Enhanced Thermoelectric Properties of Ga and Ce Double-Filled *p*-Type Skutterudites

Jungmin Kim¹, Yuji Ohishi¹, Hiroaki Muta¹ and Ken Kurosaki^{1,2,3,*}

¹Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

²Research Institute of Nuclear Engineering, University of Fukui, Fukui 910-8507, Japan

³Institute for Integrated Radiation and Nuclear Science, Kyoto University, Osaka 590-0494, Japan

Among the *p*-type filled skutterudites, Ce single-filled (Co,Fe)Sb₃ is known as a promising thermoelectric material. Here, we try to enhance the thermoelectric properties of Ce-filled (Co,Fe)Sb₃ by co-filling of Ga. We synthesize the samples in the nominal compositions Ga_xCeFe_{3.5}Co_{0.5}Sb_{12-x/3} ($x = 0.06, 0.09, 0.15, \text{ and } 0.21$) and examined their thermoelectric properties from room temperature to 773 K. It is confirmed that Ga can occupy not only the void site but also the Sb site, i.e., the chemical formula can be expressed as (Ga_{VF})_{2x/3}CeFe_{3.5}Co_{0.5}Sb_{12-x/3}(Ga_{Sb})_{x/3}, where Ga_{VF} and Ga_{Sb} mean Ga in the void and Sb sites, respectively. Ga contributes to optimize the carrier concentration as well as to reduce the lattice thermal conductivity. Owing to these Ga contributions, the material's thermoelectric figure of merit zT is enhanced and reaches 0.85 in maximum at 773 K, which is obtained for the sample with $x = 0.15$.
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1. Introduction

Thermoelectric (TE) power generation enables a direct conversion from waste heat to electricity based on the Seebeck effect of TE materials. TEs are considered to be utilized in wide applications such as waste heat recovery in automobiles.^{1,2)} The energy conversion efficiency of TEs is determined by performance of the TE materials called material's dimensionless figure of merit, defined as, $zT = S^2\sigma T/\kappa$, where S , σ , T , and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and total thermal conductivity, respectively. $S^2\sigma$ is called as power factor. Normally, κ consists of an electronic (κ_{el}) and a lattice part (κ_{lat}), i.e., $\kappa = \kappa_{\text{el}} + \kappa_{\text{lat}}$. S , σ , and κ_{el} are intimately related with each other as a function of carrier concentration of a given material, which is a major obstacle to enhance the zT . On the other hand, κ_{lat} is independent of the carrier concentration, thus, many researchers have tried to minimize the κ_{lat} for enhancement of the zT .³⁻⁶⁾

Skutterudite compounds show good TE performance at intermediate temperature range. The crystal structure of skutterudites such as CoSb₃ contains two large interstitial voids per unit cell,^{7,8)} where various elements, such as rare earths elements,⁹⁻¹²⁾ alkaline metals,^{13,14)} and group 13 elements¹⁵⁻¹⁸⁾ can be introduced to form filled skutterudites. Notably the filler elements inserted in the voids rattle and act as an effective scattering source for heat carrying phonons leading to the κ_{lat} reduction. They also act as electron donors to make *n*-type skutterudites and help adjusting the carrier concentration to optimize the power factor. Meanwhile, *p*-type ones can be made by substituting transition metals, such as Fe substitution with Co in CoSb₃.^{9,11,18-20)}

Although similar performance in both *n*- and *p*-type TE materials is required for a powerful TE module, *p*-type skutterudites show lower TE performance than *n*-type ones normally. For example, $R(\text{Co,Fe})_4\text{Sb}_{12}$ -based single-filled

p-type skutterudites, where R represents a filler element, present small Seebeck coefficient and carrier mobility compared with those of *n*-type $R\text{Co}_4\text{Sb}_{12}$. It has been reported that by increasing the filling fraction of R in $R(\text{Co,Fe})_4\text{Sb}_{12}$, the hole concentration is suppressed by electron doping, leading to the increase in the S but decrease in the σ .^{20,21)} As a result, $S^2\sigma$ can't be enhanced and remains at a low value.^{10,22-24)}

Recently, double-filled or multiple-filled skutterudites have been investigated.^{25,26)} In many cases, double-filled skutterudites exhibit higher zT values than single-filled ones. On the other hand, it has been reported that Ga can be a good filler element for *n*-type $R\text{Co}_4\text{Sb}_{12}$.²⁷⁻²⁹⁾ In addition, it has been found that besides the void site, Ga can occupy the Sb site too, in *n*-type filled skutterudites.³⁰⁾

Here, we investigate the effect of Ga on the TE properties of *p*-type (Co,Fe)₄Sb₁₂-based double-filled skutterudites. Ce is selected as the first filler element, because Ce single-filled *p*-type skutterudites show relatively good TE properties.^{26,31,32)} Then, Ga is selected as the second filler element to make Ga and Ce double-filled *p*-type skutterudites. Samples with the nominal compositions Ga_xCeFe_{3.5}Co_{0.5}Sb_{12-x/3} ($x = 0.06, 0.09, 0.15, \text{ and } 0.21$) are synthesized and their TE properties are examined from room temperature to 773 K.

