

## Growth of the $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$ Single Crystal and Mechanism of Stokes Emission

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The investigation of the properties of novel multicomponent chalcogenide single crystals is one of the principal directions of modern semiconductor optoelectronics. Particular attention is paid to the study of the photoluminescence properties of rare earth-doped chalcogenide semiconductors in the visible and near infrared range. This is due to the use of these materials in telecommunication devices, laser and sensor technology. We describe here the growth technique of the single crystal  $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$  composition by solution-melt method. X-ray diffraction methods confirm its crystallization in the space group  $\text{Pna}2_1$ . Optical absorption spectrum of the single crystal in the visible and near infrared range was studied. Using the functional dependence of  $(\alpha h\nu)^2$  on  $h\nu$  for direct transitions, the bandgap energy of the semiconductor was determined as  $1.99 \pm 0.01$  eV. The increase in the dopant concentration from 0.2 to 0.4 at. % Er does not significantly change the band structure of the single crystal, therefore the bandgap energy is unchanged as well. Narrow absorption bands were recorded that are related to the transitions  $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ ,  $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ ,  $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$  in the f-shell of erbium ions. High concentration of energy levels in the band gap associated with the structure defects of the crystal results in the high value of the optical absorption coefficient. Photoluminescence excitation was achieved by a 532 nm (2.33 eV) laser at 150 mW. Intense Stokes photoluminescence bands were recorded at 1.53 and 0.805 eV, as well as lower-intensity maxima at 1.45, 1.27, 1.88 eV. These emission bands correspond to the transitions  $^4\text{I}_{9/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ ,  $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  in  $\text{Er}^{3+}$  ions, respectively. An energy transition diagram for the f-shell of  $\text{Er}^{3+}$  ions in the  $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$  single crystal was plotted. The emission mechanism and the important role of the cross-relaxation processes between the ground and excited states of  $\text{Er}^{3+}$  ions were established. As a result of the influence of the local crystalline field on erbium ions, the Stark splitting of the  $^4\text{I}_{13/2}$ ,  $^4\text{I}_{15/2}$  levels and the widening of the photoluminescence band with the maximum at 0.805 eV is observed. Intense infrared bands of the photoluminescence (1.53 and 0.805 eV) create prerequisites for using the  $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$  single crystal in sensor technology and optoelectronic devices.

**Keywords:** Single crystal, Erbium, Absorption spectrum, Photoluminescence.

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### 1. INTRODUCTION

Recent years saw increasing interest of scientists in the chalcogenide single crystals doped with rare earth metals (RE) [1]. This is due to the use of these materials in optoelectronic devices such as infrared light sources [2], up-converters [3], optical amplifiers [4], temperature [5, 6] and radiation sensors [7]. Sulfide crystals and glasses have the largest transparency window in the visible and near infrared (IR) spectral range of all chalcogenide semiconductors [8]. In addition, they are characterized by relatively high solid solubility of RE in the amorphous or crystalline matrix of the alloy [9] and low phonon energy [10] which provides low energy losses during the excitation of RE ions and the appearance of photoluminescence (PL).

PL efficiency in glasses can be increased by selecting the optimal component composition of the matrix and the concentration of RE. In single crystals, it is impossible to broadly vary its composition. The change in the composition of a single crystal is limited by the homogeneity range of the selected compound, the solubility of RE ions, and also the local position of these ions in the crystal structure. Therefore, the study of PL is most commonly done for RE-doped glasses and less often for single crystals.

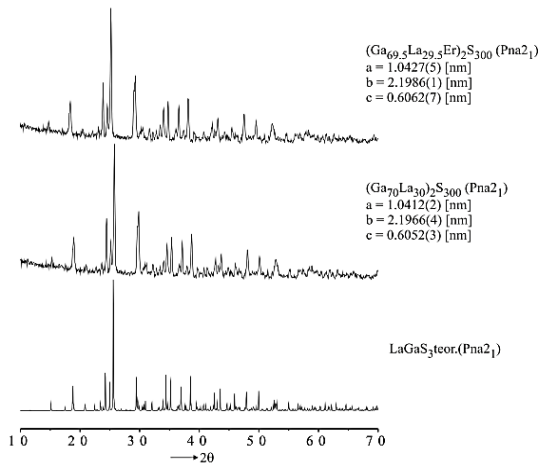
PL in chalcogenide glasses, compared to Er-doped single-crystalline semiconductors, exhibits a large number of bands in the visible and near IR ranges [11] which is due to the possibility of RE ions to occupy several positions in the amorphous matrix. It should be noted that single crystals are characterized by high intensity of PL but a small number of emission bands [3]. Therefore, the studies of single-crystalline RE-doped chalcogenides which exhibit high intensity of narrow PL bands in the visible and near-IR range are particularly interesting.

