THE INFLUENCE OF SEMICONDUCTOR PROPERTIES OF THE BASE ON LUMINESCENCE DAMPING KINETICS OF NEODYMIUM LEVEL $^4F_{3/2}$ IN THE CRYSTALS $\gamma - La_2S_3$, SULPHIDE, OXO-SULPHIDE AND SULPHIDE-OXIDE GLASSES

A.A. MAMEDOV
Institute of Physics of National Azerbaijan Academy of Sciences
Baku, Az-1143 H. Javid av., 33

The influence of semiconductor properties of the base on luminescence damping kinetics $^4F_{3/2}$ the neodymium level in the crystals $\gamma - La_2S_3$, sulphide, oxisulphide and sulphide-oxide glasses has been investigated.

The three-valency neodymium ion is the most spread activator of solid-state laser mediums [1]. This is connected with the its following peculiarities:

1) relatively intensive bands in visible region;
2) four-level generation scheme;
3) the generation wave length (λ≈1,06 и 1,35 mcm [2])which is comfortable for many practical applications;
4) the possibility to easy enough rule by the laser radiation as on the spectrum (harmony generation on nonlinear crystals), so in time (cavity damping).

The electron configuration of thrice-free ionized neodymium atom is $4f^3$. The electron number is odd one and *J* values are half-integral ones. The position of gravity centers of Nd^{3+} levels with definite *J* is close in different matrixes the same as all other three-valency rare-earth ions have. This is connected with weak interaction of 4*f* electrons with crystal field, in the comparison with spin-orbital one, as 4*f* membrane has been died and well screened by external membranes 5*s* and 5*p*. The electron transitions between membrane therms $4f^n$ are forbidden in the absence of the disturbing field. The influence of electric field of forbidden medium is partly taken and powers of oscillators of optical transitions have the order 10^{-7}. The interaction with crystal field is revealed also in Stark structure of spectrums, consisting from narrow discrete lines, which are obliged to transitions between Stark components of different therms. The number of Stark components is defined by *J* value and local symmetry of impurity center.

The metastable level $^4F_{3/2}$ is the upper laser level of neodymium, and $^4I_{11/2}$ or $^4I_{13/2}$ is lower level. In many laser crystals the degeneration taking down on the electric field is full. The $^4I_{9/2}, ^4I_{11/2}, ^4I_{13/2}, ^4I_{15/2}$ and $^4F_{3/2}$ levels are separated on 5,6,7,8 and 2Stark components correspondingly. Each Stark component stays doubly degenerate on magnetic field, i.e. is the Cramer's doublet. The main generation transition connects the $^4F_{3/2}$ and $^4I_{11/2}$ levels. The final laser level $^4I_{11/2}$ lies on 2000 cm^{-1} higher, than the main one, that causes the four-level generation scheme and laser work at the room temperature. In many laser mediums with neodymium, the relaxation speed from absorption bands into metastable state is the big enough one, anyway not less, than 10^8 cm^{-1} [3]. The bigger relaxation speed is proved by the many-phone non-radiation transitions in the result of the electron-phonon interaction. Thus, at the excitation of neodymium, the absorption bands are caused by the transitions on the superincumbent (in the comparison with $^4F_{3/2}$) levels, the absorbed energy minus the Stokes losses makes the occupancy the metastable state. Moreover, any replenishment of excited state, the velocity of which is equal to relaxation speed of metastable state is absent, thus that coming and going processes from metastable state are significantly separated in time and aren't cover the each other. The given conditions, as a rule, are carried out in known dielectric laser crystals and glasses, activated by Nd^{3+}. The situation was another one in semiconductor single crystals $\gamma - La_{2-2x}Nd_{2x}S_3$ and sulphide glasses, investigated by us. The experimental facts are:

Firstly, the non-exponentiality is observed at the activator low concentrations in crystals $\gamma - La_{2-2x}Nd_{2x}S_3$ at the excitation by the light, the wave length of which is λ=0,53 mcm on the initial region of decomposition curves of metasdtable level $^4F_{3/2}$ of neodymium.

Secondly, the neodymium deceleration takes place at the excitation of the samples $\gamma - La_{2-2x}Nd_{2x}S_3$ by the light, the wave length of which is λ=0,53 mcm on the far stages of the decomposition of metastable level $^4F_{3/2}$ of neodymium.

