Effect of Fe Doping on Thermoelectric Properties of Mechanically Alloyed CoSb$_3$

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Abstract

Fe doped skutterudite CoSb$_3$ with a nominal composition of Fe$_x$Co$_{1-x}$Sb$_{12}$ (0≤x≤2.5) have been synthesized by mechanical alloying (MA) of elemental powders, followed by vacuum hot pressing. Phase transformations during mechanical alloying and vacuum hot pressing were systematically investigated using XRD. Single phase skutterudite was successfully produced by vacuum hot pressing using as-milled powders without subsequent annealing. However, second phase of FeSb$_2$ was found to exist in case of x≥2, suggesting the solubility limit of Fe with Co in this system. Thermoelectric properties as functions of temperature and Fe contents were evaluated for the hot pressed specimens. Fe doping up to x=1.5 with Co in Fe$_x$Co$_{4-x}$Sb$_{12}$ appeared to increase thermoelectric figure of merit (ZT) and the maximum ZT was found to be 0.78 at 525K in this study.

Keywords : Skutterudite, Fe doping, Mechanical Alloying, CoSb$_3$, Thermoelectric

1. Introduction

Recently, skutterudite group has been paid great attention for higher performance, thermoelectric conversion materials [1-2]. CoSb$_3$ belongs to a skutterudite and is expected to be a promising thermoelectric material having high ZT [1-3]. The ZT is defined as $\alpha^2\sigma T/\lambda$, where α is the Seebeck coefficient, σ is the electrical conductivity, and λ is the thermal conductivity. Although high performance was expected in CoSb$_3$, binary compound itself could not provide high ZT due to relatively higher lattice thermal conductivity(λ_L) [2-4]. In general, reducing in λ_L was considered to enhance their ZT by doping and/or filling [2-4]. The preparation of δ-CoSb$_3$ involves rather complicated processes and is frequently confronted with the formation of γ-CoSb$_2$, phase decomposition and/or Sb evaporation as well as a poor tendency to form of CoSb$_3$ due to its peritectic transition [2-4]. In order to address these drawbacks, MA process was considered in this study [5]. MA is known as a unique technique, by which alloying proceeds with consecutive cold welding and fracturing, resulting in fine grain size and phase homogenization. MA materials having a fine grain size may improve thermoelectric conversion efficiency by the reduction in λ_L [5]. Fe$_x$Co$_{1-x}$Sb$_{12}$ (0≤x≤2.5) have been synthesized by MA of elemental powders, followed by vacuum hot pressing(VHP) in this study. Thermoelectric properties were measured and compared with the results of analogous studies.
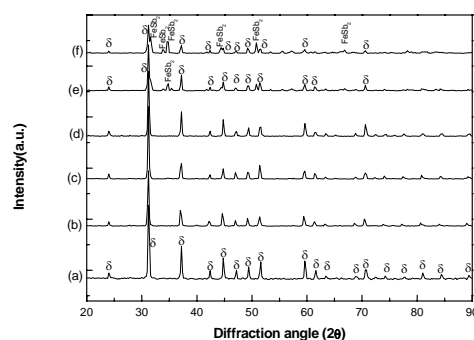
2. Experimental and Results

Fig. 1. XRD patterns of VHPed Fe$_x$Co$_{4-x}$Sb$_{12}$; (a) x=0, (b) x=0.5, (c) x=1, (d) x=1.5, (e) x=2, (f) x=2.5.

Appropriate elemental powder mixtures of -325 mesh Co (99.9%), Sb (99.9%) and Fe(99.9%) for stoichiometric Fe$_x$Co$_{1-x}$Sb$_{12}$ (0≤x≤2.5) were prepared and MAed in an attrition mill for 100hrs. XRD analysis during milling revealed that alloy development of β-CoSb and γ-(Fe,Co)Sb$_2$ phases appeared after 48 hours of milling, and proceeded further as milling time increased as in typical MA process [5]. Alloying seemed to be complete after 100 hours of milling, but single phase δ-CoSb$_3$ powders could not be obtained in this process. As-milled powder size was typically less than 10 μm. As–milled powders were VHPed at 823K with 60MPa/2hrs. All the VHPed specimens showed over 96% of theoretical density. As presented in Fig. 1, compositions of x=0.1, 0.5, 1.0 and 1.5 resulted in single phase δ-(Fe,Co)Sb$_3$, while second phase in the form of marcasite structure FeSb$_2$ was found to exist in case of x≥2.

