PHOTOLUMINESCENCE OF (Ga₂S₃)₀.₉₄:(Eu₂O₃)₀.₀₅(Tb₂O₃)₀.₀₁ CRYSTAL

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The investigations of luminescence spectra, dependence of luminescence intensity on excitation source power and also $(Ga_2S_3)_{0,94}:(Eu_2O_3)_{0,05}(Tb_2O_3)_{0,01}$ crystal luminescence kinetics in temperature interval 10 – 300K are given in the work. Stokes shifting (ΔS=0,6 eV), Huan - Rice factor (S=12±2), energy of optical phonons and lifetime of Eu^{2+} ions decreasing from 400nsec up to 200nsec with temperature increase are defined.

INTRODUCTION

Nowadays the study of inorganic materials is the modern scientific-technical direction connecting the series of tasks of quantum electronics, spectroscopy, crystallography and chemical technology in one complex problem. The activated crystals with impurity of rare-earth ions (REI) are the main objects of its study. The production of high-performance devices for visualization and lighting which are able to compete with traditional systems requires the obtaining of luminophors with specifical propeties. This necessity causes the development of new material obtaining or optimization of already existing luminophors.

Introduction of rare-earth element impurities (REE) is necessary for obtaining of radiation big quantum output at optical and electrical pumping of Ga_2S_3 crystals, moreover the effective energy transfer of excited carriers to 4f-electrons takes place. REE excitations are possible through wide matrix absorption band that decreases the excitation threshold increasing the luminescence efficiency.

The diversity of radiated transitions of REE allows us to realize the both any required lightening color and laser generation [1]. The essential peculiarity of the given materials is in the absence of concentration damping (up to 7mol% of impurity) for series of levels taking place in generation [2,3].

There are several compounds Ga_2S, GaS, Ga_4S_5, Ga_2S_3 in Ga-S system [4]. The distinctive feature of these compounds is the difference in their stability in air and corrosive medium (in mineral acids HCl, HNO_3, H_2SO_4). Ga_2S_3 is the more stable from the given compounds. It crystallizes in structures of sphalerite or wurtzite and is related to crystal-chemical group of diamond like substances.

The structure of this compound is the defect one in relation to normal structure of sphalerite or wurtzite types because of absence of gallium atoms, 1/3 part of places of which is vacant one in lattice. The impurities in compound of Ga_2S_3 type are electrically inactive ones. This peculiarity of Ga_2S_3 compound makes it closer with glassy and amorphous semiconductors. Rare-earth elements (REE) create the effective radiation centers in Ga_2S_3 and these compounds reveal the intensive luminescence at the influence of external factors (electric field, ultraviolet and roentgen radiations, electron beams and etc) [5,6].

The solid solutions of $(Ga_2S_3)_{1-x}(M_2O_3)_x$ (M-Eu, Sm, Tb) system are firstly synthesized by authors [7,8]. These crystals crystallize in monoclinic syngony.

The results of investigations of Sm^{2+} ion luminescence in Ga_2S_3 crystals at78-450K are given in [9]. The narrow bands with maxima at 610, 657, 829nm, which aren't connected by transmitted transitions $^5D_1 \rightarrow ^7F_0$, $^5D_1 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_4$ correspondingly, are observed in Ga_2S_3: Sm^{2+} crystal radiation spectrum. The luminescent properties of europium bivalent ions in Ga_2S_3 are considered in [10] at temperatures 77÷300K. There are bands with maximum at 545nm (band half-width 0.13eV) caused by $4f^65d \rightarrow ^8S_7(4f^7)$ transition are observed in spectrum. The work [11] is dedicated to the investigation of luminescence spectra $Ga_2S_3:Tb_2O_3$ in temperature interval 77÷300 K, it is shown that the observable narrow-band radiation in wave length region 400÷750 nm is connected with intracenter transitions $^5D_4 \rightarrow ^7F_6$ (492 nm), $^5D_4 \rightarrow ^7F_5$ (544 nm), $^5D_4 \rightarrow ^7F_4$ (584 nm), $^5D_4 \rightarrow ^7F_3$ (625 nm), $^5D_4 \rightarrow ^7F_2$ (680 nm) of Tb^{3+} ion.

In case if there is more than one REE in the system then the nonadditive effects being the result of their interaction. The interaction can reveal in change of absorption and radiation spectra, duration of excitation state, probability of energy transitions and series of other properties because of reconstruction of energy level system. At big concentrations or in cases of inclination from statistical distribution of REE ions there are other features of interaction in crystal lattices such as line shifting and energy redistribution in them, formation of new lines and disappearance old ones. The problem of sensitized luminescence at which the energy transfer from sensitizer resolved level to activator forbidden band plays the main role in one from developing theories in the given direction [12-15]. The strong overlapping of Eu^{2+} excitation spectrum and Tb^{3+} radiation spectrum can serve the reason of energy transfer from Tb^{3+} to Eu^{2+} [16].

