PHOTOLUMINESCENCE OF $Ca_4Ga_2S_7:Eu^{2+}$ COMPOUND

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The photoluminescence (PhL) properties of chalcogenide $Ca_4Ga_2S_7:Eu^{2+}$ semiconductors in interval of impulse laser excitation from 10 up to 10^5 Vt/cm^2 at room temperature are studied.

PhL of $Ca_4Ga_2S_7:Eu^{2+}$ compound at excitation by radiation in range 450-575nm is characterized by essential dominance of the band in the spectrum on 660 nm. PhL of $Ca_4Ga_2S_7:Eu^{2+}$ compound on wave lengths 560 nm and 660nm damps at constant times 258 nsec and 326 nsec correspondingly.

Keywords: chalcogenide semiconductors, high excitation level, luminescence efficiency.
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INTRODUCTION

The preparation of high-production devices for visualization and illumination which are able to compete with traditional systems requires the creation of luminophors with specific properties. This necessity causes to development of new materials or optimization of already existing luminophors.

In this aspect the triple alkaline-earth chalcogenide semiconductors of II-III_2-VI_4 (II-Ca, Ba, Sr; III-Ga, Al; VI-S, Se) type activated by rare-earth elements are perspective ones. In present, luminophors of above mentioned system activated by Eu ions attract investigators' attention, as they have properties required for comparably new technologies of plane screens, screens of inorganic electro-luminescence devices, including color TV and light sources [1 – 5].

$Ca_4Ga_2S_7:Eu^{2+}$ compound belongs to the group of high-performance luminophors with general formula $Ca_mGa_2S_n$:RRE (RRE is rare-earth element) where n=4,5,6,..., m = n-3 [6]. The compounds activated by 4f elements in M – Ga – S(Se) system can be active medium of semiconductor lasers, luminescence lamps, color displays and other systems of information mapping [7 – 9]. These compounds have the forbidden band width 3,0-4,4eV and effectively transform the electric field energy, roentgen and ultraviolet radiations, and also electron beams in visible light. The excitation spectrum of given compounds covers the region from vacuum ultraviolet up to 500 nm.

The investigation results of luminescence and optical properties of the crystals of $Ca_4Ga_2S_7$ type activated by Eu ions are shown in [10, 11]. The chalcogenide semiconductor $Ca_4Ga_2S_7:Eu^{2+}$ can be perspective luminophor for lighting devices on the base of InGaN-LD, however its spectral characteristics aren't studied enough. For establishment of usage possibility of this luminophor in such devices, it is necessary the study of its spectrum stability and radiation effectiveness in wide interval of excitation levels which is dedicated the present paper.

In the given paper the measurements of photoluminescence (PhL) spectra in the dependence on temperature and excitation level, excitation spectrums of photoluminescence and time-resolved photoluminescence spectra.

1. EXPERIMENT TECHNIQUE

The crystal samples $Ca_4Ga_2S_7$ are synthesized by solid-phase reaction of binary compounds CaS, Ga_2S_3 and EuF_3 at temperature 1400K taken in stoichiometric ratios in graphitized quartz ampoules evacuated up to 10^{-4} millimeter of mercury.

The obtained polycrystals are grinded with following deposition on quartz planes. The excitation spectra of photoluminescence (EPhL) are measured at excitation by monochromatic radiation of xenon lamp at temperature 300 K. The influence of excitation level on spectra and PhL efficiency in interval 10 –10^5 Vt/cm^2 is analyzed by integral PhL spectra of samples at excitation and 50 nano-sec impulse radiation of InGaN-LD on wave length 405 nm.

The investigation of damp kinetics of PhL micropowder $Ca_4Ga_2S_7:Eu^{2+}$ (5 %) is carried out at excitation by radiation of fourth harmonic of femtosecond Yb:KYW-laser on 260 nm at room temperature.

2. RESULTS AND THEIR DISCUSSION.

$Ca_4Ga_2S_7:Eu^{2+}$ (5 at.%) compound as a result of electron transitions in ions of Eu^{2+}- activator has PhL in yellow-red range in the form of two wide radiation bands with maximums on 560 and 660 nm at excitation by radiation on wave length 337 nm at room temperature (Fig.1., curve *1*).

