Improved Thermoelectric Performance of \( \text{Cu}_3\text{Sb}_{1-x-y}\text{Sn}_x\text{In}_y\text{Se}_4 \) Permingeatites Double-Doped with Sn and In

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Abstract: Cu–Sb–Se ternary chalcogenide compounds composed of earth-abundant low-toxicity elements are attracting attention as economical and ecofriendly semiconductors. Among them, permingeatite (\( \text{Cu}_3\text{SbSe}_4 \)) is a potential thermoelectric material with high Seebeck coefficient and low lattice thermal conductivity. However, it is necessary to improve its thermoelectric properties through doping, as it has low electrical conductivity due to its low intrinsic carrier concentration. In this study, samples of \( \text{Cu}_3\text{Sb}_{1-x-y}\text{Sn}_x\text{In}_y\text{Se}_4 \) \( (0.02 \leq x \leq 0.08 \) and \( 0.04 \leq y \leq 0.06) \) double-doped with In (group 13 element) and Sn (group 14 element) at the Sb (group 15 element) sites of permingeatite were synthesized and their thermoelectric performances were evaluated. All samples exhibited a single phase of permingeatite with tetragonal structure, and high relative densities of 97.4–98.9%. The lattice constants of the a- and c-axes were 0.5651–0.5654 and 1.1249–1.1257 nm, respectively, owing to the successful substitution of Sn and In at the Sb sites. As the doping concentrations of Sn and In increased, the carrier (hole) concentration increased. Thus, the Seebeck coefficient decreased, while the electrical and thermal conductivities increased. Sn doping was found to be more effective than In doping. Because \( \text{Cu}_3\text{Sb}_{0.96-x}\text{Sn}_x\text{In}_{0.04}\text{Se}_4 \) exhibits higher Seebeck coefficients than \( \text{Cu}_3\text{Sb}_{0.96-x}\text{Sn}_x\text{In}_{0.06}\text{Se}_4 \), larger power factors and higher dimensionless figures of merit (ZTs) were achieved for the \( \text{Cu}_3\text{Sb}_{0.96-x}\text{Sn}_x\text{In}_{0.04}\text{Se}_4 \) specimens. \( \text{Cu}_3\text{Sb}_{0.92}\text{Sn}_{0.04}\text{In}_{0.04}\text{Se}_4 \) achieved a maximum ZT of 0.59 at 623 K, based on its Seebeck coefficient of 161 \( \mu \text{VK}^{-1} \), electrical conductivity of \( 4.69 \times 10^4 \) Sm\(^{-1} \), thermal conductivity of 0.77 Wm\(^{-1}\)K\(^{-1} \), and power factor of 1.22 mWm\(^{-1}\)K\(^{-2} \).

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1. INTRODUCTION

The depletion of natural energy resources has increased interest in thermoelectric power generation technology which can generate electricity from waste heat [1-3]. The energy-conversion efficiency of thermoelectric power generation is determined by a dimensionless figure of merit (ZT), which depends on material factors (Seebeck coefficient: \( \alpha \), electrical conductivity: \( \sigma \), and thermal conductivity: \( \kappa \)) and operating temperature (absolute temperature: \( T \)) [4-7]:

\[
ZT = \frac{\alpha^2 \sigma}{\kappa} T
\]

Accordingly, a high ZT value can be obtained by increasing the power factor \((\alpha^2 \sigma)\) and/or reducing the thermal conductivity [8,9]. The Seebeck coefficient can be increased by adopting a large effective mass or a complex energy-band structure, and the concentration and mobility of charge carriers should be increased to increase the electrical conductivity. However, because the Seebeck coefficient decreases when the charge-carrier concentration is increased, the power factor can be maximized by optimizing the carrier concentration. Methods of reducing the thermal conductivity include using a large unit cell, reducing the mean free path of phonons, and increasing phonon scattering using impurities. However, because the Seebeck coefficient, electrical conductivity, and thermal conductivity are all dependent on the carrier concentration, it is difficult to optimize them simultaneously [1,7].

\( \text{Cu}_3\text{SbSe}_4 \) (permingeatite) has a deformed zinc-blende structure belonging to the space group \( \overline{I}42m \) and consists of SbSe\(_4\) tetrahedra with one-dimensional Sb–Se bonds and...
CuSe$_4$ tetrahedra with a three-dimensional framework of Cu–Se bonds [10–13]. It is an ecofriendly and economical compound composed of low-toxicity earth-abundant elements and has been attracting attention as a p-type thermoelectric material in the mid-temperature region owing to its narrow bandgap energy and large carrier effective mass [10,14]. However, its greatest drawback is its low electrical conductivity, due to the low carrier (hole) concentration [10].

