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A Facile Route for Synthesis of Aluminum Borate Nanowires

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Abstract: Straight single-crystalline of aluminum borate $Al_{18}B_4O_{33}$ nanowires have been successfully synthesized via simple route based on the reaction of the as-precursor powder of aluminum nitrate and sodium borate. The as-received nanowires have diameters in the range of 20-50 nm and lengths up to several micrometers. Experimental results show that the optimal synthesis temperature to fabricate nanowires of aluminum borate ($Al_{18}B_4O_{33}$) is found to be 1050°C. A self-catalytic growth mechanism was proposed to account for the growth of nanowires instead of whiskers.

Key words: Electron microscopy, ceramic material, nanowires, crystal morphology

INTRODUCTION

One-dimensional nanoscale materials, such as nanotubes, nanowires and nanobelts, have stimulated intensive research interesting, due to their great potential application in optoelectronic devices and mechanical properties (Alivisatos, 1996; Lieber, 1998). Ceramic made of nano-Al_2O_3 composites have been shown to exhibit enhanced mechanical properties such as the potential for ductile (supper-plastic) behavior. These properties are similar to those of silicon carbide whiskers, which now recognized as the best whiskers for Al-based composite material, but SiC whiskers/nanowires are expensive and sensitive to oxidation at high temperature, resulting in considerable strength and toughness degradation (Wang *et al*., 2000; Wong *et al*., 1997; Kim and Lieber, 1999). Therefore, much effort has been made to develop such whiskers/nanowires materials are that their price would be far below that of SiC whiskers. Whiskers composed of aluminum borate having these basic demands, on their excellent mechanical properties, chemical stability, low thermal expansion coefficient and potential applications in high-temperature composites (Scholze, 1956; Liu *et al*., 1998; Jaque *et al*., 2000; Peng *et al*., 1999; Hu *et al*., 2001). Aluminum borate whiskers ($Al_{18}B_4O_{33}$) is estimated to posses a high melting point approaching 1960°C and have greater potential in oxidation-resistant, whisker-reinforced composites than those observed in corresponding macroscopic single crystals due to a reduction in the number of defects per unit length (compared with larger structures) that lead to mechanical failure (Hu *et al*., 2001; Readey, 1992). Various methods have been reported for growth such whiskers composed of $Al_{18}B_4O_{33}$. Flux method has been reported to be one of the simplest techniques for preparing ceramics with the preferential orientation. A porous ceramic composed whiskers -like grains of length of 10-20 μm and the diameter of 2-3 μm and with aspect ratio lower than 10 were synthesized by firing a boric acid-stabilized aluminum acetate above 1500°C (Readey, 1992). The reaction between aluminum sulphate and boric acid in the presence of potassium sulphate flux formed the whiskers with lengths ranging from 5 to 15 μm and diameters of ~800 nm (Wada *et al*., 1996, 1991; Li *et al*., 1998; Rohmund and Smalley, 2000). It is thus reasonable to consider aluminum borate nanowires will exhibit greater strengths than previously reported in micrometer-diameter whiskers. Moreover, nanowires should be of interest and attracted much attention especially for the mechanically strengthening materials, reinforced composites materials and electronic ceramics. So we try to fabricate aluminum borate due to their unique features. Recently, nanowires of aluminum borate ($Al_{18}B_4O_{33}$) have been fabricated by thermal evaporation method (Ma *et al*., 2002; Liu *et al*., 2003) and catalyst synthesis (Cheng *et al*., 2003, 2004). However, most of these synthetic approaches involves some quantities of hydroxide boron glass and metal impurities appeared on the surface of the one-dimensional nanostructures and the nanowires usually contain transition metal at the wire end. In this research, it is reported that a simple and low cost synthetic route is put forward for the growth single phase of aluminum borate ($Al_{18}B_4O_{33}$) based long and high purity one-dimensional

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nanowires at much lower temperature 1050°C without any impurity catalyst. It requires a relative simple equipment and manipulation.

