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Investigation of Low Thermal Conductivity Materials with Potential for Thermoelectric Applications

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Investigation of Low Thermal Conductivity Materials with Potential for
Thermoelectric Applications

by

Kaya Wei

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Physics
College of Arts and Sciences
University of South Florida

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Abstract

Thermoelectric devices make it possible for direct energy conversion between heat and electricity. In order to achieve a high energy conversion efficiency, materials with a high thermoelectric figure of merit ($ZT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ is the thermal conductivity) are in great demand. The standard approach is to optimize charge carrier transport while at the same time scatter the heat transport, a task that is easier said than done. Improving the electrical properties in order to increase $ZT$ is limited since electrons also carry heat, among other reasons, resulting in higher $\kappa$ with a higher $\sigma$. Low $\kappa$ materials, whether through complexity or lattice distortion, are therefore of great interest in optimizing the materials’ thermoelectric properties.

In this thesis I will present my investigations on certain material systems that have intrinsically low $\kappa$, materials with cage-like or layer-like crystal structure and complex chalcogenides, as well as investigations on nanostructured bulk chalcogenides in order to further lower the $\kappa$. In addition, unique transport phenomena that can be described as polaronic-type conduction and lone-pair distortion have been observed in certain materials. This too will be extensively described in this thesis.
1

Introduction

Thermoelectric devices allow for the direct conversion of heat into electricity as well as solid-state refrigeration. For example, thermoelectric generators are solid-state energy converters that combine thermal and electrical properties to convert heat into electricity or electrical power into refrigeration. Due to this functionality, thermoelectric devices have moved to center stage in today’s “green technology” debate especially because of the heightened awareness of the environmental impact of global climate change as well as the reduction of all refrigerants. [1] There is currently a large interest in thermoelectric technology.

Additionally, there is clearly a great need for thermoelectric generators in a wide range of applications. Most of the world’s energy is still supplied by the combustion of fossil fuels, the main cause of the CO₂ emissions responsible for climate change. Only a fraction of the energy released by the burning of fossil fuels is converted into mechanical energy or electricity, since most of the energy is “lost” as heat, therefore the new generation of thermoelectric generators could effectively access this largely untapped source of waste heat for conversion into additional electricity. One important application of such technology is for automobiles. As indicated in Figure 1.1 from General Motor, one of several automobile manufacturers with a direct interest in this technology, approximately 40% of the combustion of fuel is wasted. With thermoelectric power generation this “wasted” energy can be “collected” and converted into electrical power to increase
the fuel efficiency of automobiles. Recently, it has been reported that gas consumption can be cut by 5-7% according to the data collected by incorporating thermoelectric devices in the drive train of a BMW 535i vehicle. [2]

Thermoelectric power generation is uniquely valuable in deep space exploration since there are no other solutions for deep space power generation. In addition, as electronic devices for spacecraft have become miniaturized and power needs have decreased, miniature power sources have become more important. A miniature or micro-device such as a sensor, an actuator or electronic components requires milliwatts of power at a few to several tens of volts. As devices shrink power needs also shrink and the development of power conversion devices in which milliwatts are provided with high specific power become important. Thermoelectric power generators can fit this need. Shrinking the size of the thermoelectric elements makes it possible to operate at much lower power with a higher heat flux leading to better performance.

Figure 1.1. Typical energy path for vehicles with gasoline fueled internal combustion engines. Reprinted from Reference 3.
1.1 Thermoelectric Module

A typical thermoelectric module consists of pairs of n and p-type semiconducting segments, or legs, as shown in Figure 1.2. These legs are electrically in series and thermally in parallel so that sufficient heat transport will be carried through the legs by the charge carriers.

As shown in Figure 1.2(a), an electric current passing through the couple results in the transfer of thermal energy via the charge carriers, thus acting as a refrigerator. On the other hand, imposing a thermal gradient across the couple generates a thermoelectric voltage. Sourcing a current through the load, can provide power, as described in Figure 1.2(b). This is the fundamental basis for thermoelectric refrigeration and power generation.

The advantages of thermoelectric refrigeration, the cooling of seats in automobiles for example, include compactness, light weight, no moving parts, low noise and environmental aspects in as much as no refrigerants are required. Other applications such as waste heat recovery and small-scale remote power generation are also of great interest. [1,4-6]

Considerable effort by NASA and other agencies has established radioisotope thermoelectric generator (RTG) as the power source for deep space missions and therefore an integral component of space exploration. The RTGs convert heat, generated by the radioactive decay of plutonium 239, into electricity thus supplying power for all the Cassini and Discovery deep space probes. This technology was used in the Voyager 1 deep space probe that was launched in 1977. It recently passed the edge of the solar system in early 2013.
Figure 1.2. Energy conversion diagrams illustrating thermoelectric (a) refrigeration and (b) power generation. The thermoelectric module is composed of a p-type and an n-type semiconducting material connected electrically in series through contact pads and thermally in parallel between ceramics.
1.2 Thermoelectric Phenomena

The behavior of a thermoelectric circuit is dependent on the Seebeck (S), Peltier (Π), and Thomson coefficients (τ). [1] For a junction made with two dissimilar uniform conductors, S defines the electric potential across the interface of this junction with an established thermal gradient. The Peltier effect refers to the heat generated (or removed) at the junction when a current is made to flow through the junction. [7,8] When the current is flowing and the temperature gradient is forming the heat generation (or absorption) flux rate is described by τ.[4] An understanding of these thermodynamic phenomena allows for the discovery and development of different materials systems that have good thermoelectric properties as well as increases the potential for technological applications. These three thermodynamic phenomena will be described in this section.

By applying a thermal gradient in a uniform conductor, the thermally excited charge carriers on the hot end will diffuse along the concentration gradient to occupy the lower energy states in the cold end, generating a voltage difference (Figure 1.3). The ratio of the voltage developed due to the temperature gradient \( \Delta T \) is related to an intrinsic property of a material defined as the Seebeck coefficient or thermopower, \( S \)[7]

\[
S_{ab} = \frac{\Delta V_{ab}}{\Delta T}.
\]  

(1)

For metals, \( S \) is typically between 1 and 10 \( \mu \text{V/K} \). For semiconductors \( S \) is in the range of \( 10^2 \) to \( 10^3 \) \( \mu \text{V/K} \). In general when electrons are the majority carriers, in n-type semiconductors for
example, a potential difference is generated in the direction of the thermal gradient resulting in a negative $S$. When holes are the majority carriers, in p-type semiconductors for example, a positive $S$ will be observed since the potential is generated in the opposite direction of the thermal gradient.

On the other hand if a current is passed through the junction of two dissimilar materials, depending on the current direction, heat will be reversibly absorbed or rejected at the junction. This is the Peltier effect, discovered a few years after the discovery of the Seebeck effect.[8] The rate of thermal exchange at the junction is given by

$$Q_p = S_{ab} IT = \Pi_{ab} I$$

(2)

where $I$ is the current through the junction at temperature $T$ and $\Pi_{ab}$ is the Peltier coefficient.

Figure 1.3 The Seebeck effect for an isolated metal in a uniform thermal gradient. Electrons (circles) diffuse from the hot end (left) to the cold end (right) leading to an electric field that produces a voltage difference.
While the Seebeck and Peltier effects define the thermoelectric properties observed in the junction between two dissimilar conductors the Thomson effect defines a thermoelectric property of a single material. That is, a current passing through a homogeneous material in a thermal gradient will result in a reversible flow of heat, defined by the Thomson coefficient,[4]

\[ \tau = \frac{1}{I} \frac{dq}{dx} \left( \frac{dT}{dx} \right)^{-1} \]  

(3)

where \( \frac{dq}{dx} \) is the rate of heating per unit length and \( \frac{dT}{dx} \) is the temperature gradient. The equations

\[ \tau_a - \tau_b = T \frac{dS_{ab}}{dT} \]  

(4)

and

\[ \Pi_{ab} = S_{ab} T \]  

(5)

describe the Kelvin relations and relate the three fundamental thermoelectric phenomena to each other, and the link between thermoelectric cooling and thermoelectric power generation.
1.3 Conversion Efficiency and Figure-of-Merit

In general, the ratio of the rate of heat extraction from the source to the rate of expenditure of electrical energy gives the coefficient of performance, for thermoelectric refrigeration, [5]

\[ \phi = \frac{Q_C}{W} = \frac{(S_p - S_n)IT_C - K\Delta T - \frac{1}{2}I^2R}{I[(S_p - S_n)\Delta T + IR]} \].  \hspace{1cm} (6)

\( T_C \) (\( T_H \)) is the temperature of the cold (hot) side, \( \Delta T = T_H - T_C \), \( K \) is the total parallel thermal conductance, and \( R \) is the total series resistance of the couple. In the absence of irreversible effects \( \phi = T_C / \Delta T \), the inverse of the Carnot limit. Similarly the efficiency of a thermoelectric power generator can be defined as

\[ \eta = \frac{W}{Q_H} = \frac{I[(S_p - S_n)\Delta T - IR]}{K\Delta T + (S_p - S_n)IT_H - \frac{1}{2}I^2R} \] \hspace{1cm} (7)

where \( W \) is the power delivered to an external load and \( Q_H \) is positive for heat flow from the source to the sink. The value of \( I \) that maximizes \( \eta \) depends upon the ratio of the cross-sectional area (\( A \)) to the length (\( L \)) of each thermoelectric segment. [1]

These relative dimensions can also be used to optimize the thermoelectric figure of merit for the couple, \( Z = \frac{(S_p - S_n)^2}{RK} \), by minimizing the product of \( RK \):

\[ \frac{L_n A_p}{L_p A_n} = \left( \frac{p_p \kappa_n}{p_n \kappa_p} \right)^{\frac{1}{2}} \].  \hspace{1cm} (8)
The figure of merit, $Z$, then becomes

$$Z = \frac{(S_p - S_n)^2}{\left[\left(\rho_p \kappa_p\right)^{1/2} + \left(\rho_n \kappa_n\right)^{1/2}\right]}.$$  \hspace{1cm} (9)

The efficiency of thermoelectric devices can also be characterized by the dimensionless thermoelectric figure of merit $ZT$,

$$ZT = \frac{S^2 \sigma}{\kappa} T,$$ \hspace{1cm} (10)

where $\sigma$ is the electrical conductivity ($\sigma = 1/\rho$, where $\rho$ is the electrical resistivity) and $\kappa$ is the thermal conductivity. This equation indicates that an ideal material system for thermoelectric applications will be one with good electrical properties (large $S$ and $\sigma$) together with poor thermal conduction (small $\kappa$). Since both of $S$ and $\sigma$ are related to the electrical properties of a material, $S^2 \sigma$ is typically defined as the power factor.

As shown in Figure 1.4, the power factor for semiconductors can be maximized only within a certain carrier concentration range, therefore in order to achieve high $ZT$ values the reduction of $\kappa$ is one approach to increase $ZT$. 
The thermal conductivity is typically understood as the sum of the electronic and lattice contributions,

\[ \kappa = \kappa_E + \kappa_L, \]  

(11)

where \( \kappa_E \) is the electrical thermal conductivity and \( \kappa_L \) is the lattice thermal conductivity.

The electronic component of the thermal conductivity, \( \kappa_E \), can be estimated using the Wiedeman-Franz relation,

\[ \kappa_E = L \sigma T \]  

(12)

where \( L \) is the Lorentz number. \( L \) varies for different materials and with temperature. The ideal Lorentz number can be written as

\[ L = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 \]  

(13)
where $k_B$ is Boltzmann’s constant, and $e$ is the charge of an electron. Since $\sigma$ is proportional to $\kappa$, efforts to reduce $\kappa$ should focus on reducing $\kappa_L$. An approach that has the potential for significantly reducing $\kappa$ for a particular material system is therefore of great interest.

