Multiphase thermoelectrics : effect of second phase in ex-SITU Cu₇Te₄-Bi_{0.4}Sb_{1.6}Te₃ and in-SITU SnTe-SnSe nanocomposites

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**MULTIPHASE THERMOELECTRICS –
EFFECT OF SECOND PHASE IN EX-SITU
 $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ and *IN-SITU* SnTe-SnSe
NANOCOMPOSITES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2014

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NANOCOMPOSITES**

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Abstract

Thermoelectric (TE) materials are a potential source of alternative energy, and have been the subject of research since the 1950s, with their figure of merit (ZT) fluctuating at about 1. Only recently were breakthroughs made in research, based on approaches like nanostructuring, presence of multiple phases or presence of these multiple phases at various length scales in the material, leading to improved ZT values of more than 2.

This thesis work focused on the use of multiphase ex-situ and in-situ nanocomposites for TE properties enhancement over the single phases. The material system for the ex-situ nanocomposites, $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ (BST), was chosen based on earlier reports on the feasibility of synthesis *via* a solid state synthesis method. Here, further improvements were made: surfactant-free nanorods of Cu_7Te_4 were fabricated *via* a facile synthesis method, where Te nanorods were used as templates, and then added to BST. The material system for in-situ nanocomposites, SnTe-SnSe , was chosen based on its phase diagram, which has two single phase regions (a SnTe-rich and a SnSe-rich solid solution) and a two phase region. The fabrication method *via* melt spinning allowed for rapid solidification and microstructural optimization through subsequent processing by ball milling and heat treatment.

In the ex-situ nanocomposite, the BST matrix alone yielded a maximum power factor of $2.46 \times 10^{-3} \text{ W/m.K}^2$ at 300 K, while the addition of 5 wt % of Cu_7Te_4 (5wtNC) nanorods increased and shifted the maximum power factor to $3.30 \times 10^{-3} \text{ W/m.K}^2$ at 345 K. The maximum ZT obtained for the 5wtNC was 1.14 at 444 K, which was nearly 23% higher than the peak ZT achieved for the BST matrix. However, issues like agglomeration of nanorods and cracking of samples were faced. To mitigate them, the focus was shifted to the use of in-situ nanocomposites instead. For the sample made up of a nominal composition 25 mol % SnSe and 75 mol % SnTe (25SnSe), a maximum power factor of $1.31 \times 10^{-3} \text{ W/m.K}^2$ was

obtained at 494 K, which was 1.5 times that of SnTe. The peak ZT of 25SnSe was 0.19 at 548 K, which was 3 times higher than the peak ZT of SnTe.

Further characterization to elucidate the reasons behind the enhancement of TE properties in 25SnSe led to the discovery of metastable behaviour in the orthorhombic second phase: the cubic SnTe-based ternary phase that formed after melt spinning transformed into a mixture of cubic and orthorhombic ternary phases (referred to as second phase) after ball milling. The mass fraction of this second phase increased with low applied pressure, and TE properties measurements carried out indicated that the second phase was important in the reduction of electrical resistivity and maintaining high Seebeck coefficient at higher temperatures.

Transmission electron microscopy showed the presence of second phase nanoprecipitates in the cubic matrix in both the ball milled and hot pressed samples, and high temperature X-ray diffraction measurements showed that the phase transformation pathway in 25SnSe was due to the movement of Te and Se atoms. Calculations using the Miedema model for the enthalpy of formation of the various phases showed that the less stable phases transformed with application of heat or pressure, to more stable compositions and/or mass fraction. These results give an insight into how the phases evolve, and how processing variables can play a role to optimize the constituent phases and further improve TE properties.

The results above indicate the effectiveness of using the multiphase concept in our work. It is concluded that (1) depending on the type of matrix, the presence of an appropriate second phase can effectively mitigate negative effects in the matrix, leading to enhanced electrical properties; (2) there is an optimum mass fraction of nano-sized second phase that will be useful for TE properties enhancement; (3) the presence of these precipitates at the micron and nano scale will be useful in scattering a larger range of phonons.

CHAPTER 1 - Introduction to Thermoelectric Materials

1.1 Background

Energy production and conversion are indispensable processes in our daily lives, and is the cornerstone of the existence of human civilization [1]. The world energy consumption in 2010 was 511 quadrillion Btu, and from Figure 1.1 (taking U.S. as an example), it is seen that more than 80% of this energy comes from fossil fuels (i.e. oil, coal, and natural gas), and less than 10% comes from renewable power sources such as geothermal, wind, solar power, and biofuels [2]. Of all the energy produced, about 60% is lost as heat [3]. Coupled with the pressing issue of the rapid depletion of fossil fuels, and the emission of greenhouse gases from their use, there is a compelling need for the development of sustainable alternative energy sources. More efficient and environmentally friendly energy conversion technologies are also required so that energy losses are minimized and there is efficient utilization of energy. Thus, the use of thermoelectric (TE) materials is highly attractive.

U.S. Energy Consumption by Energy Source, 2011

Figure 1.1: The energy consumption in U.S. by energy source in 2011.
Source: U.S. Energy Information Administration [4].

Thermoelectric materials are able to produce electricity in the presence of a heat difference, and vice versa. They have been an area of focus in alternative energy research due to advantages like not having moving parts, not producing any noise or toxic waste, and having high reliability [5, 6]. The efficiencies of TE materials are defined using a dimensionless figure of merit, ZT:

$$ZT = \left(\frac{S^2 \sigma}{\kappa} \right) T \quad (1)$$

where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the absolute temperature. The value of $S^2 \sigma$ is also defined as the power factor. Based on equation 1, good TE materials have the following properties: high Seebeck coefficient (for producing large potential difference), high electrical conductivity (so that there is low Joule heating) but low thermal conductivity (to maintain the large temperature difference) [7].

As shown in Figure 1.2, TE materials can be used across a wide range of temperatures from about 200 K – 1300 K, with different state of the art materials having peak ZTs in the range of 0.8 – 1.2 [6, 8]. Traditionally used materials are Bi_2Te_3 and its alloys for near room temperature range (200 K – 450 K), PbTe-based materials for intermediate temperature range (450 K – 850 K) and SiGe-based alloys for high temperatures (850 K – 1300 K) [6, 8]. The main uses of TE materials are in solid state cooling and power generation, but due to low efficiency, their applications are limited to niche industries where reliability and simplicity are more important than performance [9]. Nevertheless, as there are potential benefits in the utilization of TE materials, in addition to the pressing need for sustainable alternative energy sources, there is continued research in this area of study.

Figure 1.2: The ZT of state of the art and emerging materials in both bulk and nanostructured form. Reproduced from [10] with permission from The Royal Society of Chemistry and Prof Li Shi from University of Texas–Austin.

The two approaches used to increase ZT in TE materials research are decrease in thermal conductivity and increase in power factor [11]. Thermoelectrics research in recent years have focused on multiphase nanocomposites e.g. presence of multiple phases or presence of these multiple phases at various length scales, due to the ability to achieve significant improvement in TE performance over the single phases [3, 12, 13]. These enhancements are achieved through mechanisms like (1) electron filtering by the interfacial potential between different phases [12], (2) going beyond nanostructuring to take advantage of all relevant length scales in the material like mesoscale grain boundaries, endotaxial nanostructuring and atomic-scale substitutional doping [3] and (3) incorporating matrix/inclusion band alignment engineering and intra-matrix electronic structure engineering [13]. In this way, there is increased phonon scattering and maximized TE performance, as the parameters in the ZT equation are able to be optimized individually.

The use of TE materials can complement existing technologies and play a role in energy conversion and conservation (as shown in Figure 1.3). Hence there is no need for development of additional technology to allow thermoelectrics to fit

into the current energy market, and this allows more rapid implementation the TE technology.

Figure 1.3: Schematic diagram showing the various energy conversion, storage, and conservation technologies, and their interactions. Reproduced from [2] with permission from The Royal Society of Chemistry.

1.2 Objectives and Scope

In this thesis, the objective is to synthesize multiphase nanocomposites for TE enhancement over the single phases. Both ex-situ and in-situ nanocomposites will be explored: for the former, the effect of the second phase on the TE properties will be studied; for the latter, the formation of the second phase and its effect on the TE properties will be studied. Based on the findings, suggestions will be made on how to optimize the performance of the material systems. It is hoped that using these knowledge, predictions for other material systems can be made and improvements in performance can be realized.

The material systems chosen for this investigation are: $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ and SnTe-SnSe . The performance optimization of these two material systems will be carried out through composition control to obtain the appropriate mass fraction of second phases. This will lead to enhancement of Seebeck coefficient contributed

by second phase nanostructures in the matrix and reduction of thermal conductivity by increased phonon scattering from interfaces of these nanostructures.

The scope of the work will cover the study of the structure-property relationships in this material system by using characterization tools like X-ray diffraction (XRD), field emission microscopy, transmission electron microscopy (FESEM, TEM), electron microprobe analysis (EPMA), ZEM-3 and laser flash analysis.

From the characterization results, the reasons behind the improved TE properties obtained in the materials will be analyzed and validated. The parameters of focus for the discussions are:

Ex-situ nanocomposites:

- Effect of Cu_7Te_4 in $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ on TE properties
- Interface at the boundary of the two phases

In-situ nanocomposites:

- Phase transformations which occur
- What are the second phases and how they affect the TE properties
- Heat of formation of the phases in the SnTe-SnSe system

Finally, based on the understanding of the findings made, conclusions will be drawn and future directions in this area will be proposed.

1.3 Thesis Outline

The thesis outline is as follows:

In Chapter 1, a short background on TE materials, the objectives and scope of the work, and thesis outline is given.

Chapter 2 gives a more detailed literature review on the fundamentals and theory of thermoelectricity, history of TE materials research, the challenges faced and the solutions for these issues. It will also cover the motivation and hypothesis

of the thesis, the type of nanostructured multiphase material (nanocomposites) and the material systems under study.

Chapter 3 is on the materials and methods, where the experimental procedures and characterizations performed are given in detail.

Chapters 4 to 7 are on the results and discussions. In Chapters 4 and 5, the characterization and TE properties of various compositions of both ex-situ and in-situ nanocomposites will be presented and discussed. Chapters 6 and 7 focus on in-situ nanocomposites: In Chapter 6, second phase precipitation in the melt spun samples after further processing (i.e. application of pressure), its orientation relationship with the matrix and the effect of second phase on the TE properties are discussed. Chapter 7 will discuss the effect of processing parameters (i.e. application of heat and fabrication of control samples by the use of solid state synthesis and physical mixing) on the second phase of the material. The observations of the phase transformations will be supported by Miedema model theory.

In Chapter 8, both ex-situ and in-situ nanocomposites will be compared against each other. The conclusion of the work performed for the thesis and recommendations for future work will then be presented. The novelty and significance of the work is also highlighted in this chapter.

CHAPTER 2 - Literature Review

2.1 Thermoelectric Effects

Thermoelectric effects were discovered in the early 1800s, but they were not used for TE applications until the early 1900s. The process by which TE materials convert between a temperature gradient and electricity encompasses three reversible effects: the Seebeck effect, Peltier effect and Thomson effect.

The Seebeck effect was first discovered by Thomas Seebeck in 1821, and it is through this effect that electricity is produced in the presence of a temperature difference. Seebeck realized that if two dissimilar conductors were joined in a closed loop, and a temperature difference was maintained between the junctions, the conductors would respond differently to the temperature difference, and in turn creating a current loop (as shown in Figure 2.1). The voltage (V) created by this effect is proportional to the temperature (ΔT) difference and the Seebeck coefficient for the junction is defined as:

$$S_{ab} = S_a - S_b = \frac{V}{\Delta T} \quad (2)$$

The Seebeck coefficient (also known as thermopower) is an intrinsic property of the material, and can be in the order of several tens to hundreds of microvolts per Kelvin ($\mu\text{V/K}$), depending on the nature of the material [14].

Figure 2.1: Schematic diagram of Seebeck effect.
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Conversely, when supplied with electricity, heat is transferred through the Peltier effect. The Peltier effect was discovered by Jean-Charles Peltier in 1834, who observed temperature changes (i.e. heating and cooling) in the vicinity of the junction between dissimilar conductors when a current was passed through it (as shown in Figure 2.2). The rate of reversible heat absorption Q accompanying the passage of current I through the junction given by [14]:

$$Q = \pi_{ab}I \quad (3)$$

where π_{ab} is the Peltier coefficient of the junction measured in volts.

Figure 2.2: Schematic diagram of Peltier effect.
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The last effect is the Thomson effect, which describes the heating or cooling of a single homogeneous current-carrying conductor in the presence of a temperature gradient. It was predicted and subsequently experimentally observed by W. Thomson (Lord Kelvin) in 1851 after he established a relationship between the Seebeck and Peltier effect. The Thomson effect (as shown in Figure 2.3) is related to Q , the rate of generation of reversible heat which results from the passage of a current (I) along a portion of a single conductor over which there is a small temperature difference (ΔT):

$$Q = \beta I \Delta T \quad (4)$$

where β is the Thomson coefficient and its units is in V/K. β can be positive or negative, depending on the direction of current and temperature gradient – if both have the same direction, the material absorbs heat and β has a positive value, otherwise, β is negative. The Thomson effect is not of primary importance in thermoelectric devices, since its influence on performance of thermoelectric devices is very weak; but for detailed calculations, it should not be neglected. [8, 14]

Figure 2.3: Schematic diagram of Thomson effect.
Source: Francis J. DiSalvo, Cornell University [16].

The three TE effects are related by the Kelvin relationships:

$$S_{ab} = \frac{\pi_{ab}}{T} \quad (5)$$

and

$$\frac{dS_{ab}}{dT} = \frac{(\beta_a - \beta_b)}{T} \quad (6)$$

These relationships can be derived using the Onsager reciprocal relationships and the standard theory of irreversible thermodynamics. The validity of these relationships has been demonstrated for a number of thermocouple materials and is assumed to hold for all materials used in TE applications. [14]

A typical TE device, shown in Figure 2.4a, consists of arrays of alternating p- and n-type legs, connected by a metal interconnect (usually copper), and arranged electrically in series and thermally in parallel. In solid state refrigeration or cooling (Figure 2.4b), an electric power input connects to the cold junction through the p-type and n-type semiconductor, such that current flows around the

circuit. The power supply drives the electric current and heat flow, cooling the junction *via* the Peltier effect [6]. Heat is absorbed by the electrons and holes at one junction and transported away to another junction and rejected [2]. The difference in temperature between the two junctions depends on the electrical power through it. Conversely, in power generation (Figure 2.4c), due to the presence of a temperature difference across the ends of the module, the electrons and holes start to move from the heat source to the heat sink. This creates a net charge at the cold end, generating an electrostatic potential (voltage). This voltage produces an electrical current, proportional to the temperature gradient between the two junctions, through the Seebeck effect. [6, 9, 17, 18]

Figure 2.4: Schematic showing (a) a typical TE device, (b) the Peltier effect and (c) the Seebeck effect. From [18]. Reprinted with permission from AAAS.

2.2 Thermoelectric Efficiency

2.2.1 Figure of Merit (ZT)

As mentioned in Section 1.1, the measure of efficiency of a TE material is determined using $ZT = \left(\frac{S^2\sigma}{\kappa}\right) T$ (equation 1). While there is no theoretical limit (other than the Carnot efficiency) to the achievable ZT, the value for most materials has been fluctuating around the value of 1 for the past fifty years due to the interdependence of its parameters [10, 11]. These parameters are determined by the electronic structure and in turn charge carriers (electrons or holes) concentration, and thus are interrelated. As such, optimization of one factor often leads to the deterioration of another.

Figure 2.5: The relationship between electrical conductivity, Seebeck coefficient, power factor and thermal conductivity and concentration of free carriers. Republished with permission of Taylor and Francis Group LLC Books, from [8]; permission conveyed through Copyright Clearance Center, Inc.

From Figure 2.5, it is seen that the three parameters (electrical conductivity, Seebeck coefficient and thermal conductivity) are all functions of carrier concentration. On one end of the spectrum where carrier concentration is low are materials like insulators – the Seebeck coefficient values are high, but the electrical

conductivity values (and correspondingly the thermal conductivity values) are low. On the other end where carrier concentration is high, i.e. metallic materials, the reverse occurs – Seebeck coefficient values are low but electrical and thermal conductivity values are high. Maximum ZT values occur when there is optimum Seebeck coefficient and electrical conductivity (i.e. high power factor); this is often at carrier concentration values corresponding to semiconductors (10^{19} to 10^{20} charge carriers per cubic centimetre). As such, many TE materials are often (heavily doped) semiconductors [8, 19]. Of all the known TE materials, strongly doped semiconductors, or semimetals, with an electron carrier concentration about 10^{19} cm^{-3} prove to exhibit the best performance [1]. Further descriptions of the various parameters in the ZT equation will be covered in Section 2.3.

2.2.2 Conversion Efficiency of Thermoelectric Devices

When calculating the conversion efficiency of a TE device, η , the Carnot efficiency has to be taken into considerations. In power generation, the TE efficiency is defined by combining the Carnot efficiency ($\Delta T/T_{\text{hot}}$) and figure of merit of coupled material (the n- and p-type legs) [11, 20]:

$$\eta = \frac{\Delta T}{T_{\text{hot}}} \frac{\sqrt{1+ZT_{\text{avg}}} - 1}{\sqrt{1+ZT_{\text{avg}}} + \left(\frac{T_{\text{cold}}}{T_{\text{hot}}}\right)} \quad (7)$$

$$\text{And given } Z = \frac{S_{\text{ab}}^2}{\sqrt{\rho_a \kappa_a} + \sqrt{\rho_b \kappa_b}} \quad (8),$$

where T_{hot} and T_{cold} are the temperatures of the hot and cold ends in a TE module and ΔT is their temperature difference. The term $\sqrt{1+ZT_{\text{avg}}}$ varies with the average temperature T_{avg} .

Based on Figure 2.6, it is shown that with increases in Z , depending on the temperature difference (top x-axis), the predicted conversion efficiency (y-axis) can increase up to 30%, which also translates to a value near the Carnot efficiency limit (bottom x-axis) – this is highly attractive as it potentially allows TE materials to be comparable to traditional energy conversion devices.

Figure 2.6: Conversion efficiency as a function of operating temperature difference and range of values of the material's figure of merit. Republished with permission of Taylor and Francis Group LLC Books, from [8]; permission conveyed through Copyright Clearance Center, Inc.

On the other hand, for cooling devices, the maximum efficiency is determined *via* the coefficient of performance, $\Phi_{\max}$, defined as the net heat absorbed at the cold end divided by the applied electric power [8]:

$$\Phi_{\max} = \frac{T_{\text{cold}}[\sqrt{1+ZT_{\text{avg}}} - (\frac{T_{\text{hot}}}{T_{\text{cold}}})]}{(T_{\text{hot}} - T_{\text{cold}})[\sqrt{1+ZT_{\text{avg}}} + 1]} \quad (9)$$

The above discussion shows that Z affects the temperature difference that can be achieved, which will in turn affect conversion efficiency of both power generation and cooling devices. To obtain higher TE efficiencies require both high ZT values and a large temperature gradient across the TE device. [8, 21] For instance, if device ZT is increased by a factor of 4, and taking the temperature difference to be 450 K, the conversion efficiency increases to about 10%. This translated to about 30% of Carnot efficiency, comparable to domestic refrigerators [11, 22].

2.3 Parameters in the ZT equation

2.3.1 Seebeck Coefficient

As discussed in Section 2.1, the Seebeck coefficient of a material, S , is an intrinsic property and measures the magnitude of the induced TE voltage in response to a temperature difference across it: In the presence of a temperature difference, depending on the type of material, the electrons or holes diffuse from the hot side to the cold side. These carriers leave behind oppositely charged and immobile nuclei at the hot side, giving rise to a TE voltage. The separation of charges also creates an electric potential, and the buildup of carriers onto the cold side eventually ceases at some maximum value as there is an equal amount of charged carriers drifting back to the hot side due to the electric field at equilibrium. With an increase in the temperature difference, buildup of more charge carriers occurs on the cold side and lead to an increase in the TE voltage. Hence, the Seebeck coefficient can also be a measure of the entropy per charge carrier in the material. [23]

Presence of both electrons and holes in a material can contribute to the induced TE voltage, given by a weighted average to their electrical conductivity (σ) values:

$$S \approx \frac{S_e \sigma_e + S_p \sigma_p}{\sigma_e + \sigma_p} \quad (10)$$

This indicates that presence of both electrons and holes in a material will cancel out each other's contribution, making the resultant TE voltage small. It is necessary to dope the semiconductors with either donor or acceptor states to allow extrinsic conduction of the appropriate carrier type, electrons, or holes, respectively. Thus, they can have large positive or negative values of thermopower depending on the charge of the excess carriers. The sign of the thermopower is determined by the charged carriers that dominate the electric transport in both metals and semiconductors. [23]

Boltzmann transport theory describes both electronic and thermal transport in the vast majority of solids. From the point of simple theoretical considerations, and considering classical statistics in a single band model (i.e. either electron band or hole band) with the usual parabolic density-of-states distribution and assuming that the carriers obey classical statistics, the Seebeck coefficient can be expressed as:

$$S = \pm \frac{k_B}{e} \left(\frac{5}{2} + s - \xi \right) \quad (11a)$$

and

$$\xi = E_F/k_B T \quad (11b)$$

where ξ is the reduced Fermi energy, E_F is the Fermi energy, k_B is the Boltzmann's constant, T is the absolute temperature and s is the scattering parameter. The +/- sign is due to the contribution from holes or electrons respectively: a positive value means the major carriers are holes and a negative value means the major carriers are electrons.

However, the use of classical statistics to describe the behavior of the carriers is justified only in the limit of low carrier concentration. As TE materials are heavily doped in general, Fermi-Dirac statistics have to be used instead. The Seebeck coefficient is expressed in the form:

$$S = \pm \frac{k_B}{e} (\delta - \xi) \quad (12a)$$

$$\text{where } \delta = \frac{\left(s + \frac{5}{2}\right) F_{s + \frac{3}{2}}(\xi)}{\left(s + \frac{3}{2}\right) F_{s + \frac{1}{2}}(\xi)} \quad (12b)$$

The term $F_x(\xi)$ is the Fermi integral, and depending on the scattering mechanisms, the scattering parameter s takes on the values $-1/2$ for acoustic phonon scattering, $+1/2$ for polar optical mode of scattering and $+3/2$ for ionized impurities scattering. [24]

Thermopower can be expressed by the Mott–Jones relation applied to simple transport models (parabolic band model in the energy independent scattering approximation):

$$S = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left(\frac{d \ln \sigma(E)}{dE} \right)_{E=E_F} \quad (13)$$

Alternatively, it can be expressed in terms of effective mass, m^* , as:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (14)$$

where $\sigma(E)$ is the electronic conductivity determined as a function of the band filling or Fermi energy. If electronic scattering is independent of energy, then $\sigma(E)$ is just proportional to the density of states (DOS) at E . Figure 2.7 shows two hypothetical electronic DOS diagrams: In Figure 2.7a, DOS varies rapidly near E_F , and in Figure 2.7b, DOS does not. Based on equation 13, the system in Figure 2.7 with rapidly changing DOS is expected to have a larger TE power. [11]

Figure 2.7: Hypothetical density of state with (a) a large slope and (b) a small slope, near E_F . Reproduced from [11] with permission from Wiley Materials.

The Seebeck coefficient S in equation 13 is a measure of the variation in $\sigma(E)$ above and below the Fermi surface, specifically through the logarithmic derivative of σ with E , and is also a measure of the asymmetry in electronic structure and scattering rates near the Fermi level. Thus the aim should be to produce complexities in either or both electronic structure and scattering rates within a small energy interval (a few $k_B T$) near E_F . [10, 11]

How the DOS change with materials of decreasing dimensions is shown in Figure 2.8. It is seen that a reduction in dimensionality produces a more highly structured DOS compared to conventional bulk materials, leading to sharp changes in DOS. Hence, reducing dimensionality of materials is a means to increase S and in turn ZT . [25]

Figure 2.8: Schematic representation of the electronic density of states for (a) bulk material (three-dimensional), (b) quantum well (two-dimensional), (c) nanowire (one-dimensional) and (d) quantum dot (zero-dimensional). Reproduced from [10] with permission from The Royal Society of Chemistry.

The approach of reducing dimensionality to enhance the density of states (DOS) near the Fermi level, and in turn increase S , is known as quantum confinement. [10, 25] This is achieved by making the size scale of the material comparable to the spatial extent of the electronic wave function confining the electrons in one or more dimensions. If electron scattering is assumed to be energy independent (i.e. $\mu(E) = \mu$, where μ is the electron mobility), then the electrical conductivity is directly proportional to the DOS. This approach allows the decoupling of S and σ , enabling both parameters to increase concurrently.

Although the quantum confinement approach appears promising for enhancing ZT , it can be difficult to achieve due to the small confinement length requirements in many materials, potentially limiting the ability of this route to enhance ZT . [10]

Another approach to obtain high Seebeck coefficient values is through energy filtering, which can occur through band offset of the different phases. As such, low energy carriers are scattered, leaving higher energy carriers, and the net Seebeck coefficient for a given carrier concentration increases. [12, 26]

For high ZT values, large thermopower values are attractive as only a small amount of heat is necessary to induce a large voltage. This voltage can then be used to provide power. [23] Seebeck coefficient of the most commonly used materials in TE applications are typically on the order of a few tens or hundreds of microvolts per degree Kelvin. [10]

2.3.2 Electrical Conductivity

The electrical conductivity of a material, σ , is a measure of how many carriers (electrons and holes) can contribute to the electrical current along with their mobility (μ) and is given by the equation:

$$\sigma = ne\mu_n + ph\mu_p \quad (15)$$

where n (or p) is the carrier concentration, e (or h) is the carrier charge, μ_n (or μ_p) is the carrier mobility.

For n-type materials,

$$n = 2\left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2} e^{(E_F - E_C)/k_B T} \quad (16)$$

Or for p-type materials,

$$p = 2\left(\frac{2\pi m_p^* k_B T}{h^2}\right)^{3/2} e^{(E_V - E_F)/k_B T} \quad (17)$$

And,

$$\mu_n = \frac{e\langle\tau_n\rangle}{m_n^*} \quad (18)$$

Or,

$$\mu_p = \frac{h\langle\tau_p\rangle}{m_p^*} \quad (19)$$

where m_n^* (or m_p^*) is the effective mass of carrier, h is the Planck's constant and $\langle\tau_n\rangle$ (or $\langle\tau_p\rangle$) is the mean scattering times between collisions of the carriers. The values of the parameters (σ , μ_n/μ_p and n/p) can be measured experimentally through resistivity and Hall coefficient determination.

For metals, there are usually many electrons and states available for conduction, hence conductivity is high and usually on the order of $10^8 (\Omega\text{m})^{-1}$; for semiconductors for TE applications, carriers (electrons or holes) have to be excited across the band gap (E_G) for conduction to occur, electrical conductivity is represented as:

$$\sigma = \sigma_0 \exp\left(\frac{E_G}{k_B T}\right) \quad (20)$$

The two ways to achieve high electrical conductivities in semiconductors are: (1) by having a very small band gap for carriers to cross ($E_G < k_B T$) or (2) by having very high mobility carriers. In turn, typical electrical conductivity values can lie between 10^{-2} and $10^6 (\Omega\text{m})^{-1}$. [15]

The band structures of the material also play an important role in contributing to the efficiencies of TE materials. Figure 2.9 shows the schematics of two types of band structures, one simple and the other complex. In Figure 2.9a, there is only one band extremum in the valence band and one in the conduction band, while in Figure 2.9b the band structure is complex with multiple extrema in both the valence and conduction bands. It can be expected that the complex structure produces a larger power factor than the simple structure under similar carrier concentrations (either purely p-type or purely n-type). The presence of a large number of such valleys in the band structure could lead to increased ZT because the total power factor for the material derives from the summation of contributions from all extrema. [11, 27, 28]

In addition, the band gap of TE materials is important because in general, the temperature at which the ZT is maximum scales with band-gap size. For a given band gap energy there is a temperature at which thermally induced cross-gap carrier excitations occur to generate carriers of opposite sign which decrease the thermopower. It has been shown that semiconductors with a band gap of approximately $10 k_B T$ best satisfy this criterion. [29] Thus, for cooling applications small band-gap materials are best whereas for high-temperature power generation

larger gaps are necessary. Qualitatively, the higher the band gap, the higher the temperature at which the maximum in ZT will be reached before it declines. [11]

Figure 2.9: Hypothetical electronic band structure with (a) single extremum and (b) multiple extrema in the conduction and valence bands. Reproduced from [11] with permission from Wiley Materials.

