Improvement in the thermoelectric performance of highly reproducible \textit{n}-type (Bi,Sb)$_2$Se$_3$ alloys by Cl-doping

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1. The lattice parameters of Cl-doped BiSbSe$_3$.

\textbf{Figure S1.} (a) One typical XRD refinement result of BiSbSe$_3$ sample. (b) The change in lattice parameters ($a$, $b$, and $c$) of orthorhombic BiSbSe$_3$ by Cl-doping.
2. Microstructure analysis for the SPSed BiSbSe$_{3-y}$Cl$_y$ ($y = 0, 0.12, 0.18, 0.24$) and Bi$_{1.2}$Sb$_{0.8}$Se$_{3-z}$Cl$_z$ ($z = 0, 0.12, 0.18, 0.24$) samples.

**Figure S2.** SEM images of fractured surfaces for the SPSed BiSbSe$_{3-y}$Cl$_y$ ($y = 0, 0.12, 0.18, 0.24$) and Bi$_{1.2}$Sb$_{0.8}$Se$_{3-z}$Cl$_z$ ($z = 0, 0.12, 0.18, 0.24$).
3. The mole fraction of rhombohedral phase in Bi$_{1.2}$Sb$_{0.8}$Se$_{3-z}$Cl$_z$ ($z = 0, 0.12, 0.18, 0.24$).

**Table S1.** The mole fraction of rhombohedral phase in Bi$_{1.2}$Sb$_{0.8}$Se$_{3-z}$Cl$_z$ ($z = 0, 0.12, 0.18, 0.24$), which is calculated by Rietveld refinement. The relative densities of the samples measured by the Archimedes principle (AlfaMiracle, MD-300S) are also shown.

<table>
<thead>
<tr>
<th>Compositions (nominal)</th>
<th>Mole fraction</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rhombohedral</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Bi$<em>{1.2}$Sb$</em>{0.8}$Se$_3$</td>
<td>0.743</td>
<td>0.257</td>
</tr>
<tr>
<td>Bi$<em>{1.2}$Sb$</em>{0.8}$Se$<em>{2.88}$Cl$</em>{0.12}$</td>
<td>0.744</td>
<td>0.256</td>
</tr>
<tr>
<td>Bi$<em>{1.2}$Sb$</em>{0.8}$Se$<em>{2.82}$Cl$</em>{0.18}$</td>
<td>0.745</td>
<td>0.255</td>
</tr>
<tr>
<td>Bi$<em>{1.2}$Sb$</em>{0.8}$Se$<em>{2.76}$Cl$</em>{0.24}$</td>
<td>0.747</td>
<td>0.253</td>
</tr>
</tbody>
</table>
4. The lattice parameters of Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$.

**Figure S3.** (a) One typical XRD refinement result of Bi$_{1.2}$Sb$_{0.8}$Se$_3$ sample. (b) The change in lattice parameters of rhombohedral ($a$ and $c$) and orthorhombic ($a$, $b$, and $c$) phases of Bi$_{1.2}$Sb$_{0.8}$Se$_3$ by Cl-doping.
5. Phase formation in $\text{Bi}_{1.2}\text{Sb}_{0.8}\text{Se}_{2.7}\text{Cl}_{0.3}$.

Figure S4. XRD pattern of SPSed $\text{Bi}_{1.2}\text{Sb}_{0.8}\text{Se}_{2.7}\text{Cl}_{0.3}$. 
6. Calculation of electronic thermal conductivity

The electronic thermal conductivity ($\kappa_{\text{ele}}$) is estimated by the Wiedemann-Franz law ($\kappa_{\text{ele}} = L \sigma T$, where $L$, $\sigma$, and $T$ are the Lorenz number, electrical conductivity, and the absolute temperature). Temperature dependent $L$ is obtained by using Eq. S1 assuming a single parabolic band model [1].

$$L = 1.5 + \exp \left( -\frac{|S|}{116} \right)$$

Equation S1

Figure S5 shows the temperature dependences of $L$ for Cl-doped BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$.
References