

Synthesis of NaYF₄ compounds from sulfide precursors

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Abstract— The synthesis of compounds NaYF₄ by "soft chemistry" of sulphide precursors (a simple Y₂S₃ and a complex NaYS₂) is considered. Hydrofluoric acid solution (HF) having a concentration (5-45%) and a saturated aqueous solution of sodium fluoride with different content acidified by hydrofluoric acid (NaF+HF) is studied as the fluorinating component. When fluorination with hydrofluoric acid of different concentrations is decomposed, yttrium fluoride YF₃ has been formed. The composition of NaYF₄ compound is obtained as a mixture of cubic and hexagonal phases with dimensions of nanoparticles (α :30-100 nm, β :28-60 nm) with different synthesis conditions.

Keywords—fluorides, hexagonal sodium yttrium fluoride, rare earth, sulfide.

I. INTRODUCTION

The development of new strategies in optical electronics, solar cells and biomedical markers has dramatically expanded the field of up-conversion materials. Various host lattices doped with rare earth ions show efficient up-conversion emission [1]. The improved characteristics of these powders make them promising for application as laser materials [2], scintillators [3], 3D displays [4], sources of white light [5–7], catalysts [8], and laser nanoceramics [9, 10], as well as for use in medicine [11, 12], etc. Choice of material and size of particle is dependent on the application. The advantages of nanoparticles by fluoride, compared to other promising substances such as quantum dots based chalcogenides and toxic organic dyes, are: low background autofluorescence, narrow band luminescence photostability and [13]. The safety of using fluoride nanopowders for biomedical research is checked in [14-16] on the model of biological objects. Rare earth fluoride based on NCs such as binary REF₃ [12, 17, 18] and complex AREF₄ (RE= rare earth; A =alkali) [19, 20] have been the research focus in recent decades, because they normally possess a high refractive index and low phonon energy. So far, β -NaYF₄:Er³⁺ shows the highest efficiency for solar cells and photovoltaic applications [21, 22]. One of the main trends in modern research is the study of the synthesis and properties of powders, noted as NaYF₄ and NaYF₄:RE in both cubic and hexagonal phases for

biomedical applications.

The NaF-YF₃ system generated high-temperature phase of variable composition Na_{0.5-x}Y_{0.5+x}F_{2+2x} fluorite structure, melting peak 985 °C which falls on the composition of 60.5 ± 0.5 mol.% YF₃. Lowering the temperature leads to a phase of decay for eutectoid scheme with the release of the NaYF₄ low-temperature phase as well as the phase, a similar ordering of fluorite, which is stable in the temperature range of 575-700 °C. The revised phase structure corresponds to the formula Na₇Y₁₃F₄₆ (orthorhombic system), isostructural phases with Ln = Tm-Lu [23]. The paper [18] describes the phase composition NaY₂F₇, characterized by a complex low symmetric X-ray diffraction, similar to the structure of compounds with erbium and holmium. NaYF₄ connection has a dimorphic nature, a polymorphic transformation at 705 °C. Low temperature modification crystallizes in the trigonal system. High temperature version (cubic system) is capable of dissolving YF₃ in accordance with the limit composition Na_{0.345}Y_{0.655}F_{2.31} [23].

Designations α -NaREF₄ and β -NaREF₄ are used respectively in the literature for the cubic and hexagonal phases. There are following well-known methods for producing β -NaREF₄: solid phase synthesis [24, 25], hydrothermal synthesis [23], thermolysis [26], precipitation [1], pyrolysis [25]. Method efficiency depends on the size up-conversion particles of factors [27]. The highest quantum yields were submitted for micro-particles, obtained by solid synthesis [28].

