Hydrothermal synthesis of the complex fluorides $LiBaF_3$ and $KMgF_3$ with perovskite structures under mild conditions

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The complex fluorides, $LiBaF_3$ and $KMgF_3$, which are isostructural with perovskite phases, are hydrothermally synthesized at 120–240 °C and characterized by powder X-ray diffraction, thermogravimetric analysis, IR spectroscopy and scanning electron microscopy.

In recent years, complex fluorides which show various interesting structures have been extensively studied due to their particular physical properties such as piezoelectric characteristics,[1,2] photoluminescence behaviour,[3] ionic conductivity[4] and nonmagnetic insulator behaviour.[5] The preparation of complex fluorides by solid-state reactions at high temperature has been reported, but requirements for the synthetic apparatus, due to the corrosive nature of fluorides, has limited such studies on solid-state syntheses.[4] Reports on the synthesis of some binary fluorides by high-temperature hydrothermal methods above 400 °C are valuable, but were also technically challenging.[6] With an aim towards a mild condition synthesis route to complex fluorides, we studied the hydrothermal synthesis of $LiBaF_3$ and $KMgF_3$ at 120–240 °C.

Preparation and purification of the starting materials MgF_2, KF, LiF and BaF_2 were carried out in graphite crucibles in an argon flow system. All starting materials were dried to constant masses at 250 °C and treated with dried NH_4F. The initial mole ratios for the synthesis of $KMgF_3$ were $1.0KF : 1.0MgF_2 : 100H_2O$, and HF was used as a mineralizer. The typical synthetic procedure for crystalline $KMgF_3$ was as follows: 0.29 g KF and 0.31 g MgF_2 (A.R.) were added to 9 ml deionized water to which 0.04 ml HF (40 mass%, A.R.) was added with stirring. The reaction mixture (pH *ca.* 7) was sealed in a Teflon-lined stainless-steel autoclave and heated at 120–240 °C under autogenous pressure for a week. After the autoclave was cooled and depressurised, the final powder product was washed with deionized water and dried in air at room temperature.

$LiBaF_3$ was prepared by hydrothermal crystallization of a reaction mixture with a mole composition $1.0LiF : 1.0BaF_2 : 400H_2O$ in a Teflon-lined autoclave at 240 °C for 5 days. A second method for the synthesis of $LiBaF_3$ involved a combination of LiOH and $Ba(OH)_2$ solutions, to which NH_4HF_2 was added. The mole ratio of the starting materials was $2.0LiOH : 1.0Ba(OH)_2 : 2.0NH_4HF : 200H_2O$. The typical synthesis procedure was as follows: 0.21 g lithium hydroxide and 0.79 g barium hydroxide hydrate (A.R.) were dissolved in 9 ml deionized water and 0.28 g of ammonium bifluoride (A.R.) was then added dropwise to the magnetically stirred solution. Hydrofluoric acid (40 mass%, A.R.) was used to adjust the pH in the reaction system. The same crystallization procedure as above was adopted.

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 index and cell-parameter calculations were collected by a scanning mode with a step of 0.02° and a scanning rate of 0.2° min^{-1} with silicon used as an internal standard. Observation of the crystallites by SEM was performed on a Hitachi X-650 scanning electron microscope. Thermogravimetric analysis (TGA) was conducted using a TGS-2 thermogravimetric system. IR spectra were obtained with a Nicolet 5DX spectrometer using the KBr pellet technique.

Table 1 reports the hydrothermal synthesis conditions for $LiBaF_3$ and $KMgF_3$. In the syntheses, reactants, ratio of initial composition and pH of reaction system were found to be sensitive to the formation, crystallization and purity of the products.

KF, MgF_2, $Mg(OH)_2$, NH_4HF_2 and $MgCO_3$ can be used as sources for the synthesis of $KMgF_3$. When $Mg(OH)_2$ and KF are employed, NH_4HF_2 must be added and pH values in the range 3–7 must be employed; excess NH_4HF_2, however, resulted in the formation of MgF_2 as impurity owing to a reduction in pH. LiF, BaF_2, LiOH and $Ba(OH)_2$ were utilized as starting materials in the synthesis of $LiBaF_3$, in which LiOH and $Ba(OH)_2$ were the active components. NH_4HF_2 was added to supply F^- and to adjust the pH of the reaction system.

In the synthesis of $LiBaF_3$, the Li/Ba ratio is a dominating factor. Although when the Li/Ba ratio was 2, $LiBaF_3$ is formed, a larger Li/Ba ratio was favourable for crystallization, since not all of the LiOH reacts with $Ba(OH)_2$ in the hydrothermal system, and an appropriate excess of LiOH was employed. With a Li/Ba ratio < 2 an impurity phase of BaF_2 was obtained. The pH of the reaction system, depending upon the starting materials, considerably influenced the crystallization of the complex fluorides. Using KF and MgF_2 as starting materials, $KMgF_3$ could be synthesized at pH *ca.* 7, whereas when $Mg(OH)_2$ and KF were used, $KMgF_3$ could be prepared in the pH range 3–6. When the pH value was in the range 2–12, $LiBaF_3$ could be synthesized in a system with a Li/Ba ratio of 2; best crystallinity was observed at pH *ca.* 7.

