Effects of Annealing on the Thermoelectric and Microstructural Properties of Deformed n-Type Bi$_2$Te$_3$-Based Compounds

D.M. LEE,[1] C.H. LIM,[1,2] D.C. CHO,[1] Y.S. LEE,[1] and C.H. LEE[1]

1.—Department of Metallurgical Engineering, College of Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Korea. 2.—E-mail: chlim95@dreamwiz.com

We studied the effects of deformation and annealing of n-type 90Bi$_2$Te$_3$-5Sb$_2$Te$_3$-5Sb$_2$Se$_3$ thermoelectric compound. Hot-extrusion was conducted to prepare the deformed compound and then this compound was annealed at 400°C for 1–24 hr. When the undoped cast-ingot was extruded, the compound was changed from p-type to n-type due to the electrons generated during the extrusion process. For the compound extruded with SbI$_3$-doped powders, the thermoelectric properties were also varied for the extrusion process. After annealing at 400°C more than 9 hr, the powder-extruded compound was recrystallized. This caused a decrease in carrier concentration and crystallographic anisotropy. In case of the compound extruded at the ratio of 10:1, the Seebeck coefficient α and the electrical resistivity ρ increased due to recrystallization. However, thermal conductivity κ of the compound decreased. This resulted in an increase in the figure-of-merit from 1.23×10^{-3} to 1.63×10^{-3} K^{-1}.

Key words: Bi$_2$Te$_3$, thermoelectric, Seebeck coefficient, powder extrusion, deformation

INTRODUCTION

Bi$_2$Te$_3$ and its solid-solution compounds are widely used in electronic devices and areas that require precise temperature control because they have excellent cooling properties due to the Peltier effect. These compounds have been made from a single or unidirectionally solidified crystal having a high figure-of-merit as a thermoelectric material. However, their application area is very limited because their cleavage planes, which exist parallel to the growing direction (*c* axis) of crystal, make fabrication of thermoelectric devices difficult. On the other hand, Bi$_2$Te$_3$ thermoelectric compounds fabricated by powder metallurgical processes exhibit excellent mechanical properties.[1,2] However, the thermoelectric properties are inferior to those of ingot and very sensitive to the fabrication parameters such as powder oxidation,[3] vaporization of component elements,[4] and defects generated by plastic deformation.[5,6] The effect of deformation-induced defects on the thermo-

electric compound was studied by Schultz et al. and Park et al. as the compounds were fabricated by extrusion and pressing methods, respectively.[7,8] They reported that dislocations as well as point defects becoming electrical majority carriers were formed by the extrusion and pressing processes, and the carriers could be reduced by an annealing treatment. This leads to changes in the thermoelectric properties. However, the thermoelectric properties of the Bi$_2$Te$_3$-based compound are not changed by only the carrier concentration. Thermoelectric properties are varied with the carrier concentration and also with grain size and grain orientation. Thermoelectric properties with the grain size and grain orientation have been also investigated along the parallel and perpendicular directions to the loading axis[9–11] because powders showing a flaky shape are consolidated with a preferred orientation. Generally upon annealing, recovery and recrystallization take place in the compound. The recovery reduces the defects, and recrystallization causes a random grain orientation. This changes the thermoelectric properties in deformed compounds.

In this paper, we prepared the thermoelectric compound by an extrusion process. The effects of deformation and annealing on the microstructures and the thermoelectric properties of n-type $90Bi_2Te_3$-$5Sb_2Te_3$-$5Sb_2Se_3$ thermoelectric compound were further examined. Correlations between microstructures and annealing treatment for the compound after the deformation process are discussed in detail.

