Soft Chemistry Synthesis of Powders in the BaF₂–ScF₃ System

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Abstract—The BaF₂–ScF₃ system is studied using coprecipitation from aqueous solutions. Compound Ba₃Sc₂F₁₂ is found to form over a wide range (10–60 mol %) of scandium concentrations in the initial solution. At higher scandium concentrations in solution, a new phase of provisional composition BaSc₂F₈ · 2H₂O (hexagonal system, a = 9.6346 Å, c = 4.0483 Å) was obtained. Scandium fluoride hydrolysis is not observed by energy-dispersive X-ray analysis.

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Fluoride nanopowders in recent years have received appreciable attention from researchers due to the specific properties of nanosized materials and the unique set of physical and chemical properties of fluorides [1-6]. This combination opens a way to design a new generation of scintillators and white light sources and to use fluorides in biomedical applications and so on.

Scandium fluoride is the highest melting inorganic fluoride (its melting point is 1550°C [7]). The high volatility of scandium fluoride near the melting point creates difficulties in syntheses of its based materials and makes it pertinent to search for low-temperature synthetic methods. ScF₃ crystallizes in a ReO₃ type structure, space group Pm3m (with only very small trigonal distortions of the cubic lattice) [8, 9]. This constitutes a strong distinction of scandium fluoride from the other rare-earth fluorides, while formally scandium fluoride is a member of this family [10]. In terms of crystal chemistry, scandium in fluorides is close to indium [11], but its compounds are distinguished by greater chemical stability. Scandium fluoride compounds are of interest as components of antireflecting coatings with low refractive indices and as matrices to be doped with dopants having small ionic radii, in particular Cr^{3+} .

Noteworthy, scandium fluoride nanomaterials remain virtually unstudied. There are only few relevant publications [12, 13], in contrast to numerous publications concerning, for example, nanosized yttrium fluorides.

Barium fluoride crystallizes in a fluorite type structure (space group Fm3m). Its high-pressure orthorhombic phase is known to be formed during the synthesis of BaF₂ powders (space group *Pnam*) [4].

The most reliable data on the BaF_2 -ScF₃ system are those published in [14]. This system forms two compounds with close compositions: $Ba_3Sc_2F_{12}$ (space group P4/mbm, tetragonal unit cell parameters: a =9.482 Å, c = 5.587 Å), which is stable below 740°C, and the high-temperature congruently melting $Ba_5Sc_3F_{19}$ (space group *P4/mbm*, unit cell parameters: a = 21.07Å, c = 15.38 Å). Ba_{1-x}Sc_xF_{2+x} solid solution (x < 0.09) was found to exist at high temperatures; this solid solution has high fluoride-ion conductivity [15] and serves as the basis for creating a promising scintillator [16]. The scandium distribution coefficient during barium fluoride crystallization appreciably differs from unity [17], so that it is difficult to obtain samples with a uniform distribution of the dopant by melt crystallization. Ceramic synthesis using soft-chemistry methods is preferred in this context.

Barium-containing nanosized fluorides are promising theranostics due to their high X-ray contrast [5].

In continuation of our studies into the preparation of nanosized fluorides [18–29], here we study the preparation of powders in the BaF_2 –ScF₃ binary system using coprecipitation from aqueous solutions.

SYNTHESES

Syntheses were accomplished by coprecipitation from aqueous solutions. The initial chemicals used were barium nitrate (high purity grade 10-2), scandium nitrate (chemically pure grade), hydrofluoric acid (high purity grade 27-5), and aqueous ammonia (pure for analysis grade). Precipitation was accomplished in a polypropylene reactor. First, initial solutions of the nitrates were prepared in bidistilled water. The nitrate solutions were mixed and added dropwise



Fig. 1. X-ray diffraction patterns for samples precipitated from solutions in the BaF₂–ScF₃ system. Scandium percentage in the initial solution, mol %: (1) 0, (2) 5, (3) 10, (4) 50, (5) 60, (6) 65, (7) 80, (8) 95, and (9) 100.

to the magnetically stirred hydrofluoric acid solution. The white slurry formed in the course of mixing was separated from the mother solution, washed with bidistilled water, neutralized with aqueous ammonia, and dried at a temperature below $<100^{\circ}$ C. Concentrations of the nitrate solutions were varied in the range 0.1–0.2 mol/L; the hydrofluoric acid solution concentration was 11 vol %.

