

Nanosized phosphors based on $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ obtained by low-temperature methods

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Nanowires (10 to 50 nm wide, up to 2 μm long) and nanoplates (60 to 100 nm wide, 70 to 500 nm long) of europium doped gadolinium orthophosphate with narrow size distribution have been obtained by precipitation from aqueous solution using microemulsion and ultrasound treatment. The crystal structure of all nanosized samples belong to monazite structure. The size and shape of the objects has been shown to influence the luminescence spectra of activator. It is concluded that, the concentration of europium ion localization sites in low symmetry position with respect to the central ions increases in nanosized matrices as compared to $\text{GdPO}_4:\text{Eu}^{3+}$ polycrystals.

Нанонити (толщиной 10–50 нм и длиной до 2 мкм) и нанопластины (толщиной 60–100 нм и длиной 70–500 нм) ортофосфата гадолиния, активированного ионами европия, с узким распределением частиц по размеру получены методами осаждения из водных растворов с использованием микроэмульсий и обработки ультразвуком. Кристаллическая решетка всех наноразмерных образцов принадлежит структуре монацита. Показано, что размер и форма объектов влияют на спектры люминесценции активатора. Сделан вывод, что по сравнению с обычными поликристаллами $\text{GdPO}_4:\text{Eu}^{3+}$, в наноразмерных матрицах концентрация мест локализации ионов европия в низкосимметричном положении относительно центрального иона возрастает.

The synthesis and research of luminescent nanosized materials are a great interest in modern materials science. The particle size diminution of crystalline compounds and the controlled morphology thereof may result not only in new properties as compared to the bulk crystals but also in an extension of the application field. The physicochemical properties, in particular, the optical ones, of nanomaterials are known to depend heavily on the nanocrystal size and morphology. The development of a high-quality phosphor makes it necessary to solve some problems, in particular, to optimize the synthesis conditions and to study the control possibility of the growing nanocrystal shape and size.

The nanocrystals on the basis of lanthanide orthophosphates are among the materi-

als of good prospects due to the spectral features, the presence of a unique $4f$ transition in the luminescence spectrum as well as a high chemical and heat resistance. The materials are used widely as phosphors and scintillators, in luminescence devices, lasers, fluorescent probes in biology. They are promise for manufacturing of plasma displays and high-temperature proton conductors [1–6].

The use of traditional synthetic methods (hydrothermal and solid-phase ones [1, 7–13]) requires a complicated equipment and high temperatures. Such a synthesis results in formation of products with an uncontrollable granulometry that must be ground, so requiring an additional process stage. Moreover, the high-temperature synthetic processes hinder the control of the local

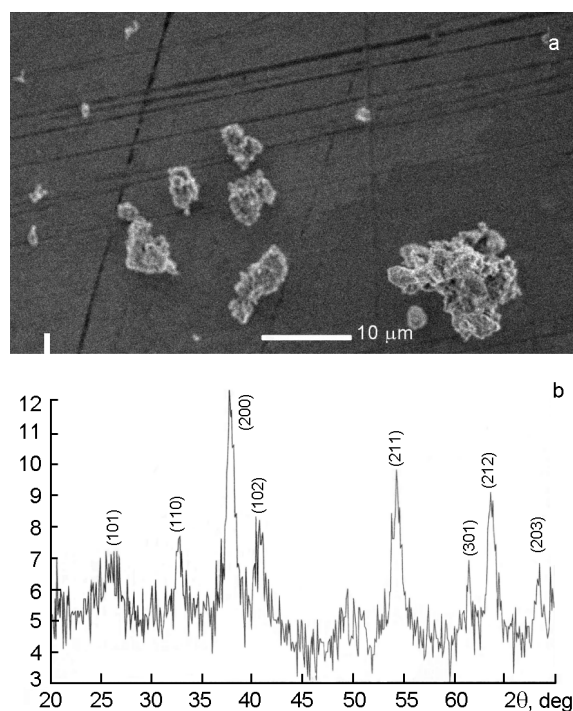


Fig. 1. Morphology (a) and XRD pattern (b) of polycrystalline $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ prepared by precipitation from aqueous solutions.

surrounding symmetry of cations in the crystal lattice and the adjustment of activating ion concentration in positions with a low local symmetry.

