Effect of Rh Substitution for Co on the Thermoelectric Properties of CoSb₃

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CoSb₃ is known as a skutterudite compound that could exhibit high thermoelectric figure of merit. However, the thermal conductivity of CoSb₃ is relatively high. In order to enhance the thermoelectric performance of this compound, we tried to reduce the thermal conductivity of CoSb₃ by substitution of Rh for Co. The polycrystalline samples of (Co_{1-x}Rh_x)Sb₃ ($x = 0, 0.1, 0.2$, and 0.3) were prepared and the thermoelectric properties such as the Seebeck coefficient, electrical resistivity, and thermal conductivity were measured in the temperature range from room temperature to 750 K. The Rh substitution for Co reduced the lattice thermal conductivity, due to the alloying scattering effect. The minimum value of the lattice thermal conductivity was $4 \text{ Wm}^{-1}\text{K}^{-1}$ at 750 K obtained for (Co_{0.7}Rh_{0.3})Sb₃.

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1. Introduction

Thermoelectric materials are capable of converting waste heat to usable electricity. The effectiveness of a material for thermoelectric applications is determined by the dimensionless figure of merit, $ZT = S^2T/\rho\kappa$, where S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity, and T is the absolute temperature.^{1,2} ZT value of the materials used in current devices is approximately 1. In recent years, several classes of bulk materials^{3,4} with high ZT have been discovered, including filled skutterudites.⁵⁻⁷

Skutterudite compounds have the composition MX_3 where M is a metal atom such as Co, Rh, or Ir and X represents a pnictogen atom such as P, As, and Sb. These compounds are body-centered cubic with 34 atoms in the unit cell and space group Im $\bar{3}$. There are two cages per unit cell in the structure. When the third atom incorporates into the cage, the formula of the compounds turns out to be RM_4X_{12} , where R is most often a rare-earth element, called filled-skutterudite structure. The R atom is bonded weakly with the other atoms and rattles. Therefore, the introduction of R atoms into the cages of the skutterudites is an effective method of reducing the lattice thermal conductivity.

In addition to the rattling effect, the lattice thermal conductivity could be reduced by the alloy scattering effect. The alloying can reduce the lattice thermal conductivity by the point defect phonon scattering while giving little influence on the electrical transport, because it does not introduce charge disorder in the crystal lattices. For example, in the systems of Si-Ge alloy,⁸ (Zr,Hf)NiSn,⁹ and Ti(Co,Rh)Sb,¹⁰ the reduction of the lattice thermal conductivity through the alloy scattering effect have been achieved.

In the CoSb₃ system, the thermoelectric properties of Co(Sb,As)₃¹¹ and (Co,Rh)Sb₃¹² were reported. In Ref. 11), homogeneous solid solutions of Co(Sb_{1-x}As_x)₃ ($x \leq 0.1$)

were prepared and the reduction of the lattice thermal conductivity with increasing As concentration was explained by the enhanced point-defect scattering due to mass fluctuations and strain field fluctuations as As atoms substitute on the Sb sublattice. On the other hand, in Ref. 12), a series of solid solutions of (Co_{1-x}Rh_x)Sb₃ ($0 \leq x \leq 1.0$) was prepared and the thermoelectric properties were measured within the wide range of composition. It was reported in Ref. 12) that the alloyed compounds resulted in dropping significantly their lattice thermal conductivity and electrical conductivity, especially for the composition of x ranging between 0.2 and 0.5.

The purposes of the present study are (1) to prepare homogeneous solid solutions of (Co_{1-x}Rh_x)Sb₃ ($x \leq 0.3$), (2) to investigate the relationships between the composition and the electrical conductivity or lattice thermal conductivity, and (3) to compare the obtained results with the literature data reported in Ref. 12). Results of such studies have been presented in the present paper.

2. Experiment

The polycrystalline samples of (Co_{1-x}Rh_x)Sb₃ ($x = 0, 0.1, 0.2$, and 0.3) were prepared from Co (99%), Rh (99.9%), and Sb (99.9%) chunks by direct reactions in sealed silica tubes. The obtained ingots were crushed into fine powders, followed by hot-pressing in graphite dies under the pressure of 45 MPa at 973 K for 4 h in an argon flow atmosphere. The obtained samples were characterized with a powder X-ray diffraction (XRD) method using Cu $K\alpha$ radiation at room temperature. The sample microstructure was observed by a scanning electron microscopy (SEM). The chemical composition of the samples was determined with an energy-dispersive X-ray (EDX) analysis in vacuum at room temperature. The density of the bulk samples was calculated based on the measured weight and dimensions. Electrical resistivity (ρ) and the

Fig. 1 Powder XRD patterns of the polycrystalline samples $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3), together with the peak positions calculated from the crystal structure of CoSb_3 .