2.3.3 Thermal Conductivity

The thermal conductivity of a material defines its ability to transport heat, and is one of the most important parameter in determining the ZT of TE materials. Thermal conduction consists of two components – the lattice contribution κ_L and the electronic contribution κ_e :

$$\kappa = \kappa_e + \kappa_L \quad (21)$$

The lattice thermal conductivity is the transport of heat by phonons (lattice vibrations) through the lattice while the electronic thermal conductivity is the transport of heat from the electrons moving through the lattice. [19] The relationship between electronic thermal conductivity and electrical conductivity is shown in the Wiedemann-Franz law, which is applicable to metallic systems and degenerate semiconductors:

$$\kappa_e = L\sigma T \quad (22)$$

where κ_e is the electronic thermal conductivity, L is the Lorenz number, and relates to the coupling between charge carriers and phonons in a given class of materials

(the Lorenz number can be expressed as: $L = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 = 2.45 \times 10^{-8} \text{ V}^2\text{K}^{-2}$ in metals and degenerate materials and $L = 2\left(\frac{k_B}{e}\right)^2 = 1.48 \times 10^{-8} \text{ V}^2\text{K}^{-2}$ for non-degenerate materials); σ is the electrical conductivity and T is the temperature in Kelvins. [1, 10, 11]

In insulators, heat is transported via phonons so the lattice contribution makes up a significant portion for the thermal conductivity. In metals, thermal conduction is mainly through the electronic component. In semiconductors, as both the electronic component and lattice component are contributors, they are usually quantified separately. In general, κ_e is small in magnitude compared to κ_L . [30]

The classical kinetic theory provides a good approximation for the lattice thermal conductivity by:

$$\kappa_L = \frac{1}{3} C_v v_s \lambda_{ph} \quad (23)$$

where C_v is the heat capacity (specific heat of the lattice), v_s is the average velocity of sound, and λ_{ph} is the phonon mean free path. [10, 11] At temperatures much higher than room temperature, the velocity of sound and the heat capacity in typical materials are independent of temperature; thus the magnitude and the temperature dependence of κ_L is basically determined by the mean free path of the phonons [31].

The thermal conductivity predicted by Callaway's model [32] is expressed as follows:

$$\kappa = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar}\right)^3 \left\{ \int_0^{\theta/T} \frac{\tau_c x^4 e^x}{(e^x - 1)^2} dx + \frac{[\int_0^{\theta/T} \frac{\tau_c}{\tau_N} \frac{x^4 e^x}{(e^x - 1)^2} dx]^2}{\int_0^{\theta/T} \frac{1}{\tau_N} (1 - \frac{\tau_c}{\tau_N}) \frac{x^4 e^x}{(e^x - 1)^2} dx} \right\} \quad (24)$$

where k_B is the Boltzmann constant, $\hbar$ is Planck's constant divided by 2π , x is the normalized frequency $\hbar\omega/k_B T$, T is the absolute temperature and v and θ are the speed of sound and Debye temperature of the material, respectively. The term τ_c is

the combined phonon scattering relaxation time, and is expressed using the Matthiessen's rule:

$$\tau_C^{-1} = \tau_B^{-1} + \tau_U^{-1} + \tau_N^{-1} + \tau_A^{-1} + \tau_{e-ph}^{-1} + \tau_D^{-1} \quad (25)$$

where τ_B is the boundary scattering, τ_U is the Umklapp scattering, τ_N is the normal scattering, τ_A is the defect or alloy scattering, τ_{e-ph} is the electron-phonon scattering and τ_D is the scattering due to presence of second phase (e.g. nanoparticles) in the material.

The lattice thermal conductivity has a wave like component, which is made up of acoustic (sound) waves and optical waves. [10] Acoustic waves are low energy phonon modes and the optical waves are higher energy phonon modes, and are named as such in relation to their response to acoustic (sound) disturbances and electromagnetic radiation, respectively. In general, acoustic phonons describe the inter-unit cell response of the lattice to external forces, like temperature or voltage, while the optical phonons describe intra-cell interactions. [30, 33] Thus, the phonon spectrum in heat transport in materials is made of up a distribution of wavelengths – short, medium and long – and these different wavelengths contribute different amounts to the heat transport. [25] Semiconducting materials possessing low sound velocities and short phonon mean free paths will have favorably low thermal conductivities, making them good candidates for high ZT TE applications. [10]

The concept of minimum lattice thermal conductivity, introduced by Slack [34], refers to the state when all phonons have a mean free path equal to the interatomic spacing of the constituent atoms in the material. Typical minimum lattice thermal conductivity values lie in the range of 0.25 W/m.K – 0.5 W/m.K, and will create a practical ZT limit for TE materials, with the predicted upper limit of ZT lying in the range of 1.5 to 4, depending on operating temperature range. [15]

2.4 Thermoelectric Materials Research

2.4.1 Motivation for Thermoelectric Materials Research

The average global primary power consumption in 2010 was approximately 14 terawatts, and this value is set to increase by more than 44% in the next few decades [2, 25]. Considering the current environmental impact from the burning of fossil fuels, to meet this increased demand, alternative energy generation techniques ranging from renewable sources to advanced energy recovery methods have to be utilized. This will allow more efficient usage of existing resources. Thus, there is much research in the areas related to clean energy e.g. lithium-ion batteries, fuel cells, solar cells, and also thermoelectrics. [25]

Although TE effects were discovered in the early 1800s, due to competing discoveries then, the potential of thermoelectrics was overlooked. Nevertheless, there was renewed interest in TE materials in the sixties, after better understanding and practical work showed the possibility for TE materials to be used in military applications [14]. Hence, interest in TE materials spanned over the last 50 years, with researchers continually trying to improve the efficiency of these materials [35].

The temperature range of application for TE materials is defined by the electronic band structure, crystal structures, and preparation methods [36]. Thus, different materials have optimized performance at different temperatures ranges, which was mentioned in Section 1.1. These TE materials have relatively good ZT values of about 0.8 – 1.2 in the working temperature range. Nevertheless, they translate to an efficiency of only about 5% to 6% (or about 10% of the Carnot efficiency) [11, 22, 37]; indeed, TE materials are not widely used due to their low efficiency (and in turn is neither cost-effective nor competitive) compared to the traditional electric generators or refrigerators, which are working at about 90% and 30% of the Carnot efficiency respectively [22].

For TE devices to be efficient enough to be competitive with market devices such as conventional electric generators and home refrigerators, ZT values have to be increased to above 1.5 for power generation, and ~2 to 4 for cooling

applications [10]. This corresponds to an increase in efficiency to about 20% and a wider operation temperature range [1, 11]. Figure 2.10 shows the efficiency of various energy conversion technologies and renewable energy technologies:

Figure 2.10: Efficiency of energy conversion technologies and renewable energy technologies. (Legend: PV – photovoltaic; CSP – concentrated solar power; Org, TE and TI – organic, thermoelectric and thermionic). Reproduced from [17] with permission from The Royal Society of Chemistry.

To allow more widespread use of TE devices, the costs involved (e.g. raw materials and technology implementation) should be considered. An upper limit of 12.5 cents per watt has been proposed for TE power generation modules for automotive applications, for which the average vehicle requirements are about 1 kW of electric power. It is estimated that current TE modules require about 1 kg of TE material to produce a 1 kW generator, suggesting an upper limit of about \$125 per module. However, higher efficiencies are likely to drive this cost down. On the other hand, as commercial TE modules are commonly based on tellurides, which are quite costly, they may not be attractive from a business point of view. Hence the use of alternative materials has to be researched. [25] Figure 2.11 gives an idea of the cost of various TE materials and its dimensions, compared to existing technologies:

Figure 2.11: The operating cost of the various types and dimensions of TE materials compared to the existing technologies. Reprinted from [38], Copyright (2014), with permission from Elsevier.

2.4.2 Development of Materials

Research on TE materials started more than 50 years ago, and Figure 2.12 gives a general overview in the direction in TE research over the years, which will be briefly discussed in the next few paragraphs:

Figure 2.12: History of thermoelectric research. Adapted from [39], Copyright (2013), with permission from Elsevier.

Research in TE materials started in the mid-20th century, where Bi₂Te₃-based alloys were widely pursued. However, there was limited progress made in the development of TE materials and the ZT obtained was stagnant at a value of approximately 1. In the material system of Bi₂Te₃-based alloys, the strategy used to obtain good TE properties traditionally was by introducing point defects through the formation of solid solutions (alloying) or doping, where atoms of different elements cause atomic mass fluctuations throughout the crystal lattice (i.e. disorder). This induces strong phonon scattering leading to significantly lower thermal conductivity and in turn increased ZT. [11]

The turning point came in the mid-1990s when more advanced TE materials were discovered, leading to increased ZT values [6]; it was also then when Hicks and Dresselhaus [27] discovered that suitable nanostructuring could lead to power factor enhancement and reduced thermal conductivity, leading to increased ZT [40]. Dresselhaus' pioneering work highlighted the potential of various low-dimensional systems like superlattices, nanowires and quantum dots, sparking renewed interest in TE materials development. Soon after, reports of high ZT obtained at 300 K were reported by other researchers: Venkatasubramanian *et al.* [41] reported on p-type Bi₂Te₃/Sb₂Te₃ superlattices with a high ZT of about 2.4, while Harman *et al.* [42] reported on PbSeTe/PbTe quantum dot superlattices with a ZT value of 1.6. Hence, a new wave of research focused on complex thermoelectrics, advanced materials or nanostructured TE materials.

Complex materials research was based on the idea proposed by Slack [34] and is referred as the “phonon glass electron crystal” (PGEC) approach. In PGEC materials, it is proposed that glass-like thermal conductivity can in principle coexist with high mobility charge carriers (i.e. conducts heat like a glass, but conducts electricity like a crystal); this class of complex materials include (but not limited to) filled skutterudites and clathrates. Due to the nature of the crystal structure, there exists “cages” or “tunnels” where weakly-bound atoms or molecules which are small enough can reside and “rattle” within the space. This leads to strong scattering of lattice phonons, but does not affect the transport of electrons adversely,

and so large reduction in thermal conductivity can be achieved and relatively high electrical conductivity can be maintained [7, 11].

On the other hand, advanced materials include tuning existing TE materials to improve their TE properties with techniques like band structure engineering [43], modulation doping [44, 45] and resonance energy level doping [46-48]. In these approaches, changes in the electronic structure are achieved through doping and composition optimization. The selected dopants usually have energy levels near the Fermi level, increasing the DOS near the Fermi level, which leads to improved Seebeck coefficient and electrical conductivity. Indeed, new research done on these materials has led to interesting increases in ZT.

Nanostructuring of TE materials is the other approach taken to improve ZT, and can be performed on new and existing material systems for TE applications. In this approach, these materials are fabricated in order to obtain them in nanometer sizes or with nano-sized features. The enhancement from nanostructuring is shown in Figure 1.2 in Chapter 1, where improved ZT values much larger than 1 can be obtained compared to the bulk material. Some methods used in the fabrication of these nanomaterials include physical and chemical processes like melt spinning [49-54], ball milling [55-57], vapour deposition [58, 59], and wet chemical synthesis methods [60-65].

Based on the results obtained in systems where $ZT > 1$, it was realized that the high values of ZT were most often due to very low lattice thermal conductivity values of the materials [6], as it is the only parameter not determined by the electronic structure and could be tuned independently [11, 15]. Thus, although nanostructuring was initially proposed because of predicted enhancements in Seebeck coefficient values, it led to increased phonon scattering and in turn reduced thermal conductivity. [66] However, as it is believed that enhancements resulting from increased thermopower are also possible, and hence much work is focused on achieving it.

2.4.3 Approaches used to increase ZT

The two main approaches used in TE materials research to increase ZT are [11]:

- 1) Decrease (lattice) thermal conductivity
- 2) Increase power factor

Techniques by which decreased thermal conductivity values can be obtained have been well established and demonstrated [25, 67], e.g. through solid-solution alloying and by nanostructuring. To maximize power factor, the product of the Seebeck coefficient and electrical conductivity has to increase. Since these two parameters are inversely related, an optimized value has to be reached. Methods used include the development of new or advanced materials, doping of existing materials to further optimize performance and the exploration of synergistic nanostructuring in materials.

As mentioned in Section 2.3.3, lattice thermal conductivity is transported via phonons, which are made up of variety of wavelengths. Phonons are scattered by defects or structures in the material, when their mean free paths are larger than the spacing between these features.

As shown in Figure 2.13, short wavelength phonons are generally scattered through methods like alloying, where there is mass difference in the material; mid to long wavelength phonons, which usually make up the transport of appreciable amounts of heat, are scattered by grain boundaries or interfaces in the material. [10, 66]

As such, nanostructuring provide the desired interfaces; however, these interfaces can also scatter charge carriers. Hence, to obtain increased ZT from this approach, phonons have to be scattered more strongly than the electrons, assuming that Seebeck coefficient does not change, or increases. To mitigate this effect, features that span across various length scales should be incorporated in the material so that scattering of phonons of various wavelengths can be done effectively without decreasing electron mean free path [3, 6, 10, 66]. Ideally, the

interfaces should have coherent structures so that there is continuity of the adjoining lattices, and the electronic structure is minimally disrupted while still being able to act as a site for phonon scattering. [66]

Figure 2.13: Schematic of various phonon scattering mechanisms in a thermoelectric material, with the path of hot and cold electrons shown. Reproduced from [33] with permission from Wiley Materials.

Apart from the possibility of quantum confinement effect, an additional benefit from nanostructuring is that interfaces may be able to act as an “energy filter”, which is an energy barrier associated with the interface. This barrier can lead to preferential scattering of low-energy charge carriers, in turn increasing the Seebeck coefficient. If there is knowledge of the mean free path of electrons and phonons in a material, e.g. silicon nanowires, it will allow design of the nanostructuring of material to scatter phonons and not electrons, and in turn reducing lattice thermal conductivity without affecting power factor. [17, 20, 25, 66, 68]

Further breakthroughs in TE materials performance may potentially allow commercialization. Hence balancing of electronic and thermal properties is critical – low thermal conductivity has to be combined with a concurrent increase in power factor of the material. One way to achieve this is through the use of nanocomposites. Bulk TE nanocomposites are an attractive direction to pursue

because of the ability to decouple the parameters in the ZT equation, leading to improved TE performance. Additional advantages include the incorporation of nanostructures, the ability to prepare them by bulk commercial fabrication processes (i.e. scale up) [30] and the ease of handling for TE properties measurement and materials characterization [69]. Further discussion on improving TE properties via the use of nanocomposites will be covered in Section 2.5

2.5 Nanocomposites

2.5.1 Introduction and Motivation

Nanocomposites is one form of nanostructuring, and refers to the inclusion of nanostructured particles of one type of material in another type of host material (matrix), a mixture of various nanostructured materials, or a bulk material consisting of nanostructured domains [9].

Shown in Figure 2.14 is the evolution of TE materials from the bulk to nanostructured form. Initially, TE materials were mostly produced in the bulk, three-dimensional (3D) form (Figure 2.14a). With the discovery made by Hicks and Dresselhaus on nanostructuring (Section 2.4.2), the sizes and morphologies have evolved to become 2D thin films (Figure 2.14b), 1D nanowires (Figure 2.14c) or 0D atomic clusters (Figure 2.14d). In recent years, different studies were made by different researchers [70-76], with the approach of incorporating nanostructures into bulk materials becoming increasingly popular. The evolution of the TE materials and the various types of nanocomposites are as follows: (i) bulk material with (micron-sized) grains (Figure 2.14e), (ii) bulk material with micron- and nano-sized grains (Figure 2.14f), (iii) bulk material with nano-sized grains (Figure 2.14g), (iv) the use of amorphous material in a bulk (Figure 2.14h), (v) normal composite with isolated distinct phases or atoms (Figure 2.14i), (vi) nanoscale dispersions located inside the grains or at grain boundaries (Figure 2.14j), (vii) nanoinclusions or nanodots, boundary modification (Figure 2.14k) and (viii) atomic doping, alloying, and vacancies (Figure 2.14l). The nanocomposites can be considered as a form of multiphase material as the nanoinclusions and matrix may or may not be

made up of the same material, thus more than one phase can be present in the nanocomposites.

Figure 2.14: Evolution of TE materials from the bulk to nanostructured form (a) 3D bulk material, (b) 2D thin films, (c) 1D nanowires, (d) 0D atomic clusters, (e) bulk material with (micro-sized) grains, (f) bulk material with micro- and nano-sized grains with different phases, (g) bulk material with nano-sized grains, (h) amorphous phases in a bulk material, (i) normal composite with isolated distinct phases or atoms, (j) nanoscale dispersions located inside the grains or at grain boundaries, (k) nanoinclusions or nanodots, boundary modification and (l) atomic doping, alloying, and vacancies. Reprinted by permission from Macmillan Publishers Ltd: NPG Asia Materials [7], copyright (2010).

The motivation for using nanocomposites is due to the fact that this approach can potentially combine reductions in thermal conductivity and increases in power factor concurrently for the following reasons:

- 1) The nanoscale phases offer a possibility to individually tune TE properties, and also contribute to increased phonon scattering.
- 2) If the nanoscale phases are small enough, i.e. comparable to the mean free path of electrons, the DOS is increased significantly due to quantum confinement; alternatively, they can act as sites for energy filtering. The result is that the Seebeck coefficient is enhanced.

- 3) The presence of phases at different length scales (nano-micron sized grains combination) allows scattering over a range of phonon wavelengths, yet allow electron transport to be preserved such that decoupling these two parameters is achieved.
- 4) The features or grains are also likely to be of different composition from the bulk, and hence can take part in controlling the TE properties through their effect on electrical conductivity.

Generally, there are two classifications of nanocomposites, in-situ and ex-situ, depending on their processing methods. These will be further discussed in Section 2.5.2 and 2.5.3.

2.5.2 Basis of Work for Ex-situ Nanocomposites

The approach of using ex-situ nanocomposites was widely used after the discovery of the benefits of nanostructuring. Typically, a host material would act as a matrix (either nanostructured or with particle sizes in the range of microns), and another nanostructured phase (which can be of similar or different composition to the matrix) would be physically mixed together [77] and then hot pressed to be consolidated into a bulk sample [70, 71]. Usually the constituent phases chosen would complement each other, e.g. the bulk matrix may have average or good Seebeck coefficient but low electrical conductivity, while the second phase possess a higher electrical conductivity to tune the overall TE properties. The aim of working with ex-situ nanocomposites is to incorporate nanostructures for phonon scattering, yet at the same time have a bulk material for ease of handling.

The matrix material can be synthesized by a variety of methods: for micron-sized material, it is usually ball milling or solid state synthesis, while the nanostructured phases are usually synthesized *via* wet chemical methods. In chemical syntheses, organic capping agents or surfactant are commonly used, and can remain as residues on the surface of the nanostructures, leading to detrimental effects on the electrical conductivity after compaction and during property measurements. It is also possible that as the matrix and nanostructured phase are just physically mixed together, they may exist as separate phases, and in some

cases not be conducive to electron movement. Thus, one common issue that can result from ex-situ nanocomposites is lowered electrical conductivity. As such, the choice of suitable materials that can be compatibly added together is important.

Approaches taken to mitigate the above effect include: taking an additional step of surfactant removal after synthesis [78], using alternative approaches like melt spinning and/or ball milling to obtain nanostructured phases [79, 80] and mixing nanostructured phases of the same composition as that of the matrix [70]. For instance, in the work done by Fan *et al.* [70], a nanocomposite formed by adding melt spun nanostructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ to bulk micron-sized $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ synthesized by solid state reaction was able to reach a peak ZT of 1.80 at 316 K, a 56% increment over the bulk sample. In yet another work utilizing melt spinning, Xie and coworkers [81] fabricated a high-performance $\text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3$ bulk material, achieving a ZT of 1.56 at 300 K. Poudel and coworkers [79] also utilized the ball milling method to achieve a maximum ZT of 1.4 at 373 K in Bi-Sb-Te alloys.

In the first part of the thesis work, the exploration of ex-situ nanocomposites based on one of the most commonly used TE material, Bi-Sb-Te, is performed. The nanostructured phase is copper telluride, and this material system will be further discussed in Section 2.6.1.

2.5.3 Basis of Work for In-situ Nanocomposites

The research on the formation of in-situ multiphase nanocomposite formation has been an approach considered in recent years to improve the properties of TE materials, and have been undertaken by researchers like M. G. Kanatzidis and coworkers from Northwestern University, and G. J. Snyder and coworkers from California Institute of Technology. Here, we explore this approach due to the following issues faced when working with ex-situ nanocomposites:

- **Difficulty in controlling agglomeration** – micron-sized aggregates of the Cu_7Te_4 phase in BST matrix
- **Possible grain growth or particle coarsening during hot press**

- **Cracks observed in some hot pressed samples**

In in-situ nanocomposites, nanostructures are formed inside the matrix during processing [77]. The fabrication of these in-situ nanocomposites are mostly *via* traditional metallurgy approaches like (a) solid state partitioning during cooling as the material crosses from a single to two-phase region in the phase diagram, (b) formation and subsequent decomposition of a metastable phase, and (c) solidification from the melt. [72] As these are often diffusion limited processes, by changing the different processing parameters, various microstructures can be obtained.

In these multiphase in-situ nanocomposites, the general idea is as follows: the second phase can exist either as (i) nanoprecipitates or (ii) as larger nano-sized, sub-micron or micron-sized precipitates. In the first approach, the bulk of the work has been done by Kanatzidis *et al.*, and is mainly based on the PbTe material system, with the second phase material composed of another compound or element. The choice of materials are based on the phase diagrams, leading to the formation of solid solutions that can form nanoinclusions through phase transformations like nucleation and growth [82, 83], or spinodal decomposition [83, 84] and heat treatment. The limited solubility of one or more element in another material (the matrix component) in the solid state can also lead to nanoinclusion formation through the matrix encapsulation method upon quenching (i.e. rapid solidification) [85, 86]. These phase transformations allow precipitates of a different phase, in the size range of a few nanometers to tens of nanometers, to form in the matrix. The net effect is an increased scattering of phonons, leading to very low thermal conductivity. It was also observed that the presence of certain elements in some systems allowed the tuning of electrical properties, while in others, interactions arising from the precipitation of the second phases leads to synergistic improvement in properties, rather than just a cumulative effect. There is also other research carried out on such in-situ nanocomposites [77, 87, 88], but they will not be elaborated here.

In the second approach, both Kanatzidis and Snyder have published results on systems like PbTe-Sb₂Te₃ [89], PbTe-PbSnS₂ [37, 90], (PbTe)_{1-x}(Ag₂Te)_x [72], PbTe-CdTe [74] and In₂Te₃-Bi₂Te₃ [87]. The basis of the choice of alloy compositions is also through the phase diagram, although heat treatment may or may not be required to form the second phase. In these nanocomposites, the net effect is reduced thermal conductivity. However, in some cases, detrimental effects on the electrical properties are also observed, which require further modifications in the electronic band structure (e.g. in PbTe-CdTe) to realize the decrease in thermal conductivity and increase in electrical properties. Thus, the potential difficulties for in-situ nanocomposites would be the choice of suitable materials that can form compatible multi-phases during processing.

There are also other types of nanocomposites, and two will be mentioned as examples. In the first type, nano-sized precipitates are formed in the matrix due to doping. These second phases can alter the electronic band structure leading to improvements in thermopower and decreased thermal conductivity. It can also, depending on the element, allow optimization of carrier concentration and thermopower, and decrease thermal conductivity. In addition, due to microstructural complexities, where there can be nano-sized structures or defects present, leading to significantly low values of thermal conductivity, and in some cases not degrading the electrical properties. [6, 46, 49, 91-93] Examples of material systems that belong to this category are PbTe-based alloys e.g. Pb_{9.6}Sb_{0.2}Te_{10-x}Se_x, PbTe_{1-x}Se_x, Ag(Pb_{1-y}Sn_y)_mSbTe_{2+m}, and Na_{1-x}Pb_mSb_yTe_{m+2}, Bi-Sb-Te alloys, (AgSbTe₂)_{0.15}(GeTe)_{0.85} (TAGS) and (AgSbTe₂)_x(PbTe)_{1-x} (LAST). In the second type, an amorphous/nanocrystal in-situ nanocomposite is formed by the solid state synthesis approach (with rapid quenching and annealing). Low thermal conductivity and improved electrical conductivity led to improved ZT. An example of this is the GeTe alloy [94].

The improvements obtained from in-situ nanocomposites are due to coherent or semi-coherent interfaces, and the ability to control the mass fraction, size and shape of the second phases. This in turn determines the interfacial area

present to scatter phonons or control electrical properties, allowing the decoupling of the parameters in the ZT equation. Hence, this is an attractive approach for exploration, which will be the focus of the second part of this thesis work.

Due to environmental and toxicity issues, the use of lead-based materials should be avoided. Hence, an alternative material system was explored – SnTe-SnSe – which will be further discussed in Section 2.6.2.

2.6 Material Systems

2.6.1 Ex-situ Nanocomposites: $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$

2.6.1.1 Cu_7Te_4

Copper telluride is reported to be a TE material with measured operation temperature up to 900 K [95-97], but there are not many reports on its TE performance. Literature data on bulk copper telluride shows that it has high electrical conductivity and relatively low Seebeck coefficient in the range of tens of $\mu\text{V/K}$ [96-98]. Usually denoted as Cu_2Te , copper telluride is better represented in the form Cu_{2-x}Te as it has a homogeneity range of 33.3 atomic % – 37.5 atomic % Te [96] (i.e. $0 \leq x \leq 0.25$). This is because Cu vacancies randomly occur as defects, resulting in the slight variation in composition [98].

Studies that have been done on this material are only in bulk or thin film form, and there are few reports on the synthesis of one dimensional copper telluride [99]. There are only a few papers on the synthesis of copper telluride nanostructures using various methods like hydrothermal, electrochemical deposition, microwave-assisted and wet chemical synthesis [95, 99-104], which require long reaction times or specialized equipment. Thus, it would be attractive if one dimensional nanostructures of copper telluride can be synthesized under facile conditions, within a short period of time, and able to be scaled up to fabricate nanocomposites for TE properties characterization.

In this work, the composition of focus is Cu_7Te_4 , due to the achievable composition from wet chemical synthesis. Cu_7Te_4 crystallizes in a hexagonal $P3m1$ structure, as seen in Figure 2.15, and has both direct and indirect band gap [98], and is known to have metallic conductivity [105].

Figure 2.15: Crystal structure of Cu_7Te_4 .

Legend: Blue atoms – Cu, Greenish-brown – Te and Pink atoms – randomly occupied Cu sites. Reprinted with permission from [106]. Copyright (2007), AIP Publishing LLC.

2.6.1.2 $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$

Bismuth antimony telluride (BST) alloys are composed of a combination of Bi_2Te_3 and Sb_2Te_3 , and are currently the most widely used and commercially available TE materials for refrigeration applications. Usually in the form of $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$, it has an indirect bandgap of about 0.15 eV, and crystallizes in a rhombohedral crystal structure (space group $R\bar{3}m$; similar to that of Bi_2Te_3 as seen in Figure 2.16) – five atomic layers are stacked along the c-axis by Van der Waals interactions, while the Bi/Sb atoms are coordinated with six Te atoms in octahedral geometry. [11]

Figure 2.16: Crystal structure of Bi_2Te_3 .
Reproduced from [11] with permission from Wiley Materials.

