Supporting Information

\(n\)-Bi\(_{2-x}\)Sb\(_x\)Te\(_3\): A Promising Alternative to Mainstream Thermoelectric Material \(n\)-Bi\(_2\)Te\(_3-x\)Se\(_x\) near Room Temperature

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### Table S1. Boiling point, electronegativity, covalent radius, and relative atomic mass of basic elements.

<table>
<thead>
<tr>
<th>Basic elements</th>
<th>Bi</th>
<th>Sb</th>
<th>Te</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point [K]</td>
<td>1837</td>
<td>1860</td>
<td>1261</td>
<td>1231</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>2.02</td>
<td>2.05</td>
<td>2.1</td>
<td>2.55</td>
</tr>
<tr>
<td>Atomic radius [Å]</td>
<td>1.60</td>
<td>1.45</td>
<td>1.40</td>
<td>1.15</td>
</tr>
<tr>
<td>Relative atomic mass</td>
<td>208.98</td>
<td>121.75</td>
<td>127.60</td>
<td>78.96</td>
</tr>
</tbody>
</table>

### Table S2. The actually chemical composition and samples’ density of the hot deformed Bi$_{2-x}$Sb$_x$Te$_3$ specimens.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Bi (at.%)</th>
<th>Sb (at.%)</th>
<th>Te (at.%)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>41.23</td>
<td>0</td>
<td>58.77</td>
<td>7.62</td>
</tr>
<tr>
<td>$x = 0.1$</td>
<td>38.8</td>
<td>3.35</td>
<td>57.86</td>
<td>7.64</td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>35.51</td>
<td>7.63</td>
<td>58.86</td>
<td>7.4</td>
</tr>
<tr>
<td>$x = 0.4$</td>
<td>32.95</td>
<td>9.92</td>
<td>57.13</td>
<td>7.22</td>
</tr>
<tr>
<td>$x = 0.5$</td>
<td>30.46</td>
<td>11.76</td>
<td>57.78</td>
<td>7.03</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>29.04</td>
<td>13.78</td>
<td>57.18</td>
<td>7.26</td>
</tr>
<tr>
<td>$x = 0.8$</td>
<td>24.96</td>
<td>18.43</td>
<td>56.61</td>
<td>7.20</td>
</tr>
<tr>
<td>$x = 1.0$</td>
<td>20.9</td>
<td>22.45</td>
<td>56.65</td>
<td>6.90</td>
</tr>
<tr>
<td>$x = 1.2$</td>
<td>16.62</td>
<td>26.62</td>
<td>56.77</td>
<td>6.88</td>
</tr>
<tr>
<td>$x = 1.3$</td>
<td>14.44</td>
<td>28.14</td>
<td>57.41</td>
<td>6.7</td>
</tr>
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</table>
Figure S1. (a) Powder XRD pattern of the Bi$_{2-x}$Sb$_x$Te$_3$ samples. (b) Lattice parameters and unit cell volume of the Bi$_{2-x}$Sb$_x$Te$_3$ samples. (c) In-plane bulk XRD pattern and (d) calculated orientation degree $F$ of (00$l$) planes for the typical Bi$_{2-x}$Sb$_x$Te$_3$ samples.
Figure S2. (a) Schematic diagram of the donor-like effect in terms of chemical, mechanical and thermal controls. Sb content dependence of room temperature (b) carrier concentration and (c) Seebeck coefficient for the SC, (M/G+HP), SPS+HD Bi$_{2-x}$Sb$_x$Te$_3$ samples.$^{1,2}$

As illustrated in Figure. S2a, the donor-like effect can be controlled chemically (compositionally), mechanically, and thermally.

The donor-like effect works as follows:$^3$

(i) In V$_2$VI$_3$ compounds, the type and concentration of intrinsic point defects through the crystal growth process from the melts is regulated by extrinsic dopants (aka chemical control). Increasing the Sb content in SC Bi$_{2-x}$Sb$_x$Te$_3$ increases the
owing to a smaller difference in $\chi$ and $r$ between Sb and Te than the counterpart between Bi and Te (Table S1).

(ii) Mechanical deformation (ball milling in this work, aka mechanical control)-induced non-basal slip produces the $V_{Bi}^{\infty}$ and $V_{Te}^{\infty}$ with a 2:3 ratio. To the first order, the net carrier charge of these vacant pairs is zero, unaffected the $n_H$. However, these vacancy pairs act as “catalysts” for the defect reaction that yields the donor-like effect. In presence of $V_{Bi}^{\infty}$, Bi atoms diffuse from Te sites back to their original sublattice sites, extra $V_{Te}^{\infty}$ and excess electrons are thus produced, aka the donor-like effect.

(iii) The spark plasma sintering (SPS) process can provide energy facilitating Bi atoms to surmount the diffusion potential barrier and thus promote the donor-like effect (aka thermal control).

