

Structure and spectral-luministic characteristics of $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--Eu}_2\text{O}_3$ powders and crystals

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Nanopowders of the concentration series $\text{ZrO}_2\text{--}(4\text{--}27 \text{ mol.}\%)\text{Y}_2\text{O}_3\text{--}(0.1 \text{ mol.}\%)\text{Eu}_2\text{O}_3$ were obtained by methods of chemical coprecipitation and hydrothermal synthesis with microwave treatment. Their morphology, dispersion, phase composition and spectral-luminescent characteristics were studied. A comparative analysis of the phase composition of nanopowders and crystals of a similar concentration series, obtained by the method of directional crystallization of the melt in a cold crucible, revealed that the phase formation processes of nanopowders are influenced by the size factor caused by additional oxygen vacancies due to the developed surface of the nanopowders. Differences in the formation of the local environment of the optical centers of Eu^{3+} ions in $\text{ZrO}_2\text{--}(4\text{--}27 \text{ mol.}\%)\text{Y}_2\text{O}_3\text{--}(0.1 \text{ mol.}\%)\text{Eu}_2\text{O}_3$ and $\text{ZrO}_2\text{--}(4\text{--}27 \text{ mol.}\%)\text{Eu}_2\text{O}_3$ nanopowders were revealed. The intensity parameters Ω_i ($i = 2, 4, 6$) for Eu^{3+} ions for $\text{ZrO}_2\text{--Eu}_2\text{O}_3$ and $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--Eu}_2\text{O}_3$ crystals with a cubic crystal structure were determined.

Keywords: solid solutions based on zirconium dioxide, nanopowders, europium ions, luminescence spectrum.

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Introduction

Zirconium dioxide solid solutions have important properties for applications: high melting temperature, chemical resistance in corrosive environment, biocompatibility, high mechanical performance, ionic conductivity at high temperatures, etc. Physical properties of zirconium dioxide materials defining their applications depend on the structure of zirconium dioxides which in turn depends on the form and concentration of stabilizing oxides. Also note that the properties of zirconium dioxide solid solutions depend considerably on local crystal structure which is defined by the oxygen vacancy position relative to zirconium ions and stabilizing oxide cations (Y_2O_3 , Sc_2O_3 , rare-earth oxides, etc.).

In [1–4], we show the results of a comprehensive study of phase composition and local structure of $\text{ZrO}_2\text{--}x \text{ mol.}\% \text{Y}_2\text{O}_3\text{--}0.1 \text{ mol.}\% \text{Eu}_2\text{O}_3$ ($x = 2.7\text{--}30$) concentration range crystals obtained by the directional melt crystallization in cold container. Eu^{3+} ions in these crystals were used as a spectroscopic probe to detect local environment of a stabilizing oxide cation. Studies [4,5] identified the local structure characteristics of $\text{ZrO}_2\text{--}x \text{ mol.}\% \text{Eu}_2\text{O}_3$ ($x = 4, 6, 8, 10, 15, 20, 27$) and $\text{ZrO}_2\text{--}x \text{ mol.}\% \text{Y}_2\text{O}_3\text{--}y \text{ mol.}\% \text{Eu}_2\text{O}_3$ ($x = 2.7, 3.6, 8, 12, 14, 16, 20, 30, 38$; $y = 0.1, 0.5$) crystals obtained by the directional melt crystallization in cold container. Results of phase formation studies and analysis of spectral luminescent

characteristics of the $\text{ZrO}_2\text{--Eu}_2\text{O}_3$ crystal and nanopowder concentration range are reported in [5–7].

Review of the existing literature indicates that spectral luminescent characteristics of the $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--Eu}_2\text{O}_3$ nanopowders have been only partially studied for single compounds with particular concentrations of the stabilizing oxide [1,3,8]. Results of a comprehensive local structure study of $\text{ZrO}_2\text{--Y}_2\text{O}_3$ nanopowders in a wide concentration variation range of stabilizing Y_2O_3 with Eu^{3+} used as a spectroscopic probe and comparison analysis of properties of crystals with similar compositions haven't been found in the literature. Therefore, this study investigated the phase composition and spectral luminescent characteristics of $\text{ZrO}_2\text{--}x \text{ mol.}\% \text{Y}_2\text{O}_3\text{--}0.1 \text{ mol.}\% \text{Eu}_2\text{O}_3$ ($x = 4, 6, 8, 10, 15, 20, 27$) concentration range nanopowders obtained via synthesis with microwave treatment, and performed a comparative analysis of properties of the same concentration range of crystals obtained via the directional melt crystallization in cold container.

Description of the subjects and methods of research

$\text{ZrO}_2\text{--}(4\text{--}27 \text{ mol.}\%)\text{Y}_2\text{O}_3\text{--}(0.1 \text{ mol.}\%)\text{Eu}_2\text{O}_3$ concentration range nanopowders were synthesized by coprecipitation and hydrothermal synthesis with microwave treatment. Milestones of synthesis of nanopowders from this concentration range are schematically shown in Figure 1, *a, b*. Nanopowder synthesis used the following reagents: ammo-

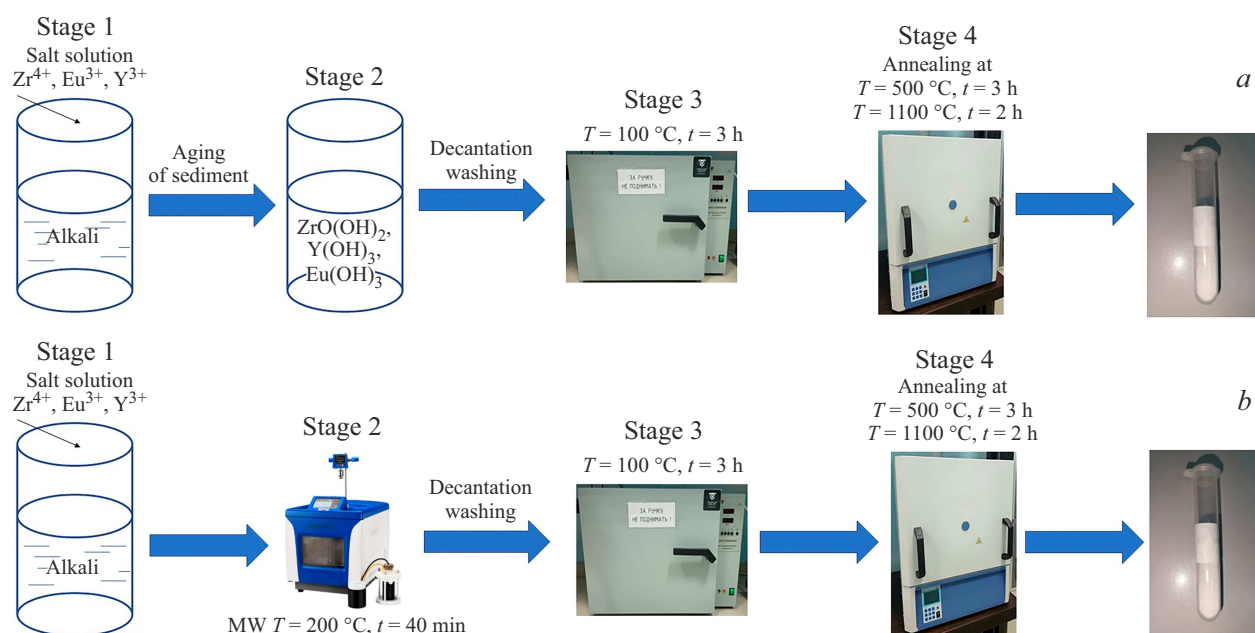


Figure 1. Milestones of the $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--Eu}_2\text{O}_3$ nanopowder synthesis techniques: coprecipitation (a) and hydrothermal synthesis with microwave treatment (b).

