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Thermoelectric Properties of Double-Filled *p*-Type $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$ Skutterudites

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La and Yb double-filled *p*-type skutterudites ($La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$; $0.25 \le z \le 0.75$ and $0.5 \le x \le 1$) were synthesized by encapsulated melting and homogenized by use of heat treatment. It was apparent from the positive signs of the Seebeck coefficient and the Hall coefficient that all specimens had *p*-type characteristics. The carrier concentration decreased with charge compensation. The thermal conductivity and the electrical conductivity decreased and the Seebeck coefficient increased with increasing substitution of Co for Fe. However, the carrier concentration was increased by increasing the Yb filling ratio. Electrical conductivity increased and the Seebeck coefficient decreased with increasing Yb filling, because the electron valence of Yb^{2+} was lower than that of La^{3+}. The thermal conductivity decreased with charge compensation, and the lattice thermal conductivity decreased with increasing Yb filling. Yb was more effective than La at reducing lattice thermal conductivity. The power factor (*PF*) and dimensionless figure of merit (*ZT*) increased with increasing temperature up to a specific temperature. The maximum $PF = 2.81\ mW/mK^2$ at 823 K was obtained for $La_{0.75}Yb_{0.25}Fe_{3.5}Co_{0.5}Sb_{12}$ and the maximum $ZT = 0.74$ at 723 K was achieved for $La_{0.5}Yb_{0.5}Fe_3CoSb_{12}$.

Key words: Thermoelectric, skutterudite, double filling

INTRODUCTION

Skutterudites have attracted much attention in thermoelectric power generation, because of their high thermoelectric performance in the middle-to-high temperature region between 500 K and 900 K.[1,2] The skutterudite structure belongs to the Im-3 space group, and takes the basic form RM_4X_{12} (M: Co, Rh, Ir, Fe, Ru, or Os, and X: P, As, or Sb) with two voids per unit cell.[3] Rare-earth and alkaline-earth atoms can fill the voids,[3,4] and the filler elements (R) cause phonon scattering by rattling, which reduces lattice thermal conductivity.[5] Filled skutterudites with a high figure of merit have been actively studied. Because the filler atom has its own resonant frequency,[6] by filling the voids two or more types of atom both high and low-frequency phonons can be effectively scattered to reduce the lattice thermal conductivity. Recently, filled skutterudites with high figures of merit, *ZT*, have been reported. Very high ($ZT > 1.4$) values were obtained for *n*-type RCo_4Sb_{12}-based skutterudites by use of double and triple-filling.[7,8] $ZT = 1.25$ at 800 K for double-filled *n*-type $Ba_{0.4}In_{0.4}Co_4Sb_{12}$ was reported by Yu et al.[9] and $ZT = 1.34$ at 800 K for triple-filled *n*-type $Ba_{0.08}Yb_{0.14}Eu_{0.1}Co_4Sb_{12}$ was reported by Shi et al.[10] However, $ZT = 0.99$ at 700 K for double-filled $La_{0.60}Yb_{0.25}Fe_{2.7}Co_{1.3}Sb_{12}$ was reported by Zhou et al.[4] and $ZT = 1.0$ at 750 K for double-filled $Ce_{0.5}Yb_{0.5}Fe_{3.25}Co_{0.75}Sb_{12}$ was reported by Ballikaya et al.;[11] these are much lower than those for *n*-type skutterudites. Therefore, active research is required on *p*-type skutterudites with *ZT* values comparable with those of *n*-type skutterudites for thermoelectric applications.

