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Single-Crystal $Al_{18}B_4O_{33}$ Microtubes

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The discovery of the carbon nanotube[1] has opened a challenging new field in materials science, solid-state physics, and chemistry, offering a wide perspective for many possible applications. This resulted in the extensive scientific interest over the past decade in tubelike micro- and nanotextures of other substances. Tube structures constructed from electrically, magnetically, or optically active ceramic materials are attractive for devices including actuators, sensors, transporters of liquids or gases. The successful synthesis of functional ceramic micro- or nanotubes such as BN, WS_2, MoS_2, VOx, TiO_2, Si_3N_4, SiC, AlN, sialon, and so forth has been reported.[2] We reveal in this communication a simple way for the production of single-crystal aluminum borate ($Al_{18}B_4O_{33}$ or $9Al_2O_3{\cdot}2B_2O_3$) microtubes.

Aluminum borates are remarkable ceramic materials with high elastic modulus and tensile strength, excellent resistance to corrosion, and thermal properties attractive for structure applications, optical electronics, and tribology.[3] Especially do aluminum borate whiskers have great potential in oxidation-resistant, whisker-reinforced composites. Mixtures of Al_2O_3 and B_2O_3 form aluminum borate whiskers at high temperature.[3a] Aluminum borate whiskers can also be fabricated by the so-called molten salt flux synthesis method where Al_2O_3 and B_2O_3 were reacted in various fluxes.[4] Gogotsi et al. also previously reported the hollow crystals with square or tetragonal cross-sections found in oxide films containing B_2O_3, Al_2O_3, and SiO_2, which were later identified as aluminum borates.[5] Recently, Guggilla et al. synthesized aluminum borate−Fe nanocomposites and studied their magnetic properties.[6] These results indicate some clues in synthesizing new structures and probing potential applications of aluminum borate. The newly discovered tube structure of aluminum borate in our present work is believed to be promising for use in composites, chemical and heat-insulating materials, and filter media.

Fumed alumina (5 g, Degussa) was impregnated with a $NaBH_4$ methanol solution for 2 h and dried at ambient temperature. Subsequently, $NiCl_2$ aqueous solution (2 M, 15 mL) and $NaBH_4$ solution (0.5 M, 20 mL) were added dropwise to the above alumina. During the addition, the solution was maintained under constant stirring with a mechanical stirrer. The precipitate was washed first with aqueous ammonia and then with methanol several times and baked in H_2 at 150 °C for 8 h. The obtained light-green powder was found to be amorphous aluminum borate particles (10−20 nm) mixed with highly dispersed nickel. The powder was then annealed in an alumina tube by a tube furnace at 1050 °C for 1 h under flowing $N_2(H_2)$ gas. After the annealing, it was observed that the light-green starting materials had been transformed into black aggregates.

The obtained products were characterized by X-ray diffractometer (XRD) and scanning electron microscopy (SEM). Sample powders were also ultrasonically dispersed in CCl_4 for 15 min. Then CCl_4 solution was dripped onto a carbon-coated-copper grid. The transmission electron microscopy (TEM) observation was carried out using a JEM-3000F (JEOL) field emission electron microscope with an electron energy loss spectra (EELS) attachment.

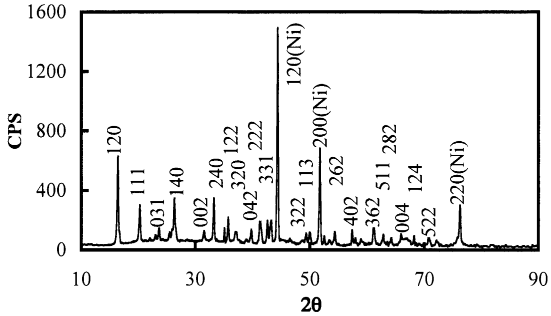

Figure 1. XRD pattern of the annealed product identifying the formation of a mixture of orthorhombic aluminum borate and cubic nickel.

The XRD pattern (Figure 1) of the product identified the formation of a mixture of orthorhombic aluminum borate (JCPDS 32-0003) and cubic nickel (JCPDS 04-0850). All the relatively sharp diffraction peaks in the pattern exhibit a good agreement concerning both the reflections profiles and intensities to the two phases. The formation of aluminum borate in the present study is similar to the process in ref 6. It involves the initial formation of boric acid (H_3BO_3) or B_2O_3 by borohydride reduction under aerobic conditions, as found in the reduction of $CoCl_2$ with $NaBH_4$ by Glavee et al.[7] Subsequently, the Al^{3+} in Al_2O_3 combines with boric acid during the hydrolysis−reduction at ambient temperatures to give amorphous aluminum borate. After annealing at higher temperatures, the crystalline aluminum borate phase is thus obtained.

Figure 2 shows the SEM observation results on the products. In Figure 2a, it is clearly seen the abundant fiberlike structures. These fibers often grow closely together. More interesting, the close-up view indicates that most of the fibers have hollow cores, namely tube-like structure (Figure 2 b−d). It appears that these tubes are usually open. The outer diameters of these tubes, as most frequently observed, are narrowly distributed at ca. 1 μm ,while the wall thickness fall in the range of about 200−450 nm. The lengths of these tubes are around 10−30 μm. From Figure 2d, it appears that some of the tubes are not seamless.

