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Synthesis and evaluation of lead telluride/bismuth antimony telluride nanocomposites for thermoelectric applications

Shreyashi Ganguly [a,1], Chen Zhou [b,1], Donald Morelli [b,*], Jeffrey Sakamoto [b,*], Ctirad Uher [c,*], Stephanie L. Brock [a,*]

[a] Department of Chemistry, Wayne State University, Detroit, MI 48202, USA
[b] Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA
[c] Physics Department, University of Michigan, Ann Arbor, MI 48109, USA

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ABSTRACT

Heterogeneous nanocomposites of p-type bismuth antimony telluride ($Bi_{2-x}Sb_xTe_3$) with lead telluride (PbTe) nanoinclusions have been prepared by an incipient wetness impregnation approach. The Seebeck coefficient, electrical resistivity, thermal conductivity and Hall coefficient were measured from 80 to 380 K in order to investigate the influence of PbTe nanoparticles on the thermoelectric performance of nanocomposites. The Seebeck coefficients and electrical resistivities of nanocomposites decrease with increasing PbTe nanoparticle concentration due to an increased hole concentration. The lattice thermal conductivity decreases with the addition of PbTe nanoparticles but the total thermal conductivity increases due to the increased electronic thermal conductivity. We conclude that the presence of nanosized PbTe in the bulk $Bi_{2-x}Sb_xTe_3$ matrix results in a collateral doping effect, which dominates transport properties. This study underscores the need for immiscible systems to achieve the decreased thermal transport properties possible from nanostructuring without compromising the electronic properties.

1. Introduction

Thermoelectric (TE) materials are those that can convert heat into electricity or transfer heat by electrical flow. Unlike conventional mechanically driven machines, TE devices use carrier's electrons and holes, to do the work, and thus require no moving parts. Consequently, the efficiency of TE devices is independent of their size and TE devices are reliable, environmentally friendly and suitable for challenging applications such as integrated circuit cooling and power for deep space exploration. However, because of their low efficiency relative to mechanical cycles, TE devices are restricted to niche applications like radioisotope thermoelectric generators (RTGs) for space probes [1]. From a materials perspective, the efficiency of a TE material is determined by its dimensionless figure of merit (FOM), $ZT=S^2\sigma T/\kappa$; where S is the Seebeck coefficient, σ the electrical conductivity, and κ the total thermal conductivity consisting of an electronic part, κ_e, and lattice thermal conductivity, κ_l. The higher a material's ZT, the greater the thermoelectric generation efficiency. The intricate relations among S, σ and κ make seeking high ZT materials hard work because a simple improvement in one parameter typically has an adverse effect on the other(s). Consequently, most conventional bulk TE materials have a $ZT<1$.

Traditional approaches to enhance ZT have focused on optimizing doping to maximize the power factor $S^2\sigma$ [1]. An alternative approach involves decoupling electrical and thermal conductivity by selectively scattering phonons while preserving charge carrier transport [2,3]. In 1993, Hicks and Dresselhaus predicted that the ZT in a 2D quantum well structure could be increased several times over the same 3D bulk materials if superlattice multilayers are properly oriented and their thickness is comparable to the unit cell parameters [3]. Proof of principle experiments in PbTe quantum well structures [4,5], Si/Ge superlattices [6], and Bi_2Te_3/Sb_2Te_3 superlattices [7] demonstrated that a $ZT>1$ is possible. All these findings marked the start of the nanostructure era of TE research.

Several methods have been explored for synthesizing TE nanocomposites. For example, Poudel et al. have reported a $Bi_{2-x}Sb_xTe_3$ nanostructure with a ZT of 1.4 prepared by hot pressing ball-milled nanoparticles into bulk ingots [8]. Also Majumdar and coworkers have observed a reduction in thermal conductivity by a factor of 2 below the alloy limit in crystalline

* Corresponding authors. Fax: +1 313 577 3102.
E-mail addresses: dmorelli@egr.msu.edu (D. Morelli), jsakamot@egr.msu.edu (J. Sakamoto), cuher@umich.edu (C. Uher), sbrock@chem.wayne.edu (S.L. Brock).
[1] These authors contributed equally and are listed in alphabetical order.

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solids of ErAs nanoparticles incorporated inside $In_{0:53}Ga_{0:47}$ by molecular beam epitaxy [1,9]. Another approach is an *in-situ* synthesis in which nanophases are created by exploiting an inherent phase segregation or decomposition in the alloy or compound system under investigation. For example, the $AgPb_mSbTe_{m+2}$ (LAST-m) family of compounds exhibit a $ZT > 1.5$ due to inhomogeneities on the nanoscale [10]. Recently, Kanatzidis and coworkers have shown that by endotaxially placing SrTe in an Na_2Te-doped PbTe matrix, the thermal conductivity could be reduced and the power factor could be enhanced, achieving a ZT of 1.7 at 800 K [11]. In another example, Zhou et al. has demonstrated a 100% enhancement of ZT in Fe compensated binary skutterudite $Co_{0.9}Fe_{0.1+x}Sb_{3+2x}$ due to the existence of a $FeSb_2$ nanophase [12]. Likewise, in In-filled $CoSb_3$ skutterudites, a significant fraction of indium reacts with Sb to form an *in situ* finely dispersed InSb nanophase in the skutterudite matrix and the combined effect of Ce and In doping results in high performance skutterudite materials with $ZT=1.43$ at 800 K [13].