Depending on heat treatment NaYF₄ powders during solid phase synthesis, as cubic and hexagonal modifications may be prepared [25]. Solid phase synthesis requires sintering in an atmosphere of HF/Argon to remove oxygen impurities disrupting the effectiveness up-conversion frequency due for multi-photon relaxation [25]. Oxygen may be removed by fluorination with NH₄F · HF or NH₄F, which is not sufficient to completely remove oxygen impurities [29] via sublimation, although limited because of low volatility of rare fluoride or by melt purification [30]. There is offered a method of converting α -NaYF₄ in β -NaYF₄ and removal of oxygen impurities [25], by pyrolysis using SnF₂ and ZnF₂ as oxygen scavengers.

Our study is based on a hypothesis, formulated on the basis of data patent RU 2445269 C1, which has been proposed a method for producing rare earth fluorides by subjecting the powders sulfides α -Ln₂S₃ hydrofluoric acid (48%), taken in an excess.

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During fluorination at room temperature, hydrogen sulfide was formed, which was removed from the reaction mixture, thus the reaction was held until the end; lanthanide fluoride precipitate was separated from the aqueous acid solution by decantation, and then subjected to dehydration in vacuum of 1 Pa at 60-80 °C [31]. This method allows the NPS to receive powders of rare-earth metal fluorides LnF₃.

The purpose of this study is the gradual development of an alternative method for producing nanostructured powder of NaYF₄ sulfide compounds by fluorination sulfide precursors.

II. EXPERIMENTAL PROCEDURES

A. Materials

The synthesis was carried out using commercially available reagents. The Y₂O₃ was 99.999 wt.% ultrapure and supplied by Uralredmed (Pyshma, Russia), the NaNO₃ and NaF were 99.99 wt. % by Vekton (St. Petersburg, Russia), the NH₄SCN was 98.5 wt. % and the HF was 99.9 wt. % by TEK System. All the chemicals were analytical grade and used without further purification.

B. Synthesis of NaYF₄ from Y₂S₃

Powder yttrium sulfide was obtained by reacting with the oxide powder gaseous decomposition products of ammonium thiocyanate (CS₂ and H₂S) [32] at 1050 °C for 20 hours. The experiment was conducted in a quartz reactor using argon as the carrier gas. Yttrium sulfide powder was treated 10-fold excess of a saturated solution of sodium fluoride to hydrofluoric acid (49%) in the ratio (10:1). All experiments were performed in Glassy carbon crucibles at ambient temperature (21-25 °C). The resulting precipitate was decanted, washed thoroughly with distilled water and dried at different temperatures in air.

C. Synthesis of NaYF₄ from NaYS₂

Yttrium oxide and sodium nitrate, taken in a stoichiometric ratio (1: 2), were annealed in alundum crucible in air at 800 °C for 20 hours and cooled in an open muffle oven mode. The obtained compound was treated with a stream NaYO₂ sulphidation agent (H₂S and CS₂) at 900 °C for 16 hours.

NaYS₂ compound powder is fluorinated in two ways: at first, by treatment with aqueous hydrofluoric acid (10-48%); secondly, by treatment with saturated aqueous NaF + HF.

D. Characterization

The chemical composition of the samples was determined by x-ray spectroscopy using a scanning electron microscope (JSM-6510LV, JEOL, Japan) with an accelerating voltage of 20 kV. The phase composition of the samples was studied by X-ray diffraction analysis (DRON diffractometer 7; Cu) Ka radiation. NaYS₂ fluorinated compound powder in two ways: by treatment with aqueous hydrofluoric acid (10-48%) and treatment with NaF+HF saturated aqueous. Evaluation crystallite size D (nm) carried by Selyakov-Scherer formula [33]:

$$D = k \frac{\lambda}{\beta \times \cos \theta},$$

where k – empiric coefficient (k ~ 1,0), λ – wave length (Å), β – X-ray diffraction peak half width (in radians), θ – the angle of diffraction.

