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Joshua Martin

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Methods of Thermoelectric Enhancement in Silicon-Germanium Alloy Type I Clathrates

and in Nanostructured Lead Chalcogenides

By

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A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
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Methods of Thermoelectric Enhancement in Silicon-Germanium Alloy Type I Clathrates and in Nanostructured Lead Chalcogenides

Joshua Martin

ABSTRACT

The rapid increase in thermoelectric (TE) materials R&D is a consequence of the growing need to increase energy efficiency and independence through waste heat recovery. TE materials enable the direct solid-state conversion of heat into electricity, with little maintenance, noise, or cost. In addition, these compact devices can be incorporated into existing technologies to increase the overall operating efficiency. High efficiency TE materials would enable the practical solid-state conversion of thermal to electrical energy. Optimizing the interdependent physical parameters to achieve acceptable efficiencies requires materials exhibiting a unique combination of properties. This research reports two methods of thermoelectric enhancement: lattice strain effects in silicon-germanium alloy type I clathrates and the nanostructured enhancement of lead chalcogenides.

The synthesis and chemical, structural, and transport properties characterization of Ba$_8$Ga$_{16}$Si$_x$Ge$_{30-x}$ type I clathrates with similar Ga-to-group IV element ratios but with increasing Si substitution (4 < x < 14) is reported. Substitution of Si within the Ga-Ge lattice framework of the type I clathrate Ba$_8$Ga$_{16}$Ge$_{30}$ results in thermoelectric performance enhancement. The unique dependences of carrier concentration, electrical
resistivity, Seebeck coefficient, and carrier effective mass on Si substitution level, may imply a modified band structure with Si substitution. These materials were then further optimized by adjusting the Ga-to-group IV element ratios.

Recent progress in a number of higher efficiency TE materials can be attributed to nanoscale enhancement. Many of these materials demonstrate increased Seebeck coefficient and decreased thermal conductivity due to the phenomenological properties of nanometer length scales. To satisfy the demands of bulk industrial applications requires additional synthesis techniques to incorporate nanostructure directly within a bulk matrix. This research investigates, for the first time, dense dimensional nanocomposites prepared by densifying nanocrystals synthesized employing a solution-phase reaction. Furthermore, the carrier concentration of the PbTe nanocomposites can be adjusted by directly doping the nanocrystals, necessary for power factor optimization. These materials were fully characterized using a low temperature TE transport measurement system, and exhibit enhanced power factors when compared to bulk polycrystalline PbTe with similar carrier concentrations.
1 INTRODUCTION TO THERMOELECTRICS

1.1 THERMOELECTRIC APPLICATIONS

Thermoelectric (TE) phenomena couple electrical and thermal currents, enabling the direct solid-state inter-conversion of thermal and electrical energy. This conversion occurs through two primary reversible phenomena: the Seebeck and the Peltier effect. The Seebeck effect describes the manifest electric potential across the interface of two dissimilar conductors within an established thermal gradient. In the corresponding Peltier effect, passing an electric current through the ohmic interface of two dissimilar conductors results in the liberation or the absorption of heat at the junction. While the low conversion efficiency of TE devices limits their commercial practicality to niche applications, they remain an integral component in NASA’s radioisotope thermoelectric generators (RTG’s) for deep space power generation, small-scale waste-heat recovery devices (i.e., TE watches and remote geothermal power generation), temperature measurement, and in reversible electronic refrigeration. In addition, TE devices are environmentally friendly (absent of hazardous coolants), require minimal maintenance, and reliably offer quiet and compact operation.

A thermoelectric device consists of pairs of n and p-type semiconducting TE segments connected electrically in series and thermally in parallel (Figure 1). This arrangement facilitates practical energy conversion by allowing sufficient heat transport
via the charge carriers.

Increased awareness in energy consumption, the environment, and dependence upon foreign fuel sources has refocused vehicle research towards maximizing fuel economy with green technologies. Since thermoelectric devices directly convert heat into electricity, several automotive companies in collaboration with the department of energy (DOE) have renewed their efforts in fabricating higher efficiency thermoelectric devices. These may also lead to reliable solid-state air conditioning. Currently, only about 25 % of the energy attained from burning gasoline is used for propulsion and powering the accessories of an automobile. Most of this energy escapes as heat. A thermoelectric device can be used to recover a portion of this waste heat and distribute the recovered energy back to the vehicle. Recent studies suggest a 20 % increase in fuel economy simply by recovering the waste heat and converting only ~ 10% into electricity.\footnote{1}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{thermoelectric_diagram.png}
\caption{Energy conversion diagrams for a thermoelectric couple. Passing an electric current through the couple results in the transfer of thermal energy via the charge carriers, providing refrigeration. Imposing a thermal gradient across the couple generates a thermoelectric voltage, sourcing a current through the load.}
\end{figure}
1.2 ORIGIN OF THERMOELECTRIC PHENOMENA

1.2.1 SEEBECK EFFECT

The Seebeck effect describes the manifest electric potential across the interface of two dissimilar conductors within an established thermal gradient. The value of this ratio yields the Seebeck coefficient. For a uniform conductor in a thermal gradient, thermally excited charge carriers in the hot end diffuse through the concentration gradient to occupy the lower energy states in the cold end, generating a voltage difference (Figure 2). This electric potential provides the dynamic equilibrium necessary to prevent further net charge transfer, resulting in the exclusive transport of kinetic energy. In n-type (p-type) semiconductors, the potential establishes in the opposite direction (same direction) of the thermal gradient resulting in a negative (positive) Seebeck coefficient. A temperature gradient $\Delta T$ across the junction of two dissimilar conductors also generates an electric potential $\Delta V_{ab}$, as in Thomas Seebeck’s$^2$ 1821 observation, where

$$S_{ab} = \frac{\Delta V_{ab}}{\Delta T}$$

represents the Seebeck coefficient for the junction.

The Seebeck coefficient is proportional to the average energy per carrier, relative to the Fermi energy $E_F$, divided by charge per carrier ($e$) and temperature ($T$):

$$S \sim \frac{1}{eT} \langle E - E_F \rangle.$$
Metals typically exhibit low Seebeck coefficients since the charges participating in electrical transport are those with energies $\sim k_B T$, resulting in a small energy per carrier. Semiconductors typically exhibit larger Seebeck coefficients since carriers exited from dopant states within the gap into the conduction band have a greater average energy per carrier (Figure 3).

**Figure 2.** Seebeck effect for an isolated conductor in a uniform thermal gradient. Electrons (blue circles) diffuse from the hot to the cold side, generating a voltage.

**Figure 3.** Ideal energy band diagrams representing electronic conduction for a metal and for n- and p-type semiconductors. Blue circles represent electrons, red circles represent holes, and open circles represent an empty state. Brackets visually indicate the average energy per carrier.
In 1834, Jean Peltier observed that the passage of an electric current through the ohmic interface of two dissimilar conductors results in the liberation or absorption of heat at the junction. Since conductors forming an ohmic contact share Fermi levels, passing a current through a metal/n-type semiconductor junction requires an electron to acquire energy as it enters the conduction band and to release energy as it passes through an n-type semiconductor/metal junction (illustrated in Figure 4). The rate of thermal exchange at each junction is given by

\[ Q_p = S_{ab}IT = \Pi_{ab}I \]  

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

Although the Seebeck and Peltier effects define the thermoelectric properties observed in the junction of two dissimilar conductors, the Thomson effect defines the bulk thermoelectric property of a single conductor. Current passing through a homogeneous material in a thermal gradient results in the reversible flow of heat, defined by the Thomson coefficient

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

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

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

(5)
and

$$\Pi_{ab} = S_{ab} T$$  \hspace{1cm} (6)

comprise the Kelvin relations and relate the three fundamental thermoelectric phenomena.

\textbf{Figure 4.} Peltier effect for a thermoelectric couple. Passing a current through the thermoelectric couple results in the transfer of thermal energy via the charge carriers. Also shown are Fermi-Dirac distribution diagrams illustrating the relative difference in occupied energy states for each metal/semiconductor junction.
2 METHODS OF THERMOELECTRIC ENHANCEMENT

2.1 TRADITIONAL METHODS OF ENHANCEMENT

The coefficient of performance for thermoelectric refrigeration, defined as the ratio of the rate of heat extraction from the source to the rate of expenditure of electrical energy, is given by: 5

\[ \phi = \frac{Q_C}{W} = \frac{(S_p - S_n) I T_C - K \Delta T - \frac{1}{2} I^2 R}{I \left[ (S_p - S_n) \Delta T + IR \right]} \]  

(7)

where \( T_C(T_H) \) 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 Carnot limit. Similarly, the efficiency of thermoelectric power generation is given by 5

\[ \eta = \frac{W}{Q_H} = \frac{I \left[ (S_p - S_n) \Delta T - IR \right]}{K \Delta T + (S_p - S_n) I T_H - \frac{1}{2} I^2 R} \]  

(8)

where \( W \) is the power delivered to an external load, \( Q_H \) is positive for heat flow from the source to the sink, and \( S_p \) and \( S_n \) are the Seebeck coefficient for the p- and n-type segments. 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. These relative dimensions also optimize the figure of merit for a thermoelectric couple, \( Z = (S_p - S_n)^2/RK \), by minimizing
the product of $RK$. This occurs when

$$
\frac{L_n A_p}{L_p A_n} = \left( \frac{\rho_p \kappa_p}{\rho_n \kappa_n} \right)^{\frac{1}{2}}
$$

(9)

and, consequently, the figure of merit becomes

$$
Z = \frac{(S_p - S_n)^2}{\left( (\rho_p \kappa_p)^{\frac{1}{2}} + (\rho_n \kappa_n)^{\frac{1}{2}} \right)^2}
$$

(10)

In these equations $\rho$ is the resistivity, $\kappa$ is the thermal conductivity, and the subscripts identify the type of the segment in the thermoelectric couple.

The dimensionless figure of merit,

$$
ZT = \frac{S^2 \alpha T}{\kappa}
$$

(11)

defines the effectiveness of individual TE materials, where $\alpha$ is the Seebeck coefficient, $\sigma$ the electrical conductivity, $T$ the absolute temperature, and $\kappa$ is the total thermal conductivity ($\kappa = \kappa_L + \kappa_e$; the lattice and electronic contributions, respectively). Optimizing these interdependent physical parameters to achieve acceptable efficiencies ($ZT > 1$) requires materials exhibiting a unique combination of properties. In addition, these materials must exhibit an optimal $ZT$ within specific target application temperatures. Several unique approaches have been developed to identify these potential thermoelectric materials.

Thermoelectric materials with optimal electrical properties exhibit carrier concentrations intrinsic to semiconductors, which led Ioffe\textsuperscript{7} to suggest the search for thermoelectric materials focus upon mixed semiconductors comprised of multiple heavy elements. This concept reduces $\kappa$ while maximizing the power factor $S^2 \sigma$ (see Figure 5).
Compounds composed of heavy elements minimize phonon energies and the sound velocity, resulting in a low intrinsic thermal conductivity. Chemical alloying further reduces the phonon contribution to the thermal conductivity but can also decrease the carrier mobility ($\mu$), however, at a slower rate. To maintain high carrier mobility requires smaller energy indirect band gap materials of $\sim 10 \ k_B T$ (but large enough to prevent intrinsic bipolar conduction), resulting in a high carrier effective mass. This will allow both high carrier concentration and mobility without the material becoming degenerate and decreasing the Seebeck coefficient. In addition, low ionicity materials with small electronegativity differences between the constituent elements limit polar optical phonon scattering of the charge carriers. Many heavy element compounds also possess large dielectric constants.\(^8\) This screens impurities to further increase the carrier mobility. However, since $Z \propto \mu (m^*)^{3/2}$, the interdependent product could optimize $Z$ with small or large $m^*$ values, depending on the specific carrier scattering mechanism and material system, preferably acoustic phonon scattering.\(^9\) Other parameters that identify potential TE materials include: complex crystal structures with a large unit cell atomic density and multivalley electronic bands near the Fermi level. These methods were largely successful in identifying the de facto industrial standard TE materials over the last three decades, including $\text{Bi}_2\text{Te}_3$ (ZT $\equiv 1$ at 300 K), PbTe (ZT $\equiv 0.8$ at 700 K), and SiGe alloys (ZT $\equiv 0.8$ at 1000 K).\(^8\)
Figure 5. Optimal electrical properties for thermoelectric applications. As shown by the power factor curve $S^2\sigma$, semiconductors should exhibit an ideal carrier concentration for thermoelectric applications.
Another approach to identify potential thermoelectric materials, proposed by G. A. Slack,\textsuperscript{10} suggests a \textit{Phonon-Glass Electron-single-Crystal} (PGEC). An ideal PGEC material would possess thermal properties similar to an amorphous material (low thermal conductivity with anomalous temperature dependence) and electrical properties similar to a ‘good’ single crystal semiconductor. Crystal systems exhibiting this low, glass-like thermal conductivity exhibit a $T^2$ temperature dependence at low temperature ($< 1$ K) and a resonant minimum at higher temperature (4 – 40 K). In addition, they may also share the following features:\textsuperscript{6}

1. They possess “loose” atoms or molecules whose translational or rotational positions are not well defined and possess two or more metastable positions.

2. There is no long-range correlation between the positions of the “loose” atoms or molecules.

3. The mass of these “loose” atoms or molecules is at least 3% of the total mass of the crystal.

4. Disorder produced by point defect scattering (monatomic substitution) cannot lead to glass-like thermal conductivity. However, some crystal systems (fluorites) with high concentrations of vacancies or interstitials can produce glass-like thermal conductivity.

Many disordered crystal systems demonstrate glass-like phonon vibrations similar
to amorphous solids: mixtures of alkali halides with cyanides, fluorite structures, feldspars (aluminosilicate crystals), and glass ceramics.\textsuperscript{11} The PGEC concept attempts to replicate this glass-like behavior of disordered crystals in semiconductor materials and reduce the lattice thermal conductivity near the theoretical minimum. Assuming a random energy transport between nearest localized quantum mechanical oscillating entities in sizes varying larger than single atoms, the minimum thermal conductivity for a solid can be expressed by modifying Einstein’s model with Debye’s model of lattice vibrations:\textsuperscript{11}

$$\Lambda_{\text{min}} = \left(\frac{\pi}{6}\right)^{\frac{2}{3}} k_B n\sum_i v_i^2 \int_0^{\Theta_i/T} x^3 e^x \left(\frac{e^x - 1}{x}\right)^2 dx,$$

(12)

where $v_i$ represents the speeds of sound (two transverse and one longitudinal), $n$ is the number atomic density, and $\Theta_i = v_i (\hbar/k_B)(6\pi^2 n)^{\frac{1}{3}}$ is the cutoff frequency for each polarization, expressed in degrees K. No bulk crystalline material has demonstrated a value lower than the model’s prediction.

An open structured covalent framework governing the band structure would define the electronic transport properties while weakly bound intercalated atoms would effectively scatter low frequency heat-carrying phonons by “rattling” about their lattice site. Such a crystal system could satisfy the ideal PGEC concept. This approach has proven successful in both the skutterudite\textsuperscript{12,13,14,15} and clathrate crystal structures,\textsuperscript{16,17,18} with optimization provided by adjusting the carrier concentration. In addition, the dynamic disorder (rattling) of the “guest” atoms incorporated within the lattice framework voids indicate low frequency scattering mechanisms replace traditional alloy phonon scattering and significantly reduce the lattice thermal conductivity.
2.3 Nanostructured Enhancement

Recent progress in a number of higher efficiency thermoelectric materials (room temperature ZT > 2) can be attributed to nanoscale enhancement.19-24 Many of these materials demonstrate increased Seebeck coefficient and decreased thermal conductivity due to the phenomenological properties of nanometer length scales, including quantum confinement effects (increased density of states, as shown in Figure 6), enhanced phonon scattering, and interfacial energy barrier filtering of charge carriers. Physically, nanostructured TE enhancement aims to split the interdependence of the electrical and thermal transport, allowing for better ZT optimization.

![Figure 6](image)

**Figure 6.** Electronic density of states for a bulk semiconductor, quantum well, quantum wire, and quantum dot, illustrating the increase in DOS with quantum confinement of energy.

One consequence of nanostructure is the increase of interfaces. These interfaces serve to scatter phonons more effectively than electrons and reduce the lattice thermal conductivity. Additionally, the presence of interfacial energy barriers filters the carrier
energy traversing the interface, restricting those energies that limit the mean carrier energy.\textsuperscript{19} This increases the Seebeck coefficient, as its value depends on the mean carrier energies relative to those at the Fermi level. Experimental evidence in epitaxial films of n- and p-type lead chalcogenides verifies the enhancement potential of this mechanism.\textsuperscript{20} Theoretical calculations further suggest a high figure of merit could result from a composite material comprised of a highly conducting base material (or metal) and thin semiconducting barrier layers.\textsuperscript{21}

As an initial exploration, Hicks and co-workers investigated the effect of a one-dimensional quantum wire structure on the thermoelectric figure of merit.\textsuperscript{22} Their calculations demonstrated the significant enhancement potential of these nanostructures when compared to bulk values. This work encouraged experimental research using thin films, heterostructures, nanowires, and other nanostructures. For example, p-type Bi\textsubscript{2}Te\textsubscript{3}/Sb\textsubscript{2}Te\textsubscript{3} 10 Å/ 50 Å superlattice structures demonstrated a room temperature ZT = 2.4, with a thermal conductivity reduced by a factor of 2 compared to other Bi\textsubscript{2}Te\textsubscript{3} alloys.\textsuperscript{23} Harman and co-workers reported a room temperature ZT = 1.6 in PbTe/PbTeSe quantum-dot superlattices (QDSLs) that contain PbTeSe nanodots imbedded in a PbTe matrix.\textsuperscript{24} Kong and co-workers also reported an enhancement in Si/Ge supperlattices.\textsuperscript{25} However, these systems require substantial fabrication costs and efforts, and may not fulfill the robust demands of high temperature bulk TE devices operating on an industrial scale (i.e., mechanical strength, economics of manufacture, operation within an excessive thermal variance, high temperature nanostructure stability). To satisfy these demands requires additional synthesis techniques to incorporate nanostructure directly within a bulk matrix.
Recently, Heremans and co-workers reported an increased Seebeck coefficient for PbTe with the inclusion of Pb precipitate nanostructures as compared to bulk PbTe. Crystals of Ag$_{m}$Pb$_{m}$SbTe$_{m+2n}$ (sometimes referred to as “LAST” materials) with self-formed nanoscale grains of PbTe also demonstrate a large figure of merit (ZT > 2) at their application temperature. Nanostructuring in these two systems requires specific cooling techniques during synthesis. Arrested precipitation in other chalcogenide systems of PbTe-x% M (where M = Sb, Bi, and InSb, and 2 ≤ x ≤ 16) upon rapid quenching kinetically traps, or encapsulates M in a nanostructured state. PbTe with a 2% Sb inclusion phase reduces the thermal conductivity to 0.8 W-m$^{-1}$K$^{-1}$, compared to the bulk value of 2.5 W-m$^{-1}$K$^{-1}$. Nanostructured chalcogenide systems prepared by thermodynamically driven compositional fluctuations also demonstrate reduced thermal conductivity when compared to similar bulk materials.

