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Photoluminescence of Erbium-Doped Glasses 70 Ga_2S_3 – 30 La_2S_3

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Glasses of the composition (70–X) mol.% Ga_2S_3 - 30 mol.% La_2S_3 - X Er_2S_3 (at X = 0, 1, 3) were synthesized and the optical absorption spectra at room temperature were studied. Photoluminescence spectra in the 2.53 - 0.73 eV range at 300 and 80 K were investigated. Intense PL maxima at 2.25, 1.88, 1.45, 1.26, 1.13, 0.81 eV were found which correspond to transitions in the f-shell of erbium ions. The redistribution of the intensity of PL peaks with temperature was analyzed based on the energy transition diagram of erbium ions.

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Introduction

Chalcogenide glasses doped with rare-earth metals attract considerable attention of scientists in recent years [1-4]. The sulfide glasses are characterized by the greatest transparency in the visible and near infrared range compared to others. This creates advantages when using them as light converters [5], active and passive elements in laser [6, 7] and in sensor technology [8-10]. Germanium and gallium sulfides are the most common among the chalcogenide glasses due to the large area of glass formation and thus a wide range of component and content variation to attain the optimal composition [11, 12]. In addition, they are non-toxic and resistant to aggressive environments.

The introduction of rare-earth metals to the composition of chalcogenide glass leads to stresses in the cation sublayer and deformation of the glass-forming matrix. This is due to the significant difference in the ionic radii of the cations of the glassy matrix and rare earth metal (e.g. $R(Ga^{3+})$ = 0.62 Å; $R(La^{3+})$ = 1.15 Å [13]). Local inhomogeneities or crystallization may occur in an amorphous matrix in the presence of high content of rare-earth metal. In addition, the concentration loss of the luminescence may occur when the content of the activating admixture (Er, Yb, Tm) increases [14]. Therefore, the choice of the optimal composition of the glass-forming matrix and the content of the doping admixture is a prerequisite for obtaining efficient luminophores and media for laser and sensor technology.

We managed to introduce 30 mol.% La_2S_3 and 1;3 mol.% Er_2S_3 in the glasses in the La_2S_3–Er_2S_3–Ga_2S_3 system. X-ray analysis showed amorphous state of alloys without any crystalline inclusions (Fig. 1). The objective of this work is to investigate the photoluminescence mechanism of erbium-doped glasses 70 mol.% Ga_2S_3 – 30 mol.% La_2S_3 in the visible and near-infrared range at low (80 K) and room (300 K) temperature.

I. Experimental

The glasses were synthesized in two stages. At the first stage, high-purity elementary components were co-melted: Ga (99.999 wt.% of the prinicipal), La, Er, (99.9 wt.%), S (99.997 wt.%, further purified by two-fold vacuum distillation). The batches were heated in shaft-type furnace at the rate of 10 K/hr to 400 K, then to 720 K, with 48 hr exposure at these stops, and to the maximum temperature of 1370 K. After 2 hours at1370 K, the furnace was switched off to cool. At the second stage, the samples were crushed into powder in an agate mortar and transferred to specially made containers of quartz glass with a neck at 1 cm from the bottom of the ampoule. The alloys were heated to 1370 K at the rate of 20 K/hr. After 2-hr exposure to this temperature, the samples were quenched into saturated NaCl solution with crushed ice [15].

Investigation of optical absorption spectra of the glasses utilized an MDR-206 monochromator and a thermostat. The signal was recorded by Si photodetector. The samples were prepared in the form of parallel-plane plates 0.8 mm in thickness. Photoluminescence (PL) spectra were studied using a Horiba Jobin-Yvon T64000 spectrometer. PL excitation was achieved by Ar laser, the output signal was recorded by CCD camera TE-1024x256 Andor and InGaAs detector.

