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Thermoelectric properties of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy with addition of BN and WO_3 powders

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Thermoelectric properties of the $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy, fabricated by mechanical alloying and hot-pressing, were investigated with addition of BN and WO_3 powders as phonon scattering centers. The Seebeck coefficient and the electrical resistivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy increased with increasing the volume fraction of BN and WO_3. Although the thermal conductivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy decreased with increasing the volume fraction of BN and WO_3 due to the reduction of κ_{el}, the lattice thermal conductivity was not lowered. The figure-of-merit of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy, 3.05×10^{-3}/K without addition of BN and WO_3, decreased with increasing the volume fraction of BN and WO_3, because the increment of the electrical resistivity was much larger than the decrement of the thermal conductivity due to the grain refinement. © *2000 Kluwer Academic Publishers*

1. Introduction

Thermoelectric modules utilizing Peltier effect have been widely utilized to cool electronic devices such as integrated circuit packages, laser diodes and IR detectors, because quick and precise control of temperature is possible with almost no noise during operation [1, 2].

As the performance of the Peltier cooling modules is determined by the figure-of-merit of thermoelectric materials, various works have been performed to improve the figure-of-merit [2–5]. Recently, It has been suggested that dispersion of fine ceramic particles in the thermoelectric materials may improve the figure-of-merit by decreasing the lattice thermal conductivity without adversely affecting the electrical resistivity [6–9]. With this method, it has been expected that the figure-of-merits of SiGe alloys [6–8] and Bi_2Te_3-based alloys [9] can be improved for 10–40% and 15–20%, respectively. Also, it has been reported that the thermal conductivity of the hot-pressed $Si_{80}Ge_{20}$ alloy decreased with addition of BN and Si_3N_4 powders [10, 11]. However, little has been reported for the thermoelectric properties of Bi_2Te_3-based alloys with addition of ceramic powders as phonon scattering centers.

Mechanical alloying is a process in which intermetallic compounds or alloy powders are fabricated from elemental powders through a sequence of collision events inside a high energy ball mill. This metallurgical process has been employed in industry since the early 1970's for production of oxide dispersion strengthened alloys and production of alloys with components which have widely different melting temperatures [12]. Recently, mechanical alloying has been applied to prepare polycrystalline thermoelectric materials, such as $(Bi,Sb)_2(Te,Se)_3$ and SiGe alloys [4, 5, 13–15]. As mechanical alloying proceeds with repeated fracture and cold welding of the elemental powders [12], it can be possible to obtain fine dispersion of ceramic powders in the polycrystalline $(Bi,Sb)_2Te_3$ alloys by mechanical alloying of $(Bi,Sb)_2Te_3$ powders with ceramic powders.

In this study, the polycrystalline $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy was fabricated by mechanical alloying and hot pressing with addition of BN and WO_3 powders as phonon scattering centers, and the thermoelectric properties of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy were characterized as a function of the volume fraction of BN and WO_3.

2. Experimental procedures

High purity (>99.99%) Bi, Sb, and Te granules were washed with 10% nitric solution, acetone, and distilled water to remove the surface oxide layer. The appropriate amounts of Bi, Sb, and Te were weighed for the $(Bi_{0.2}Sb_{0.8})_2Te_3$ composition and charged with BN and WO_3 powders (<1 μm) up to 7 vol% in a hardened tool steel vial under Ar atmosphere. Steel balls were also charged as milling media and ball-to-material weight ratio was held at 5 : 1. Mechanical alloying was conducted by shaking the vial at 1200 rpm for 5 hours using a Spex mill. After the vibro-milling process, X-ray diffraction (XRD) analysis was performed to confirm the complete formation of the alloy powders.

Gibbs formation energies (ΔG_f) for BN and WO_3 are −228.5 kJ/mole and −764.1 kJ/mole, respectively [16]. These values are much lower than ΔG_f of Bi_2Te_3 (−77.1 kJ/mole) and Sb_2Te_3 (−58.5 kJ/mole) which compose of $(Bi_{0.2}Sb_{0.8})_2Te_3$ compound [17]. Thus, it could be expected that no reactions occur between $(Bi_{0.2}Sb_{0.8})_2Te_3$ and BN or between $(Bi_{0.2}Sb_{0.8})_2Te_3$ and WO_3 during mechanical alloying and hot pressing. It can be possible to obtain fine dispersion of ceramic powders in the mechanically alloyed powders. For the Ni-Cr alloys fabricated by mechanical alloying with addition of ThO_2 and Y_2O_3 powders larger than 20 μm, it has been reported that such ceramic powders were dispersed to be a size of 10–100 nm [12]. Although BN and WO_3 powders of about 1 μm were used as starting materials in this study, thus, it could be expected that BN and WO_3 were dispersed finely much less than 1 μm in the $(Bi_{0.2}Sb_{0.8})_2Te_3$ powders fabricated by mechanical alloying process.