Another method to incorporate nanoscale dimensions into bulk materials is through ball-milling. This procedure rapidly grinds powders to sub-micron dimensions. Ball-milled Si-Ge nanocomposites demonstrated an increased Seebeck coefficient and a reduced thermal conductivity. Although the electrical conductivity also decreased, the overall thermoelectric performance of the material was enhanced. Ball-milled PbTe materials have also demonstrated thermoelectric enhancement. However, this method can cause unaccounted lattice strain effects. This effect, in combination with the need for materials in large quantities, further requires additional methods to incorporate nanostructure within a bulk material.

The reduction of thermal conductivity through the interface scattering of phonons remains the primary mechanism for increased TE performance in nanostructured systems.
However, to achieve the TE performance necessary for commercial application also requires enhancements to the power factor ($S^2\sigma$). The physical mechanisms responsible for Seebeck enhancement are not fully understood or investigated. In addition, many comparisons of nanostructured systems to traditional bulk materials do not entirely compare identical materials.

This research reports a novel approach to prepare lead chalcogenide (PbTe) dimensional nanocomposites by densifying nanocrystals synthesized employing an aqueous solution-phase reaction with a high yield and low cost. Densification using spark plasma sintering (SPS) successfully integrate disperse 100 – 150 nm PbTe nanocrystals within a bulk nanocomposite, demonstrating for the first time that nanocrystals dispersed within dense bulk polycrystalline PbTe can be prepared from solution-phase synthesized nanocrystals. Furthermore, the carrier concentration of the PbTe nanocomposites can be adjusted by directly doping the nanocrystals, necessary for power factor optimization. Directly comparing these nanocomposites with bulk polycrystalline materials yields the most direct evidence of $|S|$ enhancement due to the dispersion of nonconglomerated nanoscale PbTe grains within the PbTe nanocomposites.
3 METHODS OF PHYSICAL PROPERTIES MEASUREMENT

Investigating structure-property relationships necessitates accurate materials characterization. The measurement of key transport properties evaluates the contextual effectiveness of new materials and relates those properties to the affects of dimensional structure and compositional variations. In addition, to effectively evaluate composition-structure-property relationships requires temperature dependent measurements. This research developed a transport properties measurement system capable of examining temperature dependent resistivity, Seebeck coefficient, and thermal conductivity in the range 300 K – 12 K through specific design emphasis upon the unique challenges inherent in thermoelectric metrology (i.e. large relative Seebeck coefficient and low thermal conductivity). The system simultaneously characterizes the terms necessary to calculate a material’s ZT, benefiting accuracy through concurrent measurements on an identical sample with identical contacts and within one cryogenic cycle. National Instrument’s LabVIEW software facilitates measurement control and data acquisition.

Researchers must calibrate their apparatus and methodologies with known standards to remain consistent with characterizations in other laboratories. These practices aid in the confirmation of reported high ZT materials. Numerous Standard Reference Materials (SRM™) and measurement procedures are available through NIST (National Institute for Standards and Technology) for resistivity (stainless steel), thermal
conductivity (stainless steel, pyroceram), and some for the low Seebeck coefficient of binary metals. Round-robin laboratory research TE materials provided additional measurement calibration.

Through the Materials Science and Engineering Laboratory (MSEL), NIST recently initiated the certification of a low temperature (2 K- 400 K) Seebeck coefficient SRM™. The measurement system developed for this research was selected as one of twelve active research laboratories to participate in a round-robin measurement survey of two candidate materials, Bi$_2$Te$_3$ and constantan (55% Cu and 45% Ni). Bi$_2$Te$_3$ was selected as the prototype material and final certification is underway. A complete discussion of calibration data is located in the Appendix.
3.1 Method of Measuring Electronic Transport Properties

3.1.1 Resistivity

Accurate resistivity measurements require an indirect four-probe method in which one pair of lead wires sources current through the bulk parallelopiped and a separate pair measures the corresponding voltage drop (Figure 8). This eliminates discrete voltage contributions from lead wires and sample contacts. Concurrent dimensional measurements result in the resistivity, given by

$$\rho = \frac{V}{I l_o}$$

where $V$ is the measured voltage drop, $I$ the current sourced through the sample, $A$ the cross-sectional area, and $l_o$ the effective length between the voltage leads.

A mask is prepared to transfer the geometry of the thermocouple divots to small nickel-plated circles serving as interface contacts for the voltage wires. Positioning these voltage contacts away from the current contacts according to $l - l_o \geq 2w$ (where $l$ is the sample length and $w$ is the sample thickness) guarantees homogeneous current flow where the voltage is measured. Voltage contacts were soldered directly to these nickel-plated circles. Current contacts were soldered directly to the nickel-plated face on each specimen end. The schematic diagram in Figure 7 details the specimen connections.
Measuring resistivity in thermoelectric materials presents unique difficulties. Finite thermal gradients arising from joule heating or the Seebeck measurement superimpose a thermoelectric voltage $\Delta V = S\Delta T$ onto the resistive voltage drop. Alternating current polarity and averaging the subsequent voltage measurements eliminates these Seebeck voltage contributions

$$V_{IR} = \frac{\left[ V(I^+) + S\Delta T \right] - \left[ V(I^-) + S\Delta T \right]}{2},$$

in addition to directional inhomogeneous current flow. A more challenging problem arises from Peltier heat. The passage of current through the junction of two dissimilar materials results in the liberation or the absorption of heat at each current contact. Depending upon the direction of the current flow, attempts to measure the resistivity contribute to standing temperature gradients across the specimen and consequently increase the Seebeck voltage. Unfortunately, the reversal of current reverses the direction of both the temperature gradient and its corresponding Seebeck voltage, nullifying any
benefit incurred by averaging the two readings. While the imposed Peltier thermal gradient requires a finite time to propagate, the resistive voltage can be measured instantaneously. According to Nishida,\textsuperscript{35} this plateau region has a maximal duration of 1.1-1.3 seconds. To negate the Peltier heat requires fast switching of current polarity.

Current sourced by a Keithley 2400 SourceMeter does not necessarily indicate the actual current sourced through the specimen in a dynamic measurement. Instead, the measured voltage drop across a high precision resistor of known value in series with the specimen provides the required accuracy.

The series resistance voltage drop and the resistivity voltage drop were measured by the Keithley 2001 Multimeter with an uncertainty of 1.2 \( \mu \)V. Therefore, the contributing magnitude of this uncertainty to the total error in the resistivity measurement depends on selecting an appropriate current value as to maximize the measured voltage difference (typically > 250 mV, resulting in a negligible uncertainty \( << 0.1 \% \)).

The geometric factor \((A/l_o)\) remains the most dramatic source of error in the resistivity measurement. Utilizing a calibrated micrometer, concurrent cross-sectional geometry measurements at three longitudinally equidistant positions yield an average cross-sectional area value \((A)\). Measurement uncertainty of 0.0005” in a 2 mm span (0.0787”) results in a 0.64 % error. A Bauch and Laumb optical stereoscope provides for the practical and consistent measurement of effective length \((l_o)\). For each new magnification setting, the optical reticle built into the left eyepiece must be calibrated using a USAF resolution test target (RES-2). Comparing the measured line length for a selected group and element number to the actual calculated line length generates a correction factor. Since voltage contacts retain the potential of their centers, the optical
reticle measures voltage contact radii and the distance between the inner edge of the two contacts to calculate the effective length. Measurement uncertainty of 0.0005 for a 0.0150 diameter contact at 30 x magnification results in a 3.3 % error. The total uncertainty for the resistivity measurement is 4 % at room temperature.

**FIGURE 8.** TOP: Diagram for the resistivity measurement, where I+ and I- represent the current sourced and ΔV represents the measured voltage difference. CENTER: Diagram for the Seebeck coefficient measurement, where ΔT represents the temperature difference and TH and TC represent the hot and cold sides, respectively. BOTTOM: Diagram for the thermal conductivity measurement, where Q represents the heat flow.
3.1.2 SEEBECK COEFFICIENT

The Seebeck coefficient measures the entropy per charge carrier by relating the thermoelectric voltage to its imposing temperature gradient

$$S = \frac{\Delta V}{\Delta T} = \frac{V_H - V_C}{T_H - T_C},$$  \hspace{1cm} (15)$$

where $V_H$, $T_H$, and $V_C$, $T_C$ are the voltage and temperature of the hot side and cold side, respectively (see Figure 8).

Specimen wires soldered to contact pins in thermal contact with the sample holder serve as the thermocouple reference junction, measured by a DT-670B-CO silicon diode. Uncertainty as calibrated by four test thermocouples in reference to this temperature diode contributes a maximum of ± 0.2 K in the higher temperature range and even less at lower temperatures. The maximum uncertainty is ± 1% throughout the temperature range.

The Seebeck coefficient measurement uses a steady-state gradient sweep technique. In this method, the base temperature of the cryostat is first stabilized to within ± 10 mK at each temperature of interest (this is the resolution of the Lakeshore 331 Temperature Controller at 300 K). The Seebeck coefficient measurement follows a steady-state measurement of thermal conductivity. Due to this sequence, a stabilized thermal differential across the specimen remains as a bridge between the thermal conductivity measurement and the subsequent measurement of the Seebeck coefficient. At 300 K, this thermal differential is ≈ 0.5 K. Electrical current sourced through a small 100 Ω resistor epoxied to the free end of the specimen provides a thermal current toward
a heat sink soldered to the opposite end of the specimen (using the Keithley 2400 Sourcemeter). To measure the Seebeck coefficient, the value of electrical current maintaining the previously stabilized thermal differential is increased an additional 1 mA every 0.5 second. The voltage difference and the temperature difference across the specimen are recorded at each 0.5 s interval by measuring the appropriate voltages with the Keithley 2001 Multimeter. This sequence proceeds until one of the following events occurs: a maximum number of 20 data points is reached, a maximum heater current of 50 mA is reached, or a maximum thermal differential is reached ($\Delta T \equiv 5$ K at 300 K). The data are linearly fit using a custom LabVIEW subVI and the slope yields the measured Seebeck coefficient.

To obtain the specimen’s Seebeck coefficient, the measured Seebeck coefficient is subtracted from the Seebeck coefficient of copper generated from a polynomial fit, to correct for the wires measuring the voltage differential. A thermocouple epoxied between the differential thermocouple contacts measures the average sample temperature prior to the thermal ramp and at the final dV/dT data point to derive the average specimen temperature datum corresponding to the specimen’s Seebeck coefficient. These final data are recorded for reference with each of the dV and dT data points taken to derive the linear fit. The total measurement uncertainty for the Seebeck coefficient is $\equiv 6\%$ (for $S \equiv 100 \mu$V/K).
3.2 Method of Measuring Thermal Conductivity

Thermal conductivity remains the most challenging transport property to characterize in the figure of merit. The low thermal conductivity values of good thermoelectric materials increase the difficulty in measuring the correct input heat flux to the sample, exaggerating parasitic heat losses. These losses include heat dissipated by conduction through the surrounding medium, convection through these circulating gases, conduction through the high thermal conductivity heater and sample wires, and by radiation effects. Minimizing the contributing magnitude of these errors to the total measurement uncertainty requires both design and data analysis considerations.

To facilitate compatibility with the concurrent resistivity and Seebeck coefficient measurements, the thermal conductivity measurement requires an absolute, longitudinal steady-state method (Figure 8). In this method, electrical current sourced through a small 100 Ω resistor epoxied to the free end of the specimen provides a thermal current toward a heat sink soldered to the opposite end of the specimen, establishing a stable thermal differential. A custom programmed LabVIEW subVI monitors the thermal differential by translating the measured voltage from a chromel/constantan differential thermocouple. The thermocouple is epoxied within small divots bored into the specimen’s surface. The software continuously adjusts the heater current until this differential stabilizes within a predetermined temperature range. At 300 K, the thermal differential is ≈ 0.5 K and stable to within ± 8 mK at 300 K, increasing to ± 15 mK at 12 K. Once the subVI establishes
the required stability and drift tolerance, both the thermal differential and the heater power are recorded to calculate one $Q/\Delta T$ conductance datum. This sequence repeats twice more at acutely incremental $Q/\Delta T$ values to provide three data points. The data are linearly fit using a LabVIEW subVI and the slope yields the measured thermal conductivity according to

$$\kappa = \frac{IV}{\Delta T} \frac{l_o}{A} = \frac{Q}{\Delta T} \left( \frac{l_o}{A} \right),$$

where $I$ is the current sourced through the heater resistor, $V$ the measured resistive voltage drop across the heater, $l_o$ the effective length between the differential thermocouple contacts, and $A$ is the cross-sectional area.

Interdependent thermal errors introduce systematic offsets in the thermal differential measurement. These errors contribute to the total measurement uncertainty and require an offset correction to avoid significant deviations at low temperatures. Heater power versus $\Delta T$ traces at selected temperature intervals establish thermal stability (linear consistency) but also indicate offsets in the thermal differential measurement (Figure 9). This behavior scales dramatically as the temperature decreases. Extracting the slope from three independent and acutely increasing $Q/\Delta T$ data points eliminates the effect of this offset by essentially shifting the conductance trace to the origin. Possible sources of this offset include (but not limited to) nonuniform interface contacts, poor thermocouple contact, increased uncertainty of thermocouple voltage measurement at low temperatures, and inhomogeneities within the thermocouple wires extended across the thermal differential between the sample and the reference junction. Emphasis on the initial system design and data correction procedure limits the possible impact of these sources.
Additional thermal errors increase the difficulty in measuring the correct input heat flux to the sample, exaggerating parasitic heat losses in the Q measurement. These include heat dissipated by conduction through the surrounding medium, conduction through the high thermal conductivity heater and sample wires, and by radiation effects. Minimal design effort alleviates the severity of these losses. For example, evacuation of the sample enclosure to $10^{-5}$ torr minimizes the medium conduction losses. Thermally anchored small diameter (0.001") wires also diminish the heat conduction through sample leads, while the remaining losses can be estimated in a separate experiment to correct the measured thermal conductivity. Losses due to radiation effects further decrease input heat flux measurement accuracy. The amount of this radiation loss is given by

$$Q = \varepsilon \sigma_{S,B} A \left( T_o^4 - T_S^4 \right),$$  \hspace{1cm} (17)

where $T_o$ is the temperature of the sample, $T_S$ is the temperature of the surroundings, $\varepsilon$ is the emissivity ($0 < \varepsilon < 1$), and $\sigma_{S,B}$ is the Stephan-Boltzmann constant. A secondary radiation shield thermally anchored to the heat sink minimizes the contributing magnitude of this error to the measured thermal conductivity. These losses amount to $\approx 0.3$ W-m$^{-1}$K$^{-1}$ at room temperature.

The voltage generated for a chromel/constantan thermocouple is 68 \( \mu \)V/K at 300 K. Thus, for \( \approx 0.5 \) K \( \Delta T \) the voltage will be 34 \( \mu \)V. The stated accuracy of the 2001 Multimeter by Keithley literature in terms of \( + \) or \( - \) (ppm of reading \( + \) ppm of range), is 50 \( + \) 6, where the largest contributor is the 6 ppm of range. For the 200 mV range this is \( 6/10^6 \times 0.2 \) or 1.2 \( \mu \)V. The initial portion of the accuracy, 50 ppm of reading (or 34 \( \mu \)V \( \times \) 50/10$^6$), is negligible. Thus, the uncertainty in the meter is at most 1.2 \( \mu \)V. At room temperature for \( \approx 0.5 \) \( \Delta T \), the error from the voltage reading is \( \approx 3.5 \% \). Combined with the error in the geometric factor the total uncertainty for the thermal conductivity measurement is \( \approx 8 \% \). Note that these uncertainties do not include the uncertainty
associated with the polynomial conversion of the thermocouple voltage to the temperature gradient, which is always less than 1%.

\[ \text{F I G U R E 9. Thermal conductance traces at selected temperature intervals indicating thermal offsets in the thermal differential measurement.} \]
Clathrates form by the inclusion of atoms or molecules of one type into voids of an encapsulating crystal structure of another. The type I clathrate structure is represented by the general formula $X_8E_{46}$, where $X$ corresponds to an alkali-earth “guest” atom and $E$ to a tetrahedrally ($sp^3$) bonded group IV element, such as Si, Ge, or Sn. Type I ternary compounds also exist of the form $X_8B_{16}E_{30}$, where $B$ may represent Zn, Cd, Al, Ga, In, As, Sb, or Bi. For ternary compounds, bonding is analogous to Zintl phases. The encapsulated guest atoms donate their valence electrons to the electronegative host atoms, resulting in a stable octet (closed-valence shell). These valence electrons form the covalently bonded host framework while the guest atoms form weak bonds with the cages.

