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UDC 54.05:542 (546.33'64'161)

*ON THE PRODUCTION PROCESS OF NANOSTRUCTURED SODIUM TETRAFLUOROYTTRIATE POWDER**

SUMMARY. The purpose of this paper is to present the evolutionary development of the alternative production process of nanostructured sodium tetrafluoroyttriate powder. The problem of nanostructured compound synthesis is significant today due to the high technological potential of $NaYF_4$, its biocompatibility?, and low toxicity. These properties enable wide use of this compound in medicine and biotechnologies. The application of sodium tetrafluoroyttriate is possible provided that it is crystallized in the hexagonal system with the particle at most 50 nm in size. We consider the multiphase technique for $NaYF_4$ synthesis according to the scheme:

$$2\,NaNO_3+Y_2O_3 \xrightarrow[20\ hr]{800^\circ C} NaYO_2+H_2S+CS_2 \xrightarrow[16\ hr]{900^\circ C} NaYS_2+5NaF+HF \longrightarrow NaYF_4$$

$$NaYS_2+HF \longrightarrow YF_3+NaF_{(liq)}$$

It is fluoridated with 10 – 48 % hydrofluoric acid (1) and by aqueous caustic of sodium fluoride acidized by hydrofluoric acid (2). The size of crystallites is determined. The experimental research demonstrates the following: the fluoridation of the pre-synthesized sulfide does not enable pure compound to be obtained. When treated with aqueous solution of hydrofluoric acid of various concentrations, yttrium trifluoride with trace impurities of $NaYF_4$ (7%) is formed. When fluoridating $NaYS_2$ compound with saturated NaF + HF aqueous solution, about 10% of the original sulfide remains in the sample.

KEY WORDS. Fluorides, production process, nanocondition.

The problem of producing nanostructured sodium tetrafluoroyttriate powder is rather significant nowadays. The high technological potential of the $NaYF_4$ compound draws attention. The $NaYF_4$ (KYF_4)-based anti-Stokes luminophores are involved in the development of 3D technologies, semiconductor electronics, and can be used in biochemistry and medicine due to their low toxicity and high biocompatibility [1]. To be used in biochemistry and medicine, the $NaYF_4$ compound should be crystallized in the hexagonal system with the particles at most 50 nm in

* The experimental part of the research was carried out using the *CUC SANO&N* equipment and was financially supported by the Ministry of Education and Science of the Russian Federation (code 3.3763. 2011 (7-12)), within the Federal Target Program *Scientific and Academic Staff of Innovative Russia* No. 14.B37.21.1184.

size [2]. Besides, the change-over to nanopowders may improve the fluorescent properties of the materials [3].

In the NaF-YF_3 system, the fluorite-structured nonstoichiometric $Na_{0.5-x}Y_{0.5+x}F_{2+2x}$ high-temperature phase is formed, its highest melting point of 985 °C falls at 60.5+0.5 mol% YF_3 composition. The decrease in temperature results in the phase decomposition of a eutectoid pattern with separating the low-temperature $NaYF_4$ phase, as well as the phase similar to fluorite ordering which is stable in the range of 575-700 °C. The specified phase composition corresponds to the following formula: $Na_7Y_{13}F_{46}$ (the orthorhombic system), and it is an isostructural phase with Ln=Tm-Lu [4]. In [5] the author describes the phase of the NaY_2F_7 composition characterized by a complicated low-symmetry X-ray pattern similar to the structure of erbium and holmium compounds. The $NaYF_4$ compound is dimorphic, transiting to polymorphic at 705 °C. The low-temperature modification is crystallized in the trigonal system. The high-temperature modification (the cubic system) is able to dissolve YF_3 according to the boundary composition of $Na_{0.345}Y_{0.655}F_{2.31}$ [4].

In [4] the authors offer the technique for producing the $NaYF_4$ compound by the soft-chemistry method. The aqueous solution of NaF is added dropwise to the acid solution of yttrium nitrate in the ratio of 5 to 1. The mixture of trigonal and cubic phases is formed with the grains approximately 0.33 μm in size. In [2] there is a description of the one-phase technique for hydrothermal microwave synthesis of the $NaYF_4$:(Tb^{3+}, Yb) and KYF_4:(Tb^{3+}, Yb) nanopowders, which enables producing nanodisperse powders of the hexagonal modification with a narrow particle distribution in size. However, there is no detailed discussion of the results obtained.

