

MICROSTRUCTURE AND INTERACTION OF OPTICAL CENTERS IN CRYSTAL $Y_2SiO_5:Pr^{3+}$

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This paper is dedicated to Victor G. Bar'yakhtar on the occasion of his 75th birthday

The mechanisms of interaction between equivalent and nonequivalent optical centers in crystal $Y_2SiO_5:Pr^{3+}$, as well as the mechanisms of interaction between Pr^{3+} optical centers and the crystalline environment, have been studied. It has been demonstrated that the interaction with two-level systems makes a contribution, additional to that made by the quadratic electron-phonon interaction, to the uniform width of the resonance optical transition ${}^3H_4 \leftrightarrow {}^3P_0$ of Pr^{3+} ions. Two new mechanisms of center-to-center interaction, which are different in principle, have been revealed. The first is associated with the dipole-dipole interaction between nonequivalent Pr^{3+} optical centers, while the second is caused by the cooperative cross-relaxation of the excitation energy of term 1D_2 with the participation of Pr^{3+} optical centers of the same type.

of the necessary level of knowledge demands complex researches making use of modern methods of optical and laser spectroscopy. Only the cumulative body of experimental results obtained by different methods would allow us to form a detailed idea of the microscopic nature of an impurity center and the mechanisms of center-to-center interaction.

This review deals with a crystalline matrix $Y_2SiO_5:Pr^{3+}$ (YSO: Pr^{3+}) which belongs to a perspective family of oxyorthosilicates with the general formula $Re_2(SiO_4)O$ ($Re = Y, La-Lu$). They are the basis for intensive developments of new materials [1–5]. Until now, rather a significant extent of experimental researches [6–14] has been carried out for crystal YSO: Pr^{3+} . Those researches made it possible to reconstruct the microscopic nature of Pr^{3+} impurity centers and the mechanisms of center-to-center interaction to the full extent.

1. Introduction

From the viewpoint of modern tendencies, which are observed in the development of new optical materials on the basis of inorganic crystallophosphors activated by rare-earth ions (REIs), and demands for those materials, the complex and detailed information concerning the structures of REI spectra, the relative arrangement of electron terms of f and d shells, and the exact values of the parameters of the relaxation channels for the excitation energy becomes of the greatest importance. The application of activated crystallophosphors as optical media requires knowing the mechanisms of the outphasing of electron transitions in REIs in detail. In addition to the individual characteristics of REIs, the detailed understanding of the mechanisms of center-to-center interactions becomes extremely important. It has been accepted for a long time that the center-to-center interaction is detrimental by its effect, by quenching fluorescence. The contemporary stage of researches made it clear that the center-to-center interaction can be used for summing up the electron excitations and creating the effective scenarios of up-conversion. The achievement

2. Experimental Results and Their Discussion

2.1. Spectroscopy of crystal YSO: Pr^{3+}

Provided the temperature was low, the absorption spectrum of an YSO: Pr^{3+} crystal in the region of ${}^3H_4 \rightarrow {}^1D_2$ transitions was composed of ten spectral lines which can be divided unambiguously into two groups, five lines in each (Fig. 1). Those groups are correspondingly related to Pr^{3+} optical centers of two nonequivalent types, which was confirmed unequivocally by a selective excitation of their luminescence [6]. In the YSO: Pr^{3+} crystal, the degeneration of term 1D_2 is cancelled completely, which is caused by a low (C_1) symmetry of cation sites. Analogously, the spectral lines of two Pr^{3+} optical centers are resolved well in the region of ${}^3H_4 \rightarrow {}^3P_0$ transitions as well (Fig. 1). A certain combination of five spectral lines in the absorption spectra of nonequivalent Pr^{3+} optical centers (Fig. 1)