Two distinct face-sharing polyhedra conceptually comprise the type I cubic unit cell (space group $Pm\overline{3}n$): 2 pentagonal dodecahedra, $E_{20}$, and 6 tetrakaidecahedra, $E_{24}$, each creating a void with $\overline{3}m$ and $4m2$ symmetry, respectfully (see Figure 10). Analogous to their diamond structured compounds, the E-E-E bond angles average close to the characteristic $109.5^\circ$, ranging from $105^\circ$ to $126^\circ$. However, this clathrate structure deviates from the diamond-structured counterparts in their larger average interatomic
distances and larger (~15%) volume per group IV atom, demonstrating the relative openness of the clathrate crystal structure.\textsuperscript{37}

Interatomic distances calculated from refined atom positions allow the estimation of polyhedra size as a function of the encapsulated guest atom, assumed to reside in the center of each cage. Table I illustrates this comparison for Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}, Ba\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}, and K\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}, with bond lengths calculated by Schujman \textit{et al.},\textsuperscript{37} Eisenmann \textit{et al.},\textsuperscript{38} and Westerhaus and Schuster,\textsuperscript{39} respectively. The ideal structure\textsuperscript{37} assumes empty cages and identical nearest-neighbor interatomic distances, where actual values deviate by \(\pm 4\)% or less. With the introduction of various filler atoms, both polyhedra expand slightly. However, the tetrakaidecahedra diameters remain relatively uninfluenced by the size of the filler atom while the pentagonal dodecahedra expand minimally. This corroborates the generally weak bonding between the guest atoms and the host framework (weaker for the tetrakaidecahedra).

\textbf{Figure 10.} The type I structure is formed by two pentagonal dodecahedra and six lower symmetry tetrakaidecahedra in the cubic unit cell connected by shared faces. The dark circles represent group-IV atoms that comprise the framework while the lighter circles inside the polyhedra represent "guest" atoms. Copyright 2001, American Physical Society.
TABLE I. Comparison of interatomic distances and estimated polyhedra size for representative clathrates.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Ideal Ge$_{60}$ (Å)</th>
<th>Sr$<em>8$Ga$</em>{16}$Ge$_{30}$</th>
<th>Ba$<em>8$Ga$</em>{16}$Ge$_{30}$</th>
<th>K$<em>8$Ga$</em>{16}$Ge$_{30}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{d}$</td>
<td>2.496</td>
<td>2.495</td>
<td>2.5007</td>
<td>2.494</td>
</tr>
<tr>
<td>Me(1)-atom(2)</td>
<td>3.339</td>
<td>3.434</td>
<td>3.435</td>
<td>3.439</td>
</tr>
<tr>
<td>Me(2)-atom(3)</td>
<td>3.529</td>
<td>3.594</td>
<td>3.623</td>
<td>3.618</td>
</tr>
<tr>
<td>$r_1$ (dodecahedra)</td>
<td>2.114</td>
<td>2.187</td>
<td>2.185</td>
<td>2.192</td>
</tr>
<tr>
<td>$r_2$ (tetrakaidecahedra)</td>
<td>2.304</td>
<td>2.369</td>
<td>2.373</td>
<td>2.371</td>
</tr>
</tbody>
</table>

The average interatomic distance $\bar{d}$ is given by $13\bar{d} = 6d_1 + 5d_2 + d_3 + d_4$. The numbers 1, 2, and 3 represent the 6c, 16i, and 24k sites, respectively for the group IV atoms, and Me(1) and Me(2) represent the 2a (dodecahedra) and 6d (tetrakaidecahedra) sites, respectively of the “guest” atoms. $r_1=[2(Me(1) - atom(2) - \bar{d})/2$ and $r_2=[2(Me(2) - atom(3) - \bar{d})/2$

4.1.2 THERMAL CONDUCTION

Pioneering measurements by Nolas et al.\textsuperscript{41,42} on semiconducting Ge clathrates indicate the unique thermal conductivity of these compounds. Temperature dependent $\kappa$ for a phase-pure large grain size polycrystalline Sr$_8$Ga$_{16}$Ge$_{30}$ sample indicates glass-like thermal conduction, with a magnitude and temperature dependence similar to an amorphous material. Although $\kappa$ values exceed those of amorphous Ge (a-Ge) at room temperature, they remain less than amorphous quartz (a-SiO$_2$), above 100 K. The low temperature data ($< 1$ K) exhibits a $T^2$ temperature dependence and a resonant minimum at higher temperature (4 – 40 K), also characteristic of amorphous materials. These features cannot be explained by grain boundary or by mass fluctuation scattering. Extrapolations of the electronic contribution to the total lattice thermal conductivity using the Wiedemann-Franz relation reveal the total thermal conductivity comprised almost entirely from lattice contributions. While high frequency optic phonons in the clathrate exhibit low or zero group velocity and contribute little to the total thermal conductivity, low frequency acoustic phonons contribute the most, having the higher group velocity.
These data on $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ indicates low frequency scattering mechanisms replace traditional alloy phonon scattering.

Comparison of guest atom radii (Table II) with polyhedra size suggests smaller ions may more effectively “rattle” about within their cages, scattering lower frequency lattice phonons and suppressing the lattice thermal conduction. Figure 11 demonstrates this difference in temperature dependent thermal conductivity for several type I clathrates. Various measurement techniques, including theoretical calculations, structural information, ultrasonic attenuation measurements, and optical spectroscopy confirm the correlation between this dynamic disorder of the guest atoms and the observed effects on phonon modes. In addition, temperature dependent structural refinements from single crystal and powder $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ (and $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$) reveal comparatively larger anisotropic atomic displacement parameters (ADPs) for Sr(2) (and Eu[2]), by nearly an order of magnitude relative to the framework atoms. The large zero temperature ADP implies a static disorder for the guest atom in the tetrakaidecahedra in addition to the dynamic disorder. Neutron diffraction data on $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ also led Chakoumakos et al. to suggest a “split-site” model for Sr(2). Due to a non-uniform electrostatic potential within the polyhedra, the Sr ion may energetically favor certain sites. Thus, splitting the Sr (or Eu) position into four equivalent sites within the {100} plane may better describe the ADP data. This suggests a tunneling disorder where the guest atom “jumps” between different energetically preferred positions.

Not surprisingly then, Eu$^{2+}$ guest atoms demonstrate a greater influence in suppressing the lattice thermal conductivity than Sr$^{2+}$ atoms due to their smaller radii, larger mass (almost twice as massive), and a larger ADP. The combination of the two
ions, as in $\text{Sr}_4\text{Eu}_4\text{Ga}_{16}\text{Ge}_{30}$, introduces six discrete resonant scattering frequencies (three for each ion) and exhibits the lowest $\kappa$, comparatively. While Ba clathrates also possess a low lattice thermal conductivity, their temperature dependence is more typical of crystalline materials and differs with respect to the Eu and Sr clathrates due to the larger $\text{Ba}^{2+}$ ion size, diminishing the low-frequency heat carrying phonon scattering.

TABLE II. Ionic radii for typical type I clathrate guest atoms.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^{+}$</td>
<td>1.00</td>
</tr>
<tr>
<td>K$^{+}$</td>
<td>1.38</td>
</tr>
<tr>
<td>Rb$^{+}$</td>
<td>1.50</td>
</tr>
<tr>
<td>Cs$^{+}$</td>
<td>1.70</td>
</tr>
<tr>
<td>Eu$^{2+}$</td>
<td>1.17</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>1.18</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>1.38</td>
</tr>
</tbody>
</table>

FIGURE 11. Lattice thermal conductivity for representative polycrystalline type I clathrates. Copyright 1999, American Physical Society.42
4.1.3 Electronic Transport Properties

Clathrates have recently attracted interest as promising high temperature TE materials. Electrical transport property investigations by Kuznetsov et al.\textsuperscript{18} of several compounds over the range 100 – 870 K indicate an estimated ZT = 0.7 for Ba\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} at 700 K and 0.87 for Ba\textsubscript{8}Ga\textsubscript{16}Si\textsubscript{30} at 870 K with a room temperature carrier concentration of $6.8 \times 10^{20}$ cm\textsuperscript{-3}. A far more extensive analysis by Mudryk et al.\textsuperscript{55} characterizes a series of Ba and Eu substituted type I clathrates, including Cu-stabilized variants, with various framework substitutions. These include Al, Ga, or In atoms occupying Si or Ge host sites (see Figures 12 and 13). Although these compositions demonstrate the variety of transport properties available within the clathrate system, they do not offer direct insight into structure-property relationships or correlate these properties to carrier concentration.

Nominal compositions of Sr\textsubscript{8}Ga\textsubscript{16+x}Ge\textsubscript{30-x} prepared and characterized by Nolas et al.\textsuperscript{56} one of the first doping studies on type I clathrates. Since Ga substitution in the Ge framework produces charge compensation for the divalent Sr ions, a slight compositional change in the Ga-to-Ge ratio within a fixed Sr concentration results in varied carrier concentrations. As the carrier concentration increases, the Seebeck decreases, and decreases also with decreasing temperature, typical for heavily doped semiconductors. These data yielded a calculated ZT = 0.25 at 300 K and an estimated ZT $\geq$ 1 for T $>$ 700 K.

Transport properties of single-crystal Ba\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} using the Czochralski method\textsuperscript{57} demonstrate a large thermoelectric figure of merit at high temperature $\text{ZT} =$
Figure 12. Temperature dependent resistivity for selected type I clathrates. Reproduced with permission from Ref. 55. Copyright 2002, IOP Publishing, Ltd.

Figure 13. Temperature dependent Seebeck coefficient for selected type I clathrates. Reproduced with permission from Ref. 55. Copyright 2002, IOP Publishing, Ltd.
1.35 at 900 K). Discrete sectioning of the crystal preserved stoichiometric variations between selected disks. This allowed a direct comparison between slight deviations from the ideal 8:16:30 composition and the corresponding transport properties. The composition exhibiting the best thermoelectric properties measured a normalized Ga/Ge ratio of 0.4998. Extrapolated values for $S$, $\sigma$, and $\kappa$ estimate a ZT of 1.63 at 1100 K for this composition. Additional studies on single-crystal Ba$_8$Ga$_{16}$Ge$_{30}$ grown using the Czochralski method indicate a ZT of 0.9 at 1000 K with a room temperature carrier concentration of $2.0 \times 10^{21}$ cm$^{-3}$.

Theoretical band structure calculations by Blake et al.$^{59}$ examine the effect of changing the metal ion within the clathrate as well as varying the carrier concentration for both p and n-type doped Sr$_8$Ga$_{16}$Ge$_{30}$, Ba$_8$Ga$_{16}$Ge$_{30}$, Ba$_8$Ga$_{16}$Si$_{30}$, and Ba$_8$In$_{16}$Sn$_{30}$. These calculations estimate the band gap for Sr$_8$Ga$_{16}$Ge$_{30}$ and Ba$_8$Ga$_{16}$Ge$_{30}$ at 0.3 eV and 0.6 eV, respectively. Optical absorption data on Sr$_8$Ga$_{16}$Ge$_{30}$ estimate the band gap at 0.05 eV.$^{14}$ The larger band gap in Ba$_8$Ga$_{16}$Ge$_{30}$ gives it a higher $ZT_{\text{max}}$ (where $T_{\text{max}}$ is the temperature at which maximum ZT is observed) than Sr$_8$Ga$_{16}$Ge$_{30}$. Coupled to a higher melting point,$^{18}$ this feature potentially allows Ba$_8$Ga$_{16}$Ge$_{30}$ to operate at high temperatures. Maximal predicted ZT’s ($>1$) for p-doped samples of Sr$_8$Ga$_{16}$Ge$_{30}$ and Ba$_8$Ga$_{16}$Ge$_{30}$ indicate an optimal carrier concentration of $15.4 \times 10^{19}$ holes/cm$^3$ and $15.1 \times 10^{19}$ holes/cm$^3$, respectively, at 600 K. These calculations demonstrate pronounced differences in performance for the two n-doped samples at 600 K and with different optimal carrier concentrations. Although the Sr clathrate exhibits a calculated maximum ZT of 1.5, the theoretical ZT calculations for the Ba clathrate only approaches 0.8.

Previous work by Blake et al.$^{60}$ offers insight into why these electronic properties
differ. While bonding orbitals between the metal atoms and antibonding molecular orbitals (sp$^3$) of the framework form the lowest conduction bands, bonding between the Ga-Ge and Ge-Ge orbitals comprise the valence bands, almost completely localized on the framework. The smaller Sr ions migrate further away from the center of the tetrakaidecahedral cages than do the Ba ions, stabilizing the nearby Ga-Ge orbitals and destabilizing the further away Ge-Ge orbitals. This anisotropic interaction of Sr with the framework lowers the energy of the unit cell and perturbs the shape of the valence bands, altering the electronic properties.
4.2 Optimization Studies on $\text{Ba}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$

4.2.1 Synthesis and Structural Properties Characterization

Clathrates have recently attracted interest as promising high temperature TE materials due to their excellent thermoelectric properties, chemical stability at high temperature, and mechanical strength. The most promising example of single-crystal $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, grown using the Czochralski method, indicates a ZT of 0.9 at 1000 K.\textsuperscript{58} In this method, a seed crystal is pulled through a thermally gradated molten flux with precise speed and rotation, resulting in large single-crystal, stoichiometrically gradated ingots. This allows a direct comparison between slight deviations from the ideal 8:16:30 composition and the corresponding TE transport properties. However, the nature of these stoichiometric gradations result in only small, isolated regions of optimized clathrate. The remaining material is discarded (several grams). In addition, the optimized disks do not exhibit uniform composition, further complicating metrological implications. To fulfill the demands of bulk commercial thermoelectric devices requires additional synthesis techniques and a thorough identification of the optimal carrier concentration for high temperature operation.

Polycrystalline specimens of $\text{Ba}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$ ($0.5 \leq x \leq 1.2$) were prepared by induction melting stoichiometric quantities of high-purity elemental Ba, Ga, and Ge within pyrolitic boron nitride crucibles. These specimens were sealed within a quartz
ampoule under a nitrogen atmosphere, induction melted at 1100 °C for 10 min, and then water quenched. To facilitate homogeneity, the specimens were finely powdered under nitrogen atmosphere in an oxygen/moisture-free glove box, cold compacted at 100 MPa, and annealed at 800 °C for 3-5 days.

Figure 14 shows the powder X-ray diffraction (XRD) scans for the Ba$_{8}$Ga$_{16-x}$Ge$_{30+x}$ series. All nine specimens exhibit peaks characteristic of type I clathrates. The successive spectra are normalized and shifted in intensity for clarity. The normalized intensities were then amplified to identify low intensity diffraction peaks corresponding to secondary phases. All specimens exhibit a trace diamond-structured Ge phase, in total less than 2 vol.% estimated by comparing the ratio of areas beneath the most intense diffraction peaks of the impurity to the primary clathrate phase.

Two additional pellets (3.5 mm thick by 12 mm DIA) with nominal composition Ba$_{8}$Ga$_{16}$Ge$_{30}$ were synthesized for mechanical properties characterization at Oak Ridge National Laboratory. These properties are listed in Table III. The values of Young’s modulus are comparable to Al (70.3 MPa) and Cu (130 MPa), indicating the relative mechanical strength of these polycrystalline clathrates.$^{61}$ However, the bulk moduli are half of that reported for Sr$_{8}$Ga$_{16}$Ge$_{30}$.$^{62}$ In addition, Poisson’s ratio indicates orthogonal deformation of these materials under compression is similar to those of Cr (0.210) and W (0.280). For isotropic solids with no deformation under compression, $\nu = \frac{1}{2}$.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Density (g·cm$^{-3}$)</th>
<th>$E$ (GPa)</th>
<th>$B$ (GPa)</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP-I</td>
<td>5.749</td>
<td>100.9</td>
<td>61.8</td>
<td>0.228</td>
</tr>
<tr>
<td>MP-II</td>
<td>5.774</td>
<td>100.0</td>
<td>61.3</td>
<td>0.228</td>
</tr>
</tbody>
</table>
FIGURE 14. Standard XRD scans for the nine Ba$_8$Ga$_{16-x}$Ge$_{30+x}$ specimens. Asterisks (*) indicate a Ge impurity phase.

4.2.2 PHYSICAL PROPERTIES CHARACTERIZATION

Ba$_8$Ga$_{16-x}$Ge$_{30+x}$ specimens were powdered to 325 mesh (45 µm) and inserted within a 0.5” inner diameter cylindrical graphite die, situated between molybdenum punches and isolated via graphite foil. This isolation prevents reaction between the sample and the metal punches while simplifying release of the pellet following densification. The specimens were cold compacted and then hot pressed (Thermal Technology Inc. Hot Press, Model # HP20-4560-20) under nitrogen flow. An applied uniaxial pressure of 190 MPa at 800° C for 2 hours yielded densities ≥ 96 % of the
theoretical values (Table IV). This sintering temperature required development of custom high-Ni steel alloy hot press spacers.

Densified clathrates were cut into 2 x 2 x 10 mm³ parallelepipeds for high temperature (> 300 K) transport property measurements and 1 mm thick 12 mm diameter disks for high temperature thermal diffusivity measurements. High temperature four-probe resistivity and static DC Seebeck coefficient were measured from 300 K – 950 K at Oak Ridge High Temperature Measurement Laboratory (HTML) using an ULVAC ZEM-2 measuring system and pressure balance contact probes within an uncertainty of 3 % and 5 %, respectively. Room temperature four-probe Hall measurements were conducted at multiple positive and negative magnetic fields to eliminate voltage probe misalignment effects and thermal instabilities within a 10 % uncertainty.

