Preparation of Single Phase $\beta$-Zn$_4$Sb$_3$ Thermoelectric Materials by Mechanical Grinding Process

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Single phase $\beta$-Zn$_4$Sb$_3$ was prepared by mechanical grinding (MG). Source materials for the Zn$_4$Sb$_3$ ingots were prepared using three different processes after the direct melting of constituent elements. The ingot was obtained by quenching the melt in water within an evacuated quartz ampoule and heat-treated for a total of 200 h in two stages at 723 K and 673 K. The resultant ingots were mechanically ground and sintered at 623 K by hot pressing. The sintered materials were obtained crack-free single phase $\beta$-Zn$_4$Sb$_3$ and characterized by X-ray diffraction, differential thermal analysis (DTA) and thermoelectric property measurements. The thermal conductivity of the sintered materials was 0.88 Wm$^{-1}$K$^{-1}$ at room temperature and this was slightly lower than that reported for the materials prepared by a conventional method. Results indicate that the $\beta$-Zn$_4$Sb$_3$ single phase of the dimensionless figure of merit ranged from 1.06–1.31 at 573 K.

1. Introduction

The $\beta$-phase of Zn$_4$Sb$_3$ is a $p$-type semiconductor which has excellent thermoelectric properties in an intermediate temperature range (450–650 K).\cite{1,2} It has a relatively low cost and can potentially be used as a substitute for high performance lead tellurides that contain toxic lead.\cite{2,3} It was reported that relatively ductile Zn is more preferable to cold welding on to balls and vessels than $\gamma$-Zn$_4$Sb$_3$ which has poor ductility.\cite{1,2,3}

Figure 1 shows a phase diagram of the Zn-Sb system.\cite{4} The three modified forms of $\alpha$-, $\beta$- and $\gamma$-Zn$_4$Sb$_3$ are stable below 263 K, between 263 and 765 K, and above 765 K, respectively.

Melt growth and powder metallurgy methods have been used to prepare $\beta$-Zn$_4$Sb$_3$.\cite{5-10} $\beta$-Zn$_4$Sb$_3$ crystals, prepared by conventional melt growth contain many cracks that result from thermal stress because of the $\gamma$ to $\beta$ phase transformations. Recently, a crack-free single phase $\beta$-Zn$_4$Sb$_3$ was obtained using direct melting followed by a two-stage heat treatment and this was reported elsewhere.\cite{10}

Finely ground powder metallurgical processes such as mechanical alloying (MA) and mechanical grinding (MG) have been used to obtain homogeneous materials.\cite{11-14} In general, fine grain size materials have lower thermal conductivity than single crystals of the same materials because phonons can be scattered at grain boundaries. However, a single phase $\beta$-Zn$_4$Sb$_3$ has not been obtained by MA.\cite{11-13} It was reported that relatively ductile Zn is more preferable to cold welding on to balls and vessels than pulverizing, resulting in Zn deficiency.\cite{11}

In this study, MG was applied to the preparation of single phase $\beta$-Zn$_4$Sb$_3$ by three different heat treatment processes.

2. Experimental Procedures

The source ingot with a nominal Zn$_4$Sb$_3$ composition was synthesized at 923 K for 3 h by the direct melting of the constituent elements Zn (99.9999%) and Sb (99.9999%) in an evacuated quartz ampoule. Figure 2 shows a schematic diagram of the MG process used to prepare $\beta$-Zn$_4$Sb$_3$.

Fig. 1 A phase diagram for the Zn-Sb system.\cite{4}

In process-1, the source ingot was obtained by quenching the ampoule in water. In process-2, the ingot was heat-treated at 723 K after quenching. In process-3, the ingot was heat-treated in two stages at 723 K and 673 K after quenching. Two-stage heat treatment consisted of successively heating the ingot at 723 K and 673 K for 100 h after quenching the ampoule in water. The first stage is to change the high temperature $\gamma$-phase into the low temperature $\beta$-phase. As the $\gamma$- and $\beta$-Zn$_4$Sb$_3$ phase have different coefficients of thermal expansion, thermal stresses caused many cracks to form during material preparation. The second stage is to obtain homogeneous materials.
The resultant ingots of these three different processes were put into stainless steel vessels and milled with silicon nitride balls. The MG process was carried out in a planetary ball mill for 100 h at a maximum speed of 180 rpm. The pulverized powder was then set in stainless steel dies. The MG materials were sintered by hot pressing at a sintering temperature of 623 K under a mechanical pressure of 147 MPa in an argon atmosphere.

The density of the sintered materials was measured using the Archimedes method at room temperature. Metallographic observations were made using an optical microscope. Sintered materials were investigated by X-ray diffraction (XRD) using CuKα radiation in a 2θ range from 20–50 degrees and differential thermal analysis (DTA). DTA measurements were made by heating up to 873 K at a rate of 20 K/min in alumina containers within a N₂ atmosphere.