EXPERIMENTAL PROCEDURES

99.999%-Pure elemental Bi, Te, Se, and Sb as well as SbI_3 dopant were weighed for proper composition and vacuum-sealed at 2×10^{-5} Torr in a quartz tube of diameter 30 mm and height 50 mm to make the n-type $90Bi_2Te_3$-$5Sb_2Te_3$-$5Sb_2Se_3$ + 0.05 wt.% SbI_3 thermoelectric compound. The element mixture was heated at 750°C for 2 hr to obtain a homogeneous ingot using a rocking furnace, and it was then cooled to room temperature in the furnace. The ingot was cut and pulverized to obtain columnar bars and powders, respectively. The cut ingot was inserted into an aluminum can of diameter 30 mm and height 50 mm and then extruded at ratios of 2:1, 5:1, and 10:1 at 400°C to investigate the effects of deformation. Powders exhibiting fine flakes were sieved to prepare powders of 150–250 µm size showing lower oxygen concentrations compared with that of small-sized powders. Powders of 150–250 µm size packed into the aluminum can were extruded at ratios of 2:1 and 10:1 at 400°C. The extruded compound was annealed at 400°C for 1–24 hr.

The thermoelectric properties of the extruded compounds were measured at room temperature along the extrusion direction. The specimens with a dimension of 4 mm × 4 mm × 15 mm and 4 mm × 4 mm × 4 mm were cut out from the extruded samples for measurements of Seebeck coefficient α, electrical resistivity ρ, and thermal conductivity κ, respectively. In order to measure the Seebeck coefficient α, heat was applied to the specimen placed between two sensing Cu-discs. The thermoelectric electromotive ΔE was measured upon applying temperature difference ΔT between both ends of the specimen. The Seebeck coefficient α was determined from the $\Delta E/\Delta T$. The electrical resistivity ρ was measured by the four-point probe technique. The thermal conductivity κ was measured by the static comparative method using a transparent SiO_2 ($\kappa = 1.36$ W/(mK) at room temperature) as a standard sample in 5×10^{-5} Torr vacuum atmosphere.[12] The preferred grain orientation of the compounds was investigated by x-ray diffraction (XRD). The microstructures of the compounds were observed by optical microscope. A solution of $HNO_3/H_2O = 1:1$[13] was used in etching for the optical observations.

RESULTS AND DISCUSSION

The Seebeck coefficients of the extruded $90Bi_2Te_3$-$5Sb_2Te_3$-$5Sb_2Se_3$ compound as a function of extrusion ratio are given in Fig. 1. For the undoped ingot, as the extrusion ratio increased from 2:1–10:1 the
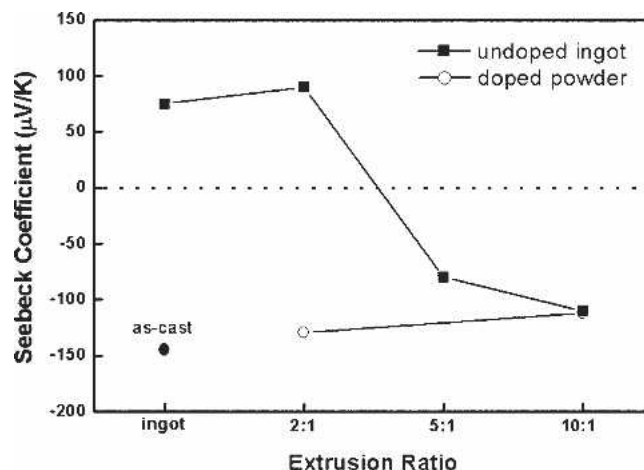

Fig. 1. Seebeck coefficient of the compounds as a function of extrusion ratio: "+" and "–" refer to p-type and n-type, respectively.