The mechanically alloyed $(Bi_{0.2}Sb_{0.8})_2Te_3$ powers were cold pressed at 425 MPa to form 5 × 5 × 10 (mm) compacts, and hot pressing was conducted in vacuum at 550 °C for 30 minutes. Seebeck coefficient (α) of the hot-pressed specimens was measured at room temperature by applying a temperature difference of 10 °C at both ends of a specimen. Electrical resistivity (ρ) and thermal conductivity (κ) were measured using Harman method [18] in a vacuum of 10^{-5} torr to minimize the thermal conduction through convection. Figure-of-merit was evaluated using the relation of $Z = \alpha^2/(\rho \times \kappa)$. Carrier concentration and mobility of the hot-pressed specimens were characterized using Hall measurements with AC magnetic field of 3000 gauss. Crystalline phase of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy was characterized by XRD analysis and microstructure was observed on the fracture surface of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy using scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 illustrates XRD patterns of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy. XRD peaks except $(Bi_{0.2}Sb_{0.8})_2Te_3$ were not observed even for the specimens with 7 vol% BN or 7 vol% WO_3, indicating that no reaction occurred between $(Bi_{0.2}Sb_{0.8})_2Te_3$ and BN or between $(Bi_{0.2}Sb_{0.8})_2Te_3$ and WO_3 during mechanical alloying and hot pressing. As shown in Figs 1(c) and (d), XRD peaks of BN or WO_3 were not observed even for the specimens fabricated with addition of 7 vol% BN or 7 vol% WO_3, which could be due to the fine dispersion of BN and WO_3 in the $(Bi_{0.2}Sb_{0.8})_2Te_3$ during mechanical alloying process. To confirm this, BN and WO_3 powders were mechanically ground for 5 hours using a Spex mill and their XRD patterns were analyzed. Fig. 2 illustrates XRD patterns of BN and WO_3 powders before and after the vibro-milling process. All diffraction peaks of BN powders disappeared completely and peak broadening occurred severely for WO_3 powders after the mechanical milling process, which could be attributed to the fact that BN and WO_3 powders were ground very finely by the mechanical milling process [19]. From the results illustrated in Fig. 2, it might be

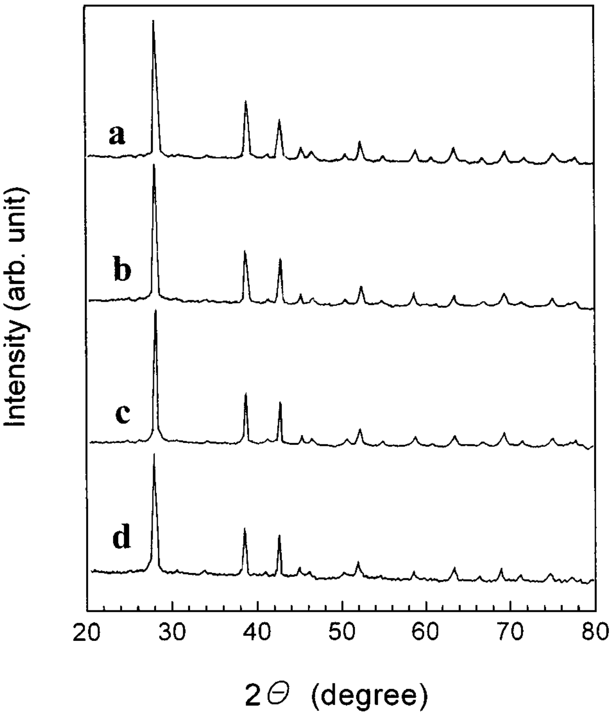

Figure 1 XRD patterns of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy with addition of (a) 0 vol% BN, (b) 3 vol% BN, (c) 7 vol% BN, and (d) 7 vol% WO_3.

