

Mechanisms of local inhomogeneity of dopant concentration in $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ nanocrystals

*V.V.Seminko, A.A.Masalov, Yu.V.Malyukin, Yu.I.Boyko**

Institute for Scintillation Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave, 61001 Kharkiv, Ukraine

*V.Karazin Kharkiv National University, 4 Svobody Sq., 61077 Kharkiv, Ukraine

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The causes of local inhomogeneity of Pr^{3+} concentration in $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ nanocrystals are discussed. To explain this effect, two physical models have been proposed: the first one based on the fact that the dopant ion force field in the near-surface layer is inhomogeneous and the second, on inhomogeneous of a nanocrystal surface curvature. The ratio between the near-surface dopant concentration and bulk one estimated according the first model is about 4, the ratio between the dopant concentrations in the different nanocrystal regions estimated within the second one is about 1.4. The quantitative estimations show clearly that the both models can be used to explain the segregation effect in $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ nanocrystals, but the contribution of the first mechanism exceeds that of the second one.

Рассмотрены причины локальной неоднородности концентрации Pr^{3+} в нанокристаллах $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$. Для объяснения этого эффекта предложены две физические модели: одна основана на неоднородности силового поля иона активатора в приповерхностном слое, а вторая - на неоднородности кривизны поверхности нанокристалла. Оценки в рамках первой модели дают отношение приповерхностной и объемной концентраций активатора около 4; согласно оценкам по второй модели, отношение концентраций активатора в различных областях нанокристалла составляет около 1,4. Количественные оценки показывают, что для объяснения эффекта сегрегации в нанокристаллах $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ могут использоваться обе модели, однако вклад первого механизма превышает вклад второго.

1. Introduction

Production of rare-earth activated luminescent materials with high activator ion concentrations is an important task for various possible applications [1–4]. However, the increase possibilities of the activator concentration are usually strongly limited (for instance, for the bulk crystals, it is connected with the limited entering coefficient of the crystal). Thus, the effect of local concentration increase in $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ nanocrystals discussed in this paper can be used in the field of creation of luminescent materials with enhanced activator concentrations. The luminescence spectra and

decay curves of $^1D_2 \rightarrow ^3H_4$ luminescence in $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ nanocrystals considered in [5–7] demonstrate unambiguously the presence of considerable amount of Pr^{3+} ion pairs separated by the minimum acceptable distance for this lattice even at small activator concentrations, that have not been observed in the bulk $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ crystals. The formation of numerous activator ion pairs at low Pr concentrations suggests the segregation of the activator ions (i.e. the formation of regions with a large concentration inhomogeneity) in $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ nanocrystals.

2. Results and discussion

We propose two possible models explaining the segregation of activator ions in $Y_2SiO_5:Pr^{3+}$ free nanocrystals (nanocrystals adjacent a gaseous phase). The first model is based on the fact that the force field created by the impurity ion having a radius larger than that of regular one will be sufficiently inhomogeneous near the crystal surface. The difference in the nanocrystal curvature can also cause a redistribution of impurity ions in the nanoparticle volume.

The first proposed model can be interpreted in terms of the uphill diffusion theory. The impurity ion diffusion processes under inhomogeneous force field (uphill diffusion) for different systems were considered in [8–12]. In our case, the Pr^{3+} impurity ion with a radius exceeding that of regular Y^{3+} ion substitutes the regular ion in the Y_2SiO_5 crystal lattice and forms the point lattice defect, a dilatation center. The radial component of elastic stress field appeared near this point defect is [13]:

$$\sigma = \frac{G\Delta\Omega}{\pi r^3}, \quad (1)$$

where G is the shear modulus; $\Delta\Omega$, the volume difference between the impurity and regular ions; r , the distance from impurity ion. To estimate the total elastic energy induced by this defect in the whole crystal (in the case when the defect is far from the surface), the next expression can be used:

$$U = \frac{1}{2G} \int \sigma^2(r) dV. \quad (2)$$

The integration in spherical coordinates in the range from the lattice constant a to the crystal size value gives the value of total elastic energy of dilatation center inside the crystal as

$$U = \frac{2}{3\pi} G(\Delta\Omega)^2 \left(\frac{1}{a^3} - \frac{1}{R^3} \right). \quad (3)$$

At the same time, if the dilatation center is located near the crystal surface, the force field becomes rather inhomogeneous. The forces acting on the impurity ion in this case do not compensate each other, thus resulting in appearance of the resultant force directed to the surface. The elastic energy component which specifies the interaction between the dilatation center and the surface can be estimated by the following expression:

$$U_s = \frac{2}{3\pi} \frac{G(\Delta\Omega)}{x^3}, \quad (4)$$

where x is the distance from dilatation center to the crystal surface. The resultant force acting on the impurity ion is

$$F = -\frac{dU_s}{dx} = -\frac{2}{\pi} \frac{G(\Delta\Omega)^2}{x^4}. \quad (5)$$

The presence of this force results in the impurity ion "attraction" by the free crystal surface. Therefore, the impurity ions move toward the crystal surface, their flow being accompanied by their segregation in the near-surface layer. This effect can be observed not only in nanocrystals as in our case, but also in bulk crystals. However, as the force acting on the impurity ion (5) is inversely proportional to the fourth power of the distance from the dilatation center to the crystal surface, only the ions placed near the crystal surface undergo the action of this force. So, the fraction of segregated ions will be appreciable only for the systems with large surface/volume ratio (for instance, for nanocrystals).

For the quantitative estimation of the activator ion redistribution, the so-called enrichment factor χ was used [14] defined as

$$\chi = \frac{C_{surf} \cdot (1 - C_{bulk})}{C_{surf} \cdot (1 - C_{bulk})}, \quad (6)$$

where C_{bulk} and C_{surf} are the bulk and surface concentration of segregated component, respectively.

