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# Sodium fluoride and rare earth trifluorides systems. Review

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### Abstract

NaF–*R*F<sub>3</sub> systems, which are composed of sodium fluorides and rare earth trifluorides, are sources of many functional materials. Data on phase formation and phase equilibria in these systems were analyzed. The polymorphism and morphotropy of rare earth fluorides were considered taking into account the influence of pyrohydrolysis. A summary series of NaF–*R*F<sub>3</sub> phase diagrams are presented and the coordinates of invariant equilibria are tabulated. The data of research by Thoma et al., performed in the sixties of the twentieth century, are now only of historical interest. In these systems,  $\alpha$ -Na<sub>0.5-x</sub>*R*<sub>0.5+x</sub>*F*<sub>2+2x</sub> (cubic, *R* = Pr-Lu, Y) and  $\beta$ -Na<sub>3x</sub>*R*<sub>2-x</sub>*F*<sub>6</sub> (hexagonal, *R* = La–Lu,Y) phases of variable composition with fluorite and gagarinite structures, respectively, are formed. In addition, solid solutions based on rare earth trifluorides with the LaF<sub>3</sub>-tysonite (*R* = La–Gd) structure and the berthollide phase of such a structure in the system with TbF<sub>3</sub> were identified. Data was presented on the concentration dependence of the lattice parameters of fluorite phases. High temperature  $\alpha$ -phases with maxima on the melting curves allow growing single crystals from the melt. A complex pattern of ordering of these phases with decreasing temperature was observed. Low-temperature syntheses of intermediate phases in these systems led, in accordance with the Ostwald's step rule, to the initial formation of nonequilibrium phases of a fluorite structure, usually designated as " $\alpha$ -Na*R*F<sub>4</sub>", which were then replaced by equilibrium low-temperature hexagonal phases of " $\beta$ -Na*R*F<sub>4</sub>". The hexagonal phase in the NaF–YF<sub>3</sub> system, doped with ytterbium and erbium (" $\beta$ -NaYF<sub>4</sub>. Yb,Er"), is one of the most well-known, efficient up-conversion phosphors.

Keywords: Sodium fluoride, Rare earth fluorides, Phase diagrams, Fluorite, Gagarinite, Morphotropy

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### 1. Introduction

The NaF– $RF_3$  systems composed of sodium fluorides and rare earth trifluorides are sources of many functional materials. These systems are also of considerable interest from the point of view of non-stoichiometry, isomorphism, morphotropy, order-disorder transition processes, and phase equilibria theory [1].

Recently, the main emphasis has been on studying the processes of synthesis of nanomaterials in these systems for use in nanophotonics and other fields [2]. Nanofluorides are used for the visualization of infrared radiation, marking and protection against counterfeiting, luminescent thermometry and vacuum measurement, increasing the efficiency of solar panels, creating anti-reflective coatings, and 2D/3D monitors [3–10]. Due to the low toxicity of nanofluorides of alkaline and rare earth fluorides, their biomedical applications is very important [10].

Up-conversion phosphors are materials characterized by anti-Stokes luminescence, i.e. the emission of light with a shorter wavelength than the exciting radiation. Among other things, they convert energy from the near infrared spectrum into the visible range using a nonlinear optical process. Operating principles of such luminophores were described in the 1960s by Ovsyankin and Feofilov [14] and Ozel [15]. More often Er<sup>3+</sup>, Tm<sup>3+</sup>, and Ho<sup>3+</sup> are used as upconversion luminescent ions, and the Yb<sup>3+</sup>ion is used as an up-conversion sensitizer, since it is characterized by a very simple energy level diagram. The most widely used matrix is the low temperature phase in the NaF-YF<sub>3</sub> system with a hexagonal structure of the gagarinite type [16-18], denoted in the literature as  $\beta$ -NaYF<sub>4</sub> [6].

Information on the low-temperature stability of the corresponding phases is essential. Methods used for the synthesis of nano- and micromaterials (co-precipitation from aqueous and non-aqueous solutions, hydrothermal synthesis, synthesis from high-boiling organics, synthesis from salt melts, sol-gel method, glass crystallization, etc.) [2, 20–27], provide limited information on phase formation in the corresponding systems, which can only indirectly be related to the problem of phase equilibria. In this preparative area of chemistry, nonequilibrium processes predominate, during which, in accordance with the Ostwald's step rule [28, 29], nonequilibrium phases are formed first. In particular, the nonequilibrium nature of the NaYF<sub>4</sub> cubic phase synthesized by coprecipitation was demonstrated in the study [30].

Since bulk single crystals are still in demand in photonics and laser technologies, growing single crystals from melt remains important. Here, the consideration of solid-liquid equilibria is essential. The main methods for growing single crystals are the Czochralski and Bridgman-Stockbarger methods. Due to the need to obtain thin laser wave guides, the micro-pulling-down ( $\mu$ -PD) method has been developed [31, 32]. The key factor is the preparation of the starting reagents and the use of a fluorinating atmosphere during the growth process [33–35].

The MF-RF<sub>3</sub> systems are model for actinides [36, 66, 121].

The aim of this review is the presentation of a complete series of phase diagrams of NaF– $RF_3$  systems and characterization of the phases formed in these systems.

# 2. Polymorphism of rare earth trifluorides

It might appear that the question of polymorphism and morphotropy in the series of rare earth element trifluorides had been finally resolved a long time ago [37–47]. However, misunderstandings arise again and again.

