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# Synthesis and thermoelectric properties of *p*-type barium-filled skutterudite $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$

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Single-phase barium-filled skutterudite compounds,  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  ( $x = 0$  to  $3.0$ ,  $y = 0$  to  $0.7$ ), were synthesized by a two-step solid-state reaction method. The maximum filling fraction of Ba ( $y_{\text{max}}$ ) in  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  increased with increasing Fe content and was found to be rather greater than that of  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . The  $y_{\text{max}}$  varied from  $0.35$  to near  $1.0$  when Fe content changed from  $0$  to  $4.0$ .  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  showed *p*-type conduction at a composition range of  $x = 0$  to  $3.0$ ,  $y = 0$  to  $0.7$ . Carrier concentration and electrical conductivity increased with increasing Fe content and decreased with increasing Ba filling fraction. The Seebeck coefficient increased with increasing Ba filling fraction and with decreasing Fe content. Lattice thermal conductivity decreased with increasing Ba filling fraction and reached a minimum at a certain Ba filling fraction ( $y = 0.3$  to  $0.4$ ). The greatest *ZT* value of  $0.9$  was obtained at  $750$  K for *p*-type  $\text{Ba}_{0.27}\text{Fe}_{0.98}\text{Co}_{3.02}\text{Sb}_{12}$ . It is expected that further investigation on the optimization of filling fraction would result in a higher *ZT* value at the moderately low Fe content region.

## I. INTRODUCTION

Filled skutterudite compounds have received great attention as potential thermoelectric materials recently.<sup>1-4</sup> It is believed that the filling of the Sb-icosahedron voids by rare-earth and other metallic atoms significantly depresses the lattice thermal conductivity due to the rattling of these atoms positioned in the oversized voids.<sup>1-3,5-8</sup> Moreover, the filling fraction of rare-earth atoms also remarkably influences carrier properties (carrier type, concentration, mobility, and effective mass) and electrical transport properties of filled skutterudite compounds. However, filling fraction is dependent on oxidation valence of filling atoms and Fe/Co ratio and is difficult to change as desirable. For example, in the  $\text{Ln}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  ( $\text{Ln} = \text{Ce}, \text{La}$ ) structure, Ce and La are generally thought of as trivalent; i.e., one Ce or La provides three electrons to the skutterudite structure.<sup>4-6,9-15</sup> Replacing Co with Fe in  $\text{CoSb}_3$  leads to the creation of one hole in the valence band.<sup>1,4,16,17</sup> The crystallographic stability and charge balance requires a match between the

filling fraction and the Fe/Co intersubstitution for charge compensation. Therefore, rare-earth ions such as  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  have only a small filling fraction because of their high oxidation valence. Furthermore, it has been found that the amount of rare-earth atoms that can be incorporated into the structure decreases significantly when Co content increases.<sup>4,10-12</sup> The low solubility of rare-earth atoms has become an obstacle for adjusting carrier concentration and optimizing thermoelectric properties in the Co-rich composition.

On the other hand, it is known that  $\text{CoSb}_3$  skutterudite decomposes at  $1147$  K by a peritectic reaction<sup>18</sup> and that the peritectic temperature decreases dramatically as Co is replaced by Fe.<sup>9</sup> For thermoelectric application, it is desirable to use thermoelectric materials that are characterized by not only high thermoelectric performance but also by good high-temperature stability. Consequently, it is necessary to find filled skutterudites on the Co-rich composition side with a high filling fraction.

From the viewpoint of crystal chemistry, it is expected

that a higher filling fraction in the Co-rich composition side would be obtained if divalent atoms, such as alkaline-earth atoms, were to fill in the Sb-icosahedron voids in the skutterudite structure. The advantage would be the ability to control and adjust carrier concentration, and further optimize and improve thermoelectric properties of filled skutterudite compounds in a wide composition range. So far, Stetson *et al.*<sup>16</sup> synthesized  $\text{BaFe}_4\text{Sb}_{12}$  and  $\text{BaRu}_4\text{Sb}_{12}$  filled by  $\text{Ba}^{2+}$ , but no report was found on the synthesis and the thermoelectric properties of  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . In the present study, *p*-type barium-filled skutterudite compounds  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  ( $x = 0$  to  $3.0$ ,  $y = 0$  to  $0.7$ ), were synthesized by a two-step solid-state reaction method. The effects of Ba filling fraction and Fe content on thermoelectric properties were investigated. The effects of the oxidation valence of filling atoms on electrical transport properties of  $\text{M}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  ( $\text{M} = \text{Ba}, \text{Ce}$ ) are discussed.

