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Synthesis and characterization of strontium chloroborate whiskers

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Single crystalline strontium chloroborate ($Sr_2B_5O_9Cl$) whiskers with uniform diameter have been synthesized by a facile route based on the calcination of precursor. The precursor was prepared by the sedimentation reaction between $SrCl_2$ and $Na_2B_4O_7$ aqueous solution. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared spectrum (FT-IR). An optimal synthesis temperature for preparing $Sr_2B_5O_9Cl$ whiskers was obtained, and the possible formation process was also presented.

1 Introduction

Whiskers are filamentary single crystals, which have less crystal defects in comparison to the bulk counterpart due to their small diameter. Therefore, they are ideal reinforcing skeletons of the composite materials with near theoretical strength [1]. For example, SiC whiskers are used as reinforcement materials for ceramic matrix composites as well as metal matrix composites [2]. Moreover, some whiskers have special functions due to their unique structures. For instance, in virtue of their unique tunnel structure [3], $Na_2Ti_6O_{13}$ whiskers have been studied as a photocatalyst for the degradation of toxic substances and the decomposition of pure water, and as oxygen electrodes in potentiometric sensors for O_2 and CO_2. $Sr_2B_5O_9Cl$ crystals exhibit an abnormally large nonlinear optical response because of their non-centrosymmetric hilgardite-type structure [4,5]. However, to the best of our knowledge, there is no study on the synthesis of $Sr_2B_5O_9Cl$ whiskers.

Flux method synthesis is one of the simplest techniques for preparing one-dimensional (1D) structural materials, such as whiskers, fibers, rods, tubes and belts [6,7]. In contrast with other synthesis approaches to 1D structures, such as solvothermal synthesis or hydrothermal synthesis, flux method synthesis needs no higher pressures or surfactants, so it is a simple and environmentally friendly process [8]. However, whiskers prepared via the traditional flux technique generally have a low purity and a wide size distribution [9]. Herein we report a simple route for the preparation of $Sr_2B_5O_9Cl$ whiskers using a two-step process: the sedimentation of precursor by reaction of aqueous solution of $Na_2B_4O_7{\bullet}10H_2O$ and $SrCl_2{\bullet}6H_2O$ and further sintering of a mixure of $SrB_6O_{10}{\bullet}5H_2O$ and KCl at 700 °C.

2 Experimental

All chemicals were of analytical grade and used without further purification. In a typical procedure, 0.09 mol of $Na_2B_4O_7{\bullet}10H_2O$ and 0.12 mol of $SrCl_2{\bullet}6H_2O$ were dissolved in 100 mL of distilled water at 90 °C, respectively. A white precipitate immediately appeared when $SrCl_2$ aqueous solution was added dropwise to the $Na_2B_4O_7$ aqueous solution. During the addition, the solution was kept stirring with a mechanical stirrer. The resulting mixture solution was evaporated at 150 °C, generating the reaction precursor as a white powder.

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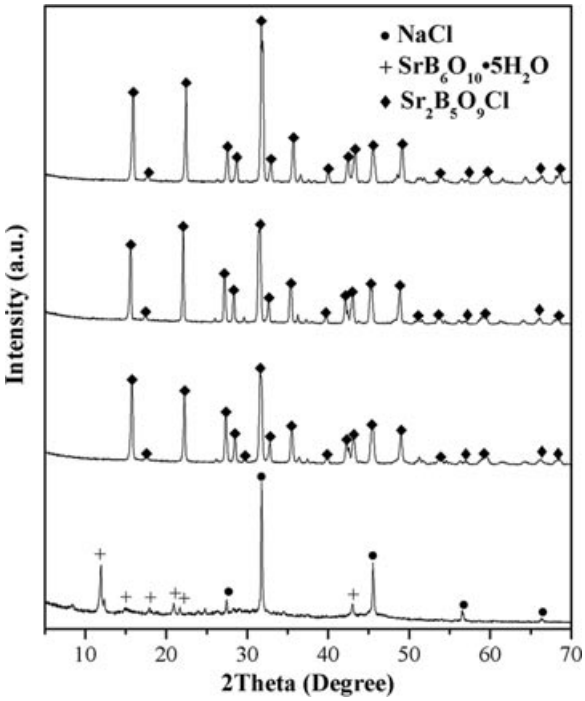


Fig. 1 XRD patterns of the precursor (a) and the samples fabricated at different temperatures (b) 600 °C; (c) 700 °C; (d) 800 °C for 8 h.

