

Processes of excitation energy transport in EuPO_4 and EuP_3O_9 nanocrystals

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Processes of excitation energy transport were investigated for EuPO_4 and EuP_3O_9 nanocrystals, in which Eu^{3+} ions form three- and one-dimensional subsystems, respectively. It was determined that for EuPO_4 nanocrystals $^5\text{D}_0$ luminescence quenching manifested itself even at low temperatures due to effective phonon-assisted energy migration. At the same time, for EuP_3O_9 nanocrystals no influence of energy migration on the luminescence quenching was observed in the whole temperature range from 10 to 293 K that can be ascribed to modification of phonon spectra for EuP_3O_9 nanocrystals as compared to their bulk counterparts.

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1. Introduction

The impact of Victor V. Eremenko to the field of physics of low-dimensional systems is substantial and his ideas have made a pathway for a number of new findings including the one shown in our paper. As was shown in the number of his papers, transport processes are modified sufficiently in one- or two-dimensional organic [1] and inorganic [2] structures. Processes of energy migration between Eu^{3+} ions in bulk crystals with different arrangement of regular ions were discussed in the 1980th [3–8]. It was shown that the processes of energy migration to quenching centres for crystal matrices with Eu^{3+} as a regular ion are very effective due to absence of intermediate states between $^5\text{D}_J$ and $^7\text{F}_J$ levels of Eu^{3+} which otherwise could stimulate nonradiative relaxation of excited state (for instance, due to multiphonon relaxation or cross-relaxation of energy between neighbour ions) [9]. Most of such matrices with Eu^{3+} as a regular ion have shown the similar temperature dependence of energy migration [10]. In the range of low temperatures (less than up to 40–100 K depending on compound) migration of energy between Eu^{3+} ions required participation of phonons, so in this range decay time of $^5\text{D}_0$ luminescence was sufficiently temperature-dependent and decreased with increase of the temperature, while at higher temperatures decay times it almost did not depend on the temperature [11]. Investigations of the

crystals with different dimensionality of Eu^{3+} subsystem have shown that the processes of energy migration possess the same temperature and concentration dependence except for energy transfer rate that was higher for 3D than for 1D systems [11].

At the same time, as was shown recently [12–16] processes of excitation energy relaxation in doped nanocrystals can be more complex than the ones observed for bulk crystals. Modification of phonon spectra [12], high or low content of lattice defects [13,14], presence of surface groups [15] and regular ions in the distorted near-surface positions [16] can have sufficient influence on the energy relaxation processes. However, the combined action of size and dimensionality restriction on the processes of excitation energy relaxation was not investigated for doped nanocrystals until now.

In this paper the investigation the influence of both size and dimensionality restriction on the energy transport processes in phosphate nanocrystals with different arrangement of regular ions is shown. Processes of energy transport in EuP_3O_9 bulk materials were investigated before in [17,18]. As was shown in [4], energy migration in EuP_3O_9 is strongly anisotropic that is determined by specific structure of EuP_3O_9 which is characterized by one-dimensional Eu^{3+} chains with ~ 4.2 Å distance between Eu^{3+} ions in the same chain and ~ 7.3 Å between chains [19]. At the same time

Eu^{3+} substructure for EuPO_4 nanocrystals is three-dimensional without any sufficient anisotropy [20]. As will be shown in our paper both different dimensionalities of Eu^{3+} subsystems and transition from bulk crystals to nanocrystals can modify sufficiently the processes of energy transport in phosphate lattices.

2. Experimental part

EuP_3O_9 and $\text{LaP}_3\text{O}_9:\text{Eu}^{3+}$ (0.01 at.%) powders were synthesized by solid state method. Europium (III) oxide (Eu_2O_3), lanthanum (III) oxide (La_2O_3), and ammonium dihydrophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) taken in required proportions were milled in agate mortar, then heated to 600°C with heating speed of 50°C/h and maintained at this temperature for 10 hours. Then the powder again was grounded in an agate mortar, and annealed at 1000°C for 15 hours.

