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SYNTHESIS OF ALUMINIUM BORATE WHISKERS THROUGH WET MOLTEN SALT METHOD

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Aluminium borate ($Al_4B_2O_9$) whiskers were successfully synthesized by the wet molten salt method at 800°C through control the aluminum/boron atomic ratio and synthesis temperature. The as-received $Al_4B_2O_9$ whiskers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermal analysis. A solution-liquid-solid (SLS) mechanism was proposed for the growth mechanism of the whiskers on the basis of the experimental phenomena and the TG-DSC data of the mixed raw materials.

INTRODUCTION

Borate whiskers as one of the one-dimensional nanostructure materials have received extensive attention due to their interesting mechanical, electrical and optical properties [1-5]. Among them, aluminum borate ($Al_4B_2O_9$) whiskers are excellent and cheap one-dimensional ceramic materials due to the unique physical properties and widely potential applications as compared with bulk materials. In addition, aluminum borate whiskers are a kind of nonpoisonous, harmless and pollution-free natural product. Because of its excellent properties and broad application prospects, some synthesis methods have been developed such as thermal evaporation [6], sol-gel [7-8], chemical vapor deposition [9] and high temperature molten salt method [10]. For example, Elssfah et al. [11] obtained single-crystalline $Al_4B_2O_9$ nanowires by a direct calcination of $Na_2B_4O_7 \cdot 10H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ at 850°C, but the borax is toxic and not conductive to environmental. Tao et al. [12] obtained single-crystalline $Al_4B_2O_9$ nanowires by a one-step combustion method at 900°C, but the synthesis temperature is a little high.

Among these methods, the high temperature molten salt method could be considered as a simple way, however, high temperature molten salt method belongs to solid reaction, it requires relatively high calcination temperature in the synthesis process, at the same time, it could cause inhomogeneous products easily, and the reaction cycle is too long to application.

In this paper, we report a simple route to synthesize the $Al_4B_2O_9$ whiskers without using any metal-catalyst at the low temperature of 800°C, we used the liquid phase method replace the solid phase method, and the reaction efficiency could be greatly increased.

EXPERIMENTAL

Raw materials

The raw materials used in this study were boric acid (H_3BO_3), aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$), sodium hydroxide (NaOH) and sodium chloride (NaCl). All materials were analytically reagents grade.

Synthesis and analysis

Appropriate amount of H_3BO_3 and NaCl were weighted and dissolved with 400 ml distilled water, and then different amount of $AlCl_3 \cdot 6H_2O$ was added into the above solution and kept the molar ratio between H_3BO_3 and $AlCl_3$ at 1, 1.5 and 2, respectively. When they totally dissolved, NaOH was added with continuous strong stirring (500 r/min) by electromagnetic stirrer, and a large amount of white precipitate was obtained. In the reaction process, the temperature of solution was kept at 80°C by super thermostatic water bath and the range kept in ± 1°C. After 2 h for reaction, the above precipitate was calcined at a certain temperature (600, 800, 1000°C) for 2 h in the air, and then washed by ethyl alcohol and dried at 120°C for 12 h. The process flow chart as follows.

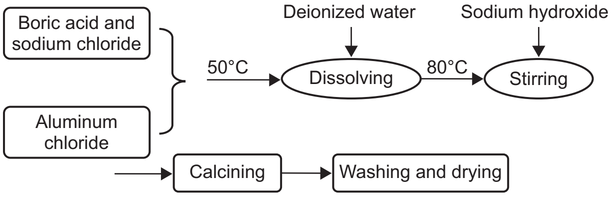
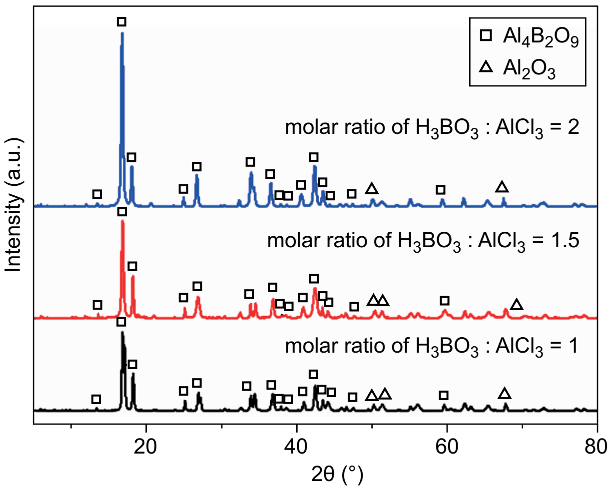


Figure 1. Process flow chart for preparing aluminium borate ($Al_4B_2O_9$) whiskers.

