Solid-State Synthesis and Thermoelectric Properties of Ge-Doped Tetrahedrites Cu$_{12}$Sb$_{4-y}$Ge$_y$S$_{13}$

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Abstract: Ge-doped tetrahedrites Cu$_{12}$Sb$_{4-y}$Ge$_y$S$_{13}$ ($y = 0.1–0.4$) were prepared using mechanical alloying and hot pressing. An X-ray diffraction analysis after mechanical alloying showed a single tetrahedrite phase without secondary phases. The tetrahedrite phase was stable after hot pressing at 723 K under 70 MPa. As the Ge content increased, the lattice constant decreased from 1.0343 to 1.0334 nm, which confirms that Ge was successfully substituted at the Sb sites. Ge-doped tetrahedrites exhibited p-type semiconductor characteristics. When Ge$^{4+}$ was substituted for Sb$^{3+}$, additional electrons were generated. Thus, the electrical conductivity decreased and the Seebeck coefficient increased due to the decrease in carrier (hole) concentration. For the Ge-doped specimen with $y = 0.1$, a maximum power factor of 0.87 mWm$^{-1}$K$^{-2}$ was obtained at 723 K. As the Ge content increased, the power factor decreased. However, as the Ge content increased, the electronic and lattice thermal conductivities decreased. Therefore, the substitutions of Ge at the Sb sites intensified both ionization impurity scattering and phonon scattering, resulting in very low thermal conductivities of 0.4–1.0 Wm$^{-1}$K$^{-1}$ at 323–723 K for $y = 0.1–0.4$. As a result, the highest dimensionless figure of merit $ZT = 0.74$ was obtained at 723 K for Cu$_{12}$Sb$_{3.8}$Ge$_{0.2}$S$_{13}$.

(Received 30 November, 2021; Accepted 12 January 2022)

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

1. INTRODUCTION

Recently, in efforts to address renewable energy and environmental issues, thermoelectric energy conversion has attracted considerable attention [1]. Tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$ has been studied as a p-type thermoelectric material, consisting of earth-abundant sulfosalt minerals and eco-friendly elements [2–4]. The tetrahedrite is composed of Cu$^I$S$_4$ tetrahedra, Cu$^{II}$S$_3$ triangles, and SbS$_3$ pyramids. It belongs to the space group I$\overline{4}$ 3 m. 58 atoms are arranged in a complex crystal structure in a cubic unit cell [5]. One of the most striking features of tetrahedrite is its very low thermal conductivity. The vertically coordinated Cu$^{II}$ atoms within the triangular plane of three S atoms vibrate anharmonically at low frequencies and high amplitudes, hindering heat transfer due to the attraction or repulsion of the active lone-pair electrons of Sb within the complex crystal structure. The reduction in heat transfer also leads to low thermal conductivity due to a low-energy state, resulting from the acoustic phonons and rattling mode of anharmonic waves due to phonon–phonon scattering [6, 7]. The composition of tetrahedrite is represented as Cu$_6^I$Cu$_2^{II}$Sb$_4$S$_{12}$S$^8$. Numerous studies have attempted to improve the compound’s thermoelectric properties by substituting some doping elements at the Cu$^{II}$, Sb, or S$^{II}$ sites [8]. The addition of dopants may affect the carrier concentration, and induce structural changes [9].

Previous studies have focused on substituting Cu with other transition elements (Zn, Fe, Ni, Mn, etc.); no extensive studies have been reported on the substitution (doping) of the Sb sites. In our previous study, Cu$_{12}$Sb$_{4-y}$Bi$_y$S$_{13}$ ($y = 0.1–0.4$) doped with Bi at Sb sites was successfully prepared by mechanical alloying (MA) and hot pressing (HP). The carrier concentration increased with the Bi doping level in the temperature range of 323–723 K. The resulting Cu$_{12}$Sb$_{3.8}$Bi$_{0.2}$S$_{13}$ exhibited a dimensionless figure of merit $ZT = 0.88$ at 723 K.
because of its high power factor and very low thermal conductivity [10]. Bouyrie et al. [11] synthesized a Te-doped Cu$_{12}$Sb$_4$Te$_3$$_{13}$ ($y = 0.52$–1.85) using encapsulated melting (EM) and spark plasma sintering (SPS) and obtained a maximum $ZT = 0.80$ at 623 K for Cu$_{12}$Sb$_{3.39}$Te$_{0.61}$S$_{13}$ because of its very low thermal conductivity. Lu et al. [12] prepared Cu$_{12}$Sb$_y$Te$_3$S$_{13}$ ($y = 0–1$) using the EM–milling–HP method and achieved a high $ZT$ of 0.92 at 723 K for Cu$_{12}$Sb$_1$Te$_3$$_{13}$.

