Phase Formation Behavior and Thermoelectric Transport Properties of S-Doped FeSe$_{2-x}$S$_x$ Polycrystalline Alloys

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Abstract: Some transition-metal dichalcogenides have been actively studied recently owing to their potential for use as thermoelectric materials due to their superior electronic transport properties. Iron-based chalcogenides, FeTe$_2$, FeSe$_2$ and FeS$_2$, are narrow bandgap (~1 eV) semiconductors that could be considered as cost-effective thermoelectric materials. Herein, the thermoelectric and electrical transport properties FeSe$_2$–FeS$_2$ system are investigated. A series of polycrystalline samples of the nominal composition of FeSe$_{2-x}$S$_x$ ($x = 0, 0.2, 0.4, 0.6, \text{and} \ 0.8$) samples are synthesized by a conventional solid-state reaction. A single orthorhombic phase of FeSe$_2$ is successfully synthesized for $x = 0, 0.2, \text{and} \ 0.4$, while secondary phases (Fe$_7$S$_9$ or FeS$_2$) are identified as well for $x = 0.6 \text{and} \ 0.8$. The lattice parameters gradually decrease gradually with S content increase to $x = 0.6$, suggesting that S atoms are successfully substituted at the Se sites in the FeSe$_2$ orthorhombic crystal structure. The electrical conductivity increases gradually with the S content, whereas the positive Seebeck coefficient decreases gradually with the S content at 300 K. The maximum power factor of 0.55 mW/mK$^2$ at 600 K was seen for $x = 0.2$, which is a 10% increase compared to the pristine FeSe$_2$ sample. Interestingly, the total thermal conductivity at 300 K of 7.96 W/mK ($x = 0$) decreases gradually and significantly to 2.58 W/mK for $x = 0.6$ owing to the point-defect phonon scattering by the partial substitution of S atoms at the Se site. As a result, a maximum thermoelectric figure of merit of 0.079 is obtained for the FeSe$_{1.8}$S$_{0.2}$ ($x = 0.2$) sample at 600 K, which is 18% higher than that of the pristine FeSe$_2$ sample.

Keywords: FeSe$_2$; FeS$_2$; thermoelectric; chalcogenides

1. Introduction

Thermoelectric materials have been widely studied in recent years, owing to their ability to convert waste thermal gradients into electrical energy [1]. The energy-conversion efficiency of thermoelectric materials can be evaluated using the dimensionless thermoelectric figure of merit, $zT$, which is expressed by the following Equation (1).

$$zT = \frac{\sigma S^2}{\kappa_{tot}} T$$

where $\sigma$, $S$, $T$, and $\kappa_{tot}$ are the electrical conductivity, Seebeck coefficient, absolute temperature, and total thermal conductivity, respectively [2–4]. Generally, $\kappa_{tot}$ is divided into two terms:

$$\kappa_{tot} = \kappa_{elec} + \kappa_{latt}$$

where $\kappa_{elec}$ and $\kappa_{latt}$ are the electrical and lattice thermal conductivities, respectively. $zT$ can be improved by increasing the power factor ($\sigma \cdot S^2$) or reducing $\kappa_{tot}$. However, the trade-off between $\sigma$ and $S$ and the proportionate relationship between $\sigma$ and $\kappa_{elec}$ make it difficult to improve $zT$. One strategy to obtain a high $zT$ is to reduce $\kappa_{latt}$ via point-defect phonon scattering, which can be achieved by doping or using a partial solid solution [5,6]. For example, Aslandiyar et al. investigated the thermoelectric properties of alloyed samples...
in an SnS–SnSe system, and they reported that the $\kappa_{\text{lat}}$ of the alloyed samples was lower than that of the nonalloyed samples, and that the $zT$ of the alloyed samples was greatly enhanced [7].

Transition-metal dichalcogenides (TMDCs) such as HfSe$_2$ [8,9], HfTe$_2$ [10], MoSe$_2$ [11], and SnSe$_2$ [12,13] have attracted significant attention because of their high potential for use as thermoelectric materials. Generally, TMDCs have a large effective mass owing to the presence of local d- or f-orbital electrons, leading to a large magnitude of $S$ [14]. Among these TMDCs, FeSe$_2$ and FeS$_2$ have been actively investigated as promising thermoelectric materials. FeSe$_2$ is a $p$-type semiconductor with a narrow direct bandgap of ~1 eV [15]. FeSe$_2$ is known to be thermally and structurally stable, as previous studies have reported [16,17]. It has a high carrier concentration, of $10^{18}$–$10^{19}$ cm$^{-3}$, and is considered a good candidate for thermoelectric applications [17,18]. FeS$_2$ is a semiconductor with a narrow bandgap (~1 eV) and is one of the most abundant sulfides in the Earth’s crust [19]. It is nontoxic, inexpensive, and is considered a promising cost-effective thermoelectric material. By combining the first-principles calculations with the Boltzmann transport theory, Harran et al. predicted that the $zT$ of FeS$_2$ could reach approximately 0.45 [20,21].