In this paper, we report a systematic study of the thermoelectric properties of p-type bismuth antimony telluride ($Bi_{2-x}Sb_xTe_3$) based nanocomposites with lead telluride (PbTe) nanoparticles as inclusions. PbTe and $Bi_{2-x}Sb_xTe_3$ were chosen because both components exhibit high ZT as single-phase materials and would benefit from decreased κ_l. We first synthesized discrete PbTe nanoparticles by solution-phase arrested precipitation [14] and bulk matrix $Bi_{2-x}Sb_xTe_3$ by standard solid state synthesis techniques [15]. The nanocomposite was prepared by incipient wetness impregnation, a well-established technique for catalyst production [16]. The method involves addition of solution-dispersed PbTe nanoparticles to the matrix followed by drying. A series of mass fractions of PbTe nanoparticles in bulk $Bi_{2-x}Sb_xTe_3$ were investigated, ranging from 0.1 wt% to 1 wt%. The resulting thermoelectric properties were measured to evaluate the efficacy of our nanocomposite approach for reduction of κ_l.

2. Experimental

2.1. Reagents

Lead acetate trihydrate ($Pb(OAc)_2 \cdot 3H_2O$) was obtained from Baker Chemicals; tellurium powder (Te, 200 mesh, 99.8%), 1-octadecene (ODE, technical grade 90%), hydrazine (anhydrous, 98%) and acetonitrile (anhydrous, 99.8%) were obtained from Aldrich; trioctylphosphine (TOP, technical grade 97%) was obtained from Strem chemicals and oleic acid (OA, technical grade, 90%), hexane and acetone were obtained from Fisher. High purity starting materials of bismuth (granule 99.997%), antimony (shot 99.999%) and tellurium (shot 99.9999%) were obtained from Alfa Aesar.

2.2. Synthesis

2.2.1. General synthesis of PbTe nanoparticles

Discrete PbTe nanoparticles were prepared by combining $Pb(OAc)_2 \cdot 3H_2O$ (1.317 g, 3 mmol) with OA (3 mL, 6 mmol) and ODE (6 mL, 18 mmol) and heating this mixture under inert atmosphere on a Schlenk line at 170 °C for 30 min to obtain a colorless solution [14]. The temperature of the solution was then reduced to 150 °C followed by rapid injection of 3 mL of 1 M TOPTe, which was formed by dissolving 1.27 g of Te in 10 mL of trioctylphosphine solution in a glove box. The resultant solution was left at 150 °C for 5 min and then the reaction was quenched by plunging the flask into a cold-water bath. The nanoparticles were precipitated inside a glove box by adding hexane as the solvent and acetone as the antisolvent, and isolated by centrifugation. Subsequently, the particles were either treated with (1) anhydrous hydrazine or (2) thermal annealing under inert atmosphere (nitrogen atmosphere) in order to remove surface ligands.

2.2.2. General synthesis of p-type bismuth antimony telluride

p-type bismuth antimony telluride with nominal composition $Bi_{0.4}Sb_{1.6}Te_3$ was employed as the matrix material for making nanocomposites. High purity elements were weighed according to the targeted ratio and sealed in a fused silica ampoule under a vacuum $> 10^{-5}$ Torr. The ampoule was heated at 750 °C for 12 h followed by rapid water quenching. The quenched ingot was annealed at 540 °C for another 3 days in order to homogenize the properties. The annealed ingot was ball milled into a fine powder in a Spex 8000 Mixer/Mill and stored inside an Ar purged glovebox before making nanocomposites.

2.2.3. General synthetic procedure for incorporation of PbTe nanoparticles in bulk $Bi_{2-x}Sb_xTe_3$ matrix

The synthesis of nanocomposites involved dispersion of an appropriate mass of PbTe nanoparticles into a minimum amount of solvent, hexane. The resulting solution was sonicated for 10 min to make a colloidal suspension. The PbTe nanoparticle sol was then added dropwise to an appropriate mass of bulk $Bi_{2-x}Sb_xTe_3$ with constant stirring, followed by solvent evaporation under ambient temperature and pressure, in a glove box.

The mixed composite powder was loaded into a graphite crucible and heated at 410 °C for 2 h (in an Ar purged glove box) in order to eliminate residual organics at the surface of the PbTe nanoparticles. The heat treated powder was then hot pressed between 350 °C and 380 °C under a pressure of 60 MPa for 15 min to form a dense pellet. A total of four samples (2 g each) with PbTe weight percentage of 0%, 0.1%, 0.5% and 1% were prepared in this way.

3. Characterization and physical measurements

3.1. Powder X-ray diffraction

Powder X-ray diffraction was collected on a Rigaku RU 200B (40 kV, 150 mA, Cu$K\alpha$ radiation) diffractometer. Samples were deposited on a quartz holder coated with a thin layer of grease and the data were acquired in the 2θ range 20–70° with a step size of 1.2°. The PXRD data obtained were processed using the Jade software package and compared to powder diffraction files (PDFs) from the International Center for Diffraction Data database (ICDD). Least-squares refinement of lattice parameters was achieved using the Jade software package with silicon as an internal standard.

3.2. Transmission electron microscopy and energy dispersive spectroscopy

Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) were performed using a JEOL 2010 transmission electron microscope operated at a voltage of 200 kV and a current of 106–108 μA with a coupled EDS detector (EDAX Inc). Images obtained from TEM measurements were analyzed by Amtv600 software (Advanced Microscopy Techniques Corporation). Samples for TEM were prepared by sonicating PbTe nanoparticles or $PbTe/Bi_{2-x}Sb_xTe_3$ nanocomposites in hexane, followed by deposition of a drop from each solution on a carbon-coated 200 mesh Cu grid (SPI) and air drying for 1 day.