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Spectral and structural characteristics of β -NaGd_{1-x}Eu_xF₄ at different concentrations of Eu³⁺ ions

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Samples of β -NaGd_{1-x}Eu_xF₄, where $0 \leq x \leq 1$, were synthesized by the hydrothermal method for the first time. The obtained materials are characterized by methods of X-ray phase analysis, electron microscopy, IR and Raman spectroscopy. For the first time, luminescence spectra and luminescence excitation spectra of β -NaGd_{1-x}Eu_xF₄ were studied in the entire range of europium concentrations. The absence of complete quenching of the luminescence of the β -NaGd_{1-x}Eu_xF₄ system was found and it was shown that the excitation of the luminescence of this system by excitation of donor ions (Gd³⁺) leads to a high quantum yield of luminescence.

Keywords: phosphors for LEDs, rare earth orthoborates, X-ray diffraction analysis, IR and Raman spectroscopy, luminescence spectra.

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1. Introduction

During recent years development of photonics, laser engineering and technologies based on quantum principles and laws is especially intensive. The double fluorides of rare earth and alkali elements doped with lanthanides are one of the materials having wide spectrum of optical properties [1]. Lanthanide ions (RE³⁺) have the characteristic features of the electronic structure and are rather effective as structural sensitive marks, as luminescence of RE³⁺-cations is due to transitions inside $4f^n$ electronic configuration. Transitions in $4f^n$ shell to a large extent are screened by external closed $5s^2$ and $5p^6$ electron shells, this ensures low width of lines in the luminescence spectra. According to selection rules the electronic transitions inside $4f^n$ — shell are prohibited, but upon ion positioning into the crystalline lattice such prohibition is partially removed, and transitions become possible [2]. Double fluorides are quite promising for use as phosphors and scintillators. The characteristic features of such compounds are large band gap (~ 8 eV) and rather narrow phonon spectrum (~ 500 cm⁻¹), this leads to minimum quenching of excited terms RE³⁺. Compound NaGdF₄ relates to class of fluorides, their composition can be described by general formula MREF₄, where (M — ion of alkali metal, RE — rare earth ion). This compound has two crystalline modifications: cube and hexagonal. From a practical point of view, the hexagonal modification β -NaGdF₄ is the most interesting one. Compounds NaYF₄ and NaGdF₄, doped with Yb³⁺ and Er³⁺ ions have good upconversion luminescent properties and are promising as luminescent materials for biomedical applications [3,4].

These compounds obtaining with crystal sizes in the nanometer range opens up wide possibilities for their use in such areas as photocatalysis, nanosensors, solar cells, IR — induced photopolymerization, and biomedical application. [3]. Promising nature of these compounds as materials for photo activated therapy shall be worth noted among biomedical applications [5].

The paper [6] presents study results of system β -NaGd_{1-x}Eu_xF₄ in concentration range $0 \leq x \leq 0.3$. In said publication for ion Eu³⁺ the probabilities of transitions $^5D_0 \rightarrow ^7F_{2,4,6}$, as well as parameters of Judd–Ofelt Ω_t luminescence are determined. Same studies were performed in paper [7], where life times are specified for excited states of ion Eu³⁺, and Judd–Ofelt model adequately describes the photophysical processes. But concentration range Eu³⁺ used in this paper is limited to 10 mol%. It is interested to study spectral luminescent characteristics of the compound β -NaGd_{1-x}Eu_xF₄ in wider concentration range of ions Eu³⁺. In present paper samples of hexagonal phase β -NaGd_{1-x}Eu_xF₄ ($0 \leq x \leq 1$) are studied, obtained by hydrothermal synthesis, and presenting mainly nanoparticles with size in accordance with data of electronic microscopy ~ 100 – 200 nm. This method of this compound synthesis in wide concentration range of europium was used for the first time. Generally, for this compound preparation in form of nanoparticles special synthesis conditions are necessary. Methods of obtaining pure hexagonal nanoscale phase β -NaGdF₄ are stated, they mainly mean high-temperature solvothermal and hydrothermal methods, thermal decomposition of rare earth trifluoroacetates at temperatures 250–330°C in presence of organic solvents and protective atmosphere [8]. As organic solvents ethylene

glycol, octadecane with oleic acid or its amine as surfactants are used.

In paper [9] nanocrystals β -NaGdF₄ doped with 5% Eu³⁺, were obtained by combined two-stage thermolysis of solutions of sodium, gadolinium and europium trifluoroacetic acid salts in trioctylphosphine oxide, first at 120°C in vacuum for 30 min, and then for 1 h at 350°C, which made it possible to control the morphology and dimensional homogeneity of the resulting product.

Use of the organic solvents, high temperatures and multi stages of the process make the known methods of β -NaGdF₄ obtaining preparatively cumbersome and ecologically stressful. Due to this reason the synthesis in aqueous environment is of special interest, but in this case the developed methods of β -NaGdF₄ obtaining can be named as simple and easy. Paper [10] informs on synthesis of phase NaGdF₄:Ce³⁺Eu³⁺ by the solvothermal method in an aqueous medium using chloride and nitrate salts. The synthesis was performed by two stages: at temperature 90°C (2 h) and at 210°C (1 h) with the separation of intermediate products by centrifugation. As a result we obtained two phases — cube and hexagonal.

In paper [11] nanoparticles NaGdF₄:Tb³⁺Eu³⁺ were synthesized in aqueous environment in presence of citric acid in two stages: obtaining particles NaGdF₄:Tb³⁺Eu³⁺ coprecipitation of citrate complexes of rare earth elements and NaF at room temperature followed by hydrothermal treatment at 180°C for 6 h. In paper [12] nanoparticles NaYF₄ were obtained by method of coprecipitation from aqueous solution at room temperature as per reaction of yttrium nitrate with excess of precipitator NaF. As a result a mixture of hexagonal and cube phases of NaYF₄ was obtained, quantitative ratio of them depended in sequence of combination of solutions of yttrium nitrate and NaF, as well as on concentration of initial solvents.

The developed by us hydrothermal single-stage method of nanoparticles β -NaGdF₄:Eu obtaining is step in way of simplification of this compound synthesis. In present paper structural and spectral characteristics are studied of the product obtained under this procedure in wide concentration range of ions Eu³⁺.

2. Experimental procedures

2.1. Sample synthesis

The nanoparticles β -NaGdF₄:Eu were obtained by coprecipitation of nitrate salts of rare-earth elements and sodium fluoride in aqueous environment. For reaction aqueous solutions of gadolinium and europium nitrates with concentration of 1.5 M, prepared by dissolving nitrate salts Gd(NO₃)₃ · 5H₂O and Eu(NO₃)₃ · 6H₂O in distilled water, and aqueous solution of sodium fluoride with a concentration of 0.9 M. All used reagents were of CP (chemically pure) grade. In teflon glass 25 ml solutions of gadolinium and europium nitrates taken in necessary ratio were poured. Total volume of nitrates was 2.5 ml.

An aqueous solution of NaF was added to this solution in amount of 20 ml, so that the excess of sodium fluoride from the stoichiometric amount was sevenfold. All procedures for the glass loading were carried out at room temperature. The glass was covered with lid and loaded in steel autoclave, which was installed in heated to temperature 210°C electric oven and held in it for 3–20 h. After this the teflon glass was removed from the oven and opened after cooling. The target product was obtained by filtering of the obtained suspension, washed in filter with water, alcohol and dried at 90°C.

