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A simple route for the synthesis single-crystalline $Mg_2B_2O_5$ nanowire bundles

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ABSTRACT

Single-crystalline magnesium borate $Mg_2B_2O_5$ nanowires in bundle form have been synthesized via a simple route based on heating a precursor powder made of aqueous solutions of magnesium chloride and de-sodium tetraborate with citric acid. The results show that each bundle composed of nanowires of high-purity with diameter of approximately ca. 90 nm and lengths up to a few micrometers. The effect of citric acid, the optimum experimental parameters and possible growth mechanism for the compound nanowires have been presented.

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Introduction

One-dimensional nanoscale materials, such as nanotubes, nanowires, and nanobelts, have attracted much attention because of their interesting properties of understanding fundamental physical concepts and for potential applications [1, 2]. Nanowires should be of interest especially for the mechanically strengthening materials, considering the important role played by tradition whisker-reinforced ceramic composites in the current commercial applications. Nanowire-like structures have been expected to effectively improve the mechanical properties of ceramic materials. As any example, SiC nanowires are particularly interesting because SiC whiskers are widely used to strengthen the ceramic materials by incorporation of SiC whiskers into these brittle matrices [3]. Recently, a delicate measurement combining atomic force microscopy and lithography techniques indicates that the strength value of SiC nanowires is a factor of 2 times the best observed previously SiC whiskers in micrometer diameter [4]. However, although the most promising ceramic composite to date is the SiC whisker-reinforced Al_2O_3 ceramics with an exceptional toughness and strength, the materials possess a difficult processing and a high cost [4, 5]. Therefore, there have been considerable interests to develop the novel whisker/nanowire materials with excellent properties and inexpensive cost. Metal borates whiskers/ nanowires meet these demands based on their excellent mechanical properties, chemical inertness, low thermal expansion coefficient, and high-temperature stability [4- 5]. Refractory compound $Al_{18}B_4O_{33}$ has a high melting point approaching 1950 °C and is considerably stable even in an oxidizing environment [6, 7, 8].

Magnesium borate whiskers/nanowires is one type of the metal borates and are well known as one of the most important technical ceramics. Up to date there are a few reports about the synthesis of magnesium borates nanostructures [9- 12]. However, magnesium borate nanowires reported in the previous work [9- 11] were mixtures of precursor powders or fiber-like boron oxide agglomerates, or each nanowire was terminated by a ball-like particle attached one end. Therefore, preparation of uncontaminated whiskers/nanowires by a cheap, effective and facile-controllable method has been of scientific and technological interest. Herein, we present an alternative with much tractable route to the synthesis magnesium borate $Mg_2B_2O_5$ wire-like bundles characterized by a comparatively low reaction temperature with the use of very simple precursor materials. This method is controllable, reproducible and environmental friendly. The $Mg_2B_2O_5$ bundle- nanowires achieved in the present work are single crystalline in nature with monoclinic structure, which differs from the $Mg_2B_2O_5$ nanowires of triclinic structure synthesized previously [13].

Experimental

The starting materials include magnesium chloride ($MgCl_2{\cdot}6H_2O$) and de-sodium tetraborate ($Na_2B_4O_7{\cdot}10H_2O$), were of commercial grades and used without further purification. A typical synthetic condition is described as follows: In beaker A, an aqueous solution was prepared by dissolving 4.92 mmol of magnesium chloride into 30 ml of deionized water and then an appropriate amount of ammonia ($NH_3{\cdot}H_2O$) was added to this solution to adjust the pH as 9-10, resulting in a milk white solution. Under continues stirring, in another beaker B, solution of borax ($Na_2B_4O_7{\cdot}10H_2O$) was also made by dissolving 5.24 mmol into 120 ml of deionized water. The 30 ml of solution A was carefully injected as dropwise into solution B. An appropriate amount ~ 5.8 mmol of citric acid monohydrate ($C_6H_8O_7.H_2O$) was dissolved in the above mixture solution as ferment and chelating agent. Then the final mixture solution was stirred strongly for 2 hours and ultimately was evaporated at 150 °C in an oven for 12 hours

Finally, the precursor powder of magnesium borate nanowires was got. After the sol-gel process, the barmy powder was placed in an alumina boat located in alumina tube, which was mounted in the traditional resistance-heated furnace (Figure 3.3). The system was rapidly heated to 850 °C and kept at this temperature for 180 minutes. High-purity argon was adopted as a protecting medium at a constant flow rate of 50 standard cubic centimeters per minute (sccm). After that, the as-obtained grey solid powder was filtered and washed several times with hot distilled water to remove the possible impurities remaining in the final products, and finally dried at 60 °C in air.