In order to obtain EuPO_4 nanocrystals, to 10 ml EuCl_3 solution (0.5 mol/l) H_3PO_4 solution (0.5 mol/l) was added till EuPO_4 precipitation. After centrifugation the precipitate was annealed at 1100°C in air during 5 hours.

The purity of crystal phase was controlled by XRD. The size of nanocrystals was controlled by TEM and average size was equal to ~ 30 nm.

Luminescence spectra of the nanocrystals were obtained using the computer-controlled setup based on the grating monochromator. Photoluminescence of the samples was excited by the fourth and second harmonic ($\lambda_{\text{exc}} = 266$ nm and 532 nm) of the neodymium-doped yttrium aluminium garnet ($\text{YAG}:\text{Nd}^{3+}$) laser EKSPLA NL-202/FH. All luminescence spectra were corrected to spectral sensitivity of the diffraction grating and normalized to intensity of ${}^5D_0 \rightarrow {}^7F_1$ (596 nm) transition.

The luminescence decay was taken using the time-correlated single-photon counting (TCSPC) technique at 10 , 77 and 300 K [21]. Decay curves were taken using ARS DE-204AE cryostat with LakeShore 335 temperature controller.

3. Results and discussion

The luminescence spectra for EuPO_4 and EuP_3O_9 nanocrystals ($\lambda_{\text{exc}} = 266$ nm) are shown in the Fig. 1. Both spectra reveal characteristic for $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$) spectral lines in the red region. For EuPO_4 nanocrystals Eu^{3+} cationic centre possesses tetragonal symmetry, which is characterized by presence of an inversion centre of symmetry, so intensity of ${}^5D_0 \rightarrow {}^7F_1$ (596 nm) transition is higher than intensity of ${}^5D_0 \rightarrow {}^7F_2$ (612 nm) one. The local symmetry of the rare-earth centre in REP_3O_9 structure is orthorhombic and lacks of the inversion symmetry making intensity of $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_2$ (616 nm) luminescence higher than intensity of ${}^5D_0 \rightarrow {}^7F_1$ (596 nm) one.

One more feature observed in the spectra of EuP_3O_9 nanocrystals is the wide intensive band with the maximum at about 540 nm which intensity depends strongly on the

