PHOTO- AND THERMO-LUMINESCENCE OF $SrGa_2S_4$:Eu CRYSTALS

B.G.TAGIYEV, S.A.ABUSHOV, O.B.TAGIYEV, F.A.KAZIMOVA
G.M. Abdullayev Institute of Physics of National Academy of Sciences,
Baku AZ1143, Azerbaijan

The photo-luminescence and thermo-luminescence (PhL and TL) of $SrGa_2S_4$ crystals activated by Eu^{2+} in temperature interval 77÷320K have been investigated. It is seen that observable wide-band PhL in temperature interval 77–300K with maximum at 535 nm is connected with intracentral transitions $4f^6 5d - 4f^7$ ($^8S_{7/2}$) of Eu^{2+} ions and narrow-band TL is caused by discrete and quasicontinuously distributed electron traps with activation energies: E_c- 0,2 и E_c-(0,25- 0,53) eV in forbidden band.

Introduction.

$SrGa_2S_4$: Eu is related to tiogallate group with general formula AB_2C_4 (A-Ca, Ba, Sr, Al; B - Ga, In; C- S, Se). The photo-luminescence (PhL) of doped and non-doped crystals of AB_2C_4 type has been investigated in the works [1-4], and thermo-luminescence (TL) of these compounds excluding $CaGa_2S_4$, $EuGa_2S_4$ и $CaGa_2Se_4$ compounds [5-7], hasn't been investigated. As these compounds are wide-band semiconductors, so trap levels in forbidden band should play the essential role in generation and recombination processes. TL investigation is the one of suitable method for definition of trap energy position directly participating in PhL and TL processes. In the given paper the results of PhL and TL investigations in $SrGa_2S_4$, activated by rare-earth ions Eu^{2+} (REI) are given.

Experiment technique.

$SrGa_2S_4$: Eu compound is synthesized from binary compounds SrS, Ga_2S_3 and EuF_3, taken in stoichiometric ratios in preliminary degasified quartz ampoules up to 10^{-2}Pa. The concentration of Eu^{2+} is varied from 1 up to 7at.%. The powder mixture of the given compounds is endured in sulfur atmosphere at temperature 1230°C. TL is investigated on technique described in [6]. The samples are excited by mercury lamp light PRK-4 at temperature of liquid nitrogen. The sample temperature is defined with the help of differential thermocouple cuprum-constantan. PhL spectrums are investigated on spectrometer CDL-1. The continuous helium-cadmium laser (λ = 441,6 nm) is used for excitation of PhL samples $SrGa_2S_4$: Eu.

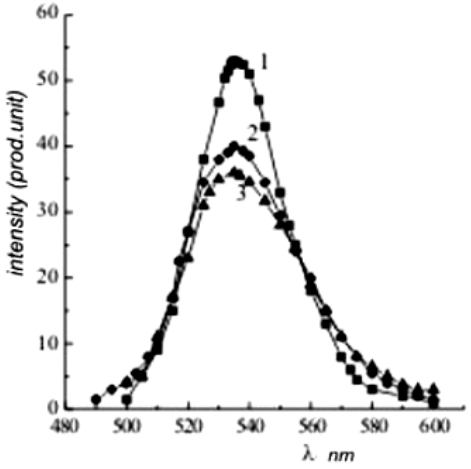

Fig.1. Photo-luminescence spectrum of $SrGa_2S_4$: Eu (5%) at temperatures: 1-140K, 2-230K, 3-286K.

PhL spectrums $SrGa_2S_4$:5%Eu at temperatures 120K, 230K and 286 K (curves 1, 2 and 3) are presented on the fig.1. It is seen that they cover the spectral region 490-600 nm and their maximums correspond to wave length 535 nm, i.e. maximum energy position doesn't change and intensity decreases with temperature increase.

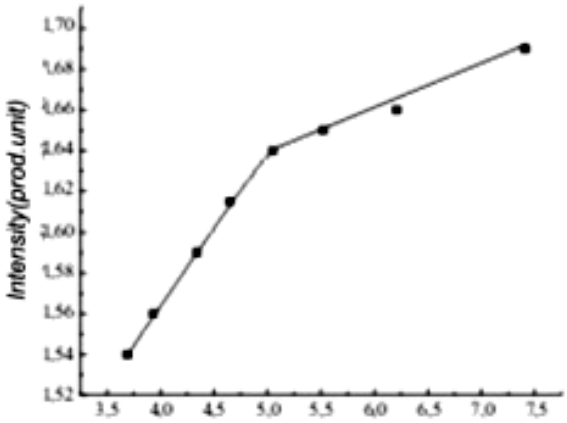

Fig.2. The dependence of photo-luminescence intensity of $SrGa_2S_4$: Eu (5%) crystals on temperature.

