Thermoelectric Properties of Si-Doped In$_2$Se$_3$ Polycrystalline Alloys

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Abstract: Post-metal chalcogenides, including InSe, In$_2$Se$_3$, and In$_4$Se$_3$, have attracted considerable attention as potential thermoelectric materials because of their intrinsically low thermal conductivity, which is attributed to their layered structure with weak van der Waals bonds. In this study, we examined the electrical and thermoelectric properties of Si-doped In$_2$Se$_3$ (In$_{1-x}$Si$_x$Se$_3$, $x = 0, 0.005, 0.01, 0.015$, and 0.02) polycrystalline samples. Hexagonal $\alpha$(2H)-In$_2$Se$_3$ phase was synthesized without any impurity, and gradual changes in the lattice parameters were observed with Si doping. Drastic changes were observed for the measured electrical and thermal transport properties at 450–500 K, due to the phase transition from $\alpha$ to $\beta$ at 473 K. The highest power factors were achieved by the sample with $x = 0.015$ for both $\alpha$ and $\beta$ phases, exhibiting the values of 0.137 and 0.0884 mW/mK$^2$ at 450 and 750 K, respectively. The total thermal conductivities of the $\alpha$ phase samples decreased gradually with increasing Si doping content, which is attributed to the point defect phonon scattering by Si doping. The total thermal conductivities of the $\beta$ phase samples significantly decreased compared to those of the $\alpha$ phase samples. Therefore, the sample with $x = 0.015$ (In$_{1.985}$Si$_{0.015}$Se$_3$) showed the maximum thermoelectric figure of merit values of 0.100 and 0.154 at 450 and 750 K, which are enhanced by 152 and 48% compared with those of the undoped $\alpha$- and $\beta$-In$_2$Se$_3$ samples, respectively.

Keywords: thermoelectric; indium selenide; In$_2$Se$_3$; doping

1. Introduction

Post-transition metal chalcogenides (PTMCs), such as Ga-, In-, and Sn-based semiconductors, have been studied in various fields. Primarily, PTMCs have been extensively investigated for transistors, photodetectors, solar cells, and thermoelectric materials [1–3]. In particular, the layered structure of most PTMCs facilitates them as thermoelectric materials; this is because the layered structure has a weak van der Waals bonding between the layers. Therefore, PTMCs have poor thermal transport properties, which indicates that they can be promising thermoelectric materials. Furthermore, thermoelectric technology directly converts temperature gradients into electrical potential, which facilitates the utilization of large amounts of waste heat from industries and automobiles, creating the potential for sustainable energy harvesting technologies [4,5]. The performance of thermoelectric materials is evaluated using dimensionless figure of merit, $zT = S^2\sigma T/\kappa_{\text{tot}}$, where $S$, $\sigma$, $\kappa_{\text{tot}}$ and $T$ are the Seebeck coefficient, electrical conductivity, total thermal conductivity, and absolute temperature, respectively. Herein, $zT$ can be improved by increasing power factor ($PF = S^2\sigma$) or decreasing $\kappa_{\text{tot}}$. However, this approach is complex because $S$ and $\sigma$ exhibit a trade-off relationship [6]. In addition, as $\sigma$ increases, $\kappa_{\text{tot}}$ also increases, because $\kappa_{\text{tot}}$ can be expressed as $\kappa_{\text{tot}} = \kappa_{\text{elec}} + \kappa_{\text{latt}}$, where $\kappa_{\text{elec}}$ and $\kappa_{\text{latt}}$ are the electronic thermal conductivity and lattice thermal conductivity, respectively. The $\kappa_{\text{elec}}$ is determined by the Wiedemann–Franz law ($\kappa_{\text{elec}} = L \cdot \sigma \cdot T$, where $L$ is the Lorentz number) [7]. Therefore, in recent years, the strategies of enhancing power factor and reducing the $\kappa_{\text{tot}}$ have been
studied [8,9]. The effective use of various scattering mechanisms is important because the $\kappa_{\text{latt}}$ is inversely proportional to the phonon scattering [9–11].