The diagram of phase transitions in the series of rare earth trifluorides is shown in Fig. 1. Lanthanum-neodymium trifluorides, as well as high-temperature modifications of fluorides



**Fig. 1.** Phase transitions in *R*F<sub>3</sub> rare-earth trifluoride series [38]

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of samarium, europium, gadolinium, crystallize in the structural type LaF<sub>z</sub> - tysonite. The tysonite structure, characterized by sp. gr.  $P\bar{3}c1$ , Z = 6, at high temperature undergoes slight anionic disordering and passes into the sp. gr.  $P6_{\pi}/mmc$ , Z = 2 [48, 49]. This transition is not accompanied by jumps in heat capacity and molar volume and has a diffuse nature. The Tb-Ho fluorides, as well as low-temperature modifications of Sm-Gd, Er-Lu, and Y trifluorides crystallize in the orthorhombic crystal system,  $\beta$ -YF<sub>3</sub> type, sp. gr. Pnma. Based on powder X-ray diffraction patterns, unquenched high-temperature modifications of Er-Lu trifluorides crystallize in the trigonal crystal system,  $\alpha$ -YF<sub>3</sub> structural type. Its structure is related to  $\alpha$ -UO<sub>3</sub> and anti-Li<sub>3</sub>N [41, 50]. Cubic fluorite-like phases, which can be stable at high pressure, are characteristic of rare earth oxofluorides and arise during intense pyrohydrolysis of rare earth trifluorides.

For example, the data of Sui et al. [51] fit well into this scheme of polymorphism and morphotropy of REE fluorides. Hexagonal modification of EuF<sub>3</sub>, which is in a nonequilibrium state at room temperature, overcomes the potential barrier upon heating and transforms into an equilibrium orthorhombic modification of the  $\beta$ -YF<sub>3</sub> type; with further heating and cooling, a reversible phase transition between equilibrium modifications is realized. In the study of Xie et al. [24] equilibrium modifications of trifluorides were obtained in the form of nanoparticles for R = La - Nd (LaF<sub>3</sub> type) and R = Tb-Lu ( $\beta$ -YF<sub>z</sub> type) during the synthesis from high-boiling organic at 300 °C. The nonequilibrium high-temperature modifications of the LaF<sub>3</sub> type were synthesized for R = Sm, Eu, and a mixture of equilibrium orthorhombic and nonequilibrium hexagonal modifications was obtained for Gd. It should be noted that, judging by the presented X-ray diffraction patterns, the hexagonal phase nanopowders obtained in this work are characterized by a high-temperature sp. gr. *P6<sub>z</sub>/mmc*.

The main difficulty in studying phase formations and obtaining materials containing rare earth fluorides is the problem of pyrohydrolysis. Hydrolysis, including pyrohydrolysis is the interaction with water vapor or water adsorbed on the surface of fluoride particles, leading to contamination of samples with hydroxyl ions, isomorphically replacing fluorine, and subsequently to the appearance of oxygen impurities, causing the formation of new oxofluoride phases [52–54]. The resistance to hydrolysis of rare earth fluorides decreases with an increase in the atomic number of the element, i.e., when moving from light to heavy lanthanides. An exception is the increased hydrolytic capacity of cerium fluoride [55]. The intensity of hydrolysis processes accelerates sharply at the nanoscale level [52, 56]. Syntheses from high-boiling organic compounds are preferable from the point of view of eliminating hydrolysis.

The partial pyrohydrolysis of rare earth trifluorides leads to an incorrect scheme of the  $RF_3$  phase transformation [57] (lower temperatures of phase transformations in Gd, Er, Tm, Yb, Lu, Y trifluorides; false polymorphic transformations in TbF<sub>3</sub>, DyF<sub>3</sub>, HoF<sub>3</sub>). These results were obtained in high-temperature X-ray diffraction experiments. Under these conditions, it is practically impossible to eliminate pyrohydrolysis, despite all precautions, since the process begins from the surface of the samples. At the same time, the action of X-ray radiation accelerates the process of pyrohydrolysis.

A good marker of the pyrohydrolysis process is the temperature of the polymorphic transformation of gadolinium fluoride GdF<sub>3</sub> [39, 57–59]. There are significant discrepancies in these data in the literature: Thoma and Brunton indicate a lower value of 900 °C [57], Spending and Henderson demonstrated 1074 °C [39]. Temperatures close to the data shown by Spending were obtained in [43,44,46]. Sobolev et al. in the study of phase equilibria in the GdF<sub>3</sub>–Gd<sub>2</sub>O<sub>3</sub> system [58], demonstrated that the low value of the polymorphic transition temperature is associated with contamination of the samples with oxygen and the formation of a solid solution based on the hightemperature polymorphic modification of  $\alpha$ -GdF<sub>3</sub>.

Recently, fantastic "cubic modifications" of rare earth trifluorides have appeared in the literature. A number of studies [22, 60, 61] contain statement that REE fluorides, such as  $YF_{32}$  CeF<sub>3</sub> and others crystallize in the sp. gr. *Fm3m*. However, there are no chemical analyses data confirming that these are  $RF_3$  compounds. There are no cubic modifications of  $RF_3$  at normal pressure [45], since they can only be stable at very high pressures [62], or they appear when the preparations are seriously contaminated with

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oxygen. Thus, cubic fluorides of both rare earth elements and bismuth trifluoride [60] are fakes.