Thus, the manufacture of RE-doped chalcogenide single crystals, which can be used as materials for optoelectronic engineering and the investigation of the PL mechanism, is an important task in solid state physics and chemistry.

### 2. EXPERIMENTAL

The method of the single crystal growth was selected based on the phase diagram of the  $\text{Ga}_2\text{S}_3\text{-La}_2\text{S}_3$  system [12]. The thermograms of the sample of the same starting composition were also recorded to determine from the cooling curves the supercooling temperature which was 70 K. The synthesis of the sample of the  $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$  stoichiometric composition was performed at 1200 K in a container with graphitized walls. The ampoule was etched with hydrofluoric acid before

graphitizing. The single crystal was later grown in the same container with the conical bottom. The container with the loaded batch was evacuated to  $1 \cdot 10^{-3}$  torr and soldered. The growth process was performed in a vertical two-zone furnace with the maximum temperature of 1200 K and temperature gradient at the solid-melt interface of 20 K/cm. After the melting of the charge, the ampoule was lowered with maximum speed until its bottom reached the supercooling temperature. After the crystallization of 10 mm of the melt, the ampoule was stopped and then raised to melt 6.0-8.0 mm of the crystallized portion. The seed was subsequently annealed for 120 hours and then grown by lowering the ampoule at the rate of 7 mm/day. After the completion of the process both zones were cooled to a temperature of 820 K at the rate of 60-70 K/day, after which the obtained single crystal was annealed for 120 hours. The set-up was cooled with the furnaces switched off. The result was a single crystal of yellow-gray color, 13 mm in diameter and 22 mm in length. The diffraction pattern was recorded from a powdered sample of the obtained single crystal (scan step  $0.05^\circ$ , exposure time 4 s), which showed the absence of other phases (Fig. 1).



**Fig. 1** – The diffraction patterns of the powdered part of the obtained  $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$  single crystal, polycrystalline sample of the  $(\text{Ga}_{70}\text{La}_{30})_2\text{S}_{300}$  composition, and the theoretical pattern of  $\text{LaGaS}_3$

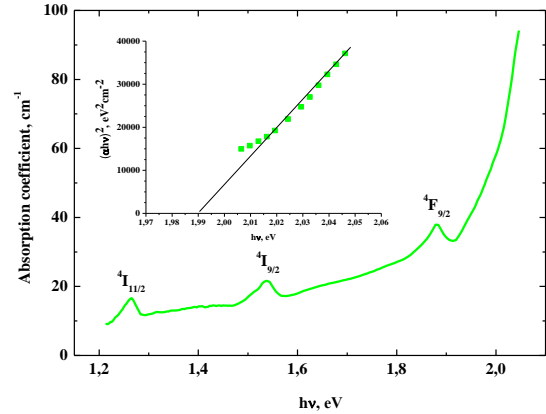
The investigation of the optical absorption spectra and PL was performed according to the standard method of synchrotrondetection,  $A \rightarrow D$  transformation, using an MDR-206 monochromator with automatic temperature control system. The PL signal was recorded from the same sample surface as the excitation. The sample for the study of the absorption spectrum was shaped as a parallel-plane polished plate of 0.8 mm thickness. The signal was registered by Si and PbS photodetectors. The luminescence excitation was effected by an LDM532U laser with the maximum power of 532 nm radiation at 150 mW.

