第 28 卷第 1 期 无 机 化 学 学 报 Vol.28 No.1
2012 年 1 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 185-190

超声化学法制备不同形貌的 CaF_2 微米晶

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摘要: 采用超声化学法,以 $CaCl_2$ 与不同氟源($NaBF_4$、K_2SiF_6)在溶液中反应,制得了不同形貌的 CaF_2 微米晶(立方体、花状、多面体)。用 XRD、SEM 及 TEM 对产物晶相及形貌进行了表征。XRD 结果显示所有产物均为结晶良好的立方相 CaF_2。SEM 及 TEM 结果表明由 $NaBF_4$ 制得的产物形貌为均匀的立方体微米晶,而由 K_2SiF_6 制得的产物为多面体。在添加配体 Na_2EDTA 的情况下,由 $NaBF_4$ 得到的产物为纳米片组成的花状结构。本文详细讨论了氟源种类、反应物比例、配体等反应参数对产物 CaF_2 形貌的影响,并提出了可能的反应机理。

关键词: CaF_2; 微结构; 超声法; Na_2EDTA
中图分类号: O614.23+1; O613.41 **文献标识码**:A **文章编号**: 1001-4861(2012)01-0185-06

Sonochemical Synthesis of Different Morphological CaF_2 Microstructures

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Abstract: Different morphological CaF_2 crystals (cubes, flowers, polyhedra) were synthesized via a mild sonochemical route from an aqueous solution of $CaCl_2$ and $NaBF_4$ or K_2SiF_6. The crystal structures and morphologies of the products were characterized by using XRD, SEM and TEM. The results show that the as-prepared products are cubic structure and with high crystallinity. Uniform microcubes and polyhedra can be easily synthesized from $NaBF_4$ and K_2SiF_6, respectively. In the presence of complex agent Na_2EDTA, uniform 3D flower-like CaF_2 hierarchical structures were prepared and assembled by numerous nanoflakes. Some reaction parameters (fluoride source, molar ratio and chelating reagent) were investigated during the process of obtaining different morphological CaF_2. Furthermore, a possible reaction mechanism for the growth of CaF_2 is proposed.

Key words: CaF_2; microstructure; sonochemical route, Na_2EDTA

0 Introduction

Ultrasound is a fast, efficient and unique heating method, therefore, sonochemical route has been developed into a powerful method for synthesis of micro/nanomaterials. When liquids are irradiated by high-intensity ultrasound, high temperatures, pressures and cooling rates can be achieved upon the collapse of the bubbles [1]. The remarkable environments provide a unique platform for the growth of nanomaterials. Up to now, a variety of inorganic materials, including metal oxides, sulfides, hydrates have been prepared via sonochemical method[2-7]. However, little work has been conducted for the fabrication of inorganic fluorides[8-9].

As an important fluoride, nanoscale CaF_2 has attracted increasing interest with respect to UV lithography,

收稿日期:2011-06-17。收修改稿日期:2011-08-24。
国家自然科学基金(No.20906052),江苏省自然科学基金(No.BK2010281,No.2009610),南通大学校级课题(No.09ZY003;10ZY004)资助项目。
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UV-transparent optical lenses, the surface conditioning of glass, promoting agents for bone/teeth reconstruction, and biocompatible luminescent markers[10-12]. Up to now, a series of CaF_2 nano/microstructures with different morphologies, such as cubes[13], plates and polyhedras[14], wires[15], hollow spheres[16-18] and flowers[19] have been fabricated by a variety of methods. The synthesis of CaF_2 nano/microstructures with wet chemical approaches involving polyol method[12], hydrothermal methods[13,17,19], thermolysis[14], coprecipitation[15-16] and reversed micelle[18]. However, to the best of our knowledge, few studies have focused on the synthesis of highly mono-dispersed CaF_2 microstructures by complex fluorides via sonochemical route. Herein, by employing $NaBF_4$ or K_2SiF_6 as fluoride sources, we present a simple, facile and effective sonochemical route to synthesize different morphological CaF_2. It is found that chelating reagent, fluoride source and molar ratio of reactants play crucial roles in the formation of products with different morphologies.

