ABSTRACT: Bi$_2$Te$_3$-based compounds are exclusive commercial thermoelectric materials around room temperature. For n-type compounds, optimal thermoelectric properties are normally obtained at temperatures higher than room temperature to suppress the bipolar effect through increased carrier concentration. We find that doping with trace amounts of Cd and the addition of excess Bi are effective ways to optimize carrier concentration and achieve enhanced room-temperature thermoelectric performance for the Bi$_2$Te$_2.7$Se$_0.3$ alloy in this work. For the Cd-doped samples, the replacement of Cd with Bi leads to not only a significant decrease in electron concentration but also apparently reduces the total thermal conductivity. The addition of excess Bi in the samples creates a Bi-rich synthetic atmosphere during the synthesis process, leading to increased Bi$_{2x}$ antisite defects, decreased electron concentration, and reduced total thermal conductivity. Doping a small amount of Cd or adding excess Bi causes optimal thermoelectric performance of the n-type Bi$_2$Te$_2.7$Se$_0.3$ sample shifts obviously toward low temperatures, and the samples with 0.4 atom % Cd and 0.8 atom % excess Bi achieve maximum $zT$ of $\sim 0.97$ at 448 K and $\sim 0.88$ at 348 K, respectively.

INTRODUCTION

With the development of science and technology, growing energy problems seriously threaten the sustainability of human society. Thermoelectric (TE) conversion technology can achieve mutual conversion between heat and electricity without generating pollution, which is applied to temperature difference power generation and solid-state refrigeration.\(^1\)\(^-\)\(^4\) TE conversion efficiency relies on the dimensionless TE figure of merit expressed as $zT = \alpha^2 \sigma T / \kappa$, where $\alpha$, $\sigma$, $T$, and $\kappa$ are Seebeck coefficient, electrical conductivity, absolute temperature, and total thermal conductivity, respectively.\(^5\)\(^-\)\(^7\) Promising TE materials should have a high $\alpha$, large $\sigma$, and as low as possible $\kappa$.\(^6\)\(^,\)\(^7\) However, due to mutual coupling between $\alpha$, $\sigma$, and $\kappa$, it is hard to obtain a high $zT$ value.\(^8\)\(^-\)\(^11\)

In recent years, Bi$_2$Te$_3$-based compounds have been widely commercialized as the best-performing room-temperature TE material. Bi$_2$Te$_3$-based compounds belong to the rhombohedral crystal system with the Te$\text{1}^-\text{-Bi}-\text{Te}^\text{2}^-\text{-Bi}-\text{Te}^\text{1}^+$ atomic layer as the basic unit repeatedly arranged in the $c$-axis direction.\(^1\)\(^,\)\(^2\)\(^,\)\(^3\) The interlayer is connected by covalent and ion bonds, while the adjacent layers are connected by a weak van der Waals force, leading to the facile cleavage along the in-plane direction. The special layered crystal structure allows the thermal and electrical properties of the Bi$_2$Te$_3$-based compounds to exhibit strong anisotropy in different directions.\(^13\)\(^-\)\(^17\) Overall, the TE performance in the vertical hot pressing (HP) direction is higher than that in parallel to the HP direction. Bi$_2$Te$_3$-based alloys exhibit $zT \approx 1$, and the TE properties of n-type are generally below p-type.\(^1\)\(^-\)\(^3\) Over the coming years, synthesis methods such as solid-phase reaction,\(^18\)\(^-\)\(^20\) ball milling,\(^21\)\(^,\)\(^22\) zone melting,\(^23\)\(^-\)\(^25\) and preparation methods such as HP\(^26\)\(^-\)\(^28\) or spark plasma sintering (SPS)\(^29\)\(^-\)\(^31\) have been widely used to enhance $zT$ of Bi$_2$Te$_3$-based alloys.

Extensive data analysis shows that defect engineering is an indispensable means to improve the TE performance of Bi$_2$Te$_3$-based compounds.\(^32\)\(^-\)\(^35\) The Bi$_2$Te$_3$-based compounds have numerous defects (for example, intrinsic antisite defects and vacancies),\(^36\)\(^-\)\(^38\) which jointly affect carrier concentration ($n$) of the compounds. Wu et al. optimized the $n$ and mobility ($\mu$), and a peak $zT$ of 1.1 was acquired for Ag$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ compounds to exhibit strong anisotropy in different directions.\(^13\)\(^-\)\(^17\) The addition of excess Bi causes optimal thermoelectric performance of the n-type Bi$_2$Te$_2.7$Se$_0.3$ sample shifts obviously toward low temperatures, and the samples with 0.4 atom % Cd and 0.8 atom % excess Bi achieve maximum $zT$ of $\sim 0.97$ at 448 K and $\sim 0.88$ at 348 K, respectively.

