

## Thermoelectric properties of Bi-Te based materials prepared by bulk mechanical alloying and shear extrusion

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Shear extrusion processing with combination of bulk mechanical alloying is proposed to yield the p-type  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$ , and n-type  $(\text{Bi}_2\text{Se}_3)_{0.05}(\text{Bi}_2\text{Te}_3)_{0.95}$  Bi-Te based materials from elemental granules. It has well-developed texture so as to improve the electric conductivity and thermoelectric properties. The shear extrusion processing in p-type, n-type alloy green compact, can afford to improve the preferred orientation factor of anisotropic crystallographic structure :  $F_p = 0.63$ ,  $F_n = 0.67$ . The electric resistivity of p-type, n-type materials is well-controlled to be  $0.989 \times 10^{-5} (\Omega\text{m})$ ,  $0.491 \times 10^{-5} (\Omega\text{m})$  respectively. Maximum power factors of p-type, n-type materials are achieved to  $4.33 \times 10^{-3} (\text{W/mK}^2)$ ,  $3.31 \times 10^{-3} (\text{W/mK}^2)$  even without any dopants. The bending strength of the material produced is also improved to be the range of 120-160MPa, six times larger than that for zone-melted specimen.

Key words: Shear extrusion processing, Bismuth telluride, Anisotropy, Orientation factor, Thermoelectric properties.

### 1. INTRODUCTION

The crystallographic structure in the  $\text{Bi}_2\text{Te}_3$  system is characterized by  $\text{Te}^{(1)}\text{-Bi-Te}^{(2)}\text{-Bi-Te}^{(1)}$  layered structure, having the weak van der Waals bonding between Te-Te layers [1-2]. This weak interlayer becomes a cleavage plane that leads to reduction of the strength in the single crystals. This weak strength is improved by sintering the materials once they are pulverized. The second feature of  $\text{Bi}_2\text{Te}_3$  system is known to have anisotropic property, in which the thermoelectricity along the a-axis is superior to that in the c-axis [3-4]. Without any post-treatment, however, the anisotropy is inevitably lost in the sintered polycrystalline materials, resulting in decrease of thermoelectric properties.

In order to attain higher bending strength and anisotropic crystallographic structure at the same time, a new method is proposed to make full use of intense plastic straining toward high performance thermoelectric materials. The shear extrusion process is employed to investigate the well-controlledness in texture development. The correlation between the developed microstructure and the thermoelectric properties is discussed to evaluate the controllability of thermoelectricity by shear extrusion.

### 2. Experimental Procedure

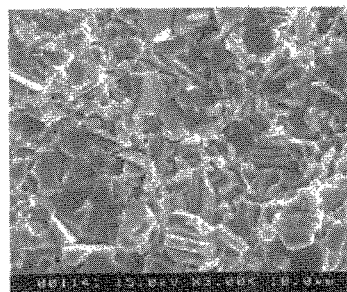
P-type  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$ , n-type  $(\text{Bi}_2\text{Se}_3)_{0.05}(\text{Bi}_2\text{Te}_3)_{0.95}$  solid solution were adopted as target thermoelectric materials. They were prealloyed and synthesized by Bulk Mechanical Alloying (BMA) [5] method ( $N=800$  cycles) from elemental granules and compacted into small preform with the size of  $\phi=10.5\text{mm}$ ,  $h=15\text{mm}$  and 85%T.D. In the shear extrusion process, the crosshead speed was kept 0.5mm/min, and the holding temperature was varied for 693-783K, 643-713K for p-type, n-type respectively, in argon atmosphere. The mechanical properties were measured at room temperature by the three-point bending test under a crosshead speed of

0.5mm/min. The van der Pauw method was employed to measure the electric resistivity at room temperature. Temperature difference by 10K was applied to both ends of the sample to measure the Seebeck coefficient at room temperature. X-ray diffraction analysis (XRD) was used to investigate the rearrangement of crystal orientation. The texture observation was conducted by scanning electron microscopy on the fractured surface.