15 g of the precursor was mixed with 15 g of KCl and the solid mixture was ground into a fine powder. The powder was firstly placed in a muffle furnace and sintered at 600 °C, 700 °C and 800 °C for 8 h respectively, then cooled down to room temperature. Subsequently, the sintered powder was washed with distilled water for several times and dried at 100 °C for 8 h.

The phase composition and crystal structure of the products were identified by means of X-ray diffraction (XRD, D/max-2500, Rigku, Japan) equipped with Cu kα radiation ($\lambda = 1.54178$ Å). The morphology, microstructure and crystalline nature of the sample were examined by scanning electron microscopy (SEM, JSM-5610LV, Japan), transmission electron microscopy (TEM, JEOL 2010) and selected area electron diffraction (SAED). Chemical bonds in the molecules of the calcined product were determined by the Fourier transform infrared spectrum (FT-IR, NEXUS 670, Nicolet, USA).

3 Results and discussion

In order to understand the formation of $Sr_2B_5O_9Cl$ whiskers and to determine the optimum reaction temperature for fabricating the whiskers, the growth process of $Sr_2B_5O_9Cl$ whiskers has been systematically investigated by analyzing the samples prepared at different stages.

The XRD patterns of the precursor formed by the sedimentation reaction between $SrCl_2$ and $Na_2B_4O_7$ aqueous solution are shown in figure 1a. It is found that after sedimentation, besides NaCl, there are some weak and broad diffraction peaks marked with "+" could be detected in the precursor. It means that new phase with poor crystallinity was formed except NaCl. XRD analysis indicates the new phase is $SrB_6O_{10}{\cdot}5H_2O$ (JCPDS Card No. 16-0495). In order to remove NaCl, the precursor was washed with deionized water for several times. The precursor consists of Sr, B and O after the final washing according the EDS spectrum (see figure 2). Figure 1b shows the XRD patterns of the sample fabricated at 600 °C for 8 h. All the peaks are in good accordance with the standard orthorhombic phase of $Sr_2B_5O_9Cl$ (JCPDS Card No. 27-0835). The lattice parameters are a = 1.1381, b = 1.1319 and c = 0.6498 nm. No XRD peaks arising from impurities could be detected, indicating that $Sr_2B_5O_9Cl$ crystal with high purity was obtained. As the temperature was further increased to 700 °C (figure 1c)

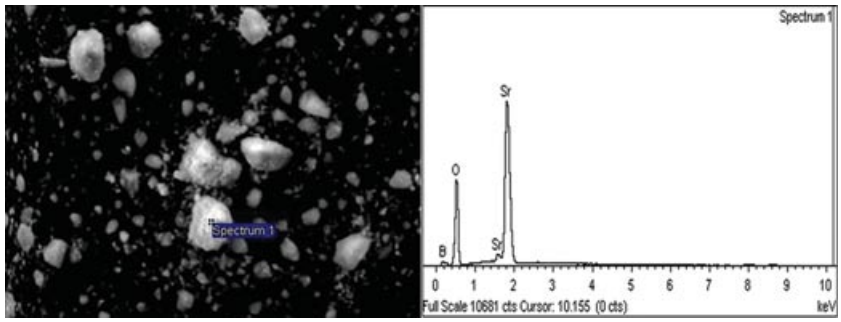


Fig. 2 EDS spectrum of the final washed precursor.

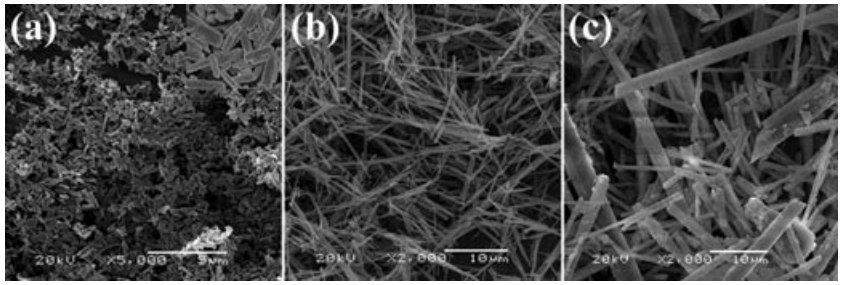


Fig. 3 SEM images of the samples fabricated at different temperatures (a) 600 °C; (b) 700 °C; (c) 800 °C for 8 h.

and 800 °C (figure 1d), all diffraction peaks of the as-prepared samples can also be attributed to the orthorhombic $Sr_2B_5O_9Cl$ phase (JCPDS Card No. 27-0835), and the diffraction intensity increased gradually.

