Investigation of Tin Chalcogenides Thermoelectric Materials for Energy Conversion

Lijuan Zhang

University of Wollongong
Investigation of Tin Chalcogenides Thermoelectric Materials for Energy Conversion

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Lijuan Zhang, B. Sc., M. Sc.

Institute for Superconducting and Electronic Materials (ISEM)

Faculty of Engineering and Information Sciences

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I, Lijuan Zhang, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials, Faculty of Engineering and Information Sciences, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Lijuan Zhang

January 18, 2018
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Abstract

The emerging global energy shortage and climate change have intensified interests in more effective means of power generation with clean energy sources. Thermoelectric materials can directly convert heat into electricity by imposing a temperature gradient between the hot and cold junction in the absence of any moving parts or liquid media. The heat can come from the combustion of fossil fuels, from sunlight, or as a by-product of various processes (i.e., combustion, chemical reactions, and nuclear decay), indicating thermoelectric materials can play a significant role in both primary power generation and energy conservation.

Lead chalcogenides are the most studied thermoelectric materials with high $ZT$ values between 1.4 and 2.2 through the synergy of the band engineering (band convergence and/or resonant levels) and all-scale hierarchical architectures (point defects, second phase nanoprecipitates and mesoscale grain boundaries). The concerns about Pb (i.e., toxicity), however, limit their large-scale applications. An alternative is tin chalcogenides including SnTe- and SnSe-based semiconductors, which are lead-free environmentally friendly thermoelectric materials.

SnTe presents the same rock-salt structure and the same multiple valence bands (light- and heavy-hole valence bands) as PbTe, indicating all the strategies used for the enhancement of lead chalcogenides thermoelectric performance can be utilized to improve the thermoelectric properties of SnTe-based materials.

Thereby in this doctoral work, we first enhance the lead-free SnTe thermoelectric performance through the adjustment of the carrier concentration and the introduction of nanoprecipitates. The lattice thermal conductivity of SnTe was first optimized through introduction of nanoprecipitates by doping Gd into SnTe. In conjunction with adjustment of the phase composition via further doping of Ag into Gd$_x$Sn$_{1-x}$Te, the carrier concentration
was reduced accompanied with the enhancement of the Seebeck coefficient. A promising $ZT$ of ~1.1 was achieved at 873 K in $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{SnTe}_{0.94}\text{Te}$ sample. Band structuring engineering is another effective strategy to improve electrical transport of SnTe. We applied neutron and synchrotron powder diffraction measurements to pristine SnTe to reveal its temperature-dependent $\Sigma$ band contribution to its Seebeck coefficient, which indicates that additional carriers with high effective mass were generated in heavy-hole valence band above 493 K. Besides the temperature dependence of $\Sigma$ band contribution to the Seebeck coefficient, the band structure of SnTe can be further engineered by the introduction of resonant levels and band convergence via co-doping with Mg&In, Ag&In and Bi&In, which leads to a notable enhancement of the thermoelectric performance over a wide temperature range. In addition, the atomic scale point defects, the nanoscale elongated screw dislocations with random directions, and the microscale grain boundaries caused by the sintering efficiently scatter a wide spectrum of heat-carrying phonons, leading to a remarkable reduction in the lattice thermal conductivity. With the benefit of these factors, a high $ZT$ of ~1 at 873 K was obtained for $\text{Mg}_{0.015}\text{In}_{0.015}\text{Sn}_{0.97}\text{Te}$ sample, being 80% higher than that of pristine SnTe. The average $ZT$ in the range of 323 to 873 K is considerably improved 2.6 times, i.e., from ~0.14 for pristine SnTe to ~0.51 for $\text{Mg}_{0.015}\text{In}_{0.015}\text{Sn}_{0.97}\text{Te}$. Recently, SnSe single crystals have produced a surge in the field of thermoelectrics as a new type of promising lead-free thermoelectric materials because of the intrinsically ultra-low thermal conductivity ($< 0.4 \text{ W m}^{-1} \text{ K}^{-1}$ at 923 K) and high $ZT$ along the $b$- and $c$-crystallographic directions ($> 2.3$ at 923 K). Nevertheless, the difficulties in large-scale synthesis of single crystals limit their practical applications, and extensive efforts have been devoted to the fabrication of high-performance polycrystalline counterparts. In this doctoral work, pristine SnSe polycrystals with novel nanolaminar structure have been fabricated via the conventional solid state reaction at high temperature by simply
controlling the reaction time. Ag- and SnCl$_2$-doped SnSe polycrystals with the same structure were also prepared by this approach. The resultant structural properties were characterized by neutron and synchrotron powder diffraction measurements to reveal a temperature-dependent three-stage inter-orthorhombic structural evolution from a low-temperature phase $Pnma$, through the coexistence of distorted $Pnma/Cmcm$ by a series of layer slips and stretches along the $a$- and $b$-directions over a wide temperature range (200 K) below the transition temperature, to a high-temperature phase $Cmcm$. This phase transition narrows the band gap and enhances the phonon capture at high temperature, which results in an enhancement of the carrier concentration and phonon scattering above 600 K. In addition, the large laminar structure can effectively enhance the carrier mobility of SnSe polycrystals, and the grain and layer boundaries can simultaneously strengthen the phonon scattering. With the benefits of these excellent features and the further enhancement of the carrier concentration by chemical doping, high thermoelectric performances of SnSe polycrystals are reached, i.e., a very high average power factor of $\sim 500 \, \mu \text{W m}^{-1} \, \text{K}^{-2}$ from 300 - 973 K, an extremely low lattice thermal conductivity (0.23 - 0.85 W m$^{-1}$ K$^{-1}$), and a new record $ZT$ of 1.3 at 773 K are achieved in Ag$_{0.015}$Sn$_{0.985}$Se polycrystals.
### Nomenclature

#### List of abbreviation

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full name</th>
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<tbody>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>ZT</td>
<td>Dimensionless figure of merit</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>SPD</td>
<td>Synchrotron powder diffraction</td>
</tr>
<tr>
<td>NPD</td>
<td>Neutron powder diffraction</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electronic Microscopy</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electronic Microscopy</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier transform</td>
</tr>
<tr>
<td>IFFT</td>
<td>Inversed fast Fourier transform</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical Property Measurement System</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>SPS</td>
<td>Spark plasma sinter</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
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<tr>
<td>RLS</td>
<td>Resonant levels</td>
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<tr>
<td>TE</td>
<td>Thermoelectric</td>
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<tr>
<td>MFP</td>
<td>The mean free path</td>
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# List of Symbols

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<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Unit</th>
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<tr>
<td>$\theta$</td>
<td>Diffraction angle</td>
<td>Degree</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Electrical conductivity</td>
<td>S.cm$^{-1}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Carrier mobility</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$n$</td>
<td>Carrier concentration</td>
<td>cm$^2$.V$^{-1}$.s$^{-1}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Seebeck coefficient</td>
<td>$\mu$V.K$^{-1}$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Thermal conductivity</td>
<td>W.m$^{-1}$.K$^{-1}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>X-ray wavelength of the incident beam</td>
<td>Å</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi energy</td>
<td>eV</td>
</tr>
<tr>
<td>$L$</td>
<td>Lorenz parameter</td>
<td>W.Ω.K$^{-2}$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap</td>
<td>eV</td>
</tr>
<tr>
<td>$D$</td>
<td>Thermal diffusivity coefficient</td>
<td>cm$^2$.s$^{-1}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>g.cm$^{-3}$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific heat capacity</td>
<td>Jg$^{-1}$K$^{-1}$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Energy conversion efficiency</td>
<td>%</td>
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# List of Organizations

<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>UOW</td>
<td>University of Wollongong</td>
</tr>
<tr>
<td>AIIM</td>
<td>Australian Institute for Innovative Materials</td>
</tr>
<tr>
<td>ISEM</td>
<td>Institute for Superconducting and Electronic Materials</td>
</tr>
<tr>
<td>EMC</td>
<td>Electron Microscopy Center</td>
</tr>
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**Figure 3.2** illustration of the synchrotron.

**Figure 3.3** illustration of the electrode constitution.

**Figure 4.1.** (a) Powder XRD patterns of Gd$_x$Sn$_{1-x}$Te ($x = 0$-0.08) samples; (b) powder synchrotron XRD pattern of Gd$_{0.06}$Sn$_{0.94}$Te sample; (c) the lattice parameter as a function of x at room temperature.

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Chapter 1. Introduction

1.1. Background

The emerging global energy shortage and climate change have intensified interests in more effective means of power generation from clean energy sources to reduce ozone depletion, greenhouse gas emissions, and fossil fuel usage. Enhancements to the existing clean energy supply are mainly focused on solar, wind and biomass energy.\(^6^8\) Another potential source of power is electricity converted from heat through the thermoelectric technology. Thermoelectric (TE) modules are solid-state devices that directly convert thermal energy into electrical energy by imposing a temperature gradient between the hot and cold junctions in the absence of any moving parts or liquid media, which can be used for power generation and TE refrigeration. The power generation is based on the “Seebeck effect”, which is the appearance of an electrical voltage caused by a temperature gradient across a material. The heat can come from the combustion of fossil fuels, sunlight, or as a by-product of various processes (\textit{i.e.}, combustion, chemical reactions, nuclear decay).\(^6^8-6^9\) Therefore, thermoelectric materials can play a role in both primary power generation and energy conservation (\textit{i.e.} waste-heat harvesting). TE-powered devices have been in production since bismuth telluride-based room-temperature materials were developed in the late 1950s. TE technology was first used to operate the sensors in infrared imaging systems for heat-seeking missiles and night-vision systems through the production of 80°C temperature gradient. Moreover, the development of silicon germanium high-temperature power-generation materials led directly to the production of heat engines for space applications with no moving parts that could operate in the absence of sunlight. Solar cells, another type of heat engine, are effective and can be used as far as the orbit of Mars, but beyond that distance, the solar radiant flux is not adequate to power spacecraft.\(^6^8\)
Another application for TE materials is refrigeration, in which a temperature gradient is generated upon the application of electrical voltage, based on the “Peltier effect”. Portable beverage and picnic coolers were an early commercial application, which combined small size, light weight, and quiet and vibration-free electric operation, opening up a new market for ice-free portable cooling systems. Recently, TE refrigeration has proven popular for replacing traditional vapor-compressor refrigeration in wine-storage cabinets, hotel room mini-refrigerators, and office water coolers. Moreover, by taking advantage of TE materials, climate-controlled seat (CCS) systems have been developed to provide rapid seat cooling in the summer and equally fast heating in the winter. The CCS system are being installed in more than 500,000 vehicles a year, which increases passenger comfort and is beginning to be used to provide a degree of comfort when the vehicle engine is off due to coasting, braking, or being stopped. In addition, TE cooling of small electronic enclosures has been used to cool various low-power computer boards which control industrial equipment, due to the advantage of their efficient and cost-effective characteristics.

The principal issue which limits broad application of TE devices is their low efficiency. Thermoelectric efficiency ($\eta$) relies directly on the temperature gradient ($\Delta T$) and a material’s dimensionless figure of merit ($ZT$) as shown in Equation (1-1).

$$\eta = \frac{\Delta T}{T_{\text{hot}}} \frac{\sqrt{1 + ZT_{\text{avg}}^{-1}}}{\sqrt{1 + ZT_{\text{avg}}^{1} + T_{\text{cold}}/T_{\text{hot}}}}$$

where $T_{\text{hot}}$, $T_{\text{cold}}$, and $ZT_{\text{avg}}$ are the temperature of the hot end, temperature of the cold end, and average dimensionless figure of merit, respectively. Thermoelectric devices currently available have a $ZT$ of ~1 and operate at an efficiency of only around 5-6%. By increasing device $ZT$ ($ZT_{\text{dev}}$) by factor of 1.3-1.7, and depending on $\Delta T$, the predicted efficiency increases to 11-15%, a highly attractive prospect.
1.2. Thermoelectric effect

1.2.1. Seebeck effect

The Seebeck effect is the conversion of temperature differences directly into electricity at the junction of different types of wire. As shown in Figure 1.1, if the junctions at the top are heated and those at the bottom are cooled, electron/hole pairs will be created at the hot end that absorb heat and transport it to the cold end. The pairs then recombine and reject heat at the cold end. A voltage potential, the Seebeck voltage, which drives the hole/electron flow, is created by the temperature difference between the hot and cold ends of the thermoelectric element. The net voltage appears across the bottom of the TE element legs, and drives an electric current in a closed circuit. In 1821, Baltic German physicist Thomas Johann Seebeck noticed this effect, and named it the Seebeck effect. The Seebeck coefficient is the Seebeck voltage per unit temperature, which can be defined by Equation (1-2):

\[ \alpha = \lim_{\Delta T \to 0} \frac{V_{ab}}{\Delta T} \]  

where \( \alpha \) is the Seebeck coefficient, \( V_{ab} \) is the Seebeck voltage, and \( \Delta T \) is the temperature gradient between the hot and cold ends.

Figure 1.1. Schematic diagram of Seebeck effect for power generation model.
1.2.2. Peltier effect

The Peltier effect is the presence of heating or cooling when electric current is maintained in a circuit of consisting of two dissimilar conductors. As shown in Figure 1.2, if voltage is applied in the right direction across a p-n junction, electron/hole pairs are created in the vicinity of the junction. Electrons will flow away from the junction in the n-type material, and holes will flow away in the p-type material. The energy for the electron/hole pairs transport comes from the junction region, which will be then cold. On the opposite end, electrons and holes stream toward the junction where pairs recombine. This process releases energy and heats the junction. In 1834, French physicist Jean Charles Athanase Peltier noticed this effect, and named it the Peltier effect. The Peltier heat generated at the junction per unit time can be defined by Equation (1-3):

\[
\frac{dQ}{dt} = I\pi_{ab}
\]  

(1-3)

where \( I \) is the electric current, and \( \pi_{ab} \) is the Peltier coefficient.

![Figure 1.2. Schematic diagram of Peltier effect for refrigeration model.](image)
1.2.3. Thomson effect

The Thomson effect is the presence of heating or cooling of a current-carrying conductor with a temperature gradient, which is based on the Seebeck effect and the Peltier effect. If an electric current passes through a single conductor that has a spatial gradient in temperature along its length, it will dissipate heat in excess of the Joule heat which is associated with the electrical resistance. In 1854, Scots-Irish physicist William Thomson noticed this effect, and named it the Thomson effect. The additional heat (absorption or release) is Thomson heat, which can be defined by Equation (1-4):

\[ Q = \beta I \Delta T \]  

(1-4)

where \( I \) is the electric current, \( \Delta T \) is the temperature gradient along the length, and \( \beta \) is the Thomson coefficient.

1.2.4. Relationship of thermoelectric parameters

As mentioned above, the TE performance is characterized by the dimensionless figure of merit, which can be defined by Equation (1-5):

\[ ZT = \frac{\alpha^2 \sigma T}{\kappa_{\text{lat}} + \kappa_{\text{ele}}} \]  

(1-5)

where \( \alpha \), \( \sigma \), \( \kappa_{\text{lat}} \), \( \kappa_{\text{ele}} \), and \( T \) are the Seebeck coefficient, the electrical conductivity, the lattice thermal conductivity, the electronic thermal conductivity, and the absolute temperature, respectively. The quantity \( \alpha^2 \sigma \) is called the power factor (PF), and a large PF means that a large voltage and a high current are generated. The challenge of receiving high \( ZT \) thermoelectric materials arises from the strong correlation among \( \alpha \), \( \sigma \), and \( \kappa \), depending upon the carrier concentration \( n \), as shown in Figure 1.3.
1.3. Objectives of the Research

The overall objective of this doctoral work is to find lead-free high thermoelectric materials for energy conversion application. Two lead-free promising candidates are selected, including SnTe-based and SnSe-based materials. For the SnTe-based materials, the investigation was mainly focused on the enhancement of thermoelectric performance through synergy of effective methods including optimization of the carrier concentration, nanostructuring, and band engineering (resonant levels, band convergence). For the SnSe-based materials, the investigation was first focused on the temperature-dependent inter-orthorhombic phase transition, and the relationship between this phase transition and the thermoelectric performance. In addition, we optimized its thermoelectric performance through modulation of microstructure and chemical doping.
1.4. Thesis Structure

The scope of the research that is carried out in this doctoral thesis is briefly outlined below as following:

Chapter 1 presents the general background of thermoelectric materials and thermoelectric technology, some major thermoelectric effects, and the challenge to receive high thermoelectric performance. The objectives and outlines of the doctoral study are also presented.

Chapter 2 presents a comprehensive literature review on the strategies to improve the electrical conductivity (via the carrier concentration and the carrier mobility), improve the Seebeck coefficient (via band degeneracy, band flattening, and resonant levels), and reduce the thermal conductivity (via point defects, nanostructuring, dislocations, and mesoscale structuring). The literature review on lead-free SnTe-based and SnSe-based bulk thermoelectric materials are also presented.

Chapter 3 presents the materials fabrication, general materials characterizations including X-ray diffraction (XRD), synchrotron powder diffraction (SPD), neutron powder diffraction (NPD), filed emission scanning electron microscopy (FESEM), scanning transmission electron microscopy (STEM), differential scanning calorimetry (DSC), physical property measuring system (PPMS), and thermoelectric performance characterizations including Ozawa Rz2001i system, Linseis LFA1000, and LFA457.

Chapter 4 presents the enhancement of lead-free SnTe-based thermoelectric performance through the adjustment of the carrier concentration and the introduction of nanoprecipitates. The lattice thermal conductivity of SnTe was first optimized through introduction of nanoprecipitates by doping Gd into SnTe. The carrier concentration and band gap were then optimized through further doping Ag into Gd-contained samples.
Chapter 5 presents the enhancement of lead-free SnTe-based thermoelectric performance through band structure engineering. The temperature-dependent heavy-hole valence band contribution to Seebeck coefficient was first investigated. The synergy of resonant levels and band convergence were then investigated through chemical modification via In&Mg, In&Ag and In&Bi co-doping.

Chapter 6 presents the investigation of lead-free SnSe-based thermoelectric materials. The temperature-dependent inter-orthorhombic phase transition, and the relationship between this phase transition and thermoelectric performance was first investigated. The enhancement of thermoelectric performance of SnSe was then investigated through modulation of microstructure and chemical doping.

Chapter 7 summarizes the conclusions we obtained from this doctoral work and providing some suggestions for further research work related to both the SnTe-based and SnSe-based thermoelectric materials.
Chapter 2. Literature Review

2.1. Strategies to improve the electrical conductivity

The electrical conductivity is a measure of the ability of a material to conduct electrical current, and is proportional to the carrier concentration \( n \) and the carrier mobility \( \mu \), \( \sigma = ne\mu \). Typical values of the electrical conductivity for good TE materials are on the order of about \( 10^5 \) S m\(^{-1}\), which can be obtained either by a high density of charge carrier or by a high carrier mobility.

2.1.1. Carrier concentration

The optimum carrier concentration for most good TE materials is in the range of \( 10^{19} \) to \( 10^{21} \) cm\(^{-3}\), which is favourable for obtaining the optimum power factors by balancing \( \alpha \) and \( \sigma \) (Figure 1.3). Generally, there are two different means of carrier-concentration control, \( i.e. \), extrinsic doping and tuning intrinsic defects.

Extrinsic doping, including alloying with elements from the neighbouring columns of the periodic table and guest atoms filling in a caged structure,\(^{73-74}\) is the mainstream methodology to alter the carrier concentration, as shown in Figure 2.1a-c. It is noteworthy, however, that, although the idea seems simple, choosing a proper dopant is not an easy thing. In some specific cases, the optimum carrier concentration cannot be achieved due to the solubility limit and the doping efficiency of the dopants, and this is part of the reason why some theoretically predicted higher TE performances have not been realized in experiments.\(^{75-76}\) Moreover, in complex semiconductors containing two or more elements, the solubility of the dopant is complicated by the chemical potential of the other elemental species. In fact, in binary semiconductors, instead of a single solubility limit, there should be at least two important solubility limits, depending on whether the semiconductors are cation or anion rich.
The excellent \( n \)-type thermoelectrics based on CoSb\(_3\) skutterudite provide a good example, where study of the dopant (filler) atom solubility has been confusing, in part because there are two solubility limits, depending on whether the materials is Co-rich or Sb-rich.\(^{77}\) It is important to mention that in most homogeneously doped semiconductors modulated by extrinsic dopants, the carrier concentration is independent on temperature, which limits the optimum \( ZT \) to a rather narrow temperature window.

Intrinsic Defects, including vacancies, interstitials, and antisites, provide another strategy to optimize the carrier concentration, as shown in Figure 2.1d-f. Typically, the intrinsic conduction behaviour in \( n \)-type \( \text{Bi}_2\text{Se}_3 \), \( p \)-type \( \text{Sb}_2\text{Te}_3 \), and \( p \)-type \( \text{Bi}_2\text{Te}_3 \), which are observed under cation-rich conditions, should actually ascribed to the presence of \( \text{V}_{\text{Se}}^+ \), \( \text{Sb}_{\text{T}e}^- \), and \( \text{Bi}_{\text{T}e}^- \), respectively. \( \text{V}_{\text{Se}}^+ \) is the positively charged anion vacancy, while \( \text{Sb}_{\text{T}e}^- \) and \( \text{Bi}_{\text{T}e}^- \) are negatively charged antisite defects formed when cation atoms occupy the vacant anion sites.\(^{78-81}\) The types and concentrations of these intrinsic point defects are very sensitive to the composition and can be manipulated by extrinsic doping. Generally, a smaller difference in the electronegativity, \( \chi \), and the covalent radius, \( r \), between the cation and the anion will favour the formation of cation antisite defects, while a bigger difference will give rise to the formation of anion vacancies.\(^{78,81}\)

Compared to the conventional methods, manipulation of the carrier concentration is also realized by taking advantage of the temperature-dependent solubility\(^2,82-83\) and magnetic transition,\(^3\) as shown in Figure 2.1g-h Temperature-dependent (\( T \)-dependent) doping is a promising control manner that can realize a gradient of \( n \), controlled only by temperature within a single material, and it is reversible in the heating-cooling process which is favourable for actual application. The key point of the \( T \)-dependent doping is to find appropriate dopants that possess an increasing solubility limit with increasing temperature. Typically, Cu, Ag, and excess Pb presents negligible solubility in PbTe at room temperature,
but they are highly soluble at elevated temperatures. Taking advantage of a temperature-dependent magnetic transition is another control strategy to manipulate carrier concentration by incorporation in a magnetic nanocomposite, which plays an ‘electron repository’ role in maintaining a high figure of merit $ZT$. Typically, in the magnetic nanocomposite of thermoelectric materials consisting of $\text{BaFe}_12\text{O}_{19}$ nanoparticles and a $\text{Ba}_0.3\text{In}_0.3\text{Co}_4\text{Sb}_{12}$ matrix, the electrical transport behaviour is controlled by the magnetic transition of $\text{BaFe}_12\text{O}_{19}$ nanoparticles from ferromagnetism to paramagnetism. $\text{BaFe}_12\text{O}_{19}$ nanoparticles trap electrons below the Curie temperature ($T_C$) and release the trapped electrons above the $T_C$, realizing a gradient of $n$ that is controlled only by the magnetic transition.\(^3\)

Normally, optimizing the carrier concentration is routine in performance optimization and always accompanied by other strategies, but it is an especially effective method for TE systems with intrinsically low thermal conductivity.

![Figure 2.1](image)

**Figure 2.1.** Schematic diagram of the carrier concentration engineering (extrinsic substitution, intrinsic vacancies, interstitials, antisites, $T$-dependent doping\(^{1,2}\) and magnetic transition\(^3\)).
2.1.2. Carrier mobility

A high level of doping provides a high carrier concentration to conduct electricity, while high carrier mobility is also required to transfer electrons in an efficient manner. In semiconductors, the carrier mobility is determined by the electronic structure of the material and the various scattering mechanisms, including acoustic phonon scattering, alloying scattering, ionized impurity scattering, polar optical phonon scattering, etc. With a simple parabolic band assumption, the carrier mobility, $\mu$, in the case of elastic scattering can be expressed by Equation (2-1):  

$$
\mu = \frac{e\tau}{m_i^*}
$$

where $\tau$ is the scattering time, and $m_i^*$ is the transport effective mass. The scattering time is related to the temperature ($T$), density-of-states (DOS) effective mass ($m_d^*$), and the carrier energy ($E$), which is dependent on the scattering mechanisms, as shown in Equation (2-2):  

$$
\tau \propto T^r T^s m_d^{st}
$$

Specifically, for acoustic phonon scattering, $r = -1/2$, $s = -1$, and $t = -3/2$, while for ionized impurity scattering, $r = 3/2$, $s = 0$, and $t = 1/2$, respectively.

