Thermoelectric properties of Bi-doped PbTe composites

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An experimental and theoretical study is presented for n-type Bi-doped PbTe composites with different grain sizes and doping levels. The bulk polycrystalline composites were prepared by spark plasma sintering of the nanocrystals synthesized via micro-emulsion and direct precipitation. This technique is particularly attractive due to its low cost, its reproducibility, and the control of the composition and nanocrystal size that it affords. The thermoelectric properties of the synthesized specimens were experimentally measured and theoretically modeled. Our calculations reveal that the inclusion of electron/grain and phonon/grain interface scattering is crucial for the correct description and interpretation of the measured properties. © 2011 American Institute of Physics. [doi:10.1063/1.3586240]

I. INTRODUCTION

Thermoelectric (TE) materials are currently of interest for enhanced performance of solid-state devices that convert heat into electrical power and for refrigeration applications. The efficiency of TE materials is characterized by the figure of merit defined as a dimensionless quantity $ZT = S^2 T/\kappa$, where $S$ is the Seebeck coefficient (or thermopower), $\sigma$ is the electrical conductivity ($=1/\rho$, where $\rho$ is the electrical resistivity), the thermal conductivity $\kappa = \kappa_e + \kappa_L$ is composed of electronic $\kappa_e$ and lattice $\kappa_L$ contributions, and $T$ is the absolute temperature. There has been extensive experimental and theoretical research directed toward enhancing the figure of merit, because larger values of $ZT$ will result in higher efficiency TE devices.

Nano-structuring has emerged as a possible way to decouple the charge and thermal transport properties in order to increase the TE performance of materials. The advantages originate from the reduction in $\kappa_L$ and the enhancement of $S$.2–4 Given that nano-structuring introduces interfaces in the material, phonon/interface and carrier/interface scattering appear to be the main reasons for such changes in the transport. This is usually accompanied by a reduction in $\sigma$; therefore, careful processing of materials or composites is necessary for $ZT$ optimization.

PbTe is a material with good TE properties above room temperature. Our recent work has reported on adapting existing synthetic techniques in preparing bulk granular composites of p-type PbTe.3,5–7 Theoretical modeling was also provided for such materials in order to determine the best combination of properties for improved TE transport.5,7 For practical applications, however, TE materials of both p- and n-types are needed.

In this work, we explore further developments of the nano-composite synthesis of n-type PbTe using Bi doping. We employ a synthesis technique based on densifying nanocrystals into a polycrystalline matrix.3,6,8 This “bottom-up approach” is particularly attractive because it allows for control of the grain size, shape, and grain distribution. We also apply theoretical modeling5,7 in order to explain the role of the granular interfaces with regard to the transport characteristics of the material. The measured $S$, $\sigma$, and $\kappa$ are interpreted using this model in terms of the relevant scattering mechanisms. This combined experimental and theoretical approach allows for a complete analysis and evaluation of the fundamental transport properties of the material system under consideration.

II. EXPERIMENTAL PROCEDURE

Two chemical processes, micro-emulsion and direct precipitation, were adopted for the synthesis of different crystal sizes of Bi-doped n-type PbTe nanocrystals. N-type PbTe nanocrystals of ~30 nm in diameter were synthesized via a low temperature reverse microemulsion process9 whereby sodium 2 bis (2-ethylhexyl) sulfosuccinate (Na-AOT), water, and n-hexane, each of high purity grade, were used as the surfactant, water phase, and oil phase, respectively. For each synthesis, a water/oil ratio of 20 was used to control the grain size of the nanocrystals. Lead nitrate (Pb(NO₃)₂), sodium tellurite (Na₂TeO₃), and bismuth nitrate (Bi(NO₃)₃) were used for sources of Pb, Te, and Bi, respectively. Initially, 1.5 gm Na-AOT was dissolved in 150 ml n-hexane, into which a 3 mmol aqueous solution of Pb(NO₃)₂ (for the undoped specimens) was added and stirred for 1 h. For the Bi doped nanocrystals, 1-25 mol% Bi(NO₃)₃·5H₂O to that of Pb(NO₃)₂ was dissolved together with the help of 2 ml of glacial acetic acid. After 1 h of homogeneous mixing, a stoichiometric amount of sodium tellurite was added to the solution, and the emulsion was heated to 60 °C. When it was completely dissolved, 22 ml hydrazine hydrate was added to the solution as a reducing agent. Heating and stirring were continued for an additional 4 h. The reaction was then cooled to room temperature, and the precipitate was filtered out by repeated centrifugation with water and ethanol. Each reaction yielded ~2 gm of Bi-doped PbTe nanocrystals.

