

# Fast preparation and thermoelectric properties of $\text{Zn}_4\text{Sb}_3$ by HPHT

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In this paper, crack-free bulk thermoelectric material  $\text{Zn}_4\text{Sb}_3$  was prepared rapidly by high pressure and high temperature (HPHT) method. Near a single-phase  $\text{Zn}_4\text{Sb}_3$  specimen was obtained using nominal stoichiometric powder mixtures, which were indexed by powder X-ray diffraction. The temperature-dependent thermoelectric properties including the Seebeck coefficient and electrical resistivity were studied. The maximum power factor of  $\text{Zn}_4\text{Sb}_3$  specimen prepared by HPHT reaches  $10.8 \mu\text{W}/(\text{cmK}^2)$  at 637 K, which is comparable to the published data. The results show that the HPHT offers potential processing route to produce the thermoelectric material  $\text{Zn}_4\text{Sb}_3$  quickly and effectively.

Keywords: *thermoelectric properties; HPHT;  $\text{Zn}_4\text{Sb}_3$*

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## 1. Introduction

Thermoelectric materials are a class of functional materials which can be used both as generators and refrigeration devices [1, 2]. These thermoelectric devices have many advantages such as compactness, silent operation, reliability, lack of any moving parts, and long period of operation [3]. Effectiveness of a material for thermoelectric applications is determined by the figure-of-merit:

$$ZT = T\sigma S^2/\kappa \quad (1)$$

where  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity, and  $\kappa$  is the thermal conductivity. The electrical properties are determined by the power factor, defined as  $\sigma S^2$  or  $S^2/\rho$  ( $\rho$  is the electrical resistivity). As can be seen from the equation of the figure of merit, a good thermoelectric material must have a large power factor and low thermal conductivity.

$\text{Zn}_4\text{Sb}_3$  is one of the best thermoelectric materials, which has a large power factor

( $\sim 10 \mu\text{W}/\text{cmK}^2$ ) and a low thermal conductivity ( $\sim 0.6 \text{ W}/\text{mK}$ ). For this reason it has drawn a great deal of attention in recent years [4–7]. It is well known that  $\text{Zn}_4\text{Sb}_3$  has three structural phase modifications, namely  $\alpha\text{-Zn}_4\text{Sb}_3$  ( $T \leq 263 \text{ K}$ ),  $\beta\text{-Zn}_4\text{Sb}_3$  ( $263 \text{ K} \leq T \leq 765 \text{ K}$ ) and  $\gamma\text{-Zn}_4\text{Sb}_3$  ( $T \geq 765 \text{ K}$ ). Due to different coefficients of thermal expansion for  $\gamma$  and  $\beta$ , the cracks formed upon cooling are the major problem [4]. Large crack-free  $\text{Zn}_4\text{Sb}_3$  samples can be obtained by the methods such as melting in evacuated quartz ampoule followed by granulation and hot consolidation [5] and bulk mechanical alloying followed by hot pressing [6]. But these methods involve rather complicated processes which are not suitable for industrial application. Other direct methods such as melting followed by slow cooling [7] were also adopted to synthesize  $\text{Zn}_4\text{Sb}_3$ . But they need a long time heat treatment, which makes the samples more expensive.

Compared with the other preparation methods for thermoelectric materials, the HPHT method has many advantages, including the ability to synthesize rapidly and cleanly, typically without introducing disorders, phase separation, or other complicat-

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ing factors [8]. In our previous studies, thermoelectric materials of PbTe and AgSbTe<sub>2</sub> were rapidly (~20 minutes) prepared by HPHT [9, 10]. Up to date, there has been no report on the Zn<sub>4</sub>Sb<sub>3</sub> sample prepared by HPHT. In this study, thermoelectric material Zn<sub>4</sub>Sb<sub>3</sub> was synthesized by HPHT rapidly and the temperature dependence of the thermoelectric properties was studied.

## 2. Experimental

Zn<sub>4</sub>Sb<sub>3</sub> was prepared in a cubic anvil HPHT apparatus (SPD-6×1200). The raw materials of Zn and Sb of 99.999 % purity were pressed into a disk after mixing them in a stoichiometric ratio. The pole shaped sample was then immediately placed in the container and compressed to 4.0 GPa at room temperature. The sample was then heated to 1050 K and melted for 20 minutes. Subsequently, the samples were cooled to 700 K and sintered for 20 minutes. Finally, the electrical power for heating was cut off and the pressure was released. The pressure was estimated by the oil press load, which was calibrated by the pressure induced phase transitions of bismuth, thallium and barium metals. The temperature was estimated by the relationship of input heater power and temperature, which was measured by the ChromelAlumel thermocouples.