2. Experimental Details

The polycrystalline samples were synthesized from starting materials of chunks of Ga (99.999%), Ce (99.999%), Fe (99.99%), Co (99.99%), and Sb (99.999%) by solid state reaction. Stoichiometric amounts of the starting materials were weighed and sealed into quartz tubes under vacuum. The nominal compositions were set as Ga_xCeFe_{3.5}Co_{0.5}Sb_{12-x/3} ($x = 0.06, 0.09, 0.15, \text{ and } 0.21$). The sealed quartz tubes were heated to 1323 K followed by quenching in an ice water bath and annealed at 873 K for 7 days to obtain the pure skutterudite phase. The obtained ingots were pulverized by hand into powders and then sintered by spark

*Corresponding author, E-mail: kurosaki@see.eng.osaka-u.ac.jp

plasma sintering (SPS) in graphite dies under an Ar flow atmosphere at a pressure of 50 MPa and temperature of 873 K for 20 min. Densities of those obtained bulk samples were calculated from the measured weight and dimensions. The obtained samples were characterized by powder X-ray diffraction (XRD) using Cu K α radiation at room temperature using a commercial apparatus (Rigaku, Ultima IV). The lattice parameters were calculated via least-squares fitting to the indexed 2θ values, using Si as an external standard by employing PDXL, Rigaku's integrated X-ray powder diffraction software. The microstructure and elemental distribution of the samples were investigated using a field emission scanning electron microscopy (FE-SEM; JEOL, JSM-6500F) equipped with an energy dispersive X-ray spectroscopy (EDS) under vacuum at room temperature. S and σ were measured using a commercial apparatus (ULVAC, ZEM-3) in a He atmosphere. Hall coefficient (R_H) was measured at room temperature using the van der Pauw method in atmosphere under an applied magnetic field of 0.5 T. Hall carrier concentration (n_H) and Hall mobility (μ_H) were calculated from R_H based on the assumptions of a single-band model and a Hall factor of 1, i.e., $n_H = 1/(eR_H)$ and $\mu_H = \sigma R_H$, where e is the elementary charge. κ was evaluated from thermal diffusivity (α), heat capacity (C_p), and sample density (d) based on the relationship $\kappa = \alpha C_p d$. C_p was estimated from the Dulong–Petit model, $C_p = 3nR$, where n is the number of atoms per formula unit and R is the gas constant. α was measured by the flash diffusivity method in vacuum using a commercially available apparatus (NETZSCH, LFA467). S , σ , and κ were evaluated from room temperature to 773 K.

3. Results and Discussion

Figure 1 shows the powder XRD patterns of the SPS bulk samples. It can be confirmed from the XRD patterns that the main phase of all the samples are the skutterudite phase. The lattice parameters of the SPS bulk samples are listed in Table 1, showing that the lattice parameters are almost constant. Generally, Ga and Ce filling into the voids expands the lattice parameter of the skutterudite structure.^{27,31} On the other hand, the substitution of Ga with the Sb site tends to shrink the lattice.²⁹ Thus, these effects compensate for each other, results in the almost constant lattice parameters. Actually, Xi *et al.* have reported that the ratio of Ga atoms

Fig. 1 Powder XRD patterns of the bulk samples of $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$ ($x = 0.06, 0.09, 0.15, \text{ and } 0.21$).

at the void site to those at the Sb sites for Ga-added *n*-type CoSb_3 is very close to be 2:1.³⁰ As summarized in Table 1, the densities of all samples are over 96% of the theoretical values.

