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Optical Absorption of Chalcogenide Glass Ga₂S₃-La₂S₃ Doped with Erbium

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The glasses of the La_2S_3-Er_2S_3-Ga_2S_3 system were synthesized from the melted samples which where quenched in to the cold 25-% solution of NaCl. Their optical absorption spectra were studied in the range of 1.2–2.9 eV at 80 K. For doped erbium glasses, there are narrow absorption bands with maxima at 2.53, 2.35, 2.27, 1.88, 1.54, 1.26 eV. With increasing of the content of La_2S_3 (30 - 40 mol. %) the bandgap width decreases (E_g = 2.83 - 2.73 eV) and the Urbach parameter increases (ΔE = 151 - 238 meV). These changes are determined by the structural disorder in the glasses.
Keywords: glassy alloys, optical absorption, Urbach's rule.

Introduction

Chalcogenide glasses are promising materials in the field of optoelectronics that are characterized as chemically stable glass-forming media, with low phonon energy [1] and relatively high solubility of metallic and rare earth admixtures [2, 3, 4]. The transparency of the chalcogenide glasses in the visible and infrared spectral region opens the prospect of their use as filters, media for optical fibers and telecommunication devices [5].

Some research on the glass formation in the Ga–La–S system was performed by A.M. Loireau-Lozac'h et al. [6, 7] back in 1970 s. The authors determined that the component composition variations suffer quite wide limits of the introduction of lanthanum. Additionally, in the Ga_2S_3–La_2S_3 system there are two compounds, $La_3Ga_{1.67}S_7$ and $LaGaS_3$. $La_3Ga_{1.67}S_7$ melts congruently at 1423 K and crystallizes in the hexagonal symmetry, S.G. $P6_3$, a = 1.015 nm, c = 0.608 nm [7]. $LaGaS_3$ forms at 1223 K in a peritectic reaction $L + La_3Ga_{1.67}S_7 \leftrightarrow LaGaS_3$ and crystallizes in the monoclinic symmetry, S.G. $P2_1/c$, a = 1.517(8) nm, b = 1.056(4) nm, c = 1.282(6) nm, β = 137.70° [8]. Acousto-optical properties of the Ga_2S_3–La_2S_3 glasses were later investigated [9] as well as the glass formation

processes upon admixture of Na_2S, CaS, In_2S_3 and the optical properties of obtained materials [10]. The use of the glasses of the Ga_2S_3–La_2S_3 system modified with various dopants is favoured as they are ecologically friendly and technologically simple to synthesize compared to the crystalline analogs.

The purpose of this work is to study the visible and near-infrared optical absorption spectra of new sulfide glasses of the Ga_2S_3–La_2S_3 system doped with erbium as promising materials for optoelectronic technology.

I. Experimental

The production of the glasses of the La_2S_3–Er_2S_3–Ga_2S_3 system started with preliminary synthesis of alloys of 1 - 1.5 g mass from the elements Ga (99.999 mass%), La, Er, (99.9 mass%), S (99.997 mass%, additionally purified by vacuum sublimation). The synthesis was performed by direct high-temperature method in shaft-type furnaces with temperature control accuracy ± 5 K. The batches were first heated to 400 K at the rate of 10 K/hr (48 hr exposure), then heated to 720 K at 10 K/hr (48 hr exposure), heated to the maximum temperature of 1370 K at 10 K/hr (2 hr exposure), followed by cooling to room temperature at 20 K/hr. Obtained alloys were

crushed into powder in an agate mortar, loaded into quartz containers with a spherical bottom of 1 cm diameter and evacuated to the residual pressure $1.33 \cdot 10^{-3}$ Pa. The powdered samples were again heated step-wise, first to 1070 K at the rate of 50 K/hr, then to 1420 K at the rate of 40 K/hr. The melts were kept at the maximum temperature for 3 hrs and then quenched into saturated saline with crushed ice. Obtained alloys were examined by XRD (DRON 4-13 diffractometer) and microstructure analysis (Leica VMHT Auto microhardness tester) for the presence or absence of crystalline inclusions.

Optical absorption spectra of the glassy alloys were investigated at T = 80 K in the range of 1 - 3 eV using an MDR-206 monochromator equipped with automatic synchrodetection system, thermostat with temperature stabilization and control. The signal was received at a Si photosensor. Parallel-plane plates of 0.5 and 0.8 mm thickness were used as samples.

II. Results and Discussion

The glasses of the La_2S_3–Er_2S_3–Ga_2S_3 system were synthesized in which Ga_2S_3 is the glass-forming agent,

La_2S_3 is a modifier of the glassy matrix, and Er_2S_3 is a dopant. The samples with the La_2S_3 content of 30, 35, 40 mol.% were prepared, with the Er_2S_3 content of 0, 1 or 3 mol.% for each version. The component composition of each sample is listed in Table 1.

