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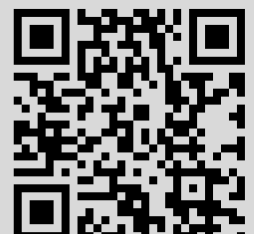
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Phosphors with different morphology, formed under hydrothermal conditions on the basis of $\text{ZrO}_2:\text{Eu}^{3+}$ nanocrystallites

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Eu^{3+} -doped ZrO_2 nanostructures in the form of rods, stars, and hollow spheres were prepared by varying hydrothermal conditions. X-ray diffraction, transmission electron microscope, ultraviolet-visible diffuse reflection spectroscopy, low-temperature nitrogen adsorption method, Raman spectroscopy and photoluminescence spectra were used to characterize the polymorph modification, surface and optical properties of the $\text{Zr}_{0.98}\text{Eu}_{0.02}\text{O}_2$ nanophosphors. The Eu^{3+} content in a zirconia monoclinic lattice, remained constant for all types of obtained nanostructures in order to reveal the morphology influence on the efficiency of electronic excitation energy transfer from the host matrix to photoactive centers. The decrease of average size of the coherent scattering regions in the series rods \rightarrow stars \rightarrow hollow spheres, is associated with increasing the specific surface area values. At that, in the photoluminescence spectrum, the splitting of the sublevels associated with the monoclinic lattice $^5\text{D}_0 \rightarrow ^7\text{F}_1$ disappears.

Keywords: hydrothermal synthesis, monoclinic zirconia, europium, solid solution, rods, stars, hollow spheres, nanocrystals, optical band gap, photoluminescence, fluorescence lifetime.

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1. Introduction

Currently, metal-oxide semiconductors doped with lanthanide ions (Ln) are widely used in solid-state lighting technologies in the manufacture of LEDs, lasers, field emission and vacuum fluorescence displays, as well as in the medical field for the visualization of drug delivery systems and monitoring changes in implant structure [1–3].

The introduction of trivalent lanthanide ions into the crystal structure of semiconductor oxide leads to weakening of the selection rules for radiative transitions, which is accompanied by splitting of the 4f energy levels [4, 5]. In this case, the prohibition of intra-configuration transitions is weakened for Ln^{3+} , since such transitions can be partially resolved by vibronic interaction or by mixing higher configurations into 4f wave functions due to the crystal field effect. However, the luminescence lifetime is usually quite large compared to radiative recombination from other types of excited states [6, 7]. Such phosphors are characterized by narrow emission lines, high color purity, large anti-Stokes shifts, an acceptable quantum yield, and a significant luminescence lifetime [8–10]. Such signs are determined by the efficiency of electron excitation energy transfer from the host matrix to photoactive centers, which is determined by the band gap, the type of crystal structure, the size and morphology of the metal-oxide semiconductor particles, and also the local environment of Ln^{3+} ions in the lattice [11, 12]. For instance, the trivalent europium ion (Eu^{3+}) can be used as a spectroscopic probe for site symmetry determination [13].

Among p-type semiconductors, zirconia is the optimal optical medium for lanthanide ions, since it has photochemical stability, a high refractive index, a large band gap, transparency in the visible and near infrared regions of the spectrum, and low phonon energy, which helps to reduce the probability of nonradiative transitions due to multiphonon relaxation [14–16]. In turn, europium (III) ions possess intense luminescence in the red region of the visible spectrum and have an advantage over other lanthanides with an even number of 4f electrons, since their initial transition levels in both the absorption spectrum and the luminescence spectrum are non-degenerate ($J = 0$), which makes absorption and luminescence spectra interpretation easy. In addition, the contribution to the integrated luminescence intensity of the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition can be used to determine whether Eu^{3+} is located in the centers of symmetry of the crystal matrix [6].

Precipitation methods [17], combustion [18], sol-gel technology [19], template synthesis [20], hydrothermal treatment [21], aerosol pyrolysis [22], anodizing [23] and impregnation [24] are used to obtain nanostructures of various morphology based on ZrO_2 doped with europium (III) ions. Among the above synthetic approaches, the hydrothermal method is the most universal, since it allows one to obtain nanomaterials with a narrow particle size distribution, high crystallinity, controlled by morphology and microstructure. Varying the pH of the hydrothermal medium and introducing various mineralizers or surfactants can limit crystallite growth along certain crystallographic directions, contributing to the formation of nanostructures of different morphology based on monoclinic zirconia [25–27]. $\text{ZrO}_2:\text{Eu}^{3+}$ nanophosphors with a baddeleyite structure, as far as we know, were obtained only in the form of rods under hydrothermal conditions. For example, Chen and colleagues obtained 1D nanostructures based on the $\text{Zr}_{0.98}\text{Eu}_{0.02}\text{O}_2$ solid solution by hydrothermal treatment a mixture of zirconium and europium hydroxides in the presence of cetyltrimethylammonium bromide [28].

The aim of this work was to synthesize nanostructures with different morphology based on monoclinic zirconia doped with Eu^{3+} by varying the hydrothermal treatment conditions. After that, it was necessary to study the influence of size, structural and surface characteristics of the obtained nanostructures (rods, stars, hollow spheres) on their optical and photoluminescent properties (excitation and emission spectrum profile, luminescence lifetime).

2. Experimental part

In this work, we synthesized nanorods, nanostars and hollow spheres of the ZrO_2 –2 mol.% $\text{EuO}_{1.5}$ composition, which are represented by the monoclinic zirconia phase in order to study the features of their photoluminescence.

To synthesize nanorods, 2.54 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 0.06 g of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 15 ml of distilled water, after that a mixture of hydroxides of the corresponding metals was precipitated with continuous stirring, dropwise adding 5 M NaOH solution. The obtained precipitate was dehydrated under hydrothermal conditions at 240 °C and 15 MPa for 24 hours.