MATERIALS AND METHODS

Aluminum nitrate $Al(NO_3)_3.9H_2O$) and sodium borate $Na_2B_4O_7 \cdot 10H_2O$ were commercial grades and used as starting materials without purification. A typical synthetic condition was described as follows: Under vigorously stirring typically, 4 g (10.66 mmol) of aluminum nitrate was dissolved into 50 mL of distilled water in beaker A. In another beaker B, 6 g (15.73 mmol) of purity sodium borate was completely dissolved in 100 mL distilled water. Then the solution A was added as drop wise under magnetic stirring to the solution B until a white precipitation appeared. The precipitate that formed is filtered, followed by washing with absolute methanol and deionized water several times to remove the adhering reactants. Then citric acid was added to above participate which is act as ferment agent. Washed precipitate was slowly dried on a hot plate at 50°C overnight. Finally, the precursor powder for aluminum borate nanowires was obtained. The as-prepared precursor powder was homogenized in an agate pestle and mortar as initial reaction constituents and then was placed in an alumina boat located in alumina tube, which was mounted in a traditional resistance-heated furnace. The sample was heated at 1050°C for 2 h under flowing Ar gas. The final product single-crystal nanowires is separated from the remnant Na salt flux by washing the products with water and dilute HCl solution and finally dried at 50°C in air. The Crystalline phase was identified by X-ray diffraction (XRD, D/max-RB), The morphology and the size of the product were observed by Scanning Electron Microscopy (SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, Phillips-CM200), with a micro-analysis system of Energy Dispersive Spectroscopy (EDS). These experiments have been carried out on November 2005 in the Department of Physics, (Nanomaterials Center) Central China Normal University.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the product fabricated by direct heating of the as-precursor powder at 1050°C by using a reaction time of 2 h. All reflections peaks in Fig. 1 can be easily indexed to orthorhombic $Al_{18}B_4O_{33}$ with cell parameters of a = 0.774 nm, b = 1.504 nm and c = 0.567 nm. These results are in good accordance with those reported in (JCPDS 32-0003) bulk crystal. The results of XRD measurements, performed on sample containing relatively large quantities of nanowires,

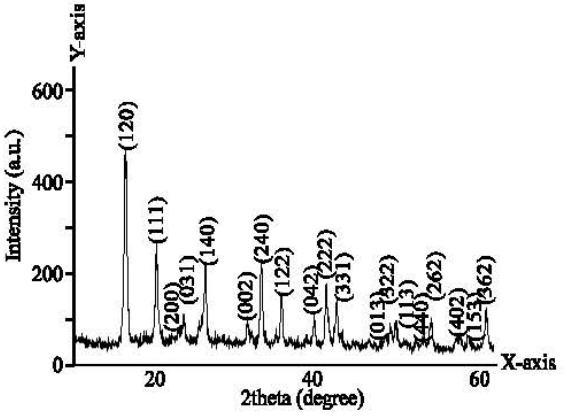

Fig. 1: X-ray diffraction (XRD) pattern of the nanowires prepared by direct heating of as-prepared precursor powder at 1050°C

