Preparation and Thermoelectric Properties of Si-Doped Tetrahedrites Cu$_{12}$Sb$_{4-y}$Si$_y$S$_{13}$

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Abstract: Si-doped Cu$_{12}$Sb$_{4-y}$Si$_y$S$_{13}$ ($y = 0.1-0.4$) compounds were prepared using solid-state synthesis. Each specimen consisted of a single tetrahedrite phase with a densely sintered body whose relative density exceeded 98.9%. The lattice constant decreased from 1.0357 nm to 1.0336 nm as the Si content increased. When the Si doping content ($y$) exceeded 0.3, the decrease in the lattice constant was reduced and residual Si appeared. This established the solubility limit of Si at the Sb sites was $y = 0.3$. The Seebeck coefficient increased with the temperature and Si content, achieving a maximum value of 178 µVK$^{-1}$ at 723 K for $y = 0.3$. For the specimens with $y \leq 0.2$, the electrical conductivity increased with temperature, and then slightly decreased at temperatures higher than 623 K, while it gradually increased with temperature for the specimens with $y \geq 0.3$. The electrical conductivity decreased as the Si content increased at a constant temperature and the highest electrical conductivity of $(2.8-3.4) \times 10^4$Sm$^{-1}$ was obtained at 323–723 K for Cu$_{12}$Sb$_{3.9}$Si$_{0.1}$S$_{13}$. When $y = 0.4$, the electrical conductivity did not decrease further, which is related to the solubility limit of Si. The power factor reached a maximum value of 0.86 mWm$^{-1}$K$^{-2}$ at 723 K for Cu$_{12}$Sb$_{3.7}$Si$_{0.3}$S$_{13}$. As the Si content increased, the thermal conductivity tended to decrease, and Cu$_{12}$Sb$_{3.8}$Si$_{0.2}$S$_{13}$ exhibited the lowest thermal conductivity of 0.85 Wm$^{-1}$K$^{-1}$ at 723 K. Hence, the highest dimensionless figure of merit, ZT = 0.63 was achieved at 723 K for Cu$_{12}$Sb$_{3.8}$Si$_{0.2}$S$_{13}$.

(Received 19 January, 2022; Accepted 11 February, 2022)

Keywords: thermoelectric, tetrahedrite, mechanical alloying, hot pressing

1. INTRODUCTION

Tetrahedrite, which exhibits p-type semiconductor characteristics, is an earth-abundant sulfosalt natural mineral that has received much attention as an economical and eco-friendly material. Studies are being conducted to improve its thermoelectric performance by doping with synthetic tetrahedrite Cu$_{12}$Sb$_{4}$S$_{13}$ [1-3]. Previous research has focused on substitution with transition metal elements (Zn, Fe, Mn, and Ni) at Cu sites [4]. Tetrahedrite has a body-centered cubic structure (space group I43m) with 58 atoms in the unit cell, and consists of three sublattices: Cu$^{II}$S$_{4}$ tetrahedra, Cu$^{II}$S$_{3}$ triangular planes, and SbS$_{3}$ triangular pyramid [5-6]. The composition of tetrahedrite can be expressed as Cu$_{10}$Cu$_{5}$Sb$_{2}$Si$_{12}$S$_{31}$ considering the charge balance and atomic occupancy, where the Cu$^{II}$ atoms form weak Cu$^{II}$-Sb$^{3+}$ bonds, leaving Sb with lone-pair electrons [7]. Accordingly, the Sb atom exists as Sb$^{3+}$ rather than Sb$^{5+}$ in the structure [8]. As a result, tetrahedrite has inherently low thermal conductivity because of the influence of the co-polyhedron composed of Cu$_3$ and Sb$_3$ groups, which contain asymmetrically adjusted Cu and Sb [9].

When tetrahedrite is synthesized using the conventional melting method, precise temperature controls (very slow heating-holding-cooling steps) are required because the boiling point of S is lower than the melting point of Cu. Phase transformation and homogenization occur only after a long period of heat treatment [10,11]. Tanaka et al. [12] required more than 260 h (approximately 11 d) to synthesize homogeneous tetrahedrite via annealing after melting. Mechanical alloying (MA) has the advantages of avoiding phase separation and enabling homogenization by preventing the volatilization of elements [13]. Therefore, in this study, MA was employed for effective solid-state synthesis to
suppress the volatilization of the constituent elements, and hot pressing (HP) was performed to sinter the synthetic tetrahedrite.

