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Thermoelectric Properties of β-Zn_4Sb_3 Synthesized by Mechanical Alloying and Pulse Discharge Sintering

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Thermoelectric power generation is a helpful method for harnessing waste thermal energy, particularly covering a middle temperature range between 500 and 800 K. A β-Zn_4Sb_3 compound has become the focus of attention as a thermoelectric material applicable to thermoelectric power generation around 700 K. In this research, a method combining the mechanical alloying with the pulse discharge sintering was adopted to obtain the sintered compact of β-Zn_4Sb_3. Pure zinc and antimony powders were used as the starting material for mechanical alloying. These powders were mixed in the stoichiometry ratio of 4 to 3, or more Zn-rich. The mechanical alloying was carried out by planetary ball milling under conditions of fixed revolution speed and variable milling time. The influence of the milling time on the synthesis of β-Zn_4Sb_3 was investigated. The sintering was executed at two sintering temperatures and under fixed conditions of sintering time, pressing pressure, and atmosphere. The influences of the sintering temperature of pulse discharge sintering on the polycrystalline grain size and the thermoelectric properties were also studied. The following results were clarified. The phases of ZnSb and Zn are easily obtained by mechanical alloying for 50 h or longer time. These phases change to a single phase of β-Zn_4Sb_3 through pulse discharge sintering under the optimum condition of Zn-rich mixing. The sintered compact of β-Zn_4Sb_3 with 1.17 of nondimensional figure of merit can be obtained at 673 K with the proposed mechanical alloying with pulse discharge sintering method.

Nomenclature

D	=	polycrystalline grain size, m
K	=	Scherrer constant
L_0	=	Lorentz number, V^2K^{-2}
T	=	absolute temperature, K
ZT	=	thermoelectric (nondimensional) figure of merit
α	=	Seebeck coefficient, VK^{-1}
β	=	full width at half-maximum of x-ray diffraction peak at diffraction angle θ, rad
θ	=	diffraction angle, rad
κ	=	thermal conductivity, $Wm^{-1}K^{-1}$
κ_E	=	electron thermal conductivity, $Wm^{-1}K^{-1}$
κ_L	=	lattice thermal conductivity, $Wm^{-1}K^{-1}$
λ	=	wavelength of x-ray source, m
ρ	=	electrical resistivity, Ωm

I. Introduction

IN MOST current energy systems, 30–70% of the primary or chemical energy originating from fossil fuels such as petroleum, natural gas, and coal is not used and is wasted during the energy conversion. It is very important from a standpoint of saving energy to generate electricity from such waste-heat resources. Thermoelectric power generation systems are solid apparatuses constructed with thermoelectric semiconductors and they can directly convert the heat energy into electrical energy. Thermoelectric devices are therefore promising to generate electricity from various heat resources such as automobiles, cogeneration systems, and waste material incinerators. The exhaust heat from various energy systems has a middle range of temperature (600–800 K). A development of high-performance thermoelectric materials applicable in this middle range of temperature is thus indispensable to realize the thermoelectric power generation systems for routine use.

It has been known that the Zn–Sb system includes the compounds of ZnSb, Zn_3Sb_2, α-Zn_4Sb_3, β-Zn_4Sb_3, and γ-Zn_4Sb_3. Soma et al. [1] studied the thermoelectric properties of the α-Zn_4Sb_3 compound in the temperature range of 4 to 260 K. The β-Zn_4Sb_3 compound has attracted increasing attention as a thermoelectric material applicable to thermoelectric power generation around 700 K, because Caillat et al. [2] reported that the sintered compact of this compound has a very low thermal conductivity, an excellent performance, and that the maximum nondimensional figure of merit ZT is 1.3 at 670 K. Yamamoto et al. [3] successfully synthesized the β-Zn_4Sb_3 compound by bulk mechanical alloying (BMA) and obtained the maximum ZT of 1.0 at 680 K. Recently, Ohzora et al. [4] succeeded in preparing the compound having the excellent ZT of 1.6 through an optimum sintering process. Here, the nondimensional figure of merit is defined as follows.

$$ZT \equiv \frac{\alpha^2 T}{\kappa \rho} \tag{1}$$

The recent studies on the β-Zn_4Sb_3 compound are summarized in Table 1. This table includes data of the mole ratio of Zn to Sb, the production process used in the study, and the maximum figure of merit ZT_{max}.

