PHOTOLUMINESCENCE OF Mn^{2+} IONS IN $CaGa_2S_4$

R.B. JABBAROV
Institute of Physics of Academy of Sciences of Azerbaycan
370143, Baku, G. Javid ave., 33

The photoluminescence (PL) for $CaGa_2S_4$: Mn and its kinetics were investigated in the temperature range 77÷300K. The samples were excited by the mercury line of 365, 313 and 254 nm.

It is found, that the PL is caused by intracentred transitions of the Mn^{2+} ions namely of ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ and ${}^4A_1\ {}^4E\ ({}^4G) \rightarrow {}^6A_1({}^6S)$.

The lifetimes of the excited states corresponding to maxima at 545 and 650 nm, are $1,3\cdot10^{-6}\div9\cdot10^{-7}$s and $2,6\cdot10^{-6}\div 4\cdot10^{-6}$ s relatively in the temperature range 77÷300K.

1. Introduction

Investigation of the luminescence of ions of elements with unfilled $3d$ and $4f$ shells in new matrices at the present time has scientific and practical interest. The partial filling internal $3d$ and $4f$ shells creates a possibility for optical transitions between of energy, levels, having of the same electronic configuration. Thus in most cases there is no essential change of interaction of the activator with surrounding ions (atoms), in bond formation with which the electrons of intermal shell do not participate. A consequent of that is the ruled nature of radiation spectra. We investigated in detail the photoluminescence properties of the compounds $CaGa_2S_4$ activated by rare-earth elements and we found that these compounds are effective photoluminescence materials with high quant exit [1-3]. In the present paper we investigate the photoluminescence properties of the compound $CaGa_2S_4$ activated by Mn^{2+} ions.

2. Experimental results and discussion

The compound $CaGa_2S_4$ was synthesized in the evacuated quartz ampoule and in the medium on the activated coal. Activation of this compounds by manganese ions was carried out in synthesize process.

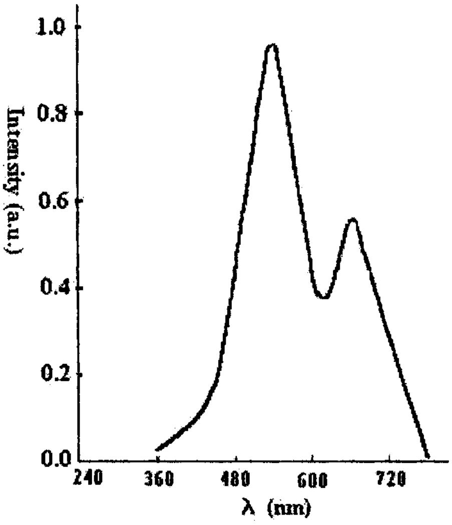


Fig. 1. PL spectra of $CaGa_2S_4$ activated by Mn at 77K

In the wide temperature range (77÷300K) crystals $CaGa_2S_4$: Mn, transform ultraviolet radiation to visible one at their excitation by the radiation of mercury lines of 365, 313, 254 nm. The results of PL investigations at 77K for $CaGa_2S_4$: Mn (excited by the radiation of mercury line –365nm) are shown in fig.1. It is seen that bands with maxima at 545 and 650 nm are observed in the PL spectrum of $CaGa_2S_4$: Mn. The ratio of these maxima values increases from 1,85 at 1% up to 3,3 at 5% Mn with increasing of the Mn concentration. The half – width of indicated maxima is equal to 0,33 and 0,25 eV for the samples containing 1% Mn. The increase of an ion concentration of Mn ions results in extinguishing and widening of maxima. It is established that the PL is caused by the intracentred transitions of Mn^{2+} ions ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ and ${}^4A_1{}^4E\ ({}^4G) \rightarrow {}^6A_1({}^6S)$.

Investigation of PL kinetics of $CaGa_2S_4$:Mn was the most interesting in wide temperature range. Measurements were made using of pulsed –nitrogen –laser LGI-21 (wave length 337 nm, length of impulses $3\cdot10^{-8}$) for determination of lifetime of the Mn^{2+} ions excited state as well as the PL kinetics in these compounds.

