Electronic Transport and Thermoelectric Properties of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ Tetrahedrites Prepared by Mechanical Alloying and Hot Pressing

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Abstract: Tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ has low lattice thermal conductivity because of the lone-pair electrons of Sb, which cause the Cu atoms to vibrate at a low frequency and high amplitude. When the Cu atoms of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ are partially substituted with a transition metal, changes in the Cu vibrations can intensify phonon scattering, thereby enhancing the thermoelectric properties. The synthesis of tetrahedrite compounds by conventional melting methods requires sophisticated reactions because the S element vaporizes at low temperature and its homogenization requires a long time. However, a homogeneous and solid-state synthesis can be carried out in a short time using mechanical alloying, because the volatilization of the constituent elements is inhibited and the subsequent heat treatment is not necessary. In this study, Zn-doped $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites were prepared by mechanical alloying (MA) and hot pressing (HP), and their electronic transport and thermoelectric properties were examined. A single tetrahedrite phase was successfully obtained by the MA-HP process without subsequent heat treatment. The lattice constant increased with the Zn content, confirming that Zn was substituted for Cu. Zn doping led to *p*-type conduction characteristics; however, it did not effectively increase the power factor. However, the thermal conductivity showed a marked decrease upon Zn doping, due to decrease in carrier contribution. A dimensionless figure of merit of 0.76 was obtained at 723 K for $\text{Cu}_{11.6}\text{Zn}_{0.4}\text{Sb}_4\text{S}_{13}$.

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Keywords: thermoelectric, tetrahedrite, mechanical alloying, hot pressing, doping

1. INTRODUCTION

The natural mineral tetrahedrite has attracted attention as a promising *p*-type thermoelectric material for intermediate temperature applications, because of its eco-friendly and earth-abundant characteristics. The synthetic tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ exhibits a very low thermal conductivity of less than $1 \text{ W m}^{-1} \text{ K}^{-1}$ at temperatures above 300 K, as well as high dimensionless figure of merit (*ZT*) values at temperatures near 723 K [1,2]. Ternary tetrahedrite exists as a $\text{Cu}_I^1\text{Cu}_2^{\text{II}}\text{Sb}_4\text{S}_{12}\text{S}^{\text{II}}$, according to the valence and coordination of its constituent elements. The active lone-pair electrons of the Sb atoms result in a low thermal conductivity, due to the low-frequency and high-amplitude vibrations of the Cu^{II} atoms out of the CuS_3 trigonal planes [3–5]. Generally, one-

third and two-thirds of the Cu^{I} sites are occupied by Cu^+ and Cu^{2+} ions, respectively, whereas the Cu^{II} site is occupied exclusively by Cu^+ [6]. The low lattice thermal conductivity is mainly related to the Cu^{II} sites. The substitution of Cu^{2+} at the Cu^{I} sites reduces the contribution of charge carriers to the thermal conductivity, mostly because it affects electrical resistivity [7–9].

M-substituted $\text{Cu}_{12-x}\text{M}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites (where M is a transition element such as Zn, Fe, Ni, Co, and Mn) have been reported to be good *p*-type thermoelectric materials [10]. Doping transition metals into the tetrahedrite structure can improve their thermoelectric performance with respect to that of lead telluride and skutterudite, and further studies on doped tetrahedrites are needed to confirm. Lu *et al.* [2] successfully synthesized $\text{Cu}_{11}\text{ZnSb}_4\text{S}_{13}$ using a melting method and obtained a *ZT* value close to 1 at 720 K; this high *ZT* value resulted from the very low lattice thermal conductivity. The low thermal conductivity of the tetrahedrite compound is caused by the peculiar

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chemical environment of some of the Cu atoms, resulting in anharmonic phonon scattering with low-frequency planar vibrations [11]. In this study, Zn-doped tetrahedrites were prepared by mechanical alloying (MA) and hot pressing (HP), and their electronic transport and thermoelectric properties were examined.

