INFLUENCE OF HEATING RATE ON THE PARAMETERS OF THERMO-LIGHTING METHOD IN $EuGa_2S_4$: Er^{3+} CRYSTALS

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The thermoluminescence of $EuGa_2S_4$: Er^{3+} crystal was investigated in the temperature range 110–310K at various heating rates using thermo-lighting curves. The thermal ionization energy, frequency factor were determined and the parameters of thermo-lighting method (dispersion, resolution, light power) were calculated. It was shown that, the thermoluminescence intensity increases and the maxima of the emission curves shift toward higher temperatures with an increase in the heating rate of the samples.

Keywords: thermo-lighting method, heating rate, dispersion, resolution, light power.
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1. INTRODUCTION

The luminescence of Er^{3+} ions has been studied in various crystal matrices. Of particular interest is the emission of Er^{3+}, due to the intra-center transitions of 4f electrons in the1530–1560nm range [1], promising for use in fiber-optic communication. Materials containing Er^{3+} can be used to make planar optical amplifiers and lasers.

The $EuGa_2S_4$:Er compound belongs to the extensive class of substances with the general formula $AB_2^{III}C_4^{VI}$ (A=Eu, Yb, Sm; B=Al, Ga, In; C=S, Se, Tl) and belongs to the tetragonal syngony (space group Fddd), with lattice parameters equal to: *a=20.716Å*, *b=20.404Å* and *c=12,200Å* [2]. The results of photo- and thermoluminescence studies and the temperature dependences of the luminescence intensity in $EuGa_2S_4$:Er crystals are presented in [3–8].

The presentedwork is devoted to the study of thermoluminescence (TL) in $EuGa_2S_4$:Er^{3+} crystals by using thermal glow curves, on the basis of which some parameters of the trap levels and the thermo-lighting method are calculated.

2. EXPERIMENTAL PROCEDURE

The $EuGa_2S_4$ crystals were synthesized from binary EuS and Ga_2S_3 compounds taken in stoichiometric ratios in evacuated to $\sim 10^{-4} \div 10^{-5}$ torr quartz ampoules by the solid-state reaction method. The synthesis was carried out at 1400 K temperature for 10 hours, after which the sample was placed on H_2S medium, which contributed to an improved placement of Er^{3+} ions in the matrix. Thermoluminescence was investigated according to the method which described in [9]. The samples were excited with a *PRK4* mercury lamp for 3 min at liquid nitrogen temperature. Thermoluminescence curves were recorded at various heating rates in the110–310K temperature range.

3. RESULT AND DISCUSSION

TL spectrum of $EuGa_2S_4$:Er^{3+} crystals are given in fig.1, taken at different heating rates, and fig. 2 shows the general view of this spectrum. It can be seen that the spectrum has a wide band and covers a temperature range of 110-310K.

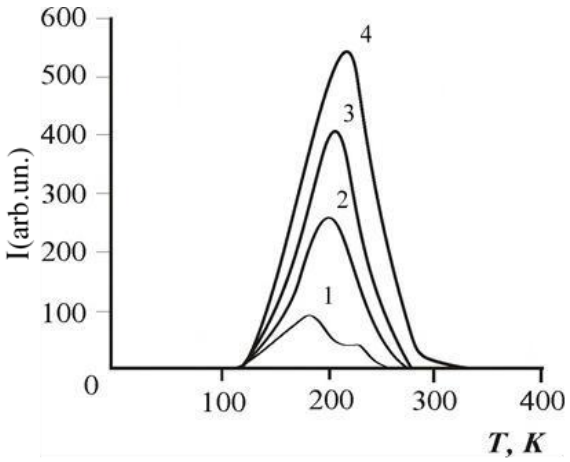

*Fig.1.*Thermoluminescence spectra of $EuGa_2S_4$: Er^{3+} (Er=7at.%) at different heating rates *β, K/s:* 1– 0.26, 2– 0.67, 3–1.35, 4–1.96.

The position of the maximum temperature T_m of the spectrum depends on the heating rate β: T_m takes values of 184, 194, 202, 215K for heating rates of 0.26; 0.67; 1.35; 1.96 K/s, respectively. The obtained measurement results were analyzed on the basis of the theory and model described in [10–14], according to which the observed maxima are characteristic of ternary alkaline-earth and rare-earth chalcogenides belonging to the $A^{II}B_2^{III}C_4^{VI}$ group. It has been established that the TL spectra are caused by electron traps with a quasicontinuous distribution of levels in the energy range of 0.1–0.3eV. Note that on the TL curve from the high temperature side at *β=0.26K/s*, a weak peak is observed at 221K, which is easily eliminated by the thermal purification method proposed in [15].

