# Thermoelectric Properties of n-type Ni-doped CoSb$_3$ Semiconductors

Machiko Wakatsuki, Hiroyuki Kitagawa, Hisanori Nagaoka and Yasutoshi Noda
Department of Materials Science, Shimane University, Matsue 690-8504, Japan
Fax: 81-852-32-6319, e-mail: s029120@matsu.shimane-u.ac.jp

We prepared Co$_{1-x}$Ni$_x$Sb$_3$ ($x$=0~0.1) by melting constituent elements in a graphite crucible followed by sintering using Spark Plasma Sintering. All samples exhibited n-type conduction and the electron carrier concentration increased with increasing Ni content. The Seebeck coefficient $\alpha$ and the electrical resistivity $\rho$ at room temperature decreased with increasing Ni content. The $\rho$ value decreased with increasing temperature and the Seebeck coefficient was at a maximum in the temperature range of 400 to 600 K, depending on Ni content. As a result, the temperature of the maximum power factor $P=\alpha^2/\rho$ shifted to a higher temperature with increasing Ni content. Based on these results, we also prepared a segmented element with a Ni content gradient. Confirmation of graded structure formation in the segmented element was carried out by Seebeck coefficient measurements and EPMA in each part and boundary. These results suggested that the segmented element is a potentially promising material for thermoelectric conversion in the middle temperature range.
Key words: thermoelectrics, skutterudite, spark plasma sintering, functionally graded materials

## 1. INTRODUCTION

CoSb$_3$ crystallizes peritectically with a cubic skutterudite structure (CoAs$_3$-type), space group Im3 and eight MPn$_3$ groups per unit cell [1-2]. The skutterudite compounds, TPn$_3$ (T: Co, Rh, Ir. Pn: P, As, Sb), are expected to be promising thermoelectric materials in the middle temperature range due to their attractive properties; i.e. large unit cell, heavy constituent atom masses, low electronegativity differences between the constituent atoms, large carrier mobility and Seebeck coefficient [3-4]. CoSb$_3$ is mainly known as a binary skutterudite compound used for thermoelectric materials. It is well known that the conduction type and thermoelectric properties of CoSb$_3$ can be controlled by impurity doping. However, pnicogen site substitution is not effective because Sb bonds directly affect the band structure [3]. Therefore, n-type CoSb$_3$ is generally prepared by substituting Ni, Pd or Pt in Co sites [5-6].

In the present study, Co$_{1-x}$Ni$_x$Sb$_3$ ($x$=0~0.1) compounds were prepared by direct melting of constituent elements followed by Spark Plasma Sintering (SPS). Crystal structures were identified by X-ray diffraction (XRD). The Hall and Seebeck effects were measured in the temperature range from 20 to 773 K, in order to investigate semiconducting and thermoelectric properties. Results are discussed in terms of temperature and Ni content. We also prepared a segmented element with a Ni content gradient, in order to obtain an excellent n-type thermoelectric element. Seebeck coefficient measurements and electron probe microanalyses (EPMA) were performed in order to evaluate the graded structure.

## 2. EXPERIMENTAL

Co (3N), Ni (3N) and Sb (4N) powders were used as starting materials. These materials were weighed to form the different Co$_{1-x}$Ni$_x$Sb$_3$ ($x$=0~0.1) compositions. They were directly melted at 1200°C in a graphite crucible (20 mm$\phi$) in the chamber of a spark plasma sintering apparatus. The heating was performed by applying a pulse current of 950 A under vacuum. After 5 minutes, the temperature was decreased to 600°C by setting a pulse current of 300 A, and this temperature was held for 20 minutes for annealing. All ingots obtained were sintered by spark plasma sintering (SPS) so that measurements of their thermoelectric and semiconducting properties could be made. The ingots were crushed and each powder was filled into a graphite die (10 mm$\phi$). A mechanical pressure of 50~75 MPa was applied through graphite punches, and the samples were heated to 550°C by a pulse current of about 250 A. The samples were kept at 550°C for 5 minutes, and then cooled down to room temperature. The sintered materials were about 1 mm thick and 10 mm in diameter, with a metallic luster.

