Electrical, Thermal, and Thermoel ectric Transport Properties of Co-Doped n-type Cu$_{0.008}$Bi$_2$Te$_{2.6}$Se$_{0.4}$ Polycrystalline Alloys

Okmin Park$^{1, *}$, TaeWan Kim$^{2, *}$, Minsu Heo$^1$, Sang Jeong Park$^1$, Se Woong Lee$^1$, Hyun Kyu Cho$^1$, and Sang-il Kim$^{1, *}$

$^1$Department of Materials Science and Engineering, University of Seoul, Seoul 02504, Republic of Korea
$^2$Department of Electrical Engineering and Smart Grid Research Center, Jeonbuk National University, Jeonju 54896, Republic of Korea

Abstract: Bi$_2$Te$_3$-based alloys have been extensively studied as thermoelectric materials near room temperature. In this study, the electrical, thermal, and thermolectric transport properties of a series of Co-doped n-type Cu$_{0.008}$Bi$_2$Te$_{2.6}$Se$_{0.4}$ polycrystalline alloys (Cu$_{0.008}$Bi$_2$-xCo$_x$Te$_{2.6}$Se$_{0.4}$, $x = 0, 0.03, 0.06, 0.09$ and $0.12$) are investigated. The electrical conductivity of the Cu$_{0.008}$Bi$_1$Te$_{2.6}$Se$_{0.4}$ ($x = 0.03$) sample was significantly enhanced, by 34%, to 1199 S/cm compared to 793 S/cm of the pristine Cu$_{0.008}$Bi$_2$Te$_{2.6}$Se$_{0.4}$ ($x = 0$) sample at 300 K, and gradually decreased to 906 S/cm for $x = 0.12$ upon further doping. Power factors of the Co-doped samples decreased compared to the 3.26 mW/mK$^2$ of the pristine Cu$_{0.008}$Bi$_2$Te$_{2.6}$Se$_{0.4}$ sample at 300 K. Meanwhile, the power factor of the Cu$_{0.008}$Bi$_{1.97}$Co$_{0.03}$Te$_{2.6}$Se$_{0.4}$ ($x = 0.03$) sample became higher at 520 K. The lattice thermal conductivities of the Co-doped samples decreased due to additional point defect phonon scattering by the Co dopant. Consequently, the $zT$ for the Cu$_{0.008}$Bi$_{1.97}$Co$_{0.03}$Te$_{2.6}$Se$_{0.4}$ alloy at 520 K was 0.83, which is approximately 15% larger than that of pristine Cu$_{0.008}$Bi$_2$Te$_{2.6}$Se$_{0.4}$, while the $zT$ of the Cu doped samples at 300 K was smaller than that of the pristine Cu$_{0.008}$Bi$_2$Te$_{2.6}$Se$_{0.4}$ sample. Electrical transport properties of the Co-doped Cu$_{0.008}$Bi$_{2-x}$Co$_x$Te$_{2.6}$Se$_{0.4}$ samples were analyzed by experimental phenomenological parameters, including the density-of-state, effective mass, weighted mobility, and quality factor.

(Received 5 December, 2022; Accepted 20 December, 2022)

Keywords: thermoelectric, Bi$_2$Te$_3$, doping

1. INTRODUCTION

Bi$_2$Te$_3$-based alloys have been extensively studied as thermoelectric materials at room temperature. These materials are semiconductors with a narrow band gap (~ 0.13 eV) [1,2]. They have excellent electrical transport properties with a high carrier concentration (~ 10$^{19}$ cm$^{-3}$) and exhibit a relatively low thermal conductivity due to layered structures with a weak Van der Waals bonding between layers [3-5], resulting in a good thermoelectric figure of merit ($zT$) at room temperature [6,7]. Thermoelectric performance is evaluated by the dimensionless Figure of merit, $zT = S^2\sigma\kappa_T$/$\kappa_{tot}$, where $S$, $\sigma$, $T$, and $\kappa_{tot}$ are Seebeck coefficient, electrical conductivity, absolute temperature, and total thermal conductivity ($\kappa_{tot} = \kappa_{ele} + \kappa_{latt}$, where $\kappa_{ele}$ and $\kappa_{latt}$ are electron and lattice thermal conductivities, respectively), respectively. At elevated temperatures Bi$_2$Te$_3$-based alloys also induce an intrinsic excitation of electron-hole pairs, resulting in a decrease in $S$ and an increase in $\kappa_{tot}$. Therefore, Bi$_2$Te$_3$-based alloys exhibit rapidly degrading thermoelectric performance above 500 K [8-10], which limits the application of Bi$_2$Te$_3$ alloys to low temperatures, of 450 K or less.

