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Synthesis and Characterization of Nanocrystalline Bismuth Telluride

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ABSTRACT

We report the first synthesis and characterization of nanocrystalline Bi_2Te_3 with particle sizes less than 10 nm. The reaction of $BiOClO_4 \cdot xH_2O$ with $(Me_3Si)_2Te$ in a reverse micelle formed by sodium dioctylsulfosuccinate and water in hexane has produced good yields (71%) of a black powder that has been characterized by elemental analysis, X-ray diffraction, and transmission electron microscopy.

Since the discovery of the thermoelectric properties of Bi_2Te_3 in 1954,[1] bismuth−tellurium-based compounds have become major components of the thermoelectric industry. However, the small improvements in thermoelectric properties of materials since that time have limited their transition to commercial applications. The possibility that low-dimensional systems such as quantum-well structures (2D) and quantum wires (1D) might exhibit enhanced thermoelectric properties compared to bulk materials has been indicated by recent theoretical calculations[2−4] and has led to renewed interest in these types of materials. Subsequent experimental results from $PbTe/Pb_{1-x}Eu_xTe$ 2D quantum wells were found to be consistent with these theoretical predictions.[5] As a logical extension of these results, it has been suggested that coupled, 0D quantum dots might provide adequate conduction paths for carriers but less effective heat conduction paths for phonons, thereby giving rise to an increase in the thermoelectric figure of merit Z.[6] However, it has also been pointed out that no systematic study of the thermoelectric properties of quantum dots has been done,[6] a situation resulting, at least in part, from a lack of suitable nanophase materials.

There have only been a few reports of the synthesis of low-dimensional and small-particle systems containing Bi_2Te_3. These include 2D superlattice structures of Bi_2Te_3/Sb_2Te_3 grown by metalorganic chemical vapor deposition,[7] and 1D nanowires of Bi_2Te_3 in the 250 and 40 nm diameter range electrodeposited in porous alumina substrates.[8,9] Several near-0D systems have been reported in which the final particle size is less than 100 nm. Ritter has described the synthesis of fine-particle Bi_2Te_3,[10,11] and Groshens et al. have isolated polycrystalline powders of annealed Bi_2Te_3 of approximately 30−50 nm,[12] which were likely smaller prior to annealing. A one-step, low-temperature reaction between bismuth oxalate and tellurium in ethylenediamine or pyridine has also produced powdered Bi_2Te_3.[13] We have recently reported the synthesis and characterization of nanocrystalline bismuth with particle sizes less than 10 nm[14] and describe here the first confirmed synthesis, to our knowledge, of nanocrystalline Bi_2Te_3 in this same size regime.

Our approach is similar to one used initially for the synthesis of nanocrystalline CdSe[15] and involves the reaction of $BiOClO_4 \cdot xH_2O$ with $(Me_3Si)_2Te$ in a reverse micelle formed by sodium dioctylsulfosuccinate (AOT) and water in hexane. Bismuth(III) perchlorate oxide hydrate and AOT were purchased from Aldrich Chemical, heated overnight in an oven at 92 °C, and subsequently handled in a glovebag filled with N_2 boil-off from liquid N_2. Trioctylphosphine (TOP) (Aldrich) was distilled in vacuo and stored in a glovebox. Triply distilled water, absolute ethanol, and reagent-grade toluene and hexane (500 mL) were purged with N_2, degassed with five freeze−pump−thaw cycles, and used in a N_2-filled glovebag. Bis(trimethylsilyl) telluride was synthesized from Li_2Te and Me_3SiCl[16] and diluted with hexane that was vacuum-distilled from sodium benzophenone. In a typical synthesis where $w = [H_2O]/[AOT] = 5$, a sample of 0.83M $BiOClO_4$ solution (0.95 mL, 0.79 mmol) was added to a 500-ml flask followed by hexane (200 mL) and AOT (4.420 g, 9.943 mmol); vigorous stirring produced an optically clear solution. A 2 mL portion of a hexane solution of $(Me_3Si)_2Te$ (326.2 mg, 1.191 mmol) was added rapidly under N_2 to the reaction flask to produce an immediate black color. Two minutes after addition, a black solid precipitated from solution when the stirring was stopped. Stirring was continued for an additional 15 min, followed by vacuum transfer of the volatile materials from the reaction flask to yield a sticky, black solid. Toluene (20 mL) was added to the solid and the suspension sonicated