Thus, mechanical deformation- and sintering process-induced donor-like effect realize the $n$-type conduction crossover when the Sb content is lower than 1.4 in SPS Bi$_{2-x}$Sb$_x$Te$_3$ polycrystalline alloys. The main stream $p$-type conduction is established when the Sb content is higher than 1.4. However, the $n_H$ of SPS Bi$_2$Te$_3$ is still too high to make good $n$-type thermoelectrics. One one hand, with increasing Sb content, the $[Bi'_{Te}]$ increases and only a portion of $Bi'_{Te}$ involves in the donor-like effect through the BM-SPS process. Extra holes induced by residual $Bi'_{Te}$ compensate for the carrier electrons induced by the donor-like defects, i.e. $V_{Te}^{\infty}$, resulting in the decrease of $n_H$ (aka the compensation effect). On the other hand, the excessive $n_H$ needs to be tuned by hot deformation.
(iv) The HD process involves heavy deformation and recovery process, which plays opposite role in tuning the $n_{H}$. Plastic deformation promotes the donor-like effect while the recovery role eliminates $V^{\infty}_{Te}$ to some extent, closely depending on the HD temperature. It is found in this study that the recovery effect is predominant in view of 773 K adopted for HD, which further reduces the $n_{H}$ of $x = 0.4 - 0.8$ to the optimized range.

In summary, ball milling and SPS realized the $p$-$n$ type transition for Bi$_{2-x}$Sb$_x$Te$_3$ with $x < 1.4$. And the compensation effect by Sb alloying and the recovery effect via high-temperature HD optimized the $n_{H}$, resulting in a high $S$ and low $\kappa_{el}$. 
Figure S3. (a) Sb and Se content dependence of band gap for the Bi$_{2-x}$Sb$_x$Te$_3$ and Bi$_2$Te$_{3-x}$Se$_x$ series.$^{4,5}$ (b) Band gap and carrier concentration dependence of temperature such that the peak $S$ occurs for the hot deformed Bi$_{2-x}$Sb$_x$Te$_3$ samples.

Figure S4. Room temperature $PF$ values in this work compared with other $n$-type Bi$_2$Te$_{3-x}$Se$_x$ compounds.$^6$-$^{11}$
Figure S5. Temperature dependences of (a) thermal diffusivity, (b) Lorenz number and (c) electrical thermal conductivity of the hot deformed Bi$_{2-x}$Sb$_x$Te$_3$ samples.

Figure S6. Calculated disorder parameter $\Gamma$ for Bi$_{2-x}$Sb$_x$Te$_3$ and Bi$_2$Te$_{3-x}$Se$_x$ series. $\Gamma$ consist of contribution from mass fluctuations $\Gamma_M$ and strain field fluctuations $\Gamma_S$:

$$\Gamma = \Gamma_M + \Gamma_S.$$
Figure S7. Lowest lattice thermal conductivity in this work in comparison with those of other $n$-type V$_2$VI$_3$ materials.$^{6,11-19}$

The present room temperature $\kappa_{ph}$ is one of the lowest reported in $n$-type V$_2$VI$_3$ system (Figure S7).

Figure S8. Temperature dependences of $\kappa$-$\kappa_{el}$ of the hot deformed $n$-type Bi$_2$Te$_3$, Bi$_{1.5}$Sb$_{0.5}$Te$_3$, Bi$_2$Te$_{2.3}$Se$_{0.7}$ and Bi$_2$Te$_{2.79}$Se$_{0.21}$ samples.
Figure S9. Measurement repeatability of the $n$-type $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$ alloys in different test round: (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity and (f) Figure of Merit $zT$.

To check the reproducibility of the present results, the $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$ sample has been re-measured three times. Highly repeatable excellent $zT$ values of $0.97 \sim 1.02$ were obtained.
Figure S10. (a) Temperature dependence of specific heat capacity for Bi$_{1.5}$Sb$_{0.5}$Te$_3$ sample measured on a DSC along with the classic Dulong-Petit law. (b) Temperature dependent $zT$ values calculated by the Dulong-Petit law in comparison with that calculated from the DSC data.
Figure S11. Low temperature thermoelectric properties of $n$-type hot deformed Bi$_{1.5}$Sb$_{0.5}$Te$_3$: (a) electrical conductivity, (b) Seebeck coefficient, (c) total thermal conductivity and (d) Figure of Merit $zT$. 
Figure S12. (a) Temperature dependence of out-of-plane thermal conductivity for the Bi$_{2-x}$Sb$_x$Te$_3$ samples. (b) Temperature dependence of the overvalued $zT$ determined by in-plane $\sigma$ and out-of-plane $\kappa$ for the Bi$_{2-x}$Sb$_x$Te$_3$ samples.

The texture of $n$-type Bi$_{2-x}$Sb$_x$Te$_3$ samples studied is reflected in the difference between the in-plane (cf. Figure 5a) and out-of-plane $\kappa_0$ (cf. Figure. S12).

It is a must to measure all the thermoelectric properties and calculate the $zT$ in the same direction. Otherwise, an overestimated $zT$ value ~ 1.6 would be obtained if the in-plane $PF$ and the out-of-plane $k$ are used for the $x = 0.5$ sample.
References:


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(18) Xu, B. A.; Feng, T. L.; Agne, M. T.; Zhou, L.; Ruan, X. L.; Snyder, G. J.; Wu, Y. Highly Porous Thermoelectric Nanocomposites with Low Thermal Conductivity and High Figure of Merit from Large-Scale Solution-Synthesized Bi\(_2\)Te\(_{2.5}\)Se\(_{0.5}\) Hollow Nanostructures. *Angew. Chem. Int. Ed.* **2017**, *56*, 3546-3551.