## II. EXPERIMENTAL

Highly pure metals of Ba (99.9%, plate), Sb (99.9999%, powder), Fe (99.99%, powder) and Co (99.99%, powder) were used as starting materials. Because the reaction between Ba and Sb or Co(Fe) is highly exothermic, it is difficult to directly melt or react a mixture of the constituent elements. In the present study, a two-step solid reaction was used. A binary compound of  $\text{Ba}_3\text{Sb}$  and a ternary compound of  $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$  were first synthesized by reacting the constituent elements in a flowing Ar atmosphere. Reaction temperature and reaction time were 903 K, 96 h and 973 K, 168 h for the synthesis of  $\text{Ba}_3\text{Sb}$  and  $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$ , respectively. For the synthesis of a  $\text{Ba}_3\text{Sb}$  compound, it is important that the samples are heated slowly ( $<1$  K/min) from room temperature to 793 K and kept at that point for 12 h before being heated to the reaction temperature (903 K). The resulting compounds,  $\text{Ba}_3\text{Sb}$  and  $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$ , were then crushed and mixed with Sb in various  $\text{Ba}:(\text{Fe} + \text{Co}):\text{Sb} = y:4:12$  molar ratios and pressed into pellets. The pellets were heated at 973 K under an Ar atmosphere for 96 h. The reacted materials were milled into fine powder and washed with  $\text{HCl} + \text{HNO}_3$  to remove a slight amount of impurity phases (Sb and  $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$ ). To form a fully dense polycrystalline solid, the obtained powder was sintered by the plasma activated sintering (PAS) method. Sintering was performed at a temperature of 873 K for 15 min. Samples of  $3 \times 4 \times 15 \text{ mm}^3$ ,  $\phi 10 \times 1.5 \text{ mm}^3$ , and  $5 \times 5 \times 0.3 \text{ mm}^3$  in size were cut from the sintered material for measurements of electrical conductivity/Seebeck coefficient, thermal conductivity, and Hall coefficient, respectively.

The constituent phases of the samples were determined by powder x-ray diffractometry (Rigaku, RAD-C, Cu  $\text{K}\alpha$ , Tokyo, Japan). The chemical compositions of the samples were analyzed by inductively coupled plasma emission spectroscopy (ICPES). The crystal structure of  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  were refined by Rietveld analysis using the x-ray powder diffraction data in a wide  $2\theta$  range (10 to  $130^\circ$ ). The Hall coefficient ( $R_H$ ) was measured using the van der Pauw method with an excitation current of 100 mA and a magnetic field of 5028 Gauss. The carrier concentration ( $p$ ) was calculated from the Hall coefficient ( $R_H$ ), using  $p = 1/R_H e$  where  $e$  is the electron charge. The electrical conductivity ( $\sigma$ ) was measured by the standard four-probe method in a flowing Ar atmosphere. The thermoelectromotive force ( $\Delta E$ ) was measured under temperature differences ( $\Delta T$ ) of 0 to 10 K, and the Seebeck coefficient ( $\alpha$ ) was obtained from the slope of  $\Delta E$  versus  $\Delta T$  plot. The thermal conductivity ( $\kappa$ ) was measured by a laser flash method (Shinkuriko, TC-7000, Yokohama, Japan) in a vacuum. All the measurements were performed in a temperature range of 300 to 800 K. The dimensionless figure of merit ( $ZT = \alpha^2 \sigma T / \kappa$ ) was calculated using measured electrical conductivity, Seebeck coefficient, and thermal conductivity.

## III. RESULTS AND DISCUSSION

### A. Synthesis and structure

When Ba and Sb were pre-reacted at 903 K for 96 h,  $\text{Sb}_3\text{Ba}$  was obtained with a slight amount of remaining Sb. When  $\text{Fe} + \text{Co} + \text{Sb}$  were pre-reacted at 973 K for 168 h,  $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$  was synthesized. After the second-step reaction at 973 K, the single phase of  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  was obtained when  $x \leq 2$ , but the reacted powder consisted of  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  as the main phase with a trace impurity phase of Sb and  $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$  when  $x > 2$ . The impurity phases (Sb and  $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$ ) were removed with a  $\text{HCl} + \text{HNO}_3$  mixed acid.

Rietveld analysis was used to determine and refine the crystal structure of the synthesized  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ .<sup>19</sup> The resulting unit cell was consistent with filled skutterudite having space group of  $Im\bar{3}$ . The refined Ba filling fraction ( $y$ ) was in good agreement with the Ba contents by ICPES analysis. Atomic coordinates for the Sb site differed slightly from those of  $\text{CoSb}_3$  but were close to those of  $\text{BaFe}_4\text{Sb}_{12}$ .<sup>16</sup> The thermal parameters ( $B$ ) of Ba, Sb, and Co/Fe were 0.61, 0.16, and 0.12, respectively. Sales *et al.*<sup>2</sup> and Chakoumakos *et al.*<sup>6</sup> have reported that the thermal parameter values (the atomic displacement parameters) can be used to determine the degree of the vibration of the atom about its equilibrium position. They also indicated that the anomalously large value of the thermal parameter of the La atom in  $\text{Ln}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  means that the La is poorly bound

in the structure and rattles about its equilibrium position. In the present study, the finding of  $B_{\text{Ba}} \gg B_{\text{Sb}}$  and  $B_{\text{Ba}} \gg B_{\text{Fe/Co}}$  supported the possibility that Ba atoms rattled in  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ .  $B_{\text{Ba}}$  was smaller than that of Ce or La in  $\text{Ln}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . This may be due to the large ionic radius of Ba,<sup>19</sup> implying that the ionic size of the filling atoms gives influence on the thermal parameters.

