

Defect-Governed Optoelectronics in Copper-based Solar Cells

To obtain the academic degree of

Doctor of Engineer (Dr.-Ing)

From the Department of
Electrical Engineering and Information Technology
Karlsruhe Institute of Technology (KIT)

Dissertation

submitted by

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Date of oral exam: 14.09.2026

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Zur Erlangung des akademischen Grades eines
Doktors der Ingenieurwissenschaften (Dr.-Ing.)

von der KIT-Fakultät für
Elektrotechnik und Informationstechnik
des Karlsruher Instituts für Technologie (KIT)

angenommene

Dissertation

von

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Geboren in: Kolkata, Indien

Tag der mündlichen Prüfung: 14.09.2026

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Kurzfassung

Kupferbasierte, bleifreie lichtabsorbierende Halbleitereröffnen einen möglichen neuen Weg zu Dünnschichtphotovoltaik indem sie die wesentlichen Vorteile der Halogenidperowskite, durch die sie inspiriert wurden, erhalten: Lösungsprozessierbarkeit, starke optische Absorption und Defekttoleranz. Gleichzeitig adressieren sie zwei grundlegende Einschränkungen der vorherrschenden organischen Bleihalogenidfamilie: das Vorhandensein von toxischem Blei und die Verwendung flüchtiger organischer A-Platz-Kationen. Der Ersatz organischer Kationen durch ein anorganisches Metallkation ist nicht lediglich eine durch Stabilitätsüberlegungen motivierte Substitution; er verändert die Chemie des Gitters, die Defektlandschaft und die Mechanismen, welche die Ladungsträgererzeugung und -extraktion bestimmen. In dieser Arbeit wird Kupfer gezielt als Designelement betrachtet: als kleines, redoxaktives Kation, das verschiedene Koordinationsumgebungen, einschließlich Zwischengitterplätzen, besetzen und dadurch Phasen stabilisieren kann, die für Perowskite mit organischen Kationen nicht zugänglich sind. Die hier entwickelte zentrale These lautet, dass das optoelektronische Verhalten kupferbasierter, bleifreier, perowskitinspirierter Halbleiter durch intrinsische Zwischengitterdefekte bestimmt wird. Ihre funktionellen Eigenschaften ergeben sich daraus, wie Kupfer in defektreiche Gitter eingebaut, innerhalb dieser umverteilt und dort immobilisiert wird, und nicht aus einer idealisierten Ausgangsstruktur. Eine weitere wesentliche Motivation dieser Arbeit ist die korrekte Zuordnung der entsprechenden Kristallphasen. Die Arbeit zeigt, dass die verbreitete Praxis, Kupfer-Pniktogen-Iodide vorwiegend anhand ihrer chemischen Formel den Strukturfamilien „Rudorffit/Caswellsilverit“ zuzuordnen irreführend sein kann: Zusammensetzungen, die in einer rudorffitähnlichen stöchiometrischen Form dargestellt werden können, weisen im Festkörper nicht zwangsläufig das kanonische Koordinationsmotiv auf.

Diese Arbeit entwickelt daher eine einheitliche Struktur-Eigenschaft-Bauelement-Beziehung, in der die Phasenidentität experimentell bestimmt und anschließend unmittelbar mit energetischer Unordnung, der Ausrichtung der Bandkanten und dem photovoltaischen Verhalten verknüpft wird. Die Dünnschichtverarbeitung, insbesondere unter lösungsbasierten Bedingungen bei geringen Temperaturen, führt zu Mikrostrukturen, die sich nicht zuverlässig erfassen lassen, wenn eine Strukturfamilie allein aus der Zusammensetzung abgeleitet wird. Für die

hier untersuchten Systeme zeigen Beugungs- und Mikrostrukturanalysen, dass Phasen mit derselben nominalen Stöchiometrie unterschiedliche Gitterstrukturen und Defektkonfigurationen annehmen können. Aus diesem Grund betrachtet diese Arbeit die experimentelle Bestimmung des Strukturmotivs und der Defektmikrostruktur als notwendigen Schritt, bevor Materialeigenschaften mit der Leistungsfähigkeit photovoltaischer Bauelemente in Beziehung gesetzt und Designregeln formuliert werden.

Die zentrale These wird anhand zweier repräsentativer Iodidsysteme entwickelt, die durch lösungsbasierte Niedertemperaturverfahren hergestellt wurden. In $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$ zeigt die Strukturanalyse ein Bi–I-Gerüst, das überschüssiges Kupfer auf Zwischengitterplätzen aufnimmt. Dadurch wird das Material nicht als einfaches Mitglied einer übernommenen Strukturfamilie, sondern als ein durch Zwischengitterbesetzung bestimmter Halbleiter neu eingeordnet. Diese durch Zwischengitterbesetzung ermöglichte Phasenbildung führt zu einer Bandlücke von 1,66 eV, thermischer Stabilität bis 333 °C und reproduzierbarem photovoltaischen Verhalten, wobei Dünnschichtbauelemente Spitzenwirkungsgrade von 0,65 % erreichen. Für Cu_3SbI_6 löst eine vergleichbare Neubewertung eine seit Langem bestehende Unklarheit: Die Schichten bilden kein wohlgeordnetes „Rudorffit“-Gerüst, sondern einen von CuI abgeleiteten, stapelungeordneten Festkörper, in dem Antimon über defektassoziierte Umgebungen eingebaut wird. Die resultierende Mikrostruktur ist intrinsisch metastabil, wird bereits durch geringe thermische oder mechanische Einwirkungen leicht umgeordnet und weist eine hohe direkte Bandlücke von 2,32 eV mit ausgeprägten Bandkantenausläufern auf. Trotz dieser Unordnung erreichen invertierte Solarzellen einen Wirkungsgrad von 1,02 %. Dies zeigt, dass die Leistungsfähigkeit letztlich durch die Kontrolle der Mikrostruktur und nicht allein durch die nominale Zusammensetzung begrenzt wird.

Um die Designregeln über Iodide hinaus zu verallgemeinern, analysiert die Arbeit außerdem die lichtabsorbierende Materialklasse von Cu_3BiS_3 (Wittichenit). Dessen starke Absorption und indirekte Bandlücke von 1,4 eV machen das Material zu einem vielversprechenden sulfidischen Kandidaten für die Dünnschichtphotovoltaik. Über Halogenide und Sulfide hinweg ergibt sich eine konsistente Schlussfolgerung: Phasenselektivität, die Regulierung von Zwischengitter- und anderen Defekten sowie das Grenzflächenmanagement bestimmen maßgeblich die Bauelementeigenschaften. Indem intrinsische Zwischengitterdefekte und Defektmikrostrukturen als gezielt nutzbare Werkzeuge der Materialentwicklung und nicht als zu beseitigende Nachteile betrachtet werden, stellt diese Arbeit einen kohärenten Rahmen für die zukünftige Entwicklung stabiler und effizienter kupferbasierter, bleifreier, perowskitinspirierter Solarzellen bereit.

Abstract

Copper-based, lead-free absorbers, inspired by halide perovskites, promise a route to thin-film photovoltaics that retains the key advantages of the perovskite solar cell paradigm: solution processability, strong optical absorption, and defect tolerance, while mitigating two fundamental limitations of the dominant organic–lead halide family: the presence of toxic lead and the use of volatile organic A-site cations. Replacing organic cations with an inorganic metal cation is not merely a substitution motivated by stability; it reshapes the chemistry of the lattice, the defect landscape, and the mechanisms that govern charge carrier generation and extraction. In this thesis, copper is treated as a purposeful design element: a small, redox-active cation that can occupy multiple coordination environments, including interstitial sites, and thereby stabilize phases that are inaccessible to organic-cation perovskites. The central claim developed here is that the optoelectronic properties of copper-based, lead-free, perovskite-inspired semiconductors is governed by native interstitials – their functional properties emerge from how copper is incorporated, redistributed, and immobilized within defect-rich lattices rather than from an idealized parent structure. Another key motivation for this work is the widespread practice of assigning copper–pnictogen iodides to “Rudorffite/ Caswellsilverite” structure families based primarily on chemical formula. The thesis shows why this shortcut can be misleading: compositions that can be written in a Rudorffite-like stoichiometric form do not necessarily realize the canonical coordination motif in the solid state.

This work establishes the phase identity of the thin films experimentally and examines how their structures influence energetic disorder, band-edge alignment, and solar cell device performance. Thin films, particularly when processed from solution at low-temperature conditions, yield microstructures; thus, the crystal structure formed in a thin film cannot be inferred solely from its nominal stoichiometry. In the systems studied here, diffraction and microstructural analyses show that phases with the same nominal stoichiometry can adopt different lattice structures and defect configurations. For this reason, experimental determination of the structural motif and defect microstructure is a necessary step before relating material properties to photovoltaic device performance and before formulating design rules.

The central thesis is developed through two representative iodide systems fabricated by low-temperature solution processing. In Cu_3SbI_6 , structural analysis shows that the films do not

form a well-ordered Rudorffite framework but instead adopt a CuI-derived stacking-disordered structure in which antimony is incorporated through defect-associated environments. The resulting structure is intrinsically metastable, readily reorganizing under mild thermal or mechanical perturbations, and exhibits a direct band gap of 2.32 eV with pronounced band-edge tailing. Despite this structural disorder, inverted solar cells based on these films reached a power conversion efficiency of more than 1 %, demonstrating photovoltaic functionality while highlighting the need for improved control of phase formation and microstructure. The structural analysis of $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$ reveals a Bi-I framework that accommodates excess copper on interstitial sites, identifying the material as an interstitially stabilized semiconductor rather than a conventional member of an established structure family. This interstitial-enabled phase exhibits a 1.66 eV band gap, thermal stability up to 333°C, and reproducible photovoltaic performance, yielding thin-film solar cells with peak efficiencies of 0.65 %.

To generalize the design rules beyond iodides, the thesis critically consolidates the absorber landscape of Cu_3BiS_3 (Wittichenite), whose strong absorption and 1.4 eV indirect band gap make it an attractive sulfide counterpart to the copper-pnictide halides. Across halides and sulfides, a consistent message emerges: phase selectivity, point-defect regulation, and interface management dominate the optoelectronic properties that influence device outcomes. By treating native interstitials and defect microstructures as engineering handles rather than imperfections to be eliminated, this work provides a coherent framework for designing copper-based, lead-free perovskite-inspired solar cells.

Publications

Published Articles

- Datta R., Herfert K.T., Többens D.M., Tischler P., Peterlechner M., Breitung B., Habrik M., Bruder J., Lemmer U., Schorr S., Colsmann A. and Röhm H., 2025. Photovoltaic properties of BiI_3 with copper interstitials. *EES Solar*, 1(5), pp.881-886.
- Datta R., Többens D.M., Habrik M., Garbev K., Peterlechner M., Schorr S., Colsmann A. and Röhm H., 2026. Defect-Stabilized Polytypism in Copper Antimony Iodide Solar Cells. (Submitted)

Articles in preparation

- Processing-Dependent Crystal Growth in Cu_3BiS_3 Thin-Films for CdS-free Solar Cells

Presentation at international conference

- Datta R., Colsmann A. and Röhm H. *Rudorffites: Lead-free Perovskite-Inspired Copper Pnictohalides For Next-Generation Photovoltaics*, MS&T24 Pittsburgh, **2024**, October 6-9, Oral presentation.

Supervised scientific work

Thesis

- Tim Effelberg, *Solution-Processed Cu_3BiS_3 for Thin Film Solar Cells*, Master thesis in Electrical Engineering and Information Technology, 2026.

Contents

Kurzfassung	i
Abstract	iii
Publications	v
Supervised scientific work	v
1 Introduction	1
1.1 Motivation and problem statement	1
1.2 From lead-halide perovskites to perovskite-inspired absorbers	6
1.2.1 From lead replacement to perovskite-inspired design	6
1.2.2 Positioning copper-based absorbers within the perovskite-inspired landscape	7
1.3 Why copper? Inorganic cation selection and defect-driven optoelectronics . . .	7
1.3.1 Copper and silver as group-IB cations in pnictohalides: similarities and differences	8
1.3.2 Why copper is inherently defect-relevant: native defects, self-doping, and disorder	8
1.3.3 Copper vs. silver: practical and mechanistic implications for lead-free photovoltaics	9
1.3.4 Extending the copper–pnictogen design space beyond halides: Cu_3BiS_3 as a sulfide benchmark	10
2 Fundamentals	13
2.1 Crystal Symmetry, Space Groups, and Relevant Crystal Structures	13
2.1.1 Unit Cells, and the 14 Bravais Lattices	13
2.1.2 Close-Packed Iodide Frameworks and Interstitial Site Logic	14
2.1.3 Caswellsilverite and Rudorffite Families	15
2.2 Point Defects in Semiconductors	17
2.2.1 Classification of Point Defects	17
	vii

2.3	Semiconductor Physics of Thin-Film Photovoltaics	18
2.3.1	Solar Cells	22
3	Experimentals and Characterizations	27
3.1	Experimental Methods	27
3.1.1	Copper Antimony Iodide (Chapter 4)	27
3.1.2	Copper Bismuth Iodide (Chapter 5)	28
3.1.3	Copper Bismuth Sulfide (Chapter 6)	29
3.2	Characterization Methods	31
3.2.1	Powder X-Ray Diffraction (PXRD)	31
3.2.2	Grazing-Incidence X-Ray Diffraction (GI-XRD)	32
3.2.3	Scanning Electron Microscopy (SEM)	33
3.2.4	Transmission Electron Microscopy: HRTEM, STEM-HAADF, and EDX	33
3.2.5	Thermogravimetric and Differential Thermal Analysis (TGA/DTA)	34
3.2.6	Ultraviolet–Visible–Near-Infrared Spectrometry (UV-Vis-NIR)	34
3.2.7	Photoluminescence Spectroscopy (PL)	36
3.2.8	White Light Interferometry	37
3.2.9	Photoelectron Spectroscopy Yield in Air (PESA)	37
3.2.10	Atomic Force Microscopy (AFM)	38
3.2.11	Confocal Raman Spectroscopy	39
3.2.12	X-Ray Fluorescence Spectroscopy (XRF)	40
3.2.13	Stylus Profilometry	41
3.2.14	Solar Cell Characterization: Current Density–Voltage Curves and Ex- ternal Quantum Efficiencies	41
4	Copper Antimony Iodide (Cu–Sb–I)	45
4.1	Background	45
4.1.1	Copper–Pnictogen Iodides in the Lead-Free Halide Landscape	45
4.1.2	Prior Work on Copper Antimony Iodide	46
4.1.3	Structural Considerations: CuI Polymorphs and Polytypism	46
4.2	Results and Discussion	47
4.2.1	Thermal Stability	47
4.2.2	Vibrational Properties of Cu–Sb–I	49
4.2.3	Compositional Analysis by X-Ray Fluorescence	50
4.2.4	Crystal Structure Determination	52
4.2.5	Microstructure and Electron Microscopy	54

4.2.6	Optoelectronic Properties	57
4.2.7	Thin-Film Quality	59
4.2.8	Solar Cell Integration and Device Performance	61
4.3	Conclusion and Outlook	63
5	Copper Bismuth Iodide (Cu–Bi–I)	65
5.1	Background and Motivation	65
5.1.1	The Cu–Bi–I Phase Space and Its Photovoltaic Relevance	65
5.2	Results and Discussion	66
5.2.1	Phase Composition and Crystal Structure	66
5.2.2	Microstructure, Electron Microscopy, and Vibrational Property	69
5.2.3	Thermal Stability and Phase Transitions	72
5.2.4	Optical Properties and Electronic Structure	73
5.2.5	Thin-Film Morphology and HTL-Dependent Film Quality	75
5.2.6	Photovoltaic Device Performance	77
5.3	Conclusions	79
6	Copper Bismuth Sulfide (Cu₃BiS₃)	81
6.1	Background	81
6.1.1	Cu ₃ BiS ₃ in the Lead-Free Absorber Landscape	82
6.1.2	Crystal Structure of Wittichenite	82
6.1.3	Optoelectronic Properties and Photovoltaic Motivation	84
6.1.4	Existing Solar Cell Literature and Performance Gap	85
6.2	Results and Discussion	86
6.2.1	Optical Absorption and Stoichiometry Dependence	86
6.2.2	Phase Identification and Lattice Parameters	87
6.2.3	Differential Thermal Analysis of the Cu₃BiS₃ Precursor System	90
6.2.4	TEM and SAED Analysis of Cu₃BiS₃	93
6.2.5	Film Topography and Microstructure	95
6.2.6	Photoluminescence and Defect Landscape	104
6.3	Solar Cell Performance	106
6.3.1	Device Architecture and As-Fabricated Performance	106
6.3.2	Effect of Post-Annealing on Device Performance	108
6.3.3	Absorption Response and External Quantum Efficiency	109
6.3.4	Role of Defects in Recombination and Transport	110
7	Conclusions and Outlook	113

7.1	Unifying Design Principles: Defect-Governed Optoelectronics	113
7.2	Outlook and Future Directions	114
7.2.1	Phase-Pure CBI through Controlled Precursor Chemistry	114
7.2.2	Tandem Integration of β -CuI:Sb	115
7.2.3	Morphological Densification of Cu_3BiS_3 Films	115
7.2.4	Defect Passivation and Interface Engineering	116
7.2.5	Extension to Mixed-Anion and Chalcogenide Frameworks	116
Declaration on the Use of AI-Assisted Tools		119
Bibliography		120
A Acknowledgements		137

1 Introduction

1.1 Motivation and problem statement

Photovoltaics (PV) has moved from a niche technology to a central contributor to electricity generation, driven by sustained cost reduction, large-scale manufacturing, and deployment across a wide range of climates and applications. Recent global deployment data highlight both the pace of growth and the scale of the remaining challenge: in 2024, worldwide cumulative PV capacity exceeded 2.2 TW and annual additions surpassed 600 GW, marking another record year for PV commissioning [1, 2]. The same sources report that PV supplied more than 10 % of global electricity consumption for the first time in 2024 [1]. These developments reinforce a broad consensus that PV will continue to expand rapidly, but they also sharpen the scientific and technological question of which absorber materials can support the next phase of growth, particularly for applications where low-temperature processing, light weight, and new form factors offer decisive advantages.

Against this background, metal-halide perovskites have emerged as a disruptive class of semiconductors because they combine strong optical absorption with the prospect of manufacturing by scalable coating and printing methods. The acceleration in certified device performance over the past decade has been documented by independent tracking efforts on power conversion efficiency. For example, the U.S. National Renewable Energy Laboratory (NREL) maintains a “best research-cell efficiencies” chart as shown in 1.1 that compiles independently verified record efficiencies across photovoltaic technologies and shows that perovskite-based architectures have reached the same performance as established thin-film technologies and have enabled very high-efficiency tandem concepts [3]. In parallel with these efficiency gains, perovskite semiconductors have attracted attention far beyond photovoltaics, reflecting the broader relevance of their optoelectronic and defect-chemical properties.

However, the most promising and operationally advanced perovskite absorbers, to date, have largely relied on lead-containing compositions and organic cations. Both aspects motivate intensive research into alternative, lead-free, fully inorganic absorber families. Lead raises environmental and health concerns that become increasingly consequential as the technology approaches large-area module deployment and end-of-life management. Quantitative studies have demonstrated that lead release can occur rapidly in scenarios relevant to real-world operation if

encapsulation fails or modules are damaged. For instance, aqueous exposure experiments report that a substantial fraction of the lead in unencapsulated perovskite devices can be leached on short time scales under rainfall-like conditions [4]. Reviews that synthesize broader leaching datasets further conclude that encapsulation alone does not eliminate risk if water ingress occurs, and that additional mitigation concepts (e.g. sequestration layers) are often required to reduce potential lead release [5]. The detailed potential environmental and human health hazards associated with lead-based perovskite photovoltaic technology are shown schematically in Figure 1.2. Complementing these materials-level observations, systems-oriented assessments emphasize that the higher solubility of lead species in perovskite modules relative to many incumbent PV technologies necessitates careful risk evaluation and the development of testing and mitigation standards as the technology matures [6]. Field-relevant studies are now emerging that explicitly target outdoor leaching and soil-impact scenarios, underscoring that lead management is not only a laboratory issue but a practical consideration for deployment [7].

In addition to lead, the presence of organic cations with halides introduces intrinsic stability challenges for many hybrid perovskite compositions. These challenges are not reducible to a single degradation pathway; rather, they reflect the combined effects of moisture, illumination, heat, and bias stress on a comparatively soft and chemically reactive lattice. A comprehensive stability perspective is provided by reviews that attribute part of this vulnerability to the organic component, halides, and low formation energies, which together can facilitate chemical and structural degradation under technologically relevant stressors [8]. Mechanistic work on methylammonium lead iodide (MAPbI_3), for example, has identified decomposition routes that produce volatile species under illumination and elevated temperature, linking device stability to both encapsulation requirements and compositional choices [9]. These insights have helped drive the search for absorber materials that retain the attractive optoelectronic features of halide perovskites while removing lead and reducing (or eliminating) dependence on volatile organic sublattices.

Copper-based, lead-free, perovskite-inspired absorbers represent one such concept. Here, copper is not simply a benign substitute for an organic cation; it is an electronically active ion that can occupy multiple coordination environments and can stabilize non-stoichiometric lattices under low-temperature thin-film processing. In this thesis, copper is deliberately chosen in order to enable fully inorganic compounds in which functional optoelectronic properties emerge from a defect-rich structural landscape. A concrete example is provided by $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$, where X-ray diffraction analysis supports a description in which copper is incorporated on interstitial sites within a Bi-I framework, and where thin films exhibit a solar-relevant band gap and measurable photovoltaic effect [10]. Importantly for the broader motivation of this work, the same study explicitly illustrates that nominal stoichiometry alone does not uniquely determine

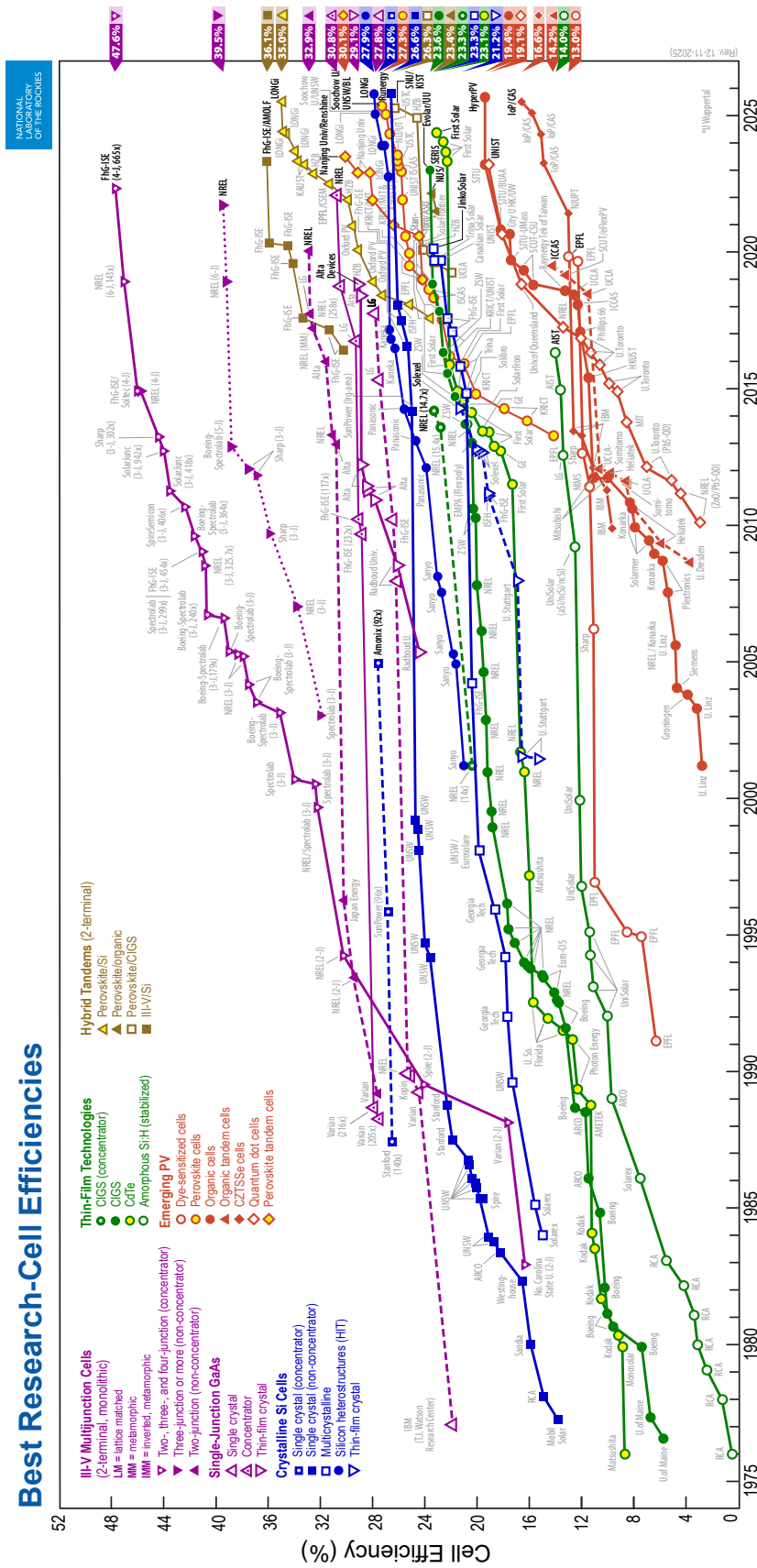
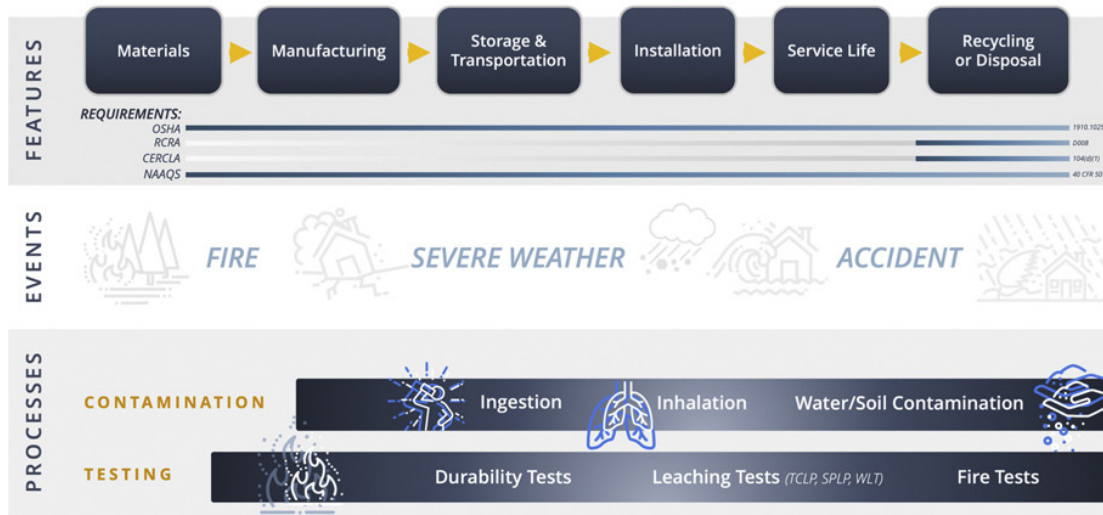


Figure 1.1: NREL Best Research-Cell Efficiencies (Rev. 03-06-2026). Figure from [3].



Perovskite Photovoltaic Module Risks

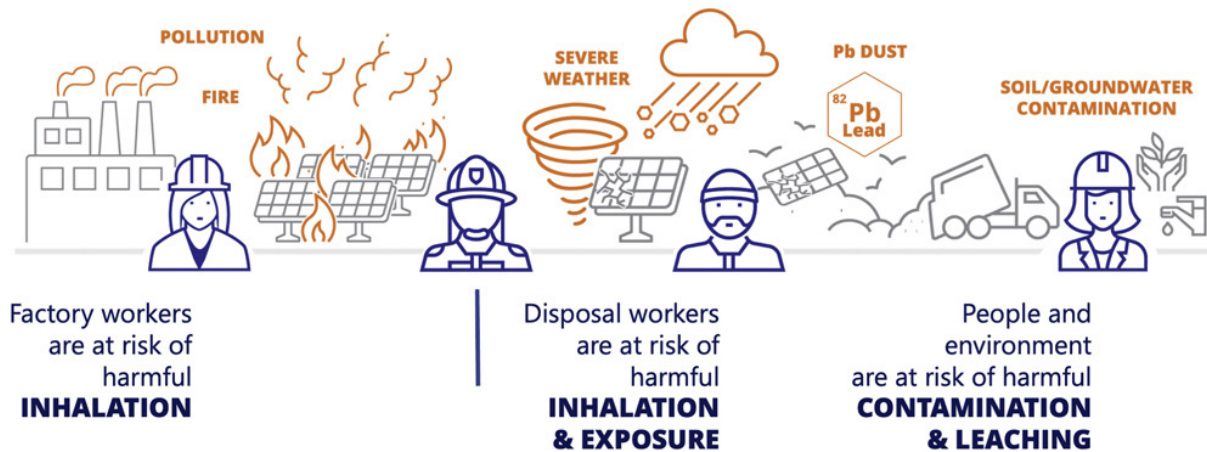


Figure 1.2: Potential environmental and human-health hazards linked to lead-perovskite photovoltaic technology across its lifecycle, along with relevant regulatory frameworks and assessment procedures. Figure from [5]

the structural motif: low-temperature synthesis can yield occupation of interstitial sites whose optoelectronic response cannot be inferred reliably from a formula label [10].

The emphasis on interstitial incorporation and native defects places this dissertation within a broader scope in photovoltaic materials science: the performance of a thin-film absorber is often determined by the energetics, densities, and mobilities of native defects, not only by the ideal crystal structure. In lead-halide perovskites, the notion of “defect tolerance” has been used to rationalize why high device performance can be achieved despite significant defect densities. Yet, careful analyses also stress that defect tolerance does not imply defect irrelevance: defect-mediated nonradiative recombination still limits performance and motivates extensive defect-passivation efforts [11]. More generally, modern defect theory identifies specific chemical and structural features that influence whether dominant intrinsic defects are shallow (defects close to the valence or conduction-band edge) or deep (defect levels farther inside the band gap and can trap carriers or promote non-radiative recombination). Shallow defects lie close to the valence- or conduction-band edges, whereas deep defects introduce levels farther within the band gap, where they can trap charge carriers and promote non-radiative recombination. These studies also emphasize that favorable electronic defect physics cannot be predicted from composition alone [12]. These considerations become particularly important in lead-free, perovskite-inspired semiconductors, where replacing Pb-based halide frameworks changes the band-edge orbital character, bonding, and structural motifs. As a result, their defect landscapes can differ markedly from those of the best-performing lead-halide perovskites.

This thesis is motivated by the view that, for copper-based, lead-free absorbers, progress toward efficient and stable photovoltaic devices requires a framework in which (i) structural identity is established experimentally for the phases formed under thin-film processing conditions and (ii) optoelectronic properties are interpreted through the lens of native defects, including interstitials and defect-stabilized microstructures. The central question addressed in this dissertation can therefore be stated as follows: *How do native defects—particularly copper interstitials and defect-derived microstructures—govern the optoelectronic properties and photovoltaic performance of copper-based, lead-free, perovskite-inspired absorbers, and which control parameters offer practical levers for improving device functionality while preserving the benefits of low-toxicity, low-temperature processing?*

The subsequent sections of the Introduction develop the context for this question by (1) positioning perovskite-inspired absorber concepts relative to established PV technologies, (2) motivating copper as a structurally and electronically versatile cation in lead-free halide frameworks, and (3) outlining how defect chemistry and microstructure control can be treated as design opportunities rather than unavoidable limitations.

1.2 From lead-halide perovskites to perovskite-inspired absorbers

The motivation outlined in Section 1.1 naturally leads to a broader materials question. How can the key advantages of lead-halide perovskites be retained while overcoming their toxicity and intrinsic stability limitations? Answering this requires distinguishing between (i) the specific ABX_3 *metal-halide perovskite* structure that underpins the most efficient hybrid devices and (ii) a wider set of *perovskite-related* and *perovskite-inspired* solids that share structural motifs, bonding characteristics, and processing routes, but do not necessarily adopt the ideal ABX_3 lattice [13, 14].

1.2.1 From lead replacement to perovskite-inspired design

An obvious approach to “lead-free perovskites” is to replace Pb^{2+} with other divalent cations while maintaining an ABX_3 topology. In practice, this strategy can preserve some structural features but introduces new constraints, including altered orbital character, different defect energetics, and in some cases additional chemical instability. As a result, a significant amount of lead-free researches have expanded beyond strict ABX_3 substitution and into a wider design space of *perovskite-related* and *perovskite-inspired* materials [13, 14]. In this dissertation, the term *perovskite-inspired* is used in this broad and pragmatic sense: materials that can be processed in perovskite-like thin-film workflows and that are built from related polyhedral building blocks, yet may differ in dimensionality, ordering, or connectivity compared to the ideal ABX_3 lattice.

Several structure families recur across the perovskite-inspired literature and are particularly relevant to lead-free absorber discovery. One important class comprises *defect-ordered* and *low-dimensional derivatives* of the perovskite lattice, often discussed for compositions such as $A_3B_2X_9$ (commonly with $B = Bi$ or Sb). Such compounds can be viewed as perovskite-related in the sense that they preserve BX_6 octahedra but reorganize their connectivity and/or incorporate ordered vacancies, which frequently reduces the structural dimensionality relative to 3D ABX_3 frameworks [14]. A second class is *cation-ordered double perovskites* with formulas such as $A_2B'B''X_6$, where heterovalent substitution replaces two Pb^{2+} sites by a monovalent and a trivalent cation (e.g., Ag^+/Bi^{3+}) while retaining a perovskite-derived octahedral network [13, 15]. A third perovskite-related family is *vacancy-ordered* “double perovskites” of the type A_2BX_6 , such as Cs_2SnI_6 , in which half of the B-site (Sn) positions are vacant in an ordered pattern. Consequently, the BX_6 octahedra are separated from one another rather than forming a continuous corner-sharing network, which weakens inter-octahedral electronic coupling and can constrain charge carrier transport compared with three-dimensional ABX_3 perovskites [13, 14, 16].

The emergence of $\text{Cs}_2\text{AgBiBr}_6$ as a benchmark lead-free double perovskite illustrates both the promise and the limitations that motivate continued exploration beyond simple composition rules. Slavney *et al.* showed that this Bi-containing double perovskite can exhibit long photoluminescence lifetimes and improved environmental robustness compared to typical hybrid lead-halide perovskites [15]. At the same time, the absorption onset and bandgap energy of $\text{Cs}_2\text{AgBiBr}_6$ constrain its performance as a single-junction solar absorber, focusing attention on bandgap engineering, defect control, and device-architecture optimization [17]. This combination of strengths and bottlenecks has helped clarify a broader lesson for lead-free perovskite-inspired photovoltaics: replacing lead is not sufficient; the structural motif, dimensionality, and defect landscape must collectively support efficient charge-carrier generation and extraction.

1.2.2 Positioning copper-based absorbers within the perovskite-inspired landscape

Copper-based, lead-free absorbers occupy a distinctive position within this broader perovskite-inspired design space. In contrast to ABX_3 hybrids where the A-site is typically electronically inert, copper is a chemically versatile cation that can participate directly in lattice stabilization and defect formation. In perovskite-inspired silver/copper pnictohalides, for example, the literature explicitly highlights that composition–structure–property relationships cannot be inferred from a single structure label, and that multiple structure types may occur across closely related chemistries [18]. This makes copper-based systems particularly suitable for a thesis centered on native-defect-mediated optoelectronics: they offer a realistic path to fully inorganic, lead-free thin films, but they also require an understanding of defects and microstructure to interpret their optoelectronic properties.

Rather than treating “lead-free” as a purely compositional constraint, the following sections develop the idea that lead-free, copper-containing absorbers must be understood as defect-chemical solids whose functional optoelectronic properties emerge from the interplay of structural motifs, dimensionality, and native defect populations. Section 1.3 narrows this discussion to the specific role of copper as an enabling (and electronically active) cation in lead-free halide frameworks, preparing the ground for the defect and interstitial-centered perspective developed throughout the remainder of the thesis.

1.3 Why copper? Inorganic cation selection and defect-driven optoelectronics

Section 1.2 introduced the transition from lead-halide perovskites to a broader design space of perovskite-inspired absorbers and emphasized that, in this expanded materials landscape, *structure must be established experimentally rather than inferred from composition*. The present

section narrows the discussion to the specific question that motivates this dissertation: *why copper as the inorganic cation*, and how does that choice connect directly to defect-mediated optoelectronic properties in lead-free photovoltaics?

1.3.1 Copper and silver as group-IB cations in pnictohalides: similarities and differences

Many lead-free perovskite-inspired iodides explored for photovoltaics fall into the broader class of group-IB/group-VA halides (often termed silver/copper pnictohalides), where A^+ is Cu^+ and/or Ag^+ and B^{3+} is Bi^{3+} and/or Sb^{3+} . A key message from field-wide assessments is that these compositions support a range of structure types and dimensionalities, and that composition alone does not uniquely specify the lattice that forms in thin films [18, 13]. This is precisely the regime where the cation choice becomes inseparable from microstructure control and defect-mediated device losses.

Copper and silver share some chemical features that make both attractive for lead-free iodide absorbers: both can occur as monovalent cations in iodide-rich environments, and both allow the construction of fully inorganic lattices that can be processed from solution in perovskite-like thin-film workflows. For example, $AgBiI_4$ has been established as a lead-free absorber candidate and has been explored in thin-film solar cells [19, 20]. Likewise, mixed $Cu/Ag/Bi$ iodides such as Cu_2AgBiI_6 have been identified as stable, inorganic, lead-free semiconductors with photovoltaic relevance, including applications where wide-bandgap absorbers are advantageous [21, 22].

The decisive differences between Cu^+ and Ag^+ become apparent when the discussion shifts from “can a phase form?” to “which defects and microstructures are likely under thin-film conditions?” A simple but informative descriptor is ionic size: Shannon radii indicate that Cu^+ is substantially smaller than Ag^+ across common coordination environments [23]. This size contrast provides a structural rationale for why Cu^+ can more readily participate in compact coordination polyhedra and can occupy interstitial-type sites in some iodide frameworks, whereas Ag^+ more often favors octahedral coordination environments. Importantly, this statement is not meant as a rigid rule: it is a geometrical constraint that influences which local motifs are accessible at low temperature and, therefore, which defect configurations and metastable microstructures can be stabilized during film formation.

1.3.2 Why copper is inherently defect-relevant: native defects, self-doping, and disorder

The same site flexibility that broadens the accessible structure space also implies that copper-based iodides are naturally discussed in the language of defect physics. A useful reference point

is CuI itself, which is widely studied as a p-type semiconductor in optoelectronics and transparent electronics. First-principles work has shown that native point defects in CuI, particularly copper vacancies, can have low formation energies and can act as shallow acceptors, providing a mechanism for intrinsic p-type conductivity without extrinsic dopants [24]. Reviews on CuI further emphasize that its electrical properties are tunable over a wide range through defect and microstructure control, making it a model case for “defect-enabled” electronic functionality [25]. While absorber layers for photovoltaics are not designed to be degenerate conductors, the CuI example illustrates a general principle that carries over to copper-based perovskite-inspired absorbers: *native defects can dominate the electronic landscape and can determine the effective doping and recombination*.

For lead-free pnictohalides, defect-mediated properties are frequently discussed in terms of (i) energetic disorder and band-tail states near the absorption edge, (ii) microstructure-dependent recombination pathways, and (iii) processing-induced metastability that modifies defect configurations over time. Comparative studies and reviews of Cu/Ag–Bi–I semiconductors emphasize that their photovoltaic outcomes depend strongly on phase purity, microstructure, and defect/disorder management rather than nominal composition alone [18, 26]. In silver bismuth iodides, for example, recent combined experimental and theoretical investigations have focused explicitly on how different silver–bismuth–iodide compositions and defect landscapes influence electronic structure and photovoltaic relevance [27]. These studies provide a useful comparison point: whereas silver-based phases can offer chemically stable, fully inorganic lattices, copper-containing analogues introduce an additional degree of freedom in the form of non-stoichiometric copper occupancy (including interstitial configurations), which can be advantageous for phase formation and tunability but also demands a structural interpretation of defects.

1.3.3 Copper vs. silver: practical and mechanistic implications for lead-free photovoltaics

The comparison between Cu^+ and Ag^+ can therefore be summarized at two complementary levels.

Practical level (materials selection): copper is far more abundant and typically less expensive than silver at the scale relevant for terawatt deployment, a point reflected in global production statistics and commodity summaries [28]. This does not make silver unusable, but it strengthens the case for copper-centered absorber concepts if the goal is a broadly scalable, lead-free thin-film PV platform.

Mechanistic level (structure and defects): Ag^+ -based absorbers such as AgBiI_4 demonstrate that perovskite-inspired, lead-free iodides can be realized as stable thin films and integrated

into devices [19, 20]. However, the smaller size and coordination flexibility of Cu^+ (relative to Ag^+) [23] increases the range of local environments accessible to copper during low-temperature film formation, including the possibility of interstitial incorporation and defect-stabilized microstructures. Evidence across copper-containing pnictohalides shows that these copper-specific structural degrees of freedom can control dimensionality and network motif [29] and can directly manifest as interstitial copper in photovoltaic absorbers [10]. Consequently, copper-based lead-free absorbers should be approached as systems where optimizing PV performance is inseparable from controlling defect chemistry and microstructure.

1.3.4 Extending the copper–pnictogen design space beyond halides: Cu_3BiS_3 as a sulfide benchmark

While the discussion above has focused on iodide-based, perovskite-inspired pnictohalides, where Cu^+ enables fully inorganic absorber lattices, and where microstructure and native defects strongly influence photovoltaic outcomes, it is equally instructive to ask whether the same *cation-choice logic* remains relevant when the anion chemistry is changed. In this dissertation, this broader perspective is provided by Cu_3BiS_3 (CBS), an orthorhombic copper–bismuth sulfide (wittichenite) that preserves the central materials premise of the thesis (Cu–Bi, lead-free, thin-film-compatible) while replacing the iodide sublattice with a sulfide framework. Cu_3BiS_3 therefore serves as a chemically adjacent, yet electronically and structurally distinct, reference point for understanding copper-governed optoelectronics in lead-free absorbers.

Cu_3BiS_3 has been investigated as a photovoltaic absorber because thin films can combine strong visible-light absorption with optical band gaps in the solar-relevant range, with reported values of 1.2–1.6 eV depending on deposition route and sulfurization techniques. A recent solution-based precursor route yielded nanocrystalline Cu_3BiS_3 films with absorption coefficients up to 10^5 cm^{-1} in the visible and a direct optical bandgap extracted near 1.55 eV, whereas, earlier studies typically reported bandgaps of 1.3–1.45 eV for films prepared by sputtering, electrodeposition, or co-evaporation [30, 31, 32]. Beyond optical metrics, Cu_3BiS_3 has also been characterized with photoelectron spectroscopy to establish band-edge energetics and surface-sensitive electronic structure; such measurements provide a device-relevant basis for discussing interface alignment and loss channels in Cu_3BiS_3 heterojunction concepts [33].

From a processing standpoint, Cu_3BiS_3 is an important complement to iodide pnictohalides because its thin films have been produced by a wide range of scalable methods, including (reactive) sputtering, co-evaporation followed by sulfurization, electrodeposition routes, and chemical-bath deposition, and recent work has expanded the set of solution-based strategies beyond classical bath deposition [31, 30, 32]. The resulting literature establishes Cu_3BiS_3 as a lead-free absorber that combines the interplay of phase purity, grain structure, and intrinsic

electronic states remains decisive for functional performance, even though the underlying lattice is not a “perovskite” structure. Within the narrative of this thesis, Cu_3BiS_3 therefore provides a controlled extension: it retains copper as the enabling cation but places it in a sulfide environment, allowing copper-driven structure–property relationships to be discussed across anion chemistries rather than within iodides alone.

2 Fundamentals

2.1 Crystal Symmetry, Space Groups, and Relevant Crystal Structures

The orbital pathways that set the bandgap, the interstitial sites available to foreign cations, and the formation energies of native defects all trace back to one thing: where the atoms are in the crystal lattice, and how the coordination polyhedra connect. In conventional semiconductors, identifying the phase also identifies the main crystallographic structure. Copper pnictohalides, however, are more structurally complex. The same chemical composition can crystallize in several closely related structural frameworks with overlapping diffraction patterns, similar nominal compositions, and markedly different optoelectronic properties. Consequently, reliable structural assignment is essential for establishing meaningful structure–property relationships and forms the basis for the discussions throughout this thesis.

2.1.1 Unit Cells, and the 14 Bravais Lattices

A *crystal* is an infinite, three-dimensionally periodic arrangement of atoms whose translational symmetry is captured by a *Bravais lattice* – one of the 14 distinct space-filling lattice geometries that tile Euclidean space by translation alone. Each lattice is fully characterized by three vectors **a**, **b**, **c** and the interaxial angles α , β , γ , whose metric and angular constraints define one of the seven *crystal systems*: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic [34, 35].

The *unit cell* is the repeating volume element that, when translated, regenerates the full crystal. Its content can be reduced to the asymmetric unit, which is the smallest set of atomic positions from which the complete structure is generated by the symmetry operations of the space group. Rietveld refinement is a whole-pattern fitting method used to refine a crystal-structure model against powder diffraction data. Starting from an assumed phase, space group, and atomic arrangement, the method calculates a diffraction pattern and adjusts structural and profile parameters, such as lattice constants, atomic positions, occupancies, displacement parameters, background, and peak shape, to obtain the best agreement with the measured pattern. Because the structural model is defined by the asymmetric unit, Rietveld refinement uses this unit as the fundamental crystallographic description of the structure. The complete crystal structure is then

generated by applying the symmetry operations of the space group. This provides the natural irreducible structural description of a crystalline compound [36].

Beyond pure translations, crystals can carry *point symmetry operations*: proper rotation axes (C), mirror planes (m), inversion centers ($\bar{i}$), and improper rotation axes (S). The set of all point operations compatible with three-dimensional periodicity defines the 32 *crystallographic point groups*. Pairing these with the 14 Bravais lattice types – and accounting for the possible positions of symmetry elements relative to the lattice – yields the 230 *space groups*, the exhaustive classification of three-dimensional crystal symmetry [34, 35].

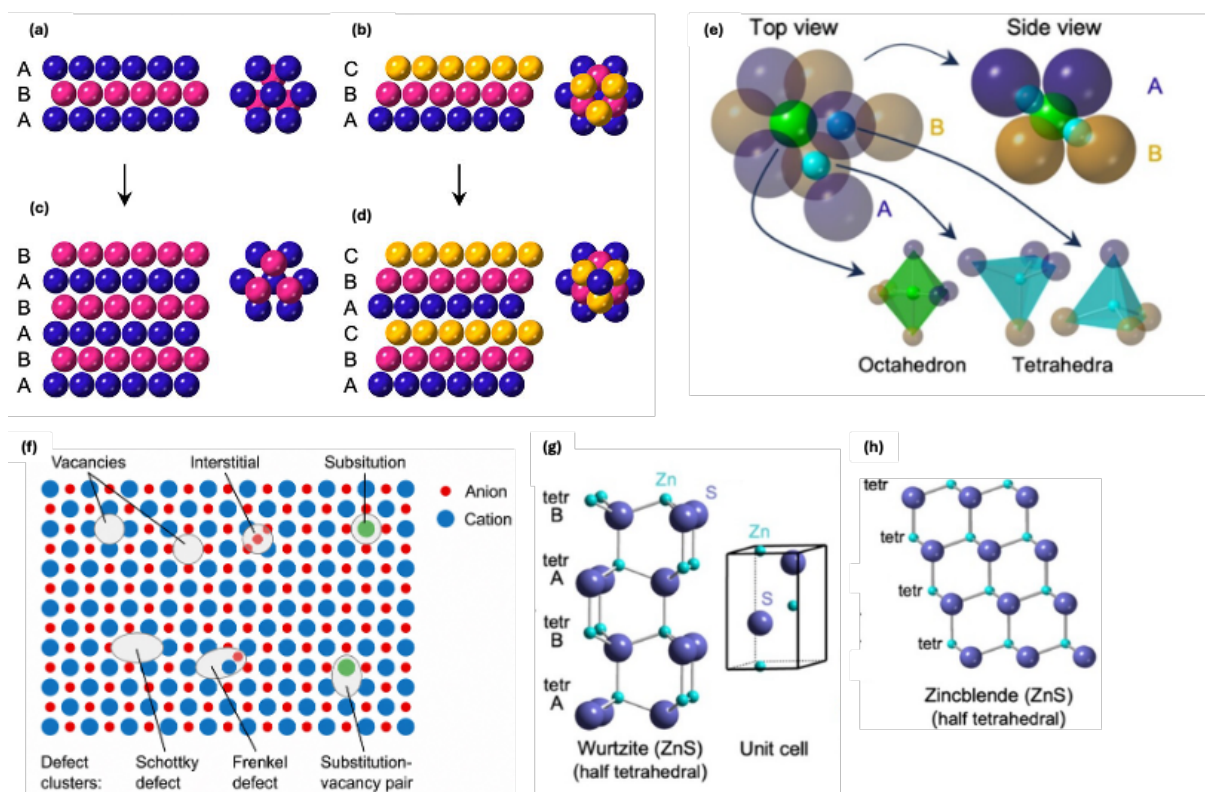


Figure 2.1: Structural motifs used to introduce close-packed halide frameworks and basic defect concepts. (a,b) Three-layer fragments of hexagonal close packing (HCP, ABAB...) and cubic close packing (CCP, ABCABC...). (c,d) Extended HCP and CCP stacking sequences. (e) Tetrahedral and octahedral voids formed between close-packed anion layers. (f) Representative point defects in an ionic lattice. (g,h) Wurtzite and zincblende ZnS structures, shown as HCP- and CCP-derived tetrahedral frameworks relevant to the discussion of CuI polytypes. Panels adapted from [37, 38]

2.1.2 Close-Packed Iodide Frameworks and Interstitial Site Logic

Many halide semiconductors are most readily understood by considering the anion sublattice first. Iodide ions are large and polarizable and, in many structures, stack into a close-packed framework into which the cations occupy the available interstitial sites. Two ideal close-packed

sequences dominate, as shown in Figure 2.1. Cubic close packing (CCP) follows an AB-CABC... stacking sequence and forms a face-centered cubic anion lattice. Hexagonal close packing (HCP) follows an ABAB... stacking sequence and forms a hexagonal anion lattice. Both pack one octahedral void and two tetrahedral voids per anion, but the connectivity between neighboring voids differs – a fact that matters when trying to figure out which cation sits where. From a structural perspective, filling all octahedral voids yields rock salt (NaCl), depending on the stacking. Whereas filling half the tetrahedral voids yields zincblende or wurtzite. Identical local coordination, different long-range stacking – which is exactly why the energy difference between CCP and HCP is often tiny in group-IB halides, and why stacking faults create coherent polytypic domains whose diffraction signals mimic a second polymorph [39, 37, 40].

