Preparation of Single-Phase ZnSb Thermoelectric Materials Using a Mechanical Grinding Process

Chinatsu Okamura*, Takashi Ueda* and Kazuhiro Hasezaki

Department of Materials Science, Shimane University, Matsue 690-8504, Japan

Single-phase zinc antimonide (ZnSb) was prepared using a mechanical grinding (MG) process. The ZnSb source ingots were prepared by direct melting of the constituent elements. Two processes were used to prepare the ingots. One of the processes involved quenching the molten material in water in an evacuated quartz ampoule. In the other process, an additional step consisting of heating for 100 h at 723 K was performed after quenching. The ground materials were obtained by mechanically grinding the resultant ingots and then hot-pressing at 673 K. The materials were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), and thermoelectric property measurements. The results indicated that the materials were crack free and single phase. The thermal conductivity of the ground materials was $1.41 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature. This value was lower than that reported in the available data for materials prepared by conventional melt growth and powder metallurgy methods. The ZnSb single phase was found to have a dimensionless figure of merit of 0.6–0.8 at 573 K.

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1. Introduction

Zinc antimonide (ZnSb) is a thermoelectric material of potentially high performance in the intermediate temperature range (450–650 K). The constituent elements of ZnSb are low cost and non-toxic.¹⁾ ZnSb is therefore more environmentally sound than lead telluride, which is toxic.

Thermoelectric energy conversion results from the Peltier and Seebeck effects. The performance of thermoelectric materials is estimated using the figure of merit ZT , defined as $ZT = \alpha^2 \sigma T \kappa^{-1}$, where α is the Seebeck coefficient (VK^{-1}), σ is the electrical conductivity ($\Omega^{-1}\text{m}^{-1}$), κ is the thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$) and T is the absolute temperature (K). Thermoelectric performance is enhanced by increasing the Seebeck coefficient and the electrical conductivity, and by decreasing the thermal conductivity.

Melt growth and powder metallurgy methods have been used to prepare ZnSb.^{2–7)} Telkes has investigated the production of solar thermoelectric generators using *p*-type ZnSb.^{2–5)} However, according to reports in the available literature,^{9,10)} preparation of single-phase ZnSb has proved to be difficult. ZnSb undergoes a peritectic reaction at 819 K, indicating that prolonged heating is necessary to obtain single-phase ZnSb.⁸⁾

Processes such as mechanical alloying (MA) and mechanical grinding (MG), which produce finely ground metal powders, have been used to obtain homogeneous materials.^{9–12)} In general, finely ground materials have lower thermal conductivities than those of single crystals of the same materials because phonons can be scattered at grain boundaries. However, single-phase ZnSb has not been obtained by MA.^{9–12)} It has been reported that ductile Zn does not participate in mechanical alloying reactions, leading to Zn deficiency.¹¹⁾ In the present study, MG was applied to ZnSb preparation, and two different methods of heat treating the melt growth ingots before grinding and sintering were investigated.

Fig. 1 Schematic diagram of the MG process for preparation of ZnSb.

2. Experimental Procedures

ZnSb was prepared using two different MG processes. Figure 1 shows a schematic diagram of the MG processes.

MG process I consisted of making source ingots from the ZnSb melt, mechanical grinding (MG), and sintering. The source ingot was prepared by direct melting of Zn (99.9999%) and Sb (99.9999%) in an evacuated quartz ampoule at 923 K for 3 h, and quenching the ZnSb melt in the ampoule in water. The resultant quenched ingot was put into a stainless steel vessel and milled with silicon nitride balls. The grinding was carried out in a planetary ball mill for 100 h at a maximum speed of 180 rpm. The pulverized powders were then sieved and passed through the size of $150 \mu\text{m}$ in diameter. The pulverized powder was then set in stainless steel dies. The ground materials were obtained by hot-pressing at a sintering temperature of 673 K under a mechanical pressure of 147 MPa in an argon atmosphere.

*Graduate Student, Shimane University

In MG process II, the quenched ingots underwent an additional heat-treatment at 723 K for 100 h to produce a homogeneous single-phase material.

The densities of the materials prepared by the MG processes were measured at room temperature using the Archimedes method. Metallographic observations were made using an optical microscope. The materials were also investigated by X-ray diffraction (XRD) using Cu K α radiation in a 2θ range of 20° – 50° , and by differential thermal analysis (DTA). DTA measurements were made by heating the material to 873 K at a rate of 20 K min^{-1} in an argon atmosphere in alumina containers.

The thermoelectric properties were measured using a ResiTest8340 (Toyo Corporation). The equipment has a measurement error of less than 1%. The Seebeck coefficients α were estimated from the linear relationship between the thermoelectromotive force (E) and a temperature difference (ΔT) of up to 3 K, under vacuum over a temperature range of 300–573 K ($\alpha = E\Delta T^{-1}$). The electrical conductivities σ were measured by the van der Pauw method under vacuum over a temperature range of 300–573 K. The thermal conductivities κ of the mechanically ground materials were measured using the self-constructed instrument of static comparison method at room temperature.¹³⁾

Thermoelectric performances were evaluated using the dimensionless thermoelectric figure of merit ZT , where $ZT = \alpha^2 \sigma T \kappa^{-1}$.