The investigation of luminescence properties of Ga_2S_3 solid solutions activated by rare-earth element ions is of interest from both points of view the (PhL) photoluminescence mechanism revealing and their practical application. The given work is dedicated to

investigation of luminescence spectra in temperature interval 10 – 300K, dependence of luminescence intensity on excitation source power and also crystal luminescence kinetics $(Ga_2S_3)_{0.94}:(Eu_2O_3)_{0.05}(Tb_2O_3)_{0.01}$.

EXPERIMENT

For formation of effective luminescence spectra in $(Ga_2S_3)_{0.95}:(Eu_2O_3)_{0.05}$ the impurity Tb in Tb_2O_3 form is introduced in synthesis process. The terbium oxide content changes from 0,1 up to 7at%. The melts are synthesized in evacuated ampoules up to 10^{-4} Pa at 1400K with periodic mixing. The samples are excited by radiation of impulse nitrogen laser (Laser LN 1000 with energy 1,4J by impulse 0,5 nsec, wavelength 337,1 nm). The luminescence spectrum is registered on spectrometer HR 460, radiation detector is CCD detector.

RESULTS AND THEIR DISCUSSION

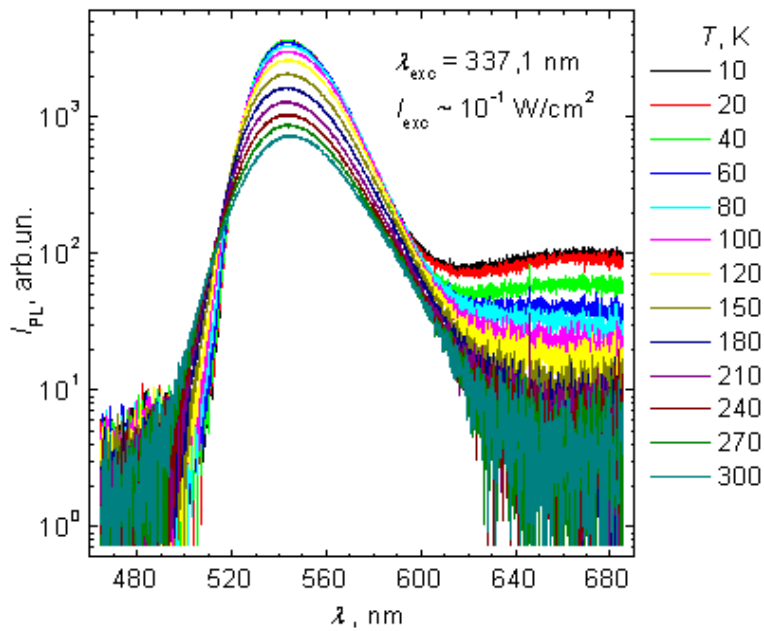PhL spectra at different temperatures are presented in fig.1.

Fig.1. PhL spectrum of $(Ga_2S_3)_{0.94}:(Eu_2O_3)_{0.05}(Tb_2O_3)_{0.01}$ at temperatures: 1-10,2-20, 3-40,4-60,5-80,6-100,7-120,8-150,9-180, 10-210,11-240,12-270,13-300K, $\lambda_{exc.}$=337.1nm, $I_{exc.}$=10^{-1}Vt/cm^2.
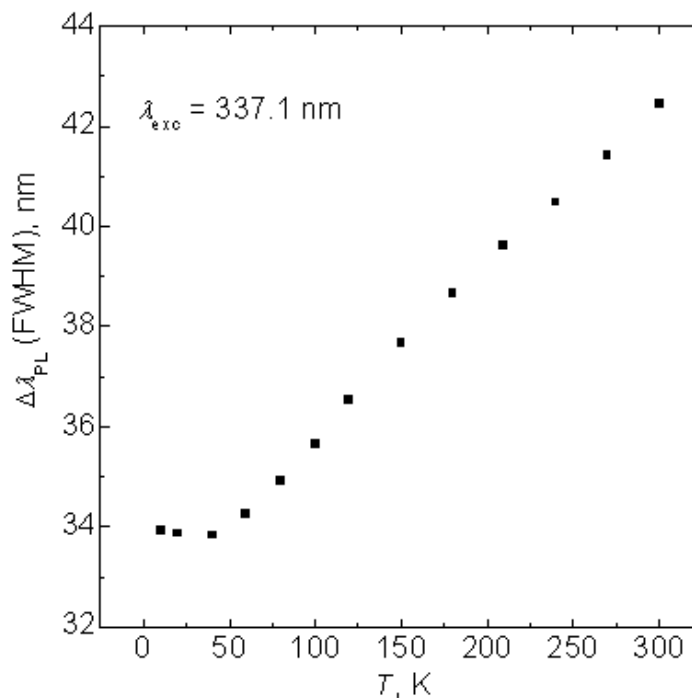

