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IMPROVEMENT IN THERMOELECTRIC PROPERTIES OF N-TYPE BISMUTH TELLURIDE NANOPOWDERS BY HYDROGEN REDUCTION TREATMENT

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Abstract. N-type bismuth telluride nanopowders were prepared by a ball milling process involving Bi, Te, and Se powders. Hydrogen reduction treatment was applied to the nanopowders to reduce remnant oxygen contents. In this study, both the as-prepared and the reduced nanopowders were consolidated by the spark plasma sintering process at 350 °C for 10 min, and then, their thermoelectric properties were investigated.

1. INTRODUCTION

Solid-state thermoelectric (TE) energy conversion devices have attracted considerable attention from the viewpoint of cooling and power generation applications as well as for use in sensory equipment. These devices can improve energy efficiency and reduce CO_2 gas emissions [1]. It is well known that bismuth-telluride-based alloys exhibit superior TE properties at temperatures in the range of 200–450K relative to other TE materials [2].

TE performance is determined by the dimensionless figure-of-merit defined as $ZT = T(\alpha^2/\rho\kappa)$, where T is the absolute temperature; α, the Seebeck coefficient; ρ, the electrical resistivity; and κ, the thermal conductivity. Recently, it has been shown that nanostructured bismuth telluride bulk materials, prepared using nanopowders by powder metallurgy (PM), show high *ZT* values that result from the significant reduction in lattice thermal conductivity caused by the increased nanoboundaries [3-7]. However, the improvement in *ZT* values achieved through grain refinement via PM has been limited owing to the difficulty of managing contamination and oxidation during the milling process. In particular, the control of oxide materials or oxygen atoms present in the bismuth telluride alloys is considered essentially because it influences their electrical properties, in that atomic-scale defects such as vacancies and impurities affect carrier behavior. However, compared to p-type bismuth tellurides [2-6], including my previous result on $Bi_{0.4}Sb_{1.6}Te_3$ powders [8], there have been few reports on the effects of controlling oxygen atoms on the TE properties of n-type bismuth telluride (NBT) systems.

In this study, we report on the influence of reduced oxygen content on the TE properties of NBT bulk prepared from nanopowders produced by a high-energy ball milling process. The sintered sample prepared using reduced n-type bismuth telluride (R-NBT) nanopowders shows an improved Seebeck coefficient and electrical conductivity, resulting in a highly improved figure-of-merit relative to that of the sintered sample prepared using as-prepared nanopowders without reduction treatment.

2. EXPERIMENTAL PROCEDURES

First, Bi_2Te_3 and Bi_2Se_3 powders were synthesized by melting and crushing Bi (99.9% purity) ingots