Bismuth antimony telluride alloys have a high ZT of 0.8 – 1.1 in the temperature range from near room temperature to about 450 K. Many studies have been performed on bulk BST, in the hope that the ZT can be further increased through various processing methods and the search continues as a much higher efficiency is required.

In this work, the BST alloy is obtained directly from Industrial Technology Research Institute (Taiwan). The composition of the as-received material is $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, close to that with optimized properties.

2.6.1.3 $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$

The first part of the thesis work is focused on ex-situ nanocomposites based on $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$. Cu_7Te_4 is selected as surfactant-free nanostructures can be obtained through a straightforward synthesis method. In addition, promising results was reported by Cui *et al.* [107] on a $\text{Cu}_4\text{Te}_3\text{-Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ bulk alloy, hence the motivation of choosing this material system.

As mentioned earlier in Section 2.5.2, the advantage of synthesizing surfactant-free copper telluride nanorods is the minimizing of the disruption of electrical conductivity in the TE material. In this work, chemically synthesized nanorods of Cu_7Te_4 will be added to bulk $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ in various amounts (5 wt %, 38

10 wt % and 15 wt %) to form nanocomposites, and the effect of these additions on TE properties compared to the bulk material alone will be discussed.

2.6.2 In-situ Nanocomposites: SnTe-SnSe

2.6.2.1 SnTe

Tin telluride (SnTe) is a narrow band gap semiconductor, with a direct band gap of bulk SnTe is 0.18 eV at 300 K [108], and is known for applications in mid-infrared photo detectors and TE heat converters [109].

SnTe crystallizes in a cubic NaCl-type lattice (space group $Fm\bar{3}m$) [110, 111], and is shown in Figure 2.17:

Figure 2.17: Crystal structure of SnTe.

Source: Katherine R. Stevens, Carthage College. [112]

Although SnTe is widely used as one of the components in TE alloys, the ZT of the SnTe phase on its own does not exceed 0.35, most likely due to low Seebeck coefficient values in the range of tens of $\mu\text{V/K}$ [113]. Hence, SnTe has to be combined with other compounds to improve the TE properties. There are various synthesis methods to form these materials, e.g. heating mixtures of the elements at high temperature for extended periods of time [114], precipitation from aqueous solutions [115] and organometallic chemical deposition [116].

2.6.2.2 SnSe

Tin selenide (SnSe) is a semiconductor material, known for its potential applications in electronic memory switching devices, solar cells, holographic recording systems [117, 118] and also in thermoelectrics [118-120].

Bulk SnSe has an indirect band gap of 0.90 eV and a direct band gap of 1.30 eV [121]. The crystal structure of SnSe is shown in Figure 2.18. SnSe usually crystallizes in an orthorhombic GeS structure (space group $Pnma$), and forms double layers that are perpendicular to the direction of the unit cell's largest axis. Each unit cell contains 8 atoms arranged in two adjacent double layers. Zigzag atoms in each of the double layer bond to their three nearest neighbours to form a chain along the direction of the minor axis of the crystal [122]. As such, it has a sheet-like structure derived from a regular NaCl structure by different interionic spacings within the octahedra [123], and it may be viewed as a highly distorted NaCl lattice [121]. As the Van der Waals bonding is more dominant in adjacent layers, the material cleaves easily along the a-b (001) planes (taking the z axis to be the longest axis). SnSe and its counterpart IV-VI compounds are reported to have an intermediate behavior between a two-dimensional and a three-dimensional material. [122]

It is found that SnSe has very high Seebeck coefficient, which increases with temperature, and low electrical conductivity [118]. It is also sensitive to pressure effects, and when subjected to increasing pressure, the band gap decreases and the materials become more conducting [124]. However, there are little reports on the ZT values of pure SnSe.

Figure 2.18: Crystal structure of SnSe. The dotted line shows the schematic of the cleavage plane in the [001] direction in SnSe. Source: Katherine R. Stevens, Carthage College. [112]

Several methods have been developed to prepare SnSe: chemical vapour deposition [125], electrodeposition [126], electron beam irradiation [127], direct vapour transport [120] and chemical synthesis [121].

SnSe, like Bi_2Te_3 , also has a layered structure, and hence it may be of interest to study its TE properties. However, as tellurium is the ninth least abundant element on earth, reliance on this element has to be reduced. In turn, we try to incorporate selenium into the material system, which is much more abundant compared to tellurium, while Sn is an earth-abundant and environmentally friendly element. The abundance of the elements is shown in Figure 2.19. By understanding this material system better, we can try to achieve improved TE properties, and reduce the reliance on the already scarce Te at the same time. [118]

Thus, for the work on in-situ nanocomposites, SnTe is combined with SnSe to form pseudo-binary or ternary phase alloys, and is initially chosen based on the phase diagram. In addition, in a recent paper [128], it was mentioned that Se–Sn–Te and its alloys have potential applications in optical and TE applications, and that the phases and microstructures of such materials are crucial in determining their material properties. However, as there are few reports on the Se–Sn–Te system, work will be performed to have a better understanding this material system. The

approach used is solid-state phase transformation, which allows for the adjustment of the microstructure and in turn the tuning of the materials' properties [129].

Figure 2.19: Graph showing the relative abundance of the various elements in the earth's crust, presented using a logarithmic scale. Reproduced from [25] with permission from The Royal Society of Chemistry.

2.6.2.3 SnTe-SnSe Phase Diagram

The pseudo-binary phase diagram of the SnTe-SnSe material system is shown in Figure 2.20:

Figure 2.20: Pseudo-binary phase diagram of the SnTe-SnSe system. From [130] with kind permission from Springer Science and Business Media.

From the phase diagram, the following are observed [130, 131]:

- The SnTe – SnSe system has a eutectic located at 55 mol % SnTe, with a melting point of about 1020 K
- For SnSe-rich region, the line indicates the γ (GeS orthorhombic) to δ (TII, orthorhombic) phase transition
- Below the solubility limit, SnSe solid solution forms, and the orthorhombic cell parameters increase with increase in SnTe content
- At the other end of the phase diagram, below the solubility limit, SnTe solid solution forms, and the cubic cell parameters decrease with increase in SnSe content
- At 773 K, solubility limit of SnSe in SnTe lies at approximately 27.3 mol %, and the solubility limit of SnTe in SnSe is approximately 32.8 mol %
- For SnTe mole percentages ranging from $27.3 < \text{SnTe} < 67.2$, SnSe and SnTe exists in two separate phases, i.e. two solid solutions

Figure 2.21: Ternary phase diagram of Sn-Te-Se [131]. Regions where the main phase is either SnTe-based or SnSe-based are as indicated [128]. Adapted from [131], Copyright (1992), with permission from Elsevier.

In this work, the nominal compositions of the various samples are 10 mol % SnSe-90 mol % SnTe, 25 mol % SnSe-75 mol % SnTe and 40 mol % SnSe-60 mol %

SnTe, and these will be referred to 10SnSe, 25SnSe and 40SnSe respectively hereon. These samples are indicated on the ternary phase diagram (Figure 2.21) as “X_{composition}”.

In the paper by Chen *et al.* [128], it was mentioned that the phases obtained in this ternary material system is actually made up of compositions represented by $\text{SnTe}_x\text{Se}_{1-x}$, instead of being purely SnTe or SnSe phases. Hence, this conclusion supports the fact that depending on the position in the phase diagram, ternary phases of SnTe-based and SnSe-based will form (indicated in Figure 2.21), allowing us to fabricate multiphase in-situ nanocomposites during processing. The results of the paper concluded that at 523 K, the solubility of Te atoms in the SnSe phase can reach 10 atomic % Te, while the solubility of Se atoms in SnTe is much lower, at a value of less than 4 atomic % Se. These limits vary slightly from that shown in the phase diagram in Figure 2.20.

2.7 Hypothesis

Based on the discussions above, the approach of ex-situ and in-situ nanocomposites is an attractive technique to undertake in this thesis work in two aspects: (i) Engineering aspect: To obtain synergistic improvements in TE properties from the combination of selected materials, and (ii) Scientific aspect: To study the reasons for the improvement in TE properties in the multiphase system.

The design of this work is based on the concept that multiphase nanostructured bulk TE materials can improve ZT values, due to increased scattering of phonons from the nanostructures, without concomitant decrease in other properties.

In the first part of the thesis work, it is hypothesized that the use of surfactant-free nanostructures will allow the benefits from nanostructuring to be achieved, yet avoiding the effect of reduced electrical conductivity. The approach incorporating metallic nanoparticles in a semiconductor matrix material has been of interest as theoretical calculations [132, 133] have predicted an enhancement in ZT.

This is due to band bending at the metal–semiconductor interface, resulting in an energy barrier which effectively blocks low energy electrons, while transmitting high energy electrons. As a result, Seebeck coefficient is enhanced for a given carrier concentration. [26] In addition, as mentioned in Section 2.6.1.1, Cu_7Te_4 has metallic conductivity and can operate up to 900 K. With the higher operation temperature range, the addition of Cu_7Te_4 may be beneficial in widening the operation temperature range the nanocomposite compared to the pure BST alloy. Thus, it is hypothesized that the mechanism by which improvement in TE properties is achieved will be different from that of in-situ nanocomposites.

In the second part of the thesis work, it is hypothesized that the use of melt spinning approach will enable multiphase nanostructured materials to be formed. This can be achieved by initially melt spinning the samples and then, through subsequent processing, form the second phase in the material. As it is expected that the major phase will be in micron-sized, while the second phase can form sub-micron or nano-sized phases, which lead to the possibility of TE properties enhancement by mechanisms similar to the percolation effect. In the percolation effect, the charge carriers will move across large grains where there is lower resistivity, while phonons do not choose their path and are scattered by the interfaces in the materials [7]. In addition, in a paper by He *et al.* [90], it was reported that the composite material of PbTe-PbSnS_2 , made up of cubic and orthorhombic crystal structures respectively, led to the formation of a superstructure along the a-axis due to the nature of these two crystal structures. From transmission electron microscopy, it was realized that there were also phase boundaries, misfit dislocations, and displacement layers present, all of which were proposed to be responsible for strong scattering of heat-carrying phonons. As our material system consists of both cubic and orthorhombic phases, it is possible that our system can also exhibit such behaviour.

In another paper by Medlin and Snyder [134], the versatility of chalcogenide compounds in adapting to changes in the composition and local environment of the material were highlighted. Due to the similarity of the different

crystal structures of the allotropes of chalcogenide compounds, changes can occur in the material, leading to phase transformations. It was reported that these changes can affect the grain boundary interfaces of the materials, which is of importance as they can have an effect on the electrical and thermal properties of the TE materials.

From these reports, it is seen that these crystal structural changes can allow phase transformations, with the effect observed most clearly in the TE properties. Thus, it is possible that such a phenomenon can occur in the SnTe-SnSe material system too, and the hypothesis will be further discussed in the subsequent chapters.

CHAPTER 3 - Experimental Methods

3.1 Ex-situ Nanocomposites

3.1.1 Introduction to Chemical Synthesis

Chemical synthesis is one of the attractive approaches taken for synthesizing nanostructures as it allows control in terms of size, morphology and composition depending on the type of reaction carried out, precursors chosen, and the parameters (e.g. time and temperature) used. In addition, nano-sized materials with narrow size distribution can be obtained. [19]

There are various types of chemical synthesis – hydrothermal/solvothermal, polyol, precipitation reactions – and various types of TE materials have been synthesized using these methods. In some reactions, the synthesis can also be scaled up from milligrams to grams scale [135, 136], facilitating the consolidation of these nanostructures into a bulk for property characterizations.

In this work, the synthesis of surfactant-free Cu_7Te_4 was performed *via* a templating method, where Te nanorods were first synthesized, after which the copper precursor was added to react with it to form copper telluride nanorods.

3.1.2 Experimental Procedures for Chemical Synthesis

Tellurium (Te) nanorods were synthesized with reference from Mayers and Xia [137]. The materials were Telluric acid ($\text{H}_6\text{Te}_6\text{O}_6$, 99.99%), Hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 98%), Copper (II) chloride dihydrate ($\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, 99+%), all purchased from Sigma Aldrich, and Ethylene glycol (EG; $\text{HOCH}_2\text{CH}_2\text{OH}$, 99%) from Alfa Aesar. In a typical synthesis using a 3-neck flask, required amounts of Telluric acid was dissolved in EG at 353 K, and slowly heated to 443 K. Meanwhile, a separate mixture of hydrazine in EG was also prepared. Upon reaching 443 K, the latter mixture was injected into the former, and immediately the solution turned to a bluish grey colour. The mixture was held at

about 443 K for 15 minutes before being removed from the heating mantle, and cooled to room temperature.

The as prepared Te nanorods were then used as templates for synthesizing copper telluride nanorods. In this synthesis, a mixture of EG and Copper (II) chloride dihydrate was prepared and then mixed with the Te nanorods. It was then left to stir at 353 K for 2 hours. The final products were then washed and centrifuged a few times using ethanol, before being stored.

The schematic of the reaction is shown in Figure 3.1:

Figure 3.1: Schematic representation of the chemical synthesis of Cu_7Te_4 nanorods.

Nanocomposites of various compositions were obtained by mixing various amounts in weight percentage (wt %) of copper telluride – 0 wt %, 5 wt %, 10 wt %, 15 wt % and 100 wt % - and $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, using the horizontal ball mill, and then hot pressed into a pellet at 723 K, 50 MPa for 30 minutes in vacuum. The densities of the hot pressed samples were found to be about 85% (for 100 wt % copper telluride) and between 92% – 99% (for nanocomposites and pure BST) of the theoretical values.

3.1.3 Experimental Procedures for Synthesis of $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$

Bismuth antimony telluride alloy of the composition $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ was obtained from Taiwan's Industrial Technology Research Institute (ITRI). It was

synthesized by the zone melting technique. The bulk material was hand ground into powders and sieved to a size smaller than 40 μm .

3.2 In-situ Nanocomposites

3.2.1 Introduction to Melt Spinning

Melt spinning (MS), as shown in Figure 3.2, is a rapid solidification approach, used for the rapid cooling of liquids (e.g. metal melts), and is the method chosen for in-situ nanocomposites fabrication. It is used to form materials that require very high cooling rates to form, such as metastable/non-equilibrium phases, metallic glasses or nanocomposites, and the cooling rates achievable by melt-spinning are of the order of $10^5 - 10^7$ K/s [138], allowing alloys with high critical cooling rate to be formed. Amorphous structures, nanocrystalline or quasi-coherent structures may be achieved in a short period of time, which is not possible in other synthesis methods.

Figure 3.2: Schematic diagram of the melt spinning process.
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The MS process has been used for synthesizing various materials for applications like electric contact materials [140], magnetic materials, metallic alloys [139] and TE materials [141, 142]. In this process, phase transitions like direct solidification and solid/liquid phase separation can lead to precipitate

formation of nano/micron scale to be achieved [140]. This can be beneficial for increasing the phonon scattering effect in TE materials.

The benefits of using MS include:

- 1) Wide range of material compositions can be formed
- 2) Possibility of achieving amorphous precursor material
- 3) Heat treatment can be done on MS material to get multiple phases
- 4) Sufficient quantities required for characterization can be synthesized in a short time.

TE material systems that have been processed by MS include Bi-Sb-Te [49, 141], half-Heusler alloys [143, 144], $(\text{GeTe})_x(\text{AgSbTe}_2)_{1-x}$ [145], $\text{Ge}_2\text{Sb}_2\text{Te}_5$ compounds [53], FeSi_2 and Fe_2Si_5 based alloys [146] and $\text{Yb}_x\text{Co}_4\text{Sb}_{12}$ [147], with the net result of improving TE properties due to grain size refinement or formation of nanostructures.

3.2.2 Experimental Procedures for Melt Spinning

In a typical experiment, depending on the compositions required, stoichiometric amounts of tin telluride (SnTe , 99.999%) and tin selenide (SnSe , 99.999%), both purchased from Alfa Aesar, were cold pressed into pellets and placed into a quartz cylinder of about 10 mm diameter with a 0.5 mm – 1 mm nozzle in the melt spinning system for rapid solidification in argon atmosphere. The pellets were inductively melted and injected onto the edge of a rotating copper roller with a working distance of 0.5 mm and a linear speed of 60 Hz. The as-obtained thin flakes were then hand ground and ball milled into powders, before being consolidated into a pellet by hot pressing in vacuum at 723 K for 30 minutes under a pressure of 50 MPa. The densities of the hot pressed samples were found to be about 96% of the theoretical values.

Pure SnSe was not prepared through melt spinning as its resistivity was too high and does not react to the induction melting coils. However, in order to obtain a

rapidly quenched sample for direct comparison of TE properties to the melt spun samples, an alternative method was carried out: As-purchased SnSe was hand grinded into powder and hot pressed under conditions as mentioned above.

To compare the differences between samples which were rapidly solidified to those obtained *via* slow cooling or by physical mixing, control samples (referred to as 25SnSe_SS and 25SnSe_phymix respectively) were also fabricated. In the former, the method used was solid state synthesis and slow cooling, based on reported references [148, 149], but with some modifications. In a typical synthesis, stoichiometric amounts of SnTe and SnSe were loaded into a quartz ampoule, sealed under vacuum at 10^{-3} millitorr, and then heated at 1223 K for 6 hours. The ingot was then cooled from 1223 K to 773 K in 4 days, and held for another 4 days at 773 K before cooling naturally to room temperature. In the latter, stoichiometric amounts of SnTe and SnSe were weighed and mixed using the horizontal ball miller, and then hot pressed under conditions mentioned above.

3.3 Characterization Techniques

Phase identification of samples was performed using X-ray diffraction (XRD) on Bruker D8 Advance using Cu K_{α} radiation ($\lambda = 1.5406 \text{ \AA}$) over 2θ range of 10° to 90° , and the microstructure, morphologies and composition were observed using a JEOL-JSM 7600F field emission scanning electron microscope (FESEM), JEOL-JEM 2100F transmission electron microscope (TEM) and JEOL JXA-8530F electron microprobe analysis (EPMA).

Thermal conductivity was obtained from the Laser Flash (Netzsch, LFA 447) over a temperature range of 300 K – 500 K. In the laser flash method, the thermal diffusivity, D , was measured, and the specific heat, C_p , determined from the comparison method with a standard sample of known specific heat tested under the same conditions. The density, ρ , was measured separately by the Archimedes' method. Using this information, thermal conductivity, κ , can be calculated using the equation, $\kappa = D.C_p.\rho$. For the work on ex-situ nanocomposites, pure copper

telluride was too brittle to be obtained in the complete pellet form, hence thermal conductivity measurements could not be carried out.

Thermoelectric properties measurements were performed using a commercial instrument ULVAC-Riko ZEM-3 (M8). The measurements were carried out on samples cut and polished into rectangular bars, sandwiched between two Ni electrodes with two probe thermocouples providing forced contacts on one side. The sample chamber was then evacuated and back-filled with Helium gas, and heated from room temperature to 500 K using an infrared furnace.

Temperature-dependent XRD was also carried out on certain samples on Siemens D5005 (with Anton Paar heat stage attached), using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over 2θ range of 10° to 90° .

The TOPAS program was used to calculate the lattice parameters, identify and calculate the weight percentages of the phases in the different samples. This was done *via* Rietveld refinement using the following equation [150]:

$$W_\alpha = \frac{S_\alpha(ZMV)_\alpha}{\sum_i (S_i(ZMV)_i)} \quad (26)$$

where W_α is the weight fraction of phase α , S is the Rietveld scale factor, Z is the number of formula units in unit cell, M is the molecular mass of formula unit and V is the unit cell volume.

CHAPTER 4 - Results and Discussion I: Ex-situ $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ Nanocomposites

4.1 Characterization of Ex-situ Nanocomposites

4.1.1 Introduction

The chemically synthesized Te and Cu_7Te_4 nanorods were characterized to determine the phases present at each step, and the purity of the phases. These will be discussed in the next few sections.

4.1.2 Morphology and Phase Identification of Chemically Synthesized Cu_7Te_4 via Field Emission Scanning Electron Microscopy and X-Ray Diffraction

Figure 4.1a-b shows the FESEM images and Figure 4.1c shows the XRD pattern of the Te nanorods after synthesis. It was noted that the size distribution of the Te nanorods was narrow. Their diameters were in the range of 70 nm to 100 nm and they had a length of a few micrometers. The XRD pattern of the Te nanorods corresponded to the Te hexagonal crystal structure (space group P3121; JCPDS card number 36-1452).

Figure 4.1: FESEM images of Te nanorods at (a) low magnification and (b) high magnification and (c) XRD pattern of Te nanorods.

(continued) Figure 4.1: FESEM images of Te nanorods at (a) low magnification and (b) high magnification and (c) XRD pattern of Te nanorods.

The FESEM images, XRD pattern and TEM micrographs of the Cu_7Te_4 nanorods that were synthesized using these Te nanorods as templates are shown in Figure 4.2:

Figure 4.2: FESEM images of Cu₇Te₄ nanorods at (a) low magnification and (b) high magnification, (c) XRD pattern of Cu₇Te₄ nanorods and TEM micrographs at (d) low magnification and (e) high magnification with the diffraction pattern in the inset. Reprinted with permission from Elsevier.

(continued) Figure 4.2: FESEM images of Cu_7Te_4 nanorods at (a) low magnification and (b) high magnification, (c) XRD pattern of Cu_7Te_4 nanorods and TEM micrographs at (d) low magnification and (e) high magnification with the diffraction pattern in the inset. Reprinted with permission from Elsevier.

From Figures 4.2a and 4.2b, the Cu_7Te_4 nanorods were observed to have diameters ranging from 70 nm to 150 nm, while the length was a few micrometers, indicating that the initial sizes of the Te nanorods were maintained. However, it was noted that the shapes of Cu_7Te_4 were not as smooth and straight as the initial Te nanorods, although the nanorod morphology was preserved. This was likely to be due to the fact that surfactants were not used, which would have been useful in maintaining the morphology. The XRD pattern (Figure 4.2c) corresponded to the Cu_7Te_4 hexagonal crystal structure (space group $P3m1$; JCPDS card number 89-2402). Figures 4.2d and 4.2e are the TEM micrographs of the Cu_7Te_4 nanorods. The lines observed across the samples may be due to its layered structure. The measured lattice parameters of 7.22 Å corresponded to the (100) and (010) planes, and the diffraction pattern in the inset indicates that the synthesized samples were single crystalline.

4.1.3 Characterization of Hot Pressed Samples

The nanocomposites were named according to their compositions in terms of wt % of Cu_7Te_4 in $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ (BST): 5 wt %, 10 wt % and 15 wt % were referred to as 5wtNC, 10wtNC and 15wtNC respectively. As shown in Figure 4.3a are the XRD patterns of the hot pressed nanocomposite samples with BST and

Cu_7Te_4 . It was noted that after hot pressing of the Cu_7Te_4 nanorods, there were some additional phases of copper telluride, which were indexed to the $\text{Cu}_{1.81}\text{Te}$ phase, and this composition lies within the range of deviation of $0 \leq x \leq 0.25$ as material for TE application. From the XRD patterns of the nanocomposites, it was seen that there were no peak shifts by the BST phases, while the slight peaks present were believed to be contributed by the Cu_7Te_4 phases, and not from $\text{Cu}_{1.81}\text{Te}$, as Cu_7Te_4 nanorods that were added initially were in low weight percentages. To further confirm that the Cu_7Te_4 phase existed separately from BST and not as a solid solution, backscattered electron imaging and energy dispersive X-ray (EDX) area mapping was carried out, as shown in Figure 4.3b and 4.3c:

Figure 4.3: (a) XRD patterns of the various hot pressed samples, (b) cross-section backscattered electron image of a 15wtNC sample and (c) the corresponding EDX mapping. Reprinted with permission from Elsevier.

(continued) Figure 4.3: (a) XRD patterns of the various hot pressed samples, (b) cross-section backscattered electron image of a 15wtNC sample and (c) the corresponding EDX mapping. Reprinted with permission from Elsevier.

The regions which were copper-rich were shown to be deficient in Sb and Bi, hence indicating that the two phases existed separately. To understand the interface between the two phases, TEM was carried out, as shown in Figure 4.4:

Figure 4.4: (a) TEM micrograph of 5wtNC showing presence of BST and Cu_7Te_4 phases, with the fast Fourier transform patterns of BST and Cu_7Te_4 on the right and left side respectively, and (b) EDX results of the line scan (as indicated by yellow line) identifying both the phases. Reprinted with permission from Elsevier.

It was seen that the interfaces between these two phases were well matched. This was likely to be due to its similarity in crystal structures, and the coherent interface being beneficial for electron transport in the material. The insets in Figure 4.4a show the fast Fourier transform patterns of the BST and Cu_7Te_4 phases on the right and left side respectively.

4.2 Thermoelectric Properties Measurements

The electrical resistivity measurements are shown in Figure 4.5a. It was seen that the nanocomposites generally had lower electrical resistivity than pure BST, with the difference being more prominent in the range of 300 K – 400 K (nearly one order of magnitude lower than BST). Due to the metallic conductivity of Cu_7Te_4 [105], the overall carrier concentration in nanocomposite samples could increase and this in turn led to improved electrical conductivity [26]. The lack of surfactant in the synthesis of the Cu_7Te_4 nanorods was likely to be beneficial towards minimizing the disruption of electrical conductivity of the TE material as well. In usual synthesis processes involving the use of surfactants, incomplete removal can affect carrier mobility (and in turn the electrical transport), resulting in degradation of TE properties [33].

Figure 4.5: Temperature dependence of thermoelectric properties of various compositions (a) Electrical resistivity, (b) Seebeck coefficient, (c) Power factor, (d) Thermal conductivity (e) Lattice thermal conductivity and (f) ZT. Reprinted with permission from Elsevier.

The temperature dependence of the electrical resistivity values of nanocomposites and BST were also different – electrical resistivity values of BST increased with temperature and reached a maximum (referred to as $T_{\max}$) at about 400 K, after which it decreased. On the other hand, for the nanocomposites, the electrical resistivity values slowly increased with temperature, and did not reach a peak value over the measured temperature range. The appearance of $T_{\max}$ had been reported by Sun *et al.* [151] and was described to be the onset of mixed conduction which is not desired in TE materials. In mixed conduction, minority carriers are being generated [152], which are of the opposite sign compared to the majority carriers (in this case electron and holes respectively). This can cancel out each other, leading to a decrease in the Seebeck coefficient.

For BST, these minority carriers affected the temperature dependence of Seebeck coefficient and electrical resistivity such that these parameters showed a transition at slightly different temperature values. A shift of $T_{\max}$ to higher temperatures was also an indication of increased carrier concentration, as reported by Kutasov *et al.* [152]. The addition of Cu_7Te_4 nanorods shifted the region of the mixed conduction to higher temperatures (> 500 K), allowing the nanocomposites to work more efficiently at higher temperatures. The presence of Cu_7Te_4 in BST also mitigated the effect of minority carriers at higher temperatures, resulting in different temperature dependence of the electrical properties.

