

Size, shape-controlled Synthesis of BaSiF₆ nanostructures in a hydrothermal process

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Abstract. Different sizes and shapes of BaSiF₆ were synthesized by a low temperature hydrothermal method using citric acid (CA) as a chelating agent and cetyltrimethylammonium bromide (CTAB) as a surfactant. The sizes and morphologies of the BaSiF₆ could be altered by controlled the molar ratio of CA to Ba²⁺. And the CTAB could help to fabricate nanoscale crystals. The as-synthesized BaSiF₆'s properties were studied using XRD, SEM, TEM and Raman. Finally, the mechanism for CA and CTAB coactive hydrothermal synthesis of the BaSiF₆ is discussed.

Introduction

Nanostructure materials have attracted considerable attention due to their unusual optical, electronic, magnetic and chemical properties and their potential applications in constructing nanoscale devices [1]. These interesting properties of nanomaterials arise from their enormous surface area, strength and the quantum size. Besides, it has been found that their properties strongly depended on not only particle size but also particle shape. Therefore, the development of methods for the synthesis of size, shape-controlled nanostructures is a major challenge [2, 3].

Barium fluosilicate (BaSiF₆), with a typical rhombohedral structure, has been extensively studied due to their particular chemical and luminescence characteristics. BaSiF₆ is an ideal material for host material that displaying unique luminescence properties when activated by rare-earth ions [4, 5]. Recently, studies on fluorides nanoparticles have shown that nanoscale fluorides exhibit enhanced luminescence and photomagnetic properties [6,7]. However, to the best of our knowledge, studies on BaSiF₆ crystal is still at bulk levels, and no work has dealt with its nanosized structures. So, the synthesis of these materials is significant.

Microemulsion-mediated hydrothermal method has been extensively used for fabricating nanostructures materials [8-12]. In this method, the surfactant has been used as template for controlling the size and shape of nanocrystals [13]. While, combined with the hydrothermal's low-temperature property, could synthesis new morphologies or structures easily.

It has been found that CA could chelate metal ions effectively. The main function of CA is to hinder metal ions mobility, which maintains local stoichiometry and minimizes precipitation of unwanted phase. Molar ratios of CA to metal ions (R) were changed, the product's properties have been affected [14-16].

Based on the characteristic of these two systems described above, we wanted to combine these two methods and research the effect on size and shape of BaSiF₆ nanocrystals by this new method. In this paper, we first report the details for the synthesis of BaSiF₆ nanorod and nanocubic by a low temperature hydrothermal route using CA as a chelating agent and CTAB as a templating agent. The objective of this study is to obtain BaSiF₆ nanocrystals with various sizes and different morphologies, and investigate the influence of the R on the properties of BaSiF₆. Furthermore, we will use this novel method to fabricate other nanomaterials. We also research the BaSiF₆'s Raman, PL and infrared properties.

Experimental

All the reagents used were analytical grade and were purchased from Beijing chemical company. The H_2SiF_6 was prepared by dissolving silica in HF (0.5 mL, 40%). As a typical synthesis, a quaternary microemulsion cetyltrimethylammonium bromide (CTAB)/water/cyclohexane/n-butanol was chosen for our study. First, two identical solutions were prepared by dissolving 2g CTAB in 50 mL cyclohexane and 2 mL n-butanol. The mixing solutions were stirred and heated at 50 °C for 30 min until they became transparent. Next, 1 mL of BaCl_2 (1M) and CA mixed aqueous solution and 1 mL of H_2SiF_6 (10%) and CA mixed aqueous solution were strongly stirred and added to the microemulsions, respectively. After substantial stirring, the two optically transparent yellow solutions were mixed and stirred for another 30 min. And then the resulting solution was transferred into Teflon lined stainless steel autoclaves, which were sealed and maintained at 120 °C for 12 h. After the reaction completed, the samples were centrifugalized, washed several times with ethanol and distilled water, dried in a vacuum at 60 °C. Finally, the different size and shape BaSiF_6 nano crystals were obtained. The importance of CA as a structural modifier was studied by varying the molar ratios of CA to Ba^{2+} concentration (CA/M were 0.5,1,2,4,6). And we also prepared products with different aging times, different temperatures and without CTAB to compare.

The crystal structure of the samples was analyzed by X-ray diffraction (XRD) (RIGAKU D/MAX 2500V/PC, Japan) from 3° to 90°. The micrographs of the samples were observed by scanning electron microscope (SEM) (Hitachi S-4800, Japan) and transmission electron microscopy (TEM) (Hitachi H-7500, Japan). The luminescence properties of the samples were analyzed by Raman spectroscopy (Jobin Yvon LABRAM-UV, France).

