Thermal Properties of Bismuth Antimony Telluride with Multi-Wall Carbon Nanotubes using Spark Plasma Sintering

C. K. Nabi, K. Ahmad, and M. A. Al-Eshaikh

Abstract— **Thermal properties play a vital role in determining the thermoelectric properties of thermoelectric materials (TE). TE materials have applications in mainly all fields of life, where there is a considerable temperature difference across a medium. Currently, they are being used in automobile, nuclear, power plants and solar thermoelectric generator (STEG) applications.**

The efficiency of a thermoelectric materials is mainly dependent on electrical conductivity, seebeck coefficient and thermal conductivity. In this research, we have studied the thermal properties of a nanocomposite material, prepared by uniform dispersion of multi-wall carbon nanotubes (MWCNTs) in BiSbTe (Bismuth Antimony Telluride) nanocomposite and consolidated using SPS (Spark Plasma Sintering). Different vol. % (0.0, 2.0) of (MWCNTs) were incorporated in bulk BiSbTe nanocomposite. MWCNTs were uniformly dispersed in BiSbTe using ultra-sonification, magnetic stirring and mild ball milling. The coarse powder was then consolidated into a disc of thickness 2mm and diameter 12.7mm by SPS for 3 minutes at temperature of 400 C and pressure of 50 MPa. Afterwards, the thermal conductivity of the material was measured using Laser Flash method (LFA-457) from temperature of 300 K to 500 K.

It was observed that the thermal conductivity was reduced by the inclusion of MWCNTs, mainly due to increased phonon scattering and enhanced thermal boundary interface. The decreasing trend of thermal conductivity can be seen in 2 vol. % MWCNTs/BiSbTe sample, with the minimum value of thermal conductivity was found 0.758 W/mK at 474 K. The overall thermal conductivity in 2 vol. % MWCNTs/BiSbTe remains less than pure BiSbTe throughout the temperature range from 300 K to 500K.

Keywords— **BiSbTe, MWCNTs, Thermal Conductivity, Thermoelectric Materials**

I. Introduction

In recent years, advancements in the field of Nano technology has open new doors in improving the efficiency of Thermoelectric (TE) materials. The rising demand of sustainable energy has urged scientists to develop new materials which can efficiently convert waste heat into electricity. Thermoelectric materials have applications in all fields of life, where there is a considerable temperature difference across a medium. Currently, they are being used in automobile, nuclear, power plants and solar thermoelectric generator (STEG) applications [1]-[4].

Considerable research has been conducted on low dimensional thermoelectric materials during the last decade to improve their efficiency as compared to those of bulk thermoelectric materials using quantum confinement effects. Significant improvements in ZT have been achieved in superlattice structures like that of Bi2Te3/Sb2Te3, PbTe/PbSeTe, and Si/Ge [5]-[6]. Such low dimensional materials are not compatible for large scale applications because of high developing cost and too thin to support considerable temperature differences. These constraints of using such materials in large-scale applications are forcing researchers to focus on bulk nanocomposite fabrication to realize nanoscale thermoelectric enhancements.

The efficiency of a TE material is closely related to the figure of merit ZT, where ZT is given by,

$$ZT = \frac{S^2 \sigma}{k} \; T \qquad (1)$$

Where S is the seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity and *T* is the absolute temperature. Therefore, the larger value of ZT requires high value of Seebeck Coefficient (S), high electrical (σ) and low thermal conductivity (k). These parameters are usually interdependent on each other in a way that an increase in S, decreases σ, while an increase in σ leads to an increase in k.

Nanoparticles dispersion into thermoelectric materials has been suggested to enhance thermal properties and hence the thermoelectric properties due to decrease in the lattice thermal conductivity without affecting the electrical resistivity adversely [7]-[8]. In this work, special attention is given to uniform dispersion of multiwall carbon nanotubes (MWCNTs) into the bulk p-type Bismuth Antimony Telluride (BiSbTe) Nano material. We have used ball milling to form BiSbTe nanostructures and incorporated different vol. % (0.0, 2.0) of MWCNTs into it. SPS (spark plasma sintering) was applied to get better consolidation without any grain growths. The main focus of this work is to enhance the thermoelectric properties of the whole mixture in a way which is cost effective and suitable for large-scale applications. The effect of Nano particle inclusion on the thermal properties of the mixture is analyzed in this work.