Pristine Bi$_2$Te$_3$ is an n-type semiconductor and is typically doped with Se into the Te-site to improve its thermoelectric performance. However, Bi$_2$Te$_3$ compositions exhibit unstable carrier transport properties because of self-defects, the formation of anti-site defects, and Te-site vacancies [11]. The unstable carrier transport properties of n-type Bi$_2$Te$_{3-x}$Se$_x$ can be stabilized by adding Cu [12-15].
Defect engineering, such as doping, addition, and solid-solution, are the most used strategies for reducing κ_{tot} by promoting point defect phonon scattering [16-19]. Doping strategies have been widely applied to enhance the thermoelectric transport properties of thermoelectric materials, particularly the n-type Bi_2Te_3-based alloys [19-22]. Lee et al. reported that using I-doping to improve the carrier transport properties of Cu_{0.008}Bi_{2.7}Te_{2.6}Se_{0.3} enhanced zT to 0.86 at 400 K [21]. A higher zT of 1.07 at 423 K was observed in CuI-doped Bi_{2.5}Te_{2.6}Se_{0.3} processed by hot-deformation [22]. Similarly, Co doping was used to enhance the electrical transport properties of pristine Bi_{2}Te_{3} and p-type Bi_{0.5}Sb_{1.5}Te_{3} [23,24].

However, Co-doping to Bi_{2}Te_{3−x}Se_{x}, a representative type of n-type Bi_{2}Te_{3} based alloy, has not yet been reported. Therefore, in this study, the electrical, thermal, and thermoelectric transport properties of Cu_{0.008}Bi_{2−x}Co_{x}Te_{2.6}Se_{0.4} (x = 0, 0.03, 0.06, 0.09 and 0.12) polycrystalline bulk alloys were investigated. The electrical transport properties of a Co-doped Cu_{0.008}Bi_{2−x}Co_{x}Te_{2.6}Se_{0.4} composition were analyzed by experimental phenomenological parameters, including the density-of-state effective mass (m^{*}), weighted mobility (μ_{w}), and quality factor (B).

2. EXPERIMENTAL

Polycrystalline Cu_{0.008}Bi_{2−x}Co_{x}Te_{2.6}Se_{0.4} (x = 0, 0.03, 0.06, 0.09 and 0.12) samples were prepared via the solid-state reaction method. Stoichiometric ratios of high purity Bi (99.999%, SN Plus), Te (99.999 %, SN Plus), and Co (99.99%, Sigma Aldrich) were sealed in a quartz tube under a pressure of 10^{-5} Torr to prevent oxidation or other reactions with air. The raw materials placed in the sealed quartz ampoules were synthesized at 1323 K for 12 h (heating rate of 3 K/min), and then slowly cooled in a box furnace. The synthesized ingots were pulverized for 5 min via high energy ball milling (SPEX 8000D, SPEX) in an Ar atmosphere. The powders placed in the graphite molds were sintered using spark plasma sintering (SPS-1030, Sumitomo Coal Mining Co., Ltd.) under 10^{6} Torr at 707 K for 5 min (heating rate = 100 K/min) under 70 MPa. The sintered bulk samples had relative densities of more than ~ 99%.

X-Ray diffraction (XRD, D8 Discover, Bruker) analysis was performed to analyze the crystal structure of the samples. The polycrystalline powder samples were excited with 0.154 nm wavelength Cu-Kα radiation. For the σ and S measurements, the sintered samples were processed into rectangular shapes with dimensions of 2 mm × 2 mm × 8 mm. The processed specimens were analyzed using ZEM-3 (Advanced-Riko) in the temperature range 300–520 K in a He atmosphere, and the power factor was calculated using the measured σ and S. The Hall carrier concentrations (n_{H}) and Hall carrier mobilities (μ_{H}) were measured using a Hall measurement system (HMS5300, Ecopia) under a magnetic field of 0.548 T; the Hall measurements were performed using the van der Paw configuration. The laser flash method (LFA457, Netzsch) was performed to obtain the thermal diffusivity (α) required to calculate κ_{tot} (κ_{tot}=α × ρ × C_{p}), where ρ and C_{p} are the sample density and heat capacity, respectively. The ρ value is the theoretical density of Bi_{2}Te_{3−x}Se_{x}—assuming a linear increase in the Bi_{2}Te_{3} (7.834 g/cm³)–Bi_{2}Se_{3} (7.664 g/cm³) system. The C_{p} value of Bi_{2}Te_{3} was determined from the empirical formulas of 108.06 + 5.53 × 10^{-2} T J/mol·K and C_{p} of Bi_{2}Se_{3} = 118.61 + 1.92 × 10^{-2} T J/mol·K [25]. The zT value was evaluated using the calculated power factor and κ_{tot}.

