Bull. Mater. Sci., Vol. 34, No. 6, October 2011, pp. 1197–1199. © Indian Academy of Sciences.

Synthesis of thorn-like $Ca_2B_2O_5 \cdot H_2O$ by hydrothermal method

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MS received 14 November 2010; revised 4 March 2011

Abstract. Thorn-like polycrystalline $Ca_2B_2O_5 \cdot H_2O$ microspheres with nano-sized slices were synthesized using boric acid and calcium hydroxide as reactants by a facile catalyst-free hydrothermal method at low temperature. The products were characterized by means of X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The XRD pattern reveals that the $Ca_2B_2O_5 \cdot H_2O$ is a monoclinic phase polycrystalline with cell parameters $a = 0{\cdot}6702$, $b = 0{\cdot}5419$ and $c = 0{\cdot}3558$ nm. SEM also reveals that the monoclinic phase polycrystalline are thorn-like microspheres composed of many flakes with an average thickness of <100 nm. Possible reaction and growth mechanism were also discussed.

Keywords. Nanomaterials; calcium borate; synthesis.

1. Introduction

Borate compounds have considerable mineralogical and industrial importance. Metal borates are remarkable compounds in ceramic materials with excellent mechanical properties, good chemical inertness, high stability under high temperature, lightweight, and low thermal expansion coefficients (Ma *et al* 2002; Zhu *et al* 2003; Tao *et al* 2007; Tao and Li 2008; Li *et al* 2009). Calcium borate has great potential for applications in ceramic coatings, glass fibres, dielectric devices, ultraviolet (UV) light sources, light emission diodes (LEDs), and luminescent phosphors (Hao and Gao 2004; Ishii *et al* 2006; Kityk *et al* 2006; Guo *et al* 2009; Santos *et al* 2009). There are many kinds of hydrated calcium borates, both natural and synthetic. Some of them are useful chemical industrial materials, which are used in glass, pottery, and porcelain enamel industries (Zhi *et al* 2006). Especially in alkali glass industry, calcium borate is used to replace boric acid and nature ascharite as it could reduce volatile ratio of boron oxide for producing glass of enhanced tensile strength and improved quality. In addition, its use helped in decreased environmental pollution (Geng 2006; Cao *et al* 2007; Li *et al* 2007).

Hydrated calcium borates are still in the research and development stage, nowadays (Wang and Feng 2003; Zhao *et al* 2004; Bao *et al* 2010). Several techniques have been developed to synthesize bulk hydrated calcium borate materials, such as solid state reactions between boric acid (boron oxide) and calcium oxide (carbonates), hydrothermal and microemulsion methods. However, hydrated calcium borates produced by these methods were found to have large particle size and low specific area that limit their applications (Zhao *et al* 2004), and to our knowledge, nanostructure of hydrated calcium borate seldom appeared in literature.

In this study, thorn-like polycrystalline microspheres with nano-sized slices of $Ca_2B_2O_5 \cdot H_2O$ were prepared using a facile catalyst-free hydrothermal method by treating boric acid and calcium hydroxide at 90°C for 24 h. Possible reaction and growth mechanism are also discussed.

2. Experimental

2.1 *Materials*

All reagents were of analytical grade and used without further purification. Calcium hydroxide, $Ca(OH)_2$ (mass fraction ≥95·0%, Sinopharm Chemical Reagent Co., Ltd) and boric acid, H_3BO_3 (mass fraction ≥99·5%, Sinopharm Chemical Reagent Co., Ltd) were also used.

2.2 *Preparation of thorn-like $Ca_2B_2O_5 \cdot H_2O$*

In a typical procedure, 7·42 g of $Ca(OH)_2$, 6·19 g of H_3BO_3 and 400 ml of distilled water were put into a stainless autoclave of 600-ml capacity, sealed tightly and heated at 90°C for 24 h. After cooling to room temperature, the product was washed for several times with distilled water and absolute ethanol. 9·59 g gray $Ca_2B_2O_5 \cdot H_2O$ powders were obtained after drying in a vacuum at 80°C for 12 h. The yield of $Ca_2B_2O_5 \cdot H_2O$ based on calcium was about 95·86 wt%.

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2.3 *Characterization*

The as-prepared powders were characterized by X-ray powder diffraction (XRD) on a XD-5A diffractometer using Cu Kα radiation (Shimadzu Corporation, $\lambda = 1{\cdot}5406$ Å, 2θ scope: 10°∼55°, 30 kV, 20 mA) and scanning electron microscopy (SEM) using a JSM-5510LV, JEOL LTD scanning electron microscope.

