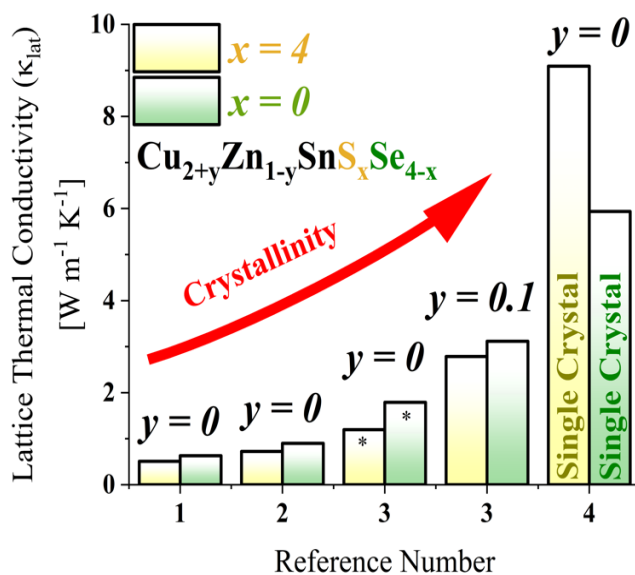
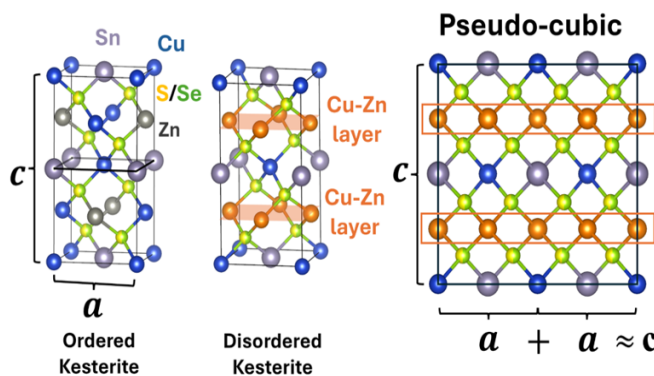


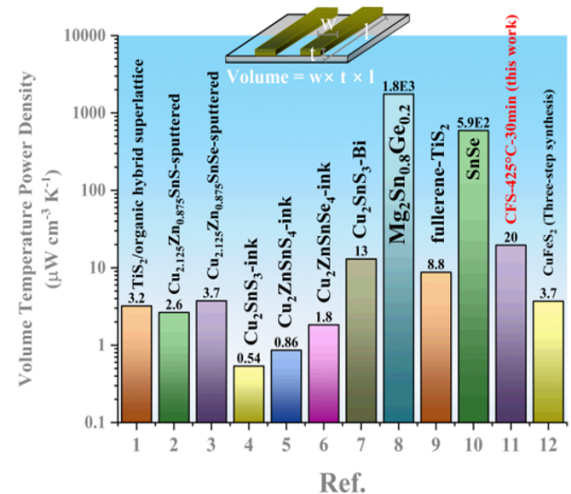
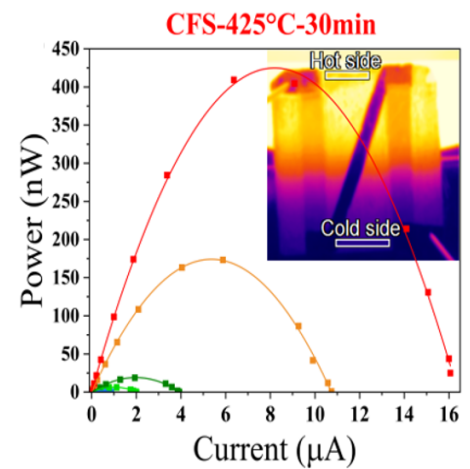
Marcelo Augusto Malagutti

Environmentally Friendly Thermoelectrics for Sustainable Energy Generation

Kesterite



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Doctoral School in Civil, Environmental and Mechanical Engineering
Topic 2. Mechanics, Materials, Chemistry and Energy - 38th cycle 2022/2026

Doctoral Thesis - May 2026

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Environmentally Friendly Thermoelectrics for Sustainable Energy Generation

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To my family

Acknowledgments

I would like to express my sincere gratitude to all those who supported me throughout my PhD journey.

First and foremost, I am deeply grateful to Prof. Paolo Scardi for his guidance and mentorship, which have been instrumental in shaping my scientific skills and broadening my understanding of the field. I would also like to thank Prof. Narges Ataollahi, whose professional guidance and personal support I deeply admire.

I am especially thankful to Prof. Eleonora Isotta for her encouragement and valuable advice at various stages of this work. I am also grateful to Prof. Carlos E. M. Campos for introducing me to this research field and encouragement throughout all the stages of my graduation. My sincere thanks go to Prof. Robert Dinnebier and Dr. Sebastian Bette for their valuable contributions to my understanding of X-ray diffraction theory and modelling. I also thank Dr. Bernd Hinrichsen and Dr. Maxwell Terban for insightful discussions on pair distribution function analysis. I acknowledge Prof. Edgardo Saucedo, Dr. Carlo Fanciulli, Prof. Rosa Di Maggio, Prof. Andy Fitch, and Prof. Umberto Anselmi-Tamburini for their valuable insights and contributions to this work.

I would also like to thank Dr. Mirco D’Incau for his kind technical and professional support. My appreciation extends to Dr. Andrea Chiappini, Dr. Gloria Ischia, Dr. Christine Stefani, Dr. Frank Adams, and Wilma Vaona. Special thanks are due to Prof. Saucedo’s collaborators, Dr. Alejandro Navarro-Guell and Dr. Ivan Caño Prades.

I am grateful to my colleagues and friends in the laboratory for the stimulating discussions, new ideas, and shared moments throughout these years, especially Dr. Binayak Mukherjee, Prof. Dr. Himanshu Nautiyal, Dr. Ketan Lohani, Dr. Varun D. N., Dr. Eleonora Tomasino, Mr. Tanguy Bernard, and Ms. Sirisha Subbareddy. I also thank the friends I met at the Max Planck Institute, including Mr. Artem Shevchenko, Ms. Anastasiia Sleptsova, Mr. Riccardo Cameli Manzo, and Mr. Erick Agnolin.

Finally, I would like to thank my family—my mother, father, and sister—for their constant support and encouragement.

Abstract

Thermoelectric devices provide a simple and practical route for converting low-grade waste heat into electrical energy. Given that more than 60% of industrial energy is lost as heat, thermoelectric generators offer a promising solution for energy recovery. They operate without moving parts, are noiseless, and require minimal maintenance. However, their widespread application is limited by the reliance on rare and expensive materials. In this context, environmentally friendly chalcogenide-based compounds with zinc-blende-derived structures, such as $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ (CZTSSe) and CuFeS_2 (CFS), are gaining attention due to their earth-abundant composition, low toxicity, and structural versatility, enabling defect engineering and control of chemical disorder.

This doctoral work investigates the synthesis of bulk and thin-film chalcogenide thermoelectric materials, their structural and transport properties, and device fabrication based on CZTSSe and CFS systems. In CZTSSe, high-energy ball milling stabilizes a metastable cubic phase at room temperature. Its origin is clarified through stacking-fault X-ray diffraction modelling and *ab initio* simulations. Upon sintering, the material transforms into an ordered tetragonal kesterite phase, with reversible disorder associated with Cu/Zn randomization. Partial Cu substitution for Zn improves electronic transport, while chalcogen substitution enhances chemical disorder, leading to an unconventional thermal conductivity trend where Se-rich compositions exhibit higher thermal conductivity due to microstructure-driven grain-boundary scattering.

For thin-film devices, CFS-based systems achieve record power density among sulfur-based thermoelectrics through a three-step process combining ball milling, thermal evaporation, and sulfurization. The coexistence of Cu_2S and Fe_2S phases enhance electronic transport by bridging CuFeS_2 grains.

Overall, this work elucidates how chemical and microstructural disorder can be tuned in zinc-blende-derived chalcogenides, develops X-ray diffraction methodologies for their characterization, and enhances the efficiency of sustainable thermoelectric energy conversion in both bulk and thin-film systems.

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Chapter 1

Introduction

1.1 The broad scope of thermoelectricity

The conversion of heat into useful work has accompanied human development since the earliest stages of civilization, from basic domestic applications such as food preparation to the development of tools through the processing of bronze and iron, often employed for defense and construction. During the Industrial Revolution, thermal energy became the primary source of mechanical power, driving rapid industrialization. Over the course of the twentieth century, however, the widespread adoption of electricity enabled the development of electronics and digital technologies, progressively replacing thermal energy as the dominant and most versatile form of energy for many applications.

At present, a new technological transformation driven by artificial intelligence and large-scale data processing is generating an unprecedented demand for energy [1], while simultaneously releasing significant amounts of heat as waste. Data centers, for instance, require extensive cooling systems, often relying heavily on water resources [2]. More broadly, in many industrial processes, thermodynamic limitations and practical inefficiencies result in a substantial portion of the input energy ($\sim 60\%$) being dissipated as heat [3, 4]. Identifying effective strategies to harvest this excess heat therefore represents a practical route toward reducing operational costs and improving overall energy efficiency.

In this context, thermoelectric generators (TEGs) have been proposed as a convenient solution. Thermoelectricity is the branch of materials science devoted to understanding the direct conversion of a temperature gradient into electrical energy through the Seebeck effect, as well as the inverse phenomenon, where an electrical current induces heat transport via the Peltier effect [5, 6]. TEGs offer several advantages: they operate without moving parts, can function continuously, require limited maintenance, and are scalable across different application ranges. For these reasons, a thorough understanding of thermoelectric principles and mechanisms is essential for advancing energy recovery technologies and enhancing efficiency in modern production systems.

1.1.1 Brief history of thermoelectricity

The history of thermoelectricity starts in 1821 with Thomas Johann Seebeck, who observed that heating the junction of two dissimilar metals in a closed circuit caused the deflection of a compass needle [5, 7]. Although Seebeck initially interpreted the phenomenon as magnetic in nature, subsequent studies in electromagnetism clarified that the needle's movement was

due to an electric current generated by the thermal gradient between the junctions. This led to the recognition of the Seebeck effect as the generation of an electromotive force in a circuit composed of two different conductors subjected to a temperature difference, establishing a direct link between heat and electricity. In 1834, Jean Peltier identified the reverse process, demonstrating that the passage of an electric current through a thermocouple could induce heating or cooling at the junction, a phenomenon now known as the Peltier effect [8].

A further milestone was achieved in 1854 by William Thomson (Lord Kelvin), who identified an additional phenomenon in which a temperature gradient along a single conductor could lead to heat absorption or release, now known as the Thomson effect [8]. Beyond its experimental observation, Thomson established the thermodynamic relationships linking Seebeck, Peltier, and Thomson effects, demonstrating that they are intrinsically connected through what is now referred to as the Kelvin relations.

Historically, the earliest materials used in thermoelectric (TE) applications were metallic [8]. During the 19th century, these metallic alloys found use in commercial applications; however, their performance was consistently limited by issues such as oxidation and melting at elevated temperatures [8, 9]. Metal alloys were gradually replaced by semiconductors after the discovery of Bi-Te, Pb-Te, Si-Ge systems in the 1950's [6, 10]. Today, Bi-Te and Sb-Te-based materials dominate commercial applications, particularly in thermoelectric cooling (TEC) devices that exploit the Peltier effect at room temperature and are widely available in consumer markets.

1.1.2 Modern applications of thermoelectrics

The most efficient way to harvest energy through thermoelectricity is by electrically connecting p- and n-type semiconductors in series while arranging them thermally in parallel, forming a thermoelectric generator module [6]. Multiple modules can then be assembled together to increase the power output per unit area of the device. Although, in principle, a TEG can operate using only one type of semiconducting material, the combination of both p- and n-type legs improves voltage generation and optimizes space utilization within the module [11].

One of the most prominent applications of TEGs is in the aerospace sector, where radioisotope thermoelectric generators (RTGs) convert the heat released by radioactive decay into electrical energy. These systems are essential for powering spacecraft operating far from the Sun, where solar energy is insufficient. A notable example is the Voyager 1 probe, launched in 1977 and still operational today [12]. Its RTGs rely on plutonium-238 as a heat source and silicon-germanium thermocouples to generate electrical power through the Seebeck effect. This application highlights the reliability and long-term stability of thermoelectric devices in extreme environments, where durability and maintenance-free operation are critical.

Thermoelectric technology has also been explored in the automotive and wearable sectors. In vehicles, TEGs can recover waste heat from exhaust systems, where a temperature gradient between the hot exhaust gases and the ambient environment generates electrical power that can support onboard electronics or reduce alternator load, contributing to improved fuel efficiency [13]. Similarly, wearable thermoelectric devices exploit the temperature difference between human skin and the surrounding air to power small sensors or medical monitoring systems [14]. Advances in microfabrication and materials engineering, including silicon-germanium and bismuth telluride alloys, have enabled the miniaturization and improved efficiency of such systems. These examples demonstrate the versatility of TEGs across scales, from large-scale space applications to compact, low-power consumer

technologies.

In recent years, growing attention has also been directed toward thermal management in high-performance electronics and data centers, where large amounts of heat are generated in confined volumes [15]. Thermoelectric coolers based on the Peltier effect are used for localized temperature control of processors, laser diodes, and sensitive electronic components, enabling precise regulation of operating conditions [16]. Similar concepts are being investigated to mitigate thermal hotspots in servers and microelectronic devices, complementing conventional cooling strategies [17]. Although thermoelectric cooling does not replace large-scale refrigeration systems, it offers a compact and controllable solution for targeted heat management, reinforcing the strategic role of thermoelectric technology in modern energy and electronic infrastructures. Overall, the widespread interest in thermoelectric devices stems from several intrinsic advantages. Being solid-state systems, they operate without moving parts, generate no mechanical noise, and require minimal maintenance. Their compactness and scalability allow integration into systems where conventional heat engines would be impractical. Moreover, thermoelectric devices can operate continuously as long as a temperature gradient is maintained, making them particularly attractive for waste-heat recovery applications. However, their main limitation lies in the relatively low conversion efficiency compared to traditional thermodynamic cycles, as performance is fundamentally constrained by material properties and the achievable temperature difference [6]. For this reason, thermoelectrics are most competitive in scenarios where heat would otherwise be dissipated and even modest efficiency gains contribute to overall system improvement.

1.2 Introduction to thermoelectric principles

1.2.1 The origin of the Seebeck effect

The Seebeck effect describes the direct conversion of a temperature difference into an electrical voltage [5]. When a temperature gradient is applied along a conductive or semiconductive material, charge carriers at the hot end acquire higher thermal energy than those at the cold end. As a result, their energy distribution becomes spatially non-uniform. Carriers on the hot side, possessing higher average kinetic energy, tend to diffuse toward the colder region. The magnitude of this voltage is proportional to the applied temperature difference and is expressed as

$$\Delta V = S \Delta T \quad (1.1)$$

where S is the Seebeck coefficient. This parameter, therefore, represents the thermoelectric sensitivity of the material.

1.2.2 Power factor and figure of merit

While the Seebeck coefficient determines how much voltage is generated from a temperature gradient, it does not alone describe the overall performance of a thermoelectric material. For practical energy conversion, both the generated voltage and the ability of the material to conduct electrical current must be considered. This leads to the definition of the power factor (PF):

$$\text{PF} = S^2 \sigma \quad (1.2)$$

where S is the Seebeck coefficient and σ is the electrical conductivity. The power factor measures the electrical power that can be extracted from a material per unit temperature

gradient. A high Seebeck coefficient is desirable, but without sufficient electrical conductivity, the generated voltage cannot translate into useful power. Conversely, a highly conductive material with a very small Seebeck coefficient will also produce limited output. Therefore, optimizing thermoelectric performance requires balancing both parameters simultaneously.

In addition, the efficiency of a thermoelectric generator is not determined solely by its electrical properties. Heat transport through the material also plays a fundamental role. If the material conducts heat too fast, their two ends will tend to equilibrate its temperature very fast, ceasing the Seebeck effect. Therefore, the overall thermoelectric performance is quantified by the dimensionless figure of merit – normalizing the PF by the thermal conductivity κ , defined as

$$zT = \frac{S^2 \sigma}{\kappa} T \quad (1.3)$$

where T is the absolute temperature. In principle, $\kappa = \kappa_e + \kappa_l$, where κ_e is the heat transported by the charge carriers and κ_l is the heat transported by the phonon waves in the material. In order to minimize κ_l , crystalline quality of the material can be tuned, whereas κ_e is more affected by the electronic properties of materials.

Since the figure of merit is directly related to the thermal-to-electrical energy conversion by the relation:

$$\eta = \frac{T_h - T_c}{T_h} \left[\frac{\sqrt{1 + zT_{\text{avg}}} - 1}{\sqrt{1 + zT_{\text{avg}}} + \frac{T_c}{T_h}} \right] \quad (1.4)$$

the thermoelectric figure of merit, zT , should be maximized to achieve high conversion efficiency. Here, T_c and T_h are the cold- and hot-side temperatures, respectively, and zT_{avg} the average figure of merit within the temperature extremes.

Overall, tuning zT is the central challenge of thermoelectric research since the transport parameters S , σ , and κ are not independent. Improving one property often affects the others, making the simultaneous optimization of electrical and thermal transport a non-trivial task. Therefore, strategies to enhance zT must consider the intrinsic coupling between these properties.

1.2.3 Intrinsic coupling between Seebeck coefficient and electrical conductivity

The interdependence between the Seebeck coefficient and electrical conductivity originates from their common dependence on charge carrier concentration and band structure. The electrical conductivity of a semiconductor is given by [5]

$$\sigma = n\mu e \quad (1.5)$$

where n is the carrier concentration, μ the carrier mobility, and e the elementary charge. Increasing the carrier concentration (e.g. via doping) generally enhances electrical conductivity, since more charge carriers are available to transport current. However, Seebeck coefficient behaves in the opposite manner. According to Boltzmann transport theory [18], under the assumption of a single parabolic band and energy-independent scattering [19], the Seebeck coefficient for degenerate semiconductors can be approximated by the Mott relation [20], which shows that

$$S \propto m_{\text{DOS}}^* T n^{-2/3} \quad (1.6)$$

where m_{DOS}^* is the density of states effective mass of the charge carriers and T is the absolute temperature. This expression highlights two important aspects. First, the Seebeck coefficient decreases as the carrier concentration increases. Second, it increases with the effective mass of the carriers.

The consequence of this relationship is a fundamental trade-off: increasing n improves electrical conductivity but reduces the Seebeck coefficient. Since the power factor depends on $S^2\sigma$, optimizing thermoelectric performance requires identifying an optimal carrier concentration that balances these competing effects. In addition, the effective mass plays a dual role. A larger effective mass enhances the Seebeck coefficient by increasing the density of electronic states near the Fermi level [21], but it typically reduces mobility, which in turn lowers electrical conductivity. Therefore, both carrier concentration and band structure must be carefully engineered to achieve meaningful improvements in thermoelectric performance.

1.2.4 Beyond the trade-off: effective mass, weighted mobility, and quality factor

Although the Seebeck coefficient and electrical conductivity are intrinsically coupled through carrier concentration and effective mass, this trade-off can be better understood by separating intrinsic band-structure effects from extrinsic doping effects. A key quantity in this context is the effective mass of the charge carriers [21]. The band effective mass m_{band}^* reflects the curvature of the electronic bands: flatter bands correspond to heavier carriers and larger Seebeck coefficients, while more dispersive bands yield higher mobility. However, the Seebeck coefficient does not depend solely on band curvature. In materials with multiple equivalent electronic valleys, the density-of-states effective mass increases according to

$$m_{DOS}^* = N_V^{2/3} m_{band}^* \quad (1.7)$$

where N_V is the valley degeneracy [22]. Increasing band degeneracy enhances the Seebeck coefficient by increasing the density of states near the Fermi level, while mobility remains primarily governed by the band effective mass. These decoupling forms the basis of the band-convergence strategy, where multiple valleys are engineered to lie close in energy in order to enhance thermopower without severely penalizing charge transport. Increasing N_V is one of the few band-structure parameters that can enhance the Seebeck coefficient without proportionally degrading mobility, making band convergence a particularly effective strategy for improving thermoelectric performance.

To evaluate the intrinsic electronic transport independently of carrier concentration, we employ the weighted mobility μ_W [23], defined as

$$\mu_W = \mu \left(\frac{m_{DOS}^*}{m_e} \right)^{3/2} \quad (1.8)$$

where $\mu = \frac{e\tau}{m_{band}^*}$ is the carrier mobility and m_e the electron mass. Unlike the PF, which depends strongly on doping level, μ_W reflects the intrinsic quality of the electronic structure and scattering mechanisms. It therefore allows direct comparison between different compositions and processing routes, even when carrier concentrations differ. Most importantly, μ_W enters directly into the thermoelectric quality factor B [23, 24], which is proportional to the ratio between weighted mobility and lattice thermal conductivity:

$$B \propto \frac{\mu_W}{\kappa_l} \quad (1.9)$$

The quality factor is particularly useful because it determines the maximum achievable zT for a given material within the single-parabolic-band framework. In other words, while the experimentally measured zT depends on the actual carrier concentration, B predicts the upper performance limit that could be reached if the doping was optimally tuned. This makes B a powerful tool to distinguish whether a material is intrinsically limited by its electronic structure (low μ_W) or by phonon transport (high κ_l). Consequently, improving thermoelectric performance requires either enhancing intrinsic electronic transport (higher μ_W , increased band degeneracy) or reducing lattice thermal conductivity—or ideally both.

On top of this, several approaches based on the single-parabolic-band model allow the extraction of m_{DOS}^* and μ_W directly from experimentally measured S , σ , and n , quantities routinely accessible in thermoelectric laboratories [21, 23]. Within the degenerate or near-degenerate regime and assuming a dominant scattering mechanism, this methodology enables rapid evaluation of intrinsic electronic quality and maximum performance potential without requiring detailed band-structure calculations. This methodology avoids the need for detailed band-structure calculations or high-field transport measurements and enables rapid screening of materials based solely on transport data. As a result, intrinsic electronic quality and optimization potential can be evaluated in a consistent and experimentally accessible manner, facilitating comparison across different compositions and processing routes.

1.3 Strategies for Enhancing Thermoelectric Performance

The discussion above has focused primarily on the chemical and crystallographic structural standpoints. However, independent of chemical tuning, microstructural features—such as the degree of disorder, microstrain, grain size, and grain-boundary density—also play a crucial role in determining thermoelectric performance. These parameters can be deliberately engineered to modify both phonon and charge-carrier transport, thereby influencing the figure of merit and the thermoelectric quality factor. In the following sub-sections, selected microstructural strategies for enhancing performance are discussed.

1.3.1 Carrier concentration optimization through doping

Carrier concentration remains one of the most effective parameters for enhancing the power factor, since increasing n directly raises the electrical conductivity and can substantially improve the PF, provided the Seebeck coefficient does not decrease too rapidly [5, 6]. In practice, this requires controlled defect engineering or aliovalent doping to shift the chemical potential toward its optimal position. However, the increase in carrier concentration must be achieved without triggering secondary phase formation or structural decomposition, which could deteriorate transport properties. Moreover, excessive defect incorporation may introduce additional scattering centers, reducing carrier mobility and offsetting the gains in conductivity. Therefore, the goal is not simply to maximize n , but to optimize it in a way that preserves phase stability and maintains sufficiently high mobility (without a significant increase in m_{band}^*), paying a closer look to the figure of merit and quality factor values for each doping configuration.

1.3.2 Chemical disorder and bonding inhomogeneity

Chemical disorder and bonding inhomogeneities, arising from the random occupation of crystallographic sites or from the incorporation of elements with different bonding characteristics, provide an effective structural route to reduce the lattice thermal conductivity κ_l .

Such disorder introduces mass fluctuations, local strain fields, and distortions of the bonding environment, all of which enhance phonon scattering. Because phonons are more sensitive to these perturbations than charge carriers, heat transport can be significantly suppressed while electrical conductivity remains comparatively less affected. At the same time, local lattice distortions may generate measurable microstrain and, in multi-component systems, can even contribute to enhanced thermodynamic stability, as observed in high-entropy materials. Zintl phases and other complex crystal structures are well-known examples in which intrinsic structural complexity and bonding diversity naturally lead to low lattice thermal conductivity [19, 25].

1.3.3 Nanostructuring

Nanostructuring offers an additional pathway to decouple electrical and thermal transport. Interfaces, grain boundaries, and nanoscale inclusions act as strong phonon scattering centers, significantly reducing κ_l [26, 27]. At the same time, properly designed nanostructures can preserve or even enhance electrical transport through mechanisms such as energy filtering, where low-energy carriers are preferentially scattered while high-energy carriers contribute to conduction. This concept is often described as achieving a phonon-glass electron-crystal (PGEC) behavior [27], in which the material blocks heat like a glass but conducts electricity like a crystalline solid.

Together, these approaches illustrate that improving thermoelectric performance is not achieved by modifying a single parameter, but rather by carefully engineering the interplay between carrier concentration, band structure, and phonon transport.

1.4 Thin film thermoelectric generators

Thin-film thermoelectric generators (TF-TEGs) operate on the same fundamental principle as bulk devices and much of the optimization techniques observed so far can also be applied. In a TF-TEG a temperature gradient is applied across p -type and n -type semiconducting elements generates a voltage difference, and when these elements are electrically connected in series and thermally in parallel, the individual voltages add up to produce usable electrical power [28, 29]. In thin-film configurations, thermoelectric materials are deposited as micrometric or sub-micrometric layers onto rigid or flexible substrates and patterned into interconnected legs. Due to the reduced thickness of the active material, the internal electrical resistance depends strongly on geometrical parameters such as leg length, width, and thickness, as well as on the quality of the metal–semiconductor contacts. Consequently, device performance is influenced not only by intrinsic material properties but also by careful geometrical and interfacial optimization [29]. In practical operation, the generated voltage drives current through an external load resistance connected in series with the device. The electrical power delivered to the load depends on the ratio between the internal resistance of the thermoelectric generator and the external load resistance. Maximum power output is achieved under the impedance-matching condition, when the load resistance equals the internal resistance of the device [6].

A key distinction between thin-film and bulk thermoelectric generators lies in heat transport management. In many thin-film systems, the substrate dominates thermal conduction, meaning that only a fraction of the external temperature gradient is effectively established across the thermoelectric layer. As a result, substrate selection, device architecture, contact engineering, and resistance optimization play a central role in determining performance.

1.4.1 Performance Metrics in Thin-Film Thermoelectric Generators

Based on what has just been said above, the PF becomes a more relevant parameter for in TF-TEGs. Since the electrical output power depends directly on the generated voltage and the internal resistance of the device, enhancing Seebeck coefficient and electrical conductivity has a more immediate effect on performance than further reducing lattice thermal conductivity. In other words, thin-film thermoelectric generators often prioritize maximizing electrical transport properties while relying on device architecture and substrate engineering to manage heat flow.

To allow meaningful comparison between devices with different geometries and dimensions, the generated power must be properly normalized. Thin-film generators are commonly evaluated using specific power metrics, such as power density normalized by active volume or surface area, and further divided by the applied temperature gradient [30, 31]. These normalized quantities enable geometry-independent comparison and provide a more accurate representation of intrinsic device performance. Raw power output alone is insufficient, as it depends strongly on device size, number of legs, and measurement conditions.

1.4.2 Fabrication Strategies for Thin-Film Thermoelectric Generators

The performance of thin-film thermoelectric generators depends not only on the intrinsic transport properties of the material, but also strongly on the synthesis route and deposition technique employed [32]. In thin films, microstructure, phase composition, density, and grain connectivity directly influence electrical conductivity and internal resistance, which in turn determine the achievable power output. Consequently, fabrication strategies must be designed to ensure homogeneity, high density, controlled thickness, and optimized interfaces.

Low-cost techniques such as spin coating, painting, and doctor-blade deposition have been widely explored due to their simplicity and scalability. However, these approaches often result in porous films with limited control over thickness and crystallographic orientation, leading to reduced electrical connectivity and lower device performance [30, 33]. In contrast, physical vapor deposition (PVD) methods, including thermal evaporation and magnetron sputtering, provide superior control over film uniformity, thickness, and density [30, 34]. These techniques allow precise tuning of deposition parameters, improving grain connectivity and reducing internal resistance, which are critical for maximizing the power factor in thin-film devices.

Furthermore, fabrication methods influence not only phase composition but also film thickness and density, which directly affect normalized power output metrics [30]. As highlighted in comparative studies, advanced deposition and patterning techniques can lead to order-of-magnitude improvements in power density relative to ink-based or solution-processed films. Therefore, in thin film thermoelectrics, synthesis optimization and microstructural engineering are as important as intrinsic material selection.

1.5 Literature review and material selection

Among earth-abundant and environmentally benign thermoelectric materials, kesterite compounds such as $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) have attracted considerable attention due to their intrinsically low lattice thermal conductivity [35–37]. Their crystal

structures exhibit strong chemical disorder, either through cation site mixing (Cu/Zn substitutions) or through anion alloying in the $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ solid solution, both of which enhance phonon scattering [35, 36, 38–40]. Disorder-induced suppression of lattice thermal conductivity has been attributed to reduced phonon group velocities and the presence of low-lying optical modes [36, 41]. From a theoretical perspective, lattice thermal conductivity scales with phonon velocity and lifetime, which are directly linked to elastic stiffness and atomic mass. Therefore, heavier atoms and softer bonding environments typically promote lower thermal conductivity [42, 43]. While Se-containing kesterites are expected to exhibit reduced κ_l due to mass effects, experimental results on polycrystalline samples reveal complex trends, suggesting that microstructural disorder and processing conditions strongly influence phonon transport. Overall, CZTSSe compounds provide a favorable platform for bulk thermoelectric applications where minimizing lattice thermal conductivity remains a primary objective.

In contrast, for thin-film thermoelectric generators, where PF optimization becomes more critical than intrinsic κ_l reduction, the Cu–Fe–S system emerges as a promising candidate. Chalcopyrite CuFeS_2 (CFS) exhibits a high Seebeck coefficient ($\sim -480 \mu\text{V K}^{-1}$) combined with appreciable electrical conductivity and tunable carrier type via stoichiometry control [44]. Although its bulk thermal conductivity is relatively high [45], this limitation is less restrictive in thin-film configurations, where substrate-dominated heat transport prevails. Furthermore, the Cu–Fe–S phase diagram allows compositional engineering through binary–ternary phase mixtures (e.g., Cu_2S and FeS_2), which have been shown to enhance the power factor via improved electrical connectivity and energy-filtering effects [31, 46–48]. Thin-film fabrication techniques such as physical vapor deposition provide precise control over phase composition, density, and microstructure, enabling further performance enhancement. For these reasons, CuFeS_2 -based systems represent a suitable choice for thin-film thermoelectric devices, while CZTSSe compounds are better positioned for bulk applications targeting low lattice thermal conductivity.

1.6 Scope and Objectives of the Thesis

This doctoral work aims to investigate environmentally friendly chalcogenide-based thermoelectric materials with Zinc-blende-derived structures, focusing on $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ (CZTSSe) and CuFeS_2 (CFS). These materials are composed of earth-abundant and low-toxicity elements and exhibit structural versatility that enables precise control of defect chemistry and chemical disorder. The scope of this research encompasses the synthesis of both bulk and thin-film thermoelectric materials, their structural and transport characterization, and the fabrication of prototype thermoelectric devices, with the objective of correlating crystal structure, microstructure, and electronic properties to thermoelectric performance.

For the CZTSSe system, the primary objective is to understand phase stability, disorder mechanisms, and their impact on transport properties. This includes stabilizing metastable phases via high-energy ball milling, investigating stacking faults and structural transitions through advanced X-ray diffraction modeling and *ab initio* simulations, and studying the reversible order–disorder behavior of the kesterite phase. Additionally, compositional engineering through Cu/Zn substitution and chalcogen tuning (S/Se ratio) is employed to control carrier concentration, band structure, and lattice thermal conductivity, with the aim of optimizing thermoelectric performance while elucidating structure–property relationships.

For thin-film thermoelectric devices, the objective is to develop scalable fabrication routes

that enhance film density, optimal phase composition, and interfacial connectivity. In the CuFeS_2 -based system, a multi-step synthesis approach combining ball milling, thermal evaporation, and sulfurization is explored to engineer phase composition and microstructure. Particular emphasis is placed on understanding how secondary sulfide phases and grain connectivity influence electronic transport and power density. Overall, this work seeks to advance sustainable thermoelectric energy conversion by integrating materials design, structural modeling, and device-level optimization in Zinc-blende-derived chalcogenide systems.

1.7 Summary

The work combines theoretical modeling, microstructural engineering, and device-level optimization to address the intrinsic coupling between electrical and thermal transport properties discussed in the previous sections.

This chapter, Chapter 1, provides the theoretical framework and contextual background of thermoelectricity, including the fundamental transport mechanisms, performance metrics, and material optimization strategies. Chapter 2 presents the structural and thermodynamic investigation of kesterite-related systems as reported in Ref. [49]. This study establishes the crystallographic and phase-stability foundations necessary to understand disorder, cation substitution, and microstructural effects in Cu-based chalcogenides.

Chapter 3 focuses on the bulk thermoelectric properties of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{Sn}_x\text{Se}_{4-x}$ (CZTSSe) compounds. Through a combination of ball milling, cold pressing, and spark plasma sintering, the interplay between chemical disorder, microstructure, grain connectivity, and anion substitution is systematically investigated. Density functional theory calculations and transport measurements reveal how intrinsic bonding softness and extrinsic microstructural effects compete in determining lattice thermal conductivity. The work clarifies the anomalous κ_l trends observed in polycrystalline samples and demonstrates that controlled disorder and microstructural engineering enable convergence of thermoelectric performance across the CZTSSe series, reaching peak values of $zT \approx 0.5$ at elevated temperatures.

Chapter 4 transitions to thin-film thermoelectric generators, where device architecture and power factor optimization become central. The study reported in Ref. [50] investigates the fabrication and performance of thin-film thermoelectric devices, emphasizing geometry, normalization metrics, and deposition strategies.

Chapter 5 further develops thin-film thermoelectrics through the Cu–Fe–S system, as detailed in ACS Applied Electronic Materials [31]. By exploiting phase regulation and compositional engineering within the $\text{CuFeS}_2 - \text{Cu}_2\text{S} - \text{FeS}_2$ system, enhanced power factor and improved device performance are achieved. The work highlights the role of microstructural control and physical vapor deposition techniques in maximizing thin-film thermoelectric output.

Finally, Chapter 6 summarizes the main findings and outlines future research directions, particularly regarding scalable sustainable thermoelectric materials, interface engineering, and advanced thin-film architecture. Together, the chapters demonstrate how thermoelectric performance can be optimized through complementary strategies in bulk and thin-film systems: minimizing lattice thermal conductivity in kesterite-based bulk materials, and maximizing power factor and device engineering in Cu–Fe–S thin-film generators. This dual approach provides a comprehensive perspective on sustainable thermoelectric material design.

Chapter 2

Investigating the cubic-to-tetragonal phase transition of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ solid solutions

Abstract

The $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ ($0 \leq x \leq 4$; $y = 0, 0.125$) system is an earth-abundant, non-toxic chalcogenide with tunable polymorphism and chemical disorder, making it a promising candidate for sustainable thermoelectric and photovoltaic applications. Recent stabilization of cubic sphalerite $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_4$ and $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnSe}_4$ via mechanochemical synthesis has demonstrated enhanced thermoelectric performance attributed to low-energy optical phonon modes and topological conduction pathways for charge carriers. In this study, we explore the role of anion substitution and Cu-induced CuZn antisite disorder in stabilizing the cubic phase and driving its transformation to the partially disordered tetragonal kesterite structure at high temperature. A combination of X-ray diffraction, Raman spectroscopy, and first-principles simulations (DFT, DFPT, AIMD) reveals that Cu-rich compositions deviate from Vegard's law, show increased stacking fault density, and exhibit pronounced distortion in the tetrahedral motifs. AIMD results indicate that the higher symmetry of the cubic phase permits a broad distribution of tetrahedral configurations, stabilizing disorder and stacking faults. Upon thermal activation, entropy favors the emergence of more stable S/Se – Cu_3Sn , S/Se – Cu_2ZnSn , and S/Se – CuZn_2Sn motifs, stabilizing the kesterite phase with a reduced quantity of microstructural defects. Notably, in compositions close to $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_2\text{Se}_2$, classified as high-entropy alloys, Baur bond and angle distortions peak, suggesting structural robustness despite high defect concentrations. This work provides a fundamental understanding of microstructural disorder from the atomic motif level, offering valuable guidelines for tuning phase stability and properties in $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ kesterite and sphalerite materials.

2.1 Introduction

$\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ (CZTSSe) is a complex multinary chalcogenide that crystallizes in zinc blende-derived structures [51, 52]. Owing to its tuneable composition and favourable electronic properties, CZTSSe has attracted significant interest for applications in batteries [53, 54], thermoelectrics (TE) [33, 55], and photovoltaics (PV) [56–58], together with other Cu-based chalcogenide materials [34, 41, 50, 59, 60]. Composed of earth-abundant and low-toxicity elements, it presents an environmentally friendly alternative to Te-based TE materials [55], and a cost-effective substitute for $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based thin-film PV technologies [61], due to its high absorption coefficient ($\sim 10^4 \text{ cm}^{-1}$) and optimal bandgap [62, 63]. In TE applications, its disordered cubic sphalerite phase is of particular interest for its low-lying optical phonon modes, which lead to ultralow thermal conductivity [35, 36]. Additionally, the S–Se solid solution in the kesterite structure enhances chemical disorder, facilitating bandgap tuning—an advantageous property for PV devices [57, 63, 64].

The CZTSSe system exhibits a rich polymorphism, as illustrated in Figure 2.1. The ordered tetragonal $I\bar{4}$ structure is composed of S/Se– Cu_2ZnSn tetrahedral motifs, in which the anion (S or Se) occupies the centre of the tetrahedron and the cations (Cu, Zn, and Sn) are positioned at its corners [65]. Upon annealing, S/Se– Cu_3Sn and S/Se– CuSnZn_2 motifs start to form, promoting a second-order phase transformation [65]. This transition is marked by the gradual randomisation of Cu and Zn cations over the Wyckoff 4d sites within the kesterite lattice, forming the so-called partially disordered $I\bar{4}2m$ tetragonal phase [55, 66]. With further increase in disorder, a cubic sphalerite-like ($F\bar{4}3m$) structure forms, typically stabilised at elevated temperatures ($\sim 1100 \text{ K}$) [66]. This cubic structure can also be synthesized at room temperature via bottom-up approaches such as high-energy ball milling, forming a metastable phase that undergoes an irreversible phase transition into the fully and partially disordered tetragonal phases upon annealing, eventually stabilising as an ordered tetragonal phase when returned to room temperature [35, 67, 68].

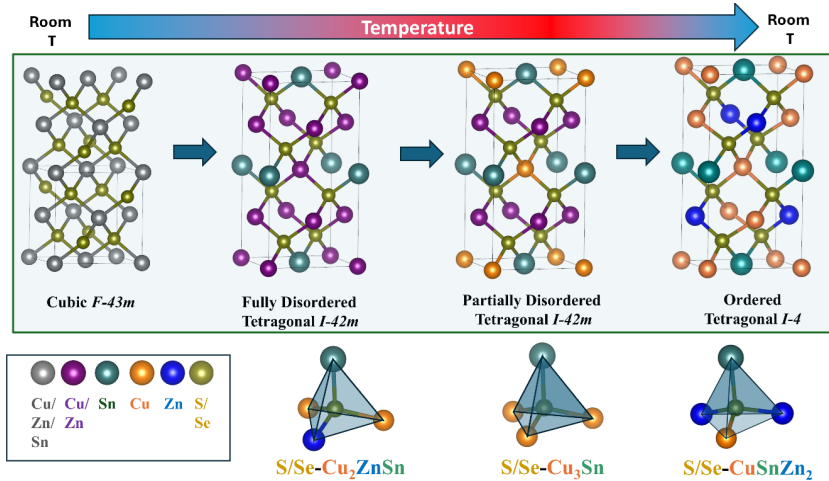


Figure 2.1: Schematic representation of the polymorphic structures in the CZTSSe system, including the ordered kesterite and disordered sphalerite phases.

The significant cation disorder in CZTSSe leads to various possible arrangements of S/Se– $\text{Cu}_i\text{Sn}_j\text{Zn}_{4-i-j}$ tetrahedral motifs that tend to form few-nanometer clusters [65]. These induce compositional fluctuations that result in Cu-rich/Zn-poor and Cu-poor/Zn-rich re-

gions within the crystalline domain. Such microstructural features can be highly desirable for TE applications, as in some systems they have been associated with thermopower enhancement via energy filtering and thermal conductivity suppression via phonon scattering [69]. Furthermore, the electrical conductivity can be improved by increasing the Cu content (i.e., increasing y in $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$), which promotes the formation of S/Se–Cu₃Sn conductive motifs, known to locally narrow the bandgap, instead of the more insulating S/Se–CuSnZn₂ tetrahedral configurations [65, 70, 71].

Besides motif clustering, stacking faults (SFs) also arise from the ball-milling synthesis process and are credited with stabilising the fully disordered sphalerite cubic phase for the CZTS compound [55, 67, 70]. Analysis of the Debye–Waller (DW) coefficients, which are proportional to the mean squared displacement (MSD) of atoms, revealed that the cubic defect structure accommodates larger MSDs, as evidenced by a static component of the DW coefficients, leading to even lower thermal conductivity [37]. Upon annealing, SF disorder is reduced, promoting the ordering of Sn atoms into Wyckoff 2a positions and forming the disordered tetragonal kesterite structure, accompanied by a reduction in MSD [67]. While this mechanism has been extensively studied in S-based materials, it remains largely unexplored for the broader CZTSSe system and its Cu-rich compositions.

This study reports, for the first time, the room-temperature synthesis of the full sphalerite-type $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ ($0 \leq x \leq 4$, $y = 0$ and 0.125) solid solution series and investigates the thermally induced phase transition into the tetragonal kesterite structure through a combination of experimental techniques and first-principles simulations. In situ high-temperature X-ray diffraction (HTXRD) enables real-time monitoring of structural and microstructural evolution, particularly the temperature-dependent behaviour of stacking fault disorder. Deviations from Vegard’s law [52] in both lattice parameters and Raman-active modes are observed for Cu-rich samples ($y = 0.125$), as confirmed by XRD and Raman spectroscopy. Furthermore, *ab initio* molecular dynamics (AIMD) simulations reveal pronounced local bond and angular distortions within tetrahedral units, especially in the compositional range $1 \leq x \leq 3$, where configurational entropy is maximised. These findings provide a comprehensive framework for understanding defect formation and phase transition mechanisms in CZTSSe, offering valuable insights for controlled synthesis and optimisation of these materials.

2.2 Materials and Methods

2.2.1 Materials

Elemental powders of Cu ($< 75 \mu\text{m}$, 99%), Zn (purum, 99%), Sn (puriss, 99%), S (puris, 98%), and Se (purum, 99.5%) supplied by Sigma-Aldrich were used for the synthesis. All chemical reagents employed in this study were of analytical grade and were used as received without further purification.

2.2.2 Synthesis Details

The powders were mechanically reacted in a planetary mill (Fritsch P4 Pulverisette) using an 80 mL WC vial containing 27 WC balls (12 mm diameter) for 120 min. The milling conditions were a jar rotation speed of $\omega = -600$ rpm, a main disk revolution speed of $\Omega = 310$ rpm, and a ball-to-powder mass ratio of 100:1.

2.2.3 Characterization

X-ray diffraction (XRD) patterns were collected using a Stadi P diffractometer (Stoe) in Debye–Scherrer geometry, employing $\text{Ag K}\alpha_1$ radiation from a $\text{Ge}(111)$ Johann-type monochromator and a triple Mythen 1K detector array (Dectris). Samples were sealed under argon in 0.3 mm quartz capillaries (Hilgenberg glass) and spun during the measurements. Heating was carried out using a GSB 1300 gas blower (FMB Oxford) at a rate of 5 K min^{-1} . High-temperature XRD (HTXRD) measurements were performed from room temperature up to 773 K in steps of 50 K, with a 10 min isothermal dwell before each acquisition to ensure thermal equilibration and a scan time of 2 h per pattern. To improve precision and counting statistics, $\text{Cu}_2\text{ZnSnSe}_4$ samples were diluted with 50 wt% quartz and measured using a single-Mythen configuration for 8 h in order to reduce absorption effects. Reproducibility was verified using a Bruker D8 Discover diffractometer in Bragg–Brentano geometry with $\text{Co K}\alpha$ radiation ($\lambda = 1.78897 \text{ \AA}$).

Raman spectra were collected using a LabRAM Aramis spectrometer (Horiba Jobin-Yvon) equipped with an optical microscope, a $100\times$ objective, and a 633 nm laser source. Alternatively, an Integra NT-MDT instrument with a similar excitation source was used. Raman data analysis, including baseline subtraction and peak fitting with Lorentzian functions, was carried out using Origin(Pro) 2023b (OriginLab Corporation, Northampton, MA, USA).

Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC822e instrument with a heating rate of 5 K min^{-1} from room temperature to 773 K under sealed argon atmosphere.

2.2.4 Simulation Details

Density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations were performed using the Vienna *Ab initio* Simulation Package (VASP) [72, 73]. Exchange–correlation effects were described within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional [74], together with scalar-relativistic PBEsol pseudopotentials [75]. For stacking-fault calculations, a plane-wave cutoff energy of 400 eV and Gaussian smearing of 0.01 eV were employed. Cubic and disordered tetragonal polymorphs of $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ and $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ were modeled using 256-atom supercells while preserving stoichiometry and introducing randomized cation disorder. Brillouin-zone sampling for geometry optimization and self-consistent field calculations was performed using a Γ -centered $2 \times 2 \times 2$ Monkhorst–Pack k -point mesh. Structural relaxations were carried out until the Hellmann–Feynman forces on all atoms were below $10^{-5} \text{ eV/\AA}$.

AIMD simulations were carried out at 300 and 700 K within the NVT ensemble using a Nosé–Hoover thermostat. A time step of 2 fs was used for 4000 steps, corresponding to a total simulation time of 8 ps. For these AIMD runs, only the Γ -point was used to sample the supercell Brillouin zone, and the electronic convergence threshold was set to 10^{-5} eV .

Density functional perturbation theory (DFPT) calculations were performed for the $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ system using a 64-atom supercell. First, a full volume relaxation was carried out, allowing both lattice parameters and atomic positions to vary. This was followed by a fixed-volume relaxation in which only the atomic coordinates were optimized, using a plane-wave cutoff energy of 450 eV. Phonon density-of-states calculations were performed using the Phonopy package [76] with a Γ -centered $4 \times 4 \times 4$ k -point mesh and an electronic convergence criterion of 10^{-8} eV .

2.3 Results and Discussion

2.3.1 Structural and microstructural analysis

The XRD patterns obtained for the as-milled $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ powders are shown in Figure 2.2(a) and (b) for $y = 0$ and 0.125, respectively. In this case, the mechanical alloying promoted the formation of the pure sphalerite phase ($F\bar{4}3m$) [35, 37]. With the addition of S in the structure (increasing x value), peaks are shifted to higher 2θ values, corresponding to a decrease in the lattice parameter a due to the smaller atomic radius of S (1.84 Å) compared to Se (1.98 Å). For a perfect solid solution, i.e., a random distribution of S and Se in the sphalerite matrix, a should increase linearly with x , respecting Vegard's law [52]. For cubic $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ (with $y = 0$), the lattice parameter is linear and follows: $a(\text{Å}) = -0.255(1)x + 5.691(1)$, as shown in Figure 2.2(c). The slope of this curve is between 0.005 Å and 0.03 Å lower than what is reported for the lattice parameter a of the ordered kesterite structure [52, 77, 78]. This is credited to the higher quantity of defects and grain boundaries in the cubic phase compared to the reported tetragonal structures [52, 77, 78], which can accommodate the strain caused by the larger anion, thereby reducing its impact on the structure size. In addition, the SF formation energies should increase linearly with x as estimated by the DFT simulations, later shown in Table 2.1. For $y = 0$, this trend is observed in Figure 2.2(e), meaning that the impact of the anion substitution in the lattice will be homogeneous for the entire x series, and no deviation from the Vegard law is expected.

However, Vegard's law does not hold for Cu-doped CZTSSe [$y = 0.125$, see Figure 2.2(d)], with deviations from the linear relation observed in the $1 \leq x \leq 3$ range. With Cu surplus in the structure, more Cu-rich tetrahedral motifs form, and this is believed to promote an increase in local motif clustering and faulting, thereby favouring structural inhomogeneities in a non-linear fashion [65]. SFs are also known to introduce local strain fields, which can contract or expand interplanar distances, also shifting the average lattice parameter in a non-Vegard fashion. Indeed, we observe a higher SF probability for $y = 0.125$ in the $1 \leq x \leq 3$ region compared to $y = 0$ system [vide Figure 2.2(f)], corroborating this fact.

One of the key indicators of the presence of SFs for sphalerite CZTSSe is the asymmetric broadening of the 111 and 200 diffraction line profiles [55, 67], which is generally accompanied by a misfit in the intensity of the latter by inappropriate modelling of the peak shape. In this case, they are modelled as twin faults in the [111] direction (see representation of SF in the centre of Figure 2.2). CZTSe materials exhibit reduced intensity for the 200 reflections due to a combination of terms in the X-ray structure factor. Consequently, accurate modelling of the 111 asymmetry, which reflects the only SF signature in the pattern, requires longer exposure times and sample dilution to mitigate X-ray absorption effects. To achieve this dilution, 50 wt% borosilicate glass was mixed with the sample powder. The profile modelling is shown in Figure 2.3(a) for CZTSe. A grid search was performed over a range of SF probabilities (3% to 10%), with the corresponding R_{wp} agreement factors plotted in Figure 2.3(b). The R_{wp} minimum points to an SF probability of 6.7(1)% for CZTSe. With the whole powder pattern modelling (WPPM) [79, 80] the crystallite size (CS) distribution could also be retrieved, showing an average of 43 nm and a standard deviation of 19 nm by considering a log-normal size distribution (Figure 2.3(c)).

In addition to faulting, microstrain (MS) features are present in the material, with values reported in Figure 2.2(e) and (f) for $y = 0$ and 0.125, respectively. The MS was modelled with a Voigt profile function, with integral breadths proportional to $\tan(\theta)$ according to the Stokes & Wilson formalism [81–83]. MS corresponds to a Gaussian distribution of

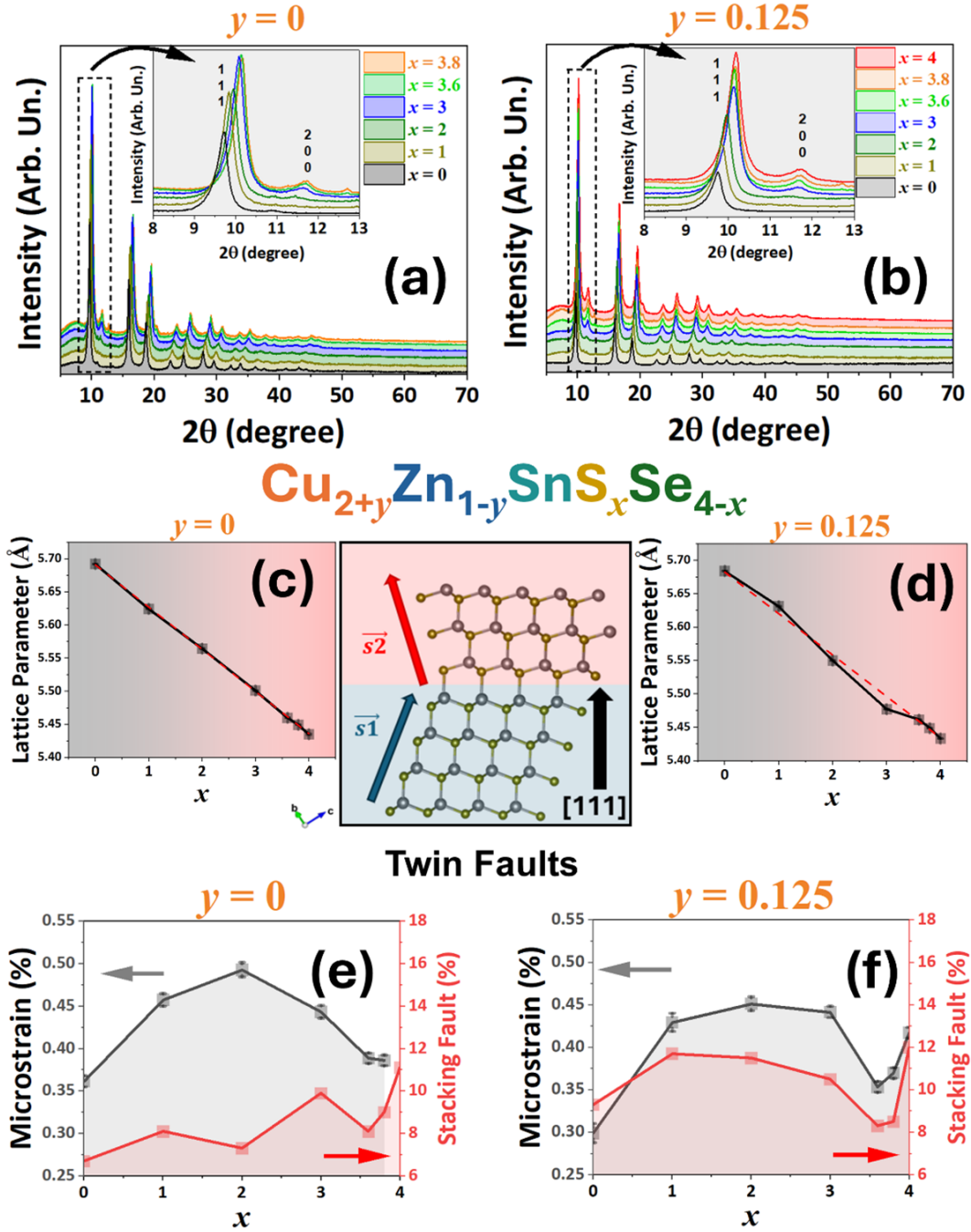


Figure 2.2: X-ray diffraction (XRD) patterns of the $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ systems for $0 \leq x \leq 4$ with (a) $y = 0$ and (b) $y = 0.125$. Corresponding lattice parameters obtained from Rietveld refinement are shown in (c) for $y = 0$ and (d) for $y = 0.125$. Values for $\text{Cu}_2\text{ZnSnS}_4$ were retrieved from [55]. Microstrain and stacking fault probability as a function of composition are presented in (e) for $y = 0$ and (f) for $y = 0.125$. The twin fault mechanism is represented in the center for the $[111]$ direction.

