Thermoelectric Properties of In$_x$FeCo$_3$Sb$_{12}$ Consisting Mainly of In-Filled p-Type Skutterudites

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Indium (In)-filled CoSb$_3$ skutterudite is known as a good n-type thermoelectric (TE) material. Its p-type samples have not been intensively studied. In this study, we tried to reduce the electron concentration of (In)-filled CoSb$_3$ by substituting Fe atoms for 1/4 of Co atoms in In$_x$Co$_{12-x}$Sb$_{12}$. Polycrystalline samples were prepared with the nominal compositions of In$_x$FeCo$_3$Sb$_{12}$ ($x = 0.3, 0.5, 0.7$, and $0.9$) and their constituent phases, microstructure, high-temperature TE properties were carefully investigated. All the samples showed positive sign of Seebeck coefficient as we expected from the nominal compositions. The filling fraction of In in In$_x$FeCo$_3$Sb$_{12}$ was revealed to extend to the value of $x = 0.43$. The largest dimensionless figure of merit $zT = 0.39$ was observed at 705 K for the sample prepared at $x = 0.5$.

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1. Introduction

Using thermoelectric (TE) generators, one can directly convert waste heat into electricity, and therefore have been intensively investigated as one of the potential energy saving technologies. The efficiency of TE generators increases intensively investigated as one of the potential energy saving technologies. The efficiency of TE generators increases using thermoelectric (TE) generators, one can directly convert waste heat into electricity, and therefore have been intensively investigated as one of the potential energy saving technologies. The efficiency of TE generators increases with increasing dimensionless figure of merit, $zT = S^2\sigma T/\kappa$ of thermoelectric materials used in the generators. Here, $S$, $\sigma$, and $\kappa$ represents Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively. It would also be important to note that both electrons and lattice vibrations contribute to the thermal conductivity, and their contributions are denoted as electron thermal conductivity $\kappa_e$ and lattice thermal conductivity $\kappa_la$, respectively. Power factor $PF = S^2/\sigma$ is also used as a measure of thermoelectric materials, because it provides us with the electrical power obtainable with a given temperature gradient. Good thermoelectric materials mean those possessing a large magnitude of $zT$ in association with a large magnitude of $PF$ and a small magnitude of $\kappa$. Novel materials such as tellurides, half-Heuslers, and clathrates are known as good thermoelectric materials. It would also be important to note that both electrons and lattice vibrations contribute to the thermal conductivity, and their contributions are denoted as electron thermal conductivity $\kappa_e$ and lattice thermal conductivity $\kappa_la$, respectively.

Skutterudite compounds have been considered as a good candidate of TE materials because of non-toxic, abundant constituent elements together with high $zT$-values. Binary skutterudite has a cubic structure with $Im-3$ symmetry, and it contains 32 atoms in the unit cell. Its chemical formula is generally expressed as $M_{32}X_{32}$, where $M$ and $X$ represent a transition metal element (Co, Fe, Ir) and a pnictogen element (P, As, Sb). The crystal structure of the skutterudite is characterized by two cage-like vacant sites in a unit cell where additional elements are capable of being involved. These atoms, called as fillers, were reported to have variation such as alkali metals and rare-earth elements. Notably filler atoms produce optical phonon branches at low energy, and sometimes causes anharmonic oscillation to greatly reduce the lattice thermal conductivity.

In sharp contrast to the n-type CoSb$_3$-based skutterudites possessing a large magnitude of $zT$, n-type CoSb$_3$-based skutterudites were rarely reported mainly because the excess holes were produced to compensate the reduction of electron concentration when element substitutions such as Fe for Co were employed to realize p-type behaviors. We considered that the formation of vacancies would be suppressed with increasing amount of fillers, because the increased electron concentration by the filler atoms presumably reduces the driving force of vacancy formation. It should be also very important to note here that the (Fe,Co)Sb$_3$-based p-type skutterudites generally indicate higher filling fraction than that in CoSb$_3$-based n-type samples due to the expanded volume of vacant sites.