3. Results and discussion

Figure 1 shows XRD pattern of the $Ca_2B_2O_5{\cdot}H_2O$ sample. All peaks (provided in table 1) can be indexed as monoclinic phase, $Ca_2B_2O_5{\cdot}H_2O$, with lattice constants of $a = 0{\cdot}6702$ nm, $b = 0{\cdot}5419$ nm and $c = 0{\cdot}3558$ nm, which are in good agreement with the values reported in the literature (JCPDS No. 51-1530, $a = 0{\cdot}6722$ nm, $b = 0{\cdot}5437$ nm, $c = 0{\cdot}3555$ nm). No diffraction peaks of impurity phases such as CaO and B_2O_3 were detected in the XRD pattern. Table 1 is the datum from XRD patterns of the $Ca_2B_2O_5{\cdot}H_2O$ sample and JCPDS No. 51-1530 with a standard deviation of about 0·2°, which showed the product is pure monoclinic phase, $Ca_2B_2O_5{\cdot}H_2O$.

Figure 2 is SEM images of $Ca_2B_2O_5{\cdot}H_2O$ sample. We can clearly see that the as-prepared $Ca_2B_2O_5{\cdot}H_2O$ having thorn-like microspheres morphology (figures 2a–b). Closer observation in larger magnification shows that these microspheres are constructed with many flakes with a thickness of <100 nm (figures 2c–d).

The hydrothermal reactions occurred as follows. First, after dissolving in distilled water, two molecules of H_3BO_3 formed and then it generated into one molecule, $(H–O)_2BOB(O–H)_2{\cdot}H_2O$. Second, the newly generated molecule, $(H–O)_2BOB(O–H)_2{\cdot}H_2O$ reacted with two molecules of $Ca(OH)_2$ to form a $Ca_2B_2O_5{\cdot}H_2O$ molecule and four molecules of water.

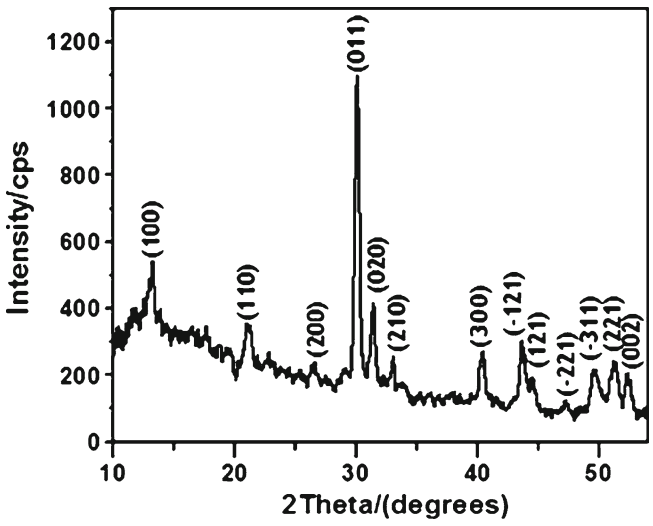

Figure 1. XRD pattern of as-prepared thorn-like $Ca_2B_2O_5{\cdot}H_2O$ microspheres sample synthesized at 90°C for 24 h.

Table 1. Datum from XRD pattern and JCPDS No. 51-1530.

No.	*h k l*	*d* value from XRD	*d* value from JCPDS No. 51-1530
1	100	6·6840	6·7300
2	110	4·2150	4·2300
3	200	3·3718	3·3540
4	011	2·9648	2·9750
5	210	2·8455	2·8500
6	020	2·7074	2·7210
7	300	2·2364	2·2370
8	−121	2·0747	2·0750
9	121	2·0356	2·0360
10	−221	1·8409	1·8420
11	−311	1·8327	1·8260
12	221	1·7892	1·7760
13	002	1·7816	1·7900
14	130	1·7479	1·7500

$$2H_3BO_3 = (H–O)_2BOB(O–H)_2{\cdot}H_2O, \quad (1)$$

$$2Ca(OH)_2 + (H–O)_2BOB(O–H)_2{\cdot}H_2O = Ca_2B_2O_5{\cdot}H_2O \downarrow + 4H_2O. \quad (2)$$