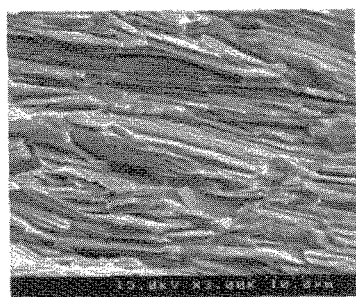
### 3. Results and Discussions

#### 3.1 Microstructure

In usual, hot pressing is frequently utilized to enhance the sintering by pressurizing. High density can be certainly obtained, but it has little controllability to arrange the crystallographic orientation. Fig.1(a) shows a typical microstructure of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  sintered at 693K by 1.2GPa for 3.6ks in argon atmosphere. Fine grains distribute with random orientation in this hot-pressed sample. On the other hand, each grain is realigned to have a laminate structure in the shear-extruded sample at the same temperature. This homogeneous rearrangement shown in Fig.1(b) must be favored for monotonic increase of electric conductivity.



(a) Hot pressed specimen



(b) Shear extruded specimen

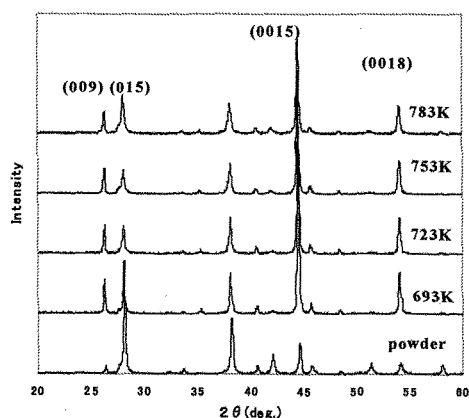
Fig.1 Microstructures of the hot pressed and shear extruded p-type  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  specimens at 693K.

### 3.2 Crystallographic anisotropy

For quantitative evaluation of the orientation distribution, the orientation factor (F) is calculated as an indicator of crystallographic anisotropy. After Ref. [6], F is defined by

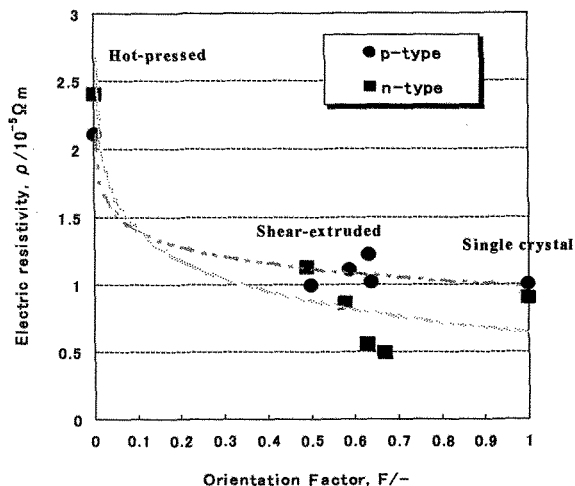
$$F = (p - p_0) / (1 - p_0), \quad (1)$$

where  $p$  and  $p_0$  are the ratios of the integrated intensity along (00 $l$ ) directions to the whole integrated intensity for all (hk $l$ ) directions, for the texture-developed and reference samples, respectively. As the reference, the powder sample was used to calculate  $p_0$ . Fig.2 compares the XRD profiles of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  between the powder sample and the extruded specimens. Higher intensities are detected along the perpendicular orientation to the shear-extruded direction : e.g., (009), (0015), and (0018). This texture development along (00 $l$ ) direction proves that significant lattice spin rotation should be accompanied with severe shear deformation to make crystalline orientation rearrangement. At the relatively low sintering temperature,  $T=693\text{K}$ , the maximum orientation factor becomes 0.63. In Ref. [7], the forward extrusion process was used to increase the orientation factor :  $F=0.22$ . The shear extrusion process provides twice higher orientation factors than attained by the conventional process, for Bi-Te-Sb solid solution.

