

# Spectroscopically detected segregation of $\text{Pr}^{3+}$ ions in $\text{YPO}_4:\text{Pr}^{3+}$ nanocrystals

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Segregation of  $\text{Pr}^{3+}$  ions in  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals was revealed by means of spectroscopic techniques. Increase of doped ions concentration in the near-surface layer of  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals was confirmed by modification of luminescence spectra and decay curves depending on the heat treatment temperature. Relaxation of excess elastic stresses created by  $\text{Pr}^{3+}$  ion with volume greater than volume of regular  $\text{Y}^{3+}$  ion was determined to be the main cause of observed effects. Theoretical estimations obtained are in a good agreement with the experimental data.

С помощью спектроскопических методов выявлена сегрегация ионов  $\text{Pr}^{3+}$  в нанокристаллах  $\text{YPO}_4:\text{Pr}^{3+}$ . Локальное концентрирование ионов активатора в приповерхностном слое нанокристаллов  $\text{YPO}_4:\text{Pr}^{3+}$  подтверждено анализом спектров люминесценции и кривых затухания в зависимости от термообработки. Было установлено, что причиной этого эффекта является релаксация избытка упругих напряжений, создаваемых примесными ионами  $\text{Pr}^{3+}$  объем которых больше, чем у регулярных ионов  $\text{Y}^{3+}$ . Теоретические оценки хорошо согласуются с экспериментальными данными.

## 1. Introduction

Segregation of impurities near the defects of the crystal lattice can sufficiently change the local properties of solids. The peculiarities of mechanical properties and diffusion processes for grain boundaries and near-surface domains have been shown in a number of theoretical and experimental works [1–3]. Recently it was revealed that for nanocrystals the change of local properties can manifest itself also in change of bulk properties (such as luminescent properties) because the scale of segregation effects becomes comparable with the average size of nanocrystal [4–7]. For instance, in [8] it was shown that abnormal low threshold of luminescence concentration quenching in  $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$  nanocrystals is caused by high quota of segregated  $\text{Pr}^{3+}$  ions. The main cause of this segregation is the relaxation

of elastic stresses created by  $\text{Pr}^{3+}$  ion, which atomic radius (1.01 Å) is greater than atomic radius of regular  $\text{Y}^{3+}$  ion (0.9 Å).

For investigation of segregation processes peculiarities in  $\text{YPO}_4$  nanocrystals  $\text{Pr}^{3+}$  ion was chosen. The pattern of  $\text{Pr}^{3+}$  luminescence quenching is well-known and the difference between volumes of  $\text{Pr}^{3+}$  and  $\text{Y}^{3+}$  ion is rather large, so the segregation of  $\text{Pr}^{3+}$  near the surface of nanocrystal can be expected.

## 2. Experimental

$\text{YPO}_4:\text{Pr}^{3+}$  (0.3, 1, 3 at.%) nanocrystals were synthesized by methods of colloidal synthesis. An average size of nanocrystals was about 20 nm. Steady state luminescence was measured with a spectrofluorimeter on the basis of a grating monochromator. Luminescence decay was taken using the time-

correlated single-photon counting (TCSPC) technique [9]. Luminescence spectra and decay curves were collected in the confocal geometry [10]. The  ${}^1D_2 \rightarrow {}^3H_4$  luminescence was excited by argon laser ( $\lambda_{\text{exc}} = 488 \text{ nm}$ ) modulated by AOM.

### 3. Results and discussion

$\text{YPO}_4$  crystals exist in two possible modifications — monoclinic (monazite structure) and tetragonal (xenotime structure). The first one is observed for  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals for heat treatment temperatures less than  $400^\circ\text{C}$ , the second one — for heat treatment temperatures more than  $400^\circ\text{C}$ . In this paper only  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals with xenotime structure (temperature treatment at  $400^\circ\text{C}$  and more) will be considered.

