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Solution-Based Bottom-Up Processing of Chalcogenide Thermoelectric Nanomaterials

Mengyao Li



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Tesi doctoral

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Solution-Based Bottom-Up Processing of Chalcogenide Thermoelectric Nanomaterials

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List of publications

My PhD research work have been disseminated in three manuscripts, which have already been published or accepted in peer-reviewed journals. A full copy of each of the publications can be found in the Annex part. The following is the list of publications included in this thesis:

1. **M. Li**, Y. Liu, Y. Zhang, Y. Zuo, J. Li, K.H. Lim, D. Cadavid, K.M. Ng, A. Cabot. Crystallographically textured SnSe nanomaterials produced from the liquid phase sintering of nanocrystals. *Dalton Transactions*, 2019, 48, 3641-3647.
2. **M. Li**, Y. Liu, Y. Zhang, X. Han, T. Zhang, Y. Zuo, C. Xie, K. Xiao, J. Arbiol, J. Llorca, M. Ibáñez, J. Liu, A. Cabot. Effect of the Annealing Atmosphere on Crystal Phase and Thermoelectric Properties of Copper Sulfide. *ACS nano*, 2021, 15, 3, 4967-4978.
3. **M. Li**, Y. Liu, Y. Zhang, T. Zhang, Y. Zuo, K. Xiao, J. Arbiol, J. Llorca, A. Cabot. Enhanced Thermoelectric Performance of N-Type Bi₂Se₃ Nanosheets through doping with Sn. *Nanomaterials* 2021, 11(7), 1827.

Authors' contributions

The work within this thesis was carried out at Advanced Material Research Department in the Catalonia Institute for Energy Research. Mengyao Li, as PhD student, contributed to the experimental work, data analysis and manuscript writing for all the publications presented in this thesis. The contributions of co-authors for each article are shown below this paragraph. The impact factor in 2021 of the journals where the manuscripts were published is provided. All of the publications belong to the 1st quartile according to the Science Citation Index. None of these papers has been previously presented in any other PhD thesis. In all the publications, Andreu Cabot conceived and guided the projects, participated in the experiment design and manuscript writing.

Chapter 2:

M. Li, Y. Liu, Y. Zhang, Y. Zuo, J. Li, K.H. Lim, D. Cadavid, K.M. Ng, A. Cabot. Crystallographically textured SnSe nanomaterials produced from the liquid phase sintering of nanocrystals. *Dalton Transactions*, 2019, 48, 3641-3647

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In this work, M. Li designed the experiments, produced the nanomaterials and wrote the first draft of the manuscript. Y. Liu, D. Cadavid and Y. Zhang participated in experiment design. Y. Zuo, J. Li, K.H. Lim, and K.M. Ng participated in data analysis. A. Cabot conceived and guided the project and supervised the work. The manuscript was corrected and improved by all authors.

Chapter 3:

M. Li, Y. Liu, Y. Zhang, X. Han, T. Zhang, Y. Zuo, C. Xie, K. Xiao, J. Arbiol, J. Llorca, M. Ibáñez, J. Liu, A. Cabot. Effect of the Annealing Atmosphere on Crystal Phase and Thermoelectric Properties of Copper Sulfide. *ACS nano*, 2021, 15, 3, 4967-4978.

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Chapter 4:

M. Li, Y. Liu, Y. Zhang, T. Zhang, Y. Zuo, K. Xiao, J. Arbiol, J. Llorca, A. Cabot. Enhanced Thermoelectric Performance of N-Type Bi_2Se_3 Nanosheets through doping with Sn. *Nanomaterials* **2021**, 11(7), 1827.

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Chapter 5:

M. Li, Y. Liu, Y. Zhang, X. Han, T. Zhang, K. Xiao, D. Yang, J. Arbiol, J. Llorca, A. Cabot. Room Temperature Synthesis of Lead Sulfide Nanoparticles for Thermoelectric Applications. (submitted).

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Prof. Andreu Cabot

Certify the information provided above is true.

Barcelona, 31th of August 2021

Preface

The chapters included in this PhD thesis cover the work developed by the PhD candidate Mengyao Li at the Catalonia Institute for Energy Research (IREC) in Sant Adrià de Besòs, Barcelona, in the period 2017-2021, supported by China Scholarship Council (No. 201706890005). The thesis is particularly focused on bottom-up engineering of high-performance thermoelectric (TE) nanomaterials with fine tuned properties.

This thesis consists of five chapters. The first chapter mainly introduces the basic concepts of thermoelectricity, and the current development status and challenges in the TE field. Chapters 2 to 5 mainly introduce the experimental part. Within the general frame of optimizing TE materials through bottom-up engineering, the work presented in this thesis aims at solving main challenges in this field: 1) Production of crystallographically textured nanomaterials. 2) Adjust the crystalline phase by annealing atmosphere to optimize electrical conductivity and thermal conductivity. 3) Increase the carrier concentration of TE nanomaterials by doping metal particles. 4) Increase the nanomaterials Seebeck coefficient by increasing bandgap with doping. In chapter two, p-type polycrystalline SnSe materials with marked crystallographic texture were produced from blends of SnSe nanocrystals (NCs) and Te nanorods (NRs) through hot-pressing them at a temperature above the Te melting point. The presence of Te promoted the material crystallization in the form of a laminar structure with the a-axis along the pressure direction. SnSe NCs consolidated in the presence of Te showed higher electrical conductivities and lower Seebeck coefficients and thermal conductivities than pure SnSe. In chapter three, I present a synthetic protocol for the potential large scale production of covellite CuS nanoparticles (NPs) at ambient temperature and atmosphere. The annealing atmosphere, temperature, and time allow adjustment of the density of copper vacancies and thus tuning of the charge carrier concentration and material transport properties. In chapter four, I present the Bi₂Se₃ nanosheets (NSs) with improve TE properties by doped with Sn. In chapter five, I present a versatile, scalable, room temperature and surfactant-free route for the synthesis of PbS NPs in aqueous solution, and I further characterize the TE properties of the obtained n-type PbS and demonstrate that the incorporation of Cu can improve the material performance.

Summary of results

TE devices are able to directly convert ubiquitous temperature gradients into electricity, to actively remove heat from local sources or temperature-sensitive devices, and to precisely control temperature without moving parts or working gases. They have countless potential application, but their high manufacturing and material costs hamper their cost-effectiveness and limit their widespread implementation. To overcome these drawbacks, TE devices must be manufactured employing high throughput technologies and using materials based on low cost and abundant elements.

Traditionally, a popular method to prepare nanostructured TE materials is to make use of a top-down approach, such as ball milling or exfoliation of materials obtained from solid state reactions at high temperature. However, most of these processes are energy consuming, complicated process or use harsh conditions, which limit their widespread application. Aqueous synthesis has received widespread attention due to its low environmental impact, low energy consumption, potential surfactant-free and high yield characteristics. This thesis focuses on the development of scalable and low consumption methods for the production of TE nanomaterials with optimized performance. In these directions, the general goals of this thesis is to develop cost-effective TE devices with improved TE conversion efficiency and low production cost. The main research objectives are: a) Exploring earth abundant, low-cost and less toxic materials with high TE performance; b) Developing a simple, scalable and cost-effective methodologies to produce TE materials and modules; c) Optimize the power factor (PF) and figure of merit (ZT) through optimized either via doping or defect engineering. d) Reduce the lattice thermal conductivity through the introduction of phonon scattering sources such as point defects, dislocations and interfaces.

The thesis is divided into 5 chapters. Chapter 1 introduces the research status and development prospects of TE materials. Chapter 2 reports p-type polycrystalline SnSe materials with marked crystallographic texture were produced from blends of SnSe NCs and Te NRs through hot-pressing them at a temperature above the Te melting point. The presence of Te promoted the material crystallization in the form of a laminar structure with the a-axis along the pressure direction. Part of the Te used for the liquid phase sintering process was found within the SnSe lattice and part in the form of element Te within the consolidated materials. The TE properties of the produced nanomaterials were measured in two perpendicular directions, along and normal to the pressure axis. SnSe NCs consolidated in the presence of Te showed higher

electrical conductivities and lower Seebeck coefficients and thermal conductivities than pure SnSe. The TE figures of merit up to $ZT \sim 1.4$ at 790 K were measured from the SnSe NCs consolidated in the presence of Te and measured along the pressing direction. Somehow surprisingly, lower ZT values were obtained in the direction normal to the pressure axis. The results in Chapter 2 were published in *Dalton Transaction* in 2019.

Chapter 3 presents a synthetic protocol for large scale production of covellite CuS NPs at ambient temperature and atmosphere, and using water as a solvent. The crystal phase and stoichiometry of the particles are afterward tuned through an annealing process at a moderate temperature under inert or reducing atmosphere. While annealing under argon results in Cu_{1.8}S nanopowder with a rhombohedral crystal phase, annealing in an atmosphere containing hydrogen leads to tetragonal Cu_{1.96}S. The annealing atmosphere, temperature, and time allow adjustment of the density of copper vacancies and thus tuning of the charge carrier concentration and materials transport properties. In this direction, the material annealed under Ar is characterized by higher electrical conductivities but lower Seebeck coefficients than the material annealed in the presence of hydrogen. By optimizing the charge carrier concentration through the annealing time, Cu_{2-x}S with record figures of merit in the middle temperature range, up to 1.41 at 710 K, is obtained. We finally demonstrate that this strategy, based on a low-cost and scalable solution synthesis process, is also suitable for the production of high performance Cu_{2-x}S layers using high throughput and cost-effective printing technologies. The results were published in *ACS nano* in 2021.

The Chapter 4 report a large scale method to synthesize N-type Bi₂Se₃ NSs. Narrow gap Bi₂Se₃ is a well-known three dimensional topological insulator with non-trivial surface states. It is also a Te-free alternative to Bi₂Te₃ as room temperature TE material. Possessing low TE properties due to its single degenerated conduction band. Here, we report a large scale method to synthesize Bi₂Se₃ NSs which have screw-dislocation-driven growth mechanism. And further doped with Sn which present notable TE performance. Incorporating Sn in Bi₂Se₃ increases the Seebeck coefficient and thus improves the power factor to 0.65 mWm⁻¹K⁻². The low thermal conductivity, down to 0.91 Wm⁻¹K⁻¹, of Bi_{1.93}Sn_{0.07}Se₃ results in ZT values well above higher than those of pure Bi₂Se₃.

The Chapter 5 report that semiconductor-metal composites are produced by just blending NPs of a sulfide semiconductor obtained in aqueous solution and at room temperature, with a metallic Cu powder. The obtained blend is annealed in a reducing atmosphere and afterwards

consolidated into dense polycrystalline pellets by means of spark plasma sintering (SPS). During the annealing process, the presence of metallic copper activates a partial reduction of the PbS, resulting in the formation of PbS-Pb-Cu_xS composites. The presence of metallic lead in the final composite leads to a strong increase of the charge carrier concentration through spillover of charge carriers enabled by the low work function of lead. We also observe a concomitant increase of the charge carrier mobility associated with a decrease of the interface energy barriers. These properties translate into power factors up to 2.1 mWm⁻¹K⁻² at ambient temperature. Besides, the presence of multiple phases in the final composite results in a notable decrease of the lattice thermal conductivity. Overall, the introduction of metallic copper in the initial blend results in a significant improvement of the TE performance of PbS, reaching a dimensionless TE figure of merit $ZT = 1.1$ at 750 K, which represents about a 400% increase over bare PbS. Besides, an average $ZT_{ave} = 0.72$ in the temperature range 320-773 K is demonstrated. The results of chapter 5 have been submitted for publication in 2021.

Finally, the main conclusions of this thesis and some perspectives for future work are presented.

Resumen de Resultados

Los dispositivos TE pueden convertir directamente los gradientes de temperatura en electricidad, eliminar activamente el calor de fuentes locales o dispositivos sensibles a la temperatura y controlar con precisión la temperatura sin piezas móviles ni gases de trabajo. Tienen innumerables aplicaciones potenciales, pero sus altos costos de fabricación y materiales obstaculizan su rentabilidad y limitan su implementación. Para superar estos inconvenientes, los dispositivos TE deben fabricarse empleando tecnologías de alto rendimiento y utilizando materiales basados en elementos abundantes y de bajo costo.

Tradicionalmente, un método popular para preparar materiales TE nanoestructurados es utilizar un enfoque de arriba hacia abajo, como la molienda o la exfoliación de materiales obtenidos de reacciones en estado sólido a alta temperatura. Sin embargo, la mayoría de estos procesos consumen energía, son procesos complicados o utilizan condiciones adversas que limitan su aplicación generalizada. La síntesis acuosa ha recibido una amplia atención debido a su bajo impacto ambiental, bajo consumo de energía, potencial libre de tensioactivos y alto rendimiento. Esta tesis se centra en el desarrollo de métodos escalables y de bajo costo para la producción de nanomateriales TE con rendimiento optimizado. En estas direcciones, los objetivos generales de esta tesis es desarrollar dispositivos TE rentables con una eficiencia de conversión TE mejorada y un bajo costo de producción. Los principales objetivos de la investigación son: a) Explorar materiales terrestres abundantes, de bajo costo y menos tóxicos con alto rendimiento en TE; b) Desarrollar metodologías simples, escalables y rentables para producir materiales y módulos de TE; c) Optimizar el factor de potencia y ZT optimizándolos ya sea mediante dopaje o ingeniería de defectos. d) Reducir el κ_L mediante la introducción de fuentes de dispersión de fonones como defectos puntuales, dislocaciones e interfaces.

La tesis se divide en 5 capítulos. El Capítulo 1 presenta el estado de la investigación y las perspectivas de desarrollo de los materiales TE. El Capítulo 2 detalla como los materiales de SnSe policristalinos de tipo p con una textura cristalográfica marcada se produjeron a partir de mezclas de NC de SnSe y Te NR mediante prensado en caliente a una temperatura por encima del punto de fusión de Te. La presencia de Te promovió la cristalización del material en forma de estructura laminar con el eje a en la dirección de la presión. Parte del Te utilizado para el proceso de sinterización en fase líquida se encontró dentro de la red de SnSe y parte en forma de elemento Te dentro de los materiales consolidados. Las propiedades TE de los

nanomateriales producidos se midieron en dos direcciones perpendiculares, a lo largo y en la normal al eje de presión. Los nanomateriales de SnSe consolidados en presencia de Te mostraron conductividades eléctricas más altas y coeficientes de Seebeck y conductividades térmicas más bajas que el SnSe puro. Figuras de mérito TE hasta $ZT \sim 1.4$ a 790 K se midieron del nanomaterial SnSe consolidado en presencia de Te a lo largo de la dirección de prensado. Sorprendentemente, se obtuvieron valores de ZT más bajos en la dirección normal al eje de presión. Los resultados del Capítulo 2 se publicaron en Dalton Transaction en 2019.

El Capítulo 3 presenta un protocolo sintético para la producción a gran escala de nanopartículas de covellite CuS a temperatura y atmósfera ambiente, y usando agua como solvente. La fase cristalina y la estequiometría de las partículas se ajustan posteriormente a través de un proceso de consolidación a una temperatura moderada en atmósfera inerte o reductora. Mientras que el tratamiento térmico en atmósfera de argón da como resultado un nanopolvo de $\text{Cu}_{1.8}\text{S}$ con una fase cristalina romboédrica, el tratamiento térmico en una atmósfera que contiene hidrógeno conduce a un $\text{Cu}_{1.96}\text{S}$ tetragonal. La atmósfera, la temperatura y el tiempo de tratamiento térmico permiten el ajuste de la densidad de las vacantes de cobre y, por lo tanto, el ajuste de la concentración del portador de carga y las propiedades de transporte de materiales. En esta dirección, el material tratado bajo Ar se caracteriza por conductividades eléctricas más altas pero coeficientes de Seebeck más bajos que el material tratado en presencia de hidrógeno. Optimizando la concentración del portador de carga a través del tiempo de tratamiento térmico, se obtiene Cu_{2-x}S con figuras de mérito récord en el rango medio de temperatura, hasta 1.41 a 710 K. Finalmente demostramos que esta estrategia, basada en un proceso de escalable y de bajo costo, también es adecuada para la producción de capas de Cu_{2-x}S utilizando tecnologías de impresión rentables y de alto rendimiento. Los resultados se publicaron en ACS nano en 2021.

El Capítulo 4 informa sobre un método a gran escala para sintetizar nanohojas de Bi_2Se_3 de tipo N. Bi_2Se_3 es un aislante topológico tridimensional bien conocido con estados superficiales no triviales. También es una alternativa sin Te al Bi_2Te_3 como material termoeléctrico a temperatura ambiente. Posee propiedades TE moderadas debido a su única banda de conducción degenerada. Aquí, presentamos un método a gran escala para sintetizar nanohojas de Bi_2Se_3 que tienen un mecanismo de crecimiento impulsado por la dislocación del tornillo. Y además dopado con Sn que presenta un notable rendimiento TE. La incorporación de Sn en Bi_2Se_3 aumenta el coeficiente de Seebeck y, por lo tanto, mejora el factor de potencia a 0.65

$\text{mWm}^{-1}\text{K}^{-2}$. La baja conductividad térmica, hasta $0.91 \text{ Wm}^{-1}\text{K}^{-1}$, de $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ da como resultado valores de ZT muy por encima de los de Bi_2Se_3 puro.

El Capítulo 5 detalla como compuestos semiconductores-metal se producen simplemente mezclando nanopartículas de un semiconductor de sulfuro obtenido en solución acuosa y a temperatura ambiente, con un polvo de Cu metálico. La mezcla obtenida se temple en atmósfera reductora y luego se consolida en gránulos policristalinos densos mediante sinterización por plasma de chispa (SPS). Durante el proceso de recocido, la presencia de cobre metálico activa una reducción parcial del PbS, lo que resulta en la formación de compuestos $\text{PbS-Pb-Cu}_x\text{S}$. La presencia de plomo metálico en el material compuesto final conduce a un fuerte aumento de la concentración de portadores de carga a través del desbordamiento de los portadores de carga habilitado por la función de bajo trabajo del plomo. También observamos un aumento concomitante de la movilidad del portador de carga asociado con una disminución de las barreras de energía de la interfaz. Estas propiedades se traducen en factores de potencia de hasta $2.1 \text{ mWm}^{-1}\text{K}^{-2}$ a temperatura ambiente. Además, la presencia de múltiples fases en el compuesto final da como resultado una disminución notable de la conductividad térmica de la red. En general, la introducción de cobre metálico en la mezcla inicial da como resultado una mejora significativa del rendimiento TE del PbS, alcanzando una cifra de TE adimensional de mérito $ZT = 1.1$ a 750 K, lo que representa un aumento de aproximadamente un 400% sobre el PbS desnudo. Además, se demuestra un ZT_{ave} promedio = 0.72 en el rango de temperatura 320-773 K. Los resultados del capítulo 5 se enviaron para su publicación en 2021.

Finalmente, se presentan las principales conclusiones de esta tesis y algunas perspectivas para trabajos futuros.

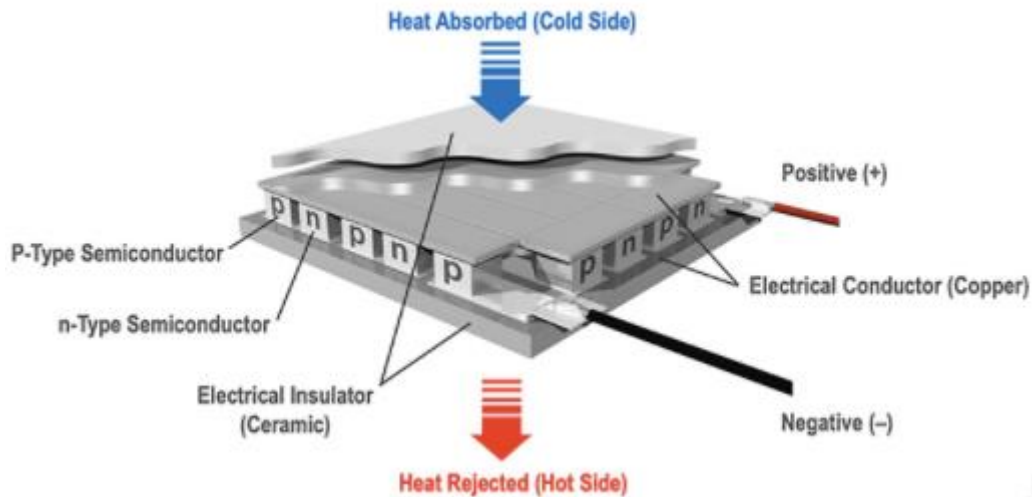
Abbreviation

TE	Thermoelectric
TEG	Thermoelectric generator
NC	Nanocrystal
NR	Nanorod
NP	Nanoparticle
NS	Nanosheet
σ	Electrical conductivity
S	Seebeck coefficient
PF	Power factor
κ	Thermal conductivity
κ_L	Lattice thermal conductivity
κ_e	Electronic thermal conductivity
ZT	TE figure of merit
n	Charge carrier concentration (electrons)
p	Charge carrier concentration (holes)
μ	Charge carrier mobility
μ_w	Weighted mobility
B	Quality factor
m^*	Charge carrier effective mass
C_p	Specific heat
λ	Thermal diffusivity
ρ	Density of the material
L	Lorenz number
XRD	X-ray diffraction
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
HRTEM	High resolution transmission electron microscopy
HAADF	High-angle annular dark-field imaging
EELS	Electron energy loss spectroscopy

XPS	X-ray photoelectron spectroscopy
EDX	Energy dispersive X-ray spectroscopy
SPS	Spark plasma sintering
HP	Hot press
DCS	Differential scanning calorimeter
SPB	Single parabolic band

Chapter 1

General Introduction



1.1 The energy challenges

Issues relating to the environment and energy are one of the greatest challenges of the 21st century. The rapid economic growth of most of the emerging and developing countries makes the discovery of new friendly environmental energy sources and energy optimization important for our societies.¹ A valuable alternative approach to improve the overall energy efficiency is to capture and recover the “waste heat”.² It is estimated that only one-third of the primary energy consumed by humans (natural gas, oil, coal, etc.) is effectively used, two-thirds are wasted, and most of them are in the form of waste heat, including residential heating and automobiles, exhaust gas, industrial processes and solar systems.³ Therefore, waste heat recovery technology is one of the best energy saving methods to make a more efficient usage of fuels to achieve environmental security.^{4,5} TE, which is directly generated electric energy from waste heat sources, shows promising results in making vital contributions to reducing greenhouse gas emissions and providing cleaner forms of energy.^{6–9} TE generators (TEG) can be used to convert heat to electricity through the Seebeck effect (Figure 1).¹⁰

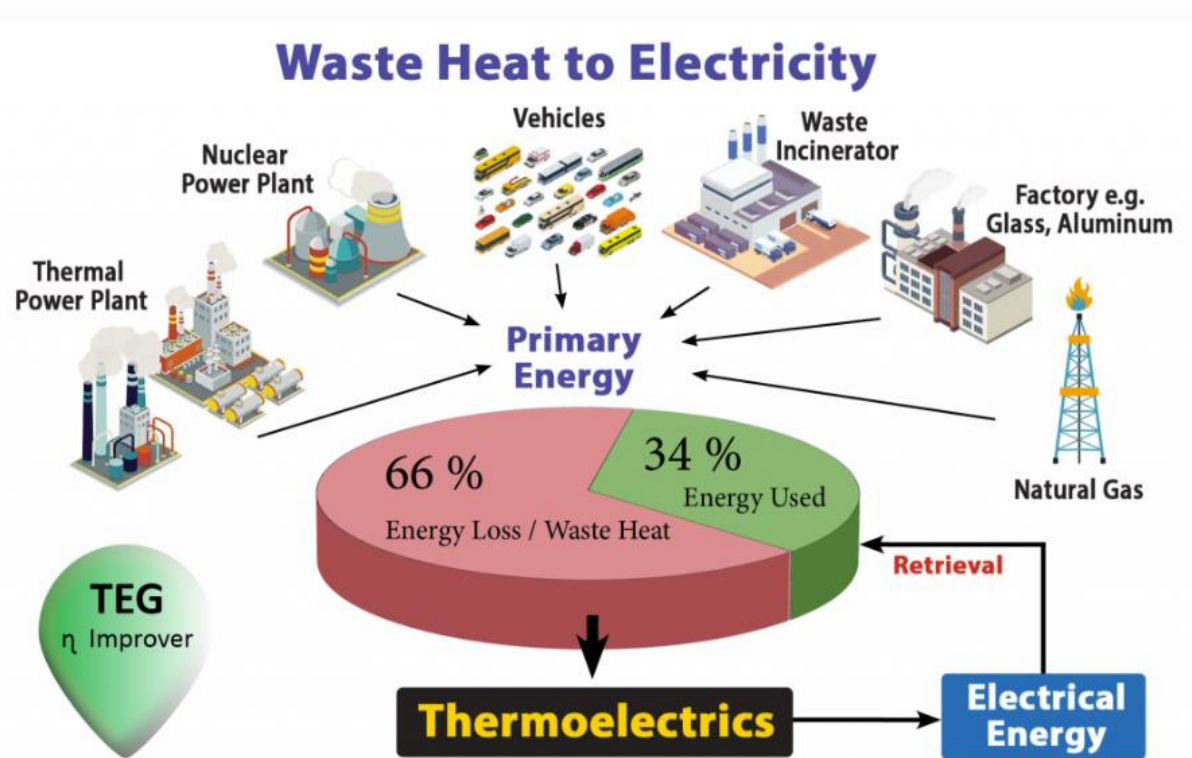


Figure 1. TEG offers a way to recapture some of the large amounts of waste energy from different industries and automobiles.¹⁰

TE systems are an environment-friendly energy conversion technology having the advantages of small size, adaptable shape, high reliability, no pollutants and feasibility in a wide temperature range.^{11–20} High performance TE materials which can directly and reversibly convert heat to electrical energy have thus drawn growing attentions of governments and research institutes in the last decades. However, most existing TE devices have relatively low conversion efficiency, so the development of high-performance TE materials becomes crucial.^{21–30}

1.2 Thermoelectricity

TE devices can convert thermal energy in the form of a temperature gradient into electrical energy. This phenomenon was discovered in 1821 and is called the “Seebeck effect,” while the reverse counterpart of this phenomenon was discovered by Peltier in 1834. As shown in Figure 2, when the TEG is subjected to a temperature difference, electrons and holes flow from the hot end to the cold end, thereby generating an electromotive force, realizing the conversion of

thermal energy into electrical energy. On the contrary, if a voltage is applied to two semiconductors, the movement of electrons and holes will produce a temperature difference.⁸

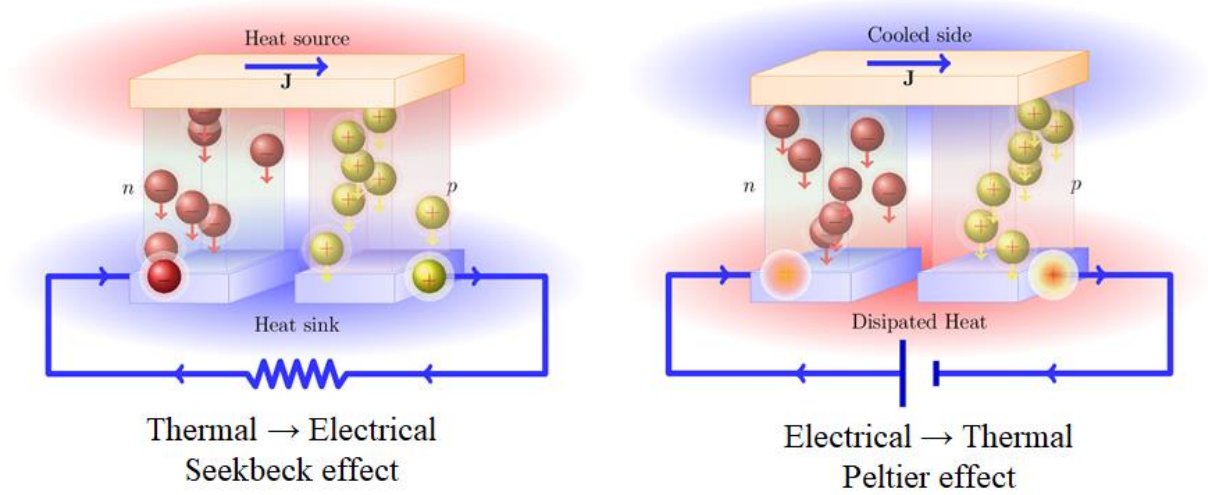


Figure 2. Working principle of a TE device.

With more and more research on thermoelectricity, the most important discoveries were related to material properties. In 1911, Altenkirch derived the TE efficiency from the TE figure of merit. Z have dimensions of T^{-1} , so it can be non-dimensionalized by multiplying by the absolute temperature T , which yields the most common form of TE figure of merit, ZT , also known as the dimensionless figure of merit. This value is given as

$$ZT = S^2\sigma T/\kappa \quad (2)$$

Where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. The product of $S^2\sigma$ is often referred to as the power factor.

The theoretical energy conversion efficiency of TE technology is as follow,

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_{avg}} - 1}{\sqrt{1 + ZT_{avg}} + T_c/T_h} \quad (1)$$

where T_c and T_h represent the temperatures at the cold and hot sides, respectively. ZT_{avg} represents the average ZT value in the relevant temperature range, and $T_h - T_c/T_h$ represents the Carnot cycle efficiency. Figure 3 displays the dependence on the hot side temperature of the energy conversion efficiency for different ZT_{avg} value, when T_c is assumed to be 300 K.²⁷ The energy conversion efficiencies of other forms of power generation, including solar, wind, nuclear, and geothermal energy, are also shown in Figure 3.

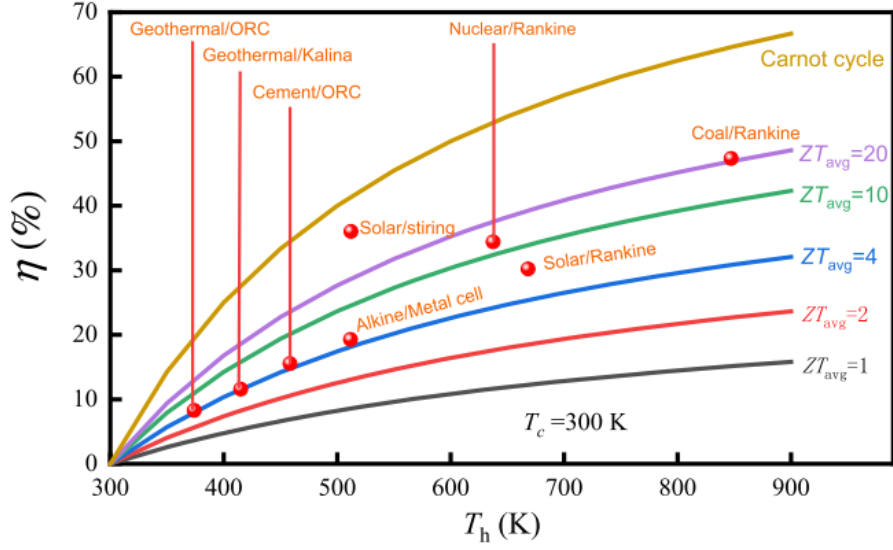


Figure 3. Hot side temperature dependence of the TE energy conversion efficiency for different ZT_{avg} value.²⁵

The three transport parameters depend on each other as a function of the band structure, carrier concentration and many other factors, which restrict each other. The relationship between the Seebeck coefficient and carrier concentration can be expressed as:

$$S = \frac{8\pi^2 \kappa_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3} \quad (3)$$

where κ_B is the Boltzmann constant, e is the carrier charge, h is Planck's constant, m^* is the effective mass of the charge carrier, and n is the carrier concentration. The relationship between electrical conductivity and carrier concentration can be defined as:

$$\sigma = ne\mu \quad (4)$$

where μ is the carrier mobility. The thermal conductivity includes the electronic κ_e and lattice κ_L , the κ_L can be expressed as follows:

$$\kappa_L = \lambda C_p \rho \quad (5)$$

where λ is the thermal diffusivity, C_p is the specific heat, ρ is the density of the material. According to the Wiedemann-Franz law, the relationship between electrical conductivity and electric thermal conductivity is defined as:

$$\kappa_E = L\sigma T \quad (6)$$

where L is the Lorenz number.²²

To maximize ZT , the optimization of the carrier concentration is key, as not only the electrical conductivity, but also the Seebeck coefficient and the electronic contribution to the thermal conductivity depend on it (Figure 4). Overall, maximum ZT are reached with relatively high charge carrier concentrations, around 10^{19} cm^{-3} .

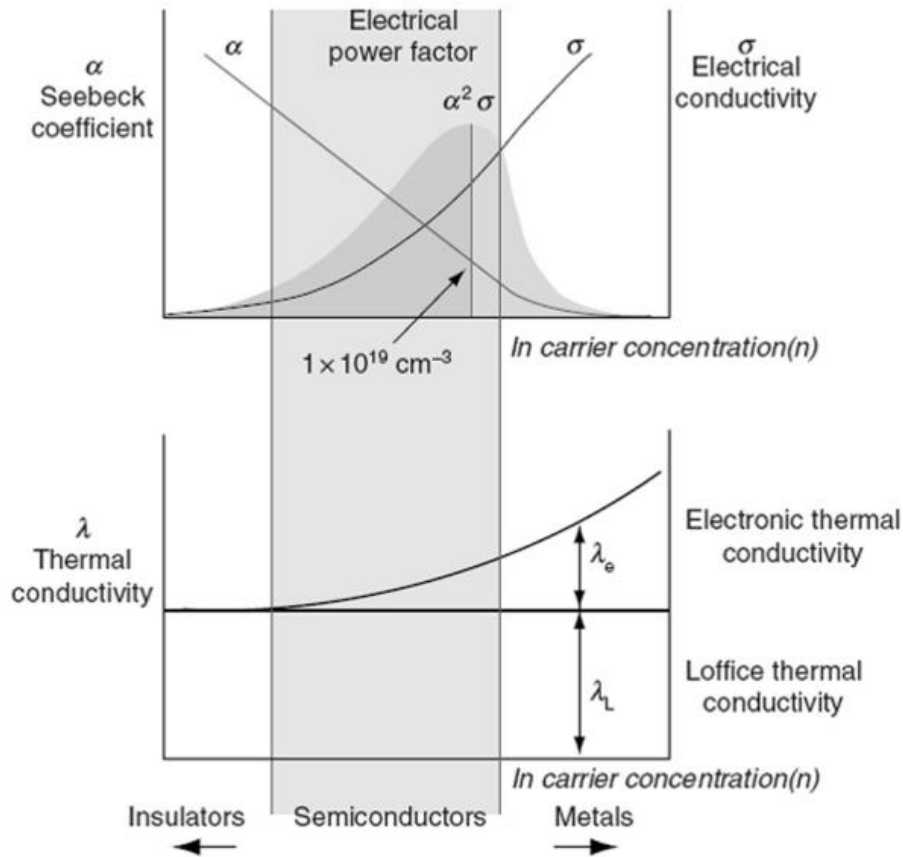


Figure 4. Schematic dependence of σ , S , PF and κ on concentration of free carriers.¹

1.3 Optimization of TE efficiency

The state of the art TE figures of merit for different high performance TE materials within their optimal operation temperatures are presented in Figure 5.²¹ The figure of merit ZT is governed by the lattice vibrations and electronic properties, and for the thermoelectromagnetic effect, the spin property must be considered in Figure 6. The conventional approach to improving the figure of merit is either to enhance the PF or to reduce the κ_L . The figure of merit ZT is governed by the lattice vibrations and electronic properties.²³ In general, the charge-carrier mobility, density-of-states effective mass and Pauling electronegativity affect the Seebeck coefficient and σ of the materials. The κ_L is related to atomic mass, bond length, bond strength, number of atoms per primitive cell, lattice symmetry, specific heat, speed of sound and lattice

anharmonicity.³¹ In addition to the separated electronic and phonon properties, the electron-phonon interaction usually plays a dominant role in determining the TE properties shown in Figure 7. Furthermore, the σ , κ , and S also depend on the sample quality, including grain size and defect concentration. Overall, improving the TE property is particularly challenging due to the complex interrelation among the aforementioned material properties.

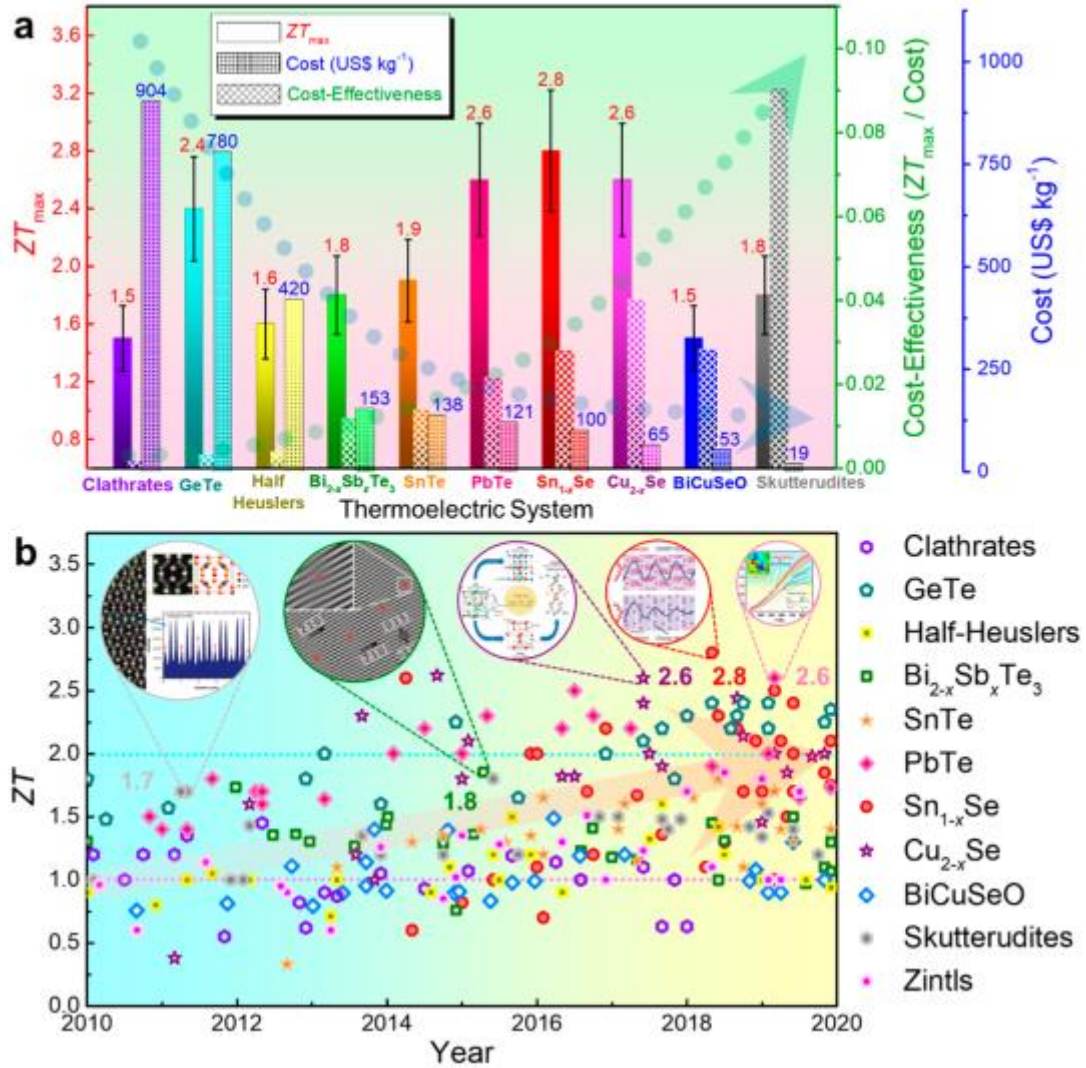


Figure 5. ZT value for state-of-the-art TE materials in the last 10 years. (a) Reported maximum ZT values (ZT_{max}) with error bars, calculated cost, and calculated cost-effectiveness (ZT_{max}/cost), and (b) timeline for the state-of -the-art TE materials.²¹

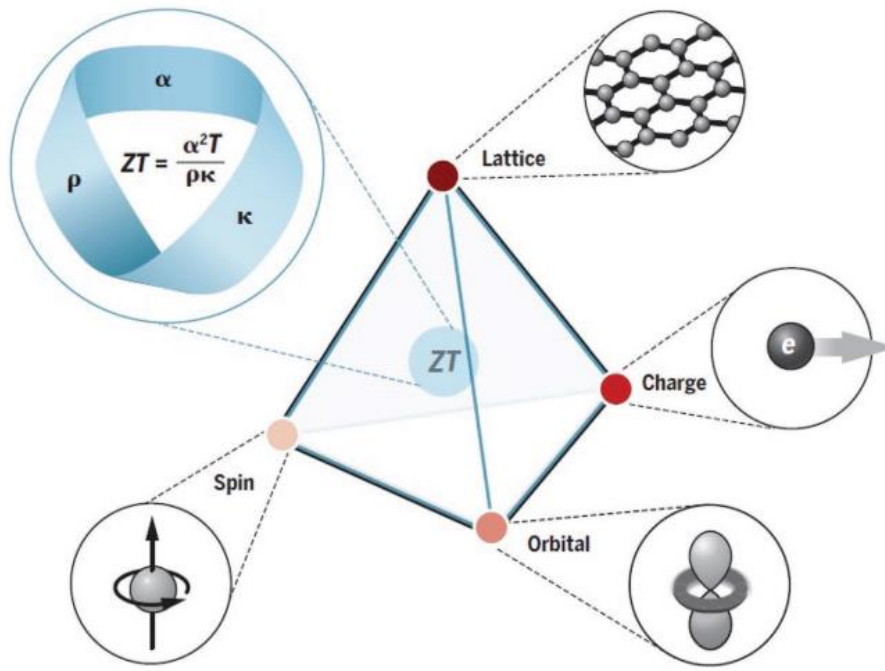


Figure 6. The TE potential of a material is evaluated by the TE figure of merit ZT . The lattice, charge, orbital, and spin are fundamental to research on TE materials.²³

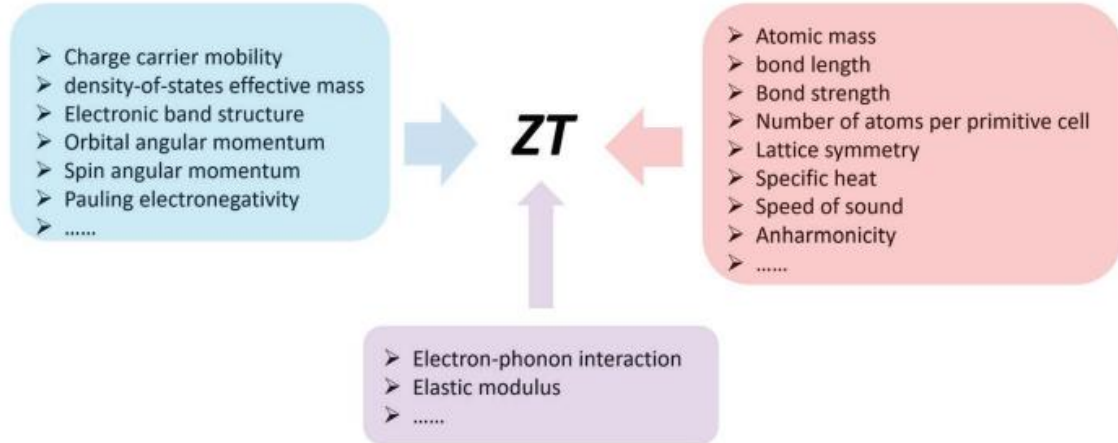


Figure 7. Factors affecting TE properties.²³

A popular and effective strategy for enhancing the PF is via the electronic band engineering. In the electronic band engineering, either the band convergence or the effective mass manipulation can be explored to increase the S or σ , respectively. In addition to the PF , the κ is also an important³² parameter that affects the ZT value. κ_L is controlled by the introduced impurities through various phonon scattering mechanisms. Another useful approach to improve ZT is to prepare nanostructured semiconducting materials. The advantages of nanostructuring

TE materials offer a pathway to decouple the correlation between the S , σ and κ .^{33–40} The quantum confinement effects associating with these nanostructures help to alter the electronic density-of-states, and therefore improve the PF . In addition, another noteworthy feature of nanostructuring is that it is able to decrease the κ_L through phonon scattering effects.^{41–45} For instance, one approach to reduce the κ_L is to minimize the phonon relaxation time through the introduction of phonon scattering sources such as point defects, dislocations and interfaces.

1.3.1 Improvement of electrical conductivity

The σ represents the material's ability to conduct electricity. A good σ requires carriers with high concentration and high mobility. Thus, the σ could be enhanced by increasing these two parameters separately or simultaneously. For semiconductor materials with poor conductivity, increasing conductivity is an effective way to improve their TE properties, such as SnS and SnSe, which have a low κ and a high S . ZT could be enhanced by achieving higher carrier concentration through improved doping together with microstructural and compositional optimization.^{46–55}

Compared with uniform doping, modulation doping was proven to be an effective approach to optimize the mobility of carriers. Figure 8 shows the difference between uniform doping and modulation doping. For uniformly doped semiconductors, the carrier mobility could be reduced due to ionized impurity scattering. For modulation doping, the dopants were incorporated into only one phase. Thus the ionized dopants would have little effect on the carriers, resulting in enhanced carrier mobility.^{56–60}

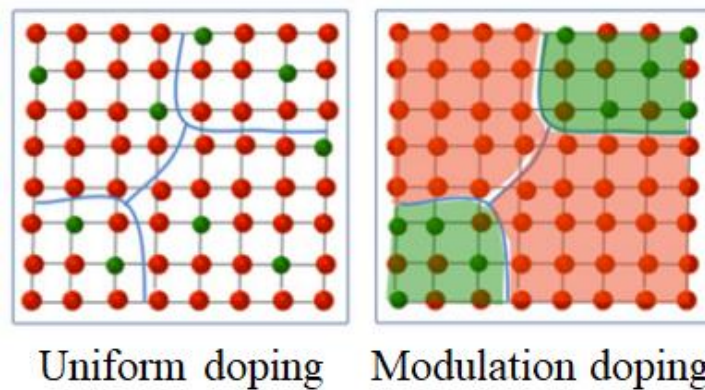


Figure 8. Comparison of uniform doping and modulation doping.²²

In addition, the σ could be enhanced by optimizing the processing parameters. For some TE materials, such as SnSe and PbS, which are more sensitive to oxygen, and the oxides will

greatly reduce the σ . In this case, the oxide can be removed by annealing in a hydrogen atmosphere to increase the σ .^{61–65} Changing the annealing atmosphere can also control the stoichiometric ratio of copper-based TE materials, thereby changing the σ .^{66–70} In addition, changing the annealing time and temperature, the time and temperature of HP can also adjust the TE properties of the material.

1.3.2 Improvement of Seebeck coefficient

The Seebeck coefficient is obtained by dividing the TE voltage by the temperature difference. Usually, the Seebeck coefficient is described by the Pisarenko relationship. The Seebeck coefficient can be changed by tuning the effective mass and carrier concentration. The reduced carrier concentration bring the two valence bands closer, leading to an enhanced Seebeck coefficient. Introducing resonant impurity levels by the dopants is an effective way to improve the Seebeck coefficient.⁷¹

Figure 9 shows the Seebeck coefficient of doped Bi₂Se₃ thin film as function of dopant concentration. The Seebeck coefficients slightly increase at the dopant concentrations of approximately 1-3% and tend to decrease with the further increase of dopant concentration. Despite the similar dependences of the Seebeck coefficient of Bi₂Se₃ thin film on Sb and Sn dopant concentrations, the mechanisms of impact of the dopants are different. The low concentrations of Sb dopant in the Bi₂Se₃ thin films suppress the bulk conductivity of the Bi₂Se₃, simultaneously lowering the Fermi level close to the conduction band edge. For the doping with Sn, the dopant concentration will result in creation of the impurity resonant level close to the conductive band edge and Fermi level thereby enhance the Seebeck value. For the Fe-doped thin film, the effect may be due to the introduction of magnetic impurities into the lattice structure of Bi₂Se₃ by substitution of Bi atoms with Fe. Probably, the introduction of magnetic impurities may result in the opening of Dirac band gap and creation of the resonant impurity levels, impacting the TE response.

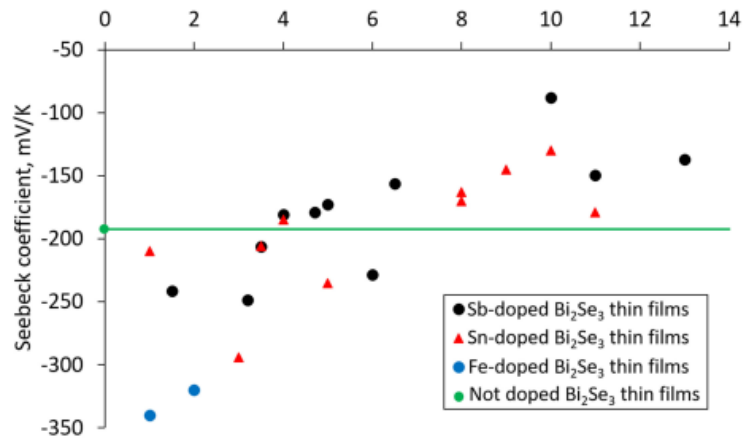


Figure 9. Seebeck coefficient of Sb, Sn and Fe doped planar Bi_2Se_3 thin film as function of dopant concentration in these film.⁷²

Moreover, nanostructuring also is an effective way to improving the TE Seebeck coefficient, which due to the energy filtering effect induced by the grain boundaries where low energy holes are scattered of the nanocomposites.^{73–80}

1.3.3 Reduction of thermal conductivity

For semiconductor materials, the total κ consists of lattice component κ_L and the electronic component κ_e , namely $\kappa = \kappa_L + \kappa_e$. In most cases, the lattice was the dominant mechanism. Since the κ and PF are coupled with each other, it is very challenging to regulate each parameter independently. Thereby, materials with low intrinsic κ have apparent advantages for further optimization of the TE performance and have received tremendous attention. Introducing nanostructures into the bulk material through doping, alloying, HP, etc can appropriately suppress the κ of the bulk materials, thereby increasing the ZT value.^{81,82}

Multiple reports have indicated that a reduction in κ_L is the main reason for enhancing TE performance in nanostructured bulk materials. The phonons with a varying wavelength in solid crystalline materials contribute to the heat transport at different scales. The κ_L is minimized due to the increased scattering of the heat-carrying phonons by the interfacial boundaries. κ minimization through nanostructuring was observed in the bulk TE systems. They attributed the decrease in the κ to the ubiquitous and spontaneous nanoscale precipitation of the secondary phase in the host material.^{83–90} Generally, the nano-crystals are embedded in the matrix endotaxially with a low lattice mismatch. A schematic of the typical interface boundaries depicting carriers' motion is presented in Figure 10.

The concept of mass fluctuations is yet another promising technique employed to reduce κ_L . Once the difference between the masses of the dopant atom and the host element is large, the lattice periodicity is disturbed and consequently increases phonon scattering, thereby minimizing the κ_L . Reduced κ_L is observed when using heavy masses with large unit cells and low spring constants. Similarly, solid solution alloying has been reported to lower the κ_L due to mass fluctuations. For the alloying approach, the constituent alloy's mass ratio significantly determines the scattering rate, and the random vacancies produced serve as scattering regions. The all-scale hierarchical approach involves the simultaneous scattering of heat-carrying phonons through the full spectrum range of their mean free path, via defect incorporation, nanoscale precipitation, and mesoscale grain boundary creation integrated to reduce the κ_L synergistically. The strategy is robust enough to bring the κ to its amorphous limit. Generally, nanostructured bulk TE materials contain some atomic defects either due to the dissolution of the dopants or partial dissolution of the second phase. Acoustic phonons are majorly responsible for the thermal transport in crystalline materials, and the phonons can be defined in terms of their mean free path and wavelength, each of which contributes to the heat transport.^{91–96} Therefore, to scatter the phonons through all mean free path ranges, from the nanoscale to microscale, the solid solution atomic defects, nanostructuring, and mesoscale approach must be integrated into a single sample as presented in Figure 11.