Fig.2 Variation of XRD profiles for the shear extruded p-type  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  specimens with increasing the holding temperature for the reference of the powder sample.

### 3.3 Correlation between texture and electric resistivity

In general, the electric resistivity in Bi-Te systems has high sensitivity to the crystallographic orientation or F. Fig.3 depicts the correlation between the orientation factor (F) and the electric resistivity ( $\rho$ ) in p-type, and n-type solid solutions. For p-type, in case of the single crystal,  $F = 1.0$  and  $\rho_{\min} = 0.995 \times 10^{-5} \Omega\text{m}$ . On the contrary, hot pressed sample has  $F = 0.02$  and  $\rho = \rho_{\text{random}} = 2.110 \times 10^{-5} \Omega\text{m}$ . In case of the shear extruded sample,  $F$  is  $0.5 < F < 0.63$ . This high F value assures that the measured resistivity becomes nearly equal to  $1 \times 10^{-5} \Omega\text{m}$ , for the single crystals with  $F = 1$ . Hence, the electric resistivity can be lowered to that for single crystals when F is increased to be higher than 0.5 by the shear extrusion process irrespectively of the holding temperature. For n-type, in case of the single crystal (doped with 0.06%  $\text{HgBr}_2$ ),  $F = 1.0$  and  $\rho = 0.950 \times 10^{-5} \Omega\text{m}$  [8]. On the contrary, hot pressed sample has  $F = 0.03$  and  $\rho = \rho_{\text{random}} = 2.400 \times 10^{-5} \Omega\text{m}$ . For the shear extruded sample ( $F > 0.6$ ), the measured resistivity becomes nearly equal to or less than that of the single crystals with  $F = 1$ .

Fig.3 Correlation between the orientation factor (F) and electric resistivity ( $\rho$ ) in p-type, n-type solid solution.

### 3.4 Classical approximation on the relationship between the Seebeck coefficient and electric resistivity

The variation of Seebeck coefficient and electric resistivity for p-type and n-type shear extruded specimens is depicted in Fig.4 and Fig.5, respectively. Variation of the Seebeck coefficient with increasing the holding temperature is similar to that of electric resistivity. The classical approximation equation [9] on the relationship between Seebeck coefficient ( $\alpha$ ) and electric resistivity ( $\rho$ ) at the temperature of T can be rewritten by

$$\alpha_{(T_H)} - \alpha_{(T_R)} = \frac{\kappa_B}{e} \left[ \ln \left( \frac{\rho_{(T_H)}}{\rho_{(T_R)}} \right) \right] + \frac{\kappa_B}{e} [s_{(T_H)} - s_{(T_R)}], \quad (2)$$

In the above,  $K_B/e$  is  $86.2 \mu V/K$ ,  $s$ , the scattering parameter,  $T_H$ , the holding temperature, and  $T_R$ , the reference temperature(783K). The first term in the right-hand side of above equation depicts the resistivity contribution to the Seebeck coefficient and the second term, the scattering contribution to  $\alpha$ .

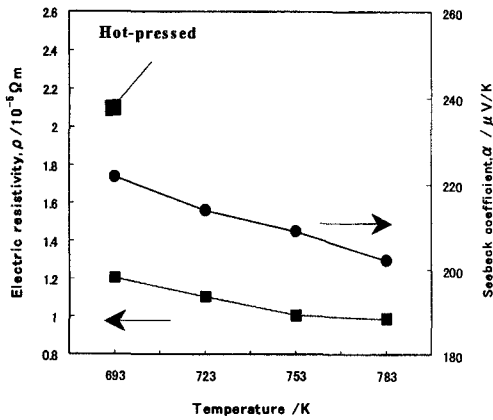


Fig. 4 Variation of the Seebeck coefficient and electric resistivity with increasing the holding temperature for p-type shear extruded specimen.