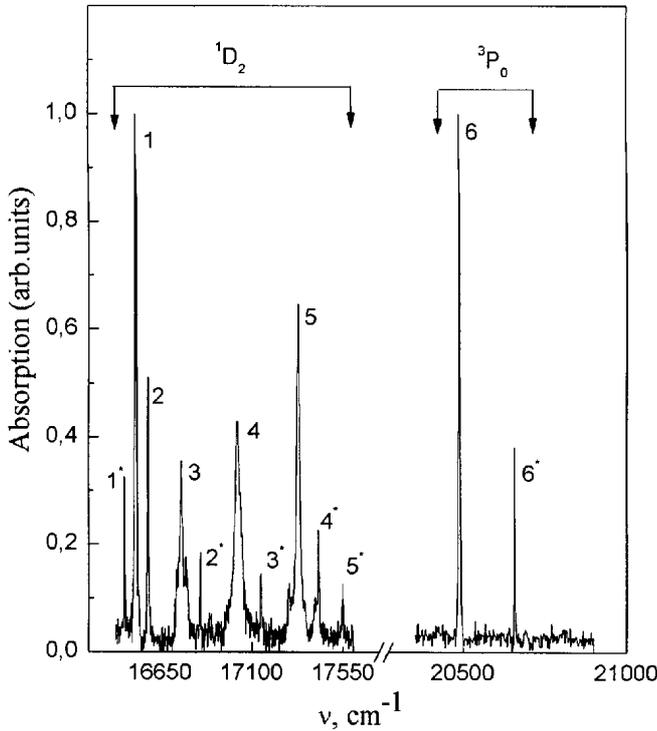


Fig. 1. Absorption spectrum of an YSO:Pr³⁺ crystal (0.3 at.% of Pr³⁺) in the region of the ${}^3H_4 \rightarrow {}^1D_2$ and ${}^3H_4 \rightarrow {}^3P_0$ optical transitions at $T = 1.5$ K. The spectral lines belonging to Pr³⁺ optical centers of the first or the second type are marked by the figures or the figures with an asterisk, respectively

allowed the conclusion about the features of the crystal field of ligands of nonequivalent cation sites in the YSO crystal [13–16] to be made. According to work [16], the cation sites of one kind are characterized by the field of a distorted octahedron, while the cation sites of the other kind by the field of a distorted tetrahedron.

2.2. Outphasing mechanisms of optical transitions in crystal YSO:Pr³⁺

The photon echo and spectral hole burning experiments were carried out engaging various optical transitions of impurity ions in crystals YSO:Pr³⁺ [10,17]. The method of photon echo was used to study the transition ${}^3H_4 \rightarrow {}^3P_0$ of Pr³⁺ optical centers of the first type (Fig. 1, spectral line 6) [10], while the spectral hole burning was realized on the ${}^3H_4 \rightarrow {}^1D_2$ optical transitions of both optical centers (Fig. 1, spectral lines 1 and 1*) [17]. The data of works [10,17] supplement each other and testify to that, besides nonequivalent Pr³⁺ optical centers related to the population of cation sites which

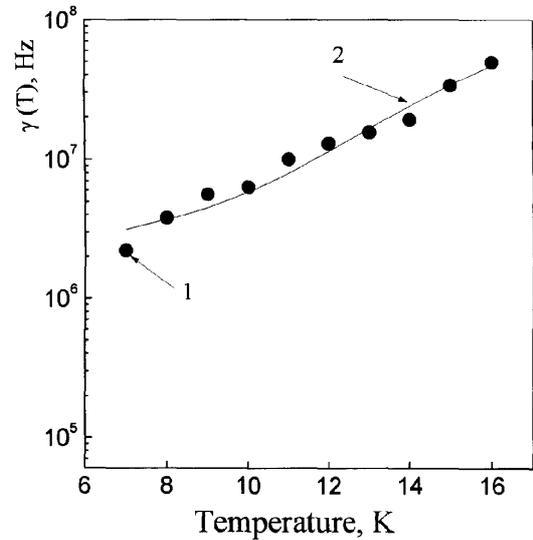


Fig. 2. Temperature dependences of the uniform width of the spectral line of the ${}^3H_4 \rightarrow {}^3P_0$ resonant transition of Pr³⁺ impurity ions in an YSO:Pr³⁺ crystal: 1 – experimental data, 2 – the result of approximation of the experimental data by relation (1)

are different by their properties, there exist nonequivalent crystals YSO:Pr³⁺ between the minima of the states of impurity ions in the scope of one site of cation localization. These nonequivalent states are described in the framework of the model of multiwell adiabatic potential [10].