### 3. RESULTS AND DISCUSSION

#### 3.1 Optical absorption

Optical absorption spectrum of the single crystal

$(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$  was investigated at room temperature in the 1.2-2.1 eV range (Fig. 2). The narrow absorption bands with the maxima of 1.27, 1.54, 1.88 eV were recorded according to the transitions from the ground state  $^4\text{I}_{15/2}$  to the excited states  $^4\text{I}_{11/2}$ ,  $^4\text{I}_{9/2}$ ,  $^4\text{F}_{9/2}$ , respectively, of erbium ions. The inset shows the graph of the dependence of  $(\alpha h\nu)^2$  on  $h\nu$ .



**Fig. 2** – The optical absorption spectrum of the single crystal  $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$

The bandgap energy of the single crystal was determined by the formula on direct transitions [13] extrapolating the straight line  $(\alpha h\nu)^2$  to zero:

$$\alpha \cdot h\nu = A(h\nu - E_g)^{\frac{1}{2}}, \quad (1)$$

where  $E_g$  is the bandgap energy,  $\alpha$  is the absorption coefficient,  $h\nu$  is the photon energy,  $A$  is a constant.

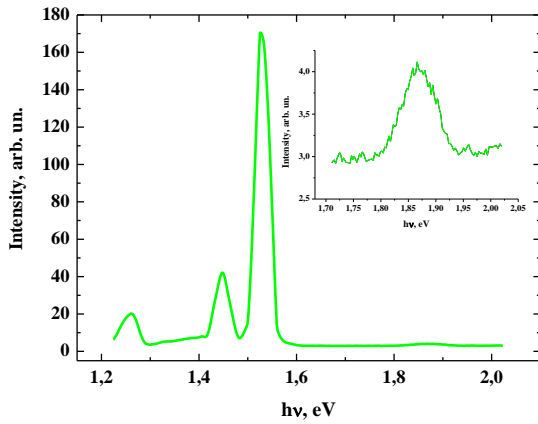
The calculated value  $E_g = 1.99 \pm 0.01$  eV coincides with the bandgap energy determined for the single crystal  $(\text{Ga}_{69.75}\text{La}_{29.75}\text{Er}_{0.5})_2\text{S}_{300}$  [3], since the modest increase in the dopant concentration (from 0.2 to 0.4 at. % Er) does not significantly change the band structure of the semiconductor.

The relatively high value of the absorption coefficient below the fundamental absorption edge (e.g.,  $14.2 \text{ cm}^{-1}$  at 1.4 eV,  $16.8 \text{ cm}^{-1}$  at 1.5 eV) is caused by the high concentration of energy levels in the band gap that are associated with the structure defects of the crystal. These defects are likely the vacancies in the cation sub-lattice of the crystal due to the cation deficiency.

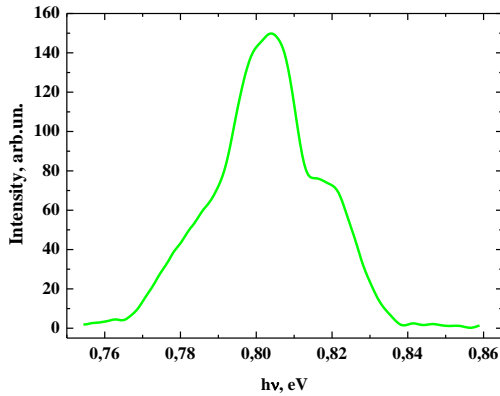
#### 3.2 Photoluminescence

Using 532 nm wavelength laser excitation (2.33 eV), Stokes PL with intense peaks of 1.53 and 0.805 eV was recorded, as well as two bands of lower intensity at 1.45, 1.27 eV, and a low-intensity maximum at 1.88 eV (Figs. 3, 4). They correspond to  $^4\text{I}_{9/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ ,  $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ , respectively, in the  $f$ -shell of  $\text{Er}^{3+}$  ions.