In this study, the electrical and thermoelectric transport properties of a series of polycrystalline FeSe$_{2-x}$S$_x$ ($x = 0, 0.2, 0.4, 0.6$, and 0.8) samples of the FeSe$_2$–FeS$_2$ system are investigated. The S substitution for the Se site was successful up to S content of $x = 0.6$. The $\sigma$ increased gradually with the S content, whereas the positive $S$ decreased gradually with the S content at 300 K. The weighted mobility of the samples is calculated and analyzed to understand the electrical transport properties better. With an increase in S content, the $\kappa_{\text{lat}}$ decreases gradually and significantly.

### 2. Experimental Section

Polycrystalline FeSe$_{2-x}$S$_x$ ($x = 0, 0.2, 0.4, 0.6$, and 0.8) samples were synthesized via a conventional solid-state reaction in vacuum-sealed quartz tubes. High-purity raw materials: Fe (99.9%, Kojundo Chemical Laboratory Co., Ltd., Tolya, Japan), Se (99.999%, 5 N Plus), and S (99.995%, Sigma-Aldrich, St. Louis, MO, USA) were weighed stoichiometrically and heated at 833 K for 48 h. The obtained ingots were pulverized into powder using a ball-milling machine (SPEX 8000D, SPEX, Costa Mesa, CA, USA). Each powder sample was densified through spark plasma sintering (SPS-1030, Sumitomo Coal Mining Co. Ltd., Japan) at 803 K for 7 min under a pressure of 75 MPa. The crystalline structures of the sintered samples were identified through X-ray diffraction (XRD, D8 Discover, Bruker, Billerica, MA, USA) using Cu K$_{\alpha}$1 radiation. Energy-dispersive X-ray spectroscopy (EDS) and EDS mapping were measured by secondary electron microscopy (SEM). The thermoelectric transport properties ($\sigma$ and $S$) of the samples were measured using a thermoelectric evaluation system (ZEM-3M8, Advance Riko, Kanagawa prefecture, Japan) in the temperature range of 300–600 K. Hall measurements were conducted in the van der Pauw configuration using a Hall measurement system (HMS-5300, Ecopia, Korea) at 300 K. The thickness of the specimen for Hall measurement were 0.75, 0.73, 0.70, and 0.70 mm for $x = 0, 0.2, 0.4$, and 0.6, respectively, and the applied electric current and magnitude of the magnetic field were 20 mA and 0.553 T, respectively. The $\kappa_{\text{tot}}$ of each sample was calculated as follows:

$$\kappa_{\text{tot}} = \kappa_{\text{lat}} + \kappa_{\text{rad}}$$

where $\kappa_{\text{rad}}$ is the radiative thermal conductivity, $\kappa_{\text{lat}}$ is the lattice thermal conductivity, $\kappa_{\text{tot}}$ is the total thermal conductivity, $\rho$ is the density, $C_p$ is the specific heat capacity, and $T$ is the temperature. The $\kappa_{\text{rad}}$ values for the samples were 7.15, 7.05, 6.93, 6.65, and 6.25 W/mK for $x = 0, 0.2, 0.4, 0.6$, and 0.8, respectively.

The bulk densities for the samples were measured using the Archimedes method, and the relative densities were obtained from $D_a$ and bulk densities. The calculated relative density values were 99.7, 98.9, 98.3, 98.3, and 97.8% for $x = 0, 0.2,$
0.4, 0.6, and 0.8, respectively. The $C_p$ for the samples was measured using a differential scanning calorimeter (DSC8000, Perkin Elmer, Waltham, MA, USA).