In the case of equilibrium, the enrichment factor can be written as the Boltzman term:

$$\chi = \exp\left(-\frac{\Delta F_a}{kT}\right), \quad (7)$$

where ΔF_a is the free Gibbs energy of adsorption; T , temperature.

The free Gibbs energy of adsorption can be estimated using the following expression [12, 15]:

$$\Delta F_a = -\frac{24\pi K G r_1 r_2 (r_1 - r_2)^2}{3K r_2 + 4G r_1}. \quad (8)$$

Here, G is the shear modulus of the host matrix; K , the bulk modulus for the impurity; r_1 and r_2 , the ionic radii of impurity and regular ions. This expression was obtained for the grain boundary segregation, but it is often used for the surface segrega-

tion as well [16, 17]. For $Y_2SiO_5:Pr^{3+}$ nanocrystals, the corresponding values are: $G = 47$ GPa; $K = 29$ GPa; $r_1 = 101.3$ pm and $r_2 = 89.3$ pm. According to (7), (8), at room temperature the enrichment factor χ is 4.26. In other words, for bulk activator concentration $C_{bulk} = 0.02$, the surface activator concentration C_{surf} will be about 0.08, i.e. four times more than the bulk one.

The second model is based on the fact that the vacancy inhomogeneity in a system may cause a redistribution of atomic components with different diffusion coefficients. For nanocrystals, the obvious difference between vacancy concentrations appears due to a variation of nanocrystal surface curvature (this effect is quite similar to the well-known effect of vacancy concentration increasing in the neck area of sintering particles) [18]. The vacancy concentration dependence on the crystal surface curvature is given as

$$C_v = C_{0v} e^{\frac{2\gamma\Omega}{RkT}}, \quad (9)$$

where C_{0v} is the vacancy concentration under the flat surface; γ , the surface tension; R , the curvature radius; and Ω , the vacancy volume.

The presence of the vacancy gradient $\text{grad } C_v$ in the n -component system results in the vacancy flux $\mathbf{j}_v = -D_v \nabla C$, which is equal to the opposite flux of atoms $\mathbf{j}_v = \sum_i \mathbf{j}_i$, where $i = 1 \dots n$. If the diffusion coefficients D_1, \dots, D_n are not equal, the segregation of different component atoms should be obtained.

For approximate estimation of segregation extent in the $Y_2SiO_5:Pr^{3+}$ nanocrystals, expression (9) can be presented in the form:

$$\frac{\Delta C_v}{C_{0v}} = \frac{2\gamma}{R} \cdot \frac{\Omega}{kT}. \quad (10)$$

Considering the nanocrystal to be of an ellipsoid shape with $a = 25$ nm, $b = 25$ nm, $c = 50$ nm and taking $\gamma \approx 1$ N/m, $\Omega \approx 10^{-30}$ m³, $T \approx 300$ K, we obtain that the dimensionless vacancy concentration change $\Delta C_v/C_{0v}$ is varied from 0.05 to 0.3 and the ratio between vacancy concentrations in the corresponding regions $C_{1v}/C_{2v} = 1.4$. The maximum ratio between Pr^{3+} concentrations in these regions of 1.4 will be obtained when the difference between diffusion coefficients of Pr^{3+} and other components is significant;

in other cases, this ratio will be less than 1.4. This fact should be considered as an additional contribution to the surface ion concentration due to segregation. At the same time, the value of impurity ion redistribution predicted by this model will be much less as compared to the one mentioned above.

3. Conclusion

The experimental results show the presence of Pr ion pairs in a considerable amount in $Y_2SiO_5:Pr^{3+}$ nanocrystals even at low activator concentrations that was not observed for corresponding bulk crystals. This anomalous formation of ion pairs can be explained by the segregation processes observed in $Y_2SiO_5:Pr^{3+}$ nanocrystals. Two possible models of the segregation have been discussed in this paper: the model based on the activator ion force field inhomogeneity in the near-surface layer and the model of inhomogeneous vacancy distribution due to variation of the nanocrystal surface curvature. The first model gives the ratio between activator concentrations in the near-surface layer and in the bulk $C_{surf}/C_{bulk} \approx 4$, the second one, to the ratio between activator concentrations $C_1/C_2 \approx 1.4$ for a nanocrystal with the size variation from 25 to 50 nm. These estimations show unambiguously that both models are applicable for the case of $Y_2SiO_5:Pr^{3+}$ nanocrystals, but the model of activator ion force field inhomogeneity in the near-surface layer provides the main contribution.

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Механізми локальної неоднорідності концентрації активатора у нанокристалах $Y_2SiO_5:Pr^{3+}$

В.В.Семінко, А.А.Масалов, Ю.В.Малюкін, Ю.І.Бойко

Розглянуто причини локальної неоднорідності концентрації Pr^{3+} у нанокристалах $Y_2SiO_5:Pr^{3+}$. Для пояснення цього ефекту запропоновано дві фізичні моделі: одна ґрунтується на неоднорідності силового поля іона активатора у приповерхневому шарі, а друга — на неоднорідності кривизни поверхні нанокристала. Оцінки в рамках першої моделі дають відношення приповерхневої та об'ємної концентрацій активатора, близьке до 4; згідно з оцінками за другою моделлю, відношення концентрацій активатора у різних областях нанокристала становить близько 1,4. Кількісні оцінки вказують, що для пояснення ефекту сегрегації у нанокристалах $Y_2SiO_5:Pr^{3+}$ можуть застосовуватися обидві моделі, проте внесок першого механізму перевищує внесок другого.