3. RESULTS AND DISCUSSION

The XRD patterns for the Cu_{0.008}Bi_{2−x}Co_{x}Te_{2.6}Se_{0.4} powder samples indicated a single rhombohedral Bi_{2}Te_{3} phase without any additional phases (Figure 1(a)). The lattice parameters, a and c were calculated using the (015) and (101) diffraction peaks (Figure 1(b)). The calculated lattice parameters gradually decreased with an increase in x values; a decreased from 4.365 to 4.348 Å and c decreased from 30.390 to 30.323 Å. This is because Co is substituted and doped at the Bi-site, that is, a Co-cation (~ 88.5 pm) with a relatively small ionic radius replaced the Bi^{3+} (117 pm).

Figures 2(a) and 2(b) show σ and S as a function of temperature, respectively, for the polycrystalline bulk samples along the direction perpendicular to the sintering pressure. The σ values of the Co-doped samples were higher than those of the undoped sample at all temperature ranges, and all samples exhibited intrinsic metal behavior. As shown in the inset of Figure 2(a), the σ values for x = 0, 0.03, 0.06,
0.09, and 0.12 were 793, 1199, 1028, 960, and 906 S/cm, respectively, at 300 K. Remarkably, the σ values systemically decreased with increases in doping level, after abruptly increasing at $x = 0.03$. The $S$ values were similar even with the increase in temperature with a decrease in the doped samples, owing to the trade-off relationship between $\sigma$ and $S$.

Therefore, the $S$ values showed the opposite trend compared to $\sigma$. The $S$ values for $x = 0, 0.03, 0.06, 0.09$ and $0.12$ were $-202, -152, -154, -163$, and $-168$ μV/K (inset of Figure 2(b)), respectively, at 300 K.

Figures 2(c) and 2(d) present the calculated power factor and weighted mobility $\mu_w$ as a function of temperature for the Cu$_{0.008}$Bi$_{2-x}$Co$_x$Te$_{2.6}$Se$_{0.4}$ ($x = 0, 0.03, 0.06, 0.09$ and $0.12$) polycrystalline bulk alloys.

0.09, and 0.12 were 793, 1199, 1028, 960, and 906 S/cm, respectively, at 300 K. Remarkably, the $\sigma$ values systemically decreased with increases in doping level, after abruptly increasing at $x = 0.03$. The $S$ values were similar even with the increase in temperature with a decrease in the doped samples, owing to the trade-off relationship between $\sigma$ and $S$.

Therefore, the $S$ values showed the opposite trend compared to $\sigma$. The $S$ values for $x = 0, 0.03, 0.06, 0.09$ and $0.12$ were $-202, -152, -154, -163$, and $-168$ μV/K (inset of Figure 2(b)), respectively, at 300 K.

Figures 2(c) and 2(d) present the calculated power factor and weighted mobility $\mu_w$ as a function of temperature for the
Cu$_{0.058}$Bi$_2$-Co$_x$Te$_2$Se$_{0.4}$ samples. As shown in Figure 2(c), the power factor for the samples decreased with the increase in temperature. The power factor of the doped samples decreased in the temperature range of 300–400 K compared to the undoped sample. However, after 450 K, the $x = 0.03$ and 0.06 samples showed a reverse trend; the power factor of the $x = 0.03$ sample increased by approximately 10% compared to the undoped sample at 520 K. The power factor values of the $x = 0$, 0.03, and 0.06 samples were 1.83, 1.99, and 1.92 mW/mK$^2$ at 520 K, respectively. The maximum power factor was 3.26 mW/mK$^2$ for the $x = 0$ sample at 300 K. The $\mu_w$ value was obtained from a simple analytical form that approximates the exact Drude–Sommerfeld free-electron model given in Equation (1) for $|S| > 20 \mu$V/K [26].

$$
\mu_w = \frac{3h^3\sigma}{8\pi e^2(2m^*kT)^{3/2}}
$$

where $k$, $m^*$, $e$, and $h$ are the Boltzmann constant, mass of the electron, elementary charge, and Planck’s constant, respectively. The $\mu_w$ parameter infers the maximum reachable power factor when $n_H$ is optimized. The $\mu_w$ value of each sample was evaluated using the measured $\sigma$ and $S$ parameters; the $\mu_w$ values showed a similar trend as the power factor. The maximum $\mu_w$ value was 373 cm$^2$/Vs for the $x = 0$ sample at 300 K.

