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Synthesis and thermoelectric properties of *p*-type- and *n*-type-filled skutterudite $R_yM_xCo_{4-x}Sb_{12}$ (R : Ce, Ba, Y; M : Fe, Ni)

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Single-phase $R_yM_xCo_{4-x}Sb_{12}$ ($x=0-3.0, y=0-0.7$) compounds filled by Ce, Ba, and Y, and substituted by Fe and Ni are synthesized by using the solid-state reaction method and melting reaction method. The structure and the thermoelectric properties of $R_yM_xCo_{4-x}Sb_{12}$ are investigated systematically. The thermal parameter (B) of Ba and Ce filled in Sb-icosahedron voids in the skutterudite structure is larger than that of Sb and Co (Fe). The maximum filling fraction of Ce and Ba (y_{\max}) for $R_yFe_xCo_{4-x}Sb_{12}$ increases with the increasing Fe content, and it is found that the maximum filling fraction of Ba (y_{\max}) is greater than that of $Ce_yFe_xCo_{4-x}Sb_{12}$. The filling atoms Ba, Ce, and Y in Sb-icosahedron voids can reduce the lattice thermal conductivity of $R_yM_xCo_{4-x}Sb_{12}$ compounds remarkably, and the lattice thermal conductivity decreases in the order of ionic radii decreasing of Ba^{2+} , Ce^{3+} , and Y^{3+} . When Ce and Ba filling fraction is 0.3–0.4, the lattice thermal conductivity of $R_yFe_xCo_{4-x}Sb_{12}$ compounds reaches a minimum value. The lattice thermal conductivity can be greatly reduced by substituting Co with Fe or Ni, and compared with Fe substitution, the substituted atoms Ni are more effective in reducing the lattice thermal conductivity. The filling atoms Ba, Ce, and Y, and the substituted atoms Fe and Ni influence electrical transport properties of $R_yM_xCo_{4-x}Sb_{12}$ compounds significantly. The carrier concentration and electrical conductivity of *p*-type $R_yFe_xCo_{4-x}Sb_{12}$ increase with the increasing Fe content but decrease with the increasing R filling fraction. At the same carrier concentration, electrical conductivity of *p*-type $Ba_yFe_xCo_{4-x}Sb_{12}$ is larger than that of *p*-type $Ce_yFe_xCo_{4-x}Sb_{12}$. Electrical conductivity of *n*-type $Ba_yNi_xCo_{4-x}Sb_{12}$ increases with the increasing Ni content remarkably. The Seebeck coefficient of *p*-type $R_yFe_xCo_{4-x}Sb_{12}$ increases with the increasing Ce and Ba filling fraction and with the decreasing Fe content, and Seebeck coefficient of *n*-type $Ba_yNi_xCo_{4-x}Sb_{12}$ decreases with the increasing Ni content. In the present study, the obtained maximum ZT values reach 1.1 and 1.25 for *p*-type Co-rich $Ce_{0.28}Fe_{1.5}Co_{2.5}Sb_{12}$ (at 750 K) and *n*-type $Ba_{0.30}Ni_{0.05}Co_{3.95}Sb_{12}$ (at 900 K), respectively. © 2005 American Institute of Physics. [DOI: 10.1063/1.1888048]

I. INTRODUCTION

Recently filled skutterudite compounds have attracted great attention as candidate thermoelectric materials.^{1–10} 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^{2–4,11–14} while maintaining the excellent electrical transport properties.⁵

At the Fe-rich composition side, Ce- and La-filled $M_yFe_xCo_{4-x}Sb_{12}$ ($M=Ce, La$) have been synthesized and their thermoelectric properties have been investigated by several researchers.^{2–5,15} The dimensionless thermoelectric figures of merit (ZT) of 1.1 and 0.9 have been reported for $Ce_{0.9}Fe_3CoSb_{12}$ (at 730 K)³ and $La_{0.9}Fe_3CoSb_{12}$ (at 750 K),²

respectively. On the other hand, it is known that $CoSb_3$ skutterudite decomposes at 1147 K by a peritectic reaction¹⁶ and that the peritectic temperature decreases dramatically as Co is replaced by Fe.¹⁷ For example, it has been reported that $Fe_{0.5}Ni_{0.5}Sb_3$ decomposes at about 1000 K,¹⁷ which is lower than the peritectic point of $CoSb_3$. From the thermoelectric application point of view, it is desirable to use thermoelectric materials that are characterized not only by high thermoelectric performance but also by good high-temperature stability. Therefore, it is necessary to find the filled skutterudites on the Co-rich composition side having high thermoelectric performance. So far, several studies on the synthesis of Co-rich $Ce_yFe_xCo_{4-x}Sb_{12}$ have been reported, and the electrical and thermal transport properties of these filled skutterudite compounds below room temperature have been investigated.^{5,6,15} However, the transport properties of these compounds at high temperatures have not been reported.

Moreover, the filling fraction of rare-earth atoms also

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influences carrier properties (carrier type, carrier concentration, carrier mobility, and carrier effective mass) and electrical transport properties of the filled skutterudite compounds remarkably. However, the filling fraction depending on oxidation valence of filling atoms and Fe/Co ratio is difficult to change as it is desired. For example, in $Ln_yFe_xCo_{4-x}Sb_{12}$ ($Ln=Ce, La$) structure, Ce and La are generally regarded as being trivalent, i.e., one Ce or La provides three electrons to the skutterudite structure.^{5,11,12,17-22} Replacing Co with Fe in $CoSb_3$ leads to the creation of one hole in the valence band.^{2,5,23,24} The crystallographic stability and charge balance require a match between the filling fraction and the Fe/Co intersubstitution for the charge compensation. Therefore, rare-earth ions such as Ce^{3+} and La^{3+} only have a small filling fraction because of their high oxidation valence. Furthermore, it has been found that the amount of rare-earth atoms which can be incorporated into the structure decreases significantly when Co content increases.^{5,15,18,19} The low solubility of rare-earth atoms has become an obstacle for adjusting carrier concentration and optimizing thermoelectric properties in the Co-rich composition. Consequently, it is necessary to find filled skutterudites on the Co-rich composition side having high filling fractions. 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 atom filled in the Sb-icosahedron voids in the skutterudite structure. This will be advantaged to control and adjust carrier concentration. Then we can further optimize and improve the thermoelectric properties of filled skutterudite compounds in a wide composition range. So far, Stetson *et al.*²³ has synthesized $BaFe_4Sb_{12}$ and $BaRu_4Sb_{12}$ filled by Ba^{2+} , but no report has been made on the synthesis and the thermoelectric properties of $Ba_yFe_xCo_{4-x}Sb_{12}$.

Still, up to now, the atoms used for filling are rare-earth elements with the relatively close ionic radii, but the effects of the filling of different ionic radii atoms (R) in the Sb-icosahedron voids and the effects of the ionic radii on the lattice thermal conductivity have not been reported yet.