The excitation spectra of short-wave band of PhL micropowder $Ca_4Ga_2S_7:Eu^{2+}$ (5 at. %) near 560 nm presents itself the wide band overlapping range from 250 up to 500 nm with maximum on 345 nm according to Fig.1 (curve *1'*). EPhL spectrum on 660 nm presents itself two wide bands overlapping

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spectral ranges from 250 up to 350 nm and from 400 up to 625 nm with maximums on 265nm and 470nm correspondingly, as it is shown in Fig.1 (curve *2′*).

The essential differences of excitation spectra of PhL bands near 560 nm and 660 nm allows us to change the luminescence color of $Ca_4Ga_2S_7:Eu^{2+}$ compound choosing the pumping source. As a result, PhL of $Ca_4Ga_2S_7:Eu^{2+}$ compounds at excitation by radiation in range 450-575 nm are characterized by significant dominance of the band in the spectrum on 660 nm in correspondence with Fig.1 (curve 1).

The obtained damp kinetics of PhL bands with maximums on 560 nm and 660 nm of $Ca_4Ga_2S_7:Eu^{2+}$ (5 at.%) solid solutions are presented in Fig.2. The constants of damping times near 560 nm and 660 nm are 258 nsec and 326 nsec, correspondingly.

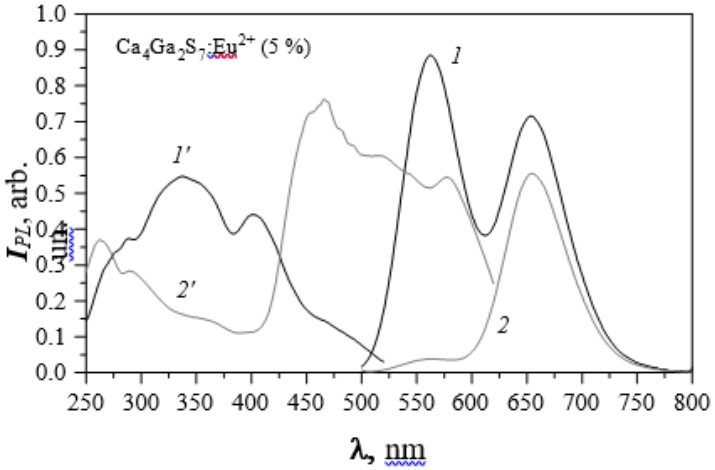

Fig.1. PhL spectra (curves *1* and *2*) and excitation PhL (curves *1′* and *2′*) $Ca_4Ga_2S_7:Eu^{2+}$ (5 at.%) compounds on wave lengths of excitation 337 nm (*1*) and 467 nm (*2*) and registration 560 nm (*1′*) and 660 nm (*2′*) at room temperature.

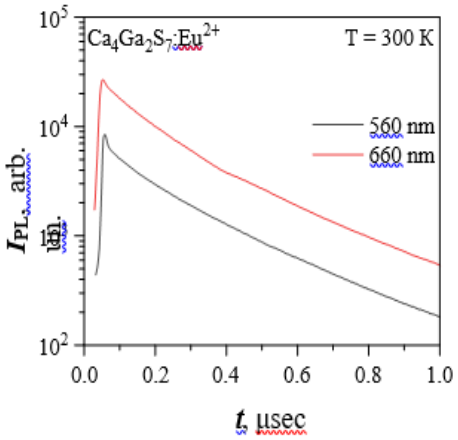

Fig.2. Damp kinetics of PhL bands with maximums on 560 nm and 660 nm of $Ca_4Ga_2S_7:Eu^{2+}$ (5 at%) solid solutions at λ_{ex} = 260 nm and room temperature.

$Ca_4Ga_2S_7:Eu^{2+}$ (5 at.%) compound has PhL in yellow-red range in the form of two wide radiation bands near 564 nm and 654 nm at temperature 10 K and excitation by continuous radiation on wave length 405 nm in correspondence with Fig.3 (a). Note that Eu^{2+} ions in different matrixes have wide bands of absorption and radiation. The radiation with wave length from ultraviolet up to red luminescence is observed in the dependence on matrix structure which is activated by Eu^{2+} ions [12]. $4f^7(^8S_{/2})$ configuration is main unexcited state of Eu^{2+} ions and $4f^65d$ configuration is excited state of Eu^{2+} ions. The intensive luminescence in yellow (564 nm) and red (654nm) spectrum region is caused by $4f^65d \rightarrow 4f^7(^8S_{/2})$ electron transitions in Eu^{2+} ions.