The crystal structure and phase purity of the product were examined by means of X-ray diffraction (XRD, D/max-RB) analysis with Cu kα radiation. The overview of the sample morphology was identified by scanning electron microscopy

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(SEM, JEOL JSM-6700F), equipped with the system of energy-dispersive X-ray (EDX) analysis. Sample powder was also ultrasonically dispersed in ethanol solution and dropped onto a carbon coated copper grid for transmission electron microscopy (TEM, JEM-210F, JEOL), with a micro-analysis system of energy dispersive spectroscopy (EDS).

Results and discussion

XRD analysis was carried out to determine the structure and the phase of the final product.

As can be seen (Fig. 1) all detectable peaks in this pattern can be assigned by their peak position to monoclinic magnesium borate $Mg_2B_2O_5$ (suanite) having lattice parameters of a = 1.233, b = 0.3122 and c = 0.9210 nm. This result is in good agreement with the standard bulk values of $Mg_2B_2O_5$ lattice parameters within experimental errors (a= 1.231, b = 0.3120 and c = 0.9205 in the JCPDS Card no: 16-0168). It should be noted that no diffraction peaks from other phases have been observed indicating a purity of as-obtained product.

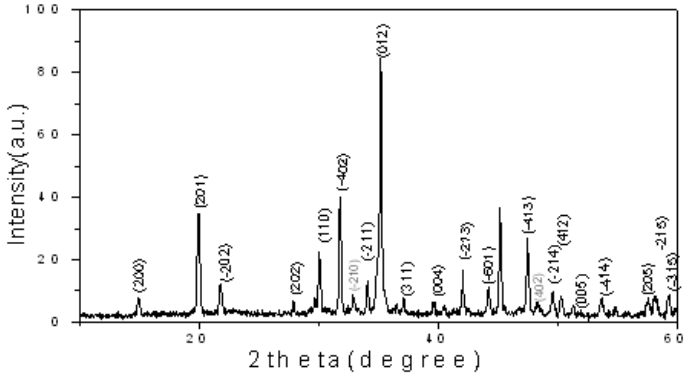

Figure 1: XRD pattern of magnesium borate ($Mg_2B_2O_5$) synthesized at temperature of 850 °C for 3 hours

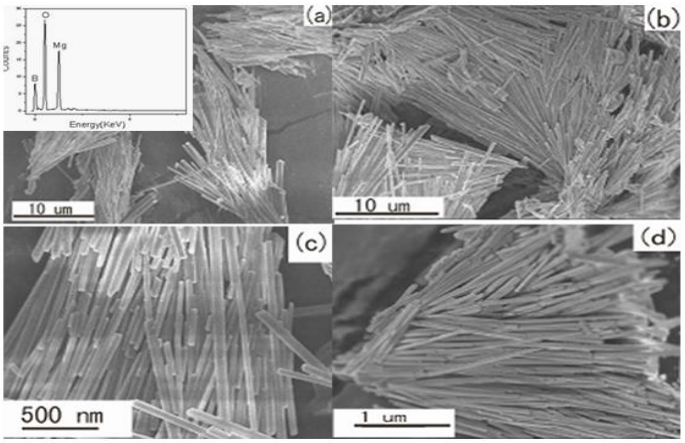

Figure 2: SEM images and EDS spectrum of $Mg_2B_2O_5$ nanowires: (a), (b) show low magnification SEM images of the nanowires; (c), (d) enlarged SEM images revealing the geometrical morphology of nanowires

Figure 2 shows SEM images of the $Mg_2B_2O_5$ nanostructures synthesized by our method. The low magnification SEM images of as synthesized $Mg_2B_2O_5$ shown in Fig. 2a and 2b, display wire-like bundles morphology. It is interesting that the nanowires in each bundle are tightly stuck together at the initiation growth and then funning out to form the typical aligned-wire-like a long bundle. The magnified SEM images in Fig. 2c and 2d reveal that the most-high purity nanowires in each bundle are straight and have uniform diameter over their entire lengths. From SEM images, we found that no particle was observed at the end of the nanowires. Energy-dispersive X-ray spectrum (EDX) was conducted for element constituents of the specimen shown in insert Figure 2a. As can be seen only elements Mg, B, O were detected. Quantitative results give the atomic ratio of 1:1:.2.8 for Mg/B/O. It was close to the ideal ratio of 1:1:2.25 considering the experimental errors.

