

Photoluminescence of $\text{EuGa}_2\text{Se}_4:\text{Nd}^{3+}$

Arif Mirjalal Pashayev^{1,2}, Bahadır Guseyn Tagiyev^{1,2}, Said Abush Abushov¹,
Ogtay Bahadır Tagiyev^{1,3}, Fatma Agaverdi Kazimova¹

¹Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan

²National Aviation Academy of Azerbaijan, Baku, Azerbaijan

³Lomonosov Moscow State University Baku Campus, Baku, Russia

Email: oktay58@mail.ru

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ABSTRACT

The photoluminescence (PL) in temperature interval 77 - 300 K is investigated in $\text{EuGa}_2\text{Se}_4:\text{Nd}$ polycrystals. It is established that broad band PL with maximum at 561 nm is caused by intracentral transitions $4f^65d - 4f^7(8S_{7/2})$ of Eu^{2+} ions. The intracentral emission of Nd^{3+} , corresponding to both transitions from ${}^4F_{3/2}$ level and higher situated levels, is observed at interband excitation. The essential intensity of transitions from ${}^2H_{11/2}$ and ${}^4F_{9/2}$ levels is the interested peculiarity of luminescence spectra of Nd^{3+} in these crystals.

Keywords: Photoluminescence; Intracentral Transitions; Europium and Neodymium Ions

1. Introduction

The series of $\text{MGa}_2\text{S}_4(\text{Se}_4)$, $\text{M}_2\text{Ga}_2\text{S}_4(\text{Se}_4)$, $\text{M}_3\text{Ga}_2\text{S}_6(\text{Se}_6)$, $\text{M}_4\text{Ga}_2\text{S}_7(\text{Se}_7)$, $\text{M}_5\text{Ga}_2\text{S}_8(\text{Se}_8)$ compounds is obtained in M-Ga-S(Se) system (where M is Ba, Sr, Ca, Eu, Yb) [1-4]. The compounds synthesized in M-Ga-S(Se) system can be combined in one group with general formula $\text{II}_n\text{-III}_2\text{-VI}_m$ (where $n = 1, 2, 3, 4, 5$; $m = n + 3$; II are bivalent cations of Eu, Yb, Sm, Ca, Ba, Sr; III are trivalent cations of Ga, Al, In; VI are S and Se chalcogens). Many $\text{II}_n\text{-III}_2\text{-VI}_m$ compounds [5] have large number of stoichiometric voids: the one-fourth fraction of free places unoccupied by cations in crystal lattice. The stoichiometric voids situated periodically in lattice, don't have the defect properties.

The compounds in M-Ga-S(Se) system, M cations of which are 4f elements (lanthanides), can be the active medium of semiconductor lasers, luminescent lamps, colored display screens and other information systems [6-8]. These compounds have the forbidden band width is 4.4 eV and effectively transform the energy of electric field, X-ray and ultraviolet emissions, and also electron beams into visible light. The excitation spectrum of these compounds covers the spectral region from near ultraviolet one up to 500 nm.

EuGa_2Se_4 is the one of comparably little-studied compounds in M-Ga-S(Se) system. EuGa_2Se_4 compound crystallizes in pseudo-orthorhombic sublattice at simultaneous existence of twinning and superstructure [9]. The lattice parameters are $a = 20.760 \text{ \AA}$, $b = 20.404 \text{ \AA}$, $c = 12.200 \text{ \AA}$ [10]. Eu atoms in EuGa_2Se_4 structure are in partial positions 16(e), 8(a) and 8(b) in space group

D_{2h}^{24} -Fddd having eight Se atoms as nearest neighbors. Crystal structure and some physical properties of this compound are described in [2]. The photoluminescence investigation of EuGa_2Se_4 activated by neodymium ions is of the interest for the photoluminescence mechanism revealing and the determination of trap level energy spectrum and also practical application.

2. Experiment

EuGa_2Se_4 compound is synthesized from binary compounds EuSe and Ga_2Se_3 , taken in stoichiometric relations, by solid-phase reaction in graphitized ampoules evacuated up to 10^{-4} millimeter of mercury. The synthesis is carried out at 1300 K in one-temperature furnace during 4 hours. The annealing during 24 hours at 1000 K is carried out after the synthesis. Activation by neodymium ions is realized using neodymium fluorides doping during synthesis process. PL is investigated in temperature interval 77 - 300 K. The continuous laser diode InGaN ($\lambda = 405 \text{ nm}$) is the excitation source. The registration of emission spectrum is carried out on Spectral Diffraction Luminescence device. The emission receiver is photoelectric multiplier-39A. The luminescence of the samples activated by neodymium is excited by laser on Rodamine 6G (range 550 - 620 nm). The luminescence registration is carried out by Diffraction Lattice Monochromator with Photoelectric Multiplier and Boxcar Integrator BC I-280.

