

Preparation of *n*-Type Bi₂Te_{2.85}Se_{0.15} Thermoelectric Semiconductor without Harmful Dopants

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Undoped *n*-type Bi₂Te_{2.85}Se_{0.15} compounds without harmful dopants were prepared by mechanical alloying (MA) and sintered by hot pressing (HP). Samples of the Bi₂Te₃-based materials had a nominal composition of Bi₂Te_{2.85}Se_{0.15}. Dopants were not added to control the carrier concentration. The constituent elements, i.e., Bi (5 N), Te (6 N), and Se (5 N), were weighed according to the target composition and milled with silicon-nitride balls. MA was carried out for 30 h. The resulting MA powder was sintered by HP in the temperature range 573–673 K under a mechanical pressure of 147 MPa in an argon atmosphere. The Seebeck coefficient α and electrical conductivity σ were measured in the temperature range 300–473 K. The thermoelectric performance was evaluated from the power factor P , where $P = \alpha^2 \sigma$. The obtained samples exhibited *n*-type conduction and the single-phase of Bi₂(Te,Se)₃. The power factor for an undoped sample sintered at 623 K was $4.4 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 313 K. This power factor was 88% of the value of $5.0 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ reported for single crystals of *n*-type doped Bi₂Te_{2.85}Se_{0.15}. These results indicated that it is not necessary to dope Bi₂Te_{2.85}Se_{0.15} prepared by an MA–HP process with harmful halide dopants to achieve carrier control. [doi:10.2320/matertrans.ME201108]

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1. Introduction

Solid solutions formed by alloying Bi₂Te₃ and Bi₂Se₃ are well known to have high thermoelectric performance at around room temperature;^{1,2)} these materials are widely used for electrical cooling devices such as small refrigerators, air conditioners, and infrared-detector parts.^{3,4)} These materials are also eco-materials because they can be used to recover exhaust heat by thermoelectric conversion.

The crystal structure of these materials is rhombohedral with an R3m space group, usually expressed by a hexagonal lattice with a sequence of atomic layer units, –Te(1)–Bi–Te(2)–Bi–Te(1), along the *c*-axis. The strong bonds between Bi and Te are ionic-covalent in character, but the Te–Te bonds are extremely weak because of their van der Waals character.⁵⁾ As a result of the presence of van der Waals bonds, Bi₂Te₃-related materials are anisotropic,¹⁾ and thus their thermoelectric properties are excellent in the *c*-plane.^{1,6)}

Eco-materials are categorized on the basis of their life-cycle and eco-efficiency. They are broadly classified into the following groups: functional environmental materials, advanced energy materials, and materials for life-cycle design.⁷⁾ Bi₂Te₃- and Bi₂Se₃-related materials are eco-materials belonging to the class of advanced energy materials. Eco-materials should contain as few hazardous substances as possible. It is well known that *n*-type Bi₂Te_{2.85}Se_{0.15} has excellent thermoelectric properties.^{6,8)} However, the production of *n*-type Bi₂Te_{2.85}Se_{0.15} with excellent thermoelectric properties by a melt-growth process requires the addition of harmful halide dopants such as CdBr, CdCl₂, HgCl₂, HgBr₂, and SbBr₃.^{1,9,10)} It is necessary to reduce the amount of harmful materials in *n*-type Bi₂Te_{2.85}Se_{0.15} if they are to be classified as eco-materials.

In the present study, undoped Bi₂Te_{2.85}Se_{0.15} thermoelectric semiconductors, without harmful halide dopants, were prepared by mechanical alloying–hot pressing (MA–

HP). The metallographies and thermoelectric properties of the resulting samples were investigated.

2. Experimental Procedures

Appropriate amounts of the constituent elements, Bi (99.999%), Te (99.9999%), and Se (99.999%), were weighted according to the composition of Bi₂Te_{2.85}Se_{0.15}. In the MA process, harmful dopants were not added to control the carrier concentration.