# 3. Phase diagrams of NaF- $RF_3$ systems

For phase diagrams of NaF–*R*F<sub>3</sub> systems it should be noted that the most widespread and frequently cited is the phase diagram scheme obtained by Thoma et al. during the implementation of the American nuclear energy project, see Fig. 2 [63–65]. The authors have considerable experience with fluoride systems, carefully studied the pyrohydrolysis and the influence of oxygen impurity on the type of phase equilibria, and eliminated this problem (with the exception of high-temperature X-ray data, see above). Thermal analysis (cooling curves) and an original gradient annealing technique were used to construct phase diagrams. According to this method, a capillary filled with powder of the studied composition was annealed in a temperature gradient, and the phase composition of the sintering products was analyzed by X-ray diffraction with reference to a specific temperature. Data on the NaF-CeF, system, studied using a similar method were used [66]. The NaF-YF, system was carefully studied in advance [63]. The results of this study were rationalized in the following extravagant way: two compounds with the compositions NaF·YF<sub>3</sub> and 5NaF.9YF<sub>3</sub> are formed in the system, each of which has two polymorphic modifications, and the high-temperature polymorphs crystallize in the fluorite structure and form a solid solution



**Fig. 2.** Phase diagrams of the NaF–*R*F<sub>3</sub> systems according to Thoma et al. [63, 64]

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between themselves. Data on other NaF– $RF_3$  systems were interpreted in a similar way [64].

It should be emphasized that the studies of Thoma et al. [63, 64] and Roy [67] were good for their time, but now these studies are of only historical interest. The conducted studies of phase equilibria in a series of NaF– $RF_3$  systems [68–76], including the polymorphism of  $RF_3$ , revealed a number of inaccuracies and errors in studies of Thoma.

Disadvantages of the Thoma scheme were as follows: an incorrect scheme of phase transformations of REE fluorides, distorted due to hydrolysis [57]; the small number of studied compositions; arbitrary schematization with postulation of 5:9 compositions and resulting from it incorrect fixation of the maxima compositions on the melting curves of intermediate phases of the fluorite structure; the incorrect determination of the compositions of ordered fluorite-like phases; the absence of solid solutions based on modifications with the tysonite structure; an impairment of the phase rule for a number of systems (R = Pr-Tb). Horizontal segments corresponding to temperatures of 860 °C (R = Pr), 800 °C (R = Nd), 773 °C (R = Sm), 806 °C (R = Eu), 767 °C (R = Gd), 742 °C (R = Tb), have no physical meaning, and their designation on phase diagrams is mistake.

A general schematic sequence of phase diagrams of NaF– $RF_3$  systems is shown in Fig. 3. The phase diagram of the most important NaF–YF<sub>3</sub> system is shown in Fig. 4a [30, 77], and the phase diagram of NaF–GdF<sub>3</sub> is shown in Fig. 4b [70]. Fig. 3 differs from the scheme shown in the article [1] in two features: the indicated low-temperature stability boundary of the NaLaF<sub>4</sub> phase and the nature of melting of the fluorite phase in the NaF–TbF<sub>3</sub> system, adjusted based on the results of growing single crystals (see below).

The methodology for studying systems [68– 76] was similar to that previously developed for studying series of  $MF_2-RF_3$  (M = Mg, Ca, Sr, Ba) systems [38, 79–83]. The initial reagents of rare earth fluorides were remelted under a fluorinating atmosphere of Teflon pyrolysis products. Differential thermal analysis was carried out in a static inert atmosphere of highpurity helium using graphite crucibles. Phase diagrams were constructed using heating curves. Phase equilibria in the solid state were studied by the X-ray diffraction of samples annealed in a fluorinating atmosphere and quenched.

In addition to the studies [68–76], correct experimental data were obtained in the studies of Cantor, Ward [84], and van der Meer et al. [36].

Low-temperature hexagonal phases with compositions close to a 1:1 ratio are formed in all NaF– $RF_3$  systems. High-temperature cubic phases with a fluorite-type structure are formed in systems with R = Pr–Lu, Y.

The coordinates of the nonvariant points are presented in Table 1. The thermal stability of the phases is shown in Fig. 5.

Both the hexagonal and cubic phases are phases of variable composition (nonstoichiometric). The representation of such phases as polymorphic  $\beta$ - and  $\alpha$ -modifications of the compounds "Na $RF_4$ ", now widely used in the literature, is a very primitive approximation, although it is used in many studies (see, for example, [6, 86, 87]). The compositions of these phases, according to the structural data, can be written as Na<sub>0.5-x</sub> $R_{0.5+x}F_{2+2x}$  (cubic) and Na<sub>3x</sub> $R_{2-x}F_6$ (hexagonal), and they generally do not coincide. For example, in the NaF–GdF<sub>3</sub> system the hexagonal phase has a homogeneity region of 52– 56 mol. % GdF<sub>3</sub>, fluorite 50–70 mol. % GdF<sub>3</sub> [70].

In [88] it was shown that the  $\alpha \rightarrow \beta$  transformation of "NaYF<sub>4</sub>", caused by the application of pressure, was accompanied by the release of YF<sub>3</sub> due to the different composition of these phases. In the NaF-YF<sub>3</sub> system (Fig. 4a) the equilibrium regions of the phases were 47–65 and ~50–53 mol. % YF<sub>3</sub>, for the cubic and hexagonal phases, respectively. The hexagonal phase is a low-temperature phase, stable up to 695 °C, the cubic phase is a high-temperature phase. The 1:1 composition for the cubic modification has a temperature stability range of 680–850 °C.

The production of cubic single crystals of stoichiometric composition NaYF<sub>4</sub> from a melt is almost impossible. The optimal composition for the production of crystals, corresponding to the maximum on the melting curve, is 60 mol. % YF<sub>3</sub>, composition Na<sub>0.4</sub>Y<sub>0.6</sub>F<sub>2.2</sub> [89, 90] (established in the study [68], in contrast to the composition of Na<sub>5</sub>Y<sub>9</sub>F<sub>32</sub> – 64.3 mol. % YF<sub>3</sub>, proposed by Thoma [63]).

