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Low temperature growth of BaFCl microcrystals by a facile one-pot refluxing method and their superhydrophobic property

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ABSTRACT

In this work, we report a facile solution route to prepare BaFCl microcrystals with different morphologies at low-temperature. The surface morphologies and chemical composition were examined by the scanning electron microscope (SEM) and X-ray powder diffraction (XRD). The wettability of the as-synthesized BaFCl microcrystals (MCs) was studied by the measuring water contact angle (CA). A static CA for water over 150° was observed, which was closely related to both the structure and chemical modification of BaFCl MCs. Furthermore, the as-prepared BaFCl MCs showed superhydrophobicity for some corrosive liquids such as acidic and basic aqueous solutions.

1. Introduction

Barium fluorochloride (BaFCl) is an alkaline-earth dihalide system which belongs to the MFX (M: Ca, Sr, Ba; X: Cl, Br, I) family. These materials attract much attention due to their various applications, such as the most efficient up and down conversion host materials [1–10]. Crystalline pure BaFCl was usually obtained at high-temperature [11]. Therefore, the controllable synthesis of crystalline pure BaFCl nano or microcrystals with specific size and morphology is very important for the applications of BaFCl. Since the 1990s, inorganic nano or microcrystals have attracted widespread research interests because of their remarkable sizes, shapes or surface dependent physical and chemical properties with respect to their bulk counterparts [12]. Many synthesis methods have been developed successfully to prepare BaFCl materials with uniform size and shape, such as the micro-emulsion method, high boiling point solvent process, precipitation method, thermolysis of organometallic precursor, ball-milling at room temperature, co-precipitation method, compressed Langmuir monolayer and hydro–or solvothermal process [13–19]. However, there are no reports on the synthesis of BaFCl by a facile one-pot refluxing method at room temperature.

In this paper, we focus our attention on the controllable synthesis of BaFCl microcrystals (MCs) via a large-scale and facile r refluxing method at low temperature. In this paper, we present the synthesis and the characterization of BaFCl MCs. The effects of the surfactant, reaction time and temperature on the morphology of BaFCl MCs have been discussed. Through adjusting the surfactant, reaction time and temperature, microcrystals of BaFCl with different sizes and aspect ratios have been obtained. The BaFCl MCs we obtained in this paper have well-defined crystal lographic facets, and show significant superhydrophobic property. Surfaces with a water contact angle greater than 150° and a small slide angle less than 10° are superhydrophobic surfaces [20]. Due to the strong electronegativity of a fluorine atom, the fluorine atom will attract the electrons when it combines with other atoms. Therefore, it is difficult to establish interactions with other groups by the Van der Waals force, which leads to its low surface energy. The BaFCl MCs showed significant superhydrophobic property with a contact angle over 150°.

2. Results and discussion

2.1. Crystal structure and morphology

The XRD patterns of BaFCl samples prepared at different reaction temperature (20 °C, 40 °C, 80 °C and 100 °C) for 6 h are presented in Fig. 1a. As shown in Fig. 1a, the XRD pattern of BaFCl MCs obtained at 20 °C is almost the same as that of BaFCl MCs

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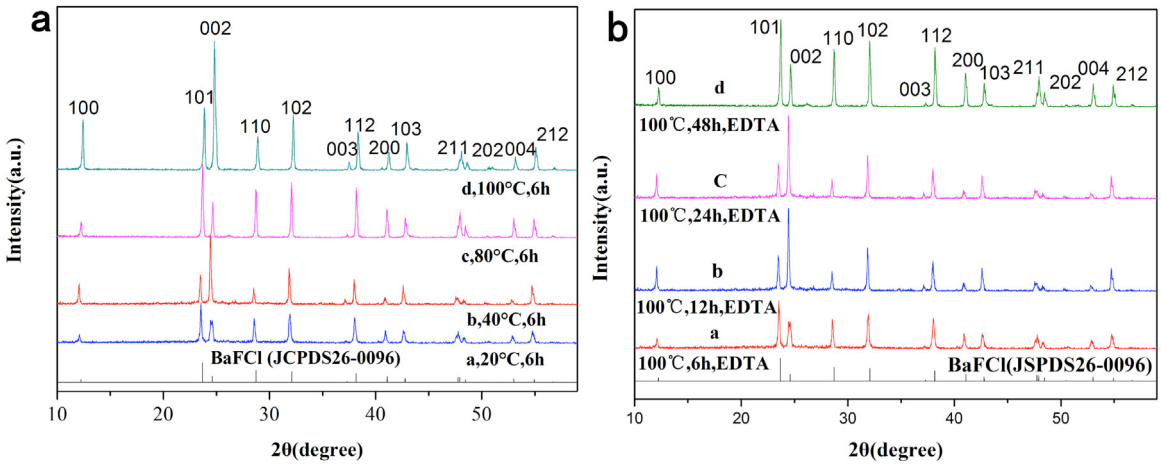

Fig. 1. XRD patterns of BaFCl MCs (a) at different reaction temperature, (b) with different reaction time.