When tetrahedrite is synthesized by a conventional melting method, because S has a boiling point (717 K) lower than the melting point (1356 K) of Cu, elaborate heating, maintenance, and cooling steps are required. In addition, a long subsequent annealing should be carried out for phase transformation and homogenization [13–14]. However, MA can be used to avoid phase separation and evaporation of elements through a low-temperature solid-state process and can synthesize and homogenize a nanopowder [15]. In this study, Cu$_{12}$Sb$_y$Ge$_3$S$_{13}$ ($y = 0.1$–0.4) partially substituted with Ge at the Sb sites, were synthesized by MA and sintered by HP and their phases and thermoelectric properties were analyzed. By doping Ge at the Sb sites, the optimal carrier concentration was adjusted to change the electrical conductivity and Seebeck coefficient and maximize the power factor. An improved dimensionless figure of merit was expected by maintaining a high power factor and reducing the thermal conductivity, due to carrier and phonon transport variations.

2. EXPERIMENTAL PROCEDURE

Ge-doped tetrahedrites Cu$_{12}$Sb$_y$Ge$_3$S$_{13}$ ($y = 0.1$, 0.2, 0.3, and 0.4) were synthesized by MA. Cu (<45 μm, purity: 99.99%), Sb (<150 μm, purity: 99.999%), Ge (<45 μm, purity: 99.99%), and S (<75 μm, purity: 99.99%) were weighed to obtain the corresponding stoichiometric compositions. Mixed powders and stainless-steel balls were placed in a hardened steel jar. Once the inside of the jar was vacuumed, Ar gas was injected and MA was performed for 24 h at a rotational speed of 350 rpm using a planetary ball mill (Fritsch Pulverisette5). The powder synthesized through MA was charged into a graphite mold and sintered by HP for 2 h at 723 K under 70 MPa in a vacuum atmosphere. The detailed MA–HP conditions are presented in our previous report [16].

The sintered specimen was cut into disks with dimensions of 1 mm (thickness) × 10 mm (diameter) to measure the Hall coefficient and thermal conductivity, and cut into a parallelepiped with dimensions of 3 mm (width) × 3 mm (depth) × 9 mm (height) to measure the Seebeck coefficient and electrical conductivity.

A phase analysis of the MA–HP specimens was performed using X-ray diffraction (XRD; Bruker D8–Advance) with Cu K$_\alpha$ radiation. The diffraction pattern was obtained at a scan speed of 0.4 s/step. The crystallinity and lattice constants were estimated by Rietveld refinement (TOPAS). The microstructures of fractured surfaces of the sintered specimens were observed using scanning electron microscopy (SEM; FEI Quanta400) equipped with energy-dispersive spectrometry (EDS; Bruker Quantax200). For the EDS analysis, elemental energy levels were used, including those of Cu L$_\alpha$ (0.928 eV), Sb L$_\alpha$ (3.604 eV), Ge L$_\alpha$ (1.188 eV), and S K$_\alpha$ (2.309 eV). Through the EDS elemental mapping, the homogeneous distribution of the constituent elements was confirmed. The Hall coefficient was measured by applying a constant magnetic field of 1 T and current of 100 mA using the van der Pauw method (Keithley 7065), and then carrier concentration and mobility were analyzed. The Seebeck coefficient ($\alpha$) and electrical conductivity ($\sigma$) were measured in a He atmosphere using the temperature differential method and direct-current (DC) four-probe method, respectively (Ulvac-Riko ZEM-3). The thermal diffusivity was measured in vacuum using the laser flash method (Ulvac-Riko TC-9000H), and then the thermal conductivity ($\kappa$) was estimated from the thermal diffusivity, specific heat, and density. Finally, the power factor (PF = $\alpha^2\sigma$) and dimensionless figure of merit ($ZT = \alpha^2\sigma\kappa^{-1}T$) were evaluated.