The transport effective mass is related to the electronic structure. For a spherical Fermi surface (isotropic band), the transport effective mass ($m_i^*$) is the same as the average DOS effective mass for each pocket (single-band DOS effective mass, $m_b^*$), and also the total DOS effective mass ($m_d^*$), which can be expressed by Equation (2-3):  

$$
m_i^* = m_b^* = m_d^*
$$

For an elliptical Fermi surface (anisotropic band), $m_i^*$ and $m_b^*$ are related to the mass tensor components $m_i^*$ along the diagonal ($i = 1, 2, 3$), which can be expressed by Equations (2-4), and (2-5):  

$$
m_i^* = 3 \left( \frac{1}{m_1^*} + \frac{1}{m_2^*} + \frac{1}{m_3^*} \right)^{-1}
$$
when the carrier pockets are isotropic (even for cubic materials), with equal values of the three mass components of $m_1^*$, $m_2^*$, and $m_3^*$, $m_i^*$ can be considered equal to $m_b^*$, although it is often only a reasonable approximation. Moreover, if the solid has a Fermi surface that consists of multiple degenerate valleys ($N_v$), $m_b^*$ and $m_d^*$ can be expressed by Equation (2-6):

\[ m_d^* = N_v^{\frac{2}{3}} m_b^* \] (2-6)

where $N_v$ is the number of degenerate carrier pockets. Therefore, the carrier mobility will decrease with increasing DOS effective mass ($m_b^*$, $m_d^*$) so long as the carriers are scattered predominately by phonons.

\[ \alpha = \frac{8\pi \kappa B e^2}{3 \hbar^2} m_d^* T \left( \frac{\pi}{3n} \right)^{\frac{2}{3}} \] (2-7)

where $k_B$, $e$, $\hbar$, and $m_d^*$ are the Boltzmann constant, carrier charge, Planck constant, and total DOS effective mass respectively. For a given carrier concentration, the Seebeck coefficient can be estimated from the total DOS effective mass, $m_d^*$. According to Equation (2-6), a large $m_d^*$ can be achieved by either high band degeneracy or a flat, narrow single-band effective mass, $m_b^*$. 

\[ m_b^* = 3\left(m_1^* m_2^* m_3^* \right)^{\frac{1}{3}} \] (2-5)
2.2.1. Band degeneracy

Band degeneracy can be evaluated by the number of band extrema \((N_v)\), which is closely related to the crystal structure symmetry, and can be large when the crystal structure is highly symmetrical, as shown in Figure 2.2a-b. Normally, band degeneracy can be improved when multiple bands have the same or comparable energy within a few \(k_B T\), and it can be divided into two situations: (i) the multiple bands have band extrema with little or no difference in energy (orbital degeneracy), or (ii) the multiple carrier pockets in the Brillouin zone are degenerate due to the symmetry of the crystal (valley degeneracy). The first strategy can be realized through converging different bands by changing temperature or alloying to obtain a higher orbital degeneracy. Typically, PbTe compounds have two valence bands. One is defined as the light-hole valence band at the L point of the highly symmetric Brillouin zone, and the other one is called the heavy-hole valence band and lies at the \(\Sigma\) point, which is energetically below the L point with a large energy separation of around \(\sim 0.3\) eV. As the temperature increases, the L band shifts down, while the energy position of the \(\Sigma\) band roughly stays constant, which leads to an effective band convergence \((N_v = 16)\) at some temperature point \((>800\) K), as shown in Figure 2.3a. Moreover, the energy separation between the L band and the \(\Sigma\) band can also be manipulated through chemical alloying (Cd, Mg, and Sr), which thus leads to convergence at low temperature. Other typical examples are SnTe and Mg\(_2\)(Si,Sn) solid solutions. Converging multiple valence (or conduction) bands to achieve high \(N_v\) has been proposed as an effective strategy to obtain high \(m^*\) and high performance in bulk thermoelectrics without explicitly reducing \(\mu\).

The second strategy can be realized through changing the symmetry of crystals to obtain a higher valley degeneracy. Typically, Bi\(_{2-x}\)Sb\(_x\)Se\(_3\) solid solution is a rhombohedral phase, but by doping Sb content to \(x = 1\), it is transformed to the orthorhombic phase, which results in a shift of the conduction-band minimum from the center of the Brillouin zone to the \(\Gamma-\Sigma\)
Figure 2.2. Schematic representation of the density of states of (a) a single valence band, (b) a converged band, (c) flattened band, and (d) the introduction of resonant levels.\(^1\)

Figure 2.3. a) Schematic diagram of temperature-induced band convergence in PbTe among the conduction band (CB), light-hole valence band (VBL), and heavy-hole valence band (VB\(\Sigma\)) \(^4\)-\(^6\); (b) structural transition-induced band convergence in Bi\(_{1-x}\)Sb\(_x\)Se\(_3\). \(^7\)

Other typical examples are tetragonal chalcopyrite, \(^{94\text{-}95}\) and CaAl\(_2\)Si\(_2\)-type Zintl compounds.\(^{96}\)

### 2.2.2. Band flattening

Theoretically, the effective mass \(m_b^*\) in a band is related to the curvature of the band and can be modified by distorting the band, which leads to an increase in the density of states in the vicinity of the Fermi level. There are two commonly adopted strategies for enhancing \(m_b^*\), i.e., band flattening \(^{97\text{-}100}\) and resonant levels, \(^{19, 39, 101\text{-}102}\) as shown in Figure 2.2c-d. Band flattening effects can be realized through the introduction of dopants containing highly
localized orbitals, which can decrease the orbital overlap. Band-structure calculations have revealed that in La-doped PbTe, the conduction band at the L point can be affected by the hybridization between La f-states (or d states if f-states are completely localized) and Pb p-states, which leads to flattening of the conduction band, resulting in an increased $m^*_b$ of the L band and a higher Seebeck coefficient.\textsuperscript{100, 103} It is noteworthy, however, although the idea seems to lead to a large Seebeck coefficient, that the increase in the increase of $m^*_b$ will result in decreased carrier mobility in most cases, according to Equation (2-1). Moreover, to make best use of the benefits of a larger $m^*_b$ through band flattening for power factor enhancement, it generally requires a much higher optimal $n$ to reach the same Fermi level as for a band with a smaller $m^*_b$. For instance, at identical carrier concentrations ($n = 1.8 \times 10^{19} \text{cm}^{-3}$), La-doped PbTe presents higher $m^*_b$, but it has a lower power factor value than those of I-doped samples due to the reduction in carrier mobility. At a higher doping level of $n$, however, La-doped PbTe samples can have comparable or even better power factors than I-doped PbTe samples, which has been demonstrated by both experimental results and theoretical predictions.\textsuperscript{97}

Specifically, in addition to the improvement of $m^*_b$, band flattening can also increase the band gap, $E_g$, according to the Kane-band model, as expressed by following Equation (2-8):\textsuperscript{104}

$$\frac{\hbar^2k^2}{2m_b^*} = E \left(1 + \frac{E}{E_g}\right)$$

(2-8)

where $\hbar$, $k$, and $E$ are the reduced Planck’s constant, the crystal momentum and the energy of electron states. The enlargement of the band gap due to band flattening is favorable to suppressing the detrimental effect of bipolar diffusion at elevated temperatures.

2.2.3. Resonant levels

Introducing resonant levels (RLs) is another strategy that is used to distort the DOS in bulk solids. Resonant levels appear when the energy level created by the impurity can lie in the
conduction or valence band of the matrix semiconductor, as shown in Figure 2.2d.\textsuperscript{105} The introduction of RLs can increase the Seebeck coefficient of metals and semiconductors through two mechanisms: \textit{i.e.}, (1) electrons in extended states (plane-wave-like wavefunction created by In impurities) can carry electricity and heat, and contribute to the Seebeck coefficient in a nearly temperature-independent way; and (2) resonant scattering presents a strong electron energy filtering effect and increases the Seebeck coefficient at low temperature where the electron-phonon interactions are weaker.\textsuperscript{106} In order to achieve the greatest benefit from the RLs, it is necessary to control two parameters, \textit{i.e.}, the position and the width of the RLs. The former not only refers to the position of the RLs relative to the band edge, but also the position of RLs relative to the Fermi level. Typically, in the case of \textit{p}-type semiconductors, if the RLs are located below the Fermi level (\textit{i.e.}, at higher energy states), they are favourable to enhance the Seebeck coefficient.\textsuperscript{70} Therefore, it is important to choose suitable dopants to adjust the positions of RLs and the Fermi level independently.\textsuperscript{107} As for the width of RLs, a value of 10-100 meV is needed to allow the Fermi energy, $E_F$, to reside inside the RLs, which indicates that the 3\textit{d}-states or \textit{f}-states are less practical than the \textit{s}- or \textit{p}-states for RLs from the aspect of their narrowness and difficulty in properly positioning $E_F$.\textsuperscript{108-109} These resonant levels are observed in Tl doped PbTe,\textsuperscript{106} Sn doped Bi$_2$Te$_3$,\textsuperscript{110} and In doped SnTe.\textsuperscript{39} It is important to note that resonant levels usually work at relatively low temperatures and are not useful in enhancing $ZT$ at high temperatures.\textsuperscript{41,106,111}

\subsection*{2.2.4. Compromise between $n$ and $\alpha$}

Under the parabolic-band approximation, the DOS has a square-root dependency on energy for a bulk material. When the Fermi level is close to the band edge, the DOS is asymmetric with respect to the Fermi level, indicating that more states take part in the carrier transport above the Fermi energy than below it (\textit{n}-type materials), and the difference between the average energy of the electrons and the Fermi level is large, resulting in a large $\alpha$. On
increasing increasing $n$, the Fermi level moves deeper into the band, the differential conductivity becomes more symmetric with respect to the Fermi level, and $\alpha$ decreases.\textsuperscript{112} The relationship between the Seebeck coefficient and the carrier concentration is well reflected in a Pisarenko curve. According to the classical statistics approximation, the optimal carrier concentration ($n_{\text{opt}}$) for a single-carrier-type system can be expressed by the following relationship \textbf{Equation (2-9)}.\textsuperscript{113}

\begin{equation}
    n_{\text{opt}} \sim (m_d^* T)^{3/2}
\end{equation}

The relationship indicates that a large DOS effective mass $m_d^*$ is favourable for increasing the Seebeck coefficient and optimal carrier concentration simultaneously. A large DOS effective mass $m_d^*$ can be realized by high band degeneracy, band flattening, and the introduction of resonant levels.

Because the value of $n_{\text{opt}}$ is proposed to be proportional to $(m_d^* T)^{3/2}$, the stabilization of $n_{\text{opt}}$ is thus a fundamental challenge for performance optimization. In most homogeneously doped semiconductors modulated by extrinsic dopants, the carrier concentration is independent of temperature, which limits the optimum of $ZT$ to a rather narrow temperature window. To realize the maximally available $ZT$ over the entire temperature range, strategies such as temperature-dependent doping,\textsuperscript{2, 82-83} and band engineering have been proposed. The aim of the temperature-dependent doping is to reduce the doping concentration at low temperature and to form a carrier concentration gradient, while band engineering aims to gain a larger $n_{\text{opt}}$ at low temperature by tuning the temperature dependence of the DOS effective mass. Typically, alloying PbTe with MgTe increases the energy gap between the L band and the conduction band faster than that of $\Sigma$ band, which leads to a decrease in the convergence temperature of these two bands.\textsuperscript{90} Thus, higher values of $N_v$ and $n_{\text{opt}}$ are obtained at low temperatures.
2.3. Strategies to reduce the thermal conductivity

The total thermal conductivity is mainly composed of the electronic thermal conductivity ($\kappa_{\text{ele}}$) and the lattice thermal conductivity ($\kappa_{\text{lat}}$). The electron contribution is assessed from the measured $\sigma$ using the Wiedemann-Franz law, $\kappa_{\text{ele}} = L\sigma T$. $L$ is the Lorenz parameter, which does not vary much from material to material, remaining in the range of $1.6$ to $2.5 \times 10^{-8}$ WΩK$^{-2}$. For most metals and degenerate semiconductors, the value of $L$ is taken to be $2.45 \times 10^{-8}$ WΩK$^{-2}$ (degenerate limit), while for heavily doped semiconductors, it varies with temperature.$^{114-115}$ According to the Wiedemann-Franz law, the electronic thermal conductivity linearly increases with the electrical conductivity, and thus, for promising thermoelectric materials, an appropriate carrier concentration is necessary. The lattice thermal conductivity can be assessed by the classical kinetic theory, which is defined by Equation (2-10):$^{116-117}$

$$\kappa_{\text{lat}} = \frac{1}{3} C_v l v_s$$  \hspace{1cm} (2-10)

where $C_v$, $l$, and $v_s$ are the specific heat at constant volume, the mean free phonon path, and the average velocity of sound, respectively. At very low temperatures (i.e., under 40 K), phonon scattering is insignificant due to the low number of excited phonons and their very long wavelength, and thus the lattice thermal conductivity is dominated by the Debye $T^3$ law for $C_v$. At high temperatures (i.e., above the Debye temperature), however, $C_v$ approaches the classical value of $3R$ (where $R$ is the ideal gas constant), and the value is related to the mean free phonon path (MFP) which is determined by phonon-phonon scattering.

It is well known that in solids, the interaction between atoms creates displacements from their equilibrium positions, resulting a set of vibrational waves with various wavelengths, which are called phonons.$^1$ These phonons, which carry most of the heat and have a spectrum of wavelengths and MFPs, propagate through the lattice, contributing to the lattice thermal conductivity.
conductivity. Crystal defects, such as point defects, nanoprecipitates, grain boundaries, and dislocations, etc., are effective barriers to block the propagation of phonons.

### 2.3.1. Point defects

The introduction of point defects is a strategy to create lattice imperfections on a length scale of one interatomic distance, or at most, a unit cell, which can be realized by the introduction of substitutions, vacancies, and interstitials (Figure 2.1). According to the thermal conductivity model developed by Klemens and Callaway, point defects scatter short MFP phonons, which is ascribed to either mass contrast or local bond strain induced by the defects, which can be governed by the scattering parameter \( \Gamma \), as defined by the following Equation (2-11).

\[
\Gamma = x(1-x) \left[ \left( \frac{\Delta M}{M} \right)^2 + \varepsilon \left( \frac{a_{\text{disorder}} - a_{\text{pure}}}{a_{\text{pure}}} \right)^2 \right] \tag{2-11}
\]

where \( x \) is the doping fraction, \( \Delta M/M \) is the rate of change of atomic mass, \( a_{\text{disorder}} \) and \( a_{\text{pure}} \) represent the lattice constants of the disordered and pure alloys, respectively, and \( \varepsilon \) is an elastic property related adjustment parameter. From Equation (2-11), a reduction in the reduction of lattice thermal conductivity can be realized through three routes, i.e., (i) introducing high doping fraction \( x \), (ii) introducing a large mass difference between the dopant and the matrix element \( \Delta M/M \), and (iii) creating high lattice disorder between the disordered phase and the matrix phase \( a_{\text{disorder}}/a_{\text{pure}} \). Because these defects have a length scale comparable to the wavelength of phonons, which involves displacements of two adjacent atoms with respect to each other, the Debye wavelength, they greatly enhance the scattering of phonons with short wavelengths. It is important to mention that the introduced point defects may also scatter the carriers, which makes the ZT enhancement subject to the trade-off between \( \kappa_{\text{lat}} \) reduction and \( \mu \) deterioration.
2.3.2. Nanostructuring

Nanostructuring is a strategy to achieve either a single phase which is assembled from nanoscale particles or a solid solution which has embedded nanoscale precipitates in the matrix. The nanoscale particles can be achieved by mechanical methods (i.e., ball milling and melt-spinning) and bottom-up processes, while the second phase precipitation can be achieved through quickly quenching a highly doped solid-state solution. The second phase candidates must have low or no solubility in the solid state, but complete solubility in the liquid state. When the corresponding melt is quenched by rapid cooling, the second phase will precipitate, since it reaches or exceeds the solid state solution limit, as shown in Figure 2.4a. The mixture of A and B gives a homogeneous melt above the solid-liquid temperature line (step 1), which then is cooled down in step 2, and after that, the sample is quenched and annealed within the single phase region (since at this stage, B is dissolved in the A matrix). In step 3, phase separation and precipitation of the second phase is achieved by cooling down after reaching the solid state solubility limit. This approach has been applied in the lead chalcogenide family, with typical successful samples being PbTe-MTe (M= Ca, Sr, Ba and Cd), PbSe-MSe (M= Ca, Sr, Ba, Zn and Cd), and PbS-MS (M= Bi, Sb, Ca, Sr, Zn and Cd). All these systems show that these B nanoscale precipitates greatly reduce the thermal conductivity of the matrix..

Nanostructures can also be achieved in A-B binary solid solutions, as shown in Figure 2.4b. The A-B system exhibits a miscibility gap where thermodynamic phase separation will occur by metastable nucleation and growth and so-called spinodal decomposition processes. Nucleation and growth and spinodal decomposition phase transformations occur because of the distinct curvature in the Gibbs free energy curve for a given isotherm over the composition range as the material transforms to reduce the overall free energy of the system.
The typical examples for this case are PbTe-PbS\textsuperscript{128-129} and PbSe-PbS systems,\textsuperscript{130} where the number density of precipitates increases with increasing PbS fraction.

It is significant to mention that all nanoprecipitation embedded materials contain large extended point defects in the matrix, which arise from the partial dissolution of the second phases in the matrix and from the dissolution of the dopants in it. The increased nanoscale grain boundaries or the thus-formed nanoscale precipitates could provide effective barriers to effectively scatter the phonons ranging from low to medium frequency, which means the scattering of more short and medium MFP phonons than solid solution alloying alone.\textsuperscript{12, 15, 40-41, 47, 124}

### 2.3.3. Dislocations

The introduction of dislocations is another strategy to suppress propagation of heat-carrying phonons with medium MFP. Dislocations can be formed by deliberate plastic deformation of the samples during the fabrication process, \textit{i.e.}, liquid-phase compaction sintering.\textsuperscript{131-132} Typically, Kim, et al.\textsuperscript{9} reported that dense dislocation arrays in Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} were formed at

**Figure 2.4.** (a) Schematic ternary diagram, which indicates a strongly temperature-dependent solubility of the second phase of B in the A matrix; (b) schematic ternary diagram for a complete solid solution that exists between the two end members A and B.\textsuperscript{8}
low-energy grain boundaries by liquid-phase compaction, which effectively scatter medium frequency phonons with a minimal effect on electron scattering, leading to a substantially lower lattice thermal conductivity, as shown in Figure 2.5.  

**Figure 2.5.** Schematic illustration showing the generation of dislocation arrays during the liquid-phase compaction process. The Te liquid (red) between the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grains flows out during the compaction process and facilitates the formation of dislocation arrays embedded in low-energy grain boundaries.

### 2.3.4. Mesoscale Structuring

As mentioned above, heat-carrying phonons with short and medium wavelengths can be scattered by point defects and second phase nanoprecipitates, although long wavelength phonons are largely unaffected and still able to transport heat. In order to scatter long wavelength phonons, samples are mainly prepared by breaking down the crystals into mesoscopic particles in the range of 100 nm to 5 µm. This is followed by sintering of the fine-grained powders, so that boundary scattering can occur in the intergrain regions. The propagation of phonons with long MFP can be limited by the finite size of a given grain. Thus, mesoscale grain boundaries mostly scatter the long wavelength phonons. Typically, Rowe et al. determined that an increase in thermal resistance of about 20% with respect to the single crystal occurs due to grain boundary scattering for a Si-Ge alloy with grain size below 5 µm, indicating the importance of the mesoscale effect towards impeding the phonon transport of bulk materials, as shown in Figure 2.6.
Figure 2.6. Schematic diagrams of microstructures of (a) single crystals or cast ingots without grain boundaries or with rather coarse grains (> 10 µm in size) and (b) polycrystalline samples with mesoscale grains (hundreds of nanometers to several microns in size). (c) Experimental study of the thermal conductivity of SiGe alloys (green circles) with different grain sizes as compared to the single crystal. Solid The solid line is a guide to the eyes. Light blue and red areas denote where the grain sizes of cast ingot and polycrystalline samples are located, respectively. 1, 10

2.3.5. All-Scale Hierarchical Architectures

As discussed above, atomic point defects caused by elemental substitution and nanoscale precipitates created by second-phase nucleation and growth can significantly scatter the short- and medium-wavelength phonons, respectively, while the mesoscale grains mainly scatter long-wavelength phonons. Therefore, achieving synergy of the multiscale phonon scattering in a single thermoelectric material is an effective strategy to obtain the lowest lattice thermal conductivity. The architectures in which this is achieved are called all-scale hierarchical architectures, as shown in Figure 2.7. Theoretical calculations indicate that, in PbTe, over 50% of the $\kappa_{\text{lat}}$ value is caused by the propagation of short-wavelength phonons with MFP less than 1nm, which can be impeded by atomic-scale point defects. The remaining
50% of the $\kappa_{\text{lat}}$ value comes equally from the medium-wavelength phonons with MFP of 1-10 nm and long-wavelength phonons with MFP of 10-1000 nm, which can be scattered by nanoscale precipitates and mesoscale grains, respectively.\textsuperscript{1} All-scale hierarchical architectures were successfully created in lead chalcogenides,\textsuperscript{126, 135-136} leading to significantly enhanced thermoelectric performance. Recently, this strategy has been applied to other lead-free materials, including SnTe,\textsuperscript{40} AgSbSe$_2$,\textsuperscript{137} Bi$_2$Te$_3$,\textsuperscript{138} and CoSb$_3$.\textsuperscript{139}

2.3.6. Compromise between $\mu$ and $\kappa$

Point defects, nanoprecipitates, dislocations, and grain boundaries as scattering centers do indeed significantly scatter phonons, but they simultaneously increase the charge carrier scattering, because for most crystalline materials, the transport for electrons and phonons shares the same set of sublattices, which leads to a compromise between $\mu$ and $\kappa_{\text{lat}}$.\textsuperscript{70}

Although an increase in the ratio of $\kappa_{\text{lat}}$ to $\mu$ can be achieved experimentally, there are still some fundamental issues that should be further addressed. For example, the accurate assessment of the mean free paths of phonons and electrons for one specific material still presents some uncertainties, which results in difficulty in choosing the right feature size for the scattering centers to effectively decrease the $\kappa_{\text{lat}}$ without explicitly reducing $\mu$. For nanostructuring in bulk materials, the deterioration in the carrier mobility is mainly caused by crystallographic mismatch and/or electronic band misalignment at the interfaces.\textsuperscript{41, 135-136}

Therefore, to avoid a reduction in the carrier mobility, both coherent interfaces (endotaxy) and energy-matched electronic bands are required, which, to some extent, achieves a decoupling of electron and phonon transport.\textsuperscript{1}

The electron and phonon scattering are strongly affected by the interface (endotaxy), the influence of which is usually determined by the degree of lattice misfit ($\xi$) between the matrix and the nanoprecipitates.\textsuperscript{140} According to their coherence, there are generally three types of
precipitate-matrix interfaces, including coherent ($\xi < 1\%$), semicoherent ($1\% < \xi < 25\%$), and incoherent ($\xi > 50\%$), as shown in Figure 2.8a-c.\textsuperscript{140-141} In the case of incoherent and semicoherent interfaces, the surrounding atomic order is strongly disrupted, leading to significant scattering of both electrons and phonons, but the nanoprecipitates and the matrix are connected coherently in the case of coherent interfaces (endotaxially) with a certain degree of strain around their interfaces, which facilitates the flow of charge carriers across the interfaces without much scattering, but strongly blocks phonon propagation, as shown in Figure 2.8d. Interface coherency has been successfully realized in lead chalcogenides,
Figure 2.8. Schematic diagrams of three types of precipitate-matrix interfaces. (a) coherent interface; (b) semi-coherent interface; (c) incoherent. (d) Schematic diagram of electron and phonon transport decoupling in nanostructured bulk materials: phonons (depicted by blue wave lines) are strongly scattered by nanoprecipitates, while the electrons (depicted by violet arrows) flow across the interfaces without restriction.

including PbTe-GeTe, PbTe-PbS, PbTe-MTe (M = Mg, Ca, Sr, Ba), PbSe-MSe (M = Ca, Sr, Ba), and SnTe-MnTe.

Although the scattering of electrons can be minimized by improving the interface coherency in nanostructured materials, the additional energy barrier caused by electronic band misalignment can also restrict the electron flow. Previous studies on GaAs/InAs (001) heterojunctions indicated that charge carriers can be transmitted freely when the band offsets are minimal. Recently, electronic band misalignment was realized for the three-dimensional bulk nanostructured lead chalcogenide family, i.e., PbTe-SrTe, PbSe-(CdS/ZnS), and PbS-MS (M = Pb, Cd, Zn, Ca and Sr). This strategy is based on the idea that, if the conduction/valence bands of the matrix are close in energy to those of the
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second phase, then electron/hole transmission through the system should be more facile. Schematic diagrams of electronic band alignment are presented in Figure 2.9a. When the energy difference of the conduction band minimum ($\Delta E_{\text{CBM}}$) or the valence band maximum ($\Delta E_{\text{VBM}}$) between the matrix and the second phase is comparable to the magnitude of the thermal energy $k_B T$ at elevated temperatures, the band alignment is realized. As shown in Figure 2.9a, phase A has a good valence band alignment with the matrix, which is favorable for seamless hole transmission across the interface, while phase B has a negligible energy difference between its conduction band minimum (CBM) and that of the matrix, and it is expected to allow facile electron transmission. A system where heat flow can be greatly inhibited without affecting the carrier mobility is realized in $p$-type PbTe with well-dispersed SrTe nanocrystals. As shown in Figure 2.9b, for a control sample of $p$-type PbTe doped with 1% Na$_2$Te, the lattice thermal conductivity of PbTe is remarkably decreased upon the addition of SrTe second phase without affecting the carrier mobility. Typically, the room-temperature carrier mobility values of pristine, 1% SrTe-containing, and 2% SrTe containing Pb$_{0.98}$Na$_{0.02}$Te are ~350, ~340, and ~340 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, and the corresponding values at 673 K have decreased to ~16, ~15, and ~21 cm$^2$ V$^{-1}$ s$^{-1}$. Apart from the PbTe-SrTe system, electronic bands misalignment has also been realized in the PbSe-(CdS/ZnS) and PbS-MS (M = Pb, Cd, Zn, Ca, and Sr) systems. The use of compositionally alloyed nanostructures is another strategy to achieve electronic band alignment when the CBM or valence band maximum (VBM) of the possible candidates lie either higher or lower in energy with respect to those of the matrix, as shown in Figure 2.9c. The CBM of the second phases AB and AC (XZ and XY) is too high or too low with respect to that of matrix for them to achieve effective conduction band alignment on their own, but if one could mix them in a proper ratio to form a solid solution $\text{AB}_{1-x}\text{C}_x$ (XY$_{1-m}$Z$_m$) then this alloy may have minimal energy offsets from the matrix. This takes place.
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Figure 2.9. (a) Schematic representation of the alignment of the valence band (VB) and conduction band (CB) energies of A and B second phase in the matrix. $\Delta E_{\text{CBM}}$ and $\Delta E_{\text{VBM}}$ denote the energy offsets of CB and VB between the second phase and the matrix, respectively. (b) Temperature dependence of lattice thermal conductivity and carrier mobilities for the PbTe-SrTe system doped with 2% Na.\textsuperscript{11-12} (c) Schematic representation of how compositionally alloyed nanostructures can achieve aligned electronic bands. (d) Temperature dependence of lattice thermal conductivity for the 2% Na-doped PbSe nanostructured with CdSe, ZnSe, CdS, and ZnS as a function of second-phase mole fraction. Insert is corresponding room-temperature carrier mobility.\textsuperscript{13}

though an interfacial reaction between the matrix and the second phase.\textsuperscript{1,8} A good example of applying this idea is $p$-type PbSe compositionally alloyed with CdS or ZnS.\textsuperscript{13} The VBM values of ZnS, CdS, ZnSe, and CdSe are 0.30, 0.27, 0.13, and 0.06 eV, respectively, which are higher or lower than that of PbSe, indicating the impossibility of electronic band alignment. When CdS/ZnS is introduced into the PbSe matrix, however, its changes the
composition, leading to solid solutions of the type CdS_{1-x}Se_x/ZnS_{1-x}Se which has intermediate VBM values between the CdS and the CdSe/ZnS and ZnSe, resulting in a reduction in the energy band offsets between the PbSe matrix and the nanostructured phases.

