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# Effect of multiwalled carbon nanotubes on the thermoelectric properties of a bismuth telluride matrix

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## ABSTRACT

Carbon nanotubes (CNTs) have been not attractive for thermal energy conversion applications because of their high thermal conductivities and low Seebeck coefficient. In other words, traditional thermoelectric materials are basically low bandgap semiconductors such as bismuth telluride and antimony telluride, which have shown outstanding performance. In this report, we studied the effect of a network consisting of CNTs as an impurity in a matrix of bismuth telluride ($Bi_2Te_3$) particles. We dispersed $Bi_2Te_3$ particles and CNTs together in a solvent and fabricated composite samples under vacuum filtration. Seven different CNTs concentration, 0, 10, 20, 50, 70, 90, 100 vol% were used to compare the influence of CNTs on electrical conductivity and thermopower of the composites. At the low contents (10 and 20 vol%) of CNTs, the electrical conductivity and the thermopower were a little increased, which can be attributed to p-typed doping effect of CNTs on $Bi_2Te_3$ particles. At the high contents (50, 70 and 90 vol%) of CNTs, the electrical conductivity and the thermopower were decreased, which can be attributed to hindered carrier mobility.

## 1. Introduction

Because we are running out of fossil fuels, many researchers naturally have studied ways to develop eco-friendly and renewable energy power generation. Among these methods, a thermoelectric power generation method has been paid attention. It includes the conversion of waste heat into electrical energy and has been very attractive fields because it uses abundant resources, i.e. heats, which are all around us and free. In most thermoelectric devices, semiconducting materials have been used because they have excess charge carriers such as electrons or holes. When a difference of temperature ($\Delta T$) is generated in a thermoelectric material, the charge carriers diffuse from the hot site to the cold site, producing an electrical potential ($\Delta V$), which is known as the Seebeck effect [1]. This is defined as $\Delta V/\Delta T$, the Seebeck coefficient ($S$) or thermopower and is an important parameter in defining a thermoelectric efficiency. The efficiency of a thermoelectric material is strongly related to its figure of merit (ZT), defined as $(S^2\sigma/\kappa)\cdot T$, where $S$, $\sigma$, $\kappa$, and $T$ indicate the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Based on this relationship, we can guess that the best thermoelectric material is one that has a higher Seebeck coefficient, higher electrical conductivity, and lower thermal conductivity.

Several articles have reported the enhanced performance of thermoelectric materials using nano- or microscale composites of several promising materials. For example, the ZT of $Sb_2Te_3$ reached 1.2 at room temperature, whereas that of $CsBi_4Te_6$ reached 0.8 at 225 K [2–6]. Recently, many researchers have paid attention to one-dimensional materials. For example, the ZT of silicon nanowires reached 1.0 at 200 K [7]. The thermoelectric performance is closely associated with charge carrier transportation as well as the mean free path of phonons and phonon scattering [5,7]. Generally, electrical conductivity of the materials is controlled by grain boundary diffusion of the charge carriers, whereas phonons do not [8]. When phonons pass through grain boundaries, thermal conductivity is considerably decreased because of their scattering effect. In the case of one-dimensional materials, they provide a larger mean free path length of electrons than that of phonons [9]. As a result, one-dimensional materials show a significantly lower thermal conductivity, without sacrificing the electrical conductivity.

As is well known, carbon nanotubes (CNTs) intrinsically have outstanding mechanical and electrical properties [10–13]. The interconnected network of CNTs provides not only a tough mechanical nanostructure but also superior electrical conductivity. The percolation conductivity of CNT network depends on their dispersions as well as their concentrations (i.e. the percolation

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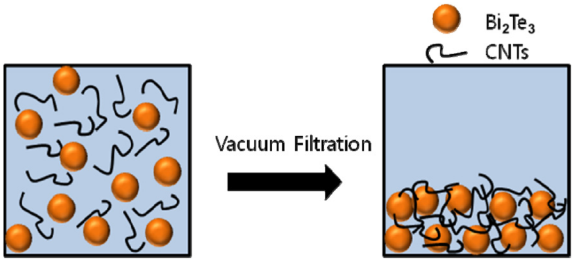

**Fig. 1.** Schematic diagram of carbon nanotubes percolating network in a bismuth telluride matrix prepared by vacuum filtration.