Seebeck coefficient (S) were measured by using a commercially available apparatus (ULVAC, ZEM-1) in a He atmosphere. Thermal conductivity (κ) was evaluated from thermal diffusivity (α), heat capacity (C_p), and sample density (d) based on the relationship $\kappa = \alpha C_p d$. The thermal diffusivity was measured by the laser flash technique in a vacuum using a commercially available apparatus (ULVAC TC-7000). The thermoelectric properties were evaluated from room temperature to 750 K.

3. Results and Discussion

The powder XRD patterns of the polycrystalline samples of $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3) are shown in Fig. 1, together with the literature data of CoSb_3 .¹³⁾ Small peaks derived from impurity phases (mainly CoSb_2) were observed in the XRD patterns as shown in circles. The lattice parameters of the skutterudite phase calculated from the XRD patterns are summarized in Table 1. It was confirmed that the lattice parameter increased linearly with increasing x , following the Vegard law. It was observed in the SEM and EDX mapping images of the samples that there were no segregation regions and Co, Rh, and Sb distributed homogeneously throughout the sample surface. The sample densities are summarized in Table 1. Very high-density samples (99% of the theoretical density) were obtained in the present study. As summarized in Table 1, the chemical compositions of the samples determined through the quantitative EDX analyses were slightly Sb-rich and Rh-poor compared with the starting compositions.

The electrical properties of the polycrystalline samples of $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3) are shown in Figs. 2(a)–(c). The electrical resistivity (ρ) of the samples decreased with temperature in the whole temperature range as shown in Fig. 2(a), indicating that the semiconductor-like behavior. The ρ values decreased with increasing Rh content, x . The Seebeck coefficient (S) values were negative and the absolute values decreased with both temperature and Rh content, as shown in Fig. 2(b). Especially, sign of the S of the $(\text{Co}_{0.7}\text{Rh}_{0.3})\text{Sb}_3$ sample turned from negative to positive at high temperature. This indicates that the carrier has mixed

Table 1 Lattice parameter, sample bulk density, and chemical composition of $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3).

		x in $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$			
		0	0.1	0.2	0.3
Lattice parameter	a (nm)	0.9034	0.9051	0.9064	0.9080
Theoretical density	d_{th} (g cm^{-3})	7.64	7.67	7.72	7.76
Measured density	d_{exp} (g cm^{-3})	7.63	7.60	7.65	7.73
Relative density	$d_{\text{exp}}/d_{\text{th}} \times 100$ (%)	99	99	99	99
Chemical composition determined through the EDX analysis (at%)	Co	24	22	20	18
	Rh	—	2	4	6
	Sb	76	76	76	76

Fig. 2 Temperature dependences of the electrical properties of the polycrystalline samples $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3); (a) electrical resistivity ρ , (b) Seebeck coefficient S , and (c) power factor $S^2 \rho^{-1}$.

conduction mechanism in high temperature region. The power factor ($S^2 \rho^{-1}$) data of the samples are plotted in Fig. 2(c) as a function of temperature. Unfortunately, the power factor was decreased by substituting Rh for Co. CoSb_3 indicated the maximum value of the power factor to be $1.2 \text{ mW m}^{-1} \text{ K}^{-2}$ at around 450 K.

