IMPROVEMENT OF THERMOELECTRIC PROPERTIES OF SKUTTERUDITE MATERIALS THROUGH MATERIAL ANALYSES USING SYNCHROTRON RADIATION

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Introduction

Several efforts to create a sustainable society are underway across various scientific fields. Our research group focuses on waste heat energy in industry. Thermoelectric materials are promising candidates for energy conversion because they utilize the thermal excitation of electrons and holes in semiconductors; therefore, materials must be selected to match the application's temperature range. We have concentrated on relatively high-temperature waste heat from industrial facilities and have been investigating technologies to convert this thermal energy into electricity.

In the high-temperature range, materials such as half-Heusler alloys, magnesium silicates, and skutterudites have attracted significant attention, and many researchers are working toward the social implementation of thermoelectric modules. Our research group recognizes that skutterudite is the closest to practical application, considering the various properties required of thermoelectric materials. Although skutterudite exhibits excellent thermoelectric performance, several material properties must be further improved to enhance its efficiency and the energy balance of thermoelectric modules.

In this paper, we discuss improvements in the thermoelectric properties of Yb-filled Co-Sb skutterudite systems. Specifically, we applied synchrotron radiation techniques, including X-ray diffraction (XRD), photoelectron emission microscopy (PEEM), and extended X-ray absorption fine structure (EXAFS) analysis, to understand and improve the material properties.

Experimental and Analyses

Sb (purity: 4N), Co (purity: 5N), and Yb (purity: 3N) were weighed according to the stoichiometric ratio of $Yb_{0.3}Co_4Sb_{12}$. These materials were melted in a high-frequency induction furnace and cast under an argon atmosphere into an iron mold coated with boron nitride powder, forming an ingot. This ingot predominantly comprised Co-Sb and Yb-Sb compounds with only a minimal skutterudite phase.

The ingot was remelted in an induction furnace under an argon atmosphere, and the molten material was cast onto a copper roll and quenched to yield a ribbon-shaped material. The ribbon was annealed at 973 K for 24 h in an argon atmosphere to form the skutterudite phase, which was then ground using a hammer mill to obtain a powdered material. The powder was placed into a 30 mm carbon die and sintered at 973 K under uniaxial hot pressing at 68 MPa for 1 h. After processing, the sintered materials were evaluated to measure the Seebeck coefficient and electrical conductivity. Thermal diffusivity was determined using an LFA 467 HT (Netzsch), and specific heat was measured using a PerkinElmer differential scanning calorimeter. The density of the sintered body was determined using the Archimedes method. The Hall effect of the obtained materials was also measured by ResiTest8400 (TOYO corporation).

XRD data were collected at beamline BL19B2, and PEEM experiments were performed at the PEEM experimental station of beamline BL25SU at SPring-8 to measure the chemical mapping of $Yb_{0.3}Co_4Sb_{12}$. Temperature-dependent EXAFS spectra of $Yb_{0.3}Co_4Sb_{12}$ were measured at beamline BL16B2 to determine the Debye-Waller factor, which is related to the material's thermal performance.

Results and Discussion

Fig. 1 shows the temperature dependence of the dimensionless figure of merit (ZT). The ZT of $Yb_{0.3}Co_4Sb_{12}$ exhibits a relatively higher value at 773 K compared with that of other Yb-filled ratio materials. The lattice component of the thermal conductivity, calculated using the Wiedemann-Franz law, is shown in Fig. 2. Clearly, the lattice component of thermal conductivity strongly influences ZT.

Fig. 3 shows the Sb contrast in chemical mapping obtained from PEEM experiments. Distinct Sb contrasts were observed in the chemical mapping. Spectral analyses of two grains (bright and dark) were performed, revealing that Sb concentration was affected by the Yb filling ratio. Furthermore, chemical mapping of Co suggests that a small amount of Co atoms may occupy Yb sites in this material.

Controlling the chemical state of Yb during material preparation may be effective. Fig. 4 shows the XAFS spectra of Yb in $Yb_{0.3}Co_4Sb_{12}$. According to XANES spectral fitting, Yb in the Co-Sb skutterudite cages exist in two ionic states (Yb^{2+} and Yb^{3+}). Because these two ionic states disturb the lattice component of thermal conductivity, controlling the Yb^{2+}/Yb^{3+} ratio is inferred to be effective for reducing thermal conductivity. To control the Yb ion ratio, sintering was performed in a hydrogen atmosphere. Although sintering in H_2 lowered thermal conductivity and improved ZT, the Yb^{2+}/Yb^{3+} ratio remained constant.

STEM observations revealed that Yb atoms were removed from the central sites of the Co-Sb skutterudite cages and migrated to the grain boundaries. These Yb compounds at the grain boundaries were primarily oxides with several defects due to the lack of O_2 in the ambient atmosphere. These grain boundary compounds decreased the thermal conductivity of $Yb_{0.3}Co_4Sb_{12}$. Because defects formed in the Yb oxides, the Yb compounds at the grain boundaries created conductive electrons, which increased electrical conductivity while reducing thermal conductivity.

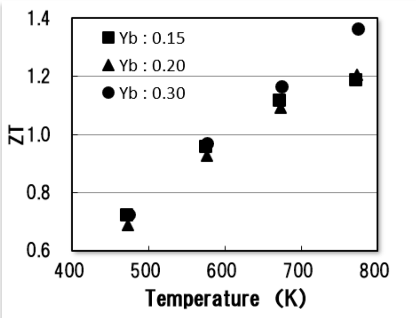

Fig. 1. Temperature dependence of ZT for $Yb_xCo_4Sb_{12}$.

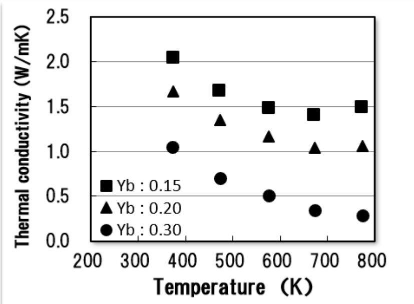

Fig. 2. Temperature dependence of lattice thermal conductivity.

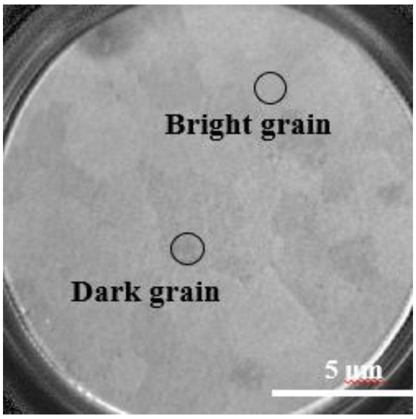

Fig. 3. Chemical mapping of Sb in $Yb_{0.3}Co_4Sb_{12}$.

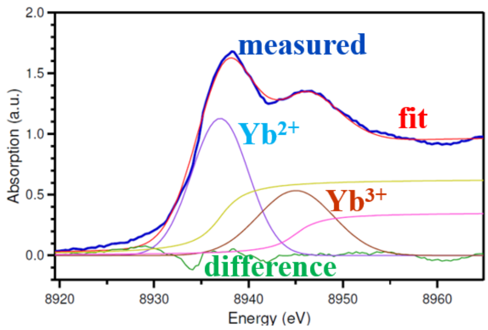

Fig. 4. XANES spectrum and its fitting analyses in $Yb_{0.3}Co_4Sb_{12}$.

Acknowledgements

We thank Dr. Hirano of Aichi synchrotron facility and Dr. Nanbu of Hitachi LTD. all contributors for their cooperation.

References

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