2.2. Research methods

X-ray diffraction examinations were performed using a Rigaku SmartLab SE diffractometer with CuK α -radiation, $\lambda = 1.54178$ Å, 40 kV, 35 mA. Angular spacing is $2\theta = 10$ – 120° . Phase analysis of the samples and calculation of lattice parameters were performed using Match and PowderCell 2.4 programs.

Samples' IR-spectra of absorption were measured using a Fourier-spectrometer VERTEX 80v in the spectral range of 30–550 cm⁻¹ with resolution 2 cm⁻¹. For measurements the suspension of polycrystalline powders in mineral oil was applied in a thin layer onto polyethylene substrate.

The sample morphology was studied using a Supra 50VP X-ray microanalyzer with an add-on for EDS INCA (Oxford).

Photoluminescence (PL) spectra and luminescence excitation spectra were studied on a unit consisting of a light source — DKSSh-150 lamp, two MDR-4 and MDR-6 monochromators (spectral range 200–1000 nm, dispersion 1.3 nm/mm). Luminescence was recorded by means of a FEU-106 photomultiplier (spectral sensitivity region 200–800 nm) and an amplification system. The MDR-4 monochromator was used to study the samples' luminescence excitation spectra, the MDR-6 monochromator was used to study luminescence spectra. The luminescence spectra were further corrected to the spectral sensitivity of FEU. The integral luminescence intensities were calculated by converting wavelengths into energy units, and then the integrals were calculated in the range 575–715 nm, where most intense luminescence bands of samples were observed. The luminescence excitation spectra were corrected to curve of lamp illumination intensity. Spectral and structural characteristics were studied at room temperature.

Raman scattering (RS) spectra were measured using spectrometer Princeton Instruments HRS 500 with CCD-detector cooled by liquid nitrogen, on diffraction grating with grooves density 1200 grooves/mm, at room temperature. For excitation laser KLM-532/SLN-100 DPSS (FTI-Optronik, Saint-Petersburg) with wavelength 532 nm was used, radiation power on sample was about 5 mW. The optical system operates in geometry of back scattering, for the laser radiation focusing and gathering of light scattered by sample lens 20× Plan Apo Mitutoyo was used (focal spot size on sample surface was ~ 3 μm). Holographic

Tydex Notch-6 filter (Tideks, Saint-Petersburg) was used to discriminate the excitation lines, and this ensures registration of RS spectra from frequency 200 cm^{-1} . Spectral resolution in this range was about 1 cm^{-1} . Measurement accuracy $\pm 1\text{ cm}^{-1}$ was achieved by spectrometer calibration by radiation lines of Ne-lamp.

Lighting kinetics of samples was studied at $T \sim 300\text{ K}$. For non-resonant excitation, an excimer ultraviolet (UV) laser with wavelength $\lambda_L = 308\text{ nm}$ was used (pulse width $\sim 10\text{ ns}$, pulse frequency 15 Hz , pulse energy $\sim 2\text{ mJ}$). The laser radiation was focused on powder loaded in the quartz cuvette into spot with diameter of $\sim 100\text{ }\mu\text{m}$, laser excitation density on sample surface P_{exc} varied using calibrated gradient filters in wide range up to $P_{\text{max}} \sim 10\text{ MW/cm}^2$ recalculated to single pulse. PL spectra were registered using MUM spectrometer equipped with cooled CCD and photomultiplier FEU-79 with registering time integrator BOXCAR Stanford SR 250, this ensured registration of both integrated over time PL spectra, and luminescence pulses with resolution $\sim 20\text{ }\mu\text{s}$.

3. X-ray diffraction studies

Diffraction patterns of powders $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$ (composition as per batch) at $0 \leq x \leq 1$ are given in Figure 1.

In full concentration range the samples are single-phase and have hexagonal structure with space group SG $P(-6)$ (174), in accordance with published data for $(\text{NaGdF}_4)_{1.5}$ (ICDD № 01-080-8787) and $(\text{NaEuF}_4)_{1.5}$ (ICDD № 01-087-2282).

Figure 2 shows change of volume of unit cell of the hexagonal phase upon change of batch composition.

In paper [6] system $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$ was studied at $0 \leq x \leq 0.3$. To monitor offset of diffraction lines during doping in this paper line (201) in angle range 2θ of 40 to 45° was selected. In present paper this diffraction line was also selected by us for comparison. Figure 3 shows offset of diffraction line (201) of hexagonal phase upon change in batch composition.

The linear change in the volume of the unit cell of the hexagonal phase upon doping corresponds to Vegard's law, Figures 2 and 3 are confirmation of the formation of solid solution $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$ in entire concentration range. Increase in volume of unit cell of hexagonal phase $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$ during x increasing confirms that ions Gd^{3+} are replaced (effective ionic radius in 9-fold coordination 1.247 \AA) by ions Eu^{3+} with larger ionic radius (1.26 \AA) [13]. Offset of the diffraction line (201), selected for monitoring, towards lower angles during x increasing also corresponds to the increase in volume of unit cell during replacement of ions Gd^{3+} by ions Eu^{3+} , having large ionic radius.

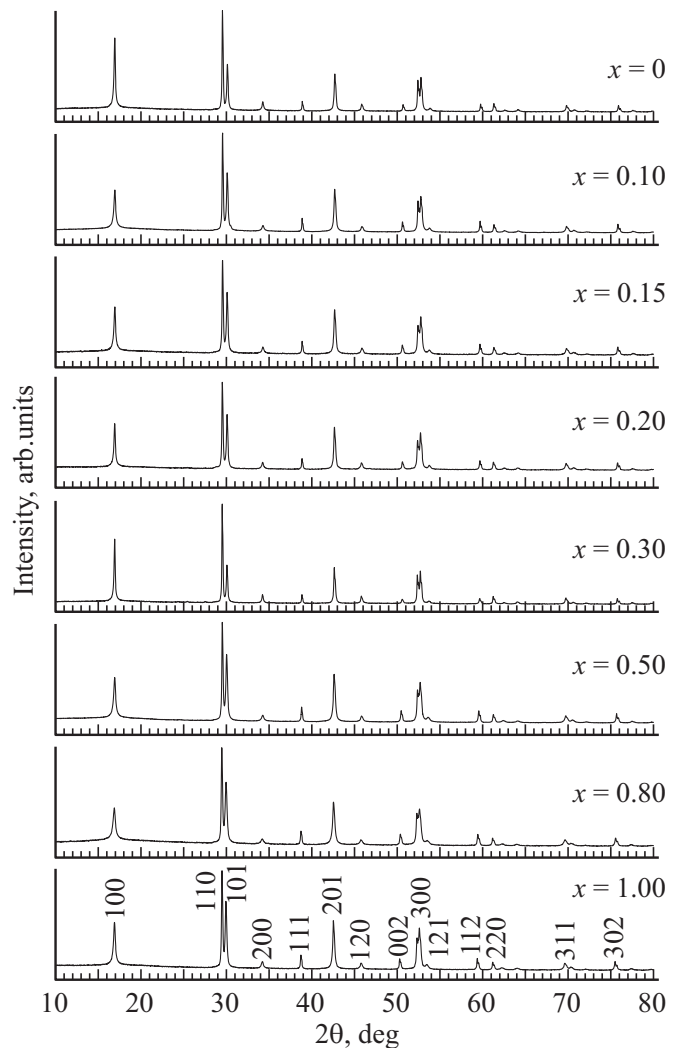


Figure 1. Diffraction patterns of powders $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$.