2. EXPERIMENTAL PROCEDURE

Zn-substituted $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ ($x = 0\text{--}1.2$) tetrahedrites were synthesized by MA. Appropriate amounts of Cu (purity 99.9%, < 45 μm , Kojundo), Zn (purity 99.9%, < 75 μm , Kojundo), Sb (purity 99.999%, < 150 μm , Kojundo), and S (purity 99.99%, < 75 μm , Kojundo) were weighed according to the stoichiometric composition. The mixed powder was charged into a hardened stainless steel jar with stainless steel balls of 5 mm diameter. The ball-to-powder weight ratio (BPR) was 20:1. MA was performed at 350 rpm for 24 h in an Ar atmosphere using a planetary mill (Fritsch Pulverisette5). The synthesized powder was loaded into a graphite mold with an inner diameter of 10 mm and then consolidated by HP at 723 K for 2 h, under 70 MPa in vacuum.

The phases of the MA powders and HP specimens were analyzed using X-ray diffraction (XRD; Bruker D8-Advance) with Cu K_α radiation ($\lambda = 0.15405$ nm). The diffraction patterns were measured in the θ - 2θ mode ($2\theta = 10^\circ\text{--}90^\circ$) with a step size of 0.02° and a scan speed of 0.4 s/step. The fractured surfaces of the HP specimens were observed using scanning electron microscopy (SEM; FEI Quanta400), while elemental analysis was carried out using energy-dispersive spectrometry (EDS; Bruker Quantax200). The thermoelectric properties were examined in the temperature range from 323 to 723 K, while the Seebeck coefficient (α) and electrical conductivity (σ) were measured using temperature differential and direct current (DC) four-probe methods in He atmosphere (Ulvac-Riko ZEM-3). The thermal conductivity (κ) was obtained by the laser flash method (Ulvac-Riko TC-9000H) after measuring thermal diffusivity, specific heat, and density. Finally, we evaluated the power factor ($\text{PF} = \alpha^2\sigma$) and the dimensionless figure of merit ($ZT = \alpha^2\sigma\kappa^{-1}T$).

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ samples synthesized by MA and sintered by HP. The diffraction peaks of all specimens matched the standard diffraction data (PDF #071-0555, space group $\bar{1}\bar{4}3m$), and no residual elements or secondary phases were identified. This indicated that the tetrahedrites were successfully synthesized by the MA-HP process. The diffraction peaks shifted to lower angles with increasing Zn content. Zn doping of the tetrahedrite structure can lead to an increase in the lattice constant, because the ionic radius of Zn^{2+} (60 pm) is larger than that of Cu^{2+} (57 pm) and Cu^+ (60 pm) [12]. As shown in Table 1, as the Zn doping level increased, the lattice constant increased from 1.0327 to 1.0361 nm. Tippireddy *et al.* [12] reported that the lattice constant increased from 1.03198 nm for $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ to 1.03391 nm for $\text{Cu}_{11}\text{ZnSb}_4\text{S}_{13}$. Suekuni *et al.* [13] reported similar results that the lattice constant increased from 1.031 nm for $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ to 1.038 nm for $\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}$. Thus, the above results confirm the successful substitution of Zn at the Cu site.

Figure 2 presents SEM images of fractured surfaces of the $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ compounds. The microstructure of the samples showed no significant variations with Zn content. Densely sintered bodies, with high relative densities of 97.1–99.2%, were obtained. Figure 3 shows the EDS elemental mappings of $\text{Cu}_{10.8}\text{Zn}_{1.2}\text{Sb}_4\text{S}_{13}$, as a typical specimen with a

Fig. 1. XRD patterns of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites prepared by the MA-HP process.

Table 1. Chemical compositions and physical properties of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites at room temperature.

Composition		Relative density	Lattice constant	Lorenz Number
Nominal	Actual	[%]	[nm]	$[10^8 \text{ V}^2\text{K}^{-2}]$
$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$	$\text{Cu}_{12.48}\text{Sb}_{4.13}\text{S}_{12.39}$	99.2	1.0327	1.71
$\text{Cu}_{11.6}\text{Zn}_{0.4}\text{Sb}_4\text{S}_{13}$	$\text{Cu}_{11.76}\text{Zn}_{0.46}\text{Sb}_{3.33}\text{S}_{13.43}$	97.1	1.0346	1.66
$\text{Cu}_{11.2}\text{Zn}_{0.8}\text{Sb}_4\text{S}_{13}$	$\text{Cu}_{11.79}\text{Zn}_{0.92}\text{Sb}_{3.99}\text{S}_{12.29}$	99.2	1.0353	1.66
$\text{Cu}_{10.8}\text{Zn}_{1.2}\text{Sb}_4\text{S}_{13}$	$\text{Cu}_{11.54}\text{Zn}_{1.19}\text{Sb}_{4.08}\text{S}_{12.17}$	99.1	1.0361	1.57