Furthermore, for thermoelectric application, both p - and n -type-filled skutterudite compounds having high thermoelectric figure of merit ZT are required simultaneously.²⁵ To date, many studies have been reported on the synthesis and thermoelectric properties of filled skutterudites.^{1-15,17-19} Such efforts have resulted in striking thermoelectric performance especially for the performance of p -type materials.^{3,19} However, few n -type skutterudite compounds have been reported so far. In our recent work, we synthesize a series of samples with composition $Ba_yCo_4Sb_{12}$,^{26,27} the result of which shows that up to 44% of the voids can be filled with Ba without any charge compensation. These compounds show low thermal conductivity as compared with the unfilled host.^{17,28,29} However, the lattice thermal conductivity of these samples still remains relatively large compared with the skutterudites filled with rare-earth atoms (Ce, La, and Yb)^{2,3,5,17,30} and other species (Tl and Sn).³¹⁻³³ To further decrease the lattice thermal conductivity of $Ba_yCo_4Sb_{12}$ -based compounds, the substitution of Co on the lattice sites with Ni, which is ex-

pected to provide additional phonon scattering, and the adjustment of the carrier characteristic should be prospective avenues for the exploration.

In this research work, $R(R:Ba,Ce,Y)$ with different ionic radii used as filling atoms and $M(M:Fe,Ni)$ used as substituted atoms are conducted. The effects of the oxidation valence and ionic radii of filling atoms, filling fraction, and substituting atoms on the structure and thermoelectric properties of $R_yM_xCo_{4-x}Sb_{12}$ compounds are systematically investigated and discussed.

II. EXPERIMENTAL DETAILS

The $R_yM_xCo_{4-x}Sb_{12}$ compounds filled with Ce and Y atoms were synthesized by melting method and one-step solid-state reaction,^{19,24} while $Ba_yM_xCo_{4-x}Sb_{12}$ compounds filled with Ba were fabricated by multistep solid-state reaction.²⁶ To form a fully dense polycrystalline solid, the obtained powder was loaded into a graphite die and sintered by a plasma-activated sintering method (Sodic Co. Ltd: PAS-V-K). 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, $Cu K\alpha$). The chemical compositions of the samples were analyzed by inductively coupled plasma emission spectroscopy (ICPES). The Hall coefficient (R_H) was measured by using the van der Pauw method with an excitation current of 100 mA and a magnetic field of 5028 G. The carrier concentration (p) was calculated from the Hall coefficient (R_H), using $p=1/R_He$ where e is the electron charge. The electrical conductivity (σ) was measured by the standard four-probe method in a flowing Ar atmosphere. The thermoelectromotive force (ΔE) was measured under the temperature differences (ΔT) from 0 to 10 K, and the Seebeck coefficient (α) was obtained from the slope of ΔE vs ΔT plot. The thermal conductivity (κ) was calculated from the measured thermal diffusivity D , specific heat C_p , and density d using the relationship $\kappa=D \times C_p \times d$. D and C_p were measured by a laser flash method (Shinkuriko: TC-7000) in a vacuum. All the measurements were performed under the temperature range from 300 to 900 K. The dimensionless figure of merit ($ZT = \alpha^2 \sigma T / \kappa$) was calculated by using the measured electrical conductivity, Seebeck coefficient, and thermal conductivity.

III. RESULTS AND DISCUSSION

A. Synthesis and structure of $R_yM_xCo_{4-x}Sb_{12}$ compounds

The typical x-ray diffraction (XRD) patterns of the final compounds $R_yM_xCo_{4-x}Sb_{12}$ is shown in Fig. 1. For $R_yFe_xCo_{4-x}Sb_{12}$, the single phase of $R_yFe_xCo_{4-x}Sb_{12}$ is obtained when $x \leq 2$, but the reacted powder consisted of $R_yFe_xCo_{4-x}Sb_{12}$ as the main phase with trace impurity phase of Sb and $(Fe,Co)Sb_2$ when $x > 2$. The impurity phase [Sb and $(Fe,Co)Sb_2$] is removed by being washed in a HCl + HNO_3 mixed acid.

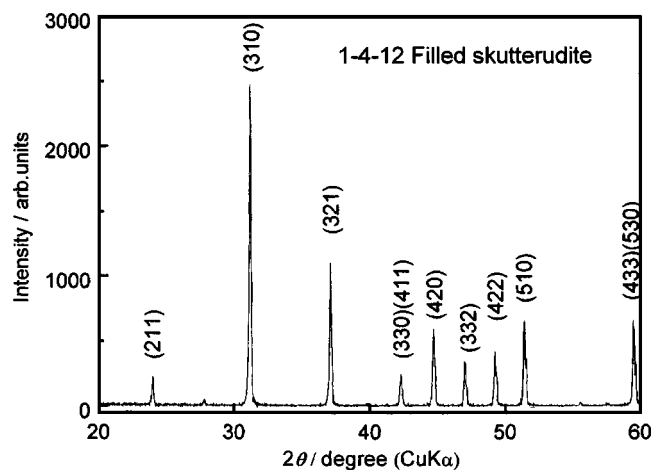


FIG. 1. X-ray diffraction patterns of Ba-filled skutterudite $\text{Ba}_{0.61}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Rietveld analysis is used to determine and refine the crystal structure of the obtained $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ by using the x-ray powder-diffraction data in a wide 2θ range (10° – 130°). The resulting unit cell is consistent with the filled skutterudite having space group of $Im\bar{3}$, and the lattice constant varies with Fe and Ba contents. As an example, Table I shows the data collection and the refinement parameters for the Rietveld analysis of $\text{Ba}_{0.61}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. The final refinement yields good reliability with the reliability factor $R_I=4.81\%$, $R_F=3.73\%$, and $S=1.17$. The refined atomic coordinates are given in Table II. The refined Ba filling fraction (y) is in good agreement with the Ba contents obtained by ICPES analysis. Atomic coordinates for Sb site differ slightly from those of CoSb_3 ,³⁴ but are close to those of $\text{BaFe}_4\text{Sb}_{12}$.²³ The thermal parameters (B) of Ba, Sb, and Co(Fe) are 0.61, 0.12, and 0.16, respectively. Several other samples with different filled atoms ($\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and $\text{Y}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$) are also examined by Rietveld analysis, and similar results

TABLE I. Powder x-ray Rietveld refinement for Ba-filled skutterudite $\text{Ba}_{0.61}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Chemical formula	$\text{Ba}_{0.61}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$
Formula weight	1778.31
Space group	$Im\bar{3}$
A(nm)	0.9118
V(nm ³)	0.7581
D(g/cm ³)	7.80
Powder color	gray
X-ray radiation	Cu $K\alpha$
Monochromator	Graphite
2θ range($^\circ$)	10.00–130.00
Step width($^\circ$)	0.01
Counting time (s/step)	4
Temperature ($^\circ\text{C}$)	20
B_{Ba}	0.61
B_{Sb}	0.16
$B_{\text{Fe/Co}}$	0.12
Reliability factor	
R_I	0.0481
R_F	0.0373
S	1.17

TABLE II. Structure parameters for Ba-filled skutterudite $\text{Ba}_{0.61}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Atom	Position	Occ.	x	y	z	B
Ba	2a	0.60	0.00	0.00	0.00	0.61
Fe/Co	8c	1.00	0.25	0.25	0.25	0.12
Sb	24g	1.00	0.00	0.1600(0)	0.3380(2)	0.16

are obtained. Sales *et al.*^{3,35} and Chakoumakos *et al.*¹² reported that the thermal parameters values (the atomic displacement parameters) can be used to determine the degree of the vibration of the atom about the La atom in $\text{R}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$, which 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 $B_{\text{Ba}} \gg B_{\text{Co,Fe}}$ supports the possibility that Ba atoms rattles in $\text{La}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. However, the thermal parameters of Ba obtained are smaller than those of Ce or La in $\text{Ln}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$.^{3,12} This may be due to the larger ionic radii of Ba, which implies that the ionic size of filling atoms gives the influence on the thermal parameters. It should be interesting to investigate the influence of ionic radii of filling atoms on the thermal conductivity.