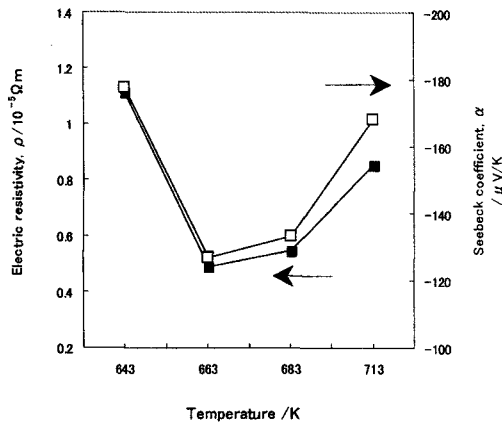


Fig. 5 Variation of the Seebeck coefficient and electric resistivity with increasing the holding temperature for n-type shear extruded specimen.

Fig.6 depicts the correlation between Seebeck coefficient and electric resistivity for p-type solid solution. The measured variation of  $\alpha$  with logarithmic  $\rho$  is estimated by equation. A little deviation is observed as a scattering effect. When  $T_H < T_R$ , the variation of Seebeck coefficient is mainly controlled by the electric resistivity rather than the scattering. It suggests that the carrier concentration should decrease in solid solution with decreasing  $T_H$ . When  $T_H = 723K$ , the scattering variation is only  $S_{(TH)} - S_{(TR)} = 0.0252$ . In general, large scattering variation is experienced in the scattering mode change between the acoustic-mode lattice scattering and ionized-impurity

scattering. Hence, no mode change takes place even with increasing  $T_H$ . The scattering deviation  $S_{(SE)}$  for the shear extruded sample is compared with those for the hot pressed and single crystal samples or  $S_{(HP)}$  and  $S_{(SG)}$ . Since  $|S_{(SG)} - S_{(SE)}| = 0.161$  and  $|S_{(HP)} - S_{(SE)}| = 0.558$ ,  $S_{(SE)}$  also approaches near to  $S_{(SG)}$  by the shear extrusion process.

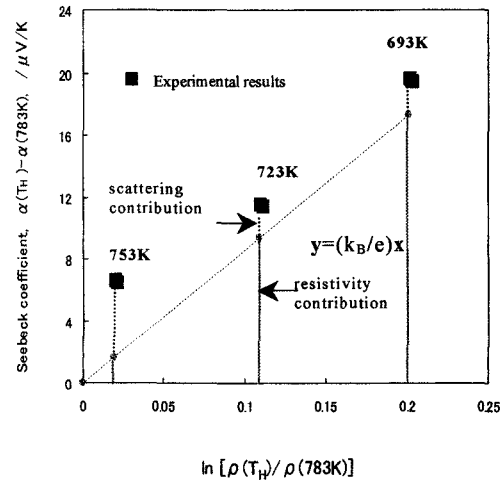


Fig.6 The correlation between the Seebeck coefficient and electric resistivity, scattering parameter for p-type solid solution.

### 3.5 Power factor

Variation of the measured power factors on the p-type materials is shown in Fig.7 with increasing the holding temperature. Every specimen has  $P \geq 4.1 \times 10^{-3} W/mK^2$  and the maximum power factor reaches  $4.33 \times 10^{-3} W/mK^2$ . Table I compares the thermoelectric properties among the single crystal, the hot pressed sample and the shear extruded sample on the p-type  $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$  materials. Significant reduction of electric resistivity takes place by shear extrusion, resulting in high power factors.

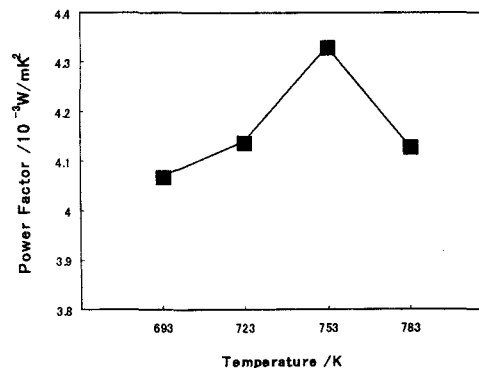


Fig.7 Variation of the power factors ( $\alpha^2/\rho$ ) for the shear extruded p-type specimen with the holding temperature in the shear extrusion.