Co_4Sb_{12} has a valence electron count (VEC) of 72 and it is electronically stable. However, *p*-type skutterudite has an unstable basic form of $[Fe_4Sb_{12}]^{4-}$ with VEC = 68. Therefore, it should be fully filled as the $R^{4+}[Fe_4Sb_{12}]^{4-}$ form to stabilize the skutterudite structure.[12] Because most filler

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atoms are either divalent or trivalent, charge compensation is needed by substituting Co or Ni for Fe, for example, $R^{3+}[Fe_3CoSb_{12}]^{3-}$ or $R^{2+}[Fe_3NiSb_{12}]^{2-}$. In this study, *p*-type $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$ skutterudites were prepared with La–Yb double filling and partial substitution of Co for Fe. $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$ skutterudites are expected to control the carrier concentration by charge compensation (by substitution) and optimize the carrier concentration by double-filling elements with different valences. The amount of Co substitution and the La-to-Yb filling ratio were varied and the thermoelectric and transport properties of the products were studied.

EXPERIMENTAL

$La_{1-z}Yb_zFe_{4-x}Fe_{4-x}Co_xSb_{12}$ ($0.25 \le z \le 0.75$ and $0.5 \le x \le 1$) skutterudites were synthesized by encapsulated melting. La (purity 99.9%, Kojundo), Yb (purity 99.9%, Sigma–Aldrich), Fe (purity 99.95%, Cerac), Co (purity 99.95%, Alfa Aesar), and Sb (purity 99.999%, LTS) were weighed according to stoichiometric ratio and loaded into a quartz ampule coated inside with carbon. The sealed quartz ampule was evacuated then heated at 1323 K for 10 h and quenched into a water bath. These synthesized ingots were annealed at 873 K for 24 h to make homogeneous skutterudite materials, then ground to a powder with a particle size of less than 75 μm. The powder obtained was sintered by hot pressing in a graphite die with an internal diameter of 10 mm at 873 K under a pressure of 70 MPa for 1 h under vacuum. For the measurement of thermoelectric properties, the sintered specimen was cut to a disk shape with the dimensions 10 mm (diameter) × 3 mm (thickness) and to a bar shape with the dimensions 3 mm × 3 mm × 10 mm.

Phases were analyzed by x-ray diffraction (XRD; Bruker D8 Advance) using Cu K_α radiation (40 kV 40 mA). The carrier transport properties (Hall coefficient, carrier concentration, and mobility) were examined at room temperature in a 1-T magnetic field and at an electric current of 50 mA. The Seebeck coefficient and electrical conductivity were measured by use of the temperature differential and four-probe methods, respectively (Ulvac-Riko, ZEM3), in an Ar atmosphere. Thermal conductivity was obtained from the density and heat capacity, and thermal diffusivity was measured by use of the laser flash method (Ulvac-Riko, TC9000H). Power factor (*PF*) and dimensionless figure of merit (*ZT*) were calculated.

RESULTS AND DISCUSSION

Figure 1 shows phase-analysis results for $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$ skutterudites. The diffraction patterns were in good agreement with standard data (ICDD PDF# 00-056-1091). The skutterudite phase was successfully synthesized for all specimens and secondary phases were not identified. Therefore, void filling and charge compensation could stabilize the skutterudite. In addition, diffraction peaks tended to shift to higher angles with increasing Co content. This means that the lattice constant decreased with increasing Co substitution. As shown in Table I, the lattice constants were 0.9135–0.9143 nm for $x = 0.5$ and were reduced to 0.9118–0.9128 nm for $x = 1$ in $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$. In contrast, the change in lattice constant with La and Yb filling fraction was not significant. Comparison of the ionic radii of Fe^{2+} (75–92 pm), Co^{3+} (68.5–75 pm), La^{3+} (117.2 pm), and Yb^{2+} (116 pm) revealed the ionic radii of La and Yb were similar, and that of Co is smaller than that of Fe.[13] Therefore, the lattice constant was reduced by substituting Co for Fe, but was nearly unchanged on varying the La/Yb filling ratio.

