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Electronic Structure and Thermoelectric Properties of $Yb_yCo_{4-x}Fe_xSb_{12}$ Compounds

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The effect of Yb filling on the electronic and thermoelectric properties of polycrystalline *p*-type $Yb_yCo_{4-x}Fe_xSb_{12}$ (x=1.5, y=0-1.0) compounds has been investigated. X-ray photoelectron spectroscopy study clearly shows that the Yb atoms have mixed valence states (Yb^{2+} and Yb^{3+}) and the contribution of Yb^{2+} f states to near the valence band top increases with increasing Yb composition. The analysis of the transport properties indicates that the density of states effective mass for *p*-type $Yb_yCo_{4-x}Fe_xSb_{12}$ increases with increasing carrier concentration, suggesting some degrees of nonparabolicity for the valence band. The effective mass for *p*-type $Yb_yCo_{4-x}Fe_xSb_{12}$ is larger than that for *p*-type $CoSb_3$, resulting in larger Seebeck coefficient and smaller Hall mobility. The carrier relaxation time is almost independent of Yb composition, suggesting that the alloy disorder scattering due to Fe substitution rather than Yb filling is a dominant scattering mechanism.

Key words: filled skutterudite, ytterbium, x-ray photoelectron spectroscopy, effective mass, Hall mobility

1. INTRODUCTION

Yb-filled $CoSb_3$ skutterudite compounds have been attracting substantial interest because of their promising thermoelectric properties. [1-3] In $Yb_yCo_4Sb_{12}$ compounds, the lattice thermal conductivity decreases with increasing Yb filling fraction due to the strong scattering of phonons from the "rattling" motions of Yb ions. [1-4] Furthermore, Yb filling has a significant influence on the electronic properties of $CoSb_3$ due to the *f*-electron effect of Yb. The optimization of Yb filling fraction as well as the carrier concentration is an important issue for improving the thermoelectric properties of Yb-filled $CoSb_3$ compounds. The limit of Yb filling fraction is, however, known to be only approximately y = 0.2 in $Yb_yCo_4Sb_{12}$. [1] 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. Recently, we reported Yb filling effect and the substitution effect on the thermoelectric properties of $Yb_yCo_4Sb_{12}$-based compounds. [5, 6]

In this study, we further investigated the effect of Yb filling on the electronic and thermoelectric properties of polycrystalline $Yb_yCo_{4-x}Fe_xSb_{12}$ (x=1.5, y=0-1.0) compounds, where Fe acts as an acceptor to charge compensate for Yb ions. We also studied the effect of Yb filling on the electronic structure of $Yb_yCo_{4-x}Fe_xSb_{12}$ compounds by x-ray photoelectron spectroscopy.

2. EXPERIMENTAL PROCEDURE

High-purity constituent elements (99.9% Yb, 99.99% Co, 99.99% Fe, and 99.9999% Sb) were used as the starting materials. A mixture of the constituent elements with slightly Sb-rich (about 4 atomic %) composition, $Yb_yCo_{4-x}Fe_xSb_{13}$ (nominal x=1.5 and y=0-1), was heated and reacted at 1000 °C for 6 h and then annealed at 600 °C for 48 h in a flowing argon atmosphere. The resulting compound was ground to fine powder (< 90 μm) and sintered into a dense polycrystalline solid by using a spark plasma sintering technique at 700 °C and 40 MPa for 90 min in an argon atmosphere. The density of sample was more than 96 % 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 curried 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 e is the electron charge. The Hall mobility μ was calculated from the electrical conductivity σ and the Hall coefficient R_H using $\mu=\sigma R_H$. X-ray photoelectron spectroscopy (XPS) measurements were performed by using the Mg K_α line (photon energy: 1253.6 eV) and a 180° hemispherical analyzer in the constant-resolution mode (pass energy: 40 eV).