The dependence of thermoelectric transport properties with temperature indicates behavior typical of degenerate (highly-doped) semiconductors (Figure 15). For all specimens, the high temperature resistivity data indicates metallic-like behavior ($d\rho/dT > 0$) with a monotonic increase with temperature. A linear and negative magnetic field dependence of the Hall resistance up to 2 T indicates dominant, single carrier n-type conduction. These carrier concentrations increase with a decrease in the nominal Ga-to-group IV element ratio (decreasing from specimen A through I), from $5.57 \times 10^{20}$ cm$^{-3}$ to $1.2 \times 10^{21}$ cm$^{-3}$, as listed in Table IV. Furthermore, the resistivity values decrease with a decrease in the nominal Ga-to-group IV element ratio, from 1.74 mΩ-cm to 0.78 mΩ-cm, at 325 K, also listed in Table IV. The lowest $\rho$ values compare well with Kuznetsov et al.,$^{18}$ Samarat et al.,$^{57}$ and Christensen et al.,$^{58}$ who report 0.66 mΩ-cm (polycrystalline), 0.67 mΩ-cm (single crystal), 0.64 mΩ-cm (single crystal), respectively at 300 K. Since

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Ga substitution produces charge compensation for the divalent Ba ions (a fixed concentration), a decrease in the Ga-to-group IV element ratio results in an increased density of charge carriers and thus lowers the resistivity. The specimen with the lowest resistivity demonstrates the largest power factor at 950 K, with an optimal room temperature carrier concentration of $9.86 \times 10^{20}$ cm$^{-3}$. This compares to room temperature values of $6.8 \times 10^{20}$ cm$^{-3}$ for a high ZT polycrystalline specimen and $2.0 \times 10^{21}$ cm$^{-3}$ for the Czochralski-pulled single crystal specimen. Although the carrier concentration for the single crystal specimen is ~ 2x larger than the optimal specimen identified by this research, it also exhibits a lower calculated mobility of $4.9 \text{ cm}^2/\text{V}\cdot\text{s}$ (7.8 cm$^2/\text{V}\cdot\text{s}$ reported), compared to $8.1 \text{ cm}^2/\text{V}\cdot\text{s}$ for specimen H.

Table IV. Percent theoretical density $D$, Seebeck coefficient $S$, resistivity $\rho$, power factor $S^2\sigma$, and mobility $\mu$, all at 325 K, and the carrier concentration $n$ at 300 K, shown in comparison to single crystal values reported by Christensen at 300 K. (*) See Reference 58.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>D (%)</th>
<th>$S$ ($\mu$V/K)</th>
<th>$\rho$ (m$\Omega$-cm)</th>
<th>$n$ (cm$^{-3}$) x $10^{20}$</th>
<th>$S^2\sigma$ ($\mu$W/K$^2$cm)</th>
<th>$\mu$ (cm$^2$/V$\cdot$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>99</td>
<td>-63</td>
<td>1.74</td>
<td>5.57</td>
<td>2.28</td>
<td>6.4</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>-58</td>
<td>1.16</td>
<td>5.94</td>
<td>2.88</td>
<td>9.1</td>
</tr>
<tr>
<td>C</td>
<td>96</td>
<td>-56</td>
<td>1.06</td>
<td>6.84</td>
<td>2.97</td>
<td>8.6</td>
</tr>
<tr>
<td>D</td>
<td>100</td>
<td>-55</td>
<td>0.99</td>
<td>6.95</td>
<td>3.03</td>
<td>9.1</td>
</tr>
<tr>
<td>E</td>
<td>99</td>
<td>-52</td>
<td>0.90</td>
<td>7.81</td>
<td>2.98</td>
<td>8.9</td>
</tr>
<tr>
<td>F</td>
<td>100</td>
<td>-55</td>
<td>0.97</td>
<td>7.90</td>
<td>3.11</td>
<td>8.1</td>
</tr>
<tr>
<td>G</td>
<td>99</td>
<td>-49</td>
<td>0.82</td>
<td>9.43</td>
<td>2.93</td>
<td>8.1</td>
</tr>
<tr>
<td>H</td>
<td>100</td>
<td>-49</td>
<td>0.78</td>
<td>9.86</td>
<td>3.06</td>
<td>8.1</td>
</tr>
<tr>
<td>I</td>
<td>96</td>
<td>-50</td>
<td>0.84</td>
<td>10.2</td>
<td>3.03</td>
<td>7.3</td>
</tr>
<tr>
<td>Christensen</td>
<td>N/A</td>
<td>-46</td>
<td>0.64</td>
<td>20</td>
<td>3.31</td>
<td>4.9*</td>
</tr>
</tbody>
</table>

Figure 15 illustrates the temperature dependence of the Seebeck coefficient. Minor discrepancies in $|S|$, $\rho$, and $n$ transport correlations can be attributed to measurement uncertainty. However, as a general trend, the room temperature $|S|$ values decrease with increasing carrier concentration and with decreasing resistivity. These
values vary between -49 µV/K and -63 µV/K at 325 K then increase to -162 µV/K and -180 µV/K at 950 K. The specimen demonstrating the largest power factor exhibits the smallest $|S|$ value throughout the measured temperature range, with a maximum value of 162 µV/K at 950 K. Compared to the Czochralski-pulled single crystal specimen at 950 K, this polycrystalline $|S|$ value is ~ 15 % larger, but also exhibits a slightly larger resistivity. No maximums were observed in the temperature dependent resistivity or Seebeck coefficient data, as the onset of minority band conduction occurs at higher temperature.\textsuperscript{18,58}

Figure 16 plots the calculated power factors for the Ba$_8$Ga$_{16-x}$Ge$_{30+x}$ specimens in comparison to power factor values extrapolated from $|S|$ and $\rho$ data reported by Christensen \textit{et al.}\textsuperscript{58} These polycrystalline specimens demonstrate a thermoelectric performance comparable to the single crystal specimen. The specimen with the lowest resistivity but the smallest $|S|$ (specimen H) demonstrates the largest power factor of 13.4 µW/K$^2$cm at 950 K, with an optimal room temperature carrier concentration of 9.86 x 10$^{20}$ cm$^{-3}$. However, this specimen does not exhibit the highest carrier concentration in the series or the largest room temperature power factor. This suggests low resistivity is the primary determinant in identifying the composition for optimal TE performance.

The thermal conductivity, $\kappa$, was calculated for specimen H using $\kappa = dDC_\rho$, where $d$ is the density, $D$ is the measured thermal diffusivity (Anther Corporation, model FL5000) using 1 mm thick, 12 mm diameter disks, and $C_\rho$ is the measured heat capacity (Netzsch, model 404 C Pegasus) at constant pressure. A maximum $ZT = 0.8$ is obtained at 950 K, the highest temperature measured. The $ZT$ has not peaked at this temperature and is comparable to the maximum values reported by Christensen \textit{et al.} (0.9 at 1000 K,
single crystal with \( \kappa \) estimated\(^{58}\) and very recently by Toberer et al. (0.8 at 1000 K, single crystal).\(^{63}\) This confirms that polycrystalline specimens synthesized using economical methods maintain the same thermoelectric performance as single crystal specimens fabricated using expensive and complex techniques.

**Figure 15.** Temperature dependence of the resistivity and Seebeck coefficient for Ba$_{8}$Ga$_{16-x}$Ge$_{30+x}$ at different carrier concentrations: $10.2 \times 10^{20}$ (●), $9.86 \times 10^{20}$ (○), $9.43 \times 10^{20}$ (▲), $7.90 \times 10^{20}$ (△), $7.81 \times 10^{20}$ (■), $6.95 \times 10^{20}$ (□), $6.84 \times 10^{20}$ (▼), $5.94 \times 10^{20}$ (▽), $5.57 \times 10^{20}$ (★).
FIGURE 16. Temperature dependence of the power factor for Ba$_{26}$Ga$_{16-x}$Ge$_{30+x}$ at different carrier concentrations: $10.2 \times 10^{20}$ ($\bullet$), $9.86 \times 10^{20}$ ($\bigcirc$), $9.43 \times 10^{20}$ ($\blacktriangle$), $7.90 \times 10^{20}$ ($\triangle$), $7.81 \times 10^{20}$ ($\blacksquare$), $6.95 \times 10^{20}$ ($\square$), $6.84 \times 10^{20}$ ($\blacktriangledown$), $5.94 \times 10^{20}$ ($\blacktriangleleft$), $5.57 \times 10^{20}$ ($\blacklozenge$).
4.3 Optimization Studies on Ba$_8$Ga$_{16}$Si$_x$Ge$_{30-x}$

4.3.1 Motivation

Compression studies on semiconducting Sr$_8$Ga$_{16}$Ge$_{30}$ indicate a three-fold improvement on the dimensionless figure of merit with the application of high pressure.$^{62}$ The absolute Seebeck coefficient increases monotonically with uniaxial compression, from -100 $\mu$V/K to -185 $\mu$V/K at $\sim$ 7 GPa. The electrical conductivity also demonstrates a 5x increase at this pressure. This conductivity increase couples to a rise in lattice thermal conductivity to raise the total thermal conductivity by a factor of 2. At ambient temperature, bulk compression results in a significant improvement in the thermoelectric properties of this material, suggesting possible enhancement at ambient pressures. Chemical methods may also tune the electronic structure. Substitution of smaller atoms within the lattice framework may cause a chemical strain, mimicking the effect of bulk compression. This initiated the effort to invoke lattice strain by substituting smaller Si atoms within the Ge-clathrate lattice framework.

A systematic investigation of the electrical properties of the Si-Ge alloy type I clathrate Ba$_8$Ga$_{16}$Si$_x$Ge$_{30-x}$ reported in comparison to Ba$_8$Ga$_{16}$Ge$_{30}$ and Sr$_8$Ga$_{16}$Si$_x$Ge$_{30-x}$ samples demonstrates transport properties in direct contrast to those expected in a typical rigid band semiconducting material.$^{64,65}$ The increasing Si substitution correlates to a slight increase in $|S|$ even as the resistivity decreases and the carrier concentration
increases, suggesting a modified band structure as compared to \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \).

Substitution of smaller Si atoms within the \( \text{Ga}_{16}\text{Ge}_{30} \) lattice framework may affect a chemical strain, mimicking the thermoelectric enhancement observed under high bulk compression.\(^{62}\) Initial indications of this effect in a \( \text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x} \) \( (3 < x < 6) \) series suggest the possibility of further enhancement on higher Si substituted alloys. The new research reports an additional series of Si-Ge alloy clathrates with \( (4 < x < 14) \). The original Master’s Thesis\(^6\) work on the \( \text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x} \) \( (3 < x < 6) \) series is covered for completeness as introductory material.

Figure 17 shows the temperature dependence of \( \rho \) and \( S \) for the \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) series. The sample with the lowest electron concentration (CLC, \( 9.3 \times 10^{19} \text{ cm}^{-3} \)) exhibits the greatest resistivity and the most pronounced semiconducting behavior \( (d\rho/dT < 0) \). The \( |S| \) and \( \rho \) values increase as the Ga-to-Ge ratio increases, with \( |S| \) increasing and \( \rho \) decreasing with increasing temperature, adhering to a rigid band model.

Figure 18 shows the temperature dependence of \( \rho \) for the \( \text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x} \) series. The sample with the lowest electron concentration (CL2, \( 8.0 \times 10^{18} \text{ cm}^{-3} \)) exhibits the greatest resistivity and the most pronounced semiconducting behavior \( (d\rho/dT < 0) \), while the sample with the highest electron concentration (CL4, \( 8.3 \times 10^{19} \text{ cm}^{-3} \)) exhibits a lower resistivity. Additionally, the large porosities significantly contribute to the elevated resistivity.

Figure 18 shows the \( S \) data for the \( \text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x} \) series. Comparison of the \( S \) values for the n-type \( \text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x} \) series to their respective carrier concentrations and \( \rho \) values illuminates an unexpected relationship: as the number of charge carriers increase the \( \rho \) values decrease but the \( S \) magnitude also increases by a modest amount. Although
the Ga-to-Ge ratios and the Ga-to-Si ratios vary, the Ga-to-group IV element ratios show no differentiation between the n-type samples within experimental error. Thus, the changes in carrier concentration do not correlate with the variations in $S$. Suppression of the lattice parameter as the Si content increases, coupled to the increase in carrier concentration suggests a deformation in the framework due to the smaller Si atoms. This lattice strain may alter the band structure and permit the simultaneous increase in carrier concentration and the $|S|$ values.

In order to determine if the atypical transport properties observed in the Ba$_8$Ga$_{16}$Si$_x$Ge$_{30-x}$ series are a function of Si substitution within the Ga$_{16}$Ge$_{30}$ framework or an interaction between the Ba and the Si-Ge alloy framework, the transport properties of a Sr-filled Si-Ge alloy series were evaluated for comparison. The $|S|$ and $\rho$ values increase as the Ga-to-group IV ratio increases as expected from a rigid band model. This suggests a different guest-framework interaction for Ba$^{2+}$ as compared to Sr$^{2+}$.

The carrier effective mass was estimated by expressing the Seebeck coefficient directly in terms of Fermi-Dirac integrals, assuming mixed ionized impurity and phonon scatterings ($r = 1/2$). The effective mass for the Ba$_8$Ga$_{16}$Ge$_{30}$ sample is similar to values previously reported.$^{16,18,47}$ For the Ba$_8$Ga$_{16}$Si$_x$Ge$_{30-x}$ series, the $m^*$ values increase with the increase in Si substitution. The $m^*$ values for these samples are one order of magnitude lower in comparison to Ba$_8$Ga$_{16}$Ge$_{30}$, suggesting a modification of the band curvature. This supports the previous indications that Si substitution in the Ga$_{16}$Ge$_{30}$ framework may alter the Ba$_8$Ga$_{16}$Ge$_{30}$ band structure. Higher Si substituted Si-Ge alloys are required to further investigate the potential enhancement of Si substitution induced lattice strain.
Figure 17. Temperature dependence of resistivity and Seebeck coefficient for the Ba$_8$Ga$_{16}$Ge$_{30}$ series. The stoichiometries are Ba$_{7.92}$Ga$_{15.26}$Ge$_{30.82}$, Ba$_{7.98}$Ga$_{15.43}$Ge$_{30.59}$, and Ba$_{7.95}$Ga$_{15.80}$Ge$_{30.25}$, for CLA, CLB, and CLC, respectively. Copyright 2005, IEEE.
Figure 18. Temperature dependence of the resistivity and Seebeck coefficient for the Ba$_8$Ga$_{16}$Si$_{30-x}$ series. The stoichiometries are Ba$_{8.08}$Ga$_{15.83}$Si$_{3.54}$Ge$_{26.54}$, Ba$_{8.09}$Ga$_{15.76}$Si$_{4.96}$Ge$_{25.19}$, and Ba$_{8.10}$Ga$_{15.82}$Si$_{5.11}$Ge$_{24.98}$, for CL2, CL3, and CL4, respectively. Copyright 2005, IEEE.
4.3.2 Synthesis

This research reports the structural, chemical, and thermoelectric transport properties of Si-Ge alloy type I clathrates, $\text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$, with high Si substitution ($4 < x < 14$) to determine the optimal Si substitution in maximizing the power factor. A new synthesis technique was employed to fully incorporate the higher Si substitution.

Previous specimens of lower Si substitution $\text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$ ($3 < x < 6$) were prepared by reacting stoichiometric quantities of high-purity elements within pyrolytic boron nitride crucibles. Subsequent to handling inside an oxygen/moisture free nitrogen glovebox, these specimens were sealed within a quartz ampoule under a nitrogen atmosphere, heated slowly at 1 °C/min to 900 °C, held at this temperature for 72 hours, then cooled to room temperature at 2 °C/min. To facilitate homogeneity, the specimens were finely powdered under nitrogen atmosphere, cold compacted at 8,000 lbs. and annealed according to the previous thermal treatment. This procedure was repeated twice. However, specimens with increasing Si substitution ($x > 5$) resulted in the formation of impurity phases in this synthesis approach.

To overcome the solubility limit imposed by the original direct powder sintering requires a modified synthesis. Stoichiometric quantities of high-purity elemental Si and Ge were arc-melted under argon first individually then combined. The resulting ingots were inverted and re-melted two additional times, then finely powdered under nitrogen atmosphere in an oxygen/moisture-free glove box. The uniformity and small scale of these powders greatly influence final clathrate specimen purity. Specimens of $\text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$ were prepared by reacting stoichiometric quantities of these Si-Ge
alloys and high-purity elemental Ba and Ga within pyrolitic boron nitride crucibles. These specimens were sealed within a quartz ampoule under a nitrogen atmosphere, heated slowly at 1 °C/min to 900 °C, held at this temperature for 72 hours, then cooled to room temperature at 2 °C/min. To facilitate homogeneity, the specimens were finely powdered under nitrogen atmosphere, cold compacted at 100 MPa, and annealed according to the previous thermal treatment. The entire annealing procedure was repeated twice. This method was successful in synthesizing a series of higher Si substituted \( (4 < x < 14) \) \( \text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x} \) clathrates.

4.3.3 Structural and Chemical Properties Characterization

Specimens were powdered to 325 mesh (45 µm) and inserted within a 0.5” inner diameter cylindrical graphite die, situated between molybdenum punches and isolated via graphite foil. This isolation prevents reaction between the sample and the metal punches while simplifying release of the pellet following densification. The specimens were cold compacted and then hot pressed (Thermal Technology Inc. Hot Press, Model # HP20-4560-20) under nitrogen flow. An applied uniaxial pressure of 190 MPa at 800° C for 2 hours yielded densities > 93 % of the theoretical values. Theoretical densities were calculated for each \( \text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x} \) specimen using chemical compositions obtained from electron probe microanalysis (EPMA) data (see Table V). Bulk theoretical density decreases with increasing Si substitution. All specimens demonstrate a similar Ga-to-group IV element ratio (within measurement uncertainty of 0.01 at. %), comparable to those obtained in previous specimens,\(^6\) with varying Si substitution. Qualitative analysis
of the EPMA elemental X-ray maps demonstrates a homogeneous composition distribution from grain to grain for each element. Impurity phases were observed to congregate into isolated grains and thus do not affect the bulk transport properties. These Ge, Si, and Si-Ge alloy phases were too small to characterize quantitatively using this standard measurement technique. No subgrain impurities were identified.

