Electronic properties of inhomogeneous Bi-Sb-Ni composite alloys

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Abstract. It is known that bismuth antimony (Bi-Sb) alloy is not only a good thermoelectric material but also a material which demonstrates some interesting phenomena at low temperatures. We have synthesized composite alloys consisting of the Bi-Sb and magnetic transition metal Ni, and measured the thermoelectric and magnetic properties. The Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ($0 \leq y \leq 1.00$) alloy ingots were synthesized by fusion method. XRD measurement revealed that the synthesized ingots were inhomogeneous polycrystalline composite. For the lower Ni concentration samples $y \leq 0.10$, the thermoelectric and magnetic properties are similar to the host Bi-Sb alloy. The dimensionless thermoelectric figure of merit $ZT$ depends on the Ni concentration $y$. Observed $ZT_{\text{max}}$ exhibits a maximum value at $y \sim 0.03$, due to an enhancement of density of states at $E_F$ by Ni doping. For the $y = 1.00$ sample, on the other hand, we have observed zero resistance below $T_c = 4.4$ K in the $\rho$-$T$ curve. Moreover, the magnetization curves below the $T_c$ show large hysteresis. These results indicate that the inhomogeneous Bi-Sb-Ni alloy is a superconductor of the second kind. It is interesting that the composite alloy including only non-superconducting elements and magnetic Ni demonstrates superconductivity.

1. Introduction
Thermoelectric conversion is the technique which realizes the direct conversion between thermal energy and electric energy using Seebeck and Peltire effects. [1] The technique is applied to electronic cooling, precise temperature regulation and thermal sensor. The materials which are used to the technique are called “thermoelectric materials”. The efficiency of the thermoelectric materials is evaluated by dimensionless thermoelectric figure of merit $ZT$ defined as,

$$ZT = \frac{S^2}{\rho \kappa}$$  \hspace{1cm} (1)

where, $S$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, $\kappa$ is the total thermal conductivity and $T$ is the absolute temperature. [1] This formula indicates that good thermoelectric materials have high Seebeck coefficient, and low electrical resistivity and low thermal conductivity. In order to enhance the Seebeck coefficient is effective for the development of thermoelectric efficiency, because the electrical resistivity and thermal conductivity of electron are related with Wiedemann-Franz law $\rho \kappa = (\pi^2 k_B^2 / 3 e^2) T$.

In this paper, we focus the thermoelectric cooling materials at low temperatures. It is known that Bi$_{1-x}$Sb$_x$ ($0 \leq x \leq 1$) alloys are n-type thermoelectric materials demonstrates high thermoelectric performance below the room temperature. [2, 3] The crystal structure of Bi$_{1-x}$Sb$_x$ is the same as bismuth and each element occupies randomly the lattice points according to the proportion $x$. The $ZT$ of Bi$_{1-x}$Sb$_x$
depends on the proportion $x$, the best performance is obtained at $x=0.12$. [3, 4] It is necessary to enhance the thermoelectric efficiency of this material to become a next generation's low temperature thermoelectric material. We have tried to dope 3d transition metals to the Bi$_{0.88}$Sb$_{0.12}$ in order to increase the density of states at Fermi level $D(E_F)$, because the absolute value of Seebeck coefficient is strongly correlated to the $D(E_F)$.

The purpose of present study is that the synthesis of polycrystalline Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ($0 \leq y \leq 1.00$) and investigation of the relation between thermoelectric properties and the Ni concentration $y$.

2. Experimental

Polycrystalline Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ($0 \leq y \leq 1.00$) samples were synthesized by fusion method. Stoichiometric starting materials Bi, Sb and Ni powders were sealed in a quartz ampoule evacuated by $5.0 \times 10^{-6}$ Torr. The powders in the quartz ampoule were melted at 1373 K for 5 hours by using of electric furnace. After that the ampoule was quenched into the room temperature water. The crystal structure of obtained ingot was measured by powder XRD and EPMA measurements.

Electrical resistivity $\rho$, Seebeck coefficient $S$, and thermal conductivity $\kappa$ were measured by ac four-probe method by Physical Property Measurement System - Thermal Transport Option (PPMS-TTO, Quantum Design Inc.). The temperature range measured was from 5 to 340 K. Dimensionless figure of merit $ZT$ was calculated from the three quantities by using of Eq. (1). Magnetization was measured by SQUID magnetometer (MPMS, Quantum Design Inc.). The temperature range measured was from 2 to 300 K, and the magnetic field was up to 3 kOe.

3. Results and discussion

Powder XRD measurement revealed that the synthesized Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ingots were polycrystalline composite. For the lower Ni concentration samples $y \leq 0.10$, the diffraction patterns were the same as the host Bi$_{0.88}$Sb$_{0.12}$. This result indicates that the Ni doping does not change the host crystal structure. On the other hand, the sample of $y = 1.00$ showed a quite different diffraction pattern from the lower Ni concentration samples; no diffraction peak of Bi$_{0.88}$Sb$_{0.12}$ was observed in the XRD pattern. It indicates that the $y = 1.00$ sample is an inhomogeneous polycrystalline alloy containing many components.

3.1. Thermoelectric properties of Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ($0 \leq y \leq 0.10$)

Figure 1 shows the temperature dependences of electrical resistivity $\rho$ of Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ($0 \leq y \leq 1.00$). The electrical resistivity of host Bi$_{0.88}$Sb$_{0.12}$ decreases with decreasing temperature, the broad peak around 100 K is an influence of thermal excited carriers thorough the semiconducting band gap. The low Ni concentration samples show the same metallic behavior. For the $y=0.10$ sample, however, the broad peak around 100 K has disappeared, indicating that the electronic structure is changed by Ni doping. The $\rho$-$T$

![Figure 1](image1.png)

**Figure 1.** Temperature dependences of electrical resistivity $\rho$ of Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ($0 \leq y \leq 1.00$).