ZT can be noticeably improved by introducing isoelectronic foreign atoms into a crystal to create defect scatterings of phonons without affecting its σ . After a series of extensive studies for seeking such type of materials, two group of crystal compounds, *i.e.*, clathrates and skutterudites, were found to be the promising candidates. The general reason for the reduction of κ in these materials is the weak bonds between host atoms and guest atom. In addition to atomic disorders, other types of disorders, like valence fluctuations, Peierls distortion and Jahn-Teller distortion, also result in a considerable reduction of κ_L .^{97,98}

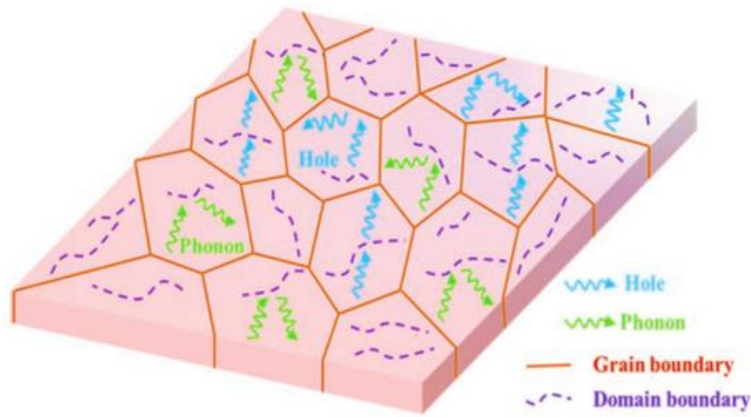


Figure 10. A schematic of the materials's grain boundaries illustrating the motions of holes and phonons.²¹

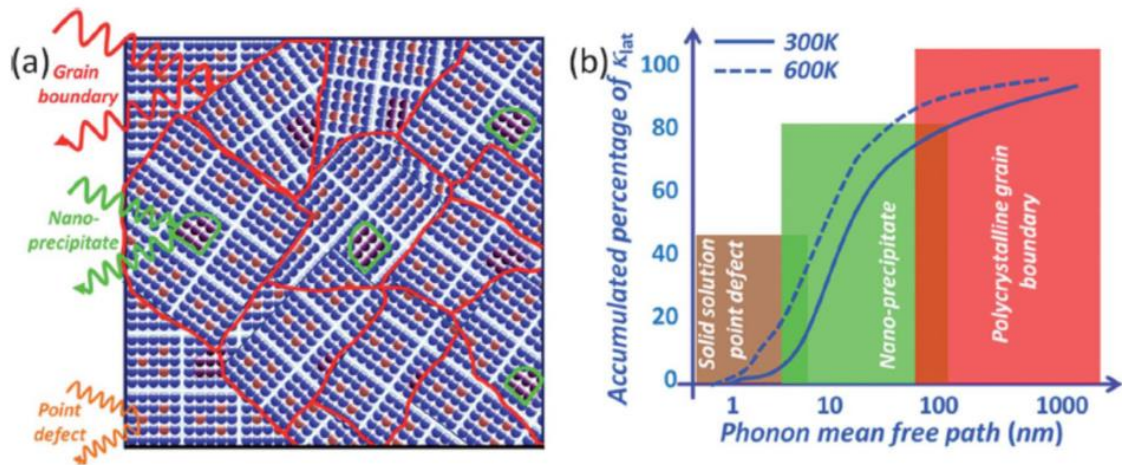


Figure 11. The all-scale hierarchical approach to minimize the κ_L showing (a) atomic defects, nano-precipitate, and mesoscale grain boundary (b) Phonons distribution according to their mean free path.²¹

1.4 TE nanomaterial synthetic approaches

Main methods to produce TE materials include solution synthesis, solid state reaction and reactive ball milling. For the ball milling, elemental powders or intermetallic compounds are loaded into a milling container with balls which can be made from stainless steel, tungsten carbides and zirconia. The containers are then loaded into a high energy ball milling machine. Normally, powders are milled under the argon atmosphere to prevent oxidation during the balling milling process. The powders will be subjected to a series of impact collisions between the ball to ball, and ball to the wall. During ball milling, the powders are constantly cold welded and fractured which will lead to the formation of nanostructured domains. Ball milling is a

simple and convenient for large-scale production method, but cannot control the morphology, particles are large, which lead to the lower TE properties.²³ For the solid state reaction, elemental powders are loaded into a tube furnace for high temperature calcination in an argon atmosphere for a period of time. This method not only cannot control the morphology but also requires higher temperature reaction.^{99,100} For the development of TE materials, nanostructuring can very effectively enhanced ZT. The high density of interfaces improves phonon scattering, decreasing the κ_L . In comparison, solution-based synthesis method is very attractive and easy to control size, shape, composition and phase. Solution-based synthesis methods include colloidal synthesis and aqueous synthesis.³¹

1.4.1 Colloidal Synthesis

Colloidal synthesis routes allow producing NCs with excellent control over their properties using low amounts of energy and low capital cost equipment. Elemental, binary, ternary, quaternary and even quinary NCs can be prepared via reaction or decomposition of multiple precursors or single-molecule sources.³¹ Reactions are usually performed under inert atmosphere in high boiling point solvents, e.g. oleylamine (OLA), octadecene (ODE), oleic acid (OA), trioctylphosphine (TOP) or ethylene glycol (EG). The typical synthesis route to produce colloidal NCs at the laboratory scale uses a Schlenk line as shown in Figure 12.

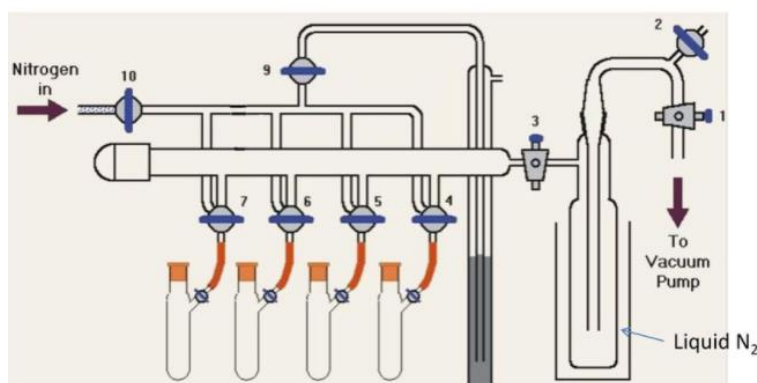


Figure 12. Colloidal synthesis Schlenk line set-up.¹⁰¹

Colloidal NC parameters can be modified to affect structural, chemical and physical properties of the resultant particles, e.g. size, shape, composition, phase, absorption, emission and conductivity. The progress to this nanoscale level of control has resulted in successful exploitation for numerous applications, particularly in the energy conversion field. In TE applications, tuning the crystal domain sizes in the proper range plays an important role in

determining transport properties and allows modifying the electronic band structure through quantum confinement effects.¹⁰²

The following reaction parameters are important to control the size and shape of colloidal NCs: i) the reaction temperature and time, ii) the injection temperature of the reactant in the case of hot-injection methods, iii) the reactivity and the concentration of precursors, iv) the ratio of the concentration of the chemicals and PH. Figure 13 represents some examples of inorganic NCs with different size and morphologies synthesized by colloidal technique in the thesis.⁸¹

Moreover, the composition and crystal phase can be also controlled by colloidal synthesis methods. NCs with multinary compositions can be produced by selecting suitable precursors and adjusting the reaction conditions. Substitution reactions are also especially powerful to control the composition of the NCs, and even to create materials with new crystallographic phases. The composition of pre-grown NCs can be also adjusted by subtractive reactions.¹⁰³

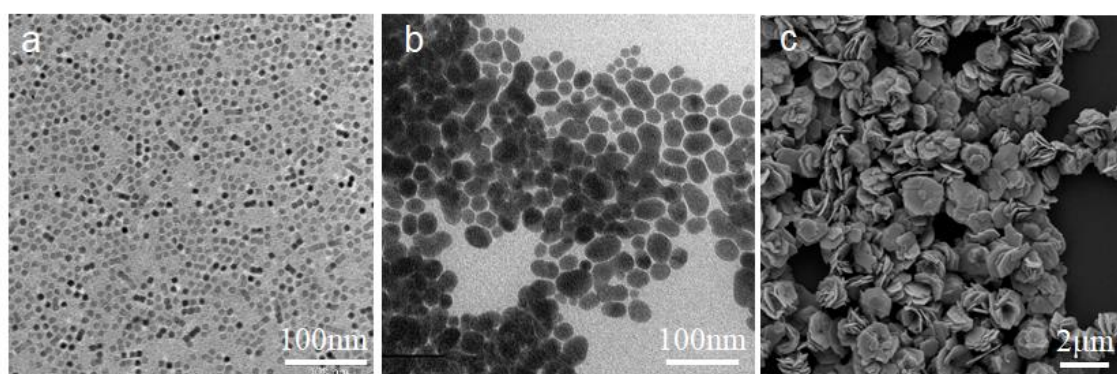


Figure 13. Examples of nanomaterials produced by means of colloidal synthesis with different size and shapes in my work. a) PbSe spheres; b) AgSe spheres and c) Bi₂Se₃ NSs (chapter 4).

1.4.2. Aqueous Synthesis

Bottom-up solution synthesis methods facilitate control of size, morphology, crystal structure, and defects. However, the organic surfactants that can control morphology through surface modification are commonly electrically insulating, which can drastically reduce the σ of the materials. Ligand replacement methods switch smaller species for long chain surfactant molecules, but sometimes involve using high toxicity chemicals, and introduce impurities, which again can adversely influence the transport behavior of the materials. For this situation, aqueous synthesis is a better choice. Aqueous synthesis is a synthesis method that simple, rapid, large scale, environmental friendly, low cost, surfactant-free and can also control the size of

the nanomaterials. There is no organic surfactants on the nanomaterials synthesized by aqueous synthesis, so in general, the TE properties of the materials will be better. Figure 14 shows the nanomaterials with different size and morphologies synthesized by aqueous synthesis.⁷⁸

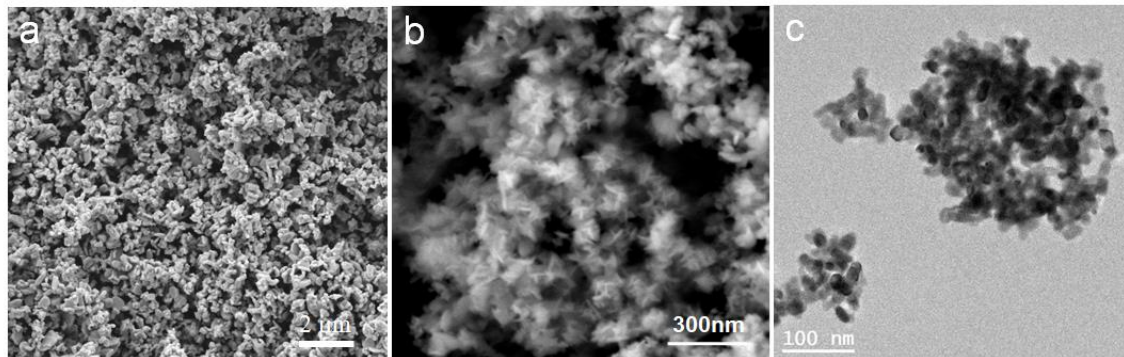


Figure 14. Examples of nanomaterials produced by means of aqueous synthesis with different size and shapes in this thesis. a) SnSe NCs (chapter 2); b) CuS NPs (chapter 3) and c) PbS NPs (chapter 5).

1.5 Objectives

The aim of this thesis is to demonstrate the production of high performance TE nanomaterials by means of the bottom-up approach using NCs obtained by cost-effective and scalable solution synthesis routes. To achieve the goals of the thesis, it will be required to overcome several main challenges encountered when aiming at the production of nanomaterials and devices using bottom-up engineering. These include to develop new synthesis methods, the control of the carrier concentration, and the consolidation of the NCs into dense and texturized bulk nanomaterials. To solve the challenges, in this thesis the following specific objectives have been defined:

- a) To develop solution synthesis strategies to produce high quality NCs of four relevant TE materials: SnSe, Cu_xS, PbS and Bi₂Se₃.
- b) To develop aqueous synthesis that simple, rapid, large scale, environmental friendly, low cost, surfactant-free and can also control the size of the NCs.
- c) To develop effective electron and hole doping strategies to control the charge carrier concentration of bottom-up assembled nanomaterials.
- d) To develop assembly and consolidation strategies that allow controlling the composition and crystallographic alignment of nanograins within nanomaterials.
- e) To establish steps toward fabricating TE devices based on molecular inks by means of printing technologies to reduce cost.

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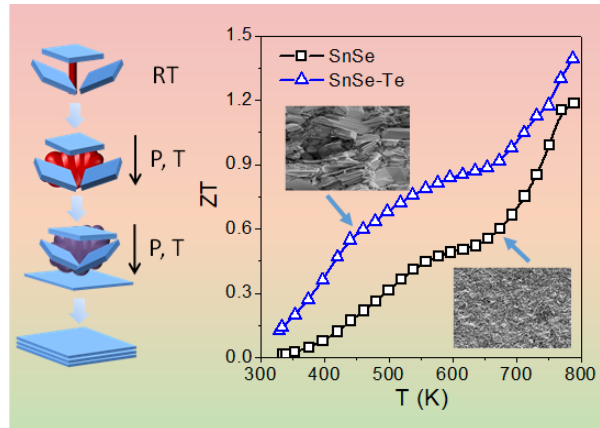
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Chapter 2 Crystallographically Textured SnSe Nanomaterials Produced from the Liquid Phase Sintering of Nanocrystals



2.1 Abstract

We report the TE performance of p-type nanocrystalline SnSe obtained from the liquid phase sintering of blends of SnSe NCs and Te NRs. A cycled HP procedure at temperature above the Te melting point promoted the formation of crystallographically textured SnSe nanomaterials with relative densities up to 93%. After consolidation, part of this Te was found within the SnSe lattice and part remained as elemental Te between the SnSe grains. The presence of Te during the SnSe consolidation resulted in SnSe nanomaterials with higher σ and lower S and κ . By adjusting the amount of Te, ZT up to 1.4 at 790 K were measured in the direction of the uniaxial pressure, coinciding with the preferential a crystallographic axis. While this value matches the highest ZT value reported at this temperature for SnSe in the [100] crystal direction, ZT values of the consolidated SnSe along the bc plane were relatively lower due to moderately low thermal conductivities in this plane.

2.2 Introduction

TE, the solid state conversion between heat and electricity, finds countless potential applications, both to harvest heat from ubiquitous temperature gradients and to precisely control temperature in endless locations and processes.¹ While TE devices are silent, easily scalable and durable, they have just impacted niche markets due to two important limitations:

i) their moderate efficiency and coefficient of performance; and ii) their relatively high price associated to the use of materials containing scarce elements such as tellurium, the complex device architectures and the elevated material processing costs.^{2,3}

In the last few years, since ZT values up to 2.6 at 923 K were reported from single crystals, SnSe has received extensive attention in the TE field.^{5,6} SnSe is a IV-VI monochalcogenide semiconductor with layered crystal structure. It is composed of reasonably abundant elements and is relatively stable. Besides a notable Seebeck coefficient and p-type electrical conductivity dominated by tin vacancies,^{7,8} the main characteristic of SnSe is its ultralow thermal conductivity in particular crystallographic directions, which has been related to a strong anharmonicity.^{2,9}

Taking into account the high cost of production of SnSe single crystals and their structural fragility, the production of polycrystalline samples with TE figures of merit as high as those obtained from single crystals is a worth endeavour. However, the strong asymmetry of the SnSe crystal structure and the related anisotropic properties inevitably result in polycrystalline samples with lower ZT , as a result of averaging them for the different crystallographic directions. Thus, to overcome this challenge, crystallographically textured polycrystalline materials are required.

Devices based on highly crystallographically textured nanomaterials produced from the bottom up consolidation of NCs could have associated not only optimized TE performance, but also reduced production cost, especially if printing technologies could be used to produce them.^{1,10,11} In this work, we blend liquid dispersions of SnSe NCs and Te NRs at different ratios (Te = 0, 10%, 15%, 20% and 25%). Taking advantage of the low Te melting point, we use a liquid phase sintering strategy to produce laminated and crystallographically textured SnSe nanomaterials, which TE properties we characterize in two directions.

2.3 Experimental section

Chemicals: Tin(II) chloride anhydrous (SnCl_2 , 98%), sodium hydroxide (NaOH, 98.5%), selenium powder (Se, $\geq 99.5\%$), sodium borohydride (NaBH_4 , $\geq 98\%$), tellurium dioxide (TeO_2 , $\geq 99\%$), potassium hydroxide (KOH, 85%), polyvinylpyrrolidone (PVP, $(\text{C}_6\text{H}_9\text{NO})_n$, average molar weight $\sim 55,000$), ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$, 99%) and hydrazine monohydrate (N_2H_4 64-65%, 98%) were purchased from Fisher. Analytical grade acetone and ethanol were obtained from various sources. All chemicals were used as received without

further purification. Syntheses were carried out using a standard vacuum/dry argon Schlenk line.

Synthesis of SnSe NCs: SnSe NCs were prepared in water following the approach developed by Guang Han et al.¹² Briefly, 100 mmol NaOH and 10 mmol $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 50 mL of deionized water and boiled to yield a transparent Na_2SnO_2 solution. 50 mL of an aqueous NaHSe solution prepared from Se and NaBH_4 was then injected into the boiling solution, leading to the immediate formation of a black precipitate. The mixture was boiled further for 2h and cooled to room temperature under Ar flow in a Schlenk line. The products were washed with deionized water and ethanol several times. The obtained product was then dried under vacuum at room temperature for 2h. Dried SnSe NCs were annealed at 400 °C for 120 min under an Ar flow inside a tube furnace.

Synthesis of tellurium NRs: Te NRs were prepared following the approach developed by Genqiang Zhang et al.¹³ In a typical synthesis, 11.2 mmol of TeO_2 , 74 mmol of KOH, 3.0 g of PVP, and 110 mL of EG were added into a 250 mL three-neck flask. The mixture was stirred and heated to 140 °C. At this temperature, 1.75 mL of a 64-65% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solution were injected into the flask. The reaction mixture was maintained at 140 °C for 1 h to allow all Te to be reduced. The solid product was collected by adding acetone to the solution and centrifuging it. In a second step, ethanol was used to re-disperse the NRs, and acetone ($V_{\text{ethanol}}/V_{\text{acetone}}=1:2$) to precipitate them again. In a third step, deionized water was added to solubilize remaining impurities and NRs were precipitated by slow centrifugation. This procedure was repeated twice. In a last step, NRs were re-dispersed with ethanol and precipitated with acetone, like in step two. Finally, NRs were dried under vacuum at room temperature.¹⁰

Bulk nanomaterial consolidation: Annealed SnSe NCs and dried Te NRs were mixed in the appropriate ratio within chloroform with the aid of an ultrasonic bath for 30 min. Then the material was dried under vacuum at room temperature. The dried mixture of SnSe NCs and Te NRs was annealed at 350 °C for 60 min under Ar flow inside a tube furnace. The annealed particles, in the form of a powder, were loaded into a graphite die and compacted into cylinders using a custom-made HP within an Ar filled glove box. The HP temperature was set at 480 °C and pressure was increased up to 50 MPa and released for 6 cycles during the 10 min that the material was kept at 480 °C. The relative densities of the compacted pellets were measured by the Archimedes' method.

Structural and chemical characterization: X-ray diffraction (XRD, 2θ angle: 20° to 80° ; scanning rate: $3^\circ/\text{min}$) analyses were carried out on a Bruker AXS D8 ADVANCE X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Size and morphology of initial NPs were examined by an Auriga Zeiss field-emission scanning electron microscopy (FESEM), operated at 5.0 kV. The material composition was analysed using an Oxford energy dispersive X-ray spectrometer (EDX) attached to the Zeiss Auriga FESEM at 20.0 kV. Refinement of the obtained diffraction patterns were done by the Rietveld method with the GSAS-II package.¹⁴

TE property measurement: Seebeck coefficients were measured using a static DC method. Electrical resistivity data was obtained by a standard four-probe method. Both the Seebeck coefficient and the electrical resistivity were measured simultaneously in a LSR-3 LINSEIS system in the temperature range between room temperature and 800 K under helium atmosphere. All samples were measured at least 3 consecutive times during heating up to around 790 K. Taking into account the system accuracy and the measurement precision, an error of ca. 4 % in the measurement of the electrical conductivity and Seebeck coefficient was estimated. κ were obtained by multiplying the λ , C_p and ρ , where $\kappa_{total} = \lambda C_p \rho$. A Xenon Flash Apparatus XFA600 was used to determine the thermal diffusivities of the samples with an estimated error of ca. 5 %. The C_p was estimated from empirical formulas by the Dulong–Petit limit (3R law). The density values were measured using the Archimedes’ method. To avoid cluttering the plots, error bars were not included in the figures.

2.4 Results and discussions

Flat SnSe NCs with 100 nm average size and 40 nm average thickness were produced from the reaction of SnCl and NaHSe in water (Figure 1a and 1b).¹² XRD analysis showed the NCs to have an orthorhombic structure with lattice parameters: $a = 11.49 \text{ \AA}$, $b = 4.44 \text{ \AA}$, and $c = 4.13 \text{ \AA}$ and space group 62 (Pnma, JCPDS No. 00-048-1224, Figure 1d).¹⁵ Te NRs with a hexagonal crystal phase, an average thickness of ca. 30 nm and an average length of 500 nm were produced within EG (Figures 1c and 1d).

The two types of particles, SnSe NCs and Te NRs, were blended in solution at different ratios (Te = 0 mol%, 10 mol%, 15 mol%, 20 mol% and 25 mol%). The mixture was dried, annealed at 350°C and subsequently hot-pressed within an inert atmosphere into cylindrical pellets 10 mm in diameter and 10 mm height. The hot-press temperature was set at 480°C and pressure was cycled from ambient to 50 MPa for 6 times during the 10 minutes that the material was

kept at 480 °C. This process resulted in cylinders with relative densities of ca. 93% of the theoretical value, as measured by the Archimedes' method.

XRD analysis of the cylindrical pellets hold in two perpendicular directions, with the diffraction plane normal and parallel to the pressing direction, showed a strong preferential orientation of the SnSe crystal domains within the pellets as noted by the differential peak intensities (Figure 2). The [100] direction was found to be preferentially aligned along the pressure axis. The presence of Te clearly promoted this alignment as observed when comparing the in-plane $I_{(400)}/I_{(011)}$ ratio of SnSe pellets obtained with and without Te. In the absence of Te, SnSe pellets with in plane $I_{(400)}/I_{(011)} = 11$ were obtained. In the presence of Te, SnSe pellets with significantly larger plane $I_{(400)}/I_{(011)}$ values, ranging from 31 to 90, were produced.

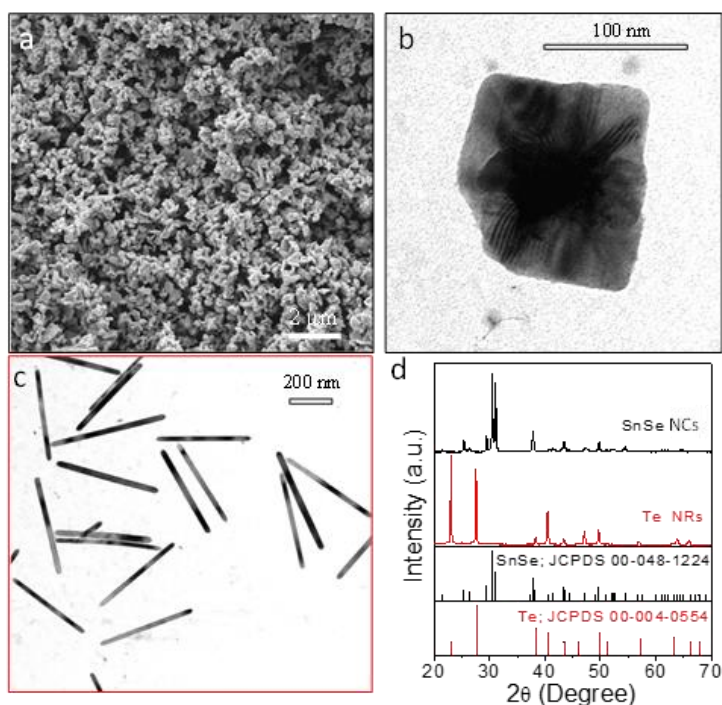


Figure 1. a) SEM micrograph of SnSe NCs. b) Representative TEM micrograph of a SnSe NC. c) TEM micrograph of Te NRs. d) XRD patterns of SnSe NCs and Te NRs. The graph includes reference patterns for orthorhombic SnSe and hexagonal Te.

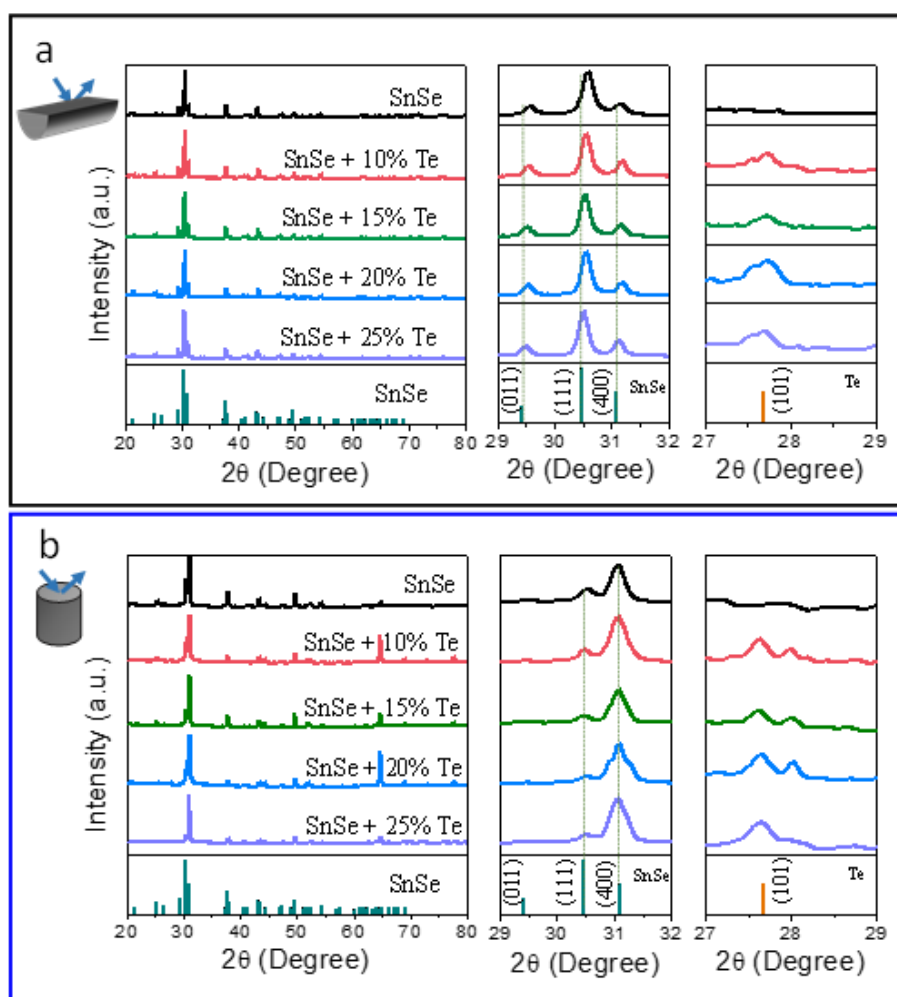


Figure 2. XRD patterns of consolidated SnSe-Te pellets measured while hold in two directions, with the press axis within (a) and normal to (b) the diffraction plane, as specified by the cartons. Expanded views of the regions corresponding to the SnSe (400) and (111) diffraction peaks and the Te (101) diffraction peak are displayed.

At increasing Te concentrations, XRD peaks of the consolidated materials systematically shifted to lower 2θ angles suggesting small amounts of Te, with a larger covalent radius, to be inserted within the SnSe lattice. Additionally, XRD analysis showed the presence of elemental Te diffraction peaks in the consolidated material, demonstrating that small amounts of elemental Te remained in the material after hot-pressing. No additional phase was identified from XRD characterization. EDX analysis quantified the total amount of Te within the final material to increase from 2.7 at% to 7.7 at% when increasing the amount of Te NRs included in the initial blend, from 10 mol% to 25 mol%, respectively (Table 1). Rietveld analysis of the XRD patterns showed the presence of a 6.8 wt% of the Te phase in the SnSe sample containing a nominal 15 mol% of Te, which corresponds to 8.8 wt% (Figure 3). After consolidation, the

amount of Te phase detected for this same sample from the Rietveld analysis of the XRD pattern decreased to 2.2 wt% (Figure 4).

Table 1. Nominal and EDX composition of the initial particle blend and the final consolidated pellets.

Nominal	EDX (%)		
	Sn	Se	Te
Sn:Se:Te			
1:1:0.00	52	48	0.0
1:1:0.10	50	47	2.7
1:1:0.15	50	47	3.1
1:1:0.20	48	46	6.4
1:1:0.25	47	45	7.7

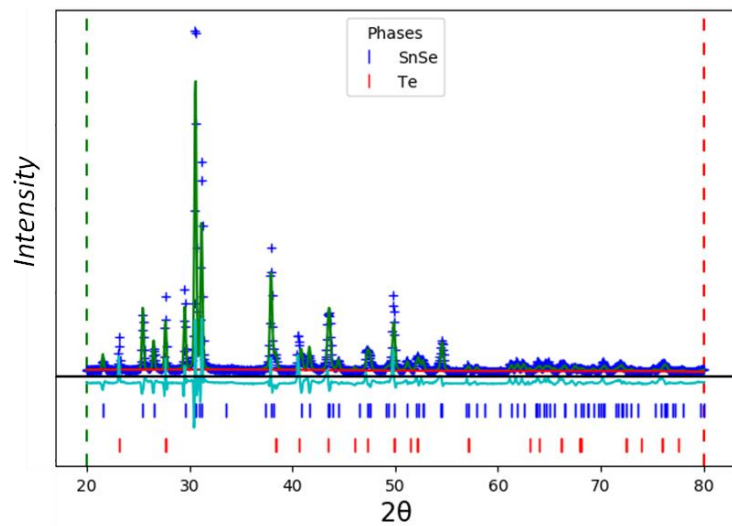


Figure 3. The refined profile fit of SnSe-15%Te powder diffraction data. Blue “+” : observed experimental data; continuous red line: modified background; continuous green line: calculated modelled structure; continuous line beneath pattern: difference between observed and calculated parameters. Upper blue tickmarcks correspond to reflections of SnSe (Pnma) unit cell, lower red ones to Te (P31,221) unit cell.

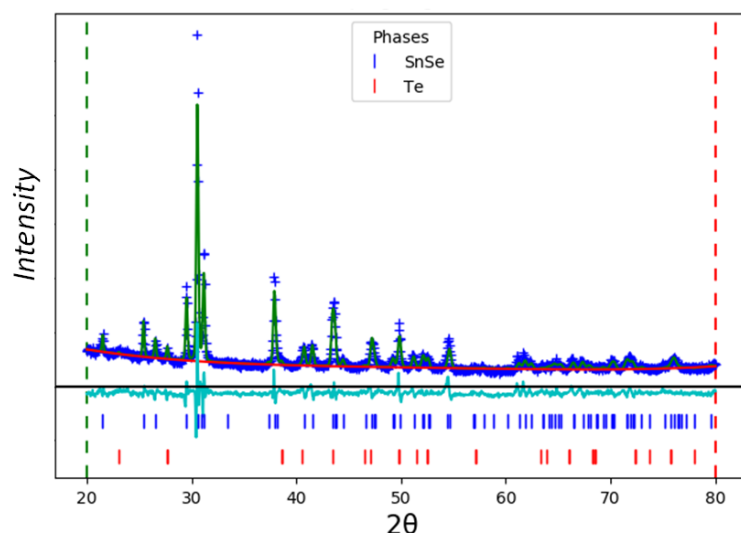


Figure 4. The refined profile fit of SnSe-15%Te pellets diffraction data. Blue “+” : observed experimental data; continuous red line: modified background; continuous green line: calculated modelled structure; continuous line beneath pattern: difference between observed and calculated parameters. Upper blue tickmarks correspond to reflections of SnSe (Pnma) unit cell, lower red ones to Te (P31,221) unit cell.

Top view and cross-section SEM images showed SnSe consolidated pellets produced without the addition of Te to consist of a dense aggregate of particles with no evident preferential orientation. On the other hand, in the presence of Te, pellets with laminar structure, containing 100 nm -1 μ m thick layers stacking in the press direction and extending several micrometres in the cylinder plane, were obtained. During the HP, Te liquefied, aiding the rotation of the asymmetric SnSe NCs towards a common preferential orientation that maximized entropy. On the other hand, Sn-Se-Te form an extended range of solid solutions in the Se-rich side as observed from the SnSe-SnTe phase diagram.^{16,17} Additionally, when moving away from the stoichiometric 1:1 composition of the tin monochalcogenides, the melting temperature strongly decreases and even an eutectic at 85 at% Te at 678 K is obtained in the Sn-Te system.¹⁸ Liquefied Te is thus able to dissolve significant amounts of SnSe, which under an uniaxial pressure reprecipitate with a preferential crystallographic orientation trapping some Te within the lattice. Under uniaxial pressure, strain energy is minimized by aligning the crystal domains with the “softer” direction parallel to the pressure axis. The lower elastic modulus of SnSe in the *a*-axis makes this the preferred crystal direction to be oriented towards the pressure axis, minimizing strain energy. At the same time, particles generally grow larger in the direction normal to the uniaxial pressure. Thus, when re-precipitating, SnSe crystals naturally grew forming plates that extended along the *bc* crystal plane, as observed from pellets consolidated

in the presence of Te.

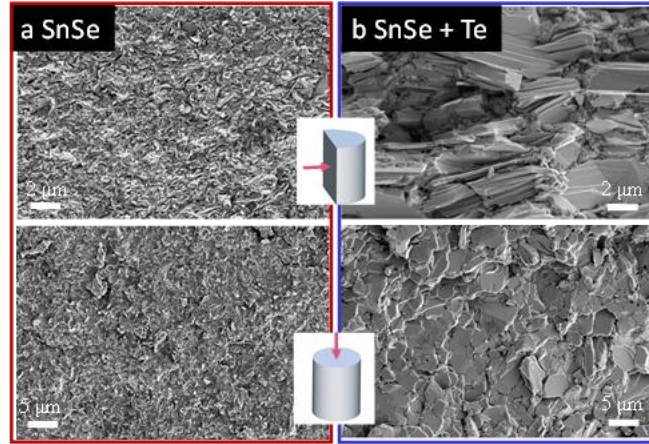


Figure 5. a) Cross section and top-view SEM micrograph of a SnSe pellet consolidated without Te. b) Cross section and top-view SEM micrograph of a SnSe pellet consolidated in the presence of a 15 mol% of Te.

From the consolidated cylinders, 8×6×1 mm rectangular bars and 1 mm thick disks were cut in-plane and out-of-plane (Figure 6). These samples were used to measure the material TE properties in two directions, parallel (//) and normal (⊥) to the pressure axis. Figures 7 and 8 display the σ , S , PF , κ , κ_L , and ZT of the SnSe pellets produced in the presence of different amounts of Te.

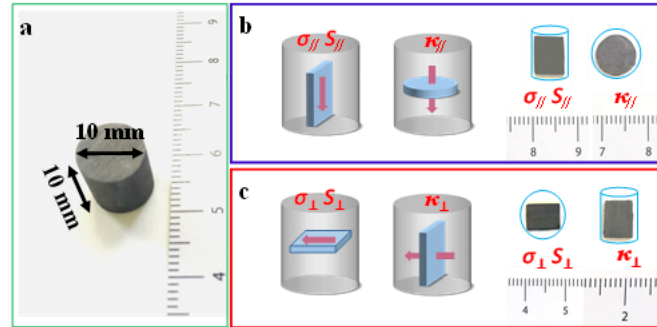


Figure 6. a) Representative photograph of one of the consolidated SnSe cylindrical pellets produced. b, c) Schematic illustrations and photographs of the samples obtained from the cylindrical pellets and used to measure σ , S and κ in both direction, parallel (b) and normal (c) to the press direction.

With the addition of Te, σ systematically increased in both directions, especially in the low-temperature range measured (Figures 7a and 8a). The presence of Te during consolidation enhanced the material crystallinity, thus improving charge carrier mobility. At the same time,

the charge carrier concentration could increase due to the presence of Te within the lattice, which reduced the material band gap, and to the increase of the concentration of Sn vacancies associated with the overall increase of the chalcogen-to-tin ratio.¹⁵ As expected, $\sigma_{\perp} > \sigma_{\parallel}$ due to the higher charge carrier mobilities in the *bc* crystal plane compared with the *a* direction and the extended size of the crystal domains in the $\perp$ direction within the layered pellets. Surprisingly, a decrease of $\sigma_{\perp}$ was observed in the sample containing the highest amount of Te. We associate this result to the scattering of charge carriers on Te domains. This scattering affects more significantly $\sigma_{\perp}$ than $\sigma_{\parallel}$ due to the former higher charge carrier mobility in the direction normal to the pressure axis.

Meanwhile, *S* decreased with the addition of increasing amounts of Te due to the increase of the charge carrier concentration. *S* started to decrease with temperature due to bipolar effects at temperatures above 600 K for SnSe and at slightly higher temperatures for SnSe-Te (Figures 7b and 8b). Moderate differences in *S* were observed when comparing the measurements done in the two different pellet directions, consistent with the low dependence of *S* on scattering.

The dependence of κ with the amount of Te was not straightforward. κ decreased with the introduction of small amounts of Te, but increased at higher Te concentrations (Figures 7e and 8e). As expected, $\kappa_{\perp} > \kappa_{\parallel}$ due to the higher intrinsic κ in the *bc* plane and to the extended size of the crystal domains in the plane $\perp$ to the press axis. The same pattern was obtained in the two directions, but minimum $\kappa_{\parallel}$ and $\kappa_{\perp}$ were obtained at different amounts of Te, *x*=0.15 and *x*=0.2, respectively. Similar values and dependences were obtained once subtracted the electronic contribution to the thermal conductivity (Figures 7e and 8e).

Overall, *ZT* values of SnSe pellets consolidated in the presence of Te were systematically higher than those of pure SnSe, both in in-plane and out-of-plane. Highest *ZT* values were obtained from the blend containing a nominal 15 mol% of Te. The increase of *ZT* with the presence of Te during consolidation was mainly related to the higher electrical and lower thermal conductivities obtained when compared with SnSe pellets consolidated without Te.

Figure 9 displays the comparison between the TE properties of pure SnSe and the best performing SnSe-Te nanomaterial, consolidated in the presence of 15 mol% of Te, measured in two normal directions in a temperature range up to 790 K. Above 700 K, σ increased and *S* decreased sharply due to the thermal activation of charge carrier across the band gap. Surprisingly, higher *ZT* values, up to 1.4 at 790 K, were reached in the out-of-plane direction, coinciding with the preferential *a*-axis orientation of SnSe. In previous works, higher *ZT* values

were usually obtained in the b and c axis due to the much higher σ and still moderate κ measured in these directions when compared with the a axis (Table 2). In our pellets, κ in the $//$ direction was comparatively small, but in the $\perp$ direction was higher than in single crystals. This could be associated to the presence of Te at the interphases and within the lattice, and potentially to a partial oxidation of the NCs.^{19,20}

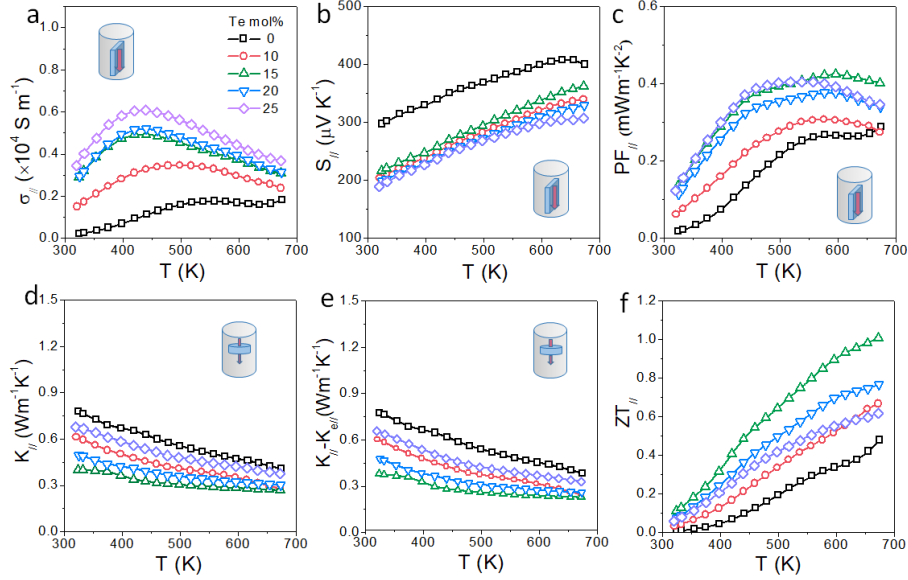


Figure 7. TE properties of SnSe and SnSe-Te nanomaterials measured along the direction of the pressure axis: a) electrical conductivity, $\sigma_{//}$; b) Seebeck coefficient, $S_{//}$; c) power factor, $PF_{//}$; d) total thermal conductivity, $\kappa_{//}$; e) thermal conductivity after subtraction of electronic component, $\kappa_{//} - \kappa_{e//}$; and f) TE figure of merit, $ZT_{//}$.

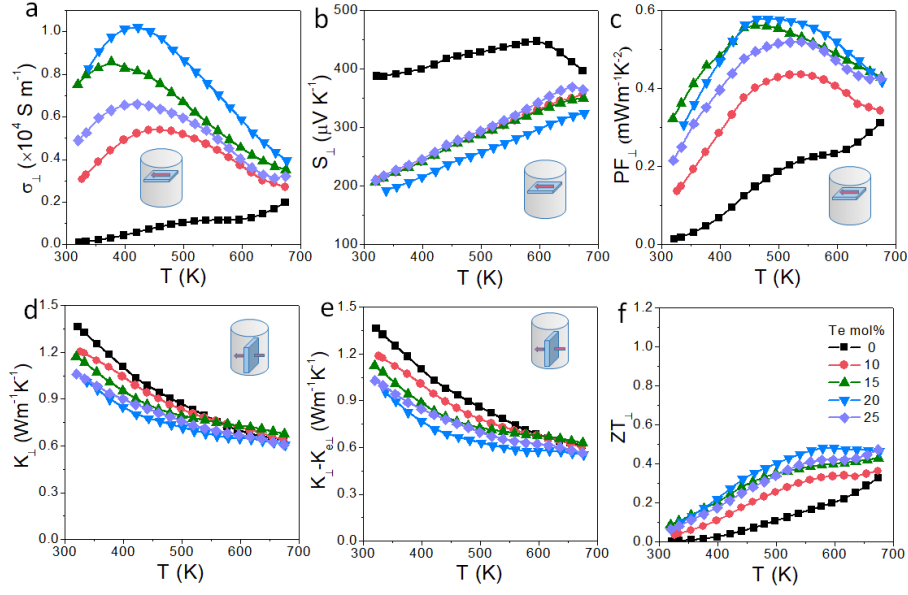


Figure 8. TE properties of SnSe and SnSe-Te nanomaterials measured in the direction normal to the pressure axis: a) electrical conductivity, $\sigma_{\perp}$; b) Seebeck coefficient, $S_{\perp}$; c) power factor, $PF_{\perp}$; d) total thermal conductivity, $\kappa_{\perp}$; e) thermal conductivity after subtraction of electronic component, $\kappa_{\perp} - \kappa_{e\perp}$ and f) TE figure of merit, $ZT_{\perp}$.

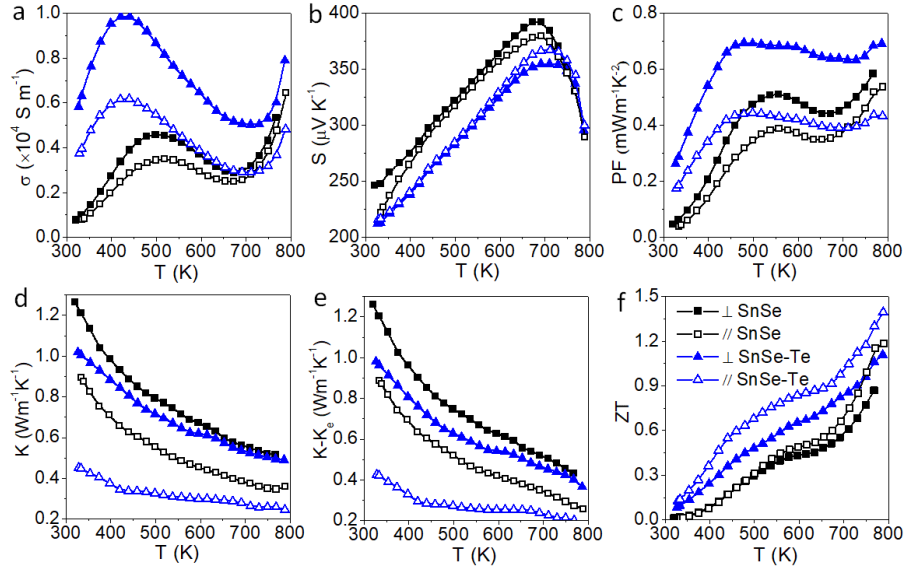


Figure 9. TE properties of SnSe and SnSe-Te (10 mol% of Te) nanomaterials measured from ambient temperature to 800 K along and normal to the pressure axis: a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) power factor, PF ; d) total thermal conductivity, κ ; e) thermal conductivity after subtraction of electronic component, $\kappa - \kappa_e$; and f) TE figure of merit, $ZT_{\parallel}$.

Table 2. Comprehensive summary on the TE performance of previously reported p-type SnSe at 790K.

P-type	Direction	ZT at 790K	Ref
Sn_{0.97}Na_{0.03}Se_{0.9}S_{0.1} (single crystal)	b	2.3 (773K)	²¹
SnSe (single crystal)	b	2.2	⁵
SnSe	a	1.4	This work
SnSe + 4% InSe_y	b	1.4	²²
Sn_{0.93}Pb_{0.02}Se	a	1.4 (773K)	²³
Sn_{0.98}Pb_{0.01}Zn_{0.01}Se	a	1.25	²⁴
Sn_{0.95}Se	a	1.25	²⁵
Sn_{0.98}Se	b	1.2	²⁶
Na_{0.005}K_{0.005}Sn_{0.99}Se	b	1.2 (773K)	²⁷
Na_{0.01}(Sn_{0.95}Pb_{0.05})_{0.99}Se	b	1.2 (773K)	²⁸
SnSe + 1% PbSe	a	1.2	²⁹
SnSe+Ag₂S	a	1.13 (773K)	³⁰
SnSe_{0.9}Te_{0.1}	b	1.1	¹⁵
Sn_{0.882}Cu_{0.118}Se	b	1.1	³¹
SnSe	b	0.8	³²
Na_{0.01}Sn_{0.99}Se	b	0.8	³³
K_{0.01}Sn_{0.99}Se	b	0.8	³³
Zn_{0.01}Sn_{0.99}Se	b	0.65	³⁴
Ag_{0.01}Sn_{0.99}Se	b	0.6 (750K)	³⁵

2.5 Conclusions

P-type polycrystalline SnSe materials with marked crystallographic texture were produced from blends of SnSe NCs and Te NRs through hot-pressing them at a temperature above Te melting point. The presence of Te promoted the material crystallization in the form of a laminar structure with the *a*-axis along the pressure direction. Part of the Te used for the liquid phase sintering process was found within the SnSe lattice and part in the form of elemental Te within the consolidated material. The TE properties of the produced nanomaterials were measured in two perpendicular directions, along and normal to the pressure axis. SnSe nanomaterials consolidated in the presence of Te showed higher electrical conductivities and lower Seebeck

coefficients and thermal conductivities than pure SnSe. TE figures of merit up to $ZT \sim 1.4$ at 790 K were measured from the SnSe nanomaterial consolidated in the presence of Te and measured along the pressing direction. Somehow surprisingly, lower ZT values were obtained in the direction normal to the pressure axis.

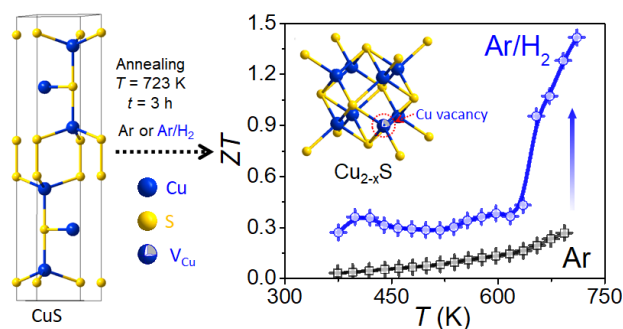
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Chapter 3 Effect of the Annealing Atmosphere on Crystal Phase and Thermoelectric Properties of Copper Sulfide



3.1 Abstract

Cu_{2-x}S has become one of the most promising TE materials for application in the middle-high temperature range. Its advantages include the abundance, low cost and safety of its elements and a high performance at relatively elevated temperatures. However, stability issues limit its operation current and temperature, thus calling for the optimization of the material performance in the middle temperature range. Here, we present a synthetic protocol for large scale production of covellite CuS NPs at ambient temperature and atmosphere, and using water as a solvent. The crystal phase and stoichiometry of the particles are afterwards tuned through an annealing process at a moderate temperature under inert or reducing atmosphere. While annealing under argon results in Cu_{1.8}S nanopowder with a rhombohedral crystal phase, annealing in an atmosphere containing hydrogen leads to tetragonal Cu_{1.96}S. High temperature XRD analysis shows the material annealed in argon to transform to the cubic phase at *ca.* 400 K, while the material annealed in the presence of hydrogen undergoes two phase transitions, first to hexagonal and then to the cubic structure. The annealing atmosphere, temperature and time allow to adjust the density of copper vacancies and thus to tune the charge carrier concentration and material transport properties. In this direction, the material annealed under Ar is characterized by higher σ but lower S than the material annealed in the presence of hydrogen. By optimizing the charge carrier concentration through the annealing time, Cu_{2-x}S with record figures of merit in the middle temperature range, up to 1.41 at 710 K, is obtained. We finally demonstrate that this strategy, based on a low-cost and scalable solution synthesis process, is also suitable for the production of high performance Cu_{2-x}S layers using high throughput and cost effective printing technologies.

3.2 Introduction

TE devices are able to directly convert ubiquitous temperature gradients into electricity, to actively cool local heat sources or sensitive devices, and to precisely control temperature without moving parts or working gases. They have countless potential applications, but their high manufacturing and materials costs hamper their cost-effectiveness and limit their widespread implementation. To overcome these drawbacks, TE devices must be manufactured employing high throughput technologies and using materials based on low cost and abundant elements.

The TE properties of copper sulfides have been explored for well over a century.^{1–4} However, it was not until this last decade that copper sulfides raised large attention not only because of the low cost and abundance of the involved elements, but also because of their outstanding TE performance in the middle-high temperature range.^{5–11}

Copper chalcogenides and particularly copper sulfides are a fascinating family of materials with exceptional characteristics:¹² i) high element abundance, low cost and minor environmental and health impact; ii) enormous structural and compositional versatility; iii) low energy of formation of defects resulting in high defect densities; iv) chalcogen atoms forming regular lattices with Cu atoms occupying not well-defined interstitial sites; v) strong influence of Cu 3d states in the chalcogenide electronic properties; vi) singular and highly tunable functional properties, including small direct band gaps, plasmonic properties, high charge carrier concentrations, high ionic conductivity, and low thermal conductivity.

Even the simplest binary Cu-S system exhibits a particularly rich phase diagram with many possible stoichiometric compositions and crystallographic phases, some of them with quite complex atomic arrangements.^{13–16} The main crystal phases in the Cu-S system at ambient temperature are the monoclinic chalcocite ($\text{Cu}_{2.0-1.997}\text{S}$), monoclinic djurleite ($\text{Cu}_{1.97}\text{S}$ - $\text{Cu}_{1.93}\text{S}$), triclinic roxbyite ($\text{Cu}_{58}\text{S}_{32}$ or $\text{Cu}_{1.81}\text{S}$), cubic digenite (Cu_9S_5 or $\text{Cu}_{1.8}\text{S}$), orthorhombic anilite (Cu_7S_4 or $\text{Cu}_{1.75}\text{S}$), and hexagonal covellite (CuS). These crystal structures are based upon approximately hexagonal (djurleite, chalcocite, roxbyite and covellite) or cubic (anilite and digenite) close-packing of the sulfur atoms, where Cu atoms occupy various interstitial sites with different statistical probabilities that depend on stoichiometry and temperature.^{15,17}

Chalcocite Cu_2S displays a monoclinic P21/c crystal structure. This is essentially a superstructure of a hexagonal lattice with slight distortions where the 36 crystallographically

distinct Wyckoff sites are fully occupied with 12 S atoms and 24 Cu atoms.^{17,18} Stoichiometric Cu_2S is considered to be intrinsically unstable at ambient conditions owing to a thermodynamic tendency towards losing Cu through oxidation in the surface.^{19,20} Thus chalcocite NPs degrade quickly into copper deficient Cu_{2-x}S phases, most notably djurleite $\text{Cu}_{1.97}\text{S}$, which is considered the thermodynamically stable stoichiometry under ambient conditions.