Direct precipitation yielded grain sizes of ~50 nm in diameter. Initially, a hot Te alkaline solution was prepared by dissolving 3 mmol of Te powder in a 40 M aqueous solution...
of KOH at 110°C. The resulting solution was dark purple in color with a pH of ~11. A 45 ml aqueous solution was then prepared by dissolving 3 mmol lead acetate (Pb(CH₃COO)₂) (for the undoped specimens) or together with 1-25 mol% Bi(NO₃)₃·5H₂O to that of Pb(CH₃COO)₂ with the help of 2 ml of glacial acetic acid. This solution was then rapidly added to the hot alkaline Te solution. The reaction was allowed to continue for 15 min. The precipitate in each case was filtered out by washing with 0.1 M nitric acid, water, and ethanol until a pH of 7 was achieved. These reactions yielded Bi-doped PbTe nanocrystals (~2.5 gm per batch).

In all cases, the products were vacuum dried at room temperature and collected for powder x-ray diffraction (XRD, Bruker AXS D8, Lynx Eye PSD detector), energy dispersive x-ray spectroscopy (EDS, Oxford Instruments INCA X sight), and scanning electron microscopy (SEM, JEOL JSM 6390 LV) analyses. For transport property measurements, approximately 1.5 gm of n-type PbTe nanocrystals were densified via spark plasma sintering (SPS) at 300°C and 60 MPa for 5 min, resulting in dense nanocomposites. Densities of 92% to 98% were achieved for the nanocomposite specimens. The bulk polycrystalline specimens were cut into 2 mm × 2 mm × 5 mm and 0.5 mm × 2 mm × 8 mm parallelepipeds for low temperature transport and room temperature Hall measurements, respectively. The four-probe resistivity, ρ, steady-state Seebeck coefficient, S, and thermal conductivity, k, (gradient sweep method) measurements on 2 mm × 2 mm × 5 mm parallelepipeds from 12 K to 300 K were conducted in a custom radiation shielded vacuum probe, with uncertainties of 4%, 6%, and 8%, respectively. Room temperature four-probe Hall measurements were conducted at multiple positive and negative magnetic fields of up to 2.5 T to eliminate voltage probe misalignment effects using a Quantum Design Physical Property Measurement System (ACT option). The Hall measurement uncertainty was 4%.

III. RESULTS AND DISCUSSION

We present results for two sets of n-type PbTe nanocomposite specimens with smaller and larger grains, with two doping levels for each size. The label S1 denotes the nanocomposite specimens consolidated from 30 nm n-type PbTe nanocrystals, and the label S2 denotes the nanocomposite specimens consolidated from 50 nm n-type PbTe nanocrystals. Figures 1(a) and 1(b) show SEM images of the nanocomposite specimens. After SPS, the grain sizes for S1 and S2 were in the range of 30–50 nm and 50–100 nm, respectively. XRD before and after SPS provided an indication of the phase purity of the specimens (Fig. 1(c)). No secondary Bi related phases were detected even in heavily doped PbTe, suggesting successful doping of the nanocrystals. EDS analysis indicated a Bi content as high as 25% in the n-type PbTe nanocomposites. EDS analysis on each specimen was accomplished by collecting spectra from over 50 different nanocrystals, suggesting a nearly uniform distribution of Bi. Elemental mapping also indicates strong homogeneity for all specimens.