Table I summarizes the transport properties of $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$ at room temperature. Hall coefficients had positive values for all specimens, indicating *p*-type conduction with holes as major carriers. Because the excess electrons were generated by Co substitution, the charge was partially compensated and the carrier concentration was therefore reduced with increasing Co content.[14] Carrier concentration increased with increasing Yb filling, because of the different valence of La^{3+} and Yb^{2+}.[15]

Figure 2 shows the temperature dependence of electrical conductivity for $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$. The electrical conductivity of all specimens decreased slightly with increasing temperature, indicating all specimens were degenerate semiconductors. This was attributed to the very high carrier concentration of 10^{20}–10^{21} cm^{-3}. Electrical conductivity increased with reduction in Co substitution and with increasing Yb filling, which was closely related to the change in the carrier concentration shown in Table I. Thus, $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$ could control the carrier concentration by charge

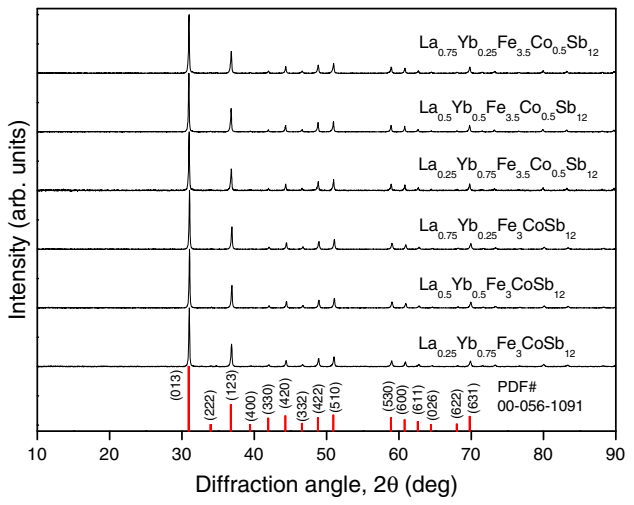

Fig. 1. X-ray diffraction patterns of the $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$ skutterudites.

Table I. Transport properties and lattice constants of $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$ at room temperature

Specimen	Hall coefficient (cm^3/C)	Mobility (cm^2/Vs)	Carrier concentration (cm^{-3})	Lattice constant (nm)
$La_{0.75}Yb_{0.25}Fe_{3.5}Co_{0.5}Sb_{12}$	3.50×10^{-3}	5.67	1.78×10^{21}	0.9135
$La_{0.5}Yb_{0.5}Fe_{3.5}Co_{0.5}Sb_{12}$	3.00×10^{-3}	5.38	2.08×10^{21}	0.9143
$La_{0.25}Yb_{0.75}Fe_{3.5}Co_{0.5}Sb_{12}$	2.73×10^{-3}	5.09	2.29×10^{21}	0.9140
$La_{0.75}Yb_{0.25}Fe_3CoSb_{12}$	6.45×10^{-3}	6.74	9.67×10^{20}	0.9118
$La_{0.5}Yb_{0.5}Fe_3CoSb_{12}$	4.08×10^{-3}	5.15	1.53×10^{21}	0.9120
$La_{0.25}Yb_{0.75}Fe_3CoSb_{12}$	3.76×10^{-3}	5.34	1.66×10^{21}	0.9128

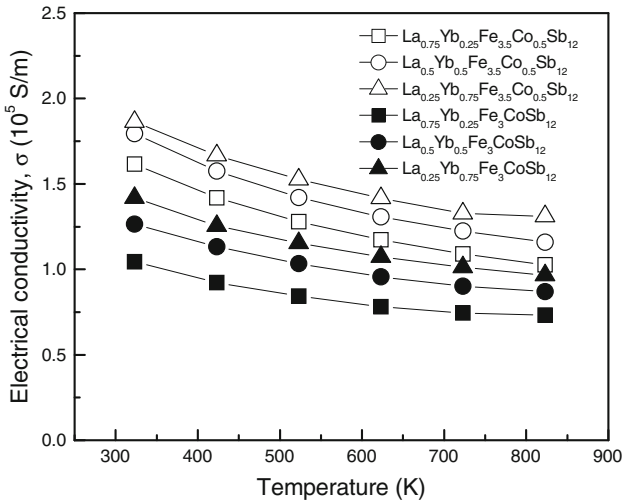

Fig. 2. Temperature dependence of electrical conductivity for $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$.

