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Structure, Mechanical and Luminescent Properties of Solid Solution $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$

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Abstract: Ceramic samples of polycomponent solid solution $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ have been prepared by sol–gel synthesis from fine powders obtained using nitrate solutions of rare earth elements REE and coprecipitated hydroxides of niobium and tantalum. The structural state of the initial powders’ crystal lattice has been investigated. The morphological features of the microstructure of the ceramics samples have been studied in dependence of temperature regimes of their preparation. The ceramics’ strength characteristics (Young’s modulus) and the critical stress intensity factor of the mode I K_{IC} have been estimated. Cathode- and photoluminescent properties of ceramic solid solutions $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ have been studied.

Keywords: solid solutions; photoluminescence; cathodoluminescence; microstructure; microhardness; Young’s modulus; crack resistance



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1. Introduction

Much attention has been paid to rare earth tantalates and niobates, in recent decades, due to their diverse physical properties and good chemical stability [1–9]. Their luminescence and scintillation characteristics are being especially closely studied due to the growing demand for dense, fast and bright scintillators for high-energy physics, medical diagnostics and safety screening devices. Orthotantalates and orthoniobates of rare earth elements (REE) with the general formula $REBO_4$ exhibit excellent luminescent properties [5–12]. Moreover, radiation in the UV-blue region upon excitation, for example, by X-rays is associated with the luminescence of the TaO_4^{3-} and NbO_4^{3-} groups of the crystal lattice of the matrix [13]. A significant increase in the emissivity of the material in the blue-green region is observed at certain ratios of NbO_4^{4-} and TaO_4^{4-} complexes in $RENb_{1-x}Ta_xO_4$ [5,8]. This occurs at $x = 3$ in $YNb_{1-x}Ta_xO_4$ solid solution (SS) [14]. This fact determined our choice of studied SS composition $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$. We expect an increase in energy transfer from the emission centers of the crystal matrix based on the TaO_4^{3-} and NbO_4^{3-} groups to the emission centers based on doping REE^{3+} cations: Eu^{3+} , Sm^{3+} , Tb^{3+} and Er^{3+} .

Additionally, the variation in $REBO_4$ of REE trivalent ions concentration provides luminescence emission from the UV to the IR region [9,15]. The contribution to the total luminescence in these phosphors can be made both by the emission centers of the main crystal lattice based on TaO_4^{3-} and NbO_4^{3-} groups and by REE^{3+} emission centers of the basic crystal matrix [9]. Moreover, luminescent radiation can be shifted to shorter or longer wavelengths by partially replacing yttrium ions in the $REBO_4$ crystal lattice with Eu^{3+} , Tb^{3+} , Gd^{3+} , Sm^{3+} , D^{3+} , and Pr^{3+} ions. Thus, increasing the complexity of lanthanide orthoniobates–orthotantalates due to an increase in the number of dopants expands the range of properties of these materials and opens up prospects for using lanthanide orthoniobates–orthotantalates as laser materials with a tunable wavelength [16].

Usually, $REMeO_4$ orthoniobates–tantalates are synthesized by the solid phase reaction from stoichiometric mixtures containing various sources of metal oxides. Works [9,13]

report a method for obtaining monoclinic YTaO_4 by thermal synthesis at temperatures above 1300°C in several stages; the synthesis is accompanied by a flux of some inorganic salts: Li_2SO_4 , LiCl or Na_2SO_4 . However, the crystalline homogeneity of the YTaO_4 powder is difficult to achieve because of the intermediate compounds involved in the mechanism of such synthesis [17,18]. Such methods of synthesis require an intensive mechanical treatment of the initial components with repeated grinding, mixing and prolonged calcination of the mixture at very high temperatures (up to 1600°C) [5,13]. This is a significant demerit of the technology. Synthesis conditions greatly affect the crystal lattice order, particle size and morphology. This determines the luminescence characteristics and the use of the material.

The sol–gel synthesis method of polycomponent SSs based on $\text{RENb}_{1-x}\text{Ta}_x\text{O}_4$ nitrate solutions of REE and co-precipitated hydroxides of niobium and tantalum suggests a more accurate adherence to the specified ratio of components. The mixture is homogenized at the atomic level. The loss of components is excluded since the stages of intensive grinding of the initial substances and the long-term high-temperature calcination of the reaction mixture are absent [19,20]. In addition, sol–gel provides control of the size of individual particles and obtains nanosized powders [20,21].

Luminescent ceramics $\text{RENb}_{1-x}\text{Ta}_x\text{O}_4$ prepared from such powders have a greater structural homogeneity. This means improved mechanical performance and increased luminescence efficiency [22,23]. The goal of this study is the sol–gel synthesis of a poly-component SS ($\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01}\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$) and the research of the regularities of the effect of heat treatment conditions of initial powders' and ceramics' sintering temperature on their structural, mechanical, and luminescent characteristics.

2. Materials and Methods

The fine powder of multicomponent SS ($\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01}\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$) was synthesized by sol–gel using nitrate solutions of REE and co-precipitated hydroxides of niobium and tantalum. Ammonia coprecipitation of niobium and tantalum hydroxides from high purity fluoride Nb and Ta-containing solutions was carried out at the first stage of the synthesis. The solutions were taken in volumes corresponding to the given one of Nb and Ta. High purity fluoride Nb- and Ta-containing solutions were obtained by dissolving Nb_2O_5 (99.9) and Ta_2O_5 (99.9) oxides (Solikamsk Magnesium Plant, Solikamsk, Russia) in HF (99.9 (not more than 10^{-5} of 27 impurities), Komponent-reaktiv Ltd., Moscow, Russia). Solutions were taken in volumes corresponding to the given value of Nb and Ta. Niobium and tantalum hydroxides were co-precipitated by ammonia (25% NH_4OH solution, 99.9 (not more than 10^{-5} of 23 impurities), Sigma Tek, Khimki, Russia) from these solutions at the first stage of the synthesis. Then, the mixture of niobium and tantalum hydroxides washed with deionized water from NH_4^+ and F^- ions and dried to a moisture content of 60–70% at 90°C was mixed with solutions of $\text{Y}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$, $\text{Sm}(\text{NO}_3)_3$, $\text{Tb}(\text{NO}_3)_3$, $\text{Er}(\text{NO}_3)_3$ in volumes that provide the given composition. Solutions of $\text{Y}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$, $\text{Sm}(\text{NO}_3)_3$, $\text{Tb}(\text{NO}_3)_3$, $\text{Er}(\text{NO}_3)_3$ of the given concentration were prepared by dissolving the corresponding oxides Y_2O_3 , Eu_2O_3 , Sm_2O_3 , Tb_4O_7 , Er_2O_3 (99.9, Himkraft, Kaliningrad, Russia) in HNO_3 (99.9 (not more than 10^{-4} of 18 impurities), Vekton Ltd., Saint Petersburg, Russia). Furthermore, the forming pulp was adjusted to $\sim\text{pH } 10$ by adding ammonia. All processes were accompanied by mixing. The obtained hydrated precipitate was washed with deionized water at a ratio of solid and liquid phases $\text{S}:\text{V}_\text{L} = 1:3$, dried at $\sim 150^\circ\text{C}$, and calcined at 700°C for 4 h. Then, the powders were ground in a ball chalcidony mill. One part of the powder was calcined for 4 h at $\sim 1200^\circ\text{C}$, and the other one for 2 h at $\sim 1400^\circ\text{C}$.