The Seebeck coefficient α was estimated from the linear relationship between the thermoelectromotive force (E) and a temperature difference (ΔT) of up to 3 K under vacuum in a temperature range from 300–573 K using α = E/ΔT. The electrical conductivity σ and the carrier concentration of the sintered materials was measured by the van der Pauw method under vacuum using a direct current of 50 mA and a magnetic field of 0.5 T in a temperature range from 300–573 K. The thermal conductivity κ was measured using the constructed static comparison method at room temperature.15)

Thermoelectric performance was evaluated by the power factor α²σ and the dimensionless thermoelectric figure of merit ZT given by ZT = α²σT/κ, where T is absolute temperature.

3. Results and Discussion

The relative density of MG materials is listed in Table 1.16) All MG materials were dense with a relative density of more than 98%. The many cracks and pores were observed in the materials before the MG process. It indicates that thermal stresses resulted during transformations after quenching. This indicates that pulverizing and sintering is necessary to obtain dense materials. Figure 3 shows XRD patterns of the bulk materials before and after the MG process. All the observed diffraction peaks were identified as those from the β-Zn₄Sb₃ single phase.

Figure 4 shows the DTA curve for the bulk materials before and after the MG process. Increasing the temperature caused the formation of a small peak at 673 K corresponding to a eutectoid reaction between β-Zn₄Sb₃ and Zn. The small peak at 723 K corresponds to a eutectoid reaction between β-Zn₄Sb₃ and ZnSb₂. The endothermic peak (II) at 773 K corresponds to a phase transition from the β- to the γ-phase. The small peak at 803 K corresponds to a peritectic reaction between γ-Zn₄Sb₃ and ZnSb. The large endothermic peak (I) at about 853 K corresponds to the melting point of Zn₄Sb₃. These XRD and DTA results indicate that a single phase β-Zn₄Sb₃ was
obtained by three different processes. It is considered that brittle Zn$_4$Sb$_3$ ingot is able to pulverize.

Figures 5–8 show plots of thermoelectric properties versus temperature for the materials prepared using the MG processes. The materials were $p$-type and their Seebeck coefficients $\alpha$ were almost similar and ranged from 139–150 $\mu$V K$^{-1}$ at room temperature. $\alpha$ values showed similar behavior to the temperature dependence as shown in Fig. 5. Their electrical conductivities $\sigma$ ranged from $2.85\times 10^2$–$3.12\times 10^2$ Ω$^{-1}$m$^{-1}$ at room temperature and showed similar behavior for all materials as shown in Fig. 6. The carrier concentration of the MG material by process-2 was $4.73 \times 10^{25}$ m$^{-3}$ at room temperature. The carrier concentration of all MG materials is expected to have a similar value because the electric conductivity does not change much between all the MG materials. The thermal conductivity, $\kappa$, of all MG materials was approximately 0.88 Wm$^{-1}$K$^{-1}$ at room temperature as listed in Table 1. This value for the MG materials was slightly lower than the values obtained for the materials prepared using the conventional method.$^{1)}$

Figure 7 shows a plot of the power factor $\alpha^2\sigma$ versus temperature. The power factor of the materials obtained by the MG process was in a range of $1.62\text{–}2.00 \times 10^{-3}$ Wm$^{-1}$K$^{-2}$ at 573 K. Thus, the estimated dimensionless

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figure of merit values ranged from 1.06–1.31 at 573 K as shown in Fig. 8. The thermal conductivity was adopted using the fixed values at room temperature.

These results indicate that heat-treatment in the MG process does not result in appreciable differences of the Seebeck coefficient, electric conductivity, power factor and dimensionless figure of merit of the materials. Therefore, process-1 is an appropriate method for the preparation of a single-phase and crack-free $\beta$-Zn$_4$Sb$_3$ phase.

4. Conclusions

In this study, MG of quenched ingots was used to prepare single phase $\beta$-Zn$_4$Sb$_3$ by three different heat treatment processes. The results are summarized as follows:

(1) Single phase $\beta$-Zn$_4$Sb$_3$ was successfully prepared by the MG process which involved the grinding of quenched ingots followed by hot-pressing. The quenched ingots had many cracks and pores and it was necessary to pulverize and sinter them to obtain dense materials.

(2) The thermal conductivity for the MG materials reached 0.88 Wm$^{-1}$K$^{-1}$ at room temperature and this was slightly lower than that of the materials prepared by a conventional method.

(3) All obtained materials were $p$-type and their dimensionless figure of merit ranged from 1.06–1.30 at 573 K.

(4) Process-1 is an appropriate method to prepare single phase and crack-free $\beta$-Zn$_4$Sb$_3$.

REFERENCES