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Effect of Filling Fraction on Thermoelectric Properties of $Yb_yFe_{4-x}Ni_xSb_{12}$ Compounds

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The effect of Yb filling fraction on the electronic and thermoelectric properties of polycrystalline *p*-type Yb-filled skutterudite compounds, the nominal formula $Yb_yFe_{4-x}Ni_xSb_{12}$ (x=1 and y=0–1), has been investigated. The thermal conductivity drastically decreases from about 0.08 W/cmK (y=0) to about 0.02 W/cmK (y=1). This can be attributed to the strong phonon scattering through the interaction between the incoherent vibration mode of Yb ions and the host lattice modes. Although the carrier concentration increases with increasing filling fraction, the Seebeck coefficient significantly increases as the filling fraction increases. The analysis of the transport properties indicates that the density of states effective mass is greatly enhanced with increasing filling fraction. The x-ray photoelectron study clearly shows the large contribution of Yb *f* states to near the valence band top. The effect of electronic states of Yb ions on the band structure and the electronic properties is also discussed.

Key words: filled skutterudite, ytterbium, thermal conductivity, Seebeck coefficient, x-ray photoelectron spectroscopy

1. INTRODUCTION

Filled skutterudite antimonides RM_4Sb_{12} (R=La, Ce, Eu, Yb, etc.; M=Fe, Co, Ni) have recently attracted great interest as Phonon Glass and Electron Crystal thermoelectric materials because they combine extremely low thermal conductivity and relatively good electronic transport properties. [1] Among them Yb-filled skutterudite compounds are particularly interesting because of the unique physical properties that are associated with heavy-fermion or intermediate-valence behavior of the Yb atoms as well as the "rattling" effect of Yb atoms. [2-6]

Nolas *et al.* [7] have reported that the dimensionless thermoelectric figure of merit ZT~1 at 600 K can be accomplished for *n*-type $Yb_{0.19}Co_4Sb_{12}$ partially filled skutterudite. We have investigated the thermoelectric properties of *n*-type $Yb_yCo_{4-x}M_xSb_{12}$ (M=Pd and Pt) filled skutterudites. [8–10] The combination of Pt doping with Yb filling resulted in a large ZT value about 1 at 700 K. On the other hand, ZT value for *p*-type $YbFe_4Sb_{12}$ remains low (about 0.5 at 700 K) because of relatively small Seebeck coefficient due to heavily doped or metallic properties. Substitution of Co or Ni for Fe in the framework is one of approaches to compensate for the high hole carrier concentration. We have reported the thermoelectric properties as a function of Ni composition on Yb-filled skutterudite compounds $Yb_yFe_{4-x}Ni_xSb_{12}$. [11] The *p*-type $Yb_yFe_{4-x}Ni_xSb_{12}$ compounds show relatively large Seebeck coefficient (about 100 μV/K at room temperature) due to enhanced effective mass at the carrier concentration range of 10^{21} cm^{-3}. It is of great importance to elucidate the electronic states of Yb and the effect of Yb filling on the electronic properties in Yb-filled skutterudite compounds.

In this study, we have investigated the dependence of the electronic and thermoelectric properties on Yb filling fraction for polycrystalline *p*-type $Yb_yFe_{4-x}Ni_xSb_{12}$ filled skutterudite compounds.

2. EXPERIMENTAL PROCEDURE

Polycrystalline *p*-type $Yb_yFe_{4-x}Ni_xSb_{12}$ samples with different Yb fractions (nominal x=1 and y=0–1) were prepared by melting stoichiometric quantities of high-purity constituent elements (99.9% Yb, 99.999% Fe, 99.99% Ni, and 99.9999% Sb) at 1000 °C in flowing argon. The obtained ingots were ground to fine powders (< 90 μm) and cold pressed into pellets. The pellets were then annealed at 580 °C for 168 h in flowing argon. The obtained materials were ground again to fine powders (< 90 μm) and sintered into a dense solid inside graphite dies at 550–560 °C and 40 MPa for 1 h in an argon atmosphere by a spark plasma sintering technique. Sample density was more than 98 % of the theoretical density. Powder x-ray diffraction measurements were performed on all samples.