The thermoelectric performance can be improved by partially substituting other elements in Cu$_2$SbSe$_4$, thereby maximizing the power factor by optimizing the carrier concentration, and by decreasing the lattice thermal conductivity through phonon scattering. Garcia et al. [15] predicted the thermoelectric performance of doped permingeatites Cu$_x$Sb$_{1−x}$M$_x$Se$_4$ (M = Al, Ga, In, Ti, Si, Ge, Sn, Pb, As, and Bi) using the density-functional theory and Boltzmann semiclassical transport theory. They reported the highest ZT value for the As-doped sample at 300 K, and decreasing ZT values for the samples doped with Bi, P, Si, Ge, Pb, Sn, In, Ti, Ga, and Al, in that order.

Various studies have been conducted on improving the thermoelectric performance by substituting group 13 (B$^3$) elements, Zhao et al. [16] obtained ZT = 0.54 at 650 K for Cu$_2$Sb$_{0.95}$Ga$_{0.05}$Se$_4$, and Zhang et al. [17] achieved ZT = 0.50 at 648 K for Cu$_2$Sb$_{0.97}$In$_{0.03}$Se$_4$. Wei et al. [18] reported ZT = 0.70 at 673 K for Cu$_2$Sb$_{0.98}$Sn$_{0.02}$Se$_4$. Pi et al. [14] obtained ZT = 0.65 at 623 K for Cu$_2$Sb$_{0.98}$Ge$_{0.02}$Se$_4$, and Chang et al. [19] achieved ZT = 0.70 at 640 K for Cu$_2$Sb$_{0.98}$Ge$_{0.02}$Se$_4$. Liu et al. [20] reported ZT = 0.81 at 648 K for Cu$_2$Sb$_{0.98}$Bi$_{0.02}$Se$_4$.

Mechanical alloying (MA) is a high-energy ball-milling process performed at room temperature, which can prevent volatilization and segregation of the chalcogen elements generated during melting. It is a practical and economical solid-state synthesis process with relatively low energy and processing time. Therefore, in this study, permingeate powders of Cu$_2$Sb$_{1−y}$Sn$_y$In$_x$Se$_4$ double-doped with Sn and In were synthesized using MA, and sintered using hot pressing (HP). Sn$^{4+}$ and In$^{3+}$ have fewer electrons than Sb$^{3+}$; thus, a possible p-type dopant (acceptor) can be expected in Cu$_2$SbSe$_4$. The changes in the thermoelectric properties according to the doping level are examined.

2. EXPERIMENTAL

To synthesize Sn/In double-doped Cu$_2$Sb$_{1−y}$Sn$_y$In$_x$Se$_4$ ($x = 0.02, 0.04, 0.06$, and $y = 0.04, 0.06$) permingeatites, elemental powders of Cu (purity 99.99%, <45 μm), Sb (purity 99.999%, <150 μm), Sn (purity 99.999%, <35 μm), In (purity 99.999%, <75 μm), and Se (purity 99.9%, <10 μm) were used. Mixed raw-material powders (20 g) and stainless-steel balls (400 g) were placed in a hardened steel jar, and MA was performed in Ar atmosphere at 350 rpm for 12 h. HP was conducted on the synthesized powders using a graphite mold and punches, under a uniaxial pressure of 70 MPa at 573 K for 2 h in vacuum.

