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

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**Abstract**

*The encapsulated induction melting and hot pressing were employed to prepare Fe-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. Iron atoms acted as electron acceptors by substituting cobalt atoms. Thermoelectric properties were remarkably improved by the appropriate doping. $Co_{0.7}Fe_{0.3}Sb_3$ was found as an optimum composition for best thermoelectric properties in this work.*

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

## 1. Introduction

Good thermoelectric materials should have thermal properties similar to that of a glass and electrical properties similar to that of a perfect single crystal material. This is so-called the PGEC (phonon-glass and electron-crystal) concept [1]. Skutterudites can meet the PGEC concept and there are a lot of research works have been reported on thermoelectric skutterudites [2,3]. $CoSb_3$ and its related materials belong to the skutterudite structure and they are expected to be the most promising thermoelectric materials, which can be semiconducting phases by doping and optimizing carrier concentration. Undoped intrinsic $CoSb_3$ shows a p-type conductivity but some reports shows that binary $CoSb_3$ is n-type at room temperature depending on carrier concentration and stoichiometry, which might be originated from residual impurities, phase changes, and slightly off-stoichiometry [4]. However, undoped $CoSb_3$ cannot be used to thermoelectric applications because its electrical resistivity and thermal conductivity are very high due to high carrier mobility. In this study, the encapsulated induction melting and vacuum hot pressing were attempted to prepare the Fe-doped $CoSb_3$ and its doping effects on the thermoelectric properties were investigated.

## 2. Experimental and Results

Fe-doped $CoSb_3$ skutterudites ($Co_{1-x}Fe_xSb_3$: x=0, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by the encapsulated induction melting (EIM). Elemental Co, Fe and Sb were mixed and melted in an encapsulated quartz ampoule with an RF electrical power of 7kW/40kHz. Subsequent isothermal heat treatment was carried out for the EIMed specimens at 773K for 24 hours in vacuum for phase transformation and homogenization as well as dopant activation. 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 Fe doping effect on the thermoelectric properties and their temperature dependence were investigated at 300K-700K.

Figure 1 shows the phase identification results analyzed by XRD for the hot-pressed $Co_{1-x}Fe_xSb_3$ using the EIMed powders followed by heat treatment in vacuum. Only δ-$CoSb_3$ was identified for the specimens of x=0 to 0.2, but as shown in Figure 1(b) and (c), it decomposed to $FeSb_2$ and Sb when the x is higher than 0.3, which means the solubility limit of Fe to Co is lower than 0.3.

Figure 2 shows the microstructure of hot-pressed $Co_{1-x}Fe_xSb_3$. 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 lower than 0.3, but the large amount of secondary phases ($FeSb_2$ and Sb) were observed for $Co_{0.6}Fe_{0.4}Sb_3$ and $Co_{0.5}Fe_{0.5}Sb_3$ specimens.

