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High efficiency Bi$_2$Te$_3$-based materials and devices for thermoelectric power generation between 100 and 300 °C

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Lattice thermal conductivity ($\kappa_L$) and bipolar thermal conductivity ($\kappa_b$)

The $\kappa_L$ data at 200-250 K was fitted by the expression of $\kappa_L = aT^{-1} + b$, where $a$ and $b$ are fitting parameters. As a typical example, Fig. S4c shows the fitting results for Bi$_{0.5}$Sb$_{1.5}$Te$_3$. Very good agreement between the experiment data and the fitting curve (red solid line) is observed. Similar agreements are also observed in all other samples. The fitted $a$ and $b$ values for the samples are listed in Table S1. The $\kappa_L$ was then extrapolated to 600 K according to the expression $\kappa_L = aT^{-1} + b$, which is shown in Fig. S4d. For sample Bi$_{0.5}$Sb$_{1.485}$Cd$_{0.015}$Te$_3$, Bi$_{0.5}$Sb$_{1.495}$Cu$_{0.005}$Te$_3$, and Bi$_{0.5}$Sb$_{1.494}$Ag$_{0.006}$Te$_3$, the $\kappa_L$ at elevated temperatures are lower than the theoretical minimum lattice thermal conductivity ($\kappa_{min} = 0.31 \text{ Wm}^{-1}\text{K}^{-1}$) in Bi$_{0.5}$Sb$_{1.5}$Te$_3$ calculated by the Cahill model.$^1$ In this case, $\kappa_{min}$ is used as the real $\kappa_L$ value instead of the extrapolated value. Finally, the $\kappa_b$ for all the samples at 300-600 K was calculated by subtracting the estimated $\kappa_L$ from experimental ($\kappa - L\sigma T$).

In n-type Bi$_2$Te$_3$-based materials, acoustic phonon scattering is also the dominant carrier scattering mechanism around 300 K. Thus, the electron mobilities ($\mu_e$) also obey the relationship of $\mu_e \sim T^{3/2}$. Based on Fig. 4a, we found that the calculated electron concentrations ($n$) for all samples varies as with the empirical relationship of $n \sim T^7$. Thus, a qualitative expression between $\mu_e$ and $n$ is derived as $\mu_e \approx Bn^{1/5}$, where $B$ is a temperature independent constant for a fixed composition. Then the electron
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Partial electrical conductivity $\sigma_e$ is calculated based on parameter $B$ and electron concentrations.

In the following numerical modeling process, $B$ is set as an adjustable parameter and listed in Table S3. Then, Equation 7 is approximately changed to

$$\kappa_b = \left(\frac{k_B}{e}\right)^2 T \left(4 + \frac{E_g}{k_B T}\right)^2 \frac{Bn^5 \cdot p \mu_h}{4 \left( Bn^5 + p \mu_h \right)}$$

where $e$ is the free electron charge, $\mu_h (=\mu_H)$ is the hole mobility, and $p (=p_H)$ is the hole concentration. The $\mu_h$ above 300 K can be extrapolated by using the measured low temperature Hall data according to the relationship of $\mu_h(T) \sim T^{-3/2}$. The $p$ values above 300 K were calculated using Equation 6. Then, the temperature dependence of $\kappa_b$ was modeled by Equation S1, which is shown in Fig. S8a. Excellent agreements between the calculations using the experimental data ($\kappa_b = \kappa - \kappa_e - \kappa_L$, symbols) and the fitted curves using Equation S1 (solid lines) are observed in a wide temperature range for all samples, suggesting the assumption and augment mentioned above is reasonable.

Lorenz number ($L$)

Lorenz number is calculated by using the single parabolic band model according to the following expression

$$L = \left(\frac{k_B}{e}\right)^2 \left\{ \frac{\left(\lambda + 7/2\right) F_{\lambda + 5/2}(\eta_h)}{\left(\lambda + 3/2\right) F_{\lambda + 1/2}(\eta_h)} - \frac{\left(\lambda + 5/2\right) F_{\lambda + 3/2}(\eta_h)}{\left(\lambda + 3/2\right) F_{\lambda + 1/2}(\eta_h)} \right\}$$

where $\lambda$ is the carrier scattering parameter which is taken as $-1/2$, $\eta_h$ is the reduced Fermi energy, $F_x$ is the Fermi integral of the order of $x$. The calculated values for our materials are listed in Table S1.
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**Fig. S1** Temperature dependences of (a) Seebeck coefficient, (b) electrical conductivity, (c) thermal conductivity, and TE figure of merit ($zT$) for commercial n-type bismuth telluride.

**Fig. S2** Temperature dependence of Hall hole concentration ($p_H$) below 300 K for Bi$_{0.5}$Sb$_{1.5}$M$_x$Te$_3$ ($M =$ Cd, Cu, and Ag) samples.
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Fig. S3 Temperature dependence of power factor ($PF$) for Bi$_{0.5}$Sb$_{1.5-x}$M$_x$Te$_3$ ($M =$ Cd, Cu, and Ag) samples.

