THERMOELECTRIC STUDY OF INSB SECONDARY PHASE BASED NANO COMPOSITE MATERIALS

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ABSTRACT

In the past several decades there has been an intensive study in the field of thermoelectric study that is basically materials driven. As the simplest technology applicable in direct heat-electricity energy conversion, thermoelectricity utilizes the Seebeck effect to generate electricity from heat or conversely achieve the solid-state cooling via the Peltier effect. With many technical merits, thermoelectric devices can be used as spot-size generators or distributed refrigerators, however, their applications are restricted by the energy conversion efficiency, which is mainly determined by the figure of merit \( ZT \) of the thermoelectric materials that these devices are made of.

A higher \( ZT (ZT = \frac{a^2 \sigma}{\kappa}) \) entails a larger Seebeck coefficient \( (a) \), a higher electrical conductivity \( (\sigma) \) and a lower thermal conductivity \( (\kappa) \). However, it is challenging to simultaneously optimize these three material parameters because they are adversely correlated. To this end, a promising approach to answer this challenge is nano-compositing or microstructuring at multiple length scales. The numerous grain boundaries in nano-composite allow for significant reduction of lattice thermal conductivity via strong phonon scattering and as well an enhanced Seebeck coefficient via, carrier energy filtering effect.

As the same grain boundaries also scatter carriers, a coherent interface between grains is needed to minimize the degradation of carrier mobilities. To this end, \textit{in-situ}, instead of \textit{ex-situ}, formation of nano-composite is preferred. It is noteworthy that electrical
conductivity can be further enhanced by the injection of high-mobility carriers introduced by the secondary nano-phase.

In view of the prevalent use of Antimony (Sb) in thermoelectric materials, Indium Antimonide (InSb) naturally becomes one of the most promising nano-inclusions since it possesses one of the largest carrier mobilities (~ 7.8 m^2/V-s) in any semiconductors, while at the same time possesses a reasonably narrow band gap (~ 0.17 eV at 300 K).

In this dissertation, I experimentally investigate whether InSb could be a “good” nano-secondary phase in two thermoelectric bulk matrix materials, FeSb_2 and half-Heusler compounds. In these in situ formed nano-composites, three mechanisms are utilized to decouple the otherwise adversely correlated Seebeck coefficient (a), electrical conductivity (σ), and thermal conductivity (κ). First, low energy carriers will be filtered out via the carrier energy filtering effect, enhancing the Seebeck coefficient without degrading the power factor (PF= α^2 σ). Second, high mobility carriers from the InSb nano-inclusions will be injected to the system to increase the electrical conductivity. Last, the numerous grain boundaries present in nano-composites allow for strong phonon scattering so as to reduce the thermal conductivity.

After the initial in situ synthesis of nano-composites with the optimized composition, further nano-structuring processes are applied in the samples of FeSb_2 with 0.5% atomic ratio of InSb. The results indicate that not all nano-structures are thermoelectrically favorable, multi-scale microstructures with the length scale comparable with the phonon
mean free path are needed to effectively scatter phonons over a wide range of wavelength.

In summary, the successful combination of the carrier energy filtering effect, high mobility carrier injection effect, and strong phonon scattering effect in the \textit{in situ} synthesized FeSb$_2$-InSb and half-Heusler-InSb nano-composites leads to a significantly enhanced $ZT$. This approach of \textit{in situ} formation of nano-composites based on InSb secondary nano-phase may also be applied to other thermoelectric materials.
DEDICATION

I would like to dedicate this dissertation to my baby girl, Chelsea Zhu, who just came to this world during the preparation of my graduation and let me understand the meaning of life, responsibility and love more deeply. In a Chinese saying, there is always a brilliant but silent woman behind a successful man. Though not succeed yet, I would like to dedicate this dissertation to my wife, Meilan Zheng, who is the woman behind me, with her full love, encouragement and support. Last, I would like to dedicate this thesis to my parents, Jianying Zhu and Huiping Rong, for their unconditional raising and leading. Thanks very much to my beloved family members.
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I would like to thank my advisor and the committee chair, Dr. Terry M. Tritt, for his motivation, guidance, and support. I would like to extend my appreciation to Dr. Jian He, Dr. Catalina Marinescu and Dr. Hye-Jung Kang for serving as my committee members.

Especially, I would like to express my sincere gratitude to Dr. Jian He for his encouragement, friendship, inspirational discussions throughout my PhD study. I am also deeply grateful to Dr. Wenjie Xie, who sparked the idea to initiate this project and cooperate with me to finish this project. I also would like to thank Dr. Catalina Marinescu and Dr. Hye-Jung Kang for the discussion in solids state Physics and neutron scattering.

Taking this chance, I want to thank the department office staffs and the machine shop staffs, who have provided us a strong documentary and hardware backup. I also would like to thank my teaching assistant supervisor, Jerry Hester, for his rigorous but kind guidance in teaching.

Finally, I would like to thank every member of the Complex and Advanced Materials Laboratory, Department of Physics and Astronomy, Clemson University, who makes the group a great team to learn from each other and work with.

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CHAPTER I

THERMOELECTRIC MATERIALS: FROM BULK TO NANO AND TO NANO-COMPOSITE

1.1 The Brief History of Thermoelectric Materials.

In the past several decades, in a wake to the growing of energy crisis, there has been an intensive study in the field of thermoelectric (TE) effects and thermoelectric materials, which can utilize the Seebeck effect to directly generate electrical power from thermal energy (waste heat) or conversely achieve the solid-state cooling by the Peltier effect\textsuperscript{1-3}.

It has been almost 200 years since thermoelectric effect was first discovered. In early 19th century, Thomas Seebeck\textsuperscript{4} (1823) and Jean Peltier\textsuperscript{5} (1834) first discovered the phenomena which are the basis for today’s thermoelectric studies. Seebeck found that if you placed a temperature gradient across the junctions of two dissimilar conductors, electric current would flow and could be probed by the displacement of a small magnetic needle, as shown in Figure 1.1. Peltier, on the other hand, observed that passing a current through two dissimilar materials could cause heat to be either emitted or absorbed at the junction of the materials.

It was only after the mid-20th century when developments in semiconductor materials and technology, that practical application for thermoelectric devices became feasible. In
1949 Abram Fedorovich Ioffe developed the modern theory of thermoelectricity using the concept of the “figure of merit” $Z$. Ioffe also strongly promoted the application of the semiconductors in investigation of thermoelectric materials and devices. He also applied semiconductor physics to analyze results and attempts to optimize thermoelectric performance. One of the first demonstrations of 0° cooling was by H. Julian Goldsmid in 1954 using $\text{Bi}_2\text{Te}_3$ based thermoelectric materials. In 1995, Glen Slack summarized the material requirements succinctly in the "phonon-glass electron-crystal" (PGEC) concept of advanced thermoelectric materials. This concept states that the phonons should be disrupted (scattered) like in a glass but the electrons or other charge carriers should have high mobility as they do in many crystalline materials.

About the same time Hicks and Dresselhaus (1993) introduced the concept of low dimensionality as a mechanism with which to obtain higher performance TE materials. More recently, Dresselhaus in 2007 proposed several new directions for low-dimensional thermoelectric materials by incorporating them into a host matrix to form TE nano-composite materials. The hope that these “engineered structures” will improve $ZT$, particularly at the nanometer scale has reinvigorated research in thermoelectric materials. Nowadays, the investigation and study of nano-structured thermoelectric materials is one of the most promising and productive directions in the field of thermoelectric materials research.
Figure 1.1 In the year of 1821, Thomas Seebeck discovered that a junction of dissimilar metals produced an electric current when exposed to a temperature gradient and the current could be detected by the movement of the magnet needle. This is now called the Seebeck effect and is the basis of thermoelectric study.

1.2 Thermoelectric Applications and Efficiency.

To a great extent, the development of civilization has evolved with the technological advent of energy production, storage, delivery and usage. As electricity will remain the dominant form of energy in the foreseeable future, eco-friendly technology to generate electricity is of the utmost importance. Heat, however, has always been an abundant but
waste heat as a form of energy comprises more than half of all the energy generated by mankind and is lost and unused. So, harvesting and directly converting the waste heat emanating from many different sources (e.g., solar, geothermal, and exhaust from automobiles or other industries) into electricity is highly desirable. One emerging market is to harvest the large amount of waste heat (≈ 2/3 of the generated power) from an automobile’s engine and convert it into “on-board” electrical energy using thermoelectric (TE) devices. Meanwhile, there has always been a strong need for solid-state cooling (heat management) in microelectronics, which often requires responsive spot size cooling instead of traditional environmental cooling. This is best satisfied by the concept of TE refrigeration, wherein the gain from temperature stabilization and device performance can be significant.

With the advantages of thermoelectric devices being a solid state technology, with no moving parts, highly reliable and environmentally friendly, thermoelectric devices can be used as spot size generators or distributed refrigerators. Most thermoelectric devices work as an array of the basic units \(^{10}\), i.e. thermoelectric couples, and is illustrated in Figure 1.2(c). As shown in Figure 1.2 (a) and (b), a basic thermoelectric couple consists of one leg made of n-type material and one leg made of p-type material in order to maximize the amount of power generated or the amount of heat absorbed. Figure 2 (a) shows the power generation mode under a temperature gradient while Figure 2(b) shows the refrigeration mode with an electrical current flowing. Then in Figure 2c is shown an array of these TE couples in a thermoelectric module where they are connected electrically in series and thermally in parallel.
Figure 1.2 The working illustration for thermoelectric devices. (a) is the power generation mode, (b) is the refrigeration mode and (c) is an array which is made of many thermoelectric couples in parallel.\textsuperscript{10}

However, the conversion efficiency of thermoelectric device restricted their usage. In 1949, Abram Ioffe formulated the Z parameter that evolved into the more modern description of the dimensionless figure of merit, $ZT$, which can be used to quantify the performance of a thermoelectric material.\textsuperscript{6} The dimensionless figure of merit, $ZT$ is defined in Eq. 1-1, where $\alpha$ is the Seebeck coefficient or thermopower, $\sigma$ is the electrical
conductivity, $\kappa$ is the thermal conductivity and $T$ is the absolute temperature, respectively. One should note the total thermal conductivity ($\kappa$) is comprised of two parts: one due to heat carried by the electrons ($\kappa_e$) and one due to heat carried by the phonons or lattice ($\kappa_l$).

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T$$  \hspace{1cm} (1-1)

In the power generation mode, the efficiency is determined by the electrical power output produced by the heat flux into the system. The power output is defined by Eq. 1-2, which consists of both Ohm’s law and the Seebeck effect ($J$ is the current density (amps/m$^2$), $E$ is the electric field and $\rho$ is the electrical resistivity). Meanwhile, the heat flux ($JQ$ on Watts/m$^2$) has a reversible Peltier heat term and an irreversible Fourier heat flow term as shown in Eq. 1-3.

$$P = EJ \quad E = \rho J - \alpha VT$$  \hspace{1cm} (1-2)

$$Q = \alpha TJ - \kappa VT$$  \hspace{1cm} (1-3)

The maximum efficiency, $\eta_{max}$, of a thermoelectric material is determined by integrating the $P/Q$ ratio at each point (each temperature) over the entire length of the sample (Eq. 1-4), where $ZT_m$ is the maximum $ZT$ which occurs at temperature $T_m$ ($T_m = \frac{T_{Hot} + T_{Cold}}{2}$) and $dx = dT/VT$. More detailed evaluation can be found in reference handbook$^{11}$.

$$\eta_{max} = \int_0^L \frac{P}{Q} dx = \int_{T_{Cold}}^{T_{Hot}} \frac{1}{VT} \frac{P}{Q} dT = \left(\frac{T_{Hot} - T_{Cold}}{T_{Hot}}\right) \left[\frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + T_{Cold}/T_{Hot}}\right]$$  \hspace{1cm} (1-4)
Similarly, in the refrigeration mode, the maximum efficiency of a thermoelectric material is defined as the $\Phi_{\text{max}}$ as given by Eq. 1-5.

$$\Phi_{\text{max}} = \left(\frac{T_{\text{Cold}}}{T_{\text{Hot}}-T_{\text{Cold}}}\right) \left(\sqrt{1+\frac{ZT_{m}}{T_{\text{Cold}}/T_{\text{Hot}}}}\right)$$  \hspace{1cm} (1-5)

In Eq. 1-4 and 1-5, the first term on the right hand side is the Carnot efficiency, which is determined by the relative temperature difference across the hot and cold end of the material. The second term, which is determined by the material thermoelectric properties, can reach unity if $ZT_{m}$ approaches to infinity. So the key point to improve the efficiency of thermoelectric materials is to enhance their dimensionless figure of merit $ZT$.

1.3 Material Parameters Pertinent to Thermoelectricity.

Per Eq. 1-1, the mathematical definition of $ZT$, there are several important physical parameters that govern the performance of a thermoelectric material: they are the Seebeck coefficient ($\alpha$), electrical conductivity ($\sigma$), and thermal conductivity ($\kappa$).