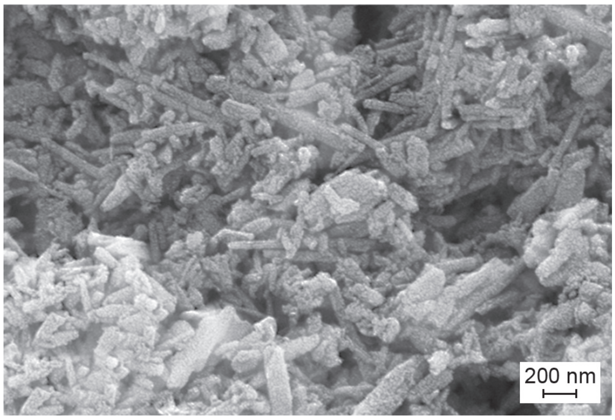
The phase compositions of obtained powders were determined with X-ray powder diffraction (XRD). The diffraction patterns were recorded on a Philips PW3040/60 X-ray diffractometer using a Cu Kα (λ = = 0.154056 nm) radiation source. The XRD scans were made from 5° to 80° in 2θ with a step rate was 5° per minute. The morphologies of the obtanied precipitation and $Al_4B_2O_9$ were observed with field emission scanning electron microscopy (FE-SEM, Zeiss-ultra plus), and the changes in mass and exothermic absorption in the heating were investigated by the thermogravimetric analysis and differential scanning calorimetry (TG-DSC).

RESULTS AND DISCUSSION

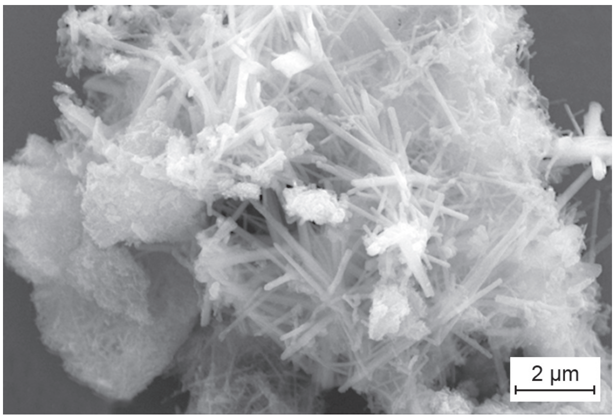
Figure 2 shows the XRD patterns and the SEM micrographs of the samples obtained by calcining the precipitate at 800°C for 2 h, and the molar ratio of $H_3BO_3/AlCl_3$ is 1, 1.5 and 2, respectively. It is easily to see from those XRD patterns (Figure 2a), $Al_4B_2O_9$ is the main phase, and a very small amount of Al_2O_3 also could be observed. At the same time, it could be seen that the crystallinity of the $Al_4B_2O_9$ phase increased with the increasing of the amount of boric acid addition. When the molar ratio of $H_3BO_3/AlCl_3$ was 2, the intensity of the diffraction peak was strongest; it means that the crystallization of the phase was best. The fitting crystalline parameters are a = 1.47460 nm, b = 1.52680 nm and c = 0.55570 nm, $\alpha = \beta = \gamma$ = 90° (reference code: 00-029-0010). It could be understood from the SEM micrographs that the molar ratio of $H_3BO_3/AlCl_3$ made a difference in $Al_4B_2O_9$ whiskers morphology (Figures 2b-d). When the molar ratio of $H_3BO_3/AlCl_3$ was 1, the whiskers showed a shorter and thicker shape, and the growth of the whiskers seemed to be messy and wide range of sizes (see Figure 2b). When the molar ratio increased to 1.5, uniform $Al_4B_2O_9$ whiskers have obtained with which the length-diameter ratio of 15 (see Figure 2c). However, it