Four-pointed nanostars of a given composition were also formed from solutions of zirconium and europium chlorides in a hydrothermal medium under the conditions presented in [29].

In the case of hollow spheres, 1.22 g of zirconyl chloride and 0.03 g of europium (III) chloride were dissolved in 60 ml of a mixture of ethanol-hydrochloric acid, taken in a ratio of 3 to 2. Then, 0.75 g urea was added to the solution, and after its dissolution, all components were transferred to an autoclave. Subsequent hydrothermal treatment was carried out at a temperature of 160 °C, a pressure of 15 MPa and an isothermal exposure time of 24 hours.

At the end of hydrothermal synthesis, all the obtained suspensions of the above described nanostructures were repeatedly washed with ethanol by centrifugation (8000 rpm) and dried in air to constant weight at 80 °C.

The elemental compositions of synthesized nanostructures were determined using a VEGA 3 SBH scanning electron microscope manufactured by Tescan (Czech Republic) with the Oxford Instruments AZtecOne Go X-ray energy dispersive microanalysis system.

X-ray diffraction (XRD) analysis of Eu^{3+} -doped ZrO_2 nanorods, nanostars and hollow spheres was performed using a Rigaku SmartLab diffractometer (Tokyo, Japan). The XRD patterns were recorded at a tube voltage of 40 kV, tube current of 40 mA, applying a scan rate of 0.5 °/min in a range of 2θ angles from 10 to 90°. The determination of zirconia crystalline phases was carried out in Crystallographica Search-Match software by comparing our experimental data with powder diffraction files from ASTM database. The average size of the coherent scattering regions was calculated from XRD line broadening of ZrO_2 –2 mol.% $\text{EuO}_{1.5}$ nanostructures in the PD-Win 4.0 program complex using the Scherrer formula.

The size, shape and phase composition of the $\text{ZrO}_2:\text{Eu}^{3+}$ nanoaggregates and crystallites forming them were established using a JEM-2100F transmission electron microscope manufactured by JEOL (Tokyo, Japan) at an acceleration voltage of 90 kV.

The specific surface area of powders of the ZrO_2 –2 mol.% $\text{EuO}_{1.5}$ composition in the form of rods, four-pointed stars and hollow spheres was measured by the low-temperature nitrogen adsorption method using a QuantaChrome Nova 4200V analyzer. Samples were degassed at 150 °C under vacuum for 16 hours before measurement. The specific surface area (S_{BET}) of samples was calculated based on the experimental data using the models: Brunauer–Emmett–Teller (BET) at 7 points in the range of partial pressures of nitrogen $P/P_0 = 0.07 \div 0.25$ and Langmuir. The pore size distribution was calculated based on the isotherms of nitrogen desorption according to the Barrett–Joyner–Halenda (BJH) method.

Raman spectra were recorded in the backscattering geometry using a Jobin Yvon T64000 triple monochromator equipped with a liquid N_2 -cooled charge coupled device detector. The excitation wavelength λ was 488 nm from an Ar^+ laser with a typical laser power of ~ 1 mW.

The photoluminescence emission spectra were recorded using a Horiba LabRAM HR Evolution system equipped with a He–Cd excitation laser emitting at 325 nm with a maximum power of 1 mW. Photoluminescence decay and excitation spectra were measured using the luminescence spectrophotometer LS-100 (PTIR, Canada).

The optical absorption edge energy of nanostructures based on zirconia was determined using diffuse reflectance spectra (Shimadzu UV-2550 spectrophotometer equipped with an ISR-2200 integrating sphere) by the standard procedure from the cross point of linear sections of the Kubelka–Munk function plot in the coordinates $(F(R) \times h\nu)^{1/2} = f(h\nu)$.

3. Results and discussion

The different morphology nanostructures based on ZrO_2 prepared in this study contained 2 at.% Eu^{3+} according to energy dispersive X-ray (EDX) spectroscopy (Table 1).

TABLE 1. EDX-analysis data of Eu^{3+} -doped ZrO_2 nanostructures with different morphology

Morphology	Zr	Eu	Hf	Na	Cl
	at., %				
Nanorods	96.8	2.1	0.6	0.5	—
Nanostars	96.7	2.0	0.6	0.7	—
Hollow spheres	96.1	2.1	0.8	—	1.0
	wt., %				
Nanorods	95.3	3.4	1.2	0.1	—
Nanostars	95.4	3.2	1.2	0.2	—
Hollow spheres	94.6	3.5	1.5	—	0.4

Phosphors in the form of nanorods were formed in a strongly alkaline medium under hydrothermal treatment of a $ZrO(OH)_2$ – $Eu(OH)_3$ mixture precipitated from solutions of their chlorides. Qualitative phase analysis based on XRD of the ZrO_2 –2 mol% $EuO_{1.5}$ one-dimensional nanostructures using the PDWin 4.0 and Crystallographica Search-Match software packages showed their greatest correspondence to the baddeleyite structure (Card No. 24-1165 according to the ASTM database [30], Fig. 1, pattern 1). The average size of coherent scattering regions calculated by the Debye–Scherrer equation was 30 ± 5 nm. The length of the nanorods was about 150 nm, and the width was 50 nm, according to TEM micrographs (Fig. 2a, line 1). In addition to twin reflections of monoclinic (*m*) ZrO_2 –2 mol.% $EuO_{1.5}$ rods elongated along the (100) plane, concentric rings indicating the presence of small crystallites with a tetragonal (*t*) structure were also observed in the electron microdiffraction image (Fig. 2b, line 1). Apparently, initially formed under hydrothermal conditions Eu^{3+} -stabilized *t*- ZrO_2 nanocrystals with an average size of $\sim 5 \pm 1$ nm (Fig. 3) gradually dissolve at high pH medium values and recrystallize along the crystallographic direction (100) with the formation of monoclinic rice-like structures.