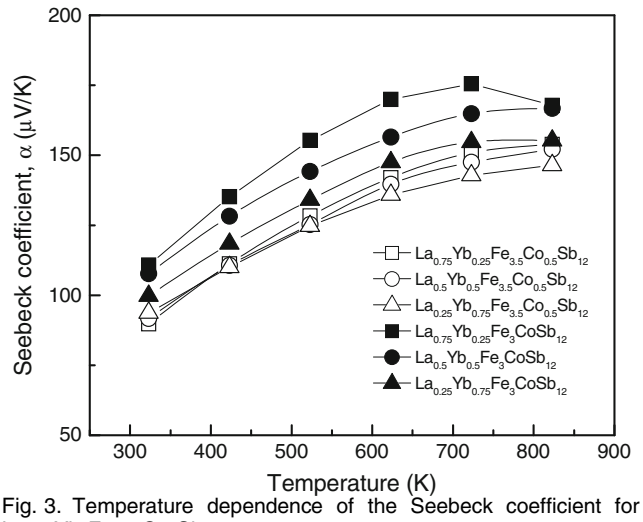

Fig. 3. Temperature dependence of the Seebeck coefficient for $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$.

compensation by substitution and optimize the carrier concentration by double-filling with elements of different valences.

Figure 3 shows the temperature dependence of the Seebeck coefficient for $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$. All specimens had positive Seebeck coefficients at all the temperatures examined. The Seebeck coefficient increased with increasing temperature, and was saturated above 723 K. As the Co and La content increased, the Seebeck coefficient increased. This was attributed to the reduced carrier concentration because of donation of excess electrons and the compensation. The Seebeck coefficient is expressed by the equation[14] $\alpha = (8/3)\pi^2 k_B^2 e^{-1} h^{-2} m^* T(\pi/3n)^{2/3}$, where k_B is the Boltzmann constant, e is the electron charge, m^* is the effective mass of the carrier, and n is the carrier concentration. Therefore, the Seebeck coefficient increased with decreasing carrier concentration. As shown in Table I, because carrier mobility did not change significantly with composition, charge carrier scattering related to mobility and effective mass did not affect the Seebeck coefficient of $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$.

Figure 4 shows the temperature dependence of the PF of $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$. All specimens had high PF values greater than 2.0 mW/mK^2 at 523–823 K. The specimens with $z \geq 0.5$ and $x = 0.5$ had larger PF values at all the temperatures examined. The maximum PF = 2.8 mW/mK^2 at 823 K was obtained for $La_{0.25}Yb_{0.75}Fe_{3.5}Co_{0.5}Sb_{12}$. This value was higher than 2.18 mW/mK^2 at 723 K for single-filled $Yb_{0.9}Fe_3CoSb_{12}$ and higher than 2.4 mW/mK^2 at 723 K to 823 K for single-filled $La_{0.9}Fe_3CoSb_{12}$, reported by Park et al.,[12,16] and was higher than 2.7 mW/mK^2 at 700 K for double-filled $La_{0.60}Yb_{0.25}Fe_{2.7}Co_{1.3}Sb_{12}$ reported by Zhou et al.[4] Consequently, double-filled $La_{1-z}Yb_zFe_xCo_xSb_{12}$ skutterudites are superior as power-generating materials.