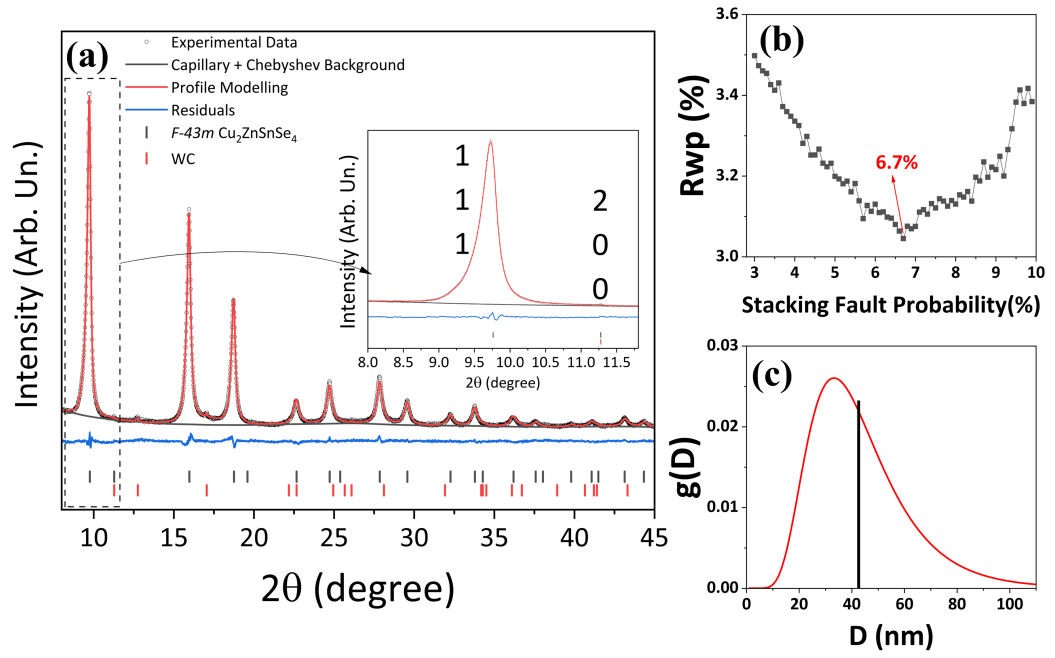


Figure 2.3: Stacking Fault modelling of $\text{Cu}_2\text{ZnSnSe}_4$. (a) XRD pattern and profile modelling. Dots represent the experimental data, red lines the profile modelling, blue lines the residuals, and black the background modelling. The black and red tick markers represent the Miller indices of the $F\bar{4}3m$ $\text{Cu}_2\text{ZnSnSe}_4$ phase and WC, respectively. (b) R_{wp} versus stacking fault probability and (c) real diameter distribution (D) retrieved from the WPPM modelling for the CS.

lattice parameters around a mean position and directly reflects the degree of structural disorder of the material. Indeed, with the increase of the anion disorder, MS reaches its maximum value at $x = 2$, credited to the higher degree of configurational disorder for both doped and undoped systems (see Figure 2.2(e) and (f)). In addition, this categorizes $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_2\text{Se}_2$ as a high-entropy alloy, being composed of five different elements with atomic proportions between 5% and 35% each, and shows enhanced stability since it bears a higher quantity of defects [84, 85]. The degree of disorder is also observed in the cation site. If doped and undoped systems are compared in Figure 2.2(e) and (f), the former shows lower MS due to the lower number of configurations possible for the cations in the doped samples.

The local lattice dynamics of the CZTSSe system can be further investigated via Raman spectroscopy, with spectra shown in Figure 2.4(a) and (b) for $y = 0$ and 0.125. Since anions have four neighboring cations in tetrahedral coordination, cation disorder in the sphalerite cubic phase exhibits a characteristic peak splitting in the Raman spectrum when compared to the kesterite phase [86]. These peaks, however, strongly overlap, [68, 86] especially due to significant microstructure-driven peak broadening. Therefore, the following analysis will only focus on two dominant vibrational modes associated with S and Se, corresponding to the kesterite A modes.

With the addition of Se into the structure, the characteristic Se-Cation vibrational modes appear at around 226 cm^{-1} , and shift towards lower wavenumbers for increasing Se content (lower x). At the same time, the intensity of Se bonding peaks increases, reaching a similar intensity as S peaks when $x = 2$. This information corroborates the fact that the added Se anion is incorporated into the structure and without forming secondary phases, which are indeed undetected with XRD. Vegard’s law for the Cation-S and Cation-Se peaks is plotted in Figure 2.4(c) and (d) for $y = 0$ and $y = 0.125$, respectively. Fits of Raman spectra are reported in Appendix A, Supplementary Note A.1. For $y = 0$, a conventional linear trend is observed, corresponding to $\omega\text{ (cm}^{-1}\text{)} = 50(7)x + 186(3)$ for the cation-Se bonding and $\omega\text{ (cm}^{-1}\text{)} = 13(1)x + 318(1)$ for the cation-S bonding. A linear relationship indicates a typical two-mode Raman band evolution as a function of composition, i.e., the vibrational characteristics of the S tetrahedral motifs behave independently of the Se motifs [52, 77, 87, 88].

However, a complete deviation from the linear trend is observed for the Cu-doped system for both Se and S-Cation peaks (see Figure 2.4(d)). This deviation was confirmed by remeasuring with a different instrument, discarding the possibility of phase decomposition during the experiment due to the laser energy (see Figures A.6 and A.7 in Appendix A, Supplementary Note A.1). A possible explanation is that the two-mode model is not valid for the Cu-doped samples. The additional Cu in the structure forms a complex Cu-rich tetrahedral network, as shown later in Figure 2.10(a), adding further complexity to the phonon vibrational modes. Unfortunately, peak overlapping prevents separating the Raman peaks corresponding to every type of bonding. Nevertheless, Raman analysis corroborates the deviation from Vegard’s law observed with XRD and further highlights that this is especially related to S-cation bonds, as these deviate the most from the linear relation. DFPT simulations (Figure A.8) were employed to investigate the phonon density of states of the CZTSSe system, but the main optical modes do not indicate a significant trend deviation. Therefore, we can conclude that the non-Vegard relationship for the Raman modes stems from microstructural effects rather than their bonding and structural characteristics.

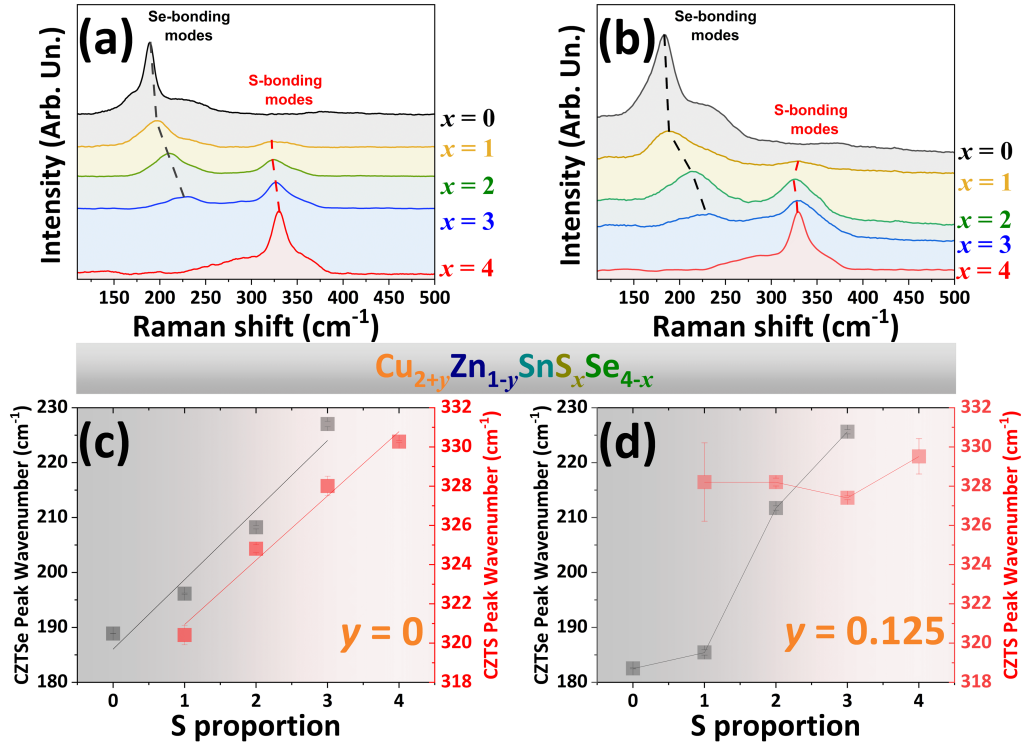


Figure 2.4: Raman spectra of the $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ system for (a) $y = 0$ and (b) $y = 0.125$. The corresponding peak positions of the main Se-cation and S-cation vibrational modes are shown for (c) $y = 0$ and (d) $y = 0.125$.

2.3.2 Temperature-dependent analysis

The microstructural characteristics of the CZTSSe system also affect its phase transformation. Upon annealing, the solid-solid phase transition from cubic Sphalerite into the fully disordered tetragonal phase occurs by the segregation of the Sn cations with the healing of microstructural defects and stacking faults.[67] A partially disordered tetragonal kesterite ($I\bar{4}2m$) phase is stabilised upon further annealing, with Cu and Zn atoms randomly occupying the 4a Wyckoff positions, as schematically illustrated in Figure 2.1.[55, 67] To estimate the phase transition temperature for each composition, in situ HTXRD measurements were conducted. The corresponding powder patterns, recorded from room temperature up to 723 K, are presented in Figure 2.5(a) for a demonstrative case of $\text{Cu}_2\text{ZnSnSe}_3\text{S}_1$. In Appendix A, Supplementary Note A.2, the patterns for the whole $y = 0$ series are shown. With annealing, the diffraction peaks become sharper, indicating CS growth and healing of other microstructural defects. In addition, the superstructure peaks of the partially disordered kesterite phase appear in the pattern, indicated by green thick markers in Figure 2.5(a). The onset temperature for this phase transition is represented in Figure 2.5(b) for all the compositions studied (marked by the green area). In general, after the initiation of the phase transition, the lattice parameters increase more quickly with temperature. The only exception is the $\text{Cu}_2\text{ZnSnSe}_4$ sample, which presents a negative thermal expansion. For this stoichiometry, we can observe that the onset of a negative thermal expansion is accompanied by stacking fault healing at around 473 K, see Figure 2.5(c). The reason behind this phenomenon is not clear, and we detect a concurrent formation of Cu_2Se at 673 K (see Figure A.9 in Appendix A, Supplementary Note A.2). For $x > 0$, the cubic-to-tetragonal onset temperature is around 650 K, with positive thermal expansion in the entire range and no formation of the Cu_2Se or Cu_2S phases. Therefore, the nature of the phase transition from cubic to tetragonal is different for the full-Se compound.

The different behaviour of the full-Se compound is also observed for the $y = 0.125$ CZTSSe system, as shown by the HTXRD analysis (details in Figure 2.6). The tetragonal phase formation is observed around 673 K for almost all the compositions, due to the emergence of superstructure peaks (highlighted in green in Figure 2.6(a)). A negative thermal expansion is present for $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnSe}_4$ just before the phase transition (see Figure 2.6(b)), similar to the $y = 0$ case, though only minor SF healing at 473 K is detected in this case (shown in Figure 2.6(c)). The striking difference compared to the $y = 0$ system is that the cation and anion DW parameters do not abruptly increase at the phase transition (see Figure 2.6(d) and (e), respectively), which will be investigated in more detail in the following section (vide Figure 2.8).

According to Schorr et al.,[66] the cubic phase forms due to increased entropy achieved at elevated temperatures (~ 1139 K). Therefore, the cubic-to-tetragonal transition observed in our case is primarily driven by the metastable nature of the cubic phase at room temperature. Upon annealing, this transition occurs predominantly through a displacive shift of the anion substructure rather than an anti-site reordering of cations.[66] Indeed, the cations order themselves after the phase transition, meaning that Cu and Zn atoms will exhibit significantly greater mobility, leading to an increase in Debye-Waller (DW) coefficients after the phase change. This behaviour is evident in Figure 2.5(d), where a notable increase in cation DW modulus indicates the onset of the phase transition around 623 K for most of the compositions. In contrast, the DW coefficients for anions, shown in Figure 2.5(e), remain largely unchanged after the transition, presenting a smooth increasing trend due to the increase in temperature. This suggests that S and Se anions do not form SSe or SeS antisites. If it should happen, the DW coefficients would increase after the phase transition,

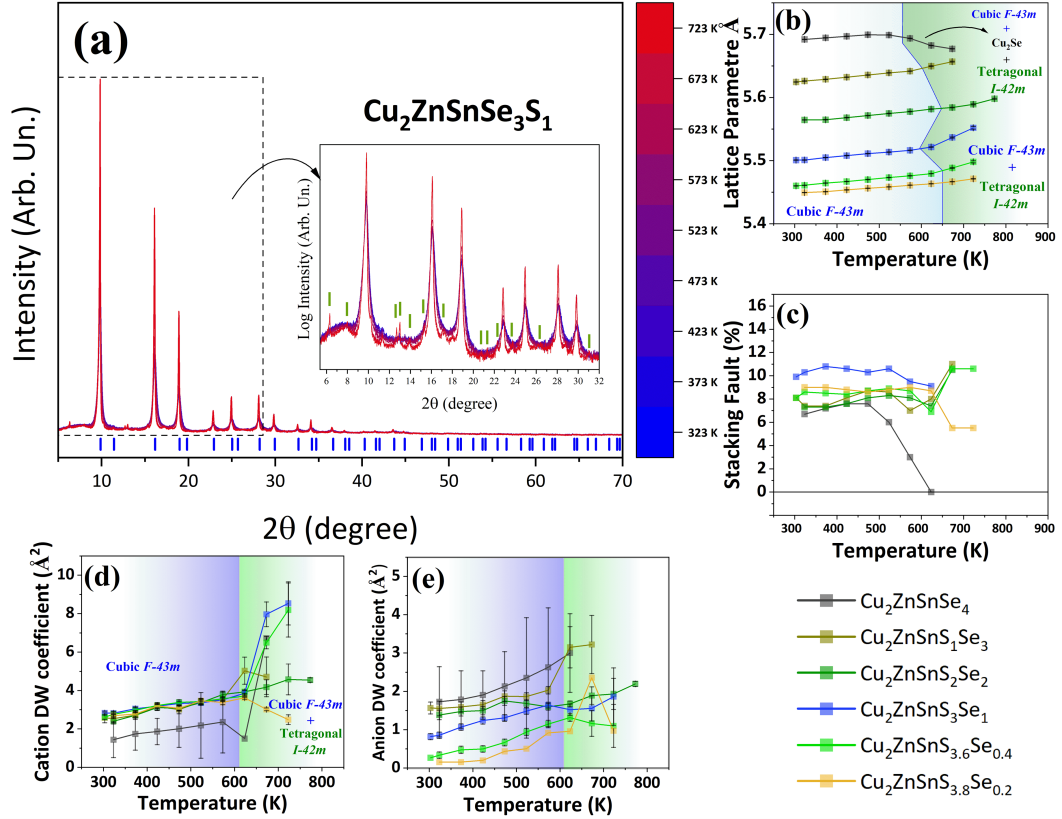


Figure 2.5: (a) In situ HTXRD of the $\text{Cu}_2\text{ZnSnSe}_3\text{S}_1$ sample collected using $\text{AgK}\alpha$ radiation. The blue markers represent the peak positions of the cubic structure, while in the inset, the green thick markers represent the positions of superstructure peaks of the tetragonal phase. The colour scale represents the temperature at which the sample was measured. (b) Lattice parameters of the Sphalerite cubic phase with temperature. The blue area represents the presence of the cubic phase, and the green area the modelling of tetragonal + cubic. (c) Stacking fault probability. (d) DW coefficients for the cations Cu, Zn, and Sn and (e) for the anions S and Se.

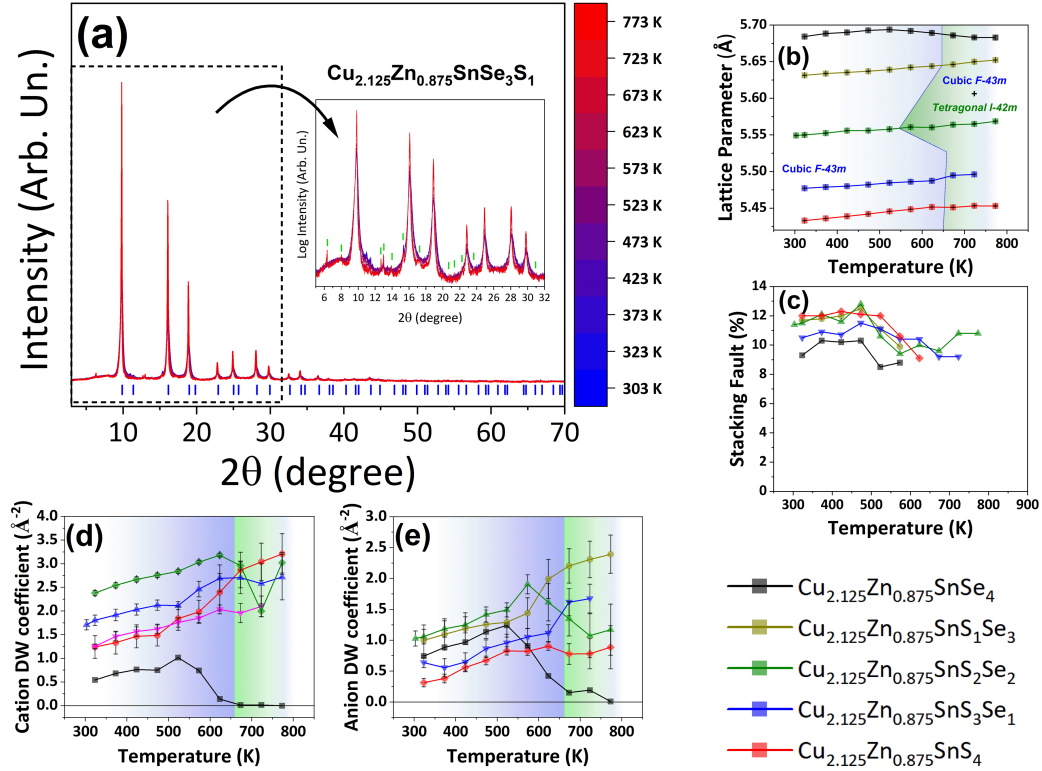


Figure 2.6: (a) In situ HTXRD of the $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnSe}_3\text{S}_1$ sample collected using $\text{AgK}\alpha$ radiation. The blue markers represent the peak positions of the cubic structure, while in the inset, the green thick markers represent the superstructure peaks of the tetragonal phase. The colour scale represents the temperature at which the sample was measured. (b) Lattice parameters of the Sphalerite cubic phase with temperature. The blue area represents the presence of the cubic phase, and the green area the modelling of tetragonal + cubic. (c) Stacking fault probability. (d) DW coefficients for the cations Cu, Zn, and Sn and (e) for the anions S and Se.

like the cations. Therefore, the dynamic behaviour of the anions, which is related to their bonding with neighbouring atoms, remains unaffected. This supports the conclusion that the cubic-to-tetragonal phase transition is driven by the static displacement of anion sites, as reported for CZTS by Schorr et al. [66], rather than by their dynamic behaviour. For the Cu-doped CZTSSe structure, a smoother change in the DW values is observed for the cations. This may be attributed to the lower configurational entropy of the doped structure, i.e., there are fewer ways to arrange the tetrahedral motifs compared to the stoichiometric CZTSSe, meaning that the cation displacements may be reduced even after transition.

DSC measurements were performed to get phase transformation temperatures for the complete Cu-doped CZTSSe series, especially to identify if the Sn ordering and stacking fault healing mechanism already commented on in previous work from some of the authors.[67] The cubic-to-tetragonal phase transition is visible by the increase in heat flow in region 5 in the DSC plots of Figure 2.7. They roughly agree with the temperatures observed for the phase transition of Figure 2.6(b) obtained via HTXRD. Two exothermal peaks are observed before the cubic-to-tetragonal phase transition, labelled as peaks 3 and 4 in Figure 2.7. It is also visible that with the increasing addition of Se into the structure, these peaks shift to a lower temperature. Their source can be attributed to two phenomena: (i) the healing of the stacking faults and microstrain, and (ii) the ordering of the Sn atoms in the 2a Wyckoff positions.[67, 86] As shown for $\text{Cu}_2\text{ZnSnS}_4$ in Ref. [67], the segregation of Sn starts a little before the decrease of stacking fault probabilities, which is accompanied by a microstrain reduction. So, peak 3 may correspond to the Sn segregation, whereas peak 4 is attributed to the stacking fault healing. Our HTXRD data lacks the temperature resolution needed to determine whether a similar phase transition occurs in the full-Se compound. However, we can observe that peak 3 in DSC data has a considerably longer tail for $\text{Cu}_2\text{ZnSnSe}_4$. From the stacking fault probability analysis, Figure 2.6(b), tailing can also be associated with early healing of stacking faults, starting already at ~ 473 K. The negative thermal expansion observed for CZTSe in Figure 2.6(b) also suggests that the mechanism of phase transition is different from the other CZTSSe materials. However, further understanding of the CZTSe phase transition is required. Peaks 1 and 2 of the DSC plots of Figure 2.7 are related to the water absorption and evaporation of sulphur, respectively (more comments are given in Appendix A, Supplementary Note A.3).

2.3.3 Computational study

So far, we concluded from the experimental point of view that the surplus of Cu in CZTSSe promotes a deviation from the conventional Vegard’s law, observed in lattice parameters and Raman modes. The Cu-surplus increases the SF probability due to the increase of Cu-rich tetrahedral motifs in the structure, inducing local motif clustering.[65] In addition, the partial substitution of sulphur for selenium leads to local distortions (due to differences in atomic radii) and affects the local dynamic of the CZTSSe system,[89] increasing the MS for $x = 2$ compositions. Due to a plethora of structural and microstructural effects present in this system, *ab initio* simulations are an effective tool to isolate and understand specific local structural effects of Cu doping. These simulations can be divided in two:[73] (i) DFT performed at 0 K to understand the local structure of the material, and formation energies of SFs; and (ii) AIMD, a technique that combines quantum mechanical calculations with classical molecular dynamics to simulate the behavior of atoms over time, providing insights on local dynamics.[73]

In the transition process, the Sn atoms need to migrate to the 2a Wyckoff position. By analysing the DW coefficients for the Sn atoms in the Sphalerite cubic phase shown

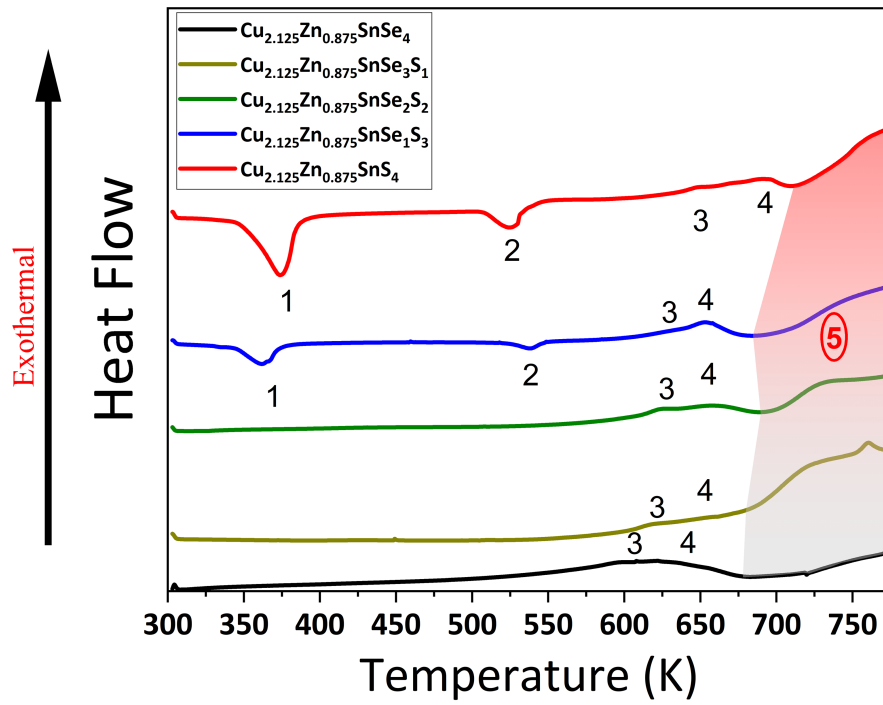


Figure 2.7: DSC measurements for the $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ samples for the series of $x = 0 - 4$.

in Figure 2.8(a) and (c) obtained via AIMD simulations – for both undoped and doped samples, respectively; we notice that its modulus is often higher than for Cu and Zn, despite being twice as heavy. Therefore, the Sn atoms are driven to migrate towards a more stable position in the Wyckoff 2a site, reducing the relative MSD and stabilising the tetragonal phase.[67]

Table 2.1 presents the SF formation energies for both cubic and tetragonal phases, showing that undoped CZTSSe ($y = 0$) requires more energy to stabilize when faulting is present compared to the Cu-rich case ($y = 0.125$). Therefore, doped CZTSSe should present a higher degree of SF. Also, the overall stacking fault energy in the tetragonal phase is lower, which means that for the system to be stable with stacking faults, it should transition to the tetragonal phase. In the transition process, the Sn atoms need to migrate to the 2a Wyckoff position. By analysing the DW coefficients for the Sn atoms in the Sphalerite cubic phase shown in Figure 2.8(a) and (c) obtained via AIMD simulations – for both undoped and doped samples, respectively; we notice that its modulus is often higher than for Cu and Zn, despite being twice as heavy. Therefore, the Sn atoms are driven to migrate towards a more stable position in the Wyckoff 2a site, reducing the relative MSD and stabilising the tetragonal phase.[67]

Table 2.1: Calculated stacking fault formation energy for $y = 0$ and $y = 0.125$ samples.

S proportion (x)	$\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$		$\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$	
	Formation	Formation Energy/atom	Formation	Formation Energy/atom
Cubic Phase				
0	-84	-0.329	-81	-0.315
1	-87	-0.342	-85	-0.332
2	-91	-0.359	-89	-0.348
3	-97	-0.379	-94	-0.366
4	-102	-0.398	-98	-0.384
Tetragonal Phase				
0	-99	-0.388	-97	-0.378
1	-103	-0.404	-101	-0.394
2	-108	-0.423	-106	-0.413
3	-113	-0.444	-111	-0.434
4	-120	-0.468	-117	-0.458

Additionally, in Cu-rich CZTSSe, CuZn antisites lead to a slight reduction in the average cation Debye-Waller (DW) factors for the kesterite phase (comparing the black squares in Figure 2.8(b) and (d)). This justifies the smaller cation DW parameters observed by HTXRD after the phase transition for the Cu-doped sample shown in Figure 2.6(d), while anions have practically the same DW coefficients with and without doping (see Figure 2.6(e)).

With the simulated AIMD trajectories, the effect of distortion can be quantitatively estimated via the Baur distortion index,[90] a quantitative measure of the deviation of a polyhedron from its ideal geometry.[90] It assesses how uniformly the bond lengths and/or bond angles are distributed around a central atom. Two types of indices can be obtained, one quantifying the deviation in bond length:

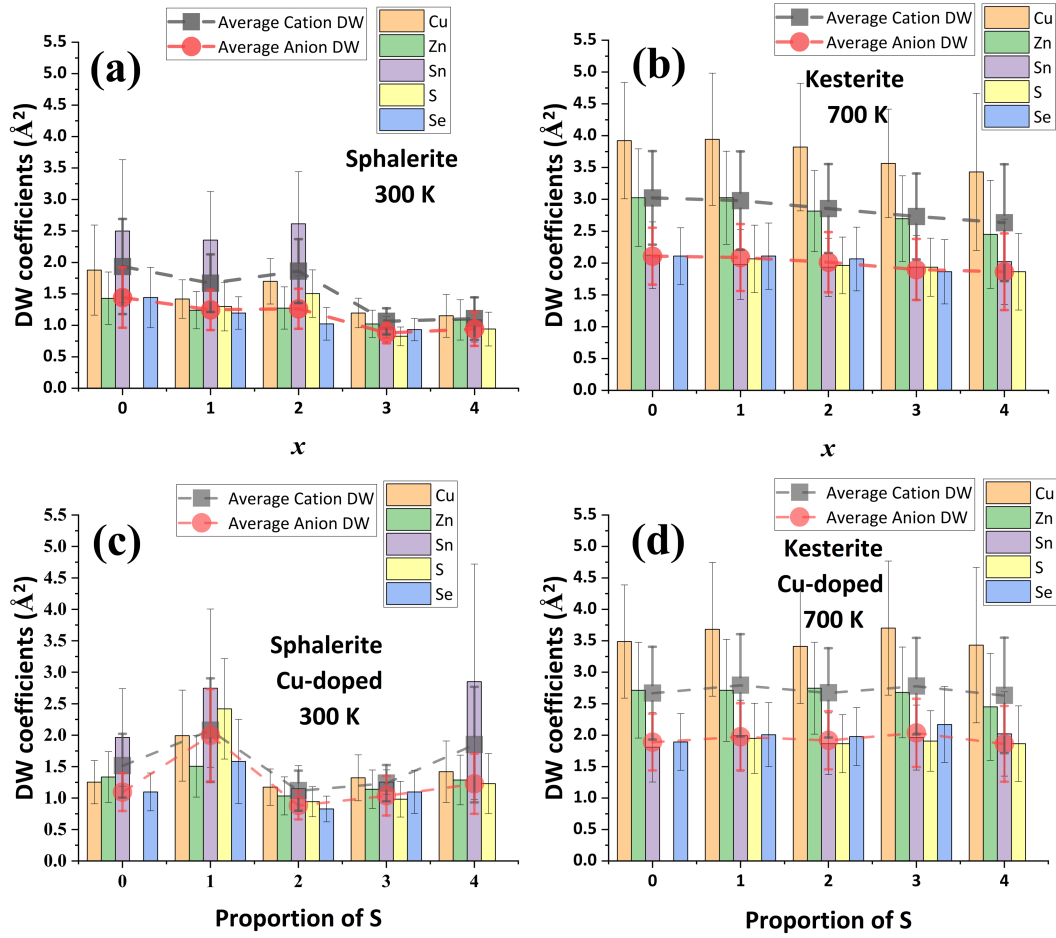


Figure 2.8: DW coefficients obtained via AIMD simulations of the (a) sphalerite phase at 300 K, (b) kesterite phase at 700 K, (c) Cu-doped sphalerite phase at 300 K, and (d) Cu-doped kesterite phase at 700 K.

$$D_{\text{bond}} = \frac{1}{4} \sum_{i=1}^4 \left| \frac{R_i - R_0}{R_0} \right| \quad (2.1)$$

with R_i being the cation-anion pair bonding distances, and R_0 the ideal crystallographic pair distance (obtained from XRD refined data), and one measuring the deviation in bond angle:

$$D_{\theta} = \frac{1}{6} \sum_{j=1}^6 \left| \frac{\theta_j - \theta_0}{\theta_0} \right| \quad (2.2)$$

Corresponding to the angle distortion from the ideal tetrahedron, where θ_j is the angle between two cation bonds, and $\theta_0 = 109.47^\circ$ is the angle for a perfect tetrahedron. Here, a time average is performed for each tetrahedron in the simulation box. The indices are also averaged over the total number of tetrahedra present in the simulation box.

Figure 2.9(a) and (b) present the calculated bond and angle distortion indices, respectively, for the cubic sphalerite and tetragonal partially disordered kesterite phases. The cubic phase exhibits markedly higher distortions, attributed to the greater number of possible tetrahedral configurations arising from enhanced chemical disorder. This compositional complexity is further illustrated in Figure 2.10(a): while only three distinct tetrahedral motifs are present in the tetragonal partially disordered structure, the cubic phase in its current configuration features 13 different motifs. The increased structural disorder is also reflected in the pair distribution function, $g(r)$. In the cubic structures, the Sn–Anion peak displays pronounced asymmetry, as shown in Figure 2.9(c) and (d), contrasting with the more symmetric peak observed in the tetragonal phase (Figure 2.9(e) and (f)). Although such asymmetry is often linked to anharmonic bonding,[91–94] in this case it stems from the broad distribution of Sn–Anion distances associated with the diverse tetrahedral environments in the cubic structure. This interpretation is supported by Figure A.15 in Appendix A, Supplementary Note A.4, which shows the Sn–Anion distance distribution from AIMD simulations of $\text{Cu}_2\text{ZnSnS}_2\text{Se}_2$. The average distorted geometries derived from AIMD simulations are displayed in Figures A.16a and A.16b for the cubic and tetragonal phases, respectively. With increasing Se content (i.e., decreasing x in CZTSSe), the average Sn–S bond length increases in both polymorphs, as shown in Figure 2.9(c-f). Conversely, the Sn–Se bond length decreases, as shown in Figure A.17. Notably, the bond lengths of other cation–anion pairs remain essentially unchanged (see Figures A.18a–A.19b), indicating that anionic substitution primarily perturbs Sn–anion interactions. This behavior can be explained by the weaker Sn–anion bond strength relative to other cations in the lattice.[41] Thus, Sn–S and Sn–Se bonds are not entirely independent, as is often assumed in the two-mode vibrational model commonly used to interpret Raman spectra of kesterite structures.[52, 77, 87, 88]

Analysis of Baur distortion reveals that the $x = 2$ composition—classified as a high-entropy alloy—displays the greatest degree of structural disorder, which aligns with the enhanced MS features observed in its diffraction patterns (see Figure 2.2(e) and (f)). The dispersion of the distortion indexes for cubic and tetragonal phases is very significant, as shown in Figure 2.9(a) and (b). This reflects the wide variability in distortion among individual tetrahedral motifs, as shown in Figure 2.10(b-e) for both structural configurations. Interestingly, the introduction of Cu-doping ($y = 0.125$) does not significantly affect the overall dispersion for the cubic phase (compare Figure 2.10(b) and (c)), indicating that the spread in distortion is an intrinsic feature of the structural complexity. Within the tetragonal phase, the inclusion of Cu into tetrahedral motifs leads to increased distortion,

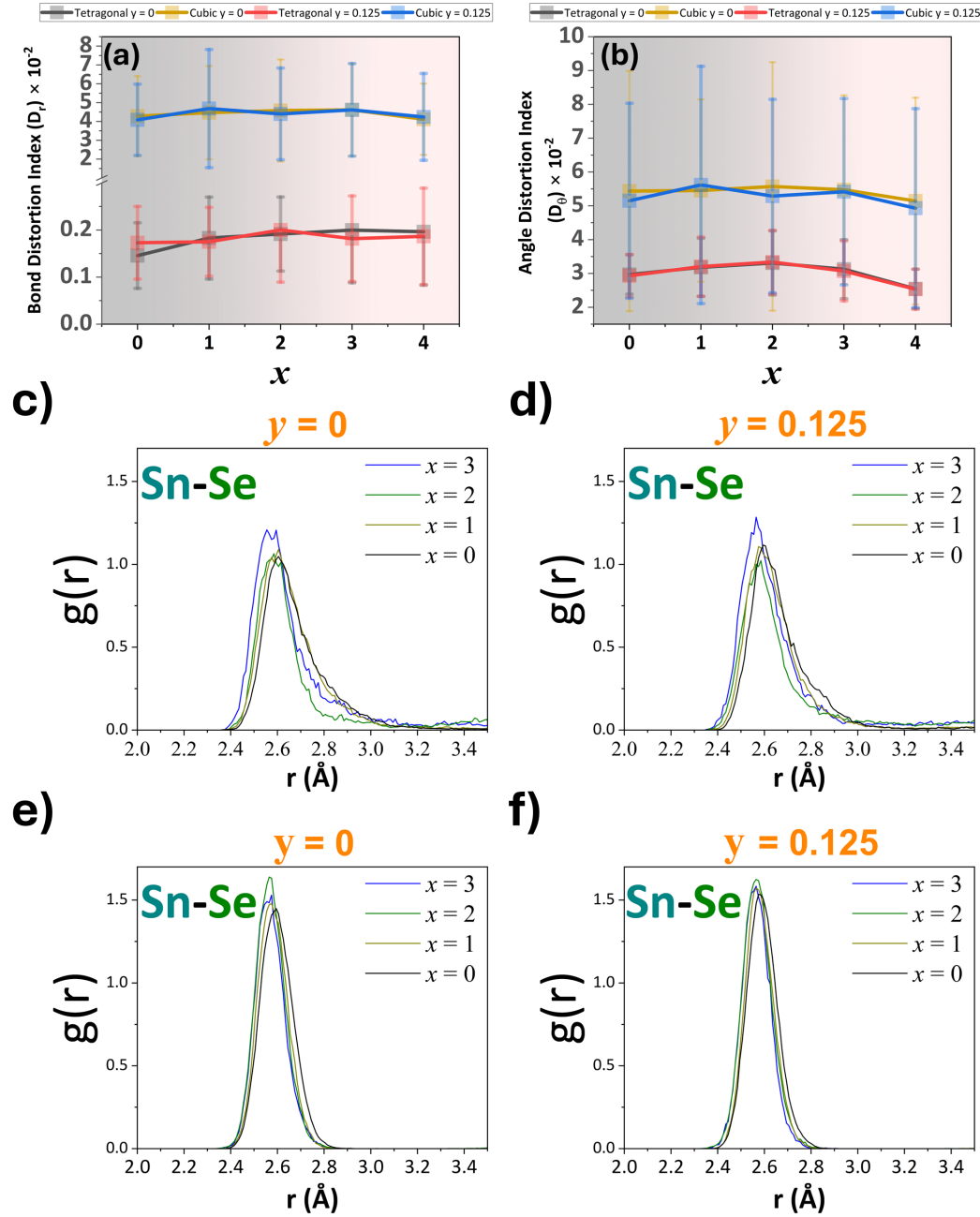


Figure 2.9: (a) Simulated Baur bond distortion index for the cubic and tetragonal phases of the $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ system and (b) their corresponding angle distortion index. PDF of the Sn-S bonds for (c) $y=0$ cubic phase, (d) $y=0.125$ cubic phase, (e) $y=0$ tetragonal phase, and (f) $y=0.125$ tetragonal phase. The colours represent the x variation.

particularly for the Cu_3Sn -Anion configurations, which are the most distorted among all (see Figure 2.10(e)). Consequently, Cu-doping in the tetragonal kesterite phase is expected to enhance MS due to the greater presence of Cu_3Sn_1 -Anion motifs in the crystal structure. This effect may be beneficial for thermoelectric applications, as it promotes the formation of CuZn and ZnCu antisite defects, thereby increasing charge carrier concentrations,[38, 95] while simultaneously increasing the quantity of microstructural defects responsible for the phonon scattering. In contrast, for PV applications, such disorder is detrimental: minimizing MS and SF effects and favoring Cu-poor environments are key to optimizing performance.[64, 96–98]

In both cubic and tetragonal CZTSSe materials, local cation ordering is governed by the octet rule.[65] In an ionic framework, this rule favors configurations in which each anion is surrounded by cations that collectively contribute eight valence electrons, ensuring charge neutrality and energetic stability. As a result, tetrahedral motifs cannot be randomly distributed but instead form correlated clusters throughout the crystal lattice. The resulting motif clustering reflects attractive entropic interactions that arise from this coupling.[99] A detailed investigation of cation clustering and formation energies in the tetragonal phase is given by P. Zawadzki et al.,[65] where DFT and Monte Carlo simulations were used to model individual tetrahedral motifs and capture entropy effects through temperature emulation. In contrast, the present study employs *ab initio* molecular dynamics (AIMD) to explore, for the first time, the distortion behavior of connected tetrahedra, thereby extending the understanding of tetrahedron–tetrahedron interactions from a dynamic, temperature-inclusive perspective. While AIMD is limited to sampling a single configuration, the simulations clearly show that the higher degree of chemical disorder in the cubic phase—along with its broader distribution of tetrahedral motifs—enables numerous local configurations that promote microstructural strain and defect formation, such as stacking faults (SF). Thus, the stabilization of the cubic phase at room temperature via stacking faults can be understood because of the increased configurational freedom and diversity of tetrahedral arrangements, which are entropically favorable under these constraints. Since the cubic-to-tetragonal phase transition involves displacement of the anion from its high-symmetry position,[66] thermal activation increases entropy, which favors the formation of the more stable CuSnZn_2 , Cu_2SnZn , and Cu_3Sn motifs.[65]

2.4 Conclusion

A comprehensive understanding of chemical disorder in sphalerite and kesterite phases is essential for tailoring the structural and functional properties of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ materials for energy applications. XRD and Raman analyses reveal that CuZn antisite formation increases microstructural disorder and stacking fault density, with Cu-rich compositions showing significant deviations from Vegard’s law. This is attributed to the non-random distribution of tetrahedral motifs, which cluster to minimize electrostatic and entropic constraints, resulting in nonlinear variations in lattice parameters and vibrational responses upon anion substitution. In situ HTXRD measurements indicate that the cubic-to-tetragonal phase transition occurs near 650 K, driven by stacking fault healing and re-ordering of cation positions, particularly the placement of Sn at Wyckoff 2a sites. Baur distortion analysis shows that the $x = 2$ composition, a high-entropy alloy, exhibits the highest structural disorder, correlating with increased defect signatures in diffraction patterns. Furthermore, Cu enrichment in tetrahedral units amplifies local disorder in kesterite structures, enhancing phonon scattering—a desirable effect for thermoelectric applications.

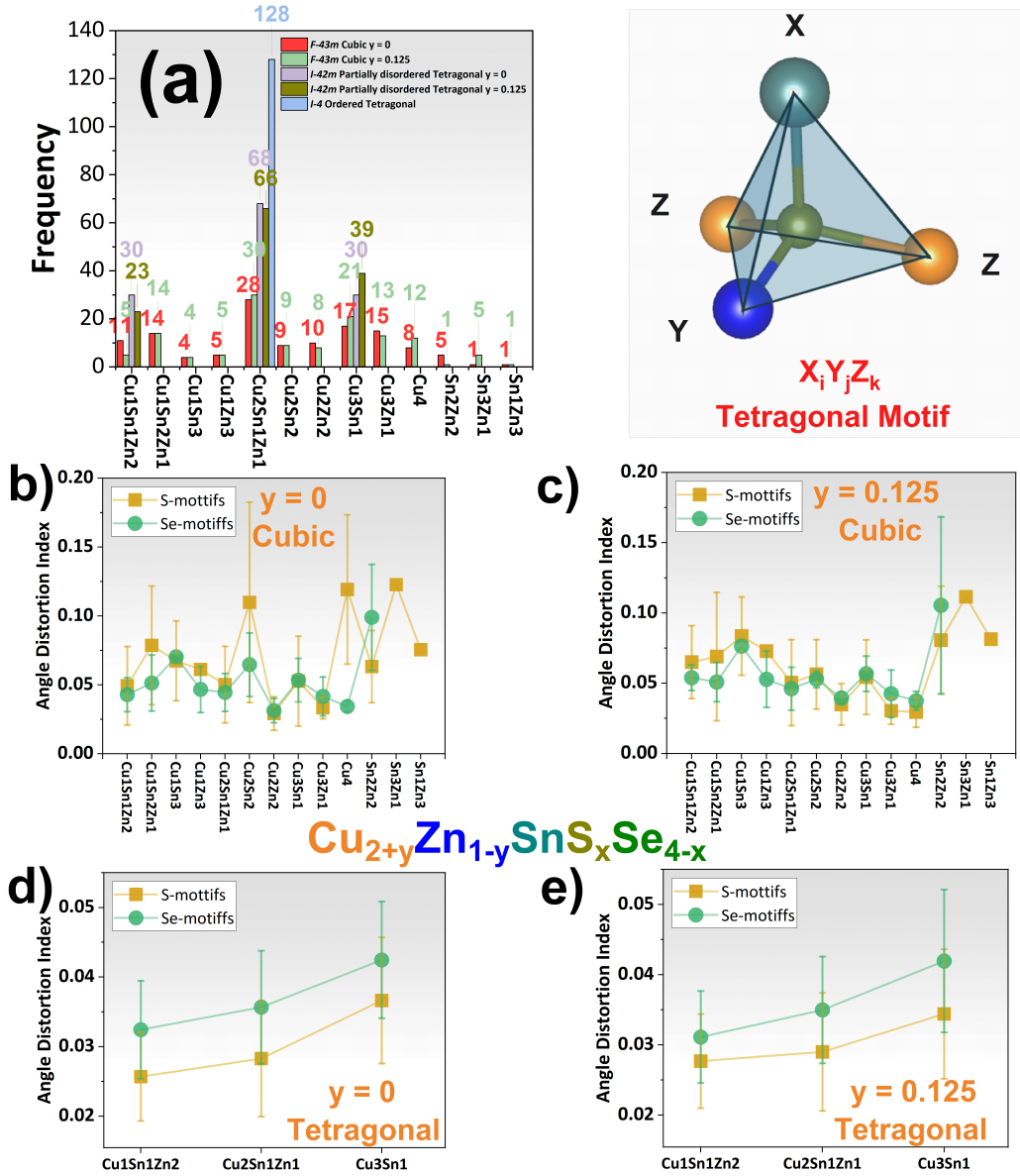


Figure 2.10: (a) Simulated Frequency distribution using AIMD first principle methods for tetrahedron motifs in cubic and tetragonal CZTSSe structures. Angle distortion indexes for the (a) cubic $y = 0$, (b) cubic $y = 0.125$, (c) tetragonal $y = 0$, and (d) tetragonal $y = 0.125$ systems. The tetrahedron label definition is represented in the figure in the upper right corner.

Conversely, Cu-poor compositions are preferred for photovoltaic devices, where reduced microstructural defects are critical for optimal performance. Ongoing work aims to further elucidate the impact of structural and microstructural features on the thermoelectric behaviour of CZTSSe materials.

Acknowledgements

Christine Stefani is acknowledged for her assistance in the HTXRD measurements. S.B. acknowledges the DFG, grant BE 7407/1-1 until February 2022 called “Joint German – Russian cooperation project” for funding. The tenth and last authors acknowledge the Italian Ministry of Education, Universities and Research (MUR) in the framework of the project DICAM-EXC (Departments of Excellence 2023-2027, grant L232/2016).

Chapter 3

Role of microstructure in the lattice thermal conductivity and thermoelectric performance of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ alloys

Abstract

Kesterite compounds of the form $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ (CZTSSe) have attracted considerable interest as sustainable thermoelectric materials due to their earth-abundant composition and intrinsically low lattice thermal conductivity. However, several studies on polycrystals report an unexpected trend in which the selenide exhibits higher lattice thermal conductivity than the sulphide, contrary to expectations based on atomic mass and lattice stiffness. In this work, we investigate the origin of this behaviour and shed light on how microstructural, chemical, and structural features affect the thermoelectric performance across the CZTSSe compositional series. First-principles calculations indicate that the intrinsic lattice dynamics favour lower lattice thermal conductivity in Se-rich compositions. In contrast, experimental results show that microstructural effects dominate phonon transport in polycrystalline samples. In particular, larger porosity, smaller grain size, and reduced grain connectivity strongly suppress the lattice thermal conductivity in sulphide-rich compounds, leading to an apparent inversion of the expected CZTS–CZTSe thermal conductivity trend. In addition, electronic transport analysis reveals an increase in weighted mobility above the order-disorder phase transition temperature, observed across all compositions, and resulting in improved performance. This effect is attributed to the band convergence effect related to the increased structural symmetry promoted by Cu-Zn disorder, approaching a pseudocubic structure. Despite the lower intrinsic carrier mobility in sulphide-rich compositions, their suppressed lattice thermal conductivity results are comparable to thermoelectric performance across the series, with zT values up to ~ 0.5 at 723 K. These results demonstrate that microstructural effects can outweigh intrinsic chemical trends and play a critical role in determining thermal transport and thermoelectric performance in kesterite materials.

3.1 Introduction

Thermoelectricity (TE) is the field of material science investigating materials that can produce electric voltage from temperature gradients due to the Seebeck effect and vice versa via the Peltier effect. The efficiency of the heat-to-electric energy conversion is proportional to the figure of merit, $zT = \frac{S^2\sigma T}{\kappa}$, where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T is the absolute temperature.[5, 6] Here, $\kappa = \kappa_e + \kappa_l$, where κ_e is the electronic thermal conductivity (heat transported by charge carriers), and κ_l is the lattice thermal conductivity (heat transported by phonons). To maximize zT , a high charge-carrier conductivity must be accompanied by strongly suppressed heat transport, yielding a high power factor ($S^2\sigma$) while maintaining a reduced κ , a concept commonly referred to as the phonon-glass electron-crystal paradigm.[100] Modifying the phase composition of a material by doping and/or alloying is a viable way to produce this effect. However, the interdependence of S , σ , and κ_e , all strongly related to the carrier concentration, makes this optimization non-trivial.[101] As a result, the thermoelectric performance is commonly improved through a combination of controlled doping, chemical disorder, and micro- and nanostructuring.

On the structural level, chemical disorder has proven particularly effective in suppressing lattice thermal conductivity.[102, 103] $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ are well-known examples among Cu-based compounds,[34–36, 50, 55] exhibiting strong disorder both in the cubic sphalerite ($F\bar{4}3m$) phase, where occupancy on the cation sites is fully randomized, and in the tetragonal disordered kesterite phase ($I\bar{4}$), where Cu and Zn partially occupy the same Wyckoff positions.[36, 55] Disorder already proved to promote ultralow thermal conductivity for these systems, which was especially attributed to low-lying optical modes and reduced phonon-group velocities,[35, 36] while simultaneously presenting features suggesting a topologically non-trivial electronic structure.[104]

Cu-doping is a common strategy to boost the σ of CZTS/Se compounds, especially by inducing Cu_{Zn} substitutions.[70, 71] In kesterites, these substitutions are energetically favourable and reinforce the intrinsic p-type character of the material.[105] Additional chemical disorder can be introduced via anion substitution in the $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ solid solution, which is structurally favourable due to the analogous local coordination environments of S and Se, and further enhances phonon scattering.[40]

The lattice thermal conductivity κ_l of crystalline solids is commonly described within the phonon gas model as

$$\kappa_l = \frac{1}{3}C_v v_s^2 \tau \quad (3.1)$$

where C_v is the specific heat capacity, v_s is an effective phonon velocity commonly approximated with the sound velocity, and τ is the phonon lifetime.[27, 106] The sound velocity is directly related to the elastic response of the lattice and scales as $v_s \propto \sqrt{C/\rho}$, where C denotes an appropriate elastic constant and ρ is the mass density. As a result, for materials within the same structural and bonding class, heavier atomic masses and longer bonds typically lead to elastic softening, reduced phonon group velocities, and ultimately lower lattice thermal conductivity. This trend aligns with Slack’s criteria for thermal conductivity[107] and has been widely discussed in the context of thermoelectric materials, as clearly illustrated, for example, by the correlation between bulk modulus softening and decreasing κ_l with increasing unit-cell volume and average atomic mass.[42, 108] Based on these considerations, Se-containing kesterites – owing to their larger unit-cell volume and mass density – are theoretically expected to exhibit lower lattice thermal conductivity than their S-based

counterparts.