Among the filler candidates, we selected In as an appropriate filler element, because group 13 elements were reported to cause excellent TE properties for n-type filled skutterudites. In deed, an indium (In) filled CoSb$_3$ exhibits the highest $zT$ exceeding unity. Besides, the positive sign of Seebeck coefficient was reported for In-filled (Co,Fe)Sb$_3$ by several different groups. Leszczynski et al. reported that the Seebeck coefficient of In$_{0.9}$Fe$_{0.5}$Co$_{0.5}$Sb$_{12}$ reached to 125 $\mu$VK$^{-1}$ at 350 K. Park et al. also reported that In$_{0.05}$Fe$_{0.15}$Co$_{0.5}$Sb$_{12}$ possesses a positive sign of Seebeck coefficient with $zT = 0.37$ at 700 K.

It was also reported that FeSb$_2$ and Sb precipitate in the...
samples prepared at $\text{In}_x(\text{Fe}_3\text{Co}_1-\gamma_3)\text{Sb}_{12}$ ($y > 1/3$), these impurity phases lead to the reduction of Seebeck coefficient.\(^{24,25}\) To avoid the heavy precipitation of impurity phases, we prepared, in the present study, the sample at $\text{In}_x\text{FeCo}_3\text{Sb}_{12}$ ($x = 0.3, 0.5, 0.7$, and $0.9$), and their TE properties were examined from room temperature to $773\ K$ to investigate the effects of the In-filling and the Fe substitution on the TE properties.

2. Experiment

The pure elements, In (99.999%), Fe (99.99%), Co (99.98%), and Sb (99.9999%), were weighed so as to the composition to be $\text{In}_x\text{FeCo}_3\text{Sb}_{12}$ ($x = 0.3, 0.5, 0.7$, and $0.9$). The weighed elements were sealed into evacuated quartz ampoules, and heated up to $1323\ K$ with the increasing rate of $1\ K\ min^{-1}$. After being kept at $1323\ K$ for 3 days, the ampoules were rapidly quenched into iced water. The quenched samples were annealed at $923\ K$ for a week to obtain the thermodynamically stable condition. The obtained ingots were ground using an agate mortar, and then sintered by means of the spark plasma sintering technique in graphite dies under an Ar flow atmosphere and the pressure of $50\ MPa$ at $923\ K$ for 15 min. The density of the bulk samples was calculated based on the measured weight and dimensions. The obtained samples were characterized by powder X-ray diffraction (XRD) using $\text{Cu K\alpha}$ radiation at room temperature in a commercially available apparatus (Rigaku, Ultima IV). The lattice parameters were calculated by a least-squares fitting using the Rietan-FP program.\(^{20}\) The microstructure and elemental distribution of the samples were investigated using field emission scanning electron microscopy (FE-SEM; JEOL, JSM-6500F) and energy dispersive x-ray spectroscopy (EDS) under vacuum at room temperature.

Electrical resistivity and Seebeck coefficient were measured using a commercially available apparatus (ULVAC, ZEM-3) in a He atmosphere. Thermal conductivity $\kappa$ was evaluated from the thermal diffusivity ($D$), heat capacity ($C_p$), and sample density ($d$) using the relationship $\kappa = D C_p d$. The value of $C_p$ was estimated from the Dulong–Petit law, $C_p = 3n k_B$, where $n$ is the number of atoms per unit volume and $k_B$ is the Boltzmann constant. Thermal diffusivity $D$ was measured by the flash method under an Ar flow atmosphere using a commercially available apparatus (NETZSCH, LFA457). The TE properties were evaluated from room temperature to $773\ K$.

3. Results and Discussion

Figure 1(a) shows the powder XRD patterns of the polycrystalline samples prepared at the nominal compositions of $\text{In}_x\text{FeCo}_3\text{Sb}_{12}$ ($x = 0.3, 0.5, 0.7$, and $0.9$). All the samples consisted mainly of skutterudite phase and a small amount of (Fe,Co)Sb$_2$ phase were precipitated as a secondary phase. The peaks of impurity phase were negligibly small in the samples prepared at $x > 0.3$, but their intensity increased with increasing $x$. The lattice parameter of skutterudite phase, shown in Fig. 1(b), slightly increased with increasing $x$ at $0 \leq x < 0.7$, and became constant at $x \geq 0.7$. By knowing that all the observed valued of lattice parameters were larger than that of previously reported In-filled CoSb$_3$\(^{18}\) and $\text{In}_x\text{Co}_{4-x}\text{Fe}_x\text{Sb}_{12}$ ($z = 0.05, 0.25; x = 0.5, 1.0, 1.5$)\(^{23}\), we considered that In atoms filled the vacancy sites in our present samples, although the variation of lattice constant was small to be involved in the error range.

