PHOTOLUMINESCENCE OF COMPOUNDS $CaGa_2S_4$:Eu AND $Ca_4Ga_2S_7$:Eu

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The compounds $CaGa_2S_4$ and $Ca_4Ga_2S_7$ have orthorhombic and cubic structure respectively. The photoluminescence of compounds $CaGa_2S_4$:Eu and $Ca_4Ga_2S_7$:Eu were investigated in the temperature rang $77 \le T \le 600$ K

Maxima at 555 and 630 nm are observed in the PL spectra of $CaGa_2S_4$:Eu and $Ca_4Ga_2S_7$:Eu respectively at excitation of the samples by light of the mercury lines (365, 313 and 254 nm.).

The excitation by the pulsed-nitrogen-laser (λ =337.1 nm and $\tau = 3 \cdot 10^{-8}$ s) leads to 4 maxima at 523, 538, 586 and 600 nm in the PL spectra of $CaGa_2S_4$:Eu. In this regime maxima at 551 and 653 nm take place in the PL spectra of $CaGa_2S_4$:Eu.

1. Introduction

The compounds $CaGa_2S_4$ and $Ca_4Ga_2S_7$ have orthorhombic and cubic structure respectively. Some experimental data were presented in [1-4] about physical properties of $CaGa_2S_4$ activated by rare earth elements (REE). There was not an information in a literature on the compound $Ca_4Ga_2S_7$. It has been synthesized and studied by us for the first time. The closeness of ionic radiuses of Ca (0.99) and Eu (1.12) creafes the favourable condition for the substitution of Ca by Eu. Therefore ternary chalcogenide semiconductors such as $CaGa_2S_4$ and $Ca_4Ga_2S_7$ are the most simple and convenient objects for the investigation of the luminescence of Eu ions. In this paper we present results of our investigations of the photoluminescence (PL) for the compounds $CaGa_2S_4$:Eu and $Ca_4Ga_2S_7$:Eu in the temperature range $77 \le T \le 600$ K. The measurements were performed in both stationary and impulsive regimes.

2. Preparation of $Ca_4Ga_2S_7$:Eu and $Ca_4Ga_2S_7$:Eu and the method of investigation

The compounds $CaGa_2S_4$ and $Ca_4Ga_2S_7$ were synthesized by methods, which were described in [2,3].

The lattice parameters $CaGa_2S_4$ a=10.021; b=6.06 and c=10.052 agree with structure data obtained in [1]. X-ray diffraction analysis of data obtained for $Ca_4Ga_2S_7$ shows that a cubic structure of a spherolite type with a=5.67 appears in the interaction of CaS and Ga_2S_3 in ratio 4:1.

The effective (PL) in stationary and dynamical regimes were investigated by the method given in [2,3]. The samples were excited by the light of mercury lines (365, 313 and 254 nm) and pulsed-nitrogen-laser LGI-21 (λ =337.1 nm and $\tau = 3 \cdot 10^{-8}$ s).

3. Results and discussion

Maxima are observed 555 and 630 nm in the PL spectra of $CaGa_2S_4$:Eu and $Ca_4Ga_2S_7$:Eu respectively at excitations of the samples by light of the mercury lines mentioned above. The excitation by pulsed-nitrogen-laser leads to four maxima at 523, 538, 586 and 600 nm in the PL spectra of $CaGa_2S_4$:Eu. In this regimes maxima take place at 551 and 653 nm.

The PL spectra of $Ca_4Ga_2S_7$:Eu (at temperature 77÷293 K are presented in Fig.1. It is seen, that the short-wave maximum corresponding to 551 nm near 300 K, decreases. The maxima in the PL spectra of $CaGa_2S_4$:Eu and maximum at 653 nm in the PL spectra of $Ca_4Ga_2S_7$ manifest in the wide temperature range (77÷600 K).