Surprisingly, several experimental studies on polycrystalline CZTS and CZTSe report the opposite trend, with CZTSe displaying higher κ_l than CZTS over a wide temperature range, particularly in ball-milled and SPS-processed samples.[35, 39, 40, 71] A summary of representative experimental results is shown in Figure 2.1. Interestingly, the only case where κ_l recovers the conventional trend of reduced κ_l with a larger unit cell volume and density (i.e., $\kappa_l(\text{CZTSe}) < \kappa_l(\text{CZTS})$) is when high-quality single crystal samples are considered.[109, 110] The absence of long-range crystalline defects in the latter case suggests that the “inverted” κ_l trends reported in the literature may arise from a combination of microstructural and chemical effects. Therefore, this work aims to clarify the origin of this unconventional behaviour, along with its impact on thermoelectric performance.

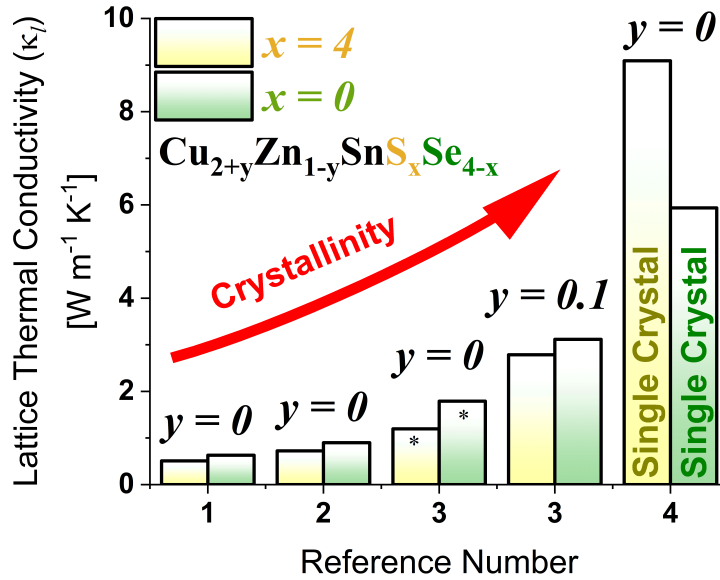


Figure 3.1: Lattice thermal conductivity collected from literature. Values are taken at 300 K, except for Ref. 3, taken at 700 K. References correspond to: (1) [40], (2) [35, 36], (3) [71], and (4) [109].

In the present work, we investigate the combined effects of nano- and micro-structuring, disorder, cation doping, and anion substitution on the thermoelectric properties of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ (CZTSSe) prepared by ball milling combined with cold pressing and spark plasma sintering. Density functional theory calculations combined with experimental transport measurements reveal that, although Se-rich compounds possess intrinsically softer bonding, enhanced grain packing and connectivity can dominate both heat and charge transport, resulting in a higher κ_l and carrier mobility for CZTSe ($x = 0$) compared to its sulphide counterpart CZTS ($x = 4$). Despite this, the substantial suppression of lattice thermal conductivity in sulphide-rich compositions leads to an enhanced thermoelectric quality factor B , particularly in the low-density cold-pressed samples. As a result, a convergence of thermoelectric performance is observed across the CZTSSe series, with peak values reaching $zT \sim 0.5$ near 725 K for all low-density samples. Notably, the CZTS composition

exhibits a higher figure of merit in the low-density state compared to its SPS counterpart, underscoring that microstructure plays a significant role in the improvement of thermoelectric performance.

3.2 Results and Discussion

3.2.1 Structural and vibrational properties

In the present study, $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ bulk pellets were synthesized by ball milling followed by cold pressing (15 tons for 5 min) and subsequent thermal treatment for compositions with $x = 0, 1, 2, 3, 4$ and $y = 0.125$. In addition, a second batch of samples was prepared by spark plasma sintering (SPS) for $x = 0$ and 4 with $y = 0$ and 0.125. The resulting pellets were shaped into disks approximately 1 mm thick and 10–16 mm in diameter. Further details are provided in the Materials and Methods section.

The X-ray diffraction patterns collected using $\text{Ag K}\alpha_1$ radiation are shown in Figure 3.2(a) for the entire compositional series of cold-pressed samples. Rietveld refinements confirm that a single-phase tetragonal kesterite structure (space group $I\bar{4}$) is stabilized at room temperature across the full anion-substitution range. Details of the refinements are provided in Supplementary Note B.1, including the SPS samples Rietveld refinements (Figures B.1–B.7). The evolution of the lattice parameters with sulphur/selenium content follows a linear Vegard-type behaviour, as shown in Figure 3.2(b). Owing to the larger ionic radius of Se^{2-} compared to S^{2-} , increasing the Se content leads to an increase in the unit-cell dimensions, in agreement with the average cation–anion bond lengths obtained from *ab initio* molecular dynamics simulations (Figure 3.2, centre). The extracted Vegard relations,

$$a \text{ (\AA)} = -0.267(9)x + 5.691(4)$$

and

$$c \text{ (\AA)} = 0.52(2)x + 11.340(8),$$

confirm the formation of a homogeneous solid solution throughout the CZTSSe series and are in good quantitative agreement with previous reports on well-crystallized CZTSSe compounds.[52] The absence of supercell reflections also confirms full statistical substitution within the anion substructures. Complementary Raman spectroscopy validates the structural evolution across the CZTSSe series (Figure B.8); the corresponding spectra and Vegard-type trends are discussed in detail in Supplementary Note B.2.

The phonon dispersion relations for the sulphide ($x = 4$) and selenide ($x = 0$) end members are shown in Figure 3.2(c) and (d), respectively, as estimated by density functional perturbation theory (DFPT) using the lattice parameters retrieved from the Rietveld refinements. DFPT emulates an infinite periodic crystal and allows isolating the intrinsic chemical contribution to the vibrational properties of the CZTSSe system. The calculated phonon dispersions reveal a clear softening in CZTSe ($x = 0$), with vibrational modes shifted toward lower frequencies compared to CZTS ($x = 4$). This behaviour is consistent with the heavier Se anion and the longer, weaker, cation–Se bonds relative to cation–S bonds. Phonon softening is reflected in the corresponding acoustic sound velocities, v_{sound} , obtained from the bulk and shear moduli.[111] The average sound velocity, combining longitudinal (v_L) and transverse (v_T) components, is given by:

$$v_{\text{sound}} = \bar{v} = \left[\frac{1}{3} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \right]^{-1/3} \quad (3.2)$$

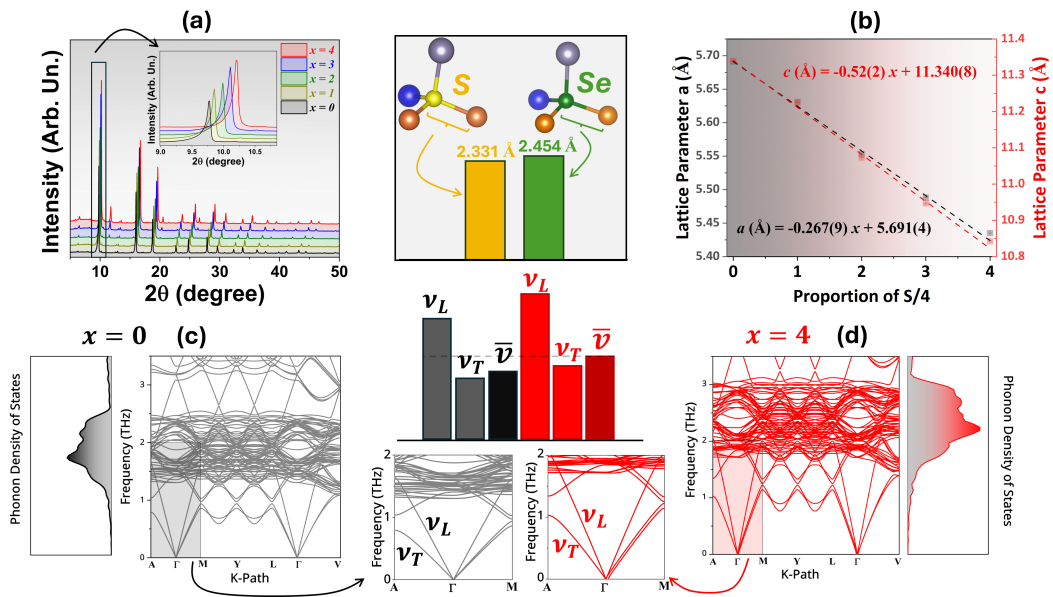


Figure 3.2: (a) X-ray diffraction patterns collected using $\text{Ag K}\alpha_1$ radiation for the cold-compressed CZTSSe series. (b) Evolution of the lattice parameters with sulphur/selenium content. The centre panel reports the average cation-anion bond lengths obtained from *ab initio* molecular dynamics simulations. (c,d) Phonon dispersion relations for the sulphide ($x = 4$) and selenide ($x = 0$) end members, respectively, as obtained by density functional perturbation theory.

Consistent with previous reports for stoichiometric CZTS-Se,[39, 112, 113] the average v_{sound} of CZTS (2867 m s^{-1}) is higher than that of CZTSe (2370 m s^{-1}), reflecting the intrinsically stiffer lattice of the sulphide end member.

The DFT-mode averaged Grüneisen parameter γ , which quantifies the degree of lattice anharmonicity, is larger for the selenide ($\gamma = 1.61$) than for the sulphide ($\gamma = 1.47$) (see Supplementary Note B.3, Figure B.9). Within the simplified Debye–Slack framework employed in Ref. [114] and references therein, the lattice thermal conductivity κ_l can be approximately estimated by accounting for acoustic (κ_a) vibrational contributions, leading to the scaling relation

$$\frac{\kappa_{l,S}}{\kappa_{l,Se}} = \frac{(\kappa_a)_S}{(\kappa_a)_{Se}} \sim \frac{\bar{M}_S \bar{v}_S^3 V_{Se}^{2/3} \gamma_{Se}^2}{\bar{M}_{Se} \bar{v}_{Se}^3 V_S^{2/3} \gamma_S^2} = 1.6 \quad (3.3)$$

Here, $\bar{M}$ is the average atomic mass and V is the atomic volume. This estimate indicates that, from a purely chemical and elastic standpoint, the sulphide is expected to exhibit a 1.6-times higher intrinsic κ_l than the selenide. While first-principles Boltzmann transport calculations by Skelton *et al.* predict the opposite trend, which they attribute to a suppression of three-phonon scattering phase space in CZTSe,[39] experimental measurements on high-quality CZTSSe single crystals report a monotonic decrease of κ_l with increasing Se content.[109, 110] These observations suggest that, in real single-crystal materials, conventional mass and lattice-stiffness effects remain dominant and support the expected correlation between elastic softening, increasing bond length, and reduced lattice thermal conductivity.[108]

3.2.2 Thermal conductivity

The measured lattice thermal conductivities, κ_l , of the cold-pressed and SPS samples are shown in Figure 3.3(a) and (b), respectively. To eliminate the effect of porosity when comparing different compositions, the matrix lattice thermal conductivity (κ_{matrix}) was estimated using an effective medium theory approximation, according to the relation

$$\kappa_{\text{matrix}} = \frac{2 + \Phi}{2 - 2\Phi} \kappa_l \quad (3.4)$$

where Φ represents the porosity.[115–117] Values are reported in Figure 3.3(c) and (d). For the cold-pressed samples, Φ , estimated from the geometrical density, ranges from 22% for the selenide to 32% for the sulphide, as reported in Figure 3.3(e). More details are given in Table B.1 of Supplementary Note B.4. It should be noted that, while compositions are referred to using their nominal stoichiometry throughout this work, EDXS analysis reveals a systematic deviation from the ideal anion/cation ratio in S-rich samples, indicating partial sulphur loss during synthesis. The corresponding measured compositions are reported in Table B.1 (Supplementary Note B.4) and schematically represented later in Figure 3.3(f), showing that the actual compositions are slightly anion-deficient, particularly at high S content.

In the cold-pressed series, the selenide exhibits higher κ_l than the sulphide, consistent with the counter-intuitive trends reported for other polycrystalline samples with analogous compositions in the literature (see Figure 3.1). Even after correcting for porosity, the samples confirm the unconventional trend of $\kappa_{\text{matrix}}(\text{CZTS}) < \kappa_{\text{matrix}}(\text{CZTSe})$. SPS samples, with porosity below 9%, display nearly identical lattice thermal conductivities for $x = 0$ and $x = 4$ (Figure 3.3(b–d)). In contrast, single-crystal measurements reported in Ref. [109]

display the opposite trend [$\kappa_l(\text{CZTSe}) < \kappa_l(\text{CZTS})$], highlighting the sensitivity of κ_l to microstructural features.

To further confirm the influence of microstructural effects, we need to compare the observed κ_l trends with the ones expected from a purely chemical perspective. Indeed, if anion chemical disorder were the dominant mechanism controlling κ_l , a minimum would be expected for intermediate compositions ($x = 2$), [118] where configurational entropy and point-defect scattering are maximized. Such behaviour is indeed observed for the dense SPS samples [Figure 3.3(b,d)]. In contrast, the behaviour is much less pronounced in the cold-pressed samples [Figure 3.3(a,c)]. Therefore, these results show that both chemical disorder and microstructure impact the absolute values of κ_l ; however, depending on porosity, microstructural effects can outweigh intrinsic alloy scattering contributions.

We note that a partial anion substitution through S–Se mixing is a well-established strategy to mitigate the anion loss effect, widely adopted in kesterite solar-cell research to improve defect tolerance and processing stability. [119, 120] A parameter sensitive to point defects and dislocations accumulated at grain boundaries is the microstrain, which can be extracted from the $\tan \theta$ law of X-ray powder diffraction (XRPD) integral breadths. [82, 83] The microstrain values, reported in Figure B.12 of Supplementary Note B.5, show a decrease upon S–Se mixing for both cold-pressed and SPS samples, indicating reduced internal stress and improved accommodation of lattice distortions at grain boundaries.

As illustrated, porosity may not be the only microstructural parameter influencing κ_l . As such, we consider crystallite size (CS) and grain/agglomerate size (GS) too. These values were obtained from XRPD and SEM (line-intercept method), respectively, and are summarized in Figure 3.4 for the cold-pressed and SPS samples (see Supplementary Note B.6 for details). Chemical maps and the remaining SEM analysis for the entire CZTSSe series are shown in Supplementary Note B.4. For both processing routes, CZTSe exhibits larger CS and GS than CZTS, with mixed-anion compositions showing intermediate behaviour (vide GS in Figure 3.4(a–d) and CS in Figure 3.4(e,f)). The larger crystallite size observed for CZTSe can be rationalized in terms of transformation-assisted grain growth. Before being subjected to thermal treatment, the as-milled powders feature a disordered cubic sphalerite-type phase ($F\bar{4}3m$). [91] Since the cubic-to-tetragonal phase transition in the Se-rich compound occurs at a lower temperature than in the sulphide counterpart, [55, 67, 91] the structural transformation is completed earlier during sintering. Consequently, a possible explanation for the larger grain size is that a greater fraction of the thermal energy supplied during sintering contributes to grain-boundary migration and defect annealing rather than being consumed as transformation enthalpy. This may promote enhanced grain growth in CZTSe compared to CZTS.

The enhanced grain growth observed in the Se-rich compositions would, in principle, influence grain-boundary phonon scattering. Crystallite- and grain-boundaries introduce an additional phonon-scattering channel, typically modelled by an effective lifetime $\tau_B = d/v_g$, where d is the characteristic crystallite or grain size and v_g the phonon group velocity. [114, 121] According to this simplified picture, larger grains should reduce boundary scattering and therefore increase κ_l . In principle, this model justifies the higher thermal conductivity for the CZTSe material, since both CS and GS are larger.

Albeit qualitatively correct, when CS and GS are compared with κ_l trends for each synthesis process, a non-monotonic behaviour emerges that cannot be rationalized within a simple grain-boundary-limited transport mechanism. For CZTS, the cold-pressed sample exhibits larger crystallites yet significantly lower κ_l than the SPS sample. Conversely, for CZTSe, both CS and GS increase markedly upon SPS processing while κ_l remains nearly unchanged (see Figure 3.3). A clear distinction between SPS and cold-pressed CZTS samples

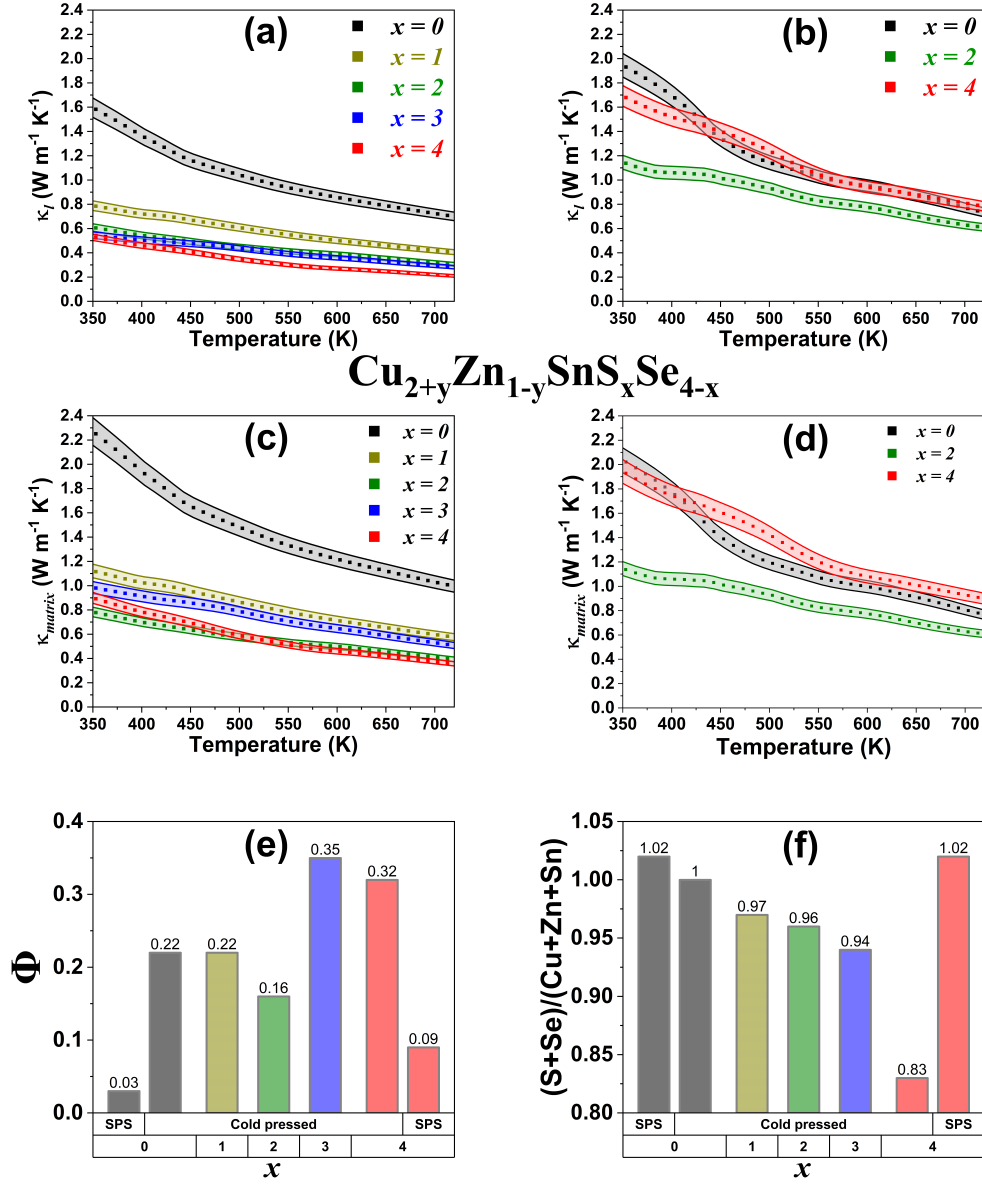


Figure 3.3: Temperature dependence of the lattice thermal conductivity, κ_l , for (a) cold-pressed and (b) spark plasma sintered (SPS) CZTSSe samples. Matrix thermal conductivity, κ_{matrix} , for the cold-pressed and SPS samples are given in items (c) and (d), respectively. Different colours correspond to the various anion stoichiometries, with $x = 0$ (CZTSe) to $x = 4$ (CZTS), as indicated in the figure. The contour lines represent the error in the measurement, estimated as 5% for all the samples. (e) Porosity (Φ) and (f) anion/cation ratio measured from EDXS for the CZTSSe samples.

arises from the effect of porosity. Despite having comparable grain sizes, the cold-pressed samples exhibit significantly lower lattice thermal conductivity, primarily due to their higher porosity (see Figure 3.4(a) and (b)). In particular, cold-pressed samples show a greater degree of crack formation compared to SPS samples. This difference can be attributed to the higher pressure applied during SPS processing, which leads to more effective densification and consequently reduced porosity. For CZTSe, a different mechanism appears to dominate. We propose that the pressure applied during SPS may lower the phase transformation temperature from the cubic to the tetragonal phase. As a result, a larger fraction of the supplied thermal energy is directed toward grain growth and defect annealing, leading to an overall increase in grain size. Although a complete phase diagram for kesterite systems is still lacking—particularly given that the cubic phase is metastable at room temperature—this hypothesis provides a plausible explanation for the observed behaviour. Additionally, CZTSe samples exhibit improved grain connectivity compared to CZTS, facilitating more continuous heat conduction pathways. Consequently, the detrimental effects of porosity on κ_l are less pronounced in CZTSe than in CZTS.

Standard grain-boundary scattering models do not account for the possibility that grain boundaries may exhibit different phonon-scattering behaviours, which instead have been shown to occur for different boundary features or synthesis routes.[43, 122, 123] In addition, effective medium theory treats porosity as an assembly of isolated, approximately spherical voids embedded in a continuous matrix.[115–117] These assumptions are likely not fully satisfied in the present samples, particularly at elevated porosity levels, where porosity manifests also in reduced grain connectivity and imperfect necking. Lattice thermal conductivity modelling via the Debye–Callaway model is widely used in thermoelectrics to elucidate the dominant mechanisms governing phonon transport.[114] However, the multinary nature of these compounds, the occurrence of phase transitions, and their significantly complex microstructure deviate from the model assumptions, preventing a clear deconvolution of the different scattering mechanisms.

SEM imaging on fracture surfaces (Figure 3.4(a–d)) shows that CZTSe grains form a more continuous and well-interconnected framework, whereas CZTS samples exhibit a higher propensity for microcrack formation and poorly bonded grain boundaries. This microstructural degradation in sulphide-rich samples may be related to the higher volatility of sulphur compared to selenium, which promotes anion depletion during sintering and may disrupt grain-boundary cohesion. This is supported by the EDXS analysis results in Figure 3.3(f), where a decrease of the anion/cation ratio is observed as the proportion of S increases, and is a widely reported occurrence in sulphide-based kesterites for photovoltaic applications.[124–126] Consequently, both the reduced grain size and the poorer grain-boundary connectivity for CZTS emerge as primary factors responsible for the inversion of the CZTSe–CZTS κ_l trends observed in polycrystalline samples.

3.2.3 Quality factor and Figure of Merit

An important question concerns how pores and microfractures influence the electronic transport properties of CZTSSe materials. To address this issue, it is first necessary to understand the intrinsic electronic transport behavior of kesterite compounds and the role of their chemical and structural characteristics.

One of the most relevant mechanisms in these materials is the formation of Cu–Zn anti-site disorder, which occurs in the Cu–Zn planes of the kesterite lattice,[41, 68, 127] as illustrated in orange in Figure 3.5(a). Since the degree of chemical disorder is proportional to the structural symmetry of kesterite, disorder can be indirectly evaluated through the

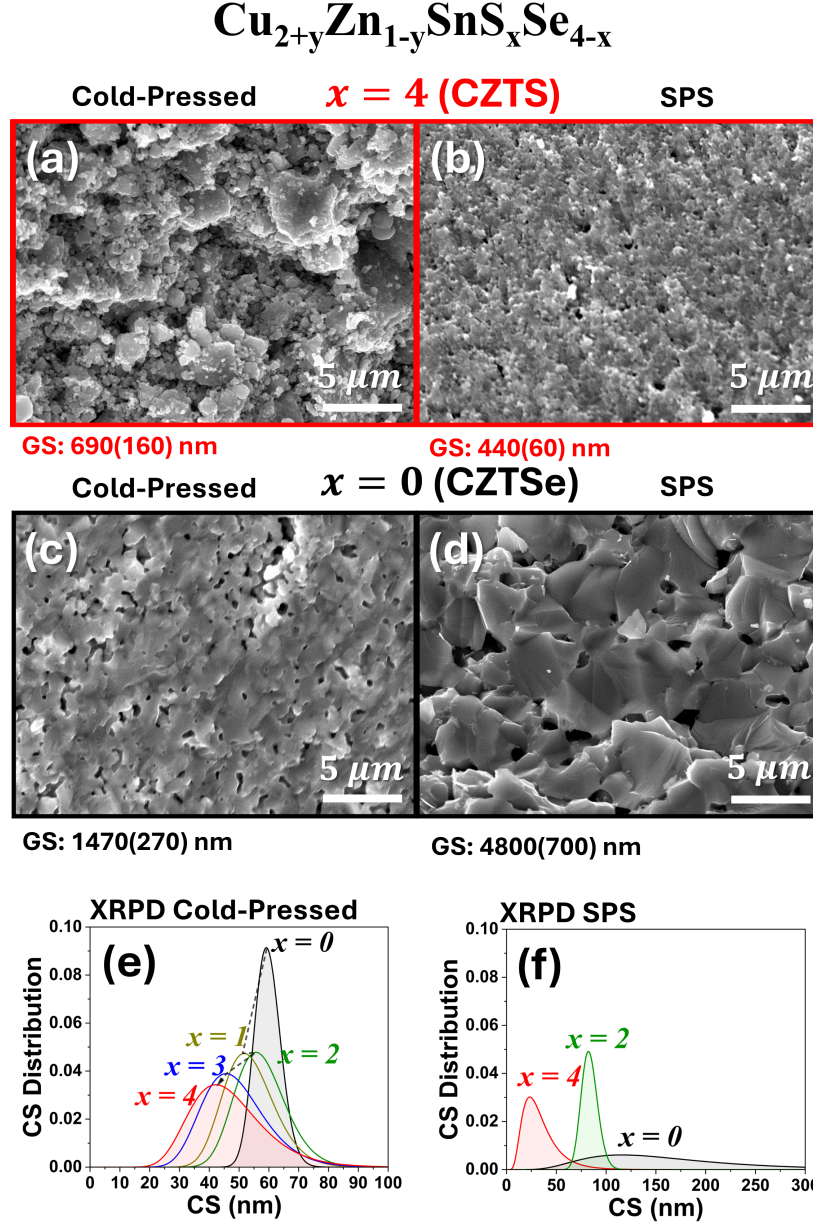


Figure 3.4: Cross-sectional SEM micrographs of cold-pressed and SPS samples for the sulphide ($x = 4$) and selenide ($x = 0$) end members: (a) cold-pressed CZTS, (b) SPS CZTS, (c) cold-pressed CZTSe, and (d) SPS CZTSe. The corresponding average grain sizes (GS) are indicated below each image. (e,f) Crystallite size (CS) distributions obtained from XRPD for cold-pressed and SPS samples, respectively, as a function of composition x .

tetragonal distortion parameter $\eta = c/2a$, [126, 128, 129] where values closer to unity indicate increased chemical disorder in the kesterite crystalline structure. Here, a and c are the tetragonal lattice parameters obtained by *in situ* high-temperature XRPD analysis.

η trends in temperature are shown in Figure 3.5(b). In this case, a sudden increase in the η values is observed around 500 K, marking the phase transition temperature from the ordered to disordered tetragonal structure, present in a similar temperature range to previous reports on CZTSSe compounds. [55, 68, 91, 127] This is sought to influence the electronic properties of the kesterite structure by promoting the band convergence effect. Due to the increase in symmetry in chalcopyrite-derived structures, the triply degenerate electronic valence band is merged, reducing the crystal-field splitting energy (Δ_{CF}) between the non-degenerate Γ_{4v} band and a doubly degenerate Γ_{5v} band. [91, 104] This is schematically represented in Figure 3.5(b), illustrating the electronic bands before and after the phase transition (Δ_{CF} values were taken from DFT simulations from Mukherjee et al. [91, 104] on CZTS and CZTSe materials). Therefore, the disordered kesterite phase presents an effective higher band degeneracy, N_v , due to the higher number of bands contributing to the hole conductivity near the Fermi level.

A convenient way to estimate experimentally the effect of band degeneracy in kesterite structures is through the weighted mobility μ_W , a parameter that can be extracted from the Seebeck coefficient (S) and electrical resistivity (ρ) following the simplified formalism developed by Snyder et al. [23] The weighted mobility condenses the effects of band structure, effective mass, and carrier scattering into a single parameter that is largely independent of carrier concentration, and is related to the carrier drift mobility μ_e as:

$$\mu_W \sim \mu_e \left(\frac{m^*}{m_e} \right)^{3/2} \quad (3.5)$$

where

$$\mu_e = \frac{e\tau}{m_{\text{band}}^*}, \quad m^* = N_v^{2/3} m_{\text{band}}^*$$

is the density-of-states effective mass, and m_e is the electron mass. Unlike the power factor ($S^2\sigma$), which depends strongly on the doping level, μ_W reflects the intrinsic electronic quality of the material and allows a more direct comparison across compositions and processing routes. [23]

The weighted mobility μ_W for both SPS and cold-pressed samples is shown in Figure 3.6(a), with the complete thermoelectric properties reported in Supplementary Note B.7. When acoustic phonons are the dominant scattering mechanism, μ_W should decrease with temperature as $T^{-3/2}$. [23] However, all compositions exhibit a clear step-increase in μ_W between ~ 450 and 550 K. This is attributed to the increased band convergence that occurs with the above-mentioned order-disorder transition from the ordered kesterite to the disordered kesterite phase, pointing to the importance of this transition for increasing the “electronic quality” of CZTSSe compounds. Here, we notice that the transition temperature shifts to higher values with increasing sulphur content for mixed anion compositions. This was also observed in the η trend in Figure 3.5(b), and is consistent with the shorter bond lengths, stronger ionic character, and larger bulk modulus of CZTS. [39, 51]

A systematic decrease in μ_W is observed with increasing sulphide content (x). This trend correlates with the increased m^* with x obtained from DFT-calculated density-of-states results (Supplementary Note B.8, Figure B.18), in agreement with previous reports for the CZTSSe system. [40, 41, 71, 130, 131] Within the $k \cdot p$ framework, [132] the curvature of the electronic bands near the band edge retrieves the m^* , which can be directly related

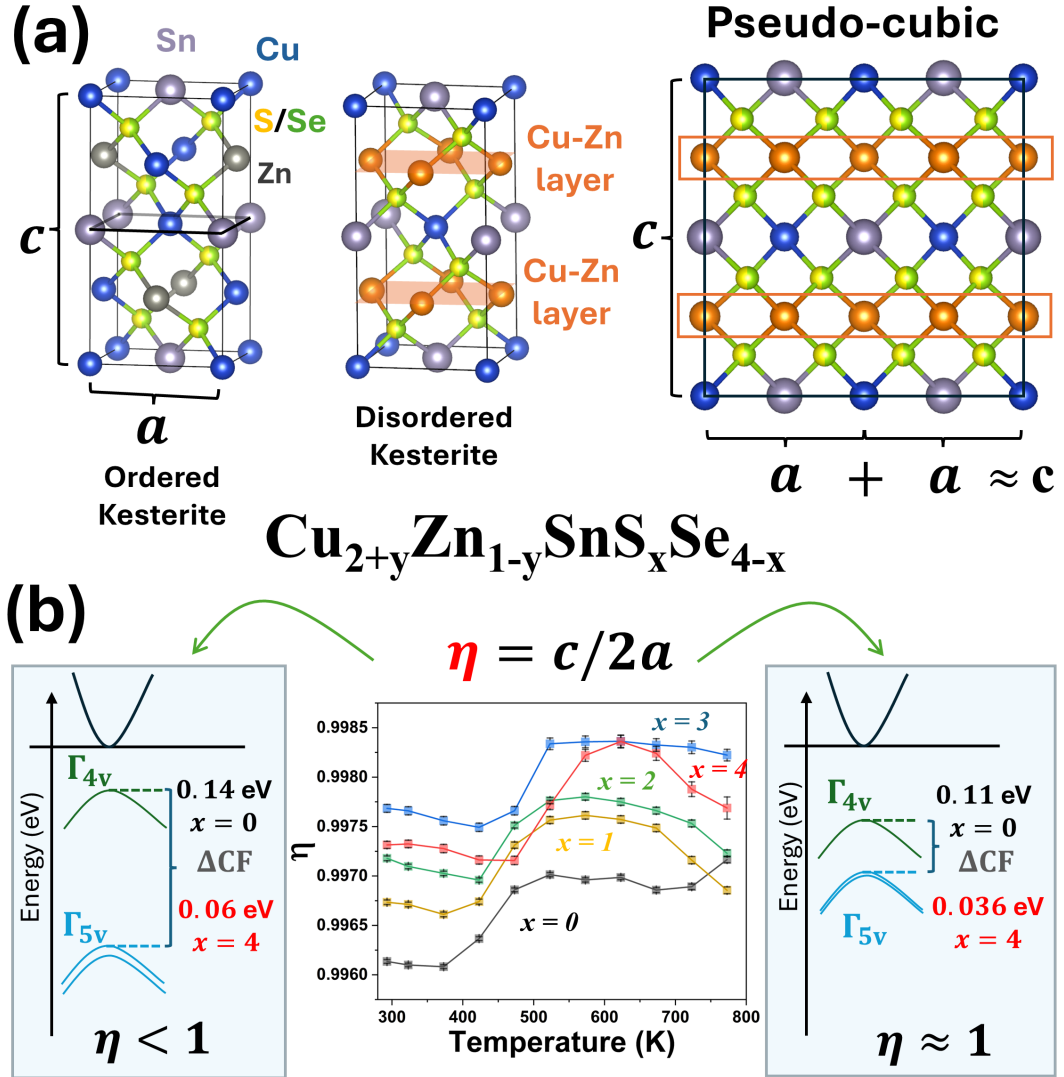


Figure 3.5: (a) Representation of the kesterite CZTSSe ordered and disordered structures and the pseudo-cubic structure. (b) η parameter estimated via high-temperature XRPD experiments. On the left side, the electronic band structure near the Γ point represents the case where $\eta < 1$. The right side illustrates the band convergence phenomenon when Cu-Zn disorder is present. Crystal field splitting values Δ_{CF} were taken from Mukherjee et al.[91, 104]

to the band gap. As sulphur substitution increases the band gap (see DoS plots in Supplementary Note B.8, Figure B.19), the valence band becomes less dispersive, resulting in a higher effective mass and, consequently, reduced carrier mobility. An independent assessment of the effective mass can be obtained by evaluating the Seebeck effective mass (m_S^*) from the experimental Seebeck coefficient and Hall carrier concentration (n_H), following the procedure developed by Snyder et al.[21] The m_S^* behavior with temperature and x is given in Supplementary Note B.8, Figure B.20. A substantial increase in m_S^* — nearly 50% for CZTS compared to CZTS_3Se_1 and almost a factor of two compared to CZTSe — is observed, following a clear compositional trend with x . This interpretation is further supported by Hall-effect measurements (Supplementary Note B.8, Figure B.21), which show a systematic decrease in transport mobility (μ_e) toward sulphide-rich compositions, in line with the increasing effective mass.

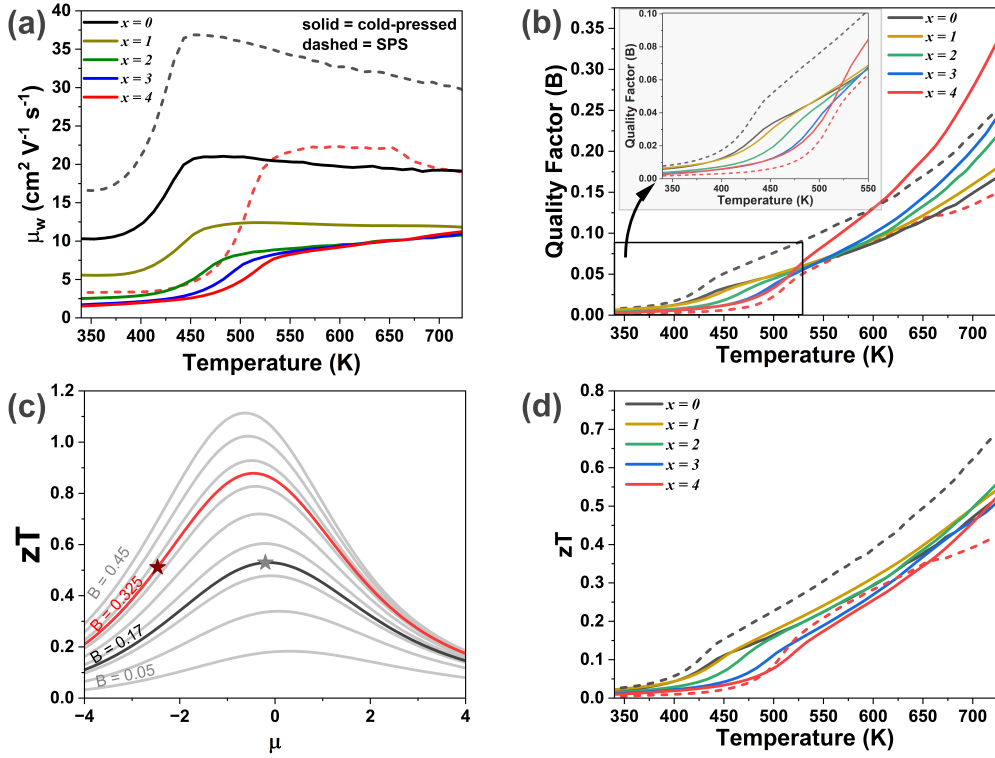


Figure 3.6: (a) Weighted carrier mobility, μ_w , and (b) thermoelectric quality factor, B , as a function of temperature for $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ samples. Solid and dashed lines correspond to cold-pressed and spark plasma sintered (SPS) samples, respectively, while colours denote the anion composition ($x = 0-4$). Panels (c) show the corresponding thermoelectric performance zT as a function of the chemical potential μ . Item (d) reports the figure of merit for all the samples.

By comparing cold-pressed with SPS samples, we observe an increase in μ_w with densification. This is justified by the increase in grain connectivity and reduced boundary scattering, increasing μ_w for both sulphide- and selenide-based materials. Even after densification, the intrinsic electronic transport remains superior in CZTSe compared to CZTS,

consistent with its smaller band gap and lower effective mass.

In contrast, microstructural densification and porosity seem to influence phonon transport more strongly than electronic transport. To assess their combined effect on thermoelectric performance, the thermoelectric quality factor B is considered.[23, 24] The quality factor represents the intrinsic potential of a material to achieve high zT , independent of carrier concentration, and is defined as a parameter proportional to the ratio between weighted mobility and lattice thermal conductivity ($B \propto \mu_W/\kappa_L$).[23, 24]

The values of B are reported in Figure 3.6(b). The trend in B with increasing sulphide content mainly follows the evolution of κ_L and is consistent with the suppressed κ_L upon anion loss, increased porosity, and lower CS (and GS). The quality factor B can also estimate the peak performance of the material if fully optimized in reduced chemical potential, μ , with the expressions reported in Refs. [5, 133]. Here, the CZTSe sample already presents an optimized level of μ in Figure 3.6(c), while in the CZTS compound, a higher carrier density would benefit its thermoelectric performance. Overall, if optimized, a potential zT of 0.88 could be achieved for the CZTS system at 723 K. Interestingly, no significant benefit to the high-temperature quality factor seems to arise from the increased alloy scattering for mixed-anion compositions. This analysis suggests that further optimization studies should focus on sulphur-rich compositions, and that overall, the increased porosity and grain-boundary density in these compositions may have a positive impact on thermoelectric performance.

By analysing the figure of merit for the cold-pressed samples in Figure 3.6(d), an interesting phenomenon is spotted. Practically all the samples presented a similar figure of merit due to a compensation between electronic and microstructural effects. In addition, the zT values for the CZTS sample are higher for the cold-pressed compared to the dense SPS samples at 723 K ($zT = 0.52$), signifying that the microstructural effects are indeed beneficial for the overall thermoelectric performance in sulphide compounds. The better densification seems to be only beneficial for the CZTSe sample, reaching a maximum of $zT = 0.7$ for the SPS sample, especially due to the markedly increased weighted mobility.

Overall, the evolution of zT across the $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ series reflects a delicate balance between intrinsic electronic structure characteristics and extrinsic microstructural effects. Sulphur substitution widens the band gap and increases the effective mass, reducing the weighted mobility and thus penalizing the electronic contribution to zT . At the same time, enhanced phonon scattering in cold-pressed samples, associated with increased porosity and increased grain boundary density, lowers the lattice thermal conductivity, partially compensating for the electronic degradation. As a result, the figure of merit remains relatively stable across compositions. Densification primarily improves electronic transport by reducing porosity and improving grain connectivity, which is particularly beneficial for CZTSe. The analysis of the thermoelectric quality factor further indicates that cold-pressed CZTSe is already close to optimal carrier concentration, whereas CZTS still offers room for improvement through targeted control of the doping level. These results highlight that further enhancement of zT in the kesterite system requires a simultaneous and delicate optimization of band convergence, carrier concentration, and phonon scattering by microstructure, beyond densification alone.

3.3 Conclusion

This study sheds light on the origin of the anomalous lattice thermal conductivity trends reported in polycrystalline $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ kesterites. Density functional theory calculations reveal that, from an intrinsic lattice-dynamical perspective, Se-rich compositions

are expected to exhibit lower lattice thermal conductivity due to their softer bonding and reduced phonon velocities. However, experimental measurements on mechanically alloyed and sintered samples show that microstructural effects dominate phonon transport. Sulphur-rich compositions display increased porosity, anion depletion, smaller grain size, and poorer grain-boundary connectivity, which significantly enhance phonon scattering and suppress lattice thermal conductivity. These microstructural effects can invert the intrinsic CZTS–CZTSe trend observed in single crystals. Furthermore, the analysis of the temperature dependence of the weighted mobility revealed that the phase transition from the ordered to the disordered kesterite structure induces a band convergence effect associated with the increase in crystalline symmetry. As a result, both the electronic transport properties and the thermoelectric quality factor are significantly enhanced. If optimized, the CZTS system could potentially achieve a zT close to 0.88 at 723 K. The interplay between intrinsic electronic structure and extrinsic microstructural effects leads to a compensation between electronic transport and phonon scattering across the CZTSSe series, resulting in comparable thermoelectric performance for different compositions, with zT values reaching ~ 0.5 at 723 K. In particular, sulphide-rich samples benefit from reduced lattice thermal conductivity despite their lower carrier mobility. These findings demonstrate that microstructural control — especially grain connectivity and porosity — plays a decisive role in determining thermal transport in kesterite thermoelectrics and must be carefully considered when interpreting compositional trends in polycrystalline materials, even among seemingly analogous compounds.

3.4 Materials and Methods

3.4.1 Materials

Elemental powders of Cu ($< 75\ \mu\text{m}$, 99%), Zn (purum, 99%), Sn (puriss, 99%), S (puris, 98%) and Se (purum, 99.5%) were employed in the synthesis, all provided by Sigma-Aldrich. All chemical reagents used in this study were analytical grade and used as received without further purification.

3.4.2 Synthesis Details

Powders were mechanically alloyed in a planetary mill (Fritsch P4 Pulverisette) inside an 80 mL WC vial containing 27 WC balls (12 mm diameter) for 120 min, with a jar rotation of $\omega = -600\ \text{rpm}$ and a main disk revolution of $\Omega = 310\ \text{rpm}$. The resulting as-milled powder was then cold-pressed into 16-mm-diameter disks ($\sim 1.5\ \text{mm}$ thick) under a 5-ton load for 3 min, followed by sintering at $300\ ^\circ\text{C}$ for 60 min and $560\ ^\circ\text{C}$ for 20 min, using a ramp rate of $20\ ^\circ\text{C}\ \text{min}^{-1}$ up to $520\ ^\circ\text{C}$ and $10\ ^\circ\text{C}\ \text{min}^{-1}$ from $520\ ^\circ\text{C}$ to $560\ ^\circ\text{C}$. The entire process was conducted inside an Ar-loaded glovebox.

High-density samples were produced by spark plasma sintering (SPS) of the as-milled powders. A pressure of 70 MPa was applied to the as-milled powders, with a temperature of $600\ ^\circ\text{C}$ for 20 min, using a 10 mm die. The thickness of the synthesized pellet remained close to 2 mm.

3.4.3 Characterization

XRPD patterns were collected using a Stadi P-Diffractometer (Stoe) in Debye–Scherrer geometry, with Ag $\text{K}\alpha_1$ radiation from a Ge(111)-Johann-type monochromator and a triple

Mythen 1K detector array (Dectris). Samples were sealed under argon in 0.3 mm quartz capillaries (Hilgenberg glass) and spun during measurement. Heating was performed using a GSB 1300 gas blower (FMB Oxford) at 5 K min^{-1} . Temperature-dependent XRPD was conducted from room temperature to 773 K in 50 K steps, with a 10 min isothermal delay before measurement for thermal equilibration and a 2 h scan time. For increased precision and counting statistics, $\text{Cu}_2\text{ZnSnSe}_4$ samples were diluted 50 wt% in quartz, measured in a single Mythen system for 8 h to reduce absorption effects. Reproducibility checks were conducted on a Bruker D8 Discover in Bragg–Brentano geometry using Co $K\alpha$ ($\lambda = 1.78897 \text{ \AA}$) radiation. Sample disks were attached to the holder and measured over an angular range of $12\text{--}94^\circ$ in 2θ . Profile modelling employed the whole powder pattern method available within the Rietveld analysis performed using TOPAS software.[79, 80, 91, 134, 135]

The Raman measurements were performed in LabRAM Aramis (Horiba Jobin-Yvon), which has an optical microscope and $100\times$ objective, with a 532 nm source wavelength. Raman spectrum analysis, including baseline extraction and peak fitting with Lorentzian profiles, was performed using Origin(Pro) 2023b (OriginLab Corporation, Northampton, MA, USA).

SEM micrographs were acquired using a JEOL JSM-7001F FEGSEM (JEOL, Tokyo, Japan), while EDXS data was collected with an Oxford INCA PentaFETx3 detector (Oxford, UK). The electron beam energy ranged from 10 to 15 keV, with a 5–10 mm working distance.

The absolute Seebeck coefficient and resistivity were measured using a four-contact configuration and a Pt standard with a Linseis LSR-3 (Linseis Messgeräte GmbH). Measurements were conducted under a static He atmosphere ($\sim 0.2 \text{ bar}$) from room temperature (RT) to 750 K, with a 10 K min^{-1} heating rate and a $\sim 10 \text{ K}$ temperature gradient across the sample. Thermal conductivity was calculated as $\kappa = \alpha \rho C_p$, where α is thermal diffusivity, ρ is geometrical density, and C_p is specific heat, calculated via the Dulong–Petit law.[136] Temperature-dependent thermal diffusivity (RT–480 K/750 K) was measured using a Linseis LFA 500 (Linseis Messgeräte GmbH) under vacuum on disk samples ($\sim 0.7 \text{ mm}$ thick). The lattice thermal conductivity, κ_l , was extracted from the $\kappa = \kappa_e + \kappa_l$ relationship, where the electronic component was estimated via the Wiedemann–Franz law using conductivity and Seebeck measurements.[5, 101, 137] Electrical transport properties, including carrier concentration and carrier mobility, were determined by Hall effect measurements using the Van der Pauw geometry with a Linseis HCS-1 system. For these measurements, a square sample with dimensions of $12.5 \text{ mm} \times 12.5 \text{ mm}$ was prepared. The experiments were conducted in a nitrogen atmosphere over a temperature range from 303 K to 473 K.

3.4.4 Simulation Details

The electronic structure and lattice dynamical properties of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ have been studied using density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP).[72, 73] The interaction between the ionic cores and the valence electrons was treated with the projector augmented wave (PAW) method. The exchange and correlation potential was treated with the generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof revised for solids (PBEsol) potential.[138]

To fulfil the condition of the desired stoichiometry of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$, and to account for the disorder of the cations, a 64-atom supercell was constructed. The supercell approach allows an accurate description of the compositional changes and maintains the overall chemical composition and local bonding environment.

Structural relaxation: All structures were fully relaxed with an energy cut-off of 500 eV. The electronic minimization threshold was set to 10^{-8} eV . Ionic relaxation was carried out

with the conjugate gradient algorithm, with the force on each atom minimized as a function of the ionic positions. Gaussian smearing with a smearing width of 0.01 eV was utilized. A Γ -centered Monkhorst–Pack k -point mesh of $4 \times 4 \times 4$ was utilized to sample the Brillouin zone of the 64-atom supercell.

Electronic density of states: After the structural relaxation, self-consistent field (SCF) calculations were carried out with a denser $8 \times 8 \times 8$ Γ -centered k -point grid for an accurate prediction of the charge density and density of states (DOS). To improve the estimation of the band gap, hybrid functional calculations were carried out with the Heyd–Scuseria–Ernzerhof (HSE06) functional.[139] In the calculations, the Hartree–Fock exchange interaction is included. To improve computational feasibility, the hybrid functional calculations were carried out with a $4 \times 4 \times 4$ k -point mesh.

Mechanical properties: The elastic constants and other mechanical properties were calculated via density functional perturbation theory (DFPT), which has been implemented in VASP.[140] The calculations have been carried out for the 64-atom supercell.

Phonon dispersion and phonon density of states: The phonon dispersion relations and the phonon density of states have been calculated via the finite displacement method, which has been implemented in the Phonopy code.[76] The force constants have been calculated via VASP for the relaxed 64-atom supercell. The Brillouin zone and supercell have been chosen for the calculations to ensure that the frequencies converge.

Mode Grüneisen parameter: The mode Grüneisen parameters (γ_i) have been calculated via the quasi-harmonic approximation (QHA). The volume dependence of the supercell has been calculated by expanding and contracting the volume by 1% above and below its relaxed volume. The mode Grüneisen parameter has then been calculated via the finite differences of the phonon frequencies with respect to volume.

Acknowledgements

The previous-to-last and last authors acknowledge the Italian Ministry of University and Research (MUR) within the framework of the DICAM-EXC project (Departments of Excellence 2023–2027, grant L232/2016). S.B. acknowledges the Deutsche Forschungsgemeinschaft (DFG) for financial support through grant BE 7407/1-1, “Joint German–Russian Cooperation Project”, until February 2022.

Chapter 4

Optimizing CuFeS₂ Chalcopyrite Thin Film Synthesis: A Comprehensive Three-Step Approach Using Ball-Milling, Thermal Evaporation, and Sulfurization Applied for Thermoelectric Generation

Abstract

CuFeS₂ (CFS) stands out as a promising narrow band-gap semiconductor for thermoelectric (TE) applications. However, its high lattice thermal conductivity is one of the factors hampering its potential for TE generation. A common strategy to tackle this problem is to produce this material in thin film form. Thus, this study aims to practically understand and optimize the synthesis of CFS 2D materials using a simple three-step approach of ball-milling, thermal evaporation, and sulphurization of the CuFe metallic precursors. The tools for thin film characterization employ X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDXS), and Hall-effect measurements. DFT phase diagrams are also used to understand the energy of formation of the secondary phases present in the film. Here, we highlight that the ball-milling mechanisms, allied with high vacuum and high energy density during evaporation, are essential for the interdiffusion of Cu and Fe during the evaporation process. The film presented a flower-like morphology and p-type semiconducting behavior. A proof-of-concept Thermoelectric Generator (TEG) was designed in an in-plane geometry, showing a power output per unit active area of 114 nW cm⁻² ($\Delta T = 180^\circ\text{C}$), comparable to other Cu-based materials, thus demonstrating the feasibility of this method of synthesis for TE applications.

4.1 Introduction

Chalcopyrites are a class of ternary materials with a diamond-like $I-42d$ crystal structure. They present an opposite heat transport mechanism to the Keyes theory [141, 142], meaning that its thermal conductivity increases with lower mean atomic mass of the compound. The best performing chalcopyrites for thermoelectric (TE) applications rely on the use of elemental Se, In, and Te [143, 144]. However, they are considered either toxic or rare, leaving the sulphide-based chalcopyrites as a cheaper option for energy applications. Among them, CuFeS₂ (CFS) stands as one of the most abundant copper ore minerals [145], presenting a narrow band-gap (0.5 eV), high electrical conductivity (σ) and Seebeck (S) coefficient ($\sim -480 \mu\text{V/K}$) [146]. For CFS, its light constituent elements and Zn blend structure mean that the lattice thermal conductivity is large, thus resulting in poor TE performance in its bulk and undoped form [147]. Other Cu-Fe-S phases such as cubic bornite Cu₅FeS₄ ($Fm-3m$) [148, 149], cubic Cu₁₈Fe₁₆S₃₂ talnakhite ($I-43m$) [150], and metastable hexagonal Wurtzite-type CuFeS₂ ($P6_3mc$) [151] do not suffer from this problem since they present significant disorder in their structure, stemming from their cation-vacancy mechanism. However, the chalcopyrite CFS phase persists as the most stable phase and is frequently employed for practical applications [152].