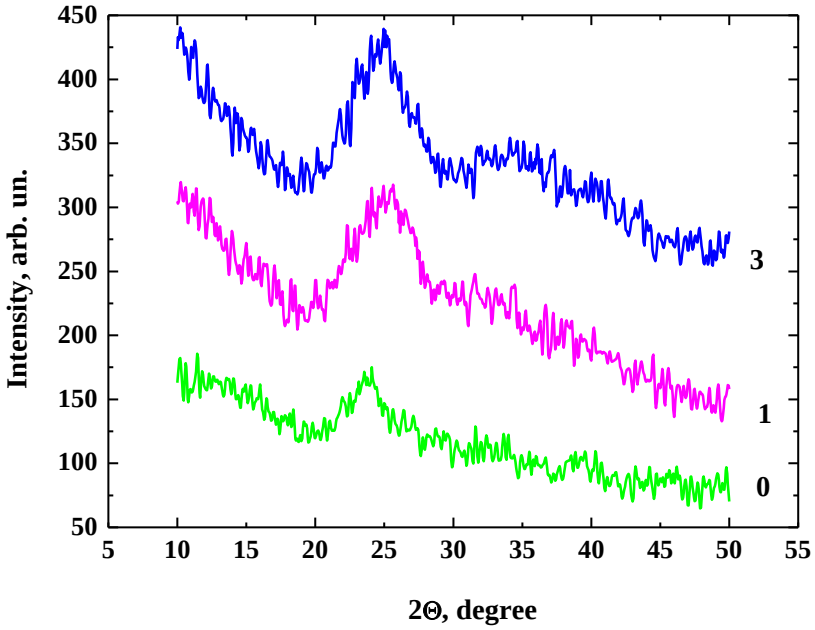


Fig. 1. X-ray diffraction patterns of the (70–X) Ga_2S_3 – 30 La_2S_3 – X Er_2S_3 glasses (numbers denote X)

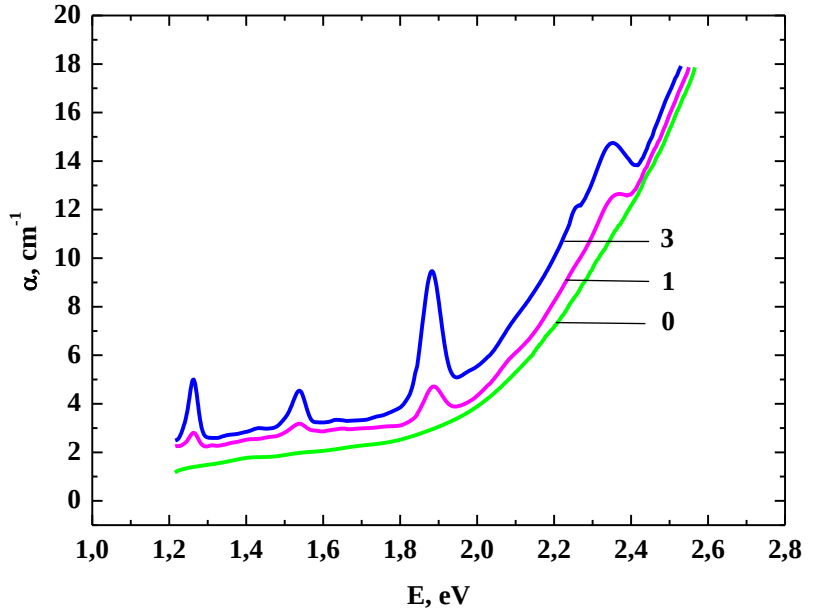


Fig. 2. Optical absorption spectra of the glasses (70–X) Ga_2S_3 – 30 La_2S_3 – X Er_2S_3 (numbers denote X).

II. Results and discussion

Optical absorption spectra in the range of 480–020 nm were investigated at room temperature (Fig. 2). Erbium-containing samples exhibit narrow absorption bands with maxima at 2.36, 2.28, 1.89, 1.55, 1.27 eV. They correspond to intra-center transitions from the ground state to the excited states $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ of Er^{3+} ions, respectively. The addition of Er_2S_3 leads also to an increase in the absorption coefficient in the visible and near infrared range.

