

Spectroscopically detected segregation of Pr³⁺ ions in Y₂SiO₅ nanocrystals

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Segregation of Pr³⁺ ions in Y₂SiO₅:Pr³⁺ nanocrystals was revealed by means of spectroscopic techniques. Increase of doped ions concentration in the near-surface layer of Y₂SiO₅:Pr³⁺ nanocrystals was confirmed by modification of luminescence spectra with the heat treatment temperature. Relaxation of excess elastic stresses created by Pr³⁺ ions with volumes greater than volume of regular Y³⁺ ion was determined to be the main cause of observed effects. Theoretical estimations clearly confirm the preliminary predictions.

Keywords: Segregation, Luminescence, Nanocrystals, Energy transfer.

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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 wide range of theoretical and experimental works [1-3]. Recently 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 range of segregation effects becomes comparable with the average size of nanocrystal. Such pattern was revealed for YAG:Nd and YAG:Ce nano-ceramics [4, 5], SnO₂:Eu³⁺ nanocomposites [6] and Y₂O₃:Eu³⁺ phosphors [7]. In [8] the abnormal low threshold of luminescence concentration quenching was revealed for Y₂SiO₅:Pr³⁺ nanocrystals. The preliminary interpretation was given [9], according to which the low concentration quenching threshold in these nanocrystals was caused by non-uniform distribution (segregation) of doped ions within the volume of nanocrystal. The main mechanism of this segregation is the relaxation of elastic stresses created by Pr³⁺ ion, which atomic radius (1.01 Å) is greater than atomic radius of regular Y³⁺ ion (0.9 Å). In this paper we confirm the preliminary interpretation and trace the processes of doped ions segregation in Y₂SiO₅:Pr³⁺ nanocrystals.

2. EXPERIMENTAL METHODS

Y₂SiO₅:Pr³⁺ nanocrystals were synthesized by the sol-gel technique [10]. The average size of nanocrystals was about 50 nm. The steady state luminescence was measured with a spectrofluorimeter on the base of a grating monochromator. The luminescence decay was taken using the time-correlated single-photon counting (TCSPC) technique [11]. Luminescence spectra and decay curves were collected in the confocal geometry [12]. The ¹D₂→³H₄ luminescence was excited by argon laser (λ_{exc} = 488 nm) modulated with AOM.

3. RESULTS AND DISCUSSION

For a wide range of Pr³⁺ doped bulk and nanocrystals the strong dependence of ¹D₂→³H₄ luminescence intensity on the Pr³⁺ concentration was shown [13, 14]. Namely, increase of Pr³⁺ concentration from 0.1 to 5 at. % manifested itself in ¹D₂→³H₄ luminescence quenching. At the same time ³P₀→³H₆ luminescence does not exhibit any observable quenching in this concentration range, so the ratio between ¹D₂→³H₄ and ³P₀→³H₆ spectral bands depends on concentration of doped ions.

The luminescence spectra of Y₂SiO₅:Pr³⁺ nanocrystals for different doped ions concentration are shown in Fig. 1.