Our study is based on the hypothesis which is presented in Patent No. RU 2445269 C1* which proposes the method for producing lanthanide trifluorides by adding hydrofluoric acid in excess (48%) to the α-Ln_2S_3 sesquisulfide powders. The fluoridation is carried out at indoor temperature until the hydrogen sulfide emission stops; the residuum of lanthanide trifluorides removed from the acid aqueous solution by decantation, it is then exposed to dehydration under vacuum up to 1 Pa at 60-80 °C [6]. This method enables obtaining nanosized powders of lanthanide trifluorides (LnF_3) [7-8].

The purpose of our study is the stage-by-stage development of an alternative technique for producing nanostructured powder of the $NaYF_4$ compound – by fluoridating the $NaYS_2$ sulfide.

The experiment. The original reactants were as follows: chemically pure (CP) $NaNO_3$, yttrium oxide (99.99%), ammonium rhodanide, hydrofluoric acid aqueous solution (48%), and extra pure (EP) NaF.

The X-ray phase analysis (RPA) was carried out using the *DRON-7* diffractometer (CuKα-radiation, Ni-filter). The L (Å) crystallite size was calculated using the Selyakov-Sherer's formula [9]:

* Invention Patent No. RU 2445269 C1 dd 30.06.2010. Authors: Petr O. Andreyev, Pavel P. Fedorov, Olga G. Mikhalkina, Andrey N. Boiko. Patentee: Tyumen State University.

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

where k is the empirical coefficient (k ~1.0), λ is the radiation wavelength (Å), β is the X-ray diffraction peak width at half height (given in radians), Θ is the diffraction angle. The investigation was carried out by the scanning electron microscopy method (SEM) using the *JSM-6510LV* scanning electron microscope (*JEOL* production).

Results and discussion. The $NaYF_4$ compound was synthesized according to the following scheme:

$$2\,NaNO_3+Y_2O_3 \xrightarrow[20\ hr]{800^\circ C} NaYO_2+H_2S+CS_2 \xrightarrow[16\ hr]{900^\circ C} NaYS_2+5NaF+HF \longrightarrow NaYF_4$$

$$NaYS_2+HF \longrightarrow YF_3+NaF_{(liq)}$$

In the first stage, a sample weight of original reactants (yttrium oxide and sodium nitrate) in the stoichiometric ratio (1:2) was annealed in an alundum crucible in the presence of atmospheric oxygen at 800 °C during 20 hours and then cooled in the top-open muffle furnace turned off. Yttrium oxide was pre-annealed at 1,000 °C for devolatilization and the removal of sorbed water. As a result, the $NaYO_2$ compound was synthesized, which was crystallized in the monoclinic system (the C2/c space group) with the following unit cell parameters (u.c.): a=1.000±0.002, b=1.320±0.002, c=0.605±0.002 nm β=33°. The data obtained within the measurement accuracy corresponded to the published data on the compound (PDF-base card No. 70-1422). Such a synthesis mode provides full interaction of the original reactants, when the active sodium ion does not react with the material of the crucible, which is confirmed by the non-occurrence of reflexes of unconverted yttrium oxide in the diffraction pattern (Fig. 1a) and the deformation of the alundum crucible.

In the second stage, the $NaYO_2$ compound underwent the sulphidation in the quartz reactor at 900 °C during 16 hours in the flow of sulphiding chemicals (H_2S and CS_2) obtained by the thermal decomposition of ammonium rhodanide at 300 °C. While being synthesized, the compound of the $NaYS_2$ composition of the orthorhombic system (sp.gr. R-3m) was obtained; its u.c. parameters were as follows: a=0.3966±0.0002, c=1.9927±0.0002 nm (Fig. 1b). When the temperature was increased to 950 °C, the interaction between the reactor and the substance was observed; as a result, the sample was depleted of sodium, it was confirmed by the reflexes of 90% $NaYS_2$ and 10% Y_2S_3 compounds in the X-ray pattern. The further increase in temperature (to 1,000 °C) resulted in the increase in the yttrium sesquisulfide percentage content in the sample.

The third stage of the treatment was the $NaYS_2$ fluorization, which was carried out in two ways: hydrofluoric acid aqueous solution (10-48%) and saturated NaF+HF aqueous solution treatments.

The $NaYS_2$ fluorization by hydrofluoric acid aqueous solution (48%) did not result in the sodium tetrafluoroyttriate formation. According to the RPA data, in the diffraction patterns the samples (Fig. 2a), there are mostly the reflexes of yttrium

fluoride and some few reflexes identified as the $NaYF_4$ compound of the hexagonal system. The occurrence of sodium in the amount of 2.25 at. % was identified by the elemental analysis. We can conclude that, when $NaYS_2$ is treated by the hydrofluoric acid aqueous solution, the compound is degraded, and sodium fluoride passes into the solution, while yttrium fluoride precipitates and remains the base component of the sample in the process of decantation. The electron micrograph of the evaporated residuum is presented in Fig. 2b. According to the SEM data, the precipitation obtained consists of parallelepiped-shaped crystallites 0.12×0.50 μm in size. The decrease in the hydrofluoric acid concentration to 10% gives no substantial results, which is caused by the nature of the $NaLnF_4$ compounds that are incongruently water soluble.