To improve a $zT$, doping strategy has been actively applied to thermoelectric PTMCs. In the case of InSe, a $zT$ for Si-doped InSe was improved to 0.18 (approximately by 210%) at 795 K, compared to pristine InSe [12]. Furthermore, a $zT$ of 0.62 was observed for SnSe$_{1.98}$Br$_{0.02}$ at 750 K, which is 50% higher than that for pristine SnSe$_2$ [13]. Rhyee et al. reported a $zT$ of 1.48 for In$_x$Se$_{3-x}$ at 705 K and a low thermal conductivity of $\sim 0.74$ Wm$^{-1}$ K$^{-1}$ [14]. Qian et al. reported a maximum $zT$ of 1.35 for Ca-doped SnTe at 873 K [15]. To enhance $zT$ of materials effectively, enhancing the effective mass, $m^*$, reducing $\kappa_{\text{latt}}$, and selecting the appropriate dopant are essential [16,17].

In$_2$Se$_3$, one of the PTMCs, has two primary phases, $\alpha$ and $\beta$. The $\alpha$ and $\beta$ phases are stable below 473 K and above 473 K, respectively, and both of them have a layered structure [18,19]. Owing to this structural characteristic, they have low thermal conductivities. Indeed, the $\alpha$ phase has two crystal structures: hexagonal (2H) and rhombohedral (3R) [20–23]. The $\alpha$(2H) phase is stable and $\alpha$(3R) phase is unstable at room temperature. The complex phase change in In$_2$Se$_3$ may imply larger possibility of the intrinsic defects [23]. To synthesize a stable $\alpha$(2H) phase, quenching process is necessary.

We investigated the effect of Si doping on the thermoelectric transport behavior of In$_2$Se$_3$. A series of In$_{2-x}$Si$_x$Se$_3$ ($x = 0, 0.005, 0.01, 0.015, 0.02$) polycrystalline samples were synthesized and their electrical and thermal transport properties were analyzed. The $zT$ were calculated to determine the optimum compositions for thermoelectric materials in Si-doped In$_2$Se$_3$.

2. Experimental Method

A series of In$_{2-x}$Si$_x$Se$_3$ compositions with nominal $x = 0, 0.005, 0.01, 0.015$ and 0.02 were synthesized via the conventional solid-state reaction in a vacuum-sealed quartz tube. High purity elements, In (99.999%, pellet), Si (99.999%, pellet), and Se (99.999%, pellet), were weighed with stoichiometric compositions. The loaded quartz ampules were heated at 1273 K for 10 h. In addition, pure $\alpha$(2H) phases were obtained by quenching in ice water. The synthesized $\alpha$(2H)-In$_2$Se$_3$ ingots were pulverized into powder using high-energy ball milling (SPEx 8000D, SPEX). All powders were densified via spark plasma sintering (SPS, SPS-1030, Sumitomo Coal Mining Co., Ltd., Tokyo, Japan) by heating at 923 K for 2 min at a pressure of 70 MPa. During sintering, the inside of the SPS chamber was kept under a vacuum ($\sim 10^{-5}$ Torr). Structural analysis of the powders was performed using X-ray diffraction (XRD, D8 Discover, Bruker) at 40 kV and 40 mA. Cu K$_\alpha$ radiation ($\lambda = 1.5406$ Å) and a scan rate of 0.02° s$^{-1}$ were used to record patterns in the 2$\theta$ range of 20°–80°. Subsequently, the lattice parameter was calculated for each synthesized sample. The thermoelectric transport properties ($S$ and $\sigma$) were simultaneously measured in the temperature range of 300–750 K using a thermoelectric property measurement system (ZEM-3, Advanced-Riko, Yokohama, Japan) in a He atmosphere along parallel direction of the SPS pressing direction, and the $PF$ was calculated by measured $S$ and $\sigma$. Hall measurement was performed in a Van der Pauw configuration at 300 K using a Hall measurement system (HMS5300, Ecopia) in the same direction. Furthermore, $\kappa_{\text{tot}}$ was calculated using the relationship, $\kappa_{\text{tot}} = \rho_\text{tot}C_p\lambda$, where $\rho_\text{tot}$, $C_p$ and $\lambda$ are the sample density, heat capacity, and thermal diffusivity, respectively, and $\rho_\text{tot}$ is the theoretical density of the $\alpha$- and $\beta$-phases of In$_2$Se$_3$. $C_p$ was measured using a differential scanning calorimeter (DSC8000, Perkin Elmer, Waltham, USA) in the temperature range of 273–473 K, and the measured values at 300 K and 473 K were used for the $\alpha$ and $\beta$ phases, respectively. The measured $C_p$ by differential scanning calorimetry (DSC) was shown in Figure S1 in Supplementary Information. $\lambda$ was measured using the laser flash method (LFA457, Netzsch, Selb, Germany) in the temperature range of 300–750 K along SPS pressing direction so the $zT$ can be calculated appropriately. The $zT$ was evaluated based on the measured data. Energy-dispersive spectroscopy (EDS) by scanning electron microscopy (SEM) was
performed for In$_{2-x}$Si$_x$Se$_3$ with nominal $x$ = 0.01 and 0.02 to verify the existence of Si dopants (See Figure S2 and Table S1 in Supplementary Materials).