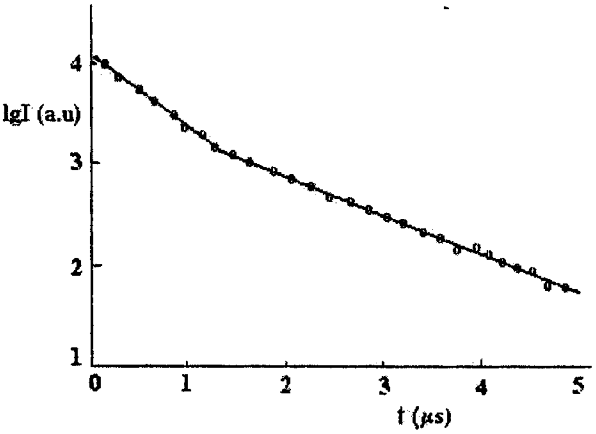


Fig.2. Time dependence of intensity in the PL spectra of $CaGa_2S_4$: Mn at 77K

The time dependence of the intensity for the maximum 545 nm in the spectra PL $CaGa_2S_4$:Mn, at 77K is presented in fig.2. The lifetimes of excited states corresponding to the maxima 545 and 650 nm in temperature range 77÷300K are equal to $1,3\cdot10^{-6}\div9\cdot10^{-7}$s and $2,6\cdot10^{-6}\div 4\cdot10^{-6}$s relatively. The linear dependence between lgI and t shows on the time decreasing of the maximum intensity in the PL spectra according to the exponential law:

$$I_t = I_0 e^{-at} , \quad (1)$$

where I_t is the luminescence intensity at moment t and I_0 is the one at t=0;

$$a = S\exp\left(-\frac{E_t}{kT}\right) , \qquad (2)$$

where S is the frequency factor.

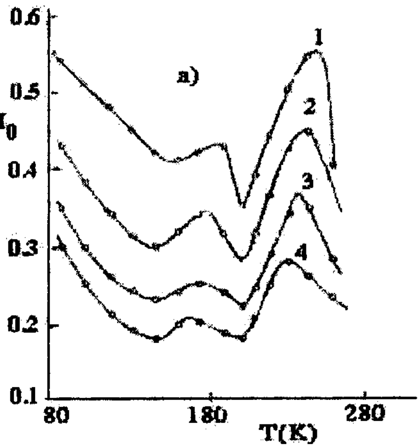


Fig.3. a) Temperature dependence ratio I_t/I_0 for the maximum 545 nm in the PL spectra $CaGa_2S_4$: Mn, at different times, t, μs: 1-0,50, 2-0,75, 3-1,00, 4-1,25.

Such dependence corresponds to the monomolecular mechanism of the luminescence. We analyzed the kinetics of the kinetics of the PL at different temperatures on the basis of the method, described in [4]. Agrees [4], for a case of the monomolecular mechanism of photoluminescence at different temperatures the ratio I_t/I_0 is obtained. There are maxima at $T=T_{max}$ on dependence I_t/I_0 from T. If to construct relation I_t/I_0 from T at different times, the value of a maximum will be increased with decreasing of time, also its position shifts in the party of heats.

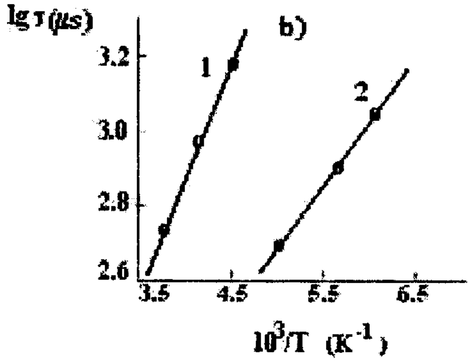
According to (1), maxima on the $I_t/I_0=f(t)$ dependence appear when $at_m=1$. In this case, t_m may be considered as the time that is equal to lifetime of the excited states of the activator ions, i.e. $t_m=\tau$. Substituting value α in (2), we have:

$$\frac{1}{\tau} = S\exp\left(\frac{E_t}{kT_{max}}\right) \qquad (3)$$

or

$$\tau = \frac{1}{S}\exp\left(\frac{E_t}{kT_{max}}\right) \qquad (4)$$

From (3) follows, that with increase τ the value T_{max} decreases. On the basis experimental data, submitted on fig.3 (a), at different temperatures τ are determined. The experimental results in the coordinates $lg\tau \sim 10^3/T_{max}$ lie down on the straight line very well. From the dependences (1)-(3) we determined the activation energies of traps which are equal to 0,12 and 0,07 (see fig.3 (b)). The same values we found earlier from the temperature dependence of the electrical conductivity and on the basis of measurements of termo-activated currents in crystals $CaGa_2S_4$:Mn.



