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Synthesis of the Complex Fluoride $LiBaF_3$ through a Solvothermal Process

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Abstract The complex fluoride $LiBaF_3$ is solvothermally synthesized at 180℃ and characterized by means of X-ray powder diffraction, scanning electron microscopy, thermogravimetric analysis and infrared spectroscopy. In the solvothermal process, the solvents, mole ratios of initial mixtures and reaction temperature play important roles in the growth of the single crystal.

Keywords: Solvothermal synthesis, complex fluoride.

Since the 1970s a number of papers[1,2] have reported the high temperature solid state synthesis of complex fluoride $LiBaF_3$ in LiF-BaF_2 system. Some complex fluorides with general formula ABF_3 (A = Li, Na, K; B = divalent element) possess the perovskite structure. The complex fluoride, ABF_3 has become important as it shows lasing action[3] when doped with a proper dopant. Various isomorphous replacements in the framework of complex fluorides lead to many controllable properties[4]. However, the solid state synthesis requires a complicated set-up because of the erosion of the fluorides. Recently, a mild hydrothermal synthesis of the complex fluorides at 120-240°C has been reported[5-8]. The oxygen content in ABF_3 synthesized by hydrothermal method is lower than that of the corresponding compound prepared by high temperature solid state reaction[9] and thus has limited the study of the fluorides. Taking into account some of the interesting properties of the complex fluorides such as piezoelectric characteristics[10], ferromagnetic[11], nonmagnetic insulators behaviour[12], and with an aim to develop new routes without complicated apparatus. Herein we report a convenient solvothermal synthesis of $LiBaF_3$ with perovskite structure.

Experimental

$LiBaF_3$ crystal was grown in a 20 mL Teflon-lined stainless steel autoclave under autogenous pressure. The starting reactants were LiF (A.R.) and BaF_2 (A.R.). The mole ratios of LiF : BaF_2 were 1.0 : 1.0. The typical synthetic procedure was as follows: 0.130 g (0.005 moL) LiF and 0.877 g (0.005 moL) BaF_2 were mixed and added into a

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Teflon-lined autoclave. Then the autoclave was filled with ethylene glycol up to 80% of the total volume. The autoclave was sealed into a stainless steel tank and heated in an oven at 180°C for 2 days. After being cooled to room temperature, the final powder product was filtered off, washed with absolute ethanol and distilled water, and then dried in air at ambient temperature.

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° • min^{-1} with silicon used as an internal standard. Observation of crystallites by SEM was performed on a JXA-840 scanning electron microscope. Thermogravimetric analysis (TGA) was conducted using a DT-30 thermogravimetric system. IR spectra were obtained with a Magna 560 spectrometer in the range 400-4000cm^{-1}. The samples for the spectral measurements were in KBr pellets.

Results and Discussion

Table 1 shows the solvothermal synthesis conditions for $LiBaF_3$. In the synthesis of $LiBaF_3$, the Li/Ba ratio and the solvent were found to be crucial to the formation, crystallization and purity of the product. When the mole ratio Li/Ba of mixture was 1, and ethylene gloycol was used as solvent, the pure and well-crystallized product was prepared. However, when the mole ratio Li/Ba was 0.5 (or 2), impurity phases BaF_2 (or LiF) appeared. Other solvents were employed to the synthesis of $LiBaF_3$, such as *n*-butanol, ethylenediamine, pyridine and phenol *etc.*, all of these solvents could not achieve the purity of the products.

Crystallization temperature was also important factor for an effective synthesis. For instance, in the LiF-BaF_2-ethylene gloycol system, $LiBaF_3$ was obtained after 1 day at 180°C, but at 150°C after 7 days could not form the pure crystals of $LiBaF_3$. The synthesis reaction can be formulated as follows:

$$LiF + BaF_2 \xrightarrow{\text{ethylene glycol 180 °C}} LiBaF_3$$

The XRD pattern of the $LiBaF_3$ is shown in **Figure 1** and can be indexed in cubic systems. The unit-cell parameters for $LiBaF_3$ is a=3.9953 Å and the value for $LiBaF_3$ is similar to that of the corresponding $LiBaF_3$ synthesized by solid-state reaction (a=3.9950 Å) [JCPDS Card 18-0715]. The powder XRD patterns show the products are pure.

The SEM observation of the product (**Figure 2**) shows that the crystallites have regular morphology and this implies that the product is pure and single phase. The complex fluoride $LiBaF_3$ has the shapes of cubic, and the average grain size is *ca.* 1.5 μm.

The thermal stability of the $LiBaF_3$ was studied by TG-DTA analysis in air. No phase transition or mass loss was observed from 25°C up to 835°C in system. This indicates that $LiBaF_3$ is not hydrated and stable in air, which was confirmed by IR at room temperature.

Table 1 Solvothermal synthesis conditions for $LiBaF_3$

Starting materials a	b	a : b mole ratio	Solvent	Reaction time/d	Reaction temp./ °C	Phases in product
LiF	BaF_2	1 : 1	Ethylene gloycol	7	180	$LiBaF_3$
LiF	BaF_2	2 : 1	Ethylene gloycol	7	180	$LiBaF_3$+LiF
LiF	BaF_2	1 : 2	Ethylene gloycol	7	180	$LiBaF_3$+BaF_2
LiF	BaF_2	1 : 1	Ethylene gloycol	4	180	$LiBaF_3$
LiF	BaF_2	1 : 1	Ethylene gloycol	2	180	$LiBaF_3$
LiF	BaF_2	1 : 1	Ethylene gloycol	1	180	$LiBaF_3$
LiF	BaF_2	1 : 1	Ethylene gloycol	1	200	$LiBaF_3$
LiF	BaF_2	1 : 1	Ethylene gloycol	7	150	$LiBaF_3$+BaF_2

Figure 1 XRD pattern of $LiBaF_3$

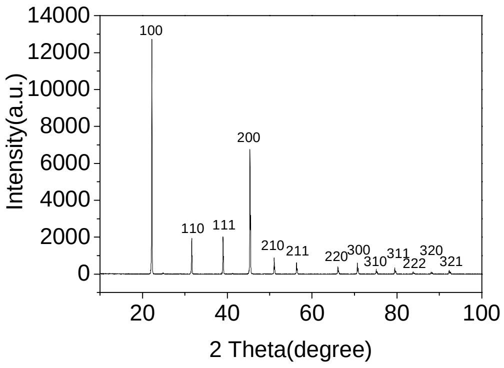

Figure 2. SEM photograph of $LiBaF_3$

In summary, a new method for the synthesis of $LiBaF_3$ by solvothermal crystallization at 180°C is presented. The solvent, mole ratios of initial mixtures and reaction temperature play an important roles in the formation of the products in the solvothermal process. The products have uniform sizes in grain shapes. The product is stable in air. Compared with traditional high temperature solid-state methods and mild hydrothermal synthesis method, the solvothermal synthesis method to complex fluorides appears advantageous in terms of lower synthesis temperature, simple operation, high purity and nice-crystallization.

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