Djurleite $\text{Cu}_{1.93-1.97}\text{S}$ also displays a monoclinic structure, but with a slightly reduced Cu concentration. The unit cell content of djurleite corresponds to $\text{Cu}_{62}\text{S}_{32}$ or $\text{Cu}_{1.93}\text{S}$. If an extra Cu atom is added, the unit cell content becomes $\text{Cu}_{63}\text{S}_{32}$ or $\text{Cu}_{1.97}\text{S}$, thus explaining the lower and higher limit of $\text{Cu}_{1.93-1.97}\text{S}$ for djurleite. Both chalcocite and djurleite are very common phases at ambient temperature and are often intermixed or intergrown.²¹

Roxbyite $\text{Cu}_{58}\text{S}_{32}$ or $\text{Cu}_{1.81}\text{S}$ is closely related to chalcocite and djurleite, but it has a triclinic structure consisting of a distorted hexagonal framework of 32 S atoms with 58 independent Cu atoms, all having triangular coordination.²² Roxbyite is uncommon in bulk, but can be readily synthesized in the form of NCs.²³

Digenite $\text{Cu}_{1.8}\text{S}$ has a cubic, but still complex structure with space group $\text{Fd}3\text{m}$.^{24,25} Sulfur atoms form a fcc structure and the copper atoms are statistically distributed over several sites. It is sometimes referred to as Cu_9S_5 but since Cu atoms are statistically distributed, the formula $\text{Cu}_{1.8}\text{S}$ is preferred.²⁶

Anilite Cu_7S_4 or $\text{Cu}_{1.75}\text{S}$ has an orthorhombic crystal phase, space group Pnma , in which S atoms approximate an fcc arrangement and Cu atoms are ordered in the interstices.^{27,28}

Finally, covellite CuS has a peculiar layered structure for such a simple stoichiometry. It is also a hexagonal phase with alternating layers of CuS and $\text{Cu-S}_2\text{-Cu}$.²⁹⁻³¹ This unusual structure is explained by the fact that it is more energetically favorable for the S atoms to covalently bond to each other than to bond with Cu atoms.²⁹

The Cu-S phase diagram is actually much more complex, with additional well-defined phases/minerals, including geerite ($\text{Cu}_{1.6}\text{S}$), spionkopite ($\text{Cu}_{1.39}\text{S}$) and yarrowite ($\text{Cu}_{1.12}\text{S}$). Furthermore, several metastable phases also exist and are commonly obtained at ambient temperature, such as a tetragonal $\text{Cu}_{1.96}\text{S}$ phase^{13,25,32,33} and a rhombohedral $\text{Cu}_{1.8}\text{S}$ structure.^{34,35}

At relatively low temperatures, just above 70-100 °C depending on stoichiometry, Cu atoms become highly mobile, which makes it difficult to determine their exact positions. Thus only a

statistical distribution of Cu atoms over the various Wyckoff positions in the lattice can be determined and the symmetry of the observed crystal structures increases.^{36,37} The ambient temperature monoclinic chalcocite phase, known as low chalcocite, transforms into a hexagonal phase known as high chalcocite at around 376 K, and to a cubic phase known as cubic chalcocite at about 709 K. Monoclinic djurite is stable up to about 363 K. At this temperature, it transforms into a combination of hexagonal chalcocite and cubic digenite phases, with the hexagonal phase disappearing as temperature further increases.²⁵ Digenite undergoes complete phase transition into a higher symmetry cubic phase at even lower temperature, 346 K.^{26,34} The high temperature digenite phase is known as high digenite, and it is identical to the cubic chalcocite.³⁶ Above 710 K only high-digenite with Cu_2S composition or cubic chalcocite, in equilibrium with copper, can be obtained.^{26,36} Anilite is also stable only to 345 K,^{36,38} transforming into the cubic high digenite phase at a higher temperature.

Phase and stoichiometry do not always go together. For instance, hexagonal digenite has been reported especially in NP form, and a cubic high chalcocite has been also described. To minimize confusion, it is wise to associate the mineral names to the crystal phase regardless of the exact composition, thus hexagonal digenite is better referred to as a Cu-deficient high chalcocite and the cubic high chalcocite as a Cu-rich high digenite.¹⁷

Phase transitions strongly depend on several parameters, including the initial phase, pressure and composition. The lower the Cu content, the lower the transition temperature to higher symmetry phases, *e.g.* from monoclinic to hexagonal and cubic phase. Besides, the phase transition temperature also strongly depends on the crystal domain size. A good example is the provided by chalcocite Cu_2S NCs, where the smaller the size, the smaller the transition temperature.³⁹ Actually, small enough NCs are reported to maintain the hexagonal high chalcocite phase even at ambient temperature.⁴⁰ The atmosphere composition, and particularly the sulfur partial pressure is another parameter that strongly influences the phase transition.²⁶

The electronic structure and functional properties of Cu_{2-x}S depend on both stoichiometry and crystal phase.^{41,42} In Cu chalcogenides, the top of the valence band has a strong contribution from the chalcogenide p orbitals and the bottom of the conduction band mainly has contributions from Cu 4s and 4p orbitals.^{12,43} It is assumed that each Cu atom contributes to bonding with one 4s electron and each chalcogen atom contributes with six p electrons. In the fully stoichiometric Cu_2S material, the valence band is completely filled and the material should behave as an intrinsic semiconductor. However, when Cu vacancies are created, holes

are generated at the top of the valence band. Cu deficiency mainly affects the valency of the chalcogen, whereas the valency of Cu remains close to +1 in all phases and stoichiometries.

The energy conversion efficiency and coefficient of performance of a TE device depend on the temperature gradient harvested/generated and on three interconnected material parameters: σ , S and κ . Besides, the thermal conductivity has two main contributions, κ_L and κ_e that is related to σ through the Wiedemann–Franz law, $\kappa_e = L\sigma T$, where L is the Lorentz number and T the absolute temperature. All these parameters combine within a TE figure of merit that is frequently expressed in its dimensionless form: $ZT = \sigma S^2 T / \kappa$. Thus, a high performance TE material is characterized by a high electrical conductivity and Seebeck coefficient, and a low thermal conductivity. Besides selecting materials with complex and/or highly anisotropic crystal structures, that contain a large defect density, a high atomic disorder and/or numerous grain boundaries to minimize thermal conductivity, a main parameter to be tuned to maximize ZT is the charge carrier concentration. The density of free charges has a strong influence on the three main material parameters. σ and thus κ_e increase with the n : $\sigma = n\mu e$, where μ is the charge carrier mobility and e is the elemental electron charge. S decreases with n through the following expression obtained for metals or degenerated semiconductors with a parabolic band and energy independent charge carrier scattering:

$$S = \frac{8\pi^2 k_B^2 T}{3eh^2} m^* \left(\frac{\pi}{3n} \right)^{2/3}$$

Where k_B and h are the Boltzmann and Planck constants, respectively, and m^* is the effective mass. Overall, the optimum charge carrier concentrations are around 10^{19} cm^{-3} . A higher charge carrier concentration results in too low S and too high κ , and a lower n leads to too low electrical conductivities.

All Cu_{2-x}S exhibit p -type electronic character with a stoichiometry-dependent hole concentration that increases with the number of Cu vacancies (x). Besides, the type of sulfur arrangement in the crystal structure also plays an important role on the electronic transport properties of the material.⁴⁴ On the other hand, the high copper disorder at moderate and high temperature gives rise not only to a virtually fluid-like ionic mobility but also to an ultralow thermal conductivity. As a drawback, this Cu mobility gives rise to copper migration instabilities. In operating TE devices, these instabilities can be overcome by proper encapsulation, by limiting the working current and operation temperature, and/or by introducing electron-conducting but ion-blocking layers.⁴⁵

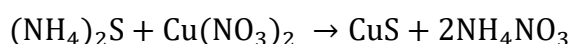
TE properties are very sensitive to the Cu deficiency, *i.e.* the Cu_{2-x}S stoichiometry, which strongly depends on the synthesis conditions, structural parameters and treatment history of the sample. Tuning the crystal structure, composition and density of intrinsic defects at the synthesis step or through post-synthesis treatments can be a very effective but still underexplored strategy to optimize TE properties of copper sulfide in the middle temperature range where this material is stable.^{46,47}

In the present work, we demonstrate a simple and low-cost room temperature aqueous phase method for the large-scale preparation of copper sulfide. Additionally, we analyze the possibilities of tuning the crystallographic phase and stoichiometry of nanocrystalline Cu_{2-x}S by means of thermal annealing at moderate temperatures under inert or reducing gas atmospheres. Finally, we analyze the TE properties of the obtained compounds as a function of the annealing temperature, time and atmosphere, and explain the obtained results taking into account the different sample stoichiometries and the phase transitions undergone by the materials when heated.

3.3 Experimental section

Chemicals: Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) and ammonium sulfide solution ((NH₄)₂S 20% in H₂O) were purchased from Fisher. Chemicals were used as received without further purification.

Copper sulfide NPs: The reaction took place at ambient atmosphere and temperature inside a fume hood. To obtain around 1 g of NPs, 10 mmol Cu(NO₃)₂·3H₂O was dissolved in 35 ml of deionized water in a centrifuge tube using ultrasounds until obtaining a clear light-blue solution. Then, 2 ml (NH₄)₂S was injected into the centrifuge tube, which was strongly shaken to force a proper mixing of the reactants. Upon (NH₄)₂S injection, the solution turned black owing to the nucleation of copper sulfide through the reaction:



After 1 min reaction, particles were recovered by centrifugation. Then, they were purified using 5 dispersion/precipitation cycles using deionized water and ethanol. Finally, NPs were dried under vacuum overnight at room temperature and stored in an Ar-filled glovebox.

Nanomaterial consolidation: Dried NPs were annealed at 450 °C for 180 min under gas flow inside a tube furnace. Two different gas atmospheres were studied: argon and 5% hydrogen in

argon (Ar/H₂). The annealed nanopowders were loaded into a 10 mm graphite die and hot-pressed at 420 °C and 60 MPa for 4 min using a custom-made HP inside the Ar-filled glovebox.^{51–55} The relative densities of the obtained pellets were measured by the Archimedes' method to be *ca.* 93% of the theoretical value.

Cu_{2-x}S layers: An ink was prepared by mixing annealed NPs with ethanol. The ink was printed on a mica tape, and let it dry for a few minutes. Then, the dried mica tape was loaded into a 10 mm graphite die and hot-pressed at 420 °C and 60 MPa for 4 min using a custom-made HP inside the Ar-filled glovebox.

Structural and chemical characterization: XRD (2θ angle: 20° to 80°; scanning rate: 1.5°/min) analyses were carried out on a Bruker AXS D8 ADVANCE X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406$ Å). Temperature-dependent XRD patterns were collected using an Anton Paar XRK 900 Reactor chamber with sample spinner with height corrections. The temperatures were ramped at a rate of 60 °C/min operating at 40 kV from 323 K to 703 K, and then isothermally held for 30 minutes at each temperature. The height of the sample was aligned, and diffraction results were collected from 20° to 60° in 2θ at a speed of 2°/min. Size and morphology of NPs were examined by TEM using a ZEISS LIBRA 120, operating at 120 kV, and field-emission SEM on an Auriga Zeiss operated at 5.0 kV. The material composition was analyzed using an Oxford EDX attached to a Zeiss Auriga SEM at 20.0 kV. Composition was also analyzed by ICP-OES using a ICPE-9820 system. For ICP measurements, samples were prepared by the digestion of crushed powder in aqua regia overnight followed by dilution in MQ-Water (Milipore). Crystallographic structure and chemical composition were analyzed by high resolution TEM (HRTEM) and electron energy loss spectroscopy (EELS), respectively, using a Tecnai F20 field-emission gun microscope at 200 keV with an embedded Gatan QUANTUM image filter. X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Specs system equipped with a Mg anode XR50 source operating at 250 W and a Phoibos 150 MCD-9 detector (Specs GmbH). The pressure in the analysis chamber was kept below 10⁻⁷ Pa. Data processing was performed with the CasaXPS program (Casa Software Ltd.).

TE Property Measurements: Seebeck coefficients were measured using a static DC method. Electrical resistivity data was obtained by a standard four-probe method. Both the Seebeck coefficient and the electrical resistivity were measured simultaneously in an LSR-3 LINSEIS system in the temperature range between room temperature and 710 K under helium atmosphere. All samples were measured at least 3 consecutive times during heating up to

around 710 K. Taking into account the system accuracy and the measurement precision, an error of *ca.* 4% in the measurement of the electrical conductivity and Seebeck coefficient was estimated. The electrical conductivity and Seebeck coefficient of the layers was measured by clamping the two ends of the mica tape with a copper electrode (Figure 7a).

κ were obtained by multiplying the λ , C_p and ρ , where $\kappa = \lambda C_p \rho$. A Xenon Flash Apparatus XFA600 was used to determine the thermal diffusivities of the samples with an estimated error of *ca.* 5 %. The C_p of the samples was evaluated using a NETZSCH DSC 404 F3 differential scanning calorimeter (DSC) at a heating rate of 10 K/min under a flow of high purity N₂ in Pt-Rh/Al₂O₃ crucible. C_p curve was calculated by NETZSCH Proteus[®] software based on C_p ratio method, with a standard sample of sapphire. The sample was first heated to 50 °C and keep for 10 min to avoid heat hook, then increase the temperature to 430 °C with a ratio of 10 K/min, and then cool inside the machine. Figure S12b displays the heat capacity measured for a sample annealed in Ar and a sample annealed in Ar/H₂ during 3h. The C_p values in the phase transition temperature range were meaningless, so we extrapolated the C_p values in the temperature regions corresponding to the phase transitions to calculate ZT. For comparison, C_p was also estimated from empirical formulas by the Dulong–Petit limit (3R law). Dulong–Petit C_p values were slightly higher than experimental C_p values. Figure 17c displays a comparison of the ZT values obtained when considering the experimental C_p or the calculated C_p . The density values were measured using the Archimedes' method. To avoid cluttering the plots, error bars were not included in the figures. Hall charge carrier concentrations and mobilities at room temperature were measured with the Van der Pauw method using a magnetic field of 0.6 T (ezHEMS, NanoMagnetics).

3.4 Results and discussion

A rapid and surfactant-free synthetic protocol was developed to produce copper sulfide NPs in water and at ambient temperature using (NH₄)₂S and Cu(NO₃)₂·3H₂O as sulfur and copper precursors, respectively (Figure 1a, see details in the experimental section). Figure 1b,c shows representative SEM and TEM micrographs of the reaction product that consisted in *ca.* 60 nm NPs with flat morphology (Figure 1c). XRD analysis showed the crystal structure of the obtained NPs to match the covellite CuS phase (JCPDS No. 01-079-2321).

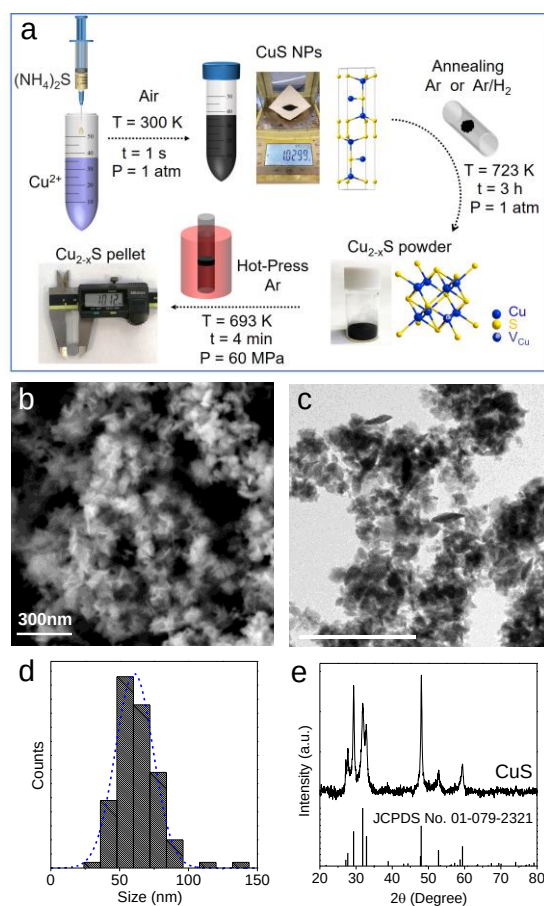


Figure 1. a) Schematic illustration of the three-step process used to produce Cu_{2-x}S pellets and which involves the synthesis of CuS NPs at ambient pressure and temperature, the annealing of the particles at 723 K in Ar or Ar/ H_2 atmosphere, and the HP of the materials at 693 K and 60 MPa. b) SEM micrograph of CuS NPs. c) TEM micrographs of CuS NPs. d) Histogram of the particle size distribution. e) XRD pattern obtained from CuS NPs.

HRTEM characterization showed the NPs to have a good crystallinity and confirmed their hexagonal covellite CuS phase (space group = $P6_3/\text{mmc}$), with $a=b=3.7917 \text{ \AA}$ and $c=16.3420 \text{ \AA}$ (Figure 2a). EELS chemical composition maps obtained from the red squared region in the high-angle annular dark-field scanning TEM micrograph displayed in Figure 2b demonstrated a homogeneous distribution of Cu and S throughout the particles.

Cu $2p_{3/2}$ and S 2p high resolution XPS spectra are displayed in Figure 2c. The Cu 2p spectrum was fitted with three bands at 933.0 eV, 935.2 eV, and 931.6 eV. The Cu $2p_{3/2}$ band at 931.6 eV was associated to Cu within a CuS chemical environment.⁴⁸ On the other hand, the two higher energy bands corresponded to two surface oxide components, probably cuprous oxide and copper sulfate.⁴⁹ The partial surface oxidation of the NPs has its origin on their manipulation and transportation in air, as observed for other materials.⁴⁸ The S 2p XPS

spectrum displayed two well-defined doublets at 161.8 eV and 168.2 eV (S 2p_{3/2}), which were assigned to lattice S within CuS and to sulfate species arising from the surface oxidation of the material, respectively.⁵⁰

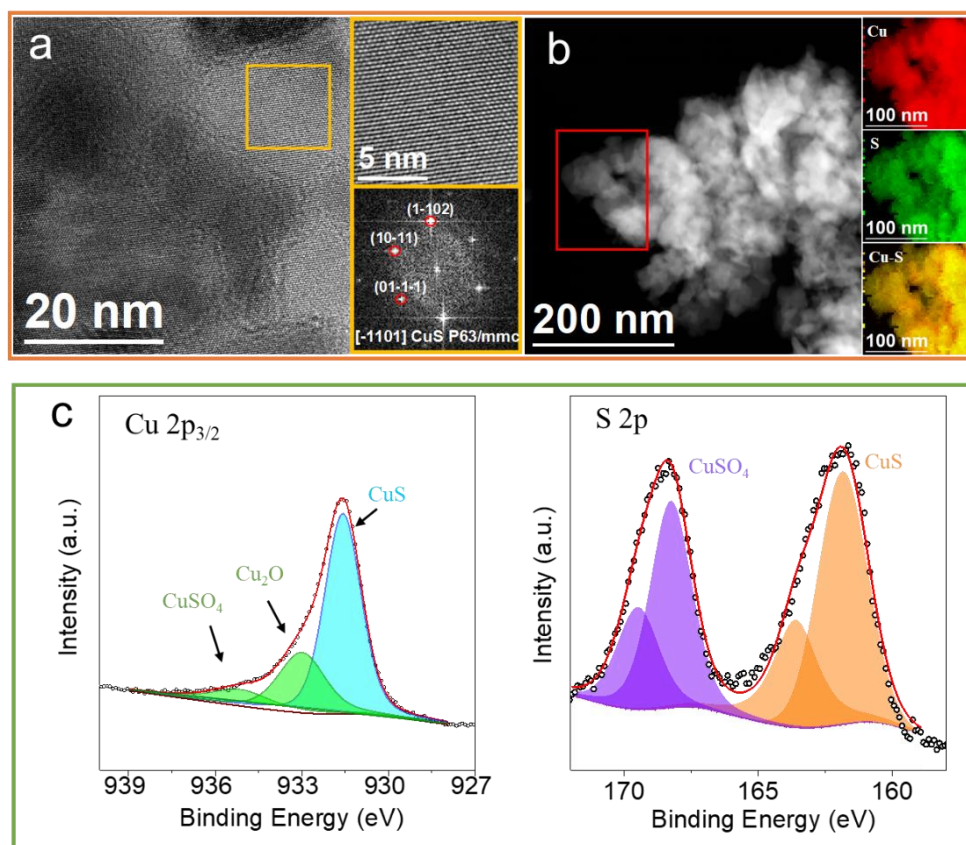


Figure 2. a) HRTEM micrograph, detail of the orange squared region and its corresponding power spectrum. CuS lattice fringe distances were measured to be 0.320 nm, 0.323 nm, and 0.304 nm, at 64.46° and 122.88° which was interpreted as the hexagonal CuS phase, visualized along its [-1101] zone axis. b) HAADF-STEM micrograph and EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Cu L_{2,3}-edges at 931 eV (red) and S L_{2,3}-edges at 165 eV (green). c) Cu 2p_{3/2} and S 2p high resolution XPS spectra obtained from CuS NPs.

CuS NPs were annealed at 723 K in a tube furnace under gas flow. Two different gases were used for the annealing treatments, Ar and 5% H₂ in Ar (Ar/H₂). The annealing time was set at 3h for Ar, and it was varied between 2 h and 4 h for Ar/H₂. Figure 3 displays the room temperature XRD patterns of the annealed powders. Covellite CuS showed to be thermally unstable in a sulfur-free atmosphere. Upon heating the particles, CuS dissociated into Cu_{2-x}S and sulfur that was lost through volatilization. The sample annealed in Ar for 3h displayed a

metastable rhombohedral $\text{Cu}_{1.8}\text{S}$ phase at ambient temperature. On the other hand, the CuS particles annealed in the presence of H_2 , displayed a larger loss of S. The sample annealed for 2 h in Ar/ H_2 displayed a combination of the metastable rhombohedral $\text{Cu}_{1.8}\text{S}$ and tetragonal $\text{Cu}_{1.96}\text{S}$ phases, being the former the dominant one. After 3 h at 450 °C in an Ar/ H_2 atmosphere, the rhombohedral phase was still identified, but the tetragonal phase became dominant and the monoclinic Cu_2S phase appeared. When increasing the annealing time to 4 h in Ar/ H_2 , a combination of monoclinic Cu_2S and tetragonal $\text{Cu}_{1.96}\text{S}$ was obtained, being the monoclinic the main phase.

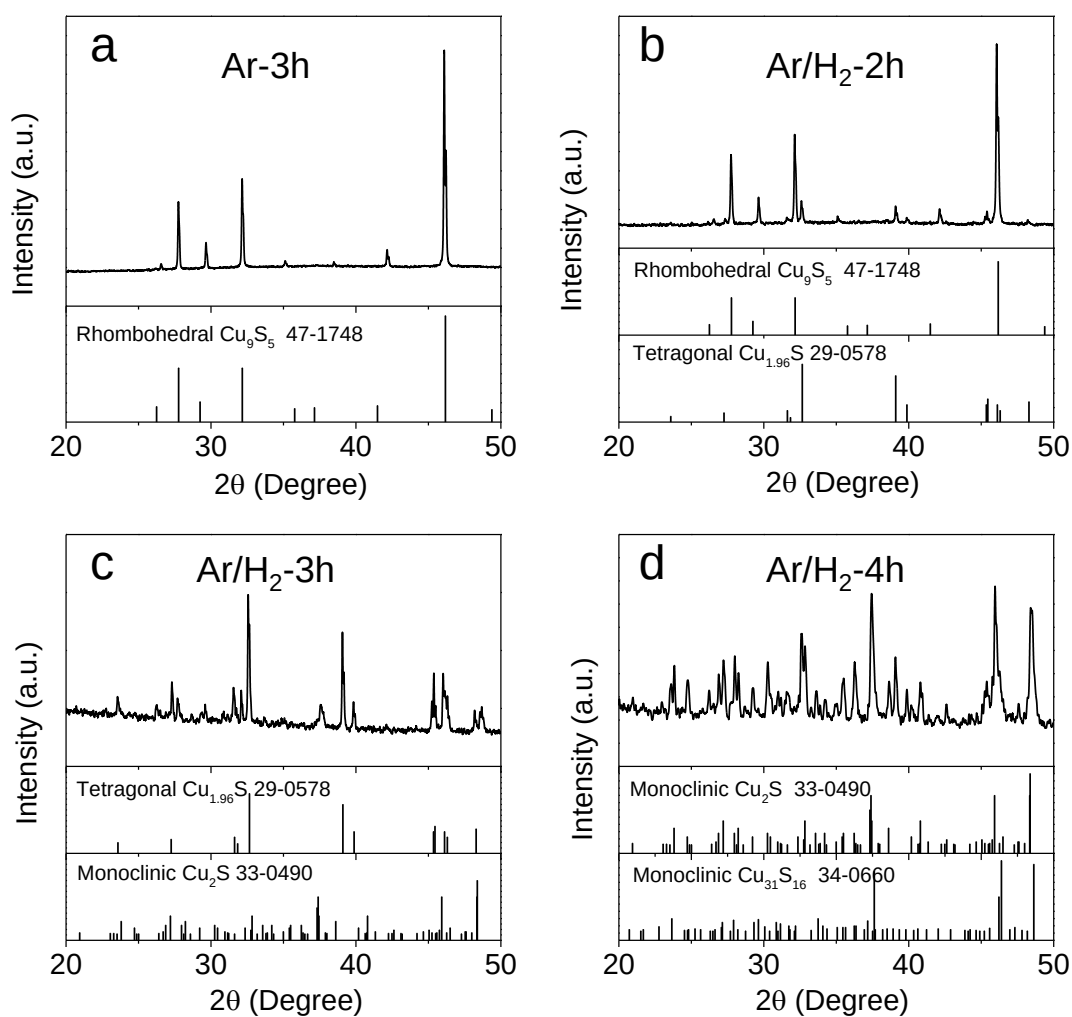


Figure 3. XRD patterns of Cu_{2-x}S powders obtained from annealing covellite CuS NPs under different gas flow, Ar or Ar/ H_2 , and different times, from 2 h to 4 h, as indicated in each pattern.

SEM characterization of the annealed powders showed the Cu_{2-x}S particles to grow during the thermal treatment, independently of the used gas flow (Figure 4). EDX analysis further confirmed the sulfur content to strongly decrease with the annealing process, and the final Cu/S

ratio to be higher for the sample annealed in the presence of H_2 (Table 1). Figures 5 and 6 display representative HRTEM images and EELS compositional maps of the samples annealed for 3 h under Ar or Ar/ H_2 flow, respectively. The power spectrum analysis of the HRTEM micrographs showed the sample annealed in Ar to display the rhombohedral $Cu_{1.8}S$ phase (space group R-3M) with $a=b=3.93$ Å and $c=48.14$ Å, consistent with XRD results. Besides, HRTEM characterization showed the sample annealed under Ar/ H_2 flow for 3 h to display crystallites with the tetragonal $Cu_{1.96}S$ structure (space group P43212) with $a=b=3.9962$ Å and $c=11.2870$ Å and crystallites with the monoclinic Cu_2S structure (space group P121/C1) with $a=15.2460$ Å, $b=11.8840$ Å, and $c=13.4940$ Å, also consistently with the measured XRD pattern. EELS chemical composition maps of both samples displayed a uniform distribution of Cu and S (Figures 5b and 6b).

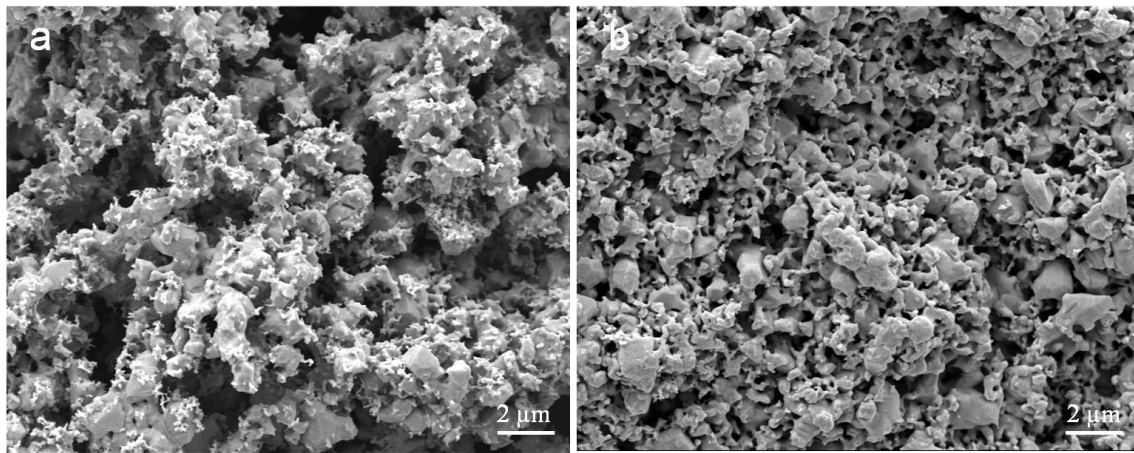


Figure 4. SEM micrographs of $Cu_{2-x}S$ nanopowder annealed during 3 h under a) Ar and b) Ar/ H_2 .

Table 1. EDX composition of CuS NPs before and after the annealing process.

Sample	Cu at%	S at%
CuS NPs	51	49
$Cu_{2-x}S$ annealed in Ar for 3 h	64	36
$Cu_{2-x}S$ annealed in Ar/ H_2 for 3 h	67	33

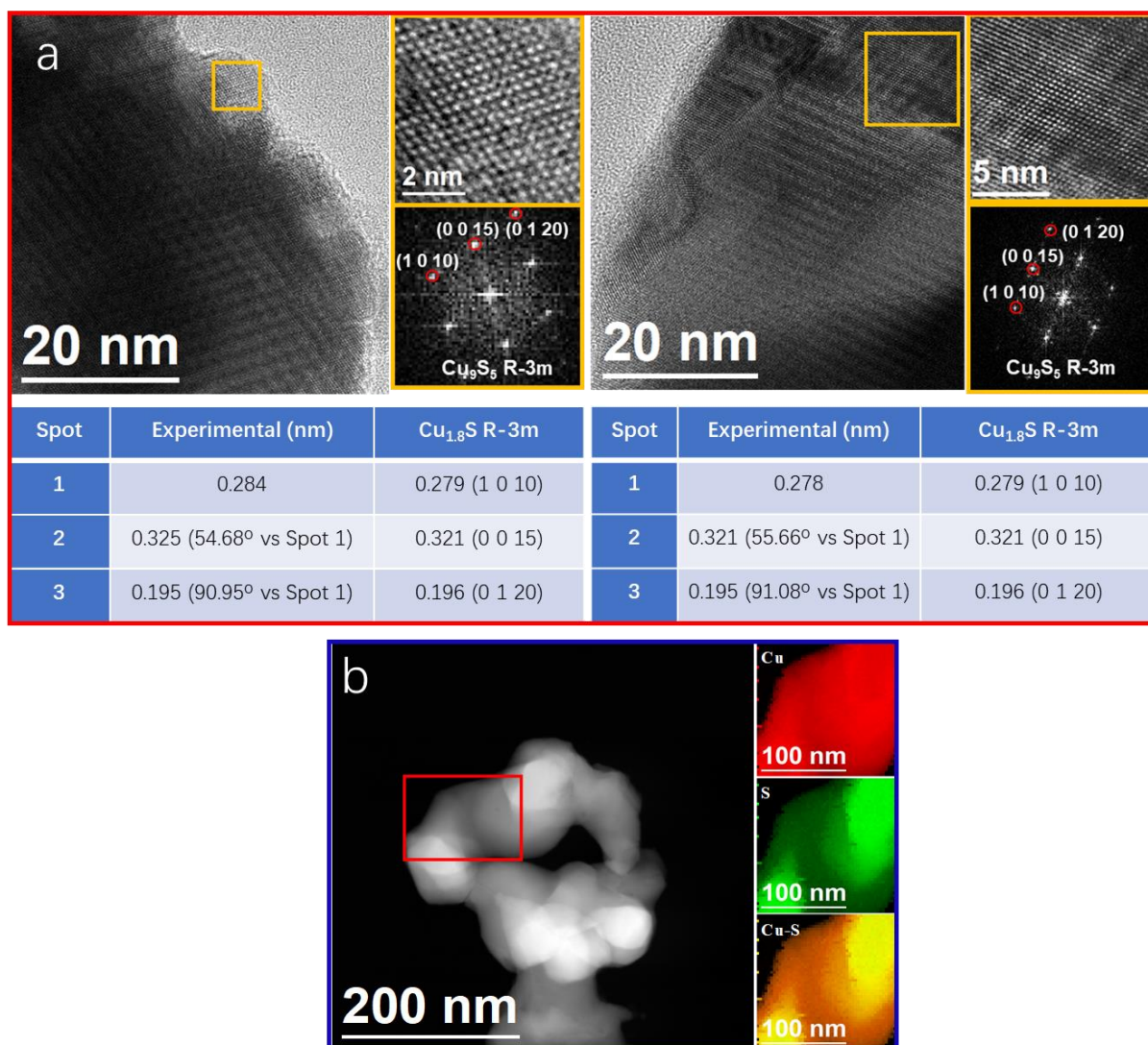


Figure 5. a) HRTEM micrographs, details of the orange squared regions and their corresponding power spectra of Cu_{2-x}S NPs annealed 3 h under Ar. The power spectra were consistent with a Cu_{1.8}S rhombohedral phase (space group R-3M) with $a=b=3.9300$ Å and $c=48.1400$ Å. Tables display the comparison between the experimental and the theoretical bulk plane spacing distances and angles between planes. b) EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Cu L_{2,3}-edges at 931 eV (red), S L_{2,3}-edges at 165 eV (green) and composites of Cu-S.

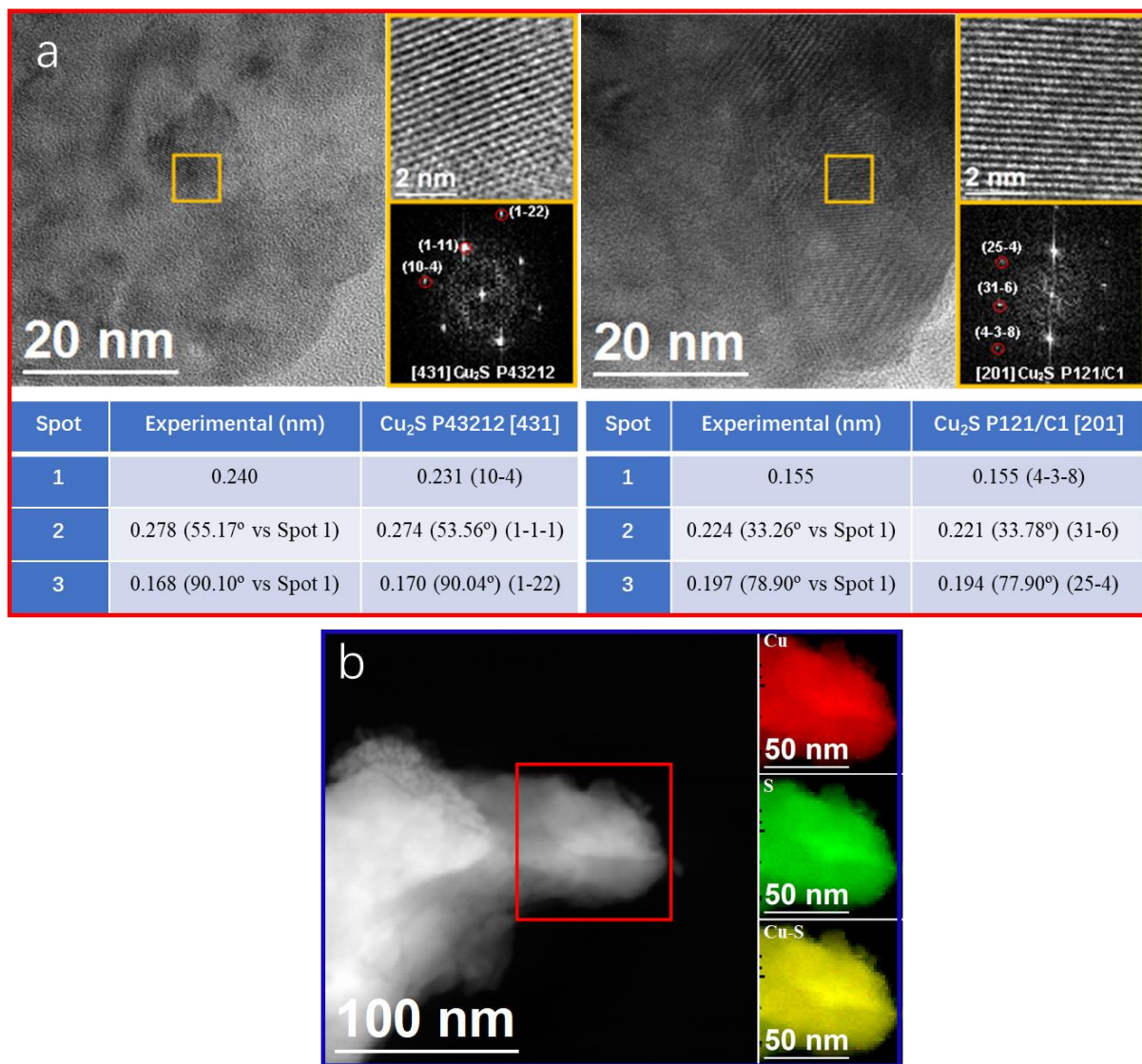


Figure 6. a) HRTEM micrographs, details of the orange squared regions and their corresponding power spectra of Cu_{2-x}S NPs annealed 3 h under Ar/H₂. HRTEM data on the left shows a crystal structure in agreement with the Cu₂S tetragonal phase (space group P43212) with $a=b=3.9962$ Å, and $c=11.2870$ Å. Lattice fringe distances were measured to be 0.240 nm, 0.278 nm, and 0.168 nm, at 55.17° and 90.10°, which could be interpreted as the tetragonal Cu₂S phase visualized along its [431] zone axis. HRTEM data on the right shows a crystal structure in agreement with the Cu₂S monoclinic phase (space group P121/C1) with $a=15.2460$ Å, $b=11.8840$ Å, and $c=13.4940$ Å. Lattice fringe distances were measured to be 0.155 nm, 0.224 nm, and 0.197 nm, at 33.26° and 78.90°, which could be interpreted as the monoclinic Cu₂S phase visualized along its [201] zone axis. Tables display the comparison between the experimental and the theoretical bulk plane spacing distances and angles between planes. b) EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Cu L_{2,3}-edges at 931 eV (red), S L_{2,3}-edges at 165 eV (green) and Cu-S composite.

Annealed powders were subsequently loaded into a 10 mm graphite die and hot-pressed at 693 K and 60 MPa for 4 min inside an Ar-filled glove box. The relative densities of the obtained pellets were *ca.* 94% of the theoretical value, as measured by the Archimedes' method (Table 2). Figure 7 displays representative cross-section SEM micrographs of the pellets, presenting a dense structure. XRD analysis showed a minor influence of the hot-press treatment on the Cu_{2-x}S crystallographic phase (Figure 8). The XRD patterns of the pellets obtained from NPs annealed in Ar and Ar/H₂ displayed the metastable rhombohedral $\text{Cu}_{1.8}\text{S}$ phase and the dominant tetragonal $\text{Cu}_{1.96}\text{S}$ structure, respectively, consistently with the results obtained from the nanopowders. The minor rhombohedral component observed on the material annealed in Ar/H₂ disappeared after the HP. Additional HRTEM characterization of the pellets confirmed the results obtained from XRD analysis (Figure 9). These pellets were used to characterize TE properties.

Table 2. Relative density of Cu_{2-x}S pellets obtained from absolute values measured by the Archimedes' method. The measured pellet density was compared with the density of Cu_2S , 5.60 g/cm³.

Sample	Measured density (g/cm ³)	Relative density
Cu_{2-x}S annealed in Ar for 3h	5.23	93.3%
Cu_{2-x}S annealed in Ar/H₂ for 2h	5.30	94.6%
Cu_{2-x}S annealed in Ar/H₂ for 3h	5.28	94.2%
Cu_{2-x}S annealed in Ar/H₂ for 4h	5.17	92.3%

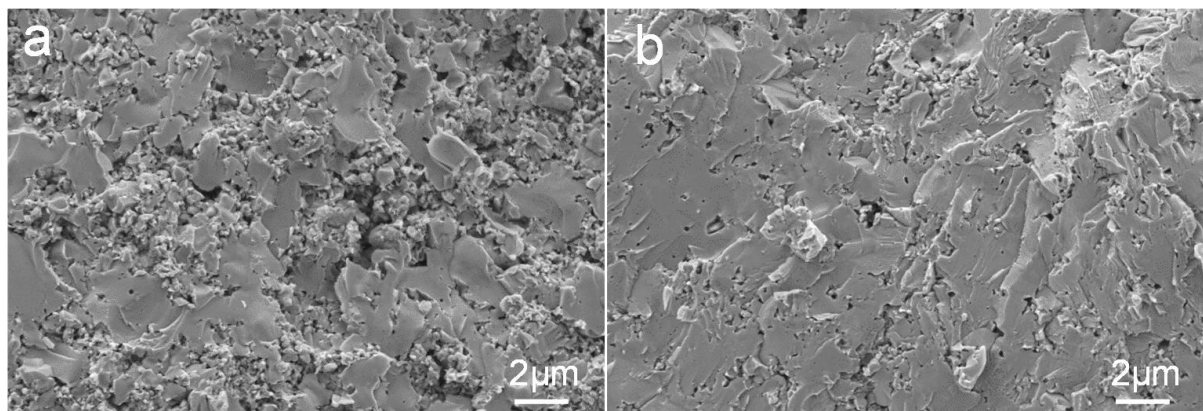


Figure 7. Cross section SEM micrographs of the pellets produced from NPs annealed 3 h under a) Ar and b) Ar/H₂.

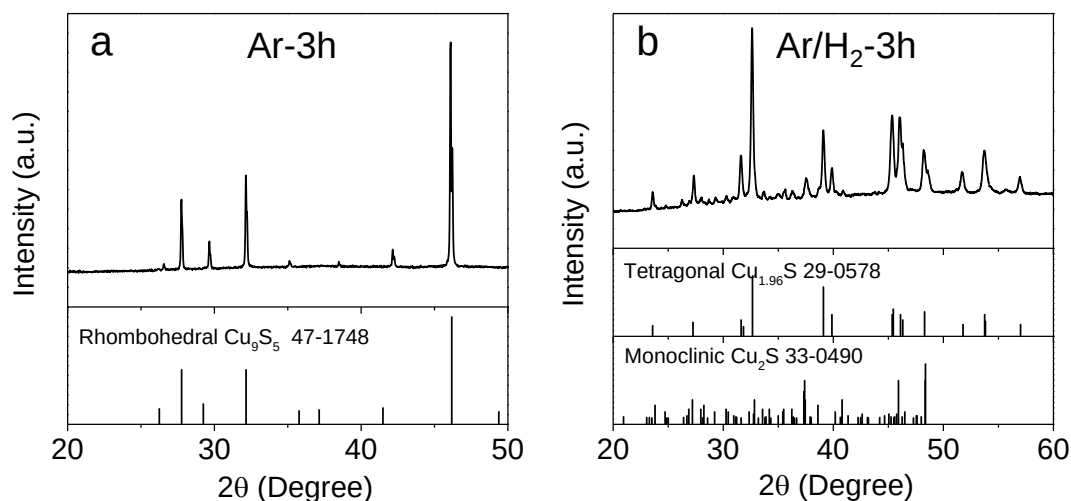


Figure 8. XRD patterns of Cu_{2-x}S pellets obtained by annealing the covellite CuS NPs for 3 h under different gas flow, Ar (a) or Ar/H_2 (b), as indicated in each pattern, and afterward HP the obtained powder at 693 K and 60 MPa.

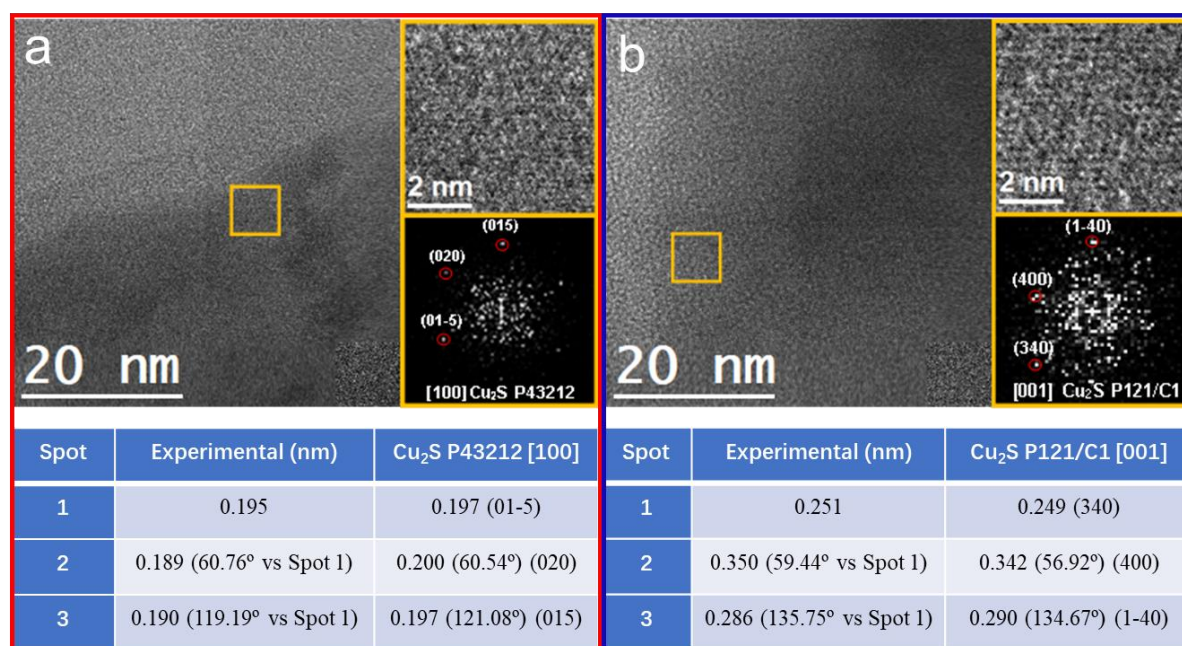


Figure 9. HRTEM micrographs, details of the orange squared regions and their corresponding power spectra from a Cu_{2-x}S pellet produced from NPs annealed 3 h under Ar/H_2 . Tables display the comparison between the experimental and the theoretical bulk plane spacing distances and angles between planes. a) The displayed crystal structure is in agreement with the Cu_2S tetragonal phase (space group P43212) with $a=b=3.9962$ Å, and $c=11.2870$ Å. Lattice fringe distances were measured to be 0.195 nm, 0.189 nm, and 0.90 nm, at 60.76° and 119.19°, which is interpreted as the tetragonal Cu_2S phase visualized along its [100] zone axis. b) The

displayed crystal structure is in agreement with the Cu_2S monoclinic phase (space group P121/C1) with $a=15.2700 \text{ \AA}$, $b=11.8900 \text{ \AA}$ and $c=13.3600 \text{ \AA}$. Lattice fringe distances were measured to be 0.251 nm, 0.350 nm, and 0.286 nm, at 59.44° and 135.75° , which is interpreted as the monoclinic Cu_2S phase visualized along its [001] zone axis.

Figure 10 displays the σ , S , and PF of the Cu_{2-x}S pellets in the temperature range 310-710 K. For all samples, the first measuring cycle showed slightly different results compared with the subsequent ones (Figure 11 and 12). After the first cycle up to 710 K, the pellet obtained from the covellite NPs annealed in Ar displayed mainly the monoclinic djurleite $\text{Cu}_{1.97}\text{S}$ phase (Figure 13). The dominance of the djurleite phase was accentuated when increasing the number of cycles. This sample also presented a sustained variation of the transport properties from cycle to cycle. It displayed a monotonous decrease of the electrical conductivity and increase of the Seebeck coefficient, that was related with a progressive loss of sulfur and consequently of copper vacancies. On the other hand, the pellet obtained from covellite particles annealed in Ar/H_2 displayed a much higher structural stability and electronic stability, presenting a similar combination of monoclinic $\text{Cu}_{1.96}\text{S}$ and Cu_2S phases and similar transport properties after the 1st and the 11th cycles (Figure 13). The transport properties obtained in the second cycle, which coincided better with results obtained in following cycles, are the ones presented in the following.

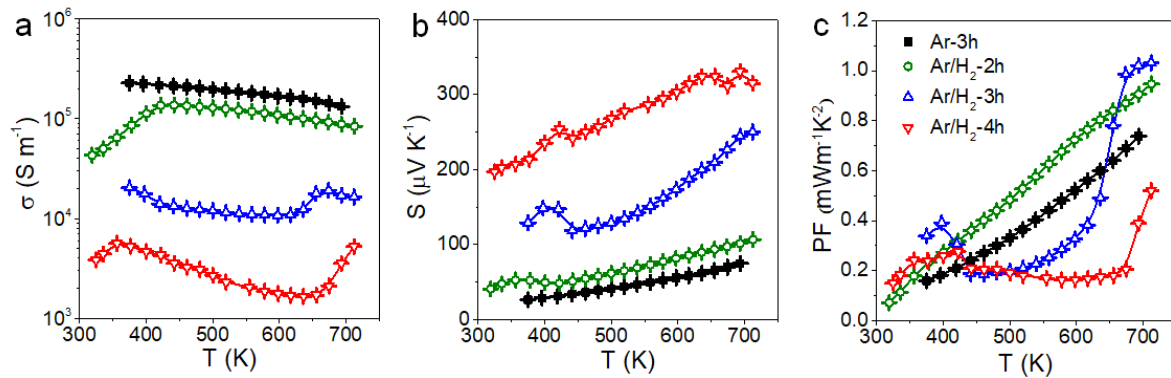


Figure 10. TE properties of Cu_{2-x}S samples annealed under different gas flow and for different times: a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) power factor, PF .

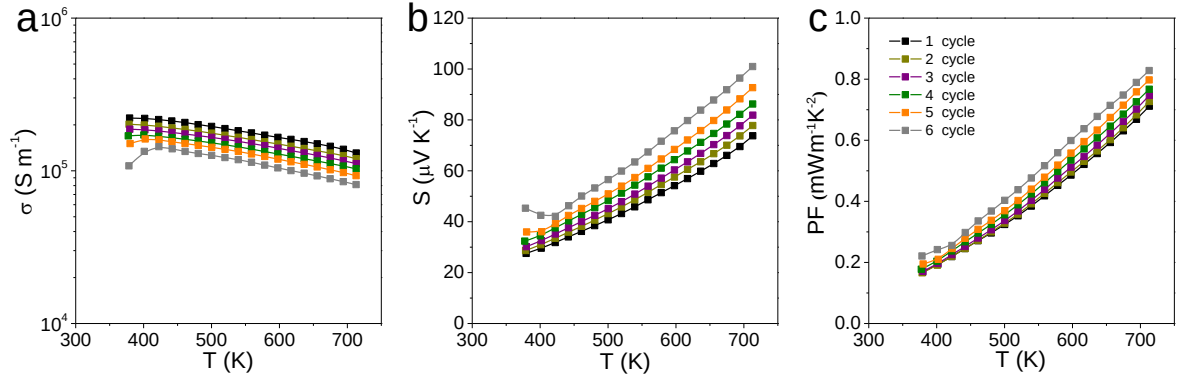


Figure 11. Temperature dependence of a) electrical conductivity, σ ; b) Seebeck coefficient, S ; and c) power factor, PF of a Cu_{2-x}S pellet obtained from NPs annealed in Ar and measured 6 consecutive cycles, from room temperature to 710 K.