obtained at 100 °C, which indicates that these two samples are almost same. The diffraction patterns of the as-synthesized BaFCl MCs can be indexed to that of the pure phase, which were in good agreement with literature data (JCPDS no. 26-0096). The sharp diffraction peaks indicated that the products were well-crystallized. No characteristic peaks for impurities or other phases were observed, which showed that the products were pure BaFCl with a single phase. Thus, our synthesis method at 20 °C can be used to obtain products of a larger scale. As shown in Fig. 1, there were some differences in the intensity of the 1 0 1 and 0 0 2 peaks of the as-prepared samples, which may be caused by the differences of growth directions of the crystals due to the different external environments, such as the electric field, the energy exchange, and some other chemical functions related to the crystallization [19].

Fig. 1b showed the XRD patterns of BaFCl samples prepared with reaction time of 6 h, 12 h, 24 h and 48 h, respectively. The reflection patterns can be indexed to that of the pure tetragonal phase of BaFCl with latice constants $a = b = 4.394$ Å and $c = 7.226$ Å, which matched well with the literature values (JCPDS no. 24-0096). No other impurity phases were detected, which indicated the lamellar structure of BaFCl. When the reaction time was 6 h, the crystals of the final product were irregular block structure (Fig. 3a). With increasing reaction time, the crystallization degree of the products got better. When the reaction time was longer than 12 h, the XRD results indicate that a phase transition process of BaFCl from lamellar micocrystals to regular flake microcrystals appeared. As the reaction time was increased to 24 h, the phase of BaFCl turned into regular lamellar completely. The experiment results showed, at such a low temperature, BaFCl crystals have been obtained by a refluxing method successfully. Thus, it is reasonable that the present method may be preferable for synthesizing flaky BaFCl crystal, indicating that we can realize the controllable synthesis of flaky BaFCl crystal by a facile and effective method at a relatively low temperature.

Fig. 2 showed the SEM photographs of the samples prepared at different temperatures for 12 h. We observed that the samples exhibited MCs with diameter of about 1–5 μm at lower temperature (20 °C). However, higher temperature favored the formation of thermodynamically stable, well-crystallized samples. With rising temperature, the samples changed from bulk to flat-shaped microstructures gradually. Thus, crystallinity, phase purity and morphological uniformity of products were considered to be highly correlative with the reaction temperature. It may be because of the surface chemical thermodynamics (SCT) mechanism [21]. As driving force, the reaction temperature affects the progress of reaction and the crystallization rate, and the reaction and crystallization rate influence the quality and morphology of crystals.

The reaction time was found to be an important factor to influence the final morphology of the BaFCl microcrystals. Fig. 3 showed the SEM images of the as-prepared products with the reaction time from 6 to 48 h (the reaction temperature was kept at 100 °C). Fig. 3a indicated that, when the reaction time was 6 h, the MCs were obtained with an average diameter of 1 μm. When the reaction time was increased to 24 h, the average diameter reduced to about 300 nm (Fig. 3c). As shown in Fig. 3d, the average diameter of products heated for 48 h was about 1 μm. Compared with the morphology of samples prepared with other reaction time, the surfaces of the sample prepared with 6 h were not clear, and presented a lamellar structure. With the increase of the reaction time to 12 and 24 h, the corresponding products obtained under these conditions were regular particles. However, all the edges of surfaces of the MCs were much clearer (Fig. 3b and c). When the reaction time was increased to 48 h, there was a change in morphology and size, and small particles appeared (Fig. 3d). From the above analysis, we find that the morphologies of the MCs transfer to regular particles with increasing the reaction time. Thus, it can be concluded that the optimal reaction time for the formation of BaFCl MCs is about 24 h.

It has been reported that the selective adhesion of the capping ligand on the surface of crystals plays an important role in the epitaxial growth of nanocrystals and microcrystals [22–25]. Surfactant can be adsorbed on the surfaces of the products effectively, and it will control the growth of the products as the capping reagent. Therefore, we investigated the important influence of surfactants on the shape of MCs in our synthesis. The water ratio, the quantity of reactants, the reaction temperature and time were kept constant (10 mL, 4 mmol, 100 °C and 24 h, respectively), and EDTA, CTAB and citric acid were selected as surfactants to investigate the effects on the shape of the BaFCl crystals. Fig. 4 shows the size and morphology of BaFCl products with EDTA, CTAB, citric acid surfactants and without surfactants, respectively. Without any surfactants, BaFCl crystals tended to grow into the regular lamellar structure with a wide distribution ranging from 2.3 to 3.8 μm, or some lamellar substances instead of bulk crystals (Fig. 4d). When CTAB was introduced into the reaction system, a noticeable change in the morphology of the crystals was observed. Fig. 4b shows typical SEM images for BaFCl sample. The as-prepared sample was almost entirely composed of such uniform particles with perfect uniformity and well-defined crystallo graphic facets. Analysis of a number of the MCs showed