The phase compositions of as-synthesized samples were determined by X-ray powder diffraction on DRON-4M and Bruker D8 diffractometers (Cu $K_{\alpha 1}$ radiation). Unit cell parameters were calculated from X-ray diffraction data using Powder 2.0 and TOPAS software. Thermogravimetric studies were carried out on a Q 1500D (MOM) derivatograph under heating to 600°C at 10 K/min. Scanning electron microscopy (SEM) studies were performed on a Carl Zeiss NVision 40 microscope. Compositions of samples were estimated from energy-dispersive X-ray analysis in a scanning electron microscope. IR spectra were recorded on an INFRALUM FT08 spectrometer equipped with an ATR (attenuated total internal reflectance) attachment.

RESULTS AND DISCUSSION

Samples were prepared with different barium and scandium contents in the initial solutions. Relevant X-ray diffraction patterns are shown in Fig. 1.

The unit cell parameter of an undoped fluorite barium fluoride sample prepared by the above-described procedure was a = 6.1903 Å. This value noticeably differs from the literature data (a = 6.200 Å [PCPDFWIN no. 04-0452]), but well corresponds with the results obtained for barium fluoride prepared by precipitation with hydrofluoric acid [29]. When the scandium content in the solution was 5 mol %, a single-phase sample of Ba_{1-x}Sc_xF_{2+x} cubic solid solution with the parameter a = 6.0421 Å was prepared. When the scandium percentage in the initial solution was 10 mol %, X-ray diffraction patterns featured distinct reflections from a second phase; these reflections corresponded to the compound Ba₃Sc₂F₁₂ (with the unit cell parameters a = 9.4923 Å, c = 5.6001 Å).

The compound $Ba_3Sc_2F_{12}$ was precipitated over a wide range of concentrations, when scandium percentages in the initial solution were 10-60 mol %. An X-ray diffraction pattern from a sample prepared when scandium percentage in the initial solution was 50 mol %, corresponded to the compound $Ba_3Sc_2F_{12}$ in a pure form. Indexing of the X-ray diffraction pattern is shown in Table 1. Calculated unit cell parameters (space group *P*4/*mbm*, a = 9.489 Å, c = 5.568 Å) correspond with the published values. Figure 2a displays SEM data for this sample. Micron-sized agglomerations composed of particles with sizes of from 30 to 500 nm can be distinguished in the SEM images. A single-phase sample was also prepared when the scandium percentage in the solution was increased to 60 mol %; the X-ray diffraction pattern for this sample corresponded to the compound $Ba_3Sc_2F_{12}$ (a = 9.469 Å, c = 5.559 Å), but particle morphology was quite different. Particles with sizes of ~30 nm are distinguishable in the SEM image (Fig. 2b).

As the scandium percentage in the initial solution increased further, $Ba_3Sc_2F_{12}$ was no longer formed.



Fig. 2. SEM images of powders with as-batch compositions: (a) $0.50BaF_2-0.50ScF_3$ and (b) $0.40BaF_2-0.60ScF_3$.

The major phase became an earlier unknown phase X. The sample obtained from the solution where the scandium percentage was 65 mol %, was a single phase; its X-ray diffraction pattern was indexed in terms of a hexagonal space group with the unit cell parameters: a =9.6346 Å, c = 4.0483 Å (Table 2). Its IR spectra featured absorption bands (at 1430, 1630, 3580 cm⁻¹) that corresponded to the vibrations of water molecules and OHgroups. Thermogravimetric studies showed that the sample lose 9.1% of its weight in the range 100-285°C. Calculations imply the chemical formula $BaSc_2F_8 \cdot 2H_2O$. According to X-ray powder diffraction, the samples after DTG were comprised of two phases: compound Ba₃Sc₂F₁₂ (a = 9.4932 Å, c = 5.9447 Å) and scandium fluoride (a = 4.014 Å). The corresponding decomposition reaction is

 $3BaSc_2F_8 \cdot 2H_2O = Ba_3Sc_2F_{12} + 4ScF_3 + 6H_2O.$

Figures 3b and 3c display SEM images of this phase. Particles having extended shapes ("rods") with diameters of 30–50 nm and lengths of up to 200 nm are distinguished in the micrograph.









Fig. 3. SEM images of powders with as-batch compositions: (a) $0.50BaF_2-0.95ScF_3$ and (b, c) $0.35BaF_2-0.65ScF_3$.

