

Rapid Communication

Thermoelectric properties of Cu-doped n-type $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0-0.2$) alloys

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Abstract

n-Type $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0-0.2$) alloys with Cu substitution for Bi were prepared by spark plasma-sintering technique and their structural and thermoelectric properties were evaluated. Rietveld analysis reveals that approximate 9.0% of Bi atomic sites are occupied by Cu atoms and less than 4.0 wt% second phase $\text{Cu}_{2.86}\text{Te}_2$ precipitated in the Cu-doped parent alloys. Measurements show that an introduction of a small amount of Cu ($x \leq 0.1$) can reduce the lattice thermal conductivity (κ_L), and improve the electrical conductivity and Seebeck coefficient. An optimal dimensionless figure of merit (ZT) value of 0.98 is obtained for $x = 0.1$ at 417 K, which is obviously higher than those of Cu-free $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ (ZT = 0.66) and Ag-doped alloys (ZT = 0.86) prepared by the same technologies. © 2007 Elsevier Inc. All rights reserved.

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1. Introduction

Thermoelectric (TE) materials and devices have received increasing attention because of their potential applications in the fields of energy conversion and TE cooling. For a compound to qualify as a efficient TE material it should exhibit highest TE figure of merit, ZT, possible at the temperature of operation, T , ZT can be defined as

$$ZT = \frac{\alpha^2 \sigma}{\kappa},$$

where α is the Seebeck coefficient, σ the electrical conductivity and κ the total thermal conductivity.

So far, many materials capable of fabricating efficient TE devices were investigated and substantial achievements were made. Several classes of TE materials with high efficiency through chemical composition and microstructure modulation were developed such as CsBi_4Te_6 [1], specially constructed $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices [2], p-type

cubic $\text{AgPb}_m\text{SbTe}_{2+m}$ [3] and $\text{Ag}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{SbTe}_{2+m}$ bulk materials by vacuum melting [4], used in low, room and mid temperature applications, respectively.

In my group, several kinds of p-type Bi–Te-based alloys with $ZT > 1$, such as $M_x\text{Bi}_{0.5}\text{Sb}_{1.5-x}\text{Te}_3$ ($M = \text{Cu}, \text{Ag}$) [5,6] and pseudo-binary $(\text{Ag}_{0.365}\text{Sb}_{0.558}\text{Te})_x-(\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3)_{1-x}$ alloys [7] simply prepared by powder metallurgy, have recently been developed. Newly developed n-type $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Ag}_x\text{Se}_3)_{0.1}$ alloys with $ZT = 0.86$ [8] also evidenced that a substitution of IB element for Bi in the n-type Bi–Te-based alloys is an effective way to achieve high performance at a specific temperature. Since element Ag has a larger atomic radius (1.75×10^{-10} m) than Cu (1.57×10^{-10} m) [9], theoretically, Cu atoms have a more possibility either to be interstitially occupied in the Bi–Se–Te layered structure or to replace parent atoms, producing more severe lattice distortion and causing a more reduction of lattice and electronic thermal conductivity. On the other hand, smaller electronegativity of element Cu (1.9) than that of Ag (1.93) [9] enables Cu-doped $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ alloys to have a larger product of effective mass and mobility of carriers than Ag-doped alloys.

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In the present work, Rietveld analysis to the Cu-doped alloys was carried out and the position of Cu atoms in the crystal lattice was determined. The relationship between the concentration of Cu and TE properties was studied to investigate what extent of ZT value can be raised by means of a substitution of Cu for Bi in the $(\text{Bi}_2\text{Te}_3)_{0.9}\text{--}(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ alloys.

2. Experimental procedures

The experiments start from powders with a high purity of 99.999%: Cu, Bi, Se and Te. These powders were weighted according to the composition formula of Bi_2Te_3 and $\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3$ ($x = 0, 0.05, 0.1$ and 0.2), and then two mixtures were sealed in two different evacuated quartz tubes and melted for 10 h at 1323 K. After quenching, the two ingots (Bi_2Te_3 and $\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3$) were once more weighted, sealed and melted in vacuum tubes according to stoichiometry of $(\text{Bi}_2\text{Te}_3)_{0.9}\text{--}(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0\text{--}0.2$). During all melting 30-s rocking every 1 h was conducted to ensure that the composition was homogenous without segregation. The obtained $(\text{Bi}_2\text{Te}_3)_{0.9}\text{--}(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ingots with different molar fraction x were subsequently ball-milled in stainless steel bowls for 5 h with a rotation rate of 350 rpm. Prior to spark plasma sintering (SPS-1030) at 633 K with a pressure of 40 MPa, the powders were dried in vacuum for 5 h at 60 °C. Eventually, each sample was cut into 3 mm slices measuring 2.5 mm × 15 mm from the sintered block with the size of $\varnothing 20$ mm × 2.5 mm for electrical property measurement.