The relationship between the maximum filling fraction ( $y_{\text{max}}$ ) of Ba and Fe content ( $x$ ) is shown in Fig. 1, similar to that observed in the  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  system.<sup>11,12,20,21</sup> The  $y_{\text{max}}$  of Ba increased with Fe content, and it was larger than that of Ce. For example, at  $x = 0$  and 1.0,  $y_{\text{max}}$  of Ba in  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  was about 0.35 and 0.5 in the present experiment, while that of Ce in  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  has been reported to be about 0.067 and 0.31. The difference between  $y_{\text{max}}$  (Ba) and  $y_{\text{max}}$  (Ce) may be caused by the difference in valence between Ba (2+) and Ce (3+). However, it is notable that the filling fraction did not change simply in proportion to the difference of valence. In other words, at lower Fe contents, the difference of filling fraction between Ba and Ce was much larger than that at higher Fe content. As Fe content increased, the difference between  $y_{\text{max}}$  (Ba) and  $y_{\text{max}}$  (Ce) decreased. At  $x = 4.0$ , the filling limits of both Ba and Ce reached nearly 1.0. The reason for the non-linear relation between the valence and filling fraction is unknown, and further investigation of the crystal structure and valence band is required. In addition, when Ba is used as filling atom and Fe content is the same, the range of filling fraction for *p*- and *n*-type filled skutterudite compounds is larger than that of Ce used as filling

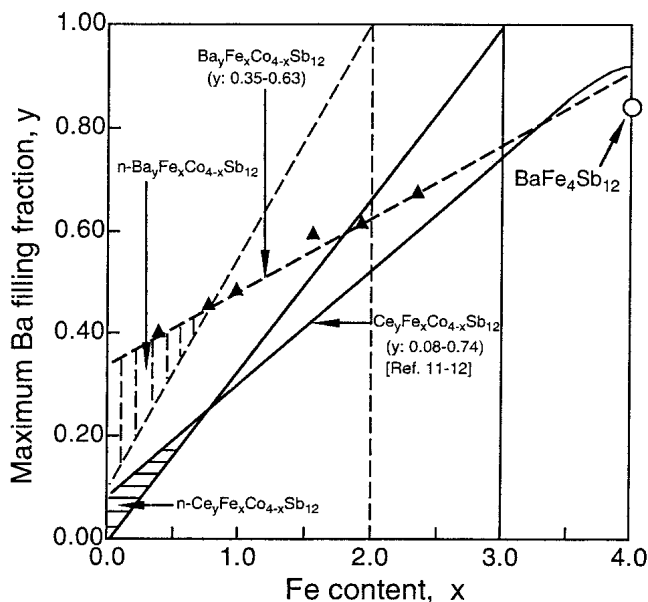


FIG. 1. Relationship between maximum Ba filling fraction and Fe content for  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . Results are compared to those obtained for  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ .<sup>11,12</sup>

atom. This implies that thermoelectric properties of  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  can be adjusted and optimized in a wide composition range when Ba is the filling atom.

## B. Electrical properties

Table I summarizes the chemical composition, Hall coefficient and carrier concentration of  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  ( $x = 0$  to 3.0,  $y = 0$  to 0.7). The Hall coefficients of all samples were plus values; therefore the  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  samples show *p*-type conduction.

Figure 2 shows the effects of Ba filling fraction and Fe content on the room-temperature carrier concentration of *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . Results are compared to those of *p*-type  $\text{Ce}_y\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ .<sup>12,21</sup> Carrier concentration of *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  decreased with increasing Ba filling fraction. In general, Ba is thought to be divalent in  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ , i.e., one  $\text{Ba}^{2+}$  provides two electrons to the skutterudite structure. With increasing Ba filling fraction, Ba provided more of the electron to skutterudite structure and therefore resulted in a decrease of hole concentration. Further, it is possible that conduction type may change from *p*-type to *n*-type if the Ba filling fraction exceeds  $y_{\text{max}}$ . At the same Ba filling fraction, carrier concentration of  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  increased with increasing Fe content. At  $y = 0.38$ , when Fe content increased from 1.0 to 1.6, carrier concentration increased from  $9.2 \times 10^{25} \text{ m}^{-3}$  to  $2.76 \times 10^{26} \text{ m}^{-3}$ . It indicated that Fe mainly showed 2+ in the skutterudite structure, thus it provided less electrons to the structure than  $\text{Co}^{+3}$ . At the same Fe content and filling fraction, carrier concentration of *p*-type  $\text{Ba}_{0.26}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$  was larger than that of *p*-type  $\text{Ce}_{0.26}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ . For example, when  $x$  is about 1.5, and  $y = 0.26$ , the carrier concentration of  $\text{Ba}_{0.26}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$  is  $3.05 \times 10^{26} \text{ m}^{-3}$ , while that of  $\text{Ce}_{0.26}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$  is  $2.67 \times 10^{26} \text{ m}^{-3}$ . This is because the electron number the  $\text{Ba}^{2+}$  provided to the skutterudite structure was less than that provided by  $\text{Ce}^{3+}$ .