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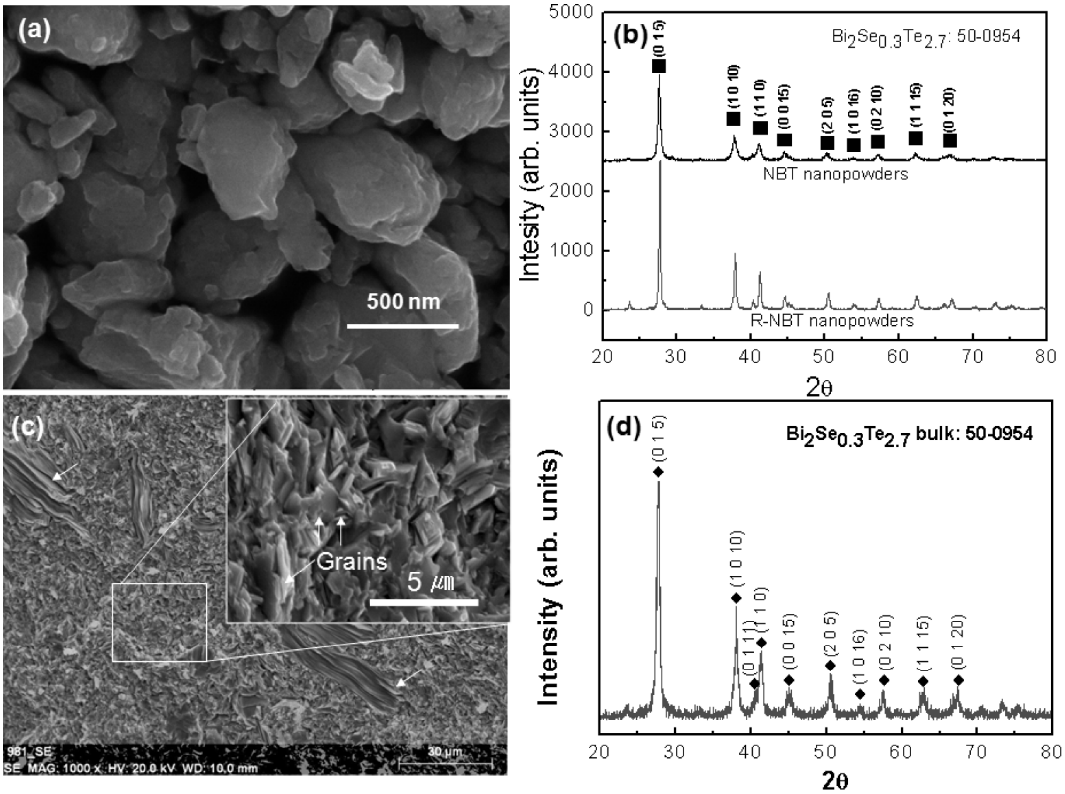

Fig. 1. (a) SEM image of R-NBT nanopowders, (b) comparison between XRD patterns of NBT nanopowders synthesized by the reduction process, (c) fracture surface, and (d) XRD pattern of the sintered body using R-NBT nanopowders.

with Te (99.9% purity) and Se (99.9% purity) ingots, respectively, the latter being used as n-type doping materials. The synthesized Bi_2Te_3 and Bi_2Se_3 powders were homogeneously mixed and alloyed into the nanopowders with a single composition of $Bi_2Se_{0.3}Te_{2.7}$ by a high-energy ball milling process using a planetary miller (Fritsch GmbH) for 4 h at 300 rpm. The synthesized NBT nanopowders were reduced to remove the remnant oxygen content in hydrogen atmosphere at 250 °C for 3 h. The R-NBT nanopowders were consolidated in a spark plasma sintering (SPS) system at 350 °C for 10 min. in a vacuum of 10^{-3} torr and under a pressure of 50 MPa. The heating rate was maintained at 150°C/min until the temperature was reached at 300 °C. To compare the effect of oxygen contents in the NBT materials, we fabricated the n-type bulk using nanopowders prepared by the same process without reduction treatment.

The oxygen contents of the nanopowders were measured using an elemental analyzer (ELTRA ON-900, oxygen/nitrogen Determinator). The phases of the nanopowders and sintered bulk were characterized using an X-ray diffractometer (XRD; Model no. X'pert MPD 3040). The microstructures of the powders and sintered n-type bulk were analyzed by field-emission scanning electron microscopy (FESEM, Hitachi S-4900). The Seebeck coefficients of the sintered bodies were measured using a 4-point probe system (Seepel, Korea) at room temperature. The electrical resistivity (ρ), carrier density, and carrier mobility at room temperature were obtained by Hall-effect measurements. The specific heat and thermal diffusivity values were evaluated by differential scanning calorimetry (DSC) and the laser flash method (Model No. LFA 447 NanoFlash; Netzsch, Germany), respectively, and the thermal conductivity was calculated using these two values and the carrier density.

3. RESULTS AND DISCUSSION

The surface morphology of the NBT nanopowders, as obtained by FESEM, is shown in Fig. 1a. The nanopowders contain ~200-nm-sized particles that are agglomerated rather than separated. The XRD pattern shown in Fig. 1b indicates that the synthesized NBT nanopowders clearly exhibit a single phase of $Bi_2Se_{0.3}Te_{2.7}$, which is defined as JCPDS (Joint Committee of Powder Diffraction Standards) card no. 50-0954. Furthermore, no additional peaks

Table 1. Comparison of oxygen contents in powders and thermoelectric properties such as relative density, electrical resistivity, carrier density, carrier mobility, and Seebeck coefficient of sintered bodies measured at room temperature.