3. Results and Discussion

Figure 1a shows the XRD patterns of the synthesized Si-doped In$_2$Se$_3$. A series of In$_{2-x}$Si$_x$Se$_3$ samples were successfully synthesized as a (2H) phase. Figure 2b shows the lattice parameters, which were calculated using the (004) and (102) diffraction peaks. The lattice parameter $a$ gradually increases from 4.03 to 4.09 Å with increasing Si content. In contrast, the lattice parameter $c$ gradually decreases from 19.3 to 19.2 Å. A gradual decrease in lattice parameter $c$ can be explained by the fact that the ionic size of Si$^{4+}$ is 54 pm, which is smaller than that of In$^{3+}$ (94 pm), even though the modest increase in the lattice parameter $a$ was seen. This unusual opposite change in lattice parameters was also seen in Si-doped InSe compounds [12]. However, these gradual changes of the lattice parameters indicate that Si is successfully substituted at the In sites. Additionally, Table 1 shows the atomic percentage directly measured by EDS-SEM for In$_{2-x}$Si$_x$Se$_3$ with $x$ = 0.01 and 0.02.

![Figure 1](image1.png)

**Figure 1.** (a) X-ray diffraction patterns and (b) calculated lattice parameters for the In$_{2-x}$Si$_x$Se$_3$ ($x = 0, 0.005, 0.01, 0.015,$ and 0.02) samples.

![Figure 2](image2.png)

**Figure 2.** (a) Electrical conductivities, (b) Seebeck coefficients and (c) power factors as a function of temperature for the In$_{2-x}$Si$_x$Se$_3$ ($x = 0, 0.005, 0.01, 0.015,$ and 0.02) samples.
The largest $|\beta|$ values for both $\alpha$ and $\beta$ phases were observed for the sample with $x = 0.01$; the value of $S$ of the sample with $x = 0.01$ was $-465.3\ \mu V/K$ at 400 K and $-950.4\ \mu V/K$ at 500 K.

Figure 2c shows the calculated $PF$ of the $\text{In}_{2-x}\text{Si}_x\text{Se}_3$ samples based on the measured $\sigma$ and $S$. The $PF$ gradually increased with increasing temperature in both the $\alpha$ and $\beta$ phases. For all the samples, the $PF$ decreased during the phase transition from $\alpha$ to $\beta$, which is mainly attributed to decreases in the $\sigma$. The maximum $PF$ for the $\alpha$ phase samples was $0.137\ \text{mW/mK}$ for $x = 0.015$ at 450 K, and that for the $\beta$ phase samples was $0.0884\ \text{mW/mK}$ for $x = 0.015$ at 750 K. Another phase transition from $\beta$ phase to $\gamma$ phase was reported in literature at $\sim 620\ \text{K}$, however, the abrupt change of electrical transport properties was not seen in the experiment [23].