To improve the thermoelectric properties of tetrahedrite, many studies have been conducted by substituting (doping) transition elements (Zn, Ni, Co, Fe, Mn, etc.) at the Cu sites [5,14-17]. The natural mineral tetrahedrite contains As, Bi, and Te as impurities at the Sb sites, and therefore, these elements can be used as dopants for synthetic tetrahedrite, however only a few studies have reported doing so [2,18,19]. In our previous study [18], Bi-doped tetrahedrites Cu_{12}Sb_{3-y}Bi_{y}S_{13} were prepared using the MA-HP process. The Cu_{12}Sb_{3.9}Bi_{0.1}S_{13} exhibited a high ZT = 0.88 at 723 K owing to the high power factor (1.02 mWm^{-1}K^{-2}) and low thermal conductivity (0.96 Wm^{-1}K^{-1}). Lu et al. [19] synthesized and consolidated Te-doped Cu_{12}Sb_{4-y}Te_{y}S_{13} by encapsulated melting (EM) and HP methods, and Cu_{12}Sb_{3}TeS_{13} achieved ZT = 0.92 at 723 K owing to the high Seebeck coefficient (194 μVK^{-1}) and low thermal conductivity (0.77 Wm^{-1}K^{-1}). Levinsky et al. [20] prepared As-doped Cu_{12}Sb_{4-y}As_{y}S_{13} using EM and spark plasma sintering (SPS), and reported ZT = 0.75 at 700 K, for Cu_{12}Sb_{2}As_{2}S_{13}, because of the very low lattice thermal conductivity (0.5 Wm^{-1}K^{-1}).

In the present study, various Cu_{12}Sb_{4-y}Si_{y}S_{13} (y = 0.1-0.4) samples were doped with Si at Sb sites and synthesized using MA and HP, and their thermoelectric properties were examined. Since additional electrons are generated by partially substituting Si^{4+} for Sb^{3+}, changes in the electrical and thermal properties were expected due to changes in carrier concentration.

### 2. EXPERIMENTAL PROCEDURE

MA was used to synthesize the Si-doped tetrahedrites Cu_{12}Sb_{4-y}Si_{y}S_{13} (y = 0.1, 0.2, 0.3, and 0.4). Elemental powders of Cu (purity 99.99%, < 45 m, Kojundo), Sb (purity 99.999%, < 150 mm Kojundo), Si (purity 99.99%, < 75 mm, Kojundo), and S (purity 99.99%, < 75 mm, Kojundo) were weighed according to their stoichiometric compositions. MA was conducted at 350 rpm for 24 h in an Ar atmosphere using a planetary ball milling system (Pulverisette5, Fritsch). The synthesized powder was sintered at 723 K for 2 h under 70 MPa via HP. The detailed MA-HP process conditions were reported in our previous study [21].

