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Tl₂S–In₂S₃–GeS₂ Glass System as Novel Promising Materials for Photonics

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It was established that minimal content of the glass-forming component GeS₂ is equal to 30 mol.% (by exploration the set of 23 different alloys with different composition). Correlation between structural properties, thermal parameters (glass transition, crystallization and melting temperatures) and optical absorption spectra along of the titled glasses system has been found. The temperatures, the band gap energy and the characteristic energy of vitreous alloys for the gastric system Tl₂S–In₂S₃–GeS₂ were investigated experimentally.

Keywords: chalcogenide glasses; optical properties; XRD diffraction patterns.

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Introduction

Third-order non-linear optical materials are recently explored very intensively researched in the recent years due to the prospect of their use in ultra-high speed switcher, triggers, light modulators, deflectors et. for optical communications [1-4]. These materials include chalcogenide glasses which have relatively high refractive indices, wide transparency spectral range, and high thermal and chemical resistance [4]. Although generally chalcogenide glasses are isotropic, they may possess promising photoinduced [5], photonics [6] and nonlinear optical [7] properties.

For instance, we have earlier demonstrated in ref. [2] the possibility of using the Tl₂S–Ga₂S₃–GeS₂ glasses as materials for effective photoinduced third harmonic generation described by fourth rank tensors. The glass-formation region in this system determined by quenching the melts from 1300 K is quite significant, the concentration of the glass-forming agent GeS₂ is varied within the 30 - 100 mol.%. Here we present the study of the glass formation for similar glass system Tl₂S–In₂S₃–GeS₂ together with the optical properties of the obtained glasses. Glass formation in the quasi-ternary systems based on the In₂S₃–GeS₂ side was studied in [2].

In particular, the region of the existence of glassy alloys in the GeS₂–Sb₂S₃–In₂S₃ system determined by quenching from 1223 K is relatively narrow and is extended along the GeS₂–Sb₂S₃ side. The maximum In₂S₃ content does not exceed 15 mol.%, and the content of Sb₂S₃ reaches about 90 mol.%. It was established that these glasses can be used in various optoelectronic and photonic devices effectively operating in the mid-IR range. The glass-formation region with potassium chloride as one of the modifiers (GeS₂–In₂S₃–KCl) is located in a space enriched with GeS₂ and extending from the GeS₂ corner down to ~50 mol.% KCl at a fixed molar ratio of In₂S₃/KCl 1:2. The minimum GeS₂ concentration is equal to 35 mol.% [8]. In a similar system involving CsCl. The location of the glass-forming region is similar, with a minimum glass-forming agent concentration equal to about 15 mol.% [9].

I. Setting the problem

Phase equilibria in the In₂S₃–GeS₂ system were studied in ref. [2]. The phase diagram is of eutectic type with additional invariant horizontal lines associated with In₂S₃ phase transitions. The existence of the In₁₆Sn₄S₃₂

compound with the spinel structure (SG *Fd-3m*, $a = 1.07551$ nm) was reported in ref. [10]. The formation of this phase can be explained within a framework of β -In₂S₃ stabilization. Glass formation in the Ge–In–S system was investigated in [9]. The Tl₂S–In₂S₃–GeS₂ glasses were obtained by vacuum synthesis (at 10^{-7} Tor) from the high purity elements, with quenching into ice-cold saline from 1273 K (for glasses with low sulphur content) or 1073 K (for sulphur-rich glasses) up to 15 at.% which could be incorporated into the glasses under such synthesis and cooling conditions. The glasses with higher sulphur content are transparent. Occurrence of yellow colour, darkening to red and black is observed with increasing germanium content. Glass transition temperature T_g in the Ge–In–S system is significantly lower than in the Ge–Ga–S system and is varied from 573 K (In₅Ge_{42.7}S_{52.3}) to 383 K (In₁₀Ge₉S₈₁). T_g increases with germanium content, while the change in indium concentration has only little effect. All the glasses are stable in air.