The mechanical alloying (MA) method is a material processing technique for assembling metal constituents with a controlled microstructure by the repeated welding, fracturing, and rewelding of a mixture of powder particles, and it is useful for synthesizing intermetallic compounds. Pulse discharge sintering (PDS), alias spark plasma sintering, is a kind of hot pressing method that has an advantage of rapid and activating sintering at relatively low temperatures. The MA–PDS method combining MA with PDS is powerful for promoting the synthesis of desired compounds and for creating a sintered body, with the fine microstructure giving a decrease of thermal conductivity and an improvement of material strength. In this study, we attempted to synthesize the β-Zn_4Sb_3 compound with this MA–PDS method as a new manufacturing process, replacing the traditional melting, crushing, and sintering

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Table 1 Recent studies on β-Zn_4Sb_3

Researchers	Mole ratio Zn/Sb	Production process[a]	ZT_{max}
Caillat et al. [2]	4/3	Melting (1023 K, 2 h) to crushing to HP to HT (673 K, 5 days)	1.3 (670 K)
Yamamoto et al. [3]	4/3, 4.1/3, 4.19/3, 4.29/3	BMA to HT (623 K, 5 h) to HP (773 k, 100 MPa, 5 h)	1.0 (680 K)
Ohzora et al. [4]	4.03/3	Melting to crushing to HP (673 K, 743 K, 39.2 MPa, 5 h) to HT (523 K, 100 h)	1.6 (673 K)
Zhang et al. [5]	3/3, 3.82/3, 3.98/3, 4.27/3, 7/3	Melting (1023 K, 2 h) to crushing to HP (733 K, 50–60 MPa, 3 h)	1.3 (673 K)

[a]HP is hot pressing, HT is heat treatment, and BMA is bulk mechanical alloying.

methods for achieving an excellent thermoelectric performance. The mixing mole ratio of zinc to antimony powders, the milling time in MA, and the sintering temperature are changed. Influences of these factors on synthesized phases and on their thermoelectric properties are investigated. The syntheses of β-Zn_4Sb_3 were confirmed reproducibly by x-ray diffraction (XRD) analysis. The thermoelectric properties were measured and the optimum conditions of MA and PDS were examined.

II. Experimental

A. Sample Powders and Mixing Ratio

The commercially available zinc powder (purity of 99.9% and size of less than 75 μm) and antimony powder (purity of greater than 99.9% and size of less than 45 μm) were used as starting powders. The two powders were blended in a stoichiometric mole ratio of β-Zn_4Sb_3 (Zn/Sb = 4/3) and in several Zn-rich mole ratios (Zn/Sb = 4.03/3, 4.06/3, 4.09/3, 4.12/3, and 4.15/3). The mixed powders of 30 g were weighed out.

B. Mechanical Alloying

A zirconia pot (capacity of 500 ml) and zirconia balls (diameter of 5 mm) were used for mechanical alloying. A weight ratio of powder to balls was 1/20. The 0.5 mass % hexane was added to the pot for preventing adhesion of the powder on the surfaces of the pot and balls during the mechanical alloying process. After substituting argon gas into the pot and making the pot airtight, the mechanical alloying process was carried out under conditions of a fixed rotation speed of 150 rpm and different milling times of 0, 50, 75, 100, 200, and 300 h, by using planetary ball milling equipment (P-5, Fritsch Japan Co. Ltd.). Subsequently, the pot was opened in a globe box filled with argon gas and the resulting MA powders were collected in the atmosphere.

C. Pulse Discharge Sintering

The MA powders were sintered in pulse discharge sintering equipment (SPS-1050, SPS Syntex, Inc.). The procedure is as follows. The MA powder was packed into a cylindrical graphite container (20-mm i.d., 40-mm o.d., and 40 mm in height). The packed powder was sandwiched between graphite punches under a compression pressure of 1 MPa, heated to 473 K, and dried for 10 min in vacuum. Subsequently, the powder was compressed under 40 MPa, sintered at 673, 723, or 753 K for 20 min in vacuum or argon atmosphere, and then cooled down to the room temperature for 360 min. Disk-type sintered samples (20 mm in diameter and 5 mm in thickness) were made under various sintering conditions. The details of the temperature and compression pressure profiles used during pulse discharge sintering are shown in Fig. 1.

