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Atom-Economic Reaction: Preparation and Mechanism of Nano-SrB_2O_4 by Solid-State Reaction

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Nano-SrB_2O_4 powder was prepared by solid-state reaction at room temperature followed by a subsequent calcination process. The highly productive method which can be operated easily confirms to the Green-chemistry principles. The XRD patters demonstrate that the component of the as-obtained sample is SrB_2O_4 after calcination at 600˚*C. Differential thermal analysis and thermogravimetriy (DTA/TG) curves suggest the process of dehydration and crystal transition from $Sr[B(OH)_4]_2$ to $SrB_2O_4{\cdot}2H_2O$. SEM image of SrB_2O_4 shows that the particles are uniform and spherical with average size of* 80 *nm in diameter. Furthermore, the mechanism of reaction was discussed. The chemical reaction of the process is assumed to be acid-base neutralization reaction. The water generated from the acid-base neutralization reaction and the release of crystal water from $Sr(OH)_2{\cdot}8H_2O$ plays an essential role in the reaction system.*

***Keywords*:** *Green-Chemistry Reaction*, *Nano-SrB_2O_4*, *Solid-State Reaction*, *Mechanism*

1. Introduction

Borates are among the most interesting and therefore the most extensively studied materials, because they show a great variety of physical properties ranging from nonlinear optical (NLO), ferroelectric to semiconducting behaviors. In addition, a boron atom may adopt triangular or tetrahedral oxygen coordination, and the BO_3 and BO_4 groups may be further linked via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets and networks, leading to rich structural chemistry [1,2].

Strontium and barium borates exhibit excellent optical properties; for instance, α-BaB_2O_4 is a new type of birefringent crystal; β-BaB_2O_4 is a nonlinear optical materials with superior performance [3]; SrB_4O_7 and SrB_6O_7 are matrix material with excellent light-emitting properties [4,5]; SrB_4O_7 is also a crystal with the multiplier effect [6]. SrB_2O_4 is also widely used in optical field [7, 8]. To date, liquid methods [9-12] have been proven to be the most commonly used techniques for the synthesis of borates. However, the liquid methods exhibit some disadvantages in some cases. For instance, the hydrothermal and ultrasonic methods generally need higher quality for equipment, and the sol-gel and microemulsion routes need complicated process. Moreover, most of the liquid methods will cause consumption of auxiliary substances. So it is desirable to develop a facile, green, and low-cost method to fabricate SrB_2O_4 products. In our present work, a new method called solid-state reaction at low temperature [13,14] has been explored to synthesize nano-SrB_2O_4. This method exhibit many advantages, such as no solvents, little pollution and highly productive, which meets the concept of green chemistry. Furthermore, the simple, green, and low-cost route may be of great significance in the synthesis of many other inorganic functional materials.

2. Materials and Methods

2.1. Preparation

Both $Sr(OH)_2{\cdot}8H_2O$ and H_3BO_3 are analytical reagents, and purchased from Tianjin Kermel chemical reagents Ltd. and Tianjin Damao reagent factory. All experiments were carried out in the deionized water. In a typical synthesis, the stoichiometric amount of $Sr(OH)_2{\cdot}8H_2O$ and H_3BO_3 (molar ratio of Sr:B is 1:2) were mixed in a mortar. Subsequently, the mixture was ground at room temperature for 30 min. Then, the solid powder transformed to wet mash. The wet samples were dried at room temperature and then calcined at 600˚C for 3 h to obtain the final product.

2.2. Characterizations

The crystal structure and composition of the products were analyzed by D8 ADVANCE X-ray Diffractomete (Bruker/Germany) with Cu Kα radiation (λ = 0.154178 nm), using an accelerating voltage of 30 kv. Powder morphology and size were characterized by JSM-7500F cold field scanning electron microscope JEOL (Japan). TG/DTA analysis was performed by TG209 F3 (NETZSCH Germany). All samples were measured at room temperature.

3. Results and Discussion

3.1. XRD Analysis of Nano-SrB_2O_4

Figure 1 shows the XRD patters of as-obtained products. When the samples was dried at room temperature, all the diffraction peaks can be well indexed to the $Sr[B(OH)_4]_2$ (JCPDS No. 74-2316), and the no diffraction peaks of impurities can be detected (**Figure 1(a)**). When the samples was calcined at 600˚C, it can be seen that the diffraction peaks of $Sr[B(OH)_4]_2$ disappeared, while all the diffraction peaks agree well with those of the pure phase of SrB_2O_4 (JCPDS No. 84-2175) (**Figure 1(b)**), indicating the formation of the SrB_2O_4 sample. The particle size can be estimated to be 85 nm according to the Scherrer equation, $D = k\lambda/\beta\cos\theta$, where k is the shape factor (0.89), λ is the x-ray wavelength (0.1542 nm), β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle, which is consistent with SEM observation (**Figure 3**).

3.2. TG-DTA Analysis

Figure 2 shows the TG-DTA analysis of as-obtained product. It can be seen from the TG curve that the weight loss of sample can be divided into two steps. In the first step, the weight loss occurs from 150˚C to 175˚C, accompanied by a sharp exothermic peak in the DTA curve at 160˚C. The weight loss can be explained by the following chemical reaction:

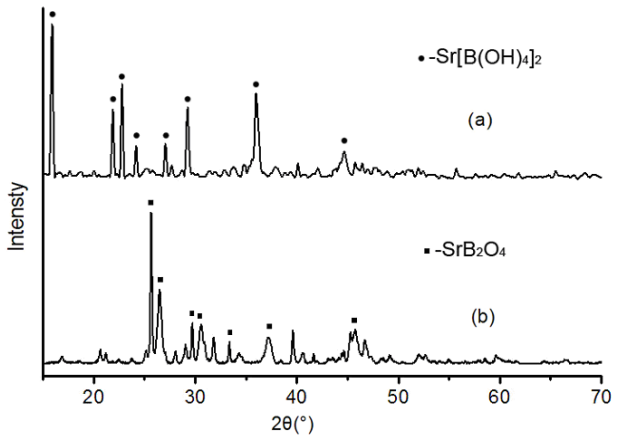

Figure 1. XRD patters of as-synthesized products (a) dried at room temperature and (b) after calcination at 600˚C.