The content of niobium and tantalum in fluoride Nb- and Ta-containing solutions was determined by the gravimetric method; fluoride ions were determined by the potentiometric method on ionomer EV-74 (Zavod izmeritel'nykh priborov, Gomel, Belarus) with an F-selective electrode EVL-1MZ (Zavod izmeritel'nykh priborov, Gomel, Belarus). Fluorine in synthesized powders ($\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01}\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$) was analyzed by pyrohydrolysis. Y, Eu, Sm, Tb, and Er in filtrates and washing solutions were determined

by atomic emission spectrometry (AES) on the spectrometer ICPE 9000 (Shimadzu, Kyoto, Japan, 2011) and by XRF on the Spectroscan MAK-S-GV (Spectron, Saint Petersburg, Russia).

Simultaneous thermal analysis (STA), including simultaneous differential scanning calorimetry (DSC) and thermogravimetry was carried out on the analyzer STA 409 PC/PG (NETZSCH, Selb, Germany) in the temperature range 30–1400 °C at the sample heating rate of 15 °C/min at air atmosphere.

The phase composition of the powders was determined on a diffractometer XRD-6000 (Shimadzu, Kyoto, Japan) with a counter speed of 1 deg·min^{−1} (CuKα radiation).

The specific surface area of (Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O₄ powders was determined by the BET method on FlowSorb II 2300 (Micromeritics, Norcross, GA, USA) and TriStar 3020 V1.03 (Micromeritics, Norcross, GA, USA).

Ceramic samples (Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O₄ were prepared in the form of tablets 10 mm in diameter and 2–3 mm in height from powders calcined at ~1200 °C and ~1400 °C. Polyvinyl alcohol was used as a binder. The tablets were pressed under a load of ~380 kg/cm². The tablets were sintered in the electric furnace KEP 14/1400P (Termal, Tryokhgorny, Russia) at 1400 °C for 3 h. Additionally, the tablets were sintered in the same furnace at 1500 °C for 2 h. Three types of ceramic samples were obtained in total, Table 1.

Table 1. Modes of preparation of ceramic samples (Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O₄.

Sample Number	Powder Calcination Temperature, T _c °C	Ceramic Sintering Temperature, T _s °C	Ceramics Sintering Time, h
1	1200	1400	3
2	1200	1500	2
3	1400	1500	2

The phase composition and structure refinement of (Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O₄ ceramic samples were performed using a diffractometer multifunctional X-ray diffractometer Rigaku (RIGAKU, Tokyo, Japan) with the SmartLab Studio II software. The counter movement speed was 2 deg·min^{−1} (CuKα radiation), the scanning range was 6–90°. ICDD databases (PDF 4, relies 2022) were used for phase identification. The structural characteristics of the phases were refined by the WPPF (Whole Powder Pattern Fitting) method of full-profile analysis of XRD patterns. The R-factor criteria were the values of the profile R-factors R_p and R_{wp} calculated using standard formulas.

The experimental density of ceramic samples ρ_{exp} (Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O₄ was determined by hydrostatic weighing. The relative density ρ_{rel}, % was also determined.

The microstructure of ceramic samples (Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O₄ was studied using the scanning electron microscope SEM LEO 420 (Carl Zeiss, Oberkochen, Germany) and analyzed using the program ScanMaster (National research nuclear university (MEPHI), Moscow Engineering Physics Institute, Russia).

The mechanical properties of (Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O₄ ceramic samples were studied by the contact method using the probe microscope nanohardness tester NanoSkan (FSBI TISNCM, Troitsk, Russia) according to the procedures described in detail in our work [19]. The obtained values of microhardness and crack resistance were averaged over ten measurements in 10 arbitrary areas 60 × 60 μm in size for each sample in order to reduce the standard error of the data.

Electron microprobe analysis and the study of the cathodoluminescence (CL) of solid solutions (Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O₄ was carried out on an electron probe microanalyzer Camebax (Cameca, Gennevilliers, France) equipped with four X-ray wave spectrometers and a CL station [23]. An electron microprobe analysis of ceramics (Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O₄ was carried out at an accelerating voltage of 20 kV, an absorbed electron current of 5–10 nA, and an electron beam diameter of 5 μm.

During the electron probe microanalysis, the sample was fixed into the cassette using Wood's alloy. To ensure the charge drain during the study of the electron probe micro-analyzer, a carbon film was additionally deposited on all samples on a JEE-4C universal vacuum station (Jeol, Japan, Tokyo).

Some of the studied ceramic samples ($Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01}$) $Nb_{0.7}Ta_{0.3}O_4$ were subjected to vacuum annealing in order to establish the effect of annealing on the features of the luminescent properties. Thermal vacuum treatment was carried out in the original installation developed in ICT RAS on the base of muffle-tube furnace SUOL-0.4.4/12 (GRANAT, Russia, Moscow) [24].

The photoluminescence spectra of the samples of ceramic solid solutions ($Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01}$) $Nb_{0.7}Ta_{0.3}O_4$ were recorded using a SOL SL-100M (SOL instruments, Belarus, Minsk) with a CCD detector FLI ML 1107 Black Illuminated (Hamamatsu PHOTONICS K.K., Hamamatsu City, Japan) in the visible region of the spectrum (380–800 nm). A cw He-Cd continuous laser (Kimmon KOHA, Fukushima, Japan), $\lambda_0 = 325$ nm, $P = 15$ mW served as the excitation source. The entrance slit of the monochromator was ~ 0.016 mm. The background signal was subtracted from each photoluminescence spectrum.

3. Results and Discussion

The AES data indicate that the concentrations of Y, Eu, Sm, Tb, and Er in the filtrates and wash solutions are in trace amounts. Therefore, Y, Eu, Sm, Tb, and Er almost completely transfer from $Y(NO_3)_3$, $Eu(NO_3)_3$, $Sm(NO_3)_3$, $Tb(NO_3)_3$, and $Er(NO_3)_3$ solutions to the hydroxide precipitate under the selected conditions. The XRF results also confirm that the contents of Y, Eu, Sm, Tb, and Er in powder samples correspond to the calculated values, the error does not exceed 2%. The concentration of fluorine in the powders is below the detection limit of the analysis method used (i.e., less than 1×10^{-3} wt%). The specific surface area of ($Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01}$) $Nb_{0.7}Ta_{0.3}O_4$ powders was at 1200 °C calcination ~ 1.87 and at 1400 °C calcination ~ 1.05 m²/g, respectively.

Electron microprobe analysis showed that the elemental ratio Nb/Ta corresponds to the given one, within the error of the method (error is 3–5% relative units), Table 2. For REE, the relative error is larger: it can reach 10% relative units due to the difficulty of determining low concentrations.

Table 2. Elemental composition of samples ($Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01}$) $Nb_{0.7}Ta_{0.3}O_4$. Values are given in formula units.

Sample	Nb	Ta	Eu	Sm	Tb	Er
($Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01}$) $Nb_{0.7}Ta_{0.3}O_4$	0.69 ± 0.02	0.31 ± 0.020	0.0072 ± 0.0010	0.0056 ± 0.0020	0.0075 ± 0.0010	0.0068 ± 0.0005

Figure 1 shows the results of the simultaneous thermal analysis of the hydrated precipitate of the precursor of yttrium niobate–tantalate doped with Eu, Sm, Tb, and Er. Additionally, the results also help to estimate the temperatures at which crystalline phases can form.

The weight loss of about 9.5% at temperatures up to ~ 250 °C is due to the evaporation of water residues and the removal of nitrogen oxides. Furthermore, when the temperature rises, intermediate oxol phases of yttrium, niobium (tantalum) containing Eu, Sm, Tb, and Er are probably formed (exothermic peak at ~ 297.7 °C). They decompose with the formation of the corresponding oxides when the temperature rises. A wide exothermal peak indicates this in Figure 1 at 500 °C. The main weight is lost in the temperature of up to 800 °C, the loss is 26.7%.

