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Synthesis and thermal stability of rare earth compounds REF₃, REF₃·nH₂O and (H₃O)RE₃F₁₀·nH₂O (RE=Tb – Lu, Y), obtained from sulfide precursors

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Highlights

- The REF₃·*n*H₂O and (H₃O)RE₃F₁₀·*n*H₂O compounds were synthesized from RE₂S₃ and HF.
- The REF₃ nH₂O compounds have an amorphous phase.
- After heat treatment the REF₃·*n*H₂O and (H₃O)RE₃F₁₀·*n*H₂O compounds moved into a REF₃ compound of crystal structure as β-YF₃.

Abstract

The nature of the interaction between sulphides of the rare-earth elements (RE) of the yttrium subgroup RE_2S_3 (Dy – Lu, Y) with hydrofluoric acid (concentration of 49%) was studied. Powders of RE_2S_3 compounds were obtained by the reaction between RE_2O_3 (Dy – Lu, Y) and Tb₄O₇ with a stream of H₂S and CS₂ in the 1000–1050 °C temperature range. The reaction between

RE₂S₃ and HF was carried out in a glassy carbon crucible in the 21-25 °C temperature range in solution, and the precipitate was washed with H₂O and dried at 90-100 °C. For the hydrates of RE fluorides with decreasing RE radius, the RE content increases the sorption of water for TbF₃·0.5H₂O; DyF₃·0.5H₂O; YF₃·0.5H₂O; HoF₃·0.8H₂O; and ErF₃·0.9H₂O. The powders of REF₃·*n*H₂O consisted of micro- and nano-sized particles containing the amorphous phase. Water loss occurs in the 50-180 °C temperature range and is accompanied by a natural increase in enthalpy: from 23.6 J/g for TbF₃·0.5H₂O to 97.8 J/g for ErF₃·0.9H₂O and from 51.1 J/g for (H₃O)Tm₃F₁₀·1.7H₂O to 64.5 J/g for (H₃O)Lu₃F₁₀·0.9H₂O. Exothermic effects of formation of polycrystalline phase REF₃ were recorded in the 200-300 °C temperature range. The reaction of RE₂S₃ (Tm, Yb, Lu) powders with HF proceeds with the formation of the zeolite type compounds (H₃O)Tm₃F₁₀·1.7H₂O, (H₃O)Yb₃F₁₀·1.0H₂O and (H₃O)Lu₃F₁₀·0.9H₂O. Thermal dissociation occurs with gradual loss of water and HF to form RE fluorides with the β-YF₃ structure as described by

 $(H_{3}O)RE_{3}F_{10} \cdot (1+n)H_{2}O \xrightarrow{\sim 50-170^{\circ}C} (H_{3}O)RE_{3}F_{10} \xrightarrow{\sim 200-350^{\circ}C} HRE_{3}F_{10} \xrightarrow{\sim 350-420^{\circ}C} 3REF_{3}.$

Keywords: rare earth fluoride, sulphides of rare earth elements, zeolite type

1. Introduction

The unique electronic structure of rare earth elements (RE) leads to the appearance of compounds with different optical, electrical [1, 2] and magnetic [3] properties, which have attracted considerable interest from researchers in recent years. Fluorides of rare earth elements are widely used in many fields (optical telecommunications, lasers, new optoelectronic devices, diagnostics and biological markers) [4-7]. In recent decades, a particularly extensive attention was devoted to rare earth fluorides (REF₃) as luminescent materials [8]. Owing to the low energy of wave oscillations, the decrease in the radiating activity of doping substances in the electronic excitation state is minimal [9, 10]. As a consequence, a high-luminescence quantum yield can be achieved [5]. Currently, fluorides of rare earth elements are used or tested in optoelectronics, optical fibres and amplifiers, lasers, and medicine. In view of their chemical stability, materials based on REF₃ could potentially be used as bioimaging fluorescent probes [5, 8].