3. RESULTS AND DISCUSSION

Fig. 1 shows the x-ray diffraction patterns of $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds with different nominal Yb compositions y. In addition to diffraction peaks due to the filled skutterudite phase, diffraction peaks due to an impurity phase (mainly $FeSb_2$) were detected for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ with y=0-0.5. The impurity phase, however, decreased and the single phase $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds were formed as the Yb composition y increased (more than y~0.5). Since the solubility limit in $Co_{1-x}Fe_xSb_3$ solid solution is low (about x=0.1), the framework ($Co_{2.5}Fe_{1.5}Sb_{12}$) of the filled skutterudite compounds seems not to be stable without Yb. Incidentally, single phase $Yb_yCo_{4-x}Fe_xSb_{12}$ compounds with y=0-1 were successfully prepared for the Fe composition x=0.4 and 1.0.

Fig. 2 shows the Yb composition measured by EPMA

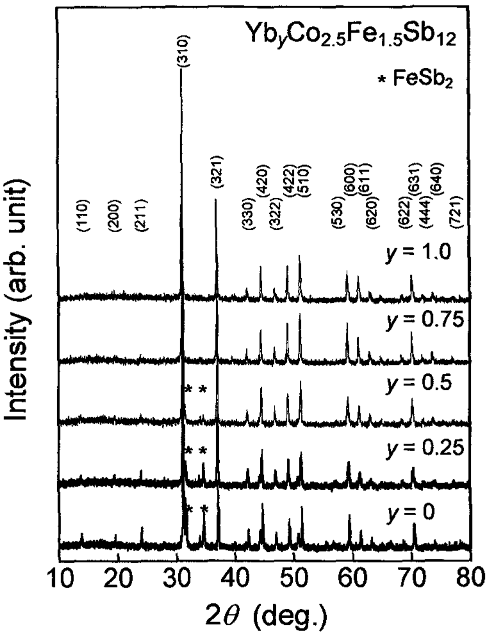

Fig. 1 X-ray diffraction patterns of $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ (y=0-1.0) compounds.

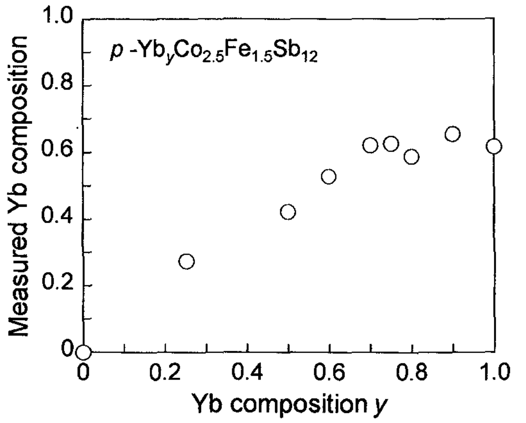

Fig. 2 Yb composition measured by EPMA as a function of nominal Yb composition y for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds.

as a function of nominal Yb composition y for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds. The measured Yb composition increases with increasing nominal y until y~0.7 and tends to be saturated for y>0.7. The lattice constant a determined from XRD analysis increased with increasing nominal y until y~0.7 and was saturated for y>0.7. Thus, it is inferred from EPMA and XRD analysis that the Yb filling fraction is approximately 0.6.

Fig. 3 shows the valence-band photoelectron spectra for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$, $YbFe_4Sb_{12}$, and $CoSb_3$ compounds. The $YbFe_4Sb_{12}$ compound clearly shows the mixed valence states (Yb^{2+} and Yb^{3+}) in the photoelectron spectrum. These *f* photoelectron structures in the valence band agree well with those observed in the typical mixed-valence material $YbAl_3$. [7] For $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds, the structures at about 0.9 and 2 eV can be identified as the Yb^{2+}-derived peaks, those between 6 and 14 eV as the Yb^{3+}-derived peaks. The divalent feature can be explained in terms of an itinerant f electron model, in which Yb $4f$ bands are strongly hybridized with Fe $3d$ and Sb $5p$ states near the top of the valence band. [8] On the other hand, the trivalent feature can be interpreted as the $4f^{12}$ final-state multiplet structures, which are shown for $YbFe_4Sb_{12}$. [9] Our photoelectron spectroscopy study clearly indicates that the density of states near the top of the valence band is enhanced when Yb composition increases due to the large contribution of the Yb^{2+} f states for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds.