compound, which is initially p-type, changed into n-type. The ingot extrusion allowed us to investigate the effect of only deformation because it would not be necessary to consider oxidation effects on the compound.[3] Considering a p-type to n-type transition of the undoped ingot during the extrusion process, it is apparently evident that the carriers formed by the deformation are electrons. As the extrusion ratio increased from 2:1–10:1 the Seebeck coefficient of the ingot-extruded compound changed from +75 to –110 µV/K, but that of the powder-extruded compound varied from –130 to –110 µV/K. The Seebeck coefficient of the two compounds was indirectly increasing with the extrusion ratio. Figure 2 plots the Seebeck coefficient with carrier concentration for p-type and n-type.[7] With increasing carrier concentration up to 10^{19} cm^{-3}, the Seebeck
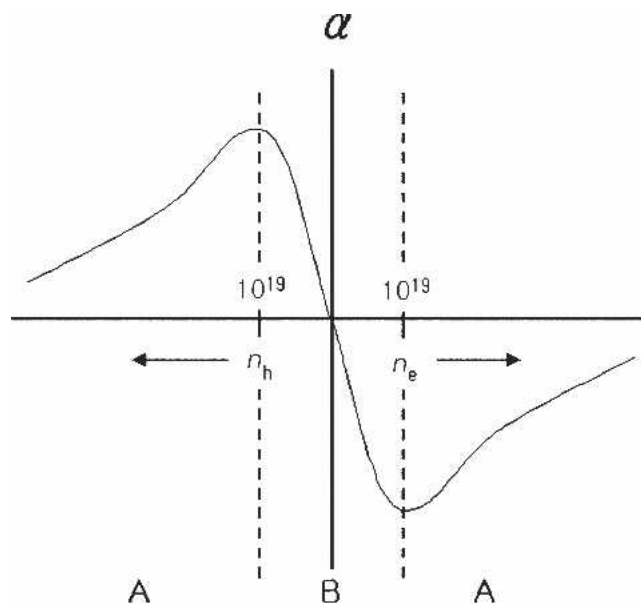

Fig. 2. Schematic plot of Seebeck coefficient α vs. carrier concentration: n_h and n_e are numbers of holes and electrons, respectively.[7] The Seebeck coefficient shows the maximum value around the carrier concentration of 10^{19} cm^{-3}. In regions A and B, α varies differently with increasing carrier concentration.

coefficient in the region A declines, whereas the Seebeck coefficient in the region B rises as the carrier concentration is over 10^{19} cm^{-3}. The carrier concentration of the undoped compound should be much lower than 10^{19} cm^{-3}. Hence, as the extrusion ratio increased the Seebeck coefficient of the undoped compound follows the curve in region B. For the compound doped with 0.05 wt.% SbI$_3$, the doping amount was optimized to have a carrier concentration of 10^{19} cm^{-3}.[14–16] In this study, the carrier concentration of the powder-extruded compound could be higher than 10^{19} cm^{-3} because the compound was doped with 0.05 wt.% SbI$_3$ and deformed by the extrusion process. Furthermore, because the powders were oxidized, the electrons could be even higher in number.[3] It is thus presumed that the Seebeck coefficients of the extruded compound with the doped powders follow the curve in region A, although no measurement of carrier concentration was performed for all the compounds.

