Effects of Preparation Methods on the Thermoelectric Performance of SWCNT/Bi$_2$Te$_3$ Bulk Composites

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Abstract: Single-walled carbon nanotube (SWCNT)/Bi$_2$Te$_3$ composite powders were fabricated via a one-step in situ reductive method, and their corresponding bulk composites were prepared by a cold-pressing combing pressureless sintering process or a hot-pressing process. The influences of the preparation methods on the thermoelectric properties of the SWCNT/Bi$_2$Te$_3$ bulk composites were investigated. All the bulk composites showed negative Seebeck coefficients, indicating n-type conduction. A maximum power factor of 891.6 μWm$^{-1}$K$^{-2}$ at 340 K was achieved for the SWCNT/Bi$_2$Te$_3$ bulk composites with 0.5 wt % SWCNTs prepared by a hot-pressing process, which was ~5 times higher than that of the bulk composites (167.7 μWm$^{-1}$K$^{-2}$ at 300 K) prepared by a cold-pressing combing pressureless sintering process, and ~23 times higher than that of the bulk composites (38.6 μWm$^{-1}$K$^{-2}$ at 300 K) prepared by a cold-pressing process, mainly due to the enhanced density of the hot-pressed bulk composites.

Keywords: single-walled carbon nanotube; Bi$_2$Te$_3$ composite; thermoelectric

1. Introduction

According to the Seebeck coefficient, thermoelectric (TE) materials can directly convert waste heat into useful electrical energy [1,2]. The TE properties of a material are judged by the figure of merit, $ZT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ is the thermal conductivity [3–6]. So far, the highest $ZT$ value of 2.6 has been reported for SnSe [7]. The actual applied TE devices near room temperature (RT) are mainly made of inorganic bulk materials, e.g., Bi–Te-based alloys due to them being one of the most widely studied TE materials and having exhibited a high $ZT$ value at RT [8–10]; however, the energy conversion efficiency of TE devices is still much lower than that of the maximum possible Carnot efficiency [2], which has limited the wide application of TE devices. In order to scale out the application of TE devices, the TE performance of inorganic bulk materials should be improved (e.g., optimizing their preparation technologies and compositions), and the conversion efficiency of thermoelectric devices should also be enhanced [11] (e.g., optimizing their geometric structures [12]).

Carbon nanotubes (CNTs) have extraordinary electrical and mechanical properties [13,14] and can form conductive network structures in a relatively low threshold value when used as fillers for preparation of composite materials; therefore, introducing CNTs into inorganic TE matrixes is an effective method to further improve the TE properties of inorganic materials [15–20]. For instance, Choi et al. [15] prepared Te nanowires using a chemical method and then synthesized flexible single-walled carbon nanotube (SWCNT)/Te nanowire films via a vacuum filtering method, and a power factor of 3.40 μWm$^{-1}$K$^{-2}$ was obtained for the composite film with 2 wt % SWCNTs at RT. Zhang et al. [16] first fabricated multi-walled carbon nanotube (MWCNT)/Bi$_2$Te$_3$ nanocomposite powders via
a cryogenic grinding method and then prepared bulk composites through a spark plasma sintering process, and a power factor (PF = $S\sigma$) of ~800 μWm⁻¹K⁻² (ZT value of ~0.3) at 300 K was obtained for the composite with 3 vol% MWCNTs. Ahmad et al. [17] first fabricated SWCNT/Bi₂Te₃ nanocomposite powders via a mechanical mixing method and then prepared bulk composites through a high-frequency induction-heated sintering furnace, and a PF of ~900 μWm⁻¹K⁻² (ZT value of ~0.32) at 300 K was obtained for the composite with 0.5 wt % SWCNTs. Kim et al. [18] prepared MWCNT/Bi₂Te₃ nanocomposite powders via a chemical route combing ball milling method and then fabricated corresponding bulk composites via a spark plasma sintering process, and a PF of 1060 μWm⁻¹K⁻² (ZT value of 0.48) at 300 K was achieved for the bulk composite with 0.7 wt % MWCNTs. Hosokawa et al. [19] firstly synthesized Bi₂Te₃ nanoplate/SWCNT composite film through a drop-casting technique, and a PF of 91 μWm⁻¹K⁻² for the composite film at 300 K was obtained after an annealing process was applied. Jin et al. [20] fabricated highly ordered Bi₂Te₃ nanocrystals anchored on an SWCNT network using a magnetron sputtering technique, and a power factor of ~1600 μWm⁻¹K⁻² (ZT value of 0.89) at RT was obtained. However, so far, systematic research of SWCNT/Bi₂Te₃ bulk composites using the hydrothermal synthesized SWCNT/Bi₂Te₃ nanopowders as raw materials, followed by a cold-pressing combing pressureless sintering process or a hot-pressing process, is limited. Herein, SWCNT/Bi₂Te₃ composite powders were fabricated via a one-step in situ reductive method, and their corresponding bulk composites were prepared by a cold-pressing combing pressureless sintering process or a hot-pressing process. The effects of the preparation methods on the composition, microstructure, and TE properties of the bulk composites were investigated.