Hydrothermal synthesis of ZrO_2 –2 mol% $EuO_{1.5}$ nanostars from the same precursors was carried out in the presence of sodium acetate. Its CH_3COO^- ions adsorbed on the surface of the germinal centers promoted the subsequent crystallization of zirconia along the direction perpendicular to the (101) planes. The resulting structures with a size of about 100 nm (Fig. 2a, line 2) have the shape of four-pointed stars with numerous outgrowth 7 nm wide according to TEM data. An electron diffraction pattern shows the presence of *m*- ZrO_2 with multiple twinning along the (100) plane (Fig. 2b, line 2). The observed diffraction maxima in the XRD pattern of ZrO_2 –2 mol.% $EuO_{1.5}$ nanostars also refer exclusively to the monoclinic phase of zirconia, and the average size of the coherent scattering regions (CSR) for this sample is 12 ± 2 nm according to calculations (Fig. 1, pattern 2).

High-temperature hydrolysis of zirconyl and europium chlorides in the presence of urea produced nanostructures in the form of hollow microspheres (Fig. 2a, line 3) using a mixture of ethanol and hydrochloric acid in a ratio of 3:2 as a hydrothermal medium. In this case, the formation of the observed structures under hydrothermal conditions occurs by the mechanism of emulsion template synthesis. Ethanol in the presence of concentrated hydrochloric acid dehydrates with increasing temperature to form diethyl ether, which, due to its low solubility in water, can exist as droplets of oil in this solution [31]. The urea present in the initial mixture slowly reacts with water, forming NH_4OH

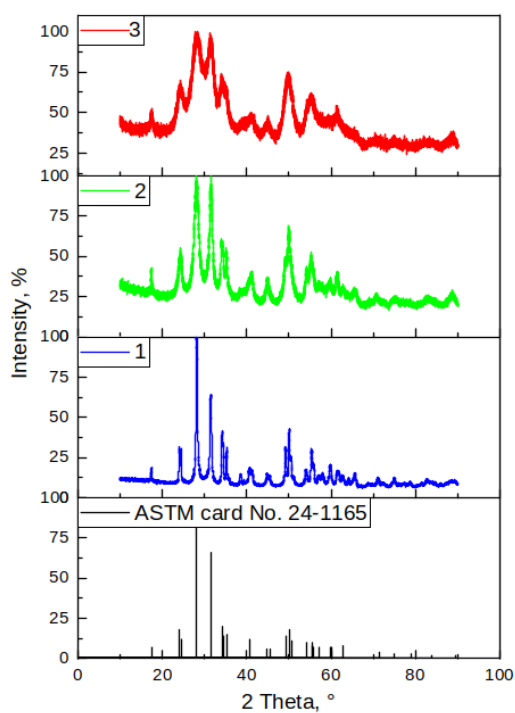


FIG. 1. XRD patterns of ZrO_2 -2 mol.% $EuO_{1.5}$ nanostructures in the form of nanorods (1), nanostars (2) and hollow spheres (3)

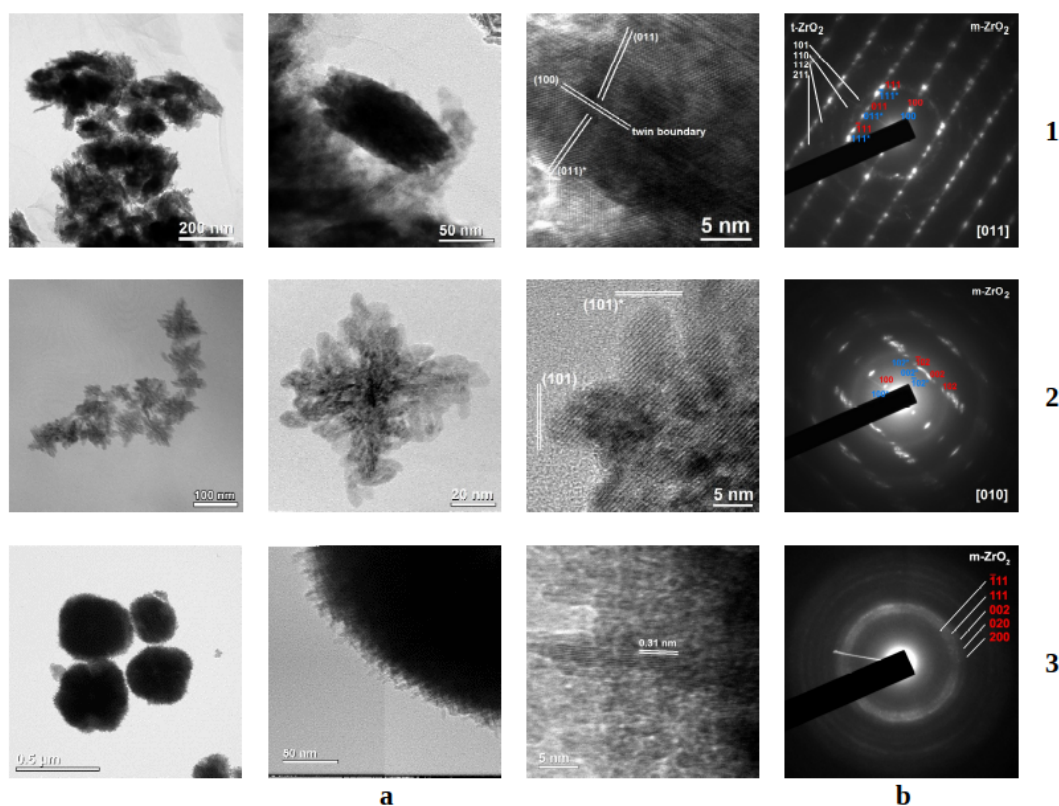


FIG. 2. TEM micrographs (a) and electron microdiffraction patterns (b) of ZrO_2 -2 mol.% $EuO_{1.5}$ nanostructures in the form of nanorods (1), nanostars (2) and hollow spheres (3)

