# CONCENTRATION QUENCHING OF LUMINESCENCE OF NEODYMIUM IONS IN $La_2S_3{\times}2Ga_2S_3$ GLASS

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The relaxation processes of neodymium upper laser level $^4F_{3/2}$ in $La_2S_3{\times}2Ga_2S_3$ glasses have been investigated. The microparameters of donor-acceptor ($C_{DA}$) and donor-donor ($C_{DD}$) interactions, and also minimal distance ($R_{min.}$) have been defined from analysis of experimental decay curves in total investigated time interval at condition of best coincidence of experimental and calculated data.

Last time the intensive searches of new laser mediums with high neodymium content for miniature lasers and elements of integrated optics have been carried out.

The phenomena of concentration quenching of luminescence is the one from the main difficulties of increase of neodymium concentration in laser mediums. The presence of suitable intermediate levels between neodymium main and excited states provides the effective cross-relaxation that essentially increases the probability of non-emitting excitation decay. Such disadvantage in neodymium level circuit leads to the fact, that its concentration in most active elements usually doesn't exceed the several percents.

The present paper is dedicated to investigation of energy relaxation processes with upper laser neodymium level $^4F_{3/2}$ in set of semiconductor glasses $(La_{1-x}Nd_x)_2S_3{\times}2Ga_2S_3$ ($x$=0.004; 0.14; 0.32). Moreover, the analysis method of decay curves of excited state after "immediate" impulse excitation [1] by laser radiation on rhodamine base 640 ($\lambda$=0.591mcm) was used by us. The impulse duration was ~15 ns. The spectral selection of radiation of investigated samples was carried out with help of monochromator MDP-2.

It is known, that analysis of curves of non-emitting decay of excited state leaded to revealing of three stages of non-emitting energy transfer: static ordered one, static disordered one and stage of migration-limited relaxation [2]. This circumstance allows to define the microparameters of donor-acceptor ($C_{DA}$) and donor-donor ($C_{DD}$) interactions, and also minimal distance ($R_{min.}$), that in one's turn allows to plot the decay curves of excited state at any promoter concentrations and consequently, to obtain the concentration dependence of luminescence quant output from upper laser level and to define the optimal concentration of working impurity.

The $R_{min.}$ value is defined by several methods. The one of them consists in measurement of velocities of static ordered quenching

$$W_H = \frac{4\pi}{3} n_A \frac{C_{DA}}{R^3_{\min.}} \tag{1}$$

where $n_A$ is acceptor concentration. It is need to note, that non-emitting decay of electron excitation in metastable state $^4F_{3/2}$ takes place in the result of cross-relaxation effect through intermediate distance of main term $^4I$. Moreover, each neodymium ion can be as quencher, so energy carrier, i.e. $n_A=n_D$, where $n_D$ is donor concentration.

Substituting in this formula the microparameter value $C_{DA}$, found on region of static disordered decay, we define $R_{min.}$. The other method consists in the following. It is known, that expression for function of non-emitting losses at static dipole-dipole energy transfer with taking into consideration of minimum distance donor-acceptor, which is not equal to zero, has the form [3]:

$$\varPi(t) = \frac{4\pi}{3} n_A R^3_{\min.} \left(e^{-y_1} - 1 + 2\sqrt{y_1} \int_0^{\sqrt{y_1}} e^{-x^2} dx\right),$$

where $$y_1 = \frac{tC_{DA}}{R^6_{\min.}} \quad . \tag{2}$$

At big times $\left[ t\rangle\rangle\tau_1 = \left(\frac{C_{DA}}{R^6_{\min.}}\right)^{-1} \right]$ we obtain:

$$\varPi(t) = -\frac{4\pi}{3} n_A R^3_{\min.} + \frac{4\pi^{3/2}}{3} n_A C_{DA}^{1/2} t^{1/2} \tag{3}$$

So extrapolating the experiment part $\varPi(\sqrt{t})$ till $t=0$, we obtain value "a":

$$a = \frac{4\pi}{3} n_A R^3{}_{\min.} \tag{4}$$

whence the value $R_{min.}$ is defined.