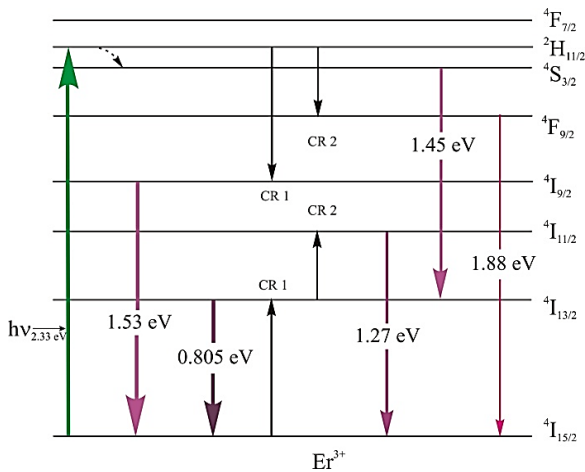
Using the energy level diagram (Fig. 5), we consider the mechanism of the appearance of excited states and radiative recombination in erbium ions. The excitation of 2.33 eV energy promotes  $\text{Er}^{3+}$  ions from the ground state to the excited state ( $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ ). After the non-radiative relaxation from  $^2\text{H}_{11/2}$  to the state  $^4\text{S}_{3/2}$ , there occurs PL with a maximum at 1.45 eV.



**Fig. 3** – PL spectrum of the (Ga<sub>69.5</sub>La<sub>29.5</sub>Er)<sub>2</sub>S<sub>300</sub> single crystal in the 1.2-2.05 eV range (inset: PL band with the maximum of 1.88 eV)

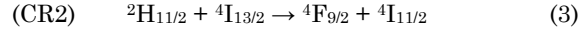
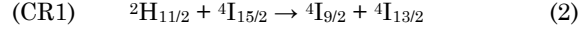


**Fig. 4** – PL spectrum of the (Ga<sub>69.5</sub>La<sub>29.5</sub>Er)<sub>2</sub>S<sub>300</sub> single crystal in the 0.75-0.86 eV range



**Fig. 5** – Energy level diagram for Er<sup>3+</sup> ions

Erbium ions cannot relax non-radiatively to lower energy states due to large energy distance between <sup>4</sup>S<sub>3/2</sub> and the states <sup>4</sup>F<sub>9/2</sub>, <sup>4</sup>I<sub>9/2</sub> and low phonon energy which is about 200-350 cm<sup>-1</sup> for sulfide crystals [10]. Therefore, we believe that these states result due to cross-relaxation processes:



According to Eq. (2), if one erbium ion is in the excited state of <sup>2</sup>H<sub>11/2</sub> and an adjacent ion is in the ground state <sup>4</sup>I<sub>15/2</sub>, an energy transfer may occur resulting in the first ion in the <sup>4</sup>I<sub>9/2</sub> state and the other in the <sup>4</sup>I<sub>13/2</sub> state. We should note that the excited state <sup>4</sup>I<sub>13/2</sub> and, consequently, the FL with the maximum at 0.805 eV result not only through CR1 but also from the radiative transition <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>13/2</sub> (the maximum at 1.45 eV). A similar energy transfer process takes place between the ions in the <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> states (Eq. (3)) resulting in <sup>4</sup>F<sub>9/2</sub> and <sup>4</sup>I<sub>11/2</sub> states of Er<sup>3+</sup> ions, respectively.

Cross-relaxation process CR1 provides a high concentration of erbium ions in the states <sup>4</sup>I<sub>9/2</sub>, <sup>4</sup>I<sub>13/2</sub>. Thus, in the case of excitation with 2.33 eV energy, two powerful emission bands at 1.53 and 0.805 eV arise in the (Ga<sub>69.5</sub>La<sub>29.5</sub>Er)<sub>2</sub>S<sub>300</sub> single crystal due to cross-relaxation CR1. The widening of the latter band is due to the Stark splitting of the <sup>4</sup>I<sub>13/2</sub>, <sup>4</sup>I<sub>15/2</sub> levels due to the effect of the crystalline field on erbium ions.

Thus, under the excitation of 2.33 eV, two powerful PL emission bands arise in the (Ga<sub>69.5</sub>La<sub>29.5</sub>Er)<sub>2</sub>S<sub>300</sub> single crystal due to the cross-relaxation process CR1. PL bands of lower intensity are associated with non-radiative relaxation to the lower energy state <sup>4</sup>S<sub>3/2</sub> and the CR2 process.