Fluorides of rare earth elements La-Nd crystallize in the tysonite (LaF₃) structure type (ST) (trigonal crystal system, space group $P\overline{3}c1$). Morphotropics changed with decreasing ionic radius [11, 12]. For fluorides of Sm-Gd, dimorphism is typically observed with the low-temperature type β -YF₃ (orthorhombic crystal system, space group Pnma) and high-temperature modifications of tysonite [13, 14]. The REF₃ (Tb-Ho) retain the modification characteristic of β -YF₃ up to their melting point, whereas for fluorides of Er-Lu, Y, in addition to the basic orthorhombic

modification (β -YF₃), the high-temperature structure with cubic α -YF₃ cubic (space group P23) can be obtained [15,16].

REF₃ are obtained by chemical and physics-chemical methods. The most common and available is the method of precipitation from aqueous solutions, referred to as "soft chemistry" [5, 17, 18]. Methods of obtaining fluorides can be divided into hydrothermal [19-22], micro-emulsion [23] and microwave [24] thermal decomposition [25] types. Synthesis of nanofluorides of RE is mainly realised by one of the following methods: pyrolysis of fluorine-containing precursors; hydrothermal synthesis; micro-emulsion method; solvo-thermal synthesis; and the sol-gel technique [26-27]. At elevated temperatures, RE fluorides participate in pyrohydrolysis reaction to form oxy-fluorides (REOF) [29-30]. The preparation of REF₃ of the cerium subgroup during the interaction of hydrofluoric acid with RE₂S₃ provides a yield of close to 100%, and does not contain rare-earth oxyfluoride impurities, because the formation of the H₂S gas product shifts the equilibrium towards fluoride formation.

RE₂S₃ compounds exist in form of 4 basic modifications. RE₂S₃ compounds with RE=Ce-Dy have a low-temperature modification of the rhombic system of α -RE₂S₃ ST α -La₂S₃, sp.gr. Pnma and high-temperature cubic modification of γ -RE₂S₃ ST Th₃P₄, sp.gr. I43d. The δ -RE₂S₃ compounds (Re=Y, Ho, Er, Tm) have the monoclinic structure of ST δ -Ho₂S₃, sp.gr. P21/m. For ϵ -Yb₂S₃ and ϵ -Lu₂S₃, the hexagonal structure of ST α -Al2O3, sp.gr. R3c is found. In the literature, there is only one report on the extent of the RE₂S_{3-x}O_x solid solutions, mainly for γ -RE₂S₃: γ -(Sm₂S₃ – Sm₂S_{2.94}O_{0.06}) [31], γ -(Gd₂S₃ – Gd₂S_{2.97}O_{0.03}) [32].

In the process of hydrothermal synthesis of fluorides of rare-earth elements (Er-Lu, Y), the interaction of lanthanide oxalates with hydrofluoric acid leads to the formation of compounds δ -(H₃O)RE₃F₁₀ · *n*H₂O [33]. A compound with the (H₃O⁺)Y₃F₁₀⁻ · *n*H₂O structure was obtained as the second (secondary) phase by the interaction of a solution of yttrium nitrates and alkaline earth metal (strontium [34], barium [35]) with hydrofluoric acid (47%). The compound is crystallized in a cubic structure and consists of octahedral diamond [RE₆F₃₂]⁻¹⁴ blocks constructed from square REF₈ anti-prisms [36]. The behaviour of water molecules and the cation-exchange properties are observed to be of the zeolite type [37]. Ionic radius of the atom RE is an important factor in the formation of stable fluoride compounds. The connection structure of diamond [38] is formed from rare earth elements *r*Ho³⁺ (coordination number (CN) is 8) = 1.015 Å - *r*Lu³⁺_(CN 8) = 0.977 Å, Y: ARE₃F₁₀ · *n*H₂O (A⁺ = K⁺, Rb⁺, NH₄⁺, Cs⁺) [33], (C₂N₂H₁₀)_{0.5}RE₃F₁₀ · *n*H₂O [22], (C₃N₂H₁₂)_{0.5}RE₃F₁₀ · *n*H₂O [39].

In this paper, the nature of the interaction of sulphides of rare earth elements RE_2S_3 (Dy -Lu, Y) with hydrofluoric acid and the reaction products are studied, and their crystal chemical, physics-chemical characteristics, and thermal stability are considered.

2. Experiment

2.1. Materials

We used 99.99 wt.% ultrapure RE₂O₃ and Tb₄O₇ (manufacturer Uralredmed, Verkhnyaya Pyshma, Russia), 99.9 wt.% pure HF and NH₄SCN (manufactured by TEK Systems) and distilled water as our starting material without further purification.