A number of very important parameters of trapping centers can be determined based on the obtained experimental results: thermal ionization energy (E_t), frequency factor (p_0), *TL* spectrum half-

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width (δ_2), etc. From the equation of the thermo-lighting curve for intensity [9,16].

$$I = n_0 p_0 \exp\left\{-\frac{E_t}{kT} - \frac{p_0}{\beta_0}\int_0^T \exp\left(-\frac{E_t}{kT}\right)dT\right\} \quad (1)$$

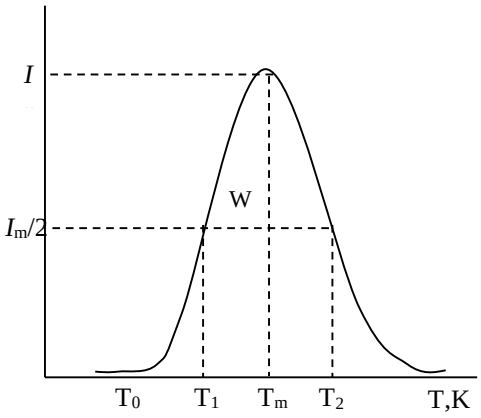

Fig. 2. General view of TL spectrum

Where n_0 is the total light sum stored at the capture levels of given depth; p_0-frequency factor is proportional to the frequency of effective collisions capable of freeing electrons from trapping levels; E_t is thermal ionization energy (capture depth); k is the Boltzmann constant($0.86 \cdot 10^{-4}$ $eV.K^{-1}$); T is absolute temperature.

Assuming the presence of levels of the same depth and without re-sticking of electrons (the monomolecular nature of the luminescence kinetics), we can calculate the values of the thermo-lighting method: dispersion, resolution and luminosity.

According to [9] the method for dispersion thermo-lighting accept value of $D = dT_m/dE_t$ which characterizes how far the maxima of thermo-lighting peaks T_m are located from each other.

Under the condition $dI/dT_{T=T_m} = 0$ from the expression (1) it turns out that

$$E_t = kT_m \ln\left(\frac{p_0}{\beta_0}\frac{kT_m^2}{E_t}\right) \quad (2)$$

replace in

$$\frac{kT_m^2}{E_t} = T_2 - T_m = \delta_2 \quad (3)$$

from (2) it follows that

$$E_t = kT_m \ln\left(\frac{p_0}{\beta_0}\delta_2\right) \quad (4)$$

consequently

$$D = \frac{dT_m}{dE_t} \cong \frac{1}{k}\frac{1}{\ln\left(\frac{p_0}{\beta_0}\delta_2\right)} \quad (5)$$

Here T_2 is the temperature on the decreasing part of the thermo-lighting peak, at which, β_0 is the sample heating rate (K/s); δ_2 is the half-width of the spectrum from the high-temperature side.

Since p_0 is considered constant for a given phosphor [16] (it varies little with temperature), according to (5), the dispersion of the method is almost constant across the entire energy spectrum at constant β_0 and δ_2.

The resolution of the thermo-lighting method is characterized by magnitude.Neglecting the asymmetry of the thermo-lighting peaks at and assuming $\delta \sim 2\delta_2$, from (3), (4) and (5), it is obtained that

$$R = \frac{1}{2E_t}\ln\left(\frac{p_0}{\beta_0}\delta_2\right) \quad (6)$$

From (6) it follows that the resolution of the method is not constant in the energy spectrum: the resolution decreaseswith an increase in E_t.

For the luminosity of thermo-lighting take value $P = I_m/n_0$. From (3) and (4), neglecting the asymmetry of the thermo-lighting peaks, we have:

$$I_m = n_0\beta_0 \frac{k}{2E_t} ln\left(\frac{\rho_0}{\beta_0}\delta_2\right) \quad (7)$$

accordingly,

$$P = \frac{I_m}{n_0} = \beta_0 \frac{k}{2E_t}\ln\left(\frac{p_0}{\beta_0}\delta_2\right) \quad (8)$$

It follows that the luminosity of the method is not constant in the energy spectrum: with an increase in E_t, the luminosity decreases.

E_t and p_0 must calculating firstly to calculate the values of D, R, P, for which different independent methods were proposed, one of which is to find them at two different rates [11,16]. Indeed, having designated the sample heating rate in β_1 in one experiment and in Tm_1 the position of the maximum of the emission intensity at this velocity and, respectively, in β_2 and Tm_2, the same values for the second experiment will be:

$$E_t = \frac{kT_{m1}{}^2}{T_{m1}-T_{m2}} \cdot ln\frac{\beta_1 T_{m2}^2}{\beta_2 T_{m1}^2} \quad (9)$$

$$lnp_0 = ln\frac{E_t}{k} + 2\frac{T_{m2}lnT_{m2} - T_{m1}lnT_{m1}}{T_{m1}-T_{m2}} + \frac{T_{m1}ln\beta 1 - T_{m2}ln\beta 2}{T_{m1}-T_{m2}} \quad (10)$$

Table 1.

The results of calculations using these formulas are given in table1.
Thermal ionization energy, frequency factor.