The crystal structure was analyzed at room temperature with X-ray diffractometer (XRD-98) using $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm), using a scan rate of 4°min^{-1} to record the patterns in the 2θ range from 10° to 110° . The quantities of second phases and atomic occupation percentages in the sublattices were examined using Rietveld refinement; the densities of the samples were measured by the Archimedes method.

Bi_2Te_3 -based alloys have strong anisotropies on TE properties for single crystals [10,11], even for the sintered specimens small anisotropies on TE properties can still be observed with respect to the pressing direction, showing that the electrical and thermal conductivities of the pressing direction are found to be small than those in the direction perpendicular to the pressing direction [12]. In the present work, the electrical properties involving Seebeck coefficients (α) and electrical conductivities (σ) were evaluated perpendicular to the pressing direction using an apparatus (ULVAC ZEM-2) in a helium atmosphere, and those for the specimens along the pressing direction were also examined at room temperature for comparison. The thermal diffusivities were measured along the pressing direction by the laser flash method (Netzsch, LFA427), the thermal conductivities were calculated from the values of densities, specific heats and thermal diffusivities.

3. Results and discussion

3.1. Rietveld analysis of X-ray diffraction profiles

The densities of the sintered samples were measured using an Archimedes method and range from 7.47 to 7.68 kg m^{-3} , the relative densities are higher than 95%.

In terms of the phase diagram of $\text{Bi}_2\text{Te}_3\text{--Bi}_2\text{Se}_3$ [13], at temperatures above 500 K Bi_2Te_3 and Bi_2Se_3 can be dissolved into each other in any proportion and form a continuous solid solution that has a tetradymite-type rhombohedral lattice. The XRD patterns indicate that the Cu-doped powders $(\text{Bi}_2\text{Te}_3)_{0.9}\text{--}(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ have the same rhombohedral lattice structure as $(\text{Bi}_2\text{Te}_3)_{0.9}\text{--}(\text{Bi}_2\text{Se}_3)_{0.1}$ (space group $R\bar{3}m$) with a small amount of second phase $\text{Cu}_{2.86}\text{Te}_2$ precipitated, shown in Fig. 1. After close Rietveld refinement to the specimen for $x = 0.1$ and 0.2 , the quantity of precipitated $\text{Cu}_{2.86}\text{Te}_2$ is less than 4.0 wt%. In the main phase of $(\text{Bi}_2\text{Te}_3)_{0.9}\text{--}(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ average 45.0% Te 1 and 50.0% Te 2 sites are, respectively, occupied by Se atoms and approximate 9.0% of Bi atomic positions by Cu atoms. This suggests that most Cu atoms are incorporated into the sublattice of Bi–Se compound, causing a decrease of the carrier concentration of Bi_2Se_3 , since the bonding of Cu–Se can increase the formation energy of Bi substitutional defects on the Se sites (Bi_{Se} antisite defects) [14].

3.2. TE properties

The temperature dependence of the Seebeck coefficient (α) of $(\text{Bi}_2\text{Te}_3)_{0.9}\text{--}(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0\text{--}0.1$) is presented in Fig. 2, where one can find that the α values are negative in the whole temperature range, showing that the majority

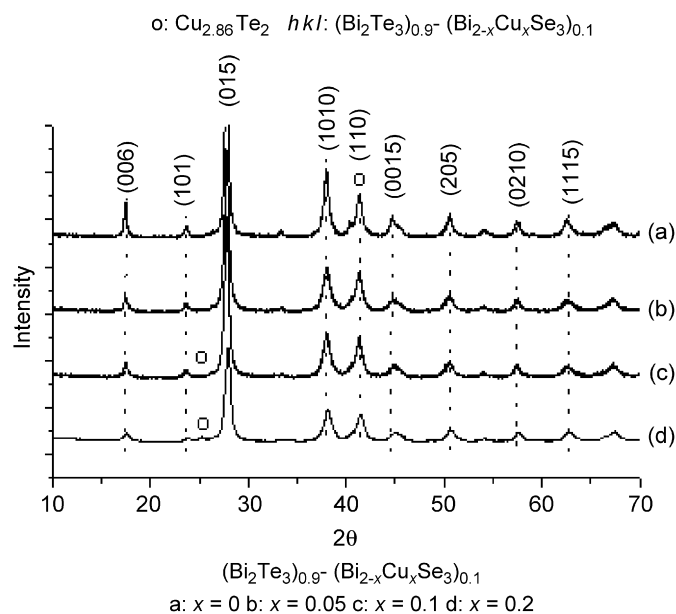


Fig. 1. X-ray diffraction patterns of the $(\text{Bi}_2\text{Te}_3)_{0.9}\text{--}(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ alloys: (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$ and (d) $x = 0.2$.