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By introducing excessive Te to optimize the \( n \), a \( zT \) as high as 1.1 was also obtained. Resulting from the optimized \( n \) owing to donor-like effect, in Bi\(_2\)Te\(_{2.7}\)Se\(_{0.3}\) + 0.067 wt % BiCl\(_3\) materials, Xiong et al. realized a maximum \( zT \) of 1.38. In the Bi\(_2\)Te\(_x\)Se\(_{3-x}\) alloys, point defects and their interaction largely change the \( n \) and \( \mu \), and a maximum \( zT \) of 0.82 has been obtained for the optimal composition of Bi\(_2\)Te\(_{2.2}\)Se\(_{0.8}\).

In this work, Bi\(_2\)Te\(_{2.7}\)Se\(_{0.3}\) samples doped with Cd/Bi were synthesized using the conventional melting technique. For Cd-doped samples, the substitution of Cd for Bi leads to decreased electron concentration and significantly decreased electronic thermal conductivity. Moreover, doping of Cd results in enhanced point-defect phonon scattering and thus decreased lattice thermal conductivity. Finally, a maximum \( zT \) of 0.97 is obtained at 448 K for the sample doped with 0.4 atom % Cd. For the samples with excess Bi, increased Bi\(_{\text{Te}}\) antisite defects lead to reduced electron concentration and enhanced point-defect phonon scattering leads to a significant reduction in lattice thermal conductivity. A peak \( zT \) of 0.88 is achieved at 348 K for the sample added with 0.8 atom % Bi. Due to decreased carrier concentration, optimal operating temperature moves toward low temperatures, which is beneficial for the commercialized n-type Bi\(_2\)Te\(_{2.7}\)Se\(_{0.3}\) alloy.

**RESULTS AND DISCUSSION**

Figure 1a,b shows XRD patterns of the as-prepared Cd\(_{0.012}\)Bi\(_{2}\)Te\(_{2.7}\)Se\(_{0.3}\) and Bi\(_{0.008}\)Te\(_{2.7}\)Se\(_{0.3}\) samples at room temperature, respectively. All of the diffraction peaks can be indexed to the rhombohedral Bi\(_2\)Te\(_3\) alloy (PDF #85-0439), and the XRD technique cannot detect any impurity phase, indicating that the samples are single-phase compounds. Sharp diffraction peaks with high intensities illustrate the high crystallinity of the samples. For all of the samples, no obvious diffraction peak shift is observed, suggesting a pretty small change or no change in the lattice constant. For the Cd-doped sample, the almost constant lattice parameters can be ascribed to the trace doping.

![Figure 1. XRD patterns of (a) Cd\(_{0.012}\)Bi\(_{2}\)Te\(_{2.7}\)Se\(_{0.3}\) and (b) Bi\(_{0.008}\)Te\(_{2.7}\)Se\(_{0.3}\) samples.](image)

![Figure 2. Temperature-dependent (a, b) \( \sigma \), (c, d) \( \alpha \), and (e, f) PF for Cd\(_{0.012}\)Bi\(_{2}\)Te\(_{2.7}\)Se\(_{0.3}\) and Bi\(_{0.008}\)Te\(_{2.7}\)Se\(_{0.3}\) samples.](image)
Cd content as well as the approximate radii of Cd\(^{2+}\) (0.95 Å) and Bi\(^{3+}\) (1.03 Å). For the sample with excess Bi, the nearly unchanged lattice constants imply that the excess Bi does not enter the crystal lattice in our synthesis condition, but the excess Bi during the synthesis process can create a Bi-rich synthetic atmosphere, leading to increased BiTe antisite defects.

Temperature dependence of the \(\sigma\), \(\alpha\), and power factor (PF) for samples with different Cd/Bi contents are depicted in Figure 2. The Bi\(_2\)Te\(_2.7\)Se\(_0.3\) alloy shows anisotropy due to the special layered structure. Therefore, characterization and analysis of TE performance should be performed while noting the anisotropy. All of the TE performances are measured perpendicular to the HP direction in this work. As shown in Figure 2a,b, \(\sigma\) of all of the samples decrease monotonously with the increase of Cd/Bi content, suggesting that the doped Cd reduces the electron concentration as an electron acceptor while the addition of excess Bi during the synthesis process decreases the \(n\) by creating more Bi\(_{\text{Te}}\) antisite defects. With the doping of Cd, the \(\sigma\) decreases significantly from 1.6 \(\times\) 10\(^3\) S·cm\(^{-1}\) for the pristine Bi\(_2\)Te\(_2.7\)Se\(_0.3\) sample to 9.6 \(\times\) 10\(^2\) S·cm\(^{-1}\) for the sample with 1.2 atom % Cd at 298 K. As the temperature increases, the \(\sigma\) of the Cd-doped samples first decrease rapidly and then decrease slowly, which can be ascribed to the intrinsic excitation at high temperatures. For the samples with excess Bi, the \(\sigma\) decreases dramatically to 9.2 \(\times\) 10\(^2\) S·cm\(^{-1}\) at 298 K by adding only 0.4 atom % Bi. The temperature-dependent \(\sigma\) shows that the \(\sigma\) of the sample with 0.8 atom % Bi starts to increase at high temperatures, implying that the intrinsic excitation temperature shifts to lower temperature due to decreased \(n\).