Figure 19 shows the X-ray diffraction (XRD) scans for the Ba$_8$Ga$_{16}$Si$_x$Ge$_{30-x}$ series. All specimens exhibit peaks characteristic of type I clathrates. The successive spectra are normalized and shifted in intensity for clarity. The normalized intensities were then amplified to identify low intensity diffraction peaks corresponding to secondary phases. All specimens exhibit trace diamond structured Si, Ge, and Si-Ge alloy phases, in total less than a few vol.% estimated by comparing the ratio of areas beneath the most intense diffraction peaks of each respective impurity to the primary clathrate phase. Specimen VI, with the highest Si substitution ($x = 13.38$), exhibits a large amount of Si impurity (< 3 vol.%). Specimens I and II exhibit a large unreacted Si-Ge alloy phase estimated below 4 vol.%. Lattice parameters (Table V) were determined from the clathrate diffraction peaks and show a linear decrease as the Si substitution increases, as shown in Figure 20, in accordance with Vegard’s law. This linear relationship indicates that Si is a compositional substitution within the lattice framework. In addition, the y-intercept (no Si substitution) is consistent with lattice parameters reported for Ba$_8$Ga$_{16}$Ge$_{30}$ clathrates ($\equiv 10.78$ Å).$^{64,69}$

Differential Scanning Calorimetry (TA Instruments, Model # SDT Q600) endotherms measured at a heating rate of 20 °C/min indicate an increase in melting temperature with an increase in Si substitution (Figure 22). These data (Table V) remain
consistent with reports on the melting temperature of Ba$_6$Ga$_{16}$Ge$_{30}$ at 957°C, and 1111°C for Ba$_8$Ga$_{16}$Si$_{30}$.$^{18}$ As shown in Figure 21, fitting a plot of the melting point vs. Si substitution with a second order polynomial yields a liquidus curve similar to those obtained in diamond structured Si-Ge alloys.$^{70}$ Repeated thermal cycling through the phase transition also shows substantial desegregation into distinct Si and Ge clathrate phases while cooling, confirming an incongruent re-crystallization.

**Figure 19.** Standard XRD scans for the six Ba$_6$Ga$_{16}$Si$_x$Ge$_{30-x}$ specimens. Asterisks (*) indicate Si-Ge alloy impurity phases. Si impurity phases are also identified by name. Reused with permission from Ref. 67. Copyright 2007, American Institute of Physics.
Figure 20. Lattice parameter vs. Si content for the six $\text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$ specimens. The dashed line is a linear fit to the data: $a_0 = -7.0014E10x + 10.7797$. Reused with permission from Ref. 67. Copyright 2007, American Institute of Physics.

Figure 21. Melting point vs. Si content for the six $\text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$ specimens. The dashed curve represents a fit to the data indicative of the liquidus curve: $T_M = -0.0037x^3 - 0.2110x^2 + 10.7397x + 919.0063$. Reused with permission from Ref. 67. Copyright 2007, American Institute of Physics.
4.3.4 Physical Properties Characterization

Densified Si-Ge alloy clathrates were cut into 2 x 2 x 5 mm³ and 2 x 2 x 10 mm³ parallelepips for low (< 300 K) and high temperature (> 300 K) transport property measurements, respectively. For low temperature measurements, electrical contacts were made by soldering directly to nickel-plated surfaces using standard techniques and thermal contacts were made using Stycast epoxy. Four-probe resistivity, Seebeck coefficient, and steady-state thermal conductivity were measured from 12 K to 300 K in a custom radiation-shielded vacuum probe. Room temperature four-probe Hall
measurements were conducted at multiple positive and negative magnetic fields to eliminate voltage probe misalignment effects and thermal instabilities within a 10 % uncertainty. High temperature four-probe resistivity and static DC Seebeck coefficient were measured from 300 K – 750 K at Oak Ridge High Temperature Measurement Laboratory (HTML) using an ULVAC ZEM-2 measuring system and pressure balance contact probes within an uncertainty of 3 % and 5 %, respectively.

Figure 23 shows the temperature dependence of the resistivity and Seebeck coefficient for the $\text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$ specimens. High temperature data (300 K – 750 K) shows very good agreement with low temperature data (12 K - 300 K). This agreement indicates the homogeneity of each specimen considering both ranges measured specimens cut from different portions of the synthesized pellet.

For all specimens, the resistivity data indicates semiconducting behavior ($d\rho/dT < 0$) with a monotonic increase at high temperatures. However, the resistivity for specimen III transitions abruptly to metallic-like behavior ($d\rho/dT > 0$) above 200 K (inset in Figure 23). This may indicate an early onset of minority carrier band population. A nonlinear magnetic field dependence of the Hall resistance at 300 K for this specimen further suggests multicarrier conduction. Therefore, a carrier concentration could not be determined with this room temperature Hall measurement technique. For the remaining specimens, a linear and negative magnetic field dependence of the Hall resistance up to 2 T indicates dominant n-type conduction. These carrier concentrations increase with increasing Si substitution, from $1.12 \times 10^{20}$ cm$^{-3}$ to $2.16 \times 10^{20}$ cm$^{-3}$, as listed in Table VI. Furthermore, the resistivity values decrease with increasing Si substitution, from 41.3 mΩ-cm to 7.9 mΩ-cm, at 300 K, also listed in Table VI. Specimen III deviates slightly
from this trend, exhibiting the lowest resistivity values in the series but also a lower Ga-to-group IV element ratio in comparison to the other specimens. Since Ga produces charge compensation for the divalent Ba ions (a fixed concentration), a decrease in the Ga-to-group IV element ratio results in an increased density of charge carriers and thus lowers the resistivity. This specimen’s $|S|$ values might also be lower due to the Ga deficiency and the possibility of dual conduction. For the other specimens, the lack of variation in the Ga-to-group IV element ratios and the strong dependence of $n$ with Si substitution may imply a continuously modified band structure with $x$ rather than an increase in conduction band population from donor states.

TABLE V. The composition obtained by EPMA, Ga-to-group IV element ratio, measured percentage of theoretical density $D$, lattice parameter $a_o$, and the melting point $T_M$ for the six $\text{Ba}_8\text{Ga}_{16}\text{Si}_{x}\text{Ge}_{30-x}$ specimens. Reused with permission from Ref. 67. Copyright 2007, American Institute of Physics.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Composition</th>
<th>Ga/group IV</th>
<th>$D$ (%)</th>
<th>$a_o$ (Å)</th>
<th>$T_M$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\text{Ba}<em>{8.06}\text{Ga}</em>{15.59}\text{Si}<em>{4.54}\text{Ge}</em>{25.71}$</td>
<td>0.519</td>
<td>94</td>
<td>10.750</td>
<td>963</td>
</tr>
<tr>
<td>II</td>
<td>$\text{Ba}<em>{8.05}\text{Ga}</em>{15.78}\text{Si}<em>{5.05}\text{Ge}</em>{25.11}$</td>
<td>0.523</td>
<td>93</td>
<td>10.744</td>
<td>968</td>
</tr>
<tr>
<td>III</td>
<td>$\text{Ba}<em>{8.00}\text{Ga}</em>{15.66}\text{Si}<em>{7.47}\text{Ge}</em>{22.80}$</td>
<td>0.517</td>
<td>96</td>
<td>10.726</td>
<td>985</td>
</tr>
<tr>
<td>IV</td>
<td>$\text{Ba}<em>{8.08}\text{Ga}</em>{15.74}\text{Si}<em>{9.05}\text{Ge}</em>{21.16}$</td>
<td>0.521</td>
<td>99</td>
<td>10.715</td>
<td>997</td>
</tr>
<tr>
<td>V</td>
<td>$\text{Ba}<em>{8.08}\text{Ga}</em>{15.76}\text{Si}<em>{10.72}\text{Ge}</em>{19.44}$</td>
<td>0.523</td>
<td>94</td>
<td>10.705</td>
<td>1005</td>
</tr>
<tr>
<td>VI</td>
<td>$\text{Ba}<em>{8.06}\text{Ga}</em>{15.84}\text{Si}<em>{13.38}\text{Ge}</em>{16.68}$</td>
<td>0.527</td>
<td>94</td>
<td>10.687</td>
<td>1016</td>
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</table>

TABLE VI. Si content obtained by EPMA, resistivity $\rho$, Seebeck coefficient $S$, power factor $S^2\sigma$, carrier concentration $n$, mobility $\mu$, and calculated effective mass, at room temperature for the six $\text{Ba}_8\text{Ga}_{16}\text{Si}_{x}\text{Ge}_{30-x}$ specimens. Reused with permission from Ref. 67. Copyright 2007, American Institute of Physics.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Si</th>
<th>$\rho$ (mΩ-cm)</th>
<th>$S$ (µV/K)</th>
<th>$S^2\sigma$ (µW/K²-cm)</th>
<th>$n$ (cm⁻³)</th>
<th>$\mu$ (cm²/V·s)</th>
<th>$m^*/m$</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>4.54</td>
<td>41.3</td>
<td>-67</td>
<td>0.11</td>
<td>1.12E+20</td>
<td>1.4</td>
<td>0.41</td>
</tr>
<tr>
<td>II</td>
<td>5.05</td>
<td>28</td>
<td>-80</td>
<td>0.23</td>
<td>1.49E+20</td>
<td>1.5</td>
<td>0.60</td>
</tr>
<tr>
<td>III</td>
<td>7.47</td>
<td>6.5</td>
<td>-96</td>
<td>1.42</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IV</td>
<td>9.05</td>
<td>10.2</td>
<td>-112</td>
<td>1.23</td>
<td>1.61E+20</td>
<td>3.8</td>
<td>0.93</td>
</tr>
<tr>
<td>V</td>
<td>10.72</td>
<td>8.7</td>
<td>-103</td>
<td>1.22</td>
<td>1.84E+20</td>
<td>3.9</td>
<td>0.92</td>
</tr>
<tr>
<td>VI</td>
<td>13.38</td>
<td>7.9</td>
<td>-88</td>
<td>0.98</td>
<td>2.16E+20</td>
<td>3.7</td>
<td>0.86</td>
</tr>
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</table>
FIGURE 23. Temperature dependence of resistivity and Seebeck coefficient for the six Ba$_x$Ga$_{16}$Si$_x$Ge$_{30-x}$ specimens, I (●), II (○), III (▲), IV (△), V (■), VI (□), with compositions indicated in Table I. Inset shows temperature dependence of the resistivity for specimen III. Reused with permission from Ref. 67. Copyright 2007, American Institute of Physics.
Figure 24 shows the temperature dependence of the lattice thermal conductivity, \( (\kappa_L) \) for the \( \text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x} \) specimens from 12 K to 300 K. The carrier contribution \( (\kappa_e) \) to the total thermal conductivity, calculated using the resistivity values in Figure 23 and the Wiedemann-Franz relation \( (\kappa_e = L_0 T/\rho) \), where the Lorenz number \( L_0 = 2.45 \times 10^{-8} \text{ V}^2\text{/K}^2 \), indicates a lattice-dominated thermal conduction with \( \kappa_e < 7 \% \) at 300 K for all specimens. The temperature dependence of \( \kappa_L \) is similar to n-type \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) clathrates previously reported\(^{18,47,71}\) with a maximum occurring between 20 K and 30 K and the absence of a plateau below 20 K as observed in \( \text{Sr}_8\text{Ga}_{16}\text{Ge}_{30} \) and \( \text{Eu}_8\text{Ga}_{16}\text{Ge}_{30} \).\(^{52,53,72}\) The addition of Si for these concentrations does not strongly reduce \( \kappa_L \), indicating the guest-framework interaction is the strongest phonon scattering mechanism in these materials.\(^{73}\) At room temperature, \( \kappa_L \approx 1.3 \text{ W/mK} \) for all specimens.

![Figure 24. Temperature dependence of the lattice thermal conductivity for the six \( \text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x} \) specimens, I (●), II (○), III (▲), IV (△), V (■), VI (□), with compositions indicated in Table I. Reused with permission from Ref. 67. Copyright 2007, American Institute of Physics.](image-url)
As shown in Figure 23, the $|S|$ values increase with increasing Si substitution, approaching a maximum in specimen IV, then decrease with further substitution. This maximum in $|S|$ occurs for a Si substitution of $x = 9.05$, exhibiting the largest power factor (disregarding Ga-deficient specimen III) and one of the largest mobilities, listed in Table III. Furthermore, the increase in $|S|$ coincides with an increasing carrier concentration, a variation from typical compound semiconductors. These trends do not adhere to a rigid-band semiconducting model and suggest a modified band structure with increasing Si substitution. The carrier effective mass was estimated by expressing the Seebeck coefficient directly in terms of Fermi-Dirac integrals\(^6\)

\[
S = \pm \frac{k_B}{e} \left[ \eta \left( \frac{r + \frac{5}{2}}{2} \right) F_{r+3/2}(\eta) - \left( \frac{r + \frac{3}{2}}{2} \right) F_{r+1/2}(\eta) \right],
\]

where $k_B$ is Boltzmann’s constant, $e$ the carrier charge, $r$ the exponent of the energy dependence of the carrier relaxation time, $F_x$ the Fermi integral of order $x$, and $\eta = E_F/k_B T$ the reduced Fermi energy. The $+$ and $-$ signs correspond to valence band carriers and conduction band carriers, respectively. This estimate requires the following assumptions: a single carrier type in a parabolic band, the absence of multiband effects, and no phonon-drag effects. The carrier concentration is given by

\[
n = \left[ \frac{4 \pi (2m_e kT)^{3/2}}{h^3} \right] \left( \frac{m^*}{m_o} \right)^{3/2} F_{1/2}(\eta),
\]

where $m_o$ is the free electron mass, $m^*$ is the effective electron mass. Assuming mixed ionized impurity and phonon scatterings ($r = 1/2$), the estimated effective mass was calculated for the Ba$_8$Ga$_{16-x}$Si$_x$Ge$_{30-x}$ specimens and is listed in Table VI. These $m^*$ values
increase with increasing Si substitution, doubling from $0.41m_o$ (specimen I) to $0.93m_o$ (specimen IV), then decrease to $0.86m_o$ with further substitution (specimen VI). In contrast, Si-Ge alloys demonstrate no $m^*$ dependence with composition. The dependence of $m^*$ with Si substitution in these $\text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$ specimens suggests a modification of the conduction band curvature, corroborating evidence in both the $\rho$ and $S$ data that changes in $x$ correlate with changes in the band structure. Substitution of Si within the Ga-Ge lattice framework may produce a chemical strain, due to the smaller bond length of Si compared to Ga and Ge, mimicking the thermoelectric enhancement effects observed in $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ under bulk compression. This lattice contraction (Figure 20) may modify the orbital interaction between the guest atoms and the framework, increasing the electron overlap and Ba’s effectiveness to hybridize with the electron-deficient Ga orbitals. Theoretical modeling indicates this interaction forms the lowest conduction bands. Furthermore, Density Functional Theory (DFT) investigations of unfilled $\text{Si}_{34-x}\text{Ge}_x$ type II clathrates also indicate a strong dependence of band gap and band curvature with composition. Figure 25 summarizes the dependence of $S$, $\rho$, and $m^*$ with increasing Si substitution for the $\text{Ba}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$ specimens, at room temperature. These data indicate the optimum Si substitution in maximizing the power factor ($S^2\sigma$) is $x = 9$, with a maximum occurring in both $|S|$ and $m^*$, and a 75 % decrease in resistivity, in comparison to the lowest Si substituted specimen.

Substitution of Si within the Ga-Ge lattice framework of the type I clathrate $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ results in thermoelectric performance enhancement. The dependence of the lattice parameter with $x$ indicates deformations in the polyhedra. This lattice contraction may modify the orbital interaction between the guest atoms and the framework, and
consequently, modify the electronic transport. The unique dependences of \( n \), \( \rho \), \( |S| \), and \( m^* \) with Si substitution, and the lack of variation in the Ga-to-group IV element ratios imply a modified band structure with \( x \) rather than an increase in conduction band population from donor states. These results indicate the thermoelectric properties of Ba\(_8\)Ga\(_{16}\)Ge\(_{30}\) type I clathrates can be enhanced upon a 20% Si substitution on the framework sites, in addition to establishing the best Ga-to-group IV element ratio to optimize the carrier concentration.

![Graph showing Resistivity, Seebeck coefficient, and calculated effective mass vs. Si substitution for Ba\(_8\)Ga\(_{16}\)Si\(_x\)Ge\(_{30-x}\) specimens.](image)

**Figure 25.** Resistivity (●), Seebeck coefficient (▲ for \( 4 < x < 14 \) and △ for the three specimens from ref. 61), and calculated effective mass (inset) vs. Si substitution for the six Ba\(_8\)Ga\(_{16}\)Si\(_x\)Ge\(_{30-x}\) specimens. The dashed curves are visual guides for the eye only. Reused with permission from Ref. 67. Copyright 2007, American Institute of Physics.
4.4 Optimization Studies on Ba$_8$Ga$_{16-x}$Si$_x$Ge$_{30+x}$

4.4.1 Synthesis

Previous specimens of Ba$_8$Ga$_{16-x}$Si$_x$Ge$_{30-x}$ were prepared by reacting stoichiometric quantities of arc-melted Si-Ge alloys with high-purity elemental Ba and Ga. This method was successful in synthesizing a series of higher Si substituted (4 < x < 14) Ba$_8$Ga$_{16-x}$Si$_x$Ge$_{30-x}$ clathrates but with similar Ga-to-group IV element ratios. To systematically modify the Ga-to-group IV element ratio requires additional synthesis techniques. Specimens of Ba$_8$Ga$_{16-x}$Si$_x$Ge$_{30+x}$, with 0.5 ≤ x ≤ 1.2 and a fixed Si substitution, were prepared by induction melting stoichiometric quantities of high-purity elemental Ba, Ga, Si, and Ge within pyrolytic boron nitride crucibles. These specimens were sealed within a quartz ampoule under a nitrogen atmosphere, induction melted at 1250 °C for 10 min, and then water quenched. This rapid cooling prevents desegregation of the liquid melt into distinct Si and Ge clathrate phases and promotes the stability of low Ga, Si-Ge clathrates. To facilitate homogeneity, the specimens were finely powdered under nitrogen atmosphere, cold compacted at 100 MPa, and annealed at 800 °C for 3-5 days. This modified synthesis method results in Si-Ge alloy type I clathrates of higher purity than the previous sintering approaches. Substitution of 20% Si within the Ga-Ge lattice framework of the type I clathrate Ba$_8$Ga$_{16}$Ge$_{30}$ results in thermoelectric performance enhancement.$^{67}$ In addition, this new synthesis technique will identify the
best Ga-to-group IV element ratio required to further optimize the carrier concentration for high temperature TE performance. These two techniques represent a complimentary strategy to identify the composition exhibiting optimal TE properties.

