Effect of Yb Filling on Thermoelectric Properties of Ge-Substituted CoSb₃ Skutterudites

Hiroshi Mori*, Hiroaki Anno¹,² and Kakuei Matsubara²

¹Department of Materials Science and Electronics, Graduate School of Science and Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda 756-0884, Japan
²Department of Electronics and Computer Science, Faculty of Science and Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda 756-0884, Japan

We report the effect of Yb filling on the thermoelectric properties of polycrystalline Ge-substituted CoSb₃ skutterudite compounds. Electrical conductivity, Seebeck coefficient, Hall effect, and thermal conductivity measurements were performed on polycrystalline Yb₀.₃Co₀.₇Ge₀.₅Sb₁₁.₅ (y = 0, 0.1, 0.2, 0.3, 0.4 and 0.5). Yb₀.₃Co₀.₇Ge₀.₅Sb₁₁.₅ shows a change in carrier concentration at low Yb compositions y = 0 and 0.1 and n-type one at high y = 0.2-0.5. Due to the effect of charge compensation for Yb ions by Ge substitution, the Yb filling fraction limit in Yb₀.₃Co₀.₇Ge₀.₅Sb₁₁.₅ is larger than that in Yb₀.₃CoSb₁₂. The lattice thermal conductivity for Yb₀.₃Co₀.₇Ge₀.₅Sb₁₁.₅ drastically decreases from 8 W/(mK) (y = 0) to 2.4 W/(mK) (y = 0.5) with increasing Yb composition. The marked reduction of the lattice thermal conductivity can be attributed to the increase in the filling fraction of Yb, whose localized thermal vibration, “rattling” motion, substantially contributes to the scattering of phonons. The influence of Ge substitution on the thermoelectric properties of Yb₀.₃Co₀.₇Ge₀.₅Sb₁₁.₅ is also discussed.

(Received October 20, 2004; Accepted April 24, 2005; Published July 15, 2005)

Keywords: skutterudite, cobalt antimonide, ytterbium filling, germanium substitution, charge compensation, thermoelectric properties, Seebeck coefficient, thermal conductivity, Hall mobility, effective mass

1. Introduction

Partially filled skutterudite antimonides RₙCoₙSb₁₂ (R = La, Ce, Eu, Yb, etc.)¹⁰ have recently attracted great interest as good thermoelectric materials based on the concept of a “Phonon Glass and Electron Crystal.”¹¹ Yb-filled skutterudite compounds are particularly interesting because of the high dimensionless thermoelectric figure of merit ZT close to one at high temperatures as well as the unique physical properties that are associated with heavy-fermion or intermediate-valence behavior of the Yb atoms.² It has been demonstrated that partial filling of the voids in the crystal structure with smaller and heavier Yb atoms causes a significant reduction in the thermal conductivity as compared to the lighter lanthanoides.³ This is attributed to strong scattering of phonons from the “rattling” motions of the void-filling atoms in their oversized local sites in the crystal structure. The lattice thermal conductivity of Yb-filled CoSb₃ is still much higher than the theoretical minimum thermal conductivity κₘᵟᵢᵦ (~0.3 W/(mK)) of CoSb₃. Accordingly, higher ZT values may be accomplished if the lattice thermal conductivity can be further reduced towards κₘᵟᵦ by increasing Yb filling fraction while maintaining the high power factors observed in Yb-filled compounds. The addition of the Yb atoms also alters the carrier concentration of the skutterudite compounds since the electrons are donated from Yb ions to CoSb₃ framework. Therefore, the control of Yb filling fraction is an important issue in optimizing the thermoelectric properties of filled skutterudite compounds. The limit of Yb filling fraction is known to be only approximately y = 0.2⁴ in Yb₀.₃Co₀.₇Sb₁₂. It can be considered that the local charge due to the Yb ions lowers the stability of the structure.⁵ To achieve high filling fraction, it is necessary to compensate for the charge of Yb ions by substitutions on either the Co site or the Sb site.⁸⁻¹⁰

In this study, we investigated the effect of Yb filling on the electronic and thermoelectric properties in polycrystalline Ge-substituted and partially filled skutterudite compounds Yb₀.₃Co₀.₇Ge₀.₅Sb₁₁.₅ (y = 0–0.5), where Ge acts as an electron acceptor to charge compensate for Yb ions. We examined the effect of Ge substitution on the Yb filling fraction limit in an effort to further decrease the lattice thermal conductivity by increasing Yb filling fraction. We also discuss the effect of Ge substitution on the thermoelectric properties in Yb₀.₃Co₀.₇Ge₀.₅Sb₁₁.₅ compounds.