For bulk CFS materials, the reduction of the thermal conductivity (κ) relies on strategies such as nanostructuring [147, 153], doping [45, 154–156], the use of a sulphur-deficient stoichiometry [152], and/or a combination of them. Nanostructuring induces the so-called phonon-glass electron-crystal behavior [100], where the grain boundaries of the crystallites scatter the phonon waves transporting heat, without a significant decrease in σ . This strategy reduced CFS thermal conductivity by 47%, although the electron-crystal behavior was compromised [147]. Other than that, lattice engineering via doping and vacancy induction can promote more obstacles to phonon propagation within the lattice. Even though intrinsic doping can significantly enhance the power factor of CFS due to the introduction of more charge carriers into the system, the drop of lattice κ is still not satisfactory. According to T. Mori *et al.* [147], the reason is that the phonon waves responsible for heat transportation have a wavelength of about 100–1000 nm. To block the propagation of these phonons, they suggest transforming the material into a thin film form, having a thickness around the value of the phonon wavelengths.

Practical ways to employ thin film materials as Thermoelectric Generators (TEG) employ an in-plane π geometry [30, 33]. For these TEGs, p- and/or n-type legs are deposited in a flat substrate, displaced electrically in series and thermally in parallel, conveniently joined by metallic contacts. Upon heating one of its extremities, electrical energy is produced. To the best of our knowledge, no CFS in-plane generator has been fabricated in this manner. Nonetheless, various techniques are employed to convert bulk CFS into thin films. They include sputtering [151] from high-density spark-plasma sintered (SPS) materials [147, 152, 157], flash methods [158, 159], spray pyrolysis [160–162], and thermal evaporation [163]. Evaporation is considered the cheapest and least complex method due to its higher deposition rate and the use of readily available powders. However, the different melting points of Cu and Fe mean that additional treatments are needed to promote the intermixing between the two. A strategy to solve this issue is proposed by Barkat *et al.* [163], where the targeted substrates are heated while multiple Cu/Fe layers are being deposited. The substrates are later exposed to a sulphur-rich atmosphere, a process called sulphurization, in order to introduce sulphur into the structure.

Thus, the current study introduces a novel three-step method for CFS fabrication using a previous ball-milling step prior to the thermal evaporation and sulphurization processes.

The optimization of every synthesis process is thoroughly discussed, with the intention of providing a clear and instructive roadmap for future fabrication of this material in thermoelectricity (TE) and other potential fields. This optimization comprises tests on the evaporation of the non-milled powders (Section 4.3.1), and the milling parameters (Section 4.3.1). Characterization of the optimized film uncovers its structural properties, phase purity, surface morphology, and stoichiometry balance through X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Electron Dispersive X-ray spectroscopy (EDXS) analysis, and Hall-effect measurements (Section 4.3.2). To gain further insights into secondary phase formations within the phase diagram, Density Functional Theory (DFT) calculations are also employed. The viability of this synthesis approach is substantiated by the fabrication of a proof-of-concept Thermoelectric Generator (TEG), having its specific power output measured using I-V curves. In Section 4.4, we provide commentary and comparisons regarding this synthesis route, along with an exploration of potential applications.

We also put forward that this method can be employed to fabricate a proof-of-concept Thermoelectric Generator (TEG), demonstrating the feasibility and practical performance of a CFS TEG made by this synthesis route.

4.2 Materials and Methods

4.2.1 Ball-milling of the metal precursors

The elemental powders of Cu (-100 ~ +325 mesh, 99.9%, Alfa Aesar) and Fe (-20 mesh, 99.9%, Alfa Aesar) were milled in three batches (namely, FeCu-01, Fe_{1.76}Cu-02, and FeCu-03) and their milling parameters are displayed in Table C.1 of Supplementary Note C.1. The milling procedure employed a Fritsch P4 planetary ball mill equipped with WC vials (80 mL of volume) and 12 mm balls of the same material, keeping a Ball-to-Powder (BPR) ratio of 100:1. The rotation was set to 310 rpm for the main disk, with a -1.80 main disk-to-planet ratio. Ethanol (99%, Sigma Aldrich) was used as a lubricant in the last batch, which helped with the retrieval of the as-milled powder from the vial and better microstructural homogenization.

4.2.2 Cu-Fe thin-film deposition by evaporation

The thin films were deposited on soda-lime glass (SLG) substrates using a thermal evaporator (Tecum AG VCM600 V1) with voltage of 12 V. The deposition parameters are displayed in Table C.2 for samples 1 to 18. Substrates were washed using a concentrated KOH solution and commercial soap, further rinsed with ultra-pure water and dried using an air gun. For some samples, the SLG substrate was polished using sandpaper to improve adhesion.

4.2.3 sulphurization processes

The sulphurization parameters were carefully chosen through a process of iterative experimentation. It was carried out in a tubular furnace (Carbonite Gero) at 500°C (heating rate: 10°C min⁻¹) and 425°C (heating rate: 20°C min⁻¹) for 1 h, using two different settings (1) static Ar atmosphere, and (2) dynamic N₂ flux, respectively. The Cu-Fe samples were placed in a carbon sample holder sided by a crucible containing 50 mg of S (-325 mesh, 99.5%, Alfa Aesar).

4.2.4 X-ray diffraction

The XRD measurements were conducted in a Bruker D8 Discover diffractometer in θ - 2θ configuration. The diffractometer was equipped with a Co K α source ($\lambda = 1.7889$ Å) and 192 microstrip channels (1D configuration) detector. The illumination area was fixed to 1×8 mm². XRD data were collected from $2\theta = 15^\circ$ to 95° , with a step size of 0.05° and a collection time of 1 s per step. The phase identification was performed using ICSD [164] and PDF4+ [165] databases. Rietveld and line profile analysis were performed using the commercial version of TOPAS 6 (Bruker) software [79]. The instrumental profile was retrieved using a LaB₆ (NIST SRM 660c) standard sample. A double-Voigt profile was employed for the microstructural analysis. One of the Voigt functions is attributed to crystallite size, where its integral breadth (β) is related to the mean volumetric crystallite size (L_{vol}) according to the Scherrer equation (vide TOPAS manual for details [79]). The microstrain (ε) is obtained by the equation $\varepsilon = \beta/(4 \tan \theta)$, where β is the full width half maximum of the diffraction peak and θ is the diffraction angle. A March-Dollase approach was employed for the estimation of preferred orientation in the prepared films [79].

4.2.5 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

SEM micrographs were collected with a JSM-7001F FEGSEM (JEOL, Tokyo, Japan) instrument equipped with an energy-dispersive X-ray spectroscopy detector (EDXS, Oxford INCA PentaFETx3, Oxford, UK). The electron beam energy was in the range of 10–15 keV, with a working distance of 5 to 10 mm. The morphology of the thin films was acquired in a top-down configuration and was later placed vertically in a stub to perform the cross-sectional analysis.

4.2.6 Computational methods

The Vienna Ab initio Simulation Package (VASP) [72, 73] was used to perform DFT calculations on the Cu-Fe-S system. The generalized gradient approximation with Perdew–Burke–Ernzerhof (PBE) [74] electron exchange–correlation was employed. The energy cut-off was set at 500 eV and the structures were relaxed using the conjugate gradient algorithm until the force on each atom was less than 0.001 eV/Å. The electronic convergence was set to 10^{-6} eV. The specific k-point mesh employed for each system were as follows: CuFeS₂ ($8 \times 8 \times 4$), Cu₃Fe ($8 \times 6 \times 8$), Cu₇S₄ ($6 \times 6 \times 4$), CuS ($4 \times 6 \times 8$), CuS₂ ($4 \times 6 \times 8$), Fe₃Cu ($8 \times 6 \times 4$), FeS ($6 \times 6 \times 4$), FeS₂ ($6 \times 6 \times 4$), bornite ($4 \times 4 \times 4$) and talnakhite ($6 \times 6 \times 6$). The Bornite and Talnakhite structures were modelled using the 160-atom and 64-atom cells, respectively, with the lattice parameters obtained from experiments in each case. Spin polarization was considered to account for the effects of electron spin interactions. The Bornite and Talnakhite structures were modelled using the 160-atom and 64-atom cells, respectively, with the lattice parameters obtained from experiments in each case. Both the compounds exhibit random occupation of Cu and Fe atoms, and pseudorandom numbers were used to model these structures.

4.2.7 Hall measurements

A Linseis HCS 1 instrument with two permanent magnets (± 0.7 T) was used to conduct the Hall effect measurements under an N₂ environment at a temperature range of 40–200°C.

4.2.8 Thin film thermoelectric generators

An in-plane π -shaped thermoelectric generator (TEG) was fabricated on an SLG substrate. The TEG comprises 2 pairs of CFS and silver (Ag) legs, electrically connected in series and thermally in parallel, with dimensions sketched in Figure 4.1a. The CFS legs were deposited using the same experimental conditions as the optimized CFS sample, i.e., Sample 18, as discussed later in the text. The silver legs (contacts) were deposited by thermal evaporation of elemental Ag pellets. The current (I), voltage (V), and power output ($P = VI = RI^2$) were measured by varying the hot side temperature and load resistance using a homemade setup, shown in Figure 4.1b. During the measurements, an active cooler was employed at the cold end of the TEG, maintaining a stable temperature of $\sim 20^\circ\text{C}$, supported on a heat dissipator (passive cooler). Foams were placed to preserve the local temperature on the hot side. Figure 4.1b also shows the TEG and the circuit employed for the measurement, where a Keithley 2611A served as the ammeter and voltmeter.

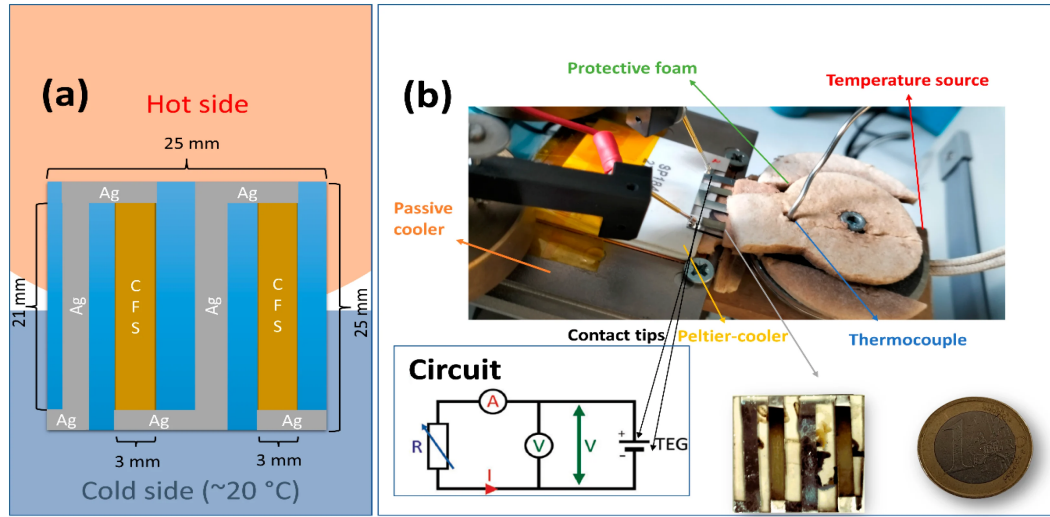


Figure 4.1: (a) TEG dimensions and layout. (b) Homemade setup for the I-V-P measurements, circuit diagram, and real-size comparison of the TEG with a one-euro coin for scale.

4.3 Results

4.3.1 Evaporation optimization

Non-milled Cu-Fe powders evaporation

To optimize the CFS thin film deposition, it is necessary to have a prior understanding of the thermal evaporation of the elemental Fe and Cu powders. Therefore, the thermal evaporation was carried out on pristine Fe and Cu, as well as in a manual mix of Fe-Cu powders (atomic ratio 1:1). The XRD patterns of the evaporated films are shown in Figure 4.2(a), and their respective evaporation parameters are summarized in Figure 4.2(b) (with full details in Table C.2 of Supplementary Note C.1). Through iterative experimentation, the evaporation current for Cu and Fe was established as 105 A and 140 A, for samples (1) and

(2), respectively. The same currents were employed during Cu-Fe blend powders evaporation for samples (3) and (4). For samples (5)–(8), an optimization of the target-to-source distance and current-step variation was performed. Fine details can be found in Supplementary Note C.2. Overall, one can notice that the melting point of Fe (1538°C) is higher than that of Cu (1085°C), so clearly, compared to Cu ($I = 105\text{A}$), the evaporation of Fe ($I = 140\text{A}$) required a higher current. This also means that, during the evaporation process of Cu-Fe mixed powders, Cu evaporates first, forming the base layer of the film, followed by the deposition of Fe, which creates the surface layer (a bilayer film). Consequently, the majority of the film's surface exhibits the bcc Fe phase.

Among all these tests (Samples 1–8), Sample 8 is the most promising due to a better intermixing of Fe-Cu in the as-evaporated film. sulphurization of sample 8 under a static Ar atmosphere resulted in the formation of two phases, namely CFS chalcopyrite ($I-42d$, PDF # 04-002-0241) as the major phase ($\sim 70\%$ weight proportion), and a minor $\text{Cu}_{18.32}\text{Fe}_{15.9}\text{S}_4$ talnakhite phase ($I-43m$, PDF # 01-071-2438) with $\sim 30\%$ weight proportion. The talnakhite phase presents low thermal conductivity [150], although in this case, the mixing of phases turns the sample poor in adhesion, as can be visualized in Figure C.14 of Supplementary Note C.5.

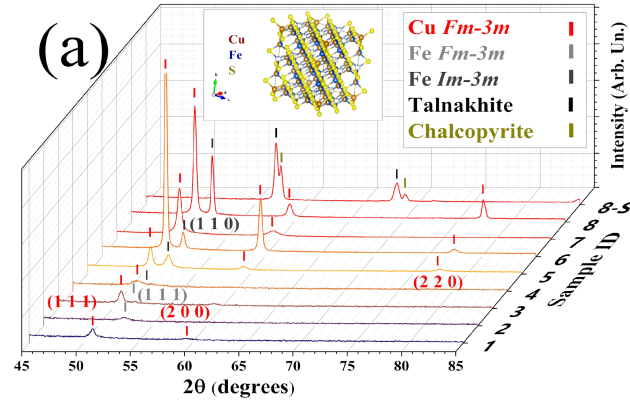
To get an insight into the multiphase formation in the thin film, the DFT phase diagram for Cu-Fe-S is presented in Figure 4.3. The gradient scale shows the formation energy per atom, which is a measure of the energy required to form one unit of the compound from its atoms. The CFS Chalcopyrite phase has a formation energy of -0.411 eV/atom , with the talnakhite and bornite phases presenting values of -0.214 eV/atom and -0.090 eV/atom , respectively. Hence, chalcopyrite is the most stable phase among the ternary compounds, however, the proximity in the formation energies of other Cu-Fe-S phases makes it challenging to obtain a pure CFS. Moreover, the binary alloys of FeS_2 and CuS_2 also have low formation energies and are likely to form.

In the literature, the Cu-Fe-S phase diagram was summarized in the work of V. Raghavan [166] from experimental information. Indeed, the complexity of the Cu-Fe-S goes beyond what is reported here using DFT, where more than 12 ternary Cu-Fe-S phases are identified to form, and a handful number of secondary phases are made present. However, one can highlight the studies on CuFeS_2 -FeS composite system shows that effect of the FeS in the system during heating [167]. CuFeS_2 chalcopyrite can only form in a pure phase if the quantity of FeS is below 5% throughout the range of temperature from 400°C to 550°C . We speculate that the presence of two distinct layers of Cu and Fe present in the films can induce the formation of Fe sulphide phases. Thus, it indicates that a better intermix of Cu and Fe must be performed. Hence, ball-milling of CuFe can be used to overcome the stoichiometry issue.

Optimization of the Ball-milled Cu-Fe

A common description of the mechanochemical reaction mechanism for ductile-ductile alloying is given by Suryanarayana [168]. As the milling starts, the ductile materials are subjected to plastic deformation and form bigger agglomerates. With milling time, the grains undergo cold hardening and eventually break, exposing fresh active surfaces. This breaking reduces the grain size and favors the exchange of electrons and ions between the reactants. Further increase in milling time leads to the formation and growth of short-range crystal order. A complete reaction is only possible if one material successfully diffuses into the other.

For CuFe alloys, M. Rabiee et al. [169] used a shaker mill and suggested that the dissolution of Fe into the Cu requires longer milling times (20 h) compared to those employed



(b)

Strategy	Non-Milled Powders							
Material	Fe	Cu					FeCu	
Setup	140 A / 1h	105 A / 1h	105 A / 1h	140 A / 1h	5 A / 3 min 105 A to 140 A Mass 0.6 g	105 A / 10 min 140 A / 1 min Target 9.5 cm Mass 0.2 g	105 A / 3 min Target 7.5 cm Mass 0.15 g	105 A / 10 min 140 A / 4 min Target 7.5 cm Mass 0.15 g
Phases	<i>Fm-3m</i>	<i>Fm-3m</i>	Cu: <i>Fm-3m</i> Fe: <i>Im-3m</i>	Fe: <i>Fm-3m</i> Cu: <i>Fm-3m</i>	Cu: <i>Fm-3m</i> Fe: <i>Im-3m</i>	Cu: <i>Fm-3m</i> Fe: <i>Im-3m</i>	Cu: <i>Fm-3m</i>	Cu: <i>Fm-3m</i> Fe: <i>Im-3m</i>
Sample ID	1	2	3	4	5	6	7	8
Sulfurization								Setup 1: Talnakhite + Chalcopyrite

Figure 4.2: (a) Diffractogram of samples 1 to 8. The tick markers represent the Bragg position of the phases, where the corresponding labelling is in the top-right corner. Sample 8-S represents sulphurized sample 8, where the process described in Section 4.2.3 was employed. The inset shows the crystal structure of CFS Talnakhite. The Rietveld refinements are available in Supplementary Note C.4. (b) Diagram with the main synthesis parameters used for the non-milled powder optimization and main results, such as element material used, current employed (A), evaporation time (h), target distance (cm), and mass of powder (g). Please refer to Table S2 for further details.

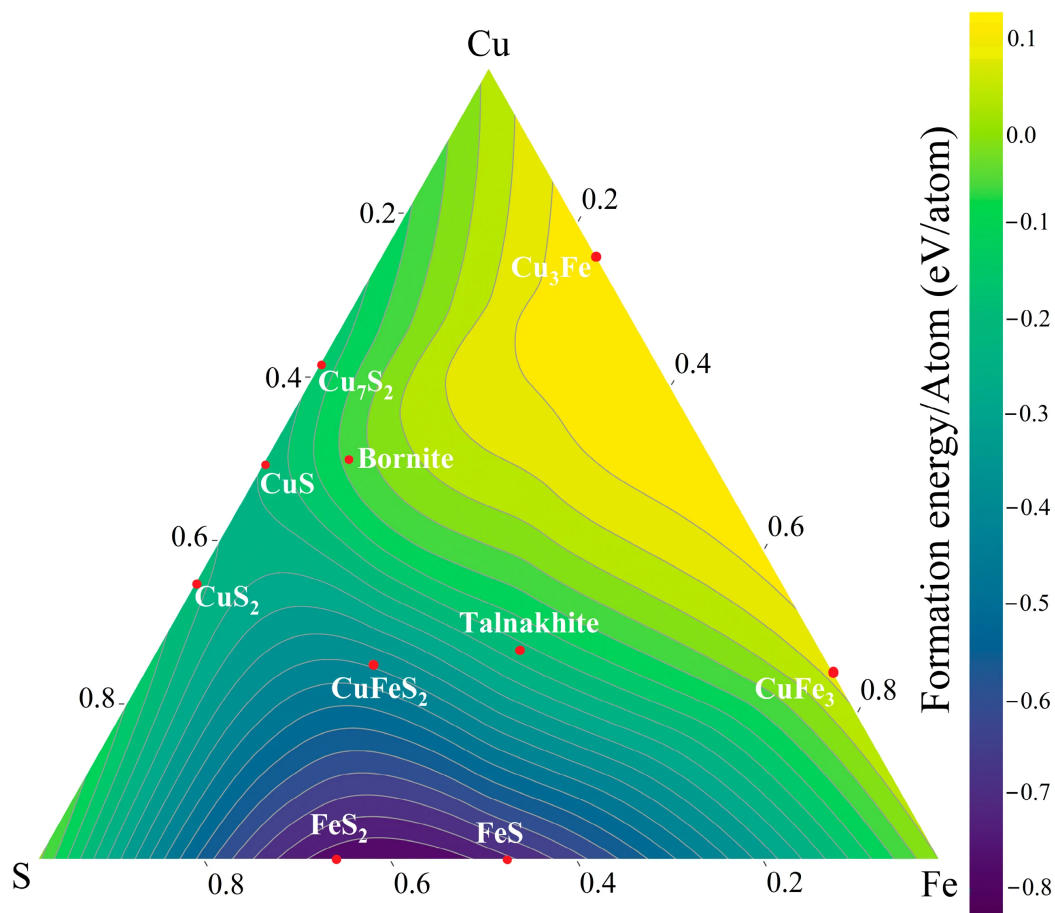


Figure 4.3: Ternary contour plot of the phase diagram of Cu, Fe, and S obtained through DFT calculations.

here (3 h) for a 20% Fe proportion. However, metastable fcc CuFe alloy with 1:1 proportion (desired for CuFeS_2) is only achieved by even longer milling times (20–360 h) for both low- and high-energy ball-milling [170, 171] or by high-pressure synthesis [172, 173]. Even upon completion, when thermally treated, CuFe alloys remain metastable and tend to decompose back into separate Cu and Fe phases [174, 175]. However, the mechanisms of milling such as plastic deformation, agglomeration, and nucleation, can still be used to better intermix Cu and Fe for the evaporation, even if the formation of the CuFe alloy is not complete. Milling can also tackle another problem observed during the evaporation of the metal precursors. As discussed earlier (Samples 3–7), the evaporation of non-milled powder results in bilayer films, where the ferromagnetic properties of fcc Fe cause significant damage to the film surface (see Figure C.14).

Therefore, three different milling conditions were tested, as described in Section 4.2.1 and Table C.1. The first (FeCu-01) and second (Fe1.76Cu-02) samples were milled for 2 h, with Fe:Cu ratio of 1:1 and 1.76:1, respectively. The third sample (with Fe:Cu = 1:1), was milled for 3 h using ethanol as a control process agent. The XRD patterns of the three as-milled Fe-Cu powders are shown in Figure 4.4. The Rietveld refinements (vide Figure C.13 of Supplementary Note C.4) show that the $\text{Cu}_{0.8}\text{Fe}_{0.2}$ (PDF4+ database entry #40031453) gives a good fit for the diffractograms for the three different samples. However, the Cu:Fe proportion might not be 0.8:0.2 for all of them. Since Cu and Fe have a similar number of electrons, this ratio is hard to be correctly retrieved by XRD, however, the incorporation of Fe into the structure can be seen by the decrease in the Fe relative intensities of samples FeCu-01 and FeCu-03. This is also observed in an increase in the lattice parameters from FeCu-01, to Fe1.76Cu-02, and to FeCu-03 of 3.6197(3) Å, 3.628(4) Å, and 3.640(4) Å, respectively.

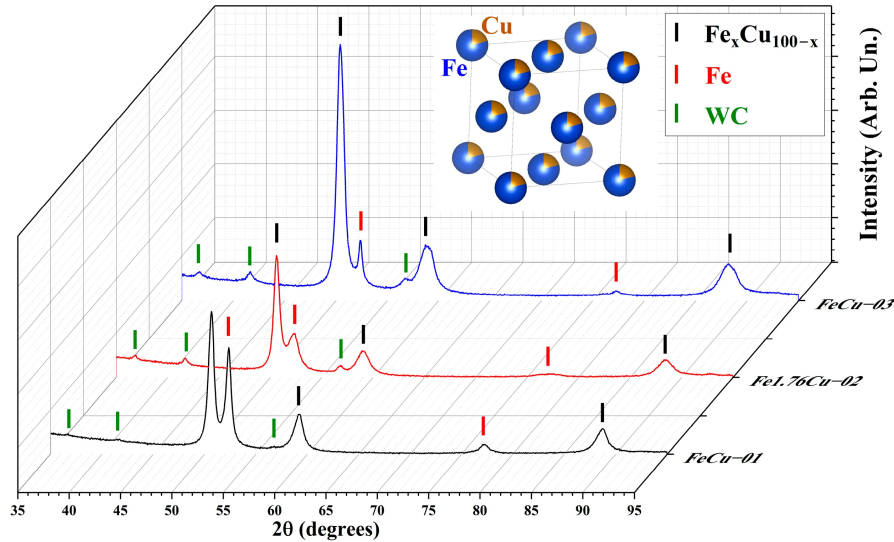


Figure 4.4: Diffractograms of the FeCu-01, Fe1.76Cu-02, and FeCu-03 ball-milled powders. Rietveld refinements are available in Figure C.13, containing Figures S18, S19, and S20. The tick markers indicate the Bragg 2θ positions of the $\text{Fe}_x\text{Cu}_{100-x}$ fcc phase (black, PDF4+ database entry #40031453), Fe bcc (red, PDF4+ database entry #40079753), and WC (green, PDF4+ database entry #40045823).

In order to investigate the effect of milling in evaporation, the first tests using the FeCu-01 milled powders were performed for Samples 9–11. All the strategies use a stepwise increase in current (see Table C.2 for reference). The diffractograms for these samples are shown in Figure 4.5(a), and the main parameters of synthesis are found in Figure 4.5(b). The strategy now consists of optimizing the source-to-target distance. Comparing Samples 9 (27 cm) and Sample 10 (7.5 cm), the crystallinity of the as-evaporated films is improved, although the adhesion is still poor. Good adhesion is only achieved when the vacuum is improved, down to 10^{-6} mbar for Sample 11. In these cases, the mass of the powder was also reduced to 0.06 g, increasing the energy per gram of material during evaporation. Further details on this optimization process can be found in Supplementary Note C.3.

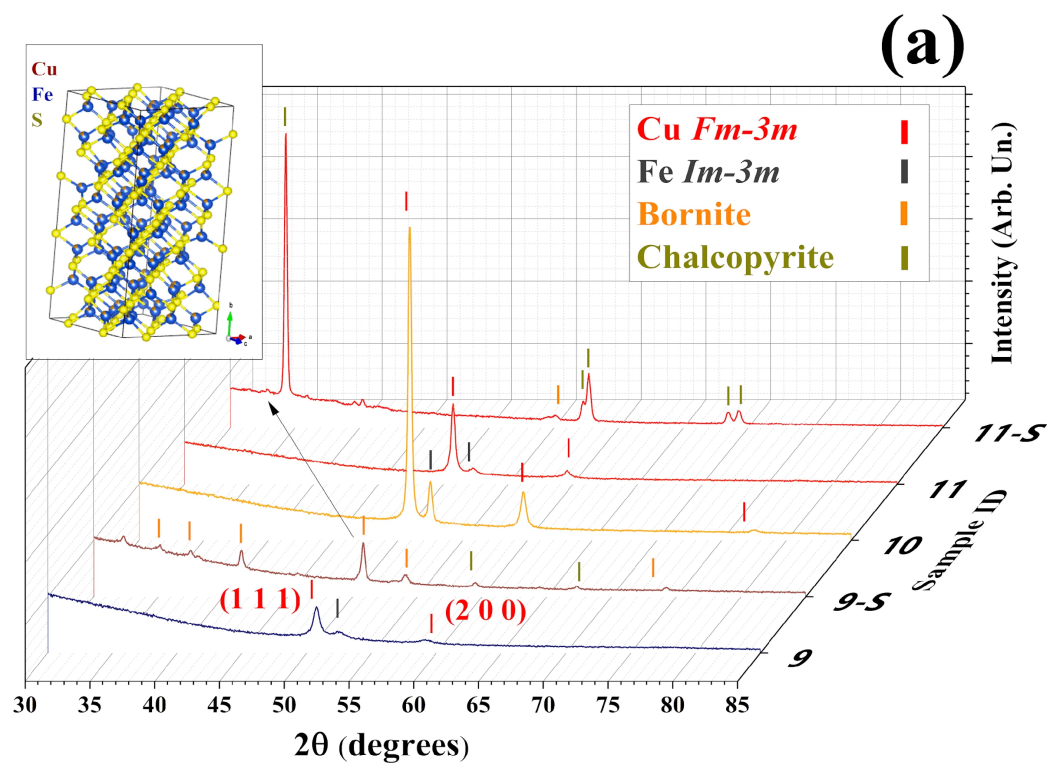
Considering the evaporation conditions of Sample 11 (using FeCu-01), the other two as-milled powders (Fe1.76Cu-02 and FeCu-03) were evaporated. Figure 4.6(a) displays diffractograms of the sulphurized films prepared using the three different milled powders. Figure 4.6(b) presents the main parameters utilized. In certain samples marked with the letter P, sandpaper was used to polish the SLG substrates before the evaporation. All the as-evaporated films exhibited fcc Cu and bcc Fe phases (refer to Figure C.15 of Supplementary Note C.5). The effect of the polishing can be observed by comparing samples 12 and 13 in Figure C.14. Overall, this strategy leads to better crystallization and weaker preferred orientation in the post-sulphurized films. However, to make a balance between purity and adhesion quality, sample 16, without polishing, was selected as the optimized film (vide Figure 4.6(a) insets). SEM and EDXS measurements of the CuFe precursor (FeCu-03, pre-sulphurized sample 18) can be visualized in Supplementary Note C.7. The use of setup 2 for the sulphurization – with a dynamic flow of N_2 , brings better results compared to setup 1 – when a static Ar atmosphere is employed. Thus, sample 11 presents the best conditions for ball-milled powder evaporation.

Considering the evaporation conditions of Sample 11 (using FeCu-01), the other two as-milled powders (Fe1.76Cu-02 and FeCu-03) were evaporated. Figure 4.6a displays diffractograms of the sulphurized films prepared using the three different milled powders. Figure 4.6b presents the main parameters utilized. In certain samples marked with the letter P, sandpaper was used to polish the SLG substrates before the evaporation. All the as-evaporated films exhibited fcc Cu and bcc Fe phases (refer to Figure C.15 of Supplementary Note C.5). The effect of the polishing can be observed by comparing samples 12 and 13 in Figure S26. Overall, this strategy leads to better crystallization and weaker preferred orientation in the post-sulphurized films. However, to make a balance between purity and adhesion quality, sample 16, without polishing, was selected as the optimized film (vide Figure 4.6a insets). More details regarding the optimization process can be found in Supplementary Note C.3.

4.3.2 Optimized CFS thin film

To assess the reproducibility of the synthesis, sample 18 was synthesized with the identical conditions as sample 16, i.e., evaporating FeCu-03 ball milled powders, with a lower vacuum (10^{-6} mbar), using a two-step current of 105 A and 140 A, followed by sulphurization with a dynamic N_2 flow. Further characterization of surface and cross-section morphology, resistivity, carrier concentration, and mobility was carried out on this sample.

Figure 4.7 shows the Rietveld refinement of the XRD data of Sample 18. The QPA shows that the sample consists mainly of the desired CFS chalcopyrite phase (PDF # 000250288), $\sim 93\%$ by weight. Nevertheless, the CuFe-bornite (PDF #40080243) and pyrite FeS_2 (PDF #000060710) phases also formed along with CFS, with a weight percentage of ~ 5 and



(b)

Strategy	Milled Powders – 1 st Optimization		
Material	FeCu-01		
Setup	Far Target 27 cm	Closer Target 7.5 cm & lower mass	High vacuum 10 ⁻⁶ mbar
Phases	Cu: <i>Fm-3m</i> & Fe: <i>Im-3m</i>	Cu: <i>Fm-3m</i> & Fe: <i>Im-3m</i>	Cu: <i>Fm-3m</i> & Fe: <i>Im-3m</i>
Sample ID	9	10	11
Sulfurization	Setup 1: Bornite 50% + Chalcopyrite 50%		Setup 2: Bornite + Chalcopyrite 96%

Figure 4.5: (a) Diffractograms for the 9 to 11. Samples 9-S and 11-S correspond to the patterns of the sulphurized samples 8 and 11, respectively. The tick markers correspond to the Bragg peaks of the phases identified in the top-right corner, and the Rietveld refinements are available in Supplementary Note 4. (b) Diagram with the main synthesis parameters used for the non-milled powder optimization, such as element material used, current employed (A), evaporation time (h), target distance (cm), and mass of powder (g). Please refer to Table S2 for further details.

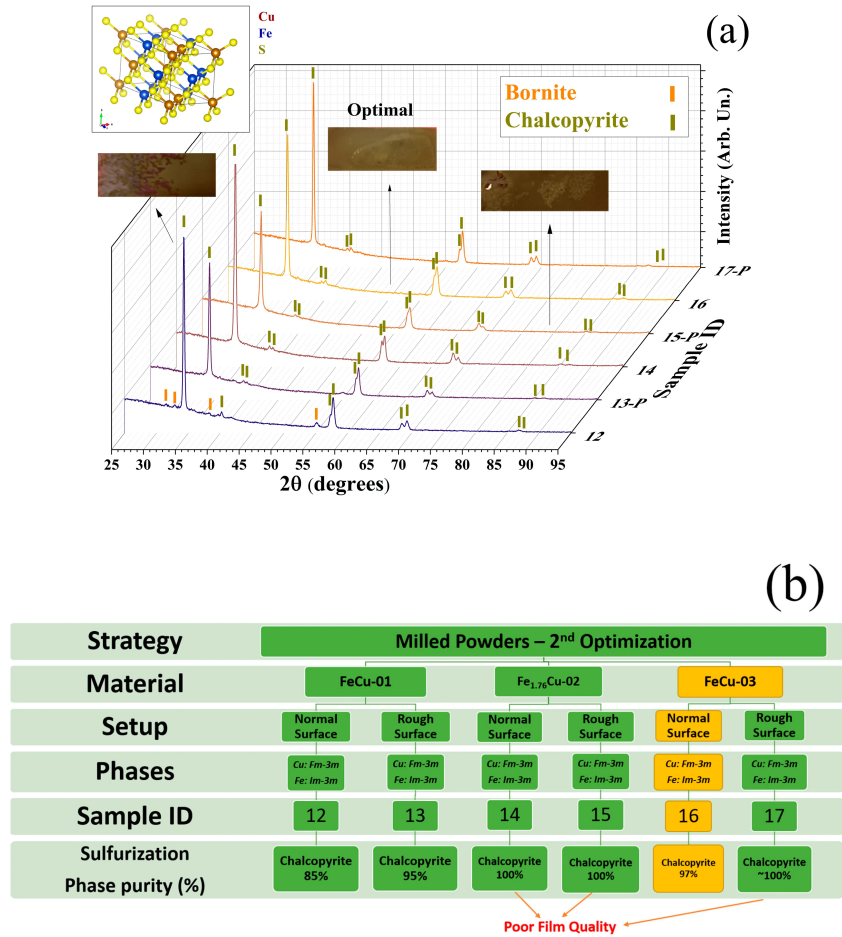


Figure 4.6: (a) Diffractograms of samples 12 to 17. The P index in the sample ID represents the polishing procedure. The markers identify the main Bragg peaks of the chalcopyrite (yellow) and bornite (orange) phases. The inset shows the crystal structure of CFS chalcopyrite. The phase percentages of chalcopyrite in the film are shown in blue. (b) Diagram with the synthesis parameters, including the milled powder employed, the polishing strategy (rough surface), the crystalline phases obtained, and the phase purity of the chalcopyrite phase after sulphurization.

2%, respectively. The chalcopyrite phase also shows a preferred orientation along the [112] direction. Good agreement is observed for the profile fitting and experimental data, as shown by the featureless residual curve. Since FeS_2 requires the lowest formation energy among the different Cu-Fe-S phases (vide Figure 4.3), its presence as a secondary phase is also expected. As is common for thin films, the contribution of crystallite size is better represented by a Gaussian profile function, which yields a volumetric crystallite size average (L_{vol}) of 61(1) nm. A relatively small microstrain of 0.4(9)% is observed for the chalcopyrite phase, with a predominant Lorentzian contribution to the line profile, see Figure 4.7.

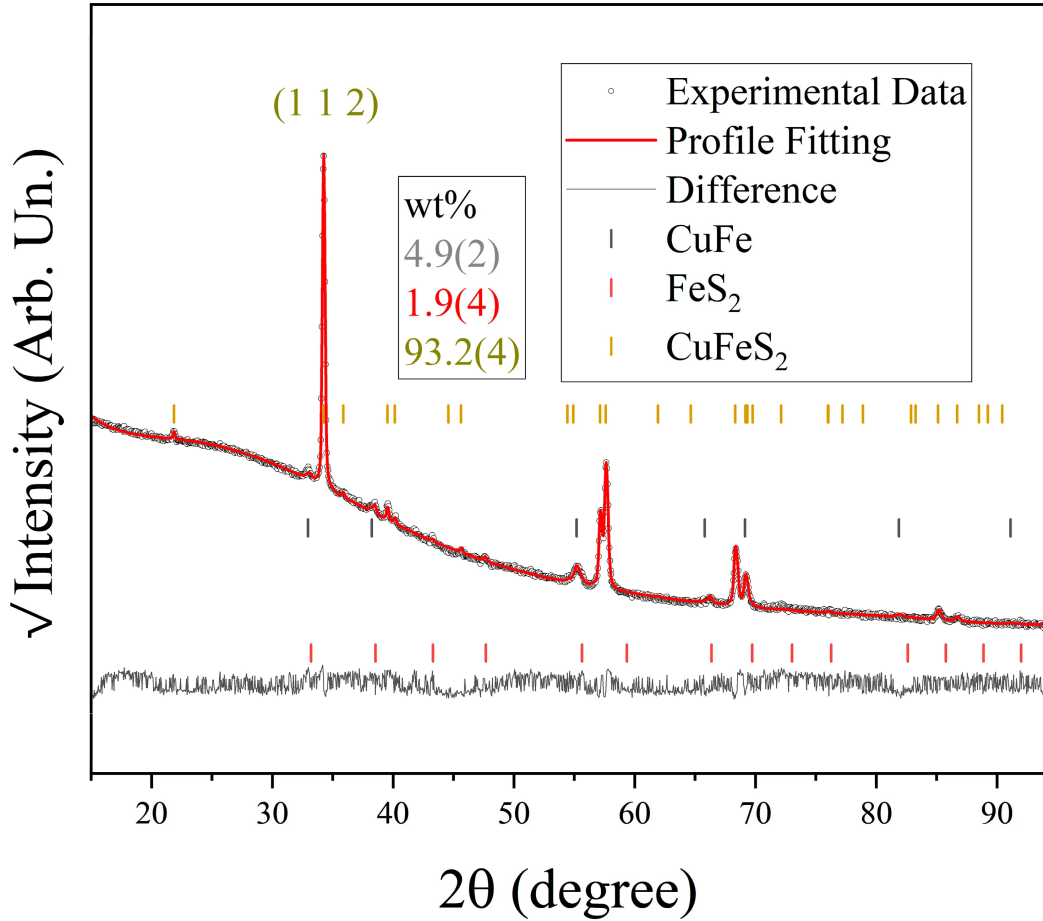


Figure 4.7: XRD pattern of the CFS-18 sample. Black dots stand for the experimentally obtained data in square root scale, while the red line represents the profile fitting. The grey line shows the residual (difference between the experimental and fitted model). The tick markers represent the Bragg reflections shown in the caption. (1 1 2) is the preferred orientation of CFS chalcopyrite.

The SEM and EDXS analyses of the sulphurized sample 18 are summarized in Figure 4.8. On the surface of the film, micrometer-sized grains form bigger polycrystalline agglomerates with an irregular plated shape microstructure (vide Figure 4.8(a)). Figure C.20 shows that this morphology is extended throughout a large area of the sample. The chemical maps

collected on the same surface suggest that Cu is homogeneously distributed throughout the sample, whereas Fe and S are more distinguished on the top surface of the grains. This reveals that even when the precursor powders are well mixed by the milling procedure, Cu tends to form the base layer of the film when evaporated, leaving the film surface Fe-rich. This also corroborates the slightly Fe-rich stoichiometry observed in the crystalline phases obtained by XRD.

SEM and EDXS measurements of the CuFe precursor (FeCu-03, pre-sulphurized sample 18) can be visualized in Supplementary Note C.7. This film shows a smooth and clean surface morphology, with a slightly copper-rich stoichiometry on the surface. For the CFS film, the average thickness is $\sim 1.7 \mu\text{m}$, as seen in the cross-section micrograph of Figure 4.8(b), left. The cross-section of the film is also Cu-rich, adding to the fact that it forms the base layer of the film.

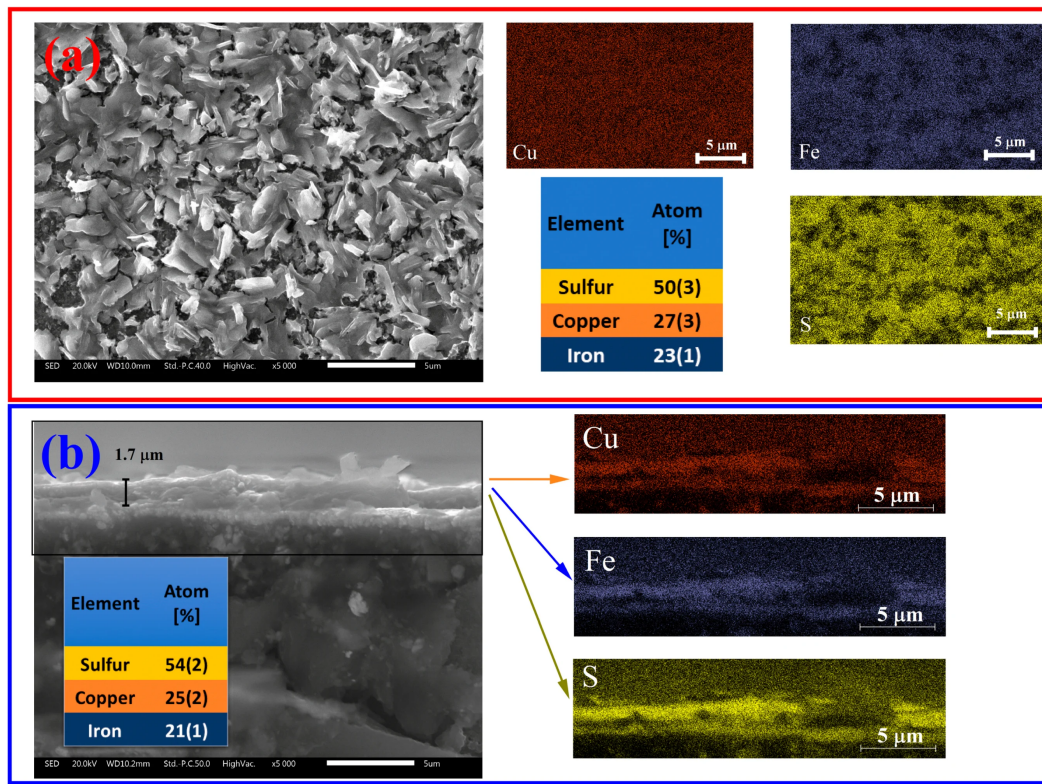


Figure 4.8: SEM and EDXS analysis of sample 18. (a) Surface scan (left), EDXS and chemical mapping (right). The table contains information on EDXS analysis of the atomic proportion of each element. (b) Cross section of the thin film.

The electrical characterization of the sulphurized Sample 18 is shown in Figure 4.9. The conductivity of the CFS film increases with the temperature and carrier concentration shows a positive value, confirming a non-degenerate p-type semiconductor nature. To explain the p-type nature, we regard that Cu is forming as the base layer of the film and CFS is believed to be Fe-rich. Since the oxidation state of CFS is often understood as $\text{Cu}^+\text{Fe}^{3+}\text{S}_2^{2-}$, the p-type nature of CFS can be stabilized by substituting Cu^{1+} with Fe^{3+} or, in general, by reducing the valence of the cations or by increasing the valence of the anions [44]. The Hall

measurement reveals that the carrier concentration does not show significant temperature variation, which is consistent with previous reports on this material (cm^{-3}) [44]. Furthermore, the carrier concentration is in the same order of magnitude and the mobility is reduced than the literature values, which can be credited to the morphology of the sample. This affects the overall conductivity, which tends to be lower than the literature reported values for p-type CFS [44, 162].

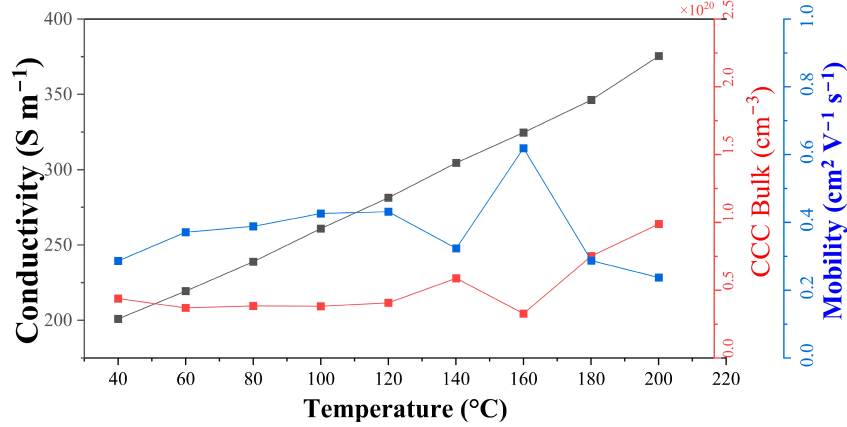


Figure 4.9: Electronic characterization of the CFS-18 samples with increasing temperature. The electrical conductivity is displayed in black squares (left axis), charge carrier concentration (CCC) in red, and electron mobility in blue, both in the right axis.

An in-plane TEG was fabricated with two couples of CFS and Ag legs. The two CFS legs were deposited following the optimized evaporation and sulphurization parameters of sample 18, as illustrated in Figure 4.1a. The current and voltage output data, shown in Figure 4.10a, were collected using a homemade setup (Figure 4.1b) by varying the hot side temperature from 50°C to 200°C . In this temperature span, the TEG shows an open circuit voltage (V_{OC}) varying from 3 to 80 mV and a short circuit (SC) current from 1 to $7.7 \mu\text{A}$. The current-voltage-power (I-V-P) curves are shown in Figure 4.10b. For a temperature difference (ΔT) of 180°C , a maximum power of 171 nW was obtained by applying a load resistance of 5 k Ω . More convenient ways to express the performance rely on dividing the power output by units of total, active, or cross-sectional areas of the generator [30]. Here, the total denotes the entire surface area of the TEG, and the actual area refers to the specific region where the CFS material is present. The thickness of the material is measured using a profilometer and the cross-sectional area is obtained by multiplying it by the width of the film. Per unit of total area, the performance reads 27 nW cm^{-2} ; in units of active area, 114 nW cm^{-2} ; and in cross-sectional area, 4 mW cm^{-2} .

The power output results are higher compared to some of the eco-friendly TEGs fabricated using hot injection and ball-milled inks. Cu_2SnS_3 , $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_{2.124}\text{Zn}_{0.875}\text{SnS}_3\text{Se}$ TEGs, for example, presented a power output per unit of active area of 59 nW cm^{-2} , 43 nW cm^{-2} , 23 nW cm^{-2} , respectively, at a ΔT 160°C [33]. The better homogeneity of the film provided by the three-step method can be the reason for the superior performance. However, a fair comparison can only be made between similar materials and, to the best of our knowledge, no device made of CFS was reported in the literature. The values reported here are still lower than the optimized TEGs for $\text{Cu}_{2+x}\text{Zn}_{1-x}\text{SnS}_4$ (152 nW cm^{-2}) and $\text{Cu}_{2+x}\text{Zn}_{1-x}\text{SnSe}_4$ (279 nW cm^{-2}) at a ΔT $^\circ\text{C}$, produced by sputtering [30]. To the best of

our knowledge, no device made of CFS was reported in the literature for a direct comparison. It is important to notice that the TEG presented in this work is a proof-of-concept device, fabricated using a noble approach where the CFS legs were deposited using the three-step method. The optimization of the CFS TEG can lead to a further enhancement in overall power output.

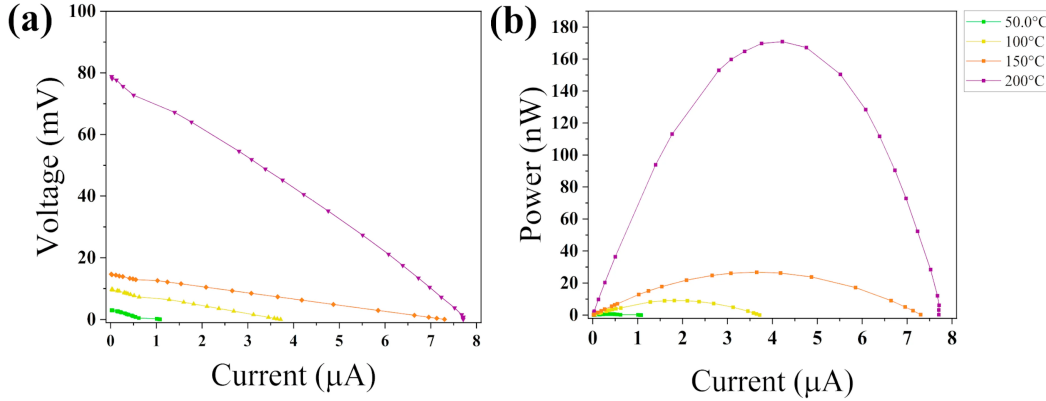


Figure 4.10: (a) I-V plots and (b) I-V-P output measurements for the CFS TEG. The temperature depicted in the figure corresponds to the hot side, while a passive cooler was employed on the cold side to maintain a temperature of approximately 20°C .

4.4 Discussion

In this study, we presented a comprehensive analysis of the three-step synthesis of CFS, examining its physical and chemical properties. Moreover, we demonstrated its successful application as a thermoelectric generator, yielding a power output comparable to similar chalcogenide-based materials [30, 33–35, 176, 177]. Comparing our proposed three-step method with existing literature can offer valuable insights into the potential applications of CFS chalcopyrite beyond thermoelectricity.

The predominant technique for producing bulk polycrystalline CFS involves wet-chemical reactions [47, 153, 154, 178–183]. This route provides control over its nanoscale dimensions enabling the tuning of its optical properties exploring the quantum confinement effect.

The polycrystalline nature also results in a higher surface-area-to-volume ratio for the material, promoting additional active sites for electrocatalysis applications [184]. Another notable attribute of CFS is its robust electrochemical stability, enabling it to endure repeated recharging cycles in battery systems [185, 186]. Furthermore, this stability has been harnessed in various applications, including its role as an electrode material for electrocatalytic oxygen reduction in fuel cells and water electrolyzers [184]. It also emerges as a promising alternative to platinum as counter electrodes in dye-sensitized solar cells [187].

The synthesis method provided here does not achieve precise control over the microstructure, although a nano flower-like morphology is observed (see Figure 4.8a). Example of similar materials with a plate-like structure have been demonstrated by Sathyaseelan et al. [188], Ding et al. [185], and Li et al. [189] as advantageous for electrochemical, Li-ion battery cathode, and magnetic applications due to its high surface-area-to-volume ratio. The difference of the three-step method compared to the above-mentioned wet-chemical process

is that it is a dry route, with no need for washing processes and the complete absence of wet chemical contaminations. However, further studies must be performed to check the stability under the aqueous (electrolyte solution) environment from our samples for electrocatalytic (battery) applications.

For thermal evaporation, Barkat et al. [163] adopted a similar synthesis route compared to the present work. They heated the substrate during the evaporation to increase the diffusion of Fe into Cu instead of ball milling. The control of stoichiometry is similar to what is reported here, although the plate-like morphology was absent. Therefore, the microstructure of the CFS film can be extremely diverse if milling is employed before powder evaporation and offers a simple alternative for improving Fe-Cu diffusion.

Moreover, the inclusion of a ball-milling step before evaporation showed the formation of three distinct Cu-Fe-S phases. We put forward that by fine-tuning specific synthesis parameters these phases can be obtained separately. Additionally, the parameters of milling can be tuned to regulate the Cu:Fe proportion in CFS, especially if aiming to modify its electrical properties from p to n-type nature.

