Synthesis and luminescent properties of (RE0.95Ln0.05)2O2S (RE = La, Y; Ln = Ho, Tm)

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SYNTHESIS AND LUMINESCENT PROPERTIES OF $RE_2O_2S:Ln^{3+}$ (RE = La, Y; Ln = Ho, Tm)

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Abstract

Solid solutions of oxysulfides $RE_2O_2S:Ln$ (RE = La, Y) were obtained by hydrogen reduction of the co-precipitated sulfates followed by sulfidation of the reaction products. The crystal chemical characteristics of the obtained compounds were refined by the Rietveld method. Morphological certification of particles in the dynamics of synthesis was carried out. The results showed an increase in particle size and the appearance of spherical holes of 50-400 nm due to elevated temperatures and the diffusion nature of reduction and sulfidation processes. Steady state luminescence properties displayed characteristic sharp bands corresponding to 4f-4f transitions. Luminescence decay curves of all studied samples showed monoexponential decay with microsecond and hundreds microsecond lifetimes depending on doping ions. Calculated color coordinates of Ho^{3+} and Tm^{3+}-doped powders make them promising candidates to be used as phosphors.

Keywords: rare earth oxysulfides, synthesis, Rietveld, luminescence, lifetime, quantum yield

1. Introduction

The rare-earth oxysulfides La_2O_2S (La^0 [Xe]$5d^16s^2$), Gd_2O_2S (Gd^0 [Xe]$4f^75d^16s^2$), Y_2O_2S (Y^0 [Xe]$5d^15s^2$), Lu_2O_2S (Lu^0 [Xe]$4f^{14}5d^16s^2$), due to the peculiarities of their electronic structure, can be regarded as unique luminescent structures for practical use and for basic research [1, 2]. Luminescence is mainly determined by the nature of the activator ion, but the host matrix into which this ion is embedded affects the intensity of the emission lines through its crystal field [3, 4].

Compounds $RE_2O_2S:Ln^{3+}$ are in great demand due to their excellent luminescent properties and color purity [5]. They can be suitable for creating thermographic phosphors (excellent candidates for fluorescence measurements of physiological temperatures using a miniature temperature sensor up to nanoscale) [6]. The authors of [7-12] synthesized and studied the properties of new materials that demonstrate unique thermal and luminescent properties.

Most phosphors are excited by ultraviolet light and exhibit temperature sensitivity, which allows them to be used to control temperature conditions in gas turbine combustion chambers in high-temperature areas of the turbine [13], as well as in X-ray diffraction and scintillation equipment [14]. These materials have the ability to store and release large volumes of oxygen under oxidation/reduction conditions, which makes them interesting as nanocatalysts [15], allows them to be used as laser detection of securities counterfeits [16], to create ultraviolet LEDs (white lamps light) [17], in photovoltaic solar cells [18], as a coating of reinforcing screens during magnetic resonance imaging [19].

Nanophosphors are a class of materials with unique properties that make them very attractive for biological applications [20]. Information about the compositions studied in this paper is rather limited. The optical fluorescence of ten trivalent lanthanide ions, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm in Y_2O_2S, La_2O_2S, and Gd_2O_2S, which was measured using X-ray excitation at 300 K., was described in [21]. La_2O_2S appears to be a more efficient host than Y_2O_2S and Gd_2O_2S for all lanthanides. The main features of the luminescence spectra and kinetics of $(Y_{1-x}Tm_x)_2O_2S$ solid solutions in the range 400–2000 nm under laser excitation at 790 and 810 nm were studied. The results were used to develop a series of IR phosphors that are “invisible” under laser excitation in the range of 790–810 nm and possess tunable and reproducible relative intensities of the three groups of IR luminescence bands in the ranges of 770–840, 1360–1520, and 1650–1980 nm, respectively [22]. The compound $La_2O_2S:Tm^{3+}$ was studied in [23]; luminescence excitation at a wavelength above 355 nm occurs mainly due to energy transfer from the host, which absorbs the exciting radiation, to the Tm^{3+} ion.

The method of obtaining new functional materials $RE_2O_2S:Ln$ by sequential processing of powders of sulfates of rare-earth elements in a stream of H_2, H_2S, used in this work, has several

advantages over solid-state synthesis methods. It is distinguished by manufacturability, productivity, the ability to produce batches of the product from tens to hundreds of grams and to conduct the process both continuously and interrupted at any time, without any significant negative consequences [24].

Thus, the aim of the work is to obtain solid solutions of oxysulfides by sequential processing of co-precipitated sulfates of rare-earth elements in an atmosphere of H_2, H_2S, and to study the morphology and optical properties of the obtained samples.