3. Results and Discussion

Many cracks and pores were observed in the quenched ingots produced by process I. This indicated that thermal stress occurred during quenching and the accompanying transformations. The relative densities of the mechanically ground materials after process I and after process II are listed in Table 1. All the materials had relative densities of more than 99%; the theoretical density was 6.38 g cm^{-3} .¹⁴⁾ The results indicate that in both process I and process II pulverizing and sintering were necessary to obtain dense materials.

Figure 2 shows the XRD patterns of the mechanically ground materials and of the quenched ingots. All the observed diffraction peaks were identified as those of the ZnSb single phase.

Figure 3 shows the DTA curves for the mechanically ground materials. Increasing the temperature caused the formation of a small endothermic peak at 780 K corresponding to a eutectoid reaction between ZnSb and Sb. The large endothermic peak at 823 K corresponds to the melting point of ZnSb. These XRD and DTA results consistently indicated that single-phase ZnSb was produced by both of the MG

Fig. 2 XRD patterns of mechanically ground materials and of quenched ingots. Single-phase ZnSb was obtained using both MG process I and MG process II.

Fig. 3 DTA curves of mechanically ground materials and of quenched ingots.

Fig. 4 Seebeck coefficient versus temperature for mechanically ground materials and for quenched ingots.

Table 1 Thermal conductivities and relative densities at room temperature for mechanically ground materials.

Sample	Thermal conductivity, κ ($\text{W m}^{-1} \text{K}^{-1}$)	Density (g cm^{-3})	Relative density (%)
process 1	1.41	6.36	99
process 2	1.36	6.34	99

(Theoretical density: 6.38 g cm^{-3})¹⁴⁾

processes. It is considered that brittle ZnSb ingots are easy to pulverize.

Figures 4–6 show plots of thermoelectric properties versus temperature for the mechanically ground materials. The materials were p -type; their Seebeck coefficients α were all similar and were in the range 400 – $500\text{ }\mu\text{V K}^{-1}$ at room temperature. α values showed similar behavior to that of the temperature dependence (Fig. 4). At room temperature, the electrical conductivities σ of the mechanically ground

Fig. 5 Electrical conductivity versus temperature for mechanically ground materials and for quenched ingots.

Fig. 6 Dimensionless thermoelectric figure of merit versus temperature for mechanically ground materials and for quenched ingots. The thermal conductivity was calculated using fixed values measured at room temperature.

materials were in the range 2.88×10^3 to $3.21 \times 10^3 \Omega^{-1}\text{m}^{-1}$, while σ values for the quenched ingots were in the range 0.54×10^3 to $0.66 \times 10^3 \Omega^{-1}\text{m}^{-1}$. The values for the quenched ingots were lower than those obtained for the mechanically ground materials. This may be because the quenched ingots had many microcracks. There were many similarities between the plots of σ values versus temperature for the quenched ingots and for the mechanically ground materials (see Fig. 5).

The thermal conductivity κ of the mechanically ground materials was $1.41 \text{ W m}^{-1}\text{K}^{-1}$ at room temperature (see Table 1), which was lower than the values reported for materials prepared using conventional melt growth and powder metallurgical methods.¹⁵⁾ This showed that the MG process produced finely ground ZnSb, resulting in decreased thermal conductivity.

Figure 6 shows a plot of the dimensionless thermoelectric figure of merit (ZT) versus temperature for the mechanically ground materials and for the quenched ingots. The ZT values

for the mechanically ground materials were 0.6–0.8 at 573 K; the fixed value room temperature thermal conductivities were adopted. For the quenched ingots, $\kappa = 2.7 \text{ W m}^{-1}\text{K}^{-1}$ was used.¹⁵⁾

These results indicated that heat-treatment in the MG process did not result in appreciable differences in the Seebeck coefficients, electrical conductivities, or dimensionless thermoelectric figures of merit of the materials. Therefore, MG process I is a simple method for the preparation of single-phase and crack-free ZnSb materials.

4. Conclusions

In the present study, two MG processes (I and II) were used to prepare single-phase ZnSb. Process II included additional heat-treatment to obtain a homogeneous material. The results are summarized as follows:

- (1) Single-phase, dense ZnSb was successfully prepared by MG processes which consisted of preparing the source ingots from a ZnSb melt, grinding the ingots, and hot-pressing. The quenched ingots had many cracks and pores. Thus, grinding and sintering were necessary to obtain dense, homogeneous materials.
- (2) The thermal conductivities of the mechanically ground materials reached $1.41 \text{ W m}^{-1}\text{K}^{-1}$ at room temperature, a value which is lower than that reported for other available materials.
- (3) All of the mechanically ground materials were p -type, with a dimensionless thermoelectric figure of merit in the range 0.6–0.8 at 573 K.
- (4) MG process I was found to be a simple method for the preparation of single-phase, crack-free ZnSb.

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