For copper pnictohalides, this has practical consequences. A diffraction peak suggesting a hexagonal CuI phase may equally arise from stacking-fault polytypism inside a dominantly cubic CuI-like matrix. Conversely, the absence of a fully ordered ternary pattern does not imply that the material is a simple binary mixture; cations can sit in interstitial or defect-complex sites within the host. The question is: which voids are occupied by which cations, and to what degree of order?

2.1.3 Caswellsilverite and Rudorffite Families

Caswellsilverites (named after Dr. Caswell Silver) or Rudorffites (named after Dr. Walter Rüdorff) belong to the same structural material category. These families are layered ternary halides with the generic formula $A_3M_2X_9$ or A_2MX_4 ($A = \text{Cu}^+, \text{Ag}^+, \text{K}^+$; $M = \text{Bi}^{3+}, \text{Sb}^{3+}$; $X = \text{I}^-, \text{Br}^-, \text{Cl}^-$), derived from the CdI_2 or NaVO_2 -type framework through ordered cation substitution [41, 42, 43].

In the Caswellsilverite type, the structural arrangement depends on the A-site cation size, where one octahedral layer sits on top of another octahedral layer in the lattice. Smaller cations (K^+, Rb^+ ; $\text{K}_3\text{Bi}_2\text{I}_9$ prototype) yield layered defect-perovskite structures, while larger cations (Cs^+, MA^+) favor 0D structures in space group $P6_3/mmc$ (No. 194) with isolated face-sharing $[\text{Bi}_2\text{I}_9]^{3-}$ dimers and monovalent cations in the interlayer positions for charge balance [44, 45]. The space group is typically $P6_3/mmc$ (No. 194) or $R\bar{3}m$ (No. 166) depending on the order of stacking layers [44, 46]. The Rudorffite type Ag_3BiI_6 is closely related, but monovalent cations partially fill octahedral sites inside the halide layers, producing a more three-dimensionally connected polyhedra network [47, 48]. The two types differ in where exactly the A-site cations sit, and how they are stacked [49].

Both families have band gaps in the 2.0–2.5 eV range for $A_3M_2X_9$ compounds, while Ag–Bi–I rudorffites such as Ag_3BiI_6 show lower direct gaps around 1.79–1.83 eV; the full family spans a

Table 2.1: Structural questions used to connect crystallographic assignment with the interpretation of optoelectronic and device properties in copper pnictohalide thin films.

Structural question	What it distinguishes	Why it matters here
Which stacking sequence is present?	Cubic γ -CuI-like ccp stacking, hexagonal β -CuI-like hcp stacking, or layered BiI_3 -type motifs.	The stacking sequence determines which structural model should be used to interpret the diffraction pattern. This is important because CuI polytypes and stacking faults can give similar diffraction signatures, making phase assignment from peak positions alone ambiguous.
Which interstitial or coordination sites are occupied?	Tetrahedral Cu^+ sites, octahedral $\text{Bi}^{3+}/\text{Sb}^{3+}$ sites, or additional Cu^+ in interstitial or intercalated positions.	Site occupancy defines whether copper acts only as a central cation or also as an interstitial species. This distinction is central to the interpretation of copper-rich phases such as $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$.
Is the cation network continuous?	A connected octahedral Caswellsilverite/Rudorffite-type framework versus a CuI-derived or defect-associated structure.	Network connectivity affects whether the material should be discussed as a true, well-defined structure or as a structurally distinct copper iodide-derived phase. This changes how its transport and defect properties should be interpreted.
Is the structure ordered, faulted, or disordered?	Long-range ordered domains versus stacking-faulted, broadened, or locally disordered structures.	Structural disorder can broaden diffraction peaks and complicate phase assignment. It is also relevant when discussing band-edge tailing, metastability, and possible recombination pathways, but these links must be tested experimentally rather than assumed from composition alone.

wide range relevant for indoor photovoltaics, LEDs, and radiation detection [50, 51]. Quantum confinement in layered geometries increases exciton binding energies and can boost photoluminescence quantum yield [52, 53]. Their relatively wide bandgap energy make them less suitable for outdoor single-junction cells. The search for narrow bandgap energy derivatives – including the copper antimony iodide phases studied here – follows directly from this consideration.

2.2 Point Defects in Semiconductors

Thin-film semiconductors often contain structural imperfections such as vacancies, interstitials, antisites, and stacking faults. In halide semiconductors, these defects can be especially relevant because the lattices are relatively soft, ions can be mobile, and defect formation energies can be low. Such defects may influence carrier concentration, reduce recombination lifetime, and contribute to features such as band-edge tailing in optical absorption. The following section introduces the defect-physics concepts used in this thesis to relate structural disorder to optoelectronic behavior.

2.2.1 Classification of Point Defects

As shown in Figure 2.1(f), point defects are classified by their structural character:

1. **Vacancies:** Missing atoms from regular lattice sites (e.g., V_{Bi} , V_I in BiI_3).
2. **Interstitials:** Atoms in sites that are empty in the ideal structure (e.g., Cu_i , Bi_i).
3. **Substitutional defects:** Foreign atoms on host sites (e.g., Sb_{Bi} , Ag_{Cu}).
4. **Antisites:** Host atoms on the wrong sublattice (e.g., Bi_I , I_{Bi}).
5. **Complexes:** Two or more defects bound together (e.g., $V_{Bi}-V_I$, Cu_i-V_{Bi}).

Each defect type can occur in different charge states by exchanging electrons with the surrounding crystal. For example, a bismuth vacancy in BiI_3 may be neutral or negatively charged, such as V_{Bi}^0 , V_{Bi}^- , V_{Bi}^{2-} , or V_{Bi}^{3-} . Which charge state is most stable depends on the Fermi-level position, i.e., the electron chemical potential within the band gap, usually referenced to the valence-band maximum. The stable charge state determines whether the defect behaves as an acceptor, donor, or carrier-trapping center [54, 55].

2.3 Semiconductor Physics of Thin-Film Photovoltaics

Band model

In an isolated atom, electrons can occupy only discrete energy levels determined by their quantum states. According to the Pauli exclusion principle, no two electrons can occupy the same quantum state simultaneously. When multiple atoms approach each other, the electrons of neighboring atoms begin to interact. Their wavefunctions overlap, causing each original discrete energy level to split into N separate levels when N atoms are involved, in order to satisfy the Pauli exclusion principle. In a crystal, the atomic density is typically on the order of 10^{22} to 10^{23} atoms per cm^3 [56, 57]. As illustrated in Figure 2.2, a very large number of energy levels form, with small energy separations merging into continuous energy bands. These bands possess a finite energy width and are separated by bandgaps, which represent no states. The width of the energy bands depends on the atomic orbitals from which they originate. Outer electron orbitals overlap more strongly than inner orbitals, whose electrons are more tightly bound to the nucleus. Consequently, outer orbitals split into broad energy bands at larger interatomic distances than inner orbitals. At a certain interatomic distance, the system reaches an equilibrium state at which the potential energy is minimized.

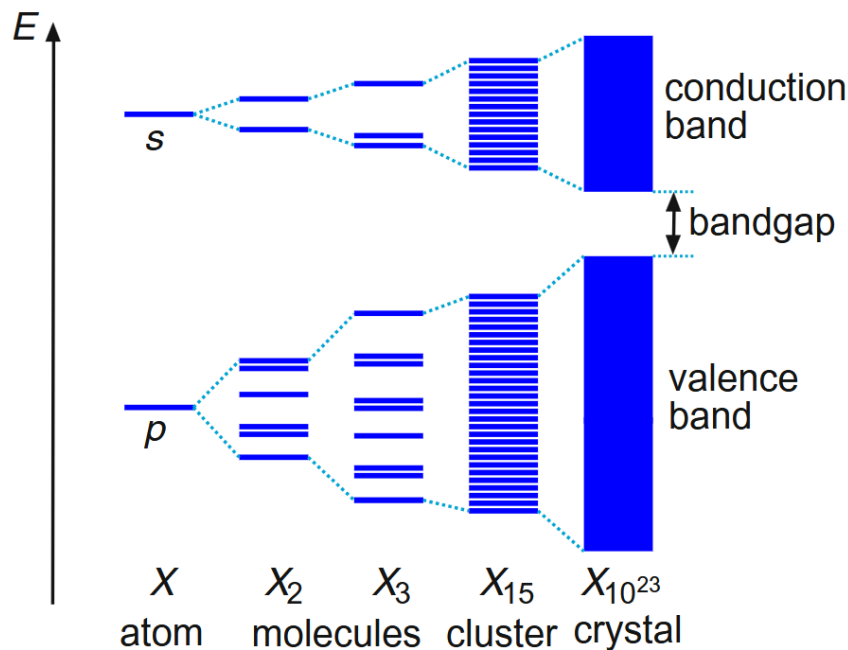


Figure 2.2: Formation of energy bands for an increasing number of atoms [57].

At a temperature of 0 K, no electrons are in excited states, and the bands are filled, starting from the lowest energy levels up to a certain energy level, above which all states remain unoccupied

[56]. If the highest occupied energy state lies within a partially filled band, the material is classified as a metal. In semiconductors and insulators, the energy bands are either completely filled or completely empty. The highest-energy band in which all states are occupied is called the valence band, while the lowest-energy empty band is referred to as the conduction band. Electrons in the conduction band are mobile and therefore contribute to electrical conductivity. In semiconductors, electrons can be thermally excited from the valence band into the conduction band as the temperature increases. In insulators, the gap between the valence and conduction bands is much larger, such that the amount of thermally excited electrons is negligible before the material is destroyed at high temperatures. As a result, insulators exhibit very low electrical conductivity.

When electrons in a semiconductor are excited into the conduction band, they leave behind an empty state in the valence band. This empty state can be treated as a quasiparticle with a positive charge equal in magnitude to the charge of an electron and is referred to as a hole. The excitation of an electron from the valence band into the conduction band thus creates an electron–hole pair.

The probability that an electron occupies a specific energy state is given by the Fermi-Dirac distribution:

$$f_e(E) = \frac{1}{1 + e^{(E-E_F)/k_B T}}, \quad (2.1)$$

where E is the energy of the state, k_B is the Boltzmann constant, T the absolute temperature and E_F the Fermi energy [58]. At thermal equilibrium, the Fermi energy corresponds to the electron electrochemical potential expressed in units of energy, describing the energy at which the occupation probability is $\frac{1}{2}$. The Fermi level does not correspond to an actual energy state. In intrinsic semiconductors, it is located within the gap between the valence band and the conduction band. The occupation probability for a hole, an empty state, can be calculated by

$$1 - f_e(E) = \frac{1}{1 + e^{(E_F-E)/k_B T}} \quad (2.2)$$

At $T = 0$ K, the Fermi-Dirac distribution is a step function, with the step occurring at the Fermi energy E_F . As shown in Figure 2.3, at temperatures above 0 K, the sharp step at the Fermi energy broadens, and the occupation probability approaches 1 at low energies and 0 at high energies. Therefore, excited electrons predominantly occupy states near the lower edge of the conduction band, whereas holes accumulate at the upper end of the valence band.

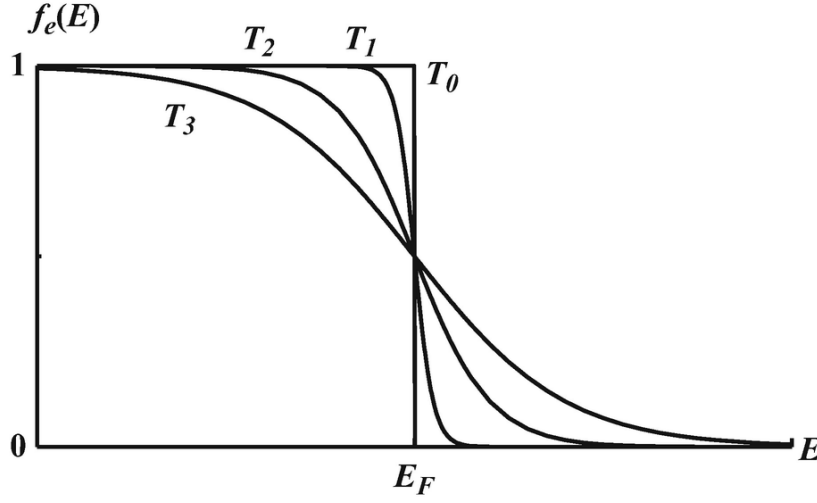


Figure 2.3: Fermi-Dirac distribution at different temperatures $T_3 > T_2 > T_1 > T_0 = 0$ K [59].

Generation and Recombination

As described in the previous section, electron-hole pairs can be generated thermally. In addition to thermal generation, free charge carriers can be introduced electrically through carrier injection from contacts or generated optically through photon absorption. The latter process is the most relevant for solar cells. Incident photons can either be reflected at the surface, absorbed within the material, or transmitted. Absorption can only occur if the energy of the incident photons $E = h\nu$, where h is the Planck constant and ν is the photon frequency, is equal to or greater than the bandgap energy of the semiconductor [60]. In this case, an electron is excited into the conduction band, thereby generating an electron-hole pair. If the photon energy exceeds the bandgap, the excess energy is dissipated as heat because the excited electron rapidly thermalizes to the conduction band minimum. These transitions must satisfy both energy and crystal-momentum conservation. In direct semiconductors, this condition is satisfied automatically because the conduction band minimum and the valence band maximum occur at the same momentum in reciprocal space. In indirect semiconductors, however, these extrema are located at different momenta. Therefore, an additional phonon is required to provide the necessary momentum for the transition. As a result, near-band-edge absorption is significantly less likely in indirect semiconductors, which generally requires thicker absorber layers for efficient light absorption. The optical generation rate in $\text{cm}^{-3}\text{s}^{-1}$ is expressed as

$$G(x) = \int_{\lambda_1}^{\lambda_2} g_{sp}(x, \lambda) d\lambda. \quad (2.3)$$

This equation describes an integration over a wavelength spectrum $\lambda_2 - \lambda_1$ of the spectral generation rate g_{sp} which is given by

$$g_{sp} = \Phi_0(\lambda)\alpha(\lambda)e^{-\alpha(\lambda)x}, \quad (2.4)$$

with the incident photon flux density Φ_0 , the absorption coefficient $\alpha(\lambda)$, and penetration depth x [61]. Therefore, the optical generation depends on the material, the intensity and wavelength of the incident radiation and the penetration depth within the material.

The opposite process of generation is recombination, in which an electron transitions from the conduction band to a free state in the valence band. In solar cells, recombination is regarded as a loss mechanism. Recombination can occur both within the bulk of the material and at the surface. For bulk recombination, three basic types can be distinguished: Radiative band to band recombination, trap-assisted Shockley-Read-Hall recombination and Auger recombination.

Radiative recombination describes the direct recombination of an electron in the conduction band with a hole in the valence band. The excess energy is released as a photon. The corresponding recombination rate depends on the electron and hole carrier densities and is commonly written as

$$R_{\text{rad}} = B(np - n_i^2),$$

where n and p are the electron and hole concentrations, n_i is the intrinsic carrier concentration, and B is the radiative recombination coefficient. Under illumination or injection, this is often approximated as $R_{\text{rad}} \approx Bnp$, showing that the recombination probability increases with both electron and hole density. Radiative recombination is most efficient in direct-band-gap semiconductors, where the band-edge transition can conserve momentum without phonon assistance [62].

Defects, such as vacancies or dislocations, can create allowed energy states within the bandgap. Electrons and holes can be trapped in these states and recombine from there. Trap states located near the center of the band gap are the most efficient recombination centers, as they can capture both electrons and holes with comparable probability [60]. The excess energy is released in the form of phonons, hence, this process is non-radiative. The recombination rate is directly proportional to the trap density. For efficient solar cells, the trap density should therefore be as low as possible [61].

Auger recombination is a three-particle process in which the energy released during the recombination of an electron-hole pair is transferred to another charge carrier, either an electron in the conduction band or a hole in the valence band. The excited charge carrier is promoted to a higher-energy state and subsequently relaxes back toward the respective band edge. During

this relaxation process, the excess energy is transferred to the lattice in the form of phonons. As multiple particles are involved, Auger recombination occurs primarily at high charge-carrier densities.

Additional trap states can be located at the surface of a crystal or at crystal grain boundaries, where the periodic lattice structure is disrupted and unsaturated valence bonds, known as 'dangling bonds', are present. This can lead to a high density of trap states and, consequently, a high recombination rate at the surface or at grain boundaries. To counteract this, surfaces can be passivated to eliminate or reduce dangling bonds. Alternatively, the grain size can be increased, thereby reducing the total number of grain boundaries within the material.

All recombination mechanisms reduce the charge carrier lifetime, which is defined as the average time that excess charge carriers exist before recombining. Closely related to the charge carrier lifetime is the diffusion length, which describes the average distance that charge carriers can travel before recombination occurs. It is given by

$$L = \sqrt{D\tau}, \quad (2.5)$$

where D is the diffusivity in m^2s^{-1} and τ is the charge carrier lifetime [61]. The diffusion length also decreases as the recombination rate increases. Both the charge carrier lifetime and the diffusion length are important parameters for solar cells and should be as high as possible to achieve efficient charge carrier extraction and high device performance.

2.3.1 Solar Cells

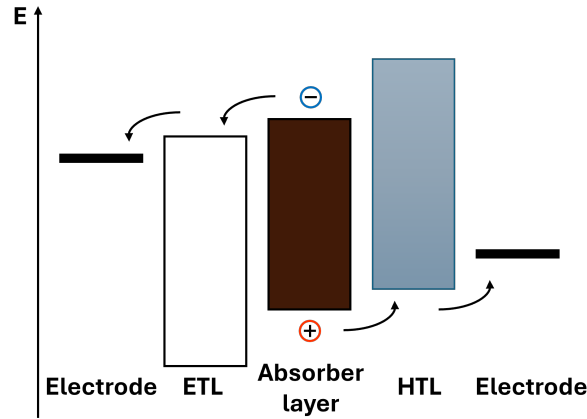


Figure 2.4: Relevant transport energies of the functional materials throughout a thin film solar cell.

Solar cells are devices that convert the energy of incident radiation to electrical energy. To achieve this, the charge carriers generated by photon absorption must be separated and collected

at the electrodes. The structure of a solar cell depends on the type of the light-absorbing layer, also referred to as the photo-active layer. The photo-active layer can be intrinsic, n-type, or p-type. Non-intrinsic conductivity can arise either by intentional doping or by native defects such as vacancies, which alter the concentration of free charge carriers by donating or accepting electrons. A typical structure of thin film solar cells with intrinsic absorber layers is shown in Figure 2.4. It consists of two electrodes, a hole transport layer (HTL), an electron transport layer (ETL), and the photo-active layer located between them. When the absorber is brought into electrical contact with the selective transport layers, their energy levels adjust, producing band bending and a built-in potential across the device. Under illumination, electrons and holes move according to gradients in their electrochemical potentials. These electrochemical potentials are represented by the electron and hole quasi-Fermi levels. The ETL and HTL then provide selective pathways for extracting electrons and holes, respectively. Efficient electron transport to the electrode requires the conduction band minimum of the electron transport layer to be energetically below that of the absorber layer. Furthermore, efficient electron extraction requires favorable energy-level alignment between the electrode and the electron transport layer, such that the contact presents little or no barrier to electron transfer. Under these conditions, the contact behaves ohmically, minimizing contact resistance and facilitating charge collection. Ideally, the valence band maximum of the electron transport layer lies below that of the absorber layer, thereby forming an energy barrier for holes that prevents them from moving towards the electrode and recombining with the collected electrons. Analogous considerations apply to the hole transport layer and the opposite electrode to ensure efficient hole extraction while blocking electrons.

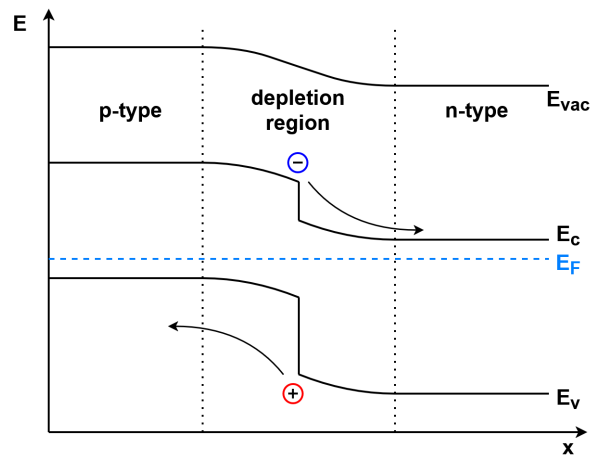


Figure 2.5: Illustration of the band diagram of a p-n-heterojunction. Charge carriers generated in the depletion region are separated and transported to the electrodes.

In the case of non-intrinsic absorber layers, separation of charge carriers can be achieved by forming a p-n junction between an n-type and a p-type semiconductor. The large charge carrier concentration gradient between the two layers causes electrons to diffuse from the n-type semiconductor to the p-type semiconductor, while the holes diffuse in the opposite direction [61]. As a result, a depletion region forms between the two layers and an electric field is created that separates generated charges. If the p-n junction is formed between differently doped regions of the same semiconductor material, it is referred to as a homojunction. If two different materials are used, this is referred to as heterojunction. In heterojunctions, discontinuities in the energy bands arise because the two materials generally possess different bandgaps and band-edge energies. An example of a p-n heterojunction band diagram is shown in Figure 2.5. Depending on the band alignment between the absorber and the transport layers, energetic barriers can form at the interfaces, impeding efficient charge-carrier extraction to the electrodes. This must be taken into account when selecting an ETL/HTL to be combined with the photo-active layer. Both layers can either be connected directly to suitable electrodes, or be combined with additional electron or hole transport layers.

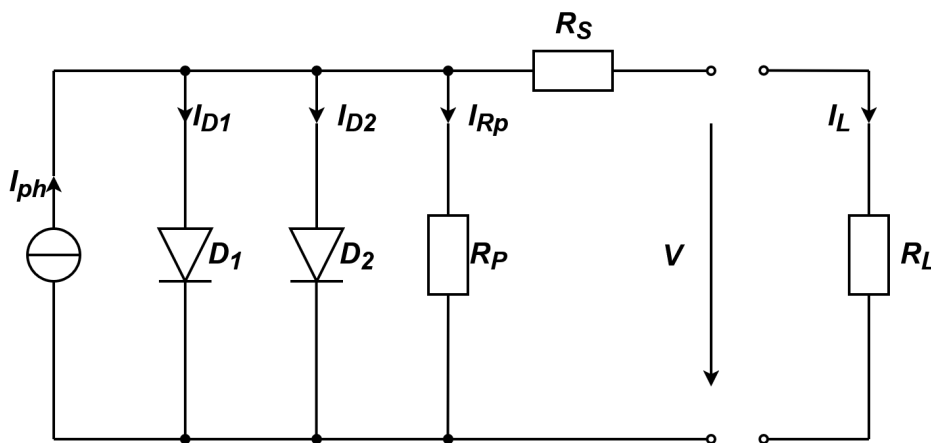


Figure 2.6: Equivalent circuit of a solar cell.

The equivalent circuit shown in Figure 2.6 describes the electrical characteristics of a solar cell. The ideal current source represents the charge carriers generated under illumination. Diode D_1 is an ideal diode connected in parallel to the current source. It originates from the p-n junction and describes the behavior of the solar cell in the dark. To account for losses caused by non-radiative recombination, a non-ideal diode D_2 is also connected in parallel. The series resistance R_s describes all series resistances in the device, including the resistances of all layers, the contact resistances, and non-zero resistances of the electrodes. Leakage currents are accounted for via

the alternative current path through resistance R_p . The current flowing through an external load resistance is then given by

$$I_L = I_{01} \left(\exp \left(\frac{q(V - I(R_s + R_L))}{k_B T} \right) - 1 \right) + I_{02} \left(\exp \left(\frac{q(V - I_L(R_s + R_L))}{n_2 k_B T} \right) - 1 \right) + \frac{V - I_L(R_s + R_L)}{R_p} - I_{ph}, \quad (2.6)$$

with voltage V between the electrodes, Boltzmann constant k_B , temperature T , ideality factor n_2 , saturation currents I_{01} and I_{02} and photo generated current I_{ph} [61]. The first term describes the dark current I_{D1} , the second term describes the current through D_2 , whilst the current I_{Rp} through R_p is described by the third term. Key parameters of a solar cell can be obtained or derived from the J - V characteristic curve which is shown in Figure 2.7. The short-circuit

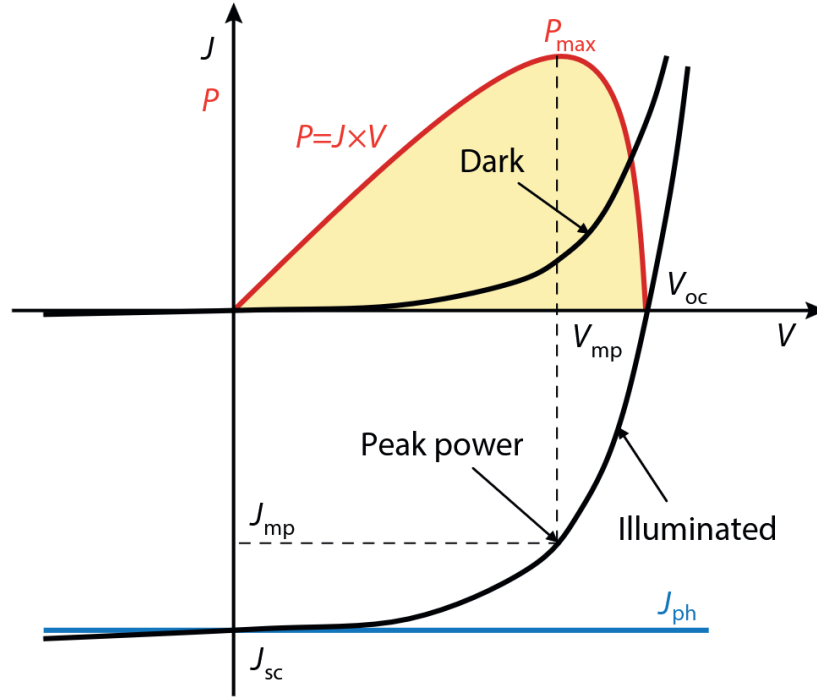


Figure 2.7: J - V characteristics of a solar cell in the dark and illuminated [61].

current density J_{sc} corresponds to the intersection of the curve with the current-density axis and describes the current density under short-circuit conditions, where the load resistance is $R_L = 0$ and therefore $V = 0$. Under open-circuit conditions, no current flows through the device; that is, the current density is zero. In this case, the open-circuit voltage V_{oc} is measured. The highest conversion efficiency is achieved at the operating point where the product of current and voltage, i.e., the power, is at its maximum. This point is referred to as the maximum power

point at current density J_{mp} and voltage V_{mp} . The ratio between the maximum power and the product of J_{SC} and V_{OC} is defined as the fill factor FF of a solar cell:

$$FF = \frac{J_{mp}V_{mp}}{J_{SC}V_{OC}} \quad (2.7)$$

The fill factor is an important parameter for evaluating the quality of a solar cell and is directly related to the power conversion efficiency. The power conversion efficiency is defined as the ratio of the electrical power generated by the solar cell to the incident optical power [61]:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{mp}V_{mp}}{P_{in}} = \frac{J_{SC}V_{OC}FF}{P_{in}} \quad (2.8)$$

Another important parameter is the external quantum efficiency $EQE(\lambda)$, which describes the ratio between the number of electron-hole pairs generated and collected at the electrodes and the number of incident photons [61]. It can be measured in a spectral response measurement setup, in which the solar cell is irradiated by monochromatic light while the resulting photocurrent is measured. The EQE is then calculated as follows:

$$EQE(\lambda) = \frac{I_{ph}(\lambda)}{e\Phi_{ph}(\lambda)}, \quad (2.9)$$

using the photocurrent I_{ph} , the elementary charge e and the incident photon flux Φ_{ph} . To determine the incident photon flux, a calibrated reference photodetector or solar cell with a known EQE can be used:

$$\Phi_{ph}(\lambda) = \frac{I_{ph,ref}(\lambda)}{eEQE_{ref}(\lambda)} \quad (2.10)$$

Substituting this in Equation 2.9 gives:

$$EQE(\lambda) = EQE_{ref}(\lambda) \frac{I_{ph}(\lambda)}{I_{ph,ref}(\lambda)} \quad (2.11)$$

By measuring the photocurrent $I_{ph}(\lambda)$ and $I_{ph,ref}(\lambda)$, the EQE can be determined.

3 Experimentals and Characterizations

3.1 Experimental Methods

Unless noted otherwise, all synthesis and device fabrication steps were performed inside a nitrogen-filled glovebox ($O_2 < 1$ ppm, $H_2O < 1$ ppm). All solutes, polymers, and solvents were of reagent grade or higher purity and were obtained from commercial suppliers without further purification.

3.1.1 Copper Antimony Iodide (Chapter 4)

Substrate Cleaning

Glass substrates (16×16 mm²) bearing pre-patterned indium tin oxide (ITO) electrodes were cleaned by sequential sonication in acetone, mechanical scrubbing with plastic swabs and glass cleaner, rinsing with isopropanol (IPA), and blow-drying with nitrogen gas. ITO substrates were subsequently treated in an oxygen plasma for 5 minutes to remove organic residues and improve surface wettability prior to the deposition of transport layers.

Powder Synthesis of Cu_3SbI_6 (β -CuI:Sb)

Solid copper(I) iodide (CuI; Thermo Scientific, 98%) and antimony(III) iodide (SbI_3 ; Sigma-Aldrich, 98%) were combined in a 3:1 molar ratio and dissolved in a hot binary solvent mixture of dimethyl sulfoxide and N,N-dimethylformamide (DMSO:DMF, 1:1 v/v) at 70°C with continuous stirring for 2 hours. The resulting solution was filtered through a 0.45 μ m polytetrafluoroethylene (PTFE) syringe filter. For powder preparation, the filtered solution was drop-cast onto cleaned glass substrates and dried at 50°C for 96 hours. The dried Cu–Sb–I was collected by carefully scraping the glass surface. Intentional grinding was avoided, as mechanical treatment induces mechano-thermal energy dissipation sufficient to cause phase segregation of the metastable Cu–Sb–I framework.

Thin-Film Fabrication of Cu_3SbI_6 (β -CuI:Sb)

Filtered Cu–Sb–I precursor solution (70 μ L, filtered through 0.45 μ m PTFE) was spin-coated onto HTL-coated substrates and thermally annealed at 55°C for 10 minutes. The annealing

temperature was kept below 100°C to preserve the integrity of the metastable Cu–Sb–I framework. Films for atomic force microscopy (AFM) characterization were deposited on cleaned, oxygen-plasma-treated ITO substrates using the same procedure.

Solar Cell Fabrication (Chapter 4)

Inverted thin-film solar cells were fabricated on ITO-coated glass substrates. Two hole-transport layer (HTL) configurations were evaluated. In the first configuration, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS; Clevios P VPA1 4083) films of 30 ± 4 nm thickness were deposited by spin-coating an aqueous dispersion at 4000 rpm for 30 s and drying at 130°C for 20 minutes. In the second configuration, 12 ± 2 nm thick tungsten suboxide (WO_{3-x}) films were deposited from nanoparticle dispersion (Avantama) by spin-coating (60 μL), 3000 rpm, ramp 1000 rpm s^{-1} , 30 s) and annealing at 120°C for 10 minutes. The Cu_3SbI_6 absorber layer was deposited onto the HTL surface as described above.

The electron transport layer (ETL) comprised [6,6]phenyl C_{71} butyric acid methyl ester (PC_{71}BM ; Lumtec, $\geq 99.8\%$, 2 wt% in anhydrous chlorobenzene; Sigma-Aldrich, 99.8%), spin-coated in two steps (50 μL filtered through 0.45 μm PTFE): 1000 rpm for 30 s (ramp: 1000 rpm s^{-1}) followed by 4000 rpm for 10 s (ramp: 1000 rpm s^{-1}). A bathocuproine (BCP; Sigma-Aldrich, 0.5 g L^{-1} in anhydrous ethanol) buffer layer was then spin-coated at 4000 rpm for 15 s (ramp: 2000 rpm s^{-1}). Silver back electrodes (100 nm) were thermally evaporated in high vacuum ($< 3 \times 10^{-6}$ mbar) at 1 $\text{\AA s}^{-1}$ for the first 10 nm and 2 $\text{\AA s}^{-1}$ for the remaining 90 nm. The complete device architecture was ITO / WO_{3-x} (12 nm) or PEDOT:PSS (30 nm) / $\beta\text{-CuI} : \text{Sb}$ / PC_{71}BM / BCP / Ag (100 nm).

3.1.2 Copper Bismuth Iodide (Chapter 5)

Substrate Cleaning

Glass substrates ($16 \times 16 \text{ mm}^2$) bearing pre-patterned ITO electrodes were cleaned by sequential sonication in acetone, mechanical scrubbing with plastic swabs and glass cleaner, rinsing with IPA, and blow-drying with nitrogen gas. Cleaned ITO substrates were treated in an oxygen plasma for 15 minutes prior to HTL deposition.

Powder Synthesis of $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$ (CBI)

Solid copper(I) iodide (CuI ; Thermo Scientific, 98%) and bismuth(III) iodide (BiI_3 ; Thermo Scientific, 99.99%) were combined in a 3:1 molar ratio and dissolved in a hot binary solvent mixture of DMSO:DMF (17:3 v/v) at 70°C with continuous stirring overnight. The solution was filtered through a PTFE syringe filter. For powder preparation, the filtered solution was

drop-cast onto cleaned glass substrates (cleaned as described above) and dried at 50°C for 96 hours. The dried material was collected by scraping and subsequently ground in a marble mortar to obtain a fine powder suitable for diffraction and thermal analysis.

Thin-Film Fabrication of $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$

Filtered CBI precursor solution (90 μL) was spin-coated onto HTL-coated substrates and thermally annealed at 60°C for 10 minutes. The influence of annealing temperature on the film morphology was investigated over the range 60 – 150°C; 60°C was identified as the optimal condition for continuous film coverage.

Solar Cell Fabrication (Chapter 5)

[2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz; TCI Chemicals, $\geq 98\%$, 2 mmol L^{-1} in anhydrous absolute ethanol; $\text{H}_2\text{O} < 0.003\%$; VWR) was filtered through a 0.22 μm PTFE membrane and spin-coated (50 μL , 3000 rpm, ramp 1000 rpm s^{-1} , 30 s) onto ITO substrates, followed by thermal annealing at 100°C for 10 minutes. A poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA; 1-Material, 0.4 wt% in anhydrous toluene; $\text{H}_2\text{O} < 0.001\%$; Sigma-Aldrich) solution was spin-coated onto the MeO-2PACz layer (60 μL , 5500 rpm, ramp 2000 rpm s^{-1} , 40 s) and annealed at 100°C for 10 minutes. To improve wettability of the hydrophobic PTAA surface, the PTAA-coated substrates were briefly rinsed with anhydrous DMF ($\text{H}_2\text{O} < 0.005\%$) immediately before CBI deposition. CBI precursor solution was then deposited as described above.

PC₇₁BM (Lumtec, $\geq 99.8\%$, 2 wt% in anhydrous chlorobenzene; Sigma-Aldrich, 99.8%) was spin-coated (45 μL) in two steps: 1000 rpm for 30 s (ramp: 1000 rpm s^{-1}) followed by 4000 rpm for 10 s (ramp: 1000 rpm s^{-1}). BCP (Sigma-Aldrich, 0.5 g L^{-1} in anhydrous ethanol) was spin-coated at 4000 rpm for 15 s (ramp: 2000 rpm s^{-1}). Silver back electrodes (100 nm) were thermally evaporated in high vacuum ($< 3 \times 10^{-6}$ mbar) at 1 $\text{\AA} \text{ s}^{-1}$ for the first 10 nm and 2 $\text{\AA} \text{ s}^{-1}$ for the remaining 90 nm. The complete device architecture was ITO / MeO-2PACz / PTAA / CBI / PC₇₁BM / BCP / Ag (100 nm).

3.1.3 Copper Bismuth Sulfide (Chapter 6)

Substrate Cleaning

Fluorine-doped tin oxide (FTO)-coated glass substrates were cleaned by sequential sonication in deionized water (10 min), mechanical brushing with glass cleaner on both sides, sonication in acetone (10 min), and sonication in isopropanol (10 min). After each sonication step, substrates

were blow-dried with nitrogen. Cleaned substrates were stored under nitrogen atmosphere; substrates stored for more than one week were re-cleaned before use.

TiO₂ Electron Transport Layer

An anatase TiO₂ electron transport layer was deposited by a solution-based process using titanium isopropoxide (TTIP) as the precursor. TTIP was dissolved in anhydrous absolute ethanol to a molarity of 0.3 M. The solution was spin-coated onto cleaned FTO substrates (50 μ L, 3000 rpm, ramp 1000 rpm s⁻¹, 90 s). Films were dried at 50°C for 10 minutes and subsequently calcined at 450°C for 1.5 hours on a preheated hotplate with a temperature ramp. Prior to Cu₃BiS₃ deposition, TiO₂ films were irradiated with UV radiation (intensity 100 mW cm⁻²) to remove surface organic contamination. All TTIP processing was performed under nitrogen atmosphere. Residual TTIP solution was wiped from substrate edges after spin-coating to expose the underlying FTO for electrical contacting.

Thin-Film Fabrication of Cu₃BiS₃ (CBS)

Cu₃BiS₃ thin films were synthesized by solution processing using metal nitrate precursors and thiourea as the sulfur source. Copper(II) nitrate (Cu(NO₃)₂) and bismuth(III) nitrate (Bi(NO₃)₃) were weighed to achieve a Cu:Bi:thiourea molar ratio of 3:1:7. Excess thiourea relative to the stoichiometric amount (3:1:3) was included to ensure complete coordination of metal ions and compensate for sulfur loss during annealing. The metal nitrates were co-dissolved in a DMF/DMSO solvent blend (4:1 v/v) at a nominal concentration of 1 mmol Cu(NO₃)₂ and 0.33 mmol Bi(NO₃)₃ per mL, with stirring for 30–60 minutes. Thiourea (2.33 mmol mL⁻¹) was dissolved separately in the same solvent blend and combined with the nitrate solution; the mixture was stirred continuously for one hour until a clear light-green color was obtained, indicating complex formation. The combined solution was filtered and used within 1–2 days to prevent bismuth oxynitrate precipitation.

Spin-coating was performed at 2500 rpm for 45 s (ramp: 1000 rpm s⁻¹) using 80 μ L of the precursor solution per layer. Each layer was immediately annealed at 165°C for 15 minutes on a preheated hotplate. Multiple layers were coated sequentially to increase total film thickness; the standard device used five layers. All spin-coating and annealing steps, except for weighing of metal nitrate precursors, were performed under nitrogen atmosphere. Additional morphological experiments employed doctor-blade coating and diluted precursor solutions (dilution ratios 1:0.33, 1:0.66, and 1:1 v/v, solution:solvent) to investigate processing-dependent crystal growth.

Solar Cell Fabrication (Chapter 6)

Solar cells were assembled using the device architecture FTO / TiO_2 / Cu_3BiS_3 / Au. Gold top electrodes were deposited by thermal evaporation at $0.5 \text{ \AA/s}$. A post-fabrication annealing step at 270°C was applied to improve photovoltaic performance; this temperature lies within the high-temperature polymorphic regime of Cu_3BiS_3 (above the second phase transition near 191°C) and its effects on device performance and phase composition are discussed in Chapter 6.

3.2 Characterization Methods

3.2.1 Powder X-Ray Diffraction (PXRD)

Powder X-ray diffraction (PXRD) was used to identify crystalline phases, determine lattice parameters, and perform quantitative phase analysis of Cu–Sb–I and Cu–Bi–I powder samples, as discussed in Chapters 4 and 5. The PXRD measurements and Rietveld refinements for these two materials were carried out by Dr. Daniel M. Töbrens and Prof. Dr. Susan Schorr at Helmholtz-Zentrum Berlin (HZB). In PXRD, monochromatic X-rays of wavelength λ irradiate a polycrystalline specimen. Constructive interference of the elastically scattered X-rays occurs when the Bragg condition $n\lambda = 2d \sin \theta$ is satisfied, where n is an integer, d is the interplanar spacing for a given set of crystallographic planes (hkl), and θ is the glancing angle. By scanning the detector over 2θ , a diffraction pattern is recorded whose peak positions and relative intensities are characteristic of the crystal structure and phase composition.

Bragg–Brentano geometry is a common reflection geometry for powder X-ray diffraction, in which a flat specimen is positioned at the center of the diffractometer circle, and the X-ray source and detector move in a coupled θ – 2θ configuration, so that diffraction is recorded from lattice planes that satisfy the Bragg condition at each angle. PXRD data were collected on a Bruker D8 diffractometer in Bragg–Brentano geometry using Cu– $\text{K}\alpha_{1,2}$ radiation. Rietveld refinement was performed using the FullProf Suite, employing the Thompson–Cox–Hastings pseudo-Voigt peak profile function and anisotropic peak broadening modeled by symmetry-adapted spherical harmonics. Phase identification was assisted by comparison with calculated diffraction patterns from structural data in the Inorganic Crystal Structure Database (ICSD) using Mercury 3.6 software. The quality of each refinement was assessed by the weighted residual factor R_{wp} , the expected residual R_{expected} , and the goodness-of-fit $\chi^2 = (R_{\text{wp}}/R_{\text{expected}})^2$. Refined quantities included lattice parameters, atomic fractional coordinates, site occupancy factors (SOFs), and isotropic atomic displacement parameters.

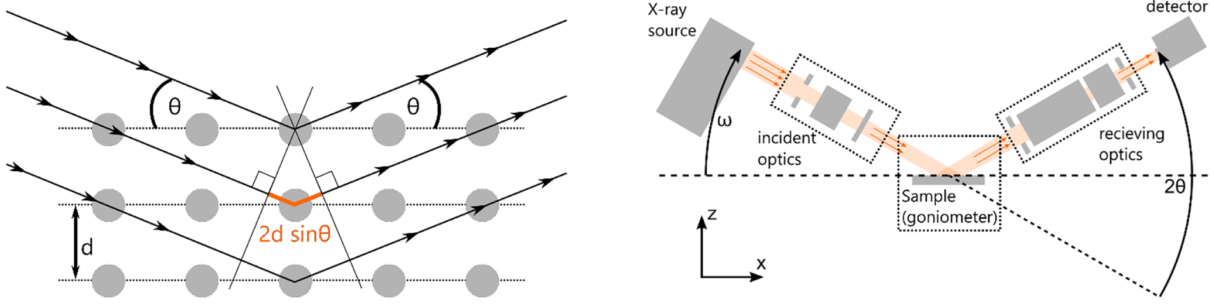


Figure 3.1: Constructive interference of X-rays in crystals and schematic representation of an X-ray diffractometer [63].

3.2.2 Grazing-Incidence X-Ray Diffraction (GI-XRD)

Grazing-incidence X-ray diffraction (GI-XRD) was used to determine the phase composition and lattice parameters of thin films. In GI-XRD, the incident X-ray beam is fixed at a small glancing angle ω to maximize the path length within the thin film and minimize signal from the underlying substrate, while the detector scans over 2θ . This geometry is particularly suited to thin polycrystalline films, which are often thinner than the X-ray penetration depth at conventional Bragg–Brentano incidence angles.

Rietveld Refinement

X-ray diffractometers provide only discrete intensity data points as a function of the diffraction angle θ . Rietveld refinement is a mathematical method used to determine a model function that best reproduces the measured diffraction pattern. The Rietveld method fits the entire diffraction pattern simultaneously and requires structural models for all crystalline phases present in the material[64]. Consequently, completely unknown or novel phases cannot be refined without prior structural information. Furthermore, several additional parameters must be known or estimated to achieve an accurate refinement. The refinement is based on a non-linear least-squares approach, in which the difference between the calculated and experimentally observed diffraction intensities is minimized:

$$S_y = \sum_i w_i |y_{io} - y_{ic}|^2 \rightarrow \min, \quad (3.1)$$

where y_{io} are observed points, y_{ic} are calculated points and w_i are weighing factors[64]. In order to assess the quality of the refinement, figures of merit can be used, including the weighted residual R_{wp}

$$R_{wp} = \sqrt{\frac{\sum_i w_i (y_{io} - y_{ic})^2}{\sum_i w_i (y_{io})^2}}, \quad (3.2)$$

and the goodness of fit

$$GOF = \sqrt{\frac{\sum_i^n w_i (y_{io} - y_{ic})^2}{n - p}}, \quad (3.3)$$

where n is the number of measurement points and p is the number of refined parameters. In addition, the difference curve between the measured and calculated intensities is typically evaluated in order to assess the quality of the refinement.

3.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to characterize the microstructure and surface characteristics of powder samples and thin films. In SEM, a focused primary electron beam is rastered across the sample surface. Interactions between the primary electrons and the specimen generate secondary electrons (SE), which carry information on surface topography, and backscattered electrons (BSE), which yield compositional contrast proportional to the mean atomic number. A photomultiplier-tube-based through-lens detector (TLD) capable of detecting both SE and BSE signals was used in conjunction with an electromagnetic immersion lens for high-resolution imaging.

SEM measurements were carried out on a Nova NanoSEM 450 instrument (FEI Deutschland GmbH) at an accelerating voltage of 15 kV with an electron beam diameter of 4 nm. Powder samples were mounted on sample holders using double-sided carbon adhesive tape.

3.2.4 Transmission Electron Microscopy: HRTEM, STEM-HAADF, and EDX

High-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy with a high-angle annular dark-field detector (STEM-HAADF), and energy-dispersive X-ray spectroscopy (TEM-EDX) were used to characterize the local crystallographic structure, lattice spacings, and elemental distribution within samples. In HRTEM, phase contrast of the transmitted electron beam is exploited to image atomic columns and lattice fringes at sub-angstrom resolution, enabling direct measurement of interplanar d -spacings. Selected-area electron diffraction (SAED) was performed to confirm crystal structure and determine zone-axis orientations of individual domains. SAED patterns were indexed using the CrystBox diffractGUI software (version 2.21), which applies the RANSAC (Random Sample Consensus) algorithm to fit a regular reciprocal lattice to the detected diffraction spots, computes zone-axis orientations, and quantifies angular and d -spacing residuals.

HRTEM measurements were conducted by Dr. Martin Peterlechner (LEM, KIT) performed on a FEI Titan³ 80–300 microscope operating at 300 kV, equipped with an image C_s -corrector and a TVIPS XF416 camera. STEM-HAADF imaging and TEM-EDX mapping were carried out

on a FEI Tecnai Osiris instrument operating at 200 kV, using a Super-X four-quadrant silicon-drift EDX detector. EDX data analysis was performed with Bruker Esprit 2.3 software and the HyperSpy Python package. HRTEM image analysis was performed using Gatan Digital Micrograph.

3.2.5 Thermogravimetric and Differential Thermal Analysis (TGA/DTA)

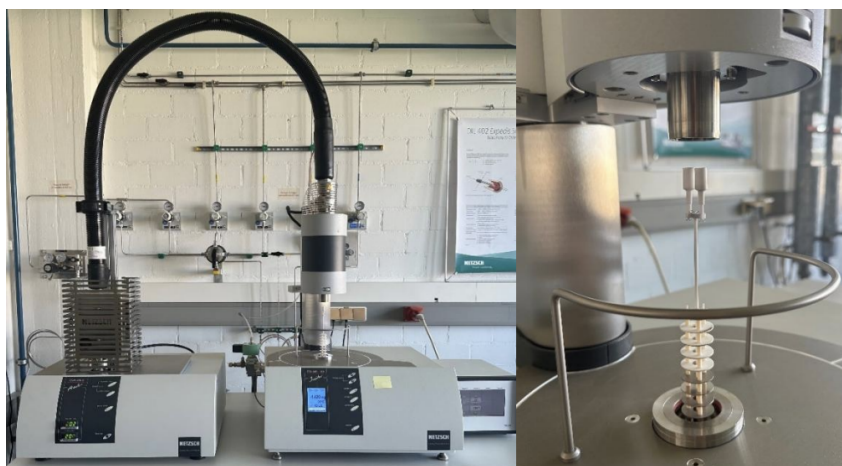


Figure 3.2: Measurement setup for TGA and DTA.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to simultaneously determine the thermal stability, decomposition temperatures, and solid-state phase-transition temperatures of the compounds. In TGA, the sample mass is recorded continuously as a function of temperature; mass-loss events indicate decomposition or evaporation of volatile species. DTA simultaneously records the temperature difference between the sample and an inert reference under identical heating conditions; endothermic and exothermic events, including solid-state phase transitions and chemical reactions, manifest as peaks in the DTA signal.