2. Materials and methods

2a. Preparative Methods

For the synthesis of $RE_2O_2S:Ln^{3+}$ compounds, calculated in a ratio of 95:5 mol. % of the amount of Ln_2O_3 (≥99.99%, ultrapure, OOO TDM-96, Russia). Oxide powders were weighed on an analytical balance to an accuracy of ± 0.0001 g. Before weighing, the oxides were calcined in a muffle furnace at 900 °C for 24 hours to remove sorbed water, as well as rare earth carbonates and hydroxides. Acids were selected using graduated pipettes with an accuracy of ± 0.1 ml. Samples of oxides were poured into a heat-resistant glass with a capacity of 100 ml, then HNO_3 (Vekton Ltd., Russia) was poured with constant stirring, with a concentration of 15 mol/L, with a volume of 10 ml, if necessary, heated to a transparent state. The result was a mixture of nitrates:

$$0{,}95RE_2O_3 + 0{,}05Ln_2O_3 + 6HNO_3 \rightarrow 2(RE_{0,95}Ln_{0,05})(NO_3)_3 + 3H_2O \quad (1)$$

Then, nitrate solutions were cooled to a temperature of 35-40 °C and 7 ml of H_2SO_4 (Vekton Ltd., Russia), with a concentration of 18 mol/L, with an excess of up to 7%, were added with a fine stream with constant stirring. As a result, crystalline hydrates of the precipitated co-crystallized sulfates were obtained according to the chemical reaction equation:

$$2(RE_{0.95}Ln_{0.05})(NO_3)_3 + 3H_2SO_4 + nH_2O \rightarrow (RE_{0.95}Ln_{0.05})_2(SO_4)_3\ nH_2O + 6HNO_3 \quad (2)$$

The resulting suspension was evaporated to dryness at 85-90 °C to remove water and nitrogen oxides, and then calcined at 600 °C for up to 12 hours to release residual sulfuric acid and achieve high crystallinity of the sample. The method of co-precipitation of sulfates allows to achieve a uniform distribution of rare-earth metal cations. The resulting precipitate was triturated to obtain a powder and sieved through a sieve with a 100 μm cell.

The sample was treated in a hydrogen stream using the setup shown in Figure S1. Hydrogen synthesis was performed using a SPECTR-6M hydrogen generator. Bidistilled water passed through a deionizer was used for electrolysis of water. A 10 g sulphate powder was placed in a quartz glass located in a reactor with a gas outlet tube placed in it. The device was carefully sealed and purged in a stream of hydrogen for 30 minutes in order to displace air from it with a gas flow rate of 7-8 l/h from the hydrogen generator, and then placed in a vertical furnace, setting the temperature mode using the Thermolux controller. After processing the sample for 1 hour at 620 °C in a stream of H_2,

the reactor was taken out of the furnace, cooled, and a sample was taken to study the phase composition. To complete the passage of chemical transformations, the treatment in a stream of hydrogen was carried out for up to 4 hours.

Processing in the H_2S stream was carried out in a similar way, only for the synthesis of hydrogen sulfide, an additional furnace was used, in which a reactor with sulfur (molten) melted at 400 °C was placed (Figure S2). The formation of hydrogen sulfide occurred by the reaction:

$H_2 + S \rightarrow H_2S$ (3)

2b. Physico-chemical Analysis Methods

X-ray phase analysis (XRD) was carried out on a BRUKER D2 PHASER diffractometer with a linear detector LYNXEYE (CuKα radiation, Ni filter). Rietveld refinement of all samples was performed using TOPAS 4.2 [25]. All fixed reflexes of the obtained phases were indexed.

Micrographs of powder particles from the processing steps in a stream of H_2, H_2S were obtained using a JEOL JSM-6510LV scanning electron microscope.

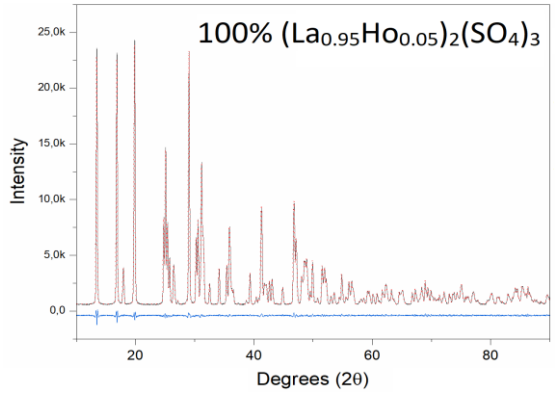
All photoluminescence measurements were carried out on a research grade spectrofluorometer Fluorolog-3 (Horiba Jobin Yvon) equipped with dual monochromators for excitation and emission channels and a 450 W xenon lamp as an excitation source. Lifetime measurements were performed at the same device using Xe-flash lamp (150 W power, 3 μs pulse width). The integration sphere (Quanta–φ, 6 inches) was used to measure the quantum yield. The measurements were carried out with powders according to the guide provided by manufacturer (four spectra-based measurement).

3. Results and discussions

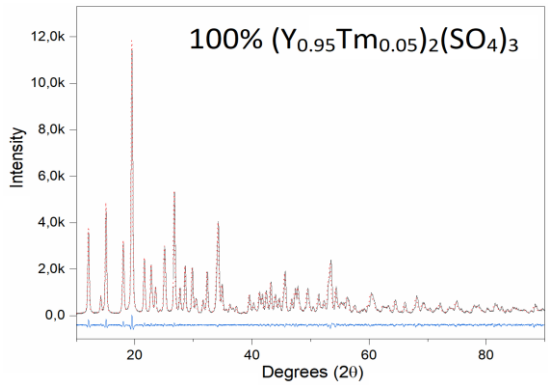
Two compositions were chosen as a model for discussing the results of sample synthesis: $La_2(SO_4)_3$: Ho^{3+} (5 mol %) and $Y_2(SO_4)_3$: Tm^{3+} (5 mol %). Figure 1 presents a complete picture of the chemical transformations that occur during the heat treatment of sulfates in a stream of H_2, H_2S. The remaining samples were synthesized by the same procedure.