Heat treatment was subsequently performed to study thermal stability of the powder-extruded compounds. Figure 3 shows optical microstructures of the compounds along the longitudinal direction after annealing at 400°C for 9 hr. Some flaky powders were observed to line up along the extrusion direction while others are somewhat deformed and recrystallized as shown in Fig. 3a and c. It is important to observe a change of the microstructures after deformation and annealing because the electrical properties are high when the powders are sintered to keep their shape in the longitudinal direction.[10] Figure 4 illustrates the powders observed by scanning electron microscope (SEM). Because the ingot is easily broken along the Te/Te layers, which are weakly bound with van der Waals forces,[17] the powders also show a flake-like shape. In addition, the powders themselves exhibit excellent thermoelectric properties along the cleavage plane, and these could be considered to be almost single crystals.[11] It is thus desirable that compounds be anisotropically extruded, which means that the powders are laminated and consolidated to keep their flaky shapes (Fig. 3). Before annealing, dynamic recrystallized phases preserving traces of the flaky powders are partially observed from 2:1 and 10:1 compounds. Af-
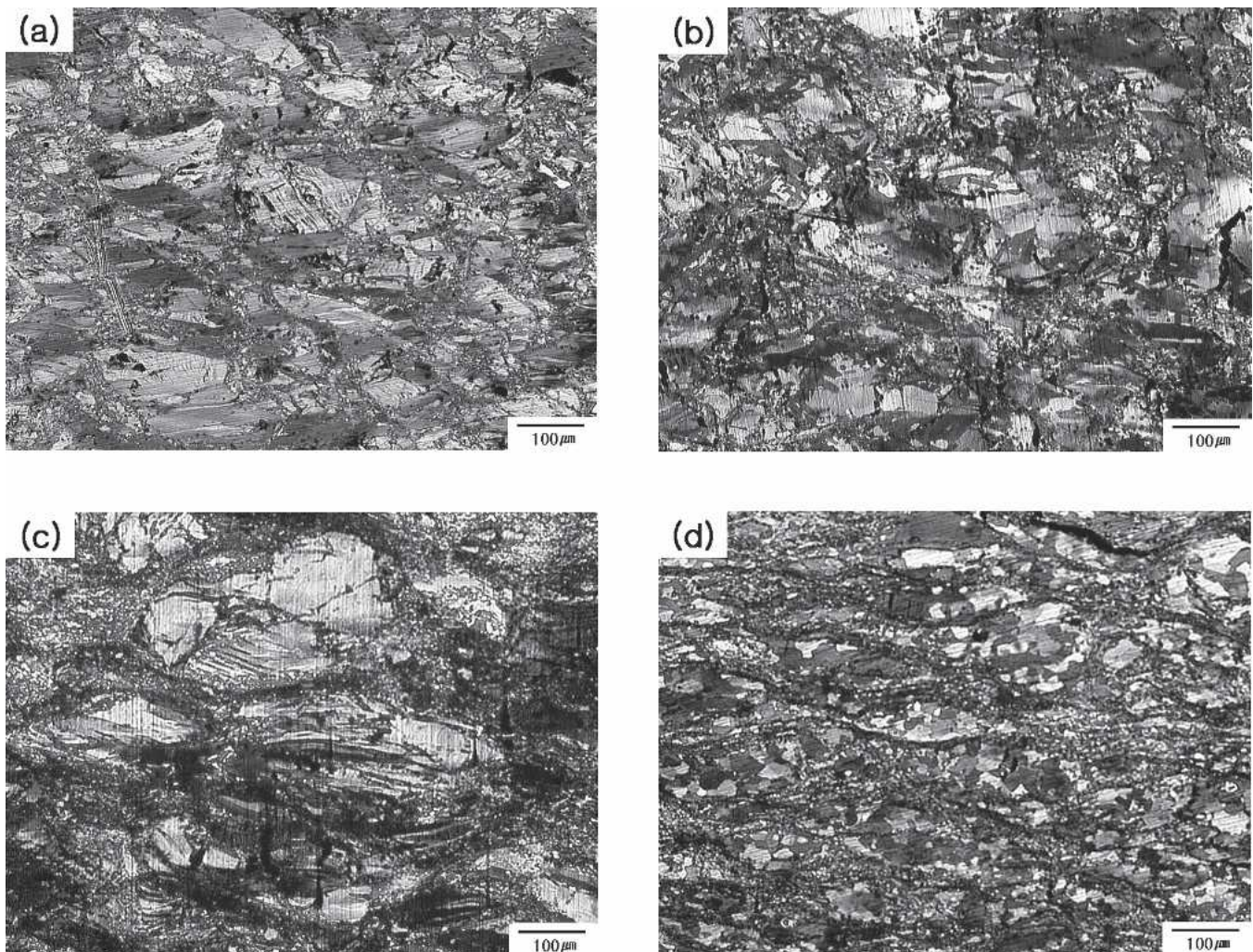