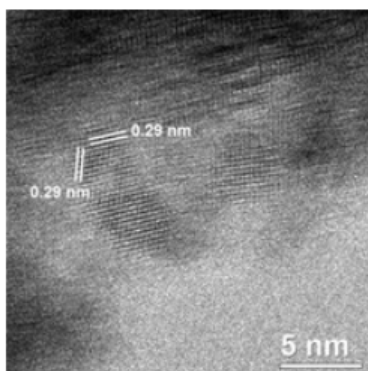


FIG. 3. TEM micrographs of quasispherical tetragonal zirconia nanoparticles of which rice-like ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ structures subsequently form under hydrothermal conditions

and CO_2 , which leads to an increase in pH and, as a result, hydrolysis of ZrOCl_2 and EuCl_3 at the “oil drop – solution” interface. A shell of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ crystallites is formed on the surface of ether drops in the process of hydroxide dehydration and subsequent isothermal exposure. In accordance with the powder XRD data, the hollow inorganic structures obtained in this way are an assembly of monoclinic zirconia crystallites with an average size of 5 ± 1 nm (Fig. 1, pattern 3). TEM images of microspheres show nanowires with a diameter of about 5 nm, assembled into spherical aggregates of submicron size (~ 400 nm, Fig. 2a, line 3). The structure of the aggregates corresponds to the monoclinic phase of zirconia (Fig. 2b, line 3).

According to the results of low-temperature nitrogen adsorption, nanocrystalline ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ powders of rods, stars, and hollow spheres are characterized by the specific surface area of 19.1, 92.3 and 151.1 m^2/g , respectively (Table 2). At the same time, the BET constant values for samples of nanoparticles collected in the form of rods and hollow spheres are equal to 508 and 745, respectively. This fact is indicative of the presence of a significant amount of micropores in these powders. Based on the foregoing, the assessment of the specific surface area for ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ powders with different morphology nanostructures was also carried out using the Langmuir model operating in the limit of monomolecular adsorption, i.e. adsorption on the surface of micropores (Table 2).

TABLE 2. The structure parameters determined using low-temperature nitrogen adsorption for powders consisting of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ nanoaggregates with different morphology

Morphology	S_{BET} , m^2/g	$S_{Langmuir}$, m^2/g	D_1 , nm	D_2 , nm	V_{pore}^* , cm^3/g
Nanorods	19.1 ± 0.2	32	2.6	42.2	0.35
Nanostars	92.3 ± 1.8	—	2.2	13.4	0.22
Hollow spheres	151.1 ± 1.5	223.9	—	—	0.14

* The specific pore volume is determined by the maximum filling ($P/P_0 = 0.99$).

According to Fig. 4, the full adsorption-desorption isotherms for these powders substantially depend on their morphology. For example, the full isotherm for a powder consisting of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ nanorods is close to the II type, which is inherent in non-porous and macroporous samples. At the same time, the weak hysteresis and a high BET constant indicate the presence of a certain amount of micro and mesopores in this sample. This hysteresis can be classified as type H1 according to IUPAC, when the material has cylindrical pores open on both sides. Thus, the full isotherm can be attributed to the combined type (Fig. 4, isotherm 1).

The full isotherm of powder consisting of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ nanostars clearly belongs to type IV, which is typical for mesoporous materials. Capillary condensation of the adsorptive can occur in the pores of such materials, which leads to the appearance of hysteresis between the adsorption and desorption isotherms (Fig. 4, isotherm 2). The course of the capillary-condensation hysteresis loop for a given nanopowder according to the IUPAC can be classified as type H2, which indicates the presence of bottle-shaped mesopores in it.

Finally, the full isotherm for a powder consisting of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ hollow spheres is close to the I-type, which is mainly fixed in microporous samples (Fig. 4, isotherm 3). Moreover, the presence of a weakly expressed loop of capillary-condensation hysteresis on the full isotherm confirms the presence of a certain amount of mesopores

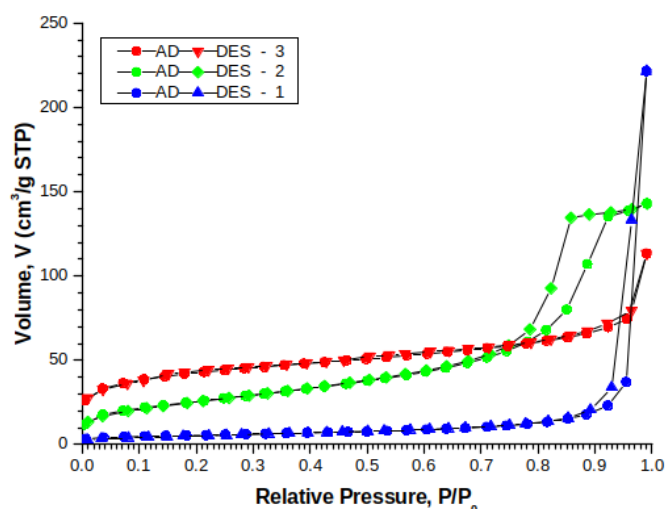


FIG. 4. Adsorption-desorption isotherms of powders consisting of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ nanostructures with different morphology: rods (1), stars (2), hollow spheres (3)

in this sample. This type H4 hysteresis according to the IUPAC classification, which is characteristic of pore slit-like form.

Pore size distributions calculated for the desorption branch according to the BJH algorithm for powders consisting of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ nanostructures with different morphology are shown in Fig. 5. Obviously, the porosity of these nanopowders substantially depends on morphology. A bimodal pore size distribution with maxima in the micro D_1 and mesopore D_2 regions is characteristic of powders containing nanostructures in the form of stars and rods (Table 2), respectively. In the case of the sample consisting of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ hollow spheres, a uniformly decreasing pore size distribution in the range from 1.5 to 40 nm is observed, which confirms the presence of both micro- and mesopores in it.

