Research Article

Fabrication and Thermoelectric Properties of Graphene/Bi₂Te₃ Composite Materials

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Graphene/Bi₂Te₃ thermoelectric materials were prepared by spark plasma sintering (SPS) using hydrothermal synthesis of the powders as starting materials. The X-ray diffraction (XRD) and field emission scanning electron microscope (FE-SEM) were used to investigate the phase composition and microstructure of the as-prepared materials. Electrical resistivity, Seebeck coefficient, and thermal conductivity measurement were applied to analyze the thermoelectric properties. The effect of graphene on the performance of the thermoelectric materials was studied. The results showed that the maximum dimensionless figure of merit of the graphene/Bi₂Te₃ composite with 0.2 vol.% graphene was obtained at testing temperature 475 K, 31% higher than the pure Bi₂Te₃.

1. Introduction

Thermoelectric (TE) materials can directly convert thermal energy to electricity and vice versa through all solid-state energy conversion. They have been considered as one of the potential solutions to energy crisis and global climate changes [1–3]. Good thermoelectric materials require a high Seebeck coefficient (α), high electrical conductivity (σ), and low thermal conductivity (κ) for a high figure of merit ($Z = \alpha^2 \sigma / \kappa$), which is related to the thermoelectric energy conversion efficiency. These parameters are not independent for a given material.

Bismuth telluride- (Bi₂Te₃-) based compounds, as one of the most excellent thermoelectric materials near room temperature, are extensively used in the area of medical appliance, microelectronic devices, biologic slug, and so on [4, 5]. Due to the wide practical applications, a great deal of research has focused on improving the TE properties of Bi₂Te₃ materials [6–12]. Nanostructure can enhance the electronic density of states near Fermi level, and the nanostructured thermoelectric materials have a large number of boundaries that will strongly scatter the phonons and carries [13]. Therefore, the Seebeck coefficient is improved,

and the thermal conductivity is reduced, which lead to the improvement of thermoelectric properties.

Graphene has become one of the most exciting topics of research in recent years. This two-dimensional material constitutes layers of carbon atoms arranged in six-membered rings. As a new kind of function materials, graphene has high conductivity, high carrier mobility, and excellent mechanical properties [14, 15]. So, it has been widely used to prepare various kinds of functional composites since the first report of the free standing graphene [16–20].

In this work, Graphene/Bi₂Te₃ nanopowders with different graphene contents were synthesized by hydrothermal synthesis, and then bulk materials were fabricated by spark plasma sintering (SPS). The TE properties of the Graphene/Bi₂Te₃ composite materials sintered body, prepared from the synthesized nanopowders, were characterized. Our studies focus on the particle morphology and sintering behavior of Graphene/Bi₂Te₃ nanopowders.

2. Experimental Procedure

All the chemicals were of analytical grade and were used without further purification. Graphene nanosheet (J&K Scientific

Inc.) was dispersed in the alcohol to form a certain concentration of solution.

In a typical procedure, BiCl_3 and Te powders with the stoichiometric ratio of $\text{Bi}:\text{Te} = 2:3$ were mixed in a beaker filled with a certain amount of distilled water. Then different quantities of graphene nanosheet (0, 0.1 vol.%, 0.2 vol.%, 2 vol.%) were dissolved in the beaker. The solution was stirred immediately following the addition of NaOH as the pH controller, hydrazine hydrate ($\text{N}_2\text{H}_4 \geq 50\% \text{ v/v}$) as the reductant, and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) in sequence. The process of ultrasonic agitation lasts 0.5 h. Finally, the solution was removed into the autoclave with the water up to 80% volume. The solution was heated to 180°C and then cooled naturally to room temperature after about 8 h. The dark-grey powders in the autoclave were centrifuged and washed with distilled water and anhydrous ethanol several times and then dried in vacuum oven at 60°C for 5 h. The phase structures of the samples were investigated by X-ray diffraction (XRD) using $\text{Cu}/\text{K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The morphologies of powders were observed by field emission scanning electron microscopy (FESEM).

The as-prepared Graphene/ Bi_2Te_3 nanopowders were sintered using spark plasma sintering (Dr. Sinter 725; Sumitomo Coal Mining Co., Tokyo, Japan). The nanopowders were loaded into cylindrical carbon dies with an inner diameter of 10 mm. The heating rate was controlled in the range of $70^\circ\text{C}/\text{min}$, and the pressure was set at 80 MPa. The final temperature was selected at 350°C for a dwelling time of 6 min. The Seebeck coefficient and electrical conductivity were measured by using temperature differential and four-probe methods, respectively, with Ulvac-Riko ZEM-3 equipment in a helium atmosphere. The thermal conductivity was estimated from the specific heat, thermal diffusivity, and density by using DSC, laser flash method (Model No. LFA 447 NanoFlash), and Archimedes immersion method, respectively. The thermoelectric figure of merit was evaluated.

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of Graphene/ Bi_2Te_3 compounds with different contents of graphene. Main diffraction peaks in Figure 1 could be indexed according to JCPDS 15-0863 for Bi_2Te_3 . Diffractions of other phases could not be found such as Te, Bi, or their compounds. It indicated that we had obtained a pure Bi_2Te_3 phase with good crystallinity. As the contents of graphene in the composites are very low, the diffraction peaks of graphene show low strength. We found that the Graphene/ Bi_2Te_3 composite powders showed the same XRD pattern as the Bi_2Te_3 .