In work [10], the key premise has been made: Pr³⁺ impurity ions can perform thermally induced transitions in adiabatic potential owing to their interaction with two-level systems [23,24]. Therefore, the uniform width of the ${}^3H_4 \rightarrow {}^3P_0$ resonant optical transition of Pr³⁺ impurity ions (Fig. 2) is determined by additive contributions related to the interaction of Pr³⁺ impurity centers with phonons and two-level systems [10]:

$$\gamma(T) = \gamma_{\text{ph}}(T) + \gamma_{\text{TLS}}(T) =$$

$$\alpha \exp\left(-\frac{\Delta\varepsilon}{kT}\right) + \lambda_{\text{sh}}^{-1} \left(\frac{\Delta}{kT}\right), \quad (1)$$

where α is the half-height width of the second Stark component of term 3H_4 , $\Delta\varepsilon$ the energy gap between the first and the second Stark component of term 3H_4 , λ the parameter of the phonon-phonon interaction, and $\Delta = \Delta_e \approx \Delta_g$ the difference between the activation energies of two-level systems in the ground and excited states of impurity ions.

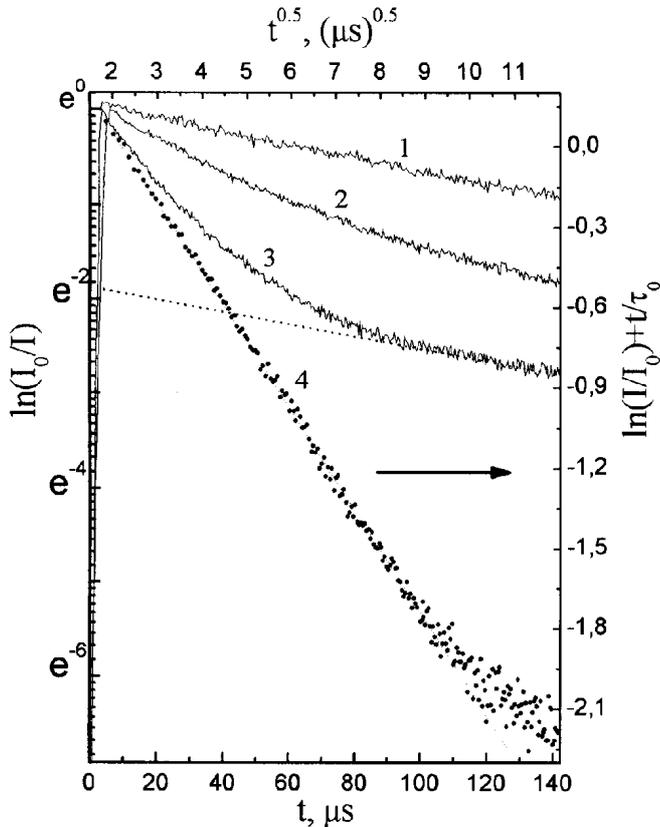


Fig. 3. Decay curves of the 1D_2 fluorescence of Pr^{3+} optical centers excited selectively through their $^3H_4 \rightarrow ^3P_0$ transition in an YSO: Pr^{3+} crystal (0.3 at.% of Pr^{3+}): the fluorescence of Pr^{3+} optical centers of the first type (donors) at $T = 1.5$ (1) and 80 K (2); the fluorescence of Pr^{3+} optical centers of the second type (acceptors) at $T = 80$ K (3), the corresponding axes being located on the left and on the bottom; and the results of the approximation of curve 3 by relation (2) (4), the corresponding axes being on the right and on the top

Relationship (1) allows the experimental data presented in Fig. 2 to be described adequately provided $\alpha = 1.04 \times 10^{10} \text{ s}^{-1}$ and $\lambda = 1.1 \times 10^5 \text{ s}^{-1}$.