The corresponding reactions are presented by Equation (2-12) and Equation (2-13):

\[
PbSe + CdS = PbSe_{1-x}S_x + CdS_{1-x}Se_x \tag{2-12}
\]

\[
PbSe + ZnS = PbSe_{1-x}S_x + ZnS_{1-x}Se_x \tag{2-13}
\]

As shown in Figure 2.9d, an increase in the second phase fraction leads to only small changes in the carrier mobility for the PbSe-(CdS/ZnS), but the lattice thermal conductivity undergoes a significant reduction. Unlike electronic band alignment by compositionally alloyed nanostructures, a decreasing trend in carrier mobility is observed on increasing the fraction of CdSe/ZnSe, although the introduction of the second phase leads to the reduction of \( \kappa_{\text{lat}} \).

### 2.4. Bulk thermoelectric materials

According to the optimal working temperature, the thermoelectric materials can be divided into three ranges, *i.e.*, (i) low-temperature TE materials below 400 K, including, Bi_{2-x}Sb_xTe_3, Bi_{2}Te_{3-y}Se_y, CsBi_4Te_6, Mg_2Sn_{1-x}Ge_x, CsBi_4Te_6, and et al., (ii) medium-temperature TE materials varying from 600 to 900 K, including PbTe, SnTe, SnSe, BiCuSeO, MgAgSb, CoSb_3, and et al., and (iii) high-temperature TE materials above 900 K, including SiGe, Cu_{2-x}Se, Cu_{2-x}S, FeNbSb, et al. Since Seebeck observed thermoelectric phenomena in 1821, TE materials have developed three generations according to \( ZT \) values, as shown in Figure 2.10. In the first generation, the TE devices can operate at ~4-5% conversion efficiency with a maximum \( ZT \) of ~1.0, as shown in the left rose part of Figure 2.10. The typically TE materials in this period are Bi_{2}Te_3, PbTe, and SiGe. The second period was ignited by size effects and push the \( ZT \) to a near doubling values in the range of 1.3-1.7 through introducing nanoscale precipitates and
**Figure 2.10.** ZT of the current bulk thermoelectric materials as a function of year: the left part indicates the three conventional thermoelectric systems with ZT < 1.0 before 1990s, Bi$_2$Te$_3$, PbTe and SiGe; the middle part elucidates that the ZTs were enhanced to about 1.7 by nanostructures (AgPb$_m$SbTe$_{m+2}$, nano-Bi$_2$Te$_3$, nano+amorphous-Bi$_2$Te$_3$, nano-SiGe, nanostructural PbS) and electronic structure engineering (Tl doped PbTe, PbTe$_{1-x}$Se$_x$, nanostructured Bi$_2$Te$_3$, nano-SiGe, nanostructural PbS) and electronic structure engineering (Tl doped PbTe, PbTe$_{1-x}$Se$_x$, SiGe, modulation doping of SiGe); the right part shows the high performance realized in synergy of band convergence and hierarchical PbTe, and promising thermoelectric materials developed recently and characterized by low-cost, earth-abundant, and low thermal conductivity, including nanoscopic PbSe, band alignment PbS, BiCuSeO, Cu$_2$S systems, SnS, Cu$_2$Se systems, Half-Heusler, and SnSe. Some materials show the ZTs > 2.0.

Compositional inhomogeneities, *i.e.*, AgPb$_m$SbTe$_{m+2}$, nanostructured Bi$_2$Te$_3$, SiGe, and PbS, and modulation doping of SiGe. Except for the reduction of lattice thermal conductivity by nanostructuring, electronic structure engineering by DOS distortion (Tl doped PbTe) and conduction/valence band convergence (PbTe$_{1-x}$Se$_x$) has also been reported to enhance Seebeck coefficient. These second-generation materials are expected to produce power generation devices with conversion efficiencies of 11-15%, as shown in the medium light blue part of Figure 2.10. The third generation of bulk thermoelectrics has been under development recently, which integrates many cutting-edge ZT enhancing approaches simultaneously, namely, enhancement of Seebeck coefficients through conduction/valence
band convergence,\textsuperscript{7, 92, 94-96} retention of the carrier mobility by matrix/precipitate interfaces endotaxy and/or electronic band alignment,\textsuperscript{71, 88, 97-98} and reduction of lattice thermal conductivity via all-scale phonon scattering (atomic-scale point defects, nanoscale endotaxial precipitates, and mesoscale grain boundaries and interfaces).\textsuperscript{13, 135-136} This third generation of bulk thermoelectrics exhibits high $ZT$, ranging from 1.8 to 2.2, depending on the temperature difference $\Delta T$, and the consequent predicted device conversion efficiency increases to $\sim 15$-20\%, as shown in the right yellow part of Figure 2.10. Typically, Tan et al.\textsuperscript{91} reported that heavily Sr alloyed PbTe not only widen the bandgap and create convergence of the two valence bands of PbTe, but also introduce endotaxial SrTe nanostructures and realize matrix/precipitate valence band alignment, leading to a record-high $ZT$ of 2.5 at 923 K by the cumulative integration of several performance-enhancing concepts in a single material system.

As shown in Figure 2.10, in the past decade, metal chalcogenides such as bismuth and lead chalcogenides have been well investigated, among which, lead chalcogenides and their alloys (PbQ, Q = S, Se, and Te) have been engineered to achieve record-high $ZT$ values between 1.4 and 2.2 through synergy of band engineering (resonant levels, band convergence/band alignment), and hierarchical all-scale phonon scattering (atomic scale point defects, nanoscale precipitates, and microscale grain boundaries). However, the concern of toxic Pb limits their wide applications. Therefore, it is significant to pursue new thermoelectric candidates which are non-toxicity, high stability and can be fabricated through simple methods.

### 2.4.1. Tin telluride based thermoelectric materials

SnTe, a lead-free IV-VI semiconductor which has a simple rocksalt structure, as shown in Figure 2.11a. Electronic structure calculations present that SnTe has a similar band structure to the lead chalcogenides, which indicates that it is a promising lead-free candidate as a good thermoelectric material.\textsuperscript{38, 168-169} As shown in Figure 2.11b, the valence and conduction band
edges of SnTe are located at the L point of the Brillouin zone with a small band gap of 0.18 eV at room temperature.\textsuperscript{141,170-171} Lying energetically below the valence band is a flatter, so-called heavy-hole band which lies along $\Sigma$. The energy offset between the light-hole valence band (L band) and the heavy-hole valence band ($\Sigma$ band) is around 0.3-0.4 eV.\textsuperscript{38,59} This energy offset is much larger than that of high performance PbTe (0.17 eV) martials, which inhibits the contribution of $\Sigma$ band to the Seebeck coefficient.\textsuperscript{172} As mentioned above, for a given carrier concentration, the Seebeck coefficient can be estimated by total DOS effective mass, $m_d^*$ (Equation (2-7)), which can be enhanced by either a high band degeneracy ($N_v$) or a flat, narrow single-band effective mass, $m_b^*$ (Equation (2-6)). For the L band, the number of degenerate carrier pockets, $N_v$, is defined as 4, and it increase to 12 for the $\Sigma$ band. Therefore, the inhibition of the contribution of $\Sigma$ band to transport directly influences the improvement of Seebeck coefficient at elevated temperature. Moreover, the very small band gap of SnTe is not helpful in retaining a high thermoelectric performance at elevated temperature because of bipolar diffusion.
Another character of SnTe materials is its ultrahigh carrier concentration (>10^{21} \text{ cm}^{-3}), caused by the very large number of intrinsic Sn lattice vacancies.\textsuperscript{59, 173} Despite this large number of vacancies and the fact that the compound is inherently off-stoichiometric, the material is still often referred to as SnTe.\textsuperscript{173} As mentioned above, the optimum carrier concentration for most good TE materials is in the range of 10^{19} to 10^{21} \text{ cm}^{-3}, which is favourable to get the optimum power factors by balancing $\alpha$ and $\sigma$. Moreover, the high carrier concentration also results in a high electronic lattice thermal conductivity. Therefore, in order
to obtain high thermoelectric performance of SnTe, we need to suppress the excess hole carrier densities, widen band gap, narrow energy offset between L and \( \Sigma \) bands, and decrease its thermal conductivity.

Recently, Zhang et al.\(^3^9\) studied the thermoelectric properties of nanostructured SnTe with different dopants, and noticed indium-doped SnTe presented extraordinarily large Seebeck coefficients that cannot be explained properly by the conventional two-valence band model, as shown in Figure 2.12a. The room-temperature Seebeck coefficient values of pristine, Bi-doped, and Cu-doped SnTe are exactly follow the Pisarenko plot, however, those of In-doped samples show the deviation values, indicating the alteration of band structure. They attributed this enhancement of Seebeck coefficients to resonant levels created by the indium impurities inside the valence band, supported by the first principles simulations, as shown in Figure 2.12b. As mentioned above, resonant levels can increase the Seebeck coefficient at low temperature by a strong electron energy filtering effect in a nearly temperature-independent way. Moreover, take advantage of ball milling, the grain size of \( \text{In}_x\text{Sn}_{1-x}\text{Te} \) (\( x = 0, 0.0025, 0.05, 0.1 \)) reduced to a small size of 100 nm, which results in a significantly reduction of lattice thermal conductivity due to the increased phonon interface scattering (Figure 2.12c). Therefore, a peak \( ZT \) of \(~1.1\) was obtained in 0.25 atom % In-doped SnTe at about 873 K, as shown in Figure 2.12d, indicating SnTe is a potentially attractive lead-free thermoelectric material. It is important to mention that, In dopant, which introduces resonant levels inside the valence bands, improve the Seebeck coefficient of SnTe at low temperature.

Tan et al.\(^4^0\) combines band engineering and nanostructuring strategies in SnTe, which results in a maximum \( ZTs \) of \(~1.3\) and \(~1.1\) at 873 K for SnCd\(_{0.03}\)Te compounds with endotaxially nanostructured CdS and ZnS, respectively. Firstly, they present that Sn self-compensation can effectively reduce the Sn vacancies and reduce the hole carrier concentration. Typically, a 3 mol % self-compensation of Sn results in a 50% improvement in
Figure 2.13. Band structures of Sn$_{27}$Te$_{27}$, Sn$_{26}$Cd$_1$Te$_{27}$, and Sn$_{25}$Cd$_2$Te$_{27}$ as functions of (a) wavevector along the path L → Σ → K in the rocksalt supercell BZ and (b) Cd concentration. In (a) the valence and conduction bands of pristine SnTe are shown as solid red lines; the valence, conduction, and Cd-defect bands of Sn$_{26}$Cd$_1$Te$_{27}$ are shown as solid black lines; and the valence, conduction, and Cd-defect bands of Sn$_{25}$Cd$_2$Te$_{27}$ are shown as dashed blue lines. In (b) the valence band at Σ (blue), valence band at L (black), conduction band at L (red), and Cd defect band (green) are shown as functions of Cd concentration in the SnTe supercell. For the Cd defect band and $x_{Cd} = 0.74$ band structures, the bands are averaged over the BZ and each Cd-Cd configuration, respectively, with vertical bars indicating the standard deviation of each average. All energies are shown relative to the valence band maximum (VBM) of pristine SnTe.$^{40}$

the figure of merit $ZT$. Moreover, according to the first-principles density functional theory calculations, they reveal the introduction of Cd is significantly alert the electronic band structure by decreasing the energy separation between the light-hole valence band and heavy-hole valence band, and widening the band gap. This type of band engineering is a crucial finding for SnTe-based materials, as shown in Figure 2.13a-b. Another important finding is that they notice CdS and ZnS nanoscale precipitates, ranging in size from 3 to 7 nm,
endotaxially embedded into SnTe matrix, which results in a significant reduction of lattice thermal conductivity to 0.56 Wm\(^{-1}\)K\(^{-1}\), as shown in Figure 2.13c-d. Differential with the resonant levels introduced by In dopant, band convergence between the light and heavy hole valence bands and an enlargement of the band gap improve the the Seebeck coefficient of SnTe in the mid- to high-temperature region.

Following with the band degeneracy between the L and Σ bands of SnTe by Cd doping, a serious of other elements have been reported, which present the same alteration for band structure, namely widening the energy offset between two valence bands and narrowing band gap, \textit{i.e.}, introduction of Mg\textsuperscript{,44} Mn\textsuperscript{,146} Ca\textsuperscript{,45} and Hg dopants\textsuperscript{,43} Among these alloying species, the multiply favorable roles that Hg plays in regulating the electron and phonon
transport of SnTe lead to a maximum $ZT$ of 1.35 at $\sim 910$ K and more importantly, a significant enhancement of average $ZT$ of $\sim 1$ in Sn$_{0.98}$Bi$_{0.02}$Te-$x\%$HgTe at the temperature range from 500 to 900 K. Moreover, synergy of resonant levels and band convergence have been also reported to be an effectively strategy to enhance the Seebeck coefficient of SnTe over a broad temperature.$^{41}$ Specifically, In dopant introduces resonant levels inside the valence bands, which enhance the Seebeck coefficient at low temperature, as shown in Figure 2.14a. Cd dopant, however, induces band convergence between the L and $\Sigma$ bands and enlarge the band gap, which improve the Seebeck coefficient from mid- to high-temperature region, as shown in Figure 2.14b. Combining the two dopants in SnTe yields enhanced Seebeck coefficient over a wide temperature range due to the synergy of resonance levels and valence band convergence, as demonstrated by the Pisarenko plot and supported by first-principles band structure calculations, as shown in Figure 2.14c-e.

Recently, Li et al.$^{53}$ reported a combination of both band convergence (Mn doping) and interstitial defects (Cu$_2$Te alloying) in SnTe, leading to a highest $ZT$ of 1.6 at 927 K, which is actually one of the highest among known $p$-type thermoelectrics other than IV-VI semiconductors,$^{26, 39-52}$ as shown in Figure 2.15a-b. It is interesting to note that at low temperatures Cu exists as Cu$_2$Te precipitates out from the matrix Sn$_{0.86}$Mn$_{0.14}$Te, however, Cu$_2$Te precipitates get dissolved in the matrix when the temperature above 700 K, leading to a strong phonon scattering by interstitial Cu, as shown in Figure 2.15c-h. Moreover, the existence of Cu$_2$Te either as precipitates (at low temperatures) or as a solvent (at high temperatures) does not play an important role on electronic transport properties. Therefore, as compared to pristine SnTe, each of these two strategies enables a $\sim 150\%$ $ZT$ enhancement, which accumulates to a $\sim 300\%$ improvement when both are applied. This work opens new possibilities for further improving this material, as well as promotes SnTe as an eco-friendly solution for PbTe thermoelectrics in $p$-type.
Figure 2.15. Temperature-dependent $ZT$ for $\text{Sn}_{0.91}\text{Mn}_{0.14}\text{Te}(\text{Cu}_2\text{Te})_{0.05}$, comparing with those of reported (a) high $ZT$ SnTe materials$^{39-47}$ and (b) thermoelectrics other than IV-VI semiconductors$^{26, 48-52}$. TEM images for $\text{Sn}_{0.85}\text{Mn}_{0.15}\text{Te}(\text{Cu}_2\text{Te})_{0.05}$ at (c) RT, (e) 473 K, and (g) 673 K. The corresponding DES mapping of Cu are presented in (d), (f), and (h), respectively.$^{53}$

2.4.2. Tin selenide based thermoelectric materials

Figure 2.16. Crystal structure of low-$T$ Pnma (a-c) and high-$T$ Cmcm (d-f): blue, Sn atoms; red, Se atoms. (a) Structure along the $b$ axis for Pnma; (b) Sn coordination polyhedron corresponding to the structures in (a); (c) Structure along the $a$ axis for Pnma; (d) Structure along the $c$ axis for Cmcm; (e) Sn coordination polyhedron corresponding to the structures in (d); (f) Structure along the $b$ axis for Cmcm.
SnSe, which is a very stable and simple compound consisting of earth-abundant elements, is another promising lead-free thermoelectric candidate. Historically, SnSe was ignored by the thermoelectric community, however, its layered and anisotropic crystal structure motivated us to explore its electrical transport properties along all axial directions. Figure 2.16 illustrates the two temperature-dependent crystal structures of SnSe. One is GeS-type orthorhombic structure \( Pnma \) which has a layered structure with two Sn-Se bilayers in the unit cell as shown in Figure 2.16a. This structure features highly distorted Sn polyhedral coordination with three short (solid bonds) and four long (dashed bonds) Sn-Se bonds, with lone pair (5s\(^2\)) electrons from the Sn\(^{2+}\) sterically accommodated between the four long Sn-Se bonds (Figure 2.16b).\(^{37, 175}\) The three stronger bonds are linked with the nearest neighbors in the same bilayer, while the other four weaker bonds cross over two bilayers, two of which are in the same bilayer, and the others are in the next bilayer.\(^{175}\) The above highly disordered bonds lead to the lattice anharmonicity, which is an important phonon scattering mechanism in SnSe-based compounds, especially along the \( a \)-direction.\(^{175-177}\) In addition, two-atom-thick SnSe bilayer is corrugated with strong Sn-Se bonding, creating a zigzagged atomic chain along the \( b \)-direction, while the two neighbored bilayers are associated with weaker Sn-Se bonding along the \( a \)-direction, resulting in easy cleavage in the \( bc \)-plane (Figure 2.16c). The \( Pnma \) orthorhombic structure of SnSe is not stable as the temperature increases, however, it gradually transforms to another orthorhombic structure (\( Cmcm \)), which preserves the bilayer stacking structure, but with the Sn coordination environment gaining higher symmetry (Figure 2.16d-f). In fact, the low temperature (low-\( T \) \( Pnma \)) structure is a subgroup of the high temperature (high-\( T \) \( Cmcm \)) structure.\(^{178}\) This means that \( Pnma \) can be considered as a distorted \( Cmcm \) phase obtained through sliding and buckling in the adjacent planes.

Recently, SnSe single crystals have produced a surge in the field of thermoelectrics as a new type of promising TE materials because of the intrinsically ultra-low thermal
conductivity (< 0.4 W m\(^{-1}\) K\(^{-1}\) at 923 K) and an unprecedented \(ZT\) along the \(b\)- and \(c\)-crystallographic directions (> 2.3 at 923 K), realizing in SnSe single crystals, as shown in Figure 2.17.\(^{37}\) Enhancements above the generally high threshold value of 2.5 have important implications for commercial deployment,\(^{8,179}\) especially for compounds free of Pb and Te. As mentioned above, however, the phase structure of SnSe present a phase transition dependent on the temperature, which leads to visible and invisible microgaps along the cleavage plane in the specimen arising from the shrinkage of the unit cell over 800 K.\(^{61-67, 154-155, 180}\) Therefore, the optimal maximum temperature for investigating the thermal and thermoelectric properties of SnSe has been verified to be around 800 K.

**Figure 2.17.** \(ZT\) values along different axial directions as a function of temperature. The \(ZT\) measurement uncertainty is about 15% (error bars). Inset images: left, a typical crystal; right, a crystal cleaved along the (00) plane, and specimens cut along the three axes and corresponding measurement directions. Inset diagram, how crystals were cut for directional measurements; \(ZT\) values are shown on the blue, red and grey arrows; colors represent specimens oriented in different directions.\(^{37}\)
Zhang et al.\textsuperscript{154} reported that sodium is an effective acceptor to SnSe materials, which significantly increase $ZT$ over a broad temperature range from 300 to 773 K. Typically, the $ZT$ value of pristine SnSe along the $b$ axis is 0.1 at 300K, which vastly increase to 0.7 after introduction of sodium, and receives to the maximum $ZT$ of 2.0 at 773 K, as shown in Figure 2.18a. The hole doped SnSe ($b$ axis) outperforms most of current state-of-the-art $p$-type materials at 300-773 K (Figure 2.18b),\textsuperscript{9,13,37,54-56} contributing to the highest device $ZT$ ($ZT_{\text{dev}}$) of ~1.34 comparing with those of other typical high performance thermoelectrics at 300-773 K (Figure 2.18c).\textsuperscript{13, 37, 57} The $ZT_{\text{dev}}$ over the entire working temperature range is important as it determines the thermoelectric conversion efficiency ($\eta$). As shown in Figure 2.18d, the projected conversion efficiency of hole doped SnSe for $T_c = 300$ K and $T_h = 773$ K is ~ 16.7\%, which is also higher than those of other high performance thermoelectrics.\textsuperscript{13, 37, 57}

Nevertheless, the difficulties in large-scale synthesis of single crystals limit their practical applications, and extensive efforts have been devoted to the fabrication of high-performance polycrystalline counterparts.\textsuperscript{60-64, 67} For example, Wei et al.\textsuperscript{61} reported a $ZT$ of ~0.8 at 800 K in 1\% Na- and K-doped SnSe, which was produced by conventional solid state reaction followed by a spark plasma sintering (SPS) treatment. Due to an impressively low lattice thermal conductivity (~0.20 W m$^{-1}$ K$^{-1}$ at 773 K) arising from the presence of coherent nanoprecipitates in the SnSe matrix, a high $ZT$ of ~1.1 at 773 K was achieved in the direction perpendicular to the pressing direction of SPS for ball-milled K-doped SnSe.\textsuperscript{63} Apart from $p$-type alkali dopants (Li, Na, K), $n$-type dopants such as I and BiCl$_3$ are also adopted to improve the performance of polycrystalline SnSe.\textsuperscript{66-67} For instance, a $ZT$ of ~0.8 at 773 K was obtained in I-doped SnSe polycrystals, which was further improved to ~1.0 by reducing the lattice thermal conductivity via alloying with SnS.\textsuperscript{67}
Figure 2.18. *ZT* values of hole doped SnSe crystals and projected efficiency. (a) *ZT* values along different axial directions comparisons of hole doped SnSe and undoped SnSe crystals\(^{37}\); the *ZT* measurement uncertainty is about 20%. (b) *ZT* values comparisons of hole doped SnSe (*b* axis) and the current state-of-the-art *p*-type thermoelectrics, BiSbTe\(^9\), MgAgSb\(^{54}\), (GeTe)\(_{0.8}^{}\)(AgSbTe)\(_{0.2}^{}\)\(^{55}\), NaPb\(_m^{}\)SbTe\(_m+2\) (SALT),\(^{56}\) PbTe-4SrTe-2Na\(^{13}\) and SnSe (*b* axis).\(^{37}\) (c) Device *ZT* values comparisons of hole doped SnSe (*b* axis), SnSe (*b* axis),\(^{37}\) PbTe-4SrTe-2Na\(^{13}\) and PbTe-30PbS-2.5K.\(^{57}\) inset is the typical hole doped SnSe crystals. The temperature range for these values is from 300-773K. (d) The calculated efficiency as a function of hot side temperature (cold side temperature is 300K) of hole doped SnSe (*b* axis), undoped SnSe (*b* axis),\(^{37}\) PbTe-4SrTe-2Na,\(^{13}\) and PbTe-30PbS-2.5K.\(^{57}\)
Chapter 3. Experimental Methods

3.1. Materials fabrication

3.1.1. Materials synthesis

The solid state reaction, also called a dry media reaction, is the most widely used method for the preparation of polycrystalline solids from a mixture of solid starting materials. Generally, in a typical solid state reaction process, raw materials are first mixed together by ball milling or by hand in an agate mortar, and then undergo a heat treatment, often above 1000 °C in order for the reaction to occur at an appreciable rate. The solid state reaction is a low cost and environmental friendly fabrication method due to the absence of organic solvents.

In this thesis, the raw powder or chunk materials were first mixed together in quartz tubes in an argon filled glove box. The tubes were flame-sealed under vacuum, and then sintered in Muffle furnace. In specific case, the sealed tube needs to be placed in larger quartz tube, evacuated, and flame-sealed again. The outer tube is used to protect the crystals from oxidation by air, in case the inner tube breaks due to the considerable difference in thermal expansion between the crystals and quartz.

3.1.2. Materials shaping

In this thesis, the synthesized powders were shaped by the thermal Technology’s spark plasma sintering (SPS) systems. SPS is a comparatively novel sintering process that allows fabrication of bulk materials from powders using a fast heating rate (i.e., up to 1000 °C min⁻¹) and short holding times (i.e., 5-10 min) at low sintering temperatures (i.e., 200-300 °C lower than most of the conventional sintering techniques). Due to advantage of high heating rate and less holding time, SPS can restrict the unwanted sintering reactions in highly reactive systems as opposed to conventional sintering and hence formation of undesirable product phases can be avoided.
3.2. Materials Characterization

3.2.1. X-ray Diffraction (XRD)

X-ray diffraction is a method for determination of the identity and crystallinity of a synthesized compound, which based on constructive interference of monochromatic X-rays and a crystalline sample, as shown in Figure 3.1. The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate them, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when the conditions satisfy Bragg’s law, as expressed by following Equation (3-1):

\[ n\lambda = 2d \sin \theta \]  

(3-1)

where \( d, \lambda, n \) and \( \theta \) are the lattice spacing between diffracting planes, the wavelength of the beam, an integer representing the order of the diffraction peak, and the diffraction angle, respectively. In this thesis, GBC-MMA X-ray diffractometer was commonly used to characterize the crystallographic materials with a Cu K\( \alpha \) radiation (\( \lambda = 1.5418 \) Å). The powder sample was placed at a small disc-shaped quartz holder with a flattened surface. The whole measurement was conducted under room temperature in air.

