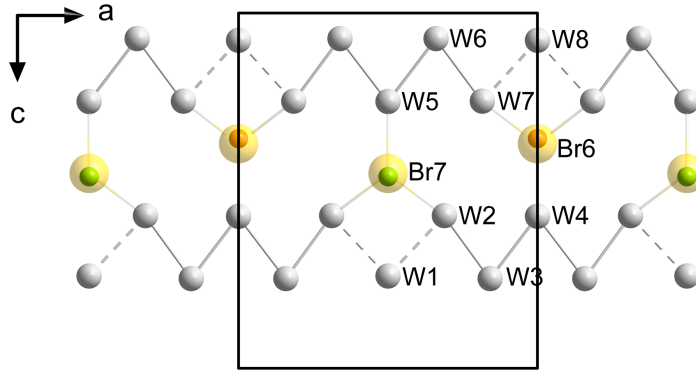


Figure 26: Section of the $\text{WTe}_2\text{Br}_{1.25}$ structure viewed along the b -axis with the unit cell highlighted. For clarity, only one interlayer section in the ac -plane of the tungsten zig-zag chains is shown. Tellurium atoms are omitted, except for Te atoms bonded to the WTe_2 layer as well as Br atoms, which are included. Note that Br7 and Br6 belong to different bromine interlayers, above and below the projected plane of W atoms. Elongated W–W contacts, indicating disruption of the tungsten chain, are highlighted by dashed lines (W: grey, Te: yellow, Br: light green/orange).^[165]

layers. In contrast, WTe_2Br_x is characterized by reversible multistage bromine uptake and release, high guest mobility, and composition-dependent interlayer ordering. Together, these results show how strongly the nature of the halogen controls the balance between modulation, staging, disorder, and host–guest bonding in anionically intercalated WTe_2 .

3.4 A New Modification of TeI_4 Possessing the Crystal Structure Proposed for WI_4 (Publication 4)

The reaction of WTe_2 with iodine had previously been reported to yield WI_4 .^[166] Since this assignment was based on a structure closely related to $\delta\text{-TeI}_4$ and the unusually high reaction temperature of 520°C already appeared questionable for a binary tungsten iodide, the system was re-investigated in detail.^[94,167] Repetition of the reported synthesis did not confirm the formation of tungsten tetraiodide, but instead yielded a new polymorph of tellurium tetraiodide, denoted $\zeta\text{-TeI}_4$. PXRD showed the product to be triclinic and essentially isotypic with the phase previously described as WI_4 . A decisive argument was obtained from the single-crystal refinement: assigning tungsten to the metal sites led to markedly inferior agreement factors, whereas refinement with tellurium gave a substantially improved structural model, demonstrating that the product is in fact TeI_4 and not a tungsten iodide. Structurally, $\zeta\text{-TeI}_4$

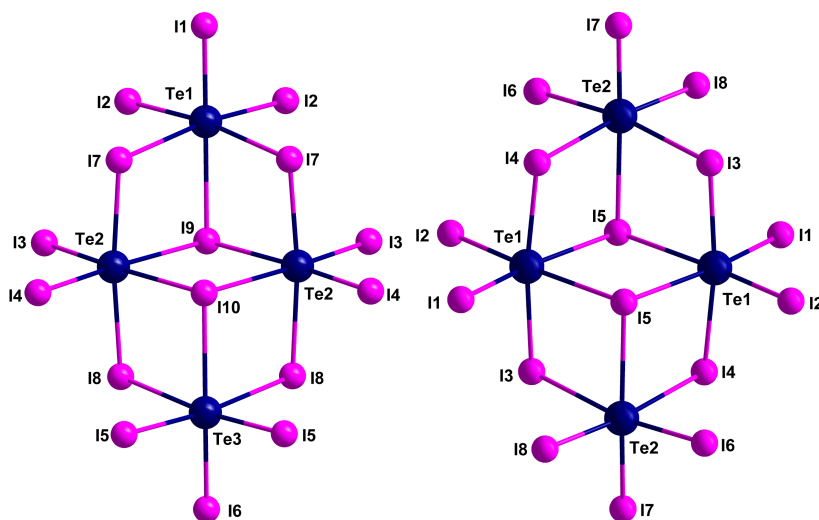


Figure 27: Te_4I_{16} units in $\delta\text{-TeI}_4$ (left) and in $\zeta\text{-TeI}_4$ (right) structures.^[96]

is built from discrete Te_4I_{16} tetramers in which each tellurium atom is surrounded by six iodide ligands in a distorted octahedral environment (see Fig. 27). This fundamental building unit is also known for $\delta\text{-TeI}_4$, so the comparison of both structures is particularly instructive.^[167] While the individual Te-I distances are very similar in the two polymorphs, the symmetry of the tetramers and, more importantly, their packing in the crystal structure differ significantly. In $\zeta\text{-TeI}_4$, the iodine arrangement can be described in terms of a defect CdI_2 -type motif with partially occupied octahedral voids (see Fig. 28), providing a useful structural interpretation of the new modification. Since both $\delta\text{-}$ and $\zeta\text{-TeI}_4$ crystallize from the gas phase, their close relationship becomes especially evident in a direct comparison of the two structure figures. The compositional assignment was corroborated by chemical analyses. Inductively

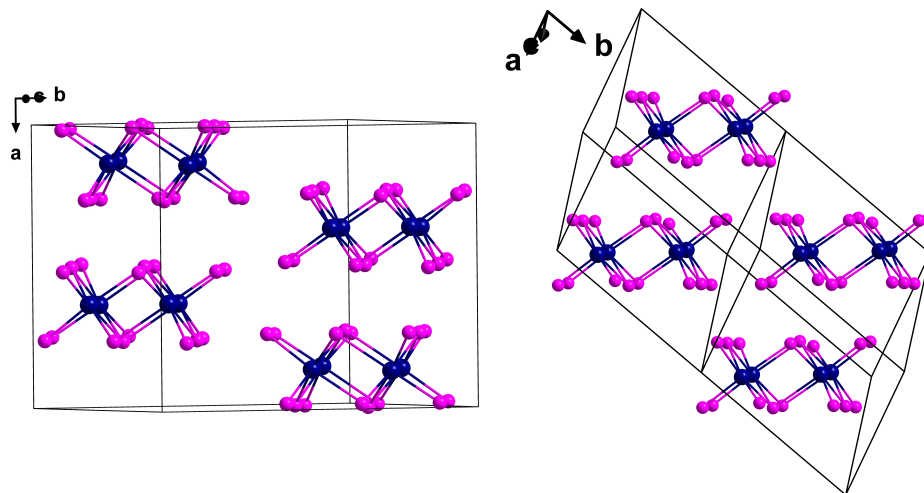


Figure 28: Crystal structures of δ -TeI₄ (top) and ζ -TeI₄ (bottom) with unit cell edges shown.^[96]

coupled plasma optical emission spectroscopy (ICP-OES) gave a Te:I ratio of 1:3.98 with only 0.005(2) % W, and electron microprobe measurements likewise yielded Te:I ratios very close to 1:4, with tungsten detected only in trace amounts at a single measurement spot. These data make a genuine tungsten-containing bulk phase highly unlikely. In addition, DFT calculations on the known TeI₄ polymorphs identified δ -TeI₄ as the thermodynamic ground state, whereas ζ -TeI₄ is metastable and must therefore form under kinetic control.^[168] This interpretation is consistent with sublimation experiments: no spontaneous interconversion between the two modifications was observed, but δ -TeI₄ could be transformed into ζ -TeI₄ at about 200 °C in the presence of small amounts of WTe₂, W(CO)₆, Mo, or Sn. The formation of ζ -TeI₄ is thus best understood as an impurity-assisted gas-phase process. Overall, the study corrects the earlier assignment of WI₄ and shows that the corresponding product is actually a new metastable polymorph of TeI₄. At the same time, it highlights how sensitively gas-phase transport reactions can respond to minor secondary phases and how easily structurally plausible, but chemically incorrect, assignments may arise in halide-rich systems.

3.5 Synthesis and Structural Characterization of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ (Publication 5)

The reaction of WTe_2 with iodine revealed an unexpected transformation from a layered transition-metal dichalcogenide into a discrete tungsten iodide cluster compound. Heating WTe_2 with iodine in a sealed silica ampoule at $250\text{ }^\circ\text{C}$ for two days afforded black, plate-like crystals of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ in high yield, while TeI_4 formed as a volatile side phase and could be removed by sublimation. The formation of an octahedral tungsten iodide cluster at such a comparatively low temperature is remarkable. In established tungsten iodide chemistry, the preparation of binary metal-rich iodides commonly proceeds through stepwise reduction and iodine loss, and the formation of octahedral tungsten clusters is usually associated with higher temperatures and more classical solid-state routes.^[169,170] Against this background, the iodination of WTe_2 opens an unusual low-temperature access to a cluster compound from a layered chalcogenide precursor.

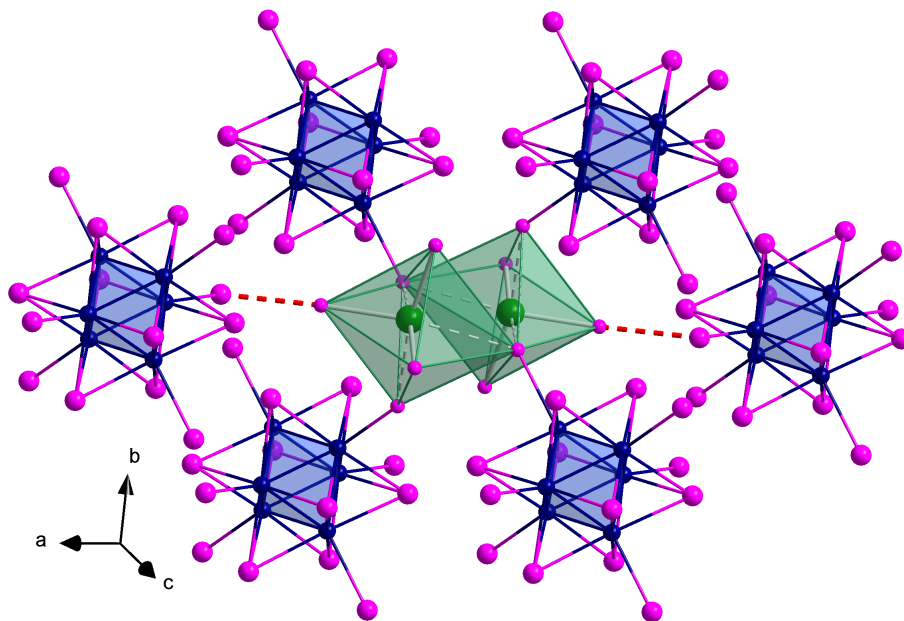


Figure 29: Section of the structure of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$, emphasizing the $[\text{W}_6\text{I}_8\text{I}_6]^{2-}$ cluster and its connectivity to tellurium atoms (green) via outer iodide ligands.^[95]

Single-crystal X-ray diffraction showed that $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ crystallizes in the triclinic space group $P\bar{1}$ and consists of discrete $[\text{W}_6\text{I}_{14}]^{2-}$ cluster anions and $(\text{TeI}_3)^+$ cations. The tungsten atoms form the well-known octahedral W_6 core, surrounded by eight inner iodide ligands and six apical iodide ligands, corresponding to the familiar $[\text{W}_6\text{I}_8\text{I}_6]^{2-}$ motif that is also found

in related inorganic $[\text{W}_6\text{I}_{14}]^{2-}$ salts.^[171] In the title compound, however, this cluster is not combined with simple alkali or organic counterions, but with $(\text{TeI}_3)^+$ cations, which gives rise to a distinctly different crystal packing. The structure can be described as an alternating layered arrangement of cations and cluster anions (see Fig. 29). This layered ordering is not inherited from the parent WTe_2 , but emerges from the ionic packing of the newly formed product.

A central structural feature is the coordination environment of tellurium. Within the cation, tellurium adopts the expected distorted trigonal-pyramidal TeI_3^+ geometry. At the same time, the cation is not fully isolated. Each tellurium atom approaches three apical iodide ligands of neighboring cluster anions, so that the local environment around Te may be described as a strongly distorted octahedron built from three short covalent Te–I bonds and three longer secondary $\text{Te} \cdots \text{I}$ contacts. The primary Te–I distances within the cation lie between 2.745(1) and 2.810(1) Å, whereas the additional contacts to cluster iodides fall in the range from 3.187(2) to 3.531(2) Å. An additional short $\text{I} \cdots \text{I}$ contact of 3.196(1) Å between one iodide of the $(\text{TeI}_3)^+$ unit and an apical cluster iodide further emphasizes that the crystal structure is not merely a simple ionic array, but is stabilized by a network of weak secondary interactions between cationic and anionic substructures. As a result, the title compound occupies an interesting structural position between classical salt-like cluster compounds and more strongly associated halide-rich solids.

Because the crystals are black, unlike many other $[\text{W}_6\text{I}_{14}]^{2-}$ -based compounds, the question arose whether this appearance might reflect defects, partial tellurium substitution within the cluster environment, or a fundamentally altered electronic structure. A crystallographic distinction between tungsten and tellurium substitution within the heavy-atom framework is difficult, so the structural model had to be evaluated in combination with chemical analysis. ICP-OES measurements yielded an average elemental ratio of $\text{W}:\text{Te}:\text{I} = 6:2.24:20.64$, already close to the idealized composition. Electron microprobe measurements on selected crystal areas refined this picture further and gave an average ratio of $\text{W}:\text{Te}:\text{I} = 6:2.17(3):21.0(1)$ for uncoated regions. At the same time, the microprobe study showed that some crystal surfaces carried a tellurium-rich amorphous coating, which explains locally elevated tellurium contents without requiring a bulk deviation from the proposed composition. These analytical results therefore support the formulation $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ and show that the unusual optical appearance is best explained by the intrinsic electronic structure of the compound rather than by extensive Te incorporation into the cluster core.

Density functional theory (DFT) calculations using the HSE06 hybrid functional corrobo-

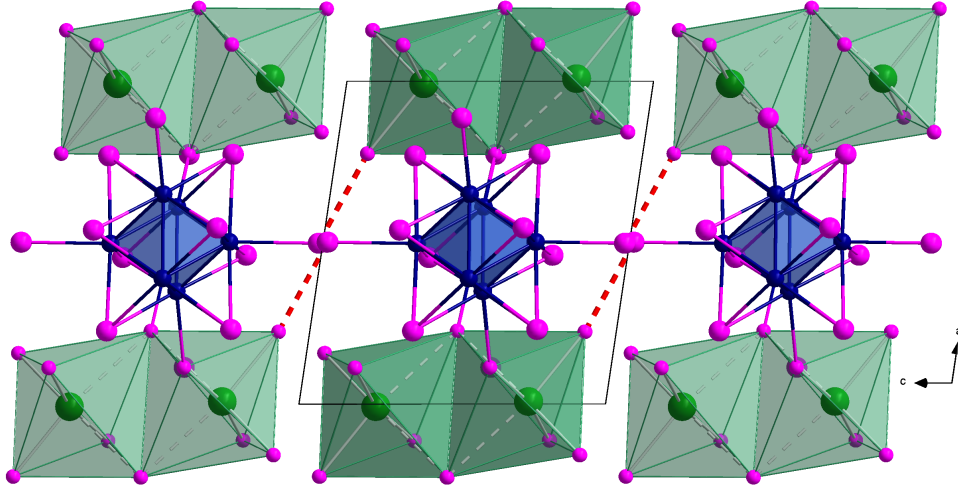


Figure 30: Projection of the crystal structure of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ forming a layered arrangement. Tungsten atoms are shown blue, iodine violet, and tellurium atoms green.^[95]

rated this interpretation and gave a consistent picture of the electronic structure (see Fig. 31). The calculated band structure exhibits rather flat bands, indicating strongly localized electronic states, and reveals an indirect band gap of about 1.8 eV. This value agrees well with the optical estimate from the Tauc evaluation, which gave approximately 1.75 eV. The upper valence band is dominated mainly by W 5*d* and I 5*p* states, whereas the bottom of the conduction band contains substantial Te 5*p* and I 5*p* contributions. This participation of tellurium states near the conduction-band minimum is particularly important, because it provides a plausible explanation for the reduced band gap. In related $[\text{W}_6\text{I}_{14}]^{2-}$ -containing compounds, band gaps are commonly reported in the range of about 2 to 3 eV, and these materials are better known for red phosphorescence and related photophysical properties than for such strong visible-light absorption.^[172,173] In $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$, by contrast, the Te-containing cation is not electronically innocent, but shifts the low-lying unoccupied states in a way that narrows the gap and accounts for the black color of the crystals.

Overall, the formation of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ demonstrates that the iodination of WTe_2 does not only lead to topochemical intercalation phenomena or simple tellurium iodides, but can also trigger a reconstructive pathway toward discrete metal-halide clusters under unexpectedly mild conditions. The compound combines three aspects that make it particularly noteworthy in the context of this dissertation: first, it documents the chemical flexibility of WTe_2 un-

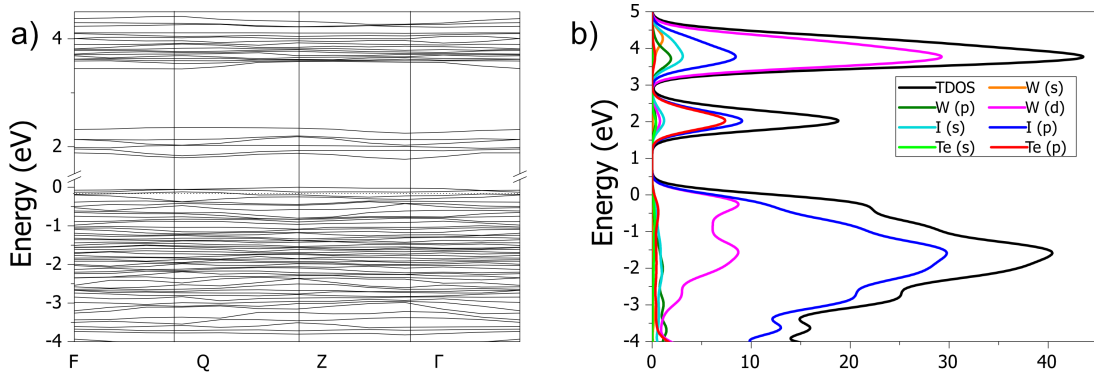


Figure 31: Calculated electronic band structure (a) and partial and total density of states (TDOS) (b) of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ based on HSE06 hybrid functional. Special points in the band structure of the Brillouin zone are Γ : (0,0,0), F: (0, 0.5, 0), Q: (0, 0.5, 0.5) and Z: (0, 0, 0.5).^[95]

der halogenating conditions; second, it links tungsten iodide cluster chemistry with tellurium iodide cations in an uncommon layered ionic arrangement; and third, it shows how the incorporation of tellurium-containing cations can substantially modify the electronic structure of a known cluster motif. The title compound therefore marks an instructive transition point between layered chalcogenide chemistry, halogen-driven decomposition, and classical tungsten iodide cluster chemistry.

3.6 Ta₄SBr₁₁: A Cluster Mott Insulator with Corrugated, Van der Waals Layered Structure (Publication 6)

Ta₄SBr₁₁ was obtained from a comproportionation reaction of tantalum, tantalum(V) bromide, and sulfur at 400 °C. Crystal growth was significantly improved by adding CsBr as a flux, which yielded platelet-like crystals with metallic luster. Their morphology already reflects the layered character of the compound.

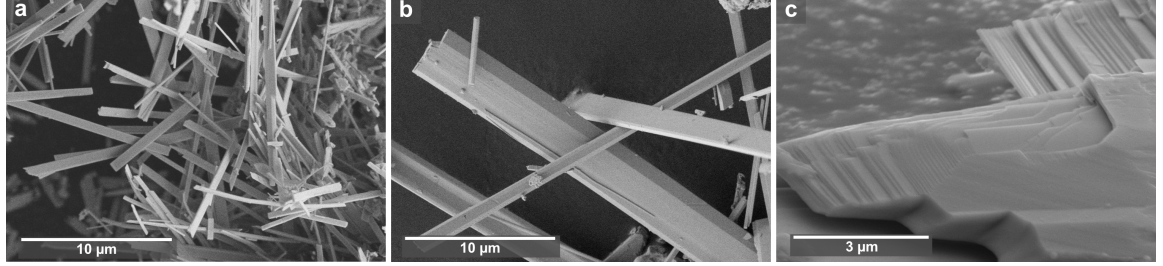


Figure 32: scanning electron microscopy (SEM) micrographs of Ta₄SBr₁₁ crystals obtained from the direct synthesis (a) and grown from a flux of CsBr (b and c).^[174]

The crystal structure is based on butterfly-shaped [Ta₄(μ₄-S)] cluster units. These clusters are linked by bromide ligands into corrugated layers, which extend in the *ab*-plane and interact only weakly with one another. The resulting arrangement can be described as a corrugated van der Waals layered structure. Single-crystal X-ray diffraction (SC-XRD) further showed that the structure is intrinsically disordered. The average structure can be refined in the space group *Pmmn*, while diffuse scattering indicates additional local ordering effects and different possible stacking arrangements of the layers.

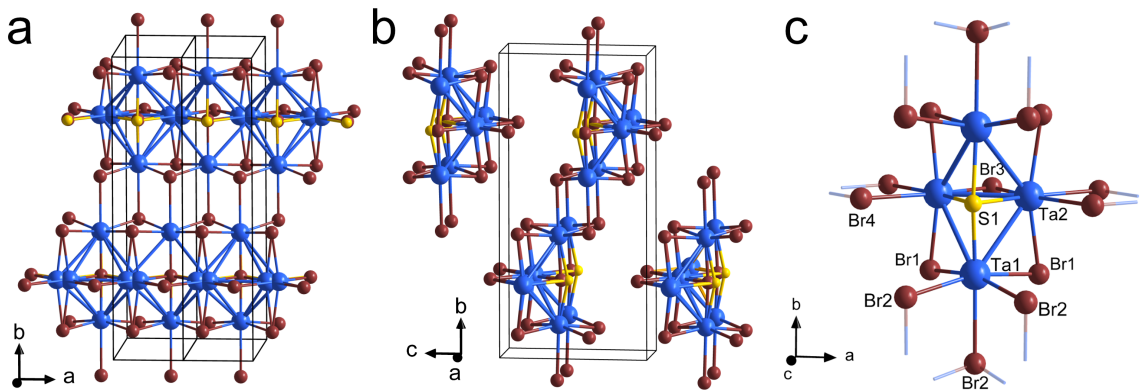


Figure 33: Refined average structure of Ta₄SBr₁₁ in two projections along *c*- and *b*-direction (a and b) and the characteristic [Ta₄(μ₄-S)] butterfly cluster in the structure of Ta₄SBr₁₁ with its connectivity pattern implied by broken bonds (c). Tantalum atoms are depicted in blue, bromine in brown and sulfur in yellow.^[174]

Each Ta₄ cluster contains seven cluster electrons and therefore one unpaired electron. This already suggests that the electronic structure should not be described by a simple closed-shell

picture. DRIFT and conductivity measurements indeed show semiconducting behavior. In the Arrhenius plot, two linear regimes are observed, indicating different activation energies above and below about 100 K. However, a low-temperature structure refinement at 80 K did not reveal any structural phase transition. The change in transport behavior is therefore not accompanied by a symmetry change of the crystal structure.

Magnetic susceptibility measurements show Curie–Weiss behavior above about 100 K and indicate predominantly antiferromagnetic interactions between the cluster moments. This is consistent with the presence of one unpaired electron per Ta_4 unit. DFT calculations initially yielded metallic band structures for the different structural variants. Only when antiferromagnetic ordering and a Hubbard- U correction were included did a small band gap open in one of the tested models, in good agreement with the experimental observations. The calculations therefore support the view that electronic correlations are essential for understanding $\text{Ta}_4\text{SBr}_{11}$.

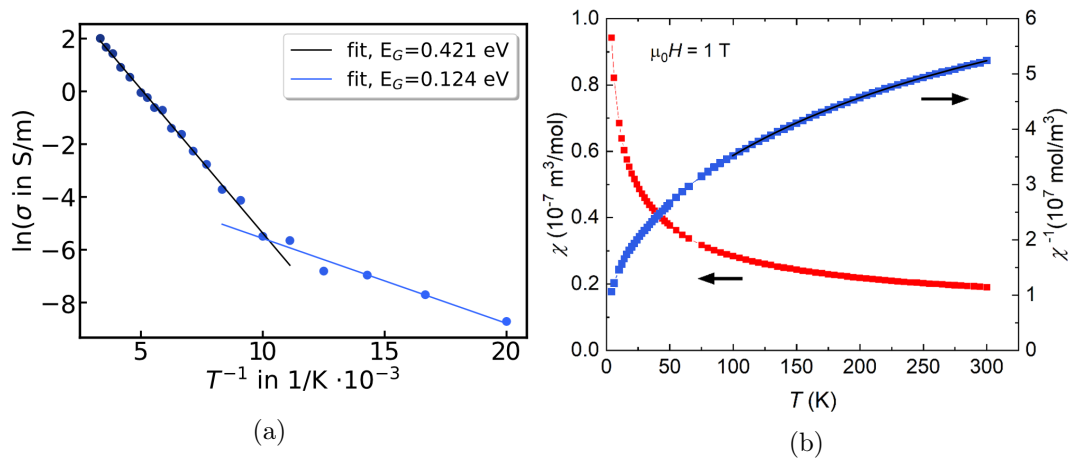


Figure 34: a) Arrhenius-plot of the temperature-dependent conductivity. Two regimes can be identified and fitted linearly to determine the electronic band gap. b) Temperature dependence of magnetic susceptibility (red squares) and inverse magnetic susceptibility (blue squares) with plotted modified Curie-Weiss fit.^[174]

Overall, $\text{Ta}_4\text{SBr}_{11}$ combines a corrugated layered structure with a seven-electron cluster motif and antiferromagnetic correlations. The experimental and theoretical results consistently indicate that it is a small-gap semiconductor whose gap cannot be explained by simple band theory alone. Instead, $\text{Ta}_4\text{SBr}_{11}$ is best described as a likely cluster Mott insulator.

3.7 The family of tetranuclear $\text{Nb}_4\text{OI}_{12-x}$ clusters ($x = 0, 1, 2$): from the molecular $\text{Nb}_4\text{OI}_{12}$ cluster to extended chains and layers (Publication 7)

A new family of tetranuclear niobium oxyiodides with the compositions $\text{Nb}_4\text{OI}_{12}$, $\text{Nb}_4\text{OI}_{11}$, and $\text{Nb}_4\text{OI}_{10}$, all based on an oxygen-centered $[\text{Nb}_4\text{O}]$ cluster core, was obtained by mild reduction of NbI_4 with $\text{Li}_2(\text{CN}_2)$ in the presence of Li_2O . These compounds establish a continuous structural sequence from isolated clusters in molecular $\text{Nb}_4\text{OI}_{12}$, through one-dimensional string structures in $\text{Nb}_4\text{OI}_{11}$, to two-dimensional layers in $\text{Nb}_4\text{OI}_{10}$ (see Fig. 35).

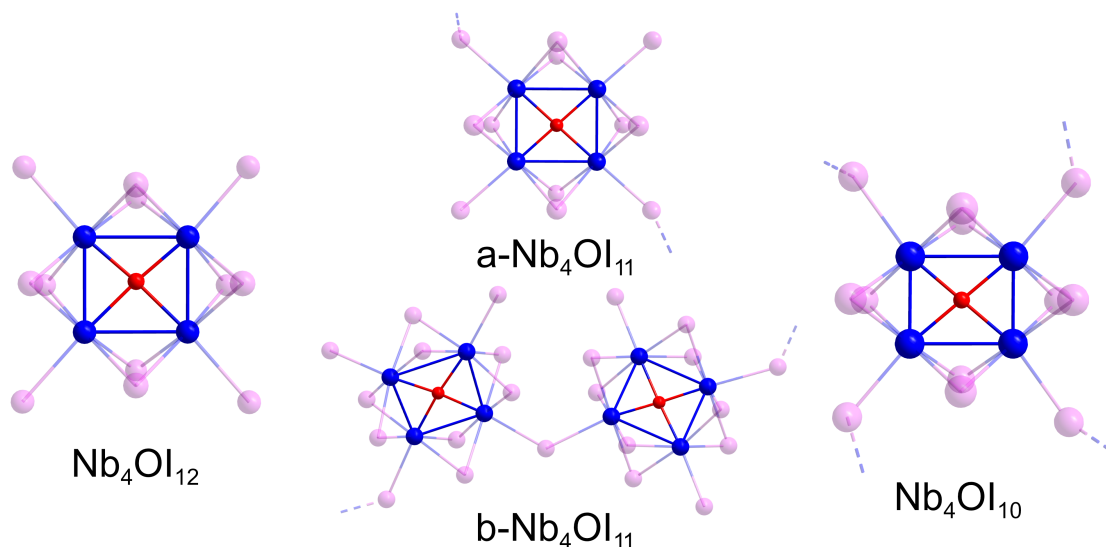


Figure 35: Sections of the crystal structures of the $\text{Nb}_4\text{OI}_{12-x}$ family, showing the smallest cluster units and their connectivity to neighboring clusters as indicated by dotted lines.

The compounds were obtained under carefully adjusted reaction conditions. Small variations in reagent ratio and temperature program were sufficient to change the crystallizing product, which reflects the sensitivity of the Nb–O–I system under heterogeneous reaction conditions. $\text{Nb}_4\text{OI}_{12}$ crystallizes as a molecular phase built from a nearly rectangular $[\text{Nb}_4\text{O}]$ core with eight bridging and four terminal iodide ligands. The two $\text{Nb}_4\text{OI}_{11}$ modifications both form iodide-bridged string structures and therefore represent one-dimensional derivatives of the same cluster motif, whereas $\text{Nb}_4\text{OI}_{10}$ adopts a layered structure as the two-dimensional end member of the series.

A central result of the work is the structural comparison across the whole series. In all compounds, the $[\text{Nb}_4\text{O}]$ unit remains preserved, but the iodide content, connectivity, and geometry change systematically. $\text{Nb}_4\text{OI}_{12}$ contains a nearly rectangular cluster core. In $\text{a-Nb}_4\text{OI}_{11}$, the clusters are linked in trans fashion into strings, whereas $\text{b-Nb}_4\text{OI}_{11}$ shows alternating cis and trans connections, which lead to a more pronounced distortion of the cluster core. In com-

parison with these phases, layered $\text{Nb}_4\text{OI}_{10}$ represents the most strongly condensed member of the series.

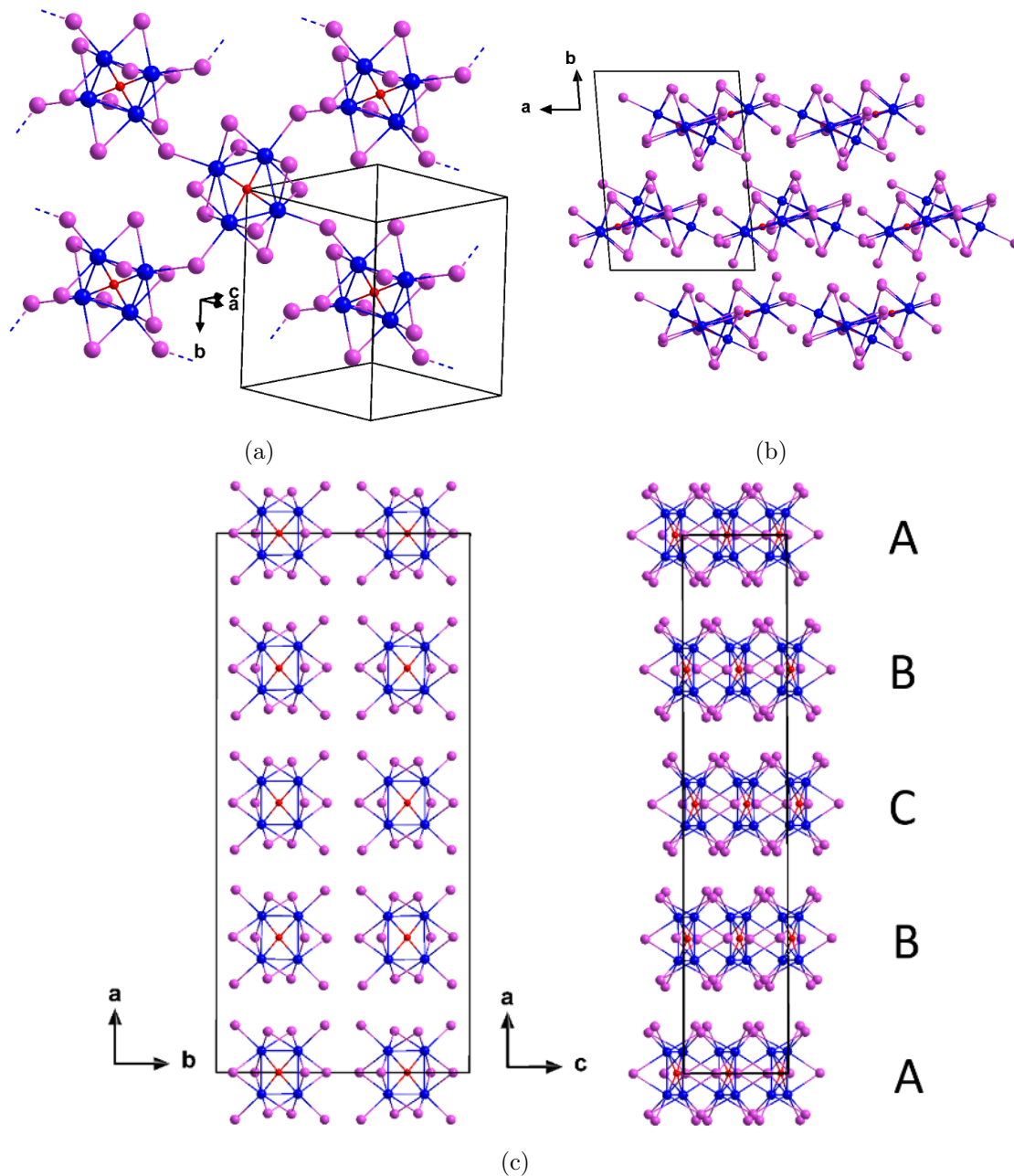


Figure 36: Sections of the crystal structures highlighting the connectivity of a) $\text{Nb}_4\text{OI}_{10}$,^[175] b) $b\text{-Nb}_4\text{OI}_{11}$ viewed along $[001]$, and c) $\text{Nb}_4\text{OI}_{12}$ viewed along c - (left) and b - (right) direction.^[176]

The Nb–Nb distances follow this trend in a systematic way. In molecular $\text{Nb}_4\text{OI}_{12}$, the $[\text{Nb}_4\text{O}]$ core shows short Nb–Nb distances of 2.793(3)–2.807(3) Å and longer contacts of 3.029(7)–3.051(3) Å. In the two $\text{Nb}_4\text{OI}_{11}$ modifications, the short Nb–Nb distances decrease to 2.7368(6)–2.7584(7) Å, whereas the longer distances remain at 3.0375(6)–3.0423(6) Å overall, although $b\text{-Nb}_4\text{OI}_{11}$ shows a stronger distortion for the cis-connected clusters. In layered

$\text{Nb}_4\text{OI}_{10}$, finally, the shortest Nb–Nb distance reaches $2.6232(2) \text{ \AA}$, while the long Nb–Nb distance is $3.1042(2) \text{ \AA}$. Overall, the longer Nb–Nb contacts remain comparatively similar, whereas the shorter Nb–Nb distances decrease continuously from $\text{Nb}_4\text{OI}_{12}$ to $\text{Nb}_4\text{OI}_{10}$. This contraction is consistent with an increasing number of electrons available for Nb–Nb bonding and was discussed in terms of a second-order Jahn-Teller (SOJT) distortion. The structural changes in the $\text{Nb}_4\text{OI}_{12-x}$ family are therefore closely connected to the electronic situation within the tetranuclear cluster.

For $\text{b-Nb}_4\text{OI}_{11}$, electrical measurements revealed semiconducting behavior. At 300 K, single crystals show a conductivity on the order of 10^{-3} S m^{-1} , and the temperature dependence corresponds to an estimated activation energy of about 0.4 eV. In addition, a photoresponse under 779 nm irradiation was observed (see Fig. 37). These results show that the structural variation within the $\text{Nb}_4\text{OI}_{12-x}$ family is accompanied by corresponding changes in the electronic properties.

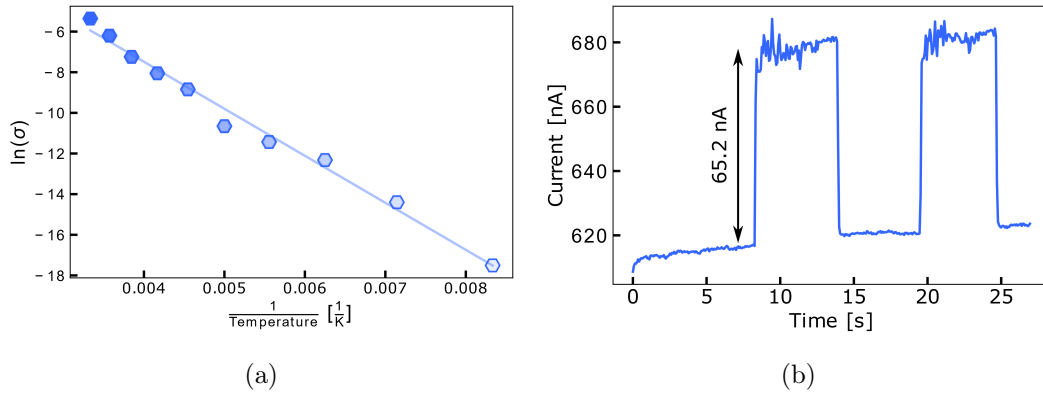


Figure 37: a) Arrhenius plot of the electrical conductivity of $\text{b-Nb}_4\text{OI}_{11}$, with 20 K temperature steps between 120–300 K. The blue line represents a linear Arrhenius fit to the data. b) Photoresponse of $\text{b-Nb}_4\text{OI}_{11}$ at 300 K toward a 779 nm laser illumination with 1 V bias applied.^[176]

Overall, the work establishes this family of tetranuclear niobium oxyiodides as a structurally coherent group in which the same oxygen-centered $[\text{Nb}_4\text{O}]$ cluster core gives rise to molecular, one-dimensional, and two-dimensional arrangements. The study therefore provides a concise picture of how small changes in composition lead to systematic changes in cluster connectivity, distortion, and semiconducting behavior.

3.8 Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicentre Nb-Nb bonding (Publication 8)

The reaction of NbI_4 with $\text{Li}_2(\text{CN}_2)$ and Li_2O gives a highly sensitive heterogeneous system in which small changes in temperature and reaction time are sufficient to redirect cluster formation. At 300 °C, an unidentified crystalline phase was obtained together with LiI , NbOI_2 , and amorphous material. Heating to 400 °C for 1 h yielded $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, whereas a prolonged treatment at the same temperature produced $\text{Nb}_5\text{O}_4\text{I}_{11}$. At 500 °C for 1 h, crystals of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$ formed on the ampoule wall, while longer heating led instead to $\text{Nb}_4\text{OI}_{10}$. Quenching experiments further supported the participation of a reactive gaseous intermediate, since black droplets appeared on the ampoule wall and transformed at room temperature into dark red filamentous crystallites that decomposed after a short time.

A central result of the study is the identification of two new oxygen-stabilized niobium cluster architectures, $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$, both structurally related to the previously known $[\text{Nb}_5\text{O}_4]$ motif.^[175] In $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, the $[\text{Nb}_7\text{O}_5]$ core can be understood as an expansion of the $[\text{Nb}_5\text{O}_4]$ unit by two additional niobium atoms and one oxygen atom. The cluster contains a central niobium atom in a trigonal-prismatic environment of six surrounding niobium atoms. This arrangement leads to six short Nb–Nb contacts of 2.7883(7) and 2.8050(4) Å between the central and outer niobium atoms, whereas the Nb1–Nb3 separations are distinctly longer at 3.0667(6) Å. The local bonding pattern therefore already indicates that the central atom plays a key role in stabilizing the expanded cluster core.

The iodide coordination of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ may be described as $(\text{Nb}_7\text{O}_5\text{I}_4)^{\text{i}}\text{I}_4^{\text{a}}\text{I}_{12/2}^{\text{a-a}}$, comprising four edge-capping, four terminal, and twelve bridging iodide ligands (see Fig. 38). These bridges connect each $[\text{Nb}_7\text{O}_5]$ cluster to six neighboring clusters and generate a three-dimensional framework. In addition, the structure is stabilized by three lithium ions and one further iodide ion. The lithium atoms occupy square-pyramidal coordination environments built from four cluster-bound iodides and the additional iodide anion. Thus, the structural role of lithium is not to form an independent substructure, but to support the extended iodide framework around the niobium cluster units.

The second compound, $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$, is closely related but shows how the addition of only one more niobium atom changes the connectivity considerably. Its $[\text{Nb}_8\text{O}_5]$ core arises from the $[\text{Nb}_7\text{O}_5]$ motif through addition of one niobium atom at the edge of the $[\text{Nb}_5\text{O}_4]$ base. The Nb–Nb distances from the central Nb2 atom to the surrounding niobium atoms remain short, ranging from 2.7911(3) to 2.8600(7) Å, whereas the contacts between outer

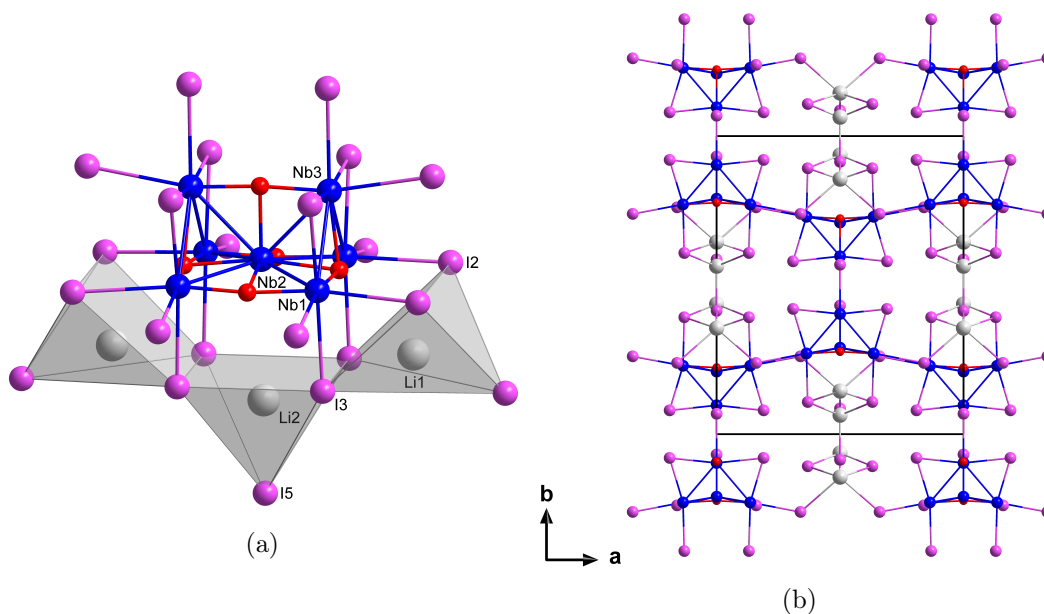


Figure 38: a) Structure of the $[\text{Nb}_7\text{O}_5]$ cluster core inside $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ with highlighted square-pyramidal coordination environment of lithium atoms (grey). b) Projection of the crystal structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, looking along the c -axis. Niobium atoms are shown in blue, oxygen in red, iodine in pink and lithium in grey.^[177]

niobium atoms are longer at 2.9981(6) to 3.1812(7) Å. The bond to the additional Nb5 atom, 3.1418(7) Å, falls into the same longer-distance regime. In this way, the $[\text{Nb}_8\text{O}_5]$ core preserves the basic bonding hierarchy of the $[\text{Nb}_7\text{O}_5]$ cluster, but modifies the overall cluster shape and its linkage to neighboring units.

This structural extension is accompanied by a clear change in iodide coordination and network dimensionality. In $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$, the coordination environment can be formulated as $(\text{Nb}_8\text{O}_5\text{I}_8^{\text{i}})\text{I}_5^{\text{a-a}}$, with eight edge-capping, five terminal, and eight bridging iodide ligands (see Fig. 39a). Because the number of bridging connections is reduced, each cluster is linked only to four neighboring clusters instead of six. As a consequence, the three-dimensional framework observed for $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ collapses into a layered arrangement with zig-zag layers extending in the ab plane (see Fig. 39b). Between these layers, channels are formed that accommodate NbI_5 units. These guests show a certain degree of disorder, which was attributed to a slight excess of iodine and the possible presence of polyiodide-like species in the interlayer region. The structural chemistry therefore shifts from a framework compound to a layered host-guest architecture once the cluster core is enlarged from $[\text{Nb}_7\text{O}_5]$ to $[\text{Nb}_8\text{O}_5]$.

Additional support for the structural characterization of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ was provided by scanning electron microscopy and EDX measurements. The crystals show a rod-like morphology with well-defined edges, and EDX gave an average Nb:I ratio of 7:15.2(6), in good agreement with the refined composition. Although this analytical result is limited to the

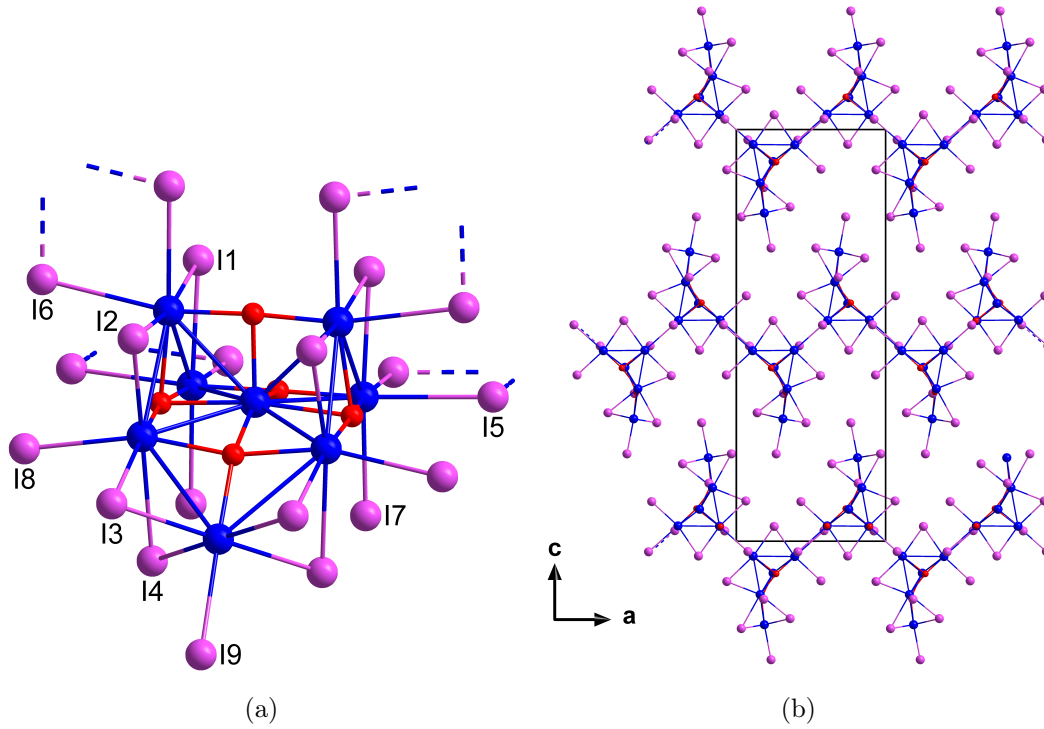


Figure 39: a) Iodide coordination of the $[\text{Nb}_8\text{O}_5]$ cluster core with eight iodide atoms with bridging functionality (indicated by dashed lines) connecting to four adjacent clusters. b) Projected structure with the $\text{Nb}_8\text{O}_5\text{I}_{17}$ section of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$. The NbI_5 molecules between the layers are omitted for clarity. Niobium atoms are colored in blue, oxygen in red and iodine in pink.^[177]

lithium-containing phase, it supports the structural model derived from single-crystal diffraction.

The discussion of bonding in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ was extended by DFT and electron localization function (ELF) calculations. The calculated band structure contains seven mainly metal-centered bands below the Fermi level, corresponding to 13 electrons available for Nb–Nb bonding within one $[\text{Nb}_7\text{O}_5]$ cluster (see Fig. 40a). Several of these bands cross the Fermi level, which indicates that the electron distribution cannot be assigned to simple localized two-center bonds only. In addition to the dominant niobium contribution, oxygen states also contribute below the Fermi level, pointing to partial Nb–O covalency. This interpretation is supported by the ELF, which shows electron density extending from oxygen into the Nb–Nb bonding region and pronounced density between Nb1, Nb2, and Nb3 (see Fig. 40b). The bonding in the cluster is therefore best described as a combination of conventional Nb–Nb interactions and multicenter bonding with oxygen participation. This can be interpreted as four three-centered bonds in addition to four Nb–Nb bonds containing some oxygen admixture, highlighting the important role of Nb d and O p orbital mixing in stabilizing the expanded cluster core.

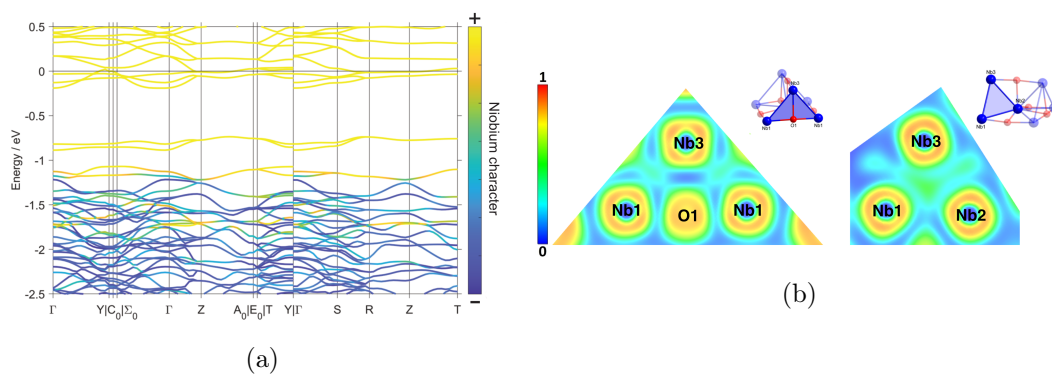


Figure 40: a) DFT-calculated electronic band structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ with bands colored by their niobium character. Special points in and paths through the Brillouin zone were chosen following the literature.^[158] b) Electron localization functions of the $[\text{Nb}_7\text{O}_5]$ cluster core in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$.^[177]

Overall, the study shows that the reaction system based on NbI_4 , $\text{Li}_2(\text{CN}_2)$, and Li_2O gives access to closely related but structurally distinct niobium oxyiodide clusters whose formation is controlled by subtle changes in reaction conditions. The two new compounds extend the known series of niobium oxyiodide cluster cores from $[\text{Nb}_4\text{O}]$ and $[\text{Nb}_5\text{O}_4]$ to $[\text{Nb}_7\text{O}_5]$ and $[\text{Nb}_8\text{O}_5]$ (see Fig. 41), while also demonstrating how a small increase in cluster nuclearity can change the connectivity from a three-dimensional framework to a layered host–guest structure. At the same time, the electronic-structure analysis shows that bonding within the $[\text{Nb}_7\text{O}_5]$ core is distinctly multicenter in nature and cannot be reduced to a simple count of isolated Nb–Nb bonds.

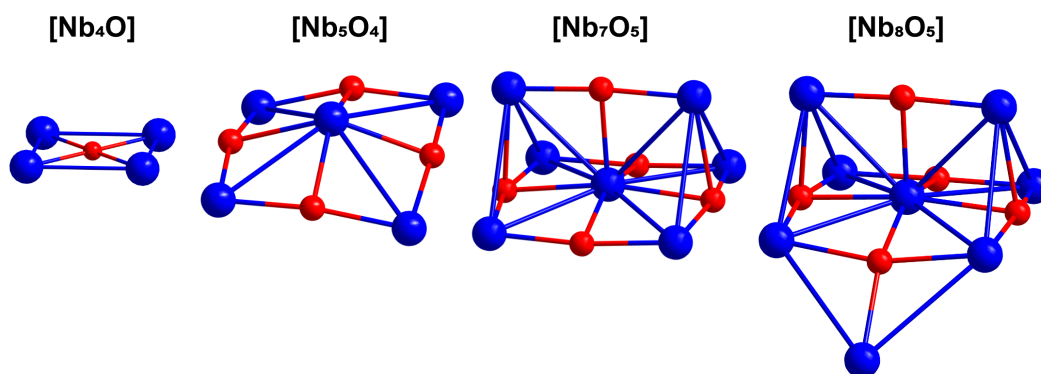


Figure 41: The expansion of cluster architectures of niobium oxide cluster cores in various niobium oxyiodides.^[177]

3.9 Hydrothermal Synthesis and Characterization of the Melamine-Based Second-Harmonic Generation Material $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ (Publication 9)

The hydrothermal reaction of HgCl_2 with melamine yielded $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ as a phase-pure, block-shaped material whose crystal structure is directly linked to its nonlinear optical behavior. Single-crystal X-ray diffraction showed that the compound crystallizes in the polar monoclinic space group $C2$. Structurally, it consists of alternating HgCl_2 layers and ordered melamine molecules stacked along the a -axis, giving rise to a distinctly polar layered arrangement (see Fig. 42).

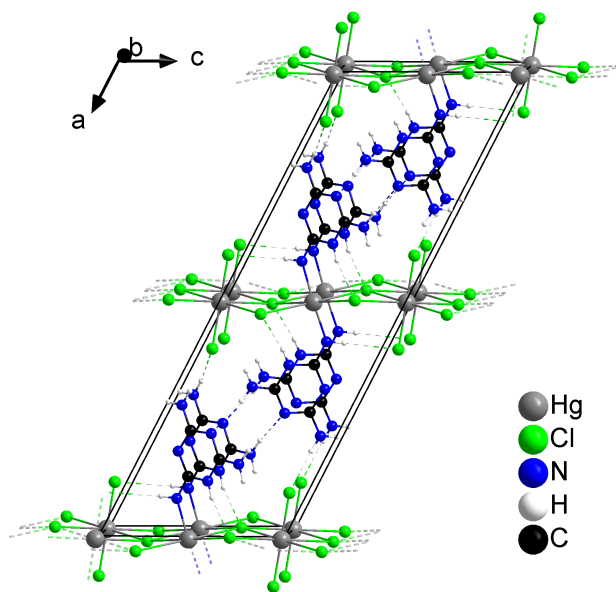


Figure 42: Section of the $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ crystal structure with viewing direction along the b -axis.^[178]

A central point of the structure discussion is that the diffraction data can at first be approximated by a higher-symmetry, centrosymmetric average model. In that description, the melamine molecules appear disordered over two symmetry-equivalent positions (see Fig. 43). Such a model, however, is incompatible with the experimentally observed second-harmonic generation (SHG) property. Refinement in the non-centrosymmetric space group therefore provides the chemically and physically more meaningful description. The crystals further refine as an inversion twin with a Flack parameter close to 0.5, which explains the pseudo-centrosymmetric diffraction behavior while remaining fully consistent with the SHG response.

The coordination environment around mercury is best described as distorted octahedral (see Fig. 44). Within the inorganic layer, bridging chloride ligands connect adjacent Hg centers

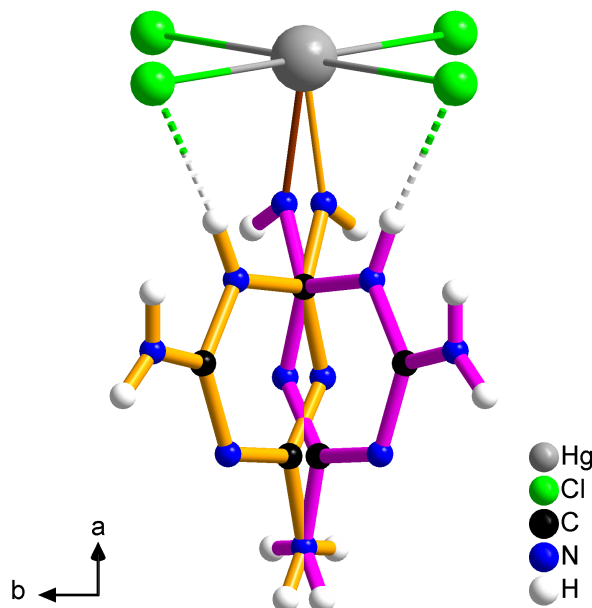


Figure 43: Section of the $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ crystal structure derived in $C2/m$ with disordered melamine molecules. The two possible position are highlighted by different bond colors (yellow and pink).^[178]

and give comparatively long Hg–Cl2 contacts of 3.026(5)–3.102(5) Å, with Cl2–Hg–Cl2 angles between 82.04(5) and 98.63(5)°. The apical positions of the distorted octahedra are occupied by terminal ligands on opposite sides of the inorganic layer, with Cl1 coordinated to Hg1 and the nitrogen atom N1 of melamine coordinated to Hg2. Accordingly, the Hg1–Cl1 distance is 2.331(2) Å, while Hg2 is coordinated by N1 with an Hg2–N1 distance of 2.0262(6) Å. This coordination motif is accompanied by a rearrangement of the hydrogen positions within the melamine molecule, in which the proton originally associated with the coordinating nitrogen N1 is shifted to another ring nitrogen N5. As a result, the structure is stabilized not only by Hg–N coordination, but also by an extended hydrogen-bonding network within and between the organic and inorganic parts of the structure. The combination of distorted HgCl_2 units, ordered melamine ligands, and hydrogen bonding therefore stabilizes the polar architecture required for second-order nonlinear optical activity.

Scanning electron microscopy showed that the product forms highly uniform block-shaped crystals with typical dimensions of about 30–50 μm in length and 5–10 μm in width. The images also reveal the layered character of the compound, which is in good agreement with the crystallographic model. Powder X-ray diffraction confirmed the phase purity of the bulk material. For comparison, the related compound $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$ was also obtained and structurally characterized. In this phase, mercury occurs as Hg_2^{2+} dumbbells with a short Hg–Hg distance of 2.5543(1) Å. These dimers are linked by chloride ligands and melamine into one-

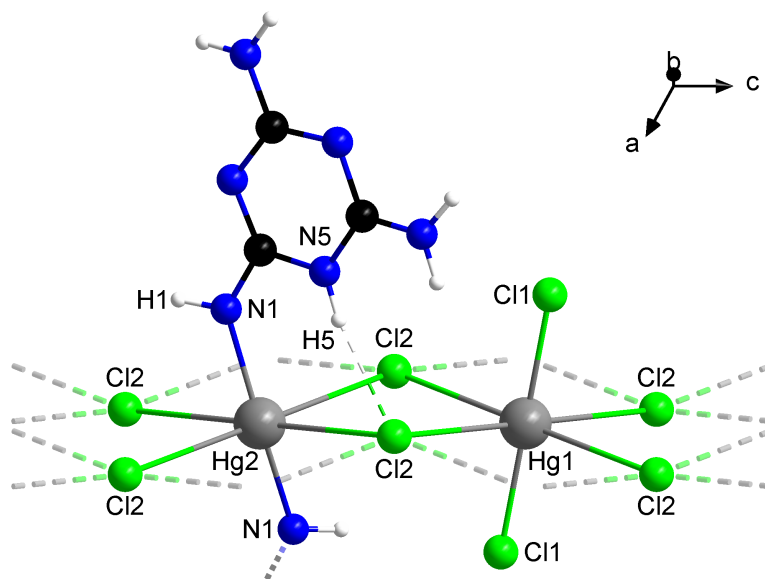


Figure 44: Section of the $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ crystal structure highlighting the HgCl_2 layers and melamine coordination to the mercury atoms.^[178]

dimensional chains. Although this second compound crystallizes in the centrosymmetric space group $P\bar{1}$ and therefore cannot exhibit SHG, it serves as a useful structural and spectroscopic reference because it illustrates how a different mercury oxidation state and connectivity can pattern lead away from the polar layered arrangement found in $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$.

Thermogravimetric analysis shows no significant mass loss below about 230 °C, indicating that the material is thermally robust and does not contain relevant amounts of incorporated solvent or volatile impurities. Above this temperature, decomposition proceeds in several steps, although the individual products could not be assigned unambiguously.

The additional spectroscopic characterization supports this structural model. Solid-state ^1H MAS-NMR spectroscopy resolves three distinct proton environments (see Fig. 45). The most intense resonance at 5.5 ppm is assigned to the primary amine protons H2 and H3, while the signal at 12.2 ppm corresponds to the proton H5 involved in hydrogen bonding to chloride. A broader resonance at 8.8 ppm is attributed to the proton H1 on the nitrogen atom that is directly linked, through coordination, to mercury. The NMR data therefore independently support the proton rearrangement inferred from the crystal structure.

The infrared spectra likewise confirm the coordination mode of melamine. Characteristic deformation vibrations of C–N–C and N–C–N units, as well as C–N and N–H stretching modes, are observed for $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$. In particular, the presence of an N–H stretching vibration indicates that mercury is coordinated by an external ring nitrogen rather than

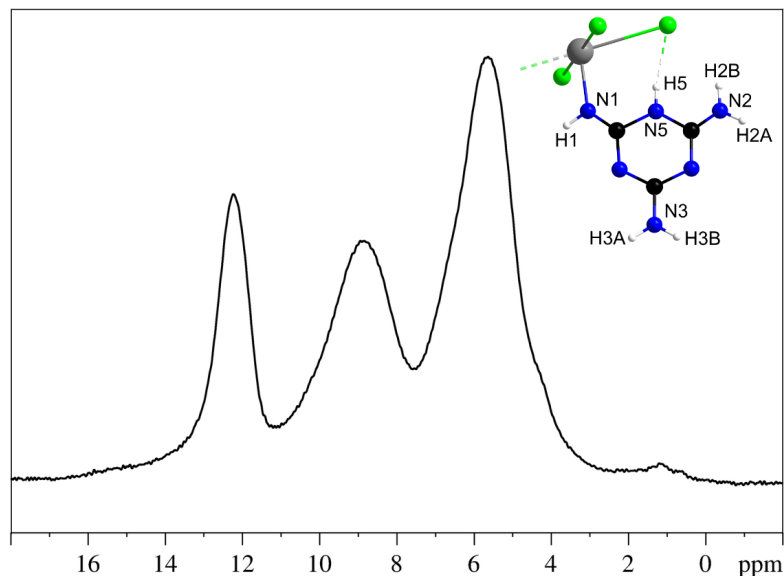


Figure 45: ^1H MAS NMR spectrum of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$.^[178]

by an inner nitrogen atom. This differs from the spectrum of $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$, in which the corresponding N–H vibration is absent because mercury is bound differently within the melamine environment. Taken together, the NMR and IR results are therefore not only complementary to the structure refinement, but also important for distinguishing the two mercury melamine chlorides spectroscopically.

The optical measurements show that $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ is a wide-band-gap material. Diffuse reflectance UV/Vis spectroscopy combined with Tauc evaluation gives a direct band gap of 4.49 eV and an indirect band gap of 4.39 eV, in agreement with the colorless and transparent appearance of the crystals. Photoluminescence measurements under 332 nm excitation reveal a broad whitish emission centered at about 490 nm at low temperatures. This emission is fully quenched above about 350 K. An additional weaker band around 570 nm is present, but its origin remains unclear. The broad character of the emission fits well with known mercury-containing compounds and suggests that the excited states are strongly broadened and not associated with narrow, highly localized emissive centers.

The nonlinear optical measurements are the key functional result of the study. SHG microscopy shows that $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ generates a second-harmonic signal of approximately the same magnitude as $\beta\text{-BaB}_2\text{O}_4$. Spatially resolved scans reveal local hot spots of enhanced SHG intensity on the crystal surfaces, but the overall signal level remains clearly comparable to the reference. The excitation-power dependence yields slopes close to 2 in a double-logarithmic representation, confirming that the detected signal indeed arises from a second-order process (see Fig. 46). These measurements show that the non-centrosymmetric crystal structure is not

only crystallographically plausible, but also functionally expressed in a strong macroscopic SHG response.

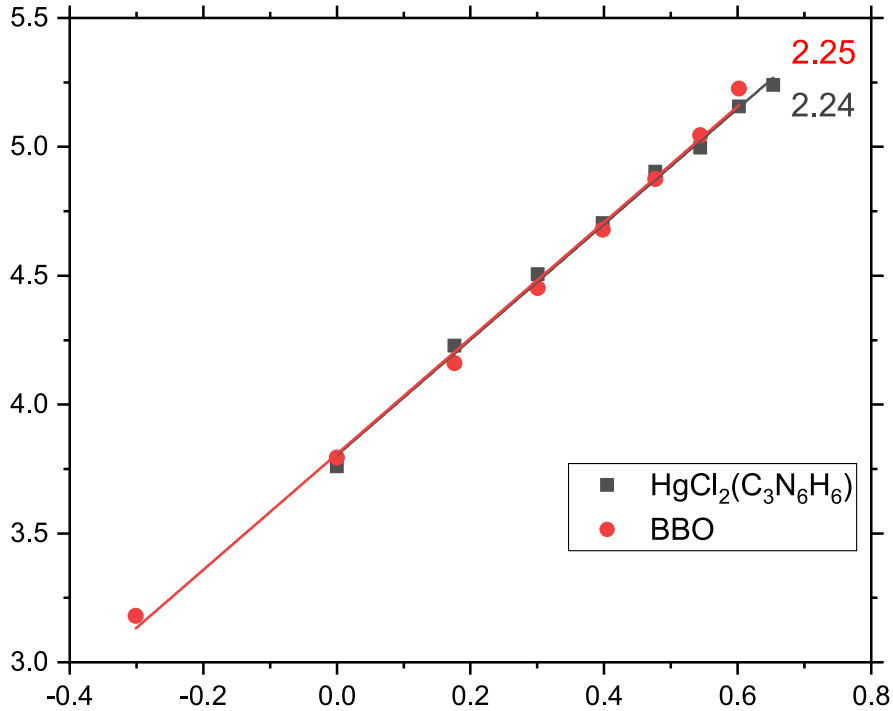


Figure 46: Nonlinear optical spectra of β -BaB₂O₄ (red) and HgCl₂(C₃N₆H₆) (gray). The excitation power dependence of the SHG signal is presented in a double logarithmic scale. Continuous lines represent the corresponding linear fits, with slopes derived from the fitted data.^[178]

DFT calculations complement the experimental findings by clarifying the electronic structure. The calculated band structure yields a direct band gap of about 3.0 eV, which is smaller than the experimental value, as expected for a GGA-based treatment. The valence-band maximum contains contributions from N, Cl, and Hg states, whereas the conduction-band minimum is dominated mainly by Cl and Hg contributions. This indicates that the optical transitions are not purely ligand-centered, but arise from cooperative contributions of the melamine framework and the mercury chloride substructure. The electronic structure analysis therefore supports the interpretation that both the polarizable Hg²⁺ centers and the π -conjugated melamine units contribute to the pronounced nonlinear optical response. Overall, the results identify HgCl₂(C₃N₆H₆) as a structurally well-defined, thermally robust, wide-band-gap SHG material in which polar layering, distorted mercury coordination, and melamine-based electronic contributions act together to generate a response comparable to that of an established benchmark compound.

3.10 Synthesis and SHG Properties of the Melamine-Based Zinc Halides $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnX}_3(\text{C}_3\text{N}_6\text{H}_6)$ ($X = \text{Cl}, \text{Br}$) (Publication 10)

The zinc halide–melamine system proved to be highly sensitive to the reaction conditions and gave access to several distinct products, including non-centrosymmetric phases with significant second-harmonic generation (SHG) activity. Hydrothermal reaction of ZnCl_2 with melamine at 110°C afforded both the hydroxide-containing phase $\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{C}_3\text{N}_6\text{H}_6)_3$ and orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnCl}_3(\text{C}_3\text{N}_6\text{H}_6)$, whereas the analogous reaction with ZnBr_2 yielded only orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnBr}_3(\text{C}_3\text{N}_6\text{H}_6)$. In addition, the chloride compound was also obtained as a second, monoclinic polymorph by a low-temperature solid-state reaction of ZnCl_2 , melaminium hydrochloride, and melamine. Elemental analysis and EDX further confirmed the expected stoichiometry of the bromide phase.

The hydrothermal synthesis leading to the SHG-active zinc halide phases also produces $\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{C}_3\text{N}_6\text{H}_6)_3$ as a by-product, which crystallizes in the centrosymmetric space group $P\bar{1}$ and therefore does not qualify as an SHG-active phase. Its structure contains three crystallographically distinct zinc atoms that are linked by hydroxide bridges into a trinuclear unit (see Fig. 47). All zinc centers adopt distorted tetrahedral coordination environments, but with different ligand combinations. Zn1 and Zn3 are each bound to two chloride ligands, one hydroxide group, and one melamine ligand through an inner ring nitrogen atom, whereas Zn2 is coordinated by two hydroxide groups and two melamine ligands. The melamine ligands connect these tetrahedral units further, so that the compound may be understood as an extended framework built from hydroxide-bridged zinc polyhedra and nitrogen-donor melamine linkers.

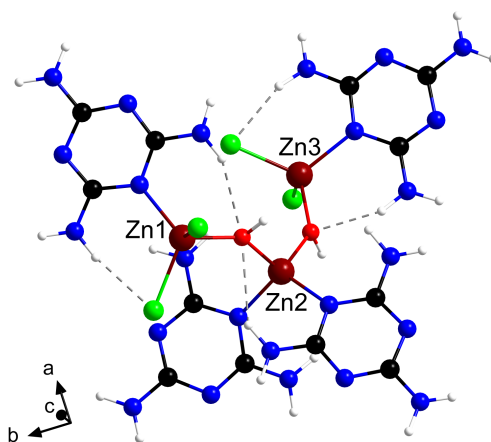


Figure 47: Section of the crystal structure of $\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{Mel})_3$, with a central trinuclear arrangement of zinc atoms, interconnected via hydroxide bridges. Each zinc atom adopts a distorted tetrahedral environment surrounded by chloride, hydroxide, and melamine ligands.^[179]

The main SHG-active phases are the melaminium zinc halides $(C_3N_6H_7)ZnX_3(C_3N_6H_6)$ with $X = Cl$ and Br . In the orthorhombic structures, both compounds crystallize isotypically in the non-centrosymmetric space group $Pna2_1$ (see Fig. 48). Their fundamental building unit is a discrete $(ZnX_3Mel)^-$ anion in which Zn^{2+} is tetrahedrally coordinated by three halide ligands and one melamine molecule through an inner nitrogen atom. Charge compensation is provided by a protonated melaminium cation. These components are arranged in layers, with melamine and melaminium ring systems stacked along the polar axis. This stacking is not perfectly parallel, but involves slight tilts between neighboring rings, which helps to generate a polar arrangement and thus enables a macroscopic second-order nonlinear response. The bromide structure is essentially the same as the chloride analogue, except for the expected lattice expansion caused by the larger bromide ion.

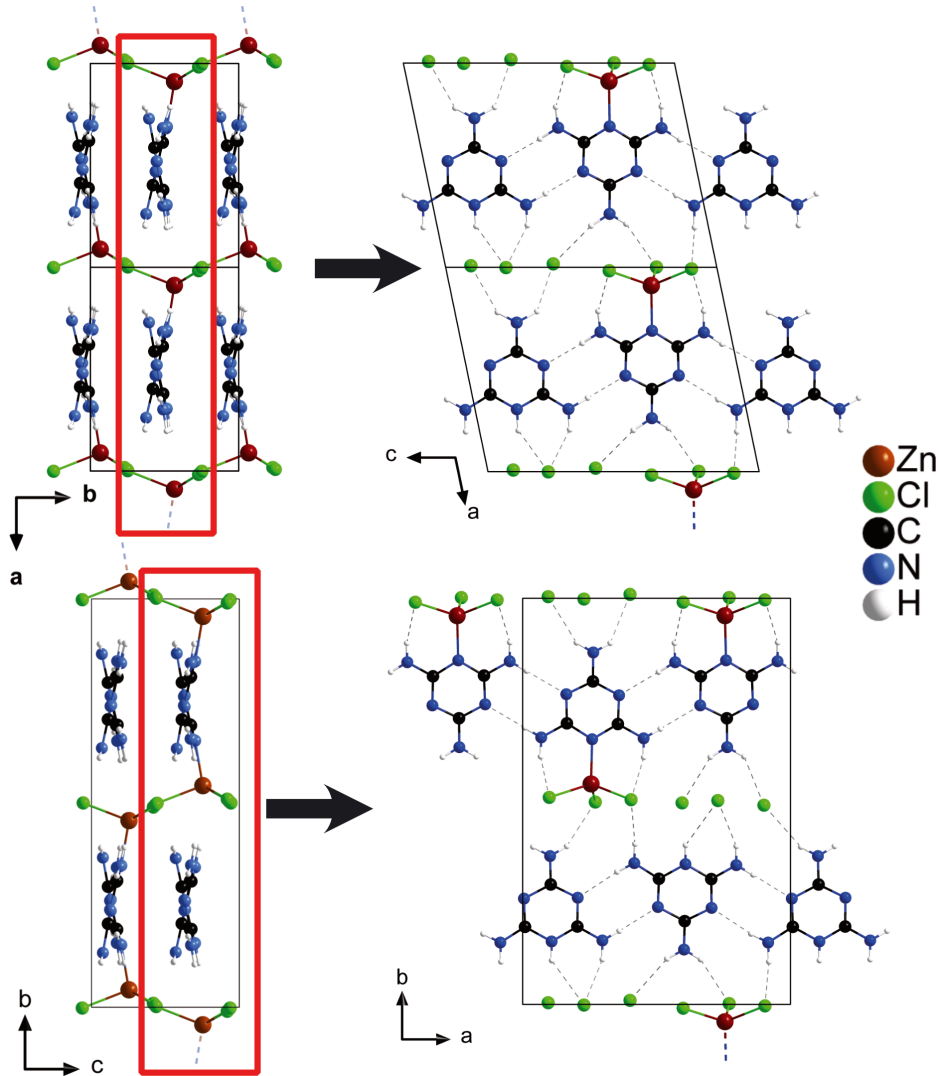


Figure 48: Two views of the monoclinic (top) and orthorhombic (bottom) modifications of $(MelH)ZnCl_3(Mel)$. The red box marks the section of the structure shown in the parent projections on the right.^[179]

The monoclinic modification of $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnCl}_3(\text{C}_3\text{N}_6\text{H}_6)$ also remains non-centrosymmetric, crystallizing in $P2_1$, and it preserves the same basic ionic building blocks as the orthorhombic polymorph. The decisive difference lies in their packing. In the monoclinic phase, the $(\text{ZnCl}_3\text{Mel})^-$ units and the melaminium cations are arranged differently, and the hydrogen-bond network is reorganized accordingly. Most importantly, the triazine-based ring systems now stack along the polar b -axis rather than along the orthorhombic c -axis. The comparison between the two chloride modifications therefore shows that the optical behavior is not determined simply by the local tetrahedral zinc coordination, but by the way in which these units are assembled into a polar crystal structure through hydrogen bonding and organic–inorganic packing.

Single-crystal SHG measurements directly confirmed that all three non-centrosymmetric zinc–melamine halides are optically active. Using potassium titanyl phosphate (KTP) as a benchmark, each compound showed a distinct SHG signal at about 390 nm under excitation at 779 nm, and power-dependent measurements yielded slopes close to 2 in double-logarithmic plots, which verifies the second-order origin of the response. The SHG intensities follow the sequence monoclinic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnCl}_3(\text{C}_3\text{N}_6\text{H}_6) >$ orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnBr}_3(\text{C}_3\text{N}_6\text{H}_6) >$ orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnCl}_3(\text{C}_3\text{N}_6\text{H}_6)$ (see Fig. 49).

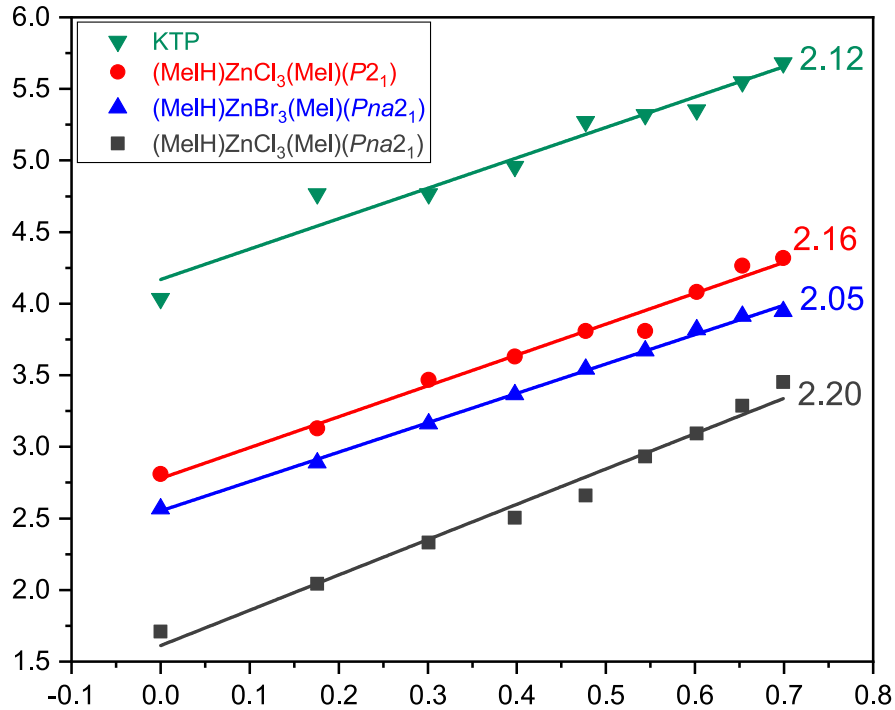


Figure 49: Nonlinear optical spectra of KTP (green), monoclinic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ ($P2_1$; red), orthorhombic $(\text{MelH})\text{ZnBr}_3(\text{Mel})$ ($Pna2_1$; blue) and orthorhombic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ ($Pna2_1$; grey). The excitation power dependence of the SHG signal is presented on a double logarithmic scale. Continuous lines represent the corresponding linear fits, with slopes derived from the fitted data.^[179]

The monoclinic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnCl}_3(\text{C}_3\text{N}_6\text{H}_6)$ thus gives the strongest signal among the investigated compounds and exhibits a remarkably strong nonlinear optical response for a melamine-based material, even though its SHG intensity remains about one order of magnitude below that of potassium titanyl phosphate. Compared to monoclinic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnCl}_3(\text{C}_3\text{N}_6\text{H}_6)$, the SHG response of $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnBr}_3(\text{C}_3\text{N}_6\text{H}_6)$ is lower by a factor of about 1.5, while orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnCl}_3(\text{C}_3\text{N}_6\text{H}_6)$ is considerably weaker still and reaches only about one seventh of the intensity of the bromide phase. Two clear structure–property relationships emerge from this comparison. First, the lower symmetry of the monoclinic phase appears to enhance the SHG efficiency. Second, for the isotypic orthorhombic structures, replacing chloride by the more polarizable bromide strengthens the nonlinear response.

Diffuse reflectance ultraviolet–visible (DRUV) spectroscopy was carried out for phase-pure orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnBr}_3(\text{C}_3\text{N}_6\text{H}_6)$ and provides a complementary picture of the electronic structure. The spectrum contains two broad absorption bands that were assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the triazine system. Compared with pure melamine, both bands are shifted to higher energy. This hypsochromic shift was attributed to coordination of melamine to Zn^{2+} together with protonation to melaminium, both of which modify the electronic structure of the conjugated ring system. Tauc analysis yielded a direct optical band gap of 4.74 eV and an indirect band gap of 4.46 eV (see Fig. 50). These values place the compound well in the UV region and agree with the observed transparency of the crystals. Infrared spectroscopy of the bromide phase, compared with the monoclinic chloride, confirmed the expected vibrational signatures of melamine and melaminium, including NH_2 stretching and characteristic triazine ring modes. The differences in the N–H stretching region are consistent with distinct hydrogen-bonding situations in the two structures (see Fig. 51).

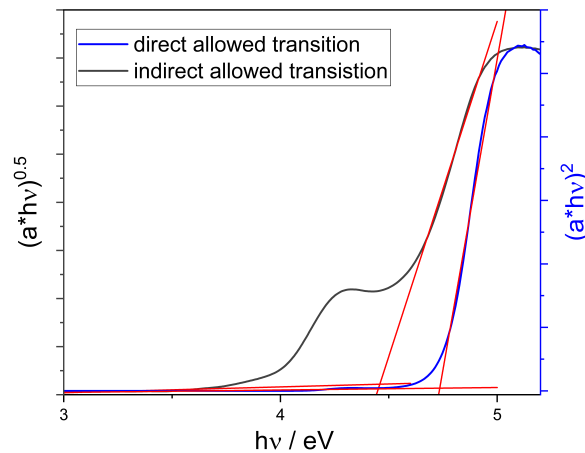


Figure 50: Tauc plots from diffuse reflectance UV/Vis spectroscopy of orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnBr}_3(\text{C}_3\text{N}_6\text{H}_6)$ showing the direct (blue) and indirect (black) transitions, with the corresponding linear fits in red.^[179]

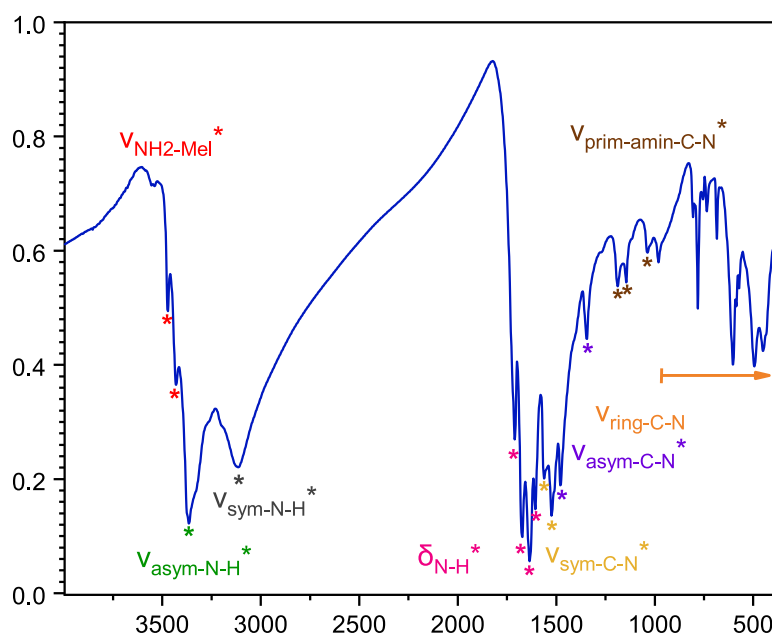


Figure 51: Infrared spectrum of orthorhombic (MelH)ZnBr₃(Mel) with band assignments of characteristic vibrational modes.^[179]

DFT calculations on orthorhombic (C₃N₆H₇)ZnCl₃(C₃N₆H₆) support the experimental optical picture and describe the compound as a wide-band-gap semiconductor with a direct band gap of about 4.1 eV at Γ . The comparatively flat valence and conduction bands are in line with the layered and rather molecular character of the structure. According to the orbital analysis, the top of the valence band is dominated mainly by nitrogen-derived states, whereas the bottom of the conduction band contains contributions from carbon and halide states with additional zinc participation. The calculations therefore indicate that the melamine-based π system is central to the electronic transitions, but that the zinc halide substructure also contributes to the polarizable electronic states relevant for the nonlinear optical behavior.

Overall, the present journal article demonstrates that the zinc halide–melamine system gives access to non-centrosymmetric hybrid zinc halides with pronounced SHG activity. The key structural feature is not only the tetrahedral ZnX₃N coordination, but also the combined polar stacking of ZnCl₃MeI[−], melamine and melaminium units, as well as the way in which this packing structure is influenced by hydrogen bonding, symmetry, and the polarizability of the halides. The comparison of the chloride polymorphs and the bromide analogue therefore demonstrates in a particularly clear way how subtle structural changes can translate into measurable differences in nonlinear optical performance.

3.11 A complete cathode recovery cycle of an exhausted and dismantled lithium battery material (Manuscript 1)

Spent graphitic $\text{Li}(\text{Ni}, \text{Mn}, \text{Co})\text{O}_2$ battery material obtained from a commercial thermomechanical recycling process was used as starting material for a complete cathode recovery sequence. The material had already been discharged, dismantled, shredded, and vacuum-dried, but still contained a complex mixture of cathode powder, graphite, residual electrolyte, lithium salts, and metallic or oxidic impurities from current collectors and cell components. Powder X-ray diffraction confirmed the presence of nickel-manganese-cobalt (NMC) cathode material together with graphite and copper. The chemical composition of the raw “black mass” was comparatively close to a conventional NMC 622 material, with an average Ni:Mn:Co ratio of 2.80(5):1.00(4):1. At the same time, the material contained significant amounts of foreign elements, especially copper, aluminium, and iron. Their variable contents reflect the inhomogeneous nature of commercially generated black mass, in which macroscopic metal flakes can remain after mechanical battery segmentation.

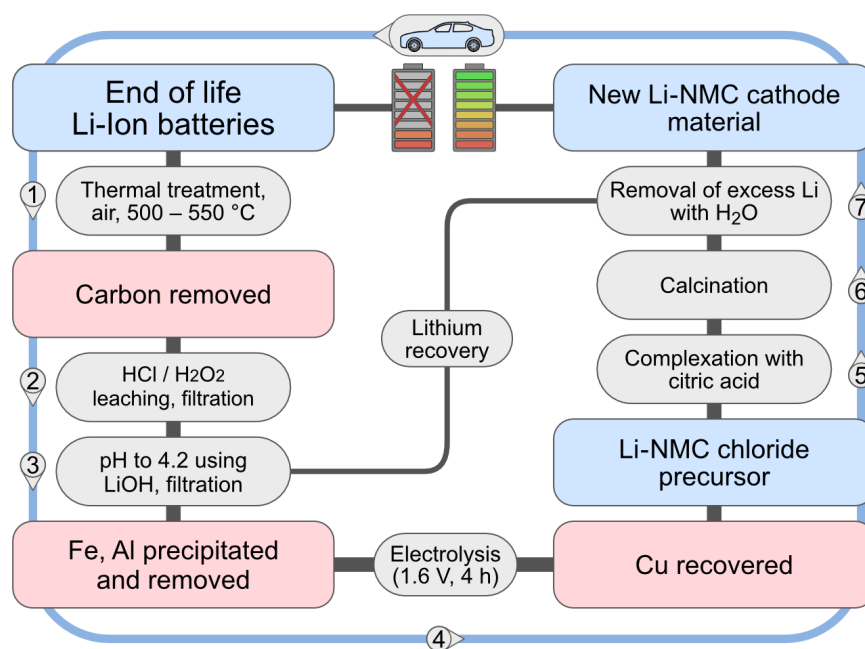


Figure 52: Recycling scheme for end of life lithium battery, departing from heat treatment for the removal of carbon, followed by acid leaching, pH dependent precipitation of impurities and electrolysis, sol-gel synthesis, involving complexation and calcination as structuring procedure for new Li-NMC cathode material.

A seven-step recycling scheme was developed to convert this material into fresh Li-NMC cathode powder without separating nickel, manganese, and cobalt from one another (see Fig. 52). The process combines thermal removal of organic and carbon-containing components, acidic leaching, pH-controlled precipitation, electrochemical copper recovery, and an aqueous

citrate sol–gel synthesis. In this approach, lithium hydroxide is not only used as a base for pH adjustment but also helps compensate the lithium deficiency of the recycled $\text{Li}_x(\text{Ni,Mn,Co})\text{O}_2$ material. Excess lithium introduced during the process can later be removed again by washing the calcined product with water.

The thermal behavior of the black mass was first investigated by TG/DTG analysis in air up to 1000 °C. The total mass loss amounted to about 40 % and occurred in three main steps. A first mass loss of 7.5 % up to 150 °C and a second loss of 8.0 % between 150 and 400 °C were assigned mainly to volatile fractions such as residual electrolyte and other organic constituents. The largest mass loss of 23.5 % between 400 and 800 °C corresponds to the oxidation of graphite and remaining binder components.

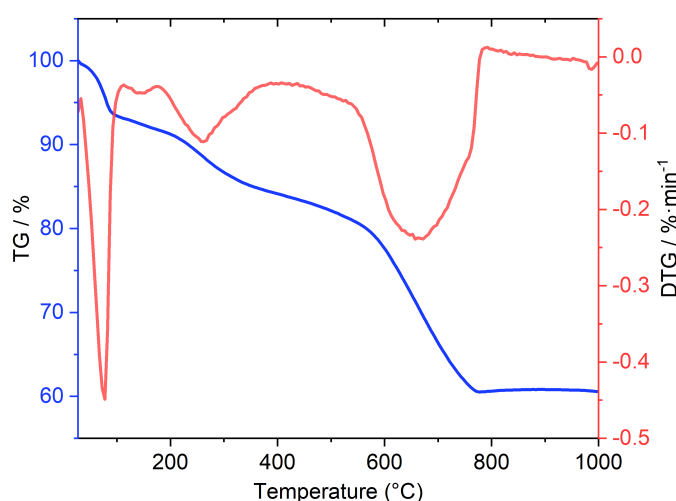


Figure 53: Thermal analysis of spent graphitic NMC LIB material heated to 1000 °C in an open corundum crucible with an airflow of 60 ml/min and a heating rate of 2 K/min (blue = thermo gravimetry; red = differential thermo gravimetry).

Additional annealing experiments showed that the graphite content can be reduced efficiently at moderate temperatures between 500 and 550 °C. At 525 °C, the graphite (002) reflection at $2\theta = 26.62^\circ$ gradually decreased with increasing reaction time and disappeared after prolonged heating. Importantly, the NMC reflections remained present, indicating that the layered cathode phase tolerates this thermal pre-treatment under the chosen conditions (see Fig. 54).

After thermal treatment, the graphite-free material was leached in an aqueous $\text{HCl}/\text{H}_2\text{O}_2$ mixture. Organic acids such as malic acid were not suitable for the present commercially derived material, because the large amount of impurity oxides promoted catalytic decomposition of H_2O_2 without sufficient dissolution of the NMC phase.^[181] In contrast, hydrochloric

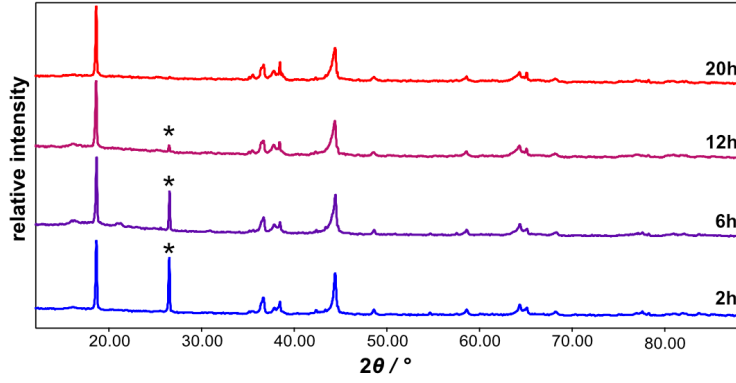


Figure 54: Powder XRD patterns ($\text{Cu-K}\alpha_1$ radiation) of the blackmass showing the decreasing graphite content over time (graphite (002)-reflection marked with *) after treatment at 525°C at 2-20 hours.^[180]

acid in combination with a small amount of hydrogen peroxide provided an effective leaching medium. The remaining insoluble residue accounted for less than 10 % of the starting mass and consisted mainly of aluminium, iron, and copper compounds, while only a minor fraction of the Ni/Mn/Co content was lost at this stage.

The purification of the leach solution was strongly controlled by the chosen pH. At pH 5.3, iron and aluminium could be removed, but a significant loss of nickel occurred and copper was still detected in the final material. As a result, the recovered cathode composition shifted toward an NMC 532 material, with an Ni:Mn:Co ratio of approximately 4.86:3.09:2.06 and about 1.6 wt. % residual copper. This result shows that pH-controlled precipitation can be used not only for impurity removal but also strongly influences the final cathode composition. For preserving the original NMC 622 ratio, the precipitation step was therefore optimized to pH 4.2. Under these conditions, iron and aluminium were removed completely, while the Ni:Mn:Co ratio in solution remained close to 6:2:2. Copper, however, stayed dissolved and was subsequently removed electrochemically. Applying 1.6 V between a graphite anode and a copper cathode for four hours enabled complete copper recovery from the solution. The final total reflection X-ray fluorescence (TXRF) analysis after this combined pH and electrolysis treatment gave an Ni:Mn:Co ratio of 6.01:2.1:1.9 and no detectable iron, aluminium, or copper contamination.

The purified precursor solution was then processed by an aqueous citrate sol-gel route. After complexation, drying, and calcination, crystalline Li-NMC material was obtained. Excess lithium was removed by washing, yielding lithium-containing by-products such as lithium chloride hydrate and Li_2CO_3 . Powder X-ray diffraction of the regenerated NMC 622 material closely matched that of a reference material prepared from pure metal nitrate precursors under similar conditions. Rietveld refinement using the LiNiO_2 -type structure in the space

group $R\bar{3}m$ showed excellent agreement between observed and calculated diffraction patterns, without detectable side phases (see Fig. 55). This confirms that nickel, manganese, and cobalt remain incorporated in the layered Li-NMC structure throughout the recycling process. The refinement also indicated about 5.8 % Ni^{2+} on lithium sites, which is consistent with a certain degree of cation mixing and with the more cubic or octahedral particle morphology observed by scanning electron microscopy.

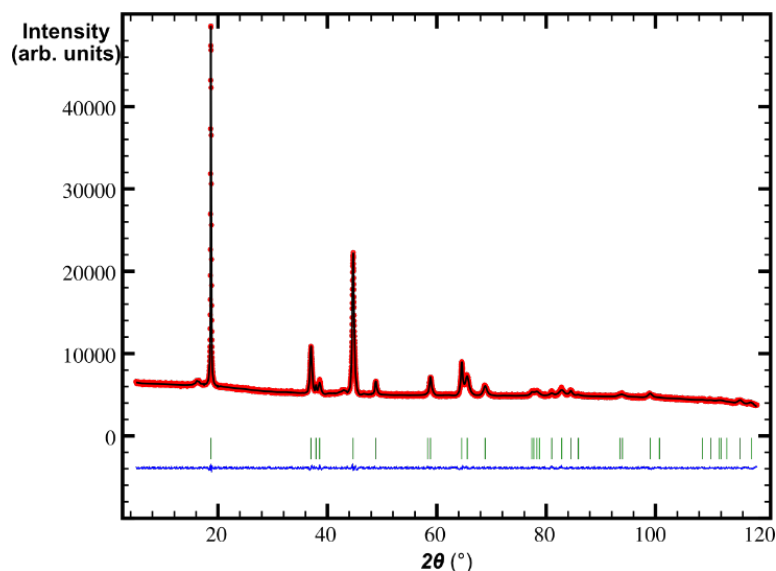


Figure 55: Rietveld fit of the $\text{Cu-K}\alpha_1$ PXRD pattern of the fresh Li-NMC material. The observed pattern (red dots) is superimposed with the calculated pattern (black line). Green ticks mark the Bragg reflections of the calcined Li-NMC 622 material. The difference curve between the observed and calculated pattern is shown in the lower part of the graph (blue line). Broad reflections at 2θ values 16.2° and 43.1° emerge from the sample carrier foil.

SEM images showed well-crystallized and rather homogeneous particles, with primary particle sizes in the range of approximately 50–250 nm. Such small particles are advantageous for lithium diffusion because they provide short transport lengths and a relatively high surface area. The study therefore establishes a practical proof of concept for converting commercially generated NMC “black mass” into a regenerated layered cathode material while retaining the original Ni/Mn/Co ratio. The most important point is that the valuable transition metals do not need to be individually separated or purified. Instead, the cathode composition can be preserved through controlled removal of graphite, iron, aluminium, copper, and excess lithium. The obtained product was structurally and chemically consistent with fresh Li-NMC 622 material, although electrochemical cell testing would still be required to evaluate its practical performance as a recovered cathode material.

4 Conclusion

This thesis demonstrates how targeted synthetic approaches can be used to modify layered, cluster-based, and hybrid inorganic materials and how these modifications directly influence their structures and properties. A central result is the establishment of WTe_2 as a versatile layered host whose structure and electronic state can be tuned by both reductive and oxidative intercalation chemistry. Alkali-metal intercalation gives access to the ordered semiconductor series $A_{0.5}\text{WTe}_2$, in which electron donation, expansion of the van der Waals gap, and distortion of the W–W chains are directly connected to the observed metal-to-semiconductor transition.

A particularly distinctive outcome of this work is the realization of anionic halogen intercalation in WTe_2 , represented by WTe_2I and the bromine series WTe_2Br_x ($x = 0.5, 1.0$, and 1.25), which constitute a particularly unusual case within layered transition-metal dichalcogenides, since cationic and molecular intercalation reactions are well established, whereas structurally well-defined anionic intercalation compounds had not been described before these studies. In these phases, oxidizing halogen species are incorporated into the van der Waals gap as integral structural components while the WTe_2 layer framework remains largely preserved. The iodine compound WTe_2I shows intrinsic commensurate and incommensurate modulation dominated by the iodine substructure, whereas the bromine series WTe_2Br_x exhibits reversible multistage bromine uptake and release with composition-dependent interlayer ordering. Together, these compounds demonstrate that anionic intercalation in WTe_2 can combine reversibility, staging, modulation, guest mobility, and strong host–guest interactions within one chemically coherent system.

Beyond intercalation chemistry, the work shows how increased halogen activity can redirect layered chalcogenides toward reconstructive transformations, including tellurium iodides and metal-halide clusters. The complementary studies on Nb/Ta oxyhalide clusters, melamine-based SHG-active hybrid halides, and recycled Li–NMC cathode materials further illustrate the central role of composition, connectivity, symmetry, and structural order in determining functional behavior. Overall, the results underline that careful synthesis combined with detailed crystallographic and spectroscopic characterization provides a powerful route to understanding and controlling structure–property relationships in complex inorganic materials.

References

- [1] J. A. Wilson, A. D. Yoffe, *Adv. Phys.* **1969**, *18*, 193–335.
- [2] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, A. Kis, *Nat. Rev. Mater.* **2017**, *2*, 17033.
- [3] S. Ahmed, X. Jiang, C. Wang, U. e. Kalsoom, B. Wang, J. Khan, Y. Muhammad, Y. Duan, H. Zhu, X. Ren, *Adv. Opt. Mater.* **2021**, *9*, 2001671.
- [4] G. H. Han, D. L. Duong, D. H. Keum, S. J. Yun, Y. H. Lee, *Chem. Rev.* **2018**, *118*, 6297–6336.
- [5] P. Miró, M. Audiffred, T. Heine, *Chem. Soc. Rev.* **2014**, *43*, 6537–6554.
- [6] M. S. Sokolikova, C. Mattevi, *Chem. Soc. Rev.* **2020**, *49*, 3952–3980.
- [7] M. Chhowalla, *Nat. Chem.* **2013**, *5*, 263–75.
- [8] M. Chhowalla, D. Jena, H. Zhang, *Nat. Rev. Mater.* **2016**, *1*, 16052.
- [9] A. Kumar, P. K. Ahluwalia, *J. Alloys Compd.* **2014**, *587*, 459–467.
- [10] J. Luxa, P. Vosecký, V. Mazánek, D. Sedmidubský, M. Pumera, P. Lazar, Z. Sofer, *ACS Catal.* **2017**, *7*, 5706–5716.
- [11] G. A. Wieggers, *Physica B+C* **1980**, *99*, 151–165.
- [12] W. S. Yun, S. W. Han, S. C. Hong, I. G. Kim, J. D. Lee, *Phys. Rev. B* **2012**, *85*, 033305.
- [13] C. Zhao, M. Hu, J. Qin, B. Xia, C. Liu, S. Wang, D. Guan, Y. Li, H. Zheng, J. Liu, J. Jia, *Phys. Rev. Lett.* **2020**, *125*, 046801.
- [14] R. H. Friend, A. D. Yoffe, *Adv. Phys.* **1987**, *36*, 1–94.
- [15] M. N. Ali, *Nature* **2014**, *514*, 205–208.
- [16] J. Wilson, F. Salvo, *Adv. Phys.* **1975**, *24*, 37–41.
- [17] E. Revolinsky, G. A. Spiering, D. J. Beerntsen, *J. Phys. Chem. Solids* **1965**, *26*, 1029–1034.
- [18] G. V. S. Rao, M. W. Shafer in *Intercalated Layered Materials*, (Ed.: F. Lévy), Springer Netherlands, Dordrecht, **1979**, pp. 99–199.
- [19] Y. Qi, P. G. Naumov, M. N. Ali, C. R. Rajamathi, W. Schnelle, O. Barkalov, M. Hanfland, S.-C. Wu, C. Shekhar, Y. Sun, V. Süß, M. Schmidt, U. Schwarz, E. Pippel, P. Werner, R. Hillebrand, T. Förster, E. Kampert, S. Parkin, R. J. Cava, C. Felser, B. Yan, S. A. Medvedev, *Nat. Commun.* **2016**, *7*, 11038.

- [20] E. Morosan, H. W. Zandbergen, B. S. Dennis, J. W. G. Bos, Y. Onose, T. Klimczuk, A. P. Ramirez, N. P. Ong, R. J. Cava, *Nat. Phys.* **2006**, *2*, 544.
- [21] R. A. Klemm, *Phys. C Supercond. Its Appl.* **2015**, *514*, 86–94.
- [22] V. Fatemi, S. Wu, Y. Cao, L. Bretheau, Q. D. Gibson, K. Watanabe, T. Taniguchi, R. J. Cava, P. Jarillo-Herrero, *Science* **2018**, *362*, 926–929.
- [23] Y. Fang, J. Pan, J. He, R. Luo, D. Wang, X. Che, K. Bu, W. Zhao, P. Liu, G. Mu, H. Zhang, T. Lin, F. Huang, *Angew. Chem. Int. Ed.* **2018**, *57*, 1232–1235.
- [24] M. N. Ali, L. Schoop, J. Xiong, S. Flynn, Q. Gibson, M. Hirschberger, N. P. Ong, R. J. Cava, *Europhys. Lett.* **2015**, *110*, 67002.
- [25] B. Amin, T. P. Kaloni, U. Schwingenschlögl, *RSC Adv.* **2014**, *4*, 34561–34565.
- [26] J. Augustin, *Phys. Rev. B* **2000**, *62*, 10812–10823.
- [27] B. E. Brown, *Acta Crystallogr.* **1966**, *20*, 268–274.
- [28] J. E. Callanan, G. A. Hope, R. D. Weir, *J. Chem. Thermodyn.* **1992**, *24*, 627–638.
- [29] Z.-S. Chen, L. Huang, W.-T. Guo, K. Zhong, J.-M. Zhang, Z. Huang, *Aip. Conf. Proc.* **2022**, *10*, 879756.
- [30] P. K. Das, D. Di Sante, F. Cilento, C. Bigi, D. Kopic, D. Soranzio, A. Sterzi, J. A. Krieger, I. Vobornik, J. Fujii, T. Okuda, V. N. Strocov, M. B. H. Breese, F. Parmigiani, G. Rossi, S. Picozzi, R. Thomale, G. Sangiovanni, R. J. Cava, G. Panaccione, *Electron. Struct.* **2019**, *1*, 014003.
- [31] W. G. Dawson, D. W. Bullett, *J. Phys. C: Solid State Phys.* **1987**, *20*, 6159–6174.
- [32] A. Eftekhari, *J. Mater. Chem. A* **2017**, *5*, 18299–18325.
- [33] C. Huang, A. Narayan, E. Zhang, Y. Liu, X. Yan, J. Wang, C. Zhang, W. Wang, T. Zhou, C. Yi, S. Liu, J. Ling, H. Zhang, R. Liu, R. Sankar, F. Chou, Y. Wang, Y. Shi, K. T. Law, S. Sanvito, P. Zhou, Z. Han, F. Xiu, *ACS Nano* **2018**, *12*, 7185–7196.
- [34] S. Kabashima, *J. Phys. Soc. Jpn.* **1966**, *21*, 945–948.
- [35] P. Li, Y. Wen, X. He, Q. Zhang, C. Xia, Z.-M. Yu, S. A. Yang, Z. Zhu, H. N. Alshareef, X.-X. Zhang, *Nat. Commun.* **2017**, *8*, 2150.
- [36] G. Liu, H. Liu, J. Zhou, X. Wan, *J. Appl. Phys.* **2017**, *121*, 045104.
- [37] H. Y. Lv, W. J. Lu, D. F. Shao, Y. Liu, S. G. Tan, Y. P. Sun, *Europhys. Lett.* **2015**, *110*, 37004.

-
- [38] Y.-Y. Lv, B.-B. Zhang, X. Li, B. Pang, F. Zhang, D.-J. Lin, J. Zhou, S.-H. Yao, Y. B. Chen, S.-T. Zhang, M. Lu, Z. Liu, Y. Chen, Y.-F. Chen, *Sci. Rep.* **2016**, *6*, 26903.
- [39] S. J. Magorrian, N. D. M. Hine, *Phys. Rev. B* **2024**, *110*, 045410.
- [40] M. J. Mleczko, R. L. Xu, K. Okabe, H.-H. Kuo, I. R. Fisher, H. S. P. Wong, Y. Nishi, E. Pop, *ACS Nano* **2016**, *10*, 7507–7514.
- [41] W. Tian, W. Yu, X. Liu, Y. Wang, J. Shi, *Materials* **2018**, *11*, 1185–1185.
- [42] M. Wang, A. Kumar, H. Dong, J. M. Woods, J. V. Pondick, S. Xu, D. J. Hynek, P. Guo, D. Y. Qiu, J. J. Cha, *Adv. Mater.* **2022**, *34*, 2200861.
- [43] Y.-M. Wu, C. Murthy, S. A. Kivelson, *Phys. Rev. Lett.* **2024**, *133*, 246501.
- [44] X. Yang, Y. Zhang, L. Chen, K. Aso, W. Yamamori, R. Moriya, K. Watanabe, T. Taniguchi, T. Sasagawa, N. Nakatsuji, M. Koshino, Y. Yamada-Takamura, Y. Oshima, T. Machida, *ACS Nano* **2025**, *19*, 13007–13015.
- [45] Y. Zhang, K. Kamiya, T. Yamamoto, M. Sakano, X. Yang, S. Masubuchi, S. Okazaki, K. Shinokita, T. Chen, K. Aso, Y. Yamada-Takamura, Y. Oshima, K. Watanabe, T. Taniguchi, K. Matsuda, T. Sasagawa, K. Ishizaka, T. Machida, *Nano Lett.* **2023**, *23*, 9280–9286.
- [46] L. Du, Z. Huang, J. Zhang, F. Ye, Q. Dai, H. Deng, G. Zhang, Z. Sun, *Nat. Mater.* **2024**, *23*, 1179–1192.
- [47] P. Schmidt, P. Schneiderhan, M. Ströbele, C. P. Romao, H.-J. Meyer, *Inorg. Chem.* **2021**, *60*, 1411–1418.
- [48] L. Zhu, Q.-Y. Li, Y.-Y. Lv, S. Li, X.-Y. Zhu, Z.-Y. Jia, Y. B. Chen, J. Wen, S.-C. Li, *Nano Lett.* **2018**, *18*, 6585–6590.
- [49] P. K. Muscher, D. A. Rehn, A. Sood, K. Lim, D. Luo, X. Shen, M. Zajac, F. Lu, A. Mehta, Y. Li, X. Wang, E. J. Reed, W. C. Chueh, A. M. Lindenberg, *Adv. Mater.* **2021**, *33*, 2101875.
- [50] W. L. Zhu, Y. Cao, P. J. Guo, X. Li, Y. J. Chen, L. J. Zhu, J. B. He, Y. F. Huang, Q. X. Dong, Y. Y. Wang, R. Q. Zhai, Y. B. Ou, G. Q. Zhu, H. Y. Lu, G. Li, G. F. Chen, M. H. Pan, *Phys. Rev. B* **2022**, *105*, 125116.
- [51] M. Wang, S. Xu, J. J. Cha, *Adv. Energ. Sust. Res.* **2021**, *2*, 2100027.
- [52] D. Fu, B. Zhang, X. Pan, F. Fei, Y. Chen, M. Gao, S. Wu, J. He, Z. Bai, Y. Pan, Q. Zhang, X. Wang, X. Wu, F. Song, *Sci. Rep.* **2017**, *7*, 12688.
- [53] M. S. Whittingham, *Prog. Solid State Ch.* **1978**, *12*, 41–99.

- [54] M. S. Dresselhaus, *MRS Bull.* **1987**, *12*, 24–28.
- [55] M. Dresselhaus, *Intercalation in Layered Materials*, Springer US, **2013**.
- [56] Z. Wang, R. Li, C. Su, K. P. Loh, *SmartMat* **2020**, *1*, e1013.
- [57] F. Lévy, *Intercalated Layered Materials*, Springer Netherlands, **2012**.
- [58] M. S. Whittingham, *Chem. Rev.* **2004**, *104*, 4271–4302.
- [59] H. Wang, Z. Lu, S. Xu, D. Kong, J. J. Cha, G. Zheng, P.-C. Hsu, K. Yan, D. Bradshaw, F. B. Prinz, Y. Cui, *Proc. Natl. Acad. Sci.* **2013**, *110*, 19701–19706.
- [60] S. I. Ali, S. Mondal, S. J. Prathapa, S. van Smaalen, S. Zörb, B. Harbrecht, *Z. Anorg. Allg. Chem.* **2012**, *638*, 2625–2631.
- [61] M. N. Ali, H. Ji, D. Hirai, M. K. Fuccillo, R. J. Cava, *J. Solid State Chem.* **2013**, *202*, 77–84.
- [62] S. I. Ali, S. Mondal, S. van Smaalen, *Z. Anorg. Allg. Chem.* **2015**, *641*, 464–469.
- [63] H. J. Crawack, C. Pettenkofer, *Solid State Commun.* **2001**, *118*, 325–332.
- [64] S. N. Patel, A. A. Balchin, *J. Mater. Sci. Lett.* **1985**, *4*, 382–384.
- [65] M. B. Dines, *Mater. Res. Bull.* **1975**, *10*, 287–291.
- [66] J. Rouxel, *Physica B+C* **1980**, *99*, 3–11.
- [67] M. B. Dines, *Science* **1975**, *188*, 1210.
- [68] E. Figueroa, J. W. Brill, J. P. Selegue, *J. Phys. Chem. Solids* **1996**, *57*, 1123–1127.
- [69] Y. Liu, Z. Wang, G. Hu, X. Chen, K. Xu, Y. Guo, Y. Xie, C. Wu, *Precis. Chem.* **2025**, *3*, 51–71.
- [70] Y. Jung, Y. Zhou, J. J. Cha, *Inorg. Chem. Front.* **2016**, *3*, 452–463.
- [71] M. Rajapakse, B. Karki, U. O. Abu, S. Pishgar, M. R. K. Musa, S. M. S. Riyadh, M. Yu, G. Sumanasekera, J. B. Jasinski, *npj 2D Mater. Appl.* **2021**, *5*, 30.
- [72] R. C. Clark, J. S. Reid, *Acta Crystallogr. A* **1995**, *51*, 887–897.
- [73] S. Whittingham, *Intercalation Chemistry*, Academic Press, New York, **1982**.
- [74] Z. Guo, F. Sun, W. Yuan, *Cryst. Growth Des.* **2017**, *17*, 2238–2253.
- [75] W. Paulus, H. Katzke, R. Schöllhorn, *J. Solid State Chem.* **1992**, *96*, 162–168.
- [76] K. Mizushima, P. Jones, P. Wiseman, J. Goodenough, *Mater. Res. Bull.* **1980**, *15*, 783–789.

-
- [77] K. Mizushima, P. Jones, P. Wiseman, J. Goodenough, *Solid State Ionics* **1981**, 3-4, 171–174.
- [78] L. Kulyuk, L. Charron, E. Fortin, *Phys. Rev. B* **2003**, 68, 075314.
- [79] L. Charron, D. Dumchenko, E. Fortin, C. Gherman, L. Kulyuk, *J. Lumin.* **2005**, 112, 45–49.
- [80] L. Kulyuk, D. Dumcehnko, E. Bucher, K. Friemelt, O. Schenker, L. Charron, E. Fortin, T. Dumouchel, *Phys. Rev. B* **2005**, 72, 075336.
- [81] L. Yang, K. Majumdar, H. Liu, Y. Du, H. Wu, M. Hatzistergos, P. Y. Hung, R. Tieckelmann, W. Tsai, C. Hobbs, P. D. Ye, *Nano Lett.* **2014**, 14, 6275–6280.
- [82] T. Kim, Y. Kim, E. K. Kim, *Sens. Actuators A* **2020**, 312, 112165.
- [83] N. T. Trung, M. I. Hossain, M. I. Alam, A. Ando, O. Kitakami, N. Kikuchi, T. Takaoka, Y. Sainoo, R. Arafune, T. Komeda, *ACS Omega* **2020**, 5, 28108–28115.
- [84] S. Prucnal, A. Hashemi, M. Ghorbani-Asl, R. Hübner, J. Duan, Y. Wei, D. Sharma, D. R. T. Zahn, R. Ziegenrucker, U. Kentsch, A. V. Krashenninnikov, M. Helm, S. Zhou, *Nanoscale* **2021**, 13, 5834–5846.
- [85] S. Pak, J. Son, T. Kim, J. Lim, J. Hong, Y. Lim, C.-J. Heo, K.-B. Park, Y. W. Jin, K.-H. Park, Y. Cho, S. Cha, *Nanotechnology* **2023**, 34, 015702.
- [86] M. Rabeel, H. Kim, M. A. Khan, M. Abubakr, I. Ahmad, M. Ahmad, S. Rehman, M.-J. Lee, M. F. Khan, D.-k. Kim, *ACS Photonics* **2023**, 10, 4425–4436.
- [87] N. Siminel, K. Sushkevich, S. Aazou, A. Micu, A. Siminel, Z. Sekkat, L. Kulyuk, *Opt. Mater. Express* **2023**, 13, 886–891.
- [88] N. Zawadzka, T. Woźniak, M. Strawski, I. Antoniazzi, M. Grzeszczyk, K. Olkowska-Pucko, Z. Muhammad, J. Ibanez, W. Zhao, J. Jadczyk, R. Stępniewski, A. Babiński, M. R. Molas, *Appl. Phys. Lett.* **2023**, 122, 042102.
- [89] D. S. Devi, N. R. Mohapatra, *ACS Omega* **2024**, 9, 50634–50641.
- [90] F.-Y. Wu, Y.-S. Cheng, K.-L. Wu, R. Wu, R. Yu, P.-L. Guan, Y.-W. Cheng, W.-J. Li, J.-L. Yang, X.-W. Wei, *J. Mater. Chem. C* **2024**, 12, 6645–6652.
- [91] Y. Garcia-Basabe, C. D. Mendoza, F. C. Vicentin, D. G. Larrude, *Phys. Chem. Chem. Phys.* **2025**, 27, 19347–19357.
- [92] H. Schäfer, *Chemische Transportreaktionen: der Transport anorganischer Stoffe über die Gasphase und seine Anwendungen*, Verlag Chemie, **1962**.

- [93] M. Binnewies, R. Glaum, M. Schmidt, P. Schmidt, *Chemische Transportreaktionen*, **2011**.
- [94] M. Ströbele, H.-J. Meyer, *Inorg. Chem.* **2019**, *58*, 12867–12872.
- [95] P. Schmidt, A. Siai, P. Schneiderhan, M. Ströbele, H.-J. Meyer, *Eur. J. Inorg. Chem.* **2020**, 716–719.
- [96] P. Schneiderhan, P. Schmidt, M. Ströbele, C. P. Romao, H.-J. Meyer, *Cryst. Growth Des.* **2020**, *20*, 3780–3784.
- [97] J. D. Franolic, J. R. Long, R. H. Holm, *J. Am. Chem. Soc.* **1995**, *117*, 8139–8153.
- [98] S. A. Shlykov, H. Oberhammer, A. V. Titov, N. I. Giricheva, G. V. Girichev, *Eur. J. Inorg. Chem.* **2008**, 5220–5227.
- [99] A. E. van Arkel, J. H. de Boer, *Z. Anorg. Allg. Chem.* **1925**, *148*, 345–350.
- [100] A. Perrin, C. Perrin, *Cr. Chim.* **2012**, *15*, 815–836.
- [101] V. E. Fedorov, A. V. Mishchenko, V. P. Fedin, *Russ. Chem. Rev.* **1985**, *54*, 408.
- [102] V. E. Fedorov, Y. V. Mironov, N. G. Naumov, M. N. Sokolov, V. P. Fedin, *Russ. Chem. Rev.* **2007**, *76*, 529–552.
- [103] J. Rijnsdorp, G. de Lange, G. Wiegers, *J. Solid State Chem.* **1979**, *30*, 365–373.
- [104] H. Schäfer, H.-G. von Schnering, *Angew. Chem-ger. Edit.* **1964**, *76*, 833–849.
- [105] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Vol. 3, Ferdinand Enke Verlag, Stuttgart, **1981**.
- [106] P. J. Schmidt, G. Thiele, *Acta Crystallogr. Sect. A* **1997**, *53*, 1743–1745.
- [107] G. V. Khvorykh, A. V. Shevelkov, V. A. Dolgikh, B. A. Popovkin, *J. Solid State Chem.* **1995**, *120*, 311–315.
- [108] M. D. Smith, G. J. Miller, *J. Solid State Chem.* **1998**, *140*, 226–232.
- [109] H. Imoto, A. Simon, *Inorg. Chem.* **1982**, *21*, 308–319.
- [110] A. Broll, A. Simon, H. G. von Schnering, H. Schäfer, *Z. Anorg. Allg. Chem.* **1969**, *367*, 1–18.
- [111] M. Ströbele, O. Oeckler, M. Thelen, R. F. Fink, A. Krishnamurthy, S. Kroeker, H.-J. Meyer, *Inorg. Chem.* **2022**, *61*, 17599–17608.
- [112] H. B. Yaich, J. C. Jegaden, M. Potel, M. Sergent, A. K. Rastogi, R. Tournier, *J. Less-Common Met.* **1984**, *102*, 9–22.

- [113] M. Ströbele, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1024–1029.
- [114] M. Ströbele, K. Eichele, H.-J. Meyer, *Inorg. Chem.* **2015**, *54*, 989–992.
- [115] M. Ströbele, H.-J. Meyer, *Russ. J. Coord. Chem.* **2012**, *38*, 178–182.
- [116] V. Kolesnichenko, D. C. Swenson, L. Messerle, *Inorg. Chem.* **1998**, *37*, 3257–3262.
- [117] A. Moś, C. Castro, S. Indris, M. Ströbele, R. F. Fink, H.-J. Meyer, *Inorg. Chem.* **2015**, *54*, 9826–9832.
- [118] M. Ströbele, A. Mos, H.-J. Meyer, *Inorg. Chem.* **2013**, *52*, 6951–6956.
- [119] X. Xie, R. E. McCarley, *Inorg. Chem.* **1996**, *35*, 2713–2714.
- [120] X. Xie, R. E. McCarley, *Inorg. Chem.* **1997**, *36*, 4665–4675.
- [121] C. Perrin, M. Sergent, *Journal of Chemical Research Synopses* **1983**, 38–39.
- [122] X. Zhong, K. Lee, D. Meggiolaro, A. H. Dismukes, B. Choi, F. Wang, C. Nuckolls, D. W. Paley, P. Batail, F. De Angelis, X. Roy, X.-Y. Zhu, *Adv. Funct. Mater.* **2019**, *29*, 1902951.
- [123] N. Le Nagard, A. Perrin, M. Sergent, C. Levy-Clement, *Mater. Res. Bull.* **1985**, *20*, 835–843.
- [124] J. A. Tulyagankhodjaev, P. Shih, J. Yu, J. C. Russell, D. G. Chica, M. E. Reynoso, H. Su, A. C. Stenor, X. Roy, T. C. Berkelbach, M. Delor, *Science* **2023**, *382*, 438–442.
- [125] A. Pisoni, J. Jacimovic, O. S. Barišić, A. Walter, B. Náfrádi, P. Bugnon, A. Magrez, H. Berger, Z. Revay, L. Forró, *J. Phys. Chem. C* **2015**, *119*, 3918–3922.
- [126] P. F. Bordui, M. M. Fejer, *Annu. Rev. Mater. Sci.* **1993**, *23*, 321–379.
- [127] P. G. Lacroix, I. Malfant, C. Lepetit, *Coordin. Chem. Rev.* **2016**, *308*, 381–394.
- [128] P. A. Franken, A. E. Hill, C. W. Peters, G. Weinreich, *Phys. Rev. Lett.* **1961**, *7*, 118–119.
- [129] S. R. Marder, J. W. Perry, W. P. Schaefer, *Science* **1989**, *245*, 626–628.
- [130] X. Liu, Z. Yang, D. Wang, H. Cao, *Crystals* **2016**, *6*, DOI 10.3390/cryst6120158.
- [131] F. Yang, L. Wang, L. Huang, G. Zou, *Coordin. Chem. Rev.* **2020**, *423*, 213491.
- [132] M. P. Warusawithana, C. S. Kengle, X. Zhan, H. Chen, E. V. Colla, M. O’Keeffe, J.-M. Zuo, M. B. Weissman, J. N. Eckstein, *Phys. Rev. B* **2021**, *104*, 085103.
- [133] C. Dirk, R. Twieg, G. Wagniere, *J. Am. Chem. Soc.* **1986**, *108*, 5387–5395.
- [134] J. Chen, C.-L. Hu, F. Kong, J.-G. Mao, *Accounts Chem. Res.* **2021**, *54*, 2775–2783.

- [135] M. Kalmutzki, M. Ströbele, F. Wackenhut, A. J. Meixner, H.-J. Meyer, *Inorg. Chem.* **2014**, *53*, 12540–12545.
- [136] M. Kalmutzki, M. Ströbele, F. Wackenhut, A. J. Meixner, H.-J. Meyer, *Angew. Chem. Int. Ed.* **2014**, *53*, 14260–14263.
- [137] X. Meng, W. Yin, M. Xia, *Coordin. Chem. Rev.* **2021**, *439*, 213916.
- [138] J. Lu, Y.-K. Lian, L. Xiong, Q.-R. Wu, M. Zhao, K.-X. Shi, L. Chen, L.-M. Wu, *J. Am. Chem. Soc.* **2019**, *141*, 16151–16159.
- [139] L. Vella-Zarb, D. Braga, A. G. Orpen, U. Baisch, *CrystEngComm* **2014**, *16*, 8147–8159.
- [140] S.-F. Li, L. Hu, Y. Ma, F.-F. Mao, J. Zheng, X.-D. Zhang, D. Yan, *Inorg. Chem.* **2022**, *61*, 10182–10189.
- [141] A. B. Wiles, D. Bozzuto, C. L. Cahill, R. D. Pike, *Polyhedron* **2006**, *25*, 776–782.
- [142] E. Bayat, M. Ströbele, M. Abbasi, S. Kroeker, J. Valenta, D. Enseling, T. Jüstel, H.-J. Meyer, *Inorg. Chem.* **2024**, *63*, 19053–19062.
- [143] E. Bayat, M. Ströbele, D. Enseling, T. Justel, H.-J. Meyer, *Dalton Trans.* **2024**, *53*, 10912–10918.
- [144] E. Bayat, M. Ströbele, D. Enseling, T. Jüstel, H.-J. Meyer, *Molecules* **2024**, *29*, 5598.
- [145] L. Liu, Z. Bai, L. Hu, D. Wei, Z. Lin, L. Zhang, *J. Mater. Chem. C* **2021**, *9*, 7452–7457.
- [146] Z. Bai, J. Lee, H. Kim, C.-L. Hu, K. M. Ok, *Small* **2023**, *19*, 2301756.
- [147] X. Dong, L. Huang, H. Zeng, Z. Lin, K. M. Ok, G. Zou, *Angew. Chem. Int. Ed.* **2022**, *61*, e202116790.
- [148] A. Cammarata, W. Zhang, P. S. Halasyamani, J. M. Rondinelli, *Chem. Mater.* **2014**, *26*, 5773–5781.
- [149] P. Schmidt, F. Strauß, M. Scheele, C. P. Romao, H.-J. Meyer, *Dalton Trans.* **2026**, *55*, 3296–3309.
- [150] N. Alcock, A. Kjekshus, *Acta Chem. Scand.* **1965**, *19*, 79.
- [151] W. W. Wendlandt, H. G. Hecht, *Reflectance spectroscopy*, Interscience, New York, **1966**.
- [152] P. Kubelka, F. Munk, *Z. Tech. Phys* **1931**, *12*, 259–274.
- [153] P. Kubelka, *J. Opt. Soc. Am.* **1948**, *38*, 448–457.
- [154] G. Kortüm, H. Koffer, *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 67–75.

- [155] G. Kortum, J. Lohr, *Reflectance Spectroscopy*, Springer, **1969**.
- [156] R. López, R. Gómez, *J. Sol-Gel Sci. Technol.* **2012**, *61*, 1–7.
- [157] A. R. Zanatta, *Sci. Rep.* **2019**, *9*, 11225.
- [158] Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, *Nato. Sc. S. Ss. Iii. C. S.* **2017**, *128*, 140–184.
- [159] B. Brown, *Acta Crystallogr.* **1966**, *20*, 264–267.
- [160] A. Mar, J. A. Ibers, *J. Solid State Chem.* **1992**, *97*, 366–376.
- [161] R. Kniep, H.-J. Beister, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 393–394.
- [162] H. M. Haendler, D. Mootz, A. Rabenau, G. Rosenstein, *J. Solid State Chem.* **1974**, *10*, 175–181.
- [163] S. Srivastava, B. Avasthi, *J. Mater. Sci.* **1985**, *20*, 3801–3815.
- [164] M. H. Whangbo, E. Canadell, P. Foury, J. P. Pouget, *Science* **1991**, *252*, 96–98.
- [165] P. Schmidt, C. Romao, H.-J. Meyer, *Dalton Trans.* **2026**, *55*, 8228–8242.
- [166] S. S. Yarovoi, A. I. Smolentsev, A. V. Ermolaev, Y. V. Mironov, *J. Struct. Chem.* **2016**, *57*, 199–201.
- [167] B. Krebs, V. Paulat, *Acta Crystallogr.* **1976**, *B32*, 1470–1476.
- [168] R. Kniep, J. Beister Heinz, D. Wald, *Z. Naturforsch. B* **1988**, *43*, 966.
- [169] M. Ströbele, C. Castro, R. F. Fink, H.-J. Meyer, *Angew. Chem-ger. Edit.* **2016**, *128*, 4894–4897.
- [170] M. Ströbele, H.-J. Meyer, *Inorg. Chem.* **2017**, *56*, 5880–5884.
- [171] T. Hummel, A. Moś-Hummel, A. Merkulova, M. Ströbele, A. Krishnamurthy, S. Kroeker, H.-J. Meyer, *Inorg. Chem.* **2018**, *57*, 2570–2576.
- [172] T. Hummel, A. Moś-Hummel, M. Ströbele, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2019**, *645*, 831–834.
- [173] A. D. Fuhrmann, F. Pachel, M. Ströbele, D. Enseling, T. Jüstel, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2020**, *646*, 1650–1654.
- [174] F. Grahlow, F. Strauss, P. Schmidt, J. Valenta, M. Ströbele, M. Scheele, C. P. Romao, H. J. Meyer, *Inorg. Chem.* **2024**, *63*, 19717–19727.
- [175] J. Beitzberger, M. Ströbele, F. Strauß, M. Scheele, C. P. Romao, H.-J. Meyer, *Eur. J. Inorg. Chem.* **2024**, *27*, e202400329.