The luminescence spectrum for  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals ( $C = 3 \text{ at. } \%$ ) is shown in Fig. 1. It consists of  ${}^1D_2 \rightarrow {}^3H_4$  and  ${}^3P_0 \rightarrow {}^3H_6$  luminescence bands and is similar to the spectrum of the bulk crystal [11]. In [11] was shown that for bulk  $\text{YPO}_4:\text{Pr}^{3+}$  crystals increase of doped ion concentration leads to quenching of  ${}^1D_2 \rightarrow {}^3H_4$  as compared to  ${}^3P_0 \rightarrow {}^3H_6$  luminescence. The same pattern of  ${}^1D_2 \rightarrow {}^3H_4$  relative intensity is observed at heat treatment temperature variation (Fig. 1, inset). So it can be supposed that increase of the heat treatment temperature leads to increase of local  $\text{Pr}^{3+}$  concentration in  $\text{YPO}_4$  nanocrystal due to segregation of  $\text{Pr}^{3+}$  ions.

The most reliable method for estimation of local doped ions concentration change is the analysis of  ${}^1D_2 \rightarrow {}^3H_4$  decay curves. Increase of doped ion concentration (or local concentration, as in our case) and consequently concentration quenching manifest itself in shortening of decay curves. Moreover, as was shown in [12] if the dipole-dipole mechanism of luminescence quenching can be supposed, the decay curve can be approximated by the expression  $I(t) = I_0 e^{-t/\tau_0 + \gamma t^{0.5}}$ , where  $\tau_0$  is the radiation time of an isolated center and  $\gamma$  is proportional to the concentration of doped ions  $\gamma \sim C$ .

To trace the segregation process in  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals with different doped ion concentrations the correspondent decay curves were measured. For  $0.3 \text{ at. } \%$  the decay curves for  $450^\circ\text{C}$  and  $700^\circ\text{C}$  coincide. The decay curves for  $1 \text{ at. } \%$  and  $3 \text{ at. } \%$  instead show the observable shortening at heat treatment temperature increase (Fig. 2).

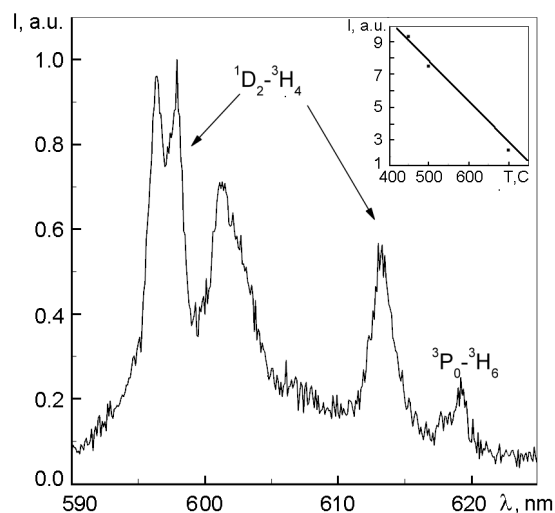


Fig. 1. Luminescence spectrum of  $\text{YPO}_4:\text{Pr}^{3+}$  ( $C = 3 \text{ at. } \%$ ) nanocrystals after heat treatment at  $T = 700^\circ\text{C}$ . Relative intensity of  ${}^1D_2 \rightarrow {}^3H_4$  luminescence band depending on the heat treatment temperature is shown in inset.

This shortening for  $3 \text{ at. } \%$  (Fig. 2b) is stronger than for  $1 \text{ at. } \%$  (Fig. 2a) and can be interpreted as quenching rate increase due to decrease of average distances between  $\text{Pr}^{3+}$  ions in nanocrystals at the heat treatment. This effect clearly confirms the idea of doped ions segregation in  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals which leads to increase of local  $\text{Pr}^{3+}$  concentration during the time of heat treatment.

To estimate the change of doped ions concentration the decay curves have been redrawn in the coordinates  $\{\ln(I/I_0) + t/\tau_0, t^{0.5}\}$ . The resulting curves are shown in Fig. 3. These curves are well fitted by  $\sim t^{0.5}$  law that allows to determine the value of  $\gamma$  as the slope of the curve to  $x$  axis. As it can be seen from Fig. 3a for  $1 \text{ at. } \%$   $\gamma$  increases from  $75 \mu\text{s}^{-0.5}$  to  $180 \mu\text{s}^{-0.5}$  as the temperature of heat treatment increases from  $450$  to  $700^\circ\text{C}$ . For  $3 \text{ at. } \%$   $\gamma$  increases from  $100 \mu\text{s}^{-0.5}$  to  $200 \mu\text{s}^{-0.5}$ . The value of the Forster constant  $\gamma$  is proportional to the concentration of doped ions:  $\gamma \sim C$ . So an increase in  $\gamma$  from  $75 \mu\text{s}^{-0.5}$  to  $180 \mu\text{s}^{-0.5}$  for samples with doped ions concentration of  $1 \text{ at. } \%$  means that local concentration of doped ions (near the surface of nanocrystal) increases during the heat treatment about 2.4 times. For  $3 \text{ at. } \%$  increase in  $\gamma$  from  $100 \mu\text{s}^{-0.5}$  to  $200 \mu\text{s}^{-0.5}$  corresponds to increase of local  $\text{Pr}^{3+}$  concentration about 2 times.

