Hydrothermal Synthesis and Characterization of Magnesium Borate Hydroxide Nanowhiskers

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Magnesium borate hydroxide ($MgBO_2(OH)$) nanowhiskers with a diameter of 20–50 nm and a length of 0.5–3 μm were synthesized via a facile hydrothermal route, using $MgCl_2 \cdot 6H_2O$, H_3BO_3, and NaOH as the reactants. $Mg_7B_4O_{13} \cdot 7H_2O$ with poor crystallinity was formed after coprecipitation of the reactant solutions at room temperature, the hydrothermal treatment of the slurry at 240 °C for 18 h led to the formation of uniform $MgBO_2(OH)$ nanowhiskers with high crystallinity and preferential growth direction along the (200) plane.

One-dimensional (1D) nanomaterials of magnesium borates have been paid much attention owing to their potential application in the manufacture of the reinforcing composites as plastics, aluminum, or magnesium alloys,[1] and also in the synthesis of the semiconductor materials.[2] It was reported that several 1D magnesium borates (such as MgB_4O_7 nanowires,[3] $Mg_3B_2O_6$ nanotubes[4] and nanobelts,[5] $Mg_2B_2O_5$ nanowires[2] and whikers[6]) can be synthesized by the sintering or the chemical vapor deposition (CVD) methods in the temperature range of 850–1100 °C. The careful control of the temperature gradient was usually needed for the growth of whiskers. In recent years, the hydrothermal method has been used for the synthesis of magnesium borate hydroxide ($MgBO_2(OH)$) whiskers, a promising candidate for the synthesis of luminescent material[7] and $Mg_2B_2O_5$ whiskers.[8] Compared with the sintering or the CVD method, the hydrothermal method has some distinct advantages such as the moderate condition, the high crystallinity of the products and the easy control of the solution components.[9–13] It was reported that $MgBO_2(OH)$ whiskers with an average diameter of 30 nm and an average length of 700 nm were formed after hydrothermal treatment of the slurry containing fine powders of B_2O_3 and MgO at 180 °C for 48 h,[7] the problem was that the length of the whiskers was relatively short, and the morphology was not uniform. $MgBO_2(OH)$ can also be produced by the hydrothermal treatment of the solution containing $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot 14H_2O$ and H_3BO_3 at 180 °C for 72 h,[14] but the morphology of $MgBO_2(OH)$ was not reported.

Herein, we reported a new moderate hydrothermal method for the synthesis of $MgBO_2(OH)$ nanowhiskers with an uniform morphology and high crystallinity, using $MgCl_2 \cdot 6H_2O$, H_3BO_3, and NaOH as the reactants. The reactions involved in the coprecipitation and hydrothermal process were investigated, and the preferential growth direction of the $MgBO_2(OH)$ nanowhiskers was discussed.

In a typical procedure, 4 mol L^{-1} NaOH solution was mixed with 3 mol L^{-1} H_3BO_3 solution and 2 mol L^{-1} $MgCl_2$ solution at room temperature, keeping the final molar ratio of NaOH: H_3BO_3:$MgCl_2$ as 4:3:2. Then 40 mL of the above slurry was put into a Teflon-lined stainless steel autoclave with a capacity of 70 mL. The autoclave was sealed and heated at 240 °C for 18 h and then cooled to room temperature on standing. The product was filtered off, washed with deionized water for several times and dried in vacuum at 60 °C for 6.0 h. All of the reagents were analytical grade and used without further purification.

The morphology and microstructure of the sample were examined with the field emission scanning electron microscopy (FESEM, JSM 7401F, JEOL, Japan), the high-resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL, Japan) and the selected area electron diffraction (SAED). The structure and composition of the sample were identified by an X-ray powder diffractometer (XRD, D/max2500, Rigaku, Japan) using Cu Kα radiation ($\lambda = 1.54178$ Å), an inductively coupled plasma (ICP, IRIS Advantage, Thermo Elemental, U.S.A.) and a thermogravimetric analyzer (TGA, TGA 2050, TA Instruments Thermal Analysis & Rheology, U.S.A.).

The typical XRD pattern, TEM image and SAED pattern of the precipitate formed after mixing of the $MgCl_2$, H_3BO_3, and NaOH solutions at room temperature are shown in Figures 1 and 2, respectively. The results indicated that the precipitate was composed of $Mg_7B_4O_{13} \cdot 7H_2O$ nanoparticles (PDF No.19-0754) with irregular shape, the weak diffraction of the XRD pattern in Figure 1 and the SAED pattern in Figure 2 revealed the poor crystallinity of the precipitate. The ICP and the TGA analyses showed that the molar ratio of Mg:B and the weight ratio of the crystal water in the precipitate was 1.76 and 23.27%, respectively, quite consistent with the theoretical values of $Mg_7B_4O_{13} \cdot 7H_2O$.

Figure 3 shows the XRD pattern of the product after the hydrothermal treatment of the slurry at 240 °C for 18 h. All of the diffraction peaks can be indexed as those of monoclinic $MgBO_2(OH)$ (PDF No. 39-1370, space group: $P2_1/a$ (No. 14)). The cell parameters correlated from the data in Figure 3 were as follows: $a = 12.610(14)$, $b = 10.431(12)$, $c = 3.139(3)$ Å, $\beta = 95.869(11)°$, which were quite consistent with the standard values ($a = 12.614$, $b = 10.418$, $c = 3.144$ Å, $\beta = 95.880°$) of $MgBO_2(OH)$. The strongest diffraction peak

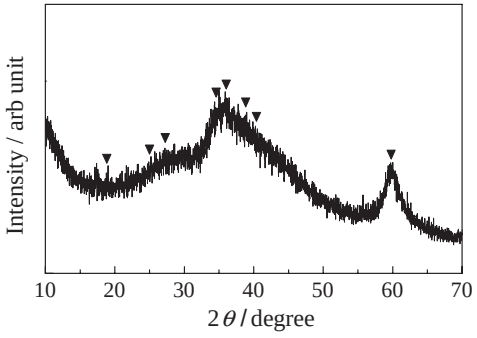

Figure 1. XRD pattern of the precipitate formed at room temperature. ▼: $Mg_7B_4O_{13} \cdot 7H_2O$.