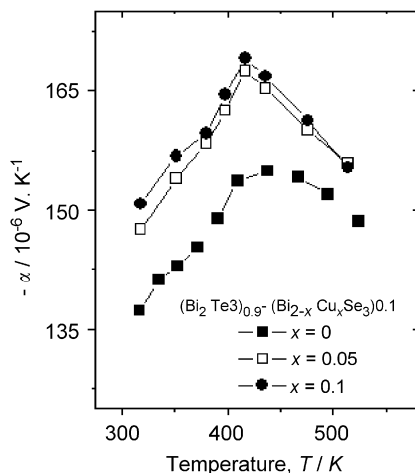


Fig. 2. The relationship between temperature and Seebeck coefficients for different $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0-0.1$) alloys prepared by spark plasma sintering.

of charge carriers are electrons. With the temperature elevation the α values increase and then continue to decrease after reaching the maximum at about 417 K, the maximum absolute α value is $170 \text{ } (\mu\text{V K}^{-1})$ for $x = 0.1$. The more the Cu concentration, the higher the α values over the entire measuring temperature range. Although an occupation of Cu in the Bi sites was reported to be able to suppress Bi'_{Se} antisite defects, according to the investigation made by Lošt'ák et al. [15–17] who found that an incorporation of Sb (In, As) atoms into the Bi_2Se_3 crystal lattice can qualitatively cause a decrease in the concentration of Se vacancies V''_{Se} and antisite defects Bi'_{Se} , resulting in a suppression of free electron concentration in the range of high Sb (In, As) content, each Cu atom can donate 0.65 electrons in Bi_2Te_3 crystals, according to Ref. [18], it is therefore estimated that the net free electron concentration can be increased in the main phase of $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$. Hence, we can suggest that increased lattice disorder and grain boundaries caused by atomic replacement of Bi with Cu and second phase $\text{Cu}_{2.86}\text{Te}_2$ precipitation play a dominant role in enhancing the scattering to carriers in the present materials. The measurements at room temperature along the pressing direction reveal that the Seebeck coefficients (α_{\parallel}) are a little higher than those in perpendicular to the pressing direction, as shown in Table 1, which might be due to the relatively low densities for the specimens, since the height of pressed cylinders in this direction is 13 mm, much higher than those perpendicular to the pressing direction, so that relatively porous specimens were obtained.

Fig. 3 shows the temperature dependence of electrical conductivity (σ). With the temperature increasing the electrical conductivity decreases, suggesting that the carriers are in an extrinsic state in the whole temperature range. Generally, the σ value increases with Cu content, its values increase from 7.6×10^4 to $8.1 \times 10^4 \text{ } (\Omega^{-1} \text{ m}^{-1})$ at 318 K and from 5.5×10^4 to $7.3 \times 10^4 \text{ } (\Omega^{-1} \text{ m}^{-1})$ at 514 K

Table 1

The electrical properties in and perpendicular to the pressing direction at room temperature for the $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0-0.1$) alloys

	$x = 0$	$x = 0.05$	$x = 0.1$
$\alpha^a \text{ } (\mu\text{V K}^{-1})$	-137.3	-147.5	-150.8
$\alpha_{\parallel}^b \text{ } (\mu\text{V K}^{-1})$	-143.8	-154.6	-156.2
$\sigma^a \text{ } (\Omega^{-1} \text{ m}^{-1})$	7.63×10^4	7.22×10^4	8.07×10^4
$\sigma_{\parallel}^b \text{ } (\Omega^{-1} \text{ m}^{-1})$	6.76×10^4	6.38×10^4	7.27×10^4

^aThe data in perpendicular to the pressing direction.

^bThe data in the pressing direction.