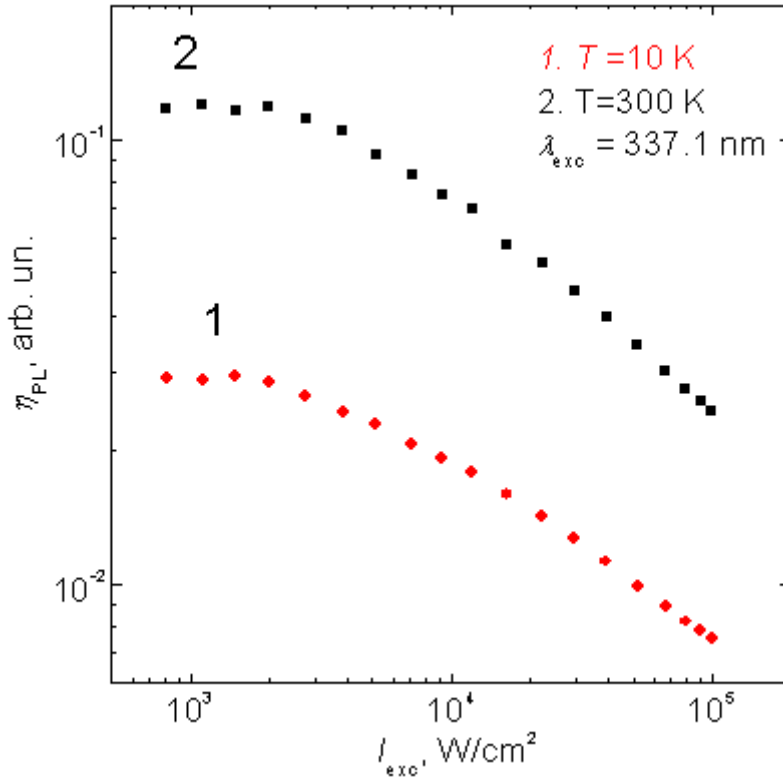*Fig.2.* The dependence of photoluminescence bandwidth with maximum at 548nm on temperature.

Fig.3. The dependence of PhL efficiency on excitation level in $(Ga_2S_3)_{0.94}$:$(Eu_2O_3)_{0,05}(Tb_2O_3)_{0,01}$ crystal at $\lambda_{exc.}$=337.1nm, 1-10, 2-300K.
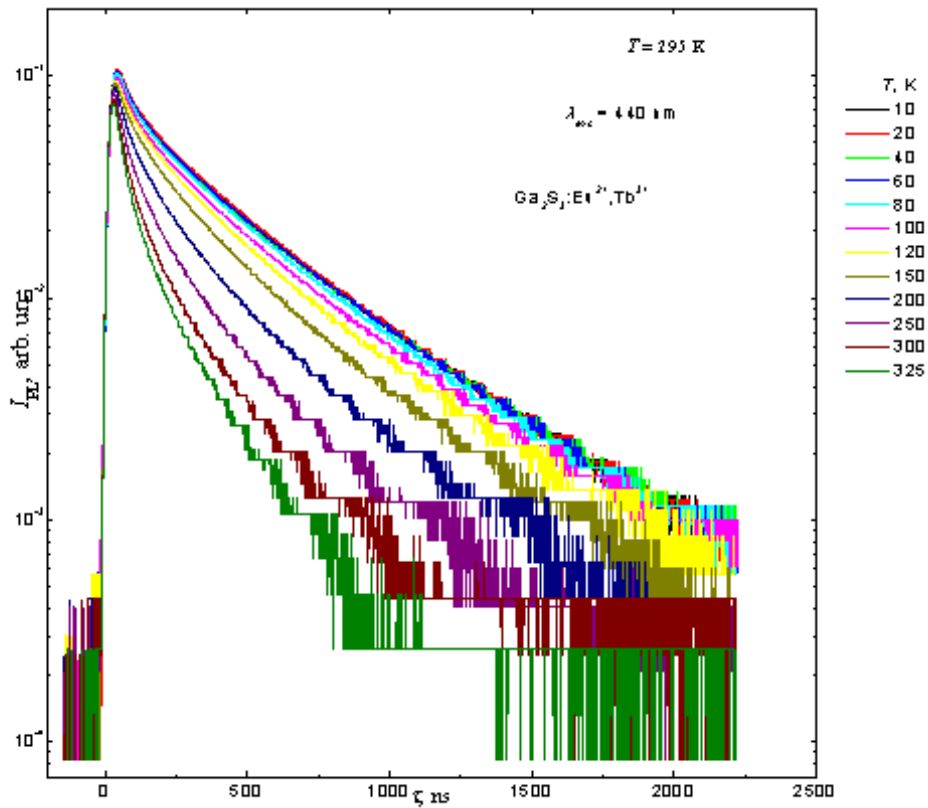
Fig.4. The kinetics of luminescence damping of $(Ga_2S_3)_{0.94}$:$(Eu_2O_3)_{0,05}(Tb_2O_3)_{0,01}$ crystal at temperatures: 1-10, 2-20, 3-40, 4-60, 5-80, 6-100,7-120, 8-150, 9-200, 10-250,11-300, 12-325K.