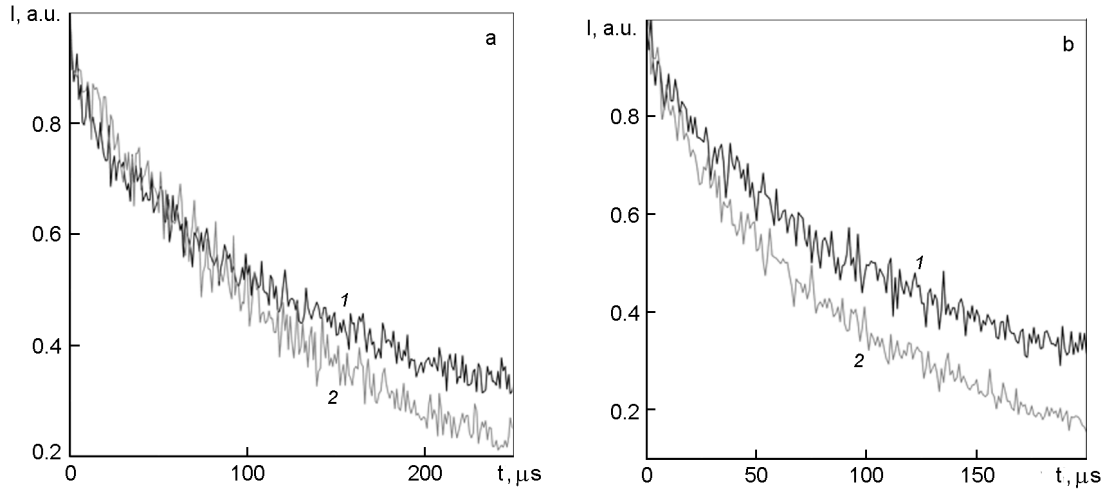


Fig. 2. Decay curves of  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals at  $\lambda_{reg} = 601 \text{ nm}$  (a — 1 at. %, b — 3 at. %).

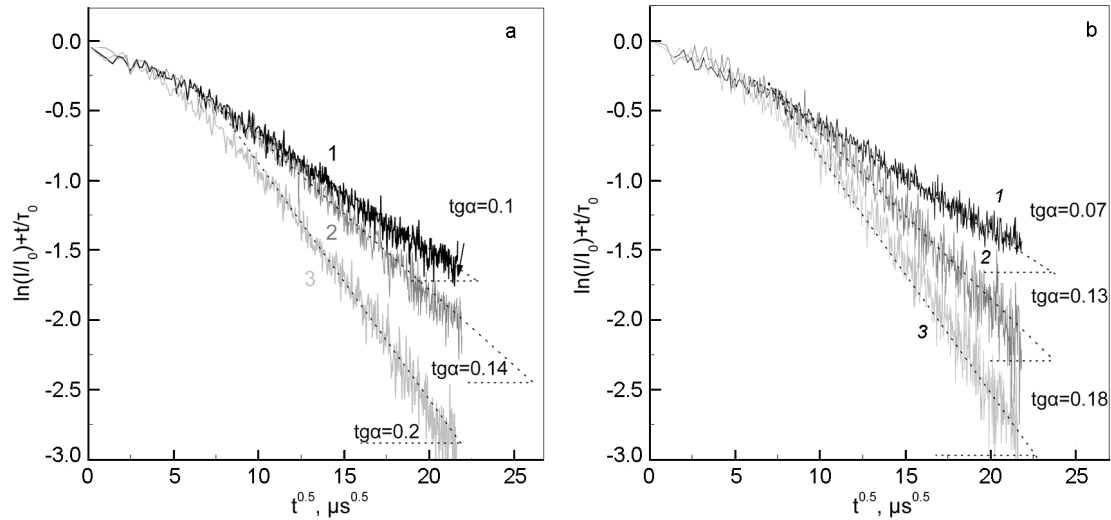


Fig. 3. Decay curves of  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals at  $\lambda_{reg} = 601 \text{ nm}$  (a — 1 at. %, b — 3 at. %) in coordinates  $\{\ln(I/I_0) + t/\tau_0, t^{0.5}\}$ .

