SCIREA Journal of Physics

http://www.scirea.org/journal/Physics

June 4, 2019

Volume 4, Issue 3, June 2019

Photo thermo-luminescence of crystal $CaGa_2Se_4$: Eu.

O.B.Taghiyev[1,2], T.Sh.Qashimova[1], K.O. Taghiyev[3]

[1]Institute of Physics, National Academy of Sciences of Azerbaijan

[2]Moscow State University, Baku branch

[3]Institute of Catalysis and Inorganic Chemistry

Abstract

Thio- and seleno- halates of rare-earth elements (Ca, Sr, Ba)Ga_2(S, Se)$_4$ are part of compounds with general formula $MA_2^{III}B_4^{VI}$(M – Ba, Sr, Ca; A^{III}- Ga, Al; B_4^{VI} – S, Se). Compounds type of $MA_2^{III}B_4^{VI}$ were first obtained by authors [1], where sulphides and selenides are part of 12 analogous composites, which crystalize in orthorhombic system. There are three studies, which contain evident of six classes of this compounds [2]. Crystal structure of three classes of the above mentioned composites - $BaAl_2Se_4$, $BaGa_2Se_4$ and $CaGa_2Se_4$– is presented in [3], where it was determined, that atoms Ba and Ca are statistically distributed and occupy anti prismatic spaced on 50%. Luminescent properties of crystals with generic formula $MA_2^{III}B_4^{VI}$ are presented in studies [4-9].

KeyWords: photoluminescence, spectra of excitation and emission, activation energy

Rare earth seleno halates of calcium are synthesized from binary components CaSe (Ca – metalic CA - 99,62%; Se – B-5(99,99999%)), Ga_2Se_3. These binary components are obtained by alloying of elements in stoichiometric relations. Doping with ions Eu^{2+} was performed by intrusion into the burden prior to the synthesis of calculated portions of EuF_3. The synthesis was performed at 1000°C in a single temperature oven over 4 hours.

Seleno halite of calcium, which was not doped intentionally, posses with significantly low quantum efficiency of luminescence at room temperature. Spectra of photoluminescence was not detected at low level of excitation (monochromatic emission of xenon lamp). Spectra of photoluminescence of non-doped crystal $CaGa_2Se_4$ (fig 1) was detected at 77K (1) and 300K (2) with excitation using continuous helium-cadmium laser (λ_{exc} =441,6nm.). Spectrum consists of three overlapping wide lines at 77K with peaks observed at 526, 596 and 636 nm, and at 300K – spectrum consists of one wide line with peak at 571 nm. Comparison of this spectrum with emission spectra of non-doped crystal shows that intensive line of emission with peak near 571nm is not observed in spectra of non-doped crystals. Intensity of this line increases with the rise of concentration of europium (up to 5%). This emission line is also observed in photoluminescence spectra of thio-halate of calcium, doped with bivalent ions of europium and it is characterized by central transfer $4f^65d \rightarrow 4f^7$ of bivalent europium, which does not depend on concentration of activator [5, 6].

Spectra of photoluminescence excitation (1) and emission (2) of $CaGa_2Se_4$: Eu at 295K are presented on Figure 2. It is evident from Figure 2 that spectrum is reasonably wide and consists of several overlapping lines. However, it was not possible to describe these lines in details. Best approximation shows positions of these lines at 380nm, 449nm, 501nm. Half-width of the lines are positioned in the range of 50-80nm.