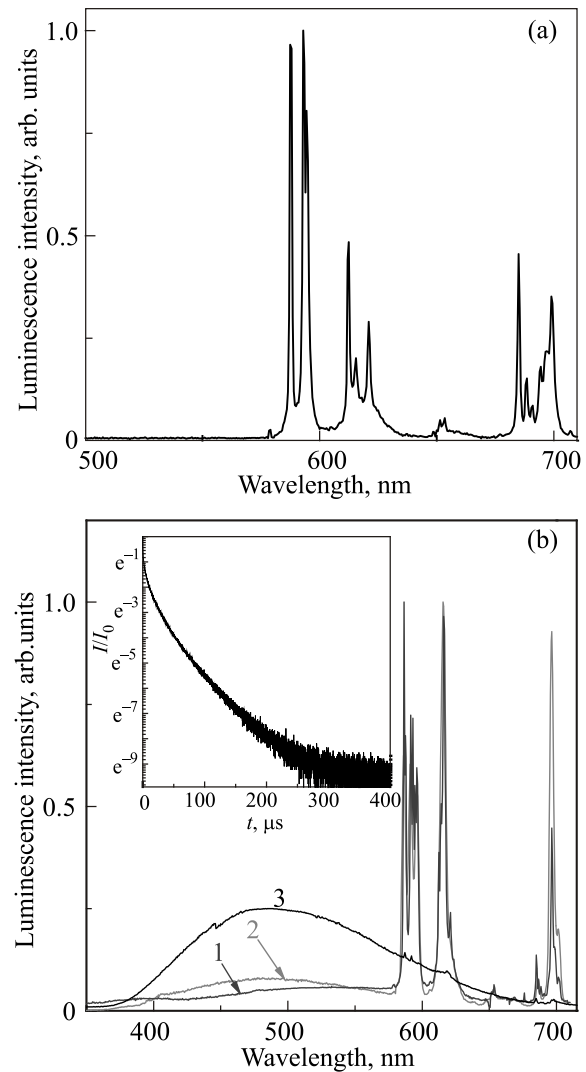


Fig. 1. Luminescence spectra of EuPO_4 nanocrystals (a): EuP_3O_9 nanocrystals (1), the same nanocrystals after treatment in vacuum (2), LaP_3O_9 nanocrystals (3) (b). $\lambda_{\text{exc}} = 266$ nm. In the inset — decay curve of 540 nm band for EuP_3O_9 nanocrystal. All spectra were taken at 293 K, corrected for spectral sensitivity and normalized to intensity of ${}^5D_0 \rightarrow {}^7F_1$ (596 nm) transition.

atmosphere of treatment. Such band was never reported previously for EuP_3O_9 or $\text{LaP}_3\text{O}_9:\text{Eu}^{3+}$ bulk materials [4,18]. Wide band with maximum at 400 nm was observed in Eu -doped LuP_3O_9 powders in [22], where authors based on the spectroscopic data and EPR analysis have determined that this band can be formed by $\text{Eu}^{2+} 5d \rightarrow 4f$ luminescence. Presence of such defect (three Eu^{2+} ions instead of two Eu^{3+} ions with the third Eu^{2+} ion between two Eu chains) could be also possible for EuP_3O_9 nanocrystals. However, the luminescence spectrum of pure LaP_3O_9 nanocrystals (Fig. 1(b)) also contains the similar band with maximum at 490 nm and it is reasonable to suppose that the bands in LuP_3O_9 and EuP_3O_9 have the same nature. Also the decay time of 540 nm band (~ 100 μs) is too long for $\text{Eu}^{2+} 5d \rightarrow 4f$ transitions, for which it is usually in the

range of few microseconds (Fig. 1(b), inset) [9]. Intensity of this band depends strongly on the atmosphere of treatment (in vacuum its intensity is more than in oxygen), one can suppose that this band has defect nature (probably, it is connected with oxygen vacancies).

In order to determine the peculiarities of energy transport within Eu^{3+} subsystems in EuPO_4 and EuP_3O_9 nanocrystals decay curves of $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_2$ (616 nm) luminescence were taken after excitation at 266 nm (via $\text{Eu}^{3+} - \text{O}^{2-}$ charge transfer band) and 532 nm (via $4f-4f$ transitions of Eu^{3+} ion) at temperature variation from 10 to 300 K. For EuPO_4 decay curves at 266 nm and 532 nm excitation coincide, so decay curves at 266 nm excitation only are shown (Fig. 2(a)). At 10 K decay curves are close to monoexponential with decay time $\tau_0 = 3$ ms. Increase of the temperature leads to quenching of Eu^{3+} luminescence and correspondent shortening of decay

