Thermoelectric Properties of Nano Structured $CoSb_3$ Synthesized by Mechanical Alloying

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Abstract

Undoped $CoSb_3$ powders were synthesized by mechanical alloying (MA) of elemental powders using a nominal stoichiometric composition. Nano-structured, single-phase skutterudite $CoSb_3$ was successfully produced by vacuum hot pressing (VHP) using MA powders without subsequent annealing. Phase transformations during synthesis were investigated using XRD, and microstructure was observed using SEM and TEM. Thermoelectric properties in terms of Seebeck coefficient, electrical conductivity, thermal conductivity and figure of merit(ZT) were systematically measured and compared with the results of analogous studies. Lattice thermal conductivity was reduced owing to increasing phone scattering in nano-structured MA $CoSb_3$, leading to enhancement in the thermoelectric figure of merit. MA associated with VHP technique offers an alternative potential processing route for the process of skutterudite.

Keywords : Skutterudite, Nano, Mechanical Alloying, $CoSb_3$, Thermoelectric

1. Introduction

$CoSb_3$ belongs to a skutterudite and is expected to be a promising thermoelectric material having high figure of merit value(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. $CoSb_3$ shows intrinsic p-type conduction at room temperature [1], but it shows an n-type in some cases at room temperature [2,4]. $CoSb_3$ is generally prepared by melting, powder metallurgy and/or hybrid methods of these [2-5]. The preparation $CoSb_3$ involves rather complicated processes and frequently involves the formation of undesirable phases such as γ-$CoSb_2$, phase decomposition and/or Sb evaporation [2,3]. Another difficulty in preparation is a poor tendency to form $CoSb_3$ due to its peritectic transition [5]. Intermetallic phases can be prepared by means of solid state synthesis such as MA process [4-6]. MA is known as a unique technique [6], by which alloying proceeds with consecutive cold welding and fracturing, resulting in fine grain size and phase homogenization. It was reported that MA materials having a fine grain size may improve thermoelectric efficiency by the reduction in lattice thermal conductivity [7]. In an effort to produce fine grain size, MA of elemental Co and Sb powders followed by hot pressing is considered in this study. Thermoelectric properties were measured and compared with the results of analogous studies.

2. Experimental and Results

Appropriate elemental powder mixtures of -325 mesh Co (99.9%) and -325 mesh Sb (99.9%) for stoichiometric $CoSb_3$ were prepared and MAed using an attrition mill for 100 hrs under an Ar atmosphere. SEM observation revealed that as-milled powders were spherical and typically less than 10 μm. As-milled powders were then hot pressed at 500-600°C with 60MPa/2hrs in vacuum. XRD analysis during milling revealed that alloy development of β-CoSb and γ-$CoSb_2$ phases appeared after 48 hours of milling, and proceeded further as milling time increased as in typical MA process [6]. Alloying seemed to be complete after 100 hours of milling, but single phase $CoSb_3$ powders could not be obtained in this process, as shown in Fig. 1. Microstructures were observed using SEM and TEM. The TEM investigation was carried out using an FEI Tecnai F30 S-Twin model operating at 300kV. MA/VHP specimen resulted in single phase δ-$CoSb_3$ with an average 95.6% of density, and it was chosen for thermoelectric property measurement. TEM observation revealed ultra fine microstructure having an average grain size of 40 nm as presented in Fig. 2. 600ºC were presented with in Table 1. The properties of hot pressed $CoSb_3$ [2], and encapsulated-induction melted and hot-pressed samples (EIM/VHP) are also presented for comparison.

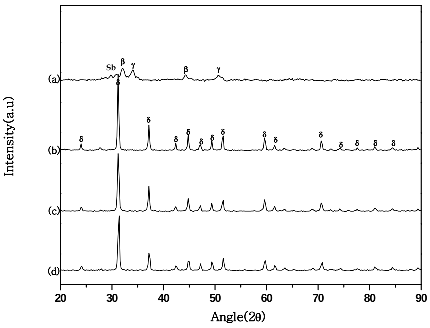

Fig. 1. XRD patterns of hot pressed $CoSb_3$ after MA for 100 hrs ; (a) As-MAed for 100 hrs, (b) VHPed at 600℃, (c) VHPed at 550℃, (d) VHPed at 500℃.