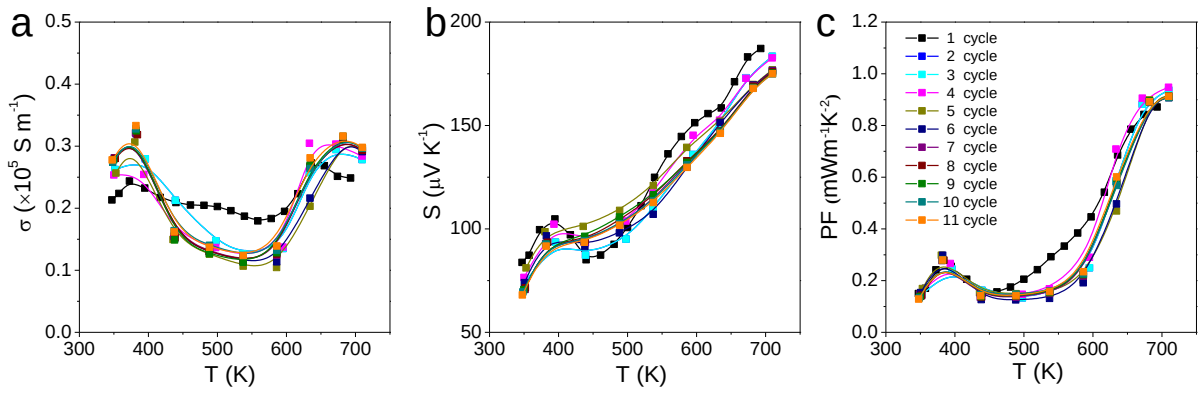


Figure 12. Temperature dependence of a) electrical conductivity, σ ; b) Seebeck coefficient, S ; and c) power factor, PF of a Cu_{2-x}S pellet obtained from NPs annealed in Ar/H_2 and measured 11 consecutive cycles, from room temperature to 710 K.

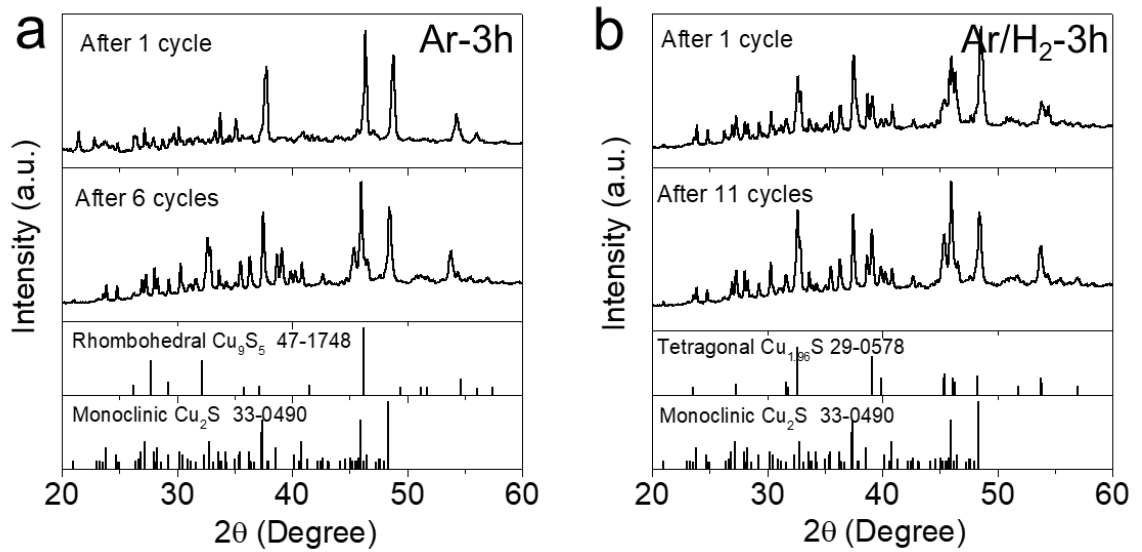


Figure 13. XRD patterns of Cu_{2-x}S pellets obtained from annealing the covellite CuS NPs for 3 h under different gas flow a) Ar and b) Ar/ H_2 . Patterns were measured after the first measurement of the pellets TE properties and several measurement cycles (6 for the Ar pellet and 11 for the Ar/ H_2 pellet).

Compared with samples annealed in Ar, an order of magnitude lower electrical conductivities were obtained for the samples annealed in the presence of H_2 for 3-4 h. This decrease of σ was correlated with a substantial increase of the Seebeck coefficient. The σ decrease and S increase were related to a strong reduction of the charge carrier concentration, from $9 \times 10^{20} \text{ cm}^{-3}$ for the sample annealed in Ar, to $6 \times 10^{19} \text{ cm}^{-3}$ for the sample annealed in Ar/ H_2 for 3 h, as measured by Hall (Table 3). This decrease of the charge carrier concentration was consistent with the higher Cu/S ratio and thus the lower density of Cu vacancies obtained in samples annealed in Ar/ H_2 , as inferred from XRD data and ICP-OES measurements (Table 4). Overall, the capability to adjust the charge carrier concentration through controlling the annealing atmosphere and time allowed its optimization and resulted in a significant increase of the maximum power factor. The largest power factors were obtained in the high temperature range tested from samples annealed in Ar/ H_2 for 3 h, and reached $1.1 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at 710 K. These results demonstrate both the large room for improvement on the TE performance of Cu_{2-x}S and the potential of tuning the Cu_{2-x}S transport properties by simply modifying the annealing parameters when using CuS NPs as precursor material.

Table 3. Room temperature Hall charge carrier concentration and mobility of Cu_{2-x}S pellets obtained from the annealing of NPs under difference atmospheres for 3 h.

Cu_{2-x}S	Annealing in Ar	Annealing in Ar/ H_2
$n_H (10^{19} \text{ cm}^{-3})$	90	6
$\mu_H (\text{cm}^2 \text{ V}^{-1} \text{ S}^{-1})$	22	13

Table 4. ICP-OES composition of Cu_{2-x}S pellets.

Sample	Cu	S
Cu_{2-x}S annealed in Ar for 3 h	1.69	1
Cu_{2-x}S annealed in Ar/ H_2 for 2 h	1.91	1
Cu_{2-x}S annealed in Ar/ H_2 for 3 h	1.95	1
Cu_{2-x}S annealed in Ar/ H_2 for 4 h	1.96	1

The transport properties of the samples annealed under Ar/H₂ showed a non-monotonous dependence on temperature. Taking the electrical conductivity as a reference (Figure 10a), the electrical conductivity increased with temperature up to 350-450 K, then decreased until 600-650 K, and then increased again. This complex behavior was reliably observed in different samples and measuring cycles (Figure 11 and 12), and it was consistent with previously reported results (Figure 14).

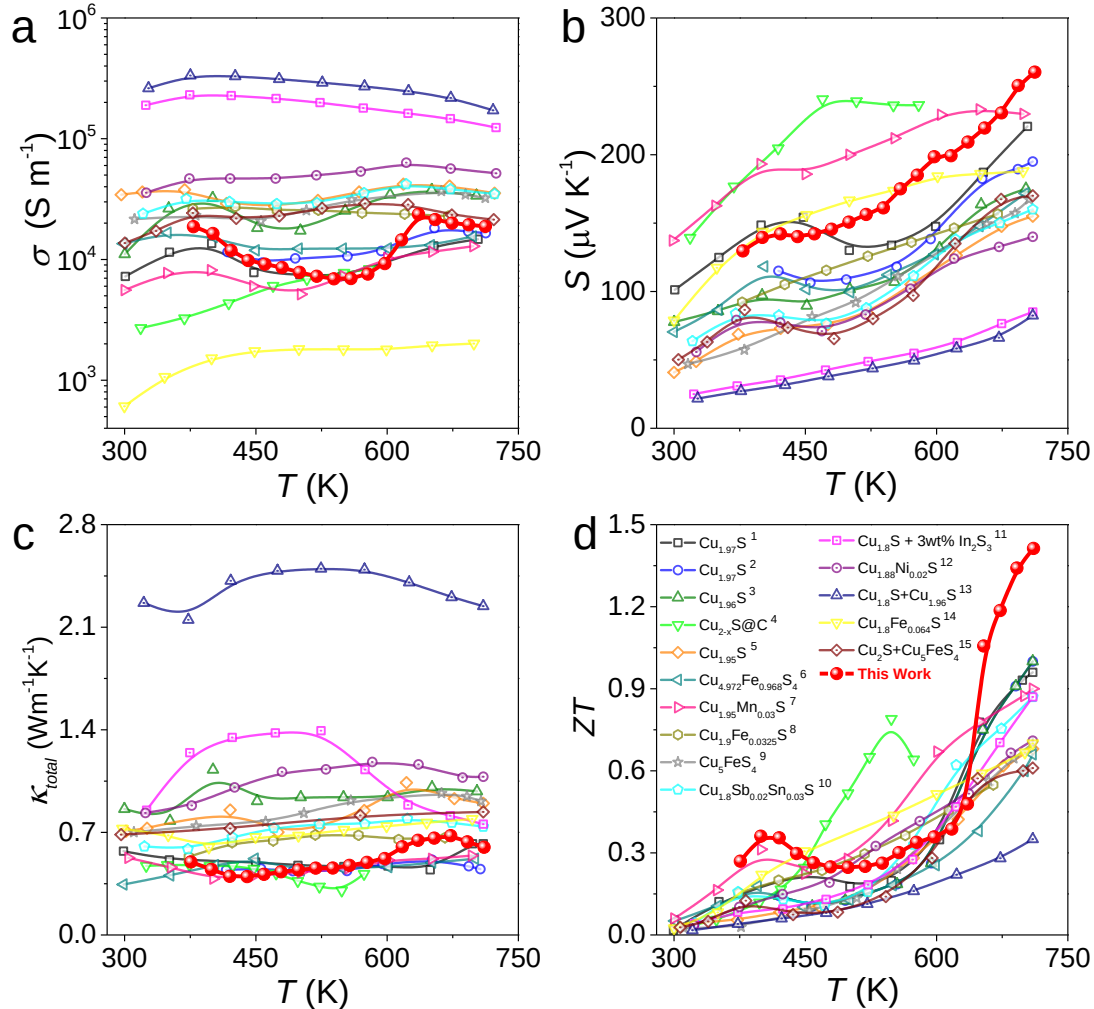


Figure 14. Comparison of the temperature dependence, up to 710 K, of a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) thermal conductivity, κ and d) TE figure of merit, ZT of state-of-the-art Cu_{2-x}S-based materials and the sample obtained from the annealing of CuS under Ar/H₂ for 3 h.

To determine the origin of this complex dependence on temperature, we analyzed the evolution of the crystal structure with temperature using the profile displayed in Figure 15. Figure 16 displays the XRD patterns measured at different temperatures from Cu_{2-x}S pellets produced

from NPs annealed in Ar (Figures 16a) and Ar/H₂ (Figures 16b). The pellets used for the high temperature XRD analysis had been previously used for the characterization of TE properties. The monoclinic djurleite phase measured at ambient temperature from the Cu_{2-x}S pellet obtained from NPs annealed in Ar evolved with temperature to a cubic Cu₂S phase. This phase transition occurred in the temperature range 350-450 K and the obtained cubic phase remained unchanged until the highest tested temperature, although a small shift of the XRD peak positions was observed at ca. 550 K. On the other hand, when increasing temperature, the Cu_{2-x}S pellet produced from NPs annealed in Ar/H₂ underwent two phase transitions, from the combination of monoclinic djurleite and chalcocite measured at ambient temperature to increasingly more symmetric structures. In the temperature range 350 - 400 K, the monoclinic phases evolved into the hexagonal high chalcocite Cu₂S phase. This transition coincided with the first anomaly in the evolution of the transport properties of this material. A second phase transition, from hexagonal to cubic Cu₂S, was observed at 500-600 K, coinciding with the second anomaly on the temperature evolution of the transport properties. DSC analyses confirmed these results (Figure 17). The DSC profile of the sample annealed in Ar displayed a clear feature at ca. 320-400 K, and an additional heat flow variation in the range 550-710 K that could be related with an irreversible loss of sulfur, consistent with the progressive decrease of σ and the increase of S measured from this sample (Figure 11). On the other hand, the DSC profile of the sample annealed in Ar/H₂ displayed additional features in the range 350-450K, and a second phase transition at ca. 550-600 K.

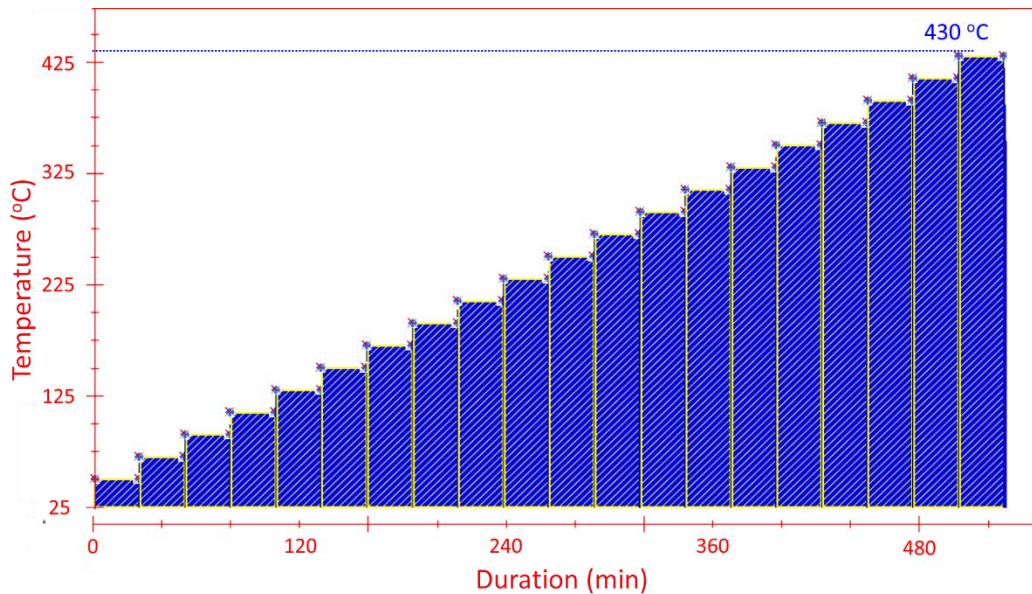


Figure 15. Temperature used to analyze the evolution of the Cu_{2-x}S crystal phase with

temperature (data shown in Figure 6).

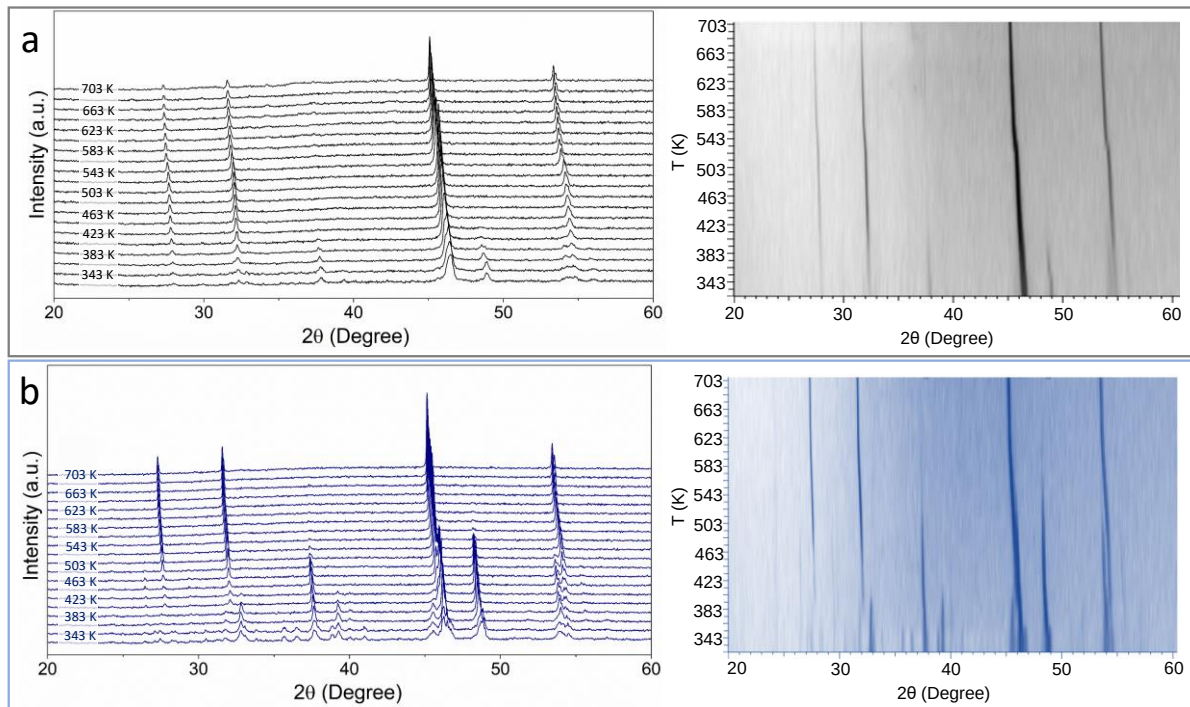


Figure 16. Temperature evolution of the XRD patterns of Cu_{2-x}S pellets obtained from NPs annealed in Ar (a) and Ar/H_2 (b) for 3 h. XRD patterns were measured on the exact same pellets previously used to measure TE properties and were obtained when increasing temperature (from bottom to top) in the temperature range from 323 K to 703 K.

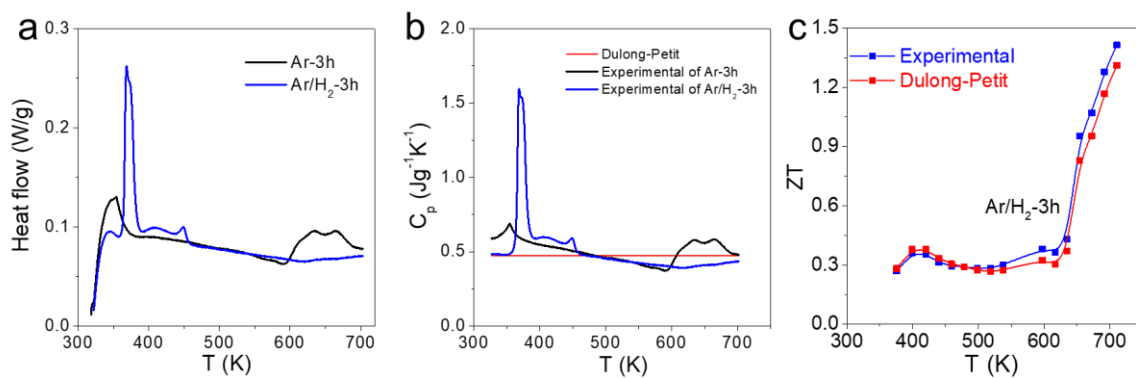


Figure 17. a) DSC profile obtained from Cu_{2-x}S pellets produced by annealing CuS NPs for 3 h under different gas flows, Ar or Ar/H_2 . b) Temperature dependence of the heat capacity of Cu_{2-x}S samples. c) Comparison of ZT values calculated by theoretical C_p and experimental C_p .

Overall, we observed CuS NPs to be intrinsically unstable with temperature. They lost sulfur

when heated at moderately high temperatures, resulting in Cu_{2-x}S nanopowders. The stoichiometry of the resulting material was found to determine its charge transport properties. Thus the annealing temperature, time and also atmosphere are key parameters to properly adjust transport properties and thus maximize TE performance. We observed CuS NPs annealed in Ar to be characterized by high Cu deficiencies that resulted in too large charge carrier concentrations. On the other hand, samples annealed in the presence of H_2 were characterized by considerably higher Cu/S ratio and thus significantly lower charge carrier concentrations that were better adjusted to maximize the power factor in the high temperature range measured ($T > 600$ K), where copper chalcogenides display best TE performance. Samples annealed in the presence of H_2 displayed an increase of electrical conductivity at around 600 K, which can be associated with a slight increase of the charge carrier concentration or mobility with the reorganization of Cu and S atoms during the phase transition to the cubic structure. While all Cu_{2-x}S pellets displayed the cubic phase at temperatures above 600 K, the slightly different Cu/S stoichiometries explain the large variation between the performances obtained from samples produced from NPs annealed in Ar or Ar/ H_2 atmospheres.

Figure 18a shows the κ of the Cu_{2-x}S pellets annealed in Ar or Ar/ H_2 for 3 h. The thermal conductivity of the sample annealed in Ar was significantly higher than that of the sample annealed in Ar/ H_2 owing to the much larger electronic contribution of the former. When subtracting the electronic thermal conductivity, we observed the lattice thermal conductivity of the two materials to be similar (Figure 18b).

The dimensionless TE figure of merit of the Cu_{2-x}S pellets annealed in Ar and Ar/ H_2 for 3 h are displayed in figure 18c. Figure 19 displays the results obtained from 3 pellets produced from 3 different batches of NPs using the same synthesis and post-treatment conditions. Data obtained from the different pellets showed an excellent reproducibility. Compared with the material annealed in Ar, the material annealed in Ar/ H_2 for 3 h was characterized by much higher figures of merit, reaching up to $ZT=1.41$ at 710 K. To the best of our knowledge, this is the highest ZT value reported for Cu_{2-x}S in this middle temperature range, where Cu_{2-x}S displays a stable behavior (Figures 18d, 14).

In figure 14 we compare the results obtained from Cu_{2-x}S pellets produced from NPs annealed in the presence of H_2 with previously reported results from Cu_{2-x}S materials. We observe that samples with similar electrical conductivities display similar trends with temperature: an initial increase of the electrical conductivity in the low temperature range, a decrease in the middle

temperature range measured, until around 600 K, and a posterior increase that coincides with the phase transition to the cubic structure. The electrical conductivity of the samples obtained from NPs annealed in the presence of H_2 was in the low electrical conductivity range of the reported values. Moderate electrical conductivities were also obtained with other copper sulfides that typically included multivalence dopants such as Fe and Mn to decrease the hole concentration. These doped samples were characterized by similar but slightly lower Seebeck coefficients than our best materials, which could be related to a lower charge carrier mobility associated with the presence of the highly ionized foreign atoms within the $Cu_{2-x}S$ lattice. The thermal conductivity of pellets produced from NPs annealed in the presence of H_2 was also in the low range of the reported thermal conductivities, as expected from the moderate contribution of the electronic component and the large density of grain boundaries present in our polycrystalline materials. Overall, the control of the annealing parameters allowed adjusting the density of Cu vacancies and thus the charge carrier concentration without adding external impurities, which resulted in the highest power factors and ZT values reported to date.

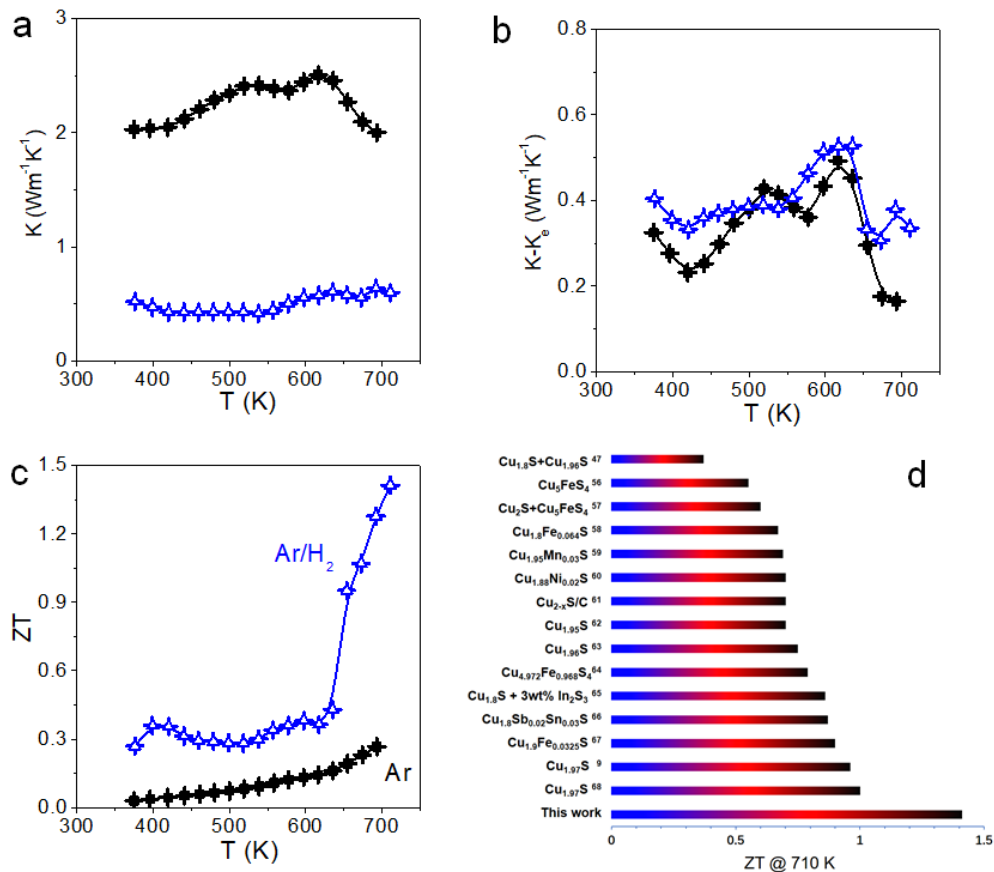


Figure 18. TE properties of $Cu_{2-x}S$ pellets obtained from NPs annealed under Ar (black solid symbols) and Ar/H₂ (blue open symbols): a) thermal conductivity, κ ; b) lattice thermal

conductivity, κ_L ; c) TE figure of merit, ZT ; d) Comparison of ZT values at 710 K for Cu_{2-x}S -based materials.

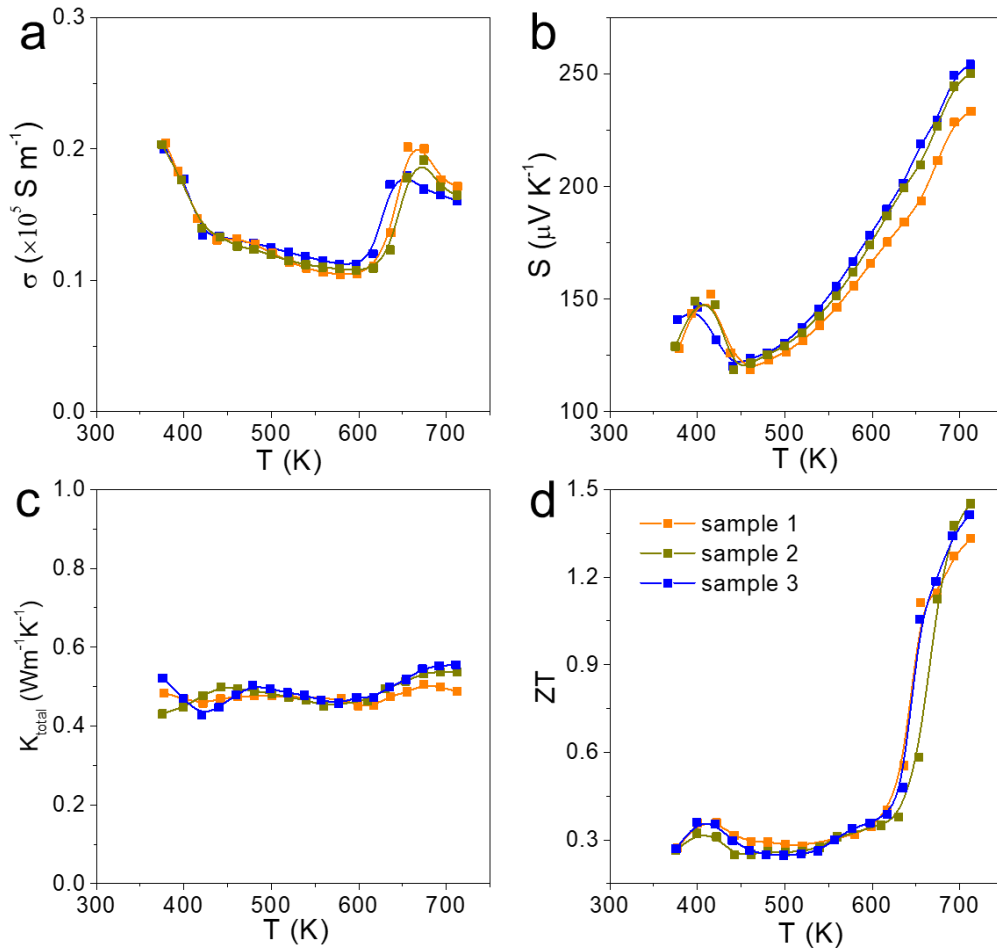


Figure 19. TE properties of three Cu_{2-x}S pellets obtained three different batches of CuS NPs produced using the same synthetic parameters and annealed and hot-pressed in the same conditions. NPs were annealed in Ar/H_2 flow for 3 h: a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) thermal conductivity, κ and d) TE figure of merit, ZT ;

The excellent performance measured from materials produced from the processing and consolidation of NPs demonstrates the high suitability of the presented material processing strategy. We believe that the synthesis of copper sulfide in the form of NPs is key both to reduce the production cost, as no large amounts of energy and time are invested in organizing atoms in large crystal domains, and to control composition by means of mild thermal annealing in a controlled atmosphere. Besides, the availability of the material in the form of NPs suspended in a low cost and safe solvent such as water or ethanol allows the scalable, high throughput and cost-effective production of devices using printing technologies. To advance

in this direction, we prepared inks from the annealed NPs, and printed them on a mica substrate (Figure 20). Then we hot-pressed the films in the same conditions as the pellets. Figure 20b-d displays the TE properties of the films obtained from Cu_{2-x}S NPs annealed under Ar or Ar/ H_2 flow for 3 h. The results obtained from the films were very similar to those obtained from pellets, which demonstrates the potential of these NP-based material to produce high performance printed TE devices.

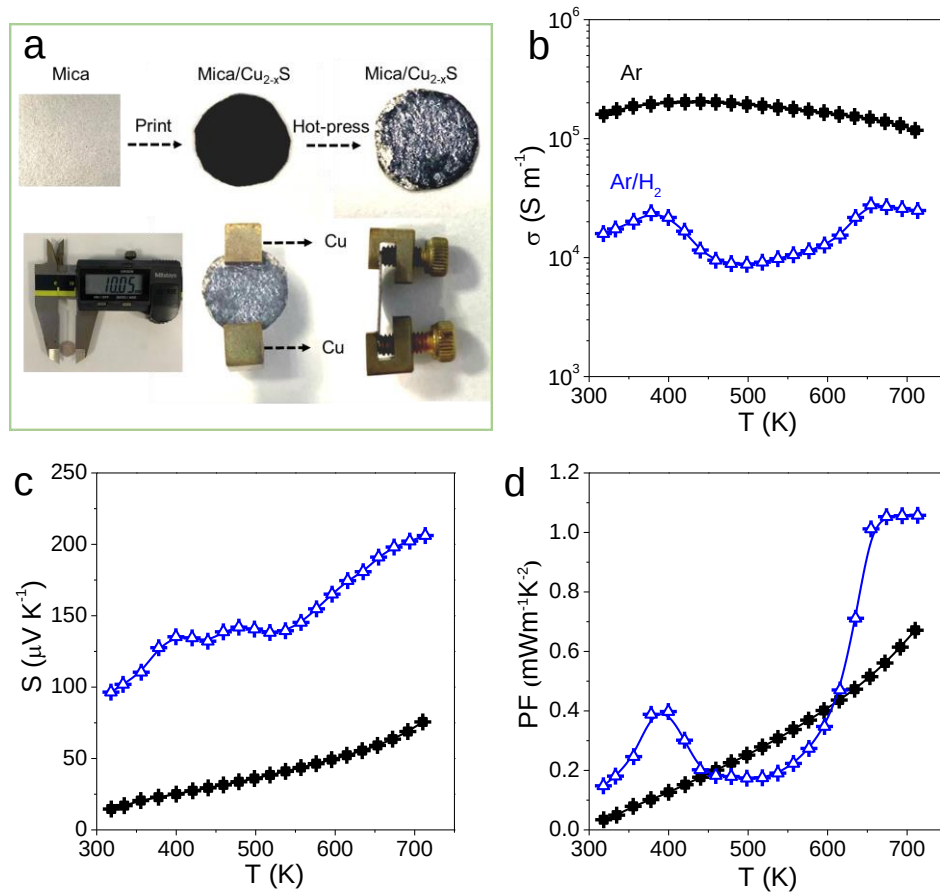


Figure 20. a) Optical images of the mica substrate, the mica/ Cu_{2-x}S film, the hot-pressed layer and the system used to measure TE properties. b-d) TE properties of the Cu_{2-x}S film on mica: a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) power factor, PF .

3.5 Conclusions

We reported a facile, scalable and low-cost method for the synthesis of covellite CuS NPs in aqueous media and at room temperature. The produced covellite NPs lost sulfur when heated under inert or reducing atmosphere, and changed their crystal phase to metastable rhombohedral $\text{Cu}_{1.8}\text{S}$ or tetragonal $\text{Cu}_{1.96}\text{S}$. The annealing atmosphere and time allowed tuning

the amount of sulfur lost and thus the stoichiometry and crystal structure of the final nanopowder. The sample stoichiometry determined the density of copper vacancies, thus the hole concentration and consequently the transport properties of the material. Comparing the material annealed in Ar with the annealed in Ar/H₂, we observed the former to be characterized by much higher charge carrier concentrations and electrical conductivities, but lower Seebeck coefficients. Finally, the material annealed in Ar/H₂ for 3 h was characterized by the highest power factors and TE figures of merit, up to 1.41 at 710 K, which is the highest *ZT* reported for Cu_{2-x}S at this temperature. Overall, this work demonstrated that: i) there is plenty of room for optimization of the TE properties of copper chalcogenides and particularly copper sulfide; ii) the annealing of CuS NPs in a controlled atmosphere and during an appropriated amount of time is a facile, convenient and highly effective strategy to tune stoichiometry, and thus the density of electronic active defects and the charge carrier concentration, which is a key parameter to optimize TE performance; iii) The use of NPs was key to provide enough surface area for effective and homogeneous removal of copper vacancies. The availability of the material in the form of NPs also allowed the direct printing of the material into layers that were characterized by similar TE performances as those obtained from the pellets.

3.6 References

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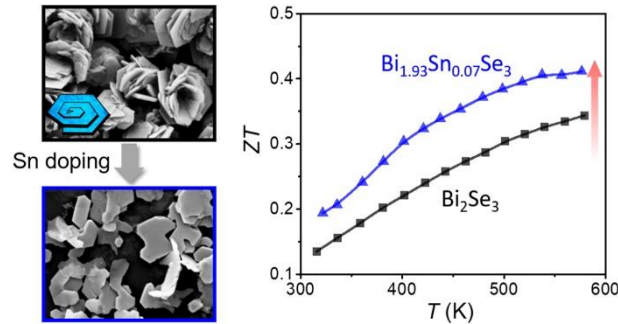
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Chapter 4 Enhanced Thermoelectric Performance of n-Type Bi_2Se_3 Nanosheets through Sn Doping



4.1 Abstract

The cost-effective conversion of low grade heat into electricity using TE devices requires developing alternative materials and material processing technologies able to reduce the current device manufacturing costs. In this direction, TE materials that do not rely on rare or toxic elements like tellurium or lead need to be produced using high-throughput technologies not involving high temperature and long processes. Bi_2Se_3 is an obvious possible Te-free alternative to Bi_2Te_3 for ambient temperature TE applications, but its performance is still low for practical applications, and additional efforts toward finding proper dopants are required. Here, we report a scalable method to produce Bi_2Se_3 NSs at low temperatures. We study the influence of different dopants on the TE properties of this material. Among the tested elements, we demonstrate Sn doping to result in best performances. Sn incorporation results in a significant improvement of the Bi_2Se_3 Seebeck coefficient and a reduction of the thermal conductivity in the direction of the press axis, overall resulting in a 60% improvement of the TE figure of merit of Bi_2Se_3 .

4.2 Introduction

TE devices that directly and reversibly convert heat to electricity find unlimited applications,¹⁻⁶ but real implementation is hampered by their low cost-effectiveness. The energy conversion efficiency of a TE device is in part determined by the properties of the TE material. These material properties are generally grouped into a dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where S , σ , T , and κ represent the Seebeck coefficient, electrical conductivity, the absolute temperature and thermal conductivity, respectively. An efficient TE material needs to be

characterized by a high power factor, $S^2\sigma$, and a low thermal conductivity, κ . However, the strong correlation between these parameters makes the optimization of the material performance extremely difficult. Several strategies have been developed to maximize ZT , including engineering the electronic band structure of the TE material through doping,⁷ the use of energy filtering interphases,⁸ and the reduction of lattice thermal conductivity through the introduction abundant grain boundaries.⁹

Commercial devices use large amounts of highly crystalline Bi_2Te_3 -based alloys as the active TE material, which accounts for a significant part of the total device cost. To reduce the device cost, it is critical to develop lower cost materials not relying on scarce Te and lower cost processing strategies not based on high temperature crystallization from high purity melts. Bi_2Se_3 presents the same structure and similar properties as Bi_2Te_3 , and thus it is an obvious possible Te-free alternative to Bi_2Te_3 . Numerous attempts have been reported to improve the ZT of this material, but with moderate success.¹⁰⁻¹⁸

To maximize the TE performance of a material, one first critical point is to optimize its charge carrier concentration. Three main strategies can be used in this direction: tuning of the material stoichiometry, introduction of atomic impurities, and introduction of secondary phases able to inject the proper charge carriers to the host material.²¹⁻³⁰ Besides optimizing the charge carrier concentration, it is fundamental to minimize the thermal conductivity using multiscale phonon scattering centres. In this direction, the introduction of atomic impurities and abundant grain boundaries are highly effective. Besides, energy barriers at grain boundaries can also introduce energy- and charge sign-dependent charge carrier scattering, which could result in significant improvements of the Seebeck coefficient.³¹

Here, we present a low temperature and high yield, solution-based strategy to prepare Bi_2Se_3 nanomaterials doped with different elements. The influence of different dopants on the TE properties of the material was tested. From the obtained results, we demonstrate Sn to have the highest potential to yield Bi_2Se_3 -based materials with improved performance. Thus we further analyse the location and chemical state of this element within Bi_2Se_3 and its effect on the material transport properties.

4.3 Experimental section

Chemicals and solvents: Bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\geq 99.99\%$), indium(III) acetate ($\text{InC}_6\text{H}_9\text{O}_6$, 99.99%) and polyvinylpyrrolidone (PVP, $(\text{C}_6\text{H}_9\text{NO})_n$, average

mol wt. ~55,000) were purchased from Sigma Aldrich. Sodium selenite (Na_2SeO_3 , $\geq 98\%$), copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%), silver nitrate (AgNO_3 , $\geq 99.9\%$), lead(II) acetate trihydrate ($\text{PbC}_4\text{H}_6\text{O}_4 \cdot 3\text{H}_2\text{O}$), potassium hydroxide (KOH , $\geq 98\%$) and ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$, 99%) were purchased from Fisher. Analytical grade acetone and ethanol were obtained from various sources. All chemicals were used as received without further purification. Syntheses were carried out using a standard vacuum/dry argon Schlenk line.

Synthesis of Bi_2Se_3 : In a typical synthesis of 5 mmol of Bi_2Se_3 , 10 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 15 mmol Na_2SeO_3 , 50 mmol KOH and 0.5 g PVP were dissolved in 200 ml of EG within a 500 ml three-neck flask by stirring under argon atmosphere at room temperature for 30 min. Then the solution was heated to 180 °C. During this process, at around 160 °C, the color of the solution gradually changed from slightly brown to black. Finally, the reaction mixture was kept at 180 °C for 3 h. After this time, the solution was naturally cooled to room temperature by removing the heating mantle. The solid product was collected by adding acetone to the solution and centrifuging it. Then ethanol was used to re-disperse the particles and acetone to precipitate them again. This step was repeated twice. Finally, particles were dried under vacuum at room temperature. This synthesis protocol was optimized to produce 3 g of material per batch.

Synthesis of $\text{Bi}_{2-x}\text{M}_x\text{Se}_3$: The procedure used to produce $\text{Bi}_{2-x}\text{M}_x\text{Se}_3$ was exactly the same used to produce Bi_2Se_3 , but replacing the proper amount of bismuth nitrate by the corresponding metal precursor, as listed in the chemical section above.

Nanomaterial consolidation: Dried Bi_2Se_3 particles were annealed at 350 °C for 60 min under Ar flow inside a tube furnace. The annealed powder was loaded into a graphite die and compacted into cylinders ($\varnothing$ 10 mm×10 mm) using a custom-made HP. The HP temperature was set at 480 °C and pressure was increased up to 50 MPa for 4min. The relative densities of the compacted pellets were measured by the Archimedes' method. To measure transport properties in the two relevant directions, cylindrical pellets were cut into 8×6×1 mm rectangular bars along the pressure axis, and 1 mm thick disks within the cylinder plane.

Structural and chemical characterization: XRD (2θ angle: 5° to 80°; scanning rate: 4°/min) analyses were carried out on a Bruker AXS D8 ADVANCE X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Size and morphology of NPs were examined by field-emission SEM on an Auriga Zeiss operated at 5.0 kV. The material composition was analyzed using an Oxford EDX attached to a Zeiss Auriga SEM at 20.0 kV. Crystallographic structure and chemical composition were analyzed by HRTEM, using a Tecnai F20 field-emission gun microscope

at 200 keV with an embedded Gatan Quantum image filter. XPS was carried out on a Specs system (Specs GmbH, Berlin, Germany) equipped with a Mg anode XR50 source operating at 250 W and a Phoibos 150 MCD-9 detector (Specs GmbH, Berlin, Germany). The pressure in the analysis chamber was kept below 10^{-7} Pa. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK).

Performance Characterization of Bulk nanomaterial: Seebeck coefficients were measured using a static DC method. Electrical resistivity data was obtained by a standard four-probe method. Both the Seebeck coefficient and the electrical resistivity were measured simultaneously in an LSR-3 Linseis system in the temperature range between room temperature and 573 K under helium atmosphere. All samples were measured at least 3 consecutive times during heating up to around 573 K. Taking into account the system accuracy and the measurement precision, an error of *ca.* 4% in the measurement of the electrical conductivity and Seebeck coefficient was estimated. κ_{total} were obtained by multiplying λ , C_p and ρ , where $\kappa_{total} = \lambda C_p \rho$. A Xenon Flash Apparatus XFA600 was used to determine the thermal diffusivities of the samples with an estimated error of *ca.* 5 %. The C_p was estimated from empirical formulas by the Dulong–Petit limit (3R law). The density values were measured using the Archimedes’ method. To avoid cluttering the plots, error bars were not included in the figures.

4.4 Results and discussion

Following the above synthesis method, Bi_2Se_3 NSs grouped into flower-like particles were produced, as shown by SEM micrographs (Figure 1a,b). Bi_2Se_3 shows a screw dislocation growth mechanism (Figure 1c). This growth mechanism is generally observed under low supersaturation synthesis conditions resulting in a layer-by-layer growth and when dendrite growth is suppressed. The axial screw dislocations provide self-perpetuating steps, which propagate in a spiral trajectory around the Burgers vector of the screw dislocation.^{15,25}

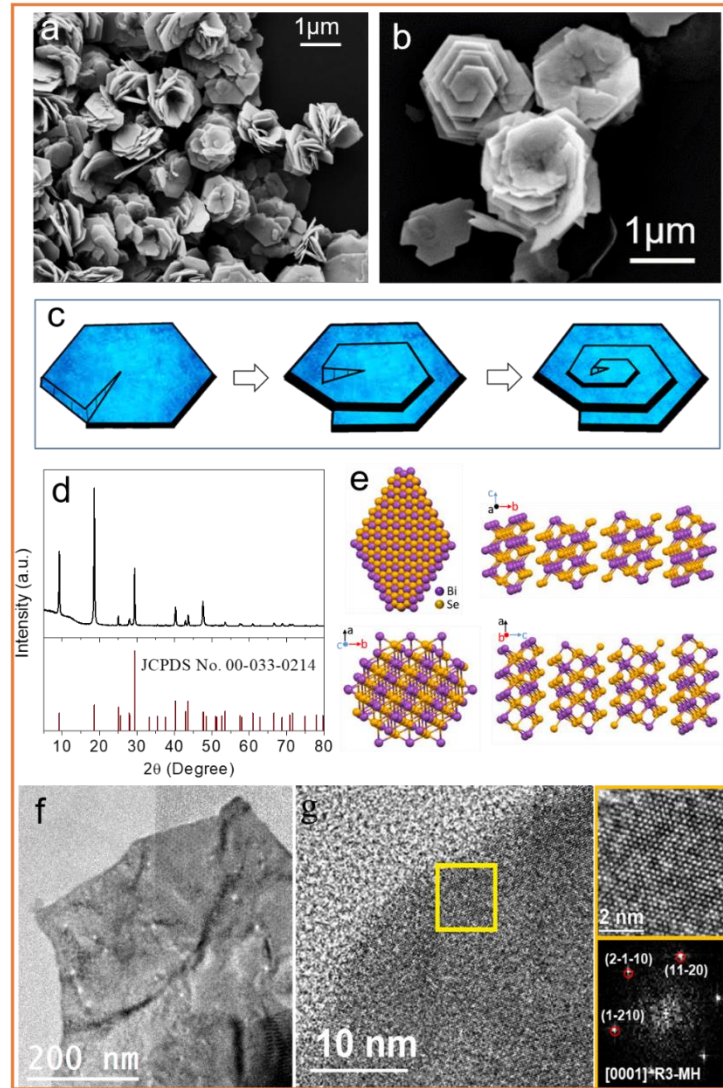


Figure 1. a and b) SEM micrographs of Bi_2Se_3 NSs. c) Schematic illustration of the screw dislocation-driven growth mechanism. d) XRD pattern of Bi_2Se_3 particles. e) layered rhombohedral crystal structure of Bi_2Se_3 . f) and g) HRTEM micrograph of Bi_2Se_3 particles, detail of the orange squared region and its corresponding power spectrum. From the crystalline domain, the Bi_2Se_3 lattice fringe distances were measured to be 0.205 nm, 0.205 nm, and 0.204 nm, at 60.96° and 120.86° which could be interpreted as the rhombohedral Bi_2Se_3 phase, visualized along its $[0001]$ zone axis.

XRD analysis showed the crystal structure of the obtained NSs to match the rhombohedral Bi_2Se_3 phase (Figure 1d, JCPDS No. 00-033-0214). Figure 1e shows the layered rhombohedral crystal structure of Bi_2Se_3 , consisting of planar quintuple layers, with five covalently bonded atomic planes Se-Bi-Se-Bi-Se. The quintuple layers are weakly bonded by van der Waals interaction. HRTEM characterization showed the material to have a good crystallinity, with a

crystal phase that could be in agreement with the Bi_2Se_3 rhombohedral phase (space group =R3-MH) with $a=b=4.1340 \text{ \AA}$ and $c=28.6300 \text{ \AA}$ (Figure 1f, g).

NSs were annealed at $350 \text{ }^\circ\text{C}$ and then hot-pressed within an inert atmosphere into cylindrical pellets 10 mm in diameter and 10 mm height. The hot-press temperature was set at $480 \text{ }^\circ\text{C}$ and pressure was cycled from ambient to 50 MPa for 4 min. This process resulted in cylinders with relative densities of ca. 93% of the theoretical value, as measured by the Archimedes' method. From the consolidated cylinders, $8 \times 6 \times 1 \text{ mm}$ rectangular bars and 1 mm thick disks were cut in-plane and out-of-plane, respectively (Figure 2). These samples were used to measure the material TE properties in two directions, parallel and normal to the pressure axis.

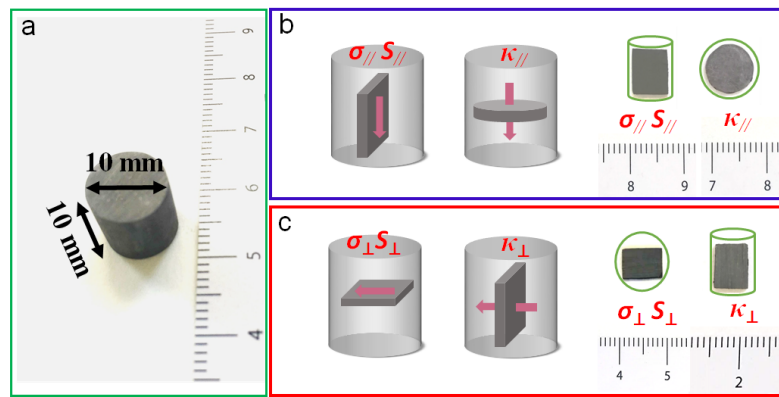


Figure 2. a) Representative photograph of one of the consolidated Bi_2Se_3 cylindrical pellets produced. b, c) Schematic illustrations and photographs of the samples obtained from the cylindrical pellets and used to measure electrical conductivities, σ ; Seebeck coefficients, S ; and thermal conductivities κ in both direction, parallel (b) and perpendicular (c) to the press direction.

Figure 3 displays the σ , S , and PF of the $\text{Bi}_{2-x}\text{M}_x\text{Se}_3$ ($\text{M} = \text{Sn}, \text{Cu}, \text{Ag}, \text{Pb}, \text{In}$) pellets perpendicular to the press direction. The electrical conductivity of the undoped material decreased with temperature, which pointed at a degenerated semiconductor behaviour. Comparing with the undoped material, the electrical conductivity of all the doped samples was slightly lower, except for Ag-doped samples. On the other hand, the samples doped with Sn and in minor extent Pb displayed an increase of the absolute value of the Seebeck coefficient. Overall, the highest power factors were obtained with the Sn doping. Thus, we decided to further study the effect of this element.

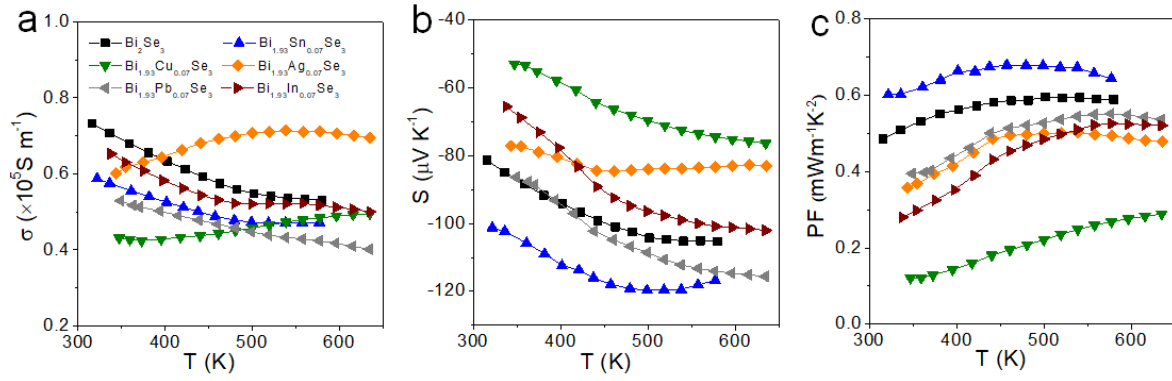


Figure 3. TE properties of $\text{Bi}_{2-x}\text{M}_x\text{Se}_3$ ($\text{M} = \text{Sn}, \text{Cu}, \text{Ag}, \text{Pb}, \text{In}$) samples measured in the plane perpendicular to the press direction: a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) power factor, PF .

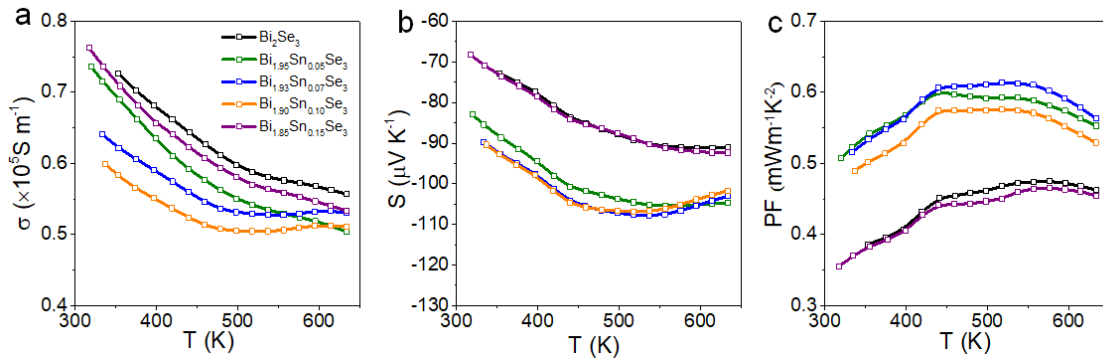


Figure 4. TE properties of $\text{Bi}_{2-x}\text{Sn}_x\text{Se}_3$ perpendicular to the press direction: a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) power factor, PF .