The raw materials were put in a stainless-steel vessel and milled with silicon-nitride balls, using a planetary ball mill, for 30 h at a maximum speed of 180 rpm. The resulting powder was passed through a 150- μm -diameter sieve, and sintered by HP at 573, 623, and 673 K under a mechanical pressure of 147 MPa in an argon atmosphere. All steps of the powder processing were performed within an argon atmosphere, with the exception that the HP mold was exposed to air during the transportation between the argon-filled glove box and HP chamber. The sintered compacts were cut into sample disks of thickness 0.8 mm and diameter 10 mm.

The structures of these HP-sintered undoped sample disks were investigated metallographically by optical microscopy (OM), by scanning electron microscopy (SEM), and by X-ray diffraction (XRD) using Cu K α radiation in the Bragg angle range $2\theta = 20\text{--}70^\circ$. The densities of the disks were measured at room temperature using the Archimedes method. Differential thermal analysis (DTA) was conducted by heating up to 900 K at a rate of 10 K min⁻¹ in quartz containers under an argon atmosphere. The Seebeck coefficients α and the electrical conductivities σ were measured using a Resitest 8340 (TOYO Corporation, Tokyo, Japan) in the temperature range 300–470 K. The electrical conductivity σ was measured by the van der Pauw method. The thermoelectromotive force E was measured at a temperature difference ΔT of about 3 K, and the Seebeck coefficient was estimated from the relationship $\alpha = E\Delta T^{-1}$.

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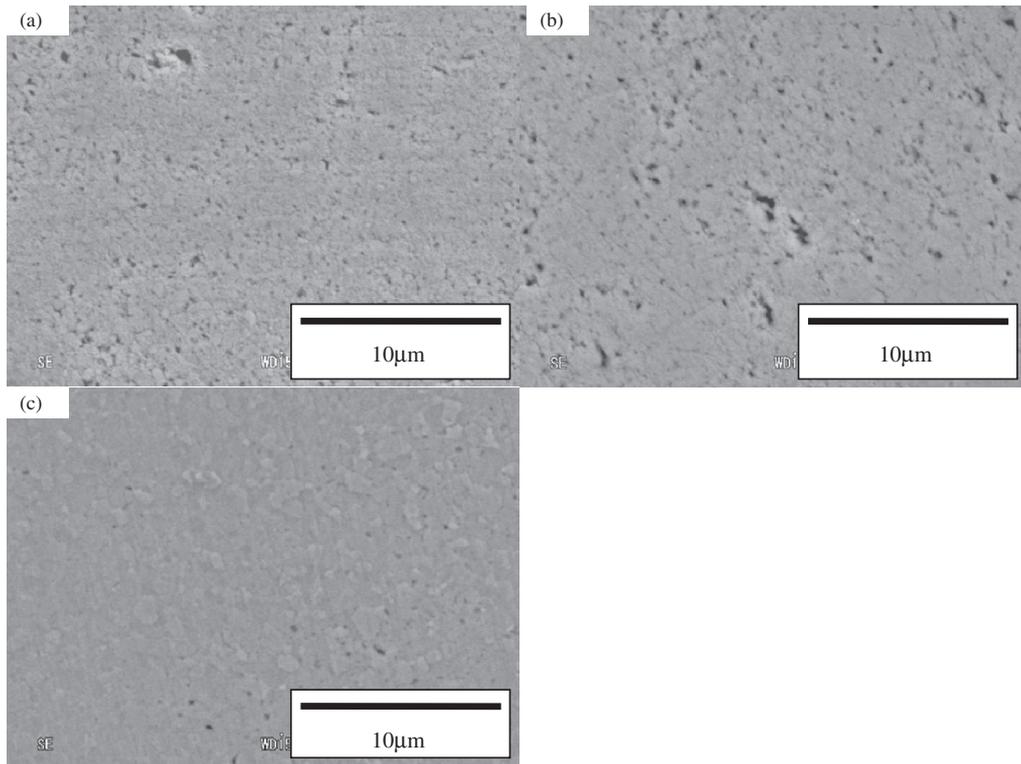


Fig. 1 SEM microphotograph of etched surfaces of undoped samples of $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}$ sintered at (a) 573 K, (b) 623 K, and (c) 673 K.

