

Synthesis and thermoelectric properties of filled skutterudite compounds $Ce_yFe_xCo_{4-x}Sb_{12}$ by solid state reaction

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Filled skutterudite compounds, $Ce_yFe_xCo_{4-x}Sb_{12}$ ($x = 0-1.0$, $y = 0-0.15$), were synthesized by solid state reaction using Co, Fe, Sb and $CeCl_3 \cdot nH_2O$ powders as source materials. The lattice constants of $Ce_yFe_xCo_{4-x}Sb_{12}$ increased with increasing substitution of Fe at Co sites and with increasing Ce filling fraction in the Sb-icosahedron voids. All specimens showed *p*-type conduction. Carrier concentration (ρ) and electrical conductivity (σ) increased with increasing substitution of Fe at Co sites and decreased with increasing Ce filling fraction. The Seebeck coefficient (α) decreased with increasing Fe content and increased with increasing Ce filling fraction. Thermal conductivity (κ) decreased with increasing substitution of Fe at Co sites and with increasing Ce filling fraction. A maximum *ZT* value of 0.8 was obtained for $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ at 750 K. © 2001 Kluwer Academic Publishers

1. Introduction

Compounds with the skutterudite structure MX_3 ($M = Co, Rh$ or Ir , $X = P, As$ or Sb) have attracted great attention recently for thermoelectric application [1–8] because they possess high carrier mobility, high electrical conductivity and relatively large Seebeck coefficients. Single crystals of skutterudites, CoP_3 , $CoAs_3$ and $CoSb_3$, were grown by a chemical vapor transport technique using chlorine as a transporting agent [2, 3]. Single crystals of *n*- and *p*-type $CoSb_3$ and $RhSb_3$ were obtained by a vertical gradient freeze technique from melts with an antimony-rich composition in a sealed quartz ampoule [4–7]. Lightly and heavily doped $CoSb_3$ and related alloys were synthesized by solid state reactions at temperatures of 873 to 1223 K [9–13]. Although skutterudite compounds possess excellent electrical properties, their relatively large thermal conductivity results in a lower thermoelectric figure of merit (*Z*). Much effort has gone into trying to reduce thermal conductivity through formation of a ternary solid solution and by controlling microstructures [1, 8, 11]. However, there is a limit to the reduction of thermal conductivity and to the improvement of thermoelectric performance through these approaches.

The skutterudite structure has two large Sb-icosahedron voids per unit which can accommodate foreign atoms such as rare-earth atoms, such a compound with a Sb-icosahedron void filled by foreign atoms is termed a filled skutterudite. Because the ionic radius

of rare-earth atoms is smaller than the radius of the voids, rare-earth atoms are weakly bonded and therefore “rattle” within the Sb cage. The rattling motion of the filling atoms can significantly reduce the lattice thermal conductivity [14–17].

Sales *et al.* [14, 15] synthesized $(Ce$ or $La)_yFe_xCo_{4-x}Sb_{12}$ compounds by melting pure Sb, Fe, Co and Ce (or La) ingots at 1273–1373 K for 24–48 hr with subsequent quenching in a water bath, followed by annealing at 973 K. $(Ce$ or $La)_yFe_xCo_{4-x}Sb_{12}$ compounds were also prepared by an arc-melting method by Chen [18], Uher [19] and Meisner *et al.* [20, 21]. In their arc-melting method, Ce and Fe (or Co) were first melted, resulting in CeFe and/or CeCo compounds. Sequentially, the obtained compounds were loaded into a pyrolytic boron nitride crucible with Sb and induction-melted at 1433 K in an Ar atmosphere. The resulting ingots were then annealed at 973 K and hot pressed into pellets.

However, all materials prepared by the above-mentioned melting methods contained some impurity phases such as $CoSb_2$ and/or Sb phases. This is because of the peritectic reaction of $CoSb_2 + liquid = CoSb_3$ at about 1147 K. It is difficult to synthesize a single phase of filled skutterudite by melting methods. Moreover, the oxidation of rare-earth metals, their reactivity with most crucible materials, and the high pressure of antimony at the optimum reaction temperature (1273–1373 K) make the process and handling very complex. For thermoelectric application, it is important to

develop a convenient method of synthesis characterized by easy handling.