As per published data values of lattice parameters $\beta\text{-NaGdF}_4$ and $\beta\text{-NaEuF}_4$ are as follows:

$$(\text{NaGdF}_4)_{1.5}: a = 6.0304\text{ \AA}, c = 3.6111\text{ \AA},$$

$$V = 113.73\text{ \AA}^3 \text{ (ICDD № 01-080-8787),}$$

$$(\text{NaEuF}_4)_{1.5}: a = 6.040\text{ \AA}, c = 3.632\text{ \AA},$$

$$V = 114.75\text{ \AA}^3 \text{ (ICDD № 01-087-2282).}$$

The obtained values are:

$$(\text{NaGdF}_4)_{1.5}: a=6.041\text{ \AA}, c=3.600\text{ \AA}, V=113.79\text{ \AA}^3,$$

$$(\text{NaEuF}_4)_{1.5}: a=6.055\text{ \AA}, c=3.626\text{ \AA}, V=115.14\text{ \AA}^3.$$

Small differences in absolute values of lattice parameters are due to, obviously, somewhat different ratio of elements in final product of synthesis, this does not affect the available patterns in change of structural parameters. Ratio of intensities of diffraction lines in studied samples differed

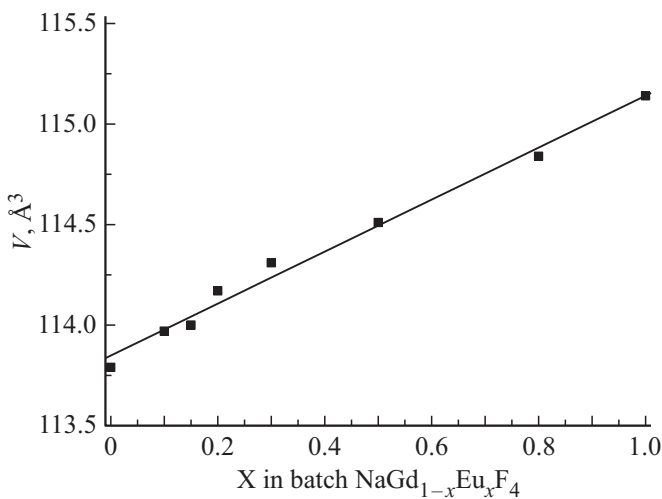


Figure 2. Volume of lattice cell β -NaGd_{1-x}Eu_xF₄ depending on batch composition.

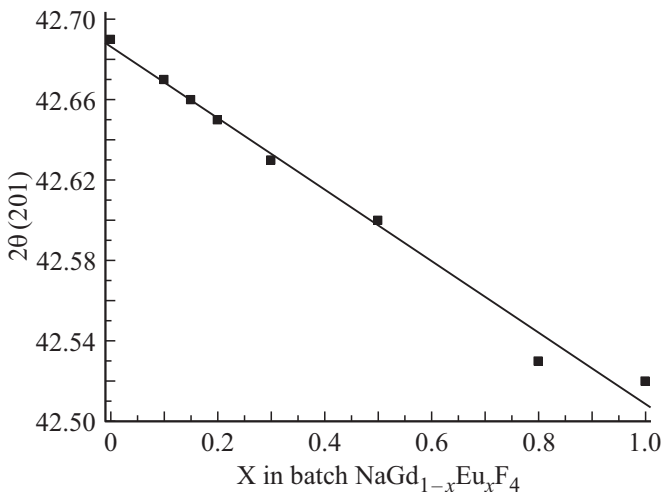


Figure 3. Position of diffraction line (201) of hexagonal phase β -NaGd_{1-x}Eu_xF₄ depending on batch composition.

from published data, this indicates presence of texture, occurred as result of samples preparation for diffractometry. So size of coherent scattering regions (CSR) in this case was evaluated considering tool broadening as per Scherrer formula over diffraction line (100), CSR size was of 20 to 90 nm.

4. Sample morphology

Figure 4 presents the electron microscopic images of samples β -NaGd_{1-x}Eu_xF₄ at $0 \leq x \leq 1$. In the entire concentration range of europium agglomerates of small microcrystals of round shape and size ~ 100 – 200 nm are observed. In samples with europium content $0 \leq x \leq 0.3$ additionally to small round microcrystals the elongated

microcrystals are observed, they have shaper of rods ~ 0.5 – $2 \mu\text{m}$ long and ~ 0.1 – $0.5 \mu\text{m}$ thick.

5. IR-spectroscopy and Raman scattering spectroscopy

Results of X-ray diffraction analysis showed that studied samples of compounds β -NaGd_{1-x}Eu_xF₄ ($x = 0, 0.1, 0.2, 0.3, 0.5, 0.8, 1$) are single-phase, nanoscale and have hexagonal structure with spatial group $P(-6)$.

Group-theoretical analysis performed for crystals NaLnF₄ (Ln = La, Ce, Pr, Sm, Eu and Gd) with space group $P(-6)$, predicts presence of 10 phonon modes in IR-spectrum [14]. In this paper, the systematic study of polarized reflection spectra was performed for bulk NaLnF₄ crystals. Two additional vibrational modes were identified in IR-spectra, and it was determined that effect of Ln ions replacement on vibrational modes of the crystal means, as a rule, the hardening of modes with decrease in ionic radius. The presence of defect modes and broad phonon bands observed in the reflection spectra of crystals, according to the opinion of authors of this paper, indicate cationic disorder allowed by this structure.

Figure 5 in frequency range 40 – 550 cm^{-1} presents IR-absorption spectra of samples of compounds NaGd_{1-x}Eu_xF₄ ($x = 0, 0.1, 0.2, 0.3, 0.5, 0.8, 1$; spectra 1–7). It follows from data of paper [14] that considered spectral range is typical for excitation of optical phonon modes of β -NaGd_{1-x}Eu_xF₄.

In measured IR-spectra of samples we can visually distinguish 7 broad absorption bands determined by lattice vibrations. Figure for spectra 1 and 7, relating to samples β -NaGdF₄ and β -NaEuF₄, respectively, contains values of frequencies of maxima of these bands, determined by positions of minima of first derivative on appropriate curves of experimental spectra. In paper [15], where dependence of IR-absorption spectra of nanocrystalline powder NaGdF₄ on size of crystallites was studied, 8 vibrational absorption bands were observed. Our spectrum β -NaGdF₄ is similar to spectrum from this paper.

The absorption bands near $65, 110, 176, 220, 283, 344$ and 380 cm^{-1} in spectrum β -NaGdF₄ in accordance with data of paper [15] can be compared as follows: low-frequency band $\sim 65 \text{ cm}^{-1}$ is associated with translation vibrations of gadolinium atoms, and rest bands — with stretching and deformation vibrations of bonds Gd–F and (Na,Gd)–F. Comparison of spectra β -NaGdF₄ and β -NaEuF₄ shows that they are similar. In spectrum β -NaEuF₄ offset of bands is observed to values near $60, 115, 174, 216, 279, 339$ and 373 cm^{-1} , respectively. In our case of ions Gd replacement by ions Eu six of seven observed vibrational modes offset by 2 – 7 cm^{-1} into red region, as the effective ionic radius Eu³⁺ (1.26 \AA) exceeds the effective ionic radius of Gd³⁺ (1.247 \AA). Opposite offset of mode 110 cm^{-1} to 115 cm^{-1} is also associated with Gd replacement by Eu. Note that