The starting materials for the synthesis of solid solutions of oxysulfides are sulfates (Figure 1, a, b), in which the doping ion is embedded in the host crystal. According to x-ray phase analysis, they are single-phase, which proves the formation of solid solutions of rare-earth sulfates.

For greater reliability, we trace the detailed formation of phases using the example of a sample of lanthanum-holmium sulfate. The appearance of gaseous reaction products at 610 °C allows processing in a stream of hydrogen at 620 °C for 1 hour in order to draw up the equations of chemical reactions based on the results of X-ray phase analysis. As a result of processing, 4 phases were found in the powder composition: $(La_{0.95}Ho_{0.05})_2(SO_4)_3$ - $(La_{0.95}Ho_{0.05})_2O_2SO_4$ - $(La_{0.95}Ho_{0.05})_2O_2S$ - $La_{0.95}Ho_{0.05})_2O_3$ (Fig. 1, c).



a)



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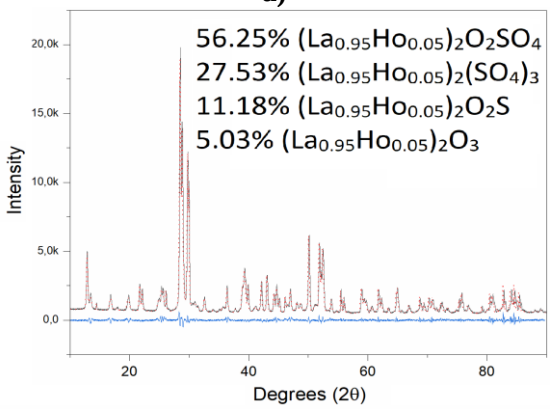
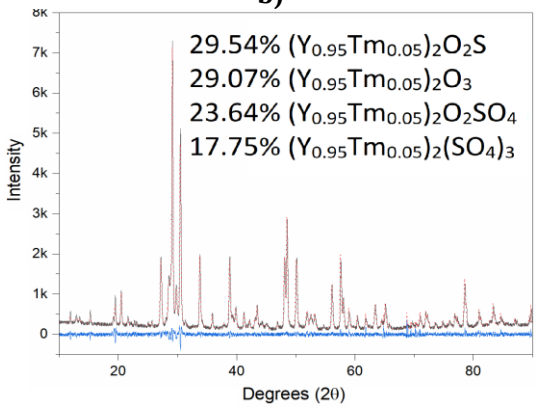
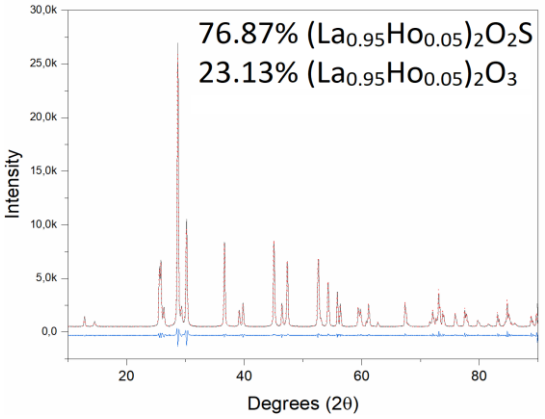


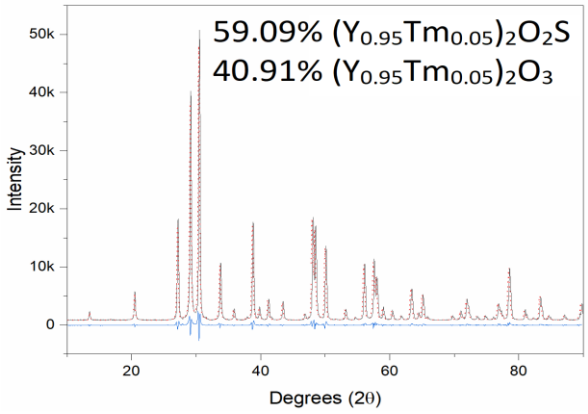
c)



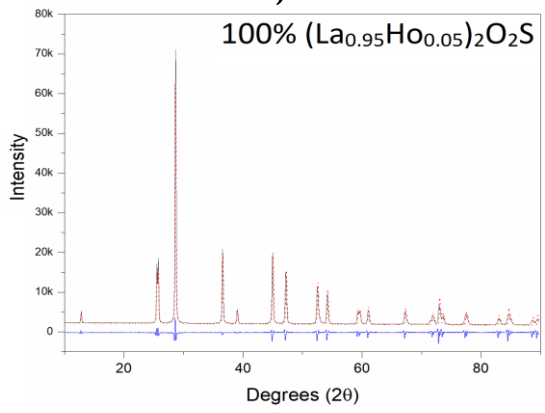
d)



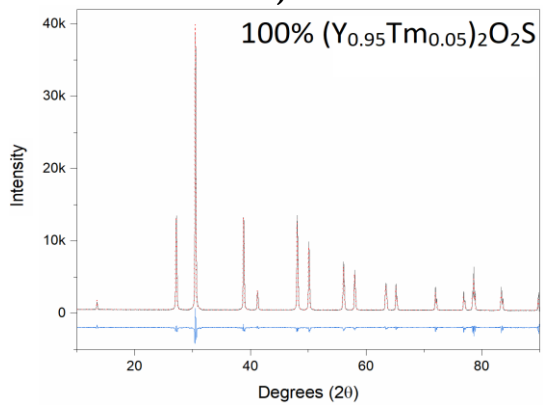
e)



f)



g)



h)