nia solution (25%, ACS, „Sigma Tec“), zirconium oxychloride octahydrate (C.P., 99.9%, „Vekton“), europium nitrate and yttrium nitrate hexahydrate (ACS, 99.99%, „Nevatorg“). Europium salt („Nevatorg“) in excess of concentrated nitric acid (65%, C.P., „Sigma Tec“) followed by evaporation. Inverse coprecipitation was used for precursor powder synthesis. The process was performed by adding salt solution (0.1 M) dropwise to the 25% diluted ammonia solution with constant stirring. After completion of this process, the solution was stirred in a magnetic stirrer for an hour. After precipitation, the precipitate was washed multiple times with distilled water by the decantation method to remove reaction products and dried in an oven at 100 °C for 3 h. $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--Eu}_2\text{O}_3$ nanopowders were prepared by consecutive annealing of precursor powders. Nanopowders were annealed in a muffle furnace for 3 h at 500 °C and for 2 h at 1100 °C.

Hydrothermal synthesis with microwave treatment used the U-Wave 2000 system with a radiation frequency of 2.45 GHz and a power of 600 W. Salt solution was added dropwise to the ammonia solution, the mixture was held in an autoclave at 200 °C for 40 min. Obtained nanoparticles were washed with water to remove by-products, dried and annealed for 3 h at 500 °C and for 2 h at 1100 °C in a muffle furnace.

Composition of $\text{ZrO}_2\text{--}(4\text{--}27 \text{ mol.}\%)\text{Y}_2\text{O}_3\text{--}(0.1 \text{ mol.}\%)\text{Eu}_2\text{O}_3$ concentration range nanopowders synthesized by the above-mentioned methods and corresponding designations are shown in Table 1. For comparative analysis, the study used $\text{ZrO}_2\text{--Eu}_2\text{O}_3$ solid solution crystals and nanopowders. Compositions of these solid solutions and corresponding designations are listed

in Table 2. $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--Eu}_2\text{O}_3$ and $\text{ZrO}_2\text{--Eu}_2\text{O}_3$ crystals used in the study for comparative analysis were obtained by the directional melt crystallization in cold container [9].

Elemental analysis of the crystal and nanopowder concentration ranges was carried out by the energy-dispersive analysis using the JSM 6480LV microscope with the INCAx-sight Energy „OXFORD instruments“ module. Results of the elemental analysis show that compositions of the given crystal and nanopowder concentration ranges correspond to the composition of feed materials within the measurement error.

Morphology analysis of $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--Eu}_2\text{O}_3$ particles was carried out by the transmission electron microscopy (TEM) using the JEOL 2100 high-resolution microscope (operating voltage 200 kV). Mean particle size was evaluated using the obtained TEM images from particle size distribution curves built in „ImageJ“. Phase analysis of $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--Eu}_2\text{O}_3$ nanopowders was carried out on the basis of diffraction patterns measured by the Empyrean PANalytical diffractometer using $\text{CuK}\alpha$ -radiation.

To study the spectral luminescent properties of nanopowders prepared by the hydrothermal synthesis with microwave treatment, cells of 14 mm in diameter and 5 mm in height were filled with the same amount of powder (0.2 g) with each of the compositions mixed with F-32LN PTFE-based varnish dissolved in isoamyle acetate. Parallel-sided plates of 2–7 mm in thickness were cut for recording crystal luminescence spectra.

Luminescence spectra of nanopowders obtained by the coprecipitation and hydrothermal synthesis with microwave treatment and of $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--Eu}_2\text{O}_3$ crystals were recorded using the Horiba FHR 1000 spectrometer and the Renishaw

Table 1. Composition of ZrO_2 –(4–27 mol.%) Y_2O_3 –(0.1 mol.%) Eu_2O_3 concentration range nanopowders and corresponding designations

№	Nanopowder composition	Designation
1	95.9 mol.% ZrO_2 –4 mol.% Y_2O_3 –0.1 mol.% Eu_2O_3	0.1 Eu_2O_3 –4YSZ
2	93.9 mol.% ZrO_2 –6 mol.% Y_2O_3 –0.1 mol.% Eu_2O_3	0.1 Eu_2O_3 –6YSZ
3	91.9 mol.% ZrO_2 –8 mol.% Y_2O_3 –0.1 mol.% Eu_2O_3	0.1 Eu_2O_3 –8YSZ
4	89.9 mol.% ZrO_2 –10 mol.% Y_2O_3 –0.1 mol.% Eu_2O_3	0.1 Eu_2O_3 –10YSZ
5	87.9 mol.% ZrO_2 –12 mol.% Y_2O_3 –0.1 mol.% Eu_2O_3	0.1 Eu_2O_3 –12YSZ
6	84.9 mol.% ZrO_2 –15 mol.% Y_2O_3 –0.1 mol.% Eu_2O_3	0.1 Eu_2O_3 –15YSZ
7	79.9 mol.% ZrO_2 –20 mol.% Y_2O_3 –0.1 mol.% Eu_2O_3	0.1 Eu_2O_3 –20YSZ
8	72.9 mol.% ZrO_2 –27 mol.% Y_2O_3 –0.1 mol.% Eu_2O_3	0.1 Eu_2O_3 –27YSZ

Table 2. Composition of ZrO_2 –(4–27 mol.%) Eu_2O_3 concentration range crystals and nanopowders and corresponding Designations

№	Crystal and nanopowder composition	Designation
1	96 mol.% ZrO_2 –4 mol.% Eu_2O_3	4EuSZ
2	94 mol.% ZrO_2 –6 mol.% Eu_2O_3	6EuSZ
3	92 mol.% ZrO_2 –8 mol.% Eu_2O_3	8EuSZ
4	90 mol.% ZrO_2 –10 mol.% Eu_2O_3	10EuSZ
5	88 mol.% ZrO_2 –12 mol.% Eu_2O_3	12EuSZ
6	85 mol.% ZrO_2 –15 mol.% Eu_2O_3	15EuSZ
7	80 mol.% ZrO_2 –20 mol.% Eu_2O_3	20EuSZ
8	73 mol.% ZrO_2 –27 mol.% Eu_2O_3	27EuSZ

Table 3. Phase composition and lattice parameters of 0.1 Eu_2O_3 –(4–27)YSZ nanopowders obtained by the coprecipitation and hydrothermal synthesis with microwave treatment

Composition	Phase composition		Lattice parameters			
	Powder (precipitation)	Powder (hydrothermal synthesis)	Powder (precipitation)		Powder (hydrothermal synthesis)	
			$a, \text{\AA}$	$c, \text{\AA}$	$a, \text{\AA}$	$c, \text{\AA}$
0.1 Eu_2O_3 –4YSZ	t- ZrO_2	t- ZrO_2	3.611(1)	5.164(1)	3.612(1)	5.164(1)
0.1 Eu_2O_3 –8YSZ	c- ZrO_2	c- ZrO_2	5.141(1)		5.144(1)	
0.1 Eu_2O_3 –10YSZ	c- ZrO_2	c- ZrO_2	5.143(1)		5.144(1)	
0.1 Eu_2O_3 –15YSZ	c- ZrO_2	c- ZrO_2	5.156(1)		5.158(1)	
0.1 Eu_2O_3 –20YSZ	c- ZrO_2	c- ZrO_2	5.167(1)		5.168(1)	
0.1 Eu_2O_3 –27YSZ	c- ZrO_2	c- ZrO_2	5.187(1)		5.185(1)	

inVia Raman spectrometer-microscope. Solid-state laser radiation with $\lambda_{exc} = 532 \text{ nm}$ was used as a $^5D_1$ excitation source of Eu^{3+} .