3. Results and Discussion

Figure 1a shows the XRD patterns of the sintered samples of FeSe$_{2-x}$S$_x$ ($x = 0, 0.2, 0.4, 0.6,$ and 0.8). The samples with $x = 0, 0.2, and 0.4$ exhibited a single orthorhombic phase (FeSe$_2$, JCPDS #01-079-1892) without any impurity. However, for the samples with higher S content ($x = 0.6$ and 0.8), a secondary phase (Fe$_7$S$_8$, JCPDS #01-089-1954) was identified. For the sample with $x = 0.8$, the peak intensity of the Fe$_7$S$_8$ secondary phase was increased and a small amount of FeS$_2$ was observed. The relative peak intensities remain similar for the samples with $x = 0, 0.2, 0.4$, and 0.6 (See Table S1 in Supplementary Materials). In addition, the grain sizes $D$ for the samples ($x = 0, 0.2, 0.4$, and 0.6) were estimated using the Scherrer equation [22]:

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where $K$, $\lambda$, $\theta$, and $\beta$ are the Scherrer constant, the wavelength of the X-ray beam, Bragg angle, and full width at half maximum, respectively. The $K$ value of 0.94 was used, assuming the spherical crystallites. The calculated $D$ values for the samples were 39.8, 39.2, 32.2, and 24.8 nm for $x = 0, 0.2, 0.4,$ and 0.6, respectively. Even though the grain size of $x = 0.6$ is a bit smaller (possibly due to secondary phase formation), it can be known that there is no large difference in microstructures between samples of $x = 0, 0.2, 0.4,$ and 0.6. The lattice parameters $a, b,$ and $c$ for the FeSe$_{2-x}$S$_x$ ($x = 0, 0.2, 0.4, 0.6,$ and 0.8) crystal structures were calculated and are shown with error bars in Figure 1b. All lattice parameters decreased gradually with an increase in S content when $x < 0.8$, which confirmed that S atoms were successfully substituted at Se sites in the FeSe$_2$ crystal structure (the ionic radii of S$^{2-}$ and Se$^{2-}$ are 170 and 184 pm, respectively). However, the lattice parameters $a, b,$ and $c$ for $x = 0.8$, exhibited values similar to that for $x = 0.6$, suggesting that further S substitution at Se sites was limited. The EDS-SEM results are shown in Figure S1 and the atomic ratios measured by EDS-SEM are shown in Table S2 (Supplementary Information). The S-excess/Se-deficient regions are seen for $x = 0.8$, where the secondary phases started to be seen. The overall compositional ratios of S increases as S doping increases (Table S2 in Supplementary Information).

Figure 1. (a) XRD patterns of the series of FeSe$_{2-x}$S$_x$ ($x = 0, 0.2, 0.4, 0.6, 0.8,$ and 1) samples. (b) Lattice parameters calculated using the XRD patterns.
Figure 2a shows the $\sigma$ values of the FeSe$_{2-x}$S$_x$ ($x = 0, 0.2, 0.4, 0.6$, and 0.8) samples. The sample with $x = 0.8$ with extensive secondary phases, which did not show the gradual decrease in lattice parameters, exhibited much higher $\sigma$ values ~440 S/cm at 300 K (Not shown in Figure 2a). The thermoelectric measurement data of the $x = 0.8$ sample is not included due to the non-systematic change due to the existence of the secondary phases. The $\sigma$ of the samples increased with temperature, exhibiting intrinsic semiconducting behavior. The $\sigma$ values were 12.4, 15.3, 19.8, and 49.6 S/cm at 300 K, and 247, 315, 353, 442, and 1170 S/cm at 600 K for $x = 0, 0.2, 0.4, 0.6$, and 0.8, respectively. The value of $\sigma$ increased gradually with an increase in S content, over the entire temperature range. The relationship between $\sigma$ and $T$ can be expressed by the Arrhenius relationship [23]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

where $k$ is the Boltzmann constant and $E_a$ is the activation energy. The inset in Figure 2b shows the Arrhenius relationship (logarithmic $\sigma$ as a function of $1000/T$) for the samples and Figure 2b shows the calculated $E_a$ with respect to $x$. Noticeable changes in the slope were observed at 400–450 K (Inset of Figure 2b). The calculated $E_a$ values of the samples were 0.033, 0.032, 0.028, 0.013, and 0.006 eV in the low-temperature range and 0.123, 0.115, 0.114, 0.108, and 0.048 eV in the high-temperature range for $x = 0, 0.2, 0.4, 0.6$, and 0.8, respectively. The $E_a$ decreased gradually with an increase in S content in both low- and high-temperature ranges.