As shown in Figure 2c,d, the \(\alpha\) of all of the samples are negative, indicating n-type conduction. The variation of the \(\alpha\) is basically consistent with that of \(\sigma\). With the doping of Cd, the absolute value of \(\alpha\) increases continuously from 138 \(\mu\)V·K\(^{-1}\) for pristine Bi\(_2\)Te\(_2.7\)Se\(_0.3\) sample to 182 \(\mu\)V·K\(^{-1}\) for the sample with 1.2 atom % Cd at 298 K. The temperature-dependent \(\alpha\) shows that the absolute \(\alpha\) first increases and then changes to decrease with the rising of temperature due to
intrinsically excited high temperatures. As the Cd doping content increases, the onset temperature of the bipolar conduction moves to a lower temperature, which can be ascribed to decreased \( n \). For samples with excess Bi, the absolute \( \alpha \) also increases with the addition of Bi, and an absolute value as high as 206 \( \mu \text{V-K}^{-1} \) at 298 K is achieved for the sample with 0.8 atom % excess Bi. The temperature-dependent \( \alpha \) shows that the intrinsic excitation temperature moves gradually from \( \sim 450 \text{ K} \) to near room temperature (\( \sim 350 \text{ K} \)). Benefiting from the dramatically increased absolute \( \alpha \), the PF of the Cd-doped and excess Bi added samples are comparable to that of the pristine Bi\(_2\)Te\(_2.7\)Se\(_0.3\) sample in the whole measured temperature range (Figure 2e,f). Particularly, the PF of the Cd-doped and excess Bi added samples are even higher than that of the pristine Bi\(_2\)Te\(_2.7\)Se\(_0.3\) sample around room temperature, which is desired for practical applications.

The room-temperature Hall effect has been measured to further elucidate the effect of Cd doping and excess Bi adding on electrical transport properties. Figure 3a shows that \( n \) decreases monotonously, while \( \mu \) increases gradually with an increase in the Cd content, further confirming that Cd doping behaves as an electron acceptor. As the Cd content increases from \( x = 0 \) to \( x = 0.012 \), \( n \) decreases from \( 1.1 \times 10^{20} \) to \( 5.3 \times 10^{19} \text{ cm}^{-3} \), while \( \mu \) increases from 86.1 to 98.9 \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1}. For the sample with excess Bi, \( n \) decreases from \( 1.1 \times 10^{20} \) to \( 4.3 \times 10^{19} \text{ cm}^{-3} \), while \( \mu \) increases from 86.1 to 118 \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1} \) when the Bi content increases from \( x = 0 \) to \( x = 0.008 \). In comparison with those of the Cd-doped samples, the changes in \( n \) and \( \mu \) of the excess Bi added samples are even more pronounced, which is consistent with the variations in \( \sigma \) and \( \alpha \). The significantly decreased \( n \) further confirms that the Bi\(_{1x}\) antisite defects increase considerably in a Bi-rich synthetic atmosphere.

The temperature-dependent thermal transport properties of Cd\(_{0.08}\)Bi\(_{1.2}\)Te\(_2.7\)Se\(_0.3\) and Bi\(_{0.08}\)Te\(_2.7\)Se\(_0.3\) samples are depicted in Figure 4. The Bi\(_2\)Te\(_2\)-based compounds show obvious bipolar conduction at high temperatures due to their small band gaps. Thus, the total thermal conductivity (\( \kappa_{\text{tot}} \)) is comprised of three contributions, i.e., electronic (\( \kappa_e \)), lattice (\( \kappa_L \)), and bipolar diffusion thermal conductivity (\( \kappa_{\text{di}} \)). According to the Wiedemann–Franz law, \( \kappa_e = L \alpha T \), where \( L \) is the Lorentz constant estimated by the single parabolic band (SPB) model in this work (refer to Figure S1). As shown in Figure 4a,b, \( \kappa_{\text{tot}} \) near room temperature decreases with the increasing content of Cd/Bi, which can be mainly attributed to the significantly decreased \( \kappa_e \) due to decreased \( \sigma \). For both Cd-doped and excess Bi added samples, \( \kappa_{\text{tot}} \) first decreases and then increases with the increase in temperature owing to the bipolar effect. As expected, \( \kappa_e \) decreases dramatically with the increasing content of Cd/Bi owing to the greatly reduced electron concentration.