F^- ion is an effective mineralizer in both aqueous and nonaqueous systems.[7–9] In the synthesis of $LiBaF_3$ and $KMgF_3$, F^- acts either as a reactant or a mineralizer. The presence of

Table 1 Hydrothermal synthesis conditions for $LiBaF_3$ and $KMgF_3$

Starting materials		a : b mole ratio	pH	Reaction time/d	Reaction temp./°C	Phases in product
a	b					
LiF	BaF_2	1 : 1	11	7	240	$LiBaF_3$
LiOH	$Ba(OH)_2$	2 : 1	2	5	240	$LiBaF_3$
LiOH	$Ba(OH)_2$	2 : 1	7	5	240	$LiBaF_3$
LiOH	$Ba(OH)_2$	2 : 1	12	5	240	$LiBaF_3$
LiOH	$Ba(OH)_2$	1.5 : 1	9	5	240	$LiBaF_3 + BaF_2$
LiOH	$Ba(OH)_2$	2 : 1	9	5	240	$LiBaF_3$
LiOH	$Ba(OH)_2$	1 : 1	4	1	240	$LiBaF_3 + BaF_2$
LiOH	$Ba(OH)_2$	1 : 1	4	3	240	$LiBaF_3 + BaF_2$
LiOH	$Ba(OH)_2$	1 : 1	4	5	240	$LiBaF_3$
LiOH	$Ba(OH)_2$	2 : 1	7	5	140	$LiBaF_3$
KF	MgF_2	1 : 1	7	8	120	$KMgF_3$
KF	MgF_2	1 : 1	7	1	240	$KMgF_3$
KF	MgF_2	1 : 1	2	8	240	$KMgF_3 + MgF_2$

excess F^- ions decreases remarkably the crystallization temperature. Crystallization temperature and time were also important factors for effective synthesis. Although $LiBaF_3$ and $KMgF_3$ can be crystallized at temperatures below 240 °C, this requires longer reaction times. For instance, in the $LiF–BaF_2–HF–H_2O$ system, $LiBaF_3$ is formed at 240 °C in one day, but some reactants are still present and for complete reaction a 5 day crystallization is needed. In the $KF–MgF_2–HF–H_2O$ system, $KMgF_3$ is obtained after 1 day at 240 °C but at 120 °C 8 days are required.

The XRD patterns of the $KMgF_3$ and $LiBaF_3$ are shown in Fig. 1 and can be indexed in cubic systems, giving refined cell parameters *a* of 3.952(2) and 3.996(9) Å, respectively. The unit cell of hydrothermally prepared $KMgF_3$ is smaller than that of $KMgF_3$ prepared by a solid-state reaction (a = 3.9889 Å). For $LiBaF_3$, both synthetic methods give almost the same unit cell size (a = 3.9950 Å for the solid-state synthesis). The XRD index results imply that the crystalline products from hydrothermal systems are pure and no oxygen insertion, which usually occurs in solid-state reactions, was evident.

The thermal stability of the as-prepared $KMgF_3$ and $LiBaF_3$ were studied by TG–DTA analyses in air. No phase transformations were observed up to 600 °C in either system and no mass loss occurred for $KMgF_3$ between 50 and 600 °C. This indicates that $KMgF_3$ is not hydrated and is stable in air. A small mass loss of *ca.* 5% surface water was evident for $LiBaF_3$ between 50 and 100 °C, as confirmed by IR in this temperature range as monitored by absorptions at 3451 and 1630 cm^{-1} due to water.[10] Upon increasing the temperature the surface water is removed.

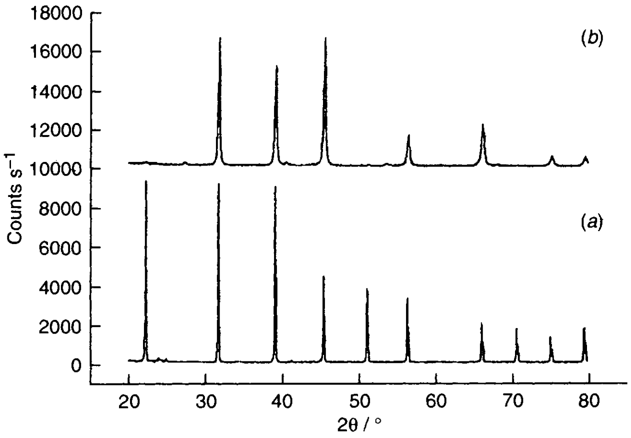

Fig. 1 XRD patterns of $LaBaF_3$ (*a*) and $KMgF_3$ (*b*)

The morphology of the samples was examined by SEM at room temperature. Uniform grain texture of $KMgF_3$ is observed and the average grain size is *ca.* 0.2 μm. The SEM morphology of $LiBaF_3$ reveals regular shapes of thin cubic sheets with a grain size of *ca.* 7.5 μm.

In summary, $KMgF_3$ and $LiBaF_3$ were hydrothermally prepared at 120–240 °C. The Li/Ba and K/Mg molar ratios and pH in the initial reaction mixture associated with the reaction temperature dominate the crystallization of the products. $KMgF_3$ and $LiBaF_3$ crystallize in cubic systems with perovskite structures and have uniform grain sizes and both are air stable. Compared with traditional high-temperature solid-state methods, the hydrothermal synthesis route to complex fluorides appears advantageous in terms of lower synthesis temperature, high purity and crystallinity with no evidence for insertion of oxygen.

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