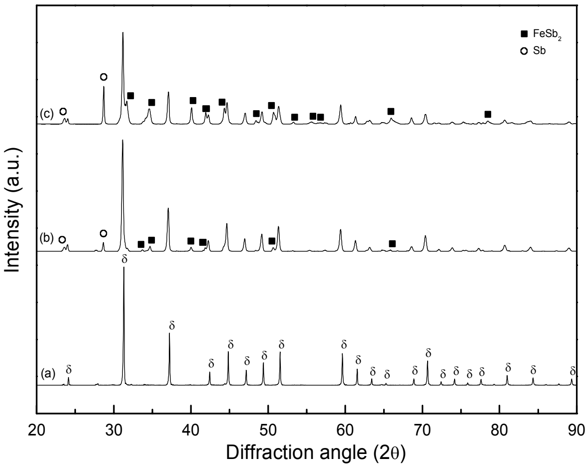


**Fig. 1. Phase identifications for hot-pressed $Co_{1-x}Fe_xSb_3$; (a) x=0, (b) x=0.3 and (c) x=0.4.**

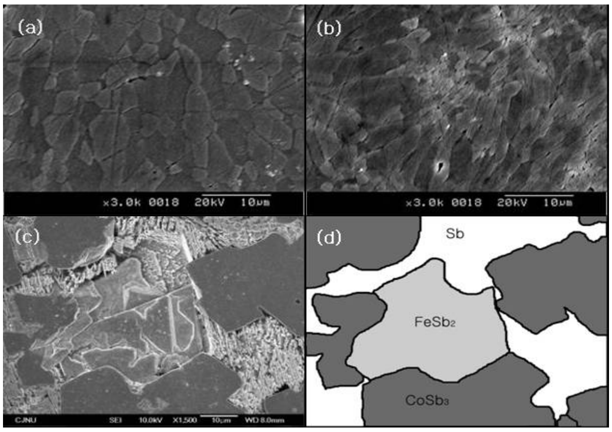


**Fig. 2. Microstructures of hot-pressed $Co_{1-x}Fe_xSb_3$; (a) x=0, (b) x=0.3, (c) x=0.4 and (d) schematic view of the (c).**

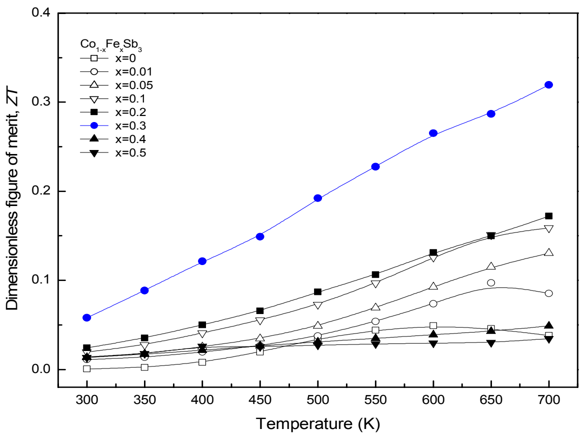


**Fig. 3. Dimensionless figure of merit (ZT) of hot-pressed $Co_{1-x}Fe_xSb_3$.**

Seebeck coefficient was considerably reduced by the Fe doping and it decreased with increasing the Fe doping amount. However, it increased with increasing temperature and reached to 109 μV/K at 700K for the $Co_{0.7}Fe_{0.3}Sb_3$ specimen. Electrical resistivity decreased with increasing the Fe doping amount. It was confirmed that the dopant atoms were well-activated by the heat treatment at 773K for 24 hours in the skutterudite structure. Electrical resistivity was almost independent of temperature for the Fe-doped $CoSb_3$, which showed from mid-$10^{-4}$ Ωcm to low-$10^{-3}$ Ωcm. Thermal conductivity was drastically reduced by doping and minimum value was obtained as around 0.02 W/cmK for the $Co_{0.7}Fe_{0.3}Sb_3$ specimen at all temperatures measured. It was confirmed that dopants contribute to electronic thermal conduction as well as phonon scattering centers, which decreases lattice thermal conductivity.

Figure 3 shows the temperature dependence of dimensionless figure of merit. Remarkable improvement was obtained by the Fe doping up to x=0.3, but it was reduced by excess doping due to decreases in Seebeck coefficient and electrical resistivity and increase in thermal conductivity. Maximum ZT was achieved as 0.32 at 700K for the $Co_{0.7}Fe_{0.3}Sb_3$ specimen and it is strongly expected to show higher value above 700K.

## 3. Summary

Fe-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 in vacuum. However, δ-$CoSb_3$ was decomposed to $FeSb_2$ and Sb when $x \geq 0.3$, which means that the solubility limit of Fe to Co is $x<0.3$. The positive signs of Seebeck coefficients for all Fe-doped specimens revealed that Fe atoms acted as p-type dopants by substituting Co atoms. Electrical resistivity and thermal conductivity decreased with increasing the Fe doping level. ZT was considerably enhanced by the Fe doping.

## 4. Acknowledgments

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