#### 4. CONCLUSIONS

A single crystal of the (Ga<sub>69.5</sub>La<sub>29.5</sub>Er)<sub>2</sub>S<sub>300</sub> composition was grown by solution-melt method and its crystallization in space group Pna2<sub>1</sub> was confirmed by X-ray diffraction. The optical absorption spectrum of the single crystal in the range of 1.2-2.1 eV and the bandgap energy were determined (1.99 eV). Using 2.33 eV laser excitation intense bands of PL were recorded at 1.88 1.53 1.45, 1.27 and 0.805 eV, that correspond to the transitions <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>I<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>13/2</sub>, <sup>4</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> in Er<sup>3+</sup>. The radiation mechanism of PL in (Ga<sub>69.5</sub>La<sub>29.5</sub>Er)<sub>2</sub>S<sub>300</sub> single crystal was determined using the energy transition diagram in Er<sup>3+</sup> ions.

The concentration of intense FL emission in only two bands (1.53 and 0.805 eV) creates prerequisites for using the (Ga<sub>69.5</sub>La<sub>29.5</sub>Er)<sub>2</sub>S<sub>300</sub> single crystal in opto-electronic technology.

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### Одержання монокристалу $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$ та механізм випромінювання стоксової фотолюмінесценції

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Дослідження властивостей нових багатокомпонентних халькогенідних монокристалів є одним із основних напрямків сучасної напівпровідникової оптоелектроніки. Особлива увага приділяється вивченню фотолюмінесцентних властивостей халькогенідних напівпровідників у видимому та близькому інфрачервоному діапазонах, які леговані рідкісноземельними металами. Це пов'язано із використанням цих матеріалів в телекомунікаційних пристроях, лазерній та сенсорній техніці. В роботі описано методику вирощування монокристалу складу  $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$  розчин-розплавним методом. Методом рентгенофазового аналізу підтверджена його кристалізація у просторовій групі  $\text{Pna}2_1$ . Досліджено спектр оптичного поглинання монокристалу у видимому та близькому інфра-червоному діапазоні. На основі функціональної залежності  $(ah\nu)^2$  від  $h\nu$  для прямих переходів визначено ширину забороненої зони напівпровідника, яка становить  $1,99 \pm 0,01$  еВ. Збільшення концентрації легуючої домішки (з 0,2 до 0,4 ат. % Er) не вносить значних змін в зонну структуру монокристалу, тому не змінює ширину забороненої зони напівпровідника. Зафіксовано вузькі смуги поглинання, які пов'язані з переходами ( $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ ,  $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ ,  $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$ ) в f-оболонці іонів ербію. Велика концентрація енергетичних рівнів в забороненій зоні, що пов'язані із структурними дефектами кристалу, обумовлюють високе значення коефіцієнта оптичного поглинання. Збудження фотолюмінесценції здійснено лазером із довжиною хвилі 532 нм (2.33 еВ) потужністю 150 мВт. Зафіксовано інтенсивні смуги стоксівської фотолюмінесценції: 1.53, 0.805 еВ, а також максимуми меншої інтенсивності: 1,45, 1,27, 1,88 еВ. Ці смуги випромінювання відповідають переходам  $^4\text{I}_{9/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ ,  $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  в  $\text{Er}^{3+}$  іонах відповідно. Побудовано діаграму енергетичних переходів в f-оболонці іонів  $\text{Er}^{3+}$  для монокристалу  $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$ . Встановлено механізм випромінювання та важливу роль процесів кросрелаксації між основним та збудженими станами іонів  $\text{Er}^{3+}$ . Внаслідок впливу локального кристалічного поля на іони ербію відбувається штарківське розщеплення рівнів  $^4\text{I}_{13/2}$ ,  $^4\text{I}_{15/2}$  і розширення смуги фотолюмінесценції із максимумом 0,805 еВ. Інтенсивні інфрачервоні смуги випромінювання (1,53 та 0,805 еВ) створюють передумови для використання монокристалу  $(\text{Ga}_{69.5}\text{La}_{29.5}\text{Er})_2\text{S}_{300}$  в сенсорній техніці та оптоелектронних приладах.

**Ключові слова:** Монокристал, Ербій, Спектр поглинання, Фотолюмінесценція.