
IR PHOTOLUMINESCENCE IN $\text{Ag}_{0.05}\text{Ga}_{0.05}\text{Ge}_{0.95}\text{S}_2\text{-Er}_2\text{S}_3$ GLASSES**V.V. HALYAN,¹ A.H. KEVSHYN,¹ G.YE. DAVYDYUK,² M.V. SHEVCHUK,³ S.V. VORONYUK¹**¹**Chair of General Physics and Physics Teaching Methodics, Volyn National University**
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The photoluminescence (PL) spectra of $\text{Ag}_{0.05}\text{Ga}_{0.05}\text{Ge}_{0.95}\text{S}_2\text{-Er}_2\text{S}_3$ glasses excited by a laser diode operating at 980 nm have been investigated. The broadening of the PL band of the glasses with increase in the Er content has been found, by calculating a full-width at half-maximum (FWHM) and the effective width $\Delta\lambda_{\text{ef}}$. Inhomogeneities with dimensions of 6–7 μm have been disclosed in the glassy alloys; their concentration increases with the erbium content and influence the width of the PL spectra.

1. Introduction

Recently, sulfide glassy alloys have been intensively investigated. They are especially interesting for their potential application in photonic devices, lasers, light amplifiers, upconvertors, *etc.* Moreover, sulfide glasses combine the low phonon energy, wide transparency window in the visual and infrared regions, high refractive index, and relatively high solubility of rare-earth elements in the host glass matrix of the alloy [1–4].

As for Er-activated sulfide glasses, the investigation of luminescent properties of the Ge–S–Ga system [5–8] in the $\sim 1.45\text{--}1.65\ \mu\text{m}$ spectral range attracts most attention. Under influence of the environment (the host glass matrix), the energy levels in the 4f-shell of an erbium ion split into collections of sublevels (Stark splitting), influencing both the bandwidth and the luminescence intensity. Varying the composition of a host glass matrix, one can obtain an environment that could increase the PL efficiency for Er^{3+} ions.

In our previous work [9], the glass formation region and features of the structure of glasses of the $\text{AgGaSe}_2 + \text{GeS}_2 \Leftrightarrow \text{AgGaS}_2 + \text{GeSe}_2$ system were studied. We chose glassy alloy $\text{Ag}_{0.05}\text{Ga}_{0.05}\text{Ge}_{0.95}\text{S}_2$ [9] in this system that has the widest transparency window in comparison with that of other glasses of the system. The subject of this work is the investigation of PL in the Er-doped glasses of the $\text{Ag}_{0.05}\text{Ga}_{0.05}\text{Ge}_{0.95}\text{S}_2\text{-Er}_2\text{S}_3$ system.

2. Experimental

The synthesis of the alloys was carried out using high-purity elements (Ag – 99.997 at.%, Ga – 99.997 at.%, Ge – 99.997 at.%, and S – 99.999 at.%) in evacuated thin quartz ampoules (0.1 Pa of residual pressure) with the initial bonding of elemental sulphur in the flame of a gas-oxygen burner and the subsequent heating (20 K/h) to 1273 K in a shaft furnace. The samples were held at 1273 K for 10 h and subsequently quenched in a 25% NaCl water solution at room temperature. The free volume of the ampoules was thermally stabilized with string asbestos to prevent losses for the vapor phase condensation. The glassy state of the alloys was confirmed by X-ray diffraction (DRON 4-13, $\text{CuK}\alpha$ -radiation) and microstructural (Leica VMHT Auto microscope) analyses.

PL was measured using an MDR-206 monochromator and a cooled PbS detector. Excitation was carried out using a KLM H980-200-5 200-mW laser diode operating at 980 nm.

3. Results and Discussion

To study PL, we chose glasses with compositions shown in Table 1 to trace the dependence of the PL efficiency on the Er content and the Ga/Er ratio.

The PL spectra are shown in Fig. 1. According to the diagram of energy levels [10], the PL excitation wavelength corresponds to the ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition, and the obtained PL does to the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in an Er^{3+} ion, respectively. Figure 1 shows that the PL intensity increases with the Er content. The position of the luminescence maximum is around 1540 nm in all samples and does not depend on the Er or Ga content.

To compare the applicability of glasses, we determined a full-width at half-maximum (FWHM) of the luminescence spectra [5, 7]. As Fig. 1 shows, the shapes of the spectra are asymmetric. Therefore, we assume that it is more reasonable to calculate the effective width $\Delta\lambda_{\text{ef}}$ of the PL spectra, by using the formula [11]

$$\Delta\lambda_{\text{ef}} = \frac{\int I(\lambda)d(\lambda)}{I_{\text{max}}}, \quad (1)$$

where $I(\lambda)$ is the emission intensity at a wavelength λ , and I_{max} is the emission intensity at the peak emission wavelength.