Figure 2 shows the relationship between the lattice constant and Fe content for $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ saturated by Ba and Ce. According to our experimental results, the lattice constant and Fe content accord with linear relation approximatively. The lattice constant increases with the increasing Fe content. It is due to the ionic radii (0.074 nm) of Fe^{2+} , which is larger than that of Co^{3+} (0.063 nm). Moreover, as Ba and Ce fill the voids, the lattice constant further increases. These results are in agreement with those reported by Morelli *et al.*,¹⁵ and suggest that Ba and Ce fill the Sb-icosahedron voids of the skutterudite structure. The lattice constants of $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ are larger than those of $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ when Fe contents are the same. It may be due to the fact that the ionic radii (0.134 nm) of Ba^{2+} is larger than that of Ce^{3+} (0.103 nm).

The relationship between the maximum filling fraction (y_{max}) of Ba and Fe content (x) is shown in Fig. 3. Similar to

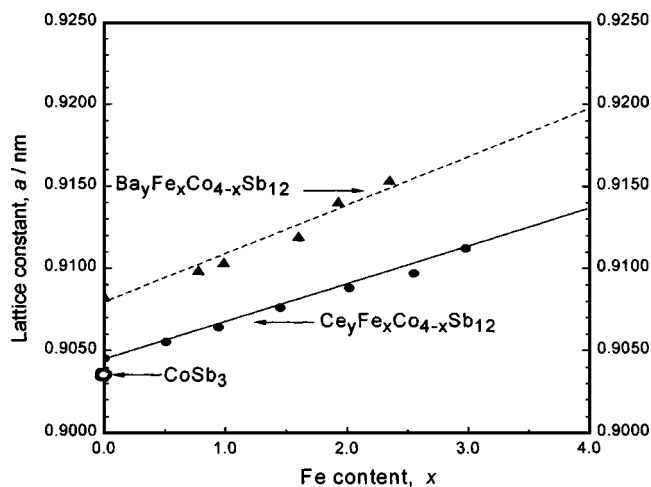


FIG. 2. Relationship between Fe content and lattice constant for $\text{R}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$.

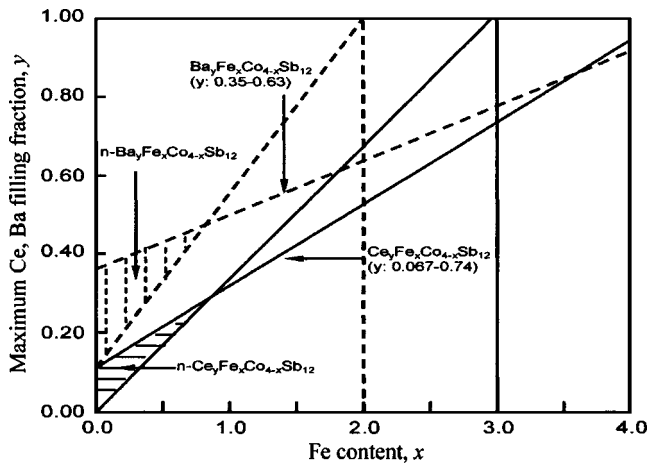


FIG. 3. Relationship between maximum Ce, Ba filling fraction and Fe content for $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ (R : Ce, Ba).

that observed in the $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ system, y_{max} of Ba increases with the increasing Fe content, and it is larger than that of Ce. For example, at $x=0$ and 1.0, y_{max} of Ba in $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ is about 0.35 and 0.5, while that of Ce in $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ is about 0.067 and 0.31. The difference between $y_{\text{max}}(\text{Ba})$ and $y_{\text{max}}(\text{Ce})$ may be caused by the difference of the valence between Ba(2+) and Ce(3+). However, it is notable that the filling fraction does not change simply in proportion to the difference of valence. In other words, at lower Fe contents, the difference of the filling fraction between Ba and Ce is much larger than that at higher Fe content. As Fe content increases, the difference between $y_{\text{max}}(\text{Ba})$ and $y_{\text{max}}(\text{Ce})$ narrows. At $x=4.0$, the filling limits of both Ba and Ce reach nearly 1.0. The reason for the nonlinear 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, the range of the filling fraction and Fe content of the obtained p - and n -type-filled skutterudite compounds are larger than those when Ce is used as filling atom. This implies that the 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 used as filling atom.

B. Thermal transport properties

The Wiedemann–Franz law ($\kappa_C = L\sigma T$) using a Lorenz number of $2 \times 10^{-8} \text{ V}^2/\text{K}^2$ is used to estimate the carrier contribution to the thermal conductivity.³ The lattice thermal conductivity (κ_L) is obtained by subtracting the carrier component (κ_C) from the total thermal conductivity (κ). The results of the lattice thermal conductivity (κ_L) of $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ saturated by Ce (i.e., filled by Ce at the maximum filling fraction) are shown in Fig. 4. In Fig. 4, the inset shows the relationship between the room-temperature lattice thermal conductivity and Fe content of Ce-saturated $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. As shown in Fig. 4, κ_L is greatly decreased either by the Ce filling in the Sb-icosahedron voids or by substituting Fe for Co sites. When the voids are filled with

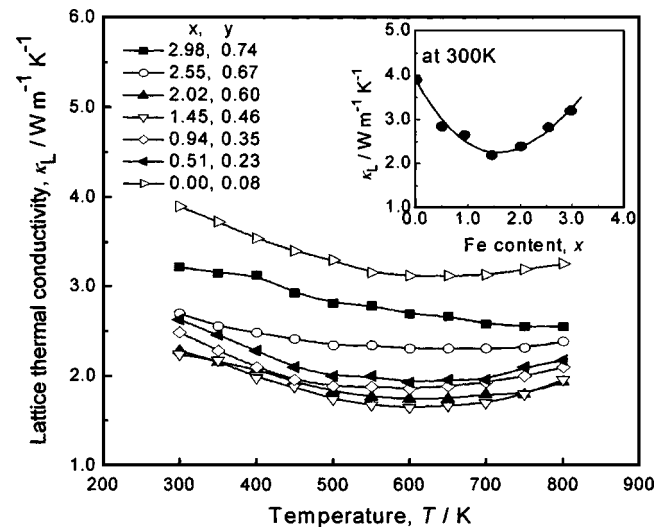


FIG. 4. Temperature dependence of lattice thermal conductivity for $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ saturated by Ce.

Ce at the maximum filling fraction, κ_L decreases with the increasing Fe content and reaches its minimum at a Fe/Co ratio of about 1.5/2.5.