The TEM image in Figure 3a shows that each bundle composed of nanowires of high-purity with diameter of ca. 90 nm. This finding corroborates the observations of SEM images (Fig. 2). Taking into account some nanowires have been broken in the process of preparing TEM sample using ultrasonic dispersion method. TEM image shown in Fig. 3b exhibits one bundle of $Mg_2B_2O_5$ the nanowires with uniform morphology and clean surface without amorphous materials seen on the surface of nanowires, which possibly have been removed by hot distilled water. Moreover, it is clearly seen that no particle could be detected at the tip of wires. Indicated in Fig. 3c is an individual $Mg_2B_2O_5$ nanowire and the corresponding SAED pattern. The selected area electron diffraction (SAED) pattern indicated that the nanowires possessed a single crystal structure consistent with the monoclinic structure of magnesium borate.

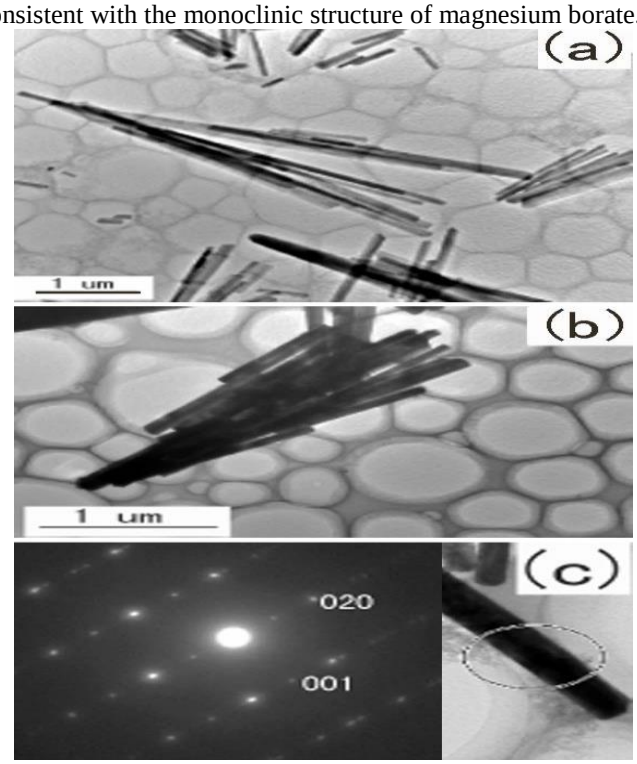

Figure 3: TEM images of the as-synthesized product: (a) low-resolution TEM image of $Mg_2B_2O_5$ nanowire bundles; (b) TEM morphology of one bundle; (c) Individual nanowire separated from the bundle, and its selected area electron diffraction pattern (inset)

To study the function of CA (citric acid), comparative experiments were also conducted using different amounts of CA and keeping other experimental conditions the same as mention above. Typical SEM images of the as synthesized products are given in Fig. 4, which clearly reveal that the morphologies of as-synthesized products in different amounts of CA are extremely different. As shown in Fig. 4a the as-obtained product is of irregular and short whiskers with an average diameter of about 1 μm obtained in the reaction system without CA. Usually, $Mg_2B_2O_5$ product exhibits whiskers like-bundle with low ratio when the amount of CA used, less than 5.00 mmol (Fig. 4b). When increasing the amount of CA up to 8.6 mmol, short whiskers capped with many nanoparticles can be observed (Fig. 4c). So we can conclude that an appropriate amount of CA is vital for the formation of $Mg_2B_2O_5$ nanowire bundles and further can effect on the diameter scale. Although, the exact roles of CA

on $Mg_2B_2O_5$ bundles growth are still unclear, we believed that the citric acid (CA) might play a role for at least one aspect: preventing the aggregation of $Mg_2B_2O_5$ nanostructures in the initial stage and kinetically controlling the growth rates of various crystallographic facets of monoclinic $Mg_2B_2O_5$ nanostructures into like-bundles.

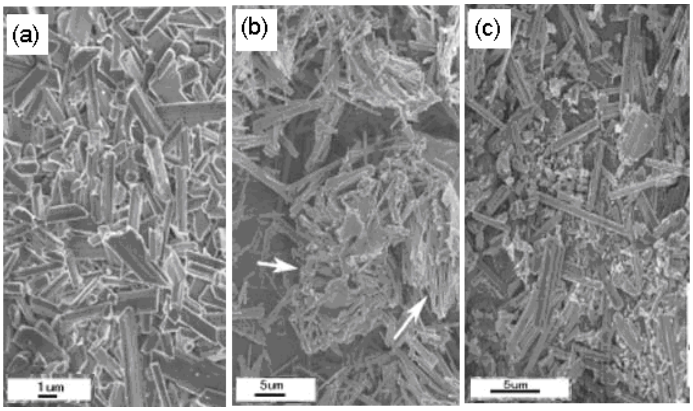

Figure 4: Shows the overview morphology of SEM images: (a) Typical morphology of sample synthesized in the absence of CA; (b), (c) SEM images of the products synthesized at the presence of 4.6 and 8.5 mmol of CA respectively