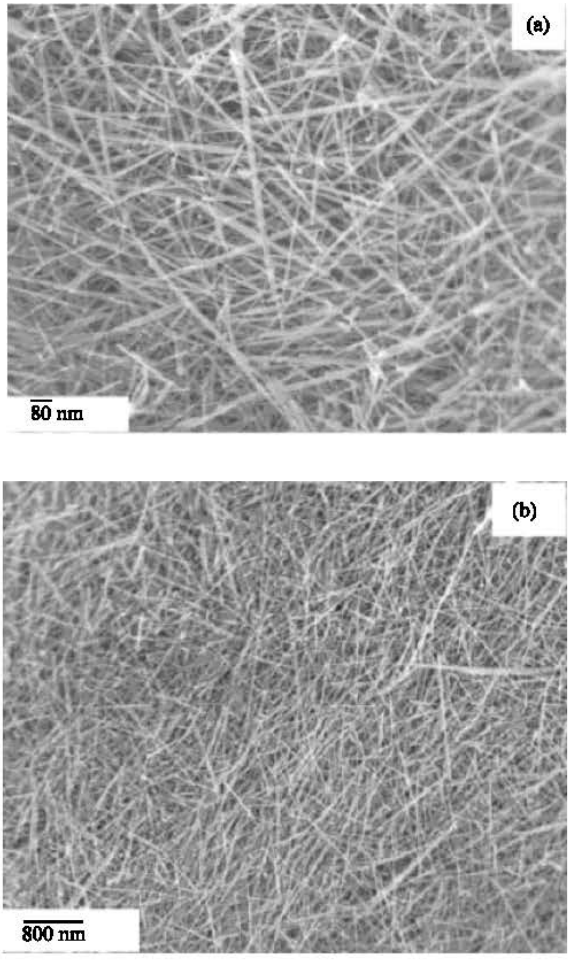

Fig. 2: SEM images, (a) High magnification of as-synthesized nanowires showing uniform diameter. (b) Low magnification of abundant and aggregation nanowires

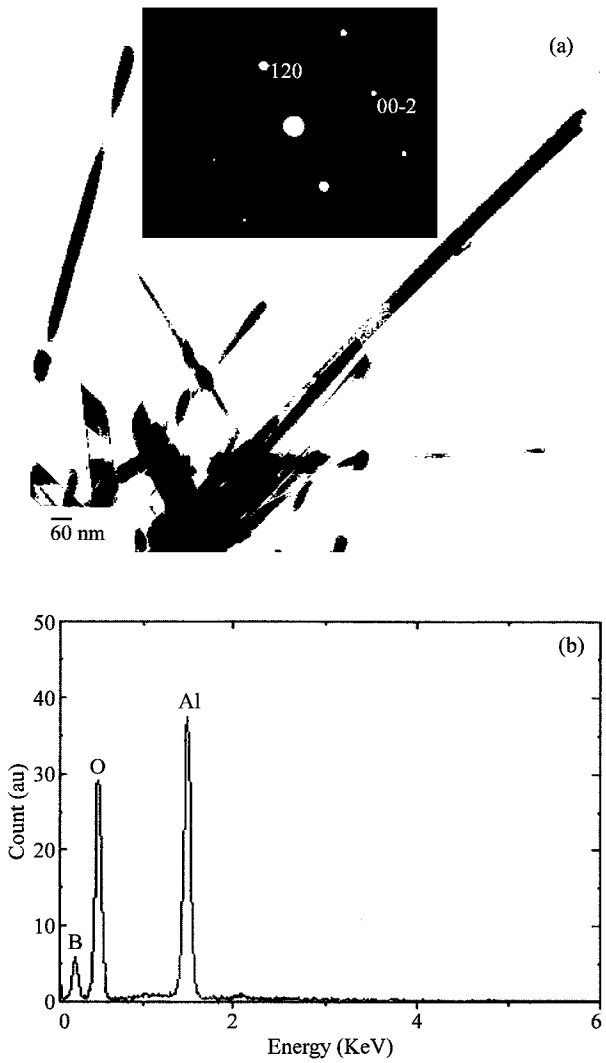

Fig. 3: TEM characterization on aluminum borate nanowires, (a) TEM image showing smooth surface nanowires and no particles at the wires end: (inset) SAED pattern taken from an individual nanowire can be index as orthorhombic phase. (b) EDS spectra confirm that the nanowires are composed of Al, B and O

indicate the high purity of $Al_{18}B_4O_{33}$ nanowires produced using the present the as-prepared powder approach.