TGA/DTA measurements were performed using a Netzsch Jupiter F449 simultaneous thermal analyzer. Samples were heated from room temperature to 900°C at a controlled ramp rate of 3 K min⁻¹, held at 900°C for 15 minutes, and cooled at the same rate. A correction run was performed prior to each sample measurement under identical conditions using an empty crucible to establish an instrument baseline and eliminate systematic measurement artifacts. All measurements were conducted under a flow of pure nitrogen gas at 80 mL min⁻¹.

3.2.6 Ultraviolet–Visible–Near-Infrared Spectrometry (UV-Vis-NIR)

Absorption, transmission, and reflection are key parameters for materials used in thin-film solar cells. The relevant spectral range includes ultraviolet (UV) radiation, visible light (Vis),

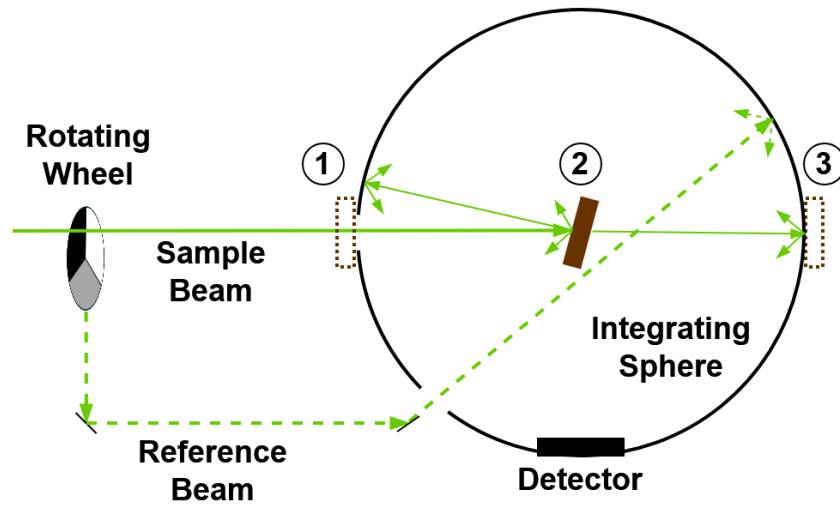


Figure 3.3: Schematic measurement setup for UV-Vis-NIR Spectroscopy. Optics like lenses, concave mirrors, and depolarizers are omitted for clarity.

and near-infrared radiation (NIR). UV-Vis-NIR spectroscopy is used to determine absorption, transmission, or reflection of samples as a function of the wavelength within this spectral range. The measurement setup is illustrated in Figure 3.3. A rotating wheel with mirrored segments divides the output of a monochromator that scans the desired wavelength range into alternating sample and reference beam paths. Between these segments, the beam is blocked completely. The depolarized sample beam is directed and focused onto the sample, and the position depends on the quantity being measured. For absorption measurements, the sample is placed at an angle inside an integrating sphere (position ②). The sample beam enters the sphere through a slit, illuminating the sample. The detector is located at the bottom of the sphere and collects all radiation that passes through the sample or is reflected by it, since the inner surface of the integrating sphere is coated with a highly reflective material. Only a small portion of the radiation is diffusely reflected out of the sphere through the entrance slit. The difference between the signal from the sample beam and the signal from the reference beam, which does not strike the sample, thus corresponds to the radiation absorbed by the sample, since the incident radiation can either be reflected, transmitted or absorbed. The absorbed fraction is referred to as the absorptance, while the transmitted fraction is called the transmittance. In optical spectroscopy, the absorptance is often expressed logarithmically as the absorbance, defined as the logarithm of the transmittance:

$$A = -\log_{10} \left(\frac{I}{I_0} \right) = -\log_{10}(T), \quad (3.4)$$

where A is the absorbance, I_0 is the incident intensity, I is the transmitted intensity and T is the transmittance. To measure the transmittance, the sample is placed in front of the integrating

sphere (position ①), so that reflected and absorbed radiation are not collected by the detector. For reflection measurements, the sample is positioned behind the integrating sphere (position ③).

Optical band gaps were extracted from Tauc plots constructed as $(\alpha h\nu)^n$ vs. $h\nu$, where α is the absorption coefficient, h is Planck constant, ν is the photon frequency, and $n = 2$ for direct-gap semiconductors and $n = 0.5$ for indirect-gap semiconductors. The linear region of the Tauc plot above the absorption onset is extrapolated to zero yield to obtain the optical band-gap energy E_g . UV-Vis-NIR absorbance measurements were carried out on an Agilent Cary 5000 spectrometer featuring a double-beam optical setup.

In this thesis, absorption spectra were measured using a Cary 5000 UV-Vis-NIR spectrometer from Agilent Technologies equipped with an integrating sphere.

3.2.7 Photoluminescence Spectroscopy (PL)

In photoluminescence spectroscopy, a sample is irradiated, exciting electrons in the semiconductor to higher energy states via absorption. The generated charge carriers rapidly thermalize to the band edges, transferring the excess energy to the lattice. Subsequent radiative recombination results in photon emission. Information about recombination mechanisms and defects can be deduced from the emitted radiation, known as photoluminescence. Photoluminescence can be divided into intrinsic and extrinsic photoluminescence. Intrinsic photoluminescence originates from direct band-to-band recombination, whereas extrinsic photoluminescence arises from recombination processes involving defects or impurities within the semiconductor [65]. In single-crystalline materials with low defect density, intrinsic photoluminescence dominates and is already observable at room temperature.

To measure extrinsic photoluminescence, it is often necessary to operate at very low temperatures, where thermal carrier excitation and peak broadening due to lattice vibrations are reduced. At low temperatures, excited electron-hole pairs form bound states through Coulomb attraction, known as excitons. These excitons are not stable at higher temperatures because they dissociate into free charge carriers. In high-purity semiconductors, excitons can diffuse freely through the crystal before recombining. Such excitons are referred to as free excitons, and their radiative recombination results in emission close to the bandgap energy, often dominating the photoluminescence spectrum in single-crystalline materials at low temperatures. As the temperature increases, free excitons dissociate more rapidly due to thermal energy, producing free charge carriers that can subsequently recombine either radiatively or non-radiatively.

In crystals with significant defect concentrations, the emission is often dominated by bound excitons. Bound excitons are free excitons that become localized at defect or impurity sites,

resulting in emission at energies below the band-gap energy. At low temperatures, the thermal energy is insufficient to ionize these localized states, allowing bound excitons to remain stable and recombine radiatively. Another recombination mechanism is donor-acceptor pair recombination, in which donor defects provide electrons while acceptor defects capture them. Donors and acceptors are spatially separated, and the recombination of an electron at a donor and a hole at an acceptor occurs via tunneling. The energy of the emitted photon then depends on the distance between the donor and acceptor sites [66]. Emission from donor–acceptor pair recombination can often be observed at higher temperatures than bound-exciton emission, since more thermal energy is required to ionize these states.

The photoluminescence measurements were carried out using a FS5 spectrofluorometer from Edinburgh Instruments with the cuvette holder attached to the integrating sphere module SC-30. For low-temperature PL, a near-infrared-sensitive setup consisting of a Fourier transform infrared spectrometer (Bruker Vertex 80) with a nitrogen-cooled germanium detector and a 10 mW continuous-wave laser diode at 375 nm. A Cryomech PT403 pulse tube cryocooler was used to cool the sample down to 3.2 K.

3.2.8 White Light Interferometry

White-light interferometry is an optical measurement technique that uses the interference of broadband light to map the topography of the samples under investigation. Light from a non-coherent light source is split into a reference beam and a sample beam. These beams can interfere if the optical path difference between them is in the order of the short coherence length of the broadband light. The resulting constructive and destructive interference signals are detected by a detector. By vertically scanning either the objective or the sample, intensity fluctuations are recorded as a function of the scan position. The position of maximum interference contrast corresponds to the local surface height at each measured point. Repeating this process for many points on the sample surface, corresponding to the detector pixels, enables reconstruction of a precise height profile and, thus, the surface topography [67]. This measurement technique requires sufficient surface reflectivity and tilt correction. Furthermore, it is sensitive to vibrations, and the lateral resolution is limited by the wavelength of the light. In this thesis, a Plu neox white-light interferometer from Sensofar atop an anti-vibration stage was used.

3.2.9 Photoelectron Spectroscopy Yield in Air (PESA)

Photoelectron spectroscopy yield in air (PESA) was used to determine the ionization potentials (IP) of thin films, which in semiconductors are close to the valence band maximum (VBM) energy referenced to the vacuum level. To determine the ionization potential, a sample is irradi-

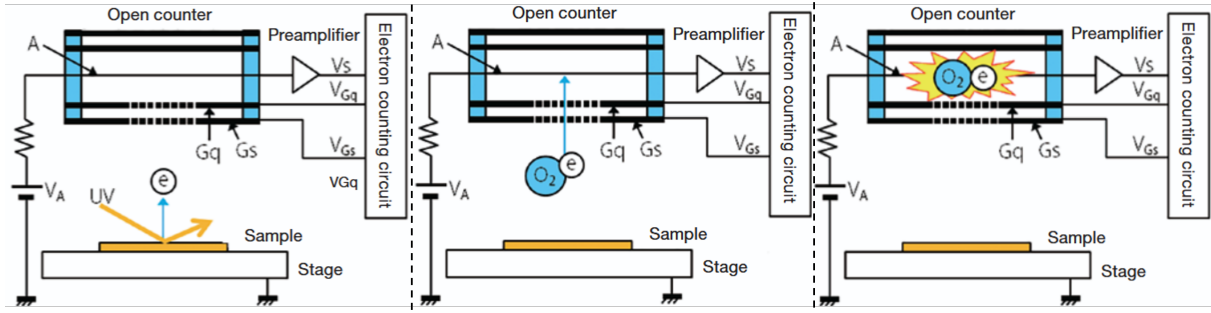


Figure 3.4: Measurement principle of photoelectron spectroscopy yield in air (PESA) [68].

ated with UV light of varying frequency. If the photon energy exceeds the ionization potential or work function, photoelectrons are emitted from the sample surface. These photoelectrons are accelerated towards the suppressor grid G_s , ionizing oxygen molecules along their path. After entering the open counter, the generated oxygen ions are drawn towards the anode A by a high voltage V_A . Near the anode, the electrons detach from the oxygen ions and are further accelerated, eventually triggering an electron avalanche through collisions and ionization of surrounding molecules. The resulting electrons are collected at the anode and detected as pulse signals by the electron-counting circuit. As soon as a pulse is detected, the grid voltages are adjusted to suppress the avalanche effect and to neutralize the generated positive ions. During this period, no additional photoelectrons can enter the counter. The system then returns to its initial state, allowing the next measurement cycle to begin. The energy of the incident UV photons is increased over time, and the square root of the electron count is plotted as a function of this photon energy. From this plot, the threshold energy is determined by extrapolating the linear region to zero, yielding the work function or ionization potential of the sample [69]. The photoelectron yield Y as a function of photon energy E follows the power-law relation $Y^{1/n} \propto (E - \text{IP})$, where $n = 2$ for a three-dimensional density of states (fitted with a power number of 0.5). The IP is extracted from the threshold energy at which the linear fit extrapolates to zero yield. The electron affinity (EA) is then estimated as $\text{EA} = \text{IP} - E_g$, where E_g is the optical band gap from UV-Vis-NIR measurements.

PESA measurements were performed on a RIKEN KEIKI AC-2E photoelectron spectrometer. Photoelectron yields were corrected for lamp intensity prior to fitting.

3.2.10 Atomic Force Microscopy (AFM)

Atomic force microscopy is a high-resolution measurement technique that allows investigation of thin-film surface topography by scanning the sample surface with a very sharp tip. It can achieve a vertical spatial resolution of 0.1 nm and a lateral resolution of 1 nm [71]. The measuring principle is illustrated in Figure 3.5. The tip is attached to a cantilever that scans

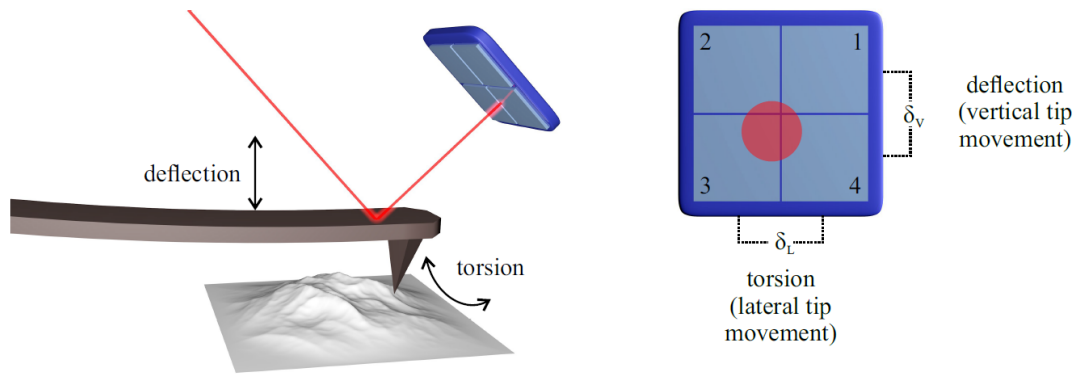


Figure 3.5: Measurement principle of atomic force microscopy (AFM). Figure adapted from [70].

across the sample surface. Interactions between the sample and the tip cause the cantilever to deflect. This deflection is measured by a laser that is focused onto the cantilever and reflected onto a four-quadrant photodiode. The difference signal between the upper and lower quadrants provides information about the vertical deflection of the cantilever, while the difference signal between the left and right quadrants indicates the lateral torsion of the tip. These differential signals serve as inputs for a feedback control loop, and the response depends on the selected measurement mode.

In contact mode, the tip is moved across the sample surface while remaining in continuous contact. During the measurement, the cantilever deflection is kept constant by the feedback loop. The corresponding control signals are used to calculate the height, resulting in a surface topography map of the sample.

In dynamic tapping mode, the cantilever, and therefore the tip, is oscillated. In this case, interaction with the surface dampens the oscillation, and the feedback loop keeps the oscillation amplitude constant [71]. As in contact mode, the resulting control signals translate into a topography of the sample surface. Since the tip is not in continuous contact with the sample, the risk of tip or sample deformation is minimized while still maintaining atomic resolution [72].

AFM measurements were performed on a Bruker Dimension Icon atomic force microscope located inside a nitrogen-filled glovebox, enabling characterization of air-sensitive thin films without atmospheric exposure. RMS roughness (R_q) was extracted from scan areas matched to the scale of the film morphology. Average grain sizes in films were determined by statistical analysis of grain boundary positions in AFM images.

3.2.11 Confocal Raman Spectroscopy

Confocal Raman spectroscopy was used to probe the local vibrational modes and bonding environments of powder and thin films, and to distinguish these materials from their binary precur-

sors. In Raman spectroscopy, incident photons interact inelastically with molecular vibrations or lattice phonon modes, generating scattered photons shifted in energy by characteristic vibrational frequencies. Confocal optics restricts the probe volume to a diffraction-limited spot, enabling spatially resolved spectral maps across heterogeneous sample areas.

Confocal Raman measurements were performed on a WITec alpha300 R instrument equipped with a UHTS300 spectrometer (300 mm focal length) and a Zeiss microscope. Excitation was provided by 488 nm and 532 nm lasers operated via adjustable TruePower modules in the range 0.4 – 1.1 mW (measured at the sample surface). Single-spot spectra were collected using 50 $\times$ (NA = 0.75) and 100 $\times$ (NA = 0.90) objectives with 600 g mm⁻¹ and 1800 g mm⁻¹ gratings, yielding spectral resolutions better than 3 cm⁻¹ and 1 cm⁻¹, respectively. Typical single-spot acquisition times were 5–10 s with 5–10 accumulations (600 g mm⁻¹ grating) or 30–50 s with 2 accumulations (1800 g mm⁻¹ grating). Raman scattering was detected with a back-illuminated CCD camera.

Spatially resolved Raman maps were recorded using a 100 $\times$ objective and 600 g mm⁻¹ grating over 100 μ m $\times$ 100 μ m areas with a step size of 1 μ m, producing 10,000 spectra per map with an acquisition time of 7 s per spectrum. Data processing was performed with WITec Project Plus v. 7.0 software and included cosmic-ray removal and polynomial background subtraction. Raman maps were generated using TrueComponent analysis and by tracking maximum peak intensities of selected bands.

3.2.12 X-Ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy (XRF) was used to determine the bulk elemental composition and average stoichiometry of powder samples. The measurements were carried out by Dr. Yvonne Tomm and Prof. Dr. Susan Schorr at Helmholtz-Zentrum Berlin (HZB). In XRF, a primary X-ray beam ejects core-shell electrons from atoms in the sample. Characteristic fluorescence X-rays are emitted as outer-shell electrons fill the resulting vacancies; the energies and intensities of these characteristic X-rays identify the elements present and allow quantification of their relative concentrations. XRF provides an area-averaged compositional measurement and cannot resolve nanoscale phase heterogeneity. Measurements were performed on a Bruker M4 Tornado instrument. Compositional analysis was repeated at multiple positions (up to 10 points) across each powder sample to assess spatial uniformity; results are reported as mean values with standard deviations.

3.2.13 Stylus Profilometry

Stylus profilometry was used to measure the thicknesses of all thin films. In this technique, a diamond-tipped stylus is mechanically dragged across a step edge created by scratching through the film to the underlying substrate. The vertical displacement of the stylus is recorded as a function of lateral position; the height step at the scratch edge provides the film thickness. Multiple measurements at different positions on each sample were averaged to obtain representative thicknesses values. Film thickness measurements were performed on a Bruker Dektak XT stylus profilometer.

3.2.14 Solar Cell Characterization: Current Density–Voltage Curves and External Quantum Efficiencies

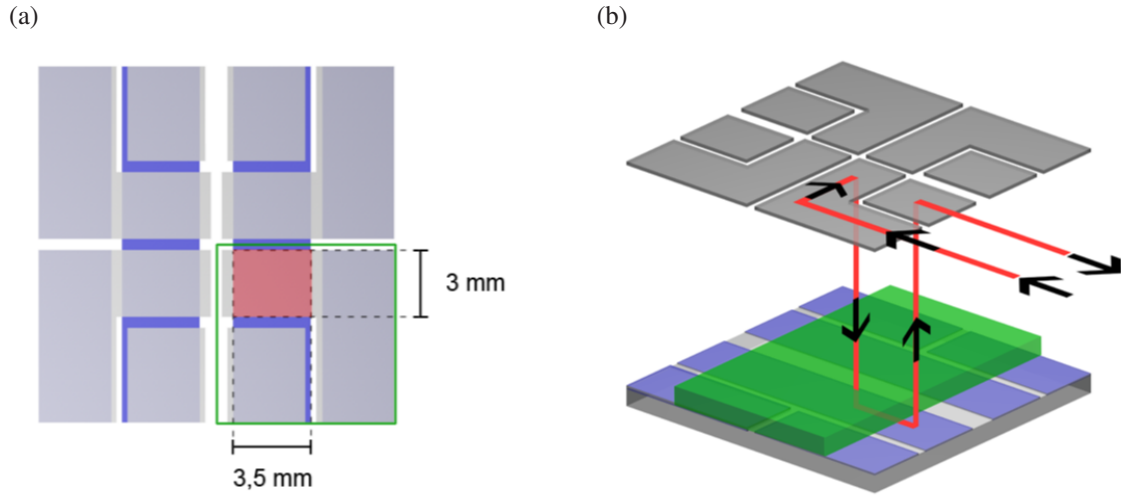


Figure 3.6: Solar cell design and current-flow geometry. **(a)** Top view of a substrate with structured electrodes. The red area marks one solar cell with a photo-active area of 10.5 mm^2 . **(b)** Schematic of the current flow in the solar cell [73].

To characterize solar cells electrically, the J - V characteristics were measured both in the dark and under illumination. The current density J can only be determined if the area of the solar cell is known. Figure 3.6a shows the solar cell design and architecture comprising a substrate with a structured transparent conductive oxide (TCO) layer, either indium tin oxide (ITO) or fluorine-doped tin oxide (FTO), the solar cell stack, and a structured top electrode. The electrode structures are designed such that the top and bottom electrodes overlap to form four solar cell pixels in the center of the substrate, each with a photo-active area of 10.5 mm^2 . The solar cell layers must be scraped off at the edges before the top electrode is deposited. The solar cells

can then be contacted at the edge of the substrate for J - V measurements, as illustrated in Figure 3.6b. A sweeping voltage is applied to the contacts and the resulting current is measured.

To obtain comparable and meaningful results, the solar cells must be illuminated by a source with a spectrum closely resembling the solar spectrum. For this purpose, a solar simulator with a 300 W xenon short-arc lamp (AX-LightLine, Sciencetech) was used in this work. It is certified to replicate the ASTM G 173 Air Mass 1.5 (AM 1.5) reference spectrum, which represents the terrestrial solar spectral irradiance at a solar incidence angle of 37° [74]. The spectrum of the solar simulator and the reference spectrum are plotted in Figure 3.7. As both the spectrum and irradiance of the lamp fluctuate initially, the lamp is ignited at least 20 minutes before the start of the measurements. The desired irradiance of 1000 W/m^2 is set using a silicon reference cell (Newport 91150-KG5). When measuring solar cells with the design described above, the edge of the substrate is shaded by a mask so that only the photo-active pixels are illuminated.

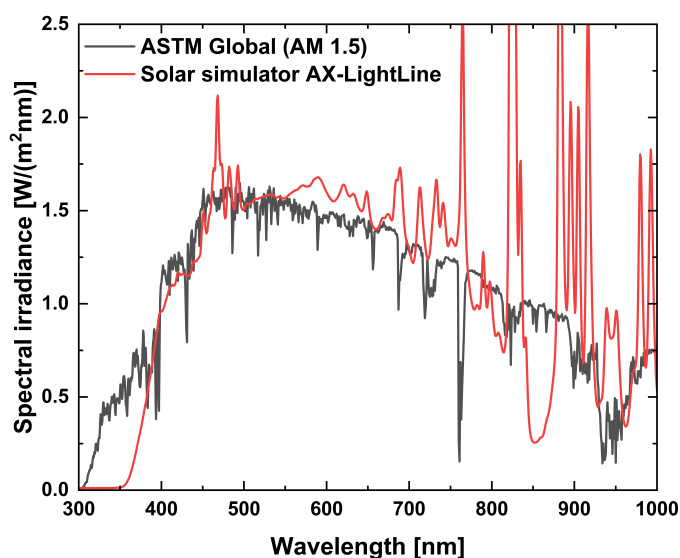


Figure 3.7: Reference ASTM Global AM 1.5 spectrum and emission spectrum of the AX-LightLine solar simulator by Sciencetech.

From J - V measurements under illumination, the following photovoltaic figures of merit were extracted: open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and power conversion efficiency (PCE). External quantum efficiency (EQE) spectra were recorded to determine the wavelength-resolved photocurrent response of each device. The EQE is defined as the fraction of incident photons at each wavelength that are converted to collected electrons. The photocurrent density J_{EQE} integrated over the solar spectrum was calculated from the EQE spectrum and compared with J_{SC} from J - V measurements for verification. In order to measure

the EQE, a spectral response setup was used in this work. This setup consists of a 450 W xenon high-pressure lamp (LSH601, LOT Oriel) and a Czerny–Turner-monochromator (Omni- λ 300, LOT Oriel) for generating monochromatic light. In addition, a chopper (C-995, Terahertz Technologies) was used to modulate the light and allow for lock-in amplification. The setup was calibrated to a reference UV-enhanced Silicon pin photodiode (Newport 818-UV-20925) with a known spectral response, leading to a known illumination intensity for the measurement.

4 Copper Antimony Iodide (Cu–Sb–I)

4.1 Background

4.1.1 Copper–Pnictogen Iodides in the Lead-Free Halide Landscape

Although lead-free perovskite and perovskite-inspired semiconductors have advanced considerably in structural characterization and device development, environmental instability and non-radiative recombination continue to limit their photovoltaic performance [75, 76]. These shortcomings have spurred growing research into perovskite-inspired materials (PIMs), often based on Sb^{3+} and Bi^{3+} , which exhibit lower or no toxicity compared to lead-based compounds [76, 18, 77]. Among PIMs, fully inorganic Caswellsilverites – formed from group IB (Cu, Ag) and group VA (Sb, Bi) halide compositions – have been reported and are often referred to as “Rudorffites” [76, 18, 77].

Caswellsilverites exhibit the general stoichiometry $\text{A}_a\text{B}_b\text{X}_y$ with charge balance $y = (a + 3b)/z$, where z is the oxidation state of X. Within this class, silver–bismuth iodides have been extensively studied, including AgBiI_4 , Ag_2BiI_5 , Ag_3BiI_6 , and Ag_2BiI_7 [76]. Replacing silver with copper at the A site is an appealing strategy owing to the greater abundance and typically lower cost of copper [78]. Replacing bismuth with antimony at the B site offers another compositional handle: Sb^{3+} carries a smaller ionic radius (0.76 Å) than Bi^{3+} (1.03 Å), influencing structural dimensionality, and antimony is substantially cheaper and more earth-abundant than bismuth [23]. The lighter Sb^{3+} also reduces the contribution of relativistic spin–orbit coupling, shifting the conduction band minimum to higher energies relative to Bi^{3+} analogs. This also leads to a blue-shift of the absorption onset toward wide bandgap energies, thereby increasing the potential for higher open-circuit voltage in indoor or tandem applications [79, 80].

The structural framework of Caswellsilverites consists of a layer of octahedrally coordinated B-site cations (Sb^{3+} or Bi^{3+}) surrounded by anions, atop another layer of octahedrally coordinated monovalent A-site cations (Cu^+ or Ag^+) within a three-dimensional layered network. This requirement for octahedral coordination of both cations is the defining structural criterion that distinguishes true Caswellsilverites from other ternary halides with similar stoichiometry but fundamentally different coordination environments.

4.1.2 Prior Work on Copper Antimony Iodide

Copper antimony iodide with the nominal composition Cu_3SbI_6 is the only copper–antimony iodide compound reported in the literature to date. Previous studies have explored its use in photovoltaic devices and resistive-switching memory, routinely classifying it as a “Rudorffite” [77, 81, 82]. However, these classifications were largely based on stoichiometric composition rather than on detailed structural characterization. The assumption that Cu_3SbI_6 adopts a Caswellsilverite structure was grounded in the expectation that the 3:1 cation ratio and the presence of a trivalent pnictogen would naturally lead to octahedral coordination of Sb^{3+} .

Theoretical calculations by Pishtshev and Karazhanov predicted that Cu_3SbI_6 should crystallize in a rhombohedral structure (space group $R\bar{3}m$) with a bandgap suitable for photovoltaic applications [83]. However, experimental validation of this prediction has been lacking. The few experimental reports that included X-ray diffraction data showed complex patterns that were not fully indexed or refined, leaving the true crystal structure ambiguous. This gap between theoretical prediction and experimental characterization has hindered a fundamental understanding of the structure–property relationships of the material.

4.1.3 Structural Considerations: CuI Polymorphs and Polytypism

Copper(I) iodide has two well-characterized polymorphs: γ -CuI (zincblende-type, cubic, space group $F\bar{4}3m$) and β -CuI (wurtzite-type, hexagonal, space group $P\bar{6}m2$) (see Chapter 2). The γ -phase adopts cubic close packing (ABC stacking), whereas the β -phase adopts hexagonal close packing (AB stacking) [84, 85]. The energy difference between these stacking sequences is small and stacking faults are common in CuI [39].

Polytypism is the phenomenon in which a material exhibits multiple structural variants (polytypes) differing only in the stacking sequence of structurally similar layers. In CuI, polytypism arises naturally from the low energy cost of stacking faults, leading to coherent intergrowth of β -CuI and γ -CuI domains within a single crystallite. X-ray diffraction patterns of polytypic CuI show reflections from both polymorphs, with relative intensities depending on the proportion and coherence length of each polytype [37].

Introducing foreign cations into the CuI lattice can stabilize specific stacking sequences or introduce additional disorder. If Sb^{3+} occupies substituted sites within the CuI framework, charge compensation requires the formation of Cu^+ vacancies. The resulting defect structure – consisting of substitution-type Sb^{3+} and compensating Cu^+ vacancies – could preferentially stabilize certain stacking faults, leading to a defect-stabilized polytypic microstructure. This mechanism would produce a material that is structurally distinct from both pure CuI and octahedrally coordinated Caswellsilverites, despite sharing a similar stoichiometric formula with the latter.

Motivation for Structural Clarification

Classifying Cu_3SbI_6 as a Caswellsilverite has significant implications for interpreting its properties and for the design strategies used to optimize its performance. If the material adopted a true Caswellsilverite/Rudorffite-type structure, both Cu^+ and Sb^{3+} would be incorporated into an iodide-based octahedral cation framework.

This thesis addresses this fundamental question through comprehensive structural characterization that combines powder X-ray diffraction with Rietveld refinement, selected-area electron diffraction (SAED), high-resolution transmission and scanning transmission electron microscopy (HRTEM/ STEM), energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy, and thermal analysis. This structural reclassification provides the foundation for further understanding the material.

4.2 Results and Discussion

4.2.1 Thermal Stability

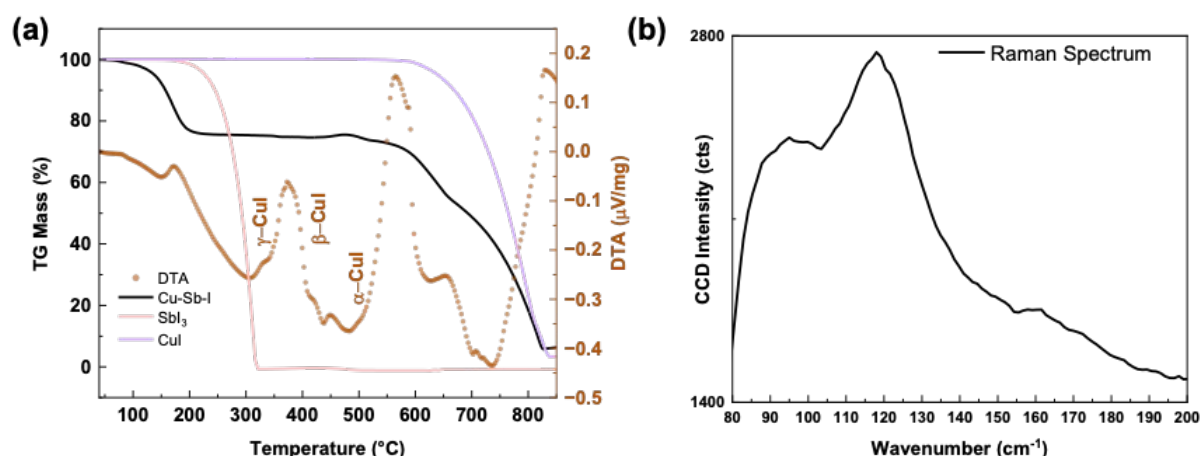


Figure 4.1: (a) TGA and DTA of a Cu-Sb-I powder sample during heating up to 900 °C and, for reference, TGA of SbI_3 and CuI . SbI_3 evaporates beyond 250 °C. The DTA of Cu-Sb-I shows the phase transition of CuI , which remains after the early thermal destabilization of the Cu-Sb-I framework. (b) Raman spectra of unground Cu-Sb-I powder.¹

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted to assess the thermal stability of Cu-Sb-I powder samples alongside the binary precursors CuI and SbI_3 . Pure SbI_3 evaporates beyond 250 °C. CuI remains nearly mass-stable up to a substantially higher temperature of approximately 620 °C and undergoes only major mass loss near the high-temperature end of the scan. During heating, CuI shows two phase transitions that have been

¹ This was measured by Dr. K. Garbev (ITC, KIT).

widely reported in the literature [84, 85]: the γ -phase (adopting the zincblende-type structure) is found below 369 °C, the β -phase (adopting the wurtzite-type structure) occurs between 369 °C and 407 °C, and the α -phase (in a superionic structure) prevails above 407 °C.

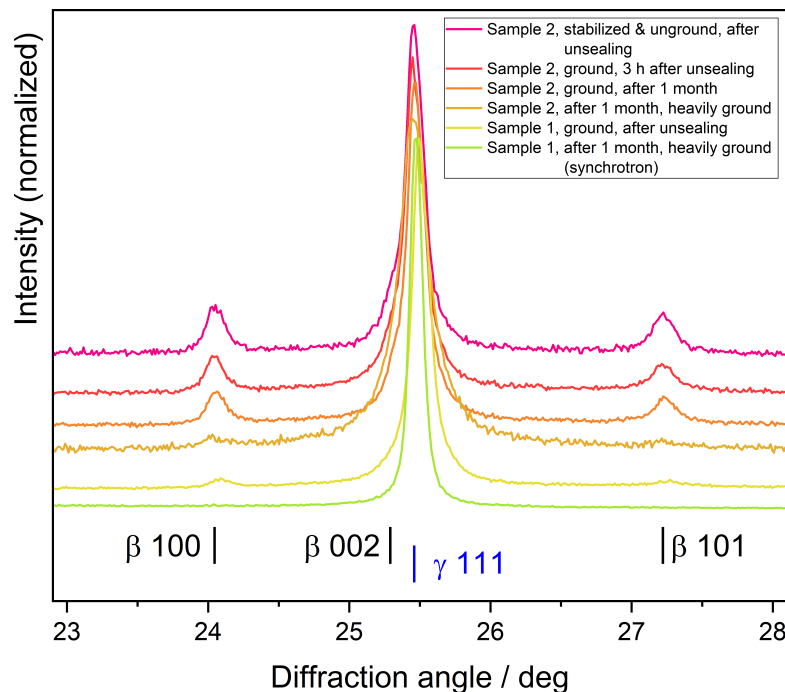


Figure 4.2: Disordered phase segregation can be observed at the 100 and 101 Bragg peaks of the β -CuI phase influenced by thermal and/or mechanical interference.²

The TGA curve (Figure 4.1a) shows that the Cu–Sb–I compound exhibits a thermal signature distinctly different from those of the binary iodide precursors. In particular, an early loss in mass begins below 100 °C – substantially lower than the onset of mass loss of either binary precursor. A subtle DTA feature in the same temperature regime accompanies this initial mass loss. This can be attributed to the early destabilization of Sb occupying metastable sites within the Cu–Sb–I framework that are less thermally stable than either binary precursor, thereby leaving a bulk CuI-rich matrix to undergo its known phase transitions at higher temperatures. The mass loss continues slowly towards higher temperatures, and this trend does not match the properties of a mere mixture of CuI and SbI₃; instead, it indicates that a Cu–Sb–I framework has formed but is not stable at elevated temperatures, thereby limiting the processing temperature without degradation to well below 100 °C.

Thermal sensitivity below 100 °C is a critical constraint for processing and device integration. Conventional powder-processing techniques such as grinding in a mortar and pestle, routinely used to homogenize precursor powders and improve thin-film quality, induce sufficient

² Measured by Dr. D. M. Töbrens (Helmholtz-Zentrum Berlin).

mechano-thermal energy dissipation to trigger phase segregation in the Cu–Sb–I compound. Repeated friction events can create short-lived local hot spots, even when the bulk sample remains near ambient temperature [86]. This mechano-thermal fragility is directly observable in Raman spectroscopy (Section 4.2.2) and X-ray diffraction measurements, where ground samples exhibit enhanced spectral features associated with phase-segregated CuI and SbI₃. Because of this effect, all subsequent experiments described here were performed deliberately on unground powder.

Post-deposition annealing – commonly used to enhance grain growth and reduce defect density in lead-halide perovskites – is not a viable strategy for Cu–Sb–I. Furthermore, the sensitivity to mechanical stress raises concerns about long-term operational stability under thermal cycling or mechanical vibration in real-world photovoltaic applications. Figure 4.2 shows the analysis of the Cu–Sb–I crystalline phase before and after grinding, demonstrating a substantial effect on the phase composition of the sample. For this reason, subsequent experiments were conducted without grinding the powder.

4.2.2 Vibrational Properties of Cu–Sb–I

Raman spectroscopy is a sensitive probe of local bonding environments and vibrational modes, making it an ideal technique for distinguishing among structural motifs in copper–antimony iodides. The Raman spectrum of unground Cu–Sb–I powder, as shown in Figure 4.1b, is dominated by intrinsic Cu–Sb–I fingerprints. The band at 93–95 cm^{−1} is assigned to the Cu–Sb–I framework, more precisely to vibrations produced by bridging iodide [87]. The feature at 115 cm^{−1} is attributed to another characteristic lattice mode of Cu–Sb–I, which lies close to the reported feature of high-temperature β -CuI (at 120 cm^{−1}) [88, 84]. The spectrum also shows features in the 124–148 cm^{−1} regime that overlap with the transverse-optic (TO) and longitudinal-optic (LO) phonon modes of γ -CuI, previously reported near 124–131 cm^{−1} and 140–148 cm^{−1} respectively [89, 90]. A very subtle shoulder feature at approximately 162 cm^{−1} is assigned to residual SbI₃, in agreement with the symmetric stretching mode of the cis-Sb–I unit and with the strongest Raman mode of bulk SbI₃ (the E_g symmetric Sb–I stretching vibration at 160.6 cm^{−1} reported by Hsueh et al. [91]). The presence of CuI-derived modes relates to a CuI-based host lattice.

Upon grinding, the Raman spectrum undergoes significant changes (Figure 4.3). Raman mapping was performed on ground powder samples using 10,000 local Raman spectra recorded over a 100 × 100 μm^2 area. The data were decomposed into three principal components labeled Minor, Major, and Intermediate, based on the cumulative area each component covered. The most significant observation relative to the unground spectrum is the pronounced evolution

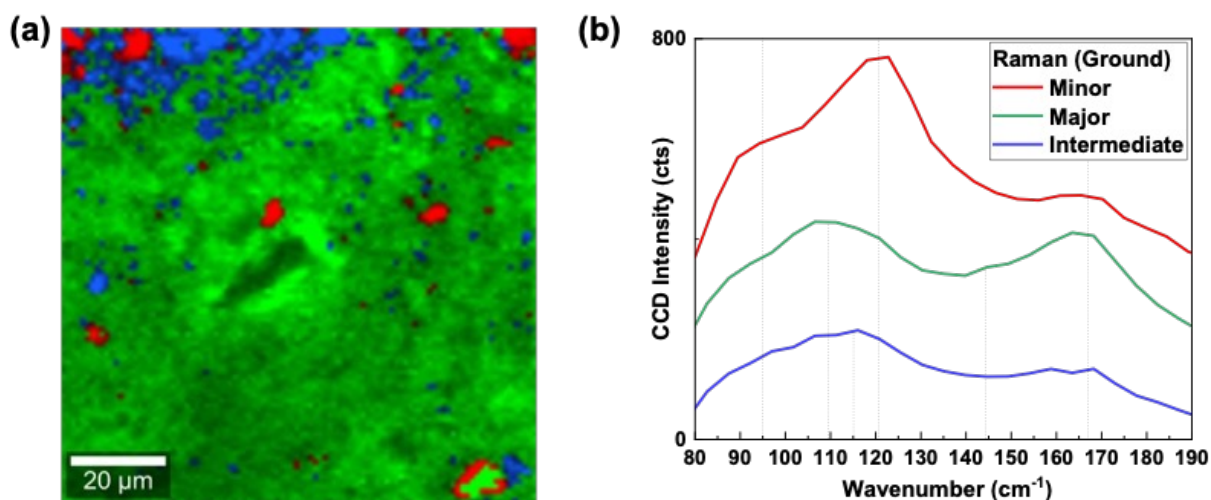


Figure 4.3: (a) Raman map distribution of the components from the ground powder sample derived from 10,000 local Raman spectra recorded over an area of $100 \times 100 \mu\text{m}^2$, and (b) corresponding components labeled as Minor (in red), Major (in green), and Intermediate (in blue) based on the cumulative area each of the components covered.³

of spectral weight in the $145\text{--}170 \text{ cm}^{-1}$ region. After grinding, the major and intermediate components show a markedly enhanced and broadened feature spanning $145\text{--}170 \text{ cm}^{-1}$, encompassing the $\gamma\text{-CuI}$ LO mode near $140\text{--}148 \text{ cm}^{-1}$ as well as the SbI_3 A_g and E_g stretching modes near 139 cm^{-1} and $162\text{--}168 \text{ cm}^{-1}$ respectively [91]. Simultaneously, the 115 cm^{-1} Cu–Sb–I lattice mode becomes noticeably broader in the ground sample, reflecting a probable loss of local structural coherence in the Cu–Sb–I framework upon mechanical perturbation. The spatial distribution of the 115 cm^{-1} Cu–Sb–I marker shows comparatively limited spatial drift in its maximum band intensity, whereas the 165 cm^{-1} feature displays a more heterogeneous distribution, confirming disordered phase segregation induced by mechano-thermal interference. Raman spectroscopy, therefore, provides direct evidence that the Cu–Sb–I compound is metastable and readily undergoes phase segregation under mechanical or thermal perturbation.

4.2.3 Compositional Analysis by X-Ray Fluorescence

The stoichiometric composition was examined after TGA/DTA and Raman spectroscopy indicated the formation of a Cu–Sb–I network distinct from the binary precursors. X-ray fluorescence (XRF) spectroscopy was used to determine the elemental composition of Cu–Sb–I thin films. Ten measurement points were selected randomly across different regions of the film to assess compositional homogeneity. The results are summarized in Table 4.1.

³ This was measured by Dr. K. Garbev (ITC, KIT).

Spectrum	Cu (at.%)	Sb (at.%)	I (at.%)	Cu/Sb
Point 1	38.39	13.77	47.85	2.79
Point 2	41.16	13.62	45.23	3.02
Point 3	43.00	12.88	44.12	3.34
Point 4	37.79	14.43	47.78	2.62
Point 5	44.36	12.82	42.82	3.46
Point 6	42.46	13.11	44.43	3.24
Point 7	45.77	12.06	42.17	3.79
Point 8	43.39	12.90	43.70	3.36
Point 9	40.61	13.73	45.66	2.96
Point 10	38.93	13.69	47.37	2.84
Mean	41.59	13.30	45.11	3.14
Std. dev.	2.68	0.67	2.04	–
Rel. std. dev. (%)	6.5	5.03	4.52	–
Conf. interval	0.87	0.22	0.66	–

Table 4.1: XRF compositional analysis of Cu–Sb–I thin films. Atomic percentages and Cu/Sb ratios are reported for ten measurement points, along with the mean, standard deviation, and confidence interval. Measured by Dr. Y. Tomm (Helmholtz-Zentrum Berlin).

The average composition is Cu: 40(5) at.%, Sb: 14(1) at.%, and I: 46(4) at.% – almost matching the Cu:Sb atomic ratio of 3:1 with which the synthesis began. The relative standard deviations (6.5% for Cu, 5.03% for Sb, 4.52% for I) indicate reasonable compositional homogeneity, though some spatial variation remains. XRF provides an averaged elemental picture of the compound produced and does not necessarily capture compositional changes or secondary phases on the nanoscale. This deviation may arise from: (1) preferential evaporation of volatile antimony species during film drying; (2) incomplete incorporation of Sb^{3+} into the CuI lattice; or (3) phase-separated CuI domains contributing to the copper signal without corresponding antimony. The XRF data alone cannot distinguish among these scenarios, but when combined with the structural evidence presented in the following sections, the results again hint at a CuI-derived host lattice in which Sb^{3+} incorporation at substitution-type sites is slightly below the nominal 3:1 Cu:Sb ratio.

4.2.4 Crystal Structure Determination

To explore whether the Cu–Sb–I powder forms the desired Caswellsilverite structure, powder X-ray diffraction (P-XRD) measurements were conducted. The diffraction pattern (Figure 4.4a) reveals a multi-phase composition consisting mostly of cubic γ -CuI in space group $F\bar{4}3m$ (ICSD 33726) [91] along with 27.7(5) wt% of trigonal β -CuI in space group $P\bar{3}m1$ (ICSD 78429) [85]. The pattern lacks the characteristic reflections expected for both octahedrally coordinated cations, Cu^+ and Sb^{3+} in a layered three-dimensional framework. Thus, this structure doesn't represent a Caswellsilverite or Rudorffite.

The β -CuI polymorph is only thermodynamically stable above 369 °C. Its appearance in the Cu–Sb–I compound synthesized at 55 °C, therefore, cannot be interpreted as equilibrium bulk β -phase formation. Instead, it is better understood as non-equilibrium, fault-stabilized polytypism: γ -CuI with zincblende-type structure (cubic) differs from β -CuI with wurtzite-type structure (hexagonal) primarily by the stacking sequence of close-packed iodide layers, so that a high density of stacking faults can generate coherent hexagonal stacking segments that produce diffraction patterns similar to β -CuI [39]. Such fault-stabilized polytypism is expected as a natural consequence of rapid, low-temperature nucleation in a system in which the free-energy difference between the zincblende and wurtzite polytypes is negligible relative to thermal energy at room temperature [40, 92].

Rietveld refinement was performed using the FullProf Suite, employing the Thompson–Cox–Hastings pseudo-Voigt profile function and anisotropic peak broadening modeled by symmetry-adapted spherical harmonics. Notably, the diffraction pattern shows no separately crystallized antimony iodide phase; Sb must therefore reside either in diffraction-weak local environments, in the surface-bound fine fraction, or at low occupancy within the CuI-derived framework. Refining Sb into γ -CuI was numerically unstable and always resulted in physically meaningless numerical values. For the β -CuI phase, there are indications in the diffraction pattern that minor amounts of antimony are indeed incorporated into the structure, hereafter denoted as β -CuI:Sb. The refined β -CuI:Sb lattice parameters ($a = 4.26826(11)$ Å, $c = 7.03472(26)$ Å) are somewhat smaller than the lattice parameters of neat β -CuI in the literature ($a = 4.279(2)$ Å, $c = 7.168(7)$ Å) [85], with a significant reduction of 1.9% along the c -axis. This contrasts with the γ -CuI phase, whose lattice parameter does not differ significantly from literature, indicating a difference in chemical composition.

Charge-balanced partial replacement of Cu^+ by Sb^{3+} resulted in decreased residuals and thus a better fit of the XRD data. However, any direct Rietveld refinement of the site-occupancy factors led to numerical instability and divergence. This is the result of the already high degree of disorder in the crystal structure of β -CuI, where Cu is located on two partially occupied split

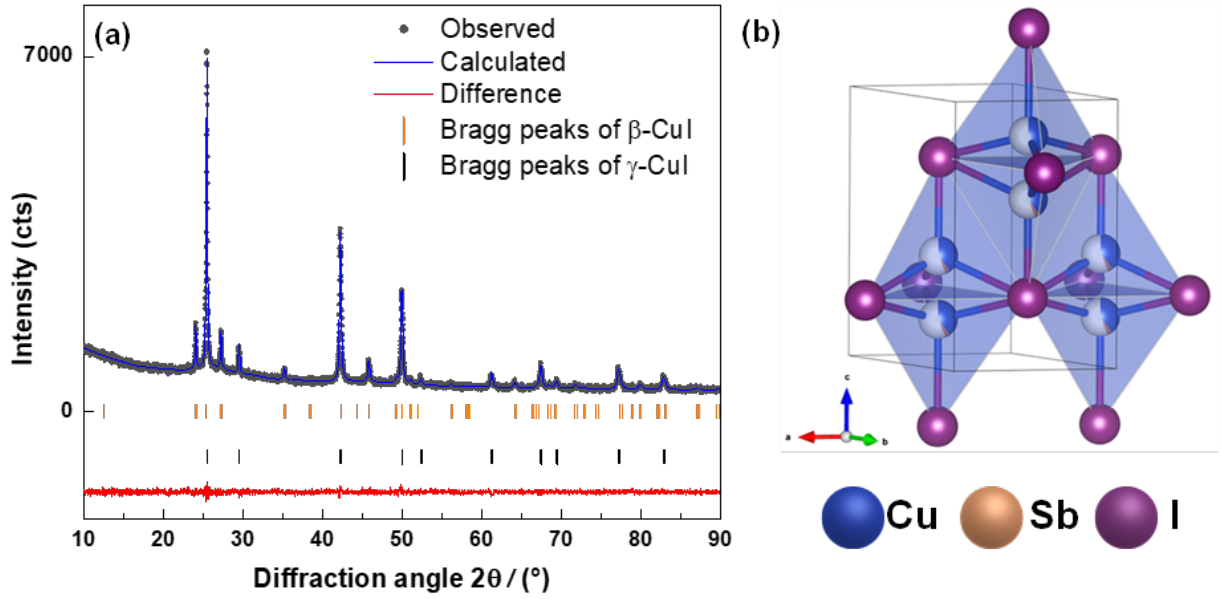


Figure 4.4: (a) Rietveld refinement of the P-XRD pattern of Cu-Sb-I powder showing the two-phase fit comprising γ -CuI ($F\bar{4}3m$) and β -CuI:Sb ($P\bar{3}m1$). (b) Crystal structure of β -CuI:Sb showing the split Cu/Sb sites on Wyckoff positions $2d$ and the CuI hexagonal framework, but with additional occupancies due to partial replacement of 3 Cu^+ by one Sb^{3+} . Adapted from [93]

Atom	Wyckoff pos.	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$	s.o.f.
I	2d	1/3	2/3	0.2470(40)	1.26(13)	1.0
Cu1	2d	1/3	2/3	0.6126(40)	2.72(40)	0.4
Sb1	2d	1/3	2/3	0.6126(40)	2.72(40)	0.0333
Cu2	2d	1/3	2/3	0.8492(40)	2.72(40)	0.4
Sb2	2d	1/3	2/3	0.8492(40)	2.72(40)	0.0333

Table 4.2: Refined structural parameters of β -CuI:Sb (space group $P\bar{3}m1$). Lattice parameters: $a = 4.26826(11) \text{ \AA}$, $c = 7.03472(26) \text{ \AA}$. Bragg R -factor = 3.75%. The "s.o.f." denotes the site occupancy factor.

sites close to each other (Wyckoff sites $2d$ in space group $P\bar{3}m1$), which is further increased by the cation replacement (Figure 4.4b). The best fit of the XRD data was obtained manually for an effective stoichiometry close to $\text{Cu}_{0.8}\text{Sb}_{0.067}\text{I}$ (β -CuI:Sb) instead of β -CuI, yielding a stoichiometry of $\text{Cu}_{6-3x}\text{Sb}_x\text{I}_6$, where $x \leq 1$ when considering 6CuI units. In this picture, the structure of β -CuI:Sb contains Cu vacancies (V'_{Cu} in Kröger-Vink notation) together with Sb substitutional defects ($\text{Sb}_{\text{Cu}}^{\bullet\bullet}$), providing a charge-balanced defect model in agreement with the bulk Cu:Sb ratio found in XRF [93].

