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Morphology preservation and crystallinity improvement in the thermal conversion of the hydrothermal synthesized MgBO₂(OH) nanowhiskers to $Mg_2B_2O_5$ nanowhiskers

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- 1. Introduction

One-dimensional (1D) nanostructures, such as nanotubes, nanowires, nanorods and nanobelts, have been the focus of intensive research owing to their unique structures and potential applications in mesoscopic physics and nanodevices [1–3]. The novel properties of 1D nanostructures greatly depend on their morphology, aspect ratio and crystallinity [4–9]; thus it is of great significance to ascertain controllable synthesis of 1D nanostructures with uniform morphology, high aspect ratio and high crystallinity. 1D nanostructures could be obtained by a variety of synthetic methods [3], among which chemical vapor deposition (CVD) has been widely used particularly for its versatility [3,10] and high crystallinity [11], e.g. noticeable semiconducting oxide

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ABSTRACT

Preservation of one-dimensional (1D) morphology and improvement of crystallinity in the thermal conversion route to magnesium borate (Mg₂B₂O₅) nanowhiskers at a relatively low temperature as 650–700 °C (200–350 °C lower than that of the literature) based on the hydrothermal synthesis of magnesium borate hydroxide (MgBO₂(OH)) nanowhiskers were investigated; the results indicated that thermal conversion at appropriate temperature with a slow heating rate was favorable for the morphology preservation and crystallinity improvement. A specific heating procedure was developed according to the recrystallization phenomenon existing in the thermal conversion of the MgBO₂(OH) nanowhiskers to produce Mg₂B₂O₅ nanowhiskers (15.0–45.0 nm in diameter, 0.2–2.0 µm in length) were synthesized by heating MgBO₂(OH) nanowhiskers (1.0 °C min⁻¹) to 650 °C for 2.0 h of isothermal condition first to preserve the 1D morphology, and thereafter to 700 °C (1.0 °C min⁻¹) for another 2.0 h of deformation could also benefit synthesis of other 1D anhydrous nanostructures via the wet chemistry-based thermal conversion route.

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nanobelts of Wang's group [2] and MgO nanowires of Xia's group [3]. However, CVD also faces problems such as high energy consumption, difficulty in scaling-up [10], and broad distributions of the size and morphology of the product.

In contrast, hydrothermal technology has been emerged as a thriving method for the synthesis of 1D nanostructures in the last decade [12-15], for its several advantages over the other conventional processes such as energy saving, better nucleation control, better shape control and lower temperature of operation, etc. [16]. However, hydrothermal synthesis readily results in 1D hydroxyl or hydrated compounds, and subsequent calcination or anneal is usually needed to obtain the corresponding 1D anhydrous compound, e.g. oxides. 1D nanostructured transition and rare earth metal oxides such as Eu₂O₃ nanorods [17], Tb₄O₇ and Y₂O₃ nanotubes [18,19], Y₂O₃:Eu nanobelts [20], Dy₂O₃ nanotubes [21] and MnO₂/Mn₂O₃/Mn₃O₄ nanorods [22] with well-preserved 1D morphology and high crystallinity have been synthesized via the calcination of the corresponding 1D precursors, probably due to the relatively low decomposition temperature and characteristics of the transition and rare earth metal compounds. Nevertheless, in more cases such as MgO



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nanorods [23] and Al₂O₃ nanorods [24,25], etc., pores, severe deformation and even rupture readily occurred in the thermal conversion process due to the dehydration or devolatilization [19,23–30]. Many efforts have been made to preserve the 1D morphology and improve the crystallinity of the calcined products, including the sintering at low temperature [18,20,22,28,29], the adaptation of the multi-step heating procedure [23] or the addition of the specific components [30–32], etc.. It is, however, still a challenge to avoid or reduce the deformation and degradation of the crystallinity of the calcined product due to the pores generated from the elimination of the volatile components [20,23,29,30].