The SEM image in Fig. 2a reveals that the product exhibits one-dimensional structure and consists of long and fairly nanowires-diameter with smooth surface. The as-received diameters of these straight nanowires ranging between 20 to 50 nm and lengths of several micrometers and the aspect ratio are high up to 200. A sample exhibiting this diameter uniformity and displays an abundant nanowires is represented by low magnification image (Fig. 2b). Figure 3 shows a typical Transmission Electron Microscopy (TEM) image of $Al_{18}B_4O_{33}$ product. It clearly reveals that the product is primarily composed of straight and pure nanowires coincidence with SEM observations and hardly to find any impurities and almost no nanoparticles can be observed at the end tips, which is the character of VLS mechanism. By comparing SEM and TEM results to the previous findings (Cheng *et al.*, 2003, 2004) all the as-synthesized nanowires represented here possess high aspect ratios, high purity one-dimensional nanowires, a very clean surface (no any impurities present in the products) and relatively much effect on the nanowires diameters. Atypical energy dispersive x-ray spectrum EDS analytic technique (Fig. 3b) indicating that the nanowire of $Al_{18}B_4O_{33}$ contains only Al, B and O elements with the Al/O ratio approaching 18/33. This is considerably different with the $Al_{18}B_4O_{33}$ nanowire structure synthesized by the catalytic growth method previously reported, (Cheng *et al.*, 2003) in which some iron nanoparticles can be observed at the ends and the growth was attributed to Fe-catalyzed liquid-liquid-solid mechanism. The Selected Area Electron Diffraction (SAED) pattern in the inset of Fig. 3a was recorded with electron beam focusing on an individual nanowire. The pattern suggests that the nanowires prepared using this method were single crystalline nature and these straight nanowires recorded from [-210] zoon axis with lattice constant consistent with XRD results presented above.

Aluminum borate has been well-known to grow into whisker-like structures by using various molten salt fluxes of Al_2O_3, boric acid, or B_2O_3. The difference in our synthesis process with the previous methods is that we did not directly mix the powders of boric acid, or B_2O_3 with Al_2O_3. In the present approach, aluminum borate $Al_{18}B_4O_{33}$ nanowires have been fabricated by improving the above-mentioned molten salt flux method, by using the as-precursor powder prepared from starting materials of $Na_2B_4O_7{\cdot}10H_2O$ and Al $(NO_3)_3.9H_2O$. Also various nanowires are fabricated over transition metal catalyst by using Vapor-Liquid-Solid (VLS) growth mechanism (Ma *et al.*, 2002; Liu *et al.*, 2003; Cheng *et al.*, 2003, 2004). However, in this mechanism the nanosized catalyst provides a seed for the growth and usually these catalysts appeared at the wire end. In the present results no tips were found at the end of the nanowires. So the VLS mechanism is not suitable for the growth of the as-prepared nanowires in this contribution. Therefore, we discuss the growth mechanism of this borate nanowires as follows: In this study a simple and easy method is used

to grow $Al_{18}B_4O_{33}$ nanowires by heating the as-precursor powder at 1050°C. It appears that the mechanism of producing $Al_{18}B_4O_{33}$ nanowires presented here is similar to that of salt synthesis (Arendt *et al*., 1979). The growth of whiskers or rods require a fluid phase in which elements of the crystal phase can easily move long distances. In this method we believe that during the synthesis boron oxide reactant (B_2O_3) will melts first and become a liquid at temperature higher than 450°C, then during the increase of temperature and at elevated temperature it is likely that a liquid clustered of Al_2O_3 will be created. The small clustered grains of Al_2O_3 will serve as nuclei for the growth of nanowires just like self-catalytic growth method previously reported (Liu *et al*., 2003. Then we expect that Al_2O_3 grains absorb the liquid B_2O_3 and diffuse rapidly to form a fluid phase of $Al_{18}B_4O_{33}$ at temperature below its melting point. Then with further heating, this liquid environment leads to the liquid phase-nanowires to stack themselves yielding in the precipitation of $Al_{18}B_4O_{33}$ nanowires at temperature 1050°C as high product Therefore, we believe that the self-catalytic mechanism may account for growth of $Al_{18}B_4O_{33}$ nanowires. The method might account one of many efforts are under way to develop high performance ceramics. Also this method may be useful to explore the many possibilities of commercial application of the single phase of these nanowires.

CONCLUSIONS

In this contribution simple and easy method to synthesis single-crystalline of $Al_{18}B_4O_{33}$ nanowires is successfully prepared by directly heating of the as-precursor of aluminum nitrate and sodium borate. The characterization of ID nanostructure through TEM and SEM shows that the nanowires possess a diameter of 20-50 nm and lengths up to several micrometers and almost are free of external catalyst contamination. Experimental results showed that the optimal synthesis temperature is 1050°C. This simple synthesis method described here may account for commercial production in order to find application in reinforcing materials.

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