The temperature increase from 10K up to 300K leads to widening of radiation bands of $Ca_4Ga_2S_7:Eu^{2+}$ compound near 564 nm and 654 nm, blurring of their structure and the shift on 5 nm and 8 nm in short-wave side, correspondingly. The integral intensity decreases on 40%.

The significant stability behavior of PhL spectrum of $Ca_4Ga_2S_7:Eu^{2+}$ compound in interval of excitation level from 10 Vt/cm^2 up to $2.2 \cdot 10^5$ Vt/cm^2 by impulse 50 nsec radiation of InGaN-LD on wave length 405 nm that is seen in Fig. 4(a), is observed [13]. PhL efficiency of $Ca_4Ga_2S_7:Eu^{2+}$ compound saves its constant value in wide interval of excitation level from 10 Vt/cm^2 up to $2 \cdot 10^4$ Vt/cm^2 as it is seen in Fig.4 (b). The reversal efficiency decrease on 40% takes place with further increase of pumping up to $4 \cdot 10^5$ Vt/cm^2.

PhL kinetics of $Ca_4Ga_2S_7:Eu^{2+}$ compound at room temperature and excitation level 2.2 μJ/cm^2 by impulse radiation of Yb:KYW-laser on wave length 260 nm and duration 140 fsec is described by two exponents with decay times 60 nsec and 240 nsec in correspondence with Fig.5. The further increase of pumping level up to 36 μJ/cm^2 leads to insignificant decrease of constant time of fast component up to 57 nsec. The presence of fast component in kinetics of PhL damping of $Ca_4Ga_2S_7:Eu^{2+}$compound at excitation by intensive laser radiation of femtosecond duration, is caused by the presence of cross-relaxation process that is character for semiconductor matrixes activated by Eu^{2+} ions.

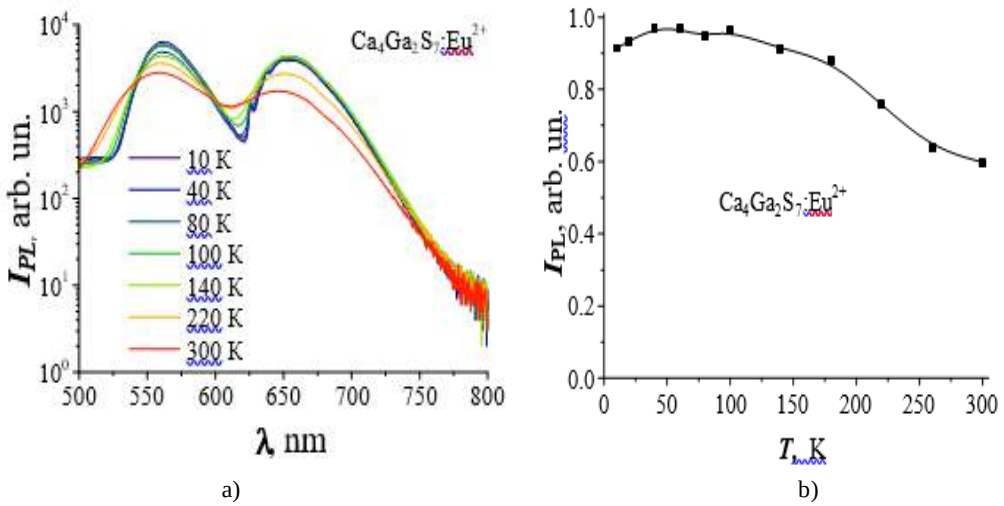

Fig.3. PhL spectra of $Ca_4Ga_2S_7:Eu^{2+}$(a) compound and dependence of integral intensity of its PhL on temperature in interval 10 – 300K at excitation by radiation on wave length 405 nm with power density by order 1Vt/cm^2 (b).