2.2. Synthesis of RE₂S₃

Powders of RE sulphides were obtained by reacting powders of Tb₄O₇ and RE₂O₃ (Dy-Lu, Y) oxides with gaseous CS₂ and H₂S. The maximum mass of one batch does not exceed 7 g. The rate of supply of sulphiding gases is 20-25 ml / min [40]. The synthesis temperature is 1000-1100 $^{\circ}$ C, and the duration is 12-18 hours [41]. The experiment was carried out in a quartz reactor, using argon as a gas carrier, at the feed rate of 10 ml / min.

2.3. Synthesis of REF_3 and $(H_3O)RE_3F_{10}$

Sulphide powders were treated with an excess of hydrofluoric acid (49%) in the ratio of 1 to 10. All experiments were carried out in glass graphite crucibles at ambient temperature (21-25 °C). The precipitate that forms in the process is decanted, washed thoroughly with distilled water and dried at various temperatures in air. The heterogeneous reaction of polycrystalline powders of RE₂S₃ with an HF aqueous solution (49 wt%, acid taken in excess) occurs within 10-15 seconds. Gaseous H₂S are isolation shifted for the equilibrium in reaction towards the reaction products. RE₂S₃ compounds are completely soluble.

Samples were dried on a sand bath at 90-100 °C for 3 hours. A solid crust of the sample was formed from the mother liquor during the heat treatment. The end of the sample drying was fixed by the cracking of its surface. Samples were stored in batches. Work with the samples was conducted in the air.

2.4. Characterization

Actual chemical composition of the samples was determined using a Philips SEM JEOL JSM-6510 LM scanning electron microscope at five different points on the surface of a sample. The chemical composition of the samples was determined by X-ray spectroscopy (EDS) using a scanning electron microscope JSM-6510LV, (JEOL, Japan) with the accelerating voltage of 20 kV. The water was monitored by IR spectroscopy FSM1201 (OOO "Monitoring", St. Petersburg, Russia).

The phase composition of the obtained samples was studied by X-ray diffraction (DRON 7 diffractometer; CuK α radiation). The processing of the experimental data, including the refinement of the crystal lattice parameters and the determination of the coherent scattering regions D, was realized in the software complex "Powder 2" and DifWin. The instrumental expansion of the diffraction reflection was applied by a survey with a standard substance, for which the line

extensions are due only to the shooting conditions. As a standard, a dispersed (less than 10 μ m) REF₃ powder annealed at 800 °C was used.

Thermal analysis is performed by using synchronously thermal analyser STA 449 F3 MOMQ-1000D (NETZSCH, Germany) (crucibles Al₂O₃, argon, 2 deg/min heating rate, weight of sample approximately 25 mg). The error in determining the mass loss is established for the TG / DSC analyses of compounds of precisely known composition: CuSO₄ · 5H₂O, ZnSO₄ · 7H₂O and RE₂(SO₄)₃ · 8H₂O. The error value was 0.3%.

3. Result and discussion

3.1. Characteristics of the precursors RE_2S_3

The RE₂S₃ formation reaction proceeds through the dioxysulfide formation stage, in which the oxide is transformed into the sulphide according to: RE₂O₃ \rightarrow RE₂O₂S \rightarrow RE₂S₃. The structure of the RE₂OS₂ compositions (Sm-Yb, Y) is presented in previous works [42, 43]. The formation of the RE₂OS₂ compound as a co-product due to the interaction of oxides of RE with gaseous carbon disulphide and hydrogen sulphide was not detected. The impurity phase RE₂O₂S is identified by X-ray diffraction when its content in the sample is less than 0.25 mol% RE₂O₂S [44]. According to the XRF data, single-phase compounds of RE₂S₃ were obtained in three modifications: γ -cubic structure, type of Th₃P₄; δ -monoclinic, type of δ -Ho₂S₃ and ϵ -rhombohedral type of α -Al₂O₃ [45, 46] (Table 1). The parameters of the cell of the connections completely correspond to the database JCDPS (Table 1) [48]. The sulphur and the rare-earth element contents in compressed powders were determined by the EDS on the JSM-6510LV. The experimental sulphur content corresponds to the theoretical value in the 0.2-0.3 wt.% range (Table 1).