The Seebeck coefficient values of the samples, presented in Figure 4.5b, were positive (p-type) and in the range of $75 \mu\text{V/K} - 180 \mu\text{V/K}$ over the measured temperature range. The addition of Cu_7Te_4 nanorods to BST caused the Seebeck coefficient values of the nanocomposites to be 2 to 3.6 times lower than BST at room temperature. As temperature increased to between 425 K and 460 K, the Seebeck coefficient values of 5wtNC and 10wtNC became higher than that of pure BST. It was also noted for the nanocomposites, the trend was an increase in Seebeck coefficient with temperature, while for BST, it decreased with temperature. The decrease in Seebeck coefficient values upon addition of nanostructures at room temperature was also reported by other authors, and was attributed to an increase in

carrier concentration [26, 151], such that there were electronic changes at the Fermi level [107]. The carrier concentration values of the samples at room temperature were measured, and it was confirmed that the carrier concentration increases with Cu_7Te_4 content: 5wtNC – $7.606 \times 10^{19} \text{ cm}^{-3}$, 10wtNC – $8.914 \times 10^{19} \text{ cm}^{-3}$ and 15wtNC – $1.452 \times 10^{20} \text{ cm}^{-3}$. The carrier concentrations of BST and Cu_7Te_4 were estimated to be in the range of about $3 \times 10^{19} \text{ cm}^{-3}$ [153] and 10^{21} cm^{-3} [154] respectively. A possible mechanism for the observed increase in the carrier concentration is as follows: In the fabrication of BST materials, Te vacancies can be formed due to the loss of tellurium during melting. [155] Some of these Te vacancies will be occupied by Bi or Sb atoms, which are known as antisite defects, and is quite common in the material system. Antisite defects produce acceptors (holes) and leads to the p-type conduction in BST. [155] In the preparation of the nanocomposites mixture, ball milling is used. Such a method has been reported to cause deformation, leading to formation of Bi-Te or Sb-Te vacancy pairs. When sufficiently abundant Bi vacancies are created, the Bi atoms occupying the Te sites would diffuse back into its original sublattices more readily, resulting in excess Te vacancies produced, leading to excess negative carriers (i.e. donor-like effect leading to n-type conduction). [156, 157] In our work, although the ball milling used is for a short time and of low energy, some deformation may still be induced and in turn forming some vacancy pairs. In addition, when the composite materials are compacted *via* hot pressing, the Bi or Sb in the antisite defects will diffuse back to the Bi or Sb positions near the “Bi-Te” or “Sb-Te” vacancy pairs, reducing the number of antisite defects. [156] This further decreases the p-type carrier concentration in the single phase material BST. However, with the presence of Cu_7Te_4 as the second phase, the “Bi-Te” or “Sb-Te” vacancy pairs tends to form near the interfaces of the two phases during ball-milling, due to the mechanical difference. Hence, it is possible that during hot pressing, some vacancy pairs will be filled by Cu and Te atoms dissolved from Cu_7Te_4 nanorods. This mitigates the donor-like effect, and increases antisite defects of another type (e.g. Cu in Te vacancies and/or Te diffusing into Te vacancies), thus p-type carrier concentration increases with the amount of Cu_7Te_4 nanorods. This is possible as the Cu_7Te_4 phase

shows the presence of a copper telluride phase with an increased Cu concentration (i.e. $\text{Cu}_{1.81}\text{Te}$) after hot pressing. This interaction of the two phases may also be the reason why they form coherent interfaces.

As seen in Figure 4.5c, the power factors of the nanocomposites were in general higher than that of the pure BST sample: both the 5wtNC and 10wtNC achieved improved power factor values across the whole temperature range measured, and this was attributed to the tuning of electrical conductivity and maintaining of Seebeck coefficient at acceptable values. The 5wtNC, 10wtNC and 15wtNC samples reached a maximum of $3.30 \times 10^{-3} \text{ W/m.K}^2$, $2.93 \times 10^{-3} \text{ W/m.K}^2$ and $2.22 \times 10^{-3} \text{ W/m.K}^2$ respectively, at about the same temperature of 345 K. A possible explanation for the improved electrical properties observed for the 5wtNC sample might be the partly similar crystal structure of the bulk BST (rhombohedral) and Cu_7Te_4 (hexagonal) phases, leading to unique electrical conducting behavior [107]. The Fermi levels in Cu_7Te_4 phase could align with the BST matrix, such that Fermi level of both phases became equivalent, leading to an increase in the hole concentration in the matrix [151].

The thermal conductivity values of the nanocomposites are shown in Figure 4.5d. With the addition of the Cu_7Te_4 nanorods, the nanocomposites' room temperature thermal conductivity value increased by 60% to 97% as compared to pure BST. The thermal conductivity of BST increased with temperature, while for the nanocomposites, the values decreased with temperature, and eventually became lower than BST in the temperature range of 430 K – 465 K.

The total thermal conductivity consists of a phonon and carrier contribution, κ_{lattice} and $\kappa_{\text{electronic}}$, respectively. As mentioned in Section 2.3.3, $\kappa_{\text{electronic}}$ is related to the electrical conductivity by the Wiedemann–Franz law: $\kappa_{\text{electronic}} = L\sigma T$, and L here is approximately equal to $1.5 \times 10^{-8} \text{ V}^2\text{K}^{-2}$ [107]. To elucidate the effect of the addition of nanorods on the thermal conductivity, lattice thermal conductivity was estimated as: $\kappa_{\text{lattice}} = \kappa - \kappa_{\text{electronic}}$. From Figure 4.5e, it is seen that the nanocomposites have lower κ_{lattice} values than the pure BST. This indicated that the addition of nanorods caused a significant suppression of lattice thermal

conductivity of the nanocomposites compared to bulk BST. Due to phonon scattering, κ_{lattice} for the nanocomposites were in the range of 0.1 W/m.K – 0.5 W/m.K, much lower than the value of 0.66 W/m.K for BST at room temperature. These values lie within the minimum lattice thermal conductivity limit defined by Slack, which has a lower limit in the range 0.1 W/m.K – 0.2 W/m.K [158].

Lattice thermal conductivity usually exhibits a temperature dependence of T^{-1} , but this behaviour was not observed in Figure 4.5e. This can be explained as follows: at lower temperatures, the phonon–phonon scattering was enhanced, leading to low κ_{lattice} . With increase in temperature, lattice vibrations were intensified, and there was a threshold limit beyond which bipolar diffusion carriers will conduct heat, which resulted in significant increases in the lattice thermal conductivity [141]. This led to the observed phenomenon of deviation from the T^{-1} dependence. The result for 5wtNC showed that it was possible that adding of a small amount of second phase nanoinclusions caused more effective phonon scattering at higher temperatures, leading to even more reduced lattice thermal conductivity. For higher levels of additions of nanostructures (10wtNC and 15wtNC), the trend is similar to that of pure BST, indicating that too high a concentration of Cu_7Te_4 nanorods present may have caused agglomeration, such that the nanostructured interfaces present were insufficient for effective scattering. The large $\kappa_{\text{electronic}}$ values observed in the nanocomposites were due to the metallic nature of Cu_7Te_4 , leading to large electrical conductivity values (and in turn large $\kappa_{\text{electronic}}$ values based on the Wiedemann–Franz law). Nevertheless, this value can be potentially suppressed by the method of inhomogeneous doping or segmentation along the TE material, leading to a significant reduction in the Lorenz number such that the electronic thermal conductivity also decreases [33].

As the improvements in electrical conductivity of the nanocomposites outweighed the concurrent increase in thermal conductivity, the ZT calculated for the 5wtNC showed an enhancement over BST (Figure 4.5f). A maximum ZT of 1.14 at 444 K was achieved for 5wtNC, which was about 4 times that of BST at the same temperature. Comparing the results here to the work done by Cui *et al.* [107]

where the maximum ZT obtained was 1.26 at 474 K, the improvement obtained here is that $ZT = 1$ was maintained across a larger temperature range, from 360 K – 500 K. Thus, the TE properties improved with the addition of nanoinclusions. Measurements showed that the material is expected to work more efficiently over a larger temperature range.

Despite these improvements, as the bulk BST matrix and Cu_7Te_4 nanorods were consolidated *via* physical mixing and hot pressing, issues like agglomeration of nanorods and cracking of samples were faced. To solve these issues, more focus was put on in-situ nanocomposites, which will be further discussed in the next chapter.

CHAPTER 5 - Results and Discussion II: In-situ SnTe-SnSe Nanocomposites

5.1 Characterization of In-situ Nanocomposites

5.1.1 Introduction

Melt spinning is a rapid solidification non-equilibrium process, and the as melt spun samples were characterized to determine the phases present, their composition, and the crystallinity. This will help to determine the properties of the material, and study any changes that occur with processing. The as melt spun samples were in the form of short ribbons or flakes with lengths of about a few millimeters. As mentioned in Section 2.6.2.3, the nominal compositions of the various samples are 10 mol % SnSe-90 mol % SnTe, 25 mol % SnSe-75 mol % SnTe and 40 mol % SnSe-60 mol % SnTe, and these will be referred to as 10SnSe, 25SnSe and 40SnSe respectively.

5.1.2 Morphology of Melt Spun Samples via Field Emission Scanning Electron Microscopy

Figure 5.1 shows the FESEM images of the various compositions of melt spun samples at the top surface, cross section and bottom surface. It was observed that the top surfaces (i.e. free surface) of the samples were generally made up of well-formed grains in the range of hundreds of nanometers to about one micrometer, depending on the composition. The cross section of the samples showed that the flakes were up to about 10 μm thick, and reflected the differences in cooling rate due to the melt spinning process. The grains on the side closer to the contact surface were about 200 nm to 350 nm thick; while towards the free surface they became larger and the columnar grains were about 2 μm long. The bottom surfaces (i.e. contact surface) were largely featureless. They only exhibited some longitudinal lines or roughness, most likely due to rapid cooling on the copper wheel, resulting in limited crystallization.

Figure 5.1: FESEM images of melt spun samples of (a) SnTe top surface, (b) SnTe cross section, (c) SnTe bottom surface; (d) 10SnSe top surface, (e) 10SnSe cross section, (f) 10SnSe bottom surface; (g) 25SnSe top surface, (h) 25SnSe cross section, (i) 25SnSe bottom surface; and (j) 40SnSe top surface, (k) 40SnSe cross section, (l) 40SnSe bottom surface. Reprinted with permission from Elsevier.

(continued) Figure 5.1: FESEM images of melt spun samples of (a) SnTe top surface, (b) SnTe cross section, (c) SnTe bottom surface; (d) 10SnSe top surface, (e) 10SnSe cross section, (f) 10SnSe bottom surface; (g) 25SnSe top surface, (h) 25SnSe cross section, (i) 25SnSe bottom surface; and (j) 40SnSe top surface, (k) 40SnSe cross section, (l) 40SnSe bottom surface. Reprinted with permission from Elsevier.

EDX analysis was also performed on the samples to compare the composition of the samples to the nominal values. The obtained values were compared to the nominal values, as shown in Table 5.1. As there is an error of about $\pm 5\%$ in the EDX, the slight differences in values were considered to be within the acceptable range.

Table 5.1: EDX values of the various melt spun samples

Element	Atomic % Sn / (Nominal value)	Atomic % Te / (Nominal value)	Atomic % Se / (Nominal value)
SnTe	50.4 / (50)	49.6 / (50)	-
10SnSe	43.5 / (49.2)	52.8 / (47.5)	3.7 / (3.3)
25SnSe	54.3 / (50.7)	36.9 / (40.9)	8.8 / (8.4)
40SnSe	55.4 / (52.3)	30.2 / (33.7)	14.4 / (13.9)

As pure SnSe could not be inductively melted for melt spinning, for comparison, as-purchased SnSe was hand ground into powder and hot pressed to form a pure SnSe sample. The FESEM image on the morphology of the hand ground SnSe powders is shown in Figure 5.2 – the hand ground powders consisted of particles in the size range of a few microns to tens of microns.

Figure 5.2: FESEM image of hand ground powders of as-purchased SnSe.

5.1.3 X-Ray Diffraction of Melt Spun Samples

The XRD patterns of the various compositions of the melt spun samples are shown in Figure 5.3. The peaks were observed to be sharp and defined, indicating

crystallinity. It was possible that the SnTe-SnSe was not amorphous after melt spinning because the supercooling from quenching of the melt was not large enough. Another reason might be the large negative heat of mixing of the system, such that the formation of compound phases instead of an amorphous one was favoured thermodynamically [159].

The diffraction peaks that appeared in the samples matched those of the cubic SnTe (JCPDS card number 065-0322), albeit with slight peak shifts. The reference SnSe XRD pattern (JCPDS card number 072-1460) is included to show that the additional peaks that appear in the 40SnSe sample match those of the SnSe phase, which has an orthorhombic crystal structure.

Figure 5.3: XRD patterns of the various as-melt spun samples. The hump observed at low angles for 40SnSe is due to the double side tape used for XRD specimen preparation.

As there were slight peak shifts from the SnTe peak positions for the as melt spun samples, TOPAS was used to obtain the lattice parameters of the cubic phase in the various samples. Using Vegard's law, the compositions were obtained and the summary of results are presented in Table 5.2 (refer to Appendix A1.1 for calculations; subsequent calculations of compositions were obtained in a similar fashion as well). It was observed that other than 40SnSe, the other samples all formed a single phase with a cubic crystal structure after melt spinning. This cubic

phase exhibited shift in lattice parameters to smaller values with increased concentrations of SnSe, indicating that a solid solution of $\text{SnTe}_x\text{Se}_{1-x}$ was forming in the melt spun samples. For the 40SnSe, due to its position in the phase diagram, an orthorhombic phase was also formed (which will be referred to as second phase) in addition to the cubic phase (which will be referred to as matrix). This orthorhombic second phase resulted in additional peaks in the XRD pattern. The lattice parameters of this second phase were also calculated in TOPAS and shown in Table 5.2. It was observed that the lattice parameters increased when compared to pure SnSe, indicating that Te atoms entered into the crystal structure of orthorhombic SnSe as well, confirming that another $\text{SnTe}_x\text{Se}_{1-x}$ solid solution compound had formed. For ease of discussion, the cubic SnTe-based phase and orthorhombic SnSe-based phase will be referred to as matrix and second phase respectively from here on.

Table 5.2: Lattice parameters and compositions of the melt spun samples calculated by TOPAS

Sample	a (Å)	b (Å)	c (Å)	Cell volume (Å ³)	Composition calculated by Vegard's Law
SnTe (JCPDS card number 065-0322)	6.304	-	-	-	-
10SnSe	6.295	-	-	-	$\text{SnTe}_{0.98}\text{Se}_{0.02}$
25SnSe	6.251	-	-	-	$\text{SnTe}_{0.84}\text{Se}_{0.16}$
40SnSe (cubic phase)	6.188	-	-	-	$\text{SnTe}_{0.64}\text{Se}_{0.36}$
40SnSe (orthorhombic phase)	4.534	4.318	11.848	231.989	$\text{SnTe}_{0.46}\text{Se}_{0.54}$
SnSe (JCPDS card number 072-1460)	4.46	4.19	11.57	216.21	-

In the calculated compositions of the samples, it was noticed that there was a deviation in composition of the single phase melt spun samples from the nominal composition, with a decrease in Se proportion. This indicated a partial loss of Se, or that Se existed in amorphous form. From the XRD pattern of 40SnSe in Figure 5.3, it is noted that there are minor peaks corresponding to the Se phase. In addition, in the characterization of some other melt spun samples of different compositions, small peaks of Sn were also detected (not shown here). It was possible that the SnSe compound was not completely stable, as Se can sublime [160], hence some SnSe might have decomposed into Sn and Se after melt spinning. This small amount of Sn and Se, when present, was taken into consideration in TOPAS calculations to determine the compositions of the matrix and second phases.

5.1.4 X-Ray Diffraction of Hot Pressed Samples

From Figure 5.4, it is observed that after hot pressing, the intensity of second phase peaks become stronger:

Figure 5.4: XRD patterns of the various hot pressed samples. The inset shows the range of angles from 25° to 35°.

Based on the phase diagram, the mass fraction of the phases in the two-phase region was calculated using the lever rule (at the tip of the solidus, ≈ 500 K,

in the phase diagram; refer to Appendix AI.2 for calculations), given by the equations below:

$$W_{\text{SnTe}} = (C_o - C_{\text{SnSe}}) / (C_{\text{SnTe}} - C_{\text{SnSe}}) \quad (27)$$

$$W_{\text{SnSe}} = (C_{\text{SnTe}} - C_o) / (C_{\text{SnTe}} - C_{\text{SnSe}}) \quad (28)$$

where $W_{\text{SnTe}}/W_{\text{SnSe}}$ are the mass fractions of the SnTe and SnSe phases respectively, C_o is the sample's composition, and $C_{\text{SnTe}}/C_{\text{SnSe}}$ is the concentration at the solidus that separates the single and two phase region.

To estimate the increase in mass fraction of the second phase from 10SnSe to 40SnSe, TOPAS was also used for the calculations (refinement images shown in Appendix AI.3) and presented together with lever rule calculations (Table 5.3). For 10SnSe, as this composition lies at the boundary between the single phase and binary phase region, the lever rule was not applied. The TOPAS calculated values were close to the nominal original composition, which was reasonable. For 25SnSe and 40SnSe, the TOPAS calculated mass fractions deviated significantly from the theoretical values, indicating that the compositions that lie near or in the two-phase region were not at the equilibrium state. This is reasonable since melt spinning is a rapid solidification non-equilibrium process.

Table 5.3: Mass fractions of phases in hot pressed samples obtained through lever rule and TOPAS calculations

Composition	Theoretical Weight percentage (from Lever rule calculation at 500 K)	Calculated Weight percentage (from TOPAS calculations)
<u>10SnSe</u>		
Matrix	-	87.7
Second phase	-	9.3
Impurity phase		Sn = 3.0

(continued) Table 5.3: Mass fractions of phases in hot pressed samples obtained through lever rule and TOPAS calculations

Composition	Theoretical Weight percentage (from Lever rule calculation at 500 K)	Calculated Weight percentage (from TOPAS calculations)
25SnSe		
Matrix	81.7	61.0
Second phase	18.3	30.0
Impurity phase(s)		Sn = 2.3, Se = 2.6, SnO ₂ = 4.2
40SnSe		
Matrix	63.4	38.8
Second phase	36.6	55.9
Impurity phase(s)		Sn = 2.5, Se = 2.9

For 10SnSe, the sample consisted of the matrix, second phase, and a small amount of Sn. For 25SnSe and 40SnSe, apart from the matrix and second phase, there were also small amounts of Sn and Se present. However, in 25SnSe, there seems to be an additional impurity phase of SnO₂, which might have formed after multiple TE properties measurements.

Both the matrix and the second phase in the hot pressed samples exhibited some shift from the reference SnTe and SnSe XRD patterns, and this was likely to be due to a phase transformation that led to changes in the lattice parameters. Based on the lattice parameters of the phases in the hot pressed samples, the corresponding compositions were obtained using TOPAS (Table 5.4).

Table 5.4: Lattice parameters and compositions of hot pressed samples calculated by TOPAS

Composition	a (Å)	b (Å)	c (Å)	Cell volume (Å ³)	Composition
<u>10SnSe</u>					
Matrix	6.282	-	-	-	SnTe _{0.942} Se _{0.05} 8
Second phase	4.538	4.317	12.057	236.242	SnTe _{0.584} Se _{0.41} 6
<u>25SnSe</u>					
Matrix	6.273	-	-	-	SnTe _{0.913} Se _{0.08} 7
Second phase	4.514	4.270	12.235	235.909	SnTe _{0.574} Se _{0.42} 6
<u>40SnSe</u>					
Matrix	6.271	-	-	-	SnTe _{0.906} Se _{0.09} 4
Second phase	4.539	4.335	11.926	234.663	SnTe _{0.538} Se _{0.46} 2
SnTe (JCPDS card number 065-0322)	6.304	-	-	-	-
SnSe (JCPDS card number 072-1460)	4.46	4.19	11.57	216.21	-

Upon a closer look at the compositions, it was noted that in all the samples, two ternary phases were present – a cubic matrix phase based on the SnTe structure, and an orthorhombic second phase based on the SnSe structure. According to papers by Aripnammal *et al.* [161, 162], in the SnTe_xSe_{1-x} systems, where $x \geq 0.6$, SnTe_xSe_{1-x} crystallized in the cubic structure; for $x < 0.6$, SnTe_xSe_{1-x} crystallized in the orthorhombic structure. Based on the calculations of the compositions of the

orthorhombic second phase, these values fit the limits given by the above-mentioned author.

There were also differences in compositions of the matrix compared to that of the melt spun samples. For the hot pressed samples, the composition of the matrix was relatively consistent, and lattice parameters did not change much (within 0.01 Å), indicating that the stable composition of the matrix was about $\text{SnTe}_{0.92}\text{Se}_{0.08}$, which is nearly the composition that corresponds to the solubility limit of SnTe according to the phase diagram at 500 K. On the other hand, the orthorhombic second phase exhibited larger changes in the lattice parameters and cell volume (within 0.1 Å and 1 Å³ respectively), but its compositions in the different samples were relatively consistent, with an average of $\text{SnTe}_{0.565}\text{Se}_{0.435}$.

As mentioned earlier in Section 2.6.2.3, the solubility of Te in the SnSe phase was reported to be about 10 atomic %, and less than 4 atomic % for Se solubility in SnTe [128]. However, the solubility of Se in SnTe and Te in SnSe in these three samples seemed to deviate from the reported values. This may be due to the rapid solidification method used, resulting in such non-equilibrium effects. Hence, comparing the theoretical mass fractions of the phases to those obtained from TOPAS calculations in column 2 and 3 of Table 5.3 respectively, a large decrease in the calculated matrix mass fraction and a corresponding increased mass fraction of orthorhombic second phase indicated that more Te was substituting into the crystal structure of SnSe in the samples than what was expected at equilibrium.

It was noted that in our material, although two different phases were identified, there was no indication of these different regions in the pseudo-binary phase diagram. Instead, the system was better represented by the ternary phase diagram, as reported by Chen *et al.* [128].

5.2 Thermoelectric Properties Measurements

The TE properties of the various samples are shown in Figure 5.5:

Figure 5.5: Temperature dependence of thermoelectric properties of various compositions, (a) Electrical resistivity, (b) Seebeck coefficient, (c) Power factor, (d) Thermal conductivity, (e) Lattice thermal conductivity and (f) ZT. Reprinted with permission from Elsevier.

As shown in Figure 5.5a, the trend of electrical resistivity was inversely related to the thermal conductivity. The highest resistivity value was observed for pure SnSe, and the lowest for pure SnTe. Pure SnTe, 10SnSe and 25SnSe had electrical resistivity values of the same order of magnitude due to significant contribution from SnTe, but 40SnSe had much higher electrical resistivity values due to the contribution from SnSe. As expected from the electrical resistivity values, pure SnSe had the highest Seebeck coefficient values (Figure 5.5b), in the range of $210 \mu\text{V/K} - 250 \mu\text{V/K}$ for the measured temperature range. Such high values are attractive for TE applications. For pure SnTe and 10SnSe, the Seebeck coefficient values were quite low, at tens of $\mu\text{V/K}$, and the values were close to each other. Although 40SnSe had a considerable amount of SnSe, it did not exhibit high values of Seebeck coefficient. Instead, it started off at the same values as 25SnSe, and the Seebeck coefficient slowly decreased with increase in temperatures. This may be because of the mass fraction of the second phase present in 40SnSe. 25SnSe had Seebeck coefficient values that increased from about $60 \mu\text{V/K}$ at room temperature to about $110 \mu\text{V/K}$ at 548 K, and this value was the highest compared to the other compositions. The differentiating factor between the samples that give good overall Seebeck coefficient values was likely to be the composition and mass fraction of orthorhombic second phase. It was expected that with the acceptable Seebeck coefficient values and low electrical resistivity values, 25SnSe would give the best power factor (Figure 5.5c). A peak value of $1.31 \times 10^{-3} \text{ W/m.K}^2$ was obtained at 494 K, which was 1.5 times the peak power factor of pure SnTe.

The thermal conductivity of the various samples is shown in Figure 5.5d. Pure SnTe, being a semi-metal, had a high thermal conductivity value of about 10 W/m.K at room temperature, and it decreased with temperature to about 7.6 W/m.K at 548 K. Pure SnSe, on the other hand, had very low thermal conductivity values of about $1.1 \text{ W/m.K} - 1.2 \text{ W/m.K}$ across the measured temperature range. The other three samples exhibit similar temperature dependence trends to SnTe and their values lie between the two parent compounds, although the thermal conductivity of 40SnSe was very close to the pure SnSe phase, possibly due to the large mass fraction of SnSe phase in this sample. It was observed that addition of

10 mol % of SnSe decreased the thermal conductivity values by 20% at room temperature, while addition of 25 mol % of SnSe decreased thermal conductivity by about 50% at room temperature. This indicated the effectiveness of adding SnSe to SnTe for thermal conductivity reduction. The lattice thermal conductivity values were obtained from the relationship $\kappa_{\text{lattice}} = \kappa - \kappa_{\text{electronic}}$, where $\kappa_{\text{electronic}} = L\sigma T$, and L was taken to be $2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ [112]. As seen in Figure 5.5e, the lattice thermal conductivity values for the nanocomposites generally lie between that of SnTe and SnSe, and decreased with increase in temperature. The values also decreased with increase in SnSe mol % in the nominal sample composition. Comparing these values to the mass fractions of the second phase in the samples, it confirmed that with larger mass fraction of second phase, there was increased scattering of phonons. It was noted that these lattice thermal conductivity values made up about 50% of the total thermal conductivity, which was close to the values reported by other authors [70, 163, 164]. However, as the total thermal conductivity was on the high side, it seems like the absolute value of lattice thermal conductivity was quite high. To further decrease the lattice thermal conductivity, solutions include further nanostructuring of the constituent phases in the material, and also to explore the possibility on whether the nucleation of the nanoscale precipitates can be controlled. These will help scatter more phonons, leading to decrease in lattice thermal conductivity.

The calculated ZT of the samples are shown in Figure 5.5f. The sample 25SnSe exhibited the best performance, while for other compositions, high electrical resistivity or thermal conductivity values or too low Seebeck coefficient values led to unfavorable power factor values, and in turn poor ZT. The peak ZT of 25SnSe was 0.19 at about 548 K, which was 3 times that of pure SnTe.

The results presented here is to select the best composition for further study. The measurements were carried out using equipment available, which had a maximum temperature limit of 548 K. However, to verify the results, another batch of samples (SnTe, SnSe and 25SnSe) was sent for laser flash measurements to higher temperatures of 673 K. The SnTe sample exhibited some oxidation due to

the high measurement temperature, while 25SnSe and SnSe also exhibited slight surface oxidation after measurements. Nevertheless, the peak performances were achieved at about 573 K (refer to Appendix AI.4). Hence it may not be practical to run samples up to such high temperatures, and it is proposed that the temperature range of measurement here is sufficient.

From the above experimental results on TE properties of the various samples, it was concluded that the best composition for this material system is 25SnSe, due to the composition and mass fraction of the second phase. Further study was performed to understand the second phase: how the phase transformations occur, how the presence of second phase affects TE properties and the heat of formation calculation to understand the stability of phases in the 25SnSe system. These will be discussed in Chapters 6 and 7.

CHAPTER 6 - Results and Discussion III: 25SnSe - Second Phase Precipitation and the Effect on Thermoelectric Properties

6.1 Second Phase Precipitation

6.1.1 Introduction

As seen in Chapter 5, different compositions of samples yielded different proportions/compositions of ternary phases, which led to different TE properties. With the focus placed on 25SnSe, it was noted that during sample preparation for characterization from powder into consolidated form, an interesting observation was made: the orthorhombic second phase appeared just by gently hand grinding the flakes, and then the mass fraction further changed with ball milling and hot pressing (as shown in Figure 6.1). This was thought to be a martensitic phase transition, which is a diffusionless, solid-to-solid phase transition where the lattice or molecular structure changes [165].

Figure 6.1: XRD patterns of the 25SnSe after melt spinning, ball milling and hot press.

This demonstrated the metastable nature of the samples, and in this chapter, more understanding on the second phase formation will be elucidated through transmission electron microscopy and also theoretical calculations *via* the Miedema model theory.

Electron microprobe analysis is first presented to confirm the presence of two phases in the hot pressed sample, then the theoretical orientation relationship between (cubic) matrix and orthorhombic phases will be discussed, after which TEM performed to observe the phases in the 25SnSe sample at various stages – as-melt spun, after ball milling, and after hot pressing – will be shown. The effect of pressure on the mass fraction of second phases, and in turn the TE properties of 25SnSe, will also be explored and discussed.