4.5 Conclusions

This study presents a novel method to fabricate CuFeS₂ chalcopyrite thin films using a three-step synthesis of ball-milling, thermal evaporation, and sulphurization. We can emphasize some points of the optimization process: (1) ball-milling the metallic precursors before evaporation is essential for effective Cu and Fe element mixing; (2) a two-step current of 105 A (for 10 min) and 140 A (for 1 min) is required due to the different melting points of Cu and Fe; (3) using a smaller quantity of mass can improve the energy-over-mass ratio during evaporation; and (4) High vacuum ($\sim 10^{-6}$ mbar) and proximity between source and target enhance film adhesion. Finally, the sulphurization requires vacuuming the furnace and sintering at 425°C for 1 h under dynamic N₂ flow. The optimized thin film exhibits a plate-like surface morphology and demonstrates p-type semiconducting behavior with a purity of 93% for the CFS Chalcopyrite phase. These features can be enjoyed for electrochemical applications, although further tests are needed to verify the stability of the material under an aqueous/ electrolyte environment. Additionally, we observed the formation of Bornite and Tlakhite phases during the optimization process. This is likely because their energy phase formation is similar to that of CFS, as determined by DFT phase-diagram calculations. We suggest that this three-step approach can synthesize these ternary phases in pure form by making specific adjustments to the synthesis parameters. A proof-of-concept CFS-based in-plane TEG fabricated using the optimized thin film showed a power output per unit active area of ~ 114 nW cm⁻² for a temperature gradient of $\sim 180^\circ\text{C}$. The performance is superior to other sulphide-based materials fabricated using ball-milling and hot injection inks due to the smaller thickness and uniformity of the thin film. However, no CFS TEG performance was reported for a direct comparison. Further studies on the CFS material's properties such as the Seebeck coefficient, electrical resistivity, and thermal conductivity, are required to understand the effect of thickness on the overall TE performance of the thin film. In short, this work provides a comprehensive step-by-step guide to fabricating CFS thin films and opens avenues to use this eco-friendly, stable, cost-effective, and sustainable material for diverse applications.

Acknowledgements

Prof. Dr Robert Dinnebier and Dr Sebastian Bette are acknowledged for useful discussion regarding DFT calculations aided by the HAWK supercomputer within the Diskete Project framework.

Chapter 5

A $\text{CuFeS}_2/\text{Cu}_2\text{S}/\text{FeS}_2$ composite to increase the performance of thin-film thermoelectric generators based on sustainable materials

Abstract

Thermoelectric devices convert waste heat into electric energy but typically depend on scarce, expensive, and toxic Te-based materials. To address these limitations, we propose the Cu–Fe–S sulphide system as a non-toxic, abundant, and environmentally friendly alternative, with enhanced properties achieved through the synergistic behavior of CuFeS_2 , Cu_2S , and FeS_2 phases in a thin-film thermoelectric generator (TF-TEG). These phases were synthesized using a three-step process: ball-milling, thermal evaporation, and sulphurization of Cu/Fe precursors, with the $\text{CuFeS}_2/\text{Cu}_2\text{S}/\text{FeS}_2$ phase ratio being tuned by adjusting sulphurization temperature and duration. The presence of binary sulphides enhances the electric connectivity between CuFeS_2 grains, which on their own exhibit poor electrical conductivity due to the formation of isolated grains during nucleation. The composite achieved a volumetric power density of $20 \mu\text{W cm}^{-3} \text{ K}^{-1}$, outperforming similar Cu-based materials such as Cu_2SnS_3 and $\text{Cu}_2\text{ZnSnS}/\text{Se}_4$, mainly due to its optimized phase composition, higher density, and the superior Seebeck coefficient and electrical conductivity achieved through nano-inclusion. The eco-friendly, low-cost Cu–Fe–S system, synthesized through scalable ball milling and thermal evaporation, presents a promising alternative to conventional materials for sustainable thermoelectric generation.

5.1 Introduction

Thin film thermoelectric generators (TF-TEGs) are solid-state devices capable of converting low-grade heat into high-grade electrical energy. These devices are composed of semiconduct-

ing legs deposited on rigid or flexible substrates, connected in series with metallic contacts. When a gradient of temperature (ΔT) is applied in the TF-TEG, commonly by heating one part of the material, electrical energy is generated due to the Seebeck effect. The perks of TF-TEGs are the absence of moving parts, ensuring a noise- and vibration-free operation for the devices, granting them a long lifespan and making them particularly suitable, e.g., for remote applications,[190] small-scale wearable electronic devices,[191] and the internet of things.[191] However, most of the commercially available TF-TEGs use either toxic or rare and expensive elements, therefore research has been devoted to discovering thermoelectric materials employing non-toxic, earth-abundant, cost-effective, and environmentally friendly alternatives.[8, 191–194]

The Cu–Fe–S system is investigated due to their earth abundance, relatively narrow band gap ($E_g \sim 0.5\text{--}0.6$ eV),[195] and a high coefficient of absorption ($10^{-5}\text{--}10^{-6}$ cm $^{-1}$)[196] that allows its use in solar cell devices. Its chalcopyrite phase, also known as copper-iron sulphide (CuFeS_2 -CFS), presents a significantly high Seebeck coefficient (S , ~ -480 $\mu\text{V K}^{-1}$) and electric conductivity (σ).[44] Moreover, its behavior can be altered between n- and p-type semiconducting nature by tuning the Cu:Fe stoichiometry.[197, 198] The naturally occurring tetragonal crystal structure ($I\bar{4}2d$)[199] with ideal stoichiometry of CFS (Cu:Fe = 1:1) leads to a switch from p-type semiconducting behaviour at low temperatures to n-type at elevated temperatures due to bipolar conduction. The attenuation of this feature was shown by Baláz et al.,[197] where the co-milling of natural and synthetic CFS was shown to boost the power factor ($PF = S^2\sigma$) with little temperature dependence. The downside of CFS is its elevated thermal conductivity κ (~ 6 W m $^{-1}$ K $^{-1}$),[45] which can be circumvented by phase regulation, when tetragonal CFS is transformed into cubic ($F\bar{4}3m$) by Al substitution of Fe.[200] Similar transformation to cubic phases has shown improve thermoelectric performance and reduced thermal conductivity for other Cu-based sulphides and selenides.[34, 36, 41, 59] Overall, several works have presented a figure of merit ($zT = S^2\sigma T/\kappa$), proportional to the heat-to-electrical energy conversion, ranging from 0.05–0.40 for CFS,[156, 201–206] and as far as we know, the best zT reported for CFS is via Ge-substitution (0.40)[207] at medium-range temperatures (400–700 K).

The Cu–Fe–S system’s phase diagram is extremely complex due to the similar formation energy of several of its binary and ternary phases.[50, 166] Binaries like FeS_2 [208–211] and Cu_2S [46, 212–214] have been investigated as mid-temperature thermoelectric materials, especially for their high PF . FeS_2 , a p-type material, exhibits a relatively stable structure among other chalcogenides,[215] whereas Cu_2S shows a phase transition to a hexagonal phase with low thermal conductivity.[213] Both sulphide binaries have been demonstrated to increase thermoelectric performance when in mixed phase. A blend of Cu_{2-x}Se – Cu_2S showed a 4-fold higher zT in comparison to pure Cu_2Se , reaching a $zT = 0.8$ at 773 K for $x = 0.1$. [46] FeS/FeS_2 and $\text{Fe}_7\text{S}_8/\text{FeS}_2$ composites also have displayed power factor enhancement using this strategy.[47, 48] This approach to improving thermoelectric efficiency is known as nano-inclusion or compositional.[216] It reduces thermal conductivity by scattering long- and mid-wavelength phonons at grain boundary interfaces, while simultaneously acting as an energy filter, where low-energy heat carriers are scattered more easily than high-energy carriers, which contribute to the Seebeck effect.

Further κ reduction can be achieved by making the material in thin film form, as simulations showed a significant drop in cross-plane effective thermal conductivity with decreasing CFS film thickness.[147] In general, low-cost and simple fabrication techniques such as spin coating,[217] painting,[218] and the use of a doctor’s blade[219] have been employed for the TF-TEG fabrication of CFS. However, the thermoelectric material performance is significantly boosted by employing physical vapour deposition (PVD) techniques, namely thermal

evaporation and magnetron sputtering, due to the best control over homogeneity, thickness, and density.[30, 220] Moreover, PVD techniques are widely used by industry and are easy to scale up. Noteworthy examples of the use of PVD for the production of TF-TEGs working at room temperature include Ag-doped Bi_2Te_3 and Sb_2Te_3 deposited on a flexible substrate, achieving a power output (P_{out}) of 2.1 mW cm^{-2} with a ΔT of 64 K.[221] Also, Ag_2Se -based TF-TEG demonstrated a maximum P_{out} of 8 mW cm^{-2} with a $\Delta T = 50 \text{ K}$.[222] For eco-friendly materials, $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_4/\text{Se}_4$ TEGs, produced via DC magnetron sputtering by Isotta et al.,[30] reported P_{out} values of $\sim 150 \text{ nW cm}^{-2}$ and 280 nW cm^{-2} with a ΔT of 150 K for the sulphide and selenide material respectively. Despite having a lower power output than the selenides and tellurides, $\text{Cu}_2\text{ZnSnS}_4/\text{Se}_4$ TEGs proved to be twice as cheap compared to Te-based materials by unit of power per active area and provide a pathway for the use of more sustainable thermoelectric materials.[30]

The present work synthesized a series of CFS and CFS/ FeS_2 / Cu_2S compounds via a three-step synthesis of ball-milling of the metallic precursors, thermal evaporation, and sulphurization.[50] TF-TEGs were fabricated with these materials in a planar N-shape configuration, where two legs of the material are connected in series using metallic contacts. The synergistic effect of the phase mixture in the performance of TF-TEGs is investigated via current-voltage-power (IVP) measurements employing a special setup for varying load resistance. Phase identification and quantification were carried out using X-ray diffraction (XRD) and Raman analysis, while scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used to determine the morphology and chemical proportions of the films, respectively. Electric properties were investigated by Van-der-Pauw conductivity experiments. The temperature and duration of the sulphurization step on the phase regulation of CFS/ FeS_2 / Cu_2S compounds are studied together with the effect on the overall power output of the TF-TEGs. This work shows how the Cu–Fe–S system’s complexity can be employed to improve the TF-TEGs performance via the phase composition of its binary and ternary phases.

5.2 Experimental Section

The elemental powders of Fe (20 mesh, 99.9%) and Cu (100–325 mesh, 99.9%) were ball-milled in a Fritsch P4 planetary mill in an atomic proportion of 1:1 and subsequently evaporated using a VCM600 V1 (tecum AG) thermal evaporation system according to a procedure described elsewhere.[50] The sulphurization was carried out in sealed tube furnaces. Beforehand, the furnace was purged (evacuating to 5×10^{-3} mbar pressure and filling with Ar twice) to ensure a minimum presence of oxygen and/or water vapour. The sulphurization process was conducted in a graphite box with 50 mg of sulphur powder. The initial pressure was chosen so that at the process temperature the pressure was close to atmospheric ($> 800 \text{ mbar}$). The heating ramp in the sulphurizations was $20 \text{ }^\circ\text{C min}^{-1}$. The samples were naturally cooled down to temperatures below $50 \text{ }^\circ\text{C}$. The parameters of sulphurization, isothermal temperature and time, are listed in Table 5.1.

The XRD data on thin films was collected using a Bruker D8 Discover diffractometer equipped with Co (K_α , $\lambda = 1.78897 \text{ \AA}$) radiation source in a pseudo-parallel beam, produced by a polycapillary collimator and collected by a 1D detector (Lynxeye XE-T). The pattern was collected from 15° to 95° in 2θ , with steps of 0.05° measured every 2 s. ICSD and PDF4+ databases were used for phase identification. Rietveld analysis, profile fitting, and quantitative phase analysis (QPA) of the XRD data were conducted using the academic version of TOPAS 7. March–Dollase approach was employed to model the preferred orientation

Table 5.1: Parameters of sulphurization.

Sample	Temperature ($^{\circ}\text{C}$)	Time (min)
CFS-400 $^{\circ}\text{C}$ -30min	400	30
CFS-400 $^{\circ}\text{C}$ -60min	400	60
CFS-425 $^{\circ}\text{C}$ -30min	425	30
CFS-425 $^{\circ}\text{C}$ -60min	425	60
CFS-500 $^{\circ}\text{C}$ -60min	500	60

of the XRD patterns.

The Raman measurements were performed in LabRAM Aramis (Horiba Jobin-Yvon), which has an optical microscope and 100 $\times$ objective, with a 532 nm source wavelength. The Origin(Pro) software, Version 2023b (OriginLab Corporation, Northampton, MA, USA) was employed for Raman spectra analysis, including baseline extraction and peak fitting with Lorentzian profiles. SEM micrographs were obtained using a JEOL JSM-7001F FEGSEM (JEOL, Tokyo, Japan), and an Oxford INCA PentaFETx3 (Oxford, UK) detector was employed for EDX data collection. The electron beam energy ranged from 10 to 15 keV at a 5–10 mm distance from the film. The film surface characteristics were acquired in a top-down configuration while for the cross-sectional micrographs, the films were placed on a 901 stub. Ag paste was added at the backside of the films for conduction.

Temperature dependent (30–200 $^{\circ}\text{C}$) electrical conductivity was measured using a Hall-effect characterization apparatus (HCS1, Linseis) in a Van-der-Pauw four-contact configuration.

The design of the TF-TEG employing the Cu–Fe–S samples is schematically represented in Figure 5.1. For each sample, two Cu–Fe–S legs were gently devised out using a precision blade, being connected electrically in series by 300 nm thick Ag layers, which were thermally evaporated using the VCM600 V1 thermal evaporation system following a similar procedure of Ref. [50]. Figure 5.1 shows the homemade setup employed in the device characterization. A hot plate in contact with the device’s back part acted as a heat source for the hot part of the TF-TEG. A metal placed in the cold part served as a passive heat dissipator. For the voltage at open circuit (V_{OC}) measurements, the voltage was acquired through a Keithley 2601A voltmeter connected in parallel to the device by two spring-loaded contacts at the edges. Adding an ammeter and a variable resistor in series with the TF-TEG (vide circuit diagram in Figure 5.1), the current–voltage–power (IVP) characteristics were obtained with hot-side temperatures ranging from 50 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$. The temperature on both edges of the material was accurately measured using an Optris PI 640i thermal camera positioned 10 cm above the TF-TEG.

5.3 Results

5.3.1 Materials Characterization

Synthesizing the Cu–Fe–S samples requires the ball milling of the Cu–Fe metal precursors, its thermal evaporation to form a Cu–Fe thin film, and a following sulphurization step. Details on the optimization of each step are given in Ref. [50]. In the present work, a different setup for the sulphurization is employed for better control over temperature homogeneity. This step is expected to produce different morphologies for the thin films and the formation of CFS/ FeS_2 / Cu_2S phase mixtures in different proportions according to the

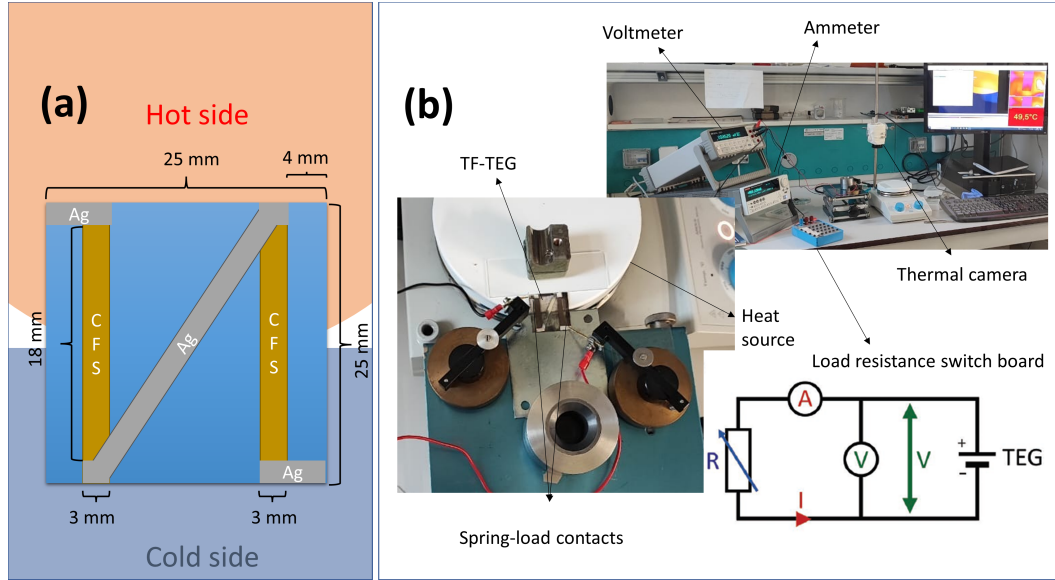


Figure 5.1: (a) Scheme and dimensions of the TEGs. (b) The setup used for the V_{OC} and IVP curve measurements.

chosen temperature and sintering time. The XRD patterns and the Rietveld profile fitting for the 400–425°C sintered samples (referred to as lower temperature sintering) are shown in Figure 5.2(a). Residuals and agreement factors are given in Figure D.1 of Supplementary Note D.1. The estimated phase percentage and crystallite size for all the phases are listed in Table D.1 of Supplementary Note D.1. The presence of multiple phases for the lower temperature synthesis is explained by the low formation energy in the Cu–Fe–S system.[50] For FeS_2 pyrite, for example, the formation energy is around -0.8 eV/atom, for Cu_2S -0.1 eV/atom, and CFS chalcopyrite, -0.4 eV/atom, all between -1 and 0 eV/atom. The $CuFeS_2$ chalcopyrite is less stable, therefore it presents higher purity when elevated temperatures are employed where entropy is higher, as observed for samples sintered at 425°C. A factor of time is also noticed, the chalcopyrite becomes major if sulphurized for longer times, whereas FeS_2 has the opposite behaviour. Therefore, we can conclude that higher temperature and sintering time promote a more entropic environment during the synthesis which favours the formation of the ternary CFS phase.

The Raman analysis of Figure 5.2(b), for samples CFS-425°C-30min and CFS-425°C-60min, shows that the CFS is the major phase along with Cu_2S and FeS_2 phases. The Raman spectra and fitting for the other samples are available in Supplementary Note D.2. The broad features of the Raman peaks suggest that the average domain size of the CFS phase is nanometric, following the XRD results (vide Table D.1). The modes of FeS_2 are given in orange in Figure 5.2(b), with E_g and A_g modes at 339 cm^{-1} and 379 cm^{-1} , respectively, and are generally shifted 4 cm^{-1} higher compared to bulk samples.[223] No match was found for the CuS phase in the literature, but the mode attributed to it is around 350 cm^{-1} . For $CuFeS_2$ chalcopyrite phase, the vibration modes are indicated as yellow in Figure 5.2(b), presenting a similar spectrum compared to Ref. [224] related to mineral ore bulk samples.

In the SEM micrographs of Figure 5.2(c), the mixing of phases can also be observed in the heterogeneous grain distribution on the surface of the thin films, where micrometre-

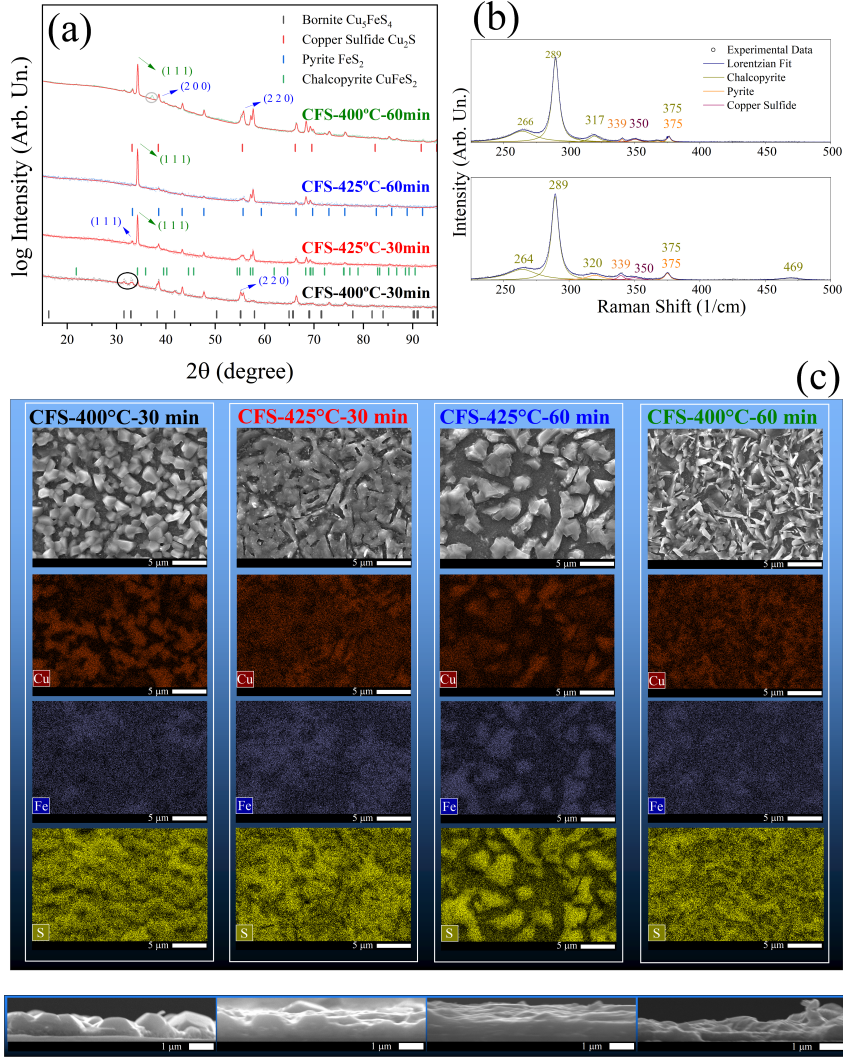


Figure 5.2: (a) Diffractograms in log-scale intensity for the low-temperature sintered samples. The dots represent the experimental data, the red lines their respective profile fitting, and the tick markers the Bragg peak positions of the main phases identified. Highlighted planes indicate their film's preferred orientations, and the circles point to unidentified reflections. (b) Raman spectra for the samples CFS-425°C-30min (top) and CFS-425°C-60min (bottom). The fitting colours represent the phases identified for each peak. (c) SEM micrographs and chemical maps for the CFS samples (top). Cross-section morphology is displayed at the bottom.

sized grains form “islands” surrounded by nanometric crystalline domains. In addition, the chemical mapping of Figure 5.2(c) reveals that the three constituent elements are inhomogeneously distributed on the film’s surface, adding to the assumption that they correspond to different phases. The thickness of the films varies from 0.6 to 1.5 μm as estimated using the cross-sectional micrographs of Figure 5.2(c). The chemical composition obtained via EDX is shown in Table 5.2 and reveals that the films are Cu-rich. As discussed in the previous work,[50] due to Cu’s lower melting point compared to Fe’s, the former evaporates first and forms a layer underneath the film that takes longer to take part in the reaction to form the Cu–Fe–S phases.

Table 5.2: The atomic proportion for Cu, Fe, and S, in %, obtained in the regions of the figure above.

Element	CFS-400°C-30min	CFS-425°C-30min	CFS-425°C-60min	CFS-400°C-60min	CFS-500°C-60min
Cu	24.7(8)	24.1(8)	25.3(8)	28.2(9)	31.1(8)
Fe	22.7(7)	23.8(6)	23.1(6)	21.0(6)	22(6)
S	50(1)	48(1)	46(1)	51(1)	47(1)

The XRD pattern of the CFS-500°C-60min sample is shown in Figure 5.3(a). The film presents 95% pure CFS in weight, with Cu_2S identified as a minor secondary phase via Rietveld-based QPA. The film is composed of micrometre-sized grains, shown in the SEM micrographs of Figure 5.3(b), but in this case, we also observe unreacted Cu in the chemical map, forming a thin base layer in the material, justifying the Cu-excess stoichiometry observed via EDXS (Table 5.2) and the formation of the Cu_2S phase. The cross-sectional micrographs reveal a film thickness of $\sim 1.8 \mu\text{m}$. As CFS is purified at higher sintering temperature, it forms isolated grains during the nucleation process, as observed in the surface micrographs of Figure 5.3(b). Similar behaviour in the CFS nucleation is observed in Refs. [163, 185, 188, 189], including the formation of a plate-like morphology for this phase, an indicative characteristic of the material formation.

In Figure 5.4, the electric conductivity (σ) trend with temperature is shown for all the samples. The samples present a non-degenerate p-type semiconducting behaviour, exhibited by increasing σ with the temperature. The lowest conductivity is observed for the CFS-rich samples, namely CFS-500°C-60min (95% CFS pure in weight) and CFS-425°C-60min sample (72% CFS pure in weight), due to the poor connection between the CFS grains. With the presence of the binary phases in the other samples, a better link between the CFS grains furnishes a path for the charge carriers to be conducted. It is worth mentioning that Cu-rich CuFeS_2 , [47, 162, 189] sulphur-poor FeS_2 pyrite, [209–211, 225] and cubic Cu_2S are p-type semiconducting phases, [226] with band gaps close to 0.6 eV, [227] 1 eV, [228] and 0.5 eV, [229] respectively. CFS exhibits a wide variation in thermoelectric properties depending on its chemical composition and synthesis methods. [44] For example, in the work of Baláz et al., [197] CFS mineral ores showed completely different behavior with temperature than what is reported here, changing from n- to p-type upon heating. The n-type behavior could only be stabilized by adding a lab-synthesized CFS alloy. Compared to CuFeS_2 pure bulk samples reported in the literature, the CFS purest sample (CFS-500°C-60min) showed a five times lower σ that reported in literature, i.e., above 50 S cm^{-1} . [147, 201] This level of conductivity can only be achieved by the $\text{CuFeS}_2/\text{Cu}_2\text{S}/\text{FeS}_2$ composite for the thin films produced here, as shown in Figure 5.4. This is due to better grain connectivity of the composite.

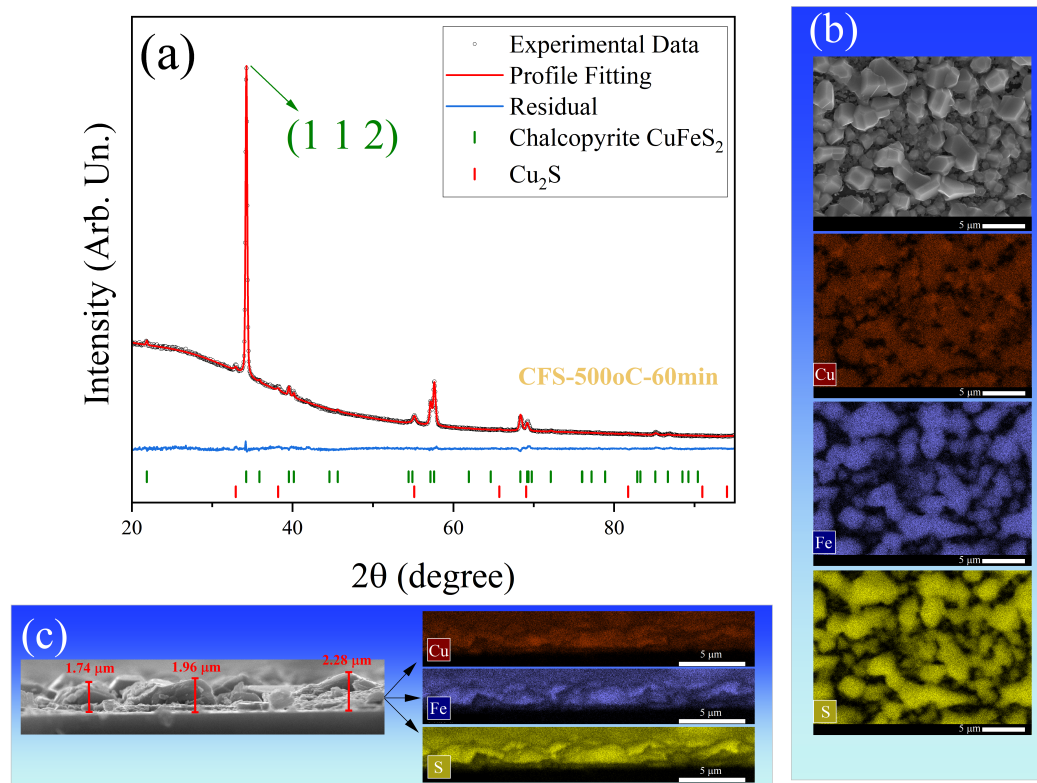


Figure 5.3: (a) Diffractogram of the CFS-500°C-60min phase. The dots represent the experimental data, the red lines their respective profile fitting, and the tick markers the Bragg peak positions of the main phases identified. (b) SEM micrographs and chemical mappings and (c) cross section morphology and its chemical mapping.

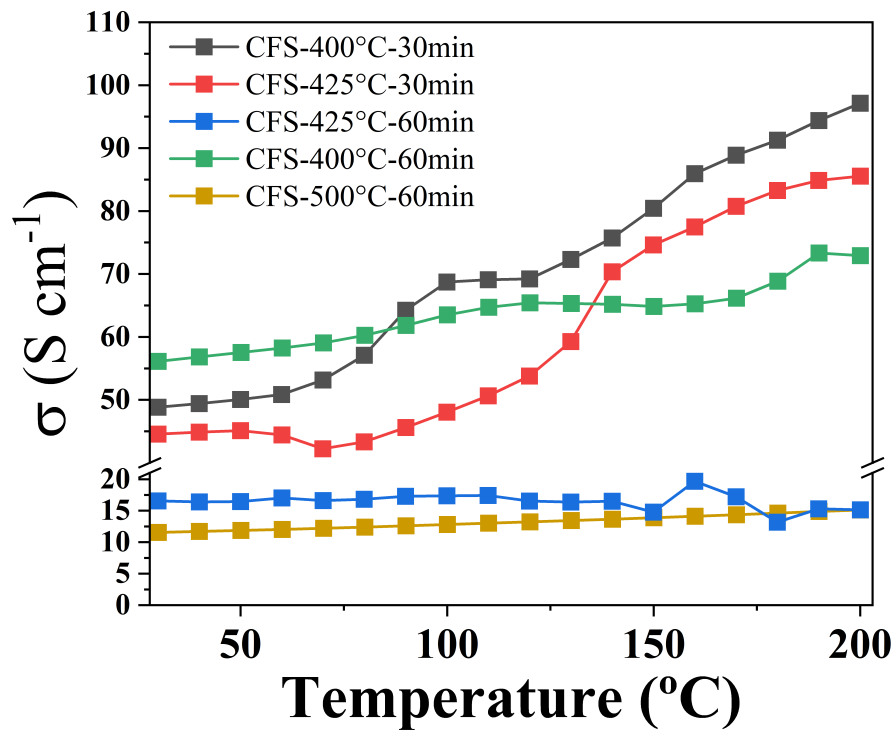


Figure 5.4: Conductivity measured with the Van-der-Pauw configuration.

5.3.2 Thin-Film Thermoelectric Generator

The thermoelectric performance of the thin film materials was characterized using IVP measurements, with the TF-TEG forming a connection in series to the load resistance as shown in Figure 5.1(b). The maximum voltage generated by the device is measured when the load resistance in the circuit is in theory infinite, leaving the TEG connected in parallel with the voltmeter. This type of measurement estimates the voltage at an open circuit (V_{OC}), reflecting the effective S of the entire device, which is defined as the voltage shift due to the thermoelectric effect:

$$V_{\text{shift}} = NS(T_h - T_c) \quad (5.1)$$

where T_h and T_c are the temperature at the hot and cold sides, respectively, and N is the number of legs. The V_{OC} of the TF-TEGs produced using the four samples sintered at lower temperatures is presented in Figure 5.5(a). The highest voltage is observed for the samples sulphurized at 425°C , and it is especially boosted when a gradient of temperature larger than 100°C is applied. All the samples show a p-type semiconducting behaviour given by the positive sign of the V_{OC} .

Generally, the trend of the Seebeck coefficient (and V_{OC}) is linear with temperature as understood by Eq. 5.1. However, the V_{OC} presents a sudden increase of S for the samples sintered at 425°C (vide Figure 5.5(a)) above 100°C ΔT . The values of the Seebeck coefficients are available in Figure D.4 of Supplementary Note D.3. We believe this method for Seebeck estimation is not reliable because the applied temperature gradient is very high, causing the Seebeck coefficient to vary significantly from one end to the other of the thin film. As a result, we capture only an average value of S that corresponds to the absolute temperature, $T_{\text{abs}} = \frac{T_h + T_c}{2}$. Nonetheless, it provides a general indication of the Seebeck coefficient's evolution with temperature and confirms that a boost in its properties happens for $T_{\text{abs}} > 100^\circ\text{C}$.

In addition, this boost in S increases for the subsequent runs of measurements performed for the CFS- 425°C -30min sample in a time interval of minutes at a T_h temperature $\sim 250^\circ\text{C}$. Their I-V-P characterization are shown in Figure D.5 of Supplementary Note D.3. For the second and third runs, the V_{OC} increases to 50 mV and 70 mV, respectively, and a threefold enhancement on the Seebeck is observed concerning the first run. The boosting of the Seebeck coefficient with time can also be observed while the material is heated at $\sim 300^\circ\text{C}$ in Supplementary Note D.3, Video 1. Comparing the internal resistance of the CFS- 425°C -30min samples we observe little to no variation with the number of runs (also available in Figure D.5), meaning that the maximum power output of the device increases. This points out the fact that the measurement itself is acting as a sintering process in the hot part and possibly promoting a chemical evolution in the sample due to volatilization of S. So far, we were not able to achieve complete stabilization of the thermoelectric properties, however, it should be the subject of further investigation.

Different mechanisms can explain the boost in the Seebeck coefficient: (i) the diffusion of Ag in the hot part of the material or (ii) the thermodynamic evolution of different phases of the Cu-Fe-S system. For hypothesis (i), SEM and EDX measurements were taken in three different regions of the TF-legs after the I-V-P characterization: (a) in the Ag contact part, (b) in the hot part, and (c) in the cold part of the TF-TEG and the micrographics are shown in Figure 5.6 for the samples sintered at 425°C . The EDX reveals that the Ag is only present in the contact part and is not diffusing through the hot part of the leg. No significant changes in the grain sizes are observed between the cold and hot parts of the TF-TEG. The second hypothesis, (ii), relies on the phase transition and evolution with the

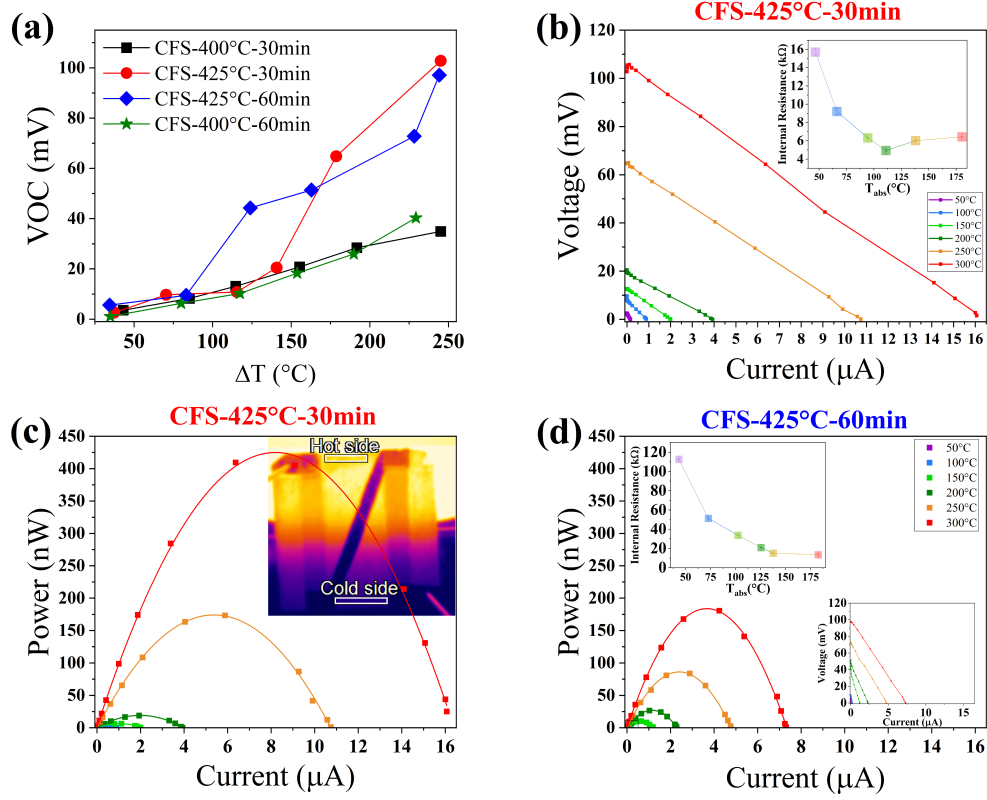


Figure 5.5: (a) Voltage at open circuit for all the samples for different temperature gradients. (b) I-V curves obtained for the CFS-425°C-30min. The inset picture represents the internal resistance of the TF-TEG with the absolute temperature. (c) P-V-I curves for the CFS-425°C-30min sample and (d) for the CFS-425°C-60min sample. The inset in (c) shows an infrared image used to measure the hot and cold side temperatures. In (d), the inset on the bottom depicts the I-V for CFS-425°C-60min, and at the top, the internal resistance of the device is presented.

sintering of the Cu_2S , FeS_2 , and CFS phases. The CuFeS_2 has a stable structure up to 557°C [166] and should not show a phase transformation during the measurement. FeS_2 is the most stable pyrite phase, with a melting point above 800°C . [214, 230, 231] On the other hand, Cu_2S has several phase transitions around 100°C . The cubic phase present in the film stabilizes at 93°C for a $\text{Cu}_{64}\text{S}_{36}$ composition and is often referred to as digenite.[232] However, this phase evolution is highly susceptible to small variations in stoichiometry. For example, with a $\text{Cu}_{66}\text{S}_{33}$ proportion, the stabilization temperature of this cubic phase increases to 435°C , [233] being a 350°C higher temperature than the $\text{Cu}_{64}\text{S}_{36}$ composition. Some reports infer that in the Cu–Fe–S system, the Cu_2S cubic phase forms congruently at elevated temperatures (1130°C). [232] Therefore, in the current work, the Cu_2S is formed as a metastable phase in the film at room temperature, and during the measurement, it undergoes several transformation processes. One common phase transition of Cu_2S is to the hexagonal high-chalcocite phase ($P6_3/mmc$), where a sharp decrease in thermal conductivity is also observed around 97°C . [213] Since the boost on the Seebeck is present solely for the samples containing Cu_2S , namely CFS- 425°C -30min (20% in wt of Cu_2S) and CFS- 425°C -60min (14% in wt of Cu_2S) — see Table D.1 of Supplementary Note D.1 — Cu_2S phase evolution with temperature is the most probable cause of power factor boost. Cu_{2-x}S also presents a p-type nature for a wide range of x , [226] therefore all the phases could contribute to increasing the Seebeck values in this range of temperature, with similar semiconducting properties than Cu-rich CFS and sulphur-poor FeS_2 .

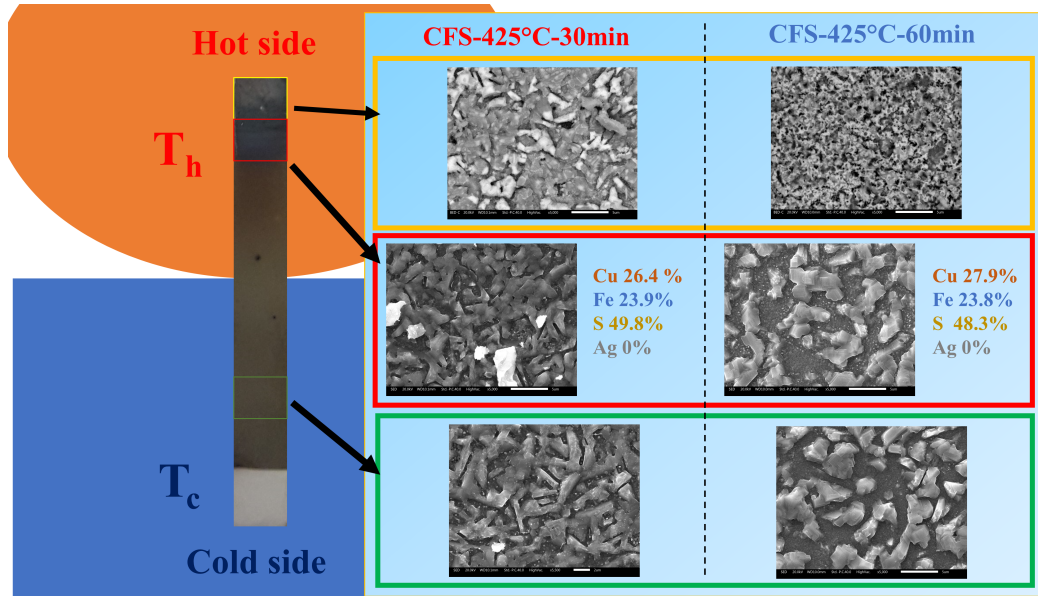


Figure 5.6: SEM micrographics of the Ag contact part (highlighted in yellow), the hot-side part (highlighted in red) and the cold-side part (highlighted in green) of the TF-TEG (on the left). The EDXS atomic proportion is given for the hot-side part region for Cu, Fe, S, and Ag elements.

The XRD patterns of the hot side of the TF-TEGs, collected after V_{OC} characterization for the Cu_2S -containing samples (CFS- 425°C -30min and CFS- 425°C -60min), are shown in Figure D.6 of Supplementary Note D.4. The patterns reveal the formation of two additional phases: CuS (PDF #00-006-0464, covellite) and Cu_9S_5 (PDF #00-047-1748, digenite), both

exhibiting excellent conducting properties[234, 235] and are more stable at room temperature than the Cu_2S cubic phases. The $\text{Ag}_{4.92}\text{Cu}_{3.08}\text{S}_4$ (PDF #01-080-2584) phase is present at the Ag contacts, and the FeS (Rudashevskyite, PDF #00-023-1123) metastable phase appears for the 30-minute sulphurization temperature. While in situ characterization is necessary to determine the exact phases at high temperatures, the observed variety of phases post-measurement suggests that these are primarily responsible for the increased performance at elevated temperatures, particularly due to the formation of the metallic phases, attributed to the higher electrical conductivity.

The complete characterization of the device performance is attained by measuring the power output, using the IVP curves. The power is calculated using the relation $P = VI = RI^2$. These measurements require a load resistance (R) to be varied from open to short circuit condition, represented in Figure 5.1(b). In Figure 5.5(b), the I-V plots for the CFS-425°C-30min sample for different hot side temperatures are displayed, varying a load resistance from 0 to 10 M Ω . The slope of the I-V curve corresponds to the internal resistance of the TF-TEG and is plotted in the inset of Figure 5.5(b) for the CFS-425°C-30min sample versus T_{abs} . Here we observe a significant decrease in the internal resistance of the films for $T_h > 100^\circ\text{C}$. This, allied with the boost in the V_{OC} shows that the phase transformation of the Cu_2S phase is increasing the thermoelectric power factor ($S^2\sigma$) of the material.

Since heat is conducted from the hot to the cold part, during the measurement, the generator tends to equilibrate its temperature and the Seebeck effect ceases. This way, the I-V and P-I measurements must be made when the highest voltage is measured, meaning that the temperature gradient is maximum. The thermal distribution is shown in the thermal picture of Figure 5.5(c) inset, seconds before the measurements take place, where the cold and hot parts correspond to half the volume of the device. The P-I plots collected at this instant are shown in Figure 5.5(c) for different temperature gradients of sample CFS-425°C-30min. Since $P = RI^2$, one expects the curve to be a parabola. Intrinsically, the circuit has a built-in resistance, and the maximum of this parabola is obtained when both the load and built-in resistance are the same. Here we observe that the power output is significantly higher when the hot side temperature is elevated above 200°C , which was also observed for the V_{OC} due to the increase of Seebeck and decrease of internal resistance shown previously. The TF-TEG characteristic curves of sample CFS-425°C-60min, richer in CFS, reveal that, despite the V_{OC} showing similar values (Figure 5.5(d) inset), the output current is half the value of the previous sample. This, in turn, results in a power output which is also reduced in half as shown in Figure 5.5(d). The trend of the internal resistance also reveals a significant decrease for $T_h > 100^\circ\text{C}$ due to the Cu_2S phase transformation. For both samples sulphurized at 400°C , the performance was significantly inferior to that of the 425°C samples. Corresponding results are available in Supplementary Note D.5.

To further demonstrate that the boost in the thermoelectric performance is due to the CFS/ FeS_2 / Cu_2S composite, the performance of the purest CFS sample (CFS-500°C-60min) is presented in Figure 5.7. A linear behaviour is observed for the V_{OC} versus temperature, with values 4 times lower than reported for the composite having an internal resistance within a similar temperature range (vide Figure 5.5(a)). The Seebeck values are given in Figure D.4, presenting a decrease with temperature, meaning that intrinsic thermal bipolaron excitation is starting to take place due to the low bandgap of this material. Nevertheless, S is at a similar order of magnitude as reported for p-type CFS materials.[47, 153] Therefore, the inclusion of p-type secondary phases in the other samples helps reduce the impact of this bipolar conduction. The maximum power output of the CFS-500°C-60min sample is 37 nW, five times smaller than the composite, with identical internal resistances.

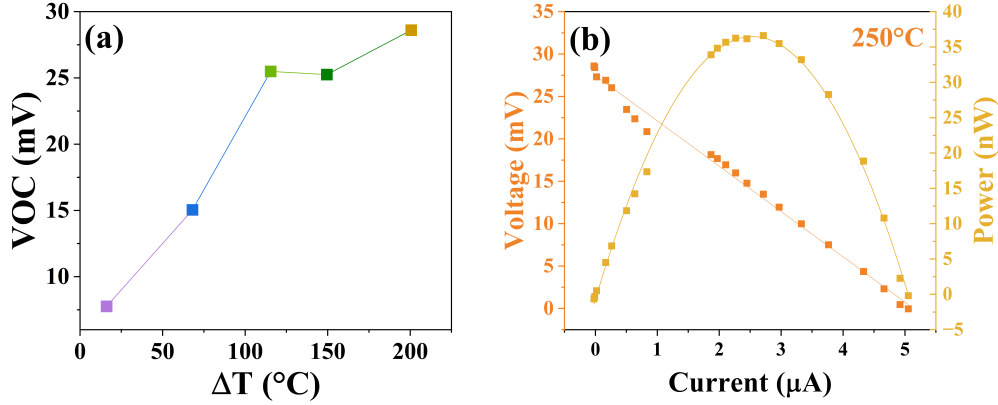


Figure 5.7: (a) Voltage at open circuit and internal resistance measured at different ΔT for the CFS-500 $^{\circ}\text{C}$ -60min sample. (b) I-V-P characteristic of the CFS-500 $^{\circ}\text{C}$ -60min at $\Delta T = 250^{\circ}\text{C}$.

5.4 Discussion

When comparing the performance of a device with literature-reported values, the maximum power output of the TF-TEG is normalized by the surface area and volume of the thermoelectric materials. In this way, analysis is made independently of the TF-TEG's geometry, i.e., how the thermoelectric materials are arranged on the surface of the device to provide the best power output. An important point is that the surface area considered in this case is only the active area of the device, where the thermoelectric material is present. Additionally, the power output must be divided by the temperature gradient (ΔT) applied.

Figures 5.8(a) and 5.8(b) show the volume temperature power density (P_{volume}) and the active area surface-specific power (P_{area}) of various Te-free and eco-friendly TF-TEG devices reported in the literature. Among the room-temperature thermoelectric devices, as far as we know, the best performance is found for the $\text{Mg}_2\text{Sn}_{0.8}\text{Ge}_{0.2}$ -based TF-TEGs developed via photolithography and dry etching, resulting in a P_{area} of $\sim 21 \text{ mW cm}^{-2}$ at ΔT of 110 K.[236] Among sulphides, TiS_2 -based TF-TEGs achieved P_{area} values of 16.8 W cm^{-2} ($\Delta T = 20 \text{ K}$) and 0.25 W cm^{-2} ($\Delta T = 70 \text{ K}$) by Wang et al.[48] and Tian et al.[237] respectively, being the second most performing material by volume-specific power. Literature also reports near-room-temperature TF-TEGs made of Mo_2C and $\text{Mo}_2\text{Ti}_2\text{C}_3$,[217] SiGe ,[238, 239] with orders of magnitude lower power outputs. As far as we know, only one report employed Cu_2S in the fabrication of TF-TEGs,[240] reaching $\sim 160 \text{ nW}$ at room temperature with a $\Delta T = 35 \text{ K}$, in a flexible device coupling five $\text{Cu}_2\text{S}:\text{PEDOT}:\text{PSS}$ and $\text{Ag}_2\text{S}/\text{PVP}$ legs (however no dimensions were provided for the normalization). In the medium temperature range, SnSe is surging as the most promising candidate for TE applications.[241–245] A TF-TEG module fabricated by thermal evaporation of SnSe with 8 legs resulted in a power output of approximately $0.09 \mu\text{W}$ at a hot side temperature of 618 K.[220] In a recent study, Ag-doped SnSe TEGs fabricated through photolithography and reactive-ion etching achieved a P_{area} of around $58.38 \mu\text{W cm}^{-2}$ at a ΔT of 147.7 K.[246] The current study, utilizing entirely sustainable, cheap, and least-toxic materials, delivered the second-best performance among TF-TEGs, following SnSe , which is considered more toxic and expensive.

Among the materials based on Cu, the Cu-Fe-S sample produced in this work pro-

vides the best performance regarding P_{volume} , and provides a five times enhancement in performance compared to the previous sulphurization process employed for the three-step synthesis.[50] This is especially attributed to the effect of synergy between the binary and ternary phases of the Cu–Fe–S system and the increased material density provided by the sulphurization process. For the P_{area} , the Cu_2SnS_3 -Bi TF-TEGs show the best performance among the Cu-based materials attributed to the higher thickness of the material ($21\ \mu\text{m}$) compared to the present work ($0.58\ \mu\text{m}$). Nevertheless, we show that the use of more advanced synthesis and deposition techniques for $\text{Mg}_2\text{Sn}_{0.8}\text{Ge}_{0.2}$ and SnSe samples is the most important factor for obtaining high performance in the materials, where one order of magnitude superior power output was obtained compared to the present work. Another example of the improvement of the synthesis process is noticed for the $\text{Cu}_2\text{ZnSnS}_4/\text{Se}_4$ samples made via sputtering[30] compared to the ink-based devices of Syafiq et al.[33] There, the performance is more than doubled using PVD techniques. Yet, CFS samples provided an equivalent performance to sputtered CZTS/Se kesterite samples, this is especially attributed to the significant power factor of Cu–Fe–S binary and ternary phases compared to that of kesterite materials. Therefore, the Cu–Fe–S system is a promising material for TF-TEGs and further steps in improving the optimization and stabilization of Cu–Fe–S are necessary to increase even more the performance of these devices.

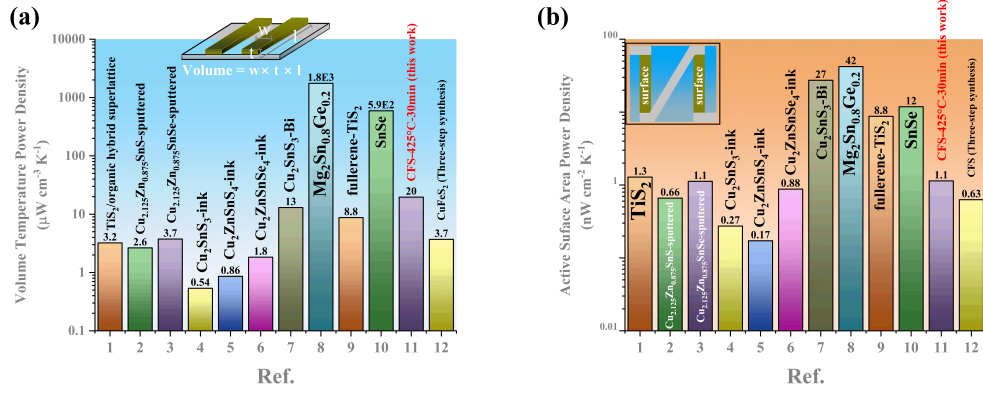


Figure 5.8: (a) Volume temperature power density for the literature reports. (b) Active surface area power density comparison with the literature-reported values for the TF-TEGs. The numbers on the x-axis correspond to the references: 1) [237], 2) [30], 3) [30], 4) [33], 5) [33], 6) [33], 7) [247], 8) [236], 9) [48], 10) [246], 11) present work, 12) [50].

5.5 Conclusions

We examined the TF-TEG characteristics of the $\text{Cu}_2\text{S}/\text{FeS}_2/\text{CuFeS}_2$ composite synthesized by the three-step method of ball-milling, thermal evaporation, and sulphurization for different sulphurization temperatures. This approach provided insights into the synergistic effects of the different phases on thermoelectric performance. During IVP measurements, the evolution of the Cu_2S phase enhanced the Seebeck coefficient of the film by three times while simultaneously reducing the internal resistance of the device by the same factor. Samples without Cu_2S did not show the boosting effect and presented a four times lower power output for a similar temperature range. The use of lower sulphurization temperature allowed the

formation of multiple phases for the Cu–Fe–S system that was shown to be crucial to maintain good electrical conductivity among the CFS grains. The $\text{Cu}_2\text{S}/\text{FeS}_2/\text{CuFeS}_2$ composite also showed the best P_{volume} comparing the Cu-based environmentally friendly TF-TEGs ($20 \mu\text{W cm}^{-3} \text{ K}^{-1}$) and show to be a promising material for thermoelectric applications.