The phase was analyzed by X-ray diffraction (XRD; D8-Advance, Bruker) using Cu-Kα radiation. The fractured surfaces of the sintered specimens were observed using a scanning electron microscope (SEM; Quanta400, FEI), and chemical compositions were analyzed using an energy dispersive spectrometer (EDS; Quantax200, Bruker). The homogeneous distribution of the elements was confirmed by EDS elemental mapping. Charge transport parameters were measured using the van der Pauw method (Model 7065, Keithley). The Seebeck coefficient (α) and electrical conductivity (σ) were measured in a He atmosphere using the temperature-differential and DC four-probe methods, respectively (ZEM-3, Advance Riko), and then the power factor (PF = α^{2}σ) was evaluated. Thermal diffusivity was measured using the laser flash method (TC-9000H, Advance Riko) in vacuum, and thermal conductivity (κ) was estimated from the thermal diffusivity, density, and specific heat. Finally, the dimensionless figure of merit (ZT = α^{2}σTκ^{-1}) was examined.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the results of the XRD analysis of sintered Cu_{12}Sb_{4-y}Si_{y}S_{13} produced by the MA-HP method. The tetrahedrite phase (ICDD PDF#024-1318) was successfully synthesized, and no Cu-Sb-S or Cu-S-based secondary phases were identified. However, diffraction peaks for...
residual Si (ICDD PDF#080-0018) were observed for Cu$_{12}$Sb$_{3.6}$Si$_{0.4}$S$_{13}$. The lattice constant calculated by the Rietveld refinement (TOPAS Program) decreased from 1.0357 to 1.0336 nm as the Si content increased (Table 1). In our previous study, the lattice constant of undoped tetrahedrite (Cu$_{12}$Sb$_{4}$S$_{13}$) was reported to be 1.0391 nm [22]. Wuensch et al. [23] reported a similar value of 1.0390 nm. The decreased lattice constant was attributed to the substitution of smaller Si$^{4+}$ ions (ionic radius: 26 pm) for Sb$^{3+}$ (ionic radius: 76 pm) [24]. When $y \geq 0.3$, the lattice constant changed little, and the solubility limit of Si for Sb was considered, as shown in Fig. 1.

Figure 2 presents SEM images of the fractured surfaces of the sintered Cu$_{12}$Sb$_{4-y}$Si$_{y}$S$_{13}$. No remarkable difference in the microstructure was observed depending on the Si content, and a high post-sintering density was confirmed. As shown in Table 1, the relative density ranged between 98.9-100.0%, and the actual compositions resembled the nominal compositions. Figure 2 shows the EDS elemental maps of Cu$_{12}$Sb$_{3.8}$Si$_{0.2}$S$_{13}$, indicating homogeneous distribution of all the constituent elements. These results indicate the MA-HP process used for solid-state synthesis suppressed the volatilization of the component elements, forming a homogeneous tetrahedrite phase.

Figure 3 shows the carrier concentration and mobility with
In the temperature range of 323-623 K, Cu$_{12}$Sb$_{3.6}$Si$_{0.4}$S$_{13}$ possessed higher Seebeck coefficients of 136-169 μVK$^{-1}$, but Cu$_{12}$Sb$_{3.7}$Si$_{0.3}$S$_{13}$ exhibited the highest Seebeck coefficient of 178 μVK$^{-1}$ at 723 K. In our previous studies, the Seebeck coefficient of undoped Cu$_{12}$Sb$_4$S$_{13}$ [22] ranged from 144-190 μVK$^{-1}$ at 323-723 K, while Bi-doped Cu$_{12}$Sb$_{3.9}$Bi$_{0.1}$S$_{13}$ [18] exhibited 154-187 μVK$^{-1}$ at 323-723 K. Lu et al. [19] reported a significantly improved Seebeck coefficient with Te doping, resulting in a high Seebeck coefficient of 194 μVK$^{-1}$ at 723 K for Cu$_{12}$Sb$_3$TeS$_{13}$. Levinsky et al. [20] reported that the Seebeck coefficient of As-doped tetrahedrite increased monotonically as the temperature increased above 300 K regardless of the As content. They explained that this was consistent with the diffusive nature expected to occur in non-degenerate semiconductors. Hence, all of the Cu$_{12}$Sb$_{4-y}$As$_y$S$_{13}$ (y = 0-4) samples exhibited almost the same Seebeck coefficient values: 120-130 μVK$^{-1}$ at 300-700 K. In this study, it was determined that the Seebeck coefficient increased with the hole concentration because of the additional electrons caused by the doping with Si$^{4+}$ at the Sb$^{3+}$ sites.

Figure 4 shows the electrical conductivity of the Cu$_{12}$Sb$_{4-y}$Si$_y$S$_{13}$. For the specimens whose Si content was y ≤ 0.2, the electrical conductivity increased with temperature and then decreased slightly after reaching a peak value at 623 K, indicating the transition to conduction behavior, from non-degenerate semiconducting to degenerate semiconducting.
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Nasonova et al. [7] proposed that the increase in electrical resistivity signified a charge-ordering metal-to-semiconductor transition that should be accompanied by structural changes. However, the specimens with $y \geq 0.3$ exhibited non-degenerate semiconductor behavior, in which the electrical conductivity increased with the temperature.

