Supporting Information

Wang et al. 10.1073/pnas.1111419109

SI Material

Additional Property Measurement. Table S1 shows the nominal composition and room temperature properties of samples discussed in the paper.

Since \( p \) and \( \kappa \) (also \( S \)) are measured along different directions, the possibility of anisotropy can be a concern. In this study, two slices were cut from a cylinder (approximately 10 mm tall, nominal composition \( \text{Pb}_{0.02}\text{Se}_{0.98}\text{Br}_{0.0018} \), with the same processing as other samples). The measurement results from each slice showed no appreciable difference beyond the measurement uncertainty (Fig. S1).

The scanning Seebeck measurement (300 K, Fig. S2) was also done on a 0.18\% Br-PbSe sample (3E19) to determine homogeneity of the material. The averaged Seebeck is \(-72 \mu V/K \) with a standard deviation of 3.7 \( \mu V/K \).

The lattice thermal conductivity, \( \kappa_L \), of n-type PbSe is found to be inherently low, similar to its p-type counterpart. However, \( \kappa_L \) obtained by subtracting electronic contribution based on the SKB model from the total thermal conductivity shows noticeable difference among samples with different doping level. Nevertheless, for a few samples with optimal carrier density and high \( zT \), the averaged value (dashed line in Fig. S3) provides a reasonable estimation which indicates approximately 0.8 W/mK around 800 K. This result is comparable with that for p-type PbSe (1) (approximately 0.6 W/mK) and as well as PbTe (approximately 0.8 W/mK for both p-type (2) and n-type (3)).

Repeatability and Reproducibility of Reported \( zT \). Four samples were individually made with the room temperature Hall carrier density close to \( 3 \times 10^{19} \text{ cm}^{-3} \) (2.9 \( \times 10^{19} \) to 3.4 \( \times 10^{19} \)). The measurements show very similar values in each of the properties, which overall give \( zT \) between 1.0 and 1.2 at 850 K (Fig. S4).

Samples were also sent to Shanghai Institute of Ceramics, Chinese Academy of Science (SIC-CAS) and National Aeronautics and Space Administration-Jet Propulsion Laboratory (JPL) for measurements. These values are also compared with recent reports of thermoelectric properties of Cl-doped PbSe (Fig. S5).

Values are taken from: sample D in ref. 4 (Northwestern high doping), sample C in ref. 4 (Northwestern low doping), and sample 1 in ref. 5 (Ioffe Institute low doping).

The differences between results from different institutes on the same (or very similar) Br-doped samples made in this work are <5\%. While measurements on different samples from different institutes but with similar \( n_H \) can be as large as 15\%, this is quite reasonable when taking into account the difference in preparation methods, sample density, dopant/composition choice, and dopant efficiency and measurement methods.

The thermal conductivity comparison is given in Fig. 1 in the main text. The reported data shown in Fig. 1 are taken from: sample 1 in ref. 5 (Ioffe Institute, p); sample C in ref. 4 (Northwestern, n, low doping); sample D in ref. 4 (Northwestern, n, high doping, solid triangles); sample “PbSe-In 3E19 electron/cm^3” in ref. 6 (Northwestern, n, high doping, open triangles filled with dots); sample “\( \text{Cl-PbSe}^+ \)” in ref. 7 (Wuhan U Tech, p, low doping); sample “Cl-PbSe” in ref. 8 (Boston College, n).

For all the samples that use laser flash method, very similar \( C_p \) was used to calculate \( \kappa \): the Caltech, SIC-CAS, and Northwestern results use experimental results reported by Blachnik; The Boston College and Wuhan Tech U results are based on measured \( C_p \) that were not directly shown, but was claimed to be 10% higher than the Dulong-Petit value above 500 K (Wuhan Tech U), or should be consistent with Blachnik’s result according to the values of a given sample (Boston College).

Single Kane Band Modeling Details. Fig. S6 shows the temperature dependence of mobilities (\( \mu = \mu_H/A \), where \( A \) is the Hall factor) of Br-doped PbSe samples. Due to the generally considered temperature dependence of effective mass (9) \( m^* \sim T^{-0.4} \) in lead chalcogenides the mobility governed by acoustic phonon scattering (\( \mu \sim \tau/m^* \sim T^{-3/2}/m^{1.5} \)) has the temperature dependence (9) of \( \mu \sim T^{-2.5} \). Such a trend can be seen in Fig. S6, thus enabling us to assume the acoustic phonon scattering is predominant, as is believed for heavily doped thermoelectric lead chalcogenides above room temperature (9).