Specimens were powdered to 325 mesh (45 µm), cold compacted, and then hot pressed (Thermal Technology Inc. Hot Press, Model # HP20-4560-20) under nitrogen flow. An applied uniaxial pressure of 190 MPa at 825 °C for 2 hours yielded densities < 90 % of the theoretical values, indicating large porosity. Theoretical densities were estimated for each Ba₈Ga₁₆Si₃Ge₃₀₋ₓ specimen using nominal compositions and Si content extrapolated from chemical data (see Table VII).

**4.4.2 STRUCTURAL AND CHEMICAL PROPERTIES CHARACTERIZATION**

Figure 26 shows the X-ray diffraction (XRD) scans for the Ba₈Ga₁₆₋ₓSi₃Ge₃₀₋ₓ series. All specimens exhibit peaks characteristic of type I clathrates. The successive spectra are normalized and shifted in intensity for clarity. The normalized intensities were then amplified to identify low intensity diffraction peaks corresponding to secondary phases. All specimens exhibit a trace Si-Ge alloy phase, in total ~ 2 vol.% estimated by comparing the ratio of areas beneath the most intense diffraction peaks of each respective impurity to the primary clathrate phase. Lattice parameters were determined from the clathrate diffraction peaks and DSC endotherms measured at a heating rate of 20 °C/min indicated specimen melting temperature (Table VII). The Si compositions were extrapolated by indexing this lattice parameter data with the linear fit obtained in Figure 27 (lattice parameter vs. EPMA Si substitution) and by indexing the
melting temperatures with the polynomial fit obtained in Figure 28 (melting temperature vs. EPMA Si substitution). The Si compositions estimated by these two techniques were consistent within 0.1 at.% and mitigated the necessity for EPMA data.

Figure 26. Standard XRD scans for the six Ba$_{16}$Ga$_{16-x}$Si$_x$Ge$_{20}$ specimens. Asterisks (*) indicate Si-Ge alloy impurity phases.
**Figure 27.** Lattice parameter vs. Si content for the six $\text{Ba}_8\text{Ga}_{16-x}\text{Si}_x\text{Ge}_{30-x}$ specimens. The dashed line is a linear fit to the data. The larger blue circles represent the lattice parameter vs. extrapolated $x$ content for the $\text{Ba}_8\text{Ga}_{16-x}\text{Si}_x\text{Ge}_{30-x}$ specimens. Fit: $a_0 = -7.0014 \times 10^3 x + 10.7797$.

**Figure 28.** Melting point vs. Si content for the six $\text{Ba}_8\text{Ga}_{16-x}\text{Si}_x\text{Ge}_{30-x}$ specimens. The dashed curve represents a second-order polynomial fit to the data indicative of the liquidus curve. The larger blue circles represent the melting point vs. extrapolated $x$ content for the $\text{Ba}_8\text{Ga}_{16-x}\text{Si}_x\text{Ge}_{30-x}$ specimens. Fit: $T_M = -0.0037 x^3 - 0.2110 x^2 + 10.7397 x + 919.0063$. 
4.4.3 Physical Properties Characterization

Densified low Ga Si-Ge alloy clathrates were cut into 2 x 2 x 10 mm³ parallelepipeds for high temperature transport property measurements. High temperature four-probe resistivity and static DC Seebeck coefficient were measured from 300 K – 950 K at Oak Ridge High Temperature Measurement Laboratory (HTML) using an ULVAC ZEM-2 measuring system and pressure balance contact probes within an uncertainty of 3 % and 5 %, respectively. Room temperature four-probe Hall measurements were conducted at multiple positive and negative magnetic fields to eliminate voltage probe misalignment effects and thermal instabilities within a 10 % uncertainty.

The dependence of ρ and |S| with temperature indicates behavior typical of degenerate semiconductors (Figure 29). For all specimens, the high temperature resistivity data indicates metallic-like behavior (dp/dT > 0) with a nonlinear increase with temperature. This rate of increase accelerates above 700 K, suggesting enhanced charge carrier-phonon scattering in the heavily Si substituted lattice framework. The decreasing resistivity values above 850 K correlate to a decrease in |S|, indicating the onset of bipolar conduction. A linear and negative magnetic field dependence of the Hall resistance up to 2 T indicates dominant, single carrier n-type conduction. These carrier concentrations increase with a decrease in the nominal Ga-to-group IV element ratio, from 2.27 x 10²⁰ cm⁻³ to 1.13 x 10²¹ cm⁻³, as listed in Table VII. Furthermore, the resistivity values decrease with a decrease in the nominal Ga-to-group IV element ratio, from 7.6 mΩ-cm to 0.93 mΩ-cm, at 300 K, also listed in Table VII. Since Ga substitution produces charge
compensation for the divalent Ba ions (a fixed concentration), a decrease in the Ga-to-group IV element ratio results in an increased density of charge carriers and thus lowers the resistivity.

The room temperature $|S|$ values decrease with increasing carrier concentration, and with decreasing resistivity and a decrease in the nominal Ga-to-group IV element ratio. These values vary between $-44 \, \mu V/K$ and $-81 \, \mu V/K$ at 300 K then increase to $-180 \, \mu V/K$ and $-220 \, \mu V/K$ at 950 K. In addition, the $|S|$ values increase with temperature, reach a maximum near 850 K, then decrease with the onset of thermally activated bipolar conduction. This dual carrier contribution affects lower $n$ carrier density specimens more severely.

Figure 30 illustrates the temperature dependence of the power factor, indicating a maximum near 850 K. The specimen with the lowest $\rho$ and the smallest $|S|$ exhibits the largest power factor in this series of $2.08 \, \mu W/K^2 cm$ with a carrier concentration of $1.13 \times 10^{21} \, cm^{-3}$, similar to the $9.86 \times 10^{20} \, cm^{-3}$ value for $Ba_8Ga_{16-x}Ge_{30+x}$ specimen H. These properties are strongly influenced by variations in the Ga-to-group IV element ratios, suggesting that small deviations from the nominal 20 at. % Si substitution do not correlate to the dynamic trends observed in the transport data. Comparing this room temperature transport data with specimen IV indicates the reduction in Ga-to-group IV element ratio results in a 10x increase in carrier concentration and a 10x decrease in the resistivity, but only a $\sim 40$ % decrease in $|S|$. This results in a 40 % increase in the room temperature power factor as compared to specimen IV (see Table VII). In addition, reducing the high porosity ($\sim 10$ %) of these specimens should further decrease the resistivity, resulting in larger power factors with a peak near 850 K.
TABLE VII. Si content obtained by extrapolating data from the lattice parameter $a_0$ and the melting point $T_M$, resistivity $\rho$, Seebeck coefficient $S$, power factor $S^2\alpha$, nominal Ga content, and carrier concentration $n$, at room temperature for the five $\text{Ba}_8\text{Ga}_{16-x}\text{Si}_9\text{Ge}_{30+x}$ specimens. *Compositions obtained from EPMA data.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Si (from $a_0$)</th>
<th>Si (from $T_M$)</th>
<th>Ga ($\mu$Ω·cm)</th>
<th>$\rho$ (mΩ·cm)</th>
<th>$S$ (μV/K)</th>
<th>$S^2\alpha$ (μW/K²·cm)</th>
<th>$n$ (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>9.05*</td>
<td>15.74*</td>
<td>15</td>
<td>10.2</td>
<td>-112</td>
<td>0.86</td>
<td>2.27E+20</td>
</tr>
<tr>
<td>SG-I</td>
<td>8.25</td>
<td>8.19</td>
<td>15.5</td>
<td>7.6</td>
<td>-81</td>
<td>1.23</td>
<td>2.67E+20</td>
</tr>
<tr>
<td>SG-II</td>
<td>8.67</td>
<td>8.6</td>
<td>15.2</td>
<td>3.1</td>
<td>-76</td>
<td>1.86</td>
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<td>SG-III</td>
<td>7.38</td>
<td>7.34</td>
<td>15.0</td>
<td>2.9</td>
<td>-58</td>
<td>1.16</td>
<td>1.1E+20</td>
</tr>
<tr>
<td>SG-IV</td>
<td>9.53</td>
<td>-</td>
<td>14.8</td>
<td>1.8</td>
<td>-47</td>
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<td>SG-V</td>
<td>10.24</td>
<td>10.06</td>
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<td>0.93</td>
<td>-44</td>
<td>2.08</td>
<td>11.3E+20</td>
</tr>
</tbody>
</table>

FIGURE 29. Temperature dependence of the resistivity and Seebeck coefficient for three of the $\text{Ba}_8\text{Ga}_{16-x}\text{Si}_9\text{Ge}_{30+x}$ specimens: SG-I (●), SG-II (○), and SG-III (▲).
Figure 30. Temperature dependence of the power factor for three of the Ba$_3$Ga$_{16-x}$Si$_9$Ge$_{30-x}$ specimens: SG-I (●), SG-II (○), and SG-III (▲).
5 Nanostructured Enhancement of Lead Chalcogenides

5.1 Introduction to Lead Chalcogenides

Lead chalcogenides form by bonding group IV (Pb) and group VI elements (S, Se, Te) in a cubic FCC crystal structure. The conduction band minima and valence band maxima located at the same point in k-space along the <111> direction, with four equivalent minima. Lead chalcogenides are polar semiconductors since bonding is only partially covalent with weak ionicity. In addition, they exhibit low carrier effective mass and narrow band gaps of 0.3-0.4 eV that increase with temperature. This gap increase raises the temperature at which minority carrier conduction limits the TE performance.

The naturally occurring crystals PbS (galenite), PbSe (clausthalite), and PbTe (altaite) were first investigated as TE materials beginning in 1865. PbTe is considered an intermediate thermoelectric material due to its moderate figure of merit, high operating temperature (900 K), strength, and chemical stability. The carrier type is heavily dependent on the stoichiometry, with Te-rich materials exhibiting p-type conduction. Adjustments to the carrier density beyond the stoichiometric solubility requires impurity doping with halogens (Cl, Br, I, with an amount of Pb, Sn, Ge, Mg, Pt, or Ni) for donor impurities and Na, Li, Tl, Ag, or O for acceptor levels. These impurity dopants produce carrier densities up to (1-2) \times 10^{20} \text{ cm}^{-3}, except for oxygen which occupies sites within the Te sublattice, resulting in hole densities only up to (3-4) \times 10^{18} \text{ cm}^{-3}. 

76
cm$^3$. Since lead chalcogenides are simple binary compounds with extensive theoretical and experimental data, they are ideal candidates for investigating nanostructured thermoelectric enhancement. Section 2.3 provides a review of nanostructured thermoelectric enhancement in a variety of materials systems.

This research reports a novel approach to prepare lead chalcogenide (PbTe) dimensional nanocomposites by densifying nanocrystals synthesized employing an aqueous solution-phase reaction with a high yield and low cost. Densification using spark plasma sintering (SPS) successfully integrates disperse 100 – 150 nm PbTe nanocrystals within a bulk nanocomposite, demonstrating for the first time that nanocrystals dispersed within dense bulk polycrystalline PbTe can be prepared from solution-phase synthesized nanocrystals. Furthermore, the carrier concentration of the PbTe nanocomposites can be adjusted by directly doping the nanocrystals, necessary for power factor optimization. Directly comparing these nanocomposites with bulk polycrystalline materials yields the most direct evidence of $|S|$ enhancement due to the dispersion of nonconglomerated nanoscale PbTe grains within the PbTe nanocomposites.
5.2 ALKALINE AQUEOUS SOLUTION SYNTHESIS OF 100 NM NANOCRSTALLINE LEAD CHALCOGENIDES

5.2.1 SYNTHESIS

Lead telluride nanocrystals were synthesized from the low temperature reaction of tellurium alkaline aqueous solution and a lead acetate trihydrate solution. To prepare the nanocrystals, monometallic precursor solutions were prepared separately at 110°C by dissolving 0.008 mol elemental Te in a 20 M KOH aqueous solution and by dissolving 0.0088 mol Pb(CH₃COO)₂·3H₂O in 40 mL distilled water. After ~ 60 minutes, the lead acetate trihydrate solution was dripped into the rapidly stirring deep purple alkaline solution to immediately form PbTe nanocrystals. After 5 minutes, the reaction mixture was removed from the heat source, quenched, and 0.1 M HNO₃ was added to flocculate the nanocrystals. The grayish-black precipitates were washed 4 times with the dilute nitric acid solution, removing lead hydroxide impurities. Excess lead acetate trihydrate in the reaction favors the formation of easily removable impurities. The precipitates were then washed 4 times with distilled water and dried overnight in a fume hood then under vacuum for 24 - 48 hours. This reaction was successful in synthesizing reproducible yields of over 2 grams per batch.

Several experiments were performed to optimize product yield by varying both the alkaline and precursor lead acetate trihydrate concentrations. Excess KOH formed a
clear solution after 1 hour, inert to the lead acetate trihydrate solution while lower KOH concentrations were unable to fully dissolve the Te. Lower concentrations of precursor lead acetate trihydrate resulted in nanocrystals of similar size and spherical morphology but far less aggregation, greatly decreasing the precipitation rate (Figure 31).

5.2.2 MODIFICATION STUDIES

Experiments were also performed to modify the nanocrystal size and morphology through sonochemical reactions. Sonochemistry utilizes high intensity ultrasonic waves to initiate cavitation and homogeneously disperse materials in aqueous solution. A 300 W ultrasonic homogenizer with a ¾” titanium horn was placed in the alkaline aqueous solution prior to the addition of the lead acetate trihydrate solution. The ultrasonic homogenizer was activated during the addition of the second solution to promote the growth of smaller crystallites and a more homogenous distribution of nanoparticle diameters. Adjustable parameters included power intensity, duration, intermittent duration, and precursor concentration. For an intensity of 60 %, increasing the ultrasonic duration over the range 5 - 20 minutes substantially increased product yield but resulted in the growth of nanorods and an overall increase in nanocrystal size. Reacting 10 x less lead acetate trihydrate concentration solutions in a 50 % intermittent ultrasonic pulse cycle for a period of 6 minutes resulted in less aggregated nanoparticles and with distinctly cubic morphologies (Figure 31). This result was also observed for other concentrations of lead acetate trihydrate in similar pulsed synthesis.
5.2.3 STRUCTURAL AND CHEMICAL PROPERTIES CHARACTERIZATION

Transmission Electron Microscopy (TEM) images (Morgani Digital Transmission Electron Microscope) indicate nanocrystal morphology for the PbTe nanopowders. Dried nanopowders were redispersed in aqueous solution by ultrasonic homogenization and dripped over carbon-coated copper TEM grids. The nanocrystals appear as polydisperse polyhedra with an average particle diameter between 100 – 150 nm (Figure 32).
In order to avoid conglomeration that occurs when nanoscale powders are mixed and densified with micron-scale powders, only the nanocrystals were densified employing SPS (Sumitomo Dr. Sinter SPS-2040). In the SPS procedure, a pulsed DC current conducts through both the graphite die and the specimen under high pressure. This heats the specimen internally, providing uniform and rapid thermal ramping while minimizing the sintering time and temperature. These characteristics limit grain growth. Two different SPS densification runs were employed at 65 MPa under vacuum, one with a maximum measured die temperature of 430°C with no hold time and the other at 425°C with a three minute hold time. Both runs used a temperature ramping rate of 30 degrees per minute, resulting in \( \equiv 2 \) mm thick pellets with densities of 7.67 g/cm\(^3\) (specimen PbTe1) and 7.75 g/cm\(^3\) (specimen PbTe2), as measured by the Archimedes method.

Figure 33 shows the X-ray diffraction (XRD) scans for the two PbTe nanocomposites in comparison to a representative PbTe nanopowder spectra. All specimens exhibit peaks characteristic of PbTe. The successive spectra are normalized and shifted in intensity for clarity. The normalized intensities were then amplified to identify low intensity diffraction peaks corresponding to secondary phases. These XRD spectra for the two nanocomposites following SPS indicate PbTe1 was nearly phase-pure, with a small amount of PbTeO\(_3\) also identified, while PbTe2 had more PbTeO\(_3\) as impurity (however, in an alternate crystal structure). These results were corroborated using electron-beam microprobe analysis (EPMA) conducted at General Motors R&D and Planning. Qualitative analysis of the obtained false-color back scattered electron (BSE) images demonstrates a homogeneous composition distribution from grain to grain for Pb and Te (Figure 34). However, a PbTeO\(_3\) impurity phase occupies discrete regions.
dispersed throughout the homogeneous PbTe matrix. Inhomogeneous contrast in the BSE image suggest the nanostructure cannot be resolved by the measurement, as distinct grain boundaries are difficult to identify.

**Figure 33.** XRD spectra for the two PbTe nanocomposites post SPS procedure and a representative nanopowder spectra (bottom). Arrows indicate PbTeO$_3$ impurity.

The representative scanning electron microscope SEM (Hitachi S-800) image of a PbTe1 fracture surface in Figure 35 indicates the preservation of nanostructure following the SPS procedure, with grains ranging from 100 nm to over 1 micron. This synthesis approach allows for dimensional nanocomposite formation with minimal conglomeration of the nanograins. Most importantly, densifying solely the nanocrystals results in a uniform dispersion of non-conglomerated nanostructure within a bulk matrix.
Collections of SEM images for each specimen demonstrate similar nanocomposite structure.

