Original articles

Stabilization of the $Ba_4Y_3F_{17}$ phase in the NaF-BaF_2-YF_3 system

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Abstract

The paper describes the study of the phase formation in the NaF-BaF_2-YF_3 system. It involved solid-phase sintering of the components in a fluorinating atmosphere at 750 °C for two weeks and quenching them in liquid nitrogen.

The prepared samples were placed in nickel capillaries, which, together with barium hydrofluoride, $BaF_2 \cdot HF$, were placed in copper containers. The containers were sealed by argon arc welding. The fluorinating atmosphere was created by pyrolysis of barium hydrofluoride, $BaF_2 \cdot HF$. X-ray powder diffraction was carried out using a Bruker D8 Advanced diffractometer ($CuK\alpha$-radiation). TOPAS, DifWin, and Powder 2.0 software were used to process X-ray diffraction patterns.

Sodium fluoride is a good sintering additive, its introduction in the amount of 5 mol % NaF was enough to synthesize sintered mass with clear X-ray diffraction patterns. The experiment revealed the formation of a solid solution based on the $Ba_4Y_3F_{17}$ compound with a trigonally distorted fluorite structure (space group R-3) with a content of up to ~ 20 mol % of NaF. The parameters of the trigonal cell were related to the parameter a_0 of the fluorite subcell by the ratios $a \sim \sqrt{7}/2a_0$ and $c \sim 2\sqrt{3}a_0$. The general formula for the resulting solid solution is $Ba_{1-x-y}Y_xNa_yF_{2+x-y}$. The introduction of sodium fluoride reduced the parameters of the trigonal lattice and was accompanied by the formation of anion vacancies. Structure stabilization expressed in the expansion of the homogeneity region of the phase based on $Ba_4Y_3F_{17}$ seems to be associated with the disappearance of interstitial fluorine ions surrounded by anions in the $Ba_4Y_3F_{17}$ structure, both in the cuboctahedral cavity of the Y_6F_{36} clusters and in the centre of the F_8 cubes.

The corresponding solid solution can be used to create new photonics materials. The NaF-BaF_2-YF_3 system is similar to the previously studied NaF-BaF_2-GdF_3 system.

Keywords: Sodium fluoride, Barium fluoride, Yttrium fluoride, Solid solution

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1. Introduction

When studying the phase diagrams of barium fluoride (BaF_2) systems with rare earth fluorides (RF_3) for R = Sm-Lu,Y , Tkachenko and Sobolev [1-3] discovered that along with solid solutions of $Ba_{1-x}R_xF_{2+x}$ fluorite structure and BaR_2F_8 (R = Ho-Lu,Y) compounds, ordered fluorite-related $Ba_4R_3F_{17}$ phases also formed. Earlier, single crystals of this phase were grown from a non-stoichiometric melt by Guggenheim and Johnson, however, they mistakenly described their composition as $BaRF_5$ [4]. Kieser and Greis [5-7] found that a slow cooling of solid solutions of $Ba_{1-x}R_xF_{2+x}$ synthesized at 1000 °C leads to their ordering and the formation of trigonally distorted phases of $Ba_4R_3F_{17}$ for R = Ce-Lu. They correctly determined the space group symmetry as *R*-3. The interpretation of the crystal structure of $Ba_4R_3F_{17}$ (R = Yb, Y) [8] confirmed that these data were correct [5]. The repeated structural study [9] did not produce any new results. Isostructural compounds $Pb_4R_3F_{17}$ (R = Sm-Lu,Y) [10], $Pb_8Y_6F_{32}O$ [11], and $Ba_4Bi_3F_{17}$ [12] were also synthesized.

A feature of BaF_2-RF_3 systems is that solid solutions of $Ba_{1-x}R_xF_{2+x}$ based on barium fluoride do not form during low-temperature syntheses. Co-precipitation from aqueous solutions results in the formation of phases of the fluorite structure containing 40–50 mol % RF_3 without any signs of ordering [13–16]. This cubic phase was also synthesized for bismuth fluoride [17]. Following the mistake of Guggenheim and Johnson, the composition of such phases is often described as $BaRF_5$ [18–21]. The absence of any signs of trigonal distortion characteristic of $Ba_4R_3F_{17}$ phases in these samples can be interpreted as a manifestation of the Ostwald's step rule [22, 23]: metastable cubic phases of the corresponding composition are precursors of ordered phases stable at synthesis temperatures.

Phases synthesized in this way have low solubility in water unlike barium fluoride nanoparticles. These phases are matrices for photonics materials [4, 18–21, 24–31].

When the phase formation was studied at 350–500 °C using BaF_2-RF_3 systems from the sodium nitrate melt and sodium fluoride as a fluorinating agent [32], it was found that for the REE of the yttrium subgroup, sodium fluoride introduced to the reaction products [33, 34] (unlike the REE of the cerium subgroup [35, 36]).

The purpose of this work was to study the NaF-BaF_2-YF_3 systems by the method of solid-phase synthesis in order to establish the composition of the formed phases.