![Figure 2](image2.png)

**Figure 2.** Temperature dependences of dimensionless thermoelectric figure of merit $ZT$ of Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ($0 \leq y \leq 1.00$).
curve of \( y = 1.00 \) sample is different from the other samples, corresponding to the difference of crystal structure.

Figure 2 shows the temperature dependences of dimensionless thermoelectric figure of merit \( ZT \) calculated by the measured \( \rho, S \) and \( \kappa \). The \( ZT \) of host Bi\(_{0.88}\)Sb\(_{0.12}\) exhibits a maximum around 200 K; this result is corresponding to the previous reports. \([2, 3]\) The maximum value \( ZT_{\text{max}} \) increases with increase of Ni concentration \( y \) up to \( y = 0.03 \), and the \( ZT_{\text{max}} \) decreases more than \( y = 0.05 \). This result indicates that the Ni doping of \( y \sim 0.03 \) improve the thermoelectric performance of Bi\(_{0.88}\)Sb\(_{0.12}\) alloy. It is noted that the prime cause of the improvement is the increase of Seebeck coefficient \( S \) by the Ni doping.

In order to examine the cause of enhancement of Seebeck coefficient at \( y \sim 0.03 \), we have measured the temperature dependences of diamagnetic magnetization \( M \) as shown in Fig. 3. The sign of the magnetization \( M \) is negative, and the temperature dependence is relatively small. No observation of Curie paramagnetism indicates that the doped Ni ions have no magnetic moment. It should be noted that the absolute value of magnetization \( |M| \) for \( y = 0.01 \) sample is larger than those of the host \( y = 0 \) and \( y = 0.10 \) samples.

It is known that the magnetic susceptibility \( \chi \) of non-magnetic alloys is written as

\[
\chi = \chi_{\text{dia}} + \chi_{L} + \chi_{P}
\]

where, \( \chi_{\text{dia}} \) is the closed shell diamagnetic susceptibility, \( \chi_{L} \) is the Landau diamagnetic susceptibility and \( \chi_{P} \) is the Pauli paramagnetic susceptibility. The \( \chi_{P} \) can be negligible comparing to \( \chi_{L} \) because the conduction carrier effective mass of the Bi-Sb alloy system is very small. The first term \( \chi_{\text{dia}} \) have to change monotonously against the Ni concentration, because the amount of closed shell diamagnetic susceptibility is directly proportional to the contents of element. Thus, the observed change in \( M \) in Fig. 3 is due to the change of Landau term \( \chi_{L} \). Landau diamagnetic susceptibility is expressed as \( \chi_{L} = -(2/3)\mu_{B}^{2} D(E_{F}) \), where \( \mu_{B}^{2} \) is the Bohr magneton. Therefore, the observed enhancement of \( |M| \) for \( y = 0.01 \) sample shown in Fig. 3 means that the density of states at \( E_{F} \) \( D(E_{F}) \) of \( y = 0.01 \) sample is larger than those of \( y = 0 \) and \( y = 0.10 \) samples. This result supports the enhancement of Seebeck coefficient around \( y \sim 0.03 \). The present result of which the doping of magnetic element to thermoelectric material improves the thermoelectric performance is useful for the development of new thermoelectric materials.

### 3.2. Superconductivity in Bi\(_{0.88}\)Sb\(_{0.12}\)Ni\(_{y}\) (\( y = 1.00 \))

Different from the lower Ni concentration samples, \( y = 1.00 \) sample exhibits poor thermoelectric performance as shown in Fig. 2.

Figure 4 shows the temperature dependence of electrical resistivity \( \rho \) of Bi\(_{0.88}\)Sb\(_{0.12}\)Ni\(_{y}\) (\( y = 1.00 \)). With decreasing temperature, the electrical resistivity \( \rho \) decreases abruptly at \( T_{c} = 4.4 \) K and exhibits a zero resistance below the \( T_{c} \). Moreover, the magnetization curves below the \( T_{c} \) demonstrate large hysteresis as...
shown in Fig. 5. These results indicate that the inhomogeneous Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ($y=1.00$) alloy is a superconductor of the second kind. The large value of magnetization $|M| \approx 8$ emu/g suggests the existence of large volume fraction indicating superconductivity. The correct composition of the superconducting phase is not unknown at this time. However, it is interesting that the composite alloy including only non-superconducting elements and magnetic Ni demonstrates superconductivity.

4. Conclusion
We have synthesized the polycrystalline Bi$_{0.88}$Sb$_{0.12}$Ni$_y$ ($0 \leq y \leq 1.00$) and investigated the relation between thermoelectric properties and the Ni concentration $y$.

For the lower Ni concentration samples $y \leq 0.10$, dimensionless thermoelectric figure of merit $ZT$ depends on the Ni concentration $y$. The observed $ZT_{\text{max}}$ exhibits a maximum value at $y=0.03$, due to an enhancement of density of states at $E_F$ by Ni doping. This result of which the doping of magnetic element to thermoelectric material improves the thermoelectric performance is useful for the development of new thermoelectric materials. For the $y=1.00$ sample, on the other hand, we have observed superconductivity of the second kind below $T_c = 4.4$ K. It is interesting that the inhomogeneous Bi-Sb-Ni alloy including only non-superconducting elements and magnetic Ni demonstrates superconductivity.

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