![Figure 3.1 Bragg’s Law defining the conditions for the occurrence of diffraction peaks](image-url)
3.2.2. Synchrotron powder diffraction (SPD)

Synchrotron powder diffraction is a high-quality X-ray diffraction. Contrast to laboratory XRD, which intensity is spread over a relatively divergent beam, synchrotron powder diffraction concentrates the intensity into a fine well-defined near-parallel X-ray beam. In the SPD, X-rays are generated by a synchrotron facility that accelerates electrons to almost the speed of light. As the electrons are deflected through magnetic fields they create extremely bright light. The light is channeled down beamlines to experimental workstations where it is used for research, as shown in Figure 3.2. In this thesis, synchrotron powder diffraction patterns were collected on the Powder Diffraction beamline at the Australian Synchrotron. The powders were ground with an agate mortar, and then packed in the quartz tube (high temperature) or boron nitride (low temperature) with a diameter of 0.3 mm using paraffin. The whole measurement was conducted under argon atmosphere.

![Figure 3.2 illustration of the synchrotron](image)

3.2.3. Neutron powder diffraction (NPD)

Neutron powder diffraction in terms of its principles of operation is similar to X-ray diffraction. Contrary to X-rays, however, which interact primarily with the electron cloud surrounding each atom of a given material, most scattering of neutrons occurs at the atom
nuclei, thus providing complementary information not accessible with X-rays. In this thesis, neutron powder diffraction patterns were collected on the high-resolution powder diffractometer ECHIDNA at the Australian Nuclear Science and Technology Organization. The powders were ground with an agate mortar, and then packed in a cylindrical alumina holder with a diameter of 8 mm.

3.2.4. **Field Emission Scanning Electronic Microscopy (FESEM)**

Scanning electronic microscopy (SEM) is a type of electron microscope that uses a high-energy electron beam scanned across the surface of the sample generates secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by detectors to form images of the sample displayed on a cathode ray tube screen. Secondary electron imaging and backscattered electron imaging mainly presents the topography of surface features, and the former focuses on the ups and downs of surface, while the latter focuses on the Z-contrast of surface. The characteristic X-rays produced by inner electron transition, showing the distribution of elements or compounds. Features seen in the SEM image may then be immediately analyzed for elemental composition using energy dispersive spectroscopy (EDS). FESEM provides topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field. Compared with convention SEM, field emission SEM produces provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. In this thesis, the microstructure of the fractured bulk surfaces was characterized by JOEL JSM-7500F field emission scanning electronic microscopy with an accelerating voltage of 5 KV, and current of 10 mA. Compositions of the samples were conducted by energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS) affixed within JOEL JSM-7500F with an accelerating voltage of 15 KV, and current of 20 mA.
3.2.5. Scanning Transmission Electronic Microscopy (STEM)

Transmission electron microscopy (TEM) can display morphology images of samples by using electrons beams transmitted through an ultra-thin sample. TEM enables the investigation of crystal structures, specimen orientations and chemical compositions of phases, precipitates and contaminants through diffraction pattern, X-ray and electron-energy analysis. Scanning transmission electron microscope (STEM) is a type of TEM. Contrast to the conventional TEM that images are formed by electrons passing through a sufficiently thin specimen, in STEM the electron beam is focused to a fine spot which is then scanned over the sample in a raster. The raster of electron beam across the sample makes it suitable for a few analysis techniques such as elemental mapping by energy dispersive X-ray (EDX) spectroscopy, electron energy loss spectroscopy (EELS) and annular dark-field imaging (ADF). These signals can be obtained simultaneously, allowing direct correlation of image and quantitative data.

In this thesis, TEM images were performed using a JEOL ARM200F microscope with an accelerating voltage of 200 kV. Elemental mapping was performed on the X-ray spectrometer attached to the JEOL ARM-200F instrument. The thin TEM specimens were prepared by two methods, one is conventional method, including cutting, grinding, dimpling, and tripod polishing, with minimal duration of Ar-ion milling with a liquid N₂ cooling stage, and the other one was sliced by focused ion beam at a moderate voltage (16 keV), which was then followed by cleaning with a lower voltage (5 keV).

3.2.6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermoanalytical technique measuring a sample and a reference sample in an increasing temperature circumstance and obtaining the difference in the amount of heat. The main application of DSC is in studying phase transitions, such as melting points, glass transitions, crystallization times and temperatures,
heats of melting and crystallization, percent crystallinity, compositional analysis, thermal stability, and heat capacity. In this thesis, the heat capacity, which used to evaluate the thermal conductivity, was measured by DSC (Netzsch 204F1) instrument which was conducted under argon atmosphere. The standard reference method is used with single crystal of Al₂O₃ as the reference, i.e., the DSC curve of empty crucible, crucible with reference, and crucible with sample is respectively collected. Then the \( C_p \) value can be evaluated by following Equation (3-2).

\[
C_p = C_R \times \frac{H_{e+s}-H_e}{H_{e+r}-H_e} \times \frac{m_R}{m_S}
\]

where \( H_e, H_{e+r}, H_{e+s}, C_R, m_R \), and \( m_S \) are heat of empty crucible, heat of empty crucible and reference, heat of empty crucible and sample, specific heat of reference, mass of reference, and mass of sample, respectively.

3.2.7. Physical Property Measurement System (PPMS)

In this thesis, the room temperature carrier concentration and carrier mobility were determined by Hall coefficient measurements conducted with a PPMS-9 system. Four contact Hall-bar geometry was used for the measurement. The Hall coefficient \( (R_H) \), carrier concentration \( (n) \) and carrier mobility \( (\mu) \) can be defined by Equation (3-3) and Equation (3-4):

\[
n = \frac{1}{eR_H}
\]

\[
\mu = \sigma R_H
\]

where \( e \) and \( \sigma \) are the electronic charge and the electrical conductivity, respectively.

3.2.8. Electrical conductivity and Seebeck coefficient measurements

In this thesis, the electrical conductivity and Seebeck coefficient were measured simultaneously by means of a static DC method using an Ozawa Rz2001i system under the helium/argon atmosphere. The fabricated samples were cut and polished into rectangular bars with a dimension of (6-8) × (2-3) × (2-3) mm³, and then two parallel platinum wires were
wrapped around the sample to tap the voltage for the electrical conductivity measurements, as shown in Figure 3.3. The temperature difference, which is used for the evacuation of Seebeck coefficient, was controlled by the cold air flowing through the quartz double tube. The values of electrical conductivity and Seebeck coefficient at every selected temperature point were measured five times, and then outputted the average values.

![Figure 3.3 illustration of the electrode constitution](image)

### 3.2.9. Thermal conductivity measurements

The thermal conductivity was calculated from $\kappa= DC_p d$, where $D$, $C_p$, and $d$ are the thermal diffusivity coefficient, heat capacity, and density, respectively. In this thesis, the thermal diffusivity coefficient was measured using the laser flash diffusivity method in a Linseis LFA1000 (Germany) and LFA457 (Germany). The fabricated samples were cut and polished into $\varnothing (6-10) \times 1 \text{ mm}^3$ disks, and coated with a thin layer of graphite to minimize errors from the emissivity of the material. The density was measured by the Archimedes method. The specific heat capacity ($C_p$) was indirectly derived from a representative sample (DSC 204) over the range of 323–573 K, and then simulated to 773 K or 873 K based on the Debye module.
4.1. Introduction

Lead chalcogenides are the most studied thermoelectric materials with high \( ZT \) values between 1.4 and 2.2, through the synergy of the band engineering (band convergence and/or resonant levels) and all-scale hierarchical architectures (point defects, second phase nanoprecipitates and mesoscale grain boundaries). The concerns about Pb (i.e., toxicity), however, limit their large-scale application. An alternative is SnTe, which is lead-free environmental friendly semiconductors with the same rock-salt structural and the same multiple valence bands (light- and heavy-hole valence bands) as PbTe, suggesting it is a promising candidate for thermoelectric material, and all the strategies used for the lead chalcogenides can be applied to the tin chalcogenides. As mentioned above, SnTe presents very high level of intrinsic Sn vacancies (\( 10^{20} - 10^{21} \) cm\(^{-3} \)), which leads to a low Seebeck coefficient and a high electronic thermal conductivity. Other concerns about SnTe are its small band gap (~0.18 eV at 300 K) and the large energy separation (0.3-0.4 eV at 300 K) between its light- and heavy-hole valence bands, which significantly suppresses the contribution of heavy holes to the Seebeck coefficient at high temperature.

In this work, we enhance the lead-free SnTe thermoelectric performance through the adjustment of carrier concentration and the introduction of nanoprecipitates. The lattice thermal conductivity of SnTe was first optimized through introduction of nanoprecipitates by doping Gd into SnTe. In conjunction with adjustment of the phase composition via further doping of Ag into Gd\(_x\)Sn\(_{1-x}\)Te, carrier concentration was reduced accompanied with the enhancement of the Seebeck coefficient. A promising \( ZT \) of ~1.1 was achieved at 873 K in
our optimized sample \(i.e., \text{Ag}_{0.11}\text{Gd}_{0.06}\text{SnTe}_{0.94}\text{Te}\), which is comparable to state-of-the-art
Mg-\(^{44}\), Cd-\(^{40}\), and In-\(^{39}\) alloyed SnTe-based materials.

### 4.2. Experimental section

#### 4.2.1. Materials

Tin (Sigma Aldrich, powders, 99.8%), tellurium (Sigma Aldrich, powders, 99.8%),
gadolinium (Sigma Aldrich, powders, 99%) and silver (Sigma Aldrich, powders, 99.9+ %)
were used for synthesis without any further purification.

#### 4.2.2. Sample preparation

Ingots (~6 g) of \(\text{Gd}_x\text{Sn}_{1-x}\text{Te} (0 \leq x \leq 0.08)\) and \(\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te} (0 \leq y \leq 0.15)\) were
synthesized by mixing appropriate ratios of high-purity Sn, Te, Gd and Ag in quartz tubes in
an argon filled glovebox. The tubes were flame-sealed under vacuum and slowly heated to
1173 K over 10 h, held at this temperature for 15 h, and then quenched in an ice water bath.
The resultant ingots were crushed into fine powders and then densified by the SPS method at
773 K for 5 min in a 20-mm-diameter graphite die under an axial compressive stress of 50
MPa in vacuum. Highly dense (>95% of theoretical density) disk-shaped pellets were
obtained, as shown in Table 4.1 and Table 4.2.

<table>
<thead>
<tr>
<th>Density</th>
<th>(\text{Gd}<em>x\text{Sn}</em>{1-x}\text{Te})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(x=0)</td>
</tr>
<tr>
<td>(D_T, \text{ g cm}^{-3})</td>
<td>6.482</td>
</tr>
<tr>
<td>(D_S, \text{ g cm}^{-3})</td>
<td>6.41</td>
</tr>
<tr>
<td>(D_R, %)</td>
<td>98</td>
</tr>
</tbody>
</table>
Table 4.2. Densities of Ag$_y$Gd$_{0.06}$Sn$_{0.94}$Te ($0 \leq y \leq 0.15$) samples.

<table>
<thead>
<tr>
<th>Density</th>
<th>y= 0</th>
<th>y= 0.03</th>
<th>y= 0.05</th>
<th>y= 0.07</th>
<th>y= 0.09</th>
<th>y= 0.11</th>
<th>y= 0.13</th>
<th>y= 0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm$^{-3}$</td>
<td>81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D$_S$, g</td>
<td>6.3</td>
<td>6.12</td>
<td>6.02</td>
<td>6.13</td>
<td>6.17</td>
<td>6.30</td>
<td>6.41</td>
<td>6.53</td>
</tr>
<tr>
<td>cm$^{-3}$</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D$_R$, %</td>
<td>96</td>
<td>97</td>
<td>97</td>
<td>98</td>
<td>97</td>
<td>97</td>
<td>98</td>
<td>98</td>
</tr>
</tbody>
</table>

4.2.3. Characterization

Samples ground in an agate mortar were used for powder X-ray diffraction (XRD). The XRD patterns were obtained with Cu K$_\alpha$ ($\lambda=1.5418$ Å) radiation in a reflection geometry on an Inel diffractometer operating at 40 kV and 25 mA, and equipped with a position sensitive detector. High resolution synchrotron X-ray diffraction was applied on representative powders of Gd$_{0.06}$Sn$_{0.94}$Te at 300 K in the Australian Synchrotron.

Scanning transmission electron microscopy (STEM) and STEM energy dispersive spectroscopy (EDS) were performed using a JEOL ARM200F microscope with an accelerating voltage of 200 kV. The thin TEM specimens were prepared by conventional methods, including cutting, grinding, dimpling, and tripod polishing, with minimal duration of Ar-ion milling with a liquid N$_2$ cooling stage.

The carrier concentration and carrier mobility were determined by Hall coefficient measurements at room temperature with a PPMS-9 system. Four contact Hall-bar geometry was used for the measurement.
The obtained highly dense pellets were cut into bars with a dimension of $8 \times 3 \times 3 \, \text{mm}^3$ to be used for simultaneous measurement of the Seebeck coefficient and the electrical conductivity on an Ozawa RZ2001i (Japan) instrument under a helium atmosphere from room temperature to 823-873 K. The left parts of pellets were cut and polished into $\varnothing 10 \times 1 \, \text{mm}^3$ disks for the thermal diffusivity coefficient ($D$) measurements using the laser flash diffusivity method in a Linseis LFA1000 (Germany). The samples were coated with a thin layer of graphite to minimize errors from the emissivity of material. The the specific heat capacity ($C_p$) was indirectly derived from a representative sample (DSC 204) over the range of 323–573 K, and then simulated to 873 K based on the Debye module. The density ($d$) was measured by the Archimedes method.

4.3. Results and discussion

The strategy for enhancing the thermoelectric performance of SnTe consists of two rational steps. First, the lattice thermal conductivity of SnTe is reduced by introducing nanoprecipitates through Gd doping. The sample with the lowest thermal conductivity is then chosen for further improvement in electrical property via adjusting carrier concentration and phase composition by doping Ag into Gd$_x$Sn$_{1-x}$Te.

4.3.1. Thermoelectric performance of SnTe by Gd doping

Figure 4.1a presents the powder XRD patterns of sintered samples of Gd$_x$Sn$_{1-x}$Te ($x = 0, 0.02, 0.04, 0.06, 0.08$). The main Bragg reflections of all the samples correspond well to the rock-salt structure, indicating SnTe as the major phase. For Gd-doping samples with dopant concentration above 0.02, some very small peaks with the $2\theta$ value around 30-33° were observed, which indicates a low solubility limit for Gd in SnTe, i.e., smaller than 0.04. In order to identify these small peaks, a representative sample of Gd$_x$Sn$_{1-x}$Te was subjected to a high resolution synchrotron X-ray diffraction measurement at 300 K. They were indexed to Sn (200), GdTe$_3$ (113) and Sn (101) with the $2\theta = \sim30.8^\circ$, $\sim31.2^\circ$, and $\sim32.1^\circ$, respectively.
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Figure 4.1. (a) Powder XRD patterns of Gd$_x$Sn$_{1-x}$Te (x = 0-0.08) samples; (b) powder synchrotron XRD pattern of Gd$_{0.06}$Sn$_{0.94}$Te sample; (c) the lattice parameter as a function of x at room temperature.

as shown in Figure 4.1b. The existence of GdTe$_3$ attributes to a “Sn-rich” system to matrix, and the excessive Sn is expected to precipitate once all the intrinsic Sn lattice vacancies are compensated.\textsuperscript{39} This can be confirmed by the changes of lattice parameter as shown in Figure 4.1c. The lattice parameter as a function of x increases gradually with increasing Gd content and then saturates at x $\geq$ 0.04. The increased lattice parameters are attributed to the Sn self-compensation until x $\sim$ 0.04. The result is close to that of Sn doped samples, which suggests that the limit for Sn compensation in SnTe is $\sim$0.03.\textsuperscript{40}

Figure 4.2a displays the total thermal conductivity, $\kappa_{tot}$, as a function of temperature for Gd$_x$Sn$_{1-x}$Te (x = 0, 0.02, 0.04, 0.06, 0.08). The thermal conductivities of these samples overall decreases with the increase of temperature. They also first gradually decrease and then increases with rising Gd content, approaching the minimum value of $\sim$1.3 W m$^{-1}$ K$^{-1}$ at optimal Gd dopant concentration (i.e., x = 0.06). The thermal diffusivity as a function of temperature for Gd$_x$Sn$_{1-x}$Te presents the similar trend with total thermal conductivity, ranging
from 6 to 0.5 mm$^2$s$^{-1}$ (Figure 4.2d). The heat capacity values are around 0.21-0.22 Jg$^{-1}$K$^{-1}$ (Figure 4.2e).
The total thermal conductivity consists of the electronic thermal conductivity, \( \kappa_{\text{ele}} \) and the lattice thermal conductivity, \( \kappa_{\text{lat}} \), as shown in Figure 4.2b-c. The contributions of \( \kappa_{\text{ele}} \) and \( \kappa_{\text{lat}} \) to the thermal transport are almost equal, which indicate the dominance of electron-phonon interactions for SnTe materials. The electronic contribution can be evaluated by the Wiedemann–Franz formula 

\[ \kappa_{\text{ele}} = L \sigma T \]

where \( L \), \( \sigma \), and \( T \) are the Lorenz number, electrical conductivity, and absolute temperature, respectively. In this work, the \( L \) value is obtained from the accepted equation 

\[ L = 1.5 + \exp\left[-|\alpha|/116\right] \]

as shown in Figure 4.2f.

The lattice thermal conductivity \( \kappa_{\text{lat}} \) is then calculated by subtracting \( \kappa_{\text{ele}} \) from \( \kappa_{\text{tot}} \), and the results are shown in Figure 4.2b. A significant decrease in \( \kappa_{\text{lat}} \) has been achieved in the Gd\(_x\)Sn\(_{1-x}\)Te (\( x = 0.08 \)) samples compared to the pristine SnTe. The \( \kappa_{\text{lat}} \) as a function of \( x \) decreases with increasing Gd concentration and then increases in a similar way to the total thermal conductivity, which suggests that there is an optimal dopant concentration for formation of nanoprecipitates to achieve the strongest phonon scattering.\(^{187}\) Gd\(_{0.06}\)Sn\(_{0.94}\)Te samples doped with 4 atom\% and 6 atom\% Gd have the similar \( \kappa_{\text{lat}} \), \( \sim 0.6 \) W m\(^{-1}\) K\(^{-1}\), and the Gd\(_{0.06}\)Sn\(_{0.94}\)Te is chosen for further Ag incorporation due to its overall lower thermal conductivity. The Gd\(_{0.06}\)Sn\(_{0.94}\)Te sample has a \( \kappa_{\text{lat}} \) of \( \sim 1.6 \) W m\(^{-1}\) K\(^{-1}\) at 323 K, decreases to the minimum (\( \sim 0.63 \) W m\(^{-1}\) K\(^{-1}\)) with the temperature increasing to 573 K, and reaches \( \sim 0.81 \) W m\(^{-1}\) K\(^{-1}\) at 873 K. The lower lattice thermal conductivity is close to the theoretical minimum, \( \kappa_{\text{min}} \) (\( \sim 0.5 \) W m\(^{-1}\) K\(^{-1}\)) for SnTe-based materials.\(^{188}\) This value is also comparable to the 0.6 W m\(^{-1}\) K\(^{-1}\) of the Hg-doped SnTe sample reported by Tan et al.\(^{43}\)

To understand the origin of the lower lattice thermal conductivity, the microstructures and chemical compositions of Gd\(_{0.06}\)Sn\(_{0.94}\)Te sample were investigated by TEM, STEM and EDS. Figure 4.3a shows low-magnification images of high-density nanoscale precipitates with a wide range of size (\( \sim 2\)–30 nm) and dark contrast. These nanoprecipitates are shown with two
morphologies (red circles for the bigger ones and yellow squares for the smaller ones). Their size distribution was counted, and most of them are in a range of 2 to 6 nm as shown in Figure 4.3b. These nanoprecipitates are the main cause of phonon scattering due to mass fluctuation between the precipitates and the matrix, especially targeting the medium

![Image](image_url)

**Figure 4.3.** Electron microscopy of the $Gd_{0.06}Sn_{0.94}Te$ specimen. (a) Low-magnification image of the specimen along the [1-11] zone axis shows both larger nanoprecipitates (red circles) and smaller nanoprecipitates (dashed yellow rectangles) in the matrix. The inset shows the corresponding SAD pattern. (b) Histograms of precipitate size for $Gd_{0.06}Sn_{0.94}Te$, with the insert showing the corresponding area used to analyse nanoprecipitate size. (c) HRTEM image of one of the smaller nanoprecipitates, with the insert presenting the IFFT image of the dashed yellow rectangle, showing that the Moiré patterns exist on the surface between the nanoprecipitate and the matrix. (d) HRTEM image of a larger nanoprecipitate. Dislocation arrays with the periodic spacing of ~2 nm were observed and are highlighted by red arrows, with the insert showing the morphology of a larger nanoprecipitate.
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Figure 4.4. STEM EDS spectrum image of Gd$_{0.06}$Sn$_{0.94}$Te. (a) Low magnification STEM image shows two precipitates highlighted by red circles and yellow squares in the matrix; (b)-(e) corresponding EDS mapping for elements Sn, Te and Gd, respectively. A blacker in color in the elementary maps corresponds to higher concentrations.

wavelength phonons. The inset of Figure 4.3a is the selected area diffraction (SAD) pattern along the [0 -1 1] orientation with an aperture that captures both the matrix and the precipitates. Two sets of Bragg diffraction spots indicate the presence of lattice mismatch between the matrix and the nanoprecipitates.

To investigate the distribution of elements in Gd$_{0.06}$Sn$_{0.94}$Te, the electron energy loss spectroscopic (EELLS) elemental mapping was performed and the images are shown in Figure 4.4. The images clearly demonstrate that the bigger nanoprecipitates (labelled with red circles) are rich in Sn, while the smaller ones (labelled with yellow squares) are rich in
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Gd, and Te is uniformly distributed. The high resolution TEM (HRTEM) image in Figure 4.3c shows a Gd-rich nanoscale precipitate (square with dashed yellow lines) embedded in the matrix. Moiré fringes are observed at interfaces due to the lattice overlap of GdTe$_3$ and the matrix $^{43}$, which can be identified by its inverse fast Fourier transform (IFFT) image inserted in Figure 4.3c. Other positions of Moiré patterns are observed in grain boundaries (Figure 4.5). The Moiré patterns indicate that the grains in precipitates and the matrix are highly crystalline, with clean interfaces and/or boundaries where obscured dislocations exist.$^9$ The Moiré patterns could deteriorate electrical properties, although they provide sufficient atomic strains to scatter heat-carrying phonons.

Figure 4.5. Low magnification STEM image shows Moiré patterns in grain boundary. The inserted is IFFT image of the dashed red rectangular.
In addition to Moiré patterns, dislocation arrays with a periodic spacing of ~2 nm were observed in Sn-rich larger nanoprecipitates, as shown by the typical HRTEM image in Figure 4.3d. These dislocation arrays target intermediate wavelength phonons which cannot be scattered sufficiently by the smaller nanoprecipitates. It is known that phonons in a material carry most of heat and have a spectrum of wavelengths and mean free paths (MFP), each of which contributes to the total thermal conductivity. In our case, the long MFP phonons are mainly scattered by mesoscopic particles around 500 nm in size that are obtained through sintering as shown in Figure 4.5. The medium MFP phonons, giving predominant contributions to the lattice thermal conductivity, are scattered by the dislocation arrays together with nanoprecipitates based on mass fluctuation. Therefore, in Gd-doped SnTe samples, the phonons were effectively scattered from nano- to micro-length scales.

Figure 4.6 shows the temperature dependence of thermoelectric properties of Gd$_x$Sn$_{1-x}$Te ($x = 0$-0.08). The room temperature electrical conductivity of the pristine SnTe is $\sim$6300 S cm$^{-1}$. It systematically decreases with dopant content $x$ increasing from 0 to 0.04, and then nearly remains unchanged at $\sim$2500 S cm$^{-1}$ when $x \geq 0.06$ (Figure 4.6a). The decrease in the electrical conductivity is ascribed to the reduced hole concentration. Moreover, the introduced nanoprecipitates, Moiré fringes and dislocation arrays also significantly influence carrier mobility. The Seebeck coefficients of Gd$_x$Sn$_{1-x}$Te ($x = 0$-0.08) samples as a function of temperature are presented in Figure 4.6b. The undoped sample possesses a low Seebeck coefficient of $\sim$26 $\mu$V K$^{-1}$ at room temperature because of its high hole concentration as mentioned above. With increase of dopant concentration $x$, their room temperature Seebeck coefficients changed slightly, however, they increase faster at high temperature, which is attributed to the increasing contribution of the heavy-hole $\Sigma$ band at high temperature due to the thermal excitation. The contribution of the heavy-hole band at high temperature can be
enhanced once a significant number of Sn vacancies was removed. The maximal Seebeck coefficient of 160 μV K⁻¹ is obtained from Gd₀.₀₆Sn₀.₉₄Te at 873 K, which is 60% enhancement over pristine SnTe. Figure 4.6c shows the temperature dependence of power factors for GdₓSn₁₋ₓTe (x = 0-0.08) samples. Their power factors are deteriorated as a result of Gd incorporation in all temperatures due to their decreased electrical conductivities, although the Seebeck coefficient is significantly increased due to the compensation of Sn vacancies. Nevertheless, due to the benefit of the significant reduction in thermal conductivity, their ZT values are enhanced with increase of Gd content over the whole temperature range. A ZT of
0.6 at 873 K is obtained in Gd$_{0.06}$Sn$_{0.94}$Te, which represents ~50% improvement over undoped SnTe.