2. Materials and Methods

2.1. Materials

Absolute ethanol (C₂H₅OH, reagent grade) and bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, analytical reagent (AR)) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Potassium borohydride (KBH₄, AR) and tellurium dioxide (TeO₂, guaranteed reagent) were purchased from Adamas Reagent Co., Ltd. (Shanghai, China). Sodium tartrate (C₄H₆Na₂O₄·2H₂O, ACS reagent) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Potassium hydroxide (KOH, AR) was purchased from General Reagent Co., Ltd. (Qionglai, China). SWCNTs were purchased from Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China) All the materials were applied without further purification or treatment.

2.2. Preparation of the SWCNT/Bi₂Te₃ Composite Powders

SWCNT/Bi₂Te₃ composite powders were prepared via a one-step in situ reductive method [21]. It mainly contained the following three steps. (1) An appropriate amount of SWCNTs was added in deionized water (80 mL) and then ultrasonicated for 1 h to form Solution I. C₄H₆Na₂O₄·2H₂O (2 g), TeO₂ (0.48 g), and KOH (4.5 g) were added to Solution I and then stirred for 0.5 h to form Solution II. Bi(NO₃)₃·5H₂O (0.97 g) was added into Solution II and then stirred for 2 h to form Solution III. KBH₄ (1.2 g) was added into Solution III and then stirred for 0.5 h to form Solution IV. (2) Solution IV was transferred to the sealed Teflon-lined autoclave and then heated for 24 h at 180 °C before naturally being cooled to RT. (3) The reaction products were washed several times by deionized water and absolute ethyl alcohol, and then dried at 60 °C for 6 h in a vacuum. The weight percentages (nominal compositions) of SWCNTs in the SWCNT/Bi₂Te₃ composite powders were 0.25, 0.5, and 0.75 wt %, respectively. Figure 1a illustrates the preparation procedures of the SWCNT/Bi₂Te₃ composite powders.

2.3. Preparation of the SWCNT/Bi₂Te₃ Bulk Composites

Cold-pressing combing pressureless sintering process: SWCNT/Bi₂Te₃ composite powders with different contents of SWCNTs from 0.25 to 0.75 wt % were cold-pressed into pellets at 30 MPa for 0.5 h, and then the bulk composites with 0.5 wt % SWCNTs were pressurelessly sintered at different
temperatures (598, 648, or 698 K) for 1 h in an argon (Ar) atmosphere, respectively, before naturally being cooled to RT. The resulting bulk composites are denoted as CNT/BT-PS-598, CNT/BT-PS-648, and CNT/BT-PS-698, respectively. The thicknesses of the as-prepared samples were ~1.3 mm. Figure 1b illustrates the preparation procedures of the SWCNT/Bi$_2$Te$_3$ bulk composites by a cold-pressing combing pressureless sintering process.

Hot-pressing process: SWCNT/Bi$_2$Te$_3$ composite powders with 0.5 wt% SWCNTs were hot-pressed into pellets in a graphite die (diameter: 12.7 mm) under vacuum at 80 MPa (648 K) for 1 h, and then naturally cooled to RT. The resulting bulk composites are denoted as CNT/BT-HP-648. The thicknesses of the hot-pressed SWCNT/Bi$_2$Te$_3$ bulk composites were ~1.55 mm. Figure 1c illustrates the preparation procedures of SWCNT/Bi$_2$Te$_3$ bulk composites by a hot-pressing process.