3. RESULTS AND DISCUSSION

Figure 1 shows the results of the XRD analysis of the Ge-doped tetrahedrites Cu$_{12}$Sb$_4$Ge$_3$S$_{13}$ prepared by the MA–HP process. All diffraction peaks were consistent with the standard diffraction data (International Center for Diffraction Data (ICDD) PDF#024-1318) for tetrahedrite. All specimens contained a single tetrahedrite phase without unreacted residual elements and secondary phases. As shown in Table

 Shares an image that cannot be rendered.
Rietveld refinement confirmed that the lattice constant decreased from 1.0343 to 1.0334 nm as the Ge content increased, because the ionic radius of Ge^{4+} (39 pm) is smaller than that of Sb^{3+} (76 pm). Thus, the lattice constant decreased with the increase in the Ge substitution at the Sb sites [17].

Figure 1 shows XRD patterns of MA and HP Cu_{12}Sb_{4-}yGe_{y}S_{13} tetrahedrites.

Table 1. Chemical compositions and physical properties of Cu_{12}Sb_{4-}yGe_{y}S_{13}.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Nominal</th>
<th>Actual</th>
<th>Relative density [%]</th>
<th>Lattice constant [nm]</th>
<th>Lorenz number [10^{-8} \text{V}^2\text{K}^{-2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_{12}Sb_{3.9}Ge_{0.1}S_{13}</td>
<td>Cu_{12.89}Sb_{3.83}Ge_{0.12}S_{12.15}</td>
<td>99.3</td>
<td>1.0343</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>Cu_{12}Sb_{3.8}Ge_{0.2}S_{13}</td>
<td>Cu_{12.42}Sb_{3.72}Ge_{0.20}S_{12.64}</td>
<td>100.0</td>
<td>1.0339</td>
<td>1.69</td>
<td></td>
</tr>
<tr>
<td>Cu_{12}Sb_{3.7}Ge_{0.3}S_{13}</td>
<td>Cu_{12.32}Sb_{3.90}Ge_{0.25}S_{12.51}</td>
<td>99.6</td>
<td>1.0337</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>Cu_{12}Sb_{3.6}Ge_{0.4}S_{13}</td>
<td>Cu_{12.44}Sb_{3.90}Ge_{0.41}S_{12.23}</td>
<td>98.5</td>
<td>1.0334</td>
<td>1.61</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 shows the chemical compositions and physical properties of Cu_{12}Sb_{4-}yGe_{y}S_{13}. Notably, no remarkable difference in the microstructure was observed according to the Ge content. Densely sintered specimens could be obtained. As shown in Table 1, all of the specimens exhibited high relative densities of 98.5%–100.0%. The actual compositions were similar to the nominal compositions. The volatilization of component elements was suppressed due to the solid-state synthesis using MA. The EDS elemental maps for Cu_{12}Sb_{3.6}Ge_{0.2}S_{13} confirmed that every element was homogeneously distributed.

Figure 2 shows SEM images of the fractured surfaces of the sintered Cu_{12}Sb_{4-}yGe_{y}S_{13}. Notably, no remarkable difference in the microstructure was observed according to the Ge content. Densely sintered specimens could be obtained. As shown in Table 1, all of the specimens exhibited high relative densities of 98.5%–100.0%. The actual compositions were similar to the nominal compositions. The volatilization of component elements was suppressed due to the solid-state synthesis using MA. The EDS elemental maps for Cu_{12}Sb_{3.6}Ge_{0.2}S_{13} confirmed that every element was homogeneously distributed.