Optical absorption spectra of the glasses of the La_2S_3–Er_2S_3–Ga_2S_3 system at 80 K are presented in Figs. 1, 2 and 3.

The optical absorption edge is shown in the insert in a semi-logarithmic scale. The linear dependence of $ln\,(a) = f\,(hn)$ in the inserts indicates that the absorption edge fits Urbach's rule which is typical of non-crystalline solids [11]:

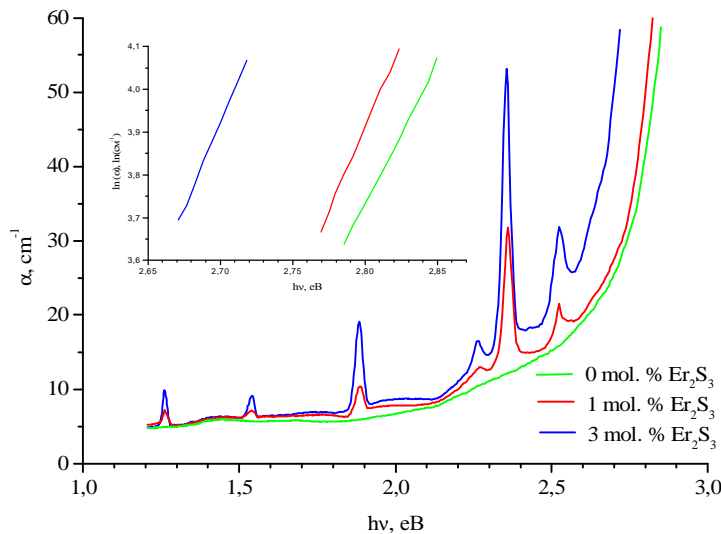$$a(hn) = a_0 \exp\left(\frac{hn - E_g}{\Delta E}\right) \qquad (1)$$

where α_0 is a constant coefficient; E_g is the bandgap energy; $\Delta E = \dfrac{\Delta(hn)}{\Delta(\ln a)}$ is the parameter that characterizes the tailing of the absorption edge.

Bandgap energy of the glasses was estimated at 50 cm⁻¹ (Table 1). The bandgap of Er-free glasses decreases with the increase of La_2S_3 content from 2.83 eV (in the sample 70 mol.% Ga_2S_3 – 30 mol.%

Table 1

Component composition and optical parameters of the La_2S_3–Er_2S_3–Ga_2S_3 glasses
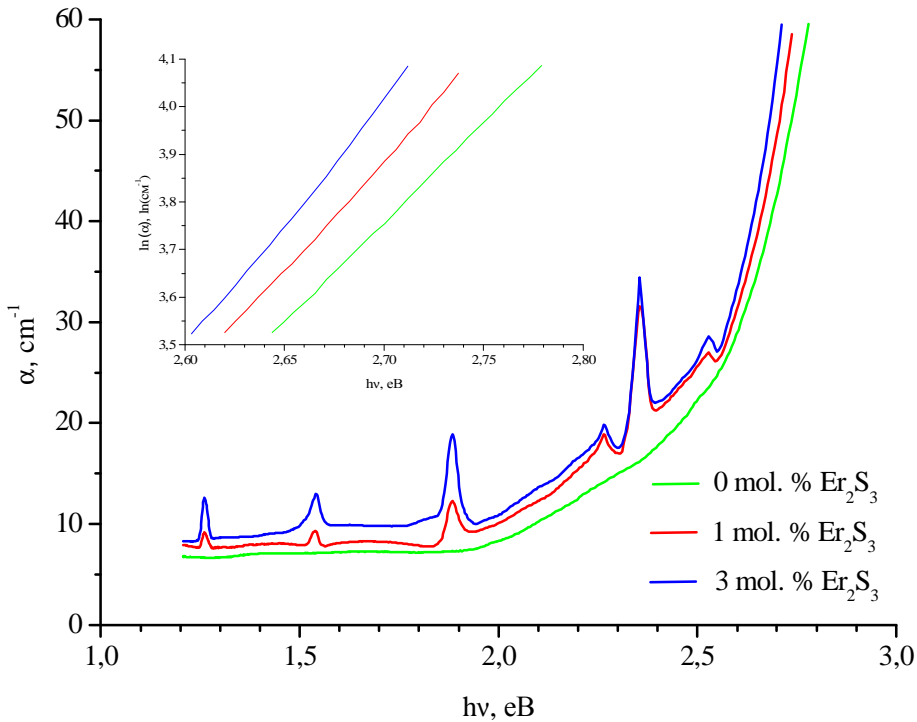
№	Ga₂S₃	La₂S₃	Er₂S₃	E_g, eV	ΔE, meV
	content, mol.%				
1	70	30	0	2.83	151
2	69	30	1	2.79	127
3	67	30	3	2.7	121
4	65	35	0	2.77	198
5	64	35	1	2.72	180
6	62	35	3	2.68	166
7	60	40	0	2.73	238
8	59	40	1	2.70	216
9	57	40	3	2.68	191

Fig. 1. Optical absorption spectra of the glasses Ga_2S_3 – (30 mol.%) La_2S_3 –Er_2S_3.