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II. Experimental Procedures

99% pure BiSbTe (American Elements) in the form of lumps and MWCNTs (EMFUTUR, Spain) in powder form were used as raw materials. Different vol. % (0.0%, 2.0%) of MWCNTs were prepared and compared to the pure BiSbTe. Initially, the lump BiSbTe were crushed by pestle mortal and ball milled in an inert environment using a Planetary Micro Mill (PULVERISETTE 7 premium line, FRITSCH Germany). MWCNTs samples of different volume % were dispersed and Deagglomerated into BiSbTe fine powder by ultra-sonification (Q500 USA). The resulted composited powders samples were then consolidated by Spark Plasma Sintering (SPS) at pressure of 50Mpa. Cylindrical Graphite mold of diameter 12.7mm was used for consolidation. The heating rate was kept at 100C/min and held for minutes at 415C during SPS. The resulted samples were is the shape of a disc with a thickness of around 2mm and diameter 12.7mm. The densities are measured by Archimedes' principle which were around 90% for 2 vol. % sample and 97% for pure BiSbTe (0 vol. %) of theoretical values. The thermal diffusivity was measured along the thickness direction using the laser flash (NETZSCH Laser Flash Apparatus LFA 457, Germany) in the temperature range of 300K to 500K under Argon atmosphere.

III. Results & Discussion

The XRD pattern of BiSbTe with x vol. % MWCNTs (x=0, x=2) is shown in fig .1. The XRD pattern is compared with the pdf reference card for BiSbTe (49-1713). The diffraction peaks match well with the standard peaks of BiSbTe. No peaks of MWCNTs are detected owing to its low content which represents phase consistency. The wider peaks in XRD pattern indicate the particles are small in size. To achieve required results of low thermal conductivity for thermoelectric applications, it is necessary for researchers to prevent oxidation. Thus, the resulted XRD pattern shows the material is in single phase and any oxidation or phase change has been prevented.

The thermal conductivity (K) of both samples is calculated by measuring the thermal diffusivity (k), using the relation,

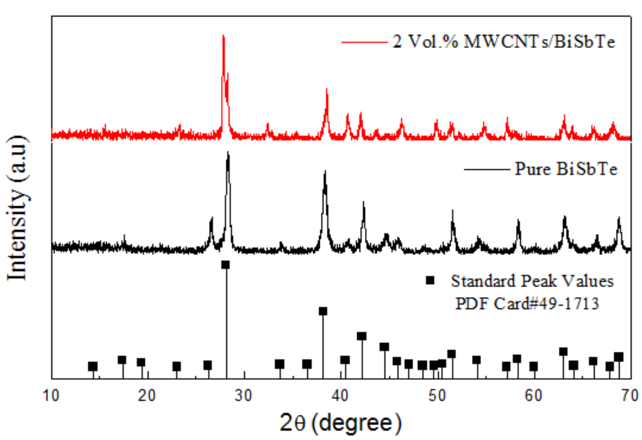

Fig. 1 XRD pattern comparison of MWCNTs/BiSbTe & BiSbTe Standard Peaks

$$K = k\,\rho\,C_p \qquad (2)$$

Where ρ is the density of the given sample, and C_p is the specific heat. The values of C_p is used as given in the database. Laser Flash method (LFA-457) is used to measure the thermal diffusivity. Temperature dependence thermal diffusivity measured by Laser Flash method has been shown in fig. 2. Although, there is a reduction in diffusivity in 2 vol. % MWCNTs/BiSbTe sample, but it is less as compared to reduction in thermal conductivity of the same. The reason is attributed to low density (90% of theoretical density) of 2 vol. % MWCNTs/BiSbTe sample, as in (2).