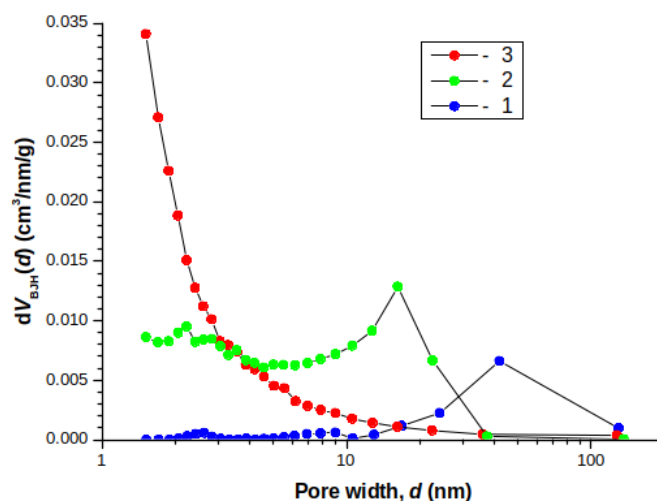


FIG. 5. Pore size distributions calculated according to the BJH algorithm for powders consisting of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ nanostructures with different morphology: rods (1), stars (2), hollow spheres (3)

An intense peak at 614 nm is observed in the luminescence spectra of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ nanostructures with different morphology and there is no component of the electric dipole transition in the region of 606 nm. This indicates the absence of cubic and tetragonal polymorphic modifications and localization of Eu^{3+} in the less symmetrical environment of the m - ZrO_2 for the synthesized phosphors (Fig. 6a). With an increase in the resolution of the luminescent equipment, one can see narrow peaks of fine splitting upon excitation at 325 nm not only in the spectral term 7F_2 ,

but also in 7F_4 for Eu^{3+} . Such a splitting pattern allows us to conclude that the monoclinic phase is exceptionally prevalent for nanorods. At the same time, for nanostars and hollow spheres the order of the monoclinic phase is disrupted due to internal stresses and a decrease in the size of crystallites. A similar violation of the long-range order also manifests itself in Raman spectra (Fig. 7) in the form of the contribution of the diffuse band in the range $400 - 700 \text{ cm}^{-1}$. Because of this, the fine splitting between 614 and 625 nm disappears in the luminescence spectra, which leads to an increase in the contribution to the luminescence band at 616 nm, as well as to the disappearance of the peak at 711 nm and a predominance of the contribution at 700 nm (compare spectrum 1 with spectra 2 and 3 in Fig. 6a).

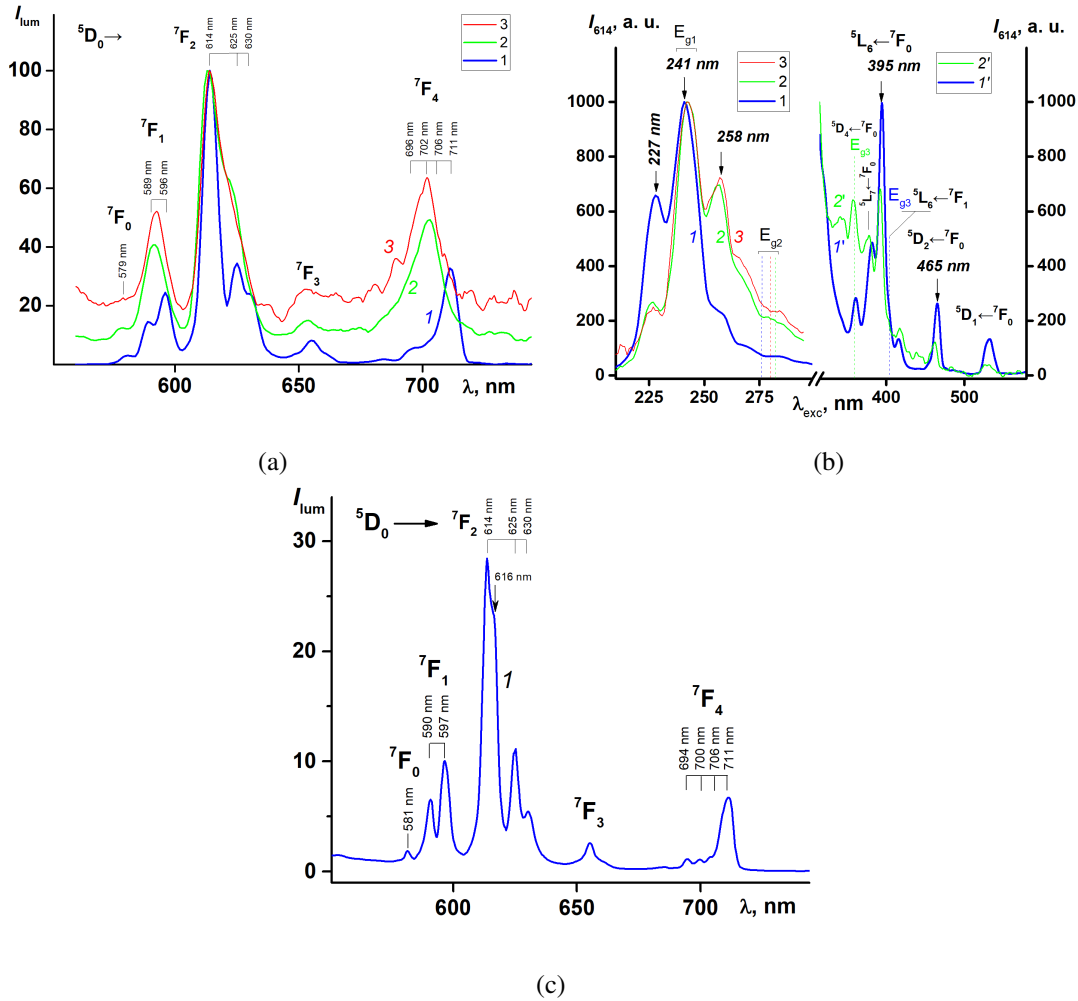


FIG. 6. Emission spectra (a, c) and excitation spectra (b) of luminescence for nanorods (1, 1'), nanostars (2, 2'), and hollow spheres (3) of the ZrO_2 -2 mol.% $\text{EuO}_{1.5}$, normalized at 614 and 241 nm, respectively. Excitation 242 (a) and 325 nm (c)