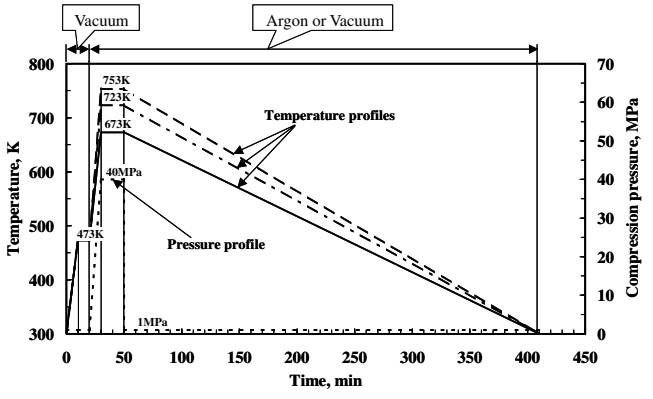


Fig. 1 Temperature profiles and compression pressure profiles during PDS.

D. Identification of Synthesized Phases and Estimation of Crystallite Size

The phases synthesized after MA and after PDS were identified by XRD analysis with Cu $K\alpha$ radiation (RINT2500TTR, Rigaku Corporation). The crystallite sizes in the MA-powder sample and in the sintered sample were also estimated from the XRD analysis. The polycrystalline grain size of the sample was obtained according to the following equation (Scherrer's equation).

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{2}$$

where the Scherrer constant K is 0.9 and the wavelength of the x-ray source λ is 0.15405 for Cu $K\alpha$ radiation. The mean value of the size D obtained from five main x-ray diffraction peaks in each sample was used as a typical polycrystalline grain size. The value might lack accuracy in the grain size a little, but it is an effective value that can indicate the state of grain refining.

E. Measurements of Thermoelectric Properties

After the sintered samples were cut into the prescribed shape, their Seebeck coefficient and electrical resistivity were measured with thermoelectric measuring equipment (ZEM-2, Ulvac-Riko, Inc.), based on steady direct-current and direct-current four-terminal methods, respectively. The thermal conductivity was measured with thermal-constant measuring equipment (TC-7000, Ulvac-Riko, Inc.), based on the laser-flash method.

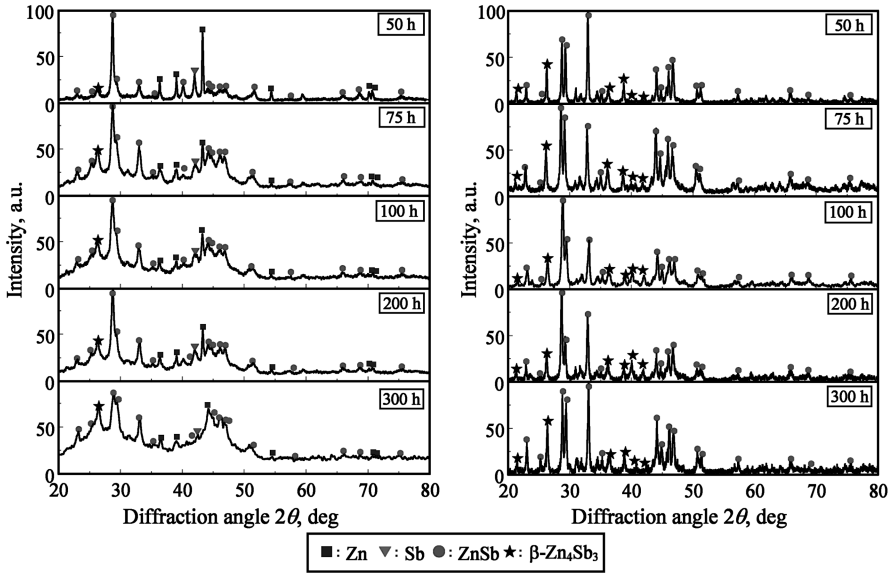
F. Outward Appearance Observation of Sintered Bodies

To survey the optimum sintering condition for making a sound or crack-free sintered body, the outward appearances of the sintered bodies made under various sintering conditions were observed and their images were taken by a digital camera. The MA powder was prepared by mechanically alloying the mixed powder (mole ratio Zn/Sb = 4.09/3) under the conditions of 150 rpm and 100 h. The samples for the observation were prepared by sintering the MA powder at 673, 723, or 753 K in vacuum or argon atmosphere.