The dominant thermal conduction mechanism in non-metals is typically $k_B$. The development of a theoretical model to understand the behavior of $\kappa_L$ was not simple and required that it be in strong agreement with experimental results. Dulong and Petit specified the high temperature limit to the heat capacity in order to try to describe temperature dependent thermal behavior from a statistical mechanics point of view. [9,10] By employing Planck’s blackbody radiation model Einstein did not obtain good agreement with the known experimental data at low temperatures. [9,10] Eventually Debye developed a method to describe the low temperature limit by modeling solids as an interacting continuous medium. This is different than the Einstein model which considers a solid to be as a series of noninteracting atoms. [9,10]

In the Debye model $\kappa_L$ is given by the integral

$$\kappa_L = \frac{k_B}{2\pi^2 v^3} \left( \frac{k_B T}{v} \right)^3 \int_0^{\theta_D / T} \frac{x^4 e^x}{\tau_C^{-1} (e^x - 1)^2} \, dx \quad (14)$$

where $x = \hbar \omega / k_B T$ is dimensionless, $\omega$ is the phonon frequency, $\theta_D$ is the Debye temperature, $v$ is the speed of sound, and $\tau_C$ is the phonon scattering relaxation time. Considering only the terms with dominant contributions, $\tau_C^{-1}$ can be written as a sum of different specific phonon scattering terms, each defines a particular phonon scattering mechanism. For typical analyses, four different
terms will be used to describe \( \tau C^{-1} \) such that

\[
\tau C^{-1} = \frac{\nu}{L} + A\omega_0^4 + B\omega_0^2 T \exp \left( -\frac{\theta_D}{3T} \right) + \frac{C\omega_0^2}{(\omega_0^2 - \omega^2)^2}
\]  

(15)

where \( L \) is the grain size, \( \omega_0 \) is the resonance frequency, and the coefficients \( A \), \( B \), and \( C \) are fitting parameters. The four terms on the right side of the equation represent grain boundary scattering, point-defect scattering, Umklapp scattering and resonance scattering, respectively. Grain boundary scattering inhibits the low temperature (longest) wavelength phonons. For polycrystalline specimens \( L \) gives an average grain size of the specimen. Point defect scattering is caused by defects or impurities resulting in a decrease in crystal periodicity and thus scatters phonons. The introduction of disorder, such as doping or modifying the atoms’ site occupation, in the crystal structure will also have an affect on \( A \). Umklapp scattering represents the interactions among phonons that tend to restore the phonon distribution to equilibrium. It refers to the interaction of two phonons giving rise to a third which leads to thermal resistance involving powers higher than quadratic in the perturbation Hamiltonian. This thermal resistance results when the total wave vector of this third phonon is greater than the reciprocal lattice.[11] At high temperatures this scattering mechanism is significant as phonon-phonon interactions are common and all phonon modes are excited.[11] The last term in the equation, resonance scattering, is essential for modeling loosely-bound atoms inside a crystal lattice, or soft modes.[9,10]
1.4 Investigation Approaches

Since the discovery of the Seebeck and Peltier effects in 1823 and 1834, respectively, theoretical stage for understanding thermoelectric phenomena has been set. Continuing efforts have been applied to thermoelectric materials research regarding a wide range of applications.[7,8] One early application is for the measurement of temperature. [4,5,7,8] By the late 1950s research on semiconducting thermocouples was underway and semiconducting thermoelectric devices were employed in terrestrial cooling and power generation applications. By the 1990s thermoelectric refrigerators can be purchased at any local department store. Starting around 2000 thermoelectrics were used in automobiles for seat cooling and cooling passengers’ beverages. Each single step of the developing of new thermoelectric devices and applications was the result of effort in thermoelectric materials investigations.

According to the definition of $ZT$, the ideal thermoelectric material will possess good electrical properties together with very poor thermal conductivity, that is, a good thermoelectric material should have thermal properties similar to that of a glass and electrical properties similar to that of a good single-crystal. This describes the Phonon-Glass Electron-Crystal, or PGEC, model. [12] As described by Slack, this model material should have the following features: (a) It should possess “loose” atoms or molecules whose translational or rotational positions are not well defined, possessing two or more metastable positions; (b) there is no long-range interaction between the positions of the “loose” atoms or molecules and (c) the mass of these “loose” atoms or molecules is relative large compared with the total mass of the compound. In addition, disorder produced by point defect scattering cannot lead to glass-like thermal conductivity.
Early studies on thermoelectric materials included three different families of compounds, $V_2VI_3$ compounds (based mainly on $Bi_2Te_3$), $IV-VI$ compounds (based on $PbTe$), and the $IV-IV$ compounds (the SiGe-alloys). [1] The $ZT$ value of these materials is limited to $\sim 1$ at their optimum temperature of operation. Since there is no theoretical limit for $ZT$, [1] materials with better thermoelectric performance can still be expected.

Some of the goals of current thermoelectric materials research include developing new materials that are either able to enhance the efficiency of thermoelectric devices (achieve higher $ZT$) or have the capability of operating at new and broader temperature regimes, particularly at lower temperatures such as $T < 200$ K for cooling applications. In this thesis, as will be discussed in the following chapters, I focus on the fundamental investigations of low $\kappa$ material systems with the potential for thermoelectric application.

Bulk $I_2-II-IV-VI_4$ and $I-II-IV-VI_3$ quaternary chalcogenides have been reported to have the potential for making good thermoelectric devices due to the complex structures associated with intrinsically low thermal conductivities.[13-16] Their different cationic valences provide a means of controlling their Fermi level by adjusting the cation ratios. In addition, the layered crystal structure allows for decoupling of the $\sigma$ from both $\kappa$ and $S$. Both bulk and nanostructured quaternary chalcogenides with different compositions were synthesized. The synthesis and transport properties of each group of compounds will be addressed in Chapter 2 and Chapter 4.

$FeSb_2$ single crystals possess huge $S$ values at cryogenic temperatures,[17-20] however, the thermoelectric performance is restricted due to a large $\kappa_L$. In order to reduce the $\kappa_L$, $FeSb_2$
nanocrystals were synthesized by an ethanol-mediated surfactant-free solvothermal approach and densified by employing spark plasma sintering (SPS). The results of the ability to form polycrystalline bulk materials from SPS processing of solution-phase synthesis of nanocrystals will be discussed in addition to the transport properties of FeSb$_2$ nanocomposites in Chapter 3.

Cage-like crystal structure offers a unique approach to reduce $\kappa$ by filling the cages with loosely bonded “guest” atoms which will rattle inside the cage to scatter phonons. Clathrate compounds have crystal structures built up from three-dimensional framework of cage-like polyhedrons. [21] This material system offers a wide range of compositional modifications. The investigations on a type-II Sn-based compound, K$_8$Ba$_{16}$Ga$_{40}$Sn$_{96}$, is discussed in Chapter 5.

In this thesis, the fundamental investigations of the crystal structure and transport properties of certain material systems will be discussed in details. Since the thermoelectric properties of most of these materials have not been previously investigated, this work is also intended as a new direction in furthering the investigation of low $\kappa$ materials for potential thermoelectric power generation and refrigeration applications.
2
Low Thermal Conductivity Bulk Metal Chalcogenides

As addressed in Chapter 1, in order to achieve high $ZT$ values finding materials with low $\kappa$ is one approach. Certain bulk materials, metal chalcogenides for example, have low $\kappa$ values and are therefore of increasing interest as potential thermoelectric materials.

2.1 Gallium Doped Cu$_2$ZnSnSe$_4$

P-type quaternary chalcogenides have shown good thermoelectric properties mainly due to their relatively low $\kappa$ in addition to the fact that good electrical properties can be achieved by appropriate modification of their compositions.[13-16] Examples include Fe doping resulted in a lower thermal conductivity for Cu$_2$ZnGeSe$_4$, [22] In doping resulted in enhanced electrical conductivity for Cu$_2$ZnSnSe$_4$, [23,24] Cu-excess on the Cd site in Cu$_{2+x}$Cd$_{1-x}$SnSe$_4$, [25] on the Zn site in Cu$_{2+x}$Zn$_{1-x}$SnSe$_4$ [26] and on the Sn site in Cu$_{2+x}$ZnSn$_{1-x}$Se$_4$ [27] resulted in an increase in electrical conductivity as well as a decrease in $\kappa$. In this study I investigated the transport properties of Ga-doped Cu$_2$ZnSnSe$_4$ with and without excess Cu and describe an approach towards enhanced thermoelectric properties as compared with other kesterite compositions.
2.1.1 Synthesis of Gallium Doped Cu₂ZnSnSe₄

The specimens in this study were synthesized by direct reaction of the elements. The Cu powder (99.9%, Alfa Aesar), Zn shot (99.9999%, Alfa Aesar), Ga pellets (99.99999%, Alfa Aesar), Sn powder (99.999%, Alfa Aesar), and Se powder (99.999%, Alfa Aesar) used for synthesizing the materials in this study were loaded into silica ampoules in the atomic ratios shown in Table 2.1. The ampoules were sealed in quartz tubes under vacuum (0.1 Pa), heated to 973 K, and subsequently held at this temperature for five days before they were air quenched to room temperature. The products were then ground into powders, cold pressed into pellets and annealed at 873 K for seven days. The resulting pellets were ground into fine powders (~ 325 mesh) and loaded into graphite dies for hot pressing. Densification was accomplished by hot pressing at 673 K and 160 MPa for 3 hours under N₂ flow. High density polycrystalline specimens (> 96% theoretical density) were obtained after hot pressing, as indicated by measurement of the dimensions and weight of each pressed pellet.

After synthesis, X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) were used to examine the purity, homogeneity, and chemical composition of the specimens. Powder XRD data were collected with a Bruker D8 Focus diffractometer in Bragg-Brentano geometry using Cu Kα radiation and a graphite monochromator. EDS analyses were accomplished with an Oxford INCA X-Sight 7582M equipped scanning electron microscope (JEOL JSM-6390LV). The homogeneity of the specimens was investigated from twelve EDS data sets obtained from random positions across the dense pellet for each specimen. The EDS data were normalized to the Cu content for each specimen in this study. The hot pressed pellets were cut using a wire saw into parallelepipeds for transport measurements and Hall measurements. High temperature \( \kappa \) values were determined.
using the equation $\kappa = D\alpha C_p$, where $D$ is the density, $\alpha$ the thermal diffusivity, and $C_p$ the specific heat. Thermal diffusivity measurements employed the laser flash method in a flowing Ar environment with a NETZSCH LFA 457 system. The uncertainty in the thermal diffusivity measurements was 5%. Heat capacity $C_p (\approx C_v)$ was estimated by the Dulong–Petit limit ($C_v = 3nR$, where $n$ is the number of atoms per formula unit and $R$ is the ideal gas constant). At high temperature this may result in an underestimate of $C_p$ thus affecting $\kappa$, however, it is a relatively good method for comparing the effect of doping and small compositional changes since it eliminates the uncertainties associated with $C_p$ measurements.[28] High temperature $S$ and $\rho$ were measured with an ULVAC ZEM-3 system (experimental uncertainty of 5%–8% for $S$ and $\rho$ at elevated temperatures). Room temperature Hall measurements were conducted on $0.5 \times 2 \times 5$ mm$^3$ parallelepipeds at multiple positive and negative magnetic fields in order to mitigate voltage probe misalignment effects (5% uncertainty).

### 2.1.2 Investigations of Gallium Doped Cu$_2$ZnSnSe$_4$

The indexed powder XRD patterns of the specimens are shown in Figure 2.1. The XRD data for all specimens can be indexed to the kesterite phase (space group $I\bar{4}$), as has been reported previously by neutron scattering employing a similar materials preparation approach [29] as well as other techniques.[30,31]
Figure 2.1. Indexed powder XRD patterns of (a) Cu$_2$ZnGa$_{0.03}$Sn$_{0.97}$Se$_4$, (b) Cu$_2$ZnGa$_{0.05}$Sn$_{0.95}$Se$_4$, (c) Cu$_2$ZnGa$_{0.07}$Sn$_{0.93}$Se$_4$, (d) Cu$_2$ZnGa$_{0.1}$Sn$_{0.9}$Se$_4$, (e) Cu$_{2.1}$Zn$_{0.9}$Ga$_{0.04}$Sn$_{0.96}$Se$_4$, (f) Cu$_{2.2}$Zn$_{0.8}$Ga$_{0.06}$Sn$_{0.94}$Se$_4$, and (g) Cu$_{2.3}$Zn$_{0.7}$Ga$_{0.12}$Sn$_{0.88}$Se$_4$. Reprinted from Reference 32.

Figure 2.2 shows the temperature dependent $\rho$ (a), $S$ (b) and $PF$ (c) of all specimens. Cu$_2$ZnSnSe$_4$ exhibits relatively high $\rho$ and $S$ values as expected for a relatively wide band gap semiconductor.[23,24] $\rho$ and $S$ of the doped specimens increase with increasing temperature indicating thermally activated semiconductor behavior. The positive sign of $S$ for all specimens implies that holes are the dominant carriers (p-type conduction), agreeing with Hall measurements (Table 2.1). The $\rho$ and $S$ values decrease with increasing Ga doping and result in an increase in $PF$ with increasing Ga content. In addition to Ga doping, an excess of Cu further reduced $\rho$, resulting
Figure 2.2. Temperature dependent (a) $\rho$ (plotted in log-linear scale), (b) $S$, and (c) $PF$ of 
$\text{Cu}_2\text{ZnSnSe}_4$ (○), $\text{Cu}_2\text{ZnGa}_{0.03}\text{Sn}_{0.97}\text{Se}_4$ (◇), $\text{Cu}_2\text{ZnGa}_{0.05}\text{Sn}_{0.95}\text{Se}_4$ (▽), $\text{Cu}_2\text{ZnGa}_{0.07}\text{Sn}_{0.93}\text{Se}_4$ (△), $\text{Cu}_2\text{ZnGa}_{0.1}\text{Sn}_{0.9}\text{Se}_4$ (□), $\text{Cu}_2.1\text{Zn}_{0.9}\text{Ga}_{0.04}\text{Sn}_{0.96}\text{Se}_4$ (◇), $\text{Cu}_2.2\text{Zn}_{0.8}\text{Ga}_{0.06}\text{Sn}_{0.94}\text{Se}_4$ (☆), and $\text{Cu}_2.3\text{Zn}_{0.7}\text{Ga}_{0.12}\text{Sn}_{0.88}\text{Se}_4$ (●). Reprinted from Reference 32.
in a significant increase in $PF$. The highest $PF$ corresponds to Cu$_{2.1}$Zn$_{0.9}$Ga$_{0.04}$Sn$_{0.96}$Se$_4$ with a carrier density of $1.72\times10^{21}$ cm$^{-3}$.

