

ENERGY DISSIPATION MECHANISM IN OXIDES WITH GARNET STRUCTURE DOPED 4f-5d TRANSITIONS RARE EARTH IONS

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The phenomenon of excitation energy dissipation was studied and corresponding mechanisms were proposed for phosphors with garnet structure on the base of $Y_3Al_5O_{12}$ - $Y_3Ga_5O_{12}$ doped by rare-earth (RE) ions with interconfiguration transitions at the Ga content increasing.

It has been shown that the change of the parameters of Ce^{3+} and Pr^{3+} ions emission under in $Y_3Al_{5-x}Ga_xO_{12}$ garnets at increasing x is caused by the decrease in both crystal stress and excitation energy dissipation of luminescence due to changes of impurity levels position with respect to band structure extrema. These mechanisms of dissipation are the transitions between these extrema and excited activator levels. In the case of Ce^{3+} , thermostimulated transitions between valence band and basic state of Ce^{3+} ions take place; for Pr^{3+} doped compounds the primary act of dissipation is the thermal „pushing” of electrons from excited 4f-5d levels to the conductivity band.

The feature of emission of solid solutions of known phosphors on the base of $Y_3Al_5O_{12}$ and $Y_3Ga_5O_{12}$ garnets doped with rare-earth (RE) ions, which have characteristic 4f-5d transitions, is the strong decrease in the quantum output of luminescence at the Ga^{3+} content growth [1]. This work concerns investigation of the nature of such phenomena.

The samples of $Y_3Al_{5-x}Ga_xO_{12}$ solid solutions were prepared by ceramics technology. $Y_3Al_5O_{12}$ ($Ce^{3+};Pr^{3+}$) single crystalline films and their bulk analogs were studied as basic objects. The samples were

prepared by the liquid phase epitaxy and the direct crystallization from melt, respectively. The concentration of Ce^{3+} and Pr^{3+} ions was about 0.1 at %.

The excitation of samples has been performed by the non-filtered x-ray emission ($\text{CrK}\alpha$) and electron beam. Absorption spectra of $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}$ doped with Pr^{3+} and Ce^{3+} ions, and diffuse reflection spectra of the $\text{Y}_3\text{Al}_{5-x}\text{Ga}_x\text{O}_{12}:\text{Ce};\text{Pr}$ solid solutions, were measured using „Specord-M40” at the room temperature.

We found [2,3] that changes of Ce^{3+} and Pr^{3+} ion emission parameters in $\text{Y}_3\text{Al}_{5-x}\text{Ga}_x\text{O}_{12}$ system at the x growth can be explained by the influence of the two factors: 1) the decrease in crystal lattice stresses; 2) changes of sites of energy levels of activator correspondingly extrema of band structure.

The first factor corresponds with the decrease in the energy distance Δ between the doublet 4f-5d absorption (excitation) peaks of Ce^{3+} and Pr^{3+} ions luminescence (see Fig. 1) and causes the shift of emission maximum to the blue region of spectrum. Influence of the second factor leads to energy dissipation due to the presence of transitions with charge exchange between states of excited Ce and Pr ions and extrema of the band structure. The phosphorence at $x>3$, the reduction of the activation energy of Ce^{3+} and Pr^{3+} ions emission at the temperature decay and decreasing the gap of garnet at the x growth (see Table) prove this conclusion.

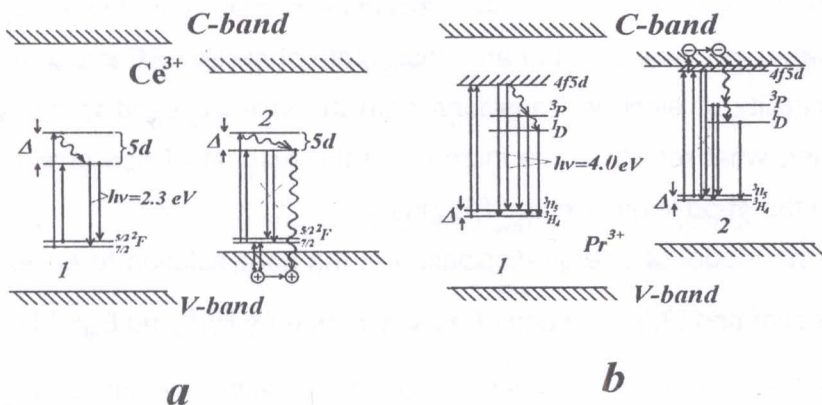


Figure 1. Optical transitions scheme of Ce³⁺ (a) and Pr³⁺ (b) ions in Y₃Al₅O₁₂ (a,1; b,1) and Y₃Ga₅O₁₂ (a,2; b,2). Possible mechanisms of luminescence decay are shown in 2,a and 2,b schemes, which are connected with interconfigurational transitions of Ce³⁺ and Pr³⁺ ions respectively.