III. Results and Discussions

A. Influences of Milling Time on Synthesized Phases and Polycrystalline Grain Size

The influences of milling time on x-ray diffraction patterns of the powders after MA (mole ratio Zn/Sb = 4/3) and of their bulk materials sintered at 723 K in argon atmosphere are shown in Figs. 2a and 2b, respectively. In the diffraction patterns after MA, the diffraction peak becomes broader after milling for the time longer than 75 h. The principal phases are ZnSb and Zn, regardless of the milling time. Though the synthesis of β-Zn_4Sb_3 progressed after PDS, the phase of ZnSb still remains as the principal phase. In both MA powder and PDS-bulk material, the identified phases hardly change for milling times of 50 to 300 h. The identification results of the phases synthesized from the mixed powder (mole ratio



a) MA powder **b) PDS-bulk material**

Fig. 2 Influences of milling time on x-ray diffraction patterns of MA powder and PDS-bulk material sintered at 723 K.

$Zn/Sb = 4/3$) after MA and after PDS at 723 K in argon atmosphere are summarized in Table 2. The results for the milling time of 0 h stand for the identified phases of mixed powder and its sintered body. It is noted from this table that the principal phases after MA are ZnSb and Zn and that the ZnSb compound is always the principal phase after PDS. The results also suggest that the phase of ZnSb is easily synthesized through the MA–PDS process at a mole ratio $Zn/Sb = 4/3$, regardless of milling time.

The polycrystalline grain sizes obtained with Scherrer's equation are shown in Fig. 3. In the MA powders in the mole ratio $Zn/Sb = 4/3$, the polycrystalline grain size decreases with the increase of milling time up to 75 h and it becomes about 15 nm for the milling time longer than 75 h. On the other hand, the minimum polycrystalline grain size after PDS at 723 K in argon atmosphere is obtained for the milling time of around 100 h. It seems that the MA process longer than 100 h causes MA powders to accumulate more internal strain, leading to the grain growth in the sintered body during the PDS process.

B. Influences of Mole Ratio Zn/Sb on Synthesized Phases

Figure 4 shows the influences of mole ratio Zn/Sb on the x-ray diffraction patterns of the powders after 100 h MA and of their bulk materials sintered at 723 K in argon atmosphere. The diffraction patterns after MA hardly change for the mole ratios Zn/Sb of 4/3 to 4.15/3. However, they drastically change after PDS, and a single phase of β-Zn_4Sb_3 is identified for the mole ratios Zn/Sb of 4.06/3 and 4.09/3. The identification results of phases synthesized after 100 h MA and after PDS at 723 K in argon atmosphere for various Zn-rich mole ratios are summarized in Table 3, together with the result of phases synthesized after PDS at 673 K in argon atmosphere for the mole ratio Zn/Sb of 4.09/3. The phases of ZnSb and Zn are identified from all MA powders, regardless of the Zn-rich mole ratio. These phases are also identified after PDS at 673 K in argon atmosphere for the mole ratio Zn/Sb of 4.09/3. The single phase of β-Zn_4Sb_3 is identified after PDS at 723 K for the mole ratios Zn/Sb of 4.06/3 and 4.09/3. Figure 3 and Table 3 indicate that the single phase of β-Zn_4Sb_3 is synthesized during sintering and that the optimum condition of mole ratio of mixed powder exists.