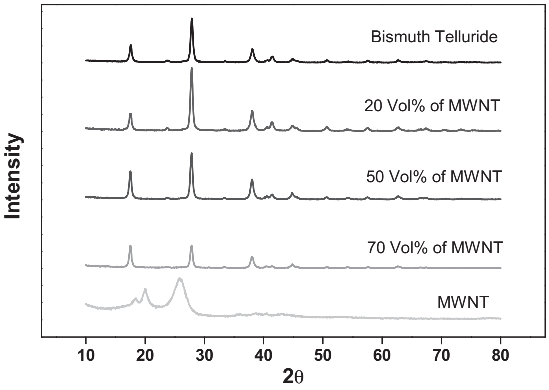

**Fig. 2.** XRD patterns of $Bi_2Te_3$/MWNTs composites.

threshold) [14]. As a result, well dispersed CNTs could provide superior electrical conductivity just with a minimum number of nanotubes.

In this study, we fabricated composites of bismuth telluride ($Bi_2Te_3$) particles and multiwalled carbon nanotubes (MWNTs) by varying amounts of multiwalled carbon nanotubes (MWNTs). $Bi_2Te_3$ particles are well known as outstanding thermoelectric materials at room temperature [15], and MWNTs are expected to provide well-connected transport paths for electrons. Fig. 1 shows a schematic diagram of our process. We prepared $Bi_2Te_3$ particles with a ball-milling process. Then, $Bi_2Te_3$ particles and MWNTs were dispersed in ethanol. In order to survey the thermoelectric properties of the $Bi_2Te_3$/MWNTs composite, bar-type samples were fabricated under high pressure after applying a vacuum filtration of $Bi_2Te_3$/MWNTs dispersions in ethanol. Then, we investigated the thermoelectric properties of the $Bi_2Te_3$/MWNTs composites. We compared the thermoelectric properties of pure $Bi_2Te_3$, pure MWNTs and their composite samples.

## 2. Experimental

### 2.1. Materials

MWNTs (CM-95), produced using chemical vapor deposition (CVD), were purchased from Hanwha Nanotech Corp. (Incheon, Korea). The diameter of the MWNTs was from 10 to 15 nm and their lengths were approximately 10 μm or longer. The nanotubes were used with no further purification. For the synthesis of $Bi_2Te_3$, commercially available bismuth and tellurium were used with purities of 99.99% or higher (Aldrich co.).

### 2.2. Fabricating $Bi_2Te_3$ particles

The bismuth and tellurium materials were weighed according to the required chemical compositions and then charged in a stainless steel vial with steel balls as the milling media under Ar atmosphere. The ball-to-powder weight ratio was held to 5:1. Mechanical alloying was conducted by shaking the vial at approximately 1200 rpm (i.e. 20 Hz) using an SPEX mixer/mill for 3 h.