Figure 3 schematically illustrates the growth processes of the thorn-like $Ca_2B_2O_5{\cdot}H_2O$ polycrystalline microspheres. At the early stage of growth, $Ca(OH)_2$ is hard to ionize into Ca^{2+} and OH^- due to the low solubility of $Ca(OH)_2$ in water. So, in the precursor solution, $Ca(OH)_2$ is in suspended precipitates state (figure 3a). The heat treatment at 90°C further lowered the solubility of $Ca(OH)_2$, resulting in more precipitates (Bao *et al* 2010). The $Ca(OH)_2$ precipitates offered energy-favoured sites for nucleation and growth of the thorn-like $Ca_2B_2O_5{\cdot}H_2O$ microspheres. While H_3BO_3, which was dissolved in the aqueous solution, reacted with Ca^+ ionized from $Ca(OH)_2$ to form $Ca_2B_2O_5{\cdot}H_2O$ at the solid–liquid (S–L) interface (figure 3b). $Ca_2B_2O_5{\cdot}H_2O$ crystals stopped growing until no more Ca^+ ionized from the encapsulated $Ca(OH)_2$.

The nuclei aggregated together through intermolecular van der Waals force to form relatively larger structures, such as nanoclusters or nanocrystals. In general, in order to lower the surface energy, nanocrystals tended to agglomerate to decrease their exposed surfaces. The same types of crystal planes then aligned with each other, and a coherent interface formed to minimize the interface stain energy (Bao *et al* 2010). Therefore, the aggregated nuclei (nanoclusters or nanocrystals) attached to each other (figure 3c), and finally three dimensional (3D) structures formed due to the anisotropic nature of $Ca_2B_2O_5{\cdot}H_2O$ crystal.

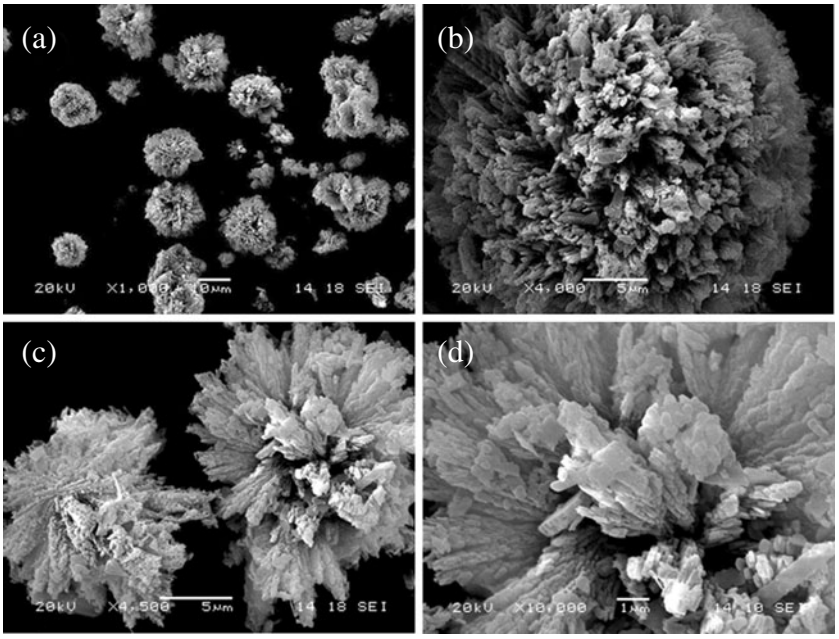

Figure 2. SEM images of thorn-like $Ca_2B_2O_5{\cdot}H_2O$ microspheres sample synthesized at 90°C for 24 h (scale bars (**a**) 10 μm, (**b**) 5 μm, (**c**) 5 μm and (**d**) 1 μm).

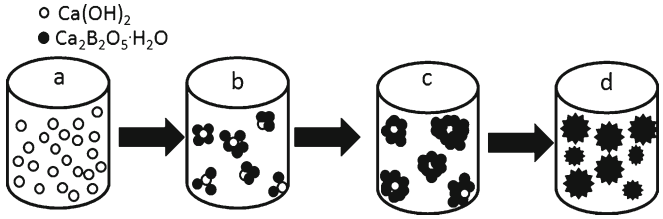

Figure 3. Schematic illustration of growth processes of thorn-like $Ca_2B_2O_5{\cdot}H_2O$ microspheres.

4. Conclusions

In summary, thorn-like polycrystalline $Ca_2B_2O_5{\cdot}H_2O$ microspheres with nano-sized slices were synthesized using $Ca(OH)_2$ and H_3BO_3 as reagents by hydrothermal method at low temperature. The microspheres composed of many flakes with an average thickness of $<$100 nm. Solid–liquid (S–L) growth mechanism was proposed to explain growth of the thorn-like polycrystalline $Ca_2B_2O_5{\cdot}H_2O$ microspheres.

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