The RE orthophosphates (in the La to Dy sequence) obtained from aqueous solutions have hexagonal crystal structure, its stability being provided by the presence of 0.5 mole crystal water per LnPO_4 formula unit within channels extending along the hexagonal axes [10]. This stipulates a thread-like or needle shape of LnPO_4 precipitated from aqueous solutions. It is the microemulsion technique [14] that provides a narrow size distribution that is a traditional method of nanocrystal synthesis. In this case, the size of the growing crystal is assumed to be limited by the size of a water droplet surrounded with a monolayer of a surfactant (SAS). The phosphor particles obtained using that technique are not aggregated, regularly shaped and show a narrow size distribution that is of importance for lanthanide orthophosphates intended for coating of plasma displays [1, 15, 16]. However, as to nanocrystals with a pronounced crystal lattice anisotropy, including the hexagonal modification of gadolinium orthophosphate, the mentioned rule may not be fulfilled due to a high stability of the

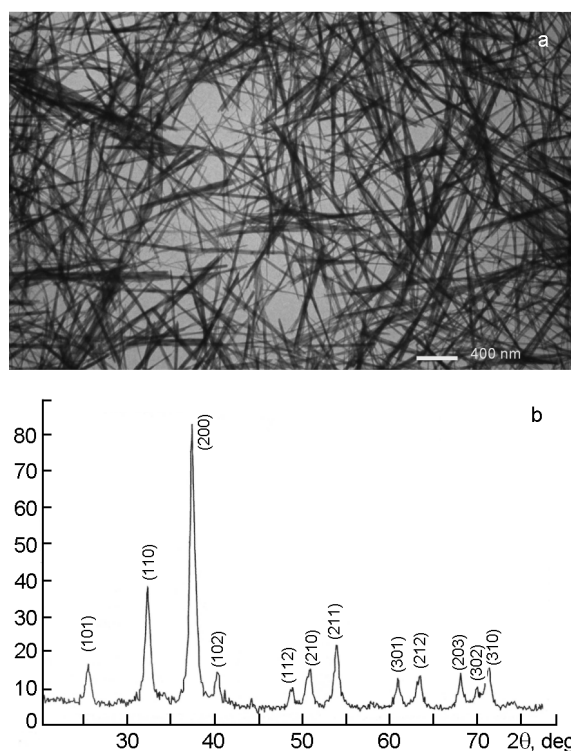


Fig. 2. Morphology (a) and XRD pattern (b) of $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ nanowires prepared by precipitation from aqueous solutions under ultrasonic treatment.

crystal lattice along the c axis and thus a predominant grow in that direction. Since the initial formation stage of RE orthophosphates consists in formation of amorphous dispersions, the crystallization process can be accelerated using ultrasonic agitation [17, 18].

The aim of this work is to study the potentials to control the length-to-diameter ratio of $\text{GdPO}_4:\text{Eu}^{3+}$ nanocrystals in the course of low-temperature synthesis from aqueous solutions as well as to study the effect of the nanocrystal morphology on the symmetry of Eu^{3+} local surrounding in the crystal lattice using the luminescence spectroscopy method.