Figure 3a shows the SEM image of the samples fabricated at 600 °C. In conjunction with their high-magnification SEM image shown in the upper-right inset of figure 3a, it can be observed that they are mainly composed of short rods and some floc-like material. When the temperature was raised to 700 °C, short rods grew into uniform whiskers (figure 3b), and the remaining floc-like material completely disappeared. The whiskers have the typical diameters in the range of 200–500 nm and the lengths of 5–20 μm. However, as the temperature was further increased to 800 °C, the diameter of the whiskers became larger obviously, as shown in figure 3c. The $Sr_2B_5O_9Cl$ particles are dispersed and confined in the solid-state salt at 600 °C, so they could not aggregate and grow overwhelmingly. On the other hand, if the temperature is increased - up to 800 °C for example, the growing rate gaps between different crystal planes reduce, which is not favorable for 1D materials growth. Thus, it is believed that the optimized calcination temperature of the $Sr_2B_5O_9Cl$ whiskers is about 700 °C.

Transmission electron microscopy (TEM) was also employed to study the structure and the morphology of the $Sr_2B_5O_9Cl$ whiskers fabricated at 700 °C for 8 h. Figure 4a exhibits the typical morphology of an individual $Sr_2B_5O_9Cl$ whisker, establishing a diameter in agreement with SEM observations shown in figure 3b. The corresponding SAED pattern of the individual whisker shown in figure 4b confirms that the whisker is single crystalline in nature and has an orthorhombic crystal structure. Meanwhile, as shown by the corresponding HRTEM image (figure 4c) of the individual whisker, the interplanar spacings of 0.563nm, 0.564 nm and 0.570nm were detected from the lattice fringes located in various sections of the whisker, being quite similar to the standard value for (101), (-101) and (200) planes of the orthorhombic $Sr_2B_5O_9Cl$ phase (JCPDS Card No. 27-0835), respectively. According to the analysis of the SAED and HRTEM results, we drew the conclusion that the whisker grew along [301] direction. The high magnification TEM image taken from the end tip of $Sr_2B_5O_9Cl$ whisker is shown in figure 4d. It is found that no particle could be found at the tip of the whisker which is the character of a VLS growth mechanism [10].

Figure 5 demonstrates the FT-IR spectrum of the $Sr_2B_5O_9Cl$ whiskers fabricated at 700 °C for 8 h. The obtained $Sr_2B_5O_9Cl$ posseses orthorhombic structure (space group Pnn2). The structure consists of Sr^{2+} cations, Cl^- and $B_5O_9^{3-}$ anions. The $B_5O_9^{3-}$ anions could be considered as three BO_4 tetrahedra and two BO_3 triangles linked by common oxygen atoms. Due to the interaction between BO_3 and BO_4 groups, the vibrational spectra of

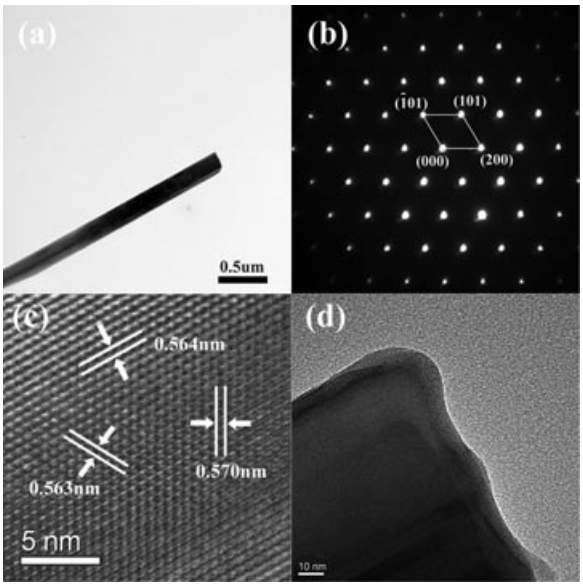


Fig. 4 TEM image (a), SAED pattern (b), HRTEM image (c) and HRTEM image taken from the end tip (d) of the $Sr_2B_5O_9Cl$ whisker fabricated at 700 °C for 8 h.