TABLE I. Nominal composition, composition, and some room-temperature properties for *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ .

Sample number and nominal composition	Composition	Hall coefficient ( $\text{cm}^3 \text{ C}^{-1}$ )	Hole concentration ( $\text{m}^{-3}$ )
1. $x: 1.6; y: 0.1$	$\text{Ba}_{0.13}\text{Fe}_{1.57}\text{Co}_{2.43}\text{Sb}_{12}$	$1.86 \times 10^{-2}$	$3.36 \times 10^{26}$
2. $x: 1.6; y: 0.2$	$\text{Ba}_{0.26}\text{Fe}_{1.56}\text{Co}_{2.44}\text{Sb}_{12}$	$1.91 \times 10^{-2}$	$3.05 \times 10^{26}$
3. $x: 1.6; y: 0.3$	$\text{Ba}_{0.38}\text{Fe}_{1.57}\text{Co}_{2.43}\text{Sb}_{12}$	$2.26 \times 10^{-2}$	$2.76 \times 10^{26}$
4. $x: 1.6; y: 0.4$	$\text{Ba}_{0.54}\text{Fe}_{1.57}\text{Co}_{2.43}\text{Sb}_{12}$	$3.28 \times 10^{-2}$	$1.90 \times 10^{26}$
5. $x: 1.6; y: 0.5$	$\text{Ba}_{0.63}\text{Fe}_{1.60}\text{Co}_{2.40}\text{Sb}_{12}$	$1.28 \times 10^{-1}$	$4.88 \times 10^{25}$
6. $x: 1.0; y: 0.1$	$\text{Ba}_{0.10}\text{Fe}_{0.93}\text{Co}_{3.07}\text{Sb}_{12}$	$3.08 \times 10^{-2}$	$2.02 \times 10^{26}$
7. $x: 1.0; y: 0.2$	$\text{Ba}_{0.19}\text{Fe}_{0.92}\text{Co}_{3.08}\text{Sb}_{12}$	$3.17 \times 10^{-2}$	$1.97 \times 10^{26}$
8. $x: 1.0; y: 0.3$	$\text{Ba}_{0.27}\text{Fe}_{0.98}\text{Co}_{3.02}\text{Sb}_{12}$	$3.65 \times 10^{-2}$	$1.72 \times 10^{26}$
9. $x: 1.0; y: 0.4$	$\text{Ba}_{0.38}\text{Fe}_{1.01}\text{Co}_{2.99}\text{Sb}_{12}$	$6.79 \times 10^{-2}$	$9.20 \times 10^{26}$
10. $x: 1.0; y: 0.5$	$\text{Ba}_{0.41}\text{Fe}_{0.98}\text{Co}_{3.02}\text{Sb}_{12}$	$1.03 \times 10^{-1}$	$6.07 \times 10^{26}$
11. $x: 1.0; y: 0.6$	$\text{Ba}_{0.46}\text{Fe}_{0.98}\text{Co}_{3.02}\text{Sb}_{12}$	$2.13 \times 10^{-1}$	$2.95 \times 10^{26}$

These results indicate that the oxidation valence of the filling atoms influenced carrier concentration of *p*-type  $\text{M}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  ( $\text{M} = \text{Ba}, \text{Ce}$ ) significantly, and larger carrier concentration would be obtained when an atom having a lower oxidation valence was used as filling atom.

The effects of Ba filling fraction on the electrical conductivity ( $\sigma$ ) of *p*-type  $\text{Ba}_y\text{FeCo}_3\text{Sb}_{12}$  is shown in Fig. 3. Results are compared to those of  $\text{FeCo}_3\text{Sb}_{12}$ <sup>20</sup> and

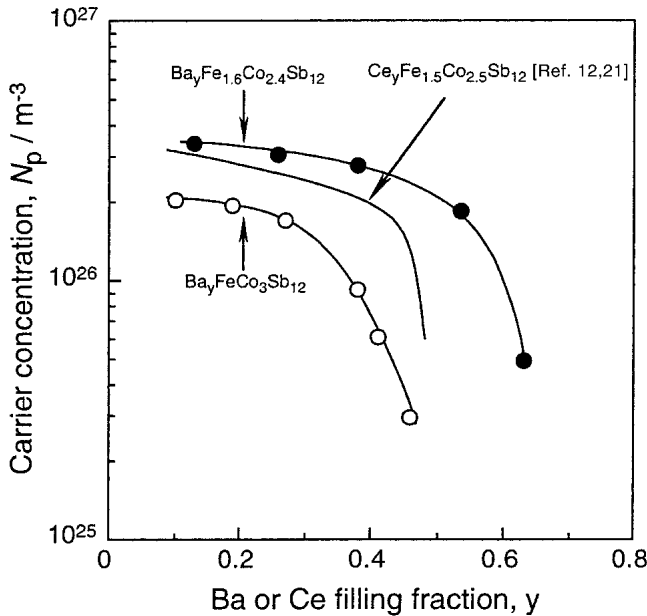


FIG. 2. Effect of Ba filling fraction and Fe content on the room-temperature carrier concentration for *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . Results are compared to those obtained for *p*-type  $\text{Ce}_y\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ .<sup>12,21</sup>