Photoluminescence spectra in the visible and near infrared range at room temperature and at 80 K were investigated (Fig. 3, 4). The PL intensity clearly increases with increasing Er_2S_3 content. Intense maxima at 2.25, 1.88, 1.26, 0.81 eV and lower-intensity bands at 2.52, 2.36, 1.53, 1.45, 1.18, 1.13, 1.00 eV were recorded at 300 K (Fig. 3 a, 4 a). A redistribution of the emission intensity occurs at low temperature of 80 K, resulting in high-intensity maxima at 2.25, 1.45, 1.26, 1.13, 0.81 eV, and lower-intensity PL bands at 2.52, 2.36 , 1.88, 1.53, 1.00 eV. All the emission maxima at room and low temperature correspond to the transitions in the *f*-shell of erbium ions.

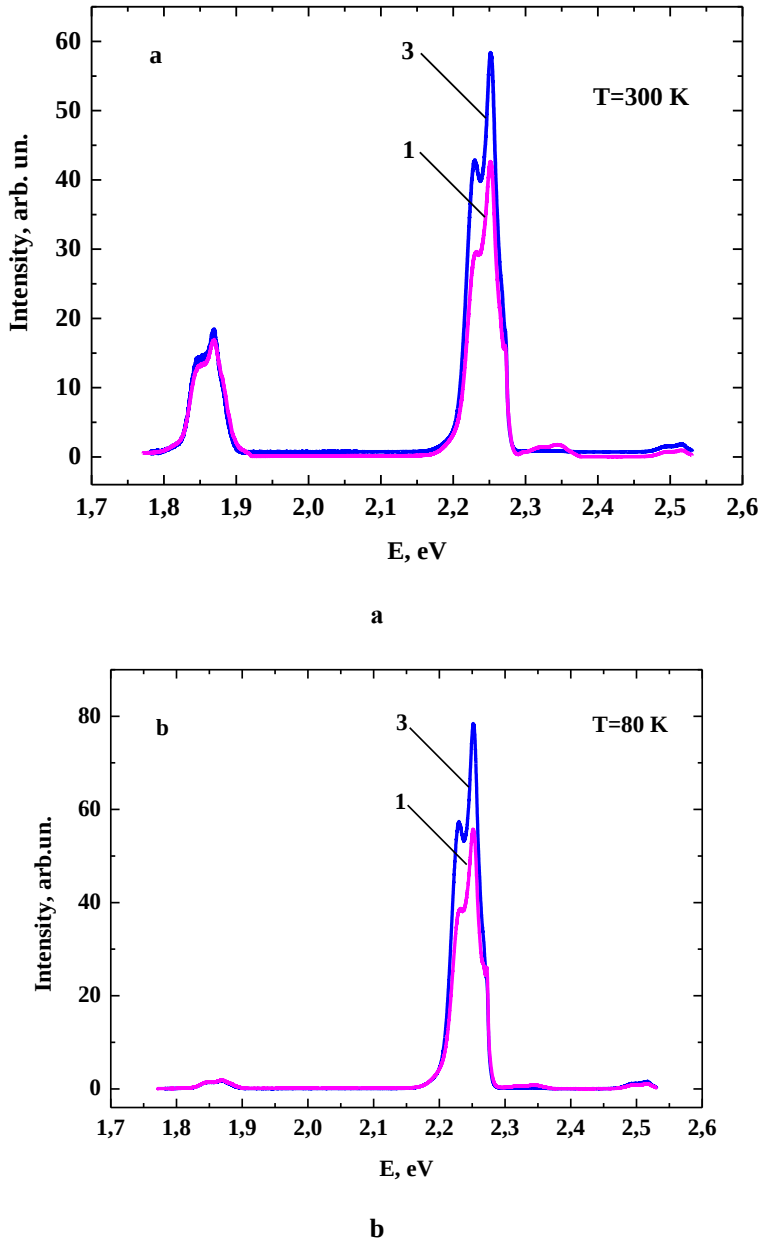


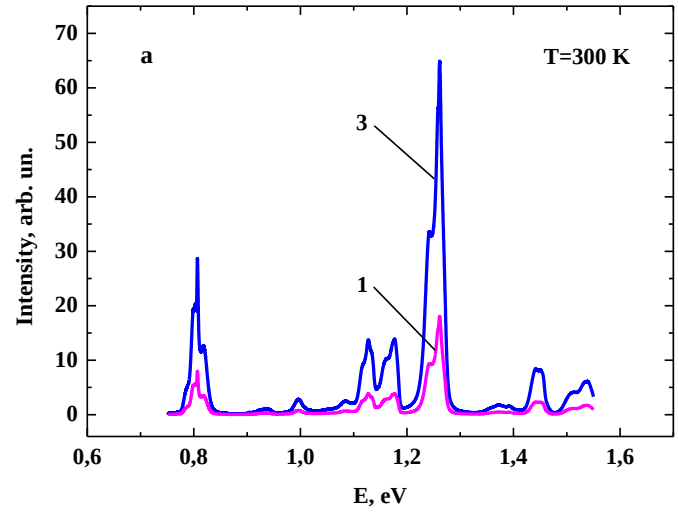
Fig. 3. Spectra PL of glasses (70 - X) Ga_2S_3 – 30 La_2S_3 – X Er_2S_3 in the visible range (numbers denote X).

It is convenient when confronted with a large number of emission bands to analyze the PL mechanism using a diagram of energy transitions in Er^{3+} ions (Fig. 5). The excitation of samples with 2.54 eV energy promotes erbium ions from the ground state to the excited state $^4F_{7/2}$. Due to small energy distance, erbium ions can then non-radiatively relax to the states $^2H_{11/2}$ and $^4S_{3/2}$. Low-temperature samples exhibit strong PL emission with maxima at 2.25 eV (transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$), 1.45 eV ($^4S_{3/2} \rightarrow {}^4I_{13/2}$), 1.13 eV ($^2H_{11/2} \rightarrow {}^4I_{11/2}$) which indicates high concentration of erbium ions in the states $^4S_{3/2}$ та $^2H_{11/2}$. The last two transitions ($^4S_{3/2} \rightarrow {}^4I_{13/2}$) and ($^2H_{11/2} \rightarrow {}^4I_{11/2}$) cause high concentration of erbium ions in the states $^4I_{13/2}$ та $^4I_{11/2}$. These create intense bands at 0.81 eV (transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$) and 1.26 eV ($^4I_{11/2} \rightarrow {}^4I_{15/2}$).

The concentration of erbium ions in various excited states changes with increasing temperature. This is caused by the changes in the phonon subsystem of the glass matrix with temperature. As a result, the probability of energy exchange between erbium ions which are in different excited states increases. Consequently, the role of cross-relaxation process (CR) increases, therefore leading to higher concentration of erbium ions in the states $^4F_{9/2}$ and $^4I_{11/2}$:

$$^2H_{11/2} + {}^4I_{13/2} \rightarrow {}^4F_{9/2} + {}^4I_{11/2}$$

The intensification of cross-relaxation processes leads to an increase in the intensity of red PL (1.88 eV) and to lower intensity of infrared bands with maxima at 1.13 and 1.45 eV. Therefore, we associate the low-intensity PL bands with low concentration of erbium ions in those excited states which correspond to radiative transitions to the states with less energy.