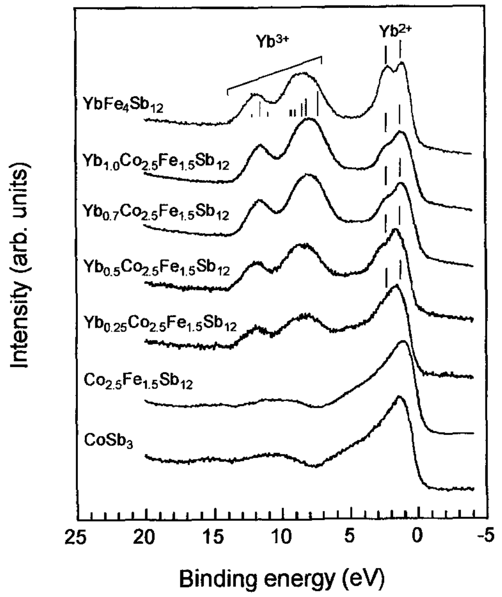

Fig. 3 Valence-band photoelectron spectra for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ (y=0-1.0), $YbFe_4Sb_{12}$, and $CoSb_3$ compounds.

Fig. 4 shows the Hall carrier concentration as a function of nominal Yb composition y for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds. The Hall carrier concentration is almost constant (~2×10^{20} cm^{-3}) for y=0-0.5, and decreases as y increases until y~0.7, then becomes almost constant for y>0.7.

Fig. 5 shows the temperature dependence of the Seebeck coefficient for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds with different nominal Yb compositions y. Relatively large Seebeck coefficient is observed for Yb compositions y=0.75 and 1.0 due to the relatively small carrier concentrations. Although the Hall carrier concentration is almost constant in the range of y=0-0.5, the Seebeck coefficient becomes large as the Yb composition increases until y=0.5, suggesting that Yb filling has an influence on the electronic properties (the density of states effective mass).

To discuss the effect of Yb filling on the thermoelectric properties, we estimated the density of states effective mass m^* from the analysis of the carrier concentration dependence of the Seebeck coefficient by assuming a single parabolic band model with predominance of acoustic phonon scattering, as described elsewhere. [10] Fig. 6 shows the density of states effective mass m^*/m_0, where m_0 is the free electron mass, at room temperature as a function of

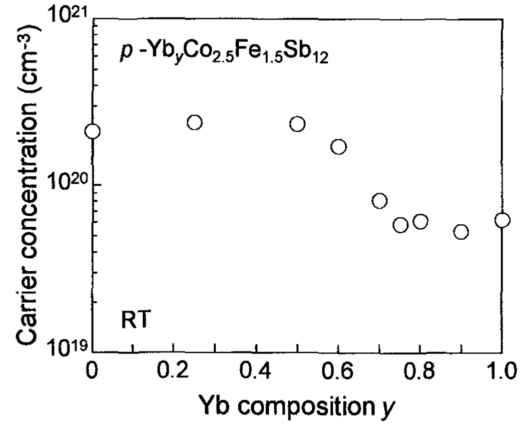

Fig. 4 Hall carrier concentration as a function of nominal Yb composition y for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds.

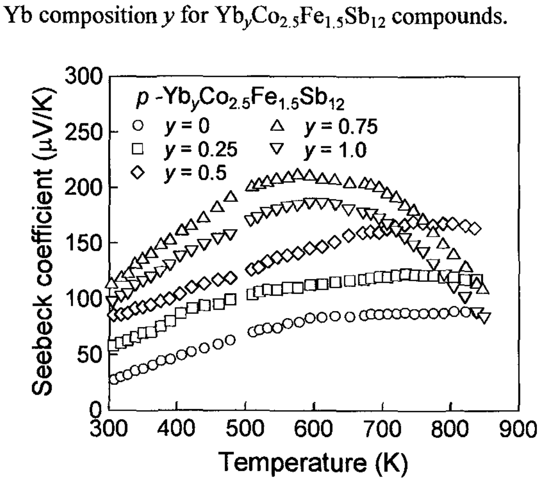

Fig. 5 Temperature dependence of the Seebeck coefficient for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ (y=0-1.0) compounds.