Fig. 2. SEM images of fractured surfaces of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites. **Fig. 3.** EDS elemental mappings of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites.

uniform distribution of the constituent elements. As shown in Table 1, the actual and nominal compositions were in almost perfect agreement.

Fig. 4. Temperature dependence of the electrical conductivity of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites.

Figure 4 shows the electrical conductivity of the $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ compounds. The non-doped specimen exhibited the maximum electrical conductivity at 623 K, while the Zn-doped specimens showed nondegenerate semiconductor behavior with a positive temperature dependence. The electrical conductivity decreased with increasing Zn content, due to the reduced hole concentration and low mobility [12]. The additional electrons generated from Zn substitution for Cu could fill the holes in the valence band and shift the Fermi level closer to the top of the valence band, thereby reducing the carrier concentration [14].

Figure 5 presents the Seebeck coefficients of the $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ compounds. All specimens showed positive Seebeck coefficient values, and the Zn-doped specimens showed higher values than undoped $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. As the Zn content increased, the Seebeck coefficient showed a marked increase. The Seebeck coefficient of a *p*-type semiconductor can be expressed as $\alpha = (8/3)\pi^2 k_B^2 m^* T e^{-1} h^{-2} (\pi/3n)^{2/3}$, where k_B , h , m^* , e , n , and T are the Boltzmann constant, Planck constant, effective carrier mass, electronic charge, carrier

Fig. 5. Temperature dependence of the Seebeck coefficient of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites.

Fig. 6. Temperature dependence of the power factor of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites.

concentration, and absolute temperature, respectively [15]. In general, the Seebeck coefficient increases with increasing temperature. However, at a certain temperature (or higher) the occurrence of the intrinsic transition leads to a rapid increase in the carrier concentration. Therefore, as the temperature increases, the contribution to reduction of the Seebeck coefficient becomes larger than to the increase in carrier concentration; therefore, the Seebeck coefficient decreases after reaching its peak value. In the present study, the specimens with $x = 0$ – 0.8 showed a similar temperature dependence of the Seebeck coefficient and no intrinsic transition occurred up to 723 K. However, in the case of the $x = 1.2$ specimen, the Seebeck coefficient showed a very weak temperature dependence and the intrinsic transition occurred at 523 K. This indicated that the intrinsic transition temperature was shifted to lower temperatures due to carrier concentration decrease in upon Zn doping, i.e., the Fermi level was shifted from the valence band to the midgap [12].

Figure 6 shows that the power factor of the $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ materials increases with the Seebeck coefficient and the electrical conductivity [16]. However, both parameters have a trade-off relationship with the carrier concentration. Therefore, optimization of the carrier concentration is necessary to maximize the PF value. In this study, PF decreased with increasing Zn content due to decrease in electric conductivity prevailed over the increase in the Seebeck coefficient caused by Zn doping. $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and

$\text{Cu}_{11.6}\text{Zn}_{0.4}\text{Sb}_4\text{S}_{13}$ exhibited maximum PFs of 0.95 and 0.75 $\text{mW m}^{-1} \text{K}^{-2}$, respectively, at 723 K. Therefore, Zn doping was not an effective strategy to increase the PF value of the tetrahedrite materials. Trippireddy *et al.* [12] reported a PF value of 0.86 $\text{mW m}^{-1} \text{K}^{-2}$ at 673 K for $\text{Cu}_{11}\text{ZnSb}_4\text{S}_{13}$ prepared by melting and hot pressing; which was slightly higher than that obtained in the present study. Harish *et al.* [17] obtained a PF value of 0.05 $\text{mW m}^{-1} \text{K}^{-2}$ at 573 K for $\text{Cu}_{10.5}\text{Zn}_{1.5}\text{Sb}_4\text{S}_{13}$ produced by mechanical alloying and spark plasma sintering obtained very low value was due to the presence of secondary phases. In this study, the decreased carrier concentration caused by the substitution of Zn at the Cu sites resulted in a decreased PF.