Room temperature $\rho$, $S$, carrier concentration, $p$, Hall mobility, $\mu_H$, and effective mass, $m^*$, for all compositions are listed in Table 2.1. Cu$_2$ZnSnSe$_4$ has a direct band gap at the $\Gamma$ point,[33] therefore we estimated $m^*$ based on a single parabolic band model where $S$ and $p$ are given by [1]

$$S = \frac{k_B}{e} \left( \frac{(2 + r)F_{1+r}(\eta)}{(1 + r)F_r(\eta)} - \eta \right)$$

and

$$p = \frac{4\pi(2m_e k_B T)^{3/2}}{\hbar^3} \left( \frac{m^*}{m_e} \right)^{3/2} F_{1/2}(\eta).$$

$r$ is the exponent of the energy dependence of the hole mean free path, $\eta = E_F k_B^{-1} T^{-1}$ where $E_F$ is the Fermi energy) is the reduced Fermi energy, $F_r$ is the Fermi integral of order $r$, [34,35] $m_e$ is the free electron mass and $\hbar$ is the Planck constant. For scattering from lattice vibrations (acoustic phonons) $r = 0$ and for ionized impurity scattering $r = 2$. Due to the high $p$ values for the doped compositions both lattice vibrations and impurity scattering are assumed thus we used $r = 1$ in our estimates of $m^*$. As shown in Table 2.1, with both Ga-doping and excess Cu $\mu_H$ increased from 1.9 cm$^2$V$^{-1}$S$^{-1}$ to 3.1 cm$^2$V$^{-1}$S$^{-1}$ and $m^*$ increased from 0.5 $m_e$ to 2.1 $m_e$. The $\mu_H$ values are comparable to that for In-doping [23,24] while $m^*$ are much larger, with the highest $PF$ among all specimens shown in Table 2.1 being that with the largest $m^*$. 

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Table 2.1. Nominal composition, EDS composition, and room temperature $\rho$, $S$, $p$, $\mu_H$, and $m^*$ of all specimens prepared for this study.

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>EDS composition</th>
<th>$\rho$ (mOhm-cm)</th>
<th>$S$ ($\mu$V/K)</th>
<th>$p$ ($10^{20}$cm$^{-3}$)</th>
<th>$\mu_H$ (cm$^2$V$^{-1}$S$^{-1}$)</th>
<th>$m^*$ (m$e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Cu$_2$ZnSnSe$_4$</td>
<td>Cu$<em>2$Zn$</em>{0.97}$Sn$<em>{0.97}$Se$</em>{3.96}$</td>
<td>1.0x10$^3$</td>
<td>353</td>
<td>0.03</td>
<td>1.9</td>
<td>0.5</td>
</tr>
<tr>
<td>(b) Cu$<em>2$ZnGa$</em>{0.03}$Sn$_{0.97}$Se$_4$</td>
<td>Cu$<em>2$Zn$</em>{1.02}$Ga$<em>{0.02}$SnSe$</em>{3.87}$</td>
<td>9.7</td>
<td>146</td>
<td>2.4</td>
<td>2.7</td>
<td>1.7</td>
</tr>
<tr>
<td>(c) Cu$<em>2$ZnGa$</em>{0.05}$Sn$_{0.95}$Se$_4$</td>
<td>Cu$<em>2$Zn$</em>{1.05}$Ga$<em>{0.05}$Sn$</em>{0.98}$Se$_{3.92}$</td>
<td>7.0</td>
<td>122</td>
<td>3.6</td>
<td>2.5</td>
<td>1.8</td>
</tr>
<tr>
<td>(d) Cu$<em>2$ZnGa$</em>{0.07}$Sn$_{0.93}$Se$_4$</td>
<td>Cu$<em>2$Zn$</em>{1.02}$Ga$<em>{0.06}$Sn$</em>{0.96}$Se$_{3.84}$</td>
<td>6.4</td>
<td>113</td>
<td>5.3</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>(e) Cu$<em>2$ZnGa$</em>{0.1}$Sn$_{0.9}$Se$_4$</td>
<td>Cu$<em>2$Zn$</em>{1.03}$Ga$<em>{0.09}$Sn$</em>{0.92}$Se$_{3.88}$</td>
<td>4.7</td>
<td>103</td>
<td>5.4</td>
<td>2.5</td>
<td>1.9</td>
</tr>
<tr>
<td>(f) Cu$<em>{2.1}$Zn$</em>{0.94}$Ga$<em>{0.04}$Sn$</em>{0.96}$Se$_4$</td>
<td>Cu$<em>{2.1}$Zn$</em>{0.94}$Ga$<em>{0.04}$Sn$</em>{0.97}$Se$_{3.95}$</td>
<td>1.5</td>
<td>57.2</td>
<td>17</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td>(g) Cu$<em>{2.2}$Zn$</em>{0.86}$Ga$<em>{0.06}$Sn$</em>{0.94}$Se$_4$</td>
<td>Cu$<em>{2.2}$Zn$</em>{0.86}$Ga$<em>{0.05}$Sn$</em>{0.96}$Se$_{3.94}$</td>
<td>1.3</td>
<td>54.1</td>
<td>18</td>
<td>2.6</td>
<td>2.1</td>
</tr>
<tr>
<td>(h) Cu$<em>{2.3}$Zn$</em>{0.74}$Ga$<em>{0.12}$Sn$</em>{0.88}$Se$_4$</td>
<td>Cu$<em>{2.3}$Zn$</em>{0.74}$Ga$<em>{0.09}$Sn$</em>{0.93}$Se$_{3.93}$</td>
<td>1.0</td>
<td>45.3</td>
<td>20</td>
<td>3.1</td>
<td>1.9</td>
</tr>
</tbody>
</table>
The temperature dependent $\kappa$ (a) and $ZT$ (b) are shown in Figure 2.3. The $\kappa$ values decrease with increasing temperature without an “upturn” at higher temperatures, indicative of little or no bipolar contribution to $\kappa$ in the measured temperature range for all specimens. Due to higher charge densities the $\kappa$ values increase with increased Ga-doping in the Cu-excess compositions; $\kappa_E$ increasing substantially with decreasing $\rho$. Cu$_2$ZnGa$_{0.05}$Sn$_{0.95}$Se$_4$ resulted in the highest $ZT$ (0.39 at 700 K) among all specimens, as compared with $ZT = 0.25$ at 700 K for In-doping.[23] This could suggest that Ga is more effective in achieving better thermoelectric properties regarding Sn site doping given the fact that Ga is much smaller and lighter compared with Sn than that of In.
In summary of this chapter, Gallium doped Cu$_2$ZnSnSe$_4$ quaternary chalcogenides with and without excess Cu were synthesized by elemental reaction and densified using hot pressing in order to investigate their high temperature transport properties. The $\rho$ and $S$ for these materials decrease with increased Ga-doping while both $\mu_H$ and $m^*$ increase with Ga doping. The $PF$ therefore increases with Ga-doping however the highest $ZT$ (0.39 at 700 K) was obtained for the composition with the lowest $\kappa$. Both Ga-doping and Cu-excess lead to enhanced $ZT$ values as compared with that of Cu$_2$ZnSnSe$_4$; however, this study demonstrated that combining Ga-doping with Cu-excess may not lead to further enhancement of $ZT$. This study suggests an approach for optimizing the thermoelectric properties of these materials and is part of the continuing effort to explore different quaternary chalcogenide compositions and structure types, as this class of materials continues to be of interest for energy-related applications.

### 2.2 PbCuSbS$_3$

Very recently, Skoug and Morelli have shown a correlation between lone-pair electrons ($s^2$ pair in group 15) and $\kappa_{\text{min}}$ (minimal thermal conductivity) in ordered crystalline solids.[36] Electrostatic repulsion between lone-pair electrons of group 15 elements and neighboring chalcogen atoms can produce low $\kappa$ by inducing unusually high lattice anharmonicity. Natural minerals such as tetrahedrites, as well as modified tetrahedrites, possess intrinsically low $\kappa$ due to Sb lone-pair electrons[37,38] and have been considered promising thermoelectric materials. Synthetic materials with crystal structures that possess lone-pair electrons should be distinguishable from other, more commonly bonded materials. This approach has, of yet, not been considered. This section reports
on the synthesis, crystal structure, and thermal conductivity of PbCuSbS₃, a compound with the bournonite crystal structure with low κ attributable to lone-pair electrons.

### 2.2.1 Synthesis of PbCuSbS₃

PbCuSbS₃ was synthesized by conventional solid state reaction from purchased binary compounds PbS (Alfa Aesar, 99.9%), Cu₂S (Alfa Aesar, 99.5%), and Sb₂S₃ (Alfa Aesar, 99.9%).[39] These binary compounds were ground together in the desired stoichiometric ratio before being loaded into a quartz ampoule. This reaction ampoule was sealed in a quartz tube, heated to 843 K and subsequently held at this temperature for 4 days before the furnace was turned off and the reaction tube was cooled to room temperature. The product was then ground into fine powder, cold pressed into a pellet and annealed at 673 K for thirty days to promote homogeneity. For densification into polycrystalline pellets, two were needed for the κ measurements, SPS was employed. The product was ground into fine powder and sieved (325 mesh) inside a nitrogen glovebox before loading into graphite dies. Densification was accomplished at 623 K and 100 MPa for 30 minutes under vacuum. The density of each pellet (~92% of theoretical density) was determined by measurement of their dimensions and weight after polishing the surfaces of the pellets.

Powder XRD data were collected with a Bruker D8 Focus diffractometer in Bragg-Brentano geometry using Cu Kα radiation and a graphite monochromator, and examined by the Rietveld method using the GSAS suite of programs.[40] EDX was employed using an Oxford INCA X-Sight 7582M equipped scanning electron microscope (SEM, JEOL JSM-6390LV). TGA and DTA measurements were carried out with a SDT Q600 (TA instruments) under N₂ flow with the
specimen heated from 293 K to 873 K at a rate of 10 K/min. Temperature dependent steady-state
κ measurements from 12 to 300 K were conducted in a custom radiation-shielded vacuum probe
with an 8 % conservative estimate of the uncertainty.[41] High temperature thermal diffusivity
measurements were made under flowing Ar with an Anter flashline system. The uncertainty in the
thermal diffusivity measurements were approximately 5 %.

2.2.2 Crystal Structure of PbCuSbS₃

Powder XRD data for PbCuSbS₃ before and after SPS consolidation are similar and EDX analyses
confirmed the phase purity. The exact composition was obtained by a combination of Rietveld
refinement and elemental analysis obtained from 12 random positions on each pellet. Thermal
gravimetric analysis (TGA) data indicated a loss of weight at 673 K then weight gain again above
795 K. The main exothermic peak from differential thermal analysis (DTA) results also appears in
this temperature region, at 785 K, corresponding to the melting point of PbCuSbS₃.[42]

Powder XRD indicated single-phase PbCuSbS₃ [43] crystallized in the non-centrosymmetric
orthorhombic phase, space group Pmn₂₁, with two 2a crystallographically independent positions
for lead, one (4b) for copper, two (2a) for antimony, and four (two 2a and two 4b) for sulfur. The
lattice parameters for this orthorhombic structure were first estimated and then refined. The initial
positional parameters for all the atoms in the structure were from previous data after
standardization.[44,45] The observed and calculated XRD pattern and difference profile are given
in Figure 2.4.
Figure 2.4. Powder XRD data for PbCuSbS₃ including profile fit, profile difference, and profile residuals from Rietvelt refinement. Reprinted from Reference 39.

Figure 2.5 shows the crystal structure of PbCuSbS₃. Pb1 is surrounded by 6 S atoms in a highly distorted octahedron (four short bonds, 2.71(2) ~ 3.02(3)Å in length, and two long bonds 3.49(2)Å each) while Pb2 is bounded by 7 S atoms in an irregular shaped geometry (five short bonds, 2.90(3) ~ 3.14(2)Å, and two long bonds 3.39(2)Å each). The short bond distances for Pb1-S and Pb2-S are close to the sum of their ionic radii.[46] The Cu atoms are located in the center of the tetrahedra that are composed of 4 S atoms with one relatively short bond length of 2.22(2)Å and three long bond lengths of 2.34(2) to 2.40(2)Å. Each Sb atom resides at a vertex of the trigonal prism with 3 more S atoms with 2.38(2) to 2.56(3)Å bond lengths. These polyhedra share their vertices and edges to form a three-dimensional network structure.
The bond valence sums and Madelung site potentials were calculated with the program EUTAX [47] with the results listed in Table 2.2. The default values of $R_{ij}$ (Pb-S = 2.55; Sb-S = 2.45; Cu-S = 1.86) for the cation–anion single bonds were used to calculate the bond valence sums. The Madelung potentials were determined by assigning ionic charges for all atoms (Pb$^{2+}$, Cu$^+$, Sb$^{3+}$, S$^{2-}$). The calculated valence sums for an atom in purely ionic compounds are expected to be close to their valence and typically calculated site potentials are approximately −10 times the formal charge of the ion. [48] The calculated Madelung site potentials listed in Table 2.2 indicate that the bond character of the metal-sulfur bonds are close to covalent, rather than ionic, in nature. These
charge valences can also be described as $[\text{Pb}^{2+}][\text{Cu}^+][][\text{Sb}^{3+}][\text{S}^{2-}]$, the bond valence sum, as expected for a closed shell diamagnetic semiconductor.