Experimental results and discussion

TEM images of 0.1 Eu_2O_3 –(4–27)YSZ solid solution concentration range particles obtained by the coprecipitation (series 1) detected that the particles were significantly agglomerated. This is illustrated in Figure 2 by TEM images and corresponding size distributions of particles with extreme concentration range compositions, 0.1 Eu_2O_3 –4YSZ and 0.1 Eu_2O_3 –27YSZ. It can be seen from the particle size distributions that the mean particle size increases insignificantly as the concentration of stabilizing Y_2O_3 increases and is equal to 75 nm for 0.1 Eu_2O_3 –4YSZ and

to 90 nm for 0.1 Eu_2O_3 –27YSZ. TEM images and size distributions of 0.1 Eu_2O_3 –4YSZ (a) and 0.1 Eu_2O_3 –27YSZ (b) nanoparticles obtained by the hydrothermal synthesis with microwave treatment (series 2) are shown in Figure 3.

It can be seen from the comparative analysis of images shown in Figure 2, 3 that in both cases particles are agglomerated, however, the degree of agglomeration of Series 2 nanoparticles is a little lower than that of Series 1 nanoparticles. Mean size of 0.1 Eu_2O_3 –4YSZ and 0.1 Eu_2O_3 –27YSZ nanoparticles obtained by hydrothermal synthesis with microwave treatment corresponds to 67 nm and 46 nm.

Figure 4, a and b shows diffraction patterns of Series 1 and 2 0.1 Eu_2O_3 –(4–27)YSZ nanopowders. An analysis of diffraction patterns shown in Figure 4 indicates that a tetragonal phase is predominant for 0.1 Eu_2O_3 –4YSZ nanopowders. Powders with concentration of Y_2O_3 higher

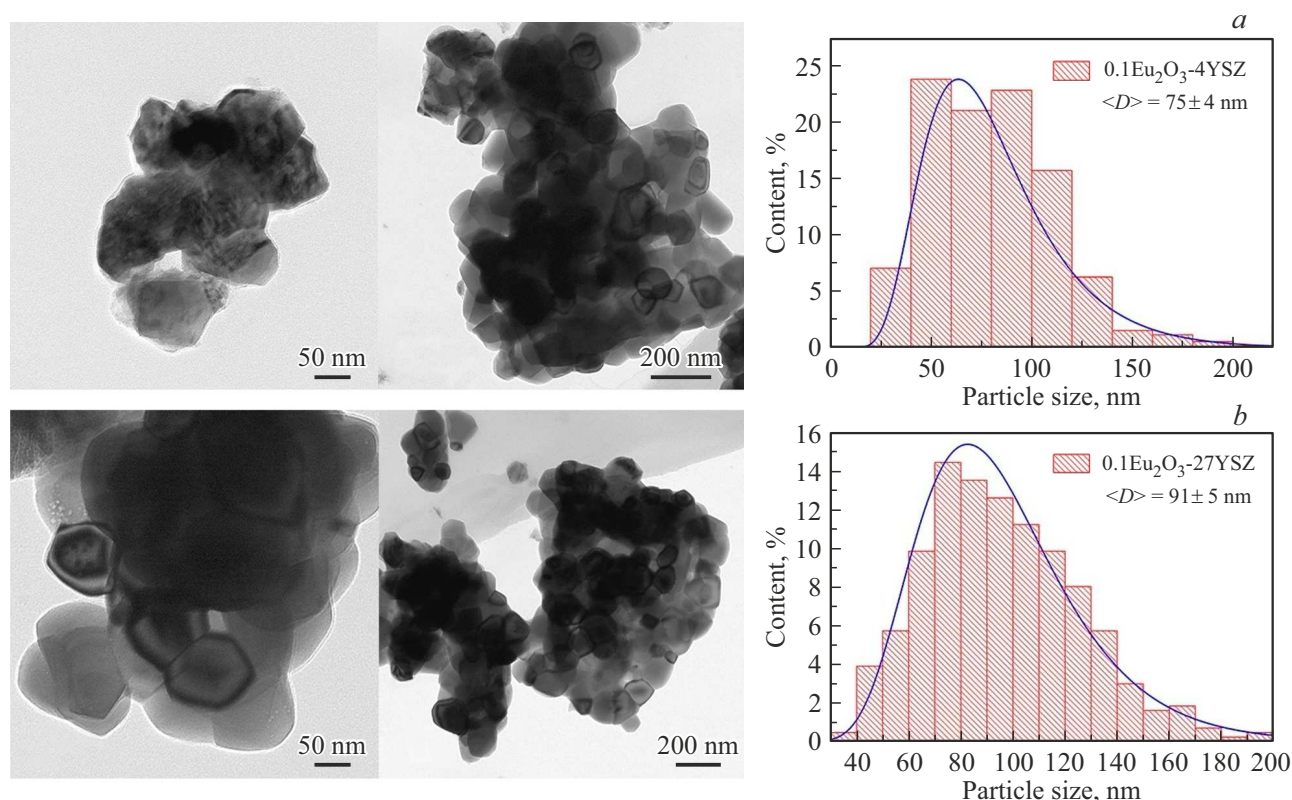


Figure 2. TEM images and size distributions of 0.1Eu₂O₃-4YSZ (a) and 0.1Eu₂O₃-27YSZ (b) nanoparticles obtained by the coprecipitation method.

than 6 mol.% feature a cubic structure. Phase composition and lattice structure parameters of Series 1 and 2 0.1Eu₂O₃-(4-27)YSZ nanopowders determined from the corresponding diffraction patterns are shown in Table 3. Similar properties for 0.1Eu₂O₃-(3.6-30)YSZ crystals obtained by the directional melt crystallization in cold container are listed in Table 4 [10,11].

Comparative phase composition analysis of ZrO₂-Y₂O₃-Eu₂O₃ series nanopowders and crystals identifies some differences. 0.1Eu₂O₃-(6-27)YSZ nanopowders synthesized by the coprecipitation and hydrothermal synthesis with microwave treatment have a cubic structure whose lattice constant increases linearly as the concentration of Y₂O₃ increases. 0.1Eu₂O₃-8YSZ crystals unlike nanopowders with the similar composition are two-phase and display the presence of cubic and tetragonal phases. It has been found that for the crystal compositions selected in the study the cubic phase is stabilized throughout the volume only beginning from 12 mol.% Y₂O₃.

Phase composition data analysis of 0.1Eu₂O₃-(4-27)YSZ concentration range crystals and nanopowders with comparative concentrations of the stabilizing oxide shows that the cubic fluorite structure gets stabilized in powders at a lower concentration of Y₂O₃ than in crystals. This is caused by the size factor and is explained by the fact that cubic phase stabilization for nanopowders at a

lower concentration of the stabilizing oxide takes place due to additional oxygen vacancies resulting from developed surface of nanoparticles.

Findings agree with the literature data according to which the size effect provides stabilization of the cubic and tetragonal phases of nanocrystalline ZrO₂ at room temperature. Thus, authors of [12] obtained amorphous ZrO₂ nanoparticles sized from 1.5 nm to 3 nm and achieved the tetragonal phase after annealing at $T = 500^\circ\text{C}$. A mixture of tetragonal and monoclinic phases was obtained by increasing the annealing time. However, it should be noted that the high-temperature synthesis method cannot give ZrO₂ crystals with a tetragonal structure at room temperature.

