Preparation of Bi Nanowires from the Reaction between Ammonia and $Bi_{1.7}V_8O_{16}$

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This paper details the synthesis of bismuth wires from the reaction of $Bi_{1.7}V_8O_{16}$ and ammonia gas at 450 °C. The Bi wires are extruded from polycrystalline pellets of $Bi_{1.7}V_8O_{16}$ and can grow to be almost a centimeter in length with diameters between 10 nm and 20 μm. X-ray diffraction, elemental analysis, and differential thermal analysis measurements confirm that the extruded wires are metallic bismuth.

Introduction

Bismuth is used in a variety of everyday applications such as solder for water pipes, medicines, and fire protection systems because it is nontoxic, expands when it cools, and melts at a low temperature, 271.5 °C.[1] There has been a great deal of fundamental interest in elemental bismuth due to the novel physical phenomena it exhibits, such as a highly anisotropic Fermi surface, low carrier concentration, and long mean free path of the carriers[2] (up to 0.4 mm at 4 K), and as a model system for quantum confinement type effects.[3−7] Bismuth nanowires have also been shown to exhibit a number of interesting phenomena, such as a semimetal to semiconductor transition with decreasing wire diameter and temperature[8] as well as large positive size-dependent magnetoresistance.[9−11] Bismuth nanowires have also been predicted to be a good thermoelectric material.[8,12,13] Recently, during attempts to synthesize the oxynitride hollandite-type compound $Bi_{1.7}V_8O_{16-x}N_x$, we succeeded in growing wires of Bi by a previously unreported technique.

Almost all reported methods to create Bi nanowires use some type of template. In 1980, Gurvitch reported the synthesis of Bi nanowires by forcing liquid Bi into Pyrex capillaries under ~150 atm pressure.[5] Zhang et al. reported the synthesis of 13−110 nm Bi nanowires by injecting liquid Bi under pressure into the nanochannels of an anodic alumina template.[7,14] Their method created a more uniform distribution of wire sizes over the previous injection method.[7,14] Bi nanowires have also been prepared using a vapor phase technique.[15] This vapor phase growth technique relies on the evaporation of Bi at elevated temperatures and low pressures followed by the subsequent cooling of the Bi vapors in a porous alumina plate.[15] The electrodeposition of Bi nanowires into narrow channels of nanoporous alumina from a Bi solution was reported in 2001 by Wang et al.[16] Kiang et al. reported the synthesis of 1 nm diameter Bi wires using single-walled carbon nanotubes as a template, in the gas phase and via solid-state reactions.[17] Gao et al. reported the solvothermal synthesis of 20−30 nm Bi wires from the reaction of bismuth nitrate, acetone, and ethylenediamine in a Teflon autoclave.[18] They postulated that the ethylenediamine acts as both a templating agent and facilitates electron transfer from N to Bi^{3+}. Yu et al. reported the synthesis of 5.9 nm Bi nanowires from the decomposition of $Bi[N(SiMe_3)_2]_3$ in a polymer and $NaN(SiMe_3)_2$ solution.[19] They also reported the synthesis of 7.0 nm Bi wires from the decomposition of photosensitized $Bi[N(SiMe_3)_2]_3$ in a polymer solution.[19] These authors suggest that the

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additives bind selectively to certain Bi faces and promote Bi wire growth orthogonally to the blocked Bi edges.[19] Recently, Cheng et al. reported the synthesis of millimeter long 30−200 nm diameter Bi nanowires via the spontaneous extrusion of Bi from a composite Bi and CrN thin film.[20] Their technique did not rely on a template but rather on compressive stresses within the film that caused the extrusion of Bi and the formation of wires.[20] Li et al. moved beyond nanowires and prepared bismuth nanotubes from the reaction of $Bi(NO_3)_3$, aqueous hydrazine, and ammonia.[21]