The electrical conductivity σ and the Seebeck coefficient S were measured in the temperature range of 300–900 K. Hall measurements were performed at room temperature by applying an external magnetic field of 1 T using the van der Pauw method. The Hall mobility μ was determined from the electrical conductivity σ and the Hall coefficient R_H using $\mu=\sigma R_H$. The thermal conductivity κ was measured by a laser flash method at room temperature using a Ni standard. 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 $Yb_yFe_3Ni_1Sb_{12}$ compounds with different Yb filling fractions. Diffraction peaks due to impurity phases (mainly Sb and $FeSb_2$), in addition to the filled skutterudite phase, were detected for $Yb_yFe_3Ni_1Sb_{12}$ with y=0. These impurity phases, however, decreased and the

single phase $Yb_yFe_3Ni_1Sb_{12}$ compounds were formed as the Yb filling fraction increased (more than y~0.7). Although $Fe_{0.5}Ni_{0.5}Sb_3$ compound is known as a stable skutterudite material, [12] the framework ($Fe_3Ni_1Sb_{12}$) of the filled skutterudite compounds seems not to be stable without Yb. Incidentally, single phase $Yb_yFe_{4-x}Ni_xSb_{12}$ compounds with y=1 could be successfully prepared in the Ni composition range of 0–2.

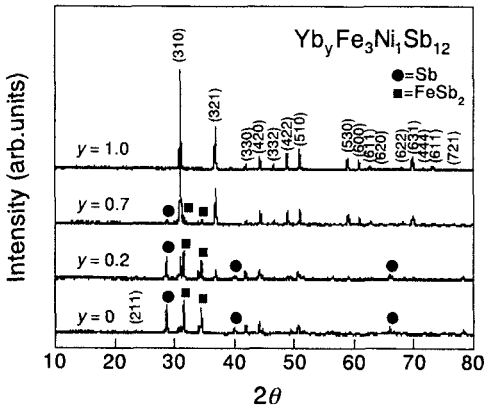

Fig. 1 X-ray diffraction patterns for $Yb_yFe_3Ni_1Sb_{12}$ compounds with different Yb filling fractions y=0−1.

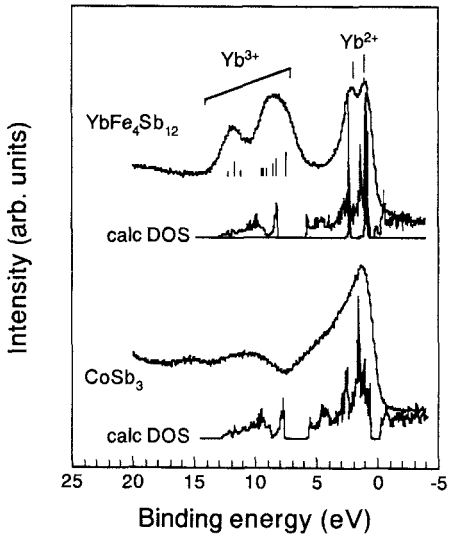

Fig. 2 Valence-band photoelectron spectra for $YbFe_4Sb_{12}$ and $CoSb_3$ compounds. The density of states (DOS) calculations are also presented. [10, 13]