The refined crystal structures are summarized in Tables 4.2 and 4.3.

Atom	Wyckoff pos.	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$	s.o.f.
I	4a	0	0	0	2.33(5)	1.0
Cu	4c	0.25	0.25	0.25	3.28(12)	1.0

Table 4.3: Refined crystal structure of γ -CuI (space group $F\bar{4}3m$). Lattice parameter: $a = 6.05235(7)$ Å. Bragg R -factor = 1.24%.

Any Sb not accounted for within the β -CuI:Sb crystallites may reside in the structurally disordered, nanoscopic surface fraction that is not resolved by XRD but is still counted by XRF.

The Rietveld refinement results demonstrate that the Cu–Sb–I compound is best described as a two-phase mixture of β -CuI and γ -CuI polytypes with Sb^{3+} accommodated at substitution-type sites within the β -CuI:Sb fraction. The coexistence of both polymorphs is characteristic of polytypism. Altogether, the following picture emerges: the bulk stoichiometry matches Cu_3SbI_6 as determined by XRF, while Rietveld refinement of the XRD data indicates that only a fraction of the Sb is incorporated substitutionally into the β -CuI framework at Cu sites. The remaining Sb is inferred to reside in a structurally disordered surface fraction that Bragg diffraction cannot resolve. The absence of reflections corresponding to both octahedrally coordinated cation sites, a defining characteristic of the Caswellsilverite structure, is another critical finding. We therefore conclude that this compound is not a Caswellsilverite (as interpreted in previously reported literature for Cu_3SbI_6), but best described as a CuI-derived, defect-stabilized phase, in which the bulk composition and local Sb incorporation together account for the Cu_3SbI_6 stoichiometry. Throughout this dissertation, the material is therefore denoted as β -CuI:Sb.

4.2.5 Microstructure and Electron Microscopy

Scanning electron microscopy (SEM) images (Figure 4.5a–d) reveal large crystallites decorated by an abundant fine fraction of sub-micron fragments adhering to their surfaces. At intermediate magnification, large crystallites are visible and are assigned to the β -CuI:Sb and γ -CuI phases identified by PXRD. Whether γ -CuI also incorporates substituted Sb cannot be determined from the present data, as Sb refinement into γ -CuI was numerically unstable. At higher magnification, the granular crust resolves into irregular fragments and compact submicron clusters that adhere to the larger crystallites, producing a rough, interface-rich surface.

The high-resolution Transmission Electron Micrograph (HRTEM) micrograph (Figure 4.5e) was collected from thin-edge regions of the large crystallites. Well-defined lattice fringes with an interplanar spacing of $d = 3.70$ Å are characteristic of the (100) lattice plane distance in β -CuI, confirming locally crystalline structures. The selected-area electron diffraction (SAED)

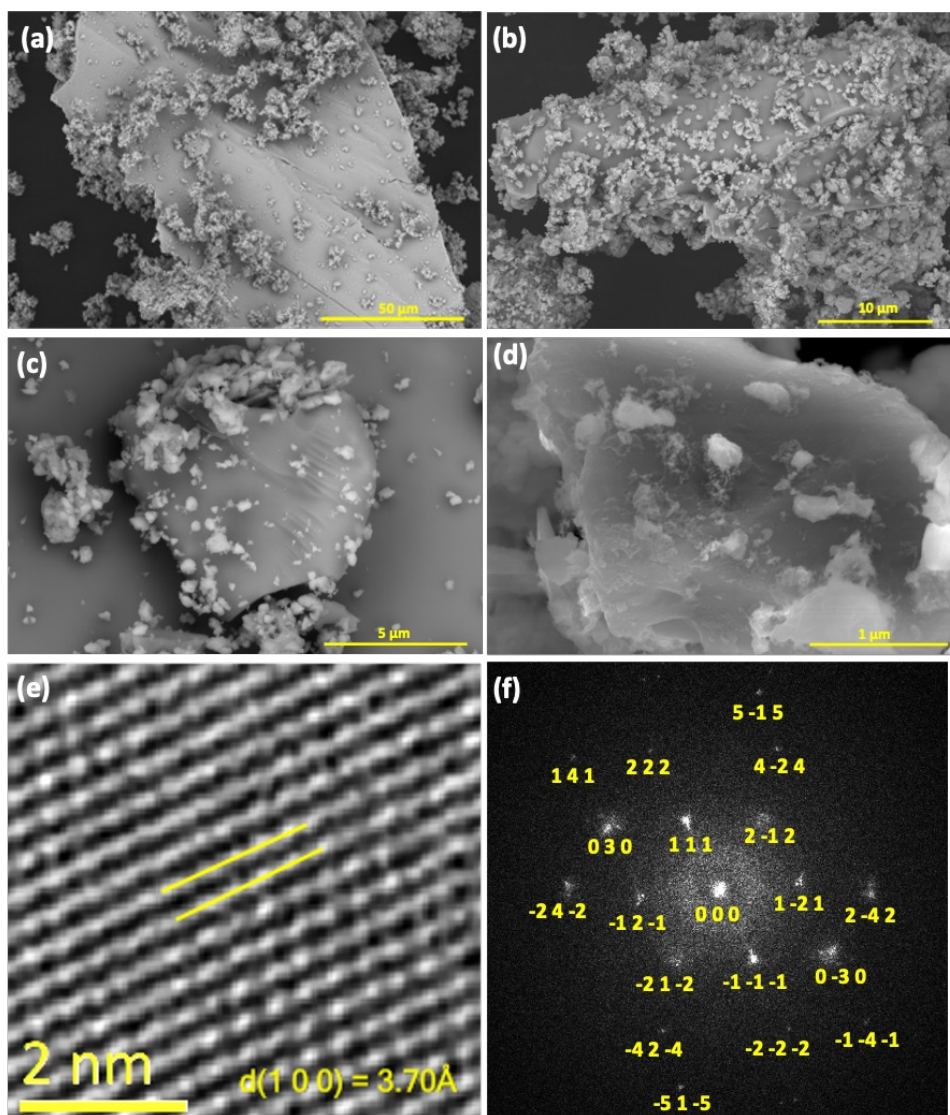


Figure 4.5: (a–d) SEM images of Cu–Sb–I powder at increasing magnification, showing large crystallites covered by a sub-micron fine fraction. (e) HRTEM micrograph with lattice fringes at $d = 3.70\text{ \AA}$ characteristic of the (100) plane of β -CuI. (f) SAED pattern indexed along the $[1\ 0\ 1]$ zone axis of β -CuI:Sb.

pattern (Figure 4.5f, Table 4.4) provides direct crystallographic validation of the polytypic CuI framework inferred from P-XRD. The SAED pattern exhibits discrete reflections resolved along the $[\bar{1}\ 0\ 1]$ zone axis of the β -CuI:Sb structure. The diffraction spots were analyzed with the CrysTBox diffractGUI software (version 2.21) using a RANSAC algorithm [94]. The total angular deviation between the experimental pattern and the ideal lattice orientation is 0.72° , and the d -spacing standard deviation is 0.0007 nm , confirming excellent agreement with the β -CuI structure. The coexistence of sharp diffraction spots and weak diffuse halos is interpreted as the signature of nanocrystalline domains.

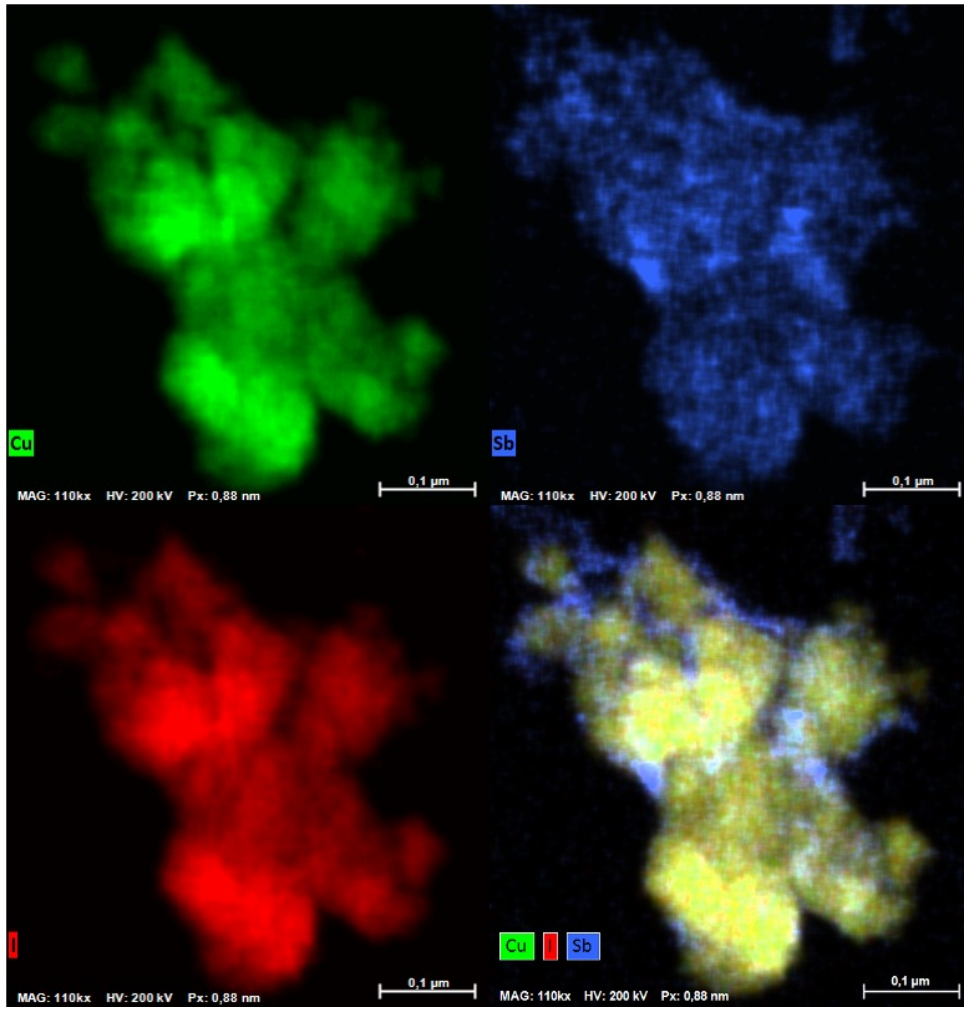


Figure 4.6: TEM-EDX analysis for elemental mapping of a β -CuI:Sb crystallite showing the spatial distributions of Cu, Sb, and I, and confirming the heterogeneous Sb distribution contrasts with the more uniform Cu and I signals.⁴

Zone axis	$[\bar{1}01]$
Total angular distance	0.72°
d -spacing STDEV	0.0007 nm

Table 4.4: SAED analysis parameters for the (β -CuI:Sb) powder along the $[\bar{1}01]$ zone axis. The low angular distance and d -spacing STDEV confirm excellent agreement with the β -CuI structure.

TEM coupled with energy-dispersive X-ray spectroscopy (EDX) analysis (TEM-EDX), as shown in Figure 4.6, confirmed the elemental distribution within the crystals. Cu and I are

⁴ Measurements conducted by Dr. M. Peterlechner (LEM, KIT).

distributed uniformly across the grains, consistent with a CuI host lattice. The Sb distribution seems heterogeneous, with regions of higher and lower Sb concentration. In combination with XRF and the absence of a separately crystallized antimony iodide phase in the XRD pattern, this suggests that at least part of the Sb is associated with the structurally disordered, surface-bound fine fraction rather than being uniformly incorporated into the crystallites. Altogether, the following picture emerges: the bulk stoichiometry matches Cu_3SbI_6 (XRF), a fraction of Sb is incorporated into the β -CuI crystal structure at substitution-type sites (Rietveld refinement), and the remainder resides in a structurally disordered surface fraction that Bragg diffraction cannot resolve.

4.2.6 Optoelectronic Properties

Optical Absorption and Bandgap Determination

For efficient solar energy conversion, photovoltaic absorbers should combine strong optical absorption with an electronic structure that supports charge-carrier generation and extraction. In thin-film solar cells, the absorber bandgap sets the principal accessible spectral range, while the sharpness of the absorption edge and the character of the photoluminescence provide insight into the degree of energetic disorder near the band edges. These properties can be extracted from UV–Vis absorption spectra, and photoluminescence (PL) spectra; and all these informations were collected from spin-coated β -CuI:Sb thin films deposited on glass substrates (Figure 4.7a). Both measurements confirm that β -CuI:Sb is a wide-bandgap semiconductor with a distinct optical onset and a broadened near-edge emission response. The primary absorption onset is at approximately 550 nm, consistent with the PL peak wavelength, and a finite low-energy tail extends below the nominal band edge. Such band-tail absorption indicates a degree of energetic disorder, in agreement with the broader structural picture established above, in which β -CuI:Sb is not an ideal single-phase semiconductor but a CuI-derived, defect-perturbed system with local structural heterogeneity.

To determine the dominant optical onset, the absorption data were analyzed using the direct-bandgap Tauc relation, $(\alpha h\nu)^2$, where α is the absorption coefficient, h is Planck's constant, and ν is the photon frequency. A linear fit to the absorbance at the edge, shown in Figure 4.7b, yields a direct optical bandgap of $E_g = 2.32 \pm 0.02$ eV. This absorption is blue shifted against Bi^{3+} as it is generally expected for Sb^{3+} -based compounds, due to reduced spin–orbit coupling and a higher conduction band minimum in antimony-based systems [79, 80].

The PL spectrum peaks close to the absorption onset but is substantially broadened. The broad near-edge emission is interpreted as recombination across a distribution of local band-edge environments, rather than as originating from a single sharply defined transition [95]. In halide

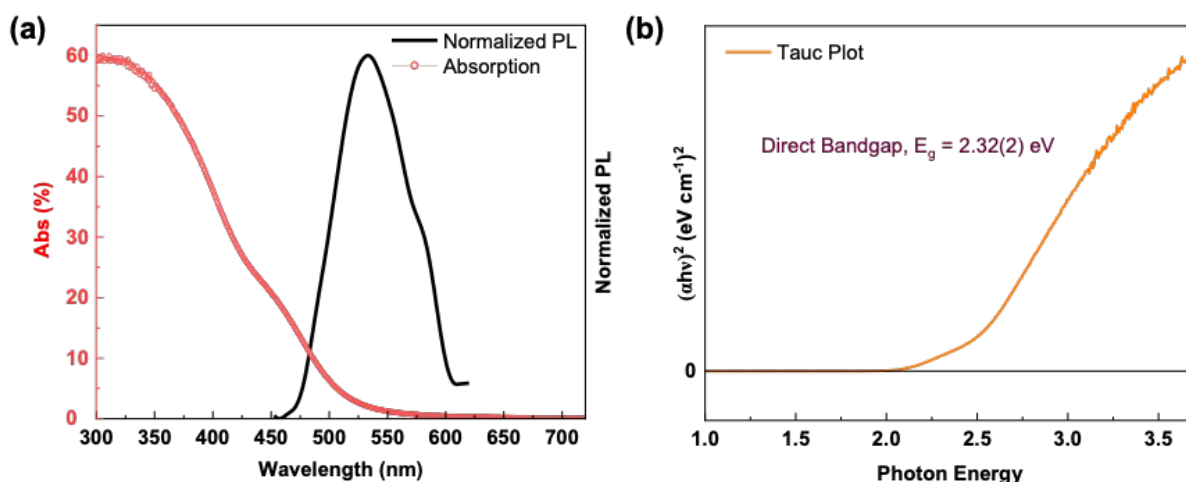


Figure 4.7: (a) UV-Vis absorption and PL spectra of β -CuI:Sb thin films on glass. The primary absorption onset at approximately 550 nm is indicated, along with the broadened PL emission near the band edge. (b) Tauc plot $(\alpha h\nu)^2$ vs. $h\nu$ for β -CuI:Sb thin films, yielding a direct optical bandgap of $E_g = 2.32(2)$ eV from the linear extrapolation to the photon-energy axis. Adapted from [93].

semiconductors, such broadening is commonly associated with energetic disorder and charge-carrier-phonon coupling, and in this material, it is consistent with the structurally heterogeneous, stacking-disorder (polytypism) framework established by diffraction and vibrational analysis [96, 24, 97].

The wide bandgap of β -CuI:Sb has both advantages and disadvantages for photovoltaic applications. The Shockley-Queisser limit for a 2.32 eV single-junction solar cell under AM1.5G illumination is approximately a power conversion efficiency of 18%, compared to 33% for the optimal bandgap of 1.34 eV for lead-halide perovskites [98]. The reduced photocurrent resulting from the wide bandgap is a fundamental limitation, though the wider bandgap is potentially attractive for indoor photovoltaic applications or as a wide-gap component in tandem solar cells.

Valence Band Maximum and Band Alignment

The ionization potential (E_{IP}) of β -CuI:Sb thin films was determined by photoelectron spectroscopy in air (PESA) measurements as shown in Figure 4.8. The photoelectron yield as a function of incident photon energy was fitted using a square-root law, yielding $E_{IP} = 5.02$ eV. The electron affinity was calculated from the ionization potential and the bandgap: $E_{EA} = E_{IP} - E_g = 5.02 - 2.32 = 2.70$ eV. These vacuum-referenced energies form the basis for selecting and evaluating charge-carrier transport layers in the device architecture are discussed below.

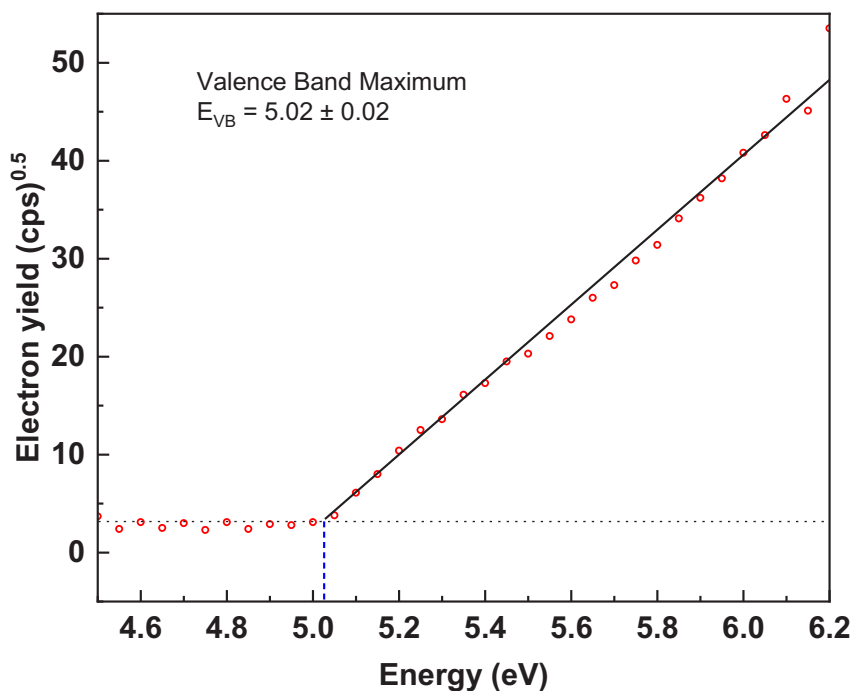


Figure 4.8: Photoelectron spectroscopy in air (PESA) measurements of Cu_3SbI_6 thin films for the determination of the valence band maximum (VBM) energy. The photoelectron yield as a function of incident photon energy was fitted using a square-root law, yielding the ionization potential (IP). The extrapolated onset energy provides the VBM energy relative to the vacuum level, which is critical for evaluating band alignment with transport layers in photovoltaic device architectures.

4.2.7 Thin-Film Quality

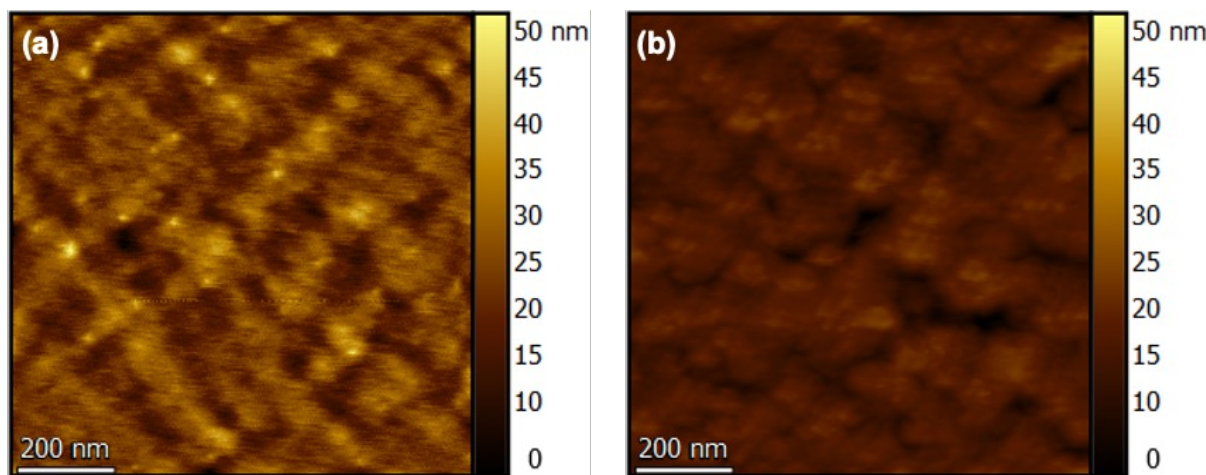


Figure 4.9: Atomic Force Micrographs show the topography of Cu_3SbI_6 deposited on (a) PEDOT:PSS, and (b) WO_{3-x} .

The processing-window constraints established by the thermal analysis (Section 4.2.1) are the same that govern thin-film morphology. The morphology of $\beta\text{-CuI:Sb}$ thin films is critical

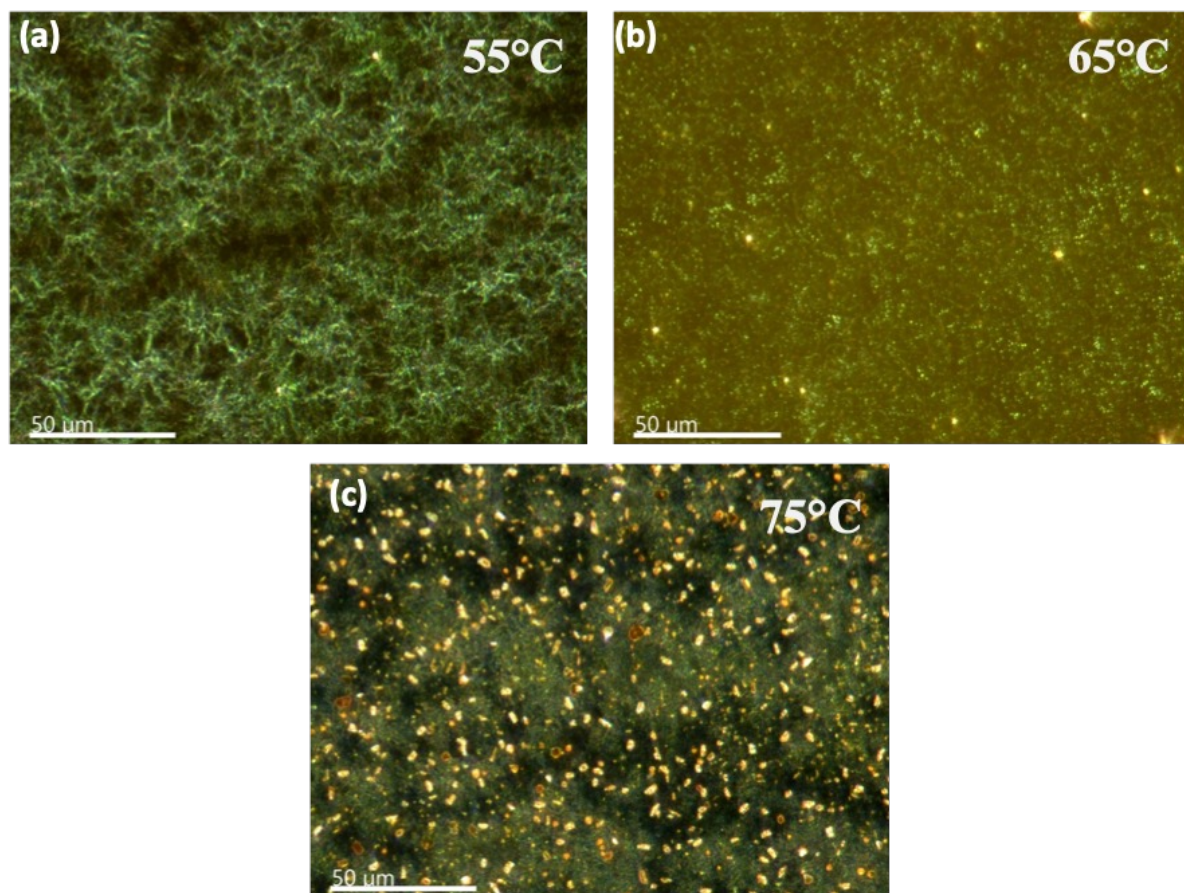


Figure 4.10: Optical microscopy images of the quality of Cu_3SbI_6 thin-films as a function of annealing temperature. (a) 55°C, (b) 65°C, and (c) 75°C.

After annealing at 55°C and 65°C, the films retain a similar appearance, but the samples annealed at 65 °C exhibit a higher density of pinholes. In contrast, annealing at 75°C produces more transparent thin-films, accompanied by islet formation, indicating that temperature alone can measurably alter the phase/defect landscape of this material.

determining device performance, as pinholes, incomplete coverage, and rough surfaces can lead to shunt pathways, increased recombination, and reduced fill factors. Atomic force microscopy (AFM) and optical microscopy were employed to characterize thin-film quality as a function of deposition conditions and substrate choice.

AFM measurements (Figure 4.9) reveal that $\beta\text{-CuI:Sb}$ films deposited on WO_{3-x} exhibit a smoother, more uniform surface with $R_q = 1.7$ nm and an average grain size of 251(37) nm. In contrast, $\beta\text{-CuI:Sb}$ atop PEDOT:PSS exhibits substantially higher roughness, $R_q = 9.2$ nm, and a smaller average grain size of 143(21) nm. The quality difference reflects the distinct surface energies and wetting properties of the two substrates, with the $\beta\text{-CuI:Sb}$ grain size depending strongly on the underlying charge-carrier transport layer.

Optical microscopy images (Figure 4.10) show the evolution of film quality as a function of annealing temperature. Films annealed at 55 °C and 65 °C retain a similar appearance, but a

higher density of pinholes is observed in the 65 °C samples. In contrast, annealing at 75 °C renders the film noticeably more transparent with islet formation, showing that temperature alone can measurably alter the phase/defect landscape of this material. This behavior is consistent with the thermal analysis (Section 4.2.1) and Raman spectroscopy (Section 4.2.2), which showed that β -CuI:Sb is thermally unstable above 100 °C. Annealing at 55 °C provides the best compromise between film quality and thermal stability.

4.2.8 Solar Cell Integration and Device Performance

To investigate the solar light-harvesting capabilities of β -CuI:Sb, thin films were integrated into solar cells in the device architecture: ITO / WO_{3-x} (12 ± 2 nm) or PEDOT:PSS (30 ± 4 nm) / β -CuI:Sb / PC₇₁BM / BCP / Ag (100 nm). In both architectures, ITO serves as the transparent conducting electrode, WO_{3-x} or PEDOT:PSS as the hole-transport layer (HTL), β -CuI:Sb as the light-absorbing layer, PC₇₁BM (phenyl-C₇₁-butyric acid methyl ester) as the electron-transport layer (ETL), BCP (bathocuproine) as a buffer layer, and Ag as the back contact (Figure 4.11(a)). Figure 4.11(b) summarizes the most relevant transport energies of the semiconductors and electrodes.

Figure 4.11(c) shows the J - V characteristics of representative WO_{3-x}-based devices measured in the dark and under 1-sun illumination (AM1.5G). Under illumination, the solar cells exhibit an average power conversion efficiency (PCE) of 0.92 ± 0.10 %, with the best device reaching PCE = 1.02 % – the highest reported for any solution-processed ternary copper pnictohalide. Across 16 devices, the average open-circuit voltage is $V_{OC} = 0.46 \pm 0.11$ V (best device: 0.57 V), the average short-circuit current density $J_{SC} = 2.67 \pm 0.22$ mA cm⁻², and the average fill factor $FF = 48 \pm 14$ %. The short-circuit current density of the champion device, $J_{SC, best} = 2.89$ mA cm⁻², is in close agreement with the photocurrent density of $J_{EQE} = 2.82$ mA cm⁻² calculated from the external quantum efficiency (EQE, Figure 4.11(d)). The EQE peaks in the visible wavelength regime and rolls off toward longer wavelengths. With an optical bandgap of 2.32 eV, β -CuI:Sb cannot be responsible for a photocurrent response extending to 700 nm; in accordance with broad experience from metal-halide perovskite solar cells, the long-wavelength EQE tail beyond 550 nm is attributed to photocurrent contributions from PC₇₁BM [99].

The J - V curves measured in ascending and descending scan directions show similar J_{SC} and FF but exhibit different V_{OC} . The scan-direction-dependent hysteresis is tentatively attributed to ionic interfacial charge redistribution during the J - V scan, analogous to mechanisms commonly discussed for metal-halide perovskite solar cells [100].

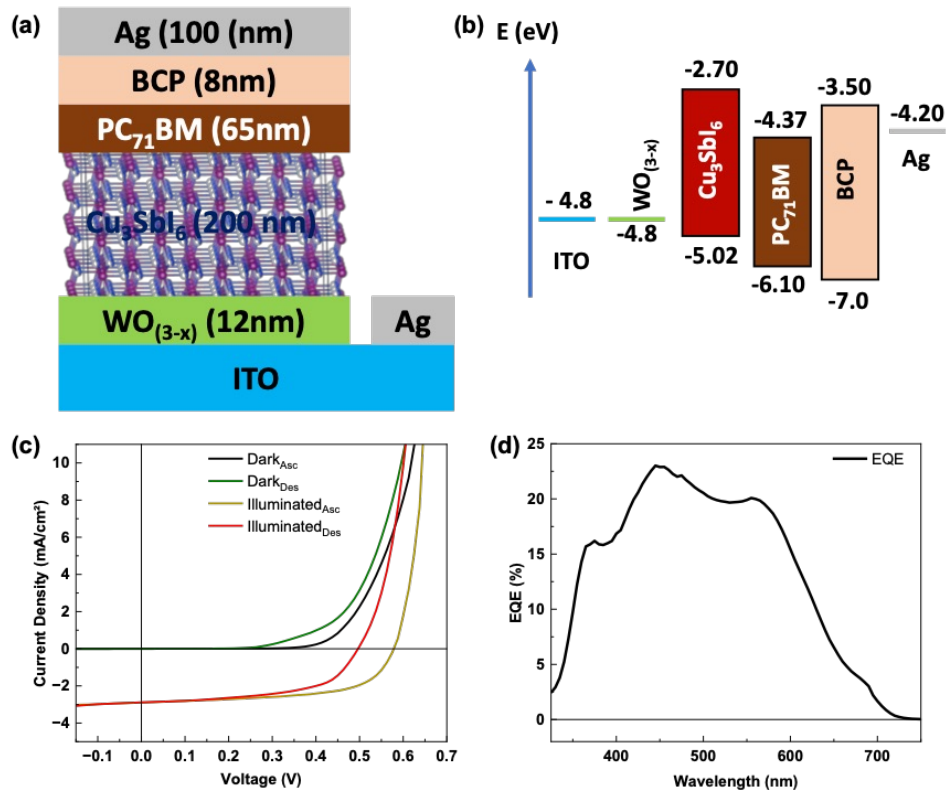


Figure 4.11: (a) Device architecture: ITO / WO_{3-x} / $\beta\text{-CuI:Sb}$ (or Cu_3SbI_6) / PC_{71}BM / BCP / Ag. (b) Energy-level diagram illustrating band alignment across the device stack. (c) J - V curves of representative WO_{3-x} -based devices in the dark and under 1-sun AM1.5G illumination, measured in ascending and descending scan directions. (d) External quantum efficiency (EQE) spectrum of the champion device; the integrated photocurrent $J_{\text{EQE}} = 2.82 \text{ mA cm}^{-2}$ is indicated. Adapted from [93]

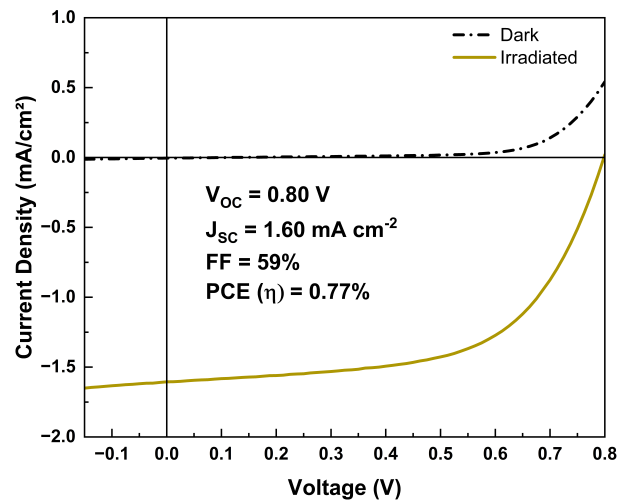


Figure 4.12: JV characteristics and parameters of the champion device from ITO / PEDOT:PSS / $\beta\text{-CuI:Sb}$ / PC_{71}BM / BCP / Ag architecture.

For reference, J - V statistics for β -CuI:Sb solar cells comprising a PEDOT:PSS transport layer are shown in Figure 4.12, yielding a champion PCE = 0.77%. The lower performance compared to WO_{3-x} -based devices can be attributed to a less favorable band alignment and a smaller grain size owing to the acidic nature of PEDOT:PSS when is used as the HTL. Although this efficiency surpasses the previous PCE record of 0.50% for the similar architecture [77].

4.3 Conclusion and Outlook

This chapter has presented a comprehensive characterization of copper antimony iodide (Cu_3SbI_6 , denoted as β -CuI:Sb), from its crystal structure to its optoelectronic properties and photovoltaic performance. The central finding is that β -CuI:Sb is not a Caswellsilverite (Rudorffite) with octahedrally coordinated Sb^{3+} , as has been routinely assumed in the literature, but a CuI-derived, defect-stabilized polytypic lattice (β -CuI:Sb) in which Sb^{3+} occupies substitution-type sites charge-compensated by Cu^+ vacancies. This structural reclassification, established through Rietveld refinement of powder XRD data, SAED analysis, HRTEM, TEM-EDX mapping, and Raman spectroscopy, fundamentally reframes how the material's properties should be understood.

The defect-stabilized polytypic microstructure of β -CuI:Sb gives rise to several key characteristics. First, the material exhibits thermal instability above approximately 100 °C and is susceptible to mechano-thermal phase segregation upon grinding. This fragility imposes severe constraints on processing conditions. Second, the material exhibits a direct bandgap of 2.32 eV, wider than the optimal bandgap for single-junction solar cells under AM1.5G illumination but potentially attractive for indoor photovoltaics or tandem architectures. Third, the material exhibits significant band-edge disorder, as evidenced by the sub-gap absorption tail and broadened PL emission, which contributes to voltage losses through increased nonradiative recombination. The correlation between microstructure and photovoltaic parameters suggests that the dominant native-defect ensemble in β -CuI:Sb is linked to both its structural arrangement and its electronic behavior. In this picture, substitutional $\text{Sb}_{\text{Cu}}^{\bullet\bullet}$ defects are charge-compensated by V_{Cu}' acceptors. The V_{Cu}' defects may contribute shallow acceptor states and support intrinsic p-type character, while Sb^{3+} incorporated at distorted tetrahedral sites may introduce Sb 5*p*-derived conduction-band character and local strain, contributing to band-edge tailing. In addition, coherent β/γ -CuI polytype disorder may introduce planar interface states and transport anisotropy, which could contribute to losses in open-circuit voltage and fill factor. Further numerical and theoretical modeling is required to verify these proposed structure–defect–property relationships.

Integration of β -CuI:Sb into thin-film solar cells yielded a champion power-conversion efficiency of 1.02%, the highest reported to date for this material. While this represents a proof-of-

concept demonstration that β -CuI:Sb can function as a photovoltaic absorber, the efficiency is far below the theoretical potential, and substantial improvements in film quality, defect passivation, and interface engineering will be required. On the structural side, controlled substitution of Cu sites with aliovalent cations could reduce V'_{Cu} density, suppressing the driving force for structural degradation and expanding the processing window. On the device side, passivating V'_{Cu} defects at grain boundaries through surface treatments or interfacial interlayers should reduce nonradiative recombination losses.

These limitations motivate a parallel exploration of the closely related copper bismuth iodide system. Replacing Sb^{3+} with Bi^{3+} at the pnictogen site addresses several structural constraints encountered here. Bi^{3+} (ionic radius 1.03 Å in octahedral coordination) is substantially larger than Sb^{3+} (0.76 Å) and is less likely to compete for the same tetrahedral sites as Cu^+ in a CuI-derived host; its incorporation follows a chemically distinct mechanism based on a BiI_3 -derived octahedral framework. In an attempt to explore the structural and thermo-mechanical stability, the copper bismuth iodide system is further investigated in the next chapter.

5 Copper Bismuth Iodide (Cu–Bi–I)

5.1 Background and Motivation

5.1.1 The Cu–Bi–I Phase Space and Its Photovoltaic Relevance

Bismuth is one of the most studied post-transition metals for lead-free perovskite-inspired photovoltaics, in large part because Bi^{3+} is an ns^2 lone-pair cation analogous to Pb^{2+} and supports comparable lone-pair-driven structural chemistry [101]. The electronic similarity underpins interest in a range of Bi-containing halide compounds, including defect-ordered perovskites such as $\text{Cs}_3\text{Bi}_2\text{I}_9$, cation-ordered double perovskites such as $\text{Cs}_2\text{AgBiX}_6$ ($X = \text{Br}, \text{I}$), and Caswellsilverite-type Ag–Bi–I phases, including AgBiI_4 , Ag_2BiI_5 , Ag_3BiI_6 , and Ag_2BiI_7 [76, 102]. A comprehensive critical review of bismuth-containing perovskite-inspired absorbers by Ünlü et al. identifies several recurring limitations across these material families: bandgaps frequently exceeding 2.0 eV, large exciton binding energies ($> 100 \text{ meV}$), strong structural anisotropy, and modest carrier transport properties. These factors collectively constrain achievable photovoltaic efficiencies, despite often favorable optical absorption characteristics such as narrow bandgap energies [14].

Compounds such as AgBiI_4 , Ag_2BiI_5 , Ag_3BiI_6 , and related silver-bismuth iodides have been explored as lead-free photovoltaic absorbers because their octahedral metal-iodide networks conceptually resemble the metal-halide frameworks that make lead-halide perovskites effective semiconductors [19, 76, 18]. Replacing Ag^+ with Cu^+ is attractive from an abundance and cost perspective, but it is not structurally trivial. The smaller ionic radius and different coordination preference of Cu^+ (tetrahedral coordination, whereas Ag^+ prefers octahedral coordination) can redirect crystallization away from the silver analog, especially at high Cu:Bi ratios.

The most established ternary copper bismuth iodide in the Caswellsilverite-related literature is CuBiI_4 , in which Cu and Bi occur in a 1:1 ratio [103]. Higher Cu contents have also been proposed for Caswellsilverite-type compositions, including Cu_3BiI_6 [104, 29]. However, precursor stoichiometry alone does not establish the crystal structure. A composition may satisfy a charge-balanced formula of the type $A_aB_bX_y$ without forming the octahedral coordination environment for both cation sublattices that is required for a true Caswellsilverite-type structure. A crystallographically resolved Cu–Bi–I phase with a Cu:Bi ratio greater than 2 has not yet been reported in the published literature.

The motivation for studying CBI is therefore threefold. First, it extends the copper-based lead-free absorber library to a Cu-rich Cu–Bi–I composition with a solar-relevant optical gap. Second, it tests the central principle of this thesis that crystal structure must be determined experimentally before optoelectronic properties can be interpreted. Third, it provides structural evidence for a Cu–Bi–I compound with $\text{Cu}:\text{Bi} > 2$, allowing the proposed Cu_3BiI_6 composition to be assessed against the structural requirements of a Caswellsilverite-type phase.

5.2 Results and Discussion

5.2.1 Phase Composition and Crystal Structure

Powder X-ray diffraction (PXRD) with Rietveld refinement (Figure 5.1a) in Bragg–Brentano geometry (Cu $K\alpha$ radiation, 2θ from 5° to 100°) revealed that the as-synthesized material obtained from a 3:1 Cu:Bi precursor solution is multi-phase. The dominant crystalline component, accounting for 56(1) wt%, is α -CuI (ICSD 33727), is identified by characteristic sharp reflections in the $\langle 111 \rangle$ directions with anisotropic broadening along $\langle 100 \rangle$. A second phase, constituting 35(1) wt%, corresponds to a previously undescribed rhombohedral phase with space group $R\bar{3}$ (trigonal), derived from the BiI_3 parent structure (ICSD 26083) via interstitial incorporation of Cu^+ . The refined unit cell parameters of this new phase are $a = 7.5171(2) \text{ \AA}$ and $c = 20.7458(10) \text{ \AA}$. An additional minor component with weak reflections at $2\theta = 12.5^\circ$ and 25.2° may be attributed to CuBiI_4 or a closely related phase. The Rietveld refinement yielded satisfactory quality indicators ($R_{\text{wp}} = 5.8\%$, $R_{\text{expected}} = 3.6\%$, $\chi^2 = 2.7$), with residuals primarily attributable to the anisotropic broadening of the 00ℓ reflections of the CBI phase, which is numerically challenging to model fully with symmetry-adapted spherical harmonics. This anisotropic broadening, confined to the 00ℓ reflections, is diagnostic of stacking fault disorder along the crystallographic c -axis rather than of limited crystallite size, indicating that while individual layers are well ordered, long-range stacking periodicity is disrupted across domains as shown in Figure 5.1b. This layered structure is similar to that of BiI_3 (Figure 5.1c), which is two-dimensional and consists of sheets of edge-sharing BiI_6 -octahedra. In BiI_3 , some octahedra in the layers are empty, forming $\square\text{I}_6$ -octahedra with $\square$ indicating a vacancy.

The closest structural analog identified in the literature is CrGeTe_3 (Figure 5.1d), which also crystallizes in a space group $R\bar{3}$ with similar lattice parameters. In CrGeTe_3 , the Ge atom is positioned near, but not exactly at, the trigonal-planar face of the octahedra, shifted slightly inward to achieve tetrahedral coordination with three Te atoms and an additional Ge atom. No compound with the CBI structure, that is, with a cation in strict threefold planar coordination at the face of an empty octahedron within a layered metal-halide framework, has been reported previously, thereby establishing CBI as a new structural prototype. For this reason, the most

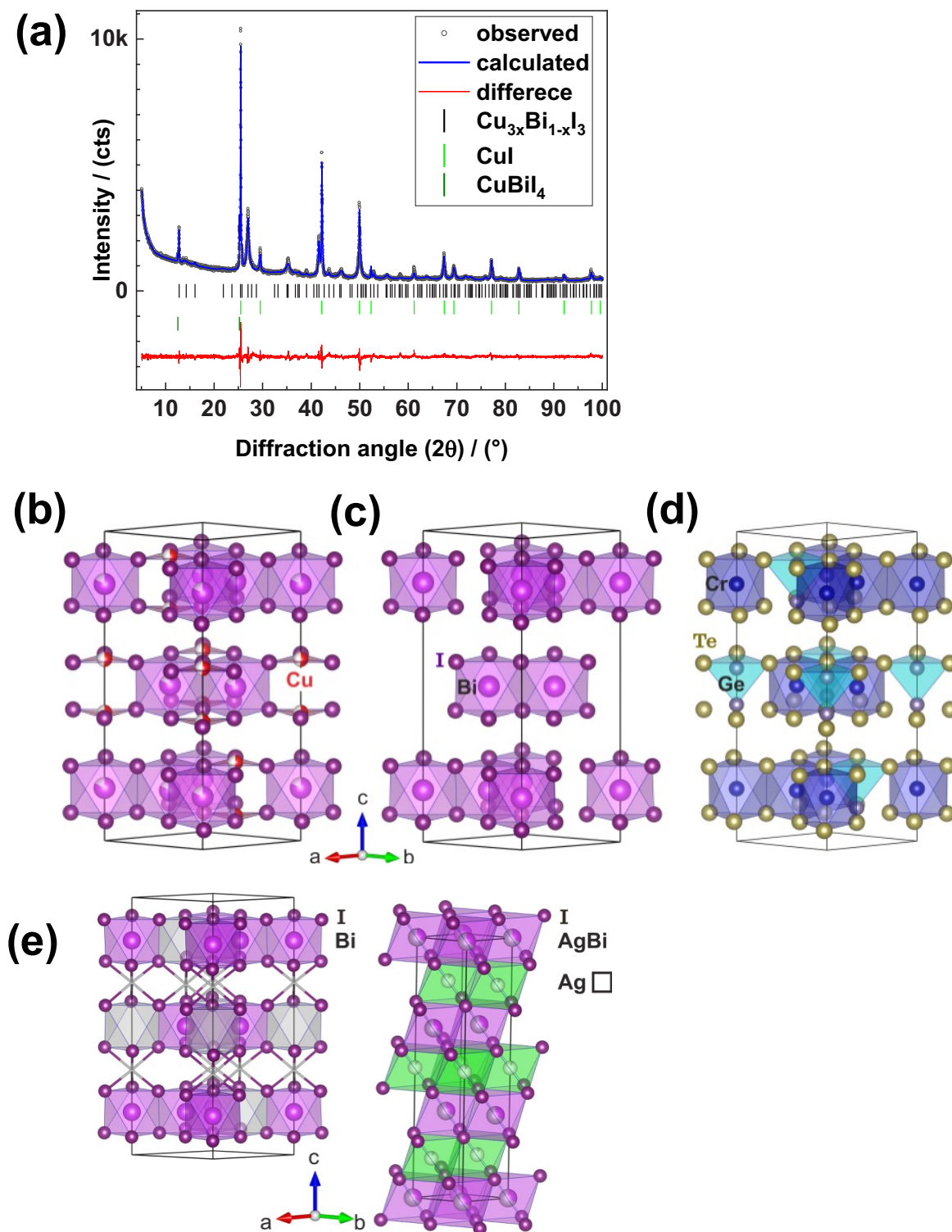


Figure 5.1: (a) Rietveld refinement of the P-XRD pattern of CBI. For (CuBiI_4), only observed peaks were included. (b) Crystal structure of $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$, (c) structure of BiI_3 , and (d) structure of CrGeTe_3 . (e) Comparison of the structure of BiI_3 and Ag_3BiI_6 . Adapted from [10]

accurate descriptor for this phase is “BiI₃ with interstitial Cu atoms,” a notation that preserves the topology of the primary building unit while explicitly indicating the nature and location of the Cu species [105].

Fig 5.1(e) displays the comparison of BiI₃ and Ag₃BiI₆ structures [106]. Ag₃BiI₆ adopts the Caswellsilverite structure type with space group $R\bar{3}m$. The lattice parameter c is similar to that of the BiI₃ cell, but the a - b base is only half as wide. Because of this smaller basal plane and the higher symmetry, all octahedra within a layer are symmetry-equivalent, in contrast to the BiI₃ structure. The topology of the individual layers, however, is identical: BiI₆ octahedra are connected into threefold rings by shared edges. The interior of each ring forms a tetrahedral space that is unoccupied. There are two fundamental differences between these structure types:

1. In the Caswellsilverite structure, the octahedra in all layers are occupied, whereas in the BiI₃-type structure, every second octahedral layer is unoccupied, separating the occupied Bi–I layers and interrupting connectivity along the stacking direction.
2. The stacking of the layers is different. In BiI₃, columns of face-sharing octahedra extend along the crystallographic c -axis. Parallel to these columns, the tetrahedra are stacked to form columns of trigonal bipyramids. In the Caswellsilverite structure, the layers are shifted relative to each other, such that in each layer the outward faces of the octahedra are capped by face-sharing tetrahedra. This produces stacks along c of the sequence octahedron–upward tetrahedron–downward tetrahedron–octahedron.