The stages of SS synthesis revealed by thermogravimetry are confirmed by the XRF results of the precipitate, Figure 2. The precipitate contained Y, Eu, Sm, Tb, Er, Nb, and Ta. It was dried at 90 °C and calcined at various temperatures in the air.

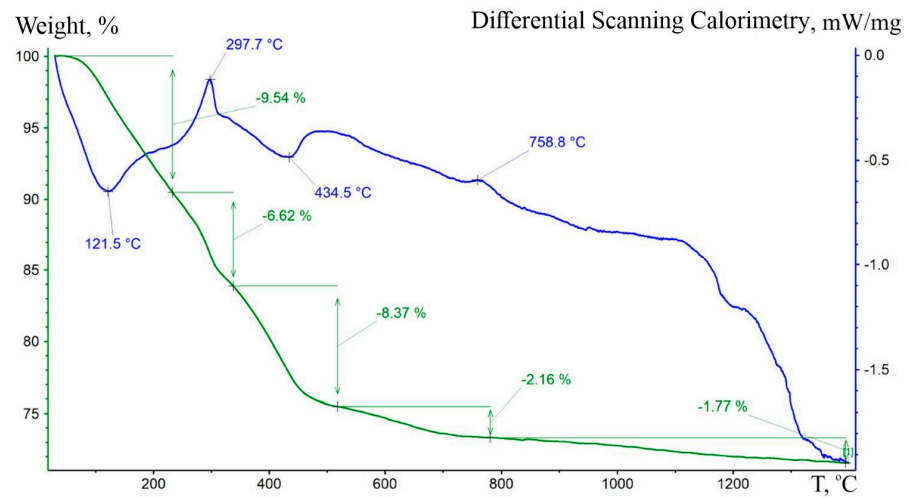


Figure 1. Thermogram and DSC curves of the hydrated precipitate of the precursor $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$.

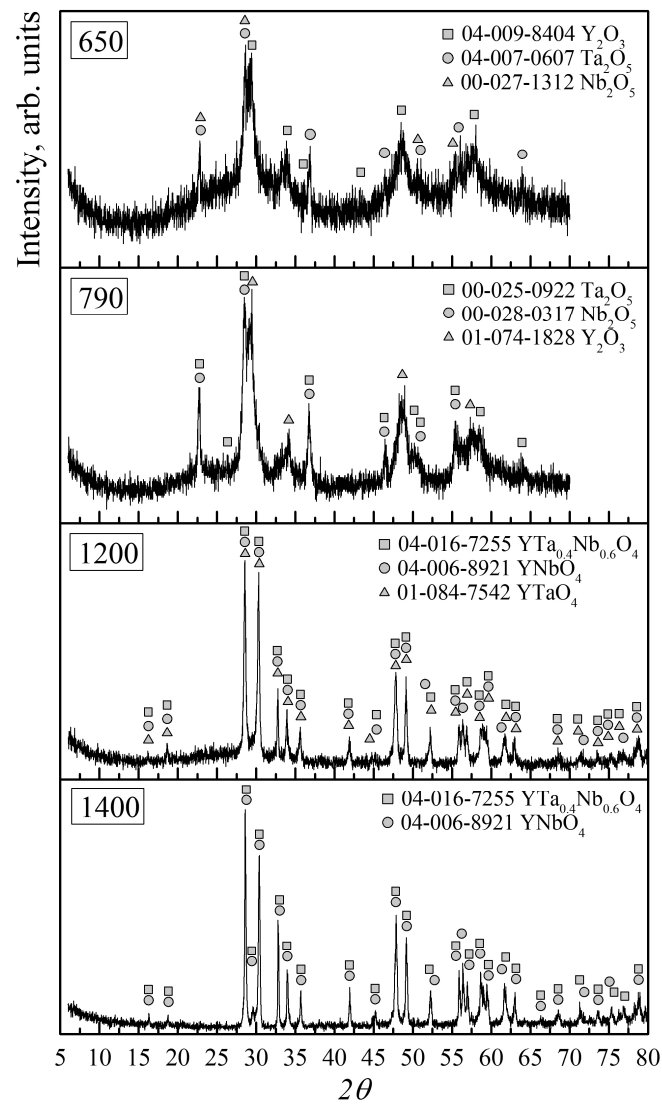


Figure 2. XRD patterns of precursor hydrate residue of $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ sintered at 650, 790, 1200 and 1400 °C.

Oxides successively crystallize in the temperature range 450–790 °C: Y_2O_3 (ICDD PDF Cards 04-009-8404 and 01-074-1828), Ta_2O_5 (ICDD PDF Cards 04-007-0607 and 00-025-0922), Nb_2O_5 (ICDD PDF Cards 00-027-1312 and 00-028-0317), as well as Eu, Sm, Tb, and E oxides isostructural to them, Figure 2. At 1200 °C the following compositions crystallize: $YTaO_4$ (ICDD Card 01-084-7542) with the space group (SPGR) I2/a (15), and $YTa_{0.4}Nb_{0.6}O_4$ (ICDD Card 04-016-7255) with the SPGR C2/c. After sintering at 1400 °C, the sample contains monoclinic modifications with SPGR C2/c (β -fergusonite), $YNbO_4$ (ICDD PDF Card 04-006-8921) and $YTa_{0.4}Nb_{0.6}O_4$ (ICDD Card 04-016-7255), Figure 2.

According to the literature, $YNbO_4$ has two structure types: T-scheelite and monoclinic distorted phase β -fergusonite [25,26]. $YTaO_4$ has a more complex polymorphism and can crystallize in three structural modifications: two monoclinic forms formed at T below 1400 °C, β -fergusonite (M'-type) with a symmetry SPGR C2/c [27] and M-fergusonite with SPGR P2/c [27,28]; tetragonal scheelite, T-phase, is formed at a temperature of about 1400–1500 °C [29–31]. The β -fergusonite phase can transfer into T-phase at heating [31–33]. At the same time, a monoclinic cell shifts into a tetragonal cell with a distorted scheelite structure: the monoclinic cell's parameters a and c are equalized, and parameter b goes to parameter c of the tetragonal cell. T-phase turns into M-phase during cooling [29–31].

Thermogravimetric and X-ray phase analyses showed the evolution of the $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ precursor from amorphous to crystalline form. It should be noted that SS based on yttrium tantalum–niobate crystallizes at temperatures as low as 1200 °C when synthesized by sol–gel, in contrast with solid-phase synthesis [9,13]. Components of sol–gel synthesized SS react completely at 1200 °C, unreacted oxide phases and intermediate compounds are absent, Figures 1 and 2.

Figure 3 demonstrates XRD patterns of ceramic $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ samples 1, 2, and 3 with the refinement of probable phases.

WPPF refinement has revealed that the structure of Sample 1 corresponds to the monoclinic phase with symmetry SPGR C2/c and a small presence of the monoclinic phase with SPGR I2/a (less than 3%). Refined values of the unit cell parameters and monoclinic angle β of Sample 1 are demonstrated in Table 3. Sample 2 corresponds exactly to the monoclinic phase with SPGR C2/c, Table 4. WPPF refinement of Sample 3 is demonstrated in Table 5.

Table 3. Refined values of the unit cell parameters, monoclinic angle β , sites population and atom coordinates of sample 1, Rwp = 12.84%, Rp = 8.34%.