1.3.1 Seebeck Coefficient.

Macroscopically, Seebeck coefficient is the ratio between the voltage difference and temperature difference as defined in Eq. 1-6, and it can be measured as shown in Figure 1.3.
Figure 1.3 A sample is heated at one end and the voltage difference between the hot and cold side is measured. The ratio between the temperature difference and the voltage drop is defined as the Seebeck coefficient, an intrinsic property of the material.

Microscopically, the Seebeck coefficient is the measurement of the heat per carrier over temperature or entropy per carrier. To see this, we start from the refrigerator mode with the definition of Peltier coefficient ($\Pi$) which is mathematically defined as the ratio of the heat current ($u$) over the charge current ($j$), as in Eq. 1-7.

$$\Pi = \frac{u}{j}$$  \hspace{1cm} (1-7)
Suppose a box of particles with a charge per particle, $e$, under an electric field but no temperature gradient. If the particles also carry heat then there will be a heat current, $u$, associated with the charge flow, $j$, as shown in Eq. 1-8.

\[ j = nev, \quad u = nQv = nSTv \]  
\[ (1-8) \]

where $n$ is the particle density, $v$ is the particle velocity, $Q$ is the heat energy per particle, $S$ is the entropy per particle and $T$ is the absolute temperature, respectively. So from Eq. 1-7 and Eq. 1-8, we can get

\[ \Pi = \frac{u}{j} = \frac{nQv}{nev} = \frac{Q}{e} = \frac{ST}{e} \]  
\[ (1-9) \]

With the Thomson relation

\[ \alpha = \frac{\Pi}{T} \]  
\[ (1-10) \]

We can get

\[ \alpha = \frac{Q}{eT} = \frac{S}{e} \]  
\[ (1-11) \]

So,

\[ \alpha = \frac{\text{heat per carrier}}{\text{charge per carrier} \cdot T} = \frac{\text{entropy per carrier}}{\text{charge per carrier}} \]  
\[ (1-12) \]
Beyond the kinetic picture of particle flow, band theory based on quantum mechanics has been widely used to interpret the thermoelectric properties. In band theory, the electrical property of semiconductor or metals is predominated by the charge carriers with energy between $E$ and $E+dE$ near the Fermi level ($E_F$), i.e. within $k_B T$ of $E_F$ (see definitions below). A more detailed model of the Seebeck coefficient is given by the Mott Relation\(^{13}\) (Eq. 1-13), where $f_0 (E)$ is the Fermi Direct distribution function, $k_B$ is the Boltzmann constant and $E_F$ is the Fermi Energy.

\[
\alpha = \pm \frac{k_B}{e} \frac{1}{\sigma} \int_0^\infty \sigma(E) \left( \frac{E-E_F}{k_B T} \right) \left( \frac{\partial f_0 (E)}{\partial E} \right) dE
\]  

(1-13)

Specifically, in metal or heavily doped semiconductors, the Mott equation for Seebeck coefficient can be further simplified to Eq. 1-14.

\[
\alpha = \pm \frac{\pi^2 k_B}{3 e k_B T} \left\{ \frac{d[\ln (\sigma(E))]}{dE} \right\}_{E=E_F}
\]  

(1-14)

1.3.2 Electrical Conductivity.

In Drude model, the electrical conductivity can be written as in Eq. 1-15, where $n$ is the carrier concentration, $e$ is the charge per carrier and $\mu$ is the carrier mobility.

\[
\sigma = ne\mu = n(E)e\mu(E)
\]  

(1-15)

where $n$ is carrier concentration, $e$ is the element charge, and $\mu$ denotes the carrier mobility.
The electrical conductivity can be further expressed in terms of the relaxation time $\tau(E)$ and effective mass $m^*$, and the mobility $\mu = e\tau(E)/m^*$ as shown in Eq. 1-16.

$$\sigma = n(E)e\mu(E) = n(E)e^2 \frac{\tau(E)}{m^*}$$  \hspace{1cm} (1-16)

1.3.3 Thermal conductivity.

Heat is transported by charge carriers and by lattice vibrations. Therefore, the total thermal conductivity $\kappa_t$ consists of two contributors, the electrical (carrier) thermal conductivity $\kappa_e$ and the lattice thermal conductivity $\kappa_l$ (or $\kappa_{ph}$), as shown in Eq. 1-17.

$$\kappa_t = \kappa_e + \kappa_l$$ \hspace{1cm} (1-17)

The electrical thermal conductivity is linearly proportional to the electrical conductivity in view of the Wiedemann-Franz relationship\textsuperscript{14}(Eq. 1-18), where $L$, the Lorenz number, is usually taken as $2.44 \times 10^{-8}$ $W\Omega/K^2$ for metals, and $T$ is the absolute temperature.

$$\kappa_e = L\sigma T$$ \hspace{1cm} (1-18)

In a classical kinetic view, the lattice thermal conductivity can be derived as shown in Eq. 1-19, where the $C_V$ is the specific heat, $v$ is the sound velocity and $l_p$ is the phonon mean free path.
\[ \kappa_t = \frac{1}{3} C_{\nu} v l_p \]

(1-19)

From Eq. 1-17 and Eq. 1-18, we infer that the thermal conductivity increases with the increase of the electrical conductivity, as illustrated in Figure 1.4. It is common belief that the inter-relation between the lattice thermal conductivity and the electrical thermal conductivity is less intimate than among other thermoelectric properties, hence they are can tuned individually to some extent.

1.4 Tuning the Thermoelectric Parameters to Enhance ZT.

As discussed in section 1.2, we need to enhance the figure of merit ZT, which is expressed in Eq. 1-1, to improve the working efficiency of thermoelectric materials.

\[ ZT = \frac{a^2 \sigma}{\kappa} T \]

(1-1)

To have a high ZT at a specific temperature, the Seebeck coefficient and the electrical conductivity need to be high whereas the thermal conductivity low. However, the Seebeck coefficient, electrical conductivity, and thermal conductivity are inversely dependent of each other and the improvement in one parameter will degrade the other parameters.

Per Eq. 1-13 and Eq. 1-14, we infer that the Seebeck coefficient will decrease with the increase of the electrical conductivity, which is illustrated in Figure 1.4. Per Eq.1-1, the contribution from the Seebeck coefficient to ZT is its squared value, so we may be able to
sacrifice some electrical conductivity to enhance the total power factor \( (PF) \), which is defined as Eq. 1-20.

\[
PF = \alpha^2 \sigma \quad (1-20)
\]

To shed light on how to increase the Seebeck coefficient, a further derivation from Eq. 1-14 and Eq. 1-15 is presented in Eq. 1-21.
Figure 1.4 The schematic relationship between electrical conductivity, Seebeck coefficient, power factor, and thermal conductivity as a function of concentration of free carrier$^{11}$. 

---

$^{11}$
\[ \alpha = \frac{\pi^2 k^2 T}{3e} \left[ \frac{d\ln(\sigma(E))}{dE} \right]_{E=E_F} = \frac{\pi^2}{3} \frac{k_B}{e} (k_B T) \left[ \frac{1}{n(E)} \frac{dn(E)}{dE} + \frac{1}{\mu(E)} \frac{d\mu(E)}{dE} \right] \] (1-21)

Per Eq. 1-21, the Seebeck coefficient has two basic contributions: the density of states (DOS) term and the scattering mechanism term that intimately affects the mobility.

For the DOS term, Dresshauls\(^9\) predicted that the quantum size effect could enhance the Seebeck coefficient significantly due to the sharp variations in the DOS to enhance ZT. In band theory, the DOS in 3D bulk materials is continuous near the Fermi level. When the 3D bulk materials are constrained into 2D, 1D or 0D structures, there will be some sharp spikes or even singularities in the DOS (Figure 1.5). However, in traditional bulk thermoelectric materials, it is difficult to constrain the charge carriers in low dimensions and also the sharp change in DOS is challenging to manipulate to be close enough to the Fermi level. As such, varying the DOS to achieve a high ZT is still under investigation thermoelectric studies.
Figure 1.5 Electronic density of states (DOS) varies as the dimensionality decreases from 3D bulk crystalline to 2D quantum well, to 1D quantum wire and 0D quantum dot\textsuperscript{69}.

Now let us look at the scattering term in Eq. 1-16, we can get $d\mu(E)/dE \sim d\tau(E)/dE$, and the scattering mechanism for $\tau(E)$ is shown as in Eq. 1-22, where $r$ is the scattering parameter\textsuperscript{11}.

$$\tau(E) = \tau_0 E^r$$  \hspace{1cm} (1-22)

In Eq. 1-22, different values of $\lambda$ correspond to different scattering mechanisms, as shown in Table 1.1. To improve $d\mu(E)/dE \sim d\tau(E)/dE$, the multiple scale scattering needs to be introduced to filter out the low energy charge carriers, i.e., the carrier energy filtering effect, which is one of the mechanisms that was utilized in this project.
<table>
<thead>
<tr>
<th>Value of $r$</th>
<th>Scattering mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1/2</td>
<td>Acoustic phonon scattering</td>
</tr>
<tr>
<td>0</td>
<td>Grain boundary defect scattering</td>
</tr>
<tr>
<td></td>
<td>Neutral impurities</td>
</tr>
<tr>
<td>3/2</td>
<td>ionized impurities</td>
</tr>
<tr>
<td>Large $r$</td>
<td>resonant scattering</td>
</tr>
</tbody>
</table>

*Table 1.1* typical values of scattering parameter for various scattering mechanisms$^{11}$.

Actually, enhancing the DOS near Fermi level or keeping the high energy charge carriers in order to increase the Seebeck coefficient can also be understood qualitatively from Eq. 1-12, since a large DOS change results in large change in entropy, and the hot charge carriers can carry more heat (or energy). This is viewed as the high energy or hot carrier injection over the grain boundary while the lower energy carriers can’t make it cross and thus do not contribute to the heat or charge flow.

To increase the electrical conductivity in view of Eq. 1-16, the carrier concentration and the carrier mobility both need to be enhanced. However, from Figure 1.4 and Eq. 1-21, the Seebeck coefficient will be suppressed with the increase of carrier concentration, leading to a lower power factor, and therefore, the best way to increase the electrical conductivity without degrading the Seebeck coefficient is to improve the carrier mobility. As for the bulk composite or nano-composite, the carrier mobility can be enhanced by
introducing high mobility carriers from the secondary phase, which is called the carrier injection effect. It is worth mentioning here, that Indium Antimonite (InSb) has the highest carrier mobility ($\mu = 7.8 \text{ m}^2/\text{V-s}$) in any semiconductor material as well as a low band gap ($E_g \approx 0.17 \text{ eV at 300K}$)\textsuperscript{15}. This is the primary reason we choose InSb as the secondary phase in the study of thermoelectric nano-composites.

As for tuning the thermal conductivity, from Eq. 1-17 to Eq. 1-19, the total thermal conductivity includes contributions from both the electrons (electrical thermal conductivity, $\kappa_e$) and the lattice (lattice thermal conductivity, $\kappa_l$). Based on Eq. 1-18, there is a limited space to decrease the electrical part since a reasonably good electrical conductivity ($\sigma \approx 1000 \Omega^{-1}\text{-cm}^{-1}$) is necessary to achieve a high power factor. The only feasible way is to decrease the lattice thermal conductivity. Per Eq. 1-19, the lattice thermal conductivity is related to three parameters, specific heat ($C_v$), sound velocity ($v$) and phonon mean free path ($l_p$). Generally, $C_v$ is determined by the material composition and there is not much room to manipulate the sound velocity since it is determined by the material density $d$ and material stiffness coefficient $K$, as in Eq. 1-23.

$$v = \sqrt{\frac{\kappa}{d}}$$

Therefore, the most effective approach to reduce the lattice thermal conductivity is to decrease the phonon mean free path ($l_p$), which means scattering phonons more frequently in space. There are several phonon scattering mechanisms in bulk materials, such as phonon-phonon scattering, phonon-electron scattering, alloy defects scattering,
and boundary scattering. Assuming these scattering processes take place in parallel, we come to the Mathiessen’s Rule (Eq. 1-24).

\[
\frac{1}{\tau_S} = \frac{1}{\tau_{imp.}} + \frac{1}{\tau_{strain}} + \frac{1}{\tau_{ph-ph}} + \frac{1}{\tau_{boud.}}
\]  

(1-24)

The phonon mean free path is thus given by: \( l_p = v\tau_s \). Therefore, the shortest scattering time will dominate the \( l_p \). However, scattering structures can also scatter charge carriers, resulting in undesirable decrease of the electrical conductivity. Consequently, a comprehensive design of the scattering centers is needed with the characteristic length of scattering close to the phonon wave length other than the charge wave length, so as to scatter the phonons more efficiently than the carriers.