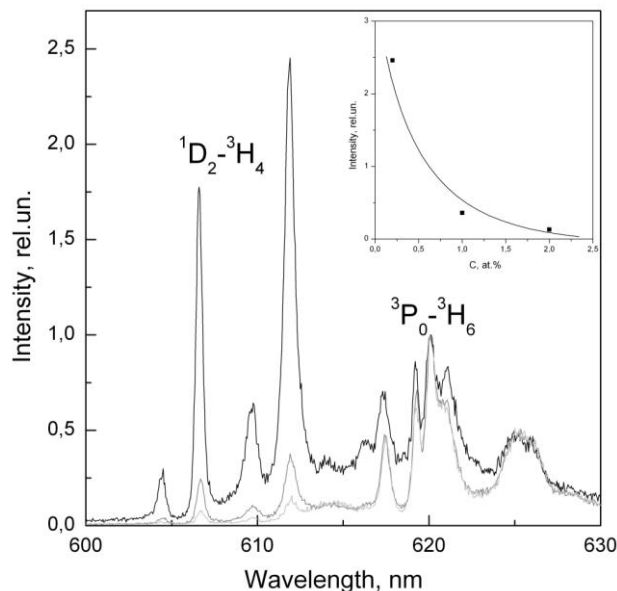


Fig. 1 – Concentration dependence of ¹D₂→³H₄ luminescence intensity for Y₂SiO₅:Pr³⁺ nanocrystals (0.2, 1 and 2 at.% are shown)

Increase of doped ion concentration leads to strong quenching of ¹D₂→³H₄ luminescence in relation to ³P₀→³H₆ luminescence. Moreover, this quenching is more strong than in the case of bulk Y₂SiO₅:Pr³⁺ crys-

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tals [13] and the threshold of luminescence concentration quenching is lower. $^1D_2 \rightarrow ^3H_4$ luminescence decay curves (Fig. 2) for $Y_2SiO_5:Pr^{3+}$ nanocrystals exhibit so-called ordered stage with linear dependence of slope angle from the time.

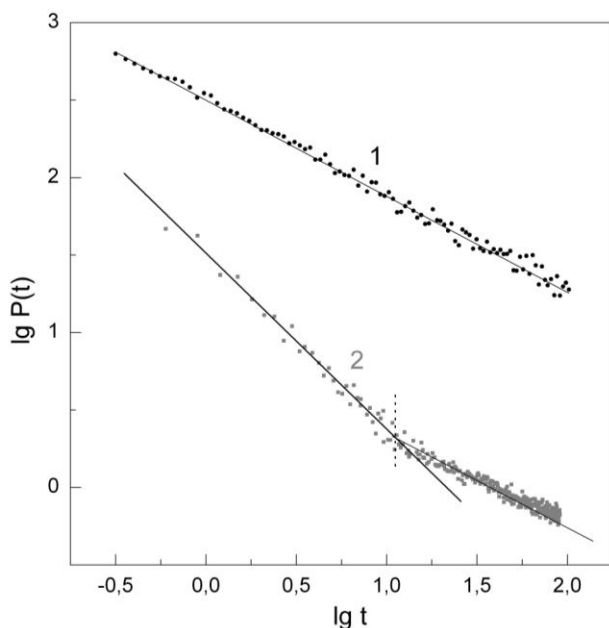


Fig. 2 – Quenching functions for $Y_2SiO_5:Pr^{3+}$ bulk (1) and nanocrystals (2) at 2 at.%

This stage occurs when in the crystal there are a lot of doped ion pairs (i.e. doped ions separated by minimal permissible distances) [15]. For the bulk $Y_2SiO_5:Pr^{3+}$ crystals this stage of quenching was never observed. Occurrence of the ordered stage in the decay curves as well as the low threshold of luminescence concentration quenching can be considered as an evidence of non-uniform doped ions distribution within the volume of nanocrystal. In another words, in $Y_2SiO_5:Pr^{3+}$ nanocrystals regions with high doped ion concentration are present. The most reliable explanation of this non-uniformity is the segregation of doped Pr^{3+} ions near the surface of nanocrystal. The same effect is observed for bulk crystals too, but, as the quota of segregated ions as compared to total doped ions quantity in this case is rather small, these segregated ions cannot manifest itself in change of luminescent properties of the crystal.

To confirm the segregation nature of this effect and to trace the segregation processes in $Y_2SiO_5:Pr^{3+}$ nanocrystals the concentration and heat treatment temperature were varied. As the segregation process is the temperature activated one, the increase of heat treatment time must lead to the increase of doped ions concentration near the surface of nanocrystal. The luminescence spectra for $Y_2SiO_5:Pr^{3+}$ nanocrystals with 0.2, 1 and 2 at.% are shown in Fig. 3.

