Hf-Doping Effect on the Thermoelectric Transport Properties of \( n \)-Type \( \text{Cu}_{0.01}\text{Bi}_{2.7}\text{Te}_{2.7}\text{Se}_{0.3} \)

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Received: 26 June 2020; Accepted: 15 July 2020; Published: 16 July 2020

Abstract: Polycrystalline bulks of Hf-doped \( \text{Cu}_{0.01}\text{Bi}_{2.7}\text{Te}_{2.7}\text{Se}_{0.3} \) are prepared via a conventional melt-solidification process and subsequent spark plasma sintering technology, and their thermoelectric performances are evaluated. To elucidate the effect of Hf-doping on the thermoelectric properties of \( n \)-type \( \text{Cu}_{0.01}\text{Bi}_{2.7}\text{Te}_{2.7}\text{Se}_{0.3} \), electronic and thermal transport parameters are estimated from the measured data. An enlarged density-of-states effective mass (from \( \sim 0.92 \) \( m_0 \) to \( \sim 1.24 \) \( m_0 \)) is obtained due to the band modification, and the power factor is improved by Hf-doping benefitting from the increase in carrier concentration while retaining carrier mobility. Additionally, lattice thermal conductivity is reduced due to the intensified point defect phonon scattering that originated from the mass difference between Bi and Hf. Resultantly, a peak thermoelectric figure of merit \( zT \) of 0.83 is obtained at 320 K for \( \text{Cu}_{0.01}\text{Bi}_{1.925}\text{Hf}_{0.075}\text{Te}_{2.7}\text{Se}_{0.3} \), which is a \( \sim 12\% \) enhancement compared to that of the pristine \( \text{Cu}_{0.01}\text{Bi}_{2.7}\text{Te}_{2.7}\text{Se}_{0.3} \).

Keywords: \( \text{Bi}_2\text{Te}_3 \); thermoelectric; Hf-doping; effective mass; lattice thermal conductivity

1. Introduction

Thermoelectric (TE) technology is widely used for cooling and energy harvesting applications, since it can directly convert thermal energy into electricity (and vice versa) by using semiconducting TE materials. \( \text{Bi}_2\text{Te}_3 \)-based alloys (\( p \)-type Sb-substituted and \( n \)-type Se-substituted \( \text{Bi}_2\text{Te}_3 \) compounds) with narrow bandgap (\( \sim 130 \) meV) semiconductor characteristics [1] are the only commercialized TE materials for solid-state cooling and low-temperature power generation. One of the most critical factors to determine the efficiency of TE systems is the performance of the TE materials, which can be denoted by a dimensionless figure of merit, \( zT \) (\( = S^2\sigma T/\kappa \), where \( S \) is the Seebeck coefficient, \( \sigma \) is the electrical conductivity, and \( \kappa \) is the thermal conductivity at a given absolute temperature \( T \)). Another issue in \( \text{Bi}_2\text{Te}_3 \)-based TE materials is their low mechanical reliability when fabricated as ingots by using a directional solidification method, such as zone melting; this because the \( 00l \) planes held together by weak van der Waals interactions are highly aligned along the growth direction [2]. Thus, many
researches have been focusing on the development of polycrystalline materials with enhanced \( zT \) due to their intrinsically high mechanical strength compared to that of ingots.

Recently, significantly enhanced \( zT \)'s have been obtained via nanostructuring approaches [3–5]; however, a \( zT \) enhancement by a facile and straightforward compositional tuning is always favorable. For \( p \)-type Sb-substituted \( \text{Bi}_2\text{Te}_3 \) alloys (Bi–Sb–Te), doping Ag, Cu, or Pb at Bi/Sb-sites has been effective to improve \( zT \), especially at higher temperatures, mainly due to the suppression of bipolar thermal conduction [6–8]. Substitutional doping also provides a chance to enhance \( zT \) due to the enlarged density-of-states (DOS) by band engineering (e.g., band flattening, band convergence, and resonant state formation) [9–12] and/or intensified phonon scattering by the formation of point defects [13]. A higher maximum \( zT (zT_{\text{max}}) \), over 1.2 times that of commercial ingot \( (zT_{\text{max}} \sim 1.0) \), has been observed in \( p \)-type Bi-Sb-Te by compositional tuning. However, the \( zT_{\text{max}} \) of \( n \)-type Se-substituted \( \text{Bi}_2\text{Te}_3 \) compounds (Bi–Te–Se) remained about 1.0 [14].

