Hydrothermal synthesis and lanthanide doping of complex fluorides, $LiYF_4$, KYF_4 and $BaBeF_4$ under mild conditions

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The complex fluorides $LiYF_4$, KYF_4, $BaBeF_4$ and AYF_4Eu_x (A = Li, K) are hydrothermally synthesized at 140–240 °C and characterized by powder X-ray diffraction, thermogravimetric analysis, IR spectroscopy, scanning electron microscopy and luminescence measurements.

Recently, we reported on a mild hydrothermal synthesis of the complex fluorides $LiBaF_3$ and $KMgF_3$ with perovskite structures at 120–240 °C,[1] which gives rise to the possibility of making new functional fluoride compounds with various structures and particular properties under mild conditions. It is well known that complex fluorides with strong potential application as luminescence materials can be prepared by solid-state reactions at high temperatures.[2,3] This solid-state synthetic apparatus however requires a complicated set-up due to the erosion of fluorides and thus has limited the study of fluoride chemistry.[4] Mild hydrothermal synthesis, as a low energy-costing and less-polluting method, can enhance the reactivity of reactants in solution and can be used to prepare important crystalline solids which are difficult to prepare or can not be prepared by solid-state reactions, such as in the case of microporous crystals. We have synthesized a number of novel oxides or complex oxides such as microporous solids and solid electrolytes by this moderate preparative technique.[5–10] As an extension of the study on hydrothermal synthesis of complex fluorides with perovskite structures (ABF_3), we have investigated the synthesis of ABF_4-type complex fluorides as well as hydrothermal doping of photo-sensitive lanthanide elements into the fluorides. The aim of our research is to search for a mild hydrothermal synthesis route to produce a variety of complex fluorides and to study the possibility for hydrothermal equilibrium doping of lanthanide ions into the fluorides.

The starting materials for the syntheses of $LiYF_4$ and KYF_4 were LiOH (A.R.), KF (A.R.), Y_2O_3 (99.99%) and HN_4HF_2 (A.R.). Under typical synthesis conditions the mole ratios of the starting materials were 2.0 LiOH : 1.0 Y_2O_3 : 10.0 NH_4HF_2 : 500 H_2O and 3.0 KF : 1.0 Y_2O_3 : 4.0 NH_4HF_2 : 300 H_2O for the syntheses of $LiYF_4$ and KYF_4, respectively. The typical synthetic procedure for crystalline $LiYF_4$ was as follows: 0.08 g LiOH, 0.23 g Y_2O_3 and 0.57 g NH_4HF_2 were added to 9 ml of deionized water (for the synthesis of KYF_4, 0.29 g KF, 0.38 g Y_2O_3 and 0.38 g NH_4HF_2 were used in this step), to form a reaction mixture with a pH of *ca.* 4. The reaction mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 240 °C under autogenous pressure for 7 days. After the autoclaves were cooled and depressurised, the final powder products were washed with deionized water and air-dried at room temperature. In the hydrothermal doping experiment, Eu_2O_3 (99.999%) was used as a reactant in the synthesis of AYF_4Eu_x (A = Li, K), and the reactant mixtures had mole compositions: 2.0 LiOH : 1.0 Y_2O_3 : 10.0 NH_4HF_2 : 500 H_2O : 0.09 Eu_2O_3 and 3.0 KF : 1.0 Y_2O_3 : 4.0 NH_4HF_2 : 300 H_2O : 0.09 Eu_2O_3, for $LiYF_4Eu_x$ and KYF_4Eu_x respectively; the reaction mixtures were heated in Teflon-lined stainless-steel autoclaves at 240 °C for 7 days.

$BaBeF_4$ was prepared by hydrothermal crystallization of a reaction mixture with a mole composition: 1.0 $Ba(OH)_2$: 2.0 BeF_2 : 2.0 NH_4HF_2 : 200 H_2O in Teflon-lined autoclaves at 140 °C for 4 days. The typical synthesis procedure was as follows: 0.79 g of barium hydroxide and 0.24 g of beryllium fluoride (A.R.) were dissolved in 9 ml of deionized water to form a solution, then 0.28 g of NH_4HF_2 (A.R.) was added dropwise to the solution under magnetic stirring. Hydrofluoric acid (40 mass%, A.R.) was used to adjust the pH to 2–4.