Based on the above fundamental discussion on tuning the thermoelectric parameters, the efforts of pursuing higher \( ZT \) have been culminated into a two pronged strategy in the past decade, depending on the type of material studied. One approach is to develop novel bulk materials in line with the concepts of “phonon-glass electron-crystal” (PGEC)\(^8\). The other approach is to search for higher \( ZT \) in nano-structured thermoelectric materials that possess reduced dimensionality or nanometer characteristic lengths, since the Seebeck coefficient can be enhanced and lattice thermal conductivity can also be reduced by the multi-scale scattering in the nano-structured thermoelectric materials.
1.5 Nano-Composite Thermoelectric Materials

Nano-structured thermoelectric materials are one of the most promising directions in current thermoelectric studies, which is largely in parallel with the discovery of new high performance TE materials. The experimental proof-of-principle studies in “custom nano-engineered” quantum dot and superlattice systems show that (i) enhancement of $\sigma$ and $\alpha$ can be achieved simultaneously with the reduction of $\kappa$ in a nano-structured material, (ii) the degradation of the electrical transport properties are minimized by an optimal choice of band offsets, and (iii) the primary gain in $ZT$ is from the reduction of $\kappa_l$, rather than the predicted enhancement of the $PF$. The observation of these experimental results has been attributed to the less-dispersed phonon modes or phonon scattering due to a strong interfacial lattice mismatch. To date, the record high $ZT$ materials is still attributed to superlattice and quantum dot systems, but the present cost of the nano-fabrication processes restricts the large-scale commercial use of these “custom nano-engineered” systems. Theoretical studies of the mechanism of heat conduction in superlattice systems suggests a thermal boundary resistance and a high density of interfaces, rather than the atomically perfect interfaces or the periodicity of nanostructures, accounts for such a significant reduction of $\kappa_l$. It naturally leads to the idea of using bulk nano-structured materials (namely, nano-composites) as a potential cost-effective and scalable alternative to these “custom nano-engineered” systems for high $ZT$ materials\textsuperscript{16}. Important advantages of nano-composites include being made using a bulk synthesis procedure and in a form
compatible with existing commercial TE devices, possessing better mechanical properties, and being more isotropic.

In nano-composites thermoelectric materials, there are several multi-scale microstructures, which play different scattering roles in the transportation of phonons and charge carriers\textsuperscript{17} (Figure 1.6). Phonons can be scattered more effectively when the phonon wavelength is close to the characteristic length scales of the microstructures. Atomic scale defects can scatter phonons due to mass or strain field fluctuation. Short wavelength phonons can be effectively scattered by atomic scale defects with wavelengths that are comparable with the defect characteristic lengths. However, the mid-to-long wavelength phonons can propagate without being significantly scattered and still contribute to heat conduction. By introducing nano-particles, a significant reduction in lattice thermal conductivity can be achieved by the additional scattering of mid and long wavelength phonons by the nano-particles and also by the grain boundaries. So a wide distribution of multi-scale microstructures in a nano-composite is preferable since it can effectively scatter different phonon modes and reduce thermal conductivity. Primarily due to these numerous multi-scale boundaries in a nano-composite, the alloy limit rule of regular composite, which states that the propriety of composite AB cannot exceeds the range between A and B, can be broken down. This is because those boundaries can be treated as a novel phase, even though their compositions are still similar to the traditional bulk materials.
Figure 1.6 The multi-scale microstructures play different roles in scattering phonons in a nano-composite\textsuperscript{17}.

The recent advent of nano-materials and nanotechnology provides a variety of ways to prepare nano-sized materials, to name a few: molecular epitaxial growth, laser ablation, chemical vapor transport, vapor-liquid-solid growth, etching, wet chemistry and hydrothermal synthesis, ball milling, mechanical alloying, melt spinning and phase separation. Among these, high energy ball milling processing is an effective scalable
method used to produce large amounts of nano-particles of a variety of compositions. Another notable nano-structuring method is the melt spinning process, which can create rich nano-structures via a highly dynamic quenching process.

In general, nano-composites can be prepared by means of *ex situ* or *in situ* methods. The *ex situ* approach is typically performed in a two-step manner: nano-materials are first prepared using the aforementioned methods, and then densified into bulk objects\(^1\). The two most widely used densification methods are hot pressing (HP) and spark plasma sintering (SPS). The SPS process can densify nano-particles in a relatively short time, compared to HP process, to avoid the undesired diffusion and growth of grains. The main drawback of the *ex situ* method is the lack of coherence in interfaces, which may severely degrade the carrier mobility. An alternative way is the *in-situ* or self-assembled preparation\(^1\), including precipitation nucleation and growth, spinodal decomposition, and matrix encapsulation (“arrested precipitation”), with the resulting interfaces being mostly coherent or semi-coherent, which is just the synthesis approach applied in this project.

Nonetheless, charge carriers are somewhat scattered by the multi-scale microstructures in nano-composite, resulting in an undesirable degraded electrical conductivity. To compensate for this disadvantage, one method is to enhance the coherency between the nano-inclusions and bulk matrix materials, which can be achieved by the *in-situ* synthesis. The other is to inject the high mobility carriers into the nano-composite by forming a secondary nano-phase that has “good” electrical properties. This will be discussed in more detail in Chapter 2.
CHAPTER II

INDIUM ANTIMONIDE: A PROMISING SECONDARY NANO-PHASE FOR NANO-COMPOSITES

As discussed in Chapter I, the nano-composite concept is a promising approach to develop higher performance thermoelectric materials, in which an appropriate secondary nano-phase (nano-inclusion) plays a crucial role. In view of the prevalent use of Antimony (Sb) in thermoelectric materials, Indium Antimonite (InSb) can be naturally considered as a promising nano-inclusion as it possesses one of the largest carrier mobilities in any semiconductor. Additionally, the simplicity of synthesizing InSb makes it feasible for the in situ formation of secondary nano-phase. There is accumulating evidence that in-situ formation of nano-inclusion is thermoelectrically favorable because the as-formed nano-inclusion-bulk matrix interfaces tend to more coherent. Finally, the intrinsic thermoelectric properties of InSb distinguish itself from other candidates of nano-inclusions for thermoelectric nano-composites, such as C_{60} and ZrO_{2}^{20, 21}.
2.1 The Synthesis of InSb

With a simple binary phase diagram\textsuperscript{22} of In and Sb (Figure 2.1) and a simple Zincblende crystal structure (Figure 2.2)\textsuperscript{23}, InSb crystals can be readily formed by slow cooling from a melt with stoichiometric amount of In and Sb\textsuperscript{24}.

![In - Sb Phase Diagram](image)

**Figure 2.1** The binary phase diagram of In-Sb elements\textsuperscript{22}. 
2.2 Thermoelectric Properties of InSb.

As a narrow direct gap semiconductor, with a band gap about 0.17 eV at 300 K (Figure 2.3)\textsuperscript{25}, InSb by itself is a fairly good thermoelectric material in the mid-range temperature. Typical thermoelectric parameters of InSb polycrystals at 500K are listed in Table 2.1\textsuperscript{26}.

\textbf{Figure 2.2} The Zincblende crystal structure of InSb, with a 0.648 nm lattice constant\textsuperscript{23}. 
Figure 2.3 The band structure of InSb with $E_g \approx 0.17$ eV at 300K.  

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Seebeck coefficient</th>
<th>Electrical conductivity</th>
<th>Thermal conductivity</th>
<th>$ZT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>InSb</td>
<td>~200 $\mu$V/K</td>
<td>&gt;7×10$^4$ S/m</td>
<td>~10W/m-K</td>
<td>~0.1</td>
</tr>
</tbody>
</table>

Table 2.1 The typical thermoelectric parameters of InSb polycrystals at 500K.
Figure 2.4 The temperature dependence of carrier mobility. The solid line is the theoretical calculation and the data points are the measured Hall mobilities.\(^{15}\)

Worth to mention, InSb possesses the highest carrier mobility, which was reported and simulated by D. L. Rode in 1971\(^{15}\). As shown in Figure 2.4, the measured mobility data matches pretty well with the predicted theoretical model.
In view of the synthesis and thermoelectric properties of InSb, we developed a strategy of in-situ synthesis of nano-composite thermoelectric materials based on the InSb secondary nano-phase to enhance the figure of merit, $ZT$. In the following chapters, this approach will be implemented in two different antimonite systems, namely, FeSb$_2$ and half-Heusler compounds. Some necessary description about the sample preparation and characterization techniques will be briefly presented in Chapter III.
CHAPTER III

BREIF INTRODUCTION OF NANO-COMPOSITE SYNTHESIS AND CHARATERAIZATION TECHNIQUES

In this chapter, we will focus on those novel synthesis techniques of nano-composites and the custom-designed low temperature property measurement systems, for example, melt spinning, hot forging, spark plasma sintering (SPS), low temperature Resistivity and Seebeck measurement system (Low RS), low temperature thermal conductivity measurement system (Low TC) and Low temperature Hall coefficient measurement by the PPMS. Those commercialized/standardized synthesis and characterization procedures of thermoelectric materials (e.g., Ball Milling, Laser Flash, ZEM, DSC, PPMS, XRD, SEM, and TEM, etc.), the models and functions of the commercial equipment utilized in the project will be listed in Appendix A.

3.1 Melt Spinning Technique.

As illustrated in Figure 3.1, melt spinning is a technique used for rapid cooling of liquid melts. A wheel is cooled internally, usually by water or liquid nitrogen, and rotated. A thin stream of liquid melt is then dripped onto the wheel and cooled, causing rapid solidification. This technique is used to develop materials that require extremely high
cooling rates in order to form, such as metallic glasses. The cooling rates achievable by melt spinning are on the order of $10^4$–$10^7$ K/s. In 1960s, this technique was first used to develop materials that require extremely high cooling rates in order to form, such as metallic glasses and magnetic materials such as NdFeB based materials. The resulting rapidly cooled materials are in the form on long thin ribbons, only a few µm (typically 5-20 µm) in thickness. In the year of 2008, Tang’s group at Wuhan University of Technology in China introduced this method in thermoelectric material synthesis to generate the amorphous and nano-crystalline phase of Bi$_2$Te$_3$. After melt spinning, the solidified ribbons can be collected for further processing. Multi-phase microstructures are observed in the ribbons after melt spinning, from amorphous to crystallites. It is shown that a combination of the melt spinning and SPS techniques can generate multi-scale nano-composite of Bi$_2$Te$_3$ with a 40% enhanced ZT$^{27}$. 
Figure 3.1 (a) An illustration of melt spinning process, and (b) the melt-spun Bi$_2$Te$_3$ ribbons $^{27}$.

3.2 Hot Forging Technique

Different from the melt spinning process, hot forging is a high pressure deformation under a high temperature below the melting point of the material, which is normally used in metallurgy to enhance the strength of alloy by introducing microstructures in the material. Zhao’s group at Zhejiang University in China successfully utilized this method in Bi$_2$Te$_3$ compounds to reduce the lattice thermal conductivity$^{28}$. During the hot forging process, a densified sample disk is sat vertically in the hot press chamber. After the
temperature reaches the sintering temperature, a pressure is applied to deform the bulk sample slowly and this procedure can be repeated by rotating the hot-forged disk by 90 degrees in the chamber (Figure 3.2).

**Figure 3.2** (a) shows the hot forging process and (b) shows the microstructures after hot forging\(^2\).

### 3.3 Spark Plasma Sintering (SPS) Technique

While hot press is the traditional sintering technique for thermoelectric study, SPS is getting more widely used nowadays, even though the SPS process has been known for well over 30 years. As shown in Figure 3.3, during the SPS process, forces are applied on the top and bottom of the sample powders that are held in a graphite die between two
graphite rods and meanwhile a huge DC pulse current (100~1000A) is driven through the sample to generate joule heating of the sample and die. Compared with the traditional sintering technique with external heating source, such as hot press(on the order of hours), SPS is a fast sintering method (on the order of minutes) with internal joule heat, which is more favorable to preserve the initial microstructures during the densification due to the limitations of grain growth with time. The holding temperature, press pressure, and holding time can be varied to get different extent of densification and re-crystallization. The as-sintered sample is typically in the form of a disc, it is then cut into rectangle bars for further characterizations.

**Figure 3.3** (a) shows the procedure of SPS and (b) is a disk sample after SPS and is cut into bars.
Figure 3.4 (a) illustrates the sample mount on the removable puck for the low RS system\textsuperscript{30} and (b) shows an actual photo of a sample mounting.
3.4 Low Temperature Resistivity and Seebeck Measurement (Low RS).

Seebeck coefficient and electrical resistivity/conductivity are simultaneously measured on a custom-designed system that employs the differential (“slewing mode”) and traditional four-probe method, respectively\(^30\). This system consists of several components, such as the computer, vacuum pump, cryo-cooler, sample chamber, power meters, and sample puck, to provide a temperature variable, high vacuum condition for the voltage reading to derive the resistivity and Seebeck coefficient values. The sample puck is removable for quick sample mount and examination (Figure 3.4).