The value of energy absorption was obtained by applying relationship of mirror symmetry between spectra of emission and excitation: $E_{abs} = 2.67 \pm 0.1$ eV ($464 \pm 1,0$nm) (fig.2.). Formulas of energy transfer of absorption *f→d* and emission *d→f* can be expressed as following [7].

$$E_{abs} = E_{free} - D \qquad \text{and} \qquad E_{emi} = E_{free} - D - \Delta S,$$

where E_{free} is difference of energy of low energetic levels $4f^7$ and $4f^6(^7F_0)5d$ for free ions, D is energy of low energetic level, so called energy of red shift and ΔS is Stocks shift. Energy of Stocks shift ΔS was calculated from spectra of absorption and emission: $\Delta S = E_{abs} - E_{em} = 0,50 \pm 0,1$eV. The known value of energy of absorption E_{abs} allows to calculate energy of red shift D or energy of the lowest transfer *f→d* in relation of energy of free ion ($E_{free} = 4.19eV$ for ion of Eu^{2+}). We calculated energy of the red shift $D = E_{free} - E_{abs} = 1,52 \pm 0,1$eV.

Energy of zero phonon line E_0 =2,42 eV (512 nm) was determined from point of overlapping of the spectra of photoluminescence and excitation. This value matches with the value of Stocks shift energy, which was determined from spectra of excitation and emission.

Spectra of thermo luminescence of crystals $CaGa_2Se_4$:Eu at heating speed 0,67 K/s (1) and 1,96 K/s are shown on Figure 3. At low heating speed (0,67 K/s) spectrum consists of two overlapping lines with peaks 150 and 220 К. Half width and intensity of the lines increase with the rise of the heating speed and peaks shift to the zone of high temperatures (162 and 230 K). New lines start to appear in spectrum with peaks at 275 and 304 К. Activation energy, which is expressed as E_t=0.22eV, was determined for the first low temperature peak T_M=162 К based on method of Qarlic-Qibson [10] (Fig. 4 line 2). Study results of thermo luminescence are presented in [11, 12]. Since all lines overlap in the spectra of thermo luminescence, it was required to split these lines on smaller parts for calculation of the activation energy of the traps from on the formulas presented in [11, 12]. Moreover, "thermic cleaning" can be applied for segregation of separate lines. The simplest way, which does not require knowledge of kinetics, is determination of the depth of trap positions from the temperature peak of the thermo emission. Therefore formula $E_t=AkT_m$ [11] was used for calculation of the activation energy of the traps, which are related to the observed wide lines of thermo luminescence, where T_m- temperature of the lines peak, k- Bolsman constant, A – constant, value of which varies in the range of 15-30 [130]. We used 22,5 as value of A. Calculation results of activation energy of the traps in CaGa2Se4:Eu are as following: at β=0,67 K/s – 0,29; 0,43; 0,52 eV; at β=1,96 K/s – 0,31; 0,44; 0,53 and 0,59 eV. Results of E_t, which were calculated from the highest low temperature peak at T_m=150 К and initial growth of the intensity based on method of Qarlic-Qibson [10] are well reproducible.

Hence, it was shown that photoluminescence in CaGa2Se4:Eu is caused by intra-central transfers $4f^65d \rightarrow 4f^7$ of the ions Eu^{2+}. Thermo luminescence in the studied rare earth seleno halates is caused by electron traps, which were formed as a result of structural defects and impurities.