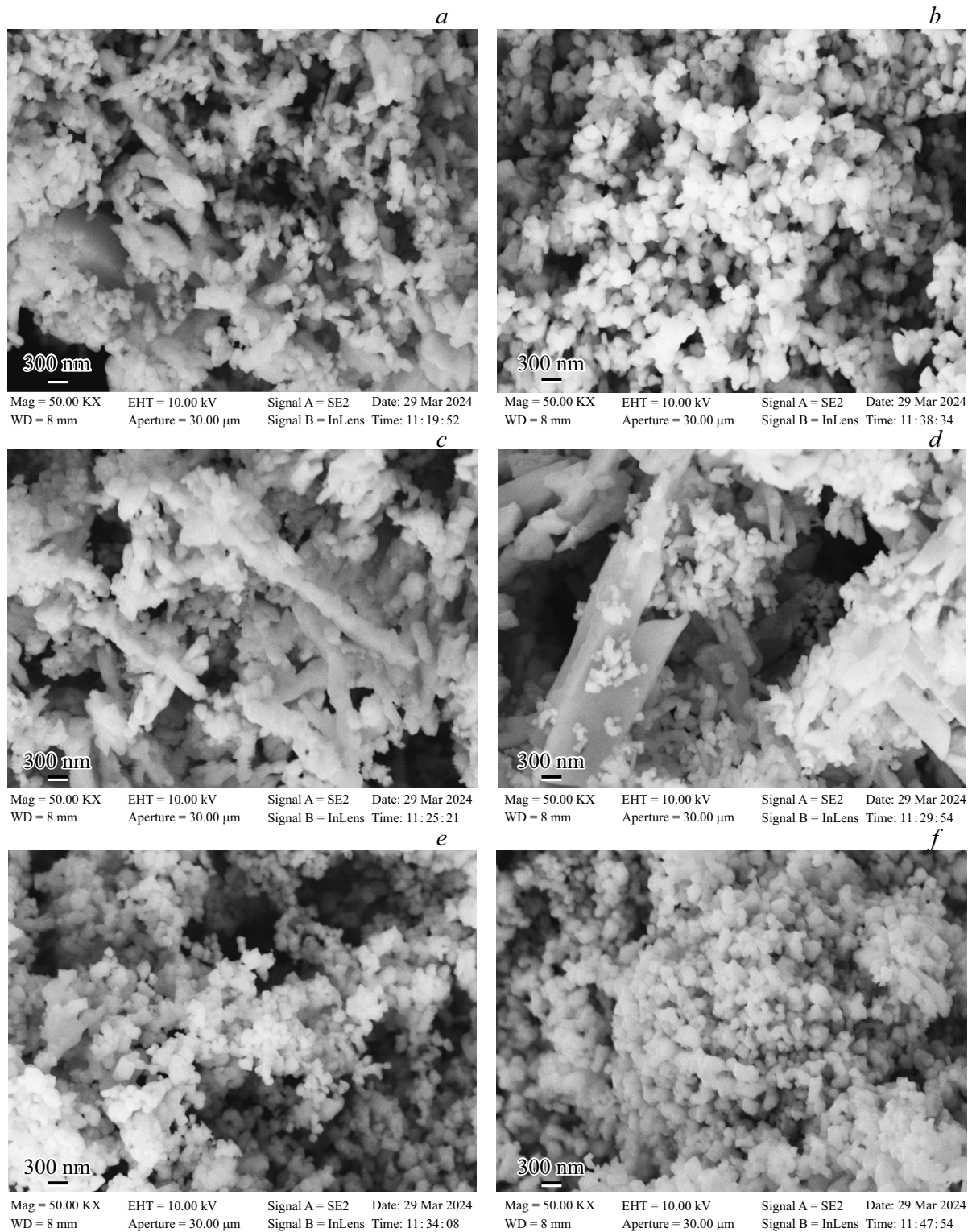


Figure 4. Electron microscopic images of β - $\text{NaGd}_{1-x}\text{Eu}_x\text{F}_4$ (x in batch): *a* — NaGdF_4 ; *b* — $\text{NaGd}_{0.9}\text{Eu}_{0.1}\text{F}_4$; *c* — $\text{NaGd}_{0.8}\text{Eu}_{0.2}\text{F}_4$; *d* — $\text{NaGd}_{0.7}\text{Eu}_{0.3}\text{F}_4$; *e* — $\text{NaGd}_{0.5}\text{Eu}_{0.5}\text{F}_4$; *f* — NaEuF_4 .

frequencies of practically all transverse optical phonons (TO) for bulk crystals NaGdF_4 and NaEuF_4 , given in paper [14], also differ insignificantly ($1\text{--}4\text{ cm}^{-1}$). In this paper frequency of mode 109 cm^{-1} for bulk crystals

NaGdF_4 during Gd replacement by Eu also do not decrease, but increase to 111 cm^{-1} . As can be seen in the figure, the substitution of gadolinium with europium and transition from one composition to another one do not change the

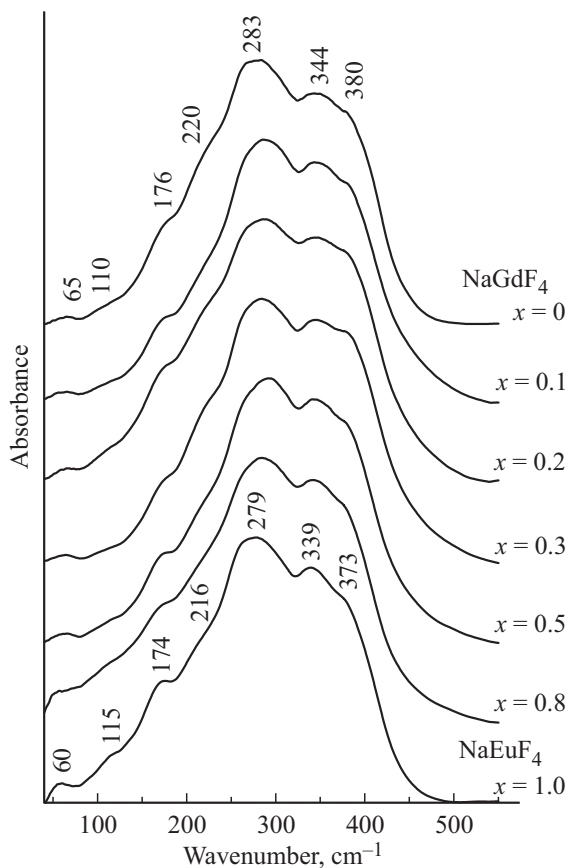


Figure 5. IR-absorption spectra of β -NaGd_{1-x}Eu_xF₄: 1 — NaGdF₄; 2 — NaGd_{0.9}Eu_{0.1}F₄; 3 — NaGd_{0.8}Eu_{0.2}F₄; 4 — NaGd_{0.7}Eu_{0.3}F₄; 5 — NaGd_{0.5}Eu_{0.5}F₄; 6 — NaGd_{0.8}Eu_{0.2}F₄; 7 — NaEuF₄.