Figure 3 shows the carrier concentration and mobility of Cu_{12}Sb_{4-}yGe_{y}S_{13}. Because of the substitution of Ge^{4+} at the Sb^{3+} sites, the carrier concentration was expected to decrease by reducing the number of holes (majority carriers) by the additionally supplied electrons (charge compensation). However, the change in the carrier (hole) concentration with the Ge content was not large, and the mobility decreased as the Ge content increased. When the Hall coefficient was measured 15 times on the same specimen, different values...
with large errors were obtained. Similar results have been reported \[3,18\], where very low Hall coefficients close to zero or very different values were obtained in repeated measurements on the same tetrahedrite sample. Therefore, the measured Hall coefficient of tetrahedrite did not have reliable accuracy.

Figure 4 shows the Seebeck coefficient for Cu$_{12}$Sb$_4$-$_y$Ge$_y$S$_{13}$. Positive Seebeck coefficients were obtained as positive signs of the Hall coefficient, which indicated that the majority carrier was holes, for a \( p \)-type semiconductor. When \( y = 0.1 \)–\( 0.3 \), the Seebeck coefficient increased with the temperature, while, when \( y = 0.4 \), the Seebeck coefficient exhibited a negative temperature dependence. In general, the Seebeck coefficient of a \( p \)-type semiconductor increases as the temperature increases \[19\]. However, when the temperature exceeds a certain value, an intrinsic transition occurs, which rapidly increases the carrier concentration, leading to a decrease in the Seebeck coefficient. In other words, as the temperature of the semiconductor increases, the Seebeck coefficient decreases after reaching the highest value at a specific temperature. In this study, the intrinsic transition only occurred in Cu$_{12}$Sb$_{3.6}$Ge$_{0.4}$S$_{13}$ and did not occur in the other specimens within the measurement temperature range. Thus, the Seebeck coefficient increased with the temperature. However, in the case of Cu$_{12}$Sb$_{3.6}$Ge$_{0.4}$S$_{13}$, the intrinsic transition seemed to occur at temperatures below 323 K. As a result, the carrier concentration rapidly increased with the temperature, while the Seebeck coefficient decreased.

As the Ge content increased at a constant temperature, the Seebeck coefficient increased. Therefore, the Ge doping reduces the carrier (hole) concentration, which increases the Seebeck coefficient. In this study, Cu$_{12}$Sb$_{3.6}$Ge$_{0.4}$S$_{13}$ exhibited the highest Seebeck coefficient of 251–224 \( \mu \)VK$^{-1}$ at 323–723 K, higher than the Seebeck coefficient of 105–140 \( \mu \)VK$^{-1}$ for an undoped Cu$_{12}$Sb$_{4}$S$_{13}$ in the temperature range of 300–690 K reported by Barbier \textit{et al.} \[4\]. Kwak \textit{et al.} \[10\] achieved a maximum of 154–187 \( \mu \)VK$^{-1}$ at 323–723 K for Cu$_{12}$Sb$_{3.9}$Bi$_{0.1}$S$_{13}$ among Cu$_{12}$Sb$_{4}$-$_y$Bi$_y$S$_{13}$ (\( y = 0.1 \)–\( 0.4 \)) specimens. Bouyrie \textit{et al.} \[11\] obtained a maximum of 190–260 \( \mu \)VK$^{-1}$ at 300–700 K for Cu$_{12}$Sb$_{2.15}$Te$_{1.85}$S$_{13}$ among Cu$_{12}$Sb$_{4}$-$_y$Te$_y$S$_{13}$ (\( y = 0.52 \)–\( 1.85 \)) specimens. Therefore, the Ge doping at Sb sites was very effective at increasing the Seebeck coefficient of tetrahedrite.