The gadolinium orthophosphate nanocrystals doped with europium ions were obtained by precipitation from aqueous solutions, microemulsion method and by a technique using ultrasound. The $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ compounds were synthesized by mixing the solutions of precursors (GdNO_3 and H_3PO_4) in a thermostated glass at constant $\text{pH} = 4$ within the temperature range 20 to 80°C. The samples under study were activated by introducing europium nitrate, $C_{\text{Eu}^{3+}}$ being 1 to 3 at %. The formed nanocrystals of doped gadolinium

orthophosphate were isolated by centrifugation, washed thrice with double-distilled water and dried for 10 h at 100°C. When preparing $\text{GdPO}_4 \cdot \text{Eu}^{3+}$ by the microemulsion technique, sodium bis (2-ethyl hexyl)sulfosuccinate (aerosol OT, $\text{C}_{20}\text{H}_{37}\text{O}_7\text{SNa}$) was used as the surfactant. The concentration ratio $W = [\text{H}_2\text{O}]/[\text{SAS}]$ was varied from 5 to 17. The nanocrystals obtained in microemulsions were centrifuged off (8.000 rpm), washed thrice with double-distilled water and ethanol, and air-dried for 8 h at 100°C. The ultrasound treatment of the working solution during the synthesis was carried out using an UZDN-A ultrasonic disperser at 20 kHz frequency.

The morphology examination of doped gadolinium orthophosphate $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ polycrystals obtained by precipitation from solutions has shown that at the initial formation stages, amorphous particles of $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ composition are formed. 4 h later, the particles are agglomerated, and after 5 h synthesis, aggregates are formed where the individual crystallites are of 200 nm to 2 μm size (Fig. 1a).

Fig. 2 presents the XPA analysis results for $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ polycrystals obtained by precipitation from aqueous solutions. The XRD patterns comprise a set of major reflections belonging to the hexagonal crystal lattice of gadolinium orthophosphate. Neither amorphous nor minor phases have been revealed, the diffraction reflections are widened.

To avoid the agglomeration during the synthesis, the reaction mixture was agitated using ultrasound. The ultrasound provided an accelerated reaction, and as early as after 10 min of synthesis, the

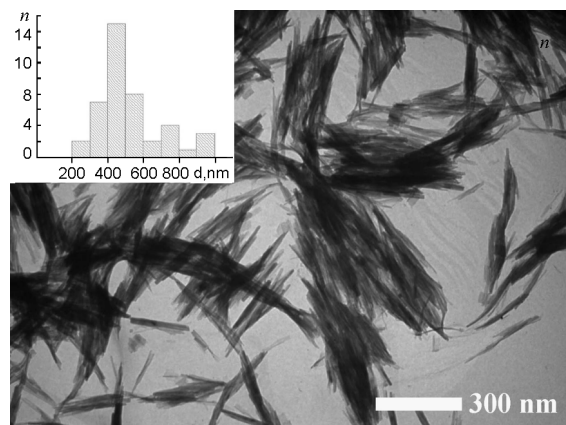


Fig. 3. TEM image of $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ prepared in microemulsions for 5 h at $T = 21^\circ\text{C}$.

$\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ was seen to form anisotropic nanocrystals (nanowires) of about 10 nm in diameter and up to 3 μm length (Fig. 2a). The XRD pattern comprises also a set of major reflections belonging to the hexagonal crystal lattice of gadolinium orthophosphate (Fig. 2b).

The lattice parameters and the coherent scatter area for polycrystals and for nanocrystals in the nanowire and nanoplate shapes have been determined from the diffractive reflection positions and are presented in Table. The lattice parameters are seen to agree with reference data and vary within the experimental error.

To stabilize the size of $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ nanowires, the synthesis was carried out using the microemulsions. The $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ nanoparticles obtained in the microemulsions under stirring by a magnetic stirrer for 5 h at room temperature are bundles consisting of needle-like fibers of 30×500 nm size (Fig. 3). Since the

