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Short communication

Rapid microwave mediated hydrothermal synthesis of complex ternary fluorides

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Abstract

Complex ternary fluorides like $LiBaF_3$, KY_3F_{10} and β-$NaYF_4$ have been synthesized by microwave mediated hydrothermal synthesis in just 10 min. The proposed synthesis is rapid, economical and needs low temperature as compared to other methods of synthesis available in the literature. Synthesized particles have been characterized by powder X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) Transmission Electron Microscopy (TEM) and BET surface area measurement.

Keywords: Fluoride; Microwave; Hydrothermal

1. Introduction

Complex fluorides have been extensively studied in recent years due to their particular physical properties such as piezoelectric characteristics, photoluminescence behavior, ionic conductivity and nonmagnetic insulator behavior [1–5]. Crystalline fluorides are highly electronic insulating materials and also exhibit enhanced ionic conductivity. Due to higher electronegativity and low polarizability of the fluoride ions, most of the fluorides are highly ionic and have very large band gap. This helps fluoride to find its application in various optical devices, such as windows, clad to wave guides, laser crystals, scintillators and phosphors etc. [6,7]. Among the complex fluorides, $LiBaF_3$, KY_3F_{10} and β-$NaYF_4$ are industrially important fluorides. There are very few synthetic methods available in the literature for the synthesis of these fluorides.

Solid state synthesis of fluoride either requires high reaction temperature or the process needs sophisticated apparatus. Many fluorides (precursors) are corrosive in nature. Synthesis of fluoride by other methods like hydrothermal and reverse micelles is either expensive or time consuming [8–12].

Hua et al. have synthesized $LiBaF_3$ by solvothermal method [13]. Solvothermal synthesis of $LiBaF_3$ has been carried out by reacting BaF_2 and LiF in a teflon container at 180 °C for 2 days. Ethylene glycol was used as a solvent in this case. They have concluded that solvent, molar ratio of initial mixture and reaction temperature play important roles in the synthesis. There are also reports on the synthesis of $LiBaF_3$ by solid state reaction [14,5]. Zhao et al. have synthesized $LiBaF_3$ by hydrothermal method [11]. Two different reaction mixture systems (LiF, BaF_2) and (LiOH, $Ba(OH)_2$, NH_4HF_2) were reacted separately for 5 days at 240 °C to get the required phases. They found that as compared with traditional high-temperature solid-state methods, the hydrothermal synthesis route for the synthesis of complex fluorides appears advantageous in terms of lower synthesis temperature and high purity. Hua et al. have synthesized $BaLiF_3$ nanocrystals by taking cetyltrimethyl ammonium bromide (CTAB)/2-octanol/H_2O microemulsion systems. Though they are not able to synthesize pure $BaLiF_3$, they conclude that particle size of the synthesized products are strongly affected by H_2O content of the reaction medium. Particle size increases with increasing H_2O content and reaction time. The solvent is found to play a key role in the synthesis of the $LiBaF_3$ nanocrystals. Zhao et al. have synthesized KYF_4 via hydrothermal synthesis by reacting KF and Y_2O_3 for seven days [10]. Though large number of studies on KY_3F_{10}

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crystals are reported, studies on KY_3F_{10} nanoparticles are very limited.

In general it was found that synthesis of complex metal fluorides either needs expensive equipment or the synthesis that is time consuming. For a decade, there was the need for the synthesis of these important materials by simple and economical route. Microwave radiation has been used to synthesize large number of inorganic solids in short time. The procedure is also economical [15–20]. Parhi et al. have synthesized KMF_3 (M=Zn, Mn, Mg and Co) by microwave mediated solid state metathesis synthesis [21].

In this communication, we have reported the synthesis of complex ternary fluorides such as $LiBaF_3$, KY_3F_{10} and β-$NaYF_4$ by microwave mediated hydrothermal route in just 10 min. This is the first report of the synthesis of $LiBaF_3$, KY_3F_{10} and β-$NaYF_4$ nanoparticle by microwave mediated hydrothermal synthesis.

2. Experimental

All chemical reagents in this experiment were of analytical grade and used as received without further purification. X-ray diffraction patterns were recorded by a Rigaku, X-ray diffractometer using Ni-filtered Cu-Kα radiation. Scanning Electron Microscopy (SEM) images were obtained using Zeiss ultra55 Scanning Electron Microscope (SEM). Transmission Electron Microscope (TEM) images were obtained by the Model FEI Technai G2 S – Twin.