- [176] J. Beitzberger, M. Martin, M. Scheele, P. Schmidt, M. Ströbele, H.-J. Meyer, *Dalton T.* **2025**, *54*, 5486–5493.
- [177] J. Beitzberger, M. Ströbele, P. Schmidt, C. P. Romao, H.-J. Meyer, *Dalton Trans.* **2025**, *54*, 14376–14383.
- [178] M. Groß, P. Schmidt, C. P. Romao, D. Ensling, T. Jüstel, M. Brytskyi, S. Kroeker, H.-J. Meyer, *Eur. J. Inorg. Chem.* **2025**, *28*, e202500256.
- [179] M. Groß, C. D. Brand, P. Schmidt, T. Parker, D. Zhang, C. P. Romao, H.-J. Meyer, *Dalton T.* **2025**, *54*, 17941–17949.
- [180] P. H. Gamlen, J. W. White, *J. Chem. Soc. Faraday Trans. 2* **1976**, *72*, 446–455.
- [181] L. Yao, H. Yao, G. Xi, Y. Feng, *RSC Adv.* **2016**, *6*, 17947–17954.

Appendix

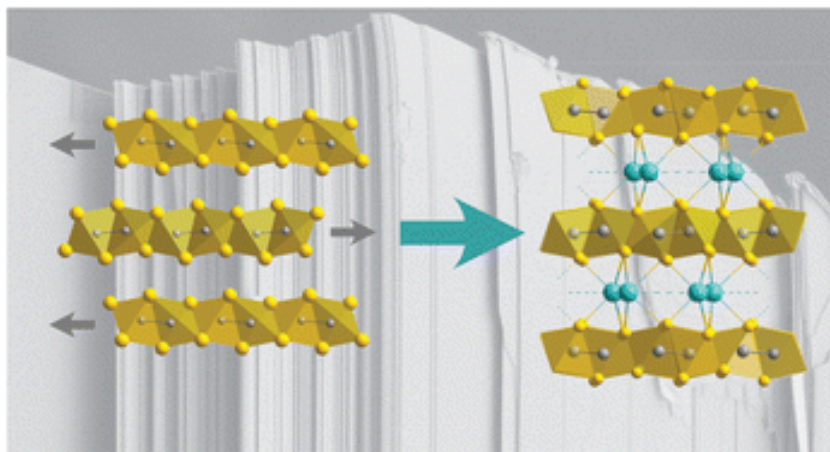
All reproduced and referenced figures are shown as they appeared in the original articles, with the exception of the figures listed below, which were modified.

- Rearranged figure panels: Figure 10, 28, 31 and 32.
- Combined two separate figures into one multi-panel figure: Figure 12, 13, 14, 34, 37, 38, 39 and 40.
- Combined three separate figures into one multi-panel figure: Figure 33 and 36.

5 Publications

Publication 1

Intercalation of alkali metal into WTe_2 , the crystal structure of $\text{A}_{0.5}\text{WTe}_2$ and observation of a metal-to-semiconductor transition Synthesis and SHG properties of the melamine-based



<https://doi.org/10.1039/d5dt02775f>

Reprinted with permission from

Dalton Trans. **2026**, 55, 3296-3309.

Copyright © 2026 The Royal Society of Chemistry

PAPER

[View Article Online](#)
[View Journal](#) | [View Issue](#)Cite this: *Dalton Trans.*, 2026, **55**, 3296Intercalation of alkali metal into WTe_2 , the crystal structure of $\text{A}_{0.5}\text{WTe}_2$ and observation of a metal-to-semiconductor transitionPatrick Schmidt,^a Fabian Strauß,^b Marcus Scheele,^b Carl P. Romao^c and Hans-Jürgen Meyer^{id} *^a

We explore the cationic intercalation of tungsten ditelluride (WTe_2) with potassium (K), rubidium (Rb), and cesium (Cs), yielding intercalation compounds of the form $\text{A}_{0.5}\text{WTe}_2$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$). Structural characterization was performed using powder X-ray diffraction (PXRD), while diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and temperature-dependent conductivity measurements were employed to investigate the electronic properties. Density functional theory (DFT) calculations were carried out to support the experimental findings and to provide insight into the intercalation mechanisms and the resulting material characteristics. All synthesized compounds display semiconducting behavior with narrow band gaps, emphasizing the influence of alkali metal intercalation on the electronic structure and transport properties of WTe_2 . These results advance the fundamental understanding of property modulation in transition-metal dichalcogenides (TMDCs) and highlight their potential for electronic device applications.

Received 19th November 2025,
Accepted 26th January 2026

DOI: 10.1039/d5dt02775f

rsc.li/dalton

Introduction

Transition metal dichalcogenides (TMDCs) represent a prominent class of two-dimensional layered materials that continue to attract significant scientific interest due to their remarkable chemical and physical properties, which can be systematically tuned by variations in composition, the number of layers, applied pressure, and intercalation chemistry.^{1–3} In these materials, transition metal atoms are sandwiched between two layers of chalcogen atoms, forming robust two-dimensional structures with strong in-plane bonds within each layer and weak van der Waals forces between layers. This structural motif enables the formation of a range of polytypes and stacking sequences and allows intercalation of guest species between the layers, similar to well-known intercalation processes in graphite.^{3–7} Such intercalation reactions can involve different atoms^{8–13} such as alkali metals, halogen atoms, or organic molecules,^{14–16} thereby producing stoichiometric or nonstoichiometric intercalation compounds whose structural, electronic, and magnetic properties can strongly differ from those of the pristine host material.^{17–20} This process can also

serve as a precursor for the exfoliation of single TMDC layers.^{21–26}

Among the TMDCs, tungsten ditelluride (WTe_2)²⁷ is distinguished by its unique low-symmetry distorted T_d structure, which can be described as a variant of the 1T structure derived from TiS_2 .²⁸ In WTe_2 , each tungsten atom is coordinated in a distorted octahedral environment by tellurium atoms and is displaced from the center of the octahedron to form distinctive W–W zigzag chains running along the a -axis (see Fig. 1). This unusual arrangement results in a semi-metallic behaviour,^{29–31}

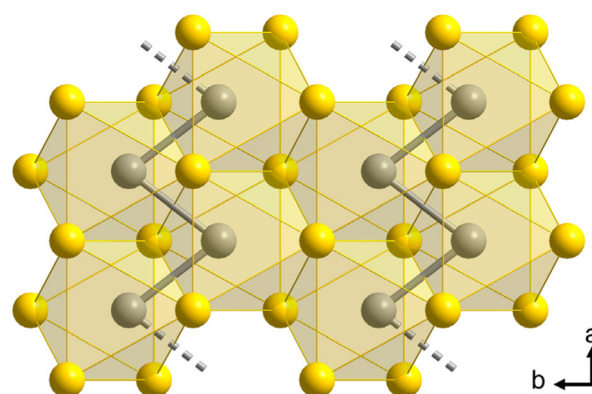


Fig. 1 Projection of the WTe_2 structure. View along the c -axis of the distorted T_d structure in which tungsten (grey) atoms follow a CDW along the a -axis. Tungsten atoms are shifted off the octahedral centers formed by tellurium (yellow) atoms.

^aSection of Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany. E-mail: juergen.meyer@uni-tuebingen.de

^bInstitute of Physical and Theoretical Chemistry, Eberhard Karls University Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

^cDepartment of Materials, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Trojanova 13, Prague 120 00, Czech Republic

large non-saturating magnetoresistance,^{32,33} and exotic phenomena such as charge density waves (CDWs),^{34–41} superconductivity,⁴² and the realization of type-II Weyl semimetal states.^{43,44} These properties have made WTe_2 a model system for studying the interplay between structural distortions, electronic topology, and transport phenomena in low-dimensional materials.

Intercalation of WTe_2 offers an effective means to tune these properties further by introducing additional charge carriers and modifying the delicate balance of bonding interactions within the layers. For example, the oxidative intercalation of iodine into WTe_2 has been shown to produce WTe_2I , a phase that displays distinctly different electronic behavior due to anion insertion.⁴⁵ Conversely, the cationic intercalation of alkali metals has long been recognized as a route to electron doping, local structural distortion, and symmetry lowering.^{46,47} Recent work on lithium intercalation is particularly notable, although single-crystal structure refinement remains challenging due to lithium's low (X-ray) scattering power. *In situ* electrochemical studies have demonstrated that lithium can be reversibly inserted into the WTe_2 lattice, driving a metal-to-semiconductor transition with the emergence of a calculated small band gap (0.392 eV)⁴⁸ and charge-density-wave (CDW) ordering.^{48,49} These findings highlight the crucial role of the electron count in modifying the W–W bonding network and lifting degeneracies at the Fermi level, providing a strong rationale for systematic studies of alkali–metal intercalation in this class of low-symmetry TMDCs.

In addition to chemical intercalation, strain and external stress could have a significant impact on the electronic properties of WTe_2 .^{50–57} Theoretical and experimental studies show that applying uniaxial or biaxial strain can open a band gap in otherwise semi-metallic WTe_2 . For instance, DFT calculations predict that moderate strain along the *b*-axis can significantly increase the band gap in monolayer or nanoribbon forms, while twisted bilayer WTe_2 can undergo semiconductor-to-metal transitions driven by strain and twist angles due to moiré effects and interlayer coupling. Such strain- and twist-driven phenomena underline how subtle lattice distortions, whether induced mechanically or *via* intercalation, play a decisive role in determining the resulting electronic structure.

A significant challenge in handling alkali intercalation compounds is their pronounced sensitivity to moisture.^{17,58–64} Initially, the co-intercalation of water is often observed, introducing additional complexities.^{65–70} This is typically followed by hydrolysis, where the intercalated metal reacts with further water, leading finally to the formation of hydroxides and the release of hydrogen gas. These reactions degrade the material, resulting in alterations to its structure and properties. To mitigate these issues, it is essential to handle intercalated compounds in inert atmospheres, such as argon-filled glove boxes, to prevent moisture exposure and the subsequent degradation reactions that compromise the material's integrity and functionality.

The synthesis and stabilization of alkali intercalation compounds require precise control of experimental conditions,

including temperature, pressure, and the stoichiometry of the reactants.^{58–61} The insertion of alkali metals into TMDCs often involves high-temperature solid-state reactions, solution chemistry or electrochemical intercalation methods, which must be carefully controlled to avoid unwanted side reactions and ensure uniform intercalation.

Determining the structure of these intercalation compounds poses another significant challenge.^{71–76} The weak van der Waals interactions and potential disorder within the layers make single-crystal structure determination particularly difficult.^{17,70,77} Single crystals of intercalated TMDCs are often of poor quality, exhibiting defects and a lack of long-range order, complicating the collection of high-quality diffraction data. As a result, it is frequently recommended to use powder X-ray diffraction (PXRD) rather than relying on single-crystal diffraction methods.⁷⁸ PXRD allows for the averaging of structural information over many crystallites, and can provide a more accurate and reliable determination of the intercalated structure.

The structural complexity of WTe_2 adds an additional layer of difficulty not only to the intercalation process but also to its accurate characterization. Unlike many TMDCs,^{79,80} which possess relatively straightforward coordination environments conducive to alkali intercalation, its distorted layers and their relative arrangement do not provide well-defined octahedral or tetrahedral voids (see Fig. 2).

In this study, we explore the cationic intercalation of WTe_2 with alkali metals, resulting in the formation of $\text{A}_{0.5}\text{WTe}_2$ (*A* = K, Rb, Cs). Our goal is to investigate the structural and electronic changes induced by cationic intercalation and to understand how these alterations influence the material's overall properties. Furthermore, we address the challenges associated with the moisture sensitivity of these compounds and the difficulties in their structural characterization, emphasizing the use of powder diffraction techniques for accurate structure determination.

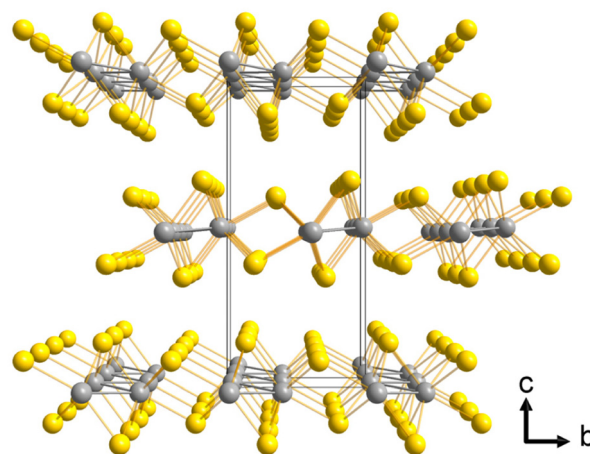


Fig. 2 Sectional view of the WTe_2 crystal structure, highlighting tungsten (grey) and tellurium (yellow) atoms. The illustration emphasizes the layered arrangement and distorted octahedral coordination environment characteristic of WTe_2 .



Results and discussion

Preparation of $A_{0.5}WTe_2$ compounds

The intercalation of WTe_2 with potassium, rubidium, and cesium was approached using various methods to ensure successful intercalation of the alkali atoms while minimizing disorder and reduction of the WTe_2 host compound.

A direct synthesis from the elements causes a violent reaction of tellurium with liquid alkali metals, resulting in the formation of a mixture of multiple alkali tellurides (A_xTe , with $A = K, Rb, Cs$; $x = 0.4-2$). Heating these reaction mixtures yielding in mixed phases containing W , WTe_2 , and tellurium-rich A_xTe compounds, highlighting the limitations of direct synthesis compared to other alkali intercalated TMDCs.⁸¹⁻⁸⁴ Given cesium's lowest melting point among the alkali metals, adding liquid cesium to WTe_2 at $\sim 35^\circ C$ also resulted in a strong exothermic reaction, yielding in Cs_xTe ,^{85,86} unreacted WTe_2 , and a small amount of $Cs_{0.5}WTe_2$. An alkali vapor intercalation approach was also attempted, in which cesium metal was placed inside an open silica ampoule in a larger, vacuum closed ampoule surrounded by WTe_2 . Despite using excess cesium, complete intercalation was not achieved, and Cs_xTe phases were observed in the temperature range of $180-300^\circ C$, reaffirming the limitations of direct alkali intercalation and synthesis. As later established, sealed-ampoule experiments show that all phase-pure $A_{0.5}WTe_2$ phases undergo slow decomposition upon heating above $\sim 100^\circ C$.

Given the inherent limitations of both, direct synthesis and alkali vapor intercalation, classical solid-state methods proved unsuitable for producing phase-pure A_xWTe_2 . This necessitated the exploration of low-temperature solution-based alternatives. A well-established approach is the use of alkali naphthalenide solutions,⁸⁷⁻⁹² which enables the intercalation of alkali atoms into the van der Waals gap at low temperatures. This slow, low-temperature process is crucial as it reduces the risk of strain- or shear-induced lattice distortion and avoids the undesirable chemical reduction of the host lattice to form A_xTe and elemental tungsten. Therefore, WTe_2 was added to a 0.2 M THF solution of alkali naphthalenide, with the reaction temperature optimized to $-80^\circ C$ for single crystals and $-50^\circ C$ for crystalline powder. While the powder reaction required typically 3.5 h, single crystals needed to be maintained at the lower temperature for over five weeks. Attempts at higher temperature (e.g. above $-40^\circ C$) resulted in rapid intercalation dynamics and a detrimental 'curly' crystal morphology (even at low concentrations of 2 mM, see Fig. S1). However, despite the successful synthesis of single crystals under these $-80^\circ C$ conditions, subsequent extreme sensitivity to moisture, air, and mechanical stress (touch) rendered single-crystal X-ray diffractometry unfeasible.

Structural studies and stability of $A_{0.5}WTe_2$

The crystallographic analysis of $A_{0.5}WTe_2$ ($A = K, Rb, Cs$) reveals significant changes to the host structure, as a consequence of alkali metal intercalation. The key structural change observed through powder X-ray diffraction (PXRD) is an

increase in the spacing between adjacent WTe_2 sheets, which confirms the successful accommodation of alkali ions into the van der Waals gaps. The increase in interlayer distance is directly linked to the size of the intercalating cation; larger ions such as cesium produce a more pronounced expansion in layer spacing than rubidium or potassium because of their greater ionic radii (see Fig. 3, spacing values are given in Table S1).

The crystal structures of $A_{0.5}WTe_2$ compounds with $A = K, Rb, Cs$ were solved from PXRD using EXPO2014,⁹³ and refined by Rietveld methods in FullProf (FP)⁹⁴ with a modified Thompson-Cox-Hastings pseudo-Voigt (TCHZ) profile function.^{95,96} The instrumental resolution function (IRF) was obtained from the NIST Si640f standard⁹⁷ and fitted in WinPLOTR.⁹⁸ Additionally, multiple texturing effects, such as particle form, size, and orientation, were included in the Rietveld refinements to enhance the accuracy of the model. The initial structure solution and indexing of $Rb_{0.5}WTe_2$, based only on the strongest reflections, yielded a monoclinic cell in $P2_1/m$. This cell ($a = 3.6904(1) \text{ \AA}$, $b = 17.8326(4) \text{ \AA}$, $c = 6.2639(1) \text{ \AA}$, $\beta = 90.5046(9)^\circ$) showed a pronounced layer expansion along b -axis, relative to the corresponding c lattice parameter in pristine WTe_2 ⁹⁹ ($a = 3.477(2) \text{ \AA}$, $b = 6.249(4) \text{ \AA}$, $c = 14.018(9)$). Despite good refinement values, this initial model featured disordered alkali sites with a refined occupancy of ~ 0.50 (Fig. S2). Incorporating weaker reflections revealed a cell of nearly double the volume and the full resolution of the disordered alkali atoms ($a = 7.29929(6) \text{ \AA}$, $b = 17.8359(2) \text{ \AA}$, $c = 7.24461(6) \text{ \AA}$, $\beta = 118.9979(4)^\circ$, see Fig. 4). The connection between the initial and final models can be rationalized by an isomorphic group-subgroup relation, illustrated for $Rb_{0.5}WTe_2$ as a Bärnighausen tree in Fig. S3. Similarly, $K_{0.5}WTe_2$ (Fig. S4) and $Cs_{0.5}WTe_2$ (Fig. S5) refine isotypically to the rubidium intercalation compound and are provided in the SI.¹⁰⁰ All relevant crystallographic parameters are summarized in Table 1.

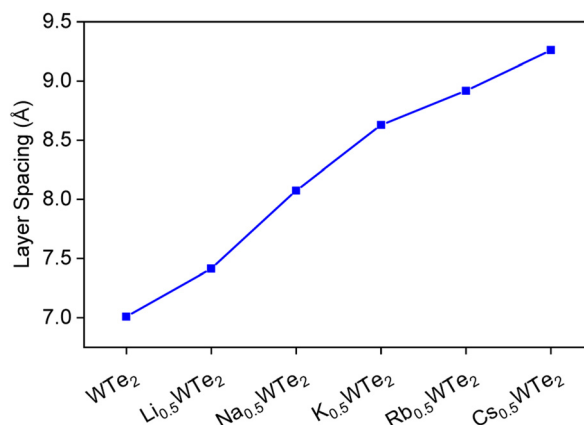


Fig. 3 Interlayer spacing of pristine WTe_2 and its alkali-metal-intercalated derivatives, determined from PXRD via the (002) Bragg reflection. Synthetic details for $Li_{0.5}WTe_2$ and $Na_{0.5}WTe_2$ are provided in the SI. The layer spacing increases systematically with cation ionic radius.



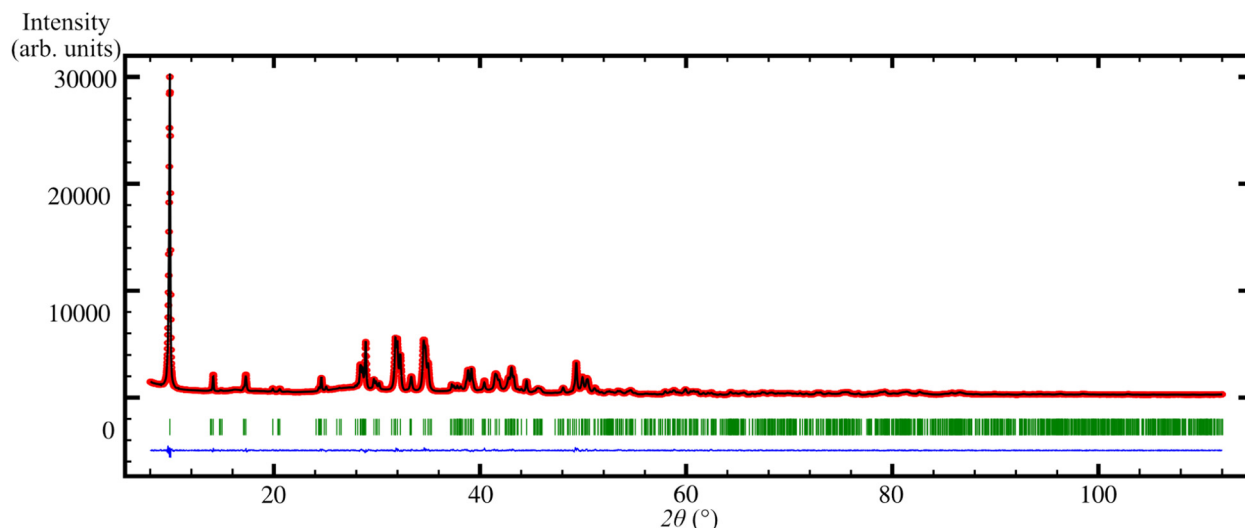


Fig. 4 PXRD structure refinement of $\text{Rb}_{0.5}\text{WTe}_2$ with the space group $P2_1/m$ at 298 K with the experimental (red) and calculated (black) intensities of the Rietveld refinement. Bragg positions (green) and the difference curve (blue) are also shown.

Table 1 Crystallographic data of pristine WTe_2 and its alkali metal-intercalated derivatives ($\text{A}_{0.5}\text{WTe}_2$, $\text{A} = \text{K}, \text{Rb}, \text{Cs}$) with additional distances and Rietveld refinement values

	WTe_2 ⁹⁹	$\text{K}_{0.5}\text{WTe}_2$	$\text{Rb}_{0.5}\text{WTe}_2$	$\text{Cs}_{0.5}\text{WTe}_2$
Formula	WTe_2	$\text{K}_2\text{W}_4\text{Te}_8$	$\text{Rb}_2\text{W}_4\text{Te}_8$	$\text{Cs}_2\text{W}_4\text{Te}_8$
Z	4	2	2	2
Space group	$Pmn2_1$	$P2_1/m$	$P2_1/m$	$P2_1/m$
$a/\text{\AA}$	3.477(2)	7.29743(8)	7.29929(6)	7.29984(6)
$b/\text{\AA}$	6.249(4)	17.2594(2)	17.8359(2)	18.5213(3)
$c/\text{\AA}$	14.018(9)	7.24144(8)	7.24461(6)	7.24484(6)
$\beta/^\circ$	90	119.1069(4)	118.9979(4)	118.9297(4)
$V/\text{\AA}^3$	304.6(3)	796.876(16)	824.93(1)	857.29(2)
Number of reflections	—	1136	1179	1383
Number of parameters	—	54	45	44
R_{Bragg}	—	1.44	1.53	1.72
R_p/R_{wp}	—	3.38/4.31	2.92/3.82	3.76/4.95
χ^2	—	1.0222	1.0012	1.1877
CCDC	73323	2392515	2390030	2390900

All intermediate and final structure models were validated with PLATON.¹⁰¹

The validity of our indexing and structure-solution strategy is substantiated by a similar unit-cell choice, including a β angle of nearly 120° , previously reported for electrochemically Li-intercalated WTe_2 by Muscher *et al.* – despite their lack of a fully refined structure.⁴⁸ For completeness of our study, we also prepared $\text{A}_{0.5}\text{WTe}_2$ with $\text{A} = \text{Li}$ and Na , with the synthetic details provided in the SI. Our structural model for $\text{Li}_{0.5}\text{WTe}_2$ was refined in the same $P2_1$ space group as previously reported by Muscher, revealing similar unit cell dimensions ($a = 7.2813(1) \text{ \AA}$, $b = 14.8109(3) \text{ \AA}$, $c = 7.2324(1) \text{ \AA}$, $\beta = 119.3428(8)^\circ$). The symmetry reduction from $P2_1/m$ to $P2_1$ is governed by the relative stacking of the WTe_2 layers with respect to one another. The Na analogue, $\text{Na}_{0.5}\text{WTe}_2$, refines in the space group $P2_1/m$, yielding distinct parameters ($a = 7.2897(2) \text{ \AA}$, $b = 16.1501(3) \text{ \AA}$, $c = 7.24837(2) \text{ \AA}$, $\beta = 119.1634(5)^\circ$). Nevertheless, the structural refinements for both compounds remain unsatisfactory

because of the weak X-ray scattering power of light atoms like Li and Na compared to WTe_2 ; we therefore report synthesis details and Le Bail fits for these intercalation compounds in the SI (Fig. S6 and S7).

As a result of the alkali metal intercalation into the van der Waals gap, the WTe_2 layers are essentially preserved, while adjacent layers undergo a significant shift relative to each other along $[10\bar{1}]$, aligning the tungsten chains along the b -axis (see Fig. 5).

The final structural model reveals an ordered, honeycomb-like arrangement of the intercalant within the van der Waals gap (Fig. 6) with representative $\text{Rb}\cdots\text{Rb}$ separations of 3.7917(7) to 5.140(1) $\text{\AA}$. The two crystallographically distinct alkali-metal positions exhibit distorted cubic coordination ($\text{CN} = 8$) environment (see Fig. 7), with $\text{Rb}\cdots\text{Te}$ distances ranging from 3.556(4) to 4.122(5) $\text{\AA}$.

Although the overall topology of individual WTe_2 layers remains largely unchanged in $\text{A}_{0.5}\text{WTe}_2$, slight distortions in



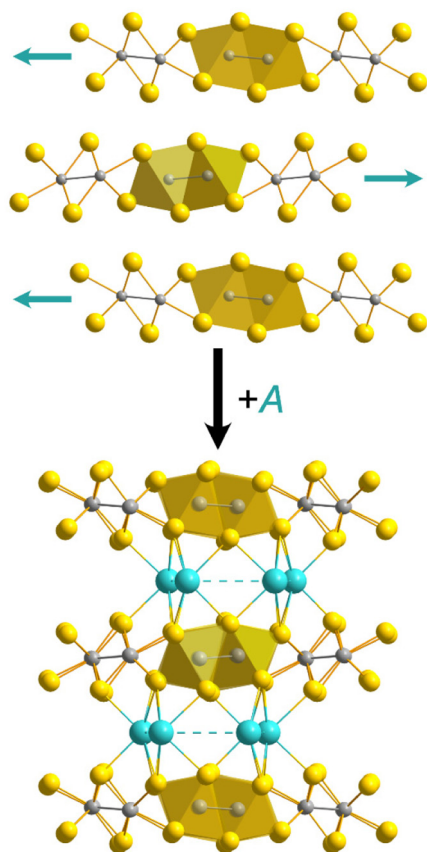


Fig. 5 Structural transformation of WTe_2 (top) to $\text{A}_{0.5}\text{WTe}_2$ (bottom) induced by alkali intercalation. The adjacent WTe_2 layers experience a significant shift, highlighted by the tungsten telluride chains (W: grey, Te: yellow, A: turquoise).

the positions of the tungsten and tellurium atoms are observed compared to those in WTe_2 . The intercalation lowers the symmetry from orthorhombic $Pmn2_1$ of the pristine WTe_2 , to monoclinic $P2_1/m$ for the intercalated $\text{A}_{0.5}\text{WTe}_2$ phases ($A = \text{K}, \text{Rb}, \text{Cs}$), or even $P2_1$ for the lithium-intercalated compound.⁴⁸ The symmetry reduction between monoclinic space groups is accompanied by a doubling of the unit cell, which in turn doubles the number of crystallographically distinct atomic sites and facilitates the observed distortions.

A closer examination of bond distances in Table 2 and Fig. 8 reveals that the distortion in the tungsten chain is likely driven by the formal addition of half an electron per WTe_2 formula unit, introduced by the alkali metal. Departing from an equidistant pattern of W–W distances in the structure of WTe_2 we note a distortion involving clustering of metal atoms when going to $\text{Rb}_{0.5}\text{WTe}_2$, with distances ranging between 2.794(3) and 3.146(3) Å (see Fig. 8(a) and (b)).

A gradually increased distortion pattern between rhenium atoms is observed in the structure of ReSe_2 (see Fig. 8c), which is another 2D TMDC with one additional d electron compared to WTe_2 . Despite crystallizing in a triclinic space group, ReSe_2 exhibits a similar layered structure with pronounced in-plane distortions of the Re–Re chains, respectively clustering. If the

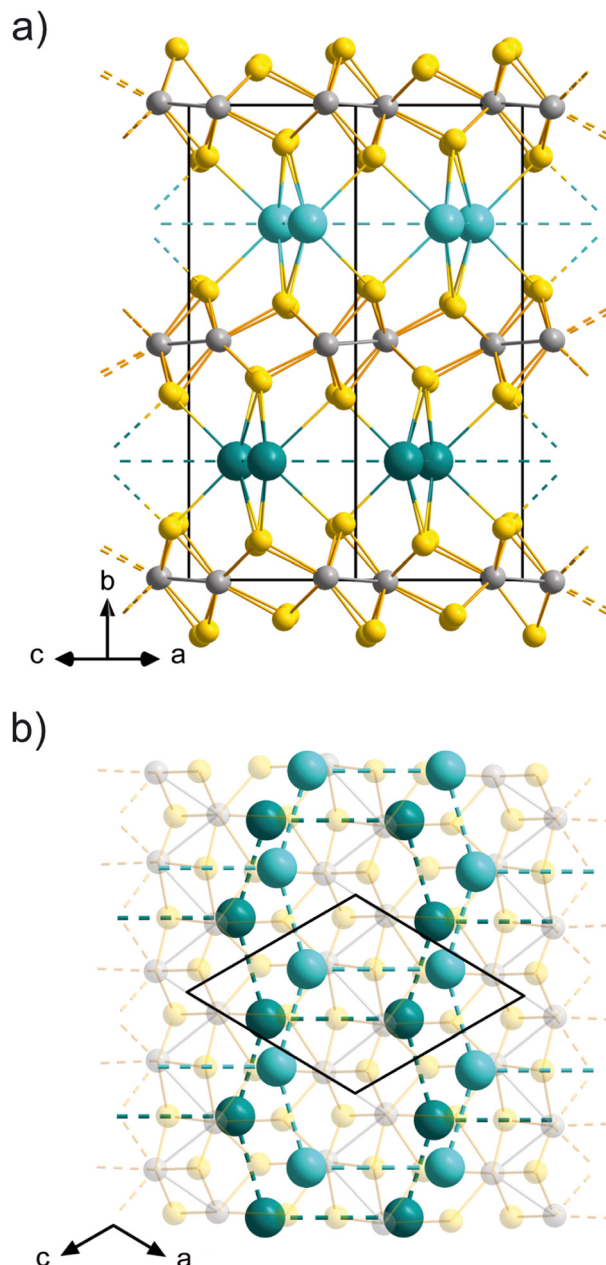


Fig. 6 Section of the $\text{Rb}_{0.5}\text{WTe}_2$ crystal structure. (a) View along the tungsten zigzag chains. (b) View along the b -axis showing the arrangements of Rb ions, shown turquoise, one of them semi-transparent (75% opacity), separated by one central WTe_2 layer (W: grey, Te: yellow).

largest bond connecting the rhenium zig-zag chains is neglected, one observes Re_4 clusters with bond lengths ranging from 2.6471(3) to 2.9273(3) Å. This highlights how electron count can drive comparable bonding and symmetry-lowering effects across group 6 and 7 dichalcogenides.^{102,103}

If we assign electrons to a series of rhombic M_4 clusters, we count 10 e^- per rhombic cluster ($\text{Rb}_2\text{W}_4\text{Te}_8$) in $\text{Rb}_{0.5}\text{WTe}_2$ and 12 e^- per rhombic cluster (Re_4Se_8) in ReSe_2 , wherein two electrons can formally be assigned to inter-cluster bonding. A comparable, isolated rhombic M_4 cluster is known in the structure



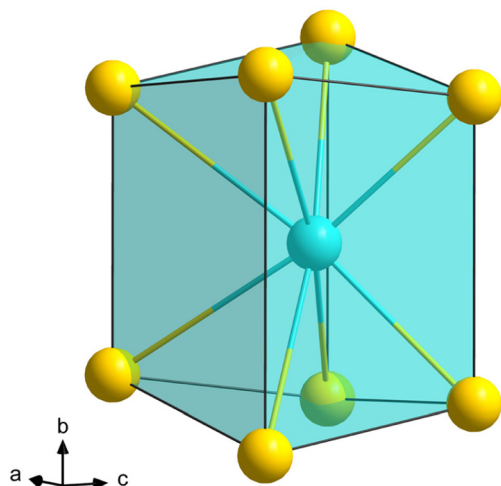


Fig. 7 Distorted cubic coordination environment of the rubidium atoms in $\text{Rb}_{0.5}\text{WTe}_2$ (W: grey, Te: yellow, Rb: turquoise).

Table 2 Selected interatomic distance (Å) for the refined structures

	WTe_2 ⁹⁹	$\text{K}_{0.5}\text{WTe}_2$	$\text{Rb}_{0.5}\text{WTe}_2$	$\text{Cs}_{0.5}\text{WTe}_2$
$d_{\text{W-W}}/\text{Å}$	2.85(1)	2.825(1), 2.860(2), 3.160(1)	2.794(3), 2.850(3), 3.146(3)	2.791(3), 2.846(3), 3.181(3)
$d_{\text{W-Te}}/\text{Å}$	2.70(1)– 2.80(1)	2.667(1)– 2.865(3)	2.691(6)– 2.860(5)	2.659(4)– 2.899(6)
$d_{\text{Te-A}}/\text{Å}$	—	3.433(1)– 3.576(1)	3.556(4)– 3.673(3)	3.712(6)– 3.821(6)

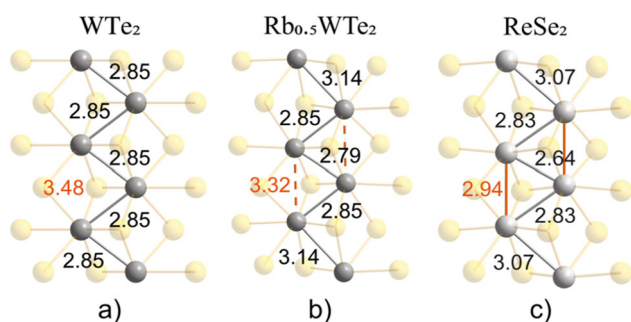


Fig. 8 Section of the (a) WTe_2 (b) $\text{Rb}_{0.5}\text{WTe}_2$ and (c) ReSe_2 structure visualizing the distortion of the metal chain with metal-to-metal distances given in Å (tungsten/rhenium in grey, chalcogens in high opacity yellow).

of $\text{CsNb}_4\text{Cl}_{11}$, which can be explained with the presence of 10 e^- being semi-localized in five metal-to-metal bonds.¹⁰⁴ This simplified assignment of cluster electrons will be corroborated by density functional theory in a following section.

All obtained alkali-intercalated phases are extremely sensitive to moisture. A time-resolved PXRD analysis of $\text{Rb}_{0.5}\text{WTe}_2$ (Fig. 9; sample placed between two Mylar foils and not hermetically sealed with Lithelen grease) reveals discrete stages of H_2O co-intercalation that precede subsequent hydrolysis. The

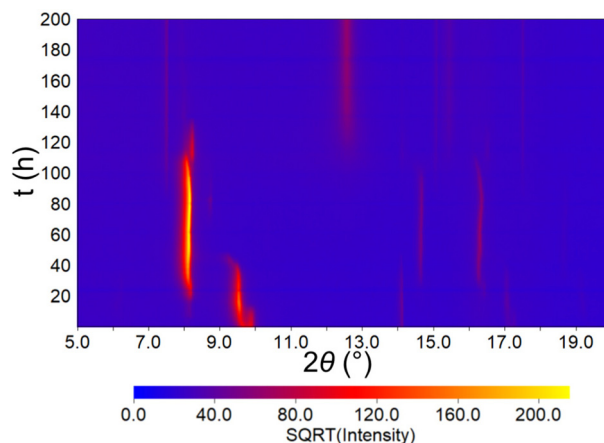


Fig. 9 Time resolved PXRD analysis of $\text{Rb}_{0.5}\text{WTe}_2$ showing structural evolution under hydrolysis (for full 2θ range see Fig. S8).

(002) reflection in the PXRD pattern – directly displaying the interlayer spacing – shifts stepwise from $2\theta = 9.91^\circ$ ($d_{002} = 8.9815 \text{ Å}$) to as low as $2\theta = 8.12^\circ$ ($d_{002} = 10.8953 \text{ Å}$), consistent with an interlayer gallery expansion of $\sim 1.91 \text{ Å}$ ($\sim 21\%$). Concurrent shifts of reflections in the $14\text{--}18^\circ$ 2θ range indicate adjustments of a and/or b lattice parameter. Upon subsequent hydrolysis/de-intercalation, Bragg intensities diminish and reflections broaden, evidencing loss of long-range order and increased stacking disorder.

ICP-OES

A chemical analysis of $\text{A}_{0.5}\text{WTe}_2$ for $A = \text{Li}, \text{K}, \text{Rb}$ by inductively coupled plasma optical emission spectrometry (ICP-OES) and RFA confirmed the identity of the product with an average elemental ratio (from a multiple measurements) corresponding to $A : \text{W} : \text{Te} = 0.50(3) : 1 : 1.98(3)$.

SEM and EDX

Scanning Electron Microscopy (SEM) analysis of $\text{Rb}_{0.5}\text{WTe}_2$ samples revealed that the crystallites exhibit a pronounced platelet morphology (see Fig. 10 and Fig. S9), indicative of their layered structure. Although individual layers and their interlayer spacings could not be resolved, the observed morphology aligns with the expected anisotropic growth patterns characteristic of such materials. This suggests a preferential growth along specific crystallographic planes, resulting in the formation of thin, plate-like structures.

The pronounced planar habitus observed in SEM images is consistent with the inherent two-dimensional nature of the crystal lattice, which promotes extensive lateral extension while limiting perpendicular growth. Consequently, the orientation of the platelets has also been considered in powder X-ray diffraction (PXRD) analysis, as it may lead to preferred orientation effects that influence the diffraction pattern.

Energy Dispersive X-ray (EDX) measurements further confirm the elemental composition of the samples, with an average ratio of $\text{Rb} : \text{W} : \text{Te} = 0.50(2) : 1 : 2.02(4)$, consistent with



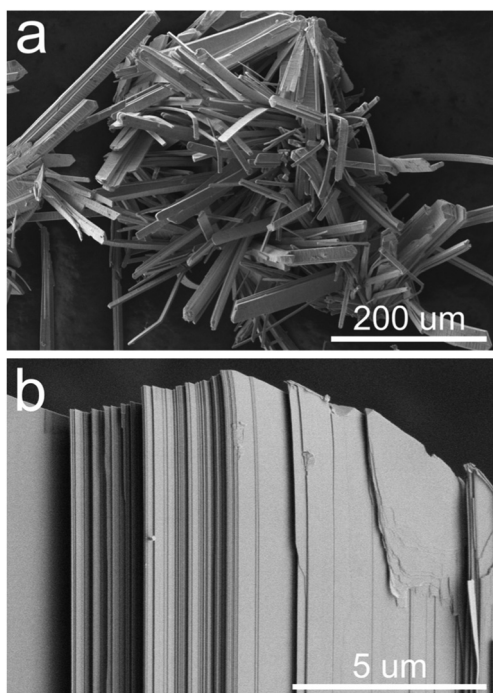


Fig. 10 Scanning electron microscopy (SEM) images of $\text{Rb}_{0.5}\text{WTe}_2$ crystals at 200 $\times$ (a) and 10 000 $\times$ (b) magnification, highlighting the layered morphology.

the stoichiometry of $\text{Rb}_{0.5}\text{WTe}_2$ (see Fig. S10). Notably, the morphology and elemental composition are representative of the analogous compounds containing potassium (K) and cesium (Cs), highlighting the broader applicability of these observations across the family of alkali-metal-intercalated WTe_2 materials.

Electrical properties

Temperature-dependent conductivity measurements were conducted on $\text{Rb}_{0.5}\text{WTe}_2$ single crystals in a range from 75 K to 300 K. Fig. 11 shows the current *vs.* voltage curves, revealing

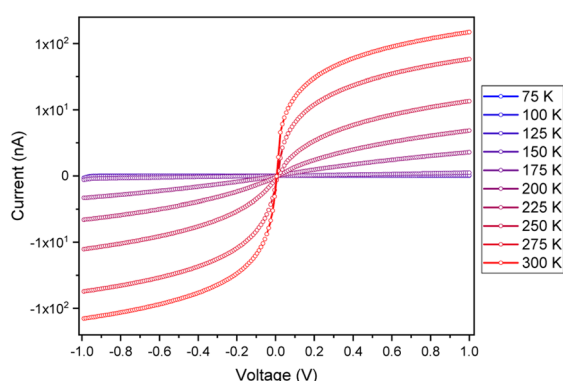


Fig. 11 Current voltage characteristic for the different temperatures measured in the range between 75 K and 300 K from -1 V to 1 V.

ohmic behavior over the entire temperature range with a maximal conductivity of $\rho = 24.3 \text{ mS m}^{-1}$ at 300 K.

Decreasing currents for decreasing voltages indicates semi-conducting behavior of the $\text{Rb}_{0.5}\text{WTe}_2$ crystals. For temperatures below 125 K, the used measurement setup is at its resolution limit and thus cannot show a reliable result. In Fig. 12, this data is presented in an Arrhenius-like plot. By fitting the conductivities from room temperature down to 150 K an activation barrier to transport of 0.476 eV can be estimated under the assumption of a fixed value of the Fermi energy.^{105–108}

Photoelectric properties

Further proof of the semiconducting behavior can be found by measuring the crystal under illumination with a 779 nm CW-laser at a constant bias of 0.2 V. The obtained photoresponse, displayed in Fig. 13, shows a rapid, steep increase which precedes a slower second component. The first rise can be tentatively attributed to photoexcited charge carriers; the second, to the effect of the crystal's concurrent heating.

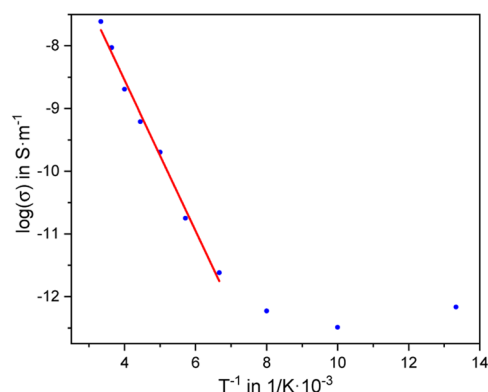


Fig. 12 Arrhenius plot of the electrical conductivity of $\text{Rb}_{0.5}\text{WTe}_2$ at temperatures in the range of 75 K to 300 K. The red line is a linear fit for the range between 150 K and 300 K.

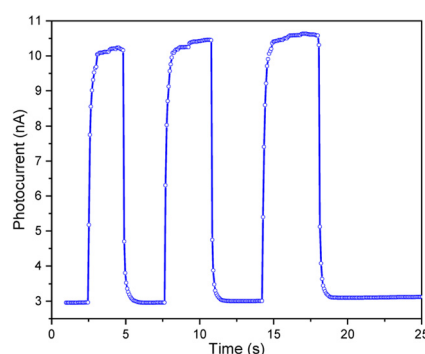


Fig. 13 Photoresponse of a $\text{Rb}_{0.5}\text{WTe}_2$ crystal toward a 779 nm laser at 250 K under a bias of 0.2 V.



Electronic structure

The electronic structures of the $A_{0.5}WTe_2$ compounds, and the general effects of cationic substitution on the electronic properties of WTe_2 were investigated using density functional theory (DFT). The calculated electronic band structures are shown in Fig. 14. All three materials ($A = K, Rb$, and Cs) are predicted by DFT to be semiconductors with indirect band gaps of 0.35 to 0.4 eV. In all cases, the valence band maximum is at the Γ (0 0 0) point in reciprocal space. The conduction band maximum is at Y_2 (−0.5 0 0) in $K_{0.5}WTe_2$ and $Rb_{0.5}WTe_2$ and at a nearby point at (−0.37 0 0) in $Cs_{0.5}WTe_2$. The minimum direct band gap of ca. 0.5 eV is located at the conduction band maximum in all cases. In all three materials, the bands near the Fermi energy have contributions from W 5d and Te 5p orbitals, with somewhat more W character. The cation orbitals are located far below the Fermi energy.

The underestimation of band gaps in DFT is a well-known problem, and therefore the significant overestimation of the indirect bandgap of $K_{0.5}WTe_2$ in DFT is not expected.¹⁰⁹ To

better understand the effects of alkali metal intercalation on WTe_2 , including the possible role of defects and disorder on the electronic structure, we performed calculations of the crystallographic and electronic structures of WTe_2 in the $P2_1/m$ space group but without cations, both in its neutral state and with a −4 charge per unit cell (W_8Te_{16} and $W_8Te_{16}^{4-}$, Fig. 15). The changes to the electronic structure are significant; the neutral form (Fig. 15a) becomes a semimetal with a negative band gap (as is expected for WTe_2), whereas the negatively charged form interestingly is also predicted to be semimetallic, but with zero band gap. This zero-gap state suggests that the very small band gap detected in $K_{0.5}WTe_2$ experimentally could be due to the presence of charged vacancies in the crystal structure.

The crystal structure of WTe_2 in the $P2_1/m$ space group also changes significantly between the charged and uncharged state (similar to Fig. 8a and Fig. S11a). The relaxed structure of the charged state closely resembles that of the intercalated compounds, featuring a reduced interlayer distance and three short W–W bond lengths ranging from 2.783(1) to 2.805(1) Å, along with one longer bond of 3.118(1) Å (similar to Fig. 8b and Fig. S11b). In the neutral state, the internal Te–W–Te angles within the layers are more linear, leading to an increased layer thickness and nearly equal W–W bond lengths of 2.827(1)–2.834 Å, closely resembling the known crystal structure of WTe_2 reported in the literature (Fig. 8a).⁹⁹ These distances are in good agreement to what has been shown in Fig. 8 and lead to a significant change in the electronic structure, as additional bands with Te character (blue) appear near the Fermi energy in Fig. 15a. Without this structural rearrange-

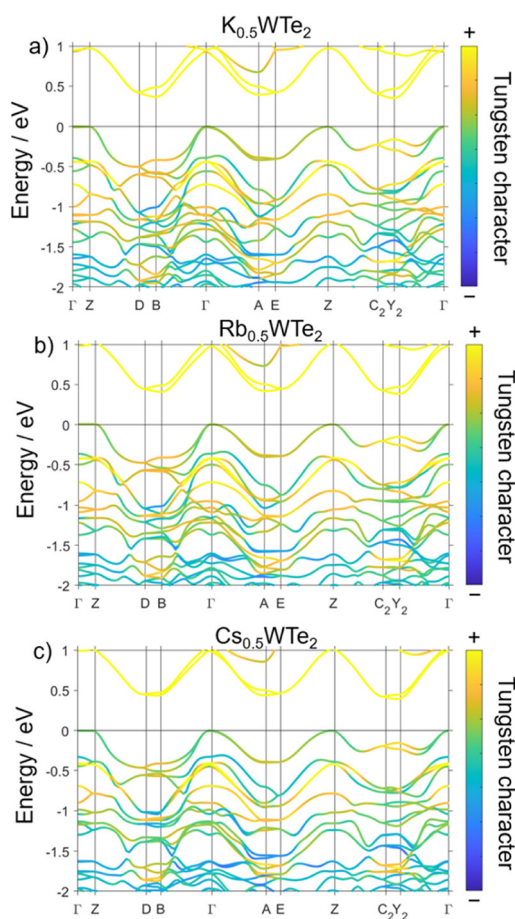


Fig. 14 Calculated electronic band structures of $K_{0.5}WTe_2$ (a), $Rb_{0.5}WTe_2$ (b), and $Cs_{0.5}WTe_2$ (c), with bands colored by their tungsten character. Special points ($\Gamma = (0\ 0\ 0)$, $Z = (0\ 0.5\ 0)$, $D = (0\ 0.5\ 0.5)$, $B = (0\ 0\ 0.5)$, $A = (-0.5\ 0\ 0.5)$, $E = (-0.5\ 0.5\ 0.5)$, $C_2 = (-0.5\ 0.5\ 0)$, $Y_2 = (-0.5\ 0\ 0)$) in and paths through reciprocal space were chosen following the literature.¹¹⁰

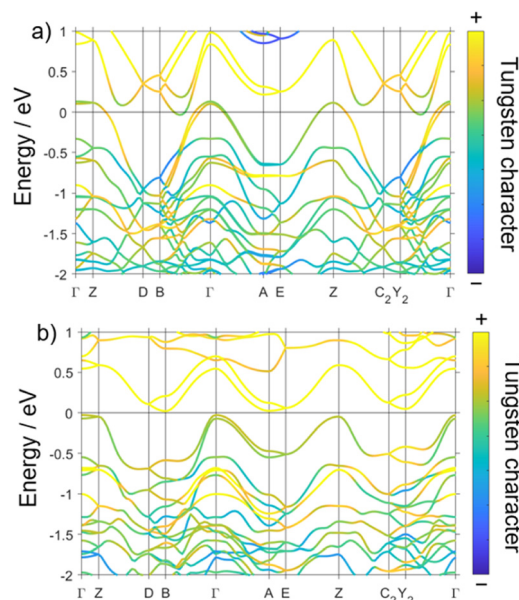


Fig. 15 Calculated electronic band structures of WTe_2 in the $P2_1/m$ space group (of the intercalated structures but with the cations removed) (a) in the neutral state and (b) with a −4 charge per unit cell. Bands are colored by their tungsten character. Special points in and paths through reciprocal space were chosen following the literature.¹¹⁰



ment, the two band structures (Fig. 15a and b) would be identical, apart from a rigid shift of the Fermi energy.

To further understand the effect of structural distortion on the electronic structure of intercalated WTe_2 , we calculated the band structure of $\text{K}_{0.5}\text{WTe}_2$ as a function of strain along the interlayer direction (Fig. 16 and 17). Interestingly, moderate compressive (Fig. 17a) and tensile (Fig. 17c) strain both decrease the band gap.

In the compressive case, the bands near the Fermi energy are largely undistorted, however in the tensile case we see a change in the curvature and character of the highest occupied band. 2% compressive strain is sufficient to turn the material metallic, whereas 2% tensile strain leads to a zero band gap semimetal due to the appearance of some unoccupied Te orbitals at the Fermi energy. These results again show how local distortions due to disorder in the material could introduce unoccupied states at or near the Fermi energy, thereby leading to the small band gap seen in the experiments. Notably, the changes in the band structure from introducing tensile strain are much more dramatic than those arising from increasing the interlayer spacing by intercalating larger cations (Fig. 14). This could indicate the importance of the electrostatic interactions between the cation and the WTe_2 layers to retain their bond geometry.

DRIFT optical band gap determination

Diffuse reflectance (DRIFT) spectra of the intercalated $\text{A}_{0.5}\text{WTe}_2$ phases were evaluated using the Kubelka–Munk transformation

$$F(R_\infty) = \frac{\alpha}{S} = \frac{(1 - R_\infty)^2}{2R_\infty},$$

with $R_\infty = \frac{R_{\text{sample}}}{R_{\text{standard}}}$ the reflectance of an infinitely thick specimen, α is the absorption and S is the scattering coefficient. For particle sizes greater than the light wavelengths measured, the scattering coefficient is understood to be approximately independent of frequency ($F(R_\infty) \sim \alpha$) and therefore $F(R_\infty)$ could be understood as a “pseudo-absorbance” coefficient.^{111–117} The transformed spectra exhibit a very broad absorption edge, typical for layered materials with weak interlayer interactions and small, anisotropic gaps. Notably, we observe that while the absolute absorption edge energy remains essentially constant

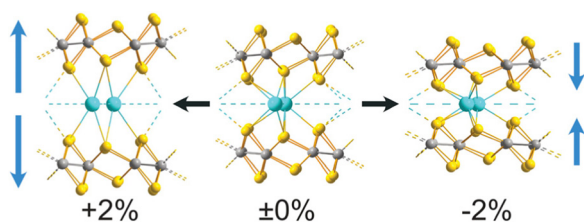


Fig. 16 Local structural arrangement of $\text{K}_{0.5}\text{WTe}_2$ in the $P2_1/m$ space group, showing the crystal structure under +2% strain (left), no strain (middle), and –2% strain (right) along the interlayer direction (viewed along the [101]-direction; W: grey, Te: yellow, K: turquoise).

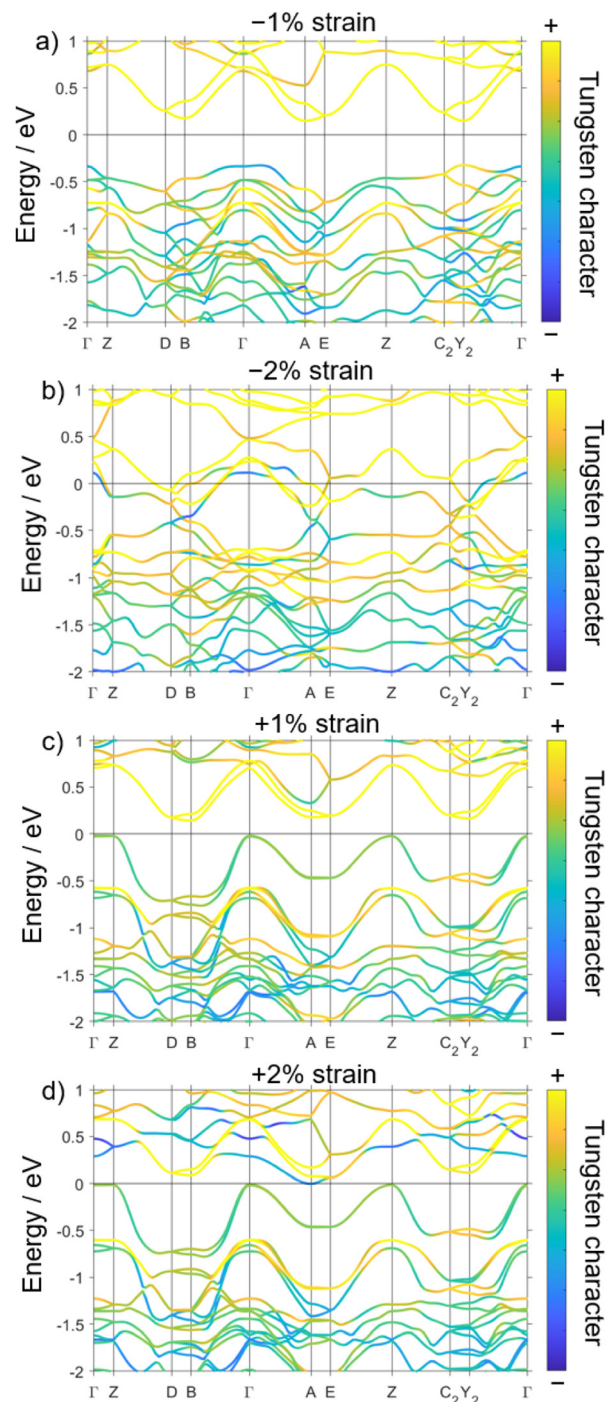


Fig. 17 Calculated electronic band structures of $\text{K}_{0.5}\text{WTe}_2$ in the $P2_1/m$ space group with compressive (negative) and tensile (positive) strain (a–d) along the interlayer direction *b*. Bands are colored by their tungsten character. Special points in and paths through reciprocal space were chosen following the literature.¹¹⁰

between different synthesis batches, the slope of the edge varies considerably, reflecting texturing effects such as disorder, stress and microstructure. Attempts to extract a band gap using conventional Tauc analysis, $[ah\nu]^n \propto (h\nu - E_g)$ with $n = 2$ for direct allowed and $n = 0.5$ for indirect allowed tran-



sitions, give highly inconsistent results. While the direct transition extrapolation results in values around 0.4–0.5 eV, the indirect treatment yields unrealistically small values.

An alternative band gap determination according to Zanatta *et al.* was performed.¹¹⁸ In this method, the energy-dependent absorption coefficient $\alpha(E)$ is fitted with a Boltzmann-type sigmoidal function:

$$\alpha(E) = \alpha_{\max} + \frac{\alpha_{\min} - \alpha_{\max}}{1 + \exp\left(\frac{E - E_0^{\text{Boltz}}}{\delta E}\right)},$$

where $\alpha_{\min}$ ($\alpha_{\max}$) stands for the minimum (maximum) absorption coefficient; E_0^{Boltz} is the energy coordinate at which the absorption coefficient is halfway between $\alpha_{\min}$ and $\alpha_{\max}$; and δE is associated with the slope of the sigmoid and indicates the energy range over which most optical transitions occur.¹¹⁸ The optical band gap is then estimated using the relation: $E_g^{\text{Boltz}} = E_0^{\text{Boltz}} - n_{\text{dir/indir}}^{\text{Boltz}} \cdot \delta E$, with $n_{\text{dir}}^{\text{Boltz}} = 0.3$ for direct and $n_{\text{indir}}^{\text{Boltz}} = 4.3$ for indirect transitions.

Both the Tauc and Zanatta approaches yield reasonable and consistent results when assuming a direct transition. However, both methods fail to produce meaningful band gap values under the assumption of an indirect transition, not due to the optical data itself but because of intrinsic limitations in the derivation of the corresponding formalisms. Despite this, the Zanatta model allows a more precise and consistent determination of the absorption edge energy E_0^{Boltz} , which represents the most robust physical observable. For $\text{K}_{0.5}\text{WTe}_2$ (see Fig. 18, Fig. S12 and S13), an analysis of Kubelka–Munk-transformed spectra with Zanatta's method yields $E_g^{\text{direct}} = 0.431$ eV ($\text{Rb}_{0.5}\text{WTe}_2 = 0.448$ and $\text{Cs}_{0.5}\text{WTe}_2 = 0.440$). These values correspond closely to the band gap of 0.476 eV determined from temperature-dependent conductivity measurements and closely to the values of the DFT-calculated band gaps (0.35–0.4 eV).

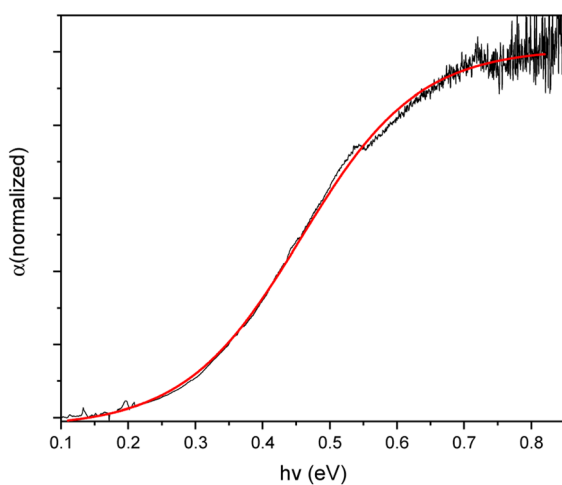


Fig. 18 Optical absorption coefficient spectrum of $\text{K}_{0.5}\text{WTe}_2$ with the Boltzmann function ($R^2 = 0.997$, $\chi^2 = 4.00 \times 10^{-4}$) used to fit α (normalized).

The broadness of the absorption edge and the mismatch between different extrapolations reflect the intrinsic sensitivity of the electronic structure to weak van der Waals bonding and distortions. Even slight shifts of the layers alter orbital overlap and band dispersion. First-principles calculations confirm that a semiconductor–metal transition can be induced in $\text{K}_{0.5}\text{WTe}_2$ by applying only $\pm 2\%$ uniaxial strain along the interlayer axis, collapsing the gap entirely under compression. Similar behavior is predicted for pristine WTe_2 , where both tensile and compressive strain change the balance of electron and hole pockets and lead to a semimetallic state. Further perturbations such as hydrostatic pressure, uniaxial stress from substrate mismatch, or moiré-type stacking in twisted bilayers also produce pronounced band structure modifications, including complete bandgap closure at twist angles of about 15° . These combined results demonstrate that the diffuse absorption edge seen experimentally does not represent a sharp bandgap in the conventional sense but rather the response of a system whose band structure is highly susceptible to strain, stacking, and interlayer distortions, making any rigid assignment of a direct or indirect gap challenging.

Experimental

Synthesis of WTe_2 and $\text{A}_{0.5}\text{WTe}_2$

All material handling and manipulations were performed in an argon-filled glove box (MBraun Labmaster 130, $\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm). All synthesis steps consistently afforded yields greater than 95%.

WTe_2 was synthesized by combining tungsten powder (1256.24 mg, 6.84 mmol, ABCR GmbH, 99.95%, particle size 0.6–0.9 μm), tellurium pieces (1830.95 mg, 14.35 mmol, Evochem, 99.999%), and tungsten(vi) chloride (WCl_6 ; 135.49 mg, 0.34 mmol, Arcos, 99.9+%) in a 1 : 2.1 : 0.05 molar ratio, with WCl_6 serving as an oxygen getter. The mixture was sealed in a dry, evacuated silica ampoule (40 mm length, 16 mm diameter) and heated in a commercial (Carbolite) furnace to 800 $^\circ\text{C}$ for 6 hours, employing heating and cooling rates of 2 K min^{-1} .

The resulting product was thoroughly ground, vacuum-sealed in a second silica ampoule (200 mm length, 16 mm diameter), and heated to 500 $^\circ\text{C}$ for 20 hours under a temperature gradient, with the opposite end of the ampoule maintained at room temperature, to facilitate the removal of excess tellurium, tungsten oxychloride impurities and unreacted WCl_6 .

$\text{A}_{0.5}\text{WTe}_2$ with $A = \text{K}, \text{Rb}, \text{Cs}$ (Strem Chemicals, 99.9+%) was synthesized by reacting WTe_2 with a 1.5 molar excess of 0.2 M alkali naphthalenide solutions (in anhydrous THF, naphthalene $\geq 99\%$ Sigma-Aldrich) at -50 $^\circ\text{C}$ for 3.5 hours under vigorous stirring with a glass stir bar. The reaction mixture was washed multiple times with absolute THF at -50 $^\circ\text{C}$ and subsequently dried under vacuum, yielding a black powder product. Single crystals were grown by maintaining the reaction at -80 $^\circ\text{C}$ for five weeks without stirring, followed by the same washing and drying procedures described above.



Powder X-ray diffraction

PXRD patterns of products were collected with a Stadi-P (STOE, Darmstadt) powder diffractometer using germanium monochromated Cu-K α_1 radiation ($\lambda = 1.5406 \text{ \AA}$) and a Mythen 1 K detector.

ICP-OES

After dissolving of $A_{0.5}WTe_2$ ($A = \text{Li, K, Rb}$) in 3.3 wt% $\text{HNO}_3/\text{H}_2\text{O}_2$ /oxalic acid, the W/Te/A ratio was determined by ICP-OES (iCAP 7400 Thermo Fisher Scientific).

TXRF (total internal reflection X-ray fluorescence) spectroscopy

TXRF studies were performed using a S2 Picofox (Bruker AXS Microanalysis, Berlin, Germany) equipped with a Mo X-ray tube, which was operated at 50 kV and 600 μA . The measurement period for each sample was 1000 s (live time). Fitting of the resulting spectra was done using the Spectra software (Bruker Nano GmbH) in the super byas mode (maximum stripping cycles of 2000).

DFT calculations

Calculations were performed using the ABINIT software package with the projector augmented-wave (PAW) method and a plane-wave basis set.^{119,120} The Perdew–Burke–Ernzerhof exchange–correlation functional was used with the vdW-DFT-D3 dispersion correction.^{121,122} PAW data files were used as received from the ABINIT library.¹²³ Methfessel–Paxton smearing was used to determine band occupation.¹²⁴ Convergence studies were used to choose a 26 Ha ($\text{K}_{0.5}\text{WTe}_2$, WTe_2), 22 Ha ($\text{Rb}_{0.5}\text{WTe}_2$), and 20 Ha ($\text{Cs}_{0.5}\text{WTe}_2$) plane wave basis set cutoff energy outside the PAW spheres; a 5 times larger cutoff was used within the spheres. The Brillouin zone was sampled with a $4 \times 2 \times 4$ ($\text{K}_{0.5}\text{WTe}_2$, $\text{Cs}_{0.5}\text{WTe}_2$, WTe_2) or $5 \times 4 \times 5$ ($\text{Rb}_{0.5}\text{WTe}_2$) grid of k -points. Structural relaxation was performed prior to calculation of the electronic structure in all cases. Negatively charged structures were simulated using a uniform background compensating positive charge. Example input files are available as part of the SI.

DRIFT (diffuse reflectance infrared Fourier transformation) spectroscopy

Samples were measured at room temperature under inert conditions in diffuse reflectance with a Harrick Praying Mantis attachment equipped with an inert chamber attachment custom-made for the original sample holder (details provided in the SI). Measurements were conducted on a Bruker Vertex 70 infrared spectrophotometer with a deuterated triglycine sulfate (DTGS) detector and KBr beam splitter. The background spectra were collected using pure dried KBr in powder form.

Electrical characterization

Conductivity measurements were performed at a Lake Shore Cryotronics CRX-6.5 K probe station with a Keithley 2636B source meter unit. Needle-shaped crystals of $\text{Rb}_{0.5}\text{WTe}_2$ were

transferred into the chamber under protective gas and contacted with silver paste on a silicon substrate with 770 nm dioxide layer. The conductive silver pads at each end of the crystals were then connected to the circuit with tungsten tips. The chamber was kept under vacuum ($<5 \times 10^{-5} \text{ mbar}$) and the temperature was varied between 20 K and 300 K. Before each measurement, sufficient time was allowed for the sample to reach the chosen temperature. Two-point conductivity measurements were performed by varying the applied source–drain voltage from -1 V to 1 V while detecting the current. For time-resolved photocurrent measurements, using a picosecond pulsed laser driver (Taiko PDL M1, PicoQuant) together with a laser head 779 nm (pulse length $<500 \text{ ps}$), the crystals were illuminated at 40 mW laser output power using the continuous wave mode while a constant voltage of 1 V was applied.

SEM and EDX

Energy Dispersive X-ray Spectroscopy (EDX) and Scanning Electron Microscopy (SEM) analyses were conducted using a HITACHI SU8030 scanning electron microscope equipped with a Bruker QUANTAX 6G EDX detector. Samples of $\text{Rb}_{0.5}\text{WTe}_2$, including both powders and crystals, were mounted on carbon tape and transferred *via* the transfer chamber technique as described by Grahlow.¹²⁵ The average elemental ratio, determined from multiple measurement points, were W : Te : Rb = $1 : 2.02(4) : 0.50(2)$ and W : Te : Cs = $1 : 1.99(5) : 0.51(4)$.

Conclusions

The successful cationic intercalation of tungsten ditelluride (WTe_2) with potassium, rubidium, and cesium resulted in the formation of $A_{0.5}\text{WTe}_2$ compounds, which exhibit notable modifications in both their structural and electronic properties. The crystallographic analysis reveals an expansion of the interlayer distance, consistent with alkali metal incorporation, leading to subtle structural distortions and a reduction in symmetry. These changes correlate with a transition from semi-metallic to semiconducting behavior, demonstrating the tunability of WTe_2 's electronic properties through alkali intercalation.

The synthesis of these intercalation compounds required careful control of conditions to accommodate the high reactivity of alkali metals. Powder X-ray diffraction and diffuse reflectance spectroscopy were key to providing accurate structural and electronic characterization of the materials.

The ability of the WTe_2 framework to accommodate different alkali metals while maintaining structural integrity highlights its potential as a versatile material for applications in electronic and energy storage devices. The tunable properties observed in $A_{0.5}\text{WTe}_2$ compounds open new possibilities for engineering the electronic characteristics of transition metal dichalcogenides, contributing to advancements in materials design for future electronic applications.



Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available on request from the corresponding author, H.-J. Meyer. Computational data are available at DOI: [10.5281/zenodo.18416912](https://doi.org/10.5281/zenodo.18416912).

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5dt02775f>.

CCDC 2392515 ($\text{K}_{0.5}\text{WTe}_2$), 2390030 ($\text{Rb}_{0.5}\text{WTe}_2$) and 2390900 ($\text{Cs}_{0.5}\text{WTe}_2$) contain the supplementary crystallographic data for this paper.^{126a-c}

Acknowledgements

The authors acknowledge support of this research by the Deutsche Forschungsgemeinschaft (Bonn) through the project ME 914/31-1 and by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no INST 40/575-1 FUGG (JUSTUS 2 cluster) is gratefully acknowledged. Carl P. Romao acknowledges support from the project FerrMion of the Ministry of Education, Youth and Sports, Czech Republic, co-funded by the European Union (CZ.02.01.01/00/22/_008/0004591).

In addition, the authors express their gratitude to Dr. Jochen Glaser (University of Tübingen) for performing ICP-OES analyses.

References

- H. Yang, S. W. Kim, M. Chhowalla and Y. H. Lee, *Nat. Phys.*, 2017, **13**, 931–937.
- M. Chhowalla, D. Jena and H. Zhang, *Nat. Rev. Mater.*, 2016, **1**, 16052.
- M. Chhowalla, *Nat. Chem.*, 2013, **5**, 263–275.
- G. H. Han, D. L. Duong, D. H. Keum, S. J. Yun and Y. H. Lee, *Chem. Rev.*, 2018, **118**, 6297–6336.
- M. J. Atherton and J. H. Holloway, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 171–198.
- H. P. Boehm, R. Setton and E. Stumpp, *Pure Appl. Chem.*, 1994, **66**, 1893.
- A. K. Geim and I. V. Grigorieva, *Nature*, 2013, **499**, 419–425.
- M. N. Ali, H. Ji, D. Hirai, M. K. Fuccillo and R. J. Cava, *J. Solid State Chem.*, 2013, **202**, 77–84.
- S. I. Ali, S. Mondal, S. J. Prathapa, S. van Smaalen, S. Zörb and B. Harbrecht, *Z. Anorg. Allg. Chem.*, 2012, **638**, 2625–2631.
- S. I. Ali, S. Mondal and S. van Smaalen, *Z. Anorg. Allg. Chem.*, 2015, **641**, 464–469.
- H. J. Crawack and C. Pettenkofer, *Solid State Commun.*, 2001, **118**, 325–332.
- J. Rouxel, *Physica B+C*, 1980, **99**, 3–11.
- S. N. Patel and A. A. Balchin, *J. Mater. Sci. Lett.*, 1985, **4**, 382–384.
- M. B. Dines, *Science*, 1975, **188**, 1210.
- E. Figueroa, J. W. Brill and J. P. Selegue, *J. Phys. Chem. Solids*, 1996, **57**, 1123–1127.
- Y. Liu, Z. Wang, G. Hu, X. Chen, K. Xu, Y. Guo, Y. Xie and C. Wu, *Precis. Chem.*, 2025, **3**, 51–71.
- Z. Wang, R. Li, C. Su and K. P. Loh, *SmartMat*, 2020, **1**, e1013.
- X. Liao, L. Liu, L. Zhang, X. Zhao, C. Wang, B. Wang, Y. Jia and J. Cho, *Phys. Rev. B*, 2025, **111**, L020505.
- Y. Ahn, G. Lee, N. Noh, C. Lee, D. D. Le, S. Kim, Y. Lee, J. Hyun, C.-Y. Lim, J. Cha, M. Jho, S. Gim, J. D. Denlinger, C.-H. Yang, J. M. Yuk, M. J. Han and Y. Kim, *Nano Lett.*, 2023, **23**, 9733–9739.
- M. Wang, S. Xu and J. J. Cha, *Adv. Energy Sustainability Res.*, 2021, **2**, 2100027.
- P. Budania, P. T. Baine, J. H. Montgomery, D. W. McNeill, S. J. N. Mitchell, M. Modreanu and P. K. Hurley, *Micro Nano Lett.*, 2017, **12**, 970–973.
- A. Sajedi-Moghaddam, C. C. Mayorga-Martinez, E. Saievar-Iranizad, Z. Sofer and M. Pumera, *Appl. Mater. Today*, 2019, **16**, 280–289.
- G. Cunningham, M. Lotya, C. S. Cucinotta, S. Sanvito, S. D. Bergin, R. Menzel, M. S. P. Shaffer and J. N. Coleman, *ACS Nano*, 2012, **6**, 3468–3480.
- S.-J. An, Y. H. Kim, C. Lee, D. Y. Park and M. S. Jeong, *Sci. Rep.*, 2018, **8**, 12957.
- X. Liu, H. Chen, J. Lin, Y. Li and L. Guo, *Chem. Commun.*, 2019, **55**, 2972–2975.
- Y. Jung, Y. Zhou and J. J. Cha, *Inorg. Chem. Front.*, 2016, **3**, 452–463.
- B. E. Brown, *Acta Crystallogr.*, 1966, **20**, 268–274.
- R. R. Chianelli, J. C. Scanlon and A. H. Thompson, *Mater. Res. Bull.*, 1975, **10**, 1379–1382.
- S. Kabashima, *J. Phys. Soc. Jpn.*, 1966, **21**, 945–948.
- J. Augustin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **62**, 10812–10823.
- W. G. Dawson and D. W. Bullett, *J. Phys. C: Solid State Phys.*, 1987, **20**, 6159–6174.
- Y.-Y. Lv, B.-B. Zhang, X. Li, B. Pang, F. Zhang, D.-J. Lin, J. Zhou, S.-H. Yao, Y. B. Chen, S.-T. Zhang, M. Lu, Z. Liu, Y. Chen and Y.-F. Chen, *Sci. Rep.*, 2016, **6**, 26903.
- H. Y. Lv, W. J. Lu, D. F. Shao, Y. Liu, S. G. Tan and Y. P. Sun, *Europhys. Lett.*, 2015, **110**, 37004.
- C. Rovira and M. H. Whangbo, *Inorg. Chem.*, 1993, **32**, 4094–4097.
- J. A. Wilson, F. J. Di Salvo and S. Mahajan, *Adv. Phys.*, 1975, **24**, 117–201.
- M. N. Ali, *Nature*, 2014, **514**, 205–208.
- N. Lu, C. Zhang, C.-H. Lee, J. P. Oviedo, M. A. T. Nguyen, X. Peng, R. M. Wallace, T. E. Mallouk, J. A. Robinson,



- J. Wang, K. Cho and M. J. Kim, *J. Phys. Chem. C*, 2016, **120**, 8364–8369.
- 38 E. Canadell and M.-H. Whangbo, *Phys. Rev. B:Condens. Matter Mater. Phys.*, 1991, **43**, 1894–1902.
- 39 B. Guster, E. Canadell, M. Pruneda and P. Ordejón, *2D Mater.*, 2018, **5**, 025024.
- 40 M. H. Whangbo, E. Canadell, P. Foury and J. P. Pouget, *Science*, 1991, **252**, 96–98.
- 41 N. Mitsuishi, Y. Sugita, M. S. Bahramy, M. Kamitani, T. Sonobe, M. Sakano, T. Shimojima, H. Takahashi, H. Sakai, K. Horiba, H. Kumigashira, K. Taguchi, K. Miyamoto, T. Okuda, S. Ishiwata, Y. Motome and K. Ishizaka, *Nat. Commun.*, 2020, **11**, 2466.
- 42 C. Huang, A. Narayan, E. Zhang, Y. Liu, X. Yan, J. Wang, C. Zhang, W. Wang, T. Zhou, C. Yi, S. Liu, J. Ling, H. Zhang, R. Liu, R. Sankar, F. Chou, Y. Wang, Y. Shi, K. T. Law, S. Sanvito, P. Zhou, Z. Han and F. Xiu, *ACS Nano*, 2018, **12**, 7185–7196.
- 43 P. Li, Y. Wen, X. He, Q. Zhang, C. Xia, Z.-M. Yu, S. A. Yang, Z. Zhu, H. N. Alshareef and X.-X. Zhang, *Nat. Commun.*, 2017, **8**, 2150.
- 44 Y. Sun, S.-C. Wu, M. N. Ali, C. Felser and B. Yan, *Phys. Rev. B:Condens. Matter Mater. Phys.*, 2015, **92**, 161107.
- 45 P. Schmidt, P. Schneiderhan, M. Ströbele, C. P. Romao and H.-J. Meyer, *Inorg. Chem.*, 2021, **60**, 1411–1418.
- 46 M. S. Whittingham, *Chem. Rev.*, 2004, **104**, 4271–4302.
- 47 H. Wang, Z. Lu, S. Xu, D. Kong, J. J. Cha, G. Zheng, P.-C. Hsu, K. Yan, D. Bradshaw, F. B. Prinz and Y. Cui, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 19701–19706.
- 48 P. K. Muscher, D. A. Rehn, A. Sood, K. Lim, D. Luo, X. Shen, M. Zajac, F. Lu, A. Mehta, Y. Li, X. Wang, E. J. Reed, W. C. Chueh and A. M. Lindenberg, *Adv. Mater.*, 2021, **33**, 2101875.
- 49 M. Wang, A. Kumar, H. Dong, J. M. Woods, J. V. Pondick, S. Xu, D. J. Hynnek, P. Guo, D. Y. Qiu and J. J. Cha, *Adv. Mater.*, 2022, **34**, 2200861.
- 50 X. Yang, Y. Zhang, L. Chen, K. Aso, W. Yamamori, R. Moriya, K. Watanabe, T. Taniguchi, T. Sasagawa, N. Nakatsuji, M. Koshino, Y. Yamada-Takamura, Y. Oshima and T. Machida, *ACS Nano*, 2025, **19**, 13007–13015.
- 51 S. J. Magorrian and N. D. M. Hine, *Phys. Rev. B*, 2024, **110**, 045410.
- 52 Z.-S. Chen, L. Huang, W.-T. Guo, K. Zhong, J.-M. Zhang and Z. Huang, *Front. Phys.*, 2022, **10**, 879756.
- 53 Y.-M. Wu, C. Murthy and S. A. Kivelson, *Phys. Rev. Lett.*, 2024, **133**, 246501.
- 54 L. Du, Z. Huang, J. Zhang, F. Ye, Q. Dai, H. Deng, G. Zhang and Z. Sun, *Nat. Mater.*, 2024, **23**, 1179–1192.
- 55 B. Amin, T. P. Kaloni and U. Schwingenschlögl, *RSC Adv.*, 2014, **4**, 34561–34565.
- 56 C. Zhao, M. Hu, J. Qin, B. Xia, C. Liu, S. Wang, D. Guan, Y. Li, H. Zheng, J. Liu and J. Jia, *Phys. Rev. Lett.*, 2020, **125**, 046801.
- 57 Y. Zhang, K. Kamiya, T. Yamamoto, M. Sakano, X. Yang, S. Masubuchi, S. Okazaki, K. Shinokita, T. Chen, K. Aso, Y. Yamada-Takamura, Y. Oshima, K. Watanabe, T. Taniguchi, K. Matsuda, T. Sasagawa, K. Ishizaka and T. Machida, *Nano Lett.*, 2023, **23**, 9280–9286.
- 58 R. Schöllhorn, *Chem. Mater.*, 1996, **8**, 1747–1757.
- 59 R. Schöllhorn and A. Weiss, *J. Less-Common Met.*, 1974, **36**, 229–236.
- 60 M. S. Dresselhaus, *Intercalation in Layered Materials*, Springer US, 2013.
- 61 M. S. Dresselhaus, *MRS Bull.*, 1987, **12**, 24–28.
- 62 M. Rajapakse, B. Karki, U. O. Abu, S. Pishgar, M. R. K. Musa, S. M. S. Riyadh, M. Yu, G. Sumanasekera and J. B. Jasinski, *npj 2D Mater. Appl.*, 2021, **5**, 30.
- 63 J. Zhou, J. Zhou, Z. Wan, Q. Qian, H. Ren, X. Yan, B. Zhou, A. Zhang, X. Pan, W. Fang, Y. Ping, Z. Sofer, Y. Huang and X. Duan, *Nature*, 2025, **643**, 683–690.
- 64 A. V. Powell, *Annu. Rep. Prog. Chem., Sect. C:Phys. Chem.*, 1993, **90**, 177–213.
- 65 R. Schöllhorn, in *Intercalation Chemistry*, ed. S. M. Whittingham, Academic Press, New York, 1982, ch. 10, pp. 315–360.
- 66 A. Lerf and R. Schöllhorn, *Inorg. Chem.*, 1977, **16**, 2950–2956.
- 67 U. Röder, W. Müller-Warmuth and R. Schöllhorn, *J. Phys. Chem.*, 1979, **70**, 2864–2870.
- 68 C. Riekel, H. G. Reznik and R. Schöllhorn, *J. Solid State Chem.*, 1980, **34**, 253–262.
- 69 W. Paulus, H. Katzke and R. Schöllhorn, *J. Solid State Chem.*, 1992, **96**, 162–168.
- 70 B. Kannen and B. Rasche, *Z. Anorg. Allg. Chem.*, 2024, **650**, e202300165.
- 71 W. P. F. A. M. Omloo and F. Jellinek, *J. Less-Common Met.*, 1970, **20**, 121–129.
- 72 R. Eppinga and G. A. Wiegers, *Physica B+C*, 1980, **99**, 121–127.
- 73 W. I. F. David and K. Shankland, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 52–64.
- 74 J. Leeman, Y. Liu, J. Stiles, S. B. Lee, P. Bhatt, L. M. Schoop and R. G. Palgrave, *PRX Energy*, 2024, **3**, 011002.
- 75 B. E. Brown, *Acta Crystallogr.*, 1966, **20**, 264–267.
- 76 P. Y. Zavalij and M. S. Whittingham, *Rigaku J.*, 2004, **21**, 2–14.
- 77 F. Ursi, S. Virga, C. Pipitone, A. Sanson, A. Longo, F. Giannici and A. Martorana, *J. Appl. Crystallogr.*, 2023, **56**, 502–509.
- 78 C.-H. Lee, E. C. Silva, L. Calderin, M. A. T. Nguyen, M. J. Hollander, B. Bersch, T. E. Mallouk and J. A. Robinson, *Sci. Rep.*, 2015, **5**, 10013.
- 79 M. S. Whittingham, *Prog. Solid State Chem.*, 1978, **12**, 41–99.
- 80 W. Rüdorff, *Angew. Chem.*, 1959, **71**, 487–491.
- 81 S. Schwarzmüller, K. Wurst, G. Heymann and H. Huppertz, *Chem. – Eur. J.*, 2024, **30**, e202302565.
- 82 F. Kopnov, Y. Feldman, R. Popovitz-Biro, A. Vilan, H. Cohen, A. Zak and R. Tenne, *Chem. Mater.*, 2008, **20**, 4099–4105.



- 83 X. Fan, H. Chen, L. Zhao, S. Jin and G. Wang, *Solid State Commun.*, 2019, **297**, 6–10.
- 84 P. J. Mulhern, *Can. J. Phys.*, 1989, **67**, 1049–1052.
- 85 I. Schewe-Miller and P. Böttcher, *Z. Kristallogr. - Cryst. Mater.*, 1991, **196**, 137–151.
- 86 P. Böttcher and U. Kretschmann, *Z. Anorg. Allg. Chem.*, 1982, **491**, 39–46.
- 87 E. Bayer and W. Rüdorff, *Z. Naturforsch., B*, 1972, **27**, 1336–1339.
- 88 J. Zheng, H. Zhang, S. Dong, Y. Liu, C. T. Nai, H. S. Shin, H. Y. Jeong, B. Liu and K. P. Loh, *Nat. Commun.*, 2014, **5**, 2995.
- 89 J. N. Coleman, M. Lotya, A. O'Neill, B. D. Shane, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grievson, K. Theuvsen, D. W. McComb, P. D. Nellist and V. Nicolosi, *Science*, 2011, **331**, 568–571.
- 90 S. M. Tan, Z. Sofer, J. Luxa and M. Pumera, *ACS Catal.*, 2016, **6**, 4594–4607.
- 91 K. Leng, Z. Chen, X. Zhao, W. Tang, B. Tian, C. T. Nai, W. Zhou and K. P. Loh, *ACS Nano*, 2016, **10**, 9208–9215.
- 92 B. B. Tian, W. Tang, K. Leng, Z. X. Chen, S. J. R. Tan, C. X. Peng, G. H. Ning, W. Fu, C. L. Su, G. Y. W. Zheng and K. P. Loh, *ACS Energy Lett.*, 2017, **2**, 1835–1840.
- 93 A. Altomare, C. Cuocci, C. Giacobozzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio, *J. Appl. Crystallogr.*, 2013, **46**, 1231–1235.
- 94 J. Rodríguez-Carvajal and T. Roisnel, *IUCr, CPD Newsl.*, 1998, **20**, 35–36.
- 95 P. Thompson, D. E. Cox and J. B. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79–83.
- 96 L. W. Finger, D. E. Cox and A. P. Jephcoat, *J. Appl. Crystallogr.*, 1994, **27**, 892–900.
- 97 D. R. Black, M. H. Mendenhall, A. Henins, J. Filliben and J. P. Cline, *Powder Diffr.*, 2020, **35**, 156–159.
- 98 T. Roisnel and J. Rodríguez-Carvajal, *Mater. Sci. Forum*, 2001, **378–381**, 118–123.
- 99 A. Mar, S. Jobic and J. A. Ibers, *J. Am. Chem. Soc.*, 1992, **114**, 8963–8971.
- 100 W. Kraus and G. Nolze, *J. Appl. Crystallogr.*, 1996, **29**, 301–303.
- 101 A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
- 102 N. Alcock and A. Kjekshus, *Acta Chem. Scand.*, 1965, **19**, 79.
- 103 B. Jariwala, A. Thamizhavel and A. Bhattacharya, *J. Phys. D: Appl. Phys.*, 2017, **50**, 044001.
- 104 A. Broll, A. Simon, H. G. von Schnering and H. Schäfer, *Z. Anorg. Allg. Chem.*, 1969, **367**, 1–18.
- 105 A. S. Hassanien and A. A. Akl, *J. Non-Cryst. Solids*, 2016, **432**, 471–479.
- 106 A. M. Al-Fa'ouri, O. A. Lafi, H. H. Abu-Safe and M. Abu-Kharma, *Arabian J. Chem.*, 2023, **16**, 104535.
- 107 M. M. A. Imran and O. A. Lafi, *Phys. B*, 2013, **410**, 201–205.
- 108 K. Kiran Kumar, M. Ravi, Y. Pavani, S. Bhavani, A. K. Sharma and V. V. R. Narasimha Rao, *Phys. B*, 2011, **406**, 1706–1712.
- 109 J. P. Perdew, *Int. J. Quantum Chem.*, 1985, **28**, 497–523.
- 110 Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba and I. Tanaka, *Comput. Mater. Sci.*, 2017, **128**, 140–184.
- 111 W. W. Wendlandt and H. G. Hecht, *Reflectance spectroscopy*, Interscience, New York, 1966.
- 112 P. Kubelka, *J. Opt. Soc. Am.*, 1948, **38**, 448–457.
- 113 P. Kubelka and F. Munk, *Z. Tech. Phys.*, 1931, **12**, 259–274.
- 114 G. Kortum and J. E. Lohr, *Reflectance Spectroscopy*, Springer, 1969.
- 115 G. Kortum and H. Koffer, *Ber. Bunsenges. Phys. Chem.*, 1963, **67**, 67–75.
- 116 A. B. Murphy, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 1326–1337.
- 117 R. López and R. Gómez, *J. Sol-Gel Sci. Technol.*, 2012, **61**, 1–7.
- 118 A. R. Zanatta, *Sci. Rep.*, 2019, **9**, 11225.
- 119 M. Torrent, F. Jollet, F. Bottin, G. Zerah and X. Gonze, *Comput. Mater. Sci.*, 2008, **42**, 337–351.
- 120 M. J. Verstraete, J. Abreu, G. E. Allemand, B. Amadon, G. Antonius, M. Azizi, L. Baguet, C. Barat, L. Bastogne, R. Béjaud, J.-M. Beuken, J. Bieder, A. Blanchet, F. Bottin, J. Bouchet, J. Bouquiaux, E. Bousquet, J. Boust, F. Briec, V. Brousseau-Couture, N. Brouwer, F. Bruneval, A. Castellano, E. Castiel, J.-B. Charraud, J. Clérouin, M. Côté, C. Duval, A. Gallo, F. Gendron, G. Geneste, P. Ghosez, M. Giantomassi, O. Gingras, F. Gómez-Ortiz, X. Gonze, F. A. Goudreaux, A. Grüneis, R. Gupta, B. Guster, D. R. Hamann, X. He, O. Hellman, N. Holzwarth, F. Jollet, P. Kestener, I.-M. Lygatsika, O. Nadeau, L. MacEnulty, E. Marazzi, M. Mignolet, D. D. O'Regan, R. Outerovitch, C. Paillard, G. Petretto, S. Poncé, F. Ricci, G.-M. Rignanese, M. Rodríguez-Mayorga, A. H. Romero, S. Rostami, M. Royo, M. Sarraute, A. Sasani, F. Soubiran, M. Stengel, C. Tantardini, M. Torrent, V. Trinet, V. Vasilchenko, D. Waroquier, A. Zabalo, A. Zadoks, H. Zhang and J. Zwaniger, *J. Phys. Chem.*, 2025, **163**, 164126.
- 121 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
- 122 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Phys. Chem.*, 2010, **132**, 154104.
- 123 <https://www.abinit.org>, (accessed 20/3/19).
- 124 M. Methfessel and A. T. Paxton, *Phys. Rev. B:Condens. Matter Mater. Phys.*, 1989, **40**, 3616–3621.
- 125 F. Grahlow, J. Beitzberger, M. Martin, E. Juriatti, H. Peisert, M. Scheele, M. Ströbele, C. P. Romao and H.-J. Meyer, *Dalton Trans.*, 2025, **54**, 16593–16604.
- 126 (a) CCDC 2392515: Experimental Crystal Structure Determination, 2026, DOI: [10.25505/fiz.icsd.cc2191xf](https://doi.org/10.25505/fiz.icsd.cc2191xf); (b) CCDC 2390030: Experimental Crystal Structure Determination, 2026, DOI: [10.25505/fiz.icsd.cc2170rm](https://doi.org/10.25505/fiz.icsd.cc2170rm); (c) CCDC 2390900: Experimental Crystal Structure Determination, 2026, DOI: [10.25505/fiz.icsd.cc217xtl](https://doi.org/10.25505/fiz.icsd.cc217xtl).



Intercalation of Alkali Metal into WTe_2 , the Crystal Structure of $\text{A}_{0.5}\text{WTe}_2$ and Observation of a Metal-to-Semiconductor Transition

Patrick Schmidt,^a Fabian Strauß,^b Marcus Scheele,^b Carl P. Romao,^c Hans-Jürgen Meyer^{*a}

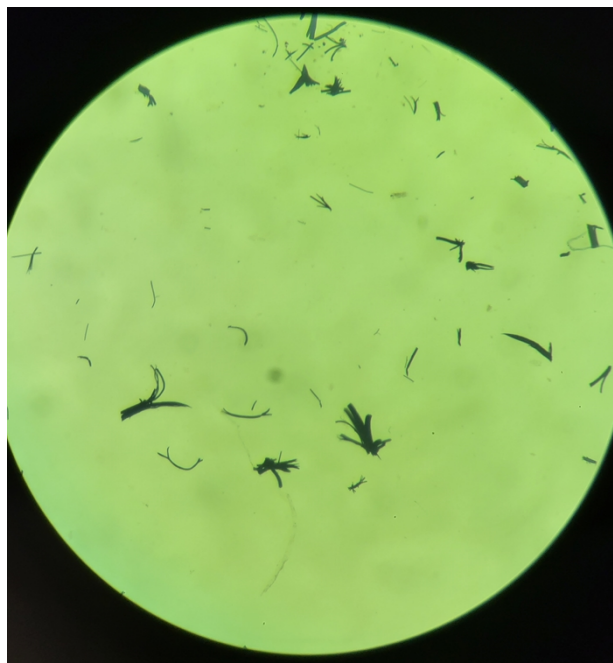


Figure S1. Microscope image (2x magnification) of WTe_2 single crystal in a 2 mM solution of rubidium naphthalenide after 30 min at room temperature.

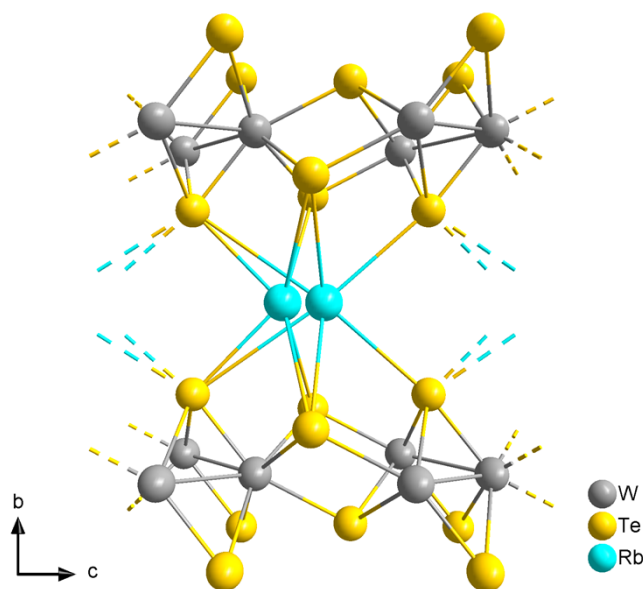


Figure S2. Section of the $\text{Rb}_{0.5}\text{WTe}_2$ initial structure solution of $\text{Rb}_{0.5}\text{WTe}_2$, showing two disordered rubidium positions with refined occupation factors close to 0.5.

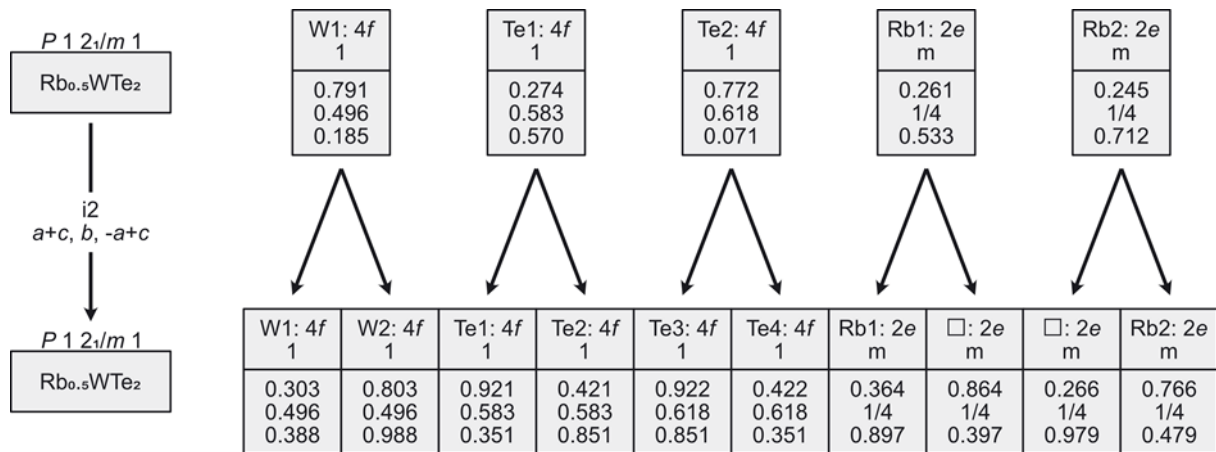


Figure S3. Bärnighausen tree: group-subgroup relation between the initial (top) and the final (bottom) structure solution of $\text{Rb}_{0.5}\text{WTe}_2$ with double cell volume and resolved disorder of the rubidium atoms.

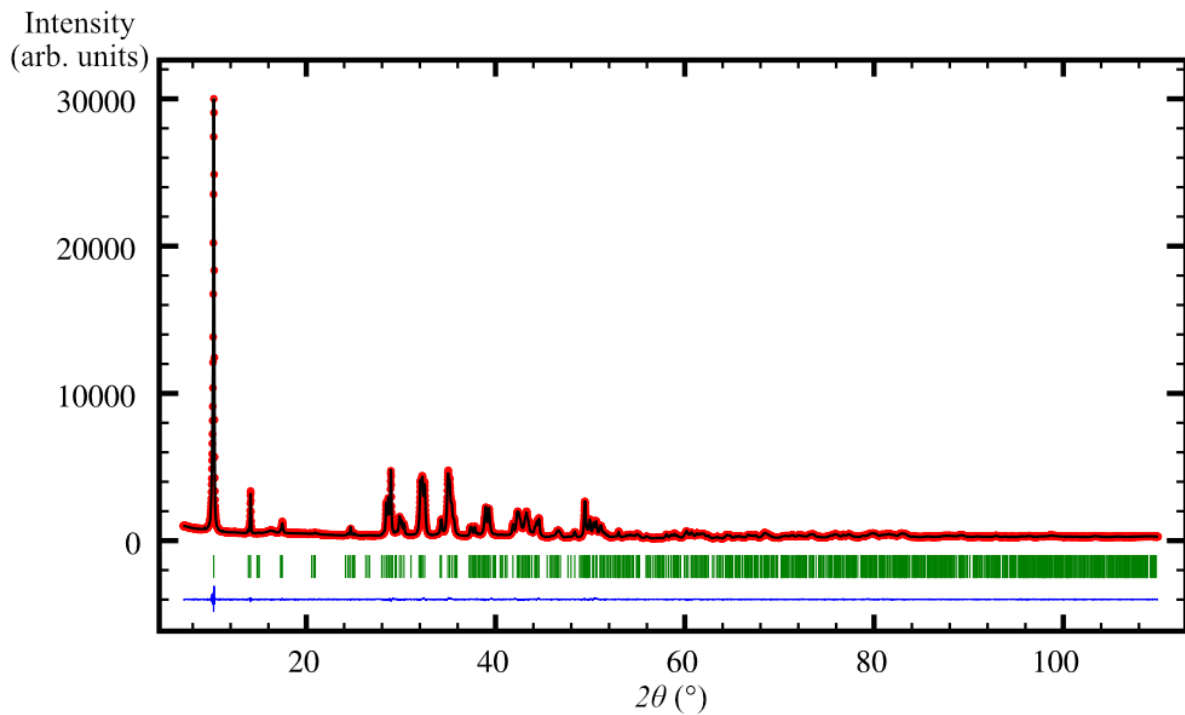


Figure S4. PXRD refinement of $\text{K}_{0.5}\text{WTe}_2$ at 298 K with the experimental (red) and calculated (black) intensities of the Rietveld refinement. Bragg positions (green) and the difference curve (blue) are also shown (CSD: 2392515).

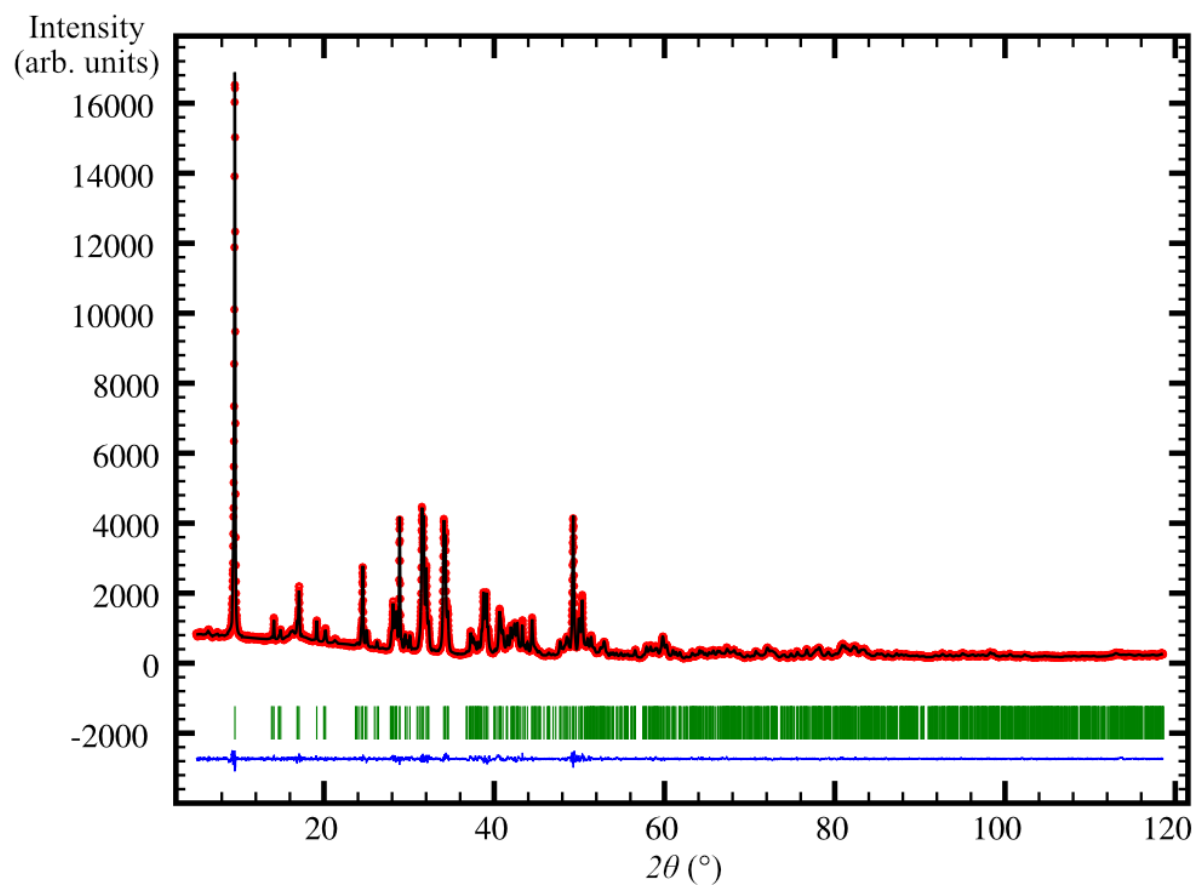


Figure S5. PXRD refinement of $\text{Cs}_{0.5}\text{WTe}_2$ at 298 K with the experimental (red) and calculated (black) intensities of the Rietveld refinement. Bragg positions (green) and the difference curve (blue) are also shown (CSD: 2390900).

Synthesis of $\text{Li}_{0.5}\text{WTe}_2$: $\text{Li}_{0.5}\text{WTe}_2$ was synthesized under an argon atmosphere by adding 10 mL of 2.5 M *n*-butyllithium (in hexane, Sigma-Aldrich) to 500 mg of WTe_2 (1.14 mmol) at room temperature. The mixture was gently agitated intermittently over five days. The solution was then decanted, and an additional 5 mL of 2.5 M *n*-butyllithium (in hexane) was added, followed by gentle shaking for another five days. After the reaction, the solution was removed, and the resulting solid was washed three times with 10 mL portions of absolute pentane. The final product was obtained as a black powder with a yield of ~95%.

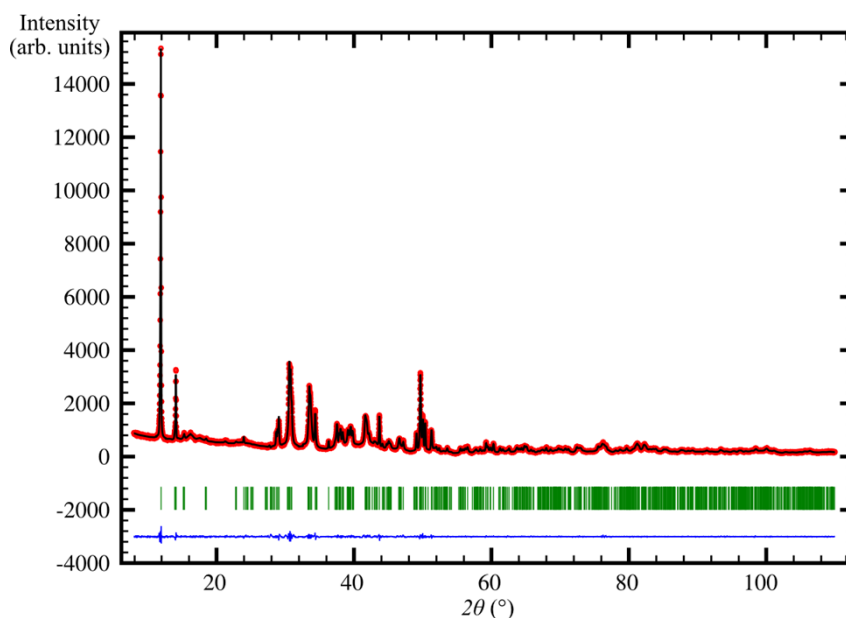


Figure S6. Le Bail profile fit to the PXRD pattern of $\text{Li}_{0.5}\text{WTe}_2$. Shown are the observed (red) and calculated (black) profiles, the difference curve (blue), and Bragg reflection positions (green). Refinement in the monoclinic space group $P2_1$ yields $a = 7.28855(6)$ Å, $b = 14.8297(2)$ Å, $c = 7.23983(6)$ Å, and $\beta = 119.3451(5)^\circ$.

Synthesis of $\text{Na}_{0.5}\text{WTe}_2$: $\text{Na}_{0.5}\text{WTe}_2$ was prepared using the same procedure as described for $\text{A}_{0.5}\text{WTe}_2$ ($A = \text{K}, \text{Rb}, \text{Cs}$) in the main text, employing sodium metal (99.95%, Sigma-Aldrich) as the alkali source. The reaction yielded a mixture of partially intercalated material with an overall yield of ~95%.

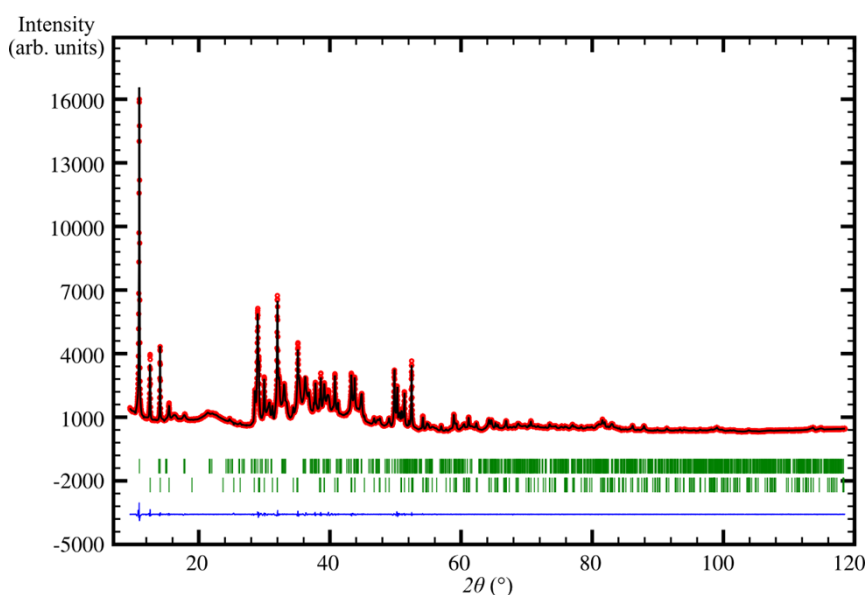


Figure S7. Le Bail profile fit to the PXRD pattern of $\text{Na}_{0.5}\text{WTe}_2$. Shown are the observed (red) and calculated (black) profiles, the difference curve (blue), and Bragg reflection positions (green, top= $\text{Na}_{0.5}\text{WTe}_2$, bottom= WTe_2). Refinement in the monoclinic space group $P2_1/m$ yields $a = 7.2897(2)$ Å, $b = 16.1501(3)$ Å, $c = 7.24837(2)$ Å, and $\beta = 119.1634(5)^\circ$. The pattern also contains ~30 mol% WTe_2 as an impurity.

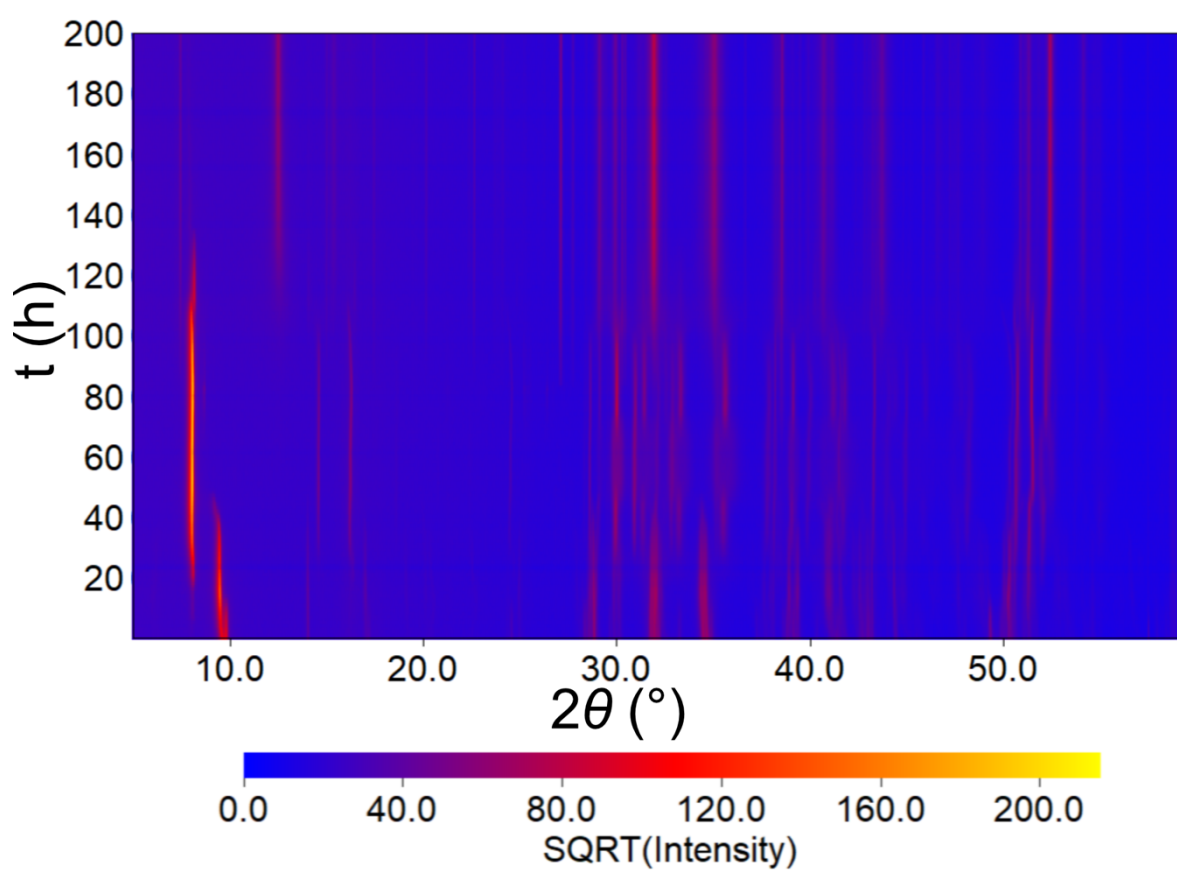


Figure S8. Time resolved PXRD analysis of $\text{Rb}_{0.5}\text{WTe}_2$ showing structural evolution upon exposure to ambient conditions. Note: Sample was mounted between two Mylar foils and was not hermetically sealed with Lithelen grease).

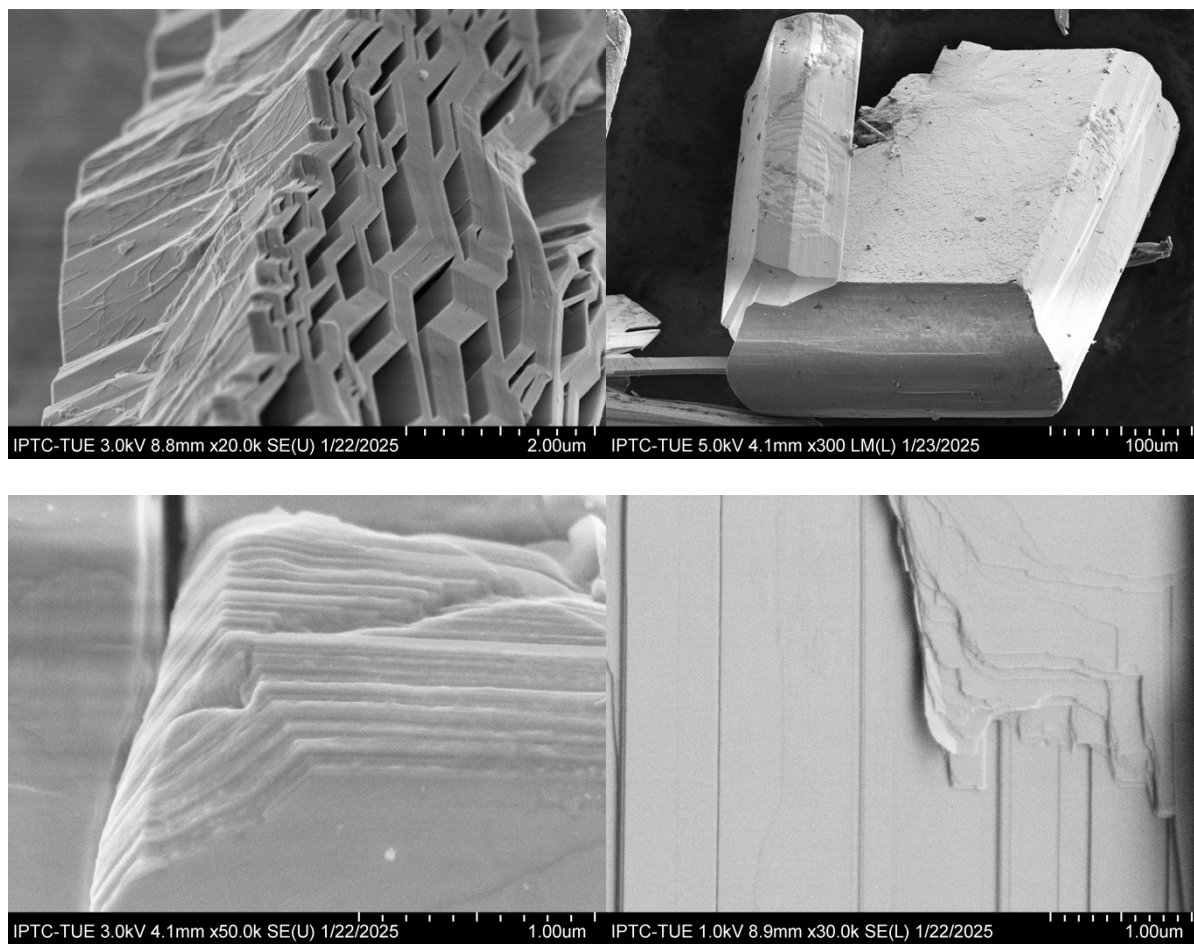


Figure S9. SEM images, highlighting the layered morphology of $\text{Rb}_{0.5}\text{WTe}_2$ crystals.

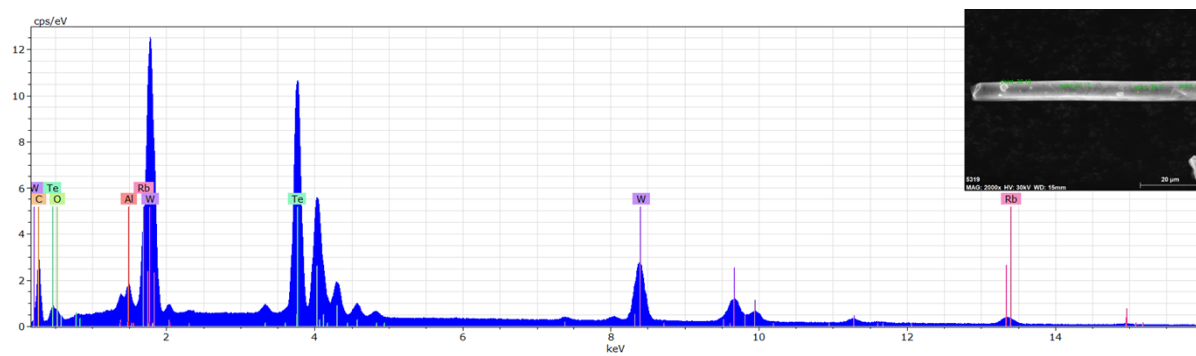


Figure S10. EDX spectra of $\text{Rb}_{0.5}\text{WTe}_2$, confirming the elemental composition and successful intercalation of rubidium. The inset SEM image indicates the precise measurement location, ensuring correlation between morphological features and compositional analysis. The presence of carbon and oxygen signals originates from the carbon tape used for sample mounting.

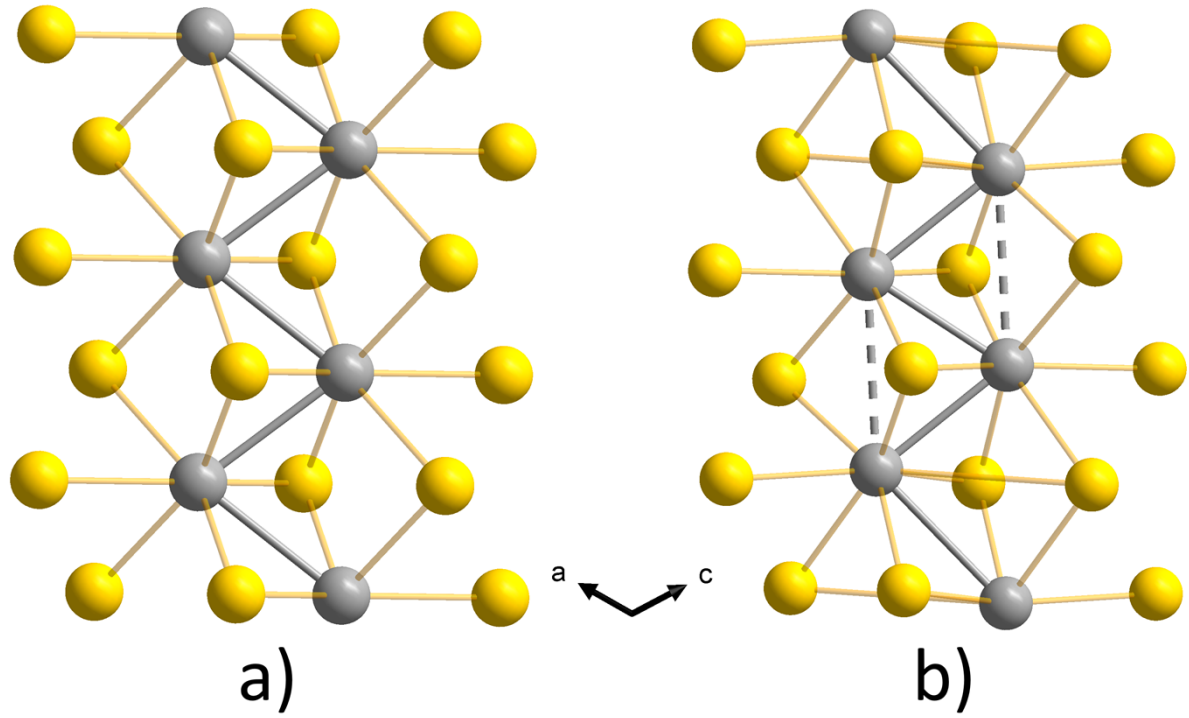


Figure S11. Local structural arrangement within a single layer of WTe_2 from DFT calculations in the $P2_1/m$ space group, showing the crystal structure without intercalating cations in (a) the neutral state and (b) with a -4 charge per unit cell (viewed along the b -axis; W: grey, Te: yellow). W_4 cluster formation is highlighted by dotted lines.

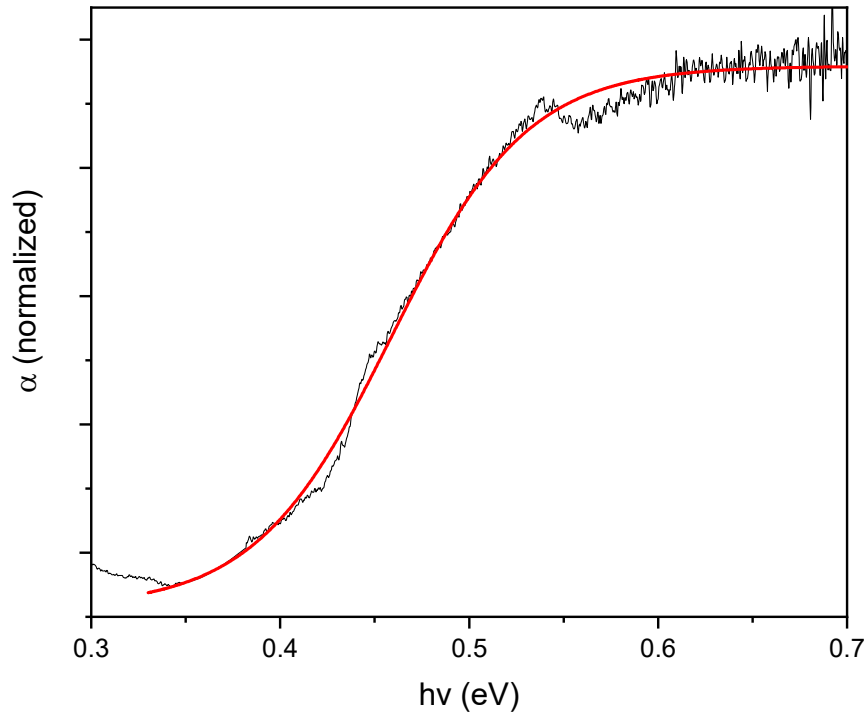


Figure S12. Optical absorption coefficient spectra of $\text{Rb}_{0.5}\text{WTe}_2$ with the Boltzmann function ($R^2 = 0.995$, $\chi^2 = 4.68 \cdot 10^{-3}$) used to fit $\alpha(\text{normalized})$ with $E_{\text{Boltz}} = 0.4589(3)$ and $dE = 0.03596(3)$.

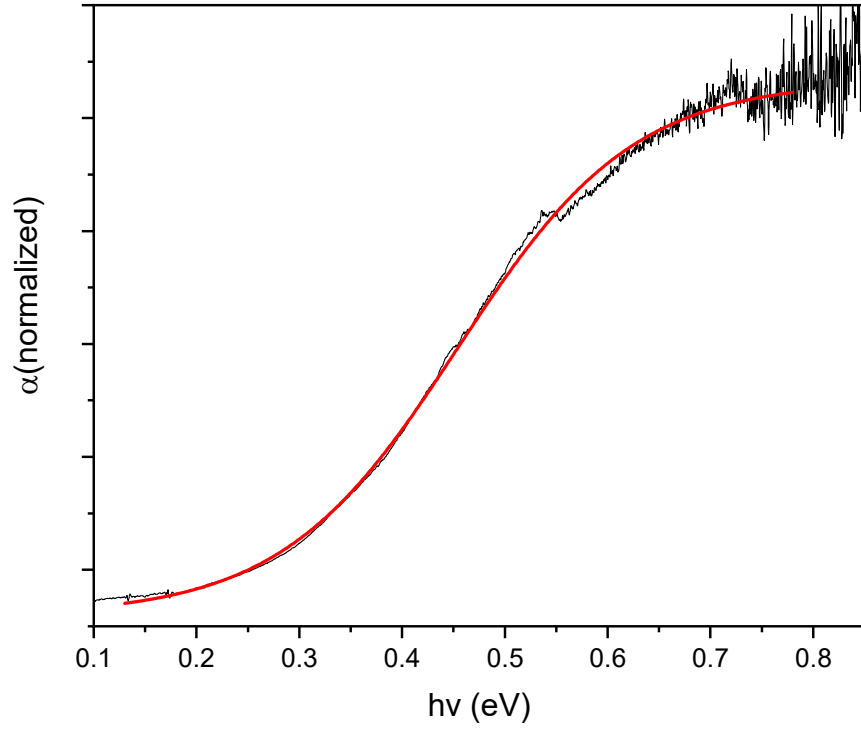


Figure S13. Optical absorption coefficient spectra of $\text{Cs}_{0.5}\text{WTe}_2$ with the Boltzmann function ($R^2 = 0.997$, $\chi^2 = 5.93 \cdot 10^{-3}$) used to fit $\alpha(\text{normalized})$ with $E_{\text{Boltz}} = 0.4542(3)$ and $dE = 0.0859(3)$.

Inert Chamber attachment for Harrick Praying Mantis Standard Sample Holder

All sample preparations were conducted under inert conditions (argon). The standard preparation procedure for DRIFT samples, including necessary adjustments, was followed. The measuring window was prepared by pressing a standard 13 mm press tool with 150 to 200 mg of KBr. The window was then fixed on top of the brass inert chamber attachment using vacuum-dried LVO 810 Lithelen grease, which was dried at 80 °C for a minimum of three days. After assembling the brass part with the sample holder, the pressure regulation hole was filled with grease to ensure a proper seal.

Although the KBr window degraded over time and was no longer intact for further measurements, the enclosed samples remained stable for at least one week when exposed to air.



Figure S14. Images of the brass inert chamber attachment (left) and the fully assembled setup (right), including the sample holder, KBr window, and sealing grease.

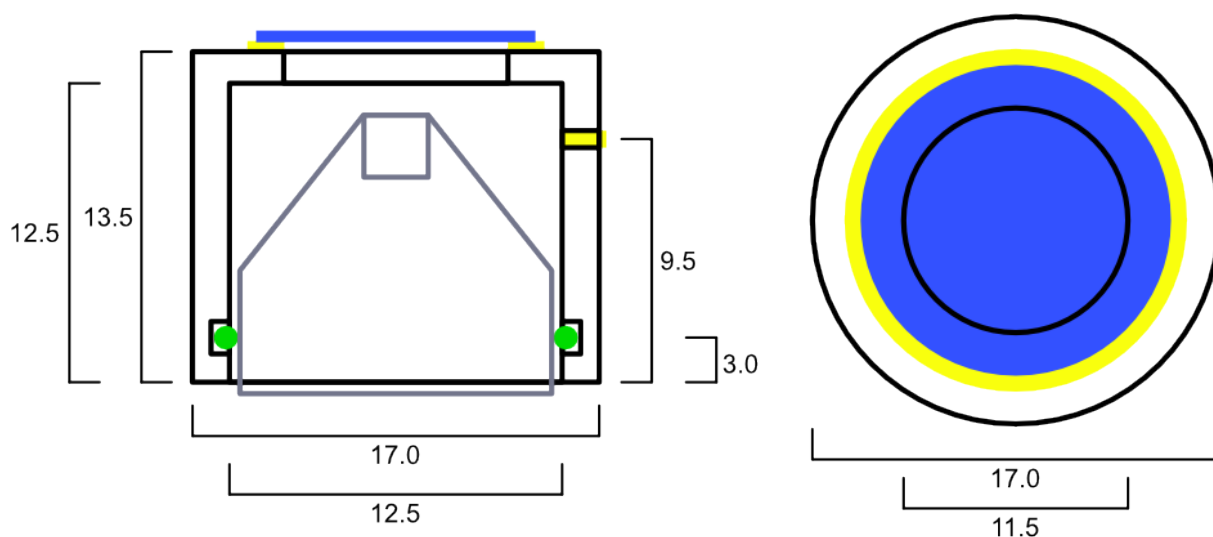


Figure S15. Schematic representation and dimensions (in mm) of the brass inert chamber attachment (black). The KBr window is shown in blue, sealing grease in yellow, rubber sealing ring in green, and the sample holder in grey.