Fig.1. Difference Rietveld plot of: a,b) $(RE_{0.95}Ln_{0.05})_2(SO_4)_3$; c,d) $(RE_{0.95}Ln_{0.05})_2(SO_4)_3$-$(RE_{0.95}Ln_{0.05})_2O_2SO_4$-$(RE_{0.95}Ln_{0.05})_2O_2S$ - $(RE_{0.95}Ln_{0.05})_2O_3$; e,f) $(RE_{0.95}Ln_{0.05})_2O_2S$ - $(RE_{0.95}Ln_{0.05})_2O_3$; g,h) $(RE_{0.95}Ln_{0.05})_2O_2S$

The same can be said about Figure 1, d; here, a similar phase composition is also observed, which is formed when the sample $Y_2(SO_4)_3$: Tm^{3+} (5 mol %) is processed in a hydrogen stream for 1 hour at 620 °C.

With an increase in the treatment time in the hydrogen stream to 4 hours, at 620 °C, two phases were detected in the sample: $(La_{0.95}Ho_{0.05})_2O_2S$ and $(La_{0.95}Ho_{0.05})_2O_3$ (Fig. 1, e), as well as $(Y_{0.95}Tm_{0.05})_2O_2S$ and $(Tm_{0.95}Ho_{0.05})_2O_3$ in Figure 1, f.

The following chemical equations correspond to the formation of the corresponding reduction products:

$(RE_{0.95}Ln_{0.05})_2(SO_4)_3 + 6H_2 \rightarrow (RE_{0.95}Ln_{0.05})_2O_2SO_4 + 2S + 6H_2O$ (4)

$(RE_{0.95}Ln_{0.05})_2(SO_4)_3 + 10H_2 \rightarrow (RE_{0.95}Ln_{0.05})_2O_2S + 2S + 10H_2O$ (5)

$(RE_{0.95}Ln_{0.05})_2(SO_4)_3 + 5H_2 \rightarrow (RE_{0.95}Ln_{0.05})_2O_3 + 2SO_2 + 5H_2O$ (6)

$(RE_{0.95}Ln_{0.05})_2O_2SO_4 + 4H_2 \rightarrow (RE_{0.95}Ln_{0.05})_2O_2S + 4H_2O$ (7)

After 4 hours of carrying out the process at this temperature, according to x-ray phase analysis, the polycrystalline products consist of two phases: $(RE_{0.95}Ln_{0.05})_2O_2S$, $(RE_{0.95}Ln_{0.05})_2O_3$ (Fig. 1, e, 1, f). In the products of intermediate transformations there are no compounds containing SO_4^{2-} ions, which indicates the complete occurrence of the redox reaction. It should be noted that the content of the by-product, which is oxide, in the case of the reduction of yttrium sulfates is much higher (40.91 mol. %) than the corresponding compounds with lanthanum (23.13 mol.%). The thermodynamic stability of La_2O_2S is higher than that of Y_2O_2S, and that of Y_2O_3 is higher than that of La_2O_3 [26]. This may be another reason for the benefits of reaction 6.

Thus, during the reduction of rare earth sulfates in a hydrogen atmosphere for 4 hours, two-phase polycrystalline intermediate products are formed with a predominant content of the oxysulfide phase, which greatly facilitated the further sulfidation procedure.

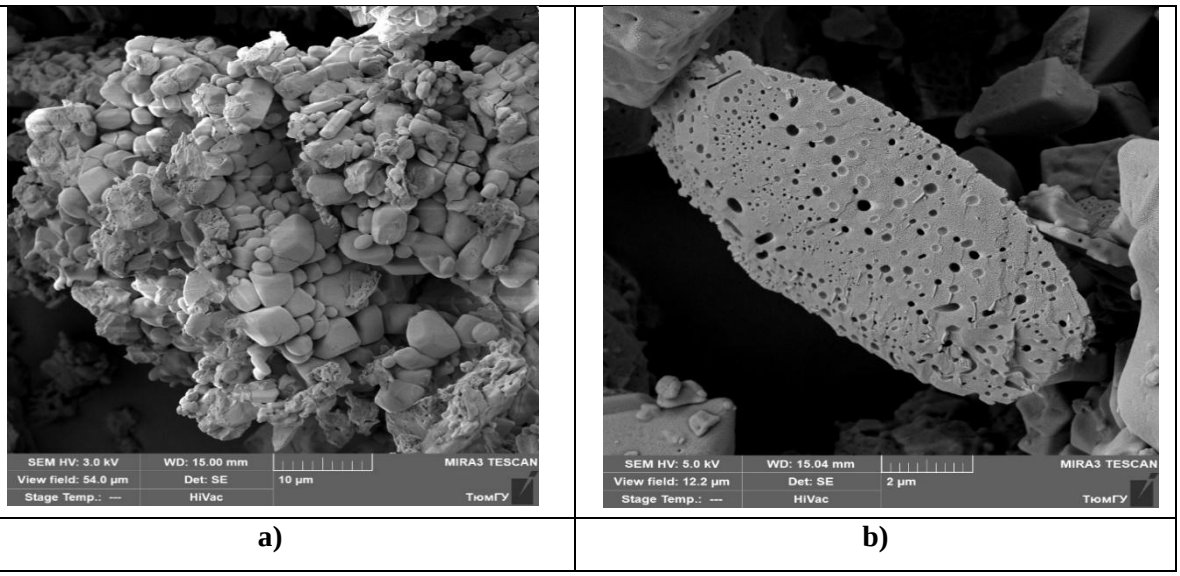
A further, final step in the synthesis is the sulfidation reaction in an H_2S atmosphere. After processing the mixture of oxysulfide and oxide in a stream of hydrogen sulfide at 1000 °C for 4 hours, according to the X-ray phase analysis, a single-phase sample of a solid solution of oxysulfide with the general formula $(RE_{0.95}Ln_{0.05})_2O_2S$ is fixed (Figure 1, g, h):