This research also began long term annealing studies of PbTe nanocomposites at device operating temperatures utilizing SEM imaging. Random SEM images were collected for each specimen following annealing at 600 K, in one and two week intervals. Figure 36 illustrates these studies, demonstrating the high temperature stability of these materials in limiting nanograins growth, necessary to retain high temperature TE performance.

![EPMA images indicating spatial distributions of targeted elements Pb, Te, and O.](image)

FIGURE 34. EPMA images indicating spatial distributions of targeted elements Pb, Te, and O.
FIGURE 35. SEM micrograph of PbTe1 fracture surface indicating 100 nm to over 1 micron grains distributed within a bulk material. Reused with permission from Ref. 79. Copyright 2007, American Institute of Physics.

FIGURE 36. Random SEM images were collected for each specimen following annealing at 600 K, in one and two week intervals, to evaluate long-term nanostructure stability at operating temperatures. These images indicate the preservation of nanostructure with enduring temperature.
Densified PbTe nanocomposites were cut into 2 x 2 x 5 mm$^3$ parallelepipeds for low (< 300 K) transport property measurements. Electrical contacts were made by soldering directly to nickel-plated surfaces using standard techniques and thermal contacts were made using Stycast epoxy. Four-probe resistivity, $\rho$, Seebeck coefficient, $S$, and steady-state thermal conductivity, $\kappa$, were measured from 12 K to 300 K in a custom radiation-shielded vacuum probe with maximum uncertainties of 4 %, 6 %, and 8 %, respectively, at 300 K. Room temperature four-probe Hall measurements were conducted at multiple positive and negative magnetic fields to eliminate voltage probe misalignment effects and thermal instabilities within a 10 % uncertainty. Temperature dependent four-probe Hall measurements were also conducted at both positive and negative magnetic fields to eliminate voltage probe misalignment effects, measured from 300 K to 5 K in a modified Magnetic Properties Measurement System (MPMS) at General Motors R&D.

As shown in Figure 37, both specimens exhibit p-type dominated conduction with large room temperature $S$ values of $\approx 325 \ \mu$V/K and similar dependences with temperature. For both specimens, a linear and positive magnetic field dependence of the Hall resistance up to 2 T confirms dominant p-type conduction. In addition, temperature dependent Hall data indicates a weak dependence with temperature (Figure 38), common in bulk PbTe below 300 K. Lead chalcogenides exhibit large dielectric permittivity ($\varepsilon$) and small effective mass ($m^*$) that merge impurity levels with the allowed energy bands.$^{76,81}$ This results in low temperature impurity ionization, with energy $\propto m^*\varepsilon^{-2}$ and
consequently, a carrier concentration independent of temperature where there is no degeneracy.\textsuperscript{82} However, the second valence band in p-type PbTe increases the carrier density near 150 K.\textsuperscript{76}

Stoichiometries calculated from EPMA data indicate an interesting correlation to the conduction type (Table VIII). In undoped PbTe, the carrier type is heavily dependent on the stoichiometry, with Te-rich materials exhibiting p-type conduction.\textsuperscript{77} However, the PbTe II specimen is Pb-rich, yet also exhibits p-type conduction similar to the Te-rich PbTe I specimen. This may be attributed to the different oxidation concentrations between the two specimens. Observations in n-type monocrystalline PbTe and PbS thin films with an oxide layer indicate carrier inversion to p-type with decreasing film thickness.\textsuperscript{83} The surface adsorption of oxygen should also form acceptor states in polycrystalline n-PbTe, drawing electrons from within the grain and increasing the hole concentration.\textsuperscript{83,84} This effect becomes more pronounced as the particle diameter shrinks, increasing the oxidized surface area/grain volume ratio, eventually resulting in an inversion from n- to p-type conduction.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>D (%)</th>
<th>$\rho$ (mΩ-cm)</th>
<th>$S$ (µV/K)</th>
<th>$p$ (cm$^{-3}$)</th>
<th>$S^2 \sigma$ (µW/K$^2$cm)</th>
<th>Pb:Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTe-I</td>
<td>94</td>
<td>24.9</td>
<td>328</td>
<td>$9.5 \times 10^{17}$</td>
<td>4.3</td>
<td>49.91 : 50.09</td>
</tr>
<tr>
<td>PbTe-II</td>
<td>95</td>
<td>12.6</td>
<td>324</td>
<td>$1.5 \times 10^{18}$</td>
<td>8.3</td>
<td>50.42 : 49.58</td>
</tr>
<tr>
<td>B-I</td>
<td>97</td>
<td>37</td>
<td>325</td>
<td>$8.0 \times 10^{17}$</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>B-II</td>
<td>97</td>
<td>19</td>
<td>250</td>
<td>$9.5 \times 10^{17}$</td>
<td>3.3</td>
<td>-</td>
</tr>
</tbody>
</table>

The low temperature $\rho$ values show activated temperature dependence ($d\rho/dT < 0$) in both specimens and a nonlinear increase with decreasing temperature down to 50 K.
Below 50 K, the resistivity values demonstrate weaker dependence with temperature. However, the carrier concentration is constant with temperature, suggesting a thermally activated conduction process different than those in typical narrow gap semiconductors (Figure 38). While the room temperature mobilities are consistent with those reported in the literature, the temperature dependence differs significantly from other lead chalcogenides since the nanocomposite mobilities decrease with decreasing temperature (inset in Figure 38), opposite of those reported in the literature for both polycrystalline and single crystal specimens.\textsuperscript{76,77,81,85,86}

The increase in $\rho$ at low temperature may be due to this decreasing mobility with decreasing temperature and suggests large impurity scattering. Additionally, the larger impurity phase for PbTe-II may indicate a greater surface oxygen adsorption for the grains and thus a larger carrier scattering, with $\mu \propto T^{-3/2}$. However, the high $\varepsilon$ in PbTe implies suppression of long-range Coulomb potentials, limiting scattering to near the internal point of an impurity (or vacancy) due to the large Bohr radius ($\propto m^*^{1/2}$, on the order of the lattice constant)\textsuperscript{82} and consequently, a small screening length. This indicates scattering by ionized impurities is not a dominant scattering mechanism in this material, especially at room temperature where the interaction time is significantly shorter.\textsuperscript{76} For nondegenerate semiconductors with the carriers scattered by long-wavelength acoustic phonons, $\mu \propto m^*^{-5/2} T^{-3/2}$. Since $m^*$ is inversely proportional to temperature, the mobility varies with $T^{-5/2}$, consistent with experimental observations in lead chalcogenides, with a weaker dependence in degenerate specimens.\textsuperscript{76} Therefore, the unique temperature dependence of the mobility for these PbTe nanocomposites suggests an additional scattering mechanism not common in bulk lead chalcogenides.
The PbTe nanocomposite carrier conduction can be effectively described as dominated by grain-boundary potential barrier scattering. Similar models have successfully described the electrical properties of doped polycrystalline silicon films,\textsuperscript{87} grain boundary recombination in silicon films,\textsuperscript{88} illumination properties of oxidized CdTe thin films,\textsuperscript{89} and the electrical conductivity of nanostructured metal oxide films.\textsuperscript{90}

Correlations between the carrier type and stoichiometry clearly indicate oxygen adsorption in the PbTe nanocomposites. Furthermore, this surface reactivity is difficult to prevent, considering the aqueous nature of the synthesis technique.\textsuperscript{79,91} The surface oxidation of PbTe is a sequential process, proceeding first through the formation of weak peroxide-like structures (up to 70 % coverage) then by the chemisorption of oxygen.\textsuperscript{91} Ab initio and DFT calculations of the surface reactivity of PbTe indicate these oxygen
complexes form chemical bonds by transferring charge from the tellurium atoms. These chemical shifts were experimentally confirmed through X-ray Photoemission Spectroscopy (XPS).\textsuperscript{91} The chemisorption of oxygen essentially forms carrier trapping acceptor states by removing electrons from the grain surface, reducing itinerant carrier density. For nanocrystalline materials, this chemisorption results in increased trapping of carriers at grain boundaries, forming energy barriers that impede the conduction of carriers between grains. Assuming a uniformly distributed concentration of ionized carrier traps, $N_t$/cm$^2$, a grain boundary thickness less than the crystallite size $L$, whose morphology and size distribution are identical, and a resistivity within the grains less than through the boundary, the effective mobility is given by:\textsuperscript{87}

$$\mu_{\text{eff}} = L q \left( \frac{1}{2 \pi m^* k T} \right)^{1/2} \exp \left( \frac{-E_B}{k T} \right),$$

(20)

where $q$ is the carrier charge, $m^*$ the effective mass, $k$ the Boltzmann constant, $T$ the temperature, and $E_B$ is the height of the energy barrier in the depletion region. A plot of the logarithm of the mobility, $\mu_B$, vs $1/kT$ for the two PbTe nanocomposites indicates activated behavior from conduction through the boundary potential barrier between grains (inset in Figure 38). Fitting the higher temperature data yields an energy barrier $E_B = 60$ meV for both specimens. Conduction through thermionic emission occurs when the average energy of the charge carriers is sufficient to overcome this energy barrier. As the temperature increases, the average energy of the charge carriers increases and therefore the electrical conductivity increases $\propto T^{-1/2}\exp(-E_B/kT)$. Furthermore, conduction through the boundary potential barrier between grains essentially filters lower energy charge carriers, increasing the average carrier energy and consequently, $|S|$. 
Figure 38. Temperature dependent carrier concentration and mobility (inset) for PbTe-I (●) and PbTe-II (△). Plotting the logarithm of $\mu_B = \mu_o (1/T)^{1/2} \exp(-E_B/kT)$ and fitting the high temperature data yields an energy barrier of 0.06 eV for both specimens. Reused with permission from Ref. 79. Copyright 2007, American Institute of Physics.

In order to directly investigate the affect of 100 – 150 nm grains within the bulk polycrystalline material, the $S$ of PbTe-I and PbTe-II is compared to that of two bulk polycrystalline PbTe specimens synthesized by water quenching induction melted ingots (one with the same Seebeck coefficient and the other with the same carrier concentration). These data are shown in Figure 39 along with data for single crystals of PbTe and theoretically calculated values, indicating $S$ for the nanocomposites are larger than that for the bulk. The $S$ for the nanocomposite specimen is larger by 23% as compared to that of the bulk polycrystalline specimen with the same carrier.
concentration, \( p \). In addition, for similar \( S \) values \( p \) is higher in the nanocomposite by 47% as compared to that of the bulk. The larger \( S \) values, in addition to similar resistivity values in the nanocomposites as compared to the bulk polycrystalline specimens, results in an enhanced room temperature power factor for these nanocomposites.

**Figure 39.** Seebeck coefficient vs. carrier concentration for the PbTe-I and PbTe-II nanocomposites (●), two polycrystalline bulk PbTe compounds synthesized for this report (○), single crystal bulk PbTe (△) and the calculated relationship (dashed line) from reference 92. Reused with permission from Ref. 79. Copyright 2007, American Institute of Physics.
5.3 DOPED LEAD TELLURIDE NANOCOMPOSITES

5.3.1 SYNTHESIS

To prepare PbTe nanocrystals with increasing carrier concentration, two precursor solutions were prepared separately at 110° C by dissolving 0.008 mol elemental Te in a 20 M KOH aqueous solution and by dissolving 0.0088 mol Pb(CH$_3$COO)$_2$·3H$_2$O and Ag Acetate in 40 mL distilled water to achieve a bimetallic solution with the desired extrinsic carrier concentration, with 2 %, 5 %, and 15 % Ag solutions. The solution’s Ag concentration may be significantly higher than in the final nanocrystallites. After ~ 60 minutes, the bimetallic silver acetate/lead acetate trihydrate solution was dripped into the rapidly stirring deep purple alkaline solution to immediately form doped PbTe nanocrystals. After 5 minutes, the reaction mixture was removed from the heat source, quenched, and 0.1 M HNO$_3$ was added to flocculate the nanocrystals. The grayish-black precipitates were washed 4 times with the dilute nitric acid solution, removing lead hydroxide impurities. Excess lead acetate trihydrate in the reaction favors the formation of easily removable impurities. The precipitates were then washed 4 times with distilled water and dried overnight in a fume hood then under vacuum for 24 - 48 hours. This reaction was successful in synthesizing Ag-doped (Ag$_2$Te) PbTe nanocrystals with reproducible yields of over 2 grams per batch.
5.3.2 **STRUCTURAL AND CHEMICAL PROPERTIES CHARACTERIZATION**

In order to avoid conglomeration that occurs when nanoscale powders are mixed and densified with micron-scale powders, only the nanocrystals were densified employing SPS, in a procedure similar to the previous PbTe nanocomposites. All runs used the same temperature ramping rate of 30 degrees per minute, resulting in ≈ 1 mm thick pellets with densities of ≈ 95% of their theoretical density.

Figure 40 shows the X-ray diffraction (XRD) scans for the four Ag-doped PbTe nanocomposites. All specimens exhibit peaks characteristic of PbTe. The successive spectra are normalized and shifted in intensity for clarity. The normalized intensities were then amplified to identify low intensity diffraction peaks corresponding to secondary phases. These XRD spectra for these nanocomposites following SPS indicate a small amount of TeO$_2$ impurity, ~ 3 vol. % for PbTe-III and PbTe-IV, with more impurity in PbTe-VI and PbTe-VI, estimated by comparing the ratio of areas beneath the most intense diffraction peaks of the impurity to the primary PbTe phase.

The representative scanning electron microscope SEM (JEOL JSM-6390LV) image of a PbTe-III fracture surface in Figure 41 indicates the preservation of nanostructure following the SPS procedure, with grains ranging from 100 nm to over 1 micron. This synthesis approach allows for dimensional nanocomposite formation with minimal conglomeration of the nanograins. In addition, densifying solely the nanocrystals results in a uniform dispersion of non-conglomerated nanostructure within a bulk matrix. Collections of SEM images for each specimen demonstrate similar nanocomposite structure.
Figure 40. XRD spectra for the four Ag-doped PbTe nanocomposites post SPS procedure. Arrows indicate TeO$_2$ impurity.

Figure 41. Representative SEM image of a PbTe-III fracture surface indicating the preservation of nanostructure following the SPS procedure.
5.3.2 **Physical Properties Characterization**

Low temperature transport properties were measured using metrology and apparatus previously described for the undoped PbTe specimens. All specimens exhibit p-type dominated conduction with large room temperature $S$ values of approximately 200 $\mu$V/K and similar dependences with temperature. These specimens exhibit a more gradual decrease in $S$ with decreasing temperature than the intrinsic specimens (Figure 42). For all specimens, a linear and positive magnetic field dependence of the Hall resistance up to 2 T confirms dominant p-type conduction. The carrier concentrations increase upon Ag-doping by a factor of $\sim$ 5-6, from $9.5 \times 10^{17}$ cm$^{-3}$ for specimen PbTe-I to $6.2 \times 10^{18}$ cm$^{-3}$ for specimen PbTe-IV, as listed in Table IX. Correspondingly, the resistivity values exhibit a significant reduction in magnitude compared to the intrinsic specimens, from 24.9 m$\Omega$-cm for the lowest carrier concentration specimen (PbTe-I) to 2.9 m$\Omega$-cm for the highest carrier concentration Ag-doped nanocomposite (specimen PbTe-IV), all with similar densities, also listed in Table IX. The carrier concentrations exceed the limits of stoichiometric variation and of oxygen doping, which result in maximum hole densities only up to $(3-4) \times 10^{18}$ cm$^{-3}$. This data suggests Ag was successfully incorporated as a dopant in these nanocomposites. In addition, specimens PbTe-V and PbTe-VI exhibit larger resistivities ($\sim$ 2x) than specimens PbTe-III and PbTe-IV despite a higher doping solution, yet possess similar carrier concentrations. This suggests a doping solubility for Ag in these nanocomposites.
TABLE IX. Room temperature percent theoretical density, resistivity $\rho$, Seebeck coefficient $S$, thermal conductivity $\kappa$, carrier concentration $p$, and power factor $S^2\sigma$.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>D (%)</th>
<th>$\rho$ (m$\Omega$-cm)</th>
<th>$S$ ($\mu$V/K)</th>
<th>$\kappa$ (W-m$^{-1}$K$^{-1}$)</th>
<th>$p$ (cm$^3$)</th>
<th>$S^2\sigma$ ($\mu$W/K$^2$cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTe-I</td>
<td>94</td>
<td>24.9</td>
<td>328</td>
<td>2.2</td>
<td>9.5 x 10$^{17}$</td>
<td>4.3</td>
</tr>
<tr>
<td>PbTe-II</td>
<td>95</td>
<td>12.6</td>
<td>324</td>
<td>2.5</td>
<td>1.5 x 10$^{18}$</td>
<td>8.3</td>
</tr>
<tr>
<td>PbTe-III</td>
<td>95</td>
<td>3.9</td>
<td>198</td>
<td>2.8</td>
<td>5.1 x 10$^{18}$</td>
<td>10.0</td>
</tr>
<tr>
<td>PbTe-IV</td>
<td>94</td>
<td>2.9</td>
<td>207</td>
<td>2.7</td>
<td>6.2 x 10$^{18}$</td>
<td>14.8</td>
</tr>
<tr>
<td>PbTe-V</td>
<td>97</td>
<td>5</td>
<td>211</td>
<td>2.7</td>
<td>6.1 x 10$^{18}$</td>
<td>8.9</td>
</tr>
<tr>
<td>PbTe-VI</td>
<td>97</td>
<td>7.9</td>
<td>222</td>
<td>2.5</td>
<td>5.9 x 10$^{18}$</td>
<td>6.2</td>
</tr>
</tbody>
</table>

The low temperature $\rho$ values for the Ag-doped specimens show activated temperature dependence ($d\rho/dT < 0$) but with a sharp peak in the $\rho$ values near 70 K (Figure 43). Below 70 K the $\rho$ values rapidly decrease with decreasing temperature. The relative heights of these peaks decrease with decreasing resistivity. This unusual dependence shows only little correlation to $S$, with a $d^2S/dT^2$ inversion between 100 K - 150 K. In addition, temperature dependent Hall data for specimens PbTe-III and PbTe-IV indicates only a weak dependence with temperature, similar to the two undoped PbTe nanocomposites. Figure 44 plots the temperature dependence of the mobility for two of the Ag-doped specimens in comparison to the two undoped nanocomposites. While the room temperature mobilities are similar, ~ 350 cm$^2$/V·s, the low temperature $\mu$ values show an order of magnitude increase as compared to the undoped specimens. The specimen with the largest carrier concentration exhibits the largest $\mu$ throughout the measured temperature range. The Ag-doped nanocomposite mobilities decrease with decreasing temperature, however, exhibit a dramatic dip in mobility (~ 20x) near 80 K, as compared to those at the lowest temperature values. Therefore, the unique temperature dependence of $\mu$ for these Ag-doped PbTe nanocomposites suggests an additional scattering mechanism not dominant in the undoped nanocomposites.
Figure 42. Temperature dependence of the Seebeck coefficient for PbTe-III (●), PbTe-IV (○), PbTe-V (▲), and PbTe-VI (△).