Thirdly, the time evolutions of population $^4F_{3/2}$ of neodymium in $\gamma - La_2S_3$ and sulphide glasses have strongly expressed maximums.

Firstly let's discuss the first two experimental facts. The crystal lattice $\gamma - La_2S_3$ is characterized by big quantity of structural vacancies, chaotically distributed (~10^{21}cm^{-3}), that leads to the quasi-amorphous lattice structure. Nowadays, it is established, that in many amorphous semiconductors, the electron states near band edges are localized, moreover, the continuous state density N(E) can take place, i.e. all states are localized in some energy interval. However, the some energy E_c, separating the localized and non-localized states, exists. From the defect crystal structure $\gamma - La_2S_3$ the quasi-continuous distribution of traps, the density maximum of which is situated on the depth 0,1-0,2 eV from conduction band bottom, takes place. In forbidden band of single crystals $\gamma - La_2S_3$, the levels with energies 1,3 and 2,6 eV below the bottom of the conduction band are revealed [4]. These levels in [4] are designated as level I and level II correspondingly.

In single crystals $\gamma - La_2S_3$ the photoluminescence band with maximum in region 1,6-1,7 eV is observed.

The luminescence spectrum at the excitation by the light, the wave length of which is 0,53 mcm, is presented on the fig.1. The spectrum consists from the one wide band.

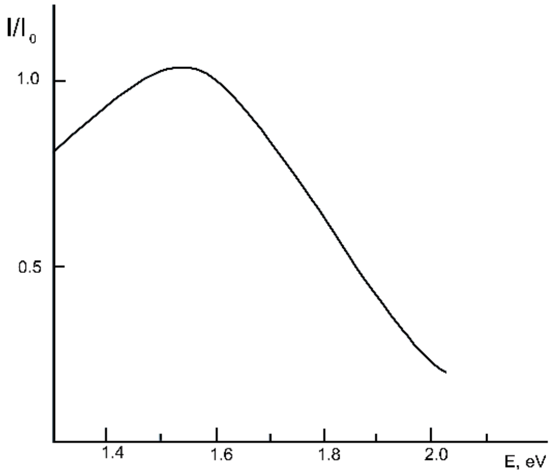

Fig.1. The luminescence spectrum of $\gamma - La_2S_3$ crystal at the excitation by the light with wave length λ=0,53 mcm (T=330K).

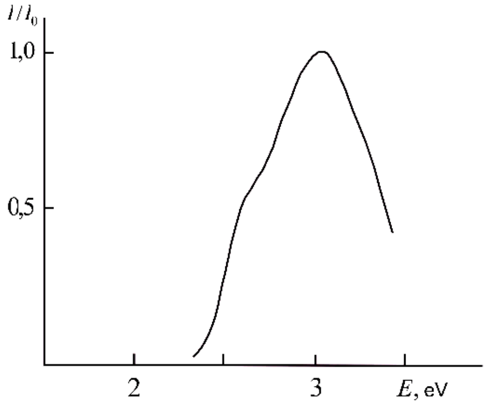

Fig.2. The luminescence excitation spectrum of $\gamma - La_2S_3$ crystal (T=300K).

The excitation spectrum of luminescence of non-doped crystal $\gamma - La_2S_3$ is given on the fig.2. It consists from wide non-elementary band, being the superposition at less of three excitation bands: the band situated in region 460-470 nm (2,6-2,7 eV), the band with maximum ~430 nm (~2,9 eV) and the band, situated in region 390-400 nm (3,1-3,2 eV), caused by the own excitation. The half-width of excitation spectrum is 0,5-0,8 eV. It is need to note, that the own luminescence $\gamma - La_2S_3$ is well excited by the light with wave length λ=0,53 mcm. Vice versa, the wideband radiation isn't observed at the crystal excitation $\gamma - La_2S_3$ by the light with wave length λ=0,6 mcm.

