Solvothermal Synthesis of Complex Fluorides $KCoF_3$ and $KNiF_3$

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(Received December 14, 2001; CL-011262)

Complex fluorides $KCoF_3$ and $KNiF_3$ with perovskite structures were solvothermally synthesized at 120–180 °C and characterized by means of X-ray powder diffraction, scanning electron microscopy, thermogravimetric analysis and infrared spectroscopy.

Perovskite-type fluorides have very interesting physical properties such as ferromagnetic,[1] piezoelectric characteristics,[2] nonmagnetic insulator behaviour,[3] thermal conductivity[4] and well photoluminescence host crystals materials,[5,6] and several ways have been employed to grow single crystals suitable for measurements of their properties. AMF_3 ($A = K$, Na, Cs, Rb; $M = Mg$, Co, Ni, Zn) is one sort of the important complex fluorides because of possible applications as a laser host.[7] Conventional synthesis routes to complex fluorides include solid state reactions[8] at high temperature and high-temperature (>400 °C), high-pressure (>100 MPa) hydrothermal technique.[9] For instance, Skrzypek et al.[10] and Garrard et al.[11] grew $KCoF_3$ crystals by the Bridgman method and a flux method, respectively. Knox[12] and Hirakawa et al.[13] grew $KCoF_3$ and $KNiF_3$ crystals from HF aqueous solutions by evaporating the solvent. Somiya et al.[14] made $KCoF_3$ and $KNiF_3$ by high-temperature (>400 °C), high-pressure (>98 MPa) hydrothermal technique. The solid state synthetic apparatus however requires a complicated set-up because of the erosion of fluorides and high-temperature, high-pressure hydrothermal technique requires special devices. The oxygen content in the complex fluorides synthesized by solid-state reaction is higher than that of the corresponding complex fluorides synthesized by hydrothermal technique[15] and thus has limited the studies of fluorides in the materials chemistry. In order to reduce the oxygen content in the complex fluorides we developed new methods for the preparation of complex fluorides. In this paper, we at the first time report a convenient method for the synthesis of $KCoF_3$ and $KNiF_3$ with perovskite structures under a solvothermal process.

Solvothermal synthesis of $KCoF_3$ and $KNiF_3$ was carried out in a Teflon-lined stainless steel autoclave under autogenous pressure. The starting reactants were KF(A.R.), NiF_2•$4H_2O$(C.P.) and CoF_2(A.R.). The mole ratios of initial mixtures for the synthesis of $KCoF_3$ and $KNiF_3$ were 1.0 KF : 1.0 CoF_2 and 1.0 KF : 1.0 NiF_2, respectively. The typical synthetic procedure for crystalline $KCoF_3$ and $KNiF_3$ was as follows: 0.291 g KF and 0.485 g CoF_2, 0.291 g KF and 0.844 g NiF_2•$4H_2O$ were mixed respectively, and added into a Teflon-lined autoclave of 20 mL capacity. Then the autoclave was filled with absolute ethanol (for the synthesis of $KCoF_3$) or ethylene glycol (for the synthesis of $KNiF_3$) 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 7days. After being cooled to room temperature naturally, the final powder products were filtered off, washed with absolute ethanol and distilled water, and then dried in air at ambient temperature.

The crystalline products were identified by X-ray powder diffraction (XRD) on a Japan Rigaku D/max-IIB diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ 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 $4.0\,°\cdot min^{-1}$ with silicon used as an internal standard. Observation of crystallites by SEM was performed on a JXA-840 scanning electron microscopy. Thermogravimetric analysis (TGA) was conducted using a DT-30 Thermogravimetric system. IR spectra were obtained with a Magna 560 spectrometer in the range 400–4000 cm^{-1}. The sample was pressed KBr pellets for the spectral measurements.

Table 1 lists the preparation conditions for $KCoF_3$ and $KNiF_3$. In the syntheses, the ratio of initial composition was found to be sensitive to the formation, crystallization, and purity of the products. As shown in Table 1, when the mole ratios K/Co (or Ni) of mixtures were 1 or 2, the pure and well-crystallized products were prepared. However, when the mole ratio K/Co (Ni) of mixtures was 0.5, unreacted CoF_2 (NiF_2) remained as an impurity. The possible reaction mechanism can be formulated