Figure 2 shows the FE-SEM images of the broken surface of the SPS bulk samples. Dense structures without any cracks or pores are observed. The grain sizes are around $\sim 10\ \mu\text{m}$. Although small amounts of nanoscale precipitates have been observed in Ce single-filled *p*-type $\text{Fe}_{3.5}\text{Co}_{1.5}\text{Sb}_{12}$ after exceeding the filling limit of Ce,^{31,33} no such precipitates are observed in the present case. Substitutions of Fe with Co increases the lattice volume, which would lead to increase in the filling limit, results in the production of no such precipitates. The actual compositions of the SPS bulk samples obtained from the quantitative EDS analyses are summarized in Table 2. The point analyses were performed at more than 15 different grains and the average values were used. Note that here, we assume that Ga is located at both the void site and the Sb site with the ratio of 2:1 according to the previous study.³⁰ Room temperature values of the ρ , n_H , and μ_H are listed in Table 3, which are obtained from the Hall

Table 1 Lattice parameter of the skutterudite phase and density of the bulk samples of $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$ ($x = 0.06, 0.09, 0.15, \text{ and } 0.21$).

Nominal composition	Lattice parameter (nm)	Density ($\text{g} \cdot \text{cm}^{-3}$)		Relative density (% T.D)
		Theoretical	Experimental	
$\text{Ga}_{0.06}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.98}$	0.9105(4)	8.01	7.97	99
$\text{Ga}_{0.09}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.97}$	0.9114(5)	8.02	7.69	96
$\text{Ga}_{0.15}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.95}$	0.9118(2)	8.03	7.88	98
$\text{Ga}_{0.21}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.93}$	0.9113(3)	8.05	7.93	99

Fig. 2 FE-SEM images of the broken surface of the bulk samples of $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$ ($x = 0.06, 0.09, 0.15$, and 0.21). (b), (d), (f), and (h) are the magnified images of the yellow regions in (a), (c), (e), and (g), respectively.

Table 2 Chemical compositions at the skutterudite phase regions of the SPS bulk sample with nominal compositions of $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$ ($x = 0.06, 0.09, 0.15$, and 0.21). The chemical composition is determined by the quantitative EDS analysis, where all the data are the average values obtained by repeating the point analyses at least 15 times.

Nominal composition	Results of the quantitative EDS analysis (at. %)					Chemical composition
	Ga	Ce	Fe	Co	Sb	
$\text{Ga}_{0.06}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.98}$	0.3 ± 0.1	5.5 ± 0.4	21.0 ± 0.7	3.0 ± 0.4	70.3 ± 0.9	$\text{Ga}_{0.05}\text{Ce}_{0.86}\text{Fe}_{3.49}\text{Co}_{0.51}\text{Sb}_{11.97}$
$\text{Ga}_{0.09}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.97}$	0.3 ± 0.2	5.6 ± 0.7	21.1 ± 1.1	2.9 ± 0.7	70.2 ± 1.7	$\text{Ga}_{0.07}\text{Ce}_{0.88}\text{Fe}_{3.50}\text{Co}_{0.50}\text{Sb}_{11.95}$
$\text{Ga}_{0.15}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.95}$	0.4 ± 0.1	5.6 ± 0.3	21.1 ± 0.4	2.9 ± 0.3	70.1 ± 1.1	$\text{Ga}_{0.11}\text{Ce}_{0.89}\text{Fe}_{3.51}\text{Co}_{0.49}\text{Sb}_{11.94}$
$\text{Ga}_{0.21}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.93}$	0.5 ± 0.2	5.5 ± 0.5	21.0 ± 0.6	3.0 ± 0.5	70.1 ± 0.8	$\text{Ga}_{0.12}\text{Ce}_{0.88}\text{Fe}_{3.49}\text{Co}_{0.51}\text{Sb}_{11.92}$

effect measurements. Here, the data for $\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ ³¹⁾ and $\text{CeFe}_3\text{CoSb}_{12}$ ²⁶⁾ are shown for comparison. With increasing x in $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$, both the n_{H} and

μ_{H} are almost constant. It is considered that the charge compensation occurs in the present case, because Ga in the void site would donate one electron while Ga in the Sb

Table 3 Electrical resistivity ρ , carrier concentration n_H , and Hall mobility μ_H of the bulk samples of $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$ ($x = 0.06, 0.09, 0.15, \text{ and } 0.21$). All the data are obtained at room temperature. The data for $\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ ^[31] and $\text{CeFe}_3\text{CoSb}_{12}$ ^[26] are shown for comparison. The uncertainty in the hall measurement is below 5%.