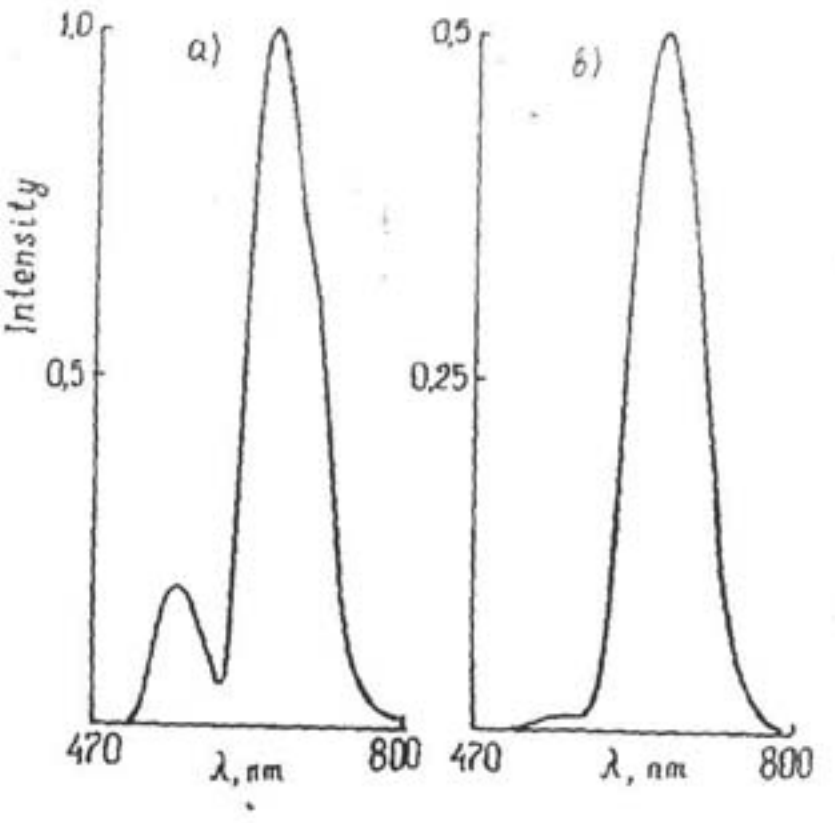

Fig.1. PL spectra for $Ca_4Ga_2S_7$:Eu at 77 K (a) and 293 K (b).

The temperature dependence of the value of the maximum at 653 nm in the PL spectra of $Ca_4Ga_2S_7$:Eu is shown in Fig. 2. It is seen that experimental data for the intensity (I) PL in the coordinates $lg\left(\frac{I_0}{I} - 1\right)$ and $10^3/T$ lie down on straight lines with different slopes. Here I_0 is a value of the PL intensity for the maximum at 653 nm, that does not depend on temperature below 120 K. The activation energies of traps determined from Fig. 2 are equal to 0.10 and 0.34 eV for $Ca_4Ga_2S_7$:Eu. Activation

energies of traps (0.10 and 0.40 eV) are found for $Ca_4Ga_2S_7$:Eu from such dependence.