1 Experimental

1.1 Preparation

$CaCl_2$, $NaBF_4$, K_2SiF_6 and Na_2EDTA (AR) were purchased from Shanghai Chemical Reagent Corporation and used without further purification. In a typical procedure, 1 mmol of $CaCl_2$ was first added to 30 mL distilled water in a 50 mL flask at room temperature, after magnetic stirring for 5 min, 0.5 mmol Na_2EDTA was introduced under stirring and was continuously stirred for 10 min to form a calcium complex, then followed by addition of 1 mmol of complex fluoride $NaBF_4$. The above mixture solution was irradiated by ultrasonic wave with 50 Hz at the ultrasonic power of 300 W for 1 h. At the end of the sonication, a temperature of about 40 ℃ was reached under ambient air without cooling. Finally, the white precipitate was centrifuged, washed with distilled water and ethanol, and dried at 70°C for 3 h.

1.2 Materials characterization

The crystalline phases of the products were analyzed by XRD on a Shimadzu XRD-6000 powder X ray diffractometer (Cu $K\alpha$ radiation, λ=0.154 18 nm), employing a scanning rate of 4.00° · min^{-1}, in the 2θ range from 20° to 80°. The operation voltage and current were maintained at 40 kV and 30 mA, respectively. The sizes and morphologies of the resulting products were studied by transmission electron microscopy (TEM, TECNAI F20S-TWIN) at 200 kV and field emission scanning electron micros copy (FE-SEM, HITACHI S-4800) at 15 kV.

2 Results and discussion

2.1 Structure characterization

The XRD patterns shown in Fig.1a are for the sample in a typical experiment, with the fixed molar ratio of $CaCl_2$/EDTA/$NaBF_4$ at 1∶0.5∶1, all diffraction peaks can be indexed to cubic structured CaF_2 (PDF No. 04-0864). No peak of impurities is observed, confirming the formation of pure CaF_2. The strong and sharp diffraction peaks indicate that the as-obtained products are well-crystalline ones.

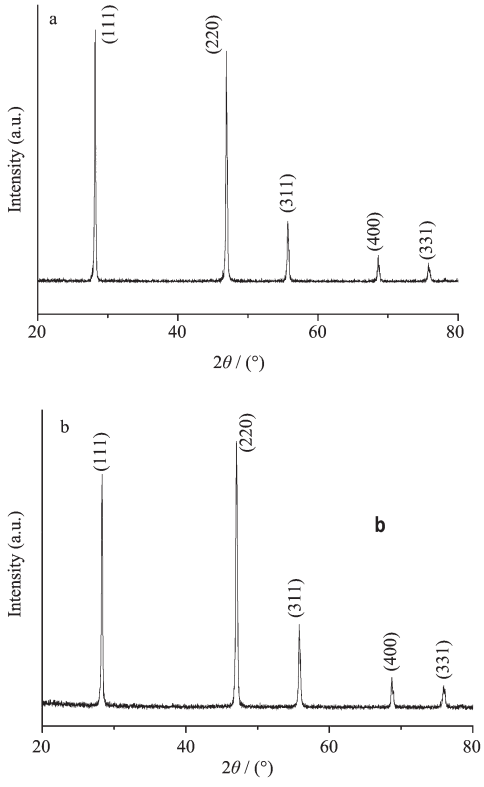


Fig.1 XRD patterns for the CaF_2 with 0.5 mmol Na_2EDTA added in (a) $NaBF_4$; (b)K_2SiF_6

2.2 Morphology characterization

Fig.2a is the low-magnification SEM image of the

sample obtained in a typical procedure. Cubic phased CaF_2 products are primarily composed of uniform flower-like structures, indicating that high yield 3D hierarchical structures can be obtained by this method. The magnified SEM image (Fig.2b) reveals that the CaF_2 flower-like structures are assembled by many nanoflakes and the flakes are interweaving together. The TEM images also imply that the flower-like CaF_2 structures are self-assembled from slightly bending nanoflakes (Fig.2c-d). The SAED pattern (inset in Fig. 2c) reveals the single-crystalline nature of the CaF_2 nanoflakes.