The following report details the synthesis of Bi nano- and microwires from a polycrystalline parent compound, $Bi_{1.7}V_8O_{16}$, using flowing ammonia. Our technique relies on the reduction of a small amount of Bi^{3+} to Bi metal, followed by the subsequent extrusion of this Bi metal during cooling. The synthesis and structure of the hollandite $Bi_{1.7}V_8O_{16}$ has been previously reported by Abraham and Mentre.[22] The structure of hollandite-type compounds, $A_xM_8O_{16}$ ($x \leq 2$), were first reported by Byström and Byström in 1950[23] and can be described as an infinite array (in the z direction) of double-rutile edge-sharing octahedral chains. Each double rutile chain shares corners with another double rutile chain to form one 2 × 2 octahedral channel and one 1 × 1 octahedral channel. The A cations are located within the larger 2 × 2 channel. Subsequent studies revealed that the Bi−V−O hollandite-type compounds can form with Bi concentrations between 1.60 and 1.80 bismuth atoms per formula unit.[24] Since hollandite-type compounds tolerate a variety of substitutions (e.g. the mineral hollandite has both O^{2-} and OH^- anions[23]) and the V is reduced in the parent compound, $V^{3.36+}$, we believed that we could substitute N^{3-} for O^{2-}, which would oxidize the V, thus forming a more stable material. The formation of vanadium oxynitrides via ammonolysis has been reported by numerous authors,[25,26] and has been shown to be a reliable way to synthesize a variety of oxynitrides.[27]

Experimental Procedures

$Bi_{1.7}V_8O_{16}$ was synthesized via the solid-state reaction between Bi_2O_3 (Alfa Aesar, 99.975%), V_2O_3 (Alfa Aesar, 99.7%), and V_2O_5 (Alfa Aesar, 99.8%). The reagents were thoroughly ground in an agate mortar and sealed in an evacuated quartz tube (pressure $= 1.0 \times 10^{-5}$ Torr). The sample was annealed at 850 °C for 24 h and then quenched by removing it from the furnace. The sample was reground, pressed into a pellet, sealed in an evacuated quartz tube, and annealed for an additional 24 h at 850 °C to complete the reaction. A sample of $Bi_{1.7}V_8O_{16}$ was then loaded onto an alumina boat and placed directly above the thermocouple in a quartz-lined tube furnace. The sample was heated in flowing ammonia (Matheson, 99.99%, 0.5 L/min), at 10 °C/min to 450 °C, and allowed to dwell for between 12 and 24 h. The samples then were allowed to cool with the furnace to room temperature in flowing ammonia. It took 30 min to cool the sample from 450 to 250 °C. Alternatively, samples were either quenched after 18 h under NH_3 by sliding the tube from the furnace or furnace-cooled after switching from ammonia to flowing argon (0.5 L/min).

Powder X-ray diffraction (PXD) data were collected on $Bi_{1.7}V_8O_{16}$ using a Scintag X1 diffractometer with Cu Kα radiation. A small amount of sample was finely ground in an agate mortar and then sprinkled onto a glass slide coated with a layer of petroleum jelly in order to remove any preferential ordering of the crystallites. Data were collected from $10° \leq 2\theta \leq 120°$ in 0.02° steps at 9 s a step. Bismuth wires were also mounted on the end of a quartz fiber drawn from the end of a quartz rod for a diffraction study of only the wires. This quartz sample rod was centered inside of a 114.6 mm Debye−Scherrer camera and subsequently mounted on a Philips XRG 3100 X-ray generator. The sample was rotated while being irradiated for 2.5 h with Mo Kα radiation at room temperature. Standard techniques were used for the development and reading of the film, while no correction was applied for film shrinkage. Attempts to study the wires using a single-crystal diffractometer failed because the wires were too small.

Electron microscopy data were obtained using a JEOL JSM-840 scanning electron microscope (SEM). Elemental mapping data were collected using an EDAX brand energy-dispersive X-rays spectroscopy (EDS) device attached to the SEM. Differential thermal analysis (DTA) data were collected on a combination DTA/TGA instrument (TA Instruments, Model SDT-Q600). Approximately 1 mg of sample was placed in a Pt pan, while a comparable amount of Al_2O_3 was used as a reference material. The sample was heated and cooled at 5 °C/min to 500 °C in flowing argon.

