Supporting Information

Soft Phonon Modes from Off-center Ge atoms Lead to Ultralow Thermal Conductivity and Superior Thermoelectric Performance in n-type PbSe-GeSe

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**Figure S1.** PXRD patterns of Pb$_{0.9955}$Sb$_{0.0045}$Se-$x\%$GeSe ($x = 0, 3, 6, 9, 12$ and $14$) samples, with all peaks indexed by the PbSe cubic phase (JCPDS #06-0354, red patterns).

**Figure S2.** Seebeck coefficient as a function of Hall carrier concentration with an effective mass of $0.35 \, m_e$ for Pb$_{0.9955}$Sb$_{0.0045}$Se-$x\%$GeSe ($x = 0, 6, 9$ and $12$). The solid curves are the theoretical Pisarenko plots at 296 K (cyan), 573 K (red) and 773 K (green) for n-type PbSe with effective mass of electrons of $0.35 \, m_e$. 
Figure S3. Temperature-dependent (a) Lorenz numbers, $L$; (b) Heat capacities, $C_p$; (c) Thermal diffusivity, $D$; and (d) Electronic thermal conductivity, $\kappa_{\text{ele}}$ for Pb$_{0.9955}$Sb$_{0.0045}$Se-$x\%$GeSe.
Figure S4. (a) Phonon dispersion curves and (b) the projected phonon density of states (PDOS) for pure PbSe.
In the Debye-Callaway model, we add defect scatterings for longitudinal and transverse modes:

\[ \tau_I'(x)^{-1} = \frac{V k_B^2}{4 \pi \hbar^4 v_L^4} x^4 T^4 \]

and

\[ \tau_I'(x)^{-1} = \frac{V k_B^2}{4 \pi \hbar^4 v_T^4} x^4 T^4 \]

where \( \Gamma = \sum_i c_i \left( \frac{m_i - m_{\text{avg}}}{m_{\text{avg}}} \right)^2 \), \( m_i \) is the atomic mass of the \( i \)th defect, \( m_{\text{avg}} = \sum_i c_i m_i \) is the average atomic mass in the system with different concentration \( c_i \), \( x = \frac{\hbar}{k_B T} \), \( T \) temperature and \( v_L, v_T \) the longitudinal and transverse phonon velocities, respectively.

The effects of Ge alloying on suppressing \( \kappa_{\text{lat}} \) is shown in the below figure:

![Figure S5](image-url)

**Figure S5.** Lattice thermal conductivity comparison of pure PbSe and with 5% and 10% Ge-alloyed samples without accounting for the off-centering Ge\(^{2+} \) defect. The effects on the thermal conductivity are small.

At 300 K, \( \kappa_{\text{lat}} \) decreases from around 2.5 Wm\(^{-1}\)K\(^{-1} \) to 2.36 Wm\(^{-1}\)K\(^{-1} \) with 5% Ge and 2.27 Wm\(^{-1}\)K\(^{-1} \) with 10% Ge alloying. Evidently, the Ge alloying effect on the lattice thermal conductivity through mass fluctuation is not as significant as the impact of the off-centering defect that induces diminished phonon vibration frequencies and phonon velocities. Thus, the main cause of the \( \kappa_{\text{lat}} \) decrease by Ge alloying originates from the Ge off-centered atomic structure. The off-centered Ge induces local lattice strain that lowers the acoustic phonon frequencies, velocities and Debye temperature yielding a decrease in \( \kappa_{\text{lat}} \) by 26% of lattice thermal conductivity relative to the pure PbSe calculated (Debye-Grüneisen) value at 300 K.

On the other hand, at high concentration (10%) of Ge impurities, the phonon-impurity scattering decreases \( \kappa_{\text{lat}} \) by 9% of pure PbSe \( \kappa_{\text{lat}} \) value at 300 K as shown in Figure S5. The off-centered Ge also induces softening of the low-lying optical phonon modes, and may cause a further decrease in the lattice thermal conductivity, but this contribution is not included in our Debye Grüneisen calculations. All these combined effects help to understand the experimental observation of \( \kappa_{\text{lat}} \) decrease by 50% of \( \kappa_{\text{lat}} \) by 12% of Ge alloying.
Figure S6. The Pb$_{0.9955}$Sb$_{0.0045}$Se-$12\%$GeSe sample was measured 3 times with almost no changes in the (a) Electrical conductivity, $\sigma$; (b) Seebeck coefficient, $S$; and (c) Power factor, $PF$, showing the good repeatability and stability. Moreover, thermal diffusion coefficient, $D$ (d) also displays the good repeatability during heating and cooling processes.
Figure S7. Comparison of the average thermoelectric figure of merit, $ZT_{avg}$, values with the temperature gradient of 300 K to 923 K for several n- and p-type PbSe-based thermoelectric materials.\textsuperscript{52-58}
Table S1. Room temperature densities of Pb$_{0.9955}$Sb$_{0.0045}$Se-x%GeSe (x = 0, 3, 6, 9, 12 and 14)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Measured Density, g cm$^{-3}$</th>
<th>Theoretical Density, $%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$<em>{0.9955}$Sb$</em>{0.0045}$Se</td>
<td>8.17</td>
<td>98.9</td>
</tr>
<tr>
<td>Pb$<em>{0.9955}$Sb$</em>{0.0045}$Se-3%GeSe</td>
<td>8.09</td>
<td>98.9</td>
</tr>
<tr>
<td>Pb$<em>{0.9955}$Sb$</em>{0.0045}$Se-6%GeSe</td>
<td>7.97</td>
<td>98.4</td>
</tr>
<tr>
<td>Pb$<em>{0.9955}$Sb$</em>{0.0045}$Se-9%GeSe</td>
<td>8.01</td>
<td>99.5</td>
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<tr>
<td>Pb$<em>{0.9955}$Sb$</em>{0.0045}$Se-12%GeSe</td>
<td>7.76</td>
<td>97.5</td>
</tr>
<tr>
<td>Pb$<em>{0.9955}$Sb$</em>{0.0045}$Se-14%GeSe</td>
<td>7.7</td>
<td>97.6</td>
</tr>
</tbody>
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References