The crystal structure was identified by X-ray diffraction from 20 to 150 degrees of diffraction angle using Cu-K$\alpha$ radiation. Lattice parameters were estimated by using the Nelson-Riley function. The electrical resistivity and the Hall and Seebeck coefficients were measured over the temperature range of 20~773 K, in order to evaluate the thermoelectric and semiconducting properties. We also prepared a segmented element that had a Ni content gradient. Each powder crushed from the ingots ($x$=0.005, 0.01, 0.03, 0.05), with a weight proportional to about a 3 mm height for each layer, was filled into a graphite die (10 mm$\phi$) in order, and sintered by SPS using the above-mentioned conditions. Seebeck coefficient measurements and electron probe microanalysis (EPMA) were performed

on each part and boundary, in order to confirm the formation of a graded structure.

## 3. RESULTS AND DISCUSSION

### 3.1 Homogeneous sintered samples

XRD patterns of all sintered materials could be assigned to the skutterudite structure and the lattice parameter increased linearly with increasing Ni content, indicating that the Ni atoms occupy the Co site in the skutterudite structure. These results indicate that Ni-doped single phase skutterudites were obtained by the method described in the Experimental section.

The temperature dependence of the carrier concentration is shown in Fig. 1 (a). The carrier concentration changed drastically with the Ni content $x$, that is, the carrier concentration can be controlled in the orders of magnitude of $10^{24}$~$10^{26}$ m$^{-3}$ at room temperature by changing the Ni content ($x$=0~0.1). The carrier concentration increased with increasing temperature in all samples. The linear increase in carrier concentration at higher temperatures is attributed to the abrupt increase in electron concentration by thermal excitation from the valence band to the conduction band. The n-type conduction is obtained over the temperature range from 20 to about 500 K. However, the sign of the Hall coefficient changes from negative to positive at the temperature of the maximum carrier concentration, as shown in Fig. 1 (b). This behavior is responsible for the light hole reported in the literature. The mobility of holes is larger than that of electrons in CoSb₃ [7]. Therefore, the sign of the Hall coefficient becomes positive in the intrinsic region because the hole contribution to conduction becomes larger than the electron contribution. Furthermore, the temperature of the maximum carrier concentration increased with increasing Ni content. This result suggests that n-type conduction can be maintained at higher temperatures by increasing Ni content. From the slope of a straight line for $x$=0 in the intrinsic region, the band gap $E_g$ was estimated to be 0.6 eV, which is very similar to available data [4,8].

The Hall mobility $\mu_H$ as a function of temperature is shown in Fig. 2. Hall mobility decreased with increasing Ni content, which may due to increasing carrier-carrier scattering caused by increasing carrier concentration. The Hall mobility increased with increasing temperature below 100 K, but decreased with increasing temperature above 200 K, in all samples. If a linear relationship between log$\mu_H$ and log$T$ is assumed, the scattering factor $s$ is represented as $\mu_H \propto T^s$. Under this assumption, the scattering factor was estimated to be $s$=1.3 for $T$<100 K, and $s$=-2.1 for $T$>200 K for $x$=0. This means that we can take the view that ionized impurity scattering is predominant at $T$<100 K, and decreasing Hall mobility at $T$>200 K is caused by acoustic phonon scattering. Similar temperature dependences for all Ni-doped materials were seen.