Results

The $Bi_{1.7}V_8O_{16}$ starting material was black and had a qualitative resistance of ∼1 Ω as measured with a hand-held multimeter. After annealing the sample in ammonia the samples remained black and conductive (resistance ∼ 0.5 Ω). Optical microscopy revealed that the samples had wires growing off the surface in all directions. Some of the wires spanned the entire surface of the pellet (1.0 cm).

PXD data on the starting material $Bi_{1.7}V_8O_{16}$ were collected and analyzed using the program GSAS.[28] The as-refined lattice parameters [space group $I4/m$; $a = 9.9312(3)$ Å, $c = 2.9139(1)$ Å] were in good agreement with the reported values for the starting compound ($a = 9.9331$ Å, $c = 2.9116$ Å).[22] The sample that was treated with ammonia was biphasic (Figure 1). The main phase was a hollandite [$a = 9.9314(3)$ Å, $c = 2.9130(1)$ Å] and the second phase was Bi metal [space group $R\bar{3}m$; $a = 4.5464(4)$ Å, $c = 11.861(2)$ Å]. The reflections for the hollandite and Bi metal are indicated by the upper and lower set of ticks in Figure 1, respectively. Debye−Scherrer diffraction data for the Bi wires were refined by a least squares program[29] and yielded lattice parameters of $a = 4.551(4)$ and $c = 11.892(3)$ Å for the hexagonal setting in the space group $R\bar{3}m$, which are in good agreement with the reported PXD data and lattice parameters of Bi ($a = 4.546$ Å, $c = 11.862$ Å)[30] and confirmed that the wires were elemental Bi.

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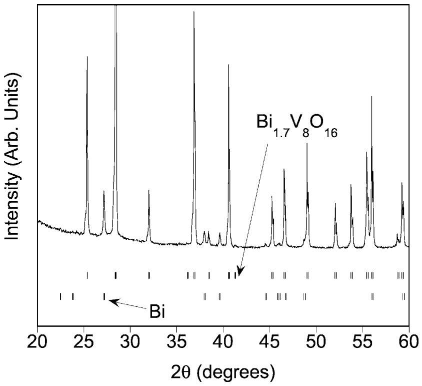

Figure 1. PXD data for the ammonia-treated $Bi_{1.7}V_8O_{16}$. The set of ticks indicate the positions for both $Bi_{1.7}V_8O_{16}$ and metallic Bi.

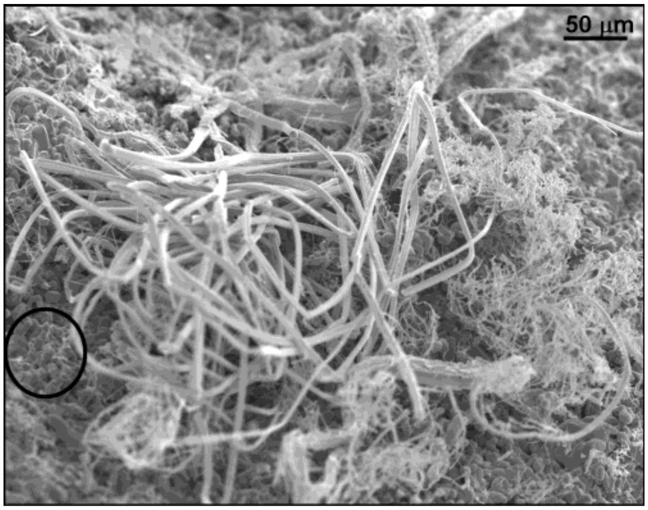

Figure 2. SEM image of the surface of the $Bi_{1.7}V_8O_{16}$ pellet after ammonolysis showing the wide variety of wire sizes and lengths. The black circle shows a region without Bi wires in order to compare the size of the $Bi_{1.7}V_8O_{16}$ crystallites and the Bi wires.