Figure 5 shows the electrical conductivity of Cu$_{12}$Sb$_4$-$_y$Ge$_y$S$_{13}$. At \( y = 0.1 \)–\( 0.3 \), the electrical conductivity initially increased with the temperature, and then decreased slightly at temperatures above 623 K. This was expected to transit the conduction mechanism of tetrahedrite from nondegenerate semiconducting to metallic (or degenerate semiconducting). However, for \( y = 0.4 \), the nondegenerate semiconductor behavior was maintained in the measured temperature range. At a constant temperature, the electrical conductivity decreased as the Ge content increased, which resulted from the reduced carrier (hole) concentration due to additional electrons with the Ge$^{4+}$ substitutions at the Sb$^{3+}$ sites. In this study, Cu$_{12}$Sb$_{3.6}$Ge$_{0.4}$S$_{13}$ exhibited the highest electrical conductivity of \( (2.8 \text{–} 3.2) \times 10^4 \) Sm$^{-1}$ at 323–723 K. Barbier \textit{et al.}
Fig. 5. Temperature dependence of the electrical conductivity of Cu$_{12}$Sb$_{4-x}$Ge$_x$S$_{13}$.

Fig. 6. Temperature dependence of the power factor of Cu$_{12}$Sb$_{4-x}$Ge$_x$S$_{13}$.

al. [4] reported an electrical conductivity of $(4.3-6.2) \times 10^4$ Sm$^{-1}$ at 300–690 K for the undoped Cu$_{12}$Sb$_{13}$. Kwak et al. [10] suggested that, as the Bi content of Cu$_{12}$Sb$_{4-x}$Bi$_x$S$_{13}$ ($y = 0.1-0.4$) increased, more Cu vacancies acting as acceptors resulted in the carrier concentration increase. As a result, Cu$_{12}$Sb$_{13}$Bi$_{0.4}$S$_{13}$ exhibited the highest electrical conductivity of $(3.1-3.6) \times 10^4$ Sm$^{-1}$ at 323–723 K. However, when the Bi content increased to $y = 0.4$, the electrical conductivity decreased to $(1.5-2.1) \times 10^4$ Sm$^{-1}$ due to the formation of a secondary phase (skinnerite; Cu$_{13}$Sb$_{3}$). Bouyrie et al. [11] reported that Cu$_{12}$Sb$_{3.48}$Te$_{0.52}$S$_{13}$ among Cu$_{12}$Sb$_{4-y}$Te$_{y}$S$_{13}$ ($y = 0.52-1.85$) specimens exhibited the highest electrical conductivity of $(10.0-6.7) \times 10^4$ Sm$^{-1}$ at 300–700 K.

Figure 6 shows the power factor for Cu$_{12}$Sb$_{4-x}$Ge$_x$S$_{13}$. The power factor is expressed by $PF = \alpha \sigma$ [20]. Because the carrier concentration has opposite effects on these two parameters, the optimal carrier concentration is necessary to obtain the maximum power factor. In this study, the PF increased as the temperature increased, which resulted from the temperature dependence of the Seebeck coefficient (Fig. 4) and electrical conductivity (Fig. 5). As the Ge content increased at a constant temperature, the PF decreased, because the decrease in the electrical conductivity was more dominant than the increase in the Seebeck coefficient due to Ge doping. Although Cu$_{12}$Sb$_{3.4}$Ge$_{0.6}$S$_{13}$ had the lowest Seebeck coefficient, due to the influence of its highest electrical conductivity, the highest PF of 0.38–0.87 mWm$^{-1}$K$^{-2}$ were obtained in the temperature range of 323–723 K. Barbier et al. [4] reported a PF of 0.60–1.02 mWm$^{-1}$K$^{-2}$ at 300–700 K for the undoped Cu$_{12}$Sb$_{13}$. Kwak et al. [10] obtained a maximum PF of 0.51–1.02 mWm$^{-1}$K$^{-2}$ at 323–723 K for Cu$_{12}$Sb$_{3.48}$Bi$_{0.52}$S$_{13}$. Bouyrie et al. [11] achieved a maximum PF of 0.96–1.48 mWm$^{-1}$K$^{-2}$ at 300–700 K for Cu$_{12}$Sb$_{3.48}$Te$_{0.52}$S$_{13}$ (calculated by the Seebeck coefficient and electrical conductivity data in the literature).