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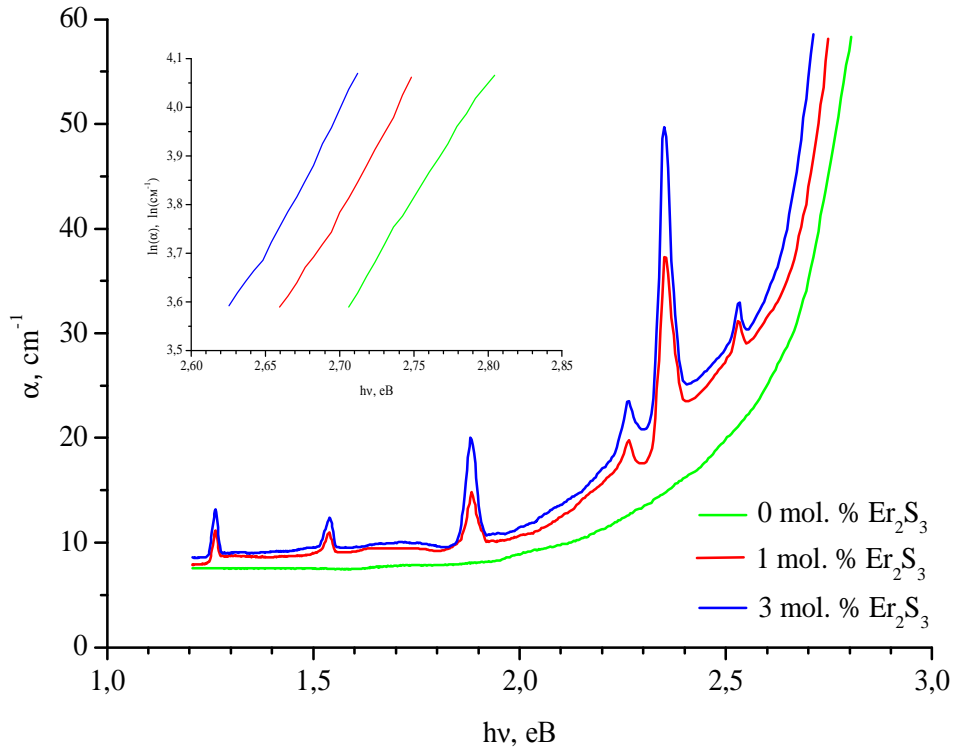
Fig. 2. Optical absorption spectra of the glasses $Ga_2S_3 – (35 mol.\%)$ $La_2S_3 – Er_2S_3$.

Fig. 3. Optical absorption spectra of the glasses $Ga_2S_3 – (40 mol.\%)$ $La_2S_3 – Er_2S_3$.

La_2S_3) to 2.73 eV (in the sample 60 mol.% Ga_2S_3 – 40 mol.% La_2S_3). Additionally, the rise of lanthanum concentration leads to increased tailing of the absorption edge and, correspondingly, to greater disorder of the glass-forming matrix. The absorption coefficient increases in the entire spectral range which results from the larger numbers of the defect centers that create energy levels in the band gap.