1D nanostructured magnesium borates, including MgB₄O₇ nanowires [33], Mg₃B₂O₆ nanotubes [34] and nanobelts [35], Mg₂B₂O₅ nanowires [36,37], nanorods [38] and whiskers [39-41], etc., have been paid much attention in recent years for their wide usage as reinforcing components in the electronic ceramics [33], the wide band gap semiconductors [36], the antiwear additive [37], and the plastics or the aluminum/magnesium [41] matrix alloys. In contrast, 1D Mg₂B₂O₅ nanomaterials [36-41] have attracted more research interests for their wider applications. Traditionally, 1D micro-/nanostructured magnesium borates were prepared at relatively high temperature within 850-1250 °C via thermal evaporation or CVD technique [33-38], flux method [39-41], or supercritical method (500-600°C, 200-1000bar, 14 days) [42]. Although the 1D Mg₂B₂O₅ nanostructures synthesized by the above methods exhibited high crystallinity, problems such as high temperature accompanied by high energy consumption, the coexistence of the particulate agglomerates [33,35,39-41] and the relatively rigorous experimental conditions [34,36,42] still needed to be solved.

The former work showed that MgBO₂(OH) could be converted into irregular particulate Mg₂B₂O₅ at temperatures above 610 °C [42], revealing the possible synthesis of 1D Mg₂B₂O₅ nanostructures from the thermal conversion of 1D MgBO₂(OH). MgBO₂(OH) nanoparticles could be synthesized under hydrothermal conditions [43-45]. Up to now little work was focused on the thermal conversion of MgBO₂(OH) to Mg₂B₂O₅. In our previous work, uniform MgBO₂(OH) nanowhiskers have been synthesized via a co-precipitation-hydrothermal reaction route [45], and here we report for the first time, to the best of our knowledge, the investigations on the preservation of 1D morphology and improvement of crystallinity in the thermal conversion of MgBO₂(OH) nanowhiskers to Mg₂B₂O₅ nanowhiskers at a relatively low temperature as 650-700 °C. Effects of the parameters such as temperature, heating rate and heating procedure on the thermal conversion route to Mg₂B₂O₅ nanowhiskers were discussed; finally Mg₂B₂O₅ nanowhiskers (diameter: 15.0–45.0 nm, length: 0.2–2.0 µm) with uniform 1D morphology and improved crystallinity were obtained. The strategies to preserve 1D morphology and improve crystallinity presented here were also subservient for the synthesis of other 1D nanostructures via the thermal conversion of the corresponding 1D nanostructured precursors.

2. Experimental methods

Monoclinic MgBO₂(OH) (PDF No. 39-1370) nanowhiskers were synthesized by co-precipitation of NaOH, MgCl₂ and H₃BO₃ solutions at room temperature followed by the hydrothermal treatment of the slurry (Mg₇B₄O₁₃ · 7H₂O) at 240 °C for 18.0 h [45]. After hydrothermal treatment, the slurry containing MgBO₂(OH) was washed with distilled water, filtrated and dried at 105 °C for 12.0 h. Then the MgBO₂(OH) powder was transferred into a horizontal tube furnace, heated (1.0–2.5 °C min⁻¹) to 650–700 °C

and kept under isothermal condition for 2.0–4.0 h. After calcination, the product was cooled down to room temperature naturally. For comparison, the MgBO₂(OH) nanowhiskers hydrothermal synthesized at 140 °C for 18 h were employed as the 1D precursors for the thermal conversion, with other conditions unchanged.

The structure of the sample was identified by the X-ray powder diffractometer (XRD, D8-Advance, Bruker, Germany) using Cu K α radiation ($\lambda = 1.54178$ Å) and a fixed power source (40.0 kV, 40.0 mA). The morphology and the microstructure of the sample were examined by a field emission scanning electron microscopy (FESEM, JSM 7401F, JEOL, Japan) and by a high-resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL, Japan). The composition of the sample was identified by an X-ray energy dispersive spectrometer (EDS, EDAX Genesis 2000, EDAX, USA). The thermal decomposition behavior of the sample was detected by a thermo-gravimetric analyzer (TGA, Netzsch STA 409C, Germany), carried out in dynamic air with a heating rate of 10.0 °C min⁻¹. The distributions of length, diameter and aspect ratio of the nanowhiskers were estimated by direct measuring about 200 particles from the typical FESEM images taken at 1.0 kV.