The collected samples were cut and polished on the surface for thermoelectric measurements. Powder X-ray diffraction (PXRD) measurements with Cu K $\alpha$  radiation were performed on an X-ray diffractometer (D/MAX-RA). The Seebeck coefficient and electrical resistivity at different temperatures from 303 K to 685 K were measured simultaneously with a ZEM-3 apparatus (ULVAC-RIKO).

## 3. Results and discussions

The PXRD patterns of Zn<sub>4</sub>Sb<sub>3</sub> synthesized by HPHT are shown in Fig. 1. All of the diffraction peak positions and (*hkl*) values match very well with the standard diffraction data of Zn<sub>4</sub>Sb<sub>3</sub>. The results indicate that the sample prepared by HPHT is near single phase Zn<sub>4</sub>Sb<sub>3</sub> with a little remnant ZnSb. As seen from the photograph for Zn<sub>4</sub>Sb<sub>3</sub> synthesized by HPHT in Fig. 2, the sample is crack free.

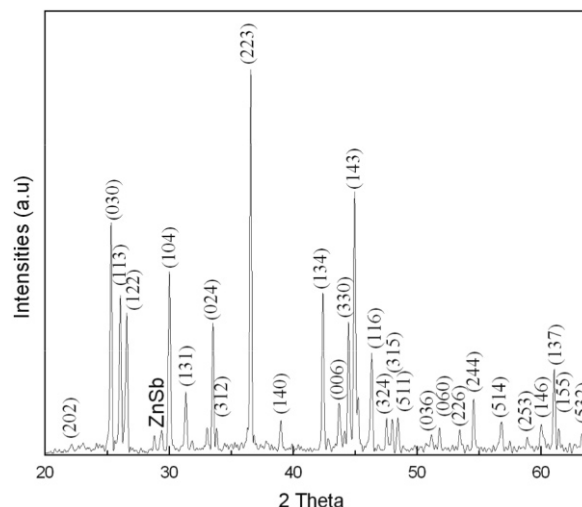


Fig. 1. Power XRD patterns of Zn<sub>4</sub>Sb<sub>3</sub> prepared by HPHT.

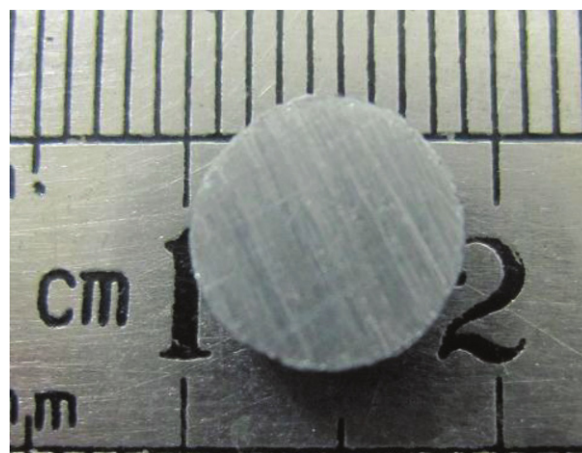


Fig. 2. Photograph of Zn<sub>4</sub>Sb<sub>3</sub> synthesized by HPHT.

The density of the Zn<sub>4</sub>Sb<sub>3</sub> sample, which is about 98.6 % of the theoretical density, was measured by the Archimedes method.

Fig. 3 presents the electrical resistivity as a function of temperature for Zn<sub>4</sub>Sb<sub>3</sub> prepared by HPHT. The electrical resistivity of Zn<sub>4</sub>Sb<sub>3</sub> has the value of  $1.83 \times 10^{-3} \Omega\text{cm}$  at room temperature which is lower than that of the same sample prepared by other methods [4–7]. The decreased electrical resistivity for Zn<sub>4</sub>Sb<sub>3</sub> prepared by HPHT could be associated with the high density obtained at high pressure. With the increase of temperature the electrical resistivity first increases and then decreases. The maximum

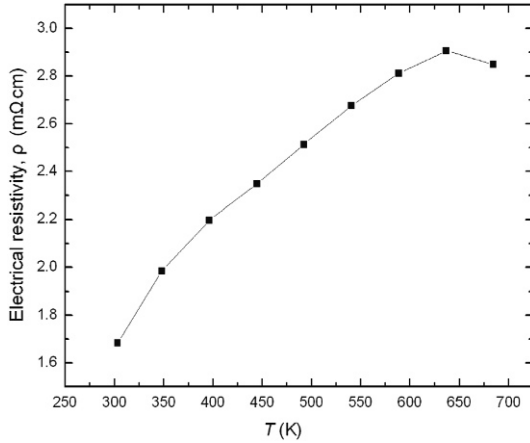


Fig. 3. Temperature dependence of the electrical resistivity for  $\text{Zn}_4\text{Sb}_3$  prepared by HPHT.