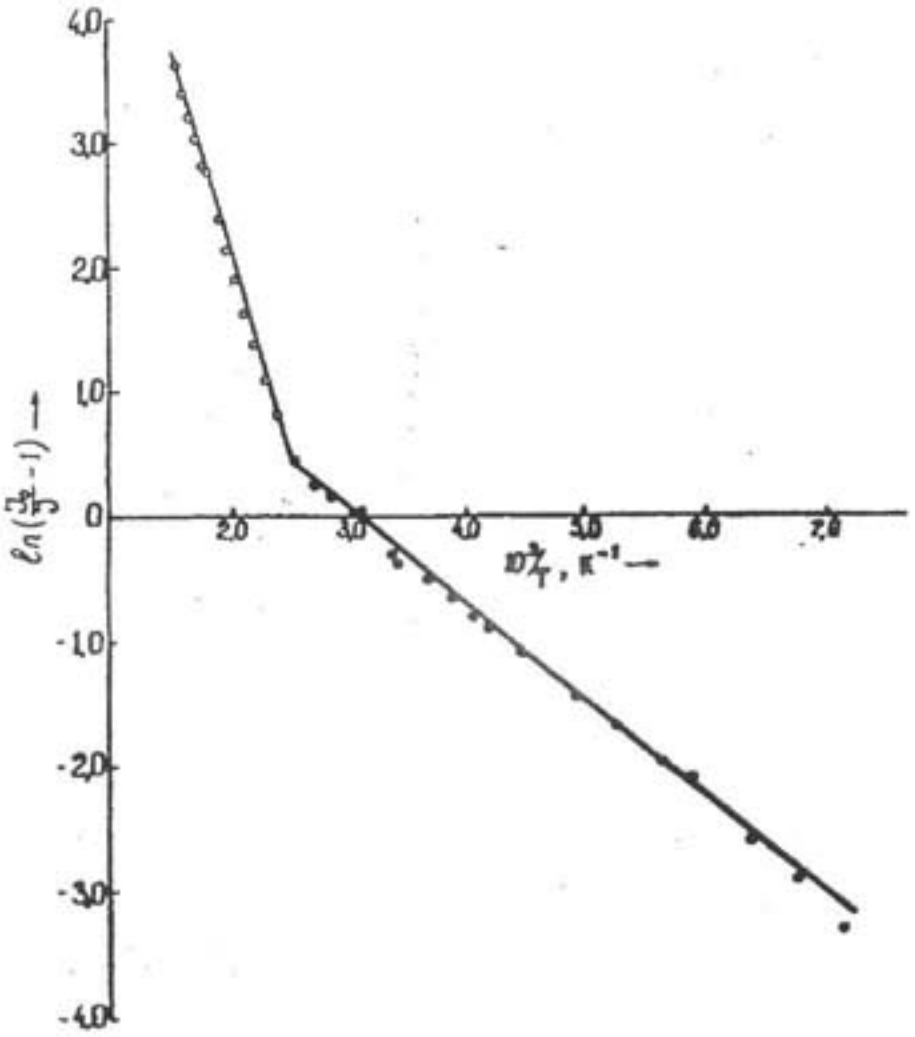

Fig. 2. Temperature dependence of the intensity of the maximum at 653 nm in PL spectra of $Ca_4Ga_2S_7$:Eu.

The excitation of samples $CaGa_2S_4$:Eu and $Ca_4Ga_2S_7$:Eu (by the pulsed-nitrogen-laser) permited to investigate the kinetics of all maxima observed in the PL spectra of these compounds.

Analysis of data shows, that intensity of maxima in PL spectra decreases by exponential law

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

where I_t is the PL intensity at the moment t, I_0 is the PL intensity at $t=0$.

$$a = S\exp(-E_t/kT) \qquad (2)$$

where S - is the frequency factor, E_t- is the activation energy of traps. The experimental data were analyzed by the method described in [5]. We find the ratio $\frac{I_t}{I_0}$ for different values of t. The dependence of $\frac{I_t}{I}$ on T have maxima for different values t, that is well illustrated in Fig. 3. It is seen, that the maxima displace in the low temperature direction with increase of time.