nominal Yb composition y for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds. It is found that as the Yb composition increases the effective mass m^* significantly increases until y=0.5 then decreases for y>0.5. This result is slightly different from the behavior observed for $Yb_yFe_{4-x}Ni_xSb_{12}$ compounds, where the effective mass greatly increases to $m^*\sim 5m_0$ with increasing Yb composition up to y=1.0. [5]

Fig. 7 shows the density of states effective mass m^*/m_0 at room temperature as a function of carrier concentration for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds with different nominal Yb compositions y. The data for p-type $CoSb_3$ single crystals [10] are also shown in Fig. 7. Caillat *et al.* [10] have reported that in p-type $CoSb_3$ the valence band effective mass increases with increasing carrier concentration, suggesting the nonparabolicity of the valence band. The behavior can be explained in terms of a linear dispersion model, where the effective mass varies as $m^* \propto p^{1/3}$ (p is the hole carrier concentration). [10, 11] It seems likely that the effective mass for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds also obeys the relation $m^* \propto p^{1/3}$. It is also found that the effective mass for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ is larger than the extrapolated curve at high carrier concentrations for p-type $CoSb_3$. The relatively large effective mass for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ is probably due to the hybridization effect of Yb $4f$ level and/or a large density of states of narrow f bands near the Fermi level, as observed in the valence-band photoelectron spectra. From the carrier concentration dependence of the effective mass, the decrease of the effective mass for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds with y>0.5, as shown in Fig. 6, can be attributed to the decrease of the carrier concentration.

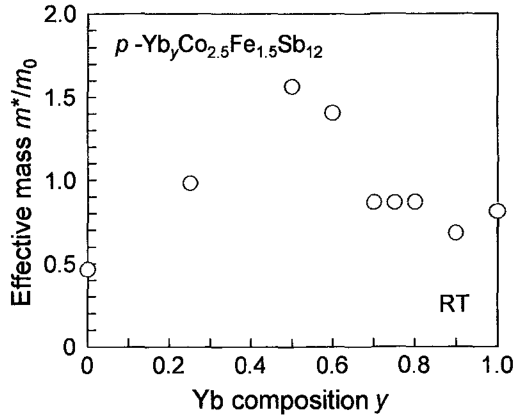

Fig. 6 Density of states effective mass m^*/m_0, where m_0 is the free electron mass, as a function of nominal Yb composition y for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds.

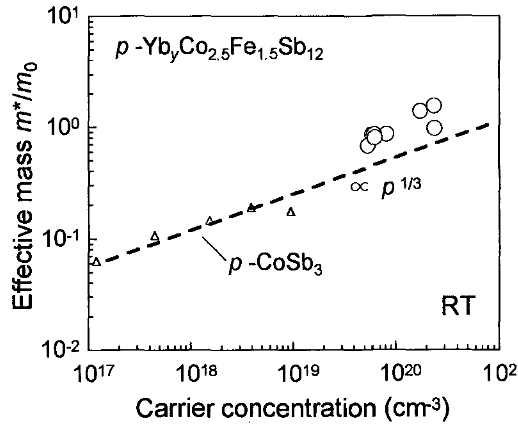

Fig. 7 Density of states effective mass m^*/m_0 as a function of carrier concentration for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ (y=0-1.0) compounds.

Fig. 8 shows the Hall mobility at room temperature as a function of carrier concentration for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds with different nominal Yb compositions y. The data for p-type $CoSb_3$ single crystals [10] and a curve ($\mu \propto p^{-1/3}$) based on the linear dispersion model are also shown in Fig. 8. The Hall mobility for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds is much smaller than that for p-type $CoSb_3$ single crystals. The relaxation time τ estimated from the relation $\mu = e\tau/m^*$ for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds was found to be almost independent of Yb composition and constant at $\sim 2\times 10^{-14}$ sec, which is about an order of magnitude smaller than that for p-type $CoSb_3$ single crystals. Thus, the alloy disorder (point defect) scattering due to Fe substitution rather than Yb filling is presumably the dominant scattering mechanism for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ compounds.