The temperature dependence of the electrical resistivity $\rho$ is shown in Fig. 3. For $x$=0~0.01, the electrical resistivity rapidly decreased with increasing temperature, which is a typical semiconducting behavior. On the other hand, for $x$=0.03~0.1, the electrical resistivity gradually increased with increasing temperature, which may be a degenerate semiconducting
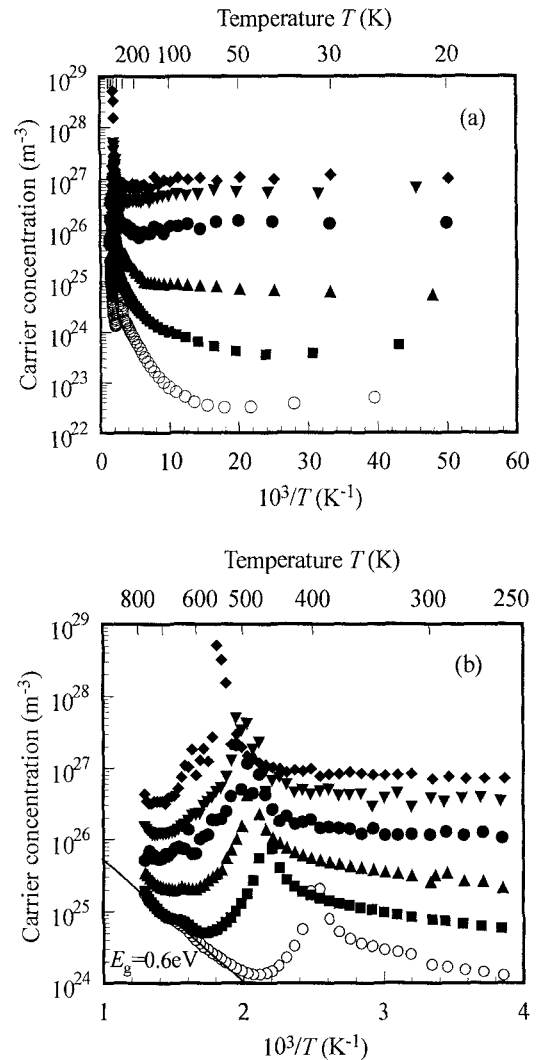


Fig. 1 (a) Temperature dependence of carrier concentration of Co$_{1-x}$Ni$_x$Sb₃ ($\bigcirc$$x$=0, $\blacksquare$$x$=0.005, $\blacktriangle$ $x$=0.01, $\bullet$ $x$=0.03, $\blacktriangledown$ $x$=0.05 and $\blacklozenge$ $x$=0.1). (b) Magnification of high temperature region in Fig. 1 (a).
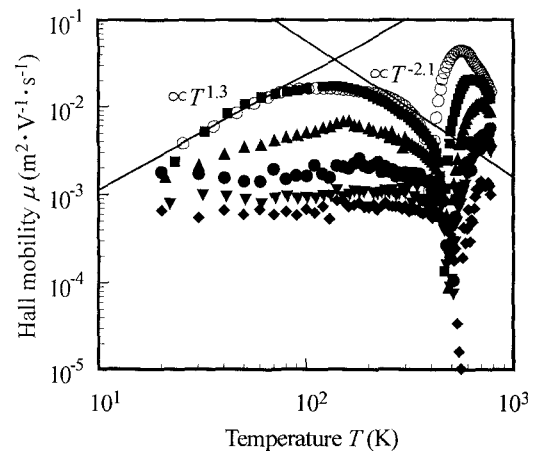


Fig. 2 Temperature dependence of Hall mobility $\mu_H$ of Co$_{1-x}$Ni$_x$Sb₃ ($\bigcirc$$x$=0, $\blacksquare$$x$=0.005, $\blacktriangle$$x$=0.01, $\bullet$ $x$=0.03, $\blacktriangledown$$x$=0.05 and $\blacklozenge$$x$=0.1).

behavior. The electrical resistivity at room temperature decreased with increasing Ni content, due to the increasing carrier concentration.

Figure 4 shows the temperature dependence of the Seebeck coefficient $\alpha$. The absolute value of the Seebeck coefficient decreased with increasing Ni content at lower temperatures, due to the increasing carrier concentration, whereas it was almost constant at higher temperatures. At lower temperatures, the Seebeck coefficient increased with increasing temperature, and it then decreased with further temperature increases, after reaching a maximum. The decrease in the Seebeck coefficient at higher temperatures is attributed to mixed conduction in the intrinsic region. The transition from a negative to a positive Seebeck coefficient sign occurred around 500 K only for $x=0$. The Seebeck coefficient decreased with increasing Ni content at lower temperatures, and the temperature of the maximum Seebeck coefficient shifted to higher temperatures with increasing Ni content, due to the increasing carrier concentration.