Sample 1					YTa _{0.4} Nb _{0.6} O ₄ with SPGR C2/c (ICDD Card 04-016-7255)		
a = 7.0175(9), b = 10.9421(2), c = 5.3060(1) Å, β = 134.01(5)°					a = 7.037, b = 10.945, c = 5.298 Å, β = 134.07°		
atom	G	x/a	y/b	z/c	x/a	y/b	z/c
O1	1.0	0.2452(1)	0.0409(1)	0.3399(2)	0.2442	0.0418	0.3374
O2	1.0	0.2839(2)	0.2847(7)	0.2983(5)	0.2919	0.2819	0.2968
Nb	0.7	0.0	0.1458(7)	0.25	0.0	0.1445	0.25
Ta _(Nb)	0.3	0.0	0.1437(3)	0.25			
Y	0.93	0.0	0.6202(1)	0.25	0.0	0.6212	0.25
Tb _(Y)	0.01	0.0	0.6333(5)	0.25			
Er _(Y)	0.007	0.0	0.6035(5)				
Eu _(Y)	0.01	0.0	0.6212(5)	0.25			
Sm _(Y)	0.005	0.0	0.6297(5)	0.25			

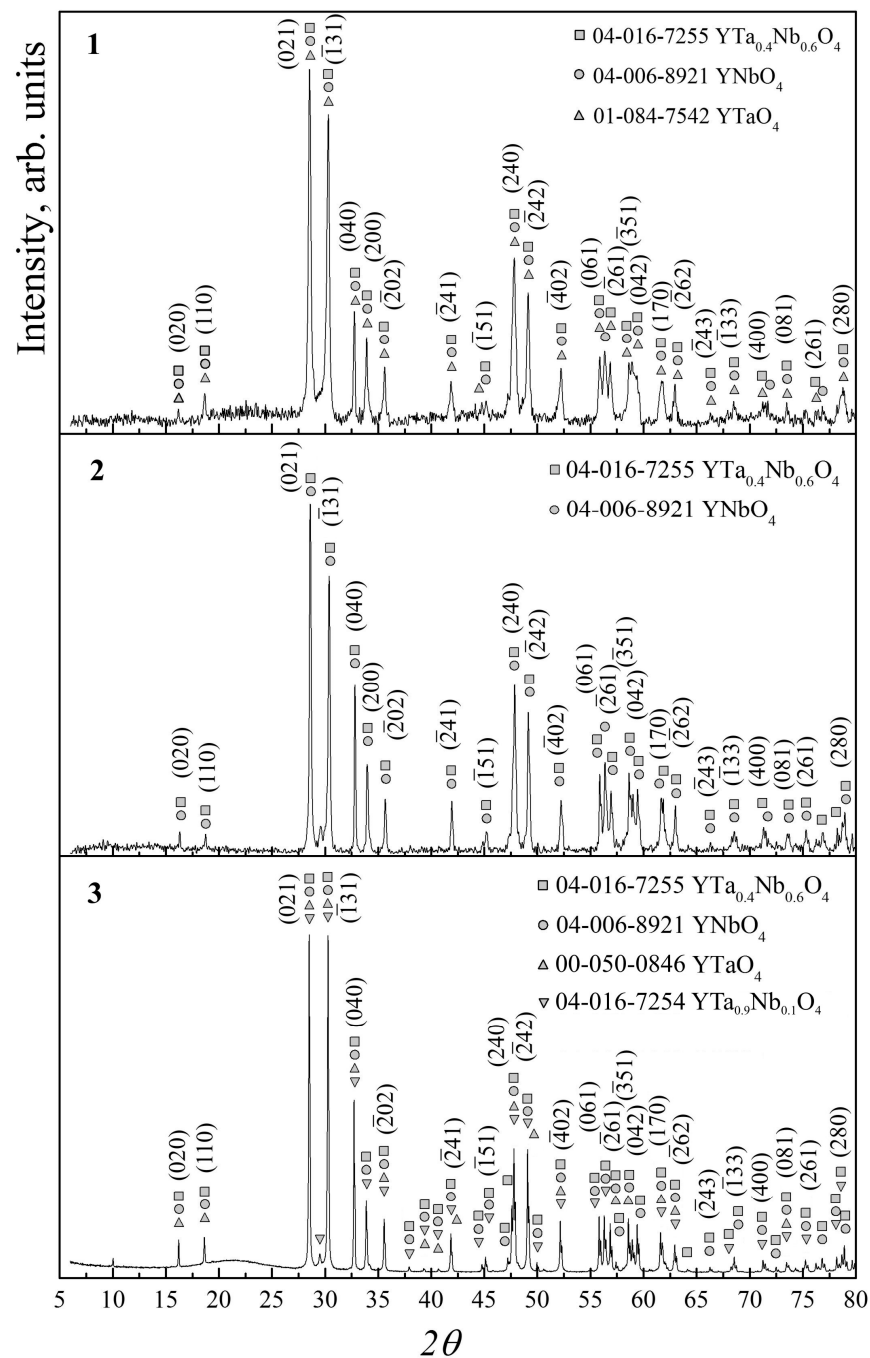


Figure 3. XRD patterns of ceramic $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ samples with the refinement of probable phases. (1) Sample 1: ■ reflections corresponding to the monoclinic $YTa_{0.4}Nb_{0.6}O_4$ phase with SPGR C2/c (ICDD Card 04-016-7255); ● reflections corresponding to the monoclinic $YNbO_4$ phase with SPGR C2/c (ICDD Card 04-006-8921); ▲ reflections corresponding to the monoclinic $YTaO_4$ phase with SPGR I2/a (ICDD Card 01-084-7542). (2) Sample 2: ■ reflections corresponding to the monoclinic $YTa_{0.4}Nb_{0.6}O_4$ phase with SPGR C2/c (ICDD Card 04-016-7255); ● reflections corresponding to the monoclinic $YNbO_4$ phase with SPGR C2/c (ICDD Card 04-006-8921). (3) Sample 3: ■ reflections corresponding to the monoclinic $YTa_{0.4}Nb_{0.6}O_4$ phase with SPGR C2/c (ICDD Card 04-016-7255); ● reflections corresponding to the monoclinic $YNbO_4$ phase with SPGR C2/c (ICDD Card 04-006-8921); ▼ reflections corresponding to the monoclinic $YTa_{0.9}Nb_{0.1}O_4$ phase with SPGR P2/c (13) (ICDD Card 04-016-7254); ▲ reflections corresponding to the tetragonal $YTaO_4$ phase with SPGR P42/mmc (131) (ICDD Card 00-050-0846).

Table 4. Refined values of the unit cell parameters of the phases of Sample 2, Rwp = 8.75%, Rp = 4.89%.

Formula ICDD Card	YTa _{0.4} Nb _{0.6} O ₄ 04-016-7255		YNbO ₄ 04-006-8921	
Syngony	Monoclinic		Monoclinic	
SPGR	C2/c, M'-type	Sample 2	C2/c, M'-type	Sample 2
a, Å	7.0089	7.01484	7.0297	7.03387
b, Å	10.9394	10.54867	10.937	10.94350
c, Å	5.0628	5.06709	5.069	5.07201
α, °	90.000	90.000	90.000	90.000
β, °	130.991	130.991	131.374	131.374
γ, °	90.000	90.000	90.000	90.000
V, Å ³	293.00	293.02	292.45	292.45
Deformation, %		0.0(3)		0.0(2)
Weight fraction in the sample, wt%		91.1(3)		8.88(19)

Table 5. Refined values of the unit cell parameters of the phases of Sample 3, Rwp = 8.75%, Rp = 4.89%.

