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Effect of Multiwall Carbon Nanotubes on the Thermoelectric Properties of BiSbTe Based Composites

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Abstract: The effects of ball milling with simultaneous addition of multiwall carbon nanotubes (MWCNTs) on the thermoelectric properties of BiSbTe based nanocomposites were investigated in the temperature range from 300 K to 500 K. The MWCNTs in 0.5 vol% and 1.0 vol% were incorporated in fine BiSbTe powder that was processed from commercially available BiSbTe lumps and consolidated through pressure assisted induction heated sintering. The results show that the electrical and thermal transport properties of the composites are altered substantially. The thermal conductivity of the composites decreases significantly from pure BiSbTe bulk due to enhanced phonon scattering caused by nanostructuring and nanoinclusion effects. While the electrical conductivity deteriorates with the addition of MWCNTs, which is attributed partly to enhanced electron scattering and predominantly, rather low densification of the composites. The figure of merit of 1.0 vol% MWCNTs/BiSbTe composite remains close to that of pristine BiSbTe, snice the decrease in electrical conductivity is compensated by the significant reduction in thermal conductivity. The result suggests that optimizing the processing parameters for enhanced densification could improve the figure of merit for BiSbTe based MWCNTs composites.

Key words: BiSbTe; multiwall carbon nanotubes; composites; thermoelectric properties

Sustainable clean energy is the biggest challenge in the 21st century and there are continued efforts for the development of viable and economical energy production technologies. Thermoelectric materials that convert waste heat into electricity offer solutions for sustainable energy challenges through improving the efficiency and providing the distribution generation of clean energy[1]. BiSbTe is the state of the art thermoelectric material and being used in energy harvesting and refrigeration applications. There are continued efforts to improve energy conversion efficiency of BiSbTe that can be quantified by the dimensionless parameter called figure of merit $ZT=S^2\sigma T/K$, where S, σ, T, K are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. The advancements in powder processing nanotechnology pave the way for the development of high performance thermoelectric bulk materials via nanostructuring through ball milling and consolidation through pressure assisted sintering[2-5]. Efforts were done to improve the figure of merit of BiSbTe through nanostructuring and nanoinclusion. Yu Pan et al. reported the effects of ball milling and spark plasma sintering on BiSbTe bulks and showed improvement in ZT and mechanical properties[6]. Similarly, Bed Poudel et al. did nanostructuring of BiSbTe and achieved improved figure of merit due to reduction in thermal conductivity[2]. Others have used nanostructuring and nanoinclusion to improve the efficiency of BiSbTe. For instance, Li Jingfeng et al. incorporated SiC in BiSbTe and reported improved *ZT* which is attributed to enhanced power factor and low thermal conductivity[3]. Li Yuanyue and coworkers incorporated 1.0 vol% of Cu_3SbSe_4 and reported significant reduction in thermal conductivity with simultaneous enhancement in power factor that leads to improved figure of merit at 476 K[7]. Most recently, Li's group incorporated graphene nanosheets in $Bi_{0.4}Sb_{1.6}Te_3$ and demonstrated simultaneous increase in electrical conductivity and reduction in thermal conductivity which resulted in improved figure of merit[8].

Multiwall carbon nanotubes (MWCNTs) possess unique electrical, mechanical and thermal properties. Their incorporation in the form of second phase have been found to improve

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electrical and mechanical properties with simultaneous deterioration in thermal conductivity[9-11]. Therefore, it is expected that addition of MWCNTs in BiSbTe will not only improve its mechanical properties but also its thermoelectric figure of merit by increasing electrical conductivity and reducing thermal conductivity.

In this work, 0.5 vol% and 1.0 vol% of MWCNTs were incorporated in fine BiSbTe powder and consolidated by the pressure assisted induction heated sintering. In addition, pristine BiSbTe bulk of coarse powder was also fabricated under similar conditions for comparison of the results. The effects of MWCNTs addition and the nanostructuring by the ball milling have been analyzed on the thermoelectric properties of the composites.

1 Experiment

Multiwall carbon nanotubes having diameter and length in the range 5~20 nm and 1~10 μm respectively were purchased from EMFUTUR Spain. BiSbTe in the form of lumps were commercially obtained from American Elements. The lumps were transformed into coarse powder and subsequently fine powder through ball milling in an inert environment. High frequency induction heated furnace was used to consolidate the composites. The density was measured by the Archimedes principle in water. The electrical conductivity and Seebeck coefficient measurements were performed on ZEM-3 (ULVAC). The thermal properties were measured on LFA-457 (NETZSCH).