For the explanation of the luminescence in single crystals $\gamma - La_2S_3$ the next model is suggested. The luminescence in single crystals $\gamma - La_2S_3$ is caused by the recombination of donor-acceptor couples, differing not only by the distance between donor and acceptor, but by the energy of donor ionization. In the capacity of donor, the quasi-continuous set of traps near conduction band takes place, and the center, causing the appearance of level II with big cross-section of capture for holes is the acceptor. The luminescence excitation is carried out firstly, at the direct neglecting of electrons from valency band on level II (this transition corresponds to the energy 2,8-2,9 eV). Moreover, the luminescence excitation is carried out at the electron transition from II level into conduction band and at the followed their capture by the quazi-continuously distributed traps (transition from energies 2,6-2,7 eV). And finally, the luminescence is excited at the creation of electron-hole couples by the light from the region of own absorption $\gamma - La_2S_3$. The big half-width of spectrum is explained by the existence of quasi-continuous distribution of donors near bottom of conduction band. The damping velocity of own luminescence decreases with time – on far stages of decomposition it becomes the significantly less, than the decomposition velocity of excited state of neodymium $^4F_{3/2}$. It is character, that the own luminescence of matrix is significantly damps at the introduction of neodymium ions, moreover, the modulation of wideband matrix radiation Nd^{3+} and also the decrease of intensity of wideband radiation there, where Nd^{3+} doesn't observe, is observed. The decomposition law of excited state of neodymium at the excitation of the sample with radiation λ=0,53 mcm on far stages of decomposition is identical to damping law by own damped luminescence (fig.3). This is suggest the idea to fact, that the superposition of neodymium and matrix radiations takes place at the excitation of activated crystal by the radiation with λ=0,53 mcm in region of neodymium luminescence. However, the coincidence of the laws of damping of own luminescence and neodymium luminescence can be then, when the energy transformation from the traps to the impurity centers of neodymium takes place, if the velocity of this transformation is less, than the decomposition velocity of excited neodymium state [5]. That fact, that luminescence isn't observed, for example, in region 0,99mc, where neodymium doesn't radiate, and decomposition kinetics of excited state of neodymium, measured in region ~0,9 mcm (transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$), coincides with decomposition energy, measured in region ~1,06 mcm (transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$), evidences about second mechanism of decomposition retardation of excited state of neodymium at the excitation by the radiation with λ=0,53 mcm. Thus, the revealed first experimental fact is caused by the slow energy transition from the traps to neodymium ions. At the temperature increase the increase of decomposition velocity is observed, and at temperature decrease is vice versa. This is connected with fact that "retardation" of luminescence on transition $^4F_{3/2} \rightarrow {}^4I_J$ disappears with temperature increase, in the result of the increase of release rate of electrons, captured by traps.

The quantum output of luminescence from metastable state $^4F_{3/2}$ Nd^{3+} in crystal $\gamma - La_2S_3 - 0{,}9\% Nd^{3+}$, at the excitation by the light with wave length λ=0,812 mcm approaches to the unit [6], i.e. the measured life time τ_m corresponds to radiational one τ_0. Thus, the decomposition of excited state $^4F_{3/2}$ of Nd^{3+} level carries out on exponential law and decomposition curves at the excitation of any level, situating higher, than ${}^4F_{3/2}$ of Nd^{3+} level should be direct ones. The other picture is observed. The decomposition curves of metastable state of neodymium ${}^4F_{3/2}$ are not direct ones at the excitation by the light with wave length λ=0,53 mcm (fig.3, curve a), not only in final, but in initial region.

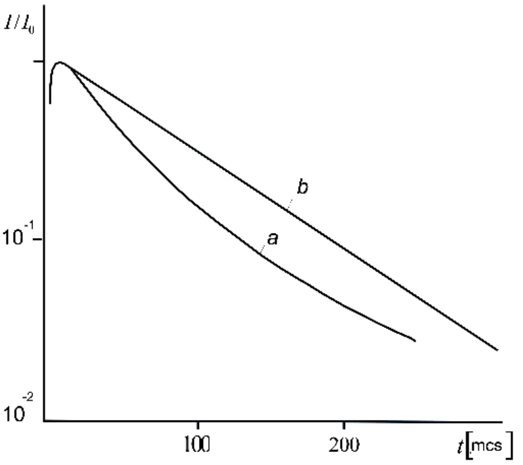

Fig.3. The decomposition curves of metastable state ${}^4F_{3/2}$ Nd^{3+} in crystal $\gamma-La_2S_3$ -0,9%Nd^{3+} at the excitation by the short impulse of the light λ=0,53 mcm (a), λ=0,6 mcm (b).