Figure 2 shows the FE-SEM images of the samples with nominal compositions $\text{In}_x\text{FeCo}_3\text{Sb}_{12}$ ($x = 0.3, 0.5, 0.7$, and $0.9$). All samples were densely compressed without showing any remarkable cracks or pores. The samples prepared at $x = 0.3$ and $0.5$ had uniformly distributed small grains (0.5–1 $\mu$m). These results on the grain size let us consider that a liquid sintering effect caused by the excess In might occur. The uniformly distributed small grains would be effective for reducing lattice thermal conductivity through the scattering of phonons. As shown in Figs. 2(f) and 2(h), the nanoparticles of less than $100\ nm$ in diameter were clearly observable at the grain boundaries in the samples prepared at $x = 0.7$ and $0.9$. Though the spatial resolution of EDS analysis prevented us from quantitatively investigating the composition of nanoparticles, we speculate that those nanoparticles would be InSb because the formation of InSb nanoparticles in In-rich samples was reported in previous papers.\(^{27,28}\)

Table 1 shows the chemical compositions of the skutterudite phase determined by the quantitative EDS analysis. The data shown here are the average values of the point analyses performed for more than $10$ different grains. The In content...
in the skutterudite phase increased with increasing $x$ at $x \leq 0.7$ and then decreased at $x > 0.7$, while the Fe/Co ratio of all samples were kept nearly constant at $0.25 \pm 0.02$. This result also indicates that the filling fraction limit of In would be $\approx 0.43$, which was determined for the sample prepared at $x = 0.7$ by means of EDS analysis. Despite the small value of In content ($\approx 0.19$), the sample prepared at $x = 0.3$ had the large lattice parameter compared to other In-filled CoSb$_3$, and this enlarged lattice parameter would be accounted for as an effect of Fe-substitution for Co. It would be important for improving the thermoelectric properties of In$_x$FeCo$_3$Sb$_{12}$.
to note here that the analyzed value of maximum In concentration (0.43) is much larger than (0.27 ± 0.01) reported previously for of In₆Co₃Sb₁₄. These results indicate that the Fe- substitution for Co increased the lattice parameter, and consequently led to the larger value of maximum In concentration in the skutterudite phase.

Figures 3(a), 3(b), and 3(c) show the temperature dependences of Seebeck coefficient $S$, electrical resistivity $\rho$, and power factor $PF = S^2/\rho$, respectively, for the polycrystalline samples prepared at nominal compositions InₓFe₃CoₓSb₁₂ ($x = 0.3, 0.5, 0.7,$ and 0.9). For comparison, we superimposed those values reported for In₀.25Fe₁.5Co₂.5Sb₁₂. The value of $\rho$ of all samples increased with temperature, indicating a typical behavior of metals having an ordered structure. $S(T)$ increased with increasing nominal In content over the whole temperature range of measurement. This tendency would be mainly attributed to the decrease of hole concentration with increasing $x$. The value of $\rho$ was monotonically increasing with increasing temperature up to around 700 K and then started to decrease after taking maximal. The reduction of Seebeck coefficient at high temperature is accounted for with the bipolar conduction. The peak temperature of $S(T)$ shifted to lower temperatures with increasing In content, because of the reduction of hole concentration.

Notably the magnitude of $S$ drastically decreased with increasing $x$ at $x > 0.5$ despite that the hole concentration was decreased. We consider that, in the samples with $x > 0.7$, the secondary phases such as (Fe,Co)Sb₂ and InSb increased. The secondary phases such as (Fe,Co)Sb₂ and InSb increased due to the large reduction of Seebeck coefficient in association with the secondary phase precipitation. This fact definitely suggests that, in order to increase $zT$ value of n-type filled skutterudite, we have to eliminate the precipitation of secondary phase.