Figure 7 (a) shows the thermal conductivity of Cu$_{12}$Sb$_{4-x}$Ge$_x$S$_{13}$. The thermal conductivity initially increased with the temperature, and then decreased at temperatures above 623 K. When the Ge content was increased at a constant temperature, the thermal conductivity decreased, and thus Cu$_{12}$Sb$_{3.48}$Ge$_{0.52}$S$_{13}$ exhibited a minimum value of 0.46–0.59 Wm$^{-1}$K$^{-1}$ at 323–723 K. Barbier et al. [4] reported relatively high thermal conductivities of 0.92–1.25 Wm$^{-1}$K$^{-1}$ at 300–690 K for the undoped Cu$_{12}$Sb$_{13}$. Kwak et al. [10] obtained a low thermal conductivity of 0.63–0.78 Wm$^{-1}$K$^{-1}$ at 323–723 K for Cu$_{12}$Sb$_{3.48}$Bi$_{0.52}$S$_{13}$ owing to phonon scattering caused by the secondary phase of skinnerite. Bouyrie et al. [11] reported low thermal conductivities of 0.45–0.60 Wm$^{-1}$K$^{-1}$ at 300–700 K for Cu$_{12}$Sb$_{3.48}$Te$_{0.52}$S$_{13}$. The thermal conductivity has two components: the lattice thermal conductivity ($\kappa_L$) and electronic thermal conductivity ($\kappa_e$). The $\kappa_L$ can be separated using the Wiedemann–Franz law ($\kappa_L = \alpha L \sigma T$, where $L$ is the Lorenz number) [21]. The Lorenz number was calculated using the equation $L \left[10^8 \text{V}^2\text{K}^{-2}\right] = 1.5 + \exp(-\alpha/116)$ [22].
As shown in Fig. 8, as the temperature increased from 323 to 723 K, the Lorenz number decreased for $y = 0.1-0.3$, while it increased slightly for $y = 0.4$. The Lorenz number decreased as the Ge content increased at a constant temperature, which reflects the behavior of a nondegenerate semiconductor. Cu$_{12}$Sb$_{3.6}$Ge$_{0.4}$S$_{13}$ exhibited the lowest value of $(1.61–1.64) \times 10^{-8}$ V$^2$K$^{-2}$ at 323–723 K. Pi et al. [23] reported higher values of $(1.76–1.69) \times 10^{-8}$ V$^2$K$^{-2}$ at 323–723 K for an undoped Cu$_{12}$Sb$_{4}$S$_{13}$.

As shown in Fig. 7 (b), the $\kappa_L$ increased with the temperature. However, the total thermal conductivity in Fig. 7 (a) decreased after reaching a maximum value at 623 K, owing to the competition between the $\kappa_L$ increase and $\kappa_E$ decrease with the increase in temperature. The $\kappa_L$ is related to electrical conductivity (carrier concentration) and Lorenz number. Thus, it is consistent with the tendency to decrease as the Ge content increases at a constant temperature. Cu$_{12}$Sb$_{3.6}$Ge$_{0.4}$S$_{13}$ exhibited the lowest $\kappa_L$ of 0.01–0.08 Wm$^{-1}$K$^{-1}$ at 323–723 K. Kim et al. [16] reported higher values of 0.13–0.34 Wm$^{-1}$K$^{-1}$ at 323–723 K for an undoped Cu$_{12}$Sb$_{4}$S$_{13}$. Kwak et al. [10] achieved a lower $\kappa_L$ of 0.09–0.25 Wm$^{-1}$K$^{-1}$ at 323–723 K for Cu$_{12}$Sb$_{3.6}$Bi$_{0.4}$S$_{13}$. Bouyrie et al. [11] obtained very low $\kappa_L$ of 0.01–0.06 Wm$^{-1}$K$^{-1}$ at 300–700 K for Cu$_{12}$Sb$_{2.15}$Te$_{1.85}$S$_{13}$. In this study, the $\kappa_L$ decreased with the increase in Ge content. Cu$_{12}$Sb$_{3.6}$Ge$_{0.4}$S$_{13}$ exhibited the lowest $\kappa_L$ of 0.45–0.55 Wm$^{-1}$K$^{-1}$ at 323–723 K. In this regard, as shown in Fig. 7 (a), the total thermal conductivity had the lowest value of 0.46–0.59 Wm$^{-1}$K$^{-1}$. Kim et al. [16] reported $\kappa_L$ of 0.60–0.43 Wm$^{-1}$K$^{-1}$ at 323–723 K for an undoped Cu$_{12}$Sb$_{4}$S$_{13}$. Kwak et al. [10] obtained the lowest $\kappa_L$ of 0.57–0.38 Wm$^{-1}$K$^{-1}$ at 323–723 K for Cu$_{12}$Sb$_{3.6}$Bi$_{0.4}$S$_{13}$. Bouyrie et al. [11] achieved the lowest $\kappa_L$ of 0.45–0.43 Wm$^{-1}$K$^{-1}$ at 300–700 K for Cu$_{12}$Sb$_{2.15}$Te$_{1.85}$S$_{13}$.