Fig. 2 shows the valence-band photoelectron spectra for $YbFe_4Sb_{12}$ and $CoSb_3$ compounds. The valence-band spectra are compared to the results of the density of states (DOS) calculation for $YbFe_4Sb_{12}$ and $CoSb_3$ by the full-potential linearized augmented-plane-wave (FLAPW) method. [10, 13] The Yb $4f^{12}$ final-state multiplets [14] are also shown. The $YbFe_4Sb_{12}$ compound clearly shows the mixed valence states (Yb^{2+} and Yb^{3+}). In Yb $4p$ and $4d$ core-level spectra, we also observed clearly photoelectron structures due to Yb^{2+} and Yb^{3+} states. These f photoelectron structures in the valence band agree well with those observed in the typical mixed-valence material $YbAl_3$. [15] The structures at about 0.9 and 2 eV can be identified as the $4f^{14}$ -> $4f^{13}$ transitions (divalent feature), those between 6 and 14 eV as the $4f^{13}$ -> $4f^{12}$ transitions (trivalent feature). The divalent feature can be explained in terms of an itinerant f electron model, as is evident from Fig. 2. On the other hand, the trivalent feature can be interpreted as the $4f^{12}$ final-state multiplet structures. [14, 15] According to the band calculation, some important points in the band structure of $YbFe_4Sb_{12}$ are as follows. (1) The narrow spin-orbit split Yb $4f$ bands, which are strongly hybridized with Fe $3d$ and Sb $5p$ states, dominate the top of the valence band. (2) There is no significant contribution from the Yb $4f$ states to the lowest lying conduction bands. (3) The conduction bands near the bottom have characters of hybridization of Yb $6s$ and $5d$ states with Fe $3d$ states. Our photoelectron spectroscopy study clearly indicates that the density of states near the top of the valence band is enhanced due to the large contribution of the Yb f states for Yb filled skutterudite compounds.

Figs. 3 and 4 show the temperature dependence of the electrical conductivity and the Seebeck coefficient

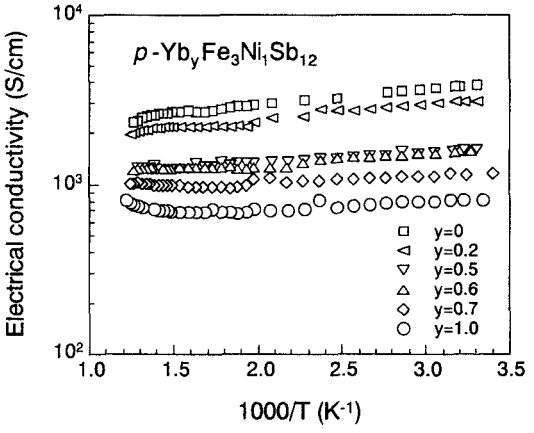

Fig. 3 Electrical conductivity as a function of inverse temperature for $Yb_yFe_3Ni_1Sb_{12}$ compounds.

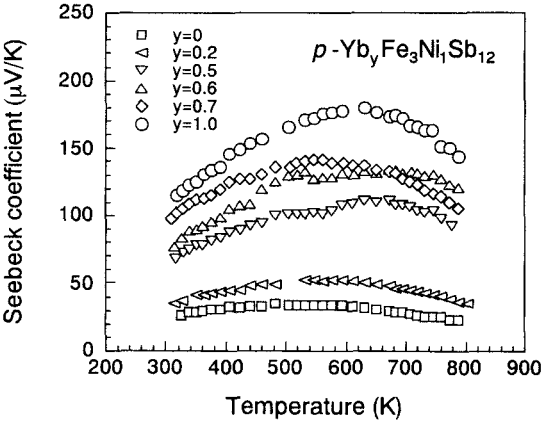

Fig. 4 Seebeck coefficient as a function of temperature for $Yb_yFe_3Ni_1Sb_{12}$ compounds.