Figure 5 shows the temperature dependence of the thermal conductivity for $La_{1-y}Yb_yFe_{4-z}Co_zSb_{12}$. The thermal conductivity (κ) is the sum of the lattice thermal conductivity (κ_L) and the electronic thermal conductivity (κ_E), which can be separated by use of measured κ and the Wiedemann–Franz law ($\kappa_E = L\sigma T$),[17] in which the Lorenz constant were assumed to be $L = 2.45 \times 10^{-8}$ V^2/K^2. As shown in Fig. 5b, the lattice thermal conductivity decreased slightly with decreasing Co substitution and increasing Yb filling. However, as shown in Fig. 5a, higher total thermal conductivity was obtained with

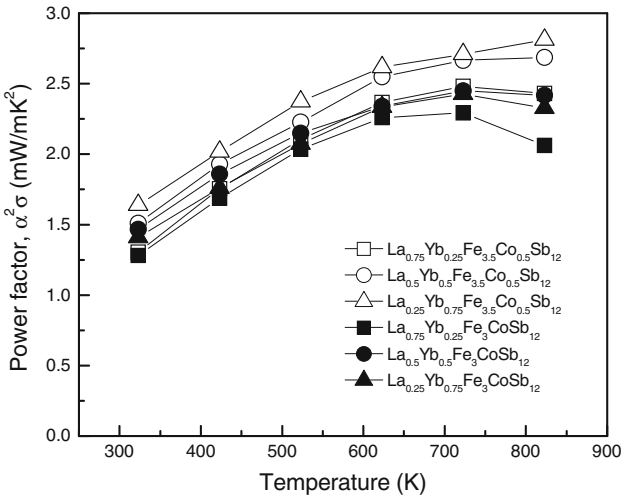

Fig. 4. Temperature dependence of the *PF* for $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$.

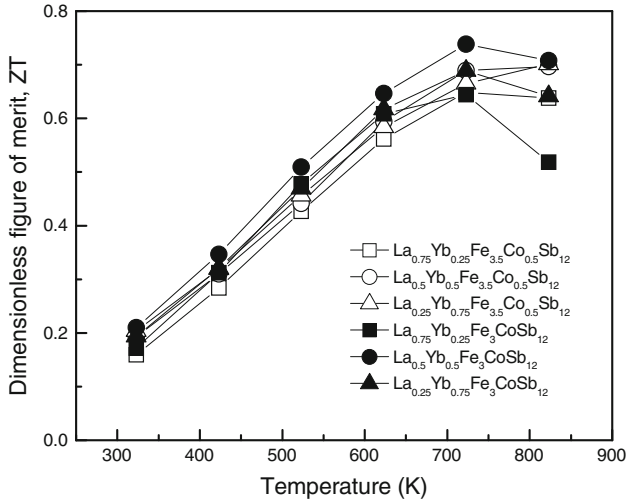

Fig. 6. Temperature dependence of the dimensionless figure of merit for $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$.