Table 3 shows that lattice constants for Series 1 and 2 nanopowders with identical compositions differ insignificantly. Data in Table 3, 4 also indicates that both 0.1Eu₂O₃-(4-27)YSZ crystals and nanopowders with cubic structure are characterized by increase in the lattice constant as the stabilizing oxide concentration increases.

Figure 5 shows luminescence spectra of the $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ optical transitions of Eu³⁺ ions for the concentrations ranges of crystals (a) and nanopowders obtained by the coprecipitation (b) and hydrothermal synthesis with microwave treatment (c), 0.1Eu₂O₃-(4-27)YSZ with excitation by radiation with

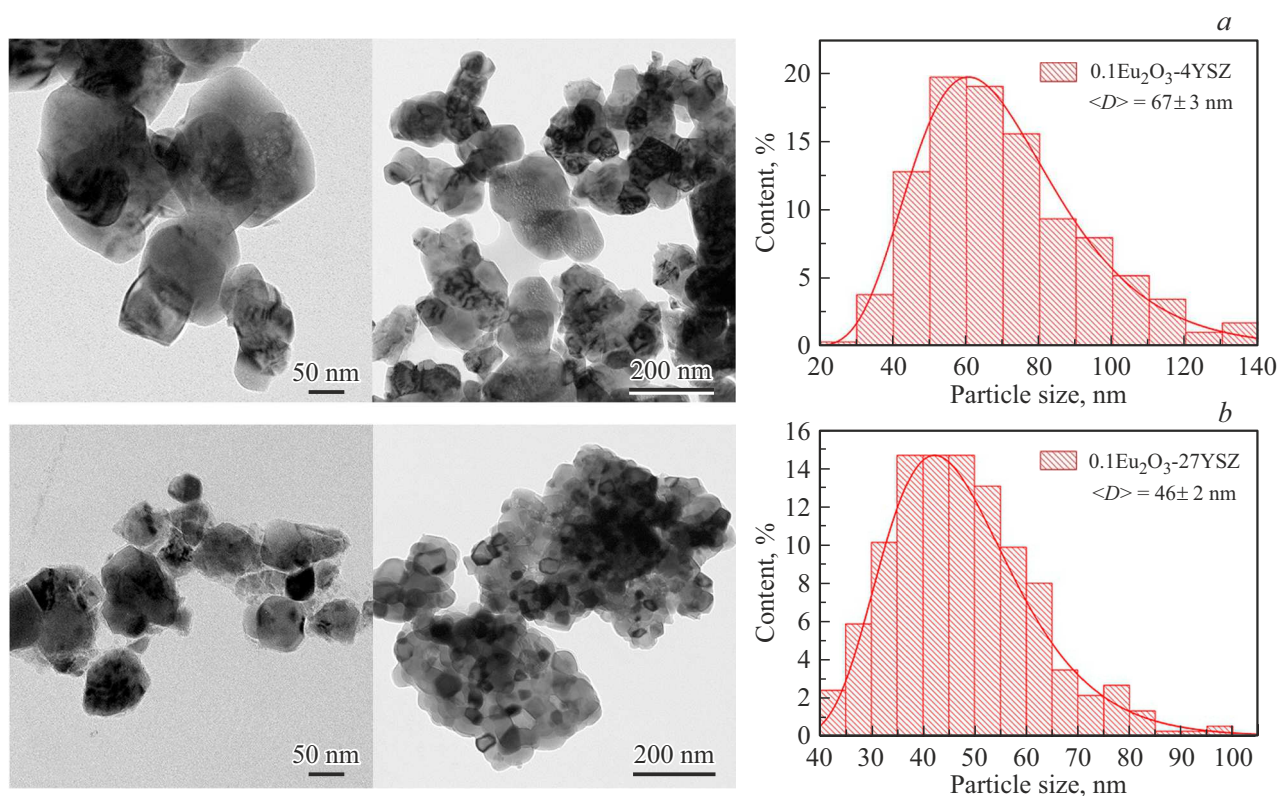


Figure 3. TEM images and size distributions of 0.1Eu₂O₃-4YSZ (a) and 0.1Eu₂O₃-27YSZ (b) nanoparticles obtained by the hydrothermal synthesis with microwave treatment.

Table 4. Phase composition and lattice constants of crystals 0.1Eu₂O₃-(3.6–30)YSZ [10,11]

Designation	Phase composition*	<i>a</i> , Å	<i>c</i> , Å	<i>c</i> /√2 <i>a</i>
0.1Eu ₂ O ₃ -3.6YSZ	t-ZrO ₂	3.606(1)	5.171(1)	1.014
	t'-ZrO ₂	3.620(1)	5.147(1)	1.005
0.1Eu ₂ O ₃ -8YSZ	c-ZrO ₂	5.138(1)		
	t''-ZrO ₂ *			
0.1Eu ₂ O ₃ -12YSZ	c-ZrO ₂	5.148(1)		
0.1Eu ₂ O ₃ -16YSZ	c-ZrO ₂	5.159(1)		
0.1Eu ₂ O ₃ -30YSZ	c-ZrO ₂	5.195(1)		

Note: *Non-transformable tetragonal t'' phase. t'' phase was identified in the 0.1Eu₂O₃-8YSZ crystal by the Raman spectroscopy method [11].

$\lambda_{\text{exc}} = 532 \text{ nm}$ at $T = 300 \text{ K}$. It can be seen from Figure 5 that the luminescence spectra of 0.1Eu₂O₃-(4–27)YSZ crystal and nanopowders with identical compositions have similar profiles, but have some differences at the same time. In luminescence spectra of nanopowders and crystals of the $^5D_0 \rightarrow ^7F_1$ optical transition of Eu³⁺ ions, as the concentration of Y₂O₃ increases, the relative intensity of a line with its maximum at $\sim 585.5 \text{ nm}$ assigned in [4] to seven-oxygen-coordinated Eu³⁺ sites increases relative to a line with its maximum at $\sim 586.5 \text{ nm}$ that is typical of Eu³⁺ without a vacancy in the first coordination sphere, but with an oxygen vacancy in the second coordination

sphere. However, if for crystals an increase in the intensity of the $\sim 585.5 \text{ nm}$ line corresponding to Eu³⁺ with a vacancy in the first coordination sphere with respect to the $\sim 586.5 \text{ nm}$ line assigned to the optical centers of Eu³⁺ with a vacancy in the second coordination sphere is typical of concentration of Y₂O₃ higher than 8 mol.%, then for nanopowders this is observed at concentrations higher than 4 mol.%.