3. The Results and Discussions

The PL spectra of EuGa_2Se_4 crystals at different tem-

peratures are shown on **Figure 1**. The one intensive broad emission band covering the wavelength region 500 - 620 nm with maximum at 561 nm and two relatively narrow bands at 709 and 745 nm are observed in PL spectra. It is known that the broad emission band is usually observed in crystals containing Eu^{2+} . The energy position of luminescence band, caused by Eu^{2+} , changes in the dependence on crystal structure and percentage of Eu^{2+} [11]. The observable PL in region 700 - 900 nm (maxima at wave lengths 709 nm and 745 nm) is caused by electron-hall recombination. The excitation and emission spectra of EuGa_2Se_4 crystal at temperature 300 K are shown on **Figure 2**. As it is seen from the figure, PL excitation spectrum is significantly broad band one and consists of overlapping bands. One of these bands at 374 nm is very clear one, but others at 404, 415, 454, 471 nm aren't allowed bands at temperature 300 K. The dependence of PL band intensity ($\lambda_{\text{max}} = 561$ nm) on temperature is shown on **Figure 3**. As it is seen from the figure the intensity in temperature region 92 - 120 K very weakly depends on temperature, in region from 120 up to 170 K slowly decreases and further temperature growth (170 - 300 K) leads to strong decrease of emission intensity, *i.e.* the strong temperature quenching of PL takes place. The activation energy of temperature quenching of PL is defined by high-temperature inclination (170 - 300 K). It is 0.09 eV. The temperature dependence of band half-width of PL with the maximum at 561 nm in $\Gamma(T)$ and $T^{1/2}$ coordinates is shown on **Figure 4**. It is seen that this dependence in temperature region 77 - 300 K is linear one and can be described by the use of configuration coordinate model and Boltzmann distribution. The fol-

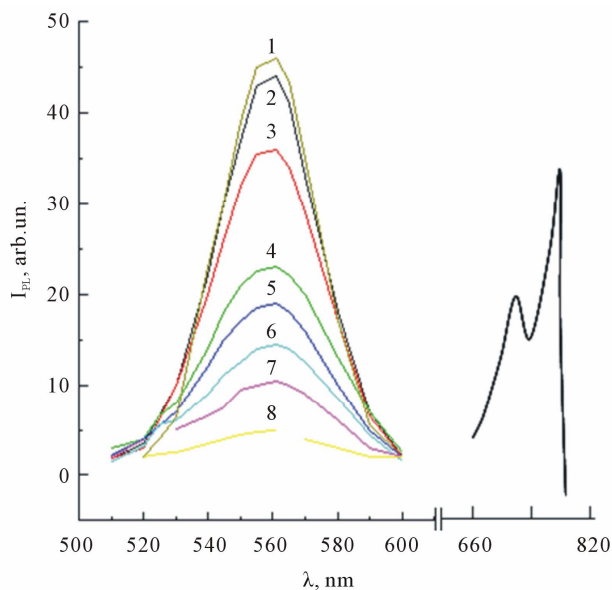


Figure 1. The PL spectra of EuGa_2Se_4 crystals at different temperatures (K): 1-92; 2-120; 3-144; 4-173; 5-184; 6-198; 7-215; 8-286.

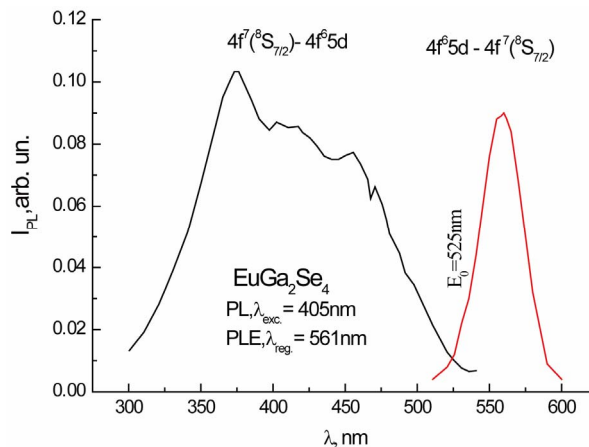


Figure 2. Excitation and emission spectra of EuGa_2Se_4 at 300 K.