Figure 43. Temperature dependence of the resistivity for PbTe-III (●), PbTe-IV (○), PbTe-V (▲), and PbTe-VI (△).
A plot of the logarithm of the mobility, $\mu_B$, vs $1/kT$ for these two Ag-doped PbTe nanocomposites indicates activated behavior from conduction through the boundary potential barrier between grains (Figure 45). Fitting the higher temperature data with equation 20 yields an energy barrier $E_B = 60$ meV for both specimens, identical to those present in the undoped specimens. This suggests the energy barriers form through a similar oxygen chemisorption mechanism in both the undoped and Ag-doped specimens. Conduction through thermionic emission occurs when the average energy of the charge carriers is sufficient to overcome the energy barrier. This mechanism dominates at higher temperature and for higher carrier densities, where the concentration of carriers with larger average energy is larger. However, an additional conduction mechanism dominates at lower temperature. When the grain boundary energy barrier is sufficiently narrow and high, the charge carriers quantum mechanically tunnel through the barrier (thermionic field emission). In equilibrium, the dependence of barrier height $E_B$ on the density of trapping states $N_t$ and the carrier concentration $p$ is given by:

$$E_B = \frac{q^2 N_t^2}{8\varepsilon \varepsilon_0 p},$$

(21)

and the barrier width (space charge region, see Figure 46) by:

$$W = \left(\frac{2\varepsilon \varepsilon_0 E_B}{q^2 p}\right)^{1/2}$$

(22)

where $q$ is the carrier charge, $\varepsilon = 414$ for PbTe at 300 K, and $\varepsilon_0$ is the vacuum permittivity. Table X lists these calculated values for the two undoped specimens in comparison to two Ag-doped specimens, PbTe-III and PbTe-IV. As the carrier concentration increases with doping, the barrier height remains constant, but promotes an
Figure 44. Temperature dependence of the mobility for Ag-doped PbTe-III (●) and PbTe-IV (▲), in comparison to PbTe-I (○) and PbTe-II (△). Lines are a guide for the eye only.

Figure 45. Temperature dependence of the mobility for Ag-doped PbTe-III (●) and PbTe-IV (▲), in comparison to PbTe-I (○) and PbTe-II (△). Plotting the logarithm of $\mu_B = \mu_o 1/T^{1/2} \exp(-E_B/kT)$ and fitting the high temperature data yields an energy barrier of 0.06 eV for all specimens.

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TABLE X. Resistivity $\rho$, carrier concentration $p$, energy barrier height $E_B$, trapping state density $N_t$, energy barrier width $W$, and effective crystallite size $L$, for the two undoped PbTe specimens and two of the Ag-doped PbTe specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$\rho$ (m$\Omega$-cm)</th>
<th>$p$ (cm$^{-3}$)</th>
<th>$E_B$ (meV)</th>
<th>$N_t$ (cm$^{-3}$)</th>
<th>$W$ (nm)</th>
<th>$L$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTe I</td>
<td>24.9</td>
<td>$9.5 \times 10^{17}$</td>
<td>60</td>
<td>$1.0 \times 10^{13}$</td>
<td>54</td>
<td>316</td>
</tr>
<tr>
<td>PbTe II</td>
<td>12.6</td>
<td>$1.5 \times 10^{18}$</td>
<td>60</td>
<td>$1.3 \times 10^{13}$</td>
<td>43</td>
<td>396</td>
</tr>
<tr>
<td>PbTe III</td>
<td>3.9</td>
<td>$5.1 \times 10^{18}$</td>
<td>60</td>
<td>$2.4 \times 10^{13}$</td>
<td>23</td>
<td>376</td>
</tr>
<tr>
<td>PbTe IV</td>
<td>2.9</td>
<td>$6.2 \times 10^{18}$</td>
<td>60</td>
<td>$2.6 \times 10^{13}$</td>
<td>21</td>
<td>416</td>
</tr>
</tbody>
</table>

increase in trapping state density. Furthermore, as the carrier concentration increases, the barrier width decreases by a factor $\propto p^{-1/2}$. This suggests an exponential increase in tunneling conduction (transmission probability) with doping.

The one-dimensional, time-independent WKB transmission probability $\tau$ for the potential barrier is given by:

$$\tau(E) = \exp\left(-2\int_{x_1}^{x_2} \left\{2m^*\left[qV(x) - E\right]\right\}^{1/2} dx / \hbar\right),$$

(23)

where $x_1$ and $x_2$ are the classical carrier turning points with energy $E$, $m^*$ is the effective mass, and $qV(x)$ is the carrier energy in the grain boundary space-charge region. Therefore, the tunneling probability is a maximum for charges with smaller effective mass. The electrical transport in p-type PbTe is complex, with a second, lower mobility heavy hole (HH) valence band below the light hole (LH) valence band at low temperature, where the light hole effective mass is an order of magnitude smaller than for the heavy holes (Figure 47). At low temperature and higher hole densities, the electrical properties are nearly exclusively dominated by these light hole carriers. As the temperature increases, the second valence band rises above the LH band and charges are transferred to the HH band. The maximums of these bands are equal near 400 K, where the top of the HH valence band and the bottom of the conduction band increase with
FIGURE 46. Simplified energy band diagram for the nanocrystalline grain-boundary interface (GB), illustrating the effective crystallite size ($L$), the width of the space-charge barrier region ($W$), and the height of the energy barrier ($E_{B}$). $C_B$, $E_F$, and $V_B$ are the conduction band, Fermi energy, and the valence band, respectively.

FIGURE 47. Temperature dependence of the energy band structure for bulk p-type PbTe, illustrating the two valence bands: a light hole (LH) band and a lower mobility heavy-hole (HH) band. The maximums of these bands are equal near 400 K, where the top of the HH valence band and the bottom of the conduction band increase with temperature to produce a band gap weakly dependent on temperature. Adapted from reference 76.
temperature to produce a band gap weakly dependent on temperature.\textsuperscript{76}

Therefore, the unique temperature dependence of the mobility for these Ag-doped PbTe nanocomposites may be modeled as follows: at low temperature and higher hole densities, the electrical properties are dominated nearly exclusively by the LH carriers, whose order of magnitude smaller effective mass results in a higher transmission probability through the grain boundary potential energy barrier. Additionally, with an increase in carrier concentration the barrier width decreases by a factor \(\propto p^{-1/2}\), with a corresponding exponential increase in the transmission probability. As the temperature increases, the second valence band rises above the LH band and charges are transferred to the HH band, resulting in a decreasing transmission probability and an increased carrier scattering. Thus, at low temperature when thermionic field emission dominates the conduction, the mobility decreases with increasing temperature for the higher carrier density specimens. At higher temperature, when the average energy of the charge carriers is sufficient to overcome the grain boundary energy barrier, conduction is dominated through thermionic emission and is \(\propto T^{-1/2}\exp(-E_B/kT)\).

The effective crystallite size was estimated using equation 20, the energy barriers obtained from fitting the temperature dependence of the mobility, the mobility values calculated from the room temperature carrier concentration, and the HH \(m^* = 1.5m_o\).\textsuperscript{76,95} These estimates indicate effective crystallite sizes between 300 and 400 nm, listed in Table X, and are consistent with the dimensional nanocomposite structure observed in the SEM images. This further confirms that grain boundary energy barrier scattering is dominated through these nanoscale features. Inclusion of LH carriers in the calculation would result in a lower effective crystallite size.
In order to directly investigate the affect of the nanograins within the bulk polycrystalline material, the $S$ for the four Ag-doped nanocomposites is compared to that of bulk polycrystalline PbTe. Figure 48 plots the nanocomposite data in comparison to a single crystal PbTe specimen and theoretically calculated values, indicating $S$ for these nanocomposites are between 10 % and 23 % larger as compared to bulk. In addition, the carrier concentration can be increased upon Ag-doping while also increasing $S$. Conduction through the boundary potential barrier between grains essentially filters lower energy charge carriers, increasing the average carrier energy and consequently, $S$. This suggests interfacial energy barrier carrier filtering arising from the surface adsorption of oxygen may be an effective method of thermoelectric performance enhancement in bulk nanocomposites. Similar carrier filtering enhancements to $S$ were also observed in InGaAs/InGaAlAs heterostructures and n-type PbTe thin-films.

![Figure 48. Seebeck coefficient vs. carrier concentration for the PbTe-I through PbTe-VI nanocomposites (●), two polycrystalline bulk PbTe compounds synthesized for this report (○), single crystal bulk PbTe (△) and the calculated relationship (dashed line) from reference 92.](image-url)
The rapid increase in thermoelectric materials R&D is a consequence of the growing need to increase energy efficiency and independence through waste heat recovery. TE materials enable the direct solid-state conversion of heat into electricity, with little maintenance, noise, or cost. In addition, these compact devices can be incorporated into existing technologies to increase the overall operating efficiency. High efficiency TE materials would enable the practical solid-state conversion of thermal to electrical energy. Optimizing the interdependent physical parameters to achieve acceptable efficiencies requires materials exhibiting a unique combination of properties. This research investigated two advanced methods of thermoelectric enhancement: lattice strain effects in silicon-germanium alloy type I clathrates and the nanostructured enhancement of lead chalcogenides. In addition, this research developed a transport properties measurement system capable of examining temperature dependent resistivity, Seebeck coefficient, and thermal conductivity in the range 300 K – 12 K through specific design emphasis upon the unique challenges inherent in thermoelectric metrology. This measurement system was recently selected by NIST as one of twelve active research laboratories to participate in a round-robin measurement survey of two candidate materials for the certification of a low temperature (2 K - 400 K) Seebeck coefficient SRM™.
Clathrates have recently attracted interest as promising high temperature TE materials due to their excellent thermoelectric properties, chemical stability at high temperature, and mechanical strength. However, many of these properties were observed in single crystal specimens using complex and wasteful synthesis techniques. This research identified the optimal polycrystalline carrier concentration that demonstrated a thermoelectric performance comparable to the single crystal specimen. This confirms that polycrystalline specimens synthesized using economical methods maintain the same thermoelectric performance as single crystal specimens fabricated using expensive and complex techniques.

This research attempted to increase the ZT through lattice strain by substituting Si within the Ga-Ge lattice framework of the type I clathrate \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \). The dependence of the lattice parameter with Si content indicates deformations in the clathrate polyhedra. This lattice contraction may modify the orbital interaction between the guest atoms and the framework, and consequently, modify the electronic transport. The unique dependences of \( n, \rho, |S|, \) and \( m^* \) with Si substitution, and the lack of variation in the Ga-to-group IV element ratios implies a modified band structure with Si content rather than an increase in conduction band population from donor states. These results indicated the thermoelectric properties of \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) type I clathrates can be enhanced upon a 20% Si substitution on the framework sites. Furthermore, the reduction in Ga-to-group IV element ratio resulted in a 10x increase in carrier concentration and a 10x decrease in the resistivity, but only a ~ 40 % decrease in \( |S| \). This results in a 40 % increase in the room temperature power factor. These two techniques represent a complimentary strategy to identify the composition exhibiting optimal TE properties.
Recent progress in a number of higher efficiency thermoelectric materials (room temperature ZT > 2) can be attributed to nanoscale enhancement. Many of these materials demonstrate increased Seebeck coefficient and decreased thermal conductivity due to the phenomenological properties of nanometer length scales, including quantum confinement effects, enhanced phonon scattering, and interfacial energy barrier filtering of charge carriers. Physically, nanostructured TE enhancement aims to split the interdependence of the electrical and thermal transport, allowing for better ZT optimization. One consequence of nanostructure is the increase of interfaces. The presence of interfacial energy barriers filters the carrier energy traversing these interfaces, restricting those energies that limit the mean carrier energy. This increases the Seebeck coefficient, as its value depends on the mean carrier energies relative to those at the Fermi level.

This research identified a novel approach to prepare lead chalcogenide (PbTe) dimensional nanocomposites by densifying nanocrystals synthesized employing an aqueous solution-phase reaction with a high yield and low cost. Densification using spark plasma sintering successfully integrates disperse 100 – 150 nm PbTe nanocrystals within a bulk nanocomposite, demonstrating for the first time that nanocrystals dispersed within dense bulk polycrystalline PbTe can be prepared from solution-phase synthesized nanocrystals. Furthermore, the carrier concentration of the PbTe nanocomposites can be adjusted by directly doping the nanocrystals with Ag, necessary for power factor optimization. Directly comparing these nanocomposites with bulk polycrystalline materials yields the most direct evidence of |S| enhancement due to the dispersion of nonconglomerated nanoscale PbTe grains within the PbTe nanocomposites.
The unique temperature dependence of the mobility observed for these PbTe nanocomposites suggests an additional scattering mechanism not common in bulk lead chalcogenides. The chemisorption of oxygen during nanocrystal synthesis results in increased trapping of carriers at grain boundaries, forming energy barriers that impede the conduction of carriers between grains. Conduction through thermionic emission occurs when the average energy of the charge carriers is sufficient to overcome this energy barrier. As the temperature increases, the average energy of the charge carriers increases and therefore the electrical conductivity increases \( \propto T^{-1/2} \exp(-E_B/kT) \). This mechanism dominates at higher temperature and for higher carrier densities, where the concentration of carriers with larger average energy is larger. However, an additional conduction mechanism dominates at lower temperature. When the grain boundary energy barrier is sufficiently narrow and high, the charge carriers quantum mechanically tunnel through the barrier.

At low temperature and higher hole densities, the electrical properties are dominated nearly exclusively by the LH carriers, whose order of magnitude smaller effective mass results in a higher transmission probability through the grain boundary potential energy barrier. Additionally, with an increase in carrier concentration the barrier width decreases by a factor \( \propto p^{-1/2} \). As the temperature increases, the second valence band rises above the LH band and charges are transferred to the HH band, resulting in a decreasing transmission probability and an increased carrier scattering. Thus, at low temperature when thermionic field emission dominates the conduction, the mobility decreases with increasing temperature for the higher carrier density specimens. At higher temperature, when the average energy of the charge carriers is sufficient to
overcome the grain boundary energy barrier, conduction is dominated through thermionic emission.

Furthermore, conduction through the boundary potential barrier between grains essentially filters lower energy charge carriers, increasing the average carrier energy and consequently, increases the Seebeck coefficient. Comparing both the undoped and the Ag-doped PbTe nanocomposites to bulk materials and to theoretically calculated values at similar carrier concentrations clearly indicates an enhanced Seebeck coefficient due to the nanostructure.
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Researchers must calibrate their apparatus and methodologies with known standards to remain consistent with characterizations in other laboratories. These practices aid in the confirmation of reported high ZT materials. Numerous Standard Reference Materials (SRM™) and measurement procedures are available through NIST (National Institute for Standards and Technology) for resistivity (stainless steel), thermal conductivity (stainless steel, pyroceram), and some for the low Seebeck coefficient of binary metals. Round-robin laboratory research TE materials provided additional measurement calibration.

Through the Materials Science and Engineering Laboratory (MSEL), NIST recently initiated the certification of a low temperature (2 K- 400 K) Seebeck coefficient SRM™. The measurement system developed for this research was selected as one of twelve active research laboratories to participate in a round-robin measurement survey of two candidate materials, Bi$_2$Te$_3$ and constantan (55% Cu and 45% Ni). Bi$_2$Te$_3$ was selected as the prototype material and final certification is underway. The following figures illustrate some of these calibration measurements using the available standards. All data was consistent within measurement uncertainty.
Figure A1. Temperature dependence of the NIST Stainless Steel SRM as measured by the Novel Materials Laboratory (●) and by NIST (○). Error bars represent the minimum 3.3% uncertainty in the effective length measurement $l_o$.

Figure A2. Temperature dependence of the Seebeck coefficient for a CoSb$_3$ skutterudite as measured by the Novel Materials Laboratory (●) and by General Motors R&D (○).
Figure A3. Temperature dependence of the Seebeck coefficient for the Bi2Te3 survey candidate reference material as measured by the Novel Materials Laboratory (●) and by statistically analyzed survey data from NIST (○).

Figure A4. Temperature dependence of the thermal conductivity for a CoSb3 skutterudite as measured by the Novel Materials Laboratory (●) and by General Motors R&D (○).
FIGURE A5. Temperature dependence of the thermal conductivity for the NIST stainless steel SRM as measured by the Novel Materials Laboratory (●) and by NIST (○).
ABOUT THE AUTHOR

Joshua Martin was graduated from the University of South Florida with a Bachelor of Science in Physics in 2003 and a Masters of Science in Physics in 2005. The research conducted during his graduate tenure as a Ph.D. candidate resulted in eight journal publications and numerous international conference presentations and proceedings, involving collaborations with government, academic, and industrial laboratories. In partial fulfillment of the Applied Physics Ph.D requirements, Joshua was awarded an internship at General Motors Research & Development.

Joshua’s research developed additional techniques to enhance the efficiency of thermoelectric materials and to advanced the synthesis and preparation procedures of nanostructured bulk materials. In addition, he constructed a low temperature transport property measurement system that was selected to participate in the certification of a new National Institute of Standards and Technology (NIST) Standard Reference Material for the Seebeck Coefficient.