In the luminescence spectra of Eu³⁺ in 0.1Eu₂O₃-(4–27)YSZ crystals with a concentration of Y₂O₃ higher than 15 mol.%, additional lines are observed, positions of which correspond to $\sim 593.9 \text{ nm}$, $\sim 598.6 \text{ nm}$ for

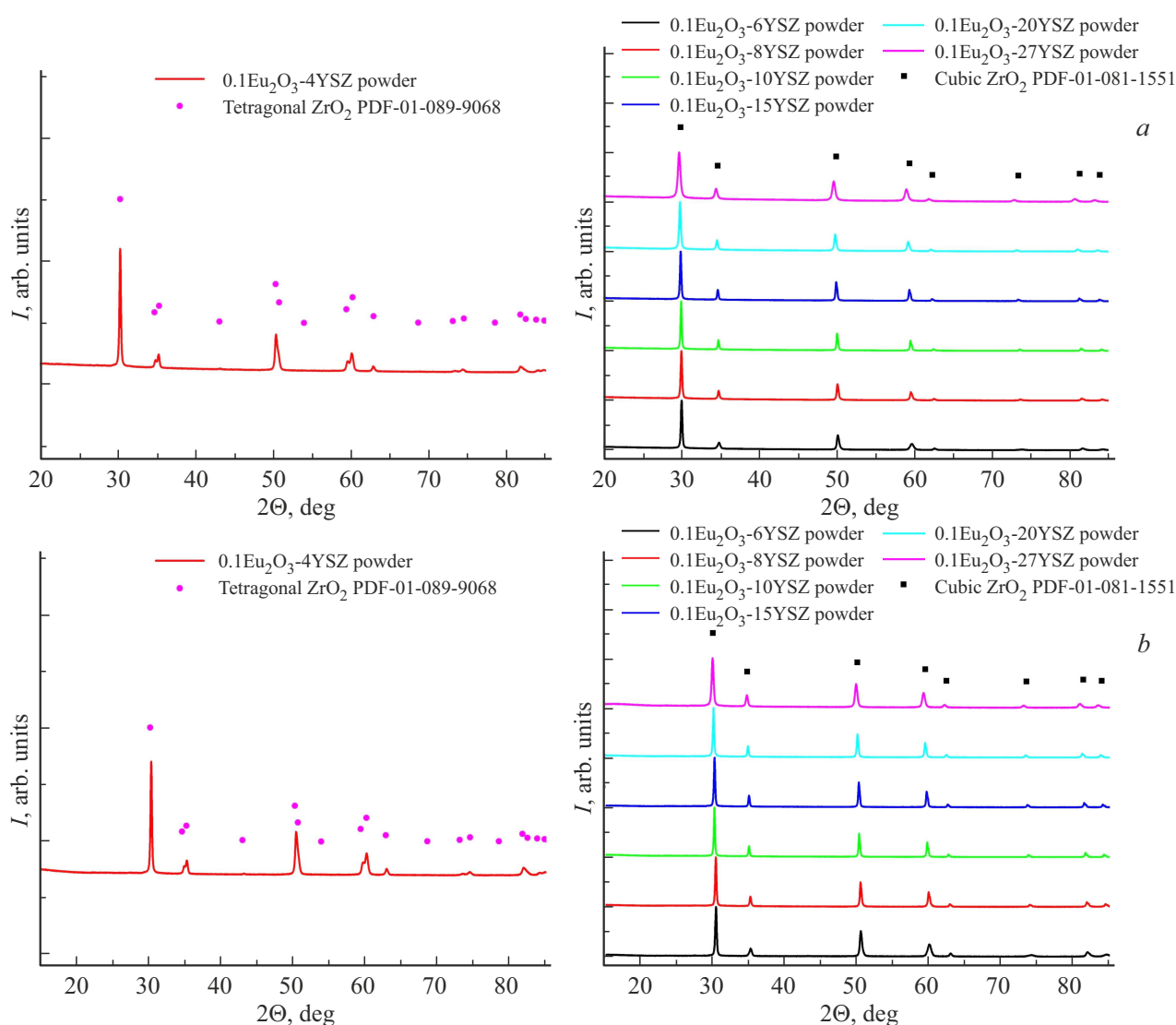


Figure 4. Diffraction patterns of $0.1\text{Eu}_2\text{O}_3\text{-(4-27)YSZ}$ concentration range nanopowders obtained by the coprecipitation (a) and hydrothermal synthesis with microwave treatment (b).

$^5D_0 \rightarrow ^7F_1$ and to ~ 611.6 nm, ~ 629.8 nm for $^5D_0 \rightarrow ^7F_2$. In accordance with findings of [1,4], these lines correspond to the optical centers of type III Eu^{3+} characterized by the presence of two oxygen vacancies located along the diagonal at a cubic lattice cell face. For nanopowders compared with crystals, these lines appear at lower concentrations of Eu^{3+} . This is visualized to a greater extent for luminescence spectra of $0.1\text{Eu}_2\text{O}_3\text{-(4-27)YSZ}$ nanopowders obtained by the hydrothermal synthesis.

Thus, comparative analysis of the luminescence spectra of $0.1\text{Eu}_2\text{O}_3\text{-(2.7-30)YSZ}$ crystals grown by the directional melt crystallization in cold container and of Series 1 and 2 $0.1\text{Eu}_2\text{O}_3\text{-(4-27)YSZ}$ nanopowders detected seven-, eight- and six-oxygen-coordinated cation sites (Y^{3+} , Eu^{3+}). As the concentration of Y_2O_3 increases, relative proportion of seven-coordinate sites with an oxygen vacancy in the first coordination sphere increases. For crystals, six-oxygen-

coordinated optical centers of Eu^{3+} are typical of stabilizing Y_2O_3 concentrations higher than 15 mol.%. In luminescence spectra of $0.1\text{Eu}_2\text{O}_3\text{-(4-27)YSZ}$ nanopowders, lines assigned to these centers are observed at Y_2O_3 4 mol.% and higher.

Results of a comprehensive study of (4–27)EuSZ crystals and nanopowders where europium oxide serves as the basic stabilizing oxide are reported in [5,6] Figure 6, a, b shows the luminescence spectra of (4–27)EuSZ crystals obtained by the directional melt crystallization in cold container and of nanopowders with the same composition obtained by the coprecipitation caused by $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} with excitation by radiation with $\lambda_{exc} = 532$ nm. Comparative analysis of luminescence spectra of $0.1\text{Eu}_2\text{O}_3\text{-(4-27)YSZ}$ and (4–27)EuSZ nanopowders and crystals as shown in Figures 5 and 6 found that luminescence spectra of $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Eu}_2\text{O}_3$ and $\text{ZrO}_2\text{-}$