2.3. Mechanisms of center-to-center interaction in crystal YSO: Pr^{3+}

The increase of the concentration of impurity ions in crystal YSO: Pr^{3+} is accompanied by the quenching of their fluorescence, which evidences for the manifestation of center-to-center interactions [16]. Varying the concentration of Pr^{3+} impurity ions (0.3, 0.6, and 1.8 at.%) affects the quenching of their 3P_0 and 1D_2 terms differently. More exactly, only the quenching of the 1D_2 fluorescence was observed, while the quenching

of the 3P_0 one was absent completely. The curves of the 3P_0 fluorescence decay were described by the exponential law with a time constant of $2.2 \mu\text{s}$. On the contrary, the curves of the 1D_2 fluorescence decay of Pr^{3+} optical centers of both types deviated strongly from the exponential law. Two different quenching mechanisms of the 1D_2 fluorescence were in action, one of them being valid only for Pr^{3+} optical centers of the first type (Fig. 1). The fluorescence quenching by this or that mechanism depended on the concentration of impurity ions and on the way of the 1D_2 term excitation [16, 27].

If 3P_0 term of Pr^{3+} optical centers of the first type had been excited selectively, some ions found themselves in the 1D_2 state owing to the $^3P_0 \rightarrow ^1D_2$ radiationless relaxation process. In this case, one can observe the quenching of the 1D_2 fluorescence provided a concentration of impurity ions of 0.3 at.% and higher. The quenching of the 1D_2 fluorescence occurred at a temperature of 80 K and disappeared if the temperature had been lowered down to 1.5 K (Fig. 3). At quenching, the fluorescence of Pr^{3+} optical centers of the second type was observed, despite the selective $^3H_4 \rightarrow ^3P_0$ excitation of Pr^{3+} optical centers of the first type. Pr^{3+} optical centers of the second type played the role of acceptors. It was confirmed unequivocally by the decay curves of Pr^{3+} optical centers of the first and second kinds (Fig. 3). The decay of the donor fluorescence deviates appreciably from the exponential law (Fig. 3, curve 2), and the decay curve of the acceptor fluorescence (Fig. 3, curve 3) includes a characteristic interval of a growth. The decay curve of the donor fluorescence (Fig. 3, curve 2) is described best by Eq. (2), provided $S = 6$ (see Fig. 3, curve 4) [26, 28]:

$$\ln I + \frac{t}{\tau_0} = \ln I_0 - \frac{4\pi}{3} n_a R_{\min}^3 (w_{d-a} t)^{3/S} \Gamma(1 - 3/S), \quad (2)$$

where I is the donor fluorescence intensity; τ_0 the time of the radiation decay of the 1D_2 fluorescence; I_0 the glowing intensity at the initial moment $t = 0$; n_a the number of acceptors per unit volume which is equivalent to the concentration of Pr^{3+} optical centers of the second type; R_{\min} the minimal distance between nonequivalent Pr^{3+} ions in the crystal lattice; w_{d-a} the energy transfer constant; Γ the gamma-function; and S equals 6, 8, or 10, depending on the type of multipole interaction

