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Thermal conductivity of cold compacted bismuth nanowires

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ABSTRACT

In contrast to their macroscale counterparts, nanostructures may exhibit a higher thermoelectric figure of merit (performance) due to their enhanced Seebeck coefficient and/or reduced thermal conductivity. Nonetheless, practical use of individual nanostructures in larger scale thermoelectric applications may not be feasible. Instead, the use of compressed materials formed from these nanomaterials may offer unique opportunities. This work explores the effects of anisotropy and particle size and shape on the thermal transport behavior in compressed materials formed from bismuth nanowires. In its bulk and nanoscale forms, bismuth and its alloys are attractive candidates as thermoelectric materials. Free standing bismuth nanowires of two different diameters, 250 nm and 20 nm, were synthesized through a vapor deposition process and compressed into pellets. Bismuth microparticles (mean diameter 100 μm) were also compressed to the same pressures for comparison. The thermal conductivity of individual nanowires with 250 nm diameter was measured to be 6.1 ± 1.2 W/m K. The compressed nanowire pellets were found to be nearly thermally isotropic with thermal conductivity of approximately 1 W/m K. The microparticle pellets showed a higher degree of anisotropy as well as higher thermal conductivity. Results indicate that thermal characteristics are a function of pellet porosity, compression pressure, and the presence of an oxide layer on the particle surface. The increase in pressure initially reduces the porosity (from 100 to 500 MPa but further compression to 3000 MPa does not influence porosity) and enhances the thermal conductivity for the microparticle samples. The results also indicate the surface oxide is breached due to compression. Some anisotropy in thermal properties due to particle shape and the direction of compression was also observed.

1. Introduction

Bismuth and its alloys have been traditionally used as thermoelectric materials for room temperature applications. Even more, bismuth nanostructures can exhibit enhanced thermoelectric properties due to quantum confinement and other nanoscale effects [1–6]. Nonetheless, practical use of individual nanostructures in real applications may not be feasible at these length scales. Instead, compressed structures formed from these nanomaterials may result in unique nanostructured materials that capture attractive nanoscale effects at the macroscale. Research interest in the formation of compressed materials from nanostructures, dubbed as nanostructured bulk materials (NBMs), has increased [7], including reports on bismuth micro- and nanoparticles [8], alloys of bismuth antimony telluride [9] and silicon germanium [10]. These materials can be formed using a variety of techniques, borrowing methods from the powder metallurgical industry such as pressureless sintering, hot pressing and cold compression [8]. NBMs can exhibit lower thermal conductivity than their bulk counterparts, which can lead to an improvement in the thermoelectric figure of merit (ZT). The ZT of a material is given by

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

where S is Seebeck coefficient expressed in units μV/K σ is the electrical conductivity in S/m, and k is the thermal conductivity of the material in W/m K.

The transport properties of cold compacted material such as those studied herein depend on a variety of factors such as the degree of particle deformation and the resulting porosity (i.e. volume fraction). The presence of a surface oxide layer on the individual particles, and the quality and quantity of particle-particle interfaces also play important roles in determining the material properties [8]. In addition, anisotropy that may arise due to the shape and orientation of the nanoparticles as well as the directionality of the compression can also lead to unique thermal transport characteristics. Modeling of the effective thermal conductivity of

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Nomenclature

k	thermal conductivity
S	seebeck coefficient
T	temperature
ZT	figure of merit

Greek symbols

ε	porosity
σ	electrical conductivity

Subscripts

e	effective property (of porous material)
s	solid particle
f	fluid
r	perpendicular to compression direction
z	compression direction

compressed *spherical* microparticles has been reported [11,12]. In fact, a review of studies that explore the deformation of spherical particles due to compaction has been presented by Kaviany [13]. Investigations of compressed *one-dimensional* nanostructures (*i.e.* nanowires or nanotubes), has received limited attention via computational simulation, but questions still remain regarding the mechanisms that influence transport [14,15]. For example, models such as the ‘interaction direct derivative micromechanics scheme’ [14,15] can predict effective thermal conductivity of carbon nanotube composites with sufficient accuracy but do not accurately account for interfacial deformation due to compaction. To date, there has not been significant experimental efforts focused on nanostructured bulk materials comprised of one-dimensional nanostructures.

For the work presented herein, bismuth nanowires of 250 nm and 20 nm diameter with corresponding lengths of 60 and 50 μm, respectively, were synthesized using a vapor deposition process. These nanowires were then compressed into pellets using pressures of 100, 500 or 3000 MPa. Directional thermal conductivities were measured using the mirage method [16]. Additionally, a modified thermal flash method was used to characterize the thermal conductivity of individual nanowires. Similar experiments were conducted with commercially available microparticles of 100 μm mean diameter, and results were compared.