Figures

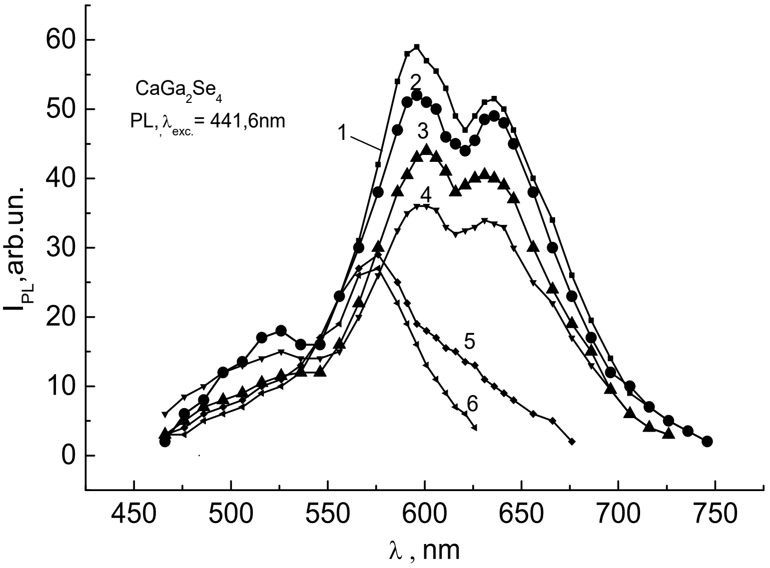

Рис.1 .Спектры фотолюминесценции нелегированного кристалла $CaGa_2Se_4$при различных температурах, К: 1 – 77, 2 – 125, 3 – 135, 4 – 169, 5 – 202, , 6 – 233.

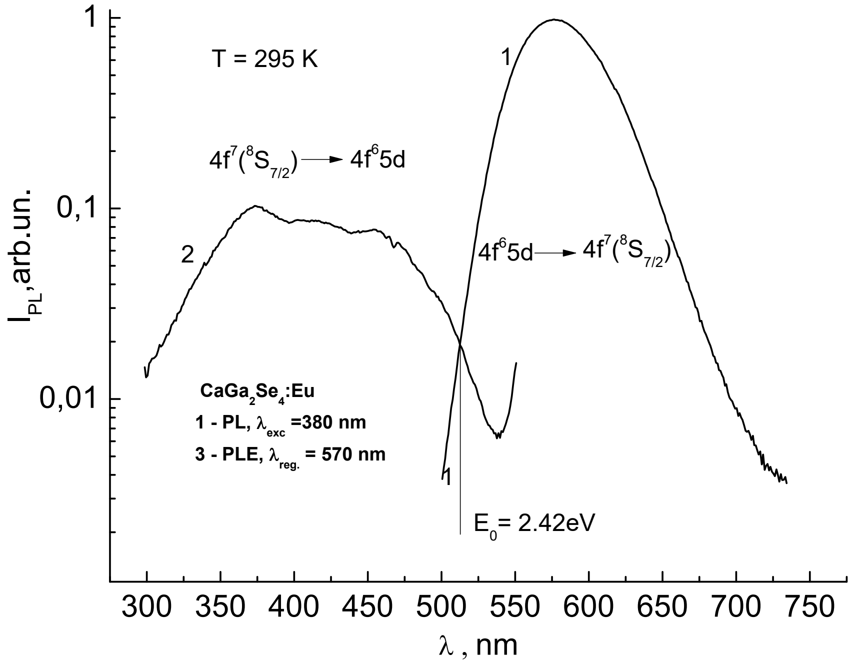

Рис.2. Спектры фотолюминесценции (1) и возбуждения фотолюминесценции(2) кристаллов Ca Ga_2Se_4:5%Eu при 295К.

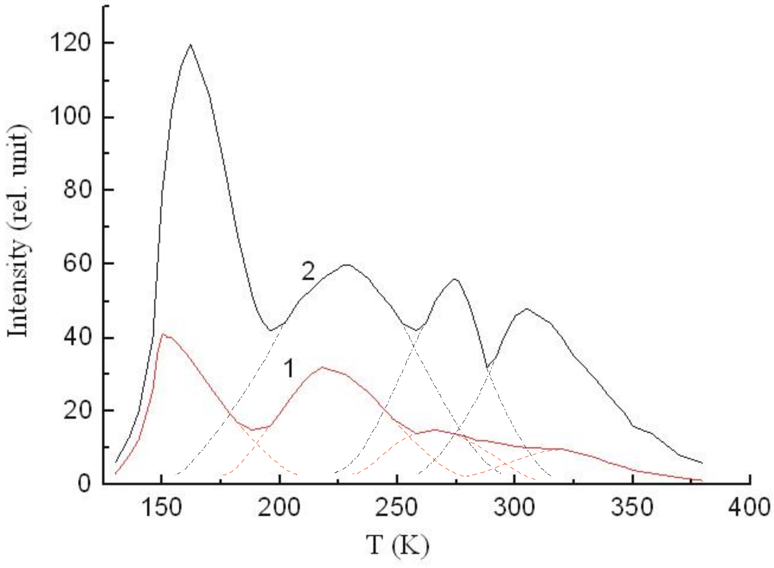

Рис.3 . Спектры термолюминесценции $CaGa_2Se_4$:Eu при двух скоростях нагрева, К/с: 1 – 0.67, 2 – 1.96.