$(RE_{0.95}Ln_{0.05})_2O_3 + H_2S \rightarrow (RE_{0.95}Ln_{0.05})_2O_2S + H_2O$ (8).

The particles of sulfate $(Y_{0.95}Tm_{0.05})_2(SO_4)_3$ studied using a scanning electron microscope represent various formations: both oval and oblong, generally irregular in shape (Fig. 2, a) with sizes from 0.2 to 6 microns. Reason differences in the shape and size of the obtained particles and their adhesion to agglomerates is probably the uneven mixing during coprecipitation and co-crystallization. The particles of oxysulfide $(La_{0.95}Tm_{0.01})_2O_2S$ obtained in the process of redox reactions are relatively large, oblong in shape, with sizes of 5 × 11 μm. The particle shown in Figure 2, b is flat, as if sanded, with small round holes d = 0.14-0.51 μm over its entire surface. The

morphological transformation is obviously due to elevated temperatures and the diffusion nature of the reduction and sulfidation processes.

The sulfate $(La_{0.95}Tm_{0.05})_2(SO_4)_3$ particles studied using a scanning electron microscope are oblong-shaped formations (Fig. 2, a) with sizes from 2.5–3 μm. The oxysulfide $(La_{0.95}Tm_{0.01})_2O_2S$ particles obtained in the process of redox reactions are represented by agglomerates of 10–15 μm (Fig. 2, b). The morphological transformation is obviously due to elevated temperatures and the diffusion nature of the reduction and sulfidation processes.



a) **b)**

Fig. 2. SEM images of a) $(La_{0.95}Tm_{0.01})_2(SO_4)_3$; b) $(La_{0.99}Tm_{0.01})_2O_2S$

The excitation and emission spectra of $Y_2O_2S:Ho^{3+}$ phosphor are presented in Fig. 3, a, 3, b. Emission spectrum of $Y_2O_2S:Ho^{3+}$ powder obtained upon 462 nm excitation consists of typical narrow lines which can be assigned to following 4f-4f transitions: $^5F_3$–$^5I_8$ (491 nm), $^5S_2$+$^5F_4$–$^5I_8$ (544 and 548 nm), $^5F_5$–$^5I_8$ (650, 655 and 663 nm) and $^5S_2$+$^5F_4$–$^5I_7$ (753 and 759 nm) [27, 28]. Majority of emission bands include several lines because of Stark splitting of energy levels. Excitation spectra of $Y_2O_2S:Ho^{3+}$ powder were measured for two transitions: $^5S_2$+$^5F_4$–$^5I_8$ (544 nm) and $^5S_2$+$^5F_4$–$^5I_7$ (759 nm). Spectral line positions did not depend on monitoring wavelength. Better resolution in the first case is explained by less spectral slit width. The observed excitation lines corresponds to $^5I_8$–$^5G_2$ (336 nm), $^5I_8$–$^5G_3$+$^3L_9$ (347 nm), $^5I_8$–$^3H_5$+$^3H_6$ (363 nm), $^5I_8$–$^5G_4$ (383 and 390 nm), $^5I_8$–$^5G_5$ (421 nm), $^5I_8$–$^5G_6$ (454, 458 and 462 nm), $^5I_8$–$^4F_2$ (470, 477 nm), $^5I_8$–$^4F_3$ (490 nm), $^5I_8$–$^5S_2$+$^5F_4$ (542 nm) [29, 30]. Fig. 3c displays luminescence decay curve of $Y_2O_2S:Ho^{3+}$ sample measured at the most prominent transition (λ_{ex} = 462 nm, λ_{em} = 544 nm). It is clearly seen, that the experimental data demonstrate single exponential behavior:

$$I = A \cdot e^{-\frac{t}{\tau}} \quad (1)$$

where τ is observed lifetime. The observed lifetime of $^5S_2+^5F_4$ excited level was found to be (50 ± 1) μs.