The phases of the sintered specimens were analyzed using X-ray diffraction (XRD; Bruker, D8-Advance) with Cu Kα radiation. To calculate the lattice constant, Rietveld refinement (TOPAS program) was performed. The microstructures of the sintered specimens were observed using scanning electron microscopy (SEM; FEI, Quantum400) in backscattered electron (BSE) mode, and elemental line scans and maps were analyzed according to the energy level of each element, using an energy-dispersive X-ray spectrometer (EDS; Bruker, XFlash4010). The carrier concentration and mobility were evaluated by measuring the Hall coefficient using the van der Pauw method (Keithley 7065). The Seebeck coefficient and electrical conductivity were measured in He atmosphere using a ZEM-3 system (Advance Riko). The thermal diffusivity was measured in vacuum by the laser flash method using TC-9000H equipment (Advance Riko), and the thermal conductivity was evaluated from the specific heat and density. From the Seebeck coefficient, electrical conductivity, and thermal conductivity, the temperature dependence of the thermoelectric power factor and ZT values were examined in the temperature range of 323–623 K.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of Cu$_2$Sb$_{1−y}$Sn$_y$In$_x$Se$_4$ prepared by the MA–HP method. All diffraction peaks correspond to a single phase tetragonal structure, consistent with the standard diffraction pattern for permingeaitte (ICDD PDF# 01-085-0003). This means that no phase transitions or decompositions occur, and no secondary phases are detected.
after HP at 573 K. Rietveld analysis was performed to
determine the changes in the lattice constant due to Sn and In
doping (substitution), and Table 1 summarizes the estimated
diffraction peak shifts, even at high diffraction angles, owing
to the small difference between the ionic radii of Sn
and In. Shannon [22] reported that the ionic radii were 76 pm for Sb
and 80 pm for In [14,21]. In this study, the double doping of Sn and In
increases the a-axis to 0.5651–0.5654 nm and c-axis to
1.1249–1.1257 nm. This implies that Sn and In have been
successfully substituted at the Sb sites; however, the change
in the lattice constant, according to the change in the doping
amount, is not significant. Shannon [22] reported that the ionic radii were 76 pm for Sb$^{3+}$, 74 pm for Sn$^{4+}$, and 80 pm for In$^{3+}$. Wei et al. [18] observed that there were no
diffraction peak shifts, even at high diffraction angles, owing
to the small difference between the ionic radii of Sn$^{4+}$ and
Sb$^{5+}$. Ghanwat et al. [23] reported that the a-axis increased
from 0.56603 to 0.56607–0.56636 nm and c-axis from
1.12843 to 1.12848–1.12876 nm, following In doping.

Figure 2 presents the BSE–SEM images of Cu$_3$Sb$_{0.92}$Sn$_{0.08}$In$_{0.04}$Se$_4$ (upper left: polished surface and upper right: fractured surface) with elemental line scans and
maps. As shown in Table 1, high relative densities of 97.4–
98.9% are obtained. Densely sintered microstructures without
pores or cracks are observed, and no secondary phases other
than the permingeatite phase are identified. This is consistent
with the results of the XRD analysis shown in Figure 1. The EDS
elemental analysis confirms that all the constituent elements
are uniformly distributed.

The charge-transport parameters of Cu$_3$Sb$_{1−x}$Sn$_x$In$_y$Se$_4$ are
shown in Table 1. The undoped CuSbSe$_4$ has a carrier
concentration of $5.2 \times 10^{18}$ cm$^{-3}$ and mobility of 49.9
cm$^2$V$^{-1}$s$^{-1}$ [14]. In this study, as the doping levels of Sn and In
increase, the carrier concentration increases to $1.46 \times 10^{19}$
cm$^{-3}$ for Cu$_3$Sb$_{0.88}$Sn$_{0.08}$In$_{0.04}$Se$_4$ and $1.87 \times 10^{19}$
cm$^{-3}$ for Cu$_3$Sb$_{0.76}$Sn$_{0.24}$In$_{0.08}$Se$_4$. In addition, the mobility increases to
517–2,352 cm$^2$V$^{-1}$s$^{-1}$ through Sn/In double doping. Wei et al.
[18] found that the carrier concentration increased while the
mobility decreased upon increasing the Sn doping level in
Cu$_3$Sb$_{1−x}$Sn$_x$Se$_4$, and reported that Cu$_3$Sb$_{0.88}$Sn$_{0.12}$Se$_4$
exhibited a carrier concentration of $(2.0–2.5) \times 10^{19}$ cm$^{-3}$
and mobility of (15–27) cm$^2$V$^{-1}$s$^{-1}$ at 300–673 K. Zhang et al.
[17] obtained a carrier concentration of $2.2 \times 10^{18}$ cm$^{-3}$ and
mobility of 65 cm$^2$V$^{-1}$s$^{-1}$ for Cu$_3$SbSe$_4$ and reported that, as
the In-doping content increased in Cu$_3$Sb$_{1−x}$In$_x$Se$_4$, the carrier
concentration increased to a maximum of $3.5 \times 10^{19}$ cm$^{-3}$ and
the mobility became $10$ cm$^2$V$^{-1}$s$^{-1}$, for Cu$_3$Sb$_{0.99}$In$_{0.01}$Se$_4$.
Liu et al. [20] reported that the carrier concentration