Formula	YTa _{0.4} Nb _{0.6} O ₄	YNbO ₄	YTa _{0.9} Nb _{0.1} O ₄	YTaO ₄		
ICDD Card	04-016-7255	04-006-8921	04-016-7254	00-050-0846		
Syngony SPGR	Monoclinic C2/c	Monoclinic C2/c	Monoclinic P2/c (13) M-type	Tetragonal P42/mmc (131)		
	Sample 3	Sample 3	Sample 3	Card	Sample 3	Card
a, Å	7.02074(13)	6.81(4)	5.26(3)	5.1107	3.654(8)	3.648(5)
b, Å	10.9490(3)	10.06(6)	5.47(4)	5.4469	3.654(8)	3.648(5)
c, Å	5.06794(10)	4.96(3)	5.11 (14)	5.2989	5.478(7)	5.466(9)
α, °	90.000	90.000	90.000	90.000	90.000	90.000
β, °	131.0853(10)	120.0(4)	96.54(1)	96.43	90.20(11)	90.000
γ, °	90.000	90.000	90.000	90.000	90.000	90.000
V, Å ³	293.633	294.350	146.62	146.58	73.18	72.74
Deformation, %	0.0(3)	2.58(18)	0.0(3)		0.0(14)	
Weight fraction in the sample, wt%	84.6(7)	6.6(4)	7.4(2)		2.3(7)	

Tantalum atoms are in a distorted octahedral coordination with six Ta–O bonds in the structure of β-fergusonite YTaO₄. At the same time, tantalum atoms are in tetrahedral coordination in M-fergusonite YTaO₄.

XRD and WPPF (Figures 2 and 3) have revealed that partial substitution of Y atoms by REE atoms Eu³⁺, Sm³⁺, Tb³⁺ and Er³⁺ in M'-YTaO₄ and M'-YNbO₄ structures does not change the basic structure. XRD data are in good agreement with previously reported data on main lattices [28–30].

It is important to pay attention to the fact that samples 2 and 3 were sintered at temperatures above phase transition to tetragonal form (1426 ± 7) °C, for RETaO₄ [33]). However, ceramic sample 2 lacks this phase. It is likely that the presence of Nb in the crystalline matrix and Eu, Sm, Tb, and Er dopants shifted the temperature of this polymorphic transformation.

Sample 3 contains not only monoclinic phases of β-fergusonite, but also tetragonal T-phase YTaO₄ with SPGR P42/mmc (131) (ICDD Card 00-050-0846) and monoclinic YTaO₄ M-type phase with SPGR P2/c (13) (ICDD Card 04-016-7254), Figure 3, Table 5. Apparently, when the sample is cooled, a high-temperature phase transformation occurs, which is a second-order transition [32] when the equilibrium tetragonal (T) phase transfers into the monoclinic (M) YTaO₄ phase.

SEM images were obtained in order to compare morphology and grain sizes in ceramic samples 1–3 with a different thermal prehistory. Figure 4 demonstrates the ceramic samples'

microstructure and size distribution. The Scan Master program, which is designed for the analysis and mathematical processing of images, was used to obtain differential particle distribution curves for $\text{YNb}_x\text{Ta}_{1-x}\text{O}_4$ ceramic samples, insets of Figure 4a–c.

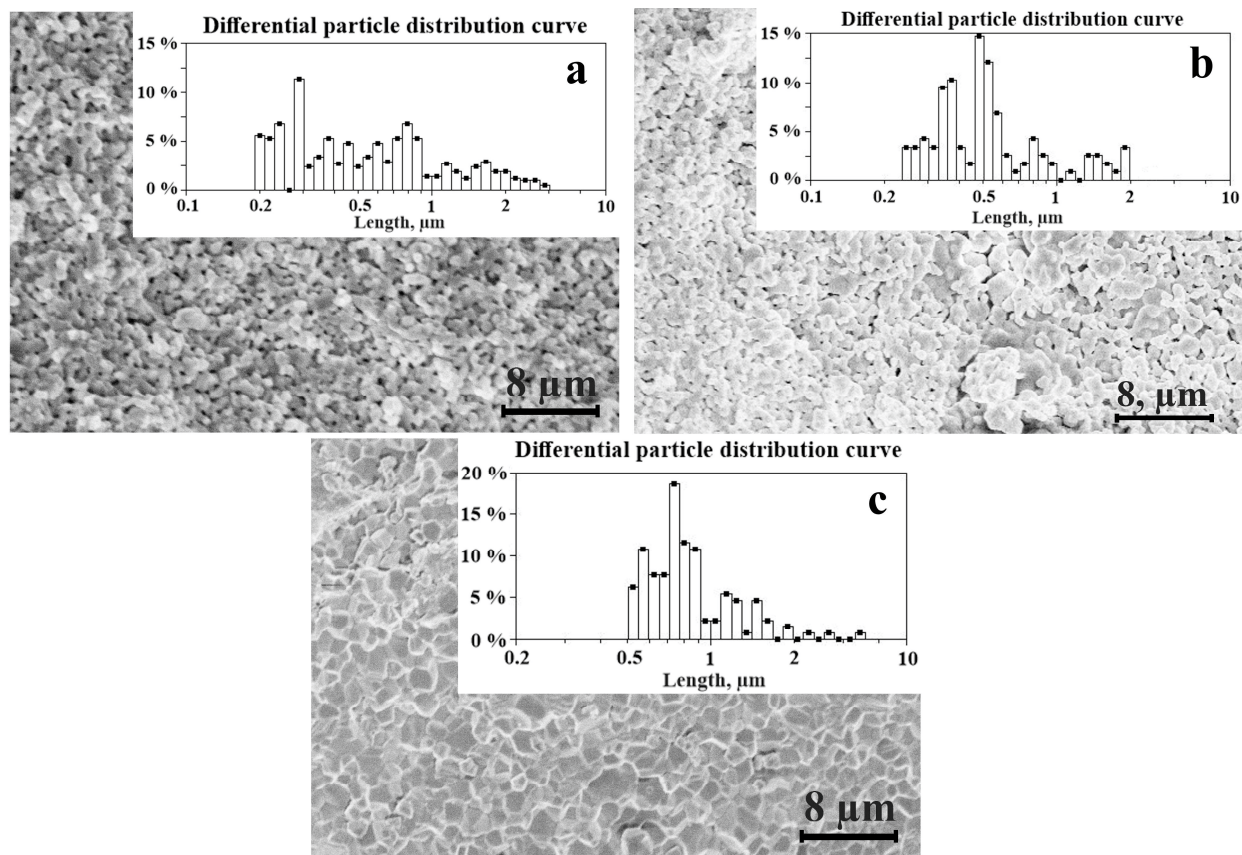


Figure 4. Microstructure and size distribution of $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramic samples (a) 1, (b) 2, (c) 3.

The structure of all studied $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramic samples is quite uniform despite the co-existence of several monoclinic phases and a small amount (approximately 3%) of tetragonal phase in Sample 3. An increase in ceramic sintering temperature leads to a slight increase in ceramic grain sizes. The shape of ceramic particles of sample 1 is close to spherical, and there are no clearly defined faceting elements. Their size varies from 0.2 to 3 μm with an average value of 0.48 μm , Figure 4a. The microstructure of sample 1 has a significant amount of pores. The particles of ceramic sample 2 also do not have a well-defined morphology. At the same time, they grow. Their size varies from 0.3 to 3 μm with an average value of 0.53 μm , Figure 4b. The microstructure of Sample 3 is the most uniform and the least porous (less than 8% pores). The structure is formed by well-cut grains from 0.5 to 4 μm with an average particle size 0.9 μm in ceramics, Figure 4c.

Phase and microstructural features of the samples are manifested in their mechanical characteristics, which have been measured due to a method described in sufficient detail in our paper [19].

Measured and calculated mechanical characteristics of $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramic samples are given in Table 6.

Table 6. Mechanical characteristics of $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramic samples.