In NaF– $RF_3$  systems with a decrease in the ionic radius of cations, a transition from peritectic

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**Fig. 3.** Phase diagrams of the NaF– $RF_3$  systems according to [1, 68–77]

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**Fig. 4.** Phase diagrams of NaF–YF<sub>3</sub>[30,78] (a) and NaF–GdF<sub>3</sub> [70](b) systems. Points – thermal analysis data, circles – single phase samples, semi black circles – two-phase samples after annealing and quenching, x – data of [84]. Phase notations: L – melt, F – Na<sub>0.5-x</sub> $R_{0.5+x}F_{2+2x}$ , G – Na<sub>3x</sub> $R_{2-x}F_6$ ,  $\alpha - \alpha$ -YF<sub>3</sub>,  $\beta - \beta$ -YF<sub>3</sub>, T – solid solution on the base  $\alpha$ -GdF<sub>3</sub>

Table	1.	<b>Co-ordinates</b>	of some	non-variant	points ir	n NaF- <i>R</i> F <sub>3</sub>	systems (	$C \pm 2$	mol %	$RF_{z}$	, <i>T</i> ±	5 °C	.)
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R	Eutectics I		Upper boundary of thermal stability of gagarinite phase		Upper boundary of thermal stability of fluorite phase		Low boundary of thermal stability of fluorite phase		Eutectic II	
	С	Т	С	Т	С	Т	$T_1$	$T_2$	С	Т
La	26	730	36	800*	_	-	_	-	-	-
Се	27	730	37	825	_	_	_	-	-	-
Pr	27	744	33	840		1050*				
Nd	28	730	35	842		1090*				
Sm	25	731	36	862		1120*		(760)	_	-
(Pm)	26	730	35	852						
Gd	28	718	52	860	67.5	1070*	856**	760***		
Tb	28	685	52	800	65.0	1056****	790**	755***	65	1056
Dy	26	650	52	780 ±10	64.0	1028	770**	730***	72	1005
Но	25	652	51	753	62.5	1004	750**	715±10***	71	988
Er	28	630	50	700	62.0	1000	696**	640±15***	73	980
Tm	29	608	50	660	60.0	980	640**	560±20***	76	940
Yb	28	598	50	600	60.0	954	561***	520±10***	75	915
Lu	28	602	50	450±40	57.5	940	550±10***	470±30***	72	895
Y	26	632	52	695	60.0	984	680**		75	955

\* – peritectic

\*\* – metatectic

\*\*\* - eutectoid

\*\*\*\* - transition point between congruent and incongruent melting



Fig. 5. Thermal stability boundaries of fluorite and gagarinite phases in series of NaF-RF<sub>3</sub> systems. F-Na<sub>0.5-</sub>  $_{x}^{N}R_{0.5+x}^{-}F_{2+2x}^{-}$  phases,  $G - Na_{3x}R_{2-x}F_{6}^{-}$  phases. Ionic radii ac-cording Shannon [85] for coordination number 8

melting of phases of the fluorite structure (R = Pr-Gd) to their congruent melting with the formation of maxima on the curves (R = Dy-Lu,Y) occurs. Changes in the compositions of the maxima on the melting curves of fluorite phases in the NaF- $RF_{3}$  systems (R = Tb-Lu) when moving along the lanthanide series [33] from  $Na_{0.37}Tb_{0.63}F_{2.26}$  [91, 92] to  $Na_{0.425}Lu_{0.575}F_{2.15}$  [93, 94] was confirmed during the growth of single crystals from the melt. At the same time, as experiments on crystal growth demonstrated [91, 92], the situation in the NaF-TbF<sub>3</sub> system is close to the transition point [95] (bifurcation of the phase diagram of B<sub>1</sub>II type according to classification [96]). According to [92],

Table	2.	Melt-grown	single	crystals
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the melting of the  $Na_{0.5-x}Tb_{0.5+x}F_{2+2x}$  solid solution of has a transitional "eutectic-peritectic" character. With directional crystallization of the melt of the  $Na_{0.37}Tb_{0.63}F_{2.26}$  composition in the initial part of the crystalline boule, an admixture of TbF<sub>3</sub> was sometimes recorded, and the central transparent part corresponds to the fluorite phase with a lattice parameter a = 5.5785(1) Å, which, according to the dependence [76], corresponds to the Na $_{0.36}$ Tb $_{0.64}$ F $_{2.28}$ composition. It should be noted that in the vicinity of the bifurcation point, fluctuations of the phase transformation type occur.

It should be emphasized that the fluorite structural phases in these systems are hightemperature ones, i.e. they are thermodynamically unstable at room temperature. This imposes restrictions on the growth of crystals from the melt, which cannot be annealed at temperatures below the eutectoid decomposition. The technological stability of single crystals in these systems increases with a decrease in the ionic radius of the lanthanide. Nominally pure and doped crystals grown by vertical directional crystallization without signs of decomposition are summarized in Table 2.

Experiments with low-temperature syntheses have shown that the NaLaF<sub>4</sub> phase has a lower stability limit, namely, it is stable only above 330±15 °C [77, 103, 104], see Fig. 3. These results are contradicted by the study [105], in which unalloyed NaLaF, powders were obtained by hydrothermal synthesis at 180 °C. However, the hydroxyl content in these samples is unknown. Calorimetric measurements performed by Yang et al. [106] recorded positive values of the enthalpy of