Figure 3a shows the low-magnification TEM image of a typical tube with the diameter ca. 1.1 μm. The selected area electron diffraction (inset in Figure 3a) taken from the longitude edge can be indexed as an orthorhombic $Al_{18}B_4O_{33}$ single crystal recorded from the $[1\bar{1}0]$ zone axis with lattice constants of $a = 0.77$ nm, $b = 1.50$ nm, and $c = 0.57$ nm. Figure 3b is the corresponding high-resolution image with the clearly resolved interplanar distance $d_{111} = 0.44$ nm. The high-resolution image also shows that the tube surface is covered by a very thin layer (1−2 nm) of amorphous phase, which also contains Al, B, and O, attributed to the glassy

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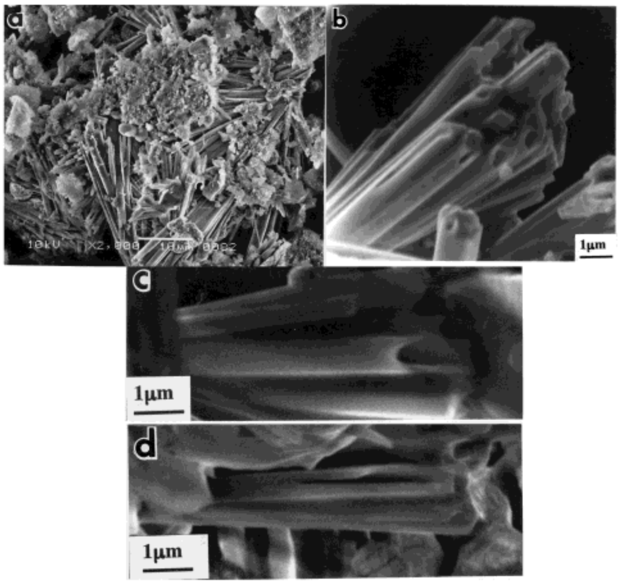

Figure 2. SEM observations on the synthesized product. (a) abundant closed-packed fiberlike structures. (b−d) Close-up view showing the fibers to be hollow tubes and usually open-end. (d) Some tubes are not completely sealed.

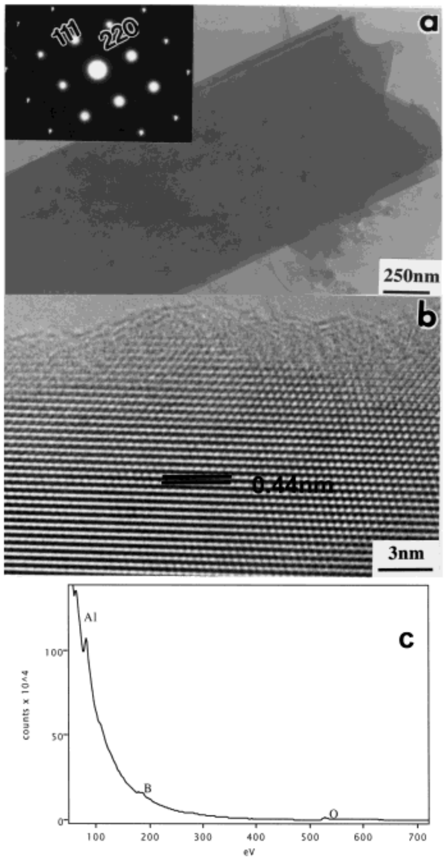

Figure 3. TEM analysis of aluminum borate tubes. (a) Low-magnification TEM image (inset) electron diffraction pattern can be indexed to an orthorhombic $Al_{18}B_4O_{33}$ single crystal. (b) HRTEM image with clearly resolved fringes of (111) planes. (c) A typical EELS spectrum taken from the microtubes exhibiting the element composition of the tube to be Al, B, and O.

aluminum borate or other ternary phases in the $Al_2O_3-B_2O_3$ system. Furthermore, the EELS measurements also confirmed the element composition of the tube to be Al, B, and O (Figure 3c). The microtubes are therefore identified undoubtedly to be single-crystal $Al_{18}B_4O_{33}$.

Aluminum borate has been well-known to form whiskerlike structures in various molten salt fluxes of Al_2O_3, boric acid, or B_2O_3.[4] The difference in our synthesis process with the previous methods is that we did not directly mix boric acid or B_2O_3 with Al_2O_3. The formation of boric acid was achieved by the borohydride reduction of $NiCl_2$ with $NaBH_4$. We also added the solution dropwise to fumed alumina to ensure that the borohydride reduction occurs on the surface of the alumina particles. The high yield of $9Al_2O_3{\cdot}2B_2O_3$ might be obtained due to the large surface-to-volume ratio of the fumed alumina which allows very efficient attack by the boron oxide. On the other hand, Ni has been extensively used as an effective metal catalyst for carbon nanotube growth.[8] It has also been previously reported that Ni could accelerate the growth of aluminum borate whiskers.[4c] We suspect that the simultaneously formed Ni metallic phase in our flux has some catalytic or promotion effect on the initiation and growth of the $Al_{18}B_4O_{33}$ tubes although it is not clear why microtubes rather than whiskers or nanotubes are obtained. Further investigations trying to elucidate the exact growth mechanism are in progress.

In summary, single-crystal aluminum borate microtubes were prepared. Such microtubes with open ends have a variety of promising applications such as being filled with other materials for protection or the fabrication of novel composites or filtering media. Further work is under way to study systematically the detailed structure and properties of this kind of novel tubular morphology, even the possibility of synthesizing nanotubes.

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