Thermoelectric Properties of Ni-doped $CoSb_3$ Prepared by Encapsulated Induction Melting and Hot Pressing

Mi-Jung Kim[1], Kwan-Ho Park[1], Jae-Yong Jung[1], Sin-Wook You[2], Jung-Il Lee[1], Soon-Chul Ur[1] and Il-Ho Kim[2,a]

[1]Department of Materials Science and Engineering/ReSEM, Chungju National University
[2]Research Center for Sustainable ECo-Devices & Materials (ReSEM), Chungju National University,
123 Geomdan-ri, Iryu-myeon, Chungju, Chungbuk 380-702, Korea
[a] ihkim@chungju.ac.kr

Abstract

Ni-doped $CoSb_3$ was prepared by the encapsulated induction melting and hot pressing, and its doping effects on the thermoelectric properties were investigated. Single phase δ-$CoSb_3$ was successfully obtained by the subsequent heat treatment at 773K for 24 hours. Nickel atoms acted as electron donors by substituting cobalt atoms. Thermoelectric properties were remarkably improved by the appropriate doping.

Keywords : thermoelectric, skutterudite, doping, induction melting, hot pressing

1. Introduction

The PGEC (phonon-glass and electron-crystal) concept has been considered to search novel thermoelectric materials [1]. Good thermoelectric materials should possess thermal properties similar to that of a glass and electrical properties similar to that of a perfect single crystal material. Skutterudites can satisfy the PGEC concept and $CoSb_3$ belongs to the skutterudite structure. It is expected to be the most promising thermoelectric material, which can be semiconducting phases by doping and optimizing carrier concentration. It was found that $CoSb_3$ is a semiconductor and its bandgap is estimated to ~0.5eV. The substitution of Co or Sb by dopants can influence the electronic structure and electrical properties, in particular substantial change of the carrier masses. Furthermore, it can be expected that doping can affect the lattice thermal conductivity due to enhanced phonon scattering on impurities [2]. Although several researchers reported the thermoelectric properties of n-type $CoSb_3$ doped with different impurities [3,4], the impurity dependence of the transport and thermoelectric properties is still an important subject to be examined. In this study, the encapsulated induction melting and hot pressing were attempted to prepare the Ni-doped $CoSb_3$ compounds and their doping effects on the thermoelectric properties were investigated.

2. Experimental and Results

Ni-doped $CoSb_3$ compounds ($Co_{1-x}Ni_xSb_3$: x=0, 0.005, 0.01, 0.03, 0.05, 0.07, 0.1 and 0.2) were prepared by the encapsulated induction melting, which is widely used to synthesize homogeneous materials. Elemental Co, Ni and Sb were mixed and melted in an encapsulated quartz ampoule with an RF electrical power of 7kW/40kHz. The EIMed ingots consisted of mixed phases of β-CoSb, γ-$CoSb_2$, and elemental Sb as well as δ-$CoSb_3$, but the phases were fully transformed to single δ-$CoSb_3$ by the subsequent heat treatment at 773K for 24 hours in vacuum. The ingot was crushed into powders and sieved to -325 mesh in a glove box in Ar atmosphere. The powders were hot pressed in a cylindrical Inconel superalloy die at 773K using a stress of 60 MPa for 2 hours in Ar atmosphere. Phase transformations were analyzed for hot-pressed specimens by the high resolution X-ray diffractometer and the field emission scanning electron microscope with the energy dispersive spectrometer. The Ni doping effect on the thermoelectric properties and their temperature dependence were investigated at 300K-700K.

Figure 1 shows the phase analysis by XRD for the hot-pressed $Co_{1-x}Ni_xSb_3$. Only δ-$CoSb_3$ was identified for the specimens of x=0 to 0.1, but as shown in Figure 1(c), it decomposed to $NiSb_2$ and Sb when the x is 0.2, which means the solubility limit of Ni to Co is lower than 0.2.

Figure 2 shows the microstructure of hot-pressed $Co_{1-x}Ni_xSb_3$. Very sound and compact microstructure with little pores and cracks could be obtained by the hot pressing. Homogeneous specimens were achieved for the x is up to 0.1, but the secondary phases ($NiSb_2$ and Sb) were observed for $Co_{0.8}Ni_{0.2}Sb_3$ specimen. This is in good agreement with the XRD analysis results.

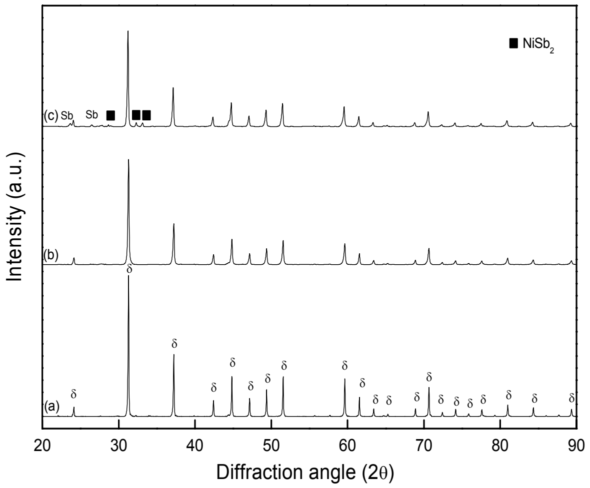

Fig. 1. Phase identifications for hot-pressed $Co_{1-x}Fe_xSb_3$; (a) x=0, (b) x=0.1 and (c) x=0.2.