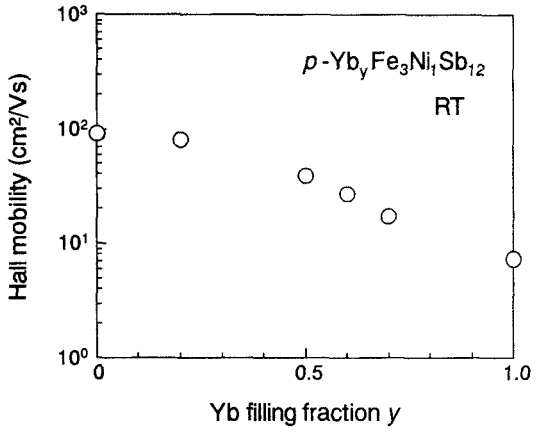

Fig. 5 Hall mobility at room temperature as a function of Yb filling fraction for $Yb_yFe_3Ni_1Sb_{12}$ compounds.

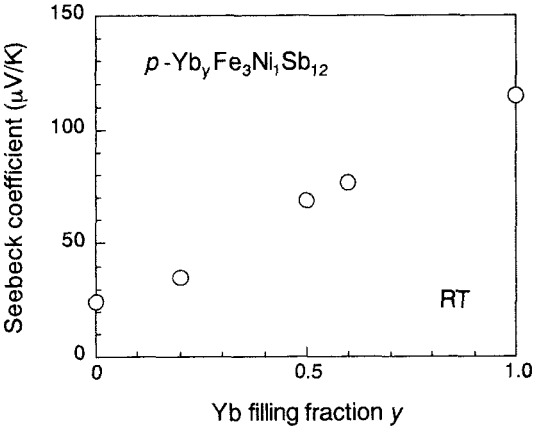

Fig. 6 Seebeck coefficient at room temperature as a function of Yb filling fraction for $Yb_yFe_3Ni_1Sb_{12}$ compounds.

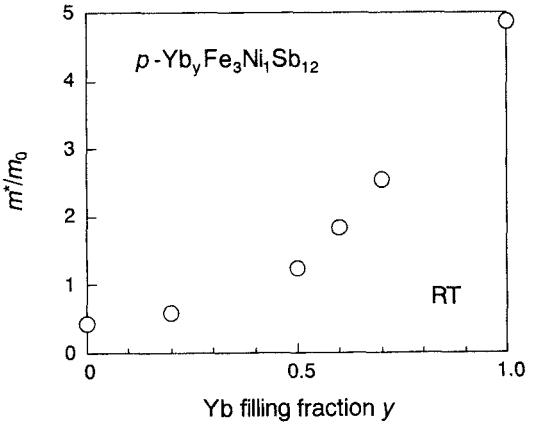

Fig. 7 Density of states effective mass m^*/m_0, where m_0 is the free electron mass, at room temperature as a function of Yb filling fraction for $Yb_yFe_3Ni_1Sb_{12}$ compounds.

for $Yb_yFe_3Ni_1Sb_{12}$ compounds with different Yb filling fractions, respectively. As the Yb filling fraction y increases, the electrical conductivity decreases and the Seebeck coefficient increases. The electrical conductivity is typical for heavily doped semiconductors and decreases almost linearly with increasing temperature. The Seebeck coefficient for y=1 reaches to about 180 μV/K at high temperatures. From Hall measurements, the carrier concentration of samples was found to increase with increasing y from ~2×10^{20} cm^{-3} (y=0) to ~8×10^{20} cm^{-3} (y=1). Thus, the dependence of the electrical conductivity and Seebeck coefficient on the Yb filling fraction can not be explained by the carrier concentration dependence.

To discuss the effect of Yb filling on the thermoelectric properties, we have investigated the electronic properties as a function of the Yb filling fraction. Figs. 5, 6, and 7 show the Hall mobility, the Seebeck coefficient, and the density of states effective mass m^*/m_0, where m_0 is the free electron mass, at room temperature as a function of Yb filling fraction for $Yb_yFe_3Ni_1Sb_{12}$ compounds, respectively. The effective mass m^*/m_0 was determined from the analysis of transport properties assuming a single parabolic band model with predominance of acoustic phonon scattering, as described elsewhere. [16] It can be clearly seen that as the Yb filling fraction increases the Hall mobility significantly decreases and the Seebeck coefficient is greatly enhanced. From Fig. 7, this behavior can be attributed to the large increase of the density of states effective mass with increasing Yb filling fraction. The density of states effective mass for p-type $Yb_yFe_3Ni_1Sb_{12}$ is estimated to be about $5m_0$ for y=1. This value is about two orders of magnitude larger than that for unfilled p-type $CoSb_3$ (~$0.05m_0$) [17] and in excellent agreement with the calculated band mass (~$4m_0$) close to the Fermi level for $YbFe_4Sb_{12}$. Therefore, the enhanced density of states effective mass can be interpreted as a large band mass due to the hybridization effect of Yb 4f level and/or a large density of states of narrow f bands near the Fermi level.