![Fig. 1. XRD patterns of Cu$_3$Sb$_{1−x}$Sn$_x$In$_y$Se$_4$ prepared by the MA–
HP process.](image)

Table 1. Relative density, lattice constant, and charge-transport parameters of Cu$_3$Sb$_{1−x}$Sn$_x$In$_y$Se$_4$

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Relative Density [%]</th>
<th>Lattice Constant [nm]</th>
<th>Carrier Concentration [$10^{19}$ cm$^{-3}$]</th>
<th>Mobility [cm$^2$V$^{-1}$s$^{-1}$]</th>
<th>Lorenz Number [10$^4$ V$^2$K$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>3$Sb$</em>{0.90}$Sn$<em>{0.10}$In$</em>{0.00}$Se$_4$</td>
<td>97.3</td>
<td>0.5654</td>
<td>1.1255</td>
<td>0.93</td>
<td>517</td>
</tr>
<tr>
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<td>98.9</td>
<td>0.5654</td>
<td>1.1257</td>
<td>0.97</td>
<td>641</td>
</tr>
<tr>
<td>Cu$<em>3$Sb$</em>{0.90}$Sn$<em>{0.04}$In$</em>{0.00}$Se$_4$</td>
<td>97.8</td>
<td>0.5651</td>
<td>1.1251</td>
<td>1.92</td>
<td>586</td>
</tr>
<tr>
<td>Cu$<em>3$Sb$</em>{0.90}$Sn$<em>{0.00}$In$</em>{0.04}$Se$_4$</td>
<td>98.3</td>
<td>0.5651</td>
<td>1.1251</td>
<td>1.46</td>
<td>2352</td>
</tr>
<tr>
<td>Cu$<em>3$Sb$</em>{0.90}$Sn$<em>{0.00}$In$</em>{0.00}$Se$_4$</td>
<td>97.9</td>
<td>0.5653</td>
<td>1.1249</td>
<td>0.96</td>
<td>736</td>
</tr>
<tr>
<td>Cu$<em>3$Sb$</em>{0.90}$Sn$<em>{0.04}$In$</em>{0.00}$Se$_4$</td>
<td>97.4</td>
<td>0.5653</td>
<td>1.1255</td>
<td>0.91</td>
<td>1279</td>
</tr>
<tr>
<td>Cu$<em>3$Sb$</em>{0.92}$Sn$<em>{0.08}$In$</em>{0.00}$Se$_4$</td>
<td>98.2</td>
<td>0.5652</td>
<td>1.1254</td>
<td>1.24</td>
<td>1000</td>
</tr>
<tr>
<td>Cu$<em>3$Sb$</em>{0.90}$Sn$<em>{0.00}$In$</em>{0.00}$Se$_4$</td>
<td>98.0</td>
<td>0.5653</td>
<td>1.1256</td>
<td>1.87</td>
<td>1819</td>
</tr>
</tbody>
</table>
increased as the Sn content increased in Cu$_{3}$Sb$_{1-x}$Sn$_x$Bi$_y$Se$_4$, but it decreased as the Bi content increased, and reached 1.0 \times 10^{20} \text{ cm}^{-3} for Cu$_{3}$Sb$_{0.88}$Sn$_{0.10}$Bi$_{0.02}$Se$_4$. Kumar et al. [24] reported that, as the Bi content increased in Cu$_{3}$Sb$_{1-x}$Bi$_x$Se$_3.99$Te$_{0.01}$, the carrier concentration increased until Cu$_{3}$Sb$_{0.92}$Bi$_{0.08}$Se$_3.99$Te$_{0.01}$ exhibited a carrier concentration of 9.62 \times 10^{18} \text{ cm}^{-3}.

In general, in nondegenerate semiconductors, as the carrier concentration increases, the mobility decreases [25]. However, in this study, the mobility tended to increase as the carrier concentration increased. This is attributed to the transition from the nondegenerate state to the degenerate state, through the double doping of Sn and In. Suzumura et al. [26] found that, in the case of degenerate semiconductors, both the carrier concentration and mobility could be increased by doping.