Table 2.2. Calculated bond valence sums and Madelung site potentials for PbCuSbS$_3$.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Input charge</th>
<th>Bond valence sum</th>
<th>Madelung site potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb1</td>
<td>+2</td>
<td>2.29</td>
<td>-17.6</td>
</tr>
<tr>
<td>Pb2</td>
<td>+2</td>
<td>1.74</td>
<td>-15.6</td>
</tr>
<tr>
<td>Cu</td>
<td>+1</td>
<td>1.16</td>
<td>-13.8</td>
</tr>
<tr>
<td>Sb1</td>
<td>+3</td>
<td>3.07</td>
<td>-24.8</td>
</tr>
<tr>
<td>Sb2</td>
<td>+3</td>
<td>3.34</td>
<td>-24.2</td>
</tr>
<tr>
<td>S1</td>
<td>-2</td>
<td>2.09</td>
<td>17.0</td>
</tr>
<tr>
<td>S2</td>
<td>-2</td>
<td>2.26</td>
<td>17.1</td>
</tr>
<tr>
<td>S3</td>
<td>-2</td>
<td>2.07</td>
<td>17.2</td>
</tr>
<tr>
<td>S4</td>
<td>-2</td>
<td>2.13</td>
<td>18.7</td>
</tr>
</tbody>
</table>

2.2.3 Investigations of PbCuSbS$_3$

The measured low temperature dependent $\kappa$ values of PbCuSbS$_3$ as a comparison to Sb$_2$S$_3$ are shown in Figure 2.6. Sb$_2$S$_3$ was synthesized using the same approach as the PbCuSbS$_3$ specimen. The $\kappa$ values of both specimens decrease rapidly up to 100 K, indicative of Umklapp scattering of phonons typical of crystalline solids. [49] Above 100 K, $\kappa$ decreases gradually with increasing temperature. Over the entire temperature range, the $\kappa$ values of PbCuSbS$_3$ are lower than that of the Sb$_2$S$_3$, indicating additional mechanism in PbCuSbS$_3$ that results in the lower $\kappa$. 
As indicated above, the oxidation states of Pb and Sb in PbCuSbS$_3$ are +2 and +3, respectively. The electron configurations are (Xe core) $4f^{14}5d^{10}6s^2$ for Pb$^{2+}$ and (Kr core) $4d^{10}5s^2$ for Sb$^{3+}$. It is well known that the heavy main group metals, such as Pb, Sb, and Bi, have 2 electrons more than the valence of that group in some compounds, the so-called inert pair effect.[50] Figure 2.7 shows the local coordination environments of Pb and Sb atoms. Obviously, the coordination is one-sided indicating that lone-pair electrons are stereoactive, projecting into the empty part of the coordination geometry. These lone-pair $6s^2$ (for Pb) and $5s^2$ (for Sb) electrons have asymmetric orbitals (stereochemically active) due to intra-atomic $s$-$p$ hybridization. These lone pairs, shown facing “outward” on one side of the metal ions in Figure 2.7, induces distorted coordination
environments with neighboring atoms, as suggested by valence shell electron pair repulsion theory.[51]

Recently it was reported that a relationship exists between the local coordination number (CN) and \( \kappa \) for compounds possessing lone-pair electrons.[36] In order to obtain lower \( \kappa \), the average angle X-M-X (where M is a metal possessing lone pair electrons and X is a neighboring atom) should be very close to 90° for CN \( \geq 6 \), 95–96° for CN = 4 or 5, and > 99° for CN = 3 with \( \kappa \) tending to decrease with an increase of the average angle.[36] In PbCuSbS\(_3\), if one considers only nearest neighbor M-X bonds, the average angles are 96.1° for Pb1, 97.5° for Pb2, 95.3° for Sb1, and 93.4° for Sb2. For Pb, both angles are very close to the value reported to result in low \( \kappa \) in Reference 36. Although the angles for Sb are smaller than that for the CN = 3 criteria, our \( \kappa \) values (0.81 W / m\( \cdot \)K at 300 K and 0.48 W / m\( \cdot \)K at 600 K) are lower than that of the CN = 3 compounds reported in Reference 36.

![Figure 2.7. The coordination environments for the Pb (gray) and Sb (blue) atoms with S (yellow) atoms in the PbCuSbS3.](image)

As a conclusion, PbCuSbS\(_3\) with a noncentrosymmetric orthorhombic crystal structure was prepared by solid state reaction of binary compounds with subsequent consolidation by SPS. The crystal structure and \( \kappa \) were investigated. The structural investigation shows that PbCuSbS\(_3\) possesses two stereochemically active lone-pair electrons (6s\(^2\) from Pb and 5s\(^2\) from Sb) resulting
in low \( \kappa \) values above 200 K. This approach in obtaining low \( \kappa \) materials can be expanded for other compositions, rocksalt-based \( \text{ABX}_2 \) compounds with \( \text{A}=\text{Cu, Ag, Au, Na, K, Rb, Cs} \) as the group I elements, with \( \text{B}=\text{As, Sb, or Bi} \) as the group V elements, and \( \text{X}=\text{S, Se, or Te} \) as the group VI elements for example, \cite{52} allowing for future investigations on materials for phase-change data storage, and thermal barriers applications in addition to thermoelectrics.

Another approach of interest is to synthesize these materials by wet-chemical bottom-up method, an approach that has proven successful for other chalcogenide materials as will be described in Chapter 4, to explore the nano-scale effects in affecting their transport properties as compared to that of the bulk. Considering that doping of thermoelectric materials can readily be accomplished by chemical synthetic approaches, \cite{53,54} and the fact that SPS densification can provide dense polycrystalline thermoelectric materials with nanoscale grains or inclusions, \cite{53-57} future work on the solution phase synthesis approach of these metal-chalcogenides is of particular interests.
FeSb₂ Nanocrystals and SPS Processing

FeSb₂ single crystals possess huge $S$ values at cryogenic temperatures, reported to be due to the existence of a band of itinerant electronic states and a thermally induced spin state transition, [17–19] however, the thermoelectric performance is restricted due to a large $\kappa_L$. Nanostructuring is one approach for reducing $\kappa$ due to increased interface scattering of phonons at the grain boundaries, as demonstrated for many thermoelectric materials systems.[46,58,59] In addition, by introducing interfacial phonon scattering and charge carrier filtering, certain nanostructured thermoelectric materials with nano-scale grains may possess enhanced thermoelectric properties, as compared to that of bulk materials, as well as the potential for broader thermoelectric applications. Fundamental research into nano-scale thermoelectrics materials may also reveal novel phenomena that can be applicable to other technologies.

In this study phase-pure $Pnma$ FeSb₂ nanocrystals with an average size of 30 nm were prepared by an ethanol mediated, low-temperature solvothermal process. [60] New reaction conditions were optimized to achieve better yield and higher purity compared with that of the former study. [61] Employing SPS densification, which will be discussed in detail at the end of this chapter, this work allowed for the preparation of polycrystalline bulk FeSb₂ with uniformly distributed nano-scale grains.
3.1 Synthesis of FeSb₂ Nanocrystals

*Pnnm* FeSb₂ nanocrystals were synthesized using a surfactant and template-free, ethanol-mediated solvothermal process. 8 mmol of iron (II) acetate [Fe (CH₃COO)₂] (97%, Acros Organics) and 8 mmol of antimony (III) acetate [Sb (CH₃COO)₃] (97%, Alfa Aesar) were used as the Fe and Sb sources, respectively. Together with 30 mmol of NaBH₄ (98%, Fisher Chemical) as the reducing agent, the chemicals were dissolved in 70 mL of anhydrous ethanol (99.5%, Acros Organics) inside a custom-designed PTFE vessel. The reactor was then inserted into a custom-designed stainless-steel chamber and sealed before reacting at 493 K for 16 h.

Figure 3.1 shows the optimization process in minimizing the impurities of the product after synthesis. The purity of the phase of FeSb₂ nanocrystals is very sensitive to the purity of the starting chemicals. By attempting with high purity chemicals (from a to b in Figure 3.1) as well as adjusting the solvent concentrations (between b to c in Figure 3.1), the impurities were minimized.

![Figure 3.1. Powder XRD patterns of *Pnnm* FeSb₂ nanocrystals synthesized by a low-temperature solvothermal process with different antimony impurity ratios: (a) 54% Sb impurity, (b) 15% Sb impurity, and (c) less than 1% Sb impurity. Asterisks (*) indicate the Sb impurity phase and pound signs (#) indicate the Fe₃O₄ impurity phase.](image-url)
3.2 Transport Properties of FeSb$_2$ Nanocrystals

Figure 3.2 shows the indexed XRD pattern of the $Pnmm$ FeSb$_2$ nanocrystals as well as that of polycrystalline FeSb$_2$ after SPS consolidation. In all cases the XRD peaks correspond to $Pnmm$ FeSb$_2$. EDS confirmed the stoichiometry for FeSb$_2$.

Figure 2 shows the low-temperature transport properties of the polycrystalline FeSb$_2$ specimens. The data for bulk FeSb$_2$ are in general agreement with that previously reported on polycrystalline FeSb$_2$ specimens.[62] All FeSb$_2$ specimens show an increasing $\rho$ with decreasing temperature from 300 K to 12 K, indicating typical thermally activated semiconductor behavior (Figure 3.3a). Although porosity will affect $\rho$, the difference in $\rho$ between the nanocomposites and the bulk specimen should also be ascribed to the large difference in average grain size between the two specimens.

Figure 3.2. Indexed XRD pattern of (a) $Pnmm$ FeSb$_2$ bulk, (b) nanocomposite specimen I, and (c) nanocomposite specimen II. Asterisks (*) indicate the Fe$_3$O$_4$ impurity phase. Reprinted from Reference 60.
The temperature dependence of $S$ for all specimens is similar (Figure 3.3b). At higher temperatures $S$ is positive then turning negative at lower temperatures, with a maximum ($S_{\text{max}}$) of $-102$ μVK$^{-1}$ and $-100$ μVK$^{-1}$ at 30 K for the two nanocomposites, and $S_{\text{max}} = -181$ μVK$^{-1}$ at 25 K for the bulk specimen. This is in agreement with the Hall concentration (inset to Figure 3.3a) where holes are the majority carriers at higher temperatures and electrons are the majority carriers at lower temperatures. An increase in the number of grain boundaries in the FeSb$_2$ nanocomposites may induce relatively large charge-carrier scattering, thereby reducing $S_{\text{max}}$.[63]

Figure 3.3. Low temperature transport properties of polycrystalline bulk FeSb$_2$ (○), specimen I (△) and specimen II (▽): (a) $\rho$, inset: carrier concentration, $n$ (b) $S$, (c) $\kappa$ and (d) $ZT$. Reprinted from Reference 60.
The effect of grain-size on $\kappa$ is most prominent at lower temperatures (Figure 3.3c). The polycrystalline FeSb$_2$ specimens with nano-scale grains have much smaller $\kappa$ values than that of the bulk polycrystalline FeSb$_2$. This result combined with the fact that $\rho$ is not much higher than that of the bulk, as was previously observed for FeSb$_2$ prepared by bottom-up solution-phase processing, results in an increase in $ZT$ for the nano-grain FeSb$_2$ as compared with that of the bulk (Figure 3.3d).

3.3 SPS Processing

Densification is an important step in obtaining dense polycrystalline specimens. However, a major challenge with densifying nanocrystals or nano-scale powders is in obtaining highly dense specimens while maintaining nano-scale domains or grains. [64]

Nowadays there are three densification techniques that are widely used: cold pressing and annealing, hot pressing, and SPS. Traditional densification processes, cold pressing and annealing and hot pressing for example, involves enhancing the grain-to-grain contact by using static pressure and subsequent sintering of the pressed powders at elevated temperatures in order to obtain dense bulk materials. Relatively long sintering times are often necessary in these processes to densify small grain powders that have a high surface-to-volume ratio. This typically promotes grain growth. In addition, due to the small particle size, nanocrystals have much lower melting
points compared with that of the bulk. This limits the annealing temperature which often results in a poor density.

The “balance” between the long processing times, where grain growth may occur, and the low annealing temperatures, typically leading to low densities, is very difficult for nanostructured materials. This is why SPS is used in the preparation of dense bulk thermoelectric materials with nano-scale domains. During SPS processing, a pulse of direct electric current is applied to our custom-designed tooling, and passes through the specimen (Figure 3.4), so that the specimen is heated both from the inside and outside.[64] This process generates internal localized heating thus allowing for the rapid, low temperature densification of fine-grain powders. Since only the surface temperature of the

![Figure 3.4. (a) A picture of the SPS system in the Novel Materials Laboratory. (b) A simplified diagram showing the die tooling with specimen during SPS densification.](image)
nanopowders rises rapidly by self-heating, grain growth is minimized. The high heating and cooling rate (up to 1273 K/min) shorten the time needed for the whole process, which also makes this process uniquely benefit the densification of nanostructured materials.