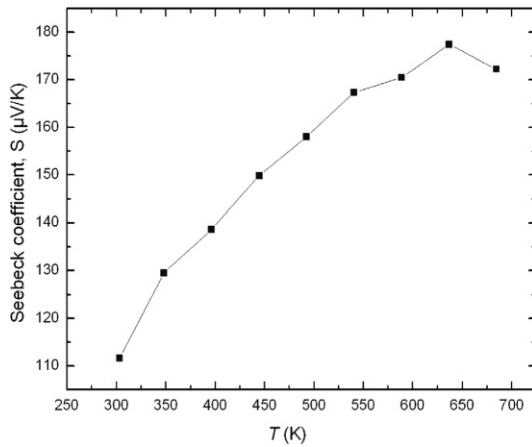


Fig. 4. Temperature dependence of the Seebeck coefficient for  $\text{Zn}_4\text{Sb}_3$  prepared by HPHT

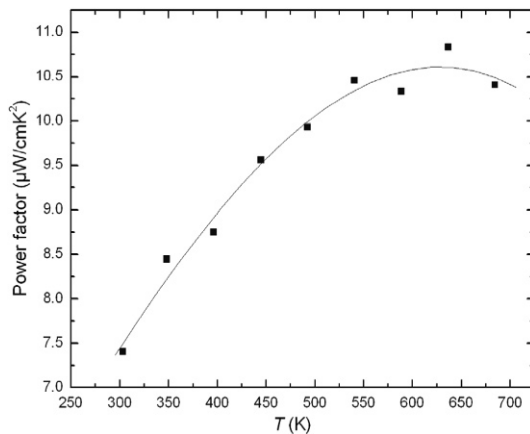


Fig. 5. Variation of power factor with temperature for  $\text{Zn}_4\text{Sb}_3$  prepared by HPHT.

value reaches  $2.9 \times 10^{-3} \Omega\text{cm}$  at the temperature of 637 K.

The temperature-dependent Seebeck coefficient of  $\text{Zn}_4\text{Sb}_3$  prepared by HPHT is shown in Fig. 4. The Seebeck coefficient has positive value, which presents *p*-type conductivity. The Seebeck coefficient for HPHT synthesized  $\text{Zn}_4\text{Sb}_3$  at room temperature is about  $106.9 \mu\text{V/K}$ , which is close to the result of Caillat ( $113 \mu\text{V/K}$ ). With increasing temperature in the extrinsic region, the Seebeck coefficient increases up to a maximum value ( $177.4 \mu\text{V/K}$ ) occurring at about 637 K, after which mixed conduction (intrinsic and extrinsic conduction) appears, lowering the Seebeck coefficient.

The power factor calculated by the value of the Seebeck coefficient and electrical resistivity for HPHT synthesized  $\text{Zn}_4\text{Sb}_3$  is shown in Fig. 5. The power factor of  $\text{Zn}_4\text{Sb}_3$  at room temperature is about  $7.4 \mu\text{W}/(\text{cmK}^2)$  which is 10 % higher than that of the result reported by Caillat. The enhanced power factor at room temperature can be due to the reduced resistivity. With the increase of temperature, the power factor increases. The largest value reaches  $10.8 \mu\text{W}/(\text{cmK}^2)$  at 637 K which is comparable to the results reported by others [4–7].

Thermal conductivity measurements were not performed in this study, so that direct estimation of  $ZT$  could not be made. However, the thermal conductivities of  $\text{PbTe}$  and  $\text{AgSbTe}_2$  prepared by HPHT are nearly identical to the same sample prepared at ambient pressure according to our early study [9, 10]. So we assume that the thermal conductivity of  $\text{Zn}_4\text{Sb}_3$  prepared by HPHT does not differ significantly from that of the sample prepared at normal pressure. The largest  $ZT$  of HPHT synthesized  $\text{Zn}_4\text{Sb}_3$  was estimated by referring to the thermal conductivity reported in the literature [4] to be about 1.02 at 684.6 K, which is comparable to that of the state-of-the art thermoelectric materials such as  $\text{Bi}_2\text{Te}_3$  and  $\text{PbTe}$ .

## 4. Conclusion

Crack free  $\text{Zn}_4\text{Sb}_3$  was rapidly synthesized by HPHT. The electrical resistivity and Seebeck coefficient of  $\text{Zn}_4\text{Sb}_3$  sample first increase and then decrease with an increase of temperature. The ther-

moelectric performances (including power factor and estimated figure of merit) for HPHT synthesized  $\text{Zn}_4\text{Sb}_3$  are comparable to the data for the same sample prepared by other methods. The results show that the HPHT method is potentially a simple and rapid method to prepare small  $\text{Zn}_4\text{Sb}_3$  samples.

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