In the present study, we tried a solid state reaction to synthesize Ce-filled skutterudite compounds: $Ce_yFe_xCo_{4-x}Sb_{12}$. In this solid state reaction, high purity powders of metallic Sb, Fe and Co were used. As the source material of cerium, cerium chloride was used because of its inertia in both oxidation and reaction with the crucible. The crystal structure and thermoelectric properties of the $Ce_yFe_xCo_{4-x}Sb_{12}$ compounds thus prepared were investigated.

2. Experimental procedure

2.1. Synthesis

High purity powders of Co (99.99%), Fe (99.99%), Sb (99.9999%), and $CeCl_3 \cdot nH_2O$ (99.9%) were used as the starting materials. The weighed starting materials were mixed and then cold-pressed into pellets. The pellets were loaded on a graphite boat and heated at 850–1100 K in an atmosphere of Ar + 7% H_2 for 172.8 ks. The obtained powders were treated with HCl + HNO_3 to remove small amounts of impurity phases such as $Fe_xCo_{1-x}Sb_2$ and Sb. A dense bulk of $Ce_yFe_xCo_{4-x}Sb_{12}$ was sintered by a plasma activated sintering method (Sodic Co. Ltd: PAS-V-K). Plasma activated sintering was performed at 873 K for 900 s in a vacuum under an unidirectional pressure of 80 MPa. The relative density of the sintered body was about 98%.

2.2. Characterization

The phase compositions of the obtained specimens were investigated by powder X-ray diffractometry (Rigaku: RAD-C, Cu $K\alpha$). The crystal structure of $Ce_yFe_xCo_{4-x}Sb_{12}$ was determined by Rietveld analysis using the diffraction data of a wide 2θ range ($2\theta = 10$ –130 degree). The compositions of the samples were determined by Inductively Coupled Plasma Emission Spectroscopy (ICPES). The Hall coefficient (R_H) was measured using the van der Pauw technique with a current of 100 mA and a magnetic field of 5028 Gauss. The carrier concentration (p) was calculated from the Hall coefficient, using $p = 1/R_H e$, where e is the electron charge. The electrical conductivity (σ) was measured by the four-probe method in a flowing Ar atmosphere. The thermoelectromotive force (ΔE) was measured under temperature differences (ΔT) of 0 to 10 K, and the Seebeck coefficient (α) was obtained from the slope of the ΔE - ΔT plot. The thermal conductivity (κ) was measured by a laser flash method (Shinkuriko: TC-7000) in a vacuum. All the measurements were performed in the temperature range of 300 to 800 K.

3. Results and discussion

3.1. Synthesis and structure of $Ce_yFe_xCo_{4-x}Sb_{12}$

The Fe contents (x) in the source materials (namely nominal Fe content) were changed from 1 to 3, and

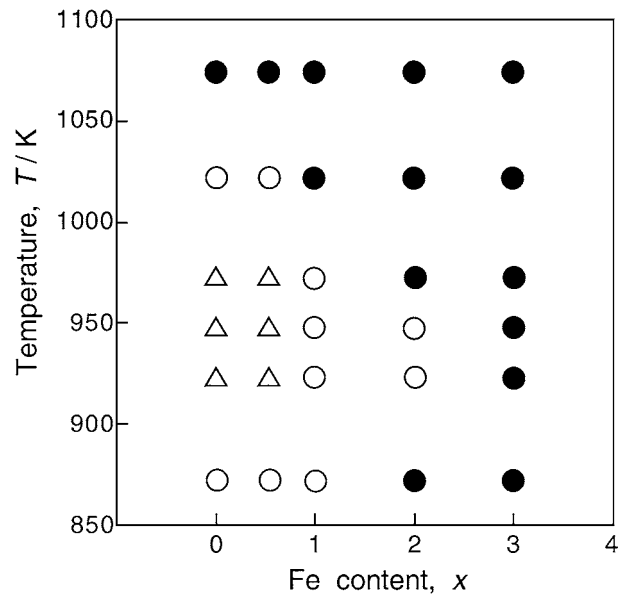


Figure 1 Effects of reaction temperature and nominal Fe content on the phase composition of the as synthesized powder. (Δ) $Ce_yFe_xCo_{4-x}Sb_{12}$, (\circ) $Ce_yFe_xCo_{4-x}Sb_{12} + (Fe_xCo_{1-x}Sb_2 + Sb)(traces)$, (\bullet) $Ce_yFe_xCo_{4-x}Sb_{12} + Fe_xCo_{1-x}Sb_2 + Sb$.