Figure 7 presents the thermal conductivity of the $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites. The thermal conductivity is the sum of the electronic thermal conductivity (κ_E), corresponding to the charge carrier contribution, and the lattice thermal conductivity (κ_L), corresponding to the phonon contribution. The electronic thermal conductivity was calculated using the Wiedemann-Franz law ($\kappa_E = L\sigma T$, where L is the Lorenz number) [18]. The Lorenz number was obtained by the relation $L [10^{-8} \text{ V}^2 \text{K}^{-2}] = 1.5 + \exp(-|\alpha|/116)$ [19], as shown in Table 1. The thermal conductivity decreased considerably with increasing Zn content; the specimen with $x = 1.2$ showed very low thermal conductivities of 0.50–0.53 $\text{W m}^{-1} \text{K}^{-1}$ in the temperature range from 323 to 723 K, which resulted from a lower κ_E due to the decreased electrical

Fig. 7. Temperature dependence of the thermal conductivities of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites: (a) total thermal conductivity and (b) electronic and lattice thermal conductivities.

conductivity (carrier concentration). However, the change in κ_L caused by Zn doping was not particularly large. Tippireddy *et al.* [12] proposed that tetrahedrite exhibited an intrinsically low thermal conductivity, and the doping of transition metal atoms substituting Cu atoms could reduce the lattice thermal conductivity through phonon scattering, bringing it close to the theoretical minimum value. In addition, they reported that the substitution of Zn for Cu led a low κ_E value due to the decrease in carrier concentration, resulting in low thermal conductivities of $0.55\text{--}0.79 \text{ W m}^{-1} \text{K}^{-1}$ at temperatures from 373 to 673 K.

Figure 8 shows the ZT values of the $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ samples. ZT increased with the temperature because the power factor increased while the thermal conductivity remained low at high temperatures, below the intrinsic transition. Among the Zn-doped specimens, $\text{Cu}_{11.6}\text{Zn}_{0.4}\text{Sb}_4\text{S}_{13}$ exhibited the highest ZT (0.76) at 723 K; however, this value was lower than that (0.86) of the undoped specimen at 723 K.

Fig. 8. Dimensionless figure of merit of $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites.

Tippireddy *et al.* [12] and Lu *et al.* [2] achieved maximum ZT values at 673 K of 0.71 and 0.80, respectively, for $\text{Cu}_{11}\text{ZnSb}_4\text{S}_{13}$ produced by melting, annealing, and hot pressing. Therefore, in this study, Zn-doped tetrahedrites could be synthesized by the MA-HP process without post-annealing, and showed good thermoelectric performance, comparable to that of specimens synthesized by the sophisticated melting method. However, Zn doping had a negative effect on the thermoelectric properties.

4. CONCLUSIONS

Zn-doped $\text{Cu}_{12-x}\text{Zn}_x\text{Sb}_4\text{S}_{13}$ ($x = 0\text{--}1.2$) tetrahedrites were successfully synthesized by MA without subsequent heat treatment. The synthesized powders were hot-pressed to obtain dense sintered bodies. The analysis of the XRD peaks and lattice constant variations confirmed the successful substitution of Zn at the Cu sites. The electrical conductivity showed a peak at 623 K for the undoped specimen, while it increased with increasing temperature for the Zn-doped specimens. As the Zn content increased, the electrical conductivity decreased and the Seebeck coefficient increased. However, Zn doping was not effective for increasing the power factor. As the Zn content increased, the thermal conductivity decreased and then reached a value close to the theoretical minimum. The contribution of the decrease in electron thermal conductivity prevailed over that of the

decrease in lattice thermal conductivity. $\text{Cu}_{11.6}\text{Zn}_{0.4}\text{Sb}_4\text{S}_{13}$ showed the highest figure of merit, $ZT = 0.76$, at 723 K.

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