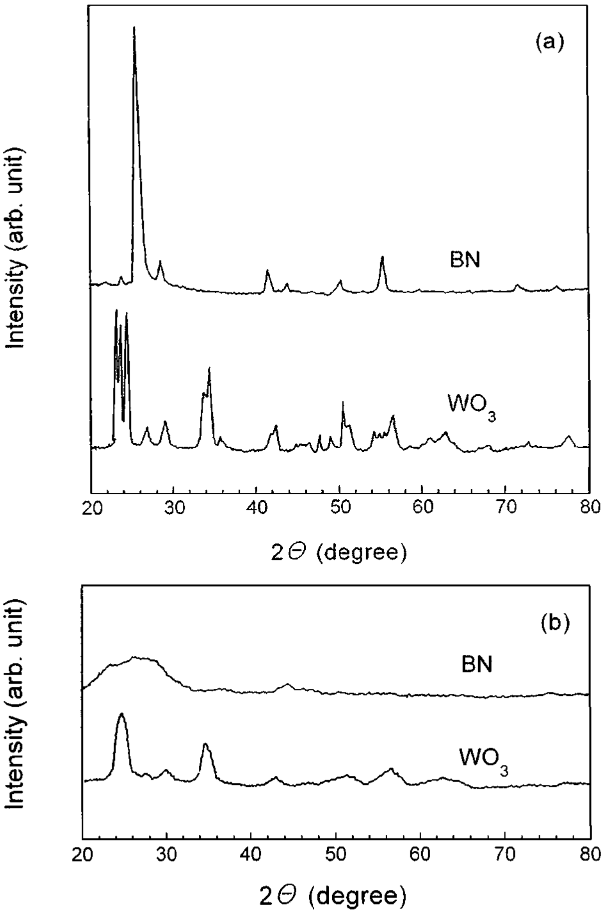

Figure 2 XRD patterns of the BN and WO_3 powders (a) before and (b) after vibro-milling for 5 hours.

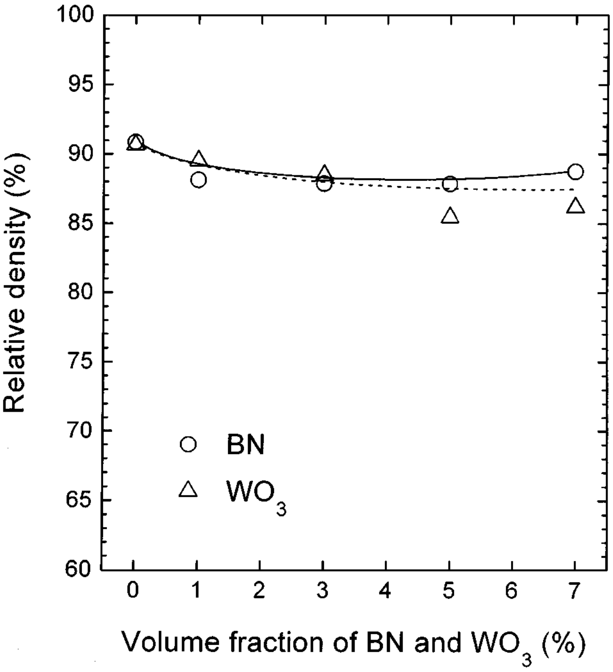

Figure 3 Relative density of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy as a function of the volume fraction of BN and WO_3.

expected that BN were dispersed more finely than WO_3 in the mechanically alloyed $(Bi_{0.2}Sb_{0.8})_2Te_3$ powders.

As shown in Fig. 3, the relative density of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy decreased slightly with increasing the volume fraction of BN and WO_3 powders. Figs 4 and 5 illustrate SEM micrographs observed on the fracture surface of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy with addition of BN and WO_3, respectively. The grain size of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy decreased with increasing the volume fraction of BN and WO_3, which could be due to the inhibition of grain growth by finely dispersed BN and WO_3. At the same volume fraction of BN and WO_3, the grain size of the specimens fabricated with BN was smaller than that of the WO_3-added specimens. Maximum grain size D_{max} of the alloys with dispersion of second phase particles is limited to $4r/3f$, where r and f are the average radius and the volume fraction of second phase particles, respectively [20]. Thus, the difference in the grain size of the specimens fabricated with BN and WO_3 might imply that BN powders were more finely dispersed in the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy.

Figs 6 and 7 illustrate the Seebeck coefficient and the electrical resistivity of the hot- pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy, respectively. The Seebeck coefficient and the electrical resistivity increased with increasing the volume fraction of BN and WO_3. Compared to the WO_3-added specimens, the $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy hot-pressed with BN exhibited lower Seebeck coefficient and higher electrical resistivity, which could be understood with the Hall measurement data in Fig. 8. As illustrated in Fig. 8, the hole concentration and mobility of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy decreased with increasing the volume fraction of BN and WO_3. At the same volume fraction of BN and WO_3, the specimens fabricated with BN exhibited higher hole concentration. However, the carrier mobility was lower in the BN-added specimens, which could be attributed to the smaller grain size. Electrical resistivity is expressed as $\rho = 1/(n_c \times e \times \mu_c)$ where n_c is the carrier concentration, e is the charge of electron and μ_c is the carrier mobility. For p-type thermoelectric materials, Seebeck coefficient is expressed as Equation [3].

$$\alpha = \frac{k_B}{e}\left[\gamma + 2 + \ln\frac{2\left(2\pi m^* k_B T\right)^{3/2}}{h^3 n_c}\right] \tag{1}$$

