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Phase formation in LaF_3–$NaGdF_4$, $NaGdF_4$–$NaLuF_4$, and $NaLuF_4$–$NaYF_4$ systems: Synthesis of powders by co-precipitation from aqueous solutions

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ABSTRACT

Detailed studies of LaF_3–$NaGdF_4$, $NaGdF_4$–$NaLuF_4$, and $NaLuF_4$–$NaYF_4$ systems have revealed that LaF_3–$NaGdF_4$ system precipitates, formed in aqueous media, contained gagarinite-type $NaGd_{1-x}La_xF_4$ ($x \leq 0.0625$) solid solution, tysonite-type $La_{1-x}Gd_xF_3$ ($x \leq 0.50$) phase, and cubic fluorite-type $NaGdF_4$-based phase, whereas $NaGdF_4$–$NaLuF_4$ precipitates contained hexagonal gagarinite-type ($x \leq 0.25$) and cubic fluorite-type ($x \geq 0.675$) $NaGd_{1-x}Lu_xF_4$ solid solutions. Furthermore, there were continuous series of single-phase cubic fluorite-type $NaLuF_4$–$NaYF_4$ solid solutions formed in the third investigated system. Crystallization of $Na_{0.5-x}Lu_{0.5+x}F_{2+2x}$ solid solutions from aqueous media occurred in an incongruent manner; the use of 5-fold excess of NaF led to precipitation of $NaLuF_4$ ($x = 0$) with almost stoichiometric composition.

Introduction

Over the last 10–15 years, inorganic nanofluorides have actively attracted the attention of scientists because of their quite wide and efficient use in modern optics, ceramics, catalysis, and medicine [1–16]. One of nanofluoride applications in the latter area is based on their up-conversion properties. Up-converters are necessary for triggering photodynamically active agents capable of generating reactive oxygen species in the vicinity of tumor cells under the influence of light of a particular wavelength. Most such photosensitizers require ca. 660 nm irradiation, but living tissues exhibit sufficient transparency for the 800–1000 nm region only, thus shielding targeted cancerous cells from radiation-initiated treatment [17]. The use of up-converting nanofluorides, such as $NaYF_4$:Yb:R (R = Er, Tm, Ho), allows one to remedy this problem: 970–980 nm light can easily reach deep tissue layers, where it is absorbed by Yb^{3+} ions and, after transfer to another rare-earth cations, some part of absorbed radiation will be converted to the higher frequency 660 nm radiation and trigger the delivery of medication. Whereas the aforementioned rare earth-doped $NaYF_4$ matrix is one of the most efficient up-converter among known nanofluorides, its efficiency depends on the selected rare earth dopants and phase composition: hexagonal $NaYF_4$:Yb:R is several times more efficient than its cubic polymorph [10]. Also preparation of hexagonal $NaYF_4$:Yb:R (R = Er, Tm, Ho) nanofluorides by precipitation from aqueous solutions is not so simple. It requires a thorough choice for the concentration of the organic catalysts, solution pH, time and order of component addition [18–20]. Very frequently, metastable cubic $NaYF_4$:Yb:R phase precipitates instead of its hexagonal polymorph. One of the possibilities to bypass these obstacles is the replacement of yttrium by different rare earth elements, such as La, Gd and Lu. The advantage of the latter metals is that they lack absorption bands and luminescence lines in the aforementioned 800–1000 nm range of spectrum, but at the same time multicomponent fluoride systems with these dopants have yet to be systematically described in the literature.

