Synthesis and Electronic Properties of Thermoelectric and Magnetic Nanoparticle Composite Materials

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Application of a magnetic field greatly enhances the thermoelectric efficiency of bismuth-antimony (Bi-Sb) alloys. We synthesized a hybrid of Bi-Sb alloy and magnetic nanoparticles, expecting improvement of the thermoelectric performance due to the magnetic field generated by the nanoparticles. Powder x-ray diffraction and magnetic measurements of the synthesized hybrid Bi0.88Sb0.12(FeSb)0.05 sample indicated that the ferromagnetic FeSb nanoparticles, with a size of about 30 nm, were distributed in the main phase of the Bi-Sb alloy. The FeSb nanoparticles act as soft ferromagnets in the diamagnetic host Bi-Sb alloy. The electrical resistivity $\rho$ of the host Bi0.88Sb0.12 sample decreased concomitantly with decreasing temperature, showing a shoulder at 80 K. In contrast, $\rho$ for the hybrid sample was enhanced below 100 K because of carrier scattering by the nanoparticles. The temperature dependence of the Seebeck coefficient $S$ was also altered by the nanoparticle addition. In contrast, the addition of magnetic nanoparticles only slightly influenced the thermal conductivity $\kappa$. These results indicate that the addition of magnetic nanoparticles to thermoelectric materials modulates the electronic structures but does not influence the lattice system.

**Key words:** Bismuth-antimony, magnetic nanoparticle, composite material, FeSb, magnetic field, carrier scattering

**INTRODUCTION**

Bismuth-antimony (Bi-Sb) alloys, which are $n$-type thermoelectric materials, show good thermoelectric performance at around 200 K.1–6 These materials are receiving attention for practical use in next-generation Peltier cooling below room temperature.

Electrical properties of Bi$_{1-x}$Sb$_{y}$ depend on the Sb concentration $y$. In the Bi-rich range of $y < 0.05$, the conduction bands at L-points overlap the valence bands at T-points, and Bi$_{1-x}$Sb$_{y}$ is a semimetal. In the range 0.05 < $y$ < 0.4, the conduction and valence band overlap disappears, and the materials are semiconductors. The maximum band gap is approximately 20 meV at $y = 0.12$.7–9 The Bi-Sb alloy shows excellent thermoelectric characteristics below 200 K. It is also apparent that the electronic transport properties depend strongly on the addition of impurities.10–13 It is noteworthy that the thermoelectric efficiency of this material is enhanced greatly by the application of a magnetic field.2,14,15 The dimensionless figure of merit reaches $ZT \approx 1.1$ under a 0.3 T magnetic field.2

As described in this paper, we propose a concept of “thermoelectric and magnetic nanoparticle hybrid materials” and present experimental results. We synthesized a hybrid of Bi-Sb alloy and magnetic nanoparticles. Thermoelectric performance is expected to be improved due to the magnetic field generated by the nanoparticles distributed in the Bi-Sb phase. Structural, magnetic, and thermoelectric properties of the thermoelectric material and magnetic nanoparticle hybrid were investigated in this study.
EXPERIMENTAL PROCEDURES

We synthesized the host Bi$_{0.88}$Sb$_{0.12}$ alloy and the Bi$_{0.88}$Sb$_{0.12}$(FeSb)$_{0.05}$ hybrid ingots using the fusion method. Stoichiometric Bi (5 N), Sb (5 N), and Fe (4 N) powders were sealed in an evacuated quartz ampoule at $3 \times 10^{-6}$ Torr. They were fused at 1273 K for 5 h using an electric furnace. The crystal structure of the obtained polycrystalline samples was checked by analyzing the powder x-ray diffraction (XRD) pattern. Spherical and rectangular samples for magnetic and thermoelectric measurements were taken, respectively, from the ingot.

Magnetic properties of the host and hybrid samples were measured using a magnetic properties measurement system (MPMS; Quantum Design) at temperatures of 2.5 K to 300 K. The temperature dependence of the magnetization was measured under field cooling (FC) and zero-field cooling (ZFC) conditions. The Seebeck coefficient $S$, electrical resistivity $\rho$, and thermal conductivity $\kappa$ were measured using a physical properties measurement system with thermal transport option (PPMS-TTO; Quantum Design) at temperatures of 10 K to 300 K. The thermoelectric figure of merit $Z$ was calculated as $Z = S^2/(\rho \kappa)$.

Moreover, we measured the thermoelectric properties of both samples under a magnetic field. Figure 1 presents a schematic of the configuration of the sample and permanent magnet. A button-type Fe-Nd-B permanent magnet is set under the sample in the sample chamber of the PPMS-TTO. The magnetic flux density $B$ is not homogeneous in this configuration, having an intensity of 190 mT and 30 mT, respectively, under the face and at the top face. The direction of the magnetic field ($B+$ and $B-$) is changed by turning the magnet upside down. The experimental errors of the thermometers and heater resistance were confirmed as less than 0.25% by application of the external magnetic field.

RESULTS AND DISCUSSION

Figure 2 depicts powder XRD patterns obtained for the host Bi$_{0.88}$Sb$_{0.12}$, hybrid Bi$_{0.88}$Sb$_{0.12}$(FeSb)$_{0.05}$, and FeSb as a reference. The XRD pattern for the host Bi$_{0.88}$Sb$_{0.12}$ shows that this sample has a rhombohedral Bi-Sb-type structure. The lattice parameters calculated from the pattern are $a = 0.453(1)$ nm and $c = 1.182(4)$ nm, consistent with reported values. The pattern for the hybrid Bi$_{0.88}$Sb$_{0.12}$(FeSb)$_{0.05}$ resembles that for the host, indicating that the main phase of the hybrid is Bi-Sb alloy. The lattice parameters $a = 0.453(1)$ nm and $c = 1.181(5)$ nm of the main phase correspond to those of the host sample. These results suggest that no composition change occurred in the Bi-Sb alloy and that no substitution of Fe ions occurred on Fe addition.

Small diffraction peaks from FeSb are observed in the hybrid Bi$_{0.88}$Sb$_{0.12}$(FeSb)$_{0.05}$ XRD pattern, as marked by circles in Fig. 2. The size of the FeSb polycrystal is estimated as about 30 nm using Scheller’s equation. These XRD results indicate that FeSb nanoparticles of 30 nm size are distributed in the Bi-Sb main phase. The magnetic properties described below also support this structural picture of the hybrid sample.

Magnetization curves of host Bi$_{0.88}$Sb$_{0.12}$ and hybrid Bi$_{0.88}$Sb$_{0.12}$(FeSb)$_{0.05}$ at $T = 2.5$ K are depicted in Fig. 3. The negative slope of the host sample $M$–$H$ curve represents a well-known diamagnetic behavior. The $M$–$H$ curve of the hybrid sample shows a sinusoidal shape with small hysteresis. The negative slope of the curve at higher magnetic field is attributed to the diamagnetism of the main Bi-Sb alloy phase. The sinusoidal component of the $M$–$H$ curve suggests the existence of ferromagnetic-like phase in the hybrid sample. This behavior is attributable to the FeSb nanoparticles. The point defect in NiAs-type materials has a