The oxygen content in the synthesized samples of RE_2S_3 can be as high as 0.2-0.3 wt.% O from the EDS data, which is generally commensurate with the accuracy of the determination method. Compositions of the synthesized samples of RE_2S_3 are in the concentration range $RE_{2.00}S_{3.02} - RE_{2.00}S_{3.00} - RE_{2.00}S_{2.98}O_{0.02}$, according to the EDS data.

Synthesized RE_2S_3 compounds do not contain impurities of oxygen-containing phases within the accuracy of XRF.

Chemical reaction of powders of RE₂S₃ compounds with an HF aqueous solution (49%) occurred within a few seconds (up to 5-10 seconds) and were accompanied by exothermal effects. The phase composition of the reaction products of the sulphides of the yttrium subgroup of rare earth elements with hydrofluoric acid is determined by the reaction conditions and the RE⁺³ radius $r_{(CN 8)}$. The relationship between the modification of the initial sulphide and the phase composition of the reaction products was not established.

3.2. X-ray analysis

Two different patterns of interaction of RE sulphides of the yttrium subgroup with an aqueous solution of hydrofluoric acid (49%) are established by the XRD method.

In the first case, diffraction patterns of samples contain fuzzy reflections of a rhombic structure of the β -YF₃ type and a "halo" at d = 4.135-2.690; 2.157-1.690 Å (Figure 1a). This picture is observed for RE (Tb - Er, Y). It can be assumed that the product of the reaction is fluoride of RE (Tb-Er, Y) and an X-ray amorphous phase, based on the XRD analysis. The intensity of the halo in the RE series naturally increases. Previously, the X-ray amorphous phase was obtained only for NdF₃ · *n*H₂O [30].

In the second case, the diffraction patterns of the samples are identical to the diffraction patterns of compound (H₃O)Yb₃F₁₀ · H₂O [48] (Figure 1b) and are identified to be in the cubic $Fd\overline{3}m$. Cell $a((H_3O)Tm_3F_{10})$ • $1.7H_{2}O) = 15.380$ Å. system parameters $a((H_3O)Yb_3F_{10} \cdot 1.0H_2O) = 15.319$ Å, $a((H_3O)Lu_3F_{10} \cdot 0.9H_2O) = 15.263$ Å are comparable with the data of [33, 38, 49]. Impurity reflexes were observed in the XRD data of samples of compounds (H₃O)RE₃F₁₀ · nH₂O (Tm, Yb). The elements Tm ($4f^{13}6s^2$) and Yb ($4f^{14}6s^2$) tend to exhibit a valence in compounds of two. Most likely, the impurity phase peaks are associated with the formation of a solid solution of the composition $(H_3O)(RE^{+3}, RE^{+2})_3F_{10} \cdot nH_2O$. This aspect has not been studied in this paper.

The X-ray diffraction patterns of REF₃ (Tb-Ho) show a significant expansion of reflections, which disappears after the thermal treatment. Expansion of diffraction peaks is due to the small size of the crystallites. According to Scherer's formula, crystallite sizes for all possible reflections of fluorides of RE (Tb-Ho, Y) were calculated (Table 2). The X-ray diffraction pattern contains three series expansions, thereby presenting the likely shape of the particle as an ellipse with a conventional dimensions $D \times 2D \times 4D$, where D ranges from 45 (Tb) and 70 (Ho) nm (Table 2).

The X-ray amorphous phase, the compounds with the composition $(H_3O)RE_3F_{10} \cdot nH_2O$, the hydrates of fluorides of RE REF₃ $\cdot nH_2O$ at 400 °C and higher are thermally dissociated to form the fluorides of RE of the β -YF₃ structure. Cell parameters of REF₃ compounds are consistent with the JCPDS data (Table 3).

Oxygen-containing impurities REOF, RE_2O_3 are not found, indicating the absence of RE hydroxides in the samples of fluorides obtained by the above described procedure.

3.3. Thermal characterization

Samples of fluorides of RE (Tb-Er, Y) and compounds of zeolite type $(H_3O)RE_3F_{10}$ (Tm-Lu) show an endothermic effect in the 50-175 °C range (Figure 2). This is ascribed to the loss of adsorbed water. The form of the thermal effect indicates the gradual removal of adsorbed water from the surface of the solid phase. The enthalpy of the effect in a list of compounds of RE gradually increases (Table 4). The magnitude of the endothermic effect in the RE series increases,

indicating an increase in the strength of the bond between the water molecules and fluoride compounds.