2. Synthesis of bismuth nanowires and compressed pellets

Bismuth nanowires were synthesized using a vapor deposition technique [5,17]. Bismuth vapor was deposited into the pores of commercially available anodic aluminum oxide (AAO) templates. A radiative reflector was used to reduce heat loss, and a steel weight over the coverplates was employed to stop the escape of bismuth vapor. The bismuth filled AAO templates were dissolved by 85% ortho-phosphoric acid for about 48–72 h. Free standing bismuth nanowires were separated from the acid solution by serial dilution and sedimentation. Scanning electron microscope (SEM) imaging revealed bismuth nanowires of mean diameter of 250 nm and a length of about 60 μm; or 20 nm and a length of approximately 50 μm, depending on the template used. The nanowires were later washed with 10% sodium do-decyl sulfate (SDS) solution to remove the phosphoric salts of aluminum. A notable increase in the purity of the nanowire sample before and after the SDS reaction was observed using an energy dispersive spectroscopy (EDS) technique. A scanning electron microscope image of the 250 nm diameter bismuth nanowires after the salt purification step is shown in Fig. 1. In total about 400 AAO templates with 250 nm pore diameter and 30 templates with pore size of 20 nm were used for this research to produce approximately one gram of nanowires.

To create sample pellets, the nanowires were uniaxially compressed with a hydraulic punch press (Ramco model number RP-50) in a 5 mm diameter die. Individual samples were made at different compression levels and at varying thicknesses. The 250 nm nanowires samples were compressed at 100, 500 and 3000 MPa, but due to complexities associated with the synthesis of the 20 nm diameter nanowires and their limited availability, only a single 20 nm nanowire-based sample could be formed at 3000 MPa. Moreover, due to issues with structural integrity, thermal conductivity measurements could only be conducted on the 250 nm nanowire-based pellets compressed at 500 and 3000 MPa. Pellets of thicknesses varying from 100 to 600 μm with diameters of 5 mm were produced. Similar pellets using bismuth *micro*particles of mean diameter of 100 μm were compressed in the same punch press at the same compression levels. The compression levels were chosen to explore the impact of particle deformation on the porosity and thermal conductivity of the

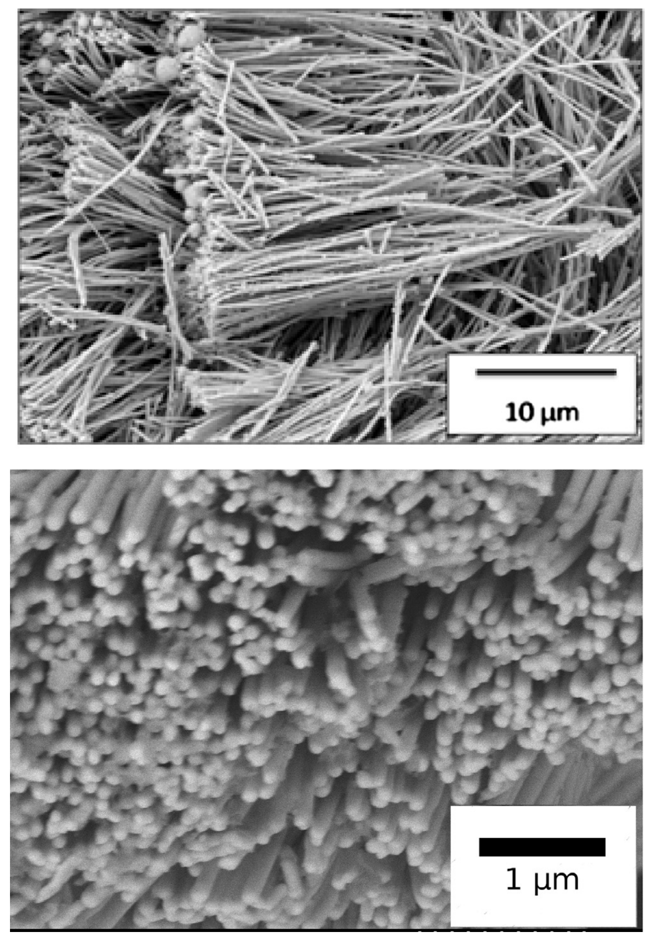

Fig. 1. Scanning electron microscope images of purified bismuth nanowires at two different levels of magnification.