Spectroscopically detected segregation of Pr\textsuperscript{3+} ions in YPO\textsubscript{4}:Pr\textsuperscript{3+} nanocrystals

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Segregation of Pr\textsuperscript{3+} ions in YPO\textsubscript{4}:Pr\textsuperscript{3+} nanocrystals was revealed by means of spectroscopic techniques. Increase of doped ions concentration in the near-surface layer of YPO\textsubscript{4}:Pr\textsuperscript{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 Pr\textsuperscript{3+} ion with volume greater than volume of regular Y\textsuperscript{3+} ion was determined to be the main cause of observed effects. Theoretical estimations obtained are in a good agreement with the experimental data.

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 Y\textsubscript{2}SiO\textsubscript{5}:Pr\textsuperscript{3+} nanocrystals is caused by high quota of segregated Pr\textsuperscript{3+} ions. The main cause of this segregation is the relaxation of elastic stresses created by Pr\textsuperscript{3+} ion, which atomic radius (1.01 Å) is greater than atomic radius of regular Y\textsuperscript{3+} ion (0.9 Å).

For investigation of segregation processes peculiarities in YPO\textsubscript{4} nanocrystals Pr\textsuperscript{3+} ion was chosen. The pattern of Pr\textsuperscript{3+} luminescence quenching is well-known and the difference between volumes of Pr\textsuperscript{3+} and Y\textsuperscript{3+} ion is rather large, so the segregation of Pr\textsuperscript{3+} near the surface of nanocrystal can be expected.

2. Experimental

YPO\textsubscript{4}:Pr\textsuperscript{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 spectrophotometer 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 ($\lambda_{\text{exc}} = 488$ nm) modulated by AOM.

3. Results and discussion

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

The luminescence spectrum for YPO$_4$:Pr$^{3+}$ nanocrystals (C = 3 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 YPO$_4$: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 Pr$^{3+}$ concentration in YPO$_4$ nanocrystal due to segregation of 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 $R(t) = I_0 e^{-t/\tau_0} + p_{0.5}$, where $\tau_0$ is the radiation time of an isolated center and $p$ is proportional to the concentration of doped ions $p \sim C$.

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

This shortening for 3 at. % (Fig. 2b) is stronger than for 1 at. % (Fig. 2a) and can be interpreted as quenching rate increase due to decrease of average distances between Pr$^{3+}$ ions in nanocrystals at the heat treatment. This effect clearly confirms the idea of doped ions segregation in YPO$_4$:Pr$^{3+}$ nanocrystals which leads to increase of local 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 $\ln(I/I_0) + t/\tau_0$, $p_{0.5}$. The resulting curves are shown in Fig. 3. These curves are well fitted by $~t^{0.5}$ law that allows to determine the value of $p$ as the slope of the curve to $x$ axis. As it can be seen from Fig. 3a for 1 at. % $\gamma$ increases from 75 $\mu$s$^{-0.5}$ to 180 $\mu$s$^{-0.5}$ as the temperature of heat treatment increases from 450 to 700°C. For 3 at. % $\gamma$ increases from 100 $\mu$s$^{-0.5}$ to 200 $\mu$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 $\mu$s$^{-0.5}$ to 180 $\mu$s$^{-0.5}$ for samples with doped ions concentration of 1 at. % means that local concentration of doped ions (near the surface of nanocrystal) increases during the heat treatment about 2.4 times. For 3 at. % increase in $\gamma$ from 100 $\mu$s$^{-0.5}$ to 200 $\mu$s$^{-0.5}$ corresponds to increase of local Pr$^{3+}$ concentration about 2 times.
Fig. 2. Decay curves of YPO₄·Pr³⁺ nanocrystals at λₘ = 601 nm (a - 1 at. %, b - 3 at. %).

Fig. 3. Decay curves of YPO₄·Pr³⁺ nanocrystals at λₘ = 601 nm (a - 1 at. %, b - 3 at. %) in coordinates (ln(I/I₀) + t/τ₀, t₀⁻¹).

The observed effect can be easily explained in the framework of segregation assumption. The difference between ionic volumes of regular and doped ions (Pr³⁺ (~1.01 Å) and Y³⁺ (~0.9 Å)) can be considered as the key factor which can lead to non-uniform distribution of doped ions in YPO₄ nanocrystal. Relaxation of elastic stresses created by doped Pr³⁺ leads to segregation of doped ions near the surface of nanocrystal.

For the quantitative estimation of the doped ion redistribution within YPO₄·Pr³⁺ nanocrystal we used the enrichment factor \( \chi = C_{\text{surf}}(1 - C_{\text{bulk}})/C_{\text{bulk}}(1 - C_{\text{surf}}) \), where \( C_{\text{bulk}} \) and \( C_{\text{surf}} \) 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]:

\[
\chi = \exp(-E_{el}/kT),
\]

where \( E_{el} = 2G^2\Delta\Omega^2/3\pi Jr_1^3 \) 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 YPO₄·Pr³⁺ nanocrystals \( G = 55 \) GPa; \( K = 74 \) GPa (the elastic constants for YPO₄·Pr³⁺ were taken from [14]); \( r_1 = 1.01 \) Å and \( r_2 = 0.9 \) Å. So the total elastic energy created by impurity ion is about 0.07 eV (\( E_{el}/kT = 3 \)). According to Eq.(2), at room temperature the enrichment factor \( \chi \) is equal to 3.62. In other words, for bulk doped ions concentration \( C_{\text{bulk}} = 1 \) at.%,
The surface concentration of doped ions $C_{\text{surf}}$ must be about 3.2 at.% and for $C_{\text{bulk}} \approx 3$ at.%, $C_{\text{surf}} = 8.9$ 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 re-distribution 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.

References


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 активації в приповерхневому шарі нанокристалів YPO$_4$:Pr$^{3+}$ було підтверджено аналізом спектрів лумінесценції і кривих загасання в залежності від термообробки. Було встановлено, що причиною цього ефекту є релаксація надміру пружних напруження які створюються іонами Pr$^{3+}$ що мають об’єм більший, ніж у регулярних іонів Y$^{3+}$. Теоретичні оцінки добре узгоджуються з експериментальними даними.