Figure 2 shows the morphologies of the as-prepared Graphene/ Bi_2Te_3 nanopowders with different concentrations of graphene. Figure 2(a) reveals the synthesized Bi_2Te_3 powders with a size of 30–200 nm, which are agglomerated and nonuniform. Figure 2(b) demonstrates the existence of graphene in the composite powders (marked by arrow), and the particle size is uniform. This is because the presence of graphene hindered the Bi_2Te_3 grain growth. Therefore, Bi_2Te_3

FIGURE 1: XRD patterns of Graphene/ Bi_2Te_3 nanopowders with different contents of graphene.

TABLE 1: Relative density of Bi_2Te_3 /graphene bulk materials fabricated by SPS.

	Content of graphene			
	0	0.1 vol.%	0.2 vol.%	2 vol.%
Actual density (g/cm^3)	7.71	7.70	7.68	7.57
Theoretical density (g/cm^3)	7.86	7.85	7.85	7.79
Relative density	98.09%	98.09%	97.83%	97.18%

grains become smaller and homogeneous. From Figures 2(c)–2(d), the existence form of graphene and Bi_2Te_3 can be observed clearly. A large number of Bi_2Te_3 particles were coated by large nanosheet of graphene. Figure 2(d) is the place that the arrow pointed in Figure 2(c). The coated Bi_2Te_3 particles can be seen clearly through the graphene.

SPS was used to densify the Bi_2Te_3 /graphene composite powders. The actual densities of Bi_2Te_3 /graphene bulk materials were calculated using the Archimedes immersion method with deionized water as the immersion medium. The theoretical densities of the samples were calculated according to the rule of mixtures. The relative densities are shown in Table 1. The results reveal that the relative densities of the Bi_2Te_3 /graphene bulk materials decrease slightly as the contents of graphene increase.

Figure 3 shows FESEM images for the fracture surface of bulk samples with different contents of graphene. Comparing pure Bi_2Te_3 sample with 2 vol.% graphene composited samples, it is easy to find that the pure Bi_2Te_3 samples are well-densified, but there are some holes (marked by arrow) in the composite. And, it is observed that the average grain sizes of the two bulk samples are obviously different. The grain size of composite sample is smaller than pure Bi_2Te_3 sample. It is suggested that the existence of graphene not only reduced the density of the sample but also decreased the size of grains. The density reduced makes the carrier concentration drop which is detrimental to the improvement of electrical conductivity. But, at the same time, the decrease of the grain size increases the ability of grain boundary scattering phonons, which is beneficial to the decrease of the thermal conductivity.

FIGURE 2: FESEM images of graphene/ Bi_2Te_3 nanopowders with different graphene contents, (a) 0, ((b)–(d)) 2 vol.%.

FIGURE 3: FESEM fractographs of bulk Bi_2Te_3 /graphene with different graphene contents, (a) 0, (b) 2 vol.%.

The temperature dependence of Seebeck coefficient is presented in Figure 4(a). The negative Seebeck coefficient confirmed that the electrical charge was transported mainly by electron and all the samples are n-type conductor. A similar varying trend of the Seebeck coefficient is showed in the whole measuring temperature range. The absolute values of Seebeck coefficient first increase and then decrease with raising the measuring temperature. The Seebeck coefficient of semiconductor can be expressed as

$$\alpha = (\gamma + C - \ln n_e) \frac{k_B}{e}, \quad (1)$$

where k_B is the Boltzmann constant, e is the electron charge, γ is the exponent of the power function in the

energy-dependent relaxation time expression, C is constant, and n_e is the electron concentration. Therefore, as shown in Figure 4(a), the Seebeck coefficient of Graphene/ Bi_2Te_3 decreased at high temperatures (>400 K) with increasing the temperature due to an increase in the carrier concentration by intrinsic conduction.

Figure 4(b) shows the temperature dependence of the electrical conductivity. All the samples show a decreasing trend in the electrical conductivity with raising the measuring temperature, which indicate a metallic conducting behavior. With the temperature rising, scattering process of lattice vibration on the carrier is strengthened gradually, and the carrier mobility is reduced. So, the conductive performance of materials declines. The highest and lowest conductivity

FIGURE 4: Temperature dependence of Seebeck coefficient (a), electrical conductivity (b), thermal conductivity (c), and ZT (d) for bulk materials of different graphene contents.

values at room temperature are $1.03 \times 10^5 \text{ S/m}$ and $0.91 \times 10^5 \text{ S/m}$, respectively. There is no big difference.

Figure 4(c) shows the temperature dependence of the total thermal conductivity on the Graphene/ Bi_2Te_3 compounds. The thermal conductivity of Bi_2Te_3 increased roughly with increasing the temperature, whereas that of the graphene/ Bi_2Te_3 composites decreased slightly with increasing the temperature. With an increase in the temperature, the total thermal conductivity of the compounds decreased roughly.

Figure 4(d) gives the dimensionless figures of merit, ZT of all composite samples. A remarkable tendency can be seen from Figure 4(d). With the temperature rising, ZT value increases and the effect of graphene is obvious. The maximum ZT of about 0.21 is obtained in the present work of the sample with 0.2 vol.% graphene. The microstructure has a certain extent effect on the performance of the material, but ZT value depends on a combination of various factors, so higher ZT could be expected by the composition optimization.

4. Conclusions

In summary, the bulk nanostructured Graphene/ Bi_2Te_3 composites have been prepared by hydrothermal synthesis followed by spark plasma sintering. In the precursor nanopowders, Bi_2Te_3 particles were coated by graphene nanosheets with a grain sizes varying from 30~200 nm. The effect of graphene composite content on the thermoelectric properties of nanostructured bulk materials is investigated in this study. The maximum ZT value of about 0.21 has been obtained at 475 K with the 0.2 vol.% content of graphene, which is 31% higher than that of pure Bi_2Te_3 materials.

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