Sample	ρ_{exp}	$\rho_{rel}, \%$	Microhardness, H, GPa	Young's Modulus, E, GPa	Crack Resistance $K_{IC}, MPa m^{0.5}$
1	4.06	69.82	4.04 ± 0.6	176.8 ± 2.5	0.88 ± 0.1
2	4.35	74.87	4.85 ± 0.5	269.9 ± 1.9	1.0 ± 0.8
3	4.68	80.55	7.2 ± 1.0	306.0 ± 5.0	1.15 ± 0.16

Table 6 demonstrates that the mechanical characteristics of samples strongly depend on the thermal prehistory of samples. Sample 3 has the highest density ($\rho_{rel} = 80.55\%$) and the best mechanical characteristics: microhardness $H = 7.2 \pm 1.0$ GPa, Young's modulus $E = 306.0 \pm 5.0$ GPa and crack resistance $K_{IC} = 1.15 \pm 0.16$ MPa $m^{0.5}$. This samples was prepared from a powder sintered at $T = 1400$ °C, ceramics calcination happened at $T = 1500$ °C. An increase in Young's modulus of sample 3 is apparently caused by the appearance of T- and M-phases with increased mechanical properties [34].

The data on the mechanical characteristics of $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramics synthesized by sol-gel in general agree with results from [34–36]. The authors of [34,35] show for the REE niobates $RENbO_4$ the following values: Young's modulus 60–170 GPa, and hardness of up to 11.48 GPa. These values are comparable with the range of our results adjusted for difference in measurement methods—nanoindentation and sclerometry. The differences in the values of the mechanical characteristics of the compared orthoniobates–tantalates are also due to the method of obtaining materials, as well as the properties and concentration of doping REE, the ratio of crystalline phases in the sample [34,37]. Whatever the absolute values of the properties, the mechanical characteristics of $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramics are quite high and sufficient for use in luminescent and scintillation devices.

Figure 5 demonstrates CL spectra of $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramic sample 1 before and after vacuum annealing. CL has revealed a relative uniformity of luminescence of ceramic SSs $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ before vacuum annealing. Spectra contain a wide luminescent halo in the blue region and a number of narrow bands of various intensities. The luminescent halo at 420 nm is caused by radiative recombination between a central atom Me^{4+} ($Me = Nb, Ta$) and a surrounding oxygen O^{2-} . The halo refers to the intrinsic glow of the ceramic matrix [15,38]. Narrow bands are due to intraconfigurational $4f^n-4f^n$ transitions of various REEs, Figure 5b: $^5D_4-^7F_J$ ($J = 6, 5, 4, 3$) transitions belong to Tb^{3+} (maxima at 490, 550, 575 and 625 nm) [39]; $^5D_0-^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions belong to Eu^{3+} (maxima at 580, 590, 615, 650 and 710 nm) [40]; $^2H_{11/2}-^4I_{15/2}$, $^4S_{3/2}-^4I_{15/2}$ transitions belong to Er^{3+} (maxima at 525 and 555 nm) [41]; $^4G_{5/2}-^6H_J$ ($J = 5/2, 7/2, 9/2, 11/2$) transitions belong to Sm^{3+} (maxima at 560, 610, 650 and 700 nm) [41]. Figure 5a demonstrates that Eu^{3+} and Sm^{3+} provide the maximal CL intensity of the studied $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ sample 1 at 625 nm. A number of bands located upon the luminescent halo in the wavelength range 420–480 nm are probably caused by the radiative recombination of these exact REEs.

Recovery annealing uniformly increases the intensity of the whole CL spectra of $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramics; the increase is in average by 44% against the maximal value at 615 nm, Figure 5a. The intensity of CL of one area of vacuum-annealed ceramics can be more than five times larger than of the other, Figures 5a and 6. Each sample contains both strongly and weakly glowing areas. However, the fraction of areas with a low CL intensity is much smaller than that of high intensity areas, Figure 6. Oxygen desorption is apparently non-uniform on the surface of the ceramic sample; the different intensity of radiative recombination indicates this. Oxygen vacancies are probably distributed unevenly; this causes formation of clusters, areas with higher and lower content of vacancy complexes. This can be determined by the annealing technology: one side of the ceramic sample tablet touches the bottom of the platinum crucible during thermal treatment, the bottom is not perfectly flat.

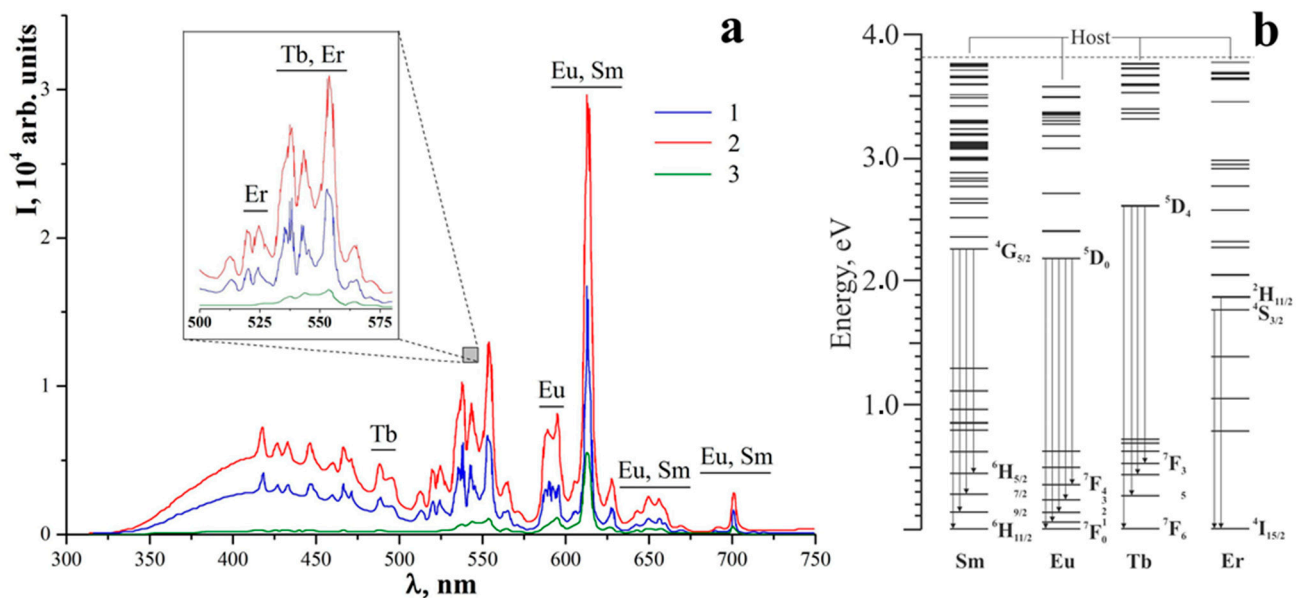


Figure 5. (a)—CL spectra of $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ sample 1: (1) Before vacuum annealing; (2) After vacuum annealing, area with a high CL intensity; (3) After vacuum annealing, area with a low CL intensity. (b)—main radiative $4f^n-4f^n$ transitions of REEs Sm, Eu, Tb and Er.