Fiq.3.b) The dependence of $lg\tau$ from $10^3/T_{max}$ for high (1) and low (2) temperature maxima.

Substituting the experimental data for τ and E_t into Eq.(3), we find the value of the frequency factor $S = 10^{10} \div 10^{11} s^{-1}$.

[1] *A.N.Georgobiani, B.G.Tagiev, O.B.Tagiev, B.M. Izzatov, R.B. Jabbarov.* Cryst: Res. Technol., 1996, v.31, Speciallssne 2, pp. 849-852.

[2] *S.Iida, T.Matsumoto, N. Mamedov, G.An. Y. Maruyama, A. Bairamov, B. Tagiev. O. Tagiev, R. Dzhabbarov.* Jpn. J. Appl. Phys., 1997, v.36, pp. L857-859.

[3] *A.N.Georgobiani, B.G.Tagiev, O.B.Tagiev, B.M. Izzatov.* Inorganic Materials 31, 1995, №1, pp.19-22.

[4] *E.A. Nakazawa.* Jpn. J. Appl. Phys., 1984, vol. 23, №10, pp. 1392-1394.

R.B. Cabbarov

Mn^{2+} İONLARININ $CaGa_2S_4$ – DƏ FOTOLÜMİNESSENSİYASI

$CaGa_2S_4$: Mn kristalının fotolüminessensiyası (FL) və kinetikası 77÷300K temperatur intervalında tədqiq edilmişdir. Nümunə 365, 313 və 254 nm civə xətləri ilə həyəcanlandırılmışdır. İonların həyəcanlanmış hallarının yaşama müddətlərini tə'yin etmək üçün impuls azot lazerindən (λ=337,1 və τ=3,10^{-8} s) istifadə olunmuşdur.

$CaGa_2S_4$: Mn birləşməsinin FL spektrində 545 və 650 nm maksimumlar müşahidə edilmişdir.

Müəyyən olunmuşdur ki, FLMn^{2+} ionlarının aşağıdakı mərkəzdaxili keçidləri ilə əlaqədardır $^4T_1(^4G)\rightarrow{}^6A_1(^6S)$ və $^4A_1{}^4E(^4G)\rightarrow{}^6A_1(^6S)$. 77÷300K temperatur intervalında 545 və 650 nm maksimumlara uyğun gələn həyəcanlanmış halların yaşama müddətləri uyğun olaraq $1{,}3\cdot10^{-6} \div 9\cdot10^{-7}$s və $2{,}6\cdot10^{-6} \div 1{,}4\cdot10^{-6}$ s -dır.

Р.Б. Джаббаров

ФОТОЛЮМИНЕСЦЕНЦИЯ ИОНОВ Mn^{2+} В $CaGa_2S_4$

Фотолюминесценция (ФЛ) $CaGa_2S_4$: Mn и ее кинетика исследованы в интервале температур 77÷300 К. Образцы возбуждались линиями ртути 365, 313 и 254 нм. Для определения времени жизни возбужденных состояний ионов Mn^{2+} и кинетики ФЛ в $CaGa_2S_4$:Mn измерения проводились с помощью импульсного азотного лазера (λ=337.1 и τ=3.10^{-8} с).

В спектре ФЛ $CaGa_2S_4$: Mn обнаружены полосы с максимумами при 545 и 650 нм.

Установлено, что ФЛ обусловлен внутрицентровыми переходами ионов Mn^{2+} $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ и $^4A_1\,^4E\,(^4G) \rightarrow {}^6A_1(^6S)$. Время жизни возбужденных состояний, соответствующее максимумам 545 и 650 нм, в интервале температур 77÷300К составляет $1,3\cdot10^{-6}\div9\cdot10^{-7}$с и $2,6\cdot10^{-6}\div1,4\cdot10^{-6}$с.

Редактор: Э.Ю. Салаев

Дата поступления: 14.03.01