In addition, the temperature is an important factor for the production of the $Mg_2B_2O_5$ nanowires bundles. If the reaction temperature is below 850 °C the as-obtained products are not nanowire bundles but indicated a large quantity of irregular short whiskers (Fig. 5a). On the other hand if the reaction temperature is 950 °C or above, the reaction is too fast and thus the morphology of the $Mg_2B_2O_5$ is not easy to control, although of that the as-obtained product consists of relatively short rods/whiskers with large diameter (Fig. 5b).

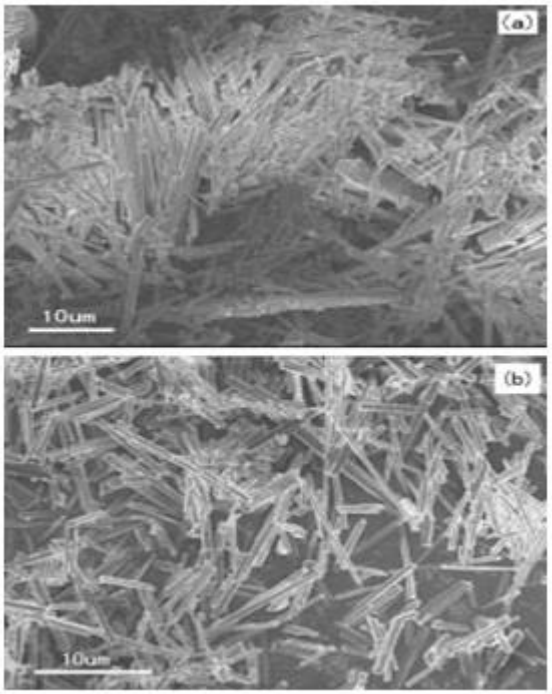

Figure 5: Shows the overview morphology of SEM images: The morphology of the samples fabricated at 800 °C (a), and 950 °C (b), in the presence of 5.8 mmol of CA

Thus, the obvious changes of the product morphology indicate that the influence of the temperature is very important in the wires formation process using this method. These experimental results assured that in the presence of 5.8 mmol of CA, the optimal conditions of the as-fabricated $Mg_2B_2O_5$ nanowires with fine diameter and with like-bundles morphology should be conducted at 850 °C for 3 h.

As for nanowires, nanorods and nanotubes preparation, the vapor-liquid-solid (VLS) and vapor-solid (VS) mechanisms have been widely used and also were discovered to be effective for the growth of metal borates [9,14- 17]. The feature of the VLS mechanism is the presence of intermediates that serve as catalyst between the vapor feed and the solid growth at elevated temperature and the morphology feature is a catalyst ball found on the tips of the nanowires [16-18]. However, no catalyst materials such as Fe, Co, or Ni were added to the starting precursors, and furthermore, our extensive TEM observations (Fig. 3) indicated that no droplets were observed at the ends of the nanowires which show that the VLS mechanism seems not to be the case in this work. We also suggest that the vapor-solid is not involved in the process. In the typical VS process, the vapor evaporated from the starting materials and deposited directly onto a lower temperature region and grows into nanowires structure determined by the super saturation [19]. Hence, in this work we expect that the most possible growth mechanism of the nanowires were basically fabricated through a catalyst-free growth rather than VLS process. Firstly, during the reaction process; when the high super saturation liquid-droplets phase of Mg-B-O takes place at elevated temperature, allows its nucleation to stack themselves and $Mg_2B_2O_5$ crystals will begin to grow from the droplets into like nanostructures. The formed nanostructures may provide the initial environment for the growth of nanowire. Secondly, with the help of the confinement of citric acid (CA) the as-produced nanostructures tend to form nanorods bundle due to the diffusion-control growth [20]. Further nucleation and epitaxial growth will take place by the diffusion of the reactants through the droplets to the growing fronts of the bundle. Thirdly, with the prolongation of the reaction time, $Mg_2B_2O_5$ nanowire bundles are formed by further growth and re-crystallization process.