6.1.2 Electron Microprobe Analysis Observation on Hot Pressed 25SnSe

Electron microprobe analysis is a high precision non-destructive technique for small-scale chemical analysis of materials. It was used to establish the presence of two phases in the hot pressed 25SnSe sample – matrix and second phase – with difference in compositions.

Presented in Figure 6.2 is the secondary electron image (SEI; Figure 6.2a) and backscattered electron image (BEI; Figure 6.2b) of a selected area in the hot pressed sample where both matrix and second phase were observed.

Figure 6.2: (a) Secondary electron image and (b) backscattered electron image of a selected area in the hot pressed sample where both matrix and second phase can be observed.

Comparing the SEI and BEI, it was confirmed that the differences in contrast were due to compositional differences. The compositional analysis is shown in Figure 6.3. It was observed that there were regions which were Se-rich and Se-deficient (and correspondingly Te-deficient and Te-rich respectively), and Sn was observed to be in slightly higher concentrations at the grain boundaries. From this analysis, we confirmed the presence of two ternary phases of $\text{SnTe}_x\text{Se}_{1-x}$, which had been established in Chapter 5.

Figure 6.3: (a) BEI image with positions where chemical analysis carried out was mapped. Elemental maps showing the concentrations of (b) Sn, (c) Se and (d) Te.

6.1.3 Theoretical Relationship between Cubic and Orthorhombic Crystal Structures

The two main components in this thesis work are SnTe and SnSe. As mentioned in Chapter 2, the crystal structure of SnTe is cubic NaCl-type, and of SnSe is orthorhombic GeS-type. Figure 6.4 shows that the transformation from the cubic to the orthorhombic structure is through the rotation of the cubic structure by 45° , and the orthorhombic unit cell overlapping at the corner, along the (101) plane of the cubic phase. It is noted that the orthorhombic unit cell is a slightly distorted version of the cubic unit cell.

Figure 6.4: Schematic of the similarity between the cubic and orthorhombic crystal structure. From [166] with kind permission from Springer Science and Business Media.

The melt spun samples crystallized in the cubic structure of $\text{SnTe}_x\text{Se}_{1-x}$, as seen in Figure 6.5, where the Se and Te atoms share the same position:

Figure 6.5: Schematic representation of the atoms of $\text{SnTe}_x\text{Se}_{1-x}$ in the $[111]$ direction.

Looking at the atom arrangements of the common plane where the two phases meet, i.e. the (101) plane of SnTe in Figure 6.6a-b and (100) interfacial plane of SnSe in Figure 6.6c, it was hypothesized that the phase transformation occurred when there was additional energy, allowing atoms from the original cubic phase to slide into positions of the common interfacial plane.

Figure 6.6: Atom arrangements of the (a) SnTe (101) plane, and the common planes of (b) SnTe (101) plane facing the (c) SnSe (100) plane (both boxed out in orange dotted lines). Source: ATOMS by Shape Software.

(continued) Figure 6.6: Atom arrangements of the (a) SnTe (101) plane, and the common planes of (b) SnTe (101) plane facing the (c) SnSe (100) plane (both boxed out in orange dotted lines). Source: ATOMS by Shape Software.

6.1.4 Transmission Electron Microscopy of Melt Spun, Ball Milled and Hot Pressed 25SnSe

Figure 6.7 shows the TEM micrograph of the as melt spun flake of 25SnSe. It was observed that the sample was made up of well-defined grains of a few hundred nanometers size. The diffraction pattern matched to a cubic phase, corresponding to the XRD pattern of 25SnSe shown in Chapter 5.

Figure 6.7: TEM micrographs of as melt spun 25SnSe (a) at low magnification and (b) indexed diffraction pattern corresponding to a cubic phase. Reprinted with permission from Elsevier.

In the TEM characterization of ball milled 25SnSe powder, it was observed that the powder was in a metastable state – upon irradiation of the electron beam, nanoprecipitates of the size of tens of nanometers were observed to be deposited on the carbon film in the region around the large particle. These TEM micrographs are shown in Figure 6.8:

Figure 6.8: TEM micrographs of (a) matrix (cubic SnTe-based) with a mixture of phase separated nanoprecipitates around the large particle at low magnification, (b) HRTEM and diffraction pattern of matrix phase in the inset, (c) HRTEM of the phase separated second phase (orthorhombic SnSe-based) nanoprecipitates and its diffraction rings in the inset, and (d) HRTEM of the second phase with the matrix phase. Reprinted with permission from Elsevier.

Figure 6.8a is a low magnification image of the ball milled powder sample, and Figure 6.8b is the HRTEM of the matrix phase with the diffraction pattern in the inset. The lattice spacing of 3.15 Å and 2.23 Å corresponded to the (0-20) and (20-2) planes (of SnTe) respectively. Figure 6.8c is a high magnification image of the nanoprecipitates of the second phase separated from the matrix, with the diffraction rings shown in the inset. Figure 6.8d is the HRTEM of the nano-sized second phase embedded in the matrix. The lattice spacing of 3.39 Å and 3.53 Å corresponded to (01-2) and (10-2) planes (of SnSe) respectively. The boundaries were observed to be generally coherent.

In the TEM observation of the hot pressed sample (Figure 6.9a), nanoscale second phases with a size of about 10 nm were observed to be embedded in the matrix. The inset shows the diffraction pattern of the cubic phase, with the second phase appearing as fainter spots. Using the software Image J, the lattice fringes were measured (Figure 6.9b) and the fast Fourier transform (FFT) of the lattice fringes was carried out to reveal the corresponding diffraction patterns (Figure 6.9c and 6.9d), which had been outlined in yellow to show the differences. This confirmed the presence of different phases in the hot pressed sample.

Figure 6.9: TEM micrographs of hot pressed samples with (a) nanoscale second phases embedded in the matrix, (b) high magnification image of second phase and FFT images of (c) the second phase and (d) matrix.

(continued) Figure 6.9: TEM micrographs of hot pressed samples with (a) nanoscale second phases embedded in the matrix, (b) high magnification image of second phase and FFT images of (c) the second phase and (d) matrix.

From the above TEM micrographs, we confirmed that from the single phase observed after melt spinning, the sample changed into a two-phase system after ball milling, with the second phase appearing as nano-sized precipitates. These nanoscale features were maintained even after hot pressing, hence the nanostructured features were retained, according to the original design concept of this work.

6.1.5 Transmission Electron Microscopy Observation on Orientation Relationship between Cubic SnTe-based Matrix and Orthorhombic SnSe-based Second Phase Crystal Structures

6.1.5.1 Ball milled samples

From the TEM micrograph in Figure 6.8d, the second phase is seen to be embedded in the matrix. Figure 6.10 is the zoomed-in image of Figure 6.8d, at the region which shows the interface between the two phases and the corresponding hkl planes of the d-spacings.

Figure 6.10: Zoomed-in image of Figure 6.8d, at the region which shows the interface between the two phases. The corresponding hkl planes are as indexed.

Examining these two phases, it was seen that the lattice spacing of the (0-20) plane of the matrix can be matched to the (10-2) plane of the second phase. The identities of these two phases were further confirmed through the diffraction patterns obtained by FFT, which was compared to the diffraction pattern from the database (Figure 6.11).

Figure 6.11: Diffraction patterns of (a) SnTe at the $[101]$ zone axis and (b) SnSe at the $[221]$ zone axis (taken from the database), compared with FFT of the matrix and second phase respectively from Figure 6.8d (as insets). Source: JEMS software. Reprinted with permission from Elsevier.

Based on the information, calculations of the lattice distances in the matrix and second phase, and their orientation relationships, are shown in Table 6.1. The projections of the atoms of the two phases are shown in Figures 6.12 and 6.13.

Table 6.1: The hkl planes and orientation relationship for the matrix and second phase

d-spacing of SnTe-based phase (Å)	hkl planes	Intersected plane at grain boundary
2.23	20-2	(11-1)
3.15	0-20	
	Zone axis = 101	
d-spacing of SnSe-based phase (Å)	hkl planes	Intersected plane at grain boundary
3.53	10-2	(0-12)
3.39	01-2	
	Zone axis = 221

Figure 6.12: Projections of SnTe at (a) zone axis [101] (indicated by the blue plane), (b) at intersection plane (11-1) of the interface boundary (indicated by the yellow plane) and (c) the cross plane view (rotated 90°) at the interface boundary of the (11-1) plane. Source: ATOMS by Shape Software. Reprinted with permission from Elsevier.

The SnSe (100) plane was used (since it is the common plane with SnTe (101) plane) together with the intersection plane of (10-2). The intersection was observed to cut across the Sn atoms as well, similar to Figure 6.12. Hence, it was predicted that this was the common plane between the two phases.

Figure 6.13: Projections of SnSe at (a) (100) plane (indicated by the blue plane), (b) at intersection plane (0-12) of the interface boundary (indicated by the yellow plane) and (c) the cross plane view (rotated 90°) at the interface boundary of the (0-12) plane. Source: ATOMS by Shape Software. Reprinted with permission from Elsevier.

From Figures 6.12c and 6.13c, it is observed that although the common planes of SnTe (11-1) and SnSe (0-12) show a hexagonal arrangement. In order to fit nicely, some distortion will be required in one of the Sn atom positions from SnSe. However, this is expected, as both phases were initially different in terms of its crystal structure. The schematics shown in Figures 6.11 to 6.13 provide insight into the crystallography of the cubic to orthorhombic transition, and how the possible transformation between cubic and orthorhombic phases may have occurred.

6.1.5.2 Hot pressed samples

Figure 6.14 is a reproduction of Figure 6.9b, but here the hkl planes are indicated instead. In this micrograph, it was observed that the second phase showed a more coherent interface compared to the ball milled powder sample (Figure 6.8d), and that matching hkl planes in both the phases indicated were different from those of the ball milled powder sample.

Figure 6.14: Reproduction of Figure 6.9b, with the hkl planes of the two phases indicated.

One possibility was that the orientation of two phases in the hot pressed sample was different from the ball milled sample, and in turn there were differences in the stability of phases. This possibility will be briefly discussed in Section 6.2. In any case, nanoprecipitates of the second phase were present in the hot pressed sample, allowing multiphase materials to be formed.

6.2 Effect of Pressure on Second Phase Precipitation and Thermoelectric Properties

6.2.1 Evolution of Second Phase Precipitation with Applied Pressure

Another observation made in the 25SnSe composition sample was that the mass fraction of second phase changed with increased applied pressure (through cold press). The evolution of phases at different stages from post ball milling to cold pressing at different pressures are shown in the XRD patterns presented in Figure 6.15 (samples are labeled S0 to S3, where S0 is the as ball milled sample, S1 is the sample cold pressed at 6.90 MPa, S2 is the sample cold pressed at 20.68 MPa and S3 is the sample cold pressed at 34.47 MPa).

Figure 6.15: XRD patterns of ball milled powder and cold pressed 25SnSe at various pressures. The inset shows the range of angles from 25° to 35°. Reprinted with permission from Elsevier.

The peak positions of the samples in Figure 6.15 do not change with pressure. This may indicate that there is an equilibrium composition for both the phases, and a change in processing parameters only changes the mass fraction of phases. Table 6.2 shows the TOPAS refinement that was carried out to determine the mass fraction of the matrix and second phases (refined images shown in Appendix AII.1) in the various samples. It was noted that in all these calculations, the values obtained were used qualitatively rather than quantitatively as there were slight differences in batch to batch synthesis.

Referring to Figure 6.15, as the change in mass fraction of the phases of the ball milled powder (S0) compared to the sample cold pressed at 6.90 MPa (S1) was quite small, their values presented in Table 6.2 were quite close. For samples S1 to S3, the mass fraction of the matrix decreased with increase in applied pressure and the reverse trend was observed for the second phase. As the applied pressure increased, the second phase seems to increase until it becomes a majority phase compared to the matrix. This observation was attributed to the metastability of the second phase in the ball milled powder, and the possible reasons for the

observation were: (i) applying pressure facilitates second phase precipitation, but did not have a prominent effect on the matrix, hence there was a decrease in proportion of the matrix phase, and (ii) the application of pressure could possibly have induced defects or disorder in the matrix, such that it formed an amorphous phase, which does not recrystallize under pressure in the absence of heat.

Table 6.2: TOPAS analysis of the mass fraction of phases in the various samples

Sample	Mass fraction of matrix (wt %)	Mass fraction of second phase (wt %)	Sn (wt %)
S0-As ball milled	70.0	25.1	4.9
S1-6.90 MPa	67.5	26.3	6.2
S2-20.68 MPa	53.1	42.0	4.9
S3-34.47 MPa	37.2	44.9	17.9

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Linking back to the appearance of the second phase after ball milling (and cold compaction, which is a form of plastic deformation), due to the creation of new atomic defects during milling as well as increased energy of the system, atomic rearrangement could have occurred to result in phase transformations [167], leading to a change in mass fractions.

It was noted that Sn was detected in the samples, due to batch to batch differences across the samples and/or decomposition of SnSe to Sn and Se. Although the mass fraction of the amount of Sn in the samples differed with increasing pressure, with the highest value observed in S3, it was likely to be due to preferred orientation (i.e. texturing) in certain directions (refer to Appendix II.1) with cold pressing. It was also possible that Sn may have existed as an amorphous phase in samples that were cold pressed at lower pressures, such that only a small amount was detected. This is possible because it is observed in the next section (Section 6.2.2) that the mass fraction of Sn phases after heating is quite similar across the three samples, which meant that initially, there should not be significant

differences between the samples. Nevertheless, Sn was also included in the refinement and subsequent calculations to give more accurate information on the two phases. The overview of the different information obtained from TOPAS and other calculations for the samples are shown in Table 6.3.

Table 6.3: TOPAS calculations on the mass fraction and compositions of the matrix and second phases for 25SnSe

Samples (C – matrix ; O – second phase)	Calculated wt %	Elemental concentration of phase in proportion to its wt % (Obtained by multiplying values in column 1 & 2)	Total elemental concentration in sample (including initially calculated Sn wt %)
S0 - As ball milled compositions			
C- SnTe _{0.877} Se _{0.123}	70.0	Sn _{0.6999} Te _{0.6138} Se _{0.0} 861	SnTe _{0.7894} Se _{0.1613}
O- SnTe _{0.700} Se _{0.300}	25.1	Sn _{0.2508} Te _{0.1756} Se _{0.0} 752	
S1 - 6.90 MPa compositions			
C- SnTe _{0.881} Se _{0.119}	67.5	Sn _{0.6747} Te _{0.5944} Se _{0.0} 802	SnTe _{0.7722} Se _{0.1654}
O- SnTe _{0.676} Se _{0.324}	26.3	Sn _{0.2630} Te _{0.1778} Se _{0.0} 852	
S2 - 20.68 MPa compositions			
C- SnTe _{0.906} Se _{0.094}	53.1	Sn _{0.5315} Te _{0.4815} Se _{0.0} 500	SnTe _{0.7758} Se _{0.1755}
O- SnTe _{0.701} Se _{0.299}	42.0	Sn _{0.4198} Te _{0.2943} Se _{0.1} 255	
S3 - 34.47 MPa compositions			
C- SnTe _{0.903} Se _{0.097}	37.2	Sn _{0.3722} Te _{0.3361} Se _{0.0} 361	SnTe _{0.6563} Se _{0.1644}
O- SnTe _{0.714} Se _{0.286}	44.9	Sn _{0.4485} Te _{0.3202} Se _{0.1} 283	

Column 1 of Table 6.3 is the composition of the phases obtained from lattice parameters calculations *via* Vegard's Law. The results indicated that the

compositions of the matrix in the samples were relatively stable and consistent, with an approximately 3.3% difference in compositions across the samples. Larger changes were observed in the second phase, with about 6.8% difference in compositions across the samples. Column 2 is the calculated weight percentages of the two phases obtained through TOPAS refinement (corresponding to the results in Table 6.2). The elemental concentration of the matrix and second phase in proportion to its wt % is presented in Column 3 (obtained by multiplying the values in Columns 1 and 2). The total elemental concentration of both phases is shown in Column 4 (which indicates the composition of the whole sample).

Theoretically, 25SnSe will consist of 78.89 wt % of SnTe phase and 21.11 wt % of SnSe phase (i.e $\text{SnTe}_{0.7889}\text{Se}_{0.2111}$). Comparing with the final calculated composition of the samples in Column 4, it was noted that initially, SnTe concentration was underestimated, while SnSe was overestimated. As mentioned in earlier chapters, SnSe can decompose, and this may be the reason for the observation of overestimation of SnSe phase. At higher pressures of 20.68 MPa and 34.47 MPa, when SnSe “became” the majority phase, the lack of SnSe was made up for, so the calculated values were close to the theoretical values.

From the results in this section, it is inferred that application of pressure led to phase transformation. The next section will discuss the effect of the second phase on TE properties.

6.2.2 Thermoelectric Properties of 25SnSe Samples Cold Pressed Samples and the Effect of Different Amounts of Pressure

The TE properties measurements of the samples cold pressed at different pressures (S1 to S3) are presented in Figure 6.16. The cold pressed samples had similar densities in order to eliminate density effects on electrical resistivity. For the cold pressed samples, as they had not been exposed to any heating cycle (unlike samples which have been consolidated *via* hot pressing), the thermal cycle during TE properties measurements acted as a heat treatment process, hence an annealing effect was observed. As a result, there was a change in its properties after the first round of measurements, with slight differences observed in subsequent

measurements. However, in the comparisons of TE properties of these samples, the data of the first runs are first presented as they were the most representative of the effect of the phases on TE properties.

Figure 6.16: Temperature dependence of thermoelectric properties of various compositions at the first run (a) Electrical resistivity, (b) Seebeck coefficient and (c) Power factor. Reprinted with permission from Elsevier.

(continued) Figure 6.16: Temperature dependence of thermoelectric properties of various compositions at the first run (a) Electrical resistivity, (b) Seebeck coefficient and (c) Power factor. Reprinted with permission from Elsevier.

Figure 6.16a shows the electrical resistivity of the samples. The differences in values were likely to be due to the different mass fraction of phases present. Thus, based on the trend, S1, with the least mass fraction of second phase, exhibited the highest resistivity values. S2, which had slightly greater mass fraction of second phase, exhibited lower resistivity values. S3, with the largest amount of second phase, had the lowest resistivity values. The electrical resistivity value of S1 was about 2.2 times higher than that of S2 and 7 times higher values than that of S3. The trend of decreased resistivity with measured temperature was due to the annealing effect of the samples.

Figure 6.16b shows the Seebeck coefficient of the samples, which lies between 30 $\mu\text{V/K}$ – 110 $\mu\text{V/K}$. The positive values indicated that the material was a p-type semiconductor. Generally, an increase in mass fraction of second phase lowered the Seebeck coefficient, although the values increased with temperature. Even though S1 and S2 had different proportions of phases, they exhibited relatively similar Seebeck values. It was possible that the contribution from the matrix and second phase precipitate was not large enough to show observable differences, or the decreased Seebeck coefficient of one phase offset the increase

from the other phase. This may be so for S2 where there were nearly equal amounts of both phases. S3 initially had a lower Seebeck coefficient value, but it was able to reach values higher than S1 and S2 from about 443 K onwards. This indicated that the second phase was more “dominant” as temperature increased, resulting in higher Seebeck coefficient values. A maximum value of 107 $\mu\text{V/K}$ was obtained for sample S3 at about 540 K, and compared to the Seebeck coefficient of hot pressed 25SnSe in Figure 5.5b (with a peak value of 111 $\mu\text{V/K}$ at 548 K), it was only about 3.7% lower. Since the values did not vary much between S3 and the hot pressed sample, it was conjectured that cold pressing could achieve equally high Seebeck coefficient values as well.

The power factors of the samples are shown in Figure 6.16c. The three samples exhibited similar power factor values from room temperature to about 398 K. However, as S3 initially had the lowest electrical resistivity values, and highest Seebeck coefficient values above 443 K, its power factor increased quickly to reach a value of $0.328 \times 10^{-3} \text{ W/m.K}^2$. This value was 1.88 times that of S2 and 3.09 times that of S1.

For this part of the work, there were no thermal conductivity measurements made initially as the samples were cold pressed in a 10 mm diameter die. Nevertheless, to understand the effect of second phase on the trend for thermal conductivity, a separate batch of samples was cold pressed in a 13 mm diameter die for thermal conductivity measurements (refer to Appendix AII.1). The trend of thermal conductivity was shown to increase with applied pressure, and the effect on the difference in thermal conductivity between the samples was less significant in comparison to the difference in power factor between them. Thus, it is predicted that S3 will yield the best TE properties. As the TE properties and thermal conductivity data obtained was from different batches, the trend of these properties, instead of using the absolute values, was considered for analysis.

It was concluded that an increase in applied pressure could increase the mass fraction of second phase, and in turn improve the TE properties. The second phase was important for the reduction of electrical resistivity, and also contributed

to improved Seebeck coefficient values, especially at higher temperatures. As the trend of thermal conductivity was shown to be less sensitive to the increase in applied pressure compared to the power factor, hence it is likely improved TE properties will be obtained with increase in applied pressure.

After TE properties measurements, XRD analysis was carried out again to study the changes (Figure 6.17).

Figure 6.17: XRD patterns of 25SnSe cold pressed at various pressures after TE properties measurements. The inset shows the range of angles from 25° to 35°. Reprinted with permission from Elsevier.

It was observed that there was dissolution of the second phase after the heat treatment, as the second phase peaks became weaker in intensity. TOPAS was used to calculate the remaining amount of phases present (Table 6.4). The TOPAS refined figures are shown in Appendix AII.2. It was noted that there was slight oxidation occurring after measurements (indicated by SnO_2 peaks), most likely on the surface of the samples. Samples S2 and S3 also had some impurities phase of Sn present.

As seen from the TOPAS calculations, the mass fraction of second phase had indeed decreased after TE measurements. The amount of second phase in S1 and S2 was quite close, while S3 had a considerably larger amount of second phase.

Table 6.4: TOPAS calculations of the mass fraction of phases after TE properties measurements

Sample	Mass fraction of matrix (wt %)	Mass fraction of second phase (wt %)	SnO ₂ (wt %)	Sn (wt %)
S1 – 6.90 MPa	91.3	5.5	3.2	-
S2 – 20.68 MPa	87.2	6.4	4.1	2.3
S3 – 34.47 MPa	81.4	12.2	3.4	3.1

The mass fraction of S3 became closer to the values calculated by the lever rule. This indicated that during TE properties measurements, the heating facilitated phase transformations back to its equilibrium state. The compositions of the phases in the three samples are shown in Table 6.5. It was observed that there was more Te and Se (compared to the initial compositions) in the matrix and second phase, respectively.

Table 6.5: TOPAS calculations on the composition of matrix and second phases before and after TE properties measurements

Sample	Lattice parameter (Å)/ Cell volume (Å ³) (after TE properties measurements)	Composition of matrix (after TE properties measurements)	Composition of second phase (after TE properties measurements)	Initial (after cold press) composition of matrix	Initial (after cold press) composition of second phase
S1 – 6.90 MPa	6.270/ 234.815	SnTe _{0.903} Se _{0.097}	SnTe _{0.542} Se _{0.458}	SnTe _{0.881} Se _{0.119}	SnTe _{0.676} Se _{0.324}
S2 – 20.68 MPa	6.265/ 237.672	SnTe _{0.887} Se _{0.113}	SnTe _{0.626} Se _{0.374}	SnTe _{0.906} Se _{0.094}	SnTe _{0.701} Se _{0.299}
S3 – 34.47 MPa	6.278/ 238.931	SnTe _{0.929} Se _{0.071}	SnTe _{0.662} Se _{0.338}	SnTe _{0.903} Se _{0.097}	SnTe _{0.714} Se _{0.286}

The TE properties measurements were repeated three times, and after the first round of measurements, the following was observed: electrical resistivity decreased slightly in each of the subsequent two cycles, while Seebeck coefficient values varied slightly between the second and third cycle. In turn, power factor was

observed to be improved in each of the measurement. The TE properties of the third cycle are presented in Figure 6.18 since it was more representative of the final microstructure.

Figure 6.18: Temperature dependence of thermoelectric properties of various compositions at the third run (a) Electrical resistivity, (b) Seebeck coefficient and (c) Power factor.

(continued) Figure 6.18: Temperature dependence of thermoelectric properties of various compositions at the third run (a) Electrical resistivity, (b) Seebeck coefficient and (c) Power factor.

In Figure 6.18a, after the initial annealing effect, the electrical resistivity values of the samples were much lower, though the trend was that it increased with temperature, which was a typical behaviour of many TE materials. S1 and S2 had values close to each other, due to the similar mass fraction of matrix phase, and a small amount of second phase in S2. S3 had the lowest resistivity value, which was expected, since the mass fraction of second phase was the largest.

The Seebeck coefficient values in Figure 6.18b generally show slightly higher room temperature values, compared to the values for the first run. The Seebeck coefficient values of S2 and S3 were quite close, while for S1, it was about 20% lower across the whole measured temperature range. Comparing S1 and S2, the presence of the second phase led to increased Seebeck values; between S2 and S3, there was no marked difference in Seebeck coefficient values. Although there were variations in the mass fractions of phases, the compositions of the second phases were quite similar. Thus, an increased amount of Te in the SnSe-rich second phase led to higher Seebeck values. From the results, increased mass fraction of

second phase increased Seebeck coefficient, but the composition of this second phase was also important in the contribution to higher Seebeck coefficient values.

Due to the lowered electrical resistivity of the samples, the power factor of the samples (Figure 6.18c) improved in the third cycle compared to the first cycle (Figure 6.16c). S3 still shows the best power factor, with a peak value of $0.395 \times 10^{-3} \text{ W/m.K}^2$ at about 540 K.

The power factor achievable by the cold pressed samples was still quite low, and was much lower than the hot pressed samples (presented in Chapter 5), which showed a peak value of $1.31 \times 10^{-3} \text{ W/m.K}^2$ at 494 K.

In this chapter, the effect of the second phase on the TE properties was studied. The effect of elevated temperature on the thermal stability of these materials was also determined. The reversible nature of the phase transformation observed in this chapter was not observed in the hot pressed samples. It was concluded that concurrent application of heat and pressure during hot pressing served to stabilize the second phases and was therefore an important processing step to be carried out. For materials to be used in TE applications, phase stability is important as the material has to survive many runs.

CHAPTER 7 - Results & Discussions IV: Effect of Processing on Second Phase, its Evolution and Theoretical Calculations of its Stability

7.1 Effect of temperature on the second phase in the absence of pressure

7.1.1 Introduction

As seen in Chapter 6, from the TE properties measurements of the cold pressed samples, after going through an elevated temperature cycle, the dissolution of the second phase was observed. This, however, was not observed in the hot pressed samples where the second phase was preserved after TE properties measurements. Hence, in order to validate the point that concurrent application of heat and pressure is required to preserve the second phases in a stable state, in this section, the behaviour of second phase with increasing temperature in the absence of pressure is studied.

7.1.2 High Temperature XRD

The ball milled 25SnSe powders were characterized using high temperature XRD, with measurements carried out at room temperature (300 K), 423 K, 573 K, 673 K and again at room temperature after the sample had cooled down. The XRD patterns are shown in Figure 7.1.

Figure 7.1: XRD patterns obtained at various temperatures for ball milled 25SnSe powders. The inset shows the range of angles from 22.5° to 45°.