Composition	R	Ref.
$Na_{0.5-x}R_{0.5+x}F_{2+2x}$	Y, Dy–Lu	[97, 98]
Na <sub>0.4</sub> R <sub>0.6</sub> F <sub>2.2</sub>	Y, Yb, Lu	[90]
$Na_{0.4}(Y,R)_{0.6}F_{2.2}$ (NYF)	Ce, Pr, Nd, Er, Tm, Yb	[90,99]
Na <sub>0.4</sub> (Lu,R) <sub>0.6</sub> F <sub>2.2</sub> (NLF)	Ce, Nd, Er, Tm,	[99]
$Na_{0.4}(Y,R)_{0.6}F_{2.2}$ (NYF)	Er	[89]
Na <sub>0.38</sub> Dy <sub>0.62</sub> F <sub>2.24</sub> (NDF)		[100]
Na <sub>0.38</sub> Ho <sub>0.62</sub> F <sub>2.24</sub>		[101]
Na <sub>0.4</sub> R <sub>0.6</sub> F <sub>2.2</sub>	Dy, Ho, Er, Tm, Yb	[102]
Na <sub>0.35</sub> Dy <sub>0.65</sub> F <sub>2.3</sub>		[102]
Na <sub>0.4</sub> (Lu,R) <sub>0.6</sub> F <sub>2.2</sub> (NLF)*	Nd, Eu	[93,94]

\* micro-pulling-down (u-PD) method

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formation of NaLaF<sub>4</sub> and NaCeF<sub>4</sub> from components. Therefore, the lower stability limit is also probable for NaCeF<sub>4</sub> at a temperature of about 100 °C.

The cubic  $NaCeF_4$  reported by Virgil et. al. [107] is information noise.

The third type of phases of variable composition in the considered systems are solid solutions with the LaF<sub>z</sub>-tysonite structure. Mansmann [48], who solved the structure of lanthanum fluoride, also pointed out that this close-packed structure should be stabilized by anion vacancies. This prediction was perfectly confirmed by studying the phase diagrams of rare earth fluoride systems with a LaF<sub>3</sub>-tysonite structure type: La–Nd trifluorides and high-temperature modifications of Sm, Eu, and Gd trifluorides. Solid solutions based on RF<sub>3</sub> with a tysonite structure are formed in all  $RF_3 - MF_2$ systems where R = La-Gd, M = Ca, Sr, Ba. In these solutions during heterovalent substitution, anion vacancies are introduced into the lattice according to the equation  $R^{3+} + F^- \rightarrow M^{2+} + V_F [80-83, 108].$ Another way of introducing anion vacancies into the tysonite lattice is the replacement of fluorine with oxygen. Again, in  $RF_3 - R_2O_3$  systems with the corresponding rare earth elements, solid solution regions are formed [58]. Therefore, the appearance of solid solutions in NaF-RF<sub>3</sub> systems based on trifluorides of the corresponding structure according to the scheme  $R^{3+} + 2F^- \rightarrow Na^+ + 2V_F$  is logical from the point of view of crystal chemistry. Such solid solutions were detected by thermal analysis in systems of NaF with trifluorides of La, Ce, Gd [70, 75]. Moreover, when the modification of the tysonite structure of REE trifluorides becomes unstable due to a decrease in the ionic radius of the cation, the phase of variable composition of the tysonite structure, stabilized by anion vacancies, is retained in the phase diagram of the NaF–TbF<sub>3</sub> system [73].

The structures of  $\alpha$ -Na<sub>0.5-x</sub> $R_{0.5+x}F_{2+2x}$  (cubic) and  $\beta$ -Na<sub>3x</sub> $R_{2-x}F_6$  (hexagonal) phases are fundamentally different. The structure of the hexagonal modification was determined not only for single crystals obtained from the melt by the Czochralski method [109–113], but also for natural crystals (enriched with calcium), which were formed in nature by a hydrothermal process (the mineral gagarinite) [114, 115]. The hexagonal modification was composed by columns of nine-vertex polyhedra (Fig. 6). The coordination polyhedron of rare earth elements is a hexagonal prism with centered lateral faces. The sodium is located in wells. There is a strong statistical disorder in the distribution of cations over crystallographic positions, typical of non-stoichiometric phases.

For the cubic  $\alpha$ -phases, the conducted structural studies [116–118] indicated that the REE do not statistically alternate with sodium in the cationic positions of the fluorite lattice, but are located in clusters of the  $R_6F_{36}$  type (Fig. 7). The



**Fig. 6.** Crystal structure of " $\beta$ -Na $RF_4$ " phase (gagarinite) [114]



Fig. 7. Embedding of  $R_6F_{36}$  clusters into the fluorite lattice according to the Bevan, Greis, and Strahle model [119]

coordination number of REE is 8, coordination polyhedra are Thompson antiprisms. Such clusters are present in  $M_{1-x}R_xF_{2+x}$  fluorite solid solutions in  $MF_2 - RF_3$  systems, M – alkaline earth element [119, 120]. The compounds of  $KY_{*}F_{10}$ type are composed from such clusters. It should be noted that the performed structural studies cover only cations of the yttrium subgroup, which are characterized by a coordination number of 8. However, it is not typical for large cations of rare earth elements of the cerium subgroup. It is possible that in the fluorite phases formed in NaF- $RF_{\pi}$  systems with large cations that the defect structure of fluorite phases is different. The formation of clusters of the  $R_4F_{23}$  type is possible  $R_4F_{23}$  with a CN of 9 is possible [33]. The diagram in Fig. 5 suggests this assumption.

The Na<sub>7</sub>Y<sub>13</sub>F<sub>46</sub> and NaY<sub>2</sub>F<sub>7</sub> compounds, present in the NaF–YF<sub>3</sub> phase diagram (Fig. 4a), are fluorite-like phases with an ordered arrangement of clusters of  $R_6F_{36}$  type (Thoma quite accurately determined the temperature limits of stability and the lattice parameters of one of the phases, but made a mistake regarding the composition [63]).

Concentration dependences of unit cell parameters *a* of non-stoichiometric  $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ 

fluorite phases [76], see Fig. 8, are well described by the equation:

$$a = 5.398 + (6.7238r - 7.259)(x + 0.13) [Å], \quad (1)$$

where r – ionic radii of REE cations for a CN of 8 according to the Shannon system [65]. These dependencies can be used to clarify the composition of the synthesized phases with a fluorite structure in these systems.