The electrical conductivity decreased as the Si content increased at a constant temperature. $\text{Cu}_{12}\text{Sb}_{3.9}\text{Si}_{0.1}\text{S}_{13}$ exhibited the highest electrical conductivity of $(2.8-3.5) \times 10^4 \text{Sm}^{-1}$ at 323-723 K, which was similar to $(2.6-3.8) \times 10^4 \text{Sm}^{-1}$ at 323–723 K for the undoped tetrahedrite $\text{Cu}_{12}\text{Sb}_{4}\text{S}_{13}$ reported in our previous study [22]. Kwak et al. [18] reported that the electrical conductivity of Bi-doped tetrahedrites increased with the Bi content, and hence, $\text{Cu}_{12}\text{Sb}_{3.7}\text{Bi}_{0.3}\text{S}_{13}$ exhibited the highest electrical conductivity of $(3.1-3.5) \times 10^4 \text{Sm}^{-1}$ at 373–723 K. However, the lowest electrical conductivity was observed for $\text{Cu}_{12}\text{Sb}_{3.6}\text{Bi}_{0.4}\text{S}_{13}$ because of the existence of a secondary phase (skinnerite $\text{Cu}_3\text{SbS}_3$). Lu et al. [19] observed that for Te-doped tetrahedrites, carrier-phonon scattering began to dominate and the mobility decreased when the temperature reached 500–600 K, resulting in increased electrical resistivity (electrical conductivity decreased). Thus, $\text{Cu}_{12}\text{Sb}_{3.9}\text{Te}_{0.1}\text{S}_{13}$ exhibited a low electrical resistivity (high electrical conductivity) of $1.5 \times 10^5 \Omega\text{m}$ $(6.7 \times 10^4 \text{Sm}^{-1})$ at 723 K. Levinsky et al. [20] reported that As-doped tetrahedrites exhibited metallic behavior, in which the electrical resistivity increased with temperature and As content at 300-700 K. Consequently, $\text{Cu}_{12}\text{Sb}_{3.6}\text{AsS}_{13}$ displayed the lowest electrical resistivity (highest electrical conductivity) of $1.2 \times 10^5 \Omega\text{m}$ $(8.3 \times 10^4 \text{Sm}^{-1})$ at 700 K.

The power factor for the $\text{Cu}_{12}\text{Sb}_{4-y}\text{Si}_y\text{S}_{13}$ is shown in Fig. 6. The power factor, which was calculated using the relation $PF = \alpha^2 \sigma$, is proportional to the Seebeck coefficient and electrical conductivity. However, the Seebeck coefficient is inversely proportional to the carrier concentration, while the electrical conductivity is proportional to the carrier concentration [26]. Thus, there is trade-off relationship with these two parameters. As the temperature increased, the power factor increased because of the temperature...
dependence of the Seebeck coefficient and electrical conductivity. When the Si content increased at a constant temperature, the power factor tended to decrease, especially at high temperatures. This indicates that the decrease in the electrical conductivity dominated over the increase in the Seebeck coefficient for the decrease in the power factor by Si doping. Cu$_{12}$Sb$_{3-y}$Si$_y$Sb$_3$ exhibited the highest power factor of 0.86 mWm$^{-1}$K$^{-2}$ at 723 K because the electrical conductivity was the highest, although the Seebeck coefficient was the lowest. In our previous study [18], Cu$_{12}$Sb$_{1.8}$Bi$_{0.2}$Sb$_3$ achieved a maximum power factor of 1.02 mWm$^{-1}$K$^{-2}$ at 723 K owing to a high Seebeck coefficient. Lu et al. [19] obtained a higher power factor of 1.22 mWm$^{-1}$K$^{-2}$ at 723 K for Cu$_{12}$Sb$_{1.9}$Te$_{0.1}$Sb$_3$ (calculated using the Seebeck coefficient and electrical resistivity reported in the literature) because of the low electrical resistivity. Levinsky et al. [20] reported the highest power factor of 1.30 mWm$^{-1}$K$^{-2}$ at 700 K for Cu$_{12}$Sb$_{3-y}$As$_y$Sb$_3$ (calculated from the Seebeck coefficient and electrical resistivity reported in the literature). Therefore, in this study, Si doping at Sb sites was ineffective at further improving the power factor of tetrahedrite.