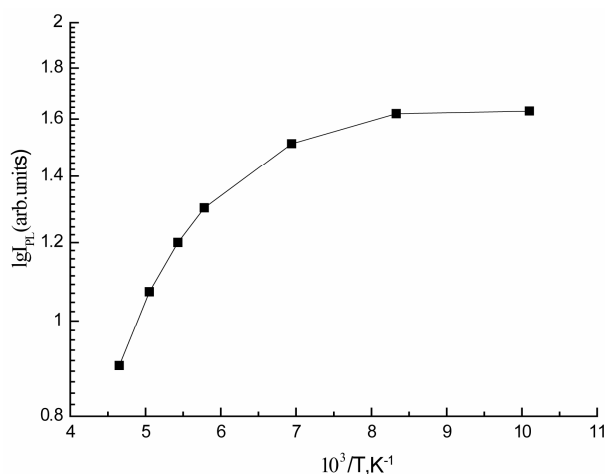


Figure 3. The temperature dependence of PL intensity of EuGa_2Se_4 .

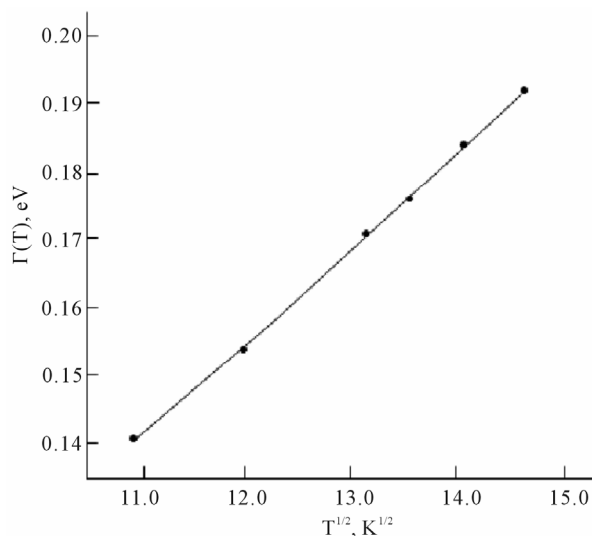


Figure 4. The dependence of PL band half-width of EuGa_2Se_4 with maximum at 561 nm on temperature.

lowing expressions, connecting Stokes shift ΔS , Huan-Rice factor s and phonon energy $\hbar\omega$ with the half-width temperature dependence $\Gamma(T)$, are obtained on the base of theoretical analysis of absorption and emission spectra in [12,13]:

$$\Delta S = (2S - 1)\hbar\omega \quad (1)$$

$$\Gamma(T) = 2.36\hbar\omega\sqrt{S}\sqrt{\coth\frac{\hbar\omega}{2KT}} \quad (2)$$

If $\hbar\omega < \kappa T$ then the expression under quadratic root in (2) can be expanded into series and limited by the first member:

$$\coth x = \frac{1}{x}, \text{ where } x = \frac{\hbar\omega}{kT} \quad (3)$$

Then expression (2) can be rewritten in the following form:

$$\Gamma(T) = 2.36\hbar\omega\sqrt{S}\sqrt{\frac{2kT}{\hbar\omega}} \quad (4)$$

or

$$\Gamma(T) = 2.36\sqrt{S}\sqrt{2kT \cdot \hbar\omega} \quad (5)$$

The Equation (5) shows that half-width Γ linearly depends on \sqrt{T} . The values of Huan-Rice factor s and Stokes shift ΔS , which are equal to 8 ± 2 and 0.33 eV correspondingly, are found by experimental results. At calculation the phonon energy $\hbar\omega$ in EuGa_2Se_4 polycrystal is considered as equal to 23 meV according to data in [14]. The red shift D is obtained using formula $D = E_{ex} - E_{em}$ [12,13] (where E_{ex} is excitation state energy and E_{em} is emission energy of Eu^{2+} ion (4.19 eV and 2.21 eV correspondingly) $D = 1.98$ eV.

The constancy of energy position of broad band emission maximum at 561 nm (**Figure 1**) with temperature variation and temperature dependence of band half-width evidence about belonging of this emission band to Eu^{2+} ions, *i.e.* to intracentral transitions $4f^65d - 4f^7(^8S_{7/2})$ of Eu^{2+} ions.