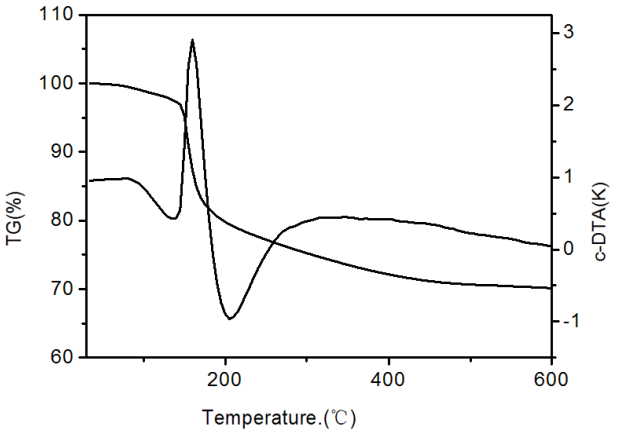

Figure 2. TG/DTA curves of $Sr[B(OH)_4]_2$.

$$Sr[B(OH)_4]_2 \rightarrow SrB_2O_4 \cdot 2H_2O + 2H_2O \quad (1)$$

The weight loss process from 150˚C to 175˚C contains the crystal transition and dehydration. The dehydration process is endothermic, and the crystal transition from $Sr[B(OH)_4]_2$ to $SrB_2O_4{\cdot}2H_2O$ is an exothermic process. As the exothermic process is dominant in the weight loss process, one can observe an exothermic peak from 150˚C to 175˚C in the DTA curve. The weight loss rate of the first step is 15.7%, which is good accordance with the theoretical value (16.0%). In the second step, the weight loss occurs from 185˚C to 545˚C, which corresponds to an endothermic peak in the DTA curve at 205˚C, which can be assigned to be a dehydration process. The weight loss can be explained by the following reaction:

$$SrB_2O_4 \cdot 2H_2O \rightarrow SrB_2O_4 + 2H_2O \quad (2)$$

SEM photograph of the powder shows that the particles are uniform and spherical with average size of 80 nm in diameter (**Figure 3**).

3.3. Chemical Reaction Mechanism

Chemical reaction motion may be as follows. As is well known, boric acid and strontium hydroxide are hard acid and hard base. As a result, the chemical reaction, in theory, should be very easy according to the Hard/Soft Acid/Base (HSAB) Principle [15]. What's more, this chemical reaction, actually, is ionic reaction in aqueous media. The water which played an essential role in chemical reaction comes not only from the released crystal water of $Sr(OH)_2{\cdot}8H_2O$ but also from the acid-base neutralization reaction reaction. Then, the pressure of grinding forced large particles rolled into small particles, meanwhile, the crystal water of $Sr(OH)_2{\cdot}8H_2O$ was re-

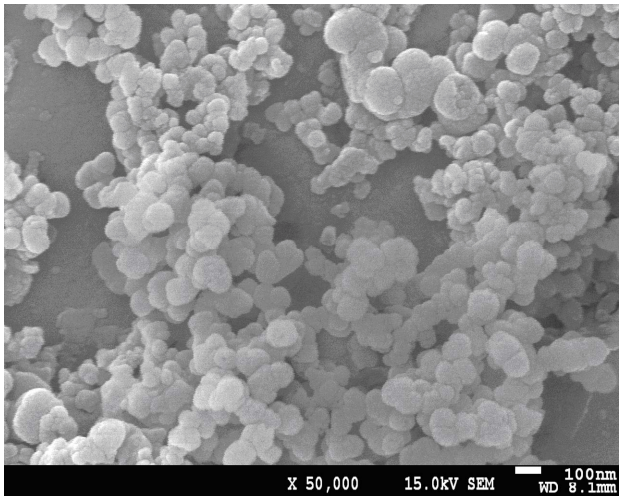

Figure 3. SEM image of Nano-SrB_2O_4 Powder.

leased. Then both $Sr(OH)_2 \cdot 8H_2O$ and H_3BO_3 dissolve into ions form. Subsequently, the nuclei formed by ions reaction in aqueous medium. With the continuous grinding, lots of nuclei quickly formed by ions reaction in aqueous medium, and the pressure of grinding can restrained the growth of nuclei. Moreover, the existence of crystal water inhibited further growth of sub-particles. Then, the $Sr[B(OH)_4]_2$ nanoparticles have been obtained by a solid-state reaction at room temperature. Finally, the nano-sized, uniform and spherical SrB_2O_4 sample was synthesized after calcination process.

4. Conclusions

The uniform and spherical SrB_2O_4 nanoparticles have been prepared by a solid-state reaction at room temperature followed by a subsequent calcination process. The method is highly productive and the synthesis process achieves economic atom reaction according to the ideas of green chemistry. The chemical reaction of the process is generally the acid-base neutralization reaction and agrees well with hard and soft (Lewis) acids and bases theory. The water generated in the synthesis process plays an essential role for the formation of the uniform SrB_2O_4 nanoparticles.

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