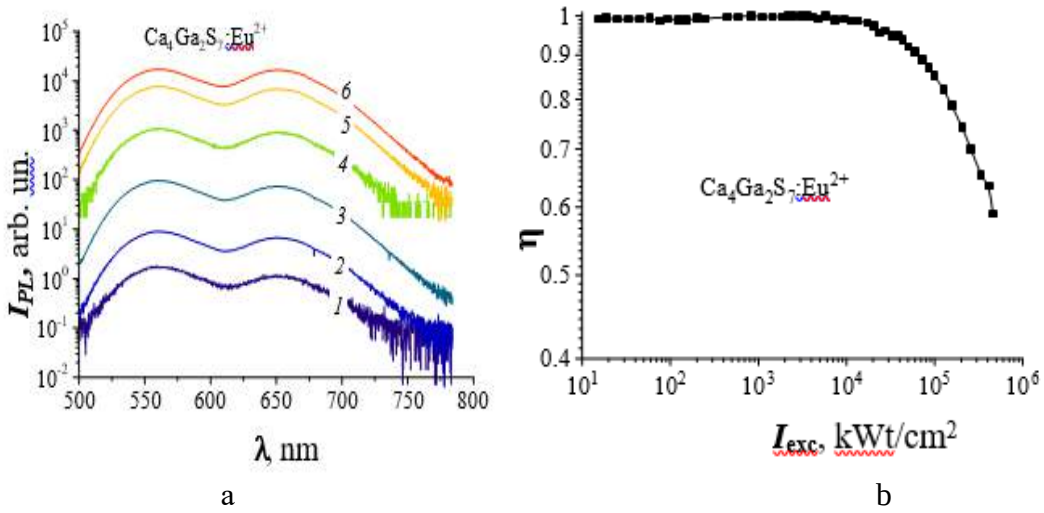

Fig.4. PhL spectra of $Ca_4Ga_2S_7:Eu^{2+}$ compound at different excitation intensities 10 (*1*), 10^2 (*2*), 10^3 (*3*), 10^4 (*4*), 10^5 (*5*), $2.2\cdot10^5$ Vt/cm^2 by LD radiation on wave length 405 nm (a) and dependence of PhL integral intensity on excitation level at 300 K (b).

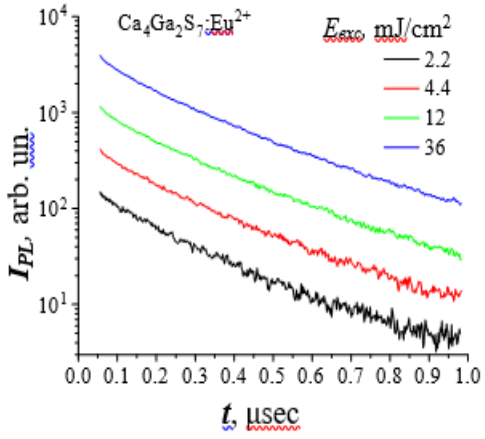

Fig.5. PhL damping kinetics of $Ca_4Ga_2S_7:Eu^{2+}$ compound at temperature 300K and excitation different levels by impulse radiation of Yb:KYW-laser with duration 140fsec on wave length 260 nm.

CONCLUSION

It is shown that $Ca_4Ga_2S_7:Eu^{2+}$ (radiated in yellow-red range) is the high-efficiency luminophors at excitation by UV-blue radiation of LD and LED (Light Emitting Diode) and have the high stability of the form and position of PhL spectrum in the excitation level interval up to ~10^4 Vt/cm^2 with further reversal PhL efficiency decrease that makes them perspective ones for the use in the capacity of luminophors excited by radiation of commercial AlGaN and InGaN lasers and light-emitting diodes for formation of sources of coherent and non-coherent radiation of "white" color with high values of colored characteristics [14 – 16].

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[1] *X. Wu, D. Carkner, H. Hamada, I. Yoshida.* Large-screen Flat Panel Displays based on Thick-Dielectric Electroluminescent (TDEL) Technology SID, 2004. vol. XXXV, Book II.- pp.1146-1149.

[2] *B.G. Tagiyev, S.A. Abushov, O.B. Ragiyev.* Journal of Applied Spectroscopy, 2010, vol.77, pp.124 – 128.