Chen *et al.*⁵ prepare Ce-saturated $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ samples in the Fe content range (x) of 2.0–4.0 and measure the thermal conductivity below the room temperature, which shows that the thermal conductivity of these samples displays a peak near 30 K and that the peaks are progressively suppressed by increasing Co content. The sample with $x=2.0$ shows the lowest peak value of κ in the Fe content range of $x=2.0$ –4.0. In the present experiment, when $x < 2.0$, the lattice thermal conductivity of Ce-saturated $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ is further reduced by increasing Co content till $x=1.5$ compared with that of $x=2.0$. Taking into account the previous and present results, it can be concluded that in the Fe content range of $x=0$ –4, the lattice thermal conductivity of the Ce-saturated $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ has its minimum near $x=1.5$. It can also be deduced that the minimum lattice thermal conductivity in the overall composition range of x and y ($x=0$ –4.0 and $y=0$ –1.0) may also exist near $x=1.5$, although lattice thermal conductivity would vary with both the Fe content and Ce filling fraction. Therefore, we further investigate the Ce filling fraction dependence of lattice thermal conductivity by fixing the Fe content at 1.5.

Figure 5 shows the temperature dependence of lattice thermal conductivity (κ_L) for $\text{Ce}_y\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$, and the inset shows the relationship between the lattice thermal conductivity and the Ce filling fraction at 300 and 800 K. κ_L for all the samples decreases significantly with the increasing temperature. κ_L decreases with the increasing Ce filling fraction, and reaches the minimum at a Ce filling fraction of about 0.3. When $y > 0.3$, κ_L begins to increase with the increasing Ce filling fraction. In other words, the lattice thermal conductivity is reduced at the maximum with the partial filling (here at 30% filling) but not with the full filling.

Figure 6 shows the temperature dependence of the lattice thermal conductivity for p -type $\text{Ba}_y\text{FeCo}_3\text{Sb}_{12}$. As shown in Fig. 6, κ_L decreases with the increasing temperature. κ_L is decreased greatly by the Ba filling in the Sb icosahedron. It

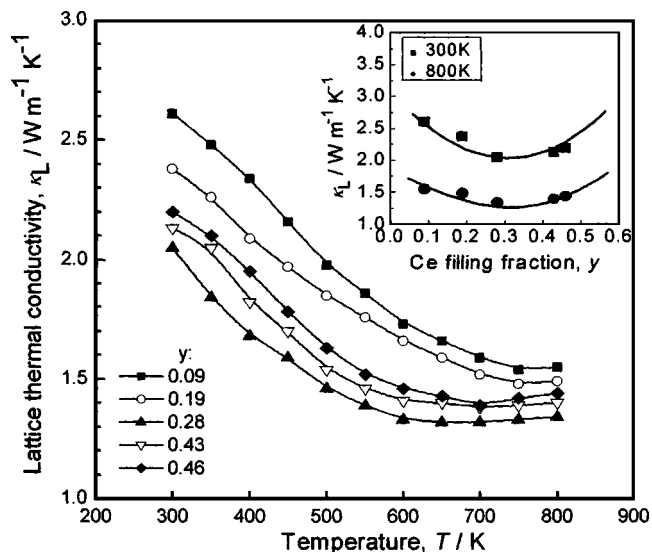


FIG. 5. Temperature dependence of lattice thermal conductivity for $\text{Ce}_y\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$.

is due to that the ionic radii of Ba ($\text{Ba}^{2+}=0.134$ nm) is smaller than the radii of the Sb-icosahedron void (0.189 nm), and thus Ba is poorly bonded in the structure and so it can rattle about its equilibrium position. Indeed, such rattling is also confirmed by the results obtained by using Rietveld analysis as what is reported above, i.e., the thermal parameters ($B=0.61$) of Ba is larger than that of Sb ($B=0.16$) and Co/Fe ($B=0.12$). The rattling of Ba atom can reduce the mean free path of the heat-carrying phonon, resulting in the decrease of the lattice thermal conductivity.

The effects of Ba filling fraction and Fe content on lattice thermal conductivity of the room temperature and 800 K are shown in Fig. 7 for *p*-type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. When $x=1.6$, κ_L decreases with the increasing Ba filling fraction, and reaches the minimum values at a Ba filling fraction of about 0.4. When $y>0.4$, κ_L begins to increase reversely with the increasing Ba filling fraction. When $x=1.0$, lattice thermal conductivity also reaches the minimum values at a cer-

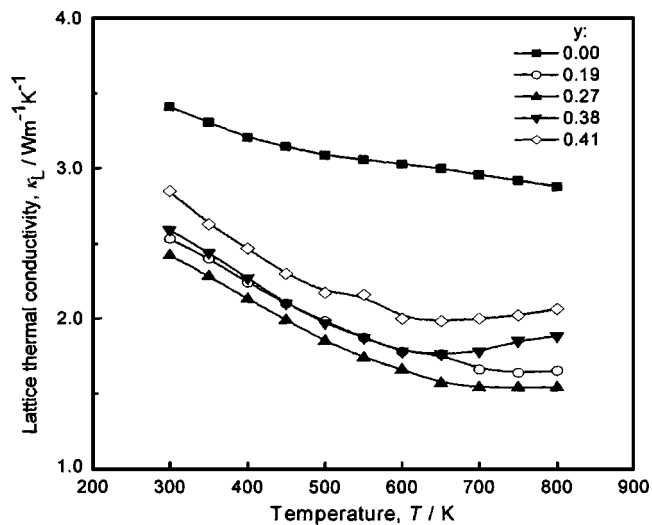


FIG. 6. Temperature dependence of lattice thermal conductivity for $\text{Ba}_y\text{FeCo}_3\text{Sb}_{12}$.

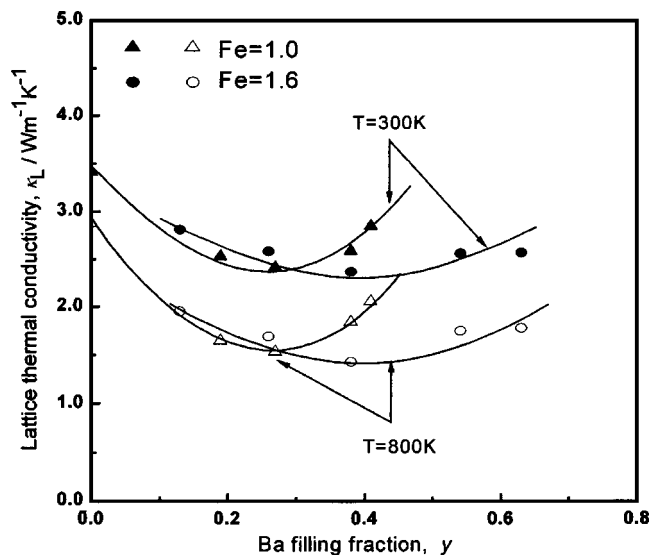


FIG. 7. Effect of Ba filling fraction and Fe content on lattice thermal conductivity for $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$.

tain Ba filling fraction (about 0.3). In other words, the lattice thermal conductivity is reduced most greatly with the partial filling but not with the full filling.

Chen *et al.*⁵ predicted that the partial filling of voids with Ce (random distribution) would provide more phonon scattering than the full filling (a regular arrangement in which all the voids are filled by Ce). Nolas *et al.*¹¹ measured the low-temperature lattice thermal conductivity of $\text{La}_x\text{Co}_4(\text{Sb}, \text{Sn})_{12}$ and reported that La scattering was most effective at $x=0.25-0.3$. The results obtained for $\text{Ce}_y\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ and $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$, and the results reported by Nolas *et al.* confirm that the random distribution of filling atoms seems to be more effective in scattering phonons than the arrangement in which all, or most, of the voids are filled.