Table S1: Interlayer spacing of pristine WTe₂ and its alkali-metal–intercalated derivatives, determined from PXRD via the (0 0 2) Bragg reflection.

Compound	Spacing / Å
WTe ₂	7.009
Li _{0.5} WTe ₂	7.4149
Na _{0.5} WTe ₂	8.0751
K _{0.5} WTe ₂	8.6297
Rb _{0.5} WTe ₂	8.9179
Cs _{0.5} WTe ₂	9.2606

Table S2: Atomic coordinates and equivalent isotropic displacement parameters (pm²) for K_{0.5}WTe₂. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	SOF
W1	0.7404(3)	0.9941(2)	0.5669(3)	0.0261(2)	1
W2	0.80081(3)	0.00456(2)	0.98707(3)	0.0261(2)	1
Te1	0.582850(6)	0.076680(2)	0.178032(6)	0.02639(2)	1
Te2	0.07637(5)	0.08472(2)	0.65191(5)	0.02639(2)	1
Te3	0.569649(5)	0.110430(2)	0.682741(5)	0.02639(2)	1
Te4	0.07680(6)	0.12008(2)	0.14999(5)	0.02639(2)	1
K1	0.77796(2)	0.25	0.48274(2)	0.0234(2)	1
K2	0.36313(2)	0.25	0.8934(2)	0.0234(2)	1

Table S3: Atomic coordinates and equivalent isotropic displacement parameters (pm²) for Rb_{0.5}WTe₂. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

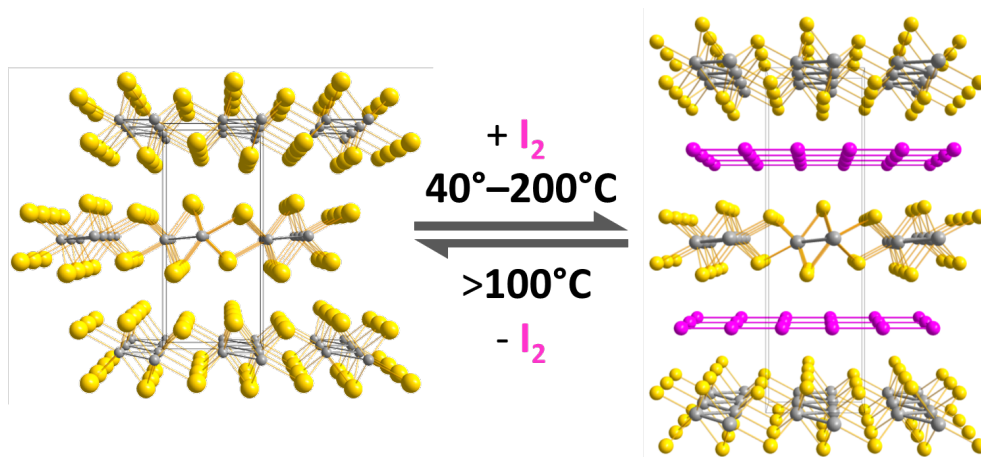
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	SOF
W1	0.8033(3)	0.4963(3)	0.9879(3)	0.0254(3)	1
W2	0.7395(3)	0.5056(2)	0.5680(3)	0.0254(3)	1
Te1	0.9213(5)	0.5832(2)	0.3514(6)	0.0269(3)	1
Te2	0.5876(6)	0.4259(2)	0.1810(6)	0.0269(3)	1
Te3	0.9216(6)	0.6175(2)	0.8506(6)	0.0269(3)	1
Te4	0.5689(5)	0.3918(2)	0.6800(6)	0.0269(3)	1
Rb1	0.36435(9)	0.25	0.89691(9)	0.03674(1)	1
Rb2	0.7664(1)	0.25	0.47853(9)	0.03674(1)	1

Table S4: Atomic coordinates and equivalent isotropic displacement parameters (pm²) for Cs_{0.5}WTe₂. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	SOF
W1	0.8036(3)	0.4964(2)	0.9880(3)	0.0183(2)	1
W2	0.7421(3)	0.50674(18)	0.5698(3)	0.0183(2)	1
Te1	0.9277(5)	0.5776(2)	0.3559(5)	0.0219(3)	1
Te2	0.5844(6)	0.4283(2)	0.1851(6)	0.0219(3)	1
Te3	0.9238(5)	0.6129(2)	0.8464(5)	0.0219(3)	1
Te4	0.5717(5)	0.3978(2)	0.6804(6)	0.0219(3)	1
Cs1	0.3697(6)	0.25	0.9041(6)	0.0310(2)	1
Cs2	0.7741(6)	0.25	0.4824(6)	0.0310(2)	1

Publication 2

Reversible Iodine Intercalation into Tungsten Ditelluride



<https://doi.org/10.1021/acs.inorgchem.0c02676>

Reprinted with permission from

Inorg. Chem. **2021**, *60*, 1411-1418.

Copyright © 2021 American Chemical Society

Reversible Iodine Intercalation into Tungsten Ditelluride

Patrick Schmidt, Philipp Schneiderhan, Markus Ströbele, Carl P. Romao,^{*,†} and Hans-Jürgen Meyer^{*,†}Cite This: *Inorg. Chem.* 2021, 60, 1411–1418

Read Online

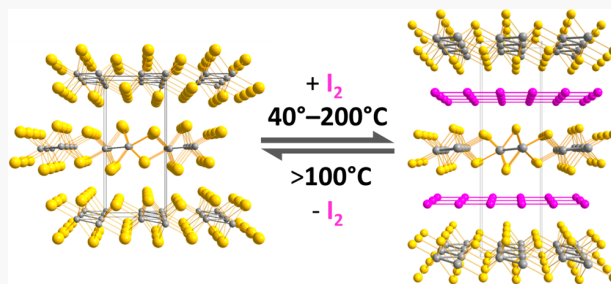
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: The new compound WTe_2I was prepared by a reaction of WTe_2 with iodine in a fused silica ampule at temperatures between 40 and 200 °C. Iodine atoms are intercalated into the van der Waals gap between tungsten ditelluride layers. As a result, the WTe_2 layer separation is significantly increased. Iodine atoms form planar layers between each tungsten ditelluride layer. Due to oxidation by iodine the semimetallic nature of WTe_2 is changed, as shown by comparative band structure calculations for WTe_2 and WTe_2I based on density functional theory. The calculated phonon band structure of WTe_2I indicates the presence of phonon instabilities related to charge density waves, leading to an observed incommensurate modulation of the iodine position within the layers.



INTRODUCTION

Transition metal dichalcogenides (TMDCs) are quasi-two-dimensional layered materials, formed by monolayers of metal atoms sandwiched between layers of chalcogen atoms. Weak van der Waals interlayer bonding between building blocks of hexagonal chalcogen layers with nearly octahedral or nearly trigonal prismatic coordinated metal atoms allow many polytypes to form.^{1–3}

The weak interlayer bonding permits intercalations, quite akin to other layered materials such as graphite,⁴ allowing the incorporation of various metal atoms^{5–10} and organic molecules^{11,12} between the layers to form stoichiometric or nonstoichiometric compounds. Depending on the intercalated species, changes in the physical properties of the host can occur. In addition, such intercalated species can be used as precursors for the exfoliation of single TMDC layers.^{13–18}

Tungsten ditelluride (WTe_2)¹⁹ is a typical TMDC that crystallizes with the so-called distorted 1T (T_d) structure. The structure resembles a distorted derivative of the TiS_2 ²⁰ structure with distorted tellurium octahedra and tungsten atoms shifted away from octahedral centers, thereby forming W–W zigzag chains along the a -axis direction (Figure 1). The arrangement of tungsten atoms in the structure plays a significant role in the remarkable electronic properties of WTe_2 . Electronic structure calculations have revealed WTe_2 to be a semimetal.^{21–23} Physical studies have revealed many unusual properties of WTe_2 , including charge density wave (CDW)^{24–31} formation, superconductivity,³² large magnetoresistance,³³ and the presence of nontrivial topological properties such as the appearance of type-II Weyl Fermions,³⁴ making this material interesting for a variety of electronic applications. Herein, we demonstrate that the oxidation of WTe_2 by iodine and the formation of the intercalated species

WTe_2I modifies the electronic structure and therefore changes the properties of this material. According to our knowledge, this type of *anionic* intercalation has not been reported before in a TMDC and may be applicable to other TMDC systems as well.

EXPERIMENTAL SECTION

Synthesis of WTe_2 and WTe_2I . Manipulations of starting materials were performed in an argon-filled glovebox (MBraun, Labmaster 130, $\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm). WTe_2 was prepared in a dry, vacuum-sealed silica ampule with a 1:2 molar ratio of tungsten powder (ABCR GmbH, 99.95%, 0.6–0.9 μm) and tellurium pieces (Evochem, 99.999%) heated at 800 °C for 24 h (total mass = 1 g). An additional 0.1 equiv of WCl_6 (Arcos, 99.9+%) was added as an oxygen getter.

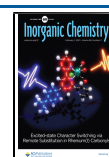
WTe_2I was prepared by heating a 1:2 molar mixture of WTe_2 and iodine (Honeywell, $\geq 99.8\%$) in a dry, vacuum-sealed silica ampule at 100 °C for 16 h. The product appeared as black powder. Excess iodine aggregated at the top of the ampule.

Synthesis of WTe_2I Single Crystals. The as-prepared WTe_2 product contained some single crystals. Carefully selected single crystals of WTe_2 were heated with an approximately 4 molar excess of iodine at 120 °C for 16 h.

Powder X-ray Diffraction. PXRD patterns of products were collected with a Stadi-P (STOE, Darmstadt) powder diffractometer using germanium monochromated $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.5406$ Å) and a Mythen 1K detector.

Received: September 7, 2020

Published: January 15, 2021



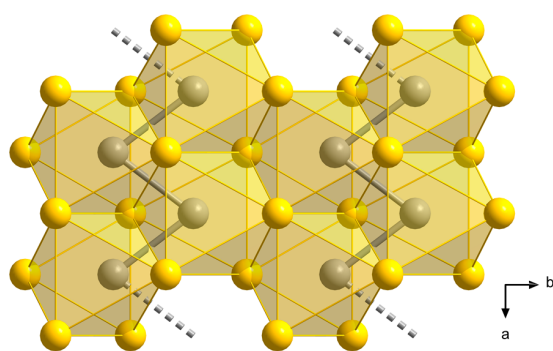


Figure 1. Projection of the WTe_2 structure. View along the c -axis of the distorted T_d structure in which tungsten (gray) atoms follow a CDW along the a -axis. Tungsten atoms are shifted off the octahedral centers formed by tellurium (yellow) atoms.

ICP-OES. After dissolution of WTe_2I in 2 wt % $\text{NaOH}/\text{H}_2\text{O}_2$, the W/Te/I ratio was determined by ICP-OES (iCAP 7400 Thermo Fisher Scientific).

Thermal Analysis. Differential thermal analysis (DTA) and thermal gravimetry (TG) measurements were performed with a Netzsch Jupiter, STA 449 F3 apparatus between room temperature and 350°C with a heating and cooling rate of 2 K min^{-1} in a bespoke silica crucible (height: 2 cm, inner diameter: 0.6 cm, thickness of wall: 0.1 cm).

DFT Calculations. Calculations were performed using the ABINIT software package with the projector augmented-wave (PAW) method and a plane-wave basis set.^{35,36} The Perdew–Burke–Ernzerhof exchange–correlation functional was used with the vdW–DFT–D3 dispersion correction.^{37,38} PAW data files were used as received from the ABINIT library.³⁹ Methfessel–Paxton smearing was used to determine band occupation.⁴⁰ Convergence studies and structural relaxation were performed prior to calculation of the electronic structure. Spin–orbit coupling was included by calculation of the electronic wave function of each spin separately, as described in ref 41. Example input files are available as part of the [Supporting Information](#).

RESULTS AND DISCUSSION

Reactions of metal dichalcogenides with halides have been reported to yield mixed chalcogenide–halide cluster compounds. An example is the formation of $\text{Re}_3\text{Se}_2\text{Br}_5$ from ReSe_2 with Br_2 (at 450°C).⁴² Following this example we have explored the reaction of WTe_2 with iodine. WTe_2 can be prepared from well-known transport reactions of the elements in fused silica tubing, like other transition metal chalcogenides.^{19,21,43–46} A detailed study of the reaction of WTe_2 with iodine in a fused silica ampule reveals several reaction steps with increasing temperature and iodine pressure. The first step is an intercalation of iodine into interlayers of the WTe_2 structure, yielding the new compound WTe_2I , which occurs following heating above 40°C in a closed vessel. When heated above 200°C , iodine and TeI_4 are released until $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ is formed at 250°C .⁴⁷

A chemical analysis of WTe_2I by inductively coupled plasma optical emission spectrometry (ICP-OES) confirmed the identity of the product with an average ratio of elements (from a number of measurements) corresponding to W:Te:I = 1:1.98:0.99.

The crystal structure of WTe_2I is closely related to that of WTe_2 but contains iodine atoms in interlayers and was refined by powder X-ray diffraction (PXRD) in the centrosymmetric space group $Pmmn$ (Figure 2).

The structure refinement converged with a conclusive crystal structure model, revealing unusually high anisotropic displacement parameters (ADPs) of the iodine atoms (Table S2). A single-crystal X-ray analysis of the reciprocal a^*/b^* plane (Figure S2) revealed perturbations of some weak Bragg reflections away from the exact regularity of the basic lattice reflections. The PXRD pattern exhibits a few additional reflections (with $I/I_{\text{max}} \cong 1/100$, marked with asterisks in Figure 2) that could not be assigned to any known compound (and the purity of all starting materials was carefully checked by EDX, ICP-OES, and RFA).

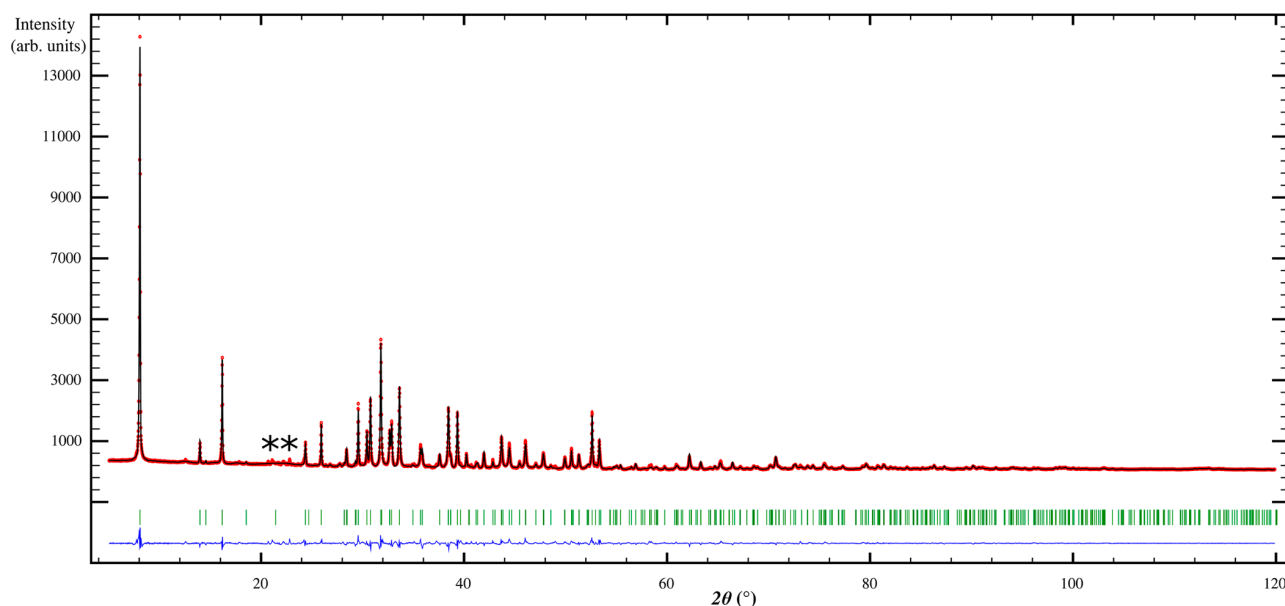


Figure 2. PXRD refinement pattern of WTe_2I at 298 K with the experimental (red) and calculated (black) patterns of the Rietveld refinement. Bragg positions (green) of WTe_2I and the difference curve (blue) are also shown. Asterisks (*) are discussed in the main text.

The observation of large ADPs of the iodine atoms can be seen to be indicative of a modulation of the iodine atom arrangement in interlayers of the structure. Hence, based on our PXRD studies, we can only provide an average location of the iodine atoms relative to the WTe_2 lattice. Low-temperature PXRD measurements (at 120 and 12 K) did not introduce a significant change in the diffraction pattern, nor in the iodine ADPs (Figure S5, Figure S6, and Table S8).

The a , b , and c axes in WTe_2I correspond to the c , a , and b axes, respectively, in WTe_2 . Individual WTe_2 layers and corresponding W–W and W–Te distances are nearly unchanged before and after the reaction with I_2 (Table 1). Therefore, the cell dimensions within the layers remain almost the same. However, due to the intercalation of iodine between adjacent WTe_2 layers, the lattice parameter along the stacking direction are approximately doubled (Table 1, compare the c -axis of WTe_2 and a -axis of WTe_2I) (Figure 3). The relative orientation of adjacent WTe_2 layers changes compared to WTe_2 in a way such that the tungsten chains are aligned parallel along the stacking axis.

Iodine atoms form nearly square (Figure 4), planar layers within the bc -plane with I–I distances of 3.18(1) Å and 3.48(1) Å. A similar arrangement of iodine layers with values of 3.32 and 3.84 Å was reported in the unusual intercalation compound $(\text{Te}_2)_2(\text{I}_2)$.⁴⁹ Another, more closely related, TMDC intercalation compound containing a planar iodine network is AuTe_2I ,⁵⁰ which has I–I distances of 4.06(1) and 4.74(1) Å.

As noted above, the incorporation of iodine atoms into the structure of WTe_2 yields a significant increase of the interlayer W–W (from 7.01 Å in WTe_2 to 10.95 Å in WTe_2I) and Te–Te (from 3.911 to 6.813 Å) distances. This increase is huge in comparison to cationic intercalation compounds like in WS_2In (increasing from 6.16 Å in WS_2 to 6.18 Å in WS_2In).⁵¹ As a result of this strong interlayer expansion and weak interaction forces between layers, dislocations are typically obtained (see Figure S1).

The intercalation reaction between iodine and WTe_2 in a sealed ampule proceeds without a detectable calorimetric feature. The deintercalation of iodine from WTe_2I under ambient pressure can be observed above 100 °C (Figure 5). The observed exothermic effect corresponds to the enthalpy of sublimation of the released iodine (in a constant argon flow of 60 mL/min) and has no correlation with the intercalation energy.

Electronic Structure. The calculated electronic band structure of WTe_2I is shown in Figure 6. This electronic structure calculation was performed on the average structure, as determined by XRPD; a discussion of the potential origins

Table 1. Crystallographic Data and W–W and W–Te Distances of WTe_2 and WTe_2I

	WTe_2 ⁴⁸	WTe_2I
space group	$Pmn2_1$	$Pmnn$
$a/\text{Å}$	3.477(2)	21.8967(2)
$b/\text{Å}$	6.249(4)	3.4759(0)
$c/\text{Å}$	14.018(9)	6.3270(1)
$V/\text{Å}^3$	304.6(3)	481.54(1)
$d(\text{W–W})/\text{Å}$	2.85(1), 3.48(1)	2.87(1), 3.48(1)
$d(\text{W–Te})/\text{Å}$	2.70(1)–2.80(1)	2.68(1)–2.83(1)
$d(\text{Te–I})/\text{Å}$	–	4.14(1)–4.36(1)
R_{Bragg}	–	5.0301

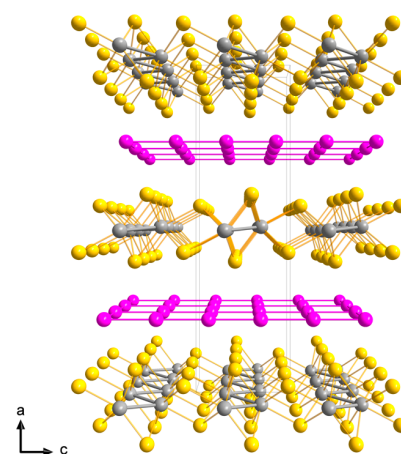


Figure 3. Perspective projection of the crystal structure of WTe_2I , showing a layered arrangement. Tungsten atoms are shown gray, iodine atoms in violet, and tellurium atoms in yellow.

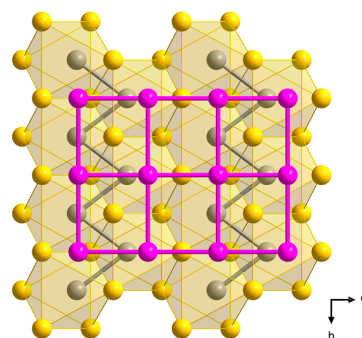


Figure 4. Arrangement of a rectangular net of iodine atoms on top of a WTe_2 layer of the WTe_2I structure (W = gray, Te = yellow, I = violet).

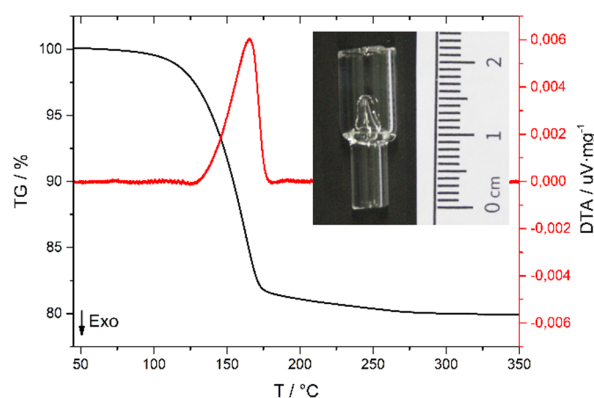


Figure 5. DTA/TG measurement of WTe_2I in an open SiO_2 container up to 350 °C with complete iodine loss (DTA: red line, TG: black line).

and effects of a modulation of the iodine positions can be found below. Comparison of Figure 6 to the band structure of WTe_2 (Figure 7) shows that the addition of iodine layers into the structure increases the density of states (DOS) at the Fermi level significantly, leading to a transition from a semimetal to a metal. These additional states are largely located between the Γ ([0 0 0]), X ([1/2 0 0]), and Z ([0 0 1/2]) points in reciprocal space. The projected density of states

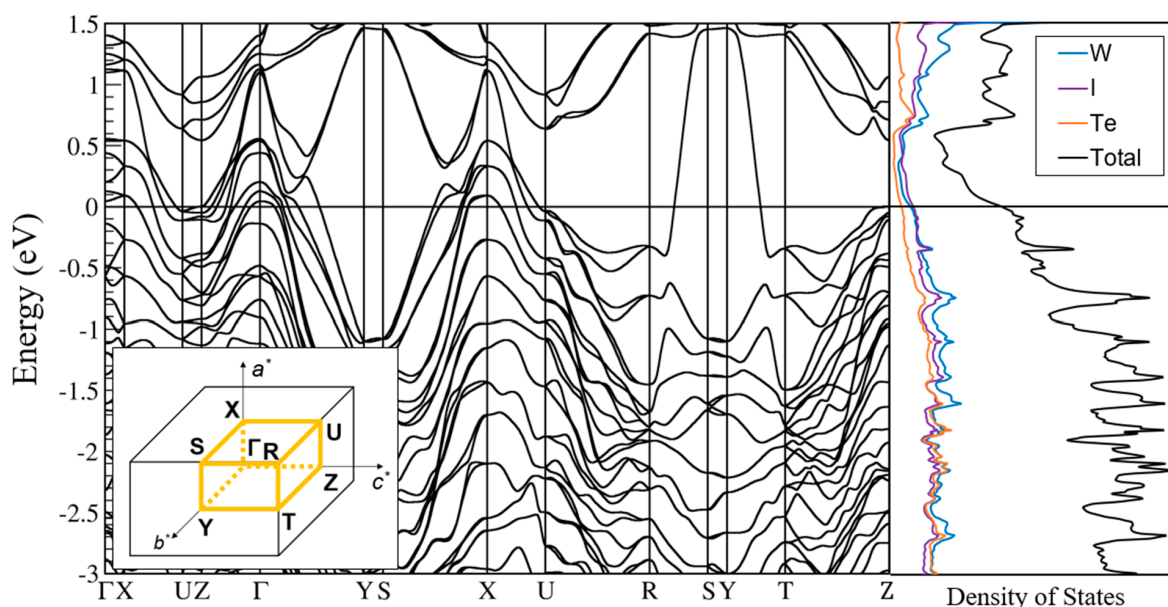


Figure 6. Electronic band structure and density of states of WTe_2I , calculated with spin–orbit coupling. The projected densities of states within the PAW spheres are shown as colored lines at right. Special points in the Brillouin zone are shown as an inset.

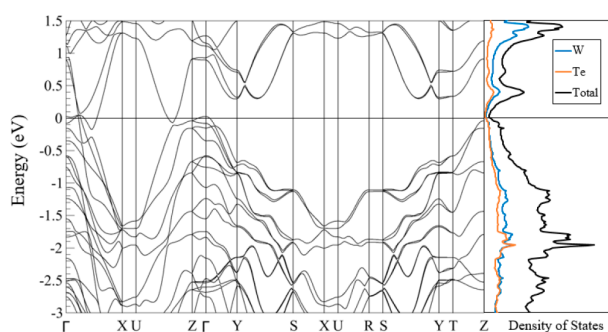


Figure 7. Electronic band structure and density of states of WTe_2 , calculated without spin–orbit coupling (see ref 8 c for the band structure with spin–orbit coupling). The projected densities of states within the PAW spheres are shown as colored lines at right.

shows that the states around the Fermi level have contributions from W, Te, and I atoms; many of the states project onto interatomic regions which cannot be assigned to a single atom.

Along the Γ –Y–S–X– Γ path in reciprocal space (Figure 6), the calculated band structure of WTe_2I closely resembles that of WTe_2 along the Γ –X–U–Z– Γ path, with the Fermi level shifted downward in energy by approximately 0.5 eV. The significant increase in the DOS at the Fermi level following the addition of iodine can therefore be partially attributed to the depletion of some electron density from the tungsten telluride layers into the iodine layers. The magnitude of this charge transfer can be estimated from the calculated density of states of WTe_2 and WTe_2I as 0.7 electrons per formula unit. In WTe_2 , an avoided crossing of two bands due to spin–orbit coupling near the Fermi level along the Γ –X direction gives rise to Weyl semimetal behavior.^{34,52} The addition of iodine to form WTe_2I moves the Fermi level away from the corresponding feature (located between Γ and Y), into a region with more conventional bands at the Fermi surface.

The addition of iodine to WTe_2 also creates additional bands at the Fermi level between R ($[1/2\ 1/2\ 1/2]$) and S

($[1/2\ 1/2\ 0]$) and between Y ($[0\ 1/2\ 0]$) and T ($[0\ 1/2\ 1/2]$) (compare Figure 6 and Figure 8). These bands have very high dispersion, indicating small effective electron masses and large charge carrier mobility. They are associated with Dirac cone-like anticrossings lying approximately 0.5 eV below the Fermi level. Several methods were used to investigate the nature of these highly dispersive bands. Projections of the wave functions near each atom onto spherical harmonics were used to determine the atomic and orbital character of the wave functions corresponding to the bands. As shown in Figure 10, this indicates that the bands of interest can be largely assigned to iodine p_z orbitals. To validate this result, the electronic band structure of the iodine layer alone was calculated, and the features between R and S and Y and T can also be found there (Figure 8).

Careful examination of the electron density around the iodine atoms (Figure 9) shows evidence of bonding (i.e., some interstitial electron density) in chains along c . Stronger bonding is indicated between iodine atoms with an interatomic distance of 3.148 Å in the XRD crystal structure. The

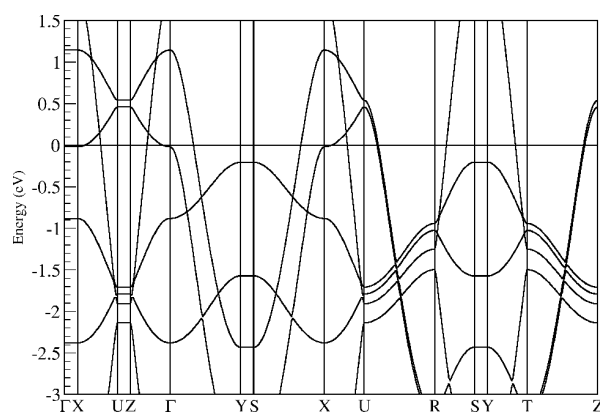


Figure 8. Electronic band structure of the iodine layers in WTe_2I .

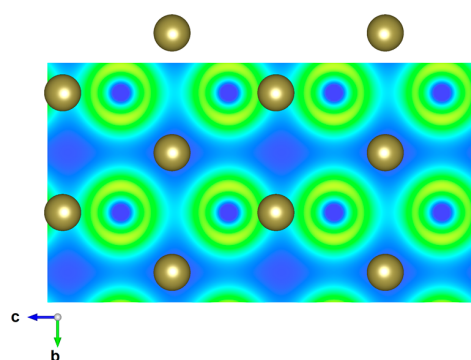


Figure 9. Density of valence electrons in a section through iodine atoms in the bc plane. A slight increase in electron density between iodine atoms along c evidence I–I bonding. The Te atoms above the plane are shown for comparison.

formation of dimers along c indicates that the bands with p_z character (Figure 10) correspond to σ bonding and antibonding orbitals.

The effects of modulation of the iodine layers upon the electronic band structure were investigated by calculation of the electronic band structure of WTe_2I with a displacement of the iodine atoms by -0.25 along c (Figure S3), in order to test the sensitivity of the band structure to the Te–I distances. The band structure was mostly unchanged, with the largest modification being a significant increase in energy of the valence band between R, S, Y, and T. This increase led to the valence band reaching the Fermi level at R and T, indicating that modulation of the iodine layers may introduce more states which contribute to electronic conductivity. Shifting the iodine atoms such that there is only one crystallographically independent I–I distance resulted in no noticeable effect on the electronic band structure (Figure S4).

Calculation of the phonon band structure of WTe_2I revealed the presence of several soft modes (modes with imaginary frequencies, shown as negative values in Figure 11). These modes indicate instabilities of the crystallographic $Pm\bar{m}n$ structure and can be identified as Kohn anomalies, that is, they indicate that a charge-density wave ordered structure is more stable at 0 K than the $Pm\bar{m}n$ structure.¹ The CDW ordering can be commensurate or incommensurate with the lattice vectors. The presence of these Kohn anomalies therefore offers

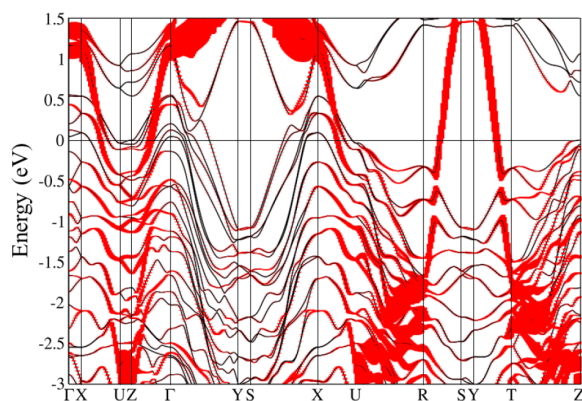


Figure 10. Projected contributions of p_z spherical harmonics to electronic bands in WTe_2I , shown in red as fatbands.

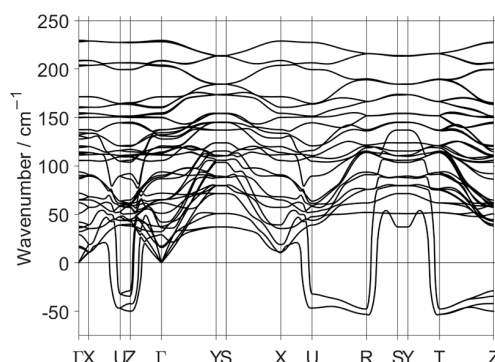


Figure 11. Calculated phonon band structure of WTe_2I .

an explanation for the modulation of the iodine layers detected by X-ray diffraction and indicate that a phase transition to a CDW disordered state can be expected on heating (although decomposition could happen prior to such a transition).

The Kohn anomalies are related to nesting vectors of the Fermi surface (Figure 12); the introduction of additional sheet-like bands crossing the Fermi level therefore opens new possibilities for such nesting. The phonon band structure also shows numerous triply degenerate nodal points between R and S and Y and T, where optic bands invert and become lower in energy than the acoustic bands. These topological features can act as additional phonon scattering centers and lead to glass-like thermal conductivity.^{53,54} There are also numerous crossings and near-crossings of bands, especially near Γ , which may correspond to Dirac points which could, by breaking the inversion symmetry, be transformed into topologically charged Weyl phonons.^{53,54}

The nature of the CDW can be determined by examination of the eigenvectors of the soft modes, which are shown in cartoon form in Figure 13. These modes all involve oscillations of iodine atoms along b , with rocking motions of the Te_2 layers being incorporated in some cases. Since the soft modes involve motions of individual iodine atoms, not rigid I_2 units, we can conclude that the CDWs are related to instabilities of the weak I–I bonds seen in the average structure and in Figure 9. This offers an interesting parallel to the dissociation of I–I bonds under pressure in solid iodine, which involves the formation of a modulated structure where some of the I–I distances vary between the values seen in the average structure.⁵⁵

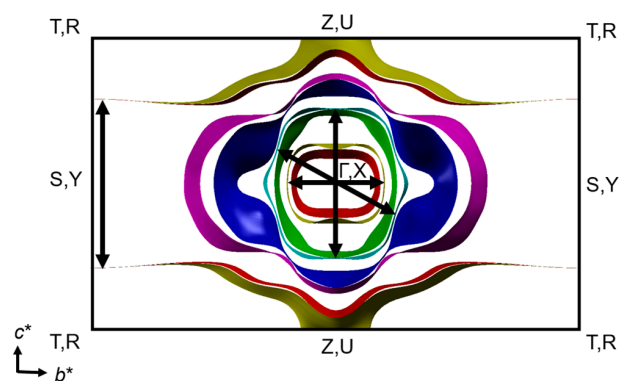


Figure 12. Calculated Fermi surface of WTe_2I . Nesting vectors (from left to right, $[0\ 0\ 0.52]$, $[0\ 0.34\ 0.20]$, $[0\ 0.28\ 0]$, and $[0\ 0\ 0.45]$) are shown as black arrows.

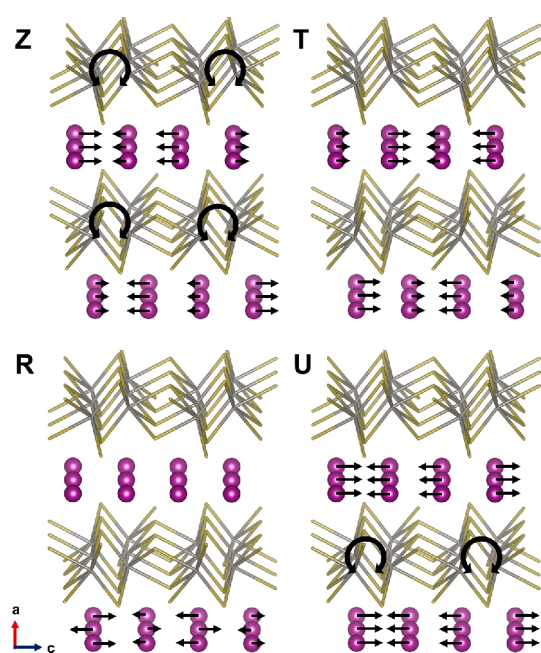


Figure 13. A cartoon view of several soft modes in WTe_2I . The modes with the largest imaginary frequency (most negative values in Figure 8) at the Z, T, R, and U points are shown. Linear oscillations of I atoms are shown as black arrows, and rocking motions of the WTe_2 layers are shown as curved arrows.

CONCLUSIONS

The reversible intercalation of iodine into the structure of WTe_2 is presented with an average crystal structure of WTe_2I obtained by PXRD. Iodide atoms in interlayers of the structure appear not fully ordered and show therefore anomalous large ADPs. Single-crystal studies have revealed additional reflections inconsistent with the Bragg reflections of the structure, leading to the assumption of the presence of an incommensurable structure.

To our knowledge, the example of WTe_2I represents the first reported halide intercalation into a dichalcogenide structure. Although other intercalation compounds of WTe_2 with alkali ions are known, no crystal structures have been reported in ICSD.⁵⁶ In light of the many unusual physical properties of WTe_2 , this intercalate with oxidized WTe_2 layers represents an interesting material for electronic applications. Electronic band structure calculations reveal WTe_2I to be metallic and to have steep bands with dominant iodine p-band character crossing the Fermi level. The phonon band structure indicates that modulation of the iodine layers is due to Kohn anomalies in the $Pmmn$ structure. Halogen intercalation is therefore demonstrated to present a potential method to reversibly modify the physical properties of WTe_2 .

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02676>.

DFT input (ZIP)

An image of a crystal of WTe_2I showing layer dislocations, PXRD patterns, and refinement information, a table of atomic coordinates, from refinement of XRD data and DFT structural optimization (PDF)

Calculated electronic band structure of WTe_2I with modified iodine positions (TXT)

Accession Codes

CCDC 2019336 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Carl P. Romao – Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany; orcid.org/0000-0002-5519-2519; Email: carl.romao@mnf.uni-tuebingen.de

Hans-Jürgen Meyer – Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany; orcid.org/0000-0003-2450-4011; Email: juergen.meyer@uni-tuebingen.de

Authors

Patrick Schmidt – Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany

Philipp Schneiderhan – Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany

Markus Ströbele – Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany; orcid.org/0000-0002-5147-5677

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.inorgchem.0c02676>

Author Contributions

[†]These authors contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors express their gratitude to Dr. Jochen Glaser (University of Tübingen) for performing ICP-OES analyses and Dipl.-Ing. Frank Adams, Dr. Sebastian Bette, and Prof. Dr. Robert Dinnebier (MPI Stuttgart) for low-temperature PXRD measurements on WTe_2I . Support of this research by the Deutsche Forschungsgemeinschaft (DFG-Bonn) through the project ME 914/31-1, by the state of Baden-Württemberg through bwHPC, and by the DFG through INST 40/467-1 FUGG (JUSTUS cluster) is gratefully acknowledged.

REFERENCES

- (1) Han, G. H.; Duong, D. L.; Keum, D. H.; Yun, S. J.; Lee, Y. H. van der Waals Metallic Transition Metal Dichalcogenides. *Chem. Rev.* **2018**, *118* (13), 6297–6336.

- (2) Atherton, M. J.; Holloway, J. H.; Thio-, Seleno-, and Tellurohalides of the Transition Metals. In *Adv. Inorg. Chem. Radiochem.*, Emeléus, H. J., Sharpe, A. G., Eds.; Academic Press: 1979; Vol. 22, pp 171–198.
- (3) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.
- (4) Boehm, H. P.; Setton, R.; Stumpp, E. Nomenclature and terminology of graphite intercalation compounds (IUPAC Recommendations 1994). *Pure Appl. Chem.* **1994**, *66* (9), 1893.
- (5) Ali, M. N.; Ji, H.; Hirai, D.; Fuccillo, M. K.; Cava, R. J. Synthesis and characterization of two crystallographic forms of $\text{Ag}_{0.79}\text{VS}_2$. *J. Solid State Chem.* **2013**, *202*, 77–84.
- (6) Ali, S. I.; Mondal, S.; Prathapa, S. J.; van Smaalen, S.; Zöhr, S.; Harbrecht, B. Self-Intercalation and Vacancy-Ordering in $6\text{R-Cu}_x\text{Ta}_{1-y}\text{S}_2$ ($x \approx 0.23$, $y = 0, 0.06$). *Z. Anorg. Allg. Chem.* **2012**, *638* (15), 2625–2631.
- (7) Ali, S. I.; Mondal, S.; van Smaalen, S. Synthesis, Superstructure, and Vacancy-Ordering in $2\text{H-Cu}_x\text{Ta}_{1-y}\text{Se}_2$ ($x, y = 0.52, 0$ and $0.16, 0.08$). *Z. Anorg. Allg. Chem.* **2015**, *641* (2), 464–469.
- (8) Crawack, H. J.; Pottenkofer, C. Calculation and XPS measurements of the Ta4f CDW splitting in Cu, Cs and Li intercalation phases of 1T-TaX_2 ($X=\text{S, Se}$). *Solid State Commun.* **2001**, *118* (7), 325–332.
- (9) Rouxel, J. Structural chemistry of layered materials and their intercalates. *Physica B+C* **1980**, *99* (1), 3–11.
- (10) Patel, S. N.; Balchin, A. A. Structural studies of lithium intercalated titanium di-telluride. *J. Mater. Sci. Lett.* **1985**, *4* (4), 382–384.
- (11) Dines, M. B. Intercalation of Metallocenes in the Layered Transition-Metal Dichalcogenides. *Science* **1975**, *188* (4194), 1210.
- (12) Figueroa, E.; Brill, J. W.; Selegue, J. P. New intercalation compounds of transition metal dichalcogenides. *J. Phys. Chem. Solids* **1996**, *57* (6), 1123–1127.
- (13) Budania, P.; Baine, P. T.; Montgomery, J. H.; McNeill, D. W.; Neil Mitchell, S. J.; Modreanu, M.; Hurley, P. K. Comparison between Scotch tape and gel-assisted mechanical exfoliation techniques for preparation of 2D transition metal dichalcogenide flakes. *Micro Nano Lett.* **2017**, *12* (12), 970–973.
- (14) Sajedi-Moghaddam, A.; Mayorga-Martinez, C. C.; Saievar-Iranizad, E.; Sofer, Z.; Pumera, M. Exfoliated transition metal dichalcogenide (MX_2 , $M=\text{Mo, W}$; $X=\text{S, Se, Te}$) nanosheets and their composites with polyaniline nanofibers for electrochemical capacitors. *Appl. Mater. Today* **2019**, *16*, 280–289.
- (15) Cunningham, G.; Lotya, M.; Cucinotta, C. S.; Sanvito, S.; Bergin, S. D.; Menzel, R.; Shaffer, M. S. P.; Coleman, J. N. Solvent Exfoliation of Transition Metal Dichalcogenides: Dispersibility of Exfoliated Nanosheets Varies Only Weakly between Compounds. *ACS Nano* **2012**, *6* (4), 3468–3480.
- (16) An, S.-J.; Kim, Y. H.; Lee, C.; Park, D. Y.; Jeong, M. S. Exfoliation of Transition Metal Dichalcogenides by a High-Power Femtosecond Laser. *Sci. Rep.* **2018**, *8* (1), 12957.
- (17) Liu, X.; Chen, H.; Lin, J.; Li, Y.; Guo, L. Exfoliation of transition-metal dichalcogenides using ATP in aqueous solution. *Chem. Commun.* **2019**, *55* (20), 2972–2975.
- (18) Jung, Y.; Zhou, Y.; Cha, J. J. Intercalation in two-dimensional transition metal chalcogenides. *Inorg. Chem. Front.* **2016**, *3* (4), 452–463.
- (19) Brown, B. E. The crystal structures of WTe_2 and high-temperature MoTe_2 . *Acta Crystallogr.* **1966**, *20* (2), 268–274.
- (20) Chianelli, R. R.; Scanlon, J. C.; Thompson, A. H. Structure refinement of stoichiometric TiS_2 . *Mater. Res. Bull.* **1975**, *10* (12), 1379–1382.
- (21) Kabashima, S. Electrical Properties of Tungsten-Ditelluride WTe_2 . *J. Phys. Soc. Jpn.* **1966**, *21*, 945–948.
- (22) Augustin, J.; Eyert, V.; Boker, T.; Frentrup, W.; Dwelk, H.; Janowitz, C.; Manzke, R. Electronic band structure of the layered compound Td-WTe_2 . *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62*, 10812–10823.
- (23) Dawson, W. G.; Bullett, D. W. Electronic structure and crystallography of MoTe_2 and WTe_2 . *J. Phys. C: Solid State Phys.* **1987**, *20*, 6159–6174.
- (24) Rovira, C.; Whangbo, M. H. Factors governing the charge density wave patterns of layered transition-metal compounds of octahedral coordination with d^2 and d^3 electron counts. *Inorg. Chem.* **1993**, *32* (19), 4094–4097.
- (25) Wilson, J. A.; Di Salvo, F. J.; Mahajan, S. Charge-density waves and superlattices in the metallic layered transition metal dichalcogenides. *Adv. Phys.* **1975**, *24* (2), 117–201.
- (26) Ali, M. N.; Xiong, J.; Flynn, S.; Tao, J.; Gibson, Q. D.; Schoop, L. M.; Liang, T.; Haldolaarachchige, N.; Hirschberger, M.; Ong, N. P.; Cava, R. J. Large, non-saturating magnetoresistance in WTe_2 . *Nature* **2014**, *514*, 205–208.
- (27) Lu, N.; Zhang, C.; Lee, C.-H.; Oviedo, J. P.; Nguyen, M. A. T.; Peng, X.; Wallace, R. M.; Mallouk, T. E.; Robinson, J. A.; Wang, J.; Cho, K.; Kim, M. J. Atomic and Electronic Structures of WTe_2 Probed by High Resolution Electron Microscopy and ab Initio Calculations. *J. Phys. Chem. C* **2016**, *120* (15), 8364–8369.
- (28) Canadell, E.; Whangbo, M.-H. Charge-density-wave instabilities expected in monophosphate tungsten bronzes. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1991**, *43* (3), 1894–1902.
- (29) Guster, B.; Canadell, E.; Pruneda, M.; Ordejón, P. First principles analysis of the CDW instability of single-layer 1T-TiSe_2 and its evolution with charge carrier density. *2D Mater.* **2018**, *5* (2), 025024.
- (30) Whangbo, M. H.; Canadell, E.; Foury, P.; Pouget, J. P. Hidden Fermi Surface Nesting and Charge Density Wave Instability in Low-Dimensional Metals. *Science* **1991**, *252* (5002), 96.
- (31) Mitsuishi, N.; Sugita, Y.; Bahramy, M. S.; Kamitani, M.; Sonobe, T.; Sakano, M.; Shimojima, T.; Takahashi, H.; Sakai, H.; Horiba, K.; Kumigashira, H.; Taguchi, K.; Miyamoto, K.; Okuda, T.; Ishiwata, S.; Motome, Y.; Ishizaka, K. Switching of band inversion and topological surface states by charge density wave. *Nat. Commun.* **2020**, *11* (1), 2466.
- (32) Huang, C.; Narayan, A.; Zhang, E.; Liu, Y.; Yan, X.; Wang, J.; Zhang, C.; Wang, W.; Zhou, T.; Yi, C.; Liu, S.; Ling, J.; Zhang, H.; Liu, R.; Sankar, R.; Chou, F.; Wang, Y.; Shi, Y.; Law, K. T.; Sanvito, S.; Zhou, P.; Han, Z.; Xiu, F. Inducing Strong Superconductivity in WTe_2 by a Proximity Effect. *ACS Nano* **2018**, *12* (7), 7185–7196.
- (33) Lv, Y.-Y.; Zhang, B.-B.; Li, X.; Pang, B.; Zhang, F.; Lin, D.-J.; Zhou, J.; Yao, S.-H.; Chen, Y. B.; Zhang, S.-T.; Lu, M.; Liu, Z.; Chen, Y.; Chen, Y.-F. Dramatically decreased magnetoresistance in non-stoichiometric WTe_2 crystals. *Sci. Rep.* **2016**, *6* (1), 26903.
- (34) Li, P.; Wen, Y.; He, X.; Zhang, Q.; Xia, C.; Yu, Z.-M.; Yang, S. A.; Zhu, Z.; Alshareef, H. N.; Zhang, X.-X. Evidence for topological type-II Weyl semimetal WTe_2 . *Nat. Commun.* **2017**, *8* (1), 2150.
- (35) Gonze, X.; Jollet, F.; Abreu Araujo, F.; Adams, D.; Amadon, B.; Applencourt, T.; Audouze, C.; Beuken, J. M.; Bieder, J.; Bokhanchuk, A.; Bousquet, E.; Bruneval, F.; Caliste, D.; Côté, M.; Dahm, F.; Da Pieve, F.; Delaveau, M.; Di Gennaro, M.; Dorado, B.; Espejo, C.; Geneste, G.; Genovese, L.; Gerossier, A.; Giantomassi, M.; Gillet, Y.; Hamann, D. R.; He, L.; Jomard, G.; Laflamme Janssens, J.; Le Roux, S.; Levitt, A.; Lherbier, A.; Liu, F.; Lukačević, I.; Martin, A.; Martins, C.; Oliveira, M. J. T.; Poncé, S.; Pouillon, Y.; Rangel, T.; Rignanese, G. M.; Romero, A. H.; Rousseau, B.; Rubel, O.; Shukri, A. A.; Stankovski, M.; Torrent, M.; Van Setten, M. J.; Van Troeye, B.; Verstraete, M. J.; Waroquiers, D.; Wiktór, J.; Xu, B.; Zhou, A.; Zwanziger, J. W. Recent developments in the ABINIT software package. *Comput. Phys. Commun.* **2016**, *205*, 106–131.
- (36) Torrent, M.; Jollet, F.; Bottin, F.; Zerah, G.; Gonze, X. Implementation of the projector augmented-wave method in the ABINIT code: Application to the study of iron under pressure. *Comput. Mater. Sci.* **2008**, *42* (2), 337–351.
- (37) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865; *Phys. Rev. Lett.* **1997**, *78* (7), 1396–1396.
- (38) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion

correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.

(39) ABINIT. www.abinit.org (accessed March 19, 2020).

(40) Methfessel, M.; Paxton, A. T. High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1989**, *40* (6), 3616–3621.

(41) Gonze, X.; Beuken, J. M.; Caracas, R.; Detraux, F.; Fuchs, M.; Rignanese, G. M.; Sindic, L.; Verstraete, M.; Zerah, G.; Jollet, F.; Torrent, M.; Roy, A.; Mikami, M.; Ghosez, P.; Raty, J. Y.; Allan, D. C. First-principles computation of material properties: the ABINIT software project. *Comput. Mater. Sci.* **2002**, *25* (3), 478–492.

(42) Solodovnikov, S. F.; Mironov, Y. V.; Yarovoi, S. S.; Virovets, A. V.; Fedorov, V. E. Crystal chemistry of octahedral clusters of rhenium chalcogenides $\text{Re}_6\text{X}_4\text{Y}_{10}$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$; $\text{Y} = \text{Cl}, \text{Br}$). *Khim. Interesakh Ustoich. Razvit.* **2000**, *8*, 285–290.

(43) Zhou, Y.; Pondick, J. V.; Silva, J. L.; Woods, J. M.; Hynek, D. J.; Matthews, G.; Shen, X.; Feng, Q.; Liu, W.; Lu, Z.; Liang, Z.; Brena, B.; Cai, Z.; Wu, M.; Jiao, L.; Hu, S.; Wang, H.; Araujo, C. M.; Cha, J. J. Unveiling the Interfacial Effects for Enhanced Hydrogen Evolution Reaction on $\text{MoS}_2/\text{WTe}_2$ Hybrid Structures. *Small* **2019**, *15* (19), 1900078.

(44) Brixner, L. H. Preparation and properties of the single crystalline AB_2 -type selenides and tellurides of niobium, tantalum, molybdenum and tungsten. *J. Inorg. Nucl. Chem.* **1962**, *24*, 257–263.

(45) Al-Hilli, A. A.; Evans, B. L. The preparation and properties of transition metal dichalcogenide single crystals. *J. Cryst. Growth* **1972**, *15* (2), 93–101.

(46) Ueno, K. Introduction to the Growth of Bulk Single Crystals of Two-Dimensional Transition-Metal Dichalcogenides. *J. Phys. Soc. Jpn.* **2015**, *84* (12), 121015.

(47) Schmidt, P.; Siai, A.; Schneiderhan, P.; Ströbele, M.; Meyer, H.-J. Synthesis of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ via Iodination of WTe_2 . *Eur. J. Inorg. Chem.* **2020**, *2020* (8), 716–719.

(48) Mar, A.; Jobic, S.; Ibers, J. A. Metal-metal vs tellurium-tellurium bonding in WTe_2 and its ternary variants TaIrTe_4 and NbIrTe_4 . *J. Am. Chem. Soc.* **1992**, *114* (23), 8963–8971.

(49) Kniep, R.; Beister, H.-J. $(\text{Te}_2)_2(\text{I}_2)$ - An Unusual Intercalation Compound. *Angew. Chem., Int. Ed. Engl.* **1985**, *24* (5), 393–394.

(50) Haendler, H. M.; Mootz, D.; Rabenau, A.; Rosenstein, G. The crystal structures of AuTe_2Cl and AuTe_2I . *J. Solid State Chem.* **1974**, *10* (2), 175–181.

(51) Srivastava, S. K.; Avasthi, B. N. Synthesis and characterization of indium intercalation compounds of tungsten disulphide: In_xWS_2 ($0 \leq x \leq 1$). *Synth. Met.* **1985**, *10* (3), 213–221.

(52) Das, P. K.; Di Sante, D.; Cilento, F.; Bigi, C.; Kopic, D.; Soranzio, D.; Sterzi, A.; Krieger, J. A.; Vobornik, I.; Fujii, J.; Okuda, T.; Strocov, V. N.; Breese, M. B. H.; Parmigiani, F.; Rossi, G.; Picozzi, S.; Thomale, R.; Sangiovanni, G.; Cava, R. J.; Panaccione, G. Electronic properties of candidate type-II Weyl semimetal WTe_2 . A review perspective. *Electron. Struct.* **2019**, *1* (1), 014003.

(53) Li, J.; Xie, Q.; Ullah, S.; Li, R.; Ma, H.; Li, D.; Li, Y.; Chen, X.-Q. Coexistent three-component and two-component Weyl phonons in TiS , ZrSe , and HfTe . *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, *97* (5), 054305.

(54) Singh, S.; Wu, Q.; Yue, C.; Romero, A. H.; Soluyanov, A. A. Topological phonons and thermoelectricity in triple-point metals. *Phys. Rev. Mater.* **2018**, *2* (11), 114204.

(55) Kenichi, T.; Kyoko, S.; Hiroshi, F.; Mitsuko, O. Modulated structure of solid iodine during its molecular dissociation under high pressure. *Nature* **2003**, *423* (6943), 971–974.

(56) Zhu, L.; Li, Q.-Y.; Lv, Y.-Y.; Li, S.; Zhu, X.-Y.; Jia, Z.-Y.; Chen, Y. B.; Wen, J.; Li, S.-C. Superconductivity in Potassium-Intercalated $\text{T}_d\text{-WTe}_2$. *Nano Lett.* **2018**, *18* (10), 6585–6590.

Supporting information

Reversible Iodine Intercalation into Tungsten Ditelluride

Patrick Schmidt,^[a] Philipp Schneiderhan,^[a] Markus Ströbele,^[a] Carl P. Romao,^{[a]*} Hans-Jürgen Meyer^{[a]*}

^[a] Section of Solid State and Theoretical Inorganic Chemistry
Institute of Inorganic Chemistry
Eberhard Karls University Tübingen
Auf der Morgenstelle 18
72076 Tübingen, Germany

Table of Contents

Figure S1. WTe ₂ I crystal with layer dislocations.....	S3
Figure S2. Reciprocal a^*/b^* plane revealing perturbations of some weak Bragg reflections away from the exact regularity of the basic lattice reflections.....	S4
Figure S3. The calculated electronic band structure of WTe ₂ I with the I atoms shifted by -0.25 along c	S6
Figure S4. The calculated electronic band structure of WTe ₂ I with the positions of the I atoms shifted along c to 0.65 and 0.15 , such that there is only one crystallographically independent I–I distance.....	S6
Figure S5. PXRD refinement pattern of WTe ₂ I at 120 K with the experimental (red) and calculated (black) patterns of the Rietveld refinement. Bragg positions (green) of WTe ₂ I and the difference curve (blue) are also shown.....	S7
Figure S6. PXRD refinement pattern of WTe ₂ I at 12 K with the experimental (red) and calculated (black) patterns of the Rietveld refinement. Bragg positions (green) of WTe ₂ I and the difference curve (blue) are also shown.....	S8
Table S1. Crystal data and structure refinement for WTe ₂ I at 298 K.....	S5
Table S2. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for WTe ₂ I. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.	S5
Table S3. Structural parameters of WTe ₂ I following DFT optimization.	S5
Table S4. Crystal data and structure refinement for WTe ₂ I at 120 K.....	S7
Table S5. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for WTe ₂ I at 120 K. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.	S7
Table S6. Crystal data and structure refinement for WTe ₂ I at 12 K.....	S8
Table S7. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for WTe ₂ I at 12 K. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.	S8
Table S8. Average equivalent isotropic displacement parameters $\langle U_{ij} \rangle$ (pm^2) at different temperatures and their ratio.....	S9

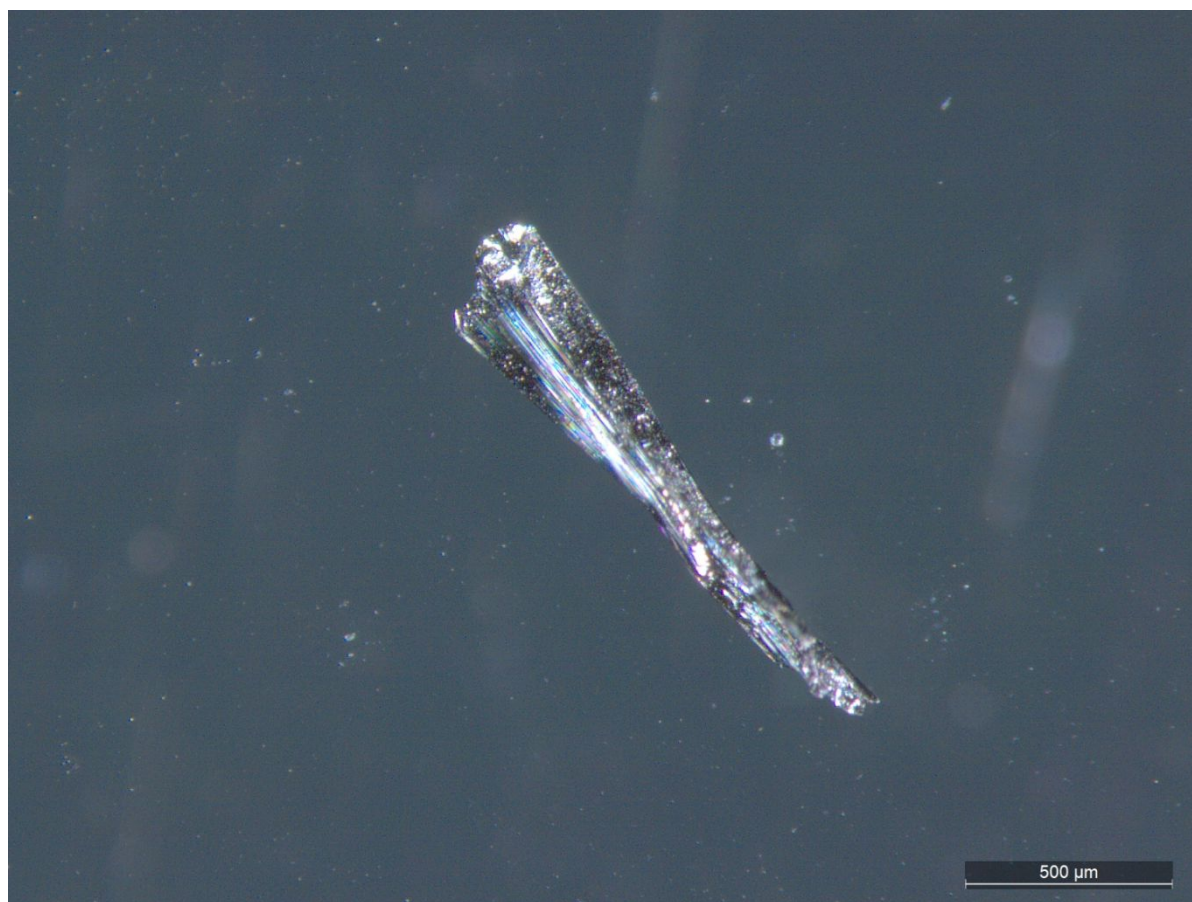


Figure S1. WTe₂I crystal with layer dislocations.

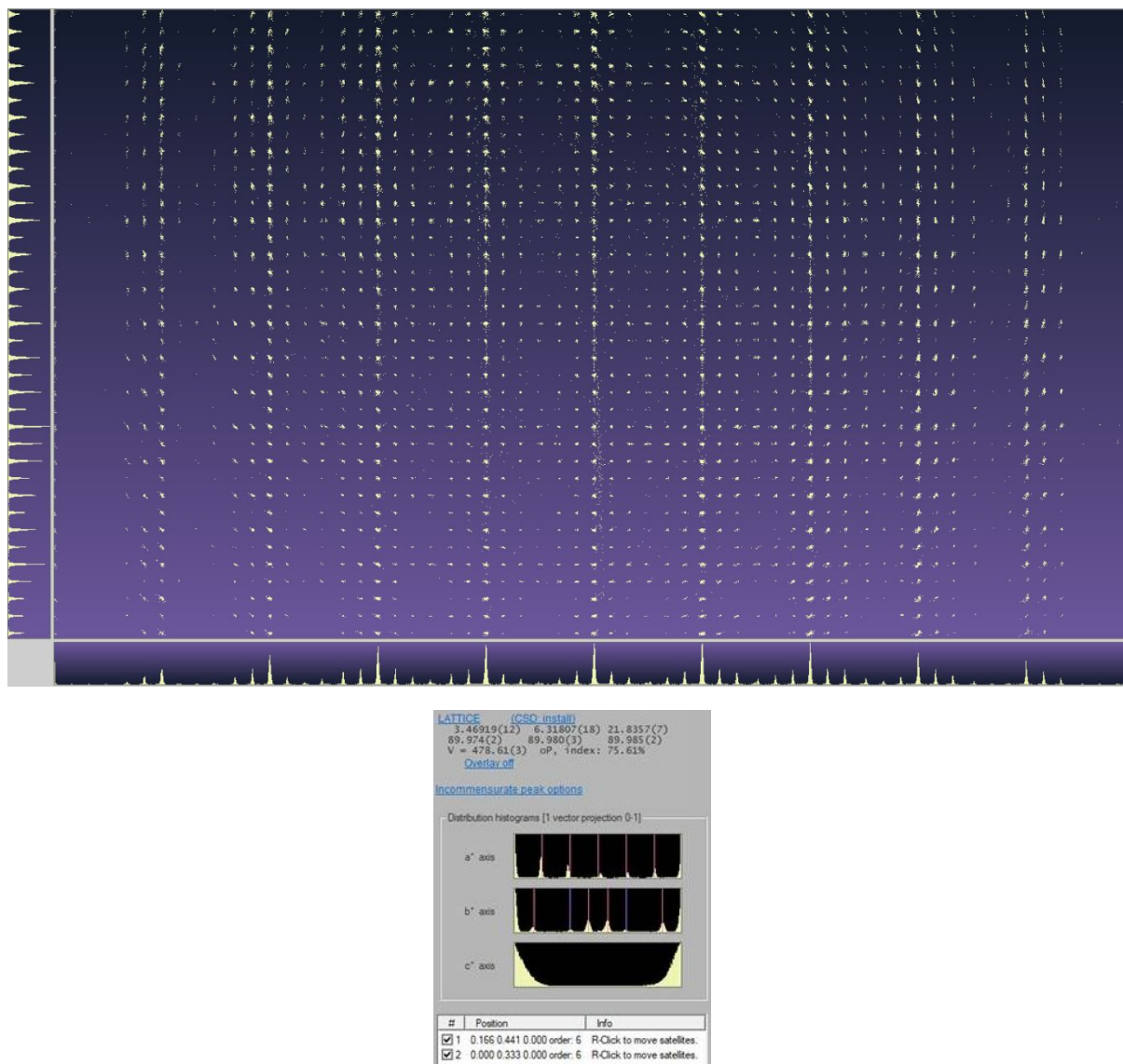


Figure S2. Reciprocal a^*/b^* plane revealing perturbations of some weak Bragg reflections away from the exact regularity of the basic lattice reflections and lattice statistic with q -vectors.

Table S1. Crystal data and structure refinement for WTe₂I at 298 K.

Identification code	CSD 2019336
Empirical formula	WTe ₂ I
Formula weight / g·mol ⁻¹	565.9945
Temperature / K	298(2)
Wavelength / Å	1.54060
Crystal system	Orthorhombic
Space group	<i>P m m n</i> (No. 59)
Unit cell dimensions / Å	a = 21.8967(2) b = 3.47586(2) c = 6.32696(6)
Volume / Å ³	481.545(8)
<i>Z</i>	4
μ (CuK α) / mm ⁻¹	186.899
Density (calculated) / g·cm ⁻³	7.806
Theta range for data collection / °	5.0 to 119.87
Total number of reflections	445
Refined structure parameters	24
R_p , R_{wp}	5.8879, 8.0924
R_{Bragg}	5.0301
χ^2	1.3882

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (pm²) for WTe₂I. *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	SOF
W1	-0.50558(9)	¼	0.3201(3)	0.0410(4)	1.00000
Te1	-0.40557(10)	¼	0.5807(4)	0.0342(6)	1.00000
Te2	-0.43444(11)	-¼	0.0710(4)	0.0405(7)	1.00000
I1	-¾	-¾	0.6681(11)	0.192(2)	1.00000
I2	-¾	-¾	0.1705(10)	0.183(2)	1.00000

Table S3. Structural parameters of WTe₂I following DFT optimization.

	<i>x</i>	<i>y</i>	<i>z</i>
W1	-0.50506	¼	0.32305
Te1	-0.39138	¼	0.58493
Te2	-0.42598	-¼	0.07194
I1	-¾	-¾	0.65535
I2	-¾	-¾	0.14979
Unit cell vector lengths	<i>a</i> = 19.2781 Å	<i>b</i> = 3.5407 Å	<i>c</i> = 6.3179 Å

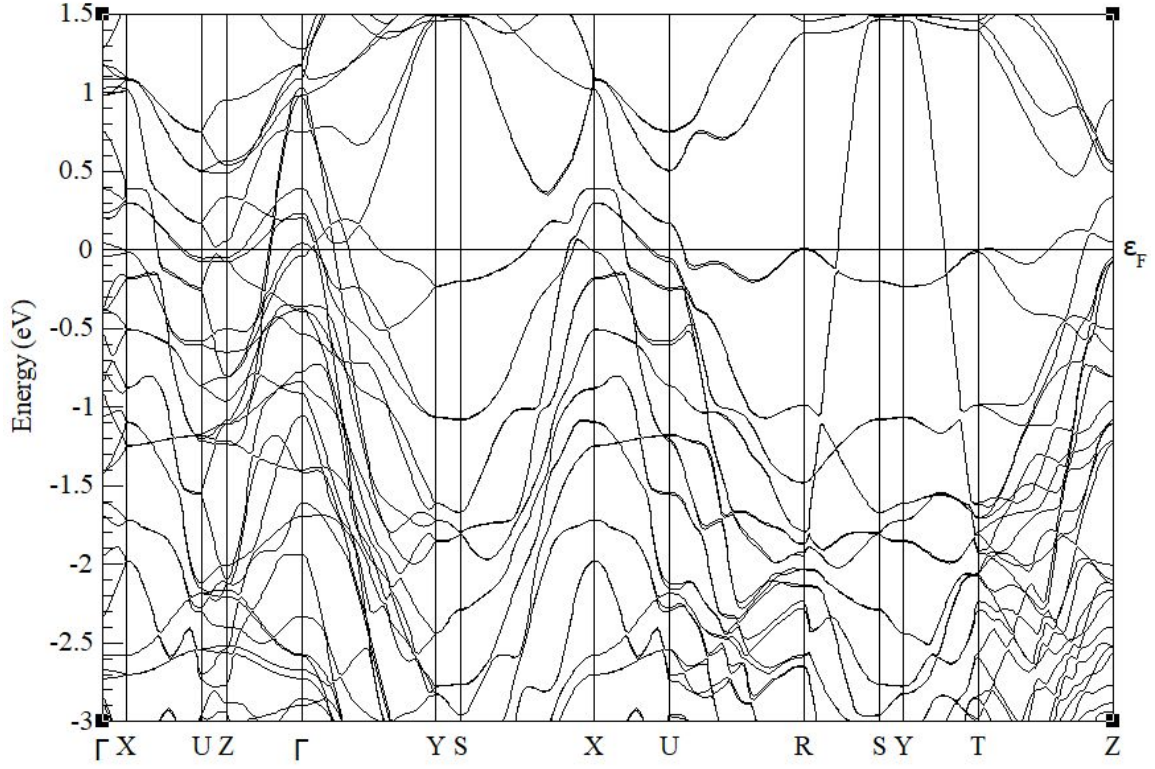


Figure S3. The calculated electronic band structure of WTe_2I with the I atoms shifted by -0.25 along c .

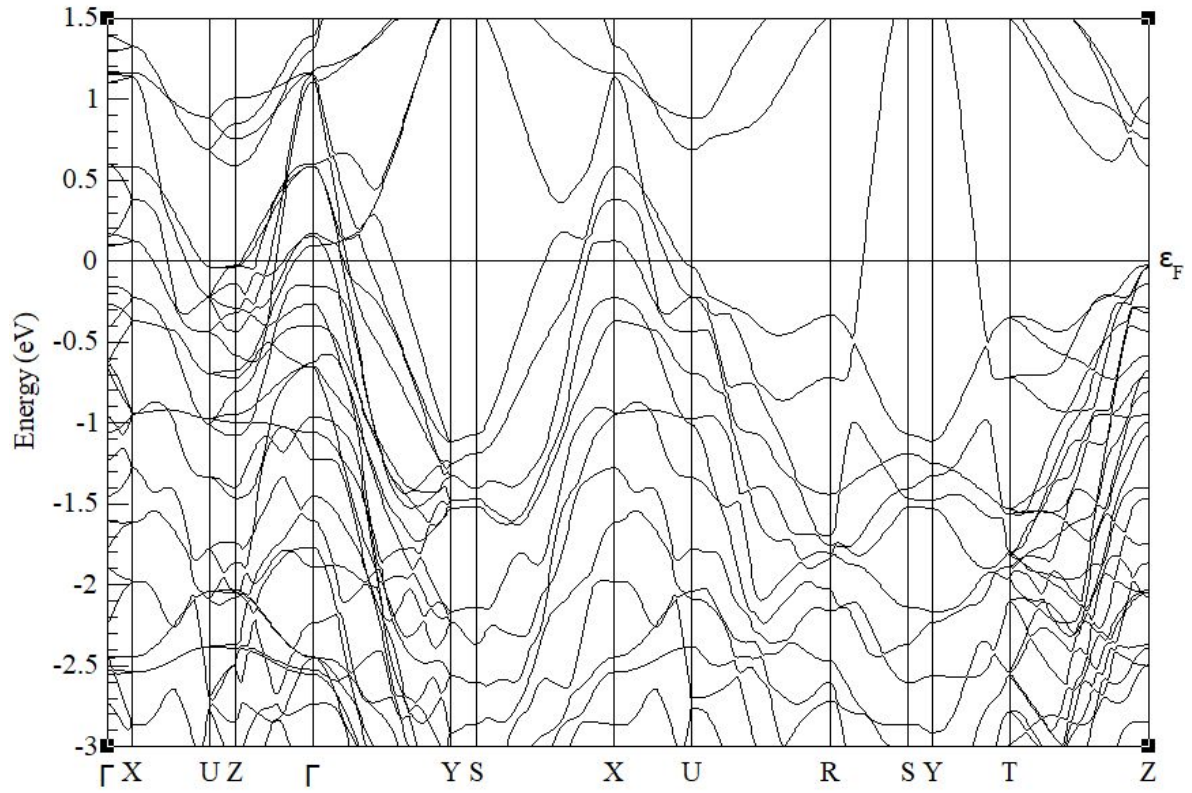


Figure S4. The calculated electronic band structure of WTe_2I with the positions of the I atoms shifted along c to 0.65 and 0.15 , such that there is only one crystallographically independent I-I distance.

Table S4. Crystal data and structure refinement for WTe₂I at 120 K.

Empirical formula	WTe ₂ I
Formula weight / g·mol ⁻¹	565.9945
Temperature / K	120(2)
Wavelength / Å	0.559407
Crystal system	Orthorhombic
Space group	<i>P m m n</i> (No. 59)
Unit cell dimensions / Å	a = 21.7849(4) b = 3.46807(7) c = 6.31444(12)
Volume / Å ³	477.07(1)
Z	4
μ (AgKa) / mm ⁻¹	22.317
Density (calculated) / g·cm ⁻³	7.808
Theta range for data collection / °	6.0 to 70.005
Total number of reflections	2510
Refined structure parameters	15
R_p , R_{wp}	4.3349, 5.6923
R_{Bragg}	4.0051
χ^2	4.1754

Table S5. Atomic coordinates and equivalent isotropic displacement parameters (pm²) for WTe₂I at 120 K. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	SOF
W1	-0.50402(7)	¼	0.3197(1)	0.0080(2)	1.00000
Te1	-0.4056(1)	¼	0.5794(3)	0.0062(4)	1.00000
Te2	-0.4344(1)	-¼	0.0655(4)	0.0120(5)	1.00000
I1	-¾	-¾	0.643(1)	0.109(2)	1.00000
I2	-¾	-¾	0.183(1)	0.117(2)	1.00000

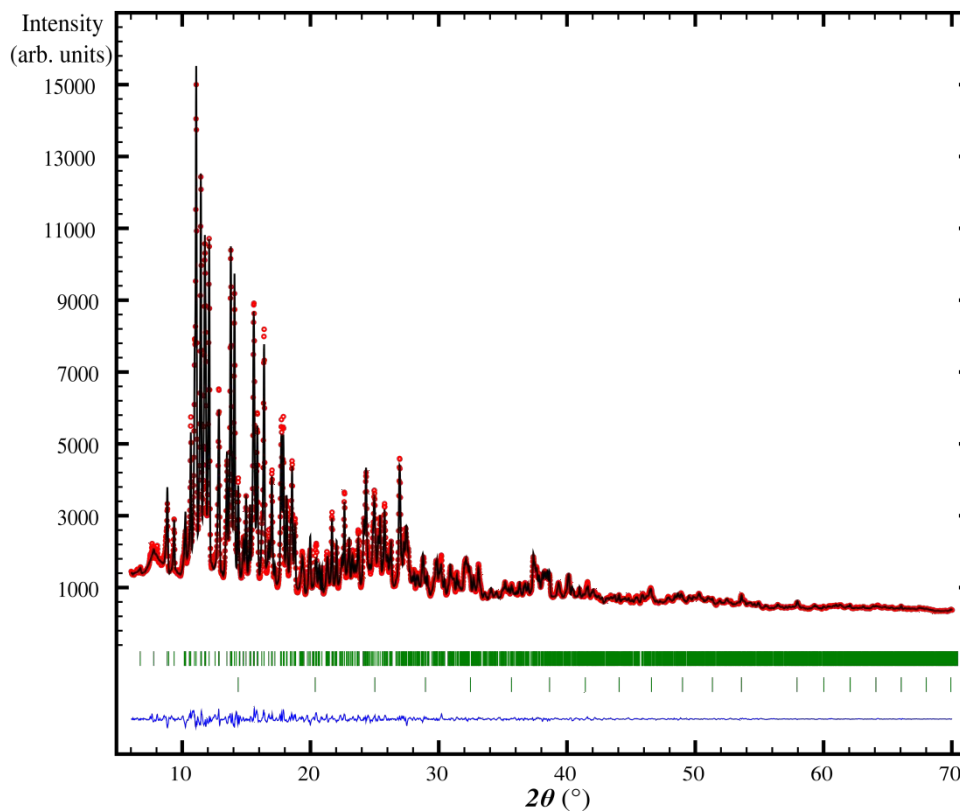
**Figure S5.** PXRD refinement pattern of WTe₂I at 120 K with the experimental (red) and calculated (black) patterns of the Rietveld refinement. Bragg positions (green) of WTe₂I and the difference curve (blue) are also shown.

Table S6. Crystal data and structure refinement for WTe₂I at 12 K.

Empirical formula	WTe ₂ I
Formula weight / g·mol ⁻¹	565.9945
Temperature / K	12(1)
Wavelength / Å	1.54060
Crystal system	Orthorhombic
Space group	<i>P m m n</i> (No. 59)
Unit cell dimensions / Å	a = 21.7269(2) b = 3.46441(6) c = 6.31172(6)
Volume / Å ³	475.09(1)
Z	4
μ (CuK α) / mm ⁻¹	187.101
Density (calculated) / g·cm ⁻³	7.913
Theta range for data collection / °	10.0 to 120.0
Total number of reflections	462
Refined structure parameters	15
R_p , R_{wp}	5.5557, 8.3462
R_{Bragg}	6.9218
χ^2	3.1899

Table S7. Atomic coordinates and equivalent isotropic displacement parameters (pm²) for WTe₂I at 12 K. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	SOF
W1	-0.50447(7)	¼	0.3208(2)	0.0172(3)	1.00000
Te1	-0.40445(9)	¼	0.5800(3)	0.0092(4)	1.00000
Te2	-0.4337(1)	-¼	0.0683(4)	0.0284(6)	1.00000
I1	-¾	-¾	0.6642(7)	0.089(2)	1.00000
I2	-¾	-¾	0.1641(7)	0.082(2)	1.00000

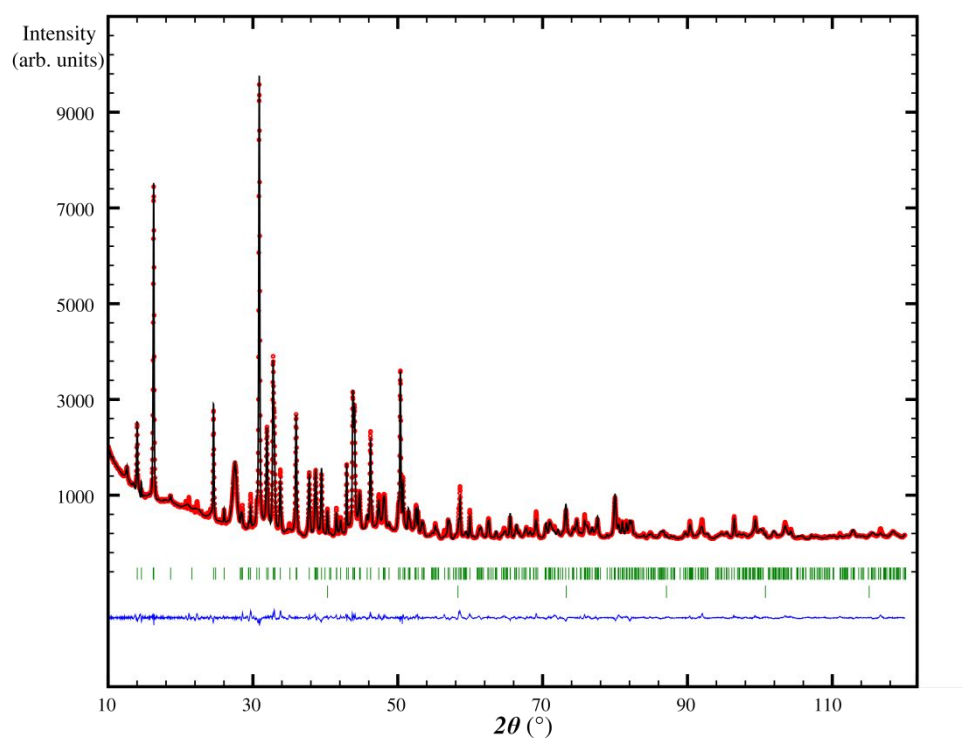
**Figure S6.** PXRD refinement pattern of WTe₂I at 12 K with the experimental (red) and calculated (black) patterns of the Rietveld refinement. Bragg positions (green) of WTe₂I and the difference curve (blue) are also shown.

Table S8. Average equivalent isotropic displacement parameters σU_{ij} (pm²) at different temperatures and their ratio.

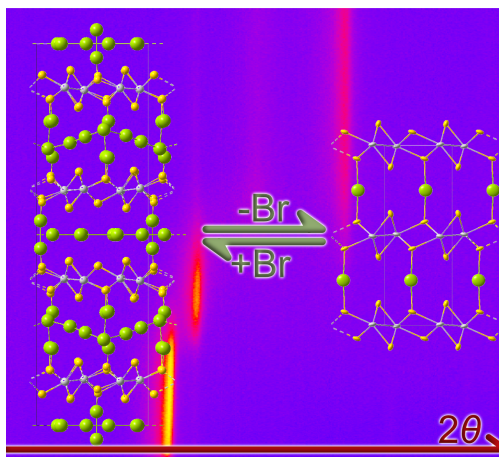
T / K	298 (CuK $_{\alpha 1}$)	120 (AgK $_{\alpha 1}$)	12 (CuK $_{\alpha 1}$)
$\sigma U_{ij}(\text{W,Te})$	0.039	0.009	0.018
$\sigma U_{ij}(\text{I})$	0.188	0.113	0.086
$\sigma U_{ij}(\text{I})/\sigma U_{ij}(\text{W,Te})$	4.862	12.939	4.681

Publication 3

Structural Evolution during Reversible Halogen Intercalation into WTe_2 :

Commensurate–Incommensurate WTe_2I and Multistage

WTe_2Br_x ($x = 0.5, 1.0$ and 1.25)



<https://doi.org/10.1039/D6DT00529B>

Reprinted with permission from

Dalton Trans. **2026**, 55, 8228–8242.

Copyright © 2026 The Royal Society of Chemistry



Cite this: *Dalton Trans.*, 2026, **55**, 8228

Structural evolution during reversible halogen intercalation into WTe_2 : commensurate–incommensurate WTe_2I and multistage WTe_2Br_x ($x = 0.5, 1.0$ and 1.25)

Patrick Schmidt, ^a Carl P. Romao ^b and Hans-Jürgen Meyer ^{*a}

Halogen intercalation into the layered material tungsten ditelluride (WTe_2) provides a unique pathway to tune its structural and electronic properties. In this study, we detail the synthesis and characterization of the new bromine-intercalated phases WTe_2Br_x ($x = 0.5, 1.0$, and 1.25), and reinvestigate the iodine-intercalated analogue, WTe_2I . A defining feature of the bromine system is its rapid and re-versible “breathing” behavior at room temperature, allowing guest molecules to be absorbed or released from the van der Waals gaps under ambient conditions. Structural analysis shows that the bromine-poor phase $\text{WTe}_2\text{Br}_{0.5}$ crystallizes in the orthorhombic space group $Pmmn$, thereby maintaining a uniform stacking sequence. In contrast, the bromine-rich $\text{WTe}_2\text{Br}_{1.25}$ phase (space group $Im\bar{m}2$) adopts an architecture where two distinct types of bromine layers alternate between the host layers. For the iodine system, the compound WTe_2I exhibits both incommensurate and commensurate ($3 + 1$)D modulated variants in the superspace group $P2_1/m(\alpha 0\gamma)00$. In the commensurate polytype, the structural modulation locks into a rational vector, $\mathbf{q} = (1/2, 0, 1/6)$, which can be described also as a 3D supercell. Electronic structure calculations show $\text{WTe}_2\text{Br}_{0.5}$ and commensurately modulated WTe_2I to be metals with flat bands at the Fermi energy arising from the intercalation. These findings demonstrate the unusual stability and structural flexibility of anionic intercalation in transition metal dichalcogenides.

Received 4th March 2026,
Accepted 28th April 2026

DOI: 10.1039/d6dt00529b

rsc.li/dalton

Introduction

Layered transition metal dichalcogenides (TMDCs) have attracted intense interest for their unique electronic, magnetic, and topological properties.^{1–3} In these materials, strong in-plane covalent bonding and weak interlayer van der Waals forces give rise to a two-dimensional architecture that is highly responsive to external perturbations, such as intercalation or the application of pressure.^{2,4} This open layered structure enables a rich intercalation chemistry in which various guest species can be incorporated. Typically, cations, neutral molecules or organic molecules can be inserted between the layers, thereby modifying the host’s structure and properties.^{5–16}

WTe_2 is a particularly intriguing member of the TMDC family and crystallizes in an orthorhombic T_d phase, where it exhibits semimetallic behavior,^{17–19} exceptionally large, non-saturating magnetoresistance,^{20,21} and complex topological

properties—ranging from a 2D topological insulator in its monolayer form to a type-II Weyl semimetal in the bulk.^{22,23} It also displays superconductivity at low temperatures²⁴ and shows a charge density wave (CDW) state,^{25–32} underscoring its rich and exotic physical properties. The crystal structure (space group $Pmn2_1$) features distorted octahedral coordination of tungsten atoms by tellurium atoms, with zigzag W–W chains running within the ab -plane along the a -axis and van der Waals gaps separating the WTe_2 layers.³³ These structural features render WTe_2 highly receptive to intercalation, offering an opportunity to tune its electronic ground state through the controlled insertion of guest species.

Cationic intercalation into the structure of WTe_2 has been reported for $\text{A}_{0.5}\text{WTe}_2$ compounds ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$), which we have previously characterized structurally and electronically, showing that alkali ions act as electron donors.³⁴ While cationic intercalation into TMDCs is well established, involving alkali metals,^{5,8–11,13,35,36} organometallic species, or molecular donors,^{12,14–16} anionic intercalation remains extremely rare. Halogen molecules ($\text{I}_2, \text{Br}_2, \text{Cl}_2$), despite their strong oxidizing nature, have largely resisted clean insertion into TMDCs in a structurally defined and stoichiometric manner. Instead, halogens have often been introduced during crystal growth as

^aSection of Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany. E-mail: juergen.meyer@uni-tuebingen.de

^bDepartment of Materials, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Trojanova 13, Prague 120 00, Czech Republic



transport agents and later found in low concentrations or as surface dopants. For example, Cl_2 and I_2 have been shown to form bound excitonic centers in MoS_2 , WS_2 , and MoSe_2 , being responsible for characteristic luminescence features at low temperatures.^{37–48} However, these guest species reside in dilute, disordered environments, without forming ordered intercalation phases or significantly expanding the host lattice. As such, these systems are better classified as halogen-doped or halogen-decorated TMDCs—rather than true intercalation compounds.

Recently, we have demonstrated that WTe_2I is the first and so far only example of a structurally confirmed anionic halogen-intercalated TMDC.^{49,50} In this compound, planar monolayers of iodine are inserted between the WTe_2 layers of the orthorhombic host, expanding the c -axis by $\sim 56\%$ and forming a fully stoichiometric intercalate. Importantly, the intercalation process was shown to be topotactically reversible: heating WTe_2I above 100°C under inert conditions fully deintercalated iodine and regenerated pristine WTe_2 . These results established WTe_2I as a prototypical system for reversible anionic intercalation in layered semimetals. The crystal structure of WTe_2I was refined an averaged three-dimensional structure from powder X-ray diffraction (PXRD) data, which revealed notably large anisotropic displacement parameters (ADPs) for iodine, already suggesting a positional modulation.

Subsequent single-crystal X-ray diffraction studies indicated the presence of an incommensurately modulated structure. Density functional theory (DFT) calculations supported these findings, indicating significant charge transfer from WTe_2 to iodine, a shift of the Fermi level, and soft phonon modes characteristic of structural instability. In this work we present an incommensurate and a commensurate structure, appearing simultaneously for WTe_2I , and for better realization we report a supercell of the structure.

Despite many reports of halogen-related doping no other halogen-intercalated TMDC compound has been structurally verified to date. The present work expands this chemistry by demonstrating that bromine, though more volatile and reactive than iodine, can also be intercalated into WTe_2 in well-defined stages. We describe the synthesis and reversible intercalation of bromine into WTe_2 , leading to the formation of stable WTe_2Br_x compounds with distinct structural and electronic signatures, representing only the second known example of an anionic halogen intercalation phase in the TMDC family. Time-resolved powder X-ray diffraction (PXRD) reveals that bromine can be reversibly inserted and removed from the van der Waals gaps, with distinct diffraction patterns for each stoichiometry ($x = 0.5, 1.0$, and 1.25), highlighting a remarkable “breathing” behavior that enables dynamic control of composition and structure under mild conditions.

Results and discussion

Incommensurate and commensurate modulations of WTe_2I

As reported previously,⁴⁹ WTe_2I forms when WTe_2 is reacted with iodine at $40\text{--}200^\circ\text{C}$. Elemental analyses confirm a stoi-

chiometry corresponding to one iodine per WTe_2 (WTe_2I) within experimental uncertainty (see Experimental section). No phase transition of WTe_2I single crystals was detected between 100 K and 270 K . The present study therefore provides an updated structural description of WTe_2I , in which the previously reported average structure is retained, while the underlying modulation is now resolved explicitly.

Single-crystal X-ray diffraction studies, performed on several crystal specimens at 150 K , revealed two closely related $(3 + 1)$ D modulated structure variants in the superspace group $P2_1/m(\alpha 0\gamma)00$ with almost identical basic lattice parameters (Table 1), in good agreement with the previously reported unit cell.⁴⁹ The incommensurate variant is described by the modulation vector $\mathbf{q} = (0.4487, 0, 0.1617)$, whereas the commensurate polytype has $\mathbf{q} = (1/2, 0, 1/6)$ and can equivalently be described as a 3D supercell. Using the transformation matrix $\begin{pmatrix} 1 & 0 & -3, & 0 & 1 & 0, & 1 & 0 & 3 \end{pmatrix}$, a primitive $P2_1/m$ supercell with $a = 12.1694(1)\text{ \AA}$, $b = 21.8799(2)\text{ \AA}$, $c = 12.1726(1)\text{ \AA}$ and $\beta = 117.635(1)^\circ$ is obtained. For ease of comparison and broader reusability, the commensurate structure was also refined as an explicit 3D superstructure in SHELXL; the resulting model is crystallographically equivalent and is provided as a reference in the deposited data (Table 1). All modulated crystals show pronounced pseudo-merohedral twinning, where the main reflections overlap, while the satellites are well separated in the incommensurate case and partially overlap for the commensurate polytype. The twin law corresponds either to a twofold rotation about c -axis or an equivalent mirror perpendicular to it; owing to the metric pseudosymmetry ($\beta \approx 90^\circ$), both descriptions are indistinguishable, and a conventional twofold twin matrix was applied, with the twin fraction of the second domain refined to $0.432(2)$. Depending on the batch, crystals were found to be fully commensurate or incommensurate (with slightly different incommensurate $\mathbf{q}$ -vectors), and some specimens contained mixed domains, combining commensurate and incommensurate regions, or even multiple distinct incommensurate modulations alongside the commensurate phase (Fig. S1). Although satellites are visible up to $m = \pm 4$, refinements were restricted to $m = \pm 2$ and carried out with the minimal, physically meaningful set of modulation waves needed to reproduce the observed atomic displacements, thereby avoiding over-parameterization. Refinement statistics are summarized in Table 1.

The average 3D structure is essentially identical to the previously reported model of WTe_2I (see Fig. 1), but requires two additional split sites, Te3 and I3. These minor positions are $\sim 15.5\%$ occupied, while the corresponding main sites (Te2, I1, and I2) are under-occupied accordingly, consistent with a local defect motif rather than a distinct bulk phase. Structurally, the splitting is initiated by a local $\sim 90^\circ$ rotation of a I_2 unit (denoted as I3) out of the iodine-net plane. This reorientation necessitates a concomitant shift of the adjacent tellurium atom. This reorientation is accommodated by a concomitant shift of the adjacent tellurium atom ($\text{Te2} \rightarrow \text{Te3}$); without this shift, the resulting Te2–I3 contact would be unrealistically small and physically prohibitive. By adopting the Te3 position,



Table 1 Crystallographic data and details of the crystal structure refinement of the different WTe_2I modifications. Refinements were performed for (in)commensurately modulated crystal structures and the corresponding supercell. Detailed information on the modulation functions is given in the crystal information file. All crystals were measured with Mo- K_α radiation at 150 K

Modification	WTe_2I		
	Incommensurate	Commensurate	Supercell
CCDC	2520418	2519690	2519736
Formula	WTe_2I	$\text{W}_6\text{Te}_{12}\text{I}_6$	
$M/\text{g mol}^{-1}$	565.95	3395.7	
Crystal system	Monoclinic		
(Super)space group	$P2_1/m(\alpha 0 \gamma)00$	$P2_1/m$	
Modulation wave vector $\mathbf{q}$	(0.4487 0 0.1617)	(1/2 0 1/6)	
$m/\text{max.}$	≤ 2	≤ 2	—
t_0	0	0	—
$a/\text{\AA}$	6.3200(2)	6.30257(5)	12.1694(1)
$b/\text{\AA}$	21.8060(6)	21.8792(3)	21.87990(2)
$c/\text{\AA}$	3.4713(2)	3.47075(3)	12.1726(1)
$\beta/^\circ$	90.057(3)	90.0268(7)	117.635(1)
V	478.40(3)	478.600(9)	2871.38(6)
Z	4	4	4
$\theta\text{-Range}/^\circ$	1.97–38.01	1.89–45.01	1.888–30.508
unique reflections/parameters	7009/193	7023/152	8947/294
twvol2 or BASF	0.432(2)	0.394(4)	0.378(2)
$R_1/\text{w}R_2/\text{GooF}$ (all data)	4.86/7.47/1.10	6.99/14.37/1.08	0.0433/0.0999/1.022
$R_1/\text{w}R_2$: (all main)	1.65/3.80	5.18/13.33	—
(All 1st order)	6.92/12.93	8.54/17.19	—
(All 2nd order)	12.09/21.07	9.13/19.37	—
Max./min. $\Delta\rho/e^- \times 10^{-6} \text{ pm}^3$	−1.02/1.25	−1.96/1.75	−4.081/4.297

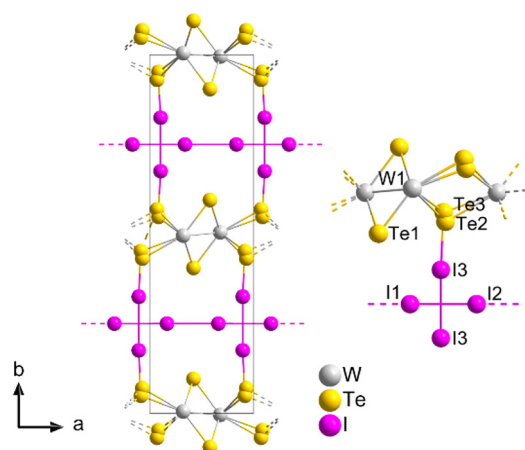


Fig. 1 Section of the average incommensurate WTe_2I structure (left) and a smaller section with atom labels (right). Note the zig-zag chains of tungsten atoms running parallel to the c -axis. The previously reported average model⁴⁹ corresponds to this structure when the minor split sites Te3 and I3 are omitted.

the system instead establishes a Te3–I3 distance of $\sim 2.77 \text{ \AA}$. This value is characteristic of a covalent bond (sum of covalent radii $\sim 2.71 \text{ \AA}$), suggesting that the local defect motif is stabilized by a degree of covalent bonding between the host layer and the guest. This localized covalent interaction likely acts as an ‘anchor’ that pins the iodine guest to the WTe_2 framework, thereby stabilizing the defect motif and dictating the specific periodicity of the long-range structural modulation.

Since the commensurate and incommensurate refinements are nearly identical apart from the modulation vector, we focus

here on the incommensurate model. The modulation is dominated by the iodine sublattice, where iodine atoms show a pronounced displacive modulation within the planar net (see Fig. 2, 4 and 3, right), whereas the WTe_2 layers exhibit only small, coupled distortions. Within the iodine layer, the displacive modulation translates into a pronounced spread of I–I distances. Over one modulation period, the shortest and longest distances within the I1/I2 planar net span $2.688(8)$ – $4.018(8) \text{ \AA}$ (see Fig. S2) and the I3–I3 distance remains comparatively long at $3.272(2) \text{ \AA}$, highlighting the strongly distorted and non-

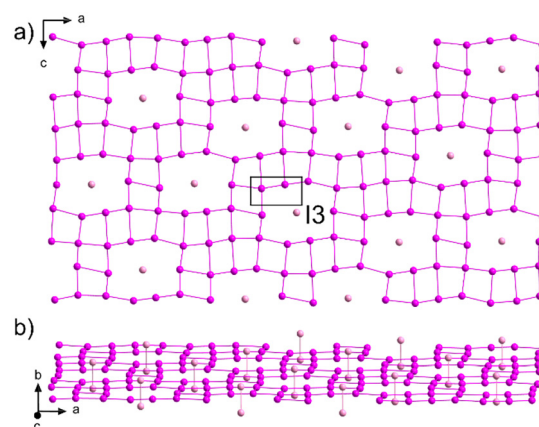


Fig. 2 Section of the incommensurate WTe_2I structure (a) only showing one iodine layer with I_2 dumbbells of I3 being aligned along the b -axis, including the projected unit cell; and (b) a corresponding view along the c -axis, emphasizing the I_2 dumbbells of I3. I1 and I2 are displayed in purple, and I3 in lighter purple.



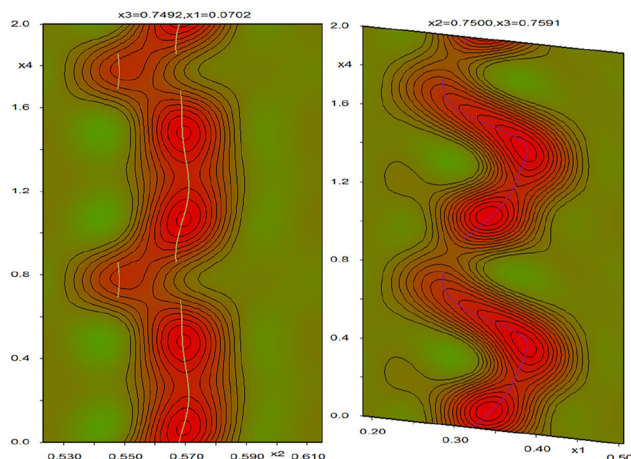


Fig. 3 de Wolff sections (F_{obs}) of x_2 - x_4 plane for Te2 and Te3 (left) and in the x_1 - x_4 plane for I1 (right). Refined atomic positions are indicated by lines (Te: yellow; I: purple); the Te2 and Te3 sections are highlighted at $x_2 = 0.57$ and $x_2 = 0.55$, respectively. The electron density is visualized as a heat map (red = high, green = low).

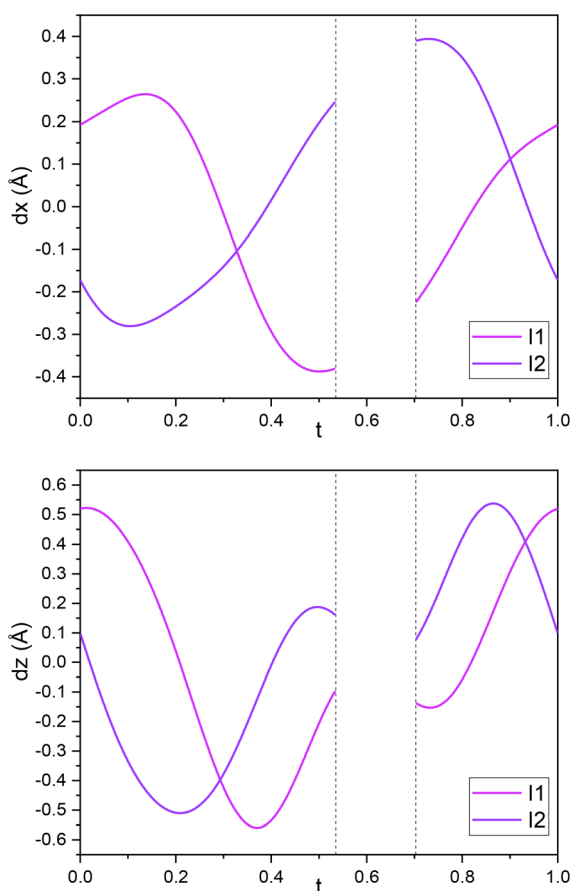


Fig. 4 The modulation functions of the deviations from the average positions for I2 and I3 along x and z directions as a function of internal phase coordinate t with crenel limits marked as dashed vertical line.

uniform iodine net. A representative section of the modulated structure at $t = 0$ is shown in Fig. 2.

The structure solution and refinement indicate that the displacement modulation of the iodine net is most pronounced in the ac -plane. Superimposed on this, an occupational modulation is required and was modeled using crenel functions (harmonics, orthogonalized to crenel interval) for the Te2/I2 and Te3/I3 split positions. The crenel intervals are $\Delta(\text{Te2/I2}) = 0.831824$ and $\Delta(\text{Te3/I3}) = 0.168176$, consistent with the intermittent appearance of the I3 site, which corresponds to a local $\sim 90^\circ$ out-of-plane reorientation of an I_2 unit out of the ac -plane that disrupts the wave-like iodine layer. The crenel functions were refined using constraints linking their origins and Δ intervals ($\Delta(\text{Te2/I1/I2}) + \Delta(\text{Te3/I3}) = 1$), ensuring a consistent occupational modulation between the split-site pairs.

To accommodate this local motif, Te2 splits into Te2/Te3 and induces subtle but observable distortions in the WTe_2 layer. The corresponding de Wolff sections (F_{obs}) through the $(3 + 1)\text{D}$ Fourier map for Te2/Te3 and I2 is shown in Fig. 3.

Although the host-layer modulations are comparatively small, they are clearly resolved. In particular, the position modulation of tungsten atom shows a characteristic saw-tooth modulation in the x_3 - x_4 section (see Fig. 6 and 7), resulting in an average W-W distance of $2.86(1)$ Å. The shortest W-W contact with $2.78(1)$ Å remains closer to the average, whereas the longest distance with $3.10(2)$ Å periodically disrupts the chain after segments of roughly ~ 12 tungsten atoms. This disruption is induced by the I3 atom, which corresponds to the out of plane I_2 dumbbell of the iodine layer above and below the projected ac -plane of W chains, shown in Fig. 5 and Fig. S3.

Apart from these interruptions, the W-W distances vary only modestly with ~ 0.08 Å (see Fig. 7, grey lines). The remaining tellurium sites exhibit similarly small displacements, with amplitudes of approximately $d_{xyz}(\text{Te1}) = \pm 0.1$ Å and $d_{xyz}(\text{Te2}) = \pm 0.06$ Å. Further refinement details, including constraints,

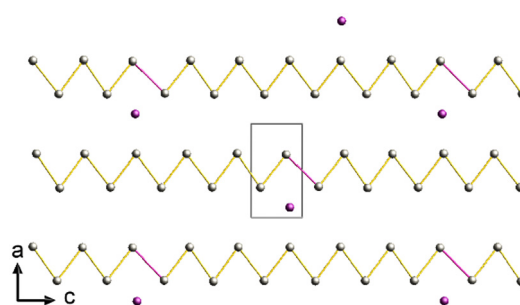


Fig. 5 Section of the incommensurate WTe_2I structure viewed along the b direction with highlighted unit cell. For clarity, tellurium atoms are omitted and only one interlayer section in the ac -plane of the tungsten zigzag chains is shown, together with the I_2 dumbbells (I3 sites) aligned along b which are directly above and beyond of the ac -plane section. Elongated W-W contacts, indicating disruption of the tungsten chain are highlighted by violet bonds (W: grey; I: violet; $t = 0.62$).



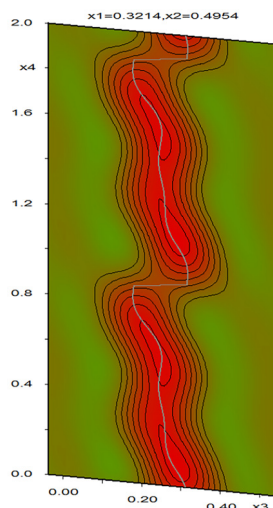


Fig. 6 de Wolff sections (F_{obs}) of x_3 – x_4 plane for W1 in WTe_2I . Refined atomic positions are indicated by a grey line. The electron density is visualized as a heat map (red = high, green = low).

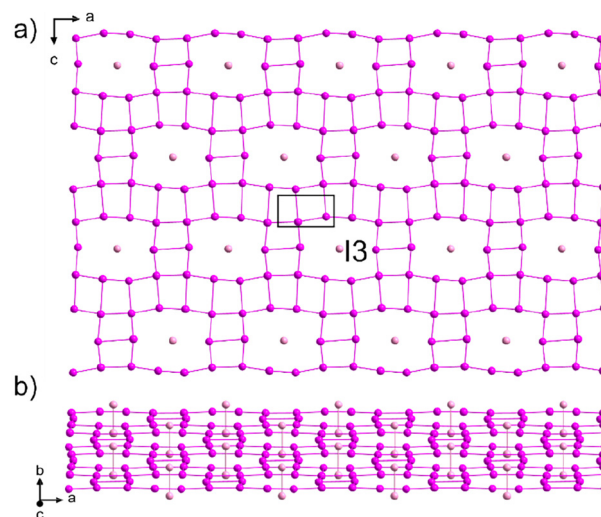


Fig. 8 Section of the commensurate WTe_2I structure only showing (a) one iodine layer with highlighted I3 units aligned along the b -axis with the unit cell shown, and (b) a corresponding view along the c -axis, emphasizing the I_2 dumbbells (I1/I2: purple; I3: lighter purple).

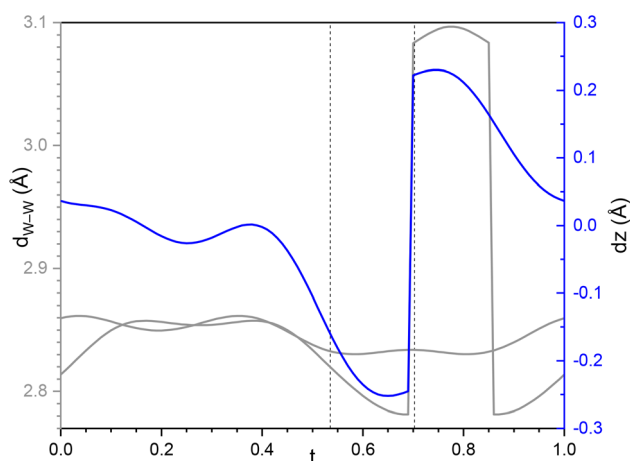


Fig. 7 t plots of the W–W distances (grey) and positional deviation (blue) of tungsten along x_3 direction in WTe_2I with crenel limits marked as dashed vertical line.

parameter correlations, and the complete list of refined variables, are provided in the deposited CIF and in the SI.

Commensurate structure and superstructure model of WTe_2I

In addition to the incommensurate variant, a commensurate polytype is occasionally obtained in which the modulation “locks in” to the rational vector $\mathbf{q} = (1/2, 0, 1/6)$ and can therefore be described as a conventional three-dimensional $P2_1/m$ superstructure. Using the transformation matrix $\begin{pmatrix} 1 & 0 & -3 \\ 0 & 1 & 0 \\ 1 & 0 & 3 \end{pmatrix}$ yields a primitive supercell ($a \approx 12.17 \text{ \AA}$, $b \approx 21.88 \text{ \AA}$, $c \approx 12.17 \text{ \AA}$, $\beta \approx 117.64^\circ$; $\text{W}_6\text{Te}_{12}\text{I}_6$), which makes the modulation periodicity explicit in real space. In this commensurate description, the iodine net adopts a regular repeating motif that mirrors the rational components of $\mathbf{q}$, where along a direc-

tion, the rotated defect motif alternates such that every second I_2 unit is rotated by $\sim 90^\circ$ out of the iodine-net plane and appears as the I3 site, while along the c direction the same motif repeats with a six-unit periodicity (Fig. 8). The commensurate structure reproduces essentially the same I–I distance distribution, but arranges the shorter and longer contacts into an exactly repeating pattern.

Refinement in the commensurate setting is advantageous over a purely 3D average-cell description because the modulation is represented explicitly rather than being “smeared out”, typically improving agreement factors and yielding cleaner residual density. Overall, the commensurate model can be viewed as a periodic approximant of the incommensurate structure that facilitates direct real-space visualization of both the iodine-net displacement wave and the ordered occurrence of the I3 defect motif. For ease of comparison and broader reusability, the commensurate structure was also refined as an explicit 3D superstructure in SHELXL; the resulting model is crystallographically equivalent and is provided as a reference in the deposited data (Table 1). Because the diffraction data are affected by twinning and residual modulation, the supercell refinement was improved by modeling the interlayer iodine net as a two-component disordered layer (atom sites $\text{I}x_a/\text{I}x_b$; $x = 2$ –11), with coupled occupancies constrained to unity and the b component accounting for $\sim 20\%$ occupancy. The minor b component represents a slightly b -rotated relative alignment of the iodine layer, whereas the out-of-plane iodine positions remain unaffected (see Fig. S4).

Synthesis and “breathing” behavior of WTe_2Br_x

WTe_2Br_x powder phases, as well as the corresponding single crystals, were obtained as black solids with a metallic luster and were prepared by Schlenk techniques by exposing ortho-



rhombic WTe_2 to an excess of bromine liquid between 0 and 30 °C. Single crystals were intercalated by bromine vapor at room temperature for 4 days or with liquid bromine at 6 °C for 2 days. Although crystallinity is generally compromised by the multiple phase transitions during bromine uptake and release, the vapor intercalation route consistently afforded crystals of higher quality than direct contact with liquid bromine. Thermal stability is a critical constraint in this system. While intercalation proceeds smoothly even near room temperature, heating WTe_2 with excess bromine in a closed vessel to 60 °C leads to decomposition of the host structure and formation of binary halides, for example TeBr_4 and WBr_6 .

A striking feature of this system is a fast and reversible “breathing” behavior, present at room temperature, which involves an uptake and release of guest bromine. The bromine content can be increased up to the maximum stage with $x = 1.25$ by supplying liquid bromine, and bromine can conversely be removed from the van der Waals gaps (at room temperature) under constant argon flow. The actual bromine content in the structure of WTe_2Br_x is highly temperature sensitive during this de-intercalation step. Evaporation of excess bromine under a constant flow of argon yields $\text{WTe}_2\text{Br}_{1.25}$ when the temperature is maintained between 0 and 5 °C, whereas the comparatively stable $\text{WTe}_2\text{Br}_{0.5}$ phase can be obtained at around 25 °C. Starting from $\text{WTe}_2\text{Br}_{0.5}$, re-intercalation to the bromine-rich stage is particularly rapid and proceeds within minutes.

Argentometric titration of the comparatively stable phase $\text{WTe}_2\text{Br}_{0.5}$ confirmed its bromine content, while the deintercalation behavior of Br_2 -saturated WTe_2Br_x supports three distinct composition regimes at $x = 0.5$, 1.0, and 1.25. Direct chemical analysis of the more bromine-rich phases was not feasible, since these compounds continuously lose bromine in the absence of sufficient bromine counterpressure, so their compositions were assigned from the crystallographic results in combination with the thermogravimetric data.

The dynamics of bromine exchange are directly captured by *in situ* PXRD studies. Starting from $\text{WTe}_2\text{Br}_{0.5}$, the bromine uptake is extremely rapid and occurs within minutes. The accompanying change in bromine content is directly reflected in the basal reflections that tracks the interlayer spacing. For the monoclinic phases, the corresponding layer-stacking reflection, indexed here as (020), shifts continuously toward lower 2θ angles as the van der Waals gap expands to accommodate bromine. Upon de-intercalation, time-resolved PXRD in Fig. 9 reveals the reverse evolution through discrete stages, and the basal reflection shifts back toward higher 2θ as bromine is released from the lattice ($2\theta = 8.21^\circ$, 8.52° and 10.56°).

This inherent reversibility also explains why $\text{WTe}_2\text{Br}_{1.0}$ is difficult to isolate and handle. Unless samples are stored under strictly controlled conditions, bromine readily diffuses in or out, and bromine contents of the sample near $x = 1.0$ often relax toward $x = 0.5$ or $x = 1.25$. As a result, mixtures are frequently obtained in which $\text{WTe}_2\text{Br}_{1.0}$ coexists with $\text{WTe}_2\text{Br}_{0.5}$ or $\text{WTe}_2\text{Br}_{1.25}$. The $\text{WTe}_2\text{Br}_{1.0}$ phase also typically shows reduced crystallinity compared with the more stable

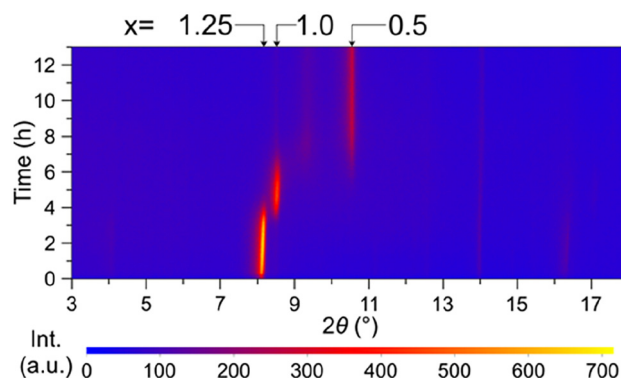


Fig. 9 Time resolved PXRD analysis of WTe_2Br_x showing structural evolution during bromine deintercalation with discrete phases from $x = 1.25$ to 1.0 and 0.5 (for full 2θ range see Fig. S5).

end members, which we attribute to ongoing bromine exchange between the two stages.

Thermogravimetric analysis (TGA) of products obtained from the reaction of WTe_2 with excess bromine provides additional support for these composition regimes. During controlled de-intercalation, distinct changes in the mass-loss rate mark transitions between the bromine-rich and bromine-poor stages. The TGA traces in Fig. 10 show an initial rapid loss of excess bromine, followed by regimes of slower mass loss and a final, near-horizontal segment with only a subtle residual mass-loss rate. At 25 °C, the first clear change in slope corresponds to a bromine content consistent with $\text{WTe}_2\text{Br}_{1.25}$, whereas at 50 °C the first change in slope is shifted to the intermediate composition $\text{WTe}_2\text{Br}_{1.0}$. In both cases, the ensuing near-horizontal segment is consistent with the comparatively stable $\text{WTe}_2\text{Br}_{0.5}$ phase, which still shows a very slow

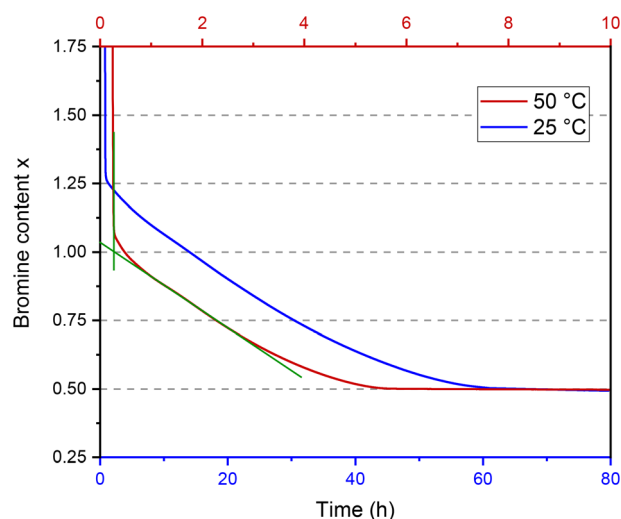


Fig. 10 TGA showing the bromine loss of bromine saturated WTe_2Br_x samples, showing steps at $x = 1.25$, 1.0, and 0.5 at constant temperature of 25 °C (blue) and 50 °C (red), under constant argon flow of 320 ml min^{-1} (an onset fit for the 50 °C measurement is shown in green).



residual bromine loss that becomes more pronounced at higher temperature. Accordingly, samples were stored cooled ($\leq 0\text{ }^{\circ}\text{C}$) or kept under a sufficient bromine counter pressure at room temperature to suppress bromine evaporation. Even though phase-pure $\text{WTe}_2\text{Br}_{1.0}$ could not be isolated and structurally characterized, the established structure of $\text{WTe}_2\text{Br}_{1.25}$ shares key motifs with WTe_2I , which suggests that the intermediate $\text{WTe}_2\text{Br}_{1.0}$ phase may follow a closely related structural principle and has a similar structure.

Owing to the highly corrosive nature of bromine, specialized reaction and measurement setups were employed, as described in the Experimental section and the SI.

Crystal structure of $\text{WTe}_2\text{Br}_{0.5}$

The bromine-intercalated phase $\text{WTe}_2\text{Br}_{0.5}$, representing the lowest bromine content in the WTe_2Br_x series, crystallizes in the orthorhombic space group $Pmmn$ with refined lattice parameters $a = 16.7450(4)\text{ \AA}$, $b = 3.67734(3)\text{ \AA}$, and $c = 6.29678(8)\text{ \AA}$. As shown by the Rietveld plot in Fig. 11, the powder diffraction pattern is well described by the refinement ($R_{\text{Bragg}} = 2.028\%$, $R_p = 5.438\%$, $R_{wp} = 7.104$, $\chi^2 = 1.268$, number of reflections/parameter 392/27), confirming a well-defined crystalline phase.

In the chosen setting, the a -axis corresponds to the stacking direction. The WTe_2 layers adopt a stacking arrangement in which the tungsten zig-zag chains of neighboring layers are brought into eclipsed alignment along the a -direction, generating an enlarged interlayer void to accommodate bromine guest atoms (Fig. 12).

The adjacent WTe_2 layers are arranged in a mirror-like fashion across the bromine-containing interlayer plane. The average W–W separation of $2.909(2)\text{ \AA}$ is slightly expanded relative to pristine WTe_2 . In contrast to WTe_2I , where a more continuous halogen layer separates adjacent WTe_2 layers, $\text{WTe}_2\text{Br}_{0.5}$ contains only half as many halogens and the bromine position is shifted such that bromine atoms align

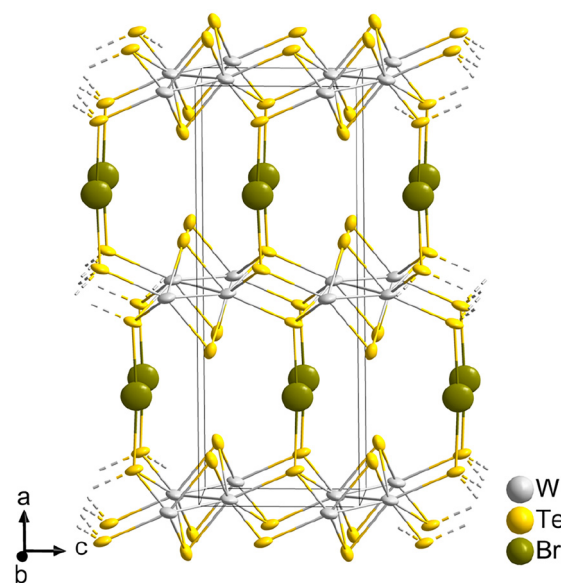


Fig. 12 Section of the $\text{WTe}_2\text{Br}_{0.5}$ crystal structure highlighting the position of bromine atoms within the van der Waals gap, with their alignment toward Te1, thereby connecting adjacent WTe_2 layers. Atomic displacement parameters are shown as anisotropic displacement ellipsoids at the 50% probability level.

along the a -axis with the tungsten-chain-bridging tellurium atom Te1, giving a short Te1–Br1 contact of $2.946(2)\text{ \AA}$ that connects neighboring WTe_2 layers. When projected onto the bc -plane, the bromine positions define a rectangular net with Br⋯Br separations fixed by the lattice dimensions ($3.6773(1)\text{ \AA}$ along b and $6.297(1)\text{ \AA}$ along the c -axis); these relatively long distances make direct Br⋯Br interactions inefficient.

A defining feature in the structure of $\text{WTe}_2\text{Br}_{0.5}$ is the exceptionally large anisotropic displacement of the bromine atom Br1, which occupies the Wyckoff $2b$ position with $mm2$ site symmetry. The bromine atom refines with $U_{\text{iso}} = 0.115(7)\text{ \AA}^2$, and anisotropic atomic-displacement parameter (ADP) refinement reveals a pronounced directional character ($U_{11} = 0.145(9)\text{ \AA}^2$, $U_{22} = 0.036(5)\text{ \AA}^2$, $U_{33} = 0.163(7)\text{ \AA}^2$) with the largest components along a - and c -direction and only a minor component along b . Attempts to improve the description by splitting the bromine position or refining the site occupancy did not yield a better model and were therefore not pursued further. These unusually large and anisotropic ADPs indicate that bromine is not sharply localized but exhibits pronounced positional disorder and/or dynamic motion within the van der Waals gap, resulting in an averaged, “smeared” electron density of bromine atoms. This crystallographic signature is consistent with the high bromine mobility inferred from the rapid and reversible bromine exchange (“breathing”) behavior observed for the WTe_2Br_x system. While the present X-ray powder diffraction data are adequately described by the average $Pmmn$ model, the presence of a weak superstructure or subtle incommensurate modulation cannot be fully excluded.

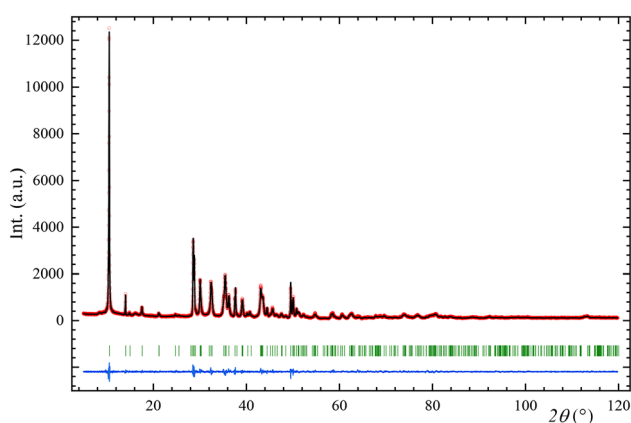


Fig. 11 Rietveld PXRd structure refinement of $\text{WTe}_2\text{Br}_{0.5}$ with the space group $Pmmn$ at 298 K with the experimental (red) and calculated (black) intensities. Bragg positions (green) and the difference curve (blue) are also shown.



Table 2 Crystallographic data and details from single-crystal X-ray refinement for **WTe₂Br_{1.25}**

Compound	WTe₂Br_{1.25}
CCDC	2438541
Formula	W ₂₄ Te ₄₈ Br ₃₀
Formula weight/g mol ⁻¹	12 934.50
Density/g cm ⁻³	7.441
Z	2
Crystal system	Orthorhombic
Space group	<i>Imm2</i>
<i>a</i> /Å	10.6218(4)
<i>b</i> /Å	43.038(3)
<i>c</i> /Å	12.6285(9)
<i>V</i> /Å ³	5773.0(6)
<i>T</i> /K	150.0(1)
Radiation type	Cu-K α
Reflections measured	25 309
Independent reflections	4856
Abs. coeff. (mm ⁻¹)	148.873
Goof (<i>F</i> ²)	1.046
<i>R</i> _{int}	0.0736
<i>R</i> ₁	0.1363
<i>wR</i> ₂	0.2842
Flack	0.56(6)

Crystal structure of WTe₂Br_{1.25}

At the maximum bromine content realized in this series, the compound **WTe₂Br_{1.25}** is obtained, which crystallizes in the orthorhombic space group *Imm2* with refined lattice parameters *a* = 10.6218(4) Å, *b* = 43.038(3) Å, and *c* = 12.6285(9) Å. The structure was determined from single-crystal X-ray diffraction at 150 K and was identified as an inversion twin (see Table 2). All measured crystals exhibited twin domains with refined Flack parameters close to 0.5. Due to multiple phase transitions during bromine uptake the resulting crystallinity is reduced and the refinement quality is modest (see Fig. S6). Such loss of crystallinity is a common intrinsic consequence of topochemical intercalation in weakly bound layered materials, where repeated guest uptake and release, changes in interlayer spacing, and minor stacking rearrangements readily deteriorate single-crystal quality. In addition, the structural model was used for Rietveld refinement of the bulk powder sample, yielding good agreement with the experimental pattern (see Fig. S7). Given the large unit cell and number of atoms, the structure refinement from PXRD data was carried out with fixed atomic coordinates, refining only lattice parameters and profile functions.

In contrast to the uniform stacking sequence in **WTe₂Br_{0.5}**, **WTe₂Br_{1.25}** adopts a structure in which two distinct bromine layer types alternate periodically within the van der Waals (vdW) gaps between adjacent WTe₂ layers, leading to a doubling of the *b*-axis (see Fig. 13). An interesting feature of the structure is that one vdW interlayer contains 0.5 Br, the other 0.75 Br per WTe₂ formula unit, corresponding to interlayer distances of 10.1573(2) Å and 11.3493(2) Å.

The WTe₂ layers in **WTe₂Br_{1.25}** are largely preserved and retain the characteristic zig-zag arrangement of tungsten atoms within a distorted WTe₂ layer. However, the W–W distances within the zig-zag chains are not equidistant, reflecting a distortion of the WTe₂ layers. Specifically, five consecutive tungsten

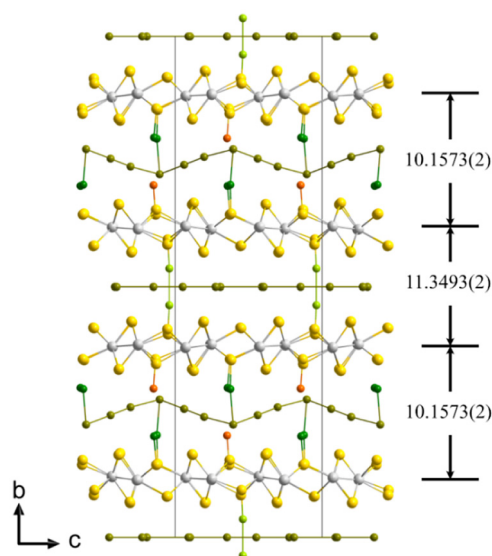


Fig. 13 Section of the **WTe₂Br_{1.25}** crystal structure viewed along the *a*-direction (W: grey, Te: yellow, Br: light green/green/olive/orange). Bromine atoms are shown in different colors to distinguish the individual bromine sites and to highlight the polybromide motifs.

atoms exhibit W–W distances along the crystallographic *a*-direction in the typical range of ~2.79 Å (2.771(9)–2.815(9) Å), followed by two distinctly elongated W–W contacts of approximately ~2.94 Å (2.925(9) Å and 2.954(9) Å, see Fig. 14).

The bromine interlayer containing 0.5 Br atoms per WTe₂ formula unit adopts an essentially planar arrangement, however, containing some out of plane Br₂ dumbbells (Br7) aligned parallel to the *b*-axis (Fig. 15, light green colored atoms), as present in the planar halogen layer observed in the commensurate **WTe₂I** structure (Fig. 8). The out of plane bromine dumbbells, with a Br–Br distance of 3.13(4) Å, establish directional contacts with Te atoms of the WTe₂ layers, via interlayer Te–Br contacts of 2.50(3) Å. This interaction, based

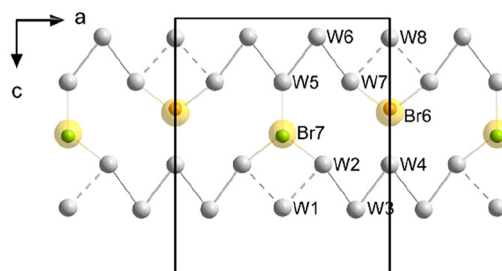


Fig. 14 Section of the **WTe₂Br_{1.25}** structure viewed along the *b*-axis with the unit cell highlighted. For clarity, only one interlayer section in the *ac*-plane of the tungsten zig-zag chains is shown. Tellurium atoms are omitted, except for Te atoms bonded to the WTe₂ layer as well as Br atoms, which are included. Note that Br7 and Br6 belong to different bromine interlayers, above and below the projected plane of W atoms. Elongated W–W contacts, indicating disruption of the tungsten chain, are highlighted by dashed lines (W: grey, Te: yellow, Br: light green/orange).