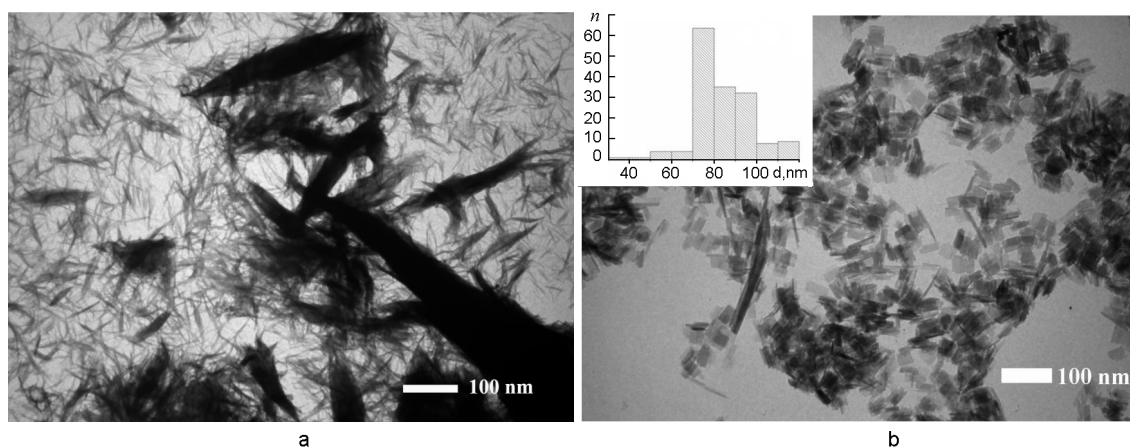


Fig. 4. TEM image of $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ prepared using ultrasound at $W = 17$ and $T = 76^\circ\text{C}$ (a) and $W = 17$, $T = 60^\circ\text{C}$ (b).

Table. Summarized results of XPA and spectral analysis of the studied $\text{GdPO}_4:\text{Eu}^{3+}$ samples

$\text{GdPO}_4:\text{Eu}^{3+}$	$L^{(002)}$, nm	a , nm	c , nm	I_{ED}/I_{MD}
polycrystals	10	0.688	0.634	0.246
Nanoplates	17	0.692	0.635	0.400
Nanowires	13	0.691	0.634	0.510

aqueous phase volume in the microemulsions is 20 to 50 nm, the reagent exchange between the water drops is hindered, therefore, ultrasonic mixing was used in all the further experiments carried out in the microemulsion systems.

The experiments have shown that the formation of isolated $\text{GdPO}_4:\text{Eu}^{3+}$ nanocrystals is possible within the concentration ratio $W = C_{\text{H}_2\text{O}}/C_{\text{AOT}}$ from 9 to 17, the variation in W does not effect significantly the nanocrystal size. At $W < 9$, mainly the conglomerates consisting of needle-like nanocrystals with a considerable size dispersion are formed. The temperature elevation to 60–80°C results in crystalline formations of up to 1 μm in length and up to 0.5 μm in diameter (Fig. 4a). The temperature drop (down to $<60^\circ\text{C}$) favors agglomeration of irregularly shaped particles. The temperature elevation within the optimum range results in formation of nanocrystals characterized by a large length-to-diameter ratio (l/d). The nanocrystals obtained in optimized conditions (Fig. 4b) are characterized by a narrow size distribution. The nanocrystal size is of 70×80 nm².

Fig. 5 presents the luminescence spectra ($\lambda_{\text{ex.}} = 253.7$ nm, $T = 21^\circ\text{C}$) of $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ nanopowders, nanowires, and nanoplates. The spectrum appearance corresponds to the main transitions ${}^5\text{D}_0-{}^7\text{F}_J$ ($J = 1, 2, 3, 4$) typical of luminescence of trivalent europium. The positions and intensities of those transitions depend on the symmetry and the crystal field strength in the europium positions. The most intense luminescence is observed for the ${}^5\text{D}_0-{}^7\text{F}_1$ transition pointing the emission in the bright orange region. The intensity ratio (K) of electric dipole transition ${}^5\text{D}_0-{}^7\text{F}_2$ (I_{ED}) and that of the magnetic dipole one ${}^5\text{D}_0-{}^7\text{F}_1$ (I_{MD}) can be considered as a symmetry measure of the coordination sphere. The higher that ratio is, the lower is the surrounding symmetry of the ion being substituted. The calculated values of