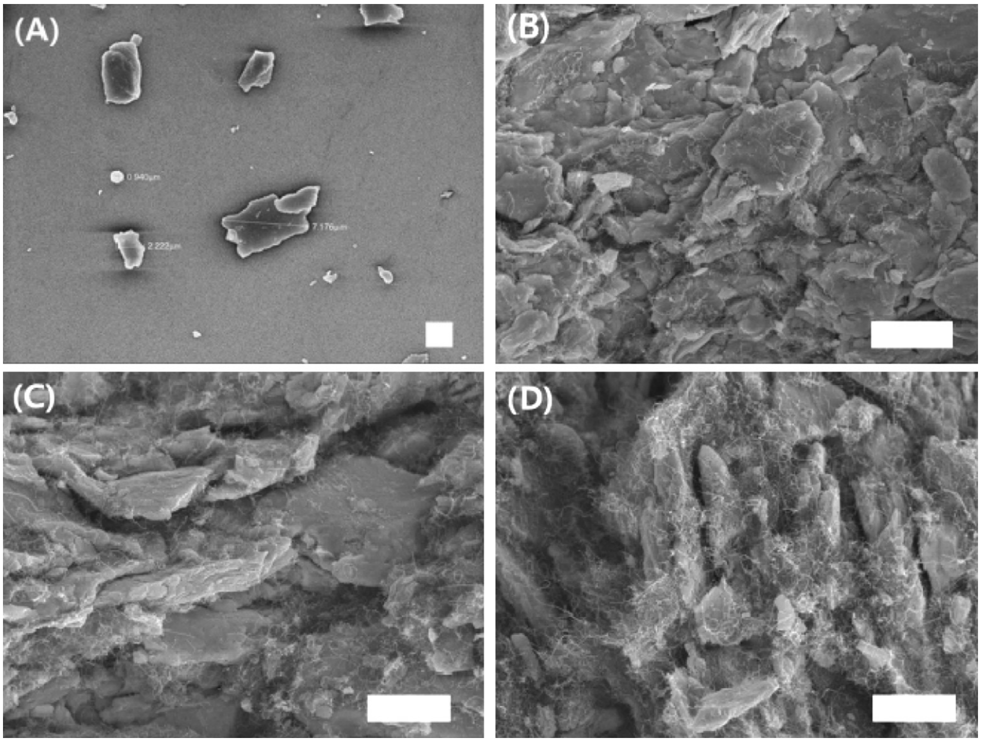

**Fig. 3.** SEM images of (A) $Bi_2Te_3$ and $Bi_2Te_3$/MWNTs composites: (B) 20 vol%, (C) 50 vol%, and (D) 70 vol% of MWNTs. All scale bars indicate 2 μm.

### 2.3. Fabricating $Bi_2Te_3$/MWNT composites

$Bi_2Te_3$ particles or MWNTs or their mixtures were dispersed in ethanol for 20 min with an ultrasonic system (750 W, Sonics & Materials Inc.), respectively. The solution was filtered by a vacuum filtration method and the filtered results were dried at 40 °C under vacuum. In order to evaluate the effect of MWNTs on the $Bi_2Te_3$ particles, we fabricated composites with 0.36, 0.8, 3.2, 7.0, and 22.3 wt% of nanotubes, which corresponded to 10, 20, 50, 70, and 90 vol%, respectively. Samples of pure $Bi_2Te_3$ particles or MWNTs were fabricated to be compared with those of their composite samples.

### 2.4. Characterization

In order to investigate the morphological and thermoelectrical properties of $Bi_2Te_3$/MWNT composites, bar-type samples ($3 \times 3 \times 10$ mm) were prepared by pressing MWNTs or $Bi_2Te_3$ or their composite samples into homemade mold at 1500 psi (i.e. 10.3 MPa). The crystal structures were surveyed by X-ray diffraction (XRD) (D/MAX 2500, Rigaku, Japan) using Cu K$\alpha$ radiation. The instrument was operated at 40 kV/200 mA and a scanning speed was 2°/min. The morphological properties were investigated using the field-emission scanning electron microscopic (FE-SEM, JSM-7401F, JEOL Ltd.). The accelerating voltage was 10.0 kV. The Seebeck coefficient and electrical conductivity of the samples were measured using a thermoelectric measurement system (ZEM-2, ULVAC-RIKO Technologies, Inc.) The temperature measuring range was approximately −100 to 800 °C. Each sample was measured under helium gas atmosphere at 50 °C.

## 3. Results and discussion

Fig. 2 illustrates the XRD patterns of pure $Bi_2Te_3$, $Bi_2Te_3$/MWNTs composites, pure MWNTs, respectively. In general, the XRD patterns of all samples were similar to that of pure $Bi_2Te_3$, with the exception of that for the pure MWNTs sample. The XRD pattern of pure $Bi_2Te_3$ was in good agreement with the results by C.-H. Kuo et al. and F. Yu et al. [16,17]. Even though the content of MWNTs was increased, the XRD patterns of nanotubes were not detected because the amount of $Bi_2Te_3$ particles was considerably higher than that of nanotubes. This phenomenon indicates that the nanotubes do not affect the crystal lattice of $Bi_2Te_3$.