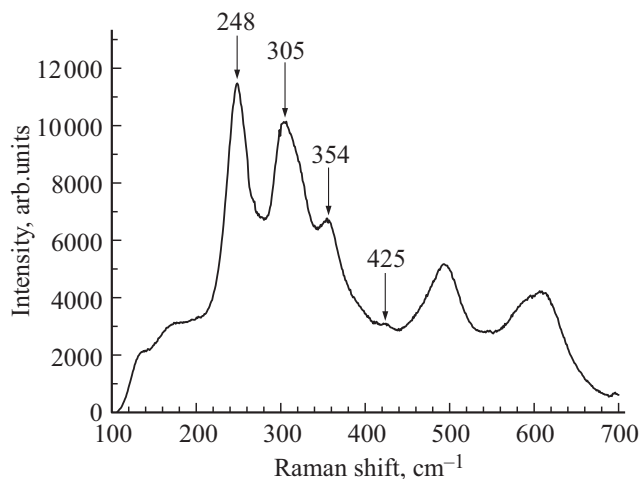


Figure 6. Experimental spectrum of Raman scattering of samples β -NaGdF₄.

spectrum, i.e. each previous and next spectra consist of same absorption bands. This confirms testifies in favor of that results of IR-study of the compound β -NaGd_{1-x}Eu_xF₄ agree with data of X-ray diffraction studies on structure keeping in wide concentration range of X-ray europium.

Figure 6 shows RS spectrum of sample NaGdF₄. Comparing the presented spectrum with the spectra of single crystals [14], we can state that the following lines are RS bands: $\sim 248, 305, 354, 425 \text{ cm}^{-1}$. Band $\sim 248 \text{ cm}^{-1}$ practically coincides with band observed in IR-spectra of single crystals, TO-phonon corresponds to it [14]. Besides, according to the same work, in RS spectra of single crystals for two orientations of the single crystal, two close bands are observed 244 and $\sim 250 \text{ cm}^{-1}$, which in the result of averaging of large number particles in powder samples can form a band $\sim 248 \text{ cm}^{-1}$. Bands $\sim 305, 354$ and 425 cm^{-1} are close to the vibrational modes observed in RS spectra of single crystals [14]. More over, the band $\sim 354 \text{ cm}^{-1}$ was observed in spectra of nanocrystalline powders samples in paper [16]. Bands ~ 500 and 600 cm^{-1} absent in spectra of single crystals, but line $\sim 500 \text{ cm}^{-1}$ was observed for nanocrystalline samples NaGdF₄ and NaYF₄ in paper [16]. Some researchers associate the presence in spectrum of bands ~ 500 and 600 cm^{-1} with the vibrational modes of Na–F [17]. Interpretation of spectra of samples doped with ions Eu³⁺, is difficult due to their luminescence in green region, so it is not provided.

6. Luminescence spectra, SC excitation spectra and curves of integral luminescence

Figures 7,8 present luminescence spectra of samples NaGd_{1-x}Eu_xF₄. The luminescence spectra of samples were obtained at two wavelengths of exciting light $\lambda_{\text{ex}} = 395 \text{ nm}$ and $\lambda_{\text{ex}} = 272.5 \text{ nm}$. The wavelength $\lambda_{\text{ex}} = 395 \text{ nm}$ corresponds to resonance excitation band of europium ions, at this excitation wavelength direct excitation of ions Eu³⁺ occurs. The resonance transition ${}^7F_0 \rightarrow {}^5L_6$ corresponds to this band. The wavelength $\lambda_{\text{ex}} = 272.5 \text{ nm}$ coincides with the resonance excitation band of ions Gd³⁺.

Said luminescence excitation bands are visible in luminescence excitation spectra (see Figure 9).

The presented luminescence excitation spectra of samples with low concentrations of europium ions were obtained at the maximum of the luminescence band at $\lambda_{\text{max}} = 615.1 \text{ nm}$. In spectral range $\lambda \sim 270\text{--}280 \text{ nm}$ the bands are determined by the resonance excitation of ions Gd³⁺ and correspond to electronic transition in ion Gd³⁺ ${}^8S_{7/2} \rightarrow {}^6I_j$, where $j = 11/2, 15/2, 13/2, 9/2, 17/2, 7/2$. The spectral bands with $\lambda \approx 305$ and 310 nm are also due to resonance excitation of ions Gd³⁺, and electronic transition ${}^8S_{7/2} \rightarrow {}^6P_j$ corresponds to them, where $j = 3/2, 5/2, 7/2$. Group of spectral bands in range $\lambda \sim 360\text{--}420 \text{ nm}$, and bands at $\lambda \approx 466 \text{ nm}$, correspond to luminescence excitation bands of ions Eu³⁺. Exciting the luminescence of sample in band $\lambda_{\text{ex}} = 272.5 \text{ nm}$ and registering in region of spectrum $575\text{--}715 \text{ nm}$, we can conclude on presence of electronic excitation transfer from gadolinium ions to ions Eu³⁺. From presented Figures 7 and 8 we see that most intense luminescence bands are bands with $\lambda_{\text{max}} \approx 592 \text{ nm}$ and

$\lambda_{\max} \approx 615$ nm, which further were used to study kinetics of samples luminescence.

During study of concentration dependences of luminescence spectra in crystals doped with rare-earth ions (RE^{3+}), the intensities of luminescence bands can unproportionally change depending on concentration of RE^{3+} [18]. Figure 10 presents dependences of integral intensity of full luminescence spectrum (Figures 7, 8) of system $\text{NaGd}_{1-x}\text{Eu}_x\text{F}_4$ in wide concentration range of europium ($0 \leq x \leq 1$). We see that maximum of integral luminescence was observed in samples with composition $x = 0.2$. At large concentrations of Eu^{3+} the integral intensity decreases insignificantly and incompletely unlike, for example, oxide systems, where complete quenching of luminescence occurs already at significantly lower concentrations (~ 10 wt.%) Eu^{3+} [18]. Figure 10 shows that in this system rather weak quenching of luminescence at $x > 0.2$ is observed.

For its explanation we need to consider mechanisms of energy transfer and quenching between rare-earth ions. Let's consider possible causes that can explain behavior of integral curves of luminescence. It is known that

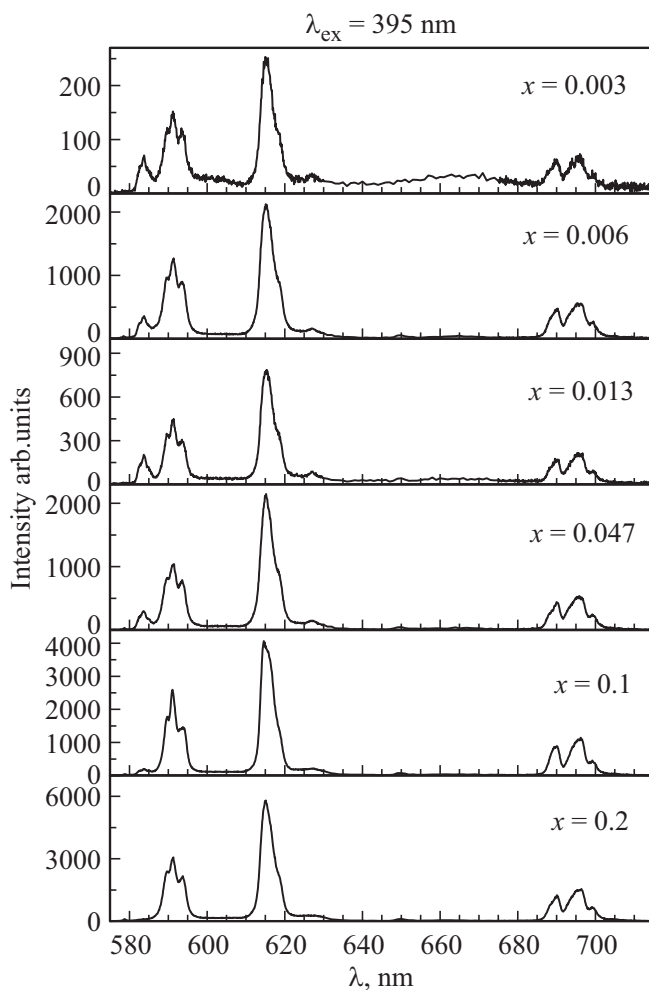


Figure 7. Luminescence spectra of $\text{NaGd}_{1-x}\text{Eu}_x\text{F}_4$ upon excitation by light with $\lambda_{\text{ex}} = 395$ nm.