For this thesis SPS consolidation was investigated by adjusting the following parameters:

- **PID settings**

  The heating process during SPS densification is controlled by a proportional-integral-derivative (PID) system based on a control loop feedback mechanism. Auto tuning allows for adjustment of the PID controller for a particular set of SPS parameters, as will be described below, resulting in the optimal performance during processing. For example optimization of the PID settings will prevent temperature overshoot during the densification process. It also allows for control of the maximum current intensity.

- **Pulse ratio**

  The SPS power supply outputs a pulsed DC current. The signal “on/off” time, or pulse ratio, directly affects the current density applied to the specimen. In effect, the “off” signal allows the system time to equilibrate to the specimen’s temperature. Since the energy that passes through the specimen is a function of the current density and the current intensity, sufficient signal on time is important in order to generate adequate power for densification. The combination of the PID settings and the pulse ratio allows control of the energy density through the specimen.

- **Holding temperature**
The maximum temperature reached during SPS processing is set to the holding temperature. Typically the higher the holding temperature is the higher the density of the specimen, however, for nanocrystals, this parameter is limited by their low melting point thus optimization of the SPS parameters is most important in densification into polycrystalline nano-scale bulk thermoelectric materials.

- Temperature ramp rate

The temperature ramp rate is a key factor during SPS processing. Increasing the ramp rate increases the energy density. The electronics will then try to adjust the power output (controlled by the PID settings and the pulse ratio) to reach this holding temperature. However, for a given set of SPS parameters, increasing the ramp rate will not result in an increase in energy through the specimen. As a result the specimen’s temperature ramp rate can be lower than that of the set ramp rate. This illustrates why optimization of the SPS parameters, the auto tune process for example, was required before densification of the nanocrystals into polycrystalline bulk materials can begin.

From these SPS tuning studies, FeSb₂ nanocrystals were successfully consolidated into dense polycrystalline pellets with equally distributed nano-scale grains. Similar studies can be applied to other thermoelectric materials in order to develop an understanding of thermoelectric properties as a function of the SPS conditions for different material systems. This can not only lead to more efficient densification processing for other nanostructured or bulk thermoelectric materials but also adequate empirical data that can then be used to model the role of the particle size on electrical and thermal transport.
By introducing interfacial phonon scattering and charge carrier filtering, nanostructured thermoelectric materials with nano-scale grains possess enhanced thermoelectric properties, as compared to that of bulk materials,[25,64,65] as well as the potential for broader thermoelectric applications. Coupled with low-cost processing techniques, this approach offers a new direction for improving thermoelectric technology. In addition, for technological applications, new materials processing approaches are typically needed in order to realize device performance gains from materials achievements in the laboratory. To this end nanocrystal synthetic approaches for quaternary chalcogenides are of interest, for example, for photovoltaics for dispersion by printing or spraying for low-cost thin-film processing [66-69] and for thermoelectrics in order to obtain enhanced thermoelectric performance from nano-scale effects after appropriate consolidation of the nanocrystals into nanostructured bulk materials.[25,64,65]

Recently the synthesis of copper-based quaternary chalcogenides nanocrystals have been reported.[67,70] Here I have developed an approach for the synthesis of Cu$_2$ZnSnQ$_4$ nanocrystals with the stannite crystal structure where Q = S, Se and Te with Ga-doping and Se-Te alloying of the nanocrystals achievable through this approach. In addition, using the same approach I have also synthesized Ag$_2$ZnSnSe$_4$ in order to investigate the low temperature transport properties of the n-type stannite compound Ag$_2$ZnSnSe$_4$ in comparison to that of p-type Cu$_2$ZnSnSe$_4$. 
4.1 Synthesis of Nanostructured Quaternary and Quinary Stannites

The chemicals used in this study were copper (II) acetate monohydrate \([\text{Cu(OOCCH}_3\text{)}\cdot\text{H}_2\text{O}]\) (98%, Alfa Aesar), silver acetate \([\text{C}_2\text{H}_3\text{AgO}_2]\) (99.99%, Sigma-Aldrich), zinc acetate dihydrate \([\text{Zn(CH}_3\text{COO)}\text{)}\cdot\text{2H}_2\text{O}]\) (97%, Alfa Aesar), tin (II) chloride dihydrate \([\text{SnCl}_2\cdot\text{2H}_2\text{O}]\) (98%, Alfa Aesar), sulfur powder (99.5%, Alfa Aesar), selenium powder (99.999%, Alfa Aesar), tellurium powder (99.997%, Sigma Aldrich), gallium pellets (99.99999%, Alfa Aesar) and Oleylamine (80%, Acros Organics). All chemicals were used as received without further purification. In a typical synthesis, 1 mmol of \([\text{Cu(OOCCH}_3\text{)}\cdot\text{H}_2\text{O}]\) or \([\text{C}_2\text{H}_3\text{AgO}_2]\) for the synthesizing of \(\text{Ag}_2\text{ZnSnSe}_4\), 0.5 mmol of \([\text{Zn(CH}_3\text{COO)}\text{)}\cdot\text{2H}_2\text{O}]\), 0.5 mmol of \([\text{SnCl}_2\cdot\text{2H}_2\text{O}]\), 2 mmol Q powder (Q = S, Se and Te) and 15 mL Oleylamine were loaded into a three-neck flask on a Schlenk line. For the Ga doping stannite nanocrystals, 0.05 mmol Ga pellets and 0.45 mmol Sn powder were used instead of 0.5 mmol Sn powder.[71,72] Similarly, 1.8 mmol Se powder and 0.2 mmol Te powder were used in synthesizing Se-Te alloy nanocrystals.

The mixture was kept at room temperature under a \(\text{N}_2\) flow for 10 min followed by degassing under vacuum for 100 min. A dark brown color was observed for all the syntheses during degassing. The solution was then heated to 383 K for 30 min followed by 553 K, the reaction temperature, for another 30 min under \(\text{N}_2\) flow for nanoparticle growth. The flask was then rapidly cooled to room temperature in an ice water bath. Scaling up is possible when all the chemical sources are increased accordingly. A typical ethanol/chloroform mixture was used to wash the products three
times in total then isolated by centrifugation at 9000 rpm for 3 min. The final products were transferred to a vacuum oven for drying before structural and chemical analyses.

Oleylamine is significant in the synthesis of these quaternary stannites as it acts as a surfactant, solvent and reducing agent. [73,74] In the first stage of synthesis, metal acetates and metal chlorides dissolve with Oleylamine at an intermediate temperature, 383 K, to form metal-oleylamine complexes that serve as secondary complex precursors. Later, while the solution is heated to a reaction temperature of 553 K, the nanocrystals begin to form. This metal-oleylamine chemical synthetic approach also shows that doping, and alloy, of quaternary stannites can be readily accomplished.

The as-synthesized products were characterized by XRD, PowderCell (PCW), transmission electron microscopy (TEM, JEOL 2010F transmission electron microscope operated at 200 kV with Cs = 1.0 mm) and EDS. TEM images and electron diffraction patterns were acquired with a Gatan Orius SC200B digital camera while EDS data was collected using an Oxford Instruments INCA EDS system. DTA (TA Instruments, Q600) was used to investigate the thermal stability and dissociation temperature of the nanocrystals.

For Cu2ZnSnSe4 and Ag2ZnSnSe4 SPS densification was carried out at 60 MPa and 583 K for 10 min with a current pulse ratio of 40:5 ms, resulting in phase-pure nanostructured polycrystalline specimens with a density of over 95% of the theoretical density, as determined by measuring the dimensions and mass of the pellets after SPS. The average grain size after densification was approximately 45 nm for Cu2ZnSnSe4 and 65 nm for Ag2ZnSnSe4, as calculated by applying the
Scherrer equation to multiple reflections from the XRD data obtained after densification. [75] After washing the products were clearly in powder-form. In addition, no indication of graphitization was observed on the punch and die after SPS, therefore any remaining surfactants in the specimens after washing was very small and did not affect the transport data. Low temperature transport properties of the two specimens were measured using the same technique described in the previous chapter.

### 4.2 Investigations of Nanostructured Quaternary and Quinary Stannites

Taking $\text{Ag}_2\text{ZnSnSe}_4$ as an example, it is instructive to think of the three-dimensional stannite crystal lattice as being made of two-dimensional $[\text{Ag}_2\text{Se}_2]$ and $[\text{ZnSnSe}_2]$ layers alternating along the crystallographic $c$-axis. The unit cell representation of $\text{Ag}_2\text{ZnSnSe}_4$, shown in Figure 4.1, is composed of two different metal-chalcogenide, $[\text{Ag}_2\text{Se}_2]$ (A) and $[\text{ZnSnSe}_2]$ (B), layers with a stacking order of $\cdots\text{ABAB’AB}\cdots$ along the crystallographic $c$ axis. Layers B and B’ are the same morphologically but B’ is translated relative to B by $\bar{4}$ symmetry along the crystallographic $a$ axis in between $[\text{Ag}_2\text{Se}_2]$ layers. All atoms are surrounded by four other atoms in a tetrahedral coordination environment such that all transition metal atoms are surrounded by four Se atoms and the Se atoms are bounded by four metal atoms (two Ag, one Zn, and one Sn).
Figure 4.1. The crystal structure of Ag$_2$ZnSnSe$_4$. The dotted-dashed lines depict the two different metal-chalcogenide layers composed of [Ag$_2$Se$_2$] and [ZnSnSe$_2$]. Reprinted from Reference 72.

Figure 4.2 shows the indexed powder XRD patterns of Cu$_2$ZnSnS$_4$, Cu$_2$ZnSnSe$_4$, Cu$_2$ZnSnTe$_4$, Ag$_2$ZnSnSe$_4$, Cu$_2$ZnGa$_{0.1}$Sn$_{0.9}$Se$_4$ and Cu$_2$Zn$_{0.8}$SnSe$_{3.4}$Te$_{0.6}$ nanocrystals. The shift in the peak positions implies a difference in lattice parameters among the six specimens. The lattice parameters obtained from the XRD data employing PowderCell are listed in Table 4.1. As expected, the lattice parameters increase with increasing size of the chalcogenide elements. In addition, the decrease in the lattice parameter of Cu$_2$ZnGa$_{0.1}$Sn$_{0.9}$Se$_4$, as compared with that of Cu$_2$ZnSnSe$_4$, can be attributed to a decrease in the unit cell upon substitution of Ga for Sn. Similarly, Te substitution for Se in Cu$_2$Zn$_{0.8}$SnSe$_{3.4}$Te$_{0.6}$ results in a larger lattice parameter as compared with that of Cu$_2$ZnSnSe$_4$. By replacing Ag with Cu the size of the unit cell increases, from 5.67 Å and 11.39 Å (for $a$ and $c$, respectively, lattice constants that are in agreement with that reported previously[34]) to 5.79 Å and 11.45 Å, due to the larger size of the Ag atom compared
Figure 4.2. Indexed powder XRD patterns of (a) Cu2ZnSnS4, (b) Cu2ZnSnSe4, (c) Cu2ZnSnTe4, (d) Ag2ZnSnSe4, (e) Cu2ZnGa0.1Sn0.9Se4 and (f) Cu2.2Zn0.8SnSe3.4Te0.6.
with that of the Cu atom. The bond length of Ag-Se in Ag₂ZnSnSe₄ is longer than that of Cu-Se in Cu₂ZnSnSe₄ [77] and results in a lowering of the energy level of the valance band maximum (VBM) which results in a larger band gap as will be discussed later in this chapter.