In Fig. 3, we show the SEM images of pure $Bi_2Te_3$ and $Bi_2Te_3$/MWNTs composites. The $Bi_2Te_3$ particles were dispersed in ethanol and dropped on the substrate (Anodisc™, pore size 0.02 μm, diameter 47 mm) to observe the size of the particles, as shown in Fig. 3(A). Generally, the particle size of $Bi_2Te_3$ was as large as approximately 10 μm. As shown in Fig. 3(B)–(D), nanotubes were well dispersed in the matrix of $Bi_2Te_3$ particles.

The electrical conductivity ($\sigma$), Seebeck coefficient ($S$), and power factor ($S^2\sigma$) are depicted in Fig. 4. Seebeck coefficient and electrical conductivity are known to have a tradeoff relationship. Low carrier concentration materials have large Seebeck coefficients. However, low carrier concentration also results in low electrical conductivity. However, Fig. 4(A) and (B) shows this inverse phenomenon as the composition of MWNTs are increased. In Fig. 4(A), the electrical conductivity of pure MWNTs was approximately 2000 S/m whereas the electrical conductivity of pure $Bi_2Te_3$ sample was nearly 8000 S/m. When the amount of nanotubes was increased, the electrical conductivity was decreased. Even though the sample with 20 vol% of MWNTs has a little larger electrical conductivity, more specifically, the electrical conductivity of composite samples was decreased significantly with an increase from 20 to 50 vol% of the MWNTs. Even though one dimensional nanotubes are expected to provide large mean free path of charge carriers, nanotubes mainly played the role of impurities among $Bi_2Te_3$ particles in composite samples and the nanotubes prevented $Bi_2Te_3$ particles from connecting with each other. As previously noted, charge carriers select a path in the grain boundary, resulting in decreasing the charge mobility and thus increasing the electrical contact resistance.