The structural solution for the CBI phase merits careful discussion, as it unambiguously distinguishes this compound from the Caswellsilverite family. The BiI₃ parent structure consists of edge-sharing BiI₆ octahedra forming two-dimensional sheets stacked along the c -axis. Within each sheet, two symmetrically independent octahedral sites exist at Wyckoff positions $3b$ (0,0,1/2) and $6c$ (0,0, z), with $z = 0.16$. In the parent BiI₃ lattice, the $6c$ site is occupied by Bi³⁺, while the $3b$ site is vacant. The layers are also separated by entirely empty interlayer spaces, making the structure strongly two-dimensional.

In CBI, Rietveld refinement of difference Fourier maps based on the BiI₃ structural model places interstitial Cu⁺ at the $6c$ Wyckoff position (0,0, z) with $z = 0.41$, which geometrically corresponds to the trigonal faces connecting two adjacent empty octahedra within the BiI₃ layer. Each Cu⁺ at this position is bonded to three I[−] atoms in the same plane, forming a triangular arrangement, a threefold planar (trigonal-planar) coordination that is highly unusual for Cu⁺, which more commonly adopts linear, tetrahedral, or octahedral coordination in halide environments. Critically, attempts to refine Cu⁺ in octahedral coordination, as would be expected for a Caswellsilverite, or in tetrahedral coordination, as found in Bi_{1.5}Cu_{1.44}I₆ (ICSD 114003),

yielded site occupation factors that refined to negligibly small or negative values, providing direct evidence against these coordination models. The Caswellsilverite topology, which requires cations at A-sites to coordinate octahedrally with halide anions within a fully occupied layered framework, is therefore structurally incompatible with the CBI phase studied here.

Rietveld refinement of atomic occupancies under the constraint of overall charge neutrality yields a mean composition of $\text{Cu}_{0.72}\text{Bi}_{0.76}\text{I}_3$, with $x = 0.24$ in the general formula $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$. The partial occupation of the Bi site (s.o.f. = 0.827 ± 0.009) and the Cu interstitial site (s.o.f. = 0.518 ± 0.009) reflect both the non-stoichiometric nature of the compound and the partial replacement of Bi^{3+} by Cu^+ on the Cu interstitial site, which serves as a mechanism of local charge compensation. It is better understood as a defect-stabilized BiI_3 -derived host in which positive $\text{Cu}_i^\bullet$ interstitials and negatively charged cation vacancies V_{Bi}''' contribute to charge balance.

This structural assignment has two implications. First, the precursor ratio and nominal formula suggest a Caswellsilverite-like compound, but the actual product is an interstitially modified BiI_3 framework. Second, it shows that the native interstitial is not a secondary defect superimposed on an otherwise ideal lattice. The interstitial defines the lattice that forms. Without Cu^+ occupying the trigonal faces of the empty octahedra, the experimentally observed CBI phase would not be structurally distinct from BiI_3 .

5.2.2 Microstructure, Electron Microscopy, and Vibrational Property

Scanning electron microscopy (SEM) of as-synthesized CBI powder (as shown in Figure 5.2a) confirms that the CBI phase grows as crystalline structures preferentially elongated along a single axis, consistent with the anisotropic *c*-axis stacking of the layered structure. Both micrometer-scale rods and nanometer-scale rod-like features were observed, the latter particularly visible in the outer regions of larger particles. The SEM micrograph of the outer crystalline area, shown in Figure 5.2b, highlights the faceted morphology and domain boundaries characteristic of the crystalline phase. The observed surface texture and grain distribution confirm the presence of well-developed crystallites in the outer regions of the sample.

High-resolution transmission electron microscopy (HRTEM) imaging (Figure 5.2c) of individual CBI micro/nanorods confirmed locally high crystallinity, with a *d*-spacing measurement of $d_{(40\bar{2})} = 1.60 \text{ \AA}$ in good agreement with the rhombohedral lattice parameters from Rietveld refinement. The selected-area electron diffraction (SAED) patterns (Figure 5.2d) acquired along the $[\bar{1}25]$ zone axis and indexed using the CrysTBox software showed sharp, well-defined spots with negligible diffuse scattering or streaking, indicating the absence of significant stacking disorder at the local scale within individual rods. SAED also yields $x = 0.16$ for $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$, indicating a composition of $\text{Cu}_{0.48}\text{Bi}_{0.84}\text{I}_3$, consistent with the Rietveld-derived average but re-

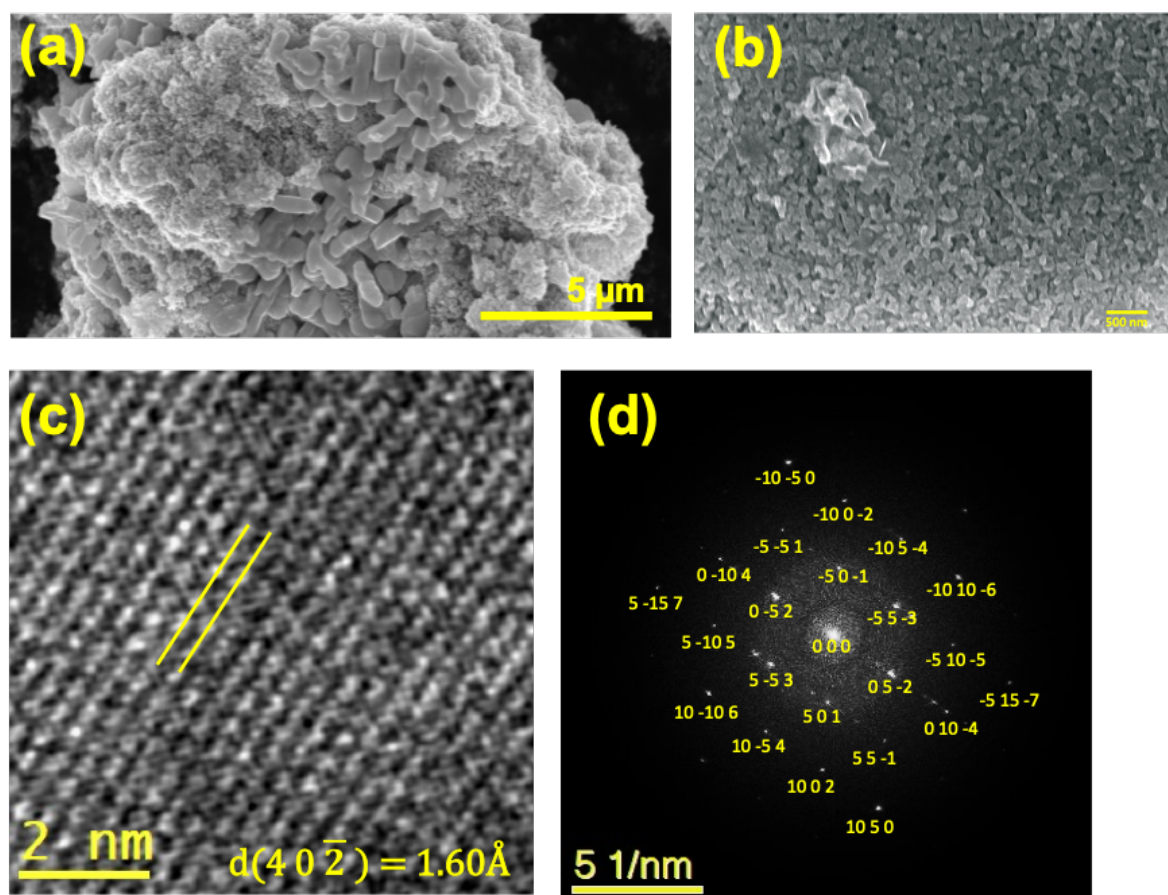


Figure 5.2: **(a)** The SEM micrograph of the powder sample shows μm -sized $\text{Cu}_3\text{Bi}_{1-x}\text{I}_3$ micro/nanorods in the center. Smaller crystalline grains are visible toward the edge of the particle, **(b)** enlarged view of those smaller crystalline grains from the outer crystalline area, **(c)** HRTEM analysis of $\text{Cu}_3\text{Bi}_{1-x}\text{I}_3$ shows the d -spacing corresponding to the $(40\bar{2})$ plane, and **(d)** the indexed SAED pattern displaying crystallographic plane. Adapted from [10].

flecting intra-sample compositional heterogeneity. The absence of a fixed stoichiometry, combined with the high degree of partial site occupation and stacking disorder, underscores that CBI is best understood as an interstitially stabilized, non-stoichiometric phase rather than a compound with a definitive stoichiometric formula. The total angular deviation of the fitted SAED lattice from the ideal orientation was 0.88° , and the d -spacing standard deviation across multiple planes was 0.0005 nm , confirming the high quality of the local structural model. The apparent discrepancy between local crystalline order in HRTEM/SAED and long-range stacking disorder in PXRD is attributed to local structural order within individual rods combined with stacking faults in the powder ensemble. The rods can therefore appear well ordered locally,

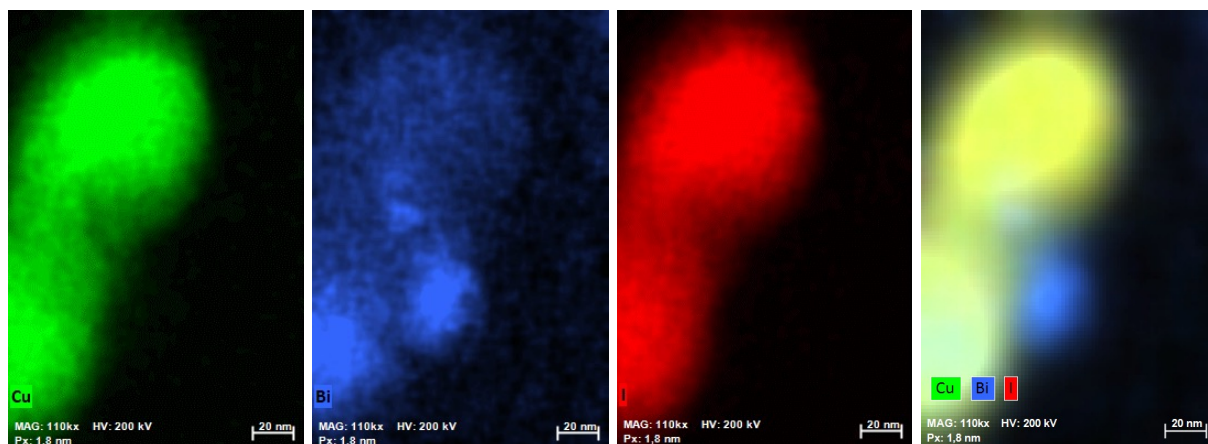


Figure 5.3: Transmission electron microscopy (TEM) coupled with energy-dispersive X-ray spectroscopy (EDX) analysis of $\text{Cu}_3\text{xBi}_{1-x}\text{I}_3$. Elemental mapping images show the spatial distribution of Cu, Bi, and I across the grains, confirming homogeneous incorporation of Cu within the BiI_3 lattice.¹

while variations in layer between adjacent stacked regions can reduce long-range periodicity and cause anisotropic peak broadening.

Energy-dispersive X-ray spectroscopy (EDX) elemental mapping acquired by STEM-HAADF (Figure 5.3) on a representative grain confirmed homogeneous spatial co-distribution of Cu, Bi, and I throughout the grain interior. No evidence of phase segregation into pure Cu or Bi-rich domains was detected at the TEM probe length scale, supporting the interpretation that Cu is genuinely incorporated within the BiI_3 framework rather than forming a separate nanoscale CuI phase dispersed within the BiI_3 matrix.

The vibrational properties are assessed using the Raman spectra of CBI thin films on glass (as displayed in Figure 5.4). Raman spectroscopy also provides phase-identification evidence in this context: the spectrum shows two additional peaks at 118 cm^{-1} and 183 cm^{-1} that are absent from the individual precursor compounds CuI and BiI_3 , confirming that a new vibrational environment is created by Cu interstitial incorporation and ruling out the possibility that the optical response arises from a simple physical mixture of precursors. The peak at 151 cm^{-1} may be attributed to a modified Bi–I stretching mode perturbed by the local lattice distortion introduced by the Cu^+ interstitials.

¹ Measurements conducted by Dr. M. Peterlechner (LEM, KIT).

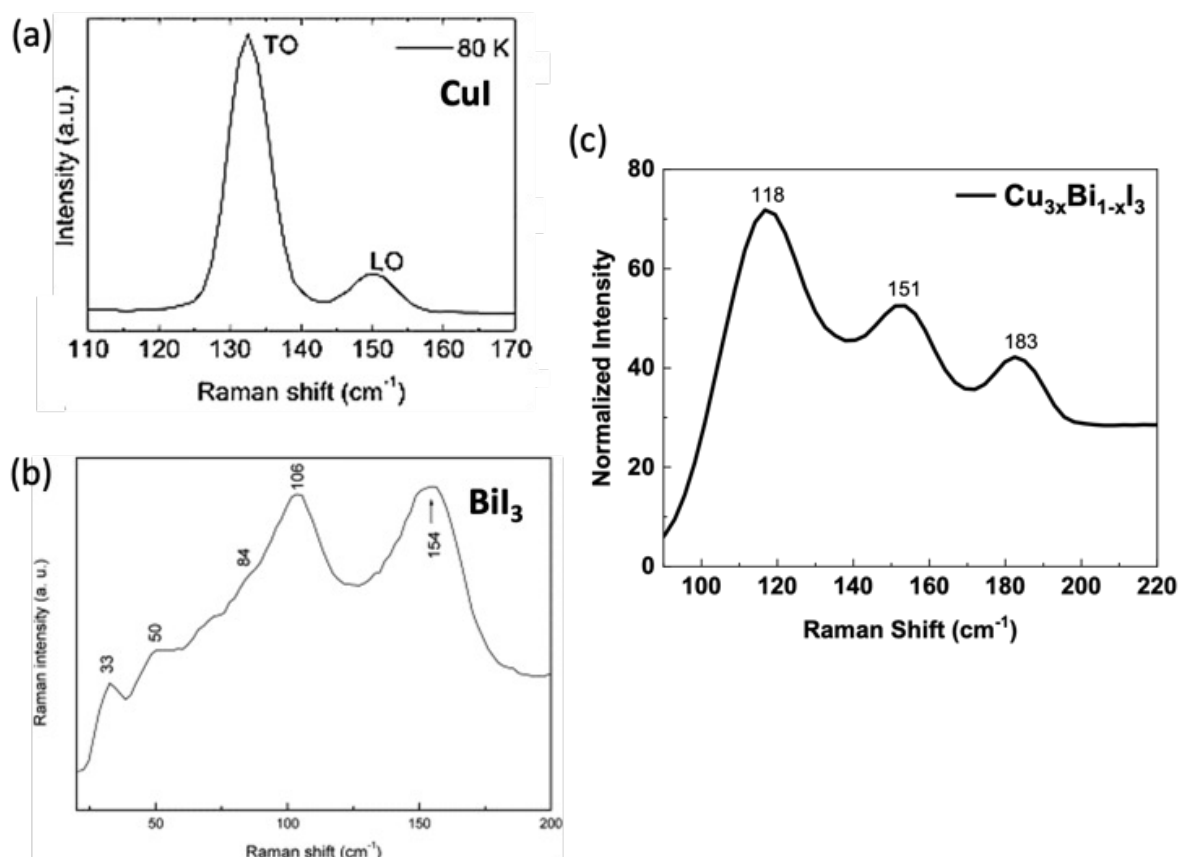


Figure 5.4: Raman spectra of (a) CuI, republished from He and Zhang [107]; (b) BiI₃, republished from Yang et al. [108]; and (c) Cu_{3x}Bi_{1-x}I₃, this work.

5.2.3 Thermal Stability and Phase Transitions

Following the structural investigation, the material properties of Cu_{3x}Bi_{1-x}I₃, which are crucial for its application in solar cells, were examined. Any novel light-harvesting semiconductor must exhibit a minimum thermal stability against decomposition to withstand the conditions in various climates and under solar illumination. Combined thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of as-synthesized CBI powder, as displayed in Figure 5.5 were conducted from room temperature to 900 °C in a nitrogen atmosphere. The TGA curve shows negligible mass loss up to 333 °C, establishing this as the practical thermal stability threshold for the compound. This value is substantially higher than the stability limit of the CuI polytypic composite identified for copper antimony iodide (β -CuI:Sb), where structural reorganization was already observable below 100 °C, and it compares favorably with the decomposition temperatures of many organic–inorganic hybrid halide perovskites. From an engineering perspective, a 333 °C stability threshold ensures that CBI absorber films can withstand any reasonable low-temperature thin-film deposition condition. Above 333 °C, sequential mass

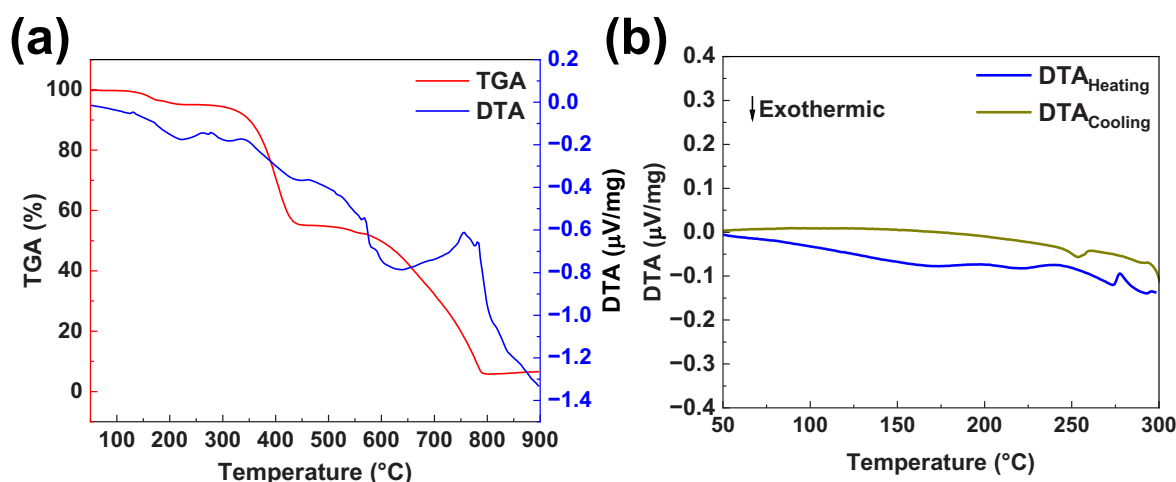


Figure 5.5: (a) TGA (red) and DTA (blue) of $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$ during heating of the sample up to 900 °C. (b) More detailed DTA during heating (blue) and cooling (green) from 50 °C to 300 °C. The peaks at 260 °C during cooling and 277 °C during heating can be attributed to a phase change.

losses are observed. The first, centered near 440 °C, corresponds to a loss of 42.5 wt%, consistent with the decomposition of the BiI_3 component and release of I_2 (theoretical mass fraction of I from BiI_3 : $253.80/589.68 \text{ g mol}^{-1} = 43 \%$). A second mass loss of 56 wt% between 580 °C and 790 °C is attributed to CuI decomposition, as trace copper was recovered in the TGA crucible after measurement completion. The Bi–I framework is the thermally labile component that decomposes first, while the residual CuI phase is more stable at higher temperatures.

High-resolution DTA reveals more nuanced thermal behavior in the 50 – 300 °C range, where TGA shows no significant mass loss. The DTA trace shows a sharp endothermic peak at 277 °C on heating and a corresponding exothermic peak at 260 °C on cooling, with negligible thermal hysteresis. The proximity of these temperatures and the absence of accompanying mass change identify this event as a reversible first-order phase transition, most likely a structural rearrangement or order–disorder transition within the interstitial sublattice of the CBI phase. Although the nature of this transition has not been characterized at the structural level by high-temperature diffraction in this work, the DTA data indicate that CBI can undergo a reversible phase change below its decomposition threshold. This has practical implications for device stability: if the phase transition involves redistribution of the interstitial Cu^+ population, it could modulate the concentration of defect states.

5.2.4 Optical Properties and Electronic Structure

The UV–Vis absorption spectrum of a representative spin-coated CBI thin film (Figure 5.6a) shows a primary absorption onset at 715 nm, corresponding to a band-edge energy of 1.73 eV.

A direct bandgap of $E_g = 1.66$ eV was determined from the Tauc plot $[(\alpha h\nu)^2 \text{ vs. } h\nu]$, consistent with direct allowed optical transitions at the band edge. The 1.66 eV bandgap is notable in several respects. First, it falls close to the Shockley–Queisser optimum of approximately 1.3 eV for single-junction solar cells, lying within the regime where the power conversion efficiency limit exceeds 30%. Second, this value is substantially narrower than the bandgap of pristine BiI_3 (1.8–1.9 eV), indicating that interstitial Cu incorporation actively modifies the band-edge electronic structure of the Bi–I host. Third, it represents a significant and favorable contrast with the 2.32 eV bandgap of copper antimony iodide (Cu_3SbI_6), which severely limits photocurrent generation in that system [98]. A secondary absorption feature was observed near 430 nm, corresponding to a photon energy well above the primary bandgap. This sub-primary absorption edge does not correspond to any characteristic energy of either precursor compound (α -CuI absorbs only in the UV above 3.0 eV; pristine BiI_3 absorbs in the visible below its band edge) and can be attributed to sub-bandgap optical transitions involving interstitial- or vacancy-derived defect states within the CBI band structure. Defect-induced sub-bandgap absorption of this type has been discussed theoretically and experimentally in the context of interstitial and vacancy states in metal oxide semiconductors and, more recently, in Cu-containing halide systems [109]. The photoluminescence (PL) spectrum of CBI thin films at room temperature (Figure 5.6b) shows a single emission peak centered at $\lambda_{\text{PL}} = 725$ nm (1.71 eV). For reference, the PL of pristine BiI_3 under identical excitation conditions is centered at 650 nm (1.91 eV). The 75 nm (0.20 eV) redshift induced by Cu^+ interstitial incorporation constitutes a qualitative indicator of how substantially the band-edge electronic structure is modified relative to the parent compound. The PL emission at 725 nm closely matches the absorption onset at 715 nm and the EQE spectral edge near 725 nm in the corresponding solar cells (Section 5.2.6), establishing a self-consistent picture in which the relevant optical and photovoltaic transitions occur at the same energy scale. The PL peak is slightly redshifted compared to the absorption edge, which may arise from lattice thermalization (electron–phonon coupling) or from a slight Stokes shift associated with localized emission from interstitial-perturbed band-tail states, as has been documented for layered metal halides under focused laser excitation [110].

Photoelectron spectroscopy in air (PESA) measurements, as shown in Figure 5.7, on CBI thin films yielded an ionization potential (IP) of 5.29 eV relative to the vacuum level, which defines the valence band maximum (VBM) energy. Combined with the 1.66 eV direct bandgap, this places the conduction band minimum (CBM) at approximately 3.55 eV below the vacuum level. The VBM energy of 5.29 eV is well matched to the IP values of the hole transport layers (HTLs) employed in the solar cell architecture, including MeO-2PACz (5.30 eV) and PTAA (5.25 eV), thereby ensuring efficient hole extraction from the absorber [10, 111, 112]. The CBM at 3.55 eV is well matched to the LUMO of PC_{71}BM (3.50 eV), which serves as the electron transport layer

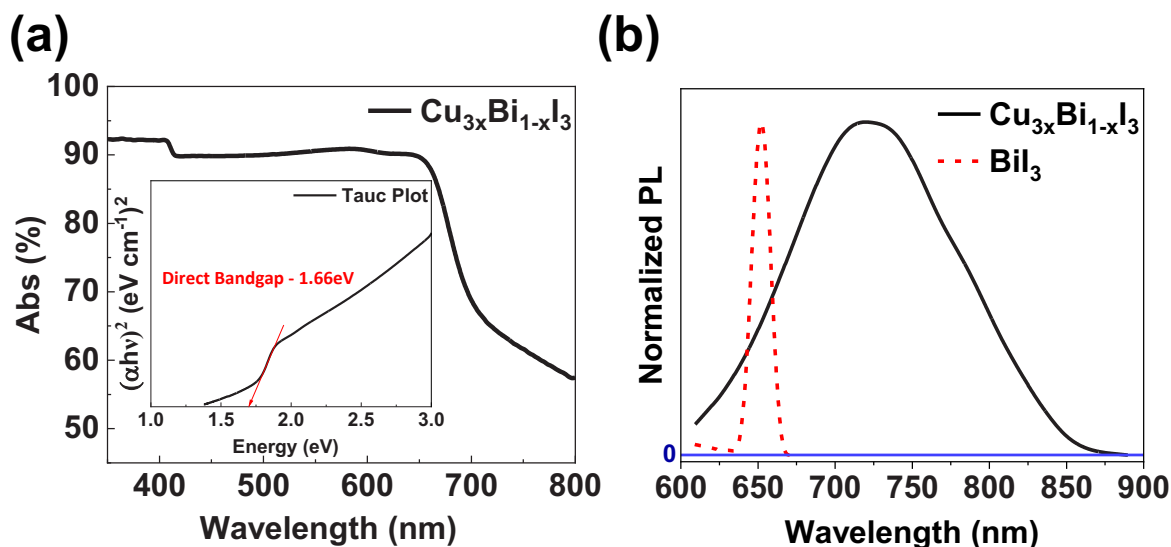


Figure 5.6: (a) Absorption spectrum of $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$. Inset: Tauc plot of the absorption, showing a direct bandgap of $E_g = 1.66\text{ eV}$. (b) Photoluminescence spectrum of $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$ with reference to the absorption of BiI_3 at room temperature. Adapted from [10].

(ETL). This energy-level alignment is near ideal for a non-inverted or conventional inverted architecture.

5.2.5 Thin-Film Morphology and HTL-Dependent Film Quality

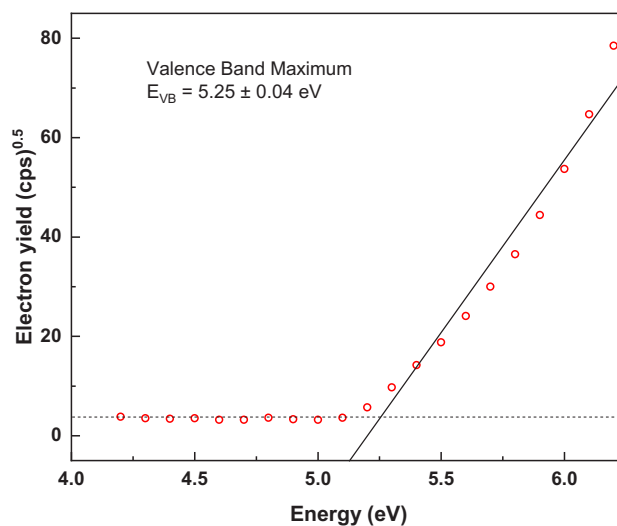


Figure 5.7: Photoelectron spectroscopy in air (PESA) measurements of $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$ thin films for determination of ionization potential (IP).

The integration of CBI into solar cell devices requires forming continuous, uniform thin films on top of the hole transport layer (HTL). Different HTLs present chemically distinct surface environments to the depositing CBI solution, and AFM characterization reveals that surface wettability critically governs film quality and morphology (Figure 5.8). To evaluate the role of the HTL surface in CBI film formation, four HTL configurations were compared: PEDOT:PSS, MeO-2PACz, PTAA, and a PTAA bilayer on top of MeO-2PACz.

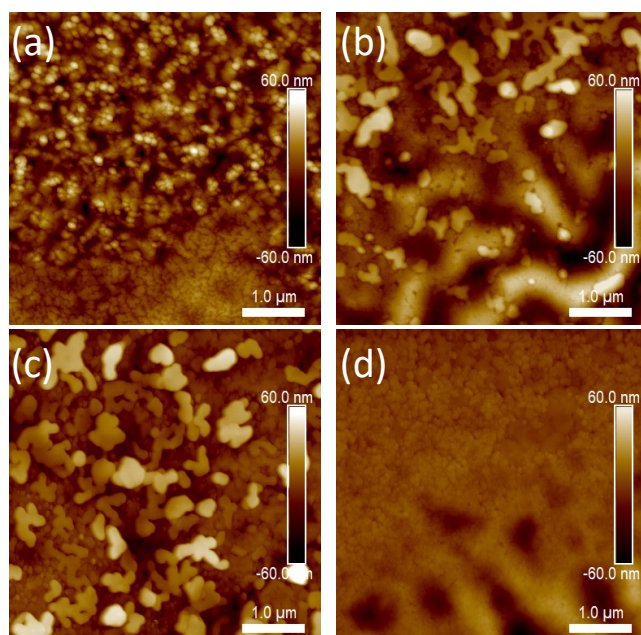


Figure 5.8: AFM images showing the topography of $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$ deposited on (a) PEDOT:PSS, (b) MeO-2PACz, (c) PTAA, and (d) PTAA on top of MeO-2PACz. The film homogeneity is satisfactory atop PEDOT:PSS and rather poor atop either MeO-2PACz or PTAA due to wetting issues. The film roughness was minimized, and the resulting device performance was maximized, using a bilayer of PTAA and MeO-2PACz, as shown in (d). Adapted from [10]

On PEDOT:PSS, CBI formed a non-homogeneous surface coverage with isolated islets, which can be attributed to poor wetting affinity between the DMSO/DMF-based CBI precursor and the hydrophilic PEDOT:PSS surface. On MeO-2PACz and PTAA individually, which present hydrophobic phosphonic acid and aromatic amine surfaces, respectively, CBI forms discontinuous patches with RMS roughness values of 13.3 nm and 12.0 nm, reflecting poor wetting on hydrophobic surfaces. The most favorable morphology is achieved on a bilayer of PTAA atop MeO-2PACz: this configuration reduces the RMS roughness to 5.4 nm and provides complete coverage of the photoactive device area, as confirmed by AFM analysis across multiple substrate positions. The improved wetting is attributed to solvent-induced modification of the PTAA surface, consistent with reports that solvent pre-washing or post-treatment can improve

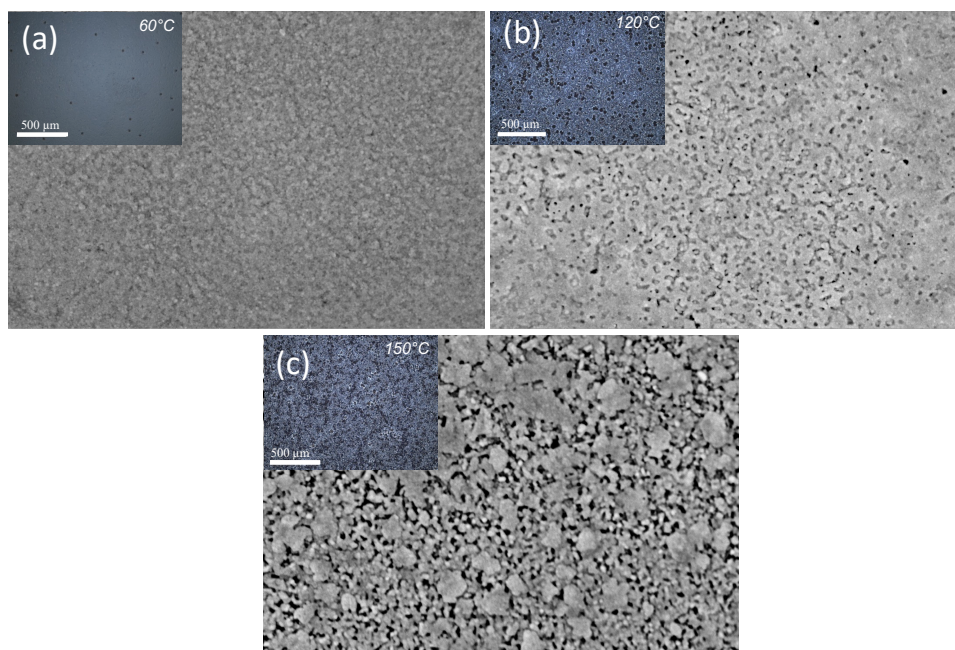


Figure 5.9: Film topography evolution of $\text{Cu}_3\text{Bi}_{1-x}\text{I}_3$ thin films as a function of annealing temperature: (a) 60°C , (b) 120°C , and (c) 150°C . SEM images reveal that as annealing temperature increases, isolated domains and crystalline islets begin to form, indicating thermally driven recrystallization. The development of inhomogeneous surface features at elevated temperatures is consistent with enhanced grain growth and partial phase separation, directly impacting thin-film coverage and device performance.

PTAA wettability and morphology [113]. Therefore, the effect is assigned to changes at the PTAA overlayer rather than to a change in the underlying MeO-2PACz layer.

A further morphological variable is the annealing temperature applied after CBI deposition, which is shown in Figure 5.9. SEM imaging on samples annealed at 60°C , 120°C , and 150°C reveals that above 120°C , discrete crystalline islets form at the film surface. This is perhaps due to thermally driven recrystallization of local micro/nano-rods as discussed earlier. At 60°C , the film coverage is continuous and homogeneous at the micrometer scale. This temperature-dependent morphological evolution is consistent with the DTA observation of no structural events below 260°C , but it demonstrates that even at temperatures well below the phase transition threshold, thermal reorganization of the film microstructure can introduce morphological heterogeneity that degrades device performance. For this reason, 60°C was identified as the optimal annealing temperature, balancing adequate crystallinity with morphological continuity.

5.2.6 Photovoltaic Device Performance

CBI thin films (thickness: $110(5)\text{ nm}$) were integrated into inverted solar cell devices with the architecture: ITO / MeO-2PACz (30 nm) / PTAA (10 nm) / CBI (110 nm) / PC_{71}BM (65 nm) / BCP (8 nm) / Ag (100 nm) (Figure 5.10a). This architecture was inspired by the standard

inverted lead-halide perovskite device stack and was adopted here because the energy level alignment is well matched to the IP and EA of CBI (Figure 5.10b). PTAA serves as electron blocking/hole-transport layer, while PC₇₁BM serves as the electron transport layer and BCP as the exciton-blocking interlayer before the Ag electrode.

Under simulated AM 1.5G illumination (1 sun, ASTM E927), (Figure 5.10c) an average PCE of 0.47% was obtained across 14 solar cells. The champion device yielded a PCE of 0.65%, with $V_{OC} = 0.53$ V, $J_{SC} = 2.54$ mA cm⁻², and FF = 34 %. Forward and reverse J–V sweeps show negligible hysteresis (PCE, V_{OC} , and J_{SC} are essentially identical in both scan directions), indicating that ion migration and interfacial charging effects are minimal under the operating conditions of these devices. The flat saturation of the dark current in the reverse bias regime confirms a sufficiently shunt-free absorber layer. The EQE spectrum (Figure 5.10d) shows photocurrent generation extending to approximately 725 nm, matching the PL emission maximum and the optical absorption onset, and confirming that the photovoltaic response derives from the CBI phase and not from the co-present α -CuI phase, whose 3.0 eV bandgap renders it inactive in the visible range. The integrated photocurrent from the EQE, $J_{EQE} = 2.41$ mA cm⁻², closely matches the J_{SC} from the J–V measurement (2.54 mA cm⁻²), validating the self-consistency of the characterization. The EQE signal well beyond the PL peak wavelength of pristine BiI₃ (650 nm) independently confirms that the photoactive material is the Cu-intercalated phase rather than unreacted BiI₃.

Despite the favorable energy alignment, the champion device efficiency of 0.65% and the low fill factor (FF = 34%) indicate that significant losses remain. The slope of the J–V curve under illumination and the FF magnitude are consistent with strong bimolecular (radiative) and/or trap-mediated non-radiative recombination. Given the multi-phase nature of the absorber (35 wt% CBI dispersed within 56 wt% α -CuI), it is plausible that grain boundaries between these phases introduce recombination-active interfaces. Additionally, the incomplete substrate coverage observed for certain HTL configurations introduces shunting pathways and non-uniform collection. The low J_{SC} relative to the available photon flux at $\lambda < 725$ nm suggests that not all absorbed photons contribute efficiently to photocurrent generation. One possible contributing factor is the presence of α -CuI within the absorber layer, which may reduce the effective photoactive volume of the CBI phase. A path toward improved device performance, therefore, requires either the elimination of the CuI co-phase or the conversion of a larger fraction of the precursor into the CBI phase, which presently appears to be constrained by the kinetics of interstitial site occupation during crystallization from solution.

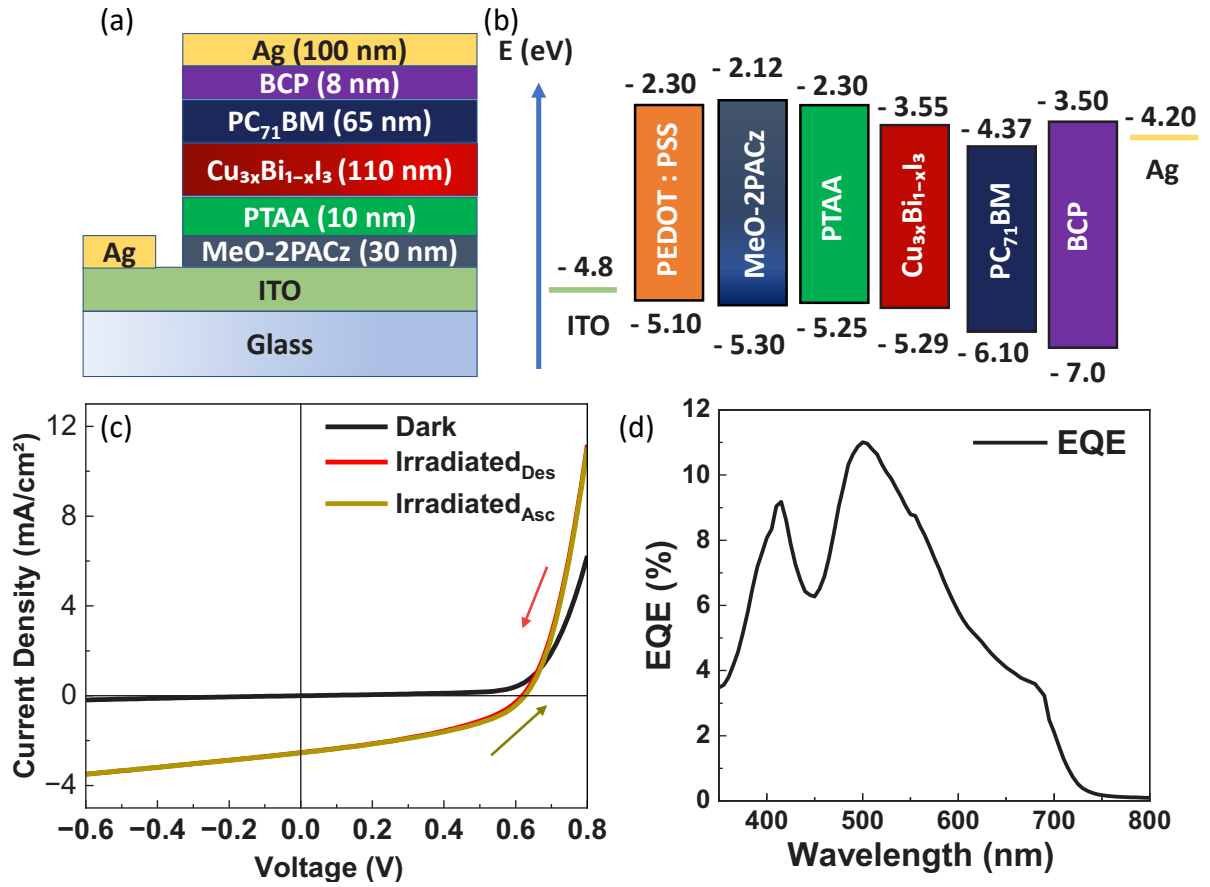


Figure 5.10: (a) Architecture of the Cu_{3x}Bi_{1-x}I₃ solar cells. (b) Relevant charge-carrier transport energies of the individual layers in the device architecture, including PEDOT:PSS. (c) J-V curve of the champion solar cell in the dark and under illumination, measured in forward and reverse directions. (d) The external quantum efficiency (EQE) shows photocurrent generation up to 740 nm, matching the optical bandgap of Cu_{3x}Bi_{1-x}I₃. [10]

5.3 Conclusions

This chapter has characterized Cu_{3x}Bi_{1-x}I₃ (CBI) as a previously undescribed, non-stoichiometric, interstitially stabilized semiconductor in which Cu⁺ occupies trigonal-planar coordination environments within the layered BiI₃ octahedra framework. Rietveld refinement, HRTEM/SAED, Raman spectroscopy, TEM-EDX elemental mapping, and optical characterization collectively establish that CBI is structurally distinct from the Caswellsilverite family, despite its nominal compatibility with the Caswellsilverite stoichiometric formula. The average composition Cu_{0.72}Bi_{0.76}I₃, with interstitial Cu⁺ at the 6c Wyckoff site of the $R\bar{3}$ space group, defines a new structural phase type with no known crystallographic prototype.

The key findings are:

- (1) CBI provides an experimentally characterized case in which native interstitial defects (Cu_i[•]) are responsible not only for stabilizing a metastable phase topology but also for

fundamentally reshaping the optoelectronic properties of the host material: the 0.20 eV bandgap reduction relative to BiI₃, the sub-bandgap trap absorption at 430 nm, and the photoluminescence redshift to 725 nm are all directly attributable to the presence and coordination chemistry of interstitial Cu⁺.

- (2) The comparison with copper antimony iodide (Chapter 4) demonstrates that swapping the host lattice and interstitial species within the copper–pnictogen–iodide family yields qualitatively different band gaps and structural outcomes, thereby providing a materials-design principle based on interstitial site control.
- (3) The demonstration of a peak PCE of 0.65% in thin-film solar cells confirms that the CBI phase is genuinely photoactive and that its bandgap of 1.66 eV is accessible for photovoltaic energy conversion, even in an incompletely optimized device architecture.

Notwithstanding these advances, CBI, as studied here, exhibits important limitations that constrain its immediate photovoltaic utility. The low fill factor (34%), modest J_{SC} (2.54 mA cm⁻²), and V_{OC} of 0.53 V all indicate substantial recombination losses, attributable in part to the high density of trap states associated with the interstitial and vacancy defects identified crystallographically. The co-presence of the photovoltaically inactive α -CuI majority phase (56 wt%) dilutes the absorber contribution and introduces potentially recombination-active phase boundaries. The inability, under the conditions studied, to synthesize CBI thin films without the α -CuI co-phase represents a fundamental processing constraint that remains unresolved.

More broadly, CBI inherits the limitations characteristic of iodide-based absorbers as a class. Halide frameworks are thermodynamically susceptible to decomposition through moisture-driven hydrolysis, producing I₂, and the reversible phase transition at 260 – 277 °C introduces a thermal sensitivity that, while well above any relevant device operating temperature, may nonetheless cause a gradual change in defect populations under accelerated aging. The volatility of I₂ as a decomposition product and the tendency of iodide-based films to undergo recrystallization at even moderate annealing temperatures, as demonstrated by the 120 °C onset of islet formation, are intrinsic to the halide framework and are not addressable by optimizing Cu interstitial chemistry alone. These stability concerns are not unique to CBI but are shared across the copper–pnictogen–iodide family, including the Cu₃SbI₆ polytypic composite examined in Chapter 4.

The recognition of these halide-specific limitations motivates a logical extension of the materials design framework developed in Chapters 4 and 5: the replacement of iodide (I⁻) by sulfide (S²⁻) as the anion framework. Sulfide frameworks generally offer substantially higher thermodynamic stability against moisture-driven decomposition than their halide counterparts.

6 Copper Bismuth Sulfide (Cu_3BiS_3)

6.1 Background

The preceding two chapters established that the optoelectronic behavior of copper-based, lead-free halide semiconductors is governed primarily by native defects and structural disorder rather than by idealized parent structures. In Cu_3SbI_6 , the target ternary phase does not crystallize as a well-ordered Caswellsilverite-type framework but assembles into a defect-stabilized polytypic composite, designated $\beta\text{-CuI:Sb}$, in which antimony occupies substitution-type tetrahedral sites within a mixed $\beta/\gamma\text{-CuI}$ host. In $\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$ (CBI), the layered BiI_3 octahedral framework accommodates interstitial Cu^+ at the 6c Wyckoff site, yielding a non-stoichiometric phase whose optical and electronic properties deviate substantially from those of the parent BiI_3 host. Across both systems, interstitial and substitution-type defect ensembles govern band-edge energies, sub-gap absorption, photoluminescence redshift, and ultimately the photovoltaic figures of merit accessible in thin-film devices.

These findings from iodide frameworks raise a natural and consequential question: do the same structure–property relationships, specifically the primacy of native defects and processing-dependent structural disorder over nominal stoichiometry, persist when the anion sublattice is changed from iodide to sulfide? The transition is motivated by well-established physicochemical differences between halide and chalcogenide frameworks. Iodide frameworks are thermodynamically susceptible to moisture-driven hydrolysis, and Cu-I and Bi-I bonds are predominantly ionic and readily disrupted by ambient humidity. The CuI -derived phases studied in Chapters 4 and 5 both exhibit limited thermal stability: $\beta\text{-CuI:Sb}$ begins to phase-segregate near 100°C , and CBI undergoes an irreversible structural change above 260°C . Replacing iodide with sulfide directly addresses this limitation because Cu-S and Bi-S covalent bonds are substantially stronger than their iodide analogs, conferring superior thermochemical stability against both moisture and thermal degradation.

Within the copper–bismuth–sulfide chemical space, Cu_3BiS_3 (wittichenite) is the most extensively documented stoichiometric ternary compound and the direct structural analog of the bismuth-containing phases examined in Chapter 5. Wittichenite is a naturally occurring mineral first described from the Wittichen locality in Germany [114] and subsequently characterized as an orthorhombic semiconductor with an indirect band gap of $1.4\text{--}1.5\text{ eV}$ and an absorption

coefficient exceeding 10^4 cm^{-1} [115, 116]. These properties make Cu_3BiS_3 an energetically competitive absorber for single-junction thin-film photovoltaics and have motivated sustained research on thin-film synthesis via both vacuum and solution routes [115, 117, 118, 119, 120, 121, 122, 30]. At the same time, the device literature reveals a stark gap between the material's intrinsic optical quality and its photovoltaic performance: the best reported power conversion efficiencies for solution-processed Cu_3BiS_3 remain below 1% and are achieved only with a cadmium sulfide (CdS) buffer layer, a toxic component that contradicts the central motivation for using a non-toxic, earth-abundant absorber [123, 124].

6.1.1 Cu_3BiS_3 in the Lead-Free Absorber Landscape

The photovoltaic absorber landscape for lead-free, solution-processable thin-film semiconductors includes several chemically distinct families. Bismuth-based halides and pnictohalides, including the systems studied in Chapters 4 and 5, form one branch. Copper-based chalcogenides constitute a complementary branch whose chemical diversity, structural richness, and superior ambient stability make them attractive for practical deployment.

Theoretical investigations have confirmed the photovoltaic promise of Cu_3BiS_3 . Density functional theory (DFT) calculations by Kumar and Persson predicted an indirect band gap of approximately 1.4 eV and high optical absorption efficiency, with the band edges determined by a hybridized manifold of Cu 3d, Bi 6s, and S 3p states [116]. A subsequent study by Kehoe et al. using hybrid DFT examined the band alignments and electronic structure of the isostructural series Cu_3MCh_3 ($\text{M} = \text{Sb, Bi}$; $\text{Ch} = \text{S, Se}$) and confirmed that Cu_3BiS_3 is the most promising candidate for photovoltaic applications within that series owing to its near-optimal direct-to-indirect gap relationship and favorable effective masses [125]. X-ray photoelectron spectroscopy and hard X-ray photoelectron spectroscopy measurements by Whittles et al. established that the valence band maximum of Cu_3BiS_3 is dominated by Cu 3d–S 3p antibonding states at -5.0 eV below the vacuum level, and that the ionization potential and electron affinity are suitable for alignment with common n-type electron transport layers [126]. These experimental band alignments provide the energetic foundation for selecting rational device architectures.

6.1.2 Crystal Structure of Wittichenite

The crystal structure of Cu_3BiS_3 was determined (as shown in Figure 6.1) by Matzat using single-crystal X-ray diffraction [127] and independently confirmed by Kocman and Nuffield [128]. The compound adopts an orthorhombic structure with space group $P2_12_12_1$ (No. 19 in the International Tables for Crystallography). Kocman and Nuffield reported lattice parameters of $a = 7.70 \text{ \AA}$, $b = 10.41 \text{ \AA}$, and $c = 6.74 \text{ \AA}$, whereas Matzat reported $a = 7.723 \text{ \AA}$, $b = 10.395$

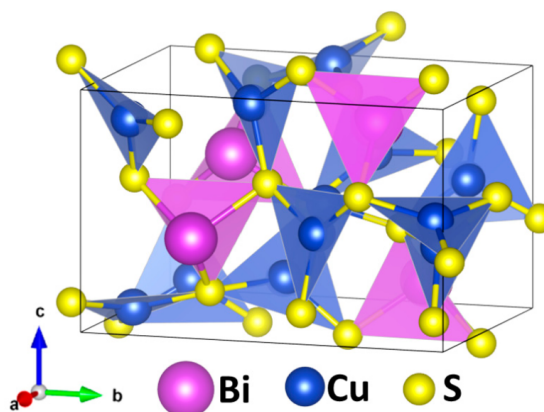


Figure 6.1: The crystal structure of Cu_3BiS_3 [127].

