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Preparation and Structure Characterization of β-BaB_2O_4 Nanowires

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A cetyltrimethylammonium bromide (CTAB)-assisted hydrothermal method was applied to prepare β-BaB_2O_4 nanowires using $Ba(NO_3)_2$ and $NaBH_4$ as reactants. After subsequent annealing in air at 700 °C, β-BaB_2O_4 nanowires with a diameter of 10–20 nm and a length up to several micrometers were obtained. The characterization results indicate that β-BaB_2O_4 nanowires are single crystalline with the preferential growth direction along [113].

One-dimensional (1D) nanostructures, such as nanotubes, nanowires, and nanorods have attracted intense attention owing to their potential application in nanodevices and understanding of the chemical and physical phenomena involving size-dependent properties. However, only a few attempts to prepare 1D nanostructures of nonlinear optical (NLO) materials have been reported. It has been reported by Magrez et al. that $KNbO_3$ nanowires can be obtained by a hydrothermal route.[1] Nakayama et al. reported an electrode-free, continuously tunable coherent visible light source compatible with physiological environments, made of individual $KNbO_3$ nanowires.[2] It indicates that 1D NLO nanostructures have much potential application in the range of physics, chemistry, materials science, and biology. As important NLO and photoluminescent materials, β-BaB_2O_4 crystals and films have been studied extensively because of their unique combination of strong nonlinear optical properties and large electronic band gaps.[3–6] Recently, β-BaB_2O_4 network-like nanostructures were prepared by sol–gel approach, and the second-harmonic generation (SHG) effect was observed.[7]

In this letter, β-BaB_2O_4 nanowires with a uniform morphology and high crystallinity were fabricated. The reaction involved in the growth of the β-BaB_2O_4 nanowires was discussed briefly, and the preferential growth direction of the β-BaB_2O_4 nanowires was also investigated.

In a typical preparation, 0.005 mol of $Ba(NO_3)_2$ and 0.01 mol of $NaBH_4$ were dissolved in distilled water to make 50 mL of mixture with Ba:B mole ratio equal to 1:2. Then 10 mL of 10% aqueous solution of CTAB was added to the mixture, and the measured pH value of the mixture, was about 11. The whole mixture was stirred for 30 min to form a homogeneous solution. It was then transferred into a stainless steel autoclave, sealed, and maintained at 220 °C for 20 h. After the reaction was completed, the white precipitate was filtered and washed several times with distilled water and absolute ethanol, respectively. The precipitate was annealed in a furnace at 700 °C in air for 1 h and then ground to powder in a mortar. All of the chemicals were of analytical grade and used without further purification.

The products were analyzed by an X-ray powder diffractometer (XRD, Rigaku D/max rA) with Cu Kα radiation ($\lambda = 0.15418$ nm). The overview of the sample morphology was checked by a field scanning electron microscope (FSEM, LEO 1530 VP) operated at an acceleration voltage of 5 kV. Sample powders were also ultrasonically dispersed in ethanol, and a drop of the solution was placed on a copper grid coated with porous carbon film for the measurement by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM), which were performed on a Philips CM300 transmission electron microscope with an acceleration voltage of 200 kV. The Fourier transform infrared (FTIR) spectra were recorded as KBr discs on a Perkin-Elmer BX-II spectrometer in the range of 400–3000 cm^{-1}.

Figure 1 shows a typical XRD pattern of the product. All of the peaks can be indexed as those of orthorhombic phase of β-BaB_2O_4 (JCPDS 80-1489) with the lattice parameters of $a = 1.253$ nm and $c = 1.272$ nm. No characteristic peaks were observed for any impurities. The strongest diffraction peak of the sample was located at $2\theta = 25.44°$, the corresponding plane was (131), and the d spacing was 0.35 nm.

The phase structure of β-BaB_2O_4 belongs to the space group C_{3v}-$R3c$. Theoretic calculations predict that the center optical mode A_1 and E of β-BaB_2O_4 are infrared active. The assignment of the FTIR absorption peaks observed in our samples was based on the FTIR data for the β-BaB_2O_4 single crystal.[8] Figure 2 shows the FTIR spectrum of the product. The absorption peaks at 1242 and 1196 cm^{-1} can be assigned to the characteristic B–O stretching mode in the $(BO_3)^{3-}$ unit, which is a component

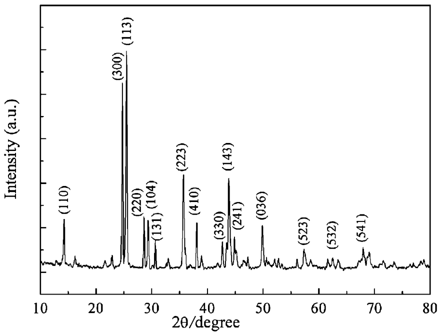

Figure 1. A typical XRD pattern of the product.

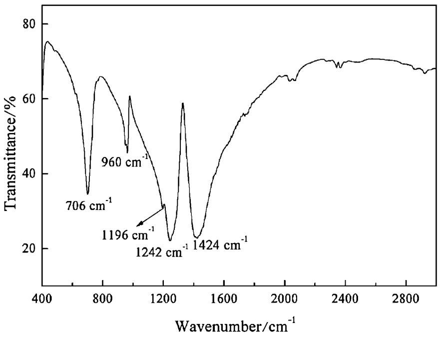

Figure 2. FTIR spectrum of the product.