In Equation 1, k_B is Boltzmann constant, e is the charge of electron, γ is the scattering factor ($\gamma = 0$ for lattice scattering and 2 for impurity scattering), m^* is the effective mass of charge, h is Plank constant and n_c is the carrier concentration. At constant temperature, the Seebeck coefficient of p-type thermoelectric materials can be simplified as Equation 2 where C is constant [21].

$$\alpha = \frac{k_B}{e}(\gamma + C \ln n_c) \tag{2}$$

Contrary to the electrical resistivity which is dependent on both the carrier concentration and mobility, the Seebeck coefficient is only dependent on the carrier concentration [2, 21]. Compared to the WO_3-added specimens, the BN-added specimens possessed higher hole concentration and much lower mobility, resulting in lower Seebeck coefficient and higher electrical resistivity.

As shown in Figs 6 and 7, the increment of the electrical resistivity with increasing the volume fraction of BN and WO_3 was much larger than the increment of the Seebeck coefficient. While the electrical resistivity is dependent on both the carrier concentration (n_c) and mobility (μ_c), the Seebeck coefficient is only dependent on the carrier concentration [2, 21]. Furthermore, the electrical resistivity is linearly proportional to $1/n_c$ and $1/\mu_c$, but the Seebeck coefficient is related only to the natural logarithm of n_c. Compared to the Seebeck coefficient, thus, the electrical resistivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy increased much largely with dispersion of BN and WO_3 due to the decrease of both the hole concentration and mobility.

Figs 9 and 10 illustrate the thermal conductivities of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy with addition of BN and WO_3, respectively. For thermoelectric materials in extrinsic conduction region, the total thermal conductivity (κ_{tot}) can be expressed as $\kappa_{tot} = \kappa_{el} + \kappa_{ph}$ where κ_{el} is the electrical contribution to the thermal conductivity and κ_{ph} is the lattice thermal conductivity [2, 3]. κ_{el} is also expressed as $\kappa_{el} = L\sigma T$ where L is the Lorenz number and σ is the electrical conductivity [2, 3]. The lattice thermal conductivity κ_{ph} of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy was obtained by calculating κ_{el} and subtracting κ_{el} from κ_{tot}. Although the total thermal conductivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy decreased with increasing the volume fraction of BN and WO_3 due to the reduction of κ_{el}, the lattice thermal conductivity κ_{ph} was not lowered. In polycrystalline alloys, phonon scattering occurs at lattice distortion,