Fig. 3. Optical micrographs of the extruded compounds observed along the extrusion direction: (a) as-extruded (2:1); (b) annealed at 400°C for 9 hr (2:1); (c) as-extruded (10:1); and (d) annealed at 400°C for 9 hr (10:1)
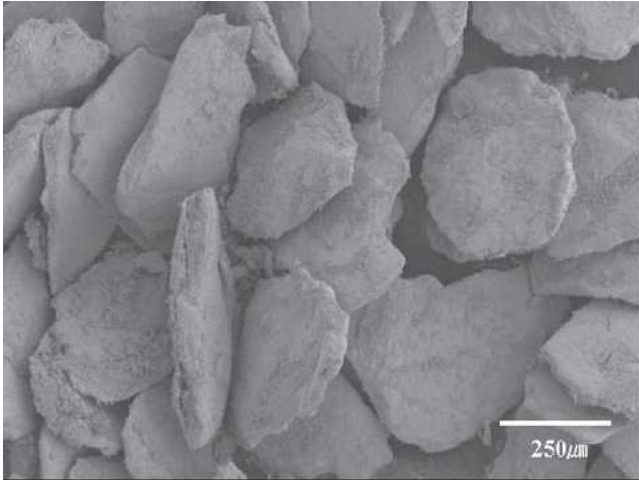
Fig. 4. SEM micrograph of flaky n-type $90Bi_2Te_3$-$5Sb_2Te_3$-$5Sb_2Se_3$ powders.

ter annealing for 9 hr, the 10:1 compound shows static recrystallized phases in most parts of the specimen, but the 2:1 compounds exhibit only a few static recrystallized phases. To investigate the preferred orientation of the grains, XRD analyses were performed. Figure 5 shows the XRD patterns of the compounds obtained from the sections parallel and perpendicular to the extrusion direction, respectively. The intensity of (0 0 6), (0 0 15), and (0 0 18) planes, which are perpendicular to the c axis, is strongly detected at the parallel section. From the XRD patterns, the degree of preferred orientation, i.e., the orientation factor f, is calculated by the following equation proposed by Lotgering:[18]

$$f = (p - p_0)/(l - p_0), \qquad (1)$$

where p and p_0 are the ratios of the sum of the in-

tensities of the (0 0 l) diffraction to the sum of the intensities of all (h k l) diffractions for the oriented and nonoriented samples, respectively. The values of orientation factor for completely nonoriented and oriented samples are 0 and 1, respectively. Table I shows the orientation factor of the extruded compounds. The orientation factor of the compound of 10:1 decreased from 0.18 to 0.12 after annealing for 9 hr, while that of the compound of 2:1 showed no variation. Because the 10:1 compound had more stored energy during the deformation process, the grains were more easily recrystallized.[19] Thus, the grains became randomly oriented, resulting in a decrease in the orientation factor.

Figure 6 shows the Seebeck coefficient of the extruded compounds as a function of annealing time at 400°C. The Seebeck coefficient of the compound of 10:1 increased considerably from −110 to −158 μV/K after annealing for 9 hr, whereas that of the compound of 2:1 shows a little variation at the same condition. In Fig. 3b and d, the 10:1 compound was more recrystallized than the compound of 2:1 after annealing. Generally, recrystallization annihilates defects in the materials. For the 10:1 compound, defects were more easily reduced than for the 2:1 compound, thereby causing carriers (e^-) to be decreased greatly. Therefore, the Seebeck coefficient of the 10:1 compound remarkably increased.