The relaxation time for the Kane band model with acoustic phonon scattering is given by (10):

\[
\tau_{ac} = \frac{\hbar C_N V}{\pi k_B T \Xi} S(e)^{-1} \left[ 1 - \frac{8a(e + e^2a)}{3(1 + 2e\alpha)^2} \right]^{-1}
\]

\[
g(e) = \frac{2^{1/2}m^{3/2}(k_B T)^{1/2}}{\pi^2 h^3} (e + e^2a)^{1/2}(1 + 2e\alpha).
\]

where \( k_B \) is the Boltzmann constant, \( h \) is the reduced Plank’s constant, \( m^* \) is the density of state effective mass taking into account the conduction band structure, \( C_N \) is the combination of the elastic constants (12), \( \Xi \) is a combination of deformation potentials for multivalley systems (11, 12), which describes the carrier scattering strength by acoustic phonons, \( N_{\text{b}} \) is the band degeneracy, \( \epsilon \) is the reduced energy, \( \alpha \) is defined by \( \alpha = k_B T/\xi_0^e \), where \( \epsilon_0^e \) is the gap between conduction and valence band at L point which is known to change with temperature via (13) \( \epsilon_0^e/eV = 0.17 + 4 \times 10^{-4} T/K \).

Within the Kane model, the transport parameters are expressed as follows:

The carrier density:

\[
n = \frac{2m^* k_B T}{3\pi^2 h^3} \frac{1}{\theta F_{0}^{3/2}}.
\]

The Seebeck coefficient:

\[
S = \frac{k_B}{\epsilon} \left[ \frac{F_{1/2}^{1}}{\theta F_{1/2}^{3/2}} - \xi \right].
\]

\( \xi \) is the reduced chemical potential \( \xi = u/k_{B} T \).

The mobility:

\[
\mu = \frac{2\pi e h^4 c_j}{m_1^*(2m_1^* k_B T)^{1/2} \Xi^2 F_0^{1/2}}.
\]

The Hall factor \( A (n = A n_H = A/eR_H) \):

\[
A = \frac{3K(K+2)\theta F_{0}^{3/2}}{K(2K + 1)^2(\theta F_{1/2}^{3/2})^2}.
\]

\( K = m_2^*/m_1^*(K = 1.75) \), assumed \( T \) independent, and the Lorenz number:
$L = \left( \frac{k_B}{e} \right)^2 \left[ \frac{1}{m_{1/2}^2} \left( \frac{F_1}{F_2} \right)^2 - \frac{1}{m_{1/2}^2} \left( \frac{F_1}{F_2} \right)^2 \right].$

In the equations above the integral \( \int F_m^m \) is defined by

$$\int F_m^m = \int_0^\infty -\frac{d}{de} e^{\eta}(e+ae)^m[(1+2ae)^2+2]^{1/2} de.$$  

Due to the anisotropy of both conduction and valence bands at the L point, the inertial effective mass \( m^*_I \), and the density of states effective mass \( m^*_D \) are governed by the effective band mass of a single pocket along two directions \( m_{1/2}^* \) and \( m_{1/2}^* \):

$$m^*_I = 3 \left( \frac{2}{m_{1/2}^*} + \frac{1}{m_{1/2}^*} \right)^{-1}, \quad m^*_D = N_x^{1/3} m_{1/2}^* = N_x^{1/3} (m_{1/2}^* m_{1/2}^*)^{1/3}.$$  

For PbSe \( m^* = 0.27 m_o \) at 300 K and changes with temperature according to \( \frac{dm^*}{dt} \) = 0.5 (Fig. S7) was determined in this study. A similar temperature dependence was observed in PbTe (14). Further extrapolating this to 77 K yields \( m^* = 0.13 m_o \), which is in good agreement with the value determined (15) by longitudinal Nernst-Ettingshausen effect (0.12 \( m_o \)).