During Low RS measurement, a temperature difference \(\Delta T\) between the top and bottom of the sample is established by the heater on the top copper block, and then the voltage drop from top to bottom is acquired by voltage meters. The contributions from the copper wire and cooper block are subtracted and the sample thermal power can be obtained from the Eq. 3-1.

\[
\alpha_{sample} = \alpha_{Cu} - \frac{V_{measured}}{\Delta T} \quad (3-1)
\]

Then the electrical resistivity is measured while the temperature difference is still maintained between the top and bottom of the sample. The measured voltage drop between two leads contains two parts, one is from the resistance \((V_R)\) and the other is from the thermoelectric effect \((\alpha\Delta T)\), as shown in Eq. 3-2.

\[
V_{measured} = V_R(I) + \alpha\Delta T \quad (2-2)
\]
By measuring the voltage between the leads with the current $I^+$, and then with the current reversed but in same magnitude, the thermoelectric voltage is removed and the Ohmic resistance of the sample between the leads can be calculated using Eq. 3-3:

$$ R = \frac{V_{\text{measured}}(I^+) - V_{\text{measured}}(I^-)}{I^+ - I^-} = \frac{[V_R(I^+) + \alpha \nabla T] - [V_R(I^-) + \alpha \nabla T]}{2I} = \frac{V_R}{I} $$

(3-3)

Then with the measured dimensions, the resistivity $\rho$ can be obtained via Eq. 3-4, where $A$ is the cross section area and $L$ is the length between two voltage leads.

$$ \rho = \frac{R \cdot A}{L} \quad \text{(3-4)} $$

One point to note, during the slow variation of system temperature $T_{\text{base}}$ sweeping from 15K to room temperature with a cooling/heating rate about 0.75K/min, the measurement of thermal power and resistivity at a specific temperature $T_{\text{measure}}$ (defined as Eq. 3-5) can be finished in 1~2 seconds. It is thus a quasi-steady state measurement (i.e., “slewing” mode). A high density data was obtained by taking measurements every 120 seconds during both cooling and heating cycles.

$$ T_{\text{measure}} = T_{\text{base}} + \frac{1}{2} \nabla T \quad \text{(3-5)} $$
Figure 3.5 (a) shows the sample mounted on the low TC puck; (b) is the side view of the sample showing the distance between thermal couple junctions and (c) is an actual photo.
3.5 Low Temperature Thermal Conductivity Measurement (Low TC) and Radiation Loss Correction

Low temperature thermal conductivity is measured by our custom designed system using a steady state technique\textsuperscript{31}. The Low TC system contains the similar parts as the Low RS system except for the removable sample puck, which is modified from the commercial pucks designed by Quantum Design for their PPMS system’s AC Transport characterization (Figure 3.5). When the system reaches a preset temperature in the range of 15 K to room temperature and stabilizes, a current $I$ will go through the heater on the top of the sample to generate a temperature difference $\Delta T$, which is measured by a differential thermocouple attached on the sample. Then the power ($P$) injected through the sample is calculated as $P=IR^2$, where $R$ is the resistance of the heater that is determined from Ohm’s law and the voltage drop across the heater. Based on the definition of thermal conductance, $P=KA\Delta T$, a sweeping plot of $P$ verse $\Delta T$ is created with the linear trend line slope telling the value of $K$. Finally, with the measured cross section area $A$ and the length between the two junctions of the thermocouple $L$, the thermal conductivity, $\kappa$ can be determined by the Eq. 3-6. Generally, the low temperature RS and TC are measured on the same rectangle bar so we do not need to consider the uncertainty of cross section area $A$ in the calculation of $ZT$.

$$\kappa = \frac{KA}{L}$$ \hspace{1cm} (3-6)
The key point of the accurate thermal conductivity measurement is to make sure that all
the heat generated at the hot end of the sample flows across the sample without loss.
Generally, heat can be carried by conduction, convection, and radiation. So a thin
thermocouple with 0.001 inch diameter is utilized and regular cooper leads are replaced
with low thermal conductive phosphor bronze in order to minimize the heat conduction ot
of the sample. In addition, a high vacuum in the sample chamber is maintained during
measurement to reduce the heat loss by convection. The sample is surrounded by a gold
plated cap to reduce the radiation, however, the radiation loss needs to be corrected above
200 K on those low thermal conductivity samples. The correction is in line with the
Stefan-Blitzmann black body radiation theory.

Figure 3.6 From (a) to (b), the electrical thermal conductivity is calculated by
Wiedemann-Franz relationship and subtracted from the total thermal conductivity.
Figure 3.6 shows an example of the radiation loss correction, the electrical thermal conductivity calculated by Wiedemann-Franz relationship (Eq. 1-18) is removed from the measured thermal conductivity, leaving the lattice thermal conductivity and the radiation loss.

According to black body theory, the total energy per unit time radiated by a black body with surface area $A$ and maintained at a temperature $T$, is known as the Stefan-Boltzmann law\(^{32}\), as shown in Eq.3-7, where $\beta$ is the Stefan-Boltzmann constant.

$$P = A\beta T^4 \sim T^4$$  \hspace{1cm} (3-7)

The radiation loss $P_{\text{loss}}$ from the sample at temperature $T+\Delta T$ to the chamber wall at temperature $T$ can be expressed as Eq. 3-8. Since $\Delta T$ is relatively small compared to $T$, $\Delta T$ terms and high order terms can be ignored. Therefore, the radiation loss $P_{\text{loss}}$ is $\sim T^3$.

$$P_{\text{loss}} = P_{\text{sample}} - P_{\text{chamber}} \sim (T + \Delta T)^4 - T^4 \sim T^3$$ \hspace{1cm} (3-8)
Figure 3.7 The radiation loss from the sample is proportional to the difference between $P_{\text{sample}}$ and $P_{\text{chamber}}$.

Now let us look at the intrinsic behavior of the lattice thermal conductivity without radiation loss. In general, the phonon-phonon interaction (i.e., the “Umklapp-process” or “U-process”) will lead to a $1/T$ dependence in the lattice thermal conductivity in semiconductors. Following this line, after subtracting the electrical thermal conductivity from the measured data, the remaining can be fitted as $A/T + B*T^3$, which are the lattice thermal conductivity term and the radiation loss term, respectively. After the value of coefficient $B$ is attained by data fitting, the radiation loss term can be removed from the whole temperature range as a radiation loss correction, which is illustrated in Figure 3.8.
Figure 3.8 (a) shows the fitting of the lattice thermal conductivity plus radiation term near room temperature to determine the value of $B$, which is $m_2$ in the insert. (b) Shows the intrinsic lattice thermal conductivity after radiation loss correction in the entire temperature range studied.

To check the validity of this $T^3$ fitting correction for radiation loss, we adopted a different approach by varying the sample surface area $A$. Based on the Stefan-Boltzmann law and Eq. 3-8, the radiation loss is proportional to the surface area $A$. Since the top and bottom surface of the sample is covered by copper block and heater, the surface area $A$ should linearly depend on the length of the sample. A Bi$_2$Te$_3$ sample with a constant cross section is measured twice at different length. We expect the difference between the
results of the two measurements arises from the difference in their radiation loss. In Figure 3.9, a linear X-Y scatter plot of measured thermal conductivity versus sample length is created at specific temperatures. The Y-intercept should be the intrinsic lattice thermal conductivity without any radiation loss, since the radiation loss should be zero when sample length is 0. Finally, the comparison between the data corrected by $T^3$ fitting and by the surface area shrink method are illustrated in Figure 3.10, they agree with each other very well. Furthermore, all these results are confirmed by the result of laser flash measurement above room temperature (section 3.6), a transient measurement technique that is inherently free of radiation loss.
Figure 3.9 (a) shows the different values of lattice thermal conductivity of the sample with different length and (b) shows the linear plot of thermal conductivity vs. sample length at 260K to get the Y-intercept value, which is the intrinsic lattice thermal conductivity.
**Figure 3.10** The comparison of the lattice thermal conductivity data from $T^3$ radiation correction and surface area normalization method, which agree each other very well.

### 3.6 Low Temperate and High Temperature Thermal Conductivity Measurements: an Indicator of Sample Texture

All three thermoelectric properties are tensor in nature and so is $ZT$. For this reason, all three thermoelectric properties should be measured in the same direction or on the same sample, if possible). However, as shown in Figure 3.11, the high temperature thermal
conductivity are measured perpendicular to the SPSed disk, which is along the SPS pressure direction, in contrast, the low temperature thermal conductivity is measured on the rectangle bar cut from the disk with the direction in plane of the disk. For some highly anisotropy thermoelectric materials, such as Bi$_2$Te$_3$, the mismatch in direction of measurement may lead to over-estimated ZT.

**Figure 3.11** The general SPS direction and characterization directions in high and low temperature range.

To check the sample texture (anisotropy) of our SPSed samples, we conduct the following procedure. As shown in Figure 3.12, to measure the thermal conductivity along the disk by laser flash, the disk is cut in rectangle disk A and then cut into rectangle bars
about 8 x 2 x 2mm. First, these bars are stacked together directly by JB Weld®, a high thermal conductive glue, to form disk B. Then, those bars are rotated by 90 degrees and then stacked together by JB Weld to form the disk C. Finally, the small rectangle bar will be measured by our home designed low temperature TC system and the disk A, B, C will be measured by the commercial laser flash for high temperature thermal characterization.

**Figure 3.12** The sample preparation process flow chart for anisotropy study between the low temperate and high temperature thermal conductivity measurements.
As shown in Figure 3.13, for a Bi$_2$Te$_3$ sample SPSed under a high pressure ~ 60 MPa, by comparing the laser flash measurement data of disk A and B, the contribution of the JB Weld® to the thermal conductivity is excluded. By the comparison of the laser flash data between Disk B and C, a discernible mismatch between the high temperature thermal conductivity is observed and the high temperature thermal conductivity data from Disk C matches with the low temperature data pretty well, since they are in the same characterization direction. The observation is well understood in that high SPS pressure can arrange the Bi$_2$Te$_3$ domains in a preferable orientation, which enhances anisotropy.
Figure 3.13 The thermal conductivity as a function of temperature of the 60MPa sample.

(a) High-temperature thermal conductivity behavior of Disk A, Disk B, and Disk C and

(b) the data matchup between high and low temperature measurements$^{33}$. 
3.7 Hall Coefficient Measurement.

From previous discussion in Chapter 1 (shown in Figure 1.4), the thermoelectric power factor may be maximized at specific carrier concentration. So it is important to determine the carrier concentration via of the Hall coefficient.

According to the Lorentz law, a force vector \( \vec{F} \) will be applied on a charge carrier with charge \( q \) and velocity \( \vec{v} \), when it is travelling in a magnetic field \( \vec{B} \), as shown in Eq. 3-9.

\[
\vec{F} = q\vec{v} \times \vec{B}
\]  

(3-9)

This magnetic force will be balanced by the electrostatic force (\( \vec{F} = q\vec{E} \)) that is generated from the deflected electrons that are accumulated at one side of the material. Writing the electric field (\( \vec{E} \)) in terms of the potential difference over the distance and the velocity (\( \vec{v} \)) in terms of the current \( I \) and then equating these two forces gives a result for the voltage \( (V_H) \) that arises due to the Hall effect in terms of the thickness of the material (\( d \)) and the carrier concentration (\( n \)), as shown in Eq. 3-10.

\[
V_H = \frac{IB}{nq\alpha}
\]  

(3-10)

Figure 3.14 schematically shows the Hall effect on a stream of electrons characterized by a current \( I \) passing through a thin layer material with thickness \( d \) in a magnetic field \( B \).

Eq. 3-10 is only valid when the voltage is measured between two points that fall on a line
perpendicular to the flow of current, which must be uniformly distributed through the cross section of the sample.

**Figure 3.14** The deflection of moving electrons in a perpendicular to a magnetic field generates the Hall voltage $V_H$.

**Figure 3.15**, five-point-mount for the Hall coefficient measurement, with a potentiometer to balance the $V$ to be 0 when $B$ is 0.
Figure 3.15 shows that a five-point configuration for the sample mount, where the positive lead for the Hall voltage is replaced by two leads attached parallel to the flow of current. These two leads are connected to the opposite ends of a high precision potentiometer, which can balance voltage to be zero when the magnetic field is zero so any voltage that arises after balance must be strictly due to the Hall effect.

Hall coefficient measurement is conducted in the temperature range of 5 – 300 K, using the configuration shown in Figure 3.15. The Hall voltage $V_H$ was measured as the magnetic field $B$ swept from -0.5 Tesla to +0.5 Tesla while the temperature and current remain constant. Based on Eq. 3-10, the slope of $V_H$ versus $B$, named as Hall coefficient $R_H$, just equals to $I/(ned)$. Then the carrier concentration $n$ can be readily obtained from the slope.