Table 1 Densities of the undoped samples of $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}$ sintered at 573, 623, and 673 K.

Sintering temperature T/K	Density $\rho/\text{g cm}^{-3}$
573	7.9
623	7.8
673	7.8

The performance of a thermoelectric material is estimated using the power factor, $P = \alpha^2 \sigma$.

3. Results and Discussion

All the undoped samples of $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}$ were n -type semiconductors. Table 1 shows that the densities of the samples sintered at 573, 623, and 673 K were 7.9, 7.8, and 7.8 g cm^{-3} , respectively. The error was estimated at $\pm 3\%$. These samples had relative densities of more than 99% of the theoretical Bi_2Te_3 density.¹⁾ Metallographic investigations using OM indicated that these samples were dense with no cracks and pores on their surfaces, before and after etching.

Figure 1 shows SEM microphotographs of samples sintered at (a) 573 K, (b) 623 K, and (c) 673 K. The grains in the sample sintered at 573 K [Fig. 1(a)] were finer than those in the samples sintered at 623 and 673 K. The grain size increased with increasing sintering temperature. However, the maximum grain size, in the sample sintered at 673 K, was less than approximately $3 \mu\text{m}$ [Fig. 1(c)].

Figure 2 shows the XRD patterns of the samples sintered at 573, 623, and 673 K. The $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}$ indices are also

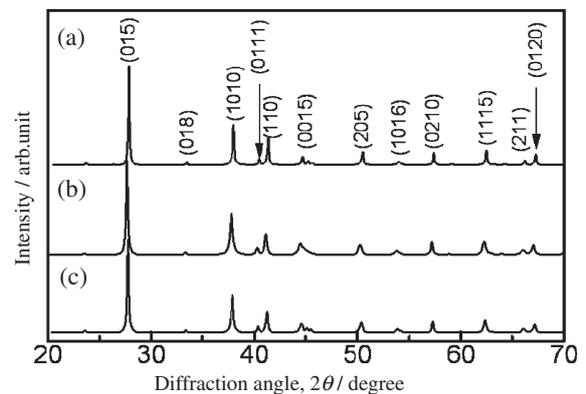


Fig. 2 XRD patterns of the undoped samples sintered at (a) 573 K, (b) 623 K, and (c) 673 K; $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}$ indices are also shown.

shown in Fig. 2. All samples were identified as single-phase Bi_2Te_3 -related materials.

Figure 3 shows the DTA curves of the undoped samples. The endothermic peaks were found at around 857 K. This peak corresponds to the melting point of Bi_2Te_3 .¹⁾ Similar DTA behaviors were observed for all the undoped samples. The DTA and XRD results indicate that these undoped HP-sintered samples were single-phase of $\text{Bi}_2(\text{Te}, \text{Se})_3$ -related materials.

Plots of the Seebeck coefficients α versus temperature for the undoped samples sintered at 573, 623, and 673 K are shown in Fig. 4. The negative values of the Seebeck coefficients indicated that these undoped HP-sintered samples had n -type conduction. The undoped sample sintered at 623 K had the maximum absolute Seebeck coefficient, i.e., $-328 \mu\text{V K}^{-1}$ at 313 K. The Seebeck coefficients of the

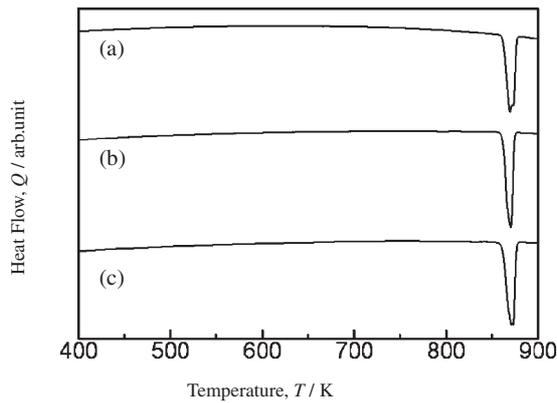


Fig. 3 DTA curves of undoped samples of Bi₂Te_{2.85}Se_{0.15} sintered at (a) 573 K, (b) 623 K, and (c) 673 K.