2. Experimental

The following reagents were used in the experiment: NaF (Reagent grade, Chimmed), BaF_2 (99.99%, LANHIT), and YF_3 (99.99%, LANHIT). The initial powders were further purified from oxygen-containing impurities by melting under CF_4 fluorinating atmosphere in graphite crucibles. The resulting polycrystalline fluorides were ground and, following stoichiometric calculations, mixtures of polycrystalline fluoride powders were prepared. The mixtures were ground in an agate mortar for 15 minutes with ethyl alcohol to achieve uniform composition, then dried at 60 °C under an IR lamp for 10 minutes and ground again for 3 minutes. The prepared powders were stored in a desiccator to avoid hydration.

The prepared samples were placed in nickel capillaries, which, together with barium hydrofluoride, BaF_2·HF, were placed in copper containers. The containers were sealed by argon arc welding. When heated, barium hydrofluoride decomposed and formed a fluorinating atmosphere.

The ground mixtures of NaF, BaF_2, and YF_3 were sintered under the following conditions: exposure temperature 750 °C, heating time 2.5 h, and exposure time 336 h. After sintering, the containers were quenched in liquid nitrogen.

The used annealing and quenching method was similar to the method which was used to study phase equilibria in the MF_2-RF_3, M = Ca, Sr, Ba systems in [1, 37, 38]. Quenching in liquid nitrogen is less efficient than quenching in water due to the low heat of vaporization of liquid nitrogen and the low heat capacity of gaseous nitrogen, however, it prevents the possibility of pyrohydrolysis of samples when water enters the container due to catastrophic cracking of welds.

The synthesized samples were examined by X-ray phase analysis and partially by thermal analysis. X-ray powder diffraction (XRD) was carried out using a Bruker D8 Advance diffractometer (Cu*K*α-radiation). TOPAS, DifWin,

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and Powder 2.0 software were used to process X-ray diffraction patterns.

3. Results and discussion

Phase equilibria in the $NaF-BaF_2-YF_3$ system are very complex. It should be noted that sintering in the binary BaF_2-YF_3 system at 750 °C for two weeks did not result in equilibrium. X-ray diffraction patterns recorded a mixture of phases, including the reflections of the BaY_2F_8 compound. It should be noted that the study of this system in [1,2] was limited to a temperature of 870 °C. The equilibrium time determined by the diffusion coefficients of cations became too long with a decrease in temperature [39], however, the addition of at least 5 mol % sodium fluoride allowed synthesis sample with clear X-ray diffraction patterns.

Fig. 1 shows a section of the phase diagram of $NaF-BaF_2-YF_3$ built using the data of the X-ray phase analysis of the annealed samples. The homogeneity region of the solid solution based on $Ba_4Y_3F_{17}$ was distinctly contoured. The maximum content of sodium fluoride in this solid solution was about 20 mol % NaF. The lattice parameters of this solid solution (*R* phase) are given in Table 1. It can be observed (Fig. 2) that an increase in the amount of sodium in the solid solution led to
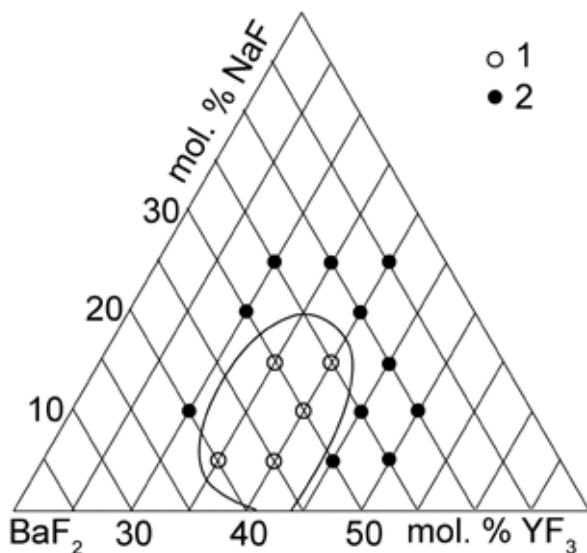
a decrease in the lattice parameters.

It should be noted that the binary BaF_2-YF_3 system had a small homogeneity region of this phase. According to [5], it is 41–44 mol % YF_3. As can be seen from Fig. 1, the introduction of sodium dramatically expanded the homogeneity region. Thus, it can be stated that the heterovalent isomorphism [40] stabilized the crystal lattice of the *R* phase. The same phenomenon was observed earlier in the $NaF-BaF_2-GdF_3$ system [41].

Naturally, we can expect a partial cationic substitution of yttrium ions of similar sizes with sodium. Such substitution takes place, for example, in the fluorite phase formed in the $NaF-YF_3$ system [3]. The study of the structure of the fluorite-like phases formed in the $NaF-BaF_2-YF_3$ system showed that sodium is also able to partially substitute barium in its crystallographic positions ($BaNa_{0.25}Y_{2.75}F_{10.5}$ phase) [34].