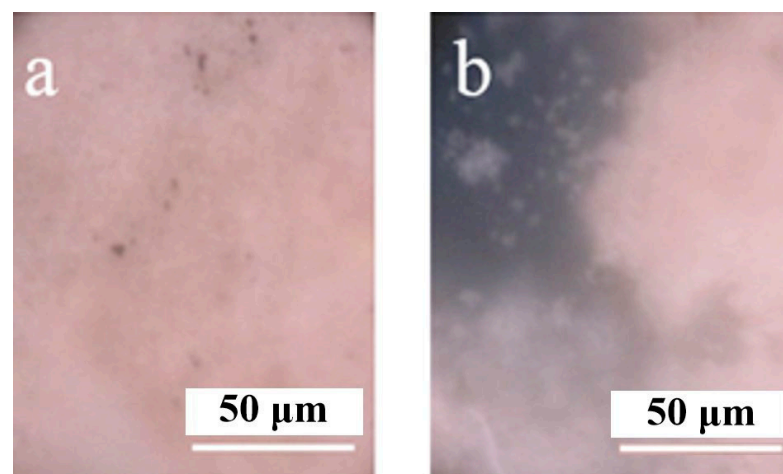


Figure 6. CL images of studied $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramics before (a) and after (b) vacuum annealing.

Oxygen vacancies form in the samples due to oxygen desorption from the surface and volume during the ceramics' recovery annealing. This changes the coordination environment of the Nb/Ta and Y metal cations, i.e., an oxygen vacancy with a localized ion forms in the first coordination sphere of Nb/Ta and Y. Defect centers of the MeO_3-V_O group types appear in the ceramics matrix along with the main luminescence centers MeO_4 -groups (Me–Nb, Ta). Electrostatic interaction changes near such a defect. This should change the mechanisms of radiative recombination involving luminescence centers of the BO_3-V_O (B–Nb, Ta) type. The centers are involved in changing the mechanism of radiative recombination and participate in the transfer of energy between luminescence centers. The position of the emission bands of doping REE elements does not change after vacuum annealing since $4f^n$ shell of REE is screened by $5s^25p^6$ shell. As a result, the crystal field of lattice surrounding the REE element hardly influences its emission. MeO_3-V_O can act as a mediator in the transition of energy from MeO_4 -groups to REE in annealed ceramics. $^5D_0-^7F_1$ and $^5D_0-^7F_2$ levels of Eu^{3+} split in the wavelength regions 590–595 nm (three bands) and 612–615 nm (two bands excluding influence of Sm^{3+} radiation) in ceramics before

annealing. Such splitting is characteristic of the monoclinic structure of M-type, where Eu^{3+} ions occupy sites with the point symmetry C_2 [15]. However, the fine structure of Eu^{3+} ion levels blurs after vacuum annealing due to an increase in disorder and the appearance of V_O defects in $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramics.

CL spectra are hardly affected by the ceramics' sintering temperature. Photoluminescence (PL) spectra of samples 2 and 3 were registered in order to establish the influence of the powders' calcination temperature. Figure 7 demonstrates PL spectra of $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramic prepared from powders calcinated at 1200 °C (sample 2) and 1400 °C (sample 3). Spectra consist of PL peaks attributed to intraconfigurational $4f^n-4f^n$ transitions of Er^{3+} , Eu^{3+} , Tb^{3+} and Sm^{3+} ions. The maximal intensity of both samples is located in the green and orange areas. The integral intensity of sample 2 spectrum is 43% larger than that of sample 3. In addition, the spectrum of sample 2 contains a wide luminescent halo in the wavelength range 380–540 nm.

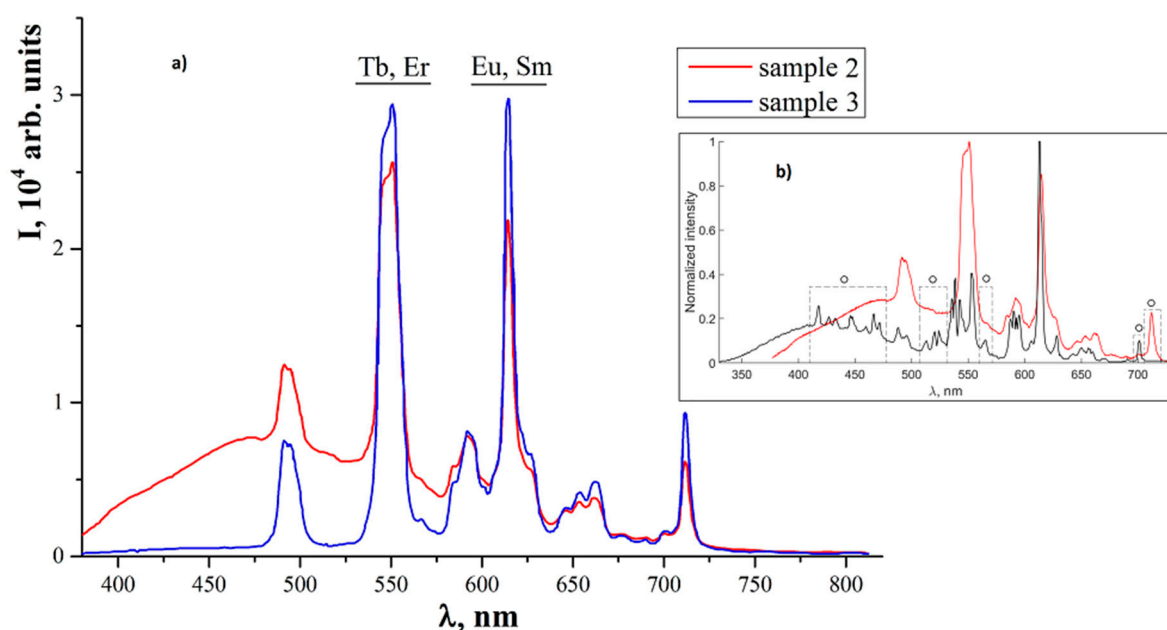


Figure 7. (a) PL spectra of $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramic sintered at 1500 °C from powders calcinated at 1200 °C (sample 2) and 1400 °C (sample 3). (b) Comparison of PL (—) and CL (—) spectra of $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramics (sample 1 (—) and sample 2 (—)); ○ denotes places with the greatest differences in the spectra.

Excitation at $\lambda_{\text{ex}} = 325$ nm shifts the luminescent halo to the long wave region ($\Delta\lambda = 40$ nm) compared to CL spectra. This might indicate the luminescence of several centers of NbO_4 groups in a monoclinic structure (M-type) of the $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramic. For example, paper [42] assumes that the excitation of luminescence by $\lambda_{\text{ex}} = 310$ nm can cause the luminescence of NbO_4 groups located near an oxygen vacancy. However, the formation of oxygen vacancies in our case is unlikely due to the technology of ceramics sintering at air. Thus, the luminescence of centers containing V_O is hardly possible.

In the crystal structure of monoclinic syngony, niobium can occupy two sites; thus, the spectrum can contain luminescence of two different NbO_4 groups [15]. In the case of CL, the excitation energy is higher than the absorption edge, the shortwave luminescence of NbO_4 groups is excited. The energy of the PL excitement in near-UV ($\lambda_{\text{ex}} = 325$ nm) is not enough to excite the luminescence of these NbO_4 groups. Only a longer-wave luminescence of the other NbO_4 group appears at PL; this is why the luminescent halo shifts to the long-wave area.