Figure 4 displays the electrical conductivity, Seebeck coefficient, and power factor of $\text{Bi}_{2-x}\text{Sn}_x\text{Se}_3$ materials containing different amounts of Sn. We observed the electrical conductivity to decrease and the absolute value of the Seebeck coefficient to increase with the amount of Sn up to a certain Sn concentration. Highest power factors were finally obtained for $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$.

Figure 5 shows representative SEM micrographs of the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ particles, which did not display the flower-like morphology observed from Bi_2Se_3 . As shown in Figure 6, XRD characterization confirmed the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ particles to maintain the rhombohedral structure. With the introduction of Sn, the XRD peaks shifted to lower 2θ angles, suggesting the incorporation of Sn within the Bi_2Se_3 lattice.⁵

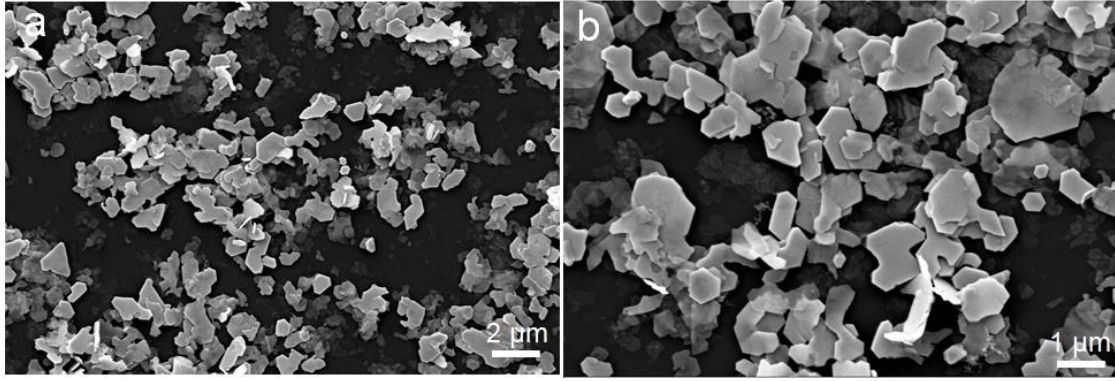


Figure 5. SEM micrographs of $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ NSs.

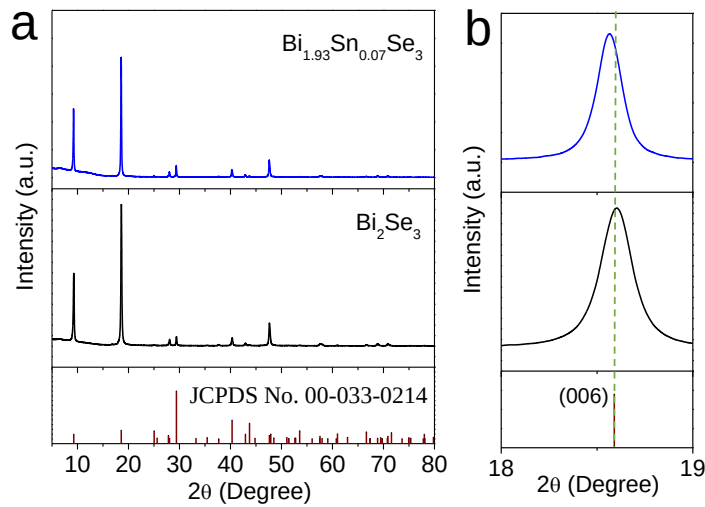


Figure 6. a) XRD patterns of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$; b) Expanded views of the regions corresponding to the Bi_2Se_3 (006) diffraction peak.

HRTEM characterization confirmed the rhombohedral phase of the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ particles (Figure 7a). EELS chemical composition maps obtained from the red squared region in the HAADF STEM micrograph shown in Figure 7b display a homogeneous distribution of Sn, Bi and Se within the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ NSs.

Bi 4f, Se 3d and Sn 3d high resolution XPS spectra of $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ particles are displayed in Figure 7c. The high resolution Bi 4f spectra was fitted with two doublets, associated with Bi^{3+} within a Bi_2Se_3 chemical environment (Bi 4f_{7/2} at 158.2 eV) and Bi within a more electronegative environment, as could be Bi_2O_3 or Bi_2SeO_2 (Bi 4f_{7/2} at 159.4 eV).³² This partial surface oxidation of the particles has its origin on their manipulation and transportation in air, as observed for other materials.⁴ The high resolution Se 3d XPS spectrum was fitted with three doublets, corresponding to Se within the Bi_2Se_3 (Se 3d_{5/2} at 53.6 eV), selenium in an elemental

or Bi_2SeO_2 environment (Se $3d_{5/2}$ at 55.2 eV), probably arising from the partial oxidation of the material surface, and Se in a SeO_2 chemical environment (Se $3d_{5/2}$ at 58.6 eV).^{32,33} Finally, the high resolution Sn 3d XPS spectrum was difficult to fit owing to the small amount of this element, but the broadness of the peaks pointed at the presence of at least two Sn chemical states that should be tentatively assigned to Sn^{x+} within a SnSe and an oxidized environment.³³

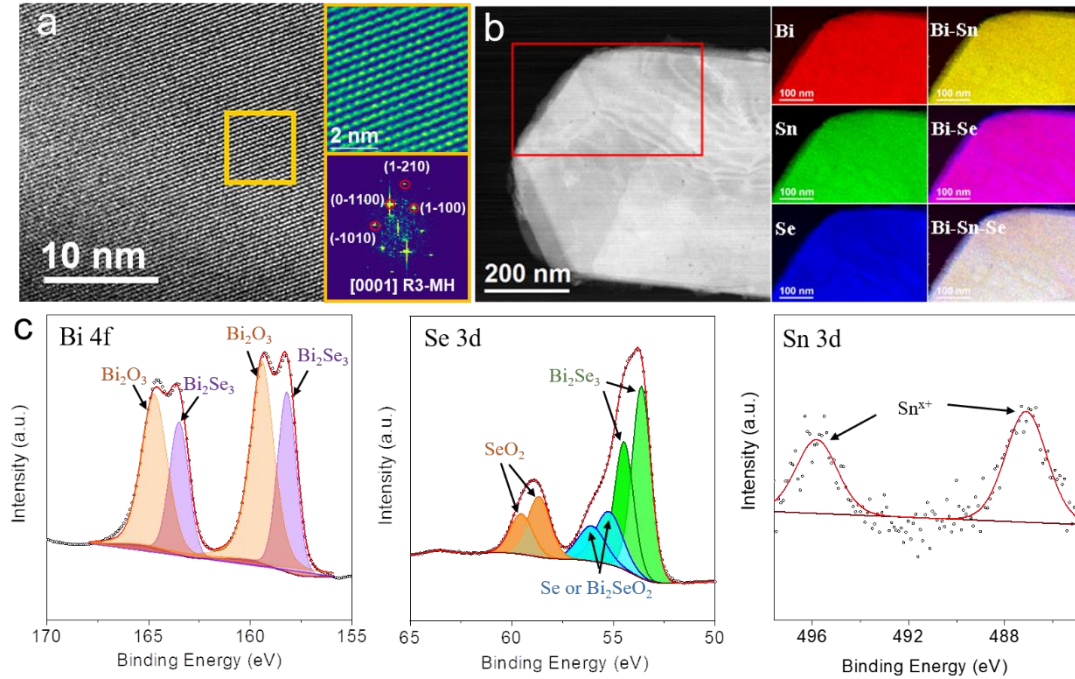


Figure 7. a) HRTEM micrograph of a $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ NSs, detail of the orange squared region and its corresponding power spectrum. Bi_2Se_3 lattice fringe distances were measured to be 0.370 nm, 0.349 nm, 0.202 nm, and 0.351 nm, at 62.89° , 92.61° and 122.99° , which could be interpreted as the rhombohedral Bi_2Se_3 phase, visualized along its $[0001]$ zone axis. b) EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Bi $N_{2,3}$ -edges at 679 eV (red), Sn $M_{4,5}$ -edges at 485 eV (green), Se $M_{2,3}$ -edges at 162 eV (blue) and composites of Bi-Sn, Bi-Se as well as Bi-Sn-Se. c) Bi 4f, Se 3d and Sn 3d high resolution XPS spectra obtained from $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ NSs.

Top view and cross-section SEM images of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ (Figure 8) showed the final pellets to present a laminar microstructure with an evident preferential orientation of the material layers. Bi_2Se_3 displayed larger and thinner layers than $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$. When comparing the XRD patterns of the sample hold in two normal directions, parallel and perpendicular to the pressure axis (Figure 8e,f), we observe the relative XRD peak intensity to clearly differ. This result confirmed the preferential crystallographic orientation of the hot-pressed materials, with the $[001]$ crystallographic direction oriented parallel to the pressure

axis.

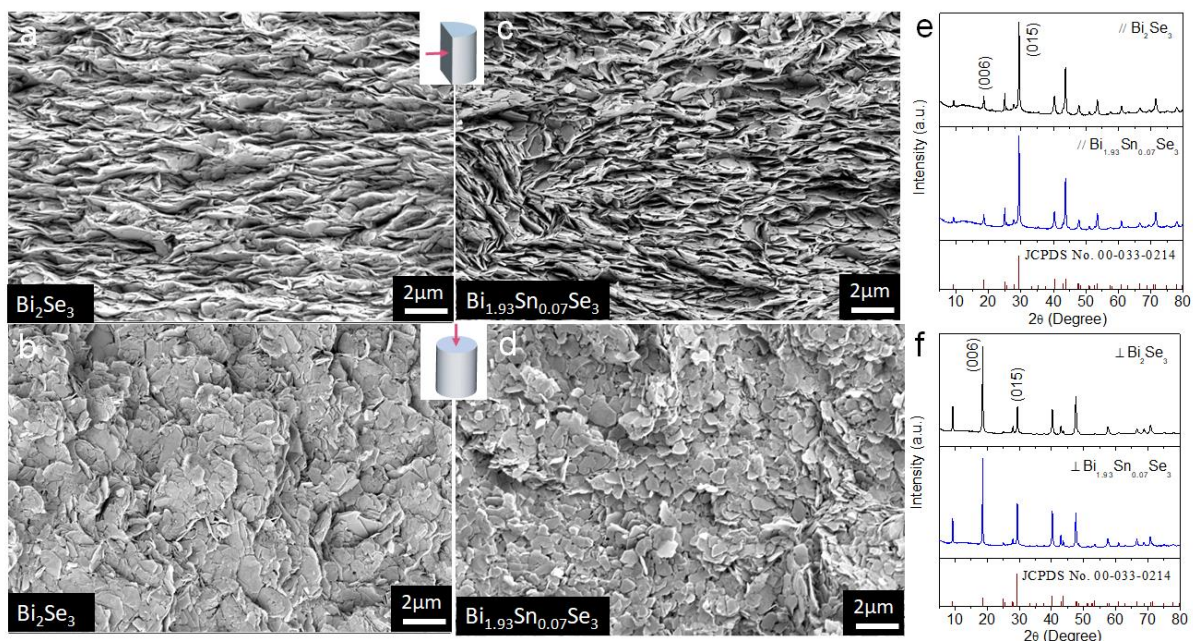


Figure. 8 a, b) Cross-section and top-view SEM micrograph of Bi_2Se_3 . c, d) Cross section and top-view SEM micrograph of $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$. e, f) XRD patterns of Bi_2Se_3 and of $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ measured in two perpendicular directions, along and perpendicular to the pressure axis.

Figure 9 displays the TE properties of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ measured in the two normal directions. As expected, $\sigma_{\perp} > \sigma_{\parallel}$ due to the higher charge carrier mobilities in the ab crystal plane compared with the c direction and the extended size of the crystal domains in the $\perp$ direction within the layered pellets. On the other hand, similar Seebeck coefficient were obtained in both directions, pointing at a minor dependence of this parameter on grain boundary scattering in this material.

When comparing the TE properties of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$, we observed $\sigma_{\perp}$ to slightly increase and $\sigma_{\parallel}$ to slightly decrease with the introduction of Sn, which could be in part related to the thinner and larger material layers observed within the layered Bi_2Se_3 pellets compared with $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$. On the other hand, with the introduction of Sn, S increased in both directions, which resulted in higher PF in both directions for the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ sample.

Table 1 displays the Hall charge carrier concentration and mobility of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ pellets at room temperature. As expected from the electrical conductivity and Seebeck coefficient measurements, we observed the Sn introduction to result in a decrease in the charge carrier concentration, from $n_H = 1.8 \times 10^{19} \text{ cm}^{-3}$ for Bi_2Se_3 to $n_H = 1.3 \times 10^{19} \text{ cm}^{-3}$ for $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$. This result is consistent with the presence of Sn^{2+} replacing Bi^{3+} ions, thus

trapping a free electron. We believe this optimization of the charge carrier concentration to be at the origin of the higher PF obtained with the introduction of Sn. We further calculated the effective mass of the Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ materials using a single parabolic band (SPB) model. For detailed calculations, the carrier transport property analysis included:³²

The Seebeck coefficient,

$$S(\eta) = \frac{\kappa_B}{e} \left[\frac{(r+5/2) \cdot F_{r+3/2}(\eta)}{(r+3/2) \cdot F_{r+1/2}(\eta)} - \eta \right] \quad (1)$$

The Hall carrier concentration,

$$n_H = \frac{1}{e \cdot R_H} = \frac{(2m^* \cdot \kappa_B T)^{3/2}}{3\pi^2 \hbar^3} \cdot \frac{(r+3/2)^2 \cdot F_{r+1/2}^2(\eta)}{(2r+3/2) \cdot F_{2r+1/2}(\eta)} \quad (2)$$

The Hall mobility,

$$\mu_H = \left[\frac{e\pi\hbar^4}{\sqrt{2}(\kappa_B T)^{3/2}} \frac{C_l}{E_{def}^2 (m^*)^{5/2}} \right] \frac{(2r+3/2) \cdot F_{2r+1/2}(\eta)}{(r+3/2)^2 \cdot F_{r+1/2}(\eta)} \quad (3)$$

where $F_x(\eta) = \int_0^\infty \frac{\varepsilon^x}{1+e^{(\varepsilon-\eta)}} d\varepsilon$ is the Fermi integral.

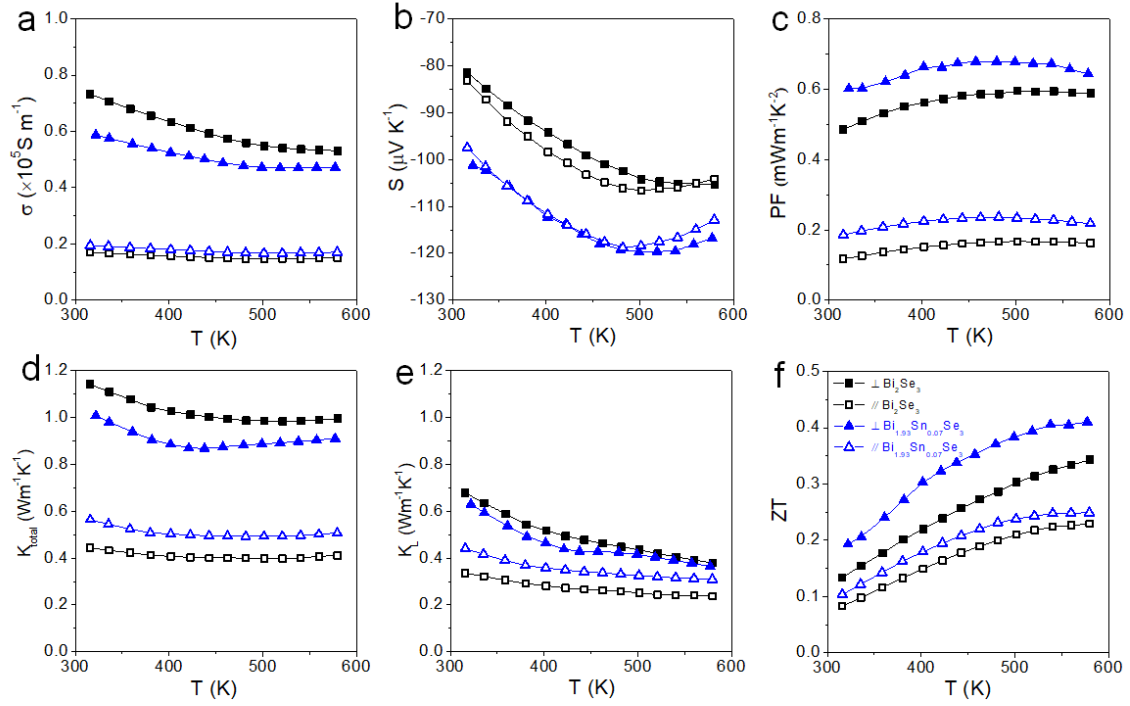
In the above equations, S , μ_H , η , κ_B , e , r , R_H , $\hbar$, C_l , E_{def} , and m^* are the Seebeck coefficient, the carrier mobility, the reduced Fermi level, the Boltzmann constant, the electron charge, the carrier scattering factor ($r = -1/2$ for acoustic phonon scattering), the Hall coefficient, the reduced plank constant, the elastic constant for longitudinal vibrations, the deformation potential coefficient, and the density of state effective mass, respectively. Using the experimental S , the reduced Fermi level η can be obtained by Equation (1). Substituting the estimated η and the measured “ n_H ” and “ μ_H ” into Equations (2) and (3), the effective mass “ m^* ” can be calculated. The results show that m^* increased slightly with the Sn doping (Table 1).

Consistently with the layered structure of the pellets and their crystallographic texture, the thermal conductivity of the materials measured in the direction normal to the pressure axis was much higher than in the pressure axis, $\kappa_\perp > \kappa_\parallel$. The introduction of Sn resulted in lower $\kappa_\perp$ but higher $\kappa_\parallel$ values, which is related to the different microstructure of the layers, with thicker and smaller $\text{Bi}_{1.93}\text{Se}_{0.07}\text{Se}_3$ plates compared with those within the Bi_2Se_3 pellet.

Overall $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ samples measured in the pellet plane displayed the highest PF and ZT values, $0.65 \text{ mWm}^{-1}\text{K}^{-2}$ and 0.41 , respectively. These values are among the higher published for Bi_2Se_3 -based materials as displayed in Table 2.

Table 1. Room temperature transport properties of Bi₂Se₃ and Bi_{1.93}Sn_{0.07}Se₃ pellets.

Materials	n_H [10^{19} cm^{-3}]	$\mu_{H\perp}$ [$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]	$\mu_{H\parallel}$ [$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]
Bi₂Se₃	1.77	178.6	41.3
Bi_{1.93}Sn_{0.07}Se₃	1.34	239.3	79.7

**Figure 9.** TE properties of Bi₂Se₃ and Bi_{1.93}Sn_{0.07}Se₃ along and perpendicular to the pressure axis: a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) power factor, PF ; d) total thermal conductivity, κ ; e) thermal conductivity after subtraction of electronic component, $\kappa - \kappa_e$; and f) TE figure of merit, ZT .**Table 2.** Comprehensive summary on the TE performance of previously reported Bi₂Se₃.

Materials	ZT at room temperature				ZT _{max}			
	$\sigma(10^4 \text{ S/m})$	$S(\mu\text{V/K})$	κ (W/mK)	ZT	$\sigma(10^4 \text{ S/m})$	$S(\mu\text{V/K})$	$\kappa(\text{W/mK})$	ZT
K _{2.5} Bi _{8.5} Se ₁₄	0.4	-100	0.6	0.05	1.8	-160	0.38	1 (873K)
Bi _{0.7} Sb _{0.3} Se	4.5	-138	0.5	0.45	4.2	-160	0.7	0.8 (425K)
Bi _{5.6} Sb _{2.4} Se ₇					4.8	-168.5	0.73	0.55 (300K)
Bi ₂ Se ₃	2	-120	0.5	0.17	1.95	-155	0.4	0.48 (427K)
Bi ₂ Se ₃	1.78	-90	0.42	0.1	3	-120.7	0.49	0.35 (400K)
Bi ₂ Se ₃ HA _{0.11} DMSO _{0.06}	14.8	-80	1.52	0.187				
Bi ₂ Se ₃	2.5	-60	0.55	0.05	2	-100	0.6	0.18 (480K)

Cu _{0.1} Bi ₂ Se ₃					1.46	-84	0.32	0.1 (290K)
Bi ₂ Se ₃	0.212	-115	0.75	0.011	0.6755	-150	0.83	0.096 (523K)
This work	5.87	-101	1	0.195	4.72	-116	0.91	0.41 (577K)

4.5 Conclutions

We report a large scale method to synthesize n-type Bi₂Se₃ NSs with different dopants. Samples doped with Sn provided the highest TE performances. The composition was optimized at Bi_{1.93}Se_{0.07}Se₃. Upon Sn doping, we observed an increase of the Seebeck coefficient and the power factor compared to pure Bi₂Se₃. As a result, a power factor up to 0.65 mWm⁻¹K⁻² and a ZT of 0.41 were obtained for the Bi_{1.93}Sn_{0.07}Se₃ pellet measured in the direction perpendicular to the pressure axis, which represents a 60% increase over pure Bi₂Se₃.

4.6 References

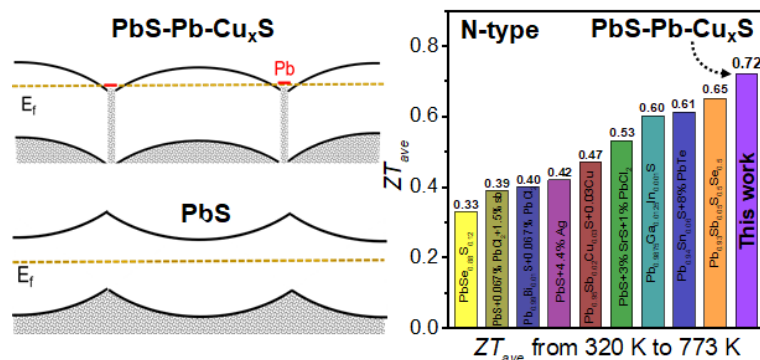
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Chapter 5 PbS-Pb-Cu_xS Composites for Thermoelectric Application



5.1 Abstract

Composite materials offer numerous advantages in a wide range of applications, including TEs. Here semiconductor-metal composites are produced by just blending NPs of a sulfide semiconductor obtained in aqueous solution and at room temperature, with a metallic Cu powder. The obtained blend is annealed in a reducing atmosphere and afterwards consolidated into dense polycrystalline pellets by means of SPS. We observe that, during the annealing process, the presence of metallic copper activates a partial reduction of the PbS, resulting in the formation of PbS-Pb-Cu_xS composites. The presence of metallic lead in the final composite leads to a strong increase of the charge carrier concentration through spillover of charge carriers enabled by the low work function of lead. We also observe a concomitant increase of the charge carrier mobility associated with a decrease of the interface energy barriers. These properties translate into power factors up to 2.1 mWm⁻¹K⁻² at ambient temperature. Besides, the presence of multiple phases in the final composite results in a notable decrease of the lattice thermal conductivity. Overall, the introduction of metallic copper in the initial blend results in a significant improvement of the TE performance of PbS, reaching a dimensionless TE figure of merit $ZT = 1.1$ at 750 K, which represents about a 400% increase over bare PbS. Besides, an average $ZT_{ave} = 0.72$ in the temperature range 320-773 K is demonstrated.

5.2 Introduction

The energy conversion efficiency of TE devices strongly depends on three key material properties: Seebeck coefficient, electrical conductivity, and thermal conductivity, which can

be grouped within a dimensionless figure of merit: $ZT = S^2 \sigma T / \kappa$. Among the numerous strategies used to maximize this TE figure of merit and thus the device efficiency, the use of composite materials offers numerous advantages.^{1–3} In composites, the thermal conductivity can be strongly reduced by effective phonon scattering at the interfaces of two dissimilar materials.^{4–8} Additionally, high electrical conductivities can be reached by adjusting the charge carrier concentration with a minor influence on the charge carrier mobility through modulation doping.^{9–13} Besides, the Seebeck coefficient can also be increased by selective scattering of minority and low energy charge carriers at interfaces.^{14,15}

A particularly interesting type of nanocomposite is obtained from combining a semiconductor host having a large Seebeck coefficient with metallic inclusions of a material providing a proper band alignment with the host. This combination offers a strong acoustic impedance mismatch between the two phases that results in an efficient interface phonon scattering.^{16–18} Additionally, metals are convenient charge pools that can adjust the host charge carrier concentration by means of charge spillover. Besides, Schottky metal-semiconductor interfaces can effectively scatter minority and low energy carriers.

PbS is regarded as a paradigmatic TE material owing to its simple binary composition and excellent charge transport properties.^{19–28} In a previous work, we presented experimental results on the thermal and electrical transport properties of PbS-metal composites produced by a versatile particle blending procedure, and where the metal work function allowed injecting electrons to the intrinsic PbS host.

In the present work, we present a simpler strategy to prepare a composite material with improved efficiency through a slightly more intricate mechanism. The composite material is obtained by blending PbS NPs produced at ambient temperature and atmosphere in aqueous solution with a commercial Cu powder. The powder blend is annealed in a reducing atmosphere to remove surface oxides, and consolidated into dense polycrystalline composites by means of SPS. Subsequently the TE properties of the obtained composites are characterized. Results show the strong and indirect effect of the presence of copper and the processing parameters on the TE properties of the obtained composites.

5.3 Experimental section

Chemicals: Lead (II) acetate trihydrate ($\text{Pb}(\text{OOCCH}_3)_2 \cdot 3\text{H}_2\text{O}$), copper (II) nitrate trihydrate

($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), and ammonium sulfide solution ($(\text{NH}_4)_2\text{S}$, 20% in H_2O) were purchased from Fisher. Copper powder ($<45 \mu\text{m}$) was purchased from Sigma. All chemicals were used as received, without further purification.

PbS NPs: All reactions were carried out under ambient temperature, pressure and atmosphere in a fume hood. To produce PbS NPs, 5 g $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ was dissolved with the help of ultrasounds in 100 ml of deionized water inside a bottle. Then, 5 ml $(\text{NH}_4)_2\text{S}$ aqueous solution was injected into the lead precursor solution. Upon injection of the $(\text{NH}_4)_2\text{S}$ solution, $(\text{NH}_4)_2\text{S}$ stoichiometrically reacted with $\text{Pb}(\text{CH}_3\text{COO})_2$ resulting in the instantaneous precipitation of PbS NPs. PbS was separated by centrifugation and washed two times with H_2O and two more times with ethanol. The product was finally dried under vacuum for 2 hours at room temperature (Figure S1).

PbS pellets: Dense PbS polycrystalline materials were produced in two steps. First, NPs were annealed at 600 °C for 180 min under a flow of reducing gas (95%Ar+5% H_2) inside a tube furnace. The annealed material was grinded into a fine powder with an agate mortar, and loaded into a graphite die within the glovebox before being sintered. The SPS process was carried out under vacuum, in an AGUS PECS SPS System-Model SPS 210Sx, that applied a pressure of 45 MPa and a temperature of 600 °C for 5 min.

PbS-Cu composites: PbS-Cu composites were produced by blending PbS NPs with commercial Cu powder within ethanol and with the aid of an ultrasonic bath for 30 min. The blend was dried under vacuum at room temperature, annealed under a flow of reducing gas, and finally SPS processed under the conditions detailed above.

Structural and chemical characterization: The relative densities of the compacted pellets were measured by the Archimedes' method. XRD patterns were measured by a Bruker AXS D8 Advance X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). SEM characterization was carried out in an Auriga Zeiss field emission SEM operated at 5.0 kV. EDX was carried out with an Oxford spectrometer attached to a Zeiss Auriga SEM at 20.0 kV. TEM, STEM, and HRTEM were carried out under the 200 keV Tecnai F20 field emission microscope. EELS and HAADF-STEM were carried out using a Gatan Quantum image filter embedded in the F20 (S)TEM. XPS was performed on a Specs system, equipped with a Mg anode XR50 source and a Phoibos 150 MCD-9 detector. XPS data was processed using the CasaXPS software.

TE properties: The Seebeck coefficient and resistivity were simultaneously measured under helium atmosphere in a LSR-3 Linseis system. All samples were tested for at least three heating

and cooling cycles. Considering the system and measurement accuracy and measurement accuracy, we estimated the measurement error of conductivity and Seebeck coefficient to be about 4%. Thermal conductivities were obtained by multiplying the λ , C_p and ρ : $\kappa_{total} = \lambda C_p \rho$. Thermal diffusivities were measured by a Xenon Flash Apparatus XFA 600 and a Laser Flash Analyzer LFA 1000, Linseis, which have an estimated error of *ca.* 5 %. The heat capacity was estimated from the Dulong–Petit limit (3R law). The Hall charge carrier concentrations and mobilities were measured by the Van der Pauw method at room temperature under a magnetic field of 0.6 T (ezHEMS, NanoMagnetics). Values provided correspond to the average of 6 measurements and the estimated error is *ca.* 10%.

5.4 Results and discussions

Quasi-spherical PbS NPs with an average size of 18 nm were produced in aqueous solution, without any surfactant, from the reaction of $(\text{NH}_4)_2\text{S}$ and $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ in air atmosphere and at ambient temperature (Figures 1 and 2a). The XRD pattern of the obtained material is consistent with a PbS cubic phase (JCPDS No. 01-077-0244, Figure 2b). Figure 2c shows a representative HRTEM micrograph of the PbS sample, with a detail of the orange squared region and its corresponding power spectrum that confirm the cubic PbS crystalline structure (space group = FM3-M) and allows determining the lattice parameter as $a=b=c=5.9360 \text{ \AA}$. EELS elemental composition maps obtained from the red squared region in the HAADF-STEM micrograph shown in Figure 2d demonstrate a uniform distribution of Pb and S through the NPs.

The high resolution Pb 4f XPS spectrum of PbS NPs was properly fitted using four bands. The bands located at 142.4 eV and 137.6 eV corresponded to Pb 4f_{5/2} and Pb 4f_{7/2} core levels of Pb²⁺ cations within a PbS chemical environment.²⁹ Bands at 142.7 eV and 137.9 eV were associated with the Pb 4f core levels of Pb²⁺ within a PbO environment.^{27,30} The presence of PbO is related to the partial surface oxidation of the material upon exposure to ambient atmosphere.^{12,31} The S 2p XPS spectrum of PbS displayed just one peak that was fitted with two bands located at 162.0 eV and 160.8 eV, and which corresponded to S 2p_{1/2} and S 2p_{3/2} core levels of S²⁻ anions within PbS.^{27,29,30}

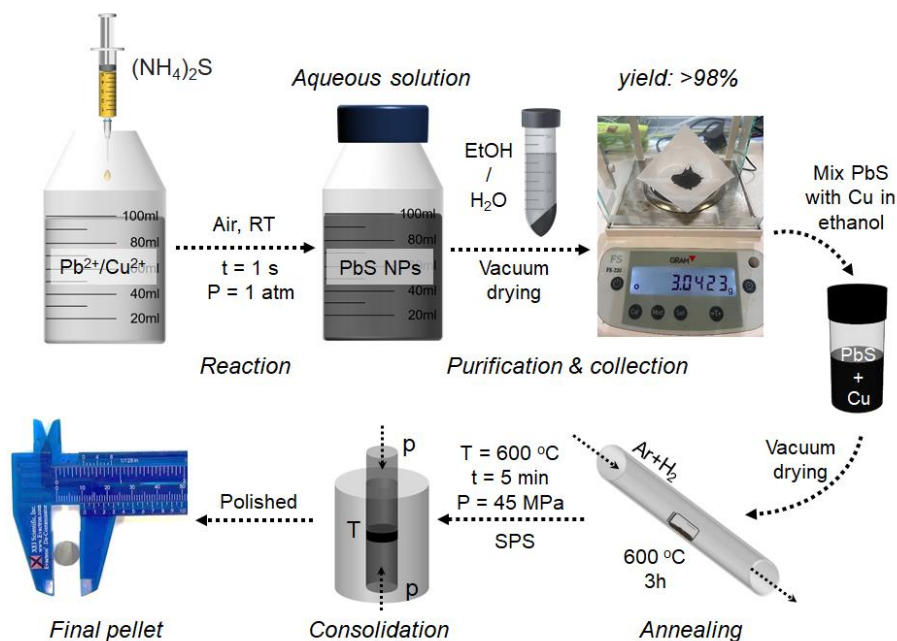


Figure 1. Schematic illustration of the process used to produce PbS pellets. The process involves the synthesis of NPs at ambient pressure and temperature, the annealing of the particles at 600°C in Ar/H_2 atmosphere, and the SPS of the materials at 600°C and 45 MPa.

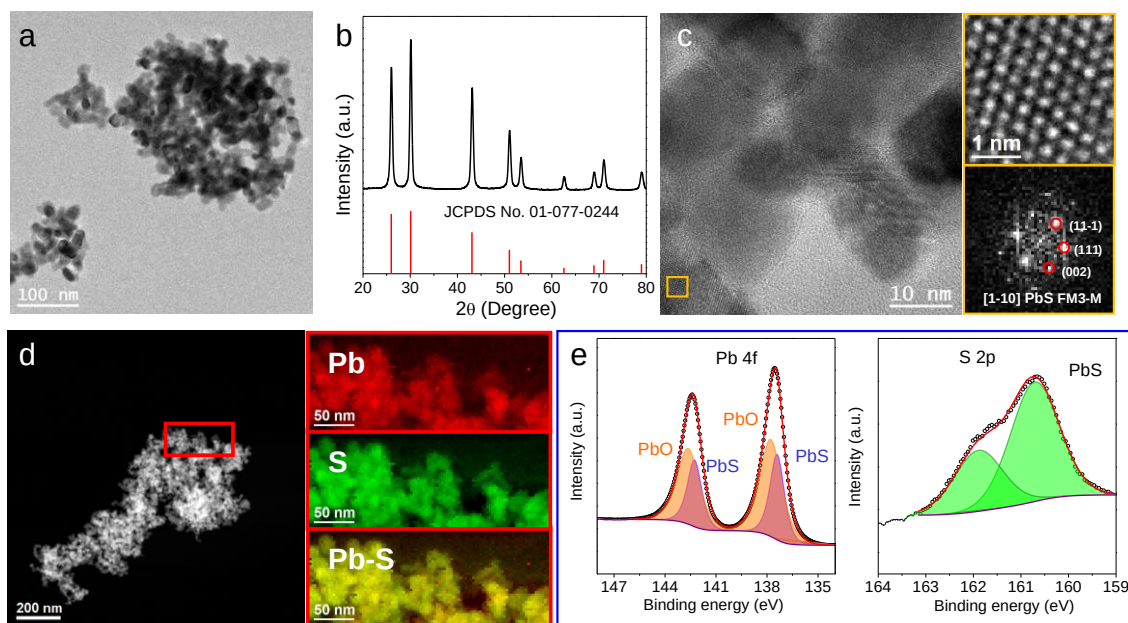


Figure 2. Structural and chemical properties of PbS NPs. a) TEM micrograph. b) XRD pattern. c) HRTEM micrograph, detail of the orange squared region and its corresponding power spectrum. From the crystalline domain, the PbS lattice fringe distances were measured to be 0.344 nm, 0.330 nm and 0.296 nm, at 70.39° and 120.78° which could be interpreted as the

cubic PbS phase, visualized along its [101] zone axis. d) EELS chemical composition maps obtained from the red squared area in the STEM micrograph. Individual Pb $N_{4,5}$ -edge at 413 eV (red), S $L_{2,3}$ -edge at 165 eV (green) and its composite. e) Pb 4f and S 2p high resolution XPS spectra.

In contrast to PbS, which typically shows an intrinsic n-type behaviour related to the presence of S vacancies, PbO shows p-type conductivity. Thus, the removal of PbO is essential to optimize the TE properties of PbS-based materials. We removed PbO by annealing the materials in an Ar/H₂ atmosphere at 600 °C during 3 h, as detailed in the experimental section. Figure 3 displays the XRD pattern of the annealed material. Upon annealing, XRD peaks became sharper, indicating a higher crystallinity, and no additional phase was detected.

The annealed material was subsequently loaded into a 10 mm graphite die and spark plasma sintered at 600°C and 45 MPa for 5 min under vacuum. The relative density of the obtained pellet was *ca.* 95% of the theoretical value, as measured by the Archimedes' method. Cross-section SEM characterization showed the size of the crystal domains within the SPS sintered material to be significantly larger ($\sim 0.5 \mu\text{m}$) than the precursor PbS NPs (Figure 4). To determine the annealing influence on the TE properties of the materials, a second pellet was produced from the unannealed PbS NPs, using the same SPS procedure.

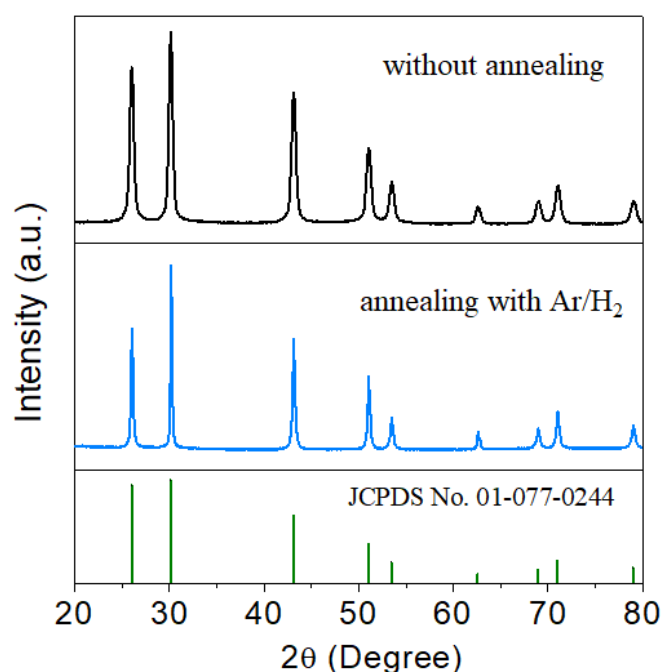


Figure 3. XRD patterns of PbS nanopowder with and without H₂-reducing/annealing step.

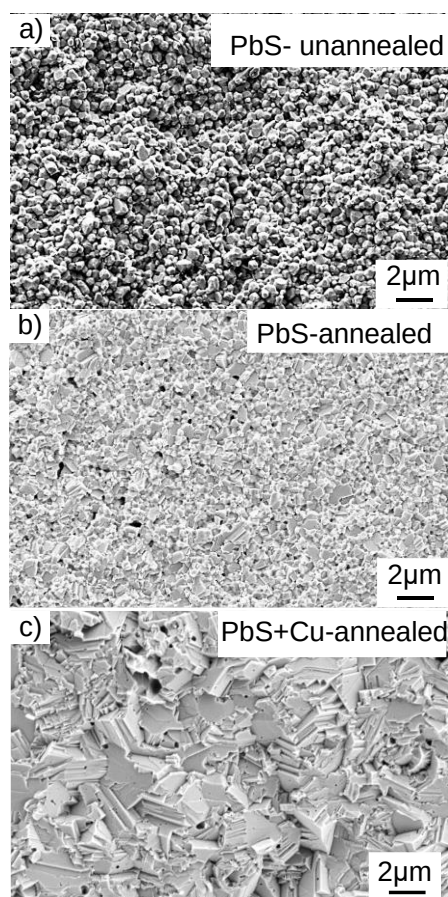


Figure 4. Cross section SEM images of unannealed and annealed PbS pellets and annealed PbS+5% Cu pellet.

As expected, the pellet obtained from the annealed PbS displayed a much higher electrical conductivity than the pellet produced from unannealed PbS NPs, especially in the low temperature range (Figure 5). This higher electrical conductivity is related both to the removal of PbO and to the formation of additional S vacancies during the annealing process. Naturally, the material pre-annealed in H_2 displayed a negative Seebeck coefficient, denoting n-type conductivity, in all the temperature range measured. In contrast, the PbS obtained from unannealed particles was characterized by a positive Seebeck coefficient at temperatures below 500 K and a negative S at higher temperatures. This change of conductivity type with temperature is consistent with previous works and has been associated to the presence of p-type PbO.¹¹ When increasing temperature, the concentration of thermally generate charge carriers eventually overcomes the hole density associated to the presence of PbO and the intrinsic n-type character of PbS becomes dominant.

The higher electrical conductivity and absolute Seebeck coefficients of the pre-annealed material resulted in much higher power factors, up to $1.1 \text{ mWm}^{-1}\text{K}^{-2}$. On the other hand, the

smaller crystal domain size of the unannealed material and the presence of an additional phase, PbO, resulted in lower thermal conductivities than those of the pre-annealed PbS. Overall the material pre-annealed in the presence of H₂ displayed significantly higher TE figures of merit than the pellet obtained from the SPS of unannealed PbS NPs. Therefore, to investigate the effect of Cu addition, a pre-annealing step was considered for all the samples.

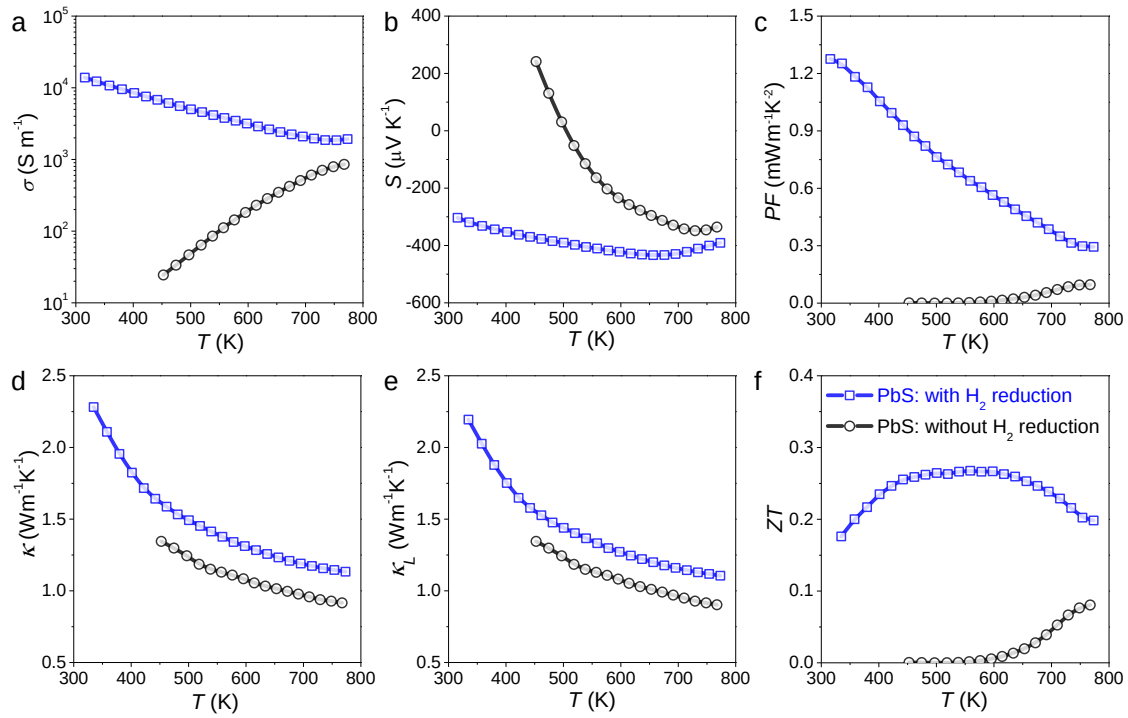


Figure 5. TE properties of PbS pellets obtained with (blue) and without (black) the annealing/reduction step: a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) power factor, PF ; d) thermal conductivity, κ_{total} ; e) lattice thermal conductivity, κ_L ; and f) figure of merit, ZT .

A representative SEM image and the XRD pattern of the commercial Cu particles used to produce PbS+Cu composites are shown in Figure 6. Composites were formed by blending in solution the proper amounts of PbS NPs and the commercial Cu powder, at different Cu molar ratios (0 mol%, 3 mol%, 5 mol%, 7 mol%). The mixture was dried and then annealed in Ar/H₂ atmosphere. The XRD patterns of the particle mixture clearly displayed the presence of PbS and metallic copper (Figure 7a). On the other hand, in addition to the fingerprint of the cubic PbS phase, the XRD pattern of the annealed samples did not display the metal copper signal but the diffraction peaks of the metallic Pb phase (Figure 7b). This result indicates that during the hydrogen reduction process, copper reacts with S from PbS, forming metallic Pb and a poor crystallinity Cu_xS phase that is not detected by XRD.

The annealed material was grinded into a fine powder with an agate mortar, and loaded into a 10 mm graphite die in the glovebox. The material was then spark plasma sintered at 600°C and 45 MPa for 5 min under vacuum. SEM characterization of the pellets showed them to be characterized by an average particle size in the micron size range (Figure 4c). The XRD patterns of the pellets containing relatively large amounts of Cu displayed the presence of PbS and metallic Pb phases, but no Cu-based phase. On the other hand, SEM-EDX elemental maps of the pellets displayed a uniform distribution of S and Pb, with areas containing a higher density of Cu (Figure 8).

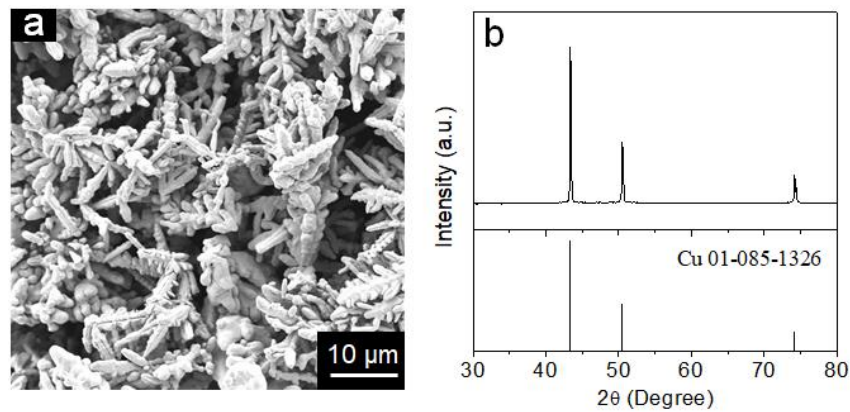


Figure 6. a) SEM image and b) XRD pattern of the commercial Cu particles.

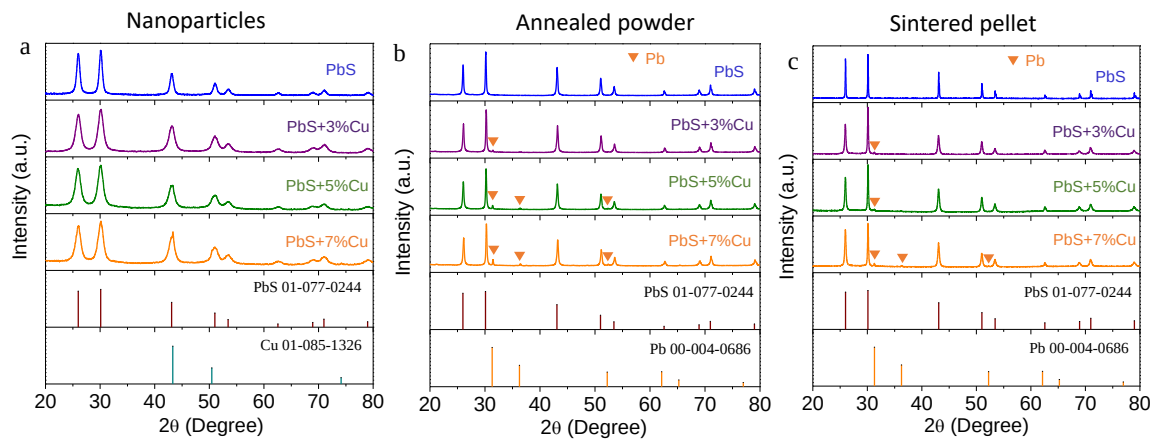


Figure 7. XRD patterns of a) PbS + x%Cu NPs, b) annealed powders, and c) SPS sintered pellets.

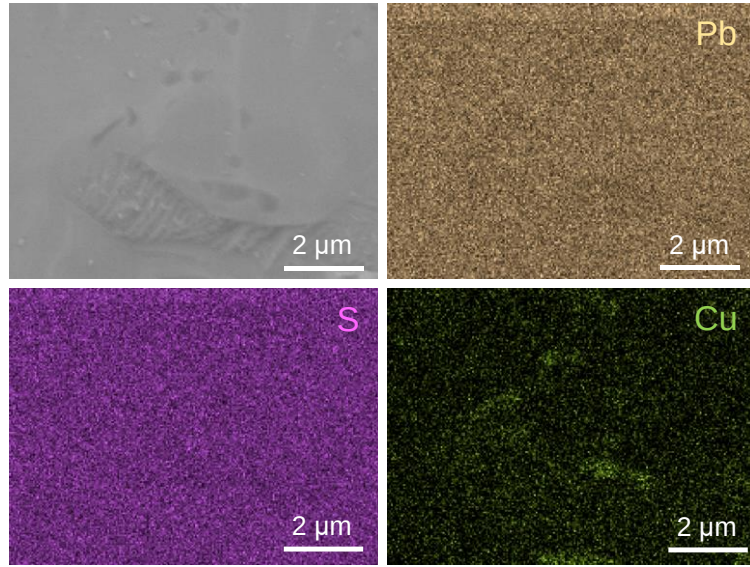


Figure 8. SEM micrograph of PbS+5%Cu pellet and corresponding EDX elemental maps.

PbS+Cu composites systematically displayed higher electrical conductivities and lower absolute values of the Seebeck coefficient than PbS (Figure 9), pointing at an increase of the charge carrier concentration with the addition of Cu. Hall measurements quantified the increase of the charge carrier concentration with the presence of Cu in one order of magnitude, from $1.8 \times 10^{18} \text{ cm}^{-3}$ for PbS to $1.7 \times 10^{19} \text{ cm}^{-3}$ for PbS+3%Cu (Figure 10a). The increase of the charge carrier concentration is associated with the injection of free electrons from the Pb domains formed during the reduction process in the pellet containing Cu. The charge injection from Pb to PbS domains is enabled by the low work function of Pb (4.14 eV) and results in a downward band bending at the PbS surface in contact with Pb domains (Figure 10b). As expected, taking into account the presence of additional charge scattering centres, Hall measurements pointed at a decrease of the charge carrier mobility for the samples containing Cu (Figure 10a).

Based on the SPB model, the Seebeck coefficient can be calculated using the following equation:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n_H} \right)^{\frac{2}{3}} \quad (1)$$

where k_B is the Boltzmann constant, h is the Planck constant, e is the elemental charge, n_H is the charge carrier concentration, and m^* is the effective mass.³² Figure 10c,d displays the weighted mobility and the Pisarenko plot including the Seebeck coefficient and charge carrier concentration of all the samples at room temperature. The introduction of copper and the annealing process in a reducing atmosphere indirectly resulted in an increase of the charge carrier concentration by one order of magnitude. Consistently with the above equation, the

Seebeck coefficient declined with increasing n_H (Figure 9b). However, the Seebeck coefficients of the samples containing Cu are slightly above the theoretical curve plotted considering the effective m^* of PbS, which we associate to a filtering effect that is observed in the form of an increase of the effective mass with the Cu content (Figure 10d). Overall, the adjustment of the Cu concentration and the indirect modulation of m^* and n_H allowed reaching high room temperature power factor, up to $2.1 \text{ mWm}^{-1}\text{K}^{-2}$ (Figure 9c), which is one of the highest values obtained for PbS-based materials at room temperature (Figure 12a).

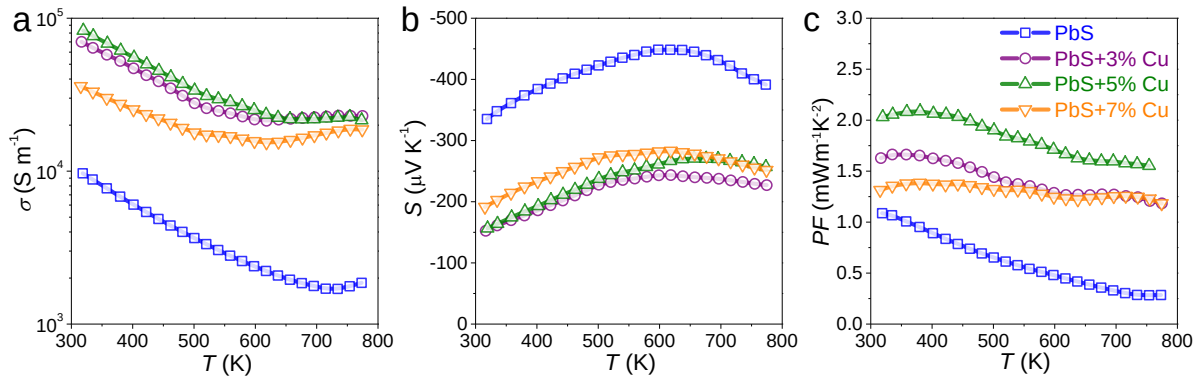


Figure 9. Electronic transport properties of PbS+xmol%Cu nanomaterials: a) electrical conductivity, σ ; b) Seebeck coefficient, S ; c) power factor, PF .