The temperature dependence of photo-luminescence band intensity with maximum 535 nm in $lgI \sim 10^3/T$ coordinates is presented on the fig.2. It is seen that intensity in temperature interval 80÷200K weakly depend on temperature, and later temperature increase lads to strong intensity decrease. The activation energy of photo-luminescence temperature quenching which is equal to 0,016 eV is defined on high-temperature inclination of this dependence.

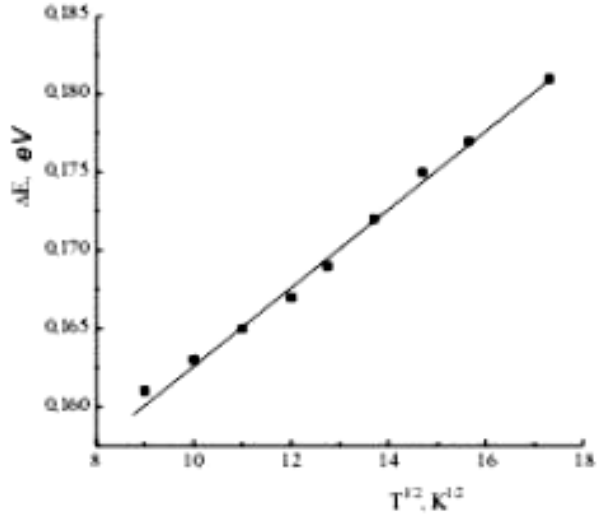

Fig.3. The dependence of PhL band half-width of $SrGa_2S_4$: Eu (5%) crystals.

The investigation of photo-luminescence spectrums, its temperature dependence of half-width and intensity of wide

band with maximum at 535 nm of $SrGa_2S_4$: Eu crystals, and also the dependence of this band intensity on activator content allows us to establish that this photo-luminescence band is connected with intracentral transitions $4f^6 5d \rightarrow 4f^7$ ($^8S_{3/2}$) of Eu^{2+} ion.

The temperature dependence of PhL band half-width with maximum at 535 nm in ΔE and $T^{1/2}$ coordinates [2] is presented on the fig.3. It is seen that this dependence has linear character. The temperature dependence of half-width is also calculated by formula [8]:

$$\Gamma(T) = \sqrt{8 \ln 2} \cdot h\nu \cdot \sqrt{s} \sqrt{coth\left(\frac{h\nu}{2kT}\right)} \qquad (1)$$

where s is Huang-Rice factor, $h\nu$ is phonon energy, k is Boltzman constant. The taken values s and hν are equal to 12 and 35meV correspondingly at $\Gamma(T)$ calculation [9]. As it is seen from fig.3, the experimental points are on the calculated straight line. The linear dependence of half-width $\Delta E=f(T)$ is connected with electron interaction in excited state with lattice high-frequency oscillations (optical phonons) [10, 11].

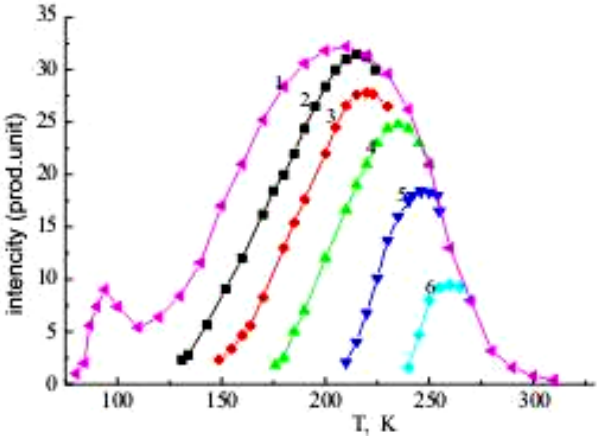

Fig.4. The thermo-luminescence spectrum of $SrGa_2S_4$: Eu crystal.

TL spectrum of $SrGa_2S_4$: 5%Eu crystals at heat rate 0,67K/c is presented on the fig.4 (curve 1). As it is seen it is wide-band one and covers the temperature interval 80÷320 K. The relative weak narrow peak with maximum at 95K(ΔT=20K) which collides with intensive wide band with maximum at 210 K is observed on this spectrum. The big half-width of TL wide band (ΔT=108 K), the complex operation of its initial increase allows supposing that this band is connected with quasicontinuously distributed trap levels in forbidden band$SrGa_2S_4$: Eu crystals. The "thermal purification" of thermo-luminescence spectrum of investigated samples is carried out by us for confirmation of this supposition.