the reaction temperatures were from 850 to 1100 K. Fig. 1 shows the effects of the reaction temperature and the nominal Fe content on the phase composition of the as-synthesized powder. When $x = 0$, $CoSb_3$ or $Ce_yCo_4Sb_{12}$ in single-phase was obtained at the temperature range of 850 to 1050 K, while above 1073 K, the reacted powder contained small amounts of $CoSb_2$ and Sb. When x was larger than 1, the reacted powder contained three phases, $Ce_yFe_xCo_{4-x}Sb_{12}$, $Fe_xCo_{1-x}Sb_2$ and Sb. The amount of $Fe_xCo_{1-x}Sb_2$ and Sb increased with increasing Fe content and reaction temperature. In the temperature range of 900 to 1000 K and the composition range of $x < 2$, $Ce_yFe_xCo_{4-x}Sb_{12}$ with trace amounts of $Fe_xCo_{1-x}Sb_2$ and Sb were obtained. The trace amounts of $Fe_xCo_{4-x}Sb_2$ and Sb could be removed by treatment with HCl + HNO_3 mixed acid. Fig. 2 shows a typical X-ray diffraction pattern of $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$. It was confirmed that the obtained samples had the structure of filled skutterudites

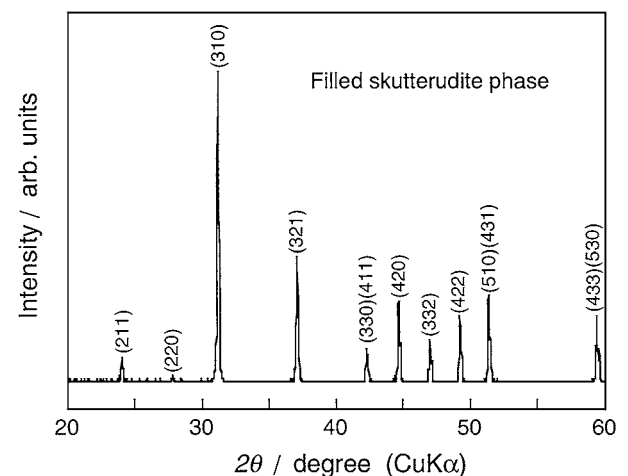


Figure 2 X-ray diffraction pattern of $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ synthesized at 923 K for 172.8 ks.

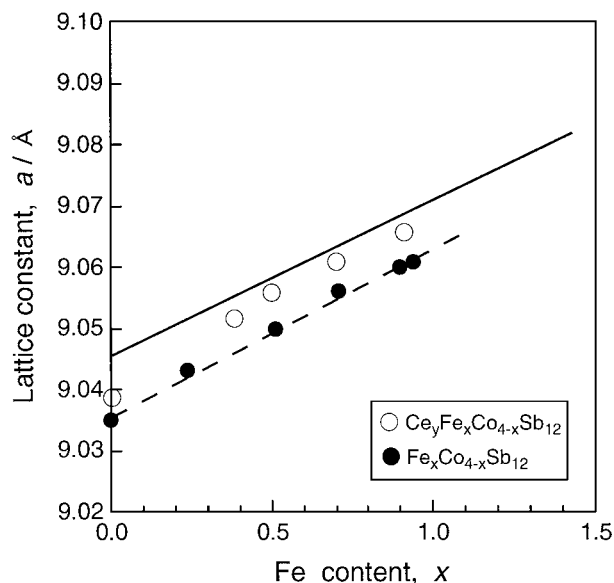


Figure 3 Relationship between lattice constant and composition for $Ce_yFe_xCo_{4-x}Sb_{12}$ ($y = 0.04-0.12$) and $Fe_xCo_{4-x}Sb_{12}$. Solid line represent Vegard's law for maximum Ce filling fraction [20].

by Rietveld analysis of X-ray powder diffraction data [22]. The filling fraction obtained from the refinement were consistent with those of ICPES analysis.