Table I. Power factors ( $\alpha^2/\rho$ ) of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  prepared via the various fabrication methods.

	$\rho(\times 10^{-5}\Omega\text{m})$	$\alpha(\mu\text{V}/\text{K})$	P.F. ( $\alpha^2/\rho$ ) ( $\times 10^{-3}\text{W}/\text{mK}^2$ )
Single crystal [10]	0.995	194	3.78
Hot pressing	2.110	224	2.37
Present Method	1.008	209	4.33

In case of n-type, the measured power factors has  $P > 3.0 \times 10^{-3} \text{W}/\text{mK}^2$  at  $T \geq 663\text{K}$ , the maximum power factor reaches  $3.31 \times 10^{-3} \text{W}/\text{mK}^2$ . With addition of BN,  $\text{Si}_3\text{N}_4$ , or  $\text{SiO}_2$  dopants, the Seebeck coefficient can be increased by increasing the electric resistivity to the same level as the doped single crystal. The power factor of shear extruded sample can be improved to that of the single crystal ( $P.F = 4.64 \times 10^{-3} \text{W}/\text{mK}^2$ ; with doping 0.06%  $\text{HgBr}_2$ ) by optimization of doping.

#### 4. Conclusion

Single crystal in Bi-Te system has a preferred anisotropy to increase the electric conductivity but low strength. Polycrystalline Bi-Te materials have sufficient high strength but little anisotropy is present in microstructure. It is noticeable that the preferred anisotropic crystallography and high strength is attained simultaneously by shear extrusion.

Owing to intense plastic straining during the shear extrusion, the crystallographic texture is improved to have higher orientation factor with 0.5 or more.

In case of p-type shear extruded materials, thermoelectric properties are enhanced : e.g., higher power factor of  $4.33 \times 10^{-3} \text{W}/\text{mK}^2$  than that for a single crystal. It has also high bending strength of 120MPa, which is six times larger than that for zone-melt specimen.

The present shear extrusion process is also effective for intense shear-straining of the bulk thermoelectric billets. It is adaptive as a new processing route to control the thermoelectric properties even when starting from the single-crystal rod.

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#### References

- [1] J. R. Drabble and C. H. L. Goodman, *J. Phys. Chem. Solid*, 5, 142 (1953).
- [2] J. D. Shim, T. Y. Seong and J. M. Kim, *J.KIMM*, 27(4), 366-373 (1989)
- [3] I. J. Ohsugi, T. Kojima, M. Sakata, M. Yamanashi and I. A. Nishida, *J.Appl. Phys.* 76(4), 2235-2239 (1994)
- [4] J. Nagao, M. Ferhat, E. Hatta and K. Mukasa,

*Phys.Stat.Sol.(b)*, 219, 347-349 (2000)

[5] T. Aizawa, J. Kihara and D. Benson, *Mater.Trans.JIM*, 36(2), 138-149 (1995)

[6] F. K. Lotgering, *J.Inorg.Nucl.Chem.* 9, 113 (1959)

[7] J. Seo, D. Cho, K. Park and C. Lee, *Materials Research Bulletin* 35, 2157-2163 (2000)

[8] I. Ohsugi and M. Sakata, *Journal of the Materials Science Society of Japan*, 32(6), 298-302 (1995)

[9] H. J. Goldsmid, *Semiconductors and Semimetals*, 69(1), 9-13 (2001)

[10] Y. Iwaisako, T. Aizawa, A. Yamamoto and T. Ohta, *J. Japan Society of Powder and Powder Metallurgy*, 47(11), 1189-1193, (2000)

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