C. Outward Appearance Observation of Sintered Bodies

It is important that the optimum sintering condition for making a sound sintered body of β-Zn_4Sb_3 compound with high thermoelectric performance is discovered. The outward appearances of the sintered samples made under various sintering conditions are shown in Fig. 5. The same MA powder (mole ratio $Zn/Sb = 4.09/3$ and 100 h MA) was used for making all samples shown in Fig. 5. The surface of each disk-type sample is polished with SiC sandpaper to see if the sample has cracks. Figure 5a shows the existence of cracks on the surface of the sample sintered at 723 K in vacuum. The sample sintered at a lower temperature of 673 K in vacuum also had cracks. Although clear cause of the cracking is uncertain, sintering in vacuum might cause the evaporation of residual zinc and the part in which zinc was lost might become the weak part in strength. Figure 5b shows the surface of the sample sintered at 723 K in argon atmosphere. The surface with metallic luster has no cracks. A similar result was obtained in the sample sintered at a lower temperature 673 K in argon atmosphere, regardless of the difference of synthesized compounds. A result of the sample sintered at 753 K in argon atmosphere is shown in Fig. 5c. Only 30-K-higher sintering temperature creates the brittle structure without metallic luster. The cracks in the sample are likely produced while the sample is pulled out of the graphite container. For making a sound sintered body, the compacted powder should be sintered at 673 or 723 K in argon atmosphere. The porosity of all bulk materials after PDS at 673 and 723 K was less than 5%.

D. Influences of Sintering Temperature on Polycrystalline Grain Size and Thermoelectric Properties

The influences of sintering temperature on the polycrystalline grain size and the thermoelectric properties were investigated for the samples mixed with the optimum mole ratio Zn/Sb of 4.09/3 and milled for 100 h. Figure 6 shows the polycrystalline grain size of the MA powder and the PDS-bulk material sintered at 673 and 723 K, respectively. The polycrystalline grain size is hardly changed by sintering at 673 K. The polycrystalline grain size in the bulk material sintered at 723 K is obviously increased 1.8 times compared with that before sintering. Figure 6, Table 3, and outward appearance

Table 2 Principal phases synthesized under different conditions in milling time

Milling time, h	0	50	75	100	200	300
MA powder	Zn + Sb	ZnSb + Zn	ZnSb + Zn	ZnSb + Zn	ZnSb + Zn	ZnSb + Zn
PDS bulk material at 723 K	ZnSb	ZnSb	ZnSb	ZnSb	ZnSb	ZnSb

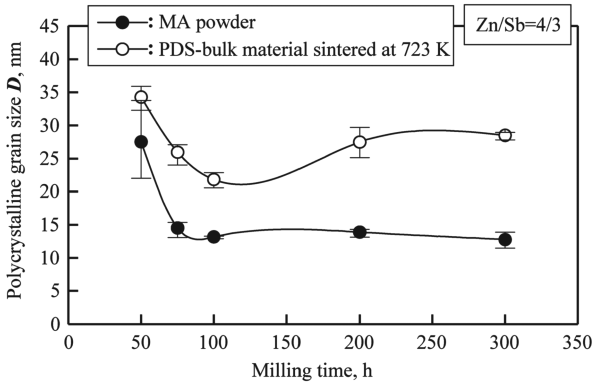


Fig. 3 Influences of milling time on polycrystalline grain sizes of MA powder and PDS-bulk material sintered at 723 K.

observation of sintered bodies indicate that although the PDS process at 673 K makes a sound sintered body, the process maintains the fine polycrystalline grain size and the phases of the MA powder. Table 3 shows that the bulk material sintered at 673 K with the mole ratio Zn/Sb of 4.09/3 has the same principal phases of ZnSb and Zn as the MA powder, whereas the bulk material sintered at 723 K with the same mole ratio has the single phase of β-Zn_4Sb_3. These results seem to be related to the thermoelectric properties.

We confirmed that the reproducibility of measurement values of the thermoelectric properties in this study was maintained with a difference less than 5%. The temperature dependencies of the electrical resistivity for the samples sintered at 673 and 723 K are shown in Fig. 7. The sample sintered at 723 K keeps the electrical resistivity lower than that sintered at 673 K over the measurement temperature range. In general, the finer polycrystalline grain size leads to the higher electrical resistivity in the same materials. But the synthesized phase of the sample sintered at 673 K is also different from that sintered at 723 K in this case. Thus, the difference in the electrical resistivity is likely attributable to the differences in both the synthesized phases and the polycrystalline grain sizes.

Figure 8 shows the comparison between the Seebeck coefficients of the two samples sintered at the different temperatures. The Seebeck coefficient of the sample sintered at 723 K is higher than that sintered at 673 K over the measurement temperature range. The Seebeck coefficient greatly depends on the materials. Thus, the difference of electrical resistivity at different sintering temperatures depends on whether the β-Zn_4Sb_3 phase exists in the sintered body.