Figure 2 shows the measured transport properties of S1 Bi-doped PbTe specimens with 20% and 25% nominal Bi doping with measured Hall carrier concentrations of
1.8 × 10^{19} \text{ cm}^{-3} \text{ and } 2.0 × 10^{19} \text{ cm}^{-3}, \text{ respectively. From Fig. 2 it is evident that } \rho \text{ exhibits the largest change with Bi concentration in the studied temperature regime. We note that these differences are larger at lower T and become less significant for T ~ 100 K. S and } \kappa \text{ have very similar values in the 20% and 25% Bi-doped specimens, although the absolute } S, \text{ I} \Sigma \text{, is larger for the 20% Bi doped specimen, as expected. Figure 3 shows the temperature dependence of the measured transport characteristics for the larger-grain specimens (S2) labeled 15% and 25% Bi, with Hall carrier concentrations of 5.8 × 10^{19} \text{ cm}^{-3} \text{ and } 7.4 × 10^{19} \text{ cm}^{-3}, \text{ respectively. Again, the largest differences occur in } \rho, \text{ while } S \text{ and } \kappa \text{ differ much less. Comparing } \rho \text{ for the two concentrations of the S2 specimens indicates that } \rho \text{ is different in the entire temperature region. In addition, } \rho \text{ and } \Sigma \text{ for the S1 specimens are larger as compared to those of the S2 specimens, whereas } \kappa \text{ seems to be slightly smaller for the S2 specimens.}

To understand the underlying mechanisms limiting the characteristics in these studied materials, we present theoretical modeling of the transport. Our goal is to apply a reliable model that will allow one to investigate the influence of the scattering mechanisms and the PbTe band structure properties simultaneously. Of particular importance here is the increased number of grain boundaries in the specimens containing nano-scale domains. Our goal is to explain the role of grain boundary scattering, because this mechanism is characteristic of composites with small nano-scale grains. For this purpose, we employ a model that was previously developed, and was successfully applied, for p-type Ag-doped PbTe granular composites.\textsuperscript{5} Given that this model led to excellent agreement with previous experimental results, it is of interest to apply it to the current material system, n-type PbTe. The model relies on the solution of the Boltzmann transport equation within the relaxation time approximation for isotropic transport:

\begin{equation}
\rho^{-1} = e^2 \int dE \left(- \frac{\partial f_0}{\partial E}\right) \Sigma(E),
\end{equation}

\begin{equation}
S = \frac{e}{\sigma T} \int dE \left(- \frac{\partial f_0}{\partial E}\right) \Sigma(E)(E - \mu),
\end{equation}

\begin{equation}
\kappa_c = \frac{1}{T} \int dE \left(- \frac{\partial f_0}{\partial E}\right) \Sigma(E)(E - \mu)^2 - T \sigma S^2,
\end{equation}

\begin{equation}
\Sigma(E) = \frac{2d^3k}{(2\pi)^3} v_t^2(k) \tau_s(k) \delta[E - E(k)],
\end{equation}

where \( e \) is the carrier charge, \( \mu \) is the chemical potential for the specific material, and \( f_0(E) \) is the Fermi distribution function. The transport distribution function \( \Sigma(E) \) includes the electronic group velocity \( v_t(k) = (1/\hbar) \nabla E(k) \) and the total electronic relaxation time \( \tau_s \). Because PbTe is a small bandgap semiconductor with ellipsoidal Fermi surfaces, the nonparabolic two-band Kane model is an adequate description for the energy band structure,\textsuperscript{12} with \( \gamma(E) = \hbar^2 k^2 / 2m^* \), where \( m^* \) is the band-edge density of states effective mass and \( \gamma(E) = E(1 + E/E_g) \), with \( E_g \) being the bandgap. This also enables one to determine the carrier group velocity, \( v_g = (2/m^*)^{1/2} \gamma(E) \gamma^2(E)^{-1} \). The relations and parameters entering \( \gamma(E) \) and \( v_g \) are given in the Appendix.