Acknowledgements

The authors acknowledge Mirco D’Incau for the technical support. This study was funded by the Italian Ministry of Universities and Research (MUR), in the framework of the project DICAM-EXC (Departments of Excellence 2023–2027, grant L232/2016). The authors acknowledge the Science Ministry of Spain projects number PID2020-116719RB-C41 (MATER-ONE) and TED2021-130265B-C21 (MIRACLE). E.S. is grateful to the ICREA Academia program.

Chapter 6

Conclusions

This thesis has addressed the development and understanding of sustainable thermoelectric materials, with particular focus on Cu-based chalcogenides, by combining experimental investigation, theoretical modelling, and advanced diffraction-based methodologies. In the broader context of energy sustainability, thermoelectric materials offer a promising route for direct heat-to-electricity conversion, yet their widespread application remains limited by the intrinsic coupling between electrical and thermal transport properties. A central challenge therefore lies in identifying material systems and design strategies capable of decoupling these properties while relying on earth-abundant and non-toxic elements.

Within this framework, the first part of this work focused on bulk $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ (CZTSSe) compounds, where a combined experimental and theoretical approach was employed to disentangle intrinsic and extrinsic contributions to thermal transport. First-principles calculations revealed that, from a purely lattice-dynamical perspective, Se-rich compositions should exhibit lower lattice thermal conductivity due to reduced phonon group velocities and enhanced anharmonicity. However, experimental observations on polycrystalline samples showed an apparent inversion of this trend, with sulphide-rich compositions displaying lower thermal conductivity. This discrepancy was rationalized by identifying microstructural effects as the dominant factor governing phonon transport in real materials.

In particular, porosity, grain size, and grain connectivity were found to play a decisive role in suppressing lattice thermal conductivity. Sulphide-rich samples exhibited higher porosity and reduced grain connectivity, leading to enhanced phonon scattering and thus lower effective thermal transport. These results demonstrate that, in polycrystalline thermoelectric materials, microstructural features can override intrinsic lattice properties, highlighting the necessity of a multiscale approach that simultaneously considers atomic-scale dynamics and mesoscale structural characteristics. In parallel, the analysis of electronic transport revealed that variations in weighted mobility and carrier concentration are closely linked to these structural features, further emphasizing the strong interdependence between microstructure and functional properties.

While bulk CZTSSe systems provide a valuable platform for understanding the interplay between intrinsic and extrinsic mechanisms, their thermoelectric performance remains limited by moderate power factors for thin film applications. This consideration motivated the exploration of alternative Cu-based chalcogenides with enhanced electronic transport properties. In this context, Cu-Fe-S (CFS) compounds were investigated in thin-film form, where significantly higher power factors can be achieved compared to kesterite-based systems. The transition from bulk to thin-film architectures also enables new opportunities

CONCLUSIONS

for device integration and microstructural control, making CFS a promising candidate for next-generation thermoelectric applications.

However, the assessment of thermoelectric performance in thin films remains a non-trivial issue. Unlike bulk materials, where figures of merit are typically defined per unit volume, thin-film devices are often evaluated using different normalization criteria, including power output per unit area, per unit volume, or per device volume/area. This lack of standardization complicates direct comparison across studies and materials systems. In this work, particular attention was therefore devoted to critically analysing performance metrics and ensuring consistent evaluation of device efficiency. Despite these challenges, CFS thin films demonstrate highly promising behaviour, achieving record performance among Cu-based thermoelectric materials when normalized to the active material volume, thus reinforcing their potential for practical applications.

Beyond the direct development of thermoelectric materials, this PhD work has been accompanied by a parallel and complementary research activity aimed at advancing the methodological framework for the investigation of complex materials through diffraction techniques. Although not always explicitly included in the core chapters of this thesis, these contributions represent an integral part of the scientific production associated with this work, and have been published in peer-reviewed journals. A detailed overview of the complete scientific output is provided in Appendix E.3.

In this context, X-ray diffraction has been employed not only as a structural characterization tool, but as a probe of microstructure, defects, and lattice dynamics. In particular, thermal diffuse scattering (TDS) has been used to access local atomic vibrations and phonon behaviour, providing direct insight into the mechanisms governing thermal transport. The studies on nanocrystalline systems and model compounds such as Ag_2O demonstrate how diffraction-based approaches can bridge the gap between atomistic dynamics and macroscopic transport properties [94, 135, 248].

Complementary to the investigation of lattice dynamics, the role of crystalline defects has been addressed through the development of the DISCO software, a general tool for the calculation of dislocation contrast factors in diffraction analysis (Malagutti et al., submitted). By enabling the quantitative incorporation of dislocation-induced strain fields into diffraction modelling, DISCO provides a robust framework for linking microstructural defects to measurable diffraction features and, ultimately, to material properties. This approach represents a significant step towards physically grounded microstructural characterization in complex materials.

In parallel, the integration of artificial intelligence methodologies into diffraction analysis has been explored as a means to accelerate data interpretation and model development [249]. The combination of simulation-driven approaches with data-driven techniques opens new perspectives for the analysis of increasingly complex datasets, enabling more efficient exploration of structure–property relationships. These developments point towards a future in which diffraction analysis evolves from a primarily interpretative tool to a predictive framework for materials design.

Taken together, the results presented in this thesis highlight that thermal transport in complex thermoelectric materials cannot be understood by considering intrinsic lattice properties alone, but requires a comprehensive description that includes microstructural features, defects, and local dynamics. Advanced diffraction techniques, combined with theoretical modelling and computational tools, provide a unique and powerful approach to access this multiscale information.

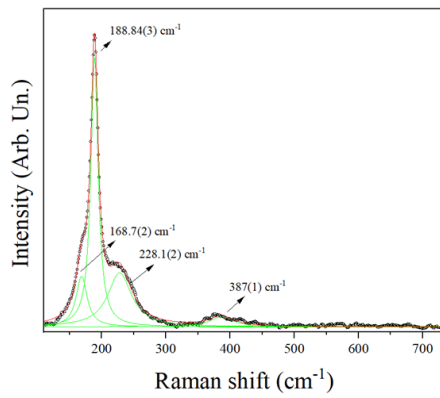
Future work should aim at further integrating these methodologies into a unified framework, combining thermal diffuse scattering, whole powder pattern modelling, and data-

driven approaches to achieve real-time, quantitative characterization of materials. Such an approach would not only deepen the fundamental understanding of transport phenomena but also enable the rational design of high-performance thermoelectric materials based on controlled manipulation of structure and defects.

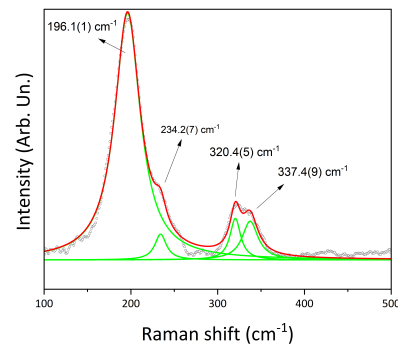
Appendix A

Supplementary Information: Investigating the cubic-to-tetragonal phase transition of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ solid solutions

A.1 Supplementary Note 1: Raman fitting of the cubic phase



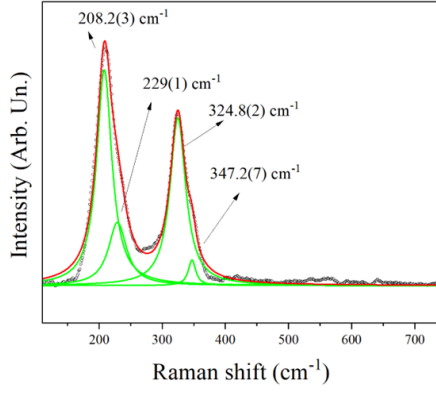
(a) $\text{Cu}_2\text{ZnSnSe}_4$.



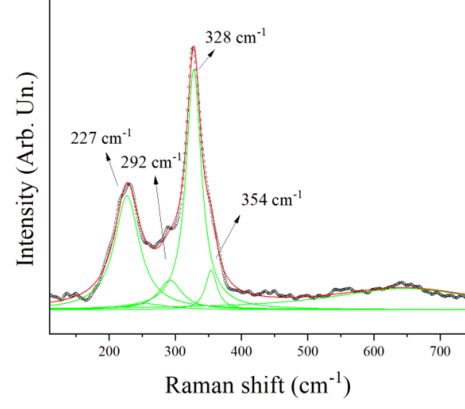
(b) $\text{Cu}_2\text{ZnSnSe}_3\text{S}_1$.

Figure A.1: Raman spectra of the undoped Se-rich compositions.

A.1. SUPPLEMENTARY NOTE 1: RAMAN FITTING OF THE CUBIC PHASE

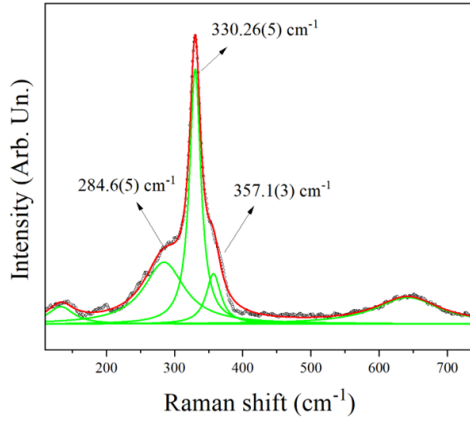


(a) Cu₂ZnSnS₂Se₂.

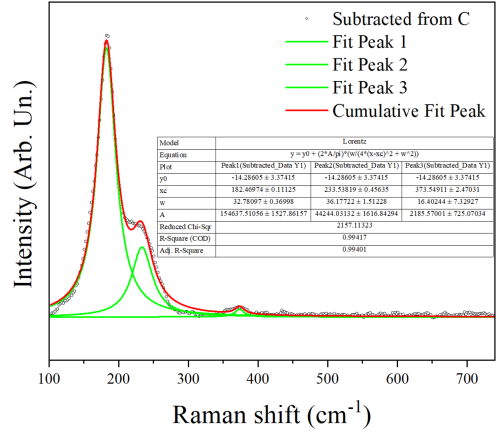


(b) Cu₂ZnSnS₃Se₁.

Figure A.2: Raman spectra of the intermediate undoped compositions.



(a) Cu₂ZnSnS₄.



(b) Cu_{2.125}Zn_{0.875}SnSe₄.

Figure A.3: Raman spectra of the S-rich undoped composition and Se-rich Cu-doped composition.

APPENDIX A. SUPPLEMENTARY INFORMATION: INVESTIGATING THE CUBIC-TO-TETRAGONAL PHASE TRANSITION OF $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ SOLID SOLUTIONS

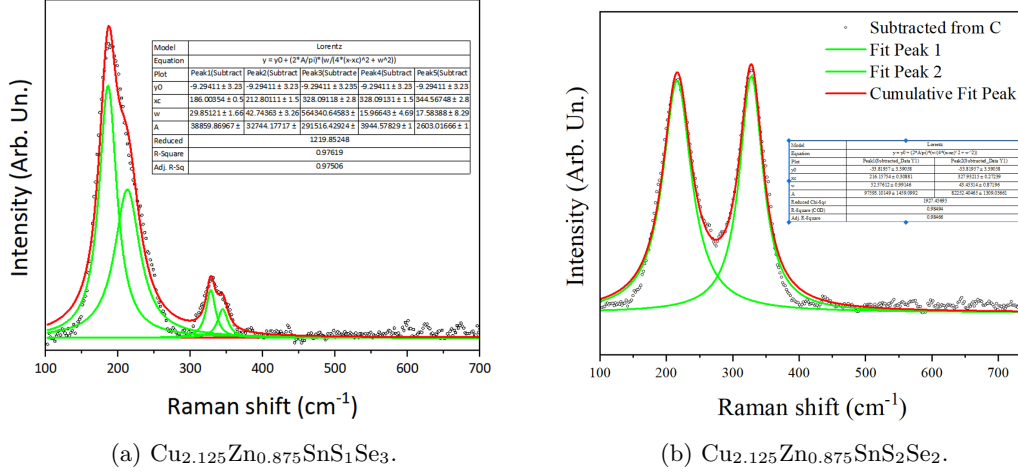


Figure A.4: Raman spectra of intermediate Cu-doped compositions.

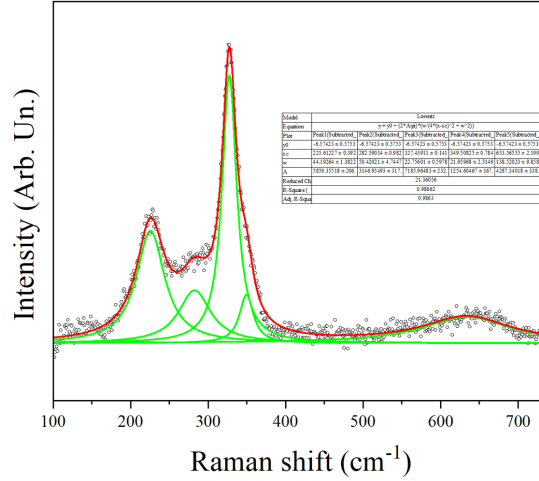


Figure A.5: Raman spectrum $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_3\text{Se}_1$.

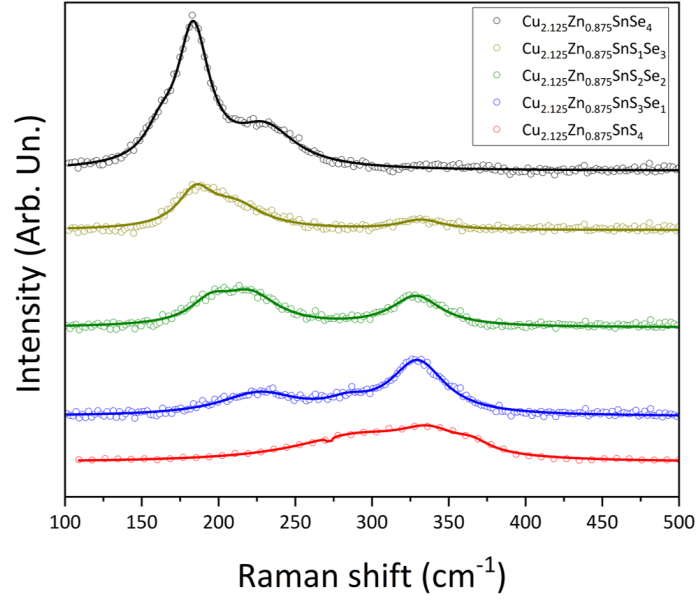


Figure A.6: Raman spectra obtained with NT-MDT NTEGRA Spectra for the as-milled $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ powder samples.

Reproducibility tests:

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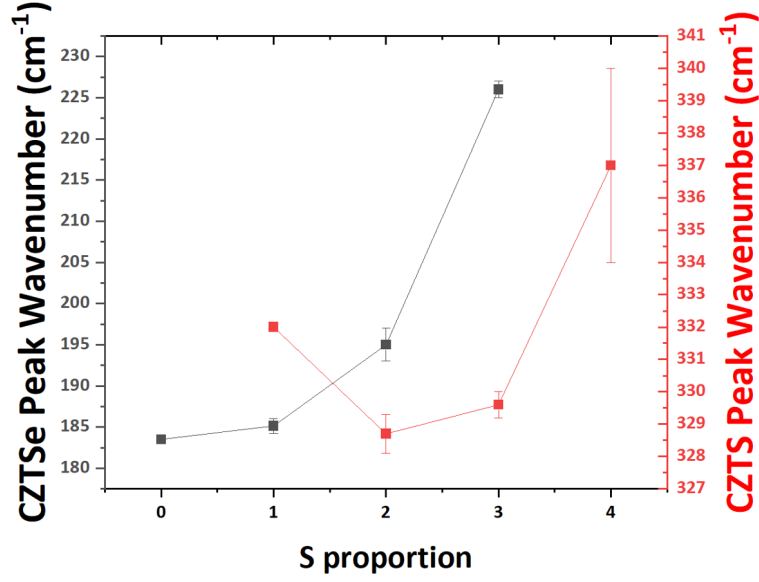


Figure A.7: Wavenumber peak positions of the main Se-cation and S-cation vibrational modes are shown for the $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ system.

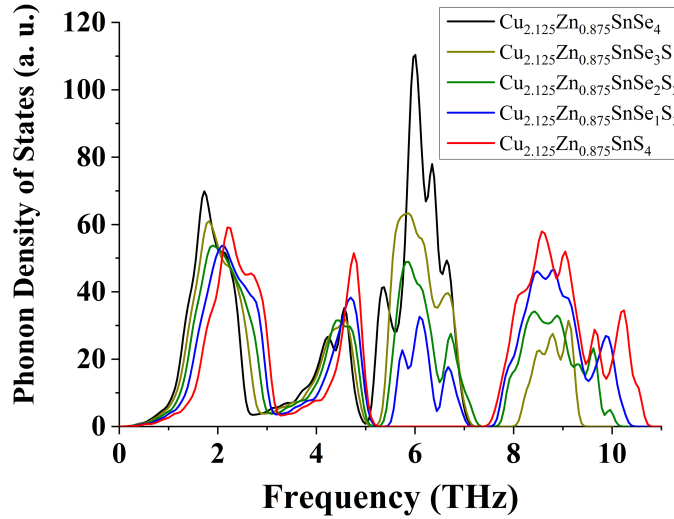


Figure A.8: Phonon density of states for the $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ system calculated via DFPT.

A.2 Supplementary Note 2: HTXRD patterns

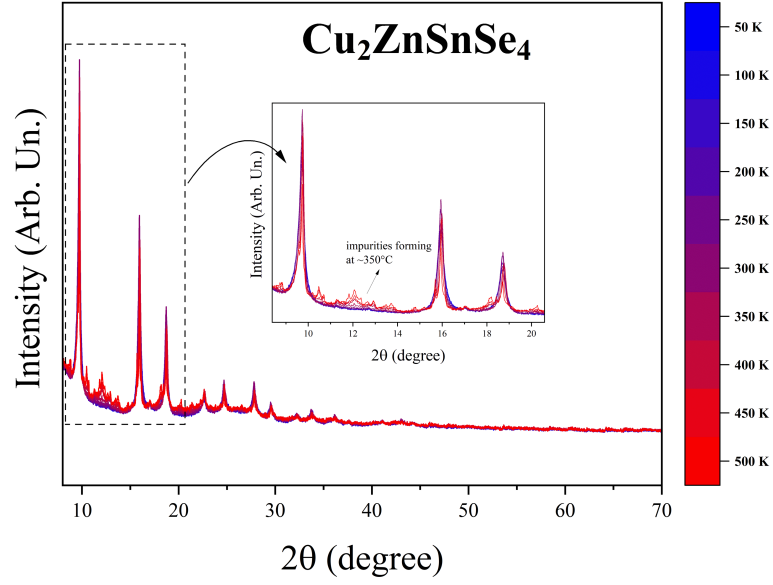


Figure A.9: In-situ HTXRD of the as-milled $\text{Cu}_2\text{ZnSnSe}_4$ powders performed using $\text{AgK}\alpha$ radiation. A phase transition to Cu_2Se is observed at around 350°C (623 K).

APPENDIX A. SUPPLEMENTARY INFORMATION: INVESTIGATING THE CUBIC-TO-TETRAGONAL PHASE TRANSITION OF $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ SOLID SOLUTIONS

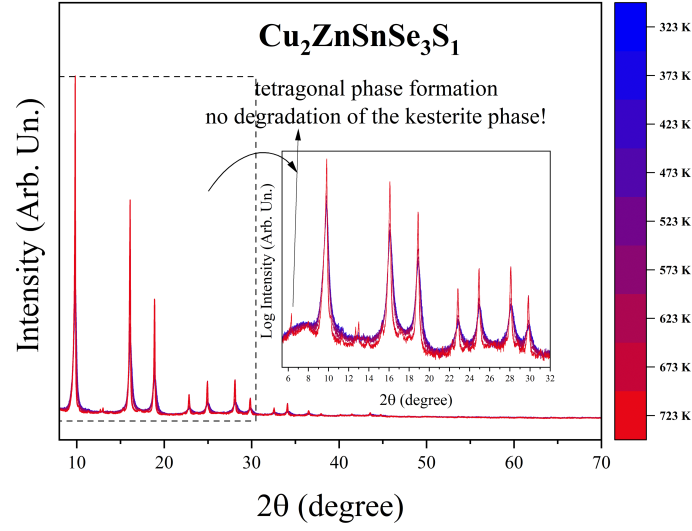


Figure A.10: In-situ HTXRD of the as-milled $\text{Cu}_2\text{ZnSnSe}_3\text{S}_1$ powders performed using $\text{AgK}\alpha$ radiation.

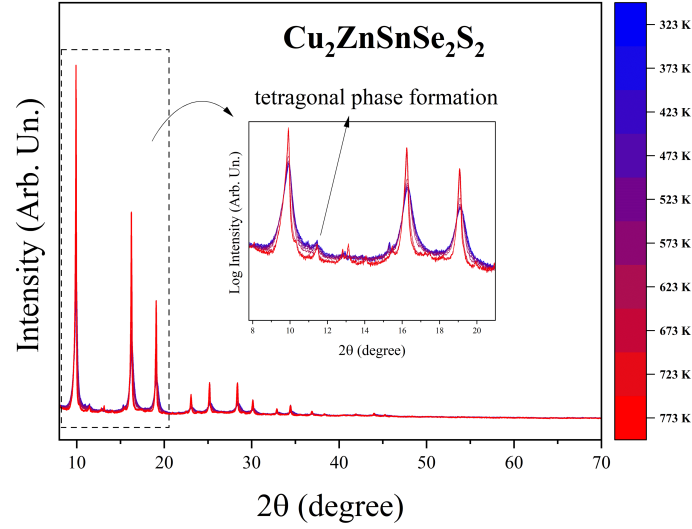


Figure A.11: In-situ HTXRD of the as-milled $\text{Cu}_2\text{ZnSnSe}_2\text{S}_2$ powders performed using $\text{AgK}\alpha$ radiation.

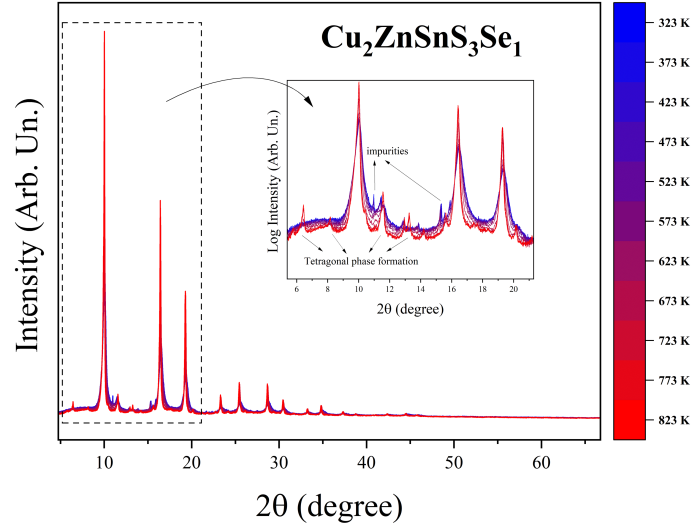


Figure A.12: In-situ HTXRD of the as-milled $\text{Cu}_2\text{ZnSnS}_3\text{Se}_1$ powders performed using $\text{AgK}\alpha$ radiation.

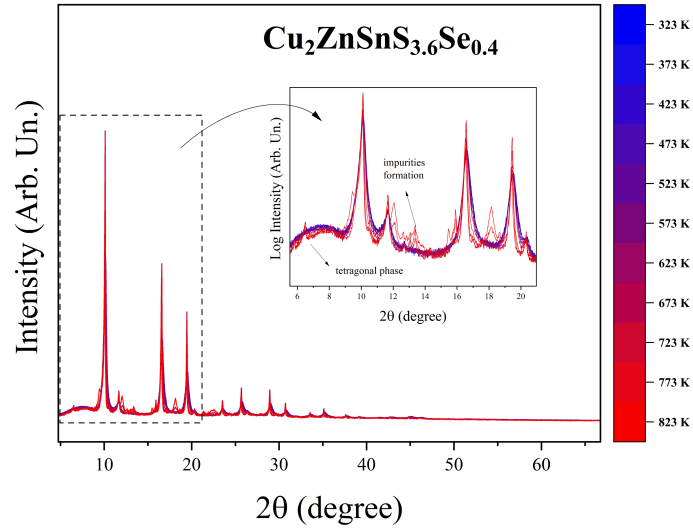


Figure A.13: In-situ HTXRD of the as-milled $\text{Cu}_2\text{ZnSnS}_{3.6}\text{Se}_{0.4}$ powders performed using $\text{AgK}\alpha$ radiation. Impurities are formed at around 623 K.

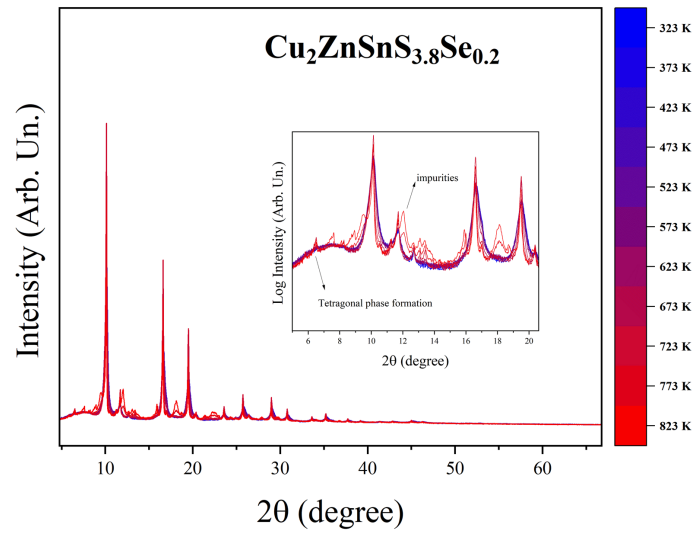


Figure A.14: In-situ HTXRD of the as-milled $\text{Cu}_2\text{ZnSnS}_{3.8}\text{S}_{0.2}$ powders performed using $\text{AgK}\alpha$ radiation.

A.3 Supplementary Note 3: Hydroscopic characteristics of the $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ system

In addition, the endothermic peaks 1 and 2 in 2.7 reveal the presence of water evaporation and crystalline sulphur degradation, respectively. The fact that both integral areas of these peaks reduce with the increasing proportion of Se is attributable to the better hydroscopic characteristic of S compared to Se, therefore confirming that Se-rich material absorbs less moisture and is less susceptible to degradation effects.

A.4 Supplementary Note 4: PDF for tetrahedral motifs

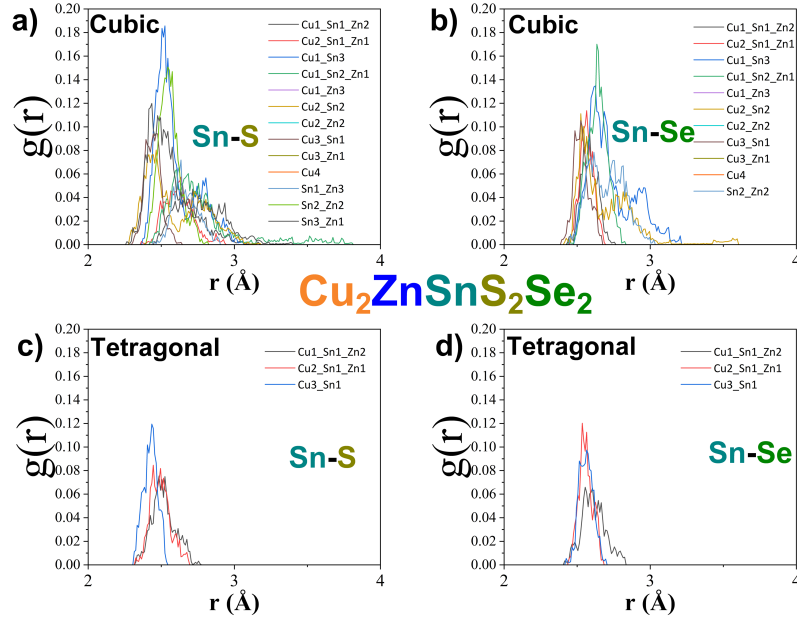


Figure A.15: PDFs for the AIMD simulated $\text{Cu}_2\text{ZnSnS}_2\text{Se}_2$ system separated by S/Se- $\text{Cu}_x\text{Zn}_y\text{Sn}_z$ tetrahedral motifs and calculated for: (a) cubic phase Sn-S pairs, (b) cubic phase Sn-Se pairs, (c) tetragonal phase Sn-S pairs, and (d) tetragonal phase Sn-Se pairs.

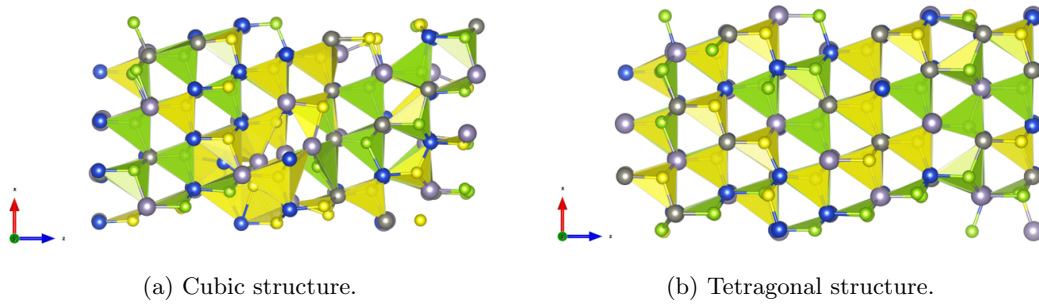


Figure A.16: $\text{Cu}_2\text{ZnSnS}_2\text{Se}_2$ tetrahedral motifs for the average positions of the atoms.

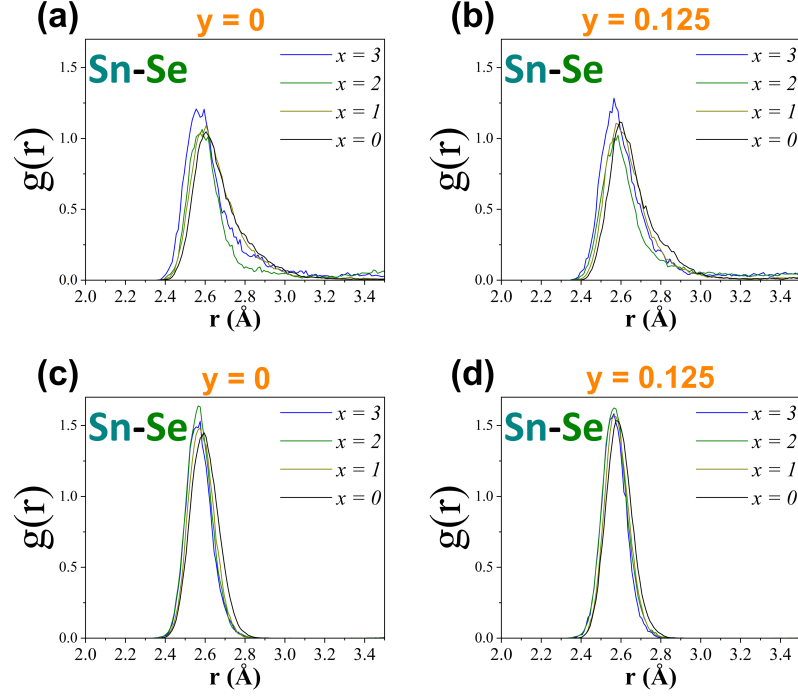
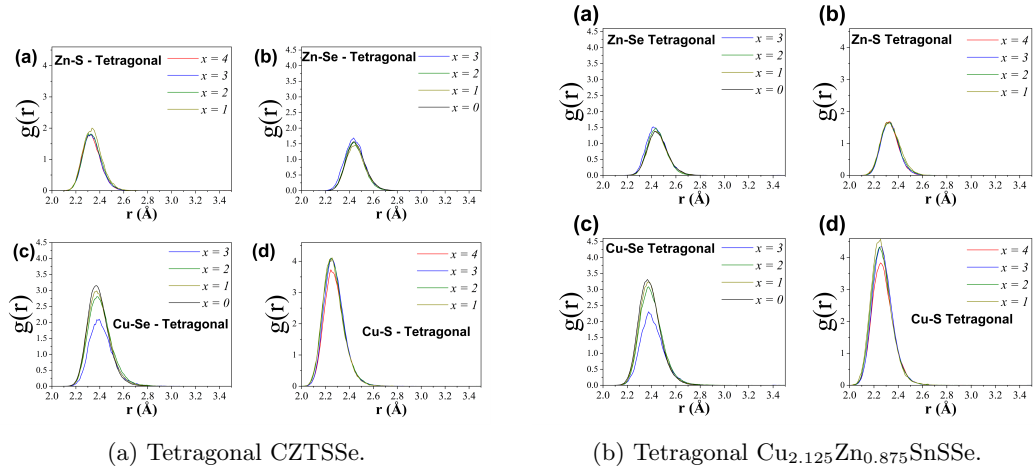


Figure A.17: PDF of the Sn-S bonds for (a) $y = 0$ cubic phase, (b) $y = 0.125$ cubic phase, (c) $y = 0$ tetragonal phase, and (d) $y = 0.125$ tetragonal phase. The colours represent the x variation.



(a) Tetragonal CZTSSe.

(b) Tetragonal $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnSe}$.

Figure A.18: Additional tetragonal structures.

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SOLUTIONS

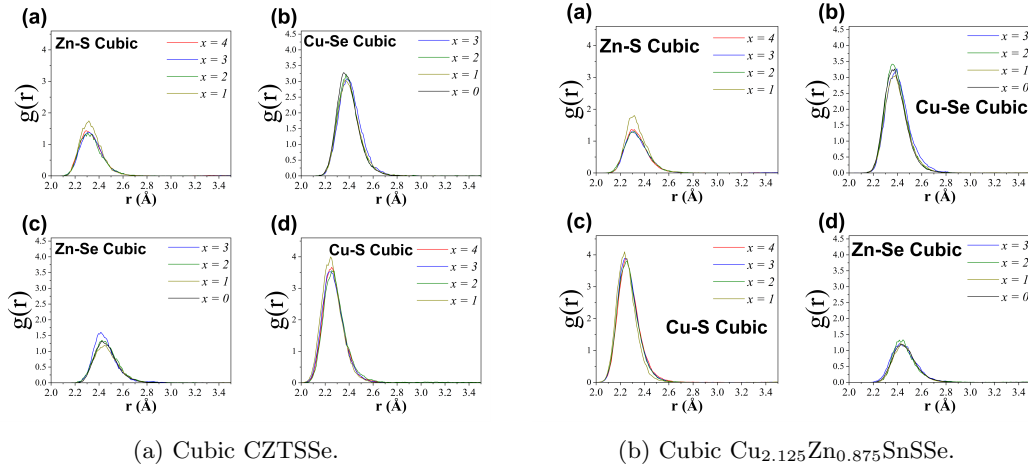


Figure A.19: Additional cubic structures.

Appendix B

Supplementary Information: Role of microstructure in the lattice thermal conductivity and thermoelectric performance of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ alloys

B.1 Supplementary Note 1: Rietveld Analysis

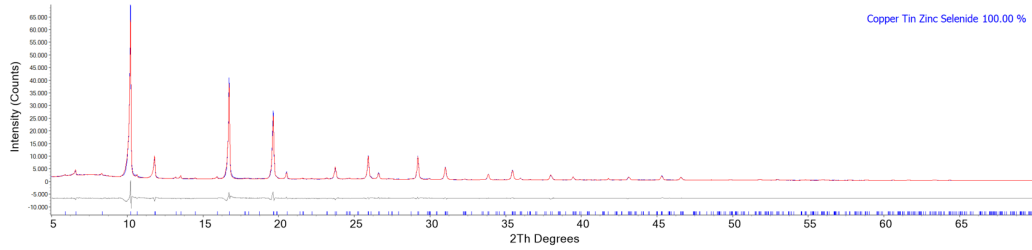


Figure B.1: Rietveld Analysis of the Cold-Pressed $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_4$. Blue line corresponds to experimental data obtained from $\text{AgK}\alpha$ radiation, red line represents the profile modelling, and gray the residuals. The blue markers correspond to the crystallographic Miller indices.

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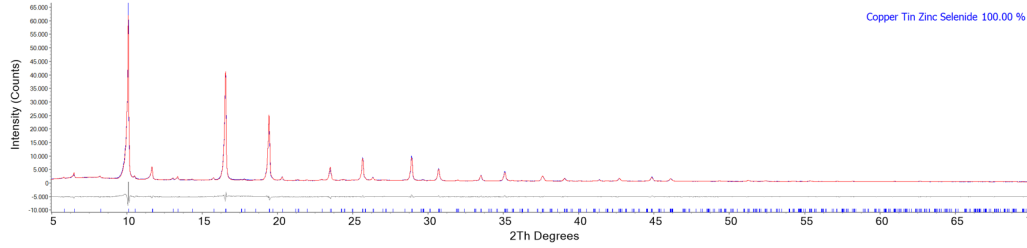


Figure B.2: Rietveld Analysis of the Cold-Pressed $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_3\text{Se}_1$. Blue line corresponds to experimental data obtained from $\text{AgK}\alpha$ radiation, red line represents the profile modelling, and gray the residuals. The blue markers correspond to the crystallographic Miller indices.

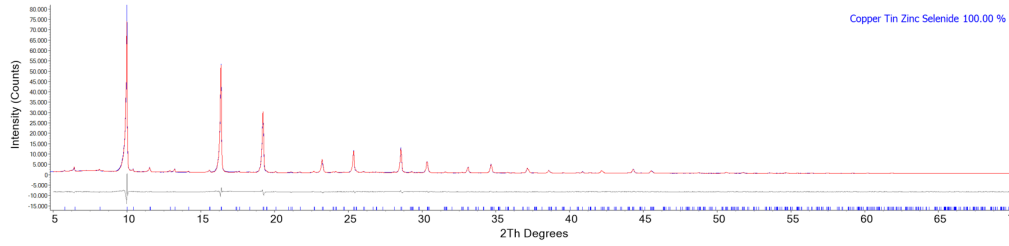


Figure B.3: Rietveld Analysis of the Cold-Pressed $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_2\text{Se}_2$. Blue line corresponds to experimental data obtained from $\text{AgK}\alpha$ radiation, red line represents the profile modelling, and gray the residuals. The blue markers correspond to the crystallographic Miller indices.

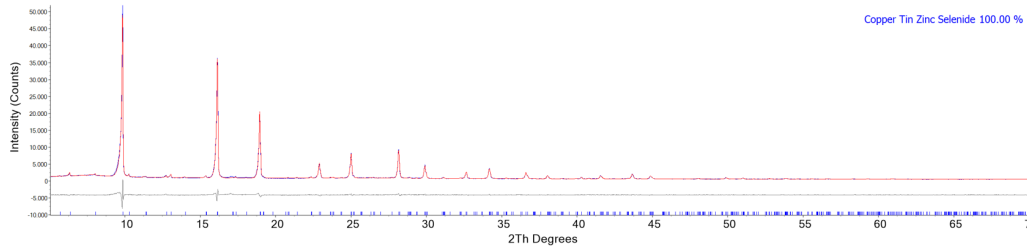


Figure B.4: Rietveld Analysis of the Cold-Pressed $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_1\text{Se}_3$. Blue line corresponds to experimental data obtained from $\text{AgK}\alpha$ radiation, red line represents the profile modelling, and gray the residuals. The blue markers correspond to the crystallographic Miller indices.

B.1. SUPPLEMENTARY NOTE 1: RIETVELD ANALYSIS

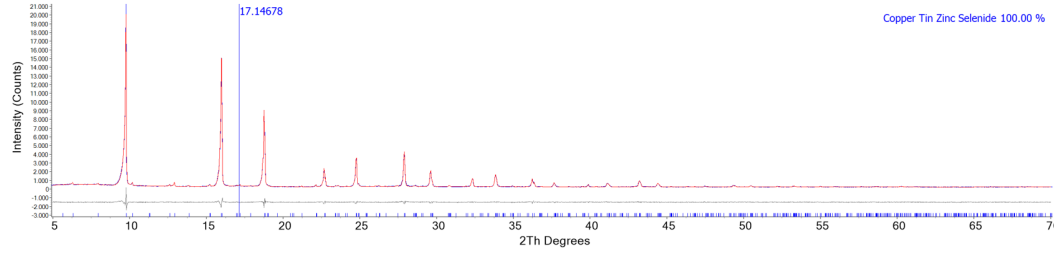


Figure B.5: Rietveld Analysis of the Cold-Pressed $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnSe}_4$. Blue line corresponds to experimental data obtained from $\text{AgK}\alpha$ radiation, red line represents the profile modelling, and gray the residuals. The blue markers correspond to the crystallographic Miller indices.

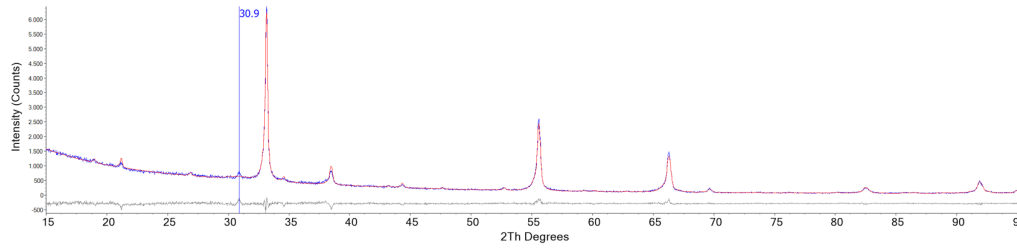


Figure B.6: Rietveld Analysis of the SPS $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_4$. Blue line corresponds to experimental data obtained from $\text{AgK}\alpha$ radiation, red line represents the profile modelling, and gray the residuals. The vertical line corresponds to C electrode employed for the SPS contact.

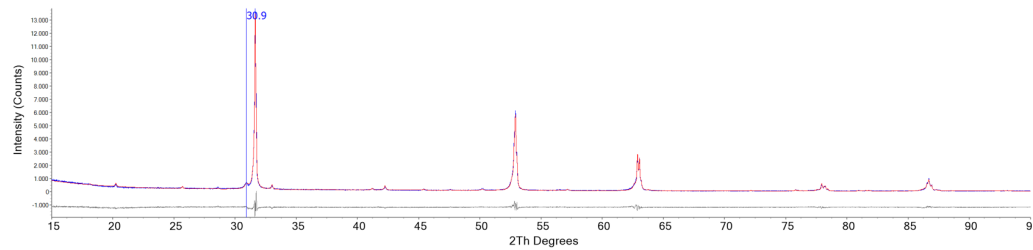


Figure B.7: Rietveld Analysis of the SPS $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnSe}_4$. Blue line corresponds to experimental data obtained from $\text{AgK}\alpha$ radiation, red line represents the profile modelling, and gray the residuals. The vertical line corresponds to C electrode employed for the SPS contact.

B.2 Supplementary Note 2: Raman analysis of the cold-pressed samples

The CuZn substitutions can be better observed via Raman analysis that are given in Figure B.8. For CZTSe, the increase on this type of substitution leads to the increase in the peak around 190 cm^{-1} [250]. In addition, the deviation from stoichiometry shifts the main 194 cm^{-1} to higher values, in this case 197 cm^{-1} , due to the excess of Cu [251] (vide Figure B.8a). For CZTS, the main A modes are identified at 337 cm^{-1} and 287 cm^{-1} [52] as shown in Figure B.8b. The other peaks are indexed as longitudinal optical modes (LO) of the polar B and E components [252]. In addition, the increased anion disorder for broadens the Raman peaks as showcased in Figure B.8c. Extracting the Vegard relations for the Se and S bonds from the Raman spectra, the relation are shown in Figure B.8. In this case, the point of $x = 3$ was not used since it deviates from the correct stoichiometry (vide EDX results in Table B.1). A similar relation is found compared to the literature for the Se bonds, but significantly deviate for the S bonds (see Figure B.8d) [52]. The deviation from linearity is also observed in recent reports and was credited to small fluctuation of the stoichiometry in this proportion region.

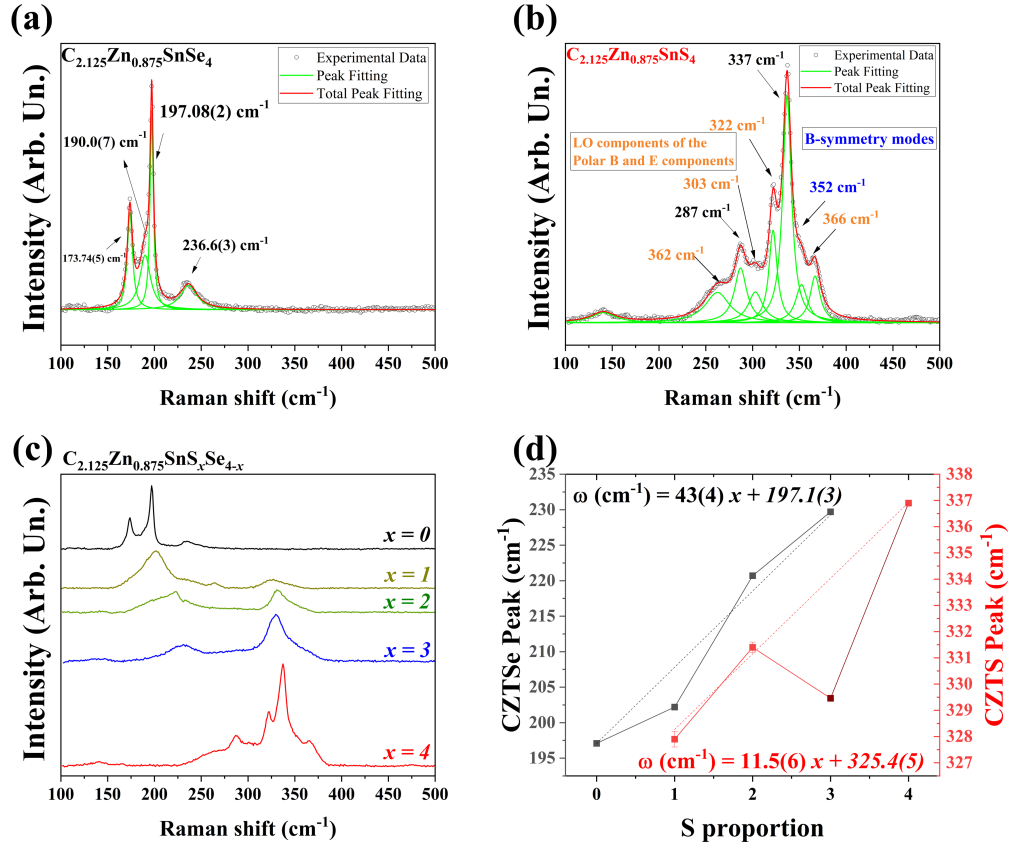


Figure B.8: Raman spectra of the (a) $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnSe}_4$ and (b) $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_4$ samples fabricated by cold-pressing and sintered at 883 K. Dots represent the experimental data, green line the Raman peaks, and the red line the summed contribution of each peak. (c) Raman spectra of the entire $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ series. (d) Vegard relations for the Se (black) and S (red)-cation bonds.

B.3 Supplementary Note 3: Mode Gruneisen parameter

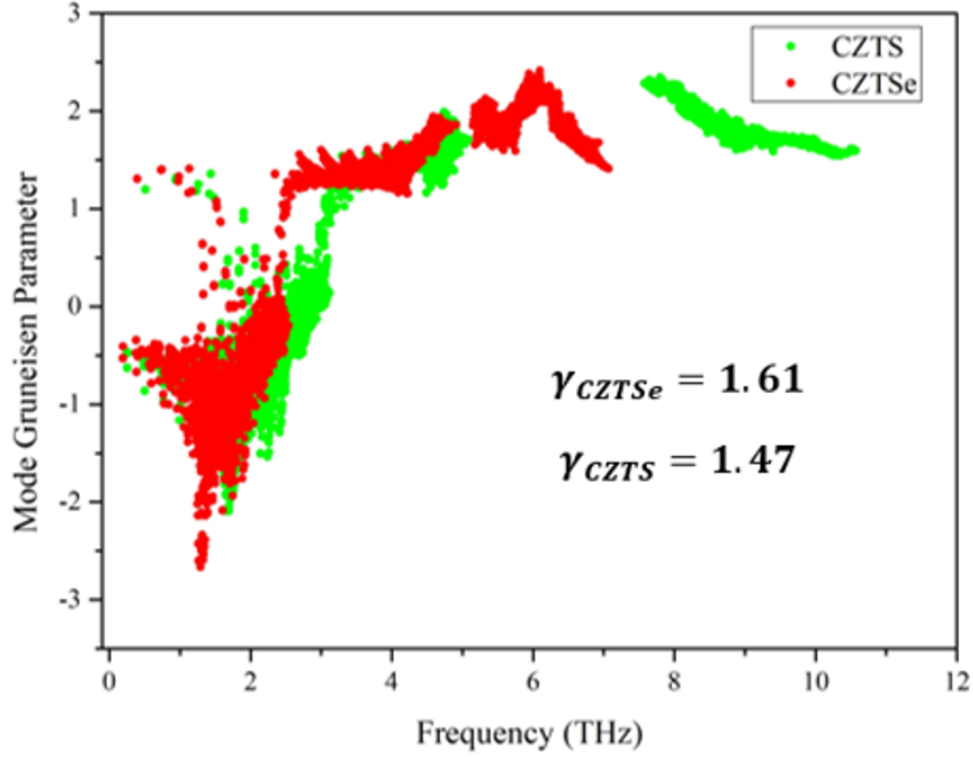


Figure B.9: Gruneisen parameter vs frequency plots for CZTS and CZTSe obtained via DFPT.

B.4 Supplementary Note 4: Electron microscopy analysis

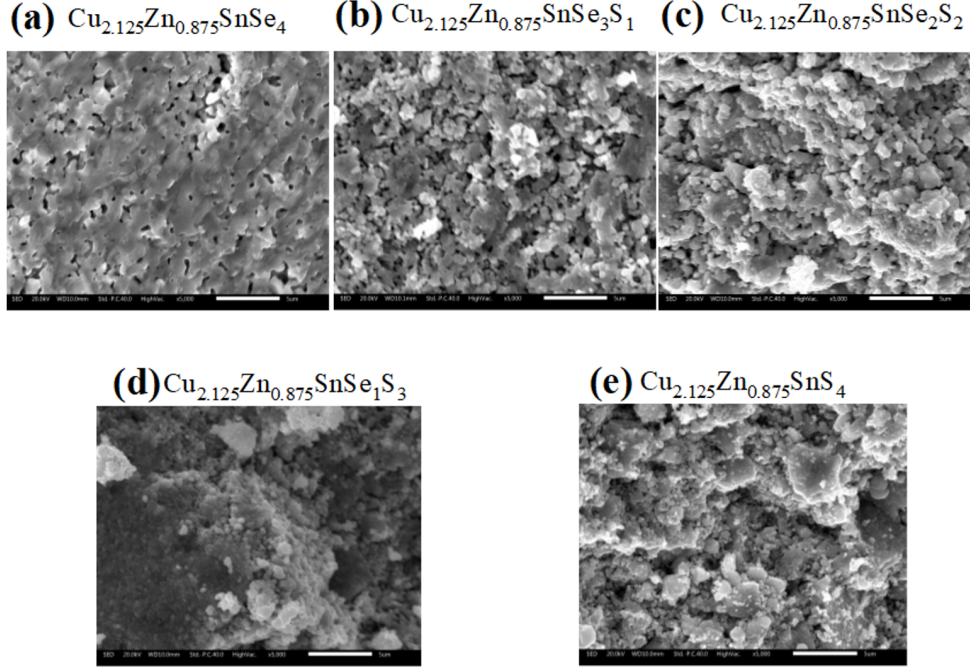


Figure B.10: SEM analysis for the cold -pressed samples.