Fig. S4 Temperature dependences of (a) total $\kappa$ and (b) $\kappa - \kappa_e$ for all samples. (c) $\kappa - \kappa_e$ as a function of temperature for Bi$_{0.5}$Sb$_{1.5}$Te$_3$. The solid line represents the expression of $\kappa_e = aT^t + b$ with $a = 78.05155$ and $b = 0.38625$. 
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\[ \kappa_L = aT^{-1} + b. \] (d) Temperature dependence of calculated lattice thermal conductivity (\(\kappa_L\)) for all samples.

**Fig. S5** Temperature dependence of experimental \(\kappa_L\) (symbols) and calculated \(\kappa_L\) (solid lines) by using Debye model for all samples.

**Fig. S6** Low-magnification TEM image for Bi\(_{0.5}\)Sb\(_{1.49}\)Cd\(_{0.01}\)Te\(_3\) sample. The insert picture is the electron diffraction pattern of the marked region, in which the nanoscale area in fig. 3d is included.
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Fig. S7 Temperature dependence of Hall hole mobility ($\mu_{HH}$) below 300 K for Cd-doped Bi$_{0.5}$Sb$_{1.5}$Te$_3$ samples.

Fig. S8 (a) Temperature dependence of experimental $\kappa_b$ for Bi$_{0.5}$Sb$_{1.5-x}$M$_x$Te$_3$ ($M = \text{Cd, Cu, and Ag}$) samples. The solid lines represent the numerical fitted $\kappa_b$ by Equation S1. The fitting parameters $B$ for all samples are shown in Table S3. (b) Experimental
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bipolar thermal conductivity ($\kappa_{b}^{Exp}$) and the fitted bipolar thermal conductivity ($\kappa_{b}^{Cal}$). The dash line stands for the relationship of $\kappa_{b}^{Exp} = \kappa_{b}^{Cal}$.

Fig. S9 Powder XRD patterns for Bi$_{0.5}$Sb$_{1.5-x}$M$_{x}$Te$_{3}$ ($M = \text{Cd, Cu, and Ag}$) samples.

Fig. S10 Schematic graph of our Bi$_{2}$Te$_{3}$-based modules. Al$_{2}$O$_{3}$ ceramic is used as the electrically isolated substrate. Cu is used as electrode. SAC305 (96.5% Sn, 3.0% Ag, 0.5% Cu) is the solder. Ni is the diffusion barrier between solder and Bi$_{2}$Te$_{3}$-based materials.
Fig. S11 SEM images of the interfaces between p-type Bi$_2$Te$_3$-based material and Ni diffusion barrier (a) before aging and (c) after aging at 250 °C for 1 hour, with the respective element line scan shown in (b) and (d) by using EDS. No obvious interdiffusions or chemical reactions are observed after high temperature aging.

**Table S1.** Calculated Lorenz number $L$ using Equation S2 and fitting parameters for all samples using the expression of $\kappa_L = aT^{-1} + b$ at 200-250 K.

<table>
<thead>
<tr>
<th></th>
<th>Bi$<em>{0.5}$Sb$</em>{1.5}$Te$_3$</th>
<th>Bi$<em>{0.5}$Sb$</em>{1.5-x}$M$_x$Te$_3$ (M = Cd, Cu, Ag)</th>
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<tr>
<td></td>
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<td>Cd: $x = 0.01$</td>
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<tr>
<td>$L$</td>
<td>1.6</td>
<td>1.7</td>
</tr>
<tr>
<td>$a$</td>
<td>78.05155</td>
<td>120.38561</td>
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<tr>
<td>$b$</td>
<td>0.38625</td>
<td>0.1027</td>
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**Table S2.** Fitting parameters for low temperature lattice thermal conductivity by using the Debye model.

<table>
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<th>Bi$<em>{0.5}$Sb$</em>{1.5-x}$M$_x$Te$_3$ (M = Cd, Cu, Ag)</th>
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<tr>
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<td>$L$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td></td>
<td></td>
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<tr>
<td>$b$</td>
<td></td>
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<table>
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<tr>
<th>$d$ (µm)</th>
<th>1.755</th>
<th>0.990</th>
<th>1.379</th>
<th>0.179</th>
<th>1.545</th>
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<td>$P$ ($10^{-41}$ s$^3$)</td>
<td>7.409</td>
<td>5.373</td>
<td>6.722</td>
<td>3.754</td>
<td>5.396</td>
</tr>
<tr>
<td>$U$ ($10^{-18}$ sK$^{-1}$)</td>
<td>9.903</td>
<td>13.682</td>
<td>18.835</td>
<td>28.775</td>
<td>13.598</td>
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**Table S3.** Calculated parameter $A$ by using Equation 1 and the carrier concentration at 300 K. Parameter $B$ is fitted from the experimental $\kappa_b$ by using Equation S1 for all Bi$_{0.5}$Sb$_{1.5-x}M_x$Te$_3$ ($M = \text{Cd, Cu, and Ag}$) samples.

| $A$ ($10^{42}$ cm$^{-6}$) | 3.1 | 2.5 | 1.6 | 1.9 | 1.7 |
| $B$ ($10^3$) | 1.67 | 2.6 | 3.5 | 2.65 | 3.7 |

**References**