[3] *R.B. Jabbarov, C. Chartier, B.G. Tagiev, O.B. Tagiev, N.N. Musayeva, C. Barthou.* Benalloul P., Journal of Physics and Chemistry of Solids, 2005, vol. 66, № 6, p.1049-1056.

[4] *A.N. Georgobiani, V.V. Sturov, V.I. Tyutyunnikov, B.G. Tagiev, O.B. Tagiev, R.B. Jabbarov.* Journal of Physics and Chemistry of Solids. 2003. vol. 64. № 9-10, pp.1519-1924.

[5] *P. Benallol, Carlos Barthou, C. Foussier, A.N. Georgobiani, L.S. Lepnev, Y.N. Emirov, A.N. Gruzintsev, B.G. Tagiev, O.B. Tagiev, R.B. Jabbarov.* Journal of the Electrochemical Society.2003. 150(1). G62-G65.

[6] *B.G. Tagiyev, O.B. Tagiyev, R.B. Jabbarov, U.F. Kasumov, N.N. Musayeva.* New Technologies-21 century, №2, 58, 1999.

[7] *SeishiLida, Tamao Matsumoto, N. Mamedov, O. Tagiev, A. Bayramov, R. Jabbarov, B. Tagiev.* Jpn,J. Appl. Phys.1997, vol 36, pp. 857- 859, part 2, N7a.

[8] *A.N. Georgobiani, B.G. Tagiev, O.B. Tagiev, R.B. Jabbarov, N.N. Musaeva, U.F. Kasumov.* Jpn. J. Appl. Phys., 2000, vol., 39, № 39 -1, pp. 434 – 439.

[9] *P. Benalloul, C. Barthou, J. Benoit.* Appl. Phys. Lett., 1993, 63(14), pp. 154-156.

[10] *B.G. Tagiyev, O.B. Tagiyev, R.B. Jabbarov, U.F. Kasumov, N.N. Musayeva.* Photoluminescence of $Ca_4Ga_2S_7$:RRE. Inorganic mat.2001, vol.17, №12, pp.1430-1434.

[11] *B.G. Tagiyev, U.F. Kasumov, N.N. Musayeva, R.B. Jabbarov, A.S. Abushov.* Optical properties of $Ca_4Ga_2S_7:Eu^{2+}$ compound, PTS, 2000, vol.34, №.10, pp. 1170-1172.

[12] *M.R. Davolos, A. Garcia, C.F. Fousser, and P. Hegenmuller.* Luminescence of Eu^{2+} in Strontium and Barium Thiogallates. J. Solid State Chemistry, 1989, 83, p. 316-323.

[13] *B.D. Urmanov.* Photoluminescence of chalcogenide semiconductors $Ca_{0.5}Ba_{0.5}Ga_2S_4:Ce^{3+}$, Sm^{3+} and $Ca_4Ga_2S_7:Eu^{2+}$ in wide interval of excitation levels by study of InGaN-laser / B.D.Urmanov and others, Collected articles of 12th Belorussian-Russian seminar, Semiconductor lasers and systems on their base, 2019, pp.170 – 173.

[14] *B.D. Urmanov.* Increase of color rendering index value of standard white light-emitting diodes because of filling of spectral notches in blue-green and red regions. B.D.Urmanov and others. Collected scientific articles of I international scientific-technical conference "OPTO-MICRO- and MICROWAVE-ELECTRONICS, Minsk, October, 22-26, 2018, pp.44-47.

[15] *B.D. Urmanov.* The improvement of white light quality of radiation sources on the base of light-emitting diodes and luminophor mixture. B.D.Urmanov, V.A.Shulenkova, M.S.Leonenya "Modern problems of physics – 2018": Proceedings of VIII international school-conference of young scientists and specialists, Minsk, 2018, pp.169-172.

[16] *B.D. Urmanov.* White light source with high values of color characteristics on the base of InGaN-LED and luminophors mixture $BaGa_2S_4:Eu^{2+}$, $CaGa_2S_4:Eu^{2+}$ и $(Ca,Sr)_2Si_5N_8:Eu^{2+}$ / B.D.Urmanov and others, Theses of reports of XV International scientific conference Youth in Science, 2018, Minsk, 2018, p.163.

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