The pristine Bi\(_2\)Te\(_2.7\)Se\(_0.3\) sample has a \( \kappa_e \) as high as 0.88 W·m\(^{-1}\)·K\(^{-1}\) at 298 K, contributing more than half of the \( \kappa_{\text{tot}} \). By doping 1.2 atom % Cd, the \( \kappa_e \) at 298 K decreases significantly to 0.49 W·m\(^{-1}\)·K\(^{-1}\), which is \( \sim 40\% \) of \( \kappa_{\text{tot}} \). For the sample with 0.8 atom % excess Bi, the \( \kappa_e \) at 298 K decreases to 0.41 W·m\(^{-1}\)·K\(^{-1}\), which is only \( \sim 32\% \) of the \( \kappa_{\text{tot}} \). As shown in Figure 4e,f, the \( \kappa_{\text{tot}} \) is comprised of three \( \kappa_e \), which is even closer to room temperature. Overall, the optimal operating temperature moves toward room temperature by doping Cd or adding excess Bi, which makes the Bi\(_2\)Te\(_2.7\)Se\(_0.3\) alloy more suitable for the current commercial requirements.

**CONCLUSIONS**

This work demonstrates that the room-temperature thermoelectric performance of the Bi\(_2\)Te\(_2.7\)Se\(_0.3\) alloy can be improved by doping with trace amounts of Cd or adding tiny excess Bi during the synthesis process. The substitution of Cd for Bi decreases electron concentration and electrical conductivity, increases the Seebeck coefficient, and reduces the total thermal conductivity, leading to enhanced n-type thermoelectric performance near room temperature. By doping with 1.2 atom % Cd, a peak \( zT \) of \( \sim 0.93 \) is attained at 373 K, which is 14% higher and 50 K lower in the temperature in comparison with the peak \( zT \) of the pristine Bi\(_2\)Te\(_2.7\)Se\(_0.3\) alloy. The addition of excess Bi during the sample synthesis creates a Bi-rich atmosphere, which is favorable for Bi\(_{1x}\) antisite defects. With the addition of excess Bi, more Bi\(_{1x}\) antisite defects are produced, resulting in decreased electron concentration and electrical conductivity but increased Seebeck coefficient. The total thermal conductivity also decreases with the addition of excess Bi because of dramatically decreased electronic thermal conductivity and increased point-defect scattering. The above combined effects of excess Bi improve the thermoelectric performance. The sample with 0.8 atom % excess Bi achieves a peak \( zT \) of \( \sim 0.88 \) at 348 K, which is closer to room temperature.

Figure 5. Temperature dependence of \( zT \) values of (a) Cd\(_{0.08}\)Bi\(_{1.2}\)Te\(_2.7\)Se\(_0.3\) and (b) Bi\(_{0.08}\)Te\(_2.7\)Se\(_0.3\) samples.
**EXPERIMENTAL SECTION**

Bi$_{2-x}$Te$_{2.7}$Se$_{0.3}$ ($x = 0, 0.004, 0.006,$ and $0.008$) and Cd$_{Bi_{2-x}}$Te$_{2.7}$Se$_{0.3}$ ($x = 0, 0.004, 0.008,$ and $0.012$) were obtained using pure elements ($Bi, 99.99\%,$ Te, $99.999\%,$ Se, $99.999\%,$ and Cd, $99.999\%$). A series of mixtures were sealed, reacted at 1073 K for $10$ h, and then annealed at 773 K after cold pressing. The powders were compacted via HP under SSMPa at 633 K for 25 min.

The phase structure of the sample was detected on a Malvern Panalytical Aera X-ray diffractometer. The $\alpha$ and $\sigma$ were measured by ULVAC-RIKO ZEM-3. The total thermal conductivity ($\kappa$) is the product of the thermal diffusion coefficient ($\lambda$), the specific heat capacity ($C_p$), and the density ($\rho$). $\lambda$ was measured on a Netzsch LFA467 laser flash device. $C_p$ was calculated by the Duron−Petty law. $\rho$ was determined by the Archimedes method. A Hall effect measurement system (Lake Shore 8400 Series) was used to measure the $n$ and $\mu$ at room temperature.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05160.

Temperature-dependent Lorentz numbers of (a) Cd$_{Bi_{2-x}}$Te$_{2.7}$Se$_{0.3}$ and (b) Bi$_2+Te_{2.7}$Se$_{0.3}$ samples (Figure S1) (PDF)

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**Notes**

The authors declare no competing financial interest.

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