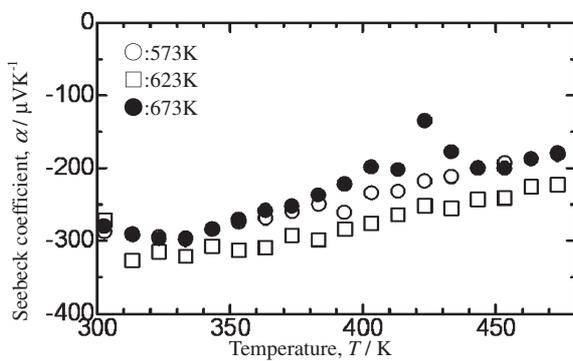


Fig. 4 Seebeck coefficient α versus temperature for undoped samples of Bi₂Te_{2.85}Se_{0.15}.

undoped samples sintered at 573 and 673 K were found to be slightly lower than that of the sample sintered at 623 K. The undoped sample sintered at 623 K had a uniformly dispersed carrier concentration as a result of grains growth, so the absolute Seebeck coefficient of this sample was greater than that of the sample sintered at 573 K. In contrast, the sample sintered at 673 K had a decreased Seebeck coefficient, and this could be caused by precipitation of Bi₂Te_{2.85}Se_{0.15} as a result of evaporation of Se and Te.^{12,13)}

Figure 5 shows the electrical conductivities σ versus temperature plots for the undoped samples sintered at 573, 623, and 673 K by HP. The electrical conductivity increases as the temperature increases. The temperature dependences of these thermoelectric properties correspond to those of a semiconductor. As is the case for the Seebeck coefficient, the electrical conductivity of the undoped sample sintered at 623 K was higher than that of the undoped sample sintered at 573 K. This was because grain growth led to an increase in the electrical conductivity. In addition, the electrical conductivity of the undoped sample sintered at 673 K was lower than that of the other samples, possibly because of precipitation of Bi₂Te_{2.85}Se_{0.15} as a result of evaporation of Se and Te.^{12,13)}

Figure 6 shows plots of the power factor P versus temperature for the undoped samples sintered at 573, 623, and 673 K by HP. The maximum power factors were $2.3 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 333 K, $4.4 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 313 K and $1.4 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 333 K for the undoped samples sintered at 573, 623, and 673 K, respectively. The maximum power factor of the undoped sample sintered at

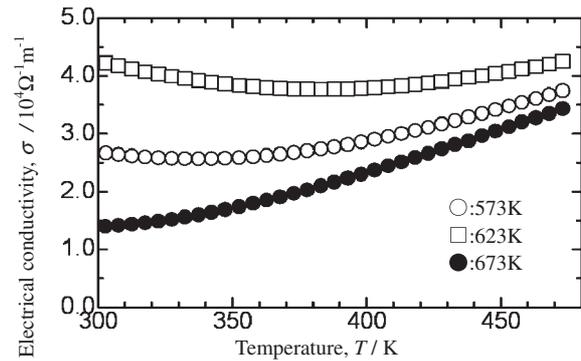


Fig. 5 Electrical conductivity σ versus temperature for undoped samples of Bi₂Te_{2.85}Se_{0.15}.