Table B.1: EDS analysis of the $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ fold cold pressed and SPS samples. The ideal proportion of $\text{Cu}/\text{Zn} = 2.43$. Measurement performed at the centre of the cross-section of the cold-pressed disk. Φ corresponds to the pore fraction.

x	Φ	Cu %	Zn %	Sn %	S %	Se %	Cu/Zn	S/(S+Se)	Anion/Cation Ratio
Cold pressed samples									
0	22%	26.9(6)	10.6(3)	12.6(6)	-	50(1)	2.5	0	0.9979
1	22%	26.9(6)	11.0(3)	12.8(6)	12.1(2)	37(1)	2.44	0.25	0.9708
2	16%	26.6(7)	11.4(3)	13.1(7)	25.9(5)	23.0(8)	2.33	0.53	0.9615
3	35%	29.9(8)	10.0(3)	11.5(7)	38.9(8)	9.6(4)	2.99	0.8	0.9433
4	32%	28.6(10)	13.0(5)	13.0(9)	45(1)	-	2.2	1	0.8333
SPS samples									
0	3%	26.9(6)	11.0(3)	11.7(6)	-	50.5(1)	2.45	0	1.02
4	9%	26.7(10)	10.8(3)	12.0(9)	50.4(1)	-	2.46	1	1.02

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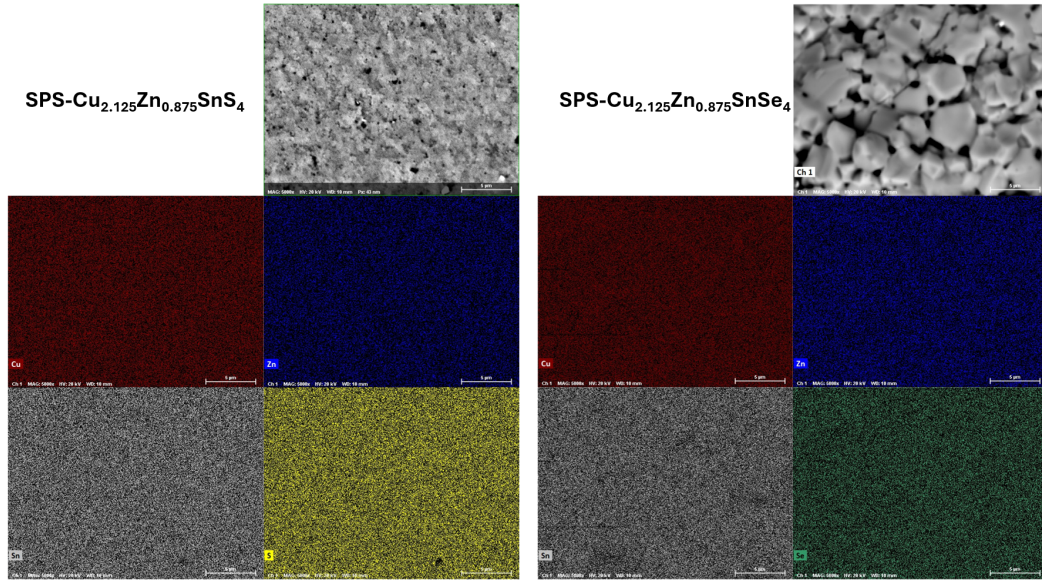


Figure B.11: SEM and chemical maps for the SPS CZTSSe samples.

B.5 Supplementary Note 5: Microstrain analysis

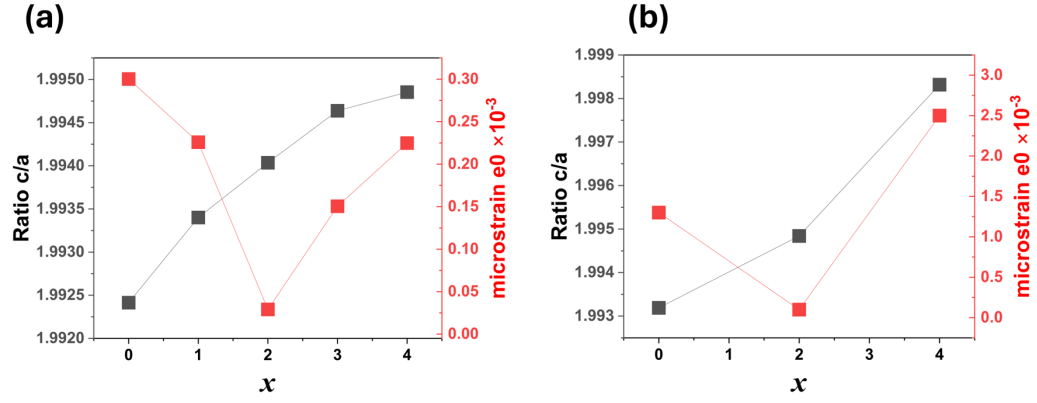


Figure B.12: Ratio of the lattice parameters c/a and microstrain for (a) cold-pressed and (b) SPS samples.

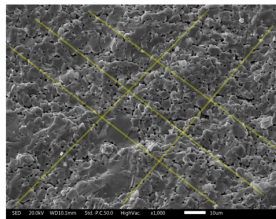
B.6 Supplementary Note 6: Crystallite and grain size analysis

The crystallite size distribution is modelled via whole powder pattern approach (WPPM) using the macros available for the TOPAS software [80, 134, 135]. It utilizes a log-normal distribution of spheres, where the log-normal mean and standard deviation are refined. For details follow details here: <https://topas.webspace.durham.ac.uk/tutorial-wppm/>.

The average grain size was estimated from SEM micrographs using the line intercept method. A set of straight test lines was superimposed on each calibrated micrograph in multiple orientations to minimize directional bias. For each line, the number of intersections with grain boundaries was counted, and the true line length was measured. The mean lineal interception length was calculated as the ratio between the total test line length and the number of grain-boundary interceptions, providing an estimate of the average grain size along that direction. The values obtained from several lines were averaged to determine the mean grain size and corresponding standard deviation. The ASTM-equivalent grain diameter was then calculated from the mean intercept length to allow comparison between samples. This stereological approach provides a statistically representative estimate of grain size, particularly suitable for irregular and porous microstructures. Values and representation is given in Figure B.13.

Size estimation via SEM

Line intercept method



SPS			
S4_X_SED_2_0005.Tif			
Line	Length (nm)	Number of Intercepts	Grain Size (nm)
1	6215.215	23	270.2267391
2	5410.615	20	270.53075
3	4194.833	19	220.7806842
4	15211.15	48	316.8989583
5	14223.987	44	323.2724318
6	10596.496	37	286.3917838
Average			281.3502245
Standard Deviation			37.2989636
ASTM average grain diameter			438.9063503
ASTM std. grain diameter			58.18638322

Cold-Pressed			
Cu2p125Zn0p875SnS4_X_SED_2_0001			
Line	Length (nm)	Number of Intercepts	Grain Size (nm)
1	10810.927	27	400.4047037
2	9801.165	28	350.0416071
3	16699.745	29	575.8532759
4	9732.963	31	313.9665484
5	28348.23	63	449.9719048
6	10935.055	20	546.75275
Average			439.498465
Standard Deviation			105.3517183
ASTM average grain diameter			685.6176054
ASTM std. grain diameter			164.3486805

SPS			
Se4_X_SED_2_0001.Tif			
Line	Length (nm)	Number of Intercepts	Grain Size (nm)
1	147473.667	38	3880.885974
2	147194.268	48	3066.54725
3	110346.84	39	2829.406154
4	109018.576	35	3114.816457
5	68342.319	26	2628.550731
Average			3104.041313
Standard Deviation			476.0581109
ASTM average grain diameter			4842.304448
ASTM std. grain diameter			742.650653

Cold-Pressed			
Cu2p125Zn0p875SnSe4_X_SED_2_0001.Tif			
Line	Length (nm)	Number of Intercepts	Grain Size (nm)
1	29449.844	42	701.1867619
2	27482.744	29	947.6808276
3	24462.494	27	906.0182963
4	18367.036	18	1020.390889
5	14934.122	13	1148.778615
Average			944.811078
Standard Deviation			164.454391
ASTM average grain diameter			1473.905282
ASTM std. grain diameter			256.54885

Figure B.13: Results obtained with the line intercept method for the SPS and cold-pressed samples.

B.7 Supplementary Note 7: Performance of tetragonal phases

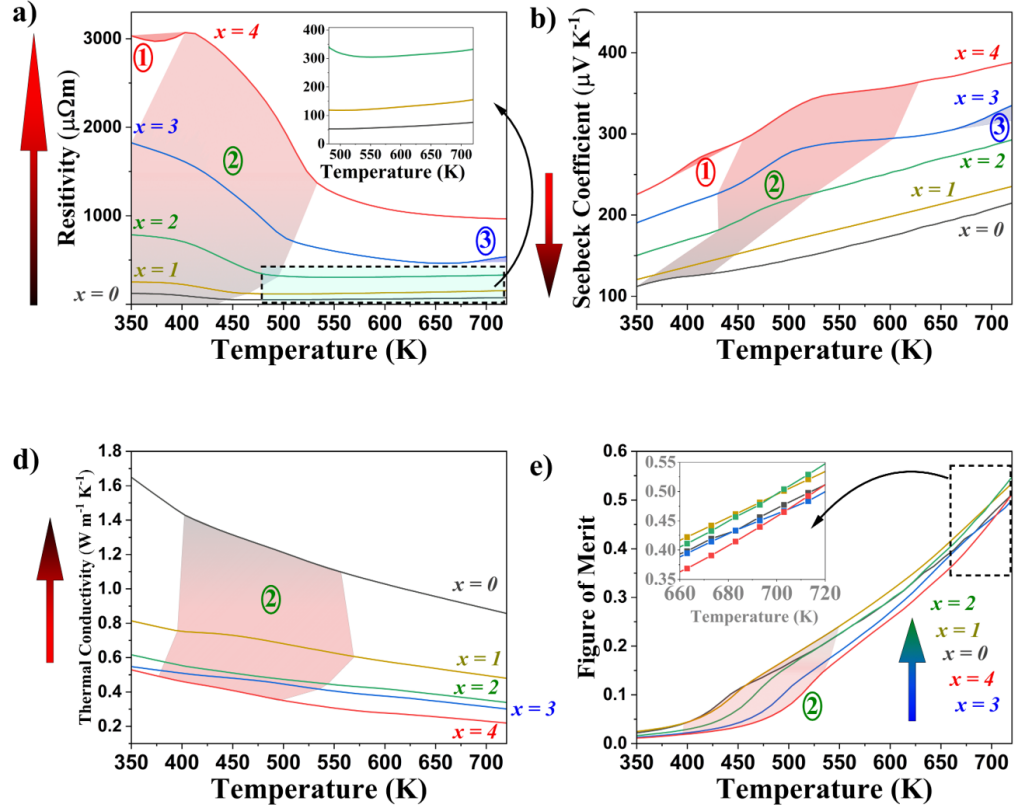


Figure B.14: (a) Resistivity, (b) Seebeck coefficient, (c) thermal conductivity, and (d) Figure of merit for the $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ series.

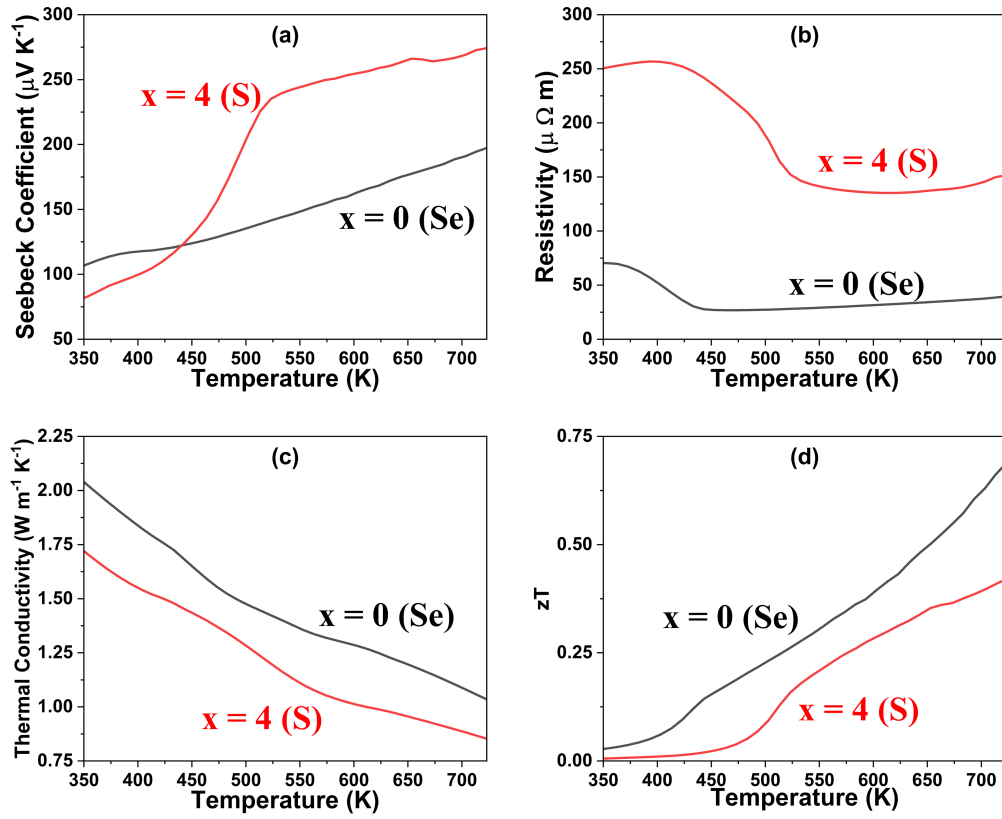


Figure B.15: (a) Resistivity, (b) Seebeck, (c) thermal conductivity, and (d) Figure of merit for the $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_x\text{Se}_{4-x}$ series.

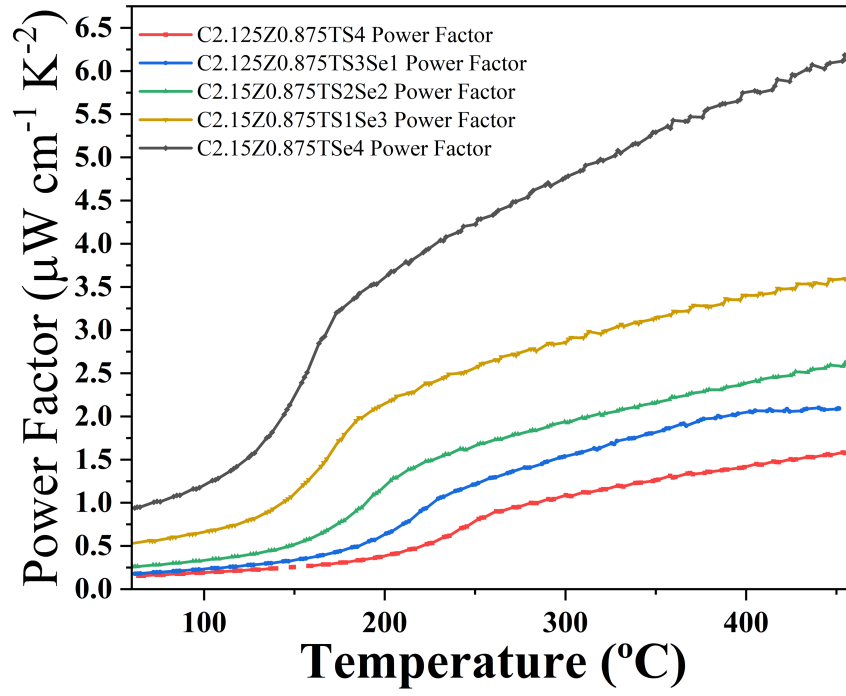


Figure B.16: Power factor obtained for the cold pressed samples.

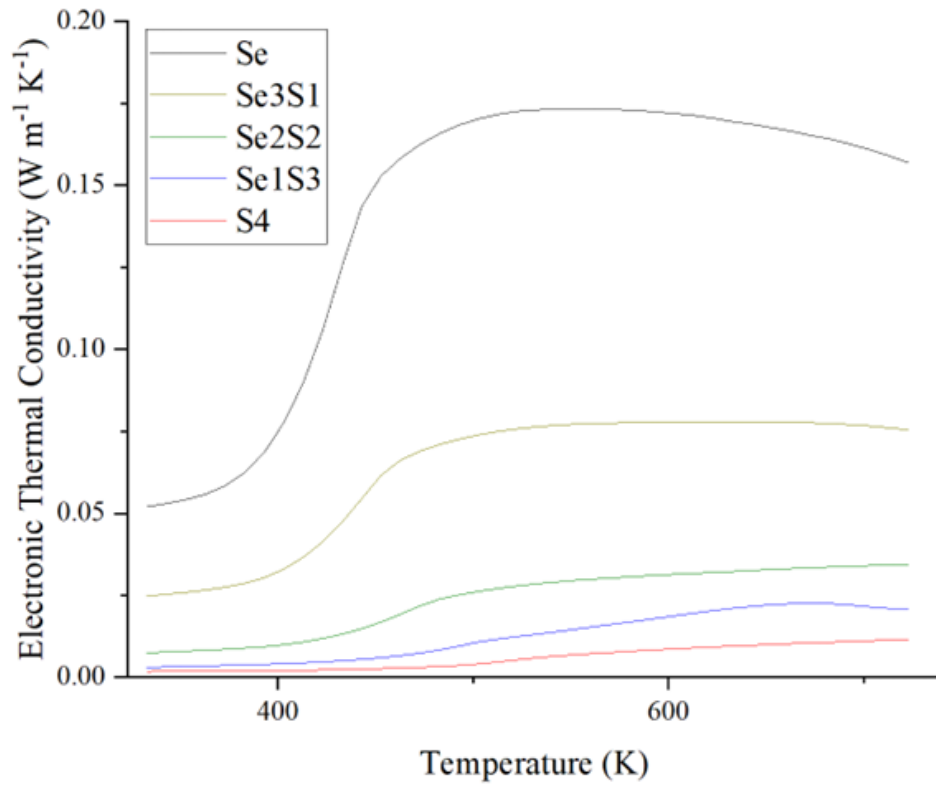


Figure B.17: Electronic thermal conductivity for the cold-pressed samples.

B.8 Supplementary Note 8: DFT analysis

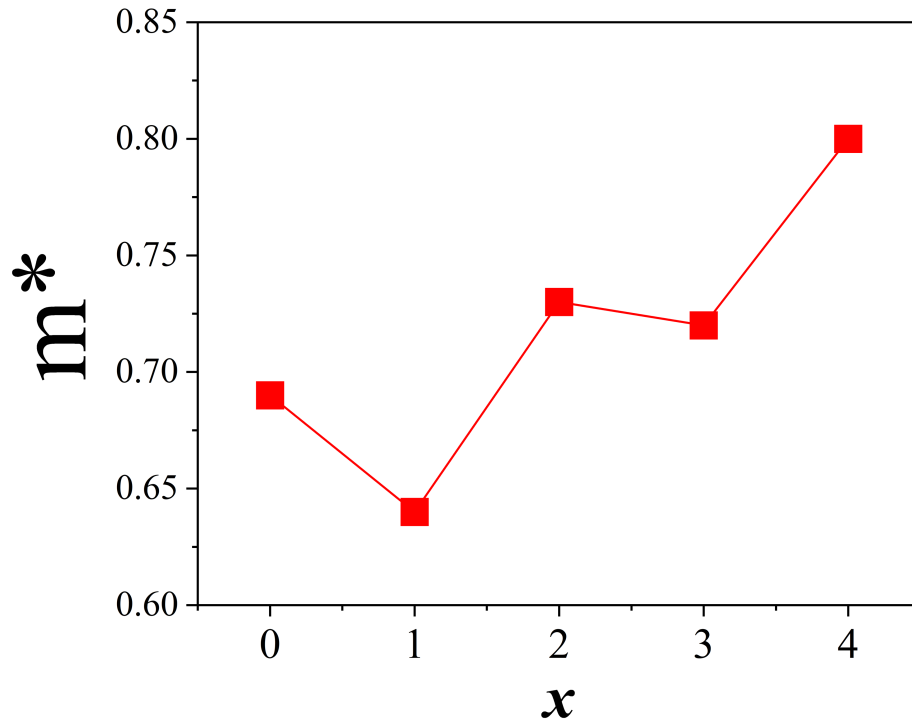


Figure B.18: DFT density of states effective mass.

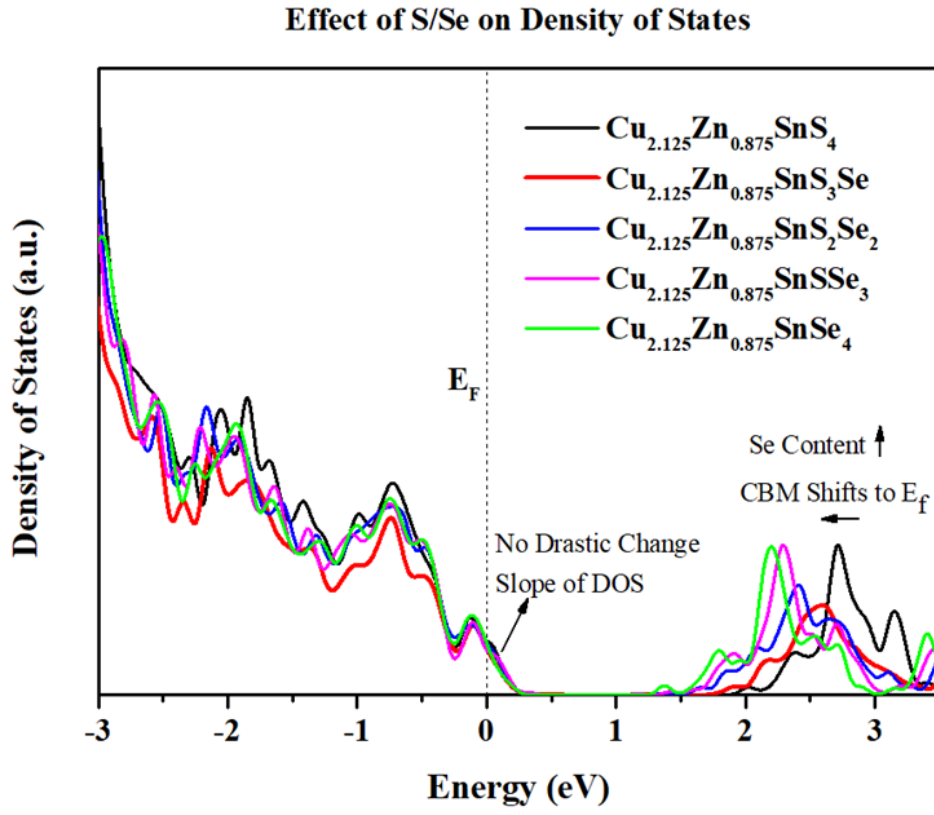


Figure B.19: DFT density of states.

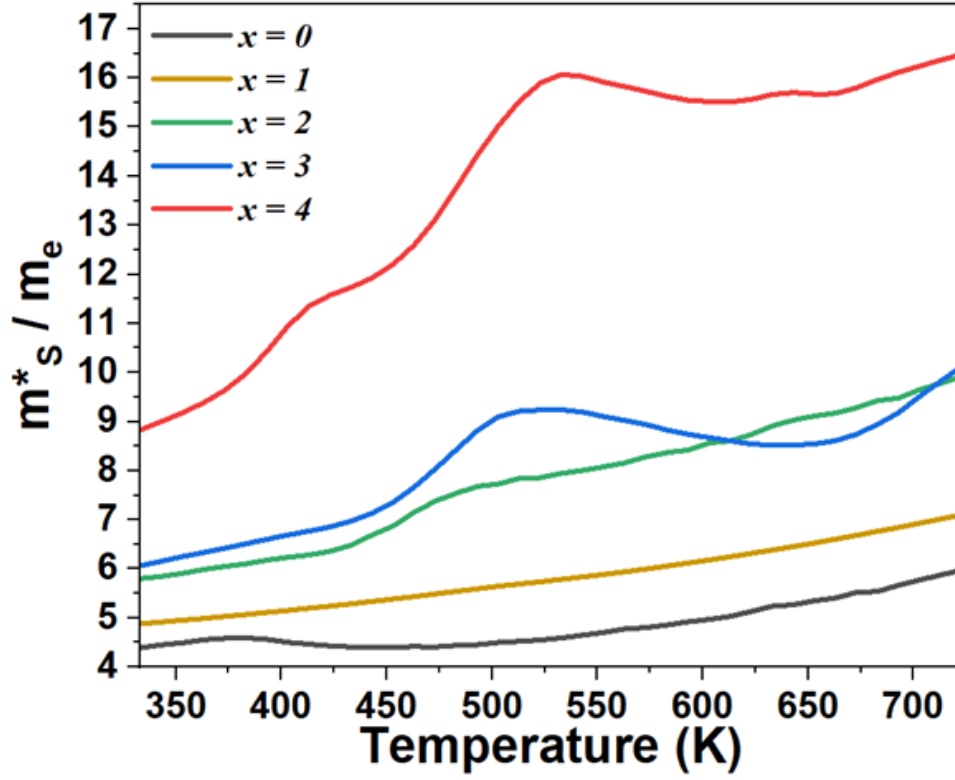


Figure B.20: Seebeck effective mass of the charge carriers.

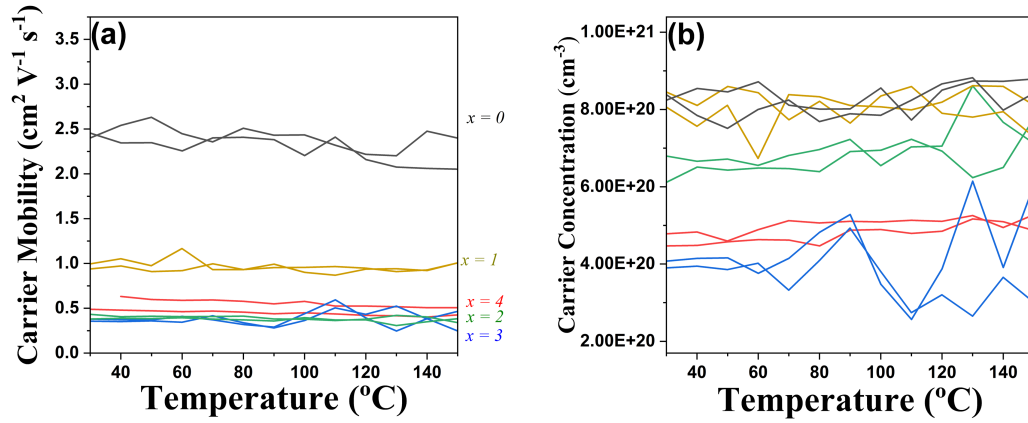


Figure B.21: Hall effect measurements of (a) carrier mobility and (b) carrier concentration for the cold-pressed samples.

B.9 Supplementary Note 9: Debye–Callaway model

Debye Callaway equations rule including all the possible scattering mechanisms [52, 250, 251] in the form:

$$\kappa_l = \frac{1}{3} \int_0^{\omega_{\max}} C_s(\omega) v_g(\omega)^2 \tau(\omega) d\omega \quad (\text{B.1})$$

Where the maximum phonon frequency is given by

$$\omega_{\max} = \left(\frac{6\pi^2}{V} \right)^{1/3} v_{\text{sound}} \quad (\text{B.2})$$

Being V the volume of the unit cell, and v_{sound} the average speed of sound between longitudinal and transverse modes. Here the phonon group speed is approximated as the speed of sound, i.e., $v_g(\omega) = v_{\text{sound}}$. At high temperatures, the spectral heat capacity ($C_s(\omega)$) can be approximated as:

$$C_s(\omega) = \frac{3k_B\omega^2}{2\pi^2 v_{\text{sound}}^3} \quad (\text{B.3})$$

k_B is the Boltzmann constant. The phonon relaxation time is modelled by a combination of Umklapp (τ_U), grain-boundary (τ_{GB}), and point defects (τ_{PD}) in the form

$$\tau^{-1} = \sum_i \tau_i^{-1} \quad (\text{B.4})$$

Umklapp scattering models the phonon scattering by the following frequency dependency:

$$\tau_U(\omega) = \frac{(6\pi^2)^{1/3}}{2} \frac{\overline{M} v_{\text{sound}}^3}{k_B V^{1/3} \gamma^2 \omega^2 T} \quad (\text{B.5})$$

Where $\overline{M}$ is the average atomic mass and γ the Gruneisen parameter. Grain-boundary scattering is governed by the following relaxation time:

$$\tau_{GB} = \frac{d}{v_{\text{sound}}} \quad (\text{B.6})$$

Where d is the SEM or XRD particle/domain size.

Point defects are modelled with both mass (m_i) and atomic radius (r_i) fluctuations residing on site with average mass and radius $\overline{m}$ and $\overline{r}$, respectively:

$$\tau_{PD} = \frac{V\omega^4}{4\pi v_{\text{sound}}^3} \left[\sum_i f_i \left(1 - \frac{m_i}{\overline{m}} \right)^2 + \sum_i f_i \left(1 - \frac{r_i}{\overline{r}} \right)^2 \right] \quad (\text{B.7})$$

The fluctuation is modelled by the occupancy fraction f_i . For vacancies, the mass of the point defects is null and we decided to omit the strain contribution

To understand the temperature dependency for the materials, we model the matrix thermal conductivity (κ_{matrix}) for the SPS samples. Since they contain no vacancies defects, only Umklapp and grain-boundary effects are modelled. The results are shown in Figure B.22. To fit well the data, the κ_l was multiplied by a constant value

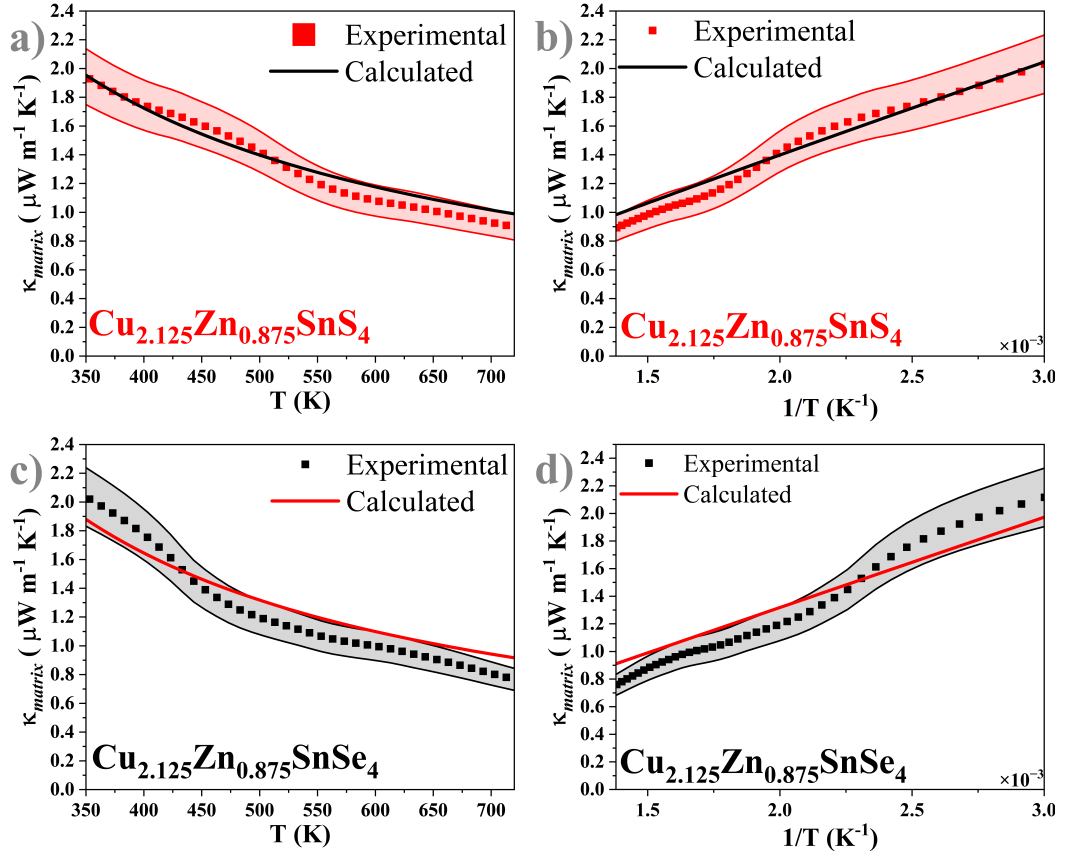


Figure B.22: Fitting of the lattice thermal conductivity using the Debye–Callaway model, considering grain-boundary and Umklapp scattering contributions to the relaxation times. Panels (a) and (b) show the fitting results for $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnS}_4$ plotted as a function of temperature (T) and its inverse (T^{-1}), respectively. Panels (c) and (d) present the corresponding plots for $\text{Cu}_{2.125}\text{Zn}_{0.875}\text{SnSe}_4$. Error bars were estimated at 10% and define the contour curves surrounding the experimental data (symbols). The model predictions are shown as solid lines.

Appendix C

Supplementary Information: Optimizing CuFeS₂ Chalcopyrite Thin Film Synthesis: A Comprehensive Three-Step Approach Using Ball-Milling, Thermal Evaporation, and Sulfurization Applied for Thermoelectric Generation

C.1 Supplementary Note 1: Parameters of Synthesis of CFS

Table C.1: FeCu milling parameters.

Sample Identifier	Atomic Proportion (Cu:Fe)	Milling Time (h)	Lubricant
FeCu-01	1:1	2	None
Fe1.76Cu-02	1:1.76	2	None
FeCu-03	1:1	3	6% weight ethanol

C.2. SUPPLEMENTARY NOTE 2: NON-MILLED CU-FE POWDERS OPTIMIZATION

Table C.2: Thermal evaporation of FeCu powders.

Sample	Milled Powder	Powder Mass (g)	Target Distance (cm)	Current Ramp	Pressure (mBar)	Surface
1	Not Milled	0.215 (Fe)	27	140 A for 1 h	$\sim 10^{-5}$	Non-Polished
2	Not Milled	0.215 (Cu)	27	105 A for 1 h	$\sim 10^{-5}$	Non-polished
3	Not milled	0.215	27	105 A for 1 h	$\sim 10^{-5}$	Non-polished
4	Not milled	0.215	27	140 A for 1 h	$\sim 10^{-5}$	Non-polished
5	Not milled	0.6	27	105 A to 140 steps of 5 A for 3 min each	$\sim 10^{-5}$	Non-Polished
6	Not milled	0.2	9.5	105 A for 10 min + 135 A for 20 s + 140 A for 1 min	$\sim 10^{-5}$	Non-polished
7	Not milled	0.15	7.5	105 A for 3 min	$\sim 10^{-5}$	Non-polished
8	Not milled	0.15	7.5	105 A for 10 min + 125 A for 20 s + 140 A for 4 min	$\sim 10^{-5}$	Non-polished
9	FeCu-01	0.215	27	110 A for 5 min + 120 A for 1 min 15 s	$\sim 10^{-5}$	Non-polished
10	FeCu-01	0.06	7.5	105 A for 3 min + 130 A for 1 min	$\sim 10^{-5}$	Non-polished
11	FeCu-01	0.06	7.5	105 A for 10 min + 140 A for 1 min	7×10^{-6}	Non-polished
12	FeCu-01	0.06	7.5	105 A for 10 min + 140 A for 1 min	7×10^{-6}	Non-polished
13	FeCu-01	0.06	7.5	105 A for 10 min + 140 A for 1 min	7×10^{-6}	Polished
14	Fe _{1.76} Cu-02	0.06	7.5	105 A for 10 min + 140 A for 1 min	7×10^{-6}	Non-Polished
15	Fe _{1.76} Cu-02	0.06	7.5	105 A for 10 min + 140 A for 1 min	7×10^{-6}	Polished
16	FeCu-03	0.06	7.5	105 A for 10 min + 140 A for 1 min	7×10^{-6}	Non-Polished
17	FeCu-03	0.06	7.5	105 A for 10 min + 140 A for 1 min	7×10^{-6}	Polished
18	FeCu-03	0.06	7.5	105 A for 10 min + 140 A for 1 min	7×10^{-6}	Non-Polished

C.2 Supplementary Note 2: Non-milled Cu-Fe powders optimization

Thermal evaporation of Fe and Cu elemental powders, respectively – corresponding to samples 1 and 2, formed a face-centred cubic (fcc) structure with the space group $Fm-3m$ (Cu: ICSD # 627117; Fe: ICSD # 53803). This means that the high-temperature phase of Fe was stabilized at room temperature and with overall good crystallinity. The Rietveld refinement of the XRD patterns revealed that the as-deposited Fe thin film sample’s average crystallite size (volumetric average) is about ~ 8 nm, half that of the Cu sample (~ 17 nm). Also, the Cu as-deposited film shows a preferred orientation along the $[111]$ direction. Figures C.1 of Supplementary Note C.4 show the Rietveld refinement for Cu and Fe, respectively.

For samples 3 and 4, a mixture of Fe and Cu was evaporated using a current of 105 A and 140 A, respectively. For the former, evaporation was expected to be of Cu only, although Fe was also present (see Figures C.1 of Supplementary Note C.4). These samples showed Fe as a major phase. As discussed in the main text, evaporation of Cu occurs at a lower current than Fe, so it is expected that the major phase on the sample’s surface is Fe. However, the possibility of Cu–Fe alloy formation is not ruled out in the refinement, although it should probably happen between the interface of Cu and Fe in the middle of the film.

To achieve better homogeneity and formation of Cu–Fe alloy, a gradual increase in current was set to start at 105 A and slowly ramp up to 140 A during the evaporation for sample 5. However, this didn’t contribute to a better homogenization of the film, meaning that the Fe and Cu form separated layers, which is detrimental to the formation of a pure CFS alloy.

As a last attempt to improve the diffusion of Fe and Cu with the non-milled powders, the substrate for samples 6, 7, and 8 was positioned closer to the W boat. Sample 6 underwent a gradual current increase from 105 A to 140 A; while for sample 7, the distance to the target was further reduced, maintaining a current of 105 A (that of the Cu). In the case of sample 8, the gradual current increase was done with the same distance as sample 7. Sample 6 showed Cu (fcc) and Fe (bcc) layers and increased crystallinity compared to the previously discussed samples (observed by the sharper Bragg peaks in Figure 4.2(a) of the main text). Sample 7 showed only Fe. However, in sample 8, better mixing of Cu and Fe on the film was observed, where the distance between source and target was minimal (7.5 cm). For this case, a current of 105 A was applied for 10 minutes, followed by an increase to 140 A lasting 1 minute. The Rietveld refinement for all the samples is displayed in Figures C.2 and C.3.

C.3 Supplementary Note 3: Optimization of the Ball-Milling Procedure

C.3.1 Effect of target distance

Here, the first comparison between milled and non-milled FeCu powders in the evaporation process is presented. The FeCu-01 sample was evaporated having the target positioned far away from the boat (27 cm) as in the first cases of the non-milled powders, using the parameters of sample 9 (vide Table C.2 for specifics). The thermal evaporation of this sample and its sulfurization in a static Ar atmosphere are displayed in Figure 4.5(a) of the main text. Sample 9 showed the formation of bcc Fe, together with a small proportion of CuFe alloy. The introduction of sulphur via sulfurization lead to the formation of two phases, i.e., bornite $\text{Cu}_{4.98}\text{Fe}_{1.02}\text{S}_4$ (Pbca, PDF # 01-071-368) and CFS chalcopyrite (PDF # 00-037-0471), the latter with preferred orientation in the [112] direction (vide Figure C.4-bottom for the refined lattice parameters). The quantitative phase analysis (QPA) reveals that bornite and chalcopyrite are in half proportion in the sample. This can also be confirmed by the dark color aspect of the film shown in Figure C.14, as chalcopyrite is known to have a golden yellow color (vide Figure 4.1(b) of the main text).

In the same fashion as the non-milled powders, the results proved to be better when the target was brought closer to the source. The crystallinity of sample 10 is significantly improved as evidenced by the sharpness of the Bragg peaks in Figure 4.5(a) when the target is positioned 7.5 cm from the source (see also Figure C.5 for profile fitting). Unfortunately, this film presented poor adhesion to the substrate. To solve this problem, for sample 11, the vacuum was improved by one order of magnitude ($\sim 10^{-6}$ mbar) during the evaporation of the FeCu-01 powder. Another key point of this test was the lower quantity of powder employed, 0.06 g, 3 times lower than the previous sample. This increased the heating energy per gram of material.

C.3.2 Changing the milling parameters

Using the FeCu-01, milled for 2 h, the sulfurization of Sample 12 without polishing still presented the Bornite phase and preferred orientation for the Chalcopyrite phase along the [111] and [044] directions (see Figure 4.6(a) of the main text and Rietveld analysis in Figure C.7). Polishing the SLG substrate for sample 13 resulted in better adhesion along with the reduction of the Bornite phase quantity in the diffractograms. However, the improvement was not adequate, and the physical aspect of the film was not satisfactory, as shown in the inset of Figure 4.6(a) (details in Figure C.14). During the evaporation of Fe_{1.76}Cu-02 powders, pure chalcopyrite is formed presenting also the characteristic golden-yellow colour (see Figure C.14 and inset of Figure 4.6(a)). In the Rietveld analysis (vide Figures C.9 and C.10), preferred orientation is present along [112] and [220] for sample 14, and [112] for sample 15 on the polished and non-polished substrates, respectively. The adhesion is only improved for samples 16 and 17 where the CuFe-03 powders were employed. Even with the polishing of sample 17, a better adhesion was found for sample 16 (vide Figure 4.6(a)), which was selected as the optimized film product.

C.4 Supplementary Note 4: Rietveld Refinement

C.4. SUPPLEMENTARY NOTE 4: RIETVELD REFINEMENT

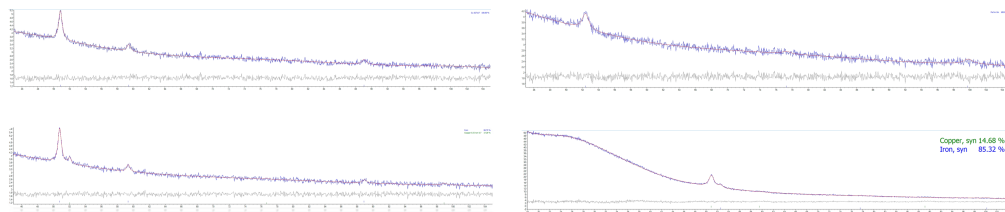


Figure C.1: Sample 1, Sample 2, Sample 3, and Sample 4.

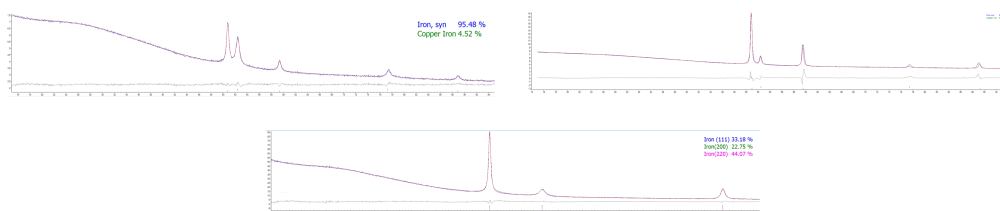


Figure C.2: Sample 5, Sample 6, and Sample 7.

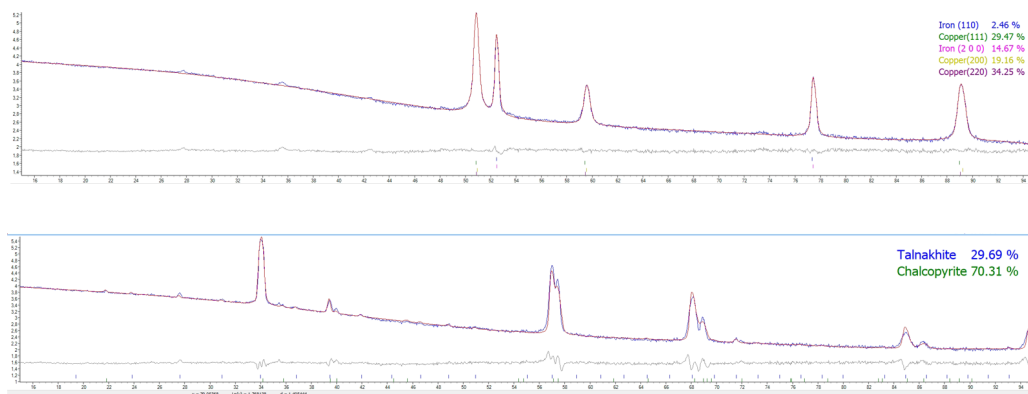


Figure C.3: Sample 8 evaporated (top) and its sulfurization using the configuration 2 (bottom).

APPENDIX C. SUPPLEMENTARY INFORMATION: OPTIMIZING CuFeS_2 CHALCOPYRITE THIN FILM SYNTHESIS: A COMPREHENSIVE THREE-STEP APPROACH USING BALL-MILLING, THERMAL EVAPORATION, AND SULFURIZATION APPLIED FOR THERMOELECTRIC GENERATION

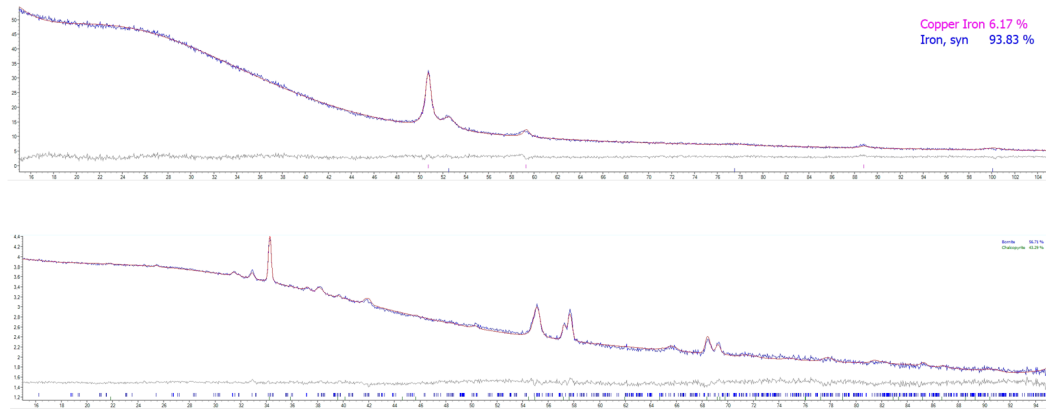


Figure C.4: Sample 9 (top) and its sulfurization employing configuration 1. The lattice parameters for the Bornite phase are retrieved by Rietveld refinement.

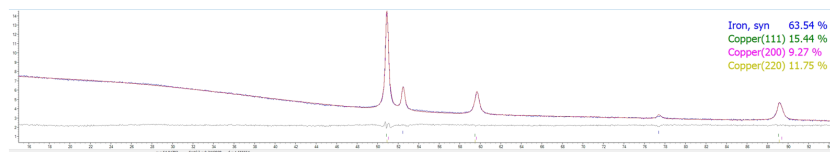


Figure C.5: Sample 10.

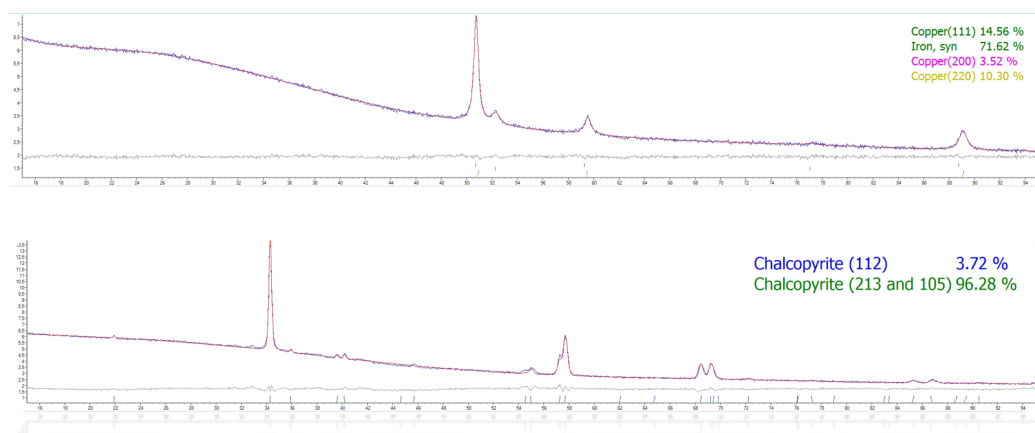


Figure C.6: Sample 11 (top) and its sulfurization using setup 1.

C.4. SUPPLEMENTARY NOTE 4: RIETVELD REFINEMENT

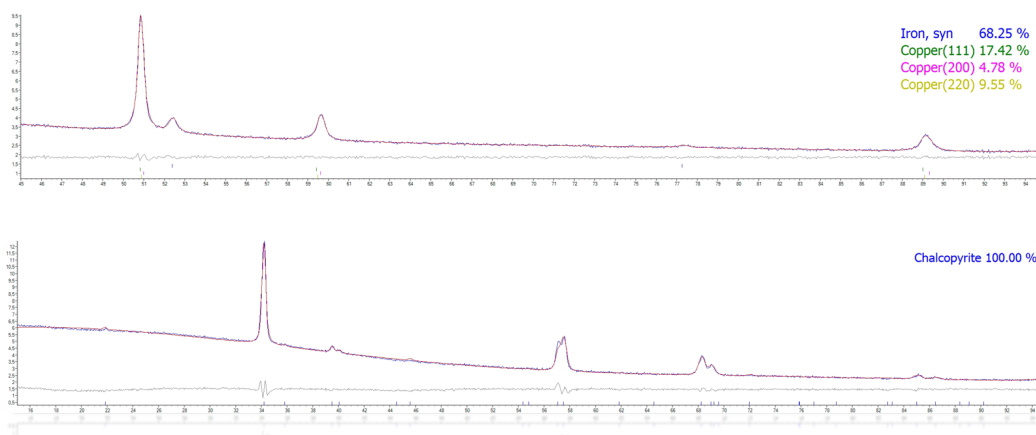


Figure C.7: Sample 12 (top) and its sulfurization employing configuration 1 (bottom).

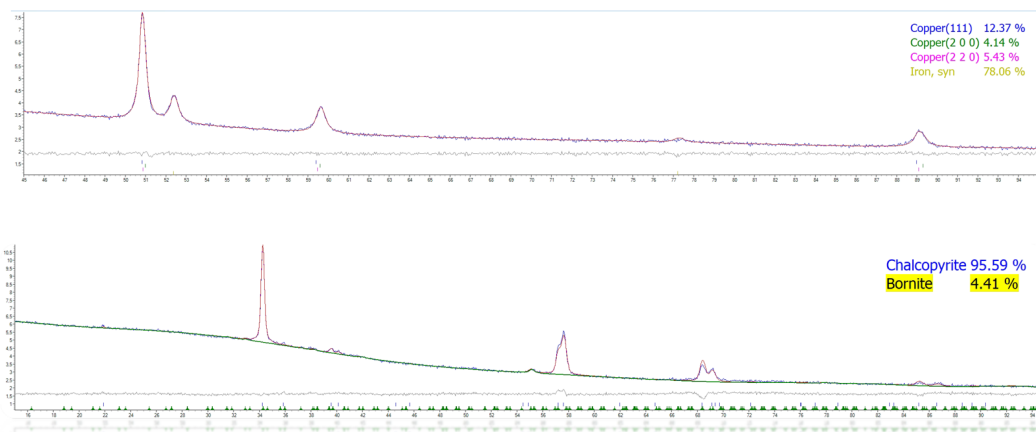


Figure C.8: Sample 13 (top) and its sulfurization using configuration 2.

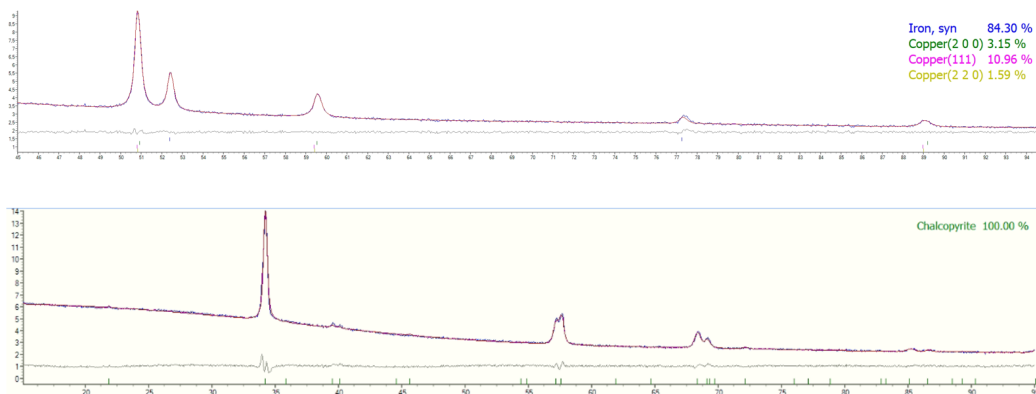


Figure C.9: Sample 14 (top) and its sulfurization using configuration 2 (bottom).

APPENDIX C. SUPPLEMENTARY INFORMATION: OPTIMIZING CUFES₂
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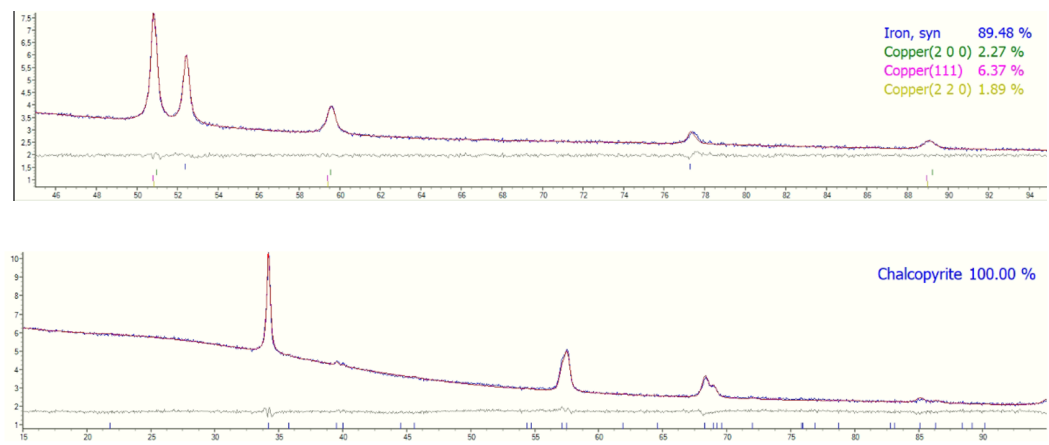


Figure C.10: Sample 15 (top) and its sulfurization using configuration 2 (bottom).