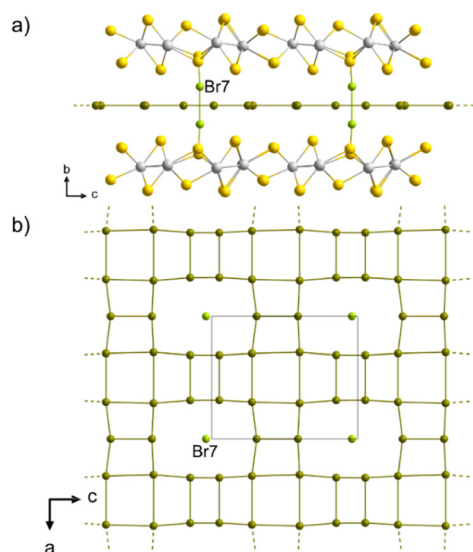


Fig. 15 Section of the crystal structure of $\text{WTe}_2\text{Br}_{1.25}$ showing interlayer bromine atoms (0.5 Br per formula unit WTe_2) (a) between adjacent WTe_2 layers and (b) the same bromine net viewed along the b -direction. (W: grey, Te: yellow, Br: green/olive). The Br_2 dumbbells (Br7) connecting adjacent WTe_2 layers are aligned along the b -axis and highlighted green.

on Br7, has an impact on the W–W distances along zig-zag chains (W1–W4), as visualized in Fig. 14 with the longer W–W bonds shown as dashed lines.

Bromine atoms within this layer organize into a rectangular network, with Br...Br separations ranging from 2.51(4) Å to 4.42(6) Å (Fig. 15). The displacement parameters of the bromine atoms within the rectangular network (Br10–Br13) behave strongly anisotropic, being extended in the ac -plane, suggesting significant positional flexibility—possibly dynamic behavior—and may indicate a tendency toward local modulation or multiple orientations of the bromine atoms.

The bromine interlayer containing 0.75 bromine per WTe_2 formula unit hosts a more complex arrangement involving polybromide species. Within this vdW interlayer, three distinct types of bromine motifs can be distinguished (see Fig. 13 and Fig. 16). First, a single bromine atom (Br6 in Fig. 14, orange color) is observed in close contact with a tellurium atom in the adjacent WTe_2 layer, with a Br5–Te12 distance of 2.48(3) Å, which perturbs the crystallographic W–W chain (W5–W8; Fig. 14). Second, a linear chain of bromine atoms is also found interacting with the WTe_2 layer (Fig. 13, green colored atoms), but without visibly perturbing the WTe_2 layers. Third, a more complex, square-pyramidal arrangement of bromine atoms is located fully within the interlayer space, forming a layer through edge-sharing connections (Fig. 13, olive colored atoms). These bromine atoms show no direct bonding to the surrounding WTe_2 framework but are connected into the polybromide chain through the apex bromine atom Br1. All Br–Br distances fall within the expected range for polybromide species (2.30–3.67 Å),^{51–53} spanning from 2.36(3) Å to 3.56(2) Å, with the shortest contacts observed at the bridging Br_2 unit between two apex bromine atoms.

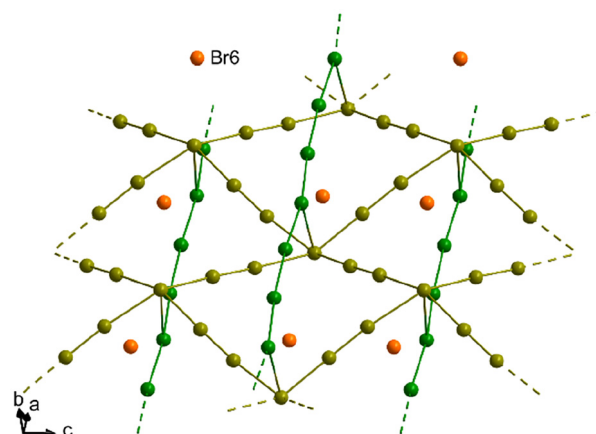


Fig. 16 Section of the crystal structure of $\text{WTe}_2\text{Br}_{1.25}$ showing interlayer bromine atoms (0.75 Br per formula unit) between adjacent WTe_2 layers. For visual clarity, distinct bromine motifs are color-coded. The bromine atoms (Br6) connecting to adjacent WTe_2 layers are highlighted in orange.

The atomic displacement parameters of these polybromide sites are relatively normal but slightly increased compared to those of the WTe_2 framework atoms. In contrast to the bromine layer forming the rectangular net, the ADPs here are less anisotropic and suggest limited flexibility or positional variation of the bromine atoms within the polybromide layer.

Crystal structure of WTe_2Br

Given the structural models of $\text{WTe}_2\text{Br}_{1.25}$, $\text{WTe}_2\text{Br}_{0.5}$ and WTe_2I , it is reasonable to assume that the intermediate phase $\text{WTe}_2\text{Br}_{1.0}$ adopts a closely related structure. Specifically, the interlayer region is expected to feature the same bromine arrangement as observed in the 0.5 Br per formula unit bromine layer configuration of $\text{WTe}_2\text{Br}_{1.25}$, *i.e.*, a planar halogen layer composed of Br_2 -like units aligned with the tungsten-chain-bridging tellurium atoms. As such, $\text{WTe}_2\text{Br}_{1.0}$ likely exhibits a uniform stacking sequence with each van der Waals gap containing the same halogen motif. This would resemble the commensurate stacking found in WTe_2I and represents a structurally balanced state between the alternating-filled architecture of $\text{WTe}_2\text{Br}_{0.5}$ and the polybromide-rich environment of $\text{WTe}_2\text{Br}_{1.25}$. Due to the fast and reversible intercalation behavior and high mobility of bromine in this system, isolation of pure $\text{WTe}_2\text{Br}_{1.0}$ remains challenging, and a final structural characterization has not yet been achieved.

Electronic band structure and phonon calculations

The electronic band structure was calculated by density functional theory (DFT) for the 3D WTe_2I supercell model derived from the commensurate refinement, which can be regarded as equivalent descriptions (shown in Fig. 17). In comparison to the band structure of unintercalated WTe_2 in the $P2_1/m$ space group, which is a semimetal,³⁴ WTe_2I shows metallic behavior due to a downward shift in energy of tungsten orbitals between A $(-\frac{1}{2} \ 0 \ \frac{1}{2})$ and E $(-\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2})$. The oxidation of the WTe_2



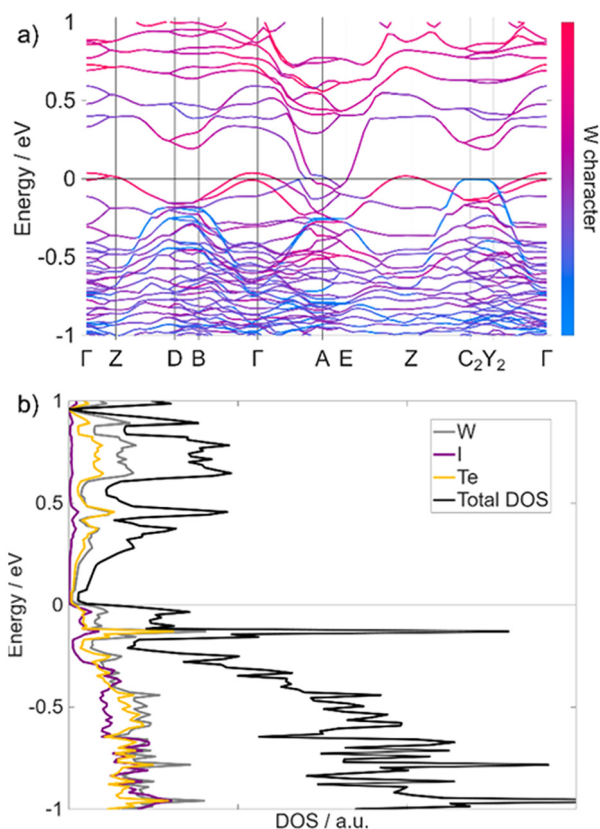


Fig. 17 Calculated electronic band structure of commensurately modulated WTe_2I , with bands colored by their tungsten character (a), and the corresponding electronic density of states (b). Special points in and paths through reciprocal space were chosen following the literature.⁵⁴

network by iodine is quite minimal, with a downward shift of the Fermi energy of only 0.04 eV.

The electronic structure of the unmodulated $Pmmn$ structure of WTe_2I ($a = 21.8967(2) \text{ \AA}$, $b = 3.4759(0) \text{ \AA}$, $c = 6.3270(1) \text{ \AA}$) has been previously reported.^{49,50} The unmodulated structure is also metallic, but shows several important differences to the supercell structure: a much higher degree of oxidation of the WTe_2 layers, and the presence of iodine bands with high dispersion crossing the Fermi level. These crossing bands lead to nesting of the Fermi surface and charge density wave (CDW) instabilities, which create the modulated structures that we have characterized here.

In supercell WTe_2I structure, some iodine states form a flat band at the Fermi energy between C_2 ($-\frac{1}{2} \frac{1}{2} 0$) and Y_2 ($-\frac{1}{2} 0 0$) (shown in blue in Fig. 17). The flatness of this band indicates a very high degree of electron localization. When moving away from the C_2 - Y_2 line, the band takes a parabolic form with many anticrossings of the W bands, which demonstrates strong coupling between the I and W states. This band is associated with the iodine atoms I2, I8 and I5, I11 which correspond to I1 and I2 in the commensurate structure at specific internal phase coordinate t (see Fig. 18, highlighted in red). The overall picture is of localized metallic electrons on

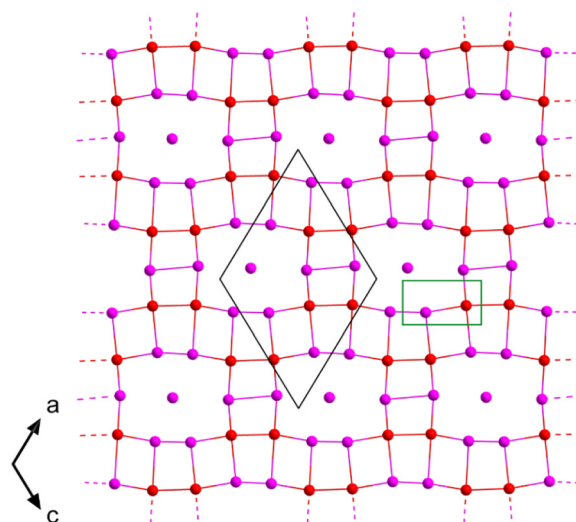


Fig. 18 Section of the WTe_2I supercell structure only showing one iodine (red/purple) layer with highlighted I2, I8 and I5, I11 iodines in red, viewed along the b -axis. Unit cells are shown in black (supercell) and green (commensurate).

some portions of the iodine layer, potentially representing frozen CDWs.⁴⁹

Electronic band structure and phonon band structure of $\text{WTe}_2\text{Br}_{0.5}$

The electronic band structure of $\text{WTe}_2\text{Br}_{0.5}$ was also calculated using density functional theory (DFT) (Fig. 19). Like WTe_2I ,

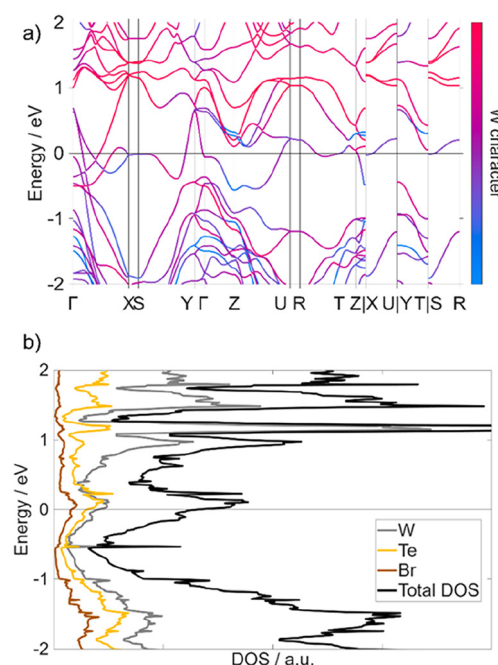


Fig. 19 Calculated electronic band structure of $\text{WTe}_2\text{Br}_{0.5}$, with bands colored by their tungsten character (a), and the corresponding electronic density of states (b). Special points in and paths through reciprocal space were chosen following the literature.⁵⁴



WTe₂Br_{0.5} is a metal, with additional bands appearing near the Fermi energy compared to **WTe₂**.⁴⁹ These include an interesting flat band at the Fermi energy between X ($\frac{1}{2}$ 0 0) and S ($\frac{1}{2}$ $\frac{1}{2}$ 0); however, unlike in the case of **WTe₂I**, there is no contribution of the Br atoms to the states near the Fermi energy, and therefore these localized metallic electrons are located within the WTe₂ layers. **WTe₂Br_{0.5}** shows a higher degree of oxidation of the WTe₂ layers than modulated **WTe₂I**, with a shift of the Fermi energy of 0.35 eV, indicating a more ionic interaction with the intercalant.

The phonon band structure of **WTe₂Br_{0.5}** was also calculated; it is shown in Fig. 20. Like unmodulated **WTe₂I**,⁴⁹

WTe₂Br_{0.5} shows many soft modes (modes with negative energy), corresponding to instabilities of the crystal structure at 0 K. These soft modes include both displacements of the Br atoms and of the WTe₂ layers. Therefore, **WTe₂Br_{0.5}**, like **WTe₂I**, has a propensity towards the formation of a disordered or modulated structure.

The observation of an unmodulated structure for **WTe₂Br_{0.5}**, in comparison to the modulated structure of **WTe₂I**, can be understood by consideration of the electronic band structure. **WTe₂Br_{0.5}** lacks the extra sheet-like bands crossing the Fermi level which lead to the formation of CDWs, CDW instabilities, and a modulated structure in **WTe₂I**.⁴⁹ Therefore, the phonon instabilities in **WTe₂Br_{0.5}** likely cause dynamic and/or static disorder, as is seen in the large ADPs. The high density of Br states below 10 meV would also contribute thermal displacements to the ADPs, although these modes contain displacements of the Br atoms in all three Cartesian directions.

Experimental

Synthesis

All material handling and manipulations were performed in an argon-filled glove box (MBraun Labmaster 130, O₂ < 1 ppm, H₂O < 1 ppm). All synthesis steps consistently afforded yields greater than 95%.

Powder

WTe₂ was synthesized by combining tungsten powder (1256.24 mg, 6.84 mmol, ABCR GmbH, 99.95%, particle size 0.6–0.9 μm), tellurium pieces (1830.95 mg, 14.35 mmol, Evochem, 99.999%), and tungsten(vi) chloride (WCl₆; 135.49 mg, 0.34 mmol, Arcos, 99.9+%) in a 1:2.1:0.05 molar ratio, with WCl₆ serving as an oxygen getter. The mixture was sealed in a dry, evacuated silica ampoule (40 mm length, 16 mm diameter) and heated in a commercial (Carbolite) furnace to 800 °C for 6 hours, employing heating and cooling rates of 2 K min^{−1}. The resulting product was thoroughly ground, vacuum-sealed in a second silica ampoule (200 mm length, 16 mm diameter), and heated to 500 °C for 20 hours under a temperature gradient, with the opposite end of the ampoule maintained at room temperature, to facilitate the removal of excess tellurium, tungsten oxychloride impurities and unreacted WCl₆.

Single crystals of WTe₂ were synthesized by combining tungsten powder (1256.24 mg, 6.84 mmol, ABCR GmbH, 99.95%, particle size 0.6–0.9 μm), tellurium pieces (1830.95 mg, 14.35 mmol, Evochem, 99.999%), and tungsten(vi) chloride (WCl₆; 135.49 mg, 0.34 mmol, Arcos, 99.9+%) in a 1:2.1:0.05 molar ratio, with WCl₆ serving as an oxygen getter. The mixture was sealed in a dry, evacuated silica ampoule (40 mm length, 16 mm diameter) and heated in a commercial (Carbolite) furnace to 800 °C for 6 hours, employing heating and cooling rates of 2 K min^{−1}.

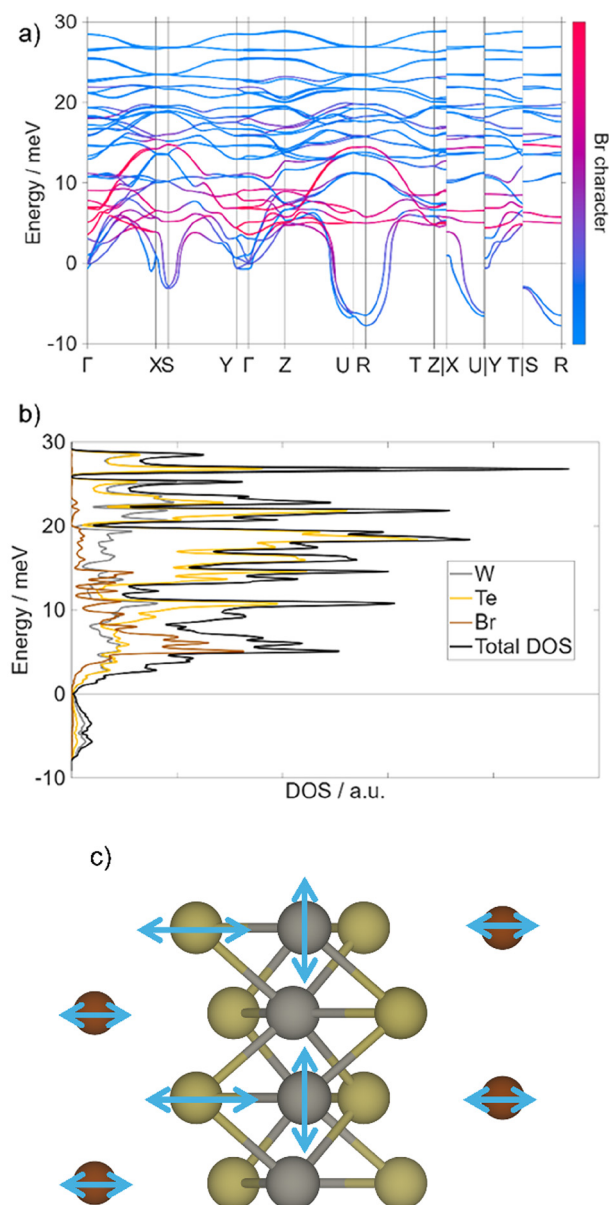


Fig. 20 Calculated phonon band structure of **WTe₂Br_{0.5}**, with bands colored by their bromine character (a), and the corresponding phonon density of states (b). A cartoon view of an unstable mode at R (0.5 0.5 0.5) along *c* is shown in (c). Special points in and paths through reciprocal space were chosen following the literature.⁵⁴



WTe₂I crystals

WTe₂ single-crystals (~100 mg) were loaded into a borosilicate glass screw-cap vial (5/20 mL for incommensurate/commensurate crystals) with four molar equivalents of iodine, and the vial was sealed with a custom-machined PEEK cap equipped with a PTFE liner. The reaction mixture was heated in a Simon-Müller laboratory oven at a rate of 2 K min⁻¹ to 120 °C, held at this temperature for 12 h, and then cooled to room temperature at the same rate and the product was obtained as black crystals.

WTe₂Br_x (x = 0.5 and 1.25)

Bromine (p.a.) was degassed and purified prior to use according to Brauer.⁵⁵ Due to the corrosive nature and high vapor pressure of bromine, all operations were performed either in an argon glovebox or using Schlenk techniques under dry argon (with appropriate cold traps). Typically, WTe₂ (powder or single crystals, *ca.* 100 mg) was reacted with a large excess of bromine (*ca.* 3 mL). WTe₂ powder was placed in a Schlenk tube, liquid bromine was added and the mixture was allowed to react for 3 h. Excess bromine was then removed by passing a constant argon flow over the sample. Because of the high density of bromine vapors, a needle was inserted through the septum and positioned directly above the sample to provide an efficient outlet for the Br₂/argon vapors and the vessel was gently shaken from time to time. For WTe₂Br_{0.5}, evaporation at room temperature was sufficient, whereas for WTe₂Br_{1.25} the Schlenk tube was cooled to 0–5 °C during the bromine removal step and needed at least 3 h. Needle-shaped WTe₂ single crystals were intercalated either (i) by exposure to bromine vapor at room temperature for 4 days or (ii) by direct contact with liquid bromine at 6 °C for 2 days. All products were obtained as black powders or black single crystals with metallic luster.

Powder X-ray diffraction

PXRD patterns of products were collected with a Stadi-P (STOE, Darmstadt) powder diffractometer using germanium-monochromated Cu-K_{α1} radiation ($\lambda = 1.5406$ Å) and a Mythen 1K detector. PXRD measurements of WTe₂Br_x (x = 0.5, 1.0, and 1.25) were performed in transmission geometry using interchangeable window materials selected according to the experimental requirements. The windows comprised ultrathin glass (Schott AF 32® eco thin glass, 30 μm), Kapton® film (25 μm), and Mylar® film (15 μm). To prevent corrosion by bromine and to enable reliable sealing, the metal parts of the original transmission holder were replaced by custom-made PTFE components (rotor disc and counter disc) and soda-lime glass components in a redesigned holder (see Fig. S8 and S9). In all experiments, WTe₂ powder was immobilized on the glass window using Lithelen grease to ensure a fixed sample position during measurement, and all samples were assembled and sealed under inert conditions (argon atmosphere). For WTe₂Br_{0.5}, a standard glass disc without a filling slit was employed; the sample was covered with a Kapton® film

window that was sealed using Lithelen grease and allowed gradual pressure equilibration *via* bromine diffusion through the Kapton film (see Fig. S8(a) and (d)). For WTe₂Br_{1.25}, a glass disc featuring a filling slit was used; ultrathin-glass windows were bonded to both sides of the disc using cyanoacrylate adhesive (superglue). Bromine was introduced through the slit under argon, and the opening was subsequently sealed with wax and additional cyanoacrylate. For *in situ* PXRD experiments, Mylar film was used as the window material to facilitate faster bromine release during the measurement. The crystal structure of WTe₂Br_{0.5} was solved from PXRD using EXPO2014,⁵⁶ and refined by Rietveld method in FullProf (FP)⁵⁷ with a modified Thompson–Cox–Hastings pseudo-Voigt (TCHZ) profile function.^{58,59} The instrumental resolution function (IRF) was obtained from the NIST Si640f standard⁶⁰ and fitted in WinPLOTR.⁶¹ Additionally, multiple texturing effects, such as particle form, size, and orientation, were included in the Rietveld refinements to enhance the accuracy of the model. All intermediate and final structure models were validated with PLATON.⁶²

Single-crystal X-ray diffraction (SC-XRD)

SC-XRD studies were performed using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix 6000HE detector using MoK_α ($\lambda = 0.71073$ Å) and CuK_α ($\lambda = 1.54184$ Å) radiation at 150 K. Data reduction, scaling and absorption corrections were performed using CrysAlis^{Pro},⁶³ taking into account the crystal shape and size.⁶⁴ The supercell structure of WTe₂I and WTe₂Br_{1.25} were solved with the ShelXT 2018/2 solution program,⁶⁵ employing dual methods and refined with ShelXL 2018/3 (Sheldrick, 2015)⁶⁶ using Olex2 1.5 (Dolomanov *et al.*, 2009)⁶⁷ as the graphical interface. The models were refined using full matrix least squares minimization on $|F|^2$. For WTe₂Br_{1.25} crystals, the needle shaped WTe₂ single crystals were selected directly from bromine layered with perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH). The modulated WTe₂I structures were solved using the charge-flipping algorithm SUPERFLIP⁶⁸ (as implemented in JANA2020), and subsequent refinements were carried out in JANA2020.^{69–72}

ICP-OES

After dissolution of WTe₂I in 2 wt% NaOH/H₂O₂, the W/Te/I ratio was determined by ICP-OES (iCAP 7400 Thermo Fisher Scientific) and yielded in averaged ratios W : Te : I of 1.0 : 1.99 (3) : 0.49(3) for WTe₂I phases.

TXRF (total internal reflection X-ray fluorescence) spectroscopy

TXRF studies were performed using a S2 Picofox (Bruker AXS Microanalysis, Berlin, Germany) equipped with a Mo X-ray tube, which was operated at 50 kV and 600 μA. The measurement period for each sample was 1000 s (live time). Fitting of the resulting spectra was done using the Spectra software (Bruker Nano GmbH) in the super byas mode (maximum stripping cycles of 2000). The average ratio for WTe₂I with W : Te : I was 1.0 : 1.98(7) : 0.51(6).



Bromide content determination (argentometric titration)

Approximately 100 mg of $\text{WTe}_2\text{Br}_{0.5}$ were dissolved in concentrated HNO_3 (5 mL) with addition of ~ 1 mL of H_2O_2 (30%). The mixture was carefully heated to *ca.* 80 °C for 30 min, allowed to cool to room temperature, and diluted with bidistilled H_2O to a final volume of 100 mL. The bromide content was determined by argentometric titration with potentiometric end-point detection using a standardized AgNO_3 solution (0.01 M). Titrations were performed on a Schott TitroLine easy automatic titrator (SI Analytics) equipped with a silver indicator electrode. The equivalence point was identified from the inflection in the electrode potential (mV), corresponding to complete precipitation of Br^- as AgBr . Repeated determinations gave bromide contents consistent with the expected composition of $\text{WTe}_2\text{Br}_{0.5}$ (W : Br = 1 : 0.49(3)).

DFT calculations

Calculations were performed using the ABINIT software package with the projector augmented-wave (PAW) method and a plane-wave basis set.^{73,74} The Perdew–Burke–Ernzerhof exchange–correlation functional was used with the vdW–DFT–D3 dispersion correction.^{75,76} PAW data files were used as received from the ABINIT library.⁷⁷ Methfessel–Paxton smearing was used to determine band occupation.⁷⁸ Convergence studies were used to choose a 18 Ha (WTe_2I) and 20 Ha ($\text{WTe}_2\text{Br}_{0.5}$), plane wave basis set cutoff energy outside the PAW spheres; a 100 Ha cutoff was used within the spheres. The Brillouin zone was sampled with a $4 \times 2 \times 4$ (WTe_2I) or $6 \times 10 \times 6$ ($\text{WTe}_2\text{Br}_{0.5}$) grid of k -points. The calculation of the phonon band structure of $\text{WTe}_2\text{Br}_{0.5}$ was performed using density functional perturbation theory on a $3 \times 5 \times 3$ grid of q -points. Structural relaxation was performed prior to calculation of the electronic and phononic structures.

Conclusions

In this work, the crystal structure of the iodine intercalate WTe_2I was reinvestigated and shown to occur in two closely related (3 + 1)D variants within $P2_1/m(\alpha 0\gamma)00$: an incommensurate form and a commensurate polytype that “locks in” to $\mathbf{q} = (1/2, 0, 1/6)$ and can be equivalently described as a 3D supercell. In both descriptions, the modulation is dominated by the iodine sublattice, while the WTe_2 host responds only by subtle, coupled distortions. A key microscopic element is a local defect motif in which an I2 unit reorients by 90° (I3 site) and is accommodated by a concomitant Te shift, consistent with localized host–guest bonding that effectively pins the modulation and periodically perturbs the tungsten chains.

Extending this chemistry from iodine to bromine, we identify a multistage series WTe_2Br_x with distinct regimes at $x = 0.5$, 1.0 and 1.25 and a striking, fast, and reversible “breathing” behavior already at room temperature. *In situ* PXRD directly captures the rapid evolution of the layer-spacing reflections during uptake and release, demonstrating that composition and structure can be cycled under mild conditions.

Structurally, $\text{WTe}_2\text{Br}_{0.5}$ ($Pm\bar{m}n$) represents a bromine-poor end member with a half-filled interlayer motif and a short Te–Br contact that links adjacent layers; its exceptionally large, anisotropic bromine displacement parameters point to pronounced positional freedom consistent with high bromine mobility. At the bromine-rich end, $\text{WTe}_2\text{Br}_{1.25}$ ($Imm2$) adopts an alternating-filled architecture with two chemically distinct interlayer environments, combining Br_2 -like bridging motifs and more complex polybromide arrangements, while the WTe_2 framework remains intact but locally distorted in response to directional Te–Br interactions. In both WTe_2I and $\text{WTe}_2\text{Br}_{0.5}$, the electronic structure of the WTe_2 layers is changed significantly by intercalation, leading to a metallic state with localized electrons in flat bands at the Fermi level. Together, these results establish WTe_2I and WTe_2Br_x as rare, structurally resolved examples of stoichiometric halogen intercalation in a TMDC, highlighting how a layered semimetal can tolerate strong oxidizing guests while retaining topotactic reversibility—opening a route to controllable oxidation (hole doping), staging, and modulation phenomena in van der Waals solids.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data are available within the article. The data that support the findings of this study are available on request from the corresponding author, H.-J. Meyer. Computational data are available at <https://doi.org/10.5281/zenodo.18420902>.

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d6dt00529b>.

CCDC 2503030 ($\text{WTe}_2\text{Br}_{0.5}$), 2519455 ($\text{WTe}_2\text{Br}_{1.25}$), 2519690 (WTe_2I , commensurate), 2519736 (WTe_2I , supercell) and 2520418 (WTe_2I , incommensurate) contain the supplementary crystallographic data for this paper.^{79a–e}

Acknowledgements

The authors acknowledge support of this research by the Deutsche Forschungsgemeinschaft (Bonn) through the project ME 914/32-1 and by the State of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no. INST 40/575-1 FUGG (JUSTUS 2 cluster). Carl P. Romao acknowledges support from the project FerrMion of the Ministry of Education, Youth and Sports, Czech Republic, co-funded by the European Union (CZ.02.01.01/00/22_008/0004591). In addition, the authors thank Dr. Jochen Glaser (University of Tübingen) for performing ICP-OES measurements and RNDr. Václav Petříček (The Czech Academy of Sciences) for assistance with solving the modulated structures.



References

- H. Yang, S. W. Kim, M. Chhowalla and Y. H. Lee, *Nat. Phys.*, 2017, **13**, 931–937.
- M. Chhowalla, D. Jena and H. Zhang, *Nat. Rev. Mater.*, 2016, **1**, 16052.
- M. Chhowalla, *Nat. Chem.*, 2013, **5**, 263–275.
- J. A. Wilson and A. D. Yoffe, *Adv. Phys.*, 1969, **18**, 193–335.
- M. S. Whittingham, *Chem. Rev.*, 2004, **104**, 4271–4302.
- M. S. Whittingham, *Prog. Solid State Chem.*, 1978, **12**, 41–99.
- Z. Wang, R. Li, C. Su and K. P. Loh, *SmartMat*, 2020, **1**, e1013.
- M. N. Ali, H. Ji, D. Hirai, M. K. Fuccillo and R. J. Cava, *J. Solid State Chem.*, 2013, **202**, 77–84.
- S. I. Ali, S. Mondal, S. J. Prathapa, S. van Smaalen, S. Zöhr and B. Harbrecht, *Z. Anorg. Allg. Chem.*, 2012, **638**, 2625–2631.
- S. I. Ali, S. Mondal and S. van Smaalen, *Z. Anorg. Allg. Chem.*, 2015, **641**, 464–469.
- H. J. Crawack and C. Pettenkofer, *Solid State Commun.*, 2001, **118**, 325–332.
- J. Rouxel, *Physica B+C*, 1980, **99**, 3–11.
- S. N. Patel and A. A. Balchin, *J. Mater. Sci. Lett.*, 1985, **4**, 382–384.
- M. B. Dines, *Science*, 1975, **188**, 1210.
- E. Figueroa, J. W. Brill and J. P. Selegue, *J. Phys. Chem. Solids*, 1996, **57**, 1123–1127.
- Y. Liu, Z. Wang, G. Hu, X. Chen, K. Xu, Y. Guo, Y. Xie and C. Wu, *Precis. Chem.*, 2025, **3**, 51–71.
- S. Kabashima, *J. Phys. Soc. Jpn.*, 1966, **21**, 945–948.
- J. Augustin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **62**, 10812–10823.
- W. G. Dawson and D. W. Bullett, *J. Phys. C: Solid State Phys.*, 1987, **20**, 6159–6174.
- Y.-Y. Lv, B.-B. Zhang, X. Li, B. Pang, F. Zhang, D.-J. Lin, J. Zhou, S.-H. Yao, Y. B. Chen, S.-T. Zhang, M. Lu, Z. Liu, Y. Chen and Y.-F. Chen, *Sci. Rep.*, 2016, **6**, 26903.
- H. Y. Lv, W. J. Lu, D. F. Shao, Y. Liu, S. G. Tan and Y. P. Sun, *Europhys. Lett.*, 2015, **110**, 37004.
- P. Li, Y. Wen, X. He, Q. Zhang, C. Xia, Z.-M. Yu, S. A. Yang, Z. Zhu, H. N. Alshareef and X.-X. Zhang, *Nat. Commun.*, 2017, **8**, 2150.
- Y. Sun, S.-C. Wu, M. N. Ali, C. Felser and B. Yan, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2015, **92**, 161107.
- C. Huang, A. Narayan, E. Zhang, Y. Liu, X. Yan, J. Wang, C. Zhang, W. Wang, T. Zhou, C. Yi, S. Liu, J. Ling, H. Zhang, R. Liu, R. Sankar, F. Chou, Y. Wang, Y. Shi, K. T. Law, S. Sanvito, P. Zhou, Z. Han and F. Xiu, *ACS Nano*, 2018, **12**, 7185–7196.
- C. Rovira and M. H. Whangbo, *Inorg. Chem.*, 1993, **32**, 4094–4097.
- J. A. Wilson, F. J. Di Salvo and S. Mahajan, *Adv. Phys.*, 1975, **24**, 117–201.
- M. N. Ali, *Nature*, 2014, **514**, 205–208.
- N. Lu, C. Zhang, C.-H. Lee, J. P. Oviedo, M. A. T. Nguyen, X. Peng, R. M. Wallace, T. E. Mallouk, J. A. Robinson, J. Wang, K. Cho and M. J. Kim, *J. Phys. Chem. C*, 2016, **120**, 8364–8369.
- E. Canadell and M.-H. Whangbo, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1991, **43**, 1894–1902.
- B. Guster, E. Canadell, M. Pruneda and P. Ordejón, *2D Mater.*, 2018, **5**, 025024.
- M. H. Whangbo, E. Canadell, P. Foury and J. P. Pouget, *Science*, 1991, **252**, 96–98.
- N. Mitsuishi, Y. Sugita, M. S. Bahramy, M. Kamitani, T. Sonobe, M. Sakano, T. Shimojima, H. Takahashi, H. Sakai, K. Horiba, H. Kumigashira, K. Taguchi, K. Miyamoto, T. Okuda, S. Ishiwata, Y. Motome and K. Ishizaka, *Nat. Commun.*, 2020, **11**, 2466.
- B. E. Brown, *Acta Crystallogr.*, 1966, **20**, 268–274.
- P. Schmidt, F. Strauß, M. Scheele, C. P. Romao and H.-J. Meyer, *Dalton Trans.*, 2026, **55**, 3296–3309.
- H. Wang, Z. Lu, S. Xu, D. Kong, J. J. Cha, G. Zheng, P.-C. Hsu, K. Yan, D. Bradshaw, F. B. Prinz and Y. Cui, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 19701–19706.
- M. B. Dines, *Mater. Res. Bull.*, 1975, **10**, 287–291.
- L. Charron, D. Dumchenko, E. Fortin, C. Gherman and L. Kulyuk, *J. Lumin.*, 2005, **112**, 45–49.
- D. S. Devi and N. R. Mohapatra, *ACS Omega*, 2024, **9**, 50634–50641.
- Y. Garcia-Basabe, C. D. Mendoza, F. C. Vicentin and D. G. Larrude, *Phys. Chem. Chem. Phys.*, 2025, **27**, 19347–19357.
- T. Kim, Y. Kim and E. K. Kim, *Sens. Actuators, A*, 2020, **312**, 112165.
- L. Kulyuk, L. Charron and E. Fortin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **68**, 075314.
- L. Kulyuk, D. Dumcehnko, E. Bucher, K. Friemelt, O. Schenker, L. Charron, E. Fortin and T. Dumouchel, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **72**, 075336.
- S. Pak, J. Son, T. Kim, J. Lim, J. Hong, Y. Lim, C.-J. Heo, K.-B. Park, Y. W. Jin, K.-H. Park, Y. Cho and S. Cha, *Nanotechnology*, 2023, **34**, 015702.
- S. Prucnal, A. Hashemi, M. Ghorbani-Asl, R. Hübner, J. Duan, Y. Wei, D. Sharma, D. R. T. Zahn, R. Ziegenrucker, U. Kentsch, A. V. Krasheninnikov, M. Helm and S. Zhou, *Nanoscale*, 2021, **13**, 5834–5846.
- M. Rabeel, H. Kim, M. A. Khan, M. Abubakr, I. Ahmad, M. Ahmad, S. Rehman, M.-J. Lee, M. F. Khan and D.-k. Kim, *ACS Photonics*, 2023, **10**, 4425–4436.
- N. T. Trung, M. I. Hossain, M. I. Alam, A. Ando, O. Kitakami, N. Kikuchi, T. Takaoka, Y. Sainoo, R. Arafune and T. Komeda, *ACS Omega*, 2020, **5**, 28108–28115.
- F.-Y. Wu, Y.-S. Cheng, K.-L. Wu, R. Wu, R. Yu, P.-L. Guan, Y.-W. Cheng, W.-J. Li, J.-L. Yang and X.-W. Wei, *J. Mater. Chem. C*, 2024, **12**, 6645–6652.
- L. Yang, K. Majumdar, H. Liu, Y. Du, H. Wu, M. Hatzistergos, P. Y. Hung, R. Tieckelmann, W. Tsai, C. Hobbs and P. D. Ye, *Nano Lett.*, 2014, **14**, 6275–6280.
- P. Schmidt, P. Schneiderhan, M. Ströbele, C. P. Romao and H.-J. Meyer, *Inorg. Chem.*, 2021, **60**, 1411–1418.
- W. L. Zhu, Y. Cao, P. J. Guo, X. Li, Y. J. Chen, L. J. Zhu, J. B. He, Y. F. Huang, Q. X. Dong, Y. Y. Wang, R. Q. Zhai,



- Y. B. Ou, G. Q. Zhu, H. Y. Lu, G. Li, G. F. Chen and M. H. Pan, *Phys. Rev. B*, 2022, **105**, 125116.
- 51 K. Sonnenberg, L. Mann, F. A. Redeker, B. Schmidt and S. Riedel, *Angew. Chem., Int. Ed.*, 2020, **59**, 5464–5493.
- 52 H. Haller and S. Riedel, *Z. Anorg. Allg. Chem.*, 2014, **640**, 1281–1291.
- 53 H. Haller, J. Schröder and S. Riedel, *Angew. Chem., Int. Ed.*, 2013, **52**, 4937–4940.
- 54 Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba and I. Tanaka, *Comput. Mater. Sci.*, 2017, **128**, 140–184.
- 55 G. Brauer, *Handbuch der präparativen anorganischen Chemie*, Ferdinand Enke, Stuttgart, 1975.
- 56 A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio, *J. Appl. Crystallogr.*, 2013, **46**, 1231–1235.
- 57 J. Rodriguez-Carvajal and T. Roisnel, *IUCr, CPD Newsl.*, 1998, **20**, 35–36.
- 58 P. Thompson, D. E. Cox and J. B. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79–83.
- 59 L. W. Finger, D. E. Cox and A. P. Jephcoat, *J. Appl. Crystallogr.*, 1994, **27**, 892–900.
- 60 D. R. Black, M. H. Mendenhall, A. Henins, J. Filliben and J. P. Cline, *Powder Diffr.*, 2020, **35**, 156–159.
- 61 T. Roisnel and J. Rodriguez-Carvajal, *Mater. Sci. Forum*, 2001, **378–381**, 118–123.
- 62 A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
- 63 Rigaku Oxford Diffraction, *CrysAlisPro Software System*, 2025.
- 64 R. C. Clark and J. S. Reid, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1995, **51**, 887–897.
- 65 G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2015, **71**, 3–8.
- 66 G. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
- 67 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- 68 L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786–790.
- 69 V. Petříček, M. Dušek and L. Palatinus, *Z. Kristallogr. – Cryst. Mater.*, 2014, **229**, 345–352.
- 70 V. Petříček, M. Dušek and J. Plášil, *Z. Kristallogr. – Cryst. Mater.*, 2016, **231**, 583–599.
- 71 V. Petříček, V. Eigner, M. Dušek and A. Čejchan, *Z. Kristallogr. – Cryst. Mater.*, 2016, **231**, 301–312.
- 72 V. Petříček, L. Palatinus, J. Plášil and M. Dušek, *Z. Kristallogr. – Cryst. Mater.*, 2023, **238**, 271–282.
- 73 X. Gonze, F. Jollet, F. Abreu Araujo, D. Adams, B. Amadon, T. Applencourt, C. Audouze, J. M. Beuken, J. Bieder, A. Bokhanchuk, E. Bousquet, F. Bruneval, D. Caliste, M. Côté, F. Dahm, F. Da Pieve, M. Delaveau, M. Di Gennaro, B. Dorado, C. Espejo, G. Geneste, L. Genovese, A. Gerossier, M. Giantomassi, Y. Gillet, D. R. Hamann, L. He, G. Jomard, J. Laflamme Janssen, S. Le Roux, A. Levitt, A. Lherbier, F. Liu, I. Lukačević, A. Martin, C. Martins, M. J. T. Oliveira, S. Poncé, Y. Pouillon, T. Rangel, G. M. Rignanese, A. H. Romero, B. Rousseau, O. Rubel, A. A. Shukri, M. Stankovski, M. Torrent, M. J. Van Setten, B. Van Troeye, M. J. Verstraete, D. Waroquiers, J. Wiktor, B. Xu, A. Zhou and J. W. Zwanziger, *Comput. Phys. Commun.*, 2016, **205**, 106–131.
- 74 M. Torrent, F. Jollet, F. Bottin, G. Zerah and X. Gonze, *Comput. Mater. Sci.*, 2008, **42**, 337–351.
- 75 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
- 76 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Phys. Chem.*, 2010, **132**, 154104.
- 77 <https://www.abinit.org>, (accessed 20/3/19).
- 78 M. Methfessel and A. T. Paxton, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1989, **40**, 3616–3621.
- 79 (a) CCDC 2503030: Experimental Crystal Structure Determination, 2026, DOI: [10.25505/fiz.icsd.cc2q0lx8](https://doi.org/10.25505/fiz.icsd.cc2q0lx8); (b) CCDC 2519455: Experimental Crystal Structure Determination, 2026, DOI: [10.25505/fiz.icsd.cc2qkprp](https://doi.org/10.25505/fiz.icsd.cc2qkprp); (c) CCDC 2519690: Experimental Crystal Structure Determination, 2026, DOI: [10.25505/fiz.icsd.cc2qkybl](https://doi.org/10.25505/fiz.icsd.cc2qkybl); (d) CCDC 2519736: Experimental Crystal Structure Determination, 2026, DOI: [10.25505/fiz.icsd.cc2qkzt3](https://doi.org/10.25505/fiz.icsd.cc2qkzt3); (e) CCDC 2520418: Experimental Crystal Structure Determination, 2026, DOI: [10.25505/fiz.icsd.cc2qlptv](https://doi.org/10.25505/fiz.icsd.cc2qlptv).



**Structural Evolution during Reversible Halogen Intercalation in WTe_2 :
Commensurate–Incommensurate WTe_2I and Multistage WTe_2Br_x ($x =$
0.5, 1.0 and 1.25)**

Patrick Schmidt,^a Carl P. Romao,^b Hans-Jürgen Meyer^{*a}

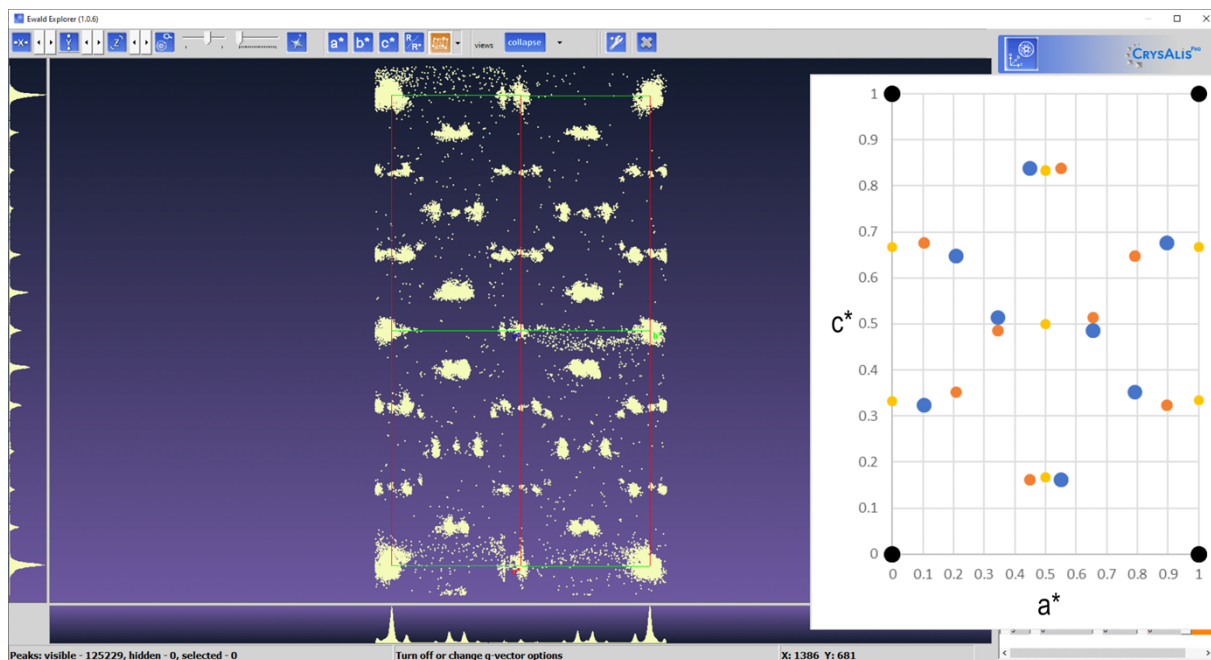


Figure S1. Screenshot from the Ewald Explorer in CrysAlisPro showing the collapsed reciprocal lattice, with a simulated satellite pattern on the right (with $m \leq \pm 4$). Black dots mark the main reflections, while red and blue dots indicate incommensurate, twinned satellite reflections. Yellow dots denote the commensurate case.

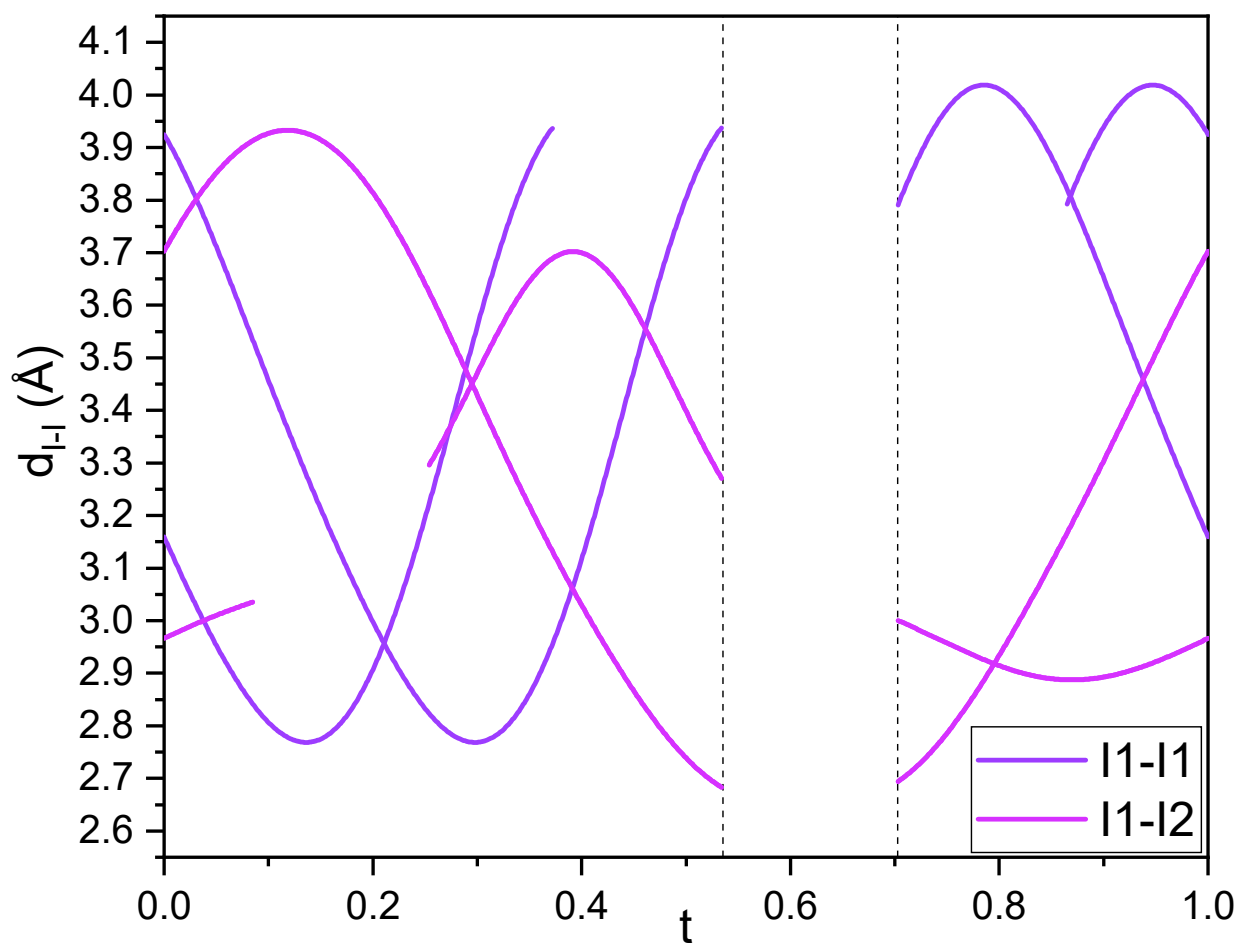


Figure S2. t plots of the distances for I1-I1 and I1-I2 in grey with crenel limits marked as dashed vertical line.

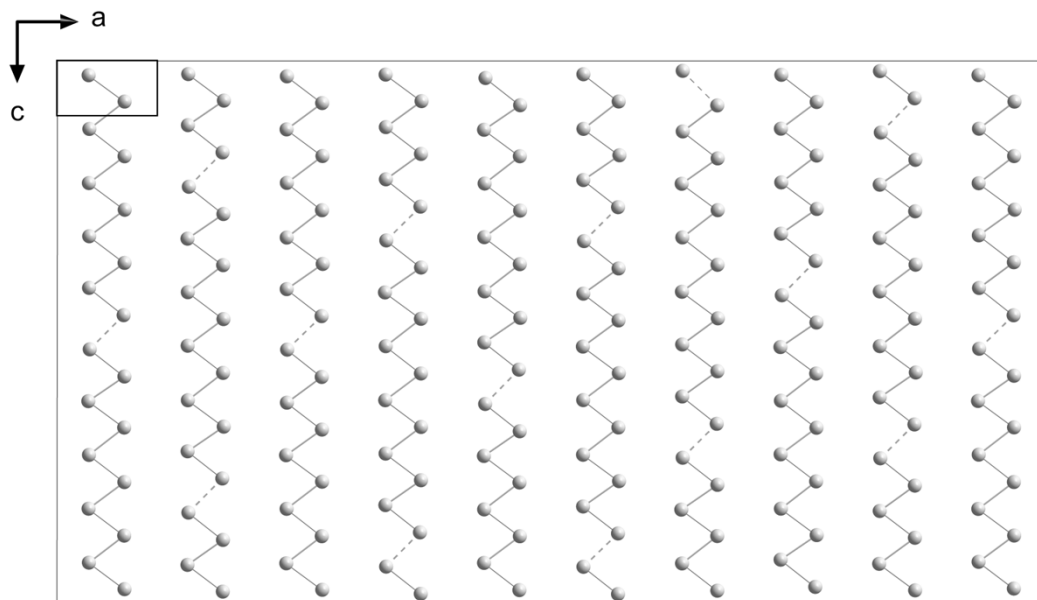


Figure S3. Section of the incommensurate WTe_2I structure showing only one layer of tungsten atoms with long bonds indicated as dashed lines. The unit cell is highlighted in the top left corner.

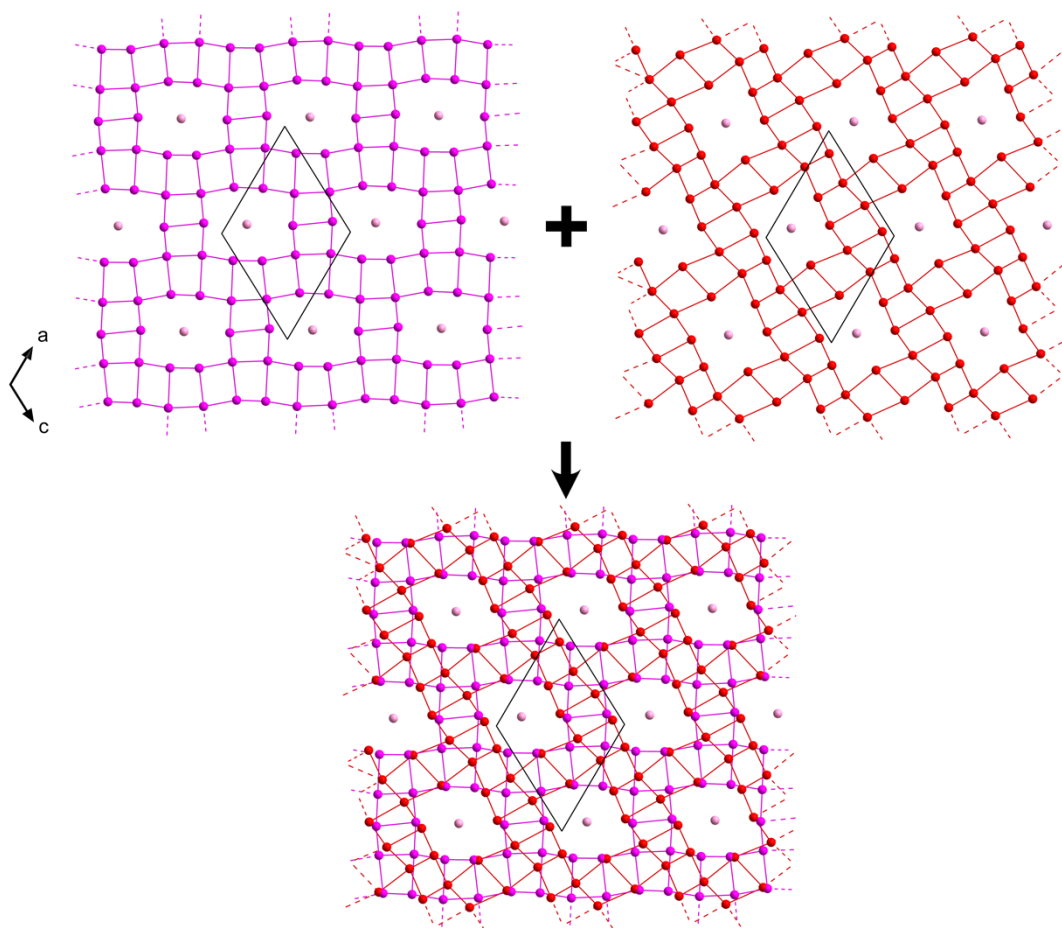


Figure S4. Sections of the WTe_2I supercell structure illustrating the iodine-layer disorder model. The top panels show the two disorder components separately (part a, purple; part b, red), while the bottom panel displays the combined iodine layer. Out-of-plane iodine atoms are highlighted in light purple. The structure is viewed along the b -axis, with the unit cell outlined.

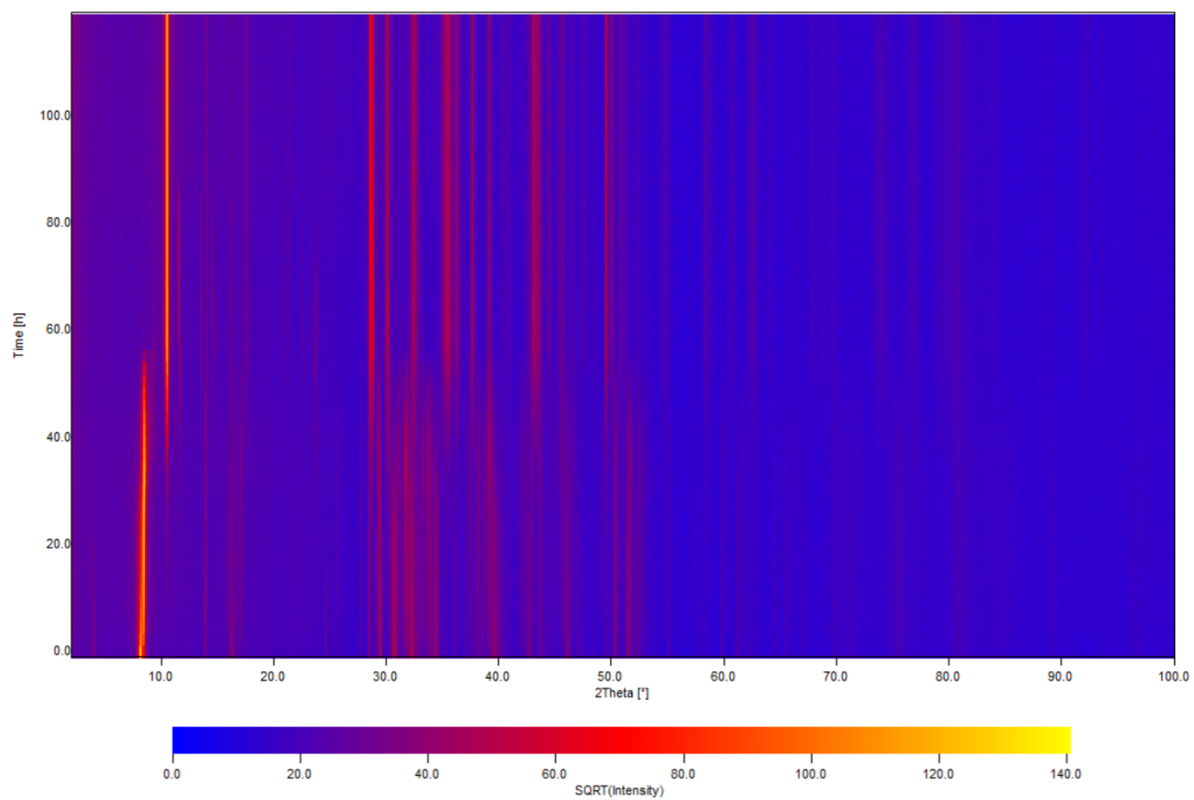


Figure S5. Time resolved PXRD analysis of WTe_2Br_x showing structural evolution while bromine deintercalation.

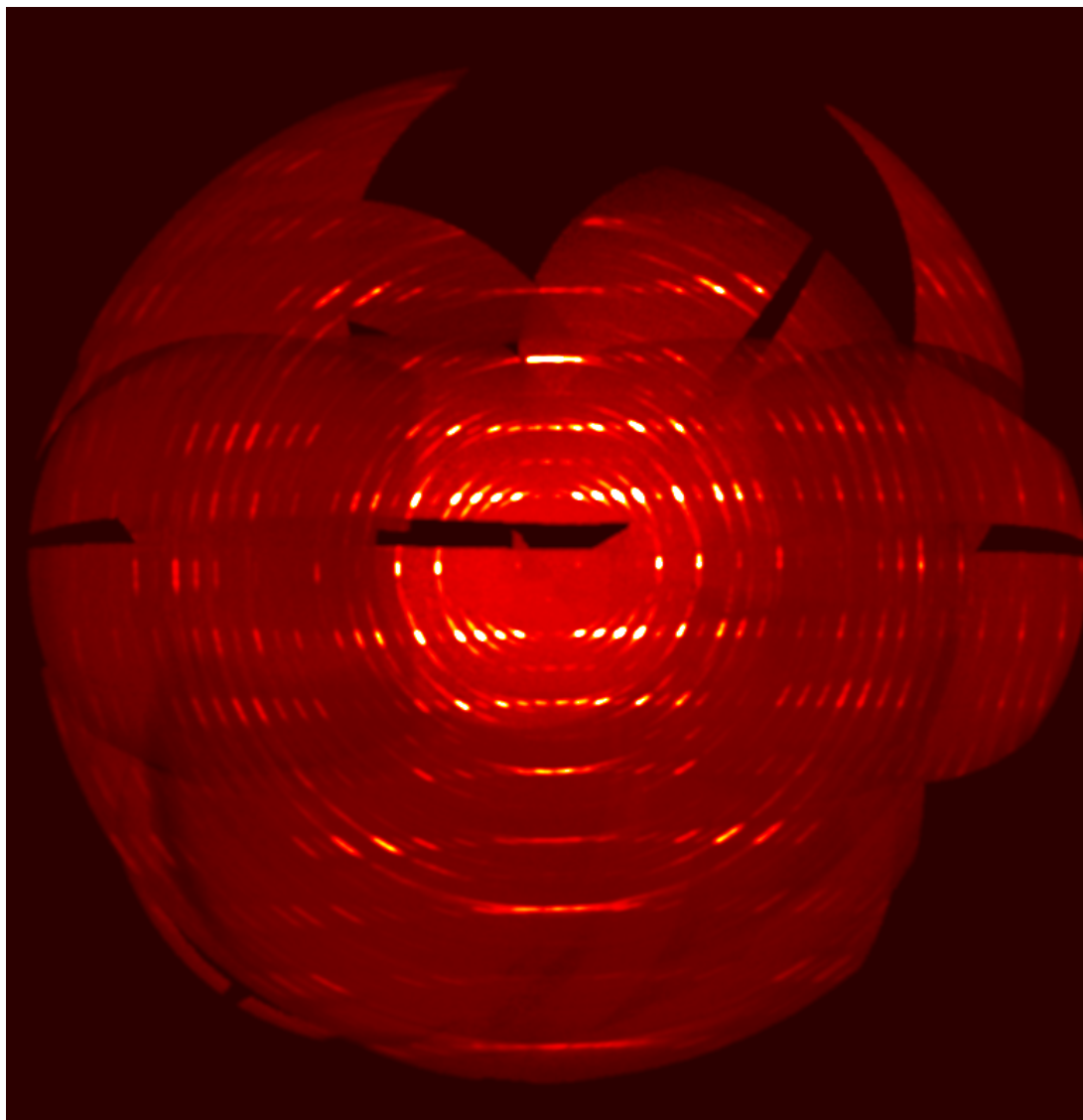


Figure S6. Reconstruction of the $(-3kn)$ of the reciprocal-space plane of $\text{WTe}_2\text{Br}_{1.25}$, highlighting reduced crystallinity due to multiple phase transitions.

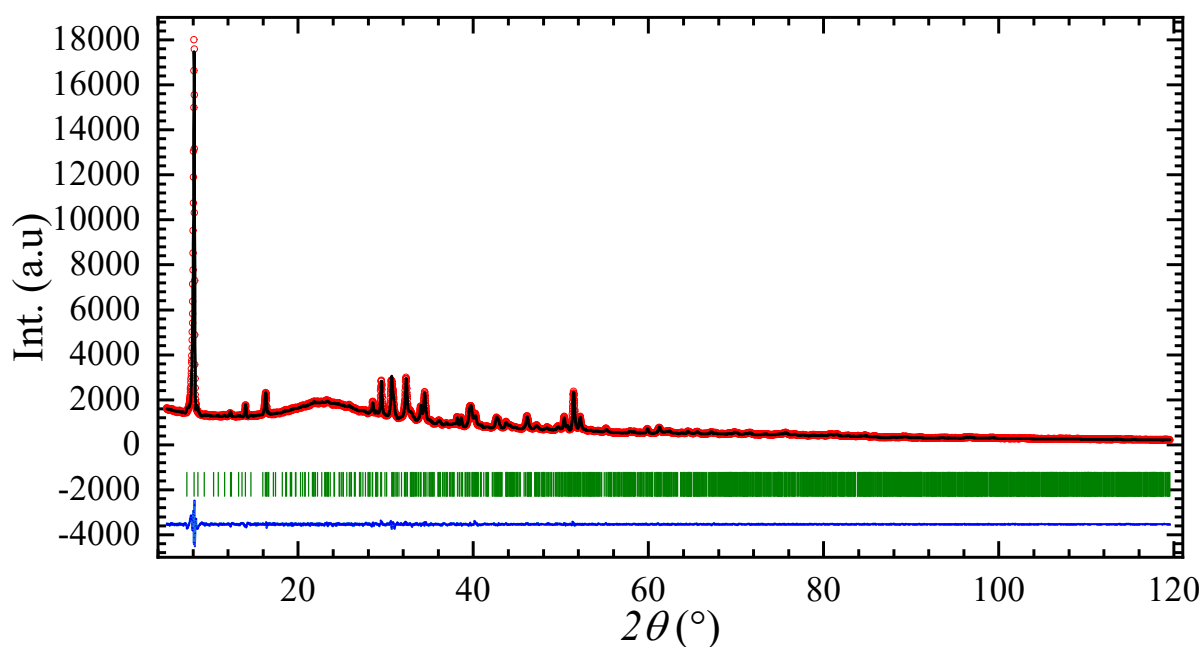


Figure S7. Rietveld refinement of $\text{WTe}_2\text{Br}_{1.25}$ using SXRD results for lattice and position parameters. The refinement shows a good agreement of PXRD and SXRD results.

Specialized Transmission Sample Holder

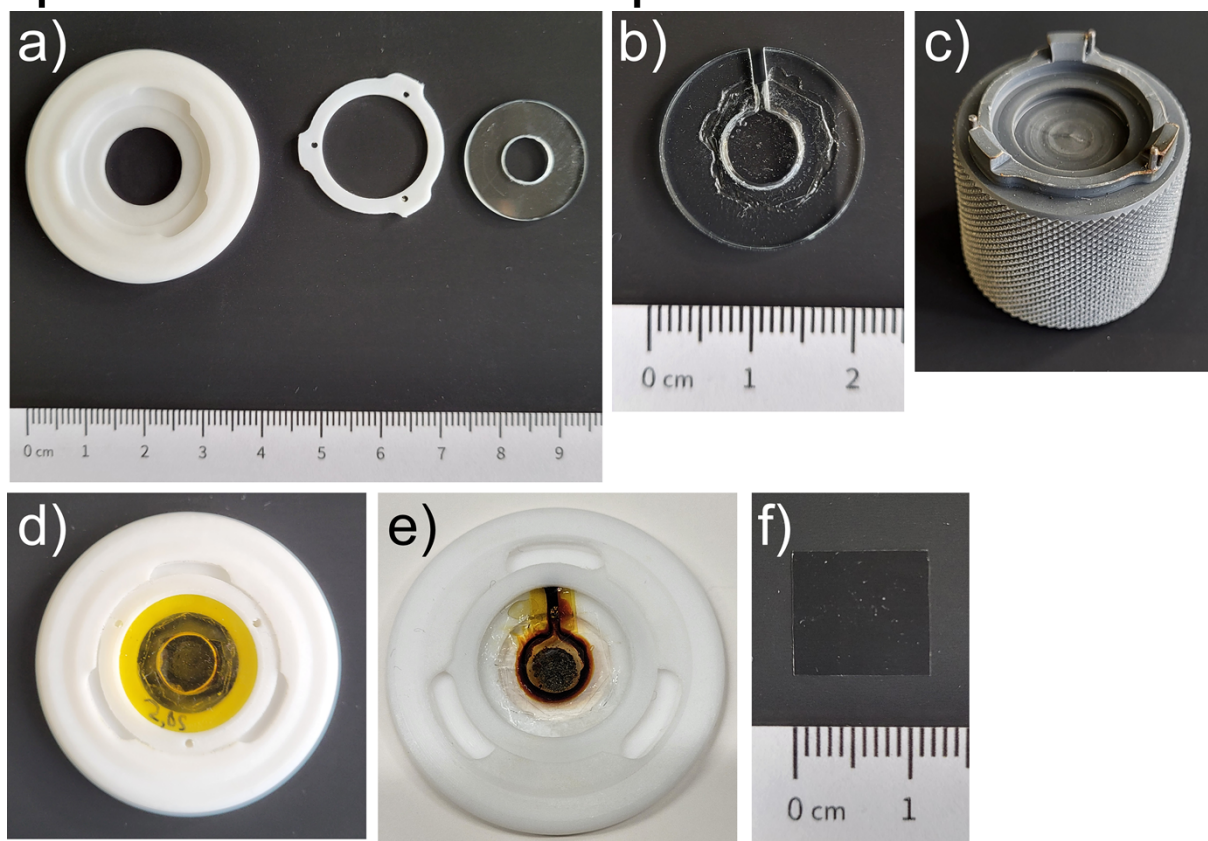
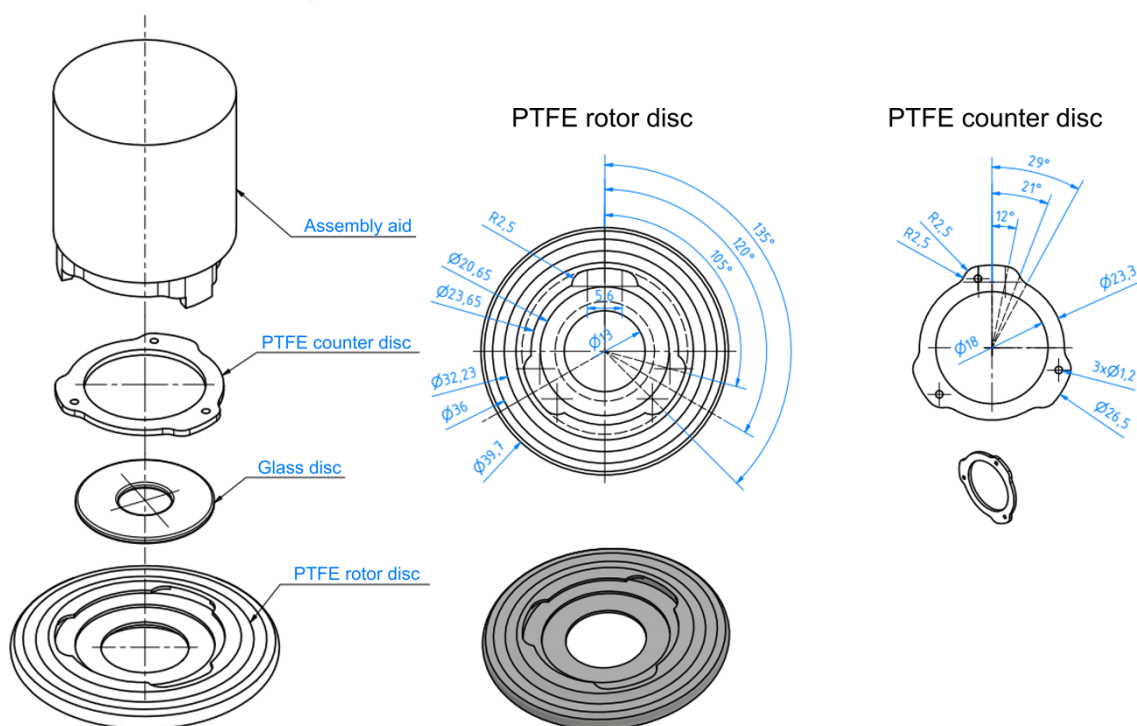
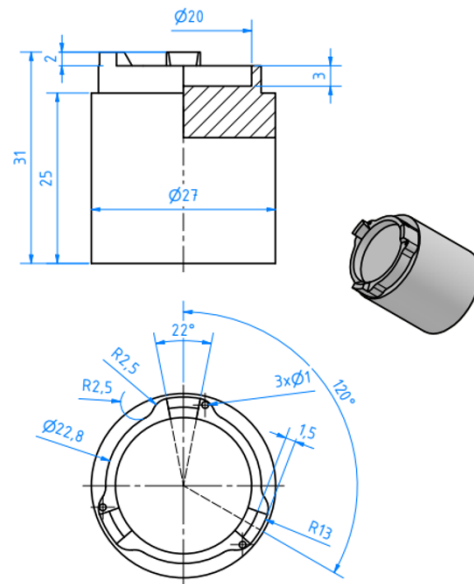


Figure S8. Components and assembly of the redesigned transmission sample holder. (a) PTFE rotor disc, PTFE counter disc, and glass disc. (b) Glass disc with an insertion slit and an ultrathin-glass window bonded to one side. (c) Assembly aid. (d) Transmission holder equipped with an assembled rotor disc (ultrathin glass on one side and Kapton on the other). (e) Examples of assembled rotor discs prepared for bromine-containing samples; for experiments with excess bromine, both sides were sealed with ultrathin glass and the perimeter was sealed with wax and cyanoacrylate under argon. (f) Ultrathin-glass window (Schott AF 32®).

Exploded view drawing



Assembly aid



Glas disc

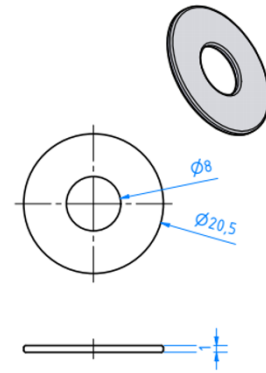


Figure S9. Engineering drawing of the redesigned transmission holder components (PTFE rotor disc, PTFE counter disc, glass disc, and assembly aid), including an exploded view and key dimensions (mm).

Crystallographic details for WTe₂I (supercell)

Table S1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **WTe₂I (supercell)**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_j .

Atom	x	y	z	U_{eq}
W1	10340.8(7)	10074.9(3)	11376.4(7)	7.57(13)
W2	12243.8(8)	10053.4(4)	9537.5(8)	8.11(14)
W3	18784.5(7)	10050.7(4)	13031.9(8)	7.03(13)
W4	16172.5(7)	9956.1(4)	12038.8(8)	7.31(13)
W5	17157.2(7)	10038.2(4)	14661.4(8)	7.08(13)
W6	14525.4(6)	9978.7(3)	13694.4(6)	6.94(11)
Te1	9174.9(11)	9090.6(5)	10028.2(11)	8.51(18)
Te2	12484.8(13)	10971.8(6)	8234.0(12)	9.0(2)
Te3	15801.4(13)	9057.9(6)	13340.0(12)	8.5(2)
Te4	14134.7(11)	9056.6(5)	14952.2(11)	7.95(18)
Te5	17459.0(13)	10958.6(6)	13354.1(12)	8.2(2)
Te6	9010.4(12)	10972.9(6)	11644.3(12)	7.4(2)
Te7	10862.9(11)	9332.5(6)	13394.7(12)	7.9(2)
Te8	20758.1(12)	10691.9(6)	14936.8(12)	7.6(2)
Te9	17602.7(11)	9298.0(5)	16706.1(11)	7.33(18)
Te10	14124.3(12)	10697.7(6)	11583.2(12)	8.0(2)
Te11	14260.3(12)	9310.0(6)	10046.9(12)	7.9(2)
Te12	12502.9(11)	9513.6(5)	11682.9(11)	8.48(17)
I1	12390.5(13)	8251.2(5)	11550.8(13)	17.6(2)
I2A	17522(5)	7500	13841(6)	52.0(13)
I3A	15352(3)	7500	11151(4)	31.9(8)
I4A	13166(6)	7500	8826(6)	36.5(11)
I5A	10319(5)	7500	6530(4)	40.1(10)
I6A	15867(6)	7500	15192(6)	58.0(14)
I7A	9118(7)	7500	8110(8)	73.7(18)
I8A	14665(5)	7500	16743(4)	39.4(10)
I9A	11810(6)	7500	14423(6)	40.6(12)
I10A	9570(4)	7500	12122(4)	34.9(8)
I11A	7449(5)	7500	9458(6)	56.5(14)
I2B	13600(20)	12500	10224(16)	58(5)
I4B	14321(17)	12500	13021(15)	44(4)
I3B	11067(17)	12500	8914(17)	44(4)
I5B	10720(20)	12500	11142(12)	50(5)
I6B	14478(12)	12500	15563(13)	29(3)
I7B	10810(20)	12500	13717(12)	50(5)
I8B	14046(17)	12500	17773(14)	38(3)
I9B	11430(20)	12500	16481(16)	51(4)
I10B	12130(30)	7500	14788(16)	50(8)
I11B	12890(30)	7500	8436(15)	43(7)

Table S2: Anisotropic Displacement Parameters ($\times 10^4$) for **WTe₂I (supercell)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	5.7(3)	10.2(3)	6.0(3)	-0.1(2)	2.0(2)	-0.5(2)
W2	6.4(3)	10.8(3)	6.0(4)	0.4(3)	1.9(3)	-1.0(3)
W3	4.9(3)	10.9(3)	5.3(3)	0.4(3)	2.3(2)	-1.1(3)
W4	5.1(3)	11.3(3)	5.7(4)	0.5(3)	2.7(2)	-1.2(3)
W5	4.8(3)	11.1(3)	5.3(4)	0.8(3)	2.3(2)	-1.3(3)
W6	4.7(4)	10.6(3)	5.4(4)	0.9(2)	2.3(2)	-1.4(2)
Te1	9.9(6)	11.5(4)	3.9(5)	1.0(4)	3.1(3)	-2.5(4)
Te2	10.5(6)	11.3(6)	6.0(6)	0.5(4)	4.5(5)	-1.7(4)
Te3	11.2(6)	11.0(5)	3.9(5)	1.0(4)	4.0(4)	-1.8(4)
Te4	11.0(6)	10.6(4)	3.3(5)	1.0(4)	4.3(3)	-1.7(4)
Te5	10.5(6)	10.9(5)	4.1(5)	1.0(4)	4.1(5)	-1.6(4)
Te6	8.7(5)	10.2(5)	5.0(5)	0.4(4)	4.6(4)	-1.0(4)
Te7	3.5(5)	13.3(5)	6.6(5)	0.2(4)	2.2(4)	-1.9(4)
Te8	3.2(5)	12.1(5)	7.8(6)	0.5(4)	2.8(4)	-1.7(4)
Te9	3.4(5)	11.4(4)	7.4(5)	0.9(4)	2.7(3)	-1.3(4)
Te10	3.7(5)	11.8(5)	8.4(6)	0.9(4)	2.8(4)	-1.4(4)
Te11	3.5(5)	12.6(5)	8.1(6)	1.3(5)	3.0(4)	-0.7(4)
Te12	4.2(5)	14.5(4)	7.7(5)	0.0(4)	3.6(3)	-1.5(4)
I1	20.0(6)	12.4(5)	20.0(7)	-1.0(5)	9.0(4)	-0.2(4)
I2A	62(3)	26.7(18)	92(4)	0	57(3)	0
I3A	39.1(19)	16.2(13)	49(2)	0	27.0(17)	0
I4A	49(3)	21.2(17)	44(3)	0	25(3)	0
I5A	63(3)	17.9(14)	49(2)	0	34(2)	0
I6A	91(4)	17.1(14)	79(4)	0	50(3)	0
I7A	100(5)	16.6(16)	110(6)	0	53(4)	0
I8A	65(3)	19.7(14)	49(2)	0	40(2)	0
I9A	53(3)	22.1(18)	52(4)	0	29(3)	0
I10A	46(2)	17.4(13)	54(2)	0	34.1(18)	0
I11A	64(3)	29.3(19)	99(4)	0	58(3)	0
I2B	91(15)	53(10)	29(8)	0	26(9)	0
I4B	55(10)	29(6)	34(7)	0	9(7)	0
I3B	56(10)	27(7)	51(10)	0	27(8)	0
I5B	97(13)	11(5)	10(5)	0	-2(7)	0
I6B	31(3)	25(3)	26(3)	0	10(2)	0
I7B	85(14)	37(7)	10(5)	0	6(6)	0
I8B	67(10)	18(5)	33(7)	0	27(7)	0
I9B	86(14)	43(8)	39(8)	0	42(9)	0
I10B	73(16)	26(8)	7(6)	0	-19(7)	0
I11B	70(15)	19(7)	5(7)	0	-13(7)	0

Table S3: Bond Lengths in Å for **WTe₂I** (supercell).

Atom	Atom	Length / Å	Atom	Atom	Length / Å
W1	W1 ¹	3.0734(14)	W5	Te5	2.6953(15)
W1	W2 ¹	2.8219(10)	W5	Te7 ²	2.8304(15)
W1	Te1	2.6803(13)	W5	Te8 ⁵	2.8419(15)
W1	Te1 ¹	2.7458(15)	W5	Te9	2.8035(14)
W1	Te6	2.6604(15)	W6	W6 ²	2.8355(14)
W1	Te7	2.7622(14)	W6	Te3	2.6978(16)
W1	Te9 ²	2.8591(13)	W6	Te4	2.7049(14)
W1	Te12	2.7676(14)	W6	Te4 ²	2.7085(13)
W2	W3 ³	2.7874(10)	W6	Te9 ²	2.8771(14)
W2	Te1 ¹	2.7594(16)	W6	Te10	2.8554(14)
W2	Te2	2.6596(15)	W6	Te12	2.7383(12)
W2	Te6 ¹	2.7211(16)	Te12	I1	2.7663(15)
W2	Te10	2.8528(16)	I2A	I3A	3.111(8)
W2	Te11	2.7641(15)	I2A	I6A	3.136(8)
W2	Te12	2.7478(15)	I3A	I4A	2.846(7)
W3	W4	2.8361(11)	I5A	I7A	2.906(9)
W3	Te2 ³	2.7492(16)	I6A	I8A	2.875(7)
W3	Te5	2.6997(16)	I7A	I11A	3.148(10)
W3	Te6 ⁴	2.7259(15)	I9A	I10A	2.863(8)
W3	Te7 ⁴	2.8329(15)	I10A	I11A	3.068(8)
W3	Te8 ⁵	2.7905(15)	I2B	I4B	3.10(2)
W3	Te8	2.8190(15)	I2B	I3B	2.73(3)
W4	W5	2.8479(10)	I4B	I6B	3.01(2)
W4	Te2 ³	2.7213(16)	I3B	I5B	2.93(3)
W4	Te3	2.6904(15)	I5B	I7B	3.09(2)
W4	Te5	2.7388(16)	I6B	I8B	2.97(2)
W4	Te10	2.8055(15)	I7B	I9B	3.09(2)
W4	Te11	2.8387(16)	I8B	I9B	2.82(3)
W4	Te11 ³	2.8393(15)			
W5	W6	2.8572(11)			
W5	Te3	2.7292(16)			
W5	Te4 ²	2.7022(16)			

¹2-x,2-y,2-z; ²3-x,2-y,3-z; ³3-x,2-y,2-z; ⁴1+x,+y,+z; ⁵4-x,2-y,3-z

Table S4: Atomic Occupancies for all atoms that are not fully occupied in **WTe₂I (supercell)**.

Atom	Occupancy	Atom	Occupancy
I2A	0.803(4)	I2B	0.197(4)
I3A	0.803(4)	I4B	0.197(4)
I4A	0.803(4)	I3B	0.197(4)
I5A	0.803(4)	I5B	0.197(4)
I6A	0.803(4)	I6B	0.197(4)
I7A	0.803(4)	I7B	0.197(4)
I8A	0.803(4)	I8B	0.197(4)
I9A	0.803(4)	I9B	0.197(4)
I10A	0.803(4)	I10B	0.197(4)
I11A	0.803(4)	I11B	0.197(4)

Crystallographic details for incommensurate WTe₂I

Table S5: Occupational waves for incommensurate WTe₂I.

Atom	Wave/Parameter	Occ
Te2	delta	0.8318(8)
	x40	0.2710(4)
Te3	delta	0.1682(8)
	x40	0.7754(5)
I1	delta	0.8318(8)
	x40	0.3929(4)
I2	delta	0.8318(8)
	x40	0.1633(4)
I3	delta	0.1682(8)
	x40	0.7865(4)

Table S6: Positional parameters for incommensurate WTe₂I.

Atom	Occ	Wave	x	y	z	Ueq/Uiso
W1	1		0.32142(3)	0.495374(9)	0.25174(13)	0.00479(7)
		s,1	-0.00194(5)	0.001783(16)	-0.0072(12)	
		c,1	0.00190(5)	-0.001740(16)	-0.0085(10)	
		s,2	-0.00203(5)	-0.000332(16)	0.0046(2)	
		c,2	0.00211(5)	-0.000476(16)	0.0091(8)	
		s,3	-0.0010(3)	0.00067(8)	-0.0068(9)	
		c,3	0.0032(2)	-0.00036(7)	0.0057(11)	
		s,4	0	0	-0.067(2)	
		c,4	0.3826(5)	1	0	
Te1	1		0.57919(5)	0.595074(13)	0.24836(18)	0.00651(7)
		s,1	-0.00264(8)	0.00038(3)	0.02596(15)	
		c,1	-0.01089(8)	-0.00028(3)	-0.01238(15)	
		s,2	0.00422(8)	-0.00187(3)	0.00920(15)	
		c,2	0.00324(8)	-0.00144(3)	-0.00400(16)	
Te2	0.8318(8)		0.07022(7)	0.56927(2)	0.7492(2)	0.00552(9)
		o,1	-0.00111(10)	0.00106(3)	0.0018(2)	
		o,2	0.00011(6)	-0.00041(2)	-0.00017(12)	
		o,3	-0.00154(8)	0.00046(3)	-0.01128(14)	
		o,4	0.00000(13)	-0.00028(4)	0.0047(3)	
Te3	0.1682(8)		0.0817(4)	0.54812(10)	0.7526(8)	0.0056(4)
		o,1	-0.0013(5)	-0.00001(17)	-0.0011(13)	
		o,2	-0.001(3)	0.0001(8)	0.006(6)	
I1	0.8318(8)		0.34767(14)	0.75	0.7591(4)	0.0218(3)
		o,1	0.02889(15)	0	0.0932(3)	
		o,2	-0.01800(15)	0	-0.0089(4)	
		o,3	0.0001(2)	0	-0.0335(4)	
		o,4	0.00596(17)	0	-0.0221(4)	
		o,5	0.0008(3)	0	0.0010(5)	
		o,6	-0.0026(2)	0	-0.0113(5)	
I2	0.8318(8)		-0.17524(15)	0.75	0.7370(4)	0.0254(3)
		o,1	-0.03392(15)	0	-0.0879(3)	
		o,2	-0.00962(16)	0	0.0148(4)	
		o,3	-0.00434(19)	0	-0.0074(5)	
		o,4	-0.0032(2)	0	0.0410(5)	
		o,5	-0.0020(2)	0	-0.0104(6)	
		o,6	-0.0011(3)	0	-0.0055(5)	
I3	0.1682(8)		0.1052(2)	0.67498(7)	0.7481(5)	0.0151(3)
		o,1	-0.0031(8)	-0.0001(2)	0.0282(15)	

o,2 -0.004(4) 0.0007(12) -0.004(7)

Table S7: ADP harmonic parameters for incommensurate WTe₂l.

Atom	Wave	U11	U22	U33	U12	U13	U23
W1		0.00241(9)	0.00714(9)	0.00482(17)	-0.00014(6)	-0.00143(14)	0.00020(12)
	s,1	-0.00019(12)	0.00021(13)	-0.0004(2)	0.00008(11)	0.00026(12)	-0.00021(13)
	c,1	0.00005(12)	-0.00017(14)	0.00099(17)	-0.00011(11)	-0.00007(13)	-0.00023(13)
Te1		0.00502(12)	0.00856(13)	0.00596(13)	-0.00101(10)	-0.0012(2)	-0.0002(2)
	s,1	0.0010(2)	0.0013(2)	0.0005(2)	-0.00105(18)	-0.00049(16)	0.00068(17)
	c,1	0.0012(2)	0.0029(2)	0.0015(2)	-0.00243(17)	0.00108(17)	-0.00133(17)
Te2		0.00326(14)	0.00726(16)	0.00603(15)	0.00004(13)	-0.0015(3)	-0.0002(3)
	o,1	-0.00010(18)	-0.0005(2)	0.0018(2)	0.00021(17)	0.00013(15)	0.00003(19)
	o,2	-0.00001(16)	0.00011(18)	-0.00068(18)	0.00009(14)	-0.00018(13)	-0.00017(14)
Te3		0.0031(4)	0.0086(6)	0.0050(9)	-0.0011(5)	-0.0010(5)	0.0001(6)
I1		0.0176(4)	0.0156(3)	0.0323(6)	0	-0.0053(4)	0
	o,1	0.0024(4)	-0.0014(4)	0.0101(6)	0	-0.0048(4)	0
	o,2	0.0025(5)	-0.0015(4)	-0.0115(7)	0	0.0078(5)	0
I2		0.0183(4)	0.0158(3)	0.0419(7)	0	-0.0045(4)	0
	o,1	0.0024(4)	-0.0014(4)	0.0123(7)	0	-0.0090(4)	0
	o,2	-0.0010(5)	0.0016(4)	0.0149(6)	0	-0.0041(5)	0
I3		0.0174(6)	0.0089(5)	0.0191(7)	-0.0002(4)	-0.0017(5)	0.0005(5)

Table S8: List of used orthogonalized functions for incommensurate WTe_2 .

[illegible]

Table S9: List of distances for incommensurate WTe₂I.

	average / Å	min / Å	max / Å
W1-W1 ⁱ	2.870(11)	2.781(16)	3.097(16)
W1-W1 ⁱⁱ	2.846(11)	2.830(14)	2.862(14)
W1-Te1	2.720(3)	2.684(3)	2.755(3)
W1-Te1 ⁱ	2.706(8)	2.555(12)	2.856(12)
W1-Te1 ⁱⁱ	2.702(8)	2.543(12)	2.851(12)
W1-Te2 ⁱⁱⁱ	2.820(7)	2.749(9)	2.905(9)
W1-Te2	2.819(7)	2.739(9)	2.889(9)
W1-Te2 ^{iv}	2.845(3)	2.813(3)	2.877(3)
W1-Te3 ⁱⁱⁱ	2.76(4)	2.73(7)	2.78(7)
W1-Te3	2.73(4)	2.45(7)	2.78(7)
W1-Te3 ^{iv}	2.74(3)	2.73(6)	2.74(6)
Te3-I3	2.77(3)	2.76(6)	2.79(6)
I1-I1 ⁱⁱⁱ	3.415(6)	2.769(8)	4.018(8)
I1-I1 ^v	3.405(6)	2.769(8)	4.018(8)
I1-I2	3.341(6)	2.688(8)	3.933(8)
I1-I2 ^{vi}	3.189(6)	2.887(8)	3.702(8)
I1-I2 ^{vii}	3.341(6)	2.688(8)	3.933(8)
I1-I2 ^{viii}	3.189(6)	2.887(8)	3.702(8)
I1-I3 ⁱⁱⁱ	4.084(9)	4.011(15)	4.255(15)
I1-I3 ^v	4.297(9)	4.140(13)	4.407(13)
I1-I3 ^{ix}	4.084(9)	4.011(15)	4.255(15)
I1-I3 ^x	4.297(9)	4.140(13)	4.407(13)
I2-I2 ⁱⁱⁱ	3.419(7)	2.765(9)	4.028(9)
I2-I2 ^v	3.416(7)	2.765(9)	4.029(9)
I2-I2 ^{ix}	3.419(7)	2.765(9)	4.028(9)
I2-I2 ^{vii}	0	0	0
I2-I2 ^x	3.416(7)	2.765(9)	4.029(9)
I2-I3 ^v	4.123(8)	4.064(14)	4.250(14)
I2-I3 ^x	4.123(8)	4.064(14)	4.250(14)
I3-I3 ⁱⁱⁱ	3.659(15)	3.659(15)	3.659(15)
I3-I3 ^v	3.658(15)	3.658(15)	3.658(15)
I3-I3 ^{vii}	3.272(11)	3.24(2)	3.29(2)
(i)	-x+1,-y+1,-z		
(ii)	-x+1,-y+1,-z+1		
(iii)	x,y,z-1		
(iv)	-x,-y+1,-z+1		
(v)	x,y,z+1		
(vi)	x+1,y,z		
(vii)	x,-y+3/2,z		
(viii)	x+1,-y+3/2,z		
(ix)	x,-y+3/2,z-1		
(x)	x,-y+3/2,z+1		
(xi)	x-1,y,z		

Table S10: List of angles for incommensurate WTe₂l.

	average / °	min / °	max / °
W1 ⁱ -W1-W1 ⁱⁱ	74.7(3)	70.4(3)	83.2(3)
W1 ⁱ -W1-Te1	57.78(14)	55.55(17)	59.50(17)
W1 ⁱ -W1-Te1 ⁱ	58.3(2)	53.7(2)	60.5(3)
W1 ⁱ -W1-Te1 ⁱⁱ	104.93(15)	102.07(12)	110.76(16)
W1 ⁱ -W1-Te2 ⁱⁱⁱ	93.3(3)	90.1(4)	96.5(4)
W1 ⁱ -W1-Te2	140.27(13)	137.64(16)	143.27(12)
W1 ⁱ -W1-Te2 ^{iv}	136.1(4)	127.6(5)	142.3(5)
W1 ⁱ -W1-Te3 ⁱⁱⁱ	82.2(14)	81.4(14)	89.2(14)
W1 ⁱ -W1-Te3	145.6(13)	145.2(14)	146.3(13)
W1 ⁱ -W1-Te3 ^{iv}	139.1(15)	138.6(15)	140.2(15)
W1 ⁱⁱ -W1-Te1	58.04(14)	54.70(18)	61.91(19)
W1 ⁱⁱ -W1-Te1 ⁱ	104.74(15)	100.93(13)	110.0(2)
W1 ⁱⁱ -W1-Te1 ⁱⁱ	58.6(2)	56.8(3)	59.9(3)
W1 ⁱⁱ -W1-Te2 ⁱⁱⁱ	140.51(12)	137.11(13)	144.01(11)
W1 ⁱⁱ -W1-Te2	92.9(3)	90.2(4)	94.1(3)
W1 ⁱⁱ -W1-Te2 ^{iv}	137.0(4)	133.2(6)	141.6(5)
W1 ⁱⁱ -W1-Te3 ⁱⁱⁱ	145.8(12)	145.2(12)	146.6(13)
W1 ⁱⁱ -W1-Te3	87.4(14)	86.4(14)	93.9(16)
W1 ⁱⁱ -W1-Te3 ^{iv}	138.3(15)	138.0(15)	138.7(15)
Te1-W1-Te1 ⁱ	116.1(3)	109.3(4)	119.9(3)
Te1-W1-Te1 ⁱⁱ	116.6(3)	111.1(4)	121.3(3)
Te1-W1-Te2 ⁱⁱⁱ	83.74(15)	81.31(14)	86.70(13)
Te1-W1-Te2	83.82(14)	81.73(17)	86.06(14)
Te1-W1-Te2 ^{iv}	155.34(14)	152.2(3)	159.93(11)
Te1-W1-Te3 ⁱⁱⁱ	85.2(12)	83.5(12)	87.7(13)
Te1-W1-Te3	87.0(13)	85.8(13)	91.8(14)
Te1-W1-Te3 ^{iv}	151.2(13)	149.5(13)	152.0(13)
Te1 ⁱ -W1-Te1 ⁱⁱ	79.86(7)	77.14(7)	84.58(9)
Te1 ⁱ -W1-Te2 ⁱⁱⁱ	99.9(3)	95.4(4)	104.4(5)
Te1 ⁱ -W1-Te2	158.24(13)	156.7(3)	160.69(10)
Te1 ⁱ -W1-Te2 ^{iv}	81.23(16)	79.4(2)	84.66(17)
Te1 ⁱ -W1-Te3 ⁱⁱⁱ	85.8(14)	84.0(14)	88.1(14)
Te1 ⁱ -W1-Te3	153.9(13)	153.6(14)	154.3(12)
Te1 ⁱ -W1-Te3 ^{iv}	85.3(14)	84.7(14)	86.3(14)
Te1 ⁱⁱ -W1-Te2 ⁱⁱⁱ	158.39(13)	156.05(10)	159.76(11)
Te1 ⁱⁱ -W1-Te2	100.1(3)	96.8(4)	103.8(5)
Te1 ⁱⁱ -W1-Te2 ^{iv}	81.39(16)	78.55(14)	85.19(17)
Te1 ⁱⁱ -W1-Te3 ⁱⁱⁱ	154.5(12)	154.2(12)	154.9(12)
Te1 ⁱⁱ -W1-Te3	86.4(14)	84.5(14)	98.7(16)
Te1 ⁱⁱ -W1-Te3 ^{iv}	85.2(14)	84.6(14)	86.1(14)
Te2 ⁱⁱⁱ -W1-Te2	75.02(8)	72.66(7)	77.19(8)
Te2 ⁱⁱⁱ -W1-Te2 ^{iv}	78.53(13)	76.69(13)	80.30(15)
Te2 ⁱⁱⁱ -W1-Te3	80.7(14)	79.8(14)	81.2(13)
Te2 ⁱⁱⁱ -W1-Te3 ^{iv}	71.7(14)	71.4(14)	72.2(14)
Te2-W1-Te2 ^{iv}	78.43(13)	76.87(16)	79.87(15)
Te2-W1-Te3 ⁱⁱⁱ	79.0(14)	78.4(14)	80.0(14)
Te2-W1-Te3 ^{iv}	71.8(14)	71.1(14)	72.2(14)
Te2 ^{iv} -W1-Te3 ⁱⁱⁱ	71.1(12)	70.7(12)	72.2(12)
Te2 ^{iv} -W1-Te3	71.9(13)	70.7(12)	74.8(14)
Te3 ⁱⁱⁱ -W1-Te3	82.8(16)	82.8(16)	82.8(16)
W1-Te1-W1 ⁱ	63.9(2)	61.8(3)	69.3(3)
W1-Te1-W1 ⁱⁱ	63.3(2)	61.3(3)	65.4(3)
W1 ⁱ -Te1-W1 ⁱⁱ	79.8(3)	75.3(3)	89.7(3)
W1-Te2-W1 ^v	73.8(3)	71.3(3)	75.8(2)
W1-Te2-W1 ^{iv}	102.09(16)	99.7(2)	105.4(2)
W1 ^v -Te2-W1 ^{iv}	102.19(16)	99.1(2)	105.36(19)
W1-Te3-W1 ^v	89.9(10)	81.8(5)	90.6(17)

W1-Te3-W1 ^{iv}	110.9(11)	110.1(17)	114.4(5)
W1-Te3-I3	113.4(11)	112(2)	119.1(5)
W1 ^v -Te3-W1 ^{iv}	111.2(11)	110.1(7)	111.6(9)
W1 ^v -Te3-I3	114.2(11)	112.3(5)	115.4(7)
W1 ^{iv} -Te3-I3	114.7(10)	113.6(4)	115.3(19)
I1 ⁱⁱⁱ -I1-I1 ^v	176.1(2)	171.3(2)	180
I1 ⁱⁱⁱ -I1-I2	89.3(2)	76.22(19)	107.0(2)
I1 ⁱⁱⁱ -I1-I2 ^{vi}	89.7(2)	82.1(2)	97.28(17)
I1 ⁱⁱⁱ -I1-I2 ^{vii}	89.3(2)	76.22(19)	107.0(2)
I1 ⁱⁱⁱ -I1-I2 ^{viii}	89.7(2)	82.1(2)	97.28(17)
I1 ⁱⁱⁱ -I1-I3 ^v	154.94(10)	152.26(10)	156.47(8)
I1 ⁱⁱⁱ -I1-I3 ^x	154.94(10)	152.26(10)	156.47(8)
I1 ^v -I1-I2	91.0(2)	81.1(2)	100.33(17)
I1 ^v -I1-I2 ^{vi}	94.6(2)	77.28(18)	99.9(2)
I1 ^v -I1-I2 ^{vii}	91.0(2)	81.1(2)	100.33(17)
I1 ^v -I1-I2 ^{viii}	94.6(2)	77.28(18)	99.9(2)
I1 ^v -I1-I3 ⁱⁱⁱ	149.64(11)	148.82(13)	151.36(8)
I1 ^v -I1-I3 ^{ix}	149.64(11)	148.82(13)	151.36(8)
I2-I1-I2 ^{vi}	167.5(2)	155.8(2)	180
I2-I1-I2 ^{vii}	0	0	0
I2-I1-I2 ^{viii}	167.5(2)	155.8(2)	180
I2-I1-I3 ⁱⁱⁱ	75.05(15)	72.67(16)	76.11(14)
I2-I1-I3 ^v	66.88(13)	65.76(11)	69.54(16)
I2-I1-I3 ^{ix}	75.05(15)	72.67(16)	76.11(14)
I2-I1-I3 ^x	66.88(13)	65.76(11)	69.54(16)
I2 ^{vi} -I1-I2 ^{vii}	167.5(2)	155.8(2)	180
I2 ^{vi} -I1-I2 ^{viii}	0	0	0
I2 ^{vi} -I1-I3 ⁱⁱⁱ	102.09(16)	101.80(18)	102.33(15)
I2 ^{vi} -I1-I3 ^v	95.29(14)	91.83(14)	102.89(12)
I2 ^{vi} -I1-I3 ^{ix}	102.09(16)	101.80(18)	102.33(15)
I2 ^{vi} -I1-I3 ^x	95.29(14)	91.83(14)	102.89(12)
I2 ^{vii} -I1-I2 ^{viii}	167.5(2)	155.8(2)	180
I2 ^{vii} -I1-I3 ⁱⁱⁱ	75.05(15)	72.67(16)	76.11(14)
I2 ^{vii} -I1-I3 ^v	66.88(13)	65.76(11)	69.54(16)
I2 ^{vii} -I1-I3 ^{ix}	75.05(15)	72.67(16)	76.11(14)
I2 ^{vii} -I1-I3 ^x	66.88(13)	65.76(11)	69.54(16)
I2 ^{viii} -I1-I3 ⁱⁱⁱ	102.09(16)	101.80(18)	102.33(15)
I2 ^{viii} -I1-I3 ^v	95.29(14)	91.83(14)	102.89(12)
I2 ^{viii} -I1-I3 ^{ix}	102.09(16)	101.80(18)	102.33(15)
I2 ^{viii} -I1-I3 ^x	95.29(14)	91.83(14)	102.89(12)
I3 ⁱⁱⁱ -I1-I3 ^{ix}	47.28(14)	44.9(2)	48.29(11)
I3 ^v -I1-I3 ^x	44.80(13)	43.19(11)	46.3(2)
I1 ^{xi} -I2-I1	168.9(2)	157.3(3)	180
I1 ^{xi} -I2-I2 ⁱⁱⁱ	94.48(18)	77.86(17)	99.7(2)
I1 ^{xi} -I2-I2 ^v	89.74(19)	82.2(2)	97.1(2)
I1 ^{xi} -I2-I2 ^{ix}	94.48(18)	77.86(17)	99.7(2)
I1 ^{xi} -I2-I2 ^{vii}	0	0	0
I1 ^{xi} -I2-I2 ^x	89.74(19)	82.2(2)	97.1(2)
I1 ^{xi} -I2-I3 ^v	105.61(14)	104.61(18)	106.13(11)
I1 ^{xi} -I2-I3 ^x	105.61(14)	104.61(18)	106.13(11)
I1-I2-I2 ⁱⁱⁱ	90.67(18)	82.37(19)	99.6(2)
I1-I2-I2 ^v	88.91(19)	76.01(17)	105.7(2)
I1-I2-I2 ^{ix}	90.67(18)	82.37(19)	99.6(2)
I1-I2-I2 ^{vii}	0	0	0
I1-I2-I2 ^x	88.91(19)	76.01(17)	105.7(2)
I1-I2-I3 ^v	73.38(13)	71.73(14)	74.28(12)
I1-I2-I3 ^x	73.38(13)	71.73(14)	74.28(12)
I2 ⁱⁱⁱ -I2-I2 ^v	175.9(2)	171.3(3)	179.53(17)
I2 ⁱⁱⁱ -I2-I2 ^{ix}	0	0	0
I2 ⁱⁱⁱ -I2-I2 ^{vii}	0	0	0

I2 ⁱⁱⁱ -I2-I2 ^x	175.9(2)	171.3(3)	179.53(17)
I2 ⁱⁱⁱ -I2-I3 ^v	148.13(10)	147.38(11)	149.85(12)
I2 ⁱⁱⁱ -I2-I3 ^x	148.13(10)	147.38(11)	149.85(12)
I2 ^v -I2-I2 ^{ix}	175.9(2)	171.3(3)	179.53(16)
I2 ^v -I2-I2 ^{vii}	0	0	0
I2 ^v -I2-I2 ^x	0	0	0
I2 ^{ix} -I2-I2 ^{vii}	0	0	0
I2 ^{ix} -I2-I2 ^x	175.9(2)	171.3(3)	179.53(17)
I2 ^{ix} -I2-I3 ^v	148.13(10)	147.38(11)	149.85(12)
I2 ^{ix} -I2-I3 ^x	148.13(10)	147.38(11)	149.85(12)
I2 ^{vii} -I2-I2 ^x	0	0	0
I2 ^{vii} -I2-I3 ^v	0	0	0
I2 ^{vii} -I2-I3 ^x	0	0	0
I3 ^v -I2-I3 ^x	46.79(13)	44.87(12)	47.60(14)
Te3-I3-I1 ⁱⁱⁱ	113.7(8)	112.1(4)	114.3(14)
Te3-I3-I1 ^v	114.6(8)	113.1(7)	115.4(4)
Te3-I3-I2 ⁱⁱⁱ	112.4(8)	110.8(4)	113.0(13)
Te3-I3-I2 ^{ix}	112.4(8)	110.8(4)	113.0(13)
Te3-I3-I3 ⁱⁱⁱ	87.8(5)	87.8(5)	87.8(5)
Te3-I3-I3 ^v	88.2(5)	88.2(5)	88.2(5)
Te3-I3-I3 ^{vii}	176.6(8)	176.4(12)	176.9(5)
I1 ⁱⁱⁱ -I3-I1 ^v	119.6(2)	118.4(3)	120.96(17)
I1 ⁱⁱⁱ -I3-I2 ⁱⁱⁱ	39.78(14)	38.23(17)	42.02(13)
I1 ⁱⁱⁱ -I3-I2 ^{ix}	39.78(14)	38.23(17)	42.02(13)
I1 ⁱⁱⁱ -I3-I3 ^v	152.4(2)	152.4(2)	152.4(2)
I1 ⁱⁱⁱ -I3-I3 ^{vii}	67.62(17)	66.9(2)	68.42(15)
I1 ^v -I3-I2 ⁱⁱⁱ	132.7(2)	132.17(16)	133.8(3)
I1 ^v -I3-I2 ^{ix}	132.7(2)	132.17(16)	133.8(3)
I1 ^v -I3-I3 ⁱⁱⁱ	146.8(4)	146.8(4)	146.8(4)
I1 ^v -I3-I3 ^{vii}	66.38(17)	65.86(13)	67.6(3)
I2 ⁱⁱⁱ -I3-I2 ^{ix}	0	0	0
I2 ⁱⁱⁱ -I3-I3 ^v	144.9(2)	144.9(2)	144.9(2)
I2 ⁱⁱⁱ -I3-I3 ^{vii}	66.62(16)	66.20(18)	67.60(15)
I2 ^{ix} -I3-I3 ^v	144.9(2)	144.9(2)	144.9(2)
I2 ^{ix} -I3-I3 ^{vii}	66.62(16)	66.20(18)	67.60(15)
I3 ⁱⁱⁱ -I3-I3 ^{vii}	89.9(4)	89.9(4)	89.9(4)
I3 ^v -I3-I3 ^{vii}	90.0(3)	90.0(3)	90.0(3)
(i)	-x+1,-y+1,-z		
(ii)	-x+1,-y+1,-z+1		
(iii)	x,y,z-1		
(iv)	-x,-y+1,-z+1		
(v)	x,y,z+1		
(vi)	x+1,y,z		
(vii)	x,-y+3/2,z		
(viii)	x+1,-y+3/2,z		
(ix)	x,-y+3/2,z-1		
(x)	x,-y+3/2,z+1		
(xi)	x-1,y,z		

Crystallographic details for commensurate WTe₂I

Table S 11: Occupational waves for commensurate WTe₂I.

Atom	Wave/Parameter	Occ
Te2	delta	0.8318
	x40	0.3211(4)
Te3	delta	0.1682
	x40	0.8231(4)
I1	delta	0.8318
	x40	0.4567(5)
I2	delta	0.8318
	x40	0.1933
I3	delta	0.1682
	x40	0.8366(5)

Table S12: Positional parameters for commensurate WTe₂I.

Atom	Occ	Wave	x	y	z	Ueq/Uiso
W1	1		0.32164(6)	0.495299(18)	0.2518(2)	0.00718(10)
		s,1	-0.00066(16)	0.00147(4)	-0.0298(10)	
		c,1	0.00256(13)	-0.00162(3)	-0.0094(4)	
		s,2	-0.00350(11)	0.00013(3)	-0.0044(6)	
		c,2	-0.00019(14)	0.00012(4)	0.0026(4)	
		s,3	0	0	-0.0949(15)	
Te1	1	c,3	0.4355	1	0	0.00847(15)
			0.57916(10)	0.59501(3)	0.2561(3)	
		s,1	-0.0039(3)	0.00054(8)	0.0279(3)	
		c,1	-0.00876(16)	-0.00040(5)	-0.0007(5)	
		s,2	-0.0009(2)	-0.00033(5)	0.0108(3)	
		c,2	0.00613(17)	-0.00235(5)	-0.0041(3)	
Te2	0.8318		0.07018(16)	0.56910(4)	0.7592(4)	0.00718(18)
		o,1	-0.0008(2)	0.00093(6)	-0.0008(6)	
		o,2	0.0002(3)	0.00012(7)	0.0029(4)	
		o,3	0.0011(4)	-0.00061(11)	-0.0175(8)	
		o,4	-0.0007(3)	0.00003(8)	-0.0030(7)	
Te3	0.1682		0.0811(4)	0.54884(10)	0.7465(8)	0.0077(4)
I1	0.8318		0.3527(6)	0.75	0.7423(14)	0.0627(11)
		o,1	0.0010(9)	0	0.0720(8)	
		o,2	-0.0266(7)	0	0.0347(12)	
		o,3	-0.0065(7)	0	-0.0358(10)	
		o,4	0.0058(11)	0	-0.0214(14)	
I2	0.8318		-0.1823(6)	0.75	0.7503(15)	0.0660(12)
		o,1	-0.0280(8)	0	0.0009(12)	
		o,2	-0.0161(8)	0	0.0755(9)	
		o,3	-0.0021(8)	0	0.0387(11)	
		o,4	0.0110(11)	0	0.0226(18)	
I3	0.1682		0.1055(4)	0.67488(9)	0.7537(9)	0.0168(5)

Table S13: ADP harmonic parameters for commensurate WTe₂l.

Atom	Wave	U11	U22	U33	U12	U13	U23
W1		0.00523(16)	0.01106(18)	0.00526(17)	-0.00038(13)	0.0000(4)	0.0020(2)
	s,1	0.0003(4)	0.0005(4)	-0.0008(3)	0.0009(3)	-0.0001(3)	0.0002(2)
	c,1	0.0002(3)	0.0000(3)	0.0004(3)	0.0002(3)	-0.0004(3)	0.0005(3)
Te1		0.0080(3)	0.0118(3)	0.0056(3)	-0.0009(2)	-0.0037(5)	0.0036(4)
Te2		0.0053(3)	0.0125(3)	0.0037(4)	-0.0006(2)	0.0026(5)	0.0027(4)
	o,1	0.0004(3)	-0.0016(4)	-0.0009(4)	0.0005(3)	0.0006(4)	-0.0009(4)
	o,2	0.0007(5)	-0.0007(5)	0.0002(5)	0.0006(4)	0.0001(2)	-0.0001(3)
Te3		0.0058(8)	0.0144(9)	0.0028(7)	0.0000(8)	0.0027(9)	-0.0003(11)
I1		0.102(2)	0.0259(9)	0.060(2)	0	0.018(2)	0
	o,1	0.005(3)	-0.0021(13)	0.0039(18)	0	-0.0057(15)	0
	o,2	-0.018(3)	0.0008(11)	-0.0075(17)	0	0.001(2)	0
I2		0.106(3)	0.0257(9)	0.067(2)	0	0.009(2)	0
	o,1	0.031(3)	-0.0012(12)	0.018(2)	0	-0.002(2)	0
	o,2	0.008(2)	0.0039(12)	0.0100(18)	0	0.0008(16)	0
I3		0.0182(9)	0.0128(8)	0.0194(9)	-0.0005(7)	-0.0014(11)	-0.0004(10)

Table S14: List of used orthogonalized functions for commensurate WTe_2 .

[illegible]

Table S15: List of distances for commensurate WTe₂I.

	average / Å	min / Å	max / Å
W1-W1 ⁱ	2.843(6)	2.825(7)	2.862(7)
W1-W1 ⁱⁱ	2.859(6)	2.775(9)	3.080(9)
W1-Te1	2.722(3)	2.689(3)	2.746(3)
W1-Te1 ⁱ	2.715(5)	2.649(6)	2.794(6)
W1-Te1 ⁱⁱ	2.696(5)	2.623(7)	2.761(7)
W1-Te2 ⁱⁱⁱ	2.802(6)	2.744(8)	2.863(8)
W1-Te2	2.837(5)	2.787(7)	2.905(7)
W1-Te2 ^{iv}	2.839(4)	2.814(6)	2.860(6)
W1-Te3 ⁱⁱⁱ	2.755(5)	2.755(5)	2.755(5)
W1-Te3	2.766(7)	2.766(7)	2.766(7)
W1-Te3 ^{iv}	2.739(3)	2.739(3)	2.739(3)
Te3-I3	2.762(3)	2.762(3)	2.762(3)
I1-I1 ⁱⁱⁱ	3.416(11)	2.900(12)	3.915(12)
I1-I1 ^v	3.416(11)	2.900(12)	3.915(12)
I1-I2	3.374(14)	2.966(18)	4.015(18)
I1-I2 ^{vi}	3.143(14)	3.051(17)	3.223(17)
I1-I3 ^v	4.164(8)	4.164(8)	4.164(8)
I1-I3 ^{vii}	4.164(8)	4.164(8)	4.164(8)
I2-I2 ⁱⁱⁱ	3.443(13)	2.967(16)	4.002(16)
I2-I2 ^v	3.443(13)	2.967(16)	4.002(16)
I2-I3 ⁱⁱⁱ	4.148(11)	4.148(11)	4.148(11)
I2-I3 ^{viii}	4.148(11)	4.148(11)	4.148(11)
I3-I3 ^{ix}	3.287(3)	3.287(3)	3.287(3)
(i)	-x+1,-y+1,-z		
(ii)	-x+1,-y+1,-z+1		
(iii)	x,y,z-1		
(iv)	-x,-y+1,-z+1		
(v)	x,y,z+1		
(vi)	x+1,y,z		
(vii)	x,-y+3/2,z+1		
(viii)	x,-y+3/2,z-1		
(ix)	x,-y+3/2,z		
(x)	x-1,y,z		

Table S16: List of angles for commensurate WTe₂I.

	average / °	min / °	max / °
W1 ⁱ -W1-W1 ⁱⁱ	74.97(16)	71.72(19)	82.50(17)
W1 ⁱ -W1-Te1	58.38(10)	57.09(11)	60.83(11)
W1 ⁱ -W1-Te1 ⁱ	58.59(12)	57.18(14)	59.34(15)
W1 ⁱ -W1-Te1 ⁱⁱ	104.87(11)	102.29(11)	109.22(11)
W1 ⁱ -W1-Te2 ⁱⁱⁱ	93.0(2)	91.9(2)	93.50(19)
W1 ⁱ -W1-Te2	140.47(16)	137.74(16)	142.44(15)
W1 ⁱ -W1-Te2 ^{iv}	136.3(3)	133.8(3)	139.1(3)
W1 ⁱ -W1-Te3 ⁱⁱⁱ	87.1(2)	87.1(2)	87.1(2)
W1 ⁱ -W1-Te3	145.68(10)	145.68(10)	145.68(10)
W1 ⁱ -W1-Te3 ^{iv}	138.87(18)	138.87(18)	138.87(18)
W1 ⁱⁱ -W1-Te1	57.67(10)	56.70(12)	58.57(10)
W1 ⁱⁱ -W1-Te1 ⁱ	105.25(11)	102.55(10)	109.73(11)
W1 ⁱⁱ -W1-Te1 ⁱⁱ	58.63(12)	54.50(15)	61.06(13)
W1 ⁱⁱ -W1-Te2 ⁱⁱⁱ	140.04(16)	138.02(16)	142.81(15)
W1 ⁱⁱ -W1-Te2	92.9(2)	91.6(2)	94.6(2)
W1 ⁱⁱ -W1-Te2 ^{iv}	136.6(3)	129.4(3)	141.9(3)
W1 ⁱⁱ -W1-Te3 ⁱⁱⁱ	145.00(12)	145.00(12)	145.00(12)
W1 ⁱⁱ -W1-Te3	82.1(2)	82.1(2)	82.1(2)

W1 ⁱⁱ -W1-Te3 ^{iv}	138.71(19)	138.71(19)	138.71(19)
Te1-W1-Te1 ⁱ	116.87(16)	114.04(17)	119.9(2)
Te1-W1-Te1 ⁱⁱ	116.29(17)	111.2(2)	119.63(17)
Te1-W1-Te2 ⁱⁱⁱ	83.75(17)	81.88(17)	85.62(16)
Te1-W1-Te2	83.27(17)	81.75(17)	85.50(16)
Te1-W1-Te2 ^{iv}	155.39(17)	153.53(17)	157.29(16)
Te1-W1-Te3 ⁱⁱⁱ	86.47(12)	86.47(12)	86.47(12)
Te1-W1-Te3	85.13(15)	85.13(15)	85.13(15)
Te1-W1-Te3 ^{iv}	150.85(9)	150.85(9)	150.85(9)
Te1 ⁱ -W1-Te1 ⁱⁱ	79.83(9)	77.81(9)	83.73(9)
Te1 ⁱ -W1-Te2 ⁱⁱⁱ	100.4(2)	97.8(2)	103.4(3)
Te1 ⁱ -W1-Te2	158.47(17)	157.59(17)	159.61(17)
Te1 ⁱ -W1-Te2 ^{iv}	80.83(18)	78.93(18)	83.49(19)
Te1 ⁱ -W1-Te3 ⁱⁱⁱ	85.48(18)	85.48(18)	85.48(18)
Te1 ⁱ -W1-Te3	154.93(12)	154.93(12)	154.93(12)
Te1 ⁱ -W1-Te3 ^{iv}	85.84(11)	85.84(11)	85.84(11)
Te1 ⁱⁱ -W1-Te2 ⁱⁱⁱ	158.18(18)	156.56(16)	160.50(18)
Te1 ⁱⁱ -W1-Te2	99.9(2)	96.6(2)	103.3(3)
Te1 ⁱⁱ -W1-Te2 ^{iv}	81.40(18)	80.4(2)	83.30(18)
Te1 ⁱⁱ -W1-Te3 ⁱⁱⁱ	153.84(12)	153.84(12)	153.84(12)
Te1 ⁱⁱ -W1-Te3	85.9(2)	85.9(2)	85.9(2)
Te1 ⁱⁱ -W1-Te3 ^{iv}	84.74(10)	84.74(10)	84.74(10)
Te2 ⁱⁱⁱ -W1-Te2	75.03(19)	73.37(17)	77.4(2)
Te2 ⁱⁱⁱ -W1-Te2 ^{iv}	78.28(18)	77.24(17)	79.01(17)
Te2 ⁱⁱⁱ -W1-Te3	78.46(15)	78.46(15)	78.46(15)
Te2 ⁱⁱⁱ -W1-Te3 ^{iv}	71.84(13)	71.84(13)	71.84(13)
Te2-W1-Te2 ^{iv}	78.91(18)	77.6(2)	80.1(2)
Te2-W1-Te3 ⁱⁱⁱ	80.69(8)	80.69(8)	80.69(8)
Te2-W1-Te3 ^{iv}	71.95(13)	71.95(13)	71.95(13)
Te2 ^{iv} -W1-Te3 ⁱⁱⁱ	71.85(15)	71.85(15)	71.85(15)
Te2 ^{iv} -W1-Te3	72.28(16)	72.28(16)	72.28(16)
W1-Te1-W1 ⁱ	63.04(13)	62.00(16)	64.18(11)
W1-Te1-W1 ⁱⁱ	63.70(13)	61.85(13)	68.81(17)
W1 ⁱ -Te1-W1 ⁱⁱ	79.82(17)	76.3(2)	89.14(18)
W1-Te2-W1 ^v	73.77(18)	71.83(16)	75.17(19)
W1-Te2-W1 ^{iv}	101.63(16)	99.85(10)	103.8(2)
W1 ^v -Te2-W1 ^{iv}	102.28(16)	100.6(2)	104.6(2)
W1-Te3-W1 ^v	89.8(2)	89.8(2)	89.8(2)
W1-Te3-W1 ^{iv}	111.06(14)	111.06(14)	111.06(14)
W1-Te3-I3	114.59(12)	114.59(12)	114.59(12)
W1 ^v -Te3-W1 ^{iv}	110.62(14)	110.62(14)	110.62(14)
W1 ^v -Te3-I3	113.31(12)	113.31(12)	113.31(12)
W1 ^{iv} -Te3-I3	114.85(10)	114.85(10)	114.85(10)
I1 ⁱⁱⁱ -I1-I1 ^v	176.2(4)	170.9(4)	179.9(5)
I1 ⁱⁱⁱ -I1-I2	90.7(4)	87.0(4)	96.3(4)
I1 ⁱⁱⁱ -I1-I2 ^{vi}	92.1(4)	83.7(4)	98.3(4)
I1 ⁱⁱⁱ -I1-I3 ^v	149.9(2)	149.9(2)	149.9(2)
I1 ⁱⁱⁱ -I1-I3 ^{vii}	149.9(2)	149.9(2)	149.9(2)
I1 ^v -I1-I2	89.7(4)	81.3(3)	98.6(4)
I1 ^v -I1-I2 ^{vi}	91.9(4)	83.5(4)	96.2(4)
I2-I1-I2 ^{vi}	169.3(4)	165.3(5)	171.8(4)
I2-I1-I3 ^v	72.03(19)	72.03(19)	72.03(19)
I2-I1-I3 ^{vii}	72.03(19)	72.03(19)	72.03(19)
I2 ^{vi} -I1-I3 ^v	100.5(2)	100.5(2)	100.5(2)
I2 ^{vi} -I1-I3 ^{vii}	100.5(2)	100.5(2)	100.5(2)
I3 ^v -I1-I3 ^{vii}	46.49(9)	46.49(9)	46.49(9)
I1 ^x -I2-I1	170.3(4)	166.8(3)	175.2(5)
I1 ^x -I2-I2 ⁱⁱⁱ	91.0(4)	82.6(3)	95.9(3)
I1 ^x -I2-I2 ^v	91.7(4)	84.3(4)	95.7(4)
I1 ^x -I2-I3 ⁱⁱⁱ	105.3(3)	105.3(3)	105.3(3)
I1 ^x -I2-I3 ^{viii}	105.3(3)	105.3(3)	105.3(3)
I1-I2-I2 ⁱⁱⁱ	89.3(4)	80.4(4)	97.3(3)
I1-I2-I2 ^v	90.2(4)	86.9(4)	96.9(4)

I1-I2-I3 ⁱⁱⁱ	70.3(3)	70.3(3)	70.3(3)
I1-I2-I3 ^{viii}	70.3(3)	70.3(3)	70.3(3)
I2 ⁱⁱⁱ -I2-I2 ^v	174.9(5)	168.3(6)	178.7(6)
I2 ^v -I2-I3 ⁱⁱⁱ	148.1(2)	148.1(2)	148.1(2)
I2 ^v -I2-I3 ^{viii}	148.1(2)	148.1(2)	148.1(2)
I3 ⁱⁱⁱ -I2-I3 ^{viii}	46.69(14)	46.69(14)	46.69(14)
Te3-I3-I1 ⁱⁱⁱ	113.92(12)	113.92(12)	113.92(12)
Te3-I3-I2 ^v	112.40(13)	112.40(13)	112.40(13)
Te3-I3-I3 ^{ix}	176.75(11)	176.75(11)	176.75(11)
I1 ⁱⁱⁱ -I3-I2 ^v	133.28(11)	133.28(11)	133.28(11)
I1 ⁱⁱⁱ -I3-I3 ^{ix}	66.75(8)	66.75(8)	66.75(8)
I2 ^v -I3-I3 ^{ix}	66.65(10)	66.65(10)	66.65(10)
(i)	-x+1,-y+1,-z		
(ii)	-x+1,-y+1,-z+1		
(iii)	x,y,z-1		
(iv)	-x,-y+1,-z+1		
(v)	x,y,z+1		
(vi)	x+1,y,z		
(vii)	x,-y+3/2,z+1		
(viii)	x,-y+3/2,z-1		
(ix)	x,-y+3/2,z		
(x)	x-1,y,z		

Crystallographic details for WTe₂Br_{0.5}

Table S17: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for WTe₂Br_{0.5}.

	x	y	z	Uiso*/Ueq
W1	−0.00516 (15)	0.25	−0.1785 (3)	0.0527 (15)
Te1	−0.07421 (12)	0.25	−0.5896 (5)	0.042 (2)
Te2	0.12012 (14)	0.25	0.0912 (5)	0.039 (2)
Br1	−0.2500	0.25	−0.6083 (13)	0.115 (7)

Table S18: for WTe₂Br_{0.5}.

	U ¹¹	U ²²	U ³³	U ¹²	U ¹³	U ²³
W1	0.0192 (14)	0.0821 (16)	0.0568 (14)	0	−0.0072 (17)	0
Te1	0.020 (3)	0.048 (3)	0.0574 (18)	0	0.013 (2)	0
Te2	0.047 (3)	0.044 (3)	0.0274 (17)	0	−0.010 (3)	0
Br1	0.145 (9)	0.036 (5)	0.163 (7)	0	0	0

Table S19: Atomic displacement parameters (Å²) for WTe₂Br_{0.5}.

W1—W1 ⁱ	3.6773 (1)	Te1—Te2 ^{vi}	3.735 (4)
W1—W1 ⁱⁱ	3.6773 (1)	Te1—Te2 ⁱⁱⁱ	3.718 (4)
W1—W1 ⁱⁱⁱ	2.909 (2)	Te1—Te2 ^{vii}	3.735 (4)
W1—W1 ^{iv}	2.909 (2)	Te1—Te2 ^{iv}	3.718 (4)
W1—Te1	2.835 (4)	Te1—Br1	2.946 (2)
W1—Te1 ^v	3.884 (4)	Te2—W1	2.699 (4)
W1—Te1 ^{vi}	2.698 (3)	Te2—W1 ⁱⁱⁱ	2.718 (3)
W1—Te1 ^{vii}	2.698 (3)	Te2—W1 ^{iv}	2.718 (3)
W1—Te2	2.699 (4)	Te2—Te1 ^v	3.825 (4)
W1—Te2 ⁱⁱⁱ	2.718 (3)	Te2—Te1 ^{vi}	3.735 (4)
W1—Te2 ^{iv}	2.718 (3)	Te2—Te1 ⁱⁱⁱ	3.718 (4)
Te1—W1 ^{viii}	3.884 (4)	Te2—Te1 ^{vii}	3.735 (4)
Te1—W1	2.835 (4)	Te2—Te1 ^{iv}	3.718 (4)
Te1—W1 ^{vi}	2.698 (3)	Te2—Te2 ⁱ	3.6773 (1)
Te1—W1 ^{vii}	2.698 (3)	Te2—Te2 ⁱⁱ	3.6773 (1)
Te1—Te1 ⁱ	3.6773 (1)	Br1—Te1	2.946 (2)
Te1—Te1 ⁱⁱ	3.6773 (1)	Br1—Te1 ^{ix}	2.946 (2)
Te1—Te1 ^{vi}	3.291 (3)	Br1—Br1 ⁱ	3.6773 (1)
Te1—Te1 ^{vii}	3.291 (3)	Br1—Br1 ⁱⁱ	3.6773 (1)
Te1—Te2 ^{viii}	3.825 (4)		

Symmetry codes: (i) x, y−1, z; (ii) x, y+1, z; (iii) −x, y−1/2, −z; (iv) −x, y+1/2, −z; (v) x, y, z+1; (vi) −x, y−1/2, −z−1; (vii) −x, y+1/2, −z−1; (viii) x, y, z−1; (ix) −x−1/2, −y+1/2, z. Table S20: for WTe₂Br_{0.5}.