Figure 2. (a) $\sigma$ as a function of the temperature for the series of FeSe$_{2-x}$S$_x$ ($x = 0, 0.2, 0.4, 0.6$, and 0.8) samples. (b) $E_a$ of the samples calculated from $\sigma$ for 300–400 K and 450–600 K. The inset of (b) shows logarithmic $\sigma$ as a function of $1000/T$ for the samples. (c) $S$ as a function of temperature for the samples. Power factors as functions of temperature for the samples in (d) p- and (e) n-type regions.

Figure 2c shows $S$ as a function of the temperature for the FeSe$_{2-x}$S$_x$ ($x = 0, 0.2, 0.4$, and 0.6) samples. The $S$ values of the samples at 300 K were 445, 146, 85, and 6 $\mu$V/K for $x = 0, 0.2, 0.4$, and 0.6, respectively. All the samples exhibited positive $S$ values at 300 K,
where \( m \) and \( n \) were 0.50, 0.55, 0.48, 0.17, and 0.051 mW/mK, respectively. The power factor of the sample with \( x = 0.2 \) was the highest, which could be attributed to an increase in \( \sigma \) and a small decrease in the magnitude of \( S \). Therefore, a maximum power factor of 0.55 mW/mK was achieved for the sample with \( x = 0.2 \) at 600 K, which was 10% higher than that of pristine FeSe\(_2\). The sample of \( x = 0.6 \) exhibits lower power factors due to a large decrease in the magnitude of \( S \).

Figure 3a,b present the Hall carrier concentration (\( n_{\text{H}} \)) and Hall mobility (\( \mu_{\text{H}} \)) of the samples, measured at 300 K. The \( n_{\text{H}} \) values were 1.67 \times 10^{19}, 1.81 \times 10^{19}, 1.91 \times 10^{19}, and 3.80 \times 10^{19} \text{ cm}^{-3} \) and the \( \mu_{\text{H}} \) values were 4.01, 4.90, 5.97, and 6.44 cm\(^2\)/Vs, for \( x = 0, 0.2, 0.4, \) and 0.6, respectively. All the samples exhibited positive \( n_{\text{H}} \) values at 300 K, and \( n_{\text{H}} \) and \( \mu_{\text{H}} \) increased gradually with an increase in \( x \). Thus, the increase in the \( \sigma \) of the samples could be due to the simultaneous increase in \( n_{\text{H}} \) and \( \mu_{\text{H}} \). Furthermore, an increase in carrier concentration generally leads to a decrease in the magnitude of \( S \), according to the Mott relationship [24]:

\[
S = \frac{8\pi^2k^2}{3\epsilon h^2} m_e^* T \left( \frac{\pi}{3m} \right)^2, \tag{6}
\]

where \( m_e^* \), \( e \), and \( h \) are the density-of-state effective mass, elementary charge, and Planck’s constant, respectively. Therefore, the decrease in the magnitude of \( S \) for the alloyed samples at 300 K could be attributed to the increase in \( n_{\text{H}} \). Figure 3c,d show the \( m_e^* \) values of the samples at 300 K calculated using the measured \( S \) and \( n_{\text{H}} \), based on the relationship in Equation (6). The \( m_e^* \) values of the samples were 1.45, 0.50, 0.30, and 0.04 for \( x = 0, 0.2, 0.4, \) and 0.6, respectively. The \( m_e^* \) values decreased gradually with an increase in \( S \) content.

Figure 3e shows the weighted mobility (\( \mu_w \)) of the samples, obtained for a better understanding of the thermoelectric properties of the samples. The \( \mu_w \) was calculated using the measured \( \sigma \) and \( S \) from a simple analytic form that approximates the exact Drude–Sommerfeld free-electron model for \( |S| > 20 \mu\text{V/K} \) [25]:

\[
\mu_w = \frac{3h^3\sigma}{8\pi^2e(2m_e kT)^{3/2}} \left[ \frac{\exp\left[\frac{|S|}{kT} - 2\right]}{1 + \exp\left[-5\left(\frac{|S|}{kT} - 1\right)\right]} + \frac{3}{5} \frac{|S|}{kT} \left|\frac{|S|}{kT} - 1\right| \right], \tag{7}
\]

where \( m_e \) is the electron mass. \( \mu_w \) is closely related to the theoretically optimum electrical performance of a thermoelectric material, and is relevant to the maximum power factor when \( n_{\text{H}} \) is tuned properly [26]. Therefore, the \( \mu_w \) trend was very similar to that of the power factor. The values of \( \mu_w \) at 600 K were 20.3, 22.7, 20.9, and 11.9 cm\(^2\)/Vs for \( x = 0, 0.2, 0.4, \) and 0.6, respectively. The \( \mu_w \) increased initially at \( x = 0.2 \) and decreased gradually at \( x > 0.2 \), which was in agreement with the power factor trend at 600 K.