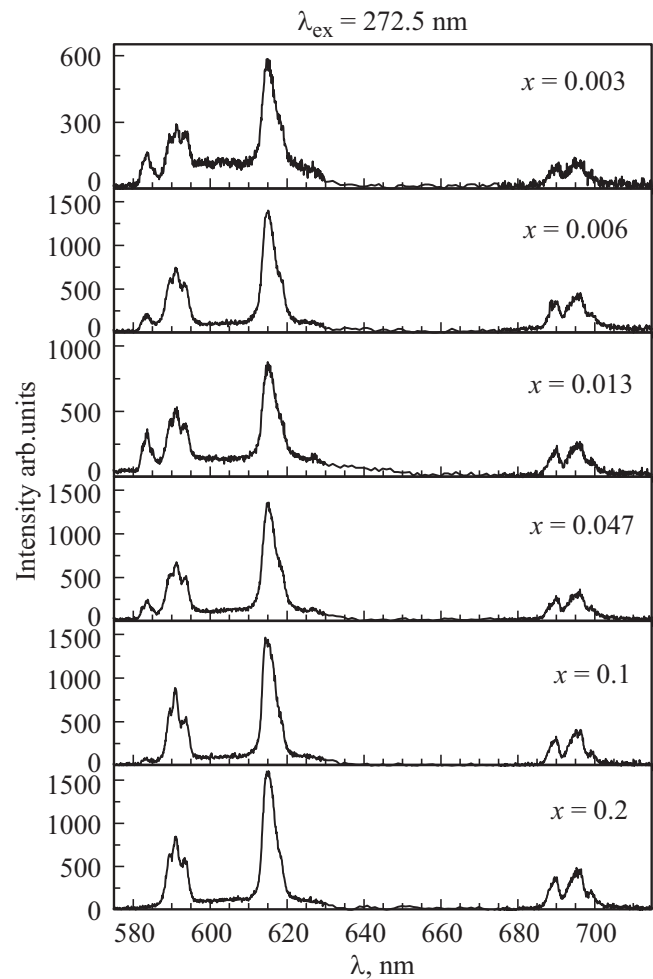


Figure 8. Luminescence spectra of $\text{NaGd}_{1-x}\text{Eu}_x\text{F}_4$ upon excitation by light with $\lambda_{\text{ex}} = 272.5$ nm.

the luminescence intensity of impurity ions of RE^{3+} is determined as

$$I_{ab} = A(ab)N_a h\nu_{ab}, \quad (1)$$

where $A(ab)$ — probability of radiative transition between levels a and b , N_a — concentration of excited ions and ν_{ab} — transition frequency, h — Planck's constant. During samples excitation by light the integral intensity increases up to europium concentration $x = 0.2$. It is obvious that this increasing is associated with N_a increasing. At low concentration of ions Eu^{3+} they can be assumed as free, i.e. we can neglect interionic interactions. For this hypothesis check the decay times of samples luminescence were determined. Figure 11 in semi-logarithmic scale presents the curves of attenuation of luminescence intensity of samples obtained at $\lambda_{\max} = 615$ nm for different concentrations of ions Eu^{3+} . Note that luminescence curves at $\lambda_{\max} = 592$ nm are similar to luminescence curves at $\lambda_{\max} = 615$ nm with accuracy to permanent multiplier, this indicates radiation from single initial state 5D_0 . These luminescence bands correspond to electro-dipole ${}^5D_0 \rightarrow {}^7F_2$ (615 nm) and magnetic dipole ${}^5D_0 \rightarrow {}^7F_1$ (592 nm) transitions. Figure shows that at low concentrations of ions

Eu^{3+} , namely $x < 0.2$, the luminescence curves are well approximated by straight lines, this indicates that the luminescence intensity is described by monoexponential law, and the ions can be considered isolated from each

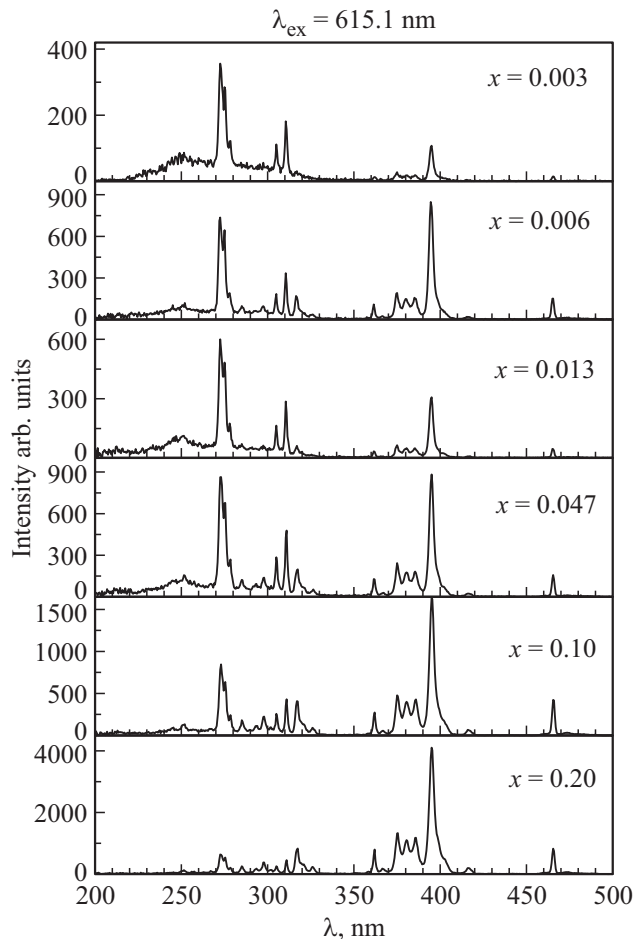


Figure 9. Luminescence excitation spectrum of $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$ ($0 \leq x \leq 0.2$), obtained at $\lambda_{\text{max}} = 615.1$ nm.

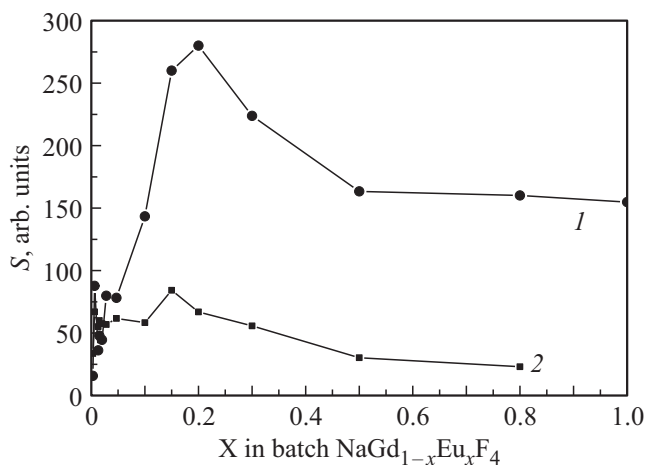


Figure 10. Concentration dependence of integral intensity of luminescence upon excitation by light: 1 — $\lambda_{\text{ex}} = 395$ nm; 2 — $\lambda_{\text{ex}} = 272.5$ nm.