Figure 7b compares normed PL spectra of $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramics obtained due to different technologies. Sample 2 PL spectrum contains a maxi-

mum at 710 nm; the maximum is attributed to the 5D_0 - 7F_4 transition of Eu^{3+} ion. Sample 3 PL spectrum (Figure 7a) contains a similar maximum. CL spectra of sample 1 lack the intense luminescence of the 5D_0 - 7F_4 transition at 710 nm, the 5D_0 - 7F_2 transition dominates with the maximum at 615 nm. This indicates the location of Eu^{3+} atoms in one non-centrosymmetrical site [43]. Vacuum treatment does not affect this fact. The ratio between the 5D_0 - 7F_2 and 5D_0 - 7F_4 transitions of Eu^{3+} ions is ~ 3.7 for sample 2 and ~ 3.3 for sample 3. Thus, Eu^{3+} localizes in two non-centrosymmetrical sites of the structure in samples 2 and 3 [43]; the fraction of Eu^{3+} ions distribution in these two sites is greater in sample 3 than in sample 2. We explain this by a formation of additional phases in sample 2 and 3 compared to sample 1; XRD analysis confirms our assumption, Tables 3–5. These phases can accumulate a part of REE atoms in positions that are not equivalent to the main phase. This can cause an intense 5D_0 - 7F_4 transition of Eu^{3+} ion at 710 nm in samples 2 and 3. This assumption is also confirmed by the quenching of part of the maxima of other REEs in spectral areas denoted by a circle on Figure 7b.

On the other hand, the absence of low-intensity maxima in the wavelength range 410–480 nm in PL spectra (Figure 7a) can be explained by the following fact. High-energy electron flow causes an additional energy transfer to occur between NbO_4 groups emitted in the short-wavelength region [44] and REEs (Sm, Eu, Tb, and Er) in the matrix of $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramics. These energy transfers cause a number of maximums of CL spectra in the range 410–480 nm, Figure 5a. In the case of PL, the spectrum is excited by $\lambda_{ex} = 325$ nm, the intrinsic luminescence of NbO_4 groups is excited in $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramics with a maximum at 460 nm (Figure 7a), while REE emission in the blue region is not activated. Consequently, the energy transfer between NbO_4 groups and REEs can either occur without the activation of these energy levels, or does not occur at all due to insufficient energy of the near-UV-exciting radiation.

PL-band intensity does depend on the powders' sintering temperatures at $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramic preparation. However, the amount and frequencies of bands are the same. Temperature regimes for obtaining powders affect the crystal structure, microstructure, the relative content of polymorphic modifications and the presence of additional phases in the samples. The positions of the luminescence bands of REEs remain the same. The absence of changes is caused by the screening of the $4f^n$ shell of REE by $5s^25p^6$ shell. The intrinsic luminescence of the matrix strongly depends on the calcination temperature of the initial powder. Intrinsic luminescence of the matrix is not observed in $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ ceramics sintered from powder calcined at 1400 °C. Non-luminescent structural units are formed under such conditions, Figure 7. The tetragonal phase of ceramics can act as such structural units (Table 5). This phase apparently does not exhibit luminescent properties. The sample contains approximately 3% of the tetragonal phase and 7% of the monoclinic phase of M-fergusonite $YT_{0.9}Nb_{0.1}O_4$. Tantalum (niobium) cations are in tetrahedral coordination in these phases, which is less favorable for the charge transfer. The absence of these phases, apparently, determines the more intense luminescent radiation and a halo in the PL spectrum in the region of 400–550 nm of sample 2.

4. Conclusions

A finely dispersed powder of a multicomponent SS $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ was obtained in this study. SS was prepared by sol-gel synthesis using nitrate solutions of REEs and co-precipitated hydroxides of niobium and tantalum. Its thermal evolution from an amorphous to a crystalline form is shown using synchronous thermogravimetric and X-ray phase analysis. Ceramic samples were prepared from finely dispersed powder calcined at different temperatures (1200 °C and 1400 °C) using traditional ceramic technology. The ceramics were sintered at 1400 °C and 1500 °C; samples 1, 2, 3 were then investigated.

The phase structure of the ceramic SS $(Y_{0.96}Eu_{0.01}Sm_{0.01}Tb_{0.01}Er_{0.01})Nb_{0.7}Ta_{0.3}O_4$ was refined by the full-profile analysis of the X-ray patterns of polycrystals depending on the

preparation conditions. The structure of ceramic sample 1, sintered at $T_{\text{sint}} = 1400\text{ }^{\circ}\text{C}$ from powder calcined at $1200\text{ }^{\circ}\text{C}$, corresponds to the structure of the monoclinic phase with SPGR symmetry $C2/c$ with a small presence of the monoclinic phase with SPGR $I2/a$ (no more than 3%). The structure of ceramic sample 2, obtained at a higher temperature sintering ($T_{\text{sint}} = 1500\text{ }^{\circ}\text{C}$) from the powder calcined at $1200\text{ }^{\circ}\text{C}$, corresponds exclusively to the monoclinic phase with SPGR $C2/c$. In ceramic sample 3, sintered at $T_{\text{sint}} = 1500\text{ }^{\circ}\text{C}$ from a powder calcined at $1400\text{ }^{\circ}\text{C}$, along with the monoclinic phases of β -fergusonite, there are tetragonal (T-phase) YTaO_4 with SPGR $P42/mmc$ (131) and monoclinic phase YTaO_4 M-type with SPGR $P2/c$ (13). Probably, during the high-temperature sintering of ceramics obtained from a powder calcined at $1400\text{ }^{\circ}\text{C}$, a monoclinic cell is distorted and a shear transition of the monoclinic phase into the tetragonal T-phase occurs. When the sample is cooled, apparently through a high-temperature polymorphic transformation, which is a second-order phase transition, the tetragonal T-phase partially transforms into the monoclinic M-phase.

The morphological features of the microstructure of ceramic samples 1–3, depending on the conditions of preparation, were studied and their mechanical characteristics were evaluated. Sample 3 has the highest density ($\rho_{\text{rel}} = 80.55\%$) and the best mechanical characteristics of all studied ceramic samples: microhardness $H = 7.2 \pm 1.0\text{ GPa}$, Young's modulus $E = 306.0 \pm 5.0\text{ GPa}$ and crack resistance $K_{\text{IC}} = 1.15 \pm 0.16\text{ MPa m}^{0.5}$.

CL and PL were investigated in $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramics in the visible region depending on the thermal history of sample preparation. PL was excited by UV light ($\lambda_{\text{ex}} = 325\text{ nm}$). The luminescent halo at $\sim 380\text{--}540\text{ nm}$ is due to the radiative recombination between the central atom Me^{4+} ($\text{Me} = \text{Nb}, \text{Ta}$) and the surrounding oxygens O^- and refers to the intrinsic luminescence of the ceramic matrix [15,36]. Many narrow lines are due to the intraconfigurational $4f^n\text{--}4f^n$ transitions of various REEs. The maximum intensity of CL of the studied ceramic samples is observed on Eu^{3+} and Sm^{3+} ions at 615 nm .

Reductive annealing in vacuum leads to a uniform increase in the luminescence intensity of the entire CL spectrum of $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramics by $\sim 44\%$. The increase can be associated with an increase in energy transfer through the defective centers $\text{MO}_3\text{--V}_\text{O}$ ($\text{M} = \text{Nb}, \text{Ta}$) to REEs. Since V_O defects are hole-trapping centers, a recombination with a fast electron flow increases the fraction of emission that is transferred to REEs. As a result, in general, the CL in vacuum annealed $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramics increases.

The intensity of PL of $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramic samples with the same set of spectral bands strongly depends on the calcination temperature of the initial powder. The thermal history (powder annealing temperature and ceramic sintering temperature) of obtaining $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ ceramics affects its crystal structure, microstructure, relative content of polymorphic modifications, and the presence of additional phases in samples. The ratio of monoclinic phases in ceramic samples $(\text{Y}_{0.96}\text{Eu}_{0.01}\text{Sm}_{0.01}\text{Tb}_{0.01}\text{Er}_{0.01})\text{Nb}_{0.7}\text{Ta}_{0.3}\text{O}_4$ is also determined by the heat treatment conditions.

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