3. Results and discussion

Fig. 1 shows the TG-DTG curves of the MgBO₂(OH) nanowhiskers, which were hydrothermally synthesized with a length of $0.5-3.0 \,\mu\text{m}$ and a diameter of $20.0-50.0 \,\text{nm}$ (Fig. S1) in advance. The sample weight decreased at a comparatively slow rate at temperature below 470 °C, at a faster rate in the temperature range of 470-620 °C, and kept almost constant at temperature above 620 °C. The DTG data showed that there was a gradual increase tendency below 470°C and a sharp peak within the temperature range of 470–620 °C, which might be connected with the elimination of the physically absorbed water and the structural water, respectively, akin to the characteristics of some other borates [46]. The weight loss between 470 and 620 °C was 10.3%, quite similar to the theoretical weight loss (10.7%) for the conversion of MgBO₂(OH) to Mg₂B₂O₅: $2MgBO_2(OH)(s) \rightarrow$ $Mg_2B_2O_5(s)+H_2O(g)$. It was noticed that the final decomposition temperature of the MgBO₂(OH) nanowhiskers (620 °C) was lower than that of the natural szaibelyite (MgBO₂(OH), 700 °C) [46], which might be attributed to the reduction of the particle size. In addition, the DTA curve (Fig. S2) indicated a remarkable exothermic peak at approx 664 °C, corresponding to the recrystallization of $Mg_2B_2O_5$ [46,47].

Effects of the temperature on the composition and morphology of the calcined products at a heating rate of $10.0 \,^{\circ}\text{Cmin}^{-1}$ are shown in Figs. 2 and 3, respectively. As shown in Fig. 2,



Fig. 1. TG-DTG curves of the MgBO₂(OH) nanowhiskers.



Fig. 2. Effect of temperature on the XRD patterns of the calcined products temperature (°C): a—no calcination, b—500, c—620, d—650, e—700, f—850; **\frac{1}{3}**: MgBO₂(OH), **\frac{1}{3}**: Mg₂B₂O₅, \overrightarrow{V} : Mg₃B₂O₆.



Fig. 3. Effect of temperature on the morphology of the products temperature (°C): a, a_1 —500, b, b_1 —620, c, c_1 —700, d, d_1 —850; heating rate (°C min⁻¹): 10.0; time (h): 2.0.

MgBO₂(OH) with poor crystallinity appeared at 500 °C and disappeared at 650 °C; triclinic Mg₂B₂O₅ (PDF No. 73-2232) with poor crystallinity occurred at 620 °C and the crystallinity was improved as the temperature increased up to 850 °C; some of the Mg₂B₂O₅ was further converted to orthorhombic Mg₃B₂O₆ (PDF



Fig. 4. Effect of heating rate on the morphology of the products heating rate (°C min⁻¹): a=10.0, b=5.5, c=2.5, d=1.0; temperature (°C): 700; time (h): 2.0.



Fig. 5. TEM image (a), SAED pattern (b) and HRTEM image (c) of the $Mg_2B_2O_5$ nanowhiskers synthesized via the normal heating procedure.

No. 38-1475) and amorphous B_2O_3 at $850 \,^{\circ}C$: $3Mg_2B_2O_5(s) \rightarrow 2Mg_3B_2O_6(s)+B_2O_3(s)$.