The addition of MWCNTs has reduced the thermal conductivity as compared to the pure BiSbTe sample, as shown in fig. 3. The thermal conductivity in semiconducting materials has two components, lattice and electrical. The effect of MWCNTs is visible on lattice thermal conductivity without effecting the electrical thermal conductivity [9]. The reductions in the lattice conductivity can be obtained by the adoption of nanostructures which is stemmed from phonon scattering on the boundaries of nano-sized grains [10]. A similar phenomenon has emerged here for the reduction of thermal conductivity, mainly due to phonon scattering at the boundaries of nanotubes and BiSbTe nano structure. Such approach is useful in the applications of thermoelectric materials as it does not affect the electrical component of thermal conductivity and thus the electrical transport properties has minimal effect. Studies show that nano structuring usually affect the lattice conductivity rather than the electronic transport properties, which is vital for high electrical conductivity and seebeck coefficient and thus to improve the thermoelectric properties of the material, which is the main aim of this research [5]-[11].

Another reason for low thermal conductivity in MWCNTs/BiSbTe sample is due to porosity. The relatively low bulk densities in 2 vol.% MWCNTs/BiSbTe sample may cause porosity [12]. As shown in the fig. 3, thermal conductivity at room temperature (300 K) has been reduced from 0.95 W/mK to 0.86 W/mK by the addition of 2 vol. % MWCNTS into bulk nano composite BiSbTe, showing a significant reduction. The

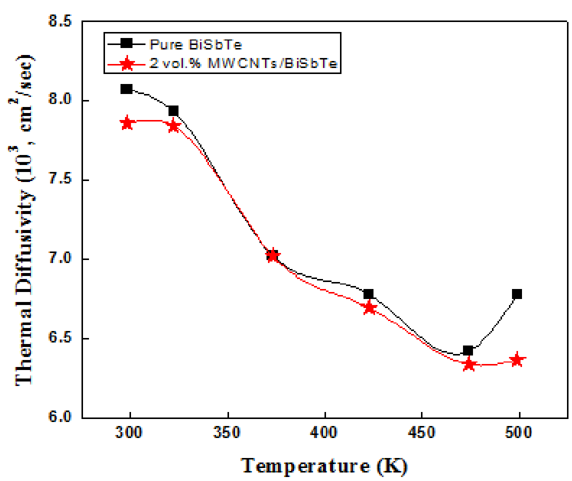

Fig. 2 Temperature dependence thermal diffusivity of pure BiSbTe & 2 Vol. % MWCNT/BiSbTe

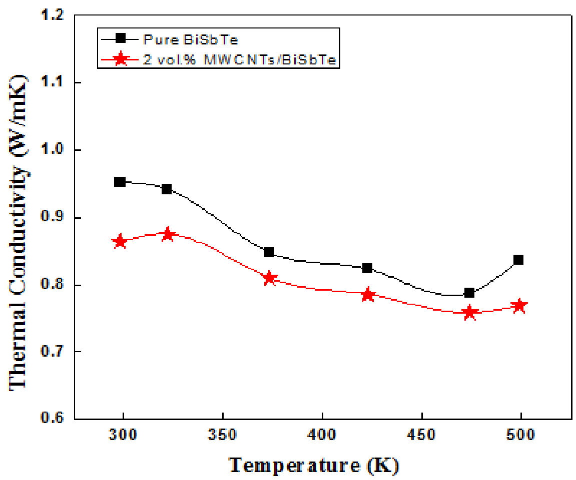

Fig. 3 Temperature dependence thermal conductivity of pure BiSbTe & 2 Vol. % MWCNT/BiSbTe

overall trend of reduced thermal conductivity can be seen throughout the temperature range from 300K to 500K. The minimum thermal conductivity 0.758 W/mK has been achieved for 2 vol. % BiSbTe/MWCNTs composites at 474 K. Overall such low thermal conductivity values in 2 vol. % BiSbTe/MWCNTs sample indicates its promising performance as a thermoelectric material, as can been seen in (1).

IV. Conclusion

The temperature dependence thermal conductivity of 2 vol. % MWCNTs/BiSbTe and pure BiSbTe has been studied and compared. Special attention is given to uniform dispersion of MWCNTs into pristine BiSbTe and SPS was later employed for consolidation. The thermal conductivity has been reduced by almost 10% at room temperature by the addition of 2 vol. % MWCNTs (0.95 W/mK to 0.86 W/mK). This study is important and unique to forecast the potential applications of using MWCNTs with BiSbTe for thermoelectric applications, as less work has been done in past using MWCNTs/BiSbTe Nano composites.

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