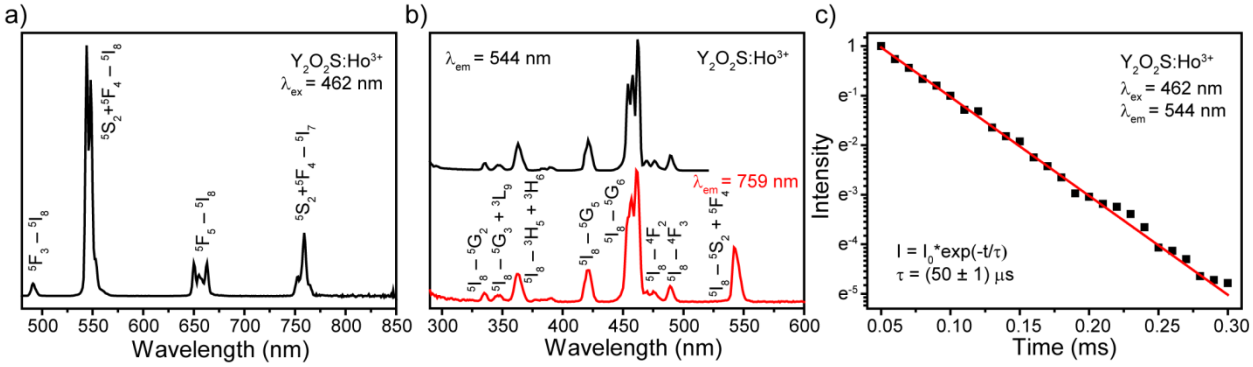


Fig. 3 a) Emission spectrum (λ_{ex} = 462 nm), b) excitation spectra (λ_{em} = 544 nm and 759 nm) and c) luminescence decay of $Y_2O_2S:Ho^{3+}$ powder.

To study host composition effect on photoluminescence properties, we regarded $La_2O_2S:Ho^{3+}$ sample. Y_2O_2S and La_2O_2S have similar structure and symmetry, the only difference is substitution of yttrium (r = 89 pm) to lanthanum (r = 102 pm) ions. Both hosts have the trigonal space group D_{3d}^3 and the point symmetry of the doping ion is C_{3v}. The crystal structure parameters of studied oxysulfides differ in such a way that La_2O_2S has the larger interionic distances than Y_2O_2S one [21]. Emission spectrum of $La_2O_2S:Ho^{3+}$ powder exhibited bands similar to those observed in case of $Y_2O_2S:Ho^{3+}$ sample: $^5F_3$–$^5I_8$ (490 nm), $^5S_2+^5F_4$–$^5I_8$ (544 and 547 nm), $^5F_5$–$^5I_8$ (650, 653 and 660 nm) and $^5S_2+^5F_4$–$^5I_7$ (751 and 757 nm) (Fig. 4, a). Small blue shift of lines and redistribution between them were observed. The observed spectral shift can be explained as follows: as the interionic distances increase, the energy levels of doping ions tend to approach the energy levels of a free ion [21]. We monitored excitation spectra of $La_2O_2S:Ho^{3+}$ phosphor for $^5S_2+^5F_4$–$^5I_8$ (544 nm) and $^5S_2+^5F_4$–$^5I_7$ (757 nm) transitions (Fig. 4, b). Both spectra are dominated by $^5I_8$–$^5G_6$ transition (454, 457 and 461 nm). Almost all excitation bands also demonstrated aforementioned blue shift. Luminescence kinetics of $La_2O_2S:Ho^{3+}$ sample was measured at the most intensive line centered at 544 nm upon 461 nm excitation (Fig. 4, c). Single exponential fitting of decay curve allowed to obtain $^5S_2+^5F_4$ lifetime for Ho^{3+}-doped La_2O_2S of (103 ± 2) μs.

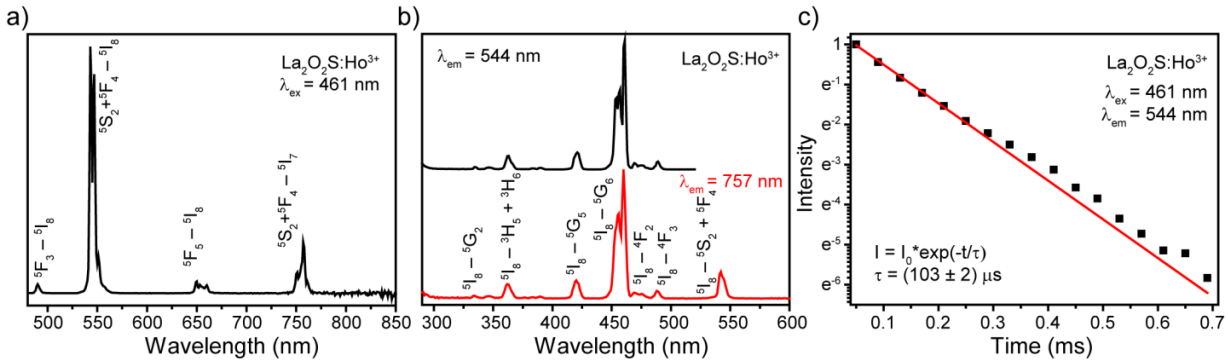


Fig. 4 a) Emission spectrum (λ_{ex} = 461 nm), b) excitation spectra (λ_{em} = 544 nm and 757 nm) and c) luminescence decay of $La_2O_2S:Ho^{3+}$ powder

