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Correlation between microstructure and drastically reduced lattice thermal conductivity in bismuth telluride/bismuth nanocomposites for high thermoelectric figure of merit

D.K. Misra [a,b,**], S. Sumithra [b], N.S. Chauhan [a], W.M. Notling [b], P.F.P. Poudeu [c], Kevin L. Stokes [b,*]

[a] Division of Physics of Energy Harvesting, CSIR National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India
[b] Dept. of Physics and the Advanced Materials Research Institute University of New Orleans LA 70148, USA
[c] Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA

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ABSTRACT

The concept of nanocomposite/nanostructuring in thermoelectric materials has been proven to be an effective paradigm for optimizing the high thermoelectric performance primarily by reducing the thermal conductivity. In this work, we have studied the microstructure details of nanocomposites derived by incorporating a semi-metallic Bi nanoparticle phase in Bi_2Te_3 matrix and its correlation mainly with the reduction in the lattice thermal conductivity. Incorporating Bi inclusion in Bi_2Te_3 bulk thermoelectric material results in a substantial increase in the power factor and simultaneous reduction in the thermal conductivity. The main focus of this work is the correlation of the microstructure of the composite with the reduction in thermal conductivity. Thermal conductivity of the matrix and nanocomposites was derived from the thermal diffusivity measurements performed from room temperature to 150 °C. Interestingly, significant reduction in total thermal conductivity of the nanocomposite was achieved as compared to that of the matrix. A detailed analysis of high-resolution transmission electron microscope images reveals that this reduction in the thermal conductivity can be ascribed to the enhanced phonon scattering by distinct microstructure features such as interfaces, grain boundaries, edge dislocations with dipoles, and strain field domains.

1. Introduction

Bi_2Te_3 and its derivative alloys are an important class of thermoelectric materials for refrigeration and power generation in the temperature range 200–400 K [1,2], having the highest figure of merit (ZT) ~1. The thermoelectric figure of merit (ZT) defined as $ZT=S^2\sigma/(K_e+K_L)T$, although has a complex interdependence between Seebeck coefficient (S), electrical conductivity (σ), electronic thermal conductivity (K_e) but lattice thermal conductivity (K_L) being an independent parameter can be tuned independently. Technological efforts in developing efficient modules for device fabrication are still restricted by insignificantly smaller ZT at room temperature that dictates thermoelectric efficiency besides parasitic losses and other device related issues. Bi_2Te_3 based thermoelectric modules offers a promising route to improve the efficiency of such devices at room temperature for its large scale application.

Several current strategies such as doping [3–6], solid solution alloying [7–11], several ideally engineered materials [12–14] and nanostructuring/nanocomposites [15–20]

* Corresponding author.
** Corresponding author at: Division of Physics of Energy Harvesting, CSIR National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India.
E-mail addresses: misradk@nplindia.org (D.K. Misra), klstokes@uno.edu (K.L. Stokes).

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have been proposed and demonstrated to improve the ZT via circumventing the interdependencies of these three competing parameters by simultaneous optimization of the power factor and reduction in the thermal conductivity. Among all these strategies, nanocomposite approach has made a marked recognition in achieving high ZT of thermoelectric materials. This approach suggests that the ZT enhancement can be realized due to nanoscale size of inclusions incorporated into bulk thermoelectric matrix enhancing the density of grain boundaries and numerous interfaces which provides easy path for electrons to transport and effectively scattering of phonons at interfaces. The high concentration of grain boundaries and interfaces is expected to lower the lattice thermal conductivity of the materials. The nanocomposite materials introduce numerous interfaces in which phonons over a large mean free path range can be scattered more effectively and preferentially than electrons, thereby reducing the lattice thermal conductivity effectively while preserving carrier mobility and electronic conduction.

In fact, theoretical calculations and experimental investigations [21–32] have also shown that in low dimensional structures the electronic transport properties can be significantly improved due to modified density of states. Moreover, incorporation of nanoscale particle in the matrix, introduces many internal interfaces which scatter phonon more effectively than electrons to reduce the thermal conductivity. Based on these facts, the enhancement in thermoelectric figure of merit could be achieved in thin film multilayers [29] and in bulk Bi_2Te_3/Sb_2Te_3 nanocomposites having a laminated nanostructure [31] where a maxima in figure of merit, ZT = 1.47 could be achieved at ~450 K. Venkatasubramanian et al. [1] and Harmans et al. [29], have been able to show significant reduction in cross-plane and in-plane lattice thermal conductivity in Bi_2Te_3/Sb_2Te_3 and PbTe/PbSeTe superlattice structures, respectively. Phonon confinement in superlattices and nanowires can alter the phonon dispersion relation and reduces the specific heat and phonon group velocity, and thereby reduces the lattice thermal conductivity.

