FLUORITE-LIKE PHASES IN THE NaF-RF$_3$ SYSTEMS FOR RARE EARTHS FROM Tb TO Lu

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Phases with variable composition having the fluorite structure which are formed in the MF_m-RF_n type systems ($m, n \leqslant 4$) [1, 2] are a are example of ionic compounds that allow anomalously high contents of structural defects – vacancies and incorporated atoms. In the $M_{1-x}R_xF_{2+x}$ phases concentrations of rare earth element (R) fluorides attain 50 mole % under normal pressure. A high defect content essentially changes physical properties of crystals such as ionic conductivity, hardness, refractive index, lattice parameter etc. As shown in [1], there is a wide range of fluorite solid solutions in the CaF_2-$NaRF_4$-RF_3 system, where R are the lanthanides and yttrium. Apparently, such solid solutions are formed in a number of similar systems of the MF_2-$NaRF_4$-RF_3 type which are parts of ternary NaF-MF_2-RF_3 ones, where M = Ca, Sr, Ba, Cd, Pb; R = lanthanides and yttrium. Transition from binary MF_2-RF_3 type systems to ternary NaF-MF_2-RF_3 systems allows one to use four different schemes of isomorphous replacements for constructing new multicomponent materials. Two of them are characterized by additional fluoride ion incorporation into the structure, one is characterized by formation of anionic vacancies and the fourth one does not affect the anionic motif. This enables variations of physical properties of the materials using combinations of structural defects of various types, that are realized in various regions of the stability field for the fluorite phase (F) in ternary system. Figure 1 shows the field of the (F) phase for the NaF-CaF_2-YF_3 system (isotherm for 900°), according to our data.

Transition to growing crystals of ternary compositions requires studies of the crystallization processes both in ternary and in binary systems involved. For the MF_2-RF_3 systems the problems of preparation of homogeneous crystals were considered in detail in [3, 4]. Such data for the NaF-RF_3 type systems are not available.

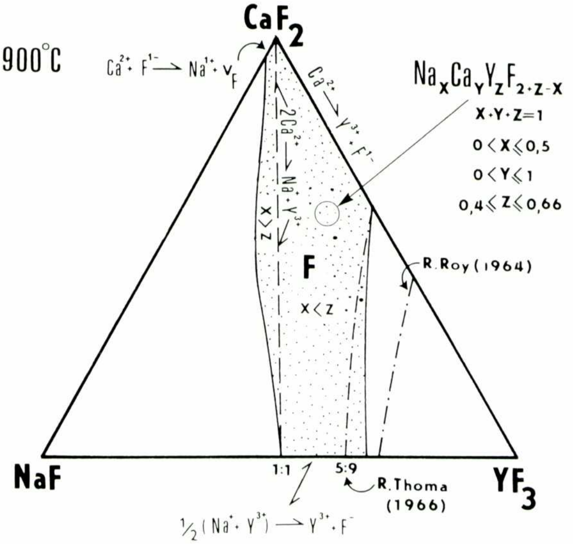

Fig. 1. Four schemes of isomorphous replacements in solid solutions with the fluorite structure exemplified by the NaF-CaF$_2$-YF$_3$ system (isothermal section 900°C).

This paper was aimed at studying specific features of preparation of single crystals of fluorite solid solution by the Bridgman technique in NaF-RF$_3$ and NaF-RF$_3$-R'F$_3$ systems, where R and R' are rare earths from Tb to Lu. This technique is the most convenient one for growing congruently melting compounds, that is why the primary task was to use $5NaF*9RF_3$ compounds (R = Gd – Lu), previously reported in [5] as congruently melting ones for the entire family of rare earth elements involved.

Our results, however, showed that compounds with the 5:9 stoichiometry melt, as a rule, incongruently, and only in some systems their behaviour is rather congruent, being, in fact, congruent only for R = Dy, Ho. Thus, the previously reported data [5] cannot be used for growing single crystals with a homogeneous in-length distribution of a rare earth component.

Refinement of the melting character of fluorite phases with a variable composition $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ (where x is the redundant rare earth elements as compared to stoichiometric NaRF$_4$) using differential thermal analysis technique for phase diagrams of NaF-RF$_3$(R = Tb – Lu), carried out following the technique described in [6] showed that the coordinates of congruently melting compositions vary upon replacement of a rare earth element by another one within the family.

