Hydrothermal Synthesis of Complex Fluorides $NaHoF_4$ and $NaEuF_4$ with Fluorite Structures under Mild Conditions

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The complex fluorides $NaHoF_4$ and $NaEuF_4$ with fluorite structures were hydrothermally synthesized and characterized by means of X-ray powder diffraction, scanning electron microscopy, thermogravimetric analysis, and infrared spectroscopy.

Introduction

Since the 1960s, a number of papers[1−3] have reported the solid-state syntheses of complex fluorides in sodium fluoride−rare-earth trifluoride systems. Some complex fluorides with general formula ABF_4 (A = Li, Na; B = trivalent transition metals and rare-earth elements) possess scheelite and fluorite structures, which are important host crystals for solid-state lasers.[2] Various isomorphous replacements in the framework of complex fluorides lead to many controllable properties.[3] However, most complex fluorides[4] were prepared from the melt under an atmosphere of HF mixed with an inert carrier gas. For instance, Shaimuradov's group[5] made some fluorides by heating a mixture of KF and HoF_3 in quartz vessel up to 1000 °C. A flux growth method[6] and high-temperature (>400 °C), high-pressure (>100 MPa) hydrothemal technique[7] were also reported. Taking into account some of the interesting properties of the complex fluorides, such as photoluminescence behavior,[8] ferromagnetic,[9] paramagnetic,[10] and magnetolastic characteristics,[11] and with an aim to develop new routes without complicated syntheses apparatus, we have made a number of complex fluorides (ABF_3) with perovskite structures[15] under mild hydrothermal conditions. In this paper, we report a hydrothermal synthesis of two complex fluorides, $NaHoF_4$ and $NaEuF_4$, both with fluorite structures.

Experiment

Hydrothemal synthesis of $NaHoF_4$ and $NaEuF_4$ was carried out in a Teflon-lined stainless steel autoclave under autogenous pressure. The starting reactants were NaOH (A.R.), NaF (A.R.), Ho_2O_3 (A.R.), Eu_2O_3 (A.R.), NH_4HF_2 (A.R.), NH_4F (A.R.), and HF (A.R.). The mole ratios of initial reaction mixtures for the synthesis of $NaHoF_4$ and $NaEuF_4$ were 6.0 NaOH:1.0 Ho_2O_3:6.0 NH_4F:6.0 HF:100 H_2O and 6.0 NaOH: 1.0 Eu_2O_3:6.0 NH_4F:6.0 HF:100 H_2O, respectively, and HF was used as a mineralizer and added with stirring to adjust the pH of the mixture. In the other method of preparing $NaHoF_4$ and $NaEuF_4$, NaF and NH_4HF_2 were used as starting materials in place of HF and NH_4F. The mole ratios of mixture were 2.0 NaF:1.0 Ho_2O_3:6.0 NH_4HF_2 and 2.0 NaF:1.0 Eu_2O_3:6.0 NH_4HF_2, respectively. Reaction mixtures were sealed with 80% fill in a Teflon-lined stainless steel autoclave for hydrothermal crystallization at 240 °C. After the autoclave was cooled and depressed, the final powder product was washed with deionized water and dried in air at room temperature.

The crystalline products were identified by X-ray powder diffraction (XRD) on a Rigaku D/Max A diffractometer using Cu Kα (λ = 1.5418 Å) radiation. 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. Silicon (99.99%) was used as an external standard. Scanning electron micrographs (SEM) were performed on a Hitachi X-650B electron microscope equipped with an X-ray energy-dispersive analyzer (EDAX). Thermogravimetric analysis (TGA) was conducted by using a TGS-2 thermogravimetric system. The IR spectra were recorded with a Nicolet 5DX Model FT spectrometer using a KBr pellet technique.

Results and Discussion

Table 1 lists the preparation conditions for $NaHoF_4$ and $NaEuF_4$. In the syntheses, the ratio of initial composition and pH of the reaction system were found to be sensitive to the formation, crystallization, and purity of the products.