Table 1. Solvothermal synthesis conditions for $KCoF_3$ and $KNiF_3$

Starting materials a	Starting materials b	a : b mole ratio	Solv.[a]	Time /d	Reaction Temp./ °C	Phases in product
KF	CoF_2	1 : 1	A	7	180	$KCoF_3$
KF	CoF_2	2 : 1	A	7	180	$KCoF_3$
KF	CoF_2	3 : 1	A	7	180	$KCoF_3$+KF
KF	CoF_2	1 : 2	A	7	180	$KCoF_3$+CoF_2
KF	CoF_2	1 : 1	A	1	180	$KCoF_3$
KF	CoF_2	1 : 1	A	2	180	$KCoF_3$
KF	CoF_2	1 : 1	A	1	150	$KCoF_3$
KF	CoF_2	1 : 1	A	2	150	$KCoF_3$
KF	CoF_2	1 : 1	A	1	120	$KCoF_3$
KF	CoF_2	1 : 1	A	2	120	$KCoF_3$
KF	NiF_2	1 : 1	B	7	180	$KNiF_3$
KF	NiF_2	2 : 1	B	7	180	$KNiF_3$
KF	NiF_2	3 : 1	B	7	180	$KNiF_3$+KF
KF	NiF_2	1 : 2	B	7	180	$KNiF_3$+NiF_2
KF	NiF_2	1 : 1	B	1	180	$KNiF_3$
KF	NiF_2	1 : 1	B	2	180	$KNiF_3$
KF	NiF_2	1 : 1	B	1	150	$KNiF_3$
KF	NiF_2	1 : 1	B	2	150	$KNiF_3$
KF	NiF_2	1 : 1	B	1	120	$KNiF_3$
KF	NiF_2	1 : 1	B	2	120	$KNiF_3$

[a] Solvent A was ethanol and B was ethylene gloycol.

as follows:

$KF \overset{H_2O}{=} K^+ + F^-$ (a trace of water is coming from the solvents)

$MF_2 + nR \rightleftharpoons MF_2 \cdot nR$

$MF_2 \cdot nR + K^+ + F^- = KMF_3 + nR$

(M = Co or Ni, R = ethanol, ethylene glycol, n = 6 and 2,)

The XRD patterns of the $KCoF_3$ and $KNiF_3$ are shown in Figure 1 and can be indexed in cubic systems with space group P_{m3m}. The unit-cell parameter for $KCoF_3$ is $a = 4.0703$ Å and for $KNiF_3$ is $a = 4.0152$ Å. The value for $KCoF_3$ is similar to that of the corresponding $KCoF_3$ synthesized by solid-state reaction ($a = 4.0708$ Å) [JCPDS Card 18-1006]. The value for $KNiF_3$ is slightly bigger than that of the corresponding $KNiF_3$ synthesized by solid-state reaction ($a = 4.0127$ Å) [JCPDS Card 21-1002]. The powder XRD patterns show that the products are pure.

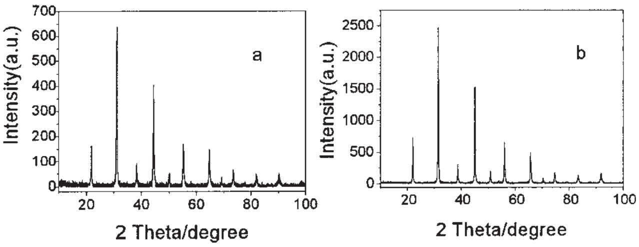

Figure 1. XRD patterns of $KCoF_3$ (a) and $KNiF_3$ (b).

The SEM observation of the product shows that the crystallites have regular morphology and this implies that the products are a pure and single phase. The two complex fluorides $KCoF_3$ and $KNiF_3$ have the same cubic shape, and the average grain sizes are ca. 8 μm and 9 μm, respectively. The analytical data for $KCoF_3$ and $KNiF_3$ crystals are in good agreement with the formulas whose mole ratio of K : Co (or Ni) is 1 : 1.

The thermal stability of the as-prepared $KCoF_3$ and $KNiF_3$ was studied by TG-DTA analysis in air. No phase transformations was observed up to 700 °C in either system and no mass loss occurred for $KCoF_3$ between 50 and 700 °C. This indicates that $KCoF_3$ is not hydrated and is stable in air. The presence of ca. 2.6% surface water was evident for $KNiF_3$ between 50–110 °C, as confirmed by IR at 3437.4 cm^{-1} and 1642.9 cm^{-1}.

In summary, a new method for the synthesis of $KCoF_3$ and $KNiF_3$ by solvothermal crystallization at 120–180 °C is presented. Both $KCoF_3$ and $KNiF_3$ crystallize in cubic systems with the perovskite structure. All the products have uniform grain shapes and sizes. The mole ratios are crucial to the synthesis. Compared with traditional high temperature solid-state methods, flux method, HF aqueous solutions method, high-temperature, high-pressure hydrothermal synthesis method 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 well-crystallization.

This work was supported by the State Key Project of Foundation Research (G1998061306) and National Nature Science Foundation of China (50072031).

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