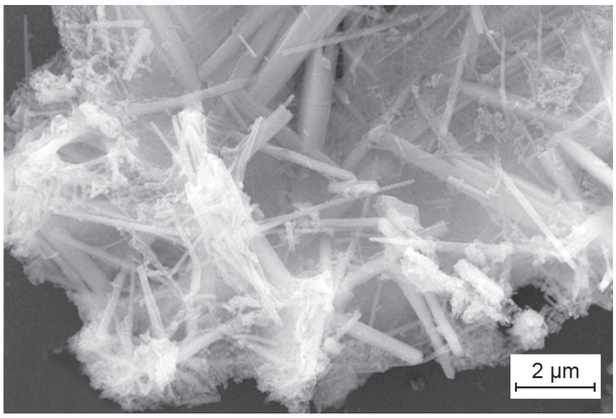
a) XRD patterns



b) molar ratio 1:1



c) molar ratio 1.5:1



d) molar ratio 2:1

Figure 2. XRD patterns (a) and SEM micrographs of samples obtained by various $H_3BO_3/AlCl_3$ molar ratio: b) 1:1, c) 1.5:1 and d) 2:1.

is worth to note that, the $Al_4B_2O_9$ whiskers not became more tenuous further but coarse when the molar ratio increased to 2, and the length-diameter ratio decreased to 10, the main reason might be that the excess of boron oxide increased the resistance of alumina movement, and alumina accumulated in the radial region of the whiskers, which resulted in radial growth and effected the length-diameter radio of the whiskers. It means that the growth of $Al_4B_2O_9$ whiskers was strictly restrained by the molar ratio of $H_3BO_3/AlCl_3$. Compared with the above SEM micrographs, the molar ratio of 1.5 was considered as a suitable for the growing of the whiskers.

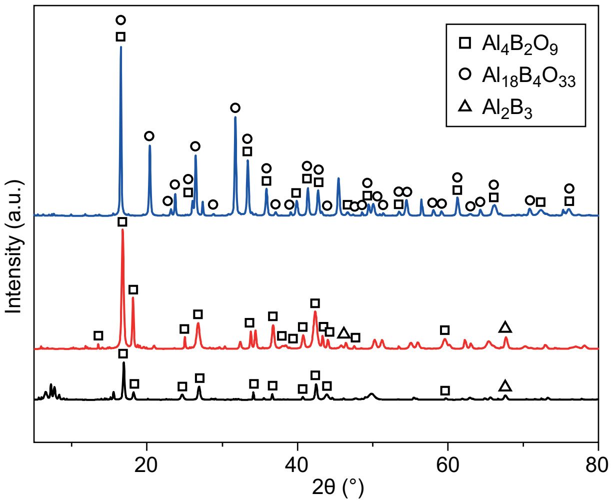
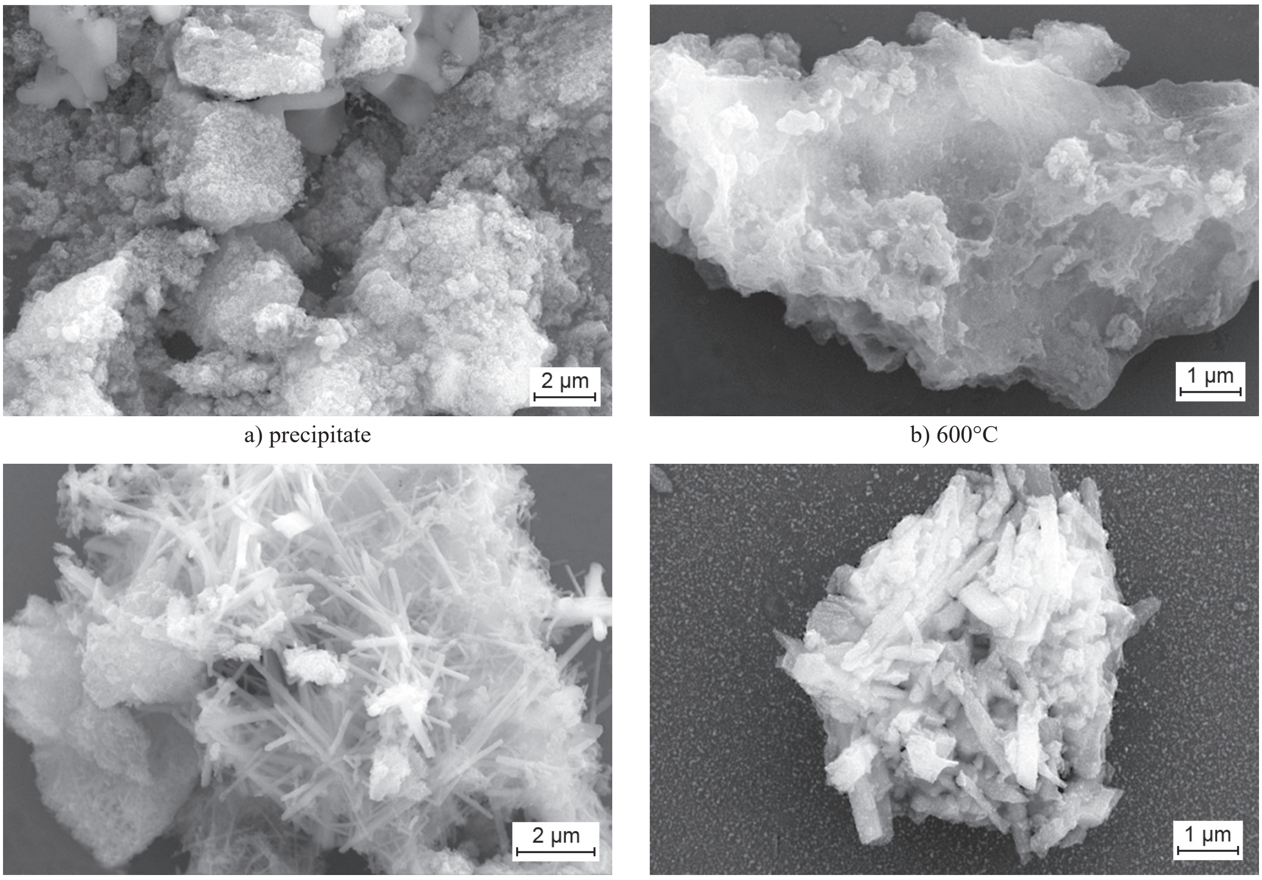