In the present study, Cu-introduced \( \text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3} \) (\( \text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3} \)) is selected as a pristine compound due to its highly reproducible TE properties as well as high \( zT \); furthermore, polycrystalline bulks of Hf-doped \( \text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3} \) are prepared by using a conventional melt-solidification process and a subsequent spark plasma sintering (SPS) technique. The electronic and thermal transport parameters are estimated to elucidate the Hf-doping effect (at Bi-sites) on the TE transport properties of \( n \)-type Bi–Te–Se alloys. The power factor is improved due to the enlarged DOS effective mass, and lattice thermal conductivity (\( \kappa_{\text{lat}} = \kappa - \kappa_{\text{ele}}, \) where \( \kappa_{\text{ele}} \) is the electronic contribution to the thermal conduction) is reduced simultaneously. Resultantly, an enhanced \( zT \) of 0.83 at 320 K is obtained in 3.75 at.% Hf-doped \( \text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3} \).

2. Materials and Methods

Firstly, the ingots of \( \text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3} \) and Hf-doped \( \text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3} \) (\( \text{Cu}_{0.01}\text{Bi}_{2-x}\text{Hf}_x\text{Te}_{2.7}\text{Se}_{0.3}, x = 0.05, 0.075, 0.1, 0.125 \)) were synthesized by using a conventional melt-solidification process. According to the stoichiometric compositions, the starting raw elements (high purity Cu, Bi, Te, Se, and Hf) were weighed and vacuum sealed (~10\(^{-3}\) Pa) in quartz tubes to prevent oxidation during the melting. The mixtures in the sealed quartz tubes were melted in a rocking furnace (rocking angle ~120°) for 5 h at 1453 K and cooled to room temperature. The acquired ingots were pulverized into powders by using a ball mill for 10 min and screened with a 325 mesh (~44 \( \mu \text{m} \)) sieve. The powders were compacted by SPS under 30 MPa for 2 min at 753 K in a dynamic vacuum. Dense polycrystalline bulks (11 mm in diameter and 13 mm in thickness) with a relative density ~96% were fabricated.

Phase formation behavior was confirmed by X-ray diffraction (XRD, Smartlab, Rigaku, Japan) with Cu Kα radiation (\( \lambda = 1.5418 \) Å). From the SPSed discs, bar-type samples (2 mm × 2 mm × 8 mm) for measurement of the electronic transport properties and cuboidal samples (10 mm × 10 mm × 1 mm) for measurement of thermal diffusivity (\( \lambda \)) were cut in a plane perpendicular and parallel to the SPS pressing direction, respectively. Thus, all three parameters (\( \rho, S, \) and \( \lambda \)) were measured along the same direction. Temperature-dependent \( S \) and \( \lambda \) were measured from 300–480 K by using a TE property measurement system (ZEM-3, ULVAC-RICO, Japan). The Hall carrier concentration (\( n_H \)) and Hall mobility (\( \mu_H \)) were obtained by Hall effect measurement at room temperature in the van der Pauw configuration (magnetic field of 0.5 T, HMS-S5500, Ecopia, South Korea). The temperature-dependent \( \kappa \) values were estimated from density (\( \rho \)), specific heat capacity (\( C_p \)), and \( \lambda \). Between 300–410 K, the \( C_p \) was measured by using a physical properties measurement system (PPMS, Quantum Design, San Diego, CA, USA) and the Dulong–Petit fitting was used to estimate the \( C_p \) up to 480 K. The temperature-dependent \( \lambda \) values were measured under vacuum by using the laser-flash method (TC-1200RH, ULVAC-RICO, Japan).