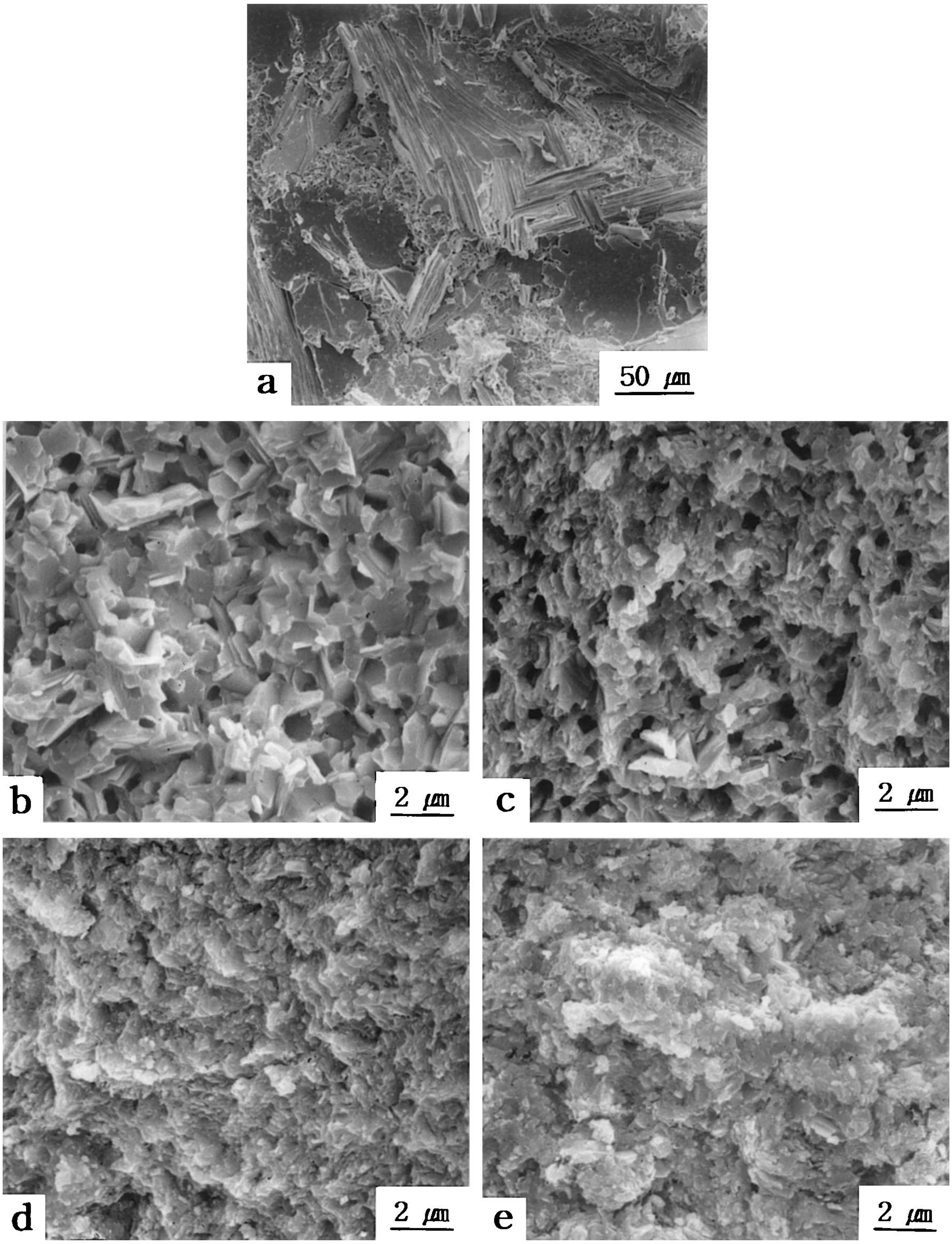

Figure 4 SEM micrographs observed on the fracture surfaces of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy with addition of (a) 0 vol% BN, (b) 1 vol% BN, (c) 3 vol% BN, (d) 5 vol% BN, and (e) 7 vol% BN.

impurities, pores, and grain boundaries. Decrease of the lattice thermal conductivity by phonon scattering is limited to a certain minimum value, however, because mean free path of phonon cannot be reduced too low [9]. Thus, it could be thought that the lattice thermal conductivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy already reached near a minimum value and was not reduced further with addition of BN and WO_3. For polycrystalline Bi_2Te_3, it has been reported that the lattice thermal conductivity was lowered from 1.2 W/K-m to 0.7 W/K-m with decreasing the grain size from 325 μm to 15 μm due to phonon scattering at grain boundaries [22]. As shown in Fig. 4, the grain size of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy decreased remarkably from 50 μm to 0.5 μm with addition of 7 vol% BN. However, the lattice thermal conductivity was little affected by such grain refinement, which might support that the lattice thermal conductivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy reached near a minimum value even without addition of BN and WO_3.