3. Synthesis of metal fluorides

All the chemicals used in this experiment are of analytical grade and were used as received. LiF, KF, YCl_3 and $BaCl_2$ starting materials were obtained from Himedia, India and were used as received. Synthesis of ternary metal fluorides $LiBaF_3$, KY_3F_{10}, $NaYF_4$ was carried out as follows. Mixture containing LiF and $BaCl_2$ (3:1 M ratio) was transferred to a 50 ml Teflon autoclave containing 20 ml of water. The autoclave was placed in a research grade microwave system (MDS-6, Sineo, China) and heated at 180 °C for 10 min. After the reaction was over, the autoclave was cooled to room temperature. The precipitates were separated by centrifugation at 15,000 rpm for 15 min in REMI ultracentrifuge, washed with de-iodized water and ethanol three times, and dried at 80 °C in oven for 3–4 h. In a similar fashion, synthesis of KY_3F_{10} and $NaYF_4$ was attempted by taking appropriate reactant precursor and necessary reaction condition as mentioned in Table 1.

4. BET surface area measurement

The nitrogen adsorption–desorption isotherm of the samples was measured at liquid nitrogen temperature with a Quantachrome Nova-3200e at −196 °C. Pre-treatment of the samples was carried out at 300 °C for 3 h under high vacuum. The surface area was determined by Brunauer–Emmett–Teller (BET) equation.

Table 1
Reaction conditions for the synthesis of ternary fluorides using microwave mediated hydrothermal technique.

Reactant A	Reactant B	Molar ratio	Method	Compound	JCPDS-no.
LiF	BaCl2	3:1	Microwave hydrothermal	LiBaF3	18-0715
KF	YCl3	4:1	Microwave hydrothermal	KY3F10	27-0465
NaF	YCl3	4:1	Microwave hydrothermal	β-NaYF4	16-0334

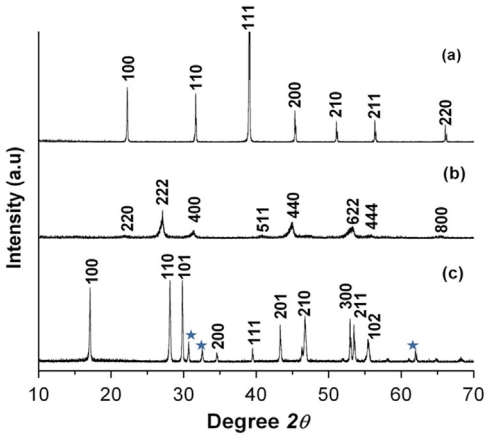

Fig. 1. Powder X-ray diffraction patterns of (a) $LiBaF_3$, (b) KY_3F_{10}, (c) β-$NaYF_4$ synthesized by microwave hydrothermal method.

5. Results and discussion

Fig. 1(a) shows XRD pattern of $LiBaF_3$ synthesized by the microwave mediated hydrothermal method. The powder pattern matches with the database. $LiBaF_3$ crystallizes in cubic system with $a=3.9950(0)$ Å (JCPDS no. 18-0715. Fig. 1 (b) shows XRD of synthesized KY_3F_{10} particle. KY_3F_{10} crystallizes in tetragonal system with $a=b=8.161$ Å and $c=11.53$ Å (JCPDS no. 27-0465). Fig. 1(c) shows XRD pattern of β-$NaYF_4$ synthesized by microwave mediated hydrothermal method. The un-indexed peaks are marked with * marks. These peaks may be as a result of impurities in the product. The XRD result confirms the synthesis of single phase $LiBaF_3$ and KY_3F_{10} whereas synthesis of β-$NaYF_4$ results in mixed phase. The crystalline size of the samples was determined from the Debye–Scherrer formula $D_{hkl}=0.89\lambda/\beta\cos\theta$, where D is the crystalline size in nm, λ is the X-ray wavelength in nm, β is the full width at half maximum intensity in radian, θ is the Bragg diffraction angle. The crystalline size, lattice parameters and unit cell volume of the samples prepared from different precursors are shown in Table 2. Yield of the synthesized products was calculated. The calculated yield for $LiBaF_3$ and KY_3F_{10} was found to be 80% and 36%, respectively.

Fig. 2(a) and (b) shows the SEM images of the synthesized metal fluorides. Well developed cube can be seen in the SEM images for $LiBaF_3$ (as shown in Fig. 2(a)). Fig. 2(b) shows