All products were characterized by X-ray diffraction (XRD) on a Rigaku D/max-γA diffractometer with a rotating target with Ni-filtered Cu-Kα radiation at room temperature. The XRD data for indexing and cell-parameter calculation were collected by a scanning mode with a step length of 0.02° and a scanning rate of 0.2° min^{-1}. Silicon was used as an internal standard. Observation of the crystallites was performed on a Hitachi X-650 scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was conducted on a TGS-2 thermogravimetric system. IR spectra were obtained with a Nicolet 5DX spectrometer using the KBr pellet technique. Optical measurements were performed at room temperature using a Spex Fluorolog 2 spectrofluorometer.

Table 1 shows the hydrothermal synthesis conditions for $LiYF_4$, KYF_4 and $BaBeF_4$. In the syntheses, ratios of initial composition and the pH of the reaction system were found to be crucial to the formation, crystallization and purity of the products. In the synthesis of $BaBeF_4$, the ratio of Ba/Be is a

Table 1 Hydrothermal synthesis conditions for $BaBeF_4$, $LiYF_4$ and KYF_4

Starting materials		a : b mole ratio	pH	*t*/day	*T*/°C	Phases in product
a	b					
$Ba(OH)_2$	BeF_2	1 : 1	4	4	140	$BaBeF_4$
$Ba(OH)_2$	BeF_2	1 : 1	4	4	180	$BaBeF_4$
$Ba(OH)_2$	BeF_2	1 : 1	4	4	200	$BaBeF_4$
$Ba(OH)_2$	BeF_2	1 : 1	4	4	240	$BaBeF_4$
$Ba(OH)_2$	BeF_2	2 : 1	4	4	240	$BaBeF_4 + BaF_2$
$Ba(OH)_2$	BeF_2	1 : 2	4	4	240	$BaBeF_4$
$Ba(OH)_2$	BeF_2	1 : 1	4	2	240	$BaBeF_4$
$Ba(OH)_2$	BeF_2	1 : 1	4	3	240	$BaBeF_4$
$Ba(OH)_2$	BeF_2	1 : 1	4	4	240	$BaBeF_4$
$Ba(OH)_2$	BeF_2	1 : 1	4	5	240	$BaBeF_4$
LiOH	Y_2O_3	1 : 1	4	7	240	$LiYF_4 + Y_2O_3$
LiOH	Y_2O_3	1 : 1	3	7	240	$LiYF_4 + Y_2O_3$
LiOH	Y_2O_3	2 : 1	4	7	240	$LiYF_4$
LiOH	Y_2O_3	2 : 1	3	7	240	$LiYF_4$
LiOH	Y_2O_3	3 : 1	13	5	240	—[a]
LiF	Y_2O_3	1 : 1	2	5	240	—[a]
KF	Y_2O_3	2 : 1	4	7	240	$KYF_4 + Y_2O_3$
KF	Y_2O_3	3 : 1	4	8	240	KYF_4
KF	Y_2O_3	3 : 1	4	7	240	KYF_4
KF	Y_2O_3	3 : 1	4	3	240	—[a]
KF	$Y(NO_3)_3$	3 : 1	2	7	240	KYF_4

[a] Unknown phases.

Table 2 Lattice parameters of $BaBeF_4$, $LiYF_4$ and KYF_4

		Lattice parameters/Å					
		Obs.			JCPDS[a]		
Compound	Symmetry	*a*	*b*	*c*	*a*	*b*	*c*
$BaBeF_4$	Orthorhombic	8.828	5.324	7.043	8.83	5.34	7.03
$LiYF_4$	Tetragonal	5.166		10.744	5.168		10.736
KYF_4	Hexagonal	8.132		10.043	8.131		10.117

[a] JCPDS cards 20-118, 17-874 and 27-466, respectively.

dominating factor. When the Ba/Be ratio was 0.5, $BaBeF_4$ was formed but when Ba/Be = 2, impurity phases appeared. In the synthesis of $LiYF_4$, when LiOH and Y_2O_3 were employed and the ratio of Li/Y was unity, NH_4HF_2 must be added and a pH of 3–4 was required, addition of a small excess of NH_4HF_2 did not result in the formation of impurities. In the synthesis of the KYF_4, when KF and Y_2O_3 were utilized as starting materials, a ratio of K/Y of 3/2 was optimal. In this case, NH_4HF_2 was also used to supply F^- and to adjust the pH to 2–4.