The thermoelectric properties were measured for eight types of Cu$_{3}$Sb$_{1-x-y}$Sn$_x$In$_y$Se$_4$-based specimens prepared in this study, and are shown in Table 1 and Figure 1. However, in this study, the thermoelectric properties of Cu$_3$Sb$_{0.92}$Sn$_{0.04}$In$_{0.04}$Se$_4$, Cu$_3$Sb$_{0.90}$Sn$_{0.06}$In$_{0.06}$Se$_4$, Cu$_3$Sb$_{0.92}$Sn$_{0.02}$In$_{0.06}$Se$_4$, and Cu$_3$Sb$_{0.88}$Sn$_{0.10}$In$_{0.06}$Se$_4$ were compared as representatives. Figure 3 shows the electrical conductivity of Cu$_3$Sb$_{1-x-y}$Sn$_x$In$_y$Se$_4$. All specimens showed negative temperature dependence, such as degenerate semiconductor behavior, decreasing the electrical conductivity upon increasing the temperature. As the Sn and In doping concentrations increase at a constant temperature, the electrical conductivity increases and the Sn doping effect becomes dominant. When Sn$^{4+}$ and In$^{3+}$ are substituted at the Sb$^{5+}$ sites of Cu$_3$SbSe$_4$, additional charge carriers (holes) are created, resulting in increased electrical conductivity. Cu$_3$Sb$_{0.92}$Sn$_{0.06}$In$_{0.06}$Se$_4$ exhibits the highest electrical conductivity of (0.9–0.6) \times 10^5 \text{ Sm}^{-1} at 323–623 K. Wei et al. [18] found that the electrical resistivity decreased (the electrical conductivity increased) as the Sn content
increased in Cu$_{3}$Sb$_{1-y}$Sn$_{y}$Se$_4$ and obtained the highest electrical conductivity of (0.2–0.5) × 10$^4$ Sm$^{-1}$ at 300–650 K for Cu$_{3}$Sb$_{0.95}$Sn$_{0.05}$Se$_4$. Zhang et al. [17] reported that the electrical conductivity increased as the Sn content increased in Cu$_{3}$Sb$_{1-y}$In$_{y}$Se$_4$ and achieved the highest electrical conductivity of (0.6–0.9) × 10$^4$ Sm$^{-1}$ at 300–650 K for Cu$_{3}$Sb$_{0.96}$In$_{0.04}$Se$_4$.

Liu et al. [20] found that the electrical conductivity of Cu$_{3}$Sb$_{1-y}$Sn$_y$Bi$_y$Se$_4$ increased as the Sn content increased and Bi content decreased, exhibiting degenerate semiconductor behavior, decreasing with increasing temperature. They obtained the highest electrical conductivity of 0.5 × 10$^4$ Sm$^{-1}$ at 300 K for Cu$_{3}$Sb$_{0.95}$Sn$_{0.05}$Bi$_{0.02}$Se$_4$. They reported anomalously high values for the Sn/Bi-double-doped samples, which were even higher than those of the Sn single-doped samples. However, Kumar et al. [24] found that Cu$_{3}$Sb$_{1-y}$Bi$_y$Se$_{1-y}$Te$_{0.01}$ exhibited typical nondegenerate semiconductor behavior, in which the electrical conductivity increased as the Bi content and temperature increased, and obtained the highest electrical conductivity of 0.3 × 10$^4$ Sm$^{-1}$ at 650 K for Cu$_{3}$Sb$_{0.95}$Bi$_{0.05}$Se$_{1-y}$Te$_{y}$$_{0.01}$. Zhao et al. [27] reported that the electrical conductivity increased upon increasing the Ag content in Cu$_{3}$In$_{1-y}$Ag$_y$Sb$_{1.95}$Bi$_{0.05}$Se$_4$, and Cu$_{3}$In$_{0.95}$Ag$_{0.05}$Sb$_{1.95}$Bi$_{0.05}$Se$_4$ exhibited the highest electrical conductivity of 0.8 × 10$^4$ Sm$^{-1}$ at 623 K. This value was greater than that of the Bi-doped samples.

Figure 4 shows the Seebeck coefficients of Cu$_{3}$Sb$_{1-y}$Sn$_y$In$_y$Se$_4$. All specimens exhibited positive values in the measured temperature range, which confirmed that the majority of carriers were holes of the n-type semiconductors [7]. Because the Seebeck coefficient is inversely proportional to the carrier concentration, as the Sn and In doping content increases, the Seebeck coefficient decreases. As the temperature increases, the Seebeck coefficient gradually increases; thus, intrinsic conduction does not occur within the measured temperature range.