Thermal experiments unambiguously determine the adsorbed nature of water in the test samples. The water present in the samples in the form of a surface film (wetness) gives rise to a separate peak of the non-invariant phase transition $H_2O_{(liquid)}$ - $H_2O_{(vapor)}$, at 100 °C. The boiling peaks of water were observed on the undried samples.

The exothermic effect is manifested for RE fluorides in the 200-270 °C range. The magnitude of the effect increases in the series of Tb-Er compounds (Table 4). Most likely, the exothermic effect is caused by the transition of the X-ray amorphous phase to the polycrystalline phase of REF₃ and these results are consistent with the XRD results. X-ray analysis showed that the maximum amount of X-ray amorphous phase was observed for ErF₃. After heat treatment at above 200-250 °C, the X-ray characteristics of the samples changed abruptly with the halo decreasing, and the reflexes becoming more narrow. The masses of RE fluorides stop decreasing at the heating temperatures of 410 °C (Tb), 410 °C (Dy), 425 °C (Y), 420 °C (Ho), and 320 °C (Er). Owing to thermal dissociation, compounds REF₃ ST β -YF₃ are formed, the crystal chemical parameters of which are in complete agreement with the JCPDS database data (Table 3).

In the series of fluorides of RE containing adsorbed water, there is a tendency to increase the content of water molecules per formula unit REF₃. The composition of freshly prepared samples varies from TbF₃ · 0.5H₂O to ErF₃ · 0.9H₂O (Table 4). In parallel experiments, the composition of REF₃ · nH₂O varies within the range $n = \pm 0.1$, but for all the samples obtained, n<0.9. When the samples of REF₃ · nH₂O are held in air, two opposite processes occur, depending on the water vapour partial pressure: moisture absorption by freshly prepared samples and weathering of water molecules.

Thermal analysis of samples of compounds $(H_3O)RE_3F_{10} \cdot nH_2O$ showed two conjugate effects, the first of which is endothermic and the second is exothermic (Figures 2 b-d, Table 4). The temperatures of the endothermic effect for samples $(H_3O)RE_3F_{10} \cdot nH_2O$ (Tm, Yb) practically coincide with the temperatures at which the sample acquires a mass close to the HRE_3F_{10} composition. It could be assumed that the endothermic effect energy is spent on the expansion of the zeolite type compound with the remaining dissociation of H_2O molecules to HRE_3F_{10} composition. Formation of a polycrystalline structure of REF_3 determines the manifestation exothermic effect. The general scheme of the thermally driven transformation of the $o(H_3O)RE_3F_{10} \cdot (1+n)H_2O$ compounds is given by the following:

$$(H_{3}O)RE_{3}F_{10} \cdot (1+n)H_{2}O \xrightarrow{\sim 50-170^{\circ}C} (H_{3}O)RE_{3}F_{10} \xrightarrow{\sim 200-350^{\circ}C} HRE_{3}F_{10} \xrightarrow{\sim 350-420^{\circ}C} 3REF_{3}.$$

Samples of the zeolite type compounds dried at 100 °C lost an average of 7.0 wt. % upon thermal dissociation to 3REF₃ (Figures 2 b-d). The maximum mass loss was shown by the compound containing thulium and reached 9.2 wt.%. For compounds with stoichiometric composition (H₃O)RE₃F₁₀ · nH₂O, the weight losses were 7.69. 7.51 and 7.45 wt. %, for RE = Tm, Yb and Lu, respectively. The composition of synthesized fluoride compounds (Table 4) under the assumption of high content of adsorbed H₂O molecules was determined. A trend of decreasing number of H₂O molecules in zeolite type compounds was found with n varying from 1.7 for RE=Tm 0.9 for Re=Yb. As the drying temperature of the sample increases, the amount of nH₂O molecules in the zeolite type compound decreases.