In Summary, several synthesis and characterization techniques for nano-composite thermoelectric materials are presented in this chapter. By using the approaches discussed here, numerous data and analysis are presented in the following chapters. However, the mismatch between high and low temperature measurements due to sample texture (anisotropy) discussed in this chapter is not a significant impact in this project: for FeSb$_2$, thermoelectric properties are mainly studied in low temperature range and half-Heusler possesses a cubic crystal structure.
CHAPTER IV

THERMOELECTRIC STUDY OF FESB$_2$ NANO-COMPOSITE WITH INSB SECONDARY NANO-PHASE$^{35}$

As a narrow-gap, strongly correlated semiconductor, FeSb$_2$ single crystal exhibits a colossal Seebeck coefficient$^{36}$ (on the order of -40000 $\mu$V/K or greater) and a relatively high lattice thermal conductivity$^{37}$ (over 300 W/m-K) at temperatures around 10K. Overall, FeSb$_2$-based materials have shown promising potential for possible thermoelectric cooling applications at cryogenic temperatures. In this project, a series of FeSb$_2$ polycrystalline samples with different amounts of additional Indium were prepared by a quench-and-anneal method followed by spark plasma sintering (SPS) procedure. Then, further microstructuring techniques, such as melt spinning, ball milling, and hot forging are applied to the sample with an optimized composition, which is FeSb$_2$ with 0.5% atomic InSb. The X-ray diffraction (XRD), scanning electron microscopy (SEM) and elemental analysis verified that the InSb nano-inclusions were formed in-situ on the boundaries of coarse FeSb$_2$ grains. The presence of such nano-inclusions and other as-formed multi-scaled microstructures introduced via ball milling can effectively scatter phonons and thus dramatically reduce the lattice thermal conductivity. Furthermore, the electrical properties can be improved because of the “injection” of high mobility carriers from the InSb nano-inclusions.
4.1 Introduction of FeSb$_2$

With an orthorhombic crystal structure$^{38}$ (as shown in Figure 4.1), FeSb$_2$ single crystals are recently reported to exhibit a huge negative Seebeck coefficient $\sim -45000 \mu$V/K (as shown in Figure 4.2) and a record high power factor of $2300 \text{W/K}^2 \text{-cm}$ at about 10K which is 65 times larger than the state-of-the-art Bi$_2$Te$_3$$^{36}$. This record high Seebeck coefficient is still questionable because no other groups repeat this result. Nonetheless, the sharp peak of Seebeck coefficient in FeSb$_2$-based systems is confirmed$^{39,40}$.

Figure 4.1 Crystal structures of FeSb$_2$. Red atoms are Fe and white atoms are Sb. The unit cell is orthorhombic with $a=5.83 \ \text{Å}$, $b=6.54 \ \text{Å}$, and $c=3.20 \ \text{Å}$ and the structure belongs to space group No. 58 (Pnmm)$^{38}$. 
Figure 4.2 The record high Seebeck coefficient of FeSb\(_2\) single crystals are reported by A. Bentien et al., showing the Seebeck coefficient temperature dependence along different direction and under different magnetic field\(^{36}\).

The mechanism underlying this sharp peak in Seebeck coefficient is still under investigation and some theoretical models are proposed, such as strong electron correlation effect. To this end, a semi-quantitative interpretation based on electron diffusion is presented by Peijie Sun et al.\(^{41}\). By comparison between the isostructural homolog RuSb\(_2\) and FeSb\(_2\), phonon drag effect is excluded since the magnitude of the
Seebeck coefficient enhancement is far beyond the limit that can be reached by phonon drag. According to the band structure calculated by A. Bentien et al\textsuperscript{38}, this colossal Seebeck coefficient is possibly caused by the strong electron correlation among the $3d$ electrons of Fe and the conduction electrons of Sb, which results in a huge electron density of state spike near the Fermi level (Figure 4.3). Per Eq. 1-21, this peak in DOS should lead to an enhancement of the Seebeck coefficient.

**Figure 4.3** The density of states $g(\varepsilon)$ of FeSb$_2$ as a function of electron energy $\varepsilon$. The horizontal dotted line represents the Fermi level. The inset shows more details near the Fermi Level\textsuperscript{38}. 
However, the thermoelectric performance of FeSb$_2$ single crystals is limited by its relatively large thermal conductivity, mostly due to the large lattice thermal conductivity $\kappa_l$. In a kinetics model, $\kappa_l = \frac{1}{3} C_V v_s l_p$, where $C_V$ is the specific heat, $v_s$ is the sound velocity, and $l_p$ is the phonon mean free path. The $l_p$ of FeSb$_2$ single crystals is approximately two orders of magnitude larger than the electron mean free path $l_e$ at about 10K$^{41}$. Based on this large difference between the mean-free path of phonons and electrons, we considered that it might be possible to reduce the thermal conductivity by introducing spatially distributed microstructures in order to scatter the propagating phonons while retaining the huge power factor in these materials. This dual purpose approach has been successfully achieved in some thin films$^{42}$ and melt spun materials$^{43}$.

In this project, we were able to form in-situ InSb nano-inclusions on the grain boundaries of FeSb$_2$ matrix. It is expected that InSb, when formed as a nano-sized secondary phase, will induce the desired interface phonon scattering and decrease the lattice thermal conductivity while inject high mobility carriers and thus increase the electrical conductivity simultaneously. Melt spinning, ball milling, and hot forging will be used to form a complex multi-scale nano-composite system to further reduce the thermal conductivity.
4.2 Experimental Procedures.

FeSb$_2$ can be synthesized by several methods$^{36-38}$. Here, according to the Fe-Sb bianray phase diagram$^{22}$ (Figure 4.4), stoichiometric amounts of Fe, Sb (with an additional 3% excess Sb to compensate for the volatile loss during the synthesis process) and Indium powders were mixed and rapidly heated to 1050°C in evacuated quartz tubes, maintained for 2 hours, and subsequently quenched in water to avoid phase separation. High crystallinity FeSb$_2$ phase can be obtained by annealing at 600°C in evacuated quartz.
tubes for two weeks. During the annealing, it was observed that as the Indium content increases, less Sb was found to be deposited on the inner wall of the quartz tube. Finally, the obtained ingots were pulverized and then spark plasma sintered at 620°C for 4 minutes in order to obtain highly densified pellets. We label these samples as sample #1, #2, #3 and #4 with 0%, 0.5%, 1%, and 3% nominal In excess, respectively. The relative densities of the resulting polycrystalline samples after the spark plasma sintering (SPS) process are over 97% of the theoretical density of single crystalline FeSb$_2$. The phase purity of the samples after the SPS process was checked by the X-ray diffraction (XRD). The micro-morphology and chemical composition of the fracture surface of the SPSed samples were checked by field emission scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDX) option. The thermal conductivity, electrical resistivity, and Seebeck coefficient have been measured from 15 to 300K with our custom designed low temperature measurement system$^{30,31}$. The Hall coefficient and heat capacity of all samples were measured with the Quantum Design PPMS.

After the composition optimization of the FeSb$_2$-InSb nano-composite for the highest $ZT$, a further microstructuring tuning upon the annealed ingot is implemented via ball milling, hot forging and melt spinning, respectively. Specifically, sample #5 and #6 are ball milled for 12 hours and 24 hours, respectively, and then SPSed. Sample #7 is synthesized by hot forging at 620 °C, 35 MPa for 30 minutes after the SPS of the annealed sample. For sample #8, melt spinning is first applied to an annealed sample to get the ribbons and then sintered by the SPS. All the SPS conditions in this project are the same, if not otherwise noted.
Figure 4.5 shows the XRD patterns of FeSb$_{2.06-x}$% In (x = 0, 0.5, 1 and 3) samples after the SPS process. In addition to the main FeSb$_2$ phases and extra Sb phase that are indexed, a small trace of InSb phase is detected with the increasing addition of Indium, and is especially evident in samples #3 and #4. Profile analysis on the X-ray powder diffraction patterns shows very similar full widths at half maximum (FWHM) for the
peaks of FeSb$_2$ in all samples, indicating the particle size distribution of FeSb$_2$ grains is practically the same for all samples.

**Figure 4.6** The low magnification SEM images of the cross sections of the samples after SPS.
Figure 4.7 The higher resolution SEM images showing the nano-inclusions.

Figure 4.8 A closer look at nano-structures in sample #1 and #2.
In Figure 4.6, the low magnification SEM photographs of the cross sections of the SPSed samples show that the crystal grains are distributed randomly within the size range of 5–20μm. Higher resolution SEM images are presented in Figure 4.7, showing that (i) uniformly distributed nano-particles with size up to 200 nm, and (ii) increasing Indium addition lead to change of the grain size, shape and distribution for nano-inclusions from sample to sample. In Figure 4.8, two more detailed SEM images for samples #1 and #2 show that the nano-particles are distributed evenly on the crystal boundaries and it is apparent that sample #2 exhibits the finest nano-structures of about 5~10nm.

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**Figure 4.9** The EDX analysis on the sample #1 cross section, with the spectrum from the nano-inclusion and the smooth grain boundary, respectively.

To check the chemical composition of these samples, the EDX analysis was performed on samples #1 and #4. The results are shown in Figure 4.9 and Figure 4.10, respectively.
It should be noted that in sample #1, the nano-particles contain an excess of Sb compared with the background matrix. Although this small fluctuation in Sb content is comparable to the uncertainty of the EDX, we infer that these nano-particles in sample #1 are Sb because of the extra amount of Sb in the starting materials as well as the Sb secondary phase shown in X-ray patterns. In Figure 4.10, the Indium content of the nano-particle in sample #4 is an order of magnitude larger than that of the matrix background, indicating that the nano-particles in sample #4 are Indium rich. Combined with the XRD analysis we can conclude that the InSb nano-particles are formed \textit{in situ} on the boundaries of the FeSb$_2$ grains and the composition of the nano-inclusions is changed from Sb to InSb with an increasing addition of Indium.

![Sample #4](image)

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\textbf{Figure 4.10} The EDX analysis on the sample #4 cross section, with the spectrum from the nano-particle and the background matrix, respectively.
The lattice thermal conductivities of the samples as a function of temperature. The inset shows the thermal conductivities of the InSb single crystals with different carrier concentrations.\(^{42}\)

The lattice thermal conductivities of these samples as a function of temperature are shown in Figure 4.11. The inset shows the thermal conductivity of the single crystal line InSb for comparison. In general, there are three main contributions to the lattice thermal conductivity: boundary scattering, the Umklapp-process of phonon-phonon scattering and mass fluctuation scattering, which dominates at the low, mid and high-temperature ranges, respectively. The low temperature lattice thermal conductivity (at temperatures
below the thermal conductivity peak) does not follow a monotonic trend. The similar particle size distribution of FeSb$_2$ grains should give rise to similar grain boundaries and grain boundary scattering. The difference of lattice thermal conductivity is more pronounced at low temperatures than high temperatures. At low temperatures the lattice thermal conductivity is dominated by long and mid-range wavelength phonons which can be effectively scattered by microstructures above the atomic scale, such as nano-particles, crystal boundaries, and interfaces. Therefore, we assert that the nano-structures should be the primary cause of the change in the lattice thermal conductivity. With more Indium excess, the lattice thermal conductivity first decreases and then increases. The increase of the lattice thermal conductivity can be understood in terms of the large thermal conductivity of the InSb itself\textsuperscript{42}, because more InSb will be formed with more Indium addition. On the other hand, the sharp drop of the lattice thermal conductivity between sample #1 and #2 is instructive, it may arise from the increasing amount of in-situ formed nano-particles residing on crystal boundaries, which can then serve to scatter more phonons. Sample #2 has the lowest lattice thermal conductivity possibly because it possesses the multi-scale nano-structures with a broader size distribution that can effectively scatter phonons over a broader range of wavelengths.

Figure 4.12 shows the electrical transport properties. In Figure 4.12, sample #2 with 0.5% Indium addition shows the lowest electrical resistivity. Figure 4.13 and Figure 4.14 present the Hall carrier concentration and Hall carrier mobility, respectively. With the increasing Indium addition and the carrier concentration will be decreased because (1) the low energy electrons will be scattered by the interfaces and (2) InSb has a lower carrier
concentration comparing with FeSb$_2$. The carrier mobility, however, is enhanced by the formation of InSb. As mentioned above, InSb is known to have one of the largest carrier mobilities among semiconductings$^{15}$. For sample #2, the carrier concentration is not degraded significantly while the carrier mobility is almost doubled, giving rise to the lowest electrical resistivity among all samples.

![Graph showing electrical resistivity versus temperature for different samples](image)

**Figure 4.12** the electrical resistivity as a function of temperature of all the samples
Figure 4.13 the Hall carrier concentrations as a function of temperature of all the samples.

Figure 4.14 the Hall carrier mobility as a function of temperature of all the samples.
Figure 4.15 displays the Seebeck coefficient of all the samples. It is apparent from these results that with the increasing Indium content, the peak of the Seebeck coefficient is first suppressed in samples #2 and #3 but then enhanced in sample #4. This trend is difficult to explain because the Seebeck coefficient of the FeSb$_2$ is anisotropic and very sensitive to sample composition$^{36-38}$. We speculated that the off-stoichiometry and orientations in all the samples may be the cause of the unusual change of the Seebeck coefficients.