Figure 5 shows the temperature dependence of the power factor $\alpha^2/\rho$ estimated from the Seebeck coefficient $\alpha$ (Fig. 4) and the electrical resistivity $\rho$ (Fig. 3). The power factor increased with increasing temperature. After reaching a maximum, it decreased with increasing temperature in the same way as the Seebeck coefficient. The temperature of the maximum power factor increased with increasing Ni content. It can be concluded that thermoelectric performance and suitable operation temperature can be controlled by Ni doping content.

### 3.2 Segmented element with graded Ni content structure

The results for homogeneous sintered samples showed that the temperature at which the power factor was large was controlled by Ni content. Thus, it was considered that a superior n-type thermoelectric element operating over the middle temperature range could be prepared by making a sample with a graded Ni content structure.

The segmented element prepared by SPS is shown in Fig. 6 (a). This element is about 12 mm in a length and 10 mm$\phi$ in diameter, and consists of four parts with Ni contents $x=0.005$, 0.01, 0.03 and 0.05. Figure 6 (b) shows the Seebeck coefficient at room temperature plotted in terms of the position on the segmented element. The black circles and dotted lines show the values for the segmented element and the homogeneous sintered samples, respectively. The values for the segmented element show good agreement with those for the homogeneous sintered samples. The electron probe microanalysis results also show that Ni concentration changes at the boundaries. These results suggest that inter-diffusion of Ni atoms did not occur during the SPS process.

Thus, a graded structure was prepared by using the SPS process in a CoSb$_3$-Ni system. However, further investigation into the design of the graded structure, taking into consideration its thermal conductivity and output properties, is necessary before this material can be used in thermoelectric elements. These issues will be addressed in a forthcoming paper.
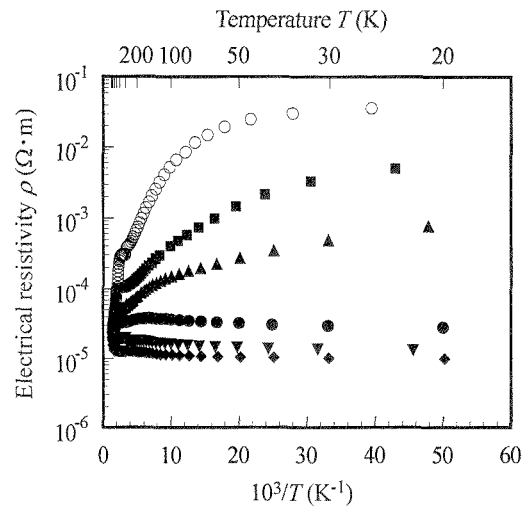


Fig. 3 Temperature dependence of electrical resistivity $\rho$ of $Co_{1-x}Ni_xSb_3$ ($\bigcirc x=0$, $\blacksquare x=0.005$, $\blacktriangle x=0.01$, $\bullet x=0.03$, $\blacktriangledown x=0.05$ and $\blacklozenge x=0.1$).
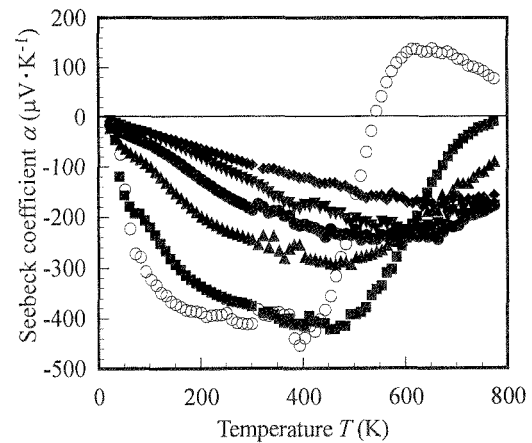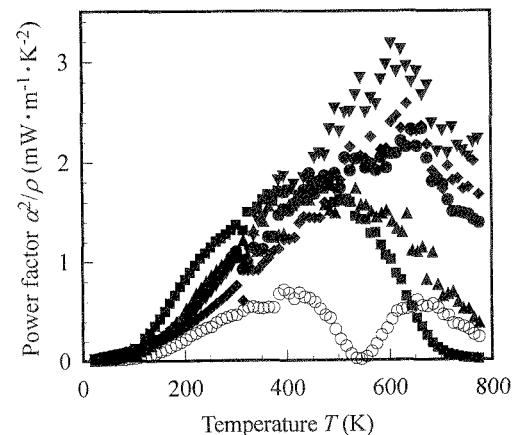