Fig. 3a–d shows that more granular particles occurred with the increase in temperature from 500 to 850 °C. Porous nanowhiskers appeared at 620 °C (Fig. 3b₁), and the pores originated from dehydration became much fewer at 700 °C (Fig. 3c₁) and finally disappeared at 850 °C (Fig. 3d₁). Since a relatively low temperature was favorable for the morphology preservation and the recrystallization of $Mg_2B_2O_5$ might cause shrinkage of the pores and improvement of the crystallinity, the calcination temperature should be controlled within 650–700 °C to produce pure phase $Mg_2B_2O_5$ nanowhiskers with uniform morphology, fewer pores and higher crystallinity.

Effect of the heating rate on the morphology of the calcined products formed at 700 °C is shown in Fig. 4. The decrease of the heating rate was favorable for the formation of nanowhiskers with high aspect ratio. With the decrease of the heating rate from 10.0

to $1.0 \,^{\circ}\text{C}\,\text{min}^{-1}$, the average length of the nanowhiskers changed approx. from 350 to 690 nm and the diameter from 65 to 25 nm, leading to the increase in the average aspect ratio approx. from 5 to 28. These results showed that the gradual dehydration of MgBO₂(OH) nanowhiskers at slower heating rate was favorable for the preservation of the 1D morphology.

Fig. 5 shows the typical TEM image, SAED pattern and the HRTEM image of the $Mg_2B_2O_5$ nanowhiskers formed at 650 °C with a heating rate of 1.0 °C min⁻¹. The observed mesopores with a typical diameter of 2–5 nm (Fig. 5a) indicated that the heating procedure still needed to be modified to produce $Mg_2B_2O_5$ nanowhiskers with fewer pores and higher crystallinity. The SAED pattern in Fig. 5b recorded from the [$\bar{1}00$] zone axis could be indexed as the triclinic $Mg_2B_2O_5$ [36,48], in accordance with XRD characterization results (Fig. 2d). The SAED pattern also revealed that the axial direction of the nanowhiskers was not only parallel to the (020) plane but also perpendicular to the (002) plane, indicating the preferential growth of the nanowhiskers along the *c*-axis. Two interplanar spacings, 0.404 and 0.223 nm, were detected from the legible lattice fringes in Fig. 5c, which were

quite similar to those of the $(\bar{1}20)$ and $(\bar{2}11)$ planes of Mg₂B₂O₅, respectively, reconfirming the preferential growth of the Mg₂B₂O₅ nanowhiskers along the *c*-axis.

The above work showed that lower temperature and heating rate were favorable for the formation of the Mg₂B₂O₅ nanowhiskers with high aspect ratio, whereas a higher temperature was favorable for the formation of the nanowhiskers with fewer pores and improved crystallinity. A specific heating procedure was thus designed based on the recrystallization of Mg2B2O5 at approx. 664 °C. MgBO₂(OH) nanowhiskers were first heated (1.0 °C min⁻¹) to 650 °C, kept under isothermal condition for 2.0 h to retain the 1D morphology, then heated $(1.0 \degree C \min^{-1})$ to 700 °C and kept in isothermal state for another 2.0 h to recrystallize. Fig. 6 shows the morphology and the SAED pattern of the calcined product via the specific heating procedure. The Mg₂B₂O₅ nanowhiskers had a diameter of 15.0–45.0 nm and a length of 0.2-2.0 µm, and the EDS analysis indicated that the nanowhiskers were composed of 36.8% of Mg, 12.7% of B and 50.5% of O, quite consistent with the theoretical composition of Mg₂B₂O₅. The explicit lattice fringes along the longitudinal





Fig. 7. Run-through formation and improvement of the morphology and crystallinity of Mg₂B₂O₅ nanowhiskers via the thermal conversion route.

direction of the nanowhiskers were detected with the interplanar spacing (0.568 nm) consistent with that (0.566 nm) of the ($\overline{1}10$) planes for the triclinic Mg₂B₂O₅, indicating the preferential growth of the nanowhiskers parallel to the *c*-axis. Hence, uniform Mg₂B₂O₅ nanowhiskers with improved crystal-linity and fewer pores were formed via the specific heating procedure.