Figure 8 shows the temperature dependence of the lattice thermal conductivity for $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ (R : Ba, Ce, Y). Experimental data were measured from 0 to 200 K. The effects of filling atoms with different ionic radii on the lattice ther-

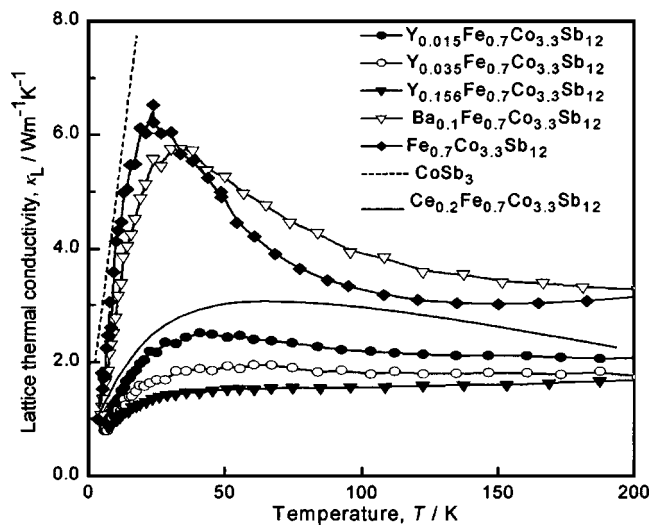


FIG. 8. Effect of Ba, Ce, and Y on lattice thermal conductivity of $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ (R : Ba, Ce, Y).

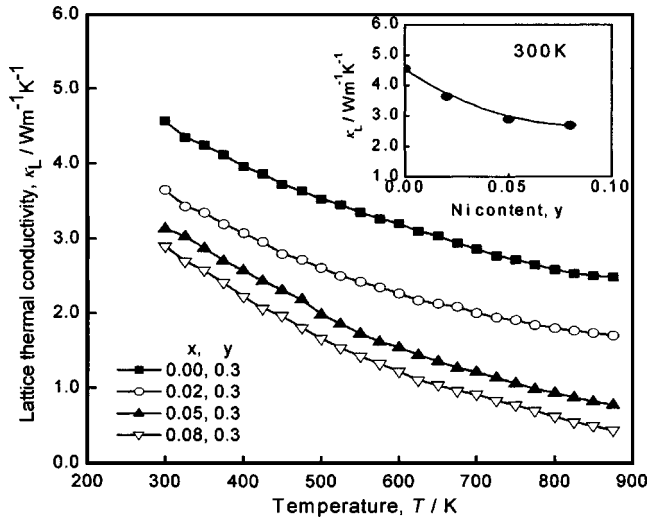


FIG. 9. Temperature dependence of lattice thermal conductivity for n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$.

mal conductivity will be discussed in the following. Figure 8 shows the relationship between the category of filling atoms and lattice thermal conductivity when the Fe content is 0.7. As shown in Fig. 8, the lattice thermal conductivity decreases in the order of Ba, Ce, and Y. The lattice thermal conductivities of filled $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$, $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$, and unfilled $\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ compounds reach their peak values at about 40 K, which indicates that these compounds possess the thermal transport characteristic of crystals. But in the case of Y filling, when the filling content is 0.015, there is almost no peak appearing in $\text{Y}_{0.015}\text{Fe}_{0.7}\text{Co}_{3.3}\text{Sb}_{17}$ compounds, which shows the thermal transport characteristic of glasses. And with the Y filling content increasing, its vitreous thermal characters are more obvious; the thermal transport characteristic of $\text{Y}_{0.156}\text{Fe}_{0.7}\text{Co}_{3.3}\text{Sb}_{17}$ compounds is extraordinarily similar to those of SiO_2 . The ionic radii of filling atoms Ba^{2+} , Ce^{3+} , and Y^{3+} are 0.134, 0.103, and 0.089 nm,

respectively, as described above; the lattice thermal conductivity of $\text{R}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ compounds decreases accordingly as the ionic radii of Ba^{2+} , Ce^{3+} , and Y^{3+} decrease. The reason probably is that the phonons scattering is enhanced when the ionic radii decrease, because the amplitudes of vibration and vibrating frequency of filling atoms in the Sb-icosahedron voids increase.

The above results indicate that filling atoms Ba, Ce, and Y in Sb-icosahedron voids act as new rattlers, which provides strong phonons scattering and results in the great reduction of the lattice thermal conductivity.

The temperature dependence of lattice thermal conductivity (κ_L) is shown in Fig. 9 for n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$. The inset shows the room-temperature lattice thermal conductivity of n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$. κ_L decreases with the increasing temperature. By substituting Ni for Co sites, κ_L decreases significantly, for example, κ_L of the room temperature reduces from 4.6 to 3.7 $\text{W m}^{-1} \text{K}^{-1}$ when Ni content is only 0.02. κ_L decreases further with increasing Ni content. The results indicate that Ni has a remarkable effect, and the effect of Ni is stronger than that of Fe in reducing the lattice thermal conductivity of $\text{R}_y\text{M}_x\text{Co}_{4-x}\text{Sb}_{12}$.

C. Electrical transport properties

Table III summarizes the chemical composition, Hall coefficient, and carrier concentration of $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. Hall coefficient of all samples is plus values, and therefore the $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ samples show p -type conduction.

Figure 10 shows the effects of Ce and Ba filling fraction, and Fe content on the room-temperature carrier concentration of p -type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and $\text{Ce}_y\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$. The carrier concentration of p -type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ decreases with the increasing of Ba filling fraction. In general, Ba is regarded as being divalent in $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$, i.e., one Ba^{2+} provides two electrons for the skutterudite structure. With the