The luminescence excitation spectra of europium (III) ions in the structure of zirconia nanostars and hollow spheres are identical (Fig. 6b, spectra 2 and 3). In the case of nanorods, a more efficient absorption of electronic excitation energy is recorded in the region of hard ultraviolet, especially at wavelengths of 227 and 241 nm (Fig. 6b, spectrum 1). This excitation band with a maximum peak at 241 nm and several additional local extrema at 227 and 258 nm corresponds to the $\text{O}^{2-}-\text{Eu}^{3+}$ charge transfer resulting from electron transitions from the 2p orbital of O^{2-} to the 4f orbital of Eu^{3+} .

In the Raman spectrum for ZrO_2 -2 mol.% $\text{EuO}_{1.5}$ nanorods, the characteristic peaks correspond to the monoclinic crystal lattice at 178, 189, 305, 380, 474, 537, 556, 612 and 631 cm^{-1} (Fig. 7, spectrum 1). For nanostars and hollow spheres in the Raman spectra region of $400 - 700 \text{ cm}^{-1}$, a diffuse scattering band is detected, which is associated with the disappearance of long-range order due to internal stresses and twinning. A similar effect of the disappearance of the long-range order of the monoclinic phase was also found in the luminescence spectra (see Fig. 6 and in the text above).

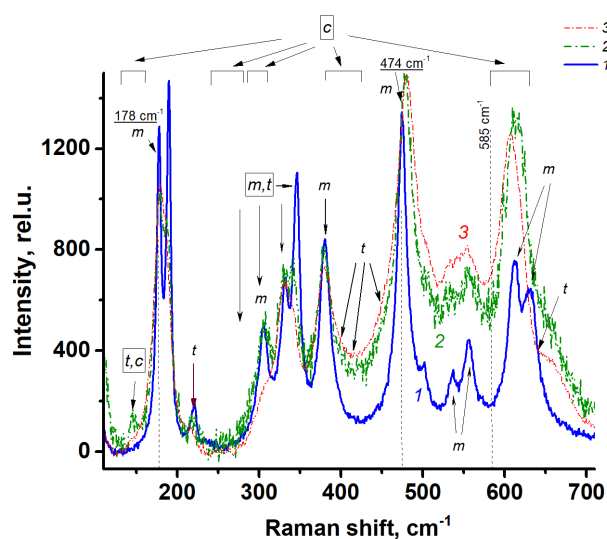


FIG. 7. Raman spectra for nanorods (1), nanostars (2) and hollow spheres (3) of ZrO_2 -2 mol.% $\text{EuO}_{1.5}$, normalized at 474 cm^{-1}

Based on the diffuse reflectance spectra $R(\lambda)$ in the visible and ultraviolet range from 1.5 to 6 eV, one calculated the Schuster–Kubelka–Munk (SKM) or remission function [32]:

$$F(R_\infty(\lambda)) = \frac{(1 - R_\infty(\lambda))^2}{2R_\infty(\lambda)} = \frac{K}{S} = \frac{2.303\varepsilon C}{S}, \quad (1)$$

where K is the absorption coefficient (twice the Beer's law absorption coefficient); S is twice the scattering coefficient of the sample; ε is the absorptivity, and C is the analyte concentration.

Using the Tauc plot of $(F(R_\infty)h\nu)^{1/\eta}$ versus energy, $h\nu$, one estimated the optical bandgap, E_g , between the conduction band and the valence one in $\text{Zr}_{0.98}\text{Eu}_{0.02}\text{O}_{1.99}$ nanoparticles (Fig. 8).

In the region of the energy obtained from 2 to 6 eV, the indirect allowed absorption transitions turned out to manifest themselves because there are linear approximations at $\eta = 2$ for all the cases under investigation [33]. At that, the E_g values of the studied nanostructures are found from 3.07 to 5.13 eV (Table 3), which is consistent with work [34]. Analysis of the Tauc spectra showed that the widest absorption edge energy (E_{g1}) of ca. 5.1 eV clearly manifests itself for all the studied zirconia nanostructures containing Eu^{3+} [35]. There is no dependence of E_{g1} on the morphology of the nanoparticles. The absorption connected with it corresponds in the luminescence excitation spectra to a maximum of 241 nm (compare Fig. 6b and Table 3).

TABLE 3. Energy gap parameters as obtained from Tauc plots for $\text{Zr}_{0.98}\text{Eu}_{0.02}\text{O}_{1.99}$ nanoparticles with a different morphology

Morphology	Coherent scattering region, nm	Energy gap parameters, eV (wavelength, nm) ¹⁾		
		$E_{g1}(\lambda_1)$	$E_{g2}(\lambda_2)$	$E_{g3}(\lambda_3)$
Nanorods	30 ± 5	5.10 (243)	4.49 (276)	3.07 (404)
Nanostars	12 ± 2	5.11 (243)	4.39 (282)	3.42 (362)
Hollow spheres	5 ± 1	5.13 (242)	4.42 (280)	3.57 (347)

¹⁾ One uses the relationship between energy in eV and corresponding wavelength in nm as $E \cdot \lambda = 1240 \text{ eV}\cdot\text{nm}$.