Fig. S8 shows the Seebeck-Pisarenko plot (Fig. S7) plotted against \( n_H \) at different temperatures. Up to 800 K, the calculated curve explains the experimental data well. Fig. S9 shows the Hall mobility \( \mu_H = R_H / \rho \) as a function of \( n_H \) at different temperatures. At 300 K, the SKB model (solid curves) successfully explains the experimental results for samples with \( n_H \) greater than \( 1.5 \times 10^{19} \) cm\(^{-3}\). The model tends to overestimate mobilities for samples with lower carrier density, which is due to other scattering mechanisms, such as polar optical phonon

scattering that usually plays an important role in lightly doped lead chalcogenides at low temperatures (11, 16). The single parabolic band (SPB) model (dashed curve), on the other hand, failed to predict the fast drop of \( \mu_H \) at higher doping level which is direct evidence that the conduction band is nonparabolic, Kane-type. As the temperature increases, the model is found to overestimate the mobility, suggesting the parameters that go into the model (such as \( C_f \)) need to be temperature dependent to improve accuracy.

This nonparabolic Kane band feature is seen in both the conduction band and the light valence band, although for p-type PbSe the heavy valence band may also play an important role in the carrier transport process at high temperatures. Thus, for relatively lightly doped samples, a comparison of the \( zT \) value (Fig. S10) of n- and p-type samples with optimal carrier density \( (n_H, 300 K \sim 1 \times 10^{19}) \) in the 300 K to 400 K temperature range provides a clear demonstration of the beneficial influence of smaller deformation potential coefficient \( \Xi \). Higher \( zT \) in n-type samples is caused by the smaller \( \Xi \) (at 300 K the ratio \( zT_n/zT_p \) = 0.24/0.10) as described in the main text.

**Additional Information on Effective Deformation Potential Coefficient \( \Xi \).** The value of deformation potentials, especially \( \Xi \) from mobility data, is reported for only a few semiconductors. In Table S2, we list the effective deformation potential coefficient \( \Xi \) determined from mobility along with other parameters (all at 300 K) including electron-electron difference (\( \Delta X \)) for systems that satisfy, or can be approximated as when \( n_H \) is small, single band conduction with acoustic phonon scattering dominant at high temperature. No obvious trend was observed, suggesting that \( \Xi \) is independent of the other parameters determining thermoelectric quality factor.

Fig. S1. Resistivity and Seebeck coefficient (A) and thermal conductivity (B) of two slices cut from a single cylinder along different directions. The curves represent results measured from each sample.

Fig. S2. Seebeck coefficient scanning on an area of $6 \times 6$ mm (0.2 mm interval) of a 0.18% Br-PbSe (3E19) sample.

Fig. S3. Lattice thermal conductivity of a few optimally doped samples as function of temperature.
Fig. S4. Temperature dependent $zT$ of five samples with optimum carrier concentration. The Caltech results are also compared with measurements from SIC-CAS and JPL. The deviation between curves is a good, direct indication of uncertainty in reported $zT$.

Fig. S5. A comparison of (A) resistivity and (B) Seebeck coefficient of a few n-type PbSe samples with similar Hall carrier concentrations, including samples from this work tested at Caltech, SIC-CAS, and JPL, as well as samples reported in the literature.

Fig. S6. Mobility as a function of temperature for Br-doped PbSe.
Fig. S7. The density of states effective mass, determined by measured Seebeck coefficient and Hall carrier density, of each sample as a function of temperature. The solid curve stands for the relation $d \ln m^*/d \ln T = 0.5$ with $m^* = 0.27 m_e$ at 300 K, which is used in the modeling of transport properties.

Fig. S8. Seebeck Pisarenko plot of Br-doped PbSe at different temperatures. The solid curves are calculated from the SKB model.

Fig. S9. Hall mobility as function of Hall carrier density for Br-doped PbSe at different temperatures. The solid curves are calculated from the SKB model and the dashed curve is from the SPB model.
Fig. S10. $zT$ values near room temperature for two lightly doped samples having similar carrier density. Higher $zT$ in n-type sample demonstrates the beneficial effect of smaller deformation potential coefficient $\Xi$.