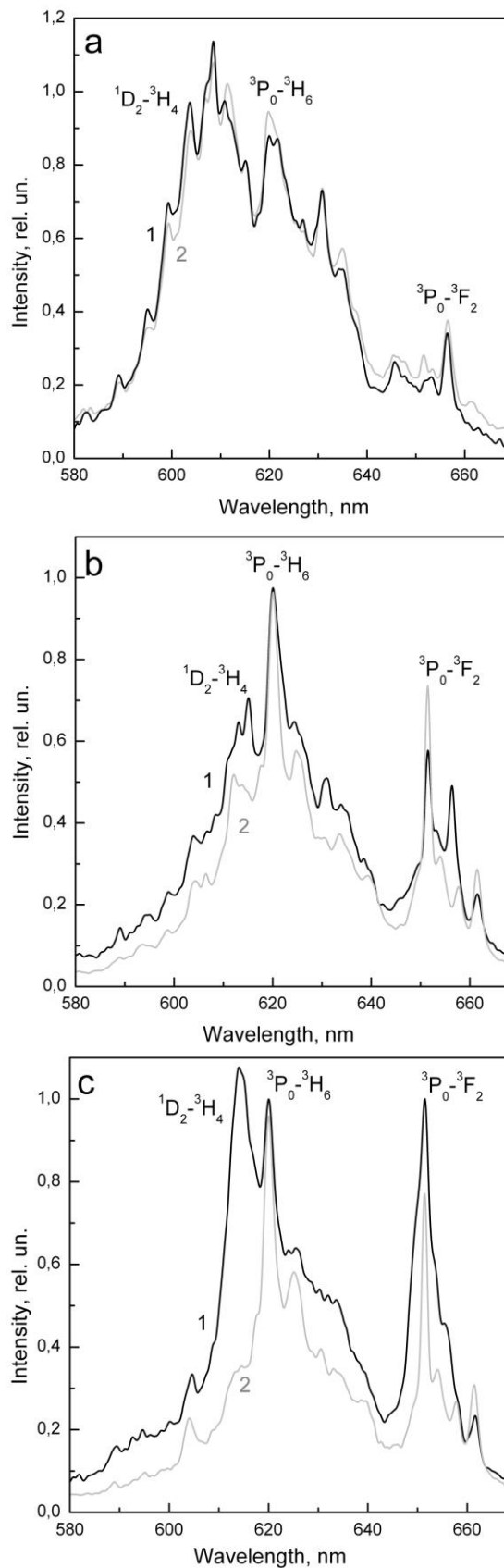


Fig. 3 – Luminescence spectra for $Y_2SiO_5:Pr^{3+}$ nanocrystals (a – 0.2 at.%, b – 1 at.%, c – 2 at.%) for 0 (curve 1) and 4 (curve 2) hours of heat treatment

For concentration of 0.2 at.% the heat treatment does not change the relative intensity of $^1D_2 \rightarrow ^3H_4$ luminescence band (3a), so in this case segregation of doped ions does not have any visible influence on the luminescence quenching processes in the nanocrystal. For concentrations of 1 and 2 at.% increase of heat treatment time from 0 to 4 hours leads to sufficient quenching of $^1D_2 \rightarrow ^3H_4$ luminescence band relative to $^3P_0 \rightarrow ^3H_6$ band. Namely, at doped ions concentration of 1 at.% relation between intensities of $^1D_2 \rightarrow ^3H_4$ for 0 and 4 hours of heat treatment is $\approx 1,2$ (Fig. 3b), while for 2 at.% $\approx 1,9$ (Fig. 3c). These results correspond well with theoretical estimations of average distances between impurity centers in the volume of nanocrystal and near its surface for different doped ions concentrations. Average distances between doped ions were estimated as $d_{vol} = (V/N)^{1/3}$ – for doped ions in the bulk of nanocrystal and $d_{surf} = (S/N)^{1/2}$ – for ions placed near the surface. Here $N = C \cdot 4/3\pi R^3$ – total quantity of doped Pr^{3+} ions in the nanocrystal, R , V and S – radius, volume and surface area of nanocrystal, respectively. Dependence of d_{vol}/d_{surf} ratio on the concentration of doped ions is shown in Fig. 4.