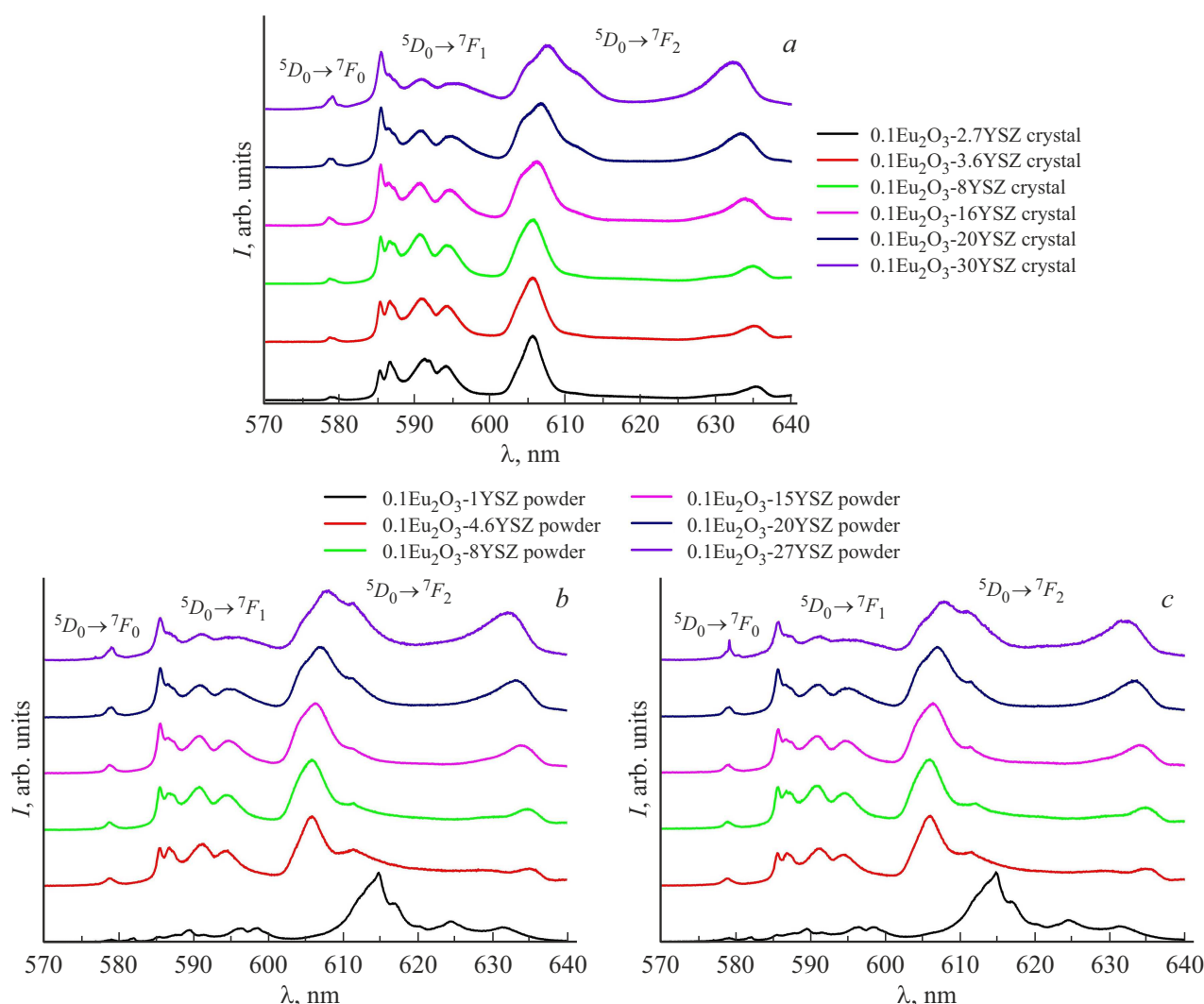


Figure 5. Luminescence spectra of the $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ optical transitions of Eu^{3+} ions, $\lambda_{exc} = 532 \text{ nm}$, $T = 300 \text{ K}$ for $0.1\text{Eu}_2\text{O}_3$ –(4–27)YSZ crystals (a) and nanpowders obtained by the coprecipitation (b) and hydrothermal synthesis with microwave treatment (c).

Eu_2O_3 solid solutions with comparable concentrations of the stabilizing oxide are very different due to different crystal environment of Eu^{3+} in these structures. Luminescence spectra of (4–27)EuSZ solid solutions have predominant spectral lines assigned to the optical centers of type II Eu^{3+} with an oxygen vacancy in the second coordination sphere. As for $0.1\text{Eu}_2\text{O}_3$ –(4–27)YSZ nanpowders, a line at 612 nm which is typical of six-oxygen-coordinated Eu^{3+} sites is observed for (4–27)EuSZ nanpowders starting from a stabilizing oxide concentration of 4 mol.% Eu_2O_3 . In spectra of (4–27)EuSZ crystals similar to $0.1\text{Eu}_2\text{O}_3$ –(4–27)YSZ crystals, this band becomes clearly visualized only at stabilizing oxide concentrations higher than 15 mol.% Eu_2O_3 .

Judd-Ofelt phenomenological theory makes it possible to fully describe the intensities of $f-f$ optical transitions of rare-earth (RE) ions by only three quantities known as

intensity parameters Ω_t ($t = 2, 4, 6$). They are important for quantitative evaluation of the probability of radiative optical transition and branching ratio. Values of these quantities are required for potential evaluation of crystal with RE ions used as phosphors and active media of solid-state lasers. Experimental measurement of Ω_t ($t = 2, 4, 6$) is also important for detecting the characteristics of the local environment of a RE ion [13,14].

Possibility of experimental measurement of Ω_t of $4f-4f$ optical transitions directly from the radiation spectrum is a unique feature of Eu^{3+} . For Eu^{3+} , experimental measurement of the intensity parameters is simplified due to the structure of its energy levels. Since the total angular momentum for the energy level $^5D_0$ is equal to zero, then in accordance with selection rules, intensity of $^5D_0 \rightarrow ^7F_2$ is defined only by Ω_2 , intensity of $^5D_0 \rightarrow ^7F_4$ — is defined by Ω_4 , and intensity of $^5D_0 \rightarrow ^7F_6$ — is defined by Ω_6 [15–17].

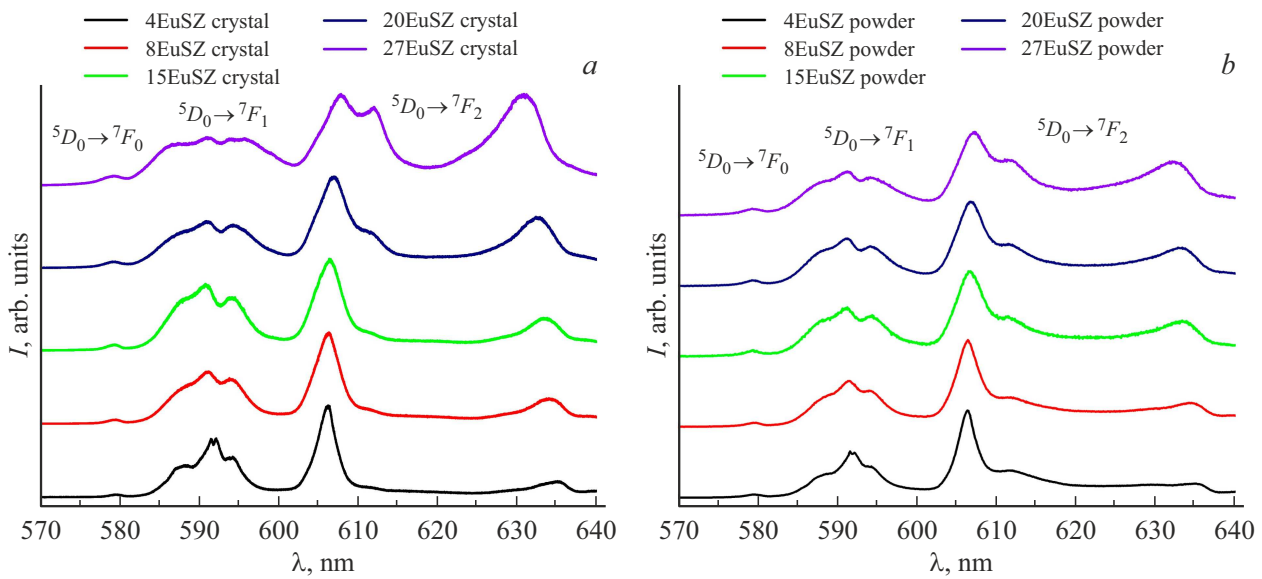


Figure 6. Luminescence spectra of $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} , $\lambda_{exc} = 532 \text{ nm}$, $T = 300 \text{ K}$ for (4–27)EuSZ crystals (a) and nanopowders (b).

In addition, Eu^{3+} ions are characterized by $^5D_0 \rightarrow ^7F_1$ which is a magnetic dipole transition. Therefore, this transition is virtually independent of the crystalline ligand field. $^5D_0 \rightarrow ^7F_1$ can be used as an internal standard to calculate the probabilities of spontaneous radiation of $^5D_0 \rightarrow ^7F_J$ ($J = 2, 4, 6$). Intensity ratios of $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ $R_{21} = \frac{I_{5D_0 \rightarrow 7F_2}}{I_{5D_0 \rightarrow 7F_1}}$ are defined by the degree of crystalline field.