It is also worth noting that despite known ability of rare earth fluorides to form metastable phases, especially, in aqueous

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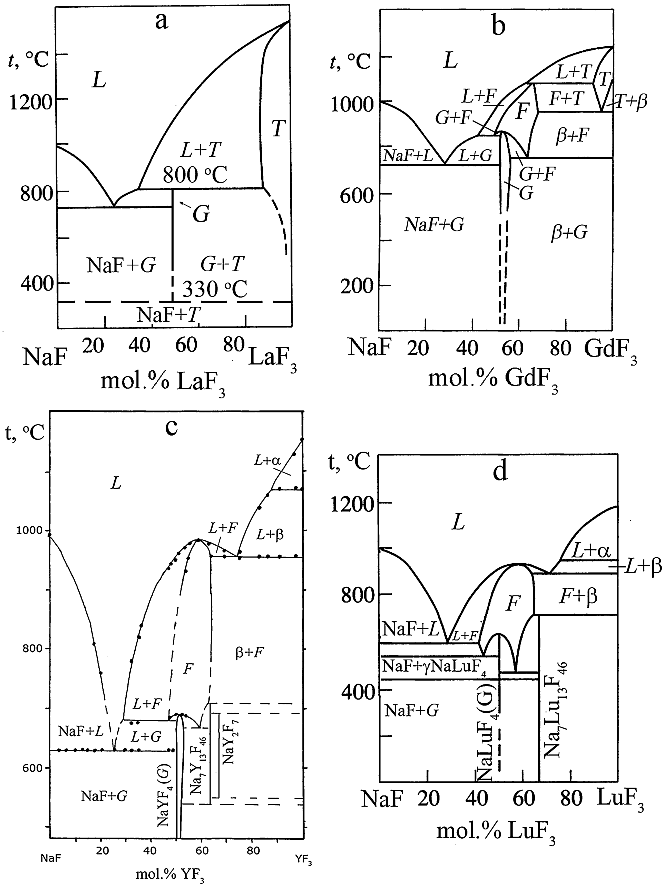

Fig. 1. Phase diagrams of NaF–LaF$_3$ (a); NaF–GdF$_3$ (b); NaF–YF$_3$ (c) and NaF–LuF$_3$ (d) systems [21–25]. L—melt; G—hexagonal gagarinite-type phase, $Na_{3x}R_{2-x}F_6$; T—hexagonal tysonite-type phase, $R_{1-y}Na_yF_{3-2y}$; F—cubic fluorite-type phase, $Na_{0.5-x}R_{0.5+x}F_{2+2x}$; α-hexagonal α-YF$_3$-type phase; β-orthorhombic β-YF$_3$-type phase; γ-hexagonal KErF$_4$-type phase.

systems [11], information about their thermodynamically stable phases is crucial for the selection of conditions and possibilities for the preparation of various fluoride materials of the aforementioned elements. For example, the high-temperature phase equilibria in the NaF-RF$_3$ (R = La, Gd, Y, Lu) systems [21–25] (Fig. 1) indicate that, in the NaF–LaF$_3$ system, the mixture of components – binary fluorides – is stable at relatively low temperature, i.e., below 330 °C. Similarly, hexagonal gagarinite-type G phases with the compositions close to NaRF$_4$ are stable in the NaF-GdF$_3$, NaF-YF$_3$ and NaF-LuF$_3$ systems. Additionally, in the latter system, the fluorite-like compound $Na_7Lu_{13}F_{46}$ is stable, too [21].

Therefore, the goal of this paper was to investigate phase formation in LaF$_3$–NaGdF$_4$, NaGdF$_4$–NaLuF$_4$, NaLuF$_4$–NaYF$_4$ systems by co-precipitation of polycrystalline powders from aqueous solutions.

Experimental

We utilized co-precipitation of nanofluorides from aqueous solutions, used in this work, that has been described in details in [19,20,25–27]. We used commercially available 99.99 wt% pure $Y(NO_3)_3{\cdot}6H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$, $Lu(NO_3)_3{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$ (Lanhit, Moscow, Russia), 99 wt% pure NaF, and doubly distilled water as starting materials. Reagents were not subjected to further purification. All experiments were carried out in polypropylene equipment (such as lid-covered reactors) at ambient temperature under air unless otherwise specified. Prepared 0.30–0.35 M aqueous solutions of rare earth nitrates (individual or mixtures of rare earth elements) were added dropwise under vigorous stirring to the appropriate amount of 0.30–0.35 M aqueous NaF (stirring continued for 2 h). The obtained precipitates were decanted or centrifuged (when necessary), washed several times with doubly distilled water (the absence of nitrate ion impurities was determined by standard qualitative reaction with diphenylamine) and dried under air.