Figure 9 compares the dimensionless figures of merit (ZT) for Cu$_{12}$Sb$_{3.6}$Ge$_y$S$_{13}$ ($y = 0.1–0.4$) produced by the MA–HP process in this study and ZT values in the literature upon doping the Sb sites of tetrahedrite. For Cu$_{12}$Sb$_{3.6}$Ge$_{0.4}$S$_{13}$, the ZT values of all specimens increased with temperature from 323 to 723 K. This resulted from the increase in the power factor and maintenance of low thermal conductivity as the temperature increased. At a constant temperature, as the Ge doping content increased, a high ZT value was maintained. However, when $y \geq 0.3$, ZT decreased, because the power
factor decreased as the Ge content increased. 

Cu$_{12}$Sb$_{3.9}$Ge$_{0.1}$S$_{13}$ exhibited the highest ZT of 0.74 at 723 K owing to the high power factor (0.77 mWm$^{-1}$K$^{-2}$) and low thermal conductivity (0.73 Wm$^{-1}$K$^{-1}$). Barbier et al. [4] reported a maximum ZT of 0.60 at 700 K for the undoped Cu$_{12}$Sb$_{4}$S$_{13}$ synthesized by EM and SPS. Therefore, the partial substitution of Ge at the Sb sites of tetrahedrite contributed to the improvement in the thermoelectric performance. Kwak et al. [10] obtained a maximum ZT of 0.88 at 723 K for Cu$_{12}$Sb$_{3.9}$Bi$_{0.1}$S$_{13}$ prepared by MA and HP. Bouyrie et al. [11] reported a maximum ZT of 0.80 at 623 K for Cu$_{12}$Sb$_{3.39}$Te$_{0.61}$S$_{13}$ synthesized and consolidated using EM and SPS. In this study, the solid-state synthesis using MA provided a single tetrahedrite phase without additional post annealing, in a relatively short time period of 24 h, and excellent thermoelectric performance of the Ge-doped tetrahedrites could be achieved.

4. CONCLUSIONS

Ge-doped tetrahedrites Cu$_{12}$Sb$_{4-y}$Ge$_{y}$S$_{13}$ ($y = 0.1$–0.4) were synthesized by MA, and then sintered by HP to produce dense specimens. The lattice constant was reduced by Ge doping, which indicated that Ge$^{4+}$ with a smaller ionic radius was substituted at the Sb$^{3+}$ sites. Ge-doped tetrahedrites are p-type nondegenerate semiconductors, as confirmed by the Hall coefficient, Seebeck coefficient, and Lorenz number. As the Ge doping level increased at a constant temperature, the electrical conductivity decreased, while the Seebeck coefficient increased. The Ge doping at Sb sites was expected to reduce the carrier (hole) concentration despite Hall measurement errors. In addition, the Ge doping reduced both electronic thermal conductivity and lattice thermal conductivity, and thus the total thermal conductivity decreased. Cu$_{12}$Sb$_{3.8}$Ge$_{0.2}$S$_{13}$ exhibited a maximum power factor of 0.87 mWm$^{-1}$K$^{-2}$ at 723 K. However, when the Ge content increased, the effect of decreasing electrical conductivity was dominant over that of increasing the Seebeck coefficient, resulting in a decrease in power factor. As a result, the highest ZT (0.74) was achieved at 723 K for Cu$_{12}$Sb$_{3.8}$Ge$_{0.2}$S$_{13}$.

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).

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