2 Results and Discussion

2.1 Powder processing and microstructure

Fig.1a shows the as received lumps that were processed to form fine BiSbTe powder. The MWCNTs and BiSbTe powder were weighed in appropriate proportions to form the 0.5 and 1.0 vol% MWCNTs/BiSbTe composites. The MWCNTs were deagglomerated through ultra-sonication in ethanol and further mixing in BiSbTe was done through magnetic stirring and ball milling. The SEM image of dried composite powder of 1.0 vol% MWCNTs/BiSbTe is shown in Fig.1b. The composite powders were consolidated by pressure assisted induction heated sintering furnace at 400 ℃ with a uniaxial pressure of 35 MPa in a 12.7 mm cylindrical graphite mold. The bulk densities of the pristine BiSbTe, 0.5 and 1.0 vol% MWCNTs/BiSbTe composites were estimated as ~97%, ~77% and ~83%. Fig.1c shows the representative microstructure of fractured surface of 1.0 vol% MWCNTs/BiSbTe consolidated composite.

The randomly oriented grains show layered structure of BiSbTe within the domain of each grain. It is hard to find MWCNTs as other report [12]. The XRD patterns of MWCNTs starting powder and consolidated pure BiSbTe, 0.5 and 1.0 vol% MWCNTs/BiSbTe bulks are shown in Fig.2. All the major peaks are well indexed with the standard BiSbTe PDF card 49-1713. The MWCNTs peaks are not detected in the consolidated composites due to its low volume fraction less than the XRD limit of detection.

2.2 Thermoelectric properties

Electrical properties of pure BiSbTe and MWCNTs/BiSbTe composites are shown in Fig.3. The electrical conductivity of BiSbTe bulks decreases with increasing temperature as shown in Fig.3a. The positive values of Seebeck coefficients exhibit p-type conduction mechanism with semi-metallic electronic transport. The conductivity decreases significantly with the addition of 0.5 vol% MWCNTs, while at 1.0 vol% it decreases moderately.

The results suggest that low density of 0.5 vol% of MWCNTs leads to significant decrease in the electrical conductivity of the composite due to poor contacts between conducting particles in the composites apart from interface scattering of charge carries. Whereas, 1.0 vol% MWCNTs/BiSbTe composite shows a less decrease in the electrical conductivity due to relatively improved density and increased volume fraction of MWCNTs. In contrast, the Seebeck coefficient increase at 0.5 vol% of MWCNTs is attributed to low electrical conductivity while rest of two samples have similar values in the measured temperature range. Since the power factor is dominated by the electrical conductivity, it exhibits similar behavior with the increasing of temperature to the electrical conductivity.

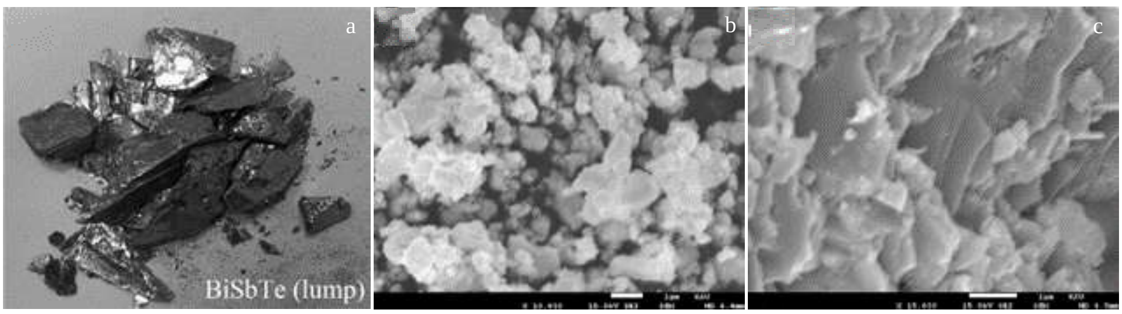

Fig.1 (a) BiSbTe lumps, (b) 1.0 vol% MWCNTs/BiSbTe composite powder, and (c) fracture surface of 1.0 vol% MWCNTs/BiSbTe bulk composite

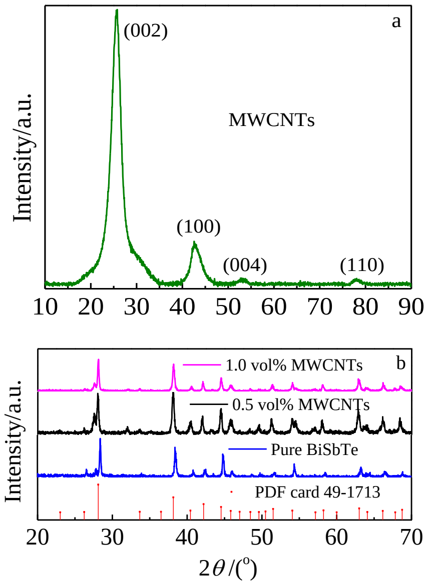

Fig.2 XRD patterns of MWCNTs (a), pure BiSbTe, 0.5 and 1.0 vol% MWCNTs/BiSbTe bulks (b)