Fig. 3 shows the relationship between the lattice constant and composition for $Ce_yFe_xCo_{4-x}Sb_{12}$ and $Fe_xCo_{4-x}Sb_{12}$. In Fig. 3, the solid line represents Vegard's law for the maximum Ce filling fraction [20]. $Fe_xCo_{4-x}Sb_{12}$ was obtained in the composition range of $x = 0-1.0$. This result suggests that the solubility of Fe in $Fe_xCo_{4-x}Sb_{12}$ should be near $x = 1.0$, though Katsuyama *et al.* [23] have reported that the solid solution limit of Fe in $Fe_xCo_{4-x}Sb_{12}$ was near 0.3. The lattice constant of $Fe_xCo_{4-x}Sb_{12}$ linearly increased with increasing Fe content. The filling of Ce resulted in an increase of lattice constant and all the lattice constant data fall between solid line (maximum Ce filling fraction) and dashed line (without Ce filling).

3.2. Electrical properties

Fig. 4 shows the temperature dependence of carrier concentration (p) for $Ce_yFe_xCo_{4-x}Sb_{12}$ ($x = 0-1.0$, $y = 0-0.12$). All specimens exhibited positive Hall coefficients showing the p -type conduction. Carrier concentration increased with increasing Fe content, but decreased with increasing Ce filling fraction. It is understood that Co and Ce atoms are trivalent, while the Fe atom is bivalent in $Ce_yFe_xCo_{4-x}Sb_{12}$ [18]. The replacement of Co with Fe produces four holes in the valence band, while the filling of Ce causes a decrease in hole concentration since one Ce provides three electrons to the valence band. The trends of the changes in hole concentration observed above are consistent with these crystal-chemical consideration.

The temperature dependence of electrical conductivity (σ) of $Ce_yFe_xCo_{4-x}Sb_{12}$ is shown in Fig. 5. The electrical conductivity decreased significantly with increasing temperature for $CoSb_3$. The temperature dependence of electrical conductivity became weaker as

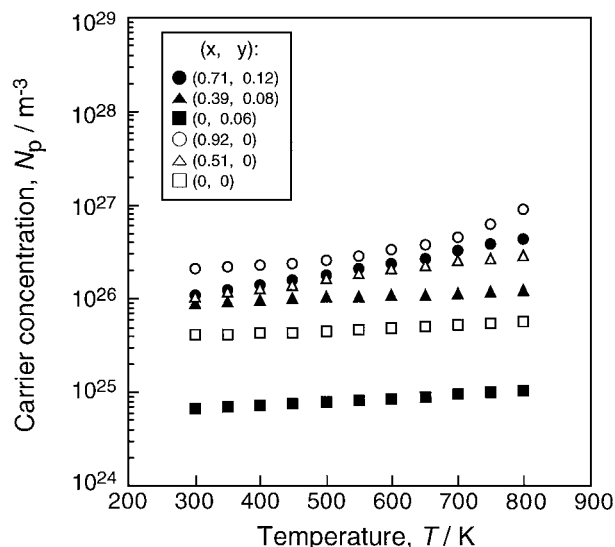


Figure 4 Temperature dependence of carrier concentration for $Ce_yFe_xCo_{4-x}Sb_{12}$.