At the density increase of excited radiation (λ=0,53 mcm), the formula of decomposition curve ${}^4F_{3/2}$ of neodymium level didn't change. This evidences about the fact, that cooperative phenomena doesn't cause the observable anomaly. The exponential potential is observed at the light excitation with wave length λ=0,6 mcm, corresponding to ${}^4I_{9/2}\rightarrow{}^4G_{5/2}+{}^4G_{7/2}$ transition. The observable anomaly was explained by the following way. The Nd^{3+} ions are excited and electrons are taken from the II level to the quasi-continuous trap levels simultaneously, at crystal $\gamma-La_2S_3-Nd^{3+}$ excitation by the light, the wave length of which is λ=0,53 mcm. In excited neodymium ions, the energy is transformed to the metastable state ${}^4F_{3/2}$. The energy, corresponding to the ${}^4F_{3/2}\rightarrow{}^4I_{13/2}$ transition (1,41 mcm or ~0,88 eV) of neodymium ions is transformed to the electrons in valency band. This energy is enough for the electron neglecting from the valency band on II level. Moreover, Nd^{3+} ions are in low excited states ${}^4I_{13/2}$. Thus, the energy transition from ${}^4F_{3/2}$ level is carried out. Because of this reason, the non-exponentiality is observed on initial stage of decomposition kinetics. The electron neglecting from the valency band on II level can only increase the life time of excited electrons in conduction band. Thus, in the difference from the wide-known dielectric matrixes, the conduction electrons interact with valency 4f-electrons in semiconductors.

Let's consider the third experimental fact. The observation of luminescence becoming flushed Nd^{3+} on ${}^4F_{3/2}\rightarrow{}^4I_J$ transitions in $\gamma-La_2S_3$ and sulphide glasses is the consequence of slow occupancy of upper laser level. In $\gamma-La_2S_3-Nd^{3+}$ crystal and sulphide glasses at the light excitation with λ=0,53 mcm, the transition possibilities from absorption bands in metastable state were significantly less ($10^5\div10^6$ sec^{-1}), that in significant degree is caused by the relatively short spectrums of own oscillations of given bases. The luminescence coming flushed on ${}^4F_{3/2}\rightarrow{}^4I_J$ transitions wasn't observed in oxo-sulphide and sulphide-oxide glasses at Stokes excitation. The comparison of the spectrums of combination light scattering of $\gamma-La_2S_3$ crystal and oxo-sulphide and sulphide-oxide glass is revealed, that the more high-frequency oscillations are present in glass, than in crystal [7]. Besides, as the spectrum of combination scattering of glassy material reflects the distribution of density spectrums and its oscillation states that it is clear, that the density maximum is on the oscillation frequencies with high energy [8]. It is clear, that these obstacles in significant degree define the big velocity of non-reflecting relaxation energy from the excitation levels and its more effective accumulation on upper laser level Nd^{3+} in oxo-sulphide and sulphide-oxide glasses in the comparison with the crystal $\gamma-La_2S_3$.

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A. Ə. Məmmədov

$\gamma - La_2S_3$ KRİSTALLARINDA SULFİD, OKSOSULFİD VƏ SULFİDOOKSİD ŞÜŞƏLƏRİNDƏ MATERİALIN YARIMKEÇİRİCİ XASSƏLƏRİNİN NEODİMİN $^4F_{3/2}$ SƏVİYYƏSİNDƏN LYUMİNESSENSİYANIN SÖNMƏ KİNETİKASINA TƏSİRİ

$\gamma - La_2S_3$ kristallarında, sulfid, oksosulfid və sulfidooksid şüşələrində materialın yarımkeçirici xassələrinin neodimin $^4F_{3/2}$ səviyyəsindən lyuminessensiyanın sönmə kinetikasına təsiri tədqiq edilmişdir.

А.А.Мамедов

ВЛИЯНИЕ ПОЛУПРОВОДНИКОВЫХ СВОЙСТВ ОСНОВЫ НА КИНЕТИКУ ЗАТУХАНИЯ ЛЮМИНЕСЦЕНЦИИ УРОВНЯ $^4F_{3/2}$ НЕОДИМА В КРИСТАЛЛАХ $\gamma - La_2S_3$, СУЛЬФИДНЫХ, ОКСОСУЛЬФИДНЫХ И СУЛЬФИДООКСИДНЫХ СТЕКЛАХ

Исследовано влияние полупроводниковых свойств основы на кинетику затухания люминесценции уровня $^4F_{3/2}$ неодима в кристаллах $\gamma - La_2S_3$, сульфидных, оксосульфидных и сульфидооксидных стеклах.

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