	Nanopowders	Sintered body				
	Oxygen Contents (wt.%)	Relative density (%)	Electrical Resistivity (mW·cm)	Carrier Density (/cm^3)	Carrier Mobility (cm^2/Vs)	Seebeck Coefficient (μV/K)
NBT	1.46	98.0	0.81	-8.04×10^{19}	101	-102
R-NBT	0.51	98.3	0.76	-5.93×10^{19}	131	-112

are observed in R-NBT nanopowders even though they are heat-treated at an elevated temperature under hydrogen atmosphere.

The SPS process, which has advantages such as the restriction of grain growth and a fast densification rate, is used to consolidate both NBT and R-NBT nanopowders. The fracture surface of bulk materials prepared from R-NBT nanopowders, shown in Fig. 1c, indicates grain sizes of the order of submicrometers and randomly oriented grains (indicated by arrows). The XRD patterns of the R-NBT bulk also show $Bi_2Se_{0.3}Te_{2.7}$ as the main peak, as shown in Fig. 1d, and this indicates that the composition and phase (defined as JCPDS card no. 50-0954) of the nanopowders remain unchanged after sintering.

The oxygen content of NBT nanopowders, 1.46 wt.%, is drastically decreased to 0.51 wt.% through a hydrogen reduction process, as shown in Table 1. This reduction in oxygen content seems to cause a variation in the two thermoelectric properties. First, the sintered bulk prepared using the R-NBT nanopowders shows specific electrical resistivity

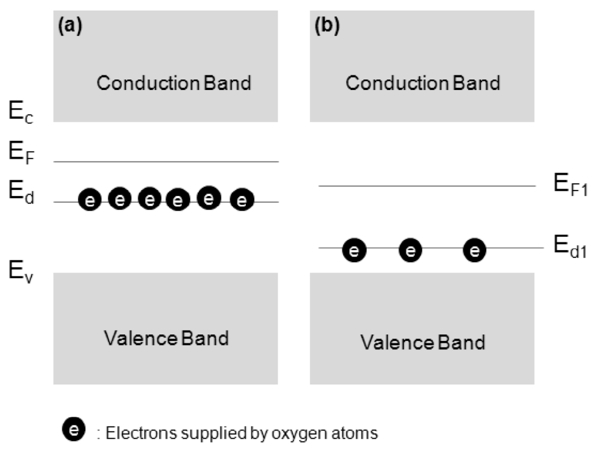

Fig. 2. Schematic illustrations of energy band diagram (a) before reduction process and (b) after reduction process at room temperature.

(ρ), 0.76 mΩ·cm, that is 5% lower than that of the NBT bulk, 0.81 mΩ·cm. It is observed that the reduction of oxygen atoms present in NBT nanopowders results in a decrease in carrier density and increase in mobility. That is, the carrier density increases from -8.04×10^{19} for the NBT bulk to -5.93×10^{19} for the R-NBT bulk, and the carrier mobility is greatly increased from 101 for the NBT bulk to 131 for the R-NBT bulk via reduction, as shown in Table 1.

Second, the Seebeck coefficient (α) of the R-NBT bulk, -112 μV/K, increases by 10% relative to that of the NBT bulk, -102 μV/K, as shown in Table 1. It can be considered that the lower Fermi energy caused by removing oxygen atoms acting as donors results in an increased Seebeck coefficient, as schematically illustrated in Fig. 2. The Fermi energy level (E_F) in the NBT bulk, as shown in Fig. 2a, shifts significantly toward E_{F1} near the band gap center because the donor level moves from E_d to E_{d1} with the reduction of oxygen atoms in hydrogen atmosphere [7].