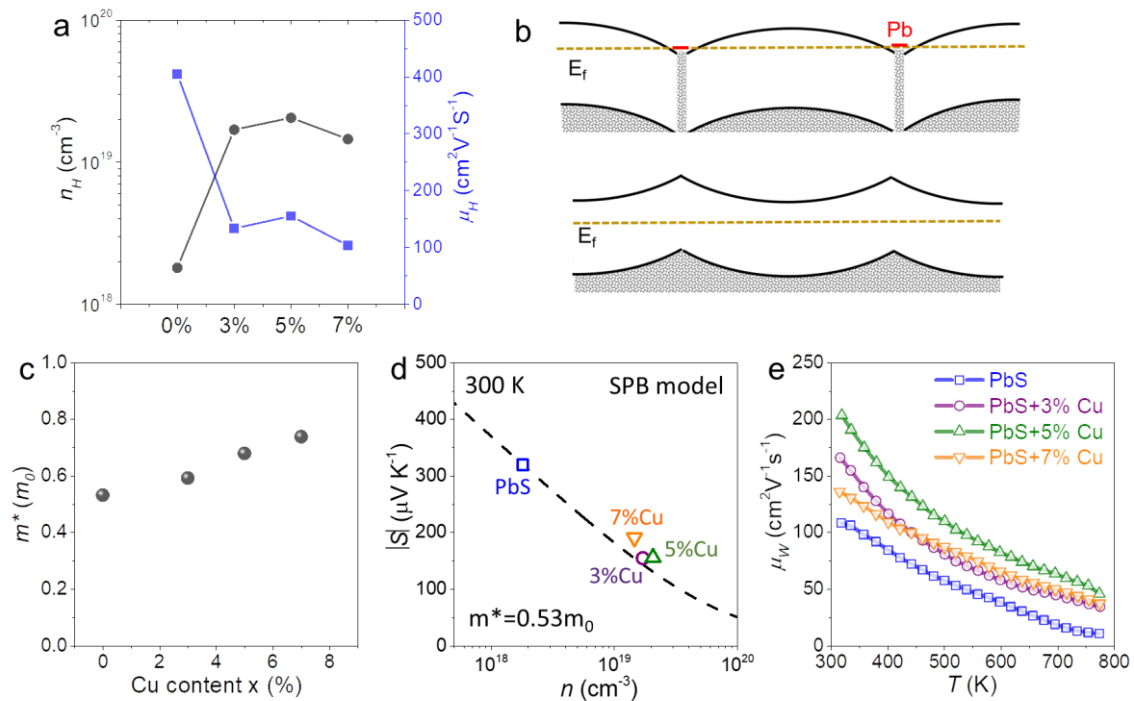


Figure 10. a) Hall charge carrier concentration n_H and mobility μ_H of PbS + x mol%Cu materials at room temperature. b) Band alignment in pure PbS (bottom) and the

PbS-Pb composite (top). c) Effective mass, m^* . d) Pisarenko relationship considering the effective mass of PbS at room temperature, $m^* = 0.53 m_0$. e) Weighted mobility, μ_w .

The weighted mobility μ_w was calculated from the electrical conductivity and Seebeck coefficient data (Figure 10e):^{26,32}

$$\mu_w = \frac{3\sigma}{8\pi e F_0(\eta)} \left(\frac{h^2}{2m_0 k_B T} \right)^{3/2} \quad (2)$$

where $F_n(\eta)$ is the Fermi integral with $n=0$ and is defined as:

$$F_n(\eta) = \int_0^\infty \frac{x^n}{1+e^{x-\eta}} dx \quad (3)$$

$$S = \pm \frac{K_B}{e} \left\{ \frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \eta \right\} \quad (4)$$

where η is the reduced chemical potential and r denotes the scattering factor, which we consider as $r=-1/2$ owing to the dominance of the acoustic scattering mechanism.³³

We observed μ_w to increase with the carrier concentration (Figure 10e), which is in contrast to the decrease of the Hall carrier mobility with the presence of Cu. The enhancement on μ_w is especially significant near room temperature, reaching very high values, up to $\sim 203 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

As expected, the processing of the material in the presence of copper reduced the κ_L over the entire temperature range (Figure 11). This reduced lattice thermal conductivity is related to the enhanced scattering at the interphase of domains with different compositions.

The quality factor B was calculated using the following equation:⁷

$$B = 9 \frac{\mu_w}{\kappa_L} \left(\frac{T}{300} \right)^{5/2} \quad (5)$$

As displayed in Figure 11c, B increased almost linearly with temperature for all samples and increased with the Cu amount over the entire temperature range.

Overall, the presence of Cu resulted in a very significant increase of ZT associated with the higher power factors and reduced κ_{lat} . Record ZT values were obtained from PbS + 5%Cu samples, reaching $ZT=1.1$ at 750 K, which is about 4 times higher than that of undoped PbS. Besides, to the best of our knowledge, the $ZT = 0.28$ obtained at room temperature from PbS + 5%Cu samples, is the highest reported for an n-type PbS-based material (Figure 11). In addition, the PbS + 5%Cu sample was characterized with a record average ZT in the range from 320 K

to 773 K, $ZT_{avg} = 0.72$. Finally, Figure 13 displays the TE properties of a PbS+5%Cu sample measured for three consecutive temperature cycles, demonstrating an excellent stability.

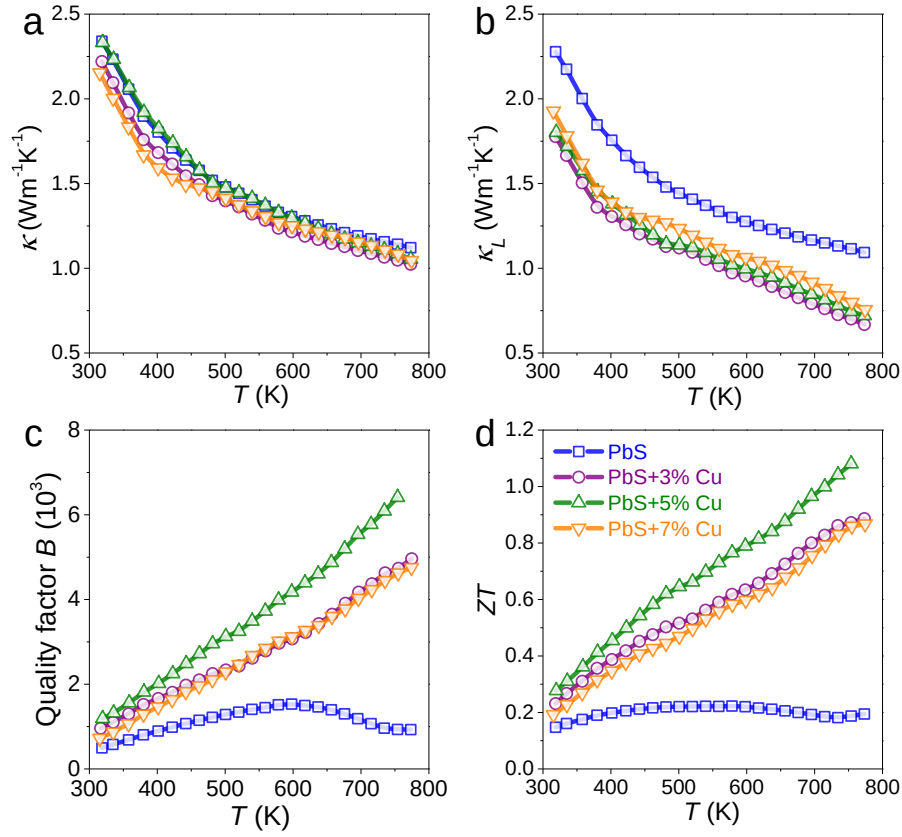


Figure 11. a) Thermal conductivity, κ . b) Lattice thermal conductivity, κ_L . c) Quality factor, B . d) TE figure of merit, ZT .

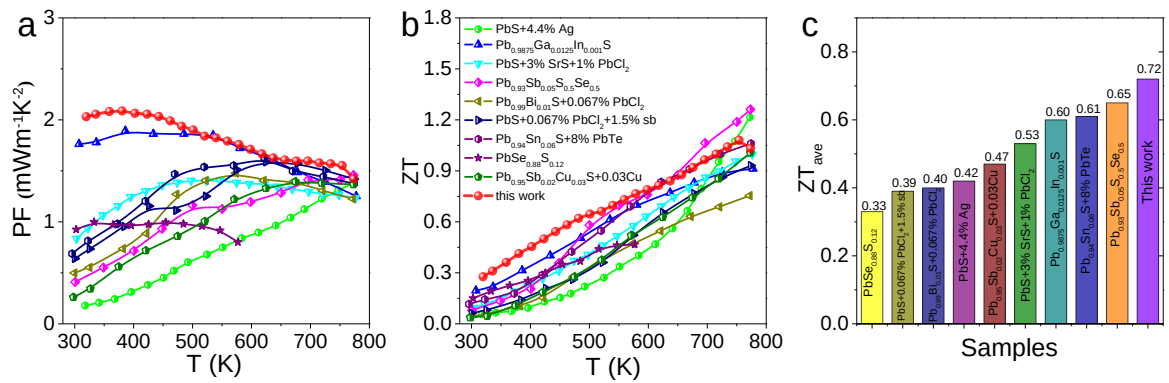


Figure 12. Performance comparison with state of the art PbS-based materials: a) PF ; b) ZT ; c) ZT_{ave} (320-773K).

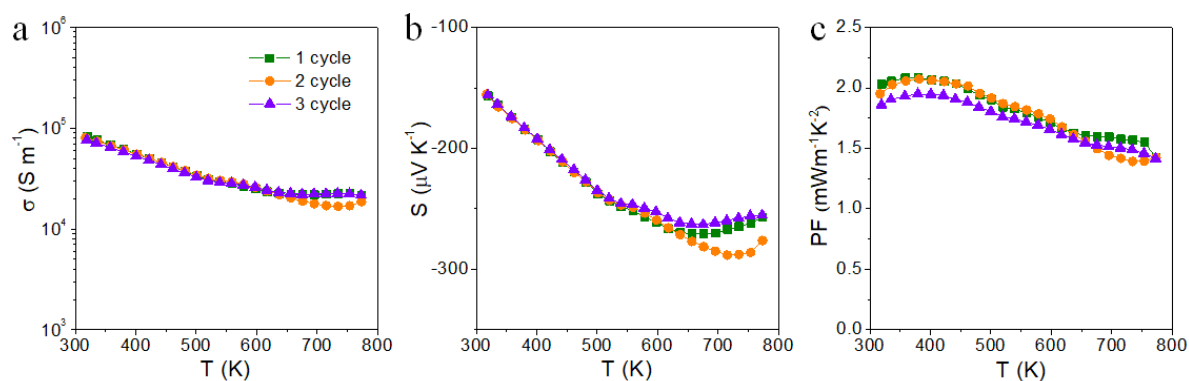


Figure 13. Temperature dependence of a) electrical conductivity, σ ; b) Seebeck coefficient, S ; and c) power factor, PF of a PbS+5%Cu pellet measured 3 consecutive cycles, from room temperature to 773 K.

5.5 Conclusions

We reported a facile rapid route, scalable and low-cost method for the synthesis of cubic PbS NPs in aqueous media and at room temperature. Lead chalcogenide materials are prone to oxidation when exposed to air with varying degrees of sensitivity, which lead to the low carrier concentration. So we removed PbO by annealing the materials in Ar/H₂ atmosphere to obtain higher electrical conductivity. Then, TE performance for n-type PbS was improved by doping Cu in our research. Firstly, we add copper acetate during the synthesis process to generate CuS NPs to achieve the purpose of doping, which can increase electrical conductivity and reduce thermal conductivity, the best ZT of PbS + 1.5%CuS reached 0.8 at 763 K. Moreover, we doped with commercial Cu particles in the PbS by blending, which can highly increase electrical conductivity and reduce lattice thermal conductivity over the whole temperature range. As a consequence, a maximum ZT value of 1.08 at 754K is acquired for PbS + 5%Cu, which is about 4 times as high as that of undoped PbS.

5.6 References

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Result and Discussions

The TE nanomaterials in this thesis are mainly produced by aqueous phase synthesis, which contain the characters of versatile, scalable, low cost and surfactant free. Firstly, we prepared the SnSe NPs using water as solvent and obtained p-type polycrystalline nanomaterials. However, the strong asymmetry of the SnSe crystal structure and the related anisotropic properties inevitably result in polycrystalline samples with low ZT , as a result of averaging them for the different crystallographic directions. Thus, to overcome this challenge, crystallographically textured polycrystalline materials are required. Devices based on highly crystallographically textured nanomaterials produced from the bottom up consolidation of NCs could have associated not only optimized TE performance, but also reduced production cost, especially if printing technologies could be used to produce them. So we blend liquid dispersions of SnSe NCs and Te NRs at different ratios. Taking advantage of the low Te melting point, we use a liquid phase sintering strategy to produce laminated and crystallographically textured SnSe nanomaterials, which TE properties we characterized in two directions. After consolidation, part of this Te was found within the SnSe lattice and part remained as elemental Te between the SnSe grains. The presence of Te during the SnSe consolidation resulted in SnSe nanomaterials with higher σ and lower S and κ , which lead to the higher TE property.

Afterwards, we use a simple and low-cost room temperature aqueous phase method for the large-scale preparation of copper sulfide. Then we analyze the possibilities of tuning the crystallographic phase and stoichiometry of nanocrystalline Cu_{2-x}S by means of thermal annealing at moderate temperatures under inert or reducing gas atmospheres. Finally, we analyze the TE properties of the obtained compounds as a function of the annealing temperature, time and atmosphere, and explain the obtained results taking into account the different sample stoichiometries and the phase transitions undergone by the materials when heated. Additionally, we use the same method to produce the lead sulfide NPs. The same procedure can be used to synthesize a range of other chalcogenide compounds, including doped materials. We further characterize the TE properties of the obtained n-type PbS and demonstrate that the incorporation of Cu can improve the material performance. Two doping strategies are tested, the incorporation of a Cu salt during the growth of PbS NPs, and the blending of PbS with preformed Cu particles. Doping through a salt allows increasing σ and reduce κ . The blending of PbS with Cu particles also results in a strong increase of σ associated with a significant

increase of the charge carrier concentration while maintaining a large charge carrier mobility, which translated into record PF at ambient temperature. Simultaneously, the κ_L decreased with the introduction of Cu, which the B increased obviously compared with pure PbS over the entire temperature range.

In addition, we use a low temperature and high yield, solution-based strategy to prepare Bi_2Se_3 NSs doped with different elements. The influence of different dopants on the TE properties of the material was tested. From the obtained results, we demonstrate Sn to have the highest potential to yield Bi_2Se_3 -based materials with improved performance. Thus we further analyse the location and chemical state of this element within Bi_2Se_3 and its effect on the material transport properties.

Conclusions

In this thesis, I detailed the production and characterization of TE nanomaterials by two main solution processed strategies, with remarkably improved TE performance by means of controllable nanoengineering. The characterization of nanomaterials has been investigated in detail in each chapter, including: NC phase, morphology, optical property, surface chemistry, etc. The TE performance has been studied by testing electric and thermal transport properties of consolidated nanomaterials in a wide temperature range. Two main optimization methodologies to achieve higher TE performance were specifically explored in this thesis: atomic doping and modulation doping approach. The related mechanism to improved TE performance was further analyzed to explain how to achieve the desired TE properties.

In the first part, p-type polycrystalline SnSe materials with marked crystallographic texture were produced from blends of SnSe NCs and Te NRs through hot-pressing them at a temperature above Te melting point. The presence of Te promoted the material crystallization in the form of a laminar structure with the a -axis along the pressure direction. Part of the Te used for the liquid phase sintering process was found within the SnSe lattice and part in the form of elemental Te within the consolidated material. The TE properties of the produced nanomaterials were measured in two perpendicular directions, along and normal to the pressure axis. SnSe nanomaterials consolidated in the presence of Te showed higher σ and lower S and κ than pure SnSe. TE figures of merit up to $ZT \sim 1.4$ at 790 K were measured from the SnSe nanomaterial consolidated in the presence of Te and measured along the pressing direction. Somehow surprisingly, lower ZT values were obtained in the direction normal to the pressure axis.

In the second part, I used a facile, scalable and low-cost method for the synthesis of covellite CuS NPs in aqueous media and at room temperature. The produced covellite NPs lost sulfur when heated under inert or reducing atmosphere, and changed their crystal phase to metastable rhombohedral $\text{Cu}_{1.8}\text{S}$ or tetragonal $\text{Cu}_{1.96}\text{S}$. The annealing atmosphere and time allowed tuning the amount of sulfur lost and thus the stoichiometry and crystal structure of the final nanopowder. The sample stoichiometry determined the density of copper vacancies, thus the hole concentration and consequently the transport properties of the material. Comparing the material annealed in Ar with the annealed in Ar/ H_2 , we observed the former to be characterized by much higher charge carrier concentrations and electrical conductivities, but lower Seebeck coefficients. Finally, the material annealed in Ar/ H_2 for 3 h was characterized by the highest

PF and *TE* figures of merit, up to 1.41 at 710 K, which is the highest *ZT* reported for Cu_{2-x}S at this temperature. The availability of the material in the form of NPs also allowed the direct printing of the material into layers that were characterized by similar *TE* performances as those obtained from the pellets.

In the third part, I used a large scale method to synthesize n-type Bi_2Se_3 NSs with different dopants. Samples doped with Sn provided the highest *TE* performances. The composition was optimized at $\text{Bi}_{1.93}\text{Se}_{0.07}\text{Se}_3$. Upon Sn doping, we observed an increase of the *S* and *PF* compared to pure Bi_2Se_3 . As a result, a *PF* up to $0.65 \text{ mWm}^{-1}\text{K}^{-2}$ and a *ZT* of 0.41 were obtained for the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ pellet measured in the direction perpendicular to the pressure axis, which represents a 60% increase over pure Bi_2Se_3 .

In the fourth part, I used the same method with CuS to synthesis of cubic PbS NPs in aqueous media and at room temperature. Lead chalcogenide materials are prone to oxidation when exposed to air with varying degrees of sensitivity, which lead to the low carrier concentration. So we removed PbO by annealing the materials in Ar/ H_2 atmosphere to obtain higher σ . Then, *TE* performance for n-type PbS was improved by doping Cu in our research. As a consequence, a maximum *ZT* value of 1.1 at 750K is acquired for PbS + 5%Cu, which is about 4 times as high as that of undoped PbS.

In summary, this thesis has detailed different strategies to improve *TE* performance of bulk nanomaterials produced from solution processed methods. In addition, it has been demonstrated that solution processed synthesis appears to be a high-throughput, high yield, low cost, feasible at ambient pressure and low temperature chemical routes, which allows production of *TE* materials with composition, size, shape and phases control to optimize their *TE* properties.

Future work

The solution processes are expected to play an important role in preparing TE nanomaterials, while the method with controllable size, morphology and surface chemistry offer a convenient route towards inexpensive and scalable TE materials. However, the practical adoption of those processes towards high quality nanomaterials still remains challenges. I will continue my research in the future in the following 3 main areas:

- i) To further improved the property of Bi_2Se_3 -based nanomaterials by doping Al and Fe, which will generate a resonance band near the Fermi level to increase the Seebeck value.
- ii) To fabricate bulk TE modules with fabricate bulk TE modules with versatile form factors. To develop composites for potential application in wearable TE devices based on high-performance p-type Cu_{2-x}S and n-type Ag_2Se .
- iii) To development the new TE materials based on solution synthesis method, which with high TE performance, and further fabrication of devices.

CURRICULUM VITAE

Personal Information

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Education

- 2017.9-present: PhD, Nanoscience, Catalonia Institute for Energy Research-IREC, University of Barcelona, Spain
Thesis: Solution-Based Bottom-Up Processing of Chalcogenide Thermoelectric Nanomaterials
Supervisor: Prof. Andreu Cabot
- 2014.9-2017.7: Master, Condensed Matter Physics, Shanghai University, China
- 2010.9-2014.7: Bachelor, Physics, Henan Normal University, China

Research Experience

My PhD research is focused on optimizing TE performance of metal chalcogenide (SnSe , Cu_xS , PbS , Bi_2Se_3) by using precisely designed nanocrystals as building blocks. My research experience mainly covers:

- ✧ Solution synthesis of nanocrystals
- ✧ Unravelling of nanocrystal surface chemistry
- ✧ Nanocrystals assemble and consolidation
- ✧ Transport properties of nanocrystal-based solid
- ✧ Bottom-up processed TE nanomaterials

Research Interests

Unravelling of structure-property relationships of nanomaterials and their use in developing efficient TE materials

Awards

- Chinese Scholarship Council (2017)
- Outstanding Graduate Student Award (2017)

Conferences

Oral presentation: "Solution processed copper chalcogenides NPs for TE application" in the Heraeus "Exciting nanostructures" Conference in Bad Honnef (July 2019)

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Annex



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Crystallographically textured SnSe nanomaterials produced from the liquid phase sintering of nanocrystals†

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We report the thermoelectric performance of p-type nanocrystalline SnSe obtained from the liquid phase sintering of blends of SnSe nanocrystals and Te nanorods. A cycled hot press procedure at a temperature above the Te melting point promoted the formation of crystallographically textured SnSe nanomaterials with relative densities up to 93%. After consolidation, part of this Te was found within the SnSe lattice and part remained as elemental Te between the SnSe grains. The presence of Te during the SnSe consolidation resulted in SnSe nanomaterials with higher electrical conductivities and lower Seebeck coefficients and thermal conductivities. By adjusting the amount of Te, thermoelectric figures of merit (ZT) up to 1.4 at 790 K were measured in the direction of the uniaxial pressure, coinciding with the preferential a crystallographic axis. While this value matches the highest ZT value reported at this temperature for SnSe in the [100] crystal direction, the ZT values of the consolidated SnSe along the bc plane were relatively lower due to moderately low thermal conductivities in this plane.

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1. Introduction

Thermoelectricity (TE), the solid state conversion between heat and electricity, has found countless potential applications, both to harvest heat from ubiquitous temperature gradients and to precisely control temperature in endless locations and processes.¹ While TE devices are silent, easily scalable and durable, they have just impacted niche markets due to two important limitations: (i) their moderate efficiency and coefficient of performance (COP) and (ii) their relatively high price associated with the use of materials containing scarce elements such as tellurium, the complex device architectures and the elevated material processing costs.^{2,3}

Without going through the trouble of fabricating thermoelectric devices and the measurement of their efficiency/COP, the performance of TE materials is generally assessed by a dimensionless figure-of-merit, $ZT = S^2\sigma T/\kappa$, where S is the

Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the total thermal conductivity. The power factor ($PF \equiv S^2\sigma$) on the numerator thus characterizes the electronic energy conversion capability, while the denominator ($\kappa = \kappa_L + \kappa_e$), which is the sum of lattice thermal conductivity (κ_L) and electronic thermal conductivity, (κ_e) characterizes heat leakage.⁴

In the last few years, since ZT values up to 2.6 at 923 K were reported from single crystals, SnSe has received extensive attention in the thermoelectric field.^{5,6} SnSe is a IV–VI monochalcogenide semiconductor with a layered crystal structure. It is composed of reasonably abundant elements and is relatively stable. Besides a notable Seebeck coefficient and p-type electrical conductivity dominated by tin vacancies,^{7,8} the main characteristic of SnSe is its ultralow thermal conductivity in particular crystallographic directions, which has been related to a strong anharmonicity.^{2,9}

Taking into account the high cost of production of SnSe single crystals and their structural fragility, the production of polycrystalline samples with TE figures of merit as high as those obtained from single crystals is a worth endeavour. However, the strong asymmetry of the SnSe crystal structure and the related anisotropic properties inevitably result in polycrystalline samples with a lower ZT , as a result of averaging them for different crystallographic directions. Thus, to overcome this challenge, crystallographically textured polycrystalline materials are required.

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Devices based on highly crystallographically textured nanomaterials produced from the bottom up consolidation of nanocrystals (NCs) could have associated with not only optimized TE performance, but also reduced production cost, especially if printing technologies could be used to produce them.^{1,10,11} In this work, we blend liquid dispersions of SnSe NCs and Te nanorods (NRs) at different ratios (Te = 0%, 10%, 15%, 20% and 25%). Taking advantage of the low Te melting point, we use a liquid phase sintering strategy to produce laminated and crystallographically textured SnSe nanomaterials, the thermoelectric properties of which we characterize in two directions.

2. Experimental

2.1 Chemicals

Tin(II) chloride anhydrous (SnCl_2 , 98%), sodium hydroxide (NaOH , 98.5%), selenium powder (Se, $\geq 99.5\%$), sodium borohydride (NaBH_4 , $\geq 98\%$), tellurium dioxide (TeO_2 , $\geq 99\%$), potassium hydroxide (KOH , 85%), polyvinylpyrrolidone (PVP, $(\text{C}_6\text{H}_9\text{NO})_n$, average molar weight $\sim 55\,000$), ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$, 99%) and hydrazine monohydrate (N_2H_4 64–65%, 98%) were purchased from Fisher. Analytical grade acetone and ethanol were obtained from various sources. All chemicals were used as received without further purification. Syntheses were carried out using a standard vacuum/dry argon Schlenk line.

2.2 Synthesis of SnSe nanocrystals

SnSe NCs were prepared in water following the approach developed by Guang Han *et al.*¹² Briefly, 100 mmol NaOH and 10 mmol $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 50 mL of deionized water and boiled to yield a transparent Na_2SnO_2 solution. 50 mL of an aqueous NaHSe solution prepared from Se and NaBH_4 was then injected into the boiling solution, leading to the immediate formation of a black precipitate. The mixture was boiled further for 2 h and cooled to room temperature under an Ar flow in a Schlenk line. The products were washed with deionized water and ethanol several times. The obtained product was then dried under vacuum at room temperature for 2 h. Dried SnSe NCs were annealed at 400 °C for 120 min under an Ar flow inside a tube furnace.

2.3 Synthesis of tellurium nanorods

Te NRs were prepared following the approach developed by Zhang *et al.*¹³ In a typical synthesis, 11.2 mmol TeO_2 , 74 mmol KOH , 3.0 g of PVP, and 110 mL of EG were added into a 250 mL three-neck flask. The mixture was stirred and heated to 140 °C. At this temperature, 1.75 mL of a 64–65% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solution were injected into the flask. The reaction mixture was maintained at 140 °C for 1 h to allow all Te to be reduced. The solid product was collected by adding acetone to the solution and centrifuging it. In the second step, ethanol was used to re-disperse the NRs, and acetone ($V_{\text{ethanol}}/V_{\text{acetone}} = 1:2$) to precipitate them again. In the third step, deionized water was

added to solubilize the remaining impurities and NRs were precipitated by slow centrifugation. This procedure was repeated twice. In the last step, NRs were re-dispersed with ethanol and precipitated with acetone, like in step two. Finally, NRs were dried under vacuum at room temperature.¹⁰

2.4 Bulk nanomaterial consolidation

Annealed SnSe NCs and dried Te NRs were mixed in an appropriate ratio with chloroform with the aid of an ultrasonic bath for 30 min. Then the material was dried under vacuum at room temperature. The dried mixture of SnSe NCs and Te NRs was annealed at 350 °C for 60 min under an Ar flow inside a tube furnace. The annealed particles, in the form of a powder, were loaded into a graphite die and compacted into cylinders using a custom-made hot press within an Ar filled glove box. The hot press temperature was set at 480 °C and the pressure was increased up to 50 MPa and released for 6 cycles during the 10 min that the material was kept at 480 °C. The relative densities of the compacted pellets were measured by the Archimedes method.

2.5 Structural and chemical characterization

X-ray diffraction (XRD, 2θ angle: 20° to 80°; scanning rate: 3° min⁻¹) analyses were carried out on a Bruker AXS D8 ADVANCE X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The size and morphology of the initial NPs were examined by using an Auriga Zeiss field-emission scanning electron microscope (FESEM), operated at 5.0 kV. The material composition was analysed using an Oxford energy dispersive X-ray spectrometer (EDX) attached to the Zeiss Auriga FESEM at 20.0 kV. The refinement of the obtained diffraction patterns was done by the Rietveld method with the GSAS-II package.¹⁴

2.6 Thermoelectric property measurement

Seebeck coefficients were measured using a static DC method. Electrical resistivity data were obtained by a standard four-probe method. Both the Seebeck coefficient and the electrical resistivity were measured simultaneously in a LSR-3 LINSEIS system in the temperature range between room temperature and 800 K under a helium atmosphere. All samples were measured at least 3 consecutive times during heating up to around 790 K. Taking into account the system accuracy and the measurement precision, an error of *ca.* 4% in the measurement of the electrical conductivity and Seebeck coefficient was estimated. Thermal conductivities (κ_{total}) were obtained by multiplying the thermal diffusivity (λ), the constant pressure heat capacity (C_p) and the density of the material (ρ), where $\kappa_{\text{total}} = \lambda C_p \rho$. A Xenon Flash Apparatus XFA600 was used to determine the thermal diffusivities of the samples with an estimated error of *ca.* 5%. The constant pressure heat capacity (C_p) was estimated from empirical formulas by the Dulong–Petit limit (3R law). The density values were measured using the Archimedes method. To avoid cluttering the plots, error bars were not included in the figures.

3. Results and discussion

3.1 Nanomaterials

Flat SnSe NCs with 100 nm average size and 40 nm average thickness were produced from the reaction of SnCl and NaHSe in water (Fig. 1a and b).¹² XRD analysis showed the NCs to have an orthorhombic structure with lattice parameters: $a = 11.49 \text{ \AA}$, $b = 4.44 \text{ \AA}$, and $c = 4.13 \text{ \AA}$ and space group 62 (*Pnma*, JCPDS No. 00-048-1224, Fig. 1d).¹⁵ Te NRs with a hexagonal crystal phase, an average thickness of *ca.* 30 nm and an average length of 500 nm were produced within EG (Fig. 1c and d).

The two types of particles, SnSe NCs and Te NRs, were blended in solution at different ratios (Te = 0 mol%, 10 mol%, 15 mol%, 20 mol% and 25 mol%). The mixture was dried, annealed at 350 °C and subsequently hot-pressed within an inert atmosphere into cylindrical pellets 10 mm in diameter and 10 mm in height. The hot-press temperature was set at 480 °C and the pressure was cycled from ambient to 50 MPa 6 times during the 10 minutes that the material was kept at 480 °C. This process resulted in cylinders with relative densities of *ca.* 93% of the theoretical value, as measured by the Archimedes method.

XRD analysis of the cylindrical pellets held in two perpendicular directions, with the diffraction plane normal and parallel to the pressing direction, showed a strong preferential orientation of the SnSe crystal domains within the pellets as noted by the differential peak intensities (Fig. 2). The [100] direction was found to be preferentially aligned along the pressure axis. The presence of Te clearly promoted this alignment as observed when comparing the in-plane $I_{(400)}/I_{(011)}$

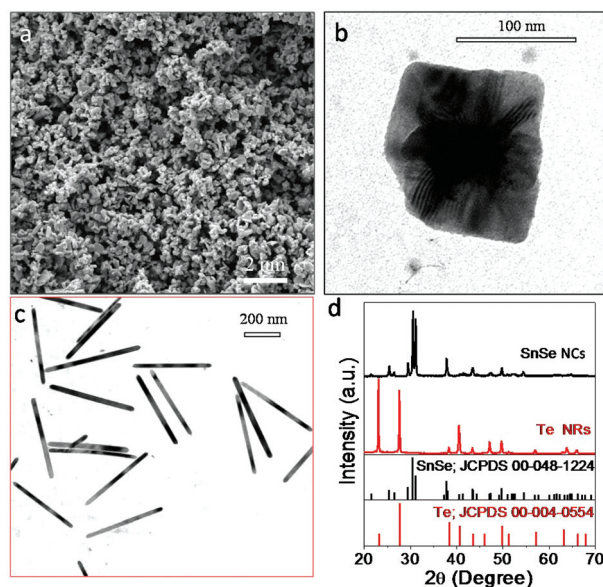


Fig. 1 (a) SEM micrograph of SnSe NCs. (b) Representative TEM micrograph of a SnSe NC. (c) TEM micrograph of Te NRs. (d) XRD patterns of SnSe NCs and Te NRs. The graph includes reference patterns for orthorhombic SnSe and hexagonal Te.

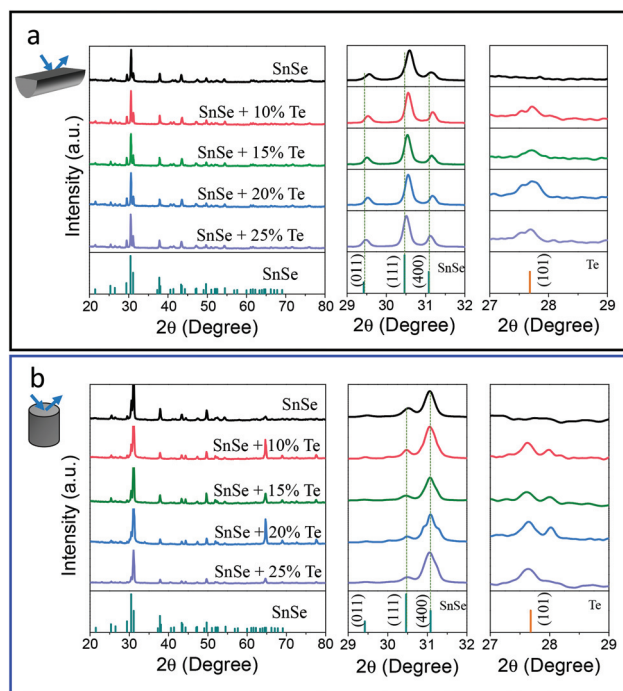


Fig. 2 XRD patterns of consolidated SnSe–Te pellets measured while held in two directions, with the press axis within (a) and normal to (b) the diffraction plane, as specified by the cartons. The expanded views of the regions corresponding to the SnSe (400) and (111) diffraction peaks and the Te (101) diffraction peak are displayed.

ratio of SnSe pellets obtained with and without Te. In the absence of Te, SnSe pellets with in-plane $I_{(400)}/I_{(011)} = 11$ were obtained. In the presence of Te, SnSe pellets with significantly larger plane $I_{(400)}/I_{(011)}$ values, ranging from 31 to 90, were produced.

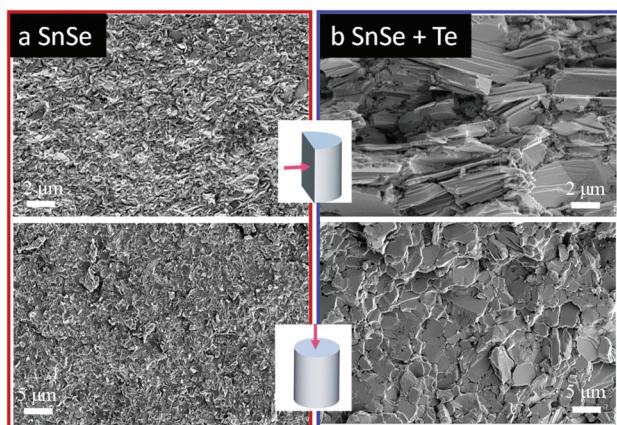
At increasing Te concentrations, the XRD peaks of the consolidated materials systematically shifted to lower 2θ angles suggesting small amounts of Te, with a larger covalent radius, to be inserted within the SnSe lattice. Additionally, XRD analysis showed the presence of elemental Te diffraction peaks in the consolidated material, demonstrating that small amounts of elemental Te remained in the material after hot-pressing. No additional phase was identified from XRD characterization. EDX analysis quantified the total amount of Te within the final material to increase from 2.7 at% to 7.7 at% when increasing the amount of Te NRs included in the initial blend, from 10 mol% to 25 mol%, respectively (Table 1). The Rietveld analysis of the XRD patterns showed the presence of 6.8 wt% of the Te phase in the SnSe sample containing a nominal 15 mol% of Te, which corresponds to 8.8 wt% (Fig. S1†). After consolidation, the amount of Te phase detected for the same sample from the Rietveld analysis of the XRD pattern decreased to 2.2 wt% (Fig. S2†).

Top view and cross-sectional SEM images show that the SnSe consolidated pellets produced without the addition of Te consist of a dense aggregate of particles with no evident preferential orientation. On the other hand, in the presence of Te,

Table 1 Nominal and EDX compositions of the initial particle blend and the final consolidated pellets

Nominal Sn : Se : Te	EDX (%)		
	Sn	Se	Te
1 : 1 : 0.00	52	48	0.0
1 : 1 : 0.10	50	47	2.7
1 : 1 : 0.15	50	47	3.1
1 : 1 : 0.20	48	46	6.4
1 : 1 : 0.25	47	45	7.7

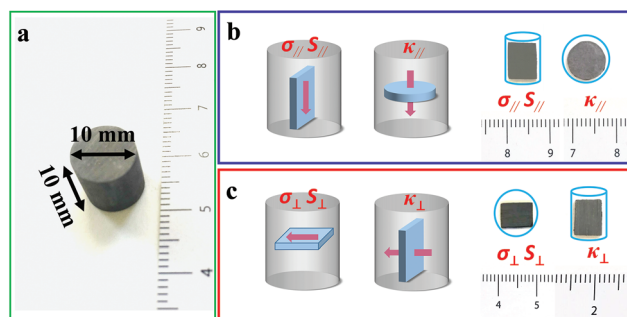
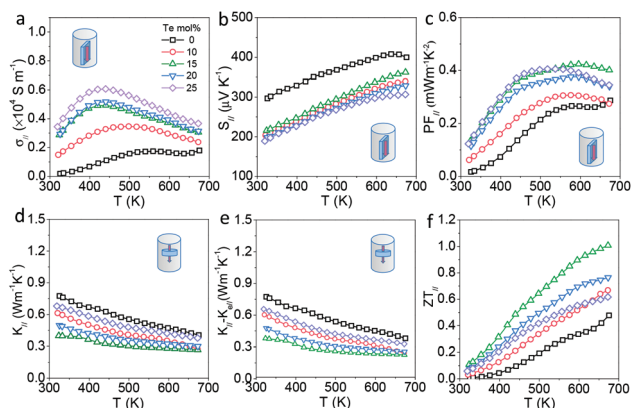
pellets with a laminar structure, containing 100 nm–1 μ m thick layers stacking in the press direction and extending several micrometres in the cylinder plane, were obtained (Fig. 3). During the hot press, Te liquefied, aiding the rotation of the asymmetric SnSe NCs towards a common preferential orientation that maximized the entropy. On the other hand, Sn–Se–Te forms an extended range of solid solutions in the Se-rich side as observed from the SnSe–SnTe phase diagram.^{16,17} Additionally, when moving away from the stoichiometric 1 : 1 composition of tin monochalcogenides, the melting temperature strongly decreases and even an eutectic at 85 at% Te at 678 K is obtained in the Sn–Te system.¹⁸ Liquefied Te is thus able to dissolve significant amounts of SnSe, which under an uniaxial pressure reprecipitates with a preferential crystallographic orientation trapping some Te within the lattice. Under uniaxial pressure, strain energy is minimized by aligning the crystal domains in the “softer” direction parallel to the pressure axis. The lower elastic modulus of SnSe in the *a*-axis makes this the preferred crystal direction to be oriented towards the pressure axis, minimizing the strain energy. At the same time, particles generally grow larger in the direction normal to the uniaxial pressure. Thus, when re-precipitating, SnSe crystals naturally grew forming plates that extended along the *bc* crystal plane, as observed from pellets consolidated in the presence of Te (Fig. 3).

**Fig. 3** (a) Cross sectional and top-view SEM micrographs of a SnSe pellet consolidated without Te. (b) Cross sectional and top-view SEM micrographs of a SnSe pellet consolidated in the presence of 15 mol% of Te.

3.2 Thermoelectric characterization

From the consolidated cylinders, 8 × 6 × 1 mm rectangular bars and 1 mm thick disks were cut in-plane and out-of-plane (Fig. 4). These samples were used to measure the material TE properties in two directions, parallel ($\parallel$) and normal ($\perp$) to the pressure axis. Fig. 5 and 6 display the electrical conductivity (σ), Seebeck coefficient (*S*), power factor (PF), total thermal conductivity (κ), the total thermal conductivity once subtracted from the electronic contribution ($\kappa - \kappa_e$), and the TE figure of merit (*ZT*) of the SnSe pellets produced in the presence of different amounts of Te.

With the addition of Te, σ systematically increased in both directions, especially in the low-temperature range measured (Fig. 5a and 6a). The presence of Te during consolidation enhanced the material crystallinity, thus improving the charge carrier mobility. At the same time, the charge carrier concentration could increase due to the presence of Te within the

**Fig. 4** (a) Representative photograph of one of the consolidated SnSe cylindrical pellets produced. (b) and (c) Schematic illustrations and photographs of the samples obtained from the cylindrical pellets and used to measure electrical conductivities (σ), Seebeck coefficients (*S*) and thermal conductivities (κ) in both directions, parallel (b) and normal (c) to the pressing direction.**Fig. 5** Thermoelectric properties of SnSe and SnSe–Te nanomaterials measured along the direction of the pressure axis ($\parallel$): (a) electrical conductivity, $\sigma_{||}$; (b) Seebeck coefficient, $S_{||}$; (c) power factor, $PF_{||}$; (d) total thermal conductivity, $\kappa_{||}$; (e) thermal conductivity after subtraction of the electronic component, $\kappa_{||} - \kappa_{e||}$; and (f) TE figure of merit, $ZT_{||}$.

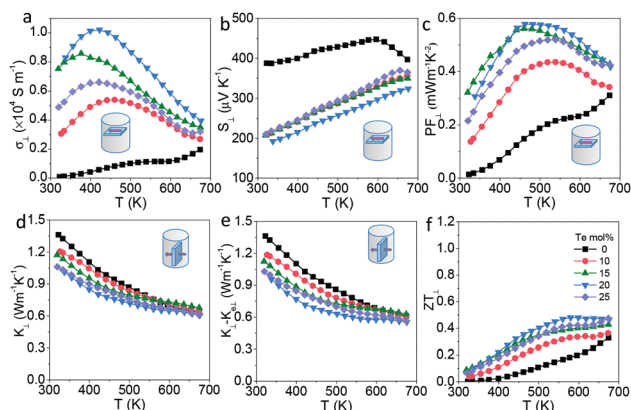


Fig. 6 Thermoelectric properties of SnSe and SnSe–Te nanomaterials measured in the direction normal to the pressure axis ($\perp$): (a) electrical conductivity, $\sigma_{\perp}$; (b) Seebeck coefficient, $S_{\perp}$; (c) power factor, $PF_{\perp}$; (d) total thermal conductivity, $\kappa_{\perp}$; (e) thermal conductivity after subtraction of the electronic component, $\kappa_{\perp} - \kappa_{e\perp}$; and (f) TE figure of merit, $ZT_{\perp}$.

lattice, which reduced the material bandgap, and due to the increase of the concentration of Sn vacancies associated with the overall increase of the chalcogen-to-tin ratio.¹⁵ As expected, $\sigma_{\perp} > \sigma_{\parallel}$ due to the higher charge carrier mobilities in the bc crystal plane compared with the a direction and the extended size of the crystal domains in the $\perp$ direction within the layered pellets. Surprisingly, a decrease of $\sigma_{\perp}$ was observed in the sample containing the highest amount of Te. We associate this result with the scattering of charge carriers on Te domains. This scattering affects more significantly $\sigma_{\perp}$ than $\sigma_{\parallel}$ due to the former higher charge carrier mobility in the direction normal to the pressure axis.

Meanwhile, S decreased with the addition of increasing amounts of Te due to the increase of the charge carrier concentration. S started to decrease with temperature due to bipolar effects at temperatures above 600 K for SnSe and at slightly higher temperatures for SnSe–Te (Fig. 5b and 6b). Moderate differences in S were observed when comparing the measurements done in the two different pellet directions, consistent with the low dependence of S on scattering.

The dependence of κ on the amount of Te was not straightforward. κ decreased with the introduction of small amounts of Te, but increased at higher Te concentrations (Fig. 5e and 6e). As expected, $\kappa_{\perp} > \kappa_{\parallel}$ due to the higher intrinsic κ in the bc plane and the extended size of the crystal domains in the plane $\perp$ to the press axis. The same pattern was obtained in the two directions, but minimum $\kappa_{\parallel}$ and $\kappa_{\perp}$ were obtained at different amounts of Te, $x = 0.15$ and $x = 0.2$, respectively. Similar values and dependences were obtained once subtracted from the electronic contribution to the thermal conductivity (Fig. 5e and 6e).

Overall, the ZT values of SnSe pellets consolidated in the presence of Te were systematically higher than those of pure SnSe, both in the in-plane and out-of-plane directions. The highest ZT values were obtained from the blend containing a nominal 15 mol% of Te. The increase of ZT with the presence

of Te during consolidation was mainly related to the higher electrical and lower thermal conductivities obtained when compared with SnSe pellets consolidated without Te.

Fig. 7 displays the comparison between the TE properties of pure SnSe and the best performing SnSe–Te nanomaterial, consolidated in the presence of 15 mol% of Te, measured in two normal directions in the temperature range up to 790 K. Above 700 K, σ increased and S decreased sharply due to the thermal activation of charge carriers across the bandgap. Surprisingly, higher ZT values, up to 1.4 at 790 K, were reached in the out-of-plane direction, coinciding with the preferential a -axis orientation of SnSe. In previous studies, higher ZT values were usually obtained in the b and c axes due to the much higher σ and still moderate κ measured in these directions when compared with the a axis (Table 2). In our pellets, κ

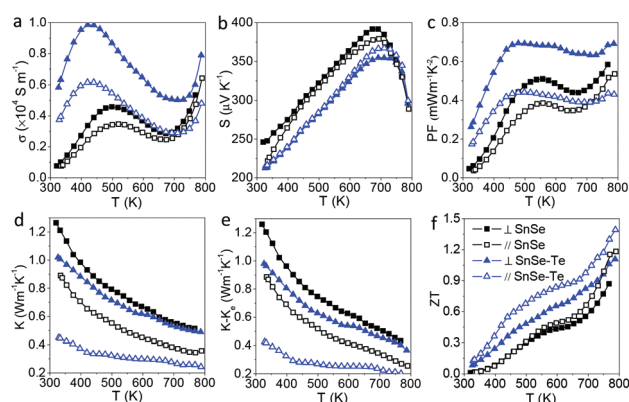


Fig. 7 Thermoelectric properties of SnSe and SnSe–Te (10 mol% of Te) nanomaterials measured from ambient temperature to 800 K along ($\parallel$) and normal ($\perp$) to the pressure axis: (a) electrical conductivity, σ ; (b) Seebeck coefficient, S ; (c) power factor, PF ; (d) total thermal conductivity, κ ; (e) thermal conductivity after subtraction of the electronic component, $\kappa - \kappa_e$; and (f) TE figure of merit, $ZT_{\parallel}$.

Table 2 Comprehensive summary on the thermoelectric performance of previously reported p-type SnSe at 790 K

p-type	Direction	ZT at 790 K	Ref.
$\text{Sn}_{0.97}\text{Na}_{0.03}\text{Se}_{0.9}\text{S}_{0.1}$ (single crystal)	b	2.3 (773 K)	21
SnSe (single crystal)	b	2.2	5
SnSe	a	1.4	This work
SnSe + 4% InSe_y	b	1.4	22
$\text{Sn}_{0.93}\text{Pb}_{0.02}\text{Se}$	a	1.4 (773 K)	23
$\text{Sn}_{0.98}\text{Pb}_{0.01}\text{Zn}_{0.01}\text{Se}$	a	1.25	24
$\text{Sn}_{0.95}\text{Se}$	a	1.25	25
$\text{Sn}_{0.98}\text{Se}$	b	1.2	26
$\text{Na}_{0.005}\text{K}_{0.005}\text{Sn}_{0.99}\text{Se}$	b	1.2 (773 K)	27
$\text{Na}_{0.01}(\text{Sn}_{0.95}\text{Pb}_{0.05})_{0.99}\text{Se}$	b	1.2 (773 K)	28
SnSe + 1% PbSe	a	1.2	29
SnSe + Ag_2S	a	1.13 (773 K)	30
$\text{SnSe}_{0.9}\text{Te}_{0.1}$	b	1.1	15
$\text{Sn}_{0.882}\text{Cu}_{0.118}\text{Se}$	b	1.1	31
SnSe	b	0.8	32
$\text{Na}_{0.01}\text{Sn}_{0.99}\text{Se}$	b	0.8	33
$\text{K}_{0.01}\text{Sn}_{0.99}\text{Se}$	b	0.8	33
$\text{Zn}_{0.01}\text{Sn}_{0.99}\text{Se}$	b	0.65	34
$\text{Ag}_{0.01}\text{Sn}_{0.99}\text{Se}$	b	0.6 (750 K)	35

in the $\parallel$ direction was comparatively small, but in the $\perp$ direction it was higher than in single crystals. This could be associated with the presence of Te at the interphases and within the lattice, and potentially with a partial oxidation of the NCs.^{19,20}

4. Conclusions

p-type polycrystalline SnSe materials with marked crystallographic texture were produced from blends of SnSe NCs and Te NRs through hot-pressing them at a temperature above the Te melting point. The presence of Te promoted the material crystallization in the form of a laminar structure with the a -axis along the pressure direction. Part of the Te used for the liquid phase sintering process was found within the SnSe lattice and part in the form of elemental Te within the consolidated material. The TE properties of the produced nanomaterials were measured in two perpendicular directions, along and normal to the pressure axis. SnSe nanomaterials consolidated in the presence of Te showed higher electrical conductivities and lower Seebeck coefficients and thermal conductivities than pure SnSe. The TE figures of merit up to $ZT \sim 1.4$ at 790 K were measured from the SnSe nanomaterial consolidated in the presence of Te and measured along the pressing direction. Somehow surprisingly, lower ZT values were obtained in the direction normal to the pressure axis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Effect of the Annealing Atmosphere on Crystal Phase and Thermoelectric Properties of Copper Sulfide

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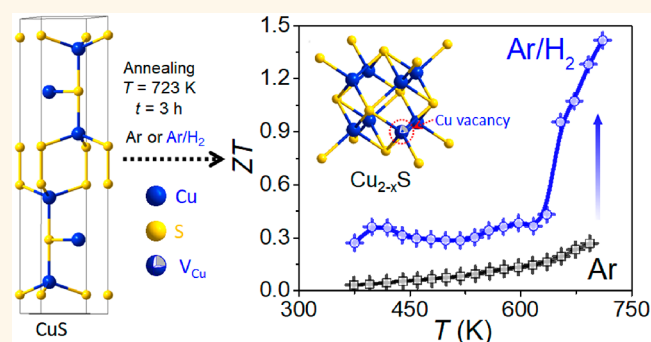
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Supporting Information

ABSTRACT: Cu_{2-x}S has become one of the most promising thermoelectric materials for application in the middle-high temperature range. Its advantages include the abundance, low cost, and safety of its elements and a high performance at relatively elevated temperatures. However, stability issues limit its operation current and temperature, thus calling for the optimization of the material performance in the middle temperature range. Here, we present a synthetic protocol for large scale production of covellite CuS nanoparticles at ambient temperature and atmosphere, and using water as a solvent. The crystal phase and stoichiometry of the particles are afterward tuned through an annealing process at a moderate temperature under inert or reducing atmosphere. While annealing under argon results in $\text{Cu}_{1.8}\text{S}$ nanopowder with a rhombohedral crystal phase, annealing in an atmosphere containing hydrogen leads to tetragonal $\text{Cu}_{1.96}\text{S}$. High temperature X-ray diffraction analysis shows the material annealed in argon to transform to the cubic phase at *ca.* 400 K, while the material annealed in the presence of hydrogen undergoes two phase transitions, first to hexagonal and then to the cubic structure. The annealing atmosphere, temperature, and time allow adjustment of the density of copper vacancies and thus tuning of the charge carrier concentration and material transport properties. In this direction, the material annealed under Ar is characterized by higher electrical conductivities but lower Seebeck coefficients than the material annealed in the presence of hydrogen. By optimizing the charge carrier concentration through the annealing time, Cu_{2-x}S with record figures of merit in the middle temperature range, up to 1.41 at 710 K, is obtained. We finally demonstrate that this strategy, based on a low-cost and scalable solution synthesis process, is also suitable for the production of high performance Cu_{2-x}S layers using high throughput and cost-effective printing technologies.