Параметры	β_1=0,67; T_{m1}=194 β_2=0,26; T_{m2}=184 β, K/s; T_m, K	β_1=1,35; T_{m1}=202 β_2=0,26; T_{m2}=184 β, K/s; T_m, K	β_1=1,35; T_{m1}=202 β_2=0,67; T_{m2}=194 β, K/s; T_m, K
E_t, eV	0,26	0,26	0,27
p_0, c^{-1}	$3{,}1\cdot10^5$	$3{,}4\cdot10^5$	$3.4\cdot10^5$

In [16] and [17], other formulas are given for finding E_t and p_0, namely: $E_t = AkT_m$, in which $A=15$ according to our calculations and $A=15\div30$ according to [18] and

$$\ln\frac{p_0 T_m}{\beta} = \frac{E_t}{kT_m} + \ln\frac{E_t}{kT_m} \qquad (11)$$

The numerical values of E_t and p_0 determined from these formulas are given in Table 2.

Table 2.

Thermo-lighting parameters

β, K/c	T_m,K	δ_2, K	E_t,eV	p_0, c^{-1}	D, K/eV	R,eV^{-1}	P, c^{-1}
0,26	184	12	0,24	$1{,}0.10^5$	758	32	$7{,}1.10^{-4}$
0,67	194	13	0,25	$1{,}7{,}10^5$	775	30	$1{,}7.10^{-3}$
1,35	202	14	0,26	$3{,}3.10^5$	775	29	$3{,}3.10^{-3}$
1,96	215	15	0,28	$5{,}2.10^5$	768	27	$4{,}5.10^{-3}$

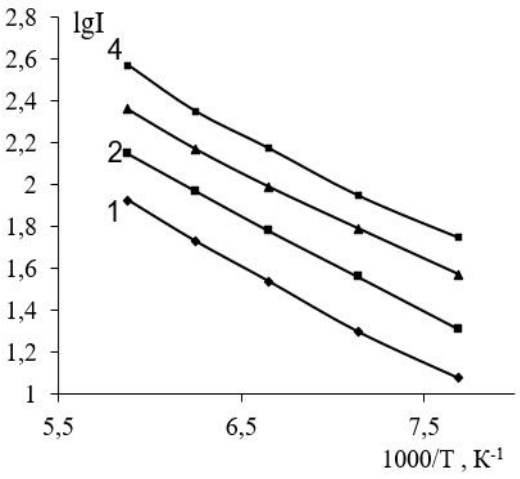

Fig.3. Temperature dependence of the intensity of thermoluminescence $EuGa_2S_4:Er^{3+}$ (Er = 7 at.%), at various heating rates β, K/s: 1-0.26, 2-0.67, 3-1.35, 4-1.96.

The thermal activation energy E_t was also determined from the initial increase in the intensity of the TL curves, which varies with temperature according to the $I=I_0e^{-E/kT}$ law. The dependence of I on T plotted in lnI coordinates from 1/T is represented by a straight line (Fig. 3), the slope of which gives the value E_t = *0.2–0.3eV*. The overlap of nearby trap levels, unfortunately, made it difficult to estimate the parameters of their capture cross section.

Finally, after the values of E_t and p_0 were calculated, as well as the half-width $\delta_2 = \frac{kT_m^2}{E_t}$ (3) for which $I=0.5I_m$, the dispersion (*D*), resolution (*R*) and luminosity (*P*) were calculated using the above formulas (5), (6) and (8) (Table 2).

CONSLUSION

Thus, in $EuGa_2S_4:Er^{3+}$ crystals, thermoluminescence was investigated at various

heating rates by using thermal emission curves.The thermal ionization energy, frequency factor were determined, the parameters of the thermal lighting method (dispersion, resolution, aperture) were calculated. It is shown thatthe thermoluminescence intensity increases and the maxima of the emission curves shift toward higher temperatures with an increase in the sample heating rate.

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$EuGa_2S_4:Er^{3+}$ KRİSTALLARINDA TERMO-İŞIQLANMA ÜSULUNUN PARAMETRLƏRİNƏ QIZMA SÜRƏTİNİN TƏSİRİ

110–310*K* temperatur inervalında və qızma sürətinin müxtəlif qiymətlərində $EuGa_2S_4:Er^{3+}$ kristallarında termik işıqlanma əyrilərinin köməyi ilə termolüminessensiya hadisəsi öyrənilmişdir.

Termik ionlaşma enerjisi və tezlik faktoru hesablanmış, termik işıqlanma metodunun parametrləri (dispersiya, ayırdetmə qabiliyyəti, işıq şıddəti) təyin edilmişdir. Göstərilir ki, qızrma sürətinin artması ilə nümunədə termolüminessensiyanın intensivliyi artır və lüminessensiya əyrilərinin maksimumu daha yüksək temperaturlara doğru sürüşür.

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ВЛИЯНИЕ СКОРОСТИ НАГРЕВА КРИСТАЛЛОВ $EuGa_2S_4:Er^{3+}$ НА ПАРАМЕТРЫ МЕТОДА ТЕРМОВЫСВЕЧИВАНИЯ

В диапазоне температур 110-310*K* при различных скоростях нагрева с помощью кривых термического высвечивания исследована термолюминесценция кристаллов $EuGa_2S_4:Er^{3+}$. Определены энергия тепловой ионизации, частотный фактор, рассчитаны параметры метода термовысвечивания (дисперсия, разрешающая способность, светосила). Показано, что с увеличением скорости нагрева образцов интенсивность термолюминесценции растет и максимумы кривых свечения смещаются в сторону высоких температур.