W1 ⁱ —W1—W1 ⁱⁱ	180	W1 ^{vii} —Te1—Br1	118.07 (13)
W1 ⁱ —W1—W1 ⁱⁱⁱ	50.80 (6)	Te1 ⁱ —Te1—Te1 ⁱⁱ	180
W1 ⁱ —W1—W1 ^{iv}	129.20 (6)	Te1 ⁱ —Te1—Te1 ^{vi}	56.03 (7)
W1 ⁱ —W1—Te1	90.00 (10)	Te1 ⁱ —Te1—Te1 ^{vii}	123.97 (7)
W1 ⁱ —W1—Te1 ^v	90.00 (8)	Te1 ⁱ —Te1—	90.00 (8)
W1 ⁱ —W1—Te1 ^{vi}	47.04 (7)	Te1 ⁱ —Te1—Te2 ^{vi}	60.51 (9)
W1 ⁱ —W1—Te1 ^{vii}	132.96 (7)	Te1 ⁱ —Te1—Te2 ⁱⁱⁱ	60.36 (9)
W1 ⁱ —W1—Te2	90.00 (10)	Te1 ⁱ —Te1—Te2 ^{vii}	119.49 (9)
W1 ⁱ —W1—Te2 ⁱⁱⁱ	47.43 (7)	Te1 ⁱ —Te1—Te2 ^{iv}	119.64 (9)
W1 ⁱ —W1—Te2 ^{iv}	132.57 (7)	Te1 ⁱ —Te1—Br1	90.00 (5)
W1 ⁱⁱ —W1—W1 ⁱⁱⁱ	129.20 (6)	Te1 ⁱⁱ —Te1—Te1 ^{vi}	123.97 (7)

$W1^{ii}-W1-W1^{iv}$ 50.80 (6)
 $W1^{ii}-W1-Te1$ 90.00 (10)
 $W1^{ii}-W1-Te1^v$ 90.00 (8)
 $W1^{ii}-W1-Te1^{vi}$ 132.96 (7)
 $W1^{ii}-W1-Te1^{vii}$ 47.04 (7)
 $W1^{ii}-W1-Te2$ 90.00 (10)
 $W1^{ii}-W1-Te2^{iii}$ 132.57 (7)
 $W1^{ii}-W1-Te2^{iv}$ 47.43 (7)
 $W1^{iii}-W1-W1^{iv}$ 78.40 (6)
 $W1^{iii}-W1-Te1$ 136.86 (16)
 $W1^{iii}-W1-Te1^{vi}$ 87.61 (13)
 $W1^{iii}-W1-Te1^{vii}$ 145.05 (13)
 $W1^{iii}-W1-Te2$ 57.84 (10)
 $W1^{iii}-W1-Te2^{iii}$ 57.20 (10)
 $W1^{iii}-W1-Te2^{iv}$ 108.26 (10)
 $W1^{iv}-W1-Te1$ 136.86 (16)
 $W1^{iv}-W1-Te1^{vi}$ 145.05 (13)
 $W1^{iv}-W1-Te1^{vii}$ 87.61 (13)
 $W1^{iv}-W1-Te2$ 57.84 (10)
 $W1^{iv}-W1-Te2^{iii}$ 108.26 (10)
 $W1^{iv}-W1-Te2^{iv}$ 57.20 (10)
 $Te1-W1-Te1^v$ 138.61 (18)
 $Te1-W1-Te1^{vi}$ 72.95 (12)
 $Te1-W1-Te1^{vii}$ 72.95 (12)
 $Te1-W1-Te2$ 153.1 (2)
 $Te1-W1-Te2^{iii}$ 84.02 (14)
 $Te1-W1-Te2^{iv}$ 84.02 (14)
 $Te1^v-W1-Te1^{vi}$ 131.55 (16)
 $Te1^v-W1-Te1^{vii}$ 131.55 (16)
 $Te1^v-W1-Te2$ 68.33 (12)
 $Te1^v-W1-Te2^{iii}$ 66.18 (11)
 $Te1^v-W1-Te2^{iv}$ 66.18 (11)
 $Te1^{vi}-W1-$ 85.92 (8)
 $Te1^{vi}-W1-Te2$ 87.57 (15)
 $Te1^{vi}-W1-Te2^{iii}$ 89.85 (13)
 $Te1^{vi}-W1-Te2^{iv}$ 156.82 (13)
 $Te1^{vii}-W1-Te2$ 87.57 (15)
 $Te1^{vii}-W1-Te2^{iii}$ 156.82 (13)
 $Te1^{vii}-W1-$ 89.85 (13)
 $Te2-W1-Te2^{iii}$ 115.04 (15)
 $Te2-W1-Te2^{iv}$ 115.04 (15)
 $Te2^{iii}-W1-Te2^{iv}$ 85.13 (8)
 $W1^{viii}-Te1-W1$ 138.61 (13)
 $W1^{viii}-Te1-W1^{vi}$ 48.45 (9)
 $W1^{viii}-Te1-$ 48.45 (9)
 $W1^{viii}-Te1-Te1^i$ 90.00 (8)
 $W1^{viii}-Te1-Te1^{ii}$ 90.00 (8)
 $W1^{viii}-Te1-$ 95.88 (11)
 $W1^{viii}-Te1-$ 95.88 (11)
 $W1^{viii}-Te1-$ 150.16 (13)
 $W1^{viii}-Te1-$ 150.16 (13)
 $W1^{viii}-Te1-Br1$ 105.03 (18)
 $W1-Te1-W1^{vi}$ 107.05 (13)
 $W1-Te1-W1^{vii}$ 107.05 (13)
 $W1-Te1-Te1^i$ 90.00 (10)
 $W1-Te1-Te1^{ii}$ 90.00 (10)
 $W1-Te1-Te1^{vi}$ 51.61 (10)
 $W1-Te1-Te1^{vii}$ 51.61 (10)
 $W1-Te1-Te2^{viii}$ 97.63 (14)
 $W1-Te1-Te2^{vi}$ 148.89 (16)
 $W1-Te1-Te2^{vii}$ 148.89 (16)
 $W1-Te1-Te2^{iv}$ 46.65 (10)

$Te1^{ii}-Te1-$ 56.03 (7)
 $Te1^{ii}-Te1-$ 90.00 (8)
 $Te1^{ii}-Te1-Te2^{vi}$ 119.49 (9)
 $Te1^{ii}-Te1-Te2^{iii}$ 119.64 (9)
 $Te1^{ii}-Te1-$ 60.51 (9)
 $Te1^{ii}-Te1-Te2^{iv}$ 60.36 (9)
 $Te1^{ii}-Te1-Br1$ 90.00 (5)
 $Te1^{vi}-Te1-$ 67.93 (7)
 $Te1^{vi}-Te1-$ 62.46 (10)
 $Te1^{vi}-Te1-$ 99.81 (13)
 $Te1^{vi}-Te1-$ 65.82 (10)
 $Te1^{vi}-Te1-$ 136.09 (13)
 $Te1^{vi}-Te1-$ 98.22 (10)
 $Te1^{vi}-Te1-Br1$ 140.20 (11)
 $Te1^{vii}-Te1-$ 62.46 (10)
 $Te1^{vii}-Te1-$ 136.09 (13)
 $Te1^{vii}-Te1-$ 98.22 (10)
 $Te1^{vii}-Te1-$ 99.81 (13)
 $Te1^{vii}-Te1-$ 65.82 (10)
 $Te1^{vii}-Te1-Br1$ 140.20 (11)
 $Te2^{viii}-Te1-$ 74.38 (10)
 $Te2^{viii}-Te1-$ 128.28 (14)
 $Te2^{viii}-Te1-$ 74.38 (10)
 $Te2^{viii}-Te1-$ 128.28 (14)
 $Te2^{viii}-Te1-Br1$ 146.01 (13)
 $Te2^{vi}-Te1-$ 115.33 (15)
 $Te2^{vi}-Te1-$ 58.99 (9)
 $Te2^{vi}-Te1-$ 156.19 (15)
 $Te2^{vi}-Te1-Br1$ 76.14 (16)
 $Te2^{iii}-Te1-$ 156.19 (15)
 $Te2^{iii}-Te1-$ 59.28 (9)
 $Te2^{iii}-Te1-Br1$ 80.04 (17)
 $Te2^{vii}-Te1-$ 115.33 (15)
 $Te2^{vii}-Te1-Br1$ 76.14 (16)
 $Te2^{iv}-Te1-Br1$ 80.04 (17)
 $W1-Te2-W1^{iii}$ 64.96 (11)
 $W1-Te2-W1^{iv}$ 64.96 (11)
 $W1-Te2-Te1^v$ 70.69 (12)
 $W1-Te2-Te1^{vi}$ 46.20 (11)
 $W1-Te2-Te1^{iii}$ 111.74 (15)
 $W1-Te2-Te1^{vii}$ 46.20 (11)
 $W1-Te2-Te1^{iv}$ 111.74 (15)
 $W1-Te2-Te2^i$ 90.00 (10)
 $W1-Te2-Te2^{ii}$ 90.00 (10)
 $W1^{iii}-Te2-W1^{iv}$ 85.13 (8)
 $W1^{iii}-Te2-Te1^{vi}$ 72.07 (12)
 $W1^{iii}-Te2-Te1^{iii}$ 49.33 (10)
 $W1^{iii}-Te2-Te1^{vii}$ 110.99 (12)
 $W1^{iii}-Te2-Te1^{iv}$ 91.00 (10)
 $W1^{iii}-Te2-Te2^i$ 47.43 (7)
 $W1^{iii}-Te2-Te2^{ii}$ 132.57 (7)
 $W1^{iv}-Te2-Te1^{vi}$ 110.99 (12)
 $W1^{iv}-Te2-Te1^{iii}$ 91.00 (10)
 $W1^{iv}-Te2-$ 72.07 (12)
 $W1^{iv}-Te2-Te1^{iv}$ 49.33 (10)
 $W1^{iv}-Te2-Te2^i$ 132.57 (7)
 $W1^{iv}-Te2-Te2^{ii}$ 47.43 (7)
 $Te1^v-Te2-Te1^{vi}$ 105.62 (13)
 $Te1^v-Te2-Te1^{iii}$ 51.72 (9)
 $Te1^v-Te2-$ 105.62 (13)
 $Te1^v-Te2-Te1^{iv}$ 51.72 (9)
 $Te1^v-Te2-Te2^i$ 90.00 (8)
 $Te1^v-Te2-Te2^{ii}$ 90.00 (8)

W1—Te1—Br1	116.36 (19)	Te1 ^{vi} —Te2—	115.33 (15)
W1 ^{vi} —Te1—W1 ^{vii}	85.92 (8)	$\bar{\text{Te1}}^{\text{vi}}$ —Te2—	58.99 (9)
W1 ^{vi} —Te1—Te1 ⁱ	47.04 (7)	$\bar{\text{Te1}}^{\text{vi}}$ —Te2—	156.19 (15)
W1 ^{vi} —Te1—Te1 ⁱⁱ	132.96 (7)	$\bar{\text{Te1}}^{\text{vi}}$ —Te2—Te2 ⁱ	60.51 (9)
W1 ^{vi} —Te1—Te1 ^{vi}	55.45 (10)	Te1 ^{vi} —Te2—Te2 ⁱⁱ	119.49 (9)
W1 ^{vi} —Te1—	101.20 (10)	Te1 ⁱⁱⁱ —Te2—	156.19 (15)
$\bar{\text{W1}}^{\text{vi}}$ —Te1—	45.29 (9)	$\bar{\text{Te1}}^{\text{iii}}$ —Te2—	59.28 (9)
$\bar{\text{W1}}^{\text{vi}}$ —Te1—Te2 ^{vi}	46.22 (10)	$\bar{\text{Te1}}^{\text{iii}}$ —Te2—Te2 ⁱ	60.36 (9)
W1 ^{vi} —Te1—Te2 ⁱⁱⁱ	102.81 (14)	Te1 ⁱⁱⁱ —Te2—Te2 ⁱⁱ	119.64 (9)
W1 ^{vi} —Te1—	88.81 (10)	Te1 ^{vii} —Te2—	115.33 (15)
$\bar{\text{W1}}^{\text{vi}}$ —Te1—Te2 ^{iv}	153.61 (14)	$\bar{\text{Te1}}^{\text{vii}}$ —Te2—Te2 ⁱ	119.49 (9)
W1 ^{vi} —Te1—Br1	118.07 (13)	Te1 ^{vii} —Te2—	60.51 (9)
W1 ^{vii} —Te1—Te1 ⁱ	132.96 (7)	$\bar{\text{Te1}}^{\text{iv}}$ —Te2—Te2 ⁱ	119.64 (9)
W1 ^{vii} —Te1—Te1 ⁱⁱ	47.04 (7)	Te1 ^{iv} —Te2—Te2 ⁱⁱ	60.36 (9)
W1 ^{vii} —Te1—	101.20 (10)	Te2 ⁱ —Te2—Te2 ⁱⁱ	180
$\bar{\text{W1}}^{\text{vii}}$ —Te1—	55.45 (10)	Te1—Br1—Te1 ^{ix}	175.42 (13)
$\bar{\text{W1}}^{\text{vii}}$ —Te1—	45.29 (9)	Te1—Br1—Br1 ⁱ	90.00 (5)
$\bar{\text{W1}}^{\text{vii}}$ —Te1—	88.81 (10)	Te1—Br1—Br1 ⁱⁱ	90.00 (5)
$\bar{\text{W1}}^{\text{vii}}$ —Te1—Te2 ⁱⁱⁱ	153.61 (14)	Te1 ^{ix} —Br1—Br1 ⁱ	90.00 (5)
W1 ^{vii} —Te1—	46.22 (10)	Te1 ^{ix} —Br1—Br1 ⁱⁱ	90.00 (5)
$\bar{\text{W1}}^{\text{vii}}$ —Te1—	102.81 (14)	Br1 ⁱ —Br1—Br1 ⁱⁱ	180

Symmetry codes: (i) $x, y-1, z$; (ii) $x, y+1, z$; (iii) $-x, y-1/2, -z$; (iv) $-x, y+1/2, -z$; (v) $x, y, z+1$; (vi) $-x, y-1/2, -z-1$; (vii) $-x, y+1/2, -z-1$; (viii) $x, y, z-1$; (ix) $-x-1/2, -y+1/2, z$.

Crystallographic details for $\text{WTe}_2\text{Br}_{1.25}$

Table S 21: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{WTe}_2\text{Br}_{1.25}$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_j .

Atom	x	y	z	U_{eq}
W4	5000	3794(2)	723(8)	55(2)
W8	5000	3803(2)	5768(8)	57(2)
W6	1607(5)	3809.8(15)	5719(5)	56(2)
W3	3417(5)	3849.9(16)	2475(5)	58(2)
W2	1886(4)	3782.2(15)	703(5)	57(2)
W5	0	3832(2)	7490(7)	55(2)
W7	3155(5)	3850.8(15)	7480(5)	58(2)
W1	0	3858(2)	2403(8)	64(3)
Te1	0	3357(3)	1159(9)	53(3)
Te3	3411(6)	3323(2)	1265(6)	52(2)
Te13	0	4055(3)	9515(10)	55(3)
Te12	5000	3538(3)	3811(9)	57(3)
Te15	3329(6)	4157(2)	-525(7)	55(2)
Te14	1712(6)	3461(2)	8708(7)	61(3)
Te10	1651(6)	3557(2)	3727(7)	60(3)
Te8	5000	4294(3)	7073(10)	55(3)
Te6	1594(7)	4313.7(17)	7032(7)	52(2)
Te16	5000	3555(3)	8679(10)	60(3)
Te9	0	4186(3)	4440(11)	57(3)
Te11	3342(6)	4177.7(19)	4490(7)	55(2)
Te5	0	3347(3)	6167(10)	59(3)
Te7	3283(7)	3357(2)	6187(7)	58(2)
Te4	5000	4313(3)	1945(12)	63(3)
Te2	1726(7)	4291(3)	1916(8)	71(3)
Br5	5000	2961(5)	3756(16)	63(5)
Br6	5000	2969(5)	8534(18)	64(5)
Br3	1794(15)	2597(4)	6973(16)	78(4)
Br4	1674(12)	2984(4)	3571(14)	71(4)
Br7	0	4636(6)	9607(19)	71(6)
Br8	3170(20)	5000	10520(20)	74(6)
Br1	5000	2249(6)	3950(20)	74(6)
Br9	3160(20)	5000	8530(20)	75(6)
Br10	0	5000	5910(60)	190(40)
Br2	3175(12)	2438(5)	5615(18)	86(5)
Br12	2920(40)	5000	6020(80)	290(50)
Br13	3020(60)	5000	2760(100)	350(80)
Br11	0	5000	3080(70)	240(60)

Table S22: Anisotropic Displacement Parameters ($\times 10^4$) for **WTe₂Br_{1.25}**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W4	31(3)	80(5)	55(5)	7(4)	0	0
W8	37(4)	79(5)	53(5)	-3(4)	0	0
W6	34(3)	77(4)	55(4)	-5(3)	1(3)	-1(2)
W3	32(3)	91(4)	51(3)	0(3)	-1(3)	0(2)
W2	31(3)	81(4)	60(4)	5(3)	-1(3)	0(2)
W5	35(4)	76(5)	55(5)	0(4)	0	0
W7	42(3)	80(4)	52(4)	1(3)	-2(3)	0(2)
W1	69(6)	70(5)	55(6)	1(4)	0	0
Te1	26(4)	76(7)	55(7)	-5(5)	0	0
Te3	31(3)	81(5)	45(4)	-2(3)	1(3)	-1(3)
Te13	23(4)	95(8)	49(6)	4(6)	0	0
Te12	24(4)	109(9)	37(6)	-5(6)	0	0
Te15	33(3)	85(5)	46(4)	0(4)	1(3)	2(3)
Te14	28(3)	104(6)	49(5)	-4(5)	2(3)	-1(3)
Te10	25(3)	100(6)	55(5)	-7(4)	1(3)	-2(3)
Te8	35(5)	73(7)	57(7)	-3(5)	0	0
Te6	43(4)	55(4)	59(5)	-5(3)	-2(4)	-1(3)
Te16	33(5)	93(8)	56(7)	-1(6)	0	0
Te9	36(5)	77(7)	58(7)	0(6)	0	0
Te11	32(3)	76(5)	57(4)	-2(4)	0(3)	0(3)
Te5	29(5)	95(9)	52(7)	-1(6)	0	0
Te7	31(3)	84(5)	58(5)	4(4)	1(3)	0(3)
Te4	24(4)	91(8)	74(8)	5(7)	0	0
Te2	20(3)	126(8)	66(6)	-2(5)	-4(3)	3(4)
Br5	20(6)	118(15)	51(11)	3(10)	0	0
Br6	60(10)	65(11)	67(13)	-8(9)	0	0
Br3	57(8)	84(9)	92(11)	-2(8)	21(8)	4(7)
Br4	41(6)	87(9)	86(11)	8(8)	1(7)	1(6)
Br7	29(7)	124(18)	58(12)	-3(11)	0	0
Br8	64(11)	65(11)	94(16)	0	10(12)	0
Br1	41(9)	102(15)	78(14)	0(12)	0	0
Br9	54(10)	92(14)	79(15)	0	13(10)	0
Br10	370(130)	60(20)	150(60)	0	0	0
Br2	36(6)	118(13)	104(13)	27(11)	9(8)	2(6)
Br12	60(20)	450(130)	370(110)	0	110(40)	0
Br13	190(50)	64(18)	800(200)	0	-300(90)	0
Br11	500(200)	50(20)	170(70)	0	0	0

Table S23: Bond Lengths in Å for **WTe₂Br_{1.25}**.

Atom	Atom	Length/Å
W4	W3	2.789(9)
W4	W3 ¹	2.789(9)
W4	Te3	2.725(11)
W4	Te3 ¹	2.725(11)
W4	Te15	2.843(11)
W4	Te15 ¹	2.843(11)
W4	Te16 ²	2.778(16)
W4	Te4	2.716(17)
W8	W7 ¹	2.925(9)
W8	W7	2.925(9)
W8	Te12	2.723(15)
W8	Te8	2.680(15)
W8	Te11	2.883(11)
W8	Te11 ¹	2.883(11)
W8	Te7	2.701(11)
W8	Te7 ¹	2.701(11)
W6	W5	2.815(9)
W6	W7	2.772(9)
W6	Te10	2.741(11)
W6	Te6	2.730(10)
W6	Te9	2.852(12)
W6	Te11	2.883(11)
W6	Te5	2.682(13)
W6	Te7	2.706(10)
W3	W2	2.781(8)
W3	Te3	2.736(11)
W3	Te12	2.735(12)
W3	Te10	2.758(10)
W3	Te11	2.910(11)
W3	Te4	2.692(13)
W3	Te2	2.706(12)
W2	W1	2.955(9)
W2	Te1	2.775(11)

Atom	Atom	Length/Å
W2	Te3	2.653(10)
W2	Te13 ²	2.763(11)
W2	Te15	2.713(10)
W2	Te14 ²	2.879(12)
W2	Te2	2.676(13)
W5	Te13	2.731(16)
W5	Te14 ³	2.866(11)
W5	Te14	2.866(11)
W5	Te6	2.738(10)
W5	Te6 ³	2.738(10)
W5	Te5	2.672(16)
W7	Te15 ⁴	2.849(11)
W7	Te14	2.750(11)
W7	Te8	2.782(11)
W7	Te6	2.653(10)
W7	Te16	2.783(11)
W7	Te7	2.685(12)
W1	Te1	2.668(15)
W1	Te10	2.748(12)
W1	Te10 ³	2.748(12)
W1	Te9	2.933(17)
W1	Te2 ³	2.685(12)
W1	Te2	2.685(12)
Te13	Br7	2.50(3)
Te12	Br5	2.48(3)
Te10	Br4	2.473(19)
Te16	Br6	2.53(2)
Br3	Br2	2.36(2)
Br8	Br9	2.51(3)

¹1-x,+y,+z; ²+x,+y,-1+z; ³-x,+y,+z; ⁴+x,+y,1+z

Table S 24: Bond Angles in ° for **WTe₂Br_{1.25}**.

Atom	Atom	Atom	Angle/°
W3 ¹	W4	W3	74.2(3)
W3 ¹	W4	Te15	140.2(4)
W3	W4	Te15 ¹	140.2(4)
W3 ¹	W4	Te15 ¹	90.9(2)
W3	W4	Te15	90.9(2)
Te3 ¹	W4	W3 ¹	59.5(2)
Te3	W4	W3	59.5(2)
Te3	W4	W3 ¹	103.8(4)
Te3 ¹	W4	W3	103.8(4)
Te3 ¹	W4	Te3	76.6(4)
Te3 ¹	W4	Te15	159.3(5)
Te3	W4	Te15	99.3(2)
Te3	W4	Te15 ¹	159.3(5)
Te3 ¹	W4	Te15 ¹	99.3(2)
Te3	W4	Te16 ²	87.6(4)
Te3 ¹	W4	Te16 ²	87.6(4)
Te15 ¹	W4	Te15	77.3(4)
Te16 ²	W4	W3 ¹	140.3(2)
Te16 ²	W4	W3	140.3(2)

Atom	Atom	Atom	Angle/°
Te16 ²	W4	Te15	71.8(4)
Te16 ²	W4	Te15 ¹	71.8(4)
Te4	W4	W3	58.5(3)
Te4	W4	W3 ¹	58.5(3)
Te4	W4	Te3 ¹	118.0(4)
Te4	W4	Te3	118.0(4)
Te4	W4	Te15	82.1(4)
Te4	W4	Te15 ¹	82.1(4)
Te4	W4	Te16 ²	146.3(6)
W7	W8	W7 ¹	84.1(3)
Te12	W8	W7 ¹	134.5(2)
Te12	W8	W7	134.5(2)
Te12	W8	Te11	74.1(4)
Te12	W8	Te11 ¹	74.1(4)
Te8	W8	W7 ¹	59.3(3)
Te8	W8	W7	59.3(3)
Te8	W8	Te12	152.7(6)
Te8	W8	Te11 ¹	84.4(4)
Te8	W8	Te11	84.4(4)

Atom	Atom	Atom	Angle/°
Te8	W8	Te7	116.1(4)
Te8	W8	Te7 ¹	116.1(4)
Te11 ¹	W8	W7 ¹	88.0(2)
Te11	W8	W7	88.0(2)
Te11 ¹	W8	W7	141.6(4)
Te11	W8	W7 ¹	141.6(4)
Te11	W8	Te11 ¹	75.3(4)
Te7	W8	W7 ¹	111.0(4)
Te7	W8	W7	56.8(3)
Te7 ¹	W8	W7	111.0(4)
Te7 ¹	W8	W7 ¹	56.8(3)
Te7 ¹	W8	Te12	83.1(4)
Te7	W8	Te12	83.1(4)
Te7	W8	Te11	95.4(3)
Te7	W8	Te11 ¹	156.9(4)
Te7 ¹	W8	Te11 ¹	95.5(3)
Te7 ¹	W8	Te11	156.9(4)
Te7	W8	Te7 ¹	84.9(5)
W5	W6	Te9	93.9(3)
W5	W6	Te11	142.8(3)
W7	W6	W5	73.7(2)
W7	W6	Te9	140.7(4)
W7	W6	Te11	91.0(3)
Te10	W6	W5	138.9(3)
Te10	W6	W7	138.7(3)
Te10	W6	Te9	73.5(4)
Te10	W6	Te11	73.3(3)
Te6	W6	W5	59.2(3)
Te6	W6	W7	57.7(2)
Te6	W6	Te10	150.8(4)
Te6	W6	Te9	83.7(3)
Te6	W6	Te11	83.9(3)
Te9	W6	Te11	76.5(3)
Te5	W6	W5	58.1(3)
Te5	W6	W7	104.8(3)
Te5	W6	Te10	84.8(4)
Te5	W6	Te6	117.3(4)
Te5	W6	Te9	99.2(3)
Te5	W6	Te11	158.1(4)
Te5	W6	Te7	80.7(3)
Te7	W6	W5	104.5(3)
Te7	W6	W7	58.7(3)
Te7	W6	Te10	84.4(3)
Te7	W6	Te6	116.3(3)
Te7	W6	Te9	157.8(4)
Te7	W6	Te11	95.3(3)
W4	W3	Te11	138.8(3)
W2	W3	W4	72.8(2)
W2	W3	Te11	137.6(3)
Te3	W3	W4	59.1(3)
Te3	W3	W2	57.5(2)
Te3	W3	Te10	86.5(3)
Te3	W3	Te11	152.9(4)
Te12	W3	W4	94.4(3)
Te12	W3	W2	143.5(4)
Te12	W3	Te3	86.5(4)
Te12	W3	Te10	80.8(3)
Te12	W3	Te11	73.5(3)
Te10	W3	W4	145.6(4)
Te10	W3	W2	90.9(3)
Te10	W3	Te11	72.6(3)
Te4	W3	W4	59.4(4)

Atom	Atom	Atom	Angle/°
Te4	W3	W2	104.0(4)
Te4	W3	Te3	118.5(4)
Te4	W3	Te12	97.6(4)
Te4	W3	Te10	154.9(5)
Te4	W3	Te11	82.9(4)
Te4	W3	Te2	80.3(3)
Te2	W3	W4	104.7(3)
Te2	W3	W2	58.4(3)
Te2	W3	Te3	115.7(4)
Te2	W3	Te12	156.0(4)
Te2	W3	Te10	91.1(3)
Te2	W3	Te11	82.5(3)
W3	W2	W1	78.5(2)
W3	W2	Te14 ²	142.4(3)
Te1	W2	W3	108.9(3)
Te1	W2	W1	55.4(3)
Te1	W2	Te14 ²	79.6(3)
Te3	W2	W3	60.4(3)
Te3	W2	W1	107.5(3)
Te3	W2	Te1	83.9(3)
Te3	W2	Te13 ²	154.7(4)
Te3	W2	Te15	104.6(3)
Te3	W2	Te14 ²	85.2(3)
Te3	W2	Te2	119.7(4)
Te13 ²	W2	W3	144.7(4)
Te13 ²	W2	W1	81.7(3)
Te13 ²	W2	Te1	82.5(3)
Te13 ²	W2	Te14 ²	71.5(4)
Te15	W2	W3	93.9(3)
Te15	W2	W1	137.1(4)
Te15	W2	Te1	156.8(4)
Te15	W2	Te13 ²	81.2(3)
Te15	W2	Te14 ²	79.7(3)
Te14 ²	W2	W1	130.2(3)
Te2	W2	W3	59.4(3)
Te2	W2	W1	56.7(3)
Te2	W2	Te1	112.0(4)
Te2	W2	Te13 ²	85.3(4)
Te2	W2	Te15	82.9(3)
Te2	W2	Te14 ²	152.7(4)
W6 ³	W5	W6	74.6(3)
W6	W5	Te14 ³	142.4(4)
W6 ³	W5	Te14 ³	91.3(2)
W6	W5	Te14	91.3(2)
W6 ³	W5	Te14	142.4(4)
Te13	W5	W6 ³	139.1(2)
Te13	W5	W6	139.1(2)
Te13	W5	Te14	72.1(4)
Te13	W5	Te14 ³	72.1(4)
Te13	W5	Te6	86.1(4)
Te13	W5	Te6 ³	86.1(4)
Te14 ³	W5	Te14	78.8(4)
Te6 ³	W5	W6	103.4(4)
Te6	W5	W6	58.9(3)
Te6 ³	W5	W6 ³	58.9(3)
Te6	W5	W6 ³	103.4(4)
Te6 ³	W5	Te14 ³	98.2(3)
Te6	W5	Te14 ³	158.0(5)
Te6 ³	W5	Te14	158.0(5)
Te6	W5	Te14	98.2(3)
Te6	W5	Te6 ³	76.4(4)
Te5	W5	W6	58.4(3)

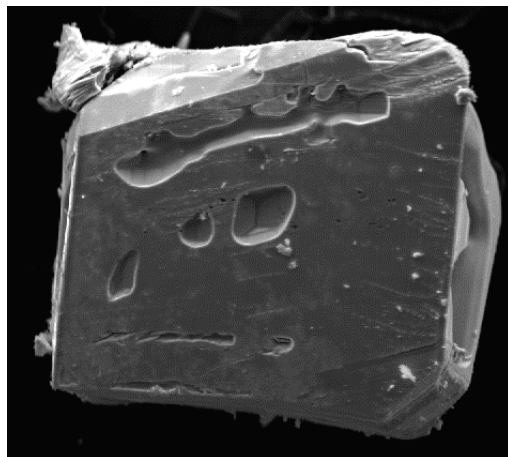
Atom	Atom	Atom	Angle/°
Te5	W5	W6 ³	58.4(3)
Te5	W5	Te13	149.2(6)
Te5	W5	Te14 ³	84.3(4)
Te5	W5	Te14	84.3(4)
Te5	W5	Te6 ³	117.3(4)
Te5	W5	Te6	117.3(4)
W6	W7	W8	78.5(2)
W6	W7	Te15 ⁴	141.0(3)
W6	W7	Te8	108.2(3)
W6	W7	Te16	145.6(4)
Te15 ⁴	W7	W8	130.0(3)
Te14	W7	W8	138.3(4)
Te14	W7	W6	94.7(3)
Te14	W7	Te15 ⁴	79.6(3)
Te14	W7	Te8	156.2(4)
Te14	W7	Te16	78.9(3)
Te8	W7	W8	55.9(3)
Te8	W7	Te15 ⁴	78.5(3)
Te8	W7	Te16	85.3(3)
Te6	W7	W8	108.3(3)
Te6	W7	W6	60.4(2)
Te6	W7	Te15 ⁴	83.2(3)
Te6	W7	Te14	103.3(3)
Te6	W7	Te8	83.5(3)
Te6	W7	Te16	154.0(4)
Te6	W7	Te7	119.8(3)
Te16	W7	W8	84.2(3)
Te16	W7	Te15 ⁴	71.6(3)
Te7	W7	W8	57.4(3)
Te7	W7	W6	59.4(2)
Te7	W7	Te15 ⁴	154.3(4)
Te7	W7	Te14	83.6(3)
Te7	W7	Te8	113.3(4)
Te7	W7	Te16	86.2(4)
W2 ³	W1	W2	85.4(3)
Te1	W1	W2 ³	58.9(3)
Te1	W1	W2	58.9(3)
Te1	W1	Te10	88.7(4)
Te1	W1	Te10 ³	88.7(4)
Te1	W1	Te9	154.8(6)
Te1	W1	Te2 ³	115.2(4)
Te1	W1	Te2	115.2(4)
Te10	W1	W2 ³	145.4(4)
Te10	W1	W2	87.6(2)
Te10 ³	W1	W2	145.4(4)
Te10 ³	W1	W2 ³	87.6(2)
Te10 ³	W1	Te10	79.3(4)
Te10 ³	W1	Te9	72.1(3)
Te10	W1	Te9	72.1(3)
Te9	W1	W2	133.6(2)
Te9	W1	W2 ³	133.6(2)
Te2 ³	W1	W2 ³	56.4(3)
Te2	W1	W2 ³	111.9(4)
Te2	W1	W2	56.4(3)
Te2 ³	W1	W2	111.9(4)
Te2 ³	W1	Te10 ³	91.8(3)
Te2	W1	Te10 ³	154.5(5)
Te2	W1	Te10	91.8(3)
Te2 ³	W1	Te10	154.5(5)
Te2	W1	Te9	82.4(4)
Te2 ³	W1	Te9	82.4(4)
Te2	W1	Te2 ³	86.1(5)

Atom	Atom	Atom	Angle/°
W2	Te1	W2 ³	92.4(4)
W1	Te1	W2	65.7(3)
W1	Te1	W2 ³	65.7(3)
W4	Te3	W3	61.4(3)
W2	Te3	W4	75.9(3)
W2	Te3	W3	62.1(3)
W2 ⁴	Te13	W2 ⁵	92.9(4)
W5	Te13	W2 ⁵	111.1(4)
W5	Te13	W2 ⁴	111.1(4)
Br7	Te13	W2 ⁵	113.5(5)
Br7	Te13	W2 ⁴	113.5(5)
Br7	Te13	W5	113.2(7)
W8	Te12	W3	110.7(5)
W8	Te12	W3 ¹	110.7(5)
W3	Te12	W3 ¹	75.9(4)
Br5	Te12	W8	116.4(7)
Br5	Te12	W3 ¹	118.3(5)
Br5	Te12	W3	118.3(5)
W4	Te15	W7 ²	106.0(4)
W2	Te15	W4	73.0(3)
W2	Te15	W7 ²	101.1(3)
W5	Te14	W2 ⁴	104.1(4)
W7	Te14	W2 ⁴	99.5(3)
W7	Te14	W5	73.3(3)
W6	Te10	W3	110.9(3)
W6	Te10	W1	111.1(4)
W1	Te10	W3	82.5(3)
Br4	Te10	W6	118.0(6)
Br4	Te10	W3	113.8(5)
Br4	Te10	W1	115.3(5)
W8	Te8	W7 ¹	64.7(3)
W8	Te8	W7	64.7(3)
W7 ¹	Te8	W7	89.5(4)
W6	Te6	W5	62.0(3)
W7	Te6	W6	62.0(2)
W7	Te6	W5	76.9(3)
W4 ⁴	Te16	W7 ¹	109.7(4)
W4 ⁴	Te16	W7	109.7(4)
W7	Te16	W7 ¹	89.5(5)
Br6	Te16	W4 ⁴	115.8(7)
Br6	Te16	W7	114.6(5)
Br6	Te16	W7 ¹	114.6(5)
W6	Te9	W6 ³	73.5(4)
W6	Te9	W1	102.9(4)
W6 ³	Te9	W1	102.9(4)
W8	Te11	W3	101.6(3)
W6	Te11	W8	77.4(3)
W6	Te11	W3	102.8(3)
W6 ³	Te5	W6	79.0(5)
W5	Te5	W6 ³	63.4(4)
W5	Te5	W6	63.4(4)
W8	Te7	W6	83.6(3)
W7	Te7	W8	65.8(3)
W7	Te7	W6	61.9(3)
W3	Te4	W4	62.1(3)
W3 ¹	Te4	W4	62.1(3)
W3 ¹	Te4	W3	77.3(5)
W2	Te2	W3	62.2(3)
W2	Te2	W1	66.9(3)
W1	Te2	W3	84.7(4)

¹1-x,+y,+z; ²+x,+y,-1+z; ³-x,+y,+z; ⁴+x,+y,1+z; ⁵-x,+y,1+z

Publication 4

A New Modification of TeI_4 Possessing the Crystal Structure Proposed for WI_4



<https://doi.org/10.1021/acs.cgd.0c00053>

Reprinted with permission from

Cryst. Growth Des. **2020**, *20*, 3780-3784.

Copyright © 2020 American Chemical Society

A New Modification of TeI_4 Possessing the Crystal Structure Proposed for WI_4

Philipp Schneiderhan, Patrick Schmidt, Markus Ströbele, Carl P. Romao, and Hans-Jürgen Meyer*



Cite This: *Cryst. Growth Des.* 2020, 20, 3780–3784



Read Online

ACCESS |



Metrics & More

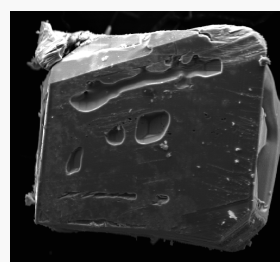


Article Recommendations



Supporting Information

ABSTRACT: A modification of TeI_4 ($\zeta\text{-TeI}_4$) was discovered in an attempt to reproduce a reported synthesis of WI_4 , beginning from WTe_2 and iodine. The crystal structure of $\zeta\text{-TeI}_4$ was solved from single-crystal data in the triclinic space group $P\bar{1}$, isotypic with the structure of the previously reported WI_4 . The crystal structure of $\zeta\text{-TeI}_4$ contains isolated tetrameric Te_4I_{16} molecules, in which tellurium atoms are coordinated by six iodine atoms. Electron microprobe and ICP-OES measurements confirm the identity of the new phase and make the formation of WI_4 via this synthesis route implausible. A comparison of $\zeta\text{-TeI}_4$ with all other TeI_4 polymorphs is drawn by DFT calculations and structural relationships. Special conditions regarding the formation of $\zeta\text{-TeI}_4$ as well as the phase transition from $\delta\text{-TeI}_4$ into $\zeta\text{-TeI}_4$ are reported.



INTRODUCTION

Metal dichalcogenides have been traditionally used for the preparation of chalcogenide–halide compounds. Syntheses of this type are exemplified by rhenium, where $\text{Re}(\text{Ch})_2$ ($\text{Ch} = \text{S}, \text{Se}$) reacts with halides to yield ReCl_2S , ReCl_2Se , or $\text{Re}_3\text{Br}_5\text{Se}_2$.¹ A similar type of reaction was reported for the preparation of WI_4 by exposure of WTe_2 to iodine.²

Studies on binary tungsten iodides were reported more than 100 years ago, including the preparation of WI_4 from a reaction of WCl_6 with HI at 110 °C.^{3,4} A convenient synthesis of tungsten iodides $\text{W}_3\text{I}_8 \cdot n\text{I}_2$ ($n = 0, 1, 2$) was developed more recently from a reaction of WCl_6 and SiI_4 at 120 °C.⁵ After the discovery of trigonal cluster compounds $\text{W}_3\text{I}_8 \cdot n\text{I}_2$, their successive transformation reactions into tetrahedral, square-pyramidal, and octahedral clusters were explored by thermal scanning to investigate the binary tungsten iodine system in more detail, resulting in the discovery of more than 15 binary tungsten iodides that have been structurally characterized.⁶ The unusually high preparation temperature reported for WI_4 (520 °C)² was also commented upon in this work.⁶ This feature and the close structural relationship between the reported crystal structure of WI_4 and that of $\delta\text{-TeI}_4$ gave cause to screen the given reaction between WTe_2 and I_2 in detail.

Although the formation of TeI_4 in this reaction is clear, we are unable to confirm the formation of WI_4 , as it seems the formation of a new modification of TeI_4 ($\zeta\text{-TeI}_4$), adopting the crystal structure reported for WI_4 , is favored. The identity of the product as TeI_4 is examined by chemical analyses. Lattice energies of the new $\zeta\text{-TeI}_4$ phase are reported in comparison with those of previously reported TeI_4 phases, and the formation, relationship, and transformation conditions are analyzed.

RESULTS AND DISCUSSION

Synthesis and Crystal Structure. TeI_4 ($\zeta\text{-TeI}_4$) was synthesized according to the method described in the literature² for WI_4 : by heating WTe_2 with elemental I_2 at 520 °C for 48 h in a fused silica tube. The resulting black crystalline powder was selected and indexed in a triclinic unit cell, isotypic with WI_4 , and the lattice parameters were refined using the LeBail method in the Fullprof Suite with the lattice parameters of WI_4 as starting values.^{7,8} The refined lattice parameters in comparison with the literature values are given in Table 1.

A stoichiometric reaction of appropriate proportions of elemental tellurium and iodine yielded crystals of $\delta\text{-TeI}_4$ (orthorhombic, $Pnma$) after cooling from 520–620 °C to room temperature.

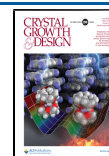
Table 1. Comparison of the Lattice Parameters of so-Called WI_4 and $\zeta\text{-TeI}_4$ Refined from Powder X-ray Diffraction Data

lattice param	WI_4 ²	$\zeta\text{-TeI}_4$
$a/\text{\AA}$	7.9291(3)	7.9345(2)
$b/\text{\AA}$	10.7695(4)	10.7734(5)
$c/\text{\AA}$	10.8117(4)	10.7991(4)
α/deg	85.688(1)	85.623(2)
β/deg	71.772(1)	71.746(2)
γ/deg	71.559(1)	71.520(3)
$V/\text{\AA}^3$	831.60(5)	831.19(5)

Received: January 13, 2020

Revised: April 17, 2020

Published: April 27, 2020



Both δ -TeI₄ and ζ -TeI₄ crystallize from the gas phase so that single crystals can be obtained quite easily; a specimen of ζ -TeI₄ is displayed in Figure 1.

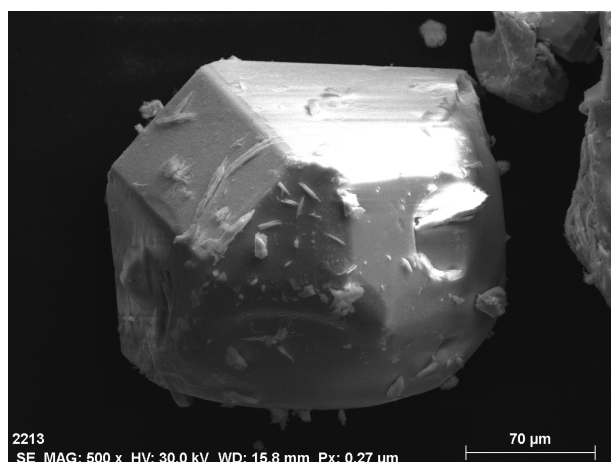


Figure 1. Electron micrograph of a ζ -TeI₄ crystal.

A single-crystal diffraction measurement was performed using suitable single crystals from the reaction $WTe_2 + I_2$ by X-ray diffraction on a STOE IPDS 2-T system as described in the Experimental Section.

A structure refinement with the metal sites occupied by tungsten resulted in $R1 = 0.0822$ and $wR2 = 0.2342$ for all 2868 independent reflections. Exchanging tungsten for tellurium improved the results of the refinement, yielding $R1 = 0.0274$ and $wR2 = 0.0491$. Details of the structure refinement, including a comparison with the literature data, are given in Tables S1 and S2 in the Supporting Information.

The crystal structure of ζ -TeI₄ is characterized by Te₄I₁₆ molecules, in which tellurium atoms are surrounded by six iodido ligands in a distorted-octahedral fashion (Figure 2). This structural pattern has been already reported for δ -TeI₄ in the literature.⁹

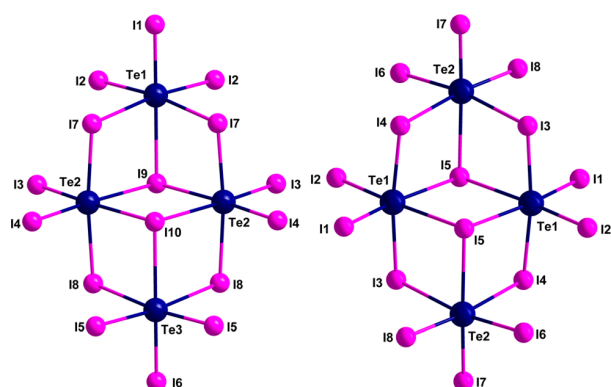


Figure 2. Te₄I₁₆ units in δ -TeI₄ (left) and in ζ -TeI₄ (right) structures.

No less than five modifications have been reported for TeI₄, prepared by evaporation from a HI solution. Their stabilities have been reported to follow the sequence $\epsilon < \alpha < \beta < \gamma < \delta$; δ -TeI₄ was considered to be the thermodynamically stable modification with a melting point of 280 °C.¹⁰

A basic difference among the structures of the α -, β -, γ -, δ -, and ζ -TeI₄ modifications is the distortion of the Te environment by iodide atoms of the Te₄I₁₆ body. A comparison of Te–I distances in the crystal structures of δ -TeI₄ (left) and in ζ -TeI₄, ranging between 272 and 331 pm, yields average values of 299.8(1) and 299.15(5) pm (Table 2).

Table 2. Comparison of Te–I Distances in δ -TeI₄ and ζ -TeI₄

δ -TeI ₄	distance/pm	ζ -TeI ₄	distance/pm
Te(1)–I(1)	277.3(2)	Te(2)–I(7)	276.33(6)
Te(1)–I(2)	275.3(1)	Te(2)–I(6)	276.81(5)
		Te(2)–I(8)	272.30(5)
Te(1)–I(7)	327.9(1)	Te(2)–I(4)	330.64(5)
		Te(2)–I(3)	322.97(5)
Te(1)–I(9)	320.0(2)	Te(2)–I(5)	319.16(5)
Te(2)–I(7)	293.3(3)	Te(1)–I(4)	294.80(5)
Te(2)–I(3)	276.6(1)	Te(1)–I(2)	273.99(5)
Te(2)–I(4)	277.0(1)	Te(1)–I(1)	274.71(5)
Te(2)–I(10)	324.7(1)	Te(1)–I(5)	323.11(4)
Te(2)–I(9)	324.1(1)	Te(1)–I(5)	329.24(5)
Te(2)–I(8)	298.9(1)	Te(1)–I(3)	295.74(5)
Te(3)–I(10)	321.4(2)	Te(2)–I(5)	319.16(5)
Te(3)–I(5)	278.9(1)	Te(2)–I(8)	272.30(5)
		Te(2)–I(6)	276.81(5)
Te(3)–I(8)	323.1(1)	Te(2)–I(3)	322.97(5)
		Te(2)–I(4)	330.64(5)
Te(3)–I(6)	276.1(2)	Te(2)–I(7)	276.33(6)

In spite of similar distances within Te₄I₁₆ tetramers, their symmetries and structural arrangements are different. The Te₄I₁₆ tetramer of δ -TeI₄ contains a vertical mirror plane, visible in Figure 2 (left). The arrangements of Te₄I₁₆ molecules in the structures of δ -TeI₄ (*Pnma*) and ζ -TeI₄ (*P1*) are shown in Figure 3.

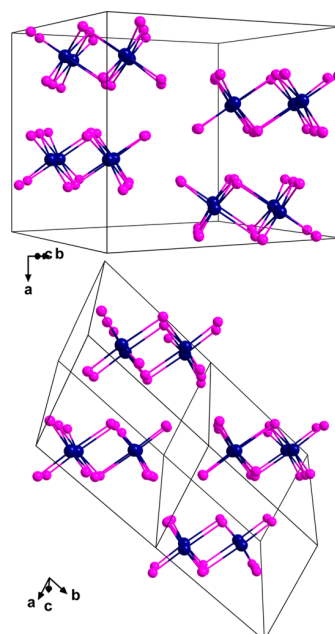


Figure 3. Crystal structures of δ -TeI₄ (top) and ζ -TeI₄ (bottom) with unit cell edges shown.

The arrangement of iodine atoms in the structures can be derived from stacking of hexagonal layers in a nearly close packing. Tellurium cations occupy one-fourth of the octahedral sites in every (δ -TeI₄) interlayer, and half of the octahedral sites in every other (ζ -TeI₄) interlayer. Hence, the arrangement of Te₄I₁₆ molecules in the structure of ζ -TeI₄ can be related to a defect CdI₂ structure with empty ($\square$) octahedral voids (Te₄ $\square$ I₁₆; see Figure S1) within metal layers.

The crystal structure of α -TeI₄ has been reported to adopt a trigonal space group ($P\bar{3}m1$) wherein tellurium atoms occupy half of the metal positions of a 2H-CdI₂ type structure with disordered Te₄I₁₆ units in the structure.¹¹ A relationship between α -TeI₄ and ζ -TeI₄ cannot be clarified due to the lack of diffraction data for α -TeI₄ in the literature.

The structure of ϵ -TeI₄ is also constituted from tetrameric Te₄I₁₆; however, it has a cubane-type structure corresponding to the crystal structures of TeCl₄ and TeBr₄.

In light of different distortion patterns evident in TeI₄ modifications with tetrameric Te₄I₁₆ units, calculations of lattice energies were undertaken.

Lattice Energies of TeI₄ Modifications. In order to rationalize the large number of observed polymorphs of TeI₄, density functional theory (DFT) calculations were performed to obtain the lattice energy (i.e., the total energy at 0 K minus the zero-point vibrational energy) of the β , γ , δ , ϵ ,¹⁰ and ζ polymorphs both in the structures determined crystallographically at 300 K (Table 3) and following structural relaxation (Table 4).

Table 3. Comparison of the Calculated Lattice Energies (E) of Several Polymorphs of TeI₄, with the Increase in Energy Compared to That of the Most Stable Form Shown as ΔE

polymorph	$E/\text{MJ mol}^{-1}$	$\Delta E/\text{kJ mol}^{-1}$
β -TeI ₄	−144.3837	6.2
γ -TeI ₄	−144.3899	2.2
δ -TeI ₄	−144.3856	0
ϵ -TeI ₄	−144.3877	4.3
ζ -TeI ₄	−144.3838	6.1

Table 4. Comparison of the Calculated Lattice Energies (E) of Several Polymorphs of TeI₄ Following Structural Relaxation, with the Increase in Energy Compared to That of the Most Stable Form Shown as ΔE

polymorph	$E/\text{MJ mol}^{-1}$	$\Delta E/\text{kJ mol}^{-1}$
β -TeI ₄	−144.5699	2.4
γ -TeI ₄	−144.5722	1.2
δ -TeI ₄	−144.5656	0
ϵ -TeI ₄	−144.5709	6.6
ζ -TeI ₄	−144.5697	2.5

The δ polymorph is predicted to be the most stable. The differences between polymorphs are relatively small—on the order of a few kJ mol^{−1}. The difference between β -TeI₄ and ζ -TeI₄ is particularly small (0.1 kJ mol^{−1}); at this energy scale differences in vibrational entropy (not included in these calculations) could be sufficient to stabilize one polymorph over another. Structural relaxation decreased the energies of all polymorphs by approximately 0.2 MJ mol^{−1}; the ordering of the stabilities was mostly unaffected, with ϵ -TeI₄ being the least stable polymorph following relaxation. Crystal structures

following structural relaxation are available as part of the Supporting Information.

Calculations of Madelung energies had previously been used to estimate the relative stability of the various polymorphs as $\epsilon < \gamma < \delta < \beta$;¹⁰ the ordering here, which also includes contributions from the energies of the electrons, shows β as the least stable polymorph rather than the most stable but otherwise is in agreement. A comparison to the reported ordering of thermal stabilities ($\epsilon < \alpha < \beta < \gamma < \delta$)¹⁰ indicates that δ -TeI₄ is likely the thermodynamic ground state at all temperatures; it is not stabilized by vibrational entropy.¹² This result indicates that all other polymorphs of TeI₄ are truly metastable and require kinetic control for synthesis and that no phase transition from the δ -TeI₄ form is expected on cooling.

Chemical Analyses. Crystals from the reaction of WTe₂ with I₂ were selected and analyzed for their elemental compositions to find out about compositional differences that may exist for ζ -TeI₄.

ICP-OES measurement results yielded averaged ratios of the elements in the sample as follows: Te:I = 1:3.98, with 0.005(2)% W.

Finally, the tellurium to tungsten ratio was inspected by electron microprobe measurements on different crystals. Averaged element ratios of the samples were determined as Te:I = 1:4.0(1). Only in one spot could a tungsten amount of 0.0065 atom % be detected. The results of this measurements are shown in Table S3.

Transformation of δ -TeI₄ into ζ -TeI₄. δ -TeI₄ is prepared from the elements Te and I₂, and the synthesis of ζ -TeI₄ was performed, departing from WTe₂ and I₂. This raises the question whether a catalytic effect could influence the formation of ζ -TeI₄. From a structural point of view, tungsten could be easily incorporated into TeI₄, as the corresponding Te–I and W–I distances are practically indistinguishable and the structure of ζ -TeI₄ contains empty voids (Figure S1) between tetramers (as in δ -TeI₄ as well). However, chemical analyses did not show a significant amount of tungsten to be present in the samples of ζ -TeI₄.

Sublimation experiments of individual phases did not show a transformation from δ -TeI₄ into ζ -TeI₄ or vice versa, so that both phases remain the same. Finally, the sublimation of δ -TeI₄ yielded a transformation into ζ -TeI₄ in the presence of small portions (single grains) of WTe₂, W(CO)₆, Mo, or Sn in vacuum-sealed silica tubes at approximately 200 °C. These experiments reveal that the presence of impurities plays a critical role in the formation of ζ -TeI₄.

CONCLUSION

The reaction between WTe₂ and iodine has produced hitherto unknown crystals with the composition TeI₄ that we call ζ -TeI₄. A previously obtained product from the given reaction was obviously assigned by mistake as WI₄,² with the same crystal structure we describe herein for ζ -TeI₄. Analytical studies confirm the composition as TeI₄. We conclude that the appearance of a WI₄ with the ζ -TeI₄ structure is not confirmed and the existence of tungsten tetraiodide remains unknown (WI₅ and WI₆ are also unknown). Tungsten tetraiodide, if existent under ambient conditions, is considered to be a thermally labile phase, because tungsten iodides are known to undergo self-reduction at temperatures as low as 100 °C.^{4,5,19}

Five modifications (α , β , γ , δ , and ϵ) have been reported for TeI₄, with all of them, except ϵ -TeI₄, containing the same tetrameric Te₄I₁₆ molecule with small dimensional derivations.

The results of DFT calculations reveal the structure of δ -TeI₄ to represent the thermodynamic ground state, and all other polymorphs of TeI₄ are truly metastable and require kinetic control for synthesis.

The formation of ζ -TeI₄ is enabled by the presence of an impurity derived from W, Mo, or Sn phases which did not turn out to be a significant constituent in the structure. δ -TeI₄ can be transformed into ζ -TeI₄ in the presence of small amounts of one of the aforementioned external phases via gas-phase reactions at approximately 200 °C. The temperature dependence of partial pressures of relevant gas-phase species such as TeI₄, TeI₂, and I₂²⁰ and the influence of a secondary phase do not provide a uniform picture of the crystallization of TeI₄ to understand the formation of ζ -TeI₄.

■ EXPERIMENTAL SECTION

Synthesis. Manipulations of starting materials, such as charging the fused silica ampules with starting materials, were performed in an argon-filled glovebox (MBraun, Labmaster 130, O₂ <1 ppm, H₂O <1 ppm).

WTe₂. WTe₂ was prepared from the elements W (ABCR GmbH, 99.95%) and Te (Evochem, 99.999%) and iodine (sublimed, 99.99%), vacuum-sealed into a silica tube in stoichiometric proportions and heated at 800 °C for 24 h.

ζ -TeI₄ (bulk). A mixture of 100 mg WTe₂ (0.23 mmol) and 300 mg of I₂ (2.4 mmol), fused into an evacuated silica tube, was heated in a Simon-Müller furnace at a rate of 2.0 K/min to 520 °C and kept at this temperature for 48 h (we note that the amount of iodine was erroneously given as 0.683 mmol instead of 6.83 mmol in ref 2). Afterward, the ampule was cooled to room temperature at a rate of 0.5 K/min. ζ -TeI₄ was obtained at the cooler part of the ampule as a black crystalline powder, in addition to crystals of (TeI₃)₂[W₆I₁₄].¹⁰

δ -TeI₄. This form was synthesized from stoichiometric proportions of Te powder and I₂ under conditions identical with those described for ζ -TeI₄.

ζ -TeI₄ (Single Crystals). Single crystals of ζ -TeI₄ were synthesized by heating 100 mg of WTe₂ (0.23 mmol) and 300 mg of I₂ (2.4 mmol) at a rate of 2.0 K/min up to 360 °C in an evacuated silica tube. The ampule was kept at this temperature for 8 h and then cooled to room temperature at a rate of 2.0 K/min. The single crystals (approximate size 0.2 mm) were found in the middle part of the ampule.

Alternative Synthesis Routes for ζ -TeI₄. With W(CO)₆, ζ -TeI₄ was obtained by reacting 50.00 mg of tellurium (0.4 mmol) and 198.91 mg of iodine (1.6 mmol) with an addition of 6.89 mg of W(CO)₆ (0.02 mmol) fused into an evacuated silica tube. The ampule with the mixture was heated at a rate of 2.0 K/min to 620 °C, kept at this temperature for 48 h, and then cooled to room temperature at a rate of 0.5 K/min. ζ -TeI₄ was obtained as a black powder at the cooler part of the ampule. Similar results were obtained in the presence of Sn or Mo.

With WTe₂. ζ -TeI₄ was obtained by reacting 50.00 mg of tellurium (0.39 mmol) and 198.91 mg of I₂ (0.78 mmol) with an addition of 8.60 mg WTe₂ (0.02 mmol) fused into an evacuated silica tube. The ampule with the mixture was heated at a rate of 2.0 K/min to 620 °C, kept at this temperature for 48 h, and then cooled to room temperature at a rate of 0.5 K/min. TeI₄ was obtained as a black powder at the cooler part of the ampule.

Powder X-ray Diffraction Studies. All reaction products were investigated by powder X-ray diffraction (PXRD) using a StadiP diffractometer (Stoe, Darmstadt) with Ge-monochromated Cu K α radiation and a Mythen1 Detector. A black crystalline powder of ζ -TeI₄ was selected and indexed as triclinic, isotypic with WI₄, and the lattice parameters were refined using the LeBail fit of the Fullprof Suite⁷ with the lattice parameters of WI₄ as starting values. The refined lattice parameters in comparison with the literature values are given in Table 1.

Single-Crystal X-ray Diffraction. Black single crystals of ζ -TeI₄ were selected and mounted on the tip of a glass fiber for an intensity measurement using a single-crystal X-ray diffractometer (STOE IPDS 2-T, Darmstadt, Germany), equipped with (graphite) monochromatic Mo K α radiation (λ = 0.71073 Å) at room temperature. Raw data intensities were corrected for Lorentz factors and polarization by the IPDS software. Absorption effects were corrected by the X-Red/X-Shape program of the STOE software. Crystal structure solutions were obtained by direct methods (SHELXS), followed by full-matrix least-squares structure refinements with SHELXL-2017.¹³ Details of the structure refinements are presented in Tables S1 and S2.

Electron Microscopy. Scanning electron microscopy (SEM) was performed on a Hitachi SU8030 scanning electron microscope at a maximum acceleration voltage of 30 kV and a free working distance of 15.0 mm. EDX investigations were performed with an acceleration voltage of 30 kV.

ICP-OES. After dissolution of TeI₄ in 2 wt % of NaOH/H₂O₂ the W:Te:I ratio was determined by ICP-OES (iCAP 7400 Thermo Scientific).

Electron Microprobe Analysis. Electron microprobe analysis was performed on a JEOL 8900 Superprobe spectrometer using an acceleration voltage of 20 kV, a probe current of 10^{−9} A, and a beam diameter of 10^{−6} m. The samples were coated with carbon prior to the measurements.

Density Functional Theory. DFT calculations were carried out using the Abinit software package with the projector-augmented wave (PAW) method.^{14,15} Convergence studies (to 1% in pressure) were used to choose a 3 × 2 × 2 Monkhorst–Pack grid¹⁶ of *k* points, an 18 Å coarse grid, and 108 fine-grid plane-wave basis set energy cutoffs. PAW data sets were used as received from the Abinit library.^{14,17,18} Example input files are available as part of the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.cgd.0c00053>.

Comparison of the results of single-crystal refinements for WI₄ and ζ -TeI₄, comparison of the atomic coordinates of WI₄ with those of ζ -TeI₄, results of the electron microprobe measurements, one layer of the crystal structure of ζ -TeI₄ highlighting the octahedral voids (some are highlighted as polyhedra) in the structure of Te₄□₄I₁₆ (PDF)

Accession Codes

CCDC 1940965 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Hans-Jürgen Meyer — Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls Universität Tübingen, D-72076 Tübingen, Germany; orcid.org/0000-0003-2450-4011; Email: juergen.meyer@uni-tuebingen.de

Authors

Philipp Schneiderhan — Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls Universität Tübingen, D-72076 Tübingen, Germany

Patrick Schmidt — Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls Universität Tübingen, D-72076 Tübingen, Germany

Markus Ströbele — Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls Universität Tübingen, D-72076 Tübingen, Germany;

orcid.org/0000-0002-5147-5677

Carl P. Romao — Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls Universität Tübingen, D-72076 Tübingen, Germany

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.cgd.0c00053>

Funding

The authors acknowledge support by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through Grant No. INST 40/467-1 FUGG (JUSTUS cluster).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors appreciate the expertise and support of the following scientists from the University of Tübingen: Dr. Jochen Glaser for the ICP-OES and Priv.-Doz. Dr. Thomas Wenzel for electron microprobe analyses.

REFERENCES

- (1) Rice, D. A. The sulphido-, seleno- and telluro-halides of the transition elements. *Coord. Chem. Rev.* **1978**, *25*, 199–227.
- (2) Yarovoi, S. S.; Smolentsev, A. I.; Ermolaev, A. V.; Mironov, Y. V. Crystal structure of Wl_4 . *J. Struct. Chem.* **2016**, *57*, 199–201.
- (3) Defacqz, E. Sur un iodure de tungstène. *C. R. Hebd. Seances Acad. Sci.* **1898**, *126*, 962–964.
- (4) Defacqz, E. Contributions a L'Étude du Tungstène et de ses Composés. *Ann. Chim. Phys.* **1901**, *22*, 239–288.
- (5) Ströbele, M.; Castro, C.; Fink, R. F.; Meyer, H.-J. A Facile Method for the Synthesis of Binary Tungsten Iodides. *Angew. Chem., Int. Ed.* **2016**, *55*, 4814–4817.
- (6) Ströbele, M.; Meyer, H.-J. Pandora's box of binary tungsten iodides. *Dalton Trans.* **2019**, *48*, 1547–1561.
- (7) Rodriguez-Carvajal, J.; Roisnel, T. FullProf.98 and WinPLOTR: New Windows 95/NT Applications for Diffraction. *IUCr-News.* **1998**, *20*, 35–36.
- (8) Roisnel, T.; Rodríguez-Carvajal, J. WinPLOTR: A Windows Tool for Powder Diffraction Pattern Analysis. *Mater. Sci. Forum* **2001**, *378–381*, 118–123.
- (9) Krebs, B.; Paulat, V. Kristallstruktur des Tellurtetraiodids TeI_4 . *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 1470–1476.
- (10) Kniep, R.; Beister, H. J.; Wald, D. Polymorphie von Tellur(IV)-iodid. *Z. Naturforsch., B: J. Chem. Sci.* **1988**, *43*, 966.
- (11) Kniep, R. *Subhalogenide des Tellurs*; Dissertation, TH Braunschweig, 1973.
- (12) Fultz, B. Vibrational thermodynamics of materials. *Prog. Mater. Sci.* **2010**, *55*, 247–352.
- (13) Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *C71*, 3–8.
- (14) Gonze, X.; Jollet, F.; Abreu Araujo, F.; Adams, D.; Amadon, B.; Applencourt, T.; Audouze, C.; Beuken, J. M.; Bieder, J.; Bokhanchuk, A.; Bousquet, E.; Bruneval, F.; Caliste, D.; Côté, M.; Dahm, F.; Da Pieve, F.; Delaveau, M.; Di Gennaro, M.; Dorado, B.; Espejo, C.; Geneste, G.; Genovese, L.; Gerossier, A.; Giantomassi, M.; Gillet, Y.; Hamann, D. R.; He, L.; Jomard, G.; Laflamme Janssen, J.; Le Roux, S.; Levitt, A.; Lherbier, A.; Liu, F.; Lukačević, I.; Martin, A.; Martins, C.;

Oliveira, M. J. T.; Poncé, S.; Pouillon, Y.; Rangel, T.; Rignanese, G. M.; Romero, A. H.; Rousseau, B.; Rubel, O.; Shukri, A. A.; Stankovski, M.; Torrent, M.; Van Setten, M. J.; Van Troeye, B.; Verstraete, M. J.; Waroquiers, D.; Wiktor, J.; Xu, B.; Zhou, A.; Zwanziger, J. W. Recent developments in the ABINIT software package. *Comput. Phys. Commun.* **2016**, *205*, 106–131.

(15) Torrent, M.; Jollet, F.; Bottin, F.; Zerah, G.; Gonze, X. Implementation of the projector augmented-wave method in the ABINIT code: Application to the study of iron under pressure. *Comput. Mater. Sci.* **2008**, *42*, 337–351.

(16) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(17) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. *77*, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.

(18) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(19) Ströbele, M.; Meyer, H.-J. The Archetype Tungsten Iodide Cluster Compound W_3I_8 . *Z. Anorg. Allg. Chem.* **2016**, *642*, 631–634.

(20) Shlykov, S. A.; Oberhammer, H.; Titov, A. V.; Giricheva, N. I.; Girichev, G. V. A Combined Gas-Phase Electron Diffraction/Mass Spectrometric Study of the Sublimation Processes of TeBr_4 and TeI_4 : The Molecular Structure of Tellurium Dibromide and Tellurium Diiodide. *Eur. J. Inorg. Chem.* **2008**, *2008*, S220–S227.

A new modification of TeI_4 possessing the crystal structure proposed for WI_4

*Philipp Schneiderhan, Patrick Schmidt, Markus Ströbele, Carl P. Romao and Hans-Jürgen
Meyer**

Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry,
Auf der Morgenstelle 18, Eberhard Karls Universität Tübingen, D-72076 Tübingen, Germany.

Table S1. Comparison of the results of single crystal refinements for Wl₄^a and ζ-TeI₄.

Parameter	Wl ₄ ^a	ζ-TeI ₄
Unit cell dimensions	a = 7.9291(3) Å b = 10.7695(4) Å c = 10.8117(4) Å α = 85.6680(10) ° β = 71.7720(10) ° γ = 71.5590(10) °	a = 7.8850(3) Å b = 10.7024(5) Å c = 10.7485(4) Å α = 85.657(3) ° β = 71.789(3) ° γ = 71.563(3) °
Volume /Å ³	831.60(5)	817.12(6)
Z	4	4
Measurement temperature	296(2)	293(2)
Crystal size	0.08 x 0.08 x 0.05 mm ³	0.27 x 0.27 x 0.15 mm ³
Independent reflections	3123	2868
Largest diff. peak and hole	7.316 and -9.786 e.Å ⁻³	0.739 and -0.538 e.Å ⁻³
R indices (all data)	R ₁ = 0.0646, wR ₂ = 0.1796	R ₁ = 0.0274, wR ₂ = 0.0491
Goodness-of-fit on F ²	1.142	1.067

^aYarovoi, S. S.; Smolentsev, A. I.; Ermolaev, A. V.; Mironov, Y. V., Crystal structure of Wl₄, *J. Struct. Chem.* **2016**, 57 (1), 199-201.

Table S2. Comparison of the atomic coordinates of Wl₄^a (left) with ζ-TeI₄ (right).

Atom Name	x	y	z	U _{eq}	x	y	z	U _{eq}
W1/Te1	0.28223(11)	0.34978(8)	0.36123(8)	0.0293(3)	0.28192(4)	0.35015(3)	0.36120(3)	0.02171(9)
W2/Te2	0.00148(11)	0.24341(8)	0.78446(8)	0.0301(3)	0.00166(4)	0.24328(3)	0.78412(3)	0.0223(1)
I1	0.36264(17)	0.24867(13)	0.11585(11)	0.0208(3)	0.36446(5)	0.25222(4)	0.11300(3)	0.0309(1)
I2	0.62254(16)	0.22089(14)	0.39562(13)	0.0273(3)	0.62384(5)	0.22237(4)	0.39633(4)	0.0328(1)
I3	0.39351(15)	0.58427(12)	0.26151(12)	0.0191(3)	0.39122(4)	0.58806(4)	0.26349(4)	0.02865(9)
I4	0.12488(18)	0.13609(13)	0.47873(11)	0.0251(3)	0.12432(5)	0.13732(4)	0.47797(3)	0.0311(1)
I5	0.13334(14)	0.49040(12)	0.65564(10)	0.0145(3)	0.13293(4)	0.48899(3)	0.65487(3)	0.02411(9)
I6	0.35977(15)	0.12213(14)	0.79693(13)	0.0241(3)	0.36329(5)	0.11902(4)	0.79311(4)	0.0328(1)
I7	-0.13321(18)	0.03290(13)	0.84930(12)	0.0277(4)	-0.13173(5)	0.02981(4)	0.84984(4)	0.0330(1)
I8	-0.13490(18)	0.35369(14)	1.03029(11)	0.0301(4)	-0.13241(5)	0.35404(4)	1.02946(3)	0.0341(1)

Table S3. Results of the electron microprobe measurements.

Crystal 1

Element	El. Wt%	Norm El%	At prop
Te	21.16	20.71	20.615
I	81.04	79.29	79.385
W	0.00	0.00	0.000

Total:	102.21	100.00	100.000
Te : I = 1:3.85			

Crystal 2

Element	El. Wt%	Norm	At prop
Te	20.93	20.45	20.356
I	81.42	79.55	79.644
W	0.00	0.00	0.000

Total:	102.35	100.00	100.000
Te : I = 1:3.91			

Crystal 3

Element	El. Wt%	Norm El%	At prop
Te	19.65	19.93	19.840
I	78.96	80.06	80.153
W	0.0093	0.0095	0.0065

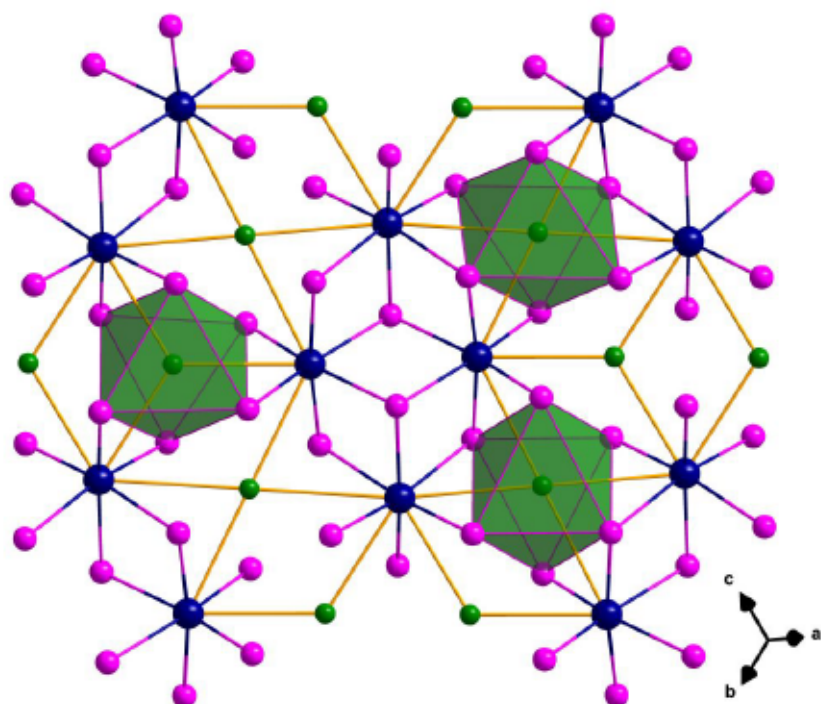
Total:	98.62	100.00	100.000
Te : I = 1:4.04			

El- Wt%: Element-weight-%

Norm El%: Normalized Element-%

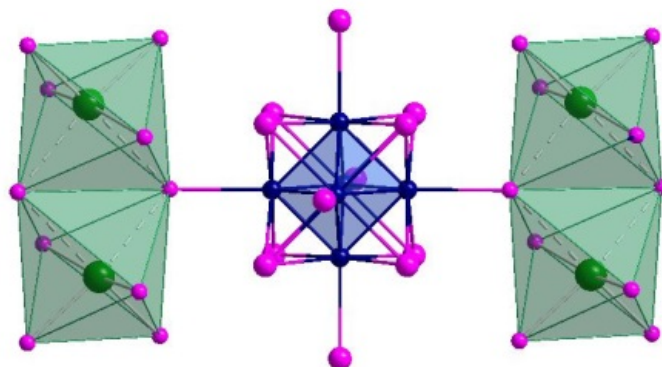
At prop: Atom proportion

Figure S1. One layer of the crystal structure of ζ -TeI₄ highlighting the octahedral voids (some are highlighted as polyhedras) in the structure (Te₄□₄I₁₆ with Te = blue, I = purple and □ = green).



Publication 5

Synthesis of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ via Iodination of WTe_2



<https://doi.org/10.1002/ejic.201901337>

Reprinted with permission from

Eur. J. Inorg. Chem. **2020**, 8, 716-719.

Copyright © 2020 Wiley-VCH GmbH

Tungsten Iodide Clusters

Synthesis of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ via Iodination of WTe_2

Patrick Schmidt,^[a] Amira Siai,^[a] Philipp Schneiderhan,^[a] Markus Ströbele,^[a] and H.-Jürgen Meyer^{*[a]}

Abstract: The new compound $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ appeared as an unforeseen product from a reaction of WTe_2 with iodine at 250 °C, representing an exceptionally low temperature for the formation of an octahedral tungsten iodide cluster. The crystal structure, as refined by single-crystal X-ray diffraction, reveals $(\text{TeI}_3)^+$ ions and the well-known $[\text{W}_6\text{I}_{14}]^{2-}$ cluster. A chemical

analysis confirms the identity of the product. The electronic structure of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ is analyzed in view of the relative position of tellurium states by density functional theory (DFT) calculations. This cluster compound exhibits an indirect band gap as confirmed by the band structure calculation based on the HSE06 hybrid functional theory.

Introduction

Our interest in the iodination of WTe_2 was stimulated by a recent report on the observation of binary WI_4 from this reaction.^[1] Nearly twenty phases have been reported to exist in the binary W–I system and a little less being confirmed.^[2] Tungsten iodides are thermally labile on heating because they are known to undergo self-reduction by release of I_2 . For example, the thermal treatment of W_3I_{12} involves the formation of several binary phases under successive release of I_2 until the most stable cluster compound W_6I_{12} is formed in excess of 300 °C.^[3] The successive reduction of WX_6 ($X = \text{Cl}, \text{Br}$) with reducing agents also leads to W_6X_{12} .^[4]

Surprisingly enough, the preparation of WI_4 was reported from a reaction at 520 °C^[1] where octahedral tungsten iodide clusters are already formed. The preparation of the herein reported $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ from WTe_2 and I_2 at 250 °C represents an unexpected low formation temperature for an octahedral tungsten iodide cluster.

Metal halide clusters with the octahedral $[\text{M}_6\text{X}_8]$ cluster core are evidenced by the binary compounds Mo_6X_{12} and W_6X_{12} ($X = \text{Cl}, \text{Br}, \text{I}$).^[5] Many compounds with the $[\text{W}_6\text{I}_{14}]^{2-}$ cluster have been developed with alkali^[6] as $\text{A}_2[\text{W}_6\text{I}_{14}]$, and alkaline earth^[7] ions as $(\text{AE})[\text{W}_6\text{I}_{14}]$. Their counterparts with organic cations like $(\text{nBu}_4\text{N})^{+}$ ^[8] can serve as soluble starting materials for the preparation of ligand substituted cluster compounds with the $[\text{W}_6\text{L}_6]^{2-}$ ion (L is an inorganic or organic ligand).^[9] These clus-

ter compounds have shown exceptional photophysical properties in solid state and in solution, related to their band gaps.^[10]

Theoretical investigations of the electronic structure of tungsten halide clusters were reported, mostly based on molecular orbital (MO) calculations. Studies of the electronic properties of isolated hexanuclear tungsten halide clusters $[\text{W}_6\text{X}_{14}]^{2-}$ ($X = \text{I}, \text{Br}, \text{Cl}$) revealed band gaps in the order of 2–3 eV.^[11]

In the present work we report the synthesis, crystal structure, electronic band structure and density of states of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$.

Results and Discussion

The reaction between WTe_2 and iodine revealed the new compound $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$. The synthesis of the starting material WTe_2 was performed straight forward from appropriate amounts of the elements tungsten and tellurium in a vacuum-sealed silica tubing at 800 °C.^[12] The phase-purity of WTe_2 was verified by X-ray powder diffraction (estimated > 95 %).

The reaction between WTe_2 and iodine was also performed in a sealed silica tube. At 250 °C black, air-stable single-crystals of the new phase $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ were obtained with $\delta\text{-TeI}_4$ ^[13] as a side phase. This emphasizes that the reaction of gaseous iodine leads to the complete consumption of WTe_2 with the formation of the cluster compound and TeI_4 , that tends to sublime into the colder region of the container. The mechanism of the formation of an octahedral tungsten cluster from the layered tungsten ditelluride structure at this low temperature is not clear.

Interestingly this type of reaction has been used for the original synthesis of rhenium chalcogenide cluster compounds $\text{Re}_3\text{Q}_2\text{X}_5$ ($\text{Q} = \text{Se}, \text{X} = \text{Cl}, \text{Br}; \text{Q} = \text{Te}, \text{X} = \text{Br}$), following the reaction of ReSe_2 and Cl_2 (at 450 °C) by Opalovskii and Fedorov.^[14]

The crystal structure of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$, as refined by single-crystal X-ray diffraction (Table 1) is represented by an octahedral $[\text{W}_6\text{I}_{14}]^{2-}$ cluster and two $(\text{TeI}_3)^+$ ions per triclinic unit cell (Figure 1) resulting from three crystallographic independent W and one Te atom. $(\text{TeI}_3)^+$ ions are known for their trigonal-py-

[a] Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany
E-mail: juergen.meyer@uni-tuebingen.de

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejic.201901337>.

© 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

ramidal structure.^[15] A typical feature of the essentially discrete chalcogen-trihalide cation is the increase of the coordination number of the chalcogen atom by halogen atoms of surrounding halometallate anions.^[16] This feature is also present for the $(\text{TeI}_3)^+$ ion in the crystal structure of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$. Each tellurium atom is comprised in a distorted octahedral environment of three iodides of the $(\text{TeI}_3)^+$ ion itself and three additional iodide ligands arising from outer iodides (I^a) of $[\{\text{W}_6\text{I}_8\}\text{I}_6]^{2-}$, shown in Figure 1.

Table 1. Crystal data from the structure refinement for $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$.

Identification code	CSD-1898645
Formula weight	3896.30 g/mol
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.2593(4) \text{ \AA}$ $\alpha = 116.621(1)^\circ$ $b = 10.2987(4) \text{ \AA}$ $\beta = 95.123(1)^\circ$ $c = 10.7267(4) \text{ \AA}$ $\gamma = 95.362(1)^\circ$
Volume	$997.76(7) \text{ \AA}^3$
Z	1
Goodness-of-fit on F^2	1.068
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.035$, $wR_2 = 0.088$
R indices (all data)	$R_1 = 0.044$, $wR_2 = 0.094$
Largest diff. peak and hole	2.77 and $-3.02 \text{ e \AA}^{-3}$

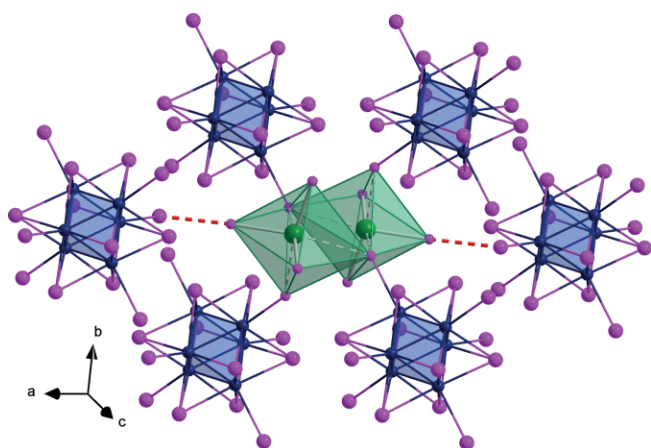


Figure 1. Section of the structure of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$, emphasizing the $[\text{W}_6\text{I}_8]\text{I}_6^{2-}$ cluster and its connectivity to tellurium atoms (green) via outer iodide ligands.

Corresponding Te–I distances within the $(\text{TeI}_3)^+$ ion are at 2.745(1) Å, 2.764(1) Å and 2.810(1) Å and three additional Te– I^a contacts with the iodides of the cluster are at 3.187(2) Å, 3.325(1) Å and 3.531(2) Å.

Another relevant interatomic contact in the structure is due to the van der Waals interactions between one iodido ligand of $(\text{TeI}_3)^+$ and an apical iodido ligand of the cluster with an I–I distance of 3.196(1) Å, emphasized in Figure 1 and Figure 2 by dashed red lines. The overall arrangement in the structure can be described by an alternating layer arrangement of $(\text{TeI}_3)^+$ and $[\{\text{W}_6\text{I}_8\}\text{I}_6]^{2-}$.

The band gap of compounds containing the $[\text{W}_6\text{I}_{14}]^{2-}$ clusters usually amounts to 2–3 eV,^[11] allowing for the unique photophysical properties of such cluster compounds with respect to photoluminescence and/or energy transfer reactions including the generation of singlet oxygen.^[11,17]

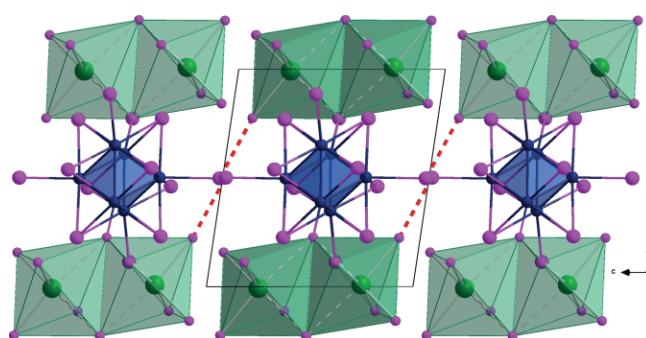


Figure 2. Projection of the crystal structure of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ forming a layered arrangement. Tungsten atoms are shown blue, iodine violet, and tellurium atoms green.

Crystals of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ appear with a black body color and may therefore be expected to have a considerably smaller band gap than other compounds containing the $[\text{W}_6\text{I}_{14}]^{2-}$ cluster. Several reasons may account for the black body color; such as defects in the crystal structure or simply a smaller band gap compared to other compounds containing $[\text{W}_6\text{I}_{14}]^{2-}$ clusters.

A partial substitution of the iodido ligand environment of the cluster by telluride could introduce a significant change to the electronic situation, including the appearance of a $[\text{W}_6\text{I}_{13}\text{Te}]^-$ cluster, having 23 instead of 24 electrons in W–W bonding states of the cluster. Tungsten and tellurium atoms appear quite indistinguishable in the crystal structure refinement, meaning that a substitution of I vs. Te can be neither detected from the refinement of individual atoms in the crystal structure nor by differences of respective (W–I and W–Te) bond lengths.

In attempt to clarify these points, a chemical analysis and an electronic structure calculation were performed.

Chemical Analysis

ICP-OES measurements on single crystals of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ yielded averaged ratios of elements in the sample as follows: W/Te/I = 6:2.24:20.64. Due to the relatively high tellurium content found in the analysis, an electron microprobe measurement on different crystals of the same batch was done (Table S1). Some crystal surfaces or surface sections were covered by an amorphous area containing tellurium (Figure S2). Averaged element ratios of (non-coated areas) of the samples were determined as W/Te/I = 6:2.17(3):21.0(1).

Electronic Structure Calculations

For the sake of an investigation of the electronic properties of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ and for prediction of the contributions of different atomic states to the valence and conduction bands, the DFT calculations of the band structure and the total and partial density of states (DOS) were carried out by using Heyd, Scuseria, and Ernzerhof screened hybrid density functional theory (HSE06).^[18] Considering that pure DFT functionals like generalized gradient approximation (GGA)^[19] and local density approximation (LDA)^[20] underestimate the band gap value by an error

that can reach 1.3 eV, the HSE06 hybrid density functional theory was found to decrease this error to 0.2 eV.^[21] In this work, the electronic calculation was carried out after structural optimization, which reveals an agreement between experimental and theoretical cell parameters. As shown in Figure 3, the band structure shows flat bands over the k-space, suggesting strong localized electron distribution in the lattice. The partial density of states calculations reveals that the maximum of the valence band under the Fermi level (set to 0 eV) is dominated by I (5p) and W (5d) orbitals. At the bottom of the conduction band, it is seen that I (5p) and Te (5p) orbitals represent the major contribution, while the W (5d) states were found to dominate at relatively higher energy level (3 eV). The band structure calculation indicates an indirect band gap (see Figure S4), which is estimated to 1.8 eV by the HSE06 Hybrid functional theory and was found to be in accord with experimental results obtained based on Tauc plot^[22] (see supporting information, Figure S3). The orbital positions at the bottom of the conduction band of Te and I, indicate the effect of tellurium in narrowing the band gap energy compared to what it has been previously estimated for the $[W_6I_{14}]^{2-}$ clusters.^[11] Indeed, the involvement of tellurium states in the bottom of the conduction band can explain the black color of $(TeI_3)_2[W_6I_{14}]$ crystals.

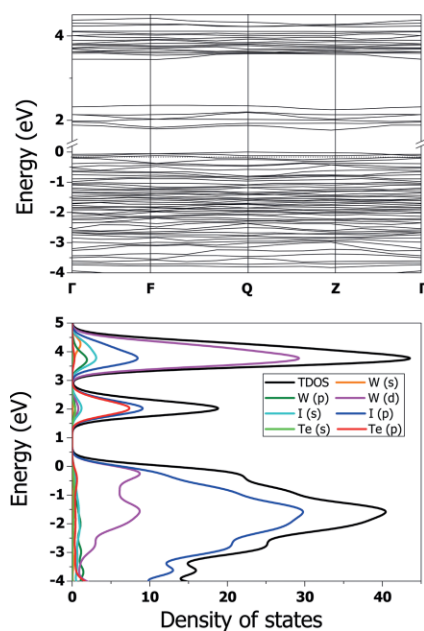


Figure 3. Calculated electronic band structure (top) and partial and total (TDOS) density of states (bottom) of $(TeI_3)_2[W_6I_{14}]$ based on HSE06 hybrid functional. Special points in the band structure of the Brillouin zone are Γ : (0,0,0), F: (0, 0.5, 0), Q: (0, 0.5, 0.5) and Z: (0, 0, 0.5).

Conclusion

Although they have been performed many decades ago, halogenation reactions of transition metal dichalcogenides are not fully explored and can provide new findings. The iodination reaction of WTe_2 involves the new compound $(TeI_3)_2[W_6I_{14}]$ with the well-known $[W_6I_{14}]^{2-}$ cluster with the formation of TeI_4 as a

second phase. The crystal structure of $(TeI_3)_2[W_6I_{14}]$ contains $(TeI_3)^+$ ions and $[W_6I_{14}]^{2-}$ clusters, arranged in a layered fashion.

The formation of the new $(TeI_3)_2[W_6I_{14}]$ with an octahedral tungsten iodide cluster at a temperature as low as 250 °C is unexpected. The calculated electronic structure of $(TeI_3)_2[W_6I_{14}]$ reveals the presence of tellurium (p) energy levels at the bottom of the conduction band. Our calculations reveal a considerably smaller band-gap of $(TeI_3)_2[W_6I_{14}]$ compared to all other compounds containing $[W_6I_{14}]^{2-}$ clusters.^[11] The calculated band structure of $(TeI_3)_2[W_6I_{14}]$ shows significant contributions tellurium and iodine p-states at the bottom of the conduction band, thereby lowering the band gap.

Experimental Section

Synthesis of WTe_2 and $(TeI_3)_2[W_6I_{14}]$: Manipulations of starting materials were performed in an argon-filled glove box (MBraun, lab-master 130, $O_2 < 1$ ppm, $H_2O < 1$ ppm). WTe_2 was prepared in a dry, vacuum sealed silica ampoule (7 mm inner diameter, 9 cm length) with a 1:2.05 molar ratio of tungsten powder (ABCR GmbH, 99.95 %, 0.6–0.9 micron) and tellurium pieces (Evochem, 99.999 %) heated in a first step with 2 K/min up to 420 °C, followed by a ramp of 1 K/min to 700 °C and kept at this temperature for one day (total mass 2 g). For removing unreacted tellurium, the compound was then displaced to one end of the ampoule and kept at a temperature of 650 °C for 24 h, while the other end of the ampoule maintained at room temperature.

$(TeI_3)_2[W_6I_{14}]$ was prepared by heating a 1:3 molar mixture of WTe_2 and iodine in a dry, vacuum sealed silica ampoule (7 mm inner diameter, 5 cm length) at 250 °C for two days. Single crystals appeared as black crystal plates besides crystals of TeI_4 , as identified by powder X-ray diffraction. TeI_4 was removed by sublimation at 200 °C. Yields were up to 95 %.

Single-crystal X-ray diffraction: A single-crystal of $(TeI_3)_2[W_6I_{14}]$ was selected for a single-crystal X-ray diffraction measurement (Stoe, IPDS, Darmstadt, Germany) with (graphite) monochromated Mo- $K\alpha_1$ radiation ($\lambda = 0.71073$ Å) at room temperature. The crystal structure refinement and solution was performed with direct methods (SHELXS) and least square refinements on F^2 (SHELXL14^[23]).

Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe. CCDC 1898645 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

ICP-OES: After dissolution of $(TeI_3)_2[W_6I_{14}]$ in 2-w% KOH/ H_2O_2 the W/Te/I ratio was determined by ICP-OES (iCAP 7400 Thermo Scientific).

Electron microprobe analysis: Electron microprobe analysis were performed on a JEOL 8900 Superprobe spectrometer using an acceleration voltage of 15 kV, Probe current 20 nA, beam diameter 5 μ m.

The samples were coated with carbon prior to the measurements.

UV/Visible near infrared spectroscopy (UV/Vis-NIR). The transmittance of $(TeI_3)_2[W_6I_{14}]$ sample prepared in KBr matrix was measured by UV/Vis-NIR spectroscopy. The measurement was performed using a fiber optic spectrometer purchased from ocean optics (Maya 2000 pro) with a spectral resolution of 3 nm.

DFT calculations. DFT calculations were performed using CASTEP simulation package.^[24] The electronic band structure and density

of states were calculated by HES06 Hybrid functional theory starting from optimized geometry of cell parameters and atomic positions. The first Brillouin zone integration using Γ -center scheme is sampled with a k -point separation on the reciprocal space path of $0.015 \text{ \AA}^{-1}$. The plane wave cut-off energy was set to 500 eV. Norm-conserving pseudo-potential was used to describe the interaction between electrons and ions. The convergence tolerance of the total energy for the wave function self-consistent is set to 5×10^{-7} eV.

Acknowledgments

The authors appreciate the expertise and support of the following scientists from the University of Tübingen: Dr. Jochen Glaser for the ICP-OES and Priv.-Doz. Dr. Thomas Wenzel for electron microprobe analyses. Support of this research by the Deutsche Forschungsgemeinschaft (Bonn) through the project ME 914/31-1 is gratefully acknowledged.

Keywords: Tungsten · Cluster compounds · Synthesis design · Structure elucidation · Band structure

- [1] S. S. Yarovoi, A. I. Smolentsev, A. V. Ermolaev, Y. V. Mironov, *J. Struct. Chem.* **2016**, *57*, 199–201.
- [2] M. Ströbele, H.-J. Meyer, *Dalton Trans.* **2019**, *48*, 1547–1561.
- [3] M. Ströbele, C. Castro, R. F. Fink, H.-J. Meyer, *Angew. Chem. Int. Ed.* **2016**, *55*, 4814–4817; *Angew. Chem.* **2016**, *128*, 4894.
- [4] M. Ströbele, A. Moś, H.-J. Meyer, *Inorg. Chem.* **2013**, *52*, 6951–6956.
- [5] H. Schäfer, H. G. V. Schnering, J. Tillack, F. Kuhn, H. Wöhrle, H. Bauermann, *Z. Anorg. Allg. Chem.* **1967**, *353*, 281–310.
- [6] a) T. Hummel, A. Moś-Hummel, A. Merkulova, M. Ströbele, A. Krishnamurthy, S. Kroeker, H.-J. Meyer, *Inorg. Chem.* **2018**, *57*, 2570–2576; b) T. Hummel, M. Ströbele, D. Schmid, D. Ensling, T. Jüstel, H.-J. Meyer, *Eur. J. Inorg. Chem.* **2016**, *2016*, 5063–5067.
- [7] T. Hummel, A. Moś-Hummel, M. Ströbele, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2019**, *645*, 831–834.
- [8] L. Riehl, A. Seyboldt, M. Ströbele, D. Ensling, T. Jüstel, M. Westberg, P. R. Ogilby, H.-J. Meyer, *Dalton Trans.* **2016**, *45*, 15500–15506.
- [9] Y. A. Vorotnikov, M. A. Mikhailov, K. A. Brylev, D. A. Piryazev, N. V. Kuratieva, M. N. Sokolov, Y. V. Mironov, M. A. Shestopalov, *Russ. Chem. Bull.* **2015**, *64*, 2591–2596.
- [10] M. N. Sokolov, K. A. Brylev, P. A. Abramov, M. R. Gallyamov, I. N. Novozhilov, N. Kitamura, M. A. Mikhaylov, *Eur. J. Inorg. Chem.* **2017**, *2017*, 4131–4137.
- [11] T. G. Gray, *Chem. Eur. J.* **2009**, *15*, 2581–2593.
- [12] A. Eftekhari, *J. Mater. Chem. A* **2017**, *5*, 18299–18325.
- [13] R. Kniep, J. Beister Heinz, D. Wald, *Z. Naturforsch. B* **1988**, *43*, 966.
- [14] a) A. A. Opalovskii, V. E. Fedorov, E. U. Lobkov, *Russ. J. Inorg. Chem.* **1971**, *16*, 790; b) A. A. Opalovskii, V. E. Fedorov, E. U. Lobkov, B. G. Erenburg, *Russ. J. Inorg. Chem.* **1971**, *16*, 1685–1688.
- [15] a) J. Beck, F. Steden, *Z. Naturforsch. B* **2003**, *58*, 711–714; b) A. Pfitzner, S. Zimmerer, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 982–984; *Angew. Chem.* **1997**, *109*, 1031; c) J. P. Johnson, M. Murchie, J. Passmore, M. Tajik, P. S. White, C.-M. Wong, *Can. J. Chem.* **1987**, *65*, 2744–2755; d) J. Passmore, G. Sutherland, P. S. White, *Can. J. Chem.* **1981**, *59*, 2876–2878.
- [16] a) J. Beck, A. Fischer, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1042–1046; b) J. Beck, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 163–172; *Angew. Chem.* **1994**, *106*, 172.
- [17] M. Bregnhøj, K. Strunge, R. J. Sørensen, M. Ströbele, T. Hummel, H.-J. Meyer, F. Jensen, P. R. Ogilby, *J. Phys. Chem. A* **2019**, *123*, 1730–1739.
- [18] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Phys. Chem. A* **2006**, *124*, 219906.
- [19] J. P. Perdew, *Phys. Rev. Lett.* **1985**, *55*, 1665–1668.
- [20] W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, A1133.
- [21] J. Heyd, G. E. Scuseria, *J. Phys. Chem. A* **2004**, *121*, 1187–1192.
- [22] J. Tauc, *Mater. Res. Bull.* **1968**, *3*, 37–46.
- [23] G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.
- [24] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, *J. Phys. Condens. Matter* **2002**, *14*, 2717–2744.

Received: December 18, 2019



Supporting Information

Synthesis of $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ via Iodination of WTe_2

Patrick Schmidt, Amira Siai, Philipp Schneiderhan, Markus Ströbele,
and H.-Jürgen Meyer*

ejic201901337-sup-0001-SupMat.pdf

INDEX:

1. Table S1. Electron microprobe results.	1
2. Figure S1. SEM image of a $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ crystal.	1
3. Figure S2. Crystal with partial tellurium rich coating.	2
4. Figure S3. Tauc plot.	2
5. Figure S4. Calculated electronic band structure.	3

Table S1. Results of the electron microprobe measurements. Crystal 3 shows partial tellurium-rich coating (3a without and 3b with coating, see also Figure S2).

Crystal	W at%	Te at%	I at%	Sum	W : Te : I
1	27.26	6.94	66.03	100.23	6 : 2.20 : 21.05
2	27.21	6.91	66.40	100.52	6 : 2.20 : 21.21
3a	27.52	6.83	66.27	100.62	6 : 2.15 : 20.93
3b	24.85	13.69	61.09	99.63	6 : 4.76 : 21.37
4	26.34	6.61	63.23	96.18	6 : 2.17 : 20.87
5	27.77	6.85	67.08	101.70	6 : 2.13 : 21.00

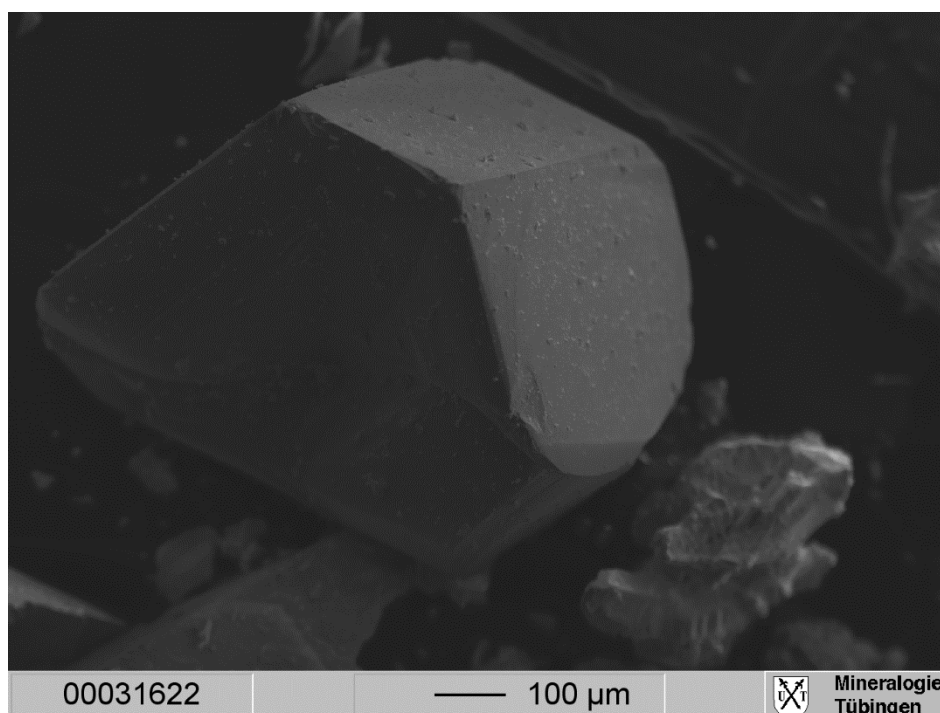


Figure S1. SEM image of a $(\text{TeI}_3)_2[\text{W}_6\text{I}_{14}]$ crystal.

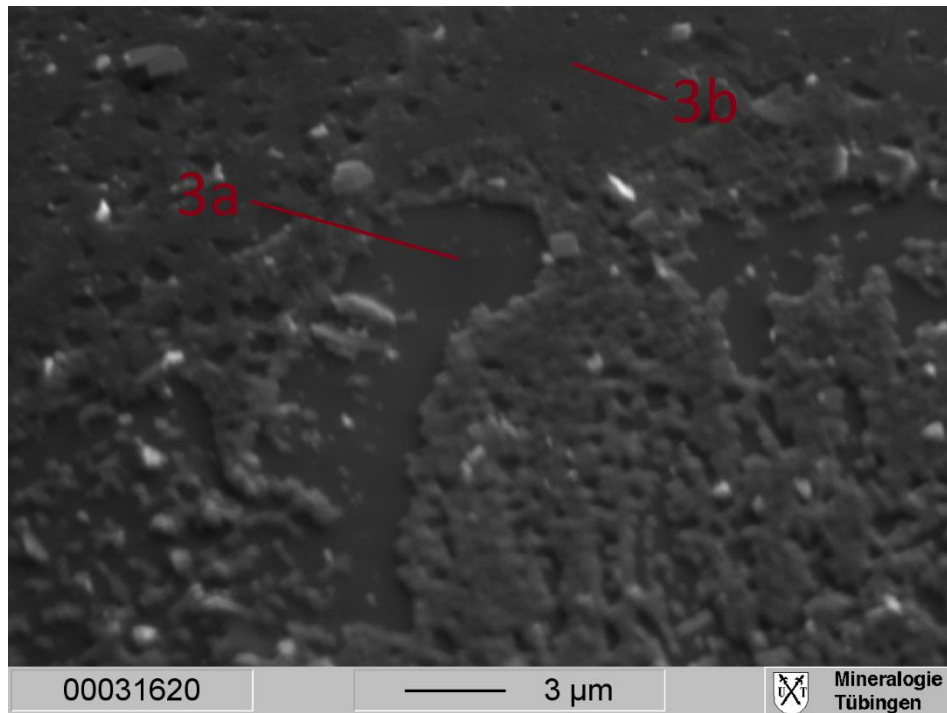


Figure S2. Crystal with partial tellurium rich coating.

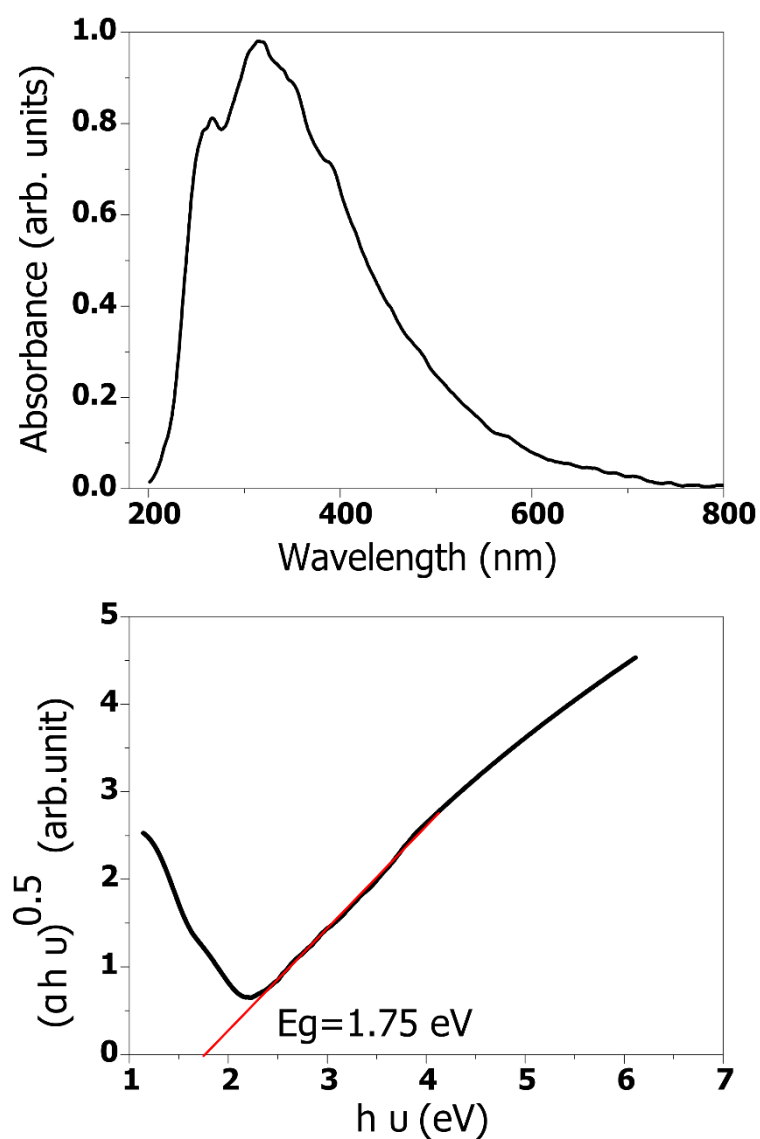


Figure S3. Absorbance spectrum (top) and Tauc plot (bottom) presented for indirect band gap as a function of photon energy.

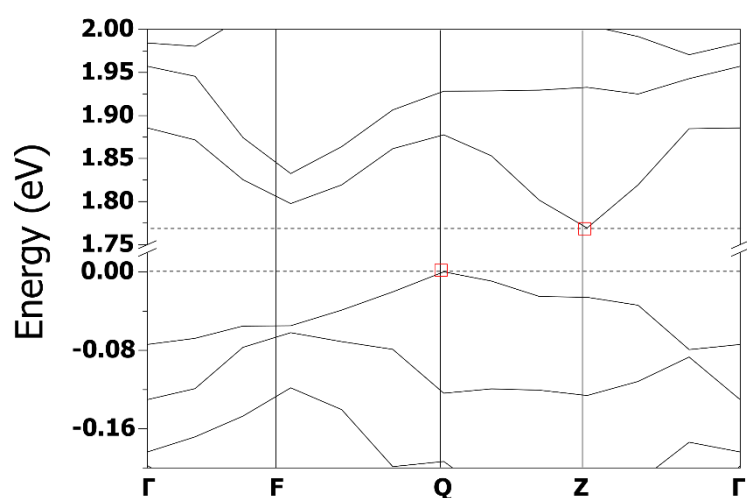
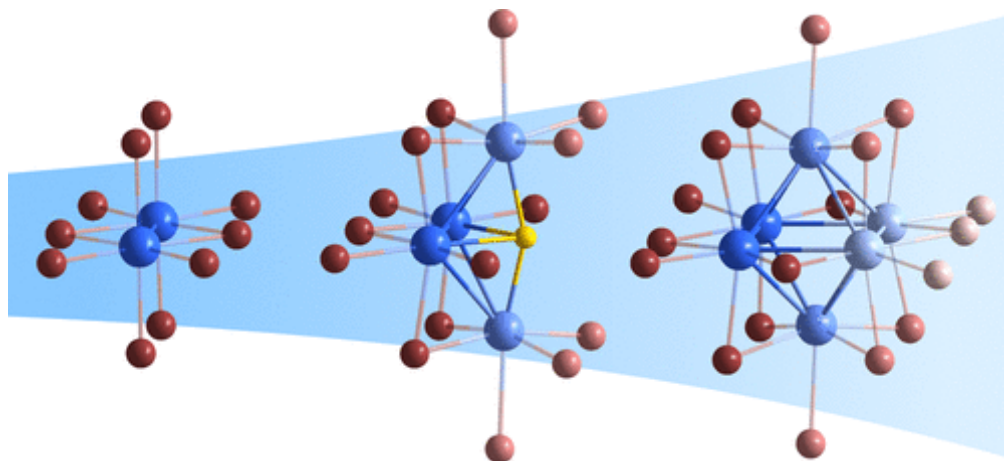


Figure S4. Calculated electronic band structure with HSE06 hybrid functional indicating indirect band gap.

Publication 6

Ta₄SBr₁₁: A Cluster Mott Insulator with a Corrugated, Van der Waals Layered Structure



<https://doi.org/10.1021/acs.inorgchem.4c02896>

Reprinted with permission from

Inorg. Chem. **2024**, *63*, 19717-19727.

Copyright © 2024 American Chemical Society

Ta₄SBr₁₁: A Cluster Mott Insulator with a Corrugated, Van der Waals Layered Structure

Fabian Grahlow, Fabian Strauß, Patrick Schmidt, Jaroslav Valenta, Markus Ströbele, Marcus Scheele, Carl P. Romao,* and Hans-Jürgen Meyer*



Cite This: *Inorg. Chem.* 2024, 63, 19717–19727



Read Online

ACCESS |



Metrics & More

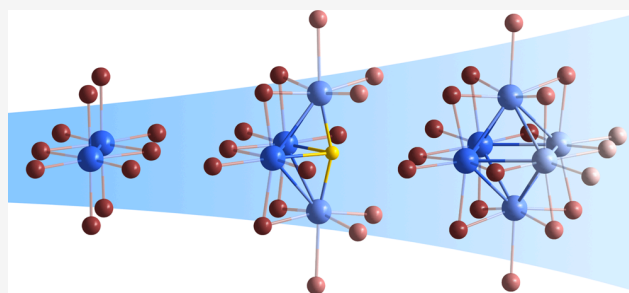


Article Recommendations



Supporting Information

ABSTRACT: The compound Ta₄SBr₁₁ was prepared by a comproportionation reaction of tantalum bromide with tantalum and elemental sulfur. The crystal structure, as refined by single-crystal X-ray diffraction, is composed of clusters with Ta₄S cores, arranged in corrugated van der Waals layers. Individual layers appear to be displaced relative to each other along one direction. Successful crystal growth in a melt of CsBr yielded black platelets of Ta₄SBr₁₁, which were used to investigate the electrical properties of the compound. The electronic structure was studied by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and by density functional theory (DFT) band structure calculations, revealing this material to be a small-gap semiconductor. DFT results, in combination with magnetic susceptibility measurements, suggest that metallicity originating from the one unpaired Ta d electron per cluster is most likely suppressed by electronic correlations, forming a cluster Mott insulator.



INTRODUCTION

The chemistry of reduced niobium and tantalum halides is dominated by cluster compounds prepared by solid-state synthesis at elevated temperatures. Their structures are characterized by octahedral metal ($M = \text{Nb}, \text{Ta}$) cluster cores $M_6X_{12}^iX_6^a$ with halide ligands ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) in edge-bridged (ⁱ) and terminal (^a) positions.¹ Average oxidation states in binary tantalum compounds Ta₆X₁₄ and Ta₆X₁₅ range from +2.33 to +2.5. The electronic structures of such compounds have been studied, revealing that the M_6X_{14} cluster with $M = \text{Nb}$ or Ta is considered electron precise with 14 electrons per cluster. These skeletal electrons reside in metal-to-metal bonds of the clusters. As a result of the separation of adjacent clusters via outer (^a) ligands, semiconducting behavior with poor electrical conductivity is observed for these crystalline compounds.^{2–4}

Another binary species, MX_4 with $M = \text{Nb}, \text{Ta}$ form infinite chain structures with alternating M – M distances, including bonding between pairs of metal atoms, which can be described by a Peierls distortion. The electrical conductivity of NbCl₄ has been reported to increase sharply (by a factor of 10^4 – 10^5) with increasing temperature (at 533 K), the Nb–Nb distances also tend to equalize, but the temperature dependence remains typical for a semiconductor.⁵

Known tantalum chalcogenide (Ch) halides include one-dimensional compounds of the type $(\text{Ta}Ch_4)_nX$ ($Ch = \text{Se}, \text{Te}; n = 1, 2, 4; X = \text{Br}, \text{I}$)^{6–8} and trinuclear niobium and tantalum cluster compounds with the stoichiometry M_3ChX_7 ($M = \text{Nb},$

Ta; $Ch = \text{S}, \text{Se}, \text{Te}; X = \text{Cl}, \text{Br}, \text{I}$).^{9–12} The latter compounds can be derived from the binary Nb₃X₈ ($X = \text{Cl}, \text{Br}, \text{I}$) structure by substituting the μ_3 -capping X atom of the cluster with a chalcogenide (Ch) atom. The structure of Nb₃Cl₈ contains seven skeletal electrons.¹³ Recently, an interlayer charge disproportionation has been proposed for Nb₃Cl₈ when lowering the temperature, resulting in a magnetic-to-non-magnetic phase transition and a structural phase transition.^{14–17} Monolayer Nb₃Cl₈ has been identified as a cluster Mott insulator, and has been the subject of significant recent interest due to its correlated flat metallic bands and the formation of a quantum spin liquid state due to magnetic frustration.¹⁸

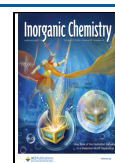
Trigonal clusters in ANb₃SBr₇ ($A = \text{Rb}, \text{Cs}$) also contain seven skeletal electrons, of which six electrons may be assigned for Nb–Nb bonding with one electron per cluster remaining unpaired.^{19,20} In their quasi-one-dimensional structure, these circumstances are expected to lead to a Luttinger liquid-like behavior.²⁰ These observations illustrate the appeal and complexity of heterohalide clusters, with their properties depending on the localized or delocalized distributions of

Received: July 11, 2024

Revised: August 27, 2024

Accepted: September 19, 2024

Published: October 7, 2024



their cluster electrons. In this context, the field of reduced tantalum halides notably lacks compounds having intermediate oxidation states between +2.5 and +4, which is of interest for the development of novel heterohalide cluster compounds.

Recently we reported niobium pnictide-halides $\text{Nb}_4\text{PnX}_{11}$, ($\text{Pn} = \text{N}, \text{P}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) containing the butterfly shaped $[\text{Nb}_4]$ niobium cluster, μ_4 -capped by a pnictogen (N or P) atom.²¹ In our current work, we describe the related compound $\text{Ta}_4\text{SBr}_{11}$, containing a butterfly shaped $[\text{Ta}_4]$ tantalum cluster compound with a μ_4 -capped sulfide atom. Specifically, we report the solid-state synthesis, crystal structure, electrical conductivity, magnetic susceptibility and the calculated band structure of $\text{Ta}_4\text{SBr}_{11}$. These results suggest that $\text{Ta}_4\text{SBr}_{11}$ is a cluster Mott insulator with a van der Waals layered structure. Other Mott insulators containing Ta include the cluster compound GaTa_4Se_8 ²² and the van der Waals material TaS_2 .²³ $\text{Ta}_4\text{SBr}_{11}$ demonstrates an interesting combination of these two structural features.

RESULTS AND DISCUSSION

Synthesis. $\text{Ta}_4\text{SBr}_{11}$ was prepared from tantalum, tantalum-(V) bromide and sulfur at 400 °C. It is obtained as black, rod-shaped platelets showing metallic luster. The compound was obtained from a high yield reaction, according to the powder XRD pattern (Figure S1). The addition of CsBr to the reaction mixture was found to improve crystal growth. In this process, CsBr and TaBr_5 form a eutectic melt allowing the reaction to proceed and promoting the formation of sizable crystals of $\text{Ta}_4\text{SBr}_{11}$. Figure 1 shows electron micrographs of $\text{Ta}_4\text{SBr}_{11}$ crystals from the direct synthesis (a) and significantly larger crystals grown from a CsBr flux (b and c).

The crystal growth process involves the compounds CsTaBr_6 ²⁴ and Cs_2TaBr_6 as intermediate products or side-phases, whose structures were characterized by means of single-crystal X-ray diffraction techniques. The as-yet unreported compound Cs_2TaBr_6 crystallizes in the space group $Fm\bar{3}m$ with $a = 10.6831(2)$ Å,²⁵ isostructural to K_2TaCl_6 .²⁶ The structure can be described as a face-centered cubic packing of $[\text{TaBr}_6]^{2-}$ octahedra with Cs^+ in cuboctahedral voids formed by bromides (Figure S3).

TXRF, EDX, and SEM. Elemental analysis of crystalline samples of $\text{Ta}_4\text{SBr}_{11}$ was performed with two techniques. Total reflection X-ray fluorescence (TXRF) measurements revealed a Ta : S : Br ratio of 4.00 : 1.05(4) : 11.08(7). Energy-dispersive X-ray spectroscopy (EDX) measurements on various spots of single crystals resulted in a emission spectrum corresponding to an average Ta : S : Br ratio of 4.00 : 1.2(± 0.23) : 11.77(± 0.76), verifying the composition determined by single-crystal XRD.

Crystal Structure. The crystal structure of $\text{Ta}_4\text{SBr}_{11}$, as refined on the basis of single-crystal XRD data (Table S1) at 150 K, was found to be intrinsically disordered (Table S2 and Figure 2). The average structure was solved and refined in the space group $Pm\bar{3}n$ and contains two distinct tantalum positions: one tantalum atom in a split position on both sides of a mirror plane and the second position with 50% occupancy. Out of four independent bromides in the structure, one (Br4) shares its position with the sulfur (50% each) in a bridging position.

Using these split positions, refinements resulted in wR_2 values below 4%, yielding a kinked van der Waals type layer structure with stacking orthogonal to the c -axis direction (Figure 2). However, all reasonable structure models require a

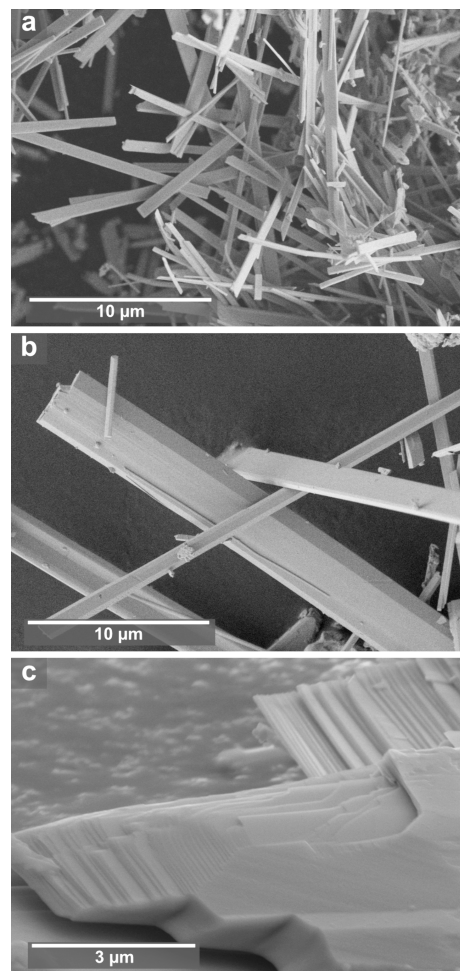


Figure 1. Scanning electron microscope (SEM) micrographs of $\text{Ta}_4\text{SBr}_{11}$ crystals obtained from the direct synthesis (a) and grown from a flux of CsBr (b and c).

doubling of the a lattice parameter and thus a superstructure. Close inspection of the diffraction patterns yielded diffuse scattering along a^* rather than sharp superstructure reflections (Figure S2). Assuming a translation period of $2a$, the disorder can be resolved and ordered structure models developed in a straightforward manner. A similar average structure was previously reported and decomposed for $\text{Nb}_4\text{PnX}_{11}$ ($\text{Pn} = \text{N}, \text{P}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$).²¹

The characteristic motif in the structure of $\text{Ta}_4\text{SBr}_{11}$ is the butterfly shaped $\text{Ta}_4(\mu_4\text{-S})$ cluster core with a capping sulfur atom (Figure 3). For each cluster, there are four bridging bromide ligands, Br3 and Br4, connecting the cluster into linear chains along $[100]$, that will be compared below with the arrangement of atoms in structure of TaBr_4 . Furthermore, the bromides Br2 connect the butterfly clusters along $[010]$. These bridging functionalities together create layers within the a,b plane of the structure.

However, the connection of Ta_4S clusters within one layer of the structure (via Br2) can be accomplished in two different ways, as can be understood from the average structure displayed in Figure S4. This leads to two possible cluster arrangements within layers of the structure, one kinked and one linear, as shown in Figure 4.

The connectivity of clusters via Br2 ligands creates an inversion center between butterfly clusters that can be

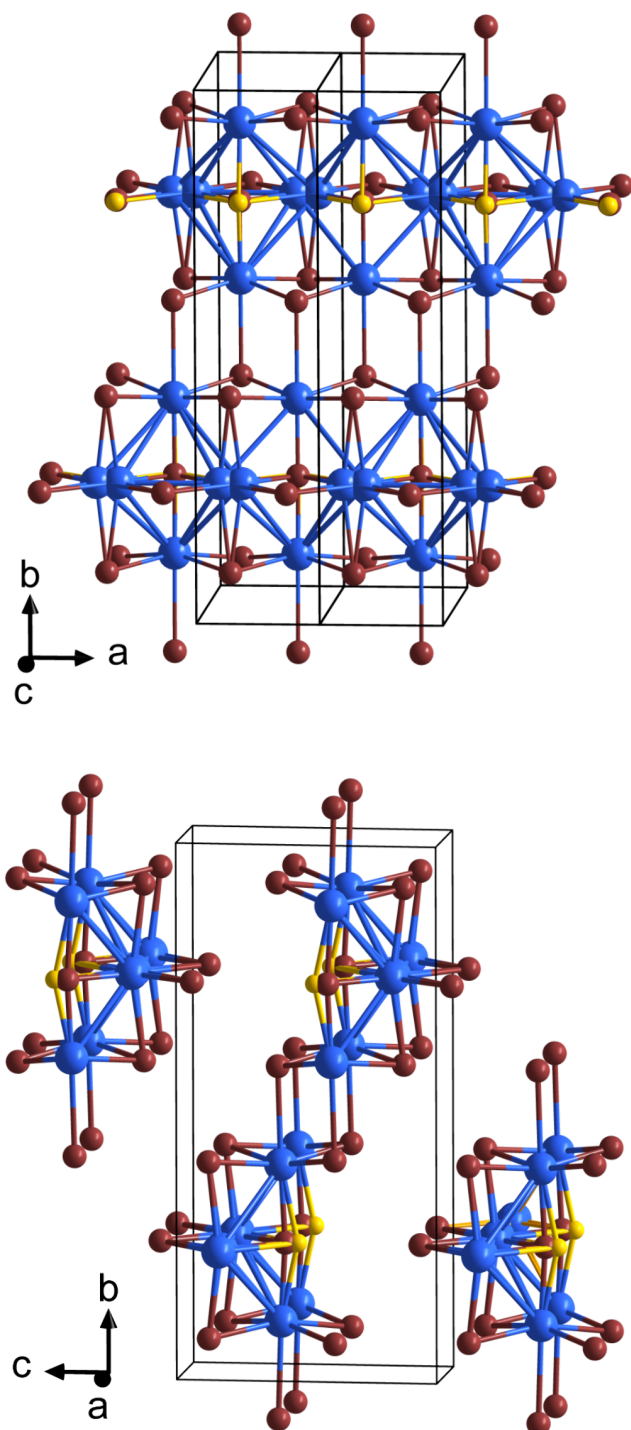


Figure 2. Refined average structure of $\text{Ta}_4\text{SBr}_{11}$ in two projections. Tantalum atoms are depicted in blue, bromine in brown and sulfur in yellow.

envisioned in Figure 5, thereby creating a sinusoidal pattern within each layer. This arrangement is further expanded in Figure 6, emphasizing the arrangement of corrugated layers in the structure. It is evident that the structure demonstrates van der Waals bonding between layers. In planar van der Waals layer structures, such as graphite or in transition metal dichalcogenides, shearing of layers may occur along different directions.^{27–29} Due to the corrugated layer structure of

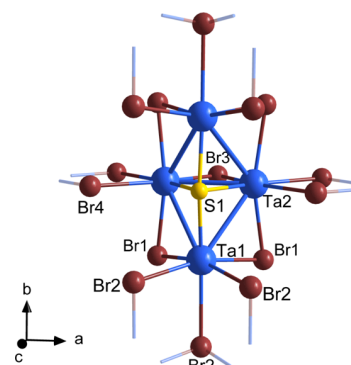


Figure 3. Characteristic $[\text{Ta}_4(\mu_4\text{S})]$ butterfly cluster in the structure of $\text{Ta}_4\text{SBr}_{11}$ with its connectivity pattern implied by broken bonds.

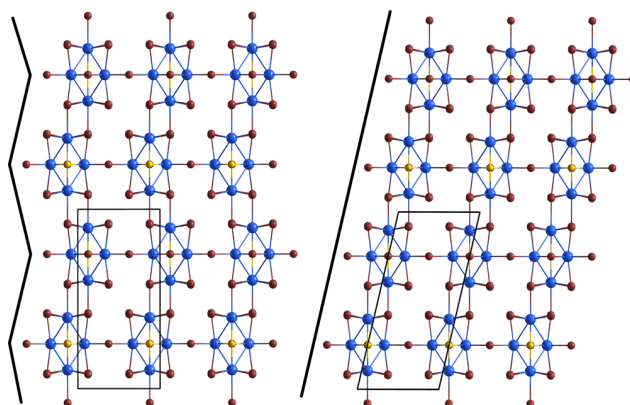


Figure 4. Two possible cluster arrangements, kinked (left) and linear (right) in a single layer of $\text{Ta}_4\text{SBr}_{11}$, shown with respective unit cells (black lines) given in Table 1.

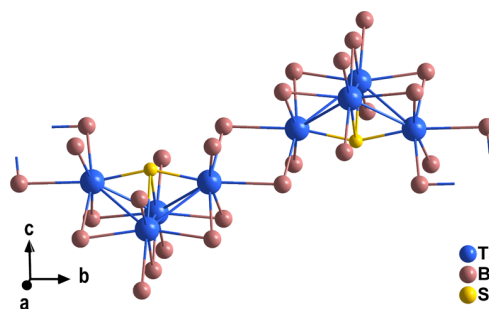


Figure 5. Section of the $\text{Ta}_4\text{SBr}_{11}$ structure, visualizing the corrugated connectivity of two clusters along the b -axis.

$\text{Ta}_4\text{SBr}_{11}$, shearing can occur only along one direction, which is along $[100]$ as indicated by the red arrow in Figure 6.

Shearing of layers parallel to $[100]$ results in essentially two different possible arrangements of layers. Figure 7 shows two possible sequences of cluster layers, held together by the van der Waals interactions, in which the stacking of clusters is eclipsed (left) or staggered (right).