Figure 3(a) shows $n_H$ as a function of $x$ for the Cu$_{0.058}$Bi$_2$-Co$_x$Te$_2$Se$_{0.4}$ samples along the direction perpendicular to the sintering pressure. The $n_H$ values showed a trend similar to the $\sigma$ values; $n_H$ increased approximately twice for the $x = 0.03$ (6.66 × 10$^9$ cm$^{-2}$) sample compared to the $x = 0$ (3.54 × 10$^9$ cm$^{-2}$) sample at 300 K and then decreased linearly with increases in $x$. The $\mu_H$ values for the Co-doped samples decreased because $\mu_H$ is inversely proportional to $n_H$; however, unlike $n_H$, the $\mu_H$ values were constant after $x = 0.06$ (Figure 3(b)). The $\mu_H$ values for the $x = 0$, 0.03, 0.06, 0.09, and 0.12 samples are 139 108, 105, 106, and 109 cm$^2$/Vs at 300 K, respectively.

The magnitude of the density of states is directly related to the density-of-state effective mass $m_d^*$ and the electrical transport behavior was interpreted in terms of changes in the electron structure by calculating $m_d^*$. Equation (2), which was optimized to a single parabolic band model, is used to plot $m_d^*$ for the samples (Figure 3(c)) [27].

$$
\log_{10}(\frac{m_d^* T}{300}) = \frac{2}{3}\log_{10}(n) - \frac{2}{3}[20.3 - (0.00508 \times |S|) + (1.58 \times 0.96^{\text{exp}})]
$$

The $m_d^*$ value of the $x = 0.03$ (1.55 $m_0$) sample was larger than that of the $x = 0$ (1.529 $m_0$) sample at 300 K because $m_d^*$ is proportional to both $|S|$ and $n_H$. This indicates that the decrease in $|S|$ for the $x = 0.03$ sample is less than the increase in $n_H$ at 300 K. The inset of Figure 3(c) shows a plot of $\log_{10}(n_H)$ as a function of $|S|$ for the samples. The $m_d^*$ becomes generally lower with the Co doping.

Figure 4(a) shows $\kappa_{tot}$ as a function of temperature for the
Cu$_{0.008}$Bi$_{2−x}$Co$_x$Te$_{2.6}$Se$_{0.4}$ samples along the direction perpendicular to the sintering pressure. The $\kappa_{\text{tot}}$ values of the $x=0.03, 0.06, 0.09$, and 0.12 samples at 300–450 K increased with the increase in $\kappa_{\text{ele}}$ (inset of Figure 4(a)). The $\kappa_{\text{ele}}$ values were calculated using $\kappa_{\text{ele}} = L\sigma T$ (where $L$ is the Lorenz number [28]) and the increase in $\kappa_{\text{tot}}$ significantly affected the increase in $\sigma$ of the Co-doped samples. Therefore, the values of $\kappa_{\text{tot}}$ for the $x=0, 0.03, 0.06, 0.09$, and 0.12 samples at 300 K were 1.08, 1.18, 1.22, 1.18, and 1.16 W/mK, respectively. In contrast, the $\kappa_{\text{tot}}$ values of the $x=0.03, 0.06$, and 0.12 samples at 520 K decreased to 1.24, 1.29, and 1.31 W/mK, respectively, from that of the $x=0$ (1.31 W/mK at 520 K) sample. Interestingly, the $\kappa_{\text{tot}}$ reached its lowest value at $x=0.03$, and increased for the higher doping samples. The physical reason behind the unusual observation for $\kappa_{\text{tot}}$ may be the complex defect structures produced by the Co doping, which requires further study.