The obtained values of FWHM and $\Delta\lambda_{\text{ef}}$ are listed in Table 2. The largest values of FWHM and $\Delta\lambda_{\text{ef}}$ were calculated for the sample with 0.27 at.% Er, and they are less for the samples with 0.16 and 0.12 at.% Er. It is worth noting that, at a smaller erbium content (0.27 at.%) as compared with that (0.35 at.%) in [7], we obtained larger value of FWHM (49 nm) (36 nm in [7]).

To analyze the effect of broadening of the PL band for the sample with the maximum Er content, we deconvoluted the PL spectra into four Gaussians (Fig. 2) with parameters presented in Table 2.

Gaussians 1 and 4 contribute the most to the PL spectra. Moreover, the positions of the Gaussians 1, 2, and 3 do not change practically, whereas the maximum of Gaussian 4 shifts from 1558 nm (0.12 at.% Er) to 1568 nm (0.27 at.% Er). The broadening of the PL band in the short-wavelength region with increase in the erbium content to 0.27 at.% is caused by an increase of the contribution of Gaussian 1 (area of the Gaussian). At the same time, the position of its maximum does

Table 1. Composition of the glassy alloys

Alloy composition	at.% Er	Ga/Er
$\text{Ag}_{12}\text{Ga}_{12}\text{Ge}_{228}\text{Er}_2\text{S}_{483}$	0.27	6
$\text{Ag}_{20}\text{Ga}_{20}\text{Ge}_{380}\text{Er}_2\text{S}_{803}$	0.16	10
$\text{Ag}_{28}\text{Ga}_{28}\text{Ge}_{532}\text{Er}_2\text{S}_{1123}$	0.12	14

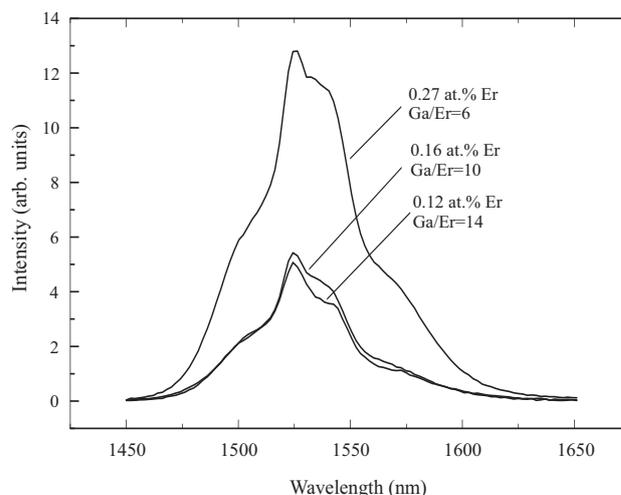


Fig. 1. PL spectra of the $\text{Ag}_{0.05}\text{Ga}_{0.05}\text{Ge}_{0.95}\text{S}_2\text{-Er}_2\text{S}_3$ glasses

not change practically. At the long-wavelength side, the broadening of the PL band occurs only due to a shift of Gaussian 4 toward longer wavelengths, because the contribution of Gaussian 4 at different erbium contents does not change practically. The broadening of the PL band in the erbium-doped glasses was referred in work [12] to the formation of clusters in the samples with $\text{Ga/Er} < 10$. Among the studied glassy alloys, the PL band broadened in the sample with 0.27 at.% Er and $\text{Ga/Er} < 10$ (see Table 2 and Fig. 2).

An increase of the erbium content in glasses can lead to an increase in the number of defects. We conducted microstructural investigations of the alloys, by using a Leica VMHT Auto microscope (magnification $\times 1894$). Before the scanning, the surface of the samples was etched

Table 2. FWHM and effective width of the PL bands, area, and position of the Gaussians of the glasses

at.% Er	FWHM (nm)	$\Delta\lambda_{\text{ef}}$ (nm)	Gaussian number	Area (arb. units)	Position of maximum
0.27	48	61	1	18	1522
			2	5	1539
			3	9	1554
			4	27	1568
0.16	42	52	1	13	1523
			2	5	1539
			3	9	1553
			4	25	1560
0.12	40	52	1	13	1523
			2	7	1539
			3	7	1555
			4	26	1558