3. Results and Discussions

Because of the anisotropic crystal structure of the \( \text{Bi}_2\text{Te}_3 \)-based alloys, their electronic and thermal transport properties are strongly influenced by the measurement directions (00l orientation characteristics). To minimize this effect, we prepared the SPSed bulks with a similar 00l orientation
by controlling the SPS conditions. As shown in Figure 1 (XRD patterns for the SPSed bulks of Cu$_{0.01}$Bi$_2$xHf$_x$Te$_{2.7}$Se$_{0.3}$ ($x = 0, 0.05, 0.075, 0.1, 0.125$)), the 00l orientation, which can be denoted by a Lotgering factor $f$ ($f_{00l} = (p_{00l} - p_0)/(1-p_0)$, where $p_{00l} = \Sigma I_{00l}/\Sigma l_{0kl}$, and $p_0 = \Sigma I_{000}/\Sigma l_{0kl}$ with $l_{0kl}$ and $I_{0kl}$ being the intensities of the ($hkl$) peaks for the textured and randomly oriented sample), for all samples are almost the same ($f = 0.13-0.15$). This suggests that the electronic and thermal transport parameters for these samples can provide reliable information to investigate the Hf-doping effect on the TE properties of Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$. It is noted that a single-phase without any Hf-related secondary phases is observed up to 5 at.% Hf-doped Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$; however, a small amount of Hf$_3$Te$_2$ is observed in 6.25 at.% Hf-doped Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$. Peak positions in all samples are nearly constant due to the similar atomic radii of Bi (~230 pm) and Hf (~225 pm). Figure 1b shows the SEM image of the fractured surface of the SPSed Cu$_{0.01}$Bi$_{1.9}$Hf$_{0.1}$Te$_{2.7}$Se$_{0.3}$. The average grain size is about 10–20 μm, and no inclusions and secondary phases were observed.

![Figure 1](image_url)  
Figure 1. (a) X-ray diffraction patterns of the spark plasma sintered (SPSed) Cu$_{0.01}$Bi$_2$xHf$_x$Te$_{2.7}$Se$_{0.3}$ ($x = 0, 0.05, 0.075, 0.1, 0.125$) bulks in the planes perpendicular to the SPS press direction. (b) SEM image of the fractured surface of the SPSed Cu$_{0.01}$Bi$_{1.9}$Hf$_{0.1}$Te$_{2.7}$Se$_{0.3}$.

Figure 2a shows the temperature dependence of $\sigma$ for the SPSed bulks of Cu$_{0.01}$Bi$_2$xHf$_x$Te$_{2.7}$Se$_{0.3}$. The measurement directions for $\sigma$ and other parameters ($S$ and $\lambda$) are illustrated in the inset of Figure 2a. The $\sigma$ value of the pristine Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ is ~712 S cm$^{-1}$ at 300 K, and it gradually increases with an increasing Hf-doping content up to $x = 0.1$. This suggests that Hf is an effective doping element at the Bi-site to generate electron carriers. The decreased $\sigma$ observed in Cu$_{0.01}$Bi$_{1.875}$Hf$_{0.125}$Te$_{2.7}$Se$_{0.3}$ is considered to be related to the generation of Hf$_3$Te$_2$ owing to the solid solution limit of Hf at the Bi-site.
Figure 2. Temperature dependences of the (a) electrical conductivity ($\sigma$) and (b) Seebeck coefficient ($S$) for the SPSed Cu$_{0.01}$Bi$_{2-x}$Hf$_x$Te$_{2.7}$Se$_{0.3}$ ($x = 0$, $0.05$, $0.075$, $0.1$, $0.125$) bulks. Insets in (a) and (b) show the thermoelectric measurement orientations and the temperature-dependent power factor ($S^2\sigma$), respectively.

On the other hand, $S$ shows the trade-off relationship with $\sigma$, as shown in Figure 2b. The calculated power factor ($S^2\sigma$) is shown in the inset of Figure 2b. The maximum power factor of $\sim$3.41 mW m$^{-1}$ K$^{-2}$ is obtained at 300 K in Cu$_{0.01}$Bi$_{1.925}$Hf$_{0.075}$Te$_{2.7}$Se$_{0.3}$, which is improved by $\sim$27% compared to that of the pristine Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ ($\sim$2.68 mW m$^{-1}$ K$^{-2}$).