Figure 5(a) illustrates the $zT$ of the Cu$_{0.008}$Bi$_{2−x}$Co$_x$Te$_{2.6}$Se$_{0.4}$ polycrystalline bulk samples. The thermoelectric performance of the Co-doped samples significantly decreased in contrast to the undoped sample at 300 K. The maximum $zT$ value of the undoped sample at 300 K was 1.0. However, the $zT$ of the undoped sample decreased above 360 K, while those of the $x=0.03$ and 0.06 samples marginally increased above 450 K. Therefore, the $zT$ values of the $x=0.03$ and 0.06 were enhanced more than the $x=0$ sample at 480 and 520 K. The $zT$ values of the $x=0.03$, and 0.06 samples were 0.91, and 0.84 at 480 K and 0.83, and 0.77 at 520 K, respectively. Further, the $zT$ values of the $x=0.03$ and 0.06 samples were enhanced to approximately 8% and 3% at 480 K and to approximately 15% and 7% at 520 K, compared with the $x=0$ (0.82 and 0.72 at 480 and 520 K, respectively), respectively.
Figure 5(b) shows the $n_H$-dependent $zT$ calculated via the single parabolic band model and experimental $zT$ at 300 K; $n_H$-dependent experimental $zT$ (denoted using symbols) and calculated $zT$ (denoted using a line), which indicates the theoretically achievable $zT$ at 300 K. The $zT$ values of all the Co-doped samples were lower than the achievable $zT$ (line in Figure 5(b)), which would infer that the band structure was unfavorably changed by the doping. Because the $n_H$ value of the $x = 0.03$ sample was the highest, it is plotted at the rightmost side ($n_H$ of $6.7 \times 10^{19}$ cm$^{-3}$) in the graph (solid red). As the doping content increases, the symbols shift toward the left, which indicates a decrease in $n_H$. However, the peak value of the calculated $zT$ was observed when $n_H$ was $2.2 \times 10^{19}$ cm$^{-3}$. Therefore, $n_H$ optimization of the samples is required. Based on the calculation, shown in Fig. 5(b), $zT$ can be increased to 0.94 at 300 K when $n_H$ is optimized (decreased) to $\sim 2.2 \times 10^{19}$ cm$^{-3}$. Dopants to decrease the mother compound Cu$_{0.08}$Bi$_{2.6}$Se$_{0.4}$ could be introduced to enhance $zT$ at 300 K.

Figure 5(c) shows the dimensionless thermoelectric quality factor $B$, which was evaluated using Equation (3) [26]:

$$B = \left(\frac{k}{e}\right)^2 \frac{8\pi e (2m_e kT)^{3/2}}{3h^3} \frac{\mu_e T}{\kappa_{\text{tot}}}$$

(3)

Based on previous studies, $B$ is proportional to the maximum $zT$ value that can be achieved for an optimized $n_H$ [29, 30]. Therefore, the general trend of $B$ is similar to that of $zT$; however, in this study, the $x = 0.03$ sample has a maximum $B$ value (0.49) at 440 K. In particular, the $B$ values for all doped samples above 480 K were less than that of the undoped sample. The $B$ values of the $x = 0, 0.03, 0.06, 0.09,$ and 0.12 samples were 0.29, 0.45, 0.37, 0.30, and 0.32, respectively, at 520 K. This indicates that in the Co-doped samples at 520 K, $zT$ can be increased to a greater extent, when $n_H$ is optimized.

4. CONCLUSIONS

In summary, the thermoelectric properties of Co-doped Bi$_2$Te$_2.6$Se$_{0.4}$, Cu$_{0.08}$Bi$_{2.6}$Co$_{0.4}$Te$_{2.6}$Se$_{0.4}$ ($x = 0, 0.03, 0.06, 0.09,$ and 0.12) polycrystalline samples were investigated. The electrical conductivity generally increased for the Co-doped samples and the $S$ values decreased. The measured power factor of the Co-doped samples was lower than 3.26 mW/mK$^2$ for the pristine Cu$_{0.08}$Bi$_{2.6}$Se$_{0.4}$ sample at 300 K. However, the power factor of the Cu$_{0.08}$Bi$_{1.97}$Co$_{0.03}$Te$_{2.6}$Se$_{0.4}$ ($x = 0.03$) sample became higher at 520 K. A decrease in lattice thermal conductivity was observed for the Co-doped samples due to additional point defect phonon scattering. Consequently, a maximum $zT$ of 1.0 was observed for the $x = 0$ sample at 300 K; however, above 440 K, the $zT$ values of the $x = 0.03$ and 0.06 samples were approximately 15% and 7% larger than that of the $x = 0$ sample, at 520 K, respectively. Furthermore, a maximum quality factor of 0.49 was observed for the $x = 0.03$ sample at 440 K, which would infer that the highest $zT$ can be obtained with the $x = 0.03$ sample at 440 K by optimizing carrier concentration.

Conflict of interest statement

There is no conflict of interest.

ACKNOWLEDGEMENT

This study was supported by the National Research Foundation of Korea (NRF-2019R1C1C1005254 and NRF-2022R1F1A1063054).

REFERENCES