![Figure 1](image.png)

**Figure 1.** (a) The preparation procedures of the single-walled carbon nanotube (SWCNT)/Bi$_2$Te$_3$ composite powders, (b) bulk composites (prepared by a cold-pressing combing pressureless sintering process), and (c) bulk composites (prepared by a hot-pressing process).

### 2.4. Sample Characterization

The compositions of the as-prepared SWCNT/Bi$_2$Te$_3$ composites were characterized by X-ray powder diffraction (XRD, D/max 2200PC, Rigaku, Tokyo, Japan). The morphologies of the samples were characterized by high-resolution transmission electron microscopy (HRTEM, Technai G2 F20, FEI, Waltham, MA, USA) and scanning electron microscopy (SEM, Philips PW6800/70, Philips, Amsterdam, The Netherlands). The Seebeck coefficient and electrical conductivity were measured simultaneously from 300 to 360 K by an MRS-3L thin-film thermoelectric test system (Wuhan Giant Instrument Technology Co., Ltd., Wuhan, China) in a low-vacuum atmosphere (≤40 Pa). The instrument test errors are 6% and 5% for the Seebeck coefficient and electrical conductivity, respectively. The thicknesses of the samples were measured by a helical micrometer (Links 150-0.01, Links, Harbin, China). By calculating the ratios of measured density/theoretical density of the SWCNT/Bi$_2$Te$_3$ bulk materials, the corresponding relative density of the as-prepared sample was obtained. The densities of Bi$_2$Te$_3$ and SWCNTs used for calculating the theoretical density of the SWCNT/Bi$_2$Te$_3$ bulk materials were 7.86 [22] and 2.1 g/cm$^3$ (from the manufacturer), respectively.

### 3. Results and Discussion

Figure 2 presents the XRD patterns of SWCNT/Bi$_2$Te$_3$ composite powders with different contents of SWCNTs from 0.25 to 0.75 wt%. The main diffraction peaks of all the SWCNT/Bi$_2$Te$_3$ composite...
powders are matched with the standard JCPDF #15-0863 for Bi\(_2\)Te\(_3\) [23,24]. No obvious characteristic peak of SWCNTs is observed as the content of SWCNTs increases from 0.25 to 0.75 wt %, mainly due to the low content of SWCNTs, which agrees with a previous report in Reference [17].

Figure 2. XRD patterns of the SWCNT/Bi\(_2\)Te\(_3\) composite powders with different contents of SWCNTs from 0.25 to 0.75 wt %.

Figure 3a–c & 3d–f shows the SEM images and TEM images of the SWCNT/Bi\(_2\)Te\(_3\) composite powders with different contents of SWCNTs, respectively. A network structure is observed for the SWCNTs in the composite powders, which agrees with the results reported in Reference [25] (Figure 3a–c), and some Bi\(_2\)Te\(_3\) particles are partially nucleated on the surfaces of SWCNTs (Figure 3d–f). The SWCNTs are homogeneously dispersed in the Bi\(_2\)Te\(_3\) matrixes. From Figure 3f, it can be seen that the lattice spacing is ~0.32 nm, which corresponds to the (015) lattice plane of Bi\(_2\)Te\(_3\), indicating good crystallinity of the Bi\(_2\)Te\(_3\) particles in the composite powders [26].