The excitation spectra registered in the region of matrix self-absorption edge (**Figure 5**) evidence about fact, that the excitation on transition band-band isn't less effective, than one on intracentral transition $^4I_{9/2} - ^4G_{5/2}$. Note that the beginning of monotonously growing excitation spectrum part lies below than the region of matrix self-absorption edge, *i.e.* the transfer of excitation energy from small donor levels to Nd^{3+} ion ones is observed. The curve 2 is obtained under the conditions when the luminescence intensity linearly depends on pumping intensity; the curve 3 corresponds to nonlinear dependence of luminescence on pumping intensity (more detail about nonlinear dependence of luminescence intensity on pumping one can see below).

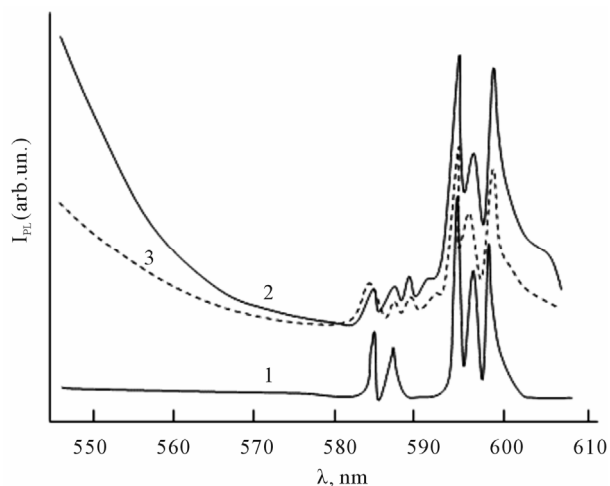


Figure 5. Excitation spectrum of $\text{EuGa}_2\text{Se}_4:1$ at % Nd^{3+} in 548 ÷ 605 nm wavelength range at 77 K (cur. 1) and 293 K (cur. 2, 3) 1 and 2 are linear parts of PL intensity dependence on pumping power 3 is nonlinear part of PL intensity dependence on pumping power.

It is interesting to note that the pumping at room temperature into matrix absorption band is more effective one for excitation of high-situated levels of Nd^{3+} , at 77 K the pumping is effective one for $^4F_{3/2}$ level. As a whole, the efficiency for excitation by means of matrix at 77 K is less than at room temperature.

Note that dependence of buildup effect of Nd^{3+} luminescence from $^4F_{3/2}$ level on excitation wavelength. The time passes of luminescence for $\text{EuGa}_2\text{Se}_4:\text{Nd}^{3+}$ at 77 K are given in the **Figure 6**. At 77 K the excitation on $^4G_{5/2}/\lambda_{exc} = 598$ nm level (curve 2) gives the clearly expressed buildup effect during ~ 15 μs . The transition to interband excitation, increase of pumping frequency $h\nu_{exc} > E_g$, $\lambda_{exc} = 545$ nm (curve 1) leads to disappearance of this effect. At room temperature the buildup isn't observed in both cases. The luminescence decay times for both cases of excitation are similar ones (~ 50 μs). At 77 K the luminescence decay times for EuGa_2Se_4 at small neodymium concentrations on transitions from $^4F_{3/2}$ and $^4F_{5/2}$ levels are equal to 50 μs and 5 μs correspondingly. Here we need to say several words about possible excitation mechanism Nd^{3+} in EuGa_2Se_4 . In EuGa_2Se_4 at 293 K and interband excitation Eu^{2+} excites and it transfers the excitation on G-levels of neodymium. At temperature decrease Eu^{2+} band narrows, the overlapping with G-levels of Nd^{3+} disappears and that's why the levels causing the broad impurity emission bands which transfer the energy on $^4F_{3/2}$ and $^4F_{5/2}$ levels, mainly take part in energy transfer on Nd^{3+} at 77 K. As a result at 77 K $^4F_{3/2}$ level excites more effectively than G-levels as it is mentioned above. Moreover, the emission from $^4F_{3/2}$ takes place without buildup because of the energy is transferred on it directly from impurity levels. As a whole at