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

Sample number	Nominal composition		Composition	Hall coefficient ($\text{cm}^3 \text{C}^{-1}$)	Hole concentration (m^{-3})
1	$x: 1.5,$	$y: 0.1$	$\text{Ce}_{0.09}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{12}$	1.85×10^{-2}	3.37×10^{26}
2	$x: 1.5,$	$y: 0.2$	$\text{Ce}_{0.19}\text{Fe}_{1.55}\text{Co}_{2.45}\text{Sb}_{12}$	1.93×10^{-2}	3.27×10^{26}
3	$x: 1.5,$	$y: 0.3$	$\text{Ce}_{0.28}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12}$	2.34×10^{-2}	2.67×10^{26}
4	$x: 1.5,$	$y: 0.5$	$\text{Ce}_{0.43}\text{Fe}_{1.50}\text{Co}_{2.50}\text{Sb}_{12}$	2.96×10^{-2}	2.11×10^{26}
5	$x: 1.5,$	$y: 0.6$	$\text{Ce}_{0.46}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{12}$	9.21×10^{-2}	6.78×10^{25}
6	$x: 1.6,$	$y: 0.1$	$\text{Ba}_{0.13}\text{Fe}_{1.57}\text{Co}_{2.43}\text{Sb}_{12}$	1.86×10^{-2}	3.36×10^{26}
7	$x: 1.6,$	$y: 0.2$	$\text{Ba}_{0.26}\text{Fe}_{1.56}\text{Co}_{2.44}\text{Sb}_{12}$	1.91×10^{-2}	3.05×10^{26}
8	$x: 1.6,$	$y: 0.3$	$\text{Ba}_{0.38}\text{Fe}_{1.57}\text{Co}_{2.43}\text{Sb}_{12}$	2.26×10^{-2}	2.76×10^{26}
9	$x: 1.6,$	$y: 0.4$	$\text{Ba}_{0.54}\text{Fe}_{1.57}\text{Co}_{2.43}\text{Sb}_{12}$	3.28×10^{-2}	1.90×10^{26}
10	$x: 1.6,$	$y: 0.5$	$\text{Ba}_{0.61}\text{Fe}_{1.60}\text{Co}_{2.40}\text{Sb}_{12}$	1.28×10^{-1}	4.48×10^{25}
11	$x: 1.0,$	$y: 0.1$	$\text{Ba}_{0.10}\text{Fe}_{0.93}\text{Co}_{3.07}\text{Sb}_{12}$	3.08×10^{-2}	2.02×10^{26}
12	$x: 1.0,$	$y: 0.2$	$\text{Ba}_{0.19}\text{Fe}_{0.92}\text{Co}_{3.08}\text{Sb}_{12}$	3.17×10^{-2}	1.97×10^{26}
13	$x: 1.0,$	$y: 0.3$	$\text{Ba}_{0.27}\text{Fe}_{0.98}\text{Co}_{3.02}\text{Sb}_{12}$	3.65×10^{-2}	1.72×10^{26}
14	$x: 1.0,$	$y: 0.4$	$\text{Ba}_{0.38}\text{Fe}_{1.01}\text{Co}_{2.99}\text{Sb}_{12}$	6.79×10^{-2}	9.20×10^{25}
15	$x: 1.0,$	$y: 0.5$	$\text{Ba}_{0.41}\text{Fe}_{0.98}\text{Co}_{3.02}\text{Sb}_{12}$	1.03×10^{-1}	6.07×10^{25}
16	$x: 1.0,$	$y: 0.6$	$\text{Ba}_{0.46}\text{Fe}_{0.98}\text{Co}_{3.02}\text{Sb}_{12}$	2.13×10^{-1}	2.95×10^{25}

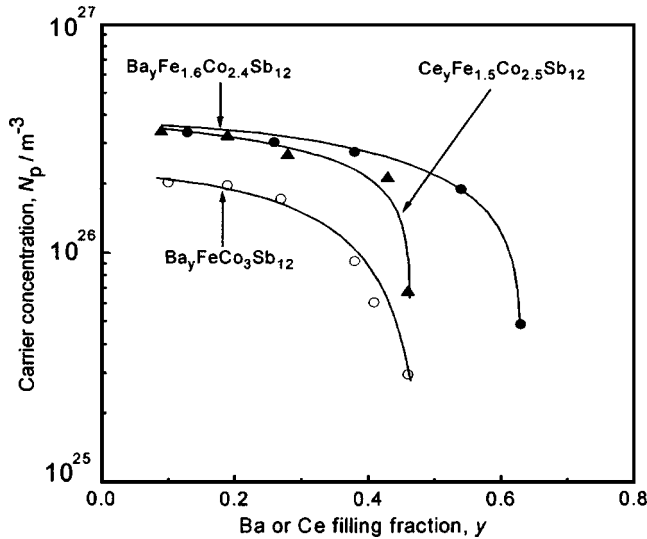


FIG. 10. Effect of Ba or Ce filling fraction and Fe content on the room-temperature carrier concentration for p -type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$.

increasing of Ba filling fraction, Ba provides more electrons for the skutterudite structure, which results in the decreasing of the hole concentration. Further, it is possible that the conduction type may change from p type to n type if Ba filling fraction exceeds y_{max} . At the same Ba filling fraction, the carrier concentration of $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ increases with the increasing of Fe content. At $y=0.38$, when Fe content increases from 1.0 to 1.6, the carrier concentration increases from 9.2×10^{25} to $2.76 \times 10^{26} \text{ m}^{-3}$. It is due to the fact that Fe provides more holes for the skutterudite structure with the increasing of Fe content, resulting in the increasing of the hole concentration. At the same Fe content and filling fraction, the carrier concentration of p -type $\text{Ba}_y\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ is larger than that of p -type $\text{Ce}_y\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$. This is due to the fact that the electron number which the Ba^{2+} provides for the skutterudite structure is less than that provided by Ce^{3+} . These results indicate that the oxidation valence of the filling atoms influences the carrier concentration of p -type $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ ($R=\text{Ba}, \text{Ce}$) significantly, and more large carrier concentration will be obtained when atoms having lower oxidation valence are used as filling atoms.

The effects of Ba filling fraction on the electrical conductivity (σ) of p -type $\text{Ba}_y\text{FeCo}_3\text{Sb}_{12}$ is shown in Fig. 11. Results are compared with those of $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Ce}_{0.35}\text{FeCo}_3\text{Sb}_{12}$. The σ values of $\text{Ba}_y\text{FeCo}_3\text{Sb}_{12}$ decreased with the increasing of Ba filling fraction. This is consistent with the changes of the carrier concentration shown in Fig. 10. At the maximum Ba filling fraction of 0.46, the electrical conductivity increases with the increasing of temperature at high temperatures, which implies 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 $0.29 \pm 0.05 \text{ eV}$ is calculated by using $\sigma = \sigma_0 \exp(-E_g/k_B T)$ (where, σ is electrical conductivity, E_g is band gap, k_B is Boltzmann constant, T is absolute temperature, and σ_0 is constant), which is close to the band-gap value ($0.4 \pm 0.1 \text{ eV}$) obtained for $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. While Fe content is the same, σ of $\text{FeCo}_3\text{Sb}_{12}$ is larger than that of $\text{Ba}_{0.38}\text{FeCo}_3\text{Sb}_{12}$ and

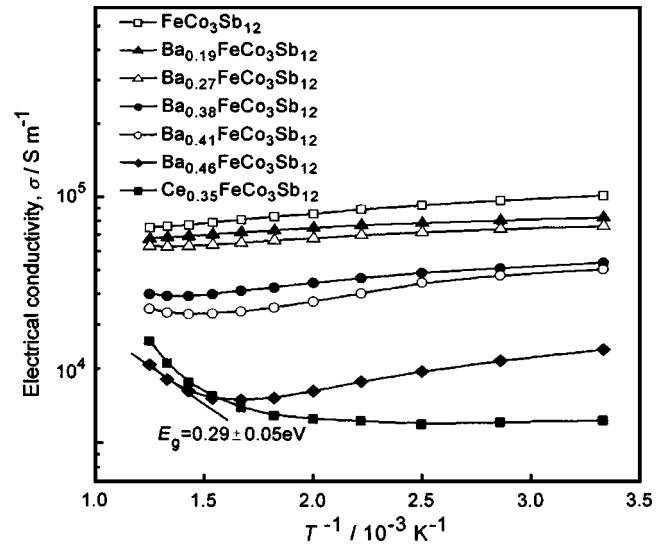


FIG. 11. Temperature dependence of electrical conductivity for p -type (Ce or Ba) $_y\text{FeCo}_3\text{Sb}_{12}$.

$\text{Ce}_{0.35}\text{FeCo}_3\text{Sb}_{12}$. While the filling fraction is the same, σ of $\text{Ba}_{0.38}\text{FeCo}_3\text{Sb}_{12}$ is 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 the carrier concentration.