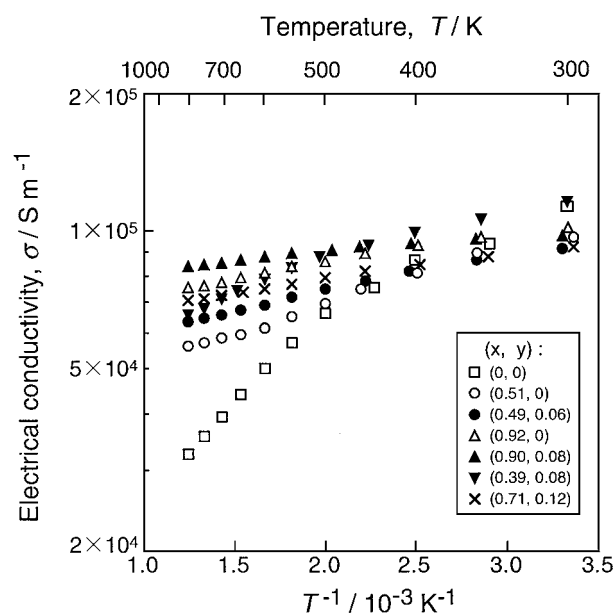


Figure 5 Temperature dependence of electrical conductivity for $Ce_yFe_xCo_{4-x}Sb_{12}$.

Fe content increased. The electrical conductivity increased with increasing Fe content and decreased with increasing Ce filling fraction. Caillat *et al.* [5] reported that electrical conductivity at room temperature increased from 5×10^3 to 2×10^5 Sm^{-1} and that the temperature coefficient of electrical conductivity changed from plus to minus as carrier concentration varied from 1×10^{23} m^{-3} to 1×10^{25} m^{-3} for p -type $CoSb_3$ single crystal. The electrical conductivity values and their temperature dependence in the present experiment were in agreement with the p -type $CoSb_3$ single crystal having a carrier concentration similar to that reported by Caillat. On the other hand, Sales *et al.* [14] synthesized a starting composition of $CeFe_xCo_{4-x}Sb_{12}$ with some impurity phases and showed that as $x < 2.0$ (Co-rich side) the electrical conductivity increased with increasing temperature, which is inconsistent with the present experiments. The difference between the present results

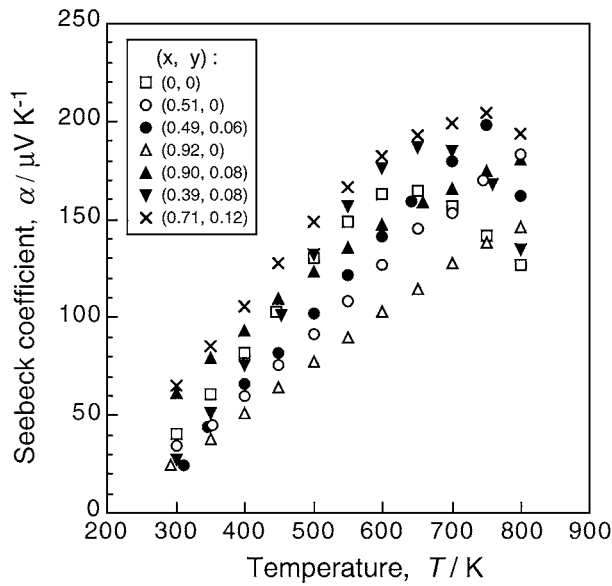


Figure 6 Temperature dependence of seebeck coefficient for $Ce_yFe_xCo_{4-x}Sb_{12}$.

and Sales' results may be mainly due to the difference in Ce filling fractions. Indeed, the $CeFe_xCo_{4-x}Sb_{12}$ ($x < 2.0$) specimens prepared by Sales *et al.* [14] had negative thermopower, showing their *n*-type conduction, and greater Ce filling.

Fig. 6 shows the temperature dependence of the Seebeck coefficient (α) for $Ce_yFe_xCo_{4-x}Sb_{12}$. The Seebeck coefficient increased with increasing temperature and then reached its maximum value at a certain temperature, T_{opt} . The T_{opt} shifted to a higher temperature with increasing Fe content, but shifted to a lower temperature with increasing Ce filling fraction. These phenomena might be caused by a change of hole concentration. The Seebeck coefficient was raised by the combination of Ce filling and Fe substitution, perhaps due to the combined effect of the increase of carrier effective mass [15] and the adjustment of carrier concentration. Among the obtained samples, $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ had the greatest Seebeck coefficient values, which reached about $200 \mu V K^{-1}$ at 750 K.