Luminescence decay times at different concentrations of ions Eu^{3+}

x in $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$	τ_{exp} , ms		Average decay time $\bar{\tau}_{\text{exp}}$, ms
	$\lambda = 615$ nm	$\lambda = 592$ nm	
0.003	9.0	8.95	8.98
0.006	9.14	8.48	8.81
0.013	9.25	8.77	9.01
0.02	9.25	8.85	9.05
0.04	8.69	8.70	8.70
0.10	7.46	7.52	7.49
0.15	7.84	7.97	7.91
0.20	7.74	7.27	7.51
0.50	3.21	3.27	3.24
0.80	2.42	2.68	2.55
1.00	2.68	2.56	2.62

other. Note that luminescence curve for the sample with composition $\beta\text{-NaGd}_{0.8}\text{Eu}_{0.2}\text{F}_4$ ($x = 0.2$) is not described by simple monoexponential law, but has several components (see Figure 11). Such complex behavior may be associated with stimulated processes, which is also indicated by the maximum of luminescence intensity at this concentration (Figure 10) and requires a separate detailed study. Table shows decay times (τ_{exp}), measured at wavelengths of luminescence $\lambda = 615$ nm and $\lambda = 592$ nm, and average values of decay time ($\bar{\tau}_{\text{exp}}$) of luminescence of samples $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$ at $0.003 \leq x \leq 1$. According to Table dependence of luminescence decay times on concentration of doping admixture is observed. $\bar{\tau}_{\text{exp}}$ decreasing, presumably, indicates increase in interionic interaction between ions Eu^{3+} with europium concentration increasing. Average luminescence decay time for samples with $x = 0.003$ is $\bar{\tau}_{\text{exp}} \sim 9$ ms, it can be considered as life time of excited state 5D_0 .

At $x = 0.5$, 0.8 and 1.0 the time dependences of luminescence have small differences from mono-exponential dependences, which also indicates weak interionic interaction of ions Eu^{3+} . At $x = 0.20$ the maximum difference of luminescence kinetics from the mono-exponential dependence is observed. In this case the average decay time was estimated as equal to [6]:

$$\tau_{\text{mean}} = \frac{\int_0^{t_{\text{max}}} I(t) dt}{\int_0^{t_{\text{max}}} I(t) dt}, \quad (2)$$

where $I(t)$ — luminescence intensity of material, t_{max} — measurement time. Calculation by formula (2) leads to values $\tau_{\text{mean}} = 7.74$ and 7.27 ms.

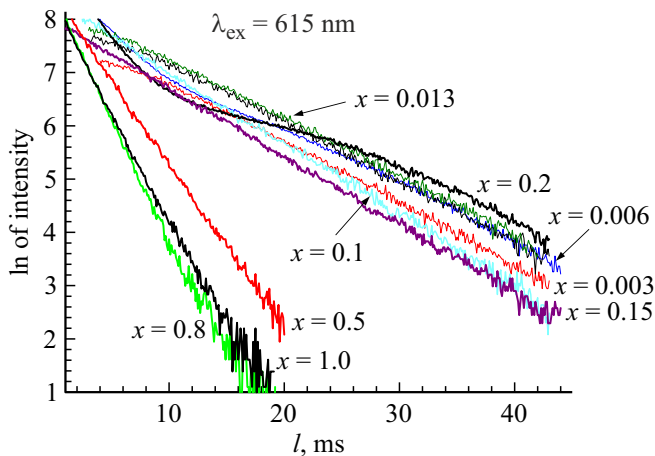


Figure 11. Curves of luminescence decay in semi-logarithmic scale taken at $\lambda_{\max} = 615$ nm.

From Table data it follows that with increase in concentration of europium ions the luminescence decay time of samples decreases, this in turn is associated with processes of luminescence quenching. It is known that life time of radiative term τ_0 is associated with probabilities of electronic transition of ion [19]:

$$\tau_0^{-1} = \sum_k A_{jk} + W. \quad (3)$$

In this formula τ_0 — the decay time of luminescence center due to intracenter transitions only, $\sum_k A_{jk}$ — sum of probabilities of radiative transition from level j to levels k . In case of ion Eu^{3+} this is sum of probabilities of transitions ${}^5D_0 \rightarrow {}^7F_J$, where $J = 1, 2, 4, 6$; W — rate of nonradiative multiphonon relaxation between excited multiplets [19]. In europium ion there is unique transition ensuring calculation of transitions probability in luminescence spectra. The fact is that the luminescence spectra contain an allowed magnetic transition ${}^5D_0 \rightarrow {}^7F_1$, its probability is practically independent of the crystal matrix and the point symmetry of the local environment of the center. Thus, comparing intensities of spectral bands we can evaluate probabilities of other spectral transitions, for example, transition ${}^5D_0 \rightarrow {}^7F_2$, and also calculate the luminescence parameters and life time of excited state. In paper [6] for the considered system $\text{NaGdF}_4:\text{Eu}$ the life time of level 5D_0 —7.5 ms was determined. Moreover, according to this paper the probability of transition ${}^5D_0 \rightarrow {}^7F_1$ is $\approx 48 \text{ s}^{-1}$. The experimental value W — rate of nonradiative multiphonon relaxation can be determined from a comparison of the radiative life times τ at given concentration and measured life time of term 5D_0 [19]. In studied samples at low concentrations Eu^{3+} the measured luminescence time $\tau_0 \sim 9$ ms is longer the time $\tau_0 = 7.5$ ms, obtained in paper [6], this can be attributed to difference in the synthesis technology. Based on the experimental data, it is possible to calculate the range of rates of nonradiative multiphonon relaxation W

(see formula (4)), which is of 0.3 to 280 s^{-1} upon change in concentration of ions Eu^{3+} from $x = 0.006$ to $x = 1.00$:

$$W = \tau_0^{-1} - \tau^{-1}. \quad (4)$$

Based on these data the quantum yield η of luminescence is [19]:

$$\eta = \sum_k A_{jk} / \left(\sum_k A_{jk} + W \right). \quad (5)$$

Calculation as per this formula gives the values $\eta \approx 30\text{--}90\%$. The made evaluations show that in the system under consideration there are small losses of electron excitation energy during laser excitation. More accurate evaluations of the quantum yield require measurement of temperature dependences $\tau_0(T)$. So, we can conclude that if the excitation of ions Eu^{3+} occurs by transfer of electron excitation energy from ions Gd^{3+} , like in studied case, this material can be considered as effective phosphor under UV excitation.