KEYWORDS: copper sulfide, vacancies, solution synthesis, thermoelectric, printing, energy conversion



INTRODUCTION

Thermoelectric devices are able to directly convert ubiquitous temperature gradients into electricity, to actively remove heat from local sources or temperature-sensitive devices, and to precisely control temperature without moving parts or working gases. They have countless potential applications, but their high manufacturing and material costs hamper their cost-effectiveness and limit their widespread implementation. To overcome these drawbacks, thermoelectric devices must be manufactured employing high throughput technologies and using materials based on low cost and abundant elements.

The thermoelectric properties of copper sulfides have been explored for well over a century.^{1–4} However, it was not until this past decade that copper sulfides raised much interest not

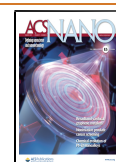
only because of the low cost and abundance of the involved elements but also because of their outstanding thermoelectric performance in the middle-high temperature range.^{5–11}

Copper chalcogenides and particularly copper sulfides are a fascinating family of materials with exceptional characteristics:¹² (i) high element abundance, low cost, and minor environmental and health impact; (ii) enormous structural and

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compositional versatility; (iii) low energy of formation of defects resulting in high defect densities; (iv) chalcogen atoms forming regular lattices with Cu atoms occupying not well-defined interstitial sites; (v) strong influence of Cu 3d states in the chalcogenide electronic properties; (vi) singular and highly tunable functional properties, including small direct band gaps, plasmonic properties, high charge carrier concentrations, high ionic conductivity, and low thermal conductivity.

Even the simplest binary Cu–S system exhibits a particularly rich phase diagram with many possible stoichiometric compositions and crystallographic phases, some of them with quite complex atomic arrangements.^{13–16} The main crystal phases in the Cu–S system at ambient temperature are the monoclinic chalcocite ($\text{Cu}_{2.0-1.997}\text{S}$), monoclinic djurleite ($\text{Cu}_{1.97}\text{S}$ – $\text{Cu}_{1.93}\text{S}$), triclinic roxbyite ($\text{Cu}_{58}\text{S}_{32}$ or $\text{Cu}_{1.81}\text{S}$), cubic digenite (Cu_9S_5 or $\text{Cu}_{1.8}\text{S}$), orthorhombic anilite (Cu_7S_4 or $\text{Cu}_{1.75}\text{S}$), and hexagonal covellite (CuS). These crystal structures are based upon approximately hexagonal (djurleite, chalcocite, roxbyite, and covellite) or cubic (anilite and digenite) close-packing of the sulfur atoms, where Cu atoms occupy a variety of interstitial sites with different statistical probabilities that depend on stoichiometry and temperature.^{15,17}

Chalcocite Cu_2S displays a monoclinic $P2_1/c$ crystal structure. This is essentially a superstructure of a hexagonal lattice with slight distortions, where 12 sulfur and 24 copper atoms fully occupy the 36 different Wyckoff positions.^{17,18} Stoichiometric Cu_2S is considered to be intrinsically unstable at ambient conditions owing to a thermodynamic tendency toward losing Cu through surface oxidation.^{19,20} Thus, chalcocite nanoparticles degrade quickly into Cu_{2-x}S , mainly djurleite $\text{Cu}_{1.97}\text{S}$ that is considered the thermodynamically stable phase in ambient atmosphere.

Djurleite $\text{Cu}_{1.93-1.97}\text{S}$ also displays a monoclinic structure. Its unit cell can be represented as $\text{Cu}_{62}\text{S}_{32}$ or $\text{Cu}_{1.93}\text{S}$ and becomes $\text{Cu}_{63}\text{S}_{32}$ or $\text{Cu}_{1.97}\text{S}$ when adding a Cu atom. Both chalcocite and djurleite are frequently observed at ambient temperature and are often intermixed or intergrown.²¹

Roxbyite $\text{Cu}_{58}\text{S}_{32}$ or $\text{Cu}_{1.81}\text{S}$ is similar to chalcocite and djurleite, but it has a triclinic structure based on a distorted hexagonal framework that contains 32 sulfur atoms and 58 copper atoms, all of them with a triangular coordination.²² Roxbyite is not a common copper sulfide structure, but it can be easily produced in the form of nanocrystals.²³

Digenite $\text{Cu}_{1.8}\text{S}$ has a cubic but still complex structure with space group $Fd\bar{3}m$.^{24,25} Sulfur atoms form an fcc structure, and copper is randomly dispersed over different sites. Digenite stoichiometry can be also displayed as Cu_9S_5 , but $\text{Cu}_{1.8}\text{S}$ is a more suitable nomenclature when taking into account the random distribution of Cu atoms.²⁶

Anilite Cu_7S_4 or $\text{Cu}_{1.75}\text{S}$ has an orthorhombic structure, space group $Pnma$. Within anilite, Cu is ordered in the interstitial sites of the fcc framework approximately defined by S atoms.^{27,28}

Finally, covellite CuS has a layered hexagonal structure consisting of alternating layers of CuS and $\text{Cu-S}_2\text{-Cu}$.^{29–31} This unusual structure is explained by the fact that S–S covalent bonds are energetically favorable over S–Cu bonds.²⁹

The Cu–S phase diagram is actually much more complex, with additional well-defined phases/minerals, including geerite ($\text{Cu}_{1.6}\text{S}$), spionkopite ($\text{Cu}_{1.39}\text{S}$) and yarrowite ($\text{Cu}_{1.12}\text{S}$). Furthermore, several metastable phases also exist and are commonly obtained at ambient temperature, such as a

tetragonal $\text{Cu}_{1.96}\text{S}$ phase^{13,25,32,33} and a rhombohedral $\text{Cu}_{1.8}\text{S}$ structure.^{34,35}

At relatively low temperatures, just above 70–100 °C depending on stoichiometry, Cu atoms become highly mobile. This high mobility prevents describing their precise positions, but just defines their statistical distribution, which increases the symmetry of the observed crystal structures.^{36,37} The ambient temperature monoclinic chalcocite phase, known as low chalcocite, transforms into a hexagonal phase known as high chalcocite at around 376 K, and to a cubic phase known as cubic chalcocite at about 709 K. Monoclinic djurleite is stable up to about 363 K. At this temperature, it transforms into a combination of hexagonal chalcocite and cubic digenite phases, with the hexagonal phase disappearing as the temperature increases further.²⁵ Digenite undergoes complete phase transition into a higher symmetry cubic phase at even lower temperature, 346 K.^{26,34} The high temperature digenite phase is known as high digenite, and it is identical to the cubic chalcocite.³⁶ Above 710 K only high-digenite with Cu_2S composition or cubic chalcocite, in equilibrium with copper, can be obtained.^{26,36} Anilite is also stable only to 345 K,^{36,38} transforming into the cubic high digenite phase at a higher temperature.

Phase and stoichiometry do not always go together. For instance, hexagonal digenite has been reported especially in nanoparticle form, and a cubic high chalcocite has been also described. To minimize confusion, it is wise to associate the mineral names to the crystal phase regardless of the exact composition; thus, hexagonal digenite is better referred to as a Cu-deficient high chalcocite, and the cubic high chalcocite, as a Cu-rich high digenite.¹⁷

Phase transitions strongly depend on several parameters, including the initial phase, pressure, and composition. The lower the Cu content, the lower the transition temperature to higher symmetry phases, e.g. from monoclinic to hexagonal and cubic phase. Besides, the phase transition temperature also strongly depends on the crystal domain size. A good example is provided by chalcocite Cu_2S nanocrystals, where the smaller the size, the smaller the transition temperature.³⁹ Actually, small enough nanocrystals are reported to maintain the hexagonal high chalcocite phase even at ambient temperature.⁴⁰ The atmosphere composition, and particularly the sulfur partial pressure, is another parameter that strongly influences the phase transition.²⁶

The electronic structure and functional properties of Cu_{2-x}S depend on the crystal phase but mainly on stoichiometry.^{41–43} Stoichiometric chalcocite Cu_2S should be an intrinsic semiconductor. However, Cu-poor phases contain large hole densities associated with the presence of numerous copper vacancies and to the fact that the Cu valence is +1 in all phases and stoichiometries, regardless of the Cu deficiency.

The energy conversion efficiency of a thermoelectric device depends on the temperature gradient harvested/generated and on three interconnected material parameters: electrical conductivity (σ), Seebeck coefficient (S), and thermal conductivity (κ). Besides, the thermal conductivity has two main contributions, the lattice (κ_l) and the electronic (κ_e) that is related to σ through the Wiedemann–Franz law, $\kappa_e = L\sigma T$, where L is the Lorentz number and T is the absolute temperature. All these parameters combine within a thermoelectric figure of merit (Z) that is frequently expressed in its dimensionless form: $ZT = \sigma S^2 T / \kappa$. Thus, a high performance thermoelectric material is characterized by a high electrical

conductivity and Seebeck coefficient, and a low thermal conductivity. Besides selecting materials with complex and/or highly anisotropic crystal structures, which contain a large defect density, high atomic disorder, and/or numerous grain boundaries to minimize thermal conductivity, a main parameter to be tuned to maximize ZT is the charge carrier concentration. The density of free charges has a strong influence on the three main material parameters. σ and thus κ_e increase with the charge carrier concentration (n): $\sigma = n\mu e$, where μ is the charge carrier mobility and e is the elemental electron charge. S decreases with n through the following expression obtained for metals or degenerated semiconductors with a parabolic band and energy independent charge carrier scattering:

$$S = \frac{8\pi^2 k_B^2 T}{3eh^2} m^* \left(\frac{\pi}{3n} \right)^{2/3}$$

where k_B and h are the Boltzmann and Planck constants, respectively, and m^* is the effective mass. Overall, the optimum charge carrier concentrations are around 10^{19} cm^{-3} . A higher charge carrier concentration results in a too low S and too high k , and a lower n leads to too low electrical conductivities.

All Cu_{2-x}S phases have p -type electronic character with a stoichiometry-dependent hole concentration that increases with the number of Cu vacancies (x). Besides, the type of sulfur arrangement in the crystal structure also plays an important role in the electronic transport properties of the material.⁴⁴ On the other hand, the high copper disorder at moderate and high temperature gives rise not only to a virtually fluid-like ionic mobility but also to ultralow thermal conductivity. As a drawback, this Cu mobility gives rise to copper migration instabilities. In operating thermoelectric devices, these instabilities can be overcome by proper encapsulation, by limiting the working current and operation temperature, and/or by introducing electron-conducting but ion-blocking layers.⁴⁵

Thermoelectric properties are very sensitive to the Cu deficiency, *i.e.* the Cu_{2-x}S stoichiometry, which strongly depends on the synthesis conditions, structural parameters, and treatment history of the sample. Tuning the crystal structure, composition, and density of intrinsic defects at the synthesis step or through postsynthesis treatments can be a very effective but still underexplored strategy to optimize thermoelectric properties of copper sulfide in the middle temperature range where this material is stable.^{46,47}

In the present work, we demonstrate a simple and low-cost room temperature aqueous phase method for the large-scale preparation of copper sulfide. Additionally, we analyze the possibilities of tuning the crystallographic phase and stoichiometry of nanocrystalline Cu_{2-x}S by means of thermal annealing at moderate temperatures under inert or reducing gas atmospheres. Finally, we analyze the thermoelectric properties of the obtained compounds as a function of the annealing temperature, time, and atmosphere and explain the obtained results taking into account the different sample stoichiometries and the phase transitions undergone by the materials when heated.

RESULTS AND DISCUSSION

A rapid and surfactant-free synthetic protocol was developed to produce copper sulfide nanoparticles in water and at ambient

temperature using $(\text{NH}_4)_2\text{S}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as sulfur and copper precursors, respectively (Figure 1a; see details in

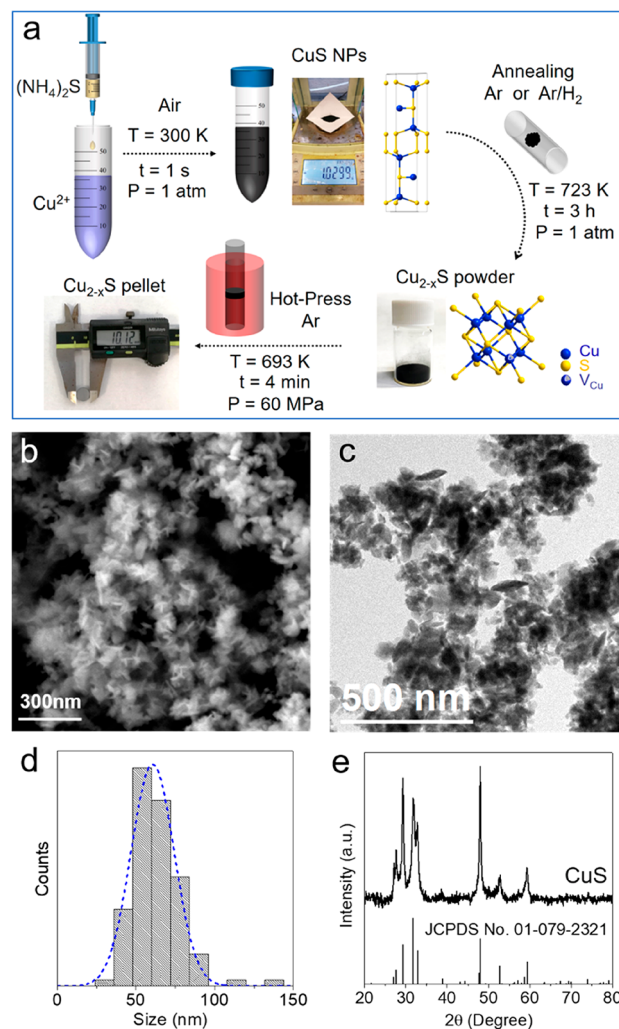


Figure 1. (a) Schematic illustration of the three-step process used to produce Cu_{2-x}S pellets and which involves the synthesis of CuS nanoparticles at ambient pressure and temperature, the annealing of the particles at 723 K in Ar or Ar/H_2 atmosphere, and the hot press of the materials at 693 K and 60 MPa. (b) SEM micrograph of CuS nanoparticles. (c) TEM micrographs of CuS nanoparticles. (d) Histogram of the particle size distribution. (e) XRD pattern obtained from CuS nanoparticles.

the Methods section). Figure 1b,c shows representative scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs of the reaction product that consisted of *ca.* 60 nm nanoparticles with flat morphology (Figures 1c and S1). X-ray diffraction (XRD) analysis showed the crystal structure of the obtained nanoparticles to match the covellite CuS phase (JCPDS No. 01-079-2321).

High resolution TEM (HRTEM) characterization showed the nanoparticles to have good crystallinity and confirmed their hexagonal covellite CuS phase (space group = $P6_3/mmc$), with $a = b = 3.7917 \text{ \AA}$ and $c = 16.3420 \text{ \AA}$ (Figure 2a). Electron energy loss spectroscopy (EELS) chemical composition maps obtained from the red squared region in the high-angle annular dark-field scanning TEM (HAADF-STEM) micrograph

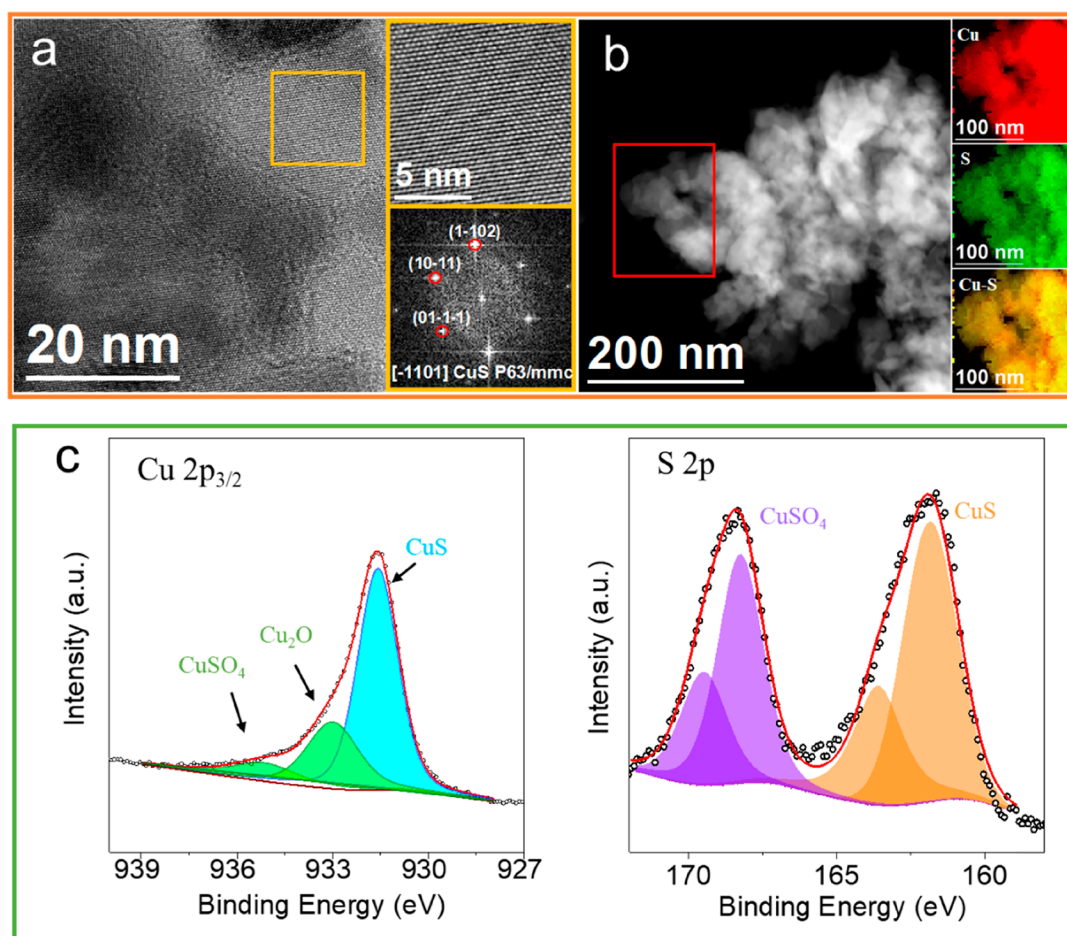


Figure 2. (a) HRTEM micrograph, detail of the orange squared region and its corresponding power spectrum. CuS lattice fringe distances were measured to be 0.320, 0.323, and 0.304 nm, at 64.46° and 122.88° , interpreted as the hexagonal CuS phase, visualized along its $[-1101]$ zone axis. (b) HAADF-STEM micrograph and EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Cu $L_{2,3}$ -edges at 931 eV (red) and S $L_{2,3}$ -edges at 165 eV (green). (c) Cu $2p_{3/2}$ and S $2p$ high resolution XPS spectra obtained from CuS nanoparticles.

displayed in Figure 2b demonstrated a homogeneous distribution of Cu and S throughout the particles.

Cu $2p_{3/2}$ and S $2p$ high resolution X-ray photoelectron spectroscopy (XPS) spectra are displayed in Figure 2c. The Cu $2p$ spectrum was fitted with three bands at 933.0, 935.2, and 931.6 eV. The Cu $2p_{3/2}$ band at 931.6 eV was associated with Cu within a CuS chemical environment.⁴⁸ On the other hand, the two higher energy bands corresponded to two surface oxide components, probably cuprous oxide and copper sulfate.⁴⁹ The partial surface oxidation of the nanoparticles has its origin on their manipulation and transportation in air, as observed for other materials.⁴⁸ The S $2p$ XPS spectrum displayed two well-defined doublets at 161.8 and 168.2 eV (S $2p_{3/2}$), which were assigned to lattice S within CuS and to sulfate species arising from the surface oxidation of the material, respectively.⁵⁰

CuS nanoparticles were annealed at 723 K in a tube furnace under gas flow. Two different gases were used for the annealing treatments, Ar and 5% H_2 in Ar (Ar/ H_2). The annealing time was set at 3 h for Ar, and it was varied between 2 and 4 h for Ar/ H_2 . Figure 3 displays the room temperature XRD patterns of the annealed powders. Covellite CuS exhibited thermal instability in a sulfur-free atmosphere. Upon heating the particles, CuS dissociated into $Cu_{2-x}S$ and sulfur that was lost through volatilization. The sample annealed in Ar for 3 h

displayed a metastable rhombohedral $Cu_{1.8}S$ phase at ambient temperature. On the other hand, the CuS particles annealed in the presence of H_2 displayed a larger loss of S. The sample annealed for 2 h in Ar/ H_2 displayed a combination of the metastable rhombohedral $Cu_{1.8}S$ and tetragonal $Cu_{1.96}S$ phases, with the former being the dominant one. After 3 h at 450 °C in an Ar/ H_2 atmosphere, the rhombohedral phase was still identified, but the tetragonal phase became dominant and the monoclinic Cu_2S phase appeared. When increasing the annealing time to 4 h in Ar/ H_2 , a combination of monoclinic Cu_2S and tetragonal $Cu_{1.96}S$ was obtained, with the monoclinic being the main phase.

SEM characterization of the annealed powders showed the $Cu_{2-x}S$ particles to grow during the thermal treatment, independently of the used gas flow (Figure S2). EDX analysis further confirmed the sulfur content to strongly decrease with the annealing process and the final Cu/S ratio to be higher for the sample annealed in the presence of H_2 (Table S1). Figures S3 and S4 display representative HRTEM images and EELS compositional maps of the samples annealed for 3 h under Ar or Ar/ H_2 flow, respectively. The power spectrum analysis of the HRTEM micrographs showed the sample annealed in Ar to display the rhombohedral $Cu_{1.8}S$ phase (space group $R\bar{3}M$) with $a = b = 3.93$ Å and $c = 48.14$ Å, consistent with XRD results. Besides, HRTEM characterization showed the sample

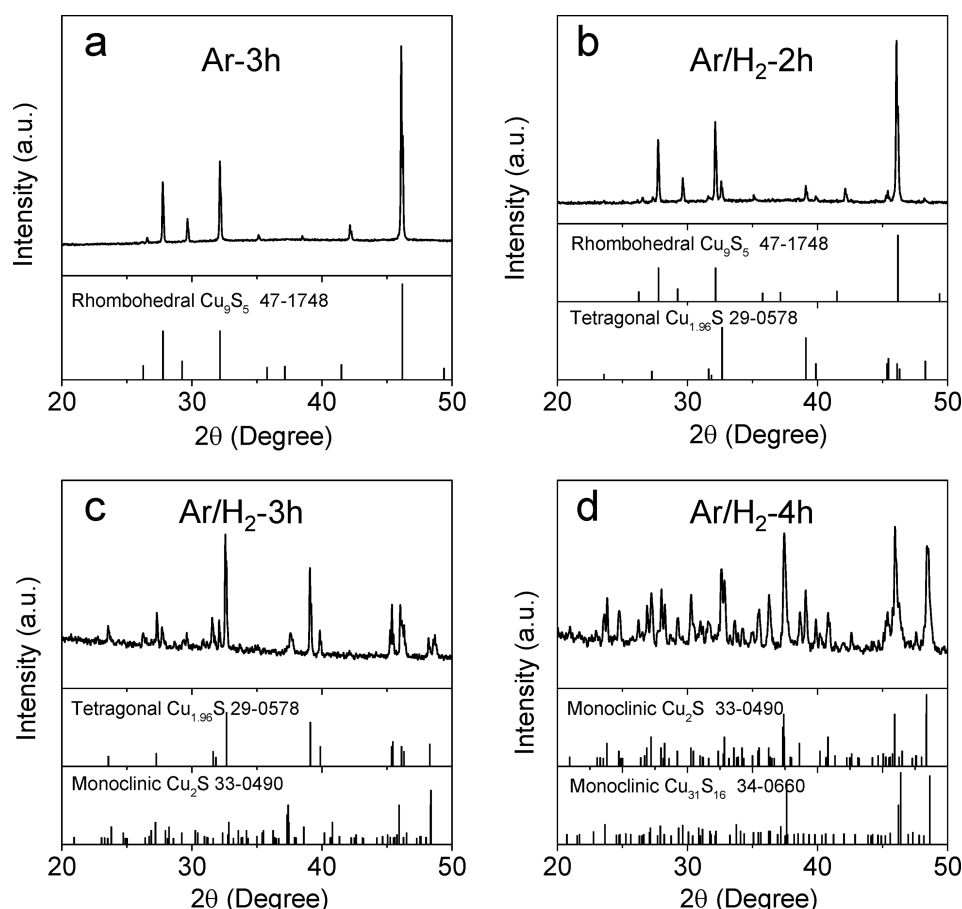


Figure 3. XRD patterns of Cu_{2-x}S powders obtained from annealing covellite CuS nanoparticles under different gas flow, Ar or Ar/H_2 , and different times, from 2 to 4 h, as indicated in each pattern.

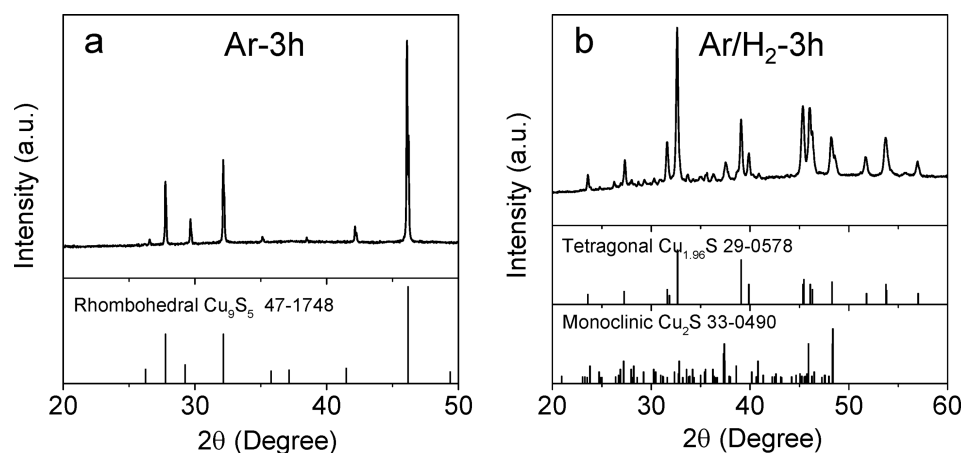


Figure 4. XRD patterns of Cu_{2-x}S pellets obtained by annealing the covellite CuS nanoparticles for 3 h under different gas flow, Ar (a) or Ar/H_2 (b), as indicated in each pattern, and afterward hot pressing the obtained powder at 693 K and 60 MPa.

annealed under Ar/H_2 flow for 3 h to display crystallites with the tetragonal $\text{Cu}_{1.96}\text{S}$ structure (space group $P43212$) with $a = b = 3.9962 \text{ \AA}$ and $c = 11.2870 \text{ \AA}$ and crystallites with the monoclinic Cu_2S structure (space group $P121/C1$) with $a = 15.2460 \text{ \AA}$, $b = 11.8840 \text{ \AA}$, and $c = 13.4940 \text{ \AA}$, also consistently with the measured XRD pattern. EELS chemical composition maps of both samples displayed a uniform distribution of Cu and S (Figures S3b and S4b).

Annealed powders were subsequently loaded into a 10 mm graphite die and hot-pressed at 693 K and 60 MPa for 4 min

inside an Ar-filled glovebox. The relative densities of the obtained pellets were *ca.* 94% of the theoretical value, as measured by the Archimedes' method (Table S2). Figure S5 displays representative cross-sectional SEM micrographs of the pellets, presenting a dense structure. XRD analysis showed a minor influence of the hot-press treatment on the Cu_{2-x}S crystallographic phase (Figure 4). The XRD patterns of the pellets obtained from nanoparticles annealed in Ar and Ar/H_2 displayed the metastable rhombohedral $\text{Cu}_{1.8}\text{S}$ phase and the dominant tetragonal $\text{Cu}_{1.96}\text{S}$ structure, respectively, consis-

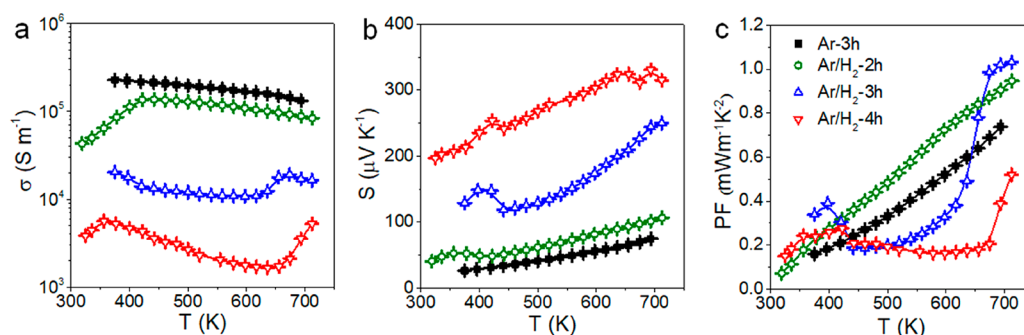


Figure 5. Thermoelectric properties of Cu_{2-x}S samples annealed under different gas flow and for different times: (a) electrical conductivity, σ ; (b) Seebeck coefficient, S ; (c) power factor, PF .

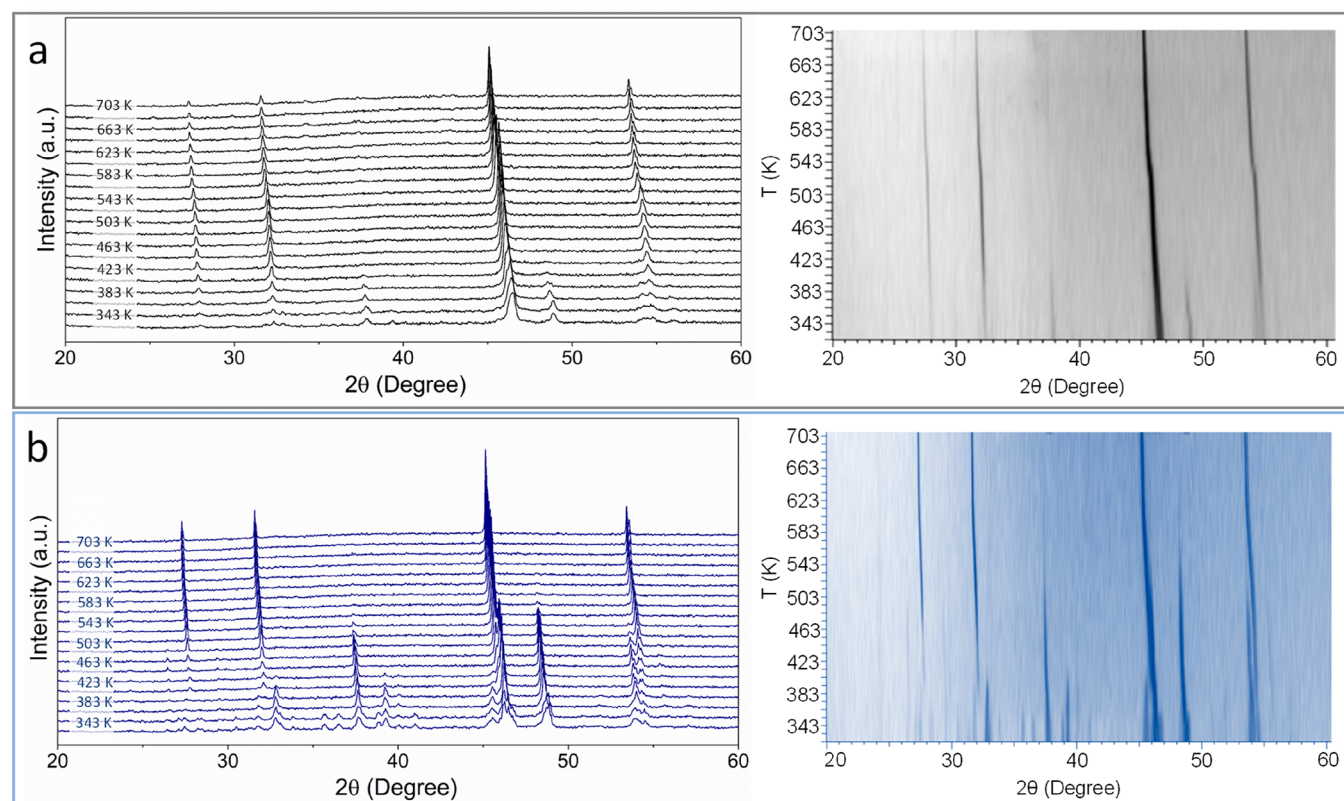


Figure 6. Temperature evolution of the XRD patterns of Cu_{2-x}S pellets obtained from nanoparticles annealed in Ar (a) and Ar/H_2 (b) for 3 h. XRD patterns were measured on the exact same pellets previously used to measure thermoelectric properties and were obtained when increasing temperature (from bottom to top) in the temperature range from 323 to 703 K.

tently with the results obtained from the nanopowders. The minor rhombohedral component observed on the material annealed in Ar/H_2 disappeared after the hot press. Additional HRTEM characterization of the pellets confirmed the results obtained from XRD analysis (Figure S6). These pellets were used to characterize thermoelectric properties.

Figure 5 displays the electrical conductivity (σ), Seebeck coefficient (S), and power factor ($PF = S^2\sigma$) of the Cu_{2-x}S pellets in the temperature range 310–710 K. For all samples, the first measuring cycle showed slightly different results compared with the subsequent ones (Figures S7 and S8). After the first cycle up to 710 K, the pellet obtained from the covellite nanoparticles annealed in Ar displayed mainly the monoclinic djurleite $\text{Cu}_{1.97}\text{S}$ phase (Figure S9). The dominance of the djurleite phase was accentuated when increasing the number of cycles. This sample also presented a sustained

variation of the transport properties from cycle to cycle. It displayed a monotonous decrease of the electrical conductivity and increase of the Seebeck coefficient that was related to a progressive loss of sulfur and consequently of copper vacancies. On the other hand, the pellet obtained from covellite particles annealed in Ar/H_2 displayed much higher structural stability and electronic stability, presenting a similar combination of monoclinic $\text{Cu}_{1.96}\text{S}$ and Cu_2S phases and similar transport properties after the first and the 11th cycles (Figure S9). The transport properties obtained in the second cycle, which coincided better with results obtained in following cycles, are the ones presented in the following.

Compared with samples annealed in Ar, an order of magnitude lower electrical conductivities were obtained for the samples annealed in the presence of H_2 for 3–4 h. This decrease of σ was correlated with a substantial increase of the

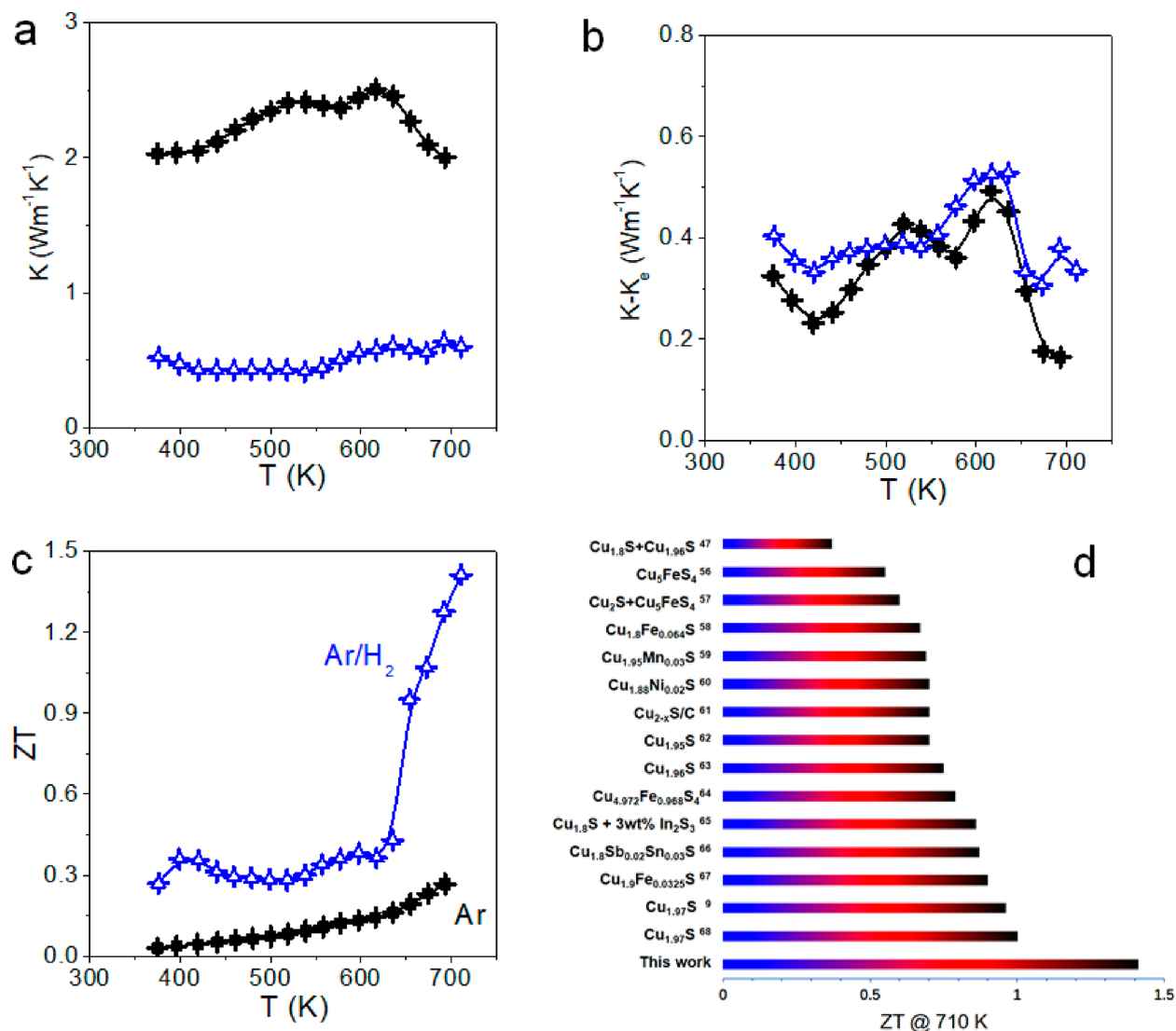


Figure 7. Thermoelectric properties of Cu_{2-x}S pellets obtained from nanoparticles annealed under Ar (black solid symbols) and Ar/H₂ (blue open symbols): (a) thermal conductivity, κ_{total} ; (b) lattice thermal conductivity, κ_L ; (c) thermoelectric figure of merit, ZT . (d) Comparison of ZT values at 710 K for Cu_{2-x}S-based materials.^{9,47,56–68}

Seebeck coefficient. The σ decrease and S increase were related to a strong reduction of the charge carrier concentration, from $9 \times 10^{20} \text{ cm}^{-3}$ for the sample annealed in Ar to $6 \times 10^{19} \text{ cm}^{-3}$ for the sample annealed in Ar/H₂ for 3 h, as measured by Hall (Table S3). This decrease of the charge carrier concentration was consistent with the higher Cu/S ratio and thus the lower density of Cu vacancies obtained in samples annealed in Ar/H₂, as inferred from XRD data and inductively coupled plasma optical emission spectrometry (ICP-OES) measurements (Table S4). Overall, the capability to adjust the charge carrier concentration through controlling the annealing atmosphere and time allowed its optimization and resulted in a significant increase of the maximum power factor. The largest power factors were obtained in the high temperature range tested from samples annealed in Ar/H₂ for 3 h and reached $1.1 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at 710 K. These results demonstrate both the large room for improvement in the thermoelectric performance of Cu_{2-x}S and the potential of tuning the Cu_{2-x}S transport properties by simply modifying the annealing parameters when using CuS nanoparticles as precursor material.

The transport properties of the samples annealed under Ar/H₂ showed a nonmonotonous dependence on temperature. Taking the electrical conductivity as a reference (Figure 5a), the electrical conductivity increased with temperature up to 350–450 K, then decreased until 600–650 K, and then increased again. This complex behavior was reliably observed in different samples and measuring cycles (Figures S7 and S8), and it was consistent with previously reported results (Figure S10).

To determine the origin of this complex dependence on temperature, we analyzed the evolution of the crystal structure with temperature using the profile displayed in Figure S11. Figure 6 displays the XRD patterns measured at different temperatures from Cu_{2-x}S pellets produced from nanoparticles annealed in Ar (Figure 6a) and Ar/H₂ (Figure 6b). The pellets used for the high temperature XRD analysis had been previously used for the characterization of thermoelectric properties. The monoclinic djurleite phase measured at ambient temperature from the Cu_{2-x}S pellet obtained from nanoparticles annealed in Ar evolved with temperature to a cubic Cu₂S phase. This phase transition occurred in the

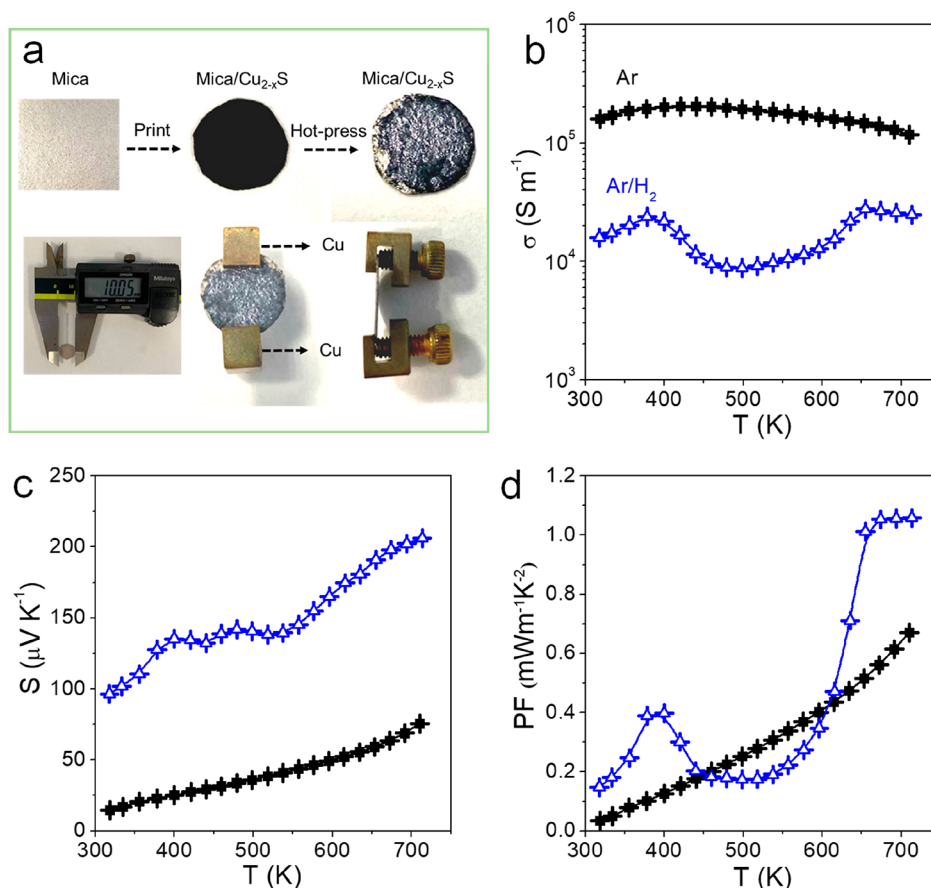


Figure 8. (a) Optical images of the mica substrate, the mica/Cu_{2-x}S film, the hot-pressed layer and the system used to measure thermoelectric properties. (b–d) Thermoelectric properties of the Cu_{2-x}S film on mica: (a) electrical conductivity, σ ; (b) Seebeck coefficient, S ; (c) power factor, PF .

temperature range 350–450 K and the obtained cubic phase remained unchanged until the highest tested temperature, although a small shift of the XRD peak positions was observed at ca. 550 K. On the other hand, when increasing temperature, the Cu_{2-x}S pellet produced from nanoparticles annealed in Ar/H₂ underwent two phase transitions, from the combination of monoclinic djurleite and chalcocite measured at ambient temperature to increasingly more symmetric structures. In the temperature range 350–400 K, the monoclinic phases evolved into the hexagonal high chalcocite Cu₂S phase. This transition coincided with the first anomaly in the evolution of the transport properties of this material. A second phase transition, from hexagonal to cubic Cu₂S, was observed at 500–600 K, coinciding with the second anomaly on the temperature evolution of the transport properties. Differential scanning calorimetry (DSC) analyses confirmed these results (Figure S12). The DSC profile of the sample annealed in Ar displayed a clear feature at ca. 320–400 K, and an additional heat flow variation in the range 550–710 K that could be related with an irreversible loss of sulfur, consistent with the progressive decrease of σ and the increase of S measured from this sample (Figure S7). On the other hand, the DSC profile of the sample annealed in Ar/H₂ displayed additional features in the range 350–450 K and a second phase transition at ca. 550–600 K.

Overall, we observed CuS nanoparticles to be intrinsically unstable with temperature. They lost sulfur when heated at moderately high temperatures, resulting in Cu_{2-x}S nanopowders. The stoichiometry of the resulting material was found

to determine its charge transport properties. Thus, the annealing temperature, time, and also atmosphere are key parameters to properly adjust transport properties and thus maximize thermoelectric performance. We observed CuS nanoparticles annealed in Ar to be characterized by high Cu deficiencies that resulted in too high charge carrier concentrations. On the other hand, samples annealed in the presence of H₂ were characterized by a considerably higher Cu/S ratio and thus significantly lower charge carrier concentrations that were better adjusted to maximize the power factor in the high temperature range measured ($T > 600$ K), where copper chalcogenides display the best thermoelectric performance. Samples annealed in the presence of H₂ displayed an increase of electrical conductivity at around 600 K, which can be associated with a slight increase of the charge carrier concentration or mobility with the reorganization of Cu and S atoms during the phase transition to the cubic structure. While all Cu_{2-x}S pellets displayed the cubic phase at temperatures above 600 K, the slightly different Cu/S stoichiometries explain the large variation between the performances obtained from samples produced from nanoparticles annealed in the Ar or Ar/H₂ atmosphere.

Figure 7a shows the thermal conductivity (κ_{total}) of the Cu_{2-x}S pellets annealed in Ar or Ar/H₂ for 3 h. The thermal conductivity of the sample annealed in Ar was significantly higher than that of the sample annealed in Ar/H₂ owing to the much larger electronic contribution of the former. When subtracting the electronic thermal conductivity, we observed

the lattice thermal conductivity of the two materials to be similar (Figure 7b).

The dimensionless thermoelectric figure of merit of the Cu_{2-x}S pellets annealed in Ar and Ar/H_2 for 3 h are displayed in Figure 7c. Figure S13 displays the results obtained from 3 pellets produced from 3 different batches of nanoparticles using the same synthesis and post-treatment conditions. Data obtained from the different pellets showed excellent reproducibility. Compared with the material annealed in Ar, the material annealed in Ar/H_2 for 3 h was characterized by much higher figures of merit, reaching up to $ZT = 1.41$ at 710 K. To the best of our knowledge, this is the highest ZT value reported for Cu_{2-x}S in this middle temperature range, where Cu_{2-x}S displays stable behavior (Figures 7d, S10).

In Figure S10 we compare the results obtained from Cu_{2-x}S pellets produced from nanoparticles annealed in the presence of H_2 with previously reported results from Cu_{2-x}S materials. We observe that samples with similar electrical conductivities display similar trends with temperature: an initial increase of the electrical conductivity in the low temperature range, a decrease in the middle temperature range measured, until around 600 K, and a posterior increase that coincides with the phase transition to the cubic structure. The electrical conductivity of the samples obtained from nanoparticles annealed in the presence of H_2 was in the low electrical conductivity range of the reported values. Moderate electrical conductivities were also obtained with other copper sulfides that typically included multivalence dopants such as Fe and Mn to decrease the hole concentration. These doped samples were characterized by similar but slightly lower Seebeck coefficients than our best materials, which could be related to a lower charge carrier mobility associated with the presence of the highly ionized foreign atoms within the Cu_{2-x}S lattice. The thermal conductivity of pellets produced from nanoparticles annealed in the presence of H_2 was also in the low range of the reported thermal conductivities, as expected from the moderate contribution of the electronic component and the large density of grain boundaries present in our polycrystalline materials. Overall, the control of the annealing parameters allowed adjusting the density of Cu vacancies and thus the charge carrier concentration without adding external impurities, which resulted in the highest power factors and ZT values reported to date.

The excellent performance measured from materials produced from the processing and consolidation of nanoparticles demonstrates the high suitability of the presented material processing strategy. We believe that the synthesis of copper sulfide in the form of nanoparticles is key both to reduce the production cost, as no large amounts of energy and time are invested in organizing atoms in large crystal domains, and to control composition by means of mild thermal annealing in a controlled atmosphere. Besides, the availability of the material in the form of nanoparticles suspended in a low cost and safe solvent such as water or ethanol allows the scalable, high throughput, and cost-effective production of devices using printing technologies. To advance in this direction, we prepared inks from the annealed nanoparticles and printed them on a mica substrate (Figure 8). Then we hot-pressed the films in the same conditions as the pellets. Figure 8b–d display the thermoelectric properties of the films obtained from Cu_{2-x}S nanoparticles annealed under Ar or Ar/H_2 flow for 3 h. The results obtained from the films were very similar to those obtained from pellets, which demonstrates

the potential of these nanoparticle-based materials to produce high performance printed thermoelectric devices.

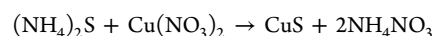
CONCLUSIONS

We reported a facile, scalable, and low-cost method for the synthesis of covellite CuS nanoparticles in aqueous media and at room temperature. The produced covellite nanoparticles lost sulfur when heated under an inert or reducing atmosphere and changed their crystal phase to metastable rhombohedral $\text{Cu}_{1.8}\text{S}$ or tetragonal $\text{Cu}_{1.96}\text{S}$. The annealing atmosphere and time allowed tuning the amount of sulfur lost and thus the stoichiometry and crystal structure of the final nanopowder. The sample stoichiometry determined the density of copper vacancies, thus the hole concentration and consequently the transport properties of the material. By comparing the material annealed in Ar with that annealed in Ar/H_2 , we observed the former to be characterized by much higher charge carrier concentrations and electrical conductivities, but lower Seebeck coefficients. Finally, the material annealed in Ar/H_2 for 3 h was characterized by the highest power factors and thermoelectric figures of merit, up to 1.41 at 710 K, which is the highest ZT reported for Cu_{2-x}S at this temperature. Overall, this work demonstrated that (i) there is plenty of room for optimization of the thermoelectric properties of copper chalcogenides and particularly copper sulfide; (ii) the annealing of CuS nanoparticles in a controlled atmosphere and during an appropriated amount of time is a facile, convenient, and highly effective strategy to tune stoichiometry, and thus the density of electronic active defects and the charge carrier concentration, which is a key parameter for optimizing thermoelectric performance; and (iii) the use of nanoparticles was key to providing enough surface area for effective and homogeneous removal of copper vacancies. The availability of the material in the form of nanoparticles also allowed the direct printing of the material into layers that were characterized by similar thermoelectric performances as those obtained from the pellets.

METHODS

Chemicals. Copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and ammonium sulfide solution ($(\text{NH}_4)_2\text{S}$ 20% in H_2O) were purchased from Fisher. Chemicals were used as received without further purification.

Copper Sulfide Nanoparticles. The reaction took place at ambient atmosphere and temperature inside a fume hood. To obtain around 1 g of nanoparticles, 10 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in 35 mL of deionized water in a centrifuge tube using ultrasound until obtaining a clear light-blue solution. Then, 2 mL of $(\text{NH}_4)_2\text{S}$ were injected into the centrifuge tube, which was strongly shaken to force a proper mixing of the reactants. Upon $(\text{NH}_4)_2\text{S}$ injection, the solution turned black owing to the nucleation of copper sulfide through the reaction:



After 1 min of reaction, particles were recovered by centrifugation. Then, they were purified using 5 dispersion/precipitation cycles using deionized water and ethanol. Finally, nanoparticles were dried under vacuum overnight at room temperature and stored in an Ar-filled glovebox.