3.4. Morphology characterization

As a result of the reaction of RE sulphides with hydrofluoric acid, the particle morphology varies greatly. The powders for γ -Tb₂S₃ show a coral-like grained structure, formed by fused elongated ovals with dimensions of $0.4 \times 0.7 \mu m$ (Figure 3a). The precipitates of REF₃ (Tb-Er, Y) fluorides have spherical grains with the size of less than 1 micron, combining into agglomerates of 2-7 μm . It is not possible to distinguish the differences in the grain characteristics of the crystalline and X-ray amorphous phases or to obtain clear images of nanosized particles (Figure 3b). The characteristics of the sediment surface did not allow us to obtain clear nanoscale images. A similar morphology for X-ray amorphous phases was also observed for sulphates of RE, for example, Eu₂(SO₄)₂ [51].

The presence of a "film" of the water phase on the particles was not detected in the samples of RE fluorides containing adsorbed water (Figure 3b). A water film is present in the raw samples and appears in the SEM image in separate areas in the form of a vague enveloping sphere, usually encapsulating several particles and/or agglomerates.

The particles of the $(H_3O)Tm_3F_{10} \cdot 1.7 H_2O$ compound have the shape of a regular octahedron with faces of 0.7-1.5 µm size and 4-8 µm particle size (Figure 3c). With a further decrease in the ionic radius, the particle shape becomes close to a sphere. The compounds $(H_3O)Yb_3F_{10} \cdot 1.0 H_2O$, $(H_3O)Lu_3F_{10} \cdot 0.9 H_2O$ are present in the form of globules with a diagonal of 0.5-1.0 µm (Figure 3d). In the spherical particles, the octahedral motif can be traced.

3.5. IR spectra

The IR spectra of anhydrous REF₃ samples contain characteristic absorption bands in the 400-500 cm⁻¹ range caused by the RE-F bond vibration (Figure 4). Samples of RE fluorides containing adsorbed water and zeolite type (H₃O)RE₃F₁₀ · nH₂O compounds have characteristic absorptions of bond stretching (3000-3800 cm⁻¹) and deformation (1630, 1440 cm⁻¹) vibrations of OH groups [52]. As the compounds of composition (H₃O)RE₃F₁₀ · nH₂O are heat treated and the

H₂O molecule content decreases, the intensity of the peaks for the OH-group oscillations decreases. The REF₃ \cdot *n*H₂O compounds show characteristic absorption peaks in the 800-1200 cm⁻

¹ range. The phase composition of one of the synthesized samples was determined by IR spectroscopy as $(H_3O)Yb_3F_{10} \cdot nH_2O + YbF_3 \cdot nH_2O$. The X-ray patterns of the sample show diffraction maxima of the zeolite type compound and the halo of the X-ray amorphous phase. In the IR spectrum of the sample, characteristic absorption lines of the zeolite structure as well as absorption lines of 800-1200 cm⁻¹ REF₃ · *n*H₂O are observed. The YbF₃ · *n*H₂O phase in the sample is present in the X-ray amorphous state (Figure 4). Peaks for the vibrations of RE-OH groups require detailed study, because there is little information on the investigations of the compounds that are the subject of the article by the IR spectroscopy.

3.6. Reaction steps

The interactions of RE₂S₃ (Tb-Er) compounds for different ionic sizes varying from $r\text{Tb}^{3+}(\text{CN 8}) = 1.040$ to $r\text{Er}^{3+}(\text{CN 8}) = 1.004$ nm with an aqueous solution of HF (49%) lead to the formation of REF₃ · *n*H₂O with the β-YF₃ structure type as described by reaction (1) (Table 4).

 $RE_2S_3 + 6HF + nH_2O = 2REF_3 \cdot nH_2O\downarrow + 3H_2S\uparrow(1)$

The precipitates of RE fluorides of (RE=Tb-Er) obtained by reaction (1) with different heat treatments retain the β -YF₃ structure type. It should be concluded that products of reaction (1) are not crystallohydrates and H₂O molecules are not a part of the structure of fluorides but are adsorbed on the surface of the grains [53]. Water molecules are bound to the solid phase only by van der Waals forces and the HO-H...F-RE²⁺ hydrogen bonds.

The REF₃ \cdot *n*H₂O composition depends on the following synthesis parameters: acid concentration, the mass ratio of the sulphide sample and the hydrofluoric acid solution, the synthesis and drying temperatures, and the storage conditions of the samples. The synthesis parameters are specified in the methods section.