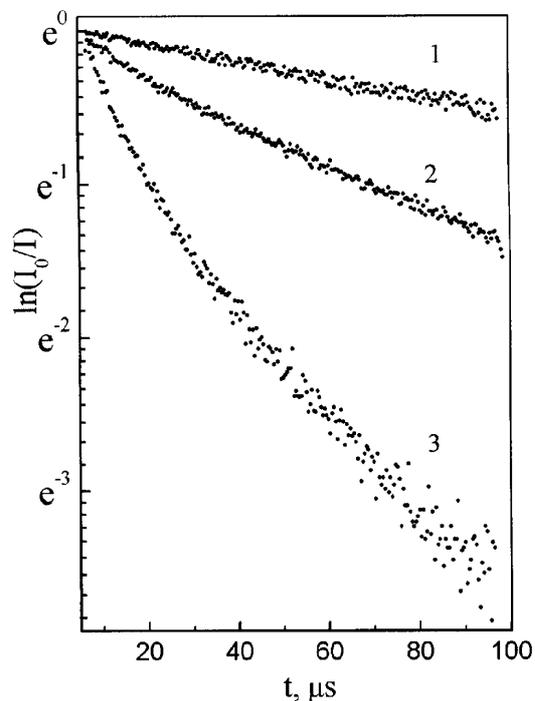


Fig. 4. Decay curves of the 1D_2 fluorescence of Pr^{3+} optical centers of the first type at their selective excitation through the ${}^3H_4 \rightarrow {}^1D_2$ transition in an $\text{YSO}:\text{Pr}^{3+}$ crystal at $T = 80$ K for various Pr^{3+} concentrations: 0.3 (1), 0.6 (2), and 1.8 at.% (3)

(dipole-dipole, dipole-quadrupole, or quadrupole-quadrupole one, respectively).

The slope of the straight line (the dependence of $\ln I + t/\tau_0$ on \sqrt{t} , see Fig. 3, curve 4) allows the energy transfer constant to be determined. If the total concentration of Pr^{3+} ions amounts to 0.3 at.%, the concentration of optical centers of the second type is $6.8 \times 10^{10} \text{ cm}^{-3}$ which is equivalent to n_a . The minimal distance between nonequivalent Pr^{3+} ions in the YSO lattice is 3.403 Å. Hence, the constant of excitation energy transfer equals $w_{d-a} = 2.5 \times 10^4 \text{ s}^{-1}$. This value of the energy transfer constant is in agreement with that calculated immediately for the interval, where the intensity of the acceptor glowing increases (Fig. 3, curve 3).

If the Pr^{3+} concentration is of 0.3 at.%, the quenching of the 1D_2 fluorescence of optical centers of both types is absent, provided those centers have been excited selectively (${}^3H_4 \rightarrow {}^1D_2$). Nevertheless, starting from 0.6 at.% of Pr^{3+} and above, the quenching appears again (Fig. 4). The curves of fluorescence decay deviate noticeably from the exponential law (Fig. 4). In contrast to the previous case (Fig. 3), the selective ${}^3H_4 \rightarrow {}^1D_2$ excitation of optical centers of one type stimulates their

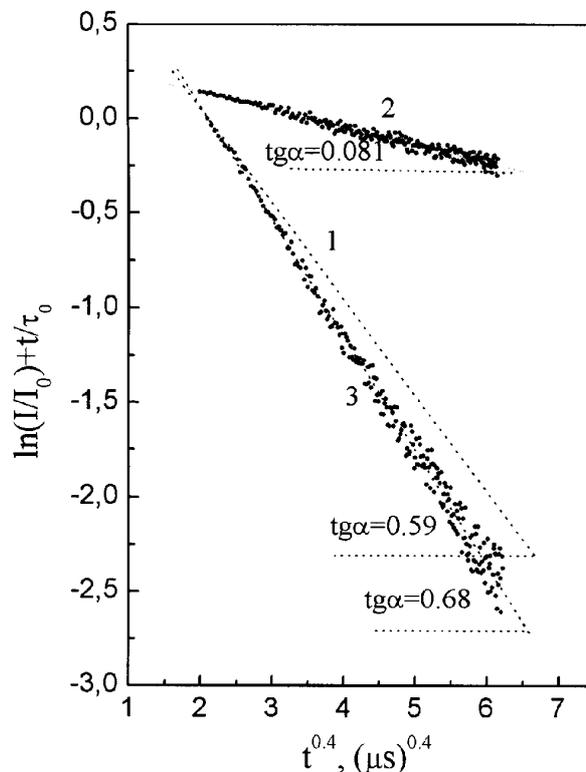


Fig. 5. Results of analysis of the decay curves of the 1D_2 fluorescence of Pr^{3+} optical centers of the first type at their selective excitation through the ${}^3H_4 \rightarrow {}^1D_2$ transition in an $\text{YSO}:\text{Pr}^{3+}$ crystal: $T = 1.5$ K, 1.8 at.% of Pr^{3+} (1); $T = 80$ K, 0.6 at.% of Pr^{3+} (2); and $T = 80$ K, 1.8 at.% of Pr^{3+} (3)