### 4.3.2. Thermoelectric performance of SnTe by Gd/Ag co-doping

To further improve the thermoelectric properties of SnTe, optimized Gd-doped SnTe sample (i.e., Gd$_{0.06}$Sn$_{0.94}$Te) was selected to dope with different contents of Ag. The XRD patterns of resultant samples (Ag$_y$Gd$_{0.06}$Sn$_{0.94}$Te, $y = 0, 0.03, 0.05, 0.07, 0.09, 0.11, 0.15$) show the NaCl-type structure as the main phase (Figure 4.7a). A trace of Ag$_4$Sn phase is detected in the samples with dopant concentration above 0.05 (i.e., $y \geq 0.05$). The absence of GdTe$_3$/Sn, which was detected in Gd$_{0.06}$Sn$_{0.94}$Te sample, suggests that doping Ag into Gd$_x$Sn$_{1-x}$Te changes the crystal structure and the composition of Gd$_x$Sn$_{1-x}$Te. Figure 4.7b shows the lattice parameter as a function of Ag concentration $y$ for Ag$_y$Gd$_{0.06}$Sn$_{0.94}$Te samples. The lattice parameter decreases gradually with increasing Ag content, and then slightly increases at $y > 0.05$. The drastic decrease in lattice parameter also suggests that Ag reacted with Sn to produce Ag$_4$Sn, not substituted for Sn. This is supported by the fact that Ag$^+$ radius (0.126 nm) is larger than that of Sn$^{2+}$ (0.093 nm), and the cell parameters of Ag$_4$Sn ($a = b = 2.966$, $c = 4.782$) are much smaller than that of SnTe ($a = 6.319$).

The trend of the room temperature carrier concentration ($n$) as a function of $y$ is in a good agreement with that of the lattice parameter Figure 4.7c. The hole concentration in undoped Gd$_{0.06}$Sn$_{0.94}$Te sample is up to ~3.6 $\times$ 10$^{21}$ cm$^{-3}$, but it clearly decreases to ~1.4 $\times$ 10$^{20}$ cm$^{-3}$ with doped Ag concentration increasing from 0 to 0.07 and then increases to ~5 $\times$ 10$^{20}$ cm$^{-3}$ with further increase of Ag content to 0.15. The decreased carrier concentration is attributed to the fact that Gd is a donor dopant for SnTe, and doping of Gd into SnTe leads to the decrease of electrical conductivity. Below the critical dopant concentration (i.e., $y < 0.07$), the formation of Ag$_4$Sn could boost the homogenous distribution of Gd in SnTe, however, the formation of Ag$_4$Sn above the critical dopant concentration ($y \geq 0.07$) leads to Sn vacancies.
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Figure 4.7. (a) Powder XRD patterns of $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ ($x = 0-0.15$) samples, with the insert showing enlarged powder XRD patterns in the range of $30^\circ$ to $43^\circ$ ($2\theta$ deg.); (b) lattice parameter and (c) carrier concentration as a function of $y$ at room temperature.

and increase of the hole concentration.

To demonstrate that Ag doping led to the homogenous distribution of Gd in SnTe, $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ samples were characterized with TEM. Figure 4.7a shows the typical low-magnification image of $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ specimen. In comparison with Gd-doped SnTe sample in Figure 4.3, only one type of uniform nanoprecipitates (red arrows) is observed in the SnTe matrix, and only one set of Bragg diffraction spots appear in the inset SAD pattern taken with an aperture that captures both the matrix and the nanoprecipitates. This result suggests no distinguishable difference between the matrix and the nanoprecipitates, owing to their small lattice mismatch. Most of the nanoscale precipitates in this sample is in the range of 5 to 7 nm (Figure 4.8b). The HRTEM image in Figure 4.8c depicts a coherent nanoscale precipitate (circled with the dashed red line) that is embedded in the matrix. No defects or discontinuities in lattice fringes are observed at the matrix/precipitate interface, confirming coherently strained nanoscale endotaxial precipitates.
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Figure 4.8. Electron microscopy of Ag$_{0.11}$Gd$_{0.06}$Sn$_{0.84}$Te specimen. (a) Low-magnification image of the specimen along the [001] zone axis shows even nanoprecipitates in the matrix. The inset shows the corresponding SAD pattern. (b) Histogram of precipitate size for Ag$_{0.11}$Gd$_{0.06}$Sn$_{0.84}$Te. (c) HRTEM image of one of the nanoprecipitates.

Figure 4.9. STEM EDS spectrum image of Ag$_{0.11}$Gd$_{0.06}$Sn$_{0.84}$Te. (a) Low magnification STEM image shows Ag-rich particles in the matrix; (b)-(e) corresponding EDS mapping for elements Ag, Gd, Sn, and Te, respectively. A whiter colour in the element maps corresponds to higher concentrations.
Figure 4.10. STEM EDX spectrum image taken at the matrix and the nanoprecipitate of Ag$_{0.11}$Gd$_{0.06}$Sn$_{0.94}$Te. The matrix is with Sn, Te and a little bit of Gd and Ag, while the precipitate is rich in Ag.

To further demonstrate the homogenous distribution of Gd in SnTe after Ag doping, elemental mapping of Ag$_{0.11}$Gd$_{0.06}$Sn$_{0.94}$Te sample was carried out. The low magnification STEM image in Figure 4.9a shows uniform nanoprecipitates with white contrast, which are proved to be Ag rich area by mapping Ag Figure 4.9b. In contrast, Sn, Te and Gd are uniformly distributed in both nanoprecipitates and the matrix, as shown in Figure 4.9c-e. Similar to the element mapping, the EDS spectra collected from the matrix and nanoprecipitates demonstrate that the matrix is SnTe doped with traces of Gd and Ag, and the nanoprecipitates have more Ag as shown in Figure 4.10.

Figure 4.11 shows the temperature dependence of the thermoelectric properties of Ag$_y$Gd$_{0.06}$Sn$_{0.94}$Te (y = 0-0.15) samples with different Ag content. Their electrical conductivities decrease with increasing temperature, as displayed in Figure 4.11a, indicating
the typical behavior of degenerate semiconductors. For all Ag/Gd codoped samples, their electrical conductivities are much lower than that of undoped SnTe. The room temperature electrical conductivity decreases from ~6 × 10^5 S m\(^{-1}\) for pristine SnTe to ~3 × 10^5 S m\(^{-1}\) for doped counterparts. Moreover, with increase of dopant Ag content, the \(\sigma\) values show a decreasing tendency, followed by increase, which is consistent with the results expected with reduced carrier concentration (Figure 4.7c). It is important to note that the electrical conductivities of \(\text{Ag}_y \text{Gd}_{0.06} \text{Sn}_{0.94}\)Te samples show a turnover at ~723 K, which suggests the occurrence of electron-hole bipolar effects in these samples with lower carrier concentrations at high temperature.\(^{40}\)

Contrast to the behaviour of the electrical conductivity, the Seebeck coefficient (\(\alpha\)) values of Gd/Ag doped samples increase in all temperature ranges without any evidence of deterioration (Figure 4.11b). Moreover, the room temperature Seebeck coefficient gradually increases with increasing Ag fraction, although the reduced \(n\) is expected to suppress the contribution of heavy holes to the Seebeck coefficient due to the higher Fermi level.\(^{40}\) This could be explained if the Gd could widen the band gap of SnTe. We could not resolve the band gap (\(E_g\)) of the \(\text{Ag}_y \text{Gd}_{0.06} \text{Sn}_{0.94}\)Te \((y = 0-0.15)\) samples by diffuse infrared (IR) reflectance spectroscopy, as the present samples are highly self-doped (carrier concentration of ~10\(^{20}\)-10\(^{21}\) cm\(^{-3}\)) due to the intrinsic Sn vacancies. In fact, the band gap is related to the Seebeck coefficient by the Goldsmid relation \(E_g \approx 2e\alpha_{\text{max}}T_{\text{max}}^{189}\). The significant increase in the Seebeck coefficients of doped samples comparing with pristine SnTe suggests that chemical doping effectively broadened the band gap of SnTe. The negligible difference in the Seebeck coefficients of \(\text{Gd}_{0.06} \text{Sn}_{0.94}\)Te and \(\text{Ag}_y \text{Gd}_{0.06} \text{Sn}_{0.94}\)Te \((y = 0-0.15)\) samples demonstrates that Gd is an effective dopant to tune the band gap of SnTe.

Figure 4.11c plots the power factors as a function of temperature for \(\text{Ag}_y \text{Gd}_{0.06} \text{Sn}_{0.94}\)Te \((y = 0-0.15)\). With the benefits of the significant enhancement in the Seebeck coefficient and
electrical conductivity at high temperature, the maximum power factor of ~1800 µW m\(^{-1}\) K\(^{-2}\) was reached in the Ag\(_{0.11}\)Gd\(_{0.06}\)Sn\(_{0.94}\)Te sample at 873 K.

The temperature dependence of the total thermal conductivity and the lattice thermal conductivity of Ag\(_y\)Gd\(_{0.06}\)Sn\(_{0.94}\)Te (y = 0-0.15) is shown in Figure 4.11d-e. The $\kappa_{\text{tot}}$ of all Gd/Ag codoped samples are significantly decreased due to the reduction in $\kappa_{\text{lat}}$. It should be noted that the $\kappa_{\text{lat}}$ values of Ag\(_y\)Gd\(_{0.06}\)Sn\(_{0.94}\)Te samples are still relatively low compared to that of Cd-\(^{40}\) and Hg-\(^{43}\) doped SnTe. Typically, the $\kappa_{\text{lat}}$ of Ag\(_{0.11}\)Gd\(_{0.06}\)Sn\(_{0.94}\)Te at room temperature is 1.8 Wm\(^{-1}\)K\(^{-1}\), which is decreased to ~0.6 W m\(^{-1}\) K\(^{-1}\) at 873 K.

Figure 4.11f presents the temperature dependence of $ZT$ of Ag\(_y\)Gd\(_{0.06}\)Sn\(_{0.94}\)Te (y = 0-0.15). The highest $ZT$ of ~1.1 at 873 K was achieved in Ag\(_{0.11}\)Gd\(_{0.06}\)Sn\(_{0.94}\)Te, which is ~200% improvement over the pristine SnTe. The higher $ZT$ obtained in our work is comparable to the previously reported maximum $ZT$ of Cd-doped SnTe (~1.3 at 873 K), \(^{40}\) Hg-doped SnTe (~1.35 at 910 K),\(^{43}\) and In-doped SnTe (~ 1.1 at 873 K) samples.\(^{39}\)

### 4.4. Conclusions

Lead-free high performance SnTe thermoelectric materials were rationally designed and prepared through chemical doping of Gd and Ag via two steps. The first step is doping Gd into SnTe to effectively reduce the lattice thermal conductivity via introduction of nanoprecipitates. The large mass contrast between the nanoprecipitates and the matrix, together with the increased grain boundaries from mesoscale grains the heat-carrying phonons strongly scattered from nanoscale to mesoscale. The second step is doping Ag into optimized Gd\(_{0.06}\)Sn\(_{0.94}\)Te to improve the Seebeck coefficient and power factor by tuning its composition to reduce the carrier density. The maximum $ZT$ of ~1.1 at 873 K was successfully obtained in Ag\(_{0.11}\)Gd\(_{0.06}\)Sn\(_{0.94}\)Te. Our research highlights the potential of SnTe-based thermoelectric materials by
engineering their compositions to tune electrical conductivity, Seebeck coefficient and thermal conductivity, as alternatives of lead chalcogenides in near future.

**Figure 4.11.** Thermoelectric properties as a function of temperature for $\text{Ag}_x\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$: (a) electrical conductivity; (b) Seebeck coefficient; (c) power factor; (d) total thermal conductivity; (e) lattice thermal conductivity; (f) $ZT$. 
Chapter 5. Band Structure Engineering for SnTe: Temperature Dependence of Self-Contribution and Synergy of Resonance Levels and Valence Band Convergence via Q/In (Q = Mg, Ag, Bi) Co-Doping

5.1. Introduction

Recent studies have significantly demonstrated that SnTe could be a promising thermoelectric material through the introduction of resonant levels (In dopant) \(^{39,41,58,190}\), valence band convergence (Cd\(^{40-41}\), Mg\(^{44}\), Hg\(^{43}\), Ag\(^{46,58}\), and Mn\(^{174}\) dopants), and optimization of the carrier concentration (Bi, Sb, and Ga dopants)\(^{43,47,191}\). Zhang et al.\(^{39}\) reported that In is an effective dopant for creating resonance levels around the Fermi level inside the valence band. With the benefit of valence band convergence via Mg doping, a high \(ZT\) of 1.2 has been achieved at 860 K\(^{44}\). It is important to note that the formation of a resonance state in the valence band significantly enhances the Seebeck coefficient of SnTe at low temperature\(^{19,106}\). In addition, the convergence of the valence band widens the band gap and lowers the energy separation, which improves the Seebeck coefficient at high temperature by improving the electronic density of states and inhibiting bipolar conduction\(^{40}\). Thus, it is a significant advance to introduce the synergetic effects of resonance levels and valence band convergence to improve the Seebeck coefficient and thermoelectric performance over a broad temperature range. Moreover, it has been demonstrated that at room temperature the \(\Sigma\) band rarely contributed to the electrical transport, but at high temperature (\(i.e., > 800\) K), additional heavy holes were involved to the enhancement of the Seebeck coefficient\(^{5,70}\). The temperature-dependent evolution of \(\Sigma\) band contribution, however, to electrical transport and its relationship to the Seebeck coefficient have not been fully investigated and understood.
In this work, neutron and synchrotron powder diffraction measurements were applied to pristine SnTe to reveal its temperature-dependent $\Sigma$ band contribution to its Seebeck coefficient, which indicates that additional carriers with high effective mass were generated in heavy-hole valence band above 493 K. These “heavy” carriers contributed to the electrical transport, and played a significant role in the enhancement of the Seebeck efficient at high temperature ($>$ 493 K). Moreover, the coexistence of resonant levels, band convergence, and/or the carrier concentration optimization induced by Mg&In, Ag&In and Bi&In co-doping has synergistically contributed to a large improvement in the Seebeck coefficients of SnTe-based materials over a wide temperature range from 323 to 873 K. In addition, the atomic scale point defects, the nanoscale elongated screw dislocations with random directions, and the microscale grain boundaries caused by the sintering efficiently scatter a wide spectrum of heat-carrying phonons, leading to a remarkable reduction in the lattice thermal conductivity. With the benefit of these factors, a high $ZT$ of ~1 at 873 K was obtained for Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te sample, being 80% higher than that of pristine SnTe. The average $ZT$ in the range of 323 to 873 K is considerably improved 2.6 times, i.e., from ~0.14 for pristine SnTe to ~0.51 for Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te.

5.2. Experimental section

5.2.1. Materials

Tin (Sigma Aldrich, 99.8%), tellurium (Alfa Aesar, 99.999+%), indium (Sigma Aldrich, 99.99%), magnesium (Sigma Aldrich, 99+%), silver (Sigma Aldrich, 99.9+%), and bismuth (Alfa Aesar, 99.99+) were used for synthesis without any further purification.

5.2.2. Sample preparation

Ingots (~6 g) of Q$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te ($Q = Mg, Ag,$ and Bi; $x = 0, 0.01, 0.02, 0.03,$ and 0.04) were synthesized by mixing appropriate ratios of high-purity Sn, Te, In, Mg, Ag and Bi in quartz tubes in an argon filled glovebox, and put inside 15-mm-diameter quartz tubes in an argon
Chapter 5. Band Structure Engineering for SnTe: Temperature Dependence of Self-Contributions and Synergy of Resonance Levels and Valence Band Convergence via Q/In (Q = Mg, Ag, Bi) Co-Doping

filled glove box. The tubes were flame-sealed under vacuum and then placed in larger 26-mm-diameter quartz tubes, which were evacuated and flame-sealed again. The outer tube was used to protect the crystals from oxidation by air, because the inner tube could break due to the considerable difference in thermal expansion between the crystals and quartz. The double sealed quartz was slowly heated to 1273 K in 10 h, held at this temperature for 8 h, and then cooled to room temperature by turning off the furnace power. In a typical experiment, 2.2504 g Te, 2.0308 g Sn, 0.0064 g Mg and 0.0304 g In were used to prepare ~ 4.318 g ingots of Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te sample. The resultant ingots were ground into fine powders and then sintered by the spark plasma sintering (SPS) method at 773 K for 5 min in a 20 mm-diameter graphite die under an axial compressive stress of 50 MPa under the vacuum. Highly dense (>95% of theoretical density) of pellets were obtained, as shown in Table 5.1.

The theoretical densities $d(t)$ of Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, and Bi$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te samples were calculated using the law of mixtures, which can be expressed by Equation (5-1). $^{41}$

$$d(t) = \sum_{i=1}^{n} t_i A_i \text{Te}$$

(5-1)

where $A_i$ represents the cationic element, $n$ is total number of the cationic elements, $t_i$ is the volume fraction of the binary telluride formed between the $i_{th}$ cationic and Te. The following theoretical densities for binary tellurides were used in the calculation: 6.532 g cm$^{-3}$ for SnTe (PDF# 65-9611), 3.810 g cm$^{-3}$ for MgTe (PDF# 50-1307), 6.831 g cm$^{-3}$ for InTe (PDF# 65-5755), 7.180 g cm$^{-3}$ for AgTe (PDF# 27-0623), and 8.250 g cm$^{-3}$ for BiTe (PDF# 15-0820). Typically, $d$ (0.01) for Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te can be calculated by $d(0.01) = 3.810 \times 0.01 \div 2 + 6.831 \times 0.01 \div 2 + 6.532 \times (1-0.01) = 6.52$ g cm$^{-3}$. 

100
Table 5.1. Densities of the $\text{Mg}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$, $\text{Ag}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$ and $\text{Bi}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$ samples.

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<th>$D_S$, g cm$^{-3}$</th>
<th>$D_R$, %</th>
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<td>6.317</td>
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<td>6.368</td>
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<td>$x=0.005$</td>
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<td>$x=0.01$</td>
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<tr>
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<td>$x=0.04$</td>
<td>6.572</td>
<td>6.423</td>
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</table>

5.2.3. Characterization

Samples ground with an agate mortar were used for PXRD characterization. The powder diffraction patterns were obtained with Cu $K_a$ ($\lambda = 1.5418$ Å) radiation in a reflection geometry on an Inel diffractometer operating at 40 kV and 25 mA, and equipped with a position-sensitive detector.

The neutron powder diffraction patterns were collected on the high-resolution powder diffractometer ECHIDNA (Australian Nuclear Science and Technology Organization) with a wavelength of 1.6215 Å. 3.5 g of SnTe powder was packed in a cylindrical alumina holder.
with a diameter of 8 mm, and heated from 300 to 700 K under vacuum on a cylindrical computer controlled furnace. The collecting time for one pattern was around 2 h over a wide 2-theta range from 6.5° to 164°. Rietveld refinements of the structure were carried out using the FULLPROF program package.

The Synchrotron powder diffraction patterns were collected on the Powder Diffraction beamline at the Australian Synchrotron. Two wavelengths (\( \lambda = 0.59002 \) Å and 0.6885 Å) were used for the synchrotron powder diffraction experiments. The short wavelength was used for pristine SnTe, and the longer one was selected for Mg&In, and Ag&In co-doped samples. 4 mg of ground SnTe powder was packed in cylindrical quartz capillary tubes with a diameter of ~0.3 mm, and heated under argon atmosphere from room temperature to 873 K. The collecting time for one pattern was around 10 min over a wide 2-theta range from 3° to 83°.

STEM and energy dispersive spectroscopy (EDS) were carried out in a JEOL JEM-ARM 200F microscope operated at 200 kV. The thin TEM specimen was prepared by focused ion beam (FIB) at a moderate voltage (16 keV), which was then followed by cleaning at a lower voltage (5 keV) to remove contaminants.

The measurement of room-temperature Hall coefficient was carried out on a Physical Properties Measurements System (Quantum Design PPMS-9) by using the four-contact Hall-bar geometry.

The obtained highly dense pellets were cut into bars with a dimension of \(-6 \times 2 \times 2 \) mm\(^3\) to be used for simultaneous measurement of the Seebeck coefficient and the electrical conductivity on an Ozawa RZ2001i (Japan) instrument under an argon atmosphere from 323 to 873 K. The samples were coated with a thin (~0.1 - 0.2 mm) layer of boron nitride to protect the instrument. The left parts of pellets were cut and polished into \(\varnothing (6-10) \times 1 \times 1 \) mm\(^3\) disks for the thermal diffusivity coefficient \((D)\) measurements using the laser flash
diffusivity method on the LFA457 instrument (Germany). The samples were coated with a thin layer of graphite to minimize errors from the emissivity of material. The specific heat capacity \(C_p\) was indirectly derived from a representative sample (DSC 204) over the range of 323–573 K, and then simulated to 873 K based on the Debye module. The density \(d\) was measured by the Archimedes method. The electron contribution is assessed by the Wiedemann-Franz law, \(\kappa_{\text{ele}} = L\sigma T\), where \(L\) is Lorenz number, \(\sigma\) is electrical conductivity, and \(T\) is absolute temperature.\(^{41}\) In this work, \(L\) is evaluated from the formula \(L = 1.5 + \exp\left[\frac{-|\alpha|}{116}\right]\), where \(L\) and \(\alpha\) are in \(10^{-8}\) W Ω K\(^{-2}\) and in µV K\(^{-1}\), respectively.\(^{115}\)

5.3. Results and discussion

5.3.1. Temperature Dependence of \(\Sigma\) band contribution to the Seebeck coefficient

As demonstrated previously, the \(\Sigma\) valence band contributes additional carriers to electrical transport at elevated temperature, leading to a significant enhancement of the Seebeck coefficient, as shown in Figure 5.1a.\(^5\),\(^70\) In order to fully understand the temperature-dependent evolution of \(\Sigma\) band contribution to electrical transport and its relationship to the Seebeck coefficient, the \textit{in situ} neutron and synchrotron powder diffraction measurements were carried out for pristine SnTe over a wide temperature range.

The neutron powder diffraction (PND) patterns were collected from 300 to 700 K (Figure 5.1b), and the corresponding unit cell volumes as a function of temperature are shown in Figure 5.1c. It can be seen that the unit cell volume grows larger as the temperature increases; however, the enlargement is diminished above 493 K. Specifically, the room-temperature unit cell volume is 251.31 Å\(^3\), it quickly increases to 254.10 Å\(^3\) at 483 K, and then slowly rises to 254.78 Å\(^3\) as the temperature increases to 700 K. This crossover temperature is also confirmed by the derivative of the unit cell volume with respect to the temperature, as shown in the inset (Figure 5.1c). According to the Dulong-Petit law plot based on the thermal expansion, the deviation of the unit cell volume could be ascribed
Figure 5.1. (a) Schematic diagram of the carriers transport of SnTe at room temperature and high temperature among the conduction band (CB), light-hole valence band (VBL), and heavy-hole valence band (VBΣ); (b) Neutron powder diffraction patterns for pristine SnTe at 300 - 700 K; (c) Corresponding Rietveld refined unit cell volume (V) as a function of temperature as it is increased in (b). Inset is the derivative of the unit cell volume with respect to temperature, presenting a downturn point at 493 K. The red line is the theoretical unit cell volume according to the Dulong-Petit law; values from previous reports of the temperature-dependent Hall coefficient are also presented; (d) Synchrotron powder diffraction patterns for pristine SnTe at 303 - 873 K; (e) Enlarged patterns in the 2-theta range of 10.5˚ - 10.8˚ for peak (200) in (d). Inset is corresponding NPD enlarged patterns for peak of (200) in (b).
to the intrinsic structural transformation of SnTe, which can be also confirmed by the endothermic peak of DSC analysis around 507 K (Figure 5.2). It is interesting to note that this discrepancy has also been observed in T-dependent Hall coefficients measurement.40 A similar crossover peak, around 523 K, was observed in the $R_H-T$ plot, which is ascribed to the presence of the heavy-hole valence band on the contribution of the electrical transport. Thus, one of the possible mechanisms for this deviation of the unit cell volume based on thermal expansion is the onset of the $\Sigma$ band to electrical transport, indicating the potential existence of valence bands convergence at elevated temperature.$^5,70$ In addition, the in situ synchrotron powder diffraction (SPD) patterns are collected over a wide temperature range from 303 to 873 K as shown in Figure 5.1d. As expected, the synchrotron diffraction presents higher resolution and it is able to distinguish the peak shifting of SnTe comparing to the neutron powder diffraction. For example, the peak of (200), which is located at the 2-theta of ~10.71° at 303 K, gradually shifts to smaller angles ~10.69°, 10.67°, 10.64°, 10.61° and 10.58° when the temperature increases from 303 K to 373, 523, 673, 773, and 873 K due to the thermal expansion (Figure 1e), which is difficult to be separated from the neutron diffraction patterns. It is interesting to note that the relative intensity of the peak of (200) presents a double increase above 523 K. Such abnormal intensity increase is observed in all the other peaks above 523 K. The peak intensity is kept when the samples are cooled from 523 K to the room temperature (Figures 5.3-5.4), which indicates that SnTe powders undergo an irreversible grain recrystallization and growth above 523 K. The abnormal intensity increase is ascribed to the introduction of strains during the preparation of SPD powders. The strain is released as the temperature increases, which promotes the grain growth, as shown in Figure 5.2. We select one sintered bulk, and cut it to two parts. One of these two parts are ground into fine powders with an agate mortar around 30 min and the operation process is similar to the preparation of SPD powders. It can be seen that one endothermic peak around 507 K is
Figure 5.2. DSC curves of SnTe powders and bulk. Powder1-1cycle: powders are heated once; Powder1-2cycle: powders are heated twice; Powder2-1cycle: the twice-heated powders are ground again, and heated once; Powder2-2cycle: the ground twice-heated powders are heated again. The results demonstrate that in comparison with bulk sample, the introduction of strains in powders induces additional thermal absorption as temperature elevated, which leads to the abnormal intensity increase of SPD patterns above 523 K (Figure 5.1d-e). Typically, the temperature of strain release is above 478 K. The endothermic peak around 507 K for all the samples is mainly attributed to the structural transformation of SnTe due to the onset of $\Sigma$ valence band (Figure 5.1b-c).

detected for pristine SnTe bulk, which is mainly attributed to the structural transformation of SnTe due to the onset of $\Sigma$ valence band (Figure 5.1b-c). Two endothermic peaks, around 478 and 507 K, are detected in the pristine SnTe powders (red solid line), however, only one peak (507 K) is left when they are heated again (red dot line). This abnormal behavior of DSC can be also observed after these twice heated powders are ground and heated again (blue solid and dot lines), which indicates that in comparison with bulk-specimen, the introduction of strain in powder-specimen induces additional thermal absorption as temperature elevated. It is supported by the abnormal intensity increase of SPD patterns.
Figure 5.3. Synchrotron powder diffraction patterns for Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te over the temperature range of 333 - 673 K for (a) 10-40°, (b) 12.4-12.6°, (c) 17.5-17.9°, (d) 21.6-21.9°, and (e) 25-15.3°.