It is worth mentioning here that the creation of random interfaces on a nanometer scale by nanostructuring, increases phonon scattering at grain boundaries and interfaces, and thereby reduces the phonon mean free path for effective reduction in lattice thermal conductivity. These nanoinclusions embedded into thermoelectric matrix, grain size reduction, and creation of grain boundary interfaces due to nanostructuring can also lead to significant micro-structural modifications of the bulk matrix for reduction in lattice thermal conductivity. Such reduction in the lattice thermal conductivity enhances the thermoelectric figure of merit which has been reported by Poudel et al. [32] and Ma et al. [27]. Significant enhancement in ZT is also reported in LAST [25] system, due to the embedded quantum nanodots into the matrix structures, which modifies the micro-structural features at nanoscale for effective phonon scattering and hence reduces the lattice thermal conductivity. These nanostructures were fabricated by encapsulating the nanodots into matrix by a melt quenching method. Similar approach was also adopted in other systems like $NaPbmSbTe_{2+m}$ and $Pb_{9.6}Sb_{0.2}Te_{10-x}Se_x$ [32,33]. Incorporation of nanopowders (insulators, metals, and semiconductors) or presence of nanosized cavities, into bulk thermoelectric materials has also been reported in several investigations [34–39] in which effective phonon scattering has been taken place to reduce the lattice thermal conductivity.

Improved materials for thermoelectric applications require that the lattice thermal conductivity be reduced while retaining favorable electronic properties. The present study aims to further improve the understanding of the correlation between microstructure and lattice thermal conductivity in nanocomposites. The electronic properties of Bi_2Te_3/Bi nanocomposites have been reported earlier in detail by our group [40]. However, in this work, we have investigated microstructural modifications of Bi_2Te_3 nanocomposites with Bi nanoinclusions on the reduction in the lattice thermal conductivity. Here, Bi has been synthesized by low temperature solvothermal route while Bi_2Te_3 has been synthesized by planetary ball milling. Finally the chemically-synthesized Bi nanoparticles were mixed in Bi_2Te_3 matrix and subsequently densified at 200 °C and 100 MPa employing conventional hot pressing technique. The melting point of the matrix ensures retention of nanostructures, grain boundary interfaces and nanograins for significant phonon scattering, compared to micron sized grains if hot pressed at high temperatures. Since transmission electron microscopy provides an appropriate means to characterize microstructural details on the nanometer scale, we report the distinct microstructure features present in these nanocomposites (with Bi nanoinclusions), which have helped in significantly reducing the lattice thermal conductivity. Aim of this article is to correlate the compositional inhomogeneties and microstructural features in these nanocomposites with the reduction in lattice thermal conductivity. The detailed synthesis procedure of the nanocomposites and the thermoelectric transport properties were reported in [41].

2. Experimental

Bi nanoparticles used as nanoinclusions in this study were synthesized by a low temperature solvothermal method. $BiCl_3$ was used as precursor and citric acid as a surface modifier, and these constituents were weighed in 1:5 molar ratios and dissolved in 40 mL of DMF used as reducing agent. The solvent was further transferred into a Teflon lined autoclave and heated at 160 °C for 6 h. Bi_2Te_3 composition was synthesized by a planetary ball milling using Bi and Te elemental shots in 2:3 ratio. The Bi and Te shots of 5 N purity (ESPI metals) were weighed in an Ar filled glove box, sealed in a stainless steel vial and subjected to ball milling for 25 h. The Bi and Bi_2Te_3 nanoparticles crystallized in rhombohedral symmetry (R-3m) and the phase purity was matched with the JCPDS data set of (015-0863) and (005-0519) respectively. The Bi_2Te_3 matrix phase and Bi (3% and 5%) nanoparticles incorporated Bi_2Te_3 nanocomposites, were uniaxially hot pressed at 200 °C and 100 MPa. The pellets could be densified upto ~95% theoretical density. Thermal diffusivity of these samples were measured using the laser flash apparatus (Netzsch LFA-457) from RT to 150 °C and the