$\text{\AA}$, and $c = 6.716 \text{ \AA}$ [128, 127]. In this structure, bismuth occupies a single crystallographically distinct site in a distorted coordination environment, while copper occupies three symmetry-inequivalent sites within a sulfide framework. The structural motif comprises BiS_3 pyramidal units and CuS_3 and CuS_4 polyhedra, reflecting the chemically distinct roles of the stereochemically active $\text{Bi}^{3+} 6s^2$ lone pair and the d^{10} -configured Cu^+ cations [125, 129]. This structural complexity is relevant for the optical properties of Cu_3BiS_3 . The stereochemically active $\text{Bi}^{3+} 6s^2$ lone pair is associated with asymmetric Bi–S coordination, while the distorted Cu–S polyhedra influence the Cu $3d$ –S $3p$ states near the valence-band edge. Published electronic-structure studies show that the valence-band edge contains mainly Cu $3d$ and S $3p$ character, whereas the conduction-band edge is dominated by Bi $6p$ and S $3p$ states; optical absorption is therefore linked to transitions between these hybridized states [126].

An important aspect of the wittichenite structure is its thermal polymorphism. Makovicky documented two successive phase transitions on heating: a first transition to a Pnma or $\text{Pn}2_1a$ structure at $118.5 \pm 2 \text{ }^\circ\text{C}$, followed by a transformation to a second Pnma polymorph at approximately $191 \text{ }^\circ\text{C}$ [130]. Above $135 \text{ }^\circ\text{C}$, the material enters a regime of enhanced ionic conductivity and has been classified as a solid electrolyte [130]. This sequence of phase transitions has direct consequences for solution-based thin-film synthesis: annealing temperatures routinely employed in prior literature (240 – $300 \text{ }^\circ\text{C}$) fall within or beyond the high-temperature polymorphic regime, meaning that the as-deposited films may not return to the room-temperature $\text{P}2_12_12_1$ phase on cooling unless the quench rate and chemical potential are carefully controlled. This structural consideration connects directly to the processing-dependent crystal growth behavior documented in Section 6.3.

6.1.3 Optoelectronic Properties and Photovoltaic Motivation

The optical properties of Cu_3BiS_3 thin films have been studied by several groups, yet a consensus on the precise band gap remains elusive. Reported values range from 1.10 to 1.72 eV, with the spread attributable in part to differences in film microstructure, secondary-phase content, and the choice of optical analysis method [115, 117, 118, 120, 121]. A recurring methodological issue is the application of the Tauc formalism to films whose microstructure deviates from the idealized, homogeneous, single-phase limit for which the Tauc plot was originally derived [131]. The native structural disorder inherent to polycrystalline films, including grain boundaries, voids, and secondary phases, introduces sub-gap optical contributions that can skew the linear extrapolation to the energy axis and yield erroneously low or high band-gap estimates. In this context, thermally evaporated Cu_3BiS_3 with 1.4–1.5 eV indirect bandgap is the most reliable reference, supported by the theoretical band-structure data of Whittles et al. [126]. Carrier mobilities reported from electrical measurements span $1\text{--}100\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, with most values falling within the $1\text{--}10\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ range [118, 120, 126, 132].

The p-type character of Cu_3BiS_3 films has been consistently reported across synthesis routes [115, 118] and is mechanistically attributed to the low formation energy of copper vacancies (V'_{Cu}) under copper-poor conditions, in direct analogy with the V'_{Cu} acceptor population identified as the dominant native defect in the CuI-derived phases of Chapters 4 and 5. In the Cu–S and Bi–S coordination environment of wittichenite, the valence band maximum is set by an antibonding combination of Cu 3d and S 3p states. V'_{Cu} creates charge-transition levels that are resonant with or just above the valence band edge, making it an effective shallow acceptor rather than a deep recombination center [126]. This property distinguishes Cu_3BiS_3 from many binary sulfide absorbers, where sulfur vacancies ($V_{\text{S}}^{\bullet\bullet}$) act as deep midgap traps, and is the electronic basis for the material's relatively benign defect tolerance.

Photoluminescence studies of Cu_3BiS_3 thin films by Yakushev et al. identified emission peaks at sub-band-gap energies attributable to donor–acceptor pair (DAP) recombination, suggesting the simultaneous presence of donor and acceptor defect populations within the gap [133]. Pan et al. reported additional PL features in electrodeposited films consistent with localized recombination states near the band edge [134]. The coexistence of donor and acceptor defects within the Cu_3BiS_3 crystal structure is consistent with the Cu–S and Bi–S chemistry: bismuth at its crystallographic site can, under non-stoichiometric conditions, form $\text{Bi}_{\text{Cu}}^{\bullet\bullet}$ antisites or interstitial configurations that act as donors, while V'_{Cu} and possible Cu_{S} antisites (Cu'_{S}) constitute the acceptor population. Correlating these competing defect types with photovoltaic figures of merit is a primary goal of the following sections.

6.1.4 Existing Solar Cell Literature and Performance Gap

Despite the material's favorable band gap and optical absorption, photovoltaic devices based on Cu_3BiS_3 have achieved only modest performance to date. Estrella et al. were among the first to report Cu_3BiS_3 thin films formed by solid-state reaction of CuS and bismuth. Semiconducting optical behavior was confirmed, but no complete device characterization was provided [115]. Gerein and Haber demonstrated a one-step synthesis of Cu_3BiS_3 by RF sputtering and confirmed optical and electrical properties consistent with a photovoltaic absorber [117]. An evaporation-derived device with the architecture ITO/CdS/ Cu_3BiS_3 /Ag showed diode-like J–V characteristics but lacked quantified fill factor, efficiency, or short-circuit current density, leaving its photovoltaic functionality undemonstrated [119].

The highest power conversion efficiency reported in the Cu_3BiS_3 literature, 1.7%, was achieved in a device with a molybdenum back contact and a ZnO/ZnO : Al front electrode. However, the absorber layer in that study contained additional secondary phases alongside Cu_3BiS_3 [135]. For phase-pure Cu_3BiS_3 , the best efficiencies have been achieved in spin-coated films deposited on molybdenum-coated glass and paired with a CdS buffer layer: Li et al. reported a best PCE of 0.48% with Ag doping, while the undoped reference achieved 0.2% with a fill factor of 45%, $V_{\text{OC}} = 233$ mV, and $J_{\text{SC}} = 2.9$ mA cm^{-2} [123, 136]. Fang et al. investigated the effect of thiourea dosage on film properties and solar cell performance, providing EQE spectra as supporting evidence for Cu_3BiS_3 -derived photocurrent [124]. More recently, Rath et al. demonstrated solution-processed Cu_3BiS_3 solar cells with interfacial modification and reported improvements in charge generation properties, though they still relied on CdS as the buffer layer and achieved efficiencies below 1% [30].

A critical survey of this literature reveals two important shortcomings that motivate the approach taken in the present chapter. First, except for Rath et al. [30], reported EQE spectra either do not align with the absorption spectra [124] or are absent entirely, leaving the origin of the photocurrent, whether from Cu_3BiS_3 or from the photoactive Bi_2S_3 secondary phase, unresolved. Second, every reported high-efficiency Cu_3BiS_3 device employs CdS, which is itself an efficient absorber in the visible spectral range and whose photovoltaic contribution to J–V and EQE characteristics may have been systematically underestimated in prior reports. The present chapter directly addresses this ambiguity by attempting to achieve phase-pure Cu_3BiS_3 , that too via low-temperature solution processing, and intentionally excluding CdS from the device architecture and using EQE measurements to unambiguously attribute photocurrent to the Cu_3BiS_3 absorber.

6.2 Results and Discussion

6.2.1 Optical Absorption and Stoichiometry Dependence

Absorption spectra of Cu_3BiS_3 films on quartz glass confirm semiconducting optical behavior across all stoichiometric variants investigated: absorption below the band edge is very low, and a steep absorption onset is followed by strong absorption above the band edge at shorter wavelengths. The reference sample prepared at the nominal $\text{Cu}:\text{Bi} = 3:1$ stoichiometry displays a well-defined onset, followed by a region of gradually rising absorption, which is qualitatively consistent with an indirect-gap semiconductor, in which the density-of-states ramp at the absorption edge is gentler than in direct-gap materials. The material does not exhibit a flat below-gap absorption plateau, distinguishing it from samples with high defect density or heavy secondary-phase contamination.

Systematic variation of the Bi content across $\text{Cu}:\text{Bi}$ ratios of 3:0.6, 3:0.8, 3:1 (reference), 3:1.2, and 3:1.4 produces a monotonic shift in the absorption onset (Figure 6.2a): copper-rich variants (3:0.6, 3:0.8) display the latest onset (highest effective gap), while bismuth-rich variants (3:1.2, 3:1.4) show progressively earlier onsets. The 3:1.4 sample exhibits a particularly extended linear absorption slope spanning approximately 400 nm, a spectral signature associated in the literature with elevated sub-gap absorption from defects. The partial contribution of film thickness changes to the observed total absorbance is noted: stylus profilometry measurements indicate that the two-layer film thickness increases from approximately 115 nm for the 3:0.6 variant to approximately 145 nm for the 3:1.4 variant, partly because a higher bismuth nitrate concentration directly increases the total precursor mass per unit volume of solution.

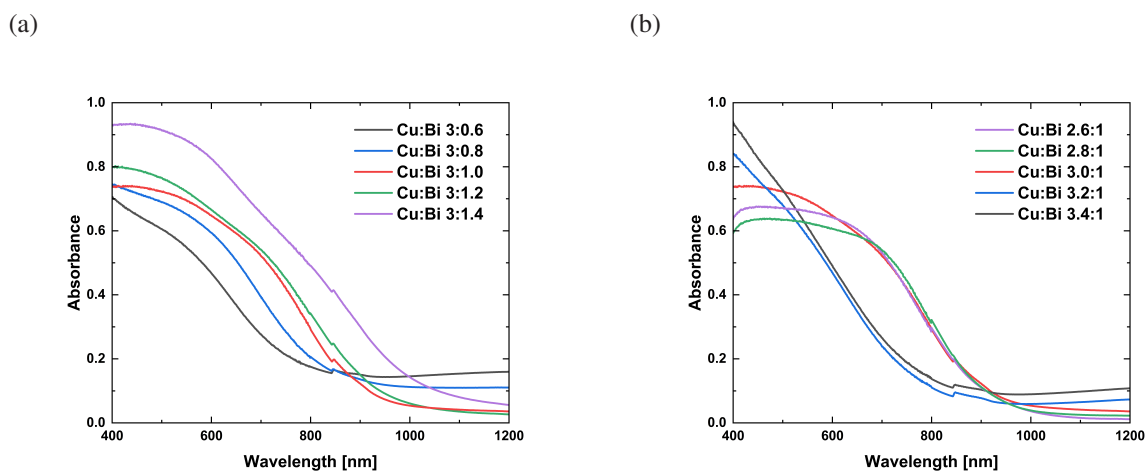


Figure 6.2: Absorption spectra of Cu_3BiS_3 thin films with varying precursor stoichiometry: (a) bismuth concentration variation and (b) copper concentration variation [137].

The dependence of the absorption onset on Bi concentration is interpreted as a composition-driven shift of the effective optical gap, arising from two nonexclusive mechanisms. First, excess bismuth may stabilize a Bi-rich secondary phase, most plausibly Bi_2S_3 , as detected by Rietveld refinement in the reference sample. Its narrower gap (approximately 1.3 eV) contributes additional below-gap absorption. Second, Bi^{3+} more than the stoichiometric Cu_3BiS_3 requirement may enter the crystal structure as Bi'_{Cu} antisite defects (Bi substituting on a Cu site) or as interstitial configurations that introduce defect states near the valence or conduction band edges, effectively narrowing the observed optical gap. The latter mechanism would be directly analogous to the interstitial Cu^+ incorporation identified in CBI (Chapter 5), in which off-stoichiometric cation incorporation reshapes the absorption spectrum without changing the material's phase.

Over the Cu:Bi range of 2.6:1 to 3.4:1, the Cu content yields a qualitatively different response (shown in Figure 6.2b). No systematic trend in absorption onset is observed for the copper-poor variants (2.6:1 and 2.8:1), consistent with the relatively minor compositional change from the reference. By contrast, the copper-rich variants (3.2:1 and 3.4:1) display a clear blue shift of the absorption onset and a flattened above-gap absorption slope, the latter indicating phase formation distinct from wittichenite. Powder samples synthesized under the same copper-rich conditions exhibit color changes from the characteristic black of Cu_3BiS_3 to dark green (3:1.2 variant) and reddish-brown (3:1.4 variant), indicating the plausible formation of copper-rich sulfides such as Cu_2S or CuS . These observations indicate that the phase purity of Cu_3BiS_3 in the DMF/DMSO precursor system is highly sensitive to the Cu:Bi precursor ratio. The sulfur-precursor amount was fixed at 7 in both series. Based on both UV–Vis plots, Cu:Bi = 3:1:7 was selected as the most suitable ratio for further investigation. This sample showed a clear absorption edge and a steady increase in absorption at photon energies above the band gap. In comparison, Bi-rich samples showed an earlier absorption onset. The most Bi-rich sample also showed a broad absorption tail below the band gap. Cu-rich samples showed a shift of the absorption edge toward shorter wavelengths and a flatter absorption response at photon energies above the band gap. These results support selecting 3:1:7 Cu:Bi:S under the tested conditions.

6.2.2 Phase Identification and Lattice Parameters

The optical trends of Section 6.2.1 cannot identify the phases present. Grazing-incidence X-ray diffraction (GI-XRD) was therefore used to determine phase identification and lattice parameters directly. Two films on quartz glass, of two and four spin-coated layers, were measured at Helmholtz-Zentrum Berlin on a PANalytical X'Pert Pro MPD diffractometer with $\text{Cu-K}\alpha_{1,2}$ radiation ($\lambda_{\text{K}\alpha_1} = 1.54056 \text{ \AA}$, $\lambda_{\text{K}\alpha_2} = 1.54439 \text{ \AA}$) at a fixed incident angle of $\omega = 0.5^\circ$. Both pat-

terns index throughout the orthorhombic Cu_3BiS_3 cell and were refined by the Le Bail method (Figure 6.3).¹

Le Bail refinement (developed by Armel Le Bail) differs from the Rietveld method in its treatment of reflection intensities. In Rietveld refinement, the integrated intensities are calculated from the structure factors of an atomic model. In Le Bail refinement, no atomic structural model is required; instead, the observed intensity is iteratively partitioned among the reflections permitted by the selected unit cell and space group while the lattice parameters, peak-profile parameters, zero-point correction and background are refined. The lattice parameters are therefore as reliable as a Rietveld result, but no atomic positions, occupancies or weight fractions follow from the fit. Decoupling intensity from structure is an advantage here, since preferred orientation and the shallow sampling depth of the grazing geometry distort relative intensities in thin films and would otherwise bias the cell.

The structural model was the Cu_3BiS_3 structure in space group $P2_12_12_1$ (No. 19), all atoms on Wyckoff $4a$ sites [127]. This modification is appropriate for films annealed at 165°C , well below the transformation to $Pnma$ near 190°C . The refinement yields $a = 7.674(2) \text{ \AA}$, $b = 10.394(4) \text{ \AA}$ and $c = 6.694(2) \text{ \AA}$ for the two-layer film and $a = 7.676(2) \text{ \AA}$, $b = 10.402(4) \text{ \AA}$ and $c = 6.699(2) \text{ \AA}$ for the four-layer film, corresponding to $533.9 \text{ \AA}^3$ and $534.9 \text{ \AA}^3$. Both lie roughly 1 % below the single-crystal volumes [128, 127], and the deviation is anisotropic: a is contracted by 0.6 % and c by 0.3 %, whereas b matches the literature value. This can be attributed to the residual compressive stress from the thermal expansion mismatch with the rigid quartz substrate during cooling from the anneal. The four-layer cell lies closer to the bulk values along all three axes, indicating partial relaxation as the film thickens.

As Figures 6.3a and 6.3b show, the quartz substrate contributes a broad amorphous feature near 21° (2θ) that is considerably more intense for the two-layer film than for the four-layer film, where it is markedly attenuated. This attenuation reflects the reduced substrate signal as additional spin-coated layers build a denser, more compact absorber. Rietveld refinement of the GI-XRD pattern from the four-layer film on quartz yields a near-phase-pure composition of $(98.8 \pm 0.6) \% \text{ Cu}_3\text{BiS}_3$ and $(0.6 \pm 0.4) \% \text{ Bi}_2\text{S}_3$. The weighted-profile residual R_{wp} , which measures the weighted difference between the observed and calculated diffraction profiles, is 7.6 %. The goodness of fit, $\text{GOF} = R_{\text{wp}}/R_{\text{exp}}$, is 1.2, indicating that the calculated pattern describes the measured data with a residual close to the statistically expected value. Because the refined amount of Bi_2S_3 is close to the instrumental detection limit, the actual Bi_2S_3 content may be lower. This value is nonetheless recorded as an upper bound on phase purity, and as a

¹ Measurements and refinements were carried out by Prof. Dr. S. Schorr and R. Schwiddessen (Helmholtz-Zentrum Berlin).

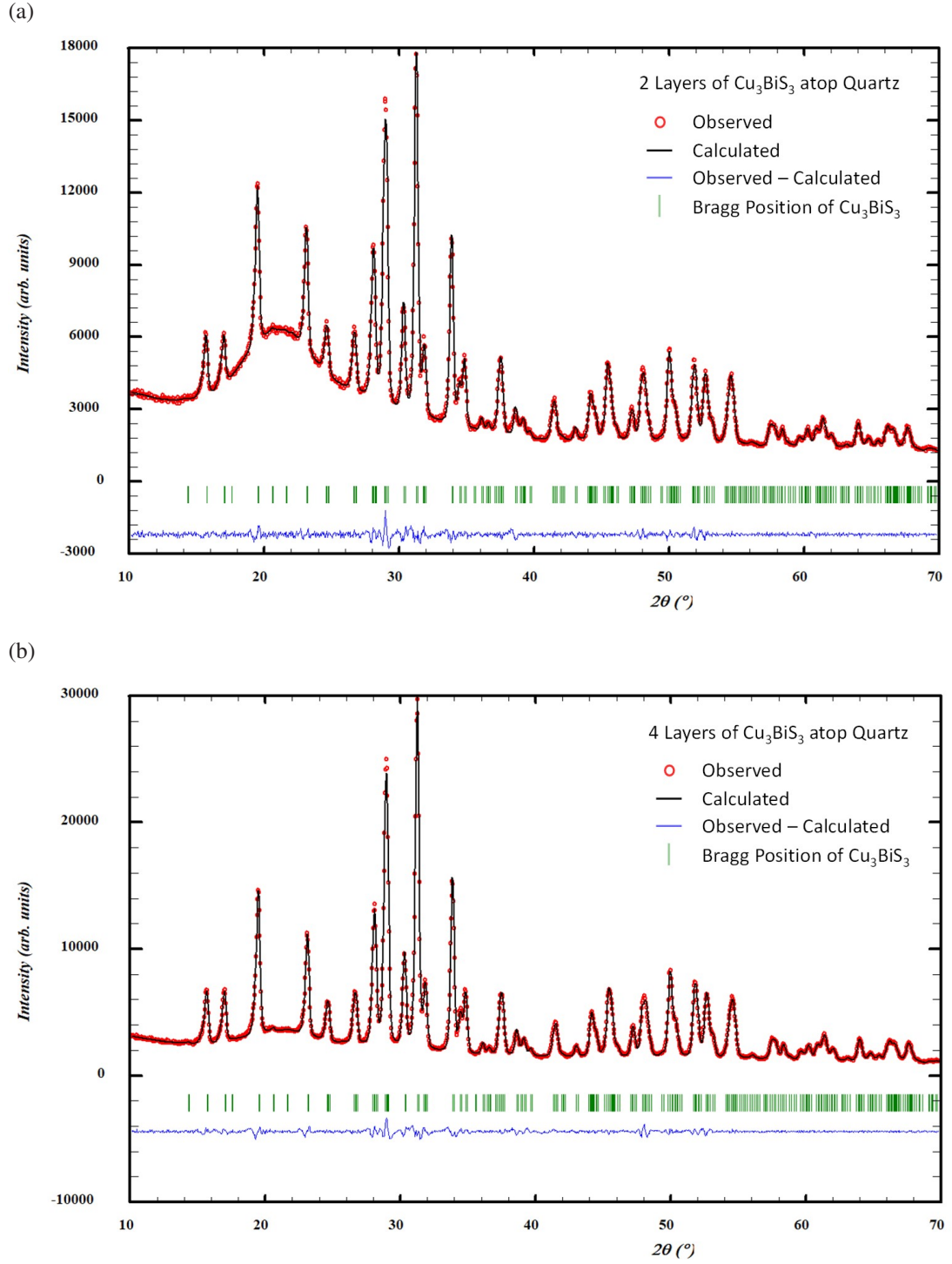


Figure 6.3: Le Bail refinement of the GI-XRD patterns of (a) two-layer and (b) four-layer Cu_3BiS_3 thin films on quartz glass, measured at $\omega = 0.5^\circ$ with $\text{Cu-K}\alpha_{1,2}$ radiation.

reminder that the chemical potential at the grain boundaries may depart from stoichiometry in precursor metal-enriched microenvironments.

6.2.3 Differential Thermal Analysis of the Cu_3BiS_3 Precursor System

Thermogravimetric analysis (TGA) was performed simultaneously with Differential Thermal Analysis (DTA) on the same dried precursor film to quantify the mass losses accompanying each thermal event and to cross-validate the chemical assignments of the DTA features. The overall weight loss from room temperature to 900 °C is approximately 37%, yielding a thermally stable residual of approximately 63% of the initial sample mass, which is attributed to the Cu_3BiS_3 product phase and residual non-volatile inorganic components. The weight-loss profile comprises four partially resolved regimes whose temperature boundaries correspond directly to the thermal events identified in the DTA trace. An initial mass loss of approximately 8 wt% between elevated room temperature and 200 °C is attributed to the progressive evaporation of residual DMF and DMSO from the precursor matrix. A secondary loss of approximately 5 wt%, extending to 300 °C, is associated with the onset of thiourea decomposition, as reported by Mahto et al. [138]. The most pronounced mass-loss step, spanning 300–450 °C and accounting for approximately 17 wt%, coincides with a cluster of sharp DTA endotherms in this region and is attributed to multi-step gaseous release accompanying the concurrent decomposition of thiourea and the metal nitrate precursor salts, which may be attributed to the loss of physisorbed water, surface hydroxyl groups, and precursor residues [138]. A shallow plateau near 450–500 °C marks the temporary completion of dominant volatile-release events. A further minor mass loss of approximately 3 wt% between 500 and 700 °C is consistent with the sulfur-reduction processes identified in the second thermal stage reported by Mahto et al. for synthesized Cu_3BiS_3 nanostructures [2]. Above 700 °C, the residual weight loss is attributed primarily to material decomposition, as identified by Mahto et al. for Cu_3BiS_3 nanostructures [138].

Differential thermal analysis (DTA) was performed on the dried precursor material to determine the sequence and nature of the thermal events during the conversion of the copper nitrate, bismuth nitrate, and thiourea precursors to the Cu_3BiS_3 phase. In DTA, the sample temperature is continuously compared with that of an inert reference; endothermic processes within the sample cause a negative deflection of the DTA signal, while exothermic processes cause a positive deflection. The measured DTA heating curve is shown in Figure 6.4. The curve is characterized by a series of overlapping negative deflections that rise from the baseline, indicating that the thermal conversion of the precursor system occurs through multiple sequential and partially concurrent endothermic processes rather than a single transformation event. This

multi-step character is expected, given that the precursor film contains residual solvent (*N,N*-dimethylformamide, b.p. at 153 °C; dimethyl sulfoxide, b.p. at 189 °C), thiourea as a solid sulfur source, and the two metal nitrate salts, all of which undergo chemically distinct thermal transformations at different temperatures [139, 140, 141].

At the lowest temperatures accessible in the measurement, the DTA signal begins to deviate from the baseline in the endothermic direction. This early deflection is attributable to the progressive evaporation and desorption of residual solvent species retained within the dried precursor film after spin coating. Both DMF and DMSO have appreciable vapor pressures below their boiling points and can be trapped within the dense precursor matrix in quantities that are not completely removed during the room-temperature drying step [139]. Solvent evaporation from a porous or dense solid is a diffusion-limited process, so the onset temperature and breadth of the corresponding DTA feature depend on the film morphology and the heating rate rather than on a sharp thermodynamic transition. This explains the broad, gradually evolving character of the initial region of the DTA curve. Incomplete removal of the solvent before annealing has practical implications for the nucleation of Cu_3BiS_3 : residual DMF or DMSO molecules coordinated to the metal nitrate precursors may suppress nucleation at lower temperatures by stabilizing dissolved metal species, thereby raising the threshold temperature for phase formation [139, 142].

The intermediate-temperature region of the DTA curve shows a sequence of more sharply defined endothermic dips, attributed to the multi-stage thermal decomposition of thiourea and the concurrent decomposition of the metal nitrate salts. The thermal decomposition of thiourea ($\text{SC}(\text{NH}_2)_2$) is well documented to proceed in multiple overlapping steps beginning at approximately 180 °C, producing gaseous products such as ammonia (NH_3) and isothiocyanic acid (HNCS), in varying proportions depending on the heating rate and atmosphere [140, 141]. Each decomposition step releases sulfur-containing reactive species into the local reaction environment of the metal nitrates. The coincidence of sulfur release from thiourea decomposition with the thermal destabilization of the metal nitrate anions creates a reactive atmosphere in which Cu^+ and Bi^{3+} cations are available for immediate sulfidation. The multiple overlapping DTA dips in this region, therefore, most likely reflect the convolution of thiourea decomposition steps, metal nitrate reduction and sulfidation, and the onset of Cu_3BiS_3 nucleation, each contributing an endothermic signature at a slightly different characteristic temperature [140, 141, 138].

The DTA events at elevated temperature, reflected in the broader shoulder beyond the sharpest dips, are consistent with structural reorganization within the newly formed Cu_3BiS_3 crystallites. As established by Makovicky from in-situ variable-temperature X-ray diffraction, the room-temperature $P2_12_12_1$ polymorph of Cu_3BiS_3 undergoes a first phase transition at 118.5 °C to a modulated Pnma polymorph, followed by a second transition to an unmodulated, high-

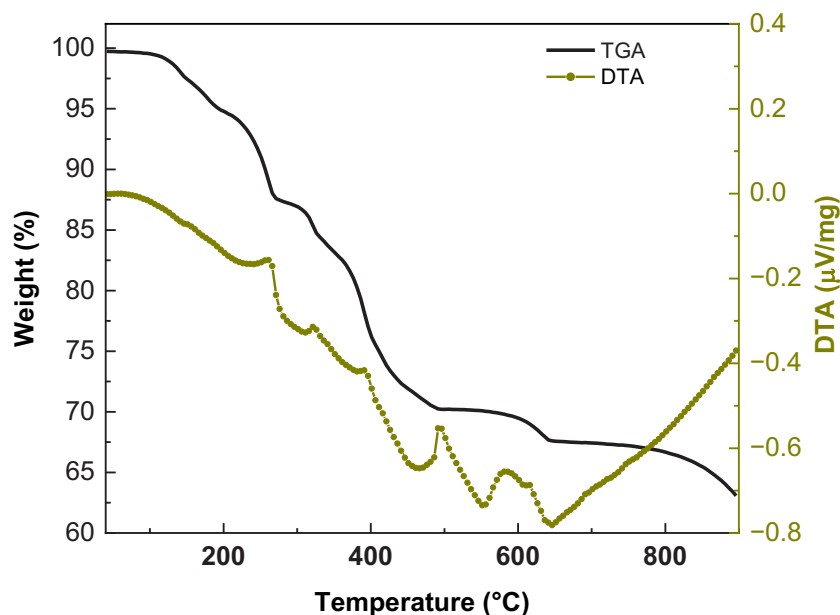


Figure 6.4: TGA and DTA curves for Cu_3BiS_3 . The heating profile shows multiple partially overlapping endothermic events rather than a single conversion event, consistent with residual solvent evaporation, thiourea decomposition, metal nitrate decomposition, sulfidation, CuBiS nucleation, and structural reorganization of the forming wittichenite phase.

temperature Pnma polymorph at 191 °C [130]. Above approximately 135 °C, copper atoms within the wittichenite structure transition from a stationary to a mobile state, conferring solid-electrolyte behavior on the compound [130]. Under continuous heating, these two transitions would each produce a DTA thermal event superimposed on the broader decomposition background. Their coincidence with the temperature range of thiourea decomposition makes it likely that the multiple dip features observed in Figure 6.4 include contributions from structural rearrangements of the forming wittichenite phase as well as from precursor decomposition. Analogous multi-feature DTA profiles during the solvothermal formation of Cu_3BiS_3 from thiourea-containing precursor systems have been reported using a choline chloride/thiourea deep eutectic solvent, where the successive DTA features were attributed to the stepwise release of sulfur from the thiourea decomposition products and the temperature-dependent formation and anisotropic growth of the ternary sulfide nanostructures [138].

The multi-stage thermal profile established by the TGA and DTA curves provides a rationalization for the synthesis conditions employed in this work and for the post-annealing behavior documented in Section 6.3. The standard annealing temperature of 165 °C falls within the temperature window between the solvent evaporation regime and the onset of complete thiourea decomposition: at this temperature, sufficient sulfur has been liberated from thiourea to initiate Cu_3BiS_3 nucleation and produce a crystalline film as confirmed by GI-XRD (Section 6.2.2),

but the conversion is incomplete and a residual population of Cu and Bi precursor species may persist at grain boundaries. The post-annealing temperature of 270 °C, which lies beyond the second Cu_3BiS_3 phase transition at 191 °C and within the ionic conductor regime, provides a thermodynamic driving force sufficient to complete sulfidation of any remaining precursor species, reduce the residual defect density, and allow copper redistribution within the wittichenite crystal structure, consistent with the improved device performance observed after this treatment [130, 143]. Mechanochemically prepared Cu_3BiS_3 has been reported to remain thermally stable up to approximately 550 K (277 °C) without decomposition or phase loss [143], which provides an upper bound above which annealing risks sulfur volatilization or irreversible structural change. The 270 °C post-annealing temperature used in this work is therefore positioned deliberately within the optimal processing window: above the second polymorph transition to ensure complete conversion and cation redistribution, yet below the reported thermal stability boundary to preserve the wittichenite phase integrity.

6.2.4 TEM and SAED Analysis of Cu_3BiS_3

Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were employed to characterize the local microstructure and crystallinity of the solution-processed Cu_3BiS_3 material at the nanoscale. These measurements complement the ensemble phase analysis obtained by GI-XRD by providing spatially resolved structural information from individual crystallites and confirming the crystalline nature of the material at length scales below those sampled by diffraction. The HRTEM image and the corresponding SAED pattern are shown in Figure 6.5.

The HRTEM image (Figure 6.5, left panel) reveals a periodic lattice fringe pattern that extends coherently across the imaged domain. The regularity and high contrast of the fringes, which are resolved at a scale of a few angstroms consistent with the scale bar of 5 Å, are characteristic of a well-ordered crystalline region in which the atomic columns are favorably oriented with respect to the electron beam direction, producing an amplitude contrast image that reflects the projected crystal potential. The absence of clearly visible amorphous patches, grain boundary interruptions, or regions of incoherent contrast within the imaged area indicates a high degree of intra-grain crystallinity. This observation is consistent with the confirmed $P2_12_12_1$ orthorhombic wittichenite phase assignment and refined lattice parameters established by Rietveld refinement in Section 6.2.2, and with the lattice fringe spacings reported for Cu_3BiS_3 nanocrystals in the literature [144]. Taken together with the AFM results of Section 6.2.5, the HRTEM data establish that the columnar crystallites comprising the film are individually well-

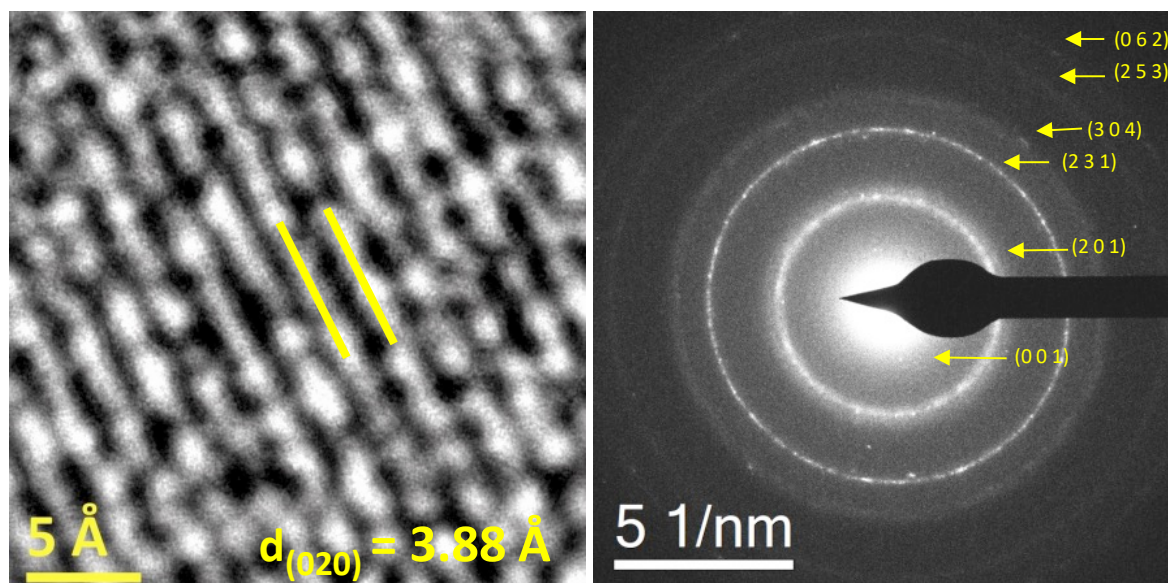


Figure 6.5: HRTEM image and selected-area electron diffraction pattern of solution-processed Cu_3BiS_3 . The HRTEM image (on the left panel) shows coherent lattice fringes and d-spacing corresponding to the (020) plane. The SAED pattern consists of concentric diffraction rings indexed to orthorhombic wittichenite Cu_3BiS_3 ; the corresponding measured and theoretical spacings are listed in Table 6.1.²

crystallized at the atomic scale, even though the macroscopic film morphology is characterized by deep inter-columnar voids.

The SAED pattern (Figure 6.5, right panel) consists of multiple concentric diffraction rings centered on the transmitted beam, with distinct rings annotated by arrows at several radial positions (scale bar: 5 nm^{-1}). The appearance of continuous rings rather than discrete spots is the diffraction signature of a polycrystalline sample in which many crystallites with random orientational distribution contribute to the electron diffraction pattern simultaneously, consistent with the randomly oriented grain microstructure established by AFM [129]. The multiplicity of well-resolved rings at different radii confirms that the crystallites scatter coherently at several distinct interplanar spacings, demonstrating long-range structural order. The observed ring spacings are consistent with the characteristic d-spacings of the Cu_3BiS_3 orthorhombic wittichenite structure, which displays prominent powder-diffraction reflections distributed broadly between $d = 4.5 \text{ Å}$ and $d = 1.5 \text{ Å}$ for the $P2_12_12_1$ space group with the refined lattice parameters $a = 7.67 \text{ Å}$, $b = 10.40 \text{ Å}$, $c = 6.70 \text{ Å}$ [128]. The SAED pattern was indexed using CrysTBox ringGUI. The measured ring positions were converted into reciprocal spacings and compared with theoretical reflections of orthorhombic wittichenite Cu_3BiS_3 , as summarized in Table 6.1. The indexed rings correspond to the (001), (201), (231), (304), (253), and (062) reflections. Except for the innermost low- g ring, the measured and theoretical d -spacings agree closely,

² Measurements were conducted by Dr. M. Peterlechner (LEM, KIT).

Reflection (hkl)	$g_{\text{theor.}} / \text{nm}^{-1}$	$g_{\text{meas.}} / \text{nm}^{-1}$	$d_{\text{theor.}} / \text{nm}$	$d_{\text{meas.}} / \text{nm}$
(001)	0.958	1.069	1.044	0.935
(201)	3.107	3.050	0.322	0.328
(231)	4.966	4.968	0.201	0.201
(304)	5.860	5.848	0.171	0.171
(253)	7.661	7.672	0.131	0.130
(062)	7.981	7.971	0.125	0.125

Table 6.1: SAED ring indexing of solution-processed Cu_3BiS_3 using CrysTBox ringGUI. The measured reciprocal spacings and d -spacings are compared with the theoretical values for the assigned reflections. Here, g denotes the reciprocal lattice spacing of a diffraction ring, defined as $g = 1/d$, where d is the corresponding real-space interplanar spacing. The subscripts “theor.” and “meas.” refer to values calculated from the reference wittichenite structure and values measured from the SAED ring positions, respectively.

supporting the assignment of the polycrystalline diffraction pattern to Cu_3BiS_3 . No prominent additional ring patterns attributable to substantial quantities of bismuthinite (Bi_2S_3) or chalcocite (Cu_2S) are identifiable, consistent with the minor secondary-phase fractions quantified by Rietveld refinement.

The finite breadth of the diffraction rings in the SAED pattern provides a qualitative indication of the coherence length of the contributing crystallites: narrower rings arise from larger coherently diffracting domains, while broader rings indicate smaller crystallites, elevated microstrain, or a combination of both [129]. The ring widths observed in Figure 6.5 are qualitatively consistent with crystallite dimensions on the order of a few to several tens of nanometers, in agreement with the grain cluster dimensions resolved in the AFM topography images of Section 6.2.5. The combined TEM and SAED evidence therefore establishes that the solution-processed Cu_3BiS_3 films consist of well-crystallized individual domains that are randomly oriented relative to the substrate plane. This microstructural picture underpins the photovoltaic analysis of Section 6.3: while the high intra-grain crystallinity reduces bulk Shockley–Read–Hall recombination within individual grains, the large number of grain boundaries between randomly oriented crystallites and the deep inter-columnar void network provide a high-density network of recombination-active interfaces that dominates the minority carrier lifetime at device operating conditions.

6.2.5 Film Topography and Microstructure

At optical-microscope resolution, as shown in Figure 6.6 the films appear smooth and uniform, indicating that the voids are sub-optical in lateral dimensions and therefore undetectable by imaging methods lacking nanometer-scale vertical resolution. AFM measurements in tapping

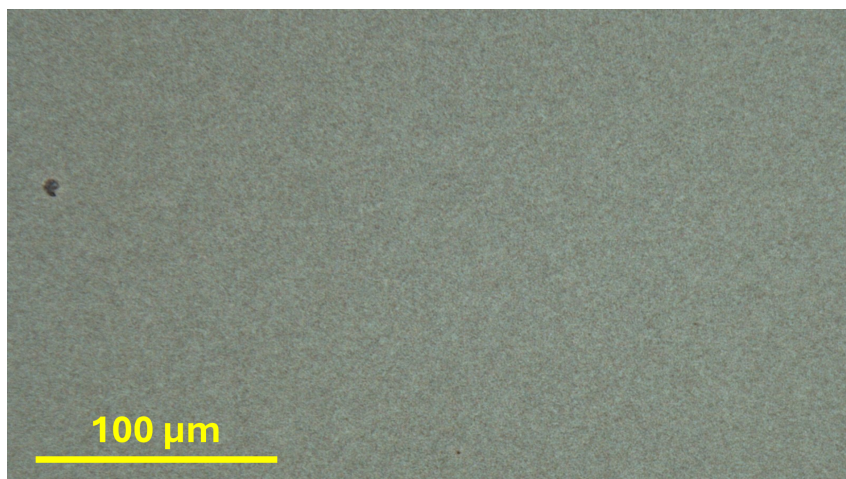


Figure 6.6: Microscope image of a two-layer thin film on ITO fabricated.

mode, as shown in Figure 6.7, reveal a characteristic columnar crystal growth pattern that is independent of processing conditions across a wide range of annealing temperatures and substrate types. Individual crystallites form elongated columns with lateral extents ranging from several tens to a few hundred nanometers, organized into larger grain clusters up to several hundred nanometers in the plane of the film. Between these clusters, voids extend in the depth direction, and $10 \times 10 \mu\text{m}^2$ AFM height distributions show tails that exceed the film thickness measured independently by stylus profilometry. For a two-layer film with a profilometry-determined thickness of approximately 125 nm, the AFM depth histogram (Figure 6.8) shows asymmetric tails at high depths, indicating that the voids penetrate the underlying ITO or glass substrate.

The columnar growth pattern and associated void topology are photovoltaically unfavorable for two independent reasons. First, when an electron transport layer (ETL) or a metal top electrode is deposited on the absorber, material can fill the deep intercolumnar voids, creating direct conductive paths between the bottom and top electrodes. In the device architecture used in this work ($\text{FTO}/\text{TiO}_2/\text{Cu}_3\text{BiS}_3/\text{Au}$), the gold electrode would penetrate the voids during thermal evaporation, thereby forming low-resistance shunt paths and, correspondingly, large reverse-bias leakage currents. Second, grain boundaries at the walls of the voids represent surfaces with disrupted coordination environments. In copper-rich sulfides, unsatisfied copper coordination at grain boundaries creates dangling-bond-like states whose charge-transition levels may lie within the band gap, serving as Shockley–Read–Hall (SRH) recombination centers for photogenerated carriers. The high grain boundary area density implied by the columnar topography, therefore, directly limits the minority carrier diffusion length and, consequently, the achievable short-circuit current density and open-circuit voltage.

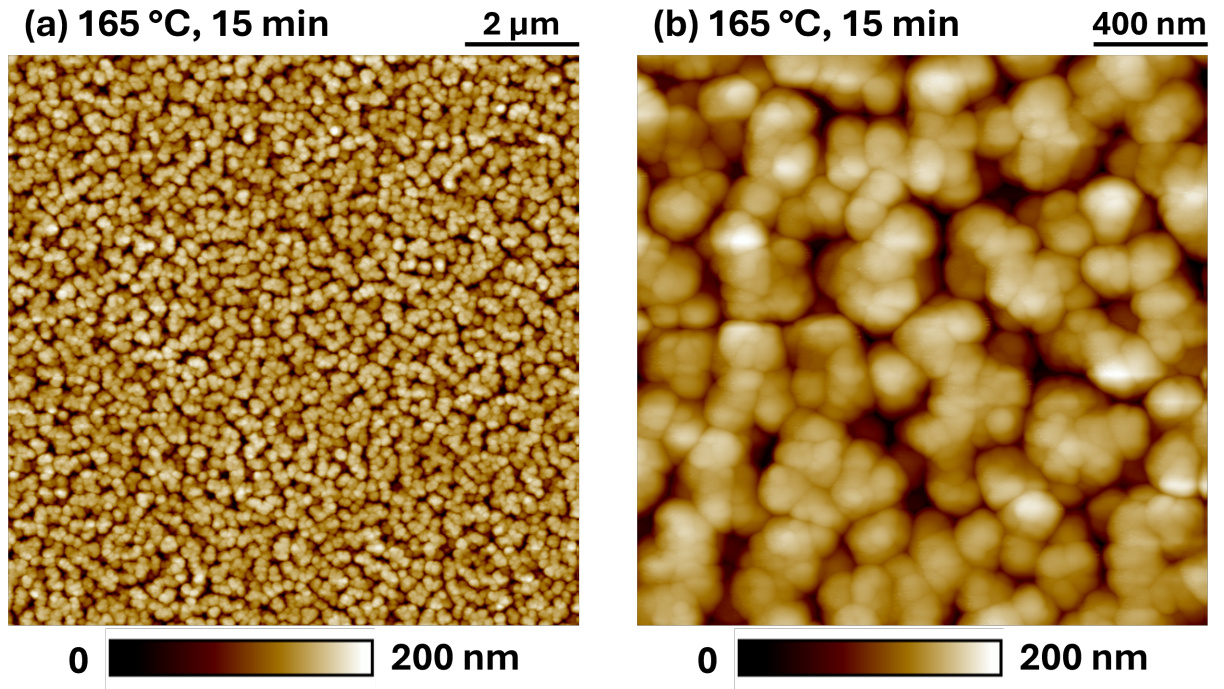


Figure 6.7: AFM topography images of a two-layer Cu_3BiS_3 thin film on ITO measured in tapping mode.

The root-mean-square roughness (R_q) of the films, measured from $10 \times 10\ \mu\text{m}^2$ AFM images, quantifies topographic roughness. For a standard two-layer film annealed at $165\ ^\circ\text{C}$, $R_q = 30.5\ \text{nm}$, and the depth parameter (the interval capturing 95% of measured height values) is $173\ \text{nm}$. Both values are substantially larger than those for a planar, closed thin film of comparable

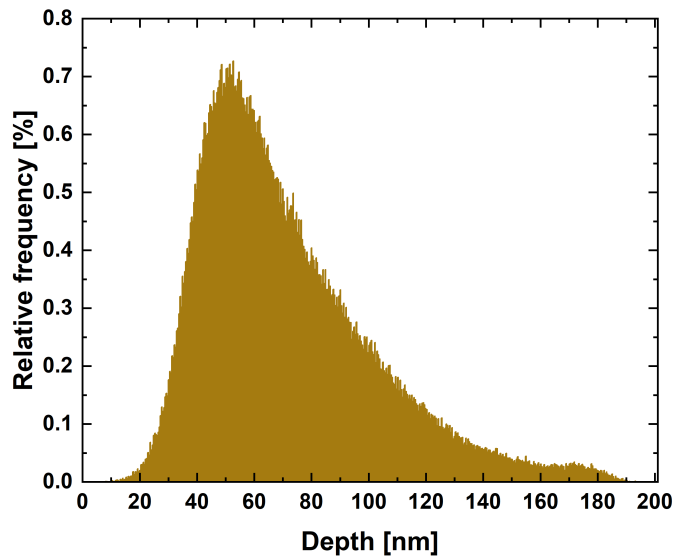


Figure 6.8: Depth histogram of the $10\ \mu\text{m}$ by $10\ \mu\text{m}$ AFM image. [137]

thickness, confirming that the effective surface area at the ETL/absorber interface is significantly greater than the geometric substrate area. Enhanced interfacial area can, in principle, increase charge collection by reducing the carrier transit distance through the absorber, but only if the interface is electronically benign. The combination of high interfacial area and substantial grain-boundary density in solution-processed Cu_3BiS_3 makes interfacial recombination the dominant loss mechanism, as confirmed by the device measurements presented in Section 6.3.

Number of Layers

A simple strategy to reduce void density is the sequential deposition of multiple layers on the same substrate. The effectiveness of this approach depends on whether additional layers fill the existing voids or simply increase the height of already formed crystal islands. To evaluate this, films with three, four, five, and ten layers were fabricated by spin coating on ITO-coated soda-lime glass. Each layer was annealed for 15 min at 165°C . The resulting topographies are shown in Figure 6.9, and the roughness parameters and film thicknesses are summarized in Table 6.2. For comparability, the same height scale was used as for the two-layer reference film discussed in Section 6.2.5.

	2 layers	3 layers	4 layers	5 layers	10 layers
R_{RMS}	30.5 nm	21.5 nm	20.1 nm	19.6 nm	16.3 nm
Depth	173 nm	118 nm	122 nm	120 nm	96 nm
Thickness	125.2 ± 0.4 nm	156.4 ± 0.3 nm	184.2 ± 1.2 nm	217.0 ± 2.7 nm	–

Table 6.2: Roughness parameters and film thicknesses of multilayer Cu_3BiS_3 thin films.

Additional layers progressively fill the voids within the film. A third layer already reduces the roughness substantially relative to the two-layer reference. The voids become shallower, and the density of crystal clusters increases. After the fourth layer, the voids narrow further and the frequency of the larger gaps decreases. Although the roughness parameters change only slightly between four and five layers, the depth distribution becomes smoother and approaches a Voigt-like distribution, as shown in Figure 6.10. In terms of surface topography, the four-layer and five-layer films are therefore nearly indistinguishable. Increasing the number of layers to ten produces a slight additional reduction in roughness. The film thickness increases by approximately 30 nm per deposited layer up to five layers.