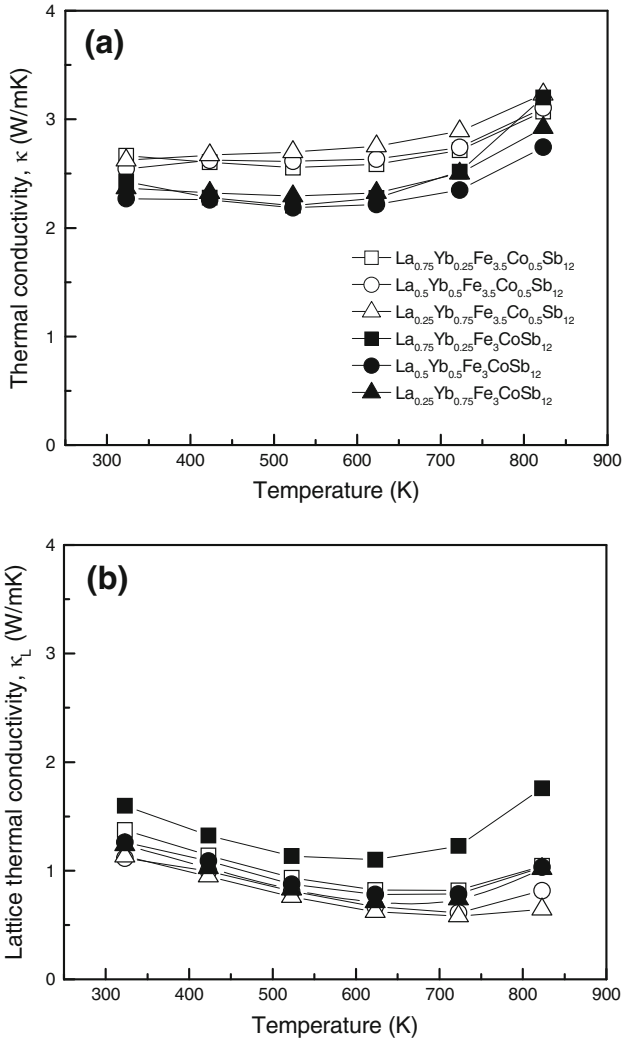

Fig. 5. Temperature dependence of (a) the thermal conductivity and (b) the lattice thermal conductivity for $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$.

a lower Co substitution. This is because of the increase in electronic thermal conductivity with increasing carrier concentration. $La_{0.5}Yb_{0.5}Fe_3CoSb_{12}$ had the lowest thermal conductivity of 2.2–2.7 W/mK from 323 K to 823 K.

Figure 6 shows the temperature dependence of the dimensionless figure of merit ($ZT = \alpha^2\sigma T\kappa^{-1}$) for $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$. The ZT value increased with increasing temperature and had a peak at 723–823 K. This was because of saturation of the Seebeck coefficient (*PF*) and increased thermal conductivity by bipolar conduction at high temperatures. $La_{0.5}Yb_{0.5}Fe_{3.5}Co_{0.5}Sb_{12}$ had a maximum ZT = 0.70 at 823 K and $La_{0.5}Yb_{0.5}Fe_3CoSb_{12}$ had the highest ZT = 0.74 at 723 K. These values were higher than ZT = 0.63 at 800 K for double-filled $BaInFe_{3.7}Co_{0.3}Sb_{13.44}$ reported by Yu et al.,[3] and higher than ZT = 0.56 at 823 K for single-filled $Yb_{0.9}Fe_3CoSb_{12}$ and higher than ZT = 0.59 at 800 K for single-filled $La_{0.9}Fe_3CoSb_{12}$ reported by Park et al.[9] However, they were lower than ZT = 0.99 at 700 K for double-filled $La_{0.60}Yb_{0.25}Fe_{2.7}Co_{1.3}Sb_{12}$ reported by Zhou et al.,[4] and lower than ZT = 1.0 at 750 K for double-filled $Ce_{0.5}Yb_{0.5}Fe_{3.25}Co_{0.75}Sb_{12}$ reported by Ballikaya et al.[11]

CONCLUSIONS

p-Type $La_{1-z}Yb_zFe_{4-x}Co_xSb_{12}$ skutterudites were successfully prepared by encapsulated melting and hot pressing, and their thermoelectric and transport properties were examined. No secondary phase was observed for any of the specimens, which confirmed that La and Yb filled the voids in the skutterudite structure. The Hall coefficient and Seebeck coefficient had positive values, indicating *p*-type conduction. Electrical conductivity decreased with charge compensation (decrease in carrier

concentration) and the Seebeck coefficient increased with increasing Co substitution; as a result, *PF* decreased. In contrast, electrical conductivity increased and the Seebeck coefficient decreased with Yb filling (increase in carrier concentration), resulting in an enhanced *PF*. The thermal conductivity decreased with increasing Co substitution, but the lattice thermal conductivity decreased with increasing Yb filling. The highest $PF = 2.8\ mW/mK^2$ was obtained at 823 K for $La_{0.25}Yb_{0.75}Fe_{3.5}Co_{0.5}Sb_{12}$ and the maximum $ZT = 0.74$ was obtained at 723 K for $La_{0.5}Yb_{0.5}Fe_3CoSb_{12}$.

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