The reaction of the s Tm_2S_3 , Yb_2S_3 , Lu_2S_3 ($rRE^{3+}_{(CN 8)}$, Table 4) compound with hydrofluoric acid proceeds by reaction (2) and leads to the formation of zeolite type (H₃O)RE₃F₁₀ · nH_2O compounds.

 $3RE_2S_3 + 20HF + (2+2n)H_2O = 2(H_3O)RE_3F_{10} \cdot nH_2O\downarrow + 9H_2S\uparrow(2)$

According to [31], the (H₃O)RE₃F₁₀·H₂O composition, the resulting interaction between the aqueous solution of oxalate rare earth elements with hydrofluoric acid (49%) is formed for rare earth elements with $rRE^{3+}(CN 8)$ smaller than 1.004 Å (Er -Lu, Y). Attempts to obtain a compound involving yttrium and erbium ions by reaction (3) were not successful. Reducing the synthesis temperature to 0 °C and processing temperature to 25 °C did not lead to a change in the results. At

different synthesis temperatures, the products of the interaction of Y_2S_3 and Er_2S_3 with an aqueous HF solution are the REF₃ · *n*H₂O and the X-ray amorphous phase.

4. Conclusions

The phase compositions of the products of the reactions of the RE₂S₃ (Tb-Lu, Y) compounds with an aqueous HF solution (49%) were established. The reactions were carried out at 21-25 °C, and the precipitate was decanted and dried at 90-100 °C. Rare earth element fluorides with the compositions $TbF_3 \cdot 0.5H_2O$, $DyF_3 \cdot 0.5H_2O$, $YF_3 \cdot 0.5H_2O$, $HoF_3 \cdot 0.8H_2O$, $ErF_3 \cdot 0.9H_2O$ were obtained. Upon heating, more than 2/3 of crystalline water passes into the gas phase in the 50-170 °C temperature range. This process is accompanied by an endothermic effect, the enthalpy of which in the RE series naturally increases. In the 200-270 °C temperature range, the exothermal effect of the formation of the polycrystalline phase of REF₃ is manifested. For the RE =Tm, Yb, Lu, zeolite type compounds with the δ -KYb₃F₁₀ · nH₂O type structure were obtained: $(H_{3}O)Tm_{3}F_{10} \cdot 1.7H_{2}O$, a = 15.380 Å; $(H_{3}O)Yb_{3}F_{10} \cdot 1.0$ H₂O, a = 15.319 Å; $(H_3O)Lu_3F_{10} \cdot 0.9 H_2O$, a = 15.263 Å. The particles of the zeolite type compound have the form of regular tetrahedra or a spherical shape with dimensions of $0.7 \times 1.5 \mu m$. Thermal evolution profiles of the zeolite phases samples contain endothermic effects at 50-170 °C accompanied by a transition of water to the gas phase, as well as exothermic effects at 200-360 °C corresponding to the formation of polycrystalline REF₃. The REF₃ (ST β -YF₃) phases are the final products of thermal treatments of the REF₃ \cdot *n*H₂O and (H₃O)RE₃F₁₀ \cdot *n*H₂O compounds. IR spectra of RE fluorides containing adsorbed water and zeolite type compounds contain peaks for bond stretching $(3000-3800 \text{ cm}^{-1})$ and deformation $(1630, 1440 \text{ cm}^{-1})$ vibrations of OH groups.

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Figure 1. XRD patterns of the samples, obtained at 100 °C a): 1- TbF₃ · 0.5H₂O; 2- DyF₃ · 0.5H₂O; 3- HoF₃ · 0.8H₂O; 4- YF₃ · 0.5H₂O; 5- ErF₃ · 0.9H₂O; b): 1- (H₃O)Tm₃F₁₀ · 1.7H₂O; 2- (H₃O)Yb₃F₁₀ · 1.0H₂O; 3- (H₃O)Lu₃F₁₀ · 0.9H₂O; 4-LuF₃, obtained at 800 °C



Figure 2. TG, DSK curves for samples dried at 100 °C: (a) $ErF_3 \cdot 0.5H_2O$, (b) $(H_3O)Tm_3F_{10} \cdot 1.7H_2O$, (c) $(H_3O)Yb_3F_{10} \cdot 1.0H_2O$, (d) $(H_3O)Lu_3F_{10} \cdot 0.9H_2O$.