In summary, the average structure of $\text{Ta}_4\text{SBr}_{11}$ (Figure 2 and Figure S4) can be explained as a superposition of in-plane and interplane disorder. Each of these types of disorder can be decomposed into two main arrangements, resulting in four ordered structures with reduced symmetries, which are presented in Table 1. The kinked arrangement of layers can be described with the monoclinic space group $P2_1/m$, with a

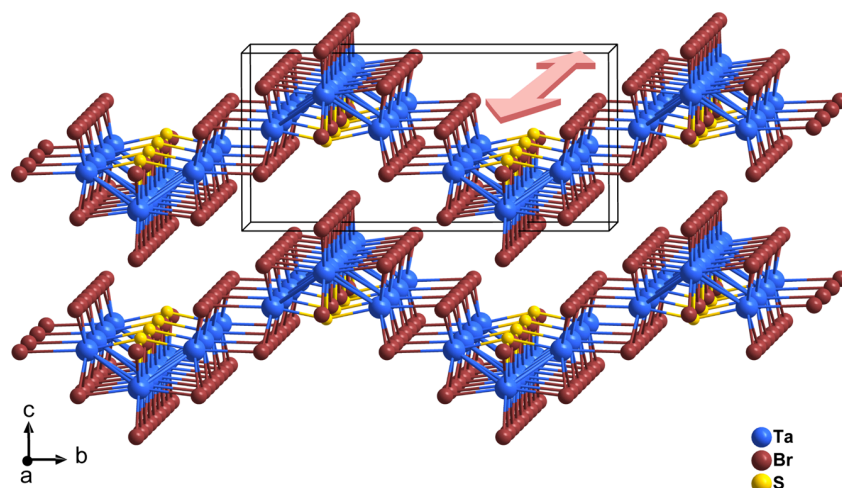


Figure 6. Corrugated layer structure of $\text{Ta}_4\text{SBr}_{11}$. The red arrow highlights the shearing direction of the layers.

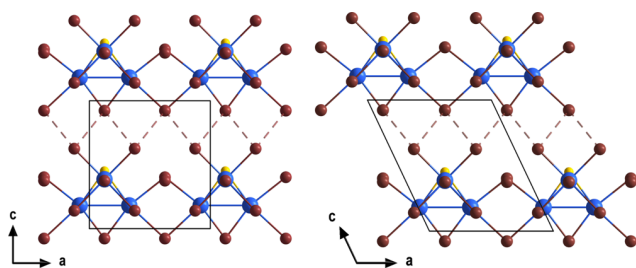


Figure 7. Possible arrangements of two parallel chains held together by a van der Waals gap (dashed lines). Clusters can be either stacked in an eclipsed (left) or staggered (right) fashion. Relevant crystallographic information for both structures are given in Table 1.

monoclinic angle (β) that is dependent on the stacking of layers (90° in eclipsed and 115.38° in staggered cluster stacking). For the linear arrangement of clusters (Figure 4, right) within layers, the resulting space groups are $P2_1/c$ (eclipsed) and $C2/c$ (staggered), where the monoclinic angle defines the arrangements of the clusters within the layers. The lattice constant a and the unit cell volume V are doubled, or even quadrupled for the linear arrangement within layers and a staggered arrangement between layers, when compared to the average structure.

Ta–Ta distances along the four edges of the butterfly cluster are equal, with $d_{\text{Ta1–Ta2}} = 309.14(3)$ pm, while the connecting edge between the cluster triangles is shorter with $d_{\text{Ta1–Ta1}} = 291.50(4)$ pm. The distance between adjacent clusters is $d_{\text{Ta1–Ta1}} = 418.46(4)$ pm, and the distances Ta–S are $d_{\text{Ta1–S}} =$

$231.0(1)$ pm and $d_{\text{Ta2–S}} = 248.5(4)$ pm. The connectivity of the 1D butterfly cluster chains along $[100]$ is comparable to that of the structure of metal tetrahalides. The Ta–Ta distances within and between the butterfly clusters in $\text{Ta}_4\text{SBr}_{11}$ are compared with the alternating short and long M–M distances in TaBr_4 and WBr_4 in Figure 8.^{30,31} The given sections of structures are easily comparable, with the appearance of alternating short and long distances between metal atoms. In TaBr_4 , the ratio of the short distance to the long distance is 0.764, and for WBr_4 it is 0.691. In $\text{Ta}_4\text{SBr}_{11}$ this ratio is 0.696. Given that two tantalum atoms in TaBr_4 form a two-center-two-electron bond, and tungsten atoms form a two-center-four-electron bond in WBr_4 , the ratio in $\text{Ta}_4\text{SBr}_{11}$ appears to be closer to the double bond character in WBr_4 .

With seven skeletal electrons, $\text{Ta}_4\text{SBr}_{11}$ contains the same number of cluster electrons as Nb_3Br_8 and $\text{CsNb}_3\text{Br}_7\text{S}$, but it is obvious that the electronic structures of these compounds are different. An odd number of electrons can give rise to different kinds of electronic behavior, which are very much dependent on the crystal structure, as outlined through the examples of Nb_3Br_8 and $\text{CsNb}_3\text{Br}_7\text{S}$ in the Introduction. In attempt to analyze the electronic properties of $\text{Ta}_4\text{SBr}_{11}$, we performed DRIFT spectroscopy as well as conductivity, magnetic measurements and electronic band structure calculations using density functional theory (DFT).

DRIFT Optical Band Gap Determination. The absorption coefficient F was obtained using Kubelka–Munk analysis following $F(R_\infty) = \frac{\alpha}{S} = \frac{(1 - R_\infty)^2}{2R_\infty}$, where $R_\infty = \frac{R_{\text{sample}}}{R_{\text{standard}}}$ is the

Table 1. Crystallographic Data of the Average Structure of $\text{Ta}_4\text{SBr}_{11}$ Compared to Those of Ordered Structures

	average structure	intralayer arrangement: kinked		intralayer arrangement: linear	
		interlayer arrangement:		interlayer arrangement:	
		eclipsed	staggered	eclipsed	staggered
space group	$Pm\bar{m}n$	$P2_1/m$	$P2_1/m$	$P2_1/c$	$C2/c$
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
a/pm	355.07(1)	710.1	710.1	710.1	710.1
b/pm	1546.90(4)	1546.9	1546.9	748.42	1496.8
c/pm	748.42(3)	748.4	828.38	1587.13	1587.13
$\beta/^\circ$	90.000	90.000	115.381	102.928	102.928
$V/\text{\AA}^3$	411.08(2)	822.15	822.15	822.15	1644.30

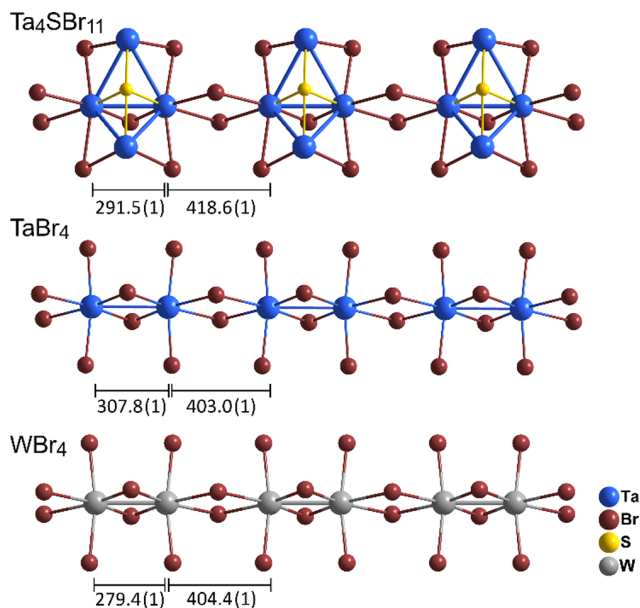


Figure 8. Comparison of 1D strands in the structures of $\text{Ta}_4\text{SBr}_{11}$, TaBr_4 ,³⁰ and WBr_4 ³¹ with metal-to-metal distances given in pm.

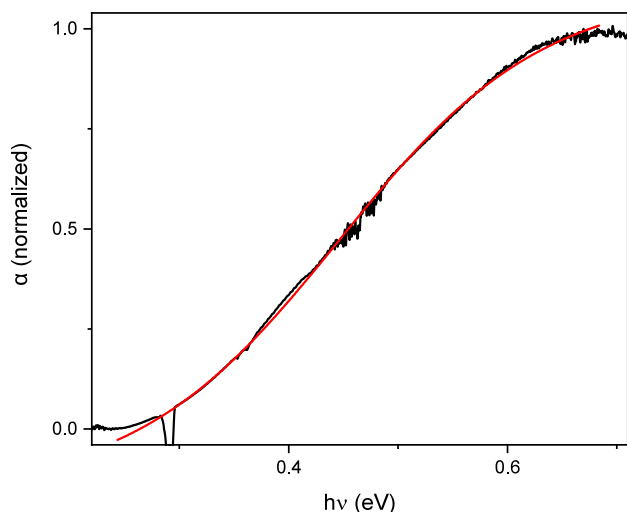


Figure 9. Optical absorption coefficient spectra of $\text{Ta}_4\text{SBr}_{11}$ with the Boltzmann function used to fit α (normalized) ($R^2 = 0.997$, $\chi^2 = 3.01 \times 10^{-4}$, signals around 0.29 eV can be assigned to atmospheric absorption bands of CO_2).

reflectance of an infinitely thick specimen, α is the absorption and S is the scattering coefficient. For particle sizes greater than the light wavelengths measured, the scattering coefficient is understood to be approximately independent of frequency ($F(R_\infty) \sim \alpha$) and therefore $F(R_\infty)$ could be understood as a “pseudoabsorbance” coefficient.^{32–38}

The observed absorption edge in the spectrum is very broad, which causes a high difference between the calculated direct and indirect bandgap. An alternative band gap determination according to Zanata et al. was performed to account for the disordered structure (see Figure 9).³⁹ The energy is plotted against the absorption coefficient α and fitted with a sigmoidal Boltzmann function:

$$\alpha(E) = \alpha_{\max} + \frac{\alpha_{\min} - \alpha_{\max}}{1 + \exp\left(\frac{E - E_0^{\text{Boltz}}}{\delta E}\right)}$$

where $\alpha_{\min}$ ($\alpha_{\max}$) stands for the minimum (maximum) absorption coefficient; E_0^{Boltz} is the energy coordinate at which the absorption coefficient is halfway between $\alpha_{\min}$ and $\alpha_{\max}$; and δE is associated with the slope of the sigmoid, indicating the energy range over which most optical transitions occur, and gives an idea of the magnitude of the disorder.³⁹

The band gap can then be calculated by following equation with $n_{\text{dir}}^{\text{Boltz}} = 0.3$ and $n_{\text{indir}}^{\text{Boltz}} = 4.3$:

$$E_g^{\text{Boltz}} = E_0^{\text{Boltz}} - n_{\text{dir}/\text{indir}}^{\text{Boltz}} \cdot \delta E$$

and results with $\delta E = 0.0933(8)$ eV in a direct $E_g^{\text{Boltz}}(\text{direct}) = 0.4181(3)$ eV and indirect $E_g^{\text{Boltz}}(\text{indirect}) = 0.044(3)$ eV bandgap. Since the center of the absorption edge is at about ~ 0.45 eV, a direct band gap can be assumed with a very broad slope of $\delta E = 0.0933(8)$ eV, originating from the disordered structure.

However, the Tauc plot ($E_{\text{dir}}^{\text{Tauc}} = 0.455$ eV and $E_{\text{indir}}^{\text{Tauc}} = 0.183$ eV with $\alpha \approx F(R_\infty)$) yielded a broad spectrum that made an unambiguous bandgap determination challenging (see Figure S6), which is why the Zanata method was preferred here.⁴⁰ We note that these values are somewhat smaller than the DFT-calculated band gap of 0.4 eV (see below). However, the DFT bandgap is dependent on the value of the adjustable phenomenological Hubbard U parameter. Therefore, the difference between the experimental and calculated gap is, in this case, an indicator of the reasonable but not perfect choice of U . Additionally, the effects of disorder are not included in the DFT calculation; disorder in general acts to transform indirect gaps to direct gaps, as indirect band gaps are necessarily reliant on the presence of translational symmetry. Relatively mild structural disorder (e.g., introduction of defects)⁴¹ can be sufficient to cause such a transition.

Electrical Properties. Further information regarding the band gap, as well as the electronic properties was obtained by temperature-dependent conductivity measurements. We performed two-point probe I–V scans (see Figure S7 for a typical measurement) to determine the electrical conductivity in the temperature range between 20 and 300 K (Figure S8 left). For each temperature the current voltage characteristic shows ohmic behavior, as exemplarily shown in Figure S7 left. In addition, an ample and rapid photoresponse to optical excitation at 779 nm was observed (Figure S8 right). Under the assumption of Arrhenius-type temperature-activated hopping transport, two distinct linear regions were obtained in the Arrhenius plots, specifically from 300–100 K and from 100–20 K (Figure 10). Assuming a position of the Fermi level in the middle of the bandgap, we derive the corresponding activation energies for the two domains and relate their values to $E_G/2$. The energy gap in electron volts can be extracted and displayed according to the following approximation:^{42–45}

$$E_g = -\text{slope} \cdot \ln(10) \cdot 2 \cdot k_B \cdot 6.25 \cdot 10^{18} \text{ eV}$$

Following this approximation gives $E_{G,1} = 0.124$ eV and $E_{G,2} = 0.424$ eV. These values are in reasonable agreement with the indirect and direct band gaps, obtained by the Zanata analysis of the DRIFT spectroscopy data. The sudden change in the temperature-dependent transport data at 100 K may indicate a

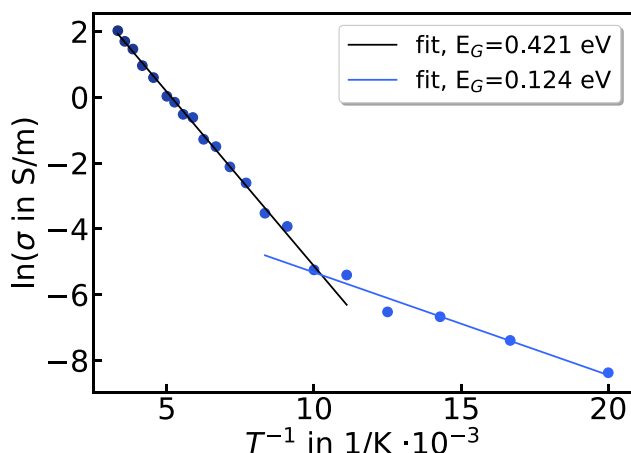


Figure 10. Arrhenius-plot of the temperature-dependent conductivity shown in Figure S8. Two regimes can be identified and fitted linearly to determine the electronic band gap.

phase transition or some other change in the electronic structure.

Crystal Structure Refinement at 80 K. Following the result of two distinct slopes in the temperature-dependent conductivity measurement, we performed another crystal-structure refinement based on a measurement at lower temperature. The crystal structure refinement data at 80 K did not show a phase-transition relative to the previously refined structure at 150 K. A comparison of refined interatomic distances in Ta₄SBr₁₁ at 150 and 80 K is given in Table 2.

Table 2. Comparison of Selected Interatomic Distances in Ta₄SBr₁₁ at 150 and 80 K

Ta ₄ SBr ₁₁ distance (pm)	150 K	80 K
Ta(1)–Ta(2)	309.14(3)	309.30(9)
Ta(2)–Ta(2)	291.50(4)	291.6(1)
	418.64(4)	417.4(1)
Ta(1)–S	231.0(1)	231.1(2)
Ta(2)–S	248.5(4)	248.9(7)

Interatomic distances within the butterfly cluster are almost identical. Only the Ta2–Ta2 distance connecting two short edges of butterfly cluster is decreased by 1.2 pm at 80 K (see Figure 3 for comparison). Although we must consider this change as significant (because it is above the 3σ limit), it is not clear if this change indicates a weaker decay of the electric conductivity (decrease of activation energy) below 100 K. However, a convergence of short and long metal-to-metal distances in the Peierls-distorted structure of NbCl₄ has been reported to increase the electrical conductivity, as mentioned in the introduction.⁵

Magnetic Properties. The temperature dependence of the magnetic susceptibility was measured at 1 and 0.5 T and proved the purity of the measured sample with paramagnetic response down to 2 K. The data for measurements at 1 T are depicted in Figure 11, showing a plot of the inverse magnetic susceptibility with a modified Curie–Weiss fit ($\chi(T) = C(T - \theta_p) + \chi_0$ wherein C , θ_p , and χ_0 are the Curie constant, the Weiss temperature, and the temperature-independent susceptibility). The magnetic susceptibility follows Curie–Weiss behavior from 100 K, and a fit to the data gives an effective magnetic moment $\mu_{\text{eff}} = 1.23(1) \mu_B$ per formula unit as well as a Weiss

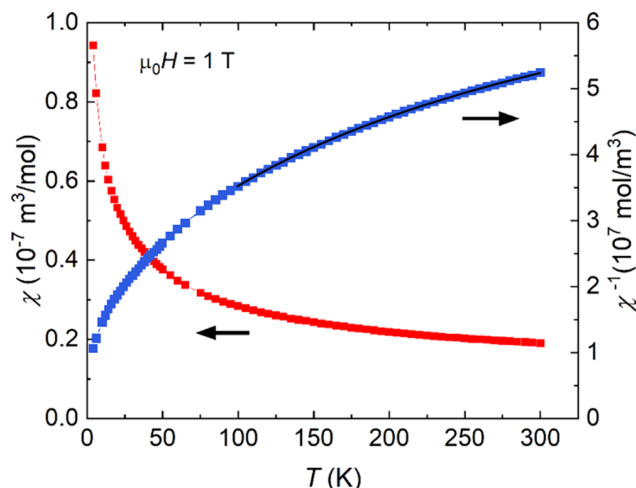


Figure 11. Temperature dependence of magnetic susceptibility (red squares) and inverse magnetic susceptibility (blue squares) with plotted modified Curie–Weiss fit.

temperature $\theta_p = -49(1)$ K, pointing to antiferromagnetic interactions and temperature-independent susceptibility $\chi_0 = 1.2(5) \times 10^{-8} \text{ m}^3/\text{mol}$. These findings are consistent with the assignment of Ta₄SBr₁₁ as a Mott insulator (see DFT results below), specifically as a paramagnet with local antiferromagnetic correlations.⁴⁶ The observed value of μ_{eff} is slightly less than the calculated value of one unpaired electron ($\mu_{\text{eff}} = 1.73 \mu_B$), which could be due to formation of electron pairs (intercluster singlet formation) at defects or domain walls within the disordered crystal.¹⁶

DFT Calculations. The electronic band structure of Ta₄SBr₁₁ was separately calculated for each of the intra- and interlayer arrangements of clusters shown in Table 1, initially without inclusion of any magnetic ordering of the unpaired spins. These calculations resulted, in all cases, in metallic band structures, with two half-occupied Ta d bands at the Fermi energy. As this finding is inconsistent with experimental results showing the material to be a semiconductor, several potential mechanisms of band gap opening were tested theoretically. First, spin–orbit coupling (SOC) was introduced into the calculations (Figure S5), since SOC can open band gaps, for example in topological insulators.⁴⁷ However, despite the significant SOC in Ta,⁴⁸ its effect on the bands near the Fermi energy was relatively small, and the material remained metallic.

Second, we consider the formation of a Mott insulator, i.e. a state where the combination of strong electronic correlations (specifically electron–electron repulsion) and antiferromagnetic exchange interactions leads to electron localization and the opening of a band gap.^{46,49} In order to model such a state using DFT, we combine an antiferromagnetic ordering of the unpaired electron spins, with the Hubbard U correction⁵⁰ on the Ta sites, which accounts for electronic correlations. A value of $U_{\text{eff}} = 4.5$ eV was chosen based on the literature.⁵¹ As DFT calculations combining the Hubbard U correction with SOC are computationally intensive, only two combinations of crystallographic and magnetic structure were trialed.

As Figure 12 shows, the combination of the linear intralayer, eclipsed interlayer arrangement with an antiferromagnetic ordering involving alternating cluster magnetic moments along c opened a band gap. This gap has a magnitude of 0.4 eV and is indirect, lying between the valence band maximum at $Z(0\frac{1}{2}0)$

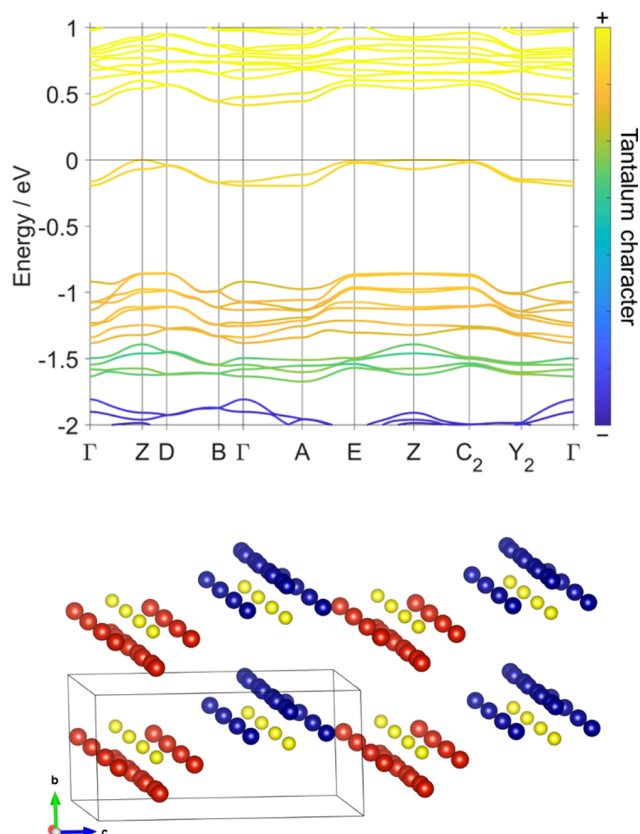


Figure 12. Calculated electronic band structure (top) of eclipsed $\text{Ta}_4\text{SBr}_{11}$ layers, with a linear intralayer arrangement of clusters and antiferromagnetic ordering of the unpaired spins (bottom), showing the opening of a gap due to strong electronic correlations and the formation of a Mott insulator. Ta atoms with spins oriented in the $+c$ direction are colored in red; those with spins oriented in the $-c$ direction are colored in blue. Br atoms are not shown for clarity. The magnetic supercell (64 atoms) used for the calculation is shown as a black outline. The bands within 1.75 eV of the Fermi level show Ta d character; the lower bands show significant hybridization with the Br p bands at -2 eV. Special points in and paths through the Brillouin zone were chosen following literature.⁵²

and the conduction band minimum at Γ (0 0 0). The DFT-calculated magnetic moments on the Ta atoms corresponded to 0.9 electronic moments per cluster, indicating a high degree of local magnetic polarization of the one unpaired electron per cluster. This polarization, in combination with the emergence of a band gap, corresponds to the formation of a Mott insulating state. The Ta d bands are found to hybridize with the Br p bands, indicating the presence of some covalent character to the Ta–Br bonding.

The second structure tested, which had the same magnetic ordering but a linear intralayer, staggered interlayer crystallographic structure, remained metallic (Figure 13). This can be attributed to the smaller degree of magnetic polarization, with only 0.6 electronic moments per cluster. Whereas in the case shown in Figure 12, the spins were aligned along $\pm c$ (along the corrugation direction), here the predominant component of the magnetic moment vector lies along $\pm a$, i.e. in an interlayer direction. Interestingly, this implies that the interlayer stacking could have a significant impact on the electronic and magnetic structure of the material. The properties of monolayers or bilayers of $\text{Ta}_4\text{SBr}_{11}$ are therefore

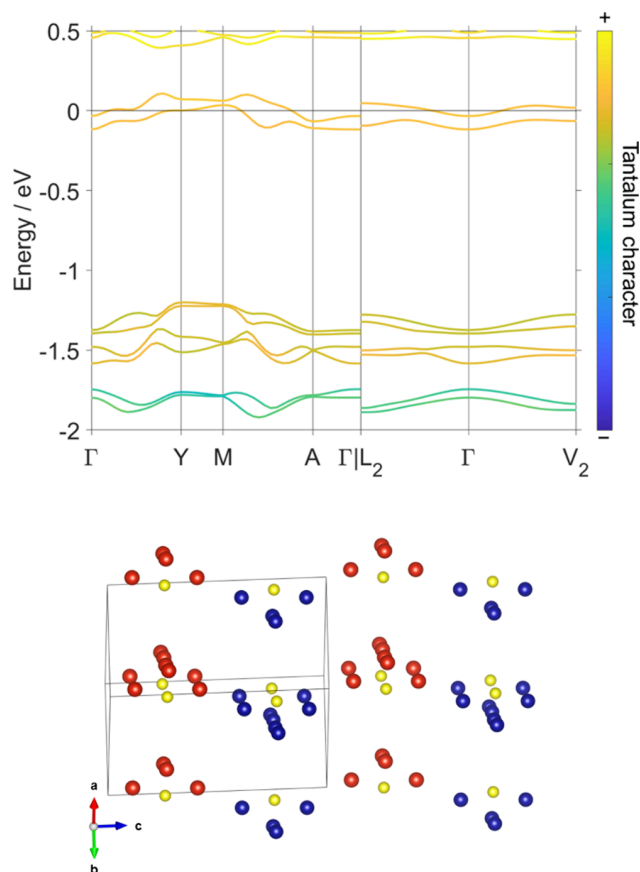


Figure 13. Calculated electronic band structure (top) of staggered $\text{Ta}_4\text{SBr}_{11}$ layers, with a linear intralayer arrangement of clusters and antiferromagnetic ordering of the unpaired spins (bottom), showing the absence of a band gap. The two magnetic sublattices (with the predominant component of the spin aligned along $\pm a$) are colored in red and blue, respectively (bottom). Br atoms are not shown for clarity. The unit cell used for the calculation is shown as a black outline. Special points in and paths through the Brillouin zone were chosen following literature.⁵²

an interesting direction for further research, especially since we note that the metallic bands shown in Figure 13 are nearly flat, an interesting phenomenon (related to superconductivity and other quantum properties) shared with monolayer Nb_3Cl_8 ¹⁷ and twisted bilayer graphene.⁵³ It is important to note that this result does not by itself demonstrate that the linear, staggered configuration should be metallic, as there are other possible magnetic orderings which were not tested due to the demanding nature of these calculations.

Another mechanism of gap opening, the charge density wave (CDW) instability (the 2-dimensional analogue of the 1-dimensional Peierls instability),^{46,49,54} was not investigated in depth, as magnetic susceptibility measurements (see above) are consistent with the Mott insulator hypothesis. However, we note that the calculated Fermi surfaces (Figure S5) show pseudo-2D bands, indicating the possibility of CDW instabilities. Such instabilities could cause structural disorder without leading to the opening of an electronic band gap, as is seen in the van der Waals material WTe_2I .⁵⁵

At first intuition, neither of the disordered arrangements within and between layers seems to be energetically favored. In order to estimate the potential energy landscape related to shearing along the van der Waals layers (see Figure 7), we

compared the lattice energy (without the inclusion of the Hubbard U or magnetic ordering) of the four arrangements shown in Table 1. The linear, staggered configuration was found to have the lowest energy, with both eclipsed configurations having energies 0.04 eV (4 kJ/mol) higher, and the kinked, staggered configuration having the highest energy at 0.1 eV (9 kJ/mol) above the minimum. These differences are significant, and are large enough that thermal effects at 80–150 K (the temperatures at which the crystal structure was determined) would not be sufficiently large to cause the observed disorder. However, the thermal energy available at the synthesis temperature (673 K), might be sufficiently large to cause disorder, which then could be frozen into the structure upon cooling. In addition, the calculated structures may not reflect the correct energy differences of the full range of possible disordered layered structures, where larger cells with more complex layer disorder would also have to be considered, exponentially increasing the computational time.

CONCLUSIONS

The new material $\text{Ta}_4\text{SBr}_{11}$ is characterized by bridged $[\text{Ta}_4(\mu_4\text{-S})]$ butterfly clusters, connected by bromides to form a corrugated van der Waals type layer structure. This compound parallels the structure of the previously reported compounds $\text{Nb}_4\text{PnX}_{11}$ ($\text{Pn} = \text{N}, \text{P}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), which represents a six-electron cluster. Both compounds exhibit complex disordering patterns, indicated by characteristic streaks in their XRD patterns. The structural disorder in $\text{Ta}_4\text{SBr}_{11}$ can be understood as a combination of in-plane disorder, due to two different cluster connectivities, and interlayer shear along the $[100]$ direction.

The connectivity of the clusters parallels the structure of NbCl_4 along one direction, where the alternation of metal-to-metal distances indicates metal–metal bonding with concomitant modification of the electronic structure. The small-gap semiconductor $\text{Ta}_4\text{SBr}_{11}$ represents another example of a seven-electron cluster, like Nb_3Cl_8 and $\text{CsNb}_3\text{Br}_7\text{S}$. In all of these compounds, the presence of an unpaired electron in each cluster, in combination with strong electronic correlations, leads to unusual properties which cannot be explained by simple band theory. Electronic structure calculations in combination with experimental results lead us to conclude that $\text{Ta}_4\text{SBr}_{11}$ is likely to be a cluster Mott insulator, like monolayer Nb_3Cl_8 . If monolayers of $\text{Ta}_4\text{SBr}_{11}$ can be prepared, they might also have interesting emergent properties such as flat electronic bands.

EXPERIMENTAL SECTION

Synthesis and Crystal Structure. Manipulations of starting materials, such as charging the silica ampules (estimated volume 5 cm^3) with starting materials were performed in an argon-filled glovebox (MBraun, labmaster 130, $\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm).

$\text{Ta}_4\text{SBr}_{11}$ Bulk Synthesis. A mixture of TaBr_5 (234.3 mg, 0.40 mmol, Sigma-Aldrich, 99.9%), Ta (59.8 mg, 0.33 mmol, Merck, 98%) and S_8 (5.9 mg, 0.18 mmol, Carl Roth GmbH, 99.9%), fused into an evacuated silica tube, was heated with 2.0 K/min in a Simon-Müller-furnace. After heating at 400 $^\circ\text{C}$ (200 h), $\text{Ta}_4\text{SBr}_{11}$ was obtained as crystalline powder.

$\text{Ta}_4\text{SBr}_{11}$ Single Crystals. CsBr (39.1 mg, 0.18 mmol, Merck, 99.9%) was added to the reaction mixture as a flux. Hereby, CsBr and TaBr_5 (234.3 mg, 0.40 mmol) react to CsTaBr_6 and Cs_2TaBr_6 as intermediate reactants, which react with Ta (59.8 mg, 0.33 mmol) and S_8 (5.9 mg, 0.18 mmol). To obtain X-ray pure phases, the powder

was resealed in a second hourglass-ampule (length: 14 cm). Unreacted TaBr_5 and TaOBr_2 were sublimed off in a temperature gradient 400 $^\circ\text{C}$ /300 $^\circ\text{C}$. Yield: 55–65%. A PXRD pattern of the product is shown in Figure S1.

Powder X-ray Diffraction. All reaction products were investigated by powder X-ray diffraction (PXRD) using a StadiP diffractometer (Stoe, Darmstadt) with Ge-monochromated $\text{Cu-K}\alpha_1$ radiation, and a Mythen1 Detector.

Single-Crystal X-ray Diffraction. Data collections were performed on a Rigaku XtaLAB Synergy-S single-crystal X-ray diffractometer equipped with HyPix-6000HE detector and monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.7107$ Å) and $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54184$ Å) at 150 and 80 K. X-ray intensities were corrected for absorption with a numerical method (crystal faces) using CrysAlisPro 1.171.41.67a (Rigaku Oxford Diffraction, 2020). This software was also used to calculate reconstructed reciprocal space sections. The average structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares methods performed with SHELXL-2014 as implemented in Olex2 1.3-ac4.44.

CCDC 2352652 contains the supplementary crystallographic data for $\text{Ta}_4\text{SBr}_{11}$ at 80 K; CCDC 2181179 for $\text{Ta}_4\text{SBr}_{11}$ at 150 K; CCDC 2327955 for Cs_2TaBr_6 . These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

EDX and SEM. Energy dispersive X-ray spectroscopy (EDX) and Scanning electron microscopy (SEM) were performed on a HITACHI SU8030 scanning electron microscope with a Bruker QUANTAX 6G EDX-detector. For this purpose, single crystals of $\text{Ta}_4\text{SBr}_{11}$ were fixed on carbon-tapes.

Electrical Conductivity. Conductivity measurements were performed in a Lake Shore Cryotronics CRX-6.5K probe station with a Keithley 2636B source meter unit. Rod-shaped crystals of $\text{Ta}_4\text{SBr}_{11}$ were contacted with silver paste on a silicon substrate with 770 nm oxide layer and transferred into the chamber under protective gas. The conductive silver pads at each end of the crystals were connected to the circuit with tungsten tips (Figure S7 right). The chamber was kept under vacuum ($< 5 \times 10^{-5}$ mbar) and the temperature was varied between 20 and 300 K. Before each measurement, sufficient time was allowed for the sample to reach the chosen temperature. Two-point conductivity measurements were performed by varying the applied source-drain voltage from -1 to 1 V while detecting the current. For time-resolved photocurrent measurements, using a picosecond pulsed laser driver (Taiko PDL M1, PicoQuant) together with a laser head 779 nm (pulse length < 500 ps) the crystals were illuminated at 40 mW laser output power using the continuous wave mode under a constant bias of 1 V. The measured crystals had the dimensions: $106 \mu\text{m} \times 16 \mu\text{m} \times 4 \mu\text{m}$ and $80 \mu\text{m} \times 15 \mu\text{m} \times 5 \mu\text{m}$.

DRIFT (Diffuse Reflectance Infrared Fourier Transformation) Spectroscopy. Samples were measured at room temperature under inert conditions in diffuse reflectance with a Harrick Praying Mantis attachment using a Bruker Vertex 70 infrared spectrophotometer with a deuterated triglycine sulfate (DTGS) detector and KBr beamsplitter. The background spectra were collected using pure dried KBr in powder form.

TXRF (Total Internal Reflection X-ray Fluorescence) Spectroscopy. TXRF studies were performed using a S2 Picofox (Bruker AXS Microanalysis, Berlin, Germany) equipped with a Mo X-ray tube, which was operated at 50 kV and 600 μA . The measurement period for each sample was 1000 s (live time). Fitting of the resulting spectra was done using the Spectra software (Bruker Nano GmbH) in the super byas mode (maximum stripping cycles of 2000).

Density Functional Theory. Density functional theory (DFT) calculations were performed within the Abinit software package (v. 10).⁵⁶ The Perdew–Burke–Ernzerhof exchange–correlation functional⁵⁷ was used with the vdw-DFT-D3(BJ) dispersion correction of Grimme.⁵⁸ Monkhorst–Pack grids of k-points were chosen with minimum real-space spacing between grid points of 30 Å.⁵⁹ Plane-wave calculations were performed using the projector augmented wave (PAW) method⁶⁰ with an energy cutoff of 24 Ha outside the

PAW spheres and a 120 Ha cutoff within them. These computational parameters were chosen following convergence studies, with convergence of the internal pressure within 1% being the criterion. The Hubbard U parameters⁵⁰ were chosen as $U = 5$ eV and $J = 0.5$ eV on the Ta sites, yielding $U_{\text{eff}} = U - J = 4.5$ eV, in accordance with previous literature results.⁶¹ Calculations performed with the Hubbard U also included spin–orbit coupling and noncollinear antiferromagnetism.

Magnetic Measurements. The magnetization measurement was performed using the magnetic property measurement system (MPMS) by Quantum Design Inc. The sample in powder form (53.9 mg) was fixed in capsule and placed to the MPMS. Diamagnetic contributions from sample holder and capsule were subtracted from observed data.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c02896>.

Additional X-ray diffraction data, figures, photographs of single crystal, band structures, Fermi surfaces, DRIFT analysis, and conductivity measurements (PDF)

Accession Codes

CCDC 2181179, 2327955, and 2352652 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Carl P. Romao – Department of Materials, ETH Zürich, Zürich 8093, Switzerland; orcid.org/0000-0002-5519-2519; Email: carl.romao@mat.ethz.ch

Hans-Jürgen Meyer – Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls Universität Tübingen, Tübingen D-72076, Germany; orcid.org/0000-0003-2450-4011; Email: juergen.meyer@uni-tuebingen.de

Authors

Fabian Grahlow – Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls Universität Tübingen, Tübingen D-72076, Germany; orcid.org/0000-0002-1308-4819

Fabian Strauß – Institute of Physical and Theoretical Chemistry, Eberhard Karls Universität Tübingen, Tübingen D-72076, Germany

Patrick Schmidt – Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls Universität Tübingen, Tübingen D-72076, Germany; orcid.org/0000-0001-6556-2088

Jaroslav Valenta – International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan; orcid.org/0000-0002-2268-7187

Markus Ströbele – Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls Universität Tübingen, Tübingen D-72076, Germany; orcid.org/0000-0002-5147-5677

Marcus Scheele – Institute of Physical and Theoretical Chemistry, Eberhard Karls Universität Tübingen, Tübingen D-72076, Germany; orcid.org/0000-0002-2704-3591

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c02896>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

DFG grant ME 914/32-1, SCHE1905-9-1

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Funding by the Deutsche Forschungsgemeinschaft through grant ME 914/32-1 and SCHE1905/9-1 is gratefully acknowledged. We like to thank Prof. Takao Mori, Dr. Jaroslav Valenta, and Dr. Naohito Tsujii, (Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan) for performing magnetic measurements, and Dr. Jochen Glaser (Univ. Tübingen) for helpful discussions and suggestions. C. P. R. was supported by ETH Zurich and by the European Union and Horizon 2020 through Grant No. 810451. Computational resources were provided by the Swiss National Supercomputing Center (CSCS) under project ID s1128. The authors thank Ms. Elke Nadler and Prof. Dr. Thomas Chassé (University Tübingen) for recording SEM images and EDX data.

■ REFERENCES

- (1) Lemoine, P.; Halet, J.-F.; Cordier, S. Inorganic Niobium and Tantalum Octahedral Cluster Halide Compounds with Three-Dimensional Frameworks: A Review on Their Crystallographic and Electronic Structures. In *Ligated Transition Metal Clusters in Solid-state Chemistry: The legacy of Marcel Sergent*, Halet, J.-F., Ed.; Springer International Publishing, 2019; pp 143–190.
- (2) Kuhn, P. J.; McCarley, R. E. Chemistry of polynuclear metal halides. I. preparation of the polynuclear tantalum halides Ta_6X_{14} . *Inorg. Chem.* **1965**, 4 (10), 1482–1486.
- (3) Simon, A.; Schnering, H. G.; Wöhrle, H.; Schäfer, H. Beiträge zur Chemie der Elemente Niob und Tantal. 44. $\text{Nb}_6\text{Cl}_{14}$ Synthese, Eigenschaften, Struktur. *Struktur. Z. Anorg. Allg. Chem.* **1965**, 339, 155–170.
- (4) Bauer, D.; Schnering, H.-G. Beiträge zur Chemie der Elemente Niob und Tantal. LXVII. Die Struktur der Tantalhalogenide $\text{Ta}_6\text{Cl}_{15}$ und $\text{Ta}_6\text{Br}_{15}$. *Z. Anorg. Allg. Chem.* **1968**, 361 (5–6), 259–276.
- (5) Blight, D. G.; Kepert, D. L. Electrical Properties of Niobium Tetrachloride. *Phys. Rev. Lett.* **1971**, 27 (8), 504–504.
- (6) Tremel, W. NbTe_4I und TaTe_4I , zwei neue Tellurid-Iodide mit Kettenstruktur. *Chem. Ber.* **1992**, 125 (10), 2165–2170.
- (7) Gressier, P.; Guemas, L.; Meerschaut, A. Preparation and structure of ditantalum iodide octaselenide, Ta_2ISe_8 . *Acta Crystallogr. Sect. B* **1982**, 38 (11), 2877–2879.
- (8) Gressier, P.; Meerschaut, A.; Guemas, L.; Rouxel, J.; Monceau, P. Characterization of the new series of quasi one-dimensional compounds $(\text{MX}_4)_n\text{Y}$ ($M = \text{Nb}, \text{Ta}$; $X = \text{S}, \text{Se}$; $Y = \text{Br}, \text{I}$). *J. Solid State Chem.* **1984**, 51 (2), 141–151.
- (9) Schmidt, P. J.; Thiele, G. A New Structural Variation of Nb_3YX_7 Compounds: Monoclinic Nb_3SI_7 . *Acta Crystallogr. Sect. C* **1997**, 53 (12), 1743–1745.
- (10) Smith, M. D.; Miller, G. J. Tantalum–Niobium Mixing in $\text{Ta}_{3-x}\text{Nb}_x\text{TeI}_7$ ($0 \leq x \leq 3$). *Z. Anorg. Allg. Chem.* **2000**, 626 (1), 94–102.

- (11) Smith, M.; Miller, G. J. Ta_3SBr_7 — A New Structure Type in the $M_3\text{QX}_7$ Family ($M=\text{Nb, Ta}$; $\text{Q}=\text{S, Se, Te}$; $\text{X}=\text{Cl, Br, I}$). *J. Solid State Chem.* **1998**, *140* (2), 226–232.
- (12) Khvorykh, G. V.; Shevelkov, A. V.; Dolgikh, V. A.; Popovkin, B. A. Niobium thiobromide, Nb_3SBr_7 , with triangle Nb_3 cluster: structure and bonding. *J. Solid State Chem.* **1995**, *120* (2), 311–315.
- (13) Ströbele, M.; Glaser, J.; Lachgar, A.; Meyer, H.-J. Struktur und elektrochemische Untersuchung von Nb_3Cl_8 . *Z. Anorg. Allg. Chem.* **2001**, *627* (8), 2002–2004.
- (14) Haraguchi, Y.; Michioka, C.; Ishikawa, M.; Nakano, Y.; Yamochi, H.; Ueda, H.; Yoshimura, K. Magnetic–Nonmagnetic Phase Transition with Interlayer Charge Disproportionation of Nb_3 Trimers in the Cluster Compound Nb_3Cl_8 . *Inorg. Chem.* **2017**, *56* (6), 3483–3488.
- (15) Pasco, C. M.; El Baggari, I.; Bianco, E.; Kourkoutis, L. F.; McQueen, T. M. Tunable Magnetic Transition to a Singlet Ground State in a 2D van der Waals Layered Trimerized Kagomé Magnet. *ACS Nano* **2019**, *13* (8), 9457–9463.
- (16) Shekelton, J. P.; Plumb, K. W.; Trump, B. A.; Broholm, C. L.; McQueen, T. M. Rearrangement of van der Waals stacking and formation of a singlet state at $T = 90$ K in a cluster magnet. *Inorg. Chem. Front.* **2017**, *4* (3), 481–490.
- (17) Grytsiuk, S.; Katsnelson, M. I.; Loon, E. G. C. P. v.; Rösner, M. Nb_3Cl_8 : a prototypical layered Mott–Hubbard insulator. *npj Quantum Mater.* **2024**, *9* (1), 8.
- (18) Hu, J.; Zhang, X.; Hu, C.; Sun, J.; Wang, X.; Lin, H.-Q.; Li, G. Correlated flat bands and quantum spin liquid state in a cluster Mott insulator. *Commun. Phys.* **2023**, *6* (1), 172.
- (19) Meyer, H.-J. $\text{CsNb}_3\text{Br}_7\text{S}$: Synthese, Struktur und Bindungsverhältnisse. *Z. Anorg. Allg. Chem.* **1994**, *620* (5), 863–866.
- (20) Grahlow, F.; Strauß, F.; Scheele, M.; Ströbele, M.; Carta, A.; Weber, S. F.; Kroeker, S.; Romao, C. P.; Meyer, H.-J. Electronic structure and transport in the potential Luttinger liquids $\text{CsNb}_3\text{Br}_7\text{S}$ and $\text{RbNb}_3\text{Br}_7\text{S}$. *Phys. Chem. Chem. Phys.* **2024**, *26* (15), 11789–11797.
- (21) Ströbele, M.; Oeckler, O.; Thelen, M.; Fink, R. F.; Krishnamurthy, A.; Kroeker, S.; Meyer, H.-J. Pnictide-Capped Butterfly Cluster in the Crystal Structure of $\text{Nb}_4\text{PnX}_{11}$ ($\text{Pn} = \text{N, P}$; $\text{X} = \text{Cl, Br, I}$). *Inorg. Chem.* **2022**, *61*, 17599.
- (22) Magnaterra, M.; Attig, J.; Peterlini, L.; Hermanns, M.; Upton, M.; Kim, J.; Prodan, L.; Tsurkan, V.; Kézsmárki, I.; van Loosdrecht, P. H. M.; Grüninger, M. Quasimolecular $J_{\text{eff}} = 3/2$ moments in the cluster Mott insulator GaTa_4Se_8 . *Phys. Rev. Lett.* **2024**, No. 046501.
- (23) Lee, J.; Jin, K.-H.; Catuneanu, A.; Go, A.; Jung, J.; Won, C.; Cheong, S.-W.; Kim, J.; Liu, F.; Kee, H.-Y.; Yeom, H. W. Honeycomb-Lattice Mott Insulator on Tantalum Disulphide. *Phys. Rev. Lett.* **2020**, *125* (9), No. 096403.
- (24) Grahlow, F.; Ströbele, M.; Meyer, H.-J. CSD 2208516: Experimental Crystal Structure Determination of CsTaBr_6 . *ICSD Commun.* **2022**.
- (25) Grahlow, F.; Ströbele, M.; Meyer, H.-J. CSD 2327955: Experimental Crystal Structure Determination of Cs_2TaBr_6 . *ICSD Commun.* **2024**.
- (26) Yun, H.; Jang, G.-J. Dicaesium hexachlorotantalate(IV), Cs_2TaCl_6 . *Acta Crystallogr. Sec. E* **2007**, *63* (1), i22–i23.
- (27) Tan, P. H.; Han, W. P.; Zhao, W. J.; Wu, Z. H.; Chang, K.; Wang, H.; Wang, Y. F.; Bonini, N.; Marzari, N.; Pugno, N.; Savini, G.; Lombardo, A.; Ferrari, A. C. The shear mode of multilayer graphene. *Nat. Mater.* **2012**, *11* (4), 294–300.
- (28) Zhang, L.; Wang, H.; Zong, X.; Zhou, Y.; Wang, T.; Wang, L.; Chen, X. Probing interlayer shear thermal deformation in atomically-thin van der Waals layered materials. *Nat. Commun.* **2022**, *13* (1), 3996.
- (29) Sheehan, P. E.; Lieber, C. M. Friction between van der Waals Solids during Lattice Directed Sliding. *Nano Lett.* **2017**, *17* (7), 4116–4121.
- (30) Grahlow, F.; Ströbele, M.; Meyer, H.-J. CSD 2202624: Experimental Crystal Structure Determination of TaBr_4 . *ICSD Commun.* **2022**.
- (31) Ströbele, M.; Meyer, H.-J. Low-temperature preparation of tungsten halide clusters: Crystal structure of the adduct $\text{W}_5\text{Br}_{12} \cdot \text{SbBr}_3$. *Russ. J. Coord. Chem.* **2012**, *38* (3), 178–182.
- (32) Wendlandt, W. W.; Hecht, H. G. *Reflectance spectroscopy*; Interscience, 1966.
- (33) Kubelka, P. New Contributions to the Optics of Intensely Light-Scattering Materials. *Part I. J. Opt. Soc. Am.* **1948**, *38* (5), 448–457.
- (34) Kubelka, P.; Munk, F. An article on optics of paint layers. *Z. Technol. Phys.* **1931**, *12* (593–601), 259–274.
- (35) Kortüm, G.; Koffer, H. Diffuse Reflexionsspektren von adsorbiertem Jod. *Ber. Bunsenges. Phys. Chem.* **1963**, *67* (1), 67–75.
- (36) Kortüm, G.; Lohr, J. E. *Reflectance Spectroscopy*; Springer My Copy UK, 1969.
- (37) Murphy, A. B. Band-gap determination from diffuse reflectance measurements of semiconductor films, and application to photoelectrochemical water-splitting. *Sol. Energy Mater. Sol. Cells* **2007**, *91* (14), 1326–1337.
- (38) López, R.; Gómez, R. Band-gap energy estimation from diffuse reflectance measurements on sol–gel and commercial TiO_2 : a comparative study. *J. Sol-Gel Sci. Technol.* **2012**, *61* (1), 1–7.
- (39) Zanatta, A. R. Revisiting the optical bandgap of semiconductors and the proposal of a unified methodology to its determination. *Sci. Rep.* **2019**, *9* (1), 11225.
- (40) Pankove, J. I. *Optical Processes in Semiconductors*; Prentice-Hall, 1971.
- (41) Hadi, M. A.; Islam, M. N.; Podder, J. Indirect to direct band gap transition through order to disorder transformation of $\text{Cs}_2\text{AgBiBr}_6$ via creating antisite defects for optoelectronic and photovoltaic applications. *RSC Adv.* **2022**, *12* (24), 15461–15469.
- (42) Imran, M. M. A.; Lafi, O. A. Electrical conductivity, density of states and optical band gap in $\text{Se}_{90}\text{Te}_6\text{Sn}_4$ glassy semiconductor. *Phys. B* **2013**, *410*, 201–205.
- (43) Al-Fa’ouri, A. M.; Lafi, O. A.; Abu-Safe, H. H.; Abu-Kharma, M. Investigation of optical and electrical properties of copper oxide - polyvinyl alcohol nanocomposites for solar cell applications. *Arabian J. Chem.* **2023**, *16* (4), No. 104535.
- (44) Kiran Kumar, K.; Ravi, M.; Pavani, Y.; Bhavani, S.; Sharma, A. K.; Narasimha Rao, V. V. R. Investigations on the effect of complexation of NaF salt with polymer blend (PEO/PVP) electrolytes on ionic conductivity and optical energy band gaps. *Phys. B* **2011**, *406* (9), 1706–1712.
- (45) Hassanien, A. S.; Akl, A. A. Electrical transport properties and Mott’s parameters of chalcogenide cadmium sulphoselenide bulk glasses. *J. Non-Cryst. Solids* **2016**, *432*, 471–479.
- (46) Redmer, R.; Holst, B.; Hensel, F. *Metal-to-nonmetal Transitions*; Springer, 2010.
- (47) Moore, J. E. The birth of topological insulators. *Nature* **2010**, *464* (7286), 194–198.
- (48) Jha, G.; Heine, T. DFTB Parameters for the Periodic Table: Part III. *Spin-Orbit Coupling. J. Chem. Theory Comput.* **2022**, *18* (7), 4472–4481.
- (49) Roy, S. B. Mott insulators and related phenomena: a basic introduction. In *Mott Insulators*; IOP Publishing Ltd, 2019; pp 3–13–35. DOI: .
- (50) Amadon, B.; Jollet, F.; Torrent, M. γ and β cerium: LDA+U calculations of ground-state parameters. *Phys. Rev. B* **2008**, *77* (15), No. 155104.
- (51) Dey, M.; Singh, A.; Singh, A. K. Formation of a Small Electron Polaron in Tantalum Oxynitride: Origin of Low Mobility. *J. Phys. Chem. C* **2021**, *125* (21), 11548–11554.
- (52) Hinuma, Y.; Pizzi, G.; Kumagai, Y.; Oba, F.; Tanaka, I. Band structure diagram paths based on crystallography. *Comput. Mater. Sci.* **2017**, *128*, 140–184.
- (53) Lisi, S.; Lu, X.; Benschop, T.; de Jong, T. A.; Stepanov, P.; Duran, J. R.; Margot, F.; Cucchi, I.; Cappelli, E.; Hunter, A.; Tamai, A.; Kandyba, V.; Giampietri, A.; Barinov, A.; Jobst, J.; Stalman, V.; Leeuwenhoek, M.; Watanabe, K.; Taniguchi, T.; Rademaker, L.; van der Molen, S. J.; Allan, M. P.; Efetov, D. K.; Baumberger, F.

Observation of flat bands in twisted bilayer graphene. *Nat. Phys.* **2021**, *17* (2), 189–193.

(54) Han, G. H.; Duong, D. L.; Keum, D. H.; Yun, S. J.; Lee, Y. H. van der Waals Metallic Transition Metal Dichalcogenides. *Chem. Rev.* **2018**, *118* (13), 6297–6336.

(55) Schmidt, P.; Schneiderhan, P.; Ströbele, M.; Romao, C. P.; Meyer, H.-J. Reversible Iodine Intercalation into Tungsten Ditelluride. *Inorg. Chem.* **2021**, *60* (3), 1411–1418.

(56) Gonze, X.; Amadon, B.; Antonius, G.; Arnardi, F.; Baguet, L.; Beuken, J.-M.; Bieder, J.; Bottin, F.; Bouchet, J.; Bousquet, E.; Brouwer, N.; Bruneval, F.; Brunin, G.; Cavignac, T.; Charraud, J.-B.; Chen, W.; Côté, M.; Cottenier, S.; Denier, J.; Geneste, G.; Ghosez, P.; Giantomassi, M.; Gillet, Y.; Gingras, O.; Hamann, D. R.; Hautier, G.; He, X.; Helbig, N.; Holzwarth, N.; Jia, Y.; Jollet, F.; Lafargue-Dit-Hauret, W.; Lejaeghere, K.; Marques, M. A. L.; Martin, A.; Martins, C.; Miranda, H. P. C.; Naccarato, F.; Persson, K.; Petretto, G.; Planes, V.; Pouillon, Y.; Prokhorenko, S.; Ricci, F.; Rignanese, G.-M.; Romero, A. H.; Schmitt, M. M.; Torrent, M.; van Setten, M. J.; Van Troeye, B.; Verstraete, M. J.; Zerah, G.; Zwanziger, J. W. The Abinitproject: Impact, environment and recent developments. *Comput. Phys. Commun.* **2020**, *248*, No. 107042.

(57) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865.

(58) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.

(59) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13* (12), 5188.

(60) Torrent, M.; Holzwarth, N. A. W.; Jollet, F.; Harris, D.; Lepley, N.; Xu, X. Electronic structure packages: Two implementations of the projector augmented wave (PAW) formalism. *Comput. Phys. Commun.* **2010**, *181* (11), 1862–1867.

(61) Hernández, J. S.; Guevara, D.; Shamshurin, M.; Benassi, E.; Sokolov, M. N.; Feliz, M. Octahedral Tantalum Bromide Clusters as Catalysts for Light-Driven Hydrogen Evolution. *Inorg. Chem.* **2023**, *62* (46), 19060–19069.

Supplementary Information

Ta₄SBr₁₁: A cluster Mott insulator with a corrugated, van der Waals layered structure

*Fabian Grahlow,^a Fabian Strauß,^b Patrick Schmidt,^a Jaroslav Valenta,^c Markus Ströbele,^a Marcus Scheele,^b Carl P. Romao,^d and Hans-Jürgen Meyer^{*a}*

^a Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Auf der Morgenstelle 18, Eberhard Karls Universität Tübingen, D-72076 Tübingen, Germany

^b Institute for Physical and Theoretical Chemistry, Auf der Morgenstelle 18, Eberhard Karls Universität Tübingen, D-72076 Tübingen, Germany

^c International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, 1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan

^d Department of Materials, ETH Zürich, Wolfgang-Pauli-Str. 27, 8093 Zürich, Switzerland

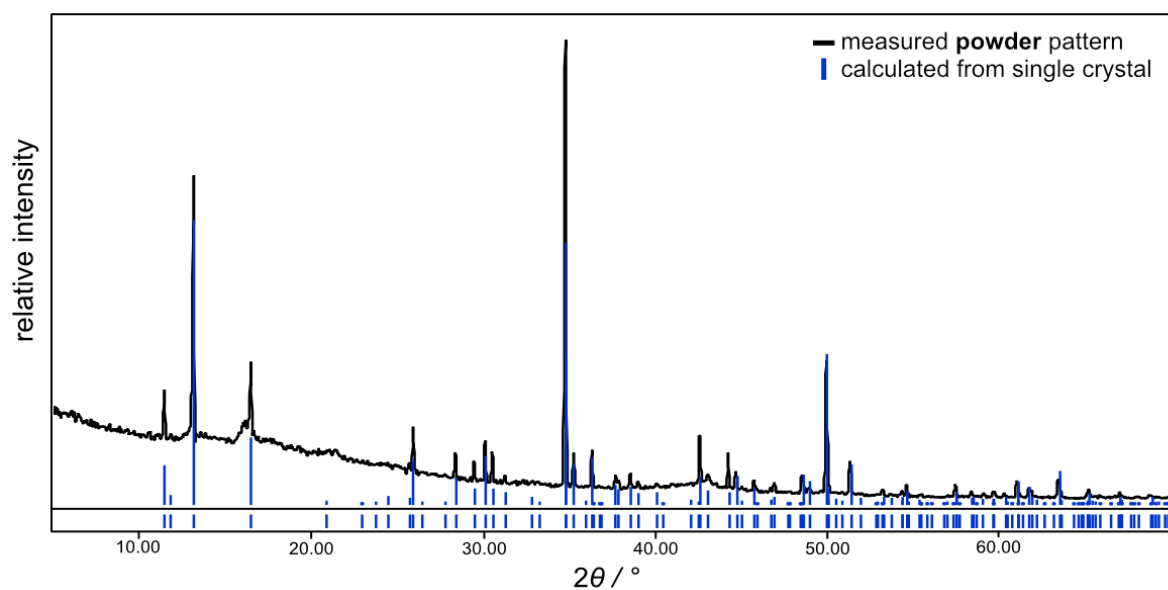


Figure S1: Powder X-Ray diffraction pattern ($\text{Cu-K}\alpha_1$) of $\text{Ta}_4\text{SBr}_{11}$.

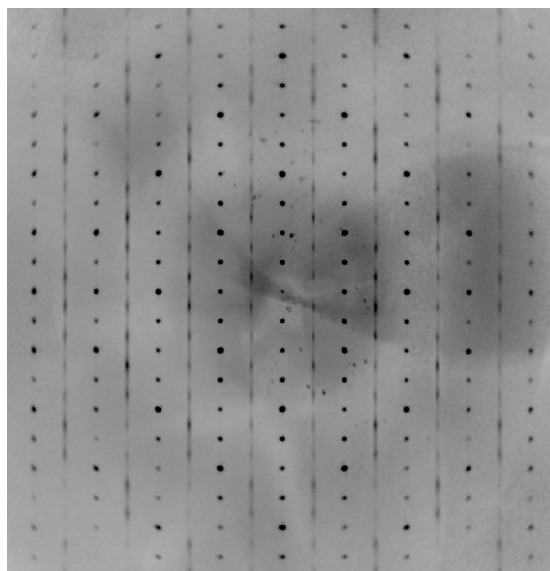


Figure S2: X-ray diffraction pattern of reciprocal lattice along the (010) direction of a $\text{Ta}_4\text{SBr}_{11}$ single crystal, showing diffuse streaks perpendicular to (100), thereby doubling the a axis locally, but not in a long-range ordered way.

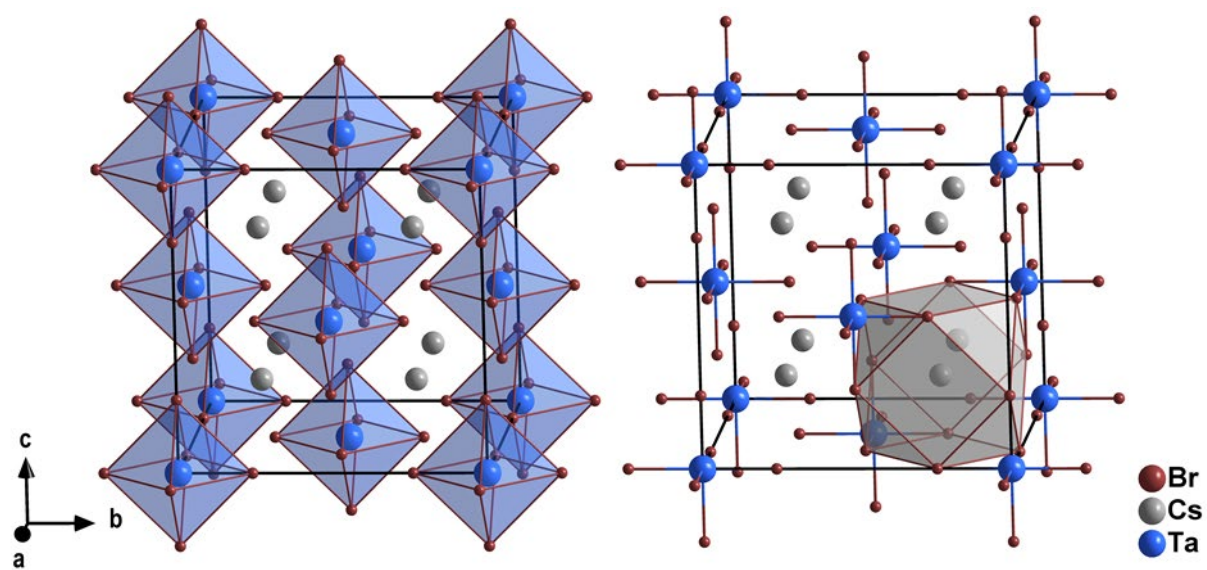


Figure S3: Unit cell of Cs_2TaBr_6 . CCDC identification code: 2327955.

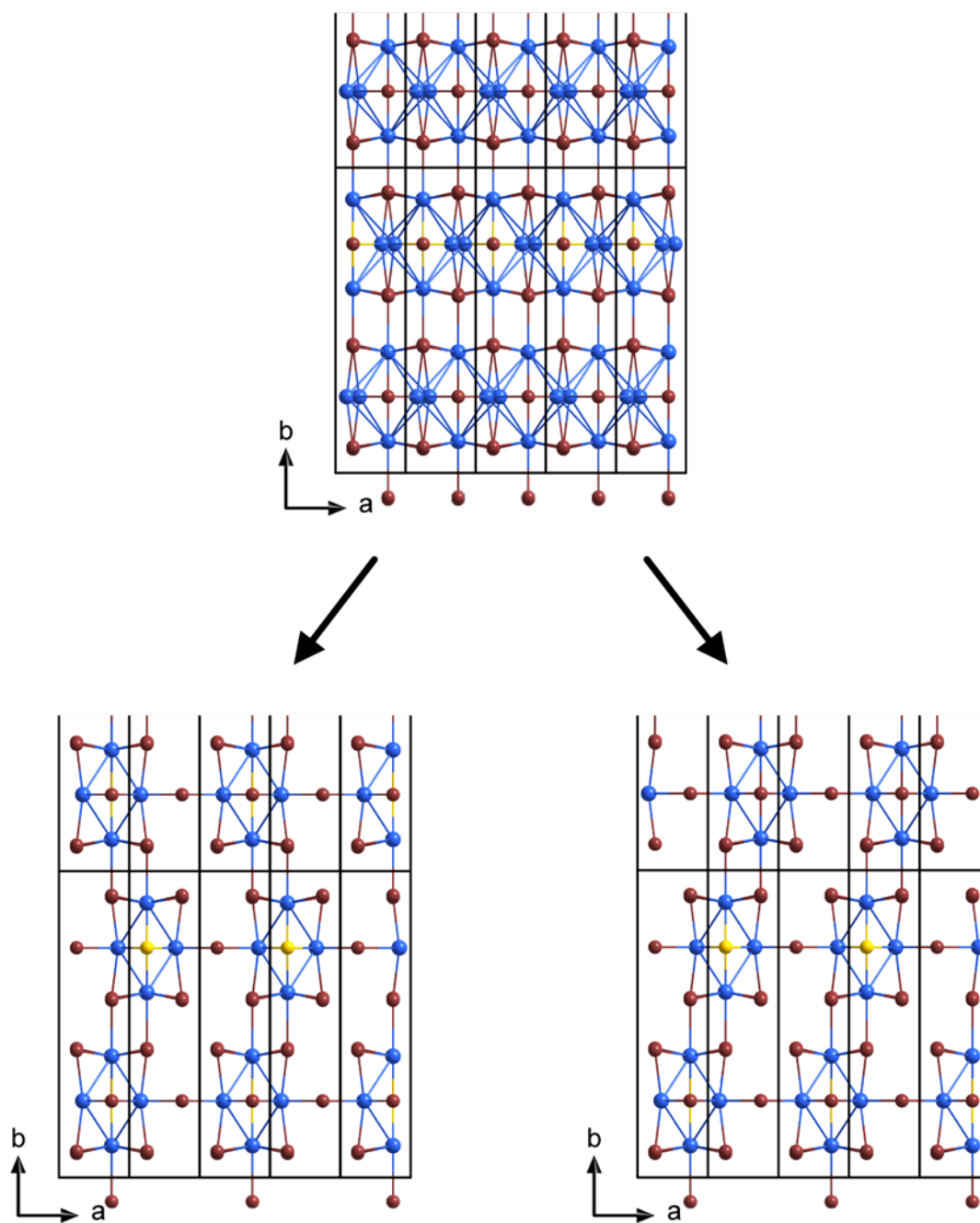


Figure S4: Two connectivity patterns (bottom left and right) within layers of $\text{Ta}_4\text{SBr}_{11}$, to resemble the average structure (top). Black lines emphasize the unit cell, with the original lattice parameter a that is to be changed to $2a$. Tantalum atoms are depicted in blue, bromine in brown and sulfur in yellow.

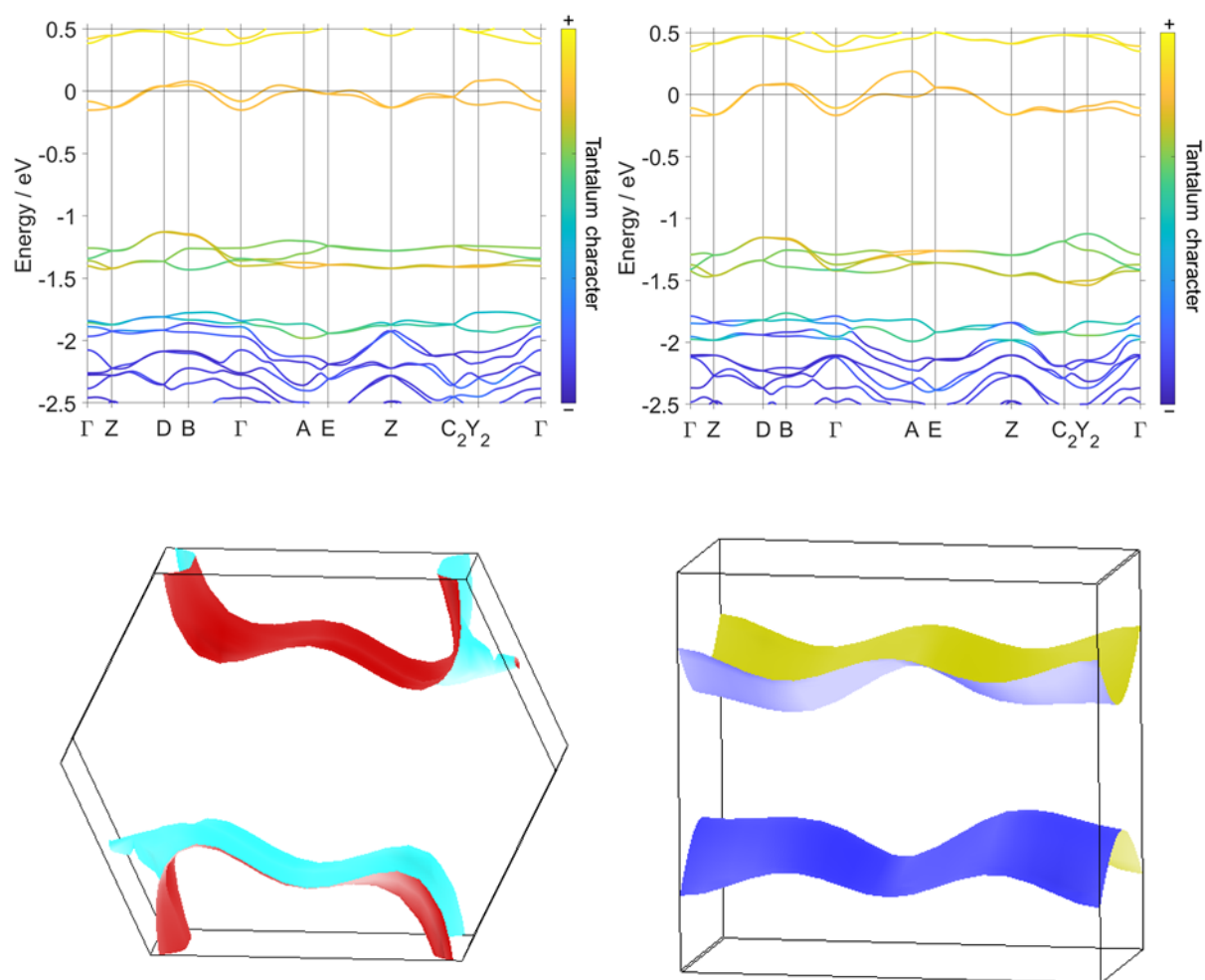


Figure S5: Electronic band structures (top) and single-band portions of the Fermi surfaces (bottom) of the staggered (left) and eclipsed (right) inter-layer arrangements of $\text{Ta}_4\text{SBr}_{11}$, with the kinked intra-layer arrangement. The displayed Fermi surfaces were calculated without spin-orbit coupling.

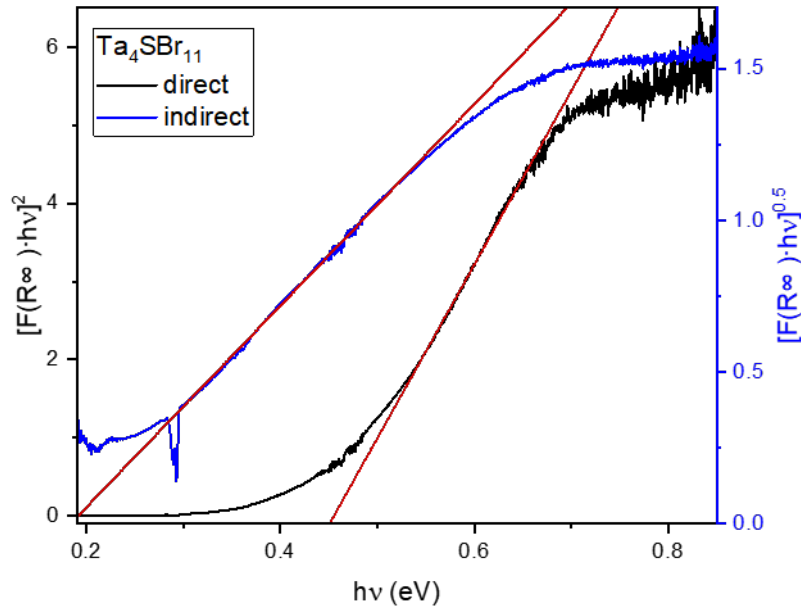


Figure S6: Tauc plot using $F(R_\infty)$ of $\text{Ta}_4\text{SBr}_{11}$ for direct (black) and indirect (blue) gap fitting along with the linear extrapolation (red) to obtain the optical band gap (signals around 0.29 eV can be assigned to atmospheric absorption bands of CO_2).

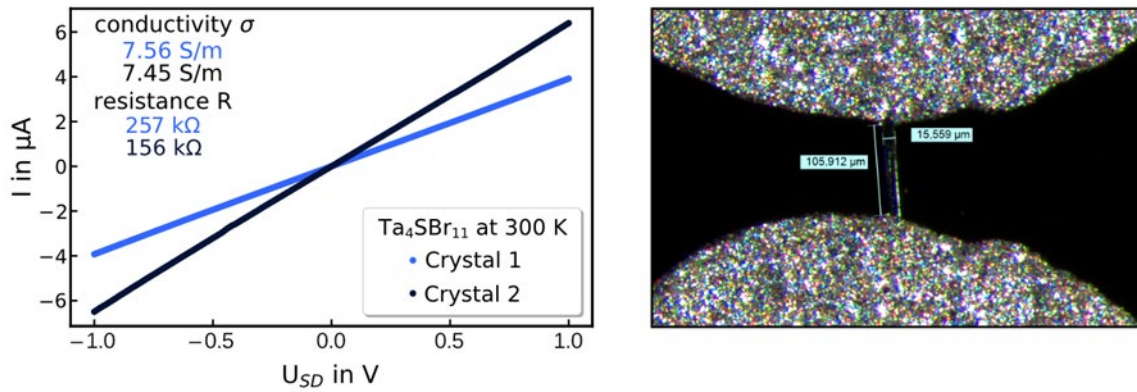


Figure S7: (left) Dark currents of $\text{Ta}_4\text{SBr}_{11}$ Crystals on silicon with 770 nm dioxide layer at 300 K. (right) Optical micrograph of one of the contacted crystals.

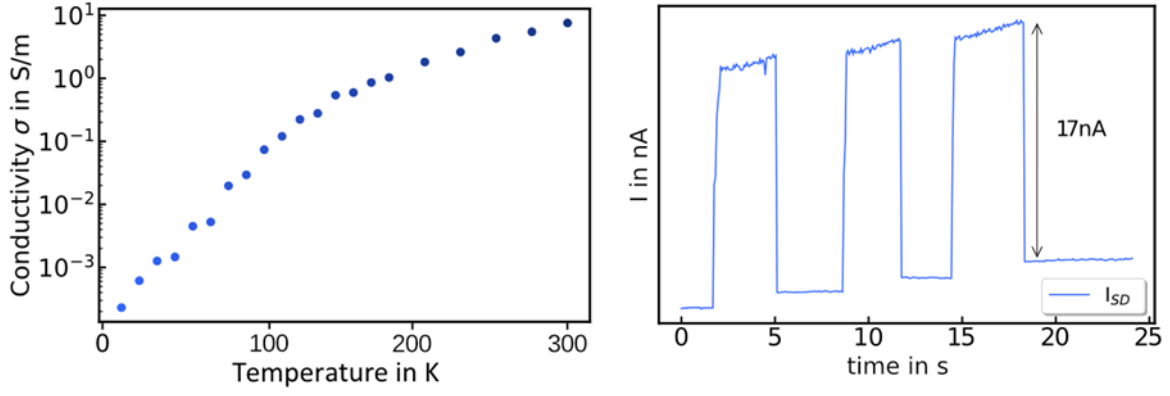
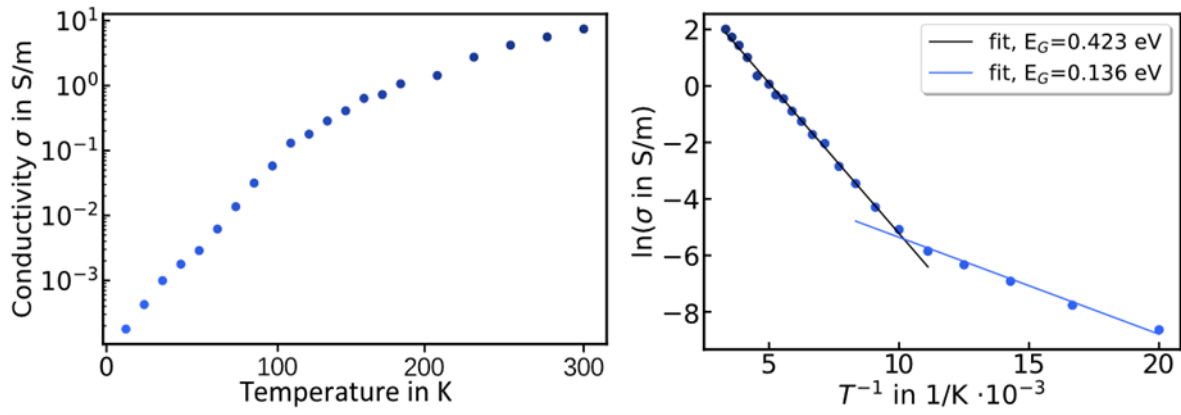


Figure S8: (left) Electrical conductivity of $\text{Ta}_4\text{SBr}_{11}$ versus set temperature in a range of 20 K to 300 K. (right) Photoresponse of a $\text{Ta}_4\text{SBr}_{11}$ crystal toward a 779 nm laser at 200 K (crystal 1).



(left) Electrical conductivity of $\text{Ta}_4\text{SBr}_{11}$ versus set temperature in a range of 20 K to 300 K. (right) Arrhenius-plot of the temperature dependent conductivity (crystal 2).

Table S1: Crystal data and structure refinement for Ta₄SBr₁₁.

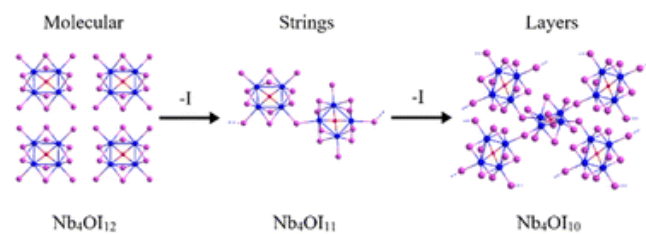
Temperature	149.9 (1) K	80.1 (1) K
CCDC Identification code	2181179	2352652
Formula weight	1634.87	1634.87
Wavelength	71.073 pm	154.184 pm
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pmmn</i>	<i>Pmmn</i>
Unit cell dimensions	$a = 3.5507(1)$ pm $b = 15.4690(4)$ pm $c = 7.4842(3)$ pm	$a = 3.5452(3)$ pm $b = 15.452(1)$ pm $c = 7.4796(4)$ pm
Volume	411.08(2) Å ³	409.74(5) Å ³
Z	1	1
Density (calculated)	6.604 g/cm ³	6.626
Absorption coefficient	53.356 mm ⁻¹	80.239 mm ⁻¹
Crystal size	0.09 × 0.01 × 0.01 mm ³	0.10 × 0.01 × 0.01 mm ³
Theta range for data collection	2.633 to 33.128°	5.727 to 77.902°
Reflections collected	21086	2824
Independent reflections	921 [$R_{\text{int}} = 0.0329$]	495 [$R_{\text{int}} = 0.0286$]
Completeness	100 % to theta = 33.128°	97.8 % to theta = 135.4°
Absorption correction	Analytical	Analytical
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	921 / 0 / 37	495 / 6 / 39
Goodness-of-fit on F2	1.139	1.068
Final R indices [$I > 2\sigma(I)$]	$R_I = 0.0180$, $wR_2 = 0.0343$	$R_I = 0.0324$, $wR_2 = 0.0874$
R indices (all data)	$R_I = 0.0202$, $wR_2 = 0.0349$	$R_I = 0.0343$, $wR_2 = 0.0887$
Largest diff. peak and hole	2.043 and -2.165 e.Å ⁻³	1.603 and -1.796 e.Å ⁻³

Table S2: Atomic coordinates and equivalent isotropic displacement parameters (pm²) for Ta₄SBr₁₁. Free refinement of the site occupancy factors (SOF) of the disordered atoms was allowed. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	SOF	x	y	z	U(eq)
Ta1	0.5	$\frac{1}{4}$	0.60399(2)	0.38585(4)	8.72(7)
Ta2	0.5	0.33952(8)	$\frac{1}{4}$	0.81816(4)	6.39(6)
Br1	1	$\frac{1}{4}$	0.08541(3)	0.85987(5)	9.15(8)
Br2	1	$\frac{1}{4}$	0.42105(3)	0.37504(6)	12.91(8)
Br3	1	$\frac{1}{4}$	$\frac{3}{4}$	0.92245(11)	19.23(14)
Br4	0.5	$\frac{1}{4}$	$\frac{3}{4}$	0.4020(3)	7.7(4)
S1	0.5	$\frac{1}{4}$	$\frac{3}{4}$	0.4508(7)	7.0(10)

Publication 7

The family of tetranuclear $\text{Nb}_4\text{OI}_{12-x}$ clusters ($x = 0, 1, 2$): from the molecular $\text{Nb}_4\text{OI}_{12}$ cluster to extended chains and layers



<https://doi.org/10.1039/D5DT00174A>

Reprinted with permission from

Dalton Trans. **2025**, *54*, 5486-5493.

Copyright © 2025 The Royal Society of Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2025, **54**, 5486

The family of tetranuclear Nb₄OI_{12-x} clusters (x = 0, 1, 2): from the molecular Nb₄OI₁₂ cluster to extended chains and layers†

Jan Beitzberger, ^a Mario Martin, ^b Marcus Scheele, ^b Patrick Schmidt, ^a Markus Ströbele ^a and H.-Jürgen Meyer ^{*,a}

Unconventional reduction reactions in the Nb–O–I system have produced a number of niobium oxyiodides containing the oxygen-centered [Nb₄O] cluster. Crystalline Nb₄OI₁₂ and two modifications of Nb₄OI₁₁ were structurally characterized by means of single-crystal X-ray diffraction studies. The new compounds can be classified as members of the Nb₄OI_{12-x} family, together with the already known Nb₄OI₁₀. Nb₄OI₁₂ is represented by a molecular structure, in which the two modifications of Nb₄OI₁₁ are forming structures with iodido-bridged strings, that can be assigned to represent one-dimensional structures. Measurements of b-Nb₄OI₁₁ single crystals reveal semiconducting behaviour, with an electrical conductivity in the order of 10⁻³ S m⁻¹ at 300 K and an electrical band gap estimated as 0.4 eV. The presence of varying numbers of cluster electrons in the given compounds is discussed in the light of second-order Jahn–Teller distortion.

Received 21st January 2025,
Accepted 26th February 2025

DOI: 10.1039/d5dt00174a

rsc.li/dalton

Introduction

Metal clusters display a broad variety in structural arrangements and oxidation states. A large number of transition metal (*M*) halide (*X*) clusters have been reported with the octahedral [*M*₆] cluster core, being represented with [*M*₆X₁₂]- and [*M*₆X₈]-type architectures.¹ The [*M*₆X₁₂]-type constitutes an octahedral *M*₆ cluster with twelve *X* atoms capping all edges of the *M*₆ core and is typically obtained for combinations of larger *M* and smaller *X* atoms. The [*M*₆X₈] cluster constitutes an octahedral cluster with eight face-capping ligands of the *M*₆ cluster and is typically obtained for combinations of smaller *M* and larger *X* atoms. The well-known niobium cluster compounds Nb₆Cl₁₄ and Nb₆I₁₁ are good examples of these two architectures, of which the latter can be described as (Nb₆I₈)I^{a-a}_{6/2} (*i* = innen or inner; *a* = außen or outer), emphasizing the presence of an [*M*₆X₈] cluster and a connectivity pattern in which six outer iodide ligands are shared between two clusters.^{2,3}

The connectivity between adjacent cluster cores and the number of cluster electrons being present has an important impact on the electronic properties of cluster compounds. A connectivity, where inner ligands simultaneously act as outer ones (*i*-*a* and *a*-*i* connectivity), is obtained in Chevrel phases like PbMo₆S₈, which is showing superconducting properties as a result of metal-to-metal interactions between adjacent clusters.⁴

A successive dimensional reduction of cluster connectivities is exemplified when going from Nb₆I₁₁ [(Nb₆I₈)I^{a-a}_{6/2}] having six shared outer ligands in three dimensions, along to W₆I₁₂ [(W₆I₈)I^{a-a}_{4/2}] having four bridging apical ligands, creating layers, and finally to BiW₆Cl₁₅ [BiCl₂(W₆Cl₈)Cl^{a-a}_{4/2}] with two bridging apical ligands, creating a linear arrangement of clusters.^{3,5} Isolated clusters like W₆Cl₁₈ ((W₆Cl₈)Cl^a₆) are held together by van der Waals forces.⁶

Metal-rich niobium iodides involve the compounds Nb₆I₁₁, Nb₃I₈, NbI₃, and NbI₄.^{3,7} A promising approach for the expansion of this chemistry is the introduction of another anion to create a heteroanionic metal cluster compound. An early outcome of this approach was the insertion of an interstitial atom (*Z*) into the octahedral [*M*₆X₁₂]-type cluster core to yield [*M*₆ZX₁₂], mostly evident with the electron-poorer d-metals (*M* = Zr, Hf).⁸ The formation of an interstitially stabilized cluster is uncommon for [*M*₆X₈]-type clusters, obviously due to an unfavorable short distance between the interstitial and the face-capping anion, causing repulsion. An exception is Nb₆I₁₁ which can incorporate a hydrogen atom to form the interstitially stabilized compound Nb₆HI₁₁.⁹

^aSection for Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry Auf der Morgenstelle 18, 72076 Tübingen, Germany.

E-mail: juergen.meyer@uni-tuebingen.de

^bInstitute of Physical and Theoretical Chemistry Auf der Morgenstelle 18, 72076 Tübingen, Germany

†Electronic supplementary information (ESI) available: IR spectra, X-ray diffraction pattern of b-Nb₄OI₁₁, photographs of crystals. CCDC 2366237, 2391069 and 2408695. For crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5dt00174a>


Generally, heteroanionic clusters can also be envisioned to constitute anion replacements in given architectures to induce a modified structure or connectivity pattern of clusters, as exemplified for $\text{Nb}_6\text{I}_9\text{S}$ (derived from Nb_6I_{11}), $\text{Nb}_3\text{X}_7\text{S}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{ANb}_3\text{Br}_7\text{S}$ with $\text{A} = \text{Rb}, \text{Cs}$ (derived from Nb_3X_8).¹⁰

The employment of oxide as a heteroanion unavoidably leads to the formation of oxyhalides NbOI_2 , NbOI_3 and NbO_2I .¹¹ However, it has been demonstrated that new oxyiodide cluster compounds can be obtained under certain conditions. A most recent example of a new oxyiodide cluster is $\text{Nb}_4\text{OI}_{10}$, which has been characterized as a small band-gap semiconductor showing photoresponse.¹² Its crystal structure can be easily derived from that of Nb_6I_{11} by cutting-off two $(\text{NbI}^{a-a}_{1/2})$ -groups of $(\text{Nb}_6\text{I}_8)\text{I}^{a-a}_{6/2}$. The resulting planar $[(\text{Nb}_4\text{OI}_8)\text{I}^{a-a}_{4/2}]$ cluster is allowing the presence of a surplus oxygen atom in the cluster center. The relaxation of inner iodide ligands in this structure is avoiding strong interanionic $\text{O}-\text{I}^-$ repulsions that would likely inhibit an oxygen centering in Nb_6I_{11} .

The preparation of niobium oxyiodide cluster compounds requires subtle control of reaction conditions and can otherwise lead to the crystallization of the thermodynamic more stable known niobium oxyiodides. Such conditions involve a highly dynamic system including elusive phases whose equilibria depend on the temperature and on local concentrations, as has been previously demonstrated with the newly discovered compound $\text{W}_2\text{O}_3\text{I}_4$ in the $\text{W}-\text{O}-\text{I}$ system.¹³ By varying the synthetic conditions, we herein describe the crystal structures of three tetranuclear niobium cluster compounds that we have characterized in the $\text{Nb}-\text{O}-\text{I}$ system. The previously reported $\text{Nb}_4\text{OI}_{10}$ and the herein described compounds are represented by a $[\text{Nb}_4\text{O}]$ cluster core that is interconnected in different ways following a dimensional reduction from layers ($\text{Nb}_4\text{OI}_{10}$) over strings ($\text{Nb}_4\text{OI}_{11}$) to isolated molecules ($\text{Nb}_4\text{OI}_{12}$).

Results and discussion

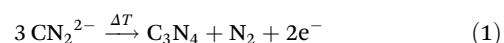
Synthesis and crystal structure

Recently, we have described the new cluster compound $\text{Nb}_4\text{OI}_{10}$ whose structure is based on a rectangular $[\text{Nb}_4\text{O}]$ core that is interconnected into layers by iodide ligands.¹² The crystal structure features a two-dimensional van der Waals material representing a small band gap semiconductor.

Slight variations of the synthesis conditions relative to those given for $\text{Nb}_4\text{OI}_{10}$ revealed the existence of a number of related compounds to exist in the $\text{Nb}-\text{O}-\text{I}$ system. These compounds are generated by changing the concentrations of reaction partners and by subtle variations of the temperature program of reactions. For a general understanding of this type of reaction we have to consider the chemical changes that occur on heating solid reactants in a heterogeneous solid-state reaction with the involvement of solid and gaseous phases. This has been already exemplified by the formation of niobium oxyiodides (NbOI_2 , NbOI_3 and NbO_2I) that were described previously.¹¹ For the preparation of reduced com-

pounds in the $\text{Nb}-\text{O}-\text{I}$ system, we are avoiding the classical pathway of a metallothermic reduction. Instead, we are exploring unconventional reduction agents with the employment of the carbodiimide ion $(\text{N}=\text{C}=\text{N})^{2-}$.

At elevated temperatures, carbodiimides have the tendency to decompose and to act as reducing agents. In this process, metal ions can be reduced, some even to form the metal state.¹⁴ The decomposition product of carbodiimide in such a reaction is not fully evidenced, as products appear X-ray amorphous. However, infrared spectra indicate the formation of C_3N_4 (Fig. S1 and S2†). A corresponding reduction mechanism could follow reaction (1).



All three compounds reported in this work crystallize as black, block-like crystals (Fig. 1). They were investigated by X-ray powder and single-crystal diffraction, providing X-ray intensity data for subsequent crystal structure determinations. The crystallographic data and refinement parameters of all tetranuclear cluster compounds are summarized in Table 1.

Syntheses of the new compounds are performed in evacuated/fused silica tubes at temperatures up to 500 °C. $\text{Nb}_4\text{OI}_{12}$ and $\text{b-Nb}_4\text{OI}_{11}$ were prepared from $\text{NbI}_4 : \text{Li}_2(\text{CN}_2) : \text{Li}_2\text{O}$ mixtures with 4 : 1 : 1 and 4 : 1.5 : 1 molar proportions, respectively. $\text{a-Nb}_4\text{OI}_{11}$ was synthesized by a reaction mixture of $\text{NbI}_4 : \text{K}_2\text{CN}_2 : \text{Cu}_2\text{O}$ in 4 : 1.5 : 1 molar ratio (see Experimental section for more details).

The $\text{Nb}_4\text{OI}_{12-x}$ system includes four structures with sum formulae $\text{Nb}_4\text{OI}_{12}$, $\text{Nb}_4\text{OI}_{11}$, and $\text{Nb}_4\text{OI}_{10}$. $\text{Nb}_4\text{OI}_{11}$ appears with two modifications, denoted as “a” and “b”.

The parent compound $\text{Nb}_4\text{OI}_{12}$ features a molecular structure based on the rectangular $[\text{Nb}_4\text{O}]$ cluster core with eight (μ_2 -) capping and four terminal iodide atoms, shown in Fig. 2. The unit cell contains eight molecules that interact through

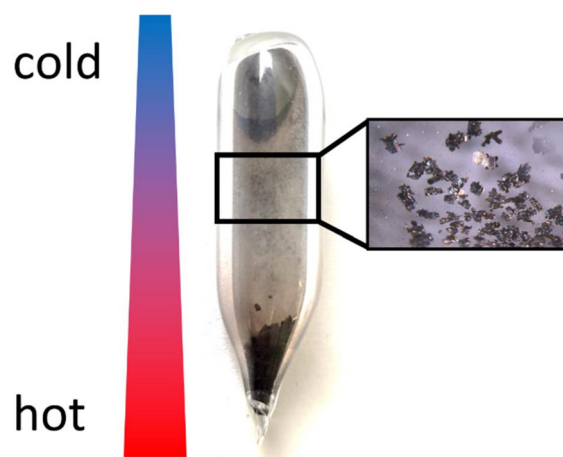


Fig. 1 A typical ampoule after the reaction is performed. The temperature gradient during the reaction is illustrated through the bar on the left side (red: hot region, blue cold region). The inset shows the reaction product $\text{b-Nb}_4\text{OI}_{11}$ (see also Fig. S4†).



Table 1 Crystal data and structure refinement parameters of Nb₄OI_{12-x} compounds

	Nb ₄ OI ₁₂	a-Nb ₄ OI ₁₁	b-Nb ₄ OI ₁₁	Nb ₄ OI ₁₀ ¹²
CCDC no.	2366237	2391069	2408695	2225618
Space group	<i>Pmc</i> 2 ₁	<i>C</i> 2/ <i>m</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	270	220	150	150
Unit cell dimensions	<i>a</i> = 37.9189(8) Å <i>b</i> = 17.8026(4) Å <i>c</i> = 7.3403(2) Å α = 90° β = 90° γ = 90°	<i>a</i> = 15.4442(3) Å <i>b</i> = 13.0449(2) Å <i>c</i> = 11.9078(2) Å α = 90° β = 105.698(2)° γ = 90°	<i>a</i> = 10.1217(2) Å <i>b</i> = 13.9844(3) Å <i>c</i> = 16.3913(3) Å α = 88.968(2)° β = 89.093(2)° γ = 85.329(2)°	<i>a</i> = 10.0435(1) Å <i>b</i> = 10.6595(1) Å <i>c</i> = 10.0594(1) Å α = 90° β = 94.193(1)° γ = 90°
Volume (Å ³)	4955.1(2)	2309.56(7)	2311.80(8)	1074.06(2)
Z	8	4	2	2
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	16.744	16.624	16.607	16.433
2 θ range for data collection	4.576 to 50.700	4.154 to 57.396	7.186 to 76.742	5.532 to 72.638
Total number of reflections	53 804	44 103	17 704	80 092
Independent reflections	9037	3115	17 704	5209
Refined parameters	418	91	290	71
<i>R</i> _{int}	0.0351	0.0189	0.020	0.0354
<i>R</i> ₁	0.0517	0.0150	0.0185	0.0117
<i>wR</i> ₂	0.1414	0.0314	0.0581	0.0282
Goodness-of-fit on <i>F</i> ²	1.086	1.430	1.037	1.093

van der Waals bonding. The crystal structure measurement was performed near room temperature because low-temperature measurements revealed incoherent scattering patterns, which could be likely indicative for the appearance of a phase-transition.

Three distinct Nb₄OI₁₂ molecules are present in the crystal structure. Each of them exhibits a (nearly) rectangular cluster core with six electrons being available for Nb–Nb bonding. The bond lengths of the cluster cores hold a small variability (Fig. 2). The short and the long interatomic distances of the cluster are in the range of 2.793(3)–2.807(3) Å and 3.029(7)–3.051(3) Å, suggesting more electron density in each shorter Nb–Nb contact. Regarding the crystal structure, the Nb₄OI₁₂ molecules are arranged in layers along the *ac*- and *bc*-planes (Fig. 3). When looking along the *b* axis (Fig. 3, right), the stacking of the molecules in the *a* direction could be explained as an ABCB sequence, although there is no closest packing of the molecules. The molecules are just arranging to each other in three different *bc*-planes (denoted in Fig. 3 as A, B and C) to reduce repulsion.

When departing from the molecular Nb₄OI₁₂ structure, the crystal structure of Nb₄OI₁₁ contains one iodide atom less and appears with two modifications. We denote these modifications with “a” and “b” because no conversion from one into the other structure could be discovered experimentally. The structure of a-Nb₄OI₁₁ is represented by a string-like connectivity of (Nb₄OI₈)I₂I_{2/2} cluster chains, in which each of the two distinct clusters is iodine bridged in a *trans* connection to the next cluster (Fig. 4). The [Nb₄O] cluster cores in this structure are as well in a rectangular shape, having two short (2.7368(6)–2.7584(7) Å) and two long (3.0375(6)–3.0423(6) Å) Nb–Nb distances.

The presence of Nb₂ atoms over all equivalent (8j) positions would create a layered structure with [Nb₄O]- and [Nb₆O]-cluster cores, shown in Fig. 5. However, the Nb₂ positions

(highlighted in light blue) are occupied by only $\frac{1}{2}$ resulting in a string connectivity. In fact, this picture (Fig. 5) represents a superposition of the alternating layers in the structure. The crystal structure of a-Nb₄OI₁₁ is characterized by two alternating layers of (Nb₄OI₈)I₂I_{2/2} that are stacked on top of each other along the [100] direction. The cluster strings within the alternating layers in the structure, each of them shown in Fig. 6, are running in two different directions ([011] and [01–1]). This arrangement affords an alternating occupation of Nb₂ positions in each layer. The adhesion between adjacent strings and layers in the structure can be described as van der Waals type, forming a hexagonal packing of strings.

Another modification of Nb₄OI₁₁ is denoted as b-Nb₄OI₁₁. The crystal structure of b-Nb₄OI₁₁ again features a string-like connectivity of two distinct [Nb₄O] clusters. However, the connectivity pattern *via* iodine atoms alternates with a *cis* and a *trans* connectivity of [Nb₄O] cores. Each *trans* connected cluster includes two short and two long Nb–Nb distance within the [Nb₄O] core. The same is true for the *cis* connected cluster. However, the *cis* connectivity induces a significant distortion to the cluster, specified in Table 2.

The unit cell of the crystal structure of b-Nb₄OI₁₁ is projected in Fig. 7. In contrast to the bidirectional arrangement of cluster strings in the structure of a-Nb₄OI₁₁, all cluster strings in b-Nb₄OI₁₁ are running parallel into one direction ([001]). A view on the projected *ab*-plane suggests that the separate strings are held together by van der Waals interactions. The given arrangement of (Nb₄OI₈)I₂I_{2/2} chains be derived from a hexagonal packing of strings, which is a typical structure pattern observed for one-dimensional structures (Fig. 8).

Electrical conductivity of b-Nb₄OI₁₁

Crystal structures like those of a- and b-Nb₄OI₁₁ with one-dimensional connectivities may be expected to act as one-



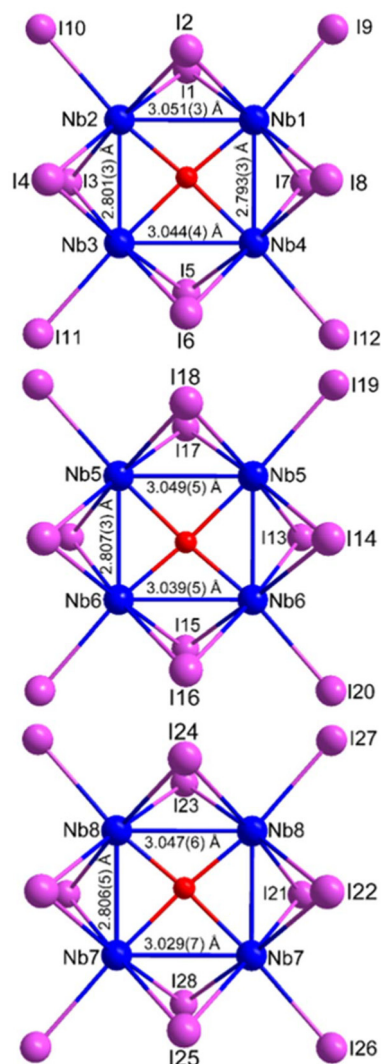


Fig. 2 Three distinct $\text{Nb}_4\text{OI}_{12}$ molecules with atom labels and Nb–Nb distances given.

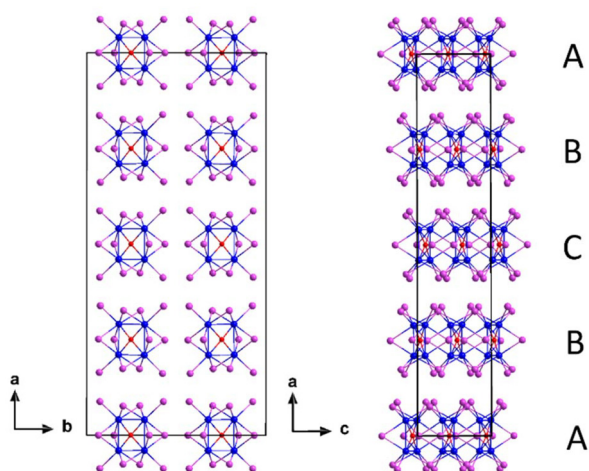


Fig. 3 Section of the crystal structure of $\text{Nb}_4\text{OI}_{12}$, looking along the c - and b -axis. Niobium atoms are coloured in blue, iodine in pink, and oxygen in red.

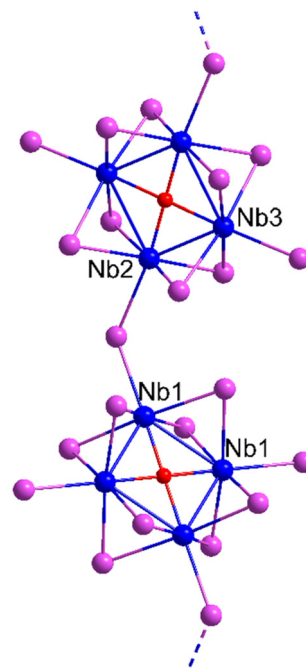


Fig. 4 String-like connectivity in the structure of $a\text{-Nb}_4\text{OI}_{11}$.

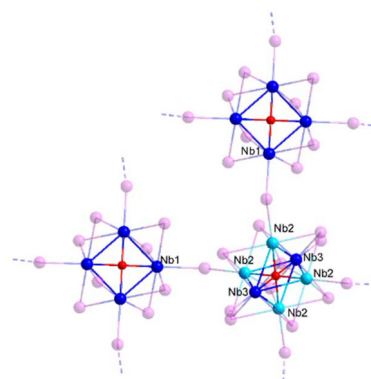


Fig. 5 Cluster connectivity in the structure of $a\text{-Nb}_4\text{OI}_{11}$ with the equivalent Nb2 positions coloured in cyan. Due to the half-occupation of Nb2 sites, only one pair of Nb2 atoms is present.

dimensional conductors. Hence, the electrical conductivity properties of single crystals of $b\text{-Nb}_4\text{OI}_{11}$ where investigated.

In Fig. 9, we display a two-point probe I - U sweep of a typical rod-shaped $b\text{-Nb}_4\text{OI}_{11}$ crystal from which we calculate the electrical conductivity as $\sigma = 4.5 \times 10^{-3} \text{ S m}^{-1}$ at 300 K.^{16,17}

The temperature-dependent conductivity measurement in Fig. 10 indicates an Arrhenius-type, temperature-activated transport, which is typical for semiconducting materials.^{12,17,18}

From this plot, we obtain an activation energy of $E_A = 0.2 \text{ eV}$. Thus, in a first-order approximation the energy difference of the Fermi level to the conduction band can be gauged as 0.2 eV. Under the assumption of an intrinsic position of the Fermi



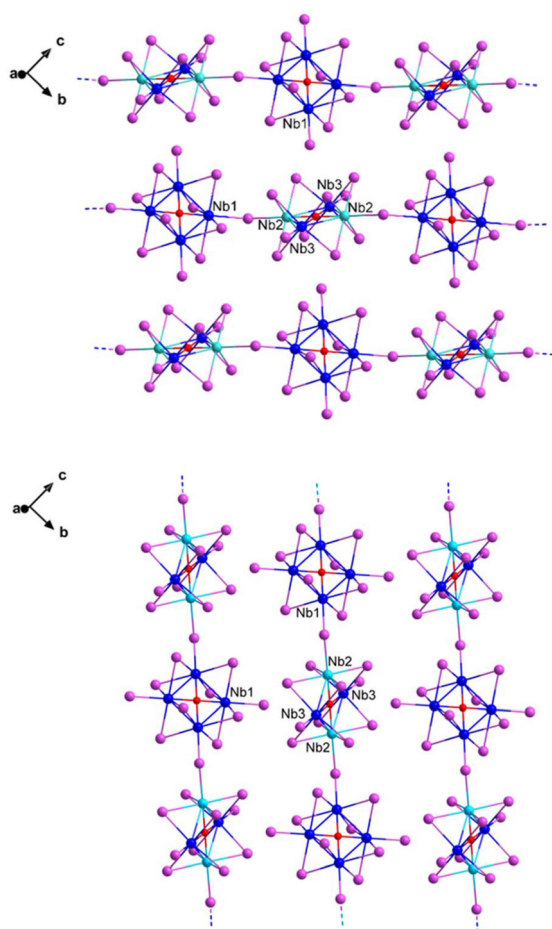


Fig. 6 Arrangement of individual cluster layers in the structure, based on string-like connectivities in the structure of a-Nb₄OI₁₁.

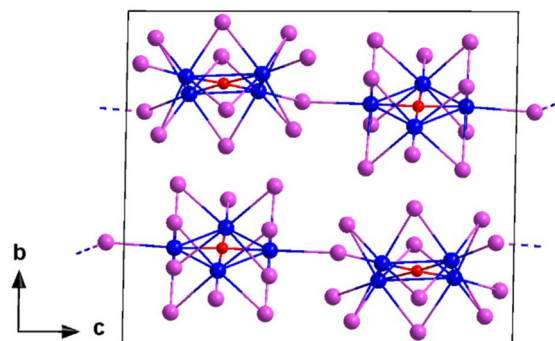


Fig. 7 Section of the crystal structure of b-Nb₄OI₁₁, looking along [100].

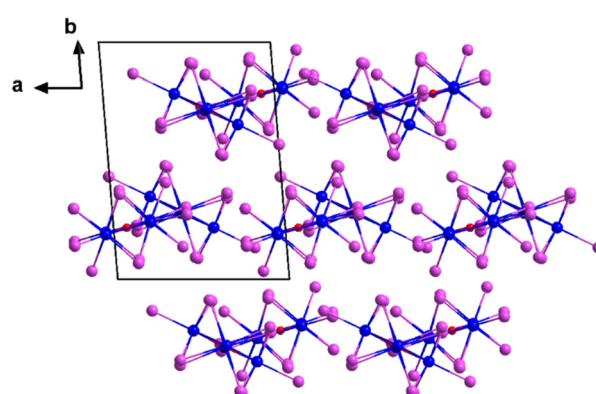


Fig. 8 Section of the crystal structure of b-Nb₄OI₁₁, following the [001] string direction.

level, this would suggest an electrical band gap on the order of 0.4 eV.

The photoresponse at 300 K of b-Nb₄OI₁₁ toward optical excitation with a 779 nm laser in continuous wave mode is shown in Fig. 11. An initial fast photocurrent of ~65 nA is followed by a slower, second component under continuous excitation. We attribute this slow component to thermal excitation by heating the crystal with the laser. At lower temperature, the photocurrent decreases substantially, *e.g.* to 12.6 pA at 160 K.

Electronic properties of Nb₄OI_{12-x} compounds

One member of the Nb₄OI_{12-x} family was already described before as Nb₄OI₁₀.¹² Nb₄OI₁₀ appears with black, plate-like crystals with an electronic band gap near 0.4 eV, according to an experimental bandgap determination and band structure calculation. This compound contains (Nb₄OI₈)I_{4/2} units that are connected into layers, through four shared apical iodide atoms (Fig. 12). The cluster core itself is rectangular with Nb–Nb distances of 2.6232(2) Å and 3.1042(2) Å. This compound was reported with an electrical conductivity of $\sigma \approx 1 \text{ S m}^{-1}$ at 300 K.

Table 2 The Nb₄OI_{12-x} family with the respective number of cluster electrons of each compound, interatomic distances with average values (Ø) and distance ranges along the short and long cluster edges, and angles within the [Nb₄O] cluster core

Distances and angles	Nb ₄ OI ₁₂ 6 cluster-e ⁻	a-Nb ₄ OI ₁₁ 7 cluster-e ⁻	b-Nb ₄ OI ₁₁ (<i>trans</i>) 7 cluster-e ⁻	b-Nb ₄ OI ₁₁ (<i>cis</i>) 7 cluster-e ⁻	Nb ₄ OI ₁₀ ¹² 8 cluster-e ⁻
short Nb–Nb (Å)	Ø 2.802 2.793(3)–2.807(3)	Ø 2.748 2.7368(6)–2.7584(7)	Ø 2.735 2.7329(8)–2.7369(8)	Ø 2.729 2.7288(8)–2.7299(8)	2.6232(2)
long Nb–Nb (Å)	Ø 3.044 3.029(7)–3.051(3)	Ø 3.040 3.0375(6)–3.0423(6)	Ø 3.054 3.0423(8)–3.0656(8)	Ø 3.056 2.9168(7)–3.1950(8)	3.1042(2)
small Nb–Nb–Nb (°)	89.81(9)–89.93(9)	87.47(2)	87.34(2)–87.88(2)	87.01(2)–87.14(2)	89.568(6)
large Nb–Nb–Nb (°)	90.11(8)–90.23(9)	92.53(1)	92.17(2)–92.60(2)	92.87(2)–92.97(2)	90.431(6)



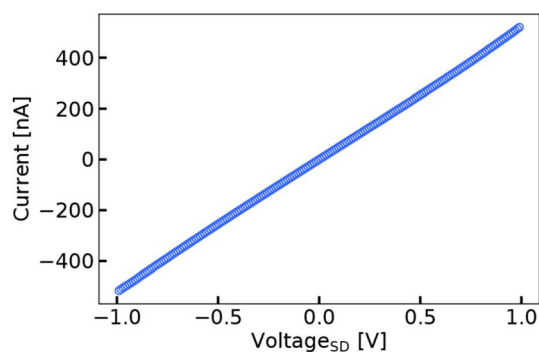


Fig. 9 I - U sweep in the dark of b-Nb₄OI₁₁ at 300 K.

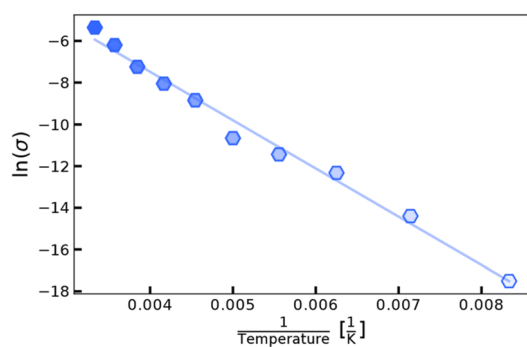


Fig. 10 Arrhenius plot of the electrical conductivity of b-Nb₄OI₁₁, with 20 K temperature steps between 120–300 K. The blue line represents a linear Arrhenius fit to the data.

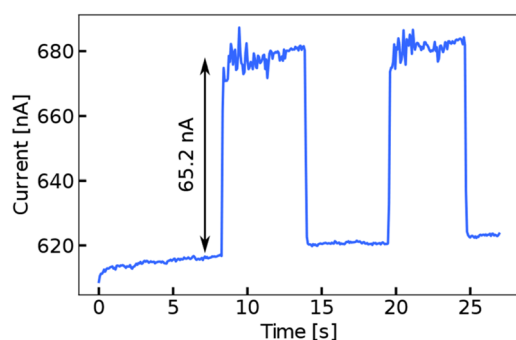


Fig. 11 Photoresponse of b-Nb₄OI₁₁ at 300 K toward a 779 nm laser illumination with 1 V bias applied.

Beside their different connectivities, the cluster compounds of the Nb₄OI_{12-x} family differ not only in their Nb–Nb bond lengths and Nb–Nb–Nb angles, but also by their numbers of cluster electrons, as summarized in Table 2.¹²

From Nb₄OI₁₂ to Nb₄OI₁₀ there is a difference of two electrons being available for niobium-to-niobium bonding. All compounds are forming nearly rectangular [Nb₄O] clusters in which the longer edges possess almost the same Nb–Nb distances (see Table 2). For the example of Nb₄OI₁₀ we already discussed the higher stability of a rectangular *versus* a square cluster core. The resulting symmetry lowering goes along with

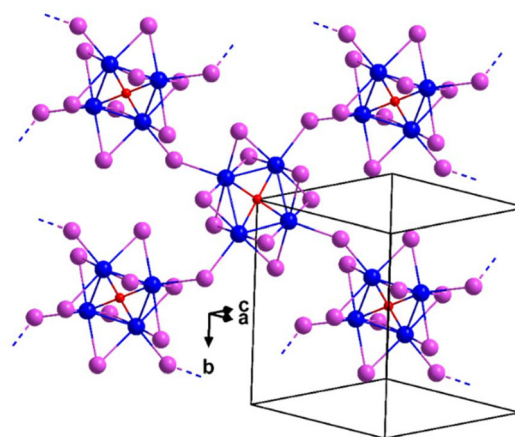


Fig. 12 Visualization of the connectivity of Nb₄OI₁₀.¹²

an increase in hybridization of molecular orbitals through a second-order Jahn–Teller distortion. In other words, the series of compounds are showing higher electron localization within the two shorter edges of [Nb₄O] cluster cores. The rectangular niobium arrangement hosts six electrons for Nb₄OI₁₂, seven electrons for Nb₄OI₁₁, and eight electrons for Nb₄OI₁₀, thereby undergoing a continuous shrinkage of the short Nb–Nb distance, with the values given in Table 2.

If there were less than six electrons for Nb–Nb bonding, the bond lengths should elongate even more. Such a compound is not yet known in the Nb–O–I system. However, the structure of Nb₄OTe₉I₄ contains an oxygen centered Nb₄ cluster core having four cluster electrons for Nb–Nb bonding.¹⁹ The cluster is distorted into a flattened tetrahedral shape with nearly equal Nb–Nb distances of 3.057(4) Å and 3.050(3) Å. These are quite close to the long distances present in the [Nb₄O] cluster cores presented in this work.

Conclusion

Cluster compounds can show a broad flexibility in their oxidation states. A well-established example is the binary tungsten-iodide system, with more than 20 different structures being reported.²⁰ The addition of oxygen leads into the W–O–I system, that is well-known because WO₂I₂ is a prominent compound in chemical vapor transport (CVT) reactions.¹³ The thermal treatment of WO₂I₂ leads to W₂O₃I₄ first, and then to WO₂. All oxides and oxyiodides in this system appear under discrete temperature conditions.

An even broader chemistry is now discovered in the Nb–O–I system for Nb₄OI_{12-x} ($x = 0, 1, 2$) compounds, with their rectangular [Nb₄O] cluster cores appearing in layers, strings, and in isolated molecules. The distinct connectivity patterns in the crystal structures involve different semiconducting properties.

These compounds could not be prepared in conventional reduction attempts through metallothermic reduction. In contrast, comparably soft reduction conditions were successful, with the carbodiimide ion as reducing agent. Hence, the formation of compounds in the Nb–O–I system involves uncon-



ventional reduction reactions in heterogeneous solid-state reactions. The product formation involves subtle equilibrium conditions related to small changes in temperature and local concentrations. These conditions appear fairly complex and are further complicated by other new compounds that exist in the given Nb–O–I system besides the herein described tetranuclear cluster compounds. The discovery of compounds with pentanuclear and heptanuclear niobium clusters in the Nb–O–I system will be reported shortly.

Experimental section

Materials and methods

Manipulations of starting materials and products were performed in a glovebox under dry argon with moisture and oxygen levels below 1 ppm. Reaction partners were charged into silica tubes ($V \approx 1.5 \text{ cm}^3$). Li_2O (ABCR, 95%) and Cu_2O (Sigma-Aldrich, 99.99%) were used as purchased. NbI_4 , $\text{Li}_2(\text{CN}_2)$ and $\text{K}_2(\text{CN}_2)$ were synthesized as described in the literature.²¹ $\text{Nb}_4\text{OI}_{10}$ was synthesized as described before.¹²

Syntheses

$\text{b-Nb}_4\text{OI}_{11}$ and $\text{Nb}_4\text{OI}_{12}$ were synthesized from NbI_4 , Li_2O and $\text{Li}_2(\text{CN}_2)$. For this purpose, NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol), and $\text{Li}_2(\text{CN}_2)$ (5.4 mg, 0.101 mmol ($\text{b-Nb}_4\text{OI}_{11}$) or 3.6 mg, 0.067 mmol ($\text{Nb}_4\text{OI}_{12}$)) were encapsulated into fused silica ampoules. The ampoules were heated from room temperature to 500 °C with a rate of 0.1 °C min^{-1} . The holding time was 24 h before the reactions were allowed to cool to room temperature with a rate of 5 °C min^{-1} for $\text{b-Nb}_4\text{OI}_{11}$ and a rate of 10 °C min^{-1} for $\text{Nb}_4\text{OI}_{12}$. Block-like crystals of $\text{b-Nb}_4\text{OI}_{11}$ and $\text{Nb}_4\text{OI}_{12}$ were found on the wall of the ampoule, along with some NbOI_2 and NbI_5 at the top of the ampoule. The products were collected mechanically. The compounds are sensitive to moisture. A powder XRD pattern of $\text{b-Nb}_4\text{OI}_{11}$ is shown in Fig. S3.† Examples of crystal specimens of $\text{b-Nb}_4\text{OI}_{11}$ and $\text{Nb}_4\text{OI}_{12}$ can be seen in Fig. S4 and S5.†

$\text{a-Nb}_4\text{OI}_{11}$ was synthesized from NbI_4 , Cu_2O and $\text{K}_2(\text{CN}_2)$. For this purpose, NbI_4 (100.7 mg, 0.168 mmol), Cu_2O (6 mg, 0.042 mmol), and $\text{K}_2(\text{CN}_2)$ (7.4 mg, 0.063 mmol) were encapsulated into a fused silica ampoule. The ampoule was heated from room temperature to 500 °C with a rate of 0.1 °C min^{-1} . The holding time was 24 h before the reaction was allowed to cool to room temperature with a rate of 5 °C min^{-1} . Block-like crystals of $\text{a-Nb}_4\text{OI}_{11}$ were found on the wall of the ampoule, along with some NbOI_2 and NbI_5 at the top of the ampoule. The product was collected mechanically. The compound is sensitive to moisture.

Instrumentation

X-ray diffraction

Black block-shaped single-crystals of $\text{a-Nb}_4\text{OI}_{11}$, $\text{b-Nb}_4\text{OI}_{11}$, and $\text{Nb}_4\text{OI}_{12}$ were mounted on a Rigaku XtaLab Synergy-S X-ray diffractometer using Mo-K_α ($\lambda = 0.71073 \text{ \AA}$) radiation. The single-crystal

was kept under N_2 cooling at 270 K for $\text{Nb}_4\text{OI}_{12}$, at 220 K for $\text{a-Nb}_4\text{OI}_{11}$ and at 150 K for $\text{b-Nb}_4\text{OI}_{11}$ during the data collection. Corrections for absorption effects were applied with CrysAlisPro (Rigaku Oxford Diffraction, 2020). The crystal structure was solved by the integrated space group and crystal structure determination routine of ShelXT²² and refined by full-matrix least-squares refinement with ShelXL-2019/3²² implemented in Olex2.²³

Reaction products were investigated by powder X-ray diffraction (PXRD) using a StadiP diffractometer (Stoe, Darmstadt) with $\text{Ge}[111]$ -monochromated Cu-K_α radiation and a mythen1 detector.

Electrical conductivity

Conductivity measurements were performed in a Lake Shore Cryotronics CRX-6.5 K probe station with a Keithley 2636B source meter unit. Block-shaped $\text{b-Nb}_4\text{OI}_{11}$ crystals were contacted with silver paste on a silicon substrate with 770 nm oxide layer and transferred into the chamber under protective gas. The conductive silver pads at each end of the crystals were connected to the circuit with tungsten tips. The chamber was kept under vacuum ($<5 \times 10^{-5}$ mbar) with 20 K temperature steps between 120 K and 300 K during the measurements. Two-point conductivity measurements were performed by varying the applied source-drain voltage from -1 V to 1 V while detecting the current. For time-resolved photocurrent measurements, using a picosecond pulsed laser driver (Taiko PDL M1, PicoQuant) together with a 779 nm laser head (pulse length $<500 \text{ ps}$) the crystals were illuminated at 40 mW laser output power using the continuous wave mode under a constant bias of 1 V.

Data availability

Crystallographic data have been deposited at the CCDC under 2366237 ($\text{Nb}_4\text{OI}_{12}$), 2391069 ($\text{a-Nb}_4\text{OI}_{11}$), and 2408695 ($\text{b-Nb}_4\text{OI}_{11}$).†

Data are available within the article.

The data that support the findings of this study are available on request from the corresponding author, H.-J. Meyer.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This research was supported by the Deutsche Forschungsgemeinschaft (ME 914-32/1 and SCHE1905/9-1).

References

- 1 L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*, Cornell University Press, 1960.



- 2 A. Simon, H. G. von Schnering, H. Wöhrle and H. Schäfer, *Z. Anorg. Allg. Chem.*, 1965, **339**, 155–170.
- 3 A. Simon, H. G. von Schnering and H. Schäufer, *Z. Anorg. Allg. Chem.*, 1967, **355**, 295–310.
- 4 O. Peña, *Phys. C*, 2015, **514**, 95–112.
- 5 M. Ströbele and H.-J. Meyer, *Z. Anorg. Allg. Chem.*, 2009, **635**, 1517–1519; M. Ströbele and H.-J. Meyer, *Inorg. Chem.*, 2017, **56**, 5880–5884.
- 6 R. Siepmann, H. G. von Schnering and H. Schäfer, *Angew. Chem.*, 1967, **79**, 650–650.
- 7 A. Simon and H. G. Von Schnering, *J. Less-Common Met.*, 1966, **11**, 31–46; L. F. Dahl and D. L. Wampler, *Acta Crystallogr.*, 1962, **15**, 903–911; P. W. Seabaugh and J. D. Corbett, *Inorg. Chem.*, 1965, **4**, 176–181.
- 8 R. P. Ziebarth and J. D. Corbett, *J. Less-Common Met.*, 1988, **137**, 21–34; R. P. Ziebarth and J. D. Corbett, *J. Solid State Chem.*, 1989, **80**, 56–67; J. Zhang and J. D. Corbett, *J. Solid State Chem.*, 1994, **109**, 265–271; J. Zhang and J. D. Corbett, *Inorg. Chem.*, 1991, **30**, 431–435; J. D. Smith and J. D. Corbett, *J. Am. Chem. Soc.*, 1984, **106**, 4618–4619; R.-Y. Qi and J. D. Corbett, *Inorg. Chem.*, 1994, **33**, 5727–5732.
- 9 A. Simon, *Z. Anorg. Allg. Chem.*, 1967, **355**, 311–322.
- 10 H.-J. Meyer and J. D. Corbett, *Inorg. Chem.*, 1991, **30**, 963–967; P. J. Schmidt and G. Thiele, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 1743–1745; G. V. Khvorykh, A. V. Shevelkov, V. A. Dolgikh and B. A. Popovkin, *J. Solid State Chem.*, 1995, **120**, 311–315; C. M. Pasco, *Electronic and Magnetic Properties of layered Two-Dimensional Materials*, Johns Hopkins University, 2021; F. Grahlow, F. Strauß, M. Scheele, M. Ströbele, A. Carta, S. F. Weber, S. Kroeker, C. P. Romao and H.-J. Meyer, *Phys. Chem. Chem. Phys.*, 2024, **26**, 11789–11797; H.-J. Meyer, *Z. Anorg. Allg. Chem.*, 1994, **620**, 863–866.
- 11 J. Rijnsdorp and F. Jellinek, *J. Less-Common Met.*, 1978, **61**, 79–82; S. Hartwig, Dissertation, Fakultät für Biologie, Chemie und Geowissenschaften, Bayreuth 2003.
- 12 J. Beitzberger, M. Ströbele, F. Strauß, M. Scheele, C. P. Romao and H.-J. Meyer, *Eur. J. Inorg. Chem.*, 2024, e202400329.
- 13 M. Löber, M. Ströbele, C. P. Romao and H.-J. Meyer, *Dalton Trans.*, 2021, **50**, 6789–6792.
- 14 K. Gibson, M. Ströbele, B. Blaschkowski, J. Glaser, M. Weisser, R. Srinivasan, H. J. Kolb and H.-J. Meyer, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1863–1870.
- 15 H. Zhao, X. Chen, C. Jia, T. Zhou, X. Qu, J. Jian, Y. Xu and T. Zhou, *Mater. Sci. Eng. B*, 2005, **122**, 90–93; H. Li, Y. Jing, X. Ma, T. Liu, L. Yang, B. Liu, S. Yin, Y. Wei and Y. Wang, *RSC Adv.*, 2017, **7**, 8688–8693.
- 16 F. Fetzter, A. Maier, M. Hodas, O. Geladari, K. Braun, A. J. Meixner, F. Schreiber, A. Schnepf and M. Scheele, *Nat. Commun.*, 2020, **11**, 6188; D. Meschede, *Gerthsen Physik*, Vol. 22, Springer, 2004.
- 17 F. Grahlow, F. Strauß, P. Schmidt, J. Valenta, M. Ströbele, M. Scheele, C. P. Romao and H.-J. Meyer, *Inorg. Chem.*, 2024, **63**, 19717–19727.
- 18 M. M. A. Imran and O. A. Lafi, *Phys. B*, 2013, **410**, 201–205; A. M. Al-Fa'ouri, O. A. Lafi, H. H. Abu-Safe and M. Abu-Kharma, *Arabian J. Chem.*, 2023, **16**, 104535; K. Kiran Kumar, M. Ravi, Y. Pavani, S. Bhavani, A. K. Sharma and V. V. R. Narasimha Rao, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **406**, 1706–1712; A. S. Hassanien and A. A. Akl, *J. Non-Cryst. Solids*, 2016, **432**, 471–479.
- 19 W. Tremel, *J. Chem. Soc., Chem. Commun.*, 1992, 709–710.
- 20 M. Ströbele and H.-J. Meyer, *Dalton Trans.*, 2019, **48**, 1547–1561.
- 21 G. Brauer, *Handbuch der präparativen anorganischen Chemie*, Enke, 1975; R. Srinivasan, M. Ströbele and H. J. Meyer, *Inorg. Chem.*, 2003, **42**, 3406–3411; M. Ströbele, E. Bayat and H.-J. Meyer, *Inorg. Chem.*, 2024, **63**, 16565–16572.
- 22 G. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
- 23 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.



Supporting Information

The Family of tetranuclear $\text{Nb}_4\text{OI}_{12-x}$ Clusters ($x = 1, 2$): From the molecular $\text{Nb}_4\text{OI}_{12}$ cluster to extended chains and layers

Jan Beitzberger,^a Mario Martin,^b Marcus Scheele,^b Patrick Schmidt,^a Markus Ströbele,^a and H.-Jürgen Meyer^{*a}

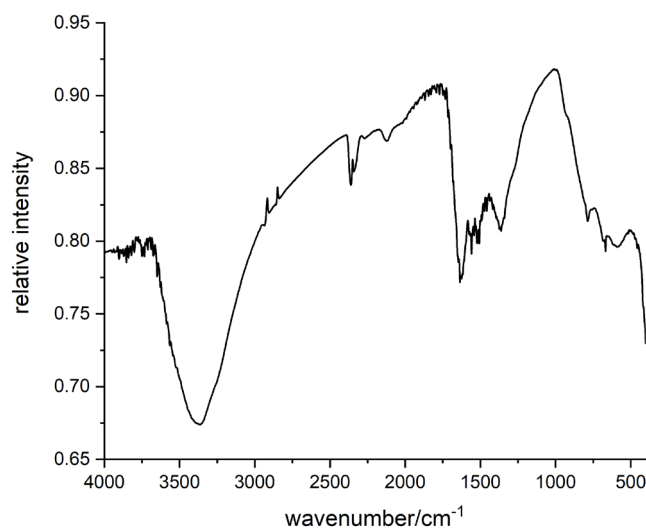


Figure S1. IR spectrum of the residual powder after the reduction of carbodiimide.