Figure 3. SEM images of the SWCNT/Bi\(_2\)Te\(_3\) composite powders with different contents of SWCNTs: (a) 0.25 wt %, (b) 0.5 wt %, and (c) 0.75 wt % SWCNTs. TEM images of SWCNT/Bi\(_2\)Te\(_3\) composite powders with different contents of SWCNTs: (d) 0.25 wt %, (e) 0.5 wt %, and (f) 0.75 wt % SWCNTs.
At 300 K, as the content of SWCNTs increases from 0.25 to 0.75 wt %, the $\sigma$ of the cold-pressed SWCNT/Bi$_2$Te$_3$ bulk composites enhances from 39.5 to 62.9 S/cm, while the absolute values of Seebeck coefficients ($|S|$) are in the range of 70–90 $\mu$V/K (the Seebeck coefficients are negative, indicating n-type conduction), and a highest power factor of 38.6 $\mu$Wm$^{-1}$K$^{-2}$ is obtained for the bulk composites with 0.5 wt % SWCNTs. In order to further enhance the TE properties of the cold-pressed samples, the pressureless sintering and hot-pressing processes were applied for the SWCNT/Bi$_2$Te$_3$ bulk composites with 0.5 wt % SWCNTs. Figure 4a–c shows the fracture surface SEM images of CNT/BT-PS-598, CNT/BT-PS-648, and CNT/BT-PS-698, respectively. Figure 4d shows the fracture surface SEM image of CNT/BT-HP-648. It can be seen that the SWCNTs are partly embedded into the Bi$_2$Te$_3$ matrix, and there are some voids both in the bulk composites prepared by the pressureless sintering process and the hot-pressing process. The content of voids in CNT/BT-HP-648 is much lower than those of CNT/BT-PS-598, CNT/BT-PS-648, and CNT/BT-PS-698, mainly because CNT/BT-HP-648 has undergone a high pressure (80 MPa). An obviously oriented microstructure was observed in CNT/BT-HP-648 (Figure 4d), mainly due to the anisotropy of Bi$_2$Te$_3$, which agrees with the results reported in Reference [24]. The peak intensity of the (0015) plane (~44.5°) significantly increases in CNT/BT-HP-648 (Figure S1) when compared with the as-prepared composite powders (Figure 2), which also confirms the oriented microstructure of CNT/BT-HP-648.

Figure 4. Fracture surface SEM images of (a) CNT/BT-PS-598, (b) CNT/BT-PS-648, (c) CNT/BT-PS-698, and (d) CNT/BT-HP-648.

Figure 5a–c shows the TE properties of CNT/BT-PS-598, CNT/BT-PS-648, and CNT/BT-PS-698, as a function of temperature from 300 to 360 K. At 300 K, as the pressureless sintering temperature rises from 598 to 698 K, the $\sigma$ increases from 117.8 to 325.8 S/cm, while the $|S|$ decreases from 101.4 to 71.8 $\mu$V/K, and a highest power factor of 167.7 $\mu$Wm$^{-1}$K$^{-2}$ is obtained for the CNT/BT-PS-698, which is ~4 times higher than that of the cold-pressed samples (38.6 $\mu$Wm$^{-1}$K$^{-2}$ at 300 K) without having undergone pressureless sintering treatment, indicating that pressureless sintering treatment is an effective method to enhance the TE properties of the cold-pressed samples. As the measurement temperature rises from 300 to 360 K, the $\sigma$ of CNT/BT-PS-598, CNT/BT-PS-648, and CNT/BT-PS-698
remains basically unchanged, while the absolute values of the Seebeck coefficient first reduce and then enhance. As a result, the power factors of CNT/BT-PS-598, CNT/BT-PS-648, and CNT/BT-PS-698 first decrease and then increase—for instance, the power factor of CNT/BT-PS-698 decreases from 167.7 (300 K) to 151.3 μWm⁻¹K⁻² (320 K), then it increases to 168.0 μWm⁻¹K⁻² at 360 K. Figure 5d presents the temperature dependence of TE properties of CNT/BT-HP-648 from 300 to 360 K. The $\sigma$ of CNT/BT-HP-648 is 782.6 S/cm at 300 K, which is higher than that of a Bi$_{3}$Te$_{5}$ nanoplate/SWCNT film (111.9 S/cm at 300 K) [19] and that of an SWCNT/Bi$_{3}$Te$_{5}$ bulk material (~700 S/cm at 300 K) [17], while close to that of an MWCNT/Bi$_{3}$Te$_{5}$ bulk (~790 S/cm at 300 K) [18]. The $|S|$ of CNT/BT-HP-648 is 101.4 μV/K at 300 K, which is higher than that of a Bi$_{3}$Te$_{5}$ nanoplate/SWCNT composite film (90.1 μV/K at 300 K) [19]; however, it is lower than those of an MWCNT/Bi$_{3}$Te$_{5}$ bulk material (113 μV/K at 300 K) [17] and an SWCNT/Bi$_{3}$Te$_{5}$ bulk material (~115 μV/K at 300 K) [17]. As the measurement temperature rises from 300 to 360 K, the $\sigma$ of CNT/BT-HP-648 shows a decreasing tendency, which suggests the degenerate semiconductor behavior of the hot-pressed bulk composites [27]. The $|S|$ of CNT/BT-HP-648 first increases and then decreases in the measurement temperature ranges from 300 to 360 K, and the $|S|$ achieves 109.2 μV/K at 340 K. The power factor of CNT/BT-HP-648 first increases and then decreases, due to the same trend of $|S|$, and a highest power factor of 891.6 μWm⁻¹K⁻² is obtained at 340 K. This value (891.6 μWm⁻¹K⁻²) is higher than those of the bulk composites prepared by a cold-pressing combing pressureless sintering process (168.0 μWm⁻¹K⁻² at 360 K) and the Bi$_{3}$Te$_{5}$ nanoplate/SWCNT composite film (91 μWm⁻¹K⁻² at 300 K) [19]; however, it is lower than those of the SWCNT/Bi$_{3}$Te$_{5}$ bulk material (~980 μWm⁻¹K⁻² at 400 K) [17] and the MWCNT/Bi$_{3}$Te$_{5}$ bulk material (~1180 μWm⁻¹K⁻² at 423 K) [18].