Figure 3. SEM images of particles of powders of phase compositions: (a) Tb_2S_3 , (b) $TbF_3 \cdot 0.5H_2O$, (c) $(H_3O)Tm_3F_{10} \cdot 1.7H_2O$, (d) $(H_3O)Lu_3F_{10} \cdot 0.9H_2O$.



Figure 4. IR spectrum of fluoride compounds

RE_2S_3	Sp.gr.	№ JCPS	Cell parameters, Å				EDS (wt.%)			
			a	b	с	α/β°	RE(exp.)	S(exp.)	S(theor)	
γ -Tb ₂ S ₃	I43d	26-1424	8.349	-	-	-	76.6	23.4	23.23	
γ -Dy ₂ S ₃	I43d	26-0594	8.298	-	-	-	77.3	22.7	22.84	
δ -Y ₂ S ₃	$P2_1/m$	79-2250	17.486	4.079	10.027	97.86	65.0	35.0	35.10	
δ-Ho ₂ S ₃	P21/m	73-0466	17.476	4.002	10.149	98.18	77.3	22.7	22.58	
δ -Er ₂ S ₃	P2 ₁ /m	81-0926	17.427	3.979	10.097	98.67	77.5	22.5	22.33	
δ -Tm ₂ S ₃	$P2_1/m$	44-1157	17.369	3.956	10.044	98.65	78.0	22.0	22.16	
ϵ -Yb ₂ S ₃	R3c	82-1182	7.208	-	-	55.82	78.4	21.6	21.75	
ϵ -Lu ₂ S ₃	R3c	85-0744	7.221	-	-	55.81	78.3	21.7	21.56	

Table 1. Crystalline chemical characteristics and the content of sulphide sulphur in the powders of RE_2S_3 compounds.

REF ₃	D, nm							
	101	020	111	210	121			
TbF ₃	43	188	49	79	93			
DyF ₃	43	169	45	87	90			
YF ₃	43	184	57	102	92			
HoF ₃	62	262	77	118	109			

Table 2. Calculation of the size of the area of coherent scattering.

REF ₃	№ JCPDS	Cell parameters, Å					
		а	b	с			
TbF ₃	84-0179	6.496	6.932	4.377			
DyF ₃	32-0352	4.472	6.919	4.383			
YF ₃	74-0911	6.379	6.874	4.409			
HoF ₃	84-0178	6.402	6.875	4.371			
ErF ₃	86-0710	6.344	6.835	4.378			
TmF ₃	32-1352	6.278	6.814	4.411			
YbF ₃	74-2178	6.213	6.782	4.430			
LuF ₃	32-0612	6.149	6.762	4.476			

Table 3. Cell parameters of REF₃ (ST β -YF₃), obtained at an annealing temperature of 400 °C.

Table 4. Phase composition of the starting compounds, the reaction (RE_2S_3 +HF) products, thermalproperties of fluoride of rare earth compounds.

		Composition	n of	Thermal effects in the sample, heated to 500 °C						SS
RE	rRE ³⁺ ,	samples	of	Thermal effects, °C			Enthalpy, J/g			lo
	[50]Å	reaction, dried at		T ₁	T ₂	T ₃	ΔH_1	ΔH_2	ΔH_3	ght %
		100 °C								/ei m,
		type	n							∇
Tb	1.040		0.5	50-175	-	200-220	23.6	-	-0.8	3.76
Dy	1.027		0.5	50-180	-	210-240	27.0	-	-1.5	4.00
Y	1.019	A*	0.5	50-150	-	270-305	45.0	-	-12.0	5.86
Ho	1.015		0.8	40-140	-	215-255	50.0	-	-50.2	5.79
Er	1.004		0.9	55-160	-	230-270	97.8	-	-64.3	6.46
Tm	0.994		1.7	65-155	170-225	225-270	51.1	23.4	-18.8	8.01
Yb	0.985	B**	1.0	70-175	280-360	360-420	55.2	18.3	-38.0	5.77
Lu	0.977		0.9	60-175	270-350	365-425	64.5	6.0	-57.5	6.07