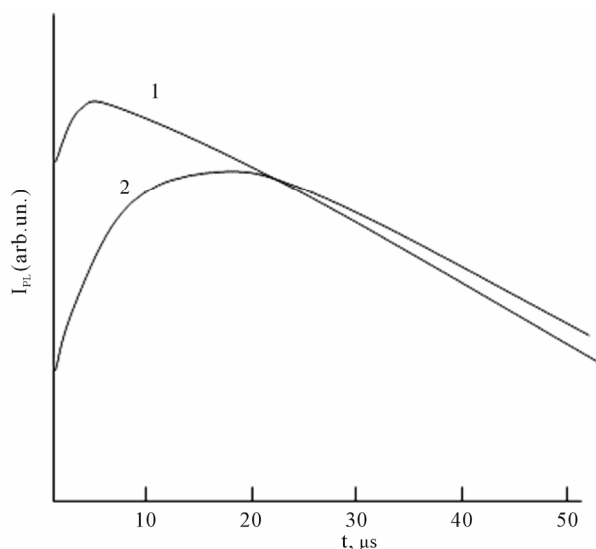


Figure 6. Time passes of PL from ${}^4F_{3/2}$ level for EuGa_2Se_4 $\langle\text{Nd}\rangle$ at 77 K; 1. $h\nu_{exc} > E_g$, $\lambda_{exc} = 545$ nm; 2. $\lambda_{exc} = 598$ nm.

77 K the efficiency of energy transfer to Nd^{3+} ion by means of the interband transition goes down. The luminescence investigation results at transitions from ${}^4F_{3/2}$ level on ${}^4I_{9/2}$, ${}^4I_{11/2}$, ${}^4I_{13/2}$ evidence about the fact that in considered crystals not one type of luminescent centers exists as Stark component number exceeds the maximum possible one. This is also confirmed by the dependence of emission spectra on excitation wave length, on delay value of registration time moment and on sample history.

The effect of intensity quick saturation with pumping growth is the interest peculiarity of neodymium luminescence at interband excitation in the investigated crystals [15]. The dependence of PL intensity on pumping power is given in **Figure 7**. In this case the excitation wave length is 552 nm and emission registration wave length is $\lambda_{reg} = 780$ nm. It is seen that emission intensity nonlinearly depends on pumping power. The saturation is observed at room temperature and at liquid nitrogen temperature. This effect can be connected with pumping energy absorption by free carriers, growth of pumping reflection at increase of free carrier number, saturation of intermediate agents by means of which the excitation is transferred from matrix to Nd^{3+} and etc. Note that luminescence intensity linearly depends on pumping power at excitation through absorption bands of Nd^{3+} .

Thus, in EuGa_2Se_4 crystals the broad band intensive luminescence is connected with intracentral transitions $4f^65d - 4f^7({}^8S_{7/2})$ of Eu^{2+} ions. The carried investigations of triple compounds with neodymium show that nearest surrounding of Nd^{3+} has the near tetragonal symmetry in investigated crystals; the luminescence of Nd^{3+} effectively excites because of interband transitions; the intensive emission of Nd^{3+} from levels situated higher ${}^4F_{3/2}$ is observed, therefore $\text{EuGa}_2\text{Se}_4:\text{Nd}^{3+}$ can be used as nar-

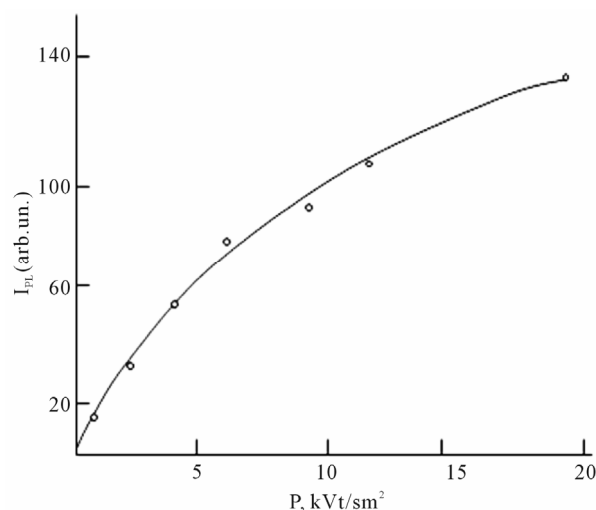


Figure 7. The dependence of PL intensity on pumping power for $\text{EuGa}_2\text{Se}_4:\text{Nd}^{3+}$, $T = 293$ K. $t_{giv} = 1$ μs . $\lambda_{reg} = 780$ nm, $\lambda_{exc} = 552$ nm.

row-band luminophors in 580 - 1090 nm range.

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