For better understanding of the electrical transport properties, Hall carrier concentration ($n_H$) and Hall mobility ($\mu_H$) were measured and are shown in Figure 3a and Figure 3b, respectively. The $n_H$ values of the samples were $-6.10 \times 10^{17}$, $-1.21 \times 10^{16}$, $-2.27 \times 10^{14}$, $-8.78 \times 10^{14}$, and $-1.02 \times 10^{18} \text{ cm}^{-3}$ for $x = 0$, 0.005, 0.01, 0.015, and 0.02, respectively. The $n_H$ values of the samples decreased up to $x = 0.01$ and then increased to the largest value beyond $x = 0.01$, which seems to be abnormal. At this stage, the clear reason for this abnormal behavior is unknown, but it can be speculated that the various intrinsic defects, including vacancies, interstitials, and antisite defects, in $\text{In}_2\text{Se}_3$, seem to play complex roles as doping increases. Various intrinsic defects exist for this complex structure of $\alpha(2H)$-$\text{In}_2\text{Se}_3$ [24]. The complex phase change in $\text{In}_2\text{Se}_3$ may imply larger possibility of the intrinsic defects [19–23]. In Figure 3b, the $\mu_H$ of all the doped samples decreased significantly, compared to pristine sample of $x = 0$. The $\mu_H$ of the sample with $x = 0$ was $147\ \text{cm}^2/\text{Vs}$, whereas the $\mu_H$ of the samples with $x = 0.005$, 0.01, 0.015 and 0.02 were 11.2, 14.0, 10.7 and $6.66\ \text{cm}^2/\text{Vs}$, respectively; the $\mu_H$ values of the doped samples decreased by more than 10 times compared with those of the undoped sample.

Figure 4a shows the temperature dependence of $\lambda$ for the $\text{In}_{2-}\text{Si}_x\text{Se}_3$ ($x = 0$, 0.005, 0.01, 0.015, and 0.02) samples. For the $\alpha$ phase samples, the $\lambda$ values gradually decreased with increasing doping contents, which is caused by the point-defect phonon scattering via Si doping. Notably, the $\lambda$ decreased significantly when the crystal structure was changed from the $\alpha$ to $\beta$ phase. The measured $\lambda$ values of the $\beta$ phase samples were very low (less than 0.15 mm$^2$/s) and increased gradually with temperature. Figure 4b shows the temperature dependence of $\kappa_{\text{tot}}$ for the samples. The $\kappa_{\text{tot}}$ values were $1.28$, $1.12$, $0.90$, $0.87$, and $0.61\ \text{W/mK}$ at $300\ \text{K}$ and $0.43$, $0.35$, $0.38$, $0.40$ and $0.36\ \text{W/mK}$ at $500\ \text{K}$ for $x = 0$, 0.005, 0.01, 0.015 and 0.02, respectively. The $\kappa_{\text{tot}}$ values decreased by 41–68% due to the phase transition from $\alpha$ to $\beta$, and the measured $\kappa_{\text{tot}}$ value for $\beta$ phase were quite low (less than 0.5 W/mK).

**Table 1.** Atomic percentage measured by energy-dispersive spectroscopy (EDS) for $\text{In}_{2-x}\text{Si}_x\text{Se}_3$ with $x = 0.01$ and 0.02.