Figure 5.4. Synchrotron powder diffraction patterns for Ag$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te over the temperature range of 318 - 673 K for (a) 10-40°, (b) 12.4-12.6°, (c) 17.5-17.9°, (d) 21.6-21.9°, and (e) 25-15.4°. The red pattern was obtained at 318 K in the cooling path from 673 K to room temperature.

above 523 K (Figure 5.1d-e, Figures 5.3-5.4). Therefore, the abnormal grain growth above 523 K is mainly attributed to the strain release as temperature elevated.

According to the Mott formula, the Seebeck coefficient can be defined by Equation (5-2):

$$\alpha = \frac{8\pi^2 k_B^2}{3 e h^2} m^* T \left( \frac{\pi}{3n} \right)^2$$  (5-2)
where $k_B$, $e$, $h$, $m_d^*$ are the Boltzmann constant, carrier charge, Plank constant, and total DOS effective mass respectively. For a given carrier concentration, the Seebeck coefficient can be estimated by total DOS effective mass, $m_d^*$, which can be defined in Equation (5-3):\(^4,8\)

$$m_d^* = N_V^{\frac{2}{3}}m_b^*$$  \hspace{1cm} (5-3)

where $N_V$ is the number of degenerate carrier pockets and $m_b^*$ is the average DOS effective mass for each pocket (single-band DOS effective mass). When the $\Sigma$ valence band contributes to electrical transport, the Seebeck coefficient will be enhanced due to the dramatically higher effective mass of carriers in the $\Sigma$ valence band by a factor of $N_V^{\frac{2}{3}}$, where $N_V$ is 4 for the L band and increases to 12 for the $\Sigma$ band.\(^8\)

Figure 5.5. Seebeck coefficient as a function of temperature for pristine SnTe. Left inset is a schematic illustration of the distribution of holes at low temperature, which indicates that the holes are mainly located in the L valence band; right inset is a schematic illustration of the distribution of holes at high temperature, indicating that additional holes are generated from the $\Sigma$ valence band as the temperature increases above 493 K.
Figure 5.5 presents the Seebeck coefficient as a function of temperature for pristine SnTe. The $\alpha$ values slowly increase from $\sim$17 $\mu$V K$^{-1}$ at room temperature to $\sim$27 $\mu$V K$^{-1}$ at 473 K, and then drastically increase to $\sim$127 $\mu$V K$^{-1}$ as the temperature increases to 873 K. This increased enhancement of the Seebeck coefficient is mainly ascribed to the contribution of the higher effective mass of carriers to the electrical transport at elevated temperature (Figure 5.1). The inset is a schematic illustration of the distribution of carriers as the temperature increases. Additional carriers with higher effective mass are generated in $\Sigma$ band arising from the thermal excitation of holes from the L to $\Sigma$ valence band above 493 K.

5.3.2. Synergy of Resonance Levels, Valence Band Convergence and carrier concentrations via Mg&In, Ag&In and Bi&In Co-doping

Besides the temperature dependence of $\Sigma$ band contribution to Seebeck coefficient, the L and $\Sigma$ valence bands can be further converged by properly doping due to the lowered Fermi level. In this part, the band structure of SnTe was engineered by co-doping with Mg&In, Ag&In and Bi&In, which leads to a notable enhancement of the thermoelectric performance over a wide temperature range. All three-types of doped samples are characterized as single cubic SnTe with the $Fm-3m$ space group, as shown in XRD patterns in the Figure 5.6, Figure 5.7, and Figure 5.8.

The Seebeck coefficient as a function of temperature for $\text{Mg}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$, $\text{Ag}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$, and $\text{Bi}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$ are presented in Figure 5.9a-c, respectively. It can be seen that the $\alpha$ values of Mg&In and Ag&In co-doped samples are strongly dependent on the dopant concentration, and the room-temperature values are notably improved 2 - 4 times in comparison with that of pristine SnTe. This significant improvement of room-temperature Seebeck coefficients is mainly attributed to the introduction of resonant levels in the valence band via In doping. $^{39, 41}$ This resonant levels, which are also observed in Tl doped PbTe and Sn doped Bi$_2$Te$_3$ samples, $^{19, 106, 110}$ can improve the Seebeck coefficient through two
Figure 5.6. XRD patterns of Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te ($0 \leq x \leq 0.04$) samples.

Figure 5.7. XRD patterns of Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te ($0 \leq x \leq 0.04$) samples.
mechanisms, \textit{i.e.}, (1) electrons in extended states (plane-wave-like wavefunction created by In impurities) can carry electricity and heat, and contribute to the Seebeck coefficient in a nearly temperature-independent way; and (2) resonant scattering presents a strong electron energy filtering effect, and increase the Seebeck coefficient at low temperature where the electron-phonon interactions are weaker.\textsuperscript{106} In addition, the $\alpha$ values present a significant improvement over a wide temperature range from 323 to 873 K, which provides an evidence of the narrowed energy separation at low temperature through Mg and Ag doping.\textsuperscript{44, 46, 58} In contrast to the cases of Mg&In and Ag&In co-doping, the $\alpha$ values are dramatically increased for Bi&In co-doped samples when compared with pristine SnTe at high temperature (\textbf{Figure 5.9c}).

To shed more light on the doping effects of the different combined dopants (Mg&In, Ag&In and Bi&In) on the Seebeck coefficients, we selected the samples with 3% doping

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.8}
\caption{XRD patterns of $\text{Ag}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$ ($0 \leq x \leq 0.04$) samples.}
\end{figure}
Chapter 5. Band Structure Engineering for SnTe: Temperature Dependence of Self- Contribution and Synergy of Resonance Levels and Valence Band Convergence via Q/In (Q = Mg, Ag, Bi) Co-Doping

Figure 5.9. Seebeck coefficient as a function of temperature for (a) Mg\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te; (b) Ag\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te; (c) Bi\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te. (d) Comparison of temperature-dependent Seebeck coefficient for pristine and doped samples with 3% doping concentration. The inset of Figure (d) is the Rietveld refined unit cell volume as a function of temperature from SPD (Mg&In and Ag&In co-doped SnTe, \(\lambda = 0.6885\) Å) and NPD (pristine SnTe, \(\lambda = 1.62150\) Å). (e) Room-temperature Pisarenko plot for Mg\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te, Ag\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te, and Bi\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te samples in comparison with reported data on In-doped,\textsuperscript{39} Mg-doped,\textsuperscript{44} Ag-doped,\textsuperscript{58} Bi-doped,\textsuperscript{47} undoped,\textsuperscript{38, 59} and In&Cd&CdS-alloyed\textsuperscript{41} SnTe. The solid line is based on the single valence band (VBM) model.\textsuperscript{39} (f) Carrier concentration and carrier mobility for pristine and doped samples with 3% doping concentration. The top inset is carrier concentration as a function of doping concentration for Mg\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te, Ag\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te, and Bi\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te samples. The bottom inset is carrier mobility as a function of doping concentration for these samples.

concentration for comparison in Figure 5.9d, since the thermoelectric properties were optimized and achieved their maximum values at 3 mol % doping fraction. It can be seen that the enhancement of Seebeck coefficients for Mg\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te and Ag\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te are similar over a broad temperature range due to the same introduction of resonant levels in the valence band via In doping, and the similar convergence of the valence band via Mg and Ag doping, as mentioned above. The improvement, however, in the case of
Bi\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te, is better identified above 473 K due to the pronounced reduction of the carrier concentration by Bi doping, which will be discussed later. Specifically, at 323 K, the Seebeck coefficients of pristine SnTe, Mg\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te, Ag\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te, and Bi\textsubscript{0.015}In\textsubscript{0.015}Sn\textsubscript{0.97}Te are ∼17, 76, 74, and 66 μV K\textsuperscript{-1}, and they increase to ∼127, 147, 137, and 160 μV K\textsuperscript{-1} at 873 K, respectively.

As mentioned above, for pristine SnTe the intrinsic T-dependent contribution of Σ valence band to the electrical transport above 493 K is observed. This behavior still exists after chemical doping. The Rietveld refined unit cell volumes of doped samples from their SPD patterns (Figures 5.3 and 5.4) as a function of temperature are shown as inset in Figure 5.9d. It can be seen that the unit cell volumes of doped samples exhibit the similar crossover temperature (∼493 K) with a slight curvature comparing with that of pristine SnTe, which provides the evidence of the presence of intrinsic structural transformation related to the onset of Σ valence band to electrical transport. It is important to note that, although the intrinsic T-dependent contribution of Σ valence band to the electrical transport presents degeneration after chemical doping, the Seebeck coefficient of co-doped SnTe shows the improvement over a broad temperature range because of the synergy of resonance levels,\textsuperscript{39,41,58} valence band convergence\textsuperscript{44,46,58} and carrier concentration\textsuperscript{43,47} via Mg&In, Ag&In and Bi&In co-doping (Figure 5.9a-c).

To further understand the change in the Seebeck coefficient due to three-types of dopants, it is significant to compare the room temperature α versus n plots for Mg\textsubscript{x/2}In\textsubscript{x/2}Sn\textsubscript{1-x}Te, Ag\textsubscript{x/2}In\textsubscript{x/2}Sn\textsubscript{1-x}Te and Bi\textsubscript{x/2}In\textsubscript{x/2}Sn\textsubscript{1-x}Te with the well-established Pisarenko plot obtained from a single valence band model (VBM).\textsuperscript{39} As shown in Figure 5.9e, the plots of pristine SnTe in this work, together with those of previously reported Bi-doped\textsuperscript{47} and undoped\textsuperscript{38,59} SnTe exactly follow the Pisarenko plot. The Seebeck coefficients of the Mg&In, Ag&In, and Bi&In co-doped SnTe in this work are much higher than the theoretical prediction, however,
which is similar to the results for Mg-44, Ag-58, and In-doped39 SnTe, but presents higher enhancement of the Seebeck coefficients than those of the individual doping cases. These higher enhancements are ascribed to the synergistic effects arising from (i) the resonant level introduced by In-dopant, (ii) the valence band convergence induced by Mg and Ag dopants, and/or (iii) the carrier concentration optimization by Mg-, Ag-, and Bi-doping.

The room temperature carrier concentration for the three-types of dopants with 3% doping concentration is shown in **Figure 5.9f**. At the identical doping fraction, the introduction of Mg&In and Ag&In co-dopants increases the carrier concentration from the $2.45 \times 10^{20}$ cm$^{-3}$ for pristine SnTe to $5.85 \times 10^{20}$ and $5.60 \times 10^{20}$ cm$^{-3}$ for Mg&In and Ag&In, respectively, but the introduction of Bi&In co-dopants leads to the reduction in $n$ value to around $1.67 \times 10^{20}$ cm$^{-3}$. The corresponding doping concentration-dependent carrier concentrations for Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, and Bi$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te are presented in the top inset. It is well known that pristine SnTe has a high hole concentration of $\sim 1.8 \times 10^{20}$ cm$^{-3}$ at room temperature because of the presence of intrinsic Sn vacancies.39-40, 47 In the case of the Mg&In and Ag&In co-doped samples, their room-temperature $n$ roughly increases with increasing doping concentration, which is consistent with expectation of the electron acceptor roles of In,39 Mg,44 and Ag58 dopants in SnTe (**Figure 5.9f**). In contrast, the carrier concentrations of Bi&In co-doped samples show a significant reduction at all doping concentrations, which is attributed to the nature of the electron donor role of Bi dopant in SnTe.47 It should be noted that the effects of the different types of dopants on the carrier concentration of SnTe are not very clear as yet. The room temperature carrier mobility ($\mu$) of three-types of dopants in **Figure 5.9f** shows a significant reduction, *i.e.*, from 162.75 cm$^2$ V$^{-1}$ s$^{-1}$ for pristine SnTe to 38.33, 36.50, and 52.54 cm$^2$ V$^{-1}$ s$^{-1}$ for Mg&In Ag&In, and Bi&In doped SnTe, respectively. The bottom inset in **Figure 5.9f** shows the room temperature carrier mobility as a function of doping concentration for Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te,
Figure 5.10. Electrical conductivity as a function of temperature for (a) Mg\(_{x/2}\)In\(_{x/2}\)Sn\(_{1-x}\)Te; (b) Ag\(_{x/2}\)In\(_{x/2}\)Sn\(_{1-x}\)Te; (c) Bi\(_{x/2}\)In\(_{x/2}\)Sn\(_{1-x}\)Te. Comparison of the temperature dependence of the electrical conductivity for the pristine and doped samples with 3\% doping concentration (d).

and Bi\(_{x/2}\)In\(_{x/2}\)Sn\(_{1-x}\)Te samples. In all cases, the carrier mobility at room temperature decreases as the doping fraction increases due to the enhanced ionization impurity scattering, and there are only minor differences between the three-types of dopants which can be ascribed to the fact that the convergence of valence band (separate pockets of Fermi surface with the same energy) introduces the large density-of-states effective mass without explicitly reducing the carrier mobility.\(^4\)
The electrical conductivity ($\sigma$) as a function of temperature for the Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, and Bi$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te samples are presented in Figure 5.10a-c, respectively. It clearly shows that the electrical conductivity of all the samples decreases steadily with increasing temperature up to 873 K, which is typical metallic conduction due to the high hole densities in these samples. With increasing doping concentration, the room temperature $\sigma$ values drastically decrease for all samples, which should be ascribed to the notable reduction in their carrier mobility, as shown in the inset in Figure 5.9f. A comparison of the temperature-dependent electrical conductivity for pristine and doped samples with 3% doping concentration is shown in Figure 5.10d. With identical doping fractions, the Bi&In co-doped samples have the lowest electrical conductivities due to the noticeable reduction in the carrier mobility and carrier concentration, and the Mg&In and Ag&In co-doped samples have intermediate values between the Bi&In co-doped and pristine samples arising from the increase of the carrier concentration (Figure 5.9f). Specifically, the room-temperature electrical conductivity of SnTe is $\sim 63.9 \times 10^4$ S m$^{-1}$, and it decreases to $\sim 35.9$, 28.9, and $13.2 \times 10^4$ S m$^{-1}$ for Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te, Ag$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te, and Bi$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te, respectively.

Because of the increased Seebeck coefficients due to the synergistic effects of the resonant level, valence band convergence, and/or the carrier concentration optimization, the power factors of all the doped samples are dramatically enhanced over a broad temperature range compared with pristine SnTe, as shown in Figure 5.11a-c. Figure 5.11d presents the comparison of their power factors at the identical doping fraction ($x = 0.03$) with previously reported values. Obviously, the co-doping of Mg and In results in a higher improvement of the electrical transport properties, and leads to a higher power factor compared to the cases of doping with Ag&In and Bi&In. In addition, previously reported In- and Mg-doped, In& Cd&CdS-,$^{44}$ Cd&CdS-,$^{40}$ Bi&HgTe-,$^{43}$ and Bi& SrTe-alloyed$^{58}$ samples are also
Figure 5.11. Power factor as a function of temperature for (a) Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te; (b) Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te; (c) Bi$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te. A comparison of temperature dependence of power factors for pristine and doped samples with 3% doping concentration is presented in (d). Previously reported In-doped,$^{39}$ Mg-doped,$^{44}$ In&Cd&CdS-alloyed,$^{41}$ Cd&CdS-alloyed,$^{40}$ Bi&HgTe-alloyed,$^{43}$ and Bi&SrTe-alloyed$^{47}$ samples are also presented.

compared. These previous works demonstrate that In contributes to the enhancement of the power factor at low temperature, and Mg contributes to the power factor at high temperature. In our case, the power factor is improved over the entire temperature range, leading to noticeably high average electrical transport properties for SnTe. Specifically, the average power factor of pristine SnTe is $\sim 0.73 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ from 300 to 873 K, it increases to $\sim 1.38 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ and $\sim 1.51 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ for Mg- and In-doped samples,
Figure 5.12. Thermal diffusivity as a function of temperature for (a) Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te; (b) Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te; (c) Bi$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te. Comparison of temperature dependence of the thermal diffusivity for pristine and doped samples with 3% doping concentration (d).

respectively, and finally reaches $\sim 2.43 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ after combining Mg and In co-dopants (Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te). Moreover, this average power factor for Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te is also higher than those reported values ($\sim 2.0 - 2.3 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$) for In&Cd&CdS$^{41}$, Bi&HgTe$^{43}$ and Bi&SrTe-alloyed$^{47}$ samples.

Figure 5.12a-c shows the thermal diffusivity ($D$) as functions of temperature for Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te and Bi$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, respectively. It can be seen that the thermal conductivity decreases with both increasing temperature and doping fraction.
Figure S13. Heat capacity as a function of temperature for (a) Mg\_\frac{x}{2}In\_\frac{x}{2}Sn\_1\_xTe; (b) Ag\_\frac{x}{2}In\_\frac{x}{2}Sn\_1\_xTe; (c) Bi\_\frac{x}{2}In\_\frac{x}{2}Sn\_1\_xTe. Comparison of temperature dependence of the heat capacity for pristine and doped samples with 3% doping concentration (d).

Moreover, the temperature dependence of thermal diffusivities seem to reach the similar low values at heavier doping fraction, i.e., $x = 0.03$ (Figure 5.12d). The heat capacity ($C_p$) as a function of temperature for Mg\_\frac{x}{2}In\_\frac{x}{2}Sn\_1\_xTe, Ag\_\frac{x}{2}In\_\frac{x}{2}Sn\_1\_xTe and Bi\_\frac{x}{2}In\_\frac{x}{2}Sn\_1\_xTe is presented in Figure 5.13a-c. All the heat capacities range from 0.21 to 0.24 J g\(^{-1}\) K\(^{-1}\) with temperature increase from 323 to 873 K. The thermal diffusivities with 3% doping concentration for three-typed dopants show the similar values over a broad temperature range (Figure 5.12d).
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Figure 5.14. Total thermal conductivity and lattice thermal conductivity as a function of temperature for (a) Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te; (b) Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te; (c) Bi$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te. Comparison of temperature dependence of the lattice thermal conductivity for pristine and Mg&In, Ag&In and Bi&In co-doped samples with 3% doping concentration, with those of previously reported In-doped, Mg-doped, Bi&HgTe-alloyed, In&Cd&CdS-alloyed, Cd&CdS-alloyed, and Bi&SrTe-alloyed samples.

Figure 5.14a-c shows the total thermal conductivity ($\kappa_{tot}$) and lattice thermal conductivity ($\kappa_{lat}$) as functions of temperature for Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te and Bi$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, respectively. The $\kappa_{tot}$ exhibits decreasing trend as the doping concentration increases for all three-types of dopants. Typically, the total thermal conductivity of pristine SnTe is $\sim$2.50 - 9.76 W m$^{-1}$ K$^{-1}$ over the temperature range of 323 - 873 K, which dramatically reduces to $\sim$2.41 - 4.15 W m$^{-1}$ K$^{-1}$ after doping 3% fraction of Mg&In, Ag&In and Bi&In. The reduction...
Figure 5.5. Electron microscope images of the Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te specimen. (a) Low-magnification image of the specimen along the [0 0 1] zone axis, showing large misfit dislocations (white arrows). The inset is the corresponding SAED pattern; (b) Enlarged view of the boxed region in (a), presenting numerous nanoscale elongated dislocations; (c) Histogram of the elongated dislocation size. The inset is the corresponding area used to count the dislocation sizes. (d) HRTEM image of a typical nanoscale elongated dislocation; (e) IFFT images of the boxed region in (d), showing a typical screw dislocation. A schematic illustration of the screw dislocations is shown in (f).

The decrease in their $\kappa_{\text{tot}}$ for Mg&In and Ag&In doped samples is mainly ascribed to the decreased lattice thermal conductivity, while for the Bi&In doped samples, it is mainly caused by the decrease in the carrier concentration (Figure 5.9f). Unlike the regular decrease of $\kappa_{\text{tot}}$, however, the temperature dependence of $\kappa_{\text{lat}}$ is irregular and independent of doping concentration or dopant types. Moreover, the $\kappa_{\text{lat}}$ values are almost half of the $\kappa_{\text{tot}}$ values for all the samples, which indicate the dominance of electron-phonon interactions for SnTe materials. It is worth noting that the lattice thermal conductivity of 3% Mg&In doped samples at 873 K is ~0.54 W m$^{-1}$K$^{-1}$, which is very close to its theoretical minimum thermal conductivity, $\kappa_{\text{min}}$ (~ 0.5 W m$^{-1}$K$^{-1}$), for SnTe-based materials.$^{188}$ This value is also lower than the reported values.
Figure 5.16. Element distribution for $\text{Mg}_{0.015}\text{In}_{0.015}\text{Sn}_{0.97}\text{Te}$, in which Sn, Te, In, and Mg are uniformly distributed in the bulk.

Figure 5.17. (a),(c) HRTEM images of typical nanoscale elongated dislocations; (b),(d) IFFT images of the boxed region in (a) and (c), respectively, showing the typical screw dislocations.

$(0.58 - 0.6 \text{ W m}^{-1} \text{ K}^{-1})$ for Bi&HgTe,\textsuperscript{43} In&Cd&CdS,\textsuperscript{41} and Cd&CdS-alloyed\textsuperscript{40} SnTe samples, as shown in Figure 5.14d.
To understand the origin of the ultralow lattice thermal conductivity, the microstructure and chemical composition of the Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te sample was investigated by TEM, STEM, and EDS, as shown in **Figure 5.15a-f.** **Figure 5.15a** shows a low-magnification image along the [0 0 1] orientation with some big misfit dislocations. These big misfit dislocations are random in length, around 100 - 500 nm. The inset of **Figure 5.15a** is the selected area electron diffraction (SAED) pattern of the corresponding area, showing perfect single cubic SnTe phase. **Figure 5.15b** shows an enlarged view of the boxed region in **Figure 5.15a,** presenting a high density of nanoscale elongated dislocations with random orientations. The size of the elongated dislocations along the length direction is around 6 - 14 nm (**Figure 5.15c**). **Figure 5.15e** shows the high resolution transmission electron microscope (HRTEM) image of a typical nanoscale elongated dislocation, which identified by the inverse fast Fourier transform (IFFT) image (**Figure 5.15e**), indicating the existence of the screw dislocation. Schematic illustration of a typical screw dislocation is shown in **Figure 5.15f.** Other typical screw dislocations and elements distribution are displayed in the **Figure 5.16** and **Figure 5.17.**

The above high-density elongated screw dislocations with random orientations can provide intensive scattering for phonons along different directions. Moreover, the size of nanoscale dislocations plays a significant role in the propagation pathways of medium wavelength phonons and thus in achieving effective nanoscale phonon scattering. In addition, the introduction of point defects by co-dopants (Mg&In, Ag&In and Bi&In) and grain boundaries by sintering also act as atomic scale and microscale barriers to scatter short and long wavelength phonons, respectively. Thus, with the benefits of this multi-scale scattering, ultralow lattice thermal conductivity (~0.54 W m$^{-1}$ K$^{-1}$) was achieved in the Mg$_{0.015}$In$_{0.015}$Sn$_{0.97}$Te sample.

The temperature dependence of $ZT$ values of Mg$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, Ag$_{x/2}$In$_{x/2}$Sn$_{1-x}$Te, and
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Figure 5.18. $ZT$ as a function of temperature for (a) $\text{Mg}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$; (b) $\text{Ag}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$; (c) $\text{Bi}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$. Comparison of the temperature dependence of $ZT$ for pristine and doped samples with 3% doping concentration (d). The inset in (d) is the corresponding average $ZT$ over the temperature range from 323 to 873 K.

$\text{Bi}_{x/2}\text{In}_{x/2}\text{Sn}_{1-x}\text{Te}$ are shown in Figures 5.16a-c, respectively. In all cases, the $ZT$ values are obviously enhanced over the entire temperature range from 323 to 873 K and are strongly dependent on the dopant type and dopant concentration. With the benefits of the higher power factor and the lower lattice thermal conductivity, a high $ZT \sim 1$ was achieved in $\text{Mg}_{0.015}\text{In}_{0.015}\text{Sn}_{0.97}\text{Te}$ at 873 K, being 80% higher than that of pristine SnTe. In addition, the
average $ZT$ over a wide temperature range from 323 to 873 K is improved considerably from ~0.14 for pristine SnTe to ~0.51 for $\text{Mg}_{0.015}\text{In}_{0.015}\text{Sn}_{0.97}\text{Te}$ sample (Figure 5.16d).