The pH of the reaction system considerably influences the crystallization of the complex fluorides. For example, using KF and Y_2O_3 as starting materials, KYF_4 can be synthesized at pH *ca.* 4, whereas when $Y(NO_3)_3$ and KF are used, KYF_4 can be prepared at pH *ca.* 2.

It is known that F^- ion is an effective mineralizer in both aqueous and non-aqueous systems.[11–13] In the synthesis of $BaBeF_4$, $LiYF_4$ and KYF_4, F^- ion was either a reactant or a mineralizer. Excess F^- ions may lower remarkably the temperature of crystallization. Thus KYF_4 can be crystallized even at 180 °C, when excess F^- ions are added. Crystallization temperature and time were also important factors for an effective synthesis. Although $BaBeF_4$ can be crystallized below 240 °C, prolonged reaction times are required. For instance, in the BeF_2–BaF_2–HF–H_2O system, $BaBeF_4$ is formed after 2 days at 240 °C, but at 140 °C 4 days are required (Table 1).

The XRD patterns of the $BaBeF_4$, $LiYF_4$ and KYF_4 can be indexed in orthorhombic, tetragonal and hexagonal systems, respectively (Table 2; full XRD data available from the authors on request). The cell of hydrothermally prepared KYF_4 is smaller then that of KYF_4 prepared by solid-state reaction. For $BaBeF_4$ and $LiYF_4$, the two synthetic methods give almost the same cell sizes.

The thermal stability of the $BaBeF_4$, $LiYF_4$ and KYF_4 were studied by TG–DTA in air. There are no phase transformations up to 600 °C in all three systems and no mass losses were observed between 50 and 600 °C. This indicates that the samples are not hydrated and are stable in air, as confirmed by IR spectroscopy in this temperature range.

The morphology of the samples was examined by SEM at room temperature. The results show that the grain size of the product particles is related to the pH of reaction solutions and the nature of cations used in the synthesis. Uniform grain texture of $BaBeF_4$ can be observed with grain sizes ranging from 0.2 to 5 μm. The SEM morphologies of $LiYF_4$ and KYF_4 show regular shapes with grain sizes in the range 0.2–10 μm.

The optimum doping concentrations of Eu^{3+} ions in $LiYF_4$ and KYF_4 were $x = 0.09$ mole in AYF_4Eu_x (A = Li, K) and the highest doping concentration of Eu^{3+} ions was $x = 0.2$. Both excitation and emission spectra show the d–f transition typical of Eu^{3+} compounds. The room-temperature excitation spectrum shows a peak at 393 nm, while the emission spectrum shows $^5D_0$–^7F_J ($J = 0, 1, 2, 3, 4$) five-line peaks and a maximum at 615 nm. All hydrothermally prepared samples showed significant luminescence properties. In the room-temperature excitation spectrum of samples obtained from hydrothermal systems, no charge transition states were observed. This indicates there is no oxygen insertion in the samples which usually occurs in solid-state reactions. A comparison of relative emission intensities for both hydrothermally and solid-state prepared samples is in progress to understand if the equilibrium doping concentration is suitable for optimizing luminescence properties.

In summary, the complex fluorides $BaBeF_4$, $LiYF_4$ and KYF_4 were hydrothermally prepared at 140–240 °C. The molar ratio and pH in the initial reaction mixture associated with the reaction temperature dominate the crystallization of the products. $BaBeF_4$, $LiYF_4$ and KYF_4 crystallize in orthorhombic, tetragonal and hexagonal systems, respectively, and all products have uniform grain sizes. The compounds are air stable and show no insertion of oxygen. Hydrothermal doping of Eu^{3+} ions into $LiYF_4$ and KYF_4 is successful and measurements of the excitation and emission spectra of AYF_4Eu_x (A = Li, K) reveal the same energy level schemes as those previously established based on samples prepared by solid-state reactions. In addition, luminescence studies demonstrate that crystallization of our samples in hydrothermal systems is complete. The hydrothermal synthesis and doping routes are apparently advantageous compared with traditional high-temperature solid-state methods.

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