![Figure 4.15](image)

**Figure 4.15** the Seebeck coefficients of all the samples as a function of temperature.

Figure 4.16 shows the low temperature heat capacity of the sample #1 with the insert showing the fitting up to 5 K by the Eq. 4-1, where $C_p$ is the heat capacity, $\gamma$ and $\beta$ are the fitting parameters.
\[ C_p = \gamma T + \beta T^3 \]  \hspace{1cm} (4-1)

From the fitting parameter $\beta$, the Debye temperature $\theta_D$ can be calculated as $\sim 328$ K by the Eq. 4-2, where $N$ is the atom number density$^{45}$.

\[ \theta_D = \left( \frac{1944N}{\beta} \right)^{1/3} \]  \hspace{1cm} (4-2)

Based on a mode proposed by David Cahill$^{46}$, the minimum limit of the lattice thermal conductivity is calculated and presented in Figure 4.17, revealing there is still a possibility for further reduction of the lattice thermal conductivity.

**Figure 4.16** the low temperature dependence of the heat capacity of the sample #1 with the insert showing the curve fitting up to 5K.
Based on the theoretical prediction shown in Figure 4.17, additional microstructuring process are applied on the annealed ingot with the composition of FeSb$_2$-0.5% InSb and compared with the thermoelectric properties of sample #2. The detailed sample preparation process flow chart of sample #5, #6, #7 and #8 are shown in figure 4.18. And then all the samples after further microstructuring process are thermoelectrically characterized with SEM images.

![Graph showing lattice thermal conductivity vs. temperature](image)

**Figure 4.17** the theoretical minimum limit for the lattice thermal conductivity of sample #1.
Figure 4.18 The preparation flow chart the preparation of sample #5, #6, #7 and #8.

Figure 4.19 shows the lattice thermal conductivity of all samples after further microstructuring process, comparing with the reference sample #2. The ball milled samples shows a lower lattice thermal conductivity and a longer time ball milling will reduce the lattice thermal conductivity further more. However, after hot forging and melt spinning, the lattice thermal conductivity is surprisingly enhanced, which is inconsistent with the results of microstructuring process in many other materials, such as Bi$_2$Te$_3$\textsuperscript{27, 28}. In the following, an explanation based on the correlation between thermoelectric properties and microstructures is presented with some SEM images.
Figure 4.19 the lattice thermal conductivity of FeSb$_2$ with 0.5% InSb after different microstructuring process.
Figure 4.20 the SEM images of sample #5 fracture surface in different magnification scale.
Figure 4.21 the SEM images of sample #6 fracture surface in different magnification scale.
From Figure 4.20, one can see that there are two types of microstructures formed after 12 Hrs ball milling and SPS. One is the uniformly distributed nano-crystalline grains with size of ~ 400 nm, and the other is the nano-particles ~ 40 nm on the grain boundaries. So after ball milling and SPS, a multi-scale nano-structure is achieved and preferable for scattering wide range of phonons. Similarly, as shown in Figure 4.21, two types of nano-structures are also found in sample #6 that is ball milled for 24 hours, with more finer nano-crystal grains with size of ~ 300 nm, which may be the reason to reduce the lattice thermal conductivity more than sample #5.
Figure 4.22. SEM images of hot forging sample #7 under different magnifications.
In the hot forged sample #7, as shown in figure 4.22, nano-inclusions are still found on the crystal boundaries, however, the matrix crystal re-crystallized during long time hot forging (~30 minutes) and grew up to 40μm, which is not very effective in scattering phonons and thus leads to a higher lattice thermal conductivity.

Figure 4.23 (a) is the SEM images of ribbons after melt spinning and (b) is the fracture surface of sample #8.
As shown in Figure 4.23, unlike the multi phases from amorphous to nano-crystals in Bi$_2$Te$_3$,$^{27,43}$ the melt spun FeSb$_2$ ribbons were found to be single-phased. Since the lattice thermal conductivity of FeSb$_2$ is much higher than the Bi$_2$Te$_3$, this may exceed the quench limit of the melt spinning method, leading to a similar cooling rate on both the contact surface and free surface of the ribbon. After SPS, crystals with uniform size up to 2µm are formed in sample #8. Also it seems there are no nano-particles on the crystal boundaries in sample #8. So after melt spinning and SPS, there is no multi-scale nano-structures formed in sample #8, resulting in the highest lattice thermal conductivity among all the FeSb$_2$ samples.
Figure 4.24 the electrical resistivity of the samples after microstructuring process, with more details shown in the inset.

Figure 4.24 shows the electrical conductivity of sample #2, #5, #6, #7, and #8. The hot forging sample (#7) shows the highest electrical resistivity since more defects and fractions introduced by hot forging can also scatter the electrons effectively. Sample #6 which was ball milled for 24 hours shows the lowest electrical resistivity since the possible off-stoichiometry and carrier concentration variation during stainless steel ball milling.
Figure 4.25 shows the Seebeck coefficient of all the samples after further microstructuring process. Aside from the effects of the composition variations, the trend of the Seebeck coefficient inversely depends on the electrical conductivity, which is shown in Eq. 1-21 and Figure 1.4. Specifically, the sample #6 has the lowest Seebeck coefficient and the highest electrical conductivity.
4.4 Summary

A series of FeSb$_2$-InSb nano-composite samples were prepared by the traditional solid-state reaction method. The in-situ nano-particles residing on the grain boundaries can scatter phonons effectively to reduce the lattice thermal conductivity. They also enhance the electrical conductivity by injecting high mobility carriers. These results exemplified the “phonon glass-electron crystal” approach suggested by Slack.

Based on the theoretical minimum limit prediction of lattice thermal conductivity on the FeSb$_2$ materials, further microstructuring process, such as melt spinning, ball milling and hot forging, are applied on the FeSb$_2$-0.5% InSb samples. Ball milling is proved to be the best approach to combine nano-secondary phase particles with nano-matrix crystals, aiming to achieve a complex multi-scale nano-composite that can reduce the lattice thermal conductivity most efficiently. Melt spinning and hot forging are not effective processes to generate multi scale nano-composites, since the lattice thermal conductivity may exceeds the cooling limit in melt spinning and the crystals re-crystalliz during long time hot forging process.

In summary, we applied three steps to reduce the lattice thermal conductivity for the FeSb$_2$ materials as well as maintaining its power factor: from single crystal to polycrystalline, then to nano-composite and finally to the multi scale nano-composite. The $ZT$ is enhanced dramatically by these microstructuring processes, which is illustrated in Figure 4.26.
**Figure 4.26** $ZT$ values of FeSb$_2$/InSb samples that are synthesized by different microstructuring processes.
CHAPTER V

THERMOELECTRIC STUDY OF HALF-HEUSLER NANO-COMPOSITE WITH INSB SECONDARY NANO-PHASE\textsuperscript{47}.

In this project, multi-scale nano-composite based on secondary InSb nano-phase, is applied to a compositionally optimized half-Heusler compounds, to achieve an enhancement in ZT. We synthesized nano-composite material composed of (TiZrHf)(CoNi)Sb bulk matrix and in-situ formed InSb nano-particles on the grain boundaries through an induction-melting and spark-plasma-sintering (SPS) synthesis process. The amount of InSb nano-inclusions can be qualitatively controlled by varying the In and Sb contents in the starting materials. The effects of the nano-inclusion formation and the matrix-nano-inclusion boundaries on the thermoelectric properties have been characterized and studied. In particular, the electron injection and electron filtering mechanisms introduced by the formation of secondary InSb nano-phase can simultaneously decrease the electrical resistivity, enhance the thermal power and reduce the thermal conductivity. A figure of merit of ZT\textasciitilde0.5 was achieved at 820 K for the sample containing 1\% atomic ratio of InSb nano-inclusions, which is a 160\% improvement over the traditional bulk half-Heusler sample. Then the experimental results are discussed in the context of the effective medium model formerly proposed by Bergman and Fel\textsuperscript{59, 60}.
5.1 Introduction of the Half-Heusler Materials.

Half-Heusler (HH) compounds are intermetallic compounds with the composition of MNiSn\textsuperscript{48,49} and MCoSb\textsuperscript{50,51} (M = Ti, Zr, or Hf) and are considered as a kind of new promising thermoelectric materials in the temperature range around 700 K and above. Based on band structure calculations, many HH systems with 18-valence electrons are narrow band gap semiconductors (E\textsubscript{g}~0.1-0.5eV)\textsuperscript{52}, which will result in a high effective mass and a large thermal power. For instance, the thermal power of TiNiSn, ZrNiSn and HfNiSn compounds are in the range of −200 to −400 \(\mu\)V/K (n-type) near room temperature\textsuperscript{53}, which is higher than that of the state-of-the-art Bi\textsubscript{2}Te\textsubscript{3} compounds\textsuperscript{54}. So, HH compounds have attracted a lot of attentions as a promising candidate material for moderate and high temperature TE power generation applications. However, the performance of the HH compounds is adversely affected by their relatively high thermal conductivity. As for the most widely studied MNiSn and MCoSb (M = Ti, Zr, or Hf) systems, the thermal conductivity is on the order of 10 W/m-K at room temperature\textsuperscript{53}, which is almost 5 times larger than that of commercial Bi\textsubscript{2}Te\textsubscript{3} compounds. Therefore, over last two decades, the main research efforts have focused extensively on significantly decreasing the thermal conductivity of these HH compounds, while simultaneously maintaining their high power factors, \(PF\) (\(PF = \alpha^2\sigma = \alpha^2/\rho\)).
Figure 5.1 the crystal structures of half-heulser compounds with composition of MNiSn and MCoSb\textsuperscript{55}.

As shown in Figure 5.1, the crystal structure of the half-Heuslers is MgAgAs structure\textsuperscript{55}, which consists of three filled and one vacant interpenetrating FCC sub-lattice. The vacant sub-lattice separates the half-Heusler compounds from the Heusler compounds, MNi\textsubscript{2}Sn, which contain an additional Ni FCC sub-lattice.

One of the first steps for enhancing ZT values for all TE materials is to tune the carrier concentration via doping. Because with an increase in carrier concentration, the electrical conductivity $\sigma$ increases and while the Seebeck coefficient $\alpha$ decreases, the power factors (PF = $\alpha^2\sigma$) typically exhibit their highest values at carrier concentrations between $10^{19}$ and $10^{21}$ carriers/cm$^3$, as already been discussed in chapter 1 (shown in Figure 1.4).
HH compounds, due to their specific structural features, it is possible to dope each of the three occupied FCC sub lattices individually for optimizing the carrier concentration. Moreover, significant doping in the HH compounds can also introduce point defects, mass fluctuations and strain field effects that can be favorable to scatter short and mid wavelength phonons, which will significantly reduce the lattice thermal conductivity. In the most widely investigated MNiSn and MCoSb (M = Ti, Zr, or Hf) systems, it is typical to vary the number of charge carriers by doping on Sn and Sb site, and simultaneously introduce disorder by isoelectronic alloying on M site with Ti, Zr and Hf. For example, in the TiNiSn system, doping 1%–5% Sb for Sn can turn the band structure effectively to reduce the resistivity. Furthermore, using isoelectronic doping on the M and Ni sites, e.g., 

$$\text{Ti}_{1-y}\text{M}_y\text{N}_{1-z}\text{R}_z\text{Sn}_{1-x}\text{Sb}_x$$ (M = Zr or Hf and R = Pd or Pt), can significantly lower the lattice thermal conductivity.

Further improvements in the thermoelectric properties of HH compounds are dependent upon new materials design techniques after the composition optimization and nano-structuring approach is one of the most promising approaches. Based on the previous study by W. Xie, a kind of n-type half-Heusler with the optimized composition of 

$$\text{Ti}_{0.5}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Co}_{0.95}\text{Ni}_{0.05}\text{Sb}$$ is chosen as the bulk matrix and the subsequent microstructuring process is applied\textsuperscript{56}.
5.2 Experimental Procedures.

Ingots of Ti$_{0.5}$Zr$_{0.25}$Hf$_{0.25}$Co$_{0.95}$Ni$_{0.05}$Sb alloys, with x = 0, 1, 3 and 7 atomic % of extra In and Sb powders, were prepared by high-frequency induction melting in an argon atmosphere. To ensure homogeneity, all the ingots were melted three times, and then annealed at 773K for 2 days, followed by further annealing at 1123K for 5 days. The ingots were pulverized into powders and then sintered by the spark-plasma sintering (SPS) technique at 1323K for 10 min in order to obtain highly densified disc samples. The density was then determined by an Archimedes’ technique. The relative packing densities of all the samples after SPS were over 98% of the theoretical density. The phase structures, chemical composition and micromorphology of the as-obtained samples were determined by X-ray diffraction (XRD), electron probe microanalysis field emission scanning electron microscopy (SEM with an energy-dispersive X-ray spectroscopy option), high-resolution field emission microscopy (STEM) and transmission electron microscopy (TEM).