The presence in the band of the PL excitation spectrum for all synthesized nanostructural forms of maxima at 227 and 240 – 243 nm, as well as the E_{g1} values of 5.10 – 5.13 eV indicate the existence of inter-configuration transitions in $m\text{-ZrO}_2$ [36]. Besides, the largest contribution occurs at 258 nm for nanostars and hollow spheres

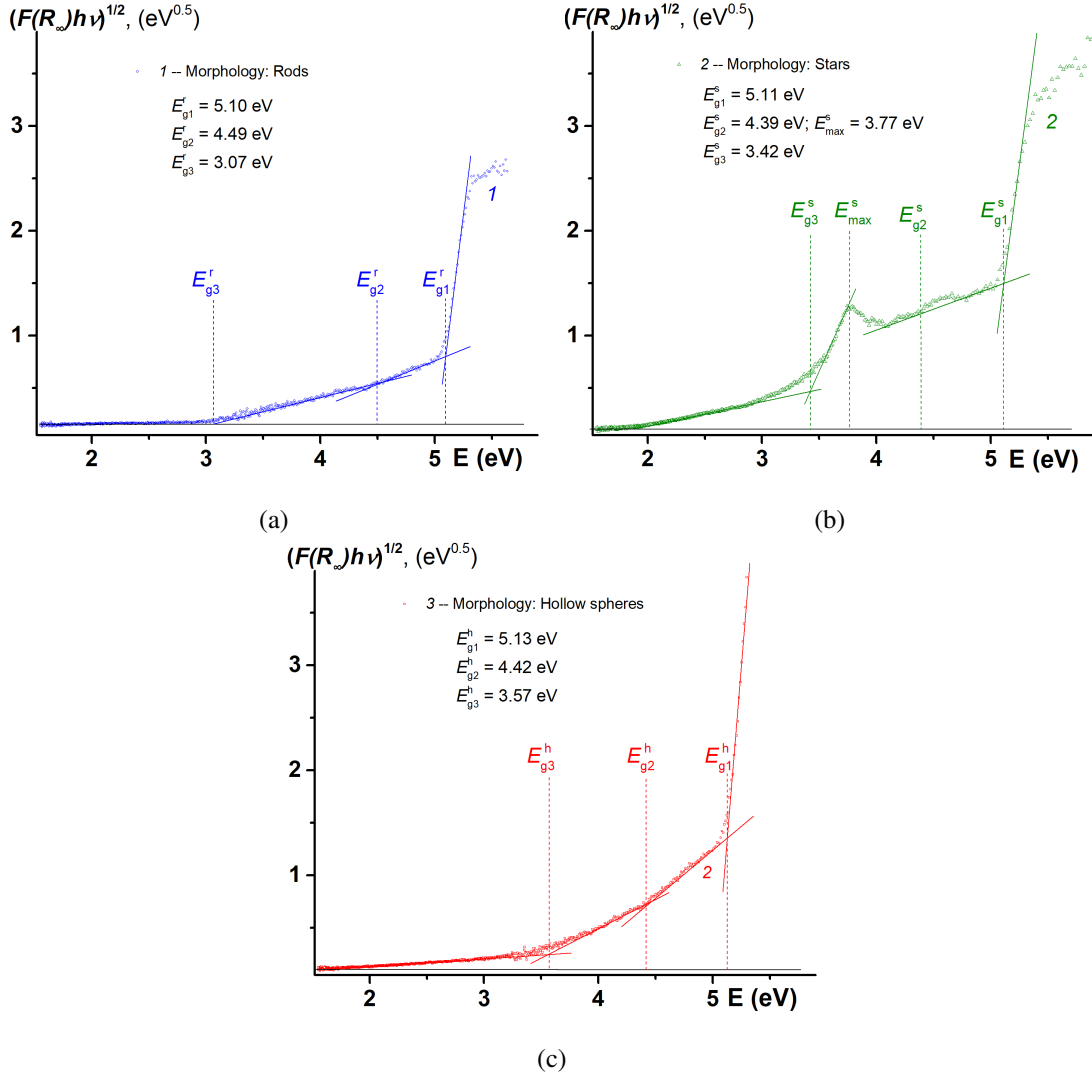


FIG. 8. Tauc plot spectra for nanorods (a), nanostars (b) and hollow nanospheres (c) of $ZrO_2-2 \text{ mol.}\% \text{ EuO}_{1.5}$

(compare normalized excitation spectra in Fig. 6b), which designates charge transfer ($\text{Eu}^{3+} \leftarrow \text{O}^{2-}$) for the type of $Zr-O$ bond of 2.1297 \AA in a monoclinic cell [35]. This indicates a perfect (with a large CSR) monoclinic phase in this case and is confirmed by other methods (XRD and RS). A change in the monoclinic modification and a decrease in its CSR (Table 3) is indicated by a shift in the excitation spectra from 241 to 243 nm during the transition to nanostars and hollow spheres. In addition, a diffuse band appears in the Raman spectra and the clear splitting of the monoclinic phase at 178 cm^{-1} disappears. As seen above, one can assume the formation of t,c-phase crystallites with a small CSR. The manifestation of the value of E_{max} 3.77 eV (Fig. 8b) for nanostars may indicate a low coordination of the bond with the $t\text{-}ZrO_2$ surface ($Zr^{4+} \leftarrow O^{2-}$) [36].