To clarify the electronic transport properties, we estimated the $n_H$ and $\mu_H$ at 300 K according to Hf-doping content (Figure 3a). The $n_H$ increases systematically with the increasing Hf-doping content up to $x = 0.1$, which suggests that Hf (Hf$^{4+}$) is an effective doping element at the Bi (Bi$^{3+}$)-site to generate electron carriers. Thus, the one of the main reasons for the decrease in $S$ by Hf-doping (Figure 2b) is increased $n_H$. On the other hand, $\mu_H$ is slightly decreased by Hf-doping due to the increase both in electron–electron scattering and carrier scattering by point defects (Hf$_{Bi}$). The significant increase in the power factor (inset of Figure 2b) observed in Cu$_{0.01}$Bi$_{1.95}$Hf$_{0.05}$Te$_{2.7}$Se$_{0.3}$ suggests that the band structure would be modified by Hf-doping. Because the DOS effective mass ($m_d^*$) is the critical parameter that determines $S$, we estimated $m_d^*$ based on the following Equation (1), assuming a single parabolic band model [15], where $e$, $h$, and $k_B$ are the elementary charge, Plank’s constant, and Boltzmann constant, respectively.

$$S = \frac{8\pi^2 k_B^2}{3eh^2} \left( \frac{\pi}{3n_H} \right)^{2/3} m_d^* T$$  \hspace{1cm} (1)

Figure 3. (a) Hall carrier concentration ($n_H$) and Hall mobility ($\mu_H$) as a function of Hf-doping content. (b) Pisarenko plot ($SI-n_H$) for the SPSed Cu$_{0.01}$Bi$_{2-x}$Hf$_x$Te$_{2.7}$Se$_{0.3}$ ($x = 0$, $0.05$, $0.075$, $0.1$, $0.125$) bulks.
Figure 3b shows the Pisarenko plot (ISI-$n_H$) for the SPSed Cu$_{0.01}$Bi$_{2-x}$Hf$_x$Te$_{2.7}$Se$_{0.3}$ bulks. Interestingly, the $n_H^*$ value at 300 K of the pristine Cu$_{0.01}$Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ ($\sim$0.92 $m_0$, where $m_0$ is the free electron mass) is increased to $\sim$1.24 $m_0$ by Hf-doping, indicating that the electronic structure of the conduction band is modified. The possible mechanisms for band modification are band convergence, band flattening, or resonant state formation by Hf-doping [16]. These results observed in the electronic transport parameters suggest that the improved power factor of Cu$_{0.01}$Bi$_{1.925}$Hf$_{0.075}$Te$_{2.7}$Se$_{0.3}$ is mainly due to the increase in $n_H^*$ without severe deterioration in $\mu_H$.

Doping of Hf at the Bi-site generates point defects (Hf$_{Bi}$), and it can act as a scattering center, especially for a high-frequency phonon. To confirm the effect of Hf-doping on the thermal transport properties of Cu$_{0.01}$Bi$_{2-x}$Hf$_x$Te$_{2.7}$Se$_{0.3}$, $\kappa_{lat}$ was calculated by subtracting $\kappa_{ele}$ from the measured $\kappa$ (Figure 4a). Figure 4b shows the temperature dependence of $\kappa_{ele}$, which is estimated based on the Wiedemann–Franz law ($\kappa_{ele} = \alpha T$). The temperature-dependent Lorenz number ($L$ in W Ω K$^{-2}$) was calculated by using the following Equation (2) [17] and represented in the inset of Figure 4b.