Figure 7 shows electrical resistivity of the extruded compounds as a function of annealing time at 400°C. With increasing annealing time, the variation of the electrical resistivity of the compounds was similar to that of Seebeck coefficient. The electrical resistivity of the compound of 2:1 gradually decreased from 0.99×10^{-5} to 0.70×10^{-5} Ωm. However, the electrical resistivity of the compound of
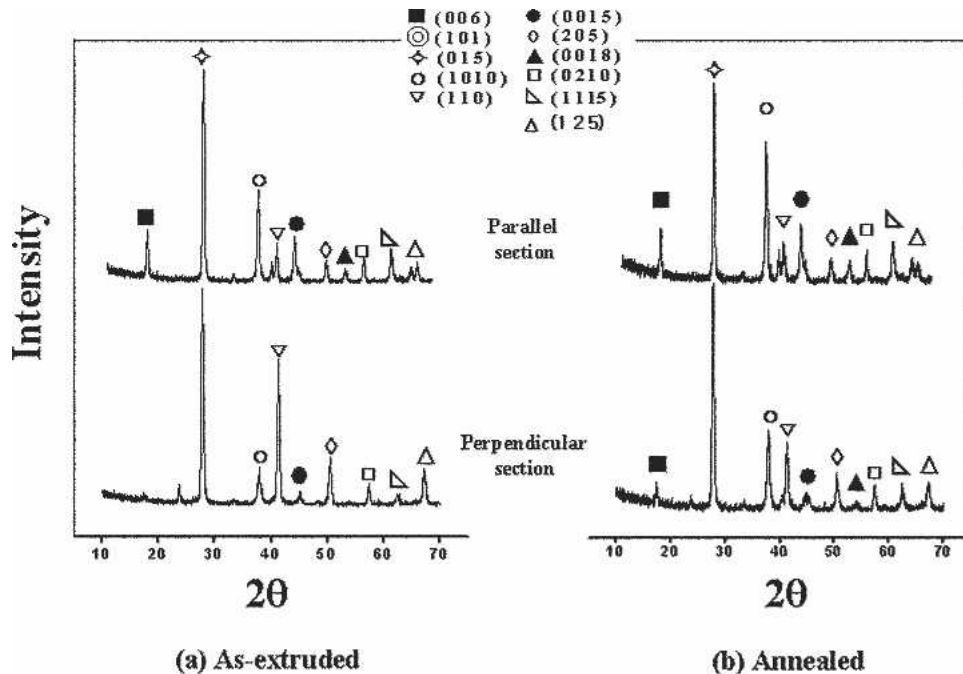

Fig. 5. XRD patterns of the compounds obtained from the parallel and perpendicular sections to the extrusion direction: (a) as-extruded (10:1), (b) annealed at 400°C for 9 hr.

Table I. Orientation Factors of the Powder-Extruded Compounds

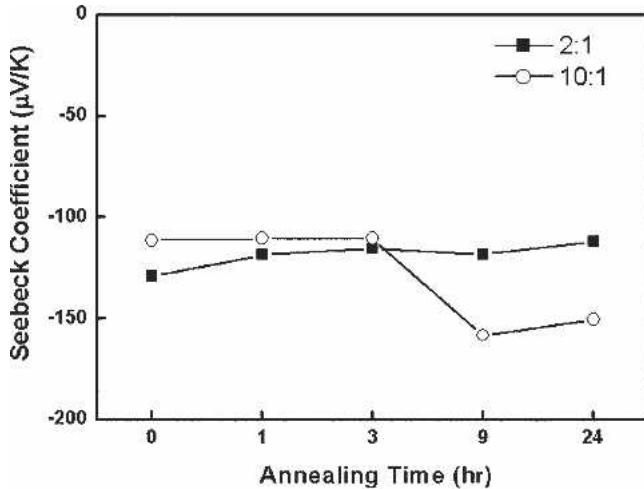| Extrusion Ratio	As-Extruded	Annealed at 400°C for 9 hr
2:1	0.11	0.11
10:1	0.18	0.12