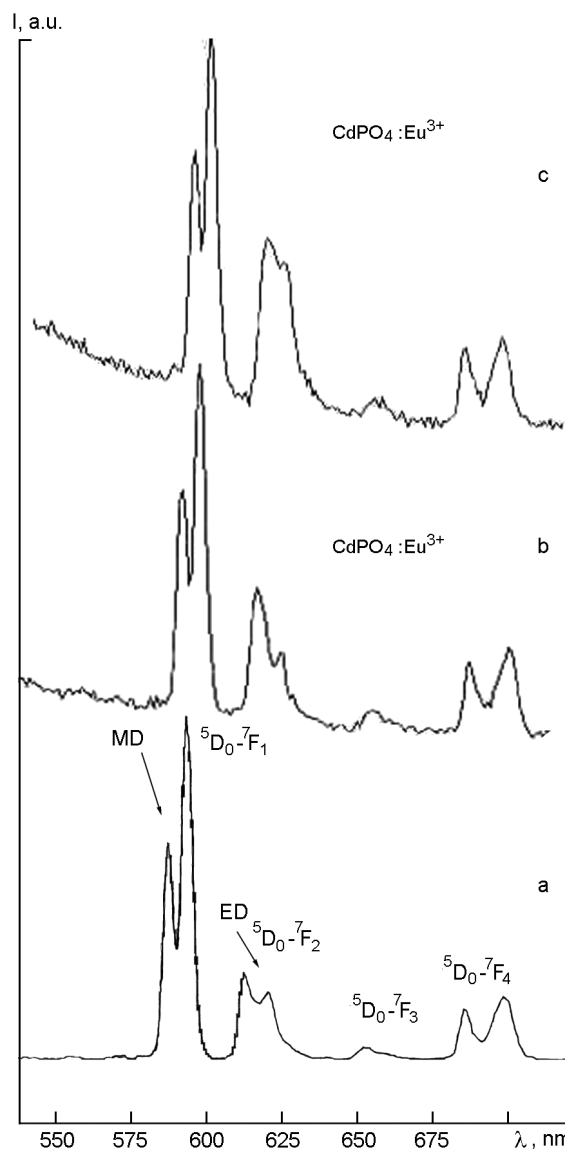


Fig. 5. Luminescence spectra of $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ polycrystals (a), nanoplates (b), nanowires (c).

K are presented in Table. The K is seen to vary depending on the sample morphology. It is appreciably higher for nanowires and nanoplates, thus indicating that in $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ nanocrystal matrices, there is an increased concentration of europium ion localization sites in low-symmetry positions with respect to the substituted cation.

Thus, isolated luminescent nanocrystals shaped as 10 to 20 nm thick nanowires of up to 2 μm length have been obtained from aqueous solutions with subsequent ultrasonic treatment. The combination of sonochemical and microemulsion techniques makes it possible to suppress the predomi-

nating growth of $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ nanocrystals and thus to control the nanocrystal size and shape. The effect of $\text{Gd}_{0.97}\text{Eu}_{0.03}\text{PO}_4$ nanocrystal morphology on the luminescence spectra thereof has been demonstrated. It has been established that in the nanocrystal matrices, an increased concentration of europium ion localization sites in low-symmetry positions with respect to the substituted cation takes place.

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Нанорозмірні фосфори на основі $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$, що отримані низькотемпературними методами

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Нанонитки (товщиною 10–50 нм та довжиною до 2 мкм) та нанопластинки (товщиною 60–100 нм та довжиною 70–500 нм) ортофосфату гадолінію, активованого іонами європію, з вузьким розподілом частинок за розміром отримані методами осадження з водних розчинів з використанням мікроемульсій та ультразвукової обробки. Кристалічна ґратка усіх нанорозмірних зразків належить до структури монациту. Показано, що розмір та форма об'єктів впливають на спектри люмінесценції активатора. Зроблено висновок, що у порівнянні зі звичайними полікристалами $\text{GdPO}_4:\text{Eu}^{3+}$, у нанорозмірних матрицях концентрація місць локалізації іонів європію у низькосиметричному положенні відносно заміщеного іона зростає.