As the scandium percentage in the initial solution increased 95 mol %, two-phase samples were precipitated; they were composed of $BaSc_2F_8 \cdot 2H_2O$ and ScF_3 in various proportions. Figure 3a displays a SEM image of a two-phase sample where the scandium percentage in the initial solution was 95 mol %. Large

hkl	$d_{\rm e}, {\rm \AA}$	2θ, deg	$I/I_0, \%$	ΔQ
200	4.736	18.72	6	1.38
111	4.287	20.70	30	-0.19
210	4.236	20.95	21	1.72
201	3.607	24.66	89	2.15
211	3.373	26.39	37	0.96
220	3.367	26.45	100	-6.88
310	3.000	29.75	19	-0.04
221	2.873	31.10	5	0.68
002	2.781	32.15	15	4.54
311	2.638	33.95	7	3.94
202	2.401	37.42	5	1.92
400	2.370	37.93	7	2.65
212	2.328	38.64	30	0.95
410	2.302	39.10	11	-1.39
330	2.238	40.26	15	-3.70
401	2.182	41.34	15	0.31
222	2.144	42.10	33	-2.27
420	2.124	42.52	36	-6.52
331	2.074	43.61	25	3.61
312	2.043	44.30	54	-3.04
322	1.913	47.49	13	0.07
113	1.790	50.96	8	-0.62
511	1.766	51.73	25	-3.50
203	1.730	52.88	13	-0.83
213	1.702	53.82	13	-1.08
521	1.680	54.57	13	-2.10
530	1.628	56.48	15	-4.41
600	1.581	58.32	11	2.08
621	1.450	64.18	18	-9.71
413	1.445	64.41	19	0.28
532	1.406	66.41	14	-10.92
602	1.376	68.08	12	-7.34
114	1.363	68.82	11	8.58
701	1.317	71.60	11	0.50

Table 1. Indexing an X-ray diffraction pattern for a $Ba_3Sc_2F_{12}$ phase

Table 2. Indexing an X-ray diffraction pattern for a $BaSc_2F_8 \cdot 2H_2O$ phase, which was precipitated from a solution where the scandium percentage was 65 mol %

hkl	$d_{\rm e}, {\rm \AA}$	2θ, deg	<i>I</i> / <i>I</i> ₀ , %	ΔQ
100	8.344	10.61	10	0.01
110	4.817	18.40	17	-0.05
200	4.172	21.28	15	0.03
101	3.642	24.42	32	-0.10
210	3.154	28.28	20	0.21
111	3.099	28.78	55	-0.16
030	2.781	32.16	21	-0.25
211	2.488	36.07	14	0.17
310	2.314	38.89	12	-0.25
301	2.292	39.27	84	-0.66
400	2.086	43.34	5	0.11
221	2.070	43.69	100	0.06
002	2.024	44.74	71	-0.36
311	2.009	45.09	10	-0.17
320	1.914	47.46	19	-0.57
112	1.866	48.76	30	-0.33
401	1.854	49.09	46	-0.85
140	1.821	50.05	16	0.77
410	1.821	50.06	49	0.77
321	1.731	52.86	5	1.93
212	1.703	53.77	28	-1.86

A primitive hexagonal lattice with the parameters: a = 9.6346 Å, c = 4.0483 Å.

group Pm3m). Noteworthy, the samples were not hydrolyzed as probed by energy-dispersive X-ray analysis, while in the BaF₂-RF₃ (R = Bi or Y) systems, hydrolysis was observed for low barium concentrations.

Low-temperature syntheses in this system yielded virtually the same phases as were identified in approaching equilibrium "from above."

In summary, a method to prepare single-phase $Ba_3Sc_2F_{12}$ powders in approaching equilibrium "from above" has been found. Noteworthy, inasmuch as this compound is stable only in a low-temperature range, its solid-phase synthesis is very difficult and would require long-term anneals, especially in view of the high melting temperatures of the constituents. A small scatter in unit cell parameters of samples may be indicative of the existence of a homogeneity range in this phase. $Ba_3Sc_2F_{12}$ served us to demonstrate the feasibility to control the dispersion of precipitations via altering the component ratio in the initial solution. The dispersion of the precipitate is of importance both for biomed-

The test sample was precipitated from a solution where the scandium and barium percentages each were 50 mol %. A primitive tetragonal lattice with the parameters: a = 9.489(1) Å, c = 5.5768(2) Å. $\Delta Q = 10^4 (1/d_e^2 - 1/d_e^2)$.

cubic particles having sizes of 100–500 nm are distinguished in the micrograph.

We also prepared scandium fluoride. The calculated unit cell parameter was a = 4.0035 Å (space

ical applications of fluoride nanopowders, and for using them as precursors for ceramics.

We have been the first to carry out systematic syntheses of samples in the BaF_2 -ScF₃ system by means of coprecipitation from aqueous solutions. We have prepared $Ba_{1-x}Sc_xF_{2+x}$ solid solution, compounds $Ba_3Sc_2F_{12}$ and ScF₃, and an earlier unknown phase whose composition has been provisionally formulated as $BaSc_2F_8 \cdot 2H_2O$ and which has been indexed in terms of the hexagonal crystal system.

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