Figure 3. XRD patterns of samples obtained by calcning the precipitate at different temperature.

Figure 3 shows XRD patterns of the samples obtained by calcining the precipitate at various heating temperature for 2 h, prepared with the molar ratio of $H_3BO_3/AlCl_3$ is 1.5. Form the Figure 3, it could be seen that the crystallinity of the whiskers became strong with the increasing of the heating temperature. At the same time, the heating temperature also affected the phase composition. When the heating temperature increased to 1000°C, besides the $Al_4B_2O_9$ phase, $Al_{18}B_4O_{33}$ was also formed. At this point, the product was not a single phase. The Figure 3a and b patterns can be indexed as orthorhombic $Al_4B_2O_9$. The fitting crystalline parameters are $a = 1.47460$ nm, $b = 1.52680$ nm and $c = 0.55570$ nm, $\alpha = \beta = \gamma = 90°$ (reference code: 00-029-0010). For pattern (c), $Al_{18}B_4O_{33}$ phase is also orthorhombic, the fitting crystalline parameters are $a = 0.76874$ nm, $b = 1.50127$ nm and $c = 0.56643$ nm, $\alpha = \beta = \gamma = 90°$ (reference code: 00-032-0003).



a) precipitate b) 600°C c) 800°C d) 1000°C

Figure 4. SEM micrographs of the precipitate and samples obtained at various heating temperature: a) precipitate, b) 600°C, c) 800°C and d) 1000°C.

Figure 4 shows the SEM micrographs of the precipitate and samples obtained by heating the precipitate at various heating temperature for 2 h. The morphology of the samples was influenced by the heating temperature obviously. The whiskers were not found in the precipitate (see the Figure 4a) and the samples obtained by heating the precipitate at 600°C for 2 h (Figure 4b). However, it was formed when the heating temperature increased to 800°C (see the Figure 4c). The whiskers were very straight with diameter ranging from 100 to 200 nm and about 2 μm at length when heated at 800°C. However, it became shorter when the heating temperature raised to 1000°C.

From the above analysis we know that the diameter of whiskers increased with the increasing of temperature after reaching a certain temperature. The reason for this phenomenon is that at a high temperature, the vapor pressure of the product was large, and the probability of collisions between atoms was high, so the initial crystal nucleus grown easily, and when it began to grow subsequently, the size of the crystal nucleus was so large that the diameter of the whiskers increased [13].

According to the previous research results, the minimum temperature for forming the $Al_4B_2O_9$ whiskers was about 780°C [12], and in the case of using the tradition method, the heating temperature was about 900°C [12] or even 1000°C [14]. However, it was decreased to 800°C by using the wet molten salt method in this study, which was largely saved the energy.