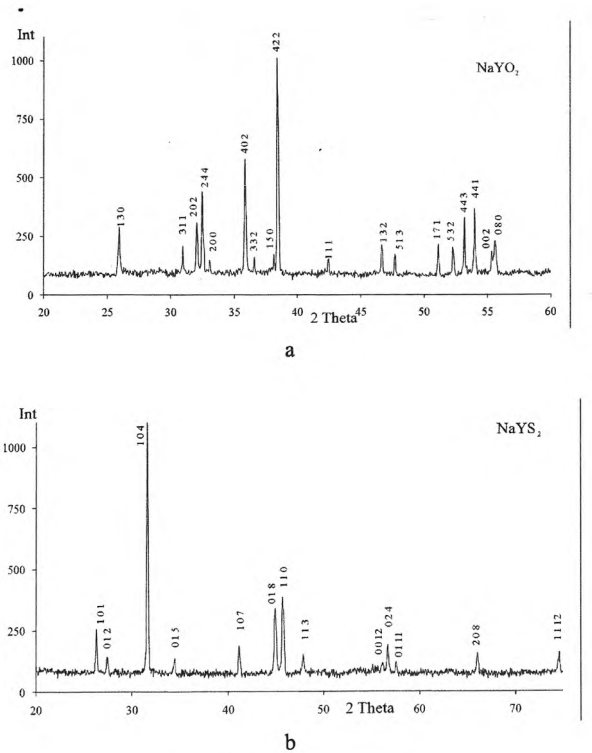
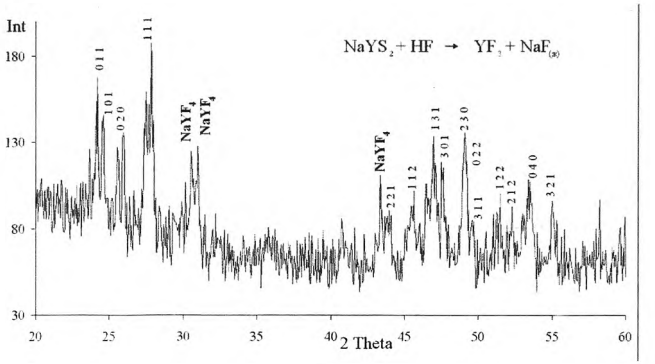


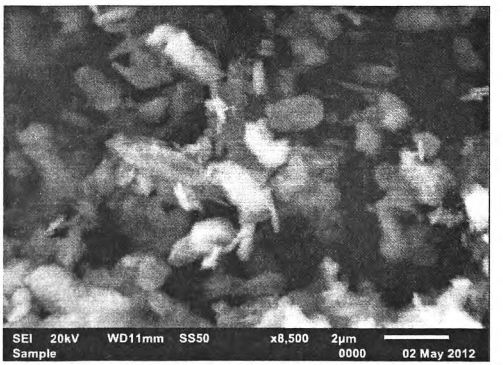
Fig. 1. The diffraction patterns:
a) the $NaYO_2$ phase obtained by annealing the Y_2O_3 and $2NaNO_3$ mix at 800 °C;
b) the $NaYS_2$ phase obtained by sulphidizing $NaYO_2$ at 900 °C during 16 hours

The $NaYS_2$ fluoridation in the excess of the saturated aqueous NaF+HF solution results in forming sodium tetrafluoroyttriate, which mainly consists of the hexagonal

phase with the following u.c. parameters: a=0.5995±0.0002 and c=0.3480±0.0002 nm, and the impure fluoride cubic phase with the u.c. parameter: a=0.5469±0.0001 nm. The calculated values of the u.c. parameter for the fluoride structure correspond to the composition of the $Na_{0.47}Y_{0.53}F_{2.06}$ compound [10]. It should be noted that the sample contains non-fluorizated $NaYS_2$. The increase in the hydrofluoric acid content in the fluoridating solution results in the side reaction where yttrium oxysulfide is formed.



a



b

Fig. 2. The sample obtained by the $NaYS_2$ fluoridation with the hydrofluoric acid aqueous solution (48%): a) the diffraction pattern; b) the electron micrograph of the residuum.