own fluorescence only. The energy transfer between nonequivalent optical centers is absent. The mechanism of quenching of the 1D_2 fluorescence differs substantially from that considered above. The quenching of the 1D_2 fluorescence occurs through the cross-relaxation of the 1D_2 term energy between Pr^{3+} centers of the same type. The only matter is: How many Pr^{3+} ions are involved in the cross-relaxation of the 1D_2 term energy? The law of $t^{0.5}$ cannot provide a satisfactory description of the fluorescence decay curves presented in Fig. 4 [27]. Relationship (2) is inapplicable at any value of the parameter S . The experimental curves are described well only making use of the law $t^{0.4}$ [27], which evidences for the cooperative quenching of the 1D_2 fluorescence by two Pr^{3+} ions in their ground states. This conclusion is confirmed by the fact that the slopes of the straight lines $\ln I + t/\tau_0$ versus $t^{0.4}$ for two Pr^{3+} concentrations — 0.6 and 1.8 at.% — are proportional to the square of their variations (Fig. 5). The efficiency of the cooperative

cross-relaxation practically does not depend on the temperature (Fig. 5). Therefore, the conditions for a resonance between the intermediate electronic terms of interacting Pr^{3+} ions are satisfied well. However, it is impossible to specify the intermediate states precisely.

3. Conclusion

Thus, there are several types of nonequivalent states of Pr^{3+} impurity ions in crystal $\text{YSO}:\text{Pr}^{3+}$. Some states are connected with the substitution of impurity ions for two nonequivalent cation sites in the YSO lattice. The cation sites are characterized by different symmetries of the crystal field of ligands. One type of the cation sites possesses the crystal field of a distorted octahedron, and the other one the crystal field of a distorted tetrahedron. Another type of nonequivalent states of the Pr^{3+} impurity ions is realized within the scope of one cation site and is connected with the specific interaction in the system “an impurity ion + the crystal field of ligands”. The latter type of nonequivalent states is described adequately in the framework of the model of multiwell adiabatic potential. The thermally induced transitions of a Pr^{3+} impurity ion between the minima of the adiabatic potential contribute to the outphasing of optical transitions. At certain concentrations of impurity ions in an $\text{YSO}:\text{Pr}^{3+}$ crystal, there emerges the center-to-center interaction which is responsible for the quenching of the Pr^{3+} luminescence. There are two different mechanisms of the fluorescence quenching for term 1D_2 which depend on the concentration, temperature, and way of excitation of Pr^{3+} impurity ions. One of them is connected with the Förster dipole–dipole transfer of the excitation energy between nonequivalent Pr^{3+} optical centers. The second mechanism is connected to the cooperative cross-relaxation of the excitation energy of the 1D_2 term among Pr^{3+} optical centers of the same type.

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МІКРОСТРУКТУРА ТА ВЗАЄМОДІЯ ОПТИЧНИХ ЦЕНТРІВ В КРИСТАЛІ $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$

В.П. Семіноженко, П.М. Жмурін, Ю.В. Малюкін

Резюме

У кристалі $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ вивчено механізми взаємодії між еквівалентними та нееквівалентними оптичними центрами, а також механізми взаємодії оптичних центрів Pr^{3+} з кристаліч-

ним оточенням. Показано, що крім квадратичної електрон-фононної взаємодії додатковий внесок в однорідну ширину резонансного оптичного переходу ${}^3H_4 \leftrightarrow {}^3P_0$ іона Pr^{3+} дає взаємодія з дворівневими системами. Встановлено існування двох принципово різних механізмів міжцентрової взаємодії. Перший пов'язаний з диполь-дипольною взаємодією між нееквівалентними оптичними центрами Pr^{3+} . Другий зумовлений кооперативною кросрелаксацією енергії збудження 1D_2 -терма за участю однотипних оптичних центрів Pr^{3+} .