The main differences between our data and the data reported in [5] are shown in figure 2. The maximum deviation of a congruently melting compo-

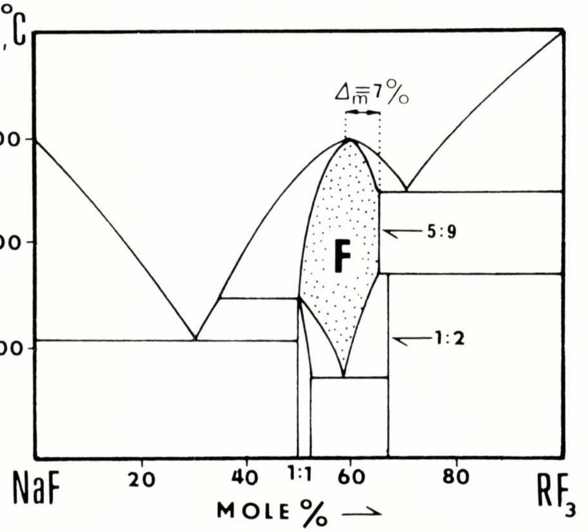

Fig. 2. General scheme of phase equilibria in the NaF – RF_3 systems for R = Er, Tm, Yb, Lu (here the main differences between our results and the data reported in [5] are shown).

sition from 5:9 is 7 mole%. The composition of the ordered phase with the fluorite-derived structure has 1:2 stoichiometry. The RF_3 content in congruently melting compositions for NaF-RF_3 systems (R = Tb – Lu) changes linearly with ionic radius (r) variations of the rare earth cations R^{3+} element and can be obtained according to the empirical equation:

$$c = (-63.5 + 124.5 * r) \pm 1 \text{ mole } \% \tag{1}$$

Temperatures of the maxima on the fusibility curves of fluorite phases vary regularly according to:

$$T = (-724.4 + 1708.1 * r) \underset{p}{\pm} 5^\circ \text{ C} \tag{2}$$

where r is the ionic radius of the rare earth element for the coordination number 8 according to the Shannon system [7]; c is the mole concentration of a rare earth element in the NaF-RF_3 system; T is the melting temperature of the compound containing RF_3 in the amount determined according to (1). In the NaF – GdF_3 system the solid solution $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ according to our data melts following peritectic reaction, in contrast to the data reported in [5].

Fluorite phases of $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ allow complete isomorphism among R = Tb – Lu cations, therefore, it is possible to grow not only binary

$Na_{0.5-x}R_{0.5+x}F_{2+2x}$ crystals but also crystals with any combinations of R, from Tb to Lu. Coordinates of congruently melting compounds are unambiguously related to the average ionic radius r_{av} of such isomorphous mixtures ($r_{av} = x_1r_1 + x_2r_2 + x_3r_3 + \ldots$; where $r_1, r_2, r_3, \ldots$ are the ionic radii of rare earth elements; $x_1, x_2, x_3, \ldots$ are mole fractions of $R_1, R_2, R_3, \ldots$, in the RF_3 mixture, related by $x_1 + x_2 + x_3 + \ldots = 1$). Thus, the compositions advantageous for growing perfect single crystals can be readily calculated.

The use of starting mixtures with compositions deduced according to (1) yielded single crystals of solid solutions $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ (R = Tb – Lu, x = 0.1C – 0.08) by the Bridgman technique, of the optical quality. The growing conditions were as follows: hot zone temperature exceeded by 50° the melting temperature of the particular compound, the annealing temperature was 200°C less than the melting temperature, gradient in the crystallization zone was 35° C/cm, rate of crucible lowering was from 2 to 20 mm/h, sample cooling rate was from 100 to 150°C/h. Crystals were grown in helium atmosphere doped with CF_4 under redundant pressure of 0.5 atm. A photo of the samples is shown in figure 3.

Admittedly, upon temperature lowering nonordered fluorite-like phases undergo decomposition or ordering. For $NaRF_4$ compounds the transi-

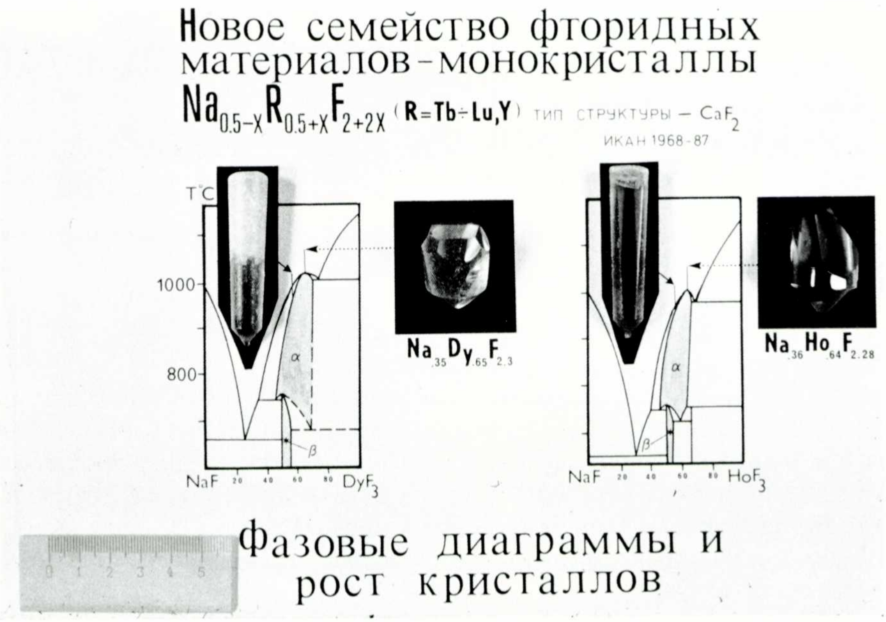

Fig. 3. Crystals of $Na_{0.5-x}R_{0.5+x}F_{2+2x}$.