It is well known that the total thermal conductivity (κ_{total}) of solids is mainly composed of two components: the lattice term (κ_{lat}) and the electronic term (κ_{el}). We roughly estimated the κ_{el} based on the Wiedemann-Franz relation using the electrical conductivity ($\sigma = 1/\rho$) data and the Lorenz number ($L = 2.45 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}$), i.e. $\kappa_{\text{el}} = L \sigma T$, and the κ_{lat} was obtained by subtracting the κ_{el} from the κ_{total} . The temperature dependences of the κ_{total} and the κ_{lat} ($= \kappa_{\text{total}} - L \sigma T$) of the polycrystalline samples of $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3) are shown in Fig. 3. It was

Fig. 3 Temperature dependences of the thermal conductivities of the polycrystalline samples $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3); (a) total (measured) thermal conductivity κ_{total} and (b) lattice thermal conductivity κ_{lat} ($= \kappa_{\text{total}} - L\sigma T$) where L is the Lorentz number ($= 2.45 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$), σ is the electrical conductivity ($= 1/\rho$), and T is the absolute temperature.

confirmed that the κ_{lat} was predominant at low temperatures, whereas the contribution of the κ_{el} became large at high temperatures. The κ_{lat} of $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ decreased with increasing temperature and also decreased with increasing Rh content, x , indicating that the alloying between Co and Rh was effective to reduce the κ_{lat} .

Next, in order to evaluate the effect of Rh substitution for Co on the κ_{lat} of CoSb_3 quantitatively, the phonon scattering parameters were calculated based on a point defect scattering theory,^{14–16} in which only the phonon-phonon scattering and the phonon-point defect scattering were taking into considered and the boundary scattering was neglected. In the present case, the relaxation time τ_{total} can be expressed as follows:

$$\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_{\text{D}}} + \frac{1}{\tau_{\text{P}}}, \quad (1)$$

where τ_{D} and τ_{P} are the relaxation times for the phonon-phonon and the phonon-point defect scatterings, respectively. τ_{D} and τ_{P} can be described by using the phonon frequency ω as follows:¹⁵

$$\frac{1}{\tau_{\text{D}}} = A\omega^4, \quad (2)$$

$$\frac{1}{\tau_{\text{P}}} = CT\omega^2. \quad (3)$$

The value of A is independent of temperature, which can be expressed by the following equation:¹⁶

$$A = \frac{\delta^3}{4\pi v^3} \sum_i \Gamma_{M,i} + \Gamma_{S,i} \\ = \frac{\delta^3}{4\pi v^3} \sum_i x_i(1-x_i) \left[\left(\frac{M_i - M}{M} \right)^2 + \varepsilon \left(\frac{r_i - r}{r} \right)^2 \right], \quad (4)$$

where δ^3 is the average atomic volume, v is the phonon velocity, x_i is the fractional concentration of the component i , M_i is the atomic mass of the substituted element, M is the average atomic mass, r_i is the atomic radius of the substituted element, and r is the average atomic radius. Γ_{M} and Γ_{S} are the phonon scattering parameters due to mass and strain-field fluctuations, respectively. Generally, the parameter ε is regarded as the adjustable parameter, normally ranging from 10 to 100.^{9,10} On the other hand, the value of C is proportional to the reciprocal of the absolute temperature, which can be expressed by the following equation:¹⁵

$$C = \frac{k_{\text{B}}^2 \theta}{2\pi^2 v \hbar T} \frac{1}{\kappa_{\text{CoSb}_3}}, \quad (5)$$

where k_{B} , θ , $\hbar$, and κ_{CoSb_3} are the Boltzmann constant, Debye temperature, the Planck constant divided by 2π , and the lattice thermal conductivity of pure CoSb_3 . By using the above-mentioned parameters, the κ_{lat} of the alloyed materials is expressed as follows:¹⁵

$$\kappa_{\text{lat}} = \frac{k_{\text{B}}}{2\pi^2 v (ACT)^{\frac{1}{2}}} \tan^{-1} \left[\frac{k_{\text{B}} \theta}{\hbar} \left(\frac{A}{CT} \right)^{\frac{1}{2}} \right]. \quad (6)$$

In the present study, the average sound velocity v_{ave} of CoSb_3 was used as the phonon velocity v . In order to evaluate the v_{ave} and θ , the samples were bonded to a 5 MHz longitudinal or shear sound wave echogenic transducer and the longitudinal (v_{l}) and shear (v_{s}) sound velocities were measured. The measurements were performed at room temperature in air. From the measured v_{l} and v_{s} the v_{ave} and θ were calculated based on the following equations:

$$v_{\text{ave}} = \left(\frac{1}{3} \left[\frac{1}{v_{\text{l}}^3} + \frac{2}{v_{\text{s}}^3} \right] \right)^{-1/3}, \quad (7)$$

$$\theta = \frac{h}{k_{\text{B}}} \left[\frac{3N}{4\pi V} \right]^{\frac{1}{3}} v_{\text{ave}}, \quad (8)$$

where N is the number of atoms in a unit cell and V is the unit cell volume. In the present study, the v_{ave} and the Debye temperature θ were evaluated to be 3684 ms^{-1} and 320 K , respectively.