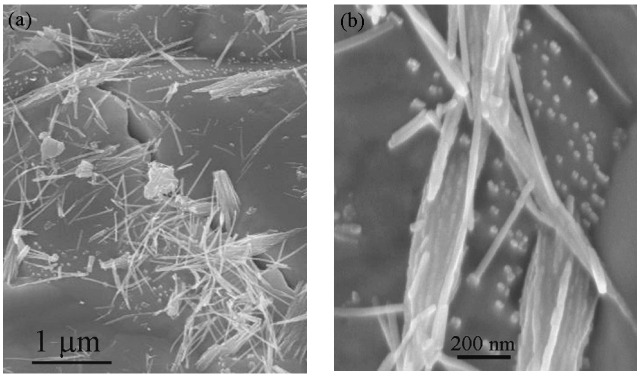

Figure 3. (a) Low-magnification and (b) high-magnification SEM images of β-BaB_2O_4 nanowires.

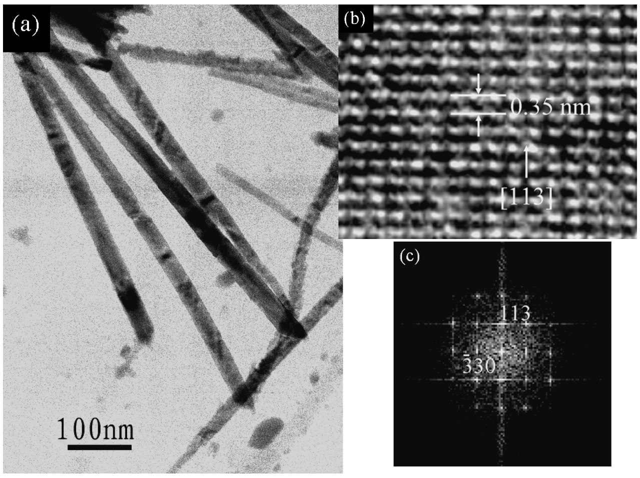

Figure 4. (a) A typical TEM image of the nanowires, (b) a representative HRTEM image of β-BaB_2O_4 nanowire, and (c) its corresponding fast FFT pattern.

of the $(B_3O_6)^{3-}$ ring. The strong absorption bands observed at 706 cm^{-1} are due to O–B–O bending vibrations of the same unit. The absorption peaks at 960 and 1424 cm^{-1} can be attributed to the stretching vibration of extra-ring B–O bonds.

The morphology of the product was observed by FESEM. Figure 3a is a low-magnification SEM image of the product and indicates that the large quantity of β-BaB_2O_4 nanowires was produced by this approach. The high-magnification SEM image in Figure 3b shows that these nanowires have a good uniform diameter of 10–20 nm and length up to several micrometers.

TEM and HRTEM observations were carried out to investigate more details of the structure and morphology of β-BaB_2O_4 nanowires. A typical TEM image of β-BaB_2O_4 nanowires is shown in Figure 4a. The results displays that the nanowires have a uniform structure and a diameter range similar to that observed by SEM. Figure 4b illustrates a representative lattice-resolved HRTEM image of the β-BaB_2O_4 nanowires and the clear lattice fringes exhibiting good crystallinity of the β-BaB_2O_4 nanowire. The lattice spacing is measured to be about 0.35 nm, which corresponds to the (113) crystal plane of β-BaB_2O_4. Figure 4c shows its corresponding fast Fourier transform (FFT), and the diffraction patterns can be indexed to the (113) and $(\bar{3}30)$ planes of the orthorhombic structure of β-BaB_2O_4, respectively. Both the HRTEM image and the FFT pattern indicate that the β-BaB_2O_4 nanowires are single-crystal structure and that the preferential growth of β-BaB_2O_4 nanowires is along the [113] direction, which is consistent with the reported analysis.[7]

The chemical reactions involved in the formation of the β-BaB_2O_4 nanowires may be considered as below. First, in hydrothermal treatment, the $BaB_2O_4{\cdot}4H_2O$ will precipitate according to reactions (1) and (2). As illustrated in the literature,[9] $BaB_2O_4{\cdot}4H_2O$ can be dehydrated consequently to form β-BaB_2O_4 according to reaction (3).

$$NaH_4B + 2H_2O \rightarrow NaBO_2 + 4H_2\uparrow \qquad (1)$$

$$2BO_2^- + Ba^{2+} + 4H_2O \rightarrow BaB_2O_4{\cdot}4H_2O\downarrow \qquad (2)$$

$$BaB_2O_4{\cdot}4H_2O \xrightarrow{700\,^{\circ}C} \beta\text{-}BaB_2O_4 + 4H_2O\uparrow \qquad (3)$$

We think that the CTAB surfactant, which has been widely used as a soft template for the formation of 1D nanostructures,[10,11] plays an important role in the fabrication of structurally uniform β-BaB_2O_4 nanowires.

Illuminated by a Q-switched mode-locked Nd:YAG laser ($\lambda = 1064$ nm), the SHG signal generated in the sample was confirmed from the emission of green radiation. The sample is still under investigation to characterize the linear and nonlinear optical properties of the β-BaB_2O_4 nanowires and will be the subject of a later publication.

In summary, single-crystalline β-BaB_2O_4 nanowires with uniform structure have been fabricated using a CTAB-assisted hydrothermal method and subsequent annealing. The preferential growth direction of the β-BaB_2O_4 nanowires was along the [113] direction.

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