The temperature dependencies of thermal conductivity of two samples sintered at the different temperatures are shown in Fig. 9. The thermal conductivity of the sample sintered at 723 K maintains a lower level than that sintered at 673 K over the measurement temperature range. This can be explained by the fact that the β-Zn_4Sb_3 phase has lower thermal conductivity than that of the ZnSb and Zn phases [5]. The thermal conductivity of thermoelectric materials is generally expressed as a total of the thermal conductivities due to the lattice and electronic contributions as follows.

$$\kappa = \kappa_L + \kappa_E \tag{3}$$

According to the Wiedemann–Franz Law, the electron thermal conductivity κ_E can be calculated as follows.

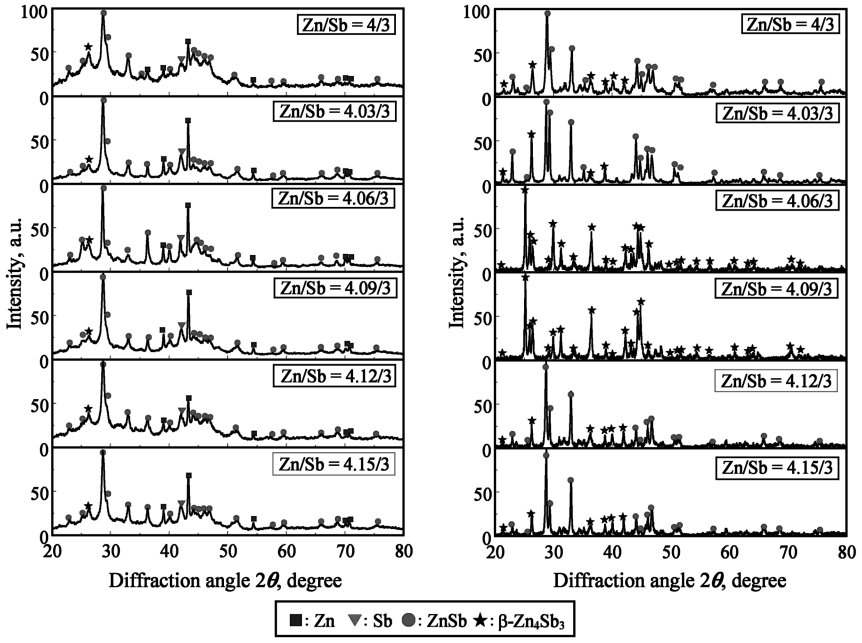
$$\kappa_E = \frac{L_0 T}{\rho} \tag{4}$$

where the Lorentz number L_0 is 2.45×10^{-8} V^2K^{-2}. The lattice thermal conductivity κ_L is estimated as a difference between the total thermal conductivity and the electron conductivity.

$$\kappa_L = \kappa - \kappa_E \tag{5}$$

Figure 10 shows the temperature dependencies of three types of thermal conductivities measured and calculated with Eqs. (4) and (5). The changes in these thermal conductivities of the samples sintered at 673 and 723 K are shown in Figs. 10a and 10b, respectively. The two types of samples sintered at the different temperatures have almost the same value change in the electron thermal conductivity. On the other hand, the lattice thermal conductivity of the sample sintered at 723 K is lower than that at 673 K over the measurement temperature range. It means that the phonon scattering in the β-Zn_4Sb_3 compound (namely, the phonon glass material) is stronger than that of the phase mixture of ZnSb and Zn (see Table 3), significantly decreasing the lattice thermal conductivity in the higher temperature range.

It becomes clear that the sintering at high temperature (723 K) creates the β-Zn_4Sb_3 compound, improving all thermoelectric properties and performance. The thermoelectric figure of merit ZT



a) MA powder **b) PDS-bulk material**

Fig. 4 Influences of mole ratio Zn/Sb on x-ray diffraction patterns of MA powder and PDS-bulk material sintered at 723 K.