III. RESULT AND DISCUSSION

In the process of synthesis there is obtained Y₂S₃ powder monoclinic structure with space group (Pr. C P21 / m), the unit cell parameters: a = 1.753 ± 0.002, b = 0.401 ± 0.002, c = 1.016 ± 0.002 nm, β = 98.603°, which are within the error consistent with the card PDF № 79-2250 base. When reducing the temperature of synthesis 1000 °C synthesis duration is increased to 30 hours or more. In this synthesis the process passes through the step of forming the first Y₂O₂S powder for 5-7 hours. Remaining time is required for the oxysulfide transition to the sulfide. Raising the temperature to 50 °C reduces synthesis time twice, but leads to sintering of the sample and disruption of the crystal lattice by forming a solid solution in the Y-S system.

NaYO₂ compound powder crystallizes in the monoclinic system (space group C2/c) with e-cell parameters: a = 1.000 ± 0.002, b = 1.320 ± 0.002, c = 0.605 ± 0.002 nm, β = 33°. These results are within the error limits are consistent with published data connection (base card PDF № 70-1422). Proposed mode of synthesis allows for complete interaction of

Table 1. Characteristics of products of interaction of sulfide precursors to HF and NaF + HF

Starting material	Fluorinating mixture	Reaction products	Lattice parameters for α-NaYF ₄ , Å	Composition of the solid solution
Y ₂ S ₃	NaF + HF (20%)	α-NaYF ₄	a=5.5406	Na _{0.34} Y _{0.66} F _{2.33}
	NaF + HF (15%)	α-NaYF ₄ + β-NaYF ₄ (~7%)	a=5.5267	Na _{0.36} Y _{0.64} F _{2.28}
	NaF + HF (10%)	α-NaYF ₄ + β-NaYF ₄ (~15%)	a=5.5203	Na _{0.37} Y _{0.63} F _{2.25}
	NaF + HF (5%)	α-NaYF ₄ + β-NaYF ₄ (~30%)	a=5.5112	Na _{0.39} Y _{0.61} F _{2.23}
NaYS ₂	HF (5-50%)	YF ₃	-	
	NaF + HF (15%)	α-NaYF ₄ + β-NaYF ₄ (~25%)	a=5.5421	Na _{0.33} Y _{0.67} F _{2.33}
	NaF + HF (10%)	α-NaYF ₄ + β-NaYF ₄ (~50%)	a=5.5122	Na _{0.39} Y _{0.61} F _{2.22}
	NaF + HF (5%)	α-NaYF ₄ + β-NaYF ₄ (~60%) + NaYS ₂	a=5.4690	Na _{0.47} Y _{0.53} F _{2.06}

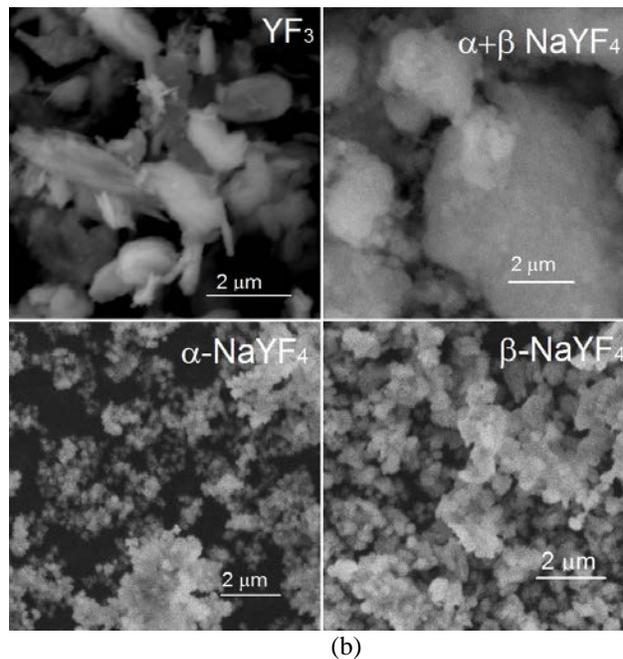
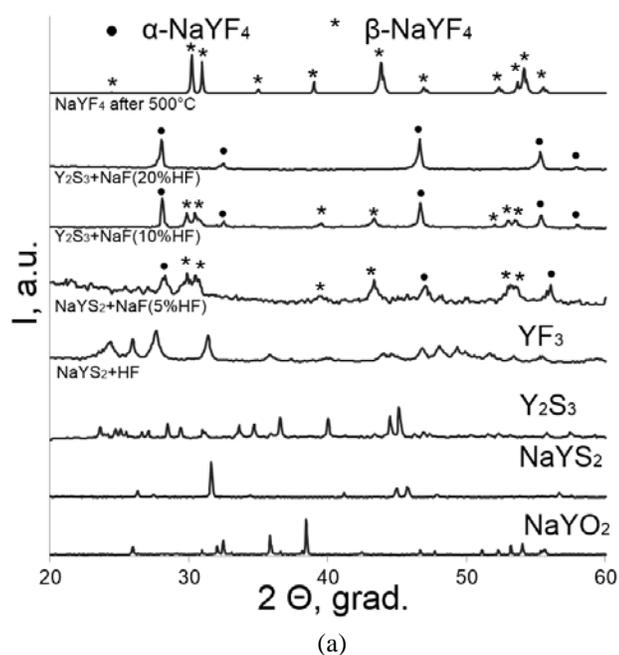