Cu$_{3}$Sb$_{0.95}$Sn$_{0.05}$In$_{0.04}$Se$_4$ exhibited the highest Seebeck coefficient of 90–161 μVK$^{-1}$ at 323–623 K. Wei et al. [18] reported that the Seebeck coefficient decreased as the Sn content increased in Cu$_{3}$Sb$_{1-y}$Sn$_y$Se$_4$, and obtained 90–170 μVK$^{-1}$ at 300–673 K for Cu$_{3}$Sb$_{0.95}$Sn$_{0.05}$Se$_4$. Zhang et al. [17] observed intrinsic conduction (degenerate state) in Cu$_{3}$Sb$_{1-y}$Sn$_y$Se$_4$ at temperatures above 475 K, and achieved 210–290 μVK$^{-1}$ at 300–650 K for Cu$_{3}$Sb$_{0.95}$In$_{0.05}$Se$_4$. Liu et al. [20] reported that, in Sn/Bi-double-doped Cu$_{3}$Sb$_{1-y}$Sn$_y$Bi$_y$Se$_4$, the Seebeck coefficient decreased as the Sn content increased, while it increased with the addition of Bi, reaching 150–255 μVK$^{-1}$ at 327–673 K for Cu$_{3}$Sb$_{0.95}$Sn$_{0.05}$Bi$_{0.02}$Se$_4$. Kumar et al. [24] found that, in Bi/Te double-doped Cu$_{3}$Sb$_{1-y}$Bi$_y$Se$_{1-y}$Te$_{0.01}$, the Seebeck coefficient decreased as the Bi content increased, and Cu$_{3}$Sb$_{0.95}$Bi$_{0.05}$Se$_{1-y}$Te$_{y}$$_{0.01}$ exhibited the highest Seebeck coefficient of 180–320 μVK$^{-1}$ at 300–650 K. Zhao et al. [27] also found that the Seebeck coefficient decreased when Bi was singly doped in Cu$_{3}$Sb$_{0.95}$Bi$_{0.05}$Se$_4$, but it increased when Bi and Ag were double-doped, resulting in the highest Seebeck coefficient of 460 μVK$^{-1}$ at 423 K for Cu$_{3}$In$_{0.95}$Ag$_{0.05}$Sb$_{0.95}$Bi$_{0.05}$Se$_4$.

Figure 5 shows the power factor of Cu$_{3}$Sb$_{1-y}$Sn$_y$In$_y$Se$_4$. According to the results of our previous studies [14,21], the power factor of Cu$_{3}$Sb$_{0.95}$Se$_4$ was as small as 0.39–0.49 mWm$^{-1}$K$^{-2}$ at 323–623 K, and its temperature dependence was relatively low. However, in this study, Sn/In double doping rapidly increases the power factor upon increasing the temperature, and thus, Cu$_{3}$Sb$_{0.95}$Sn$_{0.05}$In$_{0.04}$Se$_4$ exhibited a maximum power factor of 1.20 mWm$^{-1}$K$^{-2}$ at 623 K. Wei et al. [18] reported 0.91 mWm$^{-1}$K$^{-2}$ at 673 K for Cu$_{3}$Sb$_{0.95}$In$_{0.05}$Se$_4$, and Zhang et al. [17] obtained 0.75 mWm$^{-1}$K$^{-2}$ at 648 K for Cu$_{3}$Sb$_{0.95}$In$_{0.04}$Se$_4$. Liu et al. [20] reported 1.14 mWm$^{-1}$K$^{-2}$ at 673 K for Cu$_{3}$Sb$_{0.95}$In$_{0.05}$Se$_4$ and 0.77 mWm$^{-1}$K$^{-2}$ at 608 K for Cu$_{3}$Sb$_{0.95}$Bi$_{0.02}$Se$_4$. In addition,
they achieved an anomalously high power factor of 1.81 mW m\(^{-1}\) K\(^{-2}\) at 673 K for the Sn/Bi-double-doped Cu\(_3\)Sb\(_{0.88}\)Sn\(_{0.10}\)Bi\(_{0.02}\)Se\(_4\). Kumar et al. [24] also obtained a high power factor of 1.3 mW m\(^{-1}\) K\(^{-2}\) at 375 K for the Bi/Te-double-doped Cu\(_3\)Sb\(_{0.98}\)Bi\(_{0.02}\)Se\(_3.99\)Te\(_{0.01}\). Zhao et al. [27] reported that the power factor increased upon increasing Ag content in Cu\(_3(1-x)\)Ag\(_x\)Sb\(_{0.985}\)Bi\(_{0.015}\)Se\(_4\), resulting in (1.0–1.2) mW m\(^{-1}\) K\(^{-2}\) at 300–623 K for Cu\(_{2.79}\)Ag\(_{0.21}\)Sb\(_{0.985}\)Bi\(_{0.015}\)Se\(_4\).