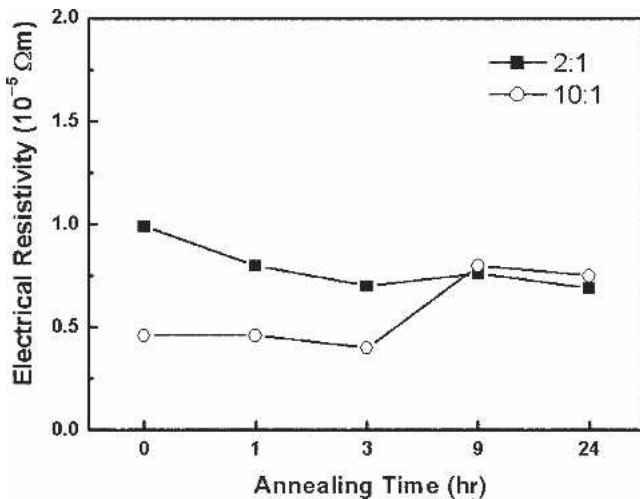Fig. 6. Seebeck coefficients of the extruded compounds with various annealing times at 400°C.

Fig. 7. Electrical resistivities of the extruded compounds with various annealing times at 400°C.
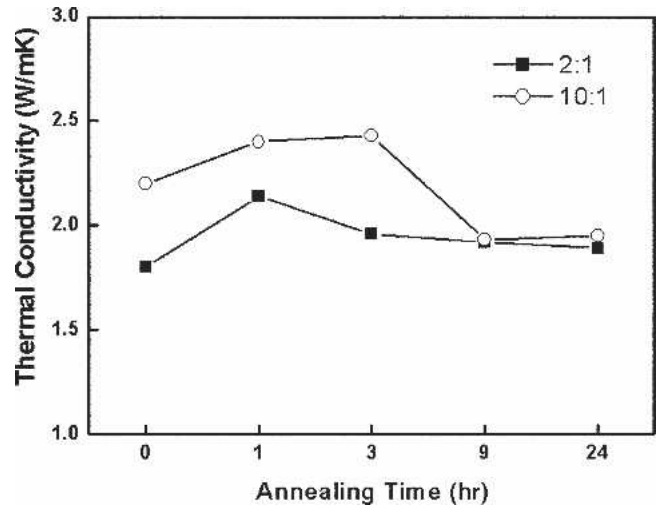

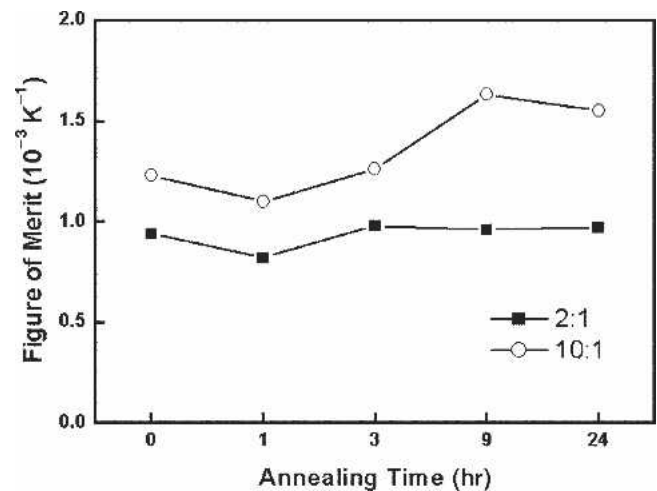Fig. 8. Thermal conductivities of the extruded compounds with various annealing times at 400°C.