Figure 3(d) shows the temperature dependences of measured thermal conductivity $\kappa$ for the samples prepared at the nominal compositions of InₓFe₃CoₓSb₁₂ ($x = 0.3, 0.5, 0.7,$ and 0.9). One may archive that the magnitude of $\kappa$ would have been underestimated since the Dulong-Petit value of the heat capacity at constant volume ($C_v \sim 0.235 \ Jg^{-1}K^{-1}$) was used to estimate the $\kappa$ without considering the thermal expansion effect. However, we confirmed that the employed value of $C_v$ was quite reasonable because it showed good consistency with the value ($C_p \sim 0.23 \ Jg^{-1}K^{-1}$) determined by the differential scanning calorimetry (DSC) measurement. In order to estimate the lattice thermal conductivity, we also calculated the value of $\kappa - \kappa_{e,calc} = \kappa - L_0T/\rho + S^2T/\rho$, where the second and the third terms indicate the contribution of electrons, and $L_0$ represents the Lorenz number = 2.45 × 10⁻⁸ WΩK⁻². Now note that the increasing tendency of $\kappa - \kappa_{e,calc}$ at high temperature was caused by the bi-polar diffusion effect to electrons. We superimposed the data reported for the polycrystalline samples prepared at nominal compositions of In₀.25Fe₁.5Co₂.5Sb₁₂. The values of $\kappa - \kappa_{e,calc}$ obtained for the samples prepared at $x = 0.3$ and 0.5 were at 705 K, and this value is close to 157 $\mu$K⁻¹ reported for $\text{Th}_8\text{FeCo}_3\text{Sb}_{12}$ at 673 K.

The value of $PF$ plotted in Fig. 3(c) was not increased with increasing $x$, but drastically reduced at $x > 0.5$ mainly due to the large reduction of Seebeck coefficient in association with the secondary phase precipitation. This fact definitely suggests that, in order to increase $zT$ value of n-type filled skutterudite, we have to eliminate the precipitation of secondary phase.

![Fig. 3](image-url) Temperature dependences of the (a) electrical resistivity $\rho$, (b) Seebeck coefficient $S$, (c) power factor $S^2/\rho$, (d) total thermal conductivity $\kappa$, (e) lattice thermal conductivity $\kappa - \kappa_{e,calc}$, and (f) dimensionless figure of merit $zT$ for polycrystalline samples with nominal compositions InₓFe₃CoₓSb₁₂ ($x = 0.3, 0.5, 0.7,$ and 0.9) and In₀.25Fe₁.5Co₂.5Sb₁₂.
smaller than that of the samples at \( x = 0.7 \) and 0.9 partly because the uniformly distributed small grains increased the scattering probability of phonons, and partly because the secondary phase possesses a larger magnitude of lattice thermal conductivity. It should be also argued that the small value of \( \kappa - \kappa_{\text{calc}} \) observed for \( x = 0.3 \) and 0.5 were slightly larger than that reported for In_{0.25}Fe_{1.5}Co_{2.5}Sb_{12} \(^{23}\), although the reason is not clear now.

The \( zT \) values of the samples were calculated from the measured thermoelectric properties and the resulting values were plotted as a function of temperature in Fig. 3(f). Notably, the value of \( zT \) of the samples prepared at \( x = 0.3 \) and 0.5 exceeded the reported value of In_{0.25}Fe_{1.5}Co_{2.5}Sb_{12} \(^{23}\) at the highest temperature range above 700 K due to the superior \( S \) values. The maximum \( zT \) value observed in this study was 0.39 at 705 K for the sample prepared at \( x = 0.5 \).

4. Summary

The TE properties of polycrystalline samples prepared at the nominal compositions of In_{x}FeCo_{3}Sb_{12} (\( x = 0.3, 0.5, 0.7, \) and 0.9) were investigated. From both the XRD and the FE-SEM/EDS analyses, the maximum filling limit of In in In_{x}FeCo_{3}Sb_{12} skutterudite phase was revealed to be less than \( x = 0.43 \). The grain size of the samples increased with increasing \( x \), meaning that excess In promoted the grain growth via a melt process. The increase of the In content led to the reduction of hole concentration, because In provided the system with conduction electrons. The samples with \( x \geq 0.7 \) exhibited lower \( S \) values than those of the samples with \( x \leq 0.5 \) most likely because of the secondary phase precipitation. The small lattice thermal conductivity caused by the rattling mode of filled In and the enhanced PF with an appropriate hole concentration led to a moderately large magnitude of \( zT \) of 0.39 at 705 K for the samples prepared at \( x = 0.5 \).

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