As it is seen from fig.4 (curves 2, 3, 4, 5, 6) the more 5 peaks with maximums at 216, 224, 235, 246 and 260 K are revealed after "thermal purification". The trap depth of occurence situated in interval 0,25-0,53 eV is defined on initial increase of these curves.

The results of thermo-luminescence measurements in investigated samples are theoretically analyzed on the model basis described in [9-13]. The wide maximums in thermo-luminescence spectrums are character for triple alkali- and rare-earth chalcogenides inluded in $M^{2+}M_2^{3+}X_4$ group. For example, thermo-luminescence spectrum $CaGa_2S_4$: Eu^{3+} consists of wide residual structure with T_{max} in interval 130 K and peak half-width is 80K [5]. It is seen by method of "thermal purification" that TL spectrums $CaGa_2S_4$: Eu^{3+} are caused by electron traps quasicontinuously distributed in energy interval E_c is (0,1-0,3) eV.

The trap activation energy in $SrGa_2S_4$: Eu^2 crystals is also defined by the method supposed in [14] on maximum temperatures of thermo-luminescence spectrum on formula:

$$E_a = AkT_m \qquad (2)$$

where E_a is trap activation energy, A is constant, k is Boltzman constant. In work [15] firstly it is theoretically shown that A value in (2) is equal to 25. The further investigations [16] show that A can has values in interval 15-30 in the dependence on private factor, heat rate and kinetic order of relaxation process. A value is taken as equal one to 5 at calculation. The trap depth of occurrence calculated by formula (2) for $SrGa_2S_4$: Eu^{2+} is 0,2eV for low-temperature peak (T_m=95K) and 0,45eV for wide band(T_m=210 K) correspondingly.

Thus, the wide-band PhL which is caused by intracentral transitions $4f^6 5d \rightarrow 4f^7$($^8S_{7/2}$) of Eu^{2+} ions is observed in $SrGa_2S_4$ activated by Eu^{2+} ions and low-temperature narrow-band and wide-band TL are connected with electron traps, discrete and quasicontinuously distributed in forbidden band $SrGa_2S_4$: Eu^{2+}. Their depth of occurrence E_c is 0,2eV and E_c is (0,25 – 0,53) eV correspondingly.

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B.H. Tağıyev, S.A. Abuşov, O.B. Tağıyev, F.A. Kazımova

$SrGa_2S_4:Eu^{2+}$ KRİSTALLARININ FOTO – VƏ TERMOLÜMİNESSENSİYASI

Eu^{2+} ionları ilə aktivləşdirilmiş $SrGa_2S_4$ kristallarının fotolüminessensiyası və termolüminessensiyası (Fl və TL) 77-320K temperatur oblastında tədqiq edilmişdir. Müəyyən edilmişdir ki, maksimumu 535 nm dalğa uzunluğunda müşahidə edilən genişzolaqlı FL Eu^{2+}ionlarının mərkəzdaxili $4f^6 5d—4f^7(^8S_{7/2})$ keçidləri ilə, maksimumları 95K və 210K olan darzolaqlı və genişzolaqlı TL isə aktivləşmə enerjiləri uyğun olaraq E_c–0.2 və Ec-(0.25-0,53)eV olan elektron tələləri ilə bağlıdır.

Б.Г. Тагиев, С.А. Абушов, О.Б. Тагиев, Ф.А. Казымова

ФОТО- И ТЕРМОЛЮМИНЕСЦЕНЦИЯ КРИСТАЛЛОВ $SrGa_2S_4$:Eu

Исследованы фотолюминесценция и термолюминесценция (ФЛ и ТЛ) кристаллов $SrGa_2S_4$, активированных Eu^{2+} в области температур 77÷320К. Показано, что наблюдаемая широкополосная ФЛ в области температур 77-300К с максимумом при 535 нм связана с внутрицентровыми $4f^65d – 4f^7$ ($^8S_{7/2}$) переходами ионов Eu^{2+},а узкополосная и широкополосная ТЛ обусловлена соответственно дискретно и квазинепрерывно распределенными в запрещенной зоне электронными ловушками с энергиями активации:E_c- 0,2 и E_c-(0,25- 0,53) эВ.

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