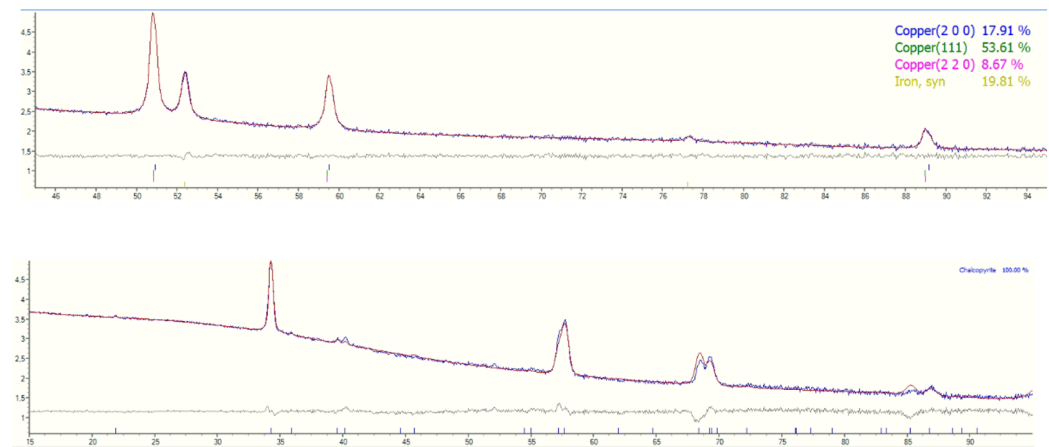


Figure C.11: Sample 16 (top) and its sulfurization using configuration 2.

C.4. SUPPLEMENTARY NOTE 4: RIETVELD REFINEMENT

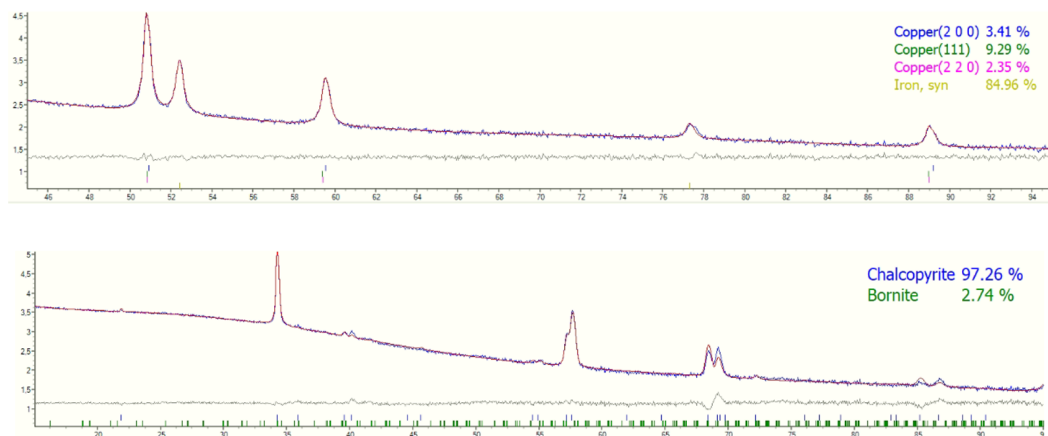


Figure C.12: Sample 17 (top) and its sulfurization (bottom).

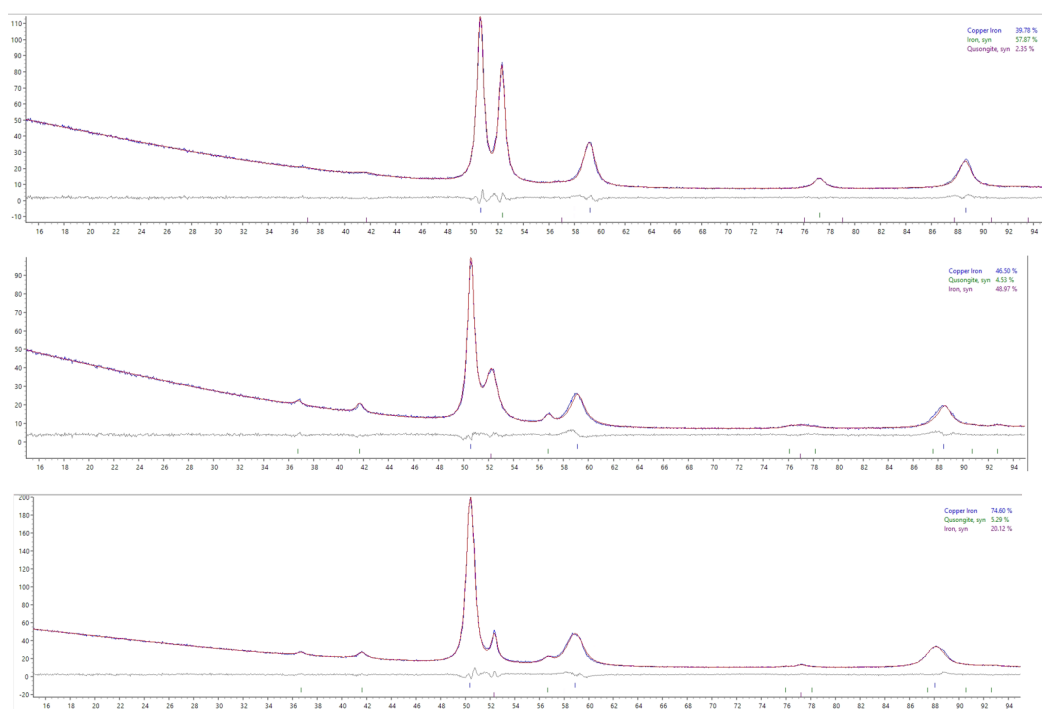


Figure C.13: FeCu-01, Fe_{1.76}Cu-02, and FeCu-03.

C.5 Supplementary Note 5: Visual inspection

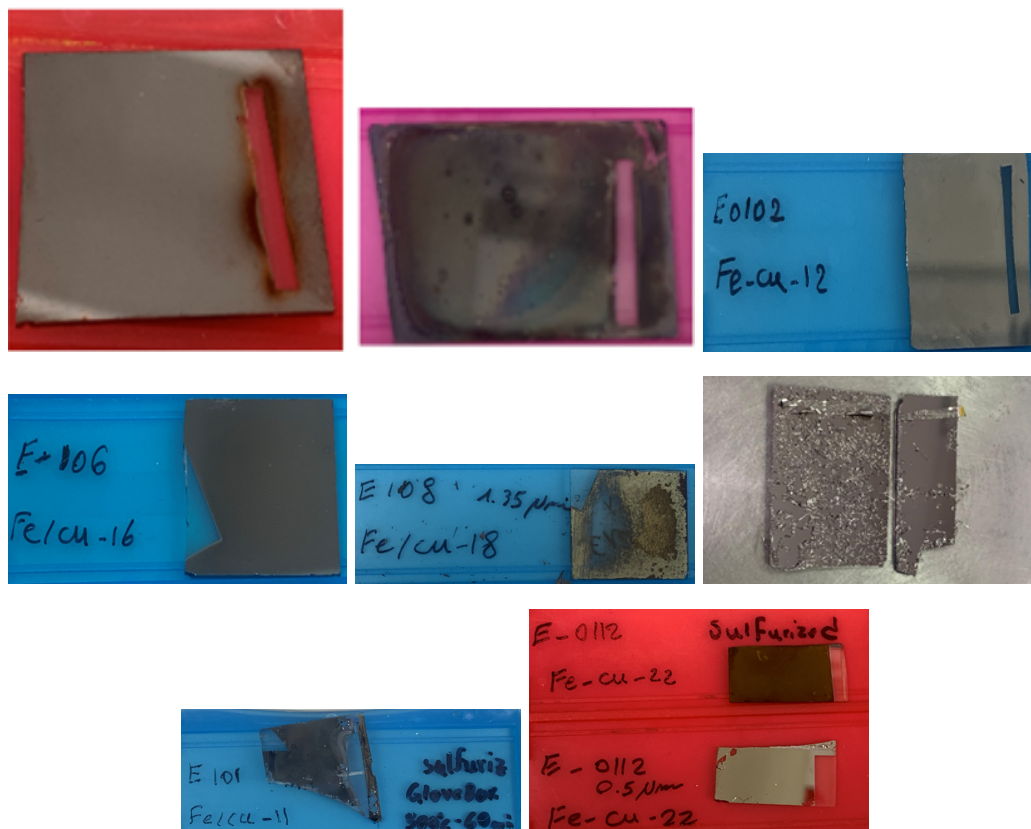


Figure C.14: Visual inspection of samples 3 to 11.

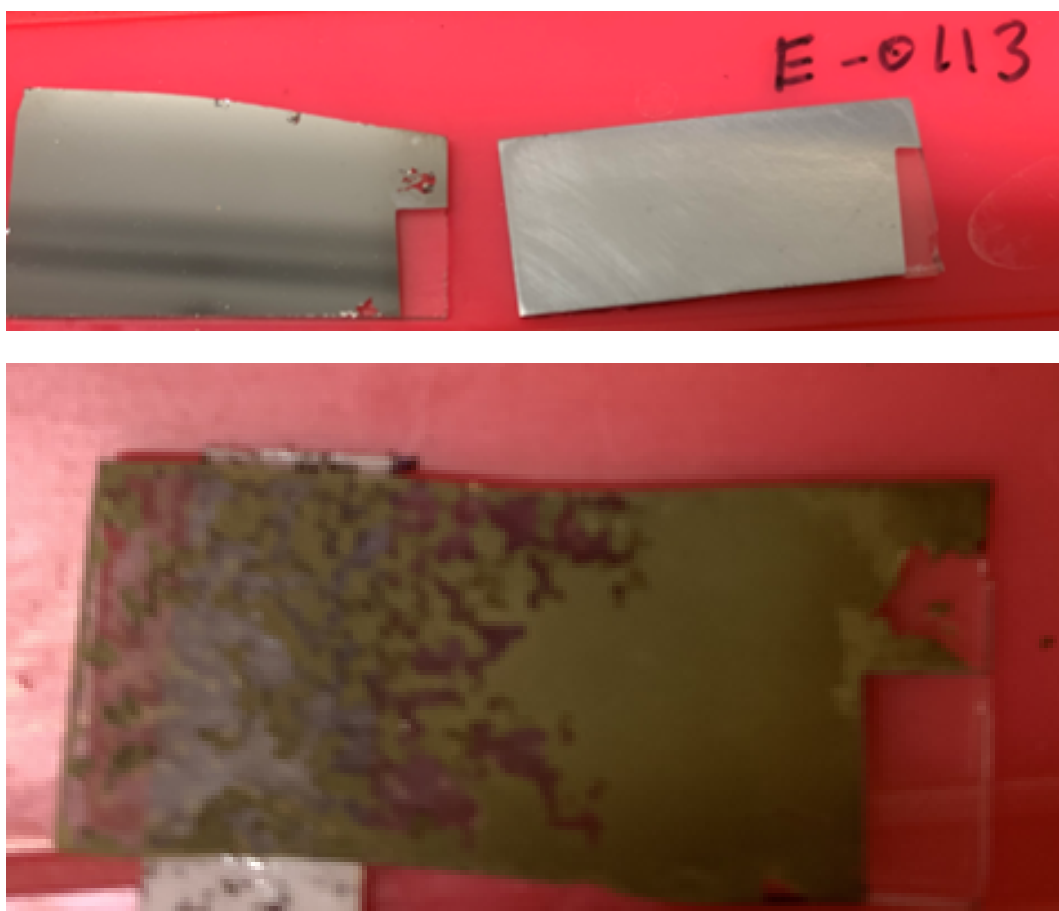


Figure C.15: Sample 12 (left-top) and 13 (right-top). Sulfurization of sample 12 (bottom).

APPENDIX C. SUPPLEMENTARY INFORMATION: OPTIMIZING CuFeS_2
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SULFURIZATION APPLIED FOR THERMOELECTRIC GENERATION

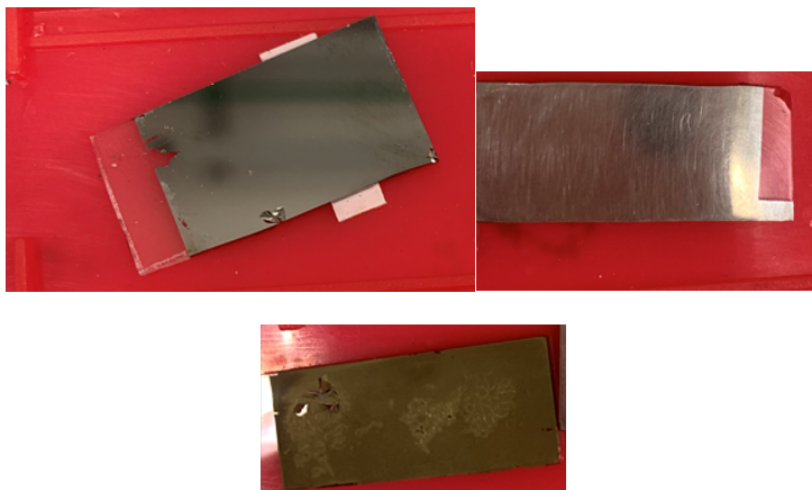


Figure C.16: Sample 14 (left-top) and 15 (right-top) and the sulfurization of sample 15 (bottom).

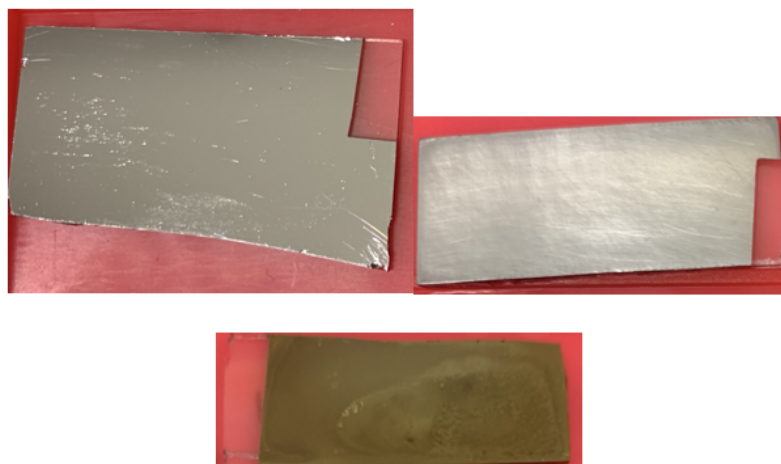


Figure C.17: Sample 16 (left-top) and 17 (right-top) and the sample 16 sulfurized (bottom).

C.6 Supplementary Note 6: Comparison of Different Ball-Milled Powders

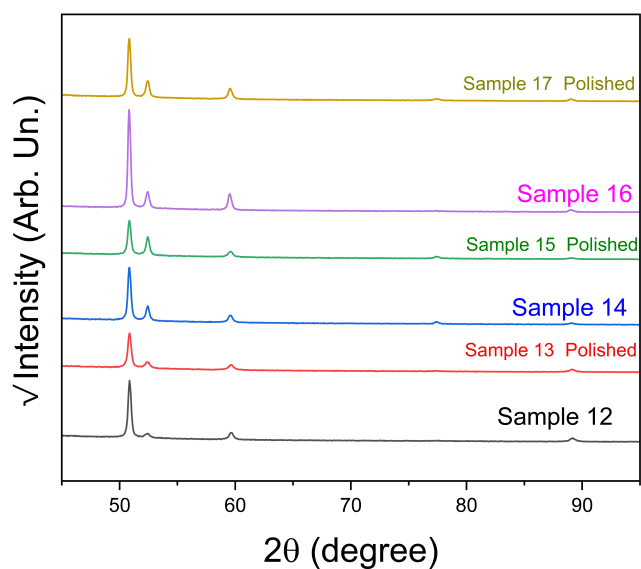


Figure C.18: Diffractograms of the samples 12 to 17.

C.7 Supplementary Note 7: Pristine film

APPENDIX C. SUPPLEMENTARY INFORMATION: OPTIMIZING CUFES₂ CHALCOPYRITE THIN FILM SYNTHESIS: A COMPREHENSIVE THREE-STEP APPROACH USING BALL-MILLING, THERMAL EVAPORATION, AND SULFURIZATION APPLIED FOR THERMOELECTRIC GENERATION

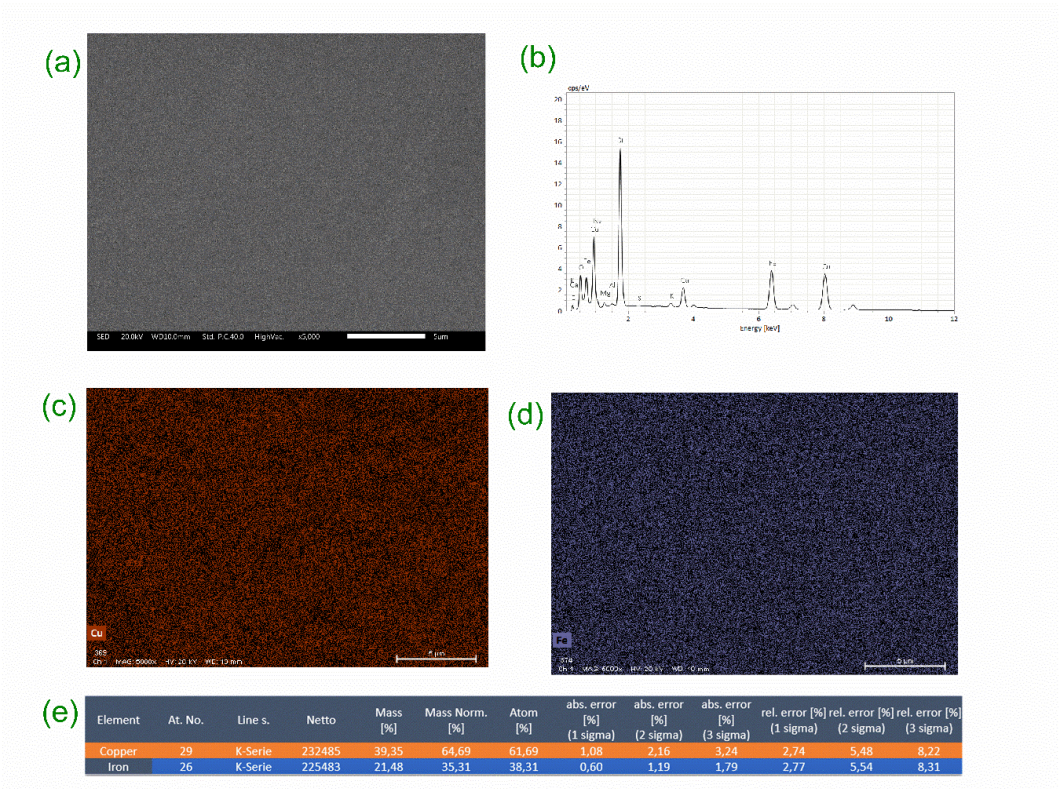


Figure C.19: (a) SEM micrography with a magnification of 5000 times. (b) EDX performed in the same region of (a). (c) Chemical mapping of Cu and (d) chemical mapping of Fe using the same region of (a). (e) EDX element quantification analysis.

C.8 Supplementary Note 8: The morphological pattern of CFS

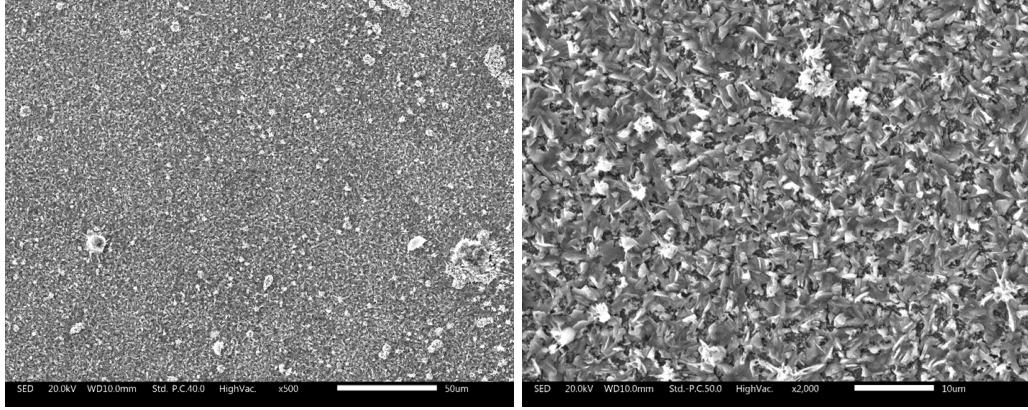


Figure C.20: Micrographics of sample 18 obtained by SEM. (a) magnification of 500 times, (b) magnification of 2000 times.

Appendix D

Supplementary Information: A CuFeS₂/Cu₂S/FeS₂ composite to increase the performance of thin-film thermoelectric generators based on sustainable materials

D.1 Supplementary Note 1: Quantitative Phase Analysis

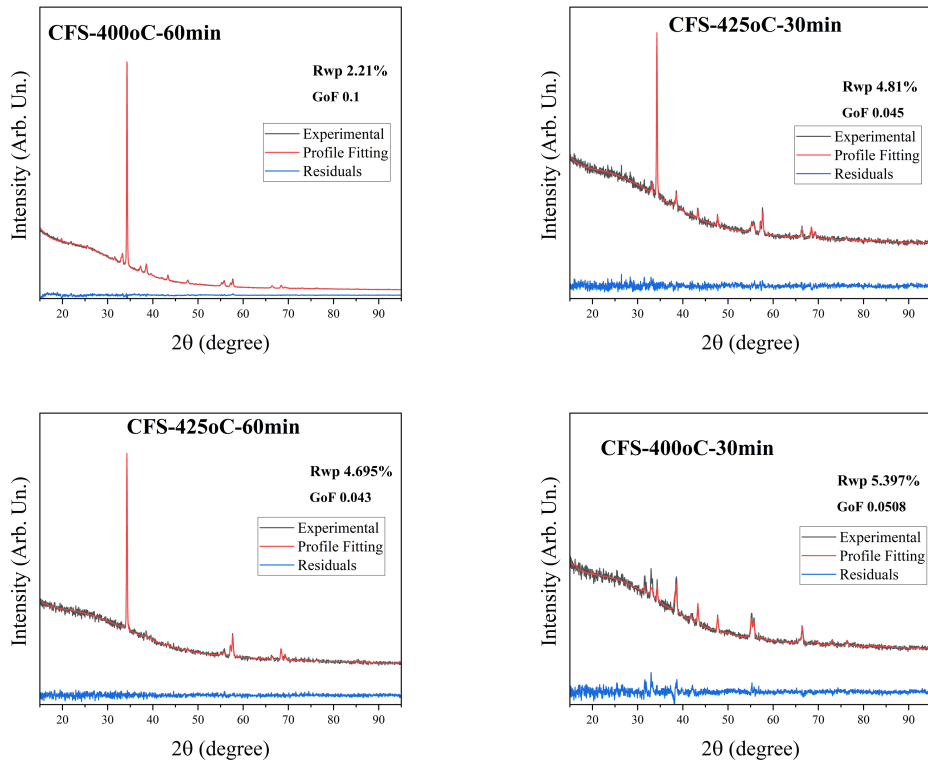


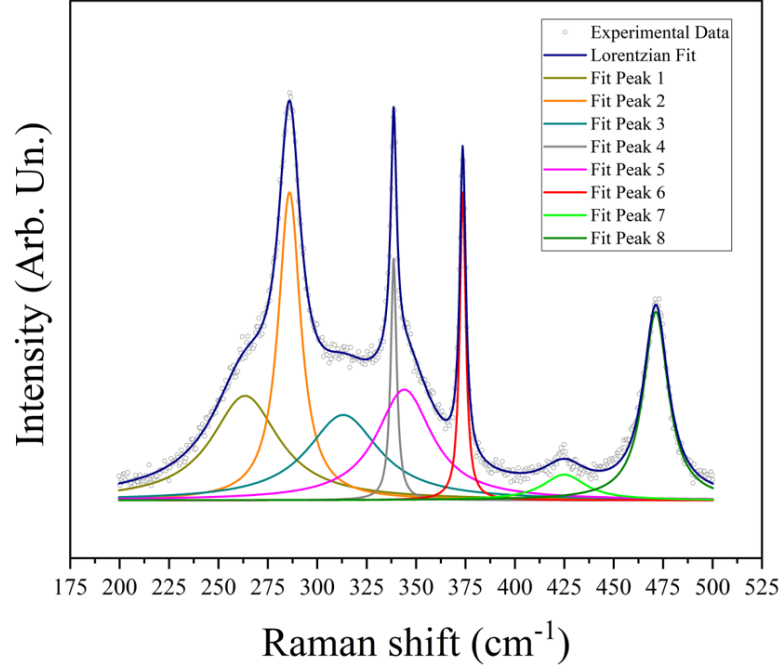
Figure D.1: XRD profile fitting for all the samples. Black lines correspond to the experimental data, red lines to the profile fitting, and blue lines to the residuals. The agreement factors for each sample are given in the plots.

APPENDIX D. SUPPLEMENTARY INFORMATION: A CUFES₂/CU₂S/FES₂
COMPOSITE TO INCREASE THE PERFORMANCE OF THIN-FILM
THERMOELECTRIC GENERATORS BASED ON SUSTAINABLE MATERIALS

Table D.1: Phase proportion, structural, and microstructural parameters obtained via profile fitting of the XRD patterns.

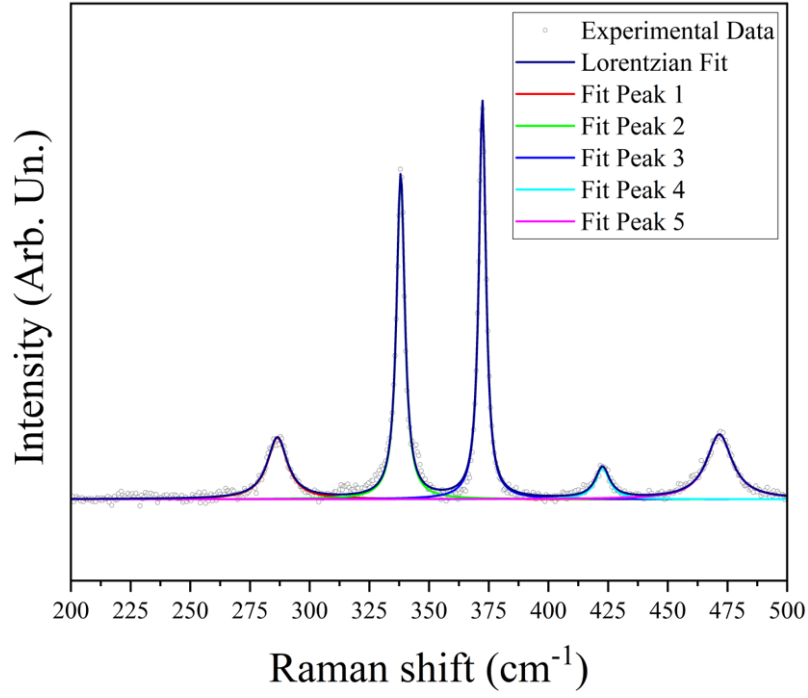
Sample ID	Phase Weight Proportion (%)	Lattice Parameters (Å)	Crystallite Size / L_{vol} (nm)
CFS-400° C-30min	CuFeS ₂ : 9 (PDF # 04-002-0241)	CuFeS ₂ : a : 5.274(6) c : 10.40(2)	CuFeS ₂ : 75 FeS ₂ : 68 Cu ₅ FeS ₄ : 21
	FeS ₂ : 71 (PDF # 04-003-1989)	FeS ₂ : a : 5.4160(5)	
	Cu ₅ FeS ₄ : 20 (PDF # 04-010-1602)	Cu ₅ FeS ₄ : a : 3.853(1) c : 18.95(1)	
CFS-425° C-30min	CuFeS ₂ : 44	CuFeS ₂ : a : 5.2833(6) c : 10.41(5)	CuFeS ₂ : 66 FeS ₂ : 204 Cu ₂ S: > 1000
	FeS ₂ : 36	FeS ₂ : a : 5.4187(8)	
	Cu ₂ S: 20 (PDF # 04-015-2234)	Cu ₂ S: a : 5.441(3)	
CFS-425° C-60min	CuFeS ₂ : 72	CuFeS ₂ : a : 5.2885(7) c : 10.418(2)	CuFeS ₂ : 61 FeS ₂ : 40 Cu ₂ S: 20
	FeS ₂ : 14	FeS ₂ : a : 5.420(2)	
	Cu ₂ S: 14	Cu ₂ S: a : 5.432(5)	
CFS-400° C-60min	CuFeS ₂ : 32	CuFeS ₂ : a : 5.2874(6) c : 10.420(2)	CuFeS ₂ : 59 FeS ₂ : 55 Cu ₅ FeS ₄ : 25
	FeS ₂ : 46	FeS ₂ : a : 5.4176(3)	
	Cu ₅ FeS ₄ : 22	Cu ₅ FeS ₄ : a : 3.861(4) c : 18.90(4)	
CFS-500° C-60min	CuFeS ₂ : 95	CuFeS ₂ : a : 5.2899(1) c : 10.4262(5)	CuFeS ₂ : 58.9(3) Cu ₂ S: 19.6(7)
	Cu ₂ S: 5%	Cu ₂ S: a : 5.4670(8)	

D.2 Supplementary Note 2: Raman Analysis



Model	Lorentz							
Equation	$y = y_0 + (2 \cdot A / \pi) \cdot (w / (4 \cdot ((x - x_c)^2 + w^2)))$							
Plot	Peak1(Subtracted_Da	Peak2(Subtracted_Da	Peak3(Subtracted_Da	Peak4(Subtracted_Da	Peak5(Subtracted_Da	Peak6(Subtracted_Da	Peak7(Subtracted_Da	Peak8(Subtracted_Da
y0	-27.34074 ± 1.84992	-27.34074 ± 1.84992	-27.34074 ± 1.84992	-27.34074 ± 1.84992	-27.34074 ± 1.84992	-27.34074 ± 1.84992	-27.34074 ± 1.84992	-27.34074 ± 1.84992
xc	263.51465 ± 0.59464	285.95605 ± 0.06657	313.14342 ± 1.1437	338.6591 ± 0.03232	344.03923 ± 0.90646	373.62709 ± 0.0246	424.94564 ± 0.81572	471.30281 ± 0.08253
w	41.42319 ± 1.83323	13.69932 ± 0.34272	44.33217 ± 6.40777	3.5615 ± 0.14883	34.16991 ± 2.12528	3.65765 ± 0.08018	26.58826 ± 3.15569	15.18357 ± 0.30343
A	8529.42722 ± 528.76	8320.29618 ± 302.69	7457.38716 ± 1567.5	1696.67529 ± 81.140	7457.64022 ± 1029.6	2223.07082 ± 39.765	1345.47743 ± 164.64	5644.20917 ± 108.27
Reduced Chi-	70.98496							
R-Square (C	0.99417							
Adj. R-Squar	0.9939							

Figure D.2: Raman analysis of the CFS-400°C-30min sample.



Model	Lorentz				
Equation	$y = y_0 + (2 \cdot A / \pi) \cdot (w / (4 \cdot (x - x_c)^2 + w^2))$				
Plot	Peak1(Subtracted_Data Y1)	Peak2(Subtracted_Data Y1)	Peak3(Subtracted_Data Y1)	Peak4(Subtracted_Data Y1)	Peak5(Subtracted_Data Y1)
y0	-3.10399 ± 1.01686	-3.10399 ± 1.01686	-3.10399 ± 1.01686	-3.10399 ± 1.01686	-3.10399 ± 1.01686
xc	286.5018 ± 0.15431	338.13151 ± 0.01834	372.38044 ± 0.01397	422.66383 ± 0.2543	471.62202 ± 0.1619
w	10.26082 ± 0.47559	4.10105 ± 0.05367	3.59873 ± 0.04077	7.31887 ± 0.75961	13.02411 ± 0.49797
A	3000.81807 ± 107.31439	6342.76353 ± 60.85556	6815.84888 ± 56.41578	1079.95173 ± 84.07524	4004.96009 ± 119.09592
Reduced Chi-Sqr	227.32643				
R-Square (COD)	0.9902				
Adj. R-Square	0.98992				

Figure D.3: Raman analysis of the CFS-400°C-60min sample.

D.3 Supplementary Note 3: V_{OC} for different runs

The Seebeck coefficient had been calculated using the following rule:

$$S = \frac{V_{OC}}{N\Delta T} \quad (D.1)$$

For each absolute temperature, in Kelvin units. N is the number of legs in the generator, equal to 2.

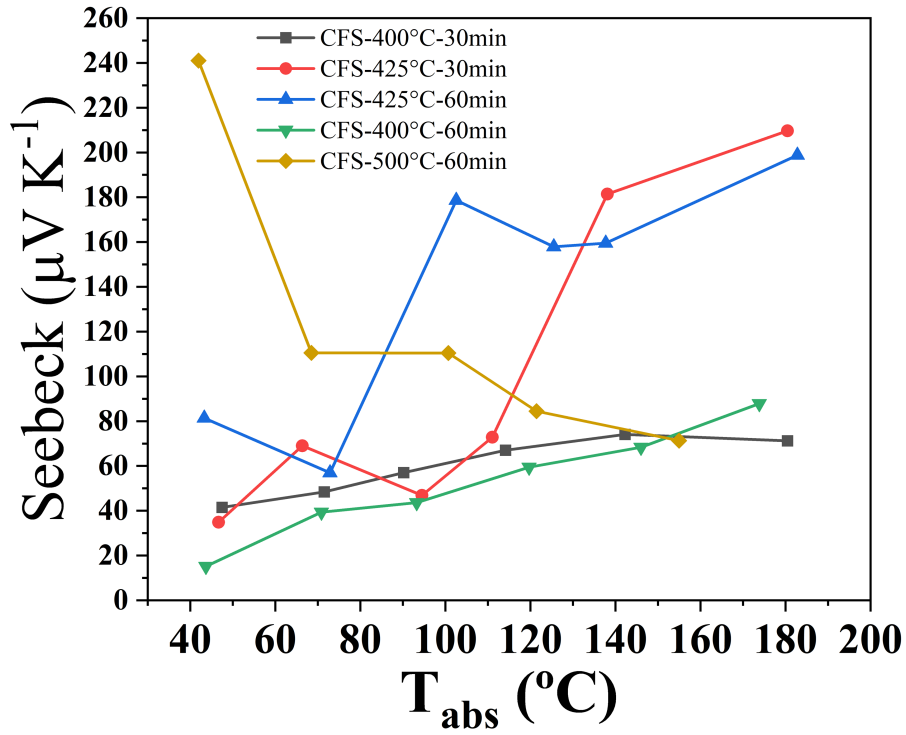


Figure D.4: Seebeck coefficients estimated by the V_{OC} and the gradient of temperature for all the samples.

Video 1 of the boosting for the CFS-02-300°C: https://drive.google.com/open?id=1WLBsmoorA5jhUYt_IhnHh3gDok0q7UK1&usp=drive_fs

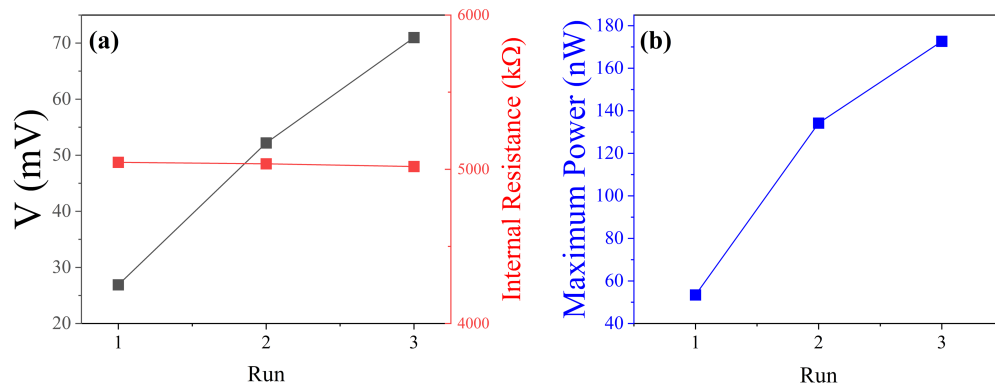


Figure D.5: (a) V_{OC} and internal resistance of the CFS-425°C-30min sample vs run number. (b) Maximum power output for different runs.

D.4 Supplementary Note 4: XRD measurements after V_{OC} estimation

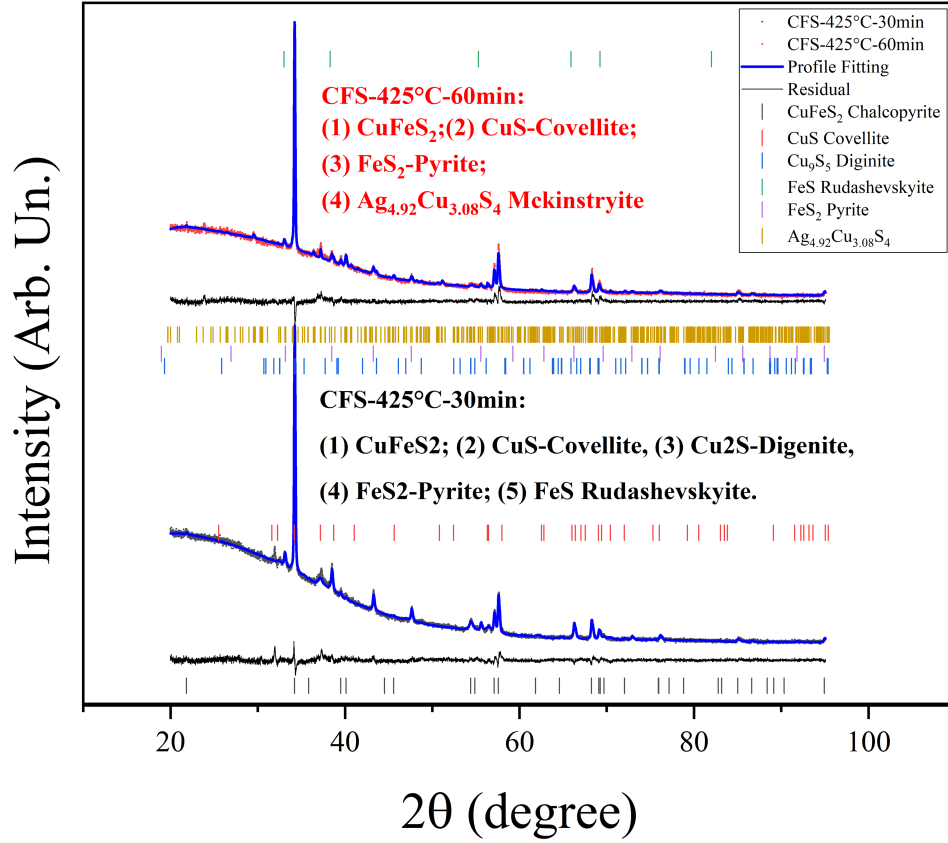


Figure D.6: XRD measurements taken after V_{OC} characterization. The black dots correspond to the CFS-425°C-30min samples and the red dots to the CFS-425°C-60min diffraction pattern. In blue is represented the profile fitting of each measurement and in black the residuals, placed below each measurement. The markers represent the Bragg position of each phase given in the legend. The phases present for the CFS-425°C-60min and CFS-425°C-30min are written in red and black, respectively.

D.5 Supplementary Note 5: Less performing power curves

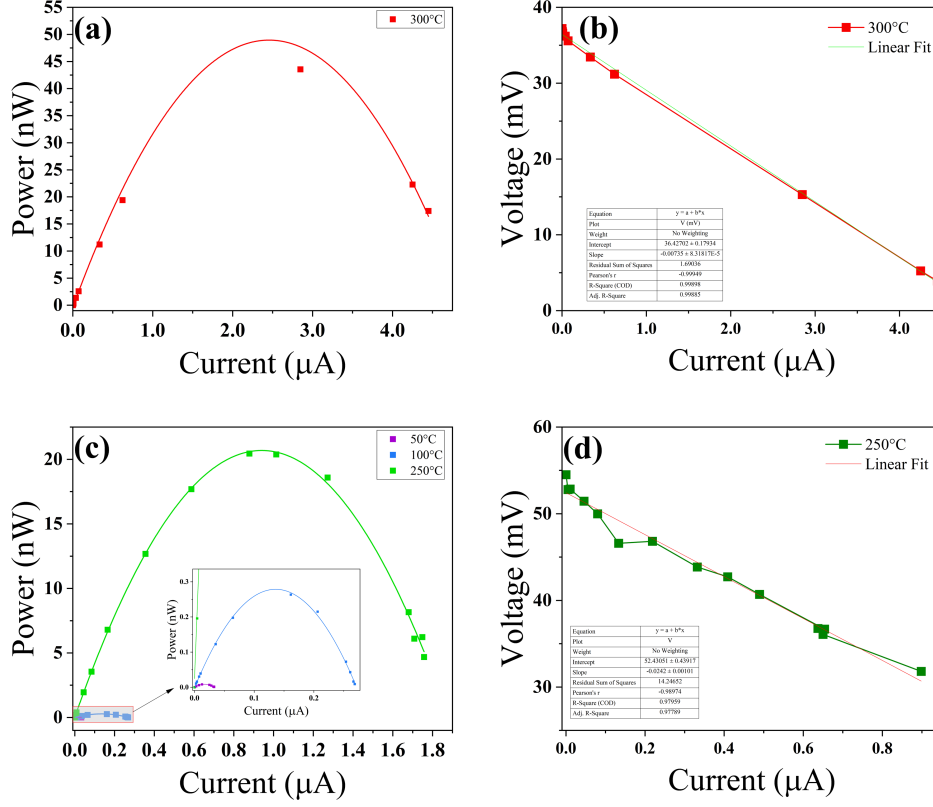


Figure D.7: P-I curves for (a) CFS-400°C-60min and (c) CFS-400°C-30min. I-V curves for (b) CFS-400°C-60min and (d) CFS-400°C-30min.

Appendix E

PhD production

E.1 Publications

E.1.1 Journal Articles Relevant to this Thesis

1. **Malagutti, M. A.**, Isotta, E., Bette, S., Nautiyal, H., Mukherjee, B., Chiappini, A., Smet, J., Maduro de Campos, C. E., Dinnebier, R., Ataollahi, N., Di Maggio, R., Scardi, P.
Investigating the Cubic-to-Tetragonal Phase Transition of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ Solid Solutions.
Crystal Growth & Design **25** (2025), 8133–8146.
DOI: <https://doi.org/10.1021/acs.cgd.5c00935>
2. **Malagutti, M. A.**, Isotta, E., Nautiyal, H., Anselmi-Tamburini, U., Chiappini, A., Bette, S., Dinnebier, R., Ataollahi, N., Scardi, P.
Role of microstructure in the lattice thermal conductivity and thermoelectric performance of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ alloys.
Journal of Materials Chemistry A, 2026.
Submitted.
3. **Malagutti, M. A.**, Lohani, K., D’Incau, M., Nautiyal, H., Ataollahi, N., Scardi, P.
Optimizing CuFeS_2 Chalcopyrite Thin Film Synthesis: A Comprehensive Three-Step Approach Using Ball-Milling, Thermal Evaporation, and Sulfurization Applied for Thermoelectric Generation.
Applied Sciences **13** (2023), 10172.
DOI: <https://doi.org/10.3390/app131810172>
4. **Malagutti, M. A.**, Lohani, K., Caño Prades, I., Navarro-Güell, A., Bernard, T., Chiappini, A., Saucedo, E., Ataollahi, N., Scardi, P.
 $\text{CuFeS}_2/\text{Cu}_2\text{S}/\text{FeS}_2$ Composite to Increase the Performance of Thin-Film Thermoelectric Generators Based on Sustainable Materials.
ACS Applied Electronic Materials **7** (2025), 21–32.
DOI: <https://doi.org/10.1021/acsaelm.4c01248>

E.1.2 Other Journal Articles as Main Author

1. Scardi, P., **Malagutti, M. A.**
Thermal Diffuse Scattering from Nanocrystalline Systems.
Crystal Growth & Design **24** (2024), 4380–4392.
DOI: <https://doi.org/10.1021/acs.cgd.3c01507>
2. Bernard, T., **Malagutti, M. A.**, Lohani, K., D’Incau, M., Ataollahi, N., Scardi, P.
Environmentally Friendly p-Type CTS-Based Thin-Film Thermoelectric Generator.
Journal of Materials Science **59** (2024), 15491–15503.
DOI: <https://doi.org/10.1007/s10853-024-10104-w>
3. **Malagutti, M. A.**, Mukherjee, B., Nautiyal, H., Bette, S. , Ataollahi, N., Dinnebier R. and Scardi, P.
Thermal diffuse scattering analysis of Ag₂O binary system via X-ray powder diffraction.
Journal of Applied Crystallography **58** (2025), 18–30. DOI: <https://doi.org/10.1107/S1600576724010756>
4. P. Scardi and **M. A. Malagutti**
Artificial intelligence in action: building simulation and analysis tools for powder diffraction.
Acta Crystallographica A **81** (2025), 401–404. DOI: <https://doi.org/10.1107/S2053273325007508>
5. P. Scardi, M. D’Incau, **M. A. Malagutti**, M. W. Terban, B. Hinrichsen and A. N. Fitch
A reference material for X-ray diffraction line profile analysis.
Journal of Applied Crystallography **58** (2025), 1764–1777. DOI: <https://doi.org/10.1107/S1600576725006946>
6. **Malagutti, M. A.**, Enriquez Camps, R., Anselmi-Tamburini, U., Dinnebier, R., Weidenthaler, C., Scardi, P., Maduro de Campos, C. E.
Effect of Oxidation on the Mechanochemical synthesis of bismuth telluride nanophases.
ACS Applied Energy Materials.
DOI: <https://doi.org/10.1021/acsaem.6c00972>
7. **Malagutti, M. A.**, D’Incau, M., Scardi, P.
DISCO: a general software tool for dislocation contrast factor calculations in diffraction analysis.
Journal of Applied Crystallography.
Submitted.

E.1.3 Other Contributions (Co-Authorship)

1. Bernard, T., **Malagutti, M. A.**, D’Incau, M., Ataollahi, N., Scardi, P.
Sustainable sulphides for π -type planar thermoelectric generators.
MRS Advances (2025).
DOI: <https://doi.org/10.1557/s43581-025-00145-2>
2. Sheikholeslami, M., Ataollahi, N., Scardi, P., **Malagutti, M. A.**
Performance evaluation of a solar dish system with hybrid nanofluid cooling.

E.2. CONFERENCE AND WORKSHOP PARTICIPATION (2023–PRESENT)

- Solar Energy Materials and Solar Cells* (2025).
DOI: <https://doi.org/10.1016/j.solmat.2025.113508>
3. Neelalochana, V.D, Tomasino, E., **Malagutti, M. A.**, Mancini, I., Chiappini, A., Shadakshari, S., Terban, M. W., Hinrichsen, B., Scardi, P., Ataollahi, N.
Impact of functionalized titanium oxide on anion exchange membranes.
Electrochimica Acta **507** (2024), 145170.
DOI: <https://doi.org/10.1016/j.electacta.2024.145170>
 4. Mukherjee, B., Isotta, E., **Malagutti, M. A.**, Lohani, K., Rebuffi, L., Fanciulli, C., Scardi, P.
Thermoelectric performance in disordered $\text{Cu}_2\text{ZnSnSe}_4$ nanostructures.
Journal of Alloys and Compounds (2023), 167756.
DOI: <https://doi.org/10.1016/j.jallcom.2022.167756>
 5. Nautiyal, H., Lohani, K., Mukherjee, B., Isotta, E., **Malagutti, M. A.**, Ataollahi, N., Pallechi, I., Putti, M., Misture, S. T., Rebuffi, L., Scardi, P.
Mechanochemical Synthesis of Sustainable Ternary and Quaternary Nanostructured Cu_2SnS_3 , $\text{Cu}_2\text{ZnSnS}_4$, and $\text{Cu}_2\text{ZnSnSe}_4$ Chalcogenides for Thermoelectric Applications.
Nanomaterials **13** (2023), 366.
DOI: <https://doi.org/10.3390/nano13020366>
 6. Tarhouni, A., **Malagutti, M. A.**, Bernard, B., Ataollahi, N., Isotta, E., Chiappini, A., Dahman, H., El Mir, L., Scardi P.
Thermoelectric Generator based on kesterite ($\text{Cu}_2\text{ZnSnS}_4$) Synthesized via Sol-Gel Method.
Materials, **19(10)**, 1971, 2026.
DOI: <https://doi.org/10.3390/ma19101971>

E.2 Conference and Workshop Participation (2023–Present)

1. *GiTe2023*. Trento, Italy (2023).
Oral presentation: *Thermoelectric Performance in Disordered $\text{Cu}_2\text{ZnSnSe}_4$ Nanostructures Driven by Ultra-Low Thermal Conductivity.*
2. *13th European Kesterite+ Workshop*. Barcelona, Spain (2023).
Oral presentation: *Quaternary Cu–Zn–Sn(S/Se)-Based Thermoelectric Generators.*
3. *19th European Conference on Thermoelectrics (ECT 2023)*. Prague, Czech Republic (2023).
Oral presentation: *Sustainable n-type CuFeS_2 Thin-Film Thermoelectric Generators.*
4. *40th International and 20th European Conference on Thermoelectrics*. Krakow, Poland (2024).
Oral presentation: *CuFeS_2 In-Plane Thermoelectric Generators Produced by Ball Milling, Thermal Evaporation, and Sulfurization.*
5. *TOPAS Meeting 2024*. Padova, Italy (2024).
Oral presentation: *The Modified Williamson–Hall Approach in TOPAS.*

6. *18th European Powder Diffraction Conference (EPDIC)*. Padova, Italy (2024).
Oral presentation: *Understanding the Structure and Stacking Faults of $\text{Cu}_2\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ Systems for Thermoelectric Applications.*
7. *21st European Conference on Thermoelectrics*. Nancy, France (2025).
Oral presentation: *Structural and Stacking Fault Modelling of Low-Density $\text{Cu}_2\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ Systems for Thermoelectric Applications.*
8. *28th Results and Review Workshop of the HLRS*. Stuttgart, Germany (2025).
Oral presentation: *Investigating the Cubic-to-Tetragonal Phase Transition of $\text{Cu}_{2+y}\text{Zn}_{1-y}\text{SnS}_x\text{Se}_{4-x}$ Alloys.*
9. *Invited talk at Max Plank Institute*. Stuttgart, Germany (2025).
Oral presentation: *Thermal diffuse scattering from nanocrystalline systems.*

E.3 Journal Covers

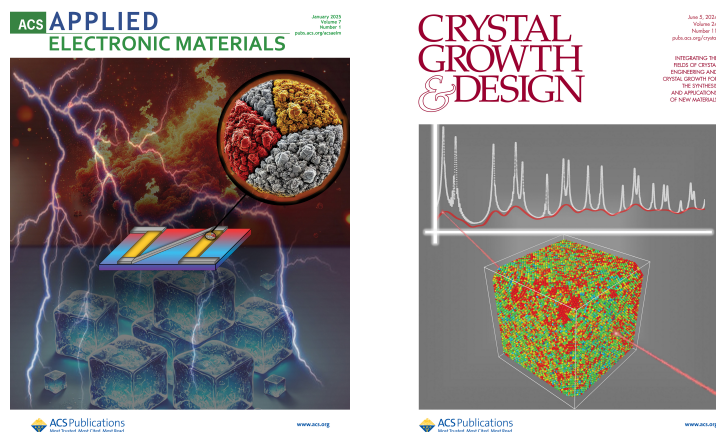


Figure E.1: Journal covers featuring publications included in this thesis.

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Thermoelectric materials enable the direct conversion of heat into electricity, offering a promising solution for energy sustainability. However, current technologies rely on Te-based compounds, which are scarce and toxic. This thesis investigates Cu-based materials as environmentally friendly alternatives, focusing on the relationship between structure, microstructure, and transport properties. Kesterite compounds (CZTSSe) exhibit strong chemical disorder and defect-rich microstructures that enhance phonon scattering and reduce thermal conductivity, while also improving electronic transport through band convergence effects. For thin-film applications, chalcopyrite materials such as CuFeS₂ show superior electronic performance, enabling high power outputs when optimized through controlled microstructure. These results provide new strategies for designing efficient and sustainable thermoelectric materials for future energy applications.

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