From the high temperature XRD data (Figure 7.1), an insight into the phase transformation behaviour of 25SnSe was obtained. It was observed that with an increase in temperature to 423 K, the two peaks corresponding to the second phase observed in the black curve at 29° and 29.5° shifted to become a hump at 30° in the red curve, indicating a decrease in lattice parameters, i.e. Te was coming out of the initial $\text{SnTe}_x\text{Se}_{1-x}$ second phase, which was confirmed by TOPAS calculations in Table 7.1. At higher temperatures of 573 K, the hump evolved into twin peaks at 30° and 30.3°. The positions of the hump and the twin peaks correspond to the reference XRD pattern of SnSe (shown in Figure 7.1). In addition, the composition of the matrix was calculated to be mainly SnTe. This may be because the Se had diffused from the matrix into the second phase. At about 673 K, the peaks of the second phase were not observable. A slight hump at about 26.5° and 33.7° was observed, which corresponded to SnO_2 peaks. This indicated that at high temperatures of 573 K to 673 K, there was some oxidation on the sample surface. Here, the composition of the matrix was calculated to be SnTe with excess Te, indicating that the second phase was dissolving in the matrix phase. To confirm if the dissolution of phases was permanent, XRD of the sample after cooling to room

temperature was performed. A single phase was detected, indicating that the dissolution was not reversible. This confirmed that for the second phase to persist, heat and pressure had to be applied concurrently.

Table 7.1 shows the calculated mass fractions and compositions of the constituent phases at different temperatures based on the lattice parameters and cell volume from TOPAS calculations (refer to Appendix III.1 for details). With changes in the composition at the various measurement temperatures, the mass fraction of the matrix and second also varied. With increase in temperatures to 423 K, the mass fraction of the matrix increased while that of the second phase decreased. Between 423 K and 573 K, the matrix phase decreased in mass fraction, while the mass fraction of the second phase increased slightly. At this point, some SnO₂ was also detected. Eventually, at 673 K, the second phase dissolved completely, leaving only “humps” at 26.5° and 33.7°, which was attributed to SnO₂.

Table 7.1: TOPAS calculations on the composition of matrix and second phases after high temperature XRD

Sample at various temperatures	Mass fraction of matrix (wt %)	Mass fraction of second phase (wt %)	Mass fraction of impurities phase (SnO ₂) (wt %)	TOPAS calculated composition of matrix	TOPAS calculated composition of second phase
300 K	71.6	28.4	-	SnTe _{0.812} Se _{0.188}	SnTe _{0.675} Se _{0.325}
423 K	78.7	21.3	-	SnTe _{0.991} Se _{0.009}	SnTe _{0.313} Se _{0.687}
573 K	71.2	23.2	5.6	SnTe _{1.004}	SnTe _{0.249} Se _{0.751}
673 K	71.2	-	28.8	SnTe _{1.027}	-
300 K – cooled down to room temperature	100.0	-	-	SnTe _{0.893} Se _{0.107}	-

7.2 Fabrication and Characterization of 25SnSe control samples

7.2.1 Introduction

The earlier chapters had shown that 25SnSe fabricated by melt spinning, ball milling and finally hot pressing led to improved TE properties due to the presence of the second phase compared to the single phases of SnTe and SnSe. To confirm the superiority of the melt spinning technique as an approach to improve TE properties, control samples of 25SnSe were synthesized by solid state synthesis (indicated as 25SnSe_SS) and by physical mixing (indicated as 25SnSe_phymix). Characterization such as XRD (and EDX for 25SnSe_SS) were performed to identify the phases in the sample, and subsequently TE properties measurements were carried out and compared with the melt spun and hot pressed 25SnSe sample.

7.2.2 Characterizations and Thermoelectric Properties of 25SnSe_SS

The EDX results of 25SnSe_SS are presented in Table 7.2 to compare the elemental concentrations in the sample. From these results, and taking into consideration the error of $\pm 5\%$, it was confirmed that the concentration of the elements of 25SnSe_SS was close to the nominal composition. TOPAS was then used to obtain composition of the phases in 25SnSe_SS (Table 7.3). Calculations (Appendix AIII.2) showed that there were some differences in composition of phases between this sample and the hot pressed sample. This was possible as 25SnSe_SS was synthesized by slow cooling, which allowed the phases to reach equilibrium. The compositions of the matrix and second phase were closer to the solubility values provided in the phase diagram.

Table 7.2: EDX values in 25SnSe_SS

25SnSe_SS after synthesis	EDX values	
Element	Average atomic percent	Theoretical atomic percent
Sn	51.2	50.7
Se	9.10	8.4
Te	39.7	40.9

The XRD pattern of the 25SnSe_SS after the solid state synthesis is shown in Figure 7.2a. As the sample was in ingot form, preferred orientation was observed in the [220] and [222] directions.

Figure 7.2: XRD patterns of solid state synthesized 25SnSe_SS (a) after synthesis and (b) after TE properties measurements. The inset shows the range of angles from 25° to 45°.

After the TE properties measurements (Figure 7.2b), the preferred orientation in the [222] direction was reduced, but there was still a strong [220] peak. For 25SnSe_SS, the second phase was not stable, and dissolved into the matrix after TE measurements (Table 7.3; refined TOPAS images in Appendix AIII.3). This observation was similar to that in Section 7.1, where the XRD pattern taken at room temperature of the ball milled powders of 25SnSe after cooling down from the high temperature XRD studies showed single phase only.

Table 7.3: Calculated mass fraction of the constituent phases and their corresponding compositions in 25SnSe_SS

25SnSe_SS after synthesis	Mass fraction (wt %)	Lattice parameter (Å) / Cell volume (Å³)	Composition
Matrix	58.3	6.269	SnTe _{0.90} Se _{0.10}
Second phase	36.8	244.244	SnTe _{0.817} Se _{0.183}
Impurities phase - Sn / Se	2.9 / 2.0	-	-
25SnSe_SS after TE properties measurements		Lattice parameter (Å) / Cell volume (Å³)	Composition
Matrix	97.0	6.270	SnTe _{0.90} Se _{0.10}
Second phase	1.7	217.193	SnTe _{0.03} Se _{0.97}
Impurities phase - Sn	1.3	-	-

The TE properties of 25SnSe_SS with cycling (i.e. run 1 to run 3) are presented in Figure 7.3. It was interesting to note that after the dissolution of the second phase (assumed to occur in the first cycle), the properties decreased slightly in subsequent measurements. There was also no annealing effect or instability in the electrical resistivity measurements performed on for 25SnSe_SS. For this part of the work, there were no thermal conductivity measurements performed throughout as the dimensions of the samples did not meet the requirements of the laser flash equipment. In addition, the density of the ingot used for measurement was about 80% of the theoretical density, limiting the accuracy of the measurements too.

Figure 7.3: Temperature dependence of thermoelectric cycling properties of 25SnSe_SS: (a) Electrical resistivity, (b) Seebeck coefficient and (c) Power factor.

(continued) Figure 7.3: Temperature dependence of thermoelectric cycling properties of 25SnSe_SS: (a) Electrical resistivity, (b) Seebeck coefficient and (c) Power factor.

From Figure 7.3a, the electrical resistivity of 25SnSe_SS is shown to be a low value of $10^{-6} \Omega \cdot \text{m}$, similar to that of 25SnSe. This was expected as they were of similar nominal compositions. However, as mentioned earlier, 25SnSe_SS was about 80% of the theoretical density, hence, the real electrical resistivity might be slightly lower. In Figure 7.3b, the Seebeck coefficient of 25SnSe was in the range of $2 \mu\text{V/K} - 52 \mu\text{V/K}$ in the measured temperature range. Compared to that of 25SnSe, these values were much lower. In fact, the minimum Seebeck coefficient value obtained in 25SnSe was higher than $52 \mu\text{V/K}$. This indicated that the second phase in the melt spun samples improves the Seebeck coefficient. The power factor (Figure 7.3c) of 25SnSe_SS was in the range from $1 \times 10^{-6} \text{ W/m.K}^2$ to nearly $6 \times 10^{-4} \text{ W/m.K}^2$, with the peak value about half of that of 25SnSe.

7.2.3 Fabrication and Characterization of 25SnSe_phymix

The XRD patterns of the 25SnSe_phymix after hot press and after TE properties measurements are shown in Figures 7.4a and 7.4b respectively. The phases were SnTe and SnSe, and it was observed that there were no changes in these phases after TE properties measurements. This indicated the stability of this physical mixture of SnTe and SnSe. It was noted that for the SnSe peaks, there was

preferred orientation in the [004] direction at 31.2° , perhaps due to the layered structure of SnSe after grinding.

Figure 7.4: XRD patterns of 25SnSe_phymix, which is prepared by physically mixing SnTe and SnSe in the molar ratio of 75:25 respectively: (a) after hot press and (b) after TE properties measurements.

The TE properties of 25SnSe_phymix are shown in Figure 7.5. As the sample was stable, only one set of measurements will be shown:

Figure 7.5: Temperature dependence of thermoelectric properties of 25SnSe_phymix (a) Electrical resistivity, (b) Seebeck coefficient, (c) Power factor, (d) Thermal conductivity and lattice thermal conductivity and (e) ZT.

From Figure 7.5a, as the nominal composition of 25SnSe_phymix was similar to that of 25SnSe_SS and 25SnSe, the electrical resistivity was also in the range of $10^{-6} \Omega \cdot \text{m}$. The Seebeck coefficient (Figure 7.5b) was in the range of $30 \mu\text{V/K} - 80 \mu\text{V/K}$. This was slightly higher than the corresponding value of 25SnSe_SS, but still about 28% lower than the peak value obtained in 25SnSe. This indicated that while the individual phases of SnTe and SnSe gave better performance than the phases obtained by slow cooling in 25SnSe_SS, the best composition and proportion of phases were still obtained from melt spinning and hot pressing. In Figure 7.5c, the power factor of 25SnSe_phymix ranged from about $2.5 \times 10^{-4} \text{ W/m.K}^2$ to $7 \times 10^{-4} \text{ W/m.K}^2$, higher than 25SnSe_SS, but still about 1.9 times lower than 25SnSe.

The thermal conductivity measurement is presented in Figure 7.5d. Since the samples were just physically mixed, the range of thermal conductivity values was simply a summation of the constituent phases. The maximum thermal conductivity at room temperature of SnTe and SnSe (in Chapter 5) was about 7.855 W/m.K and 1.185 W/m.K respectively. Taking into consideration the molar fraction, the predicted thermal conductivity value for 25SnSe_phymix = $(0.75 \times 7.855) + (0.25 \times 1.185) = 6.187 \text{ W/m.K}$, close to the room temperature thermal conductivity measured (Figure 7.5d). The lattice thermal conductivity of the 25SnSe_phymix sample had the same trend as the thermal conductivity and ranges from about 70% to 74% of the total thermal conductivity. In comparison, the lattice thermal conductivity of 25SnSe was lower, and accounted for about 61% to 72% of the total thermal conductivity. This proportion was relatively large, and gave an insight to how the presence of the phases after melt spinning led to decreased lattice thermal conductivity. The calculated ZT for 25SnSe_phymix is shown in Figure 7.5e. It was seen that the peak ZT was about 0.07. This was 2.7 times lower than the 0.19 obtained for 25SnSe, illustrating the importance of the phases present from melt spinning in improving the TE properties.

Thus from the above results, it was seen that for the same nominal composition, the obtained phases were different depending on the synthesis methods, and this difference was reflected in the TE properties.

Based on the discussions about on the two control samples of same composition prepared by solid state synthesis (25SnSe_SS) and physical mixing (25SnSe_phymix) with the hot pressed 25SnSe sample, it was validated that melt spinning had beneficial effects in the sense that the proportion and composition of the matrix and second phase formed led to synergistic improvements. As the mass fraction of the orthorhombic second phase can be altered by small applied pressure, this observed metastability with processing offers an avenue to systematically tune the microstructure, and is one of the novelties of the work. It is concluded that the melt spinning technique is superior since non-equilibrium compositions of the second phase can be obtained, leading to improved TE properties.

As metastability of the phases was observed in the ball milled and cold pressed samples, but not in the hot pressed samples, the enthalpy of formation of phases in these samples was calculated using the Miedema model theory to support the observed difference in stability and its metastable nature. This will be covered in Section 7.3.

7.3 Thermodynamics of phase transformation via Miedema Model Calculations

7.3.1 Introduction to Miedema Theory

In Section 6.1.1, it was mentioned that there was a spontaneous formation of the second phase in the ball milled samples.

In this chapter, theoretical calculations based on the Miedema model is used to rationalize why melt spun samples are metastable, and can be phase separated with small driving force. It will also be shown that the presence of these two separate phases of certain compositions and/or mass fractions are more stable

compared to the initial single phase after melt spinning and the compositions at transition stages (during cold pressing).

The heat of formation or enthalpy of formation of a compound is an indication of its stability; the more negative the value, the more stable it is. In this work, the heat of formation for the various phases was calculated to understand the spontaneous appearance of second phases upon grinding.

There are various methods used for such calculations, and it can be divided into 4 categories [168]:

- a) First principles calculations using density-functional theory,
- b) Statistical mechanics based approaches, which use atomistic simulation techniques like molecular dynamics,
- c) Solution thermodynamics based on extrapolation of experimental data, e.g. the calculation of phase diagram (CALPHAD) method, and
- d) Semi-empirical methods like Miedema's model, which is in turn based on the equivalent crystal theory.

The different methods are briefly discussed in the next few paragraphs.

First-principles calculation is a microscopic technique used to yield highly accurate values, but they have a high computing cost and prior information on the crystal structure is required. Advances in first-principles calculation based on density-functional theory have enabled the computation of thermodynamic and structural properties of phases using only atomic numbers and crystal structure information as input values. However, for a phase with a few hundred atoms per unit cell, first-principles calculation is extremely time-consuming [169].

Atomistic simulations of energy can be carried out using harmonic methods, ab-initio calculations, molecular dynamics simulations and Monte Carlo methods [168].

The CALPHAD approach is a macroscopic method used to predict the enthalpy of formation on alloy from the Gibbs energy expressions of individual phases. The expressions used are optimized from various experimental phase equilibrium and thermodynamic properties. The accuracy of this approach relies on a reasonable thermodynamic model for each phase, accurate experimental information and also the quality of thermodynamic descriptions of the lower-order systems [169].

Miedema's theory was developed by Miedema *et al.* in the 1970s, and incorporates concepts from the thermodynamics of solids and energy band theory. It has been widely used to calculate the formation enthalpies of liquids, solid solutions and compounds, and also to construct Gibbs free energy diagrams of the alloys, which could provide thermodynamic information on the relative stability of various alloy phases in the respective systems [169, 170].

The Miedema model is built on the “macroscopic atom” picture, and the assumption is that the reference can be chosen as atoms being embedded in a metal, instead of being free atoms. The essence of the model lies in estimating quantitatively the effects of the change in the Wigner–Seitz cell boundary electron density. When dissimilar cells are in contact with each other, they tend to shift their electron densities so as to remove the cell boundary discontinuities, in order to form the alloy. Elimination of such discontinuities is expected to require energy, thus the electron density difference $\Delta\eta_{ws}$ accounts for a positive contribution to the interface energy [171].

The original form of Miedema's model was applicable only to transition metals binary alloys [171]. In addition, it was found that for this model, there was a systemic deviation between the measured experimental values and the results calculated by Miedema's theory for binary alloy systems. Also, the Miedema theory does not give accurate results for ternary alloys [170]. The discrepancies are mainly due to the assumption in the original Miedema model that the third element has no effect on the other two elements when calculating the interfacial energy between them. However, such an interfacial energy is one of the several parameters

used in the Miedema model, and in multicomponent systems, it should not be ignored [169]. Instead, modifications have to be made. Many researchers have carried out extensive experimental studies to modify the Miedema model in order to apply the calculations for the thermodynamic properties of binary as well as ternary alloy systems [168, 170-173]. Details of these modifications are not in the scope of this work, and will not be discussed here.

For the Sn-Te-Se system, although the Miedema model may not be directly applicable, reports by other authors on its use for other material systems other than binary intermetallics showed that it was possible to use the modified equations, which had shown to yield relatively accurate values [170]. Hence, it was used to carry out qualitative calculations for the discussion here.

To the best of the author's knowledge, although there were reports on the enthalpy of formation of binary phases of SnTe [174] and SnSe [175], there had not been reports on the heat of formation values for the ternary Sn-Te-Se system. Thus, the value for the ternary phase was calculated qualitatively. The equations which were used have modifications made to the original Miedema model in order to give more accurate values. Why the equations were used and how they are modified is briefly discussed in the next few paragraphs.

In the qualitative calculations of heats of formation for the phases of the Sn-Te-Se system, the equations used were based on the work done by Wang *et al.* [170]. In that paper, it was mentioned that based on the Miedema model, the heat of mixing in a binary alloy system consists of a negative contribution from the electronegativity difference between the two components, and a positive contribution from their difference in electron densities. [172]. To calculate the standard formation enthalpies of the binary alloy systems, Miedema's method calculates microscopic interfacial energy, which can be described as [170]:

$$\Delta H_{\text{AinB}}^{\text{c}} = x_{\text{A}} f_{\text{B}}^{\text{A}} \Delta H_{\text{AinB}}^{\text{int}} \quad (29)$$

where x_A is the mole fraction of metal A. f_B^A is a function which accounts for the degree to which atoms of type A are surrounded by atoms of type B, and can be given by:

$$f_B^A = x_B^S [1 + \gamma(x_A^S x_B^S)^2] \quad (30)$$

and

$$x_A^S = (x_A V_A^{2/3}) / (x_A V_A^{2/3} + x_B V_B^{2/3}) \quad (31)$$

$$x_B^S = (x_B V_B^{2/3}) / (x_A V_A^{2/3} + x_B V_B^{2/3}) \quad (32)$$

The factor γ in equation 30 is an empirical parameter which is used to describe the short-range-order difference of the liquid and the ordered compound, and usually takes the values 8, 5 and 0 for intermetallics, metallic glasses and solid solutions respectively [168].

For an alloy combined by components A and B, the energy of mixing (i.e. the interfacial energy for 1 mole of metal A surrounded by 1 mole of metal B) is [170, 172]:

$$\Delta H_{AinB}^{int} = [2V_A^{2/3}/(\eta_A^{-1/3} + \eta_B^{-1/3})] \times [-P(\Delta\Phi^*)^2 + Q(\Delta\eta_{ws}^{1/3})^2 - R^*] \quad (33)$$

where V_A is the volume of 1 mole of metal A, P, Q and R^* are three empirical constants determined by Miedema. Φ^* and η_{ws} are the components' parameters: $\Delta\eta_{ws}^{1/3}$ is the electron density difference at the boundary of the Wigner–Seitz cell as derived for the pure elements in the metallic state and $\Delta\Phi^*$ describes the electronegativity difference [170].

As mentioned earlier, there were deviations observed in experimental work and the results calculated by Miedema's theory for binary alloy systems. This was due to the fact that in Miedema's theory, the contact between two dissimilar Wigner–Seitz unit cells was assumed to be ideally matched, which was not the case in reality because of the atomic size difference between the constituent metals. Thus, in the paper by Wang *et al.* [170], the calculation method was revised by

adding in an additional pre-factor $S(x)$, which was proposed to take into account the significant effect of the atomic size difference:

Thus, equation 33 becomes:

$$\Delta H_{\text{AinB}}^{\text{int}} = S(x) [2V_A^{2/3}/(\eta_A^{-1/3} + \eta_B^{-1/3})] \times [-P(\Delta\Phi^*)^2 + Q(\Delta\eta_{\text{ws}}^{1/3})^2 - R^*] \quad (34)$$

and

$$S(x) = 1 - [(C \cdot x_A x_B |V_A - V_B|)/(x_A^2 V_A + x_B^2 V_B)] \quad (35)$$

where C is an empirical parameter that describes the effect of differences in atomic size in a semi-quantitative manner. The value of C is taken as 0.5 for the liquid alloy and 2.0 for the ordered compound.

For a ternary alloy, the same approach was used, and the ternary phase could be separated into three separate binary phases. The standard formation enthalpy calculation is given as:

$$\Delta H_{\text{ABC}} = \Delta H_{\text{AinB}}^{\text{c}} + \Delta H_{\text{BinC}}^{\text{c}} + \Delta H_{\text{AinC}}^{\text{c}} \quad (36)$$

where $\Delta H_{\text{AinB}}^{\text{c}}$ is the heat of solution of metal A in metal B, and the value is calculated as per equation 29.

The assumption for the above equation is that the third metal (C) had no effect on the other two metals in the calculation of interfacial energy. However, introducing a third metal could affect the $\Delta\Phi^*$ and $\Delta\eta_{\text{ws}}$ in equation 33. Hence, Wang *et al.* [170] further proposed a two-step calculation method (TSCM) for calculation of ΔH_{ABC} to increase the precision in prediction of thermodynamic properties of ternary alloy systems.

In the TSCM hypothesis, the alloying process is split into two steps: (1) the alloying of metals A and B according to the alloy composition, and (2) the introduction of the third metal, C, into the metals A and B mixture.

As such, the heat of solution for this second step is

$$\Delta H_{CinAB}^c = x_c f_{AB}^C \Delta H_{CinAB}^{int} \quad (37)$$

In calculating ΔH_{CinAB}^c , the properties of the mixture of metals A and B comply with the following reasonable assumptions:

$$x_{AB} = x_A + x_B \quad (38)$$

$$V_{AB} = (x_A V_A + x_B V_B)/x_{AB} \quad (39)$$

$$\Phi_{AB} = (x_A \Phi_A + x_B \Phi_B)/x_{AB} \quad (40)$$

$$\eta_{wsAB} = (x_A \eta_{wsA} + x_B \eta_{wsB})/x_{AB} \quad (41)$$

By considering the entire process of alloying, the formation enthalpy could be calculated by:

$$\Delta H_{ABC} = \Delta H_{AinB}^c + \Delta H_{CinAB}^c \quad (42a)$$

Another two alternative processes that will lead to the same ternary alloy were: by first alloying metals B and C and metals A and C as the first step, respectively, and then introducing metals A and B, respectively. Thus, equation 42a could be considered equivalent to equations 42b and 42c:

$$\Delta H_{ABC} = \Delta H_{BinC}^c + \Delta H_{AinBC}^c \quad (42b)$$

$$\Delta H_{ABC} = \Delta H_{AinC}^c + \Delta H_{BinAC}^c \quad (42c)$$

Hence, taking an average from equations 42a to 42c, will achieve a best approximation as follows:

$$\Delta H_{ABC} = 1/3 [(\Delta H_{AinB}^c + \Delta H_{CinAB}^c) + (\Delta H_{BinC}^c + \Delta H_{AinBC}^c) + (\Delta H_{AinC}^c + \Delta H_{BinAC}^c)] \quad (42d)$$

The above energy calculations were for the chemical part of the interaction, which resulted from the electron factors of the constituents, and was the main contribution to the energy. Although the structural contribution to the energy of an alloy, which accounts for the difference between the valences and the crystal structure of the solute and solvent, should also be considered, it was expected to

have only a minor effect when compared with the elastic energy contribution. Hence, this term was considered in the present calculations. The elastic effect arises from the difference in atomic size of the constituents, not considered in the Miedema model [176].

In addition, one factor for the Hume-Rothery rule for the occurrence of solid solutions in a (pseudo)binary system is the size mismatch energy. The rule says that for appreciable solid solubility to occur, the atomic radii of the two constituents must not differ by more than 15% [177]. For ternary Sn-Te-Se, as SnTe was the major phase, the two constituent elements of concern were Se and Te. The atomic radius of Se was 120 pm, while that of Te was 140 pm. The difference in atomic radii was about 14.3%, and so formation of solid solution was possible; the elastic factor which considers the difference in atomic radii could also be neglected in the formation enthalpy calculations. Due to the lack of data for the required parameters in the equations and also the complexities in calculations, the elastic and structure contributions to the enthalpy of formation were not considered.

7.3.2 Calculation of Enthalpy of Formation for Ternary Sn-Te-Se System

For the calculation of enthalpy of formation, equations 29, 34, 37 and 42d were used. As the material system was a solid solution, the factor γ in equation 30 was taken to be 0. The values of the various parameters in equation 34 are shown in Table 7.4, and the value of P used was 10.7 (for metals with valency of 1 or 2), with the ratio of P/Q kept at 9.4, indicating that $Q = 1.138$ [171]. The value of R^* in equation 34 was taken to be 0 [178], while C in equation 35 was chosen to be 2 for solid solutions.

Table 7.4: Values for the various parameters of the elements Sn, Te and Se [177, 179]

Elements	$V^{2/3}$	$\eta_{ws}^{1/3}$	Φ^*
Sn	6.4	1.24	4.15
Te	5.172	1.40	5.17
Se	6.439	1.31	4.72

Calculations for the energy of mixing were carried out by substituting in the above values (from Table 7.4) for the various parameters into equation 34, and the resultant energy of mixing was tabulated (refer to Appendix AIV.1 for calculated values).

Based on the calculated values of energy of mixing for the binary compounds, the heat of solution for the ternary compounds were then calculated using equation 37, and enthalpy of formation could be calculated using the TSCM model by substituting the calculated values (refer to Appendix AIV.2 for calculated values) into equation 42d.

To calculate the total enthalpy of formation for the different samples, the common tangent method was used, as there were two phases of different compositions co-existing in equilibrium. In the common tangent method, the composite system consists of mass fraction f_1 of one solution X_{B1} (i.e. the matrix) and mass fraction f_2 of another solution X_{B2} (i.e. second phase). The enthalpy of formation of the composite system is given as:

$$\Delta H_{\text{total}} = f_1 \Delta H_{(XB1)} + f_2 \Delta H_{(XB2)} \quad (43)$$

The mass fraction values used in the calculations for the different samples were the normalized values from TOPAS calculations. The calculated values are shown in Table 7.5:

Table 7.5: Values of parameters and calculation of total enthalpy of formation of the composite system

Sample	f_1	f_2	$\Delta H_{(XB1)}$ (kJ/mol)	$\Delta H_{(XB2)}$ (kJ/mol)	ΔH_{total} (kJ/mol)
As melt spun					
$\text{Sn}_{0.5}\text{Te}_{0.42}\text{S}_{0.08}$	1	-	-17.07	-	-17.07

(continued) Table 7.5: Values of parameters and calculation of total enthalpy of formation of the composite system

Sample	f_1	f_2	$\Delta H_{(XB1)}$ (kJ/mol)	$\Delta H_{(XB2)}$ (kJ/mol)	ΔH_{total} (kJ/mol)
As ball milled					
Matrix Sn _{0.5} Te _{0.4385} Se _{0.0615}	0.7362	-	-17.83	-	-16.34
Second phase Sn _{0.5} Te _{0.350} Se _{0.150}	-	0.2638	-	-12.17	
Cold pressed at 6.90 MPa					
Matrix Sn _{0.5} Te _{0.4405} Se _{0.0595}	0.7195	-	-17.64	-	-17.24
Second phase Sn _{0.5} Te _{0.338} Se _{0.162}	-	0.2805	-	-16.23	
Cold pressed at 20.68 MPa					
Matrix Sn _{0.5} Te _{0.453} Se _{0.047}	0.5587	-	-17.16	-	-16.80
Second phase Sn _{0.5} Te _{0.3505} Se _{0.1495}	-	0.4413	-	-16.35	
Cold pressed at 34.47 MPa					
Matrix Sn _{0.5} Te _{0.4515} Se _{0.0485}	0.4535	-	-17.15	-	-16.75
Second phase Sn _{0.5} Te _{0.357} Se _{0.143}	-	0.5465	-	-16.41	

(continued) Table 7.5: Values of parameters and calculation of total enthalpy of formation of the composite system

Sample	f_1	f_2	$\Delta H_{(XB1)}$ (kJ/mol)	$\Delta H_{(XB2)}$ (kJ/mol)	ΔH_{total} (kJ/mol)
After HT XRD (cooled down to room temperature)					
Single phase Sn _{0.5} Te _{0.4465} Se _{0.0535}	1	-	-17.91	-	-17.91
Hot pressed					
Matrix Sn _{0.5} Te _{0.4565} Se _{0.0435}	0.6706	-	-17.17	-	16.30
Second phase Sn _{0.5} Te _{0.287} Se _{0.213}	-	0.3294	-	-14.53	
Cold pressed at 6.90 MPa after TE properties measurements					
Matrix Sn _{0.5} Te _{0.451} Se _{0.049}	0.9430	-	-22.82	-	-22.55
Second phase Sn _{0.5} Te _{0.271} Se _{0.229}	-	0.0570	-	-18.04	
Cold pressed at 20.68 MPa after TE properties measurements					
Matrix Sn _{0.5} Te _{0.4435} Se _{0.0565}	0.9314	-	-21.38	-	-21.19
Second phase Sn _{0.5} Te _{0.313} Se _{0.187}	-	0.0686	-	-18.59	

(continued) Table 7.5: Values of parameters and calculation of total enthalpy of formation of the composite system

Sample	f_1	f_2	$\Delta H_{(XB1)}$ (kJ/mol)	$\Delta H_{(XB2)}$ (kJ/mol)	ΔH_{total} (kJ/mol)
Cold pressed at 34.47 MPa after TE properties measurements					
Matrix $\text{Sn}_{0.5}\text{Te}_{0.4645}$ $\text{Se}_{0.0355}$	0.8700	-	-23.14	-	-22.58
Second phase $\text{Sn}_{0.5}\text{Te}_{0.331}$ $\text{Se}_{0.169}$	-	0.1300	-	-18.87	

The enthalpy of formation of SnTe and SnSe is approximately -61.2 kJ/mol [174] and -47.4 kJ/mol [175] respectively. Comparing these two values with ΔH_{total} , which was the total energy of composite system (Table 7.5), the qualitatively calculated values indicate that the individual phases had a much higher thermodynamic stability than the ternary phase. However, in the alloy composition where both SnTe and SnSe were present, formation of two types of solid solutions was favoured based on the phase diagram (Section 2.6.2.3).