Figure 5 shows the differential scanning calorimeter (DSC) and Thermogravimetry (TG) curves of the precipitate by the blue and the red line, respectively. There are two endothermic peaks and one exothermic peak on the DSC curves, corresponding to the temperature of 114.3°C 270.3°C and 798.8°C, respectively. The endothermic peaks were attributed to the interlayer water removing of H_3BO_3 and $Al(OH)_3$ decomposing, and the corresponding reaction equations were as follow:

$$2H_3BO_3\ (s) \rightarrow B_2O_3\ (s) + 3H_2O\ (l) \qquad (1)$$

$$2Al(OH)_3\ (s) \rightarrow Al_2O_3\ (s) + 3H_2O\ (l) \qquad (2)$$

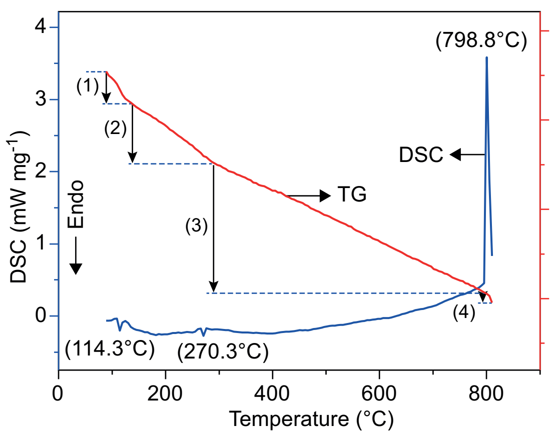


Figure 5. DSC and TG curves of the precipitate.

On the other hand, the exothermic peak at 798.8°C was attributed to the reaction between B_2O_3 and Al_2O_3, and the reaction equation was as follow:

$$2Al_2O_3\ (s) + B_2O_3\ (l) \rightarrow Al_4B_2O_9\ (l) \qquad (3)$$

In the process of whiskers growth, it is a key issue to induce 1D crystal growth in a controlled manner. At this point, many methods have been developed, such as the metal-catalyst-assisted vapor-liquid-solid (VLS) mechanism [15], the vapor-solid (VS) mechanism, and the template-assisted (TA) mechanism. Among these, the VLS mechanism is the most extensively used due to its simplicity and versatility. However, no metal-catalyst or templates were used in this study, and no tips were found at the end of the whiskers, which were considered as the mark of the VLS mechanism [16-18]. Thus, the VLS mechanism was not considered to be applied to the growth of as-prepared $Al_4B_2O_9$ whiskers.

According to the SEM micrographs and thermal analysis stated above, the formation of $Al_4B_2O_9$ could be divided into two parts in this study. The first part was the decomposition process of the initial reaction material, and the second part was that the formation and growth of whiskers nucleation. Therefore, we believe that the solution-liquid-solid (SLS) mechanism [19] is responsible for the whiskers' growth. The SLS mechanism is also called dissolution-precipitation mechanism, it means that the raw material was dissolved first and then decomposed into oxides, and then combined to form the target product, finally separated out after reaching saturation. The $Al_4B_2O_9$ whiskers were synthesized by heating the precipitate in air conditions. With the temperature increasing, H_3BO_3 first decomposed into B_2O_3 at about 250°C, and then melted at about 450°C according to phase diagram [20]. The starting liquid droplet acted a catalyst as called self-catalysts [21]. The liquid droplet might continuously dissolve the Al-contained constituent to form the Al-B-O cluster with the aid of the cosolvent. When the liquid droplets became saturate, $Al_4B_2O_9$ crystals would begin to grow from the droplets. After continuous dissolved, and the formation of the nanoscale droplets and the $Al_4B_2O_9$ crystallized at the temperature lower than its melting point, providing the necessary conditions demanded by the SLS growth mechanism.

CONCLUSIONS

In conclusion, $Al_4B_2O_9$ whiskers were synthesized by a wet molten salt method at different ratio of $H_3BO_3/AlCl_3$ and calcined temperature for the first time. XRD and SEM analysis showed that the length-diameter ratio of the whiskers was desired when the $H_3BO_3/AlCl_3$ atomic ratio is 1.5 and calcined temperature is 800°C. At the same time, a solution-liquid-solid (SLS) mechanism was proposed for the growth mechanism of the whiskers.

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