Figure 4a,b show the \( \kappa_{\text{tot}} \) and \( \kappa_{\text{latt}} \) of the samples as functions of temperature. The inset of Figure 4a shows the temperature dependence of \( \kappa_{\text{elec}} \). The \( \kappa_{\text{elec}} \) of the samples was calculated according to the Wiedemann–Franz law [27]:

\[
\kappa_{\text{elec}} = L\sigma T \tag{8}
\]
where \( L \) is the Lorenz number. Subsequently, the \( \kappa_{\text{latt}} \) was calculated by subtracting \( \kappa_{\text{elec}} \) from \( \kappa_{\text{tot}} \). The electronic contribution to \( \kappa_{\text{tot}} \) was not very significant; thus, \( \kappa_{\text{latt}} \) and \( \kappa_{\text{tot}} \) exhibited similar values. The \( \kappa_{\text{latt}} \) values of the samples were 7.96, 6.07, 4.47, and 2.58 W/mK at 300 K and 4.29, 3.85, 3.51, and 2.10 W/mK at 600 K, for \( x = 0, 0.2, 0.4, \) and 0.6, respectively. The \( \kappa_{\text{latt}} \) decreased gradually as the S content increased, over the entire temperature range, which was attributed to the point-defect phonon scattering caused by the partial substitution of S atoms at Se sites (the atomic masses of S and Se are 32.065 and 78.96 amu and the ionic radii of \( S^{2-} \) and \( Se^{2-} \) are 170 and 184 pm, respectively).
Figure 4. (a) $\kappa_{\text{tot}}$ and (b) $\kappa_{\text{latt}}$ as functions of temperature for the series of FeSe$_{2-x}$S$_x$ ($x = 0$, 0.2, 0.4, and 0.6) samples. The inset of (a) shows $\kappa_{\text{elec}}$ as a function of temperature for the samples. $zT$ as a function of temperature for the samples in (c) $p$- and (d) $n$-type regions.

4. Conclusions

A series of FeSe$_{2-x}$S$_x$ ($x = 0$, 0.2, 0.4, 0.6, and 0.8) polycrystalline samples were synthesized by a conventional solid-state reaction, and their thermoelectric transport properties were examined in an effort to search for the cost-effective thermoelectric materials. A single orthorhombic FeSe$_2$ phase was successfully synthesized for $x = 0$, 0.2, and 0.4; however, a secondary phase (Fe$_7$S$_8$ or FeS$_2$) was identified for $x = 0.6$ and 0.8. The lattice parameters decreased gradually with an increase in S content for $x < 0.8$, suggesting that S atoms were substituted at the Se sites in the FeSe$_2$ crystal structure. The electrical conductivity increased gradually with an increase in S content, whereas the magnitude of $S$ decreased gradually with an increase in S content. As a result, the sample with $x = 0.2$ exhibited a maximum power factor of 0.55 mW/mK$^2$ at 600 K. The total thermal conductivity decreased...
significantly with an increase in S content, and thus a maximum thermoelectric figure of merit value of 0.079 was obtained for the FeSe$_{1.8}$S$_{0.2}$ ($x = 0.2$) sample at 600 K, which was approximately 18% higher than that of the FeSe$_2$ ($x = 0$) sample.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/10.3390/mi13122066/s1, Figure S1: EDS-SEM results for FeSe$_{2-x}$S$_x$ ($x = 0$, 0.2, 0.4, 0.6 and 0.8); Figure S2: (a) $\sigma$, (b) $S$, and (c) $PF$ as a function of temperature for the FeSe$_2$ sample, measured after ~180 days from the initial measurement for cycling test; Figure S3: Estimated $E_g$ for the series of FeSe$_{2-x}$S$_x$ ($x = 0$, 0.2, 0.4 and 0.6) samples using Goldsmid-Sharp empirical formula; Table S1: The relative peak intensities for (111), (012), (121), (011), (200) and (103) planes for FeSe$_{2-x}$S$_x$ ($x = 0$, 0.2, 0.4, and 0.6) in the X-ray diffraction data; Table S2: Atomic ratios measured by EDS-SEM for FeSe$_{2-x}$S$_x$ ($x = 0$, 0.2, 0.4, 0.6 and 0.8). References [16,28] are cited in the supplementary materials.

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