Figure 7 shows the thermal conductivities of Cu$_{12}$Sb$_{3-y}$Si$_y$Sb$_3$, which is expressed as the sum of the electronic thermal conductivity ($\kappa_e$) of carriers and the lattice thermal conductivity ($\kappa_l$) by phonons, which can be separated by the Wiedemann-Franz law ($\kappa_e = L\sigma T$, $L$: Lorenz number) [27]. The Lorenz number was estimated using the equation $L = \frac{1.5 + \exp(-0.1/116)}{T^2}$ [28]. As shown in Fig. 7(b), the electronic thermal conductivity decreased as the Si content increased, and increased with increasing temperature. However, the lattice thermal conductivity ranged from 0.54-0.72 Wm$^{-1}$K$^{-1}$ at 323-723 K without a specific dependence on the Si content and temperature.

Hence, as shown in Fig. 7(a), the total thermal conductivity exhibited the highest values at 623 K for the specimens with $y \leq 0.3$, while it increased with the temperature for the specimens with $y = 0.4$. Thus, increasing the Si content decreased the total thermal conductivity at a constant temperature, except at 723 K. Cu$_{12}$Sb$_{3-y}$Te$_y$Sb$_3$ exhibited the lowest thermal conductivity of 0.74-0.92 Wm$^{-1}$K$^{-1}$ at 323-623 K, while Cu$_{12}$Sb$_{3-y}$Bi$_y$Sb$_3$ exhibited the lowest thermal conductivity of 0.85 Wm$^{-1}$K$^{-1}$ at 723 K. Kwak et al. [18] achieved the lowest thermal conductivity of 0.63-0.78 Wm$^{-1}$K$^{-1}$ at 323-723 K for the Bi-doped Cu$_{12}$Sb$_{3-y}$Bi$_y$Sb$_3$. Lu et al. [19] reported that the thermal conductivity of Te-doped Cu$_{12}$Sb$_{3-y}$Te$_y$Sb$_3$ decreased as the temperature increased, where the lattice thermal conductivity dominated. In their previous study [29], they estimated a low lattice thermal conductivity of 0.3-0.4 Wm$^{-1}$K$^{-1}$, and consequently, the thermal conductivity of 0.64-0.77 Wm$^{-1}$K$^{-1}$ at 300-723 K was obtained for Cu$_{12}$Sb$_{3-y}$Te$_y$Sb$_3$. Levinsky et al. [20] observed that the lattice thermal conductivity of As-doped Cu$_{12}$Sb$_{3-y}$As$_y$Sb$_3$ was very low (0.5 Wm$^{-1}$K$^{-1}$ at temperatures above 300 K), and reported that the substitution of As for the Sb sites did not enhance point defect scattering. Consequently, Cu$_{12}$Sb$_{3-y}$As$_y$Sb$_3$ exhibited a relatively high thermal conductivity of 1.2-1.3 Wm$^{-1}$K$^{-1}$ at 300-700 K.

