Single-Phase $\beta$-Zn$_4$Sb$_3$ Prepared by a Mechanical Grinding Method

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Single-phase $\beta$-Zn$_4$Sb$_3$ materials were 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. In process 1, the ingot was obtained by quenching the melt in water within an evacuated quartz ampoule. In process 2, the ingot was heat-treated for 100 h at 723 K after process 1. In process 3, the ingot was heat-treated for a total of 200 h in two stages at 723 K and 673 K after process 1. The resultant ingots were mechanically ground and sintered at 623 K by hot pressing. The sintered materials were characterized by x-ray diffraction, differential thermal analysis (DTA), and thermoelectric property measurements. The thermal conductivity of the sintered materials was 0.88 W m$^{-1}$ K$^{-1}$ at room temperature, being slightly lower than that reported for the materials prepared by a conventional method. Results indicate that the dimensionless figure of merit of the single-phase $\beta$-Zn$_4$Sb$_3$ ranged from 1.06 to 1.31 at 573 K.

Key words: Thermoelectric material, $\beta$-Zn$_4$Sb$_3$, mechanical grinding, figure of merit, zinc, antimony

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 K to 650 K).$^{1,2}$ It has a relatively low cost and can potentially be used as a substitute for high-performance lead tellurides that contain toxic lead.$^{2,3}$

The three modified forms of $\alpha$-, $\beta$-, and $\gamma$-Zn$_4$Sb$_3$ are stable below 263 K, between 263 K and 765 K, and above 765 K, respectively.$^4$ Melt-growth and powder-metallurgy methods have been used to prepare $\beta$-Zn$_4$Sb$_3$ materials.$^5$-10 $\beta$-Zn$_4$Sb$_3$ crystals prepared by conventional melt growth contain many cracks that result from thermal stress because of $\gamma$- to $\beta$-phase transformations. Recently, a crack-free single-phase $\beta$-Zn$_4$Sb$_3$ material was obtained using direct melting followed by a two-stage heat treatment, also being reported elsewhere.$^{10}$

Finely grained powder-metallurgical processes such as mechanical alloying (MA) and mechanical grinding (MG) have been used to obtain homogeneous materials.$^{11-14}$ In general, fine-grain-size materials have lower thermal conductivities 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.$^{11-13}$

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

EXPERIMENTAL PROCEDURES

The source ingot with a nominal Zn$_4$Sb$_3$ composition was synthesized at 923 K for 3 h by direct melting of the constituent elements Zn (99.9999%) and Sb (99.9999%) in an evacuated quartz ampoule. Figure 1 shows a schematic diagram of the MG process used to prepare $\beta$-Zn$_4$Sb$_3$.

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.

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 Cu Kα (radiation in a 2θ range from 20° to 50°) 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.

Measurements of the Seebeck coefficient and the electrical conductivity were performed on a Resistest8300. The Seebeck coefficient α was estimated from the linear relationship between the thermoelectromotive force (E) and a temperature difference (AT) of up to 3 K under vacuum in a temperature range from 300 K to 573 K. The electrical conductivity σ of the sintered materials were measured by the van der Pauw method under vacuum in a temperature range from 300 K to 573 K. The thermal conductivity j was measured using the constructed static comparison method at room temperature in vacuum. The measurement system consisted of a reference quartz and measurement material. Quartz (κ = 1.411 W m⁻¹ K⁻¹) was used as a reference.

Thermoelectric performance was evaluated by the power factor $z^2\alpha$ and the dimensionless thermoelectric figure of merit $ZT$ given by $ZT = z^2\alpha T/\kappa$, where $T$ is absolute temperature.

**RESULTS AND DISCUSSION**

The relative density for MG materials is listed in Table I. All MG materials were dense, with a relative density ranging from 98% to 100%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal Conductivity, $\kappa$ (W m⁻¹ K⁻¹)</th>
<th>Density (g cm⁻³)</th>
<th>Relative Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process 1</td>
<td>0.88</td>
<td>6.26</td>
<td>100</td>
</tr>
<tr>
<td>Process 2</td>
<td>0.88</td>
<td>6.11</td>
<td>98</td>
</tr>
<tr>
<td>Process 3</td>
<td>0.88</td>
<td>6.13</td>
<td>99</td>
</tr>
</tbody>
</table>

Theoretical density: 6.20 g cm⁻³.