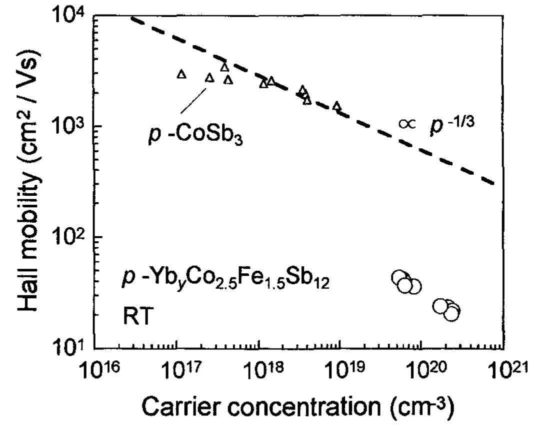

Fig. 8 Hall mobility as a function of carrier concentration for $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ (y=0-1.0) compounds.

4. CONCLUSION

We have investigated the electronic structure and thermoelectric properties of p-type $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ filled skutterudite compounds as a function of Yb composition y. X-ray photoelectron spectroscopy study shows the mixed valence states of Yb atoms (Yb^{2+} and Yb^{3+}) and the large contribution of Yb^{2+} states to near the top of the valence band. Analysis of the transport properties shows the relatively large density of states effective mass as compared to p-type $CoSb_3$, resulting in larger Seebeck coefficient and smaller carrier mobility. The effective mass of p-type $Yb_yCo_{2.5}Fe_{1.5}Sb_{12}$ depends on the Yb composition and the carrier concentration, which is probably due to the linear dispersion band as is the case for p-type $CoSb_3$. The carrier relaxation time is almost independent of Yb composition, suggesting that the Fe substitution rather than Yb filling has a great influence on the carrier scattering. The optimization of both Yb and Fe compositions is important for improving the thermoelectric properties of p-type $Yb_yCo_{4-x}Fe_xSb_{12}$ compounds.

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REFERENCES

[1] G. S. Nolas, M. Kaeser, R. T. Littleton, and T. M. Tritt, *Appl. Phys. Lett.*, **77**, 1855-1857 (2000).

[2] H. Anno, and K. Matsubara, Recent Res. Devel. Applied Phys., **3**, Transworld Research Network, Trivandrum, India (2000) pp. 47-61.

[3] H. Anno, K. Ashida, K. Matsubara, G. S. Nolas, K. Akai, M. Matsuura, and J. Nagao, *Mat. Res. Soc. Symp. Proc.*, **691**, 49-54 (2002).

[4] J. Nagao, D. Nataraj, M. Ferhat, T. Uchida, S. Takeya, T. Ebinuma, H. Anno, and K. Matsubara, *J. Appl. Phys.*, **92**, 4135-4137 (2002).

[5] H. Anno and K. Matsubara, *Transactions Materials Research Society of Japan*, **29**, 2837-2840 (2004).

[6] H. Mori, H. Anno, and K. Matsubara, *Materials Transactions*, **46**, 1476-1480 (2005).

[7] S. -J. Oh, S. Suga, A. Kakizaki, M. Taniguchi, T. Ishii, J. -S. Kang, J. W. Allen, O. Gunnarsson, N. E. Christensen, A. Fujimori, T. Suzuki, T. Kasuya, T. Miyahara, H. Kato, K. Schönhammer, M. S. Torikachvili, and M. B. Maple, *Phys. Rev. B*, **37**, 2861 (1988).

[8] K. Akai, K. Koga, K. Oshiro, and M. Matsuura, IEEE Proc. 20th Int. Conf. on Thermoelectrics, Peijing, China (2001) pp. 93-96.

[9] F. Gerken, *J. Phys. F*, **13**, 703 (1983).

[10] T. Caillat, A. Borshchevsky, and J. -P. Fleurial, *J. Appl. Phys.*, **80**, 4442-4449 (1996).

[11] D. J. Singh and W. E. Pickett, *Phys. Rev. B*, **50**, 11235-11238 (1994).

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