The phase composition of solid specimens was evaluated by X-ray diffraction (DRON-4 M diffractometer; Cu Kα radiation; graphite monochromator). Calculations of lattice parameters were performed using Powder 2.0 software, the error less than 10 taken ΔQ, where $\Delta Q = 10_4/d^2_{calc} - 10^4/d^2_{theory}$. We also used a JSM-5910LV (JEOL) scanning electron microscope for microstructure study of the obtained precipitates and the same device for the sample X-ray microanalysis (energy dispersive X-ray-EDX).

Results and discussion

As has been found earlier for NaF-RF$_3$ systems [11,25], fluorite-type solid solutions crystallize/precipitate from aqueous solutions in an incongruent manner, i.e., Na:R ratios (R = rare earth) in the solid phase differs from the one in the aqueous solution. Therefore, the initial step in our study included the determination of conditions when precipitate composition (Na:R ratio) would be the closest to the stoichiometric NaRF$_4$ (i.e., 1:1).

Therefore, we chose NaF-LuF$_3$ system as the typical one among other NaF-RF$_3$ systems and studied interaction of 0.3 M NaF with $Lu(NO_3)_3$ at Na:Lu = 1:1, 3:1, 5:1, 7.5:1, 10:1 molar ratios. Mixing the aforementioned solutions resulted in precipitation of single-phase face-centered cubic $Na_{0.5-x}Lu_{0.5+x}F_{2+2x}$ powders only (Figs. 2 and 3 and Table 1). The chemical composition of obtained $Na_{0.5-x}Lu_{0.5+x}F_{2+2x}$ solid solution was evaluated with the use of data on concentration dependence of cell parameters $a(x) = 5.4308 + 0.2318x$ [28]. The presented data indicate a non-linear correlation between the lattice parameter a and the amount of NaF used in the synthesis (Fig. 3). It is worth noting that the use of 5 eq. NaF led to the precipitation of $Na_{1.006}Lu_{0.994}F_{3.988}$, i.e., almost stoichiometric "NaLuF$_4$" (sample F483; Figs. 2 and 3 and Table 1). Similar effects were observed for the other rare earth precipitates, so further precipitation experiments were carried out at 5 eq. NaF excess with the same 0.3 M solutions.

Phase equilibria in the triple NaF–LuF$_3$-solvent water–salt(s) system are depicted in Fig. 4, which shows an incongruent crystallization of $Na_{0.5-x}Lu_{0.5+x}F_{2+2x}$ various composition phase.

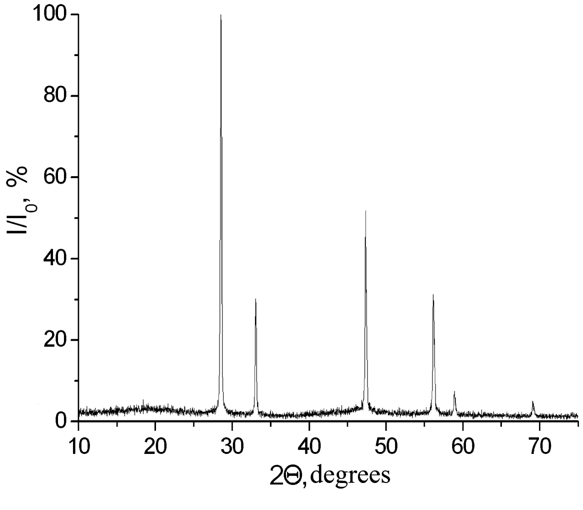

Fig. 2. Typical X-ray diffraction pattern of a NaLuF$_4$ sample (synthesized with a 5-fold excess of NaF).