HRTEM images and EDS spectra of the quaternary stannites nanocrystals are shown in Figures 4.3(a), (b), (c) and (d). Both low and high resolution TEM analysis indicates that the nanoparticles are spherical with an average size of 20 ~ 50 nm. This result is consistent with that calculated from XRD employing the Scherrer equation. The uniform contrast and diffraction patterns of the individual nanoparticles indicate that each nanoparticle is a single crystal. As indexed in the diffraction patterns all specimens appear to grow in the (112) basal plane direction. The (112) plane has the lowest surface energy among the crystallographic planes as the <112> diagonal is the longest distance in the tetragonal structure these quaternary stannites share.[78]

Table 4.1. Compositions, lattice parameters and particle sizes of Cu₂ZnSnS₄, Cu₂ZnSnSe₄, Cu₂ZnSnTe₄, Ag₂ZnSnSe₄, Cu₂ZnGa₀.₁Sn₀.₉Se₄ and Cu₂.₂Zn₀.₈SnSe₃.₄Te₀.₆.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Composition</th>
<th>Lattice parameter ((a, \text{Å}))</th>
<th>Lattice parameter ((c, \text{Å}))</th>
<th>Particle size from XRD (nm)</th>
<th>Particle size from TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Cu₂ZnSnS₄</td>
<td>5.4335(2)</td>
<td>10.7743(2)</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>(b)</td>
<td>Cu₂ZnSnSe₄</td>
<td>5.6748(2)</td>
<td>11.3866(2)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>(c)</td>
<td>Cu₂ZnSnTe₄</td>
<td>6.1852(3)</td>
<td>12.0800(3)</td>
<td>49</td>
<td>50</td>
</tr>
<tr>
<td>(d)</td>
<td>Ag₂ZnSnSe₄</td>
<td>5.7932(2)</td>
<td>11.4503(2)</td>
<td>38</td>
<td>40</td>
</tr>
<tr>
<td>(e)</td>
<td>Cu₂ZnGa₀.₁Sn₀.₉Se₄</td>
<td>5.6719(2)</td>
<td>11.3828(2)</td>
<td>29</td>
<td>30</td>
</tr>
<tr>
<td>(f)</td>
<td>Cu₂.₂Zn₀.₈SnSe₃.₄Te₀.₆</td>
<td>5.6941(2)</td>
<td>11.3318(2)</td>
<td>32</td>
<td>30</td>
</tr>
</tbody>
</table>
The fact that facets are more willing to form on the particle surfaces to increase the number of the low-symmetry planes contribute to such directional-growth behavior.[61,78] Figure 4.1(e) shows the (112) projection plane view of Cu$_2$ZnSnTe$_4$ as an example. In Figure 4.3(f), the unit cell of Cu$_2$ZnSnTe$_4$ is oriented such that it is perpendicular to the [112] direction. The dash-dotted lines represent planes where the metallic elements (Cu, Zn and Sn) are located in the structure while the dotted lines refer to the planes where the chalcogenide elements are occupying. From DTA measurements the decomposition temperatures of Cu$_2$ZnSnS$_4$, Cu$_2$ZnSnSe$_4$, Cu$_2$ZnSnTe$_4$, and Ag$_2$ZnSnSe$_4$ are 733 K, 743 K, 833 K, and 638 K respectively. It was reported that Ag$_2$ZnSnSe$_4$ ($\Delta H_r = -28.6$ kJ/mol) is easier to decompose than Cu$_2$ZnSnSe$_4$ ($\Delta H_r = -84.1$ kJ/mol).[77] Due to the similarity in morphologies the Cu$_2$ZnSnQ$_4$ nanocrystals share, their different decomposition temperatures are presumably due to the different chalcogenide elements. In addition, the small particle size results in a lower decomposition temperature than that of the bulk.[79,80]
Figure 4.3. TEM, HRTEM, and electron diffraction images of (a) Cu₂ZnSnS₄, (b) Cu₂ZnSnSe₄ and (c) Cu₂ZnSnTe₄ (d) Ag₂ZnSnSe₄ with the (112) plane indexed. The unit cell of Cu₂ZnSnTe₄ oriented in the (e) (112) projection plane view and (f) (110) projection plane view. The dash-dotted lines represent planes occupied by the metal elements (Cu, Zn and Sn) and the dotted lines refer to the planes occupied by the chalcogenide elements.

Figure 4.4 shows the HRTEM images, EDS spectra analyses of (a) Cu₂ZnGa₀.₁Sn₀.₉Se₄ and (b) Cu₂₂Zn₀.₈Sn₀.₄Te₀.₆. The same colloidal synthesis conditions resulted in the same spherical shapes as well as the same average particle size for the Ga-doping and Se-Te alloy nanocrystals. Similar with Cu₂ZnSnQ₄ nanocrystals, the HRTEM and EDS analyses both agree that each
nanoparticle of the two specimens is a single crystal. (112) selective growth has been observed in both the doping and alloy nanocrystals as expected. The slightly smaller d-spacing compared with that before doping suggests the accomplishment of the doping attempt. EDS also confirms the doping and alloy contents. The detected composition is very close to the starting element ratio, indicating the reliability of this chemical synthetic approach in growing quaternary stannite nanocrystals with doping and/or alloy contents. While doping is one approach for optimum carrier concentrations, and possible enhancement in a variety of applications, [25,53,70] the ability to process alloy nanocrystals offers additional research as well as applications possibilities. It is therefore of great interest to explore further the potential nanoscale quaternary and quinary chalcogenides possess.

Figure 4.4. TEM, HRTEM, and electron diffraction images and EDS analyses of (a) Cu$_2$ZnGa$_{0.1}$Sn$_{0.9}$Se$_4$ and (b) Cu$_{2.2}$Zn$_{0.8}$SnSe$_{3.4}$Te$_{0.6}$. Reprinted from Reference 71.
4.3 Transport Properties of Cu$_2$ZnSnSe$_4$ and Ag$_2$ZnSnSe$_4$

The low temperature $\rho$ and $S$ of the nanostructured polycrystalline bulk Cu$_2$ZnSnSe$_4$ and Ag$_2$ZnSnSe$_4$ are shown in Figure 4.5. Room temperature Hall data indicates p-type conduction for Cu$_2$ZnSnSe$_4$ and n-type conduction for Ag$_2$ZnSnSe$_4$. For Cu$_2$ZnSnSe$_4$ (Figures 4.5(a) and (b)), $\rho$ and $S$ increase with increasing temperature, with room temperature $\rho$ and $S$ values in strong agreement with that of previous results on nanostructured Cu$_2$ZnSnSe$_4$ [81] while the room temperature values for bulk are 1000 mOhm-cm and 352 µV/K, [26] respectively. This degenerate semiconductor behavior has also been observed at higher temperatures. [81]

Figure 4.5(c) shows that $\rho$ of Ag$_2$ZnSnSe$_4$ exhibits a large anomalous peak at 160K. The temperature dependent $S$ values for Ag$_2$ZnSnSe$_4$ (Figure 4.5(d)) also suggests an anomalous temperature-dependent behavior in the region of the “resistive” peak. This type of transport has been previously described by a two-component model whereby polaronic-type charge carriers are presumed to be composite polarons consisting of electrons surrounded by phonons[82] and/or magnons[83]. Eu chalcogenides,[83,84] colossal magnetoresistance compounds,[85] and Ag-doped ZnO,[86] whose carriers are primarily magnetic polarons, pentatellurides (e.g., ZrTe$_5$ and HfTe$_5$),[87] whose carriers are lattice or dielectric polarons, and SrTiO$_3$ films,[88] whose polarons are affected by electrons and vacancies, all display similar temperature dependent transport. In the case of Ag$_2$ZnSnSe$_4$ the strong electron-phonon interaction may cause self-trapping of electrons that forms a conducting band at low temperatures.[83] The coherent excitation band formed by polarons grows narrower as the temperature increases thereby increasing $\rho$ until reaching a
Figure 4.5. Temperature dependent $\rho$ and $S$ of Cu$_2$ZnSnSe$_4$, (a) and (b), and Ag$_2$ZnSnSe$_4$, (c) and (d), respectively. Solid lines are fits using the two-component model as described in the text. Reprinted from Reference 72.

maximum value while at higher temperatures the polarons become less coherent due to absorption and inelastic emission of phonons resulting in a decrease in $\rho$ with increasing temperature.[82,87] The zero crossing of $S$ correlates very well with the peak position in the $\rho$; with further decreasing temperature $S$ drops dramatically. In addition, the decreasing $dS/dT$ values below 100K implies the existence of a negative peak at lower temperatures, as is the case for polaronic materials.[82]

The solid lines in Figure 4.5 are theoretical fits to the data using the two-component model where $\rho$ and $S$ can be expressed as[82,83]

$$\rho(T) = \left[ \frac{f(T)}{\rho_{lt}(T)} + \frac{1-f(T)}{\rho_{ht}(T)} \right]^{-1}$$

(18)

$$S(T) = [f(T)] \times [-cT] + [1-f(T)] \times [S(\infty)]$$

(19)
where $\rho_{lt}$ is the low-temperature itinerant-carrier $\rho$, $\rho_{ht}$ is the high-temperature localized-carrier $\rho$, $f(T)$ is the fraction of the carriers that are in a metallic state, and $c$ and $S(\infty)$ are constants determined by the $S$ data. $\rho_{lt}$, $\rho_{ht}$, and $f(T)$ can be further expressed as

$$\rho_{ht}(T) = A_{\rho}^* T^* \exp\left(\frac{E_{\rho}}{kT}\right)$$  \hspace{1cm} (20)$$

$$\rho_{lt}(T) = B_{\rho}^* T^2$$  \hspace{1cm} (21)$$

$$f(T) = \left\{\exp\left[\frac{(T-T_0)}{\Delta}\right]+1\right\}^{-1}$$  \hspace{1cm} (22)$$

where $T_0$ is the temperature where the “resistive” peak appears and $A_{\rho}$, $E_{\rho}$, $B_{\rho}$, and $\Delta$ are fitting parameters. From our fit to the data, Figures 4.5(c) and (d), $A_{\rho}= 130.5$, $E_{\rho}/k = 1745$ K, $B_{\rho} = 2 \times 10^5$, $T_0 = 160$ K, $\Delta = 3.3$ K, $c = 0.48$, and $S(\infty) = -420$. The relatively large $A_{\rho}$ and $B_{\rho}$ values suggest a strong polaron effect. The value obtained for $E_{\rho}$, the polaron activation energy, is similar to that reported for LaMnO$_3$ ($E_{\rho}/k = 1276$ K) [89] which has been shown to have a strong adiabatic hopping of polarons, and is consistent with large $A_{\rho}$ and $B_{\rho}$ values. The small transition width, [82,83] $\Delta$, value is inferred by the sharp “resistive” peak while the ratio of the number of carriers to the number of sites, $c$, [83] indicates the polaron “band” to be about half full. $S(\infty)$ indicates the $S$ value at temperatures high enough to release all the polarons from their trapped sites. For Ag$_2$ZnSnSe$_4$ it is room temperature as suggested from Figure 4.5.

Figure 4.6 shows the $\kappa_L$ for both specimens. Employing the Wiedemann-Franz relation $\kappa_E$ can be estimated from Figures 4.5(a) and (c) by the equation $\kappa_E = L_0 \sigma T$ with $L_0$ being the Lorenz number, however, due to the relatively high $\rho$ values $\kappa_L$ is the dominant contribution to $\kappa$ in both specimens regardless of the $L_0$ value(s) used in estimating $\kappa_L$. The solid lines in Figure 4.6 are theoretical fits to the data using the Debye approximation as described in Equation (14) in Chapter 1. In our fits we use $\theta_D = 302$ K and $v = 2861$ m/s, values reported for Cu$_2$ZnSnSe$_4$ [90] since no such data is
available for Ag$_2$ZnSnSe$_4$. The parameter $\tau^{-1}$ was also been described in Chapter 1, however, since there is no loosely bound “filler” involved in the stannite-type crystal structure Equation (15) becomes

$$\tau_C^{-1} = \frac{\nu}{L} + A \omega^4 + B \omega^2 T \exp\left(-\frac{\theta_D}{3T}\right).$$  \hspace{1cm} (23)

Assuming three dominant phonon scattering mechanisms in the measured temperature range, the terms in Equation (23) represent grain boundary scattering, point defect scattering, and Umklapp scattering, respectively. The fitting parameters are listed in Table 4.2 and were uniquely defined using a minimization of the best sequence fit function compared to the data. The parameters shown in Table 4.2 yielded results with very strong agreement with the experimental data.