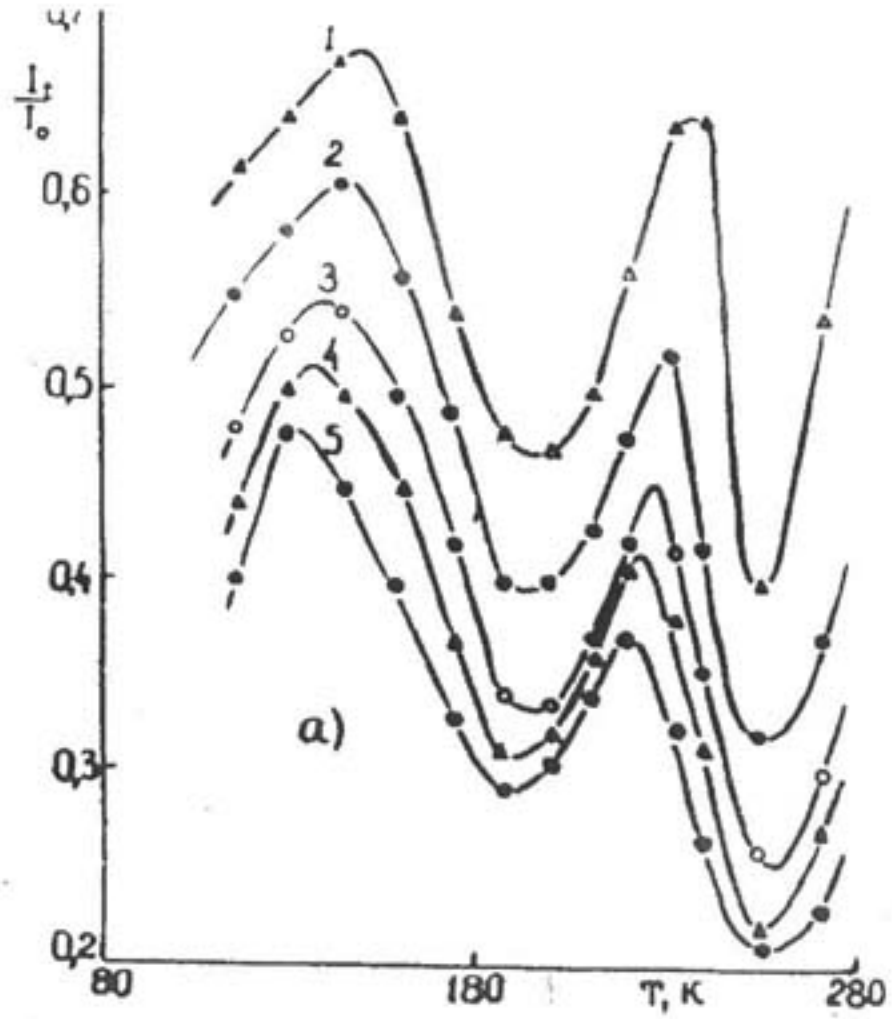

Fig. 3. The dependence of on T at different times, t, μs: 1-0.4, 2-0.6, 3-0.8, 4-1.0, 5-1.2.

In this case on the basis of experimental data we determined the following parameters: $S=10^{10}\div10^{11}$ s^{-1}, $E_t=0.10\div0.40$ eV, $\tau=10^{-6}\div10^{-7}$ s and etc. for compounds $CaGa_2S_4$:Eu and $Ca_4Ga_2S_7$:Eu. Let us note in conclusion that PL in compounds $CaGa_2S_4$:Eu and $Ca_4Ga_2S_7$:Eu is caused by the transitions $4f^65d\rightarrow4f^7$ of Eu^{2+} ions.

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$CaGa_2S_4$:Eu VƏ $Ca_4Ga_2S_7$:Eu BİRLƏŞMƏSİNİN FOTOLÜMİNESSENSİYASI

$CaGa_2S_4$:Eu və $Ca_4Ga_2S_7$:Eu birləşmələri uyğun olaraq ortorombik və kubik quruluşa malikdirlər. Bu birləşmələrin fotolüminessensiyası (FL) 77÷400 K temperatur intervalında tədqiq olunmuşdur. Nümunələr dalğa uzunluqları 365, 313 və 254 nm olan civə lampası və impuls azot lazeri (dalğa uzunluğu 337,1 nm və impulsun davametmə müddəti $3\cdot10^{-8}$ s) ilə həyəcanlaşdırılmışdır.

Civənin göstərilən xətləri ilə həyəcanlanma zamanı $CaGa_2S_4$:Eu və $Ca_4Ga_2S_7$:Eu birləşmələrinin FL spektrində 555 və 630 nm-ə uyğun maksimumlar müşahidə olunmuşdur.

Azot lazeri ilə həyəcanlanma zamanı $CaGa_2S_4$:Eu spektrində dörd maksimum 523, 538, 586 və 600 nm, $Ca_4Ga_2S_7$:Eu birləşməsində isə iki maksimum 551 və 653 nm müşahidə olunmuşdur.

Göstərilmişdir ki, Eu ionunun həyəcanlanma müddəti $10^{-7}\div10^{-6}$ san-dir.

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ФОТОЛЮМИНЕСЦЕНЦИЯ СОЕДИНЕНИЙ $CaGa_2S_4$:Eu И $Ca_4Ga_2S_7$:Eu

Соединения $CaGa_2S_4$ и $Ca_4Ga_2S_7$ имеют орторомбическую и кубическую структуры соответственно. Фотолюминесценция (ФЛ) соединений $CaGa_2S_4$:Eu и $Ca_4Ga_2S_7$:Eu исследована в интервале температур 77÷400 К. Образцы возбуждались светом линией ртути длиной волны 365, 313 и 254 нм и импульсным азотным лазером (длина волны 337.1 нм и длительность импульса $3 \cdot 10^{-8}$ с).

При возбуждении указанными линиями ртути в спектрах ФЛ соединений $CaGa_2S_4$:Eu и $Ca_4Ga_2S_7$:Eu выявлен по одному максимуму при 555 и 630 нм соответственно.

Возбуждение импульсным азотным лазером способствует появлению спектрах ФЛ соединения $CaGa_2S_4$:Eu четырех максимумов при 523, 538, 586 и 630 нм. В этом режиме в спектрах соединения $Ca_4Ga_2S_7$:Eu обнаружены максимумы при 551 и 653 нм.

Показано, что время возбужденных состояний ионов европия $CaGa_2S_4$ и $Ca_4Ga_2S_7$ равно 10^{-7} и 10^{-6} с. соответственно.

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