Fig.1 (a) XRD pattern and (b) SEM images of the sample of synthesis of compounds NaYF_4 by "soft chemistry" of sulphide precursors.

the starting materials, wherein active sodium ion does not react with the crucible material, as evidenced by the absence of reflections in the X-ray images of unreacted yttrium oxide (Fig. 1a) and a deformation of alundum crucible.

In the process of synthesis by gas stream sulphidation there was obtained NaYS_2 composition. The compound has the rhombohedral symmetry crystal system, space group $R\bar{3}m$ with the unit cell parameters: $a = 0.3966 \pm 0.0002$ and $c = 1.9927 \pm 0.0002$ nm (Fig. 1a), which corresponds to the card database PDF № 46-1051. When the temperature is raised to 950°C there is observed the interaction between the material and the reactor, as a result of which the sample is depleted of sodium, on the X-ray images reflexes 90% NaYS_2 and 10% Y_2S_3 compounds are present. A subsequent increase in temperature (1000°C) leads to an increase in the percentage of sample of yttrium sesquioxide sulfide.

During fluorination yttrium sulfide by saturated NaF , acidified with hydrofluoric acid to various content, a mixture of cubic and hexagonal phases NaYF_4 compound is formed. Thus, the use of greater content hydrofluoric acid leads to the formation of larger amounts of $\alpha\text{-NaYF}_4$ (Table 1).

As a result, the system NaF-YF_3 study allows to find NaYF_4 compounds cubic structure parameter e-cell $a = 5.448 \text{ \AA}$ [34]. However, according to [34], the cubic structure of the cell parameter can be varied over a range, that is associated with the formation of $\text{Na}_{0.5-x}\text{R}_{0.5+x}\text{F}_{2+2x}$ solid solution composition. Clarification of the solid composition of the solution takes place according to the formula $a = a_0 + kx$ [34].

The action of aqueous hydrofluoric acid on NaYS_2 compound decomposes and turns into sodium fluoride solution and yttrium fluoride precipitate; decantation process is the main component of the sample. On the X-ray images of samples there are yttrium fluoride reflexes (Fig. 1a). Electron

micrograph of the dried sludge is presented in the figure (Fig. 1b). According to the SEM, the resulting precipitate consisting of crystallites having a parallelepiped shape with dimensions of $0.12 \times 0.50 \text{ m}$. Reducing the concentration of hydrofluoric acid and 10% did not give significant results, due to the nature of NaLnF_4 compounds which are soluble in water incongruently.