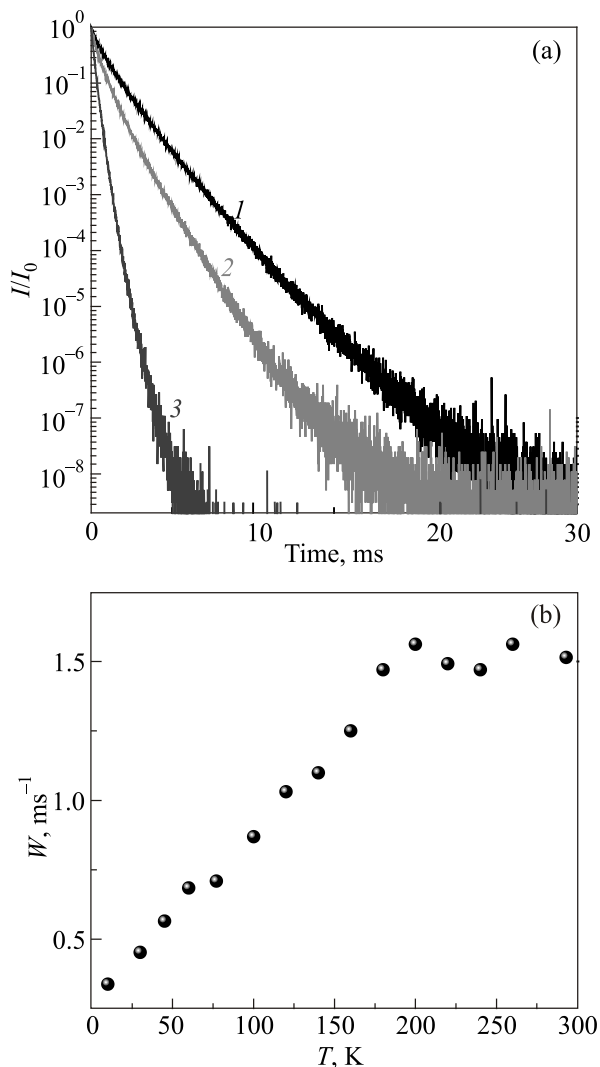


Fig. 2. (a) ${}^5D_0 \rightarrow {}^7F_2$ (612 nm) decay curves for EuPO_4 nanocrystals at different temperatures T , K: 10 (1), 77 (2), 293 (3) ($\lambda_{\text{exc}} = 266$ nm); (b) Temperature dependence of the rate of energy migration between Eu^{3+} ions obtained from analysis of decay curves.

time. Rate of energy migration can be determined from the last (exponential) stage of luminescence decay, which obeys well-known $\sim \exp(-t/\tau) = \exp(-t/\tau_0 - Wt)$ dependence, where W is the rate of migration. Fitting of the exponential stage of decay by this relation gives the dependence of the energy migration rate W on the temperature (Fig. 2(b)). According to [23] at dipole-dipole interaction between donor and acceptor of excitation energy migration rate $W = 11.404 \cdot N_a \cdot C_{DA}^{1/4} D^{3/4}$, where D is the diffusion coefficient, C_{DA} is the parameter of donor-acceptor interaction, N_a is the concentration of acceptors. In our case role of acceptors belong to defects of unknown nature (for instance, as acceptors can be considered Eu^{3+} ions in slightly distorted positions). Concentration of these defects is unknown but we can suppose with high probability its independence on the temperature. The same is true for C_{DA} , as donor-acceptor interaction usually do not depend sufficiently on the temperature. So, the increase of energy migration rate indicates an increase of diffusion coefficient.

Dependence of diffusion coefficient on the temperature can stem from the following premises. Processes of energy migration within Eu^{3+} subsystem are usually hampered by slight difference between positions of excited 5D_0 levels for nearest-neighbour ions. (This difference leads as well to the well-known effect of inhomogeneous broadening of spectral lines in absorption and luminescence spectra.) So the processes of energy transport between Eu^{3+} ions require participation of phonons, and increase of the temperature leads to more efficient migration. Moreover, at low temperatures only the lowest 7F_0 state of Eu^{3+} ion is populated and migration can take place only via ${}^5D_0 \rightarrow {}^7F_0$ transitions which are absolutely forbidden in the terms of selection rules (as $0 \leftrightarrow 0$ transitions), and so have vanishingly small oscillator strengths. At higher temperatures 7F_1 and even 7F_2 levels becomes thermally populated, so energy transport can occur via ${}^5D_0 \rightarrow {}^7F_{1,2}$ transitions do not obey $0 \leftrightarrow 0$ selection rule and so is far more effective.