Differenetly from analogue studies, the solubility limit of Fe with Co appeared to be over the limit(x=1.5), due to the formation of supersaturated solid solution which frequently occurs in MA process [5].
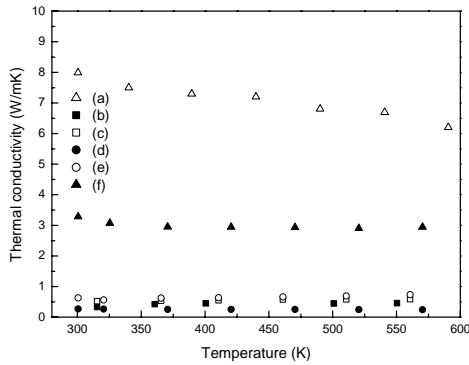

Fig. 2. Thermal conductivity as a function of temperature in VHPed $Fe_xCo_{4-x}Sb_{12}$; (a) x=0, (b) x=0.5, (c) x=1, (d) x=1.5, (e) x=2, (f) x=2.5.

Thermoelectric properties as a function of temperature were measured in terms of α, σ, and λ. Their combined values of ZT were also obtained and compared with the analogous studies. α in all the specimens at test range showed positive values, representing p-type conductivity. They increased with increasing temperature as in similar studies [2-3]. Those also show a decreasing trend as per Fe addition, possibly due to the increase in hole concentration caused by Fe substitution for Co [7,8]. σ decreased radually with increasing temperature. Interestingly, Fe doped specimens showed abrupt increase in σ with an order of magnitude. It is also attributed to the increase in hole concentration caused by Fe substitution [8]. However, no specific trend of σ variations per Fe contents was found. λ of MA $Fe_xCo_{4-x}Sb_{12}$ as a function of temperature up to 600K were presented in Fig. 2. Differently from the case of binary $CoSb_3$, λ were shown to decrease dramatically as per Fe addition. This would be attributed to the induced phonon scattering by lattice distortion which would be caused by Fe substitution [7,8]. It is also worth noting that the lowest λ is shown in the composition of x=1.5, and the λ increases at the composition of x≥2, at which $FeSb_2$ began to appear. From the values σ, α and λ, ZT values were obtained as presented in Fig. 3. Fe doping up to x=1.5 with Co in $Fe_xCo_{4-x}Sb_{12}$ appeared to increase ZT and the maximum was found to be 0.78 at 525K in this study. Fe doping in $CoSb_3$ showed to effectively act as a dopant and to reduce thermal conductivity.
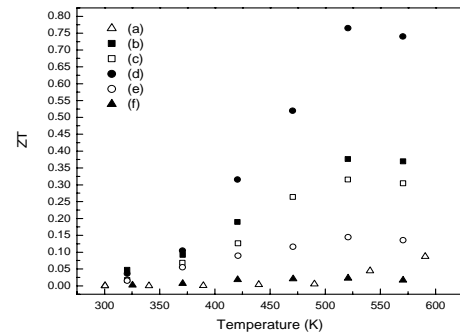

Fig. 3. ZTs as a function of temperature in VHPed $Fe_xCo_{4-x}Sb_{12}$; (a) x=0, (b) x=0.5, (c) x=1, (d) x=1.5, (e) x=2, (f) x=2.5.

3. Summary

Single phase skutterudites were successfully produced by VHP using as-MA $Fe_xCo_{1-x}Sb_{12}$ (0≤x≤2.5) powders without subsequent annealing. However, second phase in the form of marcasite structure $FeSb_2$ was found to exist in case of x≥2. Fe doping up to x=1.5 with Co in $Fe_xCo_{4-x}Sb_{12}$ appeared to increase ZT and the maximum was found to be 0.78 at 525K in this study.

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4. References

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