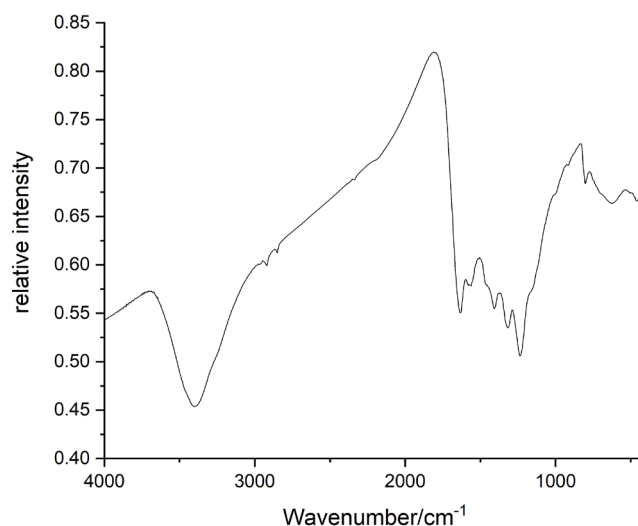


Figure S2. IR spectrum of the reaction product of amorphous C_3N_4 , made by a literature method.^[1]

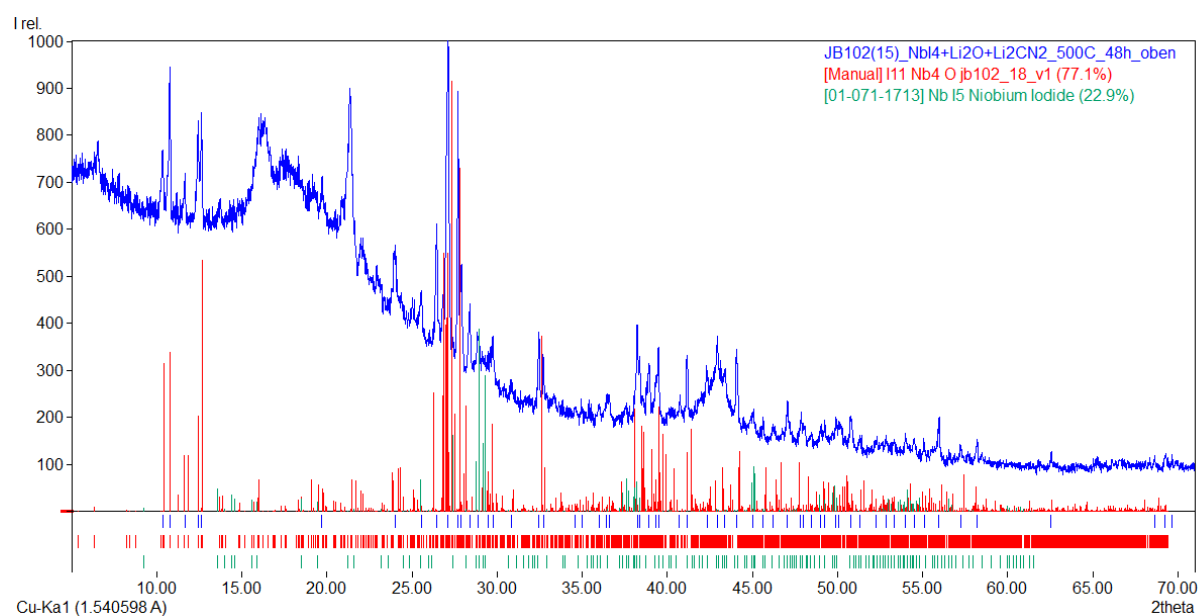


Figure S3. Measured powder X-ray diffraction pattern of $b\text{-Nb}_4\text{OI}_{11}$ with $\text{Cu-K}\alpha_1$ -radiation. In blue is the measured powder pattern, red corresponds to the calculated reflections of the single crystal X-ray measurement of $b\text{-Nb}_4\text{OI}_{11}$ and in green are the Bragg positions of coproduced NbI_5 .

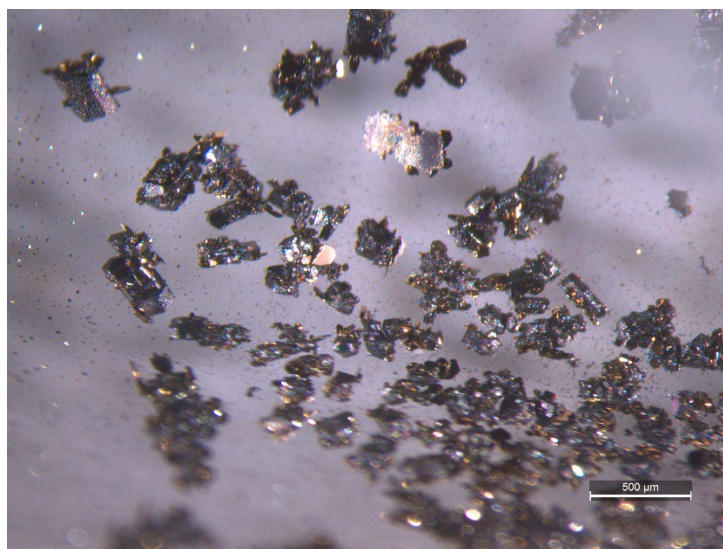


Figure S4. Example of black $b\text{-Nb}_4\text{OI}_{11}$ crystals along with some NbI_5 (golden plates).

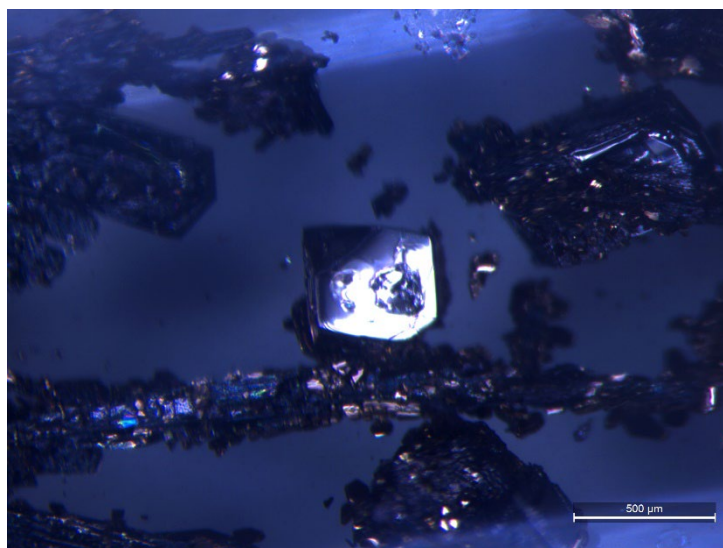
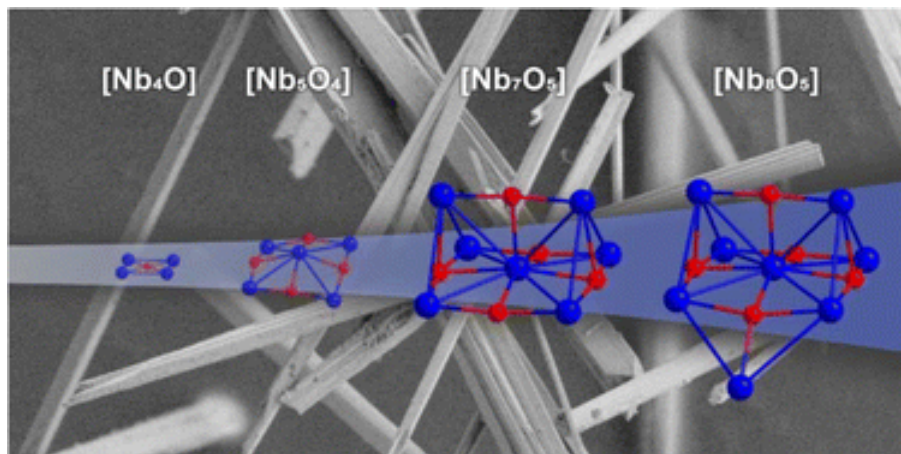


Figure S5. Example of a black Nb₄OI₁₂ crystal along with some b-Nb₄OI₁₁ aside.

- [1] H. Zhao, X. Chen, C. Jia, T. Zhou, X. Qu, J. Jian, Y. Xu, T. Zhou, *Materials Science and Engineering: B* **2005**, 122, 90-93.

Publication 8

Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicentre Nb-Nb bonding



<https://doi.org/10.1039/d5dt01819f>

Reprinted with permission from

Dalton Trans. **2025**, *54*, 14376-14383.

Copyright © 2025 The Royal Society of Chemistry

PAPER

[View Article Online](#)
[View Journal](#) | [View Issue](#)Cite this: *Dalton Trans.*, 2025, **54**, 14376**Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicentre Nb–Nb bonding**Jan Beitzberger,^a Markus Ströbele,^a Patrick Schmidt,^a Carl P. Romao^b and H.-Jürgen Meyer^{a*}

A series of niobium oxyiodide compounds has recently been identified using a non-conventional reduction method. The continuation of these studies of heterogeneous solid-state reactions in a closed system has led to the crystallization and structural analysis of two novel compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$. Both crystal structures are derived from the pentanuclear $[\text{Nb}_5\text{O}_4]$ cluster core and are expanded through the incorporation of additional niobium atoms, forming new $[\text{Nb}_7\text{O}_5]$ and $[\text{Nb}_8\text{O}_5]$ cluster cores. Furthermore, it is shown that oxyiodide clusters containing between four and eight niobium atoms can form from the same mixture of reactants by simply adjusting the composition and temperature. A comprehensive assembly model for these clusters is presented, and electronic structure calculations provide insight into the nature of niobium–niobium bonding within the $[\text{Nb}_7\text{O}_5]$ core.

Received 30th July 2025,
Accepted 19th August 2025

DOI: 10.1039/d5dt01819f

rsc.li/dalton**Introduction**

Metal-rich halide cluster compounds of group 5 and 6 transition metals are well known from the research initiated by the groups of Schäfer, von Schnering and Simon.¹ Preparations of these compounds are typically performed by metallothermic reduction, in which a metal halide (MX_n) is reacted with metal (M), which can be the same metal (M) or an electropositive alkali metal or Al.² Attempts to employ non-conventional reduction agents have been demonstrated to provide insights into the reduction pathway (namely through metal intercalation followed by metal halide elimination) by using non-conventional reduction agents, such as Cr, Fe, Co, or Ni, *etc.*, assisted by thermal scanning.³ Recently, we have successfully employed lithium carbodiimide as a reduction agent, as will be explained subsequently.⁴

The vast majority of transition metal cluster compounds is based on an octahedral cluster core of metal (M) atoms which most commonly appear with $[\text{M}_6\text{X}_8]$ with eight face-capping X or $[\text{M}_6\text{X}_{12}]$ with twelve edge-capping X halide (X) environments.⁵ In addition, interstitially (Z) stabilized octahedral clusters of the type $[\text{M}_6\text{ZX}_{12}]$ are reported for *electron-poor* group 4 metals.⁶

More than twenty binary tungsten iodide compounds have been discovered and structurally characterized; most of them are based on the $[\text{M}_6\text{X}_8]$ type cluster.⁷ In contrast, binary niobium iodide compounds involve only Nb_6I_{11} , Nb_3I_8 , NbI_3 , and NbI_4 .⁸ An interesting extension of the niobium halide chemistry has been achieved by the employment of an extra non-metal element, leading to heteroanionic cluster compounds, which may provide similar or completely distinct cluster architectures. Thus, heteroanionic clusters can be envisioned to constitute anion replacements in given architectures and to induce a modified structure or connectivity pattern of clusters, as exemplified for $\text{Nb}_6\text{I}_9\text{S}$ (derived from Nb_6I_{11}), $\text{Nb}_3\text{X}_7\text{S}$ (X = Cl, Br, I), and $\text{ANb}_3\text{Br}_7\text{S}$ with A = Rb, Cs (both derived from Nb_3X_8).⁹ Different cluster architectures are obtained in compounds with chalcogenides, such as Nb_3TeI_7 , $\text{Nb}_4\text{Se}_4\text{I}_4$, $\text{Nb}_7\text{S}_2\text{I}_{19}$, and with pnictide anions in $\text{Nb}_4\text{PnX}_{11}$ with Pn = N, P, X = Cl, Br, I.^{9b,10} Beside the difference in the number of Nb atoms forming the cluster core, the cluster design and connectivity are showing a great variety and so do the properties.

Niobium oxyiodide compounds are reported for NbOI_3 , NbO_2I , and the metal-rich example NbOI_2 .¹¹ Condensed metal–oxide–halides volatilize easily and can be crystallized only within a specific equilibrium window. This observation highlights the sensitivity of these systems to changes in conditions, such as temperature and composition, which can significantly impact the formation of different niobium oxyiodide phases.

The Nb–O–I system was recently a subject of investigations with a focus on metal-rich compounds by employing $\text{Li}_2(\text{CN}_2)$

^aSection for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Auf der Morgenstelle 18, 72076 Tübingen, Germany.

E-mail: juergen.meyer@uni-tuebingen.de

^bDepartment of Materials, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, Prague, Trojanova 339, 120 00 Nové Město, Czech Republic



as a reducing agent. The reaction, *i.e.* the reduction, involves the decomposition of the $(\text{NCN})^{2-}$ ion into C_3N_4 , as evidenced by IR spectroscopy.^{4b} Previous reactions have shown, that the interplay between NbI_4 , $\text{Li}_2(\text{CN}_2)$ and Li_2O can form a heterogeneous system in which local temperatures have an important impact on the phase formation. As a result, we have already reported the compounds $\text{Nb}_4\text{OI}_{12}$, $\text{Nb}_4\text{OI}_{11}$, and $\text{Nb}_4\text{OI}_{10}$ with their crystal structures, all based on the rectangular $[\text{Nb}_4\text{O}]$ core.^{4a} With decreasing iodide content, the series of $\text{Nb}_4\text{OI}_{12-x}$ compounds is showing structures with increasing connectivity between clusters, increasing electrical conductivities, and an increasing number of electrons from six ($x = 2$) to eight electrons ($x = 0$) per cluster. Furthermore, we have conducted a detailed analysis of the properties of oxyiodides of the type $\text{M}_5\text{O}_4\text{I}_{11}$, where $\text{M} = \text{Nb}$ or Ta .¹²

In continuation of this research, we now present two additional niobium oxyiodides, $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$, featuring $[\text{Nb}_7\text{O}_5]$ and $[\text{Nb}_8\text{O}_5]$ cluster cores, each accommodating 13 electrons available for niobium–niobium bonding.

Results and discussion

Synthesis and crystal structure

In our synthesis, NbI_4 was reacted with $\text{Li}_2(\text{CN}_2)$ and Li_2O . The specific combination of these reactants (see Experimental section) constitutes a heterogeneous reaction system governed by temperature-dependent equilibria, leading to the formation of various solid and gaseous phases. Within this system, $\text{Li}_2(\text{CN}_2)$ is proposed to function as an unconventional reducing agent for NbI_4 , thereby undergoing decomposition of the $(\text{CN}_2)^{2-}$ anion to form C_3N_4 .

To gain insight into the reaction mechanism, we performed a series of reactions at different temperatures and durations. Heating the mixture to 300 °C yielded an unknown crystalline phase, along with LiI , NbOI_2 , and an amorphous powder, as determined by powder X-ray diffraction (PXRD) (see Fig. S1, SI). Upon heating at 400 °C for 1 hour, the unidentified phase disappeared, and the compound $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ was formed, accompanied by NbOI_2 and NbI_5 . Prolonged heating at 400 °C for 24 hours resulted in the crystallization of the known $\text{Nb}_5\text{O}_4\text{I}_{11}$, which contains the $[\text{Nb}_5\text{O}_4]$ cluster core.¹²

Further heating at 500 °C for 1 hour produced crystals characterized as $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$, which were found on the walls of the ampoule. Extending the heating time at 500 °C to 24 hours led to the formation of $\text{Nb}_4\text{OI}_{10}$, a previously reported compound featuring a $[\text{Nb}_4\text{O}]$ cluster core.^{4a}

These results, while focused on solid-state products, do not account for the role of gaseous species that significantly influence the formation pathways of the observed materials. A quenching experiment of the gas phase from 400 °C to room temperature revealed the presence of a black fluid that appeared as small droplets on the ampoule walls (Fig. S2a). After 48 hours at ambient temperature, these droplets transformed into dark red, filamentous crystallites (Fig. S2b), which subsequently decomposed over time (Fig. S2c).

The two new compounds presented in this study, $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$, were structurally characterized by single-crystal X-ray diffraction (see Table 1). $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ crystallizes as rod-like crystals, whereas $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$ forms plate-like crystals. Several single crystals of the latter were refined, and in each case, the iodide content of the enclosed NbI_5 molecules were found to have slightly more than five iodide atoms, associated with the presence of some polyiodide. For clarity and simplicity, this compound will hereafter be referred to as $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$.

The crystal structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ features an oxygen-stabilized Nb_7 cluster arrangement, in which a central niobium atom (Nb2) is surrounded by six additional niobium atoms (Nb1 and Nb3), forming a trigonal prismatic coordination environment around Nb2 (Fig. 1).

Cluster cores composed of seven metal atoms are relatively rare and often adopt significantly different geometries compared to the $[\text{Nb}_7\text{O}_5]$ cluster core observed in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$. For instance, in $[\text{N}(\text{PPh}_3)_2][\text{Os}_6\text{Au}(\text{CO})_{20}\text{H}_2]$, the $[\text{Os}_6\text{Au}]$ cluster is described as two butterfly-shaped units sharing a wing tip.¹³ Another example is the asymmetric $[\text{MoFe}_6]$ cluster core in

Table 1 Crystallographic and refinement data of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$

	$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$	$\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$
CCDC	2311571	2428720
Space group	<i>Cmcm</i>	<i>Prma</i>
Temperature/K	230	200
Unit cell dimensions/Å	<i>a</i> = 14.5783(3) <i>b</i> = 17.6445(3) <i>c</i> = 13.5823(2)	<i>a</i> = 11.4282(4) <i>b</i> = 13.4336(6) <i>c</i> = 31.479(1)
Volume/Å ³	3493.7(1)	4848.1(3)
Z	4	4
Wavelength/Å	1.54184	1.54184
μ/mm^{-1}	122.292	128.729
2θ range for data collection	7.866 to 136.454	5.598 to 133.306
Total number of reflections	17 730	47 074
Independent reflections	1742	4437
Refined parameters	85	240
R_{int}	0.0316	0.0589
R_1	0.0197	0.0274
wR_2	0.0534	0.0516
Goodness-of-fit on F^2	1.060	1.036

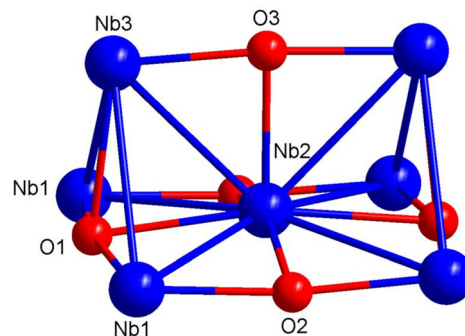


Fig. 1 Structure of the $[\text{Nb}_7\text{O}_5]$ cluster core inside $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$.



$[\text{Ph}_4\text{As}]_2[\text{MoFe}_6\text{S}_6(\text{CO})_{16}]$.¹⁴ Octahedral M_6 clusters containing a central transition-metal atom are also known, particularly among rare-earth and zirconium-based compounds.¹⁵

In contrast, the $[\text{Nb}_7\text{O}_5]$ cluster core can be regarded as an extension to the $[\text{M}_5\text{O}_4]$ cluster core found in the $\text{M}_5\text{O}_4\text{I}_{11}$ compounds ($\text{M} = \text{Nb}, \text{Ta}$) through addition of three more atoms, namely two Nb3 atoms and the O3 ion depicted in Fig. 1. The $[\text{Nb}_7\text{O}_5]$ cluster core represents six short Nb–Nb distances between the central Nb2 with the surrounding six niobium atoms measuring 2.7883(7) Å (Nb2–Nb3) and 2.8050(4) Å (Nb1–Nb2). These distances are significantly shorter than the Nb1 and Nb3 separation, which measure 3.0667(6) Å. The cluster is surrounded by iodide ligands, including four edge-capping ligands, four terminal ligands, and twelve iodide ligands that bridge between adjacent cluster cores in a 12/2 fashion, as illustrated in Fig. 2. Using the notation originally developed for octahedral cluster compounds, distinguishing between inner (i), outer (a), and outer-bridging (a–a) ligand functionalities, the connectivity pattern of the cluster can be described as $(\text{Nb}_7\text{O}_5\text{I}_4^{\text{i}})\text{I}_4^{\text{a}}\text{I}_{12/2}^{\text{a-a}}$.

This cluster fragment is further stabilized by three lithium ions and one additional iodide ion, completing the overall formula $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$. Four outer iodide ligands from the cluster, along with the additional iodide ion (I5), surround each lithium ion (Li1 and Li2) in a square-pyramidal fashion (see Fig. 3). The less flexible cluster-bound iodide ligands (I2 and I3) form the base of the square pyramid, with Li–I distances ranging from 2.904(6) to 3.17(1) Å, while the more flexible additional iodide ion (I5) occupies the apical position, showing Li–I distances of 2.64(2) Å and 2.76(1) Å.

The complete structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ is constructed by linking each $[\text{Nb}_7\text{O}_5]$ cluster to six neighbouring clusters, forming a three-dimensional framework. As illustrated in Fig. 4, a view along the c -axis of the structure reveals an alternating orientation of the adjacent clusters, highlighting the spatial arrangement and connectivity within the extended structure.

The second cluster compound obtained from the same basic reaction is $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$. The $[\text{Nb}_8\text{O}_5]$ cluster core con-

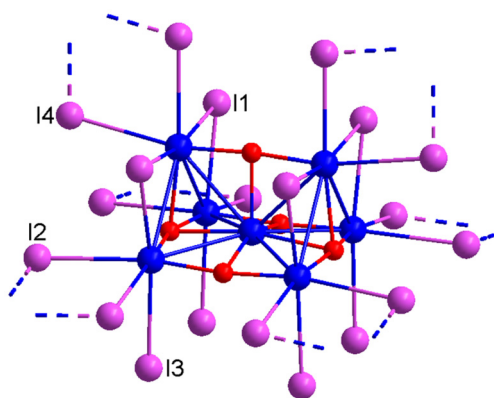


Fig. 2 Iodide coordination of the $[\text{Nb}_7\text{O}_5]$ cluster core, with twelve iodide atoms having bridging functionality (indicated by dashed lines). Niobium atoms are coloured in blue, oxygen in red and iodine in pink.

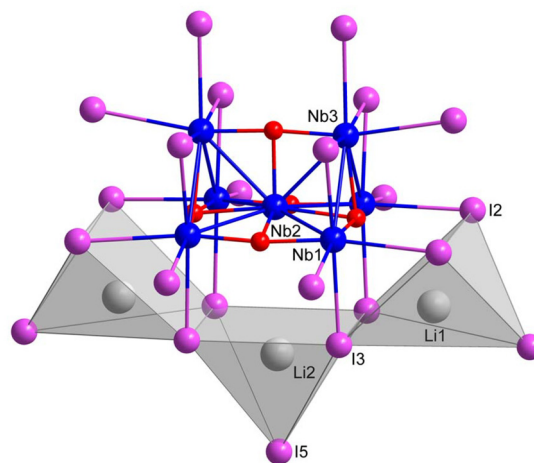


Fig. 3 Square-pyramidal lithium (grey) coordination in the structure with the additional iodide atom (I5).

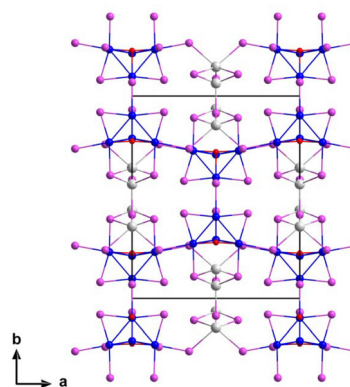


Fig. 4 Projection of the crystal structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, looking along the c -axis. Niobium atoms are shown in blue, oxygen in red, iodine in pink and lithium in grey.

tained within this compound can be viewed as an extension of the $[\text{Nb}_7\text{O}_5]$ core found in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, incorporating just one additional niobium atom. As shown in Fig. 5, this extension occurs through the addition of a niobium atom (Nb5) positioned at one edge of the $[\text{M}_5\text{O}_4]$ base, effectively expanding the cluster architecture.

As observed for the previously discussed $[\text{Nb}_7\text{O}_5]$ cluster core, the Nb–Nb distances between the central Nb2 atom and the six surrounding niobium atoms (Nb1, Nb3, Nb4) in $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ are relatively short, ranging from 2.7911(3) to 2.8600(7) Å. In contrast, the Nb–Nb distances between Nb3–Nb1 and Nb3–Nb4 are notably longer, falling in the range of 2.9981(6) to 3.1812(7) Å. The Nb–Nb distance involving the additional Nb5 atom is with 3.1418(7) Å in the same range. A comprehensive comparison of Nb–O bond lengths for both compounds is provided in Table 2. This comparison shows a good overall agreement between the structural metrics observed in the two cluster compounds.



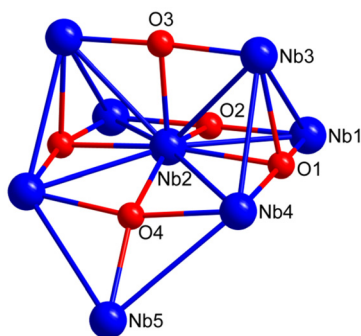


Fig. 5 The $[\text{Nb}_8\text{O}_5]$ cluster core of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$.

Table 2 Nb–O distances in the cluster cores of the two compounds and the average Nb–O distances with the corresponding coordination number (CN) of the oxygen

Compound distance/Å	$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$	$\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$
Nb1–O1	2.0005(9)	1.958(5)
Nb1–O2	1.9568(5)	1.9564(6)
Nb2–O1	2.197(6)	2.205(6)
Nb2–O2	2.097(6)	2.093(8)
Nb2–O3	2.080(8)	2.079(7)
Nb2–O4		2.084(7)
Nb3–O1	2.247(6)	2.233(5)
Nb3–O3	1.9464(6)	1.9415(7)
Nb4–O1		2.010(5)
Nb4–O4		2.122(1)
Nb5–O4		2.073(7)
$\bar{\text{O}} \text{ Nb-O1 (CN = 4)}$	2.11(1)	2.10(1)
$\bar{\text{O}} \text{ Nb-O2 (CN = 3)}$	2.00(1)	2.00(1)
$\bar{\text{O}} \text{ Nb-O3 (CN = 3)}$	1.99(1)	1.99(1)
$\bar{\text{O}} \text{ Nb-O4 (CN = 4)}$		2.10(1)

The presence of the additional niobium atom in the structure $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ alters, both the local environment and the connectivity pattern of the cluster. The connectivity changes from $(\text{Nb}_7\text{O}_5\text{I}_4)^{\text{I}}\text{I}_4^{\text{a}}\text{I}_{12/2}^{\text{a-a}}$ in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ to $(\text{Nb}_8\text{O}_5\text{I}_8)^{\text{I}}\text{I}_5^{\text{a}}\text{I}_{8/2}^{\text{a-a}}$ in $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ (Fig. 6). As a result, the number of connec-

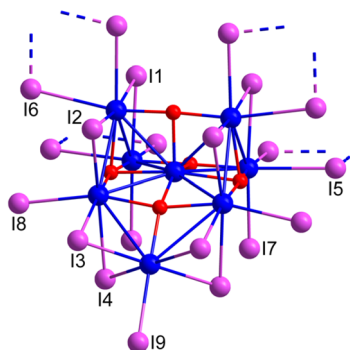


Fig. 6 Iodide coordination of the $[\text{Nb}_8\text{O}_5]$ cluster core with eight iodide atoms with bridging functionality (indicated by dashed lines) connecting to four adjacent clusters. Niobium atoms are coloured in blue, oxygen in red and iodine in pink.

tions to neighboring clusters is reduced to just four, leading to a dimensional reduction in the overall connectivity, from a three-dimensional framework in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ to a layered arrangement in $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with zig-zag layers extending along the *ab*-plane (Fig. 7).

Between the layers of the $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ structure, channels are formed that accommodate NbI_5 units (Fig. S3). The observed disorder in these regions arises from the partial incorporation of excess iodine, likely in the form of co-ordinated polyiodide species such as I_2^- or I_3^- . These species preferentially align along the crystallographic *a*-axis, contributing to the structural complexity and variability of the interlayer region.

The intercalation of molecular species within a solid-state framework is relatively uncommon but well-documented in the literature. Such molecules can reside in interlayer spaces or structural channels when the host framework provides cavities large enough to accommodate them. A notable example is the crystal structure of $\text{Nb}_7\text{S}_2\text{I}_{19}$, which can be described as $(\text{Nb}_3\text{SI}_7)_2(\text{NbI}_5)$.^{10d} In this compound, six $[\text{Nb}_3\text{S}]$ units form iodide-bridged ring arrangements that create central channels occupied by NbI_5 molecules. Another example is $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$, where TaI_5 molecules are intercalated between corrugated layers.¹² In this case, TaI_5 acts as a structural template for layer formation, as a similar cluster connectivity is observed in *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$. A comparable template effect is reported in $[\text{K}_5(\text{Ti}_2\text{Cl}_9)][(\text{Nb}_6\text{Cl}_{12}\text{O}_4)_3(\text{Ti}_3\text{Cl}_4)_2]$,¹⁶ where the complex anion $[(\text{Nb}_6\text{Cl}_{12}\text{O}_4)_3(\text{Ti}_3\text{Cl}_4)_2]^{2-}$ forms a layered framework with large channels, which are filled by $[\text{K}_5(\text{Ti}_2\text{Cl}_9)]^{2+}$ units. A related scenario is found in $\text{Cs}_3(\text{ZrCl}_5)\text{Zr}_6\text{Cl}_{15}\text{Mn}$,

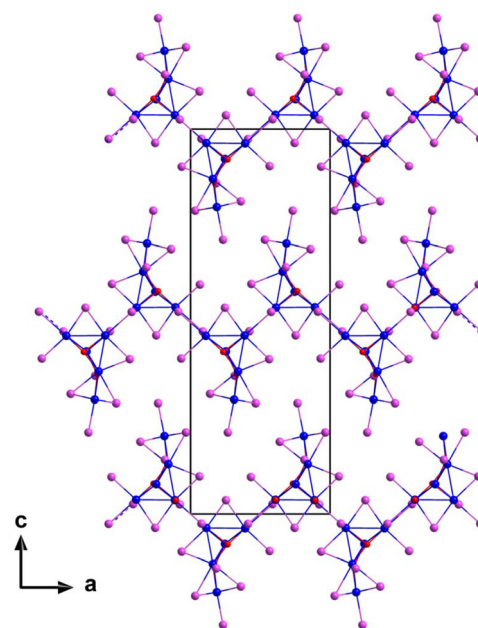


Fig. 7 Projected structure with the $\text{Nb}_8\text{O}_5\text{I}_{17}$ section of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$. The NbI_5 molecules between the layers are omitted for clarity. Niobium atoms are shown in blue, oxygen in red and iodine in pink.

where ZrCl_5^- units are incorporated into a three-dimensional framework constructed from $[\text{Zr}_6(\text{Mn})\text{Cl}_{12}]^{1-}\text{Cl}_{6/2}^{a-a}$.^{15a} Such a monoanionic molecule can also be intercalated into a simple metal halide, as demonstrated by the compound $(\text{Ta}_6\text{Br}_{15})(\text{TaBr}_6)_{0.86}$.¹⁷ These examples show how molecular species can be stabilized within solid-state matrices by occupying voids or acting as templates that influence framework formation.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Scanning electron microscopy was performed with the aid of a custom-designed vacuum transfer device to transfer the samples under inert conditions. Fig. 8 shows some crystals of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, having a rod-like morphology with right-angled edges and a rough surface.

To confirm the composition determined by X-ray diffraction of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, EDX measurements on multiple crystals were performed. These measurements result in an average Nb:I ratio of 7 : 15.2(6).

Electronic band structure and ELF calculations

The electronic structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ was investigated using density functional theory (DFT). The calculated band structure, shown in Fig. 9, reveals seven metal-centred energy bands located below the Fermi level. Among these, the highest-energy band intersects the Fermi level at multiple points in the Brillouin zone. These seven bands correspond to one formula unit of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and primarily arise from niobium-niobium bonding interactions within the $[\text{Nb}_7\text{O}_5]$ cluster, rather than in between clusters. In total, they accommodate 13 electrons per cluster. However, this number of electrons cannot be straightforwardly assigned to specific niobium-niobium contacts within the cluster core, especially when considering a notably large number of relatively short Nb–Nb distances within the cluster, discussed previously. The presence of a high density of bands at and above the Fermi level indi-

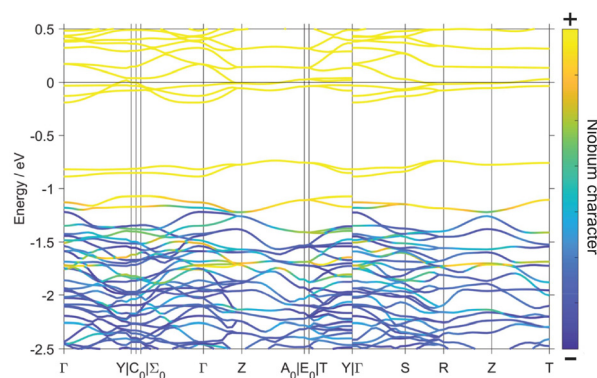


Fig. 9 DFT-calculated electronic band structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ with bands coloured by their niobium character. Special points in and paths through the Brillouin zone were chosen following the literature.¹⁸

cates delocalization of electrons across these bands. This suggests a more delocalized distribution of bonding interactions across the cluster core.

Beside the reasonably high niobium content of the bands, there is also some content arising from oxygen orbitals in bands below the Fermi energy (Fig. S4). Hence, there seems to be oxygen states hybridizing with niobium states which leads to some covalent character of some Nb–O bonds. Electron localization function (ELF) calculations of the cluster core support this interpretation. As shown in (Fig. 10, left), there is notable electron density extending from the O1 atom into the Nb1–Nb3 bonding region, indicating participation of oxygen in metal–metal bonding. Furthermore, a pronounced region of electron density is observed between Nb1, Nb2, and Nb3 (Fig. 10, right), consistent with the presence of a three-centred

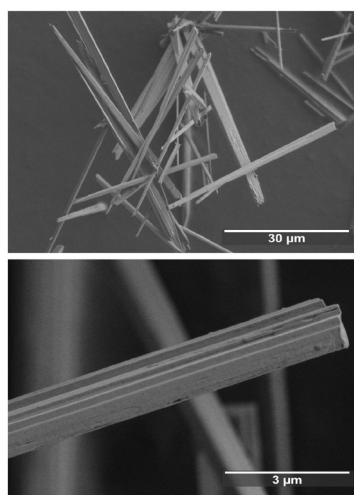


Fig. 8 Scanning electron micrographs of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$.

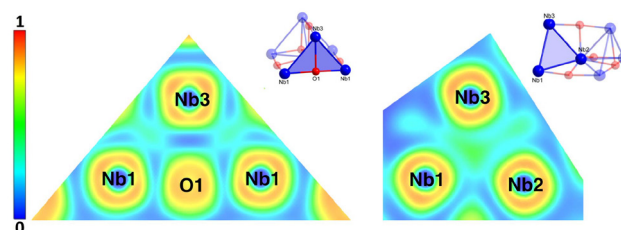


Fig. 10 Electron localisation functions of the $[\text{Nb}_7\text{O}_5]$ cluster core in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$.

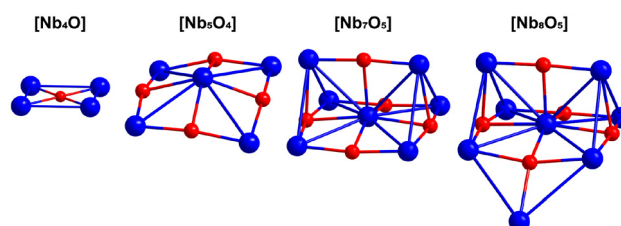


Fig. 11 The expansion of cluster architectures of niobium oxide cluster cores in various niobium oxydides.



bond. The ELF analysis suggests the presence of four such three-centred bonds, in addition to four Nb–Nb bonds with an admixture of electron density coming from oxygen within the cluster. These bonding interactions highlight the significant role of orbital mixing between niobium d-orbitals and oxygen p-orbitals in stabilizing the cluster core and the cluster framework.

Conclusion

With the discovery of the niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$, the family of cluster architectures featuring $[\text{Nb}_x\text{O}_y]$ cores is expanded by two new members. The smallest cluster in this series is the $[\text{Nb}_4\text{O}]$ core in $\text{Nb}_4\text{OI}_{12-x}$, followed by the $[\text{Nb}_5\text{O}_4]$ core in $\text{Nb}_5\text{O}_4\text{I}_{11}$, and now the $[\text{Nb}_7\text{O}_5]$ and $[\text{Nb}_8\text{O}_5]$ cores reported in the present work. These clusters are illustrated in Fig. 11.

All compounds were synthesized *via* heterogeneous solid-state reactions between NbI_4 and $\text{Li}_2(\text{CN}_2)$, which served as an unconventional reducing agent, in the presence of an oxide. The formation of the reported compounds occurs *via* temperature-dependent equilibria, influenced by slight variations in composition and the generation of various solid and gaseous phases (Fig. S5). Importantly, the gas phase and the specific gaseous species involved is thought to play a key role in guiding the formation pathways of the resulting cluster compounds.

Experimental section

Materials and methods

All manipulations of starting materials and products were performed in a glovebox under dry argon with moisture and oxygen levels below 1 ppm. Li_2O (ABCR, 95%) was used as purchased. NbI_4 and $\text{Li}_2(\text{CN}_2)$ were synthesized as described in the literature.¹⁹

Synthesis

$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ was synthesized from NbI_4 , Li_2O and $\text{Li}_2(\text{CN}_2)$. For this purpose, NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol), and $\text{Li}_2(\text{CN}_2)$ (7.2 mg, 0.135 mmol) were encapsulated into a fused silica ampoule with 3 cm length and a volume of about 1.5 cm³. The ampoule was heated in a box furnace from room temperature to 500 °C with a rate of 0.1 °C min^{−1}. The holding time was 24 h before the reaction was cooled down to room temperature with a rate of 2 °C min^{−1}. Rod-like crystals of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ were found at the bottom of the ampoule in the powder, beside LiI and an amorphous phase, produced by the decomposition of $\text{Li}_2(\text{CN}_2)$. The product was washed with dried ethanol to get rid of the LiI . A powder pattern of pure product was recorded (Fig. S6). The estimated yield of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ was about 80%; crystals appear black and decompose in air due to moisture after some time.

$\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ was synthesized from NbI_4 , Li_2O and $\text{Li}_2(\text{CN}_2)$. For this purpose, NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol) and $\text{Li}_2(\text{CN}_2)$ (7.2 mg, 0.135 mmol) were encapsulated into a fused silica ampoule with 3 cm length and a volume of about 1.5 cm³. The ampoule was heated in a Simon-Müller furnace from room temperature to 500 °C with a rate of 0.1 °C. The holding time was 1 h before the reaction was cooled down to room temperature with a rate of 2 °C min^{−1}. Plate-like crystals of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ were found at the wall in the middle of the ampoule with NbOI_2 and NbI_5 at the top of the ampoule and LiI , $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and amorphous C_3N_4 in the powder. An X-ray powder pattern of pure product was recorded (Fig. S7). Crystals appear black and decompose in air due to moisture quite fast.

Crystallography

A rod-like $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and a plate-like $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ single-crystal were mounted on a Rigaku XtaLab Synergy-S X-ray diffractometer using $\text{Cu-K}\alpha$ ($\lambda = 1.54184$ Å) radiation. The single crystal was kept under N_2 cooling at 230 K during the data collection. Corrections for absorption effects were applied with CrysAlisPro 1.171.42.70a (Rigaku Oxford Diffraction, 2022). The crystal structure was solved by the integrated space group and crystal-structure determination routine of SHELXT²⁰ and full-matrix least-squares refinement with SHELXL-2018/3²⁰ implemented in Olex2 1.5.²¹

Reaction products were investigated by powder X-ray diffraction (PXRD) using a StadiP diffractometer (Stoe, Darmstadt) with $\text{Ge}[111]$ -monochromated $\text{Cu-K}\alpha_1$ radiation and a Mythen1 detector.

Density functional theory

Density functional theory (DFT) calculations were performed using the Abinit software package (v. 9).²² The Perdew–Burke–Ernzerhof exchange–correlation functional²³ was used with the vdW–DFT–D3(BJ) dispersion correction of Grimme.²⁴ A Monkhorst–Pack grid of k -points with real-space basis vectors (3 3 0) (−2 2 0) and (0 0 3) was used to construct the electronic structure of crystalline $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$.²⁵ Plane-wave calculations were performed using an energy cutoff of 40 Ha outside of the PAW spheres and a 120 Ha cutoff inside them. Pseudopotentials sets were used as received from the Abinit library.²² These computational parameters were chosen following convergence studies.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

The data that support the findings of this study are available on request from the corresponding author, H.-J. Meyer. Computational data are available at <https://doi.org/10.5281/zenodo.15366543>.



Supplementary information is available. See DOI: <https://doi.org/10.1039/d5dt01819f>.

CCDC 2311571 ($\text{Li}_3\text{Nb}_7\text{O}_{51}\text{I}_{15}$) and 2428720 ($\text{Nb}_8\text{O}_{51}\text{I}_{17}(\text{NbI}_{5,37})$) contains the supplementary crystallographic data for this paper.^{26a,b}

Acknowledgements

This research was supported by the Deutsche Forschungsgemeinschaft (ME 914-32/1) and the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no INST 40/467-1 FUGG (JUSTUS cluster). C. P. R. acknowledges support from the project FerrMion of the Ministry of Education, Youth and Sports, Czech Republic, co-funded by the European Union (CZ.02.01.01/00/22_008/0004591), the European Union and Horizon 2020 through grant no. 810451.

References

- (a) H. Schäfer and H.-G. von Schnering, *Angew. Chem.*, 1964, **76**, 833–849; (b) A. Broll, A. Simon, H.-G. von Schnering and H. Schäfer, *Z. Anorg. Allg. Chem.*, 1969, **367**, 1–18.
- G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart, 1981, vol. 3.
- (a) A. Mos, C. Castro, S. Indris, M. Ströbele, R. F. Fink and H.-J. Meyer, *Inorg. Chem.*, 2015, **54**, 9826–9832; (b) A. Mos, M. Ströbele and H.-J. Meyer, *Z. Anorg. Allg. Chem.*, 2015, **641**, 1722–1727; (c) A. Mos, M. Ströbele and H.-J. Meyer, *J. Cluster Sci.*, 2015, **26**, 187–198; (d) A. Mos-Hummel, M. Ströbele and H.-J. Meyer, *Eur. J. Inorg. Chem.*, 2016, **2016**, 4234–4240.
- (a) J. Beitzberger, M. Ströbele, F. Strauss, M. Scheele, C. P. Romao and H.-J. Meyer, *Eur. J. Inorg. Chem.*, 2024, **27**, e202400329; (b) J. Beitzberger, M. Martin, M. Scheele, P. Schmidt, M. Ströbele and H.-J. Meyer, *Dalton Trans.*, 2025, **54**, 5486–5493.
- L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*, Cornell University Press, 1960.
- R. P. Ziebarth and J. D. Corbett, *J. Solid State Chem.*, 1989, **80**, 56–67.
- M. Ströbele and H.-J. Meyer, *Dalton Trans.*, 2019, **48**, 1547–1561.
- (a) A. Simon and H.-G. von Schnering, *J. Less-Common Met.*, 1966, **11**, 31–46; (b) A. Simon, H.-G. von Schnering and H. Schäfer, *Z. Anorg. Allg. Chem.*, 1967, **355**, 295–310; (c) P. W. Seabaugh and J. D. Corbett, *Inorg. Chem.*, 1965, **4**, 176–181; (d) L. F. Dahl and D. L. Wampler, *Acta Crystallogr.*, 1962, **15**, 903–911.
- (a) H.-J. Meyer and J. D. Corbett, *Inorg. Chem.*, 1991, **30**, 963–967; (b) P. J. Schmidt and G. Thiele, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 1743–1745; (c) G. V. Khvorykh, A. V. Shevelkov, V. A. Dolgikh and B. A. Popovkin, *J. Solid State Chem.*, 1995, **120**, 311–315; (d) C. M. Pasco, Dissertation, Johns Hopkins University, 2021; (e) F. Grahlow, F. Strauß, M. Scheele, M. Ströbele, A. Carta, S. F. Weber, S. Kroeker, C. P. Romao and H.-J. Meyer, *Phys. Chem. Chem. Phys.*, 2024, **26**, 11789–11797; (f) H.-J. Meyer, *Z. Anorg. Allg. Chem.*, 1994, **620**, 863–866.
- (a) M. Ströbele, O. Oeckler, M. Thelen, R. F. Fink, A. Krishnamurthy, S. Kroeker and H.-J. Meyer, *Inorg. Chem.*, 2022, **61**, 17599–17608; (b) M. D. Smith and G. J. Miller, *J. Alloys Compd.*, 1998, **281**, 202–205; (c) H. B. Yaich, J. C. Jegaden, M. Potel, M. Sergent, A. K. Rastogi and R. Tournier, *J. Less-Common Met.*, 1984, **102**, 9–22; (d) G. J. Miller and J. Lin, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 334–336.
- (a) J. Rijnsdorp and F. Jellinek, *J. Less-Common Met.*, 1978, **61**, 79–82; (b) S. Hartwig, Dissertation, University of Bayreuth, 2003.
- F. Grahlow, J. Beitzberger, M. Martin, E. Juriatti, H. Peisert, M. Scheele, M. Ströbele, C. P. Romao and H.-J. Meyer, unpublished work.
- B. F. G. Johnson, D. A. Kaner, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1981, 753–755.
- P. A. Eldredge, K. S. Bose, D. E. Barber, R. F. Bryan, E. Sinn, A. Rheingold and B. A. Averill, *Inorg. Chem.*, 1991, **30**, 2365–2375.
- (a) J. Zhang and J. D. Corbett, *Inorg. Chem.*, 1995, **34**, 1652–1656; (b) T. Hughbanks and J. D. Corbett, *Inorg. Chem.*, 1988, **27**, 2022–2026; (c) J. Zhang and J. D. Corbett, *Inorg. Chem.*, 1993, **32**, 1566–1572.
- T. Duraisamy, Y. Zhihua, E. V. Anokhina, C. S. Choi, C. S. Day and A. Lachgar, *J. Solid State Chem.*, 2003, **175**, 46–51.
- K. Habermehl, A.-V. Mudring and G. Meyer, *Eur. J. Inorg. Chem.*, 2010, **2010**, 4075–4078.
- Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba and I. Tanaka, *Comput. Mater. Sci.*, 2017, **128**, 140–184.
- (a) G. Brauer, *Handbuch der präparativen anorganischen Chemie*, Enke, 1975; (b) R. Srinivasan, M. Ströbele and H.-J. Meyer, *Inorg. Chem.*, 2003, **42**, 3406–3411.
- G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
- O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- X. Gonze, B. Amadon, G. Antonius, F. Arnardi, L. Baguet, J.-M. Beuken, J. Bieder, F. Bottin, J. Bouchet, E. Bousquet, N. Brouwer, F. Bruneval, G. Brunin, T. Cavignac, J.-B. Charraud, W. Chen, M. Côté, S. Cottenier, J. Denier, G. Geneste, P. Ghosez, M. Giantomassi, Y. Gillet, O. Gingras, D. R. Hamann, G. Hautier, X. He, N. Helbig, N. Holzwarth, Y. Jia, F. Jollet, W. Lafargue-Dit-Hauret, K. Lejaeghere, M. A. L. Marques, A. Martin, C. Martins, H. P. C. Miranda, F. Naccarato, K. Persson, G. Petretto, V. Planes, Y. Pouillon, S. Prokhorenko, F. Ricci,



- G.-M. Rignanese, A. H. Romero, M. M. Schmitt, M. Torrent, M. J. van Setten, B. Van Troeye, M. J. Verstraete, G. Zérah and J. W. Zwanziger, *Comput. Phys. Commun.*, 2020, **248**, 107042.
- 23 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 24 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 25 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1976, **13**, 5188–5192.
- 26 (a) J. Beitzberger, M. Ströbele, P. Schmidt, C. P. Romao and H.-J. Meyer, CCDC 2311571: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2h1ct9](https://doi.org/10.5517/ccdc.csd.cc2h1ct9); (b) J. Beitzberger, M. Ströbele, P. Schmidt, C. P. Romao and H.-J. Meyer, CCDC 2428720: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2mj8t8](https://doi.org/10.5517/ccdc.csd.cc2mj8t8).



Supporting Information

Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicenter Nb–Nb bonding

Jan Beitzberger,^a Markus Ströbele,^a Patrick Schmidt,^a Carl P. Romao,^b and H.-Jürgen Meyer^{*a}

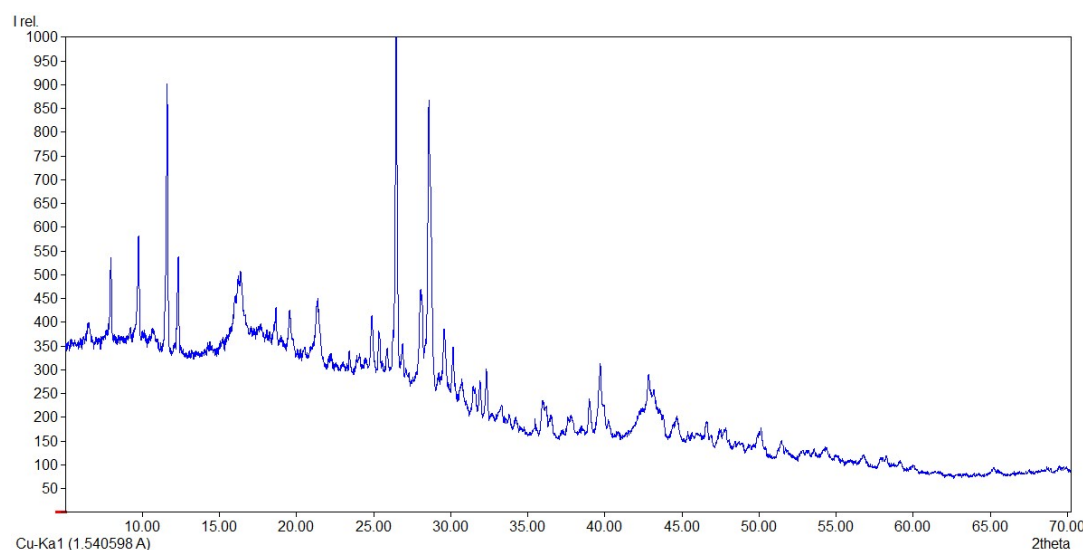


Figure S 1. Measured powder X-ray diffraction pattern of the unknown phase after the reaction of NbI_4 with Li_2CN_2 and Li_2O at 300 °C for 24 h.

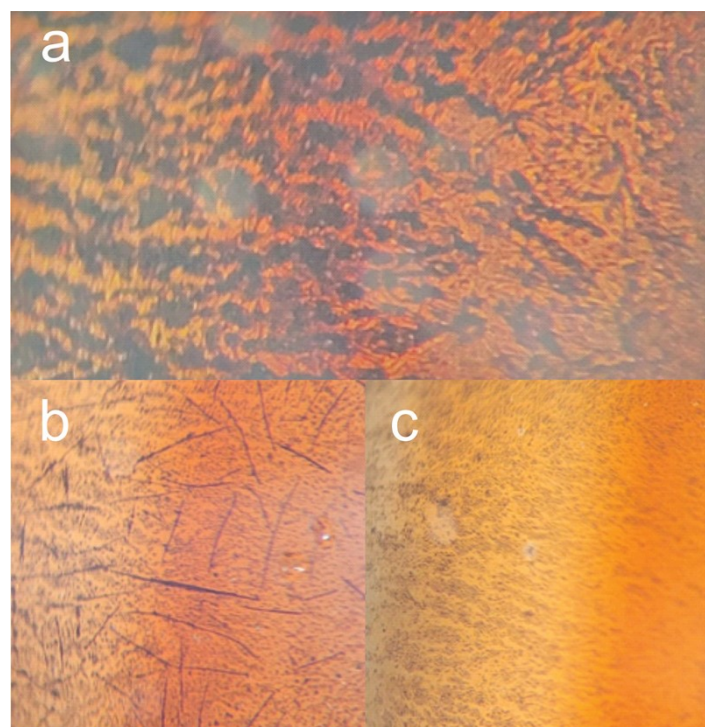


Figure S 2. Substance on the wall after quenching the reaction from 400 °C to room temperature. The product forms black droplets (a) which transform at room temperature into dark red, string-like crystallites (b). These crystallites decompose after some time at room temperature.

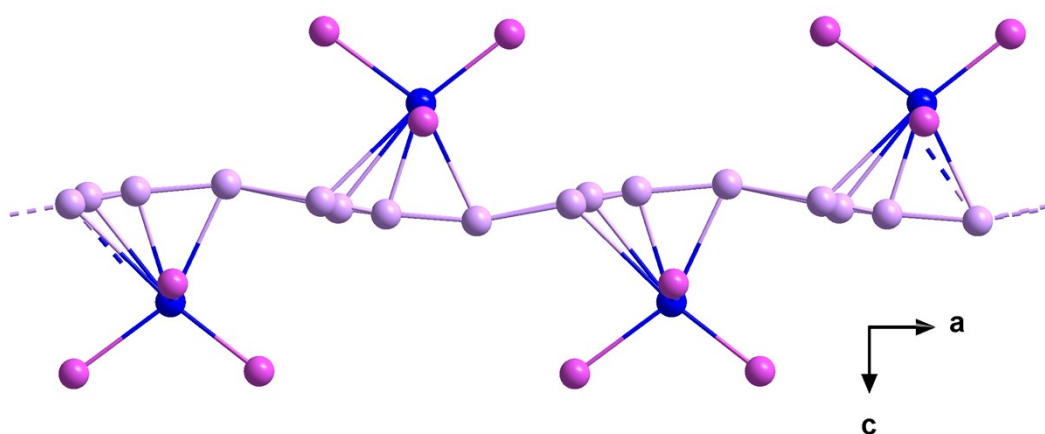


Figure S 3. " $\text{NbI}_{5.37}$ " between the layers inside the structure of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$, looking at the ac -plane.

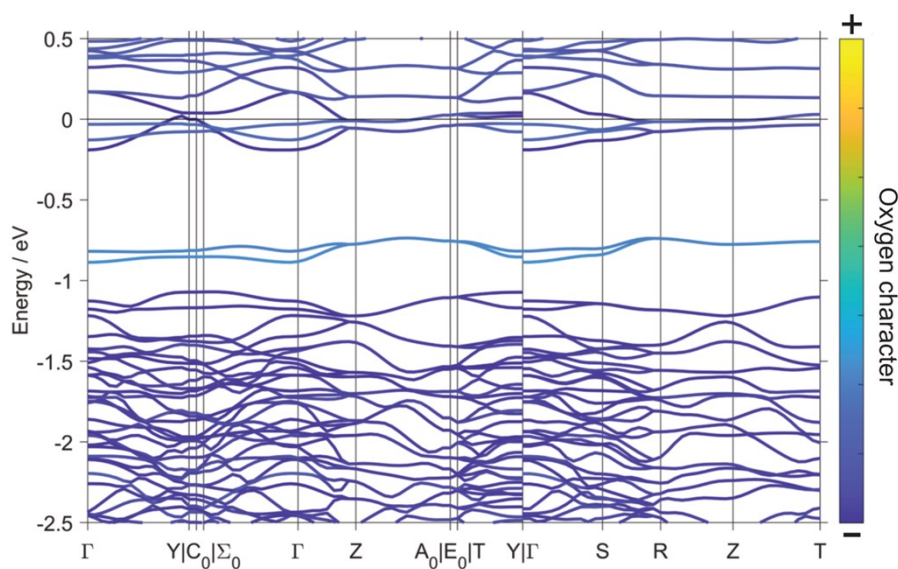


Figure S 4. DFT-calculated electronic band structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ with bands coloured by their oxygen character. Special points in and paths through the Brillouin zone were chosen following the literature.^[1]

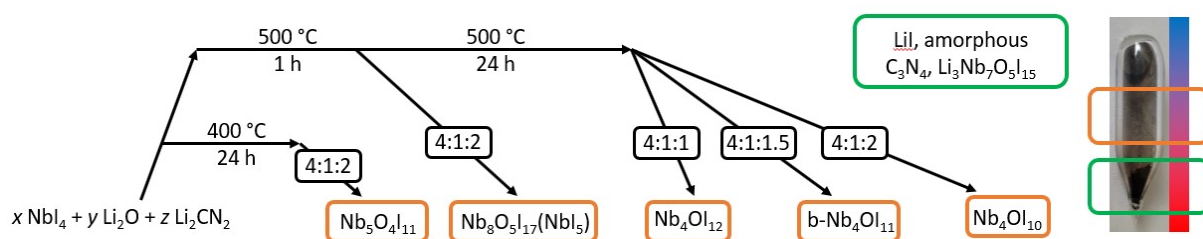


Figure S 5. Reaction conditions for the various cluster compounds, synthesized through the reaction of NbI_4 with $\text{Li}_2(\text{CN}_2)$ and Li_2O .

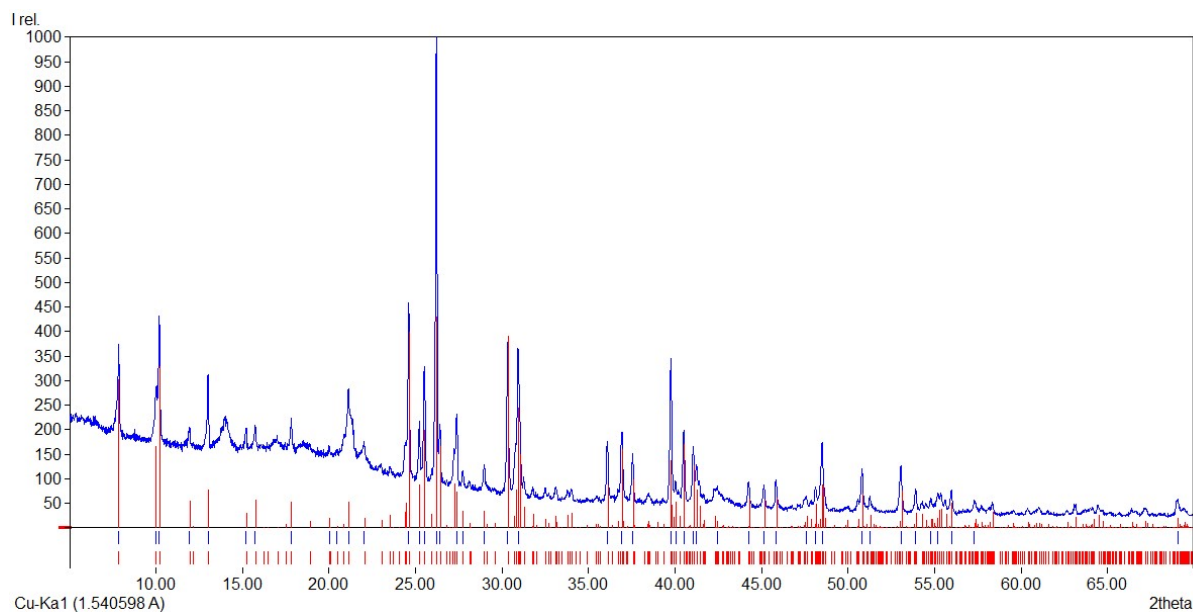


Figure S 6. Measured powder X-ray diffraction pattern of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ with $\text{Cu-K}\alpha_1$ radiation. In blue is the measured powder pattern, red correspond to the single-crystal X-ray measurement of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$.

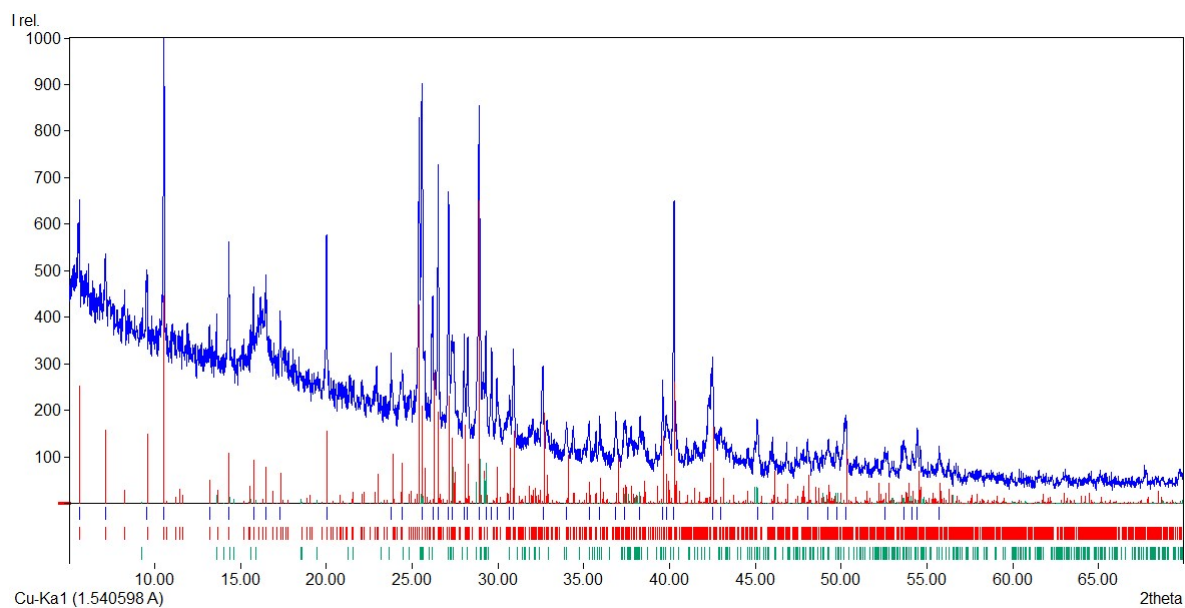
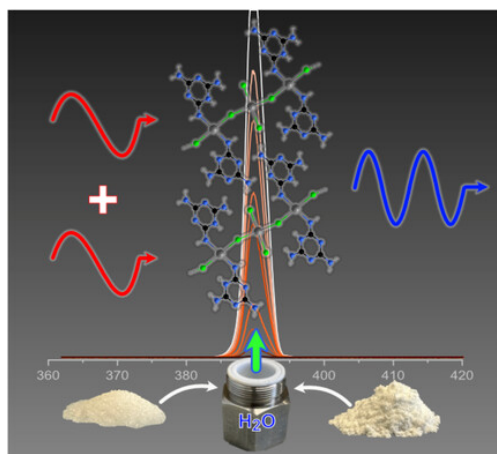


Figure S 7. Measured powder X-ray diffraction pattern of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$ with $\text{Cu-K}\alpha_1$ radiation. In blue is the measured powder pattern, red correspond to the single-crystal X-ray measurement of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$ and green are Bragg positions of coproduced NbI_5 ^[2].

- [1] Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, *Comput. Mater. Sci.* **2017**, 128, 140-184.
- [2] B. Krebs, D. Sinram, *Z. Naturforsch. B* **1980**, 35, 12-16.

Publication 9

Hydrothermal Synthesis and Characterization of the Melamine-Based
Second-Harmonic Generation Material $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ 

<https://doi.org/10.1002/ejic.202500256>

Reprinted with permission from
Eur. J. Inorg. Chem. **2025**, 28, e202500256.

Copyright © 2025 Wiley-VCH GmbH

VIP Very Important Paper

Hydrothermal Synthesis and Characterization of the Melamine-Based Second-Harmonic Generation Material $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$

Melena Groß, Patrick Schmidt, Carl P. Romao, David Enseling, Thomas Jüstel, Mykhailo Brytskyi, Scott Kroeker, and Hans-Jürgen Meyer*

The pursuit of efficient nonlinear optical materials is critical for advancing optoelectronic applications. This study focuses on the synthesis and characterization of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, a melamine-based hybrid metal halide. Structural analysis reveals a non-centrosymmetric lattice facilitated by large asymmetric secondary building units and a π -conjugated system. The

compound exhibits a strong second-harmonic generation efficiency. Density functional theory calculations, optical band gap measurements, and photoluminescence measurements specify the electronic properties. For completeness and analytical comparison, the centrosymmetric compound $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$ is also introduced.

1. Introduction

Nonlinear optical (NLO) materials are critical to the advancement of optoelectronic technologies, underpinning applications such as frequency doubling, optical switching, and high-speed telecommunications.^[1] The generation of second-order nonlinear optical effects, including second-harmonic generation (SHG), requires materials with non-centrosymmetric structures, as only such structures can exhibit the macroscopic polarization necessary for these phenomena.^[2] However, most crystalline solids, especially organic-containing compounds, tend to crystallize in centrosymmetric space groups, making the design and discovery

of non-centrosymmetric materials particularly challenging.^[3] Overcoming this “inversion symmetry trap” often requires the integration of structurally asymmetric molecular units or the introduction of lattice distortions through targeted chemical modifications.^[4,3a]

β -Barium borate (BBO) is a highly regarded NLO material, renowned for its versatility in frequency doubling, optical parametric oscillation, and electro-optic modulation. Its SHG efficiency is rooted in its non-centrosymmetric crystal structure, which features planar $(\text{B}_3\text{O}_6)^{3-}$ groups as its main building unit, enabling a strong nonlinear optical response.

The success of BBO has inspired the exploration of other structural motifs with symmetry-breaking characteristics, such as cyanurate $(\text{C}_3\text{N}_3\text{O}_3)^{3-}$ and melamine $(\text{C}_3\text{N}_6\text{H}_6)$, whereas the latter has received less attention.^[5] These planar π -conjugated groups, with delocalized π -electron systems show enhanced polarizability and offer significant potential to generate NLO properties.^[6] Most prominent candidates involve calcium cyanurate $(\text{Ca}_3(\text{C}_3\text{N}_3\text{O}_3)_2, \text{CCY})$ ^[7] and strontium cyanurate $(\text{Sr}_3(\text{C}_3\text{N}_3\text{O}_3)_2, \text{SCY})$.^[5a] Such materials could rival or even surpass the performance of traditional NLO crystals, including BBO, by leveraging the enhanced nonlinear optical properties inherent to their π -conjugated systems.

Melamine, in particular, has emerged as a promising organic component in hybrid materials due to its rich π -electron framework, planar structure, and ability to form strong hydrogen bonds.^[8] In its monovalent cationic form, melamine can serve as a templating agent for organic–inorganic systems, stabilizing structures with reduced symmetry.^[9] Despite its potential, the exploration of melamine-based NLO materials has been limited. One challenge lies in melamine’s tendency to crystallize in highly symmetric arrangements, which can negate its ability to contribute to macroscopic polarization.^[10] However, when combined with suitable inorganic units, such as transition metal halides, melamine can achieve the structural asymmetry and electronic configurations necessary for enhanced NLO performance.^[5e,5f]

M. Groß, P. Schmidt, H.-J. Meyer
Section of Solid State and Theoretical Inorganic Chemistry
Institute of Inorganic Chemistry
Eberhard Karls University Tübingen
Auf der Morgenstelle 18, 72076 Tübingen, Germany
E-mail: juergen.meyer@uni-tuebingen.de

C. P. Romao
Department of Materials
Faculty of Nuclear Sciences and Physical Engineering
Czech Technical University in Prague
Trojanova 13, Prague 120 00, Czech Republic

D. Enseling, T. Jüstel
Department of Chemical Engineering
FH Münster University of Applied Sciences
Stegerwaldstraße 39, 48565 Steinfurt, Germany

M. Brytskyi, S. Kroeker
Department of Chemistry
University of Manitoba
Winnipeg R3T 2N2, Canada

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/ejic.202500256>

© 2025 The Author(s). European Journal of Inorganic Chemistry published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Transition metal cations, particularly those with a d^{10} electronic configuration, such as Hg^{2+} , are of particular interest in NLO material design.^[11] The high polarizability of Hg^{2+} not only amplifies the nonlinear response but also induces local structural asymmetry, which is critical for achieving non-centrosymmetric structures. Among d^{10} metals, Hg^{2+} is particularly advantageous due to its heavy atomic mass and large principal quantum number, which further enhance its polarizability.^[12] This unique combination of properties brands Hg^{2+} as an interesting partner for π -conjugated organic ligands such as melamine in hybrid systems.

Recent work by Bai et al. (2023)^[50] exemplifies the potential of melamine- HgCl_2 -based compounds. They synthesized two novel melamine- HgCl_2 -based compounds, $(\text{C}_3\text{N}_6\text{H}_7)(\text{C}_3\text{N}_6\text{H}_6)\text{HgCl}_3$ and $(\text{C}_3\text{N}_6\text{H}_7)_3\text{HgCl}_5$, which exhibit NLO properties. The first compound in particular, crystallizes in an NCS polar space group due to its unique structural features, including large asymmetric secondary building units and a small dihedral angle of 2.98° between melamine molecules. These features are considered to disrupt centrosymmetry and prevent the antiparallel arrangement of molecules, which often leads to inversion symmetry. This structural asymmetry, combined with the high polarizability of the Hg^{2+} cation and the delocalized π -electron system of melamine is reported to result in an SHG efficiency five times greater than that of KH_2PO_4 (KDP), a standard reference material. Additionally, $(\text{C}_3\text{N}_6\text{H}_7)(\text{C}_3\text{N}_6\text{H}_6)\text{HgCl}_3$ exhibits a wide bandgap of 4.40 eV and giant optical anisotropy. These findings underscore the synergistic role of inorganic and organic components in driving exceptional NLO performance.

The success of $(\text{C}_3\text{N}_6\text{H}_7)(\text{C}_3\text{N}_6\text{H}_6)\text{HgCl}_3$ highlights the potential of the melamine- HgCl_2 system for producing high-performance NLO materials. Inspired by this work, we are reporting a closely related compound, $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, to evaluate its structural and optical properties. In this study, we synthesize and characterize the new compounds $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ and $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$. For $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, we investigate its SHG efficiency and electronic structure using a combination of experimental techniques and density functional theory (DFT) calculations. Our results reveal a strong SHG response and a wide bandgap, underscoring the potential of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ as a high-performance NLO material. These findings not only expand the family of melamine-based hybrid materials but also provide deeper insights into the structural and electronic factors that govern the optical performance of this family of materials.

2. Results and Discussion

2.1. Crystal Structure of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ and $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$

$\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ was synthesized via a straightforward hydrothermal reaction between HgCl_2 and melamine. Single-crystal X-ray diffraction structure solution of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ yielded a monoclinic structure with the space group $C2$ and refined lattice parameters of $a = 25.670(2) \text{ \AA}$, $b = 4.0521(3) \text{ \AA}$, $c = 9.0982(8) \text{ \AA}$, and $\beta = 117.75(1)^\circ$ (see Figure 1). The structure consists of stacked HgCl_2 layers alternating with ordered melamine

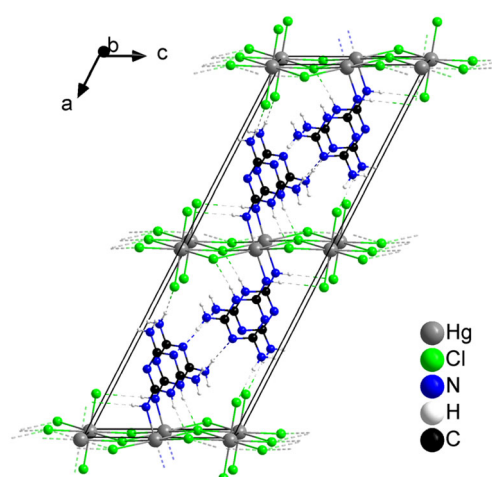


Figure 1. Section of the $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ crystal structure with viewing direction along the b -axis.

molecules along the a -axis, forming a polar architecture that supports SHG activity. Refinement as an inversion twin, with a Flack parameter of ≈ 0.5 , indicates the presence of enantiomorphic domains within the crystal. Despite their well-defined single-crystal morphology, all measured crystals exhibited pseudo-centrosymmetric behavior—a characteristic consistent with enantiomorphic domains reported in the literature.^[13]

The compound was initially modeled in the centrosymmetric space group $2/m$, which includes an inversion center; consequently, a mirror plane perpendicular to the b -axis arises from the symmetry operations. These symmetry elements necessitated disorder of the melamine units over two positions, as both orientations were symmetry-equivalent in the averaged model (Figure 2). However, this model could not account for the observed SHG response, which by nature excludes inversion symmetry.

The crystal structure consists of HgCl_2 layers in which the mercury centers adopt distorted octahedral coordination, alternately capped by chloride ions and melamine molecules. This arrangement gives rise to interleaved layers of HgCl_2 and melamine along the crystallographic a -axis (Figure 1). Each melamine molecule coordinates to a mercury center through its terminal nitrogen atom (N1) (Figure 1 and Figure 3). The layered arrangement is further stabilized by hydrogen bonding both within and between the layers, contributing to the overall structural robustness.

In the crystal structure, the coordination environment around the mercury atoms adopts a distorted octahedral geometry. For both Hg1 and Hg2, the Cl2-Hg-Cl2 bond angles range from $82.04(5)^\circ$ to $98.63(5)^\circ$, where Cl2 denotes the in-plane chloride ions within the HgCl_2 layers (Figure 3). These Cl2 atoms bridge adjacent mercury centers and are associated with relatively long Hg-Cl2 distances of $3.026(5)$ – $3.102(5) \text{ \AA}$. In contrast, the terminal, out-of-plane Cl1 atoms form shorter Hg1-Cl1 bonds of $2.331(2) \text{ \AA}$. Additionally, Hg2 coordinates to the terminal nitrogen atom (N1) of melamine with a bond length of $2.0262(6) \text{ \AA}$. A notable rearrangement of hydrogen atoms is observed, wherein the hydrogen originally bonded to N1 is relocated to N5 within the melamine molecule.

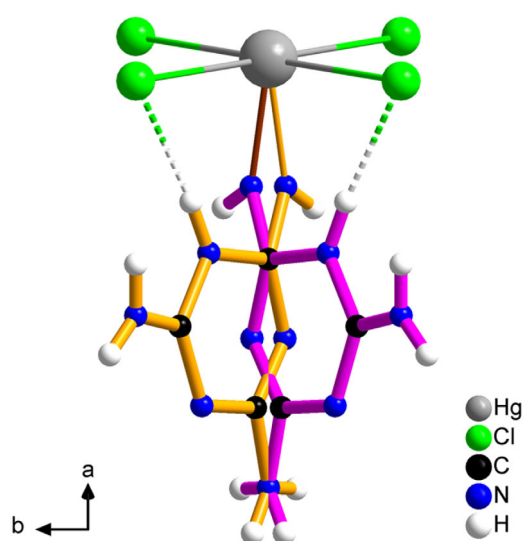


Figure 2. Section of the $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ crystal structure derived in $C2/m$ with disordered melamine molecules. The two possible positions are highlighted by different bond colors (yellow and pink).

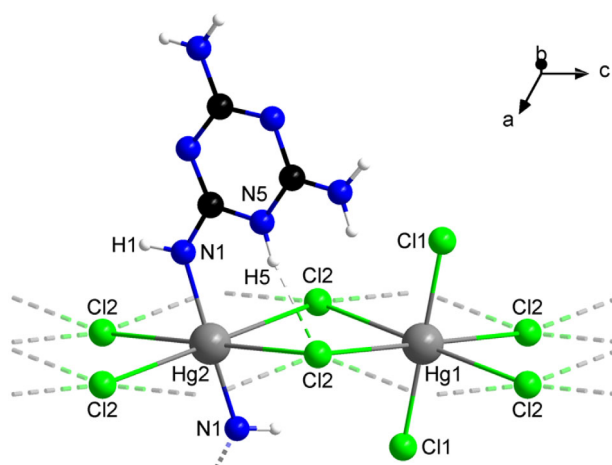


Figure 3. Section of the $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ crystal structure highlighting the HgCl_2 layers and melamine coordination to the mercury atoms.

The morphology of the synthesized $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ crystals is illustrated in the SEM images in **Figure 4**. The block-shaped crystals exhibit high uniformity, with dimensions ranging from ≈ 30 – $50\ \mu\text{m}$ in length and 5 – $10\ \mu\text{m}$ in width. The layered nature of the structure is evident in these images (**Figure 4b**), highlighting the ordered stacking of HgCl_2 and melamine layers. Powder X-ray diffraction (PXRD) analysis confirms the phase purity of the synthesized material, and the corresponding diffraction pattern is provided in the Supporting Information (see **Figure S1**, Supporting Information).

Although $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ is the primary focus of this study due to its notable SHG activity, we also report the structurally related compound $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$. This compound comprises on Hg^+ and was obtained via solid-state synthesis under inert conditions by heating a mixture of Hg_2Cl_2 and melamine to 150°C . The

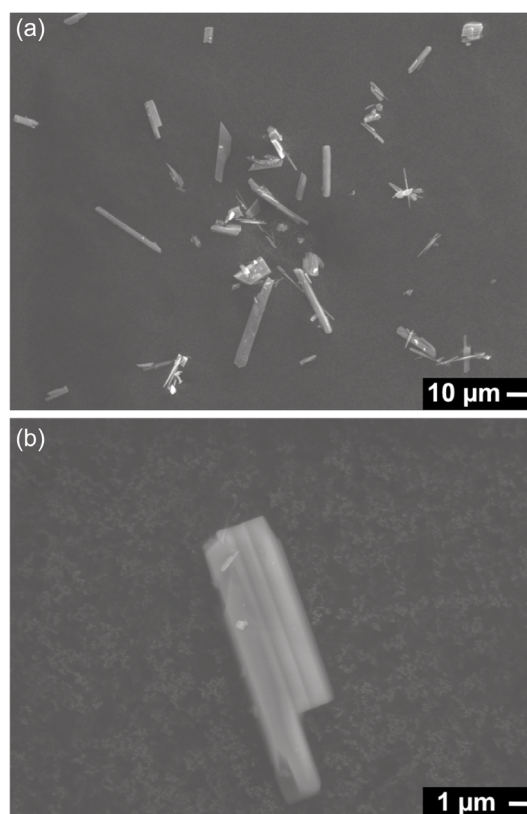


Figure 4. SEM images of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ crystals, showing their uniform, a) morphology and b) layered character.

resulting crystalline material adopts a triclinic structure in space group $P\bar{1}$ (see **Table 1**). The structure features infinite one-dimensional chains extending along the a -axis, composed of Hg–Hg dimers (dumbbells) oriented approximately orthogonal to the chain direction (see **Figure 5**). The mercury atoms within each dimer are connected by a direct Hg–Hg bond of $2.5543(1)\ \text{\AA}$. These dimers are bridged by chloride ions ($\text{Hg}–\text{Cl} = 2.6763(4)\ \text{\AA}$ and $2.8285(3)\ \text{\AA}$) and further coordinated by inner nitrogen atom (N1) of the melamine ring ($\text{Hg}–\text{N1} = 2.273(1)\ \text{\AA}$). In addition, melamine molecules engage in an extended N–H...N hydrogen-bonding network that stabilizes the crystal structure (see **Figure 6**). Currently, the compound is not known to exhibit any remarkable physical or chemical properties, but it serves as a useful structural reference for comparative analysis, particularly in infrared (IR) spectroscopic studies.

2.2. Thermogravimetric Analysis (TGA)

Thermal stability was assessed using thermogravimetric analysis (TGA), which revealed no significant weight loss below 230°C for $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, indicating that the compound is thermally robust under ambient conditions (see **Figure S2**, Supporting Information). Above this threshold, a series of discrete mass-loss steps is observed, suggesting a multistage decomposition process. However, these steps could not be reliably correlated with the release of specific decomposition products or intermediate

Table 1. Crystallographic data from the crystal structure refinement for $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$.		
	$\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$	$\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$
Space group	C2	$P\bar{1}$
$a/\text{\AA}$	25.670(2)	3.6928(1)
$b/\text{\AA}$	4.0521(3)	9.8740(2)
$c/\text{\AA}$	9.0982(8)	10.0690(2)
$\alpha/^\circ$	90	81.943(1)
$\beta/^\circ$	117.75(1)	88.320(2)
$\gamma/^\circ$	90	83.842(2)
$V/\text{\AA}^3$	837.5(1)	361.38(1)
R_1	0.0219	0.0270
wR_2	0.0486	0.0372
Goof^2	1.127	1.0299
Flack	0.49(5)	–
CCDC	2 414 165	2 178 137

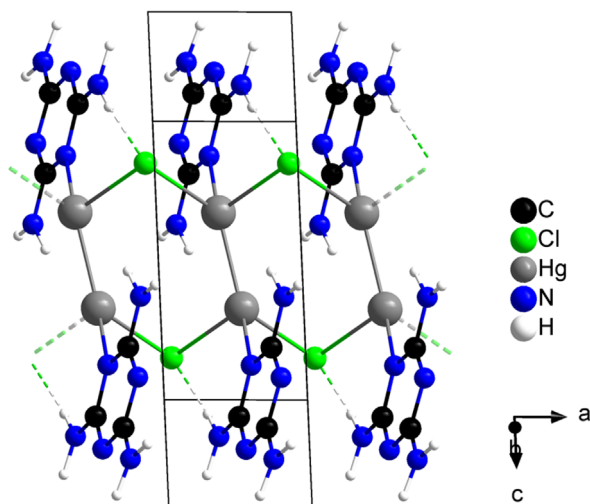


Figure 5. Section of the $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$ crystal structure.

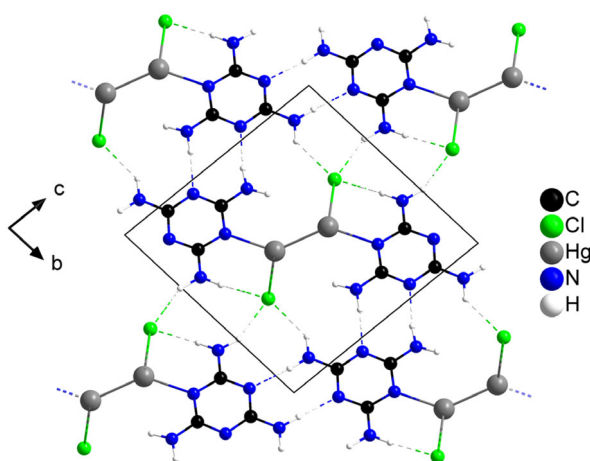


Figure 6. Section of the $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$ crystal structure with viewing direction along the a -axis.

species, likely due to the complexity of the breakdown pathway. The absence of low-temperature mass loss further supports the lack of solvent inclusion or volatile impurities, consistent with the compound's structural stability.

2.3. Solid-State NMR

^1H MAS NMR reveals the presence of three chemically distinct hydrogen environments (Figure 7) in agreement with the proposed crystal structure. The most intense peak centered at 5.5 ppm may be assigned to primary amine protons (H2 and H3). The least shielded peak at 12.2 ppm may be assigned to the melamine proton (H5) which is H-bonded to Cl, as it is most similar to analogous N-bound hydrogens found on heteroatomic rings (12.0–13.4 ppm). The middle peak at 8.8 ppm represents H1, which is bound to the nitrogen (N1) bonded to mercury. While no J-coupling can be measured in this peak, its increased breadth is likely due to unresolved $^2J(^1\text{H}, ^{199}\text{Hg})$.

2.4. Photoluminescence

Spectroscopic analysis upon 332 nm excitation at 100, 150, and 200 K showed whitish emission. This was confirmed by recording the photoluminescence spectrum at low temperatures, which shows a very broad emission band peaking at around 490 nm ($20\,400\text{ cm}^{-1}$), however, the luminescence is completely quenched at about 350°C . This broad emission is already known for other mercury compounds. For other literature-known mercury compounds, the emission typically spans a range of 150–200 nm for each individual compound but can occur anywhere within the broader region of 370–650 nm.^[14] This aligns well with our observations (see Figure 8). An additional peak is observed at 570 nm; the origin of which is currently unclear. Further investigation is warranted to determine its nature. Importantly, this peak does not affect the interpretation of the primary spectral features discussed in this work.

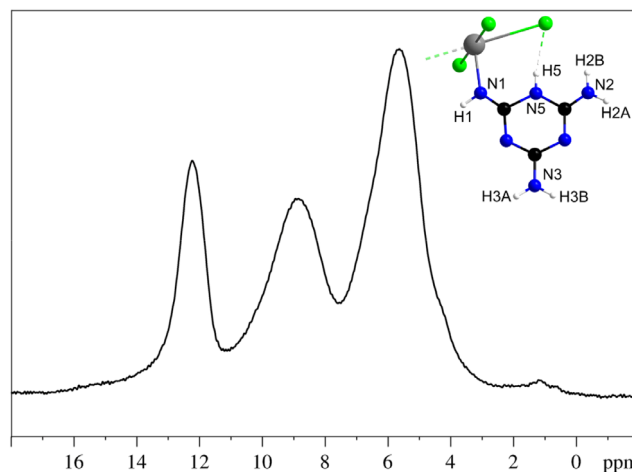


Figure 7. ^1H MAS NMR spectrum of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$.

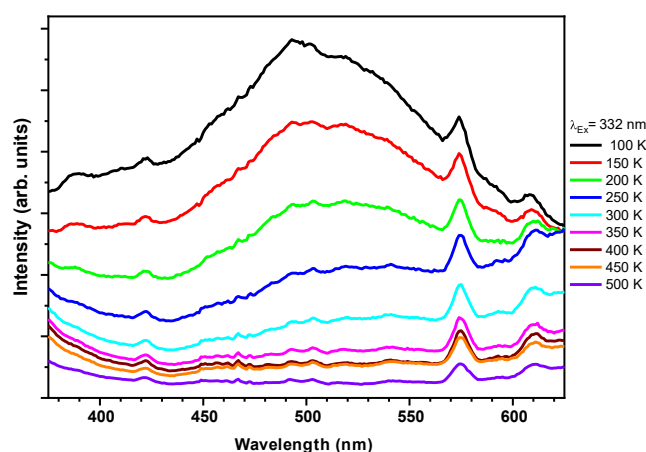


Figure 8. Photoluminescence spectrum of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ from 100 to 500 K upon 332 nm excitation.

2.5. Diffuse Reflectance UV-Vis Spectroscopy (DRUV)

Diffuse reflectance spectroscopy was used to determine the bandgap of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ via a Tauc plot.^[15] This analysis yielded a direct bandgap of 4.49 eV and an indirect bandgap of 4.39 eV (see **Figure 9**). Both bandgaps are thus located within the UV range, which match the observed formation of transparent, block-shaped crystals.

2.6. Diffuse Reflectance IR Fourier Transform Spectroscopy (DRIFT)

In the IR spectrum of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ in **Figure 10**, characteristic deformation vibrations of C–N–C, N–C–N and NH_2 could be observed, as well as valence vibrations of C–N and N–H bonds. The presence of N–H valence vibrations is a strong indicator for the binding of an external nitrogen atom of the melamine ring to the mercury atom in the structure (compare **Table 2**).

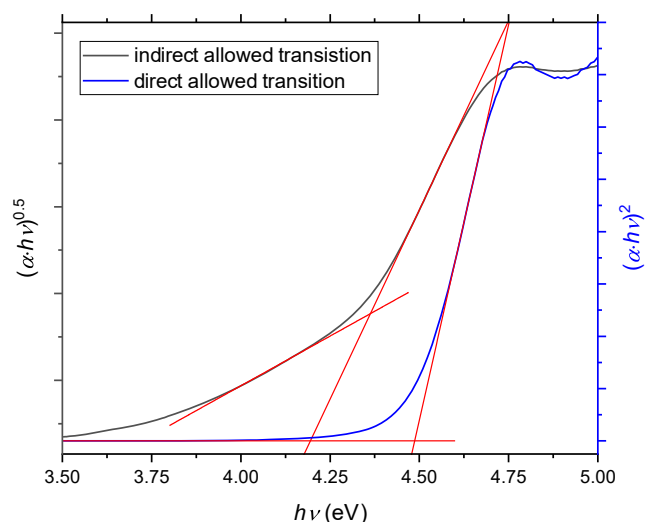


Figure 9. Tauc plot of the diffuse reflectance IR spectroscopy measurement of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$.

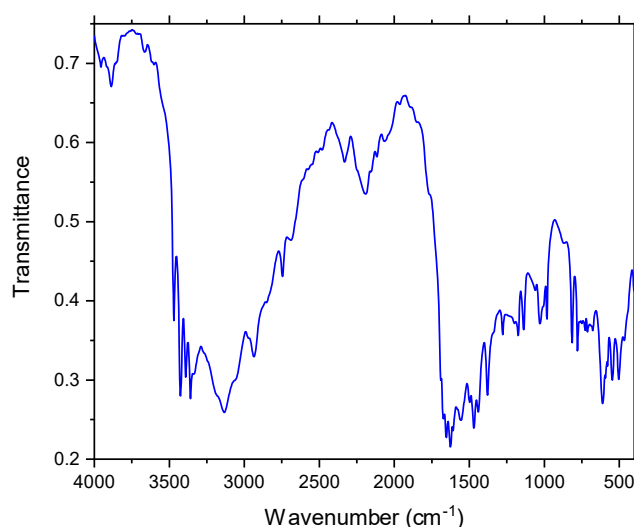


Figure 10. IR spectrum from 4000 to 480 cm^{-1} of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$.

Table 2. Assignment of the wavenumbers to the characteristic deformation and vibration oscillations in $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ and $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)$.

Wavenumber [cm^{-1}]	Assignment
$\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$	
980–1022	$\delta(\text{CNC})$, $\delta(\text{NCN})$
1375–1655	$\nu(\text{CN})$, $\delta(\text{NH}_2)$
3158, 3357, 3427–3470	$\delta(\text{NH}_2)$
3389	$\nu(\text{NH})$
$\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)$	
980–1022	$\delta(\text{CNC})$, $\delta(\text{NCN})$
1438/1539	$\nu(\text{CN})$, $\delta(\text{NH}_2)$
1654/3132/3327/3419/3469	$\delta(\text{NH}_2)$

The measured IR spectrum of $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$ shows notable similarities to that of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ (see **Figure 11**). Additionally, characteristic deformation vibrations of C–N–C, N–C–N, and NH_2 groups, as well as valence vibrations of C–N bonds, are observed. Due to the binding of mercury to the nitrogen atom within the ring, the NH vibration is absent, unlike in the IR spectrum of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$.

3. NLO Measurements

Second-harmonic generation is a second-order nonlinear optical phenomenon in which two photons interact within a material to produce a single photon of twice the energy of the original photons. This process arises from the interaction of light with the nonlinear polarization of the material.^[5a]

The SHG efficiency of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ was measured using a custom-built confocal microscope described in the Experimental Section. The material exhibited an SHG efficiency approximately equal to β -BBO, a standard reference material. This strong

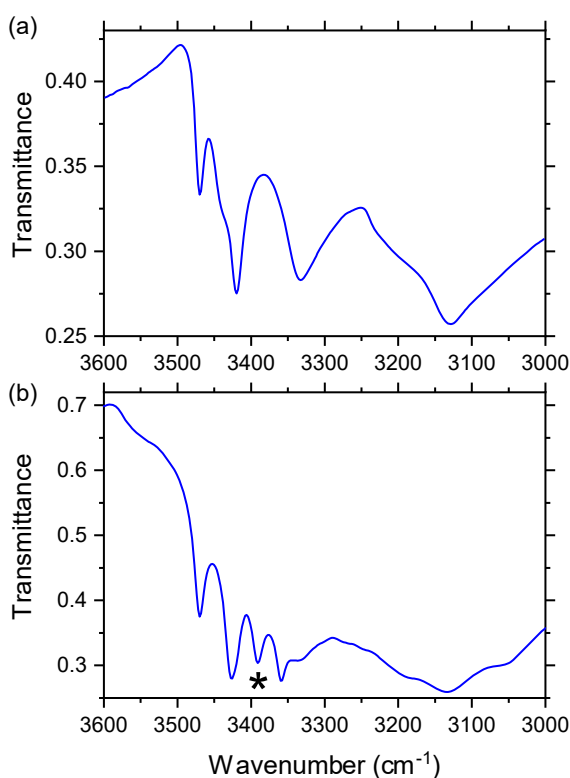


Figure 11. IR spectra from 3600 to 3000 cm^{-1} of a) $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)$ and b) $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ with the additional NH vibration signal marked with an asterisk.

nonlinear response highlights the cooperative role of the highly polarizable Hg^{2+} cations and the π -conjugated melamine framework.

The scan images presented in Figure 12 illustrate the nonlinear signal intensity of single crystals of BBO and $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$. From these images, it can be estimated that the nonlinear signal intensities of the two crystals are of similar magnitude. Regions exhibiting hotspots with enhanced SHG signals were identified and subsequently used for the spectral characterization detailed in Figure 13.

The signal intensity for a second-order nonlinear process, such as SHG is proportional to the square of the excitation power

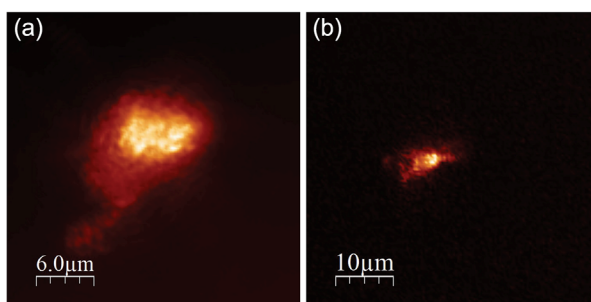


Figure 12. Scan images showing the SHG intensity of a) $\beta\text{-BaB}_2\text{O}_4$ and b) $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$. The images illustrate variations in signal intensity across the crystal surfaces, highlighting localized hotspots associated with enhanced SHG activity.

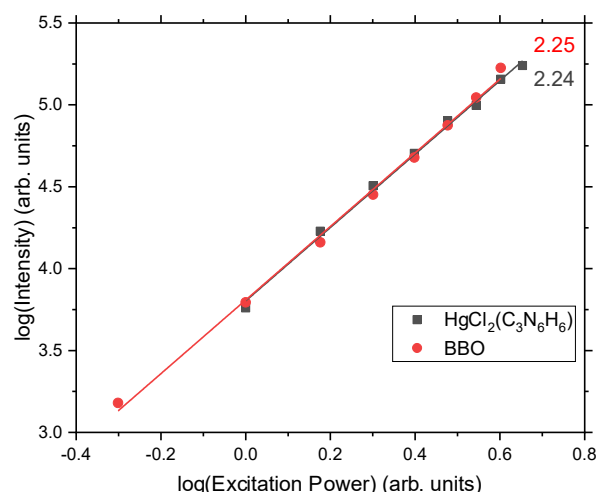


Figure 13. Nonlinear optical spectra of $\beta\text{-BaB}_2\text{O}_4$ (red) and $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ (gray). The excitation power dependence of the SHG signal is presented in a double logarithmic scale. Continuous lines represent the corresponding linear fits, with slopes derived from the fitted data.

(see Figure 13). This relationship is evident in the slopes of the linear fits, which are ≈ 2 . The linearity of the data points confirms that the observed signals arise from a two-photon process. Furthermore, the position of the peaks, appearing at half the wavelength of the excitation source, provides additional confirmation that the signal originates from SHG. As shown in Figure 13, the SHG intensity of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ is comparable in magnitude to that of BBO, highlighting the efficiency of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ as an SHG material.

3.1. Electronic Structure

DFT calculations provide deeper insights into the electronic structure and optical properties of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$. The calculated band structure (Figure S3–S7, Supporting Information) reveals a direct bandgap of 3 eV, rather consistent with the experimental bandgap value of 4.35 eV. The slight discrepancy is attributed to the limitations of the generalized gradient approximation (GGA) in underestimating band gaps. Projections of the electronic wavefunctions onto the atomic spheres in DFT showed that the valence band maximum (VBM) has contributions from N, Cl, and Hg states, while the conduction band minimum (CBM) is primarily composed of Cl and Hg states. These electronic configurations underscore the cooperative contributions of melamine and Hg^{2+} to the material's nonlinear response.

4. Experimental Section

4.1. Synthesis of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$

Crystals and powder were synthesized via a hydrothermal method, employing mild reaction conditions to promote high-quality crystal formation. HgCl_2 (750 mg, 2.76 mmol, Sigma-Aldrich $\geq 99.5\%$) and melamine (348.40 mg, 2.76 mmol,

Sigma-Aldrich 99.9%) were dissolved in 10 mL double distilled and degassed water. The reaction mixture was sealed in a Teflon-lined autoclave and heated slowly with a rate of 0.1 K min^{-1} to 110°C for 12 h and a cooling rate to room temperature of 10 K min^{-1} . The resulting crystals and powder were washed with water and dried on air at 80°C , obtained with 95 % yield.

4.2. Synthesis of $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)$

Crystals and powder were synthesized via solid-state reaction, employing mild reaction conditions. Hg_2Cl_2 (130 mg, 0.275 mmol, Sigma-Aldrich $\geq 99.5\%$) and melamine (69.5 mg, 0.551 mol, Sigma-Aldrich 99.9%) were ground in an agate mortar under inert conditions and sealed in an evacuated quartz glass ampoule and heated with a rate of 2 K min^{-1} to 150°C for 48 h and a cooling rate to room temperature of 2 K min^{-1} . The yield of this product was about 95%.

4.3. Powder X-Ray Diffraction (PXRD)

PXRD patterns of products were collected with a Stadi-P (STOE, Darmstadt) powder diffractometer using germanium monochromated $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) and a Mythen 1 K detector.

4.4. Single-Crystal X-Ray Diffraction (SC-XRD)

SC-XRD studies were performed using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix 6000HE detector using $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 220 K .^[16] The structure was solved with the ShelXT 2018/2 solution program^[17] using dual methods and by using Olex2 1.5 (Dolomanov et al., 2009)^[18] as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015)^[19] using full matrix least squares minimisation on F^2 .

4.5. Solid-State NMR

^1H magic-angle spinning (MAS) NMR was run at 11.7 T on a Bruker Avance III 500 spectrometer. Bloch-decay spectra were collected using a 1.3 mm double-resonance MAS probe at a spinning rate of 55 kHz on 2 mg of sample. Spectra of an empty rotor acquired under identical conditions were used to subtract the ^1H signal of the probe background, compromising the accuracy of the integrated intensities. 64 transients were co-added with a 90° pulse of $1.3 \mu\text{s}$, separated by a recycle delay of 30 s . The chemical shift is reported relative to TMS, as measured by the chemical shift of water at 4.75 ppm as an external reference.

4.6. Thermal Analysis

Differential thermal analysis (DTA) and thermal gravimetry (TG) measurements were performed with a Netzsch Jupiter, STA 449 F3 apparatus between room temperature and 1000°C with a heating and cooling rate of 2 K min^{-1} in a bespoke silica crucible

(height: 2 cm , inner diameter 0.6 cm , thickness of wall: 0.1 cm). The compound ($\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$) is thermally stable up to 230°C (see Figure S1, Supporting Information).

4.7. DRUV (Diffuse Reflectance UV-Vis) Spectroscopy

For recording the spectra a Maya 2000 Pro spectrometer from OceanOptics equipped with a praying mantis sample chamber from Harrick and a DH-2000-BAL (Deuterium-Tungsten-Lamp) as a light source from OceanOptics. As a software OceanView 1.6.7 (lite) from OceanOptics was used with following settings: scans to average = 40, boxcarwidth = 10 and integration time = 30 ms. The bandgap E_g of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ was calculated using following equation $(\alpha \cdot h\nu)^{1/n} = A \cdot (h\nu - E_g)$, where α is the absorption coefficient, h is the Planck constant, A is a material related constant and $h\nu$ is the photon energy. The exponent is for an indirect allowed bandgap transition $n = 2$ and for a direct allowed bandgap transition $n = 0.5$.^[15]

4.8. EDX Measurement

The EDX spectroscopy data was collected using a Hitachi SU8030 scanning electron microscope equipped with a Bruker QUANTAX 6 G EDX detector.

4.9. Electron Microscopy

SEM was carried out on a Hitachi SU8030 scanning electron microscope equipped with a Bruker QUANTAX 6 G EDX detector.

4.10. DRIFT (Diffuse Reflectance IR Fourier Transformation) Spectroscopy

Samples were measured at room temperature under inert conditions in diffuse reflectance with a Harrick Praying Mantis attachment using a Bruker Vertex 70 infrared spectrophotometer with a deuterated triglycine sulfate (DTGS) detector and KBr beamsplitter. The background spectra were collected using pure dried KBr in powder form.

4.11. Second Harmonic Generation Measurements (SHG)

For SHG measurements the samples were distributed on to clean silicon wafers. They were then imaged and spectra were collected with a home-built parabolic mirror confocal microscope. The functionality of the microscope has been confirmed on a range of samples.^[20] For excitation of the samples a pulsed laser (FemtoFiber pro, Toptica Photonics) with an emission wavelength of 779 nm and a repetition frequency of 80 MHz was used. A clean linear polarization was ensured, by placing a Glan-Taylor polarizer in the beam path. Focusing of the laser beam as well as signal collection was done by a parabolic mirror ($\text{NA} = 0.9986$ in air). To suppress both the laser line signal and the two-photon photoluminescence signal both a short pass filter and a bandpass filter with a filter wavelength of 750 nm and 390 nm (380 nm to

400 nm bandwidth) respectively were employed. The collection of SHG spectra was performed on an Acton SP2500 spectrometer with a 150 grooves/mm grating (Princeton Instruments) coupled to a Pixis 100 charge-coupled device (Princeton Instruments). For imaging the samples was scanned through the laser focus using a high-precision nano-positioning stage (Physik Instrumente/nPoint), while the intensity per pixel was recorded by an avalanche photodiode (Count, Laser Components).

4.12. DFT Calculations

Calculations were performed using the ABINIT software package^[21] with the projector augmented-wave (PAW) method and a plane-wave basis set. The Perdew–Burke–Ernzerhof exchange–correlation functional^[22] was used with the vdW-DFT-D3 dispersion correction^[23] PAW data files were used as received from the ABINIT library. Convergence studies and structural relaxation were performed prior to calculation of the electronic structure. A 120 Ha plane wave basis set energy cutoff was used inside the PAW spheres and a 24 Ha cutoff outside. A Monkhorst–Pack grid^[24] with basis vectors (−5 5 4), (4 4 12), and (−1 9 8) was used to sample reciprocal space.

5. Conclusions

This study presents the successful synthesis and detailed characterization of the melamine-based hybrid compound $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, which adopts a non-centrosymmetric layered structure essential for second-order NLO activity. The distorted octahedral coordination of Hg^{2+} , combined with the π -conjugated nature of melamine, facilitates macroscopic polarization and results in a strong SHG response comparable to that of benchmark materials such as β -BBO. Supporting spectroscopic and computational analyses confirm the wide bandgap, high optical anisotropy, and thermal robustness of the material. These findings establish $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ as a promising NLO material and underline the potential of melamine-based hybrid halides in the design of next-generation optoelectronic materials.

Supporting Information

Deposition Numbers 2414165 (for $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$), 2178137 (for $\text{Hg}_2\text{Cl}_2(\text{C}_3\text{N}_6\text{H}_6)_2$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

Support of this research by the Deutsche Forschungsgemeinschaft (Bonn) through the project ME 914/34-1 and by the State of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no INST 40/467-1

FUGG, ME914/34-1 (JUSTUS cluster) is gratefully acknowledged. S. K. is grateful to NSERC and the Canada Foundation for Innovation for research support. C.P.R. acknowledges support from the project FerrMion of the Ministry of Education, Youth and Sports, Czech Republic, co-funded by the European Union (CZ.02.01.01/00/22/_008/0004591). The authors thank Tim Parker for carrying out the SHG measurements and Peter Janoschek for performing the DRUV measurements.

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: crystal structure · electronic structure · luminescence · second harmonic generation · synthesis

- [1] a) K. Schmitt, R. P. Herr, M. Schadt, J. Fünfschilling, R. Buchecker, X. H. Chen, C. Benecke, *Liq. Cryst.* **1993**, *14*, 1735; b) A. P. Jeyakumari, S. Dhanuskodi, S. Manivannan, *Spectrochim. Acta, Part A* **2006**, *63*, 91; c) C.-Y. Pan, X.-R. Yang, L. Xiong, Z.-W. Lu, B.-Y. Zhen, X. Sui, X.-B. Deng, L. Chen, L.-M. Wu, *J. Am. Chem. Soc.* **2020**, *142*, 6423; d) P. G. Lacroix, I. Malfant, C. Lepetit, *Coord. Chem. Rev.* **2016**, *308*, 381; e) S. Aithal, P. S. Aithal, A. P. Bhat, *Poornaprajna Int. J. Basic Appl. Sci.* **2024**, *1*, 1.
- [2] P. A. Franken, A. E. Hill, C. W. Peters, G. Weinreich, *Phys. Rev. Lett.* **1961**, *7*, 118.
- [3] a) S. R. Marder, J. W. Perry, W. P. Schaefer, *Science* **1989**, *245*, 626; b) X. Liu, Z. Yang, D. Wang, H. Cao, *Crystals* **2016**, *6*.
- [4] a) F. Yang, L. Wang, L. Huang, G. Zou, *Coord. Chem. Rev.* **2020**, *423*, 213491; b) M. P. Warusawithana, C. S. Kengle, X. Zhan, H. Chen, E. V. Colla, M. O'Keeffe, J.-M. Zuo, M. B. Weissman, J. N. Eckstein, *Phys. Rev. B* **2021**, *104*, 085103.
- [5] a) M. Kalmutzki, M. Ströbele, F. Wackenhut, A. J. Meixner, H.-J. Meyer, *Inorg. Chem.* **2014**, *53*, 12540; b) X. Meng, H. Tian, Q. Wu, M. Xia, *J. Cryst. Growth* **2024**, *648*, 127930; c) X. Meng, W. Yin, M. Xia, *Coord. Chem. Rev.* **2021**, *439*, 213916; d) J. Lu, Y.-K. Lian, L. Xiong, Q.-R. Wu, M. Zhao, K.-X. Shi, L. Chen, L.-M. Wu, *J. Am. Chem. Soc.* **2019**, *141*, 16151; e) L. Liu, Z. Bai, L. Hu, D. Wei, Z. Lin, L. Zhang, *J. Mater. Chem. C* **2021**, *9*, 7452; f) Z. Bai, J. Lee, H. Kim, C.-L. Hu, K. M. Ok, *Small* **2023**, *19*, 2301756; g) B. Guo, Y. Gao, F. Guo, P. Yin, H. Xu, Z. Gu, *Optoelectron. Adv. Mater., Rapid Commun.* **2009**, *3*, 1217; h) L. Liu, C.-L. Hu, Z. Bai, F. Yuan, Y. Huang, L. Zhang, Z. Lin, *Chem. Commun.* **2020**, *56*, 14657.
- [6] a) C. Dirk, R. Twieg, G. Wagniere, *J. Am. Chem. Soc.* **1986**, *108*, 5387; b) J. Chen, C.-L. Hu, F. Kong, J.-G. Mao, *Acc. Chem. Res.* **2021**, *54*, 2775.
- [7] M. Kalmutzki, M. Ströbele, F. Wackenhut, A. J. Meixner, H.-J. Meyer, *Angew. Chem. Int. Ed.* **2014**, *53*, 14260.
- [8] L. Vella-Zarb, D. Braga, A. G. Orpen, U. Baisch, *CrystEngComm* **2014**, *16*, 8147.
- [9] S.-F. Li, L. Hu, Y. Ma, F.-F. Mao, J. Zheng, X.-D. Zhang, D. Yan, *Inorg. Chem.* **2022**, *61*, 10182.
- [10] a) E. Bayat, M. Ströbele, M. Abbasi, S. Kroeker, J. Valenta, D. Ensling, T. Jüstel, H.-J. r. Meyer, *Inorg. Chem.* **2024**, *63*, 19053; b) E. Bayat, M. Ströbele, D. Ensling, T. Jüstel, H.-J. Meyer, *Molecules* **2024**, *29*, 5598; c) A. B. Wiles, D. Bozzuto, C. L. Cahill, R. D. Pike, *Polyhedron* **2006**, *25*, 776.
- [11] X. Dong, L. Huang, H. Zeng, Z. Lin, K. M. Ok, G. Zou, *Angew. Chem. Int. Ed.* **2022**, *61*, e202116790.
- [12] A. Cammarata, W. Zhang, P. S. Halasyamani, J. M. Rondinelli, *Chem. Mater.* **2014**, *26*, 5773.

- [13] a) S. Parsons, *Acta Crystallogr. Sect. D. Biol. Crystallogr.* **2003**, *59*, 1995; b) H. D. Flack, *Helv. Chim. Acta* **2003**, *86*, 905.
- [14] a) W.-T. Chen, *Bull. Chem. Soc. Ethiop.* **2011**, *25*, 233; b) R. Fan, Y. Yang, Y. Yin, W. Hasi, Y. Mu, *Inorg. Chem.* **2009**, *48*, 6034; c) D. M. Ciurtin, N. G. Pschirer, M. D. Smith, U. H. F. Bunz, H.-C. Zur Loye, *Chem. Mater.* **2001**, *13*, 2743; d) J. Li, B. Ding, E.-C. Yang, X.-G. Wang, X.-J. Zhao, *Z. Anorg. Allg. Chem.* **2007**, *633*, 346; e) W. T. Chen, S. M. Ying, D. S. Liu, J. H. Liu, H. M. Kuang, *J. Iran. Chem. Soc.* **2010**, *7*, 510.
- [15] a) J. Tauc, *Mater. Res. Bull.* **1968**, *3*, 37; b) J. Tauc, *Amorphous and Liquid Semiconductors*, Springer, New York **1974**; c) N. F. Mott, E. A. Davis, *Electronic processes in non-crystalline materials*, Oxford University Press **2012**; d) A. R. Zanatta, *Sci. Rep.* **2019**, *9*, 11225; e) Ł. Haryński, A. Olejnik, K. Grochowska, K. Siuzdak, *Opt. Mater.* **2022**, *127*, 112205; f) J. Klein, L. Kampermann, B. Mockenhaupt, M. Behrens, J. Strunk, G. Bacher, *Adv. Funct. Mater.* **2023**, *33*, 2304523; g) P. Y. Yu, M. Cardona, *Fundamentals of semiconductors. Physics and materials properties*, Springer, Berlin, Germany **2010**; h) G. Kortüm, H. Koffer, *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 67; i) G. Kortüm, J. E. Lohr, *Reflectance Spectroscopy*, Springer My Copy UK **1969**; j) M. P. Fuller, P. R. Griffiths, *Anal. Chem.* **1978**, *50*, 1906; k) A. B. Murphy, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1326; l) R. López, R. Gómez, *J. Sol-Gel Sci. Technol.* **2012**, *61*, 1; m) Z. M. Gibbs, A. LaLonde, G. J. Snyder, *New J. Phys.* **2013**, *15*, 075020; n) P. Makula, M. Pacia, W. Macyk, *J. Phys. Chem. Lett.* **2018**, *9*, 6814; o) G. D. Gesesse, A. Gomis-Berenguer, M.-F. Barthe, C. O. Ania, *J. Photochem. Photobiol., A* **2020**, *398*, 112622.
- [16] CrysAlisPro Software System, Rigaku Oxford Diffraction **2024**.
- [17] G. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.* **2015**, *71*, 3.
- [18] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
- [19] G. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3.
- [20] a) J. Fu, N. Yang, Y. Liu, Q. Liu, J. Du, Y. Fang, J. Wang, B. Gao, C. Xu, D. Zhang, A. J. Meixner, G. Gou, F. Huang, L. Zhen, Y. Li, *Adv. Funct. Mater.* **2024**, *34*, 2308207; b) E. Gürdal, A. Horneber, A. J. Meixner, D. P. Kern, D. Zhang, M. Fleischer, *Nanoscale* **2020**, *12*, 23105; c) L. Pan, P. Miao, A. Horneber, A. J. Meixner, P.-M. Adam, D. Zhang, *Beilstein J. Nanotechnol.* **2022**, *13*, 572; d) L. Pan, P. Miao, A. Horneber, A. J. Meixner, P.-M. Adam, D. Zhang, *ACS Appl. Nano Mater.* **2023**, *6*, 6467; e) J. P. Wang, Y. Q. Fang, W. He, Q. Liu, J. R. Fu, X. Y. Li, Y. Liu, B. Gao, L. Zhen, C. Y. Xu, *Adv. Opt. Mater.* **2023**, *11*, 2300031; f) J. Wang, J. Butet, G. D. Bernasconi, A.-L. Baudrion, G. Lévêque, A. Horrer, A. Horneber, O. J. Martin, A. J. Meixner, M. Fleischer, *Nanoscale* **2019**, *11*, 23475; g) R. Wang, Q. Liu, S. Dai, C. M. Liu, Y. Liu, Z. Y. Sun, H. Li, C. J. Zhang, H. Wang, C. Y. Xu, *Small* **2024**, *20*, 2305658.
- [21] X. Gonze, B. Amadon, G. Antonius, F. Arnardi, L. Baguet, J.-M. Beuken, J. Bieder, F. Bottin, J. Bouchet, E. Bousquet, N. Brouwer, F. Bruneval, G. Brunin, T. Cavignac, J.-B. Charraud, W. Chen, M. Côté, S. Cottenier, J. Denier, G. Geneste, P. Ghosez, M. Giantomassi, Y. Gillet, O. Gingras, D. R. Hamann, G. Hautier, X. He, N. Helbig, N. Holzwarth, Y. Jia, F. Jollet, W. Lafargue-Dit-Hauret, K. Lejaeghere, M. A. L. Marques, A. Martin, C. Martins, H. P. C. Miranda, F. Naccarato, K. Persson, G. Petretto, V. Planes, Y. Pouillon, S. Prokhorenko, F. Ricci, G.-M. Rignanese, A. H. Romero, M. M. Schmitt, M. Torrent, M. J. van Setten, B. Van Troeye, M. J. Verstraete, G. Zerah, J. W. Zwanziger, *Comput. Phys. Commun.* **2020**, *248*, 107042.
- [22] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396.
- [23] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Phys. Chem.* **2010**, *132*, 154104.
- [24] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188.

Manuscript received: May 14, 2025
Revised manuscript received: July 1, 2025
Version of record online: July 2, 2025

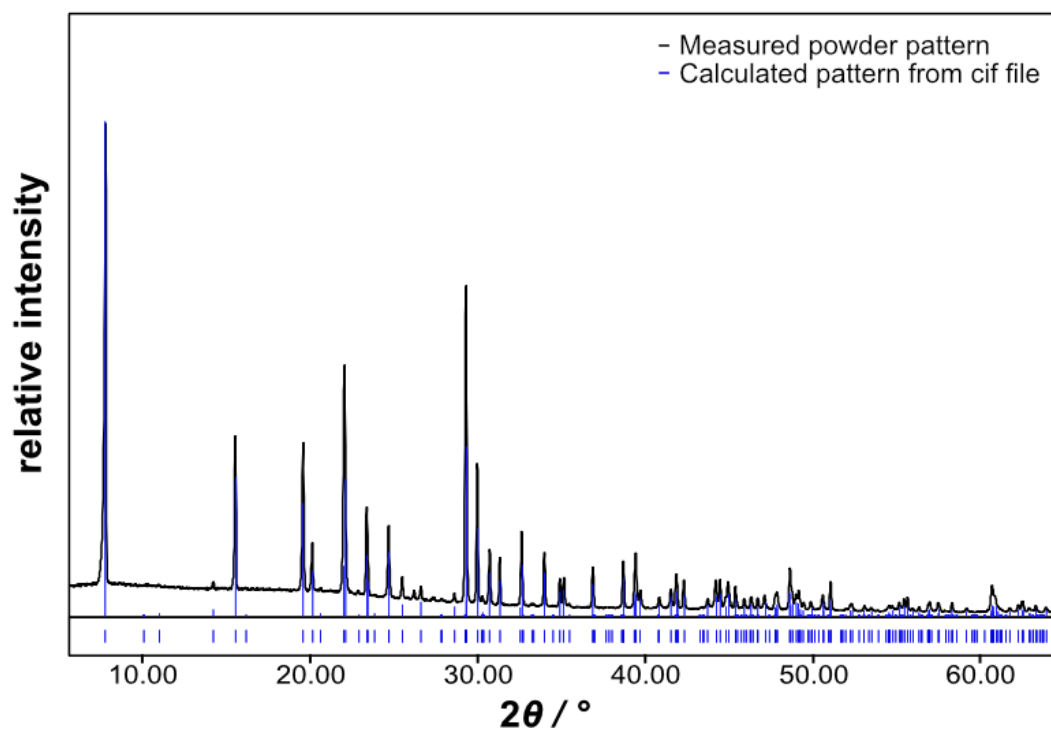


Figure S1. PXRD pattern of the measured powder with the marked Bragg positions generated from the cif file of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$ (blue).

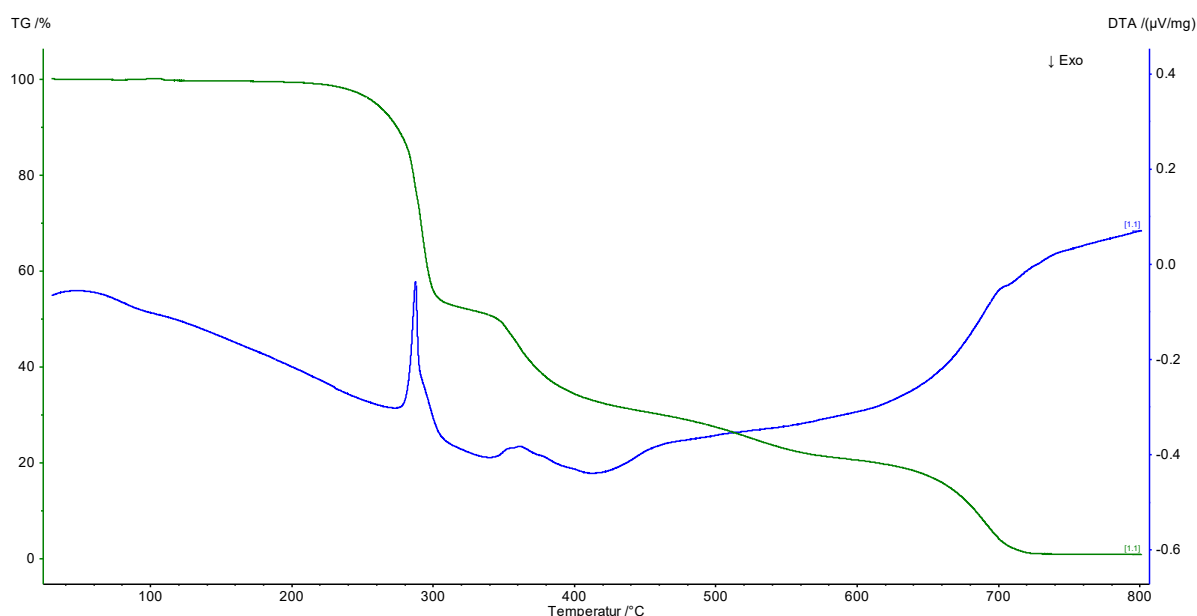


Figure S2. Thermogravimetric (TGA) and differential thermal analysis (DTA) curves of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$. No significant mass loss is observed below 230 °C, indicating high thermal stability. Above this temperature, a multi-step decomposition occurs, though the individual mass-loss steps could not be conclusively assigned to specific decomposition products.

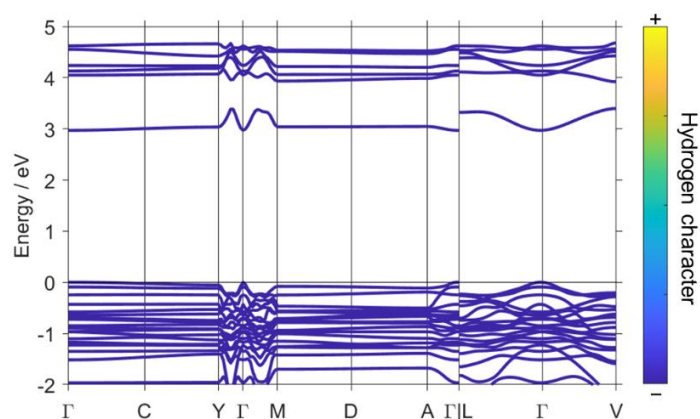


Figure S3. The electronic band structure of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, as calculated using DFT. Bands are coloured according to their hydrogen character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $C = (0.256\ 0.256\ 0)$, $Y = (-0.5\ 0.5\ 0)$, $M = (-0.5\ 0.5\ 0.5)$, $D = (-0.253\ 0.747\ 0.5)$, $A = (0\ 0\ 0.5)$, $L = (0\ 0.5\ 0.5)$, $V = (0.5\ 0\ 0)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

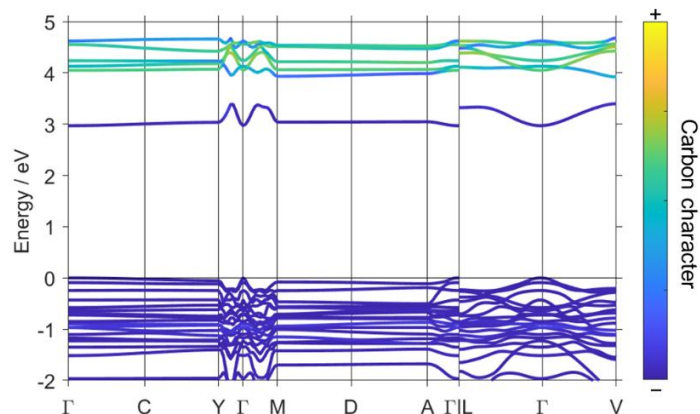


Figure S4. The electronic band structure of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, as calculated using DFT. Bands are coloured according to their carbon character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $C = (0.256\ 0.256\ 0)$, $Y = (-0.5\ 0.5\ 0)$, $M = (-0.5\ 0.5\ 0.5)$, $D = (-0.253\ 0.747\ 0.5)$, $A = (0\ 0\ 0.5)$, $L = (0\ 0.5\ 0.5)$, $V = (0.5\ 0\ 0)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

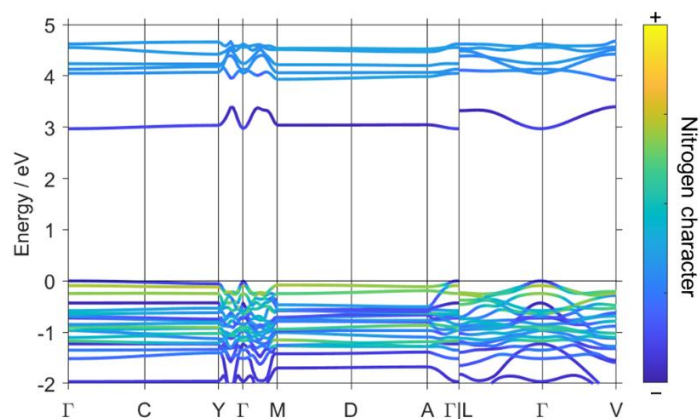


Figure S5. The electronic band structure of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, as calculated using DFT. Bands are coloured according to their nitrogen character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $C = (0.256\ 0.256\ 0)$, $Y = (-0.5\ 0.5\ 0)$, $M = (-0.5\ 0.5\ 0.5)$, $D = (-0.253\ 0.747\ 0.5)$, $A = (0\ 0\ 0.5)$, $L = (0\ 0.5\ 0.5)$, $V = (0.5\ 0\ 0)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

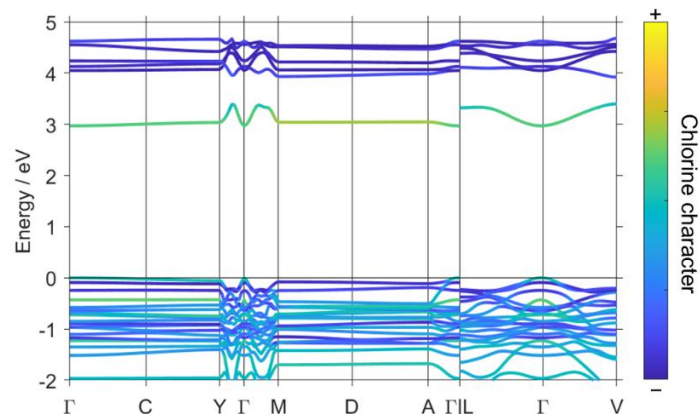


Figure S6. The electronic band structure of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, as calculated using DFT. Bands are coloured according to their chlorine character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $C = (0.256\ 0.256\ 0)$, $Y = (-0.5\ 0.5\ 0)$, $M = (-0.5\ 0.5\ 0.5)$, $D = (-0.253\ 0.747\ 0.5)$, $A = (0\ 0\ 0.5)$, $L = (0\ 0.5\ 0.5)$, $V = (0.5\ 0\ 0)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

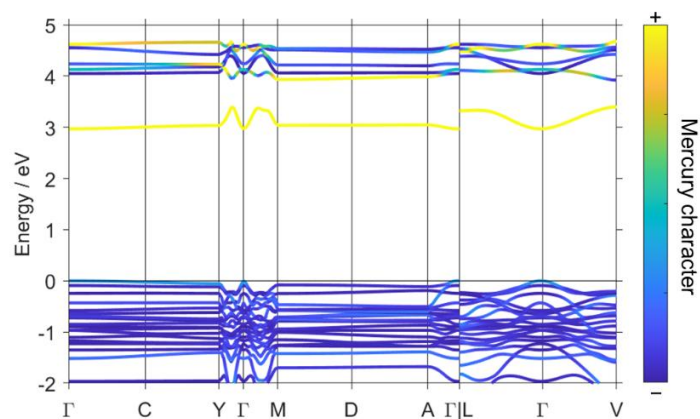
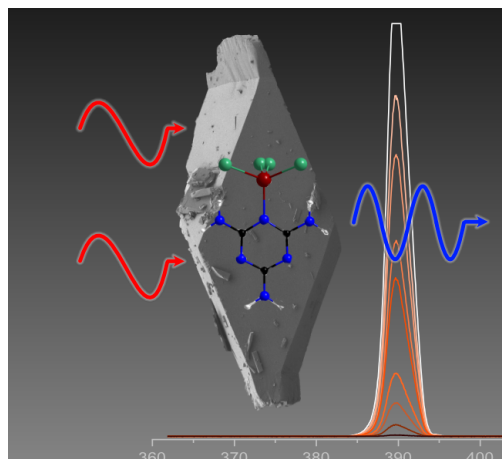


Figure S7. The electronic band structure of $\text{HgCl}_2(\text{C}_3\text{N}_6\text{H}_6)$, as calculated using DFT. Bands are coloured according to their mercury character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $C = (0.256\ 0.256\ 0)$, $Y = (-0.5\ 0.5\ 0)$, $M = (-0.5\ 0.5\ 0.5)$, $D = (-0.253\ 0.747\ 0.5)$, $A = (0\ 0\ 0.5)$, $L = (0\ 0.5\ 0.5)$, $V = (0.5\ 0\ 0)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

Publication 10

Synthesis and SHG properties of the melamine-based material
 $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnX}_3(\text{C}_3\text{N}_6\text{H}_6)$ ($X = \text{Cl}, \text{Br}$)



<https://doi.org/10.1039/d5dt02245b>

Reprinted with permission from

Dalton Trans. **2025**, *54*, 17941-17949.

Copyright © 2025 The Royal Society of Chemistry



Cite this: *Dalton Trans.*, 2025, **54**, 17941

Synthesis and SHG properties of the melamine-based material $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnX}_3(\text{C}_3\text{N}_6\text{H}_6)$ ($\text{X} = \text{Cl}, \text{Br}$)

Melena Groß,^a Catharina Darine Brand,^a Patrick Schmidt,^a Tim Parker,^b Dai Zhang,^b Carl P. Romao^c and Hans-Jürgen Meyer^{*,a}

The zinc halide–melamine system was investigated by conducting exploratory solid-state reactions and hydrothermal syntheses, yielding $\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{C}_3\text{N}_6\text{H}_6)_3$ and $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnX}_3(\text{C}_3\text{N}_6\text{H}_6)$ with $\text{X} = \text{Cl}$ and Br . All compounds were characterized by single-crystal X-ray diffraction, revealing that there are two modifications of the melaminium–zinc–chloride–melamine compound, crystallizing with non-centrosymmetric space groups ($Pna2_1$ and $P2_1$). The presence of delocalized π -electron systems in compounds containing cyclic $(\text{B}_3\text{O}_6)^{3-}$, $(\text{C}_3\text{N}_3\text{O}_3)^{3-}$, or melamine derivatives is known to give rise to significant second harmonic generation (SHG) properties, provided that the given structure has no inversion center. All crystal structures feature Zn^{2+} in a tetrahedral coordination environment, forming layered structures. Spectroscopic measurements on phase-pure orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnBr}_3(\text{C}_3\text{N}_6\text{H}_6)$ resulted in direct and indirect band gaps of 4.74 eV and 4.46 eV respectively. Measurements of the nonlinear optical response performed on single crystals of three different compounds revealed significant intensities following the sequence monoclinic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnCl}_3(\text{C}_3\text{N}_6\text{H}_6) >$ orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnBr}_3(\text{C}_3\text{N}_6\text{H}_6) >$ orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnCl}_3(\text{C}_3\text{N}_6\text{H}_6)$. Their SHG properties are compared with those of KTP, one of the most widely used SHG materials.