The data of Furuya et al. [93] for R = Lu fit well in the graph in Fig. 8b.

Enthalpies of mixing for a number of the NaF– $RF_3$  (R = La, Nd, Yb, Y) systems, defined in study [123], are the basis for the thermodynamic modelling of the considered systems. However, thermodynamic modelling is not always successful. The model for the NaF–NdF<sub>3</sub> system, proposed by Ard et al. [124], according to Thoma, is unacceptable. Interpretation of the Na<sub>0.5-x</sub>Nd<sub>0.5+x</sub>F<sub>2+2x</sub> phase of variable composition with the fluorite structure formed in this system as a solid NaF solution in the "Na<sub>5</sub>Nd<sub>9</sub>F<sub>32</sub>" compound, is extremely unsuccessful. This interpretation, invented by Thoma [63, 64], has no experimental basis. There is no evidence indicating the existence of compounds of such



**Fig. 8**. Concentration dependences of the lattice parameter *a* of phases  $Na_{0.5-x}R_{0.5+x}F_{2+2x}$  [76]. (a): data of Thoma et al. [63, 64]; *2* – data of Schmutz [121], annealing at 700 °C; *3* – the same, annealing at 900 °C; *4* – data of Pontonnie [116]; *5* – data of Hund [122]; *6* – our data, annealing at 900 °C; *7* – the same, annealing at 850 °C; *8* – the same, annealing at 720 °C; *9* – the same, annealing at 550 °C; *10* – the same, remelting under a fluorinating atmosphere after precipitation from an aqueous solution. (b): *1* – data of Thoma et al. [64]; *2* – data of Schmutz [121], annealing at 700 °C; *3* – the same, annealing at 900 °C; *4* – the same, annealing at 550 °C; *5* – our data, annealing at 700 °C; *6* – the same, annealing at 800 °C; *7* – the same, annealing at 550 °C

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composition either in this system or in other sodium fluoride systems with rare earth fluorides.

In thermodynamic modelling in studies [36, 124] the lower limit of stability of the NaLaF<sub>4</sub> phase is not taken into account and solid solutions based on  $RF_3$  tysonite modifications are not considered.

# 4. Ordering processes of non-stoichiometric phases

Formation of ordered fluorite-like phases in NaF– $RF_3$  systems was studied in detail in [73, 74, 125].

To obtain a general picture of the ordering in the series of NaF- $RF_3$  systems [125] annealing was carried out on carefully ground samples packed in Ni capillaries and placed in an hermetically sealed Ni container, inside which a fluorinating atmosphere was created by the pyrolysis of Teflon and thermal decomposition of BaF<sub>2</sub>·HF. The container was quenched in water at a cooling rate of 200°/min. Compositions with 64.3, 67, 75 mol. %  $RF_3$  (R = Dy-Lu), corresponding to  $Na_{5}R_{9}F_{32}$  compounds (Thoma's phases),  $NaR_{2}F_{7}$ and  $NaR_{3}F_{10}$  were selected. Annealing was carried out at 700 °C for 100 hours. In addition, for the NaF-HoF<sub>z</sub> system, annealings for up to 720 h were carried out [71]. The indexing of X-ray diffraction patterns of fluorite-like phases was performed using the homology method [126, 127].

The unit cell parameters of the obtained compounds are given in Table 3.

In NaF– $RF_3$  (R = La-Dy) systems ordered fluorite-like phases were not identified. The appearance of ordered phases is caused by a decrease in the ionic radius of  $R^{3+}$ .



**Fig. 9.** X-ray patterns of the phases in NaF– $RF_3$  systems. Annealing at 700 °C, 100 h,  $\lambda = CuK\alpha$  [125]

In the system with  $HoF_3$  in the studied composition range, only one phase, containing 67%  $HoF_3$  (NaHo<sub>2</sub>F<sub>7</sub>) was found. At 75%  $HoF_3$  there is an excess of trifluoride, and at 64.3 mol. %  $HoF_3$  admixture of cubic fluorite phase is present.

Samples in the system with  $\text{ErF}_3$  have a similar phase composition. The X-ray diffraction pattern of  $\text{NaEr}_2\text{F}_7$  similar to the X-ray diffraction pattern of a holmium compound, it is distinguished by a higher complexity of changes of the main fluorite

Compound	Crystal system	<i>a,</i> Å	<i>b,</i> Å	<i>c,</i> Å	comment
NaHo <sub>2</sub> F <sub>7</sub>	trigonal	3.896		9.732	Sub-cell
NaEr <sub>2</sub> F <sub>7</sub>	trigonal	3.880		9.691	Sub-cell
Na <sub>7</sub> Tm <sub>13</sub> F <sub>46</sub>	tetragonal	3.880		5.512	Sub-cell
Na <sub>0.35</sub> Yb <sub>0.65</sub> F <sub>2.3</sub>	tetragonal	3.867		5.491	Melt-grown
Na <sub>7</sub> Yb <sub>13</sub> F <sub>46</sub>	orthorhombic	7.759	38.80	5.524	
NaYb <sub>2</sub> F <sub>7</sub>	orthorhombic	3.90	13.54	28.32	
Na <sub>7</sub> Lu <sub>13</sub> F <sub>46</sub>	orthorhombic	7.744	38.58	5.508	
$\gamma$ -NaLuF $_4$	hexagonal	13.57		9.38	Medium-temperature polymorph, KEr $F_4$ type [72]
Na <sub>2</sub> Y <sub>3</sub> F <sub>11</sub>	tetragonal	12.29		10.69	Annealing of a $Na_{0.39}Y_{0.61}F_{2.22}$ single crystal at 600 °C*

Table 3. Lattice parameters of fluorite-related ordered phases in NaF-RF<sub>3</sub> systems