Figure 8 shows the temperature dependence of the Lorenz number for Cu$_{12}$Sb$_{3-y}$Si$_y$Sb$_3$. The Lorenz number decreased with increasing temperature in all the specimens, and it decreased as the Si content increased at a constant temperature. Theoretically, the Lorenz number ranges from $(1.45-2.44) \times 10^8$ V$^2$K$^{-2}$ [30], where the smaller values indicate the approach of non-degenerate semiconductor behavior. As shown in Fig. 8 and Table 1, the Lorenz number of the Si-doped tetrahedrites ranged from $1.81-1.86) \times 10^8$ V$^2$K$^{-2}$ at 323 K. Pi et al. [31] reported $1.76 \times 10^8$ V$^2$K$^{-2}$ at 323 K for undoped Cu$_{12}$Sb$_{3}$Sb$_3$, while Kwak et al. [18] obtained similar values of $(1.76-1.88) \times 10^8$ V$^2$K$^{-2}$ at 323 K for Cu$_{12}$Sb$_{3-y}$Bi$_y$Sb$_3$ ($y = 0.1-0.4$).
Figure 9 shows the dimensionless figure of merit $ZT$ for $\text{Cu}_{12}\text{Sb}_{4-y}\text{Si}_{y}\text{S}_{13}$. The $ZT$ increased as the temperature increased because of the increase in the power factor and the maintenance of low thermal conductivity. However, although the $ZT$ did not change significantly with Si doping content, it decreased at high temperatures for $y \geq 0.3$. For $\text{Cu}_{12}\text{Sb}_{3.8}\text{Si}_{0.2}\text{S}_{13}$, which exhibited a relatively low thermal conductivity ($0.90 \text{ Wm}^{-1}\text{K}^{-1}$) and high power factor ($0.79 \text{ mWm}^{-1}\text{K}^{-2}$). The maximum $ZT = 0.63$ was obtained at 723 K. In our previous study [18], Bi-doped $\text{Cu}_{12}\text{Sb}_{3.9}\text{Bi}_{0.1}\text{S}_{13}$ prepared by the MA-HP process achieved $ZT = 0.88$ at 723 K, due to the high power factor ($1.02 \text{ mWm}^{-1}\text{K}^{-2}$) and low thermal conductivity ($0.81 \text{ Wm}^{-1}\text{K}^{-1}$). Lu et al. [19] obtained $ZT = 0.92$ at 723 K for Te-doped $\text{Cu}_{12}\text{Sb}_{3.9}\text{Te}_{0.1}\text{S}_{13}$ synthesized by the EM-HP method, and suggested that the substitution of Te for the Sb sites effectively improved the thermoelectric performance of tetrahedrite. Levinsky et al. [20] achieved $ZT = 0.75$ at 700 K for As-doped $\text{Cu}_{12}\text{Sb}_{2}\text{As}_{0.1}\text{S}_{13}$ produced by the EM-SPS process, and reported that As doping at the Sb sites did not affect the thermoelectric performance of tetrahedrite.

Compared with the other studies on Sb-site doping, the $ZT$ of Si-doped tetrahedrites $\text{Cu}_{12}\text{Sb}_{3.9}\text{Si}_{0.1}\text{S}_{13}$ ($y = 0.1-0.4$) was relatively low, because of the low solubility limit of Si for Sb. Thus, the change in carrier concentration was insignificant, and the enhancement of phonon scattering by mass fluctuations was small. However, Si-doped tetrahedrites, which do not contain toxic and rare elements such as Te, As, and Bi, could be prepared using MA and HP, which are practical and relatively fast processes for solid-state synthesis and consolidation.

4. CONCLUSIONS

Densely-sintered Si-doped tetrahedrites $\text{Cu}_{12}\text{Sb}_{4-y}\text{Si}_{y}\text{S}_{13}$ ($y = 0.1-0.4$) were prepared using MA and HP. The tetrahedrite phase was successfully synthesized, and although no secondary phases were produced, residual Si elements appeared in the specimens whose Si content $y \geq 0.3$. The lattice constant decreased due to Si doping, because of the substitution of Si with a smaller ionic radius at the Sb sites. All the specimens had positive Seebeck coefficient values, confirming that they were p-type semiconductors. The Seebeck coefficient increased with the Si doping level, but the electrical conductivity decreased. $\text{Cu}_{12}\text{Sb}_{3.8}\text{Si}_{0.2}\text{S}_{13}$ achieved a maximum $ZT$ of 0.63 at 723 K, because of its lower thermal conductivity, despite the relatively low power factor.

ACKNOWLEDGMENT

This study was supported by the Basic Science Research Capacity Enhancement Project (National Research Facilities and Equipment Center) through the Korea Basic Science Institute funded by the Ministry of Education (Grant No. 2019R1A6C1010047).

REFERENCES

5. K. Suekuni, K. Tsuruta, M. Kunii, H. Nishiate, E. Nishibori,