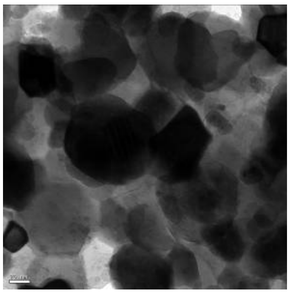

Fig. 2. TEM micrograph of hot pressed MA $CoSb_3$, showing average grain size of 40 nm.

Table 1. Properties of $CoSb_3$ at room temperature.

Sample	α(μV/K)	σ ($\Omega^{-1}cm^{-1}$)	density	Phases
Ref.[3]	-420	17.2	92-95%	δ
EIM/VHP	118.0	15.8	92%	δ
MA/VHP	-8.1	36.1	95.6%	δ

Seebeck coefficient at room temperature showed negative value in MA/VHP, representing n-type conductivity as shown in Table 1, while analogue study showed p-type [2]. This may be attributed to the possible Sb evaporation during hot pressing, resulting in the conduction type change [3]. σ at room temperature of the sample MA/VHP was shown to be similar to that of the HPed $CoSb_3$ [3], but quite lower than that of single crystal [2]. α increases with increasing temperature as in similar studies [3,4]. However, it turns to the positive from the negative, possibly due to changes in major carrier type with increasing temperature [3,4]. Similar behavior has been shown in hot pressed $CoSb_3$, due to the activation of intrinsic carriers across the band gap [4]. λ was reduced possibly due to increasing phonon scattering in nano-structured $CoSb_3$, leading to enhancement in thermoelectric figure of merit as in Fig. 3. It shows good agreement with that an ultra fine grain size as in MA microstructure may improve thermoelectric conversion efficiency by the reduction in lattice thermal conductivity [7].

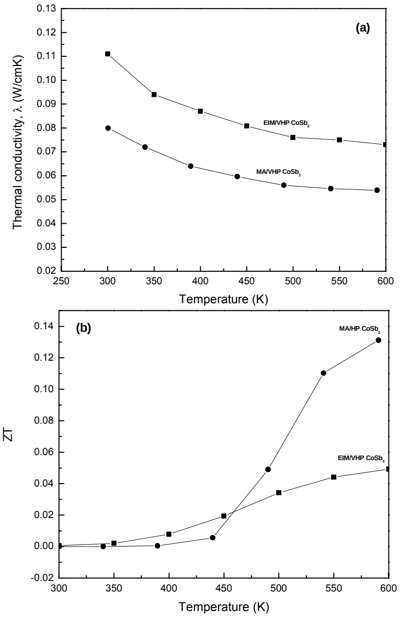

Fig. 3. Thermoelectric properties as a function of temperature for MA/VHP and EIM/VHP (a) Thermal conductivity, (b) Overall ZT.

3. Summary

Skutterudite $CoSb_3$ were produced by MA and successfully consolidated by VHP. All specimens VHPed at 500-600ºC resulted in single phase $CoSb_3$. Lattice thermal conductivity was reduced possibly owing to increasing phone scattering in nano-structured MA $CoSb_3$, leading to enhancement in the thermoelectric figure of merit.

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5. References

1. G. S. Nolas, D. T. Morelli, and T. M. Tritt, Annu. Rev. Mater. Sci., **29**, 89 (1999).
2. J. W. Sharp, E. C. Jones, R. K. Williams, P. M. Martin and B. C. Sales, J. Appl. Phys. **78(2),** 1014(1995).
3. T. Caillat, A. Borshchevski and J.-P. Fleurial, Proc. 13th ICT, Kansas City, USA, AIP, p.58 (1994).
4. Y. Kawaharada, K. Kurosaki, M. Uno, and S. Yamanaka, J. of Alloys and Comp., **315**, 193(2001).
5. J. X. Jang, Q. M. Lu, K. G. Liu, L. Zhang, and M. L. Zou, Mater. Letters, **58**, 1981 (2004).
6. S.-C. Ur, P. Nash and I.-H. Kim, J. of Alloys and Comp., **361**, 84(2003).
7. D. M. Rowe and V. S. Schukla, J. Appl. Phys., **52(12),** 7421(1981).