<table>
<thead>
<tr>
<th>$\text{In}_{2-x}\text{Si}_x\text{Se}_3$</th>
<th>In</th>
<th>Si</th>
<th>Se</th>
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<tr>
<td>$x = 0.02$</td>
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<td>0.28</td>
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Figure 2a,b show the plotted $\sigma$ and $S$ values of the $\text{In}_{2-x}\text{Si}_x\text{Se}_3$ ($x = 0$, 0.005, 0.01, 0.015, and 0.02) samples with different $x$ values, measured using ZEM-3. The $\sigma$ of all the samples decreased significantly during the $\alpha$-$\beta$ phase transition. The $\sigma$ values at 450 K for the $\text{In}_{2-x}\text{Si}_x\text{Se}_3$ samples with $x = 0$, 0.005, 0.01, 0.015 and 0.02 were $30.3$, 0.00108, 0.00322, 28.0 and $3.42\ \text{S/cm}$, respectively, and at 500 K, the $\sigma$ values decreased to $3.11$, $3.01 \times 10^{-4}$, $6.47 \times 10^{-4}$, 1.10 and $0.497\ \text{S/cm}$, respectively. Generally, the $\sigma$ exhibited semiconductor behavior in both the $\alpha$ and $\beta$ phases. The highest $\sigma$ value for $\alpha$ phase was $30.30\ \text{S/cm}$ for $x = 0$ at 400 K, and that for $\beta$ phase was $6.705\ \text{S/cm}$ for $x = 0.015$ at 750 K. Along with the $\sigma$, the magnitude of $S$ values of the samples increased due to the phase transition at 500 K. The largest $|S|$ values for both $\alpha$ and $\beta$ phases were observed for the sample with $x = 0.01$; the value of $S$ of the sample with $x = 0.01$ was $-465.3\ \mu V/K$ at 400 K and $-950.4\ \mu V/K$ at 500 K.
The state-of-the-art $zT$ was achieved for the sample with $x = 0.015$, which is attributed to its highest $\alpha$ phase. The highest $zT$ value for the $\alpha$ phase was 0.100 at 450 K for the sample with $x = 0.015$, which is attributed to its highest $PF$ and second-lowest $\kappa_{\text{tot}}$. The $zT$ decreased once at 500 K by the phase transition from $\alpha$ to $\beta$, but the $zT$ of all the $\beta$ phase samples exhibited higher $zT$ than those of the $\alpha$ phase samples, owing to their low $\kappa_{\text{tot}}$ values. For $\beta$ phase, the sample with $x = 0.015$ showed the highest $zT$ value of 0.154 at 750 K, which is improved by 48% compared to pristine $\beta$-In$_2$Se$_3$. The $zT$ of the samples shows a non-linear behavior with Si doping contents, mainly due to the abnormal behavior seen for electrical transport properties (Figures 2 and 3). As a result, the optimal Si doping for both $\alpha$ and $\beta$ phase was achieved for the sample with $x = 0.015$ ($\text{In}_{0.985}\text{Si}_{0.015}\text{Se}_3$) with the maximum $zT$ values ~0.154 at 750 K, whereas the maximum $zT$ of the intrinsic In$_2$Se$_3$ was 0.11 at 790 K. The state-of-the-art In$_2$Se$_3$ polycrystalline samples with proper doping was reported for...
Cu-doped or Ag-added In$_2$Se$_3$, which shows the maximum $zT$ values higher than 0.5–0.6 at 900 K [20,25].

![Figure 5](image-url). Thermoelectric figure of merit as a function of temperature for the In$_{2-x}$Si$_x$Se$_3$ ($x = 0, 0.005, 0.01, 0.015, $ and 0.02) samples.

4. Conclusions

We investigated the influence of Si doping on the thermoelectric transport properties of In$_2$Se$_3$ by synthesizing a series of In$_{2-x}$Si$_x$Se$_3$ ($x = 0.005, 0.01, 0.015,$ and 0.02) polycrystalline samples. Hexagonal $\alpha$(2H)-In$_2$Se$_3$ phase was synthesized without any impurity, and gradual changes in the lattice parameters were observed with Si doping. Drastic changes were observed for the measured electrical and thermal transport properties at 450–500 K, due to the phase transition from $\alpha$ to $\beta$ at 473 K. The highest power factors were reached by the sample with $x = 0.015$ for both $\alpha$ and $\beta$ phases, exhibiting the values of 0.137 and 0.0884 mW/mK$^2$ at 450 and 750 K, respectively. The total thermal conductivities of the $\alpha$ phase samples decreased gradually with increasing Si doping content, which is attributed to the point defect phonon scattering by Si doping. The total thermal conductivities of the $\beta$ phase samples significantly decreased compared to those of the $\alpha$ phase samples. As a result, the sample with $x = 0.015$ (In$_{1.985}$Si$_{0.015}$Se$_3$) showed the maximum thermoelectric figure of merit values of 0.100 and 0.154 at 450 and 750 K, which are enhanced by 152 and 48% compared with those of the undoped $\alpha$- and $\beta$-In$_2$Se$_3$ samples, respectively.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ceramics5030022/s1, Figure S1: $C_p$ of the In$_2$Se$_3$ as a function of temperature measured by differential scanning calorimetry; Figure S2: EDS results of for In$_{2-x}$Si$_x$Se$_3$ with $x = 0.01$ and 0.02; Table S1: Atomic percentage measured by energy-dispersive spectroscopy (EDS) for In$_{2-x}$Si$_x$Se$_3$ with $x = 0.01$ and 0.02.

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Conflicts of Interest: The authors declare no conflict of interest.

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