Undoped $CoSb_3$ shows positive Seebeck coefficient, which means the p-type conductivity because its hole effective mass is much smaller than electron effective mass. However, Ni-doped $CoSb_3$ showed the n-type conductivity at all temperatures examined. Therefore, Ni atoms acted as electron donors by substituting Co atoms as expected. Electrical resistivity of undoped $CoSb_3$ considerably decreased with increasing temperature, but that of Ni-doped $CoSb_3$ was almost independent of temperature. Thermal conductivity of undoped $CoSb_3$ was 0.11 W/cmK at room temperature, and it decreased to 0.07 W/cmK at 700K. Thermal conductivity was drastically reduced by doping. Dopants contribute to electronic thermal conduction as well as phonon scattering centers, which decreases lattice thermal conductivity. However, thermal conductivity of the specimen of x=0.2 was higher than that of x=0.1. The reason for this was considered as increase in electronic contribution to thermal conductivity due to excess doping.

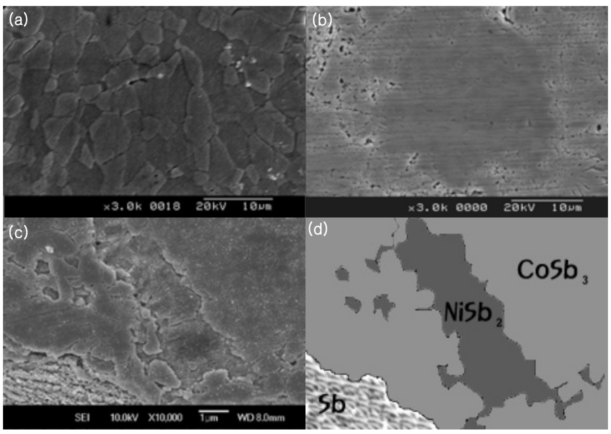

Fig. 2. Microstructures of hot-pressed $Co_{1-x}Ni_xSb_3$; (a) x=0, (b) x=0.1, (c) x=0.2 and (d) schematic view of the (c).

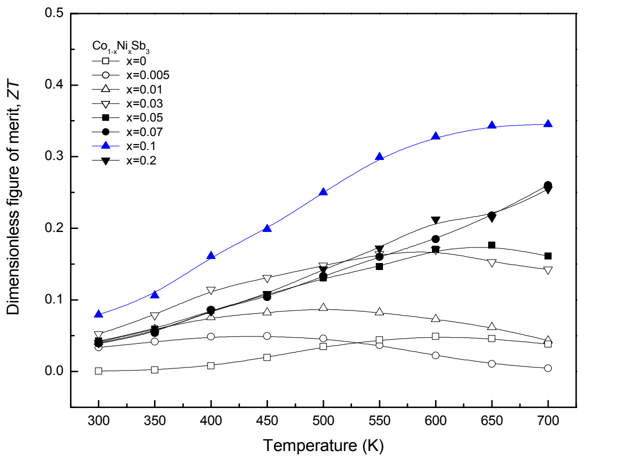

Fig. 3. Dimensionless figure of merit (ZT) of hot-pressed $Co_{1-x}Ni_xSb_3$.

Figure 3 shows the temperature dependence of dimensionless thermoelectric figure of merit (ZT). Remarkable ZT improvement was obtained by the Ni doping up to x=0.1, but it was reduced by excess doping due to decreases in Seebeck coefficient and electrical resistivity and increase in thermal conductivity.

3. Summary

The encapsulated induction melting and hot pressing were employed to prepare Ni-doped $CoSb_3$ skutterudites and their thermoelectric properties were investigated. Single phase δ-$CoSb_3$ was successfully obtained by the subsequent heat treatment at 773K for 24 hours in vacuum. However, δ-$CoSb_3$ was decomposed to $NiSb_2$ and Sb when x>0.1, which means that the solubility limit of Ni to Co is x=0.1. ZT was considerably enhanced by the Ni doping, and optimum composition was found as $Co_{0.9}Ni_{0.1}Sb_3$ for the Ni-doped $CoSb_3$ prepared by hot pressing. This was closely related with solubility limit of Ni to Co.

4. Acknowledgments

This work was supported by the Regional Innovation Center (RIC) Program conducted by the Ministry of Commerce, Industry and Energy of Korean Government.

5. References

1. G.A. Slack and V.G. Tsoukala: J. Appl. Phys. Vol. 76 (1994), p.1665.
2. K.T. Wojciechowski, J. Tobola and J. Leszczynski: J. Alloys & Comp. Vol. 361 (2003), p.19.
3. P. Feschotte and D. Lorin: J. Less-Common Metals Vol. 155 (1989), p.255.
4. Y. Nakamoto, K. Tanaka and T. Koyanagi: Proc. 17^{th} Intl. Conf. Thermoelectrics (1998), p.302.