From Judd-Ofelt theory, an expression for probabilities of spontaneous radiation for electric dipole transitions of Eu^{3+} can be written as

$$A_{0t} = \frac{32\pi^3 e^2 \chi}{3\hbar} \tilde{\nu}_{0t}^3 \times \Omega_t |\langle 5D_0 || U_t || 7F_t \rangle|^2, \quad (1)$$

where e — is the elementary electric charge, χ — is the correction factor of the local Lorentz field, Ω_t — is the intensity parameter of the $4f\text{-}4f$ optical transition, $|\langle 5D_0 || U_t || 7F_t \rangle|^2$ — is the reduced -matrix element of the rank λ unitary tensor operator ($|\langle 5D_0 || U_2 || 7F_2 \rangle|^2 = 0.0032$, $|\langle 5D_0 || U_4 || 7F_4 \rangle|^2 = 0.0023$, $|\langle 5D_0 || U_6 || 7F_6 \rangle|^2 = 0.2384$ for Eu^{3+}), $\tilde{\nu}_{0t}$ — is the mean wavenumber of $^5D_0 \rightarrow ^7F_t$ [15,18].

Expression for the probability of spontaneous radiation of allowed magnetic dipole and forbidden electric dipole transition $^5D_0 \rightarrow ^7F_1$ ($\Delta J = 1$) is written as [15]

$$A_{01} = k \tilde{\nu}_{01}^3, \quad (2)$$

where $k = 0.31 \cdot 10^{-11} n^3$, n — is the refractive index of medium, $\tilde{\nu}_{01}$ — is the mean wavenumber of $^5D_0 \rightarrow ^7F_1$. For zirconium dioxide solid solutions, $n = 2.15$.

After calculation of A_{01} , all other A_{0t} can be calculated from the relation of optical transition radiation intensities

which are proportional to areas under curves in the radiation spectrum of applicable optical transitions:

$$\begin{aligned} \frac{I_{0t}}{I_{01}} &= \left(\frac{S_{0t}}{S_{01}} \right) = \left(\frac{A_{0t}}{A_{01}} \right) \left(\frac{\sigma_{0t}}{\sigma_{01}} \right) \\ &= \frac{32\pi^3 e^2 \chi}{3\hbar k} |\langle 5D_0 || U_t || 7F_t \rangle|^2 \frac{\tilde{\nu}_{0t}^4}{\Omega_t} \tilde{\nu}_{01}^4. \end{aligned} \quad (3)$$

Figure 7 shows luminescence spectra of 0.1Eu₂O₃–15YSZ, 0.1Eu₂O₃–20YSZ, 15EuSZ, 20EuSZ crystals and nanopowders with a cubic crystal structure, for which Ω_t ($t = 2, 4, 6$) were measured. Note that as crystals and nanopowders contain several types of optical centers of Eu^{3+} , then Ω_t ($t = 2, 4, 6$) calculated using equations (1)–(3) are mean values or correspond to the dominant type of optical center.

Values of Ω_t ($t = 2, 4, 6$) and asymmetry coefficient $R_{21} = \frac{I_{5D_0 \rightarrow 7F_2}}{I_{5D_0 \rightarrow 7F_1}}$ calculated as a relation of integral intensities of spectral lines for $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ of Eu^{3+} for 0.1Eu₂O₃–15YSZ, 0.1Eu₂O₃–20YSZ, 15EuSZ, 20EuSZ crystals and nanopowders are listed in Table 5-7. It can be seen from Tables 5-7 that values of Ω_2 , which according to [13, 14] depends on the symmetry of local environment of a rare earth ion, are higher for 15EuSZ, 20EuSZ crystals than for 0.1Eu₂O₃–15YSZ, 0.1Eu₂O₃–20YSZ crystals. Also, for zirconium dioxide crystals stabilized by europium oxide, values of R_{21} are higher than those for zirconium dioxide crystals with the same concentration of the stabilizing yttrium oxide where Eu^{3+} serves as a spectroscopic probe. As noted above, zirconium dioxide crystals feature several types of optical centers of Eu^{3+} . These optical centers are defined by the oxygen vacancy position with respect to the optical center. Main optical centers of Eu^{3+} are:

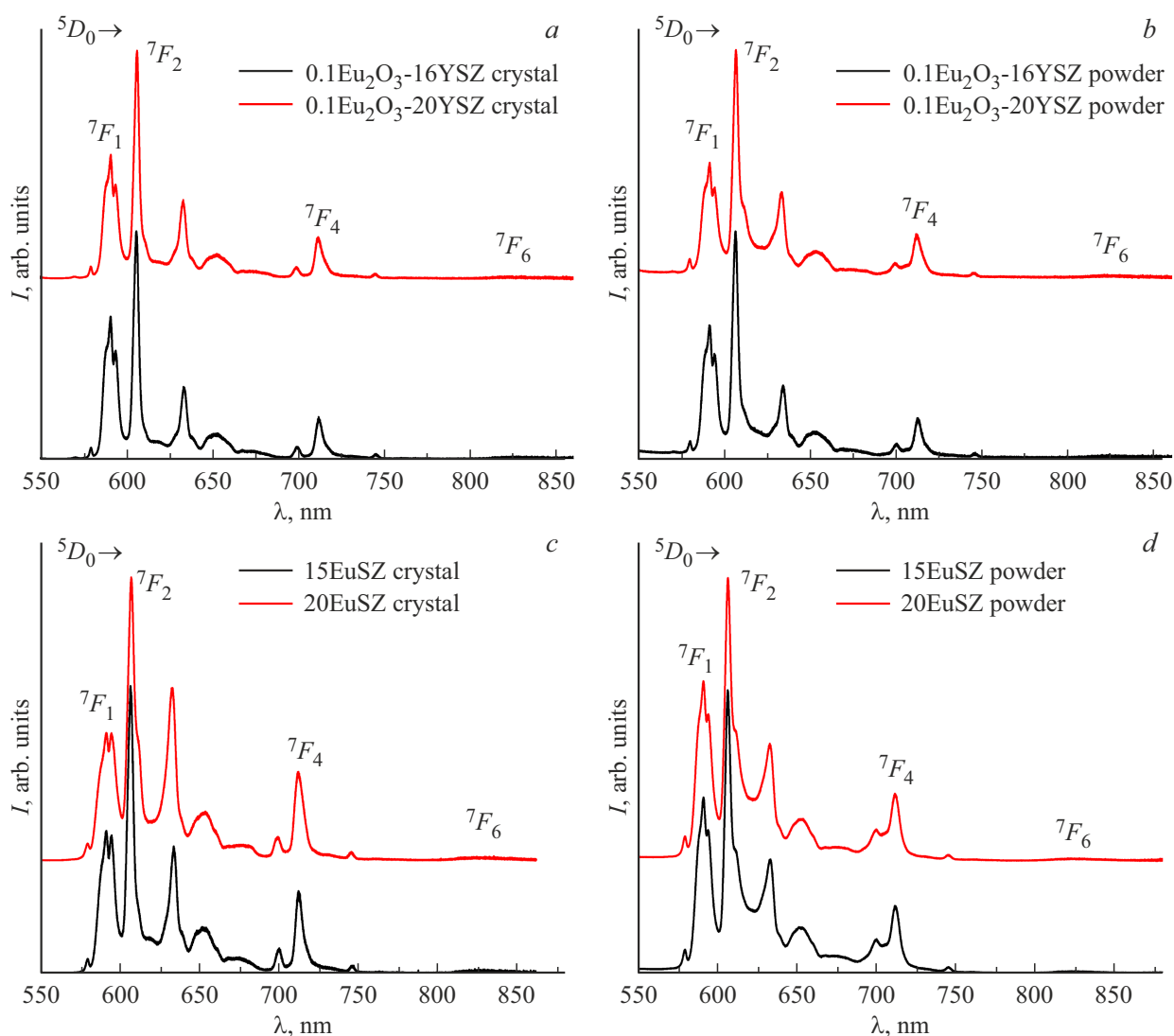


Figure 7. Luminescence spectra of 0.1Eu₂O₃–15YSZ, 0.1Eu₂O₃–20YSZ (*a, b*), 15EuSZ, 20EuSZ (*c, d*) crystals and nanopowders, $\lambda_{exc} = 465$ nm, $T = 300$ K.