Nominal composition	ρ ($10^{-4}\Omega\text{cm}$)	n_H (10^{20}cm^{-3})	μ_H ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
$\text{Ga}_{0.06}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.98}$	7.8	2.3	44
$\text{Ga}_{0.09}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.97}$	7.1	2.1	48
$\text{Ga}_{0.15}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.95}$	6.7	2.0	50
$\text{Ga}_{0.21}\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{11.93}$	7.6	2.1	48
$\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ ^[31]	7.0	2.0	49
$\text{CeFe}_3\text{CoSb}_{12}$ ^[26]	7.7	2.7	-

Fig. 3 Temperature dependences of the (a) electrical conductivity σ , (b) Seebeck coefficient S , (c) power factor $S^2\sigma$, (d) total thermal conductivity κ , (e) lattice thermal conductivity κ_{lat} ($= \kappa - \kappa_{\text{el}}$), and (f) zT for the bulk samples of $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$ ($x = 0.06, 0.09, 0.15, \text{ and } 0.21$). The literature data for $\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ ^[31] are shown for comparison.

site would donate two holes.^[28] Thus, the small decrease in the n_H is due to the increase in the Ce content in the skutterudite phase. Actually, as can be confirmed through the quantitative EDS analysis (Table 2), the Ce content increases with increasing x in $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$. On the other hand, with increasing doping level, randomness increases and thus mobility decreases usually. However, in the present case, the μ_H values are almost constant. This is probably because that the charge carriers mainly flow on the

FeCo sites with no significant influences from the randomness of the Sb sites.

The temperature dependences of σ , S , and $S^2\sigma$ of the SPS bulk samples are shown in Figs. 3(a), 3(b), and 3(c), respectively. The literature data for $\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ ^[31] are shown for comparison. The σ values increase gradually with increasing x in $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$, except for $x = 0.21$. The S values of all samples indicate positive values, i.e., the samples are *p*-type. As can be expected from the almost

constant values of the n_H , the S shows almost constant values. These less doping dependency of the S and n_H can be attributed to compensation due to the filling and substitution of Ga elements. Moreover, the S of all samples shows positive temperature dependence, while the σ shows negative one, indicating a typical behavior for degenerated semiconductors. In particular, the present samples show slightly higher S values than the Ce single-filled ones, leading to higher power factor. As a result, the sample with $x = 0.15$ shows the maximum power factor of 2.9 mW/mK^2 at 756 K. Note that here, the uncertainty of σ and S are less than 3% and 2% respectively in ZEM-3 measurement.

Figure 3(d) and 3(e) show the temperature dependences of κ and κ_{lat} for the SPS bulk samples, respectively. We evaluated the κ_{lat} using the Wiedemann-Franz law ($\kappa_{\text{el}} = L\sigma T$), where L is the Lorenz number ($L = 2.45 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$). The literature data for $\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ ³¹⁾ are also shown for comparison. The κ shows rather flat temperature dependence, while the κ_{lat} slightly decreases with temperature. The κ_{lat} decreases with increasing x in $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$ except for $x = 0.21$. The minimum κ_{lat} value is $\sim 0.59 \text{ Wm}^{-1}\text{K}^{-1}$ at 756 K obtained for the sample with $x = 0.15$, which is almost similar with the minimum value reported so far for Ce single-filled p -type skutterudites. This significant reduction in the κ_{lat} is due to the effective phonon scattering by both rattling of Ce and Ga in the void sites and substituted Ga at the Sb site.

The zT values of the SPS bulk samples calculated from the measured TE properties are shown in Fig. 3(f). The zT values of the samples except for the sample with $x = 0.06$ are higher than those of the literature data of Ce-single filled p -type skutterudites $\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$.³¹⁾ The results show that Ga co-filling into Ce-filled p -type skutterudites is effective for enhancement of zT . The sample with $x = 0.15$ exhibits the maximum zT of ~ 0.85 at 756 K.

4. Summary

The effect of Ga and Ce co-filling on the TE properties of p -type skutterudites $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$ ($x = 0.06, 0.09, 0.15$, and 0.21) were studied. Dense samples of $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$ were obtained through a solid-state reaction followed by SPS. Under the assumption that Ga is located at both the void site and the Sb site with the ratio of 2:1, the charge compensation should occur which results in a constant carrier concentration regardless of different x in $\text{Ga}_x\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12-x/3}$. Nevertheless, the hole carrier concentration decreases slightly with increasing x , which is due to the increase in the Ce content in the skutterudite phase. The present samples showed higher power factor than the Ce single-filled system due to the optimized carrier concentration. The κ_{lat} decreases with increasing x due to the rattling effect of double-filled Ga and Ce and alloying effect by substituted Ga with the Sb site. As a result, even though the present samples are p -type ones, they show very nice zT values, 0.84 in maximum at 756 K for the sample with $x = 0.15$, higher than the best value obtained for the Ce single-filled p -type skutterudites.

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