The bulk materials were cut into rectangular bars with approximate dimensions of 2 x 2 x 10mm for testing electrical conductivity and Seebeck coefficient by commercial equipment (ZEM-2) under an inert Helium gas atmosphere from 300 to 820 K. The thermal diffusivity was measured by the laser flash method and specific heat was determined by differential scanning calorimetry using a Netzsch® calorimeter. The resulting high-temperature thermal conductivity, $\kappa$, was calculated from the thermal diffusivity, $D$, specific heat, $Cp$, and density, $q$, from Eq. 5-1, as shown below.
Uncertainties in the electrical conductivity, Seebeck coefficient and thermal conductivity measurements are ±5%, ±5% and ±7%, respectively. The uncertainty is in large part from the sample dimension measurement. In order to confirm the results, we performed the electrical conductivity, thermopower and thermal conductivity measurements on the same sample by using our custom-designed low-temperature equipment from 15 to 310 K\(^{30,31}\). The results of the low temperature and high temperature measurements matched pretty well. It is also worth mentioning that in the low-temperature measurements the uncertainty in the cross-section area of the sample is eliminated (since the area cancels out) in the ZT calculation, so the uncertainty of the ZT value is around ±10%. Since the crystal structure of the HH compounds is cubic, the anisotropy from the high temperature thermal conductivity, Seebeck coefficient and electrical conductivity is not considered.

5.3. Results and Discussion.

5.3.1. Phase structure, compositions and micrographs.

Figure 5.2 shows the XRD patterns of bulk Ti\(_{0.5}\)Zr\(_{0.25}\)Hf\(_{0.25}\)Co\(_{0.95}\)Ni\(_{0.05}\)Sb –x% InSb (x = 0, 1, 3 and 7; hereafter named HH-x) samples after SPS. In addition to the indexed half-Heusler phase, small amounts of an InSb phase are detected in the HH-3 and HH-7 samples but not in HH-1 sample.
Figure 5.2 XRD patterns of the Ti$_{0.5}$Zr$_{0.25}$Hf$_{0.25}$Co$_{0.95}$Ni$_{0.05}$Sb –x% InSb nano-composites.
Figure 5.3 SEM and EDX mapping images of sample HH-1.
Scanning electron microscopy (SEM) images and EDX mapping were used to probe the presence of InSb phase in HH-1 sample, and the results are shown in Figure 5.3. The grain size of the half-Heusler matrix in the HH-1 sample is about 5–20µm, and all the elements are distributed in a homogeneous manner. It should be noted that the indium (In) seems to be distributed primarily at the grain boundaries.

Figure 5.4 Microstructures of nano-inclusions for HH-1 (a and b) and for HH-7 (c–e).
The detailed microstructures of the InSb nano-inclusions for HH-1 and HH-7 were observed by field emission SEM, and the images are shown in Figure 5.4. As shown in Figure 5.4(a) and Figure 5.4(b), many nano-particles, with a typical size of 10-30 nm, are evenly distributed at the grain boundaries. Hence the absence of InSb peaks in the XRD pattern of HH-1 sample can be attributed to the small content of inclusions. For sample HH-7, some 10-30 nm nano-inclusions are observed and shown in the inset of Figure 5.4(e); however, as shown in Figure 5.4(d), most InSb inclusions have a typical size of 200-300 nm. It appears that the typical size of InSb nano-inclusions grows rapidly, from 10 to 30 nm for sample HH-1 to 200-300 nm for sample HH-7, as the InSb content increases. The EDX results show that the larger grains are the half-Heusler composition and the nano-particles are an InSb-rich composition. The results of XRD (Figure 5.2), elemental analysis and micrographs corroborate that the InSb nano-inclusions are mainly disseminated around or at the grain boundaries.
Figure 5.5 (a) TEM image of HH-7; (b) high-resolution TEM image of the corresponding area in (a) with an inverse fast Fourier transform of the enclosed area shown in inset; (c) STEM image of nano-inclusions on grain boundary; (d and e) the EDX results of corresponding areas D and E in (c).

The STEM with EDX was utilized to get more detailed structural and compositional information of these nano-inclusions. The high-magnification TEM image inset in Figure 5.5(b) presents two inter planer spacing, of 0.198 and 0.23 nm, which correspond to the
planes (3 1 1) and (2 2 0) of InSb (JCPDS card No. 89-4299). The microstructures and EDX results of the nano-particles are shown in Figure 5.5(c-e). These confirm that the nano-particles contain indium (In), whereas the matrix does not. In view of the structure-physical property correlation, these nano-inclusions distributed around the grain boundaries are expected to influence the electron and phonon transport properties.

5.3.2. Electrical transport properties

The temperature dependence of the electrical conductivity ($\sigma$), the Seebeck coefficient ($\alpha$) and the power factor ($PF=\alpha^2\sigma$) for samples HH-x (x = 0, 1, 3 and 7) are presented in Figure 5.6 to Figure 5.8, respectively. As shown in Figure 5.6(a), the temperature dependence of the electrical conductivity for HH-x (x = 1, 3 and 7) is of a similar trend but with different magnitude, whereas the HH-0 sample behaves very differently. With increasing temperature, the HH-x (x = 1, 3 and 7) samples undergo a semiconductor-to-semimetal (SC-SM) crossover near 460 K, whereas the HH-0 sample exhibits a SM-SC crossover near 700 K. In addition, it is found that the electrical conductivity of HH-x (x = 1, 3 and 7) systematically increases with increasing InSb content at all temperatures. According to the Hall coefficient measurements, this increase is due to an increase of the effective carrier concentration. In fact, the half-Heusler alloys have a high carrier concentration ($10^{20}\text{cm}^{-3}$) and small carrier mobility ($1-10\text{cm}^2\text{V}^{-1}\text{s}^{-1}$), whereas InSb alloys have a low carrier concentration ($10^{17}\text{cm}^{-3}$) and large carrier mobility ($10^4\text{cm}^2\text{V}^{-1}\text{s}^{-1}$). Hence we propose that the high mobility electrons are introduced (electron-injection effect) and the low energy electrons are filtered at the grain boundaries (electron energy
filtering effect) by the *in situ* formation of InSb nano-inclusions. Similar results have been reported for some other thermoelectric nano-composites, such as Yb$_{0.25}$Co$_4$Sb$_{12}$ with Yb$_2$O$_3$ nano-inclusions and In$_{0.2}$Ce$_{0.15}$Co$_4$Sb$_{12}$ with InSb nano-inclusions.

According to the Bergman-Fel model, for a random dispersion of nearly spherical particles of component B (namely, InSb nano-inclusions) in a matrix medium A (namely, half-Heusler compound), the effective electrical and thermal conductivities $\sigma_E$ and $\kappa_E$ and effective Seebeck coefficient $\alpha_E$ can be calculated from the electrical conductivities $\sigma_A$ and $\sigma_B$, the thermal conductivities $\kappa_A$ and $\kappa_B$, and the Seebeck coefficients $\alpha_A$ and $\alpha_B$ of constituents A and B by the following equations.

\[
\sigma_E = \sigma_A + \frac{\phi}{D} \left( \frac{\delta_\sigma}{d_{BA}} + \frac{1-\phi}{3} * \frac{\sigma_A}{d_A} \right) \quad (5-2)
\]

\[
\kappa_E = \kappa_A + \frac{\phi}{D} \left( \frac{\delta_\kappa}{d_{BA}} + \frac{1-\phi}{3} * \frac{\kappa_A}{d_A} \right) \quad (5-3)
\]

\[
\alpha_E = \frac{1}{\sigma_E} \left[ \sigma_A * \alpha_A + \frac{\phi}{D} \left( \frac{\delta_\alpha}{d_{BA}} + \frac{1-\phi}{3} * \frac{\alpha_A \sigma_A}{d_A} \right) \right] \quad (5-4)
\]

Where $\phi$ is the volume fraction of phase B and

\[
\begin{align*}
\delta_\sigma &= \sigma_B - \sigma_A, \\
\delta_\kappa &= \kappa_B - \kappa_A, \\
\delta_\alpha &= \alpha_B \sigma_B - \alpha_A \sigma_A \\
\delta_\alpha &= \frac{\sigma_A \kappa_A}{T} - \left( \alpha_A \sigma_A \right)^2, \\
d_A &= \frac{\sigma_A \kappa_A}{T} - \alpha_A \sigma_A \\
d_{BA} &= \frac{\delta_\alpha \delta_\kappa}{T} - \delta_\alpha \sigma_A
\end{align*}
\]

And
$$D = \left( \frac{\delta_\sigma}{d_{BA}} + \frac{1-\phi}{3} \frac{\sigma_A}{d_A} \right) \times \left( \frac{\delta_\kappa}{T d_{BA}} + \frac{1-\phi}{3} \frac{\kappa_A}{T d_A} \right) - \frac{\delta_\sigma}{d_{BA}} + \frac{1-\phi}{3} \frac{\alpha_A \sigma_A}{d_A}$$ (5-7)

**Figure 5.6** (a) Temperature dependence of the electrical conductivity HH-x nano-composites, with the electrical conductivity of polycrystalline InSb shown in the inset. (b) Results for the calculated effective electrical conductivity for HH-x.
InSb polycrystalline bulk material was prepared according to Reference 61 and the electrical conductivity, Seebeck coefficient and thermal conductivity were measured from 300 to 700 K. Accordingly, the effective electrical conductivities $\sigma_E$ of samples HH-x are calculated using Eq. 4-4 and plotted in Figure 5.6(b). It should be pointed out that the overall trend and magnitude of calculated data are comparable to the measured results shown in Figure 5.6(a).

The Seebeck coefficients of the HH-x samples between 300 and 820 K are plotted in Figure 5.7(a). All the samples containing InSb nano-inclusions exhibit higher values of Seebeck coefficients than that of the sample without InSb (HH-0), with a notably different temperature dependence compared with HH-0 above 700 K. Generally, the Seebeck coefficient of a degenerate material is adversely related to electrical conductivity, as shown in Eq. 5-8 and also as seen in the Figure 1.4. Instructively, this trend is in contrary to what we observed. Based on Eq.1-22, the increased Seebeck coefficient may be attributed to an increased scattering factor $\lambda$, presumably from the potential barrier scattering effect, or named as carrier energy filtering effect$^{62}$. Similar results have been reported in ZrNiSn-based$^{63}$, PbTe-based$^{64}$ and filled skutterudite-based$^{65}$ nano-composite materials.

$$\alpha = \pm \frac{\pi^2 k_B}{3 e} k_B \left\{ \frac{d[\ln (\sigma(E))]}{dE} \right\}_{E=E_F} \quad (5-8)$$
Figure 5.7 (a) temperature dependence of the Seebeck coefficient for as prepared HH-x nano-composites with the insert showing the Seebeck coefficient of polycrystalline InSb. (b) Results for the calculated effective Seebeck coefficient for HH-x.
The effective Seebeck coefficients $\alpha_E$ for the HH-x nano-composites are calculated by Eq. 5-4 and presented in Figure 5.7(b). Unlike the case of the electrical conductivity, the experimental data are very different from those calculated Seebeck coefficient. Since the Bergman-Fel model does not take into account the phase boundary scattering, the difference between the calculated Seebeck coefficient and the measured one may be attributed to some degree to the electron filtering at the matrix-inclusion boundary. On the other hand, one cannot rule out the possibility that the nano-scaled InSb may have different physical properties compared to its bulk counterpart.

From the discussion above, it is plausible to attribute the simultaneous improvement of electrical conductivity and Seebeck coefficient to the combined “electron-filtering” and “electron-injection” mechanisms. The increased Seebeck coefficient and enhanced electron conductivity yield a much improved power factor. As shown in Figure 4.8, the sample HH-1 maintains a PF of $>1.5 \times 10^{-3}$ Wm$^{-1}$K$^{-2}$ at temperatures above 570 K, which is an increase of 100% compared with that of HH-0 sample. For comparison, the Bergman-Fel model also predicts an increased PF (the inset of Figure 5.8), though mainly due to the increased effective electrical conductivity. We note that the results of micro scale Bi-Ag composites reported by Heremans and Jaworski$^{66}$ show excellent agreement with the Bergman-Fel model at room temperature and at low doping concentration. Again, the overall effects of nano-inclusions on the power factor are subject to many factors, such as the concentration, the potential profile inside the bulk matrix and the position of the Fermi level$^{67}$. 