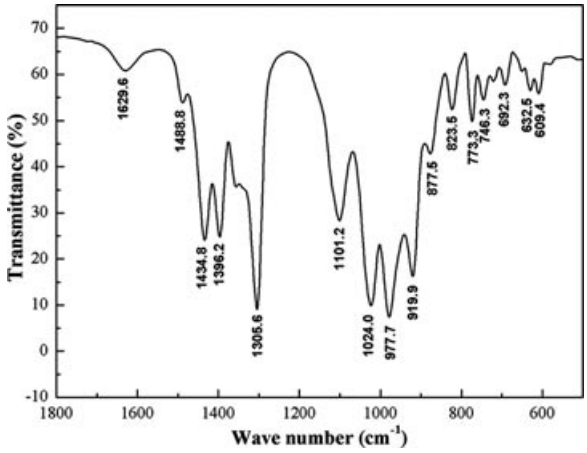
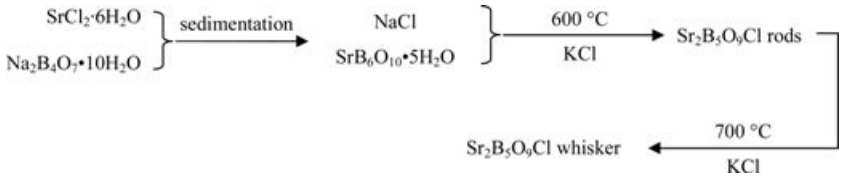


Fig. 5 FT-IR spectrum of the $Sr_2B_5O_9Cl$ whiskers fabricated at 700 °C for 8 h.

the $Sr_2B_5O_9Cl$ undergo a frequency splitting [11]. Therefore, the following assignment of spectral lines should be considered tentative to some extent. According to the FT-IR spectroscopic study results of borates [12–14], the broad and weak band at 1629.6 cm^{-1} corresponds to the H-O-H bending of the absorbed water; bands in the frequency range 1488.8-1305.6 cm^{-1} and bands at 919.9 and 877.5 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibrations of BO_3 group, respectively; bands in the frequency range 1101.2–977.7 cm^{-1} and bands at 823.5 and 773.3 cm^{-1} are owing to the asymmetric and symmetric stretching vibrations of BO_4 group; bands in the frequency range 746.3-692.3 cm^{-1} correspond to the out-of-plane bending vibrations of BO_3 group and those below 692.3 cm^{-1} can be attributed to bending of BO_3 and BO_4 groups. Moreover, the transmission peaks of BO_3 group in the $Sr_2B_5O_9Cl$ move to higher wave number, it is probably due to the inductive effect of Cl.

Through the analyses of the precursor and the as-prepared $Sr_2B_5O_9Cl$ obtained at different temperatures, we propose that the formation process of $Sr_2B_5O_9Cl$ whiskers could be illustrated as following steps.



4 Conclusion

In summary, the $Sr_2B_5O_9Cl$ whiskers with high crystallinity and uniform diameter have been successfully synthesized using a two-step process involving the sedimentation technique and sintering method. The $SrB_6O_{10}{\cdot}5H_2O$ with poor crystallinity was formed after the sedimentation reaction between $SrCl_2$ and $Na_2B_4O_7$ aqueous solution. During calcinations, $SrB_6O_{10}{\cdot}5H_2O$ with poor crystallinity transforms to rodlike shapes and finally to whisker structures. By sintering at 700 °C for 8 h, the $Sr_2B_5O_9Cl$ whiskers with orthorhombic phase and a typical diameter in the range of 200–500 nm and a length of 5-20 μm were formed. The whiskers are single crystalline and grow along [301] direction. FT-IR results show that there are trigonal BO_3 and tetrahedral BO_4 groups in the as-prepared $Sr_2B_5O_9Cl$ whiskers. This developed synthesis route may allow other metal chloroborates to be used to fabricate whiskers for fundamental research and potential applications.

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