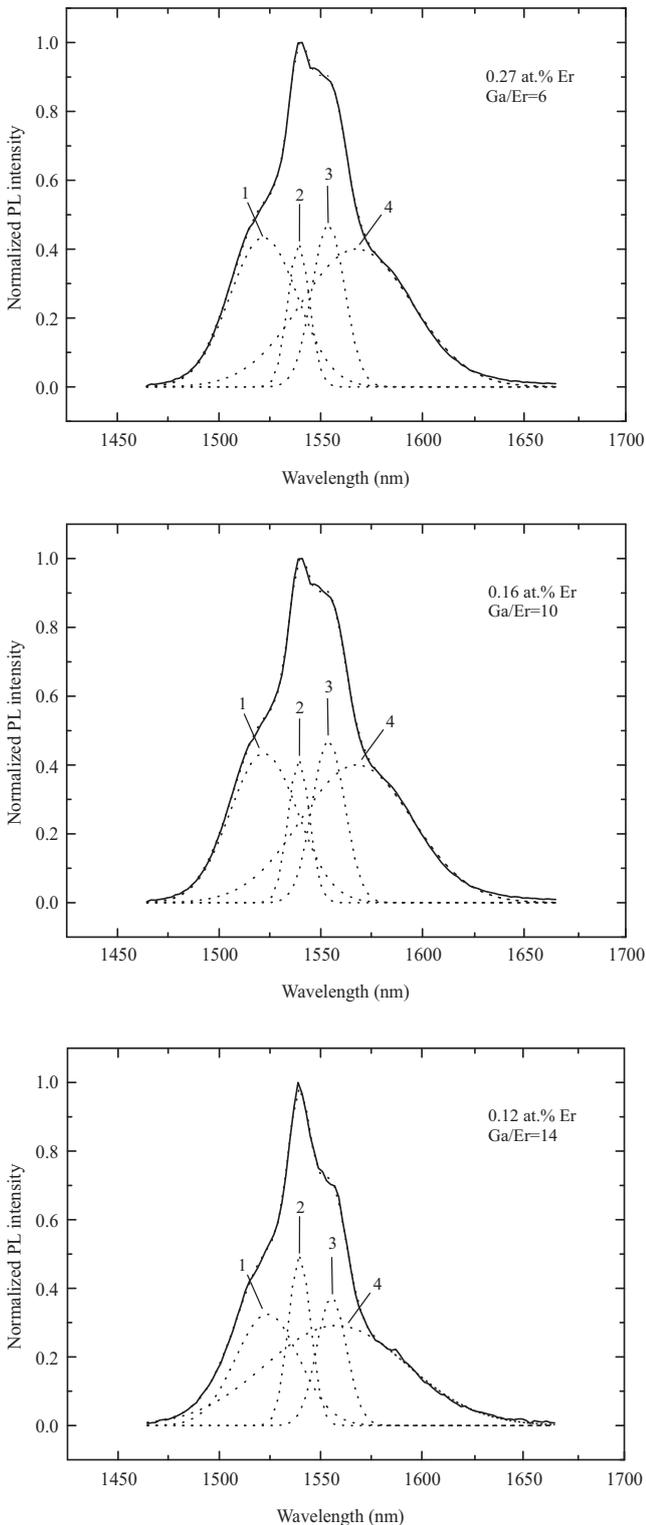


Fig. 2. Deconvoluted PL spectra of the $\text{Ag}_{0.05}\text{Ga}_{0.05}\text{Ge}_{0.95}\text{S}_2\text{-Er}_2\text{S}_3$ glasses

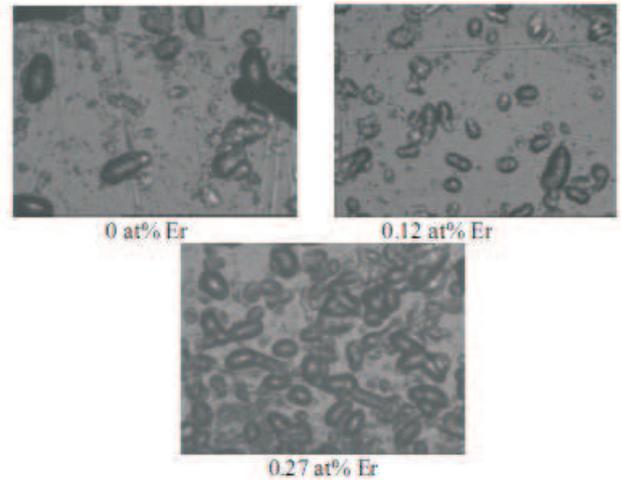


Fig. 3. Surface of the glassy alloys $\text{AgGaS}_2\text{-Ge}_2$ with a variable erbium content: 0 at%, 0.12 at% and 0.27 at% Er. Magnification $\times 1894$

for 5 min in a mixture of equal volumes of 0.5 N H_2O_2 and 1 N NaOH solutions. The results of studies are presented in Fig. 3.