The total relaxation time is obtained using Matthiessen’s rule, which assumes that each scattering mechanism is independent of the others. For PbTe, \( \tau_s \) depends on the wave vector \( k \) only through the electron energy \( E \), i.e., \( \tau_s(k) = \tau_s(E) \).\textsuperscript{12} Thus the relaxation time is obtained from \( \tau(E)^{-1} = \sum \tau_i(E)^{-1} \), where \( \tau_i(E) \) corresponds to each contributing mechanism. The most relevant \( \tau_i(E) \) for these PbTe composites are due to phonons, ionized impurities, and granular interface scatterings. Expanded expressions for the scattering relaxation times relevant for this material are given in the Appendix. The effect of screening is included for the carrier/polar optical phonon scattering, and the effect of nonparabolicity on the transition matrix element energy dependence is included for the electrons scattered by acoustic phonons through the deformation potential approximation.\textsuperscript{12}

The granular interfaces in the PbTe composites are described as an infinite series of potential barriers with average height \( E_b \), barrier region size \( w \), and grain size \( L \). \( \tau_{gr} \) can be calculated by determining the transmission probability through each barrier, and the expression is given in the Appendix. The characteristics of the granular barriers can be taken as input or adjustable parameters for modeling purposes. In a previous study,\textsuperscript{5} the role of the granular barrier on the transport properties was investigated, and that work revealed the dependence of carrier scattering due to grain boundaries and other mechanisms typical for bulk in the transport. Here, we take \( E_b = 0.06 \text{ eV} \) and \( w = 10 \text{ nm} \), and \( L \) is estimated from the experimental data (about 40 nm and 75 nm for the S1 and S2 specimens, respectively).
The lattice thermal conductivity is calculated using the Holland-Callaway model,\textsuperscript{13–15}

\[ \kappa_L = \frac{k_B}{2\pi^2v_{ph}} \left( \frac{k_B T}{h} \right)^3 \int_0^{\theta_B/T} \tau_{ph}(x) \frac{x^4 e^x}{(e^x - 1)^2} dx, \]  
\( \text{(5)} \)

where \( v_{ph} = 1771.67 \text{ m/s} \) is the average phonon group velocity, \( \theta_B = 136 \text{ K} \) is the Debye temperature,\textsuperscript{12} and \( x = \hbar \omega/k_B T \) is dimensionless. \( \tau_{ph} \) is the total phonon relaxation time, and it is given by \( \tau^{-1}_{ph} = \sum_{i} \tau^{-1}_{ph,i} \) within Matthiessen’s rule, where each \( \tau_{ph,i} \) corresponds to a phonon scattering mechanism. In the case of the doped PbTe composites,

\[ \tau^{-1}_{ph} = \tau^{-1}_{ph,U} + \tau^{-1}_{ph,d} + \tau^{-1}_{ph,e} + \tau^{-1}_{ph,b}, \]  
\( \text{(6)} \)

where the terms represent Umklapp scattering, point defect scattering, electron-phonon scattering, and grain boundary scattering, respectively. These expressions, together with the experimental data and the calculated values. The biggest difference occurs in the low temperature regions, although a decrease in \( \kappa_T \) at higher temperatures. Nevertheless, despite those with an energy larger than \( E_B \) scatter through the specimen, determining the transport. Grain interfaces with larger barriers will result in the scattering of electrons with a relative large energy distribution, whereas wider barriers and smaller grains will contribute to more frequent scattering events and a larger number of electrons being scattered. Because of the electron/grain scattering, \( \rho \) is larger, as is expected in granular materials,\textsuperscript{16,17} as compared to micron-sized grain polycrystalline bulk materials. Composites with smaller grains result in a further increase in \( \rho \), as observed in Figs. 2 and 3.