Fig. 4 Temperature dependence of Seebeck coefficient $\alpha$ of $Co_{1-x}Ni_xSb_3$ ($\bigcirc x=0$, $\blacksquare x=0.005$, $\blacktriangle x=0.01$, $\bullet x=0.03$, $\blacktriangledown x=0.05$ and $\blacklozenge x=0.1$).



Fig. 5 Temperature dependence of power factor $\alpha^2/\rho$ of $Co_{1-x}Ni_xSb_3$ ($\bigcirc x=0$, $\blacksquare x=0.005$, $\blacktriangle x=0.01$, $\bullet x=0.03$, $\blacktriangledown x=0.05$ and $\blacklozenge x=0.1$).
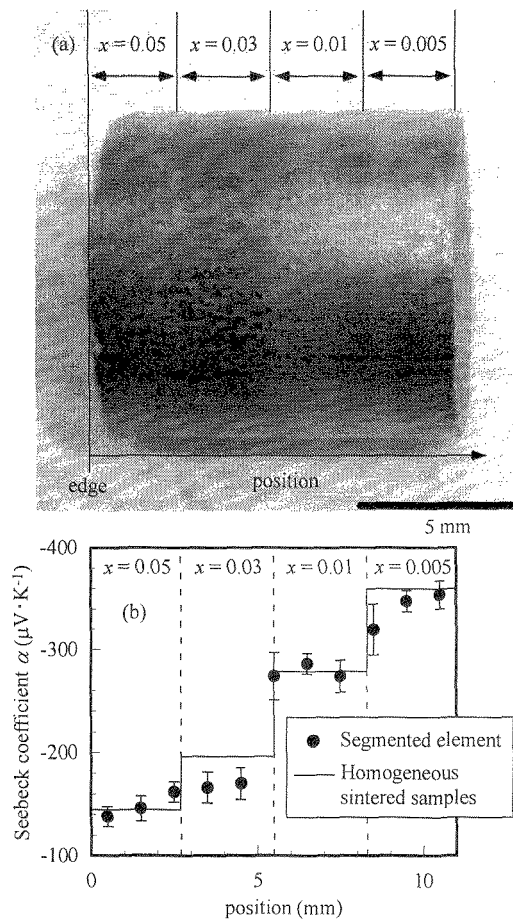
Fig. 6 (a) Segmented element with a Ni content gradient. (b) Seebeck coefficients $\alpha$ of segmented element and homogeneous sintered samples at room temperature.

References

[1] N. N. Zhurarev and G. S. Zholanov, *Soviet Physics-Crystallogr.*, 1, 404-406 (1956).

[2] K. Ishida and T. Nishizawa, *Bull. Alloy phases Diagrams*, 11, 243-248 (1996).

[3] G. S. Nolas, J. Sharp and H. J. Goldsmid, "Termoelectrics", Springer, Verlag Berlin Heidelberg, (2001) pp.178-191.

[4] T. Caillat, J. -P. Fleurial and A. Borshchevsky, *J. Crys. Growth*, 166, 722-726 (1996).

[5] H. Tashiro, Y. Notohara, T. Sakakibara, H. Anno and K. Matsubara, *Proc. 16th Int. Conf. Thermoelectrics*, 326-329 (1997).

[6] H. Kitagawa, M. Hasaka, T. Morimura, H. Nakashima and S. Kondo, *Scripta Mater.*, 43, 727-731 (2000).

[7] T. Caillat, A. Borshchevsky and J. -P. Fleurial, *Proc. 13th Int. Conf. Thermoelectrics*, 58-61 (1994).

[8] J. -P. Fleurial, A. Borshchevsky and T. Caillat, *Proc. 13th Int. Conf. Thermoelectrics*, 40-44 (1994).