Er-doped samples exhibit narrow absorption bands with the maxima at 2.53, 2.35, 2.27, 1.88, 1.54, 1.26 Ev that correspond to intra-center transitions from the ground $^4I_{15/2}$ to the excited state $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ in Er^{3+} ions. The increase of erbium content does not change the positions of the absorption bands but
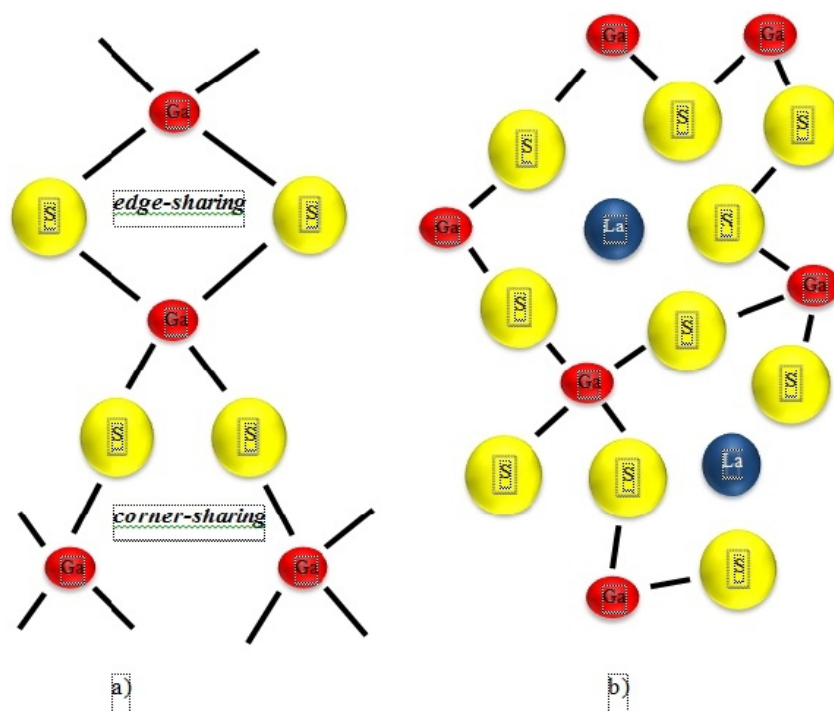
Fig. 4. Models of tetrahedra joining in the glass-forming matrix: a) formed of the [GaS$_4$] tetrahedra; b) formed of the [GaS$_4$] tetrahedra and modified with La.

leads to the increase of their intensity, with the absorption edge shifting to lower energies (Figs. 1-3).

It is known [1, 2] that the glass-forming network in Ga(Ge)$_2$S$_3$ is based on corner-sharing or edge-sharing tetrahedra [Ga(Ge)S$_4$]. The models of the tetrahedra are shown in Fig. 4.

Upon the addition of La$_2$S$_3$, edge-sharing tetrahedra transform into corner-sharing tetrahedra [2] based on [GaS$_4$] with the formation of non-bridging sulfur atoms. La^{3+} ions provide the charge balance. It should be noted that La^{3+} ionic radius (1.15 Å [12]) is much larger than that of Ga^{3+} (0.62 Å [12]) therefore the glass-forming matrix distorts; consequently appearing defects result in increasing absorption coefficient and the parameter ΔE in the glassy alloys.

Er^{3+} ions may occupy the same sites in the glass structure as La^{3+}. Additionally, erbium doping decreases the number of ethane-like units [S$_3$Ga–GaS$_3$] (typical of the glasses with the deficit of chalcogene) [1, 13] which transform into molecular units [GaS$_4$]. This is exhibited in the absorption spectra in reducing of the tailing of the absorption edge (lower ΔE, Table 1) for the glasses with the fixed content of La$_2$S$_3$.

Conclusions

Optical absorption spectra of the Ga$_2$S$_3$–La$_2$S$_3$–Er$_2$S$_3$ glasses were investigated at 80 K in the range of 1.2–2.9 eV. It was determined that the absorption edge is characterized by the exponential dependence. Bandgap energy of the glasses and its dependence on the component composition were estimated. The addition of Er$_2$S$_3$ and La$_2$S$_3$ decreases the band gap from 2.83 to 2.68 eV. The increased of erbium amount, for the fixed content of other components, leads to the decrease of the parameter ΔE (by 30 meV at 30 mol.% La$_2$S$_3$; by 32 meV at 35 mol.% La$_2$S$_3$; by 47 meV at 40 mol.% La$_2$S$_3$). The variation of the optical parameters of the chalcogenide glasses is related to the transformations of the structural units caused by the admixture of rare-earth metals.

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Оптичне поглинання халькогенідних стекол Ga₂S₃-La₂S₃, легованих ербієм

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Стекла системи La₂S₃–Er₂S₃–Ga₂S₃ були синтезовані з розплавлених зразків які були загартовані в холодному 25% розчині NaCl. Досліджено їх спектри оптичного поглинання в інтервалі 1,2 - 2,9 еВ при 80 К. Для стекол легованих Ербієм виникають вузькі смуги поглинання із максимумами 2,53; 2,35; 2,27; 1,88; 1,54; 1,26 еВ. Збільшення вмісту La₂S₃ (30 - 40 мол.%) зумовлює зменшення ширини забороненої зони (E_g = 2,83 - 2,73 еВ) та зростання характеристичного параметру Урбаха (ΔЕ = 151 - 238 меВ), що визначає структурну невпорядкованість стекол.

Ключові слова: склоподібні сплави, оптичне поглинання, правило Урбаха.