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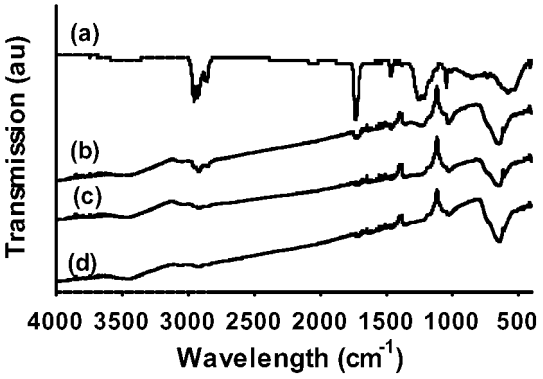

Figure 1. FTIR spectra of KBr pellets of (a) AOT; (b) Bi_2Te_3 as prepared; (c) Bi_2Te_3 washed once with toluene; (d) washed with toluene and methanol.

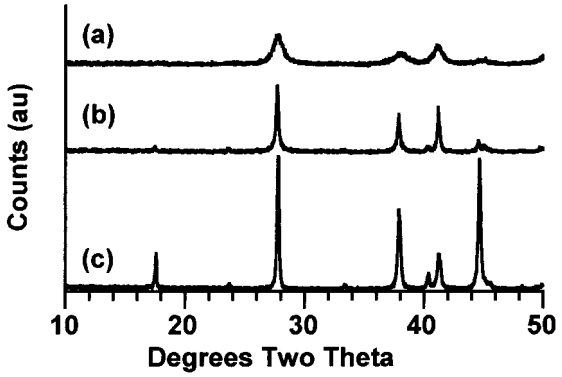

Figure 2. XRD patterns of (a) unannealed Bi_2Te_3 ($w = 5$); (b) Bi_2Te_3 annealed at 230 °C for 4 h under He; (c) commercial Bi_2Te_3 (Alfa) ground in mortar and pestle.

for fifteen minutes at ambient temperature before centrifuging at 3.5 K rpm for 5 min to yield a black solid and a clear, colorless supernatant. Washing and sonication with toluene was repeated three additional times, followed by washing and sonication once with ethanol, once with hexane, and drying in vacuo. TOP (1 mL) was added to the solid and the suspension sonicated for 1 h. Toluene (15 mL) was added to the TOP suspension and the mixture centrifuged at 3.5 K rpm for five minutes to yield a black solid and a clear, pale yellow supernatant. The supernatant was discarded, and the solid washed and sonicated five times with toluene and once with hexane to yield a black powder (223.5 mg, 0.2791 mmol, 71% yield based on Bi_2Te_3). Elemental analysis (Complete Analysis Laboratories, Inc., Parsippany NJ): wt % calcd for Bi_2Te_3: Bi, 52.20; Te, 47.80. Found: Bi, 51.73; Te, 47.38; C, 0.76; H, 0.10. The reaction was run both in the presence and in the absence of air with no observable differences in the properties of the product at this point, although X-ray photoelectron spectroscopy has shown that Bi_2Te_3 does undergo oxidation.[17] It is worth noting that in two reactions where the addition of $(Me_3Si)_2Te$ was done dropwise, elemental analysis of the products gave mole ratios of $Bi_{1.00}Te_{0.95}$ and $Bi_{1.00}Te_{1.10}$.

The washing procedure was very important in reducing the amount of AOT present in the product. The elemental analysis of one batch of material indicated a drop in the weight percentages of C and H from 9.26% and 1.69%, respectively, for a sample washed once with toluene to 3.93% C and 0.72% H in the product washed with toluene and methanol. Infrared spectra of KBr pellets containing neat AOT and these samples are shown in Figure 1. The amount of AOT was further reduced by the use of sonication in the washing procedure as described above.

The powder X-ray diffraction pattern in the 10°−50° two-theta region of the solid isolated from the $w = 5$ reaction contained broad peaks at 27.8° ($d = 3.206$, $hkl = 015$), 38.1° (2.360, 1.0.10), 41.1° (2.194, 110), and 45.0° (2.013, 116) as shown in Figure 2a. Annealing this powder under a He atmosphere at 230 °C for 4 h resulted in the sharpening of these peaks as shown in Figure 2b. Both patterns were consistent with those of a sample of commercial Bi_2Te_3 ground in a mortar and pestle as seen in Figure 2c and reported in the powder diffraction files.[18]