2. Experimental Procedure

Highly pure Yb ingot (3N), Co powder (4N), Ge grain (4N) and Sb grain (6N) were used as the starting materials. A mixture of the constituent elements with slightly Sb-rich (about 4 atomic %) composition, Yb₀.₃Co₀.₇Ge₀.₅Sb₁₁.₅ (y = 0, 0.1, 0.2, 0.3, 0.4 and 0.5), was heated and reacted at 1273 K for 6 h and then annealed at 873 K for 48 h in a flowing argon atmosphere. The resulting compound was ground into fine powder (~90 μm) and sintered into a dense polycrystalline solid by using a spark plasma sintering technique at 973 K and 40 MPa for 90 min in a argon atmosphere. The density of sample was more than 98% of the theoretical density. Powder X-ray diffraction (XRD) measurements and electron probe microanalysis (EPMA) were employed in the structural and chemical characterization of samples.

Four-probe electrical conductivity σ and steady-state Seebeck α measurements were performed in the temperature range of 300–900 K. Hall measurements were carried out at room temperature in a constant magnetic field of 1 T using a van der Pauw technique. The Hall carrier concentration n was calculated from the Hall coefficient R_H by n = 1/R_He, where
3. Results and Discussion

Figure 1 shows the powder X-ray diffraction patterns of Yb\textsubscript{3}Co\textsubscript{4}Ge\textsubscript{0.5}Sb\textsubscript{11.5} samples with different Yb compositions (y = 0, 0.1, 0.3 and 0.5). The X-ray diffraction patterns of all samples were indexed based on a cubic unit cell with the reflections corresponding to the skutterudite structure (space group Im\textbar3). As seen in Fig. 1, it was clearly observed that the intensity of (211) reflection decreased as the Yb composition y increased, indicating the formation of partially Yb-filled compounds. This decrease, however, tended to be saturated more than y = 0.4. Incidentally, the (211) reflection is completely extinguished for fully filled compound.\textsuperscript{8)\textsuperscript{9)} The EPMA result showed that the measured Yb compositions were nearly equal to the nominal compositions up to y = 0.3, but that they were lower than the nominal one at y = 0.4 and 0.5. EPMA study showed that these samples contained a small amount of impurity phase (mainly Yb-oxide), which was not detected by XRD. The maximum Yb composition was found to be approximately y = 0.34 at the nominal y = 0.5. Therefore, the XRD and EPMA results show that the Yb filling fraction limit for Yb\textsubscript{3}Co\textsubscript{4}Ge\textsubscript{0.5}Sb\textsubscript{11.5} is larger than that for Yb\textsubscript{3}CoGe\textsubscript{12} (y\textsubscript{max} \approx 0.2\textsuperscript{21)} due to the charge compensation for Yb ions by substitution of Ge.

Figure 2 shows the Hall carrier concentration at room temperature as a function of Yb composition y for Yb\textsubscript{3}Co\textsubscript{4}Ge\textsubscript{0.5}Sb\textsubscript{11.5} samples. In Fig. 2, the positive and negative signs of the Hall coefficient for these compounds are represented by open and solid symbols, respectively, which are similarly used in the other figures of this article. The carrier concentration of Yb\textsubscript{3}Co\textsubscript{4}Ge\textsubscript{0.5}Sb\textsubscript{11.5} varies widely from \(10^{25} \text{ m}^{-3}\) to \(10^{26} \text{ m}^{-3}\) with the Yb composition y. Due to the effect of Ge substitution as an electron acceptor, the carrier concentration of p-type Co\textsubscript{4}Ge\textsubscript{0.5}Sb\textsubscript{11.5} (y = 0) is about one order of magnitude larger than that of polycrystalline n-type CoSb\textsubscript{3} (\(n \approx 3 \times 10^{24} \text{ m}^{-3}\)).\textsuperscript{14,15)} The carrier conductivity changes from p-type to n-type when the Yb composition increases from y = 0.1 to 0.2 since the electrons are donated from Yb ions. In the case of Yb\textsubscript{3}CoSb\textsubscript{12}, the change of conductivity occurs at a very small amount of Yb addition.\textsuperscript{41)} The change of the carrier conductivity for Yb\textsubscript{3}Co\textsubscript{4}Ge\textsubscript{0.5}Sb\textsubscript{11.5} can be attributed to the effect of the charge compensation for Yb ions by Ge substitution. We calculated the carrier concentration based on this model by assuming “monovalent” Ge acceptor and “trivalent” Yb donor as a function of the activation rates for Ge and Yb. The best fit was obtained when the activation rates for Ge and Yb were 8% and 10%, respectively. This result is shown by the dashed line in Fig. 2.