According to the scanning electron microscopy data, the $NaYF_4$ compound obtained by the described technique consists of single spherical particles with crystallites of 50-100 nm in size and their agglomerates. The diffraction pattern of the residuum obtained after evaporation (Fig. 3a) demonstrates a significant expansion of reflexes due to the small size of crystallites, which disappears after thermal

processing. The estimation by the Selyakov-Sherrer formula indicates that the $NaYF_4$ compound obtained by the $NaYS_2$ fluorization of the aqueous NaF+HF solution is nanosized, with the cubic crystallite of 30 nm in size and hexagonal ones of 45 nm (Fig. 3b). The sizes of crystallite in the $NaYF_4$ powder obtained by evaporation are calculated according to the reflection planes as (111) and (220) for the cubic structure, and as (110), (101), and (201) for the hexagonal one. These sizes match each other and are commensurable with the particle width values obtained when scanning the surface topography.

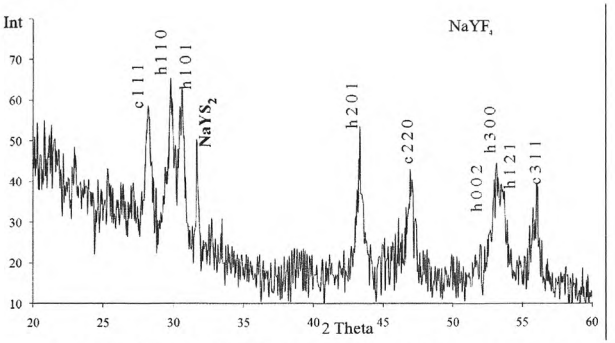


Fig. 3. The sample obtained by the $NaYS_2$ fluorization with the saturated aqueous NaF+HF solution: a) the diffraction pattern (*c* are the reflexes of the cubic system phase; *h* are the reflexes of the hexagonal system phase)

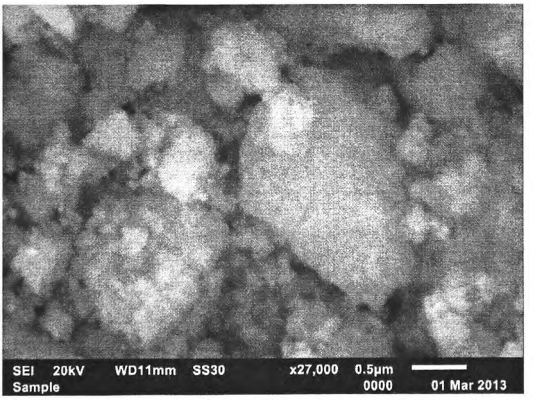


Fig. 3. The samples obtained by the $NaYS_2$ fluorization with the saturated NaF+HF aqueous solution: b) the electronic photomicrograph of the residuum.

The heat treatment of the sample at 500 ^{0}C during 1.5 hours resulted in the transition of the compound into the hexagonal phase with the following u.c. parameters: a=0.5995±0.0002, c=0.3479 ±0.0002 nm.

Conclusion. The proposed multiphase technique for the $NaYF_4$ synthesis by fluorization of the pre-synthesized sulfide $NaYS_2$ does not enable a pure compound to be obtained. When being treated by the aqueous solution of hydrofluoric acid in various concentrations, due to the incongruent dissolution of sodium tetrafluoroyttriate in water, yttrium trifluoride with trace impurities (~7%) of $NaYF_4$ is formed. The $NaYS_2$ fluorization by the saturated aqueous NaF+HF solution does not result in their full interaction. As a consequence, about 10% of the original sulfide remains in the sample. Nevertheless, the authors consider that the advantage of the proposed technique for producing sodium tetrafluoroyttriate is obvious and is as follows:

1. The yield of nanosized powder of the hexagonal phase dominates the cubic phase in percentage against the known soft-chemistry technique.

2. As the one-phase technique for the hydrothermal microwave synthesis is not explained in details by the researchers, it is impossible to estimate the productivity and economic efficiency of this technique for producing the sodium tetrafluoroyttriate powder.

Therefore, we think that to produce the nanosized $NaYF_4$ powder, the fluorization of the synthesized $NaYS_2$ sulfide by the saturated sodium fluoride aqueous solution acidified by hydrofluoric acid (48%) in the ratio of 10:1 is required. The crystallite size of the hexagonal sodium tetrafluoroyttriate powder is 45 nm.

To sum up, it is necessary to emphasize the permanent significance of developing a technique for producing the high-technology rare-earth metal compounds. Perhaps, the discussed method of synthesizing sodium tetrafluoroyttriate is not the most effective but exploratory studies in this field should be continued for the purpose of increase in the hexagonal phase yield to 99%.

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