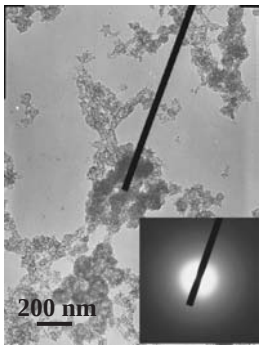

Figure 2. TEM image and SAED pattern of the precipitate formed at room temperature.

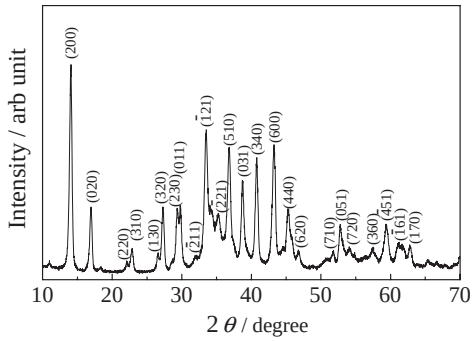

Figure 3. XRD pattern of the $MgBO_2(OH)$ nanowhiskers.

of the sample was located at $2\theta = 14.02^\circ$, the corresponding plane was (200), and the d spacing was 6.31 Å.

The reactions involved in the coprecipitation and hydrothermal reactions can be written as follows:

$$7MgCl_2 + 4H_3BO_3 + 14NaOH \rightarrow Mg_7B_4O_{13}\cdot 7H_2O + 14NaCl + 6H_2O \quad (1)$$

$$Mg_7B_4O_{13}\cdot 7H_2O + 3H_3BO_3 \rightarrow 7MgBO_2(OH) + 8H_2O \quad (2)$$

The morphology of the hydrothermal product is shown in Figure 4. Uniform nanowhiskers with a diameter of 20–50 nm and a length of 0.5–3 μm are observed.

The TEM and the HRTEM images of the hydrothermal product are shown in Figure 5. The SAED pattern (Figure 5b) which was recorded from the $[0\bar{1}1]$ zone axis and corresponding to the circled part of the nanowhisker (Figure 5a) indicated that the nanowhiskers had a preferential growth orientation along the (200) plane. The HRTEM image (Figure 5c) corresponding to

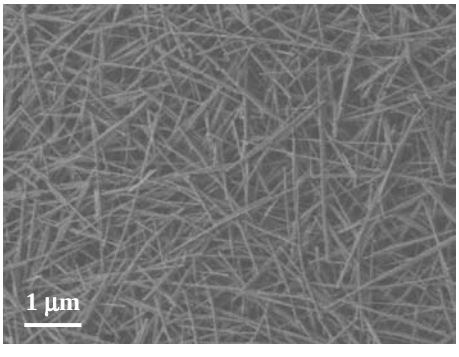

Figure 4. SEM image of the $MgBO_2(OH)$ nanowhiskers.

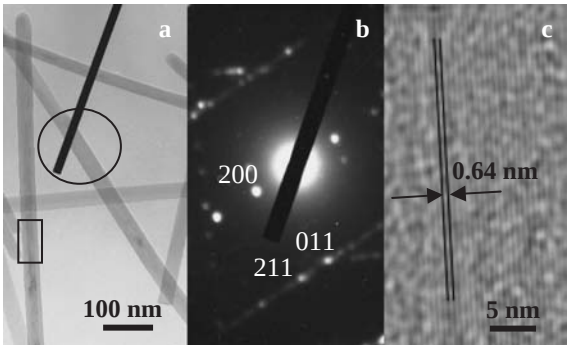

Figure 5. TEM (a), SAED (b), and HRTEM (c) images of the $MgBO_2(OH)$ nanowhiskers.

the framed part of the nanowhisker (Figure 5a) demonstrated the occurrence of the lattice fringes along the longitudinal direction of the nanowhisker. The interplanar spacing is 0.64 nm (6.4 Å), quite similar to that of the (200) plane calculated from the XRD data in Figure 3, reconfirming the preferential growth direction of the nanowhiskers along the (200) plane. The characterization of the hydrothermal product by XRD, TEM, SAED, and HRTEM confirmed the high crystallinity of the $MgBO_2(OH)$ nanowhiskers synthesized via the present coprecipitation–hydrothermal reaction route. The TGA and XRD analyses revealed that the weight loss for the conversion of the $MgBO_2(OH)$ product to $Mg_2B_2O_5$ was 12.62%, quite consistent with the theoretical weight loss and reconfirmed the high purity of the hydrothermal product.

In summary, $Mg_7B_4O_{13}\cdot 7H_2O$ with unregular shape and poor crystallinity was formed after mixing of $MgCl_2\cdot 6H_2O$, H_3BO_3, and NaOH solutions at room temperature; the hydrothermal treatment of the slurry at 240 °C for 18 h led to the formation of uniform $MgBO_2(OH)$ nanowhiskers with a diameter of 20–50 nm and a length of 0.5–3.0 μm. The preferential growth direction of the $MgBO_2(OH)$ nanowhiskers was along the (200) plane.

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