Figure 6 presents the thermal conductivity of Cu\(_3\)Sb\(_{1-x}\)Sn\(_{y}\)In\(_{y}\)Se\(_4\) and distinguishes the contributions of lattice thermal conductivity (\(\kappa_L\)) and electronic thermal conductivity (\(\kappa_E\)). The thermal conductivity is determined by these two components: the thermal conductivity of phonons and that of carriers [28,29]. As shown in Figure 6(a), the thermal conductivity decreases as the temperature increases from 323 to 623 K. Cu\(_3\)Sb\(_{0.92}\)Sn\(_{0.02}\)In\(_{0.06}\)Se\(_4\) exhibits a minimum thermal conductivity of 1.19 W m\(^{-1}\) K\(^{-1}\) at 623 K. As shown in Figure 6(b), as the temperature increases, the lattice thermal conductivity decreases, and the lattice thermal conductivity is dominant over the total thermal conductivity (Figure 6 (a)). Cu\(_3\)Sb\(_{0.92}\)Sn\(_{0.04}\)In\(_{0.02}\)Se\(_4\) exhibited a minimum \(\kappa_L\) of 0.77 W m\(^{-1}\) K\(^{-1}\) at 623 K. As shown in Figure 6(c), there is little temperature dependence for the electronic thermal conductivity, but the electronic thermal conductivity changed with the doping levels because the carrier concentration changes with the Sn and In content. The electronic thermal conductivity is expressed by the Wiedemann–Franz law:

\[ \kappa_E = L \sigma T, \]  

(2)

where \(L\) is the temperature-dependent Lorenz number [30,31], which was calculated and is presented in Table 1. As the carrier concentration is increased by the Sn and In double
doping, Cu$_2$Sb$_{0.92}$Sn$_{0.08}$In$_{0.04}$Se$_4$ exhibited a minimum $\kappa_L$ of 0.31 Wm$^{-1}$K$^{-1}$ at 623 K.

Wei et al. [18] found that the lattice thermal conductivity in Cu$_2$Sb$_{1-x}$Sn$_x$Se$_4$ decreased with $T^{-1}$ in the temperature range of 300–673 K, indicating that the Umklapp scattering was predominant in phonon transport; the thermal conductivity increased as the Sn content increased, reaching 2.0–3.6 Wm$^{-1}$K$^{-1}$ at 300–673 K for Cu$_2$Sb$_{0.96}$Sn$_{0.04}$Se$_4$. Zhang et al. [17] reported that the thermal conductivity of Cu$_2$Sb$_{1-x}$In$_x$Se$_4$ decreased with increasing temperature (300–650 K), which was associated with a decrease in lattice thermal conductivity due to the increased point-defect scattering. According to Cahill's formula, the minimum $\kappa_L$ was estimated to be 0.8 Wm$^{-1}$K$^{-1}$ at 650 K for Cu$_2$Sb$_{0.99}$In$_{0.005}$Se$_4$, and the experimentally obtained minimum $\kappa_L$ was 0.5 Wm$^{-1}$K$^{-1}$ at 648 K for Cu$_2$Sb$_{0.97}$In$_{0.003}$Se$_4$.