- 1) Eu³⁺ with a vacancy in the first coordination sphere;
- 2) Eu³⁺ with an oxygen vacancy in the second coordination sphere and without an oxygen vacancy in the first one;
- 3) Eu³⁺ with oxygen vacancies in far coordination spheres.

As the concentration of stabilizing oxide increases, crystals are characterized by Eu³⁺ with two oxygen vacancies in the near coordination sphere. For nanopowders, these optical centers are typical of the whole concentration range.

Results of [4,6] and luminescence spectra of Eu³⁺ shown in Figure 5 indicate that optical centers of Eu³⁺ with a vacancy in the second coordination sphere dominate in (4–27)EuSZ crystals compared with 0.1Eu₂O₃–(3.6–30)YSZ crystals. Point symmetry of such centers is low and corresponds to C₁. This corresponds to the fact that R_{21} for 15EuSZ and 20EuSZ crystals and nanopowders is

higher than that for 0.1Eu₂O₃–15YSZ and 0.1Eu₂O₃–20YSZ crystals.

It can be seen from Table 5, 6 that values of Ω_t ($t = 2, 4, 6$) are different for ZrO₂–Y₂O₃–Eu₂O₃ and ZrO₂–Eu₂O₃ crystals and nanopowders with identical compositions. This is due to the fact that oxygen vacancies on the surface affect the formation of optical centers of Eu³⁺ in nanopowders. As a result, notwithstanding that the same types of optical centers of Eu³⁺ were detected in ZrO₂–Y₂O₃–Eu₂O₃ and ZrO₂–Eu₂O₃ solid solution crystals and nanopowders with the same concentration ranges, relative proportions of these optical centers are different. Thus, the differences in values of Ω_t ($t = 2, 4, 6$) and asymmetry parameter of ZrO₂–Y₂O₃–Eu₂O₃ and ZrO₂–Eu₂O₃ crystals and nanopowders with the same compositions are caused by the effect of oxygen vacancies on the surface of nanopowder particles on formation of optical centers of Eu³⁺.

Table 5. Ω_t ($t = 2, 4, 6$) for $0.1\text{Eu}_2\text{O}_3\text{-15YSZ}$ and $0.1\text{Eu}_2\text{O}_3\text{-20YSZ}$ solid solutions of crystals and nanopowders obtained by the coprecipitation method

Crystals				Nanopowders			
Y_2O_3 , mol%	$\Omega_2 \times 10^{20}$, cm^2	$\Omega_4 \times 10^{20}$, cm^2	$\Omega_6^* \times 10^{20}$, cm^2	Y_2O_3 , mol%	$\Omega_2 \times 10^{20}$, cm^2	$\Omega_4 \times 10^{20}$, cm^2	$\Omega_6 \times 10^{20}$, cm^2
16	2.2 ± 0.1	1.0 ± 0.1	1.2 ± 0.2	15	2.5 ± 0.1	1.3 ± 0.1	1.2 ± 0.2
20	2.4 ± 0.1	1.1 ± 0.1	1.2 ± 0.2	20	3.0 ± 0.1	1.6 ± 0.1	1.2 ± 0.2

Table 6. Ω_t ($t = 2, 4, 6$) for 15EuSZ and 20EuSZ solid solutions of crystals and nanopowders obtained by the coprecipitation method

Crystals				Nanopowders			
Eu_2O_3 , mol%	$\Omega_2 \times 10^{20}$, cm^2	$\Omega_4 \times 10^{20}$, cm^2	$\Omega_6 \times 10^{20}$, cm^2	Eu_2O_3 , mol%	$\Omega_2 \times 10^{20}$, cm^2	$\Omega_4 \times 10^{20}$, cm^2	$\Omega_6 \times 10^{20}$, cm^2
15	2.8 ± 0.1	1.6 ± 0.1	2.1 ± 0.2	15	3.0 ± 0.1	1.7 ± 0.1	1.9 ± 0.2
20	3.4 ± 0.1	1.8 ± 0.1	2.2 ± 0.2	20	$2. \pm 0.1$	1.6 ± 0.1	1.8 ± 0.2

Table 7. R_{21} for $0.1\text{Eu}_2\text{O}_3\text{-15YSZ}$, $0.1\text{Eu}_2\text{O}_3\text{-20YSZ}$, 15EuSZ , and 20EuSZ crystals and nanopowders

Crystals				Nanopowders			
Y_2O_3 , mol. %	R_{21}	Eu_2O_3 , mol. %	R_{21}	Y_2O_3 , mol. %	R_{21}	Eu_2O_3 , mol. %	R_{21}
16	1.5	15	2	15	1.8	15	2.1
20	1.7	20	2.3	20	2.2	20	2.0

Conclusion

Coprecipitation and hydrothermal synthesis with microwave treatment were used to produce $0.1\text{Eu}_2\text{O}_3\text{-(1-27)YSZ}$ concentration range nanopowders.

Depending on the concentration of stabilizing Y_2O_3 , the mean size of nanoparticles obtained by the concentration coprecipitation is from 75 nm to 90 nm, and of nanopaticles obtained by the hydrothermal method with microwave treatment is from 67 nm to 46 nm. Nanoparticles obtained by the coprecipitation are agglomerated to a greater extent.

Comparative phase analysis of $0.1\text{Eu}_2\text{O}_3\text{-(4-27)YSZ}$ solid solution nanopowders and crystals has detected that the cubic structure for nanopowders is stabilized at lower concentrations of stabilizing Y_2O_3 . In the concentration range of Y_2O_3 from 6 mol.to 27 mol.%, $0.1\text{Eu}_2\text{O}_3\text{-(6-27)YSZ}$ nanopowders have the cubic structure. However, $0.1\text{Eu}_2\text{O}_3\text{-8YSZ}$ crystals include both cubic and tetragonal phases.

It has been detected from the luminescence spectra of Eu^{3+} that six-oxygen-coordinated optical centers of Eu^{3+} are typical of nanopowder solid solutions in the whole $0.1\text{Eu}_2\text{O}_3\text{-(6-27)YSZ}$ concentration range. For crystals, lines of these optical centers are observed in $0.1\text{Eu}_2\text{O}_3\text{-(3.6-30)YSZ}$ solid solutions at Y_2O_3 concentration higher than 16 mol.%.

It has been found that differences in Ω_t ($t = 2, 4, 6$) and $R_{21} = \frac{I_{5D0 \rightarrow 7F2}}{I_{5D0 \rightarrow 7F1}}$ of Eu^{3+} for identical crystal

and nanopowder compositions both $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Eu}_2\text{O}_3$ and $\text{ZrO}_2\text{-Eu}_2\text{O}_3$ are caused by the effect of oxygen vacancies on the surface of nanopowder particles on formation of optical centers of Eu^{3+} .

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Conflict of interest

The authors declare no conflict of interest.

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