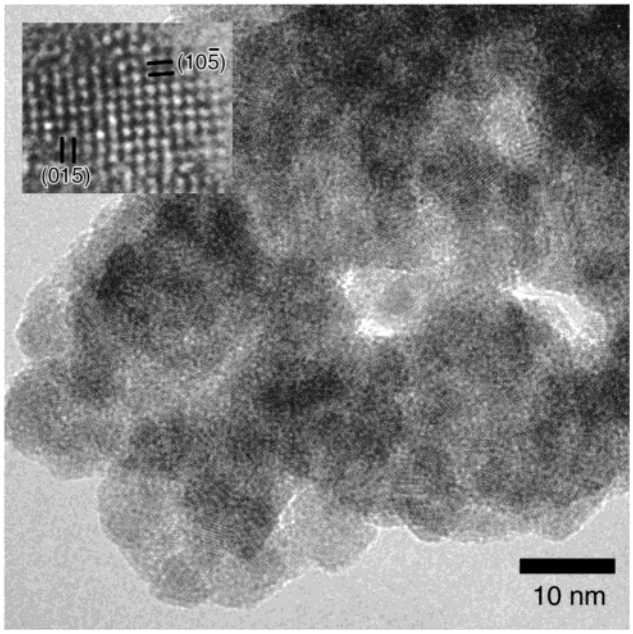

Figure 3. Transmission electron micrograph of unannealed $w = 3$ sample. Inset: Lattice image of a Bi_2Te_3 particle aligned along a [5−51] zone-axis.

Examination by transmission electron microscopy (TEM) of the unannealed powder from reactions with $w = 3$ and 5 revealed a larger particle size for the greater value of w, as expected. Transmission electron microscopy (TEM) images were obtained using a Hitachi H9000 high-resolution instrument operating at 300 kV by pipetting samples dissolved in hexane onto lacey-carbon-film-coated Cu grids. Figure 3 shows the morphology of the $w = 3$ powder; the inset shows an atomic-resolution image of one particle with a [5−51] zone-axis orientation. The average particle size of this sample as measured from the TEM images is 4.5 nm. A high-resolution image of the $w = 5$ powder is shown in Figure 4. Note that oblate as well as spherical particles are observed, likely as a result of a slightly faster growth in the (015) direction. Lattice fringes spaced 0.322 nm apart, corresponding to the (015) d spacing of Bi_2Te_3, are clearly evident on many particles. The inset shows the selected area diffraction pattern for this sample, indexed to Bi_2Te_3, in accordance with

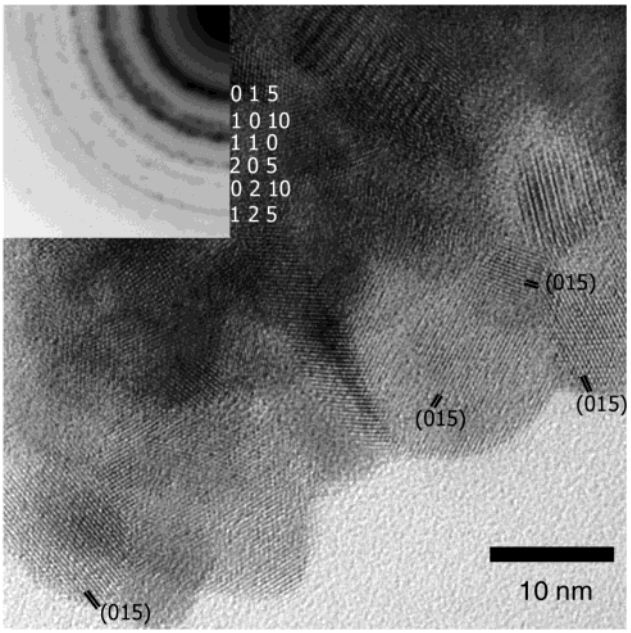

Figure 4. High-resolution transmission electron micrograph of unannealed, $w = 5$ Bi_2Te_3 sample. Inset: Selected area diffraction pattern indexed to rhombohedral Bi_2Te_3 in accordance with PDF # 15-863.

the powder diffraction files.[18] The average particle size measured from the TEM images for the $w = 5$ sample is 7.4 nm. Due to the agglomeration of the particles, it was not possible to measure enough particles to accurately report the particle size distribution for either sample. The reported particle size averages are based on measurements of 21 and 28 particles for the $w = 3$ and $w = 5$ samples, respectively. The experimental uncertainty in the average particle sizes is estimated to be <10%.

In summary, we have succeeded in synthesizing for the first time well-crystallized Bi_2Te_3 with a controllable average particle size in the sub-10 nm size regime. The approach involves a fairly standard reverse micelle reaction using AOT and water in hexane and minimizes the need for special equipment, reagents, and handling. Future work will include studying the effect of quantum confinement on the thermoelectric properties of these materials.

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