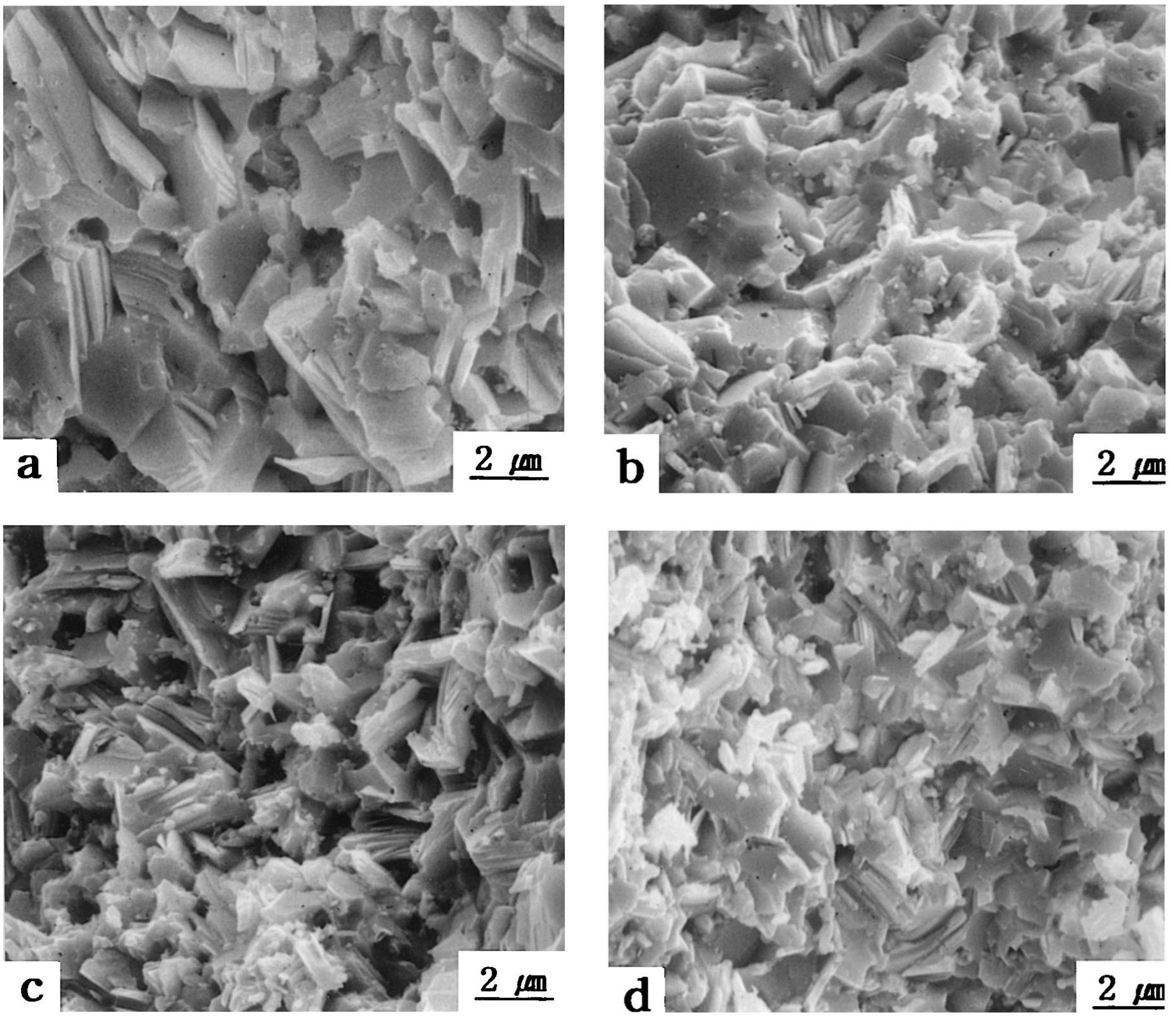

Figure 5 SEM micrographs observed on the fracture surfaces of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy with addition of (a) 1 vol% WO_3, (b) 3 vol% WO_3, (c) 5 vol% WO_3, and (d) 7 vol% WO_3.

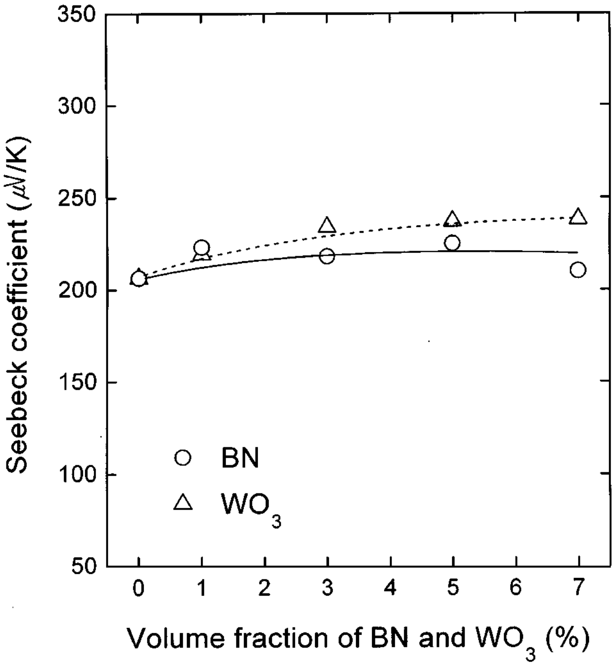

Figure 6 Seebeck coefficient of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy as a function of the volume fraction of BN and WO_3.

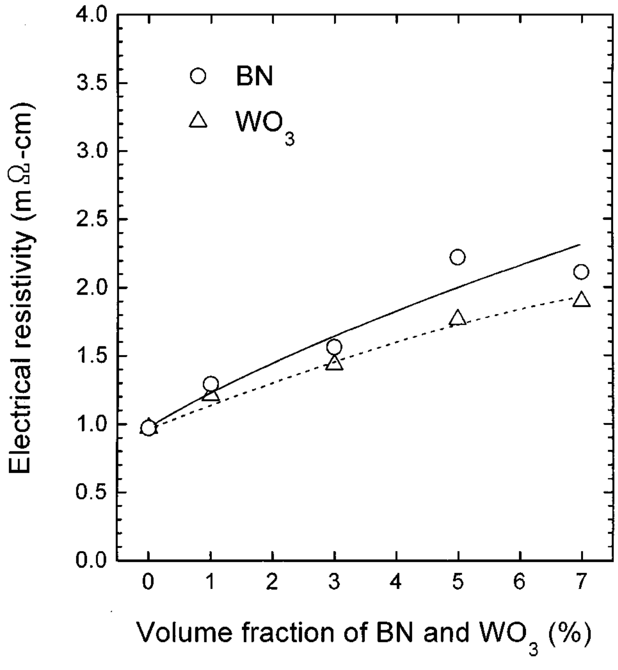

Figure 7 Electrical resistivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy as a function of the volume fraction of BN and WO_3.