\*A. Golubev, private communication

reflexes with the same superstructure. In the NaF- $TmF_{z}$  system the composition containing 64.3% is single-phase and its X-ray pattern corresponds to a weak tetragonal distortion of the fluorite lattice; TmF<sub>z</sub> lines are present on X-ray patterns of samples with a high content of  $RF_3$ . In systems with  $YbF_3$ and LuF<sub>3</sub> samples with 64.3 mol. % RF<sub>3</sub> are singlephase, characterized by the same superstructure. The splitting of the main fluorite reflections for the lutetium-containing compound corresponds to the orthorhombic nature of the distortion of the fluorite lattice. For the ytterbium compound, the splitting of the main lines is weaker and, to a first approximation, corresponds to a tetragonal distortion. In the system with LuF<sub>3</sub> samples with its high content are two-phase; the NaYb<sub>2</sub> $F_7$  phase was detected in the ytterbium system, the X-ray diffraction pattern of which differs both by the superstructure and the nature of the splitting of the main lines from the NaYb<sub>2</sub> $F_7$  (R = Ho, Er) compound.

It should be noted that we observed a very complex ordering pattern in the NaF–LuF<sub>3</sub> system in the range of 64–75 mol. % LuF<sub>3</sub> on samples annealed at 750 ° for 540 hours. In addition, a tetragonal phase, very close to the thulium phase by the X-ray diffraction pattern, was formed during the growth of single crystals from a melt in the NaF–YbF<sub>3</sub> system. The growth of a fluorite solid solution was carried out using the Bridgman method in a fluorinating atmosphere in graphite crucibles with a drawing speed of 10–12 mm/h. The tetragonal phase was observed in the lower part of the crystals with a composition of 58–62 mol. % YbF<sub>3</sub>, and its relative quantity increased with increasing concentration of  $RF_3$ .

The X-ray diffraction patterns of phases of such composition for R = Ho, Er and R = Yb are very different from each other. This indicates the presence of two structural types and a morphotropic transition in the Na $R_2F_7$  series. The X-ray diffraction patterns of sodium phases do not correspond to any of the modifications of potassium compounds of such stoichiometry.

Main lines on the X-ray diffraction pattern of NaYb<sub>2</sub>F<sub>7</sub> were indexed in a trigonal cell by the homology method with parameters  $a = 3.90 \text{ Å} \approx a_0 \sqrt{2}/2$ ,  $c = 9.44 \text{ Å} \approx a_0 \sqrt{3}$ , where  $a_0$  is the parameter of the fluorite subcell. However, superstructural reflections are not indicated in the trigonal cell with different variants of increasing

a and c parameters. In addition, subtle additional splittings of the main lines are observed, which indicate a further decrease in symmetry. The simplest option of reducing the symmetry of the trigonal cell to a orthorhombic, base-centered was considered for the interpretation of the X-ray diffraction pattern. It is assumed that equality  $b = a\sqrt{3}$ , strictly valid for trigonal symmetry, becomes approximate. This variant is omitted in the summary homology tables of splittings. The transition from trigonal to orthorhombic crystal system according to this scheme allows immediately index most of the reflections of the NaYb<sub>2</sub>F<sub>2</sub> superstructure. Full indexing is achieved by increasing the *b* parameter twice and the *c* parameter by three times.

The X-ray diffraction pattern of NaHo<sub>2</sub>F<sub>7</sub>, obtained by sintering at 700 °C for 100 hours, is well indicated in the trigonal crystal system with parameters a = 3.887 Å  $\approx a_0 \sqrt{2}/2$ , c = 9.732 Å  $\approx a_0 \sqrt{3}$ . However, with an increase in the annealing time to 700 hours, further ordering occurs, which is manifested in additional splitting of the main peaks and in the appearance of superstructural reflections (Fig. 10). The X-ray diffraction pattern of the NaEr<sub>2</sub>F<sub>7</sub> compound, obtained at 700 °C for



**Fig. 10.** Kinetics of ordering in  $NaR_2F_7$  phases. Annealing at 700 °C [125]

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100 hours has the same complex character. The general character of the splittings corresponds to triclinic crystal system. Based on these data, it is not possible to calculate the lattice parameters. It should be noted that trigonal cells, which are the prototype of Na $R_2F_7$  (R = Ho, Er) and NaYb $_2F_7$  phases (R = Ho, Er), formed by the deformation of the initial cubic cell with the opposite sign: for Ho and Er there is an extended rhombohedron (c/a = 2.50 in hexagonal packing), and for Yb – a compressed rhombohedron (c/a = 2.42). For a cubic cell in a hexagonal packing  $c/a \approx \sqrt{6} = 2.45$ .

The X-ray diffraction pattern of  $NaEr_2F_7$ similar to the X-ray diffraction pattern of a holmium compound, but differs by the greater complexity of the splitting of the main reflections with the same superstructure.