Results and discussion

The experimental conditions and the morphologies of all the samples are listed in Table 1.

Table 1 Crystal size of samples synthesized at different conditions

$[\text{Ba}^{2+}]$ (mol/L)	[CTAB] (mol/L)	R	Time (h)	Morphology	Crystal size (nm)
1	0	1	12	flower-like particles	$8\sim 10(\times 10^3)$
1	0	6	12	particles	$0.3\sim 0.8(\times 10^3)$
1	0.1	0.5	12	nanorods	$0.1 \times 0.5\sim 1(\times 10^3)$
1	0.1	1	12	nanospindles	$0.1 \times 0.5(\times 10^3)$
1	0.1	4	1	nanorods	$0.04 \times 0.1\sim 0.15(\times 10^3)$
1	0.1	4	2	nanorods	$0.04 \times 0.1\sim 0.15(\times 10^3)$
1	0.1	4	12	nanorods	$0.04 \times 0.1\sim 0.2(\times 10^3)$
1	0.1	4	24	nanorods	$0.04 \times 0.1\sim 0.2(\times 10^3)$
1	0.1	6	12	nanocubic	60

Abbreviation: $0.1 \times 0.5\sim 1(\times 10^3)$, nanorods with diameters of 100nm and lengths of 500~1 μm .

The XRD patterns of the as-prepared BaSiF_6 (Fig.1) indicate that the products are of high crystallinity. All the peaks of two XRD patterns could be well indexed based on a pure rhombohedral BaSiF_6 with lattice constants $a = 7.1854$, $c = 7.0102$, which are in good agreement with the standard values for the bulk cubic BaSiF_6 (JCPDS15-0736). As it can be seen from Fig.1, the full width at half maximum (FWHM) of the XRD pattern (c) and (d) are larger than that of the XRD pattern (a) and (b), indicating that the BaSiF_6 crystallites prepared by the CA and CTAB-mediated hydrothermal process

are smaller in size than those prepared by the CA-assisted hydrothermal process, which will be confirmed by SEM and TEM observation later.

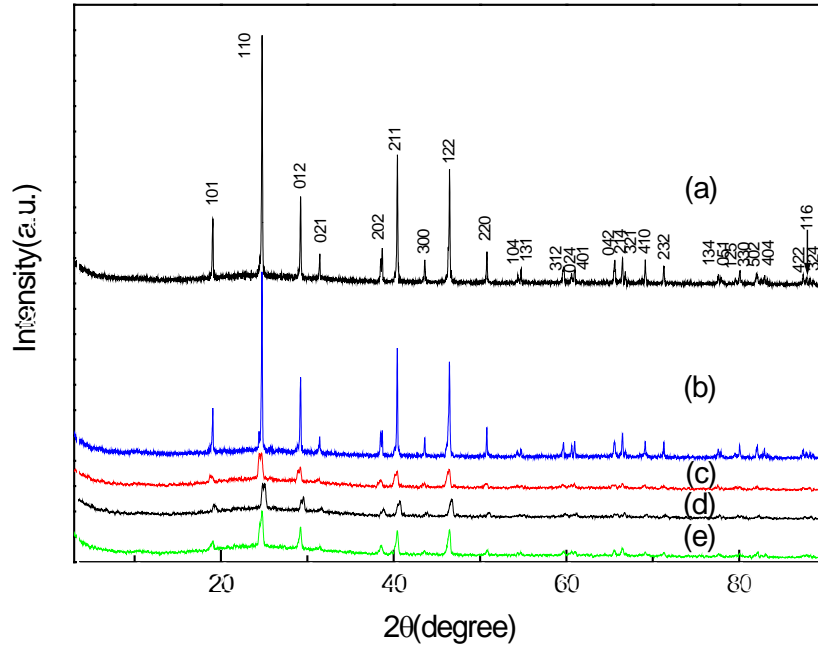


Fig. 1 XRD pattern of different morphologies of BaSiF_6 :
(a) flower-like particals; (b) oval particles; (c) nanorod; (d) nanospindle; (e) nanocubic

Fig.2 shows the spectra of the Raman measurements carried out on the BaSiF_6 samples fabricated at different conditions. The spectra suggest that the product is the same crystal and from the XRD results we know it must be BaSiF_6 . We will study Raman active mode of the three sharp Raman peaks in future work.