The decay of PL intensity ($I_{lum}(t)$) for nanoparticles can be approximated by a model of the dual exponential function:

$$I_{lum}(t) = A_1 \cdot \exp(-t/\tau_{PL1}) + A_2 \cdot \exp(-t/\tau_{PL2}) + B, \quad (2)$$

where τ_{PL1} and τ_{PL2} are the PL lifetime for the first and second emission processes; A_1 and A_2 are the first and second pre-exponential factors. Term B is a background contribution. Based on the obtained τ_{PL} and their contributions in the two-exponential approximation (Table 4), the weighted-average luminescence lifetimes, τ_{PLw} , are calculated according to the equation:

$$\tau_{PLw} = \frac{\sum_{i=1}^2 A_i \tau_{PLi}^2}{\sum_{i=1}^2 A_i \tau_{PLi}}. \quad (3)$$

TABLE 4. Photoluminescence lifetimes¹⁾ of $Zr_{0.98}Eu_{0.02}O_{1.99}$ nanoparticles of a different morphology

Morphology	A_1	τ_{PL1} , ms	$A_2 = 1A_1$	τ_{PL2} , ms	χ^2	τ_{PLw} , ms ²⁾	DWP ³⁾
Nanorods	0.452(7)	0.455(8)	0.548(8)	1.31(1)	2.147	1.120	0.518
Nanostars	0.85(2)	0.248(7)	0.15(1)	0.69(6)	0.610	0.394	1.577
Hollow spheres	0.71(6)	0.064(9)	0.29(2)	0.49(3)	1.05	0.387	1.769

¹⁾ PL lifetimes were fitted on the basis of the dual exponent decay (see Eq. 2) in minimizing a reduced χ^2 -statistics.

²⁾ Note the mean-weighted PL lifetimes, τ_{PLw} , calculated upon Eq. 3.

³⁾ Darbin–Watson statistic parameter [37].

According to the data shown in Table 4, in two-exponential approach both PL lifetimes τ_{PL1} and τ_{PL2} increase depending on morphology in series: hollow spheres to nanorods. Moreover, for the morphology of nanorods in the Raman spectra, a characteristic splitting of peaks corresponding to the monoclinic structure at 178 and 189 cm^{-1} is observed (Fig. 7). In the photoluminescence spectra for nanorods with Eu^{3+} , a fine splitting characteristic of $m\text{-ZrO}_2$ is observed in the spectral terms 7F_2 at 614, 625, 630 nm and 7F_4 at 694, 700, 706 and 711 nm (Fig. 6c). In these spectral terms, a characteristic intensity distribution pattern is observed with a maximum contribution at 614 nm in 7F_2 and at 711 nm in 7F_4 . The contributions to 7F_4 at 694, 700, and 706 nm are insignificant. In the 7F_2 term, the maximum of 614 nm has a shoulder at 616 nm. In nanorods, the formation of crystallites with a well-formed long-range order of the monoclinic phase (CSR ca. 30 nm) is also indicated by the manifestation of the ${}^5D_0 \rightarrow {}^7F_0$ optical transition in the luminescence spectrum. In addition, in this system, the ${}^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition is characterized by splitting into two peaks at 590 and 597 nm. For nanostars, the optical transition ${}^5D_0 \rightarrow {}^7F_0$ manifests itself less, and for hollow spheres it practically disappears (Fig. 6a). For nanostars and hollow spheres in the optical term 7F_1 , which is responsible for the magnetic dipole transition, fine splitting is not observed as for nanorods. The contribution at 625 nm compared to 614 nm grows in the order of nanorods \rightarrow nanostars \rightarrow hollow spheres, which leads to a greater “diffuseness” of the photoluminescence spectrum – the absence of pronounced fine splitting in the terms 7F_1 , 7F_2 and 7F_4 . This fact is consistent with Raman spectra, in which a diffuse scattering band appears during the transition from nanorods to nanostars (compare spectra 1 and 2 in Fig. 7). Moreover, the contribution of the diffuse band increases further during the transition from nanostars to hollow spheres (compare spectra 2 and 3 in Fig. 7). The appearance of a diffuse band in Raman spectra can be explained by CSR reduction in the series of nanorods \rightarrow nanostars \rightarrow hollow spheres (Table 3), and hence a decrease in the crystalline order in this series, as well as an increase in the amorphous component because of the growth of nanostructure surface area relating to volume (Table 2). This effect manifests itself if we compare the luminescence lifetimes in this order. The weighted-average luminescence lifetime decreases, indicating that the reduction in symmetry due to an increase in the contribution, which is more pronounced with a smaller CSR size and high S_{BET} values (Tables 2, 4). Thus, the most ordered monoclinic crystalline structure, in which the long-range order in the crystallite extends to 30 nm, is formed in nanorods. Disturbance of long-range order in nanostars is due to twinning, in hollow spheres – due to the presence of internal stresses. The nanostar CSR is two to three times smaller than for nanorods, which is associated with the “splitting” of the crystallite into parts. In hollow spheres, the CSR is the lowest 6 nm, since the geometry of the sphere must have the strongest internal stresses.

4. Conclusions

In this study, we examined the structure, morphology and emission properties of Eu^{3+} -doped zirconia nanophosphors using X-ray diffraction, Raman, UV-visible diffuse reflectance and photoluminescence spectroscopies. Earlier in [28], monoclinic $Zr_{0.98}Eu_{0.02}O_2$ nanorods with the lowered local site symmetry for photoactive centers were obtained by surfactant-assisted hydrothermal process. The authors observed the transformation of spherical particles of a tetragonal polymorphic modification with a size of less than 10 nm into lamellar structures of the same phase composition, which turned into $m\text{-ZrO}_2$ nanorods as basicity of the hydrothermal medium increases. In turn, we have obtained ZrO_2 nanostructures with a low content of Eu^{3+} (2 mol.%) in the form of rods, stars, and hollow spheres from the same precursors with varying hydrothermal conditions. Regardless of morphology, all synthesized nanoobjects are a monoclinic polymorphic modification of zirconia. A less defective structure of monoclinic zirconia was

formed as the size of crystallites increased in a series of hollow spheres, stars and rods. Morphology is reflected in different luminescent properties. The more regular monoclinic structure, the longer luminescence lifetime: rods have 1.12 ms versus ~ 0.4 ms for stars and hollow spheres. A comparison of the Tauc plots for the SKM function and the photoluminescence excitation spectra shows (Zr–O–Eu) charge-transfer states and energy transfer to Eu^{3+} in the ZrO_2 matrix with an absorption edge energy of 4.80 – 5.13 eV. While decreasing the coherent scattering volume, the adsorption surface area in the series rods–stars–hollow spheres increases.

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