Reference

[1] Eholie R., Gorochov O. Guittard M. et.al. Les composes de type $PbGa_2S_4$, EuM_2X_4,

et SrM_2X_4 (over –M-Al, Ga,et X-SSe) Blull. // Soc.Chim. France. 1971, 3, p.747-750.

[2] Klee W., Schafer H.Z.$CaAl_2Se_4$ and $SrAl_2Se_4$-Struktur-varianten des TlSe- Type. $CaAl_2Se_4$ and $SrAl_2Se_4$ – Variante of the TlSe- Structure.-Z. Natur-Forsch., 1978,33b,pp. 829-833.

[3] Takizawa T., C. Komatsu-Hidaka, K. Asaka, T. Isomoto, H.Matsushita. **Growthand Crystallographic Properties of II-III$_2$-VI$_4$ Compounds Focusing on the Sulfides---(Invited)** // Jpn. J. Appl. Phys. (2000),v. 39, suppl. 39-1, pp. 35-40.

[4] Davolos M.R., Garcia A., Fouassier C. and Hagenmuller P.

[5] Luminescence of Eu^{2+} in Strontium and Barium Thiogollates. // Journal of solid state chemistry. 1989, 83, p.316-323. Benalloul P., Barthou C., Foussier C., Georgobiani A. N., Lepnev

[6] L. S., Emirov Y. N., Gruzintsev A. N., Tagiev B. G., Tagiev O. B., Jabbarov R. B.. Luminescence of Eu^{2+} in Calcium Thiogallate $CaGa_2S_4$ // Journal of The Electrochemical Society, 2003, v.150, N1, pp. G62-G65.

[7] Barthou C., Banalloul P., Tagiev B.G., Georgbiani A.N., Tagiev O.B., Abushev S.A., Kazimova F.A. Energy Transfers between Eu^{2+} and Er^{3+} in $EuGa_2S_4:Er^{3+}$. Journal of Physics Condensed matter. 2004. 16, №10, p.8075-8084.

[8] Dorenbos P. f→d transition energies of divalent lanthanides in inorganic compounds. J.Phys.Condens. Matter. 2003, 15, p.575-594.

[9] Anedda A., Carbonaro C.M., Chiriu D., Corpino R., Marceddu M., RicciP.C., GeorgobianiA.N., TagievB.G., AbushevS.A., TagievO.B., Tiginyanu I.M. Photoluminescence of Ce and Pr codoped calcium thiogallate. // Physica Status Solidi (c), 2006, V.3, № 8, p.2717-2721.

[10] Yablonskii G.P., Zubialevich V.Z., Lutsenko E.V., PashaevA.M., TagievB.G., Tagiyev O.B.,Abushov S.A. Luminescence proporties of barium thio-and selenogallates doped with Eu, Ce, Eu+Ce .// Japanese Journal Appl. Phys., 2011, v.50, No.5, Issue3, p.05FG02-1-05FG02-2.

[11] Carlik G.F.J., Gibson A.F. The electrons trap mechanism of luminescence in sulphide and silicate phosphors. Proc.Phys. Soc.-London, 1948. –V. A60, pt 256.

[12] Randall J.T., Wilkins M.N.F. Phosphorescence and electron traps. Proc. Roy. Soc. London, 1945.-V.A184.-P.366-389.

[13] Rao D.R. On the Analysis of Thermo luminescence Clow Pattern. Phys. Stat. sol.(a), 1974, v.22, p.337-340.