3.3. Thermal conductivity

Fig. 7 shows the temperature dependence of thermal conductivity (κ) for $Ce_yFe_xCo_{4-x}Sb_{12}$. $CoSb_3$ showed large thermal conductivity which changed significantly with temperature. κ was greatly reduced by the substitution of Fe at Co sites. Furthermore, Ce filling lowered κ . At the same time, the temperature dependence of κ became unremarkable, as the contents of Fe and Ce increased. Among all samples, $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ showed the smallest κ values over the whole temperature range.

The Wiedemann-Frenzel law has been used to estimate the carrier component of thermal conductivity. Fig. 8 shows the temperature dependence of the carrier thermal conductivity (κ_C) and the lattice thermal conductivity (κ_L). κ_C is much smaller than κ_L and almost independent of composition. κ_L is significantly reduced by the substitution of Fe at Co sites and by Ce

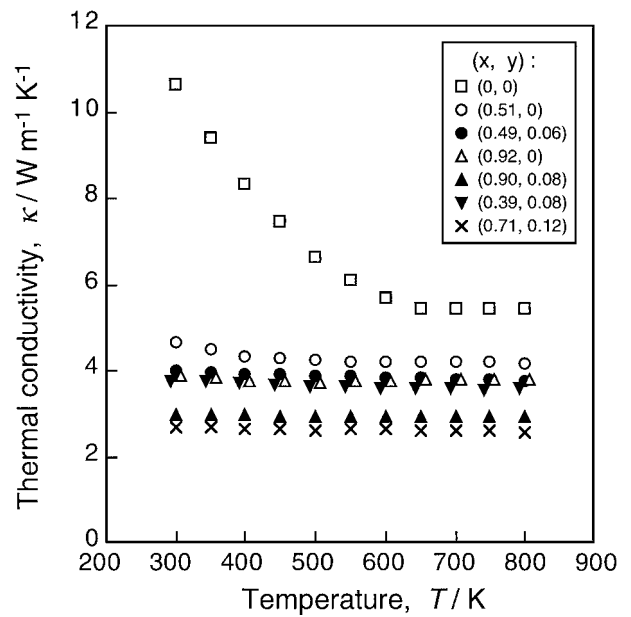


Figure 7 Temperature dependence of thermal conductivity for $Ce_yFe_xCo_{4-x}Sb_{12}$.

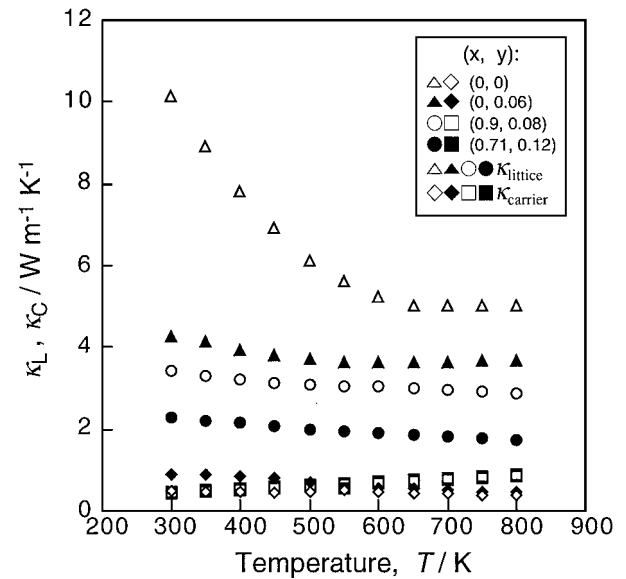


Figure 8 Temperature dependence of lattice and carrier thermal conductivity for $Ce_yFe_xCo_{4-x}Sb_{12}$.

filling. At 800 K, the ratio of κ_L to κ_C (κ_L/κ_C) is about 2.0 for $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$, as compared with 6.0 for $CoSb_3$. The decrease of lattice thermal conductivity by substitution of Fe is due to the strengthening of phonon scattering by the formation of a solid solution. Moreover, Chen *et al.* [18] suggested that Fe substitution may induce mass and strain fluctuations that can be effective in impeding heat flow. On the other hand, the ionic radius of Ce ($Ce^{3+} = 1.03 \text{ \AA}$) is smaller than the radius of the Sb-icosahedron void (1.892 \AA), and thus Ce is poorly bonded in the structure and so can rattle about its equilibrium position. The rattling of the Ce atom can significantly reduce the mean free path of the heat-carrying phonons, resulting in lowering of the lattice thermal conductivity [15]. Meisner [20] pointed out that a fractionally filled skutterudite can be thought of as a solid solution of $CeFe_4Sb_{12}$ and Co_4Sb_{12} (\square is