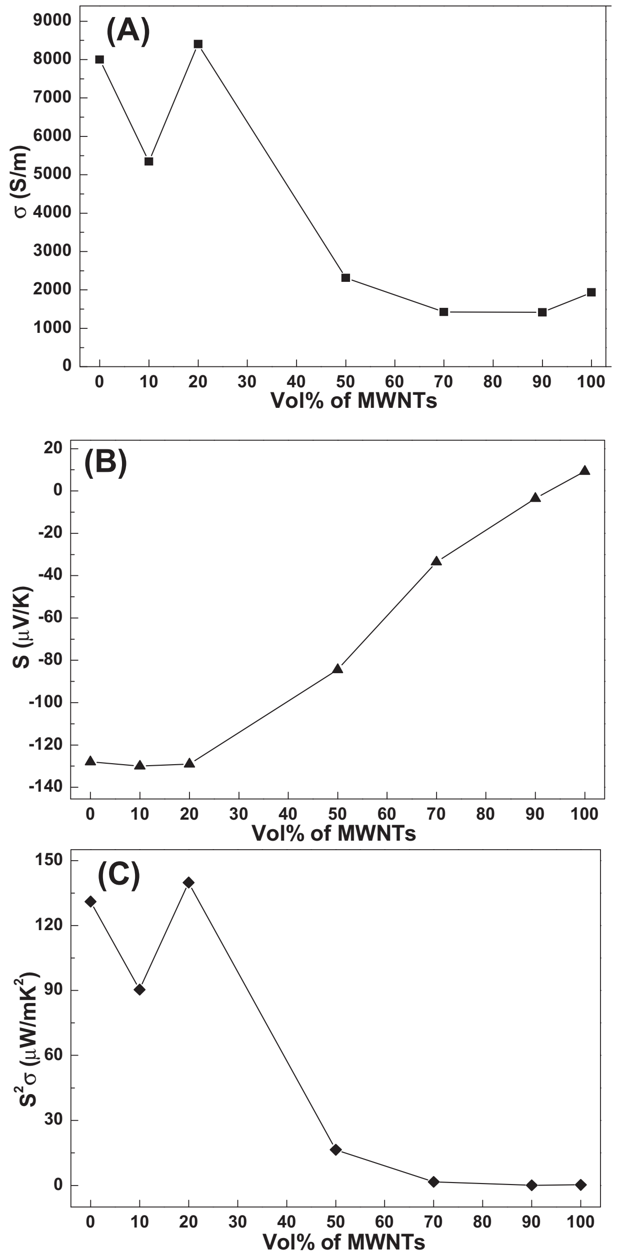

**Fig. 4.** Volume %-dependence of (A) the electrical conductivity, (B) the Seebeck coefficient, and (C) the power factor for the $Bi_2Te_3$/MWNTs composites.

In Fig. 4(B), the Seebeck coefficient of the pristine MWNTs was about +10 μV/K, whereas that of pure $Bi_2Te_3$ particles was almost −128 μV/K. The negative and positive values of Seebeck coefficients for pure $Bi_2Te_3$ particles and pure MWNTs indicate that they are n-typed and p-typed thermoelectric materials, respectively. The combination of n-typed $Bi_2Te_3$ with p-typed MWNTs would bring the p-typed doping effect on $Bi_2Te_3$ particles, i.e. the decrease of charge carrier concentrations. However, the absolute values of Seebeck coefficient also were decreased as the number of nanotubes covering $Bi_2Te_3$ particles was increased. As mentioned in explaining their electrical conductivity, it might be attributed to the decreased charge mobility. When the contents of MWNTs changed from 10 to 20 vol% in these composites, the Seebeck coefficient exhibited little change.

As the amount of MWNTs particles exceeds over 30 vol%, the absolute value of Seebeck coefficient went to be decreased. The Seebeck coefficient of the composite containing 50 vol% MWNTs was approximately −80 μV/K. The Seebeck coefficient of the composite sample containing 90 vol% MWNTs showed still a negative value (−3.61 μV/K).

The power factor ($S^2\sigma$), shown in Fig. 4(C), is one of the most important factors in monitoring thermoelectric properties. In general, the power factor of the composites was mainly dependent on their electrical conductivity. For the composites with the 10 to 20 vol% MWNTs, the power factor showed larger values than those of the composites with 50 vol% or more MWNTs. The highest power factor was as high as 140 $\mu W/mK^2$ for a composite sample with 20 vol% MWNTs, which represented the highest electrical conductivity and the largest Seebeck coefficient. The electrical conductivity and the Seebeck coefficient was a little enhanced, which can be attributed to p-typed doping effect of MWNTs on $Bi_2Te_3$ particles, even though the carrier concentration was decreased. As the contents of MWNTs were increased, the effect of hindered carrier mobility was enhanced. There was a continuous decrease in their electrical conductivity as well as the absolute values of Seebeck coefficient and then, remained constant. No significant changes were found in power factors for the composites with 50, 70 and 90 vol% MWNTs.

## 4. Conclusions

Composite samples containing MWNTs with Bi2Te3 were fabricated to survey the effect of MWNTs among $Bi_2Te_3$ particles. Seven different MWNTs concentration, 0, 10, 20, 50, 70, 90, 100 vol% were used to compare the influence of the MWNTs on electrical conductivity and thermopower of the composites. Their electrical conductivities and Seebeck coefficient values were measured for the composites. In SEM images, we found that well-dispersed MWNTs among $Bi_2Te_3$ particles. At the low contents (10 vol% and 20 vol%) of MWNTs in composite samples, the electrical conductivity and the absolute values of Seebeck coefficient were a little increased by p-typed doping effect of MWNTs on $Bi_2Te_3$ particles. We obtained the highest power factor for the composite with 20 vol % MWNTs (about 140 $\mu W/mK^2$). As the amount of nanotubes was increased, the electrical conductivity and the absolute values of Seebeck coefficient of composites were decreased because the effect of hindered carrier mobility was enhanced.

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