Figure 12 shows the relationship between the 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 with those obtained for p -type $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. The electrical conductivity increases with the increase of the carrier concentration for p -type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. But at the same carrier concentration, the electrical conductivity of p -type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ is larger than that of p -type $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. The causes for the difference of the electrical conductivity are not revealed. Calculations on $\text{LaFe}_4\text{P}_{12}$ indicate that both the interstitial cation and the framework atoms are important in determining the properties.¹⁶ It is also reported that Sb_4 ring influences the electrical transport properties of the skutterudite compound

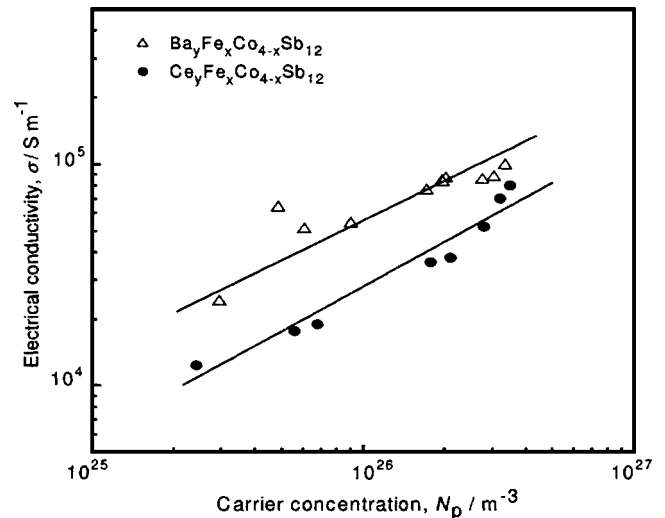


FIG. 12. Relationship between carrier concentration and electrical conductivity for p -type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$.

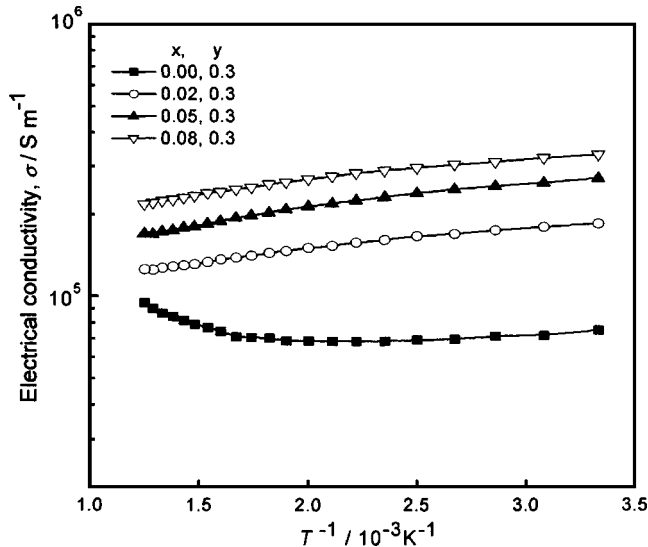


FIG. 13. Temperature dependence of electrical conductivity for n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$.

(CoSb_3) and filled skutterudite ($\text{LnFe}_x\text{Co}_{4-x}\text{Sb}_{12}$) markedly by Jung *et al.*²⁰ In CoSb_3 and $\text{LnFe}_x\text{Co}_{4-x}\text{Sb}_{12}$ structure, Sb_4 ring is (for example, in $\text{LaFe}_x\text{Co}_{4-x}\text{Sb}_{12}$ structure, Sb - Sb distances of Sb_4 ring are 2.932 and 2.982 Å, respectively). But in $\text{BaFe}_4\text{Sb}_{12}$ structure, Sb_4 ring is nearly square (Sb - Sb distance of Sb_4 ring is 2.952 and 2.959 Å, respectively).²² The difference of the 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 Sb - Sb distance of Sb_4 ring in $\text{MFe}_x\text{Co}_{4-x}\text{Sb}_{12}$ structure.

The effect of Ni content on the electrical conductivity (σ) is shown in Fig. 13 for n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$. The electrical conductivity increases with the increasing Ni content remarkably, and decreases with the rising temperature when $x \geq 0.02$. In general, Ni is regarded as being quaternary, i.e., one Ni provides four electrons for skutterudite structure with increasing Ni content so that the electron concentration increases and results in the increase of the electrical conductivity. The above results indicate that effects of Ni on thermal conductivity and electrical conductivity of $R_y\text{M}_x\text{Co}_{4-x}\text{Sb}$ are much stronger than those of Fe.

Figure 14 shows the Seebeck coefficient (α) of p -type $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$ compounds. α values of p -type $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ filled by Ce and Ba are larger than those of unfilled CoSb_3 significantly. α values increase with the temperature and reach a maximum at a certain temperature, T_{opt} for p -type $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. In general, α values increase with the decreasing carrier concentration, and increase with increasing carrier effective mass (m^*). It is shown that the carrier effective mass of $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ increases with the filling of Ce due to the strong hybridization of Ce $4f$ states with Fe $3d$ and Sb p states in the vicinity of the Fermi energy.³⁶ In the present study, the increase of α due to the Ce filling may have been caused by the decrease of the carrier concentration and the increase of the hole effective mass (m^*). As shown in Fig 14, α of p -type $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ are larger than those of p -type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ which may be due to the effect of Ce on the

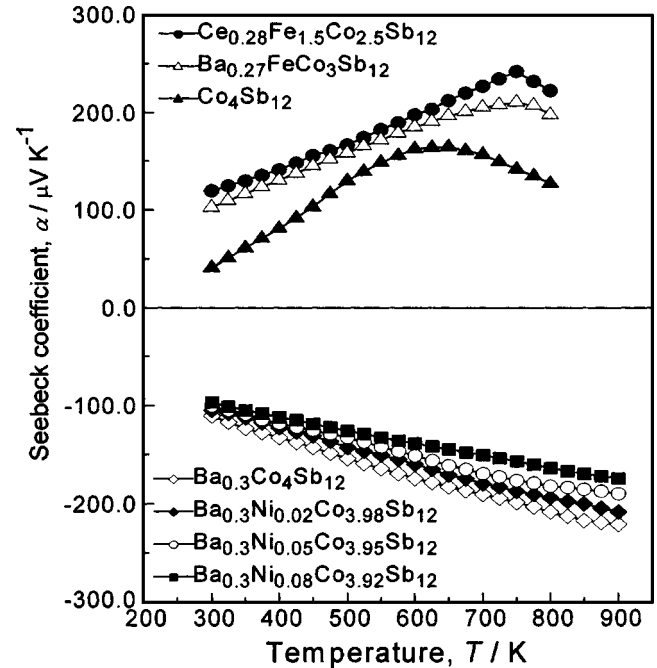


FIG. 14. Temperature dependence of Seebeck coefficient for p -type $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ (R : Ce, Ba) and n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$.

reduction of the carrier concentration, and the increasing hole effective mass (m^*) is more remarkable than that of Ba. In this work, the maximum Seebeck coefficient of $\text{Ce}_{0.28}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ reaches about $250 \mu\text{V K}^{-1}$ at 750 K.