The experimental and theoretical results show that \( \rho \) is larger for the composites with smaller grain sizes. This is directly related to the importance of the carrier scattering from the grain interfaces accounted for by the relaxation time \( \tau_{gr} \). As the grains become smaller, the carrier scattering becomes more frequent, resulting in an increase in \( \rho \). From Figs. 2 and 3 we note that \( \rho \) for S1 is larger than \( \rho \) for S2. The electron/grain scattering is also found to be responsible for the values of \( \kappa_T \), with \( \kappa \sim 1.5 \text{ Wm}^{-1}\text{K}^{-1} \) at room temperature. This value is lower by \( \sim 25\% \) as compared to that of the bulk.\textsuperscript{4,12}

\( S \) is also sensitive to the presence of granular interfaces and the carrier concentration, particularly at higher temperatures. To see this clearer, we show the dependence of \( S \) as a function of Hall concentration (Fig. 4). The solid line corresponds to Pisarenko’s curve, with acoustic phonon scattering being dominant.\textsuperscript{12} Figure 4 shows that \( S \) is larger for the composites, indicating the important role of the carrier/grains scattering. The enhancement of \( S \) is higher for nanocomposites with higher carrier concentrations.\textsuperscript{5,6,8} This was also observed for p-type PbTe and Bi\(_2\)Te\(_3\),\textsuperscript{5,6,8} and might be due to the combined effect of carrier/grain scattering and ionized impurity scattering\textsuperscript{5,6} more than to the grain size differences.

\[ \text{FIG. 4. (Color online) The Seebeck coefficient as a function of the carrier concentration for the four Bi-doped n-type PbTe nanocomposites, and the calculated relationship (solid line) from Ref. 12.} \]

The formed granular interfaces arising from the synthesis process, i.e., dense small grain polycrystalline materials, result in potential barriers between the grains that affect the electrical and heat transport. Simply stated, the carriers with an energy smaller than \( E_B \) scatter from the interfaces; however, those with an energy larger than \( E_B \) traverse through the specimen, determining the transport. Grain interfaces with larger barriers will result in the scattering of electrons with a relative large energy distribution, whereas wider barriers and smaller grains will contribute to more frequent scattering events and a larger number of electrons being scattered. Because of the electron/grain scattering, \( \rho \) is larger, as is expected in granular materials\textsuperscript{16,17} as compared to micron-sized grain polycrystalline bulk materials. Composites with smaller grains result in a further increase in \( \rho \), as observed in Figs. 2 and 3. An increase in \( \rho \) is usually accompanied by the enhancement of \( S \), because a smaller number of carriers contributes to the transport (Fig. 4).

Furthermore, grain scattering also reduces \( \kappa \). It is interesting to note that \( \kappa_T > \kappa_L \) for bulk PbTe. For example, at \( T = 300 \text{ K} \), \( \kappa_T = 4.2 \text{ Wm}^{-1}\text{K}^{-1} \) and \( \kappa_L = 2 \text{ Wm}^{-1}\text{K}^{-1} \), according to Refs. 17 and 19, and this is confirmed by our model here. Our model also shows that phonon/interface scattering is less effective for the reduction of \( \kappa_L \) at higher temperatures. It is a decrease in \( \kappa_T \) that leads to an overall decrease in \( \kappa \) at higher temperatures. Nevertheless, despite the beneficial changes due to reductions in \( \kappa \) and the increase in \( S \), the increase in \( \rho \) results in a small \( ZT \) for Bi-doped n-type PbTe. We note that the role of the carrier and phonon scattering from the granular interfaces is critical in understanding and describing the transport properties of n-type PbTe composites. If granular interface scattering is not taken into account, the transport properties cannot be described in a satisfactory manner.

**IV. CONCLUSIONS**

We have synthesized n-type PbTe (Bi-doped) composites using chemical approaches based on micro-emulsion and direct precipitation, yielding nanocrystals of different sizes. Dense polycrystalline nanocomposite specimens with grain sizes of 50 to 100 nm and 30 to 50nm were synthesized, and their transport properties were measured. The
electrical resistivity, Seebeck coefficient, and thermal conductivity were also described using a model that explicitly includes the relevant energy band-structure of PbTe within the nonparabolic Kane model, temperature dependent parameters, and relevant scattering mechanisms. Of particular importance are the electron/grain and phonon/grain interface scattering, not typically relevant for large-grain polycrystalline specimens, for the complete description of the transport properties. The increase in ρ and |s|, as well as the reduction in κ, is interpreted in terms of the “filtering” of carriers and the scattering of phonons by the potential barriers formed due to the existence of the grain boundaries, respectively. Due to the large increase in ρ, it remains of interest to find ways of optimizing the thermoelectric performance of n-type PbTe.