Received 19th September 2025,
Accepted 31st October 2025

DOI: 10.1039/d5dt02245b

rsc.li/dalton

Introduction

Nonlinear optical (NLO) materials have garnered significant interest due to their important roles in optoelectronic applications, including frequency conversion, optical data storage, and photonics.¹ A cornerstone of second-order nonlinear optical phenomena, such as second-harmonic generation (SHG), is the requirement for non-centrosymmetric structures, which enable the macroscopic polarization needed for these processes.² Cyanurate-based systems, built upon the $(\text{C}_3\text{N}_3\text{O}_3)^{3-}$ ion, have emerged as promising building blocks for NLO materials.³ These planar, π -conjugated units, isoelectronic with $(\text{B}_3\text{O}_6)^{3-}$ in $\beta\text{-BaB}_2\text{O}_4$ (BBO), display high polarizability and have demonstrated good SHG efficiencies in alkaline earth and rare-earth compounds.³ Previous works, such as the syntheses of $\text{Sr}_3(\text{C}_3\text{N}_3\text{O}_3)_2$ and $\text{Ca}_3(\text{C}_3\text{N}_3\text{O}_3)_2$, have shown that such frameworks can adopt non-centrosymmetric arrange-

ments and exhibit significant optical responses, making them strong candidates for practical applications.⁴ However, further extending these concepts to organic–inorganic systems has proven challenging. Melamine ($\text{C}_3\text{N}_6\text{H}_6$) shares structural similarities with cyanurate and offers great potential for NLO applications.⁵ Its delocalized electron system and rich chemical versatility enable it to form complex frameworks with enhanced polarizability.⁶ Unfortunately, melamine's inherent tendency to crystallize in centrosymmetric configurations often suppresses its utility for SHG applications.⁷ To circumvent this limitation, strategies such as incorporating melamine into inorganic structures and leveraging secondary building units have been explored.⁸ Recent studies on melamine-based metal halides, for example, have highlighted the potential for achieving non-centrosymmetric structures by combining heavy metal cations, such as Hg^{2+} , with melamine.^{8a} While mercury may initially seem like a promising candidate due to its high polarizability and ability to induce structural asymmetry, its toxicity significantly limits its practical applications. This highlights the importance of exploring less hazardous metals to develop environmentally safer NLO materials for broader applications.

Zinc is a particularly promising candidate for SHG-active materials due to several key properties. Zinc ions (Zn^{2+}), belonging to the d^{10} electronic configuration family, exhibit high polarizability, which is a crucial factor in enhancing SHG

^aSection of Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany. E-mail: juergen.meyer@uni-tuebingen.de

^bInstitute of Physical and Theoretical Chemistry, Eberhard Karls University Tübingen, Auf der Morgenstelle 15, 72076 Tübingen, Germany

^cDepartment of Materials, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Trojanova 13, Prague 120 00, Czech Republic



efficiency.⁹ Additionally, Zn^{2+} ions readily form diverse coordination geometries, enabling structural flexibility that facilitates the adoption of non-centrosymmetric arrangements in crystal lattices.¹⁰ Compounds incorporating Zn^{2+} , such as ZnO and its derivatives, have already demonstrated strong nonlinear responses and broad transparency ranges in the ultraviolet (UV) to visible spectrum.¹¹ Furthermore, zinc-based materials often show robust stability and processability, making them practical candidates for SHG applications.¹²

We conducted an exploratory study combining Zn^{2+} and melamine using solid-state and hydrothermal routes. This yielded a series of zinc-melamine compounds, some of which exhibit significant second-harmonic generation (SHG). These findings highlight melamine (Mel) as an effective ligand platform for the development of high-performance second-order nonlinear optical (NLO) materials.

Results and discussion

Syntheses

The hydrothermal reaction of ZnCl_2 and melamine in a Teflon-lined autoclave at 110 °C yielded two compounds: $\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{Mel})_3$, which contains melamine (Mel) as a ligand, and $(\text{MelH})\text{ZnCl}_3(\text{Mel})$, which contains melamine as a ligand and melaminium (MelH) as a counter cation. A corresponding reaction with ZnBr_2 yielded $(\text{MelH})\text{ZnBr}_3(\text{Mel})$ only.

The crystal structures of $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ and $(\text{MelH})\text{ZnBr}_3(\text{Mel})$ were refined isotypically to crystallize in the non-centrosymmetric orthorhombic space group $Pna2_1$. The lattice

parameters of the bromide containing compound are only slightly expanded compared to the chloride compound, due to the larger ionic radius of bromide (Table 1). The composition of the bromide compound was confirmed by combustion analysis ($\text{H} = 2.35\% \pm 0.157\%$) and EDX ($\text{Zn} : \text{Br} = 1 : 3.0(1)$).

A similar mercury compound $(\text{C}_3\text{N}_6\text{H}_7)(\text{C}_3\text{N}_6\text{H}_6)\text{HgCl}_3$ has been already reported with the space group $Pna2_1$ and highlighted for its SHG properties.^{8a} And finally a zinc compound $(\text{H}_7\text{C}_3\text{N}_6)(\text{H}_6\text{C}_3\text{N}_6)\text{ZnCl}_3$ obtained *via* hydrothermal synthesis has been reported to crystallize in the monoclinic space group $P2_1$.^{8b} This compound did not form under the hydrothermal conditions that were previously used, but it was synthesized by solid-state reactions of ZnCl_2 , melaminium hydrochloride, and melamine in a 1 : 1 : 1 molar ratio at 120 °C. The crystal structures and SHG properties of the compounds are reported as follows.

Structure of $\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{Mel})_3$

Single-crystal X-ray diffraction studies revealed that $\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{Mel})_3$ crystallizes in the triclinic space group $P\bar{1}$. The crystal structure is composed of three distinct zinc atoms interconnected by hydroxide groups. Each zinc atom adopts a distorted tetrahedral coordination geometry, featuring a mixed ligand environment comprising chloride, hydroxide, and melamine ligands (see Fig. 1). Zn1 and Zn3 are coordinated by two chloride ions, one hydroxide group, and one melamine ligand, bonded through an inner nitrogen atom. Zn2 is coordinated by two hydroxide groups and two melamine ligands, with each also bonded *via* inner nitrogen atoms (see Fig. 1).

Table 1 Summary of single-crystal data for $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ ($P2_1$ and $Pna2_1$), $(\text{MelH})\text{ZnBr}_3(\text{Mel})$ ($Pna2_1$), and $\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{Mel})_3$ from structure refinements

	Compound			
	$(\text{MelH})\text{ZnCl}_3(\text{Mel})$	$(\text{MelH})\text{ZnBr}_3(\text{Mel})$	$\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{Mel})_3$	
CCDC	2478821	2407677	2438541	2407380
Formula	$\text{C}_6\text{H}_{13}\text{N}_{12}\text{Cl}_3\text{Zn}$		$\text{C}_6\text{H}_{13}\text{N}_{12}\text{ZnBr}_3$	$\text{C}_{12}\text{H}_{26}\text{Cl}_4\text{N}_{24}\text{O}_2\text{Zn}_3$
Formula weight/g mol ⁻¹	425.004	425.00	558.38	876.498
Density/g cm ⁻³	1.911	1.914	2.374	2.013
Z	2	4	4	2
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_1$	$Pna2_1$	$Pna2_1$	$P\bar{1}$
<i>a</i> /Å	9.3366(2)	12.1055(4)	12.1482(2)	10.5358(1)
<i>b</i> /Å	6.6582(2)	18.3525(5)	18.8376(3)	10.5807(1)
<i>c</i> /Å	12.1344(3)	6.6402(2)	6.8263(1)	13.8676(2)
α /°	90	90	90	72.481(1)
β /°	101.703(2)	90	90	79.260(1)
γ /°	90	90	90	89.968(1)
<i>V</i> /Å ³	738.65(3)	1475.238(8)	1562.15(4)	1445.83(3)
<i>T</i> /K	150.0(1)	150.0(2)	150.0(1)	150.0(2)
Radiation type	Cu-K α	Cu-K α	Cu-K α	Cu-K α
Reflections measured	15 504	13 315	58 528	46 915
Independent reflections	2767	2486	3394	5911
Abs. coeff. (mm ⁻¹)	7.482	7.493	11.347	6.874
Goof (<i>F</i> ²)	1.0571	1.041	1.093	1.0933
<i>R</i> _{int}	0.0378	0.0419	0.0230	0.0310
<i>R</i> ₁	0.0253	0.0367	0.0200	0.0172
<i>wR</i> ₂	0.0584	0.0926	0.0590	0.0422
Flack	−0.009(8)	0.04(3)	−0.02(1)	—



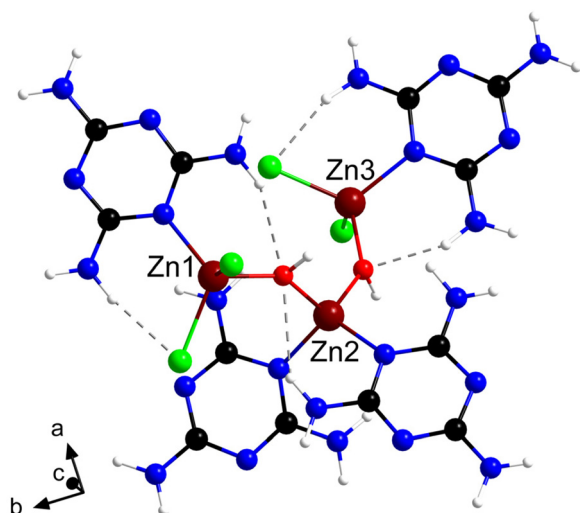


Fig. 1 Section of the crystal structure of $\text{Zn}_3(\text{OH})_2\text{Cl}_4(\text{Mel})_3$, with a central trinuclear arrangement of zinc atoms, interconnected via hydroxide bridges. Each zinc atom adopts a distorted tetrahedral environment surrounded by chloride, hydroxide, and melamine ligands.

Structure of orthorhombic and monoclinic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$

The structure of orthorhombic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ crystallizes in the non-centrosymmetric orthorhombic space group $Pna2_1$ (Fig. 2). The zinc atom in the structure is coordinated by three halide ligands and one melamine molecule through an inner nitrogen atom, forming the $(\text{ZnCl}_3\text{Mel})^-$ anion with a distorted tetrahedral coordination geometry, with $d_{\text{Zn-N}} = 2.031(1)–2.045(1)$ Å, $d_{\text{Zn-Cl}} = 2.2458(4)–2.3151(3)$ Å and $d_{\text{Zn-O}} = 1.925(1)–1.947(1)$ Å. In addition, a protonated melamine molecule is incorporated for charge compensation.

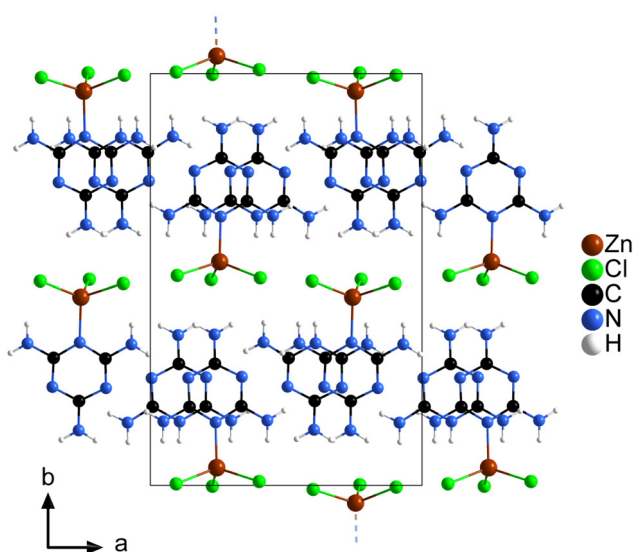


Fig. 2 Crystal structure of orthorhombic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ showing the layered character of the structure.

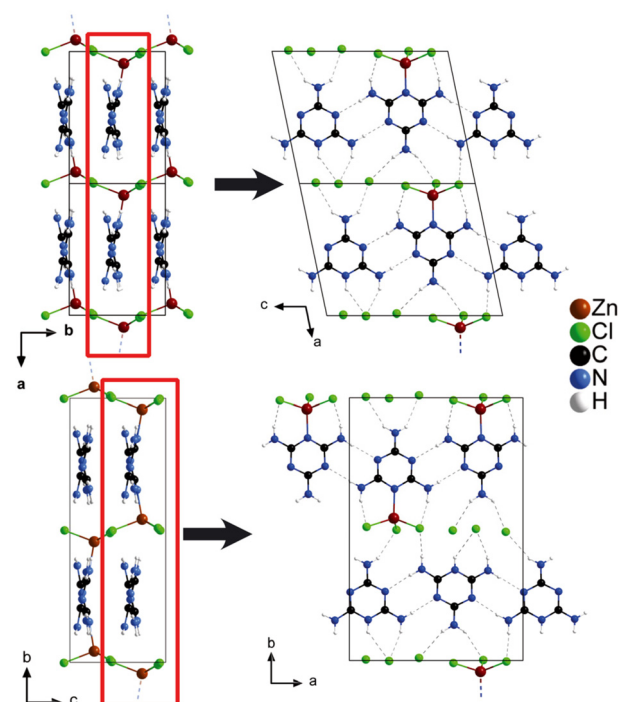


Fig. 3 Two views of the monoclinic (top) and orthorhombic (bottom) modifications of $(\text{MelH})\text{ZnCl}_3(\text{Mel})$. The red box marks the section of the structure shown in the parent projections on the right.

These moieties together form a layered arrangement, most importantly with a stacking of melamine and melaminium along the polar c -axis. When viewed along the a direction, both melamine and melaminium are slightly tilted relative to each other (see Fig. 3, left side).

The structure of monoclinic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ crystallizes in the non-centrosymmetric monoclinic space group $P2_1$ with $d_{\text{Zn-N}} = 2.053(2)$ Å and $d_{\text{Zn-Cl}} = 2.716(7)–2.2633(6)$ Å, which are in good agreement with the literature.^{8b} Herein, the $(\text{ZnCl}_3\text{Mel})^-$ and melaminium ions show different distributions in the structure, compared to the orthorhombic structure, as visualized in Fig. 3. These different arrangements are most likely a result of competing stabilizations of these structures *via* hydrogen bonding, with hydrogen bonding highlighted in Fig. 3 (right); see Tables S1–S4 for the complete list. A list of all distances surrounding the zinc atoms is provided for all compounds in Table S5. Most importantly, the melamine-based ring systems are stacked along the polar b -axis.

NLO measurements

Second harmonic generation (SHG) is a second-order non-linear optical process in which two photons combine within a material to produce a new photon with twice the energy and half the wavelength of the incident light. This phenomenon arises from the interaction between the electromagnetic field and the material's nonlinear polarization.¹³ To evaluate the SHG efficiency of the orthorhombic compounds $(\text{MelH})\text{ZnX}_3(\text{Mel})$ ($X = \text{Cl}, \text{Br}$), measurements were conducted on



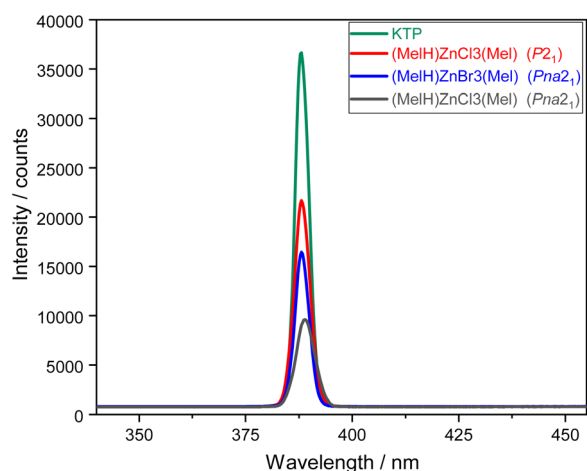


Fig. 4 Nonlinear optical spectra of KTP (green), monoclinic (MelH) $\text{ZnCl}_3(\text{Mel})$ ($P2_1$; red), orthorhombic (MelH) $\text{ZnBr}_3(\text{Mel})$ ($Pna2_1$; blue) and orthorhombic (MelH) $\text{ZnCl}_3(\text{Mel})$ ($Pna2_1$; grey) are shown for an excitation power of 5 mW. The only detectable signal is the SHG peak, which is located at approximately 390 nm.

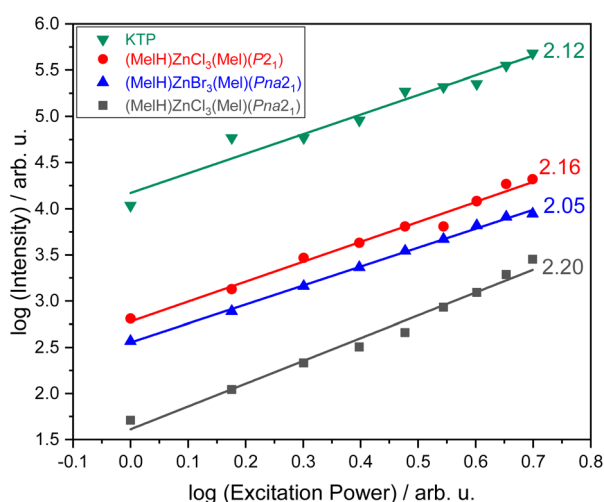


Fig. 5 Nonlinear optical spectra of KTP (green), monoclinic (MelH) $\text{ZnCl}_3(\text{Mel})$ ($P2_1$; red), orthorhombic (MelH) $\text{ZnBr}_3(\text{Mel})$ ($Pna2_1$; blue) and orthorhombic (MelH) $\text{ZnCl}_3(\text{Mel})$ ($Pna2_1$; grey). The excitation power dependence of the SHG signal is presented on a double logarithmic scale. Continuous lines represent the corresponding linear fits, with slopes derived from the fitted data.

single crystals using a custom-designed confocal microscope, as described in the Experimental section (see Fig. 4 and 5).

Among the materials studied, potassium titanyl phosphate (KTP)¹⁴ is used as a reference, which is one of the strongest SHG materials, and its intensity is approximately twice that of monoclinic (MelH) $\text{ZnCl}_3(\text{Mel})$. Nevertheless, the SHG signal of the monoclinic phase remains within the same order of magnitude as that of KTP, which is widely used as a benchmark material in nonlinear optics.

The SHG intensity of monoclinic (MelH) $\text{ZnCl}_3(\text{Mel})$ is about 1.5 times greater than that of orthorhombic (MelH)

$\text{ZnBr}_3(\text{Mel})$. This is consistent with the theoretical expectation that lower-symmetry crystal systems generally allow a greater number of non-zero components in the second-order susceptibility tensor ($\chi^{(2)}$), thereby enhancing SHG efficiency.¹⁵

In addition, the orthorhombic bromide compound exhibits an SHG response approximately twice as strong as its chloride analogue. This increase can be attributed to the higher polarizability of bromide ions compared to chloride ions, which positively influences the overall nonlinear response.

The observed SHG efficiencies likely arise from a synergistic interplay between the polarizability of the Zn^{2+} centers, the halide ions, and the delocalized π -electron system of the melamine framework, all of which contribute to an increased second-order susceptibility.¹⁶

A quadratic dependence of SHG intensity on excitation power, as shown in Fig. 5, confirms the second-order nature of the process; linear regression of the logarithmically scaled data yields slopes close to 2, consistent with second-harmonic generation. Additionally, the presence of spectral peaks at wavelengths corresponding to half the excitation wavelength provides clear evidence that the observed signals originate from second harmonic generation.

These results confirm the second-order origin of the SHG signals and highlight the potential of zinc halide-melamine complexes as promising candidates for nonlinear optical applications such as frequency conversion.

Diffuse reflectance UV/Vis (DRUV) spectroscopy

Diffuse reflectance UV/Vis spectroscopy was performed for the phase-pure orthorhombic (MelH) $\text{ZnBr}_3(\text{Mel})$ (Fig. 6). The spectrum exhibits two broad absorption bands, which are assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the aromatic triazine ring system.¹⁷ Compared to pure melamine, a hypsochromic

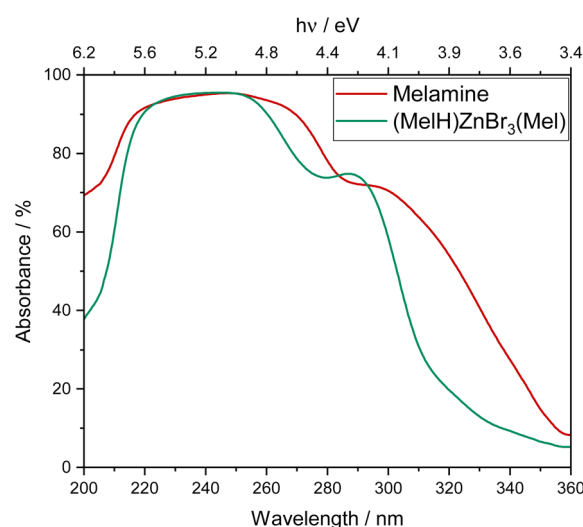


Fig. 6 Diffuse reflectance UV/Vis spectra of melamine (red) and orthorhombic (MelH) $\text{ZnBr}_3(\text{Mel})$ (green). Absorbance (%; left axis) is shown as a function of wavelength (nm) and photon energy (eV).



shift is observed, which can be attributed to the coordination of the melamine nitrogen atoms to Zn^{2+} and additional protonation at the ring nitrogen. These interactions modify the elec-

tronic structure and shift the π -system transitions to higher energies.¹⁸

The optical band gap was determined using a Tauc plot, yielding a direct band gap of 4.74 eV and an indirect band gap of 4.46 eV (Fig. 7).¹⁹ Both values lie in the UV range, consistent with the observed formation of transparent, block-shaped crystals.

Infrared (IR) spectroscopy

The infrared spectrum of orthorhombic $(\text{MelH})\text{ZnBr}_3(\text{Mel})$, shown in Fig. 8, is compared with that of the previously reported monoclinic chloride analogue $(\text{MelH})\text{ZnCl}_3(\text{Mel})$.^{8b} Assignments of the observed vibrational bands to characteristic stretching and deformation modes for both compounds are summarized in Table 2. The bromide complex exhibits an additional NH_2 stretching band at 3555 cm^{-1} , characteristic of melamine.²⁰ Since melamine typically displays two bands in this region, the absence of the second band in the chloride complex may result from band overlap, background interference, or structural effects. One possible explanation is the presence of an extended hydrogen-bonding network in the orthorhombic bromide complex, whereas no such interactions are present in the monoclinic chloride analogue. This difference in hydrogen bonding may also account for the observed blue shift in the NH_2 stretching vibrations of the bromide complex.

Electronic structure

Density functional theory (DFT) was used to calculate the electronic band structure of orthorhombic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ in order to understand the nature of the electronic states and chemical bonding in these materials. At the DFT level, orthorhombic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ has a direct band gap at Γ (0 0 0) of 4.1 eV (see the SI), with nearly dispersionless valence and conduction bands, consistent with experimental results. The highest occupied bands are predominantly associated with nitrogen, whereas the lowest unoccupied bands are associated with carbon, indicating that the C–N π bonds in these materials play an important role in their optical properties. However, hybridized states with Zn and Cl character are also found beginning at 0.5 eV below the band gap, indicating that these components all contribute to the polarizable valence states.

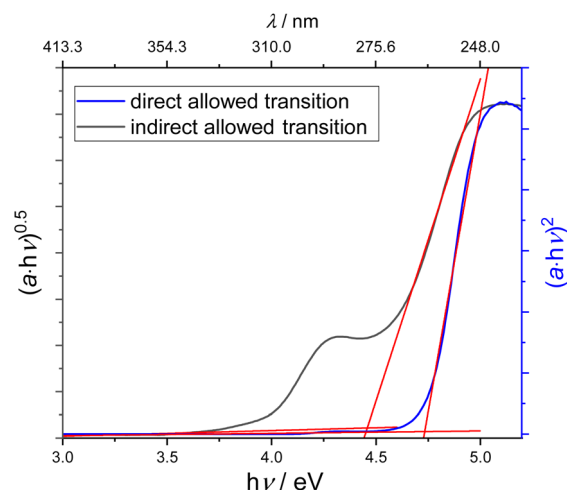


Fig. 7 Tauc plots from diffuse reflectance UV/Vis spectroscopy of orthorhombic $(\text{C}_3\text{N}_6\text{H}_7)\text{ZnBr}_3(\text{C}_3\text{N}_6\text{H}_6)$ showing the direct (blue) and indirect (black) transitions, with the corresponding linear fits in red.

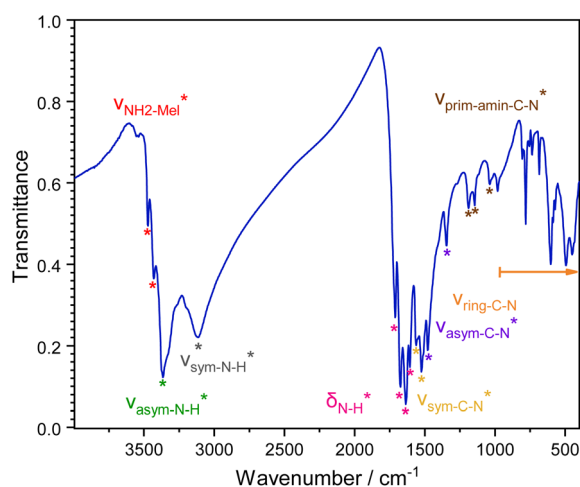


Fig. 8 Infrared spectrum of orthorhombic $(\text{MelH})\text{ZnBr}_3(\text{Mel})$ with band assignments of characteristic vibrational modes.

Table 2 Assignment of the wavenumbers to the characteristic deformation and vibration oscillations in orthorhombic $(\text{MelH})\text{ZnBr}_3(\text{Mel})$ and the published monoclinic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ ^{8b}

Orthorhombic $(\text{MelH})\text{ZnBr}_3(\text{Mel})$ Wavenumber/ cm^{-1}	Monoclinic $(\text{MelH})\text{ZnCl}_3(\text{Mel})$ Wavenumber/ cm^{-1}	Assignment	
3555, 3539	3457	$\nu_{\text{NH}_2-\text{Mel}}$	NH_2 stretching, typical of melamine
3472	3371	$\nu_{\text{asym}-\text{N}-\text{H}}$	Asymmetrical NH_2 stretching
3365	3140	$\nu_{\text{sym}-\text{N}-\text{H}}$	Symmetrical NH_2 stretching
1711–1607	1716–1645	$\delta_{\text{N}-\text{H}}$	NH_2 deformation
1562, 1524	1525, 1482	$\nu_{\text{sym}-\text{C}-\text{N}}$	1,3,5-s-Triazine ring “quadrant stretching”
1479, 1346	1480, 1347	$\nu_{\text{asym}-\text{C}-\text{N}}$	1,3,5-s-Triazine ring “semicircle stretching”
1188–1038	1200–1050	$\nu_{\text{prim-amin}-\text{C}-\text{N}}$	C–N stretching, primary amines, tertiary C
982–449	779–459	$\nu_{\text{ring}-\text{C}-\text{N}}$	1,3,5-s-Triazine ring, out-of-plane ring bending by “sextants”

Conclusions

The two-component zinc halide–melamine system was investigated by means of solvothermal synthesis and solid-state reactions, showing that this type of reaction can be easily performed to prepare compounds with potential SHG properties. We resolved the crystal structures of zinc halide–melamine compounds (MelH)ZnX₃(Mel) with X = Cl, Br, and investigated their optical spectra by means of DRUV and IR spectroscopy. (MelH)ZnCl₃(Mel) appears with two non-centrosymmetric modifications, orthorhombic and monoclinic. The monoclinic chloride polymorph corresponds to the phase reported in the literature, and an alternative solid-state synthesis was established to yield a phase-pure crystalline material. Single-crystal SHG measurements revealed an increasing SHG response following the sequence orthorhombic (Cl) > orthorhombic (Br) > monoclinic (Cl). In the case of the orthorhombic chloride and bromide compounds, the presence of Br roughly doubles the response, consistent with increasing halide polarizability. These results indicate that heavier halides strengthen the second-order response for isotopic structures, and symmetry lowering can lead to further amplification. Guided by this trend, the monoclinic iodine analogue (MelH)ZnI₃(Mel) could deliver SHG intensities comparable to the benchmark SHG material KTP.

Experimental section

Melamine hydrohalides ((C₃N₆H₆)HX with X = Cl, Br)

The melamine hydrohalides were synthesized according to the literature²¹ by adding to a suspension of melamine (5.0 g, 3.96 mmol, 1 eq.) in deionized water (250 ml) at room temperature, followed by the addition of the corresponding concentrated acids HCl (40.0 ml, 47.6 mmol, 12 eq.); HBr (26.1 ml, 47.6 mmol, 12 eq.). The mixtures were stirred overnight, filtered, and washed with 50 ml of deionized water. The resulting products were dried overnight at 80 °C. In all cases, a white powder was obtained.

Synthesis of Zn₃(OH)₂Cl₄(C₃N₆H₆)₃ and orthorhombic (C₃N₆H₇)ZnCl₃(C₃N₆H₆)

Hydrothermal synthesis was employed to produce both crystalline and powdered materials. ZnCl₂ (649 mg, 5.14 mmol, Sigma-Aldrich, ≥99.5%) and melamine (351 mg, 2.57 mmol, Sigma-Aldrich, 99.9%) were dissolved in 5 ml of double distilled and degassed water. The reaction mixture was enclosed in a Teflon-lined autoclave (volume = 15 ml) and heated slowly at a rate of 0.1 K min⁻¹ to 110 °C and maintained at this temperature for 24 hours before cooling to room temperature at a rate of 0.1 K min⁻¹. The resulting crystals and powder (yield 15%) were air-dried at 80 °C. Despite variations in the reaction conditions, the formation of Zn₃(OH)₂Cl₄(C₃N₆H₆)₃ (yield 85%) could not be further minimized in this synthesis, preventing the isolation of pure orthorhombic (C₃N₆H₇)ZnCl₃(C₃N₆H₆).

Crystals of both compounds could be well distinguished, because they formed large plates and rods.

Synthesis of monoclinic (C₃N₆H₇)ZnCl₃(C₃N₆H₆)

In addition to the previously reported hydrothermal synthesis,^{8b} this compound was prepared by a solid-state reaction of ZnCl₂ (321 mg, 2.35 mmol, 1 eq.), melamine hydrochloride (383 mg, 2.35 mmol, 1 eq.), and melamine (296 mg, 2.35 mmol, 1 eq.). The mixture was ground with an agate mortar to afford a homogeneous mixture and then sealed into a quartz ampoule. The ampoule was heated at a rate of 0.1 K min⁻¹ to 120 °C and maintained at this temperature for 14 days, followed by cooling to room temperature at a rate of 0.1 K min⁻¹. A white crystalline powder was obtained in a quantitative yield (>95%).

Synthesis of (C₃N₆H₇)ZnBr₃(C₃N₆H₆)

A hydrothermal synthesis was employed to produce the crystalline material, aiming to optimize the crystal quality. ZnBr₂ (757 mg, 3.86 mmol, Sigma-Aldrich, ≥99.5%) and melamine (343 mg, 1.93 mmol, Sigma-Aldrich, 99.9%) were dissolved in 5 ml of double distilled and degassed water. The reaction mixture was enclosed in a Teflon-lined autoclave (volume = 15 ml) and heated slowly at a rate of 0.1 K min⁻¹ to 110 °C where it was maintained for 24 hours, before cooling to room temperature at a rate of 0.1 K min⁻¹. The resulting crystals and powder (yield >95%) were dried in air at 80 °C.

Powder X-ray diffraction (PXRD)

PXRD patterns of the products were collected with a Stadi-P (STOE, Darmstadt) powder diffractometer using germanium monochromated Cu-K_{α1} radiation (λ = 1.5406 Å) and a Mythen 1K detector.

Single-crystal X-ray diffraction (SC-XRD)

SC-XRD studies were performed using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix 6000HE detector using CuK_α radiation (λ = 1.54184 Å) at 150 K. The structure was solved with the ShelXT 2018/2 solution program using dual methods and by using Olex2 1.5 as the graphical interface. The models were refined with ShelXL 2018/3 using full matrix least squares minimization on F² and Olex.refine with NoSphereA2.²² All structural models were examined using PLATON to assess for overlooked higher symmetry; however, no missed symmetry elements were detected.²³

Second harmonic generation (SHG) measurements

To perform the SHG measurements, the crystalline samples were put onto silicon wafers. The samples prepared this way could then be placed in a home-built parabolic mirror confocal microscope and the spectra and images could be collected. The ability of the microscope to measure a wide range of samples has been demonstrated in prior works.²⁴ A laser with a wavelength of 779 nm and a repetition rate of 80 MHz (FemtoFiber pro, Toptica Photonics) was used for the exci-



tation of individual crystals. A strict Gaussian beam with linear polarization was ensured through the use of a Glan-Taylor polarizer in the beam path. Both the focusing of the laser beam and the collection of the emitted signal were done through the use of a parabolic mirror, with a NA of 0.9986 in air. The scattered laser signal, as well as potentially the two-photon-photoluminescence, was blocked using a combination of a short pass filter with a filter wavelength of 750 nm and a bandpass filter with a range of 380 to 400 nm (nominal center wavelength of 390 nm). For samples, spatial intensity distribution images could be recorded using a high-precision nano-positioning stage (nPoint) where the intensity of each pixel was then collected using an avalanche photodiode. The filtered SHG spectra were then collected with a spectrometer with a 150 grooves per mm grating (Princeton Instruments) leading to a Pixis 100 charge-coupled device (Princeton Instruments).

Diffuse reflectance UV/Vis (DRUV) spectroscopy

The DRUV spectra were acquired using a Maya2000 Pro spectrometer (Ocean Optics) coupled to a Praying Mantis sample chamber (Harrick) and a DH-2000-BAL deuterium-tungsten lamp (Ocean Optics) as the illumination source. Data collection was performed using OceanView 1.6.7 Lite (Ocean Optics) under the following settings: 40 scans averaged, a boxcar width of 10, and an integration time of 30 ms. The bandgap E_g of (MeH)ZnBr₃(Me) was calculated using the following equation: $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where α is the absorption coefficient, h is the Planck constant, A is a material related constant and $h\nu$ is the photon energy. For an indirect allowed bandgap transition, the exponent $n = 2$ and for a direct allowed bandgap transition $n = 0.5$.¹⁹

Infrared (IR) spectroscopy

IR spectra were collected on a Bruker VERTEX 70 spectrometer in the range of 4000–400 cm⁻¹. Samples were prepared as KBr pellets inside a glovebox, pressed under ambient conditions, and subsequently stored under an inert atmosphere until measurement.

Density functional theory (DFT) calculations

DFT calculations were performed using the ABINIT software package (v.10).²⁵ The calculations were performed using a plane wave basis set and the PAW method,²⁶ with an energy cut-off of 26 Ha used outside the PAW spheres and 104 Ha inside. A $4 \times 4 \times 4$ Monkhorst-Pack grid²⁷ of k -points was used to sample reciprocal space. These quantities were chosen following convergence studies, with the convergence criterion being 1% of the pressure. The Perdew-Burke-Ernzerhof exchange-correlation functional was used with the dispersion correction of Grimme.²⁸ PAW data files were used as received from the ABINIT library. The structures were relaxed to an internal pressure of 5 MPa prior to calculations of the electronic band structure.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available in the supplementary information (SI) of this article. Supplementary information is available. See DOI: <https://doi.org/10.1039/d5dt02245b>. Computational data are available from DOI: <https://doi.org/10.5281/zenodo.17613259>.

CCDC 2478821, 2407677, 2438541 and 2407380 contain the supplementary crystallographic data for this paper.^{29a–d}

Acknowledgements

The support for this research from the Deutsche Forschungsgemeinschaft (Bonn) through the project ME 914/34-1 and through the bwHPC project sponsored by the state of Baden-Württemberg and the German Research Foundation (DFG) through grant no. INST 40/467-1 FUGG (JUSTUS cluster) is gratefully acknowledged. C. P. R. acknowledges the support from the project FerrMion of the Ministry of Education, Youth and Sports, Czech Republic, co-funded by the European Union (CZ.02.01.01/00/00/22_008/0004591). We thank Peter Janoschek for performing the DRUV measurements.

References

- (a) P. F. Bordui and M. M. Fejer, *Annu. Rev. Mater. Sci.*, 1993, **23**, 321–379; (b) P. Sangeetha, P. Jayaprakash, M. Nageshwari, C. R. T. Kumari, S. Sudha, M. Prakash, G. Vinitha and M. L. Caroline, *Phys. B*, 2017, **525**, 164–174; (c) Z. Qin, Y. Wen, Y. Shang, Y. Song and Y. Wan, *Appl. Phys. A*, 2007, **87**, 277–280; (d) S. K. Yesodha, C. K. S. Pillai and N. Tsutsumi, *Prog. Polym. Sci.*, 2004, **29**, 45–74; (e) S. Ahmed, X. Jiang, C. Wang, U. e. Kalsoom, B. Wang, J. Khan, Y. Muhammad, Y. Duan, H. Zhu and X. Ren, *Adv. Opt. Mater.*, 2021, **9**, 2001671; (f) X. Liu, Q. Guo and J. Qiu, *Adv. Mater.*, 2017, **29**, 1605886; (g) L. R. Dalton, A. W. Harper, R. Ghosn, W. H. Steier, M. Ziari, H. Fetterman, Y. Shi, R. Mustacich, A.-Y. Jen and K. J. Shea, *Chem. Mater.*, 1995, **7**, 1060–1081.
- P. A. Franken, A. E. Hill, C. W. Peters and G. Weinreich, *Phys. Rev. Lett.*, 1961, **7**, 118–119.
- (a) X. Meng, H. Tian, Q. Wu and M. Xia, *J. Cryst. Growth*, 2024, **648**, 127930; (b) X. Meng, W. Yin and M. Xia, *Coord. Chem. Rev.*, 2021, **439**, 213916; (c) J. Lu, Y.-K. Lian, L. Xiong, Q.-R. Wu, M. Zhao, K.-X. Shi, L. Chen and L.-M. Wu, *J. Am. Chem. Soc.*, 2019, **141**, 16151–16159; (d) F. Liang, L. Kang, X. Zhang, M.-H. Lee, Z. Lin and Y. Wu, *Cryst. Growth Des.*, 2017, **17**, 4015–4020.
- (a) M. Kalmutzki, M. Ströbele, F. Wackenhut, A. J. Meixner and H. J. Meyer, *Inorg. Chem.*, 2014, **53**, 12540–12545;



- (b) M. Kalmutzki, M. Ströbele, F. Wackenhut, A. J. Meixner and H. J. Meyer, *Angew. Chem., Int. Ed.*, 2014, **53**, 14260–14263.
- 5 (a) C. Dirk, R. Twieg and G. Wagniere, *J. Am. Chem. Soc.*, 1986, **108**, 5387–5395; (b) J. Chen, C.-L. Hu, F. Kong and J.-G. Mao, *Acc. Chem. Res.*, 2021, **54**, 2775–2783.
- 6 L. Vella-Zarb, D. Braga, A. G. Orpen and U. Baisch, *CrystEngComm*, 2014, **16**, 8147–8159.
- 7 (a) E. Bayat, M. Ströbele, M. Abbasi, S. Kroeker, J. Valenta, D. Ensling, T. Jüstel and H.-J. Meyer, *Inorg. Chem.*, 2024, **63**, 19053–19062; (b) E. Bayat, M. Ströbele, D. Ensling, T. Jüstel and H.-J. Meyer, *Molecules*, 2024, **29**, 5598; (c) A. B. Wiles, D. Bozzuto, C. L. Cahill and R. D. Pike, *Polyhedron*, 2006, **25**, 776–782.
- 8 (a) Z. Bai, J. Lee, H. Kim, C.-L. Hu and K. M. Ok, *Small*, 2023, **19**, 2301756; (b) L. Liu, Z. Bai, L. Hu, D. Wei, Z. Lin and L. Zhang, *J. Mater. Chem. C*, 2021, **9**, 7452–7457.
- 9 (a) M. Kompitsas, C. Baharis and Z. Pan, *J. Opt. Soc. Am. B*, 1994, **11**, 697–702; (b) D. Goebel, U. Hohm and G. Maroulis, *Phys. Rev. A*, 1996, **54**, 1973.
- 10 (a) D. Szunyogh, B. Gyurcsik, F. H. Larsen, M. Stachura, P. W. Thulstrup, L. Hemmingsen and A. Jancsó, *Dalton Trans.*, 2015, **44**, 12576–12588; (b) X.-L. Wang, Y.-F. Bi, G.-C. Liu, H.-Y. Lin, T.-L. Hu and X.-H. Bu, *CrystEngComm*, 2008, **10**, 349–356; (c) A. Erxleben, *Coord. Chem. Rev.*, 2003, **246**, 203–228; (d) H. Lopez-Sandoval, M. E. Londono-Lemos, R. Garza-Velasco, I. Poblano-Meléndez, P. Granada-Macías, I. Gracia-Mora and N. Barba-Behrens, *J. Inorg. Biochem.*, 2008, **102**, 1267–1276; (e) A. W. Kleij, M. Kuil, D. M. Tooke, A. L. Spek and J. N. Reek, *Inorg. Chem.*, 2005, **44**, 7696–7698.
- 11 (a) A. Zawadzka, P. Plóciennik, J. Strzelecki and B. Sahraoui, *Opt. Mater.*, 2014, **37**, 327–337; (b) K. Waszkowska, O. Krupka, O. Kharchenko, V. Figà, V. Smokal, N. Kutsevol and B. Sahraoui, *Appl. Nanosci.*, 2020, **10**, 4977–4982; (c) L.-Y. Wang, B.-Y. Shi, C.-B. Yao, Z.-M. Wang, X. Wang, C.-H. Jiang, L.-F. Feng and Y.-L. Song, *ACS Appl. Nano Mater.*, 2023, **6**, 9975–10014.
- 12 F. Jones, H. Tran, D. Lindberg, L. Zhao and M. Hupa, *Energy Fuels*, 2013, **27**, 5663–5669.
- 13 M. Kalmutzki, M. Ströbele, F. Wackenhut, A. J. Meixner and H.-J. Meyer, *Inorg. Chem.*, 2014, **53**, 12540–12545.
- 14 (a) J. D. Bierlein and H. Vanherzeele, *J. Opt. Soc. Am. B*, 1989, **6**, 622–633; (b) M. N. Satyanarayan, A. Deepthy and H. L. Bhat, *Crit. Rev. Solid State Mater. Sci.*, 1999, **24**, 103–191.
- 15 (a) A. Aghigh, S. Bancelin, M. Rivard, M. Pinsard, H. Ibrahim and F. Légaré, *Biophys. Rev.*, 2023, **15**, 43–70; (b) S. Ghimire and D. A. Reis, *Nat. Phys.*, 2019, **15**, 10–16; (c) F. Simon, S. Clevers, V. Dupray and G. Coquerel, *Chem. Eng. Technol.*, 2015, **38**, 971–983; (d) E. V. Kazantseva and A. I. Maimistov, *Opt. Spectrosc.*, 2000, **89**, 772–782.
- 16 H. Jia, X. Hou and S. Pan, *Inorg. Chem. Front.*, 2024, **11**, 7756–7774.
- 17 S. A. Kalyan, S. Elangovan, R. Karthick, N. Kanagathara, M. K. Marchewka and J. Janczak, *J. Mater. Sci.: Mater. Electron.*, 2024, **35**, 2100.
- 18 (a) L. Hynes, G. Montiel, A. Jones, D. Riel, M. Abdulaziz, F. Viva, D. Bonetta, A. Vreugdenhil and L. Trevani, *Mater. Adv.*, 2020, **1**, 262–270; (b) H. M. Vinusha, S. P. Kollur, H. D. Revanasiddappa, R. Ramu, P. S. Shirahatti, M. N. Nagendra Prasad, S. Chandrashekar and M. Begum, *Results Chem.*, 2019, **1**, 100012.
- 19 (a) J. Tauc, *Mater. Res. Bull.*, 1968, **3**, 37–46; (b) J. Tauc, *Amorphous and Liquid Semiconductors*, Springer, New York, 1974; (c) N. F. Mott and E. A. Davis, *Electronic processes in non-crystalline materials*, Oxford University Press, 2012; (d) A. R. Zanatta, *Sci. Rep.*, 2019, **9**, 11225; (e) Ł. Haryński, A. Olejnik, K. Grochowska and K. Siuzdak, *Opt. Mater.*, 2022, **127**, 112205; (f) J. Klein, L. Kampermann, B. Mockenhaupt, M. Behrens, J. Strunk and G. Bacher, *Adv. Funct. Mater.*, 2023, **33**, 2304523; (g) P. Y. Yu and M. Cardona, *Fundamentals of semiconductors. Physics and materials properties*, Springer, Berlin, Germany, 4th edn, 2010; (h) G. Kortüm and H. Koffer, *Ber. Bunsenges. Phys. Chem.*, 1963, **67**, 67–75; (i) G. Kortum and J. E. Lohr, *Reflectance Spectroscopy*, Springer My Copy UK, 1969; (j) M. P. Fuller and P. R. Griffiths, *Anal. Chem.*, 1978, **50**, 1906–1910; (k) A. B. Murphy, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 1326–1337; (l) R. López and R. Gómez, *J. Sol-Gel Sci. Technol.*, 2012, **61**, 1–7; (m) Z. M. Gibbs, A. LaLonde and G. J. Snyder, *New J. Phys.*, 2013, **15**, 075020; (n) P. Makula, M. Pacia and W. Macyk, *J. Phys. Chem. Lett.*, 2018, **9**, 6814–6817; (o) G. D. Gesesse, A. Gomis-Berenguer, M.-F. Barthe and C. O. Ania, *J. Photochem. Photobiol., A*, 2020, **398**, 112622.
- 20 X. Yuan, K. Luo, K. Zhang, J. He, Y. Zhao and D. Yu, *J. Phys. Chem. A*, 2016, **120**, 7427–7433.
- 21 (a) J. Barrio and M. Shalom, *Mater. Sci. Semicond. Process.*, 2018, **73**, 78–82; (b) G. Bertelli, G. Camino, L. Costa and R. Locatelli, *Polym. Degrad. Stab.*, 1987, **18**, 225–236.
- 22 (a) *CrysAlisPro Software System*, Rigaku Oxford Diffraction, 2024; (b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341; (c) G. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8; (d) G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8; (e) G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122; (f) L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 59–75; (g) F. Kleemiss, O. V. Dolomanov, M. Bodensteiner, N. Peyerimhoff, L. Midgley, L. J. Bourhis, A. Genoni, L. A. Malaspina, D. Jayatilaka, J. L. Spencer, F. White, B. Grundkötter-Stock, S. Steinhauer, D. Lentz, H. Puschmann and S. Grabowsky, *Chem. Sci.*, 2021, **12**, 1675–1692.
- 23 A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
- 24 (a) J. Wang, J. Butet, G. D. Bernasconi, A.-L. Baudrion, G. Lévêque, A. Horrer, A. Horneber, O. J. Martin, A. J. Meixner and M. Fleischer, *Nanoscale*, 2019, **11**, 23475–23481; (b) E. Gürdal, A. Horneber, A. J. Meixner, D. P. Kern, D. Zhang and M. Fleischer, *Nanoscale*, 2020, **12**, 23105–23115; (c) L. Pan, P. Miao, A. Horneber, A. J. Meixner,



- P.-M. Adam and D. Zhang, *Beilstein J. Nanotechnol.*, 2022, **13**, 572–581; (d) L. Pan, P. Miao, A. Horneber, A. J. Meixner, P.-M. Adam and D. Zhang, *ACS Appl. Nano Mater.*, 2023, **6**, 6467–6473; (e) J. P. Wang, Y. Q. Fang, W. He, Q. Liu, J. R. Fu, X. Y. Li, Y. Liu, B. Gao, L. Zhen and C. Y. Xu, *Adv. Opt. Mater.*, 2023, **11**, 2300031; (f) R. Wang, Q. Liu, S. Dai, C. M. Liu, Y. Liu, Z. Y. Sun, H. Li, C. J. Zhang, H. Wang and C. Y. Xu, *Small*, 2024, **20**, 2305658.
- 25 M. J. Verstraete, J. Abreu, G. E. Allemand, B. Amadon, G. Antonius, M. Azizi, L. Baguet, C. Barat, L. Bastogne and R. Bejaud, *arXiv*, 2025, preprint, arXiv:2507.08578, DOI: [10.48550/arXiv.2507.08578](https://doi.org/10.48550/arXiv.2507.08578).
- 26 M. Torrent, F. Jollet, F. Bottin, G. Zérah and X. Gonze, *Comput. Mater. Sci.*, 2008, **42**, 337–351.
- 27 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188–5192.
- 28 (a) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396–1396; (b) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Phys. Chem.*, 2010, **132**, 154104.
- 29 (a) CCDC 2478821: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2p6dz9](https://doi.org/10.5517/ccdc.csd.cc2p6dz9); (b) CCDC 2407677: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2ltd0v](https://doi.org/10.5517/ccdc.csd.cc2ltd0v); (c) CCDC 2438541: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2mvhmm](https://doi.org/10.5517/ccdc.csd.cc2mvhmm); (d) CCDC 2407380: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2lt2fy](https://doi.org/10.5517/ccdc.csd.cc2lt2fy).



Supplementary Information

Synthesis and SHG Properties of the Melamine-Based Material (C₃N₆H₇)ZnX₃(C₃N₆H₆) (X = Cl, Br)

Melena Groß, Catharina Darine Brand, Patrick Schmidt, Tim Parker, Dai Zhang, Carl P. Romao and Hans-Jürgen Meyer^{*a}

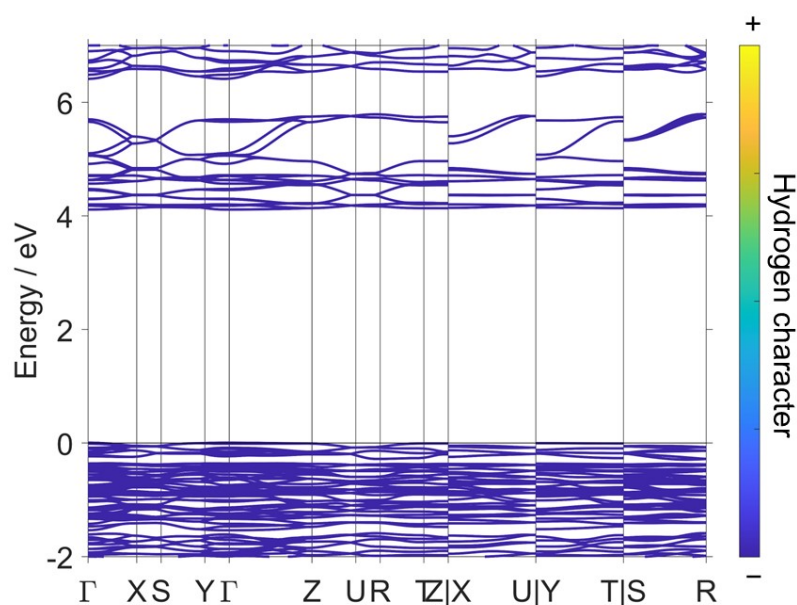


Figure S1. The electronic band structure of orthorhombic (C₃N₆H₇)ZnCl₃(C₃N₆H₆), as calculated using DFT. Bands are coloured according to their hydrogen character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $X = (0.5\ 0\ 0)$, $S = (0.5\ 0.5\ 0)$, $Y = (0\ 0.5\ 0)$, $Z = (0\ 0\ 0.5)$, $U = (0.5\ 0\ 0.5)$, $R = (0.5\ 0.5\ 0.5)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

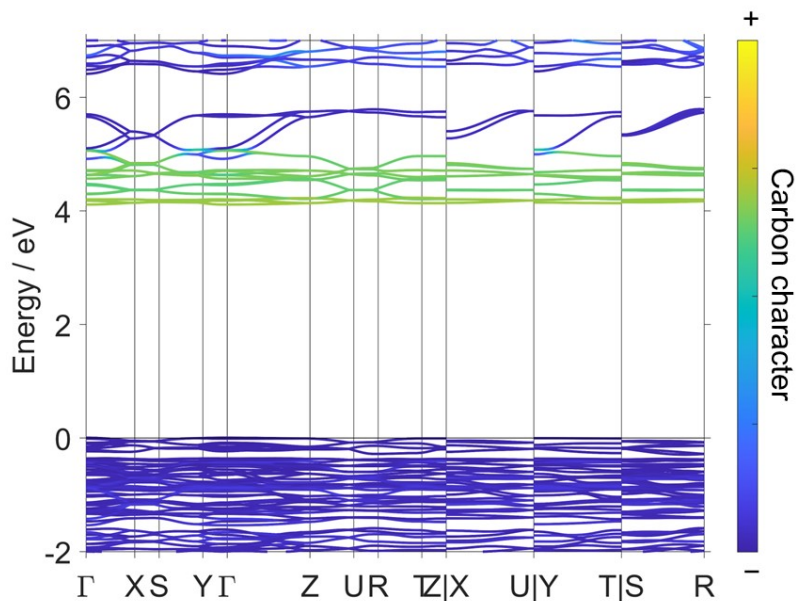


Figure S2. The electronic band structure of orthorhombic $(C_3N_6H_7)ZnCl_3(C_3N_6H_6)$, as calculated using DFT. Bands are coloured according to their carbon character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $X = (0.5\ 0\ 0)$, $S = (0.5\ 0.5\ 0)$, $Y = (0\ 0.5\ 0)$, $Z = (0\ 0\ 0.5)$, $U = (0.5\ 0\ 0.5)$, $R = (0.5\ 0.5\ 0.5)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

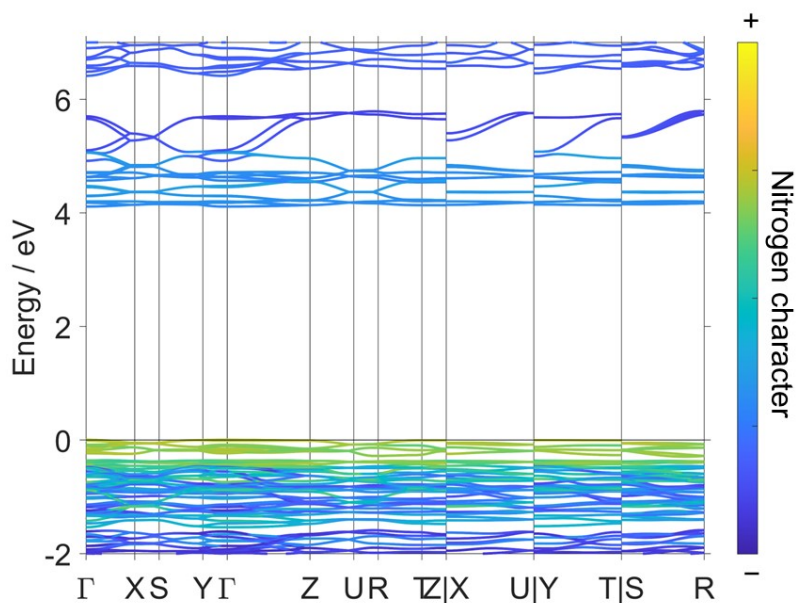


Figure S3. The electronic band structure of orthorhombic $(C_3N_6H_7)ZnCl_3(C_3N_6H_6)$, as calculated using DFT. Bands are coloured according to their nitrogen character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $X = (0.5\ 0\ 0)$, $S = (0.5\ 0.5\ 0)$, $Y = (0\ 0.5\ 0)$, $Z = (0\ 0\ 0.5)$, $U = (0.5\ 0\ 0.5)$, $R = (0.5\ 0.5\ 0.5)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

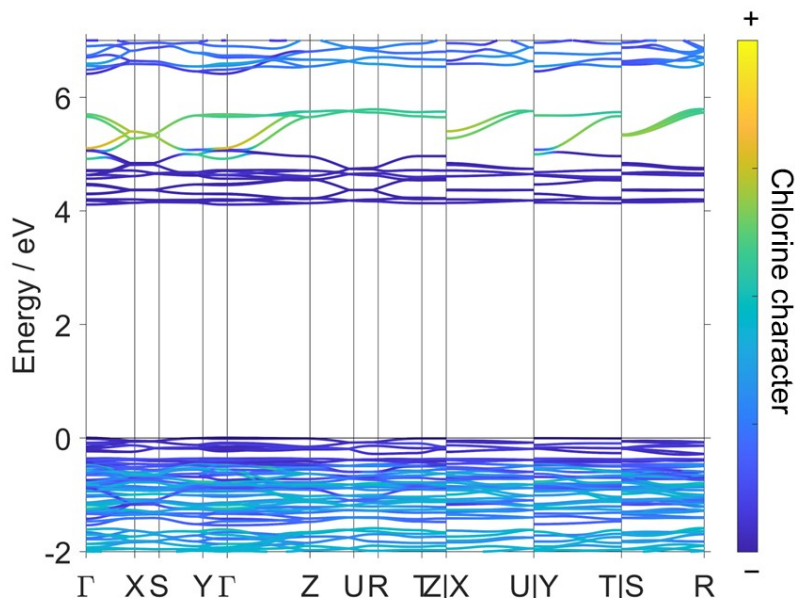


Figure S4. The electronic band structure of orthorhombic $(C_3N_6H_7)ZnCl_3(C_3N_6H_6)$, as calculated using DFT. Bands are coloured according to their chlorine character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $X = (0.5\ 0\ 0)$, $S = (0.5\ 0.5\ 0)$, $Y = (0\ 0.5\ 0)$, $Z = (0\ 0\ 0.5)$, $U = (0.5\ 0\ 0.5)$, $R = (0.5\ 0.5\ 0.5)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

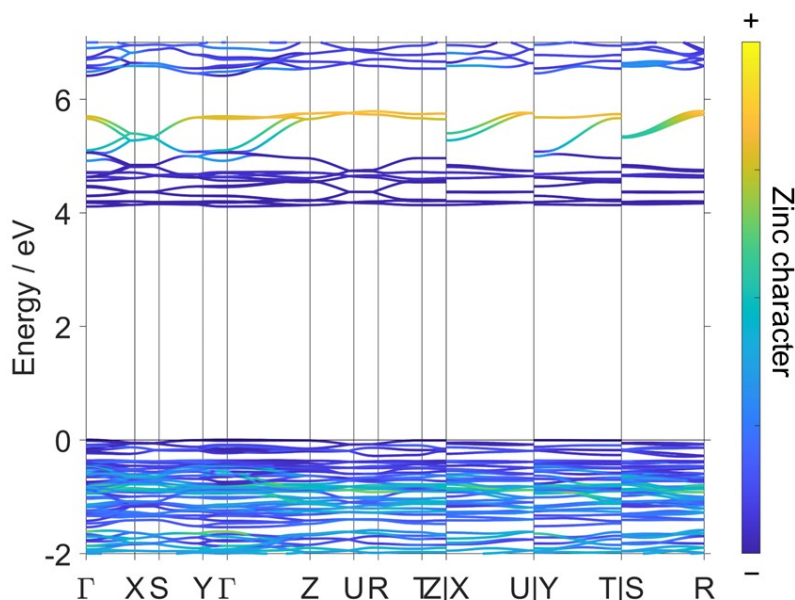


Figure S5. The electronic band structure of orthorhombic $(C_3N_6H_7)ZnCl_3(C_3N_6H_6)$, as calculated using DFT. Bands are coloured according to their zinc character. Special points in the Brillouin zone ($\Gamma = (0\ 0\ 0)$, $X = (0.5\ 0\ 0)$, $S = (0.5\ 0.5\ 0)$, $Y = (0\ 0.5\ 0)$, $Z = (0\ 0\ 0.5)$, $U = (0.5\ 0\ 0.5)$, $R = (0.5\ 0.5\ 0.5)$) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, *Comp. Mat. Sci.* 128, 140 (2017).

Table S1: Hydrogen Bond information for **monoclinic (MeH)ZnCl₃(MeI)**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N4	H4a	N9	0.98(5)	2.00(5)	2.966(3)	170(4)
N4	H4b	Cl2	0.99(4)	2.27(4)	3.197(3)	156(3)
N5	H5a	Cl3 ¹	0.87(5)	2.49(5)	3.279(3)	151(4)
N6	H6a	Cl1	0.98(4)	2.39(4)	3.293(3)	153(3)
N6	H6b	N8 ²	0.98(4)	2.00(4)	2.983(3)	175(3)
N7	H7	Cl1 ³	0.96(4)	2.59(4)	3.257(2)	127(3)
N10	H10a	Cl1 ⁴	0.98(4)	2.43(4)	3.306(3)	149(3)
N10	H10b	N3 ⁵	0.95(5)	2.08(5)	3.026(4)	177(4)
N11	H11a	Cl1 ⁶	0.98(5)	2.55(5)	3.412(3)	147(3)
N11	H11b	Cl2 ⁶	1.05(4)	2.43(4)	3.285(2)	138(3)
N12	H12a	N2	1.01(5)	1.98(5)	2.992(3)	178(4)
N12	H12b	Cl3 ⁷	0.94(4)	2.54(4)	3.348(3)	144(3)

¹1+x,y,z; ²x,x,y,-1+z; ³1-x,-1/2+y,1-z; ⁴1+x,y,1+z; ⁵x,x,y,1+z; ⁶-x,-1/2+y,1-z; ⁷1-x,1/2+y,1-z

Table S2: Hydrogen Bond information for **orthorhombic (MeH)ZnCl₃(MeI)**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N4	H4A	N3 ¹	0.88	2.11	2.986(6)	179.0
N4	H4B	Cl2	0.88	2.45	3.258(5)	153.3
N5	H5A	Cl2 ²	0.88	2.60	3.378(5)	148.7
N5	H5B	Cl1 ²	0.88	2.56	3.278(5)	138.8
N6	H6A	N2 ³	0.88	2.08	2.956(6)	174.8
N6	H6B	Cl1	0.88	2.40	3.193(5)	149.6
N7	H7	Cl2 ⁴	0.88	2.73	3.275(5)	121.1
N10	H10A	N9 ¹	0.88	2.14	3.012(7)	172.7
N10	H10B	Cl2 ⁵	0.88	2.55	3.345(6)	151.2
N11	H11A	Cl3A ²	0.88	2.50	3.301(6)	151.7
N11	H11A	Cl3B ²	0.88	2.27	2.99(3)	139.5
N11	H11B	Cl1 ⁶	0.88	2.68	3.500(5)	155.5

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N12	H12A	N8 ³	0.88	2.08	2.962(6)	175.3
N12	H12B	Cl3A	0.88	2.61	3.419(6)	152.6
N12	H12B	Cl3B	0.88	2.49	3.32(2)	157.7

¹1/2+x,3/2-y,+z; ²1/2-x,1/2+y,-1/2+z; ³-1/2+x,3/2-y,+z; ⁴+x,+y,-1+z; ⁵1-x,1-y,-1/2+z; ⁶1/2+x,3/2-y,-1+z

Table S3: Hydrogen Bond information for **(MelH)ZnBr₃(Mel)**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N4	H4A	N3 ¹	0.88	2.11	2.983(5)	174.4
N4	H4B	Br1	0.88	2.53	3.330(4)	151.2
N5	H5B	Br1 ²	0.88	2.71	3.441(4)	141.0
N6	H6A	N2 ³	0.88	2.14	3.017(5)	177.6
N6	H6B	Br2	0.88	2.55	3.365(3)	155.0
N7	H7	Br2 ⁴	0.88	2.87	3.410(4)	121.3
N10	H10A	N9 ¹	0.88	2.07	2.953(5)	175.8
N10	H10B	Br3B	0.88	2.60	3.434(11)	158.5
N11	H11A	Br3A ²	0.88	2.63	3.410(4)	148.1
N11	H11A	Br3B ²	0.88	2.44	3.163(13)	139.2
N12	H12A	N8 ³	0.88	2.14	3.021(5)	173.6
N12	H12B	Br2 ⁵	0.88	2.68	3.483(4)	153.0

¹-1/2+x,3/2-y,+z; ²1/2-x,1/2+y,-1/2+z; ³1/2+x,3/2-y,+z; ⁴+x,+y,-1+z; ⁵1-x,1-y,-1/2+z

Table S4: Hydrogen Bond information for **Zn₃(OH)₂Cl₄(Mel)₃**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	Cl2 ¹	0.91(2)	2.27(3)	3.0652(11)	145(2)
O2	H2	Cl3 ²	0.94(2)	2.25(2)	3.0923(10)	149.1(18)
N4	H4a	Cl1	0.96(3)	2.28(3)	3.2309(16)	170.9(18)
N4	H4b	Cl2 ³	0.96(2)	2.38(2)	3.2915(14)	157.3(16)
N5	H5a	N14 ⁴	0.99(2)	2.09(3)	3.0737(19)	178(2)
N5	H5b	Cl1 ⁵	0.95(3)	2.47(3)	3.2725(14)	142.2(19)
N6	H6a	N15 ⁵	0.96(2)	2.15(2)	3.1124(18)	177.7(16)
N6	H6b	O1	0.98(3)	2.34(3)	3.2392(18)	151.8(17)

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N10	H10b	Cl3 ²	0.98(2)	2.34(2)	3.2847(15)	162.2(18)
N11	H11a	Cl3 ⁶	1.00(2)	2.43(2)	3.2843(14)	144.1(17)
N11	H11b	N20 ⁷	0.94(3)	2.05(3)	2.9913(18)	172(2)
N12	H12a	N21 ⁸	0.96(3)	2.02(3)	2.9714(18)	171.0(19)
N16	H16a	Cl2 ¹	1.00(2)	2.45(2)	3.3677(15)	152.0(19)
N17	H17a	Cl2 ⁹	0.99(2)	2.44(2)	3.2903(14)	143.3(17)
N17	H17b	N2 ¹⁰	0.93(2)	2.05(2)	2.9824(19)	175.3(18)
N18	H18a	N3 ¹¹	0.97(2)	2.08(3)	3.0378(18)	169.0(19)
N18	H18b	O1	0.99(2)	2.64(2)	3.4763(19)	142.9(16)
N22	H22a	Cl3 ¹²	0.94(2)	2.48(2)	3.3597(15)	154.5(17)
N22	H22b	Cl4	0.99(2)	2.30(2)	3.2651(16)	162.8(18)
N23	H23a	N8 ¹³	0.94(2)	2.08(2)	3.0191(18)	176.7(18)
N23	H23b	Cl4 ¹⁴	0.95(2)	2.57(2)	3.3963(14)	145.9(17)
N24	H24a	N9 ¹⁴	0.96(2)	2.10(2)	3.0602(18)	174.0(18)
N24	H24b	O2	0.99(2)	2.17(2)	3.1102(18)	158.6(17)

¹1-x,1-y,1-z; ²1-x,1-y,-z; ³1-x,2-y,1-z; ⁴1+x,1+y,+z; ⁵1+x,+y,+z; ⁶1-x,2-y,-z; ⁷-1+x,1+y,+z; ⁸+x,1+y,+z; ⁹-x,1-y,1-z; ¹⁰-1+x,-1+y,+z; ¹¹-1+x,+y,+z; ¹²2-x,1-y,-z; ¹³1+x,-1+y,+z; ¹⁴+x,-1+y,+z

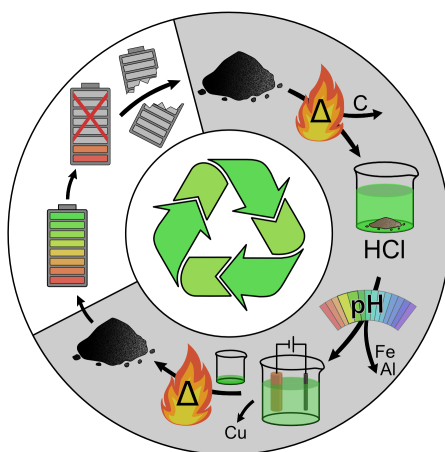
Table S5: Selected Zn–X (X = N, O, Cl, Br) bond lengths (Å). Values are refined distances with estimated standard deviations in parentheses.

Compound	Atom 1	Atom 2	Distance / Å
monoclinic (MeIH)ZnCl₃(MeI)			
	Zn1	Cl1	2.2836(6)
	Zn1	Cl2	2.2716(7)
	Zn1	Cl3	2.2633(6)
	Zn1	N1	2.053(2)
orthorhombic (MeIH)ZnCl₃(MeI)			
	Zn1	Cl1	2.269(1)
	Zn1	Cl2	2.280(1)
	Zn1	Cl3a	2.261(2)
	Zn1	Cl3b	2.240(3)
	Zn1	N1	2.050(4)
(MeIH)ZnBr₃(MeI)			
	Zn1	Br1	2.403(8)
	Zn1	Br2	2.4177(9)
	Zn1	Br3a	2.391(2)
	Zn1	Br3b	2.374(2)
Zn₃(OH)₂Cl₄(MeI)₃			
	Zn1	Cl1	2.2616(3)
	Zn1	Cl2	2.3151(4)
	Zn1	O1	1.925(1)
	Zn1	N1	2.031(1)
	Zn2	O1	1.947(1)
	Zn2	O2	1.9456(9)
	Zn2	N7	2.058(1)
	Zn2	N13	2.045(1)
	Zn3	Cl3	2.3159(3)
	Zn3	Cl4	2.2458(3)
	Zn3	O2	1.9352(9)
	Zn3	N19	2.035(1)

6 Unpublished Manuscripts

Manuscript 1

A complete cathode recovery cycle of an exhausted and dismantled lithium battery material



A complete cathode recovery cycle of an exhausted and dismantled lithium battery material

Fabian Grahlow,^[a] Patrick Schmidt,^[a] and Hans-Jürgen Meyer^{*[a]}

Abstract: One of the most important Li-ion cathode materials developed to date is lithium nickel manganese cobalt oxide (Li(Ni,Mn,Co)O₂), abbreviated as Li-NMC battery. Cathode materials of this type can refer to a variety of blends, where lower cobalt contents such as NMC 6:2:2 (LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂) or NMC 5:3:2 are preferred to reduce material costs and environmental impact. A simple and cost-effective recycling process for spent graphitic NMC Li-ion battery materials is reported for a material obtained from a commercial thermomechanical battery segmentation process. Thermo-analytical studies carried out on genuine Li-NMC/graphite material show the successive loss of electrolyte and graphite with increasing temperature. Subsequent laboratory-scale heating experiments of genuine Li-NMC/graphite materials in air confirm these findings. Impurities are removed by pH-controlled precipitation followed by electrolysis to remove and recover copper. An aqueous sol-gel process was chosen to synthesize fresh NMC cathode material. Depending on the processing conditions, the products obtained relate to an average NMC composition of 6:2:2 and 5:3:2, as shown by powder XRD measurements, structure refinement and chemical analyses.

Introduction

Following the discovery of the remarkable cathode material LiCoO₂ for lithium-ion batteries (LIBs) by Goodenough and co-workers,^[1] several developments have been undertaken for everyday application.^[2] Especially for mobile use, several requirements have to be considered: In addition to high energy densities, such as cost, safety, long-term stability and performance are important. Therefore, mixed metal oxides containing Ni, Mn and Co instead of Co alone have been developed, such as LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (referenced as NMC 622).^[2-3]

As more and more electric vehicles are sold in recent and coming years, these rechargeable batteries will play an increasingly important role in everyday transport.^[4] While there is a need to produce more and more new batteries, it is important to keep an eye on used battery materials and recycle them in order to

conserve natural resources and be sustainable.^[5] As battery manufacturers develop a wide variety of compositions, it is likely that several different types of batteries will be used in the automotive industry, requiring an elaborate recycling process.^[6] To date, there are several recycling methods, clearly summarised by Pinegar & Smith.^[7] Methods used to separate anode from cathode material are flotation, assisted by ultra-sonification and pyrolysis.^[8] Recovery of graphite requires complex laboratory installations, several intermediate treatment steps and large quantities of surfactants and waste water. Recent developments for alternative anode materials are moving towards nanostructured silicon, reducing the importance of recovering graphite in high yields, while retaining conventional cathodes.^[9] Two prominent recycling methods for NMC LIBs involve acid leaching and the pyrometallurgical processing:

Acid leaching is a well-established method for recycling battery materials on a laboratory scale.^[10] It can be carried out using both inorganic and organic acids, usually in the presence of hydrogen peroxide. Suitable organic acids reported for NMC LIBs are malic acid and acetic acid.^[11] An advantage here is the direct complexation required in the subsequent sol-gel synthesis in the case of a direct resynthesis. However, the addition of stronger acids such as sulphuric or nitric acid with H₂O₂ have been reported to result in a faster and more efficient leaching.^[7b, 11b, 12] To separate the metals from the leach solution, several extracting agents and organic solvents are necessary. The extracted metals in solution can then be successively precipitated by slowly increasing the pH of the solution.^[7b, 12b]

Pyrometallurgical processes are the most used commercial LIB recycling method. They are primarily used to recover cobalt and nickel alloys. An advantage is that LIB sorting and pre-treatment is not always required. However, parts of the battery material such as graphite and lithium are not recovered and are lost in the process. Separating metals like Co, Ni, Cu and Fe from a pyrometallurgical process generally require subsequent leaching and solvent extracting processes are required, combined with high temperature treatments.^[7a]

Thermal treatments have been reported to improve the recovery of cathode material, as a pre-treatment to remove organic binders and some of the conductive carbon, and a complete thermal removal of the carbon material in spent NMC LIBs in one step is desirable and involves a significant simplification of the whole recycling process.^[13]

Here we investigate a full recycling and recovery process by a simple combination of thermal, leaching, electrochemical and sol-gel treatment of a graphitic NMC LIB material which was obtained

[a] F. Grahlow, P. Schmidt, Prof. Dr. H.-J. Meyer
Section for Solid State and Theoretical Inorganic Chemistry
Institute of Inorganic Chemistry
Auf der Morgenstelle 18, Eberhard Karls Universität Tübingen
D-72076 Tübingen, Germany
E-mail: juergen.meyer@uni-tuebingen.de

from a commercial mechanical battery segmentation process. The thermal treatment involves the removal of (residual) electrolyte, organic binders and graphite at moderate temperatures. Removal of iron, aluminium impurities removed by pH-dependent precipitation and copper is recovered by electrolysis. The subsequent aqueous sol-gel treatment yields fresh $\text{Li}(\text{Ni,Mn,Co})\text{O}_2$ without the need for NMC metal separation as an intermediate recycling step.

Results and Discussion

The spent Li-NMC battery material (Figure 1) used in this study originates from a commercial recycling process. In this process, the batteries have been completely discharged and disassembled. The subsequent steps include shredding and an initial vacuum-drying of the spent battery material. The purpose of this treatment is to separate volatile constituents such as the electrolyte, a process that is not always complete, as will be shown later. The resulting so called 'blackmass' shown in Figure 1, is supposed to consist of a mixture of graphite, Li-NMC and lithium salts. It is important to note, that individual batteries that are being processed in a commercial recycling process might differ in terms of electrolytes, graphite content and the cathode composition, as they come from different battery manufacturers. The individual nature of these battery materials is an exclusive knowledge of the manufacturers.

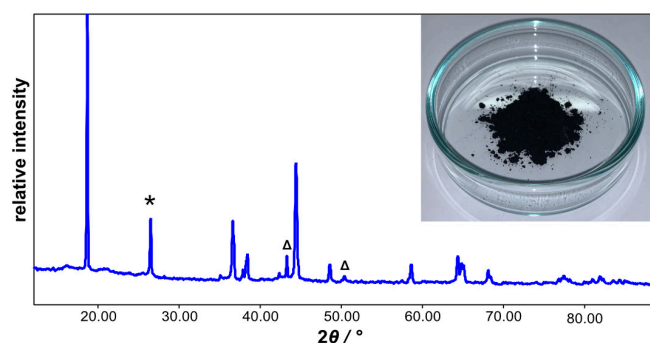


Figure 1. Powder XRD pattern ($\text{Cu-K}\alpha_1$) of spent graphitic Li-NMC battery material with a picture of the so-called "black mass" in the inset. Marked are the peaks corresponding to * graphite and Δ copper.^[15] The unlabelled peaks correspond to NMC cathode material.^[16]

Overview of the recycling process

Figure 2 illustrates the recycling scheme developed in this work, which consists of seven processing steps labelled from one to seven. In the first step a thermal treatment ($500\text{--}550\text{ }^\circ\text{C}$) of the crude 'blackmass' removes all organic compounds without alteration of the NMC material and its composition. Some aluminium and iron compounds formed in this first step do not dissolve in the following leaching step (Step 2) with chloric acid / H_2O_2 (see PXRD pattern in Figure S1). Hydrochloric acid was chosen because it is superior in dissolving the NMC material

compared to the commonly used nitric acid leaching, which in combination with H_2O_2 precipitates insoluble MnO_2 , requiring additional sulfuric or hydrochloric acid.^[14] In order to precipitate all the remaining iron and aluminium from the filtrate, the acidity of the solution was adjusted to $\text{pH} = 4.3$ using lithium hydroxide in step 3. Due to the lithium deficiency in the given $\text{Li}_x(\text{Ni,Mn,Co})\text{O}_2$ (with $x < 1$) material obtained from the commercial recycling process, the use of lithium hydroxide also ensures the formation of the desired $\text{Li}(\text{Ni,Mn,Co})\text{O}_2$ cathode material. In step 4, a voltage of 1.6 V is applied between a graphite anode and a copper cathode for 4 hours, resulting in the complete recovery of copper from solution. The remaining solution is then dried and complexated with citric acid via an aqueous sol-gel process and then calcined to yield a new Li-NMC cathode material (Step 5 and 6). Excess Li, introduced by the titration with LiOH can be recovered by washing the product with water (Step 7). Detailed procedures can be found in the Experimental Section.

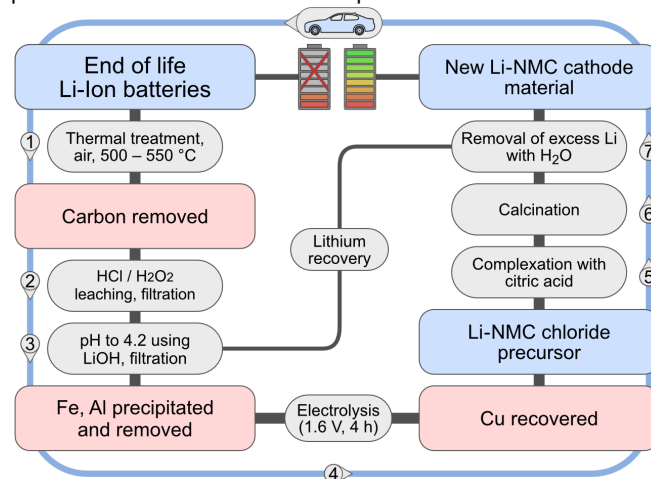


Figure 2. Recycling scheme for end of life lithium battery, departing from heat treatment for the removal of carbon, followed by acid leaching, pH dependent precipitation of impurities and electrolysis, sol-gel synthesis, involving complexation and calcination as structuring procedure for new Li-NMC cathode material.

Starting material (End of life battery material)

The TXRF analysis of the raw black mass used in this study showed a fairly consistent cathode composition with an average ratio of Ni:Mn:Co ratio of 2.80(5):1.00(4):1, which is close to the ratio of conventional NMC 622 batteries.^[3a] This indicates a reasonable sorting of the battery type in the commercial process. Additionally, multiple samples revealed iron contents between 0.9 and 3.2 wt.% (2.0 ± 0.8 wt.% on average), copper contents between 5.0 and 7.1 wt.% (6.0 ± 1.0 wt.% on average) and aluminium contents between 2.8 and 7.2 wt.% (3.6 ± 1.8 wt.% on average). These results indicate an inhomogeneity of the original material, which is due to macroscopic flakes of elemental copper and aluminium, which might be removed mechanically with improved disassembly and sorting processes.

Thermal study of the spent graphitic Li-NMC battery material

The thermal behaviour of the given spent battery material was investigated by thermogravimetric (TG) and differential thermogravimetric (DTG) analyses between room temperature and 1000 °C. Within this temperature range a total mass loss of approximately 40 % compared to the raw material is obtained. The thermolysis can be divided into three main steps, shown by the TG (blue) and DTG (red) curves in Figure 3. In the range from room temperature to 150 °C, there is a mass loss of 7.5 % and above this temperature, in the range from 150 to 400 °C the mass loss is 8.0 %. The most significant mass loss of 23.5 % occurs between 400 and 800 °C.

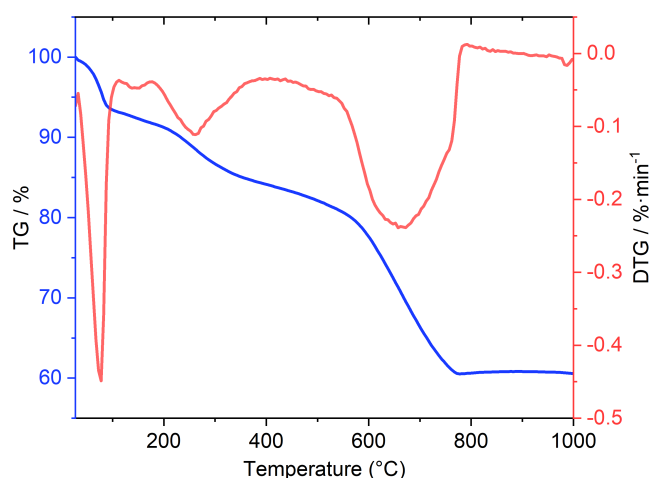


Figure 3. Thermal analysis of spent graphitic NMC LIB material heated to 1000 °C in an open corundum crucible with an airflow of 60 ml/min and a heating rate of 2 K/min (blue = thermo gravimetry; red = differential thermo gravimetry).

The mass losses obtained at lower temperatures suggest that several volatile fractions are released between 50 °C and 400 °C. These can be attributed to the volatilization of the residual electrolyte and other organic compounds, as previously described by other groups.^[8a] For our given material, different types of electrolyte have to be considered, due to different battery manufacturers. The total mass loss in this temperature range is approximately 16 %.

However, this figure should only be considered as characteristic for the given powder, which was subjected to a mechanical-vacuum-thermo pre-treatment. Multiple, separate reactions in an argon atmosphere resulted in a similar mass loss of 15-25 %, indicating the loss of electrolyte, rather than an oxidation of the binder or carbon up to 550 °C.

The mass loss of 23.5 % in the temperature range of 400 to 800 °C in air corresponds to the oxidation of graphite and organic binder.^[17] This gives a total mass loss of approximately 39 % for the thermolysis up to 800 °C. The mass loss in the region between

400 and 800 °C can be related to the loss of carbon, by oxidation in air.

Most of the organic binder is removed mechanically prior to this study, leaving only moderate amounts in the 'blackmass'. The decomposition of PVDF, the most commonly used binder, was not independently analysed in this study as it has been extensively studied by other groups. It has been shown that these compounds start decomposing at 300 °C, generating gaseous products such as HF, CO₂, H₂, and other hydrocarbon gases, which mostly react with the aluminium and lithium present in the spent battery material.^[18]

From this experiment with a continuous heating ramp of 2 K/min, the carbon loss can be seen to occur approximately above 400 °C. Subsequent steady-state annealing studies were carried out to analyse the carbon loss in more detail, showing a significant loss in the temperature range between 500 and 550 °C within a few hours.

Step 1: Thermal removal of graphite

Continuous heating of spent NMC battery material in open corundum crucibles in air at temperatures between 500 and 550 °C results in a decreasing graphite content over time. Following this finding, samples were treated at 525 °C with successively increasing reaction times, from two hours to 20 hours, and the products were periodically analysed by powder XRD, with the results shown in Figure 4.

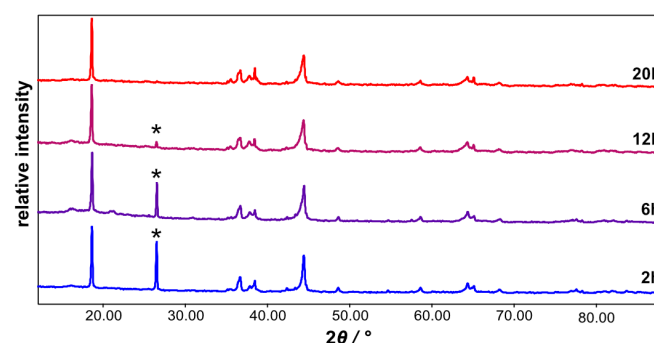


Figure 4. Powder XRD patterns (Cu-K_{α1} radiation) of the 'blackmass' showing the decreasing graphite content over time (graphite (002)-reflection marked with *) after treatment at 525 °C at 2-20 hours.^[15a]

The recorded XRD patterns of the thermally treated material show a clear signature of the original graphitic NMC material, plus the strongest PXRD (002)-reflection of graphite at $2\theta = 26.62^\circ$.^[15a] However, the intensity of this peak decreases and eventually disappears as the reaction time is prolonged from two hours (bottom) to 20 hours (top) of heating (see Figure 4).

Step 2: Acid leaching of thermally treated Li-NMC material

A simple method for acid leaching would be to use citric, malic or acetic acid, as these could directly help with the complexation required in the subsequent processing. Although the malic acid leaching has been reported for Li-NMC battery material,^[19] it was not feasible for our material, which was obtained from a commercial recycling process. Supporting the leaching with extensive amounts of H₂O₂ without the use of leaching aids (like HCl or H₂SO₄) only resulted in its catalytic decomposition in the presence of manganese oxide and iron oxide as has been extensively investigated.^[14] Due to the presence of iron oxides in the material used in this study, this issue is more significant compared to some other laboratory scale investigations, where batteries are neatly disassembled by hand.^[8c, 10c, 17, 20]

Reasonable conventional leaching procedures are to dissolve powders in aqueous solutions of stronger acids such as HNO₃ or HCl and H₂O₂, followed by citrate complexation and pyrolysis to obtain fresh Li-NMC battery material.^[21] The combination of 2 M HCl and a small quantity of H₂O₂ proved to be an effective leaching solution for the genuine, thermally treated 'blackmass' material used in this study (see experimental section for details). TXRF measurements of the solid residues (<10 % of starting mass) from the first filtration indicate that the mixture contains approximately 82 wt.% Al, Fe and Cu impurities and approximately 6 wt.% Ni, Mn, Co material, with the remainder being trace elements (Table S1).

Step 3: pH-controlled precipitation

A well-established metal separation method is the pH-controlled precipitation. We tested the feasibility of removing the aluminium, iron and copper contaminants in the obtained mixture by slowly adding LiOH to the acidic solution until the required acidity is reached. Ideally, the pH would be set to promote the precipitation of the impurities and leave the NMC-ions in solution. In practice, this method will inevitably result in some loss of nickel, manganese or cobalt, leading to a change in composition, which is affected by the acidity during precipitation. Depending on the further use of the cathode material, it is possible either to aim for a different composition or to add components to the mixture in the subsequent precursor process to obtain the desired product.

For our material, we still found 1.6 wt.% copper when precipitating at pH = 5.3 while we recorded significant loss of mainly nickel, followed by iron (Table S1). TXRF measurements of the product obtained after subsequent processing and washing revealed an Ni:Mn:Co ratio of 4.86:3.09:2.06.

Figure 5 shows PXRD patterns of new Li-NMC cathode material (bottom) which is in good accordance with Li(Ni_{0.5}Mn_{0.3}Ni_{0.2})O₂ and the recovered LiCl·H₂O and Li₂CO₃ (top).^[22-23] in terms of iron and aluminium it is therefore a fresh Li-NMC 532 product with 1.6 wt.% copper impurities. As the 'blackmass' contains copper in the form of macroscopic flakes, well-established mechanical separation methods might reduce the content even more.

The impact of specific contaminants on the functionality of NMC materials has been investigated, demonstrating that impurities

such as aluminium exert a more pronounced influence than other contaminants.^[24] This understanding enables the development of an optimised recycling process, with a particular focus on targeted impurity removal.

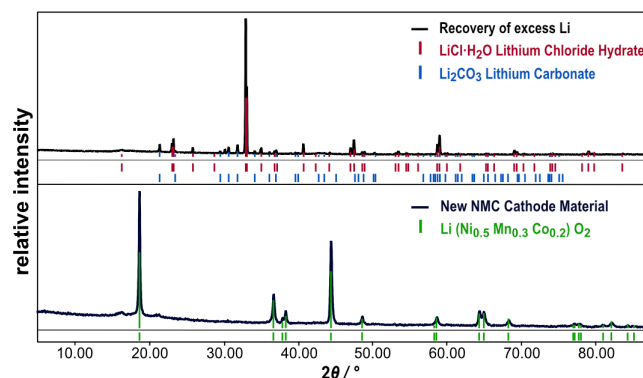


Figure 5. Recorded powder XRD patterns (Cu-K_{α1} radiation) of the washed Li-NMC material after the sol-gel processing (bottom) and recovered lithium compounds (top).^[22] The Bragg positions (in corresponding colours) are in good accordance to corresponding reference phases.^[23]

In attempt to remove the contaminants while preserving the NMC 622 composition, we optimized the pH-controlled precipitation and filtration to a pH value of 4.2 and combined it with an electrochemical processing step. The precipitation conditions are sufficient to completely remove iron and aluminium without affecting copper and NMC. TXRF measurements were conducted on the evaporated solution, which yielded an NMC ratio of 6.00:2.03:1.97. The copper content was found to be 5.8 wt.%, and no traces of aluminium or iron were detected (see Table S1). Subsequently, copper can be removed electrochemically from the filtrate leaving only NMC in the solution.

Step 4: Electrochemical removal and recovery of copper

By applying a voltage of 1.6 V between a graphite anode and copper cathode in solution, copper could be removed completely over the course of four hours of electrolysis. TXRF analysis of the obtained final product revealed an Ni:Mn:Co ratio of 6.01:2.1:1.9 which is very close to the desired 622 composition.

Step 5-7: Synthesis of fresh Li-NMC material

In general, the particle size and morphology of the as-obtained carbon-free Li-NMC 622 material can be conditioned in a subsequent process to produce a ready-to-use cathode material. Several methods have been described for the synthesis of Li(Ni,Mn,Co)O₂.^[1, 21, 25] A commonly used method for the synthesis of metal oxides such as garnets (Y₃Fe₅O₁₂)^[26] or Li(Ni,Mn,Co)O₂^[7b, 27] is the aqueous sol-gel method, as this method is known to allow precise control of the composition and morphology of these materials.

The crystalline Li-NMC material obtained from the sol-gel processing (Step 7) is compared with a Li-NMC 622 material prepared under similar conditions, but starting from pure metal nitrates solvated in H₂O, followed by citrate complexation and pyrolysis to obtain fresh Li-NMC battery material. The product of the calcination (Step 6) is washed to remove and recover excess lithium in the form of LiCl and Li₂CO₃ (Step 7, compare Figure 5). A comparison of the powder patterns of both materials after sol-gel synthesis is presented in Figure 6 and shows almost identical patterns, with Bragg positions in good agreement with the corresponding reference phases.^[16]

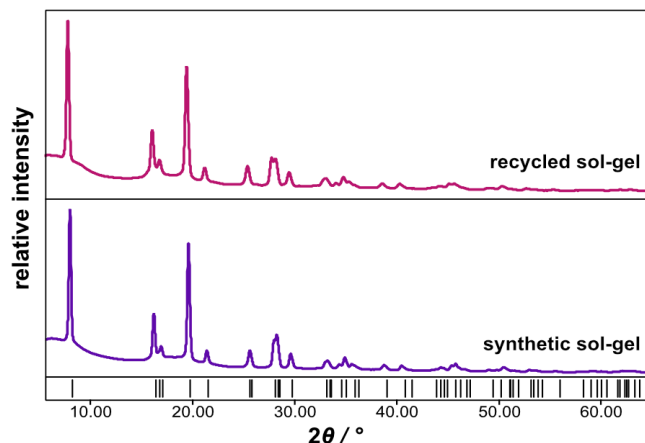


Figure 6. Recorded powder XRD patterns (Mo-K α radiation) of Li-NMC material after the sol-gel processing, departing from recycled material (top) and from metal nitrates (bottom). The Bragg positions (black) are in good accordance to corresponding reference phases.^[16]

Crystal structure refinement of graphite-free Li-NMC material

In order to evaluate the structural identity of our recycled Li-NMC 622 material (and Li-NMC 532 material, Figure S4) a full refinement with the FullProfSuite^[28] was performed on the recorded XRD pattern of the recycled material using the crystallographic data of LiNiO₂, space group $R\bar{3}m$,^[29] as starting values. The ratios of nickel, manganese and cobalt were fixed to the refined TXRF ratios. The fit between the observed (red) and calculated (black) pattern, shown in Figure 7, reveals an excellent congruence without any significant side phases being detectable. Thus, we can conclude, that the elements nickel, manganese and cobalt are still fully present in the LiNiO₂ type structure. The small particle size was considered using a spherical harmonic correction implemented in the FullProfSuite. The isotropic refinement converged in good agreement ($R_{\text{Bragg}} = 0.3802$; $\chi^2 = 1.10$; $R_p = 1.1232$, and $wR_p = 1.4175$) with around 5.8 % Ni²⁺ ions in Li⁺ sites and therefore the observed habitus (SEM, see Figure 8) is more cubic/octahedral-like compared to the ideal 2D layered structure (expected for Li⁺/Ni²⁺ mixed site <3.8 %).

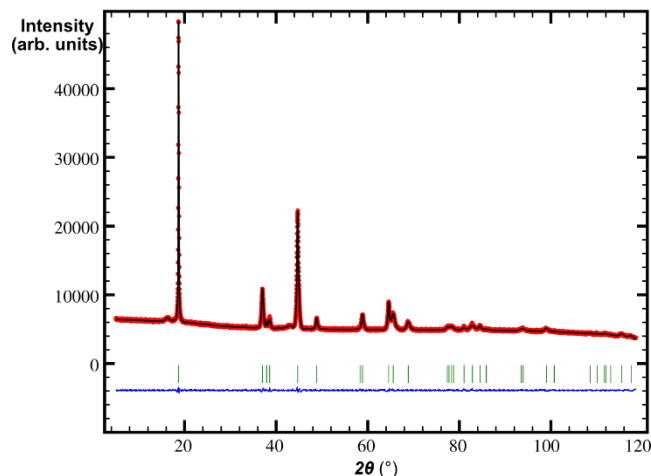


Figure 7. Rietveld fit of the Cu-K α_1 PXRD pattern of the fresh Li-NMC material. The observed pattern (red dots) is superimposed with the calculated pattern (black line). Green ticks mark the Bragg reflections of the calcined Li-NMC 622 material. The difference curve between the observed and calculated pattern is shown in the lower part of the graph (blue line). Broad reflections at 2θ values 16.2° and 43.1° emerge from the sample carrier foil.

Scanning electron microscopy (SEM) analysis of the obtained material

SEM images of the new Li-NMC 622 product are shown in Figure 8, ranging from 100x to 50.000x magnification. Homogeneous particles with high crystallinity are well distributed. The particle size ranges from 50 to 250 nm, suggesting a high surface area and short lithium diffusion lengths.

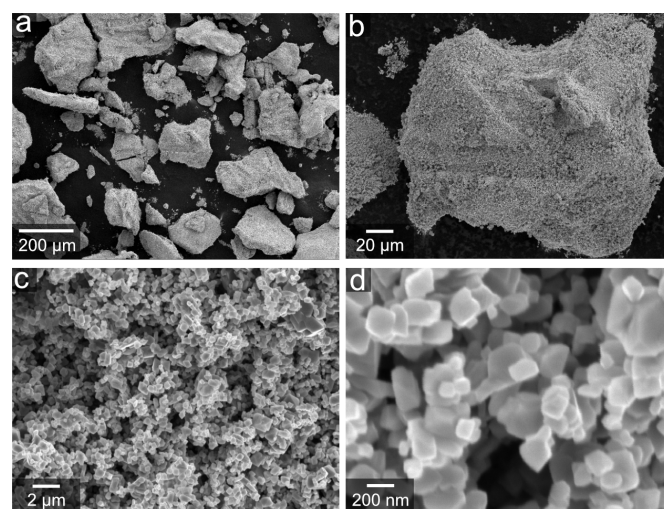


Figure 8. Electron micrographs of the obtained NMC 622 material from (a) 100 times to (d) 50000 times magnification.

Conclusions

Recycling of lithium-ion battery materials is an important process for sustainability and resource conservation. There have been several methods reported in the literature for recycling these materials, such as pyrometallurgical processes, hydrometallurgical processes, and direct recycling methods. Each method has its own advantages and challenges.

Our aim is to develop a simple and cost-efficient methodology, departing from a commercially recycled battery material that would not require a separation of the relevant elements lithium, nickel, manganese and cobalt.

The so-called 'blackmass' used in this study is a powdered mixture obtained from a commercial battery shredding process, containing the graphite anode, the Li-NMC cathode and several impurities originating from all kinds of battery components (aluminium, copper, iron, binder, etc.).

The carbon components (graphite, binder etc.) were completely removed in a moderate heating process at 550 °C. Iron and aluminium impurities were removed by precipitation at pH 4.2, and the residual copper was removed and recovered electrochemically.

The purified Li-NMC precursor solution was subjected to an aqueous sol-gel route using citric acid. After calcination and washing, fresh Li-NMC material was obtained with an unchanged initial composition. We note here, that the Li-NMC precursor solution can be used in other established synthesis routes, such as NaOH precipitation to control the morphology,^[30] or to tailor the composition for a specific application by adding nickel, manganese or cobalt.

The crystal structure of the obtained recycled crystalline $\text{Li}(\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2})\text{O}_2$ material was confirmed by X-ray and elemental analysis and its homogeneous crystallinity verified by scanning electron microscopy. However, its feasibility for the use as a new cathode material is not yet demonstrated. We suggest coin cell electrochemical performance measurements using the recycled Li-NMC cathode material to validate the performance.

It is obvious that mechanical separation and shredding of spent batteries is the first step in an industrial recycling process. However, the diverse construction of lithium batteries does make the disassembly and recycling a challenging process. We emphasise the importance of thorough battery construction to make subsequent treatments and recycling steps as lucrative as possible.

Experimental Section

Thermogravimetric analysis (TG, DTG) was performed with a Netzsch Jupiter, STA 449 F3 apparatus between room temperature and 1000 °C with a heating and cooling rate of 2 K·min⁻¹ in a corundum crucible.

Thermal treatment of the spent Li-NMC battery material was performed in a corundum boat which was inserted in a quartz tube.

The quartz tube was then inserted in a tube oven which was positioned away from the horizontal plane with an angle (ca. 10°) to allow a natural convection of the surrounding air. Reactions were performed at 500–550 °C and reaction times between 6 and 48 h. The best conditions for the removal of graphite from the Li-NMC 622 battery material were 525 °C and 20 hours.

Precursor method to process thermally treated Li-NMC battery material. The battery material, recycled via dry carbon removal was dissolved (25 g/l) in 5 M HCl and 1/10 volume equivalents of concentrated H₂O₂ (30 %). The mixture was stirred over night at room temperature and then increased to 80 °C for an hour. Insoluble components were then filtrated off. By adding 2 M LiOH the pH was slowly adjusted to 4.2 (5.3 for NMC 532), resulting in the precipitation of mostly aluminium and iron impurities. These were filtered off and the remaining solution was electrochemically treated for four hours with an applied voltage of 1.6 V using a graphite anode and a copper cathode. The solution was then dried using a citrate sol-gel method (the amount of citric acid used was four times the initial quantity of black mass, corresponding to approximately five molar equivalents of citric acid). The resulting powder was then thermally treated in a Carbolite CWF1300 oven. Hereby, it was first heated at 460 °C for 6 hours and then at 775 °C for 10 hours. All heating and cooling rates were at 5 K/min. To remove LiCl and Li₂CO₃, the powder was washed with H₂O.

A reference Li-NMC 532 cathode material was synthesised from the chlorides (735.66 mg of NiCl₂·6H₂O; 167.00 mg of MnCl₂·2H₂O; 245.47 mg of CoCl₂·6H₂O; 555.92 mg of LiOH; 3.5 g citric acid) using a similar citrate sol-gel method.

Additionally, a NMC 622 material was synthesized following a nitrate-route (294 mg of LiNO₃·3H₂O; 510 mg of Ni(NO₃)₂·6H₂O; 111 mg of Mn(NO₃)₂·6H₂O; 126 mg of Co(NO₃)₂·6H₂O), which were dissolved in water together with 5 g of citric acid and then dried. The obtained powder was then heated at 460 °C for 6 hours followed by a step at 775 °C for 10 hours. All heating and cooling rates were at 2 K/min.

Powder X-ray diffraction (PXRD). Diffraction data for PXRD studies and refinement on Li(Ni,Mn,Co)O₂ were collected using a StadiP diffractometer (Stoe, Darmstadt) with Ge monochromated Cu-K_{α1} radiation (λ = 1.54140 Å) with a Mythen1 Detector and a Rigaku XtaLab Synergy-S diffractometer with Mo-K_α radiation (λ = 0.71073 Å) and a graphite mirror. Measurements were performed with small amounts of crystalline powder, fixed to a micro loop using perfluoropolyalkylether.

Total Reflection X-ray Fluorescence spectroscopy (TXRF) studies. TXRF studies were performed using a S2 Picofox (Bruker AXS Microanalysis, Berlin, Germany) equipped with a Mo X-ray tube, which was operated at 50 kV and 600 μA. The measurement period for each sample was 1000 s (live time). Fitting of the resulting spectra was done using the Spectra software (Bruker Nano GmbH) in the super bias mode (maximum stripping cycles of 2000).

Scanning Electron Microscopy (SEM) studies. The sample surfaces were investigated with the scanning electron microscope JEOL JSM-6500F.

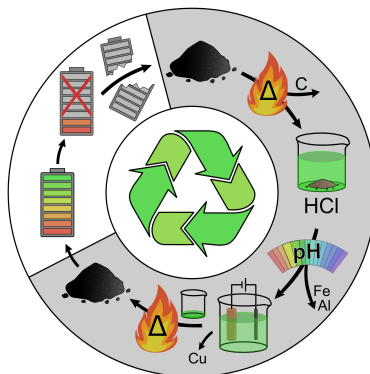
Acknowledgements

We like to express our gratitude to Priv.-Doz. Dr. Michael Marks (FB Geowissenschaften, Univ. Tübingen) for the TXRF measurements and helpful discussions, and Dr. Ronny Löffler (Center for Light-Matter-Interaction, Sensors and Analytics, LISA⁺, Univ. Tübingen) for scanning electron micrographs. Tim Werz performed electrochemical experiments during his lab course.

Keywords: Li-NMC 622 recycling • industry battery waste • pH-dependant precipitation • electrolysis • sol-gel synthesis

- [1] a) K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough, *Mater. Res. Bull.* **1980**, *15*, 783-789; b) K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough, *Solid State Ionics* **1981**, *3-4*, 171-174.
- [2] M. Winter, B. Barnett, K. Xu, *Chem. Rev.* **2018**, *118*, 11433-11456.
- [3] a) X. Chen, W. Shen, T. T. Vo, Z. Cao, A. Kapoor, in *2012 10th International Power & Energy Conference (IPEC)*, **2012**, pp. 230-235; b) F. H. Gandoman, J. Jaguemont, S. Goutam, R. Gopalakrishnan, Y. Firouz, T. Kalogiannis, N. Omar, J. Van Mierlo, *Appl. Energy* **2019**, *251*, 113343.
- [4] a) C. Pillot, in *36th Annual International Battery Seminar & Exhibit. Avicenne Energy*, **2019**; b) J. Neumann, M. Petranikova, M. Meeus, J. D. Gamarra, R. Younesi, M. Winter, S. Nowak, *Adv. Energy Mater.* **2022**, *12*, 2102917.
- [5] a) H. Chen, J. Shen, *PLOS ONE* **2017**, *12*, e0185922; b) T. Elwert, D. Goldmann, F. Römer, M. Buchert, C. Merz, D. Schueler, J. Sutter, *Recycling* **2016**, *1*, 25-60; c) G. Harper, R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines, P. Anderson, *Nature* **2019**, *575*, 75-86.
- [6] a) Y. Zhao, O. Pohl, A. I. Bhatt, G. E. Collis, P. J. Mahon, T. Rütger, A. F. Hollenkamp, *Sustain. Chem.* **2021**, *2*, 167-205; b) R. E. Ciez, J. Whitacre, *Nat. Sustain.* **2019**, *2*, 148-156; c) N. Nitta, F. Wu, J. T. Lee, G. Yushin, *Mater. Today* **2015**, *18*, 252-264.
- [7] a) H. Pinegar, Y. R. Smith, *J. Sustain. Met.* **2019**, *5*, 402-416; b) H. Pinegar, Y. R. Smith, *J. Sustain. Met.* **2020**, *6*, 142-160.
- [8] a) G. Zhang, Y. He, Y. Feng, H. Wang, X. Zhu, *ACS Sustainable Chem. Eng.* **2018**, *6*, 10896-10904; b) G. Zhang, Y. He, H. Wang, Y. Feng, W. Xie, X. Zhu, *J. Cleaner Prod.* **2019**, *231*, 1418-1427; c) L. Sun, K. Qiu, *J. Hazard. Mater.* **2011**, *194*, 378-384; d) Y. He, T. Zhang, F. Wang, G. Zhang, W. Zhang, J. Wang, *J. Cleaner Prod.* **2017**, *143*, 319-325; e) J. Yu, Y. He, Z. Ge, H. Li, W. Xie, S. Wang, *Sep. Purif. Technol.* **2018**, *190*, 45-52.
- [9] a) L. Sun, Y. Liu, R. Shao, J. Wu, R. Jiang, Z. Jin, *Energy Storage Mater.* **2022**, *46*, 482-502; b) M. A. Rahman, G. Song, A. I. Bhatt, Y. C. Wong, C. Wen, *Adv. Funct. Mater.* **2016**, *26*, 647-678; c) Y. Cui, *Nat. Energy* **2021**, *6*, 995-996.
- [10] a) J. Li, P. Shi, Z. Wang, Y. Chen, C.-C. Chang, *Chemosphere* **2009**, *77*, 1132-1136; b) J. Guan, Y. Li, Y. Guo, R. Su, G. Gao, H. Song, H. Yuan, B. Liang, Z. Guo, *ACS Sustainable Chem. Eng.* **2017**, *5*, 1026-1032; c) L. Li, J. Ge, F. Wu, R. Chen, S. Chen, B. Wu, *J. Hazard. Mater.* **2010**, *176*, 288-293; d) Y. M. Park, H. Lim, J.-H. Moon, H.-N. Lee, S. H. Son, H. Kim, H.-J. Kim, *Metals* **2017**, *7*, 303.
- [11] a) R. Gao, C. Sun, T. Zhou, L. Zhuang, H. Xie, *ChemistrySelect* **2020**, *5*, 6482-6490; b) P. Ning, Q. Meng, P. Dong, J. Duan, M. Xu, Y. Lin, Y. Zhang, *Waste Manage. (Oxford)* **2020**, *103*, 52-60; c) K. Wang, G. Zhang, M. Luo, M. Zeng, *J. Environ. Chem. Eng.* **2022**, *10*, 108250.
- [12] a) M. Esmaeili, S. O. Rastegar, R. Beigzadeh, T. Gu, *Chemosphere* **2020**, *254*, 126670; b) T. Or, S. W. Gourley, K. Kaliyappan, A. Yu, Z. Chen, *Carbon Energy* **2020**, *2*, 6-43.
- [13] G. Zhang, Z. Du, Y. He, H. Wang, W. Xie, T. Zhang, *Sustainability* **2019**, *11*, 2363.
- [14] a) F. Haber, J. Weiss, W. J. Pope, *Proc. R. Soc. London, Ser. A* **1934**, *147*, 332-351; b) S.-S. Lin, M. D. Gurol, *Environ. Sci. Technol.* **1998**, *32*, 1417-1423; c) M. A. Hasan, M. I. Zaki, L. Pasupulety, K. Kumari, *Appl. Catal., A* **1999**, *181*, 171-179; d) D. Broughton, R. Wentworth, *J. Am. Chem. Soc.* **1947**, *69*, 741-744; e) D. Broughton, R. Wentworth, M. Laing, *J. Am. Chem. Soc.* **1947**, *69*, 744-747.
- [15] a) P. H. Gamlen, J. W. White, *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 446-455; b) H. M. Otte, *J. Appl. Phys.* **1961**, *32*, 1536-1546.
- [16] a) Y.-J. Gu, Y.-B. Chen, H.-Q. Liu, Y.-M. Wang, C.-L. Wang, H.-K. Wu, *J. Alloys Compd.* **2011**, *509*, 7915-7921; b) S. C. Yin, Y. H. Rho, I. Swainson, L. F. Nazar, *Chem. Mater.* **2006**, *18*, 1901-1910.
- [17] F. Wang, T. Zhang, Y. He, Y. Zhao, S. Wang, G. Zhang, Y. Zhang, Y. Feng, *J. Cleaner Prod.* **2018**, *185*, 646-652.
- [18] a) Y. Ji, C. T. Jafvert, N. N. Zyaykina, F. Zhao, *J. Cleaner Prod.* **2022**, *367*, 133112; b) M. Wang, Q. Tan, L. Liu, J. Li, *ACS Sustainable Chem. Eng.* **2019**, *7*, 12799-12806; c) C. Hanisch, T. Loellhoeffel, J. Diekmann, K. J. Markley, W. Haselrieder, A. Kwade, *J. Cleaner Prod.* **2015**, *108*, 301-311; d) D. Song, X. Wang, E. Zhou, P. Hou, F. Guo, L. Zhang, *J. Power Sources* **2013**, *232*, 348-352; e) X. X. Zhang, Q. Xue, L. Li, E. Fan, F. Wu, R. J. Chen, *ACS Sustainable Chem. Eng.* **2016**, *4*, 7041-7049; f) Y. Chen, N. Liu, Y. Jie, F. Hu, Y. Li, B. P. Wilson, Y. Xi, Y. Lai, S. Yang, *ACS Sustainable Chem. Eng.* **2019**, *7*, 18228-18235; g) J. B. DeLisio, X. Hu, T. Wu, G. C. Egan, G. Young, M. R. Zachariah, *J. Phys. Chem. B* **2016**, *120*, 5534-5542.
- [19] L. Yao, H. Yao, G. Xi, Y. Feng, *RSC Adv.* **2016**, *6*, 17947-17954.
- [20] L. Li, X. Zhang, M. Li, R. Chen, F. Wu, K. Amine, J. Lu, *Electrochem. Energy Rev.* **2018**, *1*, 461-482.
- [21] S. Laubach, S. Laubach, P. C. Schmidt, D. Enslin, S. Schmid, W. Jaegermann, A. Thißen, K. Nikolowski, H. Ehrenberg, *Phys. Chem. Chem. Phys.* **2009**, *11*, 3278-3289.
- [22] a) Y. Idemoto, J. W. Richardson, N. Koura, S. Kohara, C.-K. Loong, *J. Phys. Chem. Solids* **1998**, *59*, 363-376; b) E. Weiss, H. Hensel, H. Kühn, *Chem. Ber.* **1969**, *102*, 632-642.
- [23] Y.-J. Gu, Q.-G. Zhang, Y.-B. Chen, H.-Q. Liu, J.-X. Ding, Y.-M. Wang, H.-F. Wang, L. Chen, M. Wang, S.-W. Fan, Q.-F. Zang, X.-L. Yang, *J. Alloys Compd.* **2015**, *630*, 316-322.
- [24] S. Krüger, C. Hanisch, A. Kwade, M. Winter, S. Nowak, *J. Electroanal. Chem.* **2014**, *726*, 91-96.
- [25] J. Yu, Z. Han, X. Hu, H. Zhan, Y. Zhou, X. Liu, *J. Power Sources* **2013**, *225*, 34-39.
- [26] E. Garskaite, K. Gibson, A. Leleckaite, J. Glaser, D. Niznansky, A. Kareiva, H. J. Meyer, *Chem. Phys.* **2006**, *323*, 204-210.
- [27] C. K. Lee, K.-I. Rhee, *J. Power Sources* **2002**, *109*, 17-21.
- [28] a) J. Rodriguez-Carvajal, *Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr*, **1990**, 127; b) J. Rodriguez-Carvajal, T. Roisnel, *IUCr-News* **1998**, *20*, 35-36.
- [29] W. Li, J. N. Reimers, J. R. Dahn, *Phys. Rev. B* **1992**, *46*, 3236-3246.
- [30] T. Entwistle, E. Sanchez-Perez, G. J. Murray, N. Anthonisamy, S. A. Cussen, *Energy Rep.* **2022**, *8*, 67-73.

A simple and cost-effective recycling process of spent graphitic Li-NMC battery material is presented for 'blackmass', obtained from a commercial thermomechanical battery segmentation process. Our procedure involves a combination of thermal treatment, leaching and electrolysis to remove impurities without altering the NMC starting composition. Fresh Li-NMC 622 cathode material is synthesized using an aqueous sol-gel method as a proof of concept.



*Fabian Grahlow, Patrick Schmidt, and
Hans-Jürgen Meyer*

Page No. – Page No.

**A complete cathode recovery cycle
of an exhausted and dismantled
lithium battery material**

Supporting Information

A complete cathode recovery cycle of an exhausted and dismantled lithium battery material

Fabian Grahlow ^a, Patrick Schmidt ^a, Hans-Jürgen Meyer ^{*a}

^a Section for Solid State and Theoretical Inorganic Chemistry, Institute of Inorganic Chemistry, Auf der Morgenstelle 18, Eberhard Karls Universität Tübingen, D-72076 Tübingen, Germany, juergen.meyer@uni-tuebingen.de

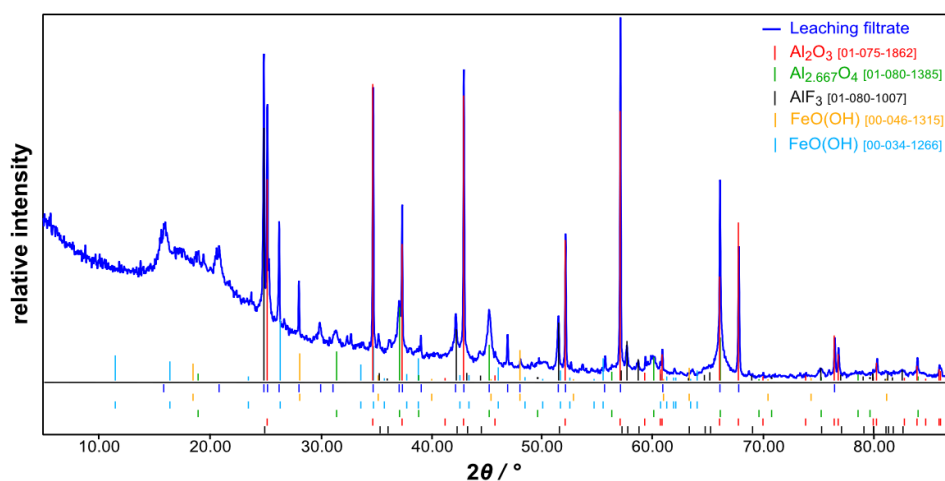


Figure S1: Powder XRD pattern ($\text{Cu-K}\alpha_1$ radiation) of the leaching filtrate containing mostly unsoluble aluminium and iron compounds.

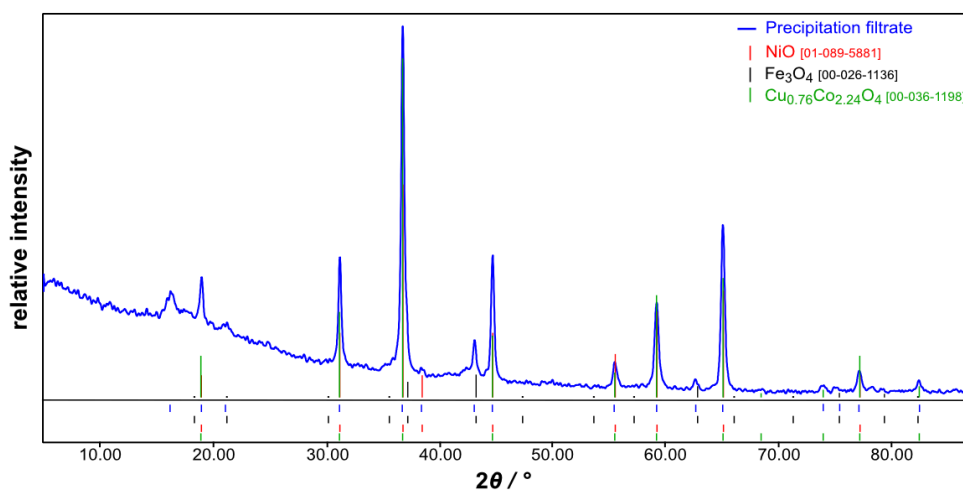


Figure S2: Powder XRD pattern ($\text{Cu-K}\alpha_1$ radiation) of the filtrate after pH-controlled precipitation of impurities.

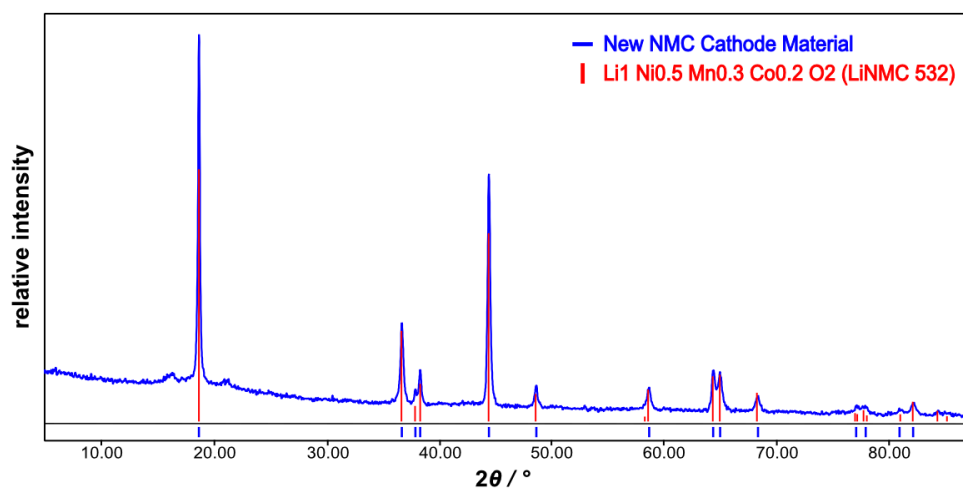


Figure S3: Powder XRD pattern (Cu-K α_1 radiation) of the fresh NMC 532 material.

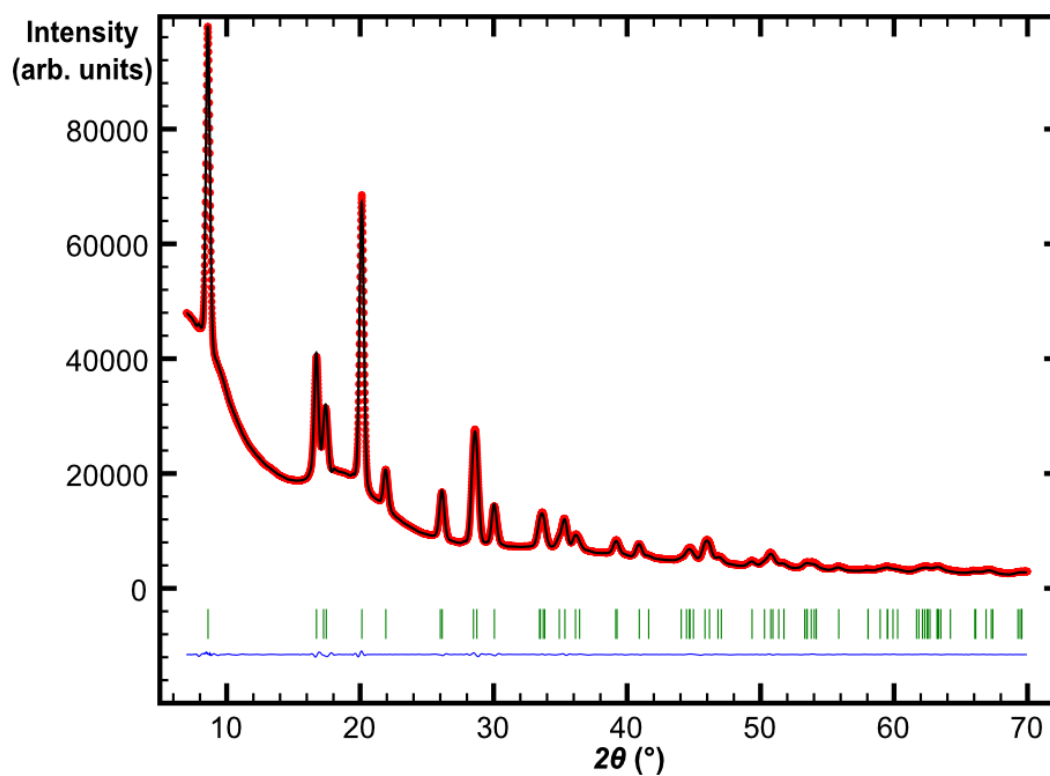


Figure S4. Rietveld fit of the Mo-K α XRD pattern of the as-obtained, graphite-free NMC LIB material. The observed pattern (red dots) is superimposed with the calculated pattern (black line). Green ticks mark the Bragg reflections of the calcined NMC 532 LIB material. The difference curve between the observed and calculated pattern is shown in the lower part of the graph (blue line).

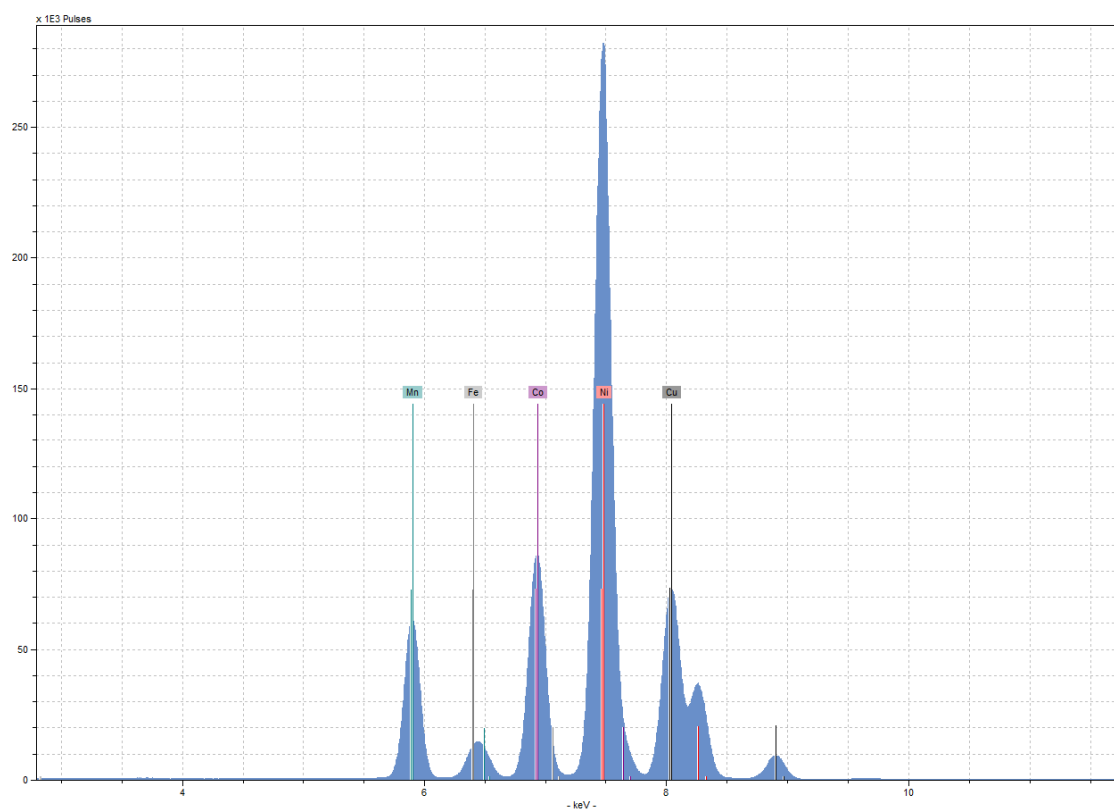


Figure S5. Section of the TXRF spectrum (Mo-K α) of the calcinated blackmass, showing copper and iron impurities.

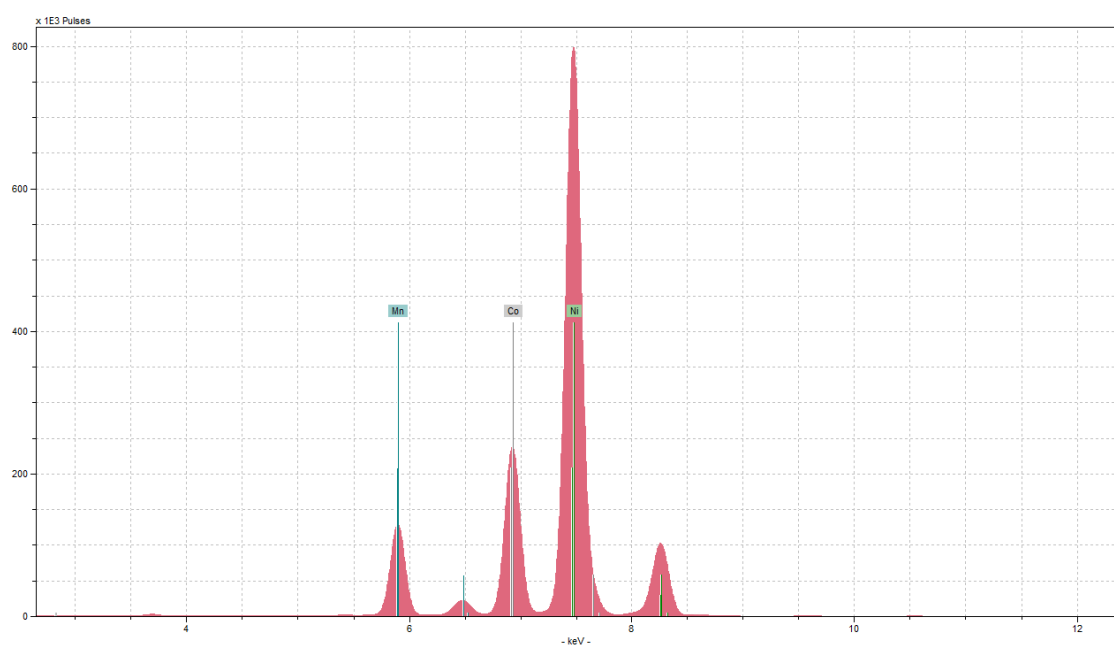


Figure S6. Section of the TXRF spectrum (Mo-K α) of the purified, fresh Li-NMC cathode material.

Table S1: Total Internal Reflection X-Ray Fluorescence (TXRF) measurements of the battery material at each step of the recycling process. The element contents are given as Mass-% of each sample.

	Raw Material	Thermally treated	Leaching Filtrate	pH = 4.2 solution	pH = 4.2 + electrolysis (NMC 622)	pH = 5.3 Precipitation Filtrate	pH = 5.3 (NMC 532)
Step	1	2	3	4-6			
Ni	52.7	52.2	3.5	57.1	60.7	38.7	48.7
Mn	18.3	20.4	0.6	18.2	17.5	5.7	29.0
Co	18.8	19.3	2.0	18.9	21.7	12.0	20.7
Fe	2.9	1.7	10.7	0.0	0.0	33.1	0.0
Cu	6.3	5.8	3.9	5.8	0.0	22.5	1.6
Al	2.1	3.2	67.5	0.0	0.0	7.1	0.0