The effect of Ni on the Seebeck coefficient of n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$ is also shown in Fig. 14. Seebeck coefficient increases with the increasing temperature, and decreases with the increasing Ni content. It is shown that the carrier effective mass of $\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ increases with the increasing Ba filling fraction.³⁷ In the present study, the increase of α of Ba-filled $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ may also have been caused by the decrease of the carrier concentration and the increase of the carrier effective mass (m^*). $\text{Ba}_{0.3}\text{Co}_4\text{Sb}_{12}$, which is not substituted by Ni, shows the maximum Seebeck coefficient, and reaches about $200 \mu\text{V K}^{-1}$ at 900 K.

D. Dimensionless thermoelectric figure of merit ZT

The dimensionless thermoelectric figure of merit (ZT) is calculated by using $ZT = \alpha^2 \sigma T / \kappa$ from the measured electrical conductivity (σ), the Seebeck coefficient (α), and the thermal conductivity (κ). Figure 15 shows the temperature dependence of ZT for p -type and n -type $R_y\text{M}_x\text{Co}_{4-x}\text{Sb}_{12}$. Of all the obtained p -type $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ samples, $\text{Ce}_{0.28}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ shows the greatest ZT values within the measured temperature range. The maximum ZT value of 1.1 is obtained at about 750 K for this sample. Sales *et al.*¹³ estimates the effect of the hole concentration on the thermoelectric performance by using Boltzmann's equation and parabolic bands. They indicated that the optimum doping level for maximizing ZT at high temperature (1000 K) is about 2×10^{27} hole m^{-3} . They synthesized a $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ sample with about 2×10^{27} hole m^{-3} , which had a ZT of 1.1 at 730 K. However, in the present study, the $\text{Ce}_{0.28}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ sample, which shows a large ZT value,

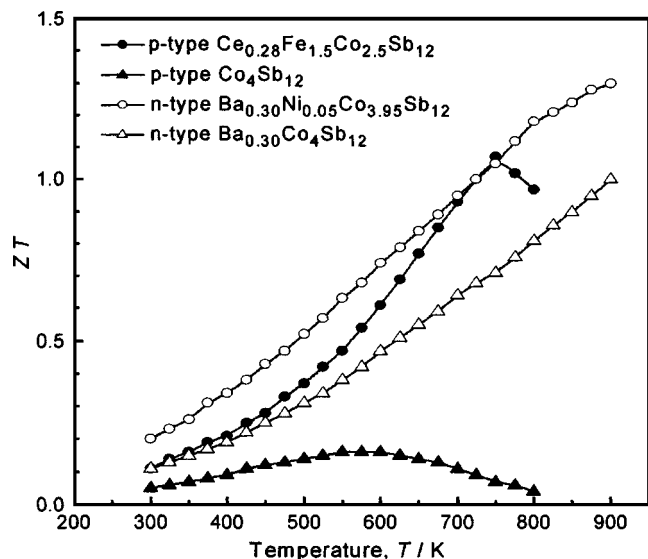


FIG. 15. Temperature dependence of ZT for p -type $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ (R : Ce, Ba) and n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$.

has a hole concentration of $2 \times 10^{26} \text{ m}^{-3}$, rather smaller than the “theoretical optimum carrier concentration (for 1000 K)” estimated by Sales *et al.* Indeed, the $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ sample prepared by Sales *et al.* does not show a peak in either ZT or α below 800 K, which corresponds to the higher hole concentration. The peaks of both α and ZT values at about 750 K for $\text{Ce}_{0.28}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ of the present study correspond to the lower carrier concentration. To develop skutterudite compounds for thermoelectric application in the medium temperature range (600–800 K), it is important to pay attention to those with a low hole concentration, i.e., those with a low Fe content.

Furthermore, of all the obtained n -type $R_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$ samples, $\text{Ba}_{0.30}\text{Ni}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$ show the greatest ZT values. The maximum ZT value of 1.25 is obtained at about 900 K for this sample.

IV. SUMMARY

Single-phase $R_yM_x\text{Co}_{4-x}\text{Sb}_{12}$ ($x=0-3.0, y=0-0.7$) compounds filled by Ce, Ba, and Y, and substituted by Fe and Ni are synthesized by using the solid-state reaction method and melting reaction method. The results of Rietveld analysis show high reliability with filling fraction values consistent with the ICPES analysis. The thermal parameter (B) of Ba and Ce is larger than that of Sb and Co (Fe). This supports the possibility of the rattling of Ba and Ce atoms in $R_yM_x\text{Co}_{4-x}\text{Sb}_{12}$. The maximum filling fraction of Ce and Ba (y_{max}) for $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ increases with the increasing Fe content, and it is found that the maximum filling fraction of Ba (y_{max}) is much greater than that of $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. The lower valence of Ba (+2) seems to allow more Ba, but less Ce, to be filled in the Sb-icosahedron voids, especially in the lower Fe content region.

The filling atoms Ba, Ce, and Y in Sb-icosahedron voids can reduce the lattice thermal conductivity of $R_yM_x\text{Co}_{4-x}\text{Sb}_{12}$ compounds significantly, and the lattice thermal conductivity decreases in the order of the decreasing of ionic radii Ba^{2+} ,

Ce^{3+} , and Y^{3+} , i.e., different ionic radii will result in different effects on lattice thermal conductivity. The smaller the ionic radii are, the stronger the effect is on the reduction of the lattice thermal conductivity. When Ce and Ba filling fraction is 0.3–0.4, the lattice thermal conductivity of $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ compounds reaches a minimum value. These indicate that when Sb-icosahedron voids in skutterudite structure are partially filled, the filling atoms provide the strongest phonons scattering. The lattice thermal conductivity can be greatly reduced by substituting Co with Fe or Ni, and with the increasing of the substitution content, the lattice thermal conductivity decreases further. Compared with Fe substitution, the substituted atoms Ni are more effective in the reduction of the lattice thermal conductivity.

The filling atoms Ba, Ce, and Y, and substituted atoms Fe and Ni influence the electrical transport properties of $R_yM_x\text{Co}_{4-x}\text{Sb}_{12}$ compounds significantly. The carrier concentration and electrical conductivity of p -type $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ increase with the increasing Fe content, and decrease with the increasing R filling fraction. In the same Fe content, the electrical conductivity of p -type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ is larger than that of p -type $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. At the same carrier concentration, the electrical conductivity of p -type $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ is also larger than that of p -type $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. The electrical conductivity of n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$ increases significantly with the increasing Ni content. The Seebeck coefficient of p -type $R_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ increases with the increasing Ce and Ba filling fraction and with the decreasing Fe content. Of all p -type samples, $\text{Ce}_{0.28}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ show the maximum Seebeck coefficient values, and it reaches about $250 \mu\text{V K}^{-1}$ at 750 K. Seebeck coefficient of n -type $\text{Ba}_y\text{Ni}_x\text{Co}_{4-x}\text{Sb}_{12}$ increases with the increasing temperature but decreases with the increasing Ni content. $\text{Ba}_{0.3}\text{Co}_4\text{Sb}_{12}$ which is not substituted by Ni, shows the maximum Seebeck coefficient, and reaches about $200 \mu\text{V K}^{-1}$ at 900 K.

In the present study, for p -type Co-rich $\text{Ce}_{0.28}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$, the maximum ZT value of 1.1 is obtained at about 750 K; for n -type $\text{Ba}_{0.30}\text{Ni}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$, the maximum ZT value of 1.25 is obtained at about 900 K.

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