The dedication of region of static disordered decay and definition of $C_{DA.}$ on this region is the "weak" place at $R_{min}$ definition by two above mentioned methods. The unit establishing process of density stationary profile of donor excitations round acceptor (moreover it can be said about non-stationary migration-accelerated quenching) takes place after sample $\delta$-excitation and it is possible to speak about extraction of static disorder quenching from this process only at $R_W$>>$R_{min}$, when the big enough quantity of seats, providing the distance dispersal donor-acceptor in different spheres (in "joint sphere") is in quenching sphere with $R_W$ radius. By other words, the ratio

$$\tau_0 >> \tau_1 \tag{5}$$

$\left(\frac{R_W}{R_{\min.}} \approx (\frac{\tau_0}{\tau_1})^{1/6}\right)$, where $\tau_0$ is more probable time of donor-donor transfer should be correct. This will be expressed in strong modulation of decay curve, i.e. it will be strongly differ from line in semi-logarithmic scale. The

$$\tau_1 << t << \tau_0 \qquad (6)$$

should be for application of usual analysis methods of static disorder decay $(e^{-\gamma\sqrt{t}})$. The condition (6) can be "softened", if we use expression $\Pi(t)$, defined by formula (2), but not the $\Pi(t) = \gamma\sqrt{t}$. Moreover, the condition (6) becomes somewhat soft:

$$0 \le t << \tau. \qquad (7)$$

The curve analysis of non-emitting decay of neodymium excitation state $^4F_{3/2}$ in $La_2S_3{\times}2Ga_2S_2$ – $Nd^{3+}$ glasses leads to the fact, that conditions (6) and (7) aren't correct and because of this fact it is impossible to dedicate the region of static disordered decay and to define the $C_{DA}$ microparameter on it. That's why in this case the specification of experimental decay curve in total investigated time interval and definition of interaction microparameters ($C_{DA}$ and $C_{DD}$) and minimum distance $R_{min.}$ from condition of best coincidence of experimental and calculated data are the uniquely right ones.

According to theory, developed in paper [4], the kinetics of migration-accelerated process, given by $N(t)$ function, is described by integral equation

$$N(t) = N_0(t)R_e(t) - \int_0^t N_0(t-t')\dot{R}_e(t-t')N(t')dt', \qquad (8)$$

where

$$R_e = e^{-\frac{t}{\tau}} \qquad (9)$$

describes the kinetics of excitation outflow, and $N_0 = \langle e^{-Wt}\rangle$ is kinetics of static quenching excitation by acceptors. Here $\tau$ is life time of excited level, and $W$ is probability of donor-acceptor interaction. In particular, $N_0$ has the following form at dipole-dipole interaction:

$$N_0 = \langle e^{-Wt}\rangle = e^{-\gamma\sqrt{t}}, \qquad (10)$$

where

$$\gamma = \frac{4}{3}\pi^{3/2} n_A C_{DA}^{1/2} \quad .$$

It is need to note, that outflow kinetics $R(t)$ coincides function (9) even in case of ordered donor position only on initial stage ($t \le \tau_0$), when excitation return on initial center can be neglected. At dipole-dipole interaction outflow kinetics [5] at particle taking into consideration return and at taking into consideration dispersal on distances between donors has the following form:

$$R(t) = \exp(-\sqrt{\frac{t}{\bar{\tau}}}) \qquad (11)$$

where $\bar{\tau}$ is average residence time on initial center.