Compositions of ordered phases proposed by Thoma for the NaF–*R*F<sub>3</sub>system correspond to single-phase (with the accuracy of X-ray phase analysis) samples in systems with  $LuF_3$ ,  $YbF_3$ , and TmF<sub>3</sub>. The X-ray diffraction patterns of the lutetium and ytterbium phases were indexed [74, 125] with the parameters provided by Thoma et al. [63, 64]  $a \approx a_0 \sqrt{2}, b \approx a_0 \sqrt{2}, c \approx a_0$ . For ytterbium compound *a* = 7.770 Å, *b* = 38.71 Å, *c* = 5.524 Å; for the lutetium phase a = 7.744 Å, b = 38.57 Å, c = 5.508 Å. It should be noted that the unit cell proposed by Thoma contains 40 cations, which does not correspond to the formula Na<sub>5</sub>R<sub>9</sub>F<sub>32</sub>, proposed in [63, 64], since with this choice Z is a fractional value. The simplest formula corresponding to this cell is  $Na_7R_{13}F_{46}$ , providing Z = 2 and a composition of 65 mol. %  $RF_3$ . A slight deviation from the 5:9 composition (64.3 mol. %  $RF_{r}$ ) may be within the sensitivity of X-ray phase analysis, especially since the second fluorite-like phase, which may be present in samples with 64.3% RF<sub>3</sub>, produces lines on X-ray diffraction patterns that overlap the reflections of ordered phases. The possibility of the existence of small areas of homogeneity based on these phases also cannot be excluded. It should be noted that in the system with HoF<sub>3</sub> we did not detect any orthorhombic ordering in the composition of 64.3 mol. % HoF<sub>3</sub>, corresponding R = Yb-Lu, although according to Thoma at this temperature it should take place. On the other hand, the temperature range indicated by Thoma for the existence of an ordered phase in the holmium system agrees well with the temperature range determined by us for the  $NaHo_2F_7$  compound. Thus, it can be assumed that in [64] a simple distortion of the fluorite lattice was recorded without detailing its nature.

In the study [69] the  $Na_7Yb_{13}F_{46}$  compound was omitted due to the fact that a significant part of the superstructural reflections of this phase and  $NaYb_2F_7$  match.

The tetragonal  $Na_2Y_3F_{11}$  phase prepared by long-time annealing of melt-grown single crystal (see Table 3), is apparently metastable.

The  $Na_{3x}R_{2-x}F_6$  hexagonal phases with the structure of gagarinite represent the second family of phases of variable composition in NaF– $RF_3$  systems. Accordingly, we can expect an ordering of these phases with decreasing temperature, especially since they demonstrate a contraction of compositions to stoichiometric Na $RF_4$ . The appearance of superstructural reflections on X-ray diffraction patterns of samples of the corresponding phases synthesized from nitrate melts was demonstrated in [87]. However, overall, further investigation of this issue is required.

# 5. Transformations of alpha-beta phases in NaF-*R*F<sub>3</sub> systems

In the process of low-temperature syntheses of samples of the "Na $RF_4$ " phases by various methods a phase formation sequence is systematically observed in NaF– $RF_3$  systems, in which cubic fluorite nanoparticles of  $\alpha$ -phase are first formed, which then transforms into the  $\beta$ -phase [86, 128-136]. This was also observed *in situ* with a sharp increase in luminescence brightness during the formation of the  $\beta$ -phase [127]. Increasing temperatures and/or increasing the duration of synthesis promote the transition  $\alpha \rightarrow \beta$ .

In these cases, at the synthesis temperature, the hexagonal  $\beta$ -phase is in equilibrium. As shown in [30, 137], nanoparticles of the cubic phase of sodium yttrium fluoride synthesized from an aqueous solution during heating transform into a hexagonal phase with a large exothermic effect. The observed phase sequence during the crystallization of sodium yttrium fluoride represents the implementation of the Ostwald step rule [28, 29].

It is obvious that in low-temperature syntheses of sodium-yttrium fluoride, a mechanism of oriented growth of nanoparticles takes place [138,

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139]. However, it does not exhaust the process. Considering the different crystal structures of the two polymorphs, it is obvious that beta phase fragments cannot be formed from alpha phase fragments. The change in the coordination number of rare earth cations during the transition from their alpha to beta phase inevitably requires complete recrystallization of the particles. In other words, in this process, there is a complete disappearance of one phase and the growth of another phase.

It should be noted that the formation of ordered fluorite-like phases in  $NaF-RF_3$  systems was not observed in low-temperature syntheses.

Currently, there are a number of chemical methods for the synthesis of nanosized particles such as  $NaYF_4$  (high-temperature co-precipitation, hydro- and solvothermal synthesis, thermolysis, etc.), see, for example, [140–142]. However, there is a problem with the reproducibility of product properties.

## 6. Conclusions

Among the unresolved problems of phase equilibria and phase formation in systems of sodium fluoride with fluorides of rare earth elements, the following can be listed.

– Structure of ordered fluorite-like phases. It is obvious that in these phases there is an ordered arrangement of  $R_6F_{36}$ -type clusters, but the specific pathways of their arrangement are unknown.

- Identification of the ordering of gagarinite phases. Obviously, the ordering must take place, since these phases are non-stoichiometric. Similar systems with bismuth fluoride demonstrate a rich set of compounds of this type.

- Intriguing cooperative transformation of ensembles of fluorite nanoparticles into the hexagonal structure of gagarinite, which is beyond the problems relating to phase equilibria.

– Possible pyrohydrolysis of samples and its influence on the functional characteristics of materials. Heat treatment in the presence of water results in the replacement of the fluoride ion by an hydroxyl ion, which is very similar in size [143]. The hydroxyl concentration should increase with increasing crystallization time and increases sharply with increasing temperature of the process. Both  $Y(OH)_3$  and La $(OH)_3$  have a hexagonal structure and is isostructural with the  $\beta$ -phase [144]. The hydrolysis process may be the driving force behind the transition of  $\alpha \rightarrow \beta$  phases in "NaRF<sub>4</sub>".

- A critical drawback of many studies devoted to the synthesis of sodium fluoride samples with rare earth elements, despite the use of modern research methods such as TEM, STEM, XRD, APT, EXAFS, is the complete disregard for monitoring the actual chemical composition of the synthesized samples and tracking their changes during the synthesis process. The composition of cubic phases can be estimated based on the lattice parameter (equation (1)), however, surprisingly, in many studies these crystallographic data are not shown and only a primitive comparison of X-ray diffraction patterns with a reference database is provided.

# 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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