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It is seen that they are broadband ones and have spectral region 480-650nm. The band intensity significantly decrease, band half-width increases (fig.2) and their maximum energy position (548nm) doesn't change with temperature increasing. On this spectrum Ga_2S_3:Tb^{3+} the maximums character for spectrum aren't observed and band intensity with maximum 548nm observed in PhL spectrum Ga_2S_3:Eu^{2+} which caused by intracenter transitions $4f^65d \rightarrow 4f^7$ ($^8S_{7/2}$) of Eu^{2+} ions, increases [10]. The absence of radiation bands corresponding to above mentioned transitions $5d \rightarrow {}^7F_6$ and $5d \rightarrow {}^7F_5$ of Tb^{3+} ion in PhL spectrum of crystals $(Ga_2S_3)_{0.94}$:$(Eu_2O_3)_{0,05}(Tb_2O_3)_{0,01,}$ activated by two REE, probably is connected with energy transfer from Tb^{3+} ion to Eu^{2+} ion. Such energy transfer between these ions is shown in [17,18]. It takes place because in these crystals the lowest excited level 5d of Tb^{3+} ion is higher than lowest excited level $4f^65d$ of Eu^{2+} ion [16]. The temperature dependence of PhL band half-width with maximum at 548nm in $\Gamma(T)$ and $T^{1/2}$ coordinates is presented in fig.2. It is seen that this dependence in temperature interval 77 – 300K is linear one and can be described by the model of configuration coordinates and Boltzmann distribution. The expressions connecting Stokes shift ΔS, Huan-Rice factor S and phonon energy $\hbar\omega$ with temperature dependence of band half-width $\Gamma(T)$ are obtained on the base of theoretical analysis of absorption and radiation spectra in [17,18]:

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

$$\Gamma(T) = 2{,}36\ \hbar\omega\sqrt{S}\ \sqrt{\coth\frac{\hbar\omega}{2kT}} \qquad (2)$$

If $\hbar\omega < kT$ then the expression under square root (2) we can expand in series and limit ourselves by the first term:

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

Then expression (2) we can rewrite in the following form:

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

or

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

Equation (5) shows that band half-width $\Gamma(T)$ linearly depends on $\sqrt{T}$. The band half-width increases with temperature increase from 34 up to 43nm. Stokes shift ($\Delta S=0,6$ eV), Huan-Rice factor ($S=12\pm2$) and energy of optical phonons ($\bar{h}\omega = 23$ MeV) are defined by experimental results. The constancy of energy position of broadband radiation maximum at 548nm with temperature change and band temperature dependence prove the belonging of this radiation band to Eu^{2+} ions, i.e. to intracenter transitions $4f^65d - 4f^7(^8S_{7/2})$ of Eu^{2+} ions (fig.1). PhL efficiency (η_{PhL}) saves its constant value at impulse excitation at wavelength 337nm in excitation level interval from 10^2 Vt/cm^2 (fig.3). The insignificant decrease of PhL intensity and practically constant PhL efficiency significantly decreases at excitation levels higher 10^2 Vt/cm^2. The further decrease of excitation level from 10^5 Vt/cm^2 up to 10^2 Vt/cm^2 leads to intensity reconstruction in previous level that evidences on absence of material degradation.

The kinetics of radiation damping for maximum 548nm at temperature interval 10 ± 335 K at excitation 440nm is shown in fig.4. As it is seen the luminescence damping in the given coordinates has the linear character, i.e. luminescence damping obeys to exponential law $I=I_0.e^{t/\tau}$. Eu^{2+} ion lifetime decreases from 400 nsec up to 200nsec in solid solutions $(Ga_2S_3)_{0.94}$:$(Eu_2O_3)_{0,05}(Tb_2O_3)_{0,01}$ with temperature increase from 10K up to 325K that can be connected with thermal activation of radiationless recombination channel.

CONCLUSION

Thus, it is shown that constancy of energy position of broadband radiation maximum at 548nm with temperature change and temperature dependence of band half-width evidences on belonging of this radiation band to Eu^{2+} ions i.e., to intracenter transitions $4f^65d - 4f^7(^8S_{7/2})$ of Eu^{2+} ions and also on the absence of material degradation in excitation level interval from 10^2 - 10^5 Vt/cm^2 and stability of position and form of PhL spectra.

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