Fig. 8 shows the thermal conductivity κ at room temperature as a function of Yb filling fraction for $Yb_yFe_3Ni_1Sb_{12}$ compounds. The lattice thermal conductivity κ_L was estimated by subtracting the electronic contribution κ_e using the Wiedemann-Franz relation ($\kappa_L=\kappa-\kappa_e$ with $\kappa_e=LT\sigma$, where L is the Lorenz number). The electronic contribution κ_e decreases with increasing Yb filling fraction since the electrical conductivity (Hall mobility) decreases with y. It is significantly interesting to see that the lattice thermal conductivity κ_L drastically decreases with increasing Yb filling fraction. The κ_L values for large Yb filling fractions are as low as ~0.015 W/cmK. The room temperature lattice thermal conductivity for ternary $Fe_{0.5}Ni_{0.5}Sb_3$ mixed valence compound is about 0.03 W/cmK. [12] Therefore, the large reduction in the lattice thermal conductivity can be essentially attributed to strong scattering of phonons through the interaction between the incoherent vibration mode of Yb ions and the host lattice modes: "rattling effect" of Yb atoms. The electron-phonon scattering due to large effective mass and point defect scattering due to Fe/Ni alloying in the framework $(Fe, Ni)_4Sb_{12}$ may also contribute to the reduction of κ_L for $Yb_yFe_{4-x}Ni_xSb_{12}$ system.

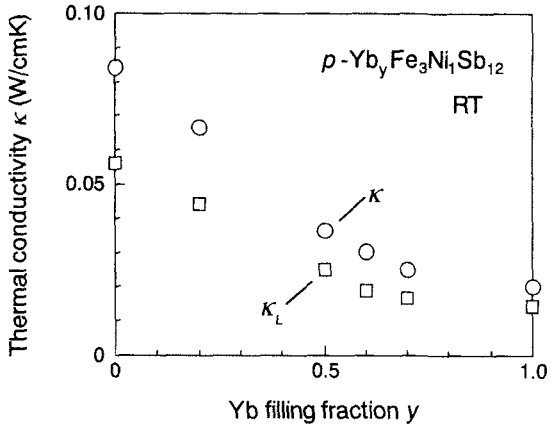

Fig. 8 Thermal conductivity κ at room temperature as a function of Yb filling fraction for $Yb_yFe_3Ni_1Sb_{12}$ compounds.

4. CONCLUSION

We have investigated the electronic structure and the electronic and thermoelectric properties of *p*-type $Yb_yFe_3Ni_1Sb_{12}$ filled skutterudite compounds as a function of Yb filling fraction *y*. X-ray photoelectron spectroscopy study indicates the mixed valence states of Yb atoms (Yb^{2+} and Yb^{3+}) and the large contribution of Yb *f* states to the valence band. This unique band structure is of great importance to the electronic and thermoelectric properties of *p*-type Yb-filled skutterudite compounds. The Seebeck coefficient is extremely enhanced by Yb filling due to the effect of a large band mass and/or a large density of states. In addition, the lattice thermal conductivity drastically decreases due to the effect of Yb filling on the phonon scattering. Therefore, the optimization of Yb filling as well as doping level is crucial for material design of Yb-filled skutterudite compounds.

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