Quite a different picture is observed for EuP_3O_9 nanocrystals. ${}^5D_0 \rightarrow {}^7F_2$ decay curves for EuP_3O_9 at different temperatures are shown in the Fig. 3(a) ($\lambda_{\text{exc}} = 266$ nm). Decay curve for EuP_3O_9 at 300 K is close to monoexponential with $\tau_0 = 4$ ms, while at lower temperatures the curve shows a sufficient deviation from monoexponential decay law at initial stage (however, the last stage of decay remain monoexponential with the same $\tau_0 = 4$ ms). Such behavior of decay curves is very untypical, because rate of energy migration usually increases with increase of the temperature [24]. This fact was especially mentioned in our previous paper [25] and even allows us to suppose that some specific kind of energy transfer is realized for these nanocrystals. However, more close investigation of luminescence spectra and decay curves have shown that such abnormal behaviour is probably determined by superposition of monoexponential decay of Eu^{3+} ions and short (~ 100 μs) decay of the defect band. Moreover, contrary to

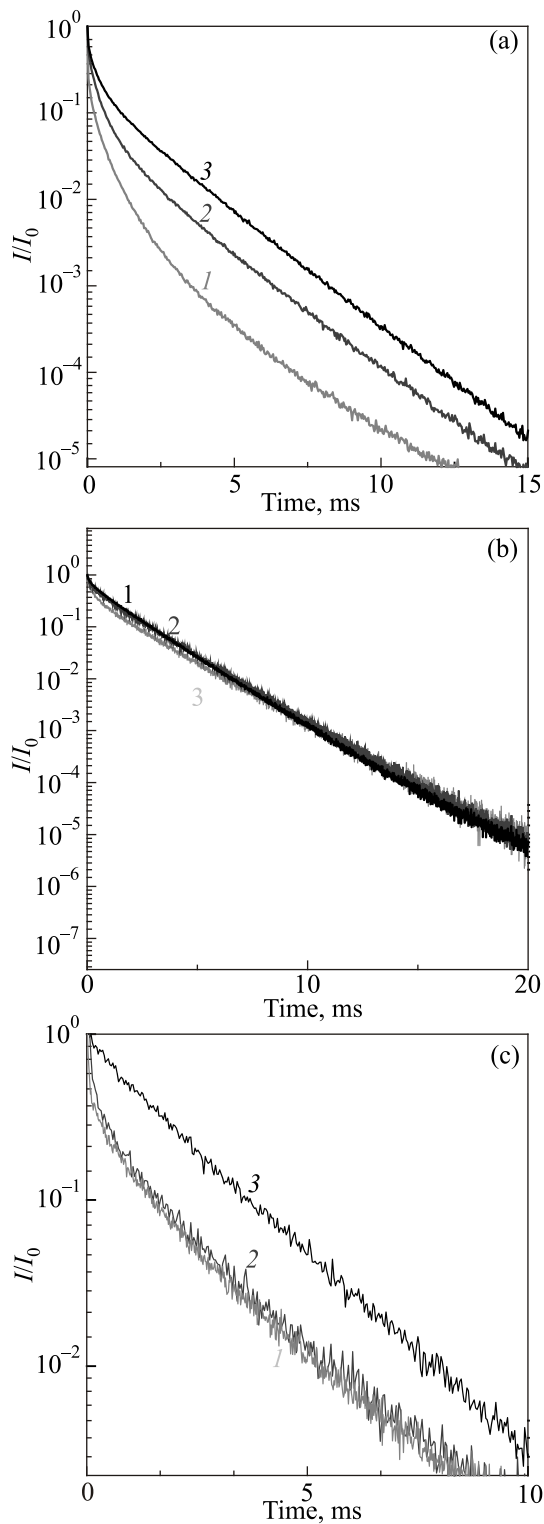


Fig. 3. ${}^5D_0 \rightarrow {}^7F_2$ (616 nm) decay curves at different T , K: (a) EuP₃O₉ nanocrystals at $\lambda_{\text{exc}} = 266$ nm 10 (1), 77 (2), 293 (3); (b) EuP₃O₉ nanocrystals at $\lambda_{\text{exc}} = 532$ nm 10 (1), 77 (2), 293 (3); (c) LaP₃O₉:Eu³⁺ at $\lambda_{\text{exc}} = 266$ nm 10 (1), 77 (2), 293 (3).