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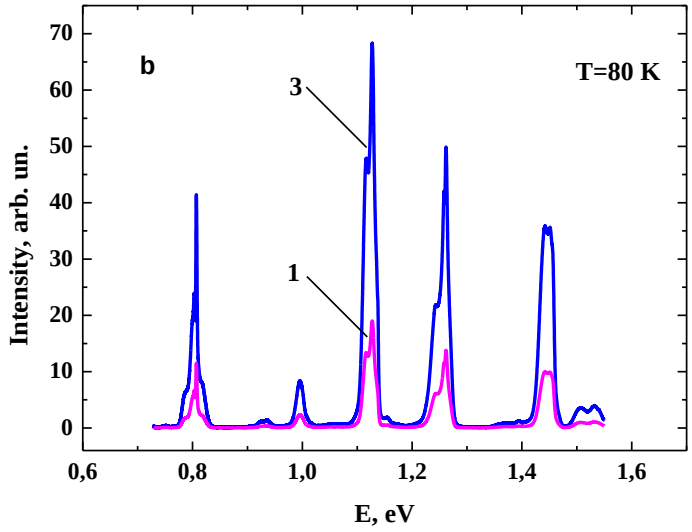

б

Fig. 4. Spectra PL of glasses (70 - X) Ga_2S_3 – 30 La_2S_3 – X Er_2S_3 in the near infrared range (numbers denote X)

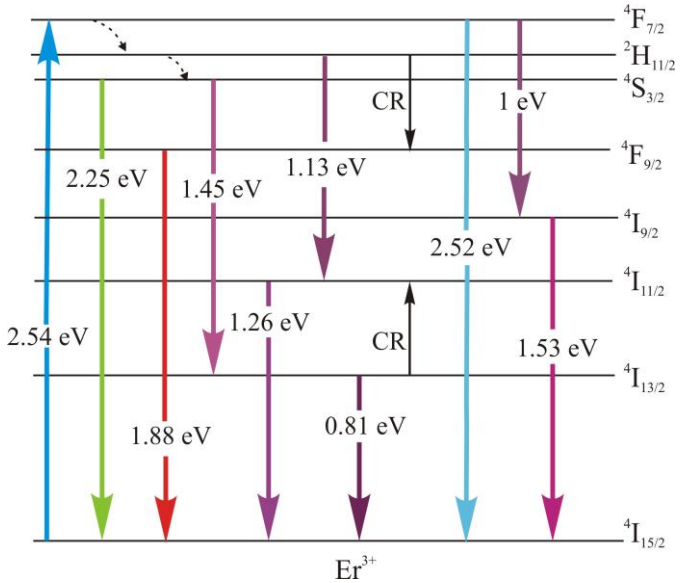

Fig. 5. Energy level diagram for Er^{3+} ions.

Conclusions

The absorption spectra of glasses (70 - X) Ga_2S_3 – 30 La_2S_3 – X Er_2S_3 (X = 0, 1, 3) at room temperature in the range of 2.60–1.22 eV were investigated. The samples with erbium show narrow absorption bands with maxima at 2.36, 2.28, 1.89, 1.55, 1.27 eV, corresponding to intra-center transitions from the ground state $^4I_{15/2}$ to excited states $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ of Er^{3+} ions, respectively.

PL spectra in the range of 2.53–0.73 eV were investigated at 300 and 80 K. All recorded emission bands are associated with transitions in the *f*-shell of erbium ions. The changes in the intensity of PL bands with increasing temperature are associated with changes in the phonon subsystem of the glass-forming matrix which result in the redistribution of erbium ion concentration in various excited states.