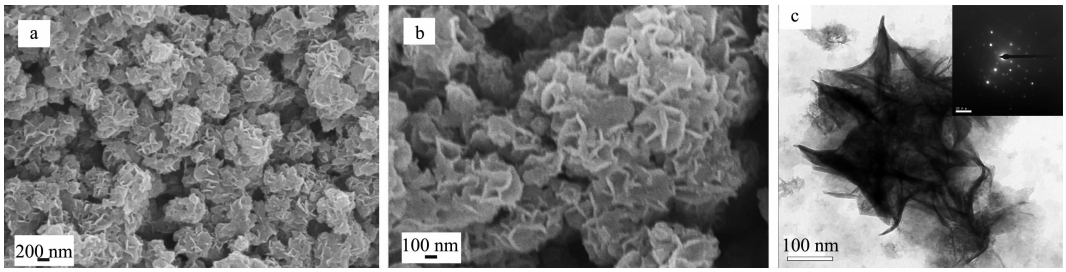
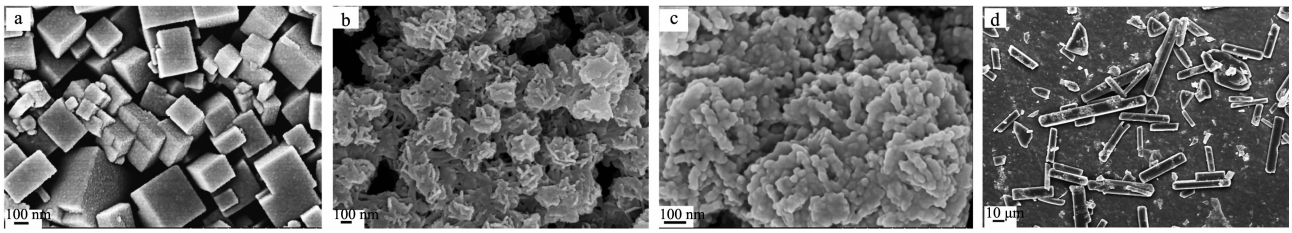


Fig.2　SEM and TEM images for the product prepared in a typical procedure

2.3　Effect of reaction parameters

Fig.3a is the SEM image for the product prepared in the absence of Na_2EDTA. It is found that the morphology of the as-prepared CaF_2 consists of highly dispersed cubes with edge length of 150~400 nm. The size of the cubes is different from each other. This observation indicates that Na_2EDTA plays a key role in controlling the morphology and size of the products. When 1 mmol Na_2EDTA is added, similar 3D flower-like CaF_2 hierarchical structures are formed, however, the edge of the flake is not clear as the former one (Fig.3b). When the amount of Na_2EDTA is increased to 2 mmol (Fig.3c), rodlike aggregates are formed. The SEM image reveals that the surfaces of the rod aggregates are not smooth and made of small nanocrystals. When we further increase the amount of Na_2EDTA to 5 mmol, only microrods are observed (Fig.3d). Therefore, the morphologies of the CaF_2 microstructures are sensitive to the amount of Na_2EDTA.



(a) 0 mmol, (b) 1 mmol, (c) 2 mmol, (d) 5 mmol

Fig.3　SEM images for the products prepared from $NaBF_4$ with different amounts of Na_2EDTA

In order to investigate the effect of fluoride source, K_2SiF_6 was used instead of $NaBF_4$ to synthesize CaF_2 by an identical procedure. Fig. 1b shows the XRD patterns of the product prepared from 0.5 mmol Na_2EDTA in the mixture of 1 mmol $CaCl_2$ and 1 mmol K_2SiF_6. All diffraction peaks of the product are perfectly indexed to the cubic phase of CaF_2 (PDF No.04-0864). It clearly reveals that the variation of fluoride source has no much effect on the crystalline phase. Fig.4 shows the SEM images for the products prepared from K_2SiF_6 with different amounts of Na_2EDTA. Fig. 4a is the SEM image of the product prepared in the absence of Na_2EDTA. The morphology of the as-prepared CaF_2 consists of irregular polyhedra. When 1 mmol Na_2EDTA is used, the as-prepared CaF_2 are all polyhedra, but the edge is much clear than former one (Fig.4b). Further increasing the amount of Na_2EDTA from 1 mmol, 2 mmol to 5 mmol, the shape of the product changes from polyhedra, urchinlike spheres to aggregated spheres. These results indicate that the chelating reagents have a