tion from nonordered fluorite structure to the gagarinite one (β-$NaCaYF_6$ type) is accompanied by heat release and is well determined by the DTA technique (reconstructive phase transition).

For the $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ phases, corresponding to composition of the maximum on the melting curves such effect is not observed. A specific feature of these compositions is the fact that, regardless of their decomposition temperature being 0.65 of their melting temperature (K), i.e. higher than the diffusion threshold in the bulk (0.52 K according to Tamman), they exhibit a marked tendency to keeping metastable state.

In order to study thermodynamic stability of $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ crystals we have carried out annealing experiments for samples where R varied from Tb to Lu. The samples were annealed in airtight nickel containers in the atmosphere of teflons pyrolysis. The samples were quenched in water at a rate of 200°C/min. The phase composition was determined on a powder diffractometer. The samples for annealing were single crystalline blocks up to 0.3 cm^3 in volume.

The primary annealing was at 550°C during 24 hours. The phase composition did not change. The secondary annealing was at 500°C during 970 hours. An X-ray analysis of these samples showed that although the shape of the blocks was retained, they contained the two-phase mixture of β-$NaRF_4$ with gagarinite and fluorite derived structure.

Thus, our results indicated that:

1) in the $NaF - RF_3$ systems (R = Tb – Lu, Y) there is no congruently melting compound with a constant composition $5NaF{*}9RF_3$ for all rare earth elements. The coordinates of the maximum on fusibility curves of fluorite solid solutions of $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ change depending on changes of ionic radiis of the rare earth elements from 66 mole% for TbF_3 to 58 mole% for LuF_3.

2) Crystals with variable composition $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ are not hygroscopic and can be used within a wide temperature range. The range 700-500°C is the worst for long usage, as the processes of phase transformations to other type structures occur here.

3) Solid solutions with the fluorite structure in MF_2-$NaRF_4$-RF_3 systems with M = Ca, Sr, Ba, Cd, Pb exhibit changes of lattice parameters from $a = 5.389$ Å for CdF_2 to $a = 6.2001$ Å for BaF_2. The refraction index varies from $n_D = 1.43338$ for CaF_2 to $n_D = 1.589$ for $Cd_{1-x}R_xF_{2+x}$, where R = Ce, Sm, Tb; x = 0.35 for Tb, x = 0.25 for Sm, x = 0.2 for Ce. Microhardness changes from 80 kg/mm^2 for BaF_2 to 420 kg/mm^2 for $Na_{0.42}Lu_{0.58}F_{2.16}$. Fluorine ionic conductivity (at 400 K) changes from $1.4 * 10^{-8}$ $(Ohm{*}cm)^{-1}$ for $Na_{0.4}Dy_{0.6}F_{2.2}$ to $1.1 * 10^{-5}$ $(Ohm\ {*}/cm)^{-1}$ for $Cd_{0.78}Tm_{0.22}F_{2.22}$, activation energy changes from 0.62 eV to 0.84 eV, respectively.

4) This family of fluoride materials with variable properties within the abo-

ve ranges due to changes in their compositions with operation parameters monitored within the above ranges can be recommended for application in the following fields:
a) optical construction materials;
b) active elements of optical quantum generators;
c) antistock luminofors and scintillators;
d) fluorine-ionic conductors for various solid state electrochemical devices.

ABSTRACT

Fluorite phases with variable compositions $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ (R = Tb-Lu, Y) have been obtained by unidirected crystallization. In NaF-RF_3 systems the compositions with congruent melting have different RF_3 contents, ranging from 66 mole% for TbF_3 to 58 mole% for LuF_3. Empirical equations have been derived which relate the temperatures and compositions of congruent melting fluorite phases with ionic radii R^{3+}. The thermal stability of $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ has been studied and a possibility of their preservation in metastable state during a long time has been shown. Limits of variations of some characteristics for fluorite phases with variable compositions in MF_2-$NaRF_4$-RF_3 systems with M = Ca, Sr, Ba, Cd, Pb have been given. A conclusion is made that phases of $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ owing to their properties can be used as optical construction materials, active elements of optical quantum generators, antistock luminofors and scintillators, fluorine-ionic conductors.

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