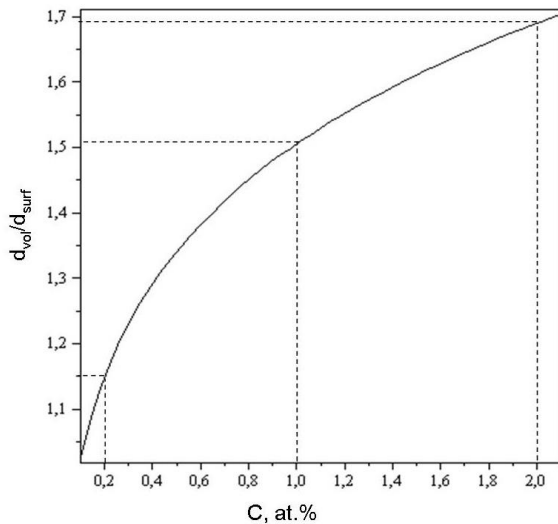


Fig. 4 – Dependence of distances ratio between doped ions in the volume and near the surface of 20 nm nanocrystal on doped ions concentration

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At doped ions concentration of 0.2 at.% even at full segregation of doped ions the decrease of average distance near the surface of nanocrystal as compared to the average distance inside the nanocrystal is about 1.15 (from 3.7 to 3.2 nm). Such a small decrease cannot lead to any obvious intensification of quenching processes in the nanocrystal, as the energy transfer probability $w_{da} \sim 1/r^6$ [15] would be negligibly small as in the first, so in the second case. The situation is rather different for concentration of 1 and 2 at.%. According to calculated dependence (Fig. 4) the average distances between subsurface ions for these concentrations will be 1.5 and 1.7 times smaller than for ions resided in the bulk. Such shortening (from 2.2 nm to 1.45 nm at 1 at.% and from 1.75 nm to 1 nm at 2 at.%) leads in turn to sufficient quenching of $^1D_2 \rightarrow ^3H_4$ luminescence in $Y_2SiO_5:Pr^{3+}$ nanocrystals at Pr^{3+} concentrations of 1 and 2 at.%.

To estimate a local concentration of doped ions near the surface of $Y_2SiO_5:Pr^{3+}$ nanocrystal we have used the theory of surface segregation [1 - 3]. According to [1], the main characteristic of this process is so-called enrichment factor $\chi = C_{surf}(1 - C_{bulk})/C_{bulk}(1 - C_{surf})$, where C_{bulk} and C_{surf} are the bulk and surface concentrations of the segregated component, respectively. In equilibrium state, the enrichment factor can be written as the Boltzman term: $\chi = \exp(-E_{el}/kT)$, where $E_{el} = 2G^2(\Delta\Omega)^2/3\pi Kr_1^3$ is the total elastic energy created by the impurity ion, G and K are the shear and the bulk modulus of the host matrix, T is the temperature.

For $Y_2SiO_5:Pr^{3+}$ nanocrystals $G = 47$ GPa; $K = 108$ GPa (the elastic constants for $Y_2SiO_5:Pr^{3+}$ were taken from [16]); $r_1 = 1.01$ Å and $r_2 = 0.9$ Å. At room temperature the enrichment factor χ is equal to 4.26. In other words, for bulk dopant concentration $C_{bulk} = 1$ at.% the surface dopant concentration C_{surf} must be equal to about 4 at.%, while for $C_{bulk} = 2$ at.% - about 8 at.%, i.e. four times higher. The high concentration of doped ions near the surface is the source of the effects described earlier (such as occurrence of ordered stage in decay curves and low threshold of concentration quenching) and it provides difference between bulk crystal and nanocrystal luminescence properties.