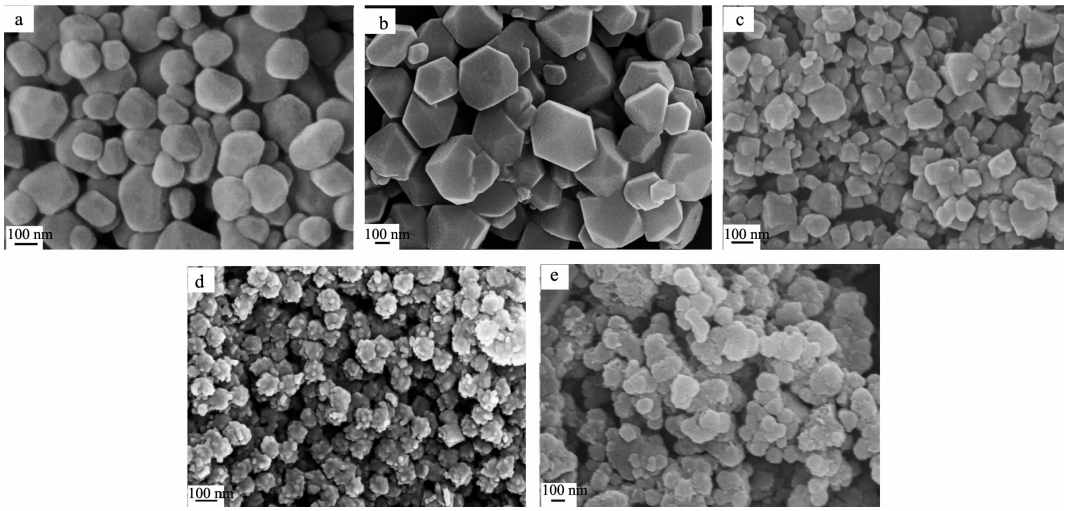


Fig.4 SEM images for the products prepared from K_2SiF_6 with different amount of Na_2EDTA

remarkable impact on the morphologies of the final products.

It is noted that the molar ratio of starting materials also plays an important role in the formation of different morphological CaF_2. A series of contrastive experiments were conducted to fabricate CaF_2 when the molar ratio of Ca^{2+}/BF_4^- or Ca^{2+}/SiF_6^{2-} varied while other reaction conditions kept constant. It should be mentioned that varying the molar ratio of the reactants does not change the phase of the CaF_2 products in our present work. All the samples involved in this study are characterized as pure cubic phased CaF_2. Here we only take CaF_2 as a typical example to explain the morphology of the products. Fig.5 shows the SEM images of the products prepared from different molar ratios of $Ca^{2+}/NaBF_4$ and Ca^{2+}/K_2SiF_6, respectively. It is clearly indicated that the as-prepared CaF_2 are all cubes, however, with the increasing of the amount of $NaBF_4$, more and more cubes aggregate together and many small particles coexist when $Ca^{2+}/NaBF_4$ is fixed at 1∶4. As shown in Fig.5d~e, changing the molar ratio of Ca^{2+}/K_2SiF_6 has no obvious effect on the shape of the CaF_2.

The ultrasonic irradiation plays an important role in the formation of different morphological CaF_2 in our current experimental conditions. In order to validate it, contrastive experiments were carried out to fabricate CaF_2 through stirring for 1 h without ultrasonication at room temperature. The XRD results indicate that the

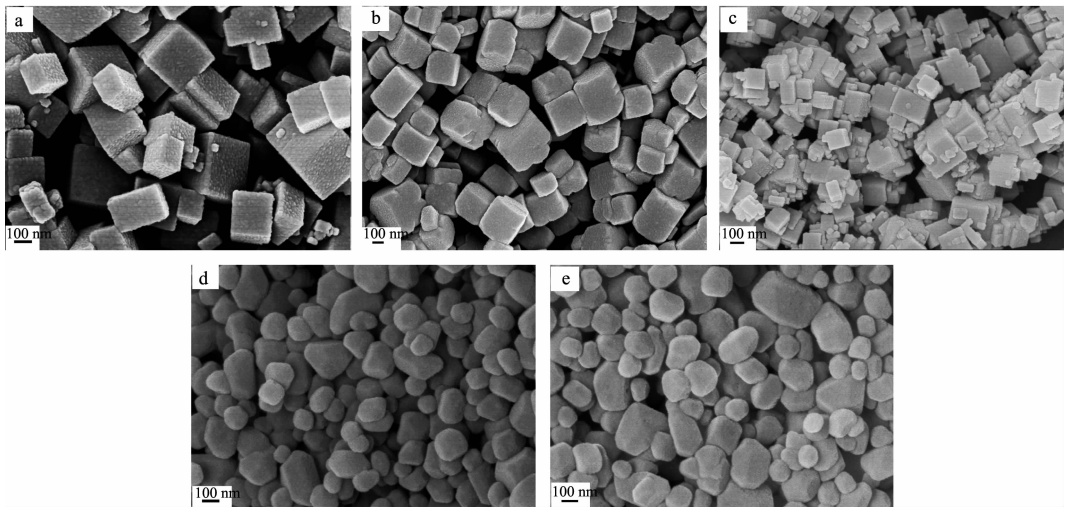
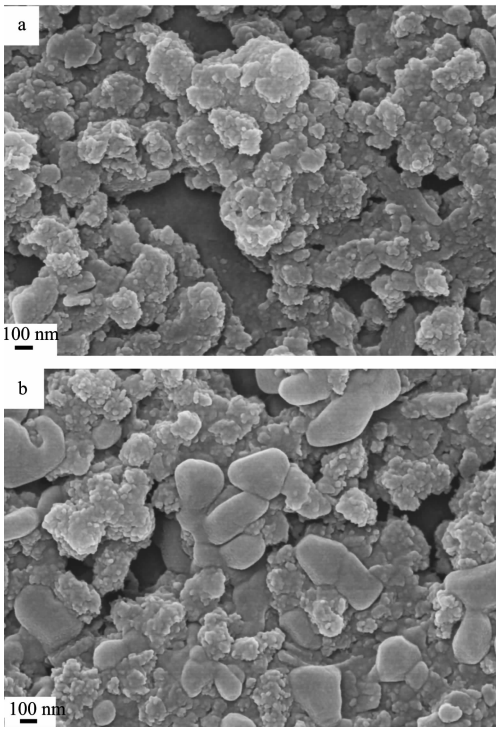