A sample of the ammonia-treated pellet was examined by SEM. Figure 2 gives a representative sampling of what the wires look like on the surface of the pellet. This image clearly shows the wide range in wire sizes produced during this reaction. The smallest observed wires have diameters of about 10 nm. The black circle is shown as an aid in order to compare the size of the $Bi_{1.7}V_8O_{16}$ crystallites (1−5 μm across) to the Bi wires. Some wires are circular while others form with more irregular cross sections. Many wires grow with striations or grooves on the surface (Figure 3). There was no evidence that these wires were hollow. The wires seemed to grow from everywhere with no obvious reason for the large range of sizes. The size dependence is probably due to the size of the pores or fractures in the pellet. Wires were observed inside of a fractured pellet; however, their concentration was much lower than those upon the surface. There was a noticeable increase in the concentration of the wires on the surface with longer reaction time up to 24 h; however, the size distribution of the wires remained the same. Elemental mapping studies using EDS indicated that the wires were pure bismuth, while the crystallites of the starting material contained Bi, V, and O. There was no evidence of the presence of N in any of the samples prepared for this study.

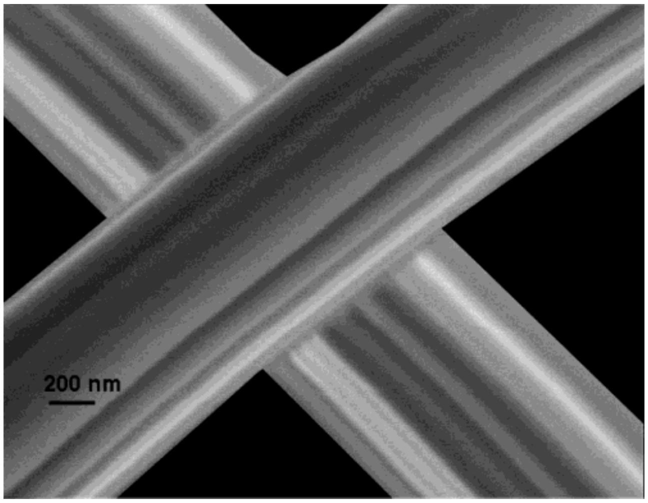

Figure 3. SEM image of two Bi wires. Note the striations on the surface from the extrusion process.

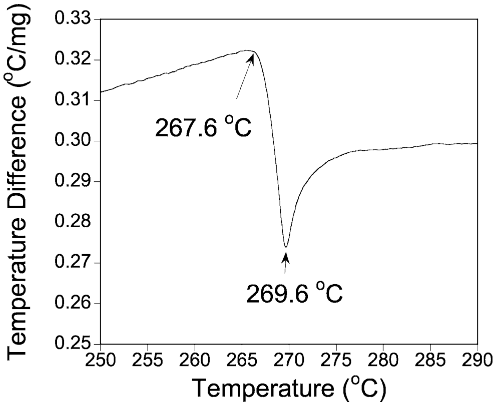

Figure 4. DTA data for the Bi wires.

Figure 4 shows the DTA data for the Bi wires. The melting point of the sample was determined to be 269.6 °C, which is within experimental error of the reported melting point of Bi in the literature of 271.5 °C.[1] No significant weight loss from the sample was observed during the heating. After the DTA measurements the Bi wires were examined by SEM and revealed the formation of Bi balls. The Bi balls were sparsely coated with small chunks of the polycrystalline starting material.

In alternate annealing experiments, when the sample was quenched from an 18 h ammonia treatment, the resulting pellet had both Bi and a hollandite-type compound in the PXD. There were also clearly Bi wires on the surface of the pellet. Alternatively, when the gas was switched to argon (0.5 L/min) during the cooling, the resulting pellet had no Bi wires on the surface, yet Bi was evident in the PXD data along with a hollandite-type phase. Last, when the sample was annealed and furnace-cooled in flowing argon (0.5 L/min), the resulting pellet had no wires on the surface and the PXD data showed a decomposition of $Bi_{1.7}V_8O_{16}$ to $BiVO_4$, $Bi_{1.33}V_2O_6$, and various V−O phases. There was no evidence of Bi or Bi_2O_3 in the PXD data.