Nanomaterial Consolidation. Dried nanoparticles were annealed at 450 °C for 180 min under gas flow inside a tube furnace. Two different gas atmospheres were studied: argon and 5% hydrogen in argon (Ar/H_2). The annealed nanopowders were loaded into a 10 mm graphite die and hot-pressed at 420 °C and 60 MPa for 4 min using a custom-made hot press inside the Ar-filled glovebox.^{51–55} The

relative densities of the obtained pellets were measured by the Archimedes' method to be *ca.* 93% of the theoretical value.

Cu₂-S Layers. An ink was prepared by mixing annealed nanoparticles with ethanol. The ink was printed on a mica tape, which was allowed to dry for a few minutes. Then, the dried mica tape was loaded into a 10 mm graphite die and hot-pressed at 420 °C and 60 MPa for 4 min using a custom-made hot press inside the Ar-filled glovebox.

Structural and Chemical Characterization. X-ray diffraction (2θ angle: 20° to 80°; scanning rate: 1.5°/min) analyses were carried out on a Bruker AXS D8 ADVANCE X-ray diffractometer with Cu K α radiation (λ = 1.5406 Å). Temperature-dependent XRD patterns were collected using an Anton Paar XRK 900 Reactor chamber with a sample spinner with height corrections. The temperatures were ramped at a rate of 60 °C/min operating at 40 kV from 323 to 703 K and then isothermally held for 30 min at each temperature. The height of the sample was aligned, and diffraction results were collected from 20° to 60° in 2θ at a speed of 2°/min. Size and morphology of nanoparticles were examined by TEM using a ZEISS LIBRA 120, operating at 120 kV, and field-emission SEM on an Auriga Zeiss operated at 5.0 kV. The material composition was analyzed using an Oxford energy dispersive X-ray spectrometer (EDX) attached to a Zeiss Auriga SEM at 20.0 kV. Composition was also analyzed by ICP-OES using an ICPE-9820 system. For ICP measurements, samples were prepared by the digestion of crushed powder in aqua regia overnight followed by dilution in MQ-Water (Milipore). Crystallographic structure and chemical composition were analyzed by HRTEM and EELS, respectively, using a Tecnai F20 field-emission gun microscope at 200 keV with an embedded Gatan QUANTUM image filter. XPS analyses were carried out on a Specs system equipped with a Mg anode XR50 source operating at 250 W and a Phoibos 150 MCD-9 detector (Specs GmbH). The pressure in the analysis chamber was kept below 10⁻⁷ Pa. Data processing was performed with the CasaXPS program (Casa Software Ltd.).

Thermoelectric Property Measurements. Seebeck coefficients were measured using a static DC method. Electrical resistivity data were obtained by a standard four-probe method. Both the Seebeck coefficient and the electrical resistivity were measured simultaneously in an LSR-3 LINSEIS system in the temperature range between room temperature and 710 K under a helium atmosphere. All samples were measured at least 3 consecutive times during heating to around 710 K. By taking into account the system accuracy and the measurement precision, an error of *ca.* 4% in the measurement of the electrical conductivity and Seebeck coefficient was estimated. The electrical conductivity and Seebeck coefficient of the layers were measured by clamping the two ends of the mica tape with a copper electrode (Figure 8a).

Thermal conductivities (κ_{total}) were obtained by multiplying the thermal diffusivity (λ), the constant pressure heat capacity (C_p), and the density of the material (ρ), where $\kappa_{\text{total}} = \lambda C_p \rho$. A Xenon Flash Apparatus XFA600 was used to determine the thermal diffusivities of the samples with an estimated error of *ca.* 5%. The specific heat capacity (C_p) of the samples was evaluated using a NETZSCH DSC 404 F3 differential scanning calorimeter (DSC) at a heating rate of 10 K/min under a flow of high purity N₂ in the Pt–Rh/Al₂O₃ crucible. The C_p curve was calculated by NETZSCH Proteus software based on the C_p ratio method, with a standard sample of sapphire. The sample was first heated to 50 °C and maintained for 10 min to avoid heat hook. Then the temperature was increased to 430 °C with a ratio of 10 K/min, followed by cooling inside the machine. Figure S12b displays the heat capacity measured for a sample annealed in Ar and a sample annealed in Ar/H₂ for 3 h. The C_p values in the phase transition temperature range were inconsequential, so we extrapolated the C_p values in the temperature regions corresponding to the phase transitions to calculate ZT. For comparison, the constant pressure heat capacity (C_p) was also estimated from empirical formulas by the Dulong–Petit limit (3R law). Dulong–Petit C_p values were slightly higher than experimental C_p values. Figure S12c displays a comparison of the ZT values obtained when considering the experimental C_p or the calculated C_p . The density values were measured using the

Archimedes' method. To avoid cluttering the plots, error bars were not included in the figures. Hall charge carrier concentrations (n_H) and mobilities (μ_H) at room temperature were measured with the Van der Pauw method using a magnetic field of 0.6 T (ezHEMS, NanoMagnetics).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.0c09866>.

Additional characterization data including TEM, HRTEM, SEM, XRD, DSC, ICP, thermoelectric properties, and literature comparison (PDF)

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Notes

The authors declare no competing financial interest.

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Article

Enhanced Thermoelectric Performance of n-Type Bi₂Se₃ Nanosheets through Sn Doping

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Abstract: The cost-effective conversion of low-grade heat into electricity using thermoelectric devices requires developing alternative materials and material processing technologies able to reduce the currently high device manufacturing costs. In this direction, thermoelectric materials that do not rely on rare or toxic elements such as tellurium or lead need to be produced using high-throughput technologies not involving high temperatures and long processes. Bi₂Se₃ is an obvious possible Te-free alternative to Bi₂Te₃ for ambient temperature thermoelectric applications, but its performance is still low for practical applications, and additional efforts toward finding proper dopants are required. Here, we report a scalable method to produce Bi₂Se₃ nanosheets at low synthesis temperatures. We studied the influence of different dopants on the thermoelectric properties of this material. Among the elements tested, we demonstrated that Sn doping resulted in the best performance. Sn incorporation resulted in a significant improvement to the Bi₂Se₃ Seebeck coefficient and a reduction in the thermal conductivity in the direction of the hot-press axis, resulting in an overall 60% improvement in the thermoelectric figure of merit of Bi₂Se₃.

Keywords: thermoelectric; Bi₂Se₃; Sn doping



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1. Introduction

Thermoelectric (TE) devices that directly and reversibly convert heat into electricity find unlimited applications [1–6], but their real implementation is hampered by their low cost-effectiveness. The efficiency of energy conversion of a TE device is in part determined by the transport properties of the TE material: Seebeck coefficient S , electrical conductivity σ , and thermal conductivity κ . These material properties are generally grouped into a dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where T is the absolute temperature. Efficient TE materials are characterized by high power factors, $S^2\sigma$, and low thermal conductivities, κ . However, the strong correlation between these parameters makes the optimization of the material performance extremely difficult. Several strategies have been developed to maximize ZT , including engineering the electronic band structure of the TE material through doping [7], the use of energy filtering interphases [8], and the reduction in lattice thermal conductivity through the introduction of abundant grain boundaries [9].

Commercial devices use large amounts of highly crystalline Bi₂Te₃-based alloys as the active TE material, which accounts for a significant part of the total cost of the device. To

reduce the device cost, it is critical to develop low-cost materials not relying on scarce Te and low-cost processing strategies not based on high-temperature crystallization from high purity melts. Bi_2Se_3 presents the same structure and similar properties as Bi_2Te_3 , and, thus, it is an obvious possible Te-free alternative to Bi_2Te_3 . Numerous attempts to improve the TE figure of merit of this material have been reported, but with moderate success [10–18].

To maximize the TE performance of a material, one first critical point is to optimize its charge carrier concentration. Three main strategies can be used in this direction: tuning of the material stoichiometry, the introduction of atomic impurities, and/or the introduction of secondary phases able to inject the proper charge carriers to the host material [19–28]. Besides optimizing the charge carrier concentration, it is fundamental to minimize the thermal conductivity using multiscale phonon scattering centers. In this direction, the introduction of atomic impurities and abundant grain boundaries are highly effective. Besides, energy barriers at grain boundaries can also introduce energy- and charge sign-dependent charge carrier scattering, which could result in significant improvements to the Seebeck coefficient [29].

Here, we present a low temperature and high yield, solution-based strategy to prepare Bi_2Se_3 nanomaterials doped with different elements. The influence of different dopants on the TE properties of the material was tested. From the results obtained, we demonstrated Sn to have the highest potential to yield Bi_2Se_3 -based materials with improved performance. Thus, we further analyzed the location and chemical state of this element within Bi_2Se_3 and its effect on the material transport properties.

2. Materials and Methods

2.1. Chemicals and Solvents

Polyvinylpyrrolidone (PVP, $(\text{C}_6\text{H}_9\text{NO})_n$, AMW ~55,000), indium(III) acetate ($\text{InC}_6\text{H}_9\text{O}_6$, 99.99%), and bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\geq 99.99\%$) were purchased from Sigma-Aldrich. Sodium selenite (Na_2SeO_3 , $\geq 98\%$), copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%), silver nitrate (AgNO_3 , $\geq 99.9\%$), ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$, 99%), lead (II) acetate trihydrate ($\text{PbC}_4\text{H}_6\text{O}_4 \cdot 3\text{H}_2\text{O}$), tin(II) chloride anhydrous (SnCl_2 , 98%), and potassium hydroxide (KOH, $\geq 98\%$) were acquired from Fisher. Analytical grade ethanol and acetone were obtained from various sources.

2.2. Synthesis of Bi_2Se_3

Bi_2Se_3 particles were produced following the approach developed by Liu et al., with slight modifications [1]. Bi_2Se_3 (5 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (10 mmol, 4.851 g), Na_2SeO_3 (15 mmol, 2.594 g), KOH (50 mmol, 2.806 g), and PVP (0.5 g) were first dissolved in a three-neck flask containing EG (200 mL) under an Ar atmosphere at an ambient temperature for 0.5 h. The solution was then heated to 180 °C and kept at this temperature for 3 h. Immediately after the reaction was completed, the solution was allowed to cool naturally to room temperature by removing the heating mantle. The solution was divided into several centrifuge tubes and acetone was added to collect the solid product by centrifugation. In the next step, ethanol was introduced to re-disperse the particles, and acetone was added to precipitate them again. This step was repeated twice. Next, purified Bi_2Se_3 particles were dried under a vacuum overnight at room temperature and kept in the glovebox for posterior use. Around 3 g of particles were obtained per batch.

2.3. Synthesis of $\text{Bi}_{2-x}\text{M}_x\text{Se}_3$

The procedure used to produce $\text{Bi}_{2-x}\text{M}_x\text{Se}_3$ was the same used to produce Bi_2Se_3 , but the proper amount of bismuth nitrate was replaced with the corresponding metal precursor, as listed in the chemical section above.

2.4. Nanomaterial Consolidation

Dried Bi_2Se_3 particles were first annealed for 1 h at 350 °C under an Ar flow in a tubular furnace. Then, the annealed material was introduced into a graphite die and

consolidated into cylinders ($\varnothing$ 10 mm $\times$ 10 mm) at 480 °C and 50 MPa of pressure for 4 min with a custom-made hot press. The relative densities of the compacted pellets were measured by Archimedes' method. To measure transport properties in the two relevant directions, cylindrical pellets were cut into ca. 8 $\times$ 6 $\times$ 1 mm rectangular bars along the pressure axis, and 1 mm thick disks along the perpendicular to the pressure axis.

2.5. Structural and Chemical Characterization

The field emission scanning electron microscope (SEM) was used to determine the nanoparticle morphology on an Auriga Zeiss. An Oxford energy dispersive X-ray spectrometer (EDX) was used to measure the material composition at 20.0 kV. X-ray diffraction (XRD) was performed on a Bruker AXS D8 Advance diffractometer. The crystal structure of the samples was analyzed under the 200 keV Tecnai F20 field emission microscope equipped with a Gatan quantum image filter. X-ray photoelectron spectroscopy (XPS) was performed on a Specs system with the material inside the chamber at a pressure below 10^{-7} Pa. Data processing was carried out using the CasaXPS program.

2.6. Performance Characterization of Bulk Nanomaterial

Seebeck coefficients and resistivities were measured by the static direct current method and by the standard four-probe method, respectively, in an LSR-3 Linseis system under helium. All samples were tested for at least three heating and cooling cycles. Considering the system accuracy and measurement accuracy, the measurement error of the conductivity and Seebeck coefficient was estimated to be about 4%. Thermal diffusivity (λ), constant pressure heat capacity (C_p), and density of the material (ρ) were used to obtain the thermal conductivities (κ_{total}), where $\kappa_{\text{total}} = \lambda C_p \rho$. The thermal diffusivities of the samples were measured by a Xenon Flash Apparatus XFA600, which has an estimated error of ca. 5%. We used a constant as the heat capacity (C_p), which was estimated from empirical formulas by the Dulong–Petit limit (3R law). Under a magnetic field of 0.6 T, the Hall charge carrier concentrations and mobilities at room temperature were measured by the Van der Pauw method. The figures in this article do not have error bars in order to avoid cluttering the plots.

3. Results and Discussion

Following the above synthesis method, Bi_2Se_3 nanosheets grouped into flower-like particles were produced, as shown by the SEM micrographs (Figure 1a,b). Bi_2Se_3 shows a screw dislocation growth mechanism (Figure 1c). This layer-by-layer growth mechanism is usually due to the low supersaturation in the synthesis conditions, which inhibits dendritic growth. Axial screw dislocation is the self-sustaining spiral growth of nanosheets around the axis [15,23].

The XRD analysis showed that the crystal structure of the obtained nanosheets matched the rhombohedral Bi_2Se_3 phase (Figure 1d, JCPDS No. 00-033-0214). Figure 1e shows the layered rhombohedral crystal structure of Bi_2Se_3 , which consists of five covalently bonded atomic planes of Se-Bi-Se-Bi-Se. Quintuple layers are weakly bonded by van der Waals. The HRTEM characterization showed that the material has good crystallinity and has a crystal phase consistent with the Bi_2Se_3 rhombohedral phase (space group = R3-MH) with $a = b = 4.1340$ Å and $c = 28.6300$ Å (Figure 1f,g).

Nanosheets were annealed at 350 °C, and the annealed powder was hot-pressed into cylindrical pellets with a diameter of 10 mm and a height of 10 mm in a glovebox filled with argon. Samples were hot-pressed for four minutes at 480 °C and 50 MPa, and then naturally cooled to an ambient temperature. The relative density of the cylinders produced by this process was about 93% of the theoretical value. From the consolidated cylinder, a rectangular bar of 8 $\times$ 6 $\times$ 1 mm was cut longitudinally, and a 1 mm thick pellet was cut transversely (Figure 2). These samples were used to measure the TE properties of materials parallel to the pressure axis ($//$) and perpendicular to the pressure axis ($\perp$).

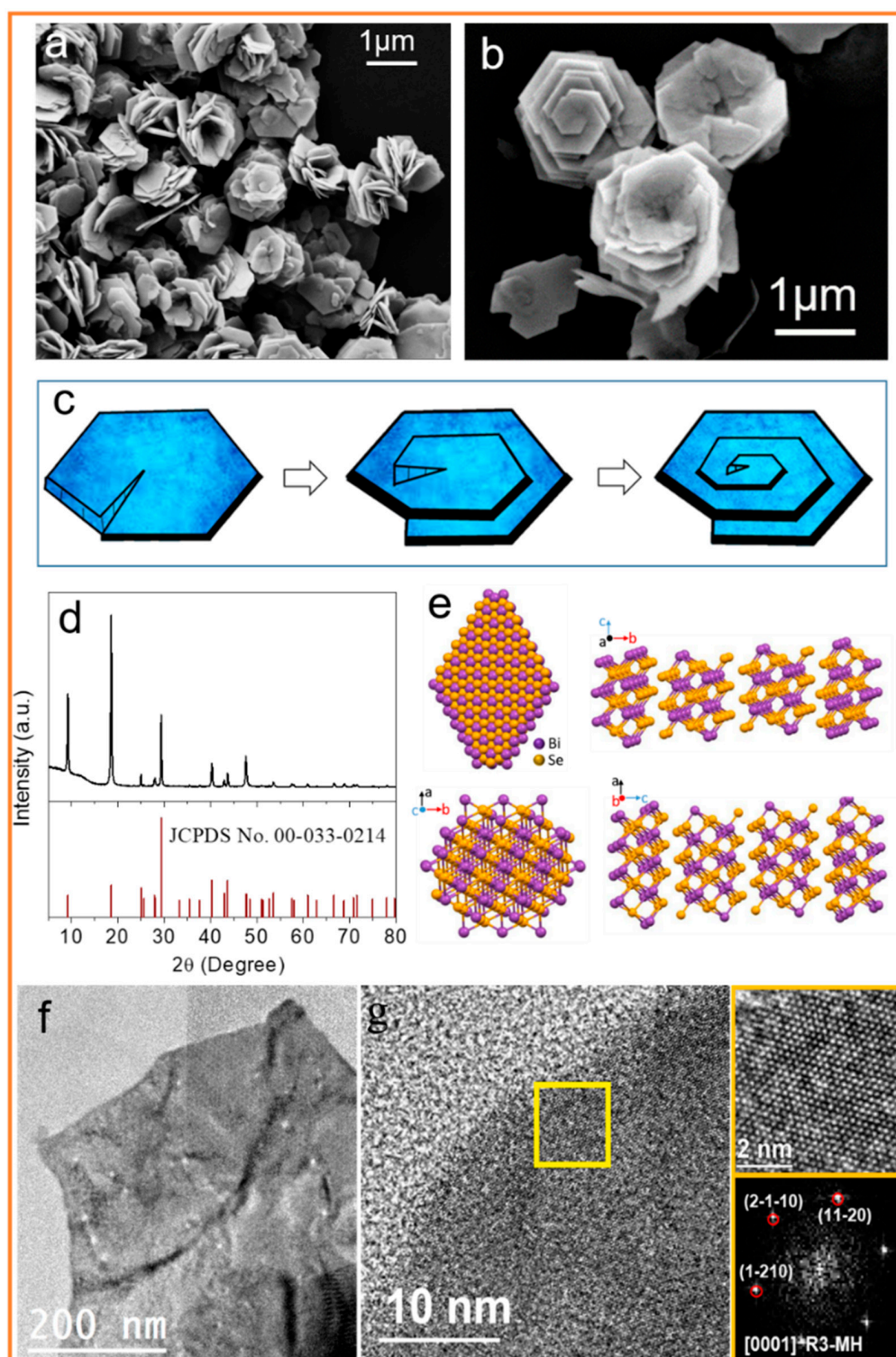


Figure 1. (a,b) SEM micrographs of the Bi_2Se_3 particles. (c) Scheme of the screw dislocation growth mechanism. (d) The XRD pattern of the Bi_2Se_3 particles. (e) The layered rhombohedral crystal structure of Bi_2Se_3 . (f) A low-resolution TEM image. (g) An HRTEM micrograph of the Bi_2Se_3 particles and its corresponding power spectrum. From the crystallographic domain, the Bi_2Se_3 lattice fringe distances were measured to be 0.205 nm , 0.205 nm , and 0.204 nm , at 60.96° and 120.86° , respectively, which could be illuminated as the rhombohedral Bi_2Se_3 phase, visualized along the $[0001]$ zone axis.

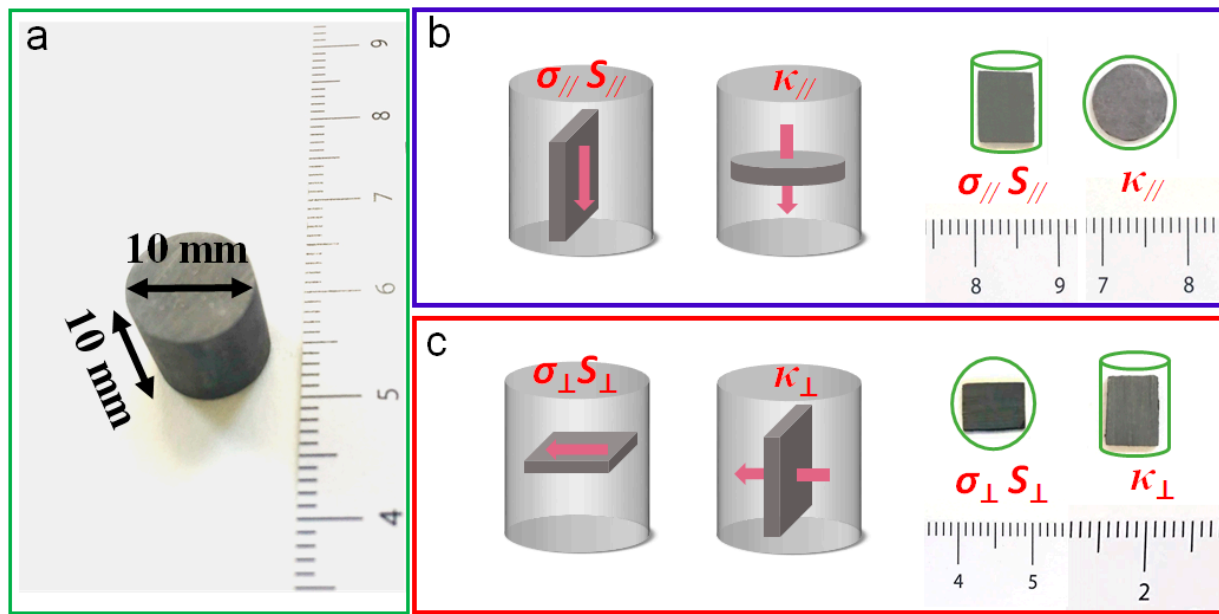


Figure 2. (a) Photograph of the consolidated Bi_2Se_3 cylinder. (b,c) Scheme and images of the samples used to measure the material transport properties in the directions parallel (b) and vertical (c) to the pressure axis.

Figure 3 displays the electrical conductivity (σ), Seebeck coefficient (S), and power factor ($PF = S^2\sigma$) of the $\text{Bi}_{2-x}\text{M}_x\text{Se}_3$ ($\text{M} = \text{Sn}, \text{Cu}, \text{Ag}, \text{Pb}, \text{In}$) pellets perpendicular to the press direction. The electrical conductivity of the undoped material decreased with temperature, which pointed to a degenerated semiconductor behavior. Compared to the undoped material, the electrical conductivity of all the doped samples was slightly lower, except for the Ag-doped samples. On the other hand, the samples doped with Sn and to a minor extent, Pb displayed an increase in the absolute value of the Seebeck coefficient. Overall, the highest power factors were obtained with the Sn doping. Thus, we decided to further study the effect of this element.

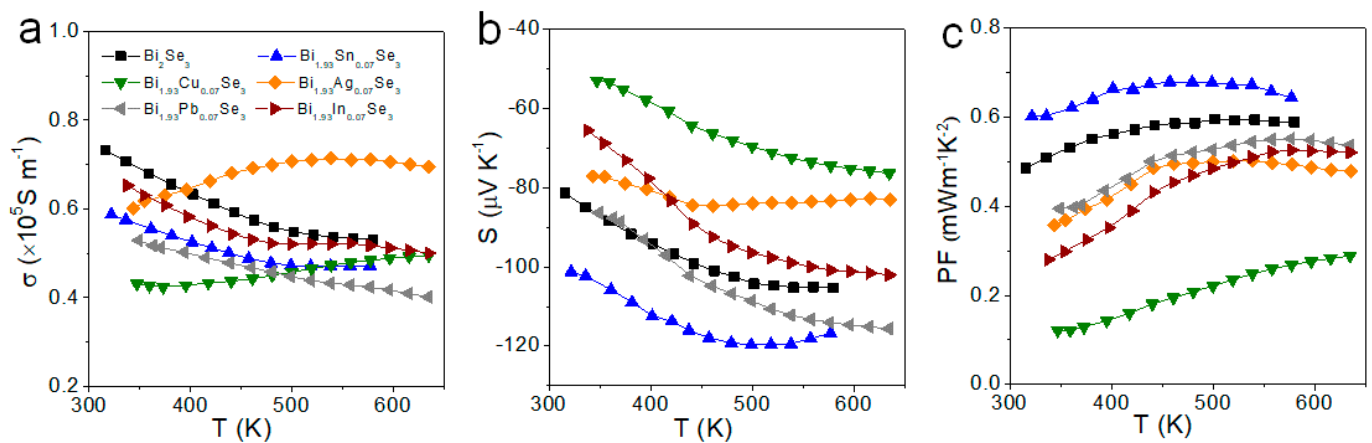


Figure 3. TE properties of $\text{Bi}_{2-x}\text{M}_x\text{Se}_3$ ($\text{M} = \text{Sn}, \text{Cu}, \text{Ag}, \text{Pb}, \text{In}$) samples measured perpendicular to the press direction: (a) electrical conductivity, σ ; (b) Seebeck coefficient, S ; (c) power factor, PF .

Figure 4 displays the electrical conductivity, Seebeck coefficient, and power factor of $\text{Bi}_{2-x}\text{Sn}_x\text{Se}_3$ materials containing different amounts of Sn. We observed that the electrical conductivity decreased and the absolute value of the Seebeck coefficient increased with the amount of Sn up to a certain Sn concentration. The highest power factors were finally obtained for $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$. The decrease in the electrical conductivity and increase in

the absolute value of the Seebeck coefficient denoted a reduction in the charge carrier concentration, which points to the presence of Sn^{2+} ions instead of Sn^{4+} at Bi^{3+} sites.

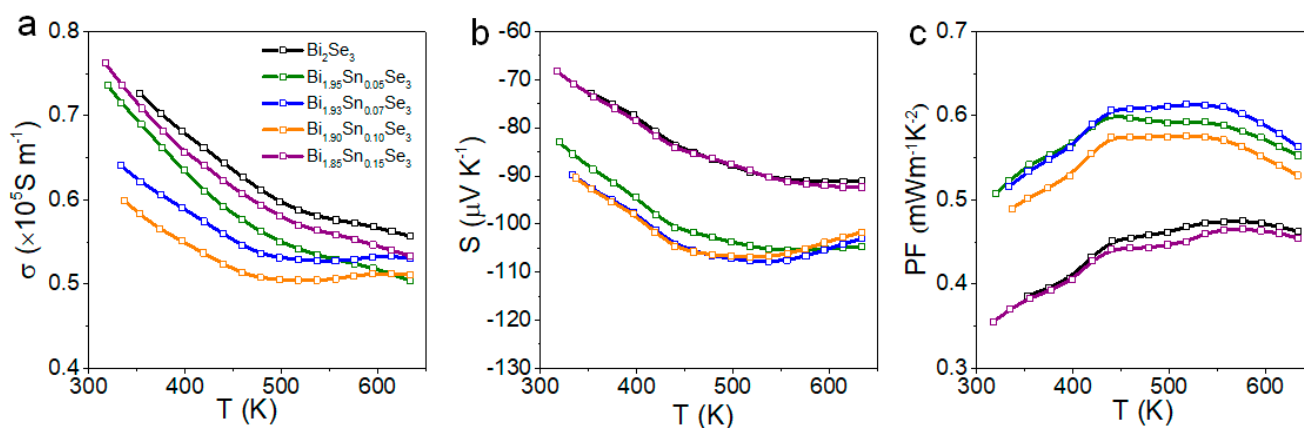


Figure 4. Thermoelectric properties of $\text{Bi}_{2-x}\text{Sn}_x\text{Se}_3$ perpendicular to the press direction: (a) electrical conductivity, σ ; (b) Seebeck coefficient, S ; (c) power factor, PF .

Figure 5 shows representative SEM micrographs of the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ particles, which had similar sizes but did not display the flower-like morphology observed from Bi_2Se_3 . As shown in Figure 6, the XRD characterization confirmed that the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ particles maintained their rhombohedral structure. With the introduction of Sn, the XRD peaks shifted to lower 2θ angles, suggesting the incorporation of Sn within the Bi_2Se_3 lattice [5].

The HRTEM characterization confirmed the rhombohedral phase of the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ particles (Figure 7a). EELS chemical composition maps obtained from the red squared region in the HAADF STEM micrograph shown in Figure 7b displayed a homogeneous distribution of Sn, Bi and Se within the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ nanosheet.

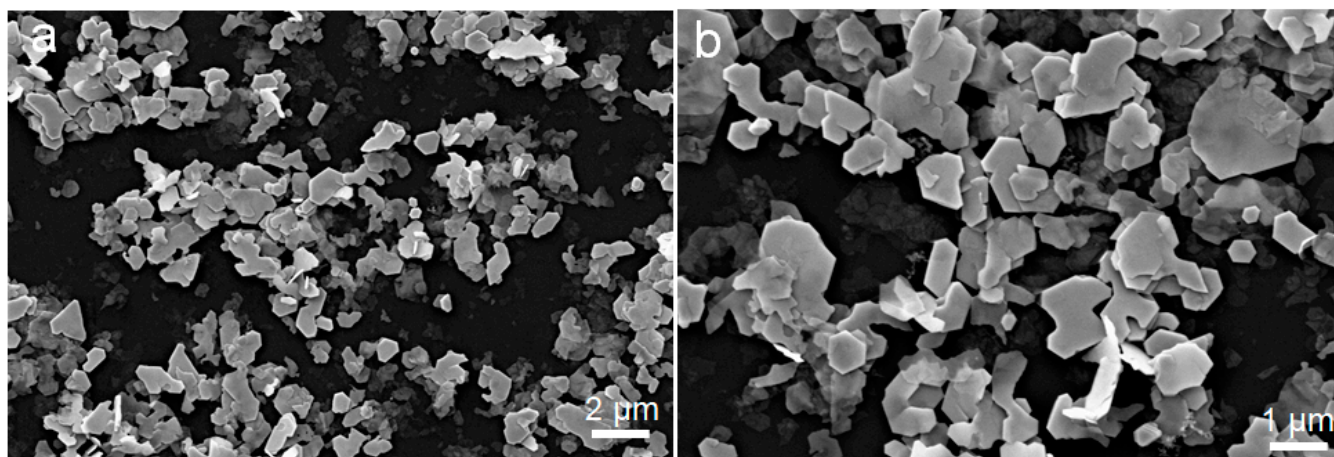


Figure 5. SEM micrographs of $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ nanosheets with different magnifications; (a) magnification 5.00 K $\times$, (b) magnification 10.00 K $\times$.

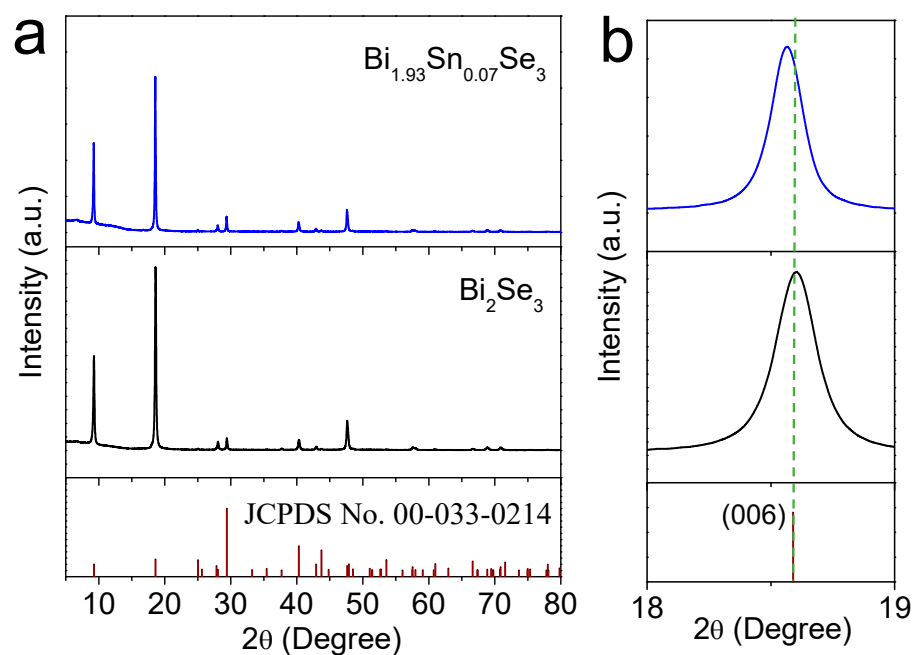


Figure 6. (a) XRD patterns of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$; (b) expansion diagram of the area corresponding to the diffraction peak of Bi_2Se_3 (006).

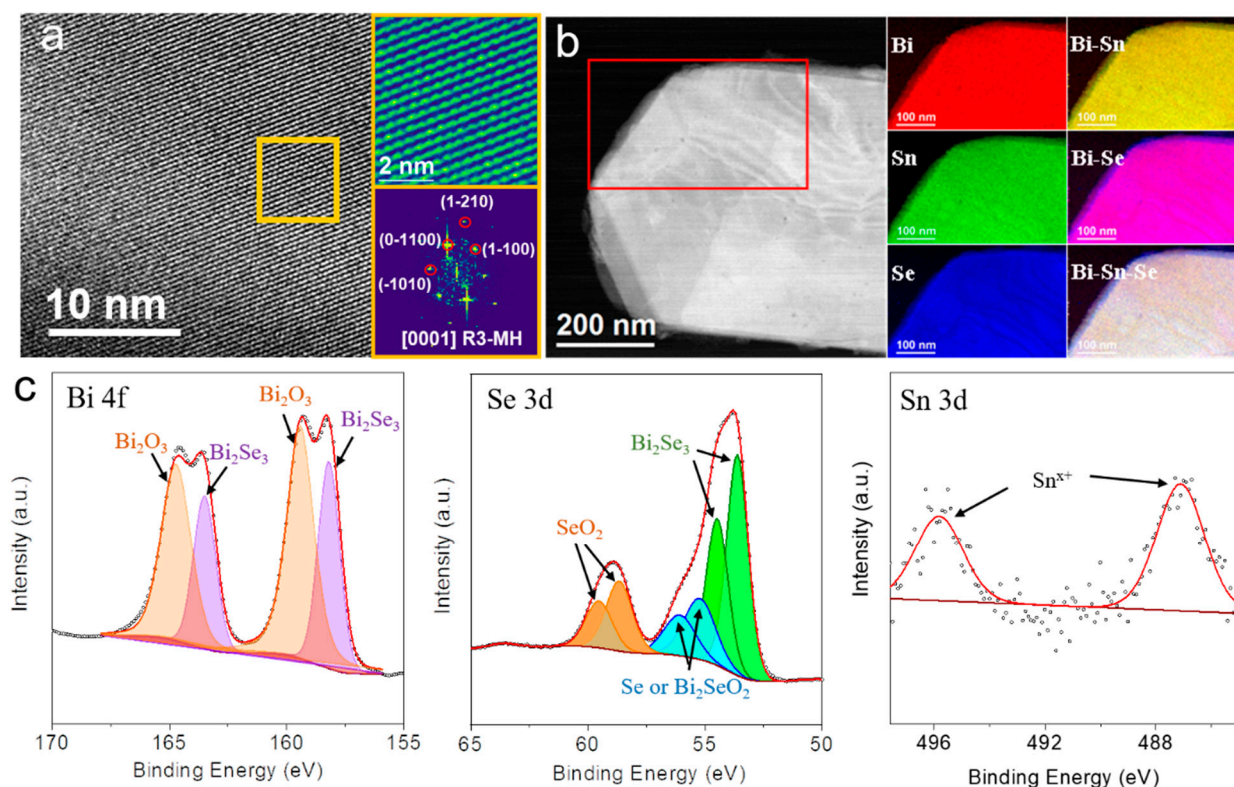


Figure 7. (a) An HRTEM micrograph of a $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ nanosheet, detailed information of the orange squared area and its corresponding power spectrum. Bi_2Se_3 lattice fringe distances were measured to be 0.370 nm, 0.349 nm, 0.202 nm, and 0.351 nm, at 62.89° , 92.61° and 122.99° , respectively, which could be illuminated as the rhombohedral Bi_2Se_3 phase, along its [0001] zone axis. (b) EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Bi $\text{N}_{2,3}$ -edges at 679 eV (red), Sn $\text{M}_{4,5}$ -edges at 485 eV (green), Se $\text{M}_{2,3}$ -edges at 162 eV (blue) and composites of Bi-Sn, Bi-Se as well as Bi-Sn-Se. (c) Bi 4f, Se 3d and Sn 3d high-resolution XPS spectra obtained from $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ nanosheets.

Bi 4f, Se 3d and Sn 3d high-resolution XPS spectra of $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ particles are displayed in Figure 7c. The high-resolution Bi 4f spectrum was fitted with two doublets, associated with Bi^{3+} within a Bi_2Se_3 chemical environment (Bi 4f_{7/2} at 158.2 eV) and Bi within a more electronegative environment, as it could be Bi_2O_3 or Bi_2SeO_2 (Bi 4f_{7/2} at 159.4 eV) [30]. This oxidation of the particles surface is related to their transport and handling in the air [4]. The high-resolution Se 3d XPS spectrum was fitted with three doublets, corresponding to Se within the Bi_2Se_3 (Se 3d_{5/2} at 53.6 eV), selenium in an elemental or Bi_2SeO_2 environment (Se 3d_{5/2} at 55.2 eV), probably arising from the partial oxidation of the material surface, and Se in a SeO_2 chemical environment (Se 3d_{5/2} at 58.6 eV) [30,31]. Finally, the high-resolution Sn 3d XPS spectrum was difficult to fit owing to the small amount of this element, but the broadness of the peaks pointed to the presence of at least two Sn chemical states that should be tentatively assigned to Sn^{x+} within a SnSe and an oxidized environment [31]. According to the electrical properties measured at the introduction of Sn, we tentatively assigned the Sn^{x+} component within SnSe to Sn^{2+} .

Top-view and cross-section SEM micrographs of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ (Figure 8) showed the final pellets presenting a laminar microstructure with an evident preferential orientation of the material layers. Bi_2Se_3 displayed larger and thinner layers than $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$. When comparing the XRD patterns of the sample held in two normal directions, parallel and perpendicular to the pressure axis (Figure 8e,f), we observed that the relative XRD peak intensity clearly differed. This result confirmed the preferential crystallographic orientation of the hot-pressed materials, with the [001] crystallographic direction oriented parallel to the pressure axis.

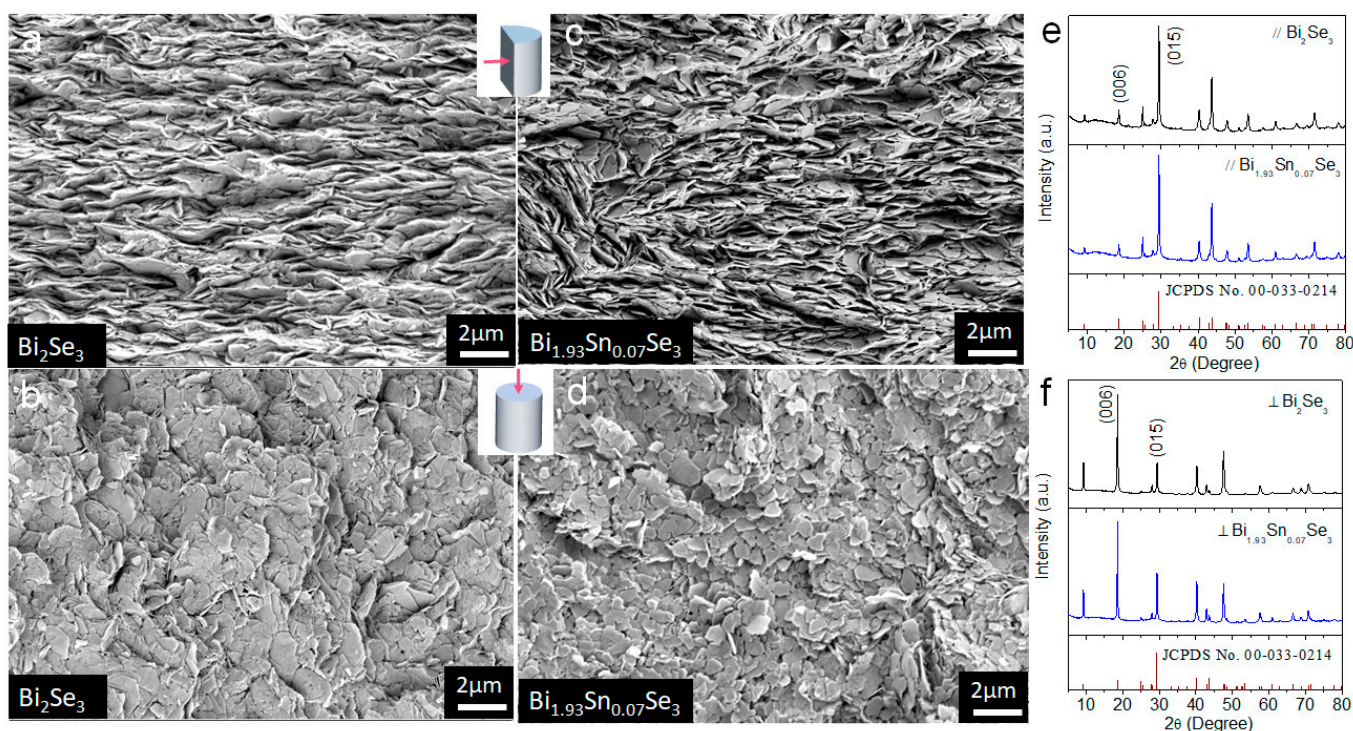


Figure 8. (a,b) Cross-section and top-view SEM micrograph of Bi_2Se_3 . (c,d) Cross-section and top-view SEM micrograph of $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$. (e,f) XRD patterns of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ measured in two perpendicular directions, along (//) and perpendicular (⊥) to the pressure axis.

Figure 9 displays the TE properties of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ measured in the two directions. We observed $\sigma_{\perp} > \sigma_{//}$, as expected from the higher charge carrier mobilities in the ab crystal plane compared with the c direction, and the extended size of the crystal domains in the direction normal to the pressure direction within the layered pellets. On

the other hand, similar Seebeck coefficients were obtained in both directions, pointing out that this parameter has little relationship with grain boundary scattering in this material.

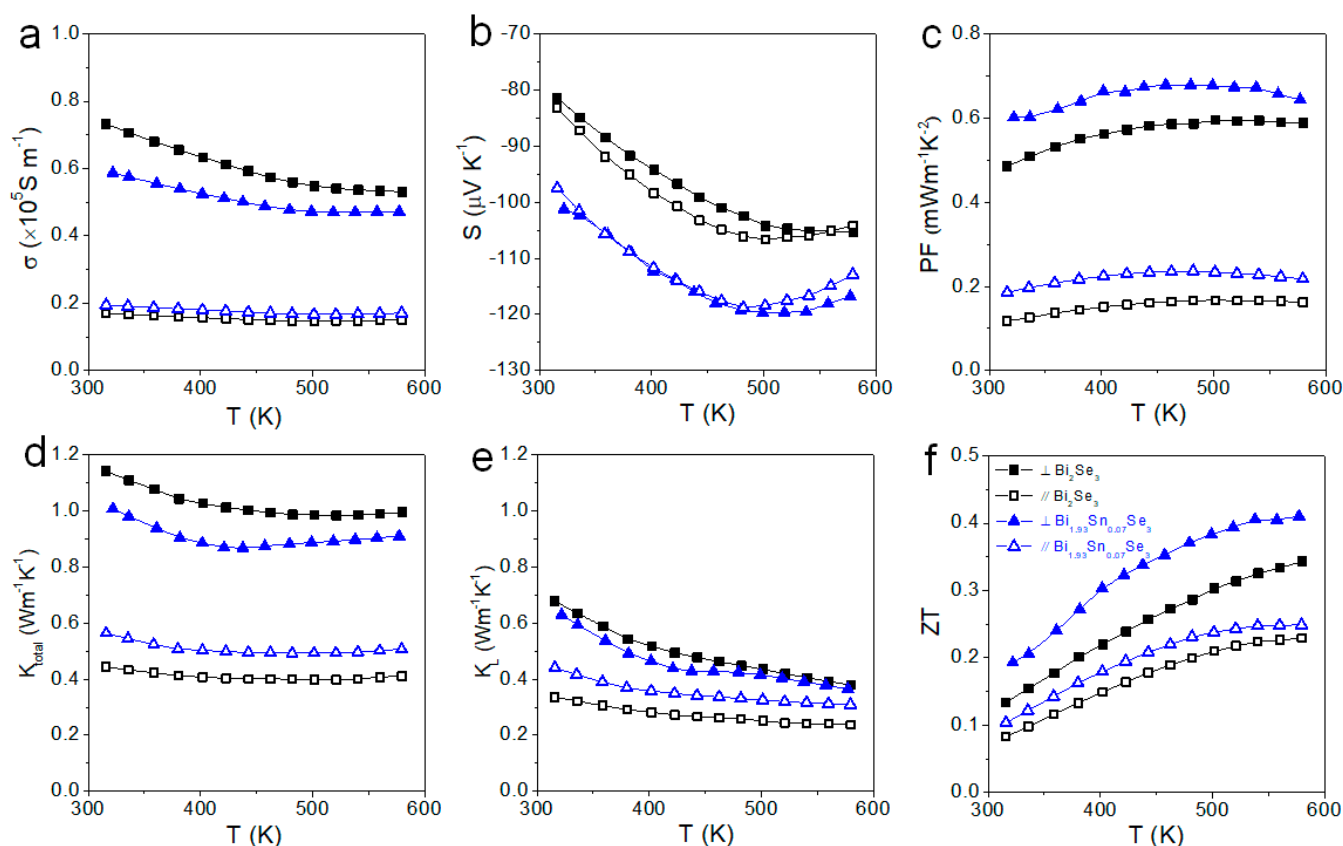


Figure 9. TE properties of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ parallel (//) and vertical ($\perp$) to the pressure axis: (a) electrical conductivity, σ ; (b) Seebeck coefficient, S ; (c) power factor, PF ; (d) total thermal conductivity, κ ; (e) lattice thermal conductivity, κ_L ; and (f) the TE figure of merit, ZT .

When comparing the TE properties of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$, we observed $\sigma_{\perp}$ to slightly increase and $\sigma_{//}$ to slightly decrease with the introduction of Sn, which could be in part related to the thinner and larger material layers observed within the layered Bi_2Se_3 pellets compared with $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$. On the other hand, with the introduction of Sn, S increased in both directions, which resulted in a higher PF in both directions for the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ sample.

Table 1 displays the Hall charge carrier concentration and mobility of Bi_2Se_3 and $\text{Bi}_{1.93}\text{Se}_{0.07}\text{Se}_3$ pellets at room temperature. As expected from the electrical conductivity and Seebeck coefficient measurements, we observed the Sn introduction to result in a decrease in the charge carrier concentration, from $n_H = 1.8 \times 10^{19} \text{ cm}^{-3}$ for Bi_2Se_3 to $n_H = 1.3 \times 10^{19} \text{ cm}^{-3}$ for $\text{Bi}_{1.93}\text{Se}_{0.07}\text{Se}_3$. This result is consistent with the presence of Sn^{2+} replacing Bi^{3+} ions, thus trapping a free electron. We believe this optimization of the charge carrier concentration to be at the origin of the higher PF obtained with the introduction of Sn. We further calculated the effective mass of the Bi_2Se_3 and $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ materials using a single parabolic band (SPB) model. For detailed calculations, the carrier transport property analysis included [32]:

Table 1. Room temperature transport properties and m^* of the Bi_2Se_3 and $\text{Bi}_{1.93}\text{Se}_{0.07}\text{Se}_3$ pellets.

Materials	n_H [10^{19} cm^{-3}]	μ_H [$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]	m^*/m_0
Bi_2Se_3	1.77	178.6	0.27
$\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$	1.34	239.3	0.29

The Seebeck coefficient,

$$S(\eta) = \frac{\kappa_B}{e} \left[\frac{(r+5/2) \cdot F_{r+3/2}(\eta)}{(r+3/2) \cdot F_{r+1/2}(\eta)} - \eta \right] \quad (1)$$

The Hall carrier concentration,

$$n_H = \frac{1}{e \cdot R_H} = \frac{(2m^* \cdot \kappa_B T)^{3/2}}{3\pi^2 \hbar^3} \cdot \frac{(r+3/2)^2 \cdot F_{r+1/2}^2(\eta)}{(2r+3/2) \cdot F_{2r+1/2}(\eta)} \quad (2)$$

The Hall mobility,

$$\mu_H = \left[\frac{e\pi\hbar^4}{\sqrt{2}(\kappa_B T)^{3/2}} \frac{C_l}{E_{def}^2 (m^*)^{5/2}} \right] \frac{(2r+3/2) \cdot F_{2r+1/2}(\eta)}{(r+3/2)^2 \cdot F_{r+1/2}(\eta)} \quad (3)$$

where $F_x(\eta) = \int_0^\infty \frac{\varepsilon^x}{1+e^{(\varepsilon-\eta)}} d\varepsilon$ is the Fermi integral.

In the above equations, S , μ_H , η , κ_B , e , r , R_H , $\hbar$, C_l , E_{def} , and m^* are the Seebeck coefficient, the carrier mobility, the reduced Fermi level, the Boltzmann constant, the electron charge, the carrier scattering factor ($r = -1/2$ for acoustic phonon scattering), the Hall coefficient, the reduced plank constant, the elastic constant for longitudinal vibrations, the deformation potential coefficient, and the density of state effective mass, respectively. Using the experimental S , the reduced Fermi level η can be obtained by Equation (1). Substituting the estimated η and the measured “ n_H ” and “ μ_H ” into Equations (2) and (3), the effective mass “ m^* ” can be calculated. The results show that m^* increased slightly with the Sn doping (Table 1).

Consistent with the layered structure of the pellets and their crystallographic texture, the thermal conductivity of the materials measured in the direction normal to the pressure axis was much higher than in the pressure axis, $\kappa_\perp > \kappa_\parallel$. The introduction of Sn resulted in lower $\kappa_\perp$ but higher $\kappa_\parallel$ values, which is related to the different microstructure of the layers, with thicker and smaller $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ plates compared to those within the Bi_2Se_3 pellet.

Overall, the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ samples measured in the pellet plane displayed the highest PF and ZT values, $0.65 \text{ m W m}^{-1} \text{ K}^{-2}$ and 0.41, respectively. These values are among the highest published for Bi_2Se_3 -based materials, as displayed in Table 2.

Table 2. A comprehensive summary of the thermoelectric performance of the previously reported Bi_2Se_3 .

Materials	ZT at Room Temperature				ZT _{max}			
	σ (10^4 S/m)	S ($\mu\text{V/K}$)	κ (W/mK)	ZT	σ (10^4 S/m)	S ($\mu\text{V/K}$)	κ (W/mK)	ZT
$\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ [33]	0.4	−100	0.6	0.05	1.8	−160	0.38	1 (873 K)
$\text{Bi}_{0.7}\text{Sb}_{0.3}\text{Se}$ [34]	4.5	−138	0.5	0.45	4.2	−160	0.7	0.8 (425 K)
$\text{Bi}_{5.6}\text{Sb}_{2.4}\text{Se}_7$ [35]					4.8	−168.5	0.73	0.55 (300 K)
Bi_2Se_3 [28]	2	−120	0.5	0.17	1.95	−155	0.4	0.48 (427 K)
Bi_2Se_3 [21]	1.78	−90	0.42	0.1	3	−120.7	0.49	0.35 (400 K)
Bi_2Se_3								
$\text{HA}_{0.11}\text{DMSO}_{0.06}$ [36]	14.8	−80	1.52	0.187				
Bi_2Se_3 [12]	2.5	−60	0.55	0.05	2	−100	0.6	0.18 (480 K)
$\text{Cu}_{0.1}\text{Bi}_2\text{Se}_3$ [37]					1.46	−84	0.32	0.1 (290 K)
Bi_2Se_3 [20]	0.212	−115	0.75	0.011	0.6755	−150	0.83	0.096 (523 K)
This work	5.87	−101	1	0.195	4.72	−116	0.91	0.41 (577 K)

4. Conclusions

We report here a large-scale method to synthesize n-type Bi_2Se_3 nanosheets with different dopants. Samples doped with Sn provided the highest TE performances. The composition was optimized at $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$. Upon Sn doping, we observed an increase in the Seebeck coefficient and the power factor compared to pure Bi_2Se_3 . As a result, a

power factor up to $0.65 \text{ m W m}^{-1} \text{ K}^{-2}$ and a ZT of 0.41 were obtained for the $\text{Bi}_{1.93}\text{Sn}_{0.07}\text{Se}_3$ pellet measured in the direction perpendicular to the pressure axis, which represents a 60% increase over pure Bi_2Se_3 .

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Data Availability Statement: Data are contained within the article.

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