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[1] D.W. Hewak, D. Brady, R.J. Curry, G. Elliott, C.C. Huang, M. Hughes, K. Knight, A. Mairaj, M.N. Petrovich, R.E. Simpson and C. Sproat, Photonic Glasses and Glass-Ceramics. Kerala, State of, IN. Research Signpost. 29 (2010).
[2] A.H. Kevshin, V.V. Halyan, G.Ye. Davydyuk, O.V. Parasyuk I.I. Mazurets, Glass Phys. Chem. 36(1), 27 (2010) (doi:10.1134/S1087659610010050).
[3] I.V. Kityk, V.V. Halyan, A.H. Kevshyn, I.A. Ivashchenko, I.D. Olekseyuk, O.O. Lebed, G. Lakshminarayana, M. Piasecki, Journal of Materials Science: Materials in Electronics 28(19), 14097 (2017) (doi:10.1007/s10854-017-7262-2).
[4] P. Kostka, J. Zavadil, M. Iovu, Z. Ivanova, D. Furniss, A. Seddon, J All Comp. 648, 237 (2015) (doi:10.1016/j.jallcom.2015.05.135).
[5] V.V. Halyan, O.Y. Khyzhun, I.A. Ivashchenko, A.H. Kevshyn, I.D. Olekseyuk, P. Tyshchenko, O.P. Vovk, Y.V. Bulik, Physica B: Condensed Matter. 544, 10 (2018) (doi:10.1016/j.physb.2018.05.023).
[6] T. Schweizer, B. N. Samson, R. C. Moore, D. W. Hewak and D. N. Payne, Electon. Lett. 33, 414 (1997) (doi:10.1049/el:19970270).
[7] T. Schweizer, D.W. Hewak, D.N. Payne, T. Jensen, and G. Huber, Electron. Lett. 32, 666 (1996) (doi:10.1049/el:19960430).
[8] I.V. Kityk, K. Ozga, V. Halyan, I.A. Ivashchenko, M. Piasecki, MRS Advances. 3(31), 1783 (2018) (doi:10.1557/adv.2018.337).
[9] V. V. Halyan, I. V. Kityk, A. H. Kevshyn, I. A. Ivashchenko, G. Lakshminarayana, M. V. Shevchuk,
[10] A. Fedorchuk, M. Piasecki, Journal of Luminescence 181, 315 (2017) (doi:10.1016/j.jlumin.2016.09.022).
[11] V. V. Halyan, I. A. Ivashchenko, A. H. Kevshyn, I. D. Olekseyuk, A. P. Tretyak, P. V. Tishchenko, Sens. elektron. mikrosist. tehnol. 15 (1), 44 (2018).
[12] V.V. Halyan, M.V. Shevchuk, G.Ye. Davydyuk, S.V. Voronyuk, A.H. Kevshyn, V.V. Bulatetsky, Semicond. phys., Quantum Electron. Optoelectron 12 (2), 138 (2009).
[13] Yicong Huang, Feifei Chen, Ruiqiang Lin, Xiaoyu Zhang, Shixun Dai, Qiuhua Nie, and Xianghua Zhang, Opt. Mater. Exp. 6 (10), 3053 (2016) (doi:10.1364/OME.6.003053).
[14] W.B. Pearson, Chrystallochimija i Physica Metallov i Splavov (Mir, Moscow, 1977).
[15] Yu. Tver'yanovich, Glass Phys Chem. 29(2), 166 (2003) (doi:10.1023/A:1023407125519).
[16] I. D. Alekseyuk, I. A. Ivashchenko, I. V. Danylyuk, V. V. Galyan, A. G. Kevshin, P. V. Tishchenko, Scientific Herald Uzhhorod Un-ty (Ser. Chemistry) 38 (2), 18 (2017).

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Фотолюмінесценція стекол 70Ga_2S_3 – 30La_2S_3 легованих Ербієм

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Синтезовано стекла (70-X) mol % Ga_2S_3 - 30 mol % La_2S_3 - X Er_2S_3 (при X = 0, 1, 3) та досліджено спектри оптичного поглинання за кімнатної температури. Проаналізовано спектри фотолюмінесценції в діапазоні 2,53 - 0,73 еВ при температурі 300 та 80 К. Встановлено інтенсивні ФЛ максимуми 2,25, 1,88, 1,45, 1,26, 1,13, 0,81 еВ, що відповідають переходам в f-оболонці іонів Ербію. На основі діаграми енергетичних переходів в іонах Ербію проаналізовано перерозподіл інтенсивності між максимумами ФЛ при зміні температури.