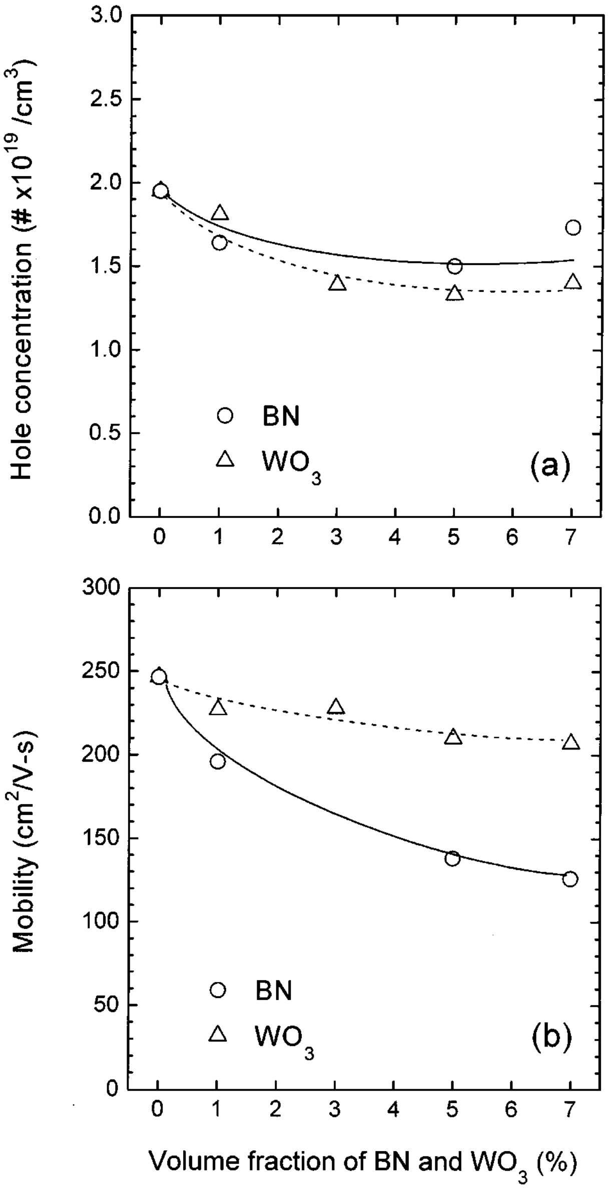

Figure 8 (a) Hole concentration and (b) mobility of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy as a function of the volume fraction of BN and WO_3.

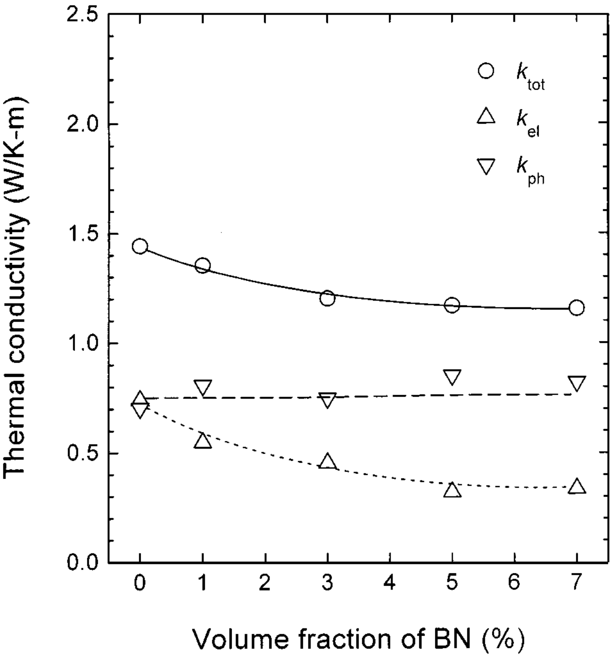

Figure 9 Thermal conductivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy as a function of the volume fraction of BN.