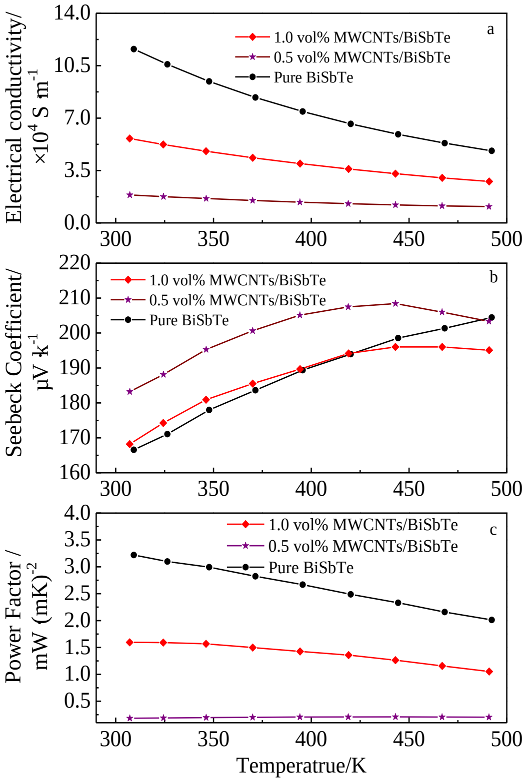

Fig.3 Electrical conductivity (a), Seebeck coefficient (b), and power factor (c) of pure BiSbTe, 0.5 and 1.0 vol% MWCNTs/BiSbTe composites

The thermal conductivity of pure BiSbTe and MWCNTs/BiSbTe composites is shown in Fig.4a. The thermal conductivity decreases drastically from pristine BiSbTe to 1.0 vol% and 0.5

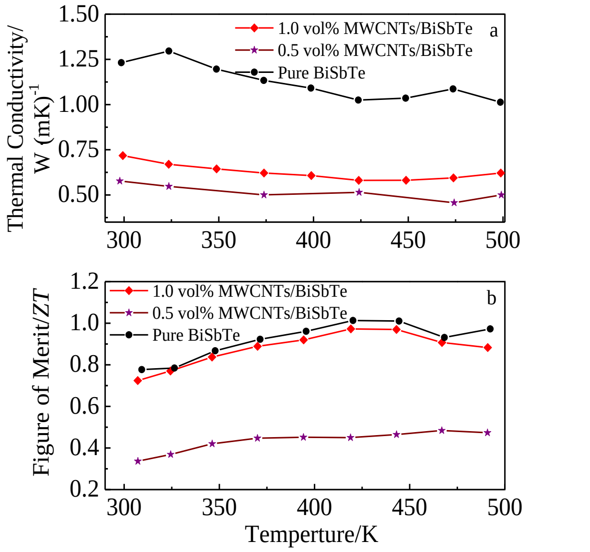

Fig.4 Thermal conductivity (a) and figure of merit (b) of pure BiSbTe, 0.5 and 1.0 vol% MWCNTs/BiSbTe composites

vol% MWCNTs composites. The decrease in thermal conductivity is partly attributed to enhanced phonon scattering caused by the reduction in lattice thermal conductivity and partly to the porosity. The decrease in lattice thermal conductivity was observed by other researchers with the addition of nanostructures[13,14]. The relatively less decrease in the thermal conductivity of 1.0 vol% MWCNTs/BiSbTe composite is due to increased density and more electronic contribution by the MWCNTs. The dimensionless figure of merits is shown in Fig.4b. The temperature dependent figure of merit values of pure BiSbTe and 1.0 vol% MWCNTs/BiSbTe composite are almost the same. The decrease in electrical conductivity of the composite has been compensated by the reduction in thermal conductivity. The results suggest that optimizing the processing parameters for improved density could enhance figure of merit at 1.0 vol% of MWCNTs.

3 Conclusions

1) The incorporation of MWCNTs accompanied by the ball milling reduces the electrical and thermal conductivity of pristine BiSbTe bulk.

2) Moderate reduction in electrical conductivity accompanied by the considerable decrease in thermal conductivity leads same figure of merit as the pristine BiSbTe for 1.0 vol% MWCNTs/BiSbTe composite.

3) Optimizing the processing parameters for improved density may lead to better figure of merit at 1.0 vol% of MWCNTs.

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多壁碳纳米管复合 **BiSbTe** 材料的热电性能

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摘 要：研究了 BiSbTe/多壁碳纳米管(MWCNTs)复合材料的球磨法制备及其热电性能(300~500 K)。采用商用 BiSbTe 块体作为基体材料，利用球磨及压力辅助的感应加热烧结进行致密化得到了不同复合比的 BiSbTe/0.5、1.0 vol% MWCNTs 复合材料。复合 MWCNTs 后，引入的纳米复合结构增强了声子散射，大幅降低了热导率，同时由于载流子散射的增强和较低的致密度使电导率恶化。尽管电导率降低但热导率得到抑制，BiSbTe/1.0 vol% MWCNT 复合材料的热电优值与 BiSbTe 基体接近。结果表明，优化加工参数获得更高的致密度可以优化 BiSbTe/MWCNTs 复合材料的热电性能。

关键词：BiSbTe；多壁碳纳米管(MWCNTs)；复合材料；热电性能

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