The available mechanisms of energy dissipation in the specified temperature range for Y₃Al_{5-x}Ga_xO₁₂-Ce (a) and Y₃Al_{5-x}Ga_xO₁₂-Pr (b) systems in the case of excitation in the 4f-5d transitions region are different (2,3) and may be presented by the two models (see Fig.1. a,2 and Fig.1. b,2)

With the growth of x, the energy splits between the conductivity band and the 4f5d-(5d-) levels of RE ion, decreases and becomes equal to the activation energy E_a. As a result, the increase in probability of temperature electron jump to conductivity band from 4f5d-(5d-) levels takes place. The next stage is non-emission electron transition from the conductivity band to the basic states of excited RE ion. Moreover, this model assumes that probability of such transitions is greater than transition probability on 4f5d-(5d-) levels.

With the x growth, the model assumes decrease in the energy split between the valence band and basic state of excited RE ion. In this case probability of electron transitions from the valence band to this level is higher, what results in the increase in the number of non emission acts from the 4f-5d levels excited RE ions.

For the model of energy dissipation in the solid solution to be establish, we estimated [3] the values of activation energy E_a^1 and E_a^2 of decay of Ce^{3+} ion photo-luminescence connected with the interconfiguration transitions excited at $h\nu_{max}=2,39\text{eV}$ in $Y_3Al_3Ga_2O_{12}$ at 4f-5d transitions with $h\nu_{max}^1=3,59\text{ eV}$ and $h\nu_{max}^2=2,86\text{ eV}$ (see Table 1.), taking into account corresponding temperature dependencies of absorption intensity changes in the mentioned bands. Closeness of the experimental values of the $E_a^1=0,38\text{ eV}$ and $E_a^2=0,54\text{ eV}$ energies to the value of the energy distance between the absorption (0,73 eV) 4f-5d levels of supports our model shown in Fig.1. a,2.

Table 1. Spectral features of absorption and emission of $Y_3Al_{5-x}Ga_xO_{12}$ solid solutions doped with Pr^{3+} and Ce^{3+} ions. The absorption and emission are also connected with the $5d-4f$ and $4f5d-4f$ interconfigurational transitions

Garnet structure	x	Energy position of most intensive emission peak, eV	Energy gap Δ between 4f-5d-absorption band, eV	Correspondent intensity of emission, %	Activation energy of thermal decay, eV
$Y_3Al_{5-x}Ga_xO_{12}:Pr$	0	$4f5d \rightarrow {}^3H_4$ 4.01 3.98	${}^3H_5 \rightarrow 4f5d$ ${}^3H_4 \rightarrow 4f5d$ 0.87	$4f5d \rightarrow {}^3H_4, {}^3H_5$ (80K) 100	0.42
	1	3.97	0.80	86	0.37
	2	3.93	0.77	67	0.30
	3	3.90	0.64	44	0.16
	4	3.87	0.61	19	0.07
	5		0.50	7	-
	$Y_3Al_{5-x}Ga_xO_{12}:Ce$	0	$5d \rightarrow {}^2F_{7/2}$ 2.28	${}^2F_{5/2} \rightarrow 5d$ ${}^2F_{7/2} \rightarrow 5d$ 0.94	$5d \rightarrow {}^2F_{7/2, 5/2}$ (300K) 100
1		2.34	0.84	54	0.26
2		2.39	0.73	48	0.19
3		2.44	0.62	34	0.11
4		2.48	0.58	29	0.09
5		2.52	0.55	27	0.08

Decrease in the quantum yield, caused by interconfigurational transitions UV luminescence at $h\nu_{\max}=3,5$ eV for the $Y_3Al_{5-x}Ga_xO_{12}:Pr^{3+}$ system, may be connected with the thermal absorption of the excited 4f5d- states of Pr^{3+} by conductivity band (Fig.1. b). If we assume that in the investigated system (case 2 on Fig. b) this model of energy dissipation takes place, then the ratio of intensities of the $^3P \rightarrow ^3H_5, ^3H_4$ and $D \rightarrow ^3H_4$ transitions between terms of 4f-band (visible spectrum) at variation of solid solution composition and temperature would not reveal so dramatic changes (what is a feature of 4f-5d transitions in the UV ($h\nu \sim 4.0$ eV) spectral region), as it has been experimentally observed [2].

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