![Figure 5](image1.png)

**Figure 5.** (a) Temperature dependence of electrical conductivity, (b) Seebeck coefficient, and (c) power factors of CNT/BT-PS-598, CNT/BT-PS-648, and CNT/BT-PS-698. (d) Temperature dependence of electrical conductivity, Seebeck coefficient, and power factor of CNT/BT-HP-648.

The relative densities of CNT/BT-PS-598, CNT/BT-PS-648, CNT/BT-PS-698, and CNT/BT-HP-648 are shown in Table 1. As the pressureless sintering temperature rises from 598 to 698 K, the relative densities increase slowly from 78.19% to 81.72%. The relative density of CNT/BT-HP-648 (91.51%) is much higher than those of CNT/BT-PS-598, CNT/BT-PS-648, and CNT/BT-PS-698, which is beneficial to improve the $\sigma$, as well as the power factor of the as-prepared samples, and it might be the main reason for the higher TE properties of the hot-pressed bulk composites, when compared with the bulk composites prepared by the cold-pressing combing pressureless sintering process. Additionally, it is noted there are still a lot of voids in the bulk composites, which could scatter the phonons and...
charge carriers, decrease the thermal conductivity, and then improve the $ZT$ value of the bulk composites [28].

| Samples        | Relative Densities (%) |
|----------------|------------------------|
| CNT/BT-PS-598  | 78.19                  |
| CNT/BT-PS-648  | 79.53                  |
| CNT/BT-PS-698  | 81.72                  |
| CNT/BT-HP-648  | 91.51                  |

4. Conclusions

SWCNT/Bi$_2$Te$_3$ bulk composites were prepared by a cold-pressing combing pressureless sintering process or a hot-pressing process, using the hydrothermal synthesized SWCNT/Bi$_2$Te$_3$ nanopowders as raw materials. For the bulk composites with 0.5 wt % SWCNTs prepared by a cold-pressing combing pressureless sintering process, as the pressureless sintering temperature increased from 598 to 698 K, the electrical conductivity was enhanced, while the absolute value of Seebeck coefficient reduced, and a power factor of 168.0 $\mu$Wm$^{-1}$K$^{-2}$ at 360 K was obtained, which is much higher than that of the bulk composites (38.6 $\mu$Wm$^{-1}$K$^{-2}$ at 300 K) prepared by a cold-pressing process; however, it is much lower than that of the bulk composites prepared by a hot-pressing process (891.6 $\mu$Wm$^{-1}$K$^{-2}$ at 340 K); the main reason is that the hot-pressed SWCNT/Bi$_2$Te$_3$ bulk composites have much higher relative densities. To this end, the hot-pressing process is a better choice than the cold-pressing or cold-pressing combing pressureless sintering processes, although it needs expensive equipment. The TE performance of the SWCNT/Bi$_2$Te$_3$ bulk composites could be further improved by enhancing their relative densities via optimizing the parameters for the hot-pressing process, or controlling the parameters of the gradient cooling process for the cold-pressing combing pressureless sintering process. The as-prepared SWCNT/Bi$_2$Te$_3$ bulk composites have a potential for thermoelectric devices.

Supplementary Materials: The following are available online at www.mdpi.com/1996-1944/13/11/2636/s1, Figure S1: XRD patterns of the CNT/BT-HP-648.

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