Figure 4.6. Temperature dependent $\kappa$ of Cu$_2$ZnSnSe$_4$ (square) and Ag$_2$ZnSnSe$_4$ (circle). The solid lines are theoretical fits to the data using the Debye approximation. The star represents data for bulk Cu$_2$ZnSnSe$_4$. [26] Reprinted from Reference 72.
Table 4.2. Values of the $\kappa_L$ fit parameters for Cu$_2$ZnSnSe$_4$ and Ag$_2$ZnSnSe$_4$.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>L (nm)</th>
<th>$A \times 10^{-43}$ s$^3$</th>
<th>$B \times 10^{-18}$ s K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$ZnSnSe$_4$</td>
<td>45</td>
<td>179</td>
<td>13</td>
</tr>
<tr>
<td>Ag$_2$ZnSnSe$_4$</td>
<td>76</td>
<td>215</td>
<td>21</td>
</tr>
</tbody>
</table>

The average grain size, $L$, are in good agreement with that calculated from the XRD data obtained after SPS densification. At low temperatures, below 70K, the larger average grain size of the Ag$_2$ZnSnSe$_4$ specimen, as compared with that of the Cu$_2$ZnSnSe$_4$ specimen, results in higher $\kappa_L$ values. Parameter $A$ which represents the point defect scattering is larger for the Ag$_2$ZnSnSe$_4$ specimen than that of Cu$_2$ZnSnSe$_4$. This is likely due to the fact that Ag is much heavier and larger than Cu, and may be the reason for the lower $\kappa_L$ values for Ag$_2$ZnSnSe$_4$ than that for Cu$_2$ZnSnSe$_4$ above 70K. The probability of anharmonic phonon scattering may however increase for Ag$_2$ZnSnSe$_4$ compared with that of Cu$_2$ZnSnSe$_4$ as implied by the larger fitting parameter $B$. The calculated Grüneisen parameter for Cu$_2$ZnSnSe$_4$ has been reported to be 2.37 at 300 K [91] while for Cu$_2$ZnGeSe$_4$ the Grüneisen parameter has been experimentally reported to be 0.8. [92] In any case, no information is available on the Grüneisen parameter for Ag$_2$ZnSnSe$_4$, to the best of my knowledge. The star in Figure 4.6 denotes room temperature $\kappa_L$ of bulk Cu$_2$ZnSnSe$_4$.[26] The $\kappa_L$ values for the nanostructured Cu$_2$ZnSnSe$_4$ are much lower than that of the bulk, as expected due to the significant grain boundary phonon scattering.[1,64,81] As a result, the room temperature $ZT$ value of nanostructured Cu$_2$ZnSnSe$_4$, 0.02, is higher than that of the bulk, 0.001. For Ag$_2$ZnSnSe$_4$ $ZT = 2 \times 10^{-7}$ due to its poor conductance as suggested by the extremely high $\rho$ values.
Nanostructured PbCuSbS₃ was synthesized using a similar technique as that used for the stannite nanocrystals. [93] Lead (IV) acetate [Pb(CH₃CO₂)₄] (95%, Sigma-Aldrich), copper (II) acetate monohydrate [Cu(OOCCH₃)·H₂O] (98%, Alfa Aesar), antimony (III) chloride [SbCl₃] (99.99%, Sigma-Aldrich), sulfur powder (99.5%, Alfa Aesar) and Oleylamine (80%, Acros Organics) were used as chemical sources. All chemicals were used as received without further purification. In a typical synthesis, 1 mmol of Pb(CH₃CO₂)₄, 1 mmol of Cu(OOCCH₃)·H₂O, 1 mmol of SbCl₃, 3 mmol S powder and 40 mL Oleylamine were loaded into a three-neck flask on a Schlenk line. The mixture was kept at room temperature under a N₂ flow for 10 min followed by degassing under vacuum for 100 min. A dark brown color was observed during degassing. The solution was then heated to 383 K for 30 min to dissolve all constituent reactants followed by heating to 553 K. Three separate syntheses were carried out and differ in the dwell time at 280 °C with lengths of 5 min, 20 min, and 60 min. The dwell time was varied as a means of controlling the particle size of the final product, as will be discussed below. The flask was then rapidly cooled to room temperature in an ice water bath.

In a typical synthesis the total yield is approximately 0.3 g (40 % of the starting chemical weight). Scaling up to larger batch sizes is possible by proportionally increasing all chemical sources, however much larger batch sizes will presumably necessitate modifications and further optimization of this process. A typical ethanol/chloroform mixture was used to wash the products.
three times before the product was isolated by centrifugation at 9000 rpm for 3 min. The final products were transferred to a vacuum oven for drying prior to structural and chemical analysis.

Indexed XRD pattern of 200 nm PbCuSbS$_3$ after synthesis is shown in Figure 4.7. In the first stage of the synthesis, metal acetates and metal chloride dissolve in Oleylamine at an intermediate temperature, 383 K, to form metal-oleylamine complexes that serve as secondary complex precursors.[73,74] Later, while the solution is heated at 553 K, PbCuSbS$_3$ crystals begin to form. 200 nm crystal size makes the small peaks visible, not the case for smaller sizes.

HRTEM and electron diffraction images are shown in Figure 4.8. TEM analyses indicate a plate-like morphology, HRTEM analyses indicate lateral facets corresponding to (030) planes (0.289 nm d-spacing).[44] and the uniform electron diffraction patterns indicate a high degree of crystallinity.

![Indexed XRD pattern of 200 nm PbCuSbS$_3$. Reprinted from Reference 93.](image)
The data of room temperature UV-Vis spectrum of 200 nm PbCuSbS3 are shown in Figure 4.9, suggesting an optical band-gap of 1.3 eV, a value similar to that reported for mineral bournonite (1.24 eV), [94] polycrystalline PbCuSbS3 (1.27 eV), [94] and PbCuSbS3 single crystals prepared by a modified zone-melting method (1.20 eV). [95] Figure 4.10 shows DTA measurements and indicates a decomposition temperature of 633 K (the decomposition starts round 600K). TGA data, also shown in Figure 4.10, indicates a weight loss at 633 K due to decomposition of PbCuSbS3 to stibnite and oxidation compounds of the sulfides, as suggested by the XRD results after TGA. The main exothermic peak also appears at this temperature, corresponding to the decomposition temperature of PbCuSbS3. This decomposition temperature for our PbCuSbS3 nanocrystals described here is lower than that reported for large-boule bulk materials, [96] likely due to the increased surface-to-volume ratio of our much small-sized crystals.
Figure 4.9. Room temperature UV-Vis spectra of 200 nm PbCuSbS$_3$. Reprinted from Reference 93.

Figure 4.10. TGA (blue) and DTA (red dashed) data of 200 nm PbCuSbS$_3$. Reprinted from Reference 93.
Calorimetric measurements were used to obtain $C_p$ from 2 K to 350 K for 1.4 mg of 200 nm PbCuSbS$_3$, shown in Figure 4.11. The inset in Figure 4.11 shows $C_p/T$ versus $T^2$ data below 10 K. The solid line in the inset is a fit to the data of the form $C_p/T = \gamma + \beta T^2$, where $\gamma$ is the Sommerfeld coefficient of the electronic contribution to the specific heat and $\beta$ is the coefficient of the lattice contribution. [97,98] From this fit we obtain $\gamma = 10.9$ mJ mol$^{-1}$ K$^{-2}$ and $\beta = 3.0$ mJ mol$^{-1}$ K$^{-4}$, values that are relatively high compared with that of metals and lower than that of oxides and other wide band gap semiconductors. [99-101] This is in line with the band gap value estimated using the data shown in Figure 4.9.

From the low temperature $C_p$ data an estimation of the Density of States (DOS) at the Fermi Level, $N(E_F)$, can be obtained by using the relation [97,102]

![Figure 4.11. Temperature dependent $C_p$ of 200 nm PbCuSbS$_3$. The inset shows $C_p/T$ versus $T^2$ data below $T=10K$. The solid line through the data in the inset is a fit by the expression $C_p/T = \gamma + \beta T^2$. Reprinted from Reference 93.](image-url)
\[ \gamma = \frac{\pi^2 k_B^2}{3} N(E_F)(1 + \lambda_{e-ph}), \]  

(24)

where \( \lambda_{e-ph} \) is the electron-phonon coupling constant. \( \lambda_{e-ph} \) is set to zero as a first approximation then we estimate \( N(E_F) = 4.6 \) states eV\(^{-1} \) per formula unit. This value is small compared with typical thermoelectric materials, such as YbFe\(_4\)Sb\(_{12}\) \( (N(E_F) = 60.1 \) states eV\(^{-1} \) per formula unit) [103] for example, indicating the DOS near the Fermi level is low with few channels for the charge carriers to flow, consistent with a very low electrical conductivity. [104] Using the relation

\[ \theta_D = \left( \frac{12\pi^4 R n_a}{5\beta} \right)^{\frac{1}{3}}, \]

(25)

where \( R \) is the molar gas constant and \( n_a \) is the number of atoms per formula unit \( (n_a=6 \) for PbCuSbS\(_3\), we estimate a \( \theta_D \) of 157 K. In the Debye model, \( \theta_D \) is linearly proportional to the Debye cutoff frequency \( \omega_D \), \( \theta_D = \hbar \omega_D / k_B \), with \( \omega_D \) being proportional to the average group velocity \( V_g \) \( (\omega_D \approx v_g K_D \) where \( K_D \) is the maximum allowable value). [102] A relatively small \( V_g \) can be a direct indication of low hardness, and possible “loose” bonding environment, [105] both suggesting that PbCuSbS\(_3\) should possess low thermal conductivity.

The magnetic susceptibility for 200 nm PbCuSbS\(_3\) particles is shown in Figure 4.12. It displays diamagnetic behavior at low temperatures. The relatively strong temperature dependence at low temperatures can be attributed to a trace amount of a paramagnetic impurity that cannot be detected by XRD. Considering the charge balancing scheme Pb\(^{2+}\)Cu\(^{1+}\)Sb\(^{3+}\)(S\(^2-\))\(_3\), all constituent ions are expected to be closed shell therefore exhibiting diamagnetic susceptibility. This behavior is consistent with our findings.[106]
As shown in Figure 4.13, the synthetic method used in this study resulted in particle sizes that can be varied with reaction time. As the reaction time was increased from 5 min to 60 min, the size of the particles increased from $5 \pm 2$ nm to $200 \pm 38$ nm, all other synthesis parameters being equal. The average particle size of the specimen, in the case of the 5 nm particle size, was confirmed by employing the Scherrer equation to the XRD data. From these observations it is clear that the reaction time is very effective in controlling the particle size up to 200 nm for synthesizing PbCuSbS$_3$. [107] However, reaction time longer than 60 min did not result in further increase of the particle size presumably due to the fact that the capping agent, Oleylamine, was used in our synthetic approach.[108,109] The XRD results show the same crystallinity for all three specimens.
In summary of this chapter, the synthesis and investigations of Cu$_2$ZnSnQ$_4$ nanocrystals (where Q = S, Se and Te) with the stannite crystal structure and with Ga-doping and Se-Te alloying of the nanocrystals, as well as nanocrystals of Ag$_2$ZnSnSe$_4$, were studied. I also investigated the low temperature transport properties of dense polycrystalline nanostructured Cu$_2$ZnSnSe$_4$ and Ag$_2$ZnSnSe$_4$. Cu$_2$ZnSnSe$_4$ shows metallic-like conduction while Ag$_2$ZnSnSe$_4$ shows polaronic-type conduction. At room temperature $\kappa_L$ of Cu$_2$ZnSnSe$_4$ is greatly reduced as compared to that of the bulk due to enhanced grain boundary phonon scattering. Replacing Cu with Ag also resulted in additional point defect scatterings that contributes to lower $\kappa_L$ for Ag$_2$ZnSnSe$_4$ compared to Cu$_2$ZnSnSe$_4$ above 70 K. In addition, another nanostructured quaternary chalcogenide, PbCuSbS$_3$, was investigated. The room temperature UV-Vis spectrum indicates an optical band-gap of 1.3 eV and DTA data indicates a decomposition temperature of 633 K. The fit to the low temperature $C_p$ data implies $N(E_F) = 4.6$ states eV$^{-1}$ per formula unit and $\theta_D$ of 157 K while magnetic susceptibility
measurements indicate PbCuSbS₃ to be diamagnetic. These investigations offer opportunities for improving thermoelectric properties of these materials by doping and alloying on the nanocrystals, affecting the transport in bulk form. Further studies may include elemental substations in order to lower the $\rho$. This synthetic approach can also be employed for the synthesis of other quaternary and quinary materials thus allowing for the potential for new avenues of investigation for a host of new materials for energy-related applications.
Type-II Sn-Clathrates

Inorganic clathrates continue to be of interest for thermoelectric, [21] magnetocaloric, [110] and photovoltaic applications, [111] as a result of their attractive physical properties including low $\kappa$, [21] magnetism, [112] and superconductivity. [113] Different synthetic approaches have been developed over the last few years in order to produce clathrate compounds, in single-crystal and microcrystalline form, with different structures and compositions. [21]

As documented previously, [21] densification of group 14 based materials presents unique challenges primarily due to the native oxide layer that easily forms on the surface of silicon based compositions. A promising method for producing high density polycrystalline materials is SPS. [114] This technique has proven very effective for the sintering, consolidation, and densification of numerous materials, [114-116] while a fundamental understanding of the mechanisms involved in SPS process are still being developed. In a typical SPS densification experiment, a pulsed DC electrical current is passed directly through the powder specimen while uniaxial pressure is applied. The specimen is therefore heated internally by joule heating, in contrast to conventional hot-pressing where the sample is typically heated using an external resistance heater. Moreover the high DC electrical current promotes substantial sintering and diffusion between grains, and through the native oxide layer present in the group 14 based clathrates. In this chapter I will present my work on the synthesis, densification, and characterizations of clathrate-II tin based compounds $K_3Ba_{13}Ga_{25}Sn_{113}$ and $K_3Ba_{9}Ga_{25}Sn_{113}$. 
5.1 Synthesis of Type-II Sn-Clathrates

Reaction of the elements at relatively high temperatures produces high alkali vapor pressures. We therefore employ a sealed stainless steel vessel in order to react the elements to synthesize the Type-II Sn-clathrates studied in this chapter. Potassium chunk (99.99%, Alfa Aesar), Ba shot (99.9999%, Alfa Aesar), Ga pellets (99.99999%, Alfa Aesar), and Sn powder (99.999%, Alfa Aesar) were used as source materials. According to the stoichiometric ratio of the target compounds, all pure elements were loaded into a stainless steel ampoule inside a glovebox and tightened in a custom-designed stainless steel vessel. In a typical synthesis, 4% Ga excess was used to compensate for weight loss during sample preparation. The stainless steel vessel was then transferred into a glass tube and sealed under vacuum. The glass tube was put into a furnace at 923 K for 15 hours followed by slowly cooling down to 723 K at a rate of 1 K/minute. The sample was then air cooled to room temperature. Diluted acid, a mixture of 10 mL HCl, 10 mL HNO₃, and 80 mL DI water, was used to remove any remaining flux in the as synthesized product. After grinding, the sample powder was filtered using a 400 mesh sieve (37 µm) after grinding before densification using SPS.

