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Synthesis of Barium Lithium Fluoride Nanocrystals Using Reverse Micelles as Microemulsion

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Abstract: Barium lithium fluoride nanocrystals were synthesized in cetyltrimethylammonium bromide (CTAB)/ *2*-octanol/ water microemulsion systems. The impurity peaks in XRD patterns were not determined. The result of SEM confirmed that the average sizes and shape of the $BaLiF_3$ nanocrystals. The formation of $BaLiF_3$ and particles size were strongly affected by water content. With increasing water content and reaction times, the size of the particle increases. Meanwhile, the solvent was also found to play a key role in the synthesis of the $BaLiF_3$ nanocrystals.

Keywords: Barium lithium fluoride, microemulsion, nanocrystal.

ABF_3 (A= Li, Na, K; B= divalent element) compounds have become important as they show lasing action[1] when they are doped with a proper dopant. Various isomorphous replacements in the framework of complex fluorides lead to many controllable properties[2]. Formation of defect-free crystals, however, can be time-consuming, expensive, and requires specialized equipment, or may even be impossible for many materials. Beecroft *et al.*[3] have used a composite consisting of light-amplifying nanoparticles placed in a glass or polymer matrix to circumvent these problems.

Many nanoparticles of different chemical compositions, shapes, and size distributions have been prepared by different kinds of methods such as gas evaporation[4], laser vaporization[5], ionized beam deposition[6], sol-gel process[7], hydrothermal[8] and solvothermal process[9], *etc*. In comparison, the synthesis of nanoparticles in reverse microemulsion is more attractive than that of many other methods. Since Boutonnet *et al.* have reported the synthesis of the monodispersed metallic particles of Pt, Pd, Rh, and Ir using microemulsions[10], reverse microemulsions have been successfully utilized for the synthesis of nanoparticles such as Y_2O_3:Eu[11], Gd_2O_2S:Eu[12], nickel ferrite[13], cobalt ferrite[14] and CdE (E=S, Se, Te) semiconductor[15], and so on. In particular, Bender *et al.*[16] described that reverse microemulsions were used to synthesize barium fluoride doped with 0-65 mol% neodymium nanoparticles. The products were polydisperse,

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average particles size below 100 nm was achieved. The aim of this paper is a detailed study of synthesis for complex fluoride $BaLiF_3$ nanocrystals to test the reactive conditions in CTAB/ *2*-octanol/ water microemulsion systems.

Experimental

All the chemicals used in this study were reagent grade without further purification. Microemulsions were made by dissolving 7 g of cetyltrimethylammonium bromide in 42 g of *2*-octanol in a 100 mL beaker. This mixture was stirred magnetically for 1 h, and then 6.30 mL of an aqueous salt solution containing $Ba(NO_3)_2$ (0.523 g, 0.002 mol) and $LiNO_3$ (0.172 g, 0.0025 mol) was added slowly. In a similar fashion, a fluoride microemulsion was made in a 200 mL beaker by substituting 6.20 mL of a NH_4F (0.370 g, 0.01 mol) solution for the barium salt and lithium salt solution. These two microemulsions were stirred separately for 2 h, and then were combined and stirred for 5-15 min before collection of the product. Finally, the emulsion mixture was centrifuged at 4000 rpm for 30 min, which caused sedimentation of the nanoparticles and allowed removal of the mother liquor. The particles were washed with ethanol (5×10 mL) and centrifuged (20 min, 4000 rpm), dried for 40 min, lightly crushed in mortar .

All products were characterized by X-ray powder diffraction (XRD), using a Japan Rigaku D/max-ⅡB diffractometer with Cu $K\alpha_1$ radiation (λ=1.5405 Å). The XRD data for index and cell-parameter calculations were collected by a scanning mode with a step of 0.02° in the 2θ range from 10° to 100° and a scanning rate of $4.0^{\circ}\cdot min^{-1}$ with silicon used as an internal standard. Observation of crystallites by SEM was performed on a Hitachi S-570 scanning electron microscopy. Powdered samples (2 mg) were dispersed in 2 mL absolute ethanol by ultrasonication for 10 min in a KQ-250B ultrasonic bath, and allowed to dry on a glass slice. IR spectra were obtained with a Magna 560 spectrometer in the range 400-4000cm^{-1}.

Results and Discussion

Table 1 shows the microemulsion synthesis conditions for $BaLiF_3$ nanocrystals. From **Table 1**, it can be seen, only when water content is more than 10.6% (w/w), the $BaLiF_3$ can be obtained. While the water content is less than 10.6% (w/w), the impurity phase of BaF_2 appeared whatever adjusted the ratio of initial composition, and surfactant and solvent. The reaction time is also an important factor for an effective synthesis. As increasing the reaction times from 5 min to 15 min, the size of crystals increases from 60 nm to 160 nm. As a result, the reaction times were typically kept less than 15 min. When the reaction time is within five minutes, increasing the amount of surfactant (from *2*-octanol: CTAB =6:1 to 4:1), the size of crystals decreases. Other system such as Igepal CO-520/cyclohexane/water[16], was used to synthesize $BaLiF_3$, the products were BaF_2 and multiphase. While octanol was used to replace 2-octanol, and cetyltrimethylammonium bromide was used as surfactant, the products are $BaLiF_3$ and BaF_2. The particles size is large than 60 nm demonstrates that microemulsion do not consist of hard spheres that strictly limit particles growth. Particles size is larger than the swollen micelle size have been reported previously [17].