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APPENDIX

In order to make the presentation self-consistent, we give some relations for the description of the dispersion relations and the scattering mechanisms. We use a modified two-band Kane dispersion model to account for the nonparabolicity and anisotropy of the PbTe energy bands at the L-point:

\[ \gamma(E) = E(1 + E/E_g) = \frac{\hbar^2 k^2_{\|}}{2m^*_T} + \frac{\hbar^2 k^2_{\perp}}{2m^*_T}, \tag{A1} \]

where \( E_g(T) = 0.19 + 0.42 \times 10^{-3} \times T \) eV is the energy bandgap, and \( k_{\|}, \, k_{\perp}, \, m^*_T, \) and \( m^*_T \) denote the carrier wave vector and effective mass components parallel and perpendicular to the ⟨111⟩ pocket direction, respectively. The density of states effective mass is then defined as \( m^*_T = (m^2_{\|} m^2_{\perp})^{1/3}, \) with \( m^2_{\|}(T)/m_0 = 0.194 \times E_g(T)/0.255 \) and \( m^2_{\perp}(T)/m_0 = 0.023 \times E_g(T)/0.255, \) respectively.

The carrier scattering mechanisms in PbTe considered here are due to electron/nonpolar acoustic phonons (npa), electron/nonpolar optical phonons (npo), electron/polar optical phonons (po), and electron/impurity (imp) scatterings, given as follows:

\[ \tau_{\text{po}} = \frac{\pi C_f \hbar^3}{2^{1/2} m^3 D_a k_B T \gamma^{1/2}(E) \Gamma(E)}, \tag{A2} \]

\[ \Gamma(E) = 1 - \frac{8\gamma(E)}{3E_E^{\prime}(E)\gamma^\prime(E)}, \tag{A3} \]

\[ \tau_{\text{npo}} = \frac{2\hbar^2 a^2 \rho(h\omega_0)^2}{\pi D_0^2 k_B T (2m^3_T)^{1/2} \gamma^{1/2}(E) \Gamma(E)} \tag{A4} \]

\[ \tau_{\text{nal}} = \frac{\pi D_0^2 k_B T (2m^3_T)^{1/2} \gamma^{1/2}(E) \Gamma(E)}{2\gamma(E) E_E^\prime(E)}, \tag{A5} \]

\[ \tau_{\text{imp}} = \frac{16\pi(2m^3_T)^{1/2} E_0^2}{Z^2 \omega_0^4 \ln(1 + (2E/E_g)^2)} E^{3/2}, \tag{A6} \]

where \( C_f \) is the average elastic constant, \( D_a \) and \( D_0 \) are the acoustic and optical deformation potential constants, respectively, \( \rho \) is the material density, \( a \) is the lattice constant, \( \omega_0 \) is the optical phonon frequency, and \( \varepsilon_\infty, \, \varepsilon_0, \) and \( E_0 \) are the high frequency, static, and vacuum permittivities, respectively. Their values are given in Table I.

In addition, \( E_g \) is the carrier potential energy at the screening length \( r_\infty, \) and \( \delta = 1/(2r_\infty)^2. \) The screening length is calculated as

\[ 1/r_\infty^2 = \frac{e^2}{\varepsilon_\infty} \int_0^{\infty} \left(-\frac{\partial \phi_0}{\partial E}\right) g(E) dE, \tag{A7} \]

with

\[ g(E) = \frac{2^{1/2} (m^*_T)^{3/2}}{\pi^2 \hbar^2} \left(\frac{\gamma(E)}{\gamma_E}\right)^{1/2} \gamma^\prime(E) \]

being the density of states.