The SPS densification process was optimized, as described in Chapter 3, to determine the appropriate parameters before applying to the sample powder at 400 MPa and 483 K for 10 min with a current pulse ratio of 20:5 ms, resulting in phase-pure bulk specimens with a relative density of 90% as determined by measuring the dimensions and mass of the pellets after SPS. XRD and electron probe analyses were used to examine the purity and chemical composition of the specimens. Powder XRD data were collected with a Bruker D8 Focus diffractometer in Bragg–
Brentano geometry using Cu $K_{\alpha,\beta}$ radiation and a graphite monochromator. EDX of the pellets was accomplished with an Oxford INCA X-Sight 7582M equipped SEM (JEOL JSM-6390LV). The average atomic ratios were calculated from at least twelve data sets obtained from random positions of the pellet for each specimen.

High temperature $S$ and $\rho$ were measured on parallelepipeds (2 mm $\times$ 2 mm $\times$ 10 mm), cut from the pellets using wire saw, with an ULVAC ZEM-3 system (experimental uncertainty of 5–8% for $S$ and $\rho$ at elevated temperatures). High temperature $\kappa$ values were determined using the equation $\kappa = DaC_p$, described in details in Chapter 2. Thermal diffusivity measurements employed the laser flash method in a flowing He environment with a NETZSCH LFA 457 system. The uncertainty in the thermal diffusivity measurements were $\sim$5%. Heat capacity $C_p$ ($\approx C_v$) was estimated with the Dulong-Petit limit.

5.2 Characterization of K$_{8+x}$Ba$_{16-x}$Ga$_{40}$Sn$_{96}$

The open-framework of the type-II clathrates ($Fd\overline{3}m$, No. 227-2) comprises of 136 tetrahedrally coordinated framework atoms per unit cell, locating on the crystallographic 96$g$, 32$e$, and 8$a$ sites as shown in Figure 5.1 and 5.2. Typically the framework is comprised of Si, Ge, or Sn with possible partial substitution by Group 12 elements, Group 13 elements, and late transition metals.[21,116] The “guest” atoms are based on alkali metals, alkaline earth metals, or the rare earth metal Eu.[21] In the (K,Ba)$_{16}$Ga$_x$Sn$_{136-x}$ clathrates the framework is composed of Ga and Sn while the “guest” atoms are Ba and K.
Figure 5.1. Unit cell representation of (K,Ba)$_{16}$Ga$_{x}$Sn$_{136-x}$; K/Ba (white), Ga/Sn (green), and Sn (pink), along a-axis.

Figure 5.2. Unit cell representation of (K,Ba)$_{16}$Ga$_{x}$Sn$_{136-x}$; K/Ba (white), Ga/Sn (green), and Sn (pink), perpendicular to b-axis.
As another typical representation of the crystal structure the framework in type-II structure can be thought of as being built up of two types of polyhedra: (Ga,Sn)_{20} dodecahedra centered at the 16c crystallographic site (0 0 0), and (Ga,Sn)_{28} hexakaidecahedra centered at the 8b crystallographic site (3/8 3/8 3/8), as shown in Figure 5.3. [117-120] There are sixteen dodecahedra and eight hexakaidecahedra per conventional unit cell. It has been reported that the combination of Ba and K, 1.75 Å and 1.78 Å for Ba^{2+} and K^{+}, respectively, results in mixed occupancy in the (Ga,Sn)_{20} dodecahedra but not in the (Ga,Sn)_{28} hexakaidecahedra. [120]

Figure 5.3. A representation of the polyhedral cages in (K,Ba)_{16}Ga_{x}Sn_{136-x}; K/Ba (white), Ga/Sn (green), and Sn (pink).
Figure 5.4 shows $S$, $\rho$, and $PF$ of the two polycrystalline Sn clathrates. Temperature dependent $S$ indicates that both specimens are n-type, however, the decrease of the peak value of $S$ at high temperatures indicates possible bipolar diffusion. Such behavior has been observed by Koda et al. [118] Theoretical studies also suggest that the valence bands of $(K, Ba)_{16}Ga_{x}Sn_{136-x}$ are due to Ga and Sn while the conduction bands are formed by all the atoms forming the crystal structure.[118] For the $K_{3}Ba_{13}Ga_{23}Sn_{113}$ specimen the amount of Ga, which is the electron acceptor dopant, is less than the number of electrons donated by the filler ions. Therefore the $\rho$ of this specimen shows a metallic temperature dependence. For the $K_{7}Ba_{9}Ga_{25}Sn_{113}$ specimen the amount of Ga is the same as the donated electrons, resulting in a more semiconducting temperature dependence of the transport properties. Similar behavior has been observed by varying the vacancy content in the framework while keeping the number of “guest” atoms constant.[119] $PF$ of both specimens reached around $4 \ \mu W/cm-K^2$ at $575 \ K$. 


Figure 5.4. $S$, $\rho$, and $PF$ of $\text{K}_3\text{Ba}_{13}\text{Ga}_{23}\text{Sn}_{113}$ (empty circle) and $\text{K}_7\text{Ba}_9\text{Ga}_{25}\text{Sn}_{113}$ (filled circle).
κ_L and κ of the two polycrystalline clathrates are shown in Figure 5.5. In a cage-like crystal structure, the phonon scattering caused by mass fluctuation between cages with “guests” with different weight, for example the cage with K as the “guest” atom and the cage with Ba as the “guest” atom, is dominant in affecting κ_L. In addition, the large unit cell and complex crystal structure also contribute to the competitively low κ_L, lower than most of the existing thermoelectric materials.[1] When the electronic contribution is considered κ of both specimens are relatively similar. The “up-turn” of κ at higher temperatures in both specimens is caused by bipolar thermal diffusion, as also observed in the S data.[118]
Similar $PF$ and $\kappa$ values above 500 K for both specimens result in two relatively close $ZT$ values with the higher $ZT$ value corresponding to the K$_3$Ba$_{13}$Ga$_{23}$Sn$_{113}$ specimen. Overall a $ZT$ value of 0.6 was achieved for K$_3$Ba$_{13}$Ga$_{23}$Sn$_{113}$ at 575 K, with potentially higher $ZT$ values possible at higher temperatures (Figure 5.6). By further adjusting the compositions, reducing the Ba/K ratio for example, better thermoelectric properties may be expected.
Figure 5.6. $ZT$ of $\text{K}_3\text{Ba}_{13}\text{Ga}_{23}\text{Sn}_{113}$ (empty circle) and $\text{K}_7\text{Ba}_9\text{Ga}_{25}\text{Sn}_{113}$ (filled circle).
Thermoelectric devices have moved to center stage in today’s “green technology” debate especially because of the heightened awareness of the environmental impact of global climate change as well as the reduction of all refrigerants. There is currently large interest in thermoelectrics technology. Fundamental research on novel materials and materials with potential for thermoelectrics applications is therefore the focus of this thesis.

I$_2$–II–IV–VI$_4$ quaternary chalcogenides have the potential for good thermoelectric performances due to their complex crystal structures, resulting in intrinsically low $\kappa$. Their different cationic valences provide a means of controlling the electrical properties by adjusting the cation ratios, as described in Chapter 2. In addition, the layered structure allows for decoupling of $\sigma$ from both $\kappa$ and $S$, to some extent. By introducing nanostructuring lower $\kappa$ was achieved compared with that of the bulk. A more interesting phenomena, described in Chapter 4, was also observed; Cu$_2$ZnSnSe$_4$ is p-type and displays typical degenerate semiconducting behavior while Ag$_2$ZnSnSe$_4$ is n-type and displays polaronic-type conduction. The large peak in $\rho$ for Ag$_2$ZnSnSe$_4$ at 160 K indicates a strong coupling between electrons and phonons. In terms of thermoelectric research, when synthesizing Cu$_2$ZnSnSe$_4$ with excess Cu and Ga-doping improved thermoelectric properties were observed as described in Chapter 2. It may also be of interest to apply similar compositional and structural modifications to bulk Ag$_2$ZnSnSe$_4$ in order to study the effects on the polaronic-type conduction.
Lone-pair electrons introduce anharmonic phonon scattering and result in an additional reduction of $\kappa$ in $\text{PbCuSbS}_3$. The $\kappa$ value of this material is lower than many thermoelectric materials, as discussed in Chapter 2, however such affects also degrade the electron transport, leading to poor $PF$. Since the distorted coordination environment is dominated by the electrostatic repulsion between the $s^2$ pair electrons from neighboring Sb and Pb atoms, it is reasonable to think of improving the electrical properties, for thermoelectric applications, by doping on the Cu site, with Ni for p-type or Zn for n-type for example.

As one promising method to improve the thermoelectric properties of materials, nanostructuring significantly reduces $\kappa$ due to increased interface scattering of phonons at the grain boundaries, as demonstrated for many thermoelectric materials systems.[1,64] In Chapter 3 and Chapter 4 I discussed using solvothermal synthesis to grow $\text{FeSb}_2$ nanocrystals and colloidal synthesis for $\text{Q}_2\text{ZnSnX}_4$ ($\text{Q}=\text{Ag, Cu}$ and $X=\text{S, Se, Te}$) and $\text{PbCuSbS}_3$ nanocrystals. I then consolidated the nanocrystals into dense polycrystalline nanostructured bulk materials and investigated their physical properties, the so called “bottom-up” approach described in Chapter 3. In addition, I also applied other solution-phase synthetic methods for the synthesis of different nanostructured materials, including direct precipitation for $\text{PbX}$ and polyol synthesis for $\text{Bi}$ and $\text{Bi}_{x}\text{Sb}_{1-x}$. Developing a suitable synthetic approach is very important in producing phase-pure, high quality and high crystallinity nanocrystals. Although the availability of different synthetic approaches offers greater flexibility, this may also add difficulty in establishing the best synthetic approach for a specific material. Depending on the chemical properties, certain synthesis techniques have limitation when being applied to certain materials. Investigating the dominant factors in materials preparation is therefore of interest.
To be able to investigate the physical properties of dense bulk nanostructured materials densification of the nanocrystals is a very important step. Due to the high surface to volume ratio, nanocrystals generally have lower melting points compared with that of the bulk. SPS is therefore unique in achieving high density at relatively low temperatures. This process generates internal localized heating, allowing for the rapid, low temperature densification of fine-grain powders, and minimizes grain growth since only the surface temperature of the nanocrystals rises rapidly by self-heating. The flexibility in controlling all densification parameters independently, only for certain models of SPS, also contributes to better adapting SPS for densifying nanocrystals. This precise control of the different SPS parameters also enables SPS to densify bulk materials that have low melting points. The sensitivity to densification with different SPS parameters is not universal for all materials. Understanding of the detailed mechanisms warrants further study, for instance it may require an understanding of the thermal stability of the materials.

As addressed in Chapter 3 and 4, thermal transport in materials with nano-scale grains is greatly affected by the high density of interfaces. This also affects the charge transport. Balancing thermal and electrical transport is therefore critical for nanostructured bulk materials. One approach, described herein, involves introducing higher degrees of complexity, for example the topics of quantitative microstructure control and panoscopic approach.[121,122] More research can be conducted following a similar concept. For instance, it would be interesting to have well oriented larger grains with un-oriented smaller grains in a nanocomposite to potentially encourage electrical transport and penalize thermal transport, using materials with size dependent magnetic properties for example. Fundamental research into thermoelectric materials with nano-scale features, or grains, may reveal novel phenomena that can be applicable to other technologies.
The last part of my thesis focused another well-known material system that continues to be of interest for thermoelectric applications. Type-II clathrate compounds such as K₃Ba₁₃Ga₂₃Sn₁₁₃ and K₇Ba₉Ga₂₅Sn₁₁₃ both offer sufficient room for compositional modifications. The numbers of charge carriers can be balanced or varied by adjusting the Ga to Sn ratio, for holes, and K or Cs to Ba ratio, for electrons. A $ZT$ value of 0.6 was achieved at 575 K, with higher $ZT$ possible at higher temperatures. The experience gained during the crystal growth and investigations, including tuning the structures in other clathrate-II compounds, is very valuable and will benefit my future research.

The research described in this thesis involves the design, synthesis, and characterization of novel materials for thermoelectric applications, including structure-property relationships of novel inorganic materials and novel synthesis routes for inorganic materials. This research has also contributed to a better understanding of the fundamental physics of these material systems.
References


[43] PbCuSbS₃, 488.7 amu, 3 dimension, Orthorhombic, Pmn2₁ (#31), a = 7.8101 (2) Å, b = 8.1504 (2) Å, c = 8.7009 (3) Å, V = 553.86 (4) Å³, Z = 4, ρcalc. = 5.860 g/cm³, Graphite monochromated Cu Kα (1.54056 Å), wRp = 0.0710, Rp = 0.0519, GSAS, Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-427413 for PbCuSbS₃.