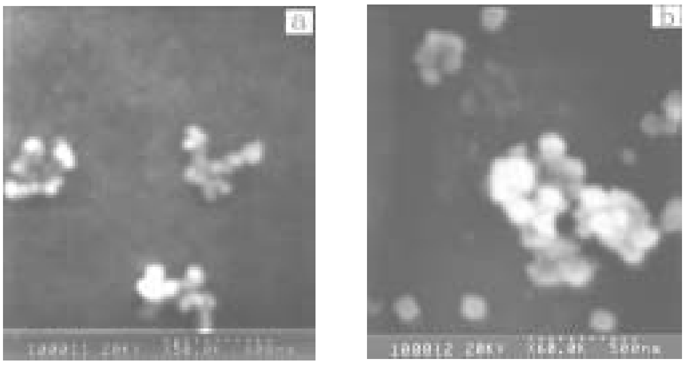
The XRD patterns of $BaLiF_3$ can be indexed in cubic system. The unit-cell parameter is calculated by the primitive cubic system[18] and the value a = 4.0060 (Esd= 0.0031, R%= 100). The value for $BaLiF_3$ is slightly larger than that of the corresponding $BaLiF_3$ synthesized by solid-state reaction (a=3.9950 Å) [JCPDS Card 18-0715]. The impurity peaks in XRD patterns were not determined.

Table 1 Synthesis of $BaLiF_3$ nanocrystals in microemulsion of cetyltrimethylammonium bromide (CTAB)/ *2*-octanol/water

a : b : c molar ratio*	2-octanol/ CTAB (w/w)	water (wt %)	reaction temp./℃	reaction time/min	phase in product	crystal diam./nm
1 : 1 : 3	6/1	12.36	20	15	$BaLiF_3$	160
1 : 1 : 5	6/1	10.60	20	15	$BaLiF_3$	90
1 : 1 : 5	6/1	10.6	20	5	$BaLiF_3$	90
1 : 1 : 5	6/1	7.72	20	15	$BaLiF_3$+BaF_2	
1 : 1.5 : 5	6/1	7.84	20	15	$BaLiF_3$+BaF_2	
1 : 2.5 : 10	6/1	7.84	20	15	$BaLiF_3$+BaF_2	
1 : 1 : 5	4/1	10.60	20	15	$BaLiF_3$+BaF_2	
1 : 1.5 : 5	4/1	10.60	20	15	$BaLiF_3$+BaF_2	
1 : 2 : 9	4/1	10.60	20	15	$BaLiF_3$	90
1 : 2 : 9	4/1	10.60	20	5	$BaLiF_3$	65
1 : 1 : 5	4/1	7.84	20	15	$BaLiF_3$+BaF_2	
1 : 2.5 : 5	4/1	7.84	20	15	$BaLiF_3$+BaF_2	

* a is $Ba(NO_3)_2$, b is $LiNO_3$, and c is NH_4F

Figure 1 Scanning electron micrographs of microemulsion reaction products



(a) $BaLiF_3$ from a 5 min reaction (2-octanol : CTAB=4 : 1, water content is 10.60%);
(b) $BaLiF_3$ from a 5 min reaction (2-octanol : CTAB=6 : 1, water content is 10.60%);

SEM was useful for qualitative assessment of the reaction products despite the inevitable aggregation of particles that occurred during sample preparation. **Figure 1** shows that the products of $BaLiF_3$ nanocrystals. As increasing the water content and reaction times, the crystals size increase from 60 nm to 160 nm. The photo showed that individual particles are aggregative and sightly smaller than others in diameter.

IR spectra were used to determine whether surfactant and other anions were removed from the products after washing. Being used nitrate salts in the synthesis, the weakly asymmetric stretching vibration for NO_3^- was observed in the IR spectrum at

1385 cm^{-1}. This results shows that there are trace NO_3^- were not removed from the products after washing with ethanol. Trace water, or possibly hydroxyl groups, was also found to be present in the powders as shown by weak absorptions at 3423 cm^{-1} and 1635 cm^{-1}. This result is consistent with the report previously[16].

In summary, a new method for the synthesis of $BaLiF_3$ nanocrystals by the cetyltrimethylammonium bromide/*2*-octanol/ water microemulsion systems is presented. The water content and reaction time play important roles in the formation of the products in the microemulsion process. With increasing water content and reaction times, the average particle sizes of the products increase from 60 to 160 nm. The solvent was also found to play a key role in the synthesis of the $BaLiF_3$ nanocrystals. The products have uniform sizes in cubic shapes. The impurity peaks showed in XRD patterns were not determined. IR spectrum showed that there is trace NO_3^- in the products.

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