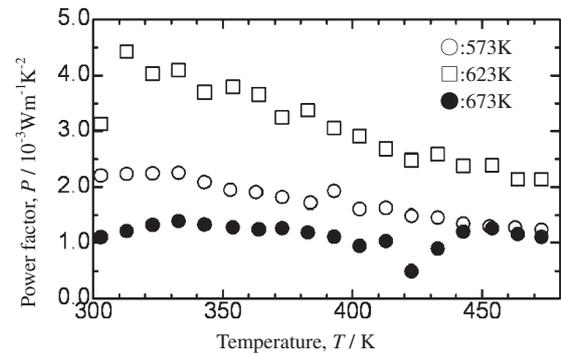


Fig. 6 Power factor P versus temperature for undoped samples of Bi₂Te_{2.85}Se_{0.15}.

623 K was found to be 88% that of the value of $5.0 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ reported for single crystals of *n*-type doped Bi₂Te_{2.85}Se_{0.15}.⁸⁾

These results indicated that doping with harmful halides of Bi₂Te_{2.85}Se_{0.15} compounds prepared by the MA-HP process is not necessary for carrier control.

4. Conclusions

In the present study, undoped Bi₂Te_{2.85}Se_{0.15} compounds without harmful dopants were prepared by MA and sintered by HP, and their thermoelectric properties were investigated. The results are summarized as follows.

- (1) The undoped samples sintered at 573 K had finer grains than those in the undoped samples sintered at 623 and 673 K. The grain sizes increased with increasing sintering temperature. The maximum grain size of the undoped samples sintered at 673 K was less than 3 μm .
- (2) The XRD patterns and DTA curves showed that all the HP-sintered undoped samples were single-phase of Bi₂(Te, Se)₃-related materials.
- (3) All the undoped samples of Bi₂Te_{2.85}Se_{0.15} were *n*-type semiconductors. The maximum power factors were $2.3 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 333 K, $4.4 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 313 K and $1.4 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 333 K for the undoped samples sintered at 573, 623, and 673 K, respectively. The maximum power factor of the undoped sample sintered at 623 K was found to be 88% that of the value of $5.0 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ reported for *n*-type doped Bi₂Te_{2.85}Se_{0.15} single crystal.

These results indicated that doping with harmful halide dopants of $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}$ compounds prepared by the MA-HP process is not necessary for carrier control.

REFERENCES

- 1) H. Scherrer and S. Scherrer: *Thermoelectric Handbook: macro to nano*, ed. by D. M. Rowe, (CRC Press, Taylor & Francis Group, 2006) ch27.
- 2) N. Fuschillo, J. N. Bierly and F. J. Donahoe: *J. Phys. Chem. Solids* **8** (1959) 430–433.
- 3) K. Uemura and I. Nishida: *Thermoelectric Semiconductor and Its Application*, (Nikkankogyo Shinbunsha, Tokyo, 1988) pp. 59–88.
- 4) J. G. Stockholm, L. Pujol-Soulet and P. Sernat: Proc. 4th ICTEC, (1982) pp. 136–140.
- 5) S. Nakajima: *J. Phys. Chem. Solids* **24** (1963) 479–485.
- 6) H. Kaibe, Y. Tanaka, M. Sakata and I. Nishida: *J. Phys. Chem. Solids* **50** (1989) 945–950.
- 7) K. Halada, K. Yamada, K. Ijima and Y. Soeno: *J. Japan Inst. Metals* **68** (2004) 939–945.
- 8) K. Uemura and I. Nishida: *Thermoelectric Semiconductor and Its Application*, (Nikkankogyo Shinbunsha, Tokyo, 1988) p. 179.
- 9) H. T. Kaibe, M. Sakata and I. A. Nishida: *J. Phys. Chem. Solids* **51** (1990) 1083–1087.
- 10) D. Perrin, M. Chitrob, S. Scherrer and H. Scherrer: *J. Phys. Chem. Solids* **61** (2000) 1687–1691.
- 11) L. E. Shelimova, V. S. Zemskov, V. I. Kosyakov and D. V. Malakhov: *Inorg. Mater.* **30** (1994) 1–8.
- 12) M. Sakata: *Thermoelectric Conversion*, (Syokabou, Tokyo, 2005) p. 183.
- 13) Y. Suga: *Nestudennhandoutai*, (Makisuyoten, Tokyo, 1966) p. 317.