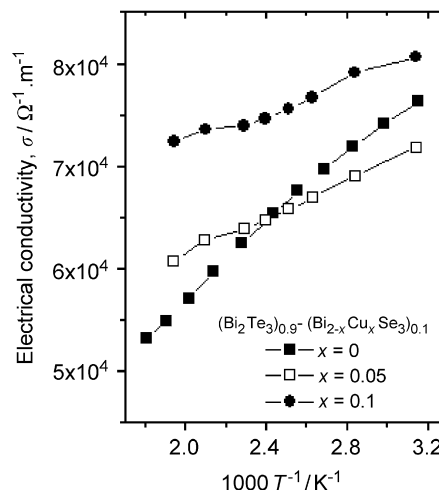


Fig. 3. The dependence of electrical conductivities on temperature for different $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0-0.1$) alloys prepared by spark plasma sintering.

with x increasing from 0 to 0.1, respectively. Because of the possible decrease of mobility μ and increase of free carrier concentration n , as was discussed above, we suggest that the best combination for the two competing factors, mobility μ and carrier concentration n , be achieved for the present alloy with $x = 0.1$, based on the formula: $\sigma = ne\mu$. On the other hand, the effective band gap can become small because the second phase $\text{Cu}_{2.86}\text{Te}_2$ might introduce impurity levels within the gap, which alters the basic conducting mechanism. The reduced activation energy, due to the introduction of $\text{Cu}_{2.86}\text{Te}_2$, can also facilitate the transports of the carriers both for electrons and holes according to the expression $\sigma = \sigma_0 \exp(-\Delta E_{\sigma}/k_{\text{B}}T)$ [19], where k_{B} is the Boltzmann's constant, ΔE_{σ} the thermal activation energy and σ_0 is the pre-exponential conductivity, leading to the increasing of σ values. The room temperature electrical conductivities (σ_{\parallel}) along the pressing direction show the lower values than those in perpendicular to pressing direction (Table 1), as was expected.

Fig. 4(a) shows the thermal conductivities versus temperature. There are three contributions to the thermal conductivity, lattice (κ_{L}), electronic (κ_{carrier}) and ambipolar (κ_{am}) component, i.e., $\kappa = \kappa_{\text{L}} + \kappa_{\text{carrier}} + \kappa_{\text{am}}$. The electronic component (κ_{carrier}) depends on the electrical conductivity

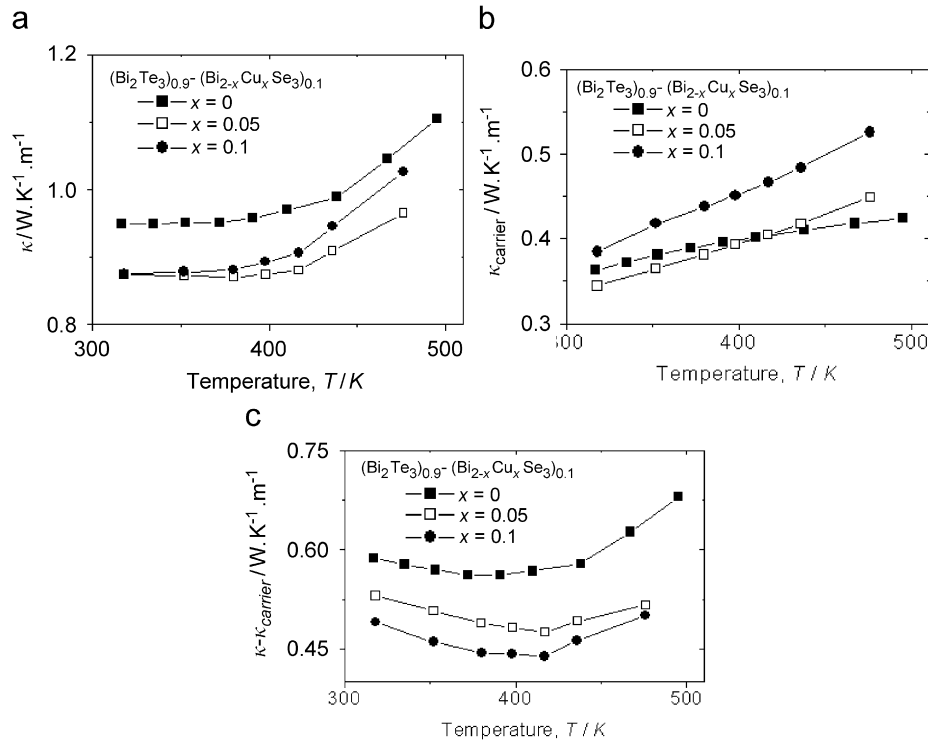


Fig. 4. The temperature dependence of thermal conductivities for different $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0-0.1$) alloys prepared by spark plasma sintering: (a) $\kappa - T$, (b) $\kappa_{\text{carrier}} - T$ and (c) $\kappa - \kappa_{\text{carrier}} - T$.