The calculated lattice thermal conductivity (κ_{calc}) for $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3) are summarized in Table 2, together with the experimental lattice thermal conductivity (κ_{lat} at 330 K). In calculating the κ_{lat} , the adjustable parameter ε was determined by fitting. The parameter ε is a phenomenological adjustable parameter that characterizes anharmonicity of the lattice. Although the value of $\varepsilon \approx 15$ was reported in the $\text{Co}(\text{Sb}_{1-x}\text{As}_x)_3$ system,¹¹ the value of $\varepsilon = 48$ was determined in the $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ system.

It was confirmed that the calculated κ_{lat} were well consistent with the experimental data. The Γ_{M} and Γ_{S} values are also summarized in Table 2. The values of Γ_{S} and Γ_{M} were similar to each other, indicating that the strain-field

Table 2 Phonon scattering parameters due to mass and strain-field fluctuations (Γ_M and Γ_S), experimental (κ_{lat} at 330 K) and calculated (κ_{calc}) lattice thermal conductivities of $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3); The Γ_S was calculated under the adjustable parameter $\varepsilon = 48$.

Composition	Γ_M	Γ_S	κ_{lat} at 330 K ($\text{Wm}^{-1}\text{K}^{-1}$)	κ_{calc} ($\text{Wm}^{-1}\text{K}^{-1}$)
CoSb ₃	...	...	7.2	7.2
(Co _{0.9} Rh _{0.1})Sb ₃	0.0066	0.0060	5.87	5.95
(Co _{0.8} Rh _{0.2})Sb ₃	0.0118	0.0107	5.38	5.36
(Co _{0.7} Rh _{0.3})Sb ₃	0.0155	0.0140	5.12	5.04

Fig. 4 (a) Electrical conductivity, σ and (b) lattice thermal conductivity, κ_{lat} vs. Rh content, x for $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ at around room temperature.

fluctuation effect and the mass fluctuation effect were comparable in reducing the κ_{lat} of CoSb₃ by substituting Rh for Co to the same degree.

Figure 4 shows the relationships between electrical conductivity, σ or lattice thermal conductivity, κ_{lat} for $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ at around room temperature and Rh content, x . In this figure, the literature data¹²⁾ are also shown for comparison (gray lines). Although it was reported¹²⁾ that both σ and κ_{lat} for $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ significantly decreased in the composition range between $x = 0.2$ and 0.5 , such trend was not observed in the present study. That is, the σ slightly increased and the κ_{lat} gradually decreased with Rh content, x . Unfortunately, the authors did not have a clear solution to this difference between the previous and the present results on the composition dependences of the transport properties of $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$. However, it can be said that the present results on the reduction of the κ_{lat} with increasing Rh concentration was explained by the well-known alloy scattering effect between Co and Rh atoms.

Fig. 5 Temperature dependences of the dimensionless figure of merit ZT of the polycrystalline samples $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3).

Finally, the temperature dependence of the ZT of the polycrystalline samples of $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3) is shown in Fig. 5. Since the Rh substitution for Co caused decrease in the κ_{lat} but further decrease in the power factor, the ZT values decreased with increasing Rh content. The maximum ZT obtained in the present study was 0.15 at around 500 K for CoSb₃.

4. Summary

In the present study, the polycrystalline samples of $(\text{Co}_{1-x}\text{Rh}_x)\text{Sb}_3$ ($x = 0, 0.1, 0.2$, and 0.3) were prepared and the thermoelectric properties were examined. All samples indicated single phase of the skutterudite structure. The Seebeck coefficient (S) values were negative. Both the electrical resistivity (ρ) and the absolute S values decreased with increasing Rh content. The power factor ($S^2\rho^{-1}$) was decreased by substituting Rh for Co. On the other hand, the lattice thermal conductivity (κ_{lat}) decreased with increasing Rh content due to the alloy scattering effect between Co and Rh. Unfortunately, the Rh substitution decreased the dimensionless figure of merit (ZT). The maximum ZT obtained in the present study was 0.15 at around 500 K for CoSb₃.

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