The granular interfaces in the PbTe composites are described as an infinite series of potential barriers with average height \( E_b, \) barrier region size \( w, \) and grain size \( L. \) Taking into account the characteristics of each grain and the quantum transmission probability of the electrons through each barrier, the relaxation time is found to be

\[ \tau_E(E) = \begin{cases} \frac{L}{v_c(E)} \left[ 1 + \frac{4}{\sinh^2 \left( \frac{2m^*_T E_b w^2}{R^2} \left(1 - \frac{E}{E_b}\right) \right) \right], & \text{if } E < E_b \\ \frac{L}{v_c(E)} \left[ 1 + \frac{4}{\sin^2 \left( \frac{2m^*_T E_b w^2}{\hbar^2} \left(1 - \frac{E}{E_b}\right) \right) \right], & \text{if } E > E_b \end{cases} \]

Finally, the total phonon scattering relaxation time (Eq. (6)) is written explicitly as

<p>| Table I. Material parameters used in calculating the Bi-doped PbTe transport properties. |
|---------------------------------|----------|--------|-------------|--------|--------|----------|----------|</p>
<table>
<thead>
<tr>
<th>( D_a ) (eV)</th>
<th>( D_0 ) (eV)</th>
<th>( \varepsilon_\infty ) (( \varepsilon_0 )) (nm)</th>
<th>10^3 kg/m^3</th>
<th>( \rho )</th>
<th>( C_f )</th>
<th>10^3 N/m^2</th>
<th>( \omega_0 ) (10^13 s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.3</td>
<td>33.172</td>
<td>33</td>
<td>400</td>
<td>0.6462</td>
<td>8.24</td>
<td>83</td>
<td>6.28</td>
</tr>
</tbody>
</table>
\[ \frac{1}{\tau_{\text{ph}}} = B\omega^4 T \exp \left( -\frac{\theta_D}{3T} \right) + A\omega^4 + C\omega^2 + \frac{v_{\text{ph}}}{L}, \tag{A9} \]

where the first term corresponds to the phonon Umklapp, the second term to the phonon/point defect, the third term to the electron/phonon, and the last term to the phonon/grain boundary scatterings. The parameters A, B, and C are taken to be adjustable, and their values are given in Table II.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>L (nm)</th>
<th>A ( \times 10^{-33} \text{s}^3 )</th>
<th>B ( \times 10^{-18} \text{sK}^{-1} )</th>
<th>C ( \times 10^{-15} \text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 25%</td>
<td>40</td>
<td>1</td>
<td>0.43</td>
<td>0.82</td>
</tr>
<tr>
<td>S1 20%</td>
<td>40</td>
<td>0.82</td>
<td>0.43</td>
<td>0.64</td>
</tr>
<tr>
<td>S2 25%</td>
<td>75</td>
<td>0.91</td>
<td>0.43</td>
<td>0.7</td>
</tr>
<tr>
<td>S2 15%</td>
<td>75</td>
<td>0.77</td>
<td>0.43</td>
<td>0.45</td>
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</table>

\(^7\text{A. Popescu and L. M. Woods, \textit{Appl. Phys. Lett.} 97, 052102 (2010).} \)
\(^11\text{J. Martin, G. S. Nolas, H. Wang, and J. J. Yang, \textit{J. Appl. Phys.} 102, 103719 (2007).} \)
\(^12\text{Y. I. Ravich, B. A. Efimova, and I. A. Smirnov, \textit{Semiconducting Lead Chalcogenides} (Plenum, New York, 1970).} \)
\(^13\text{J. Callaway, \textit{Phys. Rev.} 113, 1046 (1959).} \)
\(^14\text{M. G. Holland, \textit{Phys. Rev.} 132, 2461 (1963).} \)
\(^15\text{J. He, S. N. Girard, M. G. Kanatzidis, and V. P. Dravid, \textit{Adv. Funct. Mater.} 20, 764 (2010).} \)
\(^17\text{Q. Zhang, T. Sun, F. Cao, M. Li, M. Hong, J. Yuan, Q. Yan, H. H. Hng, N. Wud, and X. Liu, \textit{Nanoscale} 2, 1256 (2010).} \)
\(^18\text{Y. I. Ravich \textit{Lead Chalcogenides: Physics and Applications}, edited by D. Khokhlov (Taylor & Francis, New York, 2003).} \)