Liu et al. [20] achieved a low $\kappa_L$, owing to the increased point-defect density and lattice distortion caused by the incorporation of Sn and Bi, and as a result, low thermal conductivity values were reported: 0.9–2.1 Wm$^{-1}$K$^{-1}$ at 327–673 K for Cu$_2$Sb$_{0.99}$Sn$_{0.01}$Se$_4$, 0.6–1.0 Wm$^{-1}$K$^{-1}$ at 327–648 K for Cu$_2$Sb$_{0.98}$Bi$_{0.02}$Se$_4$, and 0.8–1.2 Wm$^{-1}$K$^{-1}$ at 327–673 K for Cu$_2$Sb$_{0.96}$Sn$_{0.02}$Bi$_{0.02}$Se$_4$. Kumar et al. [24] found that the thermal conductivity of Cu$_2$Sb$_{1-x}$Bi$_x$Se$_2$$_{0.95}$Te$_{0.01}$ decreased as the temperature and Bi content increased, owing to an increase in the phonon scattering. As a result, Cu$_2$Sb$_{0.98}$Bi$_{0.02}$Se$_{1.99}$Te$_{0.01}$ exhibited a minimum thermal conductivity of 0.7–1.5 Wm$^{-1}$K$^{-1}$ at 300–650 K. Zhao et al. [27] reported that the thermal conductivity of Cu$_2$(In$_{1-y}$Ag$_y$)$_{3-x}$Sb$_{0.98}$Bi$_{0.03}$Se$_4$ decreased with increasing temperature, and Cu$_2$(Ag$_{0.05}$In$_{0.01}$)$_{3-x}$Sb$_{0.98}$Bi$_{0.01}$Se$_4$ exhibited a minimum thermal conductivity of 0.7 Wm$^{-1}$K$^{-1}$ ($\kappa_L = 0.6$ Wm$^{-1}$K$^{-1}$) at 673 K.

Figure 7 shows the dimensionless figure of merit (ZT) of Cu$_2$Sb$_{1-x}$Sn$_x$In$_{0.04}$Se$_4$. In our previous studies [14,21], undoped Cu$_2$SbSe$_4$ exhibited a maximum ZT of 0.39 at 623 K. In comparison, the ZT values of Cu$_2$Sb$_{0.92}$Sn$_{0.08}$In$_{0.04}$Se$_4$ were higher than those of Cu$_2$SbSe$_4$, particularly at high temperatures, and we achieved a maximum ZT of 0.59 at 623 K. The Cu$_2$Sb$_{0.96}$Sn$_{0.04}$In$_{0.04}$Se$_4$ specimens exhibited higher ZT values than Cu$_2$Sb$_{0.94}$Sn$_{0.06}$In$_{0.04}$Se$_4$, because of their higher Seebeck coefficients and power factors.

Wei et al. [18] reported a ZT of 0.70 at 673 K for Cu$_2$Sb$_{0.96}$Sn$_{0.04}$Se$_4$ fabricated by MA and spark plasma sintering. Zhang et al. [17] obtained a ZT of 0.50 at 648 K for Cu$_2$Sb$_{0.99}$In$_{0.005}$Se$_4$ prepared through a multistep process (conventional melting, quenching, hand grinding, annealing, pulverizing, and HP), which was 47% higher than the ZT value of Cu$_2$SbSe$_4$. Liu et al. [20] reported a ZT of 1.26 at 673 K for Cu$_2$Sb$_{0.99}$Sn$_{0.01}$Bi$_{0.02}$Se$_4$ nanocrystals produced by solution processing followed by HP. Kumar et al. [24] achieved a ZT of 0.76 at 650 K for Bi/Te double-doped Cu$_2$Sb$_{0.94}$B$_{0.06}$Se$_{1.90}$Te$_{0.01}$ fabricated by melt growth, ball milling, and spark plasma sintering. Zhao et al. [27] reported a ZT of 0.51 at 673 K for Ag/Bi-double-doped Cu$_2$Ag$_{0.15}$Sb$_{0.85}$Bi$_{0.01}$Se$_4$ prepared by vacuum melting, quenching, annealing, pulverizing, and HP.

This study determined that the double doping of Sn and In is effective for improving the thermoelectric performance of permingeaitite. In addition, the solid-state synthesis process involving MA and HP is a simple and practical one that does not require subsequent crushing and/or heat-treatment to produce doped permingeaitite compounds. Further improvement in the thermoelectric performance can be expected through detailed study of the combinations and portions of the double-doping elements, and doping sites.

4. CONCLUSIONS

In this study, we prepared double-doped Cu$_2$Sb$_{1-x}$Sn$_x$In$_{0.04}$Se$_4$ ($x = 0.02$–0.08, $y = 0.04$–0.06) permingeaitites using MA.
followed by HP. We investigated the effects of double doping (partial substitution) of Sn and In at the Sb sites on the phase change, microstructure, charge transport, and thermoelectric properties. A single phase of permegateite with a tetragonal structure was produced without post-annealing treatment, and a high relative density was obtained for the HP specimens. All the doped samples exhibited positive Seebeck and Hall coefficients, indicating p-type conduction characteristics. Double doping with Sn and In significantly increased the coefficients, indicating p-type conduction characteristics.

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