Run-through formation and improvement of the morphology and crystallinity of Mg₂B₂O₅ nanowhiskers via the thermal conversion route are illustrated in Fig. 7. Crystalline MgBO₂(OH) nanowhiskers were obtained by hydrothermal treatment of amorphous irregular Mg₇B₄O₁₃·7H₂O nanoparticles [45], and the subsequent thermal conversion of the nanowhiskers at appropriate temperature with relatively slow heating rate led to the mesoporous 1D $Mg_2B_2O_5$. Distribution of length, diameter as well as the aspect ratio of the hydrothermal and calcined products (Fig. S3) demonstrated that the dehydration of MgBO₂(OH) nanowhiskers and subsequent recrystallization (650-700 °C) resulted in somewhat shorter and thinner Mg₂B₂O₅ nanowhiskers with lower aspect ratio as a result of the shrinkage of the mesopores. It is worth noting that, since hydrothermal technique was introduced into the synthesis of Mg₂B₂O₅ 1D nanostructures, the advantages of hydrothermal processing such as energy saving (200-350 °C of decrease in reaction temperature) and moderate experimental conditions (easy control and no need of any catalyst) were well transmitted down via the appropriate selection of calcination temperature, precise control of the heating rate and procedure, compared with 1D nanostructured Mg₂B₂O₅, derived from other traditional methods [36-41].

In addition to the parameters in course of thermal conversion, the hydrothermal procedure [49] determined the 1D morphology of the MgBO₂(OH) nanowhiskers and could further influence the morphology of the final calcined Mg₂B₂O₅ nanowhiskers. Hydrothermal conditions are favorable for the formation of the unique crystal structure containing water in lattice; the unique structure can contribute to porous structure by dehydration and the active porous whiskers can finally form high-crystallinity nanowhiskers via recrystallization. As a consequence, short MgBO₂(OH) nanowhiskers obtained under ordinary hydrothermal conditions (140 °C,18 h) readily resulted in short Mg₂B₂O₅ nanowhiskers, as shown in Fig. S4.

As indicated above, Mg₂B₂O₅ nanowhiskers with uniform morphology and improved crystallinity could be formed via the specific heating procedure designed according to the recrystallization phenomenon existing in the thermal conversion of the MgBO₂(OH) nanowhiskers in which the 1D morphology was firstly well preserved during dehydration at appropriate temperature with relatively slow heating rate and the crystallinity was then greatly improved via the recrystallization. On the other hand, excessively high calcination temperature and fast heating rate might accelerate the coalescence rather than shrinkage of the mesopores, leading to severe deformation and even rupture of the calcined nanowhiskers.

4. Conclusions

Mg₂B₂O₅ nanowhiskers with a diameter of 15.0-45.0 nm, a length of 0.2–2.0 µm and a preferential growth along the *c*-axis were synthesized via a facile thermal conversion of MgBO₂(OH) nanowhiskers at a relatively low temperature as 650-700 °C for 2.0-4.0 h. Appropriate calcination temperature (650-700 °C) and relatively slow heating rate (1.0–2.5 °C min⁻¹) were favorable for the preservation of the 1D morphology and improvement of the crystallinity of Mg₂B₂O₅ nanowhiskers. A specific heating procedure was developed to produce Mg₂B₂O₅ nanowhiskers with uniform morphology, improved crystallinity and fewer pores, by which the MgBO₂(OH) nanowhiskers were first heated (1.0 °C min⁻¹) to 650 °C and kept under isothermal condition for 2.0 h to retain the 1D morphology, thereafter heated to 700 °C $(1.0 \,^{\circ}\text{Cmin}^{-1})$ and kept in isothermal state for another 2.0 h of recrystallization. Thus, the preservation of 1D morphology and improvement of crystallinity could be achieved individually and successively in course of the dehydration of the 1D hydrated precursors. Also, the designed specific heating procedure to reduce the mesopores and deformation could also benefit synthesis of other 1D nanostructures via the wet chemistry-based thermal conversion route.

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Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcrysgro.2008.06.072.

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