and can roughly be estimated using the Wiedemann–Franz law, $\kappa_{\text{carrier}} = L\sigma T$, where L is the Lorenz constant ($L = 1.5 \times 10^{-8} \text{V}^2 \text{K}^{-2}$) for a degenerate semiconductor [2]. Lattice component (κ_{L}) depends on structural details such as structure type and lattice disorder. In Fig. 4(a), one can observe that κ values are weakly changed with temperature below 400.0 K and increase relatively rapidly after that, for the alloy with $x = 0.1$ the κ value increases from 0.88 to 1.03 ($\text{W} \cdot \text{K}^{-1} \cdot \text{m}^{-1}$) with temperature increasing from 318 to 474 K. An introduction of a small amount of Cu ($x \leq 0.1$) can lead to a reduction of κ values for the entire temperature range.

Electronic component κ_{carrier} against temperature is plotted in Fig. 4(b). The κ_{carrier} value gradually increases with temperature and shows similar temperature dependence to σ . The temperature dependence of $\kappa - \kappa_{\text{carrier}}$ is illustrated in Fig. 4(c), the $\kappa - \kappa_{\text{carrier}}$ values in $x = 0.1$ are much lower than those in Cu-free sample over the entire temperature range, and the minimum value of 0.44 ($\text{W} \cdot \text{K}^{-1} \cdot \text{m}^{-1}$) can be obtained at 417 K. It appears that, as was presumed above, an occupation of Cu atoms in the Bi sites as well as the precipitation of $\text{Cu}_{2.86}\text{Te}_2$ can cause a more severe scattering to phonons, leading to the reduction of the lattice thermal conductivity. When temperature is elevated to about 417 K the $\kappa - \kappa_{\text{carrier}}$ values begin to increase with temperature for all specimens, this apparent increase is caused by ambipolar contribution arising from the diffusion of electron–hole pairs with the onset of intrinsic contribution that is apparently indicated in the $\alpha - T$ curves, shown in Fig. 2.

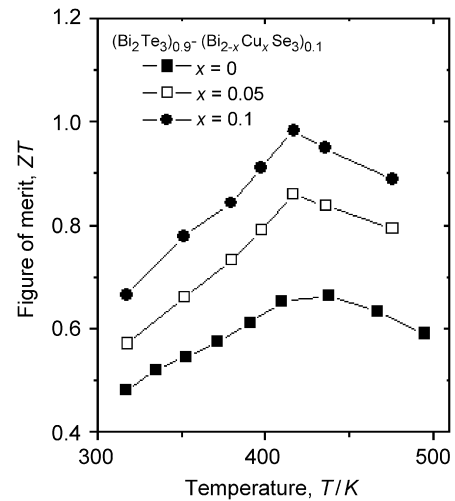


Fig. 5. The temperature dependence of dimensionless thermoelectric figure of merit ZT for different $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0-0.1$) alloys prepared by spark plasma sintering.

The ZT values for the alloys $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0-0.1$) were calculated from the relation $ZT = \alpha^2 \sigma T / \kappa$ using the experimental data, the results are indicated in Fig. 5, the ZT values increase with temperature until reach the maximum at about 417 K, for the alloy with $x = 0.1$ the highest ZT value of 0.98 is obtained, which is about 0.32 and 0.12 higher than those of Cu-free $\text{Bi}_2\text{Se}_3\text{Te}_{2.7}$ and the Ag-doped alloys $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Ag}_x\text{Se}_3)_{0.1}$ ($x = 0.4$) [8], respectively, but a little lower than those obtained by Yamashita [20,21]. Besides, to make the ZT value as high

as possible, a proper selection of other substituted elements and an optimization of chemical compositions are essential to the improvement of TE performance; henceforth, it is strongly desired that further experiments would be performed later on.

4. Conclusions

To summarize, the Seebeck coefficients (α) can increase with Cu concentration for the alloys $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ($x = 0-0.1$), possibly due to a dominant enhancement of scattering to carriers caused by lattice disorder. A small amount of Cu ($x \leq 0.1$) seems to be efficient to improve the electrical conductivity and reduce the lattice thermal conductivity, a proper combination of electrical and thermal properties enable a good TE property with the ZT value of 0.98 to be obtained for the alloy with $x = 0.1$ at 417 K. The results obtained suggest that the Cu-doped alloy is superior to that of the corresponding Ag-doped alloys, and further improvement of TE performance can be expected if a proper selection of other substituted elements and an optimization of chemical compositions are made.

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