That's why in equation (8) $R_e$ can be replace by $R$, after that instead of formula (8)we will obtain the following kinetic equation for quenching

$$N(t) = N_0(t)R(t) - \int_0^t N_0(t-t')\dot{R}(t-t')N(t')dt' \cdot \qquad (12)$$

The minimum distance donor-acceptor didn't take into consideration in equation (12). As it has been more than once noted, the damping law of donor number with taking into consideration "forbidden volume" differs from non-exponential decay (10) and has the form:

$$N_0^{'} = \exp\left\{-\frac{4\pi}{3}n_A R_{\min}^3\left(e^{-y_1} - 1 + 2\sqrt{y_1}\int_0^{\sqrt{y_1}} e^{-x^2}dx\right)\right\},$$

where $$y_1 = \frac{tC_{DA}}{R_{\min.}^6} \quad . \qquad (13)$$

That's why in order to take into consideration the minimal distance donor-acceptor $N_0$ should be replaced by $N_0'$ in equation (12). After this replacement we obtain the following equation:

$$N(t) = N_0'(t)R(t) - \int_0^t N_0(t-t')\dot{R}(t-t')N(t')dt' \cdot \qquad (14)$$

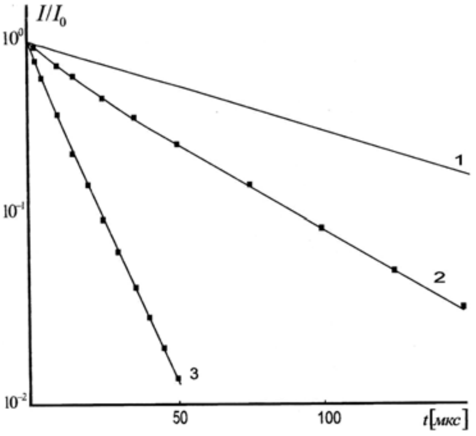

*Fig.1.* The experimental (entire lines) and calculated (points) of decay curves of metastable state $^4F_{3/2}Nd^{3+}$ in $(La_{1-x}Nd_x)_2S_3{\times}2Ga_2S_3$: glasses: 1- $x$=0.004; 2- $x$=0.14; 3- $x$=0.32.

It is impossible to solve this equation in analytic form and $N(t)$ can be investigated by only numerical methods. Thus, solving equation (14) numerically, it is possible to obtain $C_{DD}$, $C_{DA}$ and $R_{min.}$ microparameters from condition of best coincidence of experimental and calculated curves. The experimental decay curves are given by entire lines and calculated decay curves are given by points on the fig.1. From condition of best coincidence of experimental and calculated data for neodymium ions in $La_2S_3{\times}2Ga_2S_2$ glass on specification of decay curves in total investigated time interval the following parameter values have been defined:

$$R_{\min.} = 5{,}4\overset{0}{A}$$

$$C_{DA} = 2{,}5\times10^{-39}cm^6s^{-1}$$

$$C_{DD} = 1\times10^{-38}cm^6s^{-1}$$

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## $La_2S_3$×$2Ga_2S_3$ ŞÜŞƏLƏRİNDƏ NEODİM İONLARININ LYUMİNESSENSİYASININ KONSENTRASİON SÖNMƏSİ

$La_2S_3$×$2Ga_2S_3$ şüşələrində neodim ionlarının $^4F_{3/2}$ yuxarı lazer səviyyəsinin relaksasiyası tədqiq edilmişdir. Mikroparametrlər donor-akseptor ($C_{DA}$), donor-donor ($C_{DD}$) həmçinin minimal məsafə ($R_{min.}$) eksperimental parçalanma əyrilərinin bütün tədqiqat aparılan zaman intervalında analiz etməklə eksperimental və hesablama nöqtələrinin ən yaxşı üst-üstə düşmələrinə görə təyin edilmişdir.

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## КОНЦЕНТРАЦИОННОЕ ТУШЕНИЕ ЛЮМИНЕСЦЕНЦИИ ИОНОВ НЕОДИМА В СТЕКЛЕ $La_2S_3$×$2Ga_2S_3$

Исследованы процессы релаксации верхнего лазерного уровня неодима $^4F_{3/2}$ в стеклах $La_2S_3$×$2Ga_2S_3$. Из анализа экспериментальных кривых распада во всем исследованном временном интервале при условии наилучшего совпадения экспериментальных и расчетных данных были определены микропараметры взаимодействий донор – акцептор ($C_{DA}$), и донор – донор ($C_{DD}$) а также минимальное расстояние ($R_{min.}$).

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