The observed effect can be easily explained in the framework of segregation assumption. The difference between ionic volumes of regular and doped ions ( $\text{Pr}^{3+}$  ( $\sim 1.01 \text{ \AA}$ ) and  $\text{Y}^{3+}$  ( $\sim 0.9 \text{ \AA}$ )) can be considered as the key factor which can lead to non-uniform distribution of doped ions in  $\text{YPO}_4$  nanocrystal. Relaxation of elastic stresses created by doped  $\text{Pr}^{3+}$  leads to segregation of doped ions near the surface of nanocrystal.

For the quantitative estimation of the doped ion redistribution within  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystal we used the enrichment factor  $\chi = C_{surf} \cdot (1 - C_{bulk}) / C_{bulk} \cdot (1 - C_{surf})$ , where  $C_{bulk}$  and  $C_{surf}$  are bulk and surface concentrations of the segregated component, respectively [1, 13]. In equilibrium state, the

enrichment factor can be written as Boltzman term [1]:

$$\chi = \exp(-E_{el}/kT), \quad (1)$$

where  $E_{el} = 2G^2(\Delta\Omega^2/3\pi K r_1^3)$  is the total elastic energy created by the impurity ion,  $G$  and  $K$  are shear and bulk modulus of the host matrix,  $T$  is temperature.

For  $\text{YPO}_4:\text{Pr}^{3+}$  nanocrystals  $G = 55 \text{ GPa}$ ;  $K = 74 \text{ GPa}$  (the elastic constants for  $\text{YPO}_4:\text{Pr}^{3+}$  were taken from [14]);  $r_1 = 1.01 \text{ \AA}$  and  $r_2 = 0.9 \text{ \AA}$ . So the total elastic energy created by impurity ion is about  $0.07 \text{ eV}$  ( $E_{el}/kT \approx 3$ ). According to Eq.(2), at room temperature the enrichment factor  $\chi$  is equal to 3.62. In other words, for bulk doped ions concentration  $C_{bulk} = 1 \text{ at.}\%$ , the

surface concentration of doped ions  $C_{surf}$  must be about 3.2 at.% and for  $C_{bulk} = 3$  at.%,  $C_{surf} \approx 8.9$  at.%, i.e. about three times higher. These results correlate with ones obtained from the decay curves analysis.

#### 4. Conclusions

The influence of doped ions segregation on the luminescence properties was shown for doped  $YPO_4:Pr^{3+}$  nanocrystals. Increase of local  $Pr^{3+}$  concentration at heat treatment temperature increase was confirmed by luminescence spectra and decay curves modification. Estimations of doped ions redistribution value have shown that concentration of  $Pr^{3+}$  ions near the surface of  $YPO_4:Pr^{3+}$  nanocrystal must be about three times higher than in the bulk (about 2.8 at.% for bulk concentration of 1 at.% and about 8.9 at.% for bulk concentration of 3 at.%). This estimation is in a good agreement with the results obtained from the analysis of correspondent decay curves.

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## Спектроскопічно виявлена сегрегація іонів $Pr^{3+}$ у нанокристалах $YPO_4:Pr^{3+}$

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За допомогою спектроскопічних методів була виявлена сегрегація іонів  $Pr^{3+}$  в нанокристалах  $YPO_4:Pr^{3+}$ . Підвищення концентрації іонів активатора в приповерхневому шарі нанокристалів  $YPO_4:Pr^{3+}$  було підтверджено аналізом спектрів люмінесценції і кривих загасання в залежності від термообробки. Було встановлено, що причиною цього ефекту є релаксація надлишку пружних напружень які створюються іонами  $Pr^{3+}$  що мають об'єм більший, ніж у регулярних іонів  $Y^{3+}$ . Теоретичні оцінки добре узгоджуються з експериментальними даними.