NaYF_4 compound is formed by fluorination NaYS_2 compound in excess of saturated NaF+HF aqueous solution; it which consists mainly of hexagonal phase unit cell parameters: $a = 0.5995 \pm 0.0002$ and $c = 0.3480 \pm 0.0002$ nm with an admixture of the cubic phase with a fluorite structure cell parameter, presented in Table 1. Note, in the sample there is NaYS_2 compound, which is not subjected to fluorination. Increasing the content of hydrofluoric acid in the solution leads to a fluorinating side reactions. Yttrium oxysulfide is formed in a side process.

Based on the calculated values of the cell parameter fluorite structure, obtained from different sulfide precursors, corresponds to the composition, which is given in Table 1.

According to the scanning electron microscopy, described above by the procedures, obtained NaYF_4 compound consists of individual spherical particles with a crystallite size of 30-100 nm and agglomerates. On the X-ray images (Fig. 1a) of the precipitate, obtained after evaporation, there are significant expansion reflexes, associated with small crystallite size, which disappears after heat treatment. Based on Selyakov-Scherer formula [33], the NaYF_4 compound, fluorinating the resulting aqueous NaF+HF sulfide precursors is nanoscale crystallites with parameters, given in Table 2. To allow for expansion of the tool used diffraction reflection shooting with a standard substance for which the extension of the line is due only to the shooting conditions. The particulate used as a

reference (below 10 μm) powder $\alpha\text{-NaYF}_4$, annealed at 750 $^\circ\text{C}$, and the powder $\beta\text{-NaYF}_4$, annealed at 500 $^\circ\text{C}$. Dimensions of NaYF_4 compound powder crystallite, obtained after evaporation of the cubic structure and evaluated by reflection planes (111), (200), (220), (311) and (222); hexagonal - (110), (101), (111), (201) and (121). The dimensions are comparable with each other and are commensurate with the width of the particle data obtained by scanning the surface topography.

Table 2. Summary of average crystallite size (D) of α - and $\beta\text{-NaYF}_4$

Starting material	Fluorinating mixture	D from XRD for $\alpha\text{-NaYF}_4$, nm	D from XRD for $\beta\text{-NaYF}_4$, nm
Y_2S_3	NaF + HF (20%)	100	-
	NaF + HF (15%)	70	35
	NaF + HF (10%)	60	32
	NaF + HF (5%)	55	28
NaYS_2	NaF + HF (15%)	60	60
	NaF + HF (10%)	42	47
	NaF + HF (5%)	30	45

Heat treatment at a temperature 500 $^\circ\text{C}$ sample for 1.5 hours resulted in a shift in the compound with a hexagonal syngony parameters cell $a = 0,5995 \pm 0.0002$ and $c = 0,3479 \pm 0.0002$ nm.

IV. CONCLUSION

The proposed multi-step method for the synthesis of compound NaYF_4 by fluorination pre-synthesized sulfides Y_2S_3 and NaYS_2 does not allow the output connection in a hexagonal structure. When processing NaYS_2 powder with an aqueous solution of hydrofluoric acid of different concentrations in an incongruent NaYF_4 dissolving in water yttrium fluoride is formed. Fluorination Y_2S_3 and NaYS_2 compounds by NaF + HF aqueous saturated leads to the NaYF_4 formation of the cubic and hexagonal structures in the mixture. The content of the hexagonal pattern is inversely related to the content of hydrofluoric acid in the solution is fluorinated. Nevertheless, the overall result (advantage of the proposed method for producing sodium), according to the author's opinion, provides a basis for definite conclusions. According to this methodic, hexagonal phase nanopowder in a percentage of the cubic phase dominates as opposed to known technique, when as a starting material of yttrium salt solution (e.g., yttrium nitrate) is used. A prerequisite for obtaining NaYF_4 nanopowder, we believe, sulfide precursor fluorination with saturated aqueous sodium fluoride, hydrofluoric acid-acidified (2.7%) is necessary. The dimensions of the crystallites of powder $\beta\text{-NaYF}_4$ are 45 nm. The described method of NaYF_4 synthesis may be not the optimal, so the search operation in this direction in order to increase the yield hexagonal phase up to 99% must be continued.

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