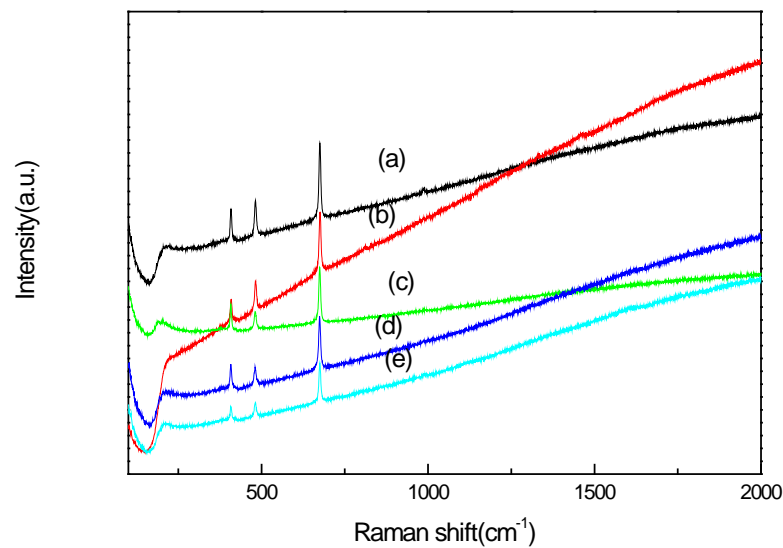


Fig. 2 Raman spectra of different morphologies of BaSiF_6 :
(a) flower-like particals; (b) oval particles; (c) nanorod; (d) nanospindle; (e) nanocubic

Fig.3 shows the typical SEM and TEM (inset in Fig.3) images of the samples produced under different conditions. Fig.3a and 3b shows the morphologies of the sample produced without CTAB conditions. As shown in Fig.3a, the samples display a flower-like morphology with the size of about 8~10 μm consists of the triangle leaves with the size of 2 μm . Other particles may be the initial stage of the flower-like morphology. Fig.3b shows the oval particles with diameter of 300~800 nm were obtained by the $R = 6$. It indicated that the sample is smaller and rounder with the R is 6 than when it is 1. This must because of the CA chelated the Ba^{2+} , and the BaSiF_6 crystal growth was restricted. The conclusion is confirmed from the Fig.3c-3e. Then, with the $[\text{CTAB}] = 0.1 \text{ mol/L}$, the morphologies of the resulting samples under different R are shown in Fig.3c-3e. It can be seen that with the increase of the R , the samples getting uniform and shorter, from nanorods to nanocubic particles. Fig.3c shows the nanorods with diameters of 100 nm and lengths of 0.5~1 μm . Spindle nanostructures with diameters of 100 nm and lengths about 500 nm were obtained by the $R = 1$ (Fig.3d). In addition, all Spindle nanoparticles have two cusped-shaped ends. When the R up to 6, the image of BaSiF_6 is shown in Fig.3e. It can be seen that the uniform nanocubic particles with the size of about 60 nm. Compared Fig.3b and 3e, the conditions of those two samples were identical except $[\text{CTAB}]$, indicating the CTAB has significant effect on the size of BaSiF_6 .

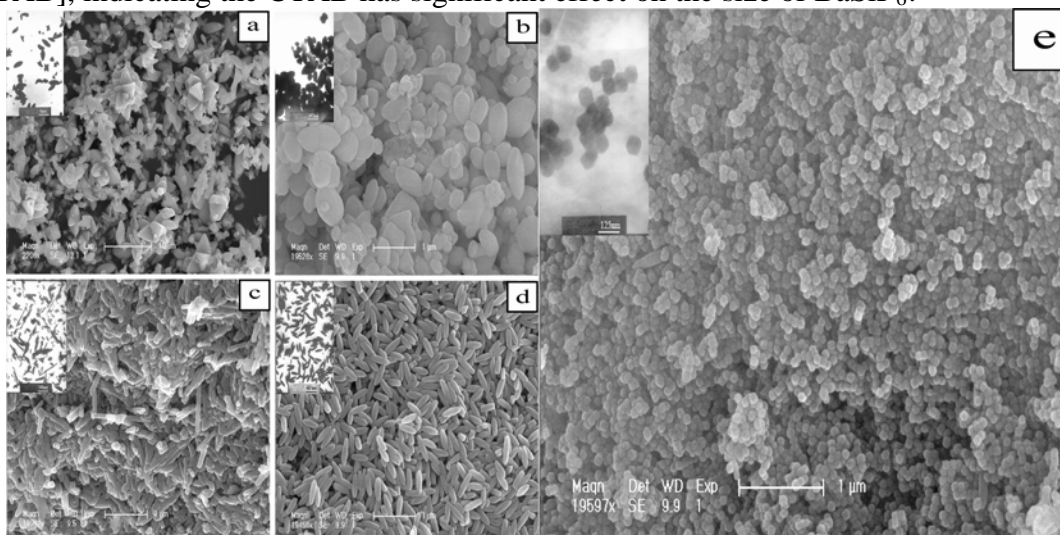


Fig. 3 SEM images of the samples produced under different conditions: (a) $R = 1$ and without CTAB. (b) $R = 6$ and without CTAB. (c) $R = 0.5$ and $[\text{CTAB}] = 0.1 \text{ mol/L}$. (d) $R = 1$ and $[\text{CTAB}] = 0.1 \text{ mol/L}$. (e) $R = 6$ and $[\text{CTAB}] = 0.1 \text{ mol/L}$. The upper left inset respectively corresponds to their TEM pattern.