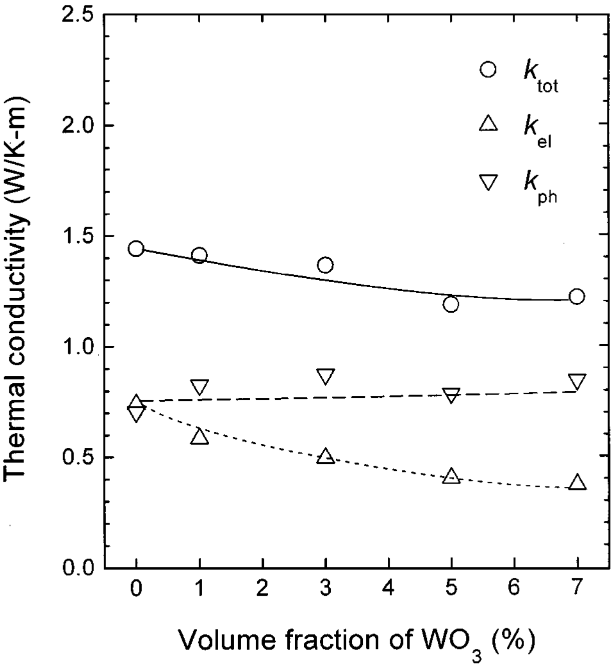

Figure 10 Thermal conductivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy as a function of the volume fraction of WO_3.

As shown in Fig. 11, the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy exhibited a figure-of-merit of $3.05 \times 10^{-3}/K$ without addition of BN and WO_3. However, the figure-of-merit decreased with increasing the volume fraction of BN and WO_3, because the increment of the electrical resistivity was much larger than the decrement of the thermal conductivity due to the grain refinement. It has been expected that the figure-of-merits of SiGe and Bi_2Te_3-based alloys can be improved for 10–40% and 15–20%, respectively, with fine dispersion of ceramic powders as phonon scattering centers [6–9]. However, the figure-of-merits of SiGe and $(Bi_{0.25}Sb_{0.75})_2Te_3$ alloys decreased with addition of BN and MgO due to the large increase of the electrical resistivity caused by the grain refinement [11, 23], which were not considered in the theoretical works [6–9]. To improve of the figure-of-merit of polycrystalline thermoelectric materials with addition of fine ceramic powders as phonon scattering centers, thus, it is definitely necessary to prevent large increase of the electrical resistivity by prohibiting the grain refinement. However, the maximum grain size D_{max} of the alloys with dispersion of second phase particles is limited to $4r/3f$, where r and f are the average radius and the volume fraction of second phase particles, respectively [20]. As there are few ways to prohibit the grain refinement of the alloys with fine dispersion of second phase particles, thus, it would be difficult in reality to improve the figure-of-merit of polycrystalline thermoelectric materials with addition of fine ceramic powders as phonon scattering centers.

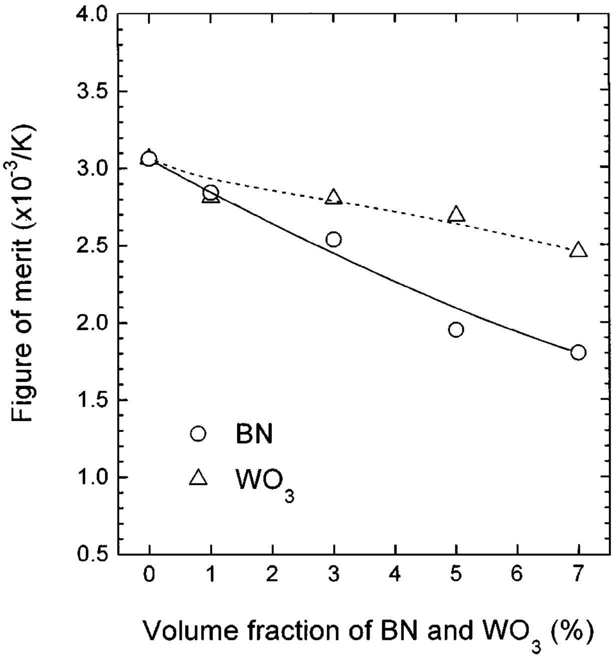

Figure 11 Figure-of-merit of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy as a function of the volume fraction of BN and WO_3.

4. Conclusions

(1) The Seebeck coefficient and the electrical resistivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy increased with increasing the volume fraction of BN and WO_3. Compared to the specimens fabricated with addition of WO_3, the BN-added specimens which possessed higher hole concentration and much lower mobility exhibited lower Seebeck coefficient and higher electrical resistivity,

(2) The total thermal conductivity of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy decreased with increasing the volume fraction of BN and WO_3 due to the reduction of κ_{el}. However, the lattice thermal conductivity was not lowered.

(3) The figure-of-merit of the hot-pressed $(Bi_{0.2}Sb_{0.8})_2Te_3$ was 3.05×10^{-3}/K without addition of BN and WO_3. However, the figure-of-merit decreased with increasing the volume fraction of BN and WO_3, because the increment of the electrical resistivity was much larger than the decrement of the thermal conductivity due to the grain refinement.

(4) As there are few ways to prohibit the grain refinement of the alloys with fine dispersion of second phase particles, it would be difficult in reality to improve the figure-of-merit of polycrystalline thermoelectric materials with addition of fine ceramic powders as phonon scattering centers.

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