In the syntheses of $NaHoF_4$ and $NaEuF_4$, F^- acts both as a reactant and as a mineralizer.[12−15] From Table 1, when the mole ratios F/Ho of mixture was 7, the pure and well-crystallized product was prepared. However, when the mole ratio F/Ho of mixture was 5, unreacted Ho_2O_3 remained as an impurity. Therefore, excess F^- is necessary for obtaining a pure product.

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(1) Thoma, R. E. *Proc. Conf. Rare Earth Res.*, fourth, Phoenix, 1964, pp 561−70 (published 1956).

(2) Insley, H.; Hebert, G. M. *Inorg. Chem.* **1966**, *5*, 1222−9.

(3) Della, M.; Roy, J. *Electrochem. Soc.* **1964**, *111*, 421−9.

(4) Pastor, R. C.; Robinson, M.; Akutagawa, W. M. *Mater. Res. Bull.* **1975**, *10*, 501−9.

(5) Shaimuradov, I. B.; Reshetnikova, L. P.; Novoselova, A. V. *Vestn. Mosk. Univ., Khim.* **1973**, *14*, 367−9.

(6) Wanklyn, B. M. *J. Mater. Sci.* **1975**, *10*, 1487−93.

(7) Demianets, L. N. *Prog. Cryst. Growth Charact.* **1990**, *21*, 299−355.

(8) Zakaria, D.; Fournier, M. T.; Mahiou, R.; Ccosseins, J. C. *J. Alloys Compd.* **1992**, *188*, 250−4.

(9) Cooke, A. H.; Jones, D. A.; Silva, J. F. A.; Wells, M. R. *J. Phys. C* **1975**, *8*, 4083−8.

(10) Janssen, P.; De groot, P.; De vos, G.; Herlach, F.; Witters, J. *High field Magn., Proc. Int. Symp.* **1982**, 241−3.

(11) Abdulsabirov, R.Yu.; Kazei, Z. A.; Korablev, S. L.; Terpilovskii, D. N. *Fiz. Tverd. Tela (St. Peterburg)* **1993**, *35*, 1876−80.

(12) Guth, J. L.; Kessler, H.; Wey, R. *Proc. 7th Int. Zeolite Conf., Tokyo* 1986, 121.

(13) Estermann, M.; Mclusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* **1991**, 352.

(14) Bukovec, P.; Bukuvel, N.; Demsar, A. J. *Therm. Anal.* **1990**, *36*, 1751.

(15) Chunyan, Z.; Shouhua, F. *J. Chem. Soc., Chem. Commun.* **1996**, 1641.

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Table 1. Hydrothermal Synthesis Conditions for $NaHoF_4$ and $NaEuF_4$

starting materials								
a	b	c	d	a:b:c:d mole ratio	PH value	react temp (°C)	react time (days)	phases in product
NaF	Ho_2O_3	NH_4HF_2		2:1:3	10.0	240	7	$NaHoF_4$ + multiphase
NaF	Ho_2O_3	NH_4HF_2		2:1:3.5	8.0	240	7	$NaHoF_4$ + multiphase
NaF	Ho_2O_3	NH_4HF_2		2:1:4	7.0	240	7	$NaHoF_4$ + multiphase
NaF	Ho_2O_3	NH_4HF_2		2:1:5	5.0	240	7	$NaHoF_4$
NaF	Ho_2O_3	NH_4HF_2		2:1:6	4.0	240	5	$NaHoF_4$
NaOH	Ho_2O_3	NH_4F	HF	6:1:6:6	3.5	240	5	$NaHoF_4$
NaF	Ho_2O_3		HF	2:1: :3	2.0	240	7	$NaHoF_4$ + multiphase
NaF	Ho_2O_3		HF	2:1: :6	1.5	240	7	$NaHoF_4$ + multiphase
NaF	Eu_2O_3	NH_4HF_2		2:1:4	7.0	240	7	$NaEuF_4$ + multiphase
NaF	Eu_2O_3	NH_4HF_2		2:1:6	4.0	240	7	$NaEuF_4$
NaOH	Eu_2O_3	NH_4F	HF	6:1:6:6	4.0	240	7	$NaEuF_4$
NaF	$Eu(NO_3)_3$	NH_4HF_2		1.1:1:3	4.0	240	7	$NaEuF_4$