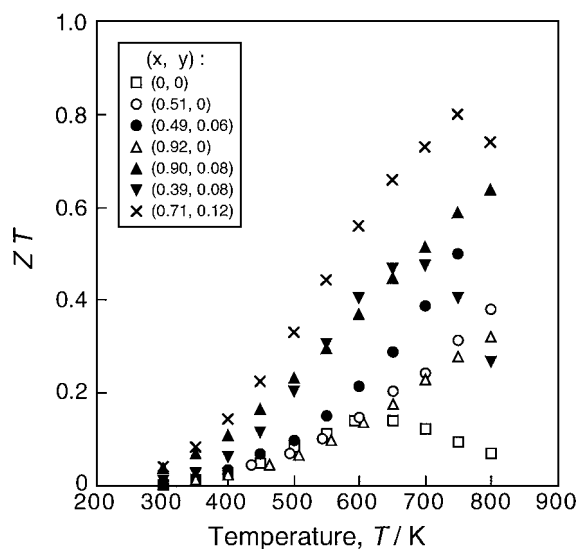


Figure 9 Temperature dependence of ZT for $Ce_yFe_xCo_{4-x}Sb_{12}$.

the vacancy) and that lowering of thermal conductivity is due to the point defect scattering. Basing on this speculation, the lowest lattice thermal conductivity can be obtained at a certain Ce filling fraction but not at the complete Ce filling. The relationship between the Ce filling fraction and lattice thermal conductivity has still not been revealed. Study aimed at clarifying the relationship between the Ce filling fraction and lattice thermal conductivity would be of interest and important for the development of a new skutterudite with high thermoelectric performance.

3.4. Thermoelectric performance

The dimensionless thermoelectric figure of merit (ZT) calculated from the electrical conductivity (σ), the Seebeck coefficient (α), and thermal conductivity (κ) is shown in Fig. 9. For all specimens, ZT increased with increasing temperature and then decreased after reaching a maximum value at a certain temperature, T_{opt} . The T_{opt} for ZT shifted to a higher temperature as Fe content increased, while it shifted to a lower temperature as the Ce filling fraction increased. ZT was greatly improved by the combination of Ce filling and Fe substitution, since these factors contributed to the reduction of lattice thermal conductivity and the adjustment of carrier concentration due to their opposite doping effects. In this study, a maximum ZT value of 0.8 was obtained for $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ at 750 K.

4. Conclusions

Cobalt-rich filled skutterudite compounds, $Ce_yFe_xCo_{4-x}Sb_{12}$ ($x=0-1.0$, $y=0-0.15$), were synthesized by a solid state reaction using Co, Fe, Sb and $CeCl_3 \cdot nH_2O$ powders as source materials. The crystal structure of filled skutterudites was confirmed by Rietveld analysis of X-ray diffraction data. Lattice constants of $Ce_yFe_xCo_{4-x}Sb_{12}$ increased with increasing Fe content and Ce filling fraction.

All specimens showed p -type conduction. Carrier concentration (p) increased with increasing Fe content and decreased with increasing Ce filling fraction. The Seebeck coefficient was not raised by the individual effect of either the substitution of Fe or the Ce fill-

ing. Only when the substitution of Fe and Ce filling were simultaneously applied, could the improvement of Seebeck coefficient be realized due to the effect of adjustment carrier concentration and increasing carrier effective mass.

The lattice thermal conductivity was reduced by both the substitution of Fe at Co sites and by Ce filling of the Sb-icosahedron voids, while the carrier thermal conductivity was not so sensitive to the composition.

The thermoelectric performance was improved by the combinational effects of Fe substitution and Ce filling. In this study, a maximum dimensionless thermoelectric figure of merit (ZT) of 0.8 was obtained for $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ at 750 K.

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Received 11 August 2000
and accepted 8 August 2001