Table 3 Principal phases synthesized under different conditions in mole ratio Zn/Sb

Mole ratio Zn/Sb	4.03/3	4.06/3	4.09/3	4.12/3	4.15/3
MA powder	ZnSb + Zn	ZnSb + Zn	ZnSb + Zn	ZnSb + Zn	ZnSb + Zn
PDS-bulk material at 673 K	N.A.	N.A.	ZnSb + Zn	N.A.	N.A.
PDS-bulk material at 723 K	ZnSb	β-Zn_4Sb_3	β-Zn_4Sb_3	ZnSb	ZnSb

defined with Eq. (1) is a useful index of thermoelectric performance. Figure 11 shows the temperature dependencies of the thermoelectric figure of merit for the samples sintered at the different temperatures. The sample sintered at 723 K has the maximum $\boldsymbol{ZT}$ of 1.17 at the measurement temperature of 673 K. This leads to high thermoelectric performance.

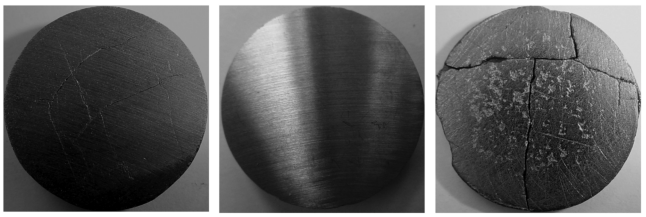


Fig. 5 Outward appearance pictures of samples sintered under different conditions.

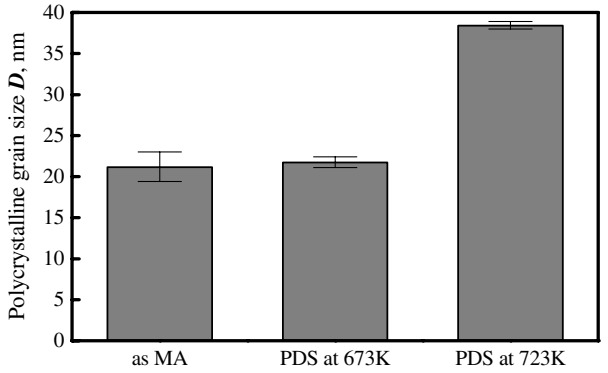


Fig. 6 Change in polycrystalline grain size at different sintering temperatures.

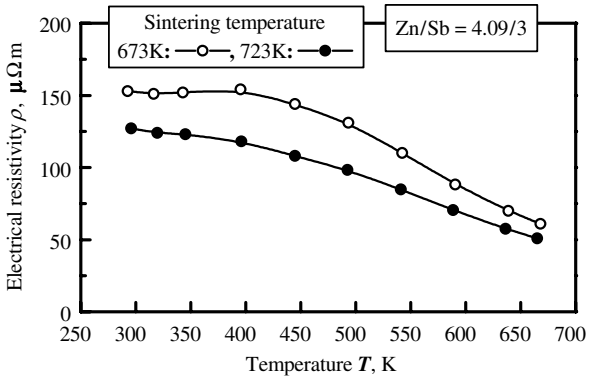


Fig. 7 Comparison between electrical resistivities of two samples sintered at different temperatures.

IV. Conclusions

The synthesis of β-Zn_4Sb_3 compound was attempted by using the MA–PDS method. The results obtained in this study are summarized as follows.

1) In the samples mixed with mole ratio Zn/Sb of 4/3 and milled for 50 to 300 h, the ZnSb compound is easily synthesized by PDS at 723 K.

2) The polycrystalline grain size of the sample powder with mole ratio Zn/Sb = 4/3 decreases with the milling time up to 75 h and it becomes about 15 nm in the milling time longer than 75 h. The minimum polycrystalline grain size after PDS is obtained in the milling time of around 100 h.

3) For making a sound sintered body, the compacted powder should be sintered at 673 or 723 K in argon atmosphere.

4) The β-Zn_4Sb_3 compound can be synthesized from the powder mixed with the mole ratio Zn/Sb of 4.06/3 or 4.09/3 and milled for 100 h by sintering at 723 K.

5) The β-Zn_4Sb_3 compound exceeds the mixture of ZnSb and Zn in all the thermoelectric properties (namely, the electrical resistivity, the Seebeck coefficient, and the thermal conductivity) and leads to the good thermoelectric performance.

6) The high-performance thermoelectric compact $\boldsymbol{ZT} > 1$ can be produced under the conditions of the optimum mole ratio of mixed powder and high sintering temperature (723 K).