Table 2. XRD Data for $NaHoF_4$

h	*k*	*l*	d_{obs}/Å	d_{cal}/Å	I/I_0
1	0	0	5.2066	5.1888	95
1	1	0	2.9979	2.9958	100
1	0	1	2.9253	2.9227	93
2	0	0	2.5950	2.5944	14
1	1	1	2.2862	2.2861	19
2	0	1	2.0917	2.0920	74
2	1	0	1.9604	1.9612	13
0	0	2	1.7681	1.7686	13
3	0	0	1.7290	1.7296	38
2	1	1	1.7145	1.7152	57
1	0	2	1.6743	1.6740	10

Table 3. XRD Data for $NaEuF_4$

h	*k*	*l*	d_{obs}/Å	d_{cal}/Å	I/I_0
1	0	0	5.2690	5.2477	71
1	1	0	3.0342	3.0298	92
1	0	1	2.9865	2.9826	100
2	0	0	2.6261	2.6239	12
1	1	1	2.3266	2.3247	17
2	0	1	2.1267	2.1255	75
2	1	0	1.9842	1.9835	11
0	0	2	1.8130	1.8125	15
3	0	0	1.7497	1.7492	40
2	1	1	1.7404	1.7400	65
1	1	2	1.5555	1.5554	14
2	2	0	1.5149	1.5149	10

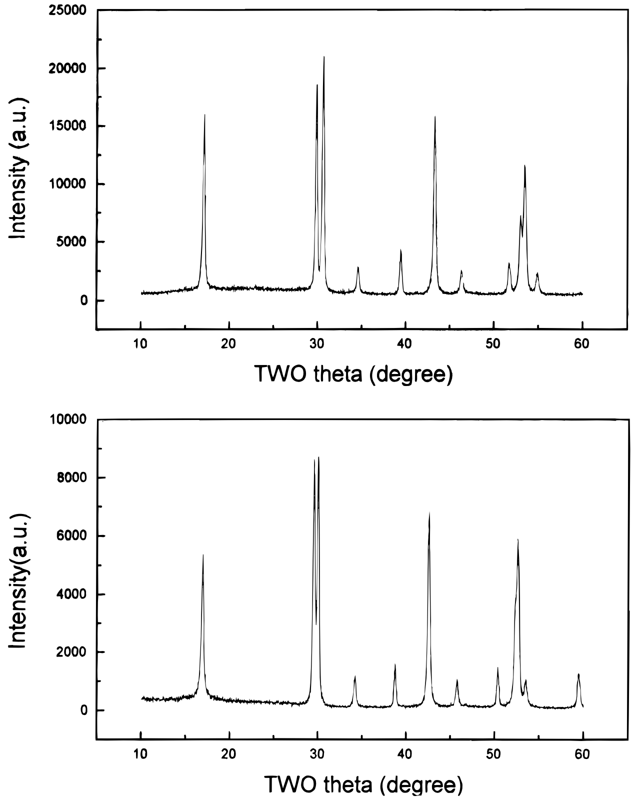

Figure 1. XRD patterns of $NaHoF_4$ (up) and $NaEuF_4$ (down).

A pH value of 4 was found to favor the formation of $NaHoF_4$ and $NaEuF_4$. Therefore, NH_4HF_2 can be used instead of HF to provide a pH value of ca. 4 and eliminate possible air pollution by HF.

Figure 1 shows the XRD of $NaHoF_4$ and $NaEuF_4$, respectively. These two compounds crystallize in a hexagonal system with space group P_6. The unit-cell parameters for $NaHoF_4$ are a = 5.991 Å, c = 3.537 Å, and for $NaEuF_4$, a = 6.059 Å, c = 3.625 Å. The values for $NaHoF_4$ are similar to those for the corresponding $NaHoF_4$ synthesized by solid-state reaction (a = 5.991 Å, c = 3.536 Å) [3, JCPDS Card 18-1253]. The values for $NaEuF_4$ were slightly bigger than those for the corresponding $NaEuF_4$ synthesized by solid-state reaction (a = 6.044 Å, c = 3.613 Å) [JCPDS Card 28-1085]. The powder XRD patterns show the product free of impurities.