The proposed overview on such (meta)stability observed in the material system at different stages of processing (based on the total enthalpy of formation data in Table 7.5) is presented in Figure 7.6.

Figure 7.6: Proposed (meta)stability of material system at different stages of processing after melt spinning and ball milling (a) cold press then thermal cycling, (b) thermal cycling through HT XRD and (c) hot press.

From earlier discussions, the compositions of the matrix and second phase differed depending on the processing methods: (a) melt spinning, (b) ball milling, (c) application of pressure and (d) hot press. From the values of enthalpy of formation, the ball milled sample appeared to have a slightly lower stability (~4.3%) than the as melt spun sample. This may be because it was in a metastable state, such that additional processing, e.g. cold pressing, led to changes in mass fraction of the phases. In the ball milled sample, although it was lower in stability, the second phase appeared due to the external energy that was supplied to it through ball milling, such that the energy barrier was overcome. The cold pressed sample at 6.90 MPa exhibited more negative values of total enthalpy compared to the as melt spun and as ball milled sample, confirming that it was indeed more stable.

Nevertheless, comparing the enthalpy of formation values across the cold pressed samples, the stability seemed to decrease with cold pressing at higher pressures, although the difference in values were quite small (~2.9%). It was proposed that cold compaction also provided the energy to cross the activation energy barrier such that more second phase was formed, although the phases were still metastable. This hypothesis was supported by the fact that after the TE properties measurements, much of the second phase dissolved into the matrix. The corresponding enthalpy of formation for these remaining phases were much higher (about 26% to 34.9%) than after cold pressing, indicating that this final state (of mass fraction and composition of the phases) was more stable than before. There were also similar observations from the sample at 300 K after cooling down from high temperature XRD measurements. It was seen that at this state, the material was more stable than the ball milled samples, such that changes occurred from an initial two phases to a final single phase.

From the above experimental observations, it was seen that while there was spontaneous formation of second phase from processing, the second phase could be metastable. Thus, following high temperature XRD measurements, or after the TE properties measurements, the material system moved towards equilibrium, which was the single phase in the former case, and a mixture of mainly single phase with a small proportion of second phase in the latter case.

Based on this understanding and comparing it to the enthalpy of formation of the hot pressed sample the following conclusion was made: Hot pressed 25SnSe was the most stable experimentally, but actually had theoretical stability values close to that of ball milling and cold pressing. Hence it was believed that due to hot pressing, when heat and pressure were supplied concurrently, the phases in terms of the composition and mass fractions of that specific pressure condition was achieved. In addition, with the heat present, any defects and strain in the material that may have contributed to its metastability or instability was relieved. Thus there was an observed difference in stability between the hot pressed and other samples.

It was concluded that the single phase material obtained after melt spinning was metastable, and changes occurred in the system with processing, e.g. ball milling and cold pressing. These changes were reflected through the differences in mass fraction of the constituent phases (i.e. matrix and second phase) and their compositions. Using the Miedema model to carry out calculations of the stability of the phases, it was seen that these phase transformations were thermodynamically induced, due to the free energy of the system at different stages. With the application of heat only or application of pressure and then subsequently application of heat, the material attained different metastable stages until it reached equilibrium. It was only in the presence of an applied heat and pressure (i.e. hot press), that a stable multiphase material was formed.

Although differential scanning calorimetry (DSC) can provide the formation energy experimentally in the absence of applied pressure, the samples that were being studied in this work involved specific processing conditions (like cold pressing at different pressures). The small sample size required by DSC meant that the cold pressed sample needs to be cut into a smaller size, which might cause artefacts to be introduced to it. In addition, based on the measurements in the earlier chapters, the phases were shown to be sensitive to temperature. Thus, it was possible that during DSC measurements, there might be dynamic changes occurring with temperature, such that the measured data would not be representative of the final phase that was present. As such, a theoretical calculation where the values could be obtained qualitatively and compared against one another was used here instead.

CHAPTER 8 - Conclusion and Recommendations for Future Work

8.1 Comparison between Ex-situ and In-situ Nanocomposites

In Chapters 4 to 7, the effect of the second phase (Cu_7Te_4 and orthorhombic $\text{SnTe}_x\text{Se}_{1-x}$) on TE properties in their respective material system was elucidated and discussed. The similarities and differences of both the ex-situ and in-situ nanocomposites are summarized as follows:

Table 8.1: Comparison of similarities and differences of ex-situ $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ and in-situ SnTe-SnSe nanocomposites

Material System	$\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	SnTe-SnSe
Similarities	Of the prepared compositions of samples tested under the operation temperature range, a particular composition gave improved TE properties over the single parent phases.	
	Interface between the two different phases were generally observed to be coherent.	
Differences	Matrix was a semiconductor with mixed conduction from 400 K.	Matrix was semi-metallic with no mixed conduction observed over the measured temperature range.

(continued) Table 8.1: Comparison of similarities and differences of ex-situ $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ and in-situ SnTe-SnSe nanocomposites

Material System	$\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	SnTe-SnSe
Differences	Nanorods of Cu_7Te_4 were agglomerated, such that the phase was observable at micron scale; Cu_7Te_4 observed at nanoscale was in the range of $\gg 10$ nm.	The orthorhombic second phase was observable at micron scale, and there were also nanoprecipitates in the size of tens of nanometers embedded in the matrix.
	Increase in hole concentration was attributed to the possible occurrence of antisite defects and the mitigation of donor-like effects. Partly similar crystal structures of both phases could also have led to unique electrical conducting behavior: alignment of Fermi levels in Cu_7Te_4 phase with BST matrix.	Presence of orthorhombic second phase led to reduced resistivity and improved Seebeck coefficient at higher temperatures.
	Apart from 5wtNC, other samples showed a trend of increase in κ_{lattice} with temperature; κ_{lattice} of 5wtNC was stable with temperature.	All samples showed a trend of decrease in κ_{lattice} with temperature.

(continued) Table 8.1: Comparison of similarities and differences of ex-situ $\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ and in-situ SnTe-SnSe nanocomposites

Material System	$\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	SnTe-SnSe
Differences	Agglomeration of nanostructured phase and cracking in sample was observed.	Problem of agglomeration and cracking observed in ex-situ nanocomposites was mitigated.

The conclusions are:

- Depending on the type of matrix, the presence of second phase can effectively mitigate any negative effects in the matrix (e.g. mixed conduction or low Seebeck coefficient), leading to enhanced the electrical properties.
- Usually the constituent phases chosen would complement each other, e.g., the matrix may have average or good Seebeck coefficient but low electrical conductivity, while the second phase possess a higher electrical conductivity to tune the overall TE properties.
- There is an optimum mass fraction of nano-sized second phase which is useful for TE properties enhancement, and the presence of the second phase at the micron and nano scale will be useful in scattering phonons.
- Addition of the second phase improves ZT (either partially or completely) over the measured operating temperature range as compared to the single phase, improving overall TE performance.
- The hypothesis in Section 2.7 that crystal structural changes can allow phase transformations, and in turn affect the TE properties, is supported in the work performed on SnTe-SnSe .

8.2 Conclusion

The results obtained in this work confirmed that the use of chemically synthesized surfactant-free Cu_7Te_4 nanostructures in the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ matrix is a suitable approach for ex-situ nanocomposites. The approach of melt spinning for the fabrication of SnTe-SnSe in-situ multiphase nanocomposites with improved TE properties is another useful technique. It is concluded that multiphase nanocomposites are beneficial for enhancement in TE properties, if the following conditions are met: (1) the constituent phases must be compatible and (2) nanostructured phases should ideally be present. These will allow both improvement in electrical properties, and reduction in thermal conductivity, such that synergistic improvements can be obtained. The results are summarized as follows:

- In the first part of Chapter 4, for the work on ex-situ nanocomposites ($\text{Cu}_7\text{Te}_4\text{-Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$), the best TE properties were observed in the 5wtNC sample. This was attributed to the fact that the presence of the nanostructured Cu_7Te_4 phase led to:
 - Reduced electrical resistivity by nearly one order of magnitude compared to the matrix phase.
 - Additional carriers (holes) in the material system such that the onset of mixed conduction behaviour that was dominant in the matrix was shifted back to higher temperatures.
 - Decreased thermal conductivity at higher temperatures.

In addition, the interface between the matrix and second phase was well matched, which was an important factor for good electrical properties.

- In Chapter 5, the best TE performance was obtained for 25SnSe, due to this alloy composition having the optimum mass fraction and compositions of the constituent phases to maximize TE properties. A maximum power factor of $1.31 \times 10^{-3} \text{ W/m.K}^2$ was obtained at 494 K, which was 1.5 times that of SnTe. The peak ZT of 25SnSe was 0.19 at 548 K, which was 3 times higher than the peak ZT of SnTe.

- In Chapter 6, the prediction of the orientation relationship between the matrix and second phase was validated by TEM. The presence of nanostructured second phase after ball milling and hot pressing was also observed.
- The metastability of the second phase under low applied pressure was observed, with the conclusion that the presence of second phase decreased electrical resistivity. The improvement in Seebeck coefficient at higher temperatures was also sensitive to the mass fraction and composition of the second phase. Although the approach of cold pressing and hot pressing the samples could both lead to equally high Seebeck coefficient values, hot pressing was required to stabilize the second phases.
- In Chapter 7, through high temperature XRD, the second phase was shown to dissolve back into the matrix in the presence of heat and absence of pressure. This was not reversible upon cooling down back to room temperature.
- Two control samples, 25SnSe_SS and 25SnSe_phymix, were prepared and characterized to confirm the superiority of the melt spinning technique as an approach to improve TE properties. For 25SnSe_SS, it was seen that for the same nominal composition, the obtained phases differ in mass fraction and composition depending on the synthesis methods. For 25SnSe_phymix, the phases present were purely SnTe and SnSe only. The effect of the differences in compositions and mass fractions of phases were reflected in the TE properties. Thus, the use of the melt spinning technique was superior in the sense that the proportion and composition of the matrix and second phase formed after hot pressing led to synergistic improvements.
- In the final section of Chapter 7, the Miedema model was used to calculate the enthalpy of formation. This revealed the stability of the samples for various processing techniques, i.e. as melt spun, after ball milling, after cold compaction at various pressures, cold compacted samples after TE properties measurements, after high temperature XRD measurements and

after hot pressing. The results of the calculations supported the observation of the metastable nature of the phases formed after processing. Generally, the material moved towards equilibrium with accompanying changes in mass fraction of the phases and composition. Although the enthalpy of formation of the hot pressed sample was close to that of after ball milling, as it was subjected to both pressure and temperature concurrently, the additional heat energy may have reduced the defects and strains in the samples, such that it became thermodynamically stable.

From the above summary of conclusions from the various chapters, the effectiveness of using the multiphase concept in our work, and the processing-property relationship for 25SnSe has been established.

In addition, the objectives of the thesis work stated in Section 1.2 have also been answered:

- a. The presence of Cu_7Te_4 nanorods in $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ led to enhancement in TE properties. This was attributed to the generally coherent interface between the two phases, and also similarity in band structure such that electronic movements were facilitated.
- b. The composition 25SnSe of the SnTe-SnSe system yielded an appropriate mass fraction and composition of second phase which led to enhanced TE properties.
- c. Enhancement of Seebeck coefficient in 25SnSe was obtained due to the nanostructured second phase in the matrix. This was linked to the composition of the second phase.
- d. Reduction of thermal conductivity by the increased phonon scattering from addition of SnSe to SnTe and due to the presence of interfaces and second phase nanostructures were achieved.

Comparing the types of nanocomposites, it is acknowledged that there are limitations in the use of ex-situ nanocomposites, and the approach of in-situ nanocomposites is more attractive. This is because nanoscale precipitates will most

likely be present in the matrix, and hence the issue of physical agglomeration of the nanostructures is avoided or reduced.

Bux *et al.* [19] highlighted the challenges in fabrication of nanocomposites. There are also four considerations to be made in the developing of synthesis techniques to obtain bulk materials with nanoscale features for practical applications: (1) the chosen synthesis method has to be scalable and cost effective (since commercial applications usually require materials in kilograms-scale), and also provide good control over particle size, distribution and morphology; (2) the final material obtained should be of sufficiently high density ($\geq 95\%$ of theoretical density, for device integration and operational purposes); (3) the performance of the nanostructured (bulk) material should be significantly enhanced over the bulk or available state of the art materials, and lastly, (4) the nanostructured material should exhibit thermal stability at operational temperatures.

The significance of the results obtained is that phase transformation that occurs naturally during processing in the material system is used to our advantage – the use of the melt spinning approach is attractive and allows control of parameters to tune the composition of the second phase in the material. Non-equilibrium phases can be obtained, which leads to improved TE properties compared to the parent single phase.

As a number of commercial TE materials are based on tellurides, the work performed here shows that reducing the use of scarce Te and replacing some of it with more widely available Se to obtain better performing TE materials is viable, which can lead to decreased material costs. The use of industrially available technique of melt spinning, ball milling and hot pressing means that commercialization can be more easily integrated. However, the shortfall of the work performed here is that the ZT is not yet comparable to state-of-the-art materials. Due to the limited time available for the thesis work, recommendations on the future work to be done are discussed in Section 8.4, to further understand the system and to achieve breakthroughs in performance of the material.

8.3 Novelty of Work

The novelty of this work is as follows:

- Synthesis of surfactant-free nanostructured Cu_7Te_4 by a facile two-step wet chemical method using Te nanorods as a template. The scalable synthesis of surfactant-free copper telluride nanorods can be done under facile conditions and within a short period of time.
- Addition of these Cu_7Te_4 nanorods to $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ leads to enhanced TE properties.
- The SnTe-SnSe system is reported to be a potential TE material system, but it has not been widely studied yet.
- The mass fraction of the orthorhombic second phase $\text{SnTe}_x\text{Se}_{1-x}$ can be altered by small applied pressure, and the effect of this second phase on the TE properties is reported for the first time. This observed metastability with processing offers an avenue to systematically tune the microstructure.

8.4 Recommendations for Future Work

8.4.1 Future Work I

In Chapter 4, for the work performed for ex-situ nanocomposites (Cu_7Te_4 - $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$), as the bulk matrix and nanostructures were physically mixed, issues like agglomeration of nanostructures and cracking of samples were faced. Hence, even though enhancement was observed, the effect of energy filtering was not observed in this system. Thus, the first future work is to develop suitable chemical synthesis methods to obtain even smaller nano-sized of copper telluride, and also possibly surfactant-free, for addition into $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$. This further exploration will allow us to gain a better understanding of the theory of the metallic nanoinclusions-semiconductor matrix approach.

Subsequently, further characterizations in terms of the effect of Cu atoms from the Cu_7Te_4 phase have to be done: The diffusion, occupancy or segregation of Cu

atoms (if any) in the BST matrix to elucidate its effect on the carrier concentration of the material system. More studies on the thermodynamic stability of the Cu_7Te_4 in BST have to be done so that the material system can be optimized to work into higher temperatures.

8.4.2 Future Work II

In Chapter 5, for the work on in-situ nanocomposites, from additional TE properties measurements that was carried out to higher temperature, some oxidation was observed. Hence future work can focus on what can be done to increase thermal stability of the material at higher temperatures. This is because similar material systems like PbTe-PbSe show that they can be used for intermediate temperature range. Some approaches that can be taken include improving the vacuum conditions at the various processing steps, and monitoring the materials closely to determine under what conditions the oxidation sets in. This will also help in achieving the best properties of the samples.

For Chapter 6, further exploration on the effect of pressure and temperature on the material system can be done through varying of hot pressing conditions, to see if any differences in TE properties are exhibited. Provided that the densities of the obtained samples are high enough, the thermal conductivity and TE properties can be measured to attain the ZT to gain deeper insight on the relationship between processing and performance.

In the optimized samples, perhaps more work can be done to further elucidate the atomic level changes in the material and its effect on TE properties, in particular (lattice) thermal conductivity. There is a report on the study of a bulk TE system consisting of solid solution and nanoscale precipitates, and how the role of nanoscale precipitates and point defects in reducing lattice thermal conductivity can be differentiated [180].

8.4.3 Future Work III

The approach of melt spinning is a top-down approach, and to fully explore the potential of the multiphase material in terms of different morphologies at the nanoscale, a bottom-up approach through chemical synthesis can be explored.

The advantages of using chemical synthesis has been mentioned in Section 3.1.1, and the ability to scale up the synthesis also allows the production large quantities of the desired compound, which is attractive for formation of bulk TE materials. [19]

Solution phase synthesis is a widely used method for obtaining materials in many other different applications like solar cells, supercapacitors and lithium-ion batteries. In particular, for TE materials, various authors have reported on the success of fabrication of the required compounds, with enhancements in TE properties obtained in certain works [63, 78, 181].

Thus, it is proposed that a bottom up approach *via* solution phase synthesis method be used to synthesize nanostructures of SnTe, SnSe and SnTe-SnSe or $\text{SnTe}_x\text{Se}_{1-x}$. By tuning the composition, optimum TE properties can be obtained, and the trend of composition versus performance can be used to compare with the bulk material. This will enhance the understanding of the effect of the compositions of the various phases on TE performance. In addition, as the nanostructures may have different morphologies and possibly also be formed at different length scales, chemical synthesis of nanoparticles will be beneficial to TE properties as it allows scattering of a larger spectrum of phonons, while allowing electron movement.

The other advantages of this method are that the chemical synthesis of oxide-free SnTe and/or SnSe nanomaterials with the reported TE properties has not been performed. In addition, if good TE properties are obtained, there is a potential for the materials to be used in ink-jet printing, allowing for fabricating of devices, and in turn commercialization and wide spread utilization in TE devices.

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Appendix I

AI.1 TOPAS calculations

Composition of the as melt spun samples was calculated using Vegard's Law: For the cubic phase, the lattice parameter is used; for the orthorhombic phase, the cell volume is used.

In the cubic phase calculation, lattice parameter values of the two end members, cubic SnTe (6.304 Å) and the cubic phase of SnSe (5.99 Å) is used. Figure A1 shows the graph and the corresponding linear equation. By substituting in the lattice parameter obtained in TOPAS as the y value, the composition is obtained as x, where x is the composition in $\text{SnTe}_x\text{Se}_{1-x}$.

Cubic Phase	$\text{SnTe}_x\text{Se}_{1-x}$
x =	Lattice parameter (Å)
0	5.99
1	6.304

Figure A1: Graph of lattice parameter versus composition

For the orthorhombic phase, as lattice parameters a , b and c are different, comparison by these values are not so straightforward. Hence, its cell volume is used for comparison instead. Here, the cell volume of cubic SnTe ($250.52 \text{ \AA}^3$) and orthorhombic SnSe ($216.21 \text{ \AA}^3$) is used.

Orthorhombic Phase	$\text{SnTe}_x\text{Se}_{1-x}$
$x =$	Cell volume ($\text{\AA}^3$)
0	216.21
1	250.52

Figure A2: Graph of cell volume versus composition

AI.2 Lever Rule calculations at 500 K

The solubility limit in the phase diagram is 0.08 for SnSe in SnTe and 0.1 for SnSe in SnTe. Lever rule calculations give the following mass fractions for SnTe (W_{SnTe}) and SnSe (W_{SnSe}):

25SnSe

$$W_{\text{SnTe}} = (0.75 - 0.08 / 0.9 - 0.08) = \underline{0.8171}$$

$$W_{\text{SnSe}} = (0.9 - 0.75 / 0.9 - 0.08) = \underline{0.1829}$$

40SnSe

$$W_{\text{SnTe}} = (0.6 - 0.08 / 0.9 - 0.08) = \underline{0.6341}$$

$$W_{\text{SnSe}} = (0.9 - 0.6 / 0.9 - 0.08) = \underline{0.3659}$$

AI.3 Graphs for TOPAS refinement of various hot pressed samples

(a) 10SnSe

(b) 25SnSe

(c) 40SnSe

Figure A3: TOPAS refined graphs of hot pressed (a) 10SnSe, (b) 25SnSe and (c) 40SnSe.

AI.4 Thermoelectric properties for laser flash measurements up to 673 K (performed at Zhejiang University)

Figure A4: Temperature dependence of thermoelectric properties: (a) Thermal conductivity, (b) Seebeck coefficient, (c) Electrical resistivity, (d) Power factor and (e) ZT.

Appendix II

AII.1 Graphs for TOPAS refinement and XRD patterns after cold press

Figure A5: TOPAS refined graphs of 25SnSe (a) as ball-milled and samples cold pressed at (b) 6.90 MPa, (c) 20.68 MPa, (d) 34.47 MPa, (e) reproduction of Figure 5.13 with hkl planes of Sn peaks which exhibit increased intensity with applied pressure indicated in red fonts and (f) temperature dependence of thermal conductivity measurements.

(d) 25SnSe cold pressed at 34.47 MPa

(e) Reproduction of Figure 5.13, with hkl planes of Sn peaks which exhibit increased intensity with applied pressure indicated in red fonts

(continued) Figure A5: TOPAS refined graphs of 25SnSe (a) as ball-milled and samples cold pressed at (b) 6.90 MPa, (c) 20.68 MPa, (d) 34.47 MPa, (e) reproduction of Figure 5.13 with hkl planes of Sn peaks which exhibit increased intensity with applied pressure indicated in red fonts and (f) temperature dependence of thermal conductivity measurements.

(f) Temperature dependence of thermal conductivity measurements

(continued) Figure A5: TOPAS refined graphs of 25SnSe (a) as ball-milled and samples cold pressed at (b) 6.90 MPa, (c) 20.68 MPa, (d) 34.47 MPa, (e) reproduction of Figure 5.13 with hkl planes of Sn peaks which exhibit increased intensity with applied pressure indicated in red fonts and (f) temperature dependence of thermal conductivity measurements.

AIL.2 Graphs for TOPAS refinement of various samples after TE properties measurements

(a) 25SnSe cold pressed at 6.90 MPa

(b) 25SnSe cold pressed at 20.68 MPa

(c) 25SnSe cold pressed at 34.47 MPa

Figure A6: TOPAS refined graphs after TE measurements of 25SnSe cold pressed at (a) 6.90 MPa, (b) 20.68 MPa and (c) 34.47 MPa.

Appendix III

AIII.1 Vegard's law calculations on phase compositions in temperature dependent XRD for ball milled 25SnSe

Composition of the samples at various temperatures during the temperature dependent XRD are calculated using Vegard's Law, similar to the procedures in AI.1. For the cubic phase, taking into account the variation of the lattice parameters, another reference data file of SnTe with a larger lattice parameter is used.

In the cubic phase calculation, the lattice parameter values of the two end members, cubic SnTe (6.324 Å) and the cubic phase of SnSe (5.99 Å) is used. Figure A7 shows the graph and the corresponding linear equation. By substituting in the lattice parameter obtained in TOPAS as the y value, the composition is obtained as x, where x is the composition in $\text{SnTe}_x\text{Se}_{1-x}$.

Cubic Phase	$\text{SnTe}_x\text{Se}_{1-x}$
x =	Lattice parameter (Å)
0	5.99
1	6.324

Figure A7: Graph of lattice parameter versus composition

For the orthorhombic phase, as lattice parameters a , b and c are different, comparison by these values are not so straightforward. Hence, cell volume is used for comparison instead. Here, the cell volume of cubic SnTe ($252.92 \text{ \AA}^3$) and orthorhombic SnSe ($216.21 \text{ \AA}^3$) is used.

Orthorhombic Phase	$\text{SnTe}_x\text{Se}_{1-x}$
$x =$	Cell volume ($\text{\AA}^3$)
0	216.21
1	252.92

Figure A8: Graph of cell volume versus composition

Temperature	Lattice Parameter ($\text{\AA}$)	Cell Volume ($\text{\AA}^3$)
300 K	6.261	240.999
423 K	6.321	227.713
573 K	6.326	225.334
673 K	6.333	-
300 K cooled down to room temperature	6.288	-

Graphs for TOPAS refinement of ball milled 25SnSe after temperature dependent XRD

(a) Temperature dependent XRD at 300 K

(b) Temperature dependent XRD at 423 K

(c) Temperature dependent XRD at 573 K

Figure A9: TOPAS refined graphs of HT XRD of 25SnSe (a) 300 K, (b) 423 K, (c) 573 K, (d) 673 K and (e) 300 K (cooled down to room temperature).

(d) Temperature dependent XRD at 673 K

(e) Temperature dependent XRD at 300 K (cooled down to room temperature)

(continued) Figure A9: TOPAS refined graphs of HT XRD of 25SnSe (a) 300 K, (b) 423 K, (c) 573 K, (d) 673 K and (e) 300 K (cooled down to room temperature).

AIII.2 Calculations of overall phase composition in 25SnSe and 25SnSe SS

25SnSe	Mass fraction (wt %)	Composition	Proportion of phases (Obtained by multiplying values in column 1 and 2)	Total composition (including initially calculated Sn and Se amount)
Matrix	60.95	$\text{SnTe}_{0.913}\text{Se}_{0.087}$	$\text{Sn}_{0.6095}\text{Te}_{0.5565}\text{Se}_{0.0530}$	$\text{Sn}_{0.9738}\text{Te}_{0.7284}\text{Se}_{0.2067} \approx \text{SnTe}_{0.7500}\text{Se}_{0.2122}$
Second phase	29.94	$\text{SnTe}_{0.574}\text{Se}_{0.426}$	$\text{Sn}_{0.2994}\text{Te}_{0.1719}\text{Se}_{0.1275}$	
Sn / SnO ₂ / Se	2.27 / 4.22 / 2.62	-	-	
25SnSe_SS after synthesis	Mass fraction (wt %)	Composition	Proportion of phases (Obtained by multiplying values in column 1 and 2)	Total composition (including initially calculated Sn and Se amount)
Matrix	58.34	$\text{SnTe}_{0.90}\text{Se}_{0.10}$	$\text{Sn}_{0.5834}\text{Te}_{0.5251}\text{Se}_{0.0583}$	$\text{Sn}_{0.9805}\text{Te}_{0.8254}\text{Se}_{0.1451} \approx \text{SnTe}_{0.8518}\text{Se}_{0.1478}$
Second phase	36.76	$\text{SnTe}_{0.817}\text{Se}_{0.183}$	$\text{Sn}_{0.3676}\text{Te}_{0.3003}\text{Se}_{0.0673}$	
Sn / Se (wt %)	2.95 / 1.95	-	-	

AIII.3 Graphs for TOPAS refinement of 25SnSe_SS

(a) 25SnSe_SS after synthesis

(b) 25SnSe_SS after TE properties measurements

Figure A10: TOPAS refined graphs of 25SnSe_SS (a) after synthesis 300 K and (b) after TE properties measurements.