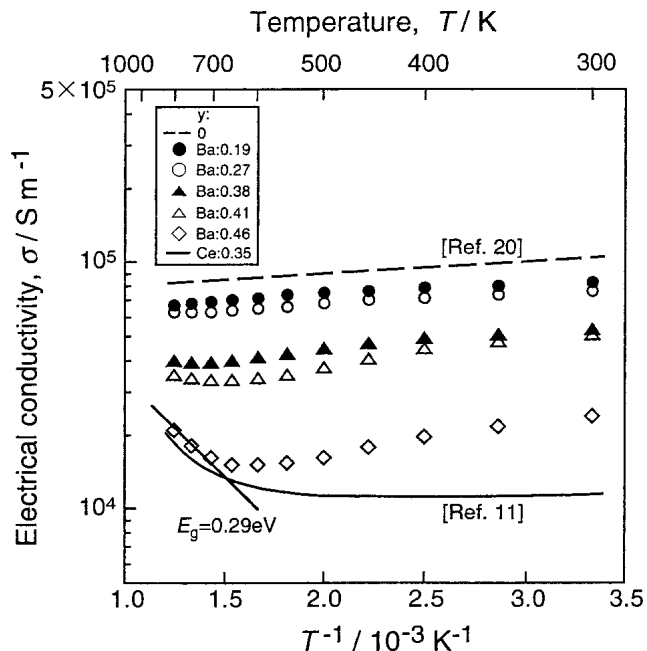


FIG. 3. Temperature dependence of electrical conductivity for *p*-type  $\text{Ba}_y\text{FeCo}_3\text{Sb}_{12}$ . Results are compared to those obtained for  $\text{FeCo}_3\text{Sb}_{12}$  and  $\text{Ce}_{0.35}\text{FeCo}_3\text{Sb}_{12}$ .<sup>11,20</sup>

$\text{Ce}_{0.35}\text{FeCo}_3\text{Sb}_{12}$ .<sup>11</sup> The  $\sigma$  values of  $\text{Ba}_y\text{FeCo}_3\text{Sb}_{12}$  decreased with increasing Ba filling fraction. This is consistent with the changes of carrier concentration shown in Fig. 2. At the maximum Ba filling fraction of 0.46, the positive temperature dependence at high temperatures was observed, implying the possibility of intrinsic behavior at high temperatures. From the slope of the  $\ln\sigma - 1/T$  plot at high temperatures, a band gap ( $E_g$ ) value of 0.29 eV was calculated using  $\sigma = A \exp(-E_g/kT)$  (where,  $\sigma$  is electrical conductivity,  $E_g$  is band gap,  $k$  is Boltzmann constant,  $T$  is absolute temperature, and  $A$  is a constant), which is close to the band gap value ( $0.4 \text{ eV} \pm 0.1$ ) reported previously for  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ .<sup>2</sup> While Fe content was the same,  $\sigma$  of  $\text{FeCo}_3\text{Sb}_{12}$  was larger than that of  $\text{Ba}_{0.38}\text{FeCo}_3\text{Sb}_{12}$  and  $\text{Ce}_{0.35}\text{FeCo}_3\text{Sb}_{12}$ . While filling fraction was the same,  $\sigma$  of  $\text{Ba}_{0.38}\text{FeCo}_3\text{Sb}_{12}$  was larger than that of  $\text{Ce}_{0.35}\text{FeCo}_3\text{Sb}_{12}$ . This is consistent with the effect of oxidation valence of filling atoms on carrier concentration.