5.4. Conclusions

In summary, the temperature-dependent evolution of $\Sigma$ band contribution to the Seebeck coefficient of SnTe was first revealed in situ by neutron and synchrotron powder diffraction over a wide temperature range. The results present that high effective mass of carriers are created in $\Sigma$ valence band arising from the thermal excitation of holes from the L to $\Sigma$ band above 493 K. These “heavy” holes contribute to the electrical transport, and significantly enhance the Seebeck coefficient at high temperature. In addition, the coexistence of resonant levels (due to In dopant), band convergence (due to Mg and Ag dopants), and/or the carrier concentration optimization (due to Mg, Ag, and Bi dopants) has synergistically led to a large improvement in the Seebeck coefficient of SnTe over a broad temperature range. Moreover, the atomic scale point defects (due to In and Mg co-doping), the nanoscale elongated screw dislocations with random directions, and the microscale grain boundaries caused by the sintering efficiently scatter a wide spectrum of heat-carrying phonons, leading to a significant reduction of the lattice thermal conductivity. With the benefit of these factors, a high $ZT$ of ~1 at 873 K was achieved for $\text{Mg}_{0.015}\text{In}_{0.015}\text{Sn}_{0.97}\text{Te}$ sample. These results suggest that SnTe-based materials could be an important lead-free thermoelectric candidate for power generation, and provide insights for synergistically engineering multiband thermoelectric materials with high performance.
Chapter 6. Three-Stage Inter-Orthorhombic Evolution and High Thermoelectric Performance in Ag-doped Nanolaminar SnSe Polycrystals

6.1. Introduction

Recently, SnSe single crystals have produced a surge in the field of thermoelectrics as a new type of promising lead-free TE materials because of the intrinsically ultra-low thermal conductivity (\(< 0.4 \text{ W m}^{-1} \text{ K}^{-1} \) at 923 K) and high \( ZT \) along the \( b \)- and \( c \)-crystallographic directions (\( > 2.3 \text{ at 923 K} \)).\(^{37} \) A new record of \( ZT_{\text{dev}} \sim 1.34 \) from 300 - 773 K along the \( b \)-crystallographic direction was achieved in thermoelectric device fabricated from hole-doped SnSe single crystal.\(^{154} \) Nevertheless, the difficulties in large-scale synthesis of single crystals limit their practical applications, and extensive efforts have been devoted to the fabrication of high-performance polycrystalline counterparts.\(^{60-64,67} \) For example, Wei et al.\(^{61} \) reported a \( ZT \) of \( \sim 0.8 \) at 800 K in 1% Na- and K-doped SnSe, which was produced by conventional solid state reaction followed by a spark plasma sintering (SPS) treatment. Due to an impressively low lattice thermal conductivity (\( \sim 0.20 \text{ W m}^{-1} \text{ K}^{-1} \) at 773 K) arising from the presence of coherent nanoprecipitates in the SnSe matrix, a high \( ZT \) of \( \sim 1.1 \) at 773 K was achieved in the direction perpendicular to the pressing direction of SPS for ball-milled K-doped SnSe.\(^{63} \) Apart from \( p \)-type alkali dopants (Li, Na, K), \( n \)-type dopants such as I and BiCl\(_3\) are also adopted to improve the performance of polycrystalline SnSe.\(^{66-67} \) For instance, a \( ZT \) of \( \sim 0.8 \) at 773 K was obtained in I-doped SnSe polycrystals, which was further improved to \( \sim 1.0 \) by reducing the lattice thermal conductivity via alloying with SnS.\(^{67} \)

The above examples clearly illustrate that SnSe polycrystals could be engineered into promising thermoelectric materials by diverse approaches, such as \( n \)-type and \( p \)-type doping,\(^{61,64-67} \) alloying,\(^{62,66-67} \) nanostructuring\(^{62-63} \) and microstructure modulation.\(^{60,193} \) The highest \( ZT \) is only \( \sim 1.1 \) achieved at 773 K\(^{63} \), however, and it is highly significant to develop a
fruitful approach to further improve the $ZT$ values of polycrystalline counterparts. In addition, SnSe-based TE materials exhibits a second-order inter-orthorhombic phase transition from low-symmetry GeS-type ($Pnma$) to high-symmetry TII-type ($Cmcm$) phase at high temperature, however, this temperature-dependent evolution and its relationship with their thermoelectric performance have not been fully investigated and understood.\textsuperscript{178, 194}

In this work, pristine SnSe polycrystals with novel nanolaminar structure have been fabricated via conventional solid state reaction at high temperature by simply controlling the reaction time. Ag- and SnCl\textsubscript{2}-doped SnSe polycrystals were also prepared with the same structure by this approach. The resultant structural properties were characterized by neutron and synchrotron powder diffraction measurements to reveal a temperature-dependent three-stage inter-orthorhombic structural evolution from a low-temperature phase $Pnma$, through the coexistence of distorted $Pnma/Cmcm$ by a series of layer slips and stretches along the $a$- and $b$-directions over a wide temperature range (200 K) below the transition temperature, to a high-temperature phase $Cmcm$. This phase transition narrows the band gap and enhances the phonon capture at high temperature, which results in an enhancement of the carrier concentration and phonon scattering above 600 K. In addition, the large laminar structure can effectively enhance the carrier mobility of SnSe polycrystals, and the grain and layer boundaries can simultaneously strengthen the phonon scattering. With the benefits of these excellent features and the further enhancement of carrier concentration by chemical doping, high thermoelectric performances of SnSe polycrystals are reached, \textit{i.e.}, a very high average power factor of $\sim 500 \, \mu W \, m^{-1} \, K^{-2}$ from 300 - 973 K, an extremely low lattice thermal conductivity (0.23 - 0.85 W m\textsuperscript{-1} K\textsuperscript{-1}), and a new record $ZT$ of 1.3 at 773 K are achieved in Ag\textsubscript{0.015}Sn\textsubscript{0.985}Se polycrystals.
6.2. Experimental section

6.2.1. Materials

Tin (Sigma Aldrich, 99.8%), selenium (Alfa Aesar, 99.999+%), silver (Sigma Aldrich, 99.9+%), and Tin(II) chloride (Sigma Aldrich, 98%) were used for synthesis without any further purification.

6.2.2. Sample preparation

Ingots of SnSe, Ag$_{0.015}$Sn$_{0.985}$Se, and SnSe$_{0.985}$Cl$_{0.015}$ were synthesized by mixing appropriate ratios of high-purity Sn, Se, Ag, and SnCl$_2$ in 15-mm-diameter quartz tubes in an argon filled glove box. The tubes were flame-sealed under vacuum and then placed in larger 26-mm-diameter quartz tubes, evacuated, and flame-sealed again. The outer tube is used to protect the crystals from oxidation by air, because the inner tube could break due to the considerable difference in thermal expansion between the crystals and quartz, as well as the expansion in the volume due to the phase transition during cooling. The double sealed quartz was slowly heated to 1273 K over 10 h, held at this temperature for 8 h, and then slowly cooled to 873 K within 6 days and to room temperature within 3 days. In a typical experiment, 7.1866 g of Sn, 4.8530 g of Se, and 0.0994 g of Ag were used to prepare ~12 g of Ag$_{0.015}$Sn$_{0.985}$Se. Highly dense (> 95% of theoretical density) ingots were obtained with dimensions of 15 mm (diameter) × 20 mm (length). The densities of SnSe, Ag$_{0.015}$Sn$_{0.985}$Se, and SnSe$_{0.985}$Cl$_{0.015}$ are presented in Table 6.1.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>$D_T$, g cm$^{-3}$</th>
<th>$D_S$, g cm$^{-3}$</th>
<th>$D_R$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSe</td>
<td>6.190</td>
<td>6.039</td>
<td>97.6%</td>
</tr>
<tr>
<td>Ag$<em>{0.015}$Sn$</em>{0.985}$Se</td>
<td>6.200</td>
<td>6.002</td>
<td>96.8%</td>
</tr>
<tr>
<td>SnSe$<em>{0.985}$Cl$</em>{0.015}$</td>
<td>6.184</td>
<td>5.911</td>
<td>95.6%</td>
</tr>
</tbody>
</table>
6.2.3. Characterization

A thin cleavage plane was used for XRD characterization. The XRD patterns were obtained with Cu Kα (λ = 1.5418 Å) radiation in a reflection geometry on an Inel diffractometer operating at 40 kV and 25 mA, and equipped with a position sensitive detector.

The neutron powder diffraction patterns were collected on the high-resolution powder diffractometer ECHIDNA (Australian Nuclear Science and Technology Organization) with a wavelength of 1.6215 Å. 4 g of as-synthesized SnSe was ground into powder in an agate mortar and packed in a cylindrical alumina holder (diameter ~8 mm). The counting time for one pattern over the range $7^\circ < 2\theta < 165^\circ$ was around 2 h. The NPD temperature ranged from room temperature to 973 K. Rietveld refinements of the structure were carried out using the FULLPROF program package.

The Synchrotron powder diffraction patterns were collected on the Powder Diffraction beamline at the Australian Synchrotron with a wavelength of 0.590028 Å. 5 mg of as-synthesized SnSe was ground into powder in an agate mortar, and packed in cylindrical quartz capillary tubes (diameter ~0.3 mm). The counting time for one pattern over the range $4^\circ < 2\theta < 30.5^\circ$ was around 10 min. The SPD temperature ranged from room temperature to 770 K.

STEM and energy dispersive spectroscopy (EDS) were performed using a JEOL ARM200F microscope with an accelerating voltage of 200 kV. The thin TEM specimens were sliced by focused ion beam (FIB) at a moderate voltage (16 keV), which was then followed by cleaning with a lower voltage (5 keV). After the cleaning to remove contaminants, the damaged layer was negligible as it was less than 2 - 5 nm.

The carrier concentration and carrier mobility were determined by Hall coefficient measurements at room temperature using a Physical Properties Measurements System.
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(Quantum Design PPMS-9). The four-contact Hall-bar geometry was used for the measurements.

The obtained highly dense ingots were cut into bars perpendicular to the cleavage plane with dimensions of $\sim 6 \times 2 \times 2 \text{ mm}^3$ to be used for simultaneous measurements of the Seebeck coefficient and the electrical conductivity on an Ozawa RZ2001i (Japan) instrument under helium atmosphere from room temperature to 973 K. The samples were coated with a thin (~0.1 - 0.2 mm) layer of boron nitride to protect the instrument. Bulks along the cleavage plane were cut and polished into $\Phi 6 \times 1 \text{ mm}^3$ disks for the thermal diffusivity measurements. The samples were coated with a thin layer of graphite to minimize errors from the emissivity of the material. The thermal diffusivity coefficient ($D$) was measured using the laser flash diffusivity method in a LFA457 (Germany), and the specific heat capacity ($C_p$) was indirectly derived from a representative sample (DSC 204) over the range of 323 - 573 K, and then simulated to 773 K based on the Debye model. The density ($d$) was measured by the Archimedes method. The electron contribution is assessed by the Wiedemann-Franz law, $\kappa_{\text{ele}} = L\sigma T$, where $L$ is Lorenz number, $\sigma$ is electrical conductivity, and $T$ is absolute temperature. In this work, $L$ is evaluated from the formula $L = 1.5 + \exp \left[-|\alpha|/116\right]$, where $L$ and $\alpha$ are in $10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ and in $\mu\text{V} \cdot \text{K}^{-1}$, respectively.

6.3. Results and discussion

6.3.1. Inter-orthorhombic phase transition of SnSe from Pnma to Cmcm

As mentioned above, SnSe-based thermoelectric materials exhibit high thermoelectric performance due to their unique crystal structures. At room temperature, it presents GeS-type orthorhombic structure $Pnma$ which has a layered structure with two Sn-Se bilayers in the unit cell as shown in Figure 2.16a. The $Pnma$ orthorhombic structure of SnSe is not stable as the temperature increases, however, it gradually transforms to another orthorhombic structure.

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(Cmcm), which preserves the bilayer stacking structure, but with the Sn coordination environment gaining higher symmetry (Figure 2.16d-f).

In order to fully understand this inter-orthorhombic evolution as a function of temperature, neutron and synchrotron diffraction measurements were conducted on the as-synthesized SnSe powders. Figure 6.1a displays the neutron powder diffraction patterns of pristine SnSe over the temperature range of 300 - 975 K, and demonstrates a continuous distortion from the low-symmetry structure to the higher symmetric one with the increase of temperature. The enlarged NPD with temperature in the 2-theta ranges of 41˚ - 47˚ and 53˚ - 59˚ further demonstrates the continuous distortion of the phase transition within the orthorhombic structures (Figure 6.1b-c). It clearly shows that the diffraction peaks of the (002) and (020) crystal planes, which belong to the Pnma structure, gradually approach to each other and then displaced by the (200) and (002) planes of the Cmcm structure above 825 K. The diffraction peaks of the (200) and (002) planes seem to merge into one peak, although there are two Bragg positions around 44˚ above 825 K. This is ascribed to the fact that (i) the Cmcm is a more highly symmetric phase with similar a and c lattice parameters, and (ii) the resolution used for neutron diffraction is insufficient to detect these neighboring positions. Similarly, the reflections of the (402) and (420) planes in the low-T structure are displaced by those of the (240) and (042) planes in the high-T structure.

Table 6.2 shows the details of the refined parameters for the neutron diffraction patterns, including lattice parameters, unit cell volumes, and coexistence phase fractions, as well as refinement agreement factors. The values for the profile R-factor ($R_p$) and the weighted profile R-factor ($R_{wp}$) are 5.77% and 7.32% at 300 K, and decreases to 3.88% and 5.38% at 975 K, respectively. At 300 K, the space group of SnSe is refined to be Pnma orthorhombic phase (Figure 6.1d), which is symmetrized to the Cmcm orthorhombic phase at 975 K (Figure 6.1f). The results also demonstrate the coexistence of the Pnma and Cmcm structures
Figure 6.1. Neutron powder diffraction patterns for pristine SnSe over the temperature range of 300 - 975 K for (a) 20° - 120°; (b) 41° - 47°; and (c) 53° - 59°. Corresponding Rietveld refinements using the FULLPROF program at (d) 300 K; (e) 750 K; and (f) 975 K. Observed, calculated, Bragg position, and difference profiles are displayed by black crosses, red full lines, green vertical bars and blue full line at the bottom. The wavelength is 1.6215 Å.

over a wide temperature range, i.e., 600 < T < 825 K, which spreads over more than 200 K below the reported critical temperature (807 K), indicating this phase transition is first- and not second-order transition.178, 194 Typically, SnSe consists of 30.46% Pnma and 69.54%
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Cmcm in its structure at 750 K, as shown in Figure 6.1e. For an ideal first-order phase transition, thermodynamic theory predicts that \( C_p(T)_H \) of the system during the transition should be infinite due to the discontinuous change of the entropy at constant temperature,\(^{195}\) however, in practice, first-order phase transition in solids even for the simplest systems always occurs within a certain temperature range, presenting a sharp but finite increase of heat capacity.\(^{196-200}\) Typically, Jesche et al.\(^ {198}\) reported a sharp peak of specific heat for SrFe\(_2\)As\(_2\) at elevated temperature, which responds to the first-order transition from orthorhombic to tetragonal structure. In fact, this sharp peak of specific heat was also observed in pristine SnSe and S-doped SnSe alloys\(^ {67}\), which provides the evidence of the first-order transition for SnSe from Pnma to Cmcm structure. Therefore, this inter-orthorhombic transition above 600 K presents coexistence temperature range, although this transition evolution is continuous.

Table 6.2. The coexistence phase fractions, unit cell volumes, and lattice parameters as a function of temperature for SnSe according to the refined neutron data.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Volume (Å(^3))</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Ratio %</th>
<th>Volume (Å(^3))</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Ratio %</th>
<th>Agreement Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>211.62</td>
<td>11.493</td>
<td>4.151</td>
<td>4.436</td>
<td>100</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>5.77 6.32</td>
</tr>
<tr>
<td>500</td>
<td>213.65</td>
<td>11.574</td>
<td>4.194</td>
<td>4.401</td>
<td>100</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>4.66 6.30</td>
</tr>
<tr>
<td>700</td>
<td>215.03</td>
<td>11.643</td>
<td>4.249</td>
<td>4.347</td>
<td>51.33</td>
<td>214.89</td>
<td>4.342</td>
<td>11.634</td>
<td>4.254</td>
<td>48.67</td>
<td>4.08 5.60</td>
</tr>
<tr>
<td>775</td>
<td>216.96</td>
<td>11.746</td>
<td>4.306</td>
<td>4.289</td>
<td>10.67</td>
<td>216.15</td>
<td>4.297</td>
<td>11.700</td>
<td>4.299</td>
<td>89.33</td>
<td>4.57 6.10</td>
</tr>
<tr>
<td>825</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>216.52</td>
<td>4.299</td>
<td>11.701</td>
<td>4.305</td>
<td>100</td>
<td>4.13 5.65</td>
</tr>
<tr>
<td>875</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>217.07</td>
<td>4.303</td>
<td>11.710</td>
<td>4.308</td>
<td>100</td>
<td>3.99 4.56</td>
</tr>
<tr>
<td>925</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>217.74</td>
<td>4.306</td>
<td>11.721</td>
<td>4.314</td>
<td>100</td>
<td>3.99 5.59</td>
</tr>
<tr>
<td>950</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>218.07</td>
<td>4.307</td>
<td>11.727</td>
<td>4.318</td>
<td>100</td>
<td>3.90 5.40</td>
</tr>
<tr>
<td>975</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>218.43</td>
<td>4.310</td>
<td>11.733</td>
<td>4.320</td>
<td>100</td>
<td>3.88 5.38</td>
</tr>
</tbody>
</table>
In addition to the wide transition temperature between *Pnma* and *Cmcm* phases, this phase transition is also reversible, as shown in Figure 6.2, which helps to preserve a high power factor for SnSe. According to the refined NPD data in Table 6.1, the lattice parameters as a function of temperature are shown in Figure 6.3a. At 300 K, the parameters of SnSe are calculated to be $a_l = 11.493$ Å, $b_l = 4.151$ Å, and $c_l = 4.436$ Å. The spatial directions of high-*T* SnSe are defined as $a_h = b_l$ and $b_h = a_l$. It is interesting to note that the values of parameters $b$ and $c$ approach to each other with the temperature increasing from 300 to 600 K, and then overlap and remain almost the same when the temperature is above 700 K. This is consistent with the variation of the temperature-dependent crystal diffraction peaks in the 2-theta 41° - 47° and 53° - 59° ranges (Figure 6.1b-c). The variation of parameter $b$ versus $c$ with temperature is displayed in Figure 6.3b. The ratio continuously increases from $b/c < 1$ to $b/c \approx 1$, indicating the increase in symmetry from *Pnma* to *Cmcm*. In contrast to the trends in parameters $b$ and $c$, the parameter $a$ increases gradually with temperature. The

---

![Graph showing the variation of intensity with 2-theta](image-url)
Figure 6.2. Neutron powder diffraction patterns of pristine SnSe at 500 K. The red pattern was obtained at 500 K in the heating path from room temperature to 975 K, while the blue pattern was obtained at 500 K in the cooling path from 975 K to room temperature. These two patterns present a perfect coincidence, indicating the reversibility of the phase transition above 600 K.

Corresponding unit cell volumes as a function of temperature are shown in Figure 6.3b. A continuous increase in the volume of the unit cell with temperature is observed, although the Cmcm structure has a shrink volume compared to the Pnma one at the same temperature. Typically, the unit cell volume of the Pnma structure is 214.33 Å³ at 600 K, and it decreases to 213.72 Å³ for Cmcm at the same temperature.

Although the neutron diffraction characterization solves the essential issues relating to the temperature region of the phase transition, and the corresponding ratios of the coexisting phases at some isolated temperatures according to their characteristic peaks, evidence on the dynamic transition which relates to minor and overlapping peaks is absent, due to the relatively low resolution of the neutron detection (Figure 6.1b-c). In order to acquire the missing information, a high resolution synchrotron powder diffraction measurement at selected temperatures was applied to the pristine SnSe sample.

Figure 6.4a shows its synchrotron powder diffraction patterns in the temperature range of 308 - 770 K. As expected, the synchrotron diffraction presents the information of (i) strong nanostructuring along the a crystallographic axis, and (ii) elaboration of the structural evolution, especially the minor and overlapping peaks. The right inset is an enlargement of the pattern at 308 K for 2θ = 10.8° - 12.2°, indicating the high preferred orientation of the as-synthesized SnSe sample, which is consistent with the XRD results from a thin sliced cleavage plane (Figure 6.5). In fact, SnSe polycrystals consist of many stacked sheets, and each of them is presumed to be single-crystalline with a large surface perpendicular to the a crystallographic axis, which results in a strong preferred orientation as seen in Figure 6.6. The thickness of the individual sheets (inset in Figure 6.6) is assessed to be about 150 nm. This nanolaminar structure is induced by two factors: (i) the characteristics of its crystal
structure (Figure 1) which determines the preferred growth orientation ($bc$- plane), and (ii) the extremely slow cooling rate which promotes the growth of the $bc$- plane.

![Figure 6.3](image)

**Figure 6.3.** (a) Lattice parameters and (b) lattice parameter ratio $b/c$ and unit cell volume as a function of temperature for SnSe.

This strong nanolaminar structure, accounting for its low lattice thermal conductivity, is also responsible for its high carrier mobility, which will be discussed later.

The presence of the (060) peak for $Cmcm$ above 600 K in the patterns enlarged in the left inset indicates the start of the coexistence structure, which coincides with the neutron
refinement results (Table 6.2). At room temperature, as seen from Figure 6.4a, the peaks for the \textit{Pnma} (200), (101), (111), (400), (311), (501), (112), (511), (221), (412), (022), (711), and (800) planes, indicated by the red color, are gradually transformed to the (020), (110), (111), (040), (131), (150), (112), (151), (221), (241), (202), (171), and (080) planes of \textit{Cmcm} with increasing temperature, indicating a closer intercepts between the \textit{a}- and \textit{c}-directions via shortening the distance in \textit{a}-direction and extending the distance in \textit{b}-direction, which is consistent with the result of parameters in neutron diffraction (Figure 6.3a). Moreover, the coupled peaks (201)/(210), (401)/(410), (601)/(610), and (512)/(521) of low-\textit{T Pnma} are merged into single peaks for the (021), (041), (061), and (152) planes of high-\textit{T Cmcm} with similar $|a|$ and $|c|$ crystal indices, respectively (Figure 6.4b-f) accompanied by the disappearance of the peaks of the (011), (102), (411), (302), (502), (122), and (322) planes, as shown in Figure 6.4a, Figure 6.4f, and Figure 6.4g. Similarly, the coupled peaks of (002)/(020) and (402)/(420) in the low-\textit{T} structure are replaced by (002)/(200), and (042)/(240) in the high-\textit{T} structure, which is consistent with the trend of the neutron diffraction with successful separation of the neighboring positions (Figure 6.1b-c, Figure 6.4g-h).

According to the neutron and synchrotron diffraction results, it can be concluded that the GeS-type (\textit{Pnma}) orthorhombic SnSe experienced a series of layer slips and stretches along the \textit{a}- and \textit{b}-axes over the wide range of 200 K, leading to an inter-orthorhombic transition to a high-symmetry TII-type (\textit{Cmcm}) phase. The phase transition is also observed in Ag- and SnCl$_2$-doped SnSe polycrystals fabricated by the same method. The detailed information for SnCl$_2$-doped SnSe, including neutron powder diffraction patterns over the temperature range of 300 - 975 K and the corresponding Rietveld refinements are shown in the Figure 6.7 and Table 6.3, which demonstrate the same inter-orthorhombic evolution and similar phase fractions at various temperatures.
Figure 6.4. Synchrotron powder diffraction patterns for pristine SnSe over the temperature range of 308 - 770 K for $2\theta = (a) 5^\circ - 25^\circ$; (b) $9^\circ - 10.5^\circ$; (c) $13^\circ - 15^\circ$; (d) $13.9^\circ - 14.1^\circ$; (e) $19^\circ - 19.6^\circ$; (f) $23^\circ - 24^\circ$; (g) $15^\circ - 16.5^\circ$; and (h) $19.1^\circ - 2.4^\circ$. The wavelength is 0.590028 Å. The left inset in (a) is the enlargement of pattern for $2\theta = 17^\circ - 18^\circ$. The presence of the (060) peak for Cmcm above 600 K indicates the start of the coexistence structure. The right inset is an enlargement of the pattern for $2\theta = 10.8^\circ - 12.2^\circ$ at 308 K, indicating the highly oriented phase for the as-synthesized SnSe sample.
Figure 6.5. XRD patterns of pristine and Ag-doped SnSe at room temperature. The black and red patterns were detected from the pristine and Ag-doped SnSe powders, while the blue one was detected from the cleavage plane for Ag-doped SnSe slice, indicating a strong textured structure along $a$ crystallographic axis. The inset is the SEM image for the corresponding cleavage plane.

Figure 6.6. (a) SEM images of nanolaminar SnSe polycrystals. The insert is an enlarged image for solid red rectangle in main panel.
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Figure 6.7. Neutron powder diffraction patterns for SnCl₂-doped SnSe over the temperature range of 300 - 875 K in (a) 20° - 120°; (b) 41° - 47°; (c) 53° - 59°. The corresponding refined Neutron diffraction patterns by using FULLPROF program at (d) 300 K; (e) 700 K; (f) 875 K. Observed, calculated, Bragg position and difference profiles are displayed by black cross, red full line, green vertical bar and blue full line at the bottom. The wavelength is 1.6215 Å.