These results indicate that the films can be considered effectively closed after four layers within the resolution limits of the AFM measurements. The depth distribution becomes smoother, and additional layers do not substantially reduce the surface roughness. Since the width of the

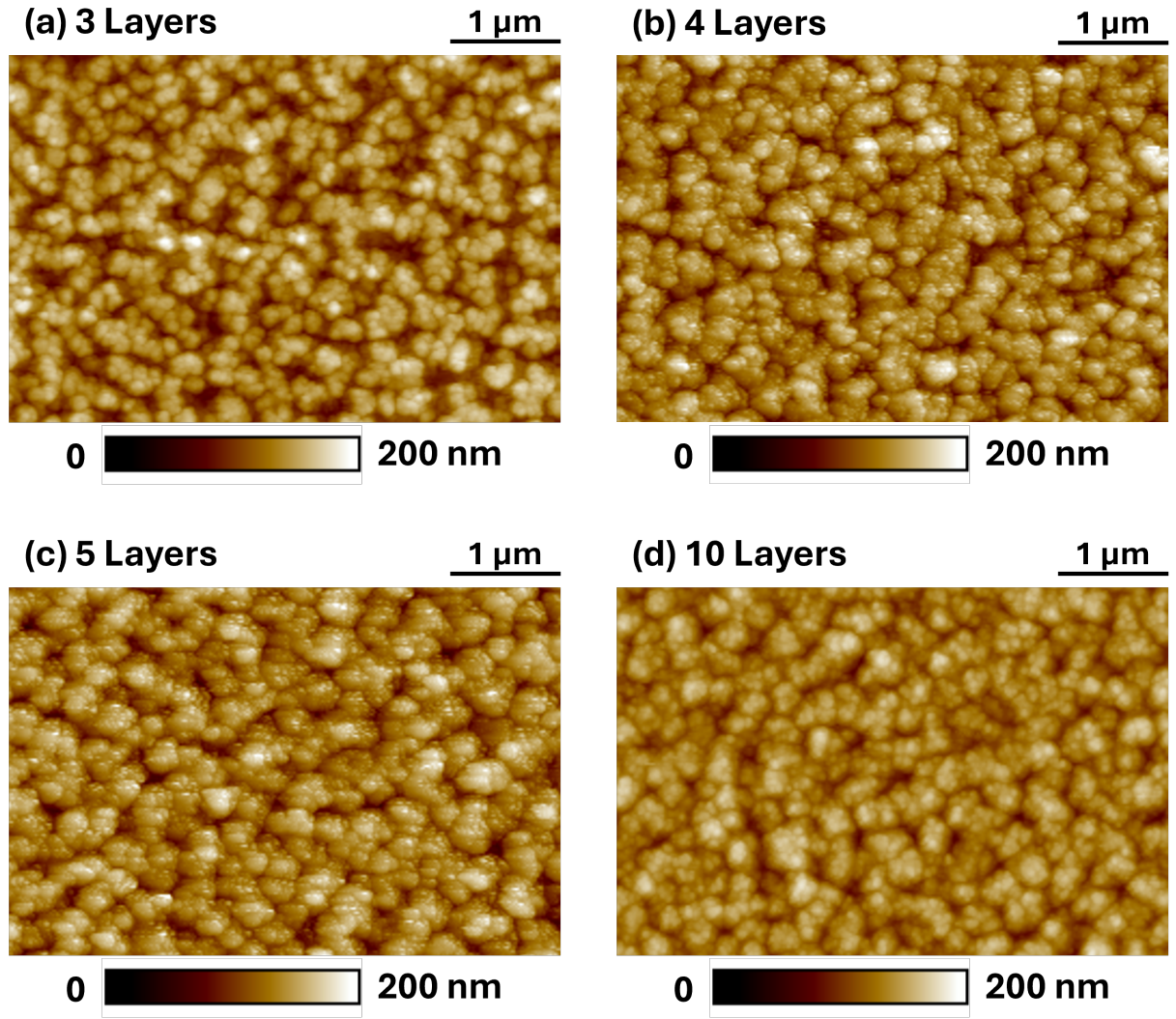


Figure 6.9: AFM topography of multilayer Cu_3BiS_3 thin films. [137]

depth distribution is smaller than the total film thickness, the remaining voids are unlikely to extend to the substrate and are therefore less likely to form direct shunt paths. This conclusion is based on the assumption that the AFM tip can accurately access the narrowest voids. If the tip cannot fully penetrate the voids because of its geometry or insufficient tapping force, a similar apparent stagnation in roughness would be observed. Nevertheless, the multilayer strategy clearly produces denser and more compact films.

Solvent

Solvent engineering is widely used in perovskite solar cells to control crystal growth, reproducibility, film quality, stability, and device performance [145, 146, 147, 148]. For Cu_3BiS_3 ,

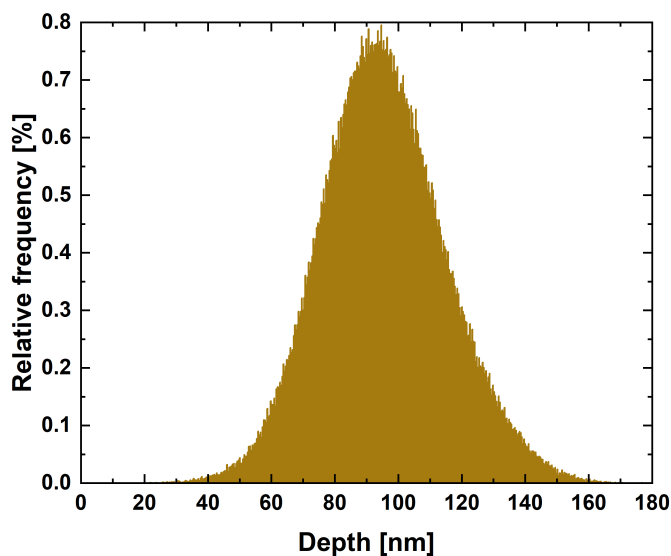


Figure 6.10: Depth histogram of a 10 μm by 10 μm AFM image for a film consisting of five layers. The distribution is smoothened, and there is no longer a tail at higher depth values.

however, the influence of solvent chemistry has not yet been investigated systematically. The most efficient solution-processed Cu_3BiS_3 devices reported to date were fabricated from DMSO-based precursor solutions [123, 149]. Those studies reported closed films and larger crystal grains.

To determine whether DMSO can modify the crystal growth behavior in the present precursor system, thin films were prepared using a DMSO-based solution. Both metal nitrates and thiourea were soluble in DMSO, yielding a precursor solution with a color similar to that of the DMF/DMSO blend. Because the viscosity of DMSO is substantially higher than that of the solvent blend, the spin coater speed was increased to 3000 rpm. The annealing temperature was also adjusted to account for the higher boiling point of DMSO. A temperature of 190 °C for 15 min was selected to slightly exceed the boiling point of DMSO (189 °C). Two-layer and five-layer films were fabricated under these conditions. For comparison, additional two-layer and five-layer films were annealed at 270 °C for two minutes, following conditions reported as favorable for DMSO-based precursor systems.

The topographies of the DMSO-based films are shown in Figure 6.11. At 190 °C, the films exhibit the same island-like growth behavior as the films prepared from the DMF/DMSO blend. As in the previous experiments, additional deposited layers yield more compact films with densely packed crystal clusters. The two-layer films annealed at 270 °C show behavior similar to that observed for high-temperature annealing in the blended-solvent system. The films become rougher, and the crystal clusters grow more prominently. The clusters in the DMSO-based films are smaller than those in the blend-based multilayer films.

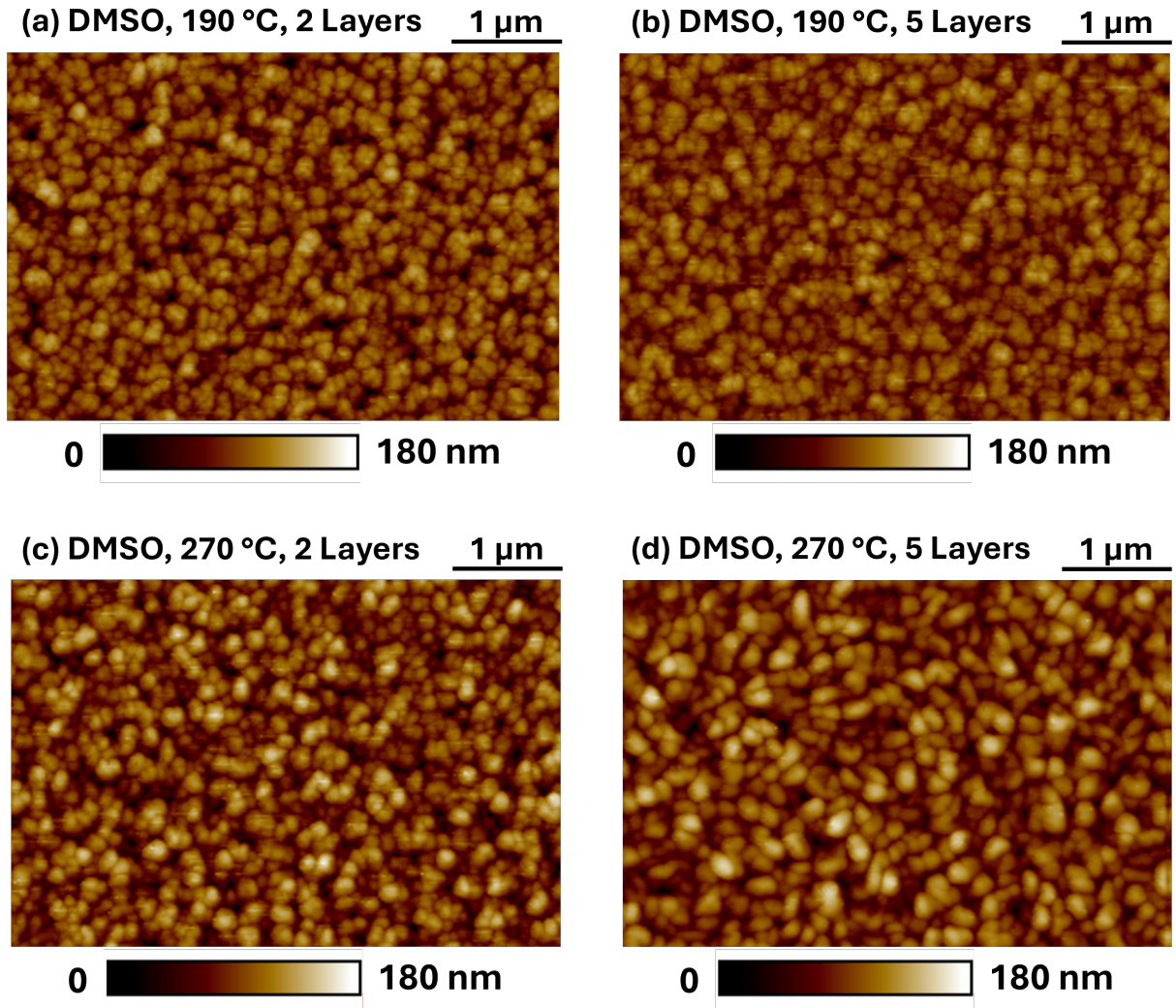


Figure 6.11: AFM topography of Cu_3BiS_3 thin films fabricated from a DMSO-based precursor solution.

The five-layer film annealed at 270°C shows a noticeable change in grain shape and size. The clusters develop into more elongated individual grains, which may result from the longer cumulative thermal exposure at 270°C , since each deposited layer was annealed individually for two minutes. Based on this experiment alone, it cannot be determined whether this behavior is caused primarily by the higher temperature or by the solvent environment. Although the five-layer high-temperature films are promising with respect to grain enlargement, all DMSO-based samples show a high density of pinholes. From the second layer onward, the macroscopic film quality deteriorates visibly. This may be related to the high viscosity of DMSO, which can produce thicker wet films even at elevated spin speeds. In addition, insufficient wetting of the already deposited Cu_3BiS_3 layer may contribute to the deterioration of film quality.

Although this route was not pursued further in the present work, solvent engineering remains a promising strategy for controlling crystal growth and improving Cu_3BiS_3 -based device performance.

Solution Concentration

The precursor concentration can influence nucleation and growth during liquid-phase film formation. Crystal growth begins when supersaturation is reached [150], and the concentration of the precursor solution is one of the parameters that determines how quickly this condition is achieved. If the initial concentration is too high, rapid nucleation can produce many small crystallites that grow on top of one another rather than forming a compact film [151]. To test whether the island-like morphology originates from an excessively high precursor concentration, films were fabricated from diluted solutions.

A solution with the standard concentration (3.66 M) was prepared first and then diluted with the DMF/DMSO 4 : 1 blend to solution:solvent ratios of 1 : 0.33, 1 : 0.66, and 1 : 1, yielding total precursor concentrations of 2.75 M, 2.20 M, and 1.83 M, respectively. For each dilution, five-layer and ten-layer films were deposited on ITO-coated soda-lime glass. All layers were annealed at 165 °C for 15 min. The topographies of the five-layer and ten-layer films are shown in Figure 6.12. The corresponding roughness parameters are given in Table 6.3, and the film thicknesses of the five-layer samples are listed in Table 6.4. The two-layer variants were not fully closed and are therefore not discussed in detail.

Solvent Ratio	Number of layers	R_{RMS}	Depth
1:0.33	5	13.4 nm	80 nm
1:0.33	10	12.2 nm	72 nm
1:0.66	5	8.9 nm	58 nm
1:0.66	10	9.4 nm	60 nm
1:1	5	7.7 nm	54 nm
1:1	10	7.2 nm	48 nm

Table 6.3: Roughness parameters of Cu_3BiS_3 thin films fabricated from precursor solutions with different dilution ratios.

The precursor concentration has a pronounced influence on film thickness, crystallite size, and surface roughness. Films prepared from the 1 : 0.33 dilution still resemble those prepared from the standard solution, but the roughness and film thickness are reduced. With further dilution, the grain size decreases substantially. Closed films are still not obtained directly, but the layers

	1:0.33, 5Layers	1:0.66, 5Layers	1:1, 5Layers
Thickness	137.1 ± 1.1 nm	96.4 ± 2.4 nm	78.9 ± 1.2 nm

Table 6.4: Film thicknesses of five-layer Cu_3BiS_3 films fabricated from precursor solutions with different dilution ratios, measured by stylus profilometry.

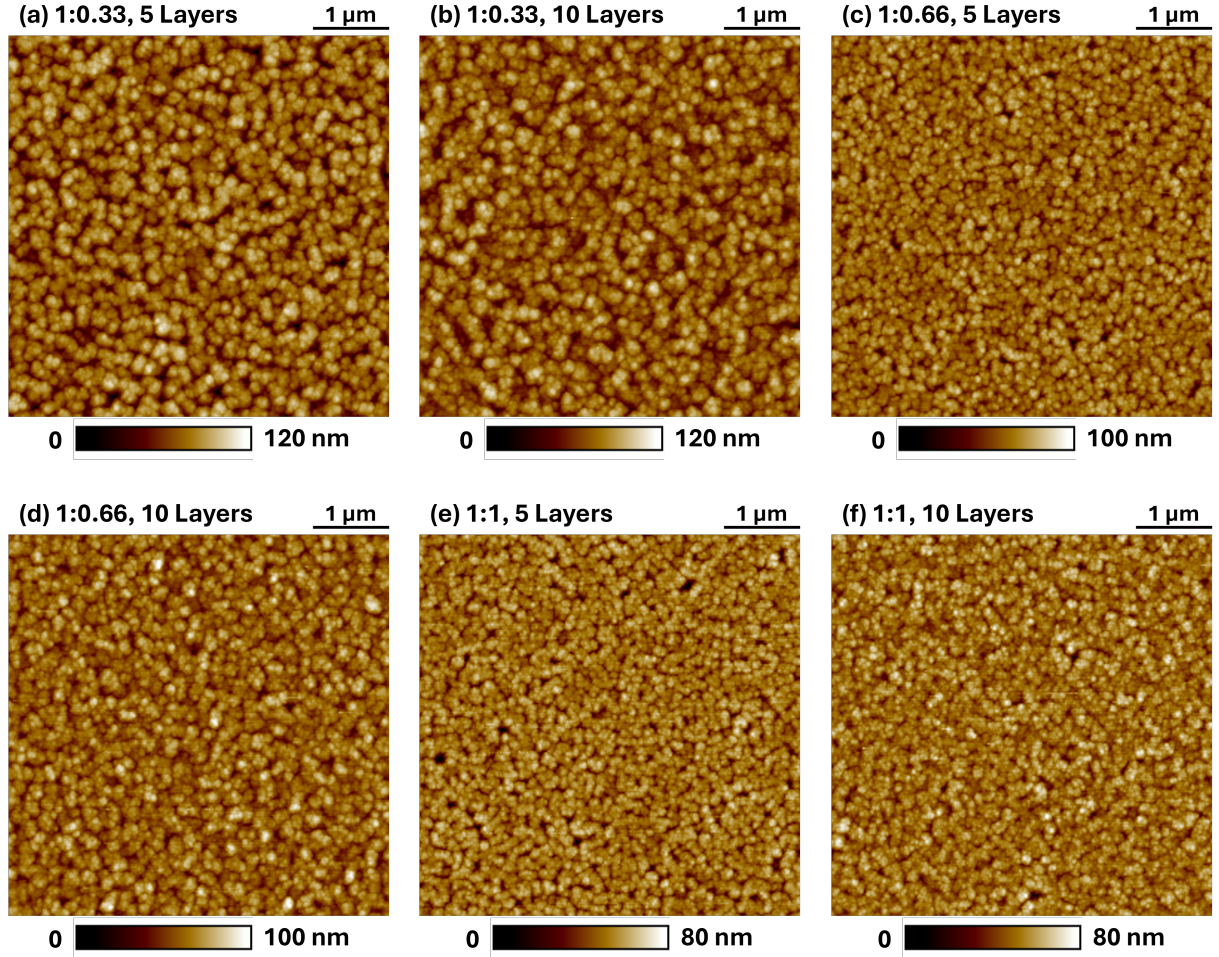


Figure 6.12: AFM topography of Cu_3BiS_3 thin films fabricated from diluted precursor solutions.

become increasingly compact as the number of deposited layers increases, and the voids become smaller.

The depth distributions of all five-layer films retain a tail toward larger depths, indicating that the films may still not be fully closed after five layers. More than five layers are therefore required to obtain completely compact films at these dilution levels. At the same time, stronger dilution produces thinner layers, meaning that a larger number of layers is required to obtain absorber films with sufficient optical density. Nevertheless, dilution is a promising route for producing compact films with low surface roughness. A combined deposition strategy may be particularly

useful, for example by first depositing compact smooth layers from diluted solutions and then adding thicker layers from more concentrated solutions, or by using diluted solutions to fill voids in rougher high-concentration films.

The thicknesses of the ten-layer films could not be measured because the films could no longer be scratched cleanly. Scratching with a metal cannula left only shallow marks without exposing the substrate. This suggests that a different or mechanically modified material state may have formed. Possible explanations include the longer total annealing time of the ten-layer samples, aging of the precursor solution, or chemical interaction with the substrate. Since the known ternary and binary sulfide phases, as well as metallic copper and bismuth, are comparatively soft, a purely phase-based explanation is not sufficient. Processes such as ion migration, oxidation, or substrate interaction could increase the apparent hardness. Further investigation, particularly by XRD, would be required to clarify the origin of this behavior.

6.2.6 Photoluminescence and Defect Landscape

Room-temperature photoluminescence measurements of Cu_3BiS_3 thin films at the nominal 3:1 stoichiometry yield only a very weak, noisy signal that cannot be unambiguously attributed to radiative recombination within the absorber. This observation is consistent with the high defect density and large grain boundary area density implied by the AFM topography: at room temperature, thermally activated non-radiative SRH recombination via deep and shallow defect states efficiently competes with and outcompetes radiative recombination, thereby suppressing PL emission below the apparatus's detection threshold. Low-temperature measurements at 3.2 K and 100 K, conducted on the reference 3:1 stoichiometry sample, reveal distinct emission features that provide insight into the defect landscape as displayed in Figure 6.13.

At 3.2 K, two overlapping emission peaks are resolved: one near 1.20 μm and a second near 1.43 μm . Both emission features lie well below the photon energy of the semiconductor's absorption onset, indicating sub-band-gap radiative recombination rather than free-exciton or band-to-band emission. Upon warming to 100 K, the 1.20 μm peak vanishes entirely, while the 1.43 μm emission persists, albeit with a sixfold reduction in integrated intensity and a discernible redshift relative to the 3.2 K position.

The distinct thermal quenching behavior of the two emission features indicates different recombination mechanisms. The complete disappearance of the 1.20 μm peak at 100 K is the spectroscopic signature of bound exciton (BE) emission: below the exciton ionization threshold, free excitons are captured by defect sites and recombine radiatively from bound states at lower energy than the free exciton. As the temperature rises, thermal energy kT becomes comparable to the exciton binding energy, dissociating the bound complexes and transferring population to

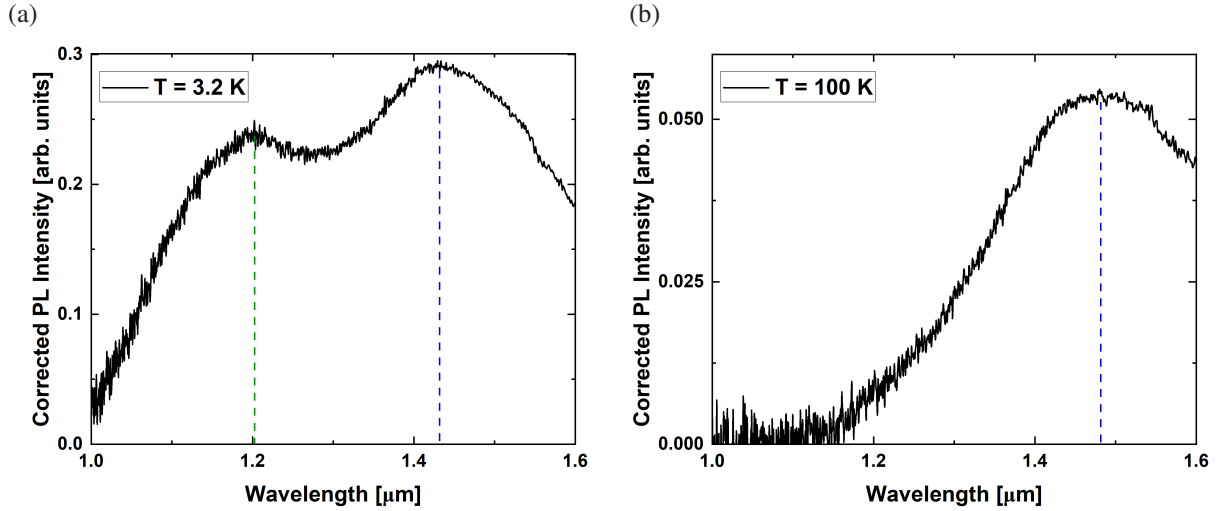


Figure 6.13: Photoluminescence spectra of Cu_3BiS_3 thin films measured at (a) 3.2 K and (b) 100 K.

free-carrier channels where non-radiative recombination dominates. In crystals with significant defect density, bound exciton quenching temperatures typically fall within 50–150 K, consistent with the behavior observed here [133]. By contrast, the persistence of the $1.43 \mu\text{m}$ emission at 100 K is characteristic of donor–acceptor pair (DAP) recombination, in which an electron at a donor site and a hole at an acceptor site recombine by tunneling. DAP emission persists to higher temperatures than BE emission because the ionization energy of the participating defects determines the quenching temperature rather than a small exciton binding energy [152].

These low-temperature PL results match with those reported by Yakushev et al. for Cu_3BiS_3 thin films, although those authors attributed both peaks to DAP recombination, based on the simultaneous quenching of both features with increasing temperature in their samples [133]. The distinction between the two peaks observed here, one clearly bound-excitonic and the other donor–acceptor, implies the simultaneous presence of at least two distinct types of radiatively active defects: a shallow state acting as the exciton capture center for the $1.20 \mu\text{m}$ emission, and a deeper DAP pair responsible for the $1.43 \mu\text{m}$ emission. The identity of the defects responsible for the PL features cannot be determined from the present PL spectra alone. Previous low-temperature PL studies of Cu_3BiS_3 reported broad emission bands that were preliminarily assigned to donor–acceptor-pair-type recombination involving deep donor and deep acceptor states, together with a shallower defect level with an activation energy of about 40 meV [133]. However, these studies did not identify the species of microscopic defects. Therefore, the PL bands observed here are assigned more cautiously to defect-related recombination in Cu_3BiS_3 , rather than to specific defects such as V_{Cu}' , $V_{\text{S}}^{\bullet\bullet}$, or $\text{Bi}_{\text{Cu}}^{\bullet\bullet}$. Defect-resolved calculations or com-

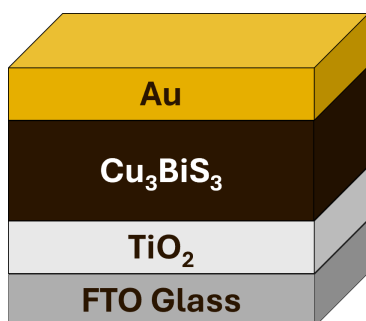
plementary measurements, such as temperature- and excitation-dependent PL combined with electrical characterization, would be required to identify the responsible native defects.

6.3 Solar Cell Performance

6.3.1 Device Architecture and As-Fabricated Performance

Solar cells were fabricated using the FTO/ TiO_2 / Cu_3BiS_3 /Au architecture (Figure 6.14b), in which a solution-processed anatase TiO_2 electron-transport layer is sandwiched between the fluorine-doped tin oxide (FTO) bottom electrode and the Cu_3BiS_3 absorber, and a gold top electrode serves as the hole-collecting contact. This architecture was selected for three reasons. First, it is architecturally simple and omits CdS as a buffer layer, directly testing whether photovoltaic function can be realized in a fully non-toxic device stack. Second, the band alignment at the TiO_2 / Cu_3BiS_3 interface is expected to support charge separation, since the conduction-band minimum of anatase TiO_2 (-4.0 eV below vacuum) lies below the electron affinity of Cu_3BiS_3 and provides a driving force for electron transfer toward the FTO electrode [30, 153, 154]. Third, the work function of gold (approximately 5.1 eV) is close to the ionization potential of Cu_3BiS_3 films measured by PESA at 4.99 eV, as shown in Figure 6.14b, providing the energetic basis for an ohmic or near-ohmic back contact with the p-type absorber.

(a) Solar cell architecture.



(b) PESA yield spectrum with linear fit of the photoemission onset.

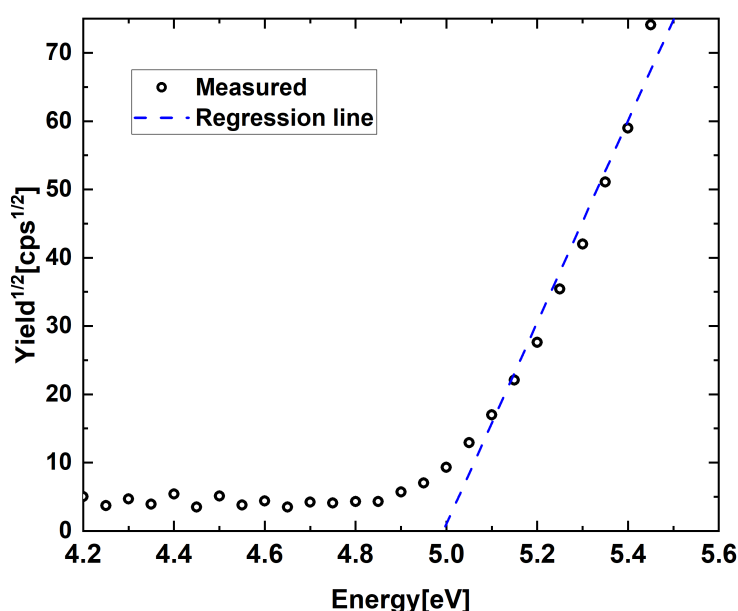


Figure 6.14: Device architecture and photoelectron spectroscopy in air measurement of the Cu_3BiS_3 thin film. The PESA yield spectrum gives an ionization potential of 4.99 eV from the linear fit of the photoemission onset.

As-fabricated devices, without any post-fabrication thermal treatment, exhibit extremely poor photovoltaic performance. Table 6.5 summarizes the J–V parameters extracted from these devices. The fill factor and PCE could not be determined by the measurement software because the J–V curves lacked a definable maximum power point, a consequence of the very large reverse-bias leakage current. The J–V curves exhibit diode-like rectification, confirming the presence of a built-in electric field at the $\text{TiO}_2/\text{Cu}_3\text{BiS}_3$ junction, but the shunt resistance is too low to sustain a meaningful open-circuit voltage. A small photocurrent that exceeds the dark current can be identified near zero voltage, but $J_{\text{SC}} = 0.34 \pm 0.04 \text{ mA cm}^{-2}$ and $V_{\text{OC}} = 3.72 \pm 2.15 \text{ mV}$ are negligible for photovoltaic purposes.

Variation	J_{SC} (mA cm^{-2})	V_{OC} (mV)	FF (%)	PCE (%)
As-fabricated (5L, standard)	0.34 ± 0.04	3.72 ± 2.15	N/D	N/D
Alternating 1:0 + 1:1 solution layers	0.34 ± 0.04	3.72 ± 2.15	N/D	N/D
8L 1:1 + 2L 1:0 solution layers	0.12 ± 0.04	1.44 ± 0.36	N/D	N/D
10L 1:0.33 diluted solution	0.23 ± 0.07	1.38 ± 1.19	N/D	N/D
5L standard + MoO_x/Ag electrode	0.038 ± 0.01	0.48 ± 0.23	N/D	N/D
Post-annealed at 270 °C (average)	1.64 ± 0.20	28 ± 12.3	23.2 ± 3.9	0.012 ± 0.006
Post-annealed at 270 °C (champion)	1.9	57	27	0.03

Table 6.5: Solar cell parameters for $\text{FTO}/\text{TiO}_2/\text{Cu}_3\text{BiS}_3/\text{Au}$ devices in different configurations. Values are means $\pm$ standard deviations across all pixels of each batch. PCE and FF were not determinable (N/D) for as-fabricated devices due to insufficient shunt resistance

Several modifications to the absorber layer and device architecture were evaluated to determine whether film coverage was the primary cause of poor performance. As shown in Figure 6.15a, absorber films prepared from diluted precursor solutions (1:0.33 and 1:1 dilution ratios), which produce more compact morphologies with reduced pinhole density as described in Section ??, showed no improvement in J–V performance relative to standard films. Devices fabricated with a ten-layer absorber prepared from alternating undiluted and 1:1-diluted solution layers performed equivalently to the as-fabricated baseline. Replacing the gold top electrode with a 10 nm $\text{MoO}_x/100 \text{ nm Ag}$ bilayer, which provides a larger work-function difference relative to the absorber to improve contact selectivity, resulted in decreased performance, with J_{SC} and V_{OC} an order of magnitude below the baseline. The large reverse-bias leakage current indicates that MoO_x -terminated devices are dominated by shunting through pinholes: where MoO_x and TiO_2 make direct contact through a pinhole, the resulting $\text{MoO}_x/\text{TiO}_2$ junction forms a rectifying

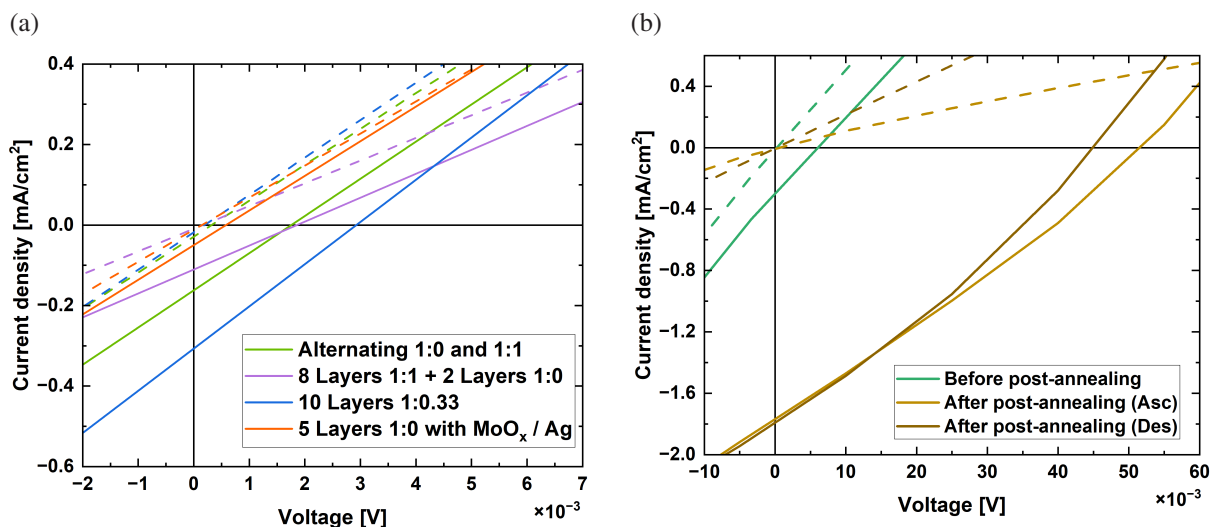


Figure 6.15: J - V curves of Cu_3BiS_3 solar cells. (a) The panels show devices with variations in the absorber layer or device architecture, (b) along with a representative solar cell before and after post-annealing.

contact in the opposite polarity to the intended device, eliminating any net photovoltaic function. The universally poor performance of the as-fabricated devices across all architectural variations confirms that film compactness is not likely the primary limiting factor and instead points to the absorber microstructure or the $\text{TiO}_2/\text{Cu}_3\text{BiS}_3$ interface as the dominant source of loss.

6.3.2 Effect of Post-Annealing on Device Performance

In order to investigate how Pnma-orthorhombic Cu_3BiS_3 (phase stability range: $191^\circ\text{C} - 290^\circ\text{C}$) behaves under illumination, a post-fabrication annealing treatment at 270°C , applied after gold electrode deposition. It does produce a dramatic improvement in device performance. The treatment involved slow heating to 270°C at a rate determined by the hotplate response, a 15-minute dwell at the target temperature, and slow cooling to room temperature while the substrates remained on the cooling hotplate. The J - V curves of a representative $\text{FTO}/\text{TiO}_2/\text{Cu}_3\text{BiS}_3/\text{Au}$ device before and after the post-annealing step are shown in Figure 6.15b. Both J_{SC} and V_{OC} increase by approximately one order of magnitude after the treatment, yielding an analyzable fill factor of $23.2 \pm 3.9\%$. The batch-averaged best device achieves a PCE of 0.03% .

Despite the improvement, the post-annealed devices still remain far from the performance levels projected for the material's 1.4 eV band gap. The very low V_{OC} (average: $28 \pm 12.3\text{ mV}$, compared with a radiative-limit value near 1.15 V for a 1.4 eV gap absorber) represents a voltage deficit exceeding 1.1 V . This large deficit suggests severe non-radiative recombination and/or shunting, most likely associated with defect states, imperfect interfaces, or incomplete film cov-

erage. The fill factor of 23.2% is well below the threshold associated with standard pn-junction behavior, reflecting large shunt conductance that is consistent with residual pinholes and the enhanced diffusion of gold through grain boundaries during the high-temperature post-annealing step. A pronounced hysteresis is present between ascending and descending sweep directions. The hysteresis does not affect the short-circuit current, which is identical in both sweep directions, confirming that the photocurrent is genuinely photogenerated and not a capacitive or ionic contribution. Ion migration within the Cu_3BiS_3 absorber layer during voltage sweep, facilitated by the high cation mobility of copper-rich sulfides above 135 °C, which is the ionic conductivity onset for Cu_3BiS_3 [130], is the most likely origin of the hysteresis.

6.3.3 Absorption Response and External Quantum Efficiency

Absorption spectra measured before and after post-annealing on five-layer Cu_3BiS_3 films on both FTO/ TiO_2 and glass substrates reveal a reproducible, substrate-independent change, which is shown in Figure 6.16a. After annealing, absorption decreases across the 400–700 nm range and in the infrared beyond the band edge, while the absorption onset energy changes only minimally. The reduction in below-gap absorption after thermal treatment is consistent with a decrease in the sub-gap defect state density within the Cu_3BiS_3 absorber: defect states with charge-transition levels within the gap contribute directly to below-gap optical transitions, and their partial passivation or annihilation during annealing reduces this contribution. Alternatively, the reduction could reflect the removal of a minor bismuth-rich secondary phase with a narrower gap, though the absence of a sharp spectral feature at a specific sub-gap energy makes this interpretation less likely. The fact that both FTO/ TiO_2 and glass substrates show the same behavior confirms that the change is intrinsic to the Cu_3BiS_3 layer and not a consequence of altered interfacial chemistry with TiO_2 .

External quantum efficiency (EQE) measurements on post-annealed devices unambiguously attribute the photocurrent to the Cu_3BiS_3 absorber. The EQE spectrum of a representative post-annealed FTO/ TiO_2 / Cu_3BiS_3 /Au device is shown in Figure 6.16b alongside the absorbance spectrum of a five-layer Cu_3BiS_3 film on TiO_2 . Because the TiO_2 electron transport layer has a band gap of approximately 3.2 eV, it does not contribute photocurrent at wavelengths longer than 390 nm. The measured EQE extends well beyond 400 nm, up to the absorption edge of Cu_3BiS_3 , confirming that the photocurrent originates from the Cu_3BiS_3 absorber layer and not from TiO_2 . This measurement resolves the primary interpretational ambiguity that compromises a significant portion of the prior Cu_3BiS_3 device literature, in which EQE spectra were not provided and the possible contribution of a photoactive CdS buffer layer to the measured photocurrent could not be excluded.

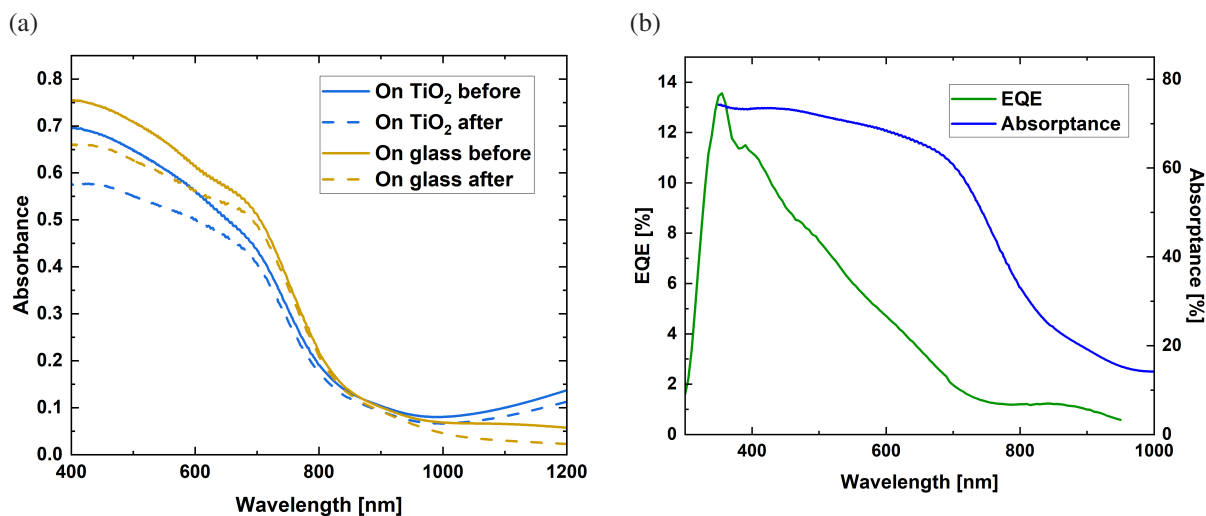


Figure 6.16: Optical and photoresponse characteristics after post-annealing. (a) Absorption spectra before and after the post-annealing step for samples on TiO_2 and glass. (b) EQE of a solar cell and absorptance of a five-layer Cu_3BiS_3 thin film on TiO_2 after post-annealing at 270°C .

The shape of the EQE spectrum provides additional information on collection efficiency within the absorber. Above the Cu_3BiS_3 absorption edge, the EQE does not follow the absorptance spectrum but instead decreases approximately linearly with increasing wavelength (decreasing photon energy). This behavior, in which higher-energy, more strongly absorbed photons produce relatively fewer collected carriers than lower-energy photons with greater penetration depth, is consistent with two scenarios. In the first scenario, carriers generated near the absorber surface by high-energy photons experience strong surface recombination at the $\text{Cu}_3\text{BiS}_3/\text{Au}$ interface, while lower-energy carriers generated deeper in the film are collected more efficiently by the $\text{TiO}_2/\text{Cu}_3\text{BiS}_3$ junction field. In the second scenario, the high defect density in the bulk of the as-annealed film introduces a spatially non-uniform collection probability, with regions near the TiO_2 interface exhibiting longer effective diffusion lengths than the absorber bulk. Analogous EQE shapes for CIGS solar cells with elevated bulk defect densities have been reproduced by numerical device simulation, supporting the second interpretation [155]. A combination of time-resolved photoluminescence to quantify the carrier lifetime and drift-diffusion modeling would be needed to definitively distinguish these mechanisms.

6.3.4 Role of Defects in Recombination and Transport

The evolution of Cu_3BiS_3 solar-cell performance, from negligible photovoltaic response in as-fabricated devices to measurable response after high-temperature post-annealing, suggests that several loss pathways are affected by the post-treatment. These may include bulk recombi-

nation through gap states, recombination at grain boundaries or void-rich regions, and shunt pathways associated with incomplete absorber coverage or pinholes. These loss mechanisms are consistent with the microstructural features observed by AFM and GI-XRD, although further electrical and spectroscopic measurements would be required to distinguish their individual contributions.

The low-temperature PL results in Section 6.2.6 establish the simultaneous presence of donor and acceptor defects in the Cu_3BiS_3 films. SRH recombination rate through a defect state is maximized when the state energy lies near the midgap, and the trap density N_t is large. The sub-bandgap optical absorption observed in the 400–700 nm spectral range indicates that absorption extends below the main optical onset. This behavior is consistent with band-edge tailing and/or defect-related sub-gap absorption, which are commonly observed in polycrystalline semiconductors with structural disorder. However, absorption data alone do not allow the microscopic origin of these states to be assigned. Therefore, the feature is discussed here as evidence of optical disorder rather than as proof of specific defect species or grain-boundary-related defect potentials [126, 133]. The voltage deficit of more than 1.1 V in the post-annealed devices indicates that non-radiative recombination is dominant through these gap states.

Compared with a dense film composed of laterally compact grains, the columnar morphology of the Cu_3BiS_3 films introduces a larger internal interface area through intercolumnar voids. Such grain-boundary and void-wall regions may contribute to recombination losses, as electronically active grain boundaries have been reported in Cu_3BiS_3 and modeled in polycrystalline thin-film absorbers more generally [154, 156]. If the voids or pinholes remain connected through the absorber layer, they may also provide leakage pathways between charge-selective contacts. In copper-rich sulfide semiconductors, dangling bonds at grain boundaries involve Cu, Bi, and S atoms in configurations that differ from the bulk tetrahedral and pyramidal coordination environments. These configurations are expected to produce electronic states deep within the band gap, based on the charge-state arguments developed in Section 6.1.3. The improvement in J_{SC} by a factor of approximately five and in V_{OC} by approximately eight upon post-annealing at 270 °C can be attributed to a partial reduction of this grain boundary state density. Shunt conduction through pinholes is the third loss mechanism and is directly responsible for the negligible fill factor and the large reverse-bias leakage of the as-fabricated devices.

7 Conclusions and Outlook

This thesis has investigated three copper-based, lead-free absorber materials, copper antimony iodide β -CuI : Sb, also formulated as Cu_3SbI_6 , copper bismuth iodide ($\text{Cu}_{3x}\text{Bi}_{1-x}\text{I}_3$, CBI), and copper bismuth sulfide (Cu_3BiS_3 , wittichenite), with the aim of establishing a consistent structure–property framework for their synthesis, structural identity, and photovoltaic behavior. Rather than treating each absorber in isolation, the experimental program was designed to reveal the extent to which a single unifying principle, the engineering of native defect populations and host-lattice microstructure, governs photovoltaic outcomes across compositionally and structurally distinct material families.

7.1 Unifying Design Principles: Defect-Governed Optoelectronics

Taken together, the three experimental chapters lead to four main conclusions.

Structural identity precedes all property interpretation. In both the Cu–Sb–I and Cu–Bi–I systems, the published literature had assigned structural identities, caswellsilverite, rudorffite, and various double-salt designations, that are demonstrably incorrect at the level of diffraction and electron microscopy. These misassignments are not merely taxonomic: they carry implicit assumptions about coordination geometry, valence electron count, and defect formation energetics that propagate into erroneous design conclusions. The work presented here demonstrates that rigorous structural determination by combined powder diffraction, Rietveld refinement, and TEM/SAED must precede any interpretation of optical or electronic properties. This principle is sufficiently general that it should be treated as a prerequisite step in any program investigating new ternary or quaternary absorber phases.

Structural identity is necessary for assigning optical properties. The measured bandgaps of the iodide absorbers must be assigned to the structures that actually form, rather than to structure families inferred from nominal composition. The 2.32 eV bandgap of β -CuI : Sb belongs to a CuI-derived, stacking-disordered structure with Sb incorporation, whereas the 1.66 eV bandgap of CBI belongs to a BiI_3 -derived framework containing interstitial Cu. These values should therefore not be interpreted as properties of ideal Caswellsilverite or Rudorffite phases. The main conclusion is that experimental structure determination is required before optical properties can be meaningfully assigned to a material phase.

Low-temperature solution processing can stabilize non-equilibrium structures and microstructures. None of the halide absorbers behaves as a simple equilibrium bulk phase under the processing conditions used here. The stacking-disordered CuI-derived structure in β -CuI : Sb, and the partially occupied interstitial Cu sites in CBI reflect the influence of low-temperature film formation. These features are not necessarily disadvantages, but they show that processing history, solvent removal, and annealing temperature must be treated as central variables in phase formation and device behavior.

Native defects and microstructure are central variables in device performance. Across the three absorber systems, the major performance limitations are linked to disorder-sensitive loss pathways: metastability in β -CuI : Sb, voltage deficit and phase mixture in CBI, and recombination or leakage losses in Cu_3BiS_3 . These observations have been logically attributed to the influence of native defects, phase disorder, grain boundaries, and incomplete film coverage. However, the microscopic identity of every defect cannot be determined from the present measurements alone. The results therefore support a cautious design principle: precursor stoichiometry, annealing conditions, phase purity, and interface selection must be controlled together in order to improve photovoltaic performance.

An important cross-cutting observation is that the substitution from iodide to sulfide anion frameworks dramatically improves ambient phase stability while preserving the defining characteristic of copper-cation mobility. The iodide systems are susceptible to halide-volatility-driven degradation above modest temperatures, whereas wittichenite remains structurally intact under conditions compatible with standard photovoltaic encapsulation. This stability advantage motivates a progressive compositional strategy in which structural and defect-engineering lessons learned from the more tractable iodide systems are transferred to the less analytically accessible but more robust sulfide and mixed-anion frameworks.

7.2 Outlook and Future Directions

The findings of this thesis suggest several future directions that address unresolved questions in phase control, film formation, defect passivation, and device integration.

7.2.1 Phase-Pure CBI through Controlled Precursor Chemistry

The most immediate challenge in the Cu–Bi–I system is to suppress the co-formation of α -CuI while retaining the interstitially modified BiI_3 -derived CBI phase. The present results indicate that CBI forms only within a narrow processing window: too little available Cu limits interstitial incorporation into the BiI_3 -derived framework, whereas excess Cu promotes CuI precipitation. A systematic study should therefore vary the CuI: BiI_3 precursor ratio, solvent polarity, and

annealing temperature while monitoring the resulting phase fractions by PXRD/GI-XRD and Rietveld refinement. This would allow the phase boundary between CBI, BiI₃-rich compositions, and CuI-rich mixtures to be mapped more precisely. Complementary defect calculations could clarify which Cu interstitial sites are energetically favored under different Fermi-level and chemical-potential conditions. Together, such experimental and computational work would test whether the 1.66 eV bandgap and carrier behavior are intrinsic to the CBI framework or are influenced by the mixed-phase microstructure of the present films.

7.2.2 Tandem Integration of β -CuI:Sb

The 2.32 eV direct bandgap and 1.02% single-junction PCE of β -CuI : Sb motivate its evaluation as a wide-gap top cell in a two-terminal tandem architecture, where the efficiency ceiling is set by current-matching constraints rather than by the Shockley–Queisser limit of the individual sub-cells. The principal challenge for tandem integration is the thermal fragility of the polytypic structure, which undergoes irreversible transformation above approximately 100°C: this temperature ceiling is incompatible with the deposition conditions of most established bottom-cell absorbers, which typically require annealing above 150°C. Two complementary approaches merit investigation. First, low-temperature bottom-cell candidates, including CBI itself, once phase-pure, and bismuth-based double perovskites, could in principle be co-deposited with β -CuI : Sb without exceeding the stability window. Second, the thermal fragility of β -CuI : Sb is directly linked to the low stacking-fault energy of the CuI polytypes. Thus, aliovalent doping strategies that increase the activation energy for stacking-fault migration could, in principle, extend the operational temperature ceiling without eliminating the beneficial interstitial chemistry. Any such modification would need to be validated by in situ high-temperature PXRD to confirm that the polytypic disorder is retained rather than annealed out.

7.2.3 Morphological Densification of Cu₃BiS₃ Films

In the Cu₃BiS₃ system, the columnar void morphology identified by AFM is the single most impactful performance-limiting factor: it simultaneously enables shunt conduction, increases grain-boundary recombination area, and degrades contact geometry. Chapter 6 demonstrated that progressive multilayer deposition closes voids and reduces roughness, but at the cost of increased total film thickness, thereby lengthening carrier collection paths. Further optimizations could include: (i) modification of the DMF/DMSO solvent ratio to increase precursor solution viscosity, slowing solvent evaporation and suppressing the capillary-driven void formation that appears to accompany rapid drying; (ii) addition of solvent additives, such as 1,8-diiodooctane or thiourea excess, that are known to retard crystallization in related sulfide systems and may

similarly promote lateral grain growth over columnar nucleation; (iii) staged annealing protocols that leverage the ionic conductivity regime of Cu_3BiS_3 , identified in the literature above 200°C , to drive cation redistribution and pore closure before the final densification anneal. Each of these modifications could be screened rapidly against the AFM and photoluminescence metrics established in Chapter 6 without requiring full device fabrication.