Fig. 9. Figures-of-merit of the extruded compounds with various annealing times at 400°C.

$$\kappa = \kappa_{ph} + \kappa_{el}. \tag{2}$$

κ_{el} is related to electrical conductivity σ ($= 1/\rho$) by the Wiedemann-Franz law:

$$\kappa_{el} = L_0 \sigma T, \tag{3}$$

where L_0 is the Lorenz number and T is the absolute temperature. In case of a single crystal, the electronic thermal conductivity κ_{el} contributes to about ¼ of the total thermal conductivity κ.[20] Although this compound is a polycrystal, the contribution of electronic thermal conductivity κ_{el} in the total thermal conductivity κ is considered to be approximately 25% because the carrier concentration is optimized around 10^{19} cm^{-3} to have a maximum figure-of-merit. However, the total thermal conductivity of the 10:1 compound was changed largely after annealing for 9 hr. Because the contribution of electronic thermal conductivity κ_{el} in the total thermal conductivity κ is small, the large decrease in the total thermal conductivity could not be explained by only the decrease in carrier concentra-

10:1 largely increased from 0.46×10^{-5} to 0.80×10^{-5} Ωm by annealing for 9 hr. This resulted from the decrease in the orientation factor as well as defects after the annealing.

Thermal conductivity of the extruded compounds as a function of annealing time at 400°C is given in Fig. 8. With increasing annealing time, the thermal conductivity of the 2:1 compound showed a little variation within 1.80 and 1.96 W/(mK), but that of the 10:1 compound showed a steep fall from 2.20–1.93 W/(mK) by the annealing for 9 hr. Thermal conductivity κ is composed of the phonon thermal conductivity κ_{ph} and the electronic thermal conductivity κ_{el} as follows:

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tion, just like the results of the Seebeck coefficient and the electrical resistivity as shown in Figs. 6 and 7, respectively. This is explained by the fact that a decrease in the phonon thermal conductivity as well as the electronic thermal conductivity can lower the total thermal conductivity simultaneously. The phonon thermal conduction can be interfered by scattering of short-wavelength phonon at the grain boundaries that have a high energy and are highly disordered. It was reported that a phonon-grain boundary scattering has a significant effect on reducing the phonon thermal conductivity of BiTe and SiC compounds.[21–23] As shown in Fig. 3d, the grains in the annealed compound are finely and homogeneously recrystallized. This causes the phonon-grain boundary scattering to increase. Therefore, the total thermal conductivity can be decreased so greatly.

From the measured thermoelectric properties, figure-of-merit Z was calculated by the following equation:

$$Z = \alpha^2/(\rho\kappa). \tag{4}$$

The figure-of-merit of the as-extruded and annealed compounds is given in Fig. 9. The figure-of-merit of the 10:1 compound increased from 1.23×10^{-3} to 1.63×10^{-3} K^{-1} after annealing at 400°C for 9 hr. This resulted from the increase in the Seebeck coefficient and the decrease in the thermal conductivity, although the electrical resistivity increased. However, the 2:1 compound showed little improvement in the figure-of-merit.

CONCLUSIONS

The effects of the deformation and annealing on the microstructures and thermoelectric properties of the n-type 90Bi$_2$Te$_3$-5Sb$_2$Te$_3$-5Sb$_2$Se$_3$ thermoelectric compound were investigated by means of the extrusion process. Undoped compound appeared to be changed from p- to n-type as the extrusion ratio increased. This was due to the electrons that were generated during the extrusion process. The thermoelectric properties of the SbI$_3$-doped compound also varied with the extrusion process. As a result, the Seebeck coefficient and the thermal conductivity of the compound increased, the electrical resistivity decreased owing to the formation of deformation-induced electrons. Annealing of the extruded compounds resulted in the reduction of electrons by the annihilated defects and the decrease of orientation factor by the recrystallized grains. When the compound was annealed at 400°C for 9 hr, the thermo-

electric properties of the 10:1 compound showed remarkable changes accompanying a recrystallization. The Seebeck coefficient and the electrical resistivity of the compound increased, and the thermal conductivity decreased. Therefore, the figure-of-merit of the compound was enhanced from 1.23×10^{-3} to 1.63×10^{-3} K^{-1}. However, the compound extruded at the ratio of 2:1, whose degree of deformation was smaller than that of 10:1, showed a little variation in thermoelectric properties during the same annealing time.

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