Fig. 5, a shows emission spectrum of $Y_2O_2S:Tm^{3+}$ sample upon 363 nm excitation measured within spectral range of 400–850 nm. It displays narrow bands assigned to the 4f-4f transitions, which are centered at 457 nm ($^1D_2$–$^3F_4$), 666 and 673 nm ($^1G_4$–$^3F_4$), 760 nm ($^3F_{2,3}$–$^3H_6$) and 789, 800, 813 nm ($^3H_4$–$^3H_6$) [31, 32]. Low-intensity bands near 550 nm are most probably attributed to the emission of Er^{3+} impurity ions situated in the sample. As luminescence of Tm^{3+} ions in Y_2O_2S is quite weak, we have also observed broad host emission situated in the 400–550 nm spectral region. Excitation spectra of $Y_2O_2S:Tm^{3+}$ phosphor were monitored at two transitions: $^1D_2$–$^3F_4$ (457 nm) and $^3H_4$–$^3H_6$ (800 nm). Contrary to Ho^{3+}-doped samples, we measured excitation spectra for transitions originated from different excited levels: $^1D_2$ and $^3H_4$, respectively. These spectra consist of sharp lines corresponding to intra-configurational f-f transitions: $^3H_6$–$^1D_2$ (363 nm), $^3H_6$–$^1G_4$ (468 nm) and $^3H_6$–$^3F_{2,3}$ (694 nm) [31-32]. Noteworthy, $^3H_6$–$^1D_2$ transition presented on both spectra had the same spectral position. We monitored luminescence decay curve of $Y_2O_2S:Tm^{3+}$ powder for the most intense transition – $^1D_2$–$^3F_4$. Experimental data were fitted with single exponential decay with sufficient accuracy (Adj. R^2 = 0.984). The observed $^1D_2$ lifetime was determined to be (6.5 ± 0.3) μs.

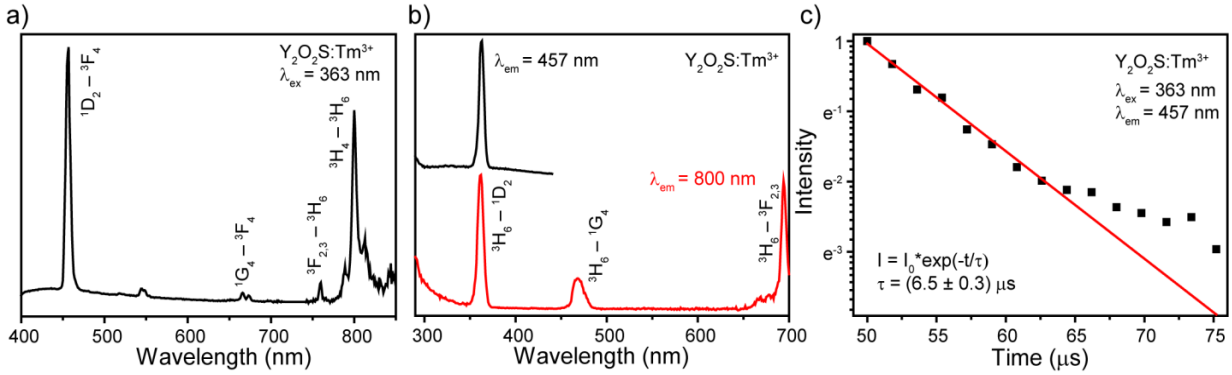


Fig. 5 a) Emission spectrum (λ_{ex} = 363 nm), b) excitation spectra (λ_{em} = 457 nm and 800 nm) and c) luminescence decay of $Y_2O_2S:Tm^{3+}$ powder

The steady state luminescence spectra and luminescence kinetics of $La_2O_2S:Tm^{3+}$ phosphor are presented in Fig. 6. Host change led to the insignificant blue shift of spectral lines and intensity redistribution. Emission spectrum includes $^1D_2$–$^3F_4$ (456 nm), $^1G_4$–$^3F_4$ (666 and 672 nm), $^3F_{2,3}$–$^3H_6$ (758 nm) and $^3H_4$–$^3H_6$ (800 nm) transitions. Excitation spectrum consists of $^3H_6$–$^1D_2$ (362 nm), $^3H_6$–$^1G_4$ (471 nm) and $^3H_6$–$^3F_{2,3}$ (695 nm) transitions. Luminescence decay curve of $^1D_2$–$^3F_4$ transition presented single exponential behavior, and $^1D_2$ lifetime was found to be (6.4 ± 0.3) μs.

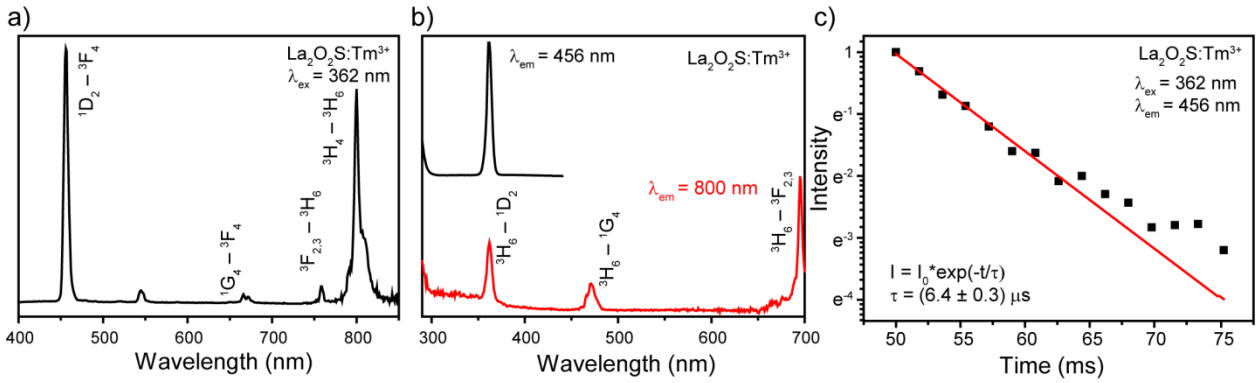


Fig. 6 a) Emission spectrum (λ_{ex} = 362 nm), b) excitation spectra (λ_{em} = 456 nm and 800 nm) and c) luminescence decay of $La_2O_2S:Tm^{3+}$ powder.