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

As shown in Figure 4a, the acquired temperature-dependent behavior is not ruled by a typical $T^{-1}$ relationship, suggesting that the bipolar thermal conduction (\(\kappa_{bp}\)) is included, and its contribution increases with temperature. To clarify the point defect phonon scattering effect, we compared the room temperature $\kappa_{lat}$ values since the $\kappa_{bp}$ can be neglected at low temperatures. The $\kappa_{lat}$ value of the pristine Cu$_{0.01}$Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ ($\sim$0.785 W m$^{-1}$ K$^{-1}$) at 300 K is gradually reduced with the Hf-doping content up to $x = 0.1$, and reaches the minimum value of $\sim$0.612 W m$^{-1}$ K$^{-1}$ due to the intensified alloy scattering of the phonons. Phonon scattering by Hf$_{Bi}$ is determined by (1) the fraction of the point defect (Hf$_{Bi}$); (2) the mass difference between the doping element (Hf) and host atom (Bi); and (3) the lattice mismatch between the disordered and pure alloys according to the Callaway model and following the phonon scattering parameter ($\Gamma$) in Equation (3), where $x$ is the fraction of the doping element, $\Delta M/M$ is the rate of change of the atomic mass, $\epsilon$ is the elastic property, and $a_{disorder}$ and $a_{pure}$ are the lattice parameters of the disordered and pure alloys, respectively [18,19].

$$\Gamma = x(1-x)\left[\left(\frac{\Delta M}{M}\right)^2 \epsilon \left(\frac{a_{disorder} - a_{pure}}{a_{pure}}\right)^2\right]$$

Thus, the $\kappa_{lat}$ reduction by Hf-doping might be related both with mass fluctuation (by the atomic mass difference between Bi ($M_{Bi} = 208.98$) and Hf ($M_{Hf} = 178.49$)) and strain field fluctuation (by
the atomic radius difference between Bi (230 pm) and Hf (225 pm). Despite the small mass and size difference between Bi and Hf, \( k_{\text{lat}} \) is reduced ~25%, since high-frequency phonons are dominant in Bi–Te-based alloys [6]. A slightly increased \( k_{\text{lat}} \) value in Cu\(_{0.01}\)Bi\(_{1.825}\)Hf\(_{0.125}\)Te\(_{2.7}\)Se\(_{0.3}\) is owing to the formation of the secondary phase (Hf\(_3\)Te\(_2\)). Figure 4c shows the temperature dependences of the \( zT \) values for the Cu\(_{0.01}\)Bi\(_{1.925}\)Hf\(_{0.075}\)Te\(_{2.7}\)Se\(_{0.3}\) bulks. An enhanced \( zT \) of 0.83 is obtained at 320 K in Cu\(_{0.01}\)Bi\(_{1.925}\)Hf\(_{0.075}\)Te\(_{2.7}\)Se\(_{0.3}\) due to the simultaneous improvement of the electronic and thermal transport properties by Hf-doping.

4. Conclusions

In summary, we demonstrate the important role of Hf-doping at the Bi-site to enhance the thermoelectric performance of \( n \)-type Cu\(_{0.01}\)Bi\(_{1.825}\)Te\(_{2.7}\)Se\(_{0.3}\) based on the theoretical and experimental considerations for the transport parameters. Hf-doping induces the modification of the conduction band, which results in the enlarged density-of-states effective mass. Additionally, lattice thermal conductivity is significantly reduced due to the mass-difference (between Bi and Hf) in phonon scattering, especially in the high-frequency region. A peak \( zT \) of 0.83 at 320 K is obtained for Cu\(_{0.01}\)Bi\(_{1.925}\)Hf\(_{0.075}\)Te\(_{2.7}\)Se\(_{0.3}\). The acquired \( zT \) in the present study is moderate considering the higher \( \kappa \) values for the Cu\(_{0.01}\)Bi\(_{1.925}\)Hf\(_{0.075}\)Te\(_{2.7}\)Se\(_{0.3}\) of 0.83 is obtained at 320 K in Cu\(_{0.01}\)Bi\(_{1.925}\)Hf\(_{0.075}\)Te\(_{2.7}\)Se\(_{0.3}\) due to the simultaneous improvement of the electronic and thermal transport properties by Hf-doping.

Author Contributions: H.-S.K. and K.H.L. conceived and led the research; J.Y.H., S.C., S.-i.K., J.-H.L., S.-M.C. and H.Y. prepared the samples, measured the thermoelectric properties, and the performed analysis; All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) project (Grant 2013M3A6B1078870). This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2019R1A6A1A03031833) and NRF-2019R1A6A1A03058660.

Conflicts of Interest: The authors declare no conflict of interest.

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