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Figure 5.8 Temperature dependence of the power factor for as prepared HH-x nano-composites. Results of the calculated effective power factor for HH-x are shown in the inset.
Figure 5.9 (a) temperature dependence of the thermal conductivity with the inset showing the calculated value and (b) lattice thermal conductivity with the inset comparing the lattice thermal conductivity of bulk InSb and HH-0 sample.
5.3.3. Thermal transport properties

Figure 5.9 shows the temperature dependence of the total thermal conductivity and the lattice thermal conductivity for all samples. The lattice thermal conductivity, \( \kappa_l \), is estimated from the Eq. 5-9.

\[
\kappa_t = \kappa_e + \kappa_l 
\]  
(5-9)

The Wiedemann–Franz relationship is invoked to estimate \( \kappa_e \) as shown in Eq. 5-10, where the Lorentz number, L, is usually taken as \( 2.0 \times 10^{-8} \, \text{V}^2\text{K}^{-2} \) for degenerate systems.

\[
\kappa_e = L\sigma T 
\]  
(5-10)

As shown in Figure 5.9(b), the \( \kappa_l \) of HH-x compound first is reduced and then increased with an increased amount of InSb nano-inclusions over the temperature range of 300–820K. At mid-range temperatures, \( \kappa_l \) is presumably governed by the phonon-phonon interactions (“Umklapp processes”), leading to a \( 1/T \) dependence, as Figure 5.9(b). The additional decrease in the magnitude of \( \kappa_l \) as compared to that of the HH-0 sample should be due mainly to the enhanced phonon scattering at the matrix-nano-inclusion boundaries. On the other hand, as shown in the insert of Figure 5.9(b), \( \kappa_l \) of InSb is much higher than that of Ti\(_{0.5}\)Zr\(_{0.25}\)Hf\(_{0.25}\)Co\(_{0.95}\)Ni\(_{0.05}\)Sb matrix and may thus be acting as a two-phase composite system that increases the effective thermal conductivity of the nano-composite. For comparison, the effective thermal conductivities, \( \kappa_e \), for the HH-x nano-composites are calculated by Eq.5-3 and presented in the inset of Figure 5.9(a). The calculated
effective thermal conductivity of HH-x is between that of HH-0 and bulk InSb, which obeys Bergman and Fel’s conclusion. With an increase in InSb content, the effective thermal conductivity of HH-x systematically increases. We note that the experimental $\kappa$ and $\kappa_L$ of HH-1 and HH-3 samples fall below the lower bound set by the HH-0 sample. Once again, since the Bergman-Fel model does not take into account the scattering on the phase boundary, this might be due to the enhanced phonon scattering on the matrix-nano-inclusion boundary. As the $\kappa_L$ and $\kappa$ of HH-7 and those of HH-0 sample are very close, it appears that the high $\kappa_L$ and $\kappa$ of the InSb phase have been cancelled out by the phonon scattering at the matrix-inclusion boundaries. We conclude this part of the discussion by saying that for a two-phase system with one nano-phase the thermal conductivity is very complicated and hard to interpret in the context of two-bulk phase model without taking into account the phase interface scattering.

5.3.4. Dimensionless thermoelectric figure of merit ZT

We now proceed to the dimensionless figure of merit, ZT, curves for all samples between 300 and 820K (Figure 5.10). Figure 5.10(b) shows the various properties of the HH samples with InSb nano-inclusions normalized by the corresponding properties of the HH-0 sample. By doing so, we easily show the itemized contributions from $\sigma$, $\kappa$ and $\sigma$ to the improvement of ZT. The largest ZT value of ~0.5 was obtained at 820 K for the HH-1 sample, a 160% improvement over the HH-0 sample.
**Figure 5.10** (a) Temperature dependence of $ZT$ values for as-prepared HH-x nano-composites; (b) resulting enhancement of TE figure of merit at 820 K. The thermoelectric figure of merit $Z$, Seebeck coefficient and thermal conductivity are normalized by the corresponding values of the bulk reference HH-0 (the dot-dashed line in the figure shows where the bulk reference is).
5.4. Summary

(Ti,Zr,Hf)(Co,Ni)Sb-InSb nano-composites were prepared by a high-frequency induction melting method combined with a subsequent SPS process. By the *in situ* formation of InSb nano-inclusions, we have experimentally shown that the Seebeck coefficient, electrical conductivity and thermal conductivity can be tuned somewhat individually, albeit in a small portion of the parameter space. The combined “electron-filtering” and electron-injection” mechanisms help decouple the otherwise interrelated Seebeck coefficient, electrical conductivity and thermal conductivity; meanwhile, the phonon scattering is enhanced at the matrix-nano-inclusion interfaces. Although simultaneous improvement of all three TE quantities was observed in all the samples with nano-inclusions, it is noteworthy that the degree of improvement decreases when the typical size of nano-inclusions becomes larger. In the HH-1 sample, which contains InSb inclusions of typical size 10-30nm, the combination of the aforementioned mechanisms achieve the best improvement in the ZT. The ZT of the HH-1 sample achieved an improvement of 160% over the HH-0 sample.

Future work might be focused on the aspects of optimizing composition and tuning the size of the nano-inclusions to achieve similar results, especially in the inclusion regime <1%. Further modeling study based on the Boltzmann transport theory is highly desirable to quantify the contribution of the grain boundary.
5.5 The Most Recent Updates on the P-typer Half-Heusler Nano-Composite with InSb Nano-Secondary Phase\textsuperscript{68}.

Recently, another project on p-typer half- Heusler nano-composite with InSb nano-secondary phase is conducted\textsuperscript{68} during thesis preparation and will be briefly introduced.

The same nano-composite approach is adopted to the p-type half-Heusler compound Ti(Co,Fe)Sb. The results of resistivity, Seebeck coefficient, thermal conductivity and Hall coefficient measurements indicate that the combined high mobility electron injection, low energy electron filtering and boundary scattering, again, lead to a simultaneous improvement in all three individual thermoelectric properties; enhanced Seebeck coefficient and electrical conductivity as well as reduced lattice thermal conductivity. A figure of merit ZT \(\approx 0.33\) was achieved at 900 K for the sample containing 1.0\% atomic ratio of InSb nano-inclusions, which is a \(~450\%\) improvement over the nano-inclusion-free sample. This represents a rare case that the same nano-structuring approach works successfully for both p-type and n-type thermoelectric materials of the same class, hence pointing to a promising materials design route for higher performance half-Heusler materials in the future and hopefully will realize similar improvement in thermoelectric devices based on such half-Heusler alloys.
Chapter VI

SUMMARIES AND FUTURE WORK

6.1 Summaries

As presented in the above chapters, now I would like to conclude my dissertation as following:

1. In the FeSb$_2$ and half-Heusler nano-composites based on InSb secondary nano-phase, the combination of the carrier energy filtering effect, high mobility carrier injection effect and phonon scattering effect can increase Seebeck coefficient and electrical conductivity as well as reducing the thermal conductivity simultaneously, leading to a dramatically enhanced figure of merit, $ZT$.

2. Among the series of FeSb$_2$-InSb nano-composites, the sample #6 with the composition of FeSb$_2$ and 0.5% atomic of InSb prepared by 24-hour ball milling followed by spark plasma sintering process, shows the largest enhanced $ZT \sim 0.015$ at 35K.

3. Among the series of $n$-type half-Heusler (TiZrHf)(CoNi)Sb nano-composites, the melt pun spark plasma sintered sample #1 with the composition of Ti$_{0.5}$Zr$_{0.25}$Hf$_{0.25}$Co$_{0.95}$Ni$_{0.05}$Sb and 1% atomic of InSb exhibits the largest enhanced $ZT \sim 0.5$ at 800K.
4. As for the FeSb$_2$-InSb nano-composites, further microstructuring processes such as ball milling can form multi-scale microstructures contains nano-crystals and nano-particles on matrix boundaries, which can further reduce the lattice thermal conductivity.

5. As illustrated by sample #8 in the series of FeSb$_2$-InSb nano-composites, melt spinning is not effective to reduce the lattice thermal conductivity for high thermal conductivity materials since more uniform microstructures can be formed after melt spinning. Not all kinds of nano-structures are effective to reduce the lattice thermal conductivity and the multi-scale nano-structures with the length scale comparable to the phonon mean free path are most favorable.

6. Comparing with hot press or hot forging, spark plasma sintering technique can preserve the as prepared nano and micro structures, which is preferable for the synthesis of nano-composite thermoelectric materials.

6.2 Future Work

Although multi-scale nano-composite based on InSb secondary nano-phase is proved to be a promising approach to enhance $ZT$, some future works are still needed and summarized as follow:

1. A more detailed and quantitative model is strongly needed to analyze the relations between the strong electron correlation and the enhancement of Seebeck coefficient.
Especially, the effects of the sample composition on the strong electron correlation need to be further studied and verified.

2. A more detailed and quantitative model about alloy rule is strongly needed to manipulate with the element A, element B and their nano-scale interface, to mathematically describe the behavior of thermoelectric parameters in multi-scale nano-composites.

3. The stability of the secondary nano-phase needs to be verified in nano-composite thermoelectric materials, especially in high temperature range, such as half-Heusler materials.

4. More thermoelectric study of FeSb$_2$ single crystals in ultralow temperature range (0~5K) is still needed for further understanding of the strong correlation effects on thermoelectric properties.

5. The approach of nano-composite synthesis based on InSb secondary nano-phase may be extended and applied to some other antimonide thermoelectric materials, such as BiSb and In$_4$Se$_3$. 
# APPENDIX A

## SYNTHESIS AND CHARACTERIZATION EQUIPMENT DETAILS

<table>
<thead>
<tr>
<th>Name</th>
<th>Model</th>
<th>Manufacturer</th>
<th>Function</th>
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<tbody>
<tr>
<td>ZEM</td>
<td>ZEM-2</td>
<td>ULVAC Technologies, Inc.</td>
<td>Seebeck coefficient and electrical conductivity measurement from room temperature to 1000K.</td>
</tr>
<tr>
<td>Laser flash</td>
<td>LFA 457</td>
<td>Netzsch</td>
<td>Thermal diffusivity measurement from room temperature to 1000K.</td>
</tr>
<tr>
<td>DSC</td>
<td>Pegasus 404C</td>
<td>Netzsch</td>
<td>Heat captivity measurement from room temperature to 1000K.</td>
</tr>
<tr>
<td>XRD</td>
<td>MiniFlex Desktop X-ray diffractometer</td>
<td>Rigaku</td>
<td>X-ray pattern detect and analysis.</td>
</tr>
<tr>
<td>Ball milling</td>
<td>Mixer/Mill 8000M</td>
<td>SPEX SamplePrep.</td>
<td>High energy ball mill to generate nano-size particles.</td>
</tr>
<tr>
<td>SPS</td>
<td>SPS-1050</td>
<td>Sumitomo Coal Mining Co., Ltd</td>
<td>Sample densification.</td>
</tr>
<tr>
<td>Hot press</td>
<td>HP20-4560-20</td>
<td>Thermal Technology Inc</td>
<td>Hot sintering under heating and pressure to from compact disk.</td>
</tr>
<tr>
<td>Box furnace</td>
<td>1500</td>
<td>Barnstead Thermolyne</td>
<td>Heat sample up to 1700K.</td>
</tr>
<tr>
<td>SEM</td>
<td>4800 and 3600</td>
<td>Hitachi</td>
<td>Micro structure observation.</td>
</tr>
<tr>
<td>STEM</td>
<td>HD2000</td>
<td>Hitachi</td>
<td>Micro structure observation.</td>
</tr>
<tr>
<td>TEM</td>
<td>HD9500</td>
<td>Hitachi</td>
<td>Micro structure observation.</td>
</tr>
<tr>
<td>PPMS</td>
<td></td>
<td>Quantum Design</td>
<td>Low temperature physical property measurement</td>
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### APPENDIX B

#### STARTING MATERIAL DETAILS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
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<th>Condition</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Iron</td>
<td>99.5%</td>
<td>pieces</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Sb</td>
<td>Antimony</td>
<td>99.99%</td>
<td>shots</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>In</td>
<td>Indium</td>
<td>99.99%</td>
<td>pieces</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
<td>99.99%</td>
<td>powders</td>
<td>Alfa Aesar</td>
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<tr>
<td>Zr</td>
<td>Zirconium</td>
<td>99.6%+</td>
<td>sponges</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Hf</td>
<td>Hafnium</td>
<td>99.6%</td>
<td>sponges</td>
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<tr>
<td>Co</td>
<td>Cobalt</td>
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<td>pieces</td>
<td>Alfa Aesar</td>
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<tr>
<td>Ni</td>
<td>Nickel</td>
<td>99.99%+</td>
<td>powders</td>
<td>Aldrich Chemical</td>
</tr>
</tbody>
</table>
APPENDIX C

AUTHOR’S PUBLICATION LIST


4) “Identifying the Specific Nanostructures Responsible for the High Thermoelectric Performance of (Bi,Sb)$_2$Te$_3$ Nanocomposites”, Wenjie Xie, Jian He, Hye Jung Kang, Xinfeng Tang, Song Zhu, Mark Laver, Shanyu Wang, John R. D. Copley, Craig M. Brown, Qingjie Zhang, and Terry M. Tritt, Nano-Letter, 10, 3283 (2010).

5) “High-Temperature Thermoelectric Properties of Co$_4$Sb$_{12}$-Based Skutterudites with Multiple Filler Atoms: Ce$_{0.1}$In$_x$Yb$_y$Co$_4$Sb$_{12}”$, JENNIFER GRAFF, SONG ZHU, TIM


9) “Thermoelectric properties and Kondo behavior in indium incorporated p-type Ce$_{0.9}$Fe$_{3.5}$Ni$_{0.5}$Sb$_{12}$ skutterudites”, Pooja Puneet, Jian He, Song Zhu, and Terry M. Tritt, JOURNAL OF APPLIED PHYSICS 112, 033710 (2012).


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