Discussion

The above results have clearly demonstrated the formation of Bi wires from the reaction of $Bi_{1.7}V_8O_{16}$ and flowing ammonia, along with the critical role a reducing gas plays in this synthesis. The decomposition forming elemental Bi leaves behind a hollandite phase with slightly less Bi. This is not surprising considering the rigidity of the octahedral channels and the fact that the Bi concentration can be as low as 1.6.[24] There are several possible scenarios for the formation of metallic bismuth under these conditions. The first is a redox reaction between V^{3+} and Bi^{3+}, where the V gets oxidized while the Bi gets reduced. However, this route is improbable because such a redox reaction would also have occurred during the formation of the starting material $Bi_{1.7}V_8O_{16}$. A second possible mechanism may be the incorporation of three interstitial H^+ and the subsequent reduction of Bi^{3+} to Bi^0. A third possible mechanism that we propose is that small amounts of O^{2-} are being removed from the structure in order to compensate for the reduction of the Bi and maintain a reduced state of V. There have been some reports of oxygen-deficient hollandite-type compounds in the literature,[31] which are formed under high-temperature reducing conditions and partial pressure of oxygen $\sim 10^{-14}-10^{-18}$. In our case, the ammonia gas is sufficiently reducing to maintain the reduced V in the hollandite, reduce the Bi^{3+} to Bi, and concurrently remove some oxygen atoms to maintain charge neutrality. On the other hand, the argon used for the annealing experiment is not reducing enough to maintain the reduced V oxidation state in the hollandite and eventually leads to the decomposition of the starting material into slightly more oxidized Bi−V−O compounds, such as $BiVO_4$ and $Bi_{1.33}V_2O_6$. The Bi wires do not form by switching from ammonia to argon during the cooling; however, Bi is evident in the PXD. Under these conditions, the hollandite does not have time to decompose, the Bi begins to reoxidize, and a small amount of metallic bismuth is trapped in the pellet or forms balls. Attempts to look for subtle changes in the hollandite structure via PXD after Bi extrusion were unsuccessful. To definitively state the formation mechanism, a combination of neutron diffraction, due to the sensitivity of neutrons to hydrogen and oxygen, as well as in-situ SEM studies needs to be performed.

Upon cooling, the molten Bi solidifies and expands by 3.32%.[1] When it solidifies, this volume change forces it to be rapidly extruded from the polycrystalline starting material, via the path of lowest resistance, to form wires. The SEM data clearly shows the presence of striations and grooves in the wires, which are consistent with the extrusion of Bi through narrow pores formed by the crystallites. This also explains the lower concentration of wires within the pellet.

The extrusion of the Bi wires from the polycrystalline sample opens the possibility of using this technique to produce large amounts of Bi nanowires. We note that wires with diameters of around 10 nm have been obtained using our method, which if they could be harvested may be useful for a variety of experiments or applications. If a suitable mask with the right porosity could be prepared, one may be able to selectively extrude wires with a fixed diameter. This technique may prove feasible to develop, since the extrusion of the Bi wires is controlled by the pressure generated from the cooling of the Bi and not from an external pressure forcing the Bi into a narrow orifice. This technique may also be useful to explore the Bi−V−O phase diagram, since small amounts of Bi can be removed from the parent compound and may lead to the formation of other unique phases.

Conclusion

We have prepared Bi nanowires and Bi wires from the reaction of ammonia with $Bi_{1.7}V_8O_{16}$. Wires with diameters down to 10 nm have been prepared using this technique. We have shown that the hollandite starting material is stable under our reaction conditions and that Bi can be selectively removed from the parent compound, reduced, and extruded to form the observed wires.

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