Figure 3 shows the electrical conductivity as a function of inverse temperature for Yb\textsubscript{3}Co\textsubscript{4}Ge\textsubscript{0.5}Sb\textsubscript{11.5} samples with different Yb compositions. At room temperature, the electrical conductivity first decreases as the Yb composition increases up to y \approx 0.2, and then begins to increase. This behavior corresponds to the change of the carrier concentration at room temperature. The electrical behavior of the samples changes from semiconducting temperature dependence to metallic one, which is expected from a heavily doped semiconductor, depending on the carrier concentration.

Figure 4 shows the Seebeck coefficient as a function of temperature for Yb\textsubscript{3}Co\textsubscript{4}Ge\textsubscript{0.5}Sb\textsubscript{11.5} samples with different Yb compositions. The sign of the Seebeck coefficient agrees with that of the Hall coefficient at room temperature except for a sample with y = 0.1. At room temperature, the magnitude of the Seebeck coefficient for n-type Yb\textsubscript{3}Co4-
addition may play a significant role in electrical transport. For concentration levels, the electron conduction due to Yb

**Fig. 4** Seebeck coefficient $\alpha$ as a function of temperature for Yb$_4$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ with different Yb compositions.

Co$_4$Sb$_{12}$ is much larger than that for $p$-type one, suggesting that the electron mass is larger than the hole mass. The Seebeck coefficient increases with increasing temperature and drops at elevated temperatures due to the intrinsic conduction, which is reasonably observed in the electrical conductivity. The drop of the Seebeck coefficient at high temperatures becomes small for heavily doped $n$-type samples ($y = 0.4$ and $0.5$).

Figure 5 shows the Seebeck coefficient at room temperature as a function of carrier concentration for Yb$_4$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ with different Yb compositions. The data for $n$-type Yb$_4$Co$_4$Sb$_{12}$ and $p$-type CoSb$_{12}$ are also shown by dashed lines for comparison. The Seebeck coefficient for unfilled $p$-type Co$_4$Ge$_{0.5}$Sb$_{11.5}$ ($y = 0$) seems to agree with the extrapolation of the experimental trend for $p$-type CoSb$_{12}$. Although the carrier concentration for $p$-type Yb$_4$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ with $y = 0.1$ is smaller than that for $p$-type Co$_4$Ge$_{0.5}$Sb$_{11.5}$ ($y = 0$), the Seebeck coefficient for $y = 0.1$ is remarkably small. This suggests that at these low carrier concentration levels, the electron conduction due to Yb addition may play a significant role in electrical transport. For $n$-type Yb$_4$Co$_4$Ge$_{0.5}$Sb$_{11.5}$, as discussed later, since the electron mass is about one order of magnitude larger than the hole mass, the donor electrons dominate the Seebeck coefficient values. Furthermore, the Seebeck coefficient for $n$-type Yb$_4$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ is larger than that for $n$-type Yb$_4$Co$_4$Sb$_{12}$ at similar carrier concentrations. This result suggests that the Ge substitution has a great influence on the conduction band as compared to the valence band.

To discuss the electronic properties, we estimated the effective mass for Yb$_4$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ by assuming a single parabolic band and the energy dependence of the carrier relaxation time $\tau \propto E^{-1/2}$, which corresponds to the acoustic phonon scattering or the alloy disorder scattering, as a dominant carrier scattering mechanism at room temperature. Acoustic phonon scattering is commonly cited as the dominant scattering mechanism near room temperature in filled and unfilled skutterudites.$^{1,14,15}$ We first calculated the reduced Fermi energy $\eta$ from the experimental Seebeck coefficient data using

$$\alpha = \frac{-k_B}{e} \left[ \frac{2F_1(\eta)}{F_0(\eta)} - \eta \right],$$

where $k_B$ is Boltzmann’s constant and $F_1$ is a Fermi integral of order $x$. The carrier concentration $n$ can be expressed as