Based on the experimental data presented in this Section the following reasoning can be drawn. At low concentrations of europium ions, they can be considered isolated from each other, which is confirmed by the luminescence decay curves. Curves of integral luminescence of samples show that in samples complete quenching of LPO is absent, this in turn is associated with mechanism of energy transfer between ions of gadolinium and europium. One of the possible mechanisms of energy transfer is the resonance mechanism. [20,21]. As it is known, its implementation requires the overlap of the luminescence spectra of the donor with the absorption spectrum of the acceptor. In considered system it is necessary that luminescence spectrum of Gd^{3+} will be mainly overlapped by absorption spectrum Eu^{3+} . Luminescence excitation spectrum of samples $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$ at $0.003 \leq x \leq 0.1$ contain spectral bands Gd^{3+} , which shall be overlapped with luminescence excitation bands of ions Eu^{3+} , existing in range of wavelength $\sim 360\text{--}420$ nm. We can state that overlapping of spectra practically absent, and the resonance mechanism is not implemented. The most likely mechanism of excitation transfer is non-resonant energy transfer mechanism, which requires the donor radiation to be shorter wavelength than the acceptor radiation. [20,21]. This is implemented in case of pairs $\text{Gd}^{3+}\text{--}\text{Eu}^{3+}$, observed most intense bands Gd^{3+} are at $\lambda \sim 273$ and ~ 311 nm. At $x > 0.2$ the available minor deviation of the luminescence decay curves from the straight line dependences indicates that interionic interaction exists. Table shows that at $x > 0.15\text{--}0.20$ the luminescence decay time decreases for samples $\beta\text{-NaGd}_{1-x}\text{Eu}_x\text{F}_4$, which indicates increase in interionic interactions and possible process of migration of electron excitation energy [22]. It can be assumed that the migration of electron excitation during excitation of ions Gd^{3+} occurs efficiently, this is indicated by values of parameter of the nonradiative multiphoton relaxation $W \approx 0.3\text{--}280 \text{ cm}^{-1}$ and values of quantum yield of luminescence $\eta \approx 30\text{--}90\%$.

7. Conclusion

In present paper for the first time by method of hydrothermal synthesis the samples β -NaGd_{1-x}Eu_xF₄ are obtained, where $0 \leq x \leq 1$, their structure, morphology, IR and RS spectra, luminescence spectra and luminescence excitation spectra are studied, and the luminescence decay times of the synthesized samples are determined.

By method of X-ray diffraction analysis it is shown that considered samples are single-phase in entire concentration range. Obtained linear dependences of volume of unit cells of samples, as well offset of the diffraction line (201) selected for monitoring on the batch composition ensure an unambiguous conclusion about obtaining the solid solution β -NaGd_{1-x}Eu_xF₄. According to the results of electron microscopy, the obtained samples are mainly nanocrystals with particles size ~ 100 – 200 nm.

The measured spectra of IR-absorption of compound β -NaGd_{1-x}Eu_xF₄ agree with data of X-ray studies on keeping structure in entire concentration range of europium.

Luminescence spectra and luminescence excitation spectrum of solid solutions β -NaGd_{1-x}Eu_xF₄ are first studied in the entire concentration range $0 \leq x \leq 1$. Absence of complete luminescence quenching of system β -NaGd_{1-x}Eu_xF₄ is identified, and it is shown that luminescence excitation of this system by excitation of donor ions (Gd³⁺) leads to high quantum yield of luminescence ($\eta \approx 30$ – 90%), which indicates the possibility of this system use as effective phosphor, including for medical and biological problems.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] P.P. Fedorov, V.V. Semashko, S.L. Korableva. **58**, 3, 235 (2022). (in Russian).
- [2] M.A. Elyashevich, *Spektry redkikh zemel*. GITTL, M. (1953). 456 s. (in Russian).
- [3] D.N. Karimov, P.A. Demina, A.V. Koshelev, V.V. Rocheva, A.V. Sokovikov, A.N. Generalova, V.P. Zubov, E.V. Khaidukov, M.V. Kovalchuk, V.Ya. Panchenko. *Ros. nanotekhnologii*, **15**, 6, 699 (2020). (in Russian).

- [4] Ch. Liu, Zh. Gao, J. Zeng, Yi Hou, F. Fang, Y. Li, R. Qiao, L. Shen, H. Lei, W. Yang, M. Gao. *ACS Nano* **7**, 8, 7227 (2013).
- [5] D.V. Pominova, A.S. Bogatova, V.Yu. Proidakova, I.D. Romanishkin, E.V. Akhlyustina, S.V. Kuznetsov, T.A. Savelyeva, E.A. Lukyanets, V.B. Loschenov. *Biomed. Photon.* **10**, 4, 23 (2021).
- [6] Y. Cheroura, Z. Smara, A. Potdevin, D. Boyer, A. Chafa, O. Ziane, R. Mahiou. *Mater. Res. Bull.* **125**, 110809 (2020).
- [7] S.A. Burikov, O.D. Kotova, O.E. Sarmanova, S.V. Kuznetsov, V.Yu. Proidakova, V.V. Voronov, P.P. Fedorov, S.V. Patsaeva, T.A. Dolenko. *Pis'ma v ZhETF*, **111**, 9, 625 (2020). (in Russian).
- [8] H. Mai, Y. Zhang, L. Sun, C. Yan. *J. Phys. Chem.* **111**, 13730 (2007).
- [9] M. Banski, A. Podhorodeski, J. Misiewicz, M. Afzaal, A.L. Abdelhady, P. O'Brien. *J. Mater. Chem. C* **1**, 801 (2013).
- [10] M.A. Soldatov, P.V. Medvedev, V.V. Butova, i dr. *Poverkhnost. Rentgenovskie, sinkhrotronnye i nejtronnye issledovaniya*, **1**, 10 (2021). (in Russian).
- [11] M. Ranasinghe, Md. Arifuzzaman, A.C. Rajamanthilage, W.R. Willoughby, A. Dickey, C. McMillen, J.W. Kolis, M. Bolding, J.N. Anker. *RSC Adv.* **11**, 31717 (2021).
- [12] D.S. Yasyrkin. *Kand. dis. „Razrabotka metodov sinteza nanodispersnogo lyuminofera NaYF₄:Yb,Er dlya biomeditsinskikh issledovaniy“*. M. (2014)
 //chrome-extension://efaidnbmnnnibpcajpcgclefindmkaj/
 http://www.issp.ac.ru/ebooks/disser/Yasyrkina_D.S.pdf
- [13] Y.Q. Jia. *J. Solid State Chem.* **95**, 184 (1991).
- [14] M.M. Lage, R.L. Moreira, F.M. Matinaga, J.-Y. Gesland. *Chem. Mater.* **17**, 4523 (2005).
- [15] A. Bednarkiewicz, M. Mączka, W. Strek, J. Hanuza, M. Karbowski. *Chem. Phys. Lett.* **418**, 75 (2006).
- [16] M. Banski, A. Podhorodecki, J. Misiewicz, M. Afzaal, Ah.L. Abdelhady, P. O'Brien. *J. Mater. Chem. C* **1**, 4, 801 (2013).
- [17] D. Yuan, M.Ch. Tan, R.E. Riman, G.-M. Chow. *J. Phys. Chem.* **117**, 25, 13297 (2013).
- [18] M.I. Gaiduk, V.F. Zolin, L.S. Gaigerova. *Spektry lyuminesentsii evropiya*. Nauka, M. (1974). 195 s. (in Russian).
- [19] A.M. Tkachuk, M.V. Petrov, A.V. Khilko. *V sb.: Spektroskopija kristallov / Pod red. A.A. Kaplyanskogo*. Nauka, L., (1983). S. 106. (in Russian).
- [20] G.M. Zverev, I.I. Kuratev, A.M. Onishchenko. *V sb.: Spektroskopija kristallov / Pod red. A.A. Kaminskogo i dr.* Nauka, M. (1975), S. 184. (in Russian).
- [21] M.N. Tolstoj. *V sb.: Spektroskopija kristallov / Pod red. S.V. Grum-Grzhimailo i dr.* Nauka, M. (1970). S. 124. (in Russian).
- [22] N.V. Znamensky, Yu.V. Malyukin. *Spektry i dinamika opticheskikh perekhodov redkozemel'nykh ionov v kristallakh*. Fizmatlit, M., (2008), 192 s. (in Russian).

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