The SEM observation (Figure 2) of the product shows that the crystallites have regular morphology and this implies that the product is a pure and single phase. The two complex fluorides have different shapes. The morphology of $NaHoF_4$ is blocklike, and the average grain size is ca. 0.83 × 1.33 μm, the $NaEuF_4$ crystallites are needlelike with average grain size of ca. 0.2 × 1.33 μm. The contents obtained by EDAX for $NaHoF_4$ and $NaEuF_4$ are in good agreement with the formulas whose mole ratio of Na:Ho (or Eu) is 1:1.

The thermal stability of the as-prepared $NaHoF_4$ and $NaEuF_4$ were studied by TG-DTA analyses in air. No phase transition or mass loss was observed from 25 °C up to 650 °C in either system. These observations indicate that $NaHoF_4$ and $NaEuF_4$ are not hydrated and are stable in dry air, which was confirmed by IR measurement in the temperature range 25−150 °C.

Conclusions

In summary, a new method for the synthesis of $NaHoF_4$ and $NaEuF_4$ by mild hydrothermal crystallization at 240 °C is presented. Both $NaHoF_4$ and $NaEuF_4$ crystallize in hexagonal systems. All the products have uniform grain sizes. The two compounds are stable in air and free of impurities. The molar ratios and pH values are effective for the syntheses. Excess F^- and

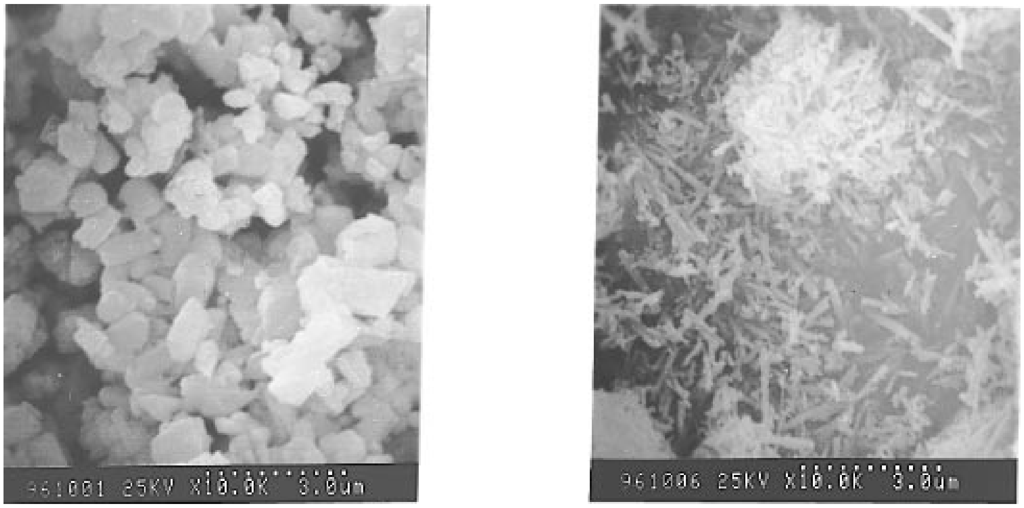

Figure 2. SEM photographs of $NaHoF_4$ (left) and $NaEuF_4$ (right).

soluble sources (NaF, NaOH) dominate the crystallization of the product. Using NH_4HF_2 as a starting material not only provides F^- reactant but also adjusts the mixture to a suitable pH value and avoids air pollution due to HF. Compared with traditional high-temperature solid-state methods, flux methods, and melt methods, the mild hydrothermal synthesis method presents a considerable potential for syntheses of high-purity complex fluoride at low temperatures and low pressures and involved no pollution of the atmosphere.

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