The studied *R* phase is a derivative of the structural type of fluorite. Its general formula can be written as follows: $Ba_{1-x-y}Y_xNa_yF_{2+x-y}$. The parameters of the trigonal cell were related to the parameter a_0 of the fluorite subcell by the ratios $a \sim \sqrt{7}/2a_0$ and $c \sim 2\sqrt{3}a_0$ [5, 8]. The structure of $Ba_4Y_3F_{17}$ has Y_6F_{37} complexes of 6 yttrium ions with an internal cuboctahedral cavity formed by anions, which includes an additional fluorine ion located in a single-charge environment (F8 positions in [8, 12]). In addition, there are

Fig. 1. Concentration region of the R phase in the $NaF-BaF_2-YF_3$ system at 750 °C. (1) single-phase samples, (2) two- or three-phase samples
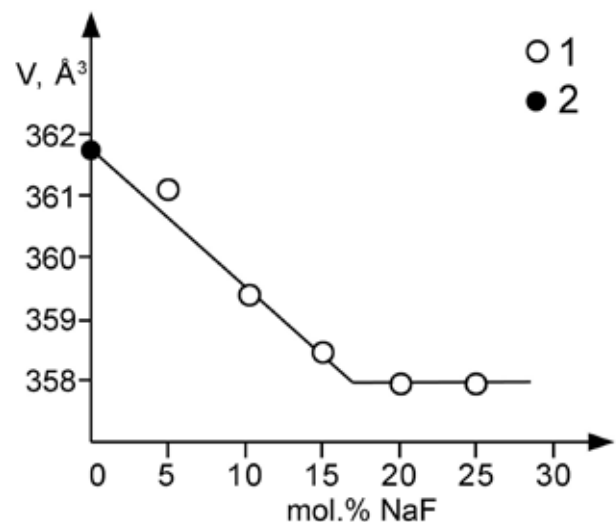

Fig. 2. Change in molar volume of the R phase at constant content of yttrium fluoride (40 mol % YF_3). *(1)* our data, *(2)* data of Greis and Kieser [6], extrapolation to 40 mol % YF_3

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Table 1. X-ray characteristics of the solid solution (*R* phase). Trigonal crystal system, space group *R*-3, Z = 6 when calculated for the formula $Ba_4R_3F_{17}$

Composition of the fluoride mixture, mol%	Lattice parameters *R* phase, Å	Unit cell volume, Å³	Mole volume, Å³
5% NaF – 60% BaF₂ – 35% YF₃ single–phase sample	a = 11.141 c = 20.57	2211.5	368.6
5% NaF – 55% BaF₂ – 40% YF₃, single–phase sample	a = 11.074 c = 20.41	2167.0	361.2
5% NaF – 50% BaF₂ – 45% YF₃	a = 11.046 c = 20.36	2150.9	358.5
5% NaF – 45% BaF₂ – 50% YF₃	a = 11.081 c = 20.35	2163.9	360.7
10% NaF – 60% BaF₂ – 30% YF₃	a = 11.131 c = 20.63	2213.2	368.9
10% NaF – 50% BaF₂ – 40% YF₃ single–phase sample	a = 11.055 c = 20.37	2156.2	359.4
10% NaF – 45% BaF₂ – 45% YF₃	a = 11.040 c = 20.36	2149.1	358.2
10% NaF – 40% BaF₂ – 50% YF₃	a = 11.049 c = 20.35	2151.9	358.7
15% NaF – 50% BaF₂ – 35% YF₃ single–phase sample	a = 11.101 c = 20.47	2184.5	364.1
15% NaF – 45% BaF₂ – 40% YF₃ single–phase sample	a = 11.044 c = 20.36	2150.7	358.5
15% NaF – 40% BaF₂ – 45% YF₃	a = 11.040 c = 20.36	2148.8	358.1
15% NaF – 35% BaF₂ – 50% YF₃	a = 11.068 c = 20.41	2164.9	360.8
20%NaF – 50%BaF₂ – 30%YF₃	a = 11.146 c = 20.60	2215.8	369.3
20% NaF – 40% BaF₂ – 40% YF₃	a = 11.038 c = 20.36	2147.9	358.0
25%NaF – 40%BaF₂ – 35%YF₃	a = 11.065 c = 20.39	2162.0	360.3
25% NaF – 35% BaF₂ – 40% YF₃	a = 11.038 c = 20.36	2148.0	358.0
25% NaF – 30% BaF₂ – 45% YF₃	a = 11.042 c = 20.36	2149.3	358.2
30% NaF – 30% BaF₂ – 40% YF₃	a = 11.040 c = 20.36	2149.2	358.2

the same interstitial fluorine ions in the cubic environment (F7 positions according to [8, 12]). These interstitial fluorine ions should disappear with the appearance of anionic vacancies, which results in the crystal structure stabilization.

4. Conclusions

Therefore, the study showed that in the ternary NaF-BaF_2-YF_3 system, the introduction of sodium fluoride stabilizes the $Ba_4Y_3F_{17}$ phase and expands its homogeneity region. The corresponding solid solution can be used to create new photonics materials.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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