Fig.4 shows the TEM micrographs of the samples synthesized at different reaction time. The Fig.4a indicates that the nanorod BaSiF_6 crystals were formed after react 1h, and with the increasing of the reaction time, the size of the sample growth slightly. Because the reaction time has a little effect on the crystals growth, it is more easier to control the form of crystals by this method.

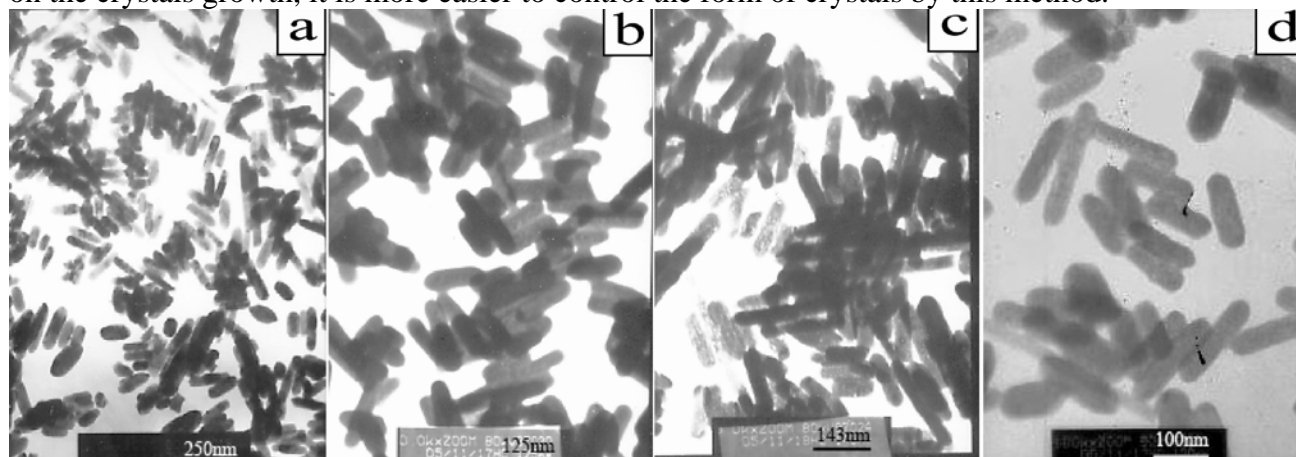


Fig. 4 TEM of the BaSiF_6 samples produced under different reaction time: (a) 1 h; (b) 2 h; (c) 12 h; (d) 24 h

In our synthetic experiments, the different morphologies of BaSiF₆ crystallites formed as mentioned above imply that CA and CTAB greatly impact on the form of BaSiF₆ crystallites. As a chelating agent, the CA's chelating ability is proven by the formation of different shape samples under different R. We could speculate that at higher R, there is enough CA to complex the surface of BaSiF₆ nuclei and prevent its growth [16]. From the SEM and TEM, we know it could restrict longitudinal growth effectively. Many papers had reported the fabrication nanostructures by using CTAB as a surfactant [8-11]. In this system, a water-in-oil (w/o) microemulsion is a transparent and isotropic liquid medium with nanosized water pools dispersed in a continuous phase and stabilized by CTAB and n-butanol at the water/oil interface. These water pools offer ideal microreactors for the formation of nanoparticles. The BaSiF₆ nanoparticles formed within the water pools will grow along a preferential direction under hydrothermal conditions [2]. Under the CA and CTAB coaction, the size and shape controlled BaSiF₆ nanocrystals were obtained.

Conclusions

In conclusion, we have synthesized size and shape controlled BaSiF₆ nanocrystals via a CA and CTAB coaction hydrothermal process. The best conditions is [CTAB] = 0.1 mol/L, R = 1 and 6 to fabricate uniform BaSiF₆ nanocrystals. Increasing R value, the samples get shorter along a particular direction. Concerning the effect of CTAB, it plays a key role to control the size and morphology of the products. The products are stable and growing slightly with reaction time. It is possible to synthesis other complex fluoride nanostructures using this method. We will study the luminescence characteristics of rare-earth ions doped BaSiF₆ nanocrystals in our future work.

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