Figure 4 shows the relationship between carrier concentration and electrical conductivity for *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  at 300 K. Results are compared to those obtained for *p*-type  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ .<sup>12,21</sup> Electrical conductivity increased with carrier concentration increasing for *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  and  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . At the same carrier concentration, however, electrical conductivity of *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  was larger than that of *p*-type  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . The reasons for the difference of electrical conductivity are not revealed. Calculations on  $\text{LaT}_4\text{P}_{12}$  indicate that both the interstitial cation and the Pn framework are important in determining the properties.<sup>16</sup> It was also reported by Jung *et al.* that the  $\text{Sb}_4$ -ring markedly influenced electrical transport

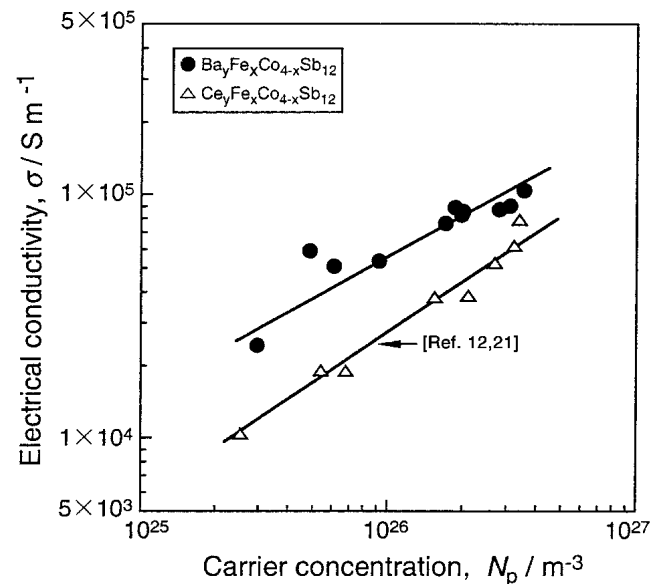


FIG. 4. Relationship between carrier concentration and electrical conductivity for *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  at 300 K. Results are compared to those obtained for *p*-type  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ .<sup>12,21</sup>

properties of the skutterudite compound ( $\text{CoSb}_3$ ) and filled skutterudite ( $\text{LnFe}_x\text{Co}_{4-x}\text{Sb}_{12}$ ).<sup>13</sup> In  $\text{CoSb}_3$  and  $\text{LnFe}_x\text{Co}_{4-x}\text{Sb}_{12}$  structure, the  $\text{Sb}_4$ -ring was rectangular (for example, in the  $\text{LaFe}_x\text{Co}_{4-x}\text{Sb}_{12}$  structure,  $\text{Sb-Sb}$  distances of the  $\text{Sb}_4$ -ring were 2.932 and 2.982 Å, respectively). But in the  $\text{BaFe}_4\text{Sb}_{12}$  structure, the  $\text{Sb}_4$ -ring was nearly square ( $\text{Sb-Sb}$  distances of  $\text{Sb}_4$ -ring are 2.952 and 2.959 Å, respectively).<sup>15</sup> The difference of electrical transport properties for  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  and  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  may be related to different effects of Ba and Ce on the  $\text{Sb-Sb}$  distances of the  $\text{Sb}_4$ -ring in  $\text{MFe}_x\text{Co}_{4-x}\text{Sb}_{12}$  structure.

Figure 5 shows temperature dependence of the Seebeck coefficient ( $\alpha$ ) for *p*-type  $\text{Ba}_y\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ . The  $\alpha$  values increased with increasing temperature and reached a maximum at a certain temperature,  $T_{\text{opt}}$ . The  $T_{\text{opt}}$  shifted to the high temperature side as the Ba filling fraction decreased. In general,  $\alpha$  values increase with decreasing carrier concentration and increase with increasing carrier effective mass ( $m^*$ ). It was shown that the carrier effective mass of  $\text{Ba}_y\text{Co}_4\text{Sb}_{12}$  increases with filling of Ba.<sup>22</sup> In the present study, the increase in  $\alpha$  of Ba-filled  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  may have been caused by the decrease of carrier concentration and the increase of carrier effective mass ( $m^*$ ).

### C. Thermal conductivity

The Wiedemann–Franz law ( $\kappa_C = L\sigma T$ ) using a Lorenz number of  $2 \times 10^{-8} \text{ V}^2/\text{K}^2$  was used to estimate the carrier concentration contribution to the thermal conductivity.<sup>2</sup> The lattice thermal conductivity ( $\kappa_L$ ) was obtained by subtracting the carrier component ( $\kappa_C$ ) from the

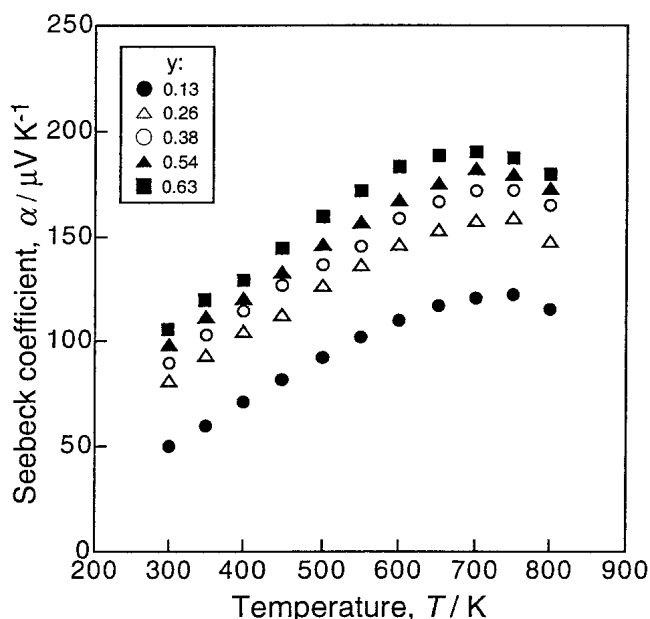


FIG. 5. Temperature dependence of Seebeck coefficient for *p*-type  $\text{Ba}_y\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ .

total thermal conductivity. Figure 6 shows temperature dependence of lattice thermal conductivity for *p*-type  $\text{Ba}_y\text{FeCo}_3\text{Sb}_{12}$ . As shown in Fig. 6,  $\kappa_L$  decreased with increasing temperature. The  $\kappa_L$  was decreased greatly by the Ba filling in the  $\text{Sb}$ -icosahedron. The ionic radius of Ba ( $\text{Ba}^{2+} = 1.34 \text{ \AA}$ ) is smaller than the radius of the  $\text{Sb}$ -icosahedron void (1.892 Å); thus Ba poorly bonded in the structure and can rattle about its equilibrium position. Indeed, such rattling was also confirmed by results obtained using Rietveld analysis as reported above; i.e., the thermal parameter ( $B = 0.61$ ) of Ba was larger than that of  $\text{Sb}$  ( $B = 0.16$ ) and  $\text{Co/Fe}$  ( $B = 0.12$ ). The rattling of the Ba atom can reduce the mean free path of the heat-carrying phonon, resulting in lowering of the lattice thermal conductivity.

The effects of Ba filling fraction and Fe content on lattice thermal conductivity at room temperature and 800 K is shown in Fig. 7 for *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . When  $x = 1.6$ ,  $\kappa_L$  decreased with increasing Ba filling fraction and reached a minimum value at a Ba filling fraction of about 0.4. When  $y > 0.4$ ,  $\kappa_L$  began to increase with increasing Ba filling fraction. When  $x = 1.0$ , lattice thermal conductivity also reached the minimum values at a certain Ba filling fraction (about 0.3). In other words, the lattice thermal conductivity was more greatly reduced when  $\text{Sb}$ -icosahedron voids are partially filled. We reported that lattice thermal conductivity reached minimum values when Ce filling fraction was 0.3 for  $\text{Ce}_y\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ .<sup>12,20</sup> Chen *et al.* predicted that partial filling of voids with Ce (random distribution) would provide more phonon scattering than full filling (a regular arrangement in which all the voids are filled by Ce).<sup>4</sup>

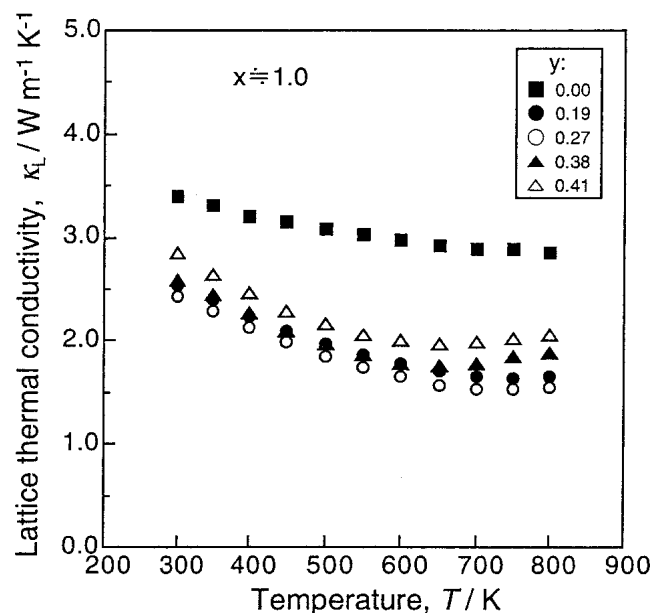


FIG. 6. Temperature dependence of lattice thermal conductivity for *p*-type  $\text{Ba}_y\text{FeCo}_3\text{Sb}_{12}$ .

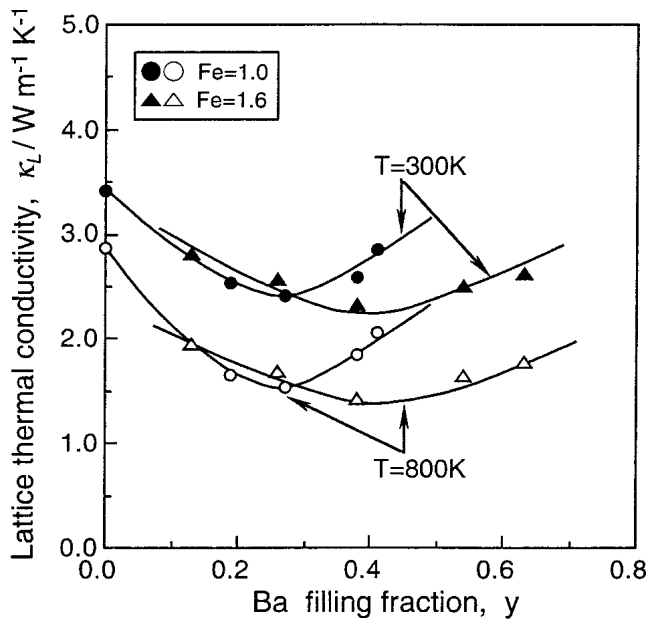


FIG. 7. Effect of Ba filling fraction and Fe content on lattice thermal conductivity of *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ .

Nolas *et al.* measured the low-temperature lattice thermal conductivity of  $\text{La}_x\text{Co}_4(\text{Sb},\text{Sn})_{12}$  and reported that La scattering is most effective at  $x = 0.25$  to  $0.3$ .<sup>5</sup> The present experimental results, results obtained for  $\text{Ce}_y\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ , and results reported by Nolas *et al.* confirmed that the random distribution of filling atoms seems to be more effective in scattering phonons than an arrangement in which all, or most, of the voids are filled.

#### D. The dimensionless thermoelectric figure of merit $ZT$

The dimensionless thermoelectric figure of merit ( $ZT$ ), was calculated using  $ZT = \alpha^2\sigma T/\kappa$  from the measured electrical conductivity ( $\sigma$ ), the Seebeck coefficient ( $\alpha$ ), and thermal conductivity ( $\kappa$ ). The maximum  $ZT$  values obtained at temperature range of 300 to 800 K for *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  are plotted as a function of Ba filling fraction and Fe content in Fig. 8. The maximum  $ZT$  values increased with Ba filling fraction and reached their maximum at some certain filling fraction. At  $x = 1.6$ ,  $ZT$  showed a maximum value (0.7) at  $y = 0.4$ . At  $x = 1.0$ ,  $ZT$  showed a maximum value at  $y = 0.3$ , for which a  $ZT_{\text{max}}$  value of 0.9 was obtained. A larger  $ZT$  value would be expected by optimizing Ba filling fraction at a moderately low Fe content region.

#### IV. SUMMARY

Single-phase barium-filled skutterudite compounds,  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  ( $x = 0$  to  $3.0$ ,  $y = 0$  to  $0.7$ ), were synthesized by a two-step solid-state reaction method. The maximum filling fraction of Ba ( $y_{\text{max}}$ ) in

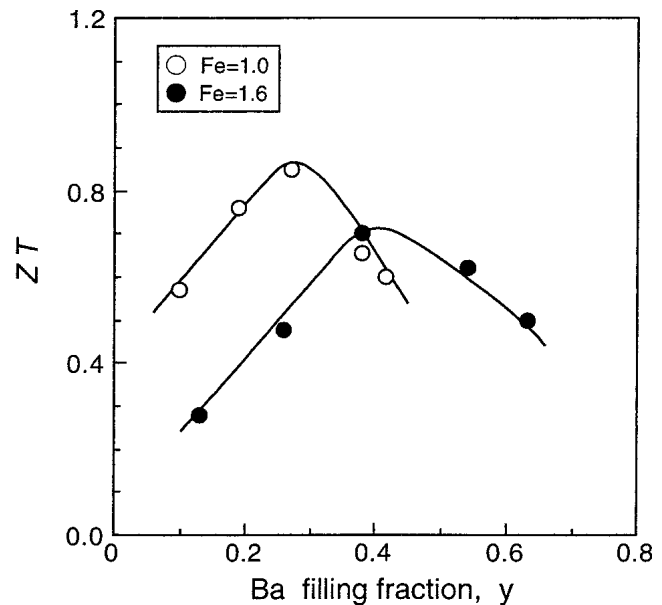


FIG. 8. Effect of Ba filling fraction and Fe content on maximum  $ZT$  for *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  (300–800 K).

$\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  increased with increasing Fe content and was found to be rather greater than that of  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . The  $y_{\text{max}}$  varied from 0.35 to near 1.0 when Fe content changed from 0 to 4.0.

$\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  showed *p*-type conduction at composition range of  $x = 0$  to  $3.0$ ,  $y = 0$  to  $0.7$ . Carrier concentration and electrical conductivity increased with increasing Fe content, and decreased with increasing Ba filling fraction. At the same carrier concentration, electrical conductivity of *p*-type  $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$  was larger than that of *p*-type  $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ . The Seebeck coefficient increased with increasing Ba filling fraction and with decreasing Fe content. Lattice thermal conductivity decreased with increasing Ba filling fraction and reached the minimum at a certain Ba filling fraction ( $y = 0.3$  to  $0.4$ ). The greatest  $ZT$  value of 0.9 was obtained at 750 K for *p*-type  $\text{Ba}_{0.27}\text{Fe}_{0.98}\text{Co}_{3.02}\text{Sb}_{12}$ . It is expected that further investigation on the optimization of filling fraction would result in a higher  $ZT$  value at a moderately low Fe content region.

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