The calculated power factor (α^2/ρ) of the bulk using R-NBT nanopowders is 26% higher than that of the bulk using as-prepared NBT nanopowders, as shown in Fig. 3a. It is confirmed that the enhancement of the power factor results from both the decreased electrical resistivity and the increased Seebeck coefficient when the oxygen contents are decreased by the reduction treatment of NBT nanopowders.

On the other hand, the thermal conductivities (κ) are not changed significantly by the hydrogen reduction process. As shown in Fig. 3b, the thermal conductivities of the NBT and R-NBT bulk show similar values and behavior over a temperature range from 25 to 200 °C. This implies that the reduction of oxygen atoms causes changes in electrical properties by varying energy-bands but does not affect the thermal conductivity of bismuth telluride materials.

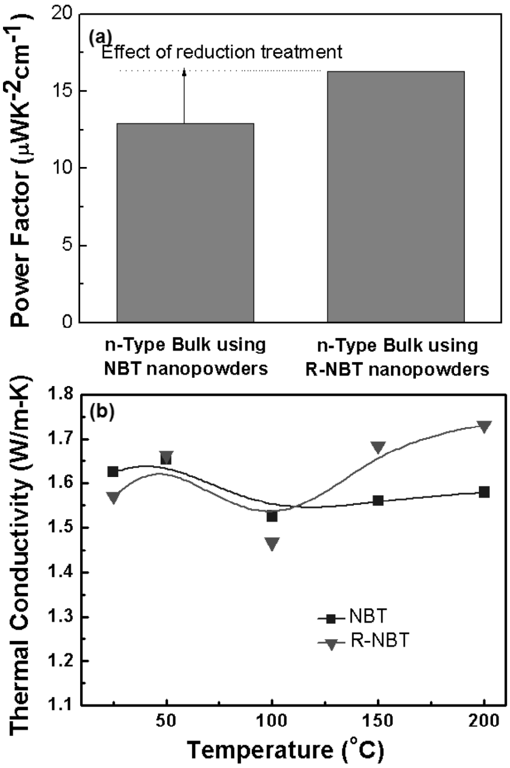

Fig. 3. Comparison between (a) power factors and (b) thermal conductivity of the sintered sample by the reduction treatment.

Fig. 4 compares the *ZT* values of the sintered samples using NBT and R-NBT nanopowders. The room-temperature *ZT* of NBT nanopowders, 0.58, is significantly improved to 0.70 because of enhanced electrical conductivity and increased Seebeck coefficient resulting from the control of the oxygen content of the NBT materials. These results suggest that hydrogen reduction treatment is essential to achieve high TE performance in TE materials prepared by PM.

4. CONCLUSION

In summary, we synthesized NBT nanopowders with a composition of $Bi_2Se_{0.3}Te_{2.7}$ using a high-energy mechanical milling process. The synthesized NBT nanopowders were reduced in hydrogen atmosphere to decrease the oxygen content. The bulk material using R-NBT nanopowders shows an enhanced Seebeck coefficient and a slightly improved electrical conductivity, while the thermal conductivity did not change significantly following the reduction process. The *ZT* value of the bulk using R-NBT nanopowders is enhanced by 25%; this improvement can be mainly attributed to the improved electrical properties resulting from the decreased number of oxygen atoms that would act as donors in bismuth telluride materials.

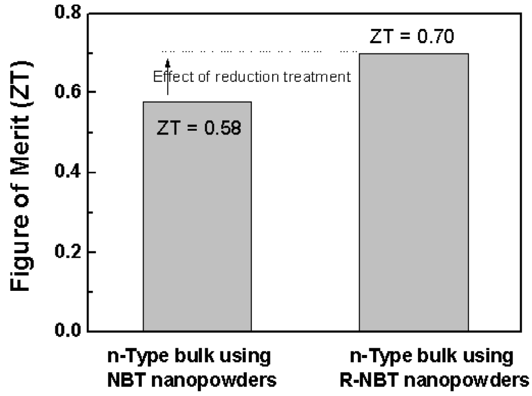

Fig. 4. Comparison of thermoelectric performance (*ZT*) of $Bi_2Se_{0.3}Te_{2.7}$ bulk materials.

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