The above interesting inter-orthorhombic transition accounts for the excellent thermoelectric performance of SnSe-based materials. As mentioned previously, their thermoelectric performance can be enhanced by the introduction of multiscale (point defects, nanoscale, and mesoscale) structures through chemical doping. The micro/nano-structure and chemical
Table 6.3. The coexistence phase fractions, unit cell volumes, and lattice parameters as a function of temperature for SnCl$_2$-doped SnSe according to the refined neutron data.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( Pnma )</th>
<th>( Cmcm )</th>
<th>Agreement Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume (( \text{Å}^3 ))</td>
<td>( a ) (( \text{Å} ))</td>
<td>( b ) (( \text{Å} ))</td>
</tr>
<tr>
<td>300</td>
<td>211.44</td>
<td>11.489</td>
<td>4.150</td>
</tr>
<tr>
<td>425</td>
<td>212.70</td>
<td>11.539</td>
<td>4.174</td>
</tr>
<tr>
<td>475</td>
<td>213.19</td>
<td>11.557</td>
<td>4.184</td>
</tr>
<tr>
<td>500</td>
<td>213.51</td>
<td>11.570</td>
<td>4.191</td>
</tr>
<tr>
<td>520</td>
<td>213.69</td>
<td>11.578</td>
<td>4.197</td>
</tr>
<tr>
<td>575</td>
<td>214.03</td>
<td>11.595</td>
<td>4.211</td>
</tr>
<tr>
<td>775</td>
<td>216.46</td>
<td>11.736</td>
<td>4.307</td>
</tr>
<tr>
<td>800</td>
<td>---</td>
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<td>---</td>
</tr>
<tr>
<td>825</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>850</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>875</td>
<td>---</td>
<td>---</td>
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</tr>
</tbody>
</table>

The composition of the Ag-doped SnSe polycrystals were investigated by TEM, STEM, and EDS.

**Figure 6.8a** shows the structure of Ag-doped SnSe as determined by atomic resolution high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images. The top inset is the distance profile of adjacent layers along the dotted line AB in the image, showing that the space between two layers is around 0.498 nm. The bottom inset is the corresponding atomic model, indicating a perfect quasi-laminar structure along the [0-11] orientation. Due to the overlapping spatial positions of the Sn and Se, and the similar Z contrast (atomic number contrast) between Sn (50) and Ag (47), it is impossible to distinguish them in the HAADF-STEM image from the [0-11] orientation.

**Figure 6.8b** presents the selected area electron diffraction (SAED) pattern along the [0-11] orientation, which clearly shows the difference between them. In the SAED pattern, the
Chapter 6. Three-Stage Inter-Orthorhombic Evolution and High Thermoelectric Performance in Ag-doped Nanolaminar SnSe Polycrystals

Figure 6.8. Structural characterization for Ag-doped SnSe polycrystals. (a) Atomic resolution HAADF image. Bottom inset: corresponding atomic model along the [0 -1 1] zone axis, where the blue balls correspond to Sn and the red ones to Se; top inset: the line profile along the dotted line AB in the main panel, showing the spacing of a bilayer; (b) The corresponding SAED pattern along the [0 -1 1] orientation; (c) Low-magnification image of the specimen, which contains two dark stripes, indicated by red rectangles. (d) Magnified observation of one stripe; (e-g) Corresponding EDX mapping for elements Se, Sn, and Ag, respectively. A darker colour in the element maps corresponds to lower concentration.

bigger and brighter dots are attributed to the Sn/Ag atoms due to their higher atomic number (50/47), and the smaller ones are ascribed to Se atoms (atomic number of 34).

It is interesting to note that there are long stripe-like structural defects with higher contrast, which are indicated by red solid rectangles in Figure 6.8c. The dimensions of these stripes are estimated to be ~250 nm in length and ~12 nm in width. The magnified image and corresponding EDX mappings of a typical stripe are presented in Figure 6.8d-g, showing the presence of Sn-poor defects, in contrast to the uniform distribution of Se and Ag. The high resolution transmission electron microscope (HRTEM) images of these Sn-poor defects are shown in Figure 6.9. In contrast to the normal section which maintains a high quality
crystalline structure, the structure of the dark stripes is quite complicated. In the most cases they appear to be amorphous as shown in Figure 6.9a-b. Some crystalline-like stripes are also observed, as shown in Figure 6.9c-d. These amorphous and crystalline-like Sn-poor defects could significantly improve the phonon scattering and reduce the thermal conductivity, leading to the excellent thermoelectric performance as discussed in the following section.

6.3.2. Thermoelectric properties of pristine, Ag- and SnCl$_2$-doped SnSe polycrystals

Electrical transport properties of pristine, Ag- and SnCl$_2$-doped SnSe polycrystals as a function of temperature are shown in Figure 6.10a-d. The temperature dependence of the electrical conductivity ($\sigma$) is presented in Figure 6.10a. In order to measure the thermal and electrical performance in the same direction, we select one cleavage plane ($bc$- plane) as the cutting reference. The inset is the schematic diagram for the cutting direction. The electrical
conductivity for all samples shows a similar temperature dependence, which can be divided into three regions where the three-stage inter-orthorhombic structural transition occurred (Figure 6.1, Figure 6.3 and Figure 6.4). The first region is from 323 to 600 K, in which the $\sigma$ values of the pristine and Ag-doped samples decrease quickly as the temperature increases, indicating their metal-like behavior. In contrast, there is no big difference in electrical conductivity for the SnCl$_2$-doped SnSe sample in this temperature range. The second region is from 600 to 825 K, where the electrical conductivity of the three types of samples rapidly increases and shows semiconductor-like transport behavior. The rapid increase in the electrical conductivity above 600 K is mainly ascribed to the structural transition from $Pnma$ to $Cmcm$, according to the neutron and synchrotron diffraction results (Figure 6.1, Figure 6.3 and Figure 6.4). In addition, the thermal excitation of carriers could also contribute to the rapid increase in the electric conductivity.\(^{37, 61-62, 65, 193}\) It is well known that the high-$T$ $Cmcm$ SnSe has a narrower band gap ($\sim 0.39$ eV) than its corresponding low-$T$ $Pnma$ structure ($\sim 0.61$ eV).\(^{37}\) Once the $Cmcm$ phase structure appears at high temperature, the shrinkage of the band gap makes the thermal excitation of carriers easier, leading to a remarkable enhancement of the carrier concentration.\(^{8, 63}\) For SnSe materials the carrier concentration is dominated by Sn vacancies.\(^{201}\) This means that the increase in carrier concentration is due to the creation of additional Sn vacancies during the phase transition. The third region is from 825 K to 973 K, where the electrical conductivity of pristine and SnCl$_2$-doped SnSe samples is notably decreased in comparison with that of Ag-doped SnSe polycrystals. The decrease in the electrical conductivity implies intrinsic metal-like behavior for the high-$T$ $Cmcm$ structure.

It should be noted that Ag doped SnSe bulks exhibit excellent conductivity, especially at low temperature. The room-temperature electrical conductivity is as high as $0.8 \times 10^4$ S m$^{-1}$, and such high electrical conductivity in the Ag doped samples is related to (i) the enhanced
carrier concentration \((n)\) and (ii) the ultrahigh carrier mobility \((\mu)\). The room-temperature carrier concentration for Ag-doped SnSe is about \(8 \times 10^{18} \text{ cm}^{-3}\), which is about 10 times and 80 times those of pristine SnSe \((9 \times 10^{17} \text{ cm}^{-3})\) and SnCl\(_2\)-doped SnSe \((1 \times 10^{17} \text{ cm}^{-3})\), respectively. This value is 40 times that of a reported pure single crystal \((2 \times 10^{17} \text{ cm}^{-3})\) perpendicular to the cleavage plane at the same temperature, as shown in Figure 6.11a. The values of carrier mobility in our work are 115, 60 and 90 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for pristine, Ag- and SnCl\(_2\)-doped SnSe bulks, respectively (Figure 6.11a), which are nearly 5 - 20 times higher than those of recently reported polycrystalline samples,\(^{61-63}\) and also much higher than that of single crystals perpendicular to the cleavage plane \((25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\).\(^{37}\) The significant increase in carrier mobility is mainly ascribed to the strongly oriented nanolaminar sheets (Figure 6.6), which have large surfaces providing expressways for carrier transport, as shown in Figure 6.11b. It should be noted that the growth direction of the sheets in different stacks is randomly orientated, indicating the nature of nanolaminar SnSe polycrystals, which can be further supported by the low-magnification SEM image in Figure 6.12. In addition, the width of the laminar sheets can be adjusted by chemical doping. Typically, the width of the laminar sheets is reduced to half that of pristine SnSe after Ag doping (Figures 6.13 and Figures 6.14). The temperature-dependent Seebeck coefficients \((\alpha)\) for pristine and doped SnSe are shown in Figure 6.10b. The gradual decrease in \(\alpha\) above 600 K coincides with the rising trend in the electrical conductivity. Above 825 K, a degeneration of the \(\alpha\) value is observed, suggesting the appearance of bipolar conduction due to the low carrier concentration and the decreased band gap at high temperature.\(^{37}\) The \(\alpha\) value of Ag-doped SnSe is in the range of \(300 - 450 \mu \text{W m}^{-1} \text{ K}^{-2}\), which is comparable to those in previous reports,\(^{61-63}\) although it is lower than those of pristine and SnCl\(_2\)-doped SnSe samples due to the increased carrier concentration. With the benefits of keeping the high Seebeck coefficient and the excellent
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Figure 6.10. (a) Electrical conductivity; (b) Seebeck coefficient; (c) Power factor as a function of temperature for pristine, Ag- and SnCl$_2$-doped SnSe polycrystals. (d) Comparison of the average power factor of the current nanolaminar SnSe polycrystals with those of the previously reported pristine,$^{60}$ $p$-type doped (Li, Na, K, Ag),$^{61-65}$ and $n$-type doped (I and BiCl$_3$)$^{66-67}$ SnSe polycrystals from 300 - 823 K. The inset in (d) is the corresponding power factors as a function of temperature.

electrical conductivity, a high average power factor ($PF$) from 323 to 973 K, about 500 $\mu$Wm$^{-1}$K$^{-2}$, is obtained for the Ag-doped sample (Figure 6.10c). The comparison of the average $PF$ with previous reports in the range of 300 - 800 K is presented in Figure 6.10d.
Ag-doped nanolaminar SnSe polycrystals show much higher average $PF$ than pristine and SnCl$_2$-doped analogues, as well as previous reports. The results indicate that both large laminar structure and Ag doping are effective for improving the electrical properties of SnSe polycrystals.
Figure 6.12. SEM image of as-synthesized pristine SnSe bulk. SnSe polycrystals consist of many stacked sheets, and each of them is presumed to be single-crystalline with a large surface perpendicular to the $a$ crystallographic axis. In addition, the growth direction of the sheet in different stacks is randomly orientated, indicating the formation of nanolaminar SnSe polycrystals.

Figure 6.13. (a) SEM images of nanolaminar pristine SnSe polycrystals; (b) and (c) The enlarged images for solid red and yellow rectangle in (a).
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**Figure 6.14.** (a) SEM images of nanolaminar Ag-doped SnSe polycrystals; (b) and (c) The enlarged images for solid red and yellow rectangle in (a). Obviously, the introduction of Ag restrains the growth of nanolaminar sheets for SnSe polycrystals.

**Figure 6.15.** (a) Heat capacity; (b) Lorenz number; (c) Thermal diffusivity as a function of temperature for pristine, Ag- and SnCl$_2$-doped SnSe polycrystals.

The heat capacity as a function of temperature for pristine, Ag- and SnCl$_2$-doped SnSe polycrystals is presented in **Figure 6.15a**. All the heat capacities range from 0.28 to 0.34 J g$^{-1}$ K$^{-1}$ with temperature increase from 323 to 773 K. In this work, Lorenz number is evaluated from the formula $L = 1.5 + \exp \left[-|\alpha|/116\right]$, where $L$ and $\alpha$ are in $10^{-8}$ W Ω K$^{-2}$ and in μV K$^{-1}$, respectively. The $L$ values for pristine, doped SnSe polycrystals range from 1.51-1.58 $10^{-8}$ W Ω K$^{-2}$ (Figure 6.15b). **Figure 6.15c** shows the thermal diffusivity as functions of
temperature for pristine, Ag- and SnCl$_2$-doped SnSe polycrystals. It can be seen that the thermal conductivity decreases with both increasing temperature and introducing Ag and SnCl$_2$ dopants. Moreover, the temperature dependence of thermal diffusivities seems to reach the similar low values at 773 K.

The thermal conductivities of pristine, Ag- and SnCl$_2$-doped SnSe polycrystals as a function of temperature are shown in Figure 6.1a-d. Recent reports have demonstrated that the optimal maximum temperature for investigating the thermal and thermoelectric properties of SnSe is around 800 K, due to the presence of the visible and invisible microgaps along the cleavage plane in the specimen arising from the shrinkage of the unit cell over 800 K caused by the phase transition.$^{61-67, 154-155, 180}$ Therefore, a temperature range of 323 - 773 K was selected for the investigation of thermal performance for our samples. The total thermal conductivity is composed of the electronic thermal conductivity ($\kappa_{\text{ele}}$) and the lattice thermal conductivity ($\kappa_{\text{lat}}$). As shown in Figure 6.1a, the total thermal conductivity ($\kappa$) is around 0.3 - 0.9 W m$^{-1}$ K$^{-1}$, and the electronic thermal conductivity is less than 0.05 W m$^{-1}$ K$^{-1}$, which indicates the dominance of phonon-phonon interactions for SnSe materials.

The dependence of $\kappa_{\text{lat}}$ of all samples on temperature is displayed in Figure 6.1b. Their $\kappa_{\text{lat}}$ decreases with increasing temperature from 323 to 773 K, with a turning point at $\sim$600 K. The temperature dependence of decreased lattice thermal conductivity is mainly ascribed to the enhancement of the phonon-phonon interactions in SnSe materials, however, the enhanced decrease above 600 K is attributed to the presence of high-temperature phase Cmcm (Figure 6.1, Figure 6.4, and Table 6.2). Moreover, the $\kappa_{\text{lat}}$ value is significantly lower than most of reported polycrystalline samples (0.2 - 1.5 W m$^{-1}$ K$^{-1}$)$^{60-62, 64-66}$, as shown in Figure 6.1c. Typically, $\kappa_{\text{lat}}$ is in the range of 0.23 - 0.85 W m$^{-1}$ K$^{-1}$ for Ag-doped SnSe. The extremely low lattice thermal conductivity for our polycrystals are most likely related to
(i) their strong textures formed during the synthesis and (ii) the evolution of *Cmcm* phase at high temperature.

Although the as-synthesized samples are highly textured, it should be noted that they have no epitaxial structure or single-crystal-like atomic arrangement. There are many nanoscale and mesoscale boundaries (layer boundaries and/or grain boundaries) in the samples (Figure 6.11b), which are particularly effective for scattering phonons, and result in an extremely low thermal conductivity for these polycrystals. Furthermore, the *Cmcm* phase formed in the *Pnma* matrix above 600 K is also effective for capturing phonons and enhancing the scattering at high temperature, as schematically shown in Figure 6.11b. In addition, the presence of point defects and Sn-poor defects (Figure 6.8 and Figure 6.9) also contribute to the low lattice thermal conductivity. All the above results illustrate that the electrical conductivity, the Seebeck coefficient, and the thermal conductivity of SnSe polycrystals could be engineered to achieve excellent performance. A new record *ZT* of 1.3 among the reported SnSe polycrystals\(^{60-67}\) has been achieved in Ag-doped nanolaminar SnSe polycrystals at 773 K (Figure 6.16d). This is the highest *ZT* value reported for polycrystalline SnSe-based thermoelectric materials.

### 6.4. Conclusions

In summary, the complete inter-orthorhombic evolution for SnSe has been demonstrated from a low-symmetry phase *Pnma* structure at room temperature, which experiences a series of layer slips and stretches along the *a*- and *b*-axes over the wide range of 200 K as the temperature rise, to a more highly symmetric phase, the *Cmcm* structure. This phase transition contributes to the enhancement of the carrier concentration and phonon scattering above 600 K. The evidence of nanolaminar polycrystal significantly influencing their thermoelectrics via promoting carrier mobility and simultaneously strengthening the phonon
scattering was revealed. The thermoelectric performance of SnSe polycrystals was further improved by Ag- and SnCl₂-doping. Ag-doped nanolaminar SnSe polycrystals have a record of average power factor (~500 μWm⁻¹K⁻²) from room temperature to 973 K, extremely low lattice thermal conductivity (0.23 - 0.85 W m⁻¹K⁻¹), and a new record of $ZT = 1.3$ at 773 K.

Figure 6.16. (a) Total thermal conductivity and electron thermal conductivity; (b) Lattice thermal conductivity; and (d) $ZT$ as a function of temperature for pristine, Ag- and SnCl₂-doped SnSe polycrystals. Comparisons of the thermal conductivity and $ZT$ of current nanolaminar SnSe polycrystals with those of the previously reported pristine, $p$-type doped (Li, Na, K, Ag), and $n$-type doped (I and BiCl₃) SnSe polycrystals are shown in (c) and (d).
This work provides insights for the fabrication of new highly textured, layered thermoelectric materials with unprecedented efficiency in heat conversion.
Chapter 7. General Conclusions and Outlook

7.1. General conclusions

In this doctoral work, tin telluride based and tin selenide based lead-free thermoelectric materials have been developed. The TE performance was enhanced through the optimization of carrier concentration, band engineering, and all-scale hierarchical architectures. Conclusions can be made as following:

(1) Gd is an effective dopant for SnTe to reduce the lattice thermal conductivity via introduction of nanoprecipitates. The large mass contrast between the nanoprecipitates and the matrix, together with the increased grain boundaries from mesoscale grains the heat-carrying phonons can be strongly scattered from nanoscale to mesoscale.

(2) Ag dopant can effectively increase the solubility limit of Gd into the SnTe matrix via the formation of Ag₄Sn, which reduce the carrier density and improve the Seebeck coefficient and power factor. A maximum ZT of ~1.1 at 873 K was successfully obtained in Ag₀.₁₁Gd₀.₀₆Sn₀.₉₄Te sample.

(3) Temperature-dependent evolution of Σ band contribution to the Seebeck coefficient of SnTe was first revealed in situ by neutron and synchrotron powder diffraction over a wide temperature range. The results present that high effective mass of carriers is created in Σ valence band arising from the thermal excitation of holes from the L to Σ band above 493 K. These “heavy” holes contribute to the electrical transport, and significantly enhance the Seebeck coefficient at high temperature.

(4) Synergy of resonant levels, band convergence, and optimization of carrier concentration through Mg&In, Ag&In, and Bi&In results in a large improvement in the Seebeck coefficient of SnTe over a broad temperature range. Moreover, the atomic scale point defects, the
nanoscale elongated screw dislocations with random directions, and the microscale grain boundaries caused by the sintering efficiently scatter a wide spectrum of heat-carrying phonons, leading to a significant reduction of the lattice thermal conductivity. With the benefit of these factors, a high $ZT$ of $\sim 1$ at 873 K was achieved for $\text{Mg}_{0.015}\text{In}_{0.015}\text{Sn}_{0.97}\text{Te}$ sample.

(5) A complete inter-orthorhombic phase transition for SnSe from $Pnma$ to $Cmcm$ structure has been demonstrated in situ by neutron and synchrotron powder diffraction over a wide temperature range. SnSe, from a low-symmetry phase $Pnma$ structure at room temperature, undergoes the coexistence of distorted $Pnma/Cmcm$ by a series of layer slips and stretches along the $a$- and $b$-directions over a wide temperature range (200 K) below the transition temperature, to a more highly symmetric phase, the $Cmcm$ structure. This phase transition contributes to the enhancement of the carrier concentration and phonon scattering above 600 K.

(6) Nanolaminar SnSe polycrystals were successfully fabricated through simply solid state reaction with slowly cooling rate. This nanolaminar structure significantly enhances their thermoelectric performance via promoting carrier mobility and simultaneously strengthening the phonon scattering.

(7) Ag is an effective electron acceptor for SnSe, which significantly improve the carrier concentration. With the benefits of the nanolaminar structure, a very high average power factor of $\sim 500 \, \mu\text{W m}^{-1}\text{K}^{-2}$ from 300 to 973 K was obtained with an extremely low lattice thermal conductivity ($0.23 - 0.85 \, \text{W m}^{-1}\text{K}^{-1}$), leading to a new record $ZT$ of 1.3 at 773 K in $\text{Ag}_{0.015}\text{Sn}_{0.985}\text{Se}$ polycrystals.
7.2. Future work

7.2.1. Future work on tin telluride based thermoelectric materials

In this doctoral work, the thermoelectric performance of lead-free SnTe-based materials have been developed through (i) nanostructuring by the introduction of nanoprecipitates via Gd/Ag doping, and (ii) band structure engineering by synergy of resonant levels, band convergence, and optimization of carrier concentration via Mg & In, Ag & In, and Bi & In co-doping. High $ZT$ values (~1.0) were obtained, however, the drawbacks of SnTe have not been fully overcome in comparison with those of lead chalcogenides. Therefore, the thermoelectric performance of tin telluride based materials can be further enhanced by the following strategies:

1. Introduce nanostructuring to In and Mg co-doped SnTe thermoelectric materials to further reduce lattice thermal conductivity, \textit{i.e.}, CdS\textsuperscript{40} and SrTe\textsuperscript{47} nanoprecipitates which were assumed to be endotaxial orientation with respect to the SnTe matrix, resulting in the enhancement of phonon scattering without explicit reduction of carrier mobility.

2. Try to introduce hybridizing organic/inorganic materials at nanometer or molecular scales to SnTe. Nunna et al.\textsuperscript{162} reported the \textit{in situ} growth of Cu$_2$Se on the surface of carbon nanotubes (CNTs), by utilizing the special interaction between metal Cu and CNTs, leading to large reductions in lattice thermal conductivity and carrier concentration.

3. Try to introduce temperature-dependent interstitial defects to In and Mg co-doped SnTe thermoelectric materials to further reduce lattice thermal conductivity, \textit{i.e.}, Cu$_2$Te which presents temperature-dependent doping in SnTe alloys, leading to a strong phonon scattering by interstitial Cu when the temperature above 700 K.\textsuperscript{53}

4. Try to introduce temperature-dependent magnetic transition to SnTe-based thermoelectric
materials to optimize the electron and phonon transport properties simultaneously through thermoelectromagnetic effects, \textit{i.e.}, Fe, Co, and Ni superparamagnetic nanoprecipitates which were assumed to improve the carrier concentration via charge transfer from superparamagnetic nanoparticles to matrix, enhance the Seebeck coefficient through a temperature-dependent multiple scattering, and reduce the lattice thermal conductivity by the random turning of the magnetic domain for superparamagnetic nanoparticles. \textsuperscript{72}

(5) Enhance the thermoelectric performance of SnTe through synergy of the band convergence (\textit{i.e.}, Mn), temperature-dependent magnetic transition (\textit{i.e.}, Fe, Co, and Ni superparamagnetic nanoprecipitates), and temperature-dependent interstitial defects (\textit{i.e.}, Cu\textsubscript{2}Te).

\textbf{7.2.2. Future work on tin selenide based thermoelectric materials}

In this doctoral work, the thermoelectric performance of lead-free SnSe-based materials have been developed by the investigation of temperature-dependent inter-orthorhombic phase transition, the design of the nanolaminar structure, and the modification of the electrical transport through Ag and SnCl\textsubscript{2} doping, leading to a high $ZT$ of 1.35 in SnSe polycrystals. The fabrication process, however, is time demanding and the optimized $ZT$ of SnSe polycrystals is still much lower than those of SnSe single crystals. Therefore, the thermoelectric performance of tin selenide based materials can be further enhanced by the following strategies:

(1) Adjust Ag doping concentration in SnSe, and obtain the optimum doping fraction for further enhancement of thermoelectric performance.

(2) Fabricate the SnSe polycrystals by simple method such as ball milling and spark plasma sintering.
(3) Optimization of carrier concentration via the introduction of $p$-type dopant, \textit{i.e.}, P, As, Na&P, and Na&As.

(4) Try to introduce temperature-dependent interstitial defects, \textit{i.e.}, Cu$_{2-x}$Se, to SnSe thermoelectric materials to enhance the carrier concentration at elevated temperatures, and realize the improvement of the electrical transport.

(5) Try to introduce temperature-dependent magnetic transition to SnSe thermoelectric materials to optimize the electron and phonon transport properties simultaneously through thermoelectromagnetic effects, \textit{i.e.}, Fe, Co, and Ni superparamagnetic nanoprecipitates which were assumed to improve the carrier concentration via charge transfer from superparamagnetic nanoparticles to matrix, enhance the Seebeck coefficient through a temperature-dependent multiple scattering, and reduce the lattice thermal conductivity by the random turning of the magnetic domain for superparamagnetic nanoparticles.$^{72}$

(6) Enhance the electrical transport of SnSe through synergy of the optimization of carrier concentration (\textit{i.e.}, P, As, Na&P, and Na&As), temperature-dependent interstitial defects (\textit{i.e.}, Cu$_{2-x}$Se), and temperature-dependent magnetic transition (\textit{i.e.}, Fe, Co, and Ni superparamagnetic nanoprecipitates).
Reference


105. König, J. D.; Nielsen, M. D.; Gao, Y.-B.; Winkler, M.; Jacquot, A.; Böttner, H.;


Appendix

Appendix A: List of Publications.


Appendix B: Conference.

1. 5th Australia-China Symposium for Materials Science.


Place: Wollongong, Australia.

Form: Poster.

Title: Lead-free SnTe-based thermoelectrics: enhancement of thermoelectric performance by doping with Gd/Ag.

2. 10th World Congress of Chemical Engineering

Time: October 1 - 5, 2017.

Place: Barcelona, Spain.

Title: Three-Stage Inter-Orthorhombic Evolution and High Thermoelectric Performance in Ag-doped Nanolaminar SnSe Polycrystals.
Appendix C: Received Awards.

1. International Postgraduate Tuition Award (IPTA), 2013-2017, University of Wollongong

2. University Postgraduate Award (UPA), 2013-2018, University of Wollongong

3. Student Travel Grant to Attend International Conference, 2017, University of Wollongong.

4. Travel Grant to Synchrotron Diffraction, 2014-2017, Australia Synchrotron

5. Travel Grant to Neutron Diffraction, 2014-2017, Australian Nuclear Science and Technology Organization