In the studied samples, heterogeneities with dimensions of 6–7 μm were disclosed. Their concentration increases with the erbium content. Since heterogeneities are present in the undoped samples, they are obviously related to defects in the host matrix. Thus, some portion of Er is evenly distributed throughout the volume of the glass, and some portion is close to the heterogeneities that are good drains for various defects. Under influence of the field of the host glass matrix, the energy levels of Er^{3+} ions that are evenly distributed throughout the volume of the alloy and that are close to the heterogeneities split differently. According to Table 2, in the sample with 0.27 at.% Er that has a large concentration of heterogeneities, the broadening of the PL spectrum is due to a shift of Gaussian 4 toward longer wavelengths. This is due to an increase of the contribution to PL from Er^{3+} ions which are close to heterogeneities [13]. The shift of Gaussian 4 toward longer wavelengths indicates a reduction in the radiation energy in transitions from the lower sublevels of the $^4I_{13/2}$ collection into the upper empty sublevels of the $^4I_{15/2}$ collection. Thus, in the erbium ions that are close to heterogeneities, a bigger Stark splitting of the $^4I_{13/2}$ and $^4I_{15/2}$ levels caused by the field of the host glass matrix takes place.

4. Conclusions

We have investigated the PL spectra of the $\text{Ag}_{0.05}\text{Ga}_{0.05}\text{Ge}_{0.95}\text{S}_2\text{-Er}_2\text{S}_3$ glasses with 0.12, 0.16, and 0.27 at.% Er. The position of the PL maximum is around 1540 nm and does not depend practically on the erbium content. The PL intensity increases, and the PL band broadens with increase in the erbium content. This can be attributed to both the influence of the field of the host glass matrix on erbium ions that are close to heterogeneities and the corresponding Stark splitting of the $^4I_{13/2}$ and $^4I_{15/2}$ levels of an Er^{3+} ion.

1. A. Zakery and S.R. Elliot, *J. Non-Cryst. Solids* **330**, 1 (2003).
2. A.M. Yamaguchi, T. Shibata, and K. Tanaka, *J. Non-Cryst. Solids* **232–234**, 715 (1998).
3. J. Heo, J.M. Yoon, and S.Y. Ryon, *J. Non-Cryst. Solids* **238**, 115 (1998).
4. A. Tverjanovich, Ya.G. Grigoriev, S.V. Degtyarev, A.V. Kurochkin, A.A. Man'shina, and Yu.S. Tver'yanovich, *J. Non-Cryst. Solids* **288**, 89 (2001).
5. Z.G. Ivanova, E. Cernoskova, and Z. Cernosek, *J. Phys. Chem. Solids* **68**, 1260 (2007).
6. D.T. Tonchev, K.V. Koughia, Z.G. Ivanova, and S.O. Kasap, *J. Optoelectron. Adv. Mater.* **9**, 337 (2007).
7. Z.G. Ivanova, Z. Aneva, K. Koughia, D. Tonchev, and S.O. Kasap, *J. Non-Cryst. Solids* **353**, 1330 (2007).
8. Z.G. Ivanova, K. Koughia, Z. Aneva, D. Tonchev, V.S. Vassilev, and S.O. Kasap, *J. Optoelectron. Adv. Mater.* **7**, 349 (2005).
9. V.V. Halyan, M.V. Shevchuk, G.Ye. Davydyuk, S.V. Voronyuk, A.H. Kevshyn, and V.V. Bulatetsky, *J. Optoelectron. Adv. Mater.* **12**, 138 (2009).
10. J. Fick, E.J. Knystautas, A. Villeneuve, F. Schiettekatte, S. Roorda, and K.A. Richardson, *J. Non-Cryst. Solids* **272**, 200 (2000).
11. I.I. Opera, H. Hesse, and K. Betzler, *Opt. Mater.* **28**, 1136 (2006).
12. K. Koughia, M. Munzar, D. Tonchev, C.J. Haugen, R.G. Decorby, J.N. McMullin, and S.O. Kasap, *J. Luminesc.* **112**, 92 (2005).
13. A.M. Gurvich, *Introduction to Physical Chemistry of Phosphorus-Based Crystals* (Vysshaya Shkola, Moscow, 1982), (in Russian).

Received 01.07.10

ВПЛИВ ВМІСТУ Er НА ШИРИНУ СМУГИ ФОТОЛЮМІНЕСЦЕНЦІЇ В СТЕКЛАХ $\text{Ag}_{0.05}\text{Ga}_{0.05}\text{Ge}_{0.95}\text{S}_2\text{-Er}_2\text{S}_3$

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Резюме

Досліджено спектри фотолюмінесценції (ФЛ) стекол $\text{Ag}_{0.05}\text{Ga}_{0.05}\text{Ge}_{0.95}\text{S}_2\text{-Er}_2\text{S}_3$, які збуджені діодним лазером із максимумом 980 нм. Обчислюючи повну ширину на половині максимуму та ефективну ширину $\Delta\lambda_{\text{ef}}$, зафіксовано розширення смуги ФЛ стекол при збільшенні вмісту Er. У склоподібних сплавах виявлено неоднорідності розмірами 6–7 мкм, концентрація яких зростає зі збільшенням вмісту ербію та впливає на ширину спектрів ФЛ.