$$n = 4\pi \left( \frac{2m^*k_B T}{\hbar^2} \right)^{3/2} F_1(\eta),$$

where $m^*$ is the effective mass, $T$ is the temperature, and $\hbar$ is Plank’s constant. Thus, the effective mass was calculated by using the calculated $\eta$ and the experimental carrier concentration $n$. In Fig. 6, the effective mass $m^*/m_0$, where $m_0$ is the free electron mass, at room temperature is plotted as a function of carrier concentration for Yb$_4$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ samples with different Yb compositions. The data for $n$-type Yb$_4$Co$_4$Sb$_{12}$ and $p$-type CoSb$_{12}$ are also shown by dashed lines for comparison. The anomalously small effective mass ($m^*/m_0 \sim 10^{-2}$) calculated for a $p$-type Yb$_4$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ ($y = 0.1$) sample may come from neglecting the significant contribution from electrons in the analysis, as described.
already. In the system of CoSb₃, the hole effective mass is much smaller than the electron effective mass. The increase of the effective mass with increasing carrier concentration in CoSb₃ system can be described in terms of a two-band Kane model. The hole effective mass for p-type Co₄Sb₁₁.₅ is larger than that for n-type Yb₄Co₂Sb₁₂ at similar carrier concentrations. Therefore, the observed enhancement of the Seebeck coefficient can be attributed to the increased electron effective mass for Yb₄Co₄Ge₀.₅Sb₁₁.₅.

Figure 7 shows the Hall mobility at room temperature as a function of carrier concentration n for Yb₄Co₄Ge₀.₅Sb₁₁.₅ with different Yb compositions. The Hall mobility drastically decreases by Ge substitution, suggesting that the influence of Ge substitution on the carrier scattering is significantly large. For n-type Yb₄Co₄Ge₀.₅Sb₁₁.₅, the Hall mobility is smaller than that for n-type Yb₄Co₂Sb₁₂ due to the increased effective mass.

The lattice thermal conductivity \( \kappa_L \) at room temperature as a function of Yb composition y is shown in Fig. 8. The data for Yb₄Co₂Sb₁₂ are also shown by dashed line for comparison. Substitution of Ge for Sb in CoSb₃ host lattice reduces substantially the lattice thermal conductivity as compared to CoSb₃, \( \kappa_L = 10 \text{ W/(m·K)} \), due to the alloy disorder scattering of phonons. It is noted that partial filling of the voids with Yb ions causes the significant reduction of the lattice thermal conductivity. In addition, due to the increase of the Yb filling fraction, the lattice thermal conductivity still decreases slowly until the Yb composition reaches to \( y = 0.5 \). The minimum value of \( \kappa_L \) is about \( 2.4 \text{ W/(m·K)} \) at \( y = 0.5 \). On the other hand, the reduction of \( \kappa_L \) for Yb₄Co₂Sb₁₂ tends to be saturated at the Yb filling fraction limit \( y = 0.2 \). The significant reduction of the lattice thermal conductivity by Yb filling can be essentially attributed to the strong scattering of phonons through the interaction of the incoherent vibration modes of Yb ions with the phonon modes of the host lattice.\(^4\)\(^1\)\(^7\)\(^1\)\(^8\)

4. Conclusions

We have investigated the electronic and thermoelectric properties of Yb₄Co₄Ge₀.₅Sb₁₁.₅ as a function of Yb composition y. The Yb filling fraction limit in Yb₄Co₄Ge₀.₅Sb₁₁.₅ increases as compared to Yb₄Co₂Sb₁₂ due to the effect of charge compensation for Yb ions by Ge substitution. Although the reduction of the lattice thermal conductivity is saturated at about \( y = 0.2 \) for Yb₄Co₂Sb₁₂, the lattice thermal
conductivity for Yb$_x$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ drastically decreases to 2.4 W/(m·K) as the Yb composition increases up to $y=0.5$. The large reduction in Yb$_x$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ can be attributed to the increase of the filling fraction of Yb atoms, which act as strong scattering centers of phonons. We also discussed the effect of Ge substitution on the thermoelectric properties of Yb$_x$Co$_4$Ge$_{0.5}$Sb$_{11.5}$. The Seebeck coefficient for $n$-type Yb$_x$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ is larger than that for $n$-type Yb$_x$Co$_4$Sb$_{12}$. However, the Hall mobility for $n$-type Yb$_x$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ is smaller than that for $n$-type Yb$_x$Co$_4$Sb$_{12}$. The analysis of the properties shows that the conduction band effective mass is enhanced as compared to Yb$_x$Co$_4$Sb$_{12}$, suggesting that the Ge substitution has a significant influence on the conduction band structure. Finally, the maximum value of the thermoelectric power factor for Yb$_x$Co$_4$Ge$_{0.5}$Sb$_{11.5}$ was estimated to be about $2.9 \times 10^{-3}$ W/(m·K$^2$) (590 K), which is smaller than that for Yb$_x$Co$_4$Sb$_{12}$, about $5 \times 10^{-3}$ W/(m·K$^2$). Further research, including void filling effect and substitution effect, is therefore necessary to improve the thermoelectric figure of merit.

Acknowledgments

The authors would like to thank Prof. T. Koyanagi and Dr. K. Kishimoto of Yamaguchi University for the use of the electron probe microanalyzer and the laser flash thermal constant analyzer.

REFERENCES