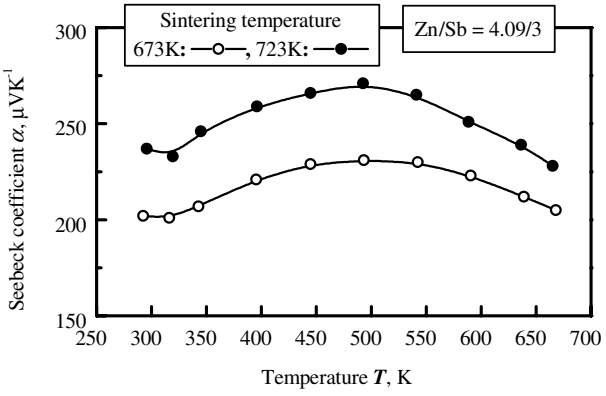


Fig. 8 Comparison between Seebeck coefficients of two samples sintered at different temperatures.

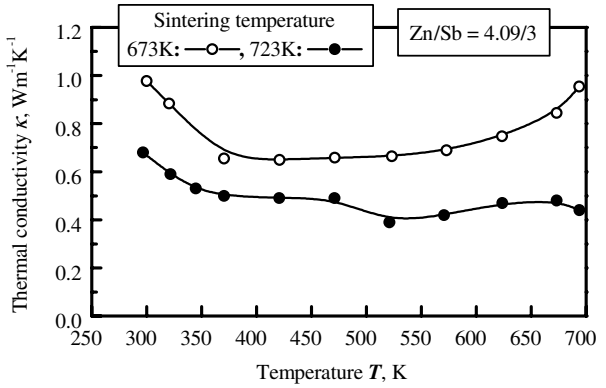


Fig. 9 Comparison between thermal conductivities of two samples sintered at different temperatures.

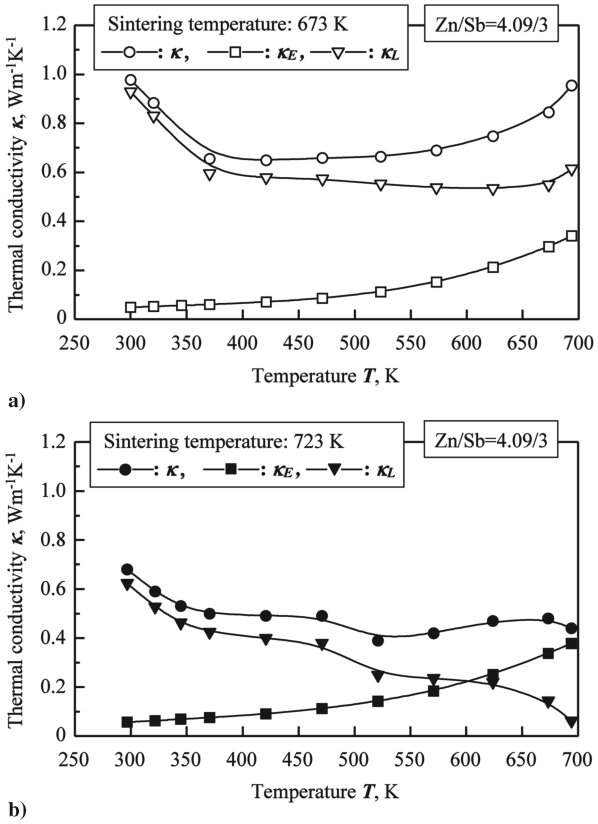


Fig. 10 Three types of thermal conductivities of two samples sintered at different temperatures.

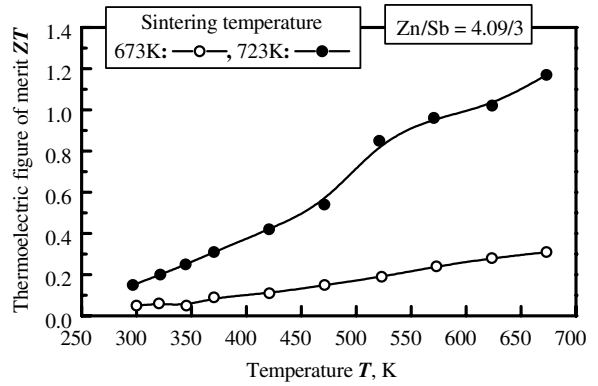


Fig. 11 Comparison between thermoelectric figures of merits of two samples sintered at different temperatures.

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