Appendix IV

AIV.1

Calculated values for the various parameters of the compounds SnTe, Se-Te, Te-Se and SnSe to be used in intermediate calculations

Compound/ calculated values	x_A^S	x_B^S	S(x) (C=2 used)	f_B^A ($\gamma = 0$ used)
SnTe	0.55	0.45	0.68	0.45
Se _{0.08} Te _{0.42}	0.19	0.81	0.86	0.81
Se _{0.0615} Te _{0.4385}	0.15	0.85	0.89	0.85
Te _{0.350} Se _{0.150}	0.65	0.35	0.73	0.35
Se _{0.0595} Te _{0.4405}	0.14	0.86	0.90	0.86
Te _{0.338} Se _{0.162}	0.63	0.37	0.72	0.37
Se _{0.047} Te _{0.453}	0.11	0.89	0.92	0.89
Te _{0.3505} Se _{0.1495}	0.65	0.35	0.74	0.35
Se _{0.0485} Te _{0.4515}	0.12	0.88	0.92	0.88
Te _{0.357} Se _{0.143}	0.67	0.33	0.75	0.33
Se _{0.0535} Te _{0.4465}	0.13	0.87	0.91	0.87
Se _{0.0435} Te _{0.4565}	0.11	0.89	0.93	0.89
Te _{0.287} Se _{0.213}	0.52	0.48	0.67	0.48
SnSe	0.50	0.50	0.99	0.50

Calculated values for the energy of mixing based on the compositions of the matrix and second phase at different stages of processing determined by TOPAS refinements

Compound (AB)/ calculated values	$\Delta H_{A \text{ in } B}^{\text{int}}$
SnTe	$\Delta H_{\text{Sn in Te}}^{\text{int}} = -63.83$
Se _{0.08} Te _{0.42}	$\Delta H_{\text{Se in Te}}^{\text{int}} = -16.15$
Se _{0.0615} Te _{0.4385}	$\Delta H_{\text{Se in Te}}^{\text{int}} = -16.81$
Te _{0.350} Se _{0.150}	$\Delta H_{\text{Te in Se}}^{\text{int}} = -11.09$
Se _{0.0595} Te _{0.4405}	$\Delta H_{\text{Se in Te}}^{\text{int}} = -16.88$
Te _{0.338} Se _{0.162}	$\Delta H_{\text{Te in Se}}^{\text{int}} = -10.83$
Se _{0.047} Te _{0.453}	$\Delta H_{\text{Se in Te}}^{\text{int}} = -17.31$
Te _{0.3505} Se _{0.1495}	$\Delta H_{\text{Te in Se}}^{\text{int}} = -11.10$
Se _{0.0485} Te _{0.4515}	$\Delta H_{\text{Se in Te}}^{\text{int}} = -17.26$
Te _{0.357} Se _{0.143}	$\Delta H_{\text{Te in Se}}^{\text{int}} = -11.25$
Se _{0.0535} Te _{0.4465}	$\Delta H_{\text{Se in Te}}^{\text{int}} = -17.08$
Se _{0.0435} Te _{0.4565}	$\Delta H_{\text{Se in Te}}^{\text{int}} = -17.43$
Te _{0.287} Se _{0.213}	$\Delta H_{\text{Te in Se}}^{\text{int}} = -10.16$
SnSe	$\Delta H_{\text{Sn in Se}}^{\text{int}} = -28.04$
Se _{0.049} Te _{0.451}	$\Delta H_{\text{Se in Te}}^{\text{int}} = -18.80$
Te _{0.271} Se _{0.229}	$\Delta H_{\text{Te in Se}}^{\text{int}} = -10.12$

(continued) Calculated values for the energy of mixing based on the compositions of the matrix and second phase at different stages of processing determined by TOPAS refinements

Compound (AB)/ calculated values	$\Delta H^{\text{int}}_{\text{A in B}}$
$\text{Se}_{0.0565}\text{Te}_{0.4435}$	$\Delta H^{\text{int}}_{\text{Se in Te}} = -18.52$
$\text{Te}_{0.313}\text{Se}_{0.187}$	$\Delta H^{\text{int}}_{\text{Te in Se}} = -10.41$
$\text{Se}_{0.0355}\text{Te}_{0.4645}$	$\Delta H^{\text{int}}_{\text{Se in Te}} = -19.30$
$\text{Te}_{0.331}\text{Se}_{0.169}$	$\Delta H^{\text{int}}_{\text{Te in Se}} = -10.70$

*Note: Calculations are as follows: Sn in Te and Se in SnTe for cubic phase, and Sn in Se, and Te in SnSe for orthorhombic phase.

AIV.2

Calculated values of the various parameters to be used for heat of solution calculation for ternary phases (equation 37)

Sample/ X in YZ	X_{AB}	$V_{AB} / V_{AB}^{2/3}$	Φ_{AB}	$\eta_{WSYZ} / \eta_{WSYZ}^{1/3}$	S(x)	$\Delta H_{XinY}^{int} / Z$	$f_{AB}^A = \chi_{AB}^S$
As melt spun single phase/matrix $Sn_{0.5}Te_{0.42}Se_{0.08}$							
C in AB	0.92	14.17 / 5.89	4.62	2.29 / 1.32	0.97	-0.96	0.91
A in BC	0.5	12.49 / 5.39	5.10	2.66 / 1.39	0.74	-59.8	0.46
B in AC	0.58	16.21 / 6.41	4.23	1.95 / 1.25	0.71	-46.00	0.63
As ball milled matrix $Sn_{0.5}Te_{0.4385}Se_{0.0615}$							
C in AB	0.9385	14.12 / 5.84	4.63	2.30 / 1.32	1.00	-0.78	0.93
A in BC	0.5	12.33 / 5.34	5.11	2.68 / 1.39	0.73	-60.71	0.45
B in AC	0.5615	16.21 / 6.40	4.21	1.94 / 1.25	0.81	-54.14	0.61
As ball milled second phase $Sn_{0.5}Te_{0.350}Se_{0.150}$							
C in AB	0.85	14.37 / 5.91	4.57	2.25 / 1.31	0.96	-1.95	0.84
A in BC	0.5	13.14 / 5.57	5.04	2.60 / 1.37	1.00	-1.43	0.47
B in AC	0.65	16.23 / 6.41	4.28	1.99 / 1.26	0.76	-43.58	0.70

(continued) Calculated values of the various parameters to be used for heat of solution calculation for ternary phases (equation 37)

Sample/ X in YZ	X_{AB}	V_{AB} / $V_{AB}^{2/3}$	Φ_{AB}	η_{WSYZ} / $\eta_{WSYZ}^{1/3}$	S(x)	ΔH_{XinY}^{int} Z	$f_{AB}^A =$ χ_{AB}^S
Cold pressed at 6.90 MPa matrix $Sn_{0.5}Te_{0.4405}Se_{0.0595}$							
C in AB	0.9405	14.12 / 5.84	4.63	2.30 / 1.32	0.98	-0.74	0.93
A in BC	0.5	12.31 / 5.33	5.12	2.69 / 1.39	0.73	-60.83	0.45
B in AC	0.5595	16.21 / 6.40	4.21	1.94 / 1.25	0.79	-52.71	0.61
Cold pressed at 6.90 MPa second phase $Sn_{0.5}Te_{0.338}Se_{0.162}$							
C in AB	0.838	15.84 / 6.31	4.56	2.24 / 1.31	0.99	-2.24	0.84
A in BC	0.5	13.25 / 5.60	5.02	2.58/ 1.37	0.80	-54.40	0.47
B in AC	0.662	16.23 / 6.41	4.29	1.99 / 1.26	0.76	-43.30	0.71
Cold pressed at 20.68 MPa matrix $Sn_{0.5}Te_{0.453}Se_{0.047}$							
C in AB	0.953	13.42 / 5.65	4.63	2.30 / 1.32	0.98	-0.64	0.95
A in BC	0.5	12.19 / 5.30	5.13	2.70 / 1.39	0.72	-61.51	0.45
B in AC	0.547	16.20 / 6.40	4.20	1.94 / 1.25	0.70	-47.83	0.60

(continued) Calculated values of the various parameters to be used for heat of solution calculation for ternary phases (equation 37)

Sample/ X in YZ	X_{AB}	V_{AB} / $V_{AB}^{2/3}$	Φ_{AB}	η_{WSYZ} / $\eta_{WSYZ}^{1/3}$	S(x)	ΔH_{XinY}^{int} Z	$f_{AB}^A =$ χ_{AB}^S
Cold pressed at 20.68 MPa second phase $Sn_{0.5}Te_{0.3505}Se_{0.1495}$							
C in AB	0.8505	14.37 / 5.91	4.57	2.25 / 1.31	0.95	-1.93	0.84
A in BC	0.5	13.13 / 5.57	5.04	2.60 / 1.37	0.79	-55.25	0.47
B in AC	0.6495	16.23 / 6.41	4.28	1.99 / 1.26	0.75	-43.59	0.70
Cold pressed at 34.47 MPa matrix $Sn_{0.5}Te_{0.4515}Se_{0.0485}$							
C in AB	0.9515	14.09 / 5.83	4.63	2.30 / 1.32	0.98	-0.66	0.95
A in BC	0.5	12.21 / 5.30	5.13	2.70 / 1.39	0.72	-61.43	0.45
B in AC	0.5485	16.20 / 6.40	4.20	1.93 / 1.25	0.70	-47.70	0.60
Cold pressed at 34.47 MPa second phase $Sn_{0.5}Te_{0.357}Se_{0.143}$							
C in AB	0.857	14.35 / 5.90	4.57	2.26 / 1.31	0.96	-1.82	0.85
A in BC	0.5	13.07 / 5.55	5.04	2.60 / 1.38	0.79	-55.69	0.46
B in AC	0.643	16.22 / 6.41	4.28	1.98 / 1.26	0.75	-43.76	0.69

(continued) Calculated values of the various parameters to be used for heat of solution calculation for ternary phases (equation 37)

Sample/ X in YZ	X_{AB}	$V_{AB} / V_{AB}^{2/3}$	Φ_{AB}	$\eta_{WSYZ} / \eta_{WSYZ}^{1/3}$	S(x)	$\Delta H_{XinY}^{int} / Z$	$f_{AB}^A = \chi_{AB}^S$
After HT XRD (cooled down to room temperature) Single phase/matrix $Sn_{0.5}Te_{0.4465}Se_{0.0535}$							
C in AB	0.9465	14.10 / 5.84	4.63	2.30 / 1.32	0.98	-0.70	0.94
A in BC	0.5	12.25 / 5.31	5.12	2.69 / 1.39	0.84	-71.15	0.45
B in AC	0.5535	16.21 / 6.40	4.21	1.94 / 1.25	0.70	-47.42	0.61
Hot pressed matrix $Sn_{0.5}Te_{0.4565}Se_{0.0435}$							
C in AB	0.956	14.08 / 5.83	4.64	2.31 / 1.32	0.99	-0.62	0.95
A in BC	0.5	12.16 / 5.29	5.13	2.70 / 1.39	0.72	-61.70	0.45
B in AC	0.5435	16.20 / 6.40	4.20	1.93 / 1.25	0.70	-48.05	0.60
Hot pressed second phase $Sn_{0.5}Te_{0.287}Se_{0.213}$							
C in AB	0.787	14.58 / 5.97	4.52	2.21 / 1.30	0.94	-3.32	0.77
A in BC	0.5	13.71 / 5.73	4.97	2.53 / 1.36	0.83	-36.05	0.47
B in AC	0.713	16.24 / 6.41	4.32	2.01 / 1.26	0.80	-42.39	0.75

(continued) Calculated values of the various parameters to be used for heat of solution calculation for ternary phases (equation 37)

Cold pressed at 6.90 MPa after TE properties measurements matrix $\text{Sn}_{0.5}\text{Te}_{0.451}\text{Se}_{0.049}$							
C in AB	0.951	14.09 / 5.83	4.63	2.30 / 1.32	0.98	-0.66	0.95
A in BC	0.5	12.21 / 5.30	5.13	2.70 / 1.39	0.72	-61.63	0.45
B in AC	0.549	16.20 / 6.40	4.20	1.94 / 1.25	0.70	-47.70	0.60
Cold pressed at 6.90 MPa after TE properties measurements second phase $\text{Sn}_{0.5}\text{Te}_{0.271}\text{Se}_{0.229}$							
C in AB	0.771	14.63 / 5.98	4.51	2.20 / 1.30	0.94	-3.77	0.76
A in BC	0.5	13.86 / 5.77	4.96	2.52 / 1.36	0.84	-49.60	0.47
B in AC	0.729	16.24 / 6.41	4.33	2.01 / 1.26	0.81	-42.17	0.77
Cold pressed at 20.68 MPa after TE properties measurements matrix $\text{Sn}_{0.5}\text{Te}_{0.4435}\text{Se}_{0.0565}$							
C in AB	0.9435	14.11 / 5.84	4.63	2.30 / 1.32	0.98	-0.73	0.93
A in BC	0.5	12.28 / 5.32	5.12	2.69 / 1.39	0.73	-60.99	0.45
B in AC	0.5565	16.21 / 6.40	4.21	1.94 / 1.25	0.70	-33.11	0.61

(continued) Calculated values of the various parameters to be used for heat of solution calculation for ternary phases (equation 37)

Cold pressed at 20.68 MPa after TE properties measurements second phase							
$\text{Sn}_{0.5}\text{Te}_{0.313}\text{Se}_{0.187}$							
C in AB	0.813	14.49 / 5.94	4.54	2.23 / 1.31	0.94	-2.68	0.80
A in BC	0.5	13.47 / 5.66	5.00	2.56 / 1.37	0.82	-52.65	0.47
B in AC	0.687	16.23 / 6.41	4.31	2.00 / 1.26	0.78	-42.80	0.73
Cold pressed at 34.47 MPa after TE properties measurements matrix							
$\text{Sn}_{0.5}\text{Te}_{0.4645}\text{Se}_{0.0355}$							
C in AB	0.9645	14.06 / 5.83	4.64	2.27 / 1.31	0.99	-0.55	0.96
A in BC	0.5	12.09 / 5.27	5.14	2.71 / 1.39	0.74	-62.12	0.45
B in AC	0.5355	16.20 / 6.40	4.19	1.93 / 1.24	0.69	-48.60	0.590
Cold pressed at 34.47 MPa after TE properties measurements second phase							
$\text{Sn}_{0.5}\text{Te}_{0.331}\text{Se}_{0.169}$							
C in AB	0.831	14.43 / 5.926	4.56	2.24 / 1.31	0.95	-2.28	0.82
A in BC	0.5	13.31 / 5.616	5.02	2.58 / 1.37	0.80	-53.90	0.47
B in AC	0.669	16.23 / 6.410	4.29	2.00 / 1.26	0.77	-43.15	0.71

Summary of the calculated heat of solution and the enthalpy of formation values to be used in the common tangent construction method

Sample with normalized composition (i.e. A+B+C = Sn+Te+Se = 1)	ΔH^c_{AinB} (kJ/mol) $\Delta H^c_{\text{Sn in Te}}$	$\Delta H^c_{\text{CinAB}}$ (kJ/mol) $\Delta H^c_{\text{SeinSnTe}}$	ΔH^c_{BinC} or ΔH^c_{CinB} (kJ/mol) $\Delta H^c_{\text{Se in Te}}$ or $\Delta H^c_{\text{Te in Se}}$	$\Delta H^c_{\text{AinBC}}$ (kJ/mol) $\Delta H^c_{\text{SninTeSe}}$	ΔH^c_{AinC} (kJ/mol) $\Delta H^c_{\text{Sn in Se}}$	$\Delta H^c_{\text{BinAC}}$ (kJ/mol) $\Delta H^c_{\text{TeinSnSe}}$
As melt spun						
Single phase/ matrix Sn _{0.5} Te _{0.42} Se _{0.08}	-15.78	-0.07	-2.50	-13.66	-7.01	-12.19
ΔH_{ABC} (kJ/mol)	-17.07					
As ball milled						
Matrix Sn _{0.5} Te _{0.4385} Se _{0.0615}	-15.78	-0.05	-2.13	-13.80	-7.01	-14.71
ΔH_{ABC} (kJ/mol)	-17.83					
Second phase Sn _{0.5} Te _{0.350} Se _{0.150}	-15.78	-0.24	-2.52	-0.33	-7.01	-10.63
ΔH_{ABC} (kJ/mol)	-12.17					

(continued) Summary of the calculated heat of solution and the enthalpy of formation values to be used in the common tangent construction method

Sample with normalized composition (i.e. A+B+C = Sn+Te+Se = 1)	ΔH^c_{AinB} (kJ/mol) $\Delta H^c_{\text{Sn in Te}}$	$\Delta H^c_{\text{CinAB}}$ (kJ/mol) $\Delta H^c_{\text{SeinSnTe}}$	ΔH^c_{BinC} or ΔH^c_{CinB} (kJ/mol) $\Delta H^c_{\text{Se in Te}}$ or $\Delta H^c_{\text{Te in Se}}$	$\Delta H^c_{\text{AinBC}}$ (kJ/mol) $\Delta H^c_{\text{SninTeSe}}$	ΔH^c_{AinC} (kJ/mol) $\Delta H^c_{\text{Sn in Se}}$	$\Delta H^c_{\text{BinAC}}$ (kJ/mol) $\Delta H^c_{\text{TeinSnSe}}$
Cold pressed at 6.90 MPa						
Matrix Sn _{0.5} Te _{0.440} Se _{0.0595}	-15.78	-0.04	-2.08	-13.82	-7.01	-14.19
ΔH_{ABC} (kJ/mol)	-17.64					
Second phase Sn _{0.5} Te _{0.338} Se _{0.162}	-15.78	-0.30	-2.54	-12.69	-7.01	-10.36
ΔH_{ABC} (kJ/mol)	-16.23					
Cold pressed at 20.68 MPa						
Matrix Sn _{0.5} Te _{0.453} Se _{0.047}	-15.78	-0.03	-1.75	-13.93	-7.01	-12.98
ΔH_{ABC} (kJ/mol)	-17.16					

(continued) Summary of the calculated heat of solution and the enthalpy of formation values to be used in the common tangent construction method

Sample with normalized composition (i.e. A+B+C = Sn+Te+Se = 1)	ΔH^c_{AinB} (kJ/mol) $\Delta H^c_{\text{Sn in Te}}$	$\Delta H^c_{\text{CinAB}}$ (kJ/mol) $\Delta H^c_{\text{SeinSnTe}}$	ΔH^c_{BinC} or ΔH^c_{CinB} (kJ/mol) $\Delta H^c_{\text{Se in Te}}$ or $\Delta H^c_{\text{Te in Se}}$	$\Delta H^c_{\text{AinBC}}$ (kJ/mol) $\Delta H^c_{\text{SninTeSe}}$	ΔH^c_{AinC} (kJ/mol) $\Delta H^c_{\text{Sn in Se}}$	$\Delta H^c_{\text{BinAC}}$ (kJ/mol) $\Delta H^c_{\text{TeinSnSe}}$
Cold pressed at 20.68 MPa						
Second phase Sn _{0.5} Te _{0.350} Se _{0.1495}	-15.78	-0.24	-2.51	-12.85	-7.01	-10.64
ΔH_{ABC} (kJ/mol)	-16.35					
Cold pressed at 34.47 MPa						
Matrix Sn _{0.5} Te _{0.451} Se _{0.0485}	-15.78	-0.03	-1.80	-13.92	-7.01	-12.90
ΔH_{ABC} (kJ/mol)	-17.15					
Second phase Sn _{0.5} Te _{0.357} Se _{0.143}	-15.78	-0.22	-2.50	-12.93	-7.01	-10.79
ΔH_{ABC} (kJ/mol)	-16.41					

(continued) Summary of the calculated heat of solution and the enthalpy of formation values to be used in the common tangent construction method

Sample with normalized composition (i.e. A+B+C = Sn+Te+Se = 1)	ΔH^c_{AinB} (kJ/mol) $\Delta H^c_{\text{Sn in Te}}$	$\Delta H^c_{\text{CinAB}}$ (kJ/mol) $\Delta H^c_{\text{SeinSnTe}}$	ΔH^c_{BinC} or ΔH^c_{CinB} (kJ/mol) $\Delta H^c_{\text{Se in Te}}$ or $\Delta H^c_{\text{Te in Se}}$	$\Delta H^c_{\text{AinBC}}$ (kJ/mol) $\Delta H^c_{\text{SninTeSe}}$	ΔH^c_{AinC} (kJ/mol) $\Delta H^c_{\text{Sn in Se}}$	$\Delta H^c_{\text{BinAC}}$ (kJ/mol) $\Delta H^c_{\text{TeinSnSe}}$
After HT XRD (cooled down to room temperature)						
Single phase/ matrix $\text{Sn}_{0.5}\text{Te}_{0.446}$ $_{5}\text{Se}_{0.0535}$	-15.78	-0.04	-1.93	-16.14	-7.01	-12.82
ΔH_{ABC} (kJ/mol)	-17.91					
Hot pressed						
Matrix $\text{Sn}_{0.5}\text{Te}_{0.456}$ $_{5}\text{Se}_{0.0435}$	-15.78	-0.03	-1.65	-13.96	-7.01	-13.07
ΔH_{ABC} (kJ/mol)	-17.17					
Second phase $\text{Sn}_{0.5}\text{Te}_{0.287}$ $\text{Se}_{0.213}$	-15.78	-0.55	-2.54	-8.53	-7.01	-9.18
ΔH_{ABC} (kJ/mol)	-14.53					

(continued) Summary of the calculated heat of solution and the enthalpy of formation values to be used in the common tangent construction method

Sample with normalized composition (i.e. A+B+C = Sn+Te+Se = 1)	ΔH^c_{AinB} (kJ/mol) $\Delta H^c_{\text{Sn in Te}}$	$\Delta H^c_{\text{CinAB}}$ (kJ/mol) $\Delta H^c_{\text{SeinSnTe}}$	ΔH^c_{BinC} or ΔH^c_{CinB} (kJ/mol) $\Delta H^c_{\text{Se in Te}}$ or $\Delta H^c_{\text{Te in Se}}$	$\Delta H^c_{\text{AinBC}}$ (kJ/mol) $\Delta H^c_{\text{SninTeSe}}$	ΔH^c_{AinC} (kJ/mol) $\Delta H^c_{\text{Sn in Se}}$	$\Delta H^c_{\text{BinAC}}$ (kJ/mol) $\Delta H^c_{\text{TeinSnSe}}$
Cold pressed at 6.90 MPa after TE properties measurements						
Matrix Sn _{0.5} Te _{0.451} Se _{0.049}	-15.78	-0.03	-18.80	-13.91	-7.01	-12.93
ΔH_{ABC} (kJ/mol)	-22.82					
Second phase Sn _{0.5} Te _{0.271} Se _{0.229}	-15.78	-0.65	-10.12	-11.76	-7.01	-8.79
ΔH_{ABC} (kJ/mol)	-18.04					
Cold pressed at 20.68 MPa after TE properties measurements						
Matrix Sn _{0.5} Te _{0.443} 5Se _{0.0565}	-15.78	-0.04	-18.52	-13.85	-7.01	-8.93
ΔH_{ABC} (kJ/mol)	-21.38					

(continued) Summary of the calculated heat of solution and the enthalpy of formation values to be used in the common tangent construction method

Sample with normalized composition (i.e. A+B+C = Sn+Te+Se = 1)	ΔH^c_{AinB} (kJ/mol) $\Delta H^c_{\text{Sn in Te}}$	$\Delta H^c_{\text{CinAB}}$ (kJ/mol) $\Delta H^c_{\text{SeinSnTe}}$	ΔH^c_{BinC} or ΔH^c_{CinB} (kJ/mol) $\Delta H^c_{\text{Se in Te}}$ or $\Delta H^c_{\text{Te in Se}}$	$\Delta H^c_{\text{AinBC}}$ (kJ/mol) $\Delta H^c_{\text{SninTeSe}}$	ΔH^c_{AinC} (kJ/mol) $\Delta H^c_{\text{Sn in Se}}$	$\Delta H^c_{\text{BinAC}}$ (kJ/mol) $\Delta H^c_{\text{TeinSnSe}}$
Cold pressed at 20.68 MPa after TE properties measurements						
Second phase Sn _{0.5} Te _{0.313} Se _{0.187}	-15.78	-0.40	-10.41	-12.36	-7.01	-9.80
ΔH_{ABC} (kJ/mol)	-18.59					
Cold pressed at 34.47 MPa after TE properties measurements						
Matrix Sn _{0.5} Te _{0.464} 5Se _{0.0355}	-15.78	-0.02	-19.30	-14.02	-7.01	-13.28
ΔH_{ABC} (kJ/mol)	-23.14					
Second phase Sn _{0.5} Te _{0.331} Se _{0.169}	-15.78	-0.32	-10.70	-12.60	-7.01	-10.21
ΔH_{ABC} (kJ/mol)	-18.87					

Publication List

“N-type CNTs/Ag₂Te Nanohybrid Buckypaper and Their Thermoelectric Properties”, Weiyun Zhao, Huiteng Tan, Li Ping Tan, Shufen Fan, Huey Hoon Hng, Freddy Boey, Igor Beloborodov, Qingyu Yan, *ACS Applied Materials & Interfaces*, 6 (7), 2014, 4940 – 4946.

“Fabrication of Flexible Thermoelectric Thin Film Devices by Inkjet Printing”, Ziyang Lu, Michael Layani, Xiaoxu Zhao, Li Ping Tan, Ting Sun, Shufen Fan, Qingyu Yan, Shlomo Magdassi, Huey Hoon Hng, *Small*, 2014, DOI: 10.1002/sml.201303126.

“Facile precipitation of two phase alloys in SnTe_{0.75}Se_{0.25} with improved power factor”, Li Ping Tan, Ting Sun, Shufen Fan, R. V. Ramanujan, Huey Hoon Hng, *Journal of Alloys and Compounds*, 587 (2014), 420 – 427.

“Aqueous Solution Synthesis of (Sb,Bi)₂(Te,Se)₃ Nanocrystals with Controllable Composition and Morphology”, Ziyang Lu, Li Ping Tan, Xiaoxu Zhao, Michael Layani, Ting Sun, Shufen Fan, Qingyu Yan, Shlomo Magdassi and Huey Hoon Hng, *Journal of Materials Chemistry C*, 1 (2013), 6271 – 6277.

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“Germanium Nanowires-based Carbon Composite as Anodes for Lithium-ion Batteries”, Li Ping Tan, Ziyang Lu, Hui Teng Tan, Jixin Zhu, Xianhong Rui, Qingyu Yan and Huey Hoon Hng, *Journal of Power Sources*, 206 (2012), 253 – 258.

Conferences Attended

Oral Presentation

“Melt Spun $(\text{SnTe})_{1-x}(\text{SnSe})_x$ and the Observed Enhancement in Power Factor” by Li Ping Tan, Ady Suwardi, Shufen Fan, Ting Sun, R. V. Ramanujan and Huey Hoon Hng, **Materials Research Society (MRS) Fall 2012, November 2012.**

Poster Presentations

“Germanium Nanowires Growth on Different Carbonaceous Compounds and Its Effect on Lithium-ion Batteries Performance” by Li Ping Tan, Ziyang Lu, Hui Teng Tan, Jixin Zhu, Xianhong Rui, Qingyu Yan and Huey Hoon Hng, **International Conference of Young Researchers on Advanced Materials (ICYRAM) 2012, July 2012.**

“Enhanced Power Factor of Cu_7Te_4 - $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Nanocomposites” by Li Ping Tan, Lay Yong Ng and Huey Hoon Hng, **Joint Symposium 2011, June 2011.**