Conclusion

In summary, single-crystalline nanowires bundles were successfully synthesized by directly heating the precursor powder made of aqueous solutions from magnesium chloride and de-sodium tetraborate with citric acid as additive. The characterization of the nanostructure through TEM and SEM shows the nanowires are gathering together in a form of bundles with approximately ca.90 nm in diameter and almost are free of contamination. The nanowires's growth is attributed as a catalyst-free growth. This simple and low-cost method may account for commercial production in order to find applications such as reinforcing materials and thermoluminescence phosphor.

References

[1] Jiang Z, Zongquan L, Zhang B, " Formation and structure of single crystalline magnesium borate ($Mg_3B_2O_6$) nanobelts " Mater. Chem. Phys., vol. 98 , pp. 195-197 , August 2006.

[2] Alivisatos A P, "Semiconductor Clusters, Nanocrystals, and Quantum Dots" Science,
vol. 271, pp. 933-937, February 1996.

[3] Lieber C M, One-dimensional Nanostrutures: Chemistry, Physics & Applications" Solid State Commun., vo.107. pp. 607-616, April 1998.

[4] Wong E W, Sheehan P E, Lieber C M, Science, "Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes" vol. 277. pp. 1971-1975, Sebtember 1997.

[5] Víctor Vl, Antonio P, "Novel Ribbon-Shaped α-Al_2O_3 Fibers" Advanced Material, vol.10, pp.1370-1373, November 1998.

[6] Jaque D, Enguita O, Sole J G., Jiang A D, Luo Z D, " Infrared continuous-wave laser gain in neodymium aluminum borate: A promising candidate for microchip diode-pumped solid state lasers" Appl. Phys. Lett., vol.76, pp. 2176-2179, April 2000.
[7] Readey M J, "Formation and Sintering Characteristics of Aluminum Borate Whiskers" J. Amer. Ceram. Soc., vol.75, pp. 3452- 3456, December 1992.
[8] Scholze H, "Aluminum borate" Z. Anorg. Allg. Chemie., vol. 284, pp. 272- 277, March 1956.
[9] Hu Z, Shi Y, Ma Z, Bi J, Wang F, Chan H, Dong J, " Study on antiwear and reducing friction additive on nanometer aluminum borate" Luber. Eng., vol. 57, pp. February 23-27,2001.
[10] Ma R, Bando Y, Sato T, "Nanowires of metal borates" , Appl. Phys. Lett., vol.81, pp. 2467-1269, October 2002.
[11] Yang L, Zhiyong F, Jia G, Chang R P H, Chem. Mater.," Synthesis of mahnesium borate ($Mg_2B_2O_5$) nanowires by Chemical Vapor Deposition Method " , vol. 16, 2512-2525, Jun 2004.
[12] E.M Elssfa, A. Alsanousi "Synthesis of magnesium borate nanorods" M. Letters, vol. 61, pp. 4385-4361, Sebtembe 2007.
[13] Jiang Z, Zongquan L, Zhang B, "Formation and structure of single crystalline magnesium borates ($Mg_3B_2O_6$)nanobelts, Mater. Chem. Phys., vol. 98, pp.195-197, August 2006.
[14] Azmi S, Emek M and Sabriye Piskin, Magnesium Borate Synthesis by Microwave Energy :A New Method, J. Chmestry, Article ID 329238, 6 pages , March 2013,
[15] Cheng C, Tang C, Ding X X, Huang X T, Huang Z X, Qi SR, Hu L, Li Y X, "Catalytic Synthesis of aluminum borate Nanowires " Chem. Phys. Lett., vol.373, pp. 626-629, April 2006.
[16] Duan X, Huang Y, Agarwal R, Lieber M C, " Single-Nanowires Electrically Driven Laser" Nature, vol. 421, pp.241-245, November 2003.
[17] Ma R Z, Bando Y, Golberg D, Angew. Chem. Ed., " Nanotubes of Magnesium Borate" vol.42, pp. 1836- 1838, April 2003.
[18] Zhang J, Huang Y, Lin J, Ding X X, Tang C, Qi S R, J. " Large Scale Preparation of aluminum borate- coated aluminum oxide nanowires" Solid State Chem., vol.178, pp.2263-2266, July 2005.
[19] Zhang H Z, Kong Y C, Wang Y Z, Du X, Bai Z G, Wang T T, Yu D P, Ping Y, Hang Q L, Feng S Q, " Ga_2O_3 nanowires prepared by physical evaporation" Solid State Commun., vol. 109, pp. 677-682, March 1999.
[20] Valcareel V, Souto A, Guitian F, "Development of Single-Crystal α-Al_2O_3 Fibers by Vapor–Liquid–Solid Deposition (VLS) from Aluminum and Powdered Silica " Adv. Mater., vol.10, pp. 138.-141, January 1998.