Table S1. A list of samples and some of their room temperature properties at 300 K

<table>
<thead>
<tr>
<th>Label</th>
<th>Composition</th>
<th>$n_v$ ($10^{19}$ cm$^{-3}$)</th>
<th>$S$ (µV/K)</th>
<th>$\mu$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7E18</td>
<td>Pb$<em>{1.002}$Se$</em>{0.996}$Br$_{0.004}$</td>
<td>0.72</td>
<td>-114.2</td>
<td>-1,215</td>
</tr>
<tr>
<td>1E19</td>
<td>Pb$<em>{1.002}$Se$</em>{0.999}$Br$_{0.0005}$</td>
<td>0.95</td>
<td>-99.7</td>
<td>-1,171</td>
</tr>
<tr>
<td>2E19</td>
<td>Pb$<em>{1.002}$Se$</em>{0.988}$Br$_{0.0012}$</td>
<td>1.8</td>
<td>-76.0</td>
<td>-1,012</td>
</tr>
<tr>
<td>3E19</td>
<td>Pb$<em>{1.002}$Se$</em>{0.982}$Br$_{0.0018}$</td>
<td>3.0</td>
<td>-52.1</td>
<td>-828</td>
</tr>
<tr>
<td>4E19</td>
<td>Pb$<em>{1.002}$Se$</em>{0.976}$Br$_{0.0024}$</td>
<td>3.8</td>
<td>-46.5</td>
<td>-719</td>
</tr>
<tr>
<td>5E19</td>
<td>Pb$<em>{1.002}$Se$</em>{0.979}$Br$_{0.0003}$</td>
<td>4.5</td>
<td>-42.8</td>
<td>-645</td>
</tr>
<tr>
<td>6E19</td>
<td>Pb$<em>{1.002}$Se$</em>{0.996}$Br$_{0.004}$</td>
<td>5.8</td>
<td>-38.3</td>
<td>-573</td>
</tr>
</tbody>
</table>

Table S2. $\Xi$ and other material parameters for some semiconductors at 300 K

<table>
<thead>
<tr>
<th>Material</th>
<th>$\mu_0 m_v^{3/2}$ (cm$^2$/Vs)</th>
<th>$\Xi$ (eV)</th>
<th>$m_v^*/m_0$</th>
<th>$N_v$ (Pa)</th>
<th>$C_1 \times 10^{-10}$</th>
<th>$\Delta X$</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSe(n)</td>
<td>160</td>
<td>25</td>
<td>0.27</td>
<td>4</td>
<td>9.1</td>
<td>0.22</td>
<td>our modeling results</td>
</tr>
<tr>
<td>PbSe(p)</td>
<td>110</td>
<td>35</td>
<td>0.27</td>
<td>4</td>
<td>7.1</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>PbTe(n)</td>
<td>200</td>
<td>22</td>
<td>0.26</td>
<td>4</td>
<td>11.1</td>
<td>0.25</td>
<td>ref. 1</td>
</tr>
<tr>
<td>PbTe(p)</td>
<td>100</td>
<td>25</td>
<td>0.26</td>
<td>4</td>
<td>115.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbS</td>
<td>160</td>
<td>20</td>
<td>0.41</td>
<td>4</td>
<td>11.1</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Diamond (n)</td>
<td>5,370</td>
<td>9</td>
<td>1.84</td>
<td>6</td>
<td>115.7</td>
<td></td>
<td>ref. 1</td>
</tr>
<tr>
<td>Si(n)</td>
<td>1,700</td>
<td>8</td>
<td>1.1</td>
<td>6</td>
<td>18</td>
<td></td>
<td>ref. 2. $\Xi$ consistent with refs. 3 and 4</td>
</tr>
<tr>
<td>Ge(n)</td>
<td>1,900</td>
<td>10</td>
<td>0.55</td>
<td>4</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>InSb(n)</td>
<td>95</td>
<td>33</td>
<td>0.011</td>
<td>1</td>
<td>8.2</td>
<td>0.27</td>
<td>ref. 2. $\Xi$ from refs. 4 and 5</td>
</tr>
<tr>
<td>InP (n)</td>
<td>114</td>
<td>21</td>
<td>0.077</td>
<td>1</td>
<td>12</td>
<td>0.41</td>
<td>$C_1$, $\Xi$ from ref. 4</td>
</tr>
<tr>
<td>GaAs(n)</td>
<td>160</td>
<td>20</td>
<td>0.067</td>
<td>1</td>
<td>14.1</td>
<td>0.37</td>
<td>ref. 2. $\Xi$ consistent with ref. 4. Secondary</td>
</tr>
<tr>
<td>GaN</td>
<td>31</td>
<td>25</td>
<td>0.2</td>
<td>1</td>
<td>36.3</td>
<td>1.23</td>
<td>band minimum close to gap</td>
</tr>
</tbody>
</table>