Fig.5 SEM images of the products prepared from different molar ratios of $Ca^{2+}/NaBF_4$ as (a)1∶0.5, (b) 1∶2, (c) 1∶4 and Ca^{2+}/K_2SiF_6 as (d)1∶0.5, (e)1∶2

as-prepared products are pure cubic phased CaF_2. However, the shape of the corresponding product is irregular, as shown in Figs.6a and 6b. In the results presented here, the instantaneous high-temperature and high-pressure field developed during ultrasonic irradiation will help to control the particle growth of CaF_2, possibly because of the short collapse between a few nucleation centers in collapsing bubbles. Therefore, the ultrasonic irradiation is a key factor in the growth of CaF_2.



(a) $n_{CaCl_2}/n_{EDTA}/n_{NaBF_4}$=1:0.5:1; (b) $n_{CaCl_2}/n_{EDTA}/n_{K_2SiF_6}$=1:0.5:1

Fig.6　SEM images of the CaF_2 prepared through stirring for 1 h without ultrasonication at room temperature

2.4　Possible formation mechanism

$$Ca^{2+}+EDTA^{2-} \rightarrow Ca\text{-}EDTA \quad (1)$$

$$BF_4^-+3H_2O \rightarrow H_3BO_3+3HF+F^- \quad (2)$$

$$SiF_6^{2-}+3H_2O \rightarrow 2F^-+H_2SiO_3+4HF \quad (3)$$

$$Ca\text{-}EDTA+2F^- \rightarrow CaF_2+EDTA^{2-} \quad (4)$$

Based on the above experimental results, the probable reaction process for the formation of CaF_2 may be summarized as Eqs (**1~4**). In the current study, Ca^{2+} and EDTA[2] form Ca-EDTA complexes at the beginning. It is known that $NaBF_4$ (or K_2SiF_6) yields F by hydrolysis of BF_4 (or SiF_6^{2-}). The Eqs(2~3) were reported earlier[20-21]. The F^- ions released from $NaBF_4$ (or K_2SiF_6) then react with the Ca^{2+} ions (released from the Ca-EDTA complex) to form CaF_2 nanoparticles. Once the CaF_2 nanoparticles formed, the EDTA molecules and the decomposed products from $NaBF_4$ and K_2SiF_6 can be selectively adsorbed onto certain crystallographic planes of the CaF_2 seeds. In a further crystallization process, the unequal growth rates of different crystal facets (*i.e.*, anisotropic growth), will lead to the preferential growth of some specific crystalline planes[19]. As a result, CaF_2 microstructures with different morphologies are synthesized via a mild sonochemical route. The ultrasonic waves may accelerate the hydrolysis of $NaBF_4$ or K_2SiF_6, which is presumably helpful to the nucleation and growth of CaF_2 microstructures. Furthermore, the cavitation and shock wave created by the ultrasound can accelerate solid particles to high velocities, leading to the interparticle collision and effective fusion at the point of collision.

3　Conclusions

Cubic phased CaF_2 microcrystals with different shapes (cubes, flowers, polyhedra) were synthesized by tuning the reaction parameters via a simple sonochemical route. The fluoride sources, molar ratio and chelating reagent are all key factors in the formation of products with different morphologies.

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