7.2.4 Defect Passivation and Interface Engineering

Across all three absorber systems, the dominant photovoltaic loss mechanism is non-radiative recombination at sub-gap defect states, and this recombination is accelerated at grain boundaries and absorber/transport-layer interfaces. Two well-established strategies from the perovskite literature have not yet been systematically applied to these copper-based absorbers. Surface passivation by thin organic or inorganic capping layers, for example, ammonium iodide treatments for the iodide systems, or thiol-based ligand exchange for the sulfide, could passivate dangling bonds and undercoordinated surface sites without requiring a change in bulk synthesis chemistry. Interface band alignment engineering, by replacement of the PEDOT:PSS hole-transport layer, which is known to etch the absorber surface, with self-assembled monolayer HTLs such as 2PACz or MeO-2PACz already demonstrated in the CBI architecture, offers a second independent lever for reducing interface recombination velocity. Systematic V_{OC} transient measurements as a function of HTL chemistry would provide a direct metric for the effectiveness of each passivation strategy and allow recombination pathways to be decomposed into bulk and interface contributions.

7.2.5 Extension to Mixed-Anion and Chalcohalide Frameworks

The structural and defect-chemical insights developed in this thesis for the iodide and sulfide endpoints of the copper–pnictogen–anion phase space suggest a broader exploration of mixed-anion (chalcohalide) compositions of the general form Cu–Bi–(S/I) and Cu–Sb–(S/I) . Such compositions have attracted theoretical interest because partial anion substitution can tune the bandgap continuously between the iodide and sulfide endpoints while potentially combining the high electron affinity of the sulfide framework with the benign grain-boundary character of the iodide systems. Experimentally, solution-processed chalcohalide synthesis is substantially less explored than either the pure iodide or pure sulfide routes, and the phase diagram is correspondingly poorly mapped. Systematic synthesis at fixed metal stoichiometry with varying S:I anion ratio, characterized by the Rietveld refinement established in this thesis, would establish which compositions correspond to thermodynamically stable phases and which are accessi-

ble only as metastable kinetic products, precisely the information needed to target intentional phase-selective synthesis by chemical potential control.

Declaration on the Use of AI-Assisted Tools

The author declares that, during the preparation of this thesis, Grammarly was used as an AI-assisted proofreading and language-refinement tool. The use of Grammarly was restricted to spelling, grammar, punctuation, readability, and stylistic clarity of the written text.

No generative AI system was used to produce scientific arguments, interpret experimental results, perform data analysis, generate figures, write code, or draw conclusions. All scientific content, including the conception of the research, experimental work, analysis, interpretation, and conclusions, was developed by the author, unless explicitly stated otherwise.

All suggested language modifications were critically reviewed by the author before acceptance. The author assumes full responsibility for the accuracy, originality, and integrity of the thesis.

Bibliography

- [1] Gaëtan Masson, Adrien Van Rechem, Melodie de l'Epine, and Arnulf Jäger-Waldau. Snapshot 2025.
- [2] Gaëtan Masson, Melodie de l'Epine, Izumi Kaizuka, and Junko Okazaki. Trends in photovoltaic applications 2025.
- [3] National Renewable Energy Laboratory (NREL). Best research-cell efficiency chart, 2026. Accessed 2026-03-10.
- [4] Dong Yan, Xingwen Lu, Shiyi Zhao, Zuhong Zhang, Mingxia Lu, Jiangtao Feng, Jingchao Zhang, Kate Spencer, Trystan Watson, Meng Li, et al. Lead leaching of perovskite solar cells in aqueous environments: a quantitative investigation. *Solar RRL*, 6(9):2200332, 2022.
- [5] Christa E Torrence, Cara S Libby, Wanyi Nie, and Joshua S Stein. Environmental and health risks of perovskite solar modules: Case for better test standards and risk mitigation solutions. *Iscience*, 26(1), 2023.
- [6] Mitchell L Rencheck, Cara Libby, Angelique Montgomery, and Joshua S Stein. Managing potential environmental and human health risks of lead halide perovskite photovoltaic modules. *Solar Energy*, 269:112337, 2024.
- [7] Anika Sidler, Felix Schmidt, Bastien Vallat, Fionnuala Grifoni, Severin N Habisreutinger, Riikka Suhonen, Henry J Snaith, Andreas Schäffer, and Markus Lenz. Assessment of soil impacts from lead release by lead-halide perovskite solar cells based on outdoor leaching tests. *EES Solar*, 2026.
- [8] Byung-wook Park and Sang Il Seok. Intrinsic instability of inorganic–organic hybrid halide perovskite materials. *Advanced Materials*, 31(20):1805337, 2019.
- [9] Emilio J Juarez-Perez, Luis K Ono, Maki Maeda, Yan Jiang, Zafer Hawash, and Yabing Qi. Photodecomposition and thermal decomposition in methylammonium halide lead perovskites and inferred design principles to increase photovoltaic device stability. *Journal of Materials Chemistry A*, 6(20):9604–9612, 2018.

- [10] Rupam Datta, Kai Trombotto Herfert, Daniel M Többsen, Pirmin Tischler, Martin Peterlechner, Ben Breitung, Marcel Habrik, Jan Bruder, Uli Lemmer, Susan Schorr, Alexander Colsmann, and Holger Röhme. Photovoltaic properties of BiI_3 with copper interstitials. *EES Solar*, 1(5):881–886, 2025.
- [11] Basita Das, Zhifa Liu, Irene Aguilera, Uwe Rau, and Thomas Kirchartz. Defect tolerant device geometries for lead-halide perovskites. *Materials Advances*, 2(11):3655–3670, 2021.
- [12] Rachel C Kurchin, Prashun Gorai, Tonio Buonassisi, and Vladan Stevanovic. Structural and chemical features giving rise to defect tolerance of binary semiconductors. *Chemistry of Materials*, 30(16):5583–5592, 2018.
- [13] Robert L. Z. Hoyer, Philip Schulz, Laura T. Schelhas, Aaron M. Holder, Kevin H. Stone, John D. Perkins, Derek Vigil-Fowler, Sebastian Siol, David O. Scanlon, Andriy Zakutayev, Aron Walsh, Ian C. Smith, Brent C. Melot, Rachel C. Kurchin, et al. Perovskite-inspired photovoltaic materials: Toward best practices in materials characterization and calculations. *Chemistry of Materials*, 29(5):1964–1988, 2017.
- [14] Feray Ünlü, Meenal Deo, Sanjay Mathur, and Thomas Kirchartz. Bismuth-based halide perovskite and perovskite-inspired light absorbing materials for photovoltaics. *Journal of Physics D: Applied Physics*, 55(11):113002, 2022.
- [15] Andrew H. Slavney, Tianwei Hu, Aaron M. Lindenberg, and Hemamala I. Karunadasa. A bismuth-halide double perovskite with long carrier recombination lifetime for photovoltaic applications. *Journal of the American Chemical Society*, 138(7):2138–2141, 2016.
- [16] Jiaming Wang, Saad Ullah, Peixin Yang, Linlin Liu, Shi-E Yang, Tianyu Xia, Haizhong Guo, and Yongsheng Chen. A feasible process for lead-free Cs_2SnI_6 films using vapor-assisted deposition method with Sn and I_2 powders as reactants. *Journal of Physics D: Applied Physics*, 54(14):145101, 2021.
- [17] Wolfgang Tress and Maximilian T. Sirtl. $\text{Cs}_2\text{AgBiBr}_6$ double perovskites as lead-free alternatives for perovskite solar cells? *Solar RRL*, 6(2):2100770, 2022.
- [18] Abhisek Chakraborty, Narendra Pai, Jing Zhao, Blair R Tuttle, Alexandr N Simonov, and Vincenzo Pecunia. Rudorffites and beyond: Perovskite-inspired silver/copper pnictohalides for next-generation environmentally friendly photovoltaics and optoelectronics. *Advanced Functional Materials*, 32(36):2203300, 2022.

- [19] Harry C Sansom, George FS Whitehead, Matthew S Dyer, Marco Zanella, Troy D Manning, Michael J Pitcher, Thomas J Whittles, Vinod R Dhanak, Jonathan Alaria, John B Claridge, and Matthew J. Rosseinsky. AgBiI₄ as a lead-free solar absorber with potential application in photovoltaics. *Chemistry of Materials*, 29(4):1538–1549, 2017.
- [20] Chaojie Lu, Jing Zhang, Hongrui Sun, Dagang Hou, Xinlei Gan, Ming-hui Shang, Yuanyuan Li, Ziyang Hu, Yuejin Zhu, and Liyuan Han. Inorganic and lead-free AgBiI₄ rudorffite for stable solar cell applications. *ACS Applied Energy Materials*, 1(9):4485–4492, 2018.
- [21] Harry C. Sansom, Giulia Longo, Adam D. Wright, Leonardo RV Buizza, Suhas Mahesh, Bernard Wenger, Marco Zanella, Mojtaba Abdi-Jalebi, Michael J. Pitcher, Matthew S. Dyer, Troy D. Manning, Richard H. Friend, Laura M. Herz, Henry J. Snaith, John B. Claridge, and Matthew J. Rosseinsky. Highly absorbing lead-free semiconductor Cu₂AgBiI₆ for photovoltaic applications from the quaternary CuI–AgI–BiI₃ phase space. *Journal of the American Chemical Society*, 143(10):3983–3992, 2021.
- [22] G Krishnamurthy Grandhi, Sami Toikkonen, Basheer Al-Anesi, Vincenzo Pecunia, and Paola Vivo. Perovskite-inspired Cu₂AgBiI₆ for mesoscopic indoor photovoltaics under realistic low-light intensity conditions. *Sustainable Energy & Fuels*, 7(1):66–73, 2023.
- [23] Robert D Shannon. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Foundations of Crystallography*, 32(5):751–767, 1976.
- [24] Jing Wang, Jingbo Li, and Shu-Shen Li. Native p-type transparent conductive CuI via intrinsic defects. *Journal of Applied Physics*, 110(5), 2011.
- [25] Ao Liu, Huihui Zhu, Myung-Gil Kim, Junghwan Kim, and Yong-Young Noh. Engineering copper iodide (CuI) for multifunctional p-type transparent semiconductors and conductors. *Advanced Science*, 8(14):2100546, 2021.
- [26] Huimin Zhu, Ivan Turkevych, Hugh Lohan, Pengjun Liu, Robert W. Martin, Fabien C.P. Massabuau, and Robert L.Z. Hoyer. Progress and applications of (Cu–) Ag–Bi–I semiconductors, and their derivatives, as next-generation lead-free materials for photovoltaics, detectors and memristors. *International Materials Reviews*, 69(1):19–62, 2024.
- [27] Marko Mladenovic, Farzaneh Jahanbakhshi, Jeong-Hyeok Im, Jovana V. Milic, M. Ibrahim Dar, Jingshan Luo, Shaik Mohammed Zakeeruddin, Michael Gratzel, and Ursula Rothlisberger. Silver bismuth iodides for photovoltaic applications: Insights from ab initio calculations and experimental analysis. *ACS Applied Energy Materials*, 8(11):7424–7432, 2025.

- [28] U.S. Geological Survey. Mineral commodity summaries 2025, 2025.
- [29] Harry C. Sansom, Leonardo RV Buizza, Marco Zanella, James T. Gibbon, Michael J Pitcher, Matthew S Dyer, Troy D. Manning, Vinod R. Dhanak, Laura M. Herz, Henry J. Snaith, John B. Claridge, and Matthew J. Rosseinsky. Chemical control of the dimensionality of the octahedral network of solar absorbers from the CuI–AgI–BiI₃ phase space by synthesis of 3D CuAgBiI₅. *Inorganic Chemistry*, 60(23):18154–18167, 2021.
- [30] Thomas Rath, Jose M Marin-Beloqui, Xinyu Bai, Astrid-Caroline Knall, Marco Sigl, Fernando G. Warchomicka, Thomas Griesser, Heinz Amenitsch, and Saif A. Haque. Solution-processable Cu₃BiS₃ thin films: Growth process insights and increased charge generation properties by interface modification. *ACS Applied Materials & Interfaces*, 15(35):41624–41633, 2023.
- [31] Sampat G. Deshmukh and Vipul Kheraj. A comprehensive review on synthesis and characterizations of Cu₃BiS₃ thin films for solar photovoltaics. *Nanotechnology for Environmental Engineering*, 2(1):15, 2017.
- [32] Maxwell Santana Libório, José César Augusto de Queiroz, Sivabalan Maniam Sivasankar, Thercio Henrique de Carvalho Costa, António Ferreira da Cunha, and Carlos de Oliveira Amorim. A review of Cu₃BiS₃ thin films: A sustainable and cost-effective photovoltaic material. *Crystals*, 14(6):524, 2024.
- [33] Thomas J. Whittles, Tim D. Veal, Christopher N. Savory, Peter J. Yates, Philip A. E. Murgatroyd, James T. Gibbon, Max Birkett, Richard J. Potter, Jonathan D. Major, Ken Durose, David O. Scanlon, and Vinod R. Dhanak. Band alignments, band gap, core levels, and valence band states in Cu₃BiS₃ for photovoltaics. *ACS Applied Materials & Interfaces*, 11:27033–27047, 2019.
- [34] M. J. Buerger. *Elementary Crystallography: An Introduction to the Fundamental Geometrical Features of Crystals*. Wiley, New York, 1956.
- [35] C. Giacovazzo, H. L. Monaco, G. Artioli, D. Viterbo, M. Milanesio, G. Gilli, P. Gilli, G. Zanotti, and M. Catti. *Fundamentals of Crystallography*. Oxford University Press, Oxford, 3rd edition, 2011.
- [36] R. A. Young. *The Rietveld Method*. Oxford University Press, Oxford, 1993.
- [37] Katelyn J. Baumler and Raymond E. Schaak. Tutorial on describing, classifying, and visualizing common crystal structures in nanoscale materials systems. *ACS Nanoscience Au*, 4(5):290–316, 2024.

- [38] Chiara Ricca and Ulrich Aschauer. Mechanisms for point defect-induced functionality in complex perovskite oxides. *Applied Physics A*, 128(12):1083, 2022.
- [39] Chin-Yu Yeh, ZW Lu, S Froyen, and Alex Zunger. Zinc-blende–wurtzite polytypism in semiconductors. *Physical Review B*, 46(16):10086, 1992.
- [40] Vincenzo Esposito and Ivano E Castelli. Metastability at defective metal oxide interfaces and nanoconfined structures. *Advanced Materials Interfaces*, 7(13):1902090, 2020.
- [41] Bayrammurad Saparov and David B Mitzi. Organic–inorganic perovskites: structural versatility for functional materials design. *Chemical Reviews*, 116(7):4558–4596, 2016.
- [42] Walter Rüdorff and Hans Becker. Die strukturen von LiVO_2 , NaVO_2 , LiCrO_2 und NaCrO_2 . *Zeitschrift für Naturforschung B*, 9(9):614–615, 1954.
- [43] Akihiko Okada and Klaus Keil. Caswellsilverite, NaCrS_2 : a new mineral in the norton county enstatite achondrite. *American Mineralogist*, 67(1-2):132–136, 1982.
- [44] Anna J. Lehner, Douglas H. Fabini, Hayden A. Evans, Claire-Alice Hébert, Sara R. Smock, Jerry Hu, Hengbin Wang, Josef W. Zwanziger, Michael L. Chabiny, and Ram Seshadri. Crystal and electronic structures of complex bismuth iodides $\text{A}_3\text{Bi}_2\text{I}_9$ (A= K, Rb, Cs) related to perovskite: aiding the rational design of photovoltaics. *Chemistry of Materials*, 27(20):7137–7148, 2015.
- [45] Biplab Ghosh, Sudip Chakraborty, Hao Wei, Claude Guet, Shuzhou Li, Subodh Mhaisalkar, and Nripan Mathews. Poor photovoltaic performance of $\text{Cs}_3\text{Bi}_2\text{I}_9$: an insight through first-principles calculations. *The Journal of Physical Chemistry C*, 121(32):17062–17067, 2017.
- [46] Byung-Wook Park, Bertrand Philippe, Xiaoliang Zhang, Håkan Rensmo, Gerrit Boschloo, and E.M. Johansson. Bismuth Based Hybrid Perovskites $\text{A}_3\text{Bi}_2\text{I}_9$ (A: Methylammonium or Cesium) for Solar Cell Application. *Advanced Materials (Deerfield Beach, Fla.)*, 27(43):6806–6813, 2015.
- [47] Mohamedally Kurmoo, Hitoshi Kumagai, Mark A. Green, Brendon W. Lovett, Stephen J. Blundell, Arzhang Ardavan, and John Singleton. Two modifications of layered cobaltous terephthalate: Crystal structures and magnetic properties. *Journal of Solid State Chemistry*, 159(2):343–351, 2001.
- [48] Padinhare Cholakkal Harikesh, Hemant Kumar Mulmudi, Biplab Ghosh, Teck Wee Goh, Yin Ting Teng, Krishnamoorthy Thirumal, Mark Lockrey, Klaus Weber, Teck Ming Koh, Shuzhou Li, Subodh Mhaisalkar, and Nripan Mathews. Rb as an alternative cation for

- templating inorganic lead-free perovskites for solution processed photovoltaics. *Chemistry of Materials*, 28(20):7496–7504, 2016.
- [49] Jan-Christoph Hebig, Irina Kuhn, Jan Flohre, and Thomas Kirchartz. Optoelectronic properties of $(\text{CH}_3\text{NH}_3)_3\text{Sb}_2\text{I}_9$ thin films for photovoltaic applications. *ACS Energy Letters*, 1(1):309–314, 2016.
- [50] Byung-wook Park, Sagar M. Jain, Xiaoliang Zhang, Biplab Philippe, Tomas Edvinsson, Håkan Rensmo, Gerrit Boschloo, and Erik M. J. Johansson. Resonance raman and excitation energy dependent charge transfer mechanism in halide-substituted hybrid perovskite solar cells. *ACS Nano*, 9(2):2088–2101, 2015.
- [51] Thomas M. Brenner, David A. Egger, Leeor Kronik, Gary Hodes, and David Cahen. Hybrid organic—inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties. *Nature Reviews Materials*, 1(1):1–16, 2016.
- [52] Leonardo R.V. Buizza, Adam D. Wright, Giulia Longo, Harry C. Sansom, Chelsea Q. Xia, Matthew J. Rosseinsky, Michael B. Johnston, Henry J. Snaith, and Laura M. Herz. Charge-carrier mobility and localization in semiconducting $\text{Cu}_2\text{AgBiI}_6$ for photovoltaic applications. *ACS Energy Letters*, 6(5):1729–1739, 2021.
- [53] Jun Pan, Li N. Quan, Yongbiao Zhao, Wei Peng, Banavoth Murali, Smritakshi P. Sarmah, Mingjian Yuan, Lutfan Sinatra, Noktan M. Alyami, Jiakai Liu, Emre Yassitepe, Zhenyu Yang, Oleksandr Voznyy, Riccardo Comin, Mohamed N. Hedhili, Omar F. Mohammed, Zheng H. Lu, Dong H. Kim, Edward H. Sargent, and Osman M. Bakr. Highly efficient perovskite-quantum-dot light-emitting diodes by surface engineering. *Advanced Materials*, 28(39):8718–8725, 2016.
- [54] Chris G. Van de Walle and Jörg Neugebauer. First-principles calculations for defects and impurities: Applications to III-nitrides. *Journal of Applied Physics*, 95(8), 2004.
- [55] Stephan Lany and Alex Zunger. Assessment of correction methods for the band-gap problem and for finite-size effects in supercell defect calculations: Case studies for ZnO and GaAs. *Physical Review B—Condensed Matter and Materials Physics*, 78(23):235104, 2008.
- [56] Vimal Kumar Jain. *Band Theory*, pages 251–293. Springer, 2022.
- [57] Karl W. Böer and Udo W. Pohl. *The origin of band structure*, pages 193–217. Springer, 2023.
- [58] Mykhaylo Evstigneev. *Crystal Structure of Solids*, pages 41–59. Springer, 2022.

-
- [59] Manijeh Razeghi. *Electrons and Energy Band Structures in Crystals*, pages 149–201. Springer, 2018.
- [60] Peter Würfel. *Physics of solar cells*. 2005.
- [61] Arno Smets, Klaus Jäger, Olindo Isabella, René Van Swaaij, and Miro Zeman. *Solar Energy: The physics and engineering of photovoltaic conversion, technologies and systems*. Bloomsbury Publishing, 2016.
- [62] Yatendra P. Varshni. *Physica*, 34:149, 1967.
- [63] George Frederick Harrington and José Santiso. Back-to-basics tutorial: X-ray diffraction of thin films. *Journal of Electroceramics*, 47:141 – 163, 2021.
- [64] Lothar Spieß, Gerd Teichert, Robert Schwarzer, Herfried Behnken, and Christoph Genzel. *Phasenanalyse*, pages 235–274. Springer, 2019.
- [65] Shivam Swaraj and Amodini Mishra. *Understanding Photoluminescence Spectroscopy: Principles, Applications, and Insights into Material Properties*, pages 163–186. Springer Nature Switzerland, Cham, 2025.
- [66] Arkadii Petrovich Levanyuk and Vladimir Vasil’evich Osipov. Edge luminescence of direct-gap semiconductors. *Phys. Usp.*, 24(3):187–215, 1981.
- [67] Jürgen Beyerer, Fernando Puente León, Christian Frese, and Johannes Meyer. *Automatische Sichtprüfung: Grundlagen, Methoden und Praxis der Bildgewinnung und Bildauswertung*. Springer, 2012.
- [68] Ltd. Riken Keiki Co. Atmospheric photoemission yield spectrometers - general catalog - pc9-0331-191110, 2019.
- [69] Tongyan Pan and Lu Sun. Sub-Microscopic Phenomena of Metallic Corrosion Studied by a Combined Photoelectron Spectroscopy in Air (PESA) and Scanning Kelvin Probe Force Microscopy (SKPFM) Approach. *International Journal of Electrochemical Science*, 7(10):9325–9344, 2012.
- [70] Holger Röhm. *Ferroelektrizität in Methylammoniumbleiiodid-Solarzellen*. PhD thesis, Karlsruher Institut für Technologie (KIT), 2019.
- [71] Q. Zhong, D. Inniss, K. Kjoller, and V.B. Elings. Fractured polymer/silica fiber surface studied by tapping mode atomic force microscopy. *Surface Science*, 290(1):L688–L692, 1993.
- [72] Franz J. Giessibl. Advances in atomic force microscopy. *Reviews of modern physics*, 75(3):949, 2003.

- [73] Holger Röhm. Prozessentwicklung zur skalierbaren Herstellung von Perowskit-Solarzellen an Luft. Master thesis, Karlsruher Institut für Technologie (KIT), 2014.
- [74] ASTM International. ASTM G173-23 Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface. Technical report, ASTM International, 2023.
- [75] Zhixin Jin, Zheng Zhang, Jingwei Xiu, Haisheng Song, Teresa Gatti, and Zhubing He. A critical review on bismuth and antimony halide based perovskites and their derivatives for photovoltaic applications: recent advances and challenges. *Journal of Materials Chemistry A*, 8(32):16166–16188, 2020.
- [76] Ivan Turkevych, Said Kazaoui, Eisuke Ito, Toshiyuki Urano, Koji Yamada, Hiroshi Tomiyasu, Hideo Yamagishi, Michio Kondo, and Shinji Aramaki. Photovoltaic rudorffites: lead-free silver bismuth halides alternative to hybrid lead halide perovskites. *ChemSusChem*, 10(19):3754–3759, 2017.
- [77] Xue Jia and Liming Ding. A low-temperature solution-processed copper antimony iodide rudorffite for solar cells. *Science China Materials*, 62(1):54–58, 2019.
- [78] Busheng Zhang, Yan Lei, Ruijuan Qi, Haili Yu, Xiaogang Yang, Tuo Cai, and Zhi Zheng. An in-situ room temperature route to CuBiI₄ based bulk-heterojunction perovskite-like solar cells. *Science China Materials*, 62(4):519–526, 2019.
- [79] Huimin Zhu, Axel Erbing, Hua Wu, Gabriel J. Man, Soham Mukherjee, Chinnathambi Kamal, Malin B. Johansson, Håkan Rensmo, Michael Odelius, and Erik M.J. Johansson. Tuning the bandgap in silver bismuth iodide materials by partly substituting bismuth with antimony for improved solar cell performance. *ACS Applied Energy Materials*, 3(8):7372–7382, 2020.
- [80] Marcello Righetto, Sebastián Caicedo-Dávila, Maximilian T Sirtl, Vincent J-Y Lim, Jay B Patel, David A Egger, Thomas Bein, and Laura M Herz. Alloying effects on charge-carrier transport in silver–bismuth double perovskites. *The Journal of Physical Chemistry Letters*, 14(46):10340–10347, 2023.
- [81] Yuchan Wang, Yiming Yuan, Wenxia Zhang, Fei Qi, Nan Zhang, Ting Liu, and Xiaosheng Tang. Flexible resistive switching device based on air-stable lead-free Cu₃SbI₆ perovskite film for nonvolatile memory application. *Applied Physics Letters*, 120(26), 2022.
- [82] Idris K. Popoola, Mohammed A. Gondal, Luqman E. Oloore, and AbdulJelili Popoola. Inorganic antimony-based rudorffite photo-responsive electrochemical capacitor utilizing

- non-aqueous polyvinylpyrrolidone polymer gel electrolyte for hybrid energy harvesting and storage applications. *Materials Science and Engineering: B*, 291:116373, 2023.
- [83] A. Pishtshev and S Z. Karazhanov. Structure-property relationships in cubic cuprous iodide: A novel view on stability, chemical bonding, and electronic properties. *The Journal of Chemical Physics*, 146(6), 2017.
- [84] Gerald Burns, F.H. Dacol, M.W. Shafer, and Richard Alben. The raman spectra of the superionic conductor CuI in its three phases. *Solid State Communications*, 24(11):753–757, 1977.
- [85] D.A. Keen and S. Hull. Determination of the structure of β -CuI by high-resolution neutron powder diffraction. *Journal of Physics: Condensed Matter*, 6(9):1637–1644, 1994.
- [86] Stuart L. James, Christopher J. Adams, Carsten Bolm, Dario Braga, Paul Collier, Tomislav Frišćić, Fabrizia Grepioni, Kenneth D. M. Harris, Geoff Hyett, William Jones, Anke Krebs, James Mack, Lucia Maini, A. Guy Orpen, Ivan P. Parkin, William C. Shearouse, Jonathan W. Steed, and Daniel C. Waddell. Mechanochemistry: opportunities for new and cleaner synthesis. *Chemical Society Reviews*, 41(1):413–447, 2012.
- [87] Hela Ferjani, Rim Bechaieb, Diego M. Gil, and Axel Klein. The 1d hybrid material allylimidazolium iodoantimonate: A combined experimental and theoretical study. *Inorganics*, 13(7):243, 2025.
- [88] Robert Nemanich and J.C. Mikkelsen. Raman scattering from the copper halides CuI, CuBr and CuCl in the high temperature phases. In *Paper from the 14th International Conference on the Physics of Semiconductors, 14th*, pages 661–664. Institute of Physics, 1979.
- [89] J.E. Potts, R.C. Hanson, C.T. Walker, and C Schwab. Raman scattering from CuBr and CuI. *Solid State Communications*, 13(3):389–392, 1973.
- [90] Gerald Burns, Richard Alben, FH Dacol, and MW Shafer. Lattice dynamic measurements and calculations of the superionic conductor CuI. *Physical Review B*, 20(2):638, 1979.
- [91] H.C. Hsueh, Roger K. Chen, H Vass, S.J. Clark, G.J. Ackland, W.C.K. Poon, and J. Crain. Compression mechanisms in quasimolecular XI_3 ($X = \text{As, Sb, Bi}$) solids. *Physical Review B*, 58(22):14812, 1998.

- [92] Heribert Hernández-Cocoletzi, Gregorio H Cocoletzi, JF Rivas-Silva, A Flores, and Noboru Takeuchi. Density Functional Study of the Structural Properties of Copper Iodide: LDA vs GGA Calculations. *Journal of Nano Research*, 5:25–30, 2009.
- [93] Rupam Datta, Daniel M. Töbrens, Michael Habrik, Krassimir Garbev, Markus Peterlechner, Susan Schorr, Alexander Colsmann, and Holger Röhm. Defect-stabilized polytypism in copper antimony iodide solar cells. Manuscript in preparation, 2026.
- [94] Miloslav Klinger and Aleš Jäger. Crystallographic Tool Box (CrysTBox): automated tools for transmission electron microscopists and crystallographers. *Applied Crystallography*, 48(6):2012–2018, 2015.
- [95] I. Pelant and J. Valenta. *Luminescence Spectroscopy of Semiconductors*. Oxford University Press, Oxford, 2012.
- [96] Aron Walsh, David O Scanlon, Shiyu Chen, X.G. Gong, and Su-Huai Wei. Self-regulation mechanism for charged point defects in hybrid halide perovskites. *Angewandte Chemie International Edition*, 54(6):1791–1794, 2015.
- [97] Ao Liu, Huihui Zhu, Myung-Gil Kim, Junghwan Kim, and Yong-Young Noh. Engineering Copper Iodide (CuI) for multifunctional p-type transparent semiconductors and conductors. *Advanced Science*, 8(14):2100546, 2021.
- [98] Sven Rühle. Tabulated values of the shockley–queisser limit for single junction solar cells. *Solar Energy*, 130:139–147, 2016.
- [99] Thomas M. Brenner, David A. Egger, Leeor Kronik, Gary Hodes, and David Cahen. Hybrid organic—inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties. *Nature Reviews Materials*, 1(1):1–16, 2016.
- [100] Christopher Eames, Jarvist M. Frost, Piers R.F. Barnes, Brian C. O’regan, Aron Walsh, and M. Saiful Islam. Ionic transport in hybrid lead iodide perovskite solar cells. *Nature communications*, 6(1):7497, 2015.
- [101] Praveen Kumar, Khursheed Ahmad, and Shaikh M. Mobin. Improved photovoltaic performance of Pb-free AgBi_2I_7 based photovoltaics. *Nanoscale Advances*, 5(6):1624–1630, 2023.
- [102] G. Krishnamurthy Grandhi, Noolu. Srinivasa Manikanta Viswanath, Marcello Righetto, Sara Domenici, Mokurala Krishnaiah, Marco Moroni, Adriana Pecoraro, Ana Belén Muñoz-García, Michele Pavone, Lorenzo Malavasi, Teresa Gatti, and Paola Vivo. Silver–bismuth perovskite-inspired materials: chemistry, optoelectronic properties, and emerging applications in photovoltaics and beyond. *Journal of Materials Chemistry A*, 2025.

- [103] P. Fourcroy, D. Carre, F. Thevet, and J. Rivet. Structure du Tétraiodure de Cuivre(I) et de Bismuth(III), CuBiI_4 . *Acta Crystallographica Section C: Crystal Structure Communications*, 47(10):2023–2025, 1991.
- [104] Ajay Kumar Baranwal, Hideaki Masutani, Hidetaka Sugita, Hiroyuki Kanda, Shusaku Kanaya, Naoyuki Shibayama, Yoshitaka Sanehira, Masashi Ikegami, Youhei Numata, Kouji Yamada, Tsutomu Miyasaka, Tomokazu Umeyama, Hiroshi Imahori, and Seigo Ito. Lead-free perovskite solar cells using sb and bi-based $\text{A}_3\text{B}_2\text{X}_9$ and A_3BX_6 crystals with normal and inverse cell structures. *Nano Convergence*, 4:26, 2017.
- [105] V. Carteaux, D. Brunet, G. Ouvrard, and G. André. Crystallographic, magnetic and electronic structures of a new layered ferromagnetic compound $\text{Cr}_2\text{Ge}_2\text{Te}_6$. *Journal of Physics: Condensed Matter*, 7(1):69–87, 1995.
- [106] T. Oldag, T. Aussieker, H. L. Keller, C. Preitschaft, and A. Pfitzner. Solvothermale synthese und bestimmung der kristallstrukturen von AgBiI_4 und Ag_3BiI_6 . *Zeitschrift für Anorganische und Allgemeine Chemie*, 631(4):677–682, 2005.
- [107] H. He and Z. Zhang. Decay mechanism of optical phonons in $\gamma\text{-CuI}$. *AIP Advances*, 9(5), 2019.
- [108] Y. Yang, C. Wang, J. Hou, and J. Dai. Raman scattering, far infrared spectrum of BiI_3 nanocrystallites. *Materials Letters*, 57(15):2185–2188, 2003.
- [109] Anderson Janotti and Chris G. Van de Walle. New insights into the role of native point defects in ZnO . *Journal of Crystal Growth*, 287(1):58–65, 2006.
- [110] Ke Wei, Zhongjie Xu, Runze Chen, Xin Zheng, Xiangai Cheng, and Tian Jiang. Temperature-dependent excitonic photoluminescence excited by two-photon absorption in perovskite CsPbBr_3 quantum dots. *Optics Letters*, 41(16):3821–3824, 2016.
- [111] Yueming Wang, Samah Akel, Benjamin Klingebiel, and Thomas Kirchartz. Hole transporting bilayers for efficient micrometer-thick perovskite solar cells. *Advanced Energy Materials*, 14(5):2302614, 2024.
- [112] Sachin A. Pawar, Abdurashid Mavlonov, Hiroki Mori, Yu Kawano, Kensuke Kojima, Jun Azuma, Takayuki Negami, and Takashi Minemoto. Band engineering of a PTAA hole transporting layer in the n–i–p architecture of MAPbI_3 -based perovskite solar cells. *Sustainable Energy & Fuels*, 9(10):2689–2697, 2025.
- [113] Yang Li, Chao Liang, Gaopeng Wang, Jielei Li, Shi Chen, Shihe Yang, Guichuan Xing, and Hui Pan. Two-step solvent post-treatment on PTAA for highly efficient and stable inverted perovskite solar cells. *Photonics Research*, 8(10):A39–A49, 2020.

- [114] E. W. Nuffield. Studies of mineral sulpho-salts; XI, Wittichenite (klaprothite). *Economic Geology*, 42(2):147–160, 1947.
- [115] V. Estrella, M. T. S. Nair, and P. K. Nair. Semiconducting Cu_3BiS_3 thin films formed by the solid-state reaction of CuS and bismuth thin films. *Semiconductor Science and Technology*, 18(2):190–194, 2003.
- [116] M. Kumar and K. A. Persson. Cu_3BiS_3 as a potential photovoltaic absorber with high optical efficiency. *Applied Physics Letters*, 102(6):062109, 2013.
- [117] N. J. Gerein and J. A. Haber. One-step synthesis and optical and electrical properties of thin-film Cu_3BiS_3 for use as a solar absorber in photovoltaic devices. *Chemistry of Materials*, 18(26):6297–6302, 2006.
- [118] F. Mesa and G. Gordillo. Optical and structural properties of Cu_3BiS_3 thin films grown by co-evaporation. *Journal of Physics: Conference Series*, 167:012019, 2009.
- [119] Arshad Hussain, Jing Ting Luo, Ping Fan, Guangxing Liang, Zhenghua Su, R. Ahmed, Nisar Ali, Qiuping Wei, Shabbir Muhammad, Aijaz Rasool Chaudhry, and Yong Qing Fu. p-type Cu_3BiS_3 thin films for solar cell absorber layer via one stage thermal evaporation. *Applied Surface Science*, 505:144597, 2020.
- [120] U. Chalapathi, P.R. Prasad, C.P. Reddy, S. Sambasivam, P. Rosaiah, M. Ouladsmene, S. Alhammadi, S. Lee, and S. Park. Synthesis of wittichenite Cu_3BiS_3 thin films by sulfurizing thermally evaporated Cu-Bi metallic stacks. *Chalcogenide Letters*, 20(11):797–802, 2023.
- [121] Sheng Liu, Xuebin Wang, Longying Nie, Lijin Chen, and Ruo Yuan. Spray pyrolysis deposition of Cu_3BiS_3 thin films. *Thin Solid Films*, 585:72–75, 2015.
- [122] Diego Colombara, Laurence M. Peter, Kyle Hutchings, Keith D. Rogers, Stefan Schäfer, Jesse T.R. Dufton, and M. Saiful Islam. Formation of Cu_3BiS_3 thin films via sulfurization of Bi-Cu metal precursors. *Thin Solid Films*, 520(16):5165–5171, 2012.
- [123] Jiajia Li, Xiuxun Han, Yun Zhao, Jian Li, Min Wang, and Chen Dong. One-step synthesis of Cu_3BiS_3 thin films by a dimethyl sulfoxide (dmso)-based solution coating process for solar cell application. *Solar Energy Materials and Solar Cells*, 174:593–598, 2018.
- [124] Yi Fang, Wenning Zhao, Wenhui Li, and Xiuxun Han. Effects of thiourea dosage on the structural, optical and electrical properties of one-step solution processed Cu_3BiS_3 film for photovoltaic application. *Applied Physics A*, 127:9, 2021.

- [125] A. B. Kehoe, G. W. Watson, and D. O. Scanlon. Cu_3MCh_3 ($\text{M} = \text{Sb, Bi}$; $\text{Ch} = \text{S, Se}$) as candidate solar cell absorbers: insights from theory. *Physical Chemistry Chemical Physics*, 15:15477–15484, 2013.
- [126] Thomas J. Whittles, Tim D. Veal, Christopher N. Savory, Peter J. Yates, Philip A. E. Murgatroyd, James T. Gibbon, Max Birkett, Richard J. Potter, Jonathan D. Major, Ken Durose, David O. Scanlon, and Vinod R. Dhanak. Band alignments, band gap, core levels, and valence band states in Cu_3BiS_3 for photovoltaics. *ACS Applied Materials & Interfaces*, 11(30):27033–27047, 2019.
- [127] E. Matzat. Die Kristallstruktur des Wittichenits, Cu_3BiS_3 . *Tschermaks Mineralogische und Petrographische Mitteilungen*, 18(4):312–316, 1972.
- [128] V. Kocman and E.W. Nuffield. The crystal structure of wittichenite, Cu_3BiS_3 . *Structural Science*, 29(11):2528–2535, 1973.
- [129] Maxwell Santana Libório, José César Augusto de Queiroz, Sivabalan Maniam Sivasankar, Thercio Henrique de Carvalho Costa, António Ferreira da Cunha, and Carlos de Oliveira Amorim. A review of Cu_3BiS_3 thin films: A sustainable and cost-effective photovoltaic material. *Crystals*, 14(6):524, 2024.
- [130] E. Makovicky. The phase transformations and thermal expansion of the solid electrolyte Cu_3BiS_3 between 25 and 300 °C. *Journal of Solid State Chemistry*, 49(1):85–92, 1983.
- [131] A. R. Zanatta. Revisiting the optical bandgap of semiconductors and the proposal of a unified methodology to its determination. *Scientific Reports*, 9:11225, 2019.
- [132] U. Chalapathi, P. Reddy Prasad, Sangaraju Sambasivam, K. Mallikarjuna, P. Rosaiah, Salh Alhammadi, Ammar M. Tighezza, Krithikaa Mohanarangam, and Si-Hyun Park. Two-stage growth of Cu_3BiS_3 thin films: Influence of the Cu/Bi ratio. *Journal of Materials Research and Technology*, 26:2443–2450, 2023.
- [133] M. V. Yakushev, P. Maiello, T. Raadik, M. J. Shaw, P. R. Edwards, J. Krustok, A. V. Mudryi, I. Forbes, and R. W. Martin. Electronic and structural characterization of Cu_3BiS_3 thin films for the absorber layer of sustainable photovoltaics. *Thin Solid Films*, 562:195–199, 2014.
- [134] Yanlin Pan, Hongmei Deng, Dongliang Sus Zheng, Jianxin Chen, Yilian Zhong, Jiahua Tao, Pingxiong Yang, and Junhao Chu. Co-electrodeposition of Cu_3BiS_3 thin films in weakly alkaline aqueous solutions for photovoltaic application. *Journal of Materials Science: Materials in Electronics*, 33:585–595, 2022.

- [135] Yanbo Yang, Xiaolu Xiong, Hongxing Yin, Ming Zhao, and Junfeng Han. Study of copper bismuth sulfide thin films for the photovoltaic application. *Journal of Materials Science: Materials in Electronics*, 30(2):1832–1837, 2019.
- [136] W. Zhao, Y. Fang, W. Li, and X. Han. Impact of ag doping on Cu_3BiS_3 solar cell performance. *Solar Energy*, 221:109–113, 2021.
- [137] Tim Effelberg. Solution-processed Cu_3BiS_3 for thin film solar cells. Master’s thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2026. Unpublished.
- [138] B. Mahto, A. A. Khan, A. Barhoi, and S. Hussain. Hierarchical Cu_3BiS_3 nanostructures with thermally controlled morphology for photoconductive, photothermal, and catalytic applications. *ACS Applied Nano Materials*, 6(8):6784–6797, 2023.
- [139] V. Mauritz and R. W. Crisp. Unravelling the intricacies of solvents and sulfur sources in colloidal synthesis of metal sulfide semiconductor nanocrystals. *Journal of Materials Chemistry C*, 12(30):11319–11334, 2024.
- [140] L. Stradella and M. Argentero. A study of the thermal decomposition of urea, of related compounds and thiourea using DSC and TG-EGA. *Thermochimica Acta*, 219:315–323, 1993.
- [141] S. Wang, Q. Gao, and J. Wang. Thermodynamic analysis of decomposition of thiourea and thiourea oxides. *The Journal of Physical Chemistry B*, 109(36):17281–17289, 2005.
- [142] A. A. Shults, G. Lu, J. D. Caldwell, and J. E. Macdonald. Role of carboxylates in the phase determination of metal sulfide nanoparticles. *Nanoscale Horizons*, 8(10):1386–1394, 2023.
- [143] Erika Dutková, Petr Levinský, Jiří Hejtmánek, Karel Knížek, Lenka Findoráková, Matej Baláž, Martin Fabián, Katarína Gáborová, Viktor Puchý, and Peter Baláž. Mechanochemically synthesized skinnerite Cu_3SbS_3 and wittichenite Cu_3BiS_3 nanocrystals and their promising thermoelectric properties. *Crystals*, 15(6):511, 2025.
- [144] C. Yan, E. Gu, F. Liu, Y. Lai, J. Li, and Y. Liu. Colloidal synthesis and characterizations of wittichenite copper bismuth sulfide nanocrystals. *Nanoscale*, 5(5):1789–1792, 2013.
- [145] Bing Cai, Wen-Hua Zhang, and Jieshan Qiu. Solvent engineering of spin-coating solutions for planar-structured high-efficiency perovskite solar cells. *Chinese Journal of Catalysis*, 36(8):1183–1190, 2015.
- [146] Bin Li, Jiangjian Shi, Jianfeng Lu, Wen Liang Tan, Wenping Yin, Jingsong Sun, Liangcong Jiang, Robert T. Jones, Paul Pigram, Christopher R. McNeill, Yi-Bing Cheng, and

- Jacek J Jasieniak. Facile deposition of mesoporous PbI_2 through DMF: DMSO solvent engineering for sequentially deposited metal Halide perovskites. *ACS Applied Energy Materials*, 3(4):3358–3368, 2020.
- [147] Namyoung Ahn, Dae-Yong Son, In-Hyuk Jang, Seong Min Kang, Mansoo Choi, and Nam-Gyu Park. Highly reproducible perovskite solar cells with average efficiency of 18.3% and best efficiency of 19.7% fabricated via lewis base adduct of lead(ii) iodide. *Journal of the American Chemical Society*, 137(27):8696–8699, 2015. PMID: 26125203.
- [148] Influence of DMSO/DMF ratio on the crystal growth and optical properties of Sn-based perovskite films. *Micro and Nano Engineering*, 28:100302, 2025.
- [149] Fucheng Yu, Zengguang Huang, Jinghong Zhang, and Sihua Zhong. Non-toxic Cu_3BiS_3 thin film solar cells with Al doped TiO_2 as electron-transport layers. *Physica Scripta*, 100(1):015948, 12 2024.
- [150] Pablo Cubillas and Michael W. Anderson. Synthesis mechanism: Crystal growth and nucleation. *Zeolites and Catalysis: Synthesis, Reactions and Applications*, pages 1–55, 2010.
- [151] Richard J. Staples. Getting crystals your crystallographer will treasure: a beginner’s guide. *Acta Crystallographica Section E*, 81(10):895–905, 10 2025.
- [152] Arkadii Petrovich Levanyuk and Vladimir Vasil’evich Osipov. Edge luminescence of direct-gap semiconductors. *Soviet Physics Uspekhi*, 24(3):187–215, 1981.
- [153] Q. Fatima, A. A. Haidry, H. Zhang, A. El Jery, and M. Aldrdery. A critical review on advancement and challenges in using TiO_2 as electron transport layer for perovskite solar cell. *Materials Today Sustainability*, 27:100857, 2024.
- [154] Fredy Mesa, William Chamorro, William Vallejo, Robert Baier, Thomas Dittrich, Alexander Grimm, Martha C. Lux-Steiner, and Sascha Sadewasser. Junction formation of Cu_3BiS_3 investigated by kelvin probe force microscopy and surface photovoltage measurements. *Beilstein Journal of Nanotechnology*, 3:277–284, 2012.
- [155] O. Oladapo, B. Marí Soucase, and B. Aka. Numerical simulation and performance optimization of $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells. *IOSR Journal of Applied Physics*, 8(4):1–11, 2016.
- [156] Benoit Gaury and Paul M Haney. Analytical description of charged grain boundary recombination in polycrystalline thin film solar cells. In *2017 IEEE 44th Photovoltaic Specialist Conference (PVSC)*, pages 2438–2442. IEEE, 2017.

A Acknowledgements

The work presented in this thesis represents a scientific journey shaped by research, collaboration, and continuous personal and professional growth. When I joined the OPV group at KIT, I was a foreigner newly arrived in Germany, trying to understand not only a new research environment but also a new culture, language, and way of life. Every day brought something unfamiliar. Many of those experiences became easier, warmer, and more joyful because of the people who supported me during this time.

First and foremost, I would like to express my sincere gratitude to my supervisors, Apl. Prof. Dr. Alexander Colsmann and Dr. Holger Röhm. I am deeply thankful to Prof. Colsmann for welcoming me into the OPV group, for giving me the opportunity to pursue this work, and for helping me grow into a better researcher than I was when I first arrived. His guidance, trust, and scientific perspective shaped the way I learned to think about materials, devices, and research questions. I am equally grateful to Dr. Holger Röhm for the trust he placed in me and for supervising this thesis with patience, clarity, and constant support. His scientific insight, constructive criticism, and encouragement were essential throughout this work. I thank both of them for creating an environment in which learning and mistakes, both became a part of growth, and research became a meaningful experience.

I would also like to thank all collaborators and co-authors who contributed to the publications and scientific work that form the foundation of this thesis. My special thanks go to Prof. Dr. Susan Schorr, Dr. Daniel M. Többens (Helmholtz-Zentrum Berlin), and Dr. Martin Peterlechner (LEM, KIT) for conducting important measurements, sharing their valuable expertise, and providing scientific insights that became an integral part of this thesis. I am also grateful to all co-authors of my publications for their contributions, discussions, and support. I would also like to extend my sincere gratitude to Prof. Dr. Susan Schorr for kindly agreeing to serve as the second referee of this dissertation.

My sincere thanks go to all current and former members of the OPV group at KIT: Dr. Christian Sprau, Dr. Karen Fischer, Dr. Ibrahim Simsek, Dr. Alexander Schulz, Dr. Jonas Armleder, Dr. Simon Petrick, Marcel Habrik, Sebastian Coen, Yunan Chen, Sven Fischer, Kerstin Märkle, Jan Bruder, and Leon Salomon. The collaborative spirit, scientific discussions, technical help,

and everyday support I received in the group were fundamental to this thesis. During a PhD, some colleagues become much more than people one works with. They become friends whose presence makes difficult days lighter and good days more memorable. I am especially thankful to Kai Trombotto Herfert, Marcel Habrik, and Srikanth Dodapaneni for their encouragement, good wishes, friendship, and for all the laughter we shared along the way.

I would like to thank my former professors and mentors, whose encouragement helped me reach where I am today. I am especially thankful to Prof. Chitragada Das Mukhopadhyay (IEST Shibpur), Dr. Mitrajit Ghosh (Uniklinikum Düsseldorf), and Prof. Sushil A. Mujumdar (NOMOL, TIFR Mumbai). Their faith in me, guidance, and support gave me confidence at important stages of my academic journey.

This thesis is dedicated to my inspiration, my hero, my father, Mr. Bimal Krishna Datta, who left this world during the COVID period in 2022. I carry his values with me and try to follow his ideology in my own life: to become kinder, calmer, and better than I was the day before. And to my greatest strength and greatest teacher, my mother, Mrs. Lopita Datta, I owe more than words can express. Even though I am more than 8000 km apart, the distance has never weakened the courage, motivation, and confidence she gives me every single day. Her love has always been my safest place. I would also like to thank all my relatives and in-laws for their love and support. Their warmth has been a source of comfort and strength during this journey. I want to express my deepest gratitude to my maternal uncle, Mr. Gopal Acharya. Even when I doubt myself, he has been a constant anchor, always lifting my confidence and believing in me. To my cousins, Ritam Chakraborty and Swarnava Sinha Ray, thank you for all the fun, laughter, and for keeping my sense of humor in check when I needed it most.

Finally, I would like to express my deepest appreciation to the brightest light of my life, my steadfast supporter, my loudest cheer, and my greatest happiness, my wife, Ms. Debapriya Dhar. Your love, patience, belief, and constant encouragement carried me through many difficult moments. This journey became more meaningful because you were by my side. Meeting you has been the greatest fortune of my life. Thank you for being my home, my strength, and my joy.

Thank you all so much.