266 nm excitation, at intracenter $4f-4f$ excitation ($\lambda_{\text{exc}} = 532$ nm) ${}^5D_0 \rightarrow {}^7F_2$ luminescence decay curves are monoexponential at all temperatures (Fig. 3(b)).

${}^5D_0 \rightarrow {}^7F_2$ decay curves for LaP₃O₉:Eu³⁺ (0.01 at.%) at 77 K and 300 K ($\lambda_{\text{exc}} = 266$ nm) are shown in Fig. 3(c). Decay curve for LaP₃O₉:Eu³⁺ at 300 K is monoexponential with decay time ~ 4 ms. Decay curve for LaP₃O₉:Eu³⁺ at 77 K similar to EuP₃O₉ decay curve consists of two stages: initial non-monoexponential stage and subsequent exponential decay (~ 4 ms). At such a low Eu³⁺ concentration processes of energy migration between Eu³⁺ ions can be neglected, so decay time of 4 ms can be associated with intrinsic decay of Eu³⁺ centers and short initial decay is also determined by impact of decay of the wide band ($\lambda_{\text{max}} = 540$ nm, see Fig. 1(b)).

So, contrary to EuPO₄ nanocrystals, for EuP₃O₉ nanocrystals no impact of excitation energy migration on the processes of Eu³⁺ 5D_0 luminescence quenching was observed up to room temperature. This result agrees well with supposition [11] that in one- or two-dimensional systems processes of energy transport are generally less effective than for their three-dimensional counterparts. However, as was shown in [4], for bulk EuP₃O₉ with one-dimensional Eu³⁺ substructure migration of excitation energy being less effective than for their three-dimensional analogues (transfer rate for one-dimensional EuP₃O₉ $\approx 2 \cdot 10^4$ s⁻¹, for three-dimensional $\approx 7 \cdot 10^5$ s⁻¹) still can be observed via two phonon-assisted energy transfer. So, one can suppose that the processes of energy migration in EuP₃O₉ nanocrystals do not lead to any observable Eu³⁺ luminescence quenching not only due to one-dimensional arrangement of Eu³⁺ ions making possible energy transfer within Eu³⁺ chains only, but also due to hampering of phonon-assisted transfer of energy. The cause of this effect can be a subject of discussions, but it can be determined by the same premises as previously observed effects of luminescence from the upper Stark components of Pr³⁺ levels [26] and abnormal narrowing of Eu³⁺ spectral lines [27], namely, by depletion of phonon spectra in nanocrystals [4]. Modification of phonon spectra can be observed as for EuP₃O₉, so for EuPO₄ nanocrystals, but for EuP₃O₉ it would have more sufficient influence on the processes of energy migration as the excitation can be transferred only within the same chain. So, in this way restrictions of size and dimensionality can lead to hampering of energy migration processes in nanocrystals.

4. Conclusions

Peculiarities of energy migration in phosphate nanocrystals (EuP₃O₉ and EuPO₄) with different dimensionality of Eu³⁺ subsystem were revealed. It was shown that as the restriction of size, so the lowering of dimensionality of Eu³⁺ subsystem lead to hampering of phonon-assisted energy migration processes. While for EuPO₄ nanocrystals with three-dimensional arrangement of Eu³⁺ ions energy migration provides effective quenching of 5D_0 luminescence even for low temperatures, for EuP₃O₉

nanocrystals with one-dimensional arrangement of Eu^{3+} ions no influence of energy migration on the luminescence quenching processes was observed. This effect can be considered as the result of combined action of lower dimensionality of Eu^{3+} subsystem and of depletion of phonon spectra in nanocrystals.

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