An important parameter of phosphor is quantum yield (**φ**), which shows conversion efficiency of absorbed photons into emitted ones. We measured quantum yield of synthesized powders via absolute technique using integrating sphere. The obtained **φ** values as well as previously obtained photoluminescence characteristics are summarized in Table 1. The best quantum yield of about 12% was found for $La_2O_2S:Ho^{3+}$ sample. Analyzing obtained experimental results, we can conclude that La_2O_2S is better host for holmium and thulium doping compared with Y_2O_2S. The same situation was observed for other lanthanides in these oxysulfide hosts [21].

Material	**λ_{em}, nm**	**τ, μs**	**φ, %**	**CIE1931 chromaticity coordinates**
$Y_2O_2S:Ho^{3+}$	491, 541, 663, 759	50 ± 1	2.7	(0.296, 0.684)
$La_2O_2S:Ho^{3+}$	490, 544, 650, 757	103 ± 2	12.3	(0.278, 0.704)
$Y_2O_2S:Tm^{3+}$	457, 544, 666, 760, 800	6.5 ± 0.3	0.1	(0.189, 0.133)
$La_2O_2S:Tm^{3+}$	456, 545, 666, 758, 800	6.4 ± 0.3	0.3	(0.171, 0.083)

Table 1. Main emission lines (**λ_{em}**), lifetime (**τ**), quantum yield (**φ**) and CIE1931 chromaticity coordinates of $RE_2O_2S:Ln^{3+}$ samples.

Possible application of synthesized powders as a phosphor was studied via photometric characterization. The Commission Internationale de L'Eclairage (CIE) chromaticity coordinates calculated from measured emission spectra are listed in Table 1 and presented in Fig. 7. Despite small spectral shift of emission lines in Y_2O_2S and La_2O_2S doped samples, chromaticity coordinates vary significantly. Such behavior is elucidated by considerable intensity redistribution between emission lines. Noteworthy, chromaticity coordinates of Ho^{3+} and Tm^{3+}-doped La_2O_2S samples are close to green (0.300, 0.600) and blue (0.150, 0.060) colors – most commonly used primary colors for display monitors and TV's (ITU-R BT.709 standard primaries). It makes synthesized powders suitable for efficient green and blue phosphors application.

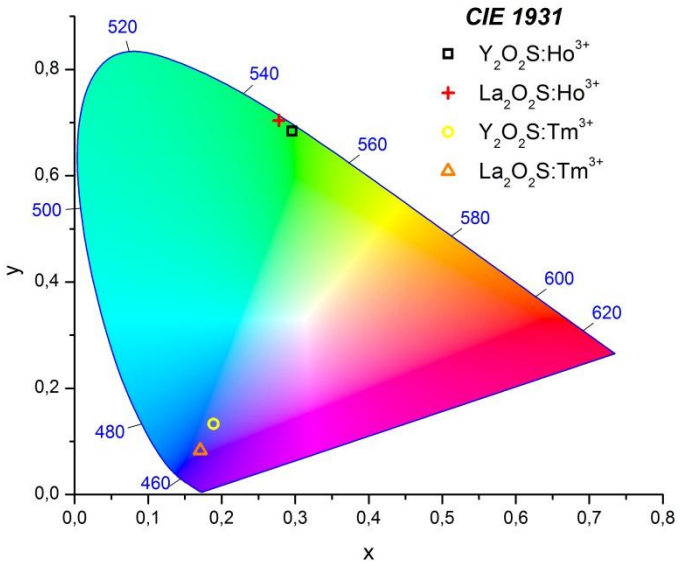


Fig. 7. CIE1931 chromaticity coordinates of synthesized samples.

4. Conclusion

The sequence of phase formation of sulfates doped with rare earth elements ($(La_{0.95}Ln_{0.05})_2(SO_4)_3$ and $(Y_{0.95}Ln_{0.05})_2(SO_4)_3$ (Ln = Ho^{3+}, Tm^{3+})) was studied during their sequential processing in a stream of H_2, H_2S. The phase and morphological certification of the obtained solid solutions of rare earth oxysulfides were carried out. Excitation and emission spectra of $La_2O_2S:Ln^{3+}$ и $Y_2O_2S:Ln^{3+}$ (Ln^{3+}= Ho, Tm) included characteristic narrow bands corresponding to the 4f-4f intra-configurational transitions. Change of Y_2O_2S host to La_2O_2S resulted in small blue shift of emission lines which is caused by the larger interionic distances in the latter case. Study of luminescence decay showed that Ho^{3+}-doped La_2O_2S powder had twice bigger lifetime compared with Ho^{3+}-doped Y_2O_2S one, whereas Tm^{3+}-doped samples have similar lifetime independently on host. The best quantum yield of about 12% was found for $La_2O_2S:Ho^{3+}$ sample. Chromaticity coordinates of Ho^{3+} and Tm^{3+}-doped La_2O_2S powders were close to green and blue standard colors, which makes them perspective for phosphor applications.

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