The glass-formation region for the GeS₂–In₂S₃ system, according to [10], exists in the range of 0 - 30 mol.% In₂S₃. The glass transition temperature in the same work is reported within the temperature region 622–733 K. The crystallization of the glasses containing 80 and 70 mol.% GeS₂ is described by two exothermal effects (the first one is varied between 698–818 K, the second one – 814 - 828 K). The first peak is likely due to the crystallization of β -In₂S₃, the second reflects the crystallization of GeS₂. The melting point (T_m) of the studied glasses is in the range of 1007 - 1090 K. The analysis of the criteria for thermal stability indicates high glass-forming ability and possibility to obtain optical fibers from these glasses. The values of characteristic temperatures decrease with increasing In₂S₃ content which may be related to the formation of the eutectic in the GeS₂–In₂S₃ system. And additionally it may be caused by the change in the order of the formation of the structural units of glass. The structure of the glasses of the Ge–In–S system was studied by Raman and IR spectroscopy [11, 12]. Main structural units of the glasses are [GeS₄] tetrahedra are connected by corners and edges, [InS₄] tetrahedra and [InS₆] octahedra are connected by sulphide bridges. Non-linear optical properties of the several types of the chalcogenide glasses confirm that they can be used as promising materials for optical commutation devices.

The Tl₂S–GeS₂ system features the Tl₄GeS₄, Tl₂GeS₃ and Tl₂Ge₂S₅ compounds which melt congruently at 677 K, 763 K and 868 K. The last two compounds may be obtained both in crystalline and glassy state. Glass formation in the Tl–Ge–S system using quenching in air allows over 30 at.% Thallium in the composition of the glassy alloys. It was established that their thermal stability is significantly reduced with increasing Tl content. The value of the glass transition temperature decreases from 593 to 463 K. The results of DTA of the glasses of the Tl₂S–GeS₂ system shown that the addition of thallium significantly diminishes the glass transition temperature from 786 K in the case of pure GeS₂ to 538 K for the composition (GeS₂)₉₀Tl₁₀. According to the

recent studies [2] during quenching from 1300 K, the maximum content of Tl₂S in the glassy alloys in the Tl₂S–GeS₂ system is 66.7 mol.%.

Thallium increases the ability of the glass formation with the chalcogenides of Group IV-a elements due to the fact that effectively interacts not only with chalcogen but also with both components of the binary chalcogenide glass. In this case, the glass contains complex structural units which possess all three components. The composition and geometry of the structural units formed in the glass are close to those of individual ternary compounds. The covalent component of the chemical bond in such ternary compounds is higher than for the binary metal chalcogenides.

In the present article the glass formation studies in the quasi-ternary system Tl₂S–In₂S₃–GeS₂ are presented for the first time. It is known that the TlInS₂–GeS₂ section of this system features quaternary compounds TlInGe₃S₈ [13], TlInGeS₄ [14], and TlInGe₂S₆ [15]. Therefore, based on the previous research, the goal of our work is to combine the best features of components in one system, when chemical composition allows a modification of properties. We performed absorbance measurements and determined the band gap of the titled glasses. Finally the studies of the photoinduced birefringence have been done to investigate the composition effect. More over, knowledge of the phase diagram allows further for modification (for example by annealing) of the obtained glasses towards to broadening optical features by activate their nonlinear optical properties for the generation of SHG [5] as it was just shown for the system GeS₂–Ga₂S₃–Li₂S [16]. It should be emphasized that such a procedure allows obtaining optical functionality similar to crystals, with much simpler technology and free choice of the shape.

II. Experimental

Glass-formation region for the Tl₂S–In₂S₃–GeS₂ system was determined by exploration of the synthesized 23 alloys with different composition. The all batches contained high-purity elements (at least 99.99 wt.%; Aldrich Germany). The precisely calculated amounts of the starting substances were placed into quartz crucible that were evacuated to a precise equal to about $1.33 \cdot 10^{-2}$ Pa and soldered. The ingredients were preliminarily synthesized by heating in the oxygen-gas burner flame for the bonding of elementary sulphur under visual control of the reaction process. Then the ampoules were placed in shaft-type furnaces and heated at the rate of 20 - 30 K/h up to 1300 K. Upper parts of the ampoules have been insulated by asbestos rope to avoid splashing the melts during quenching and to minimize the losses for the condensation of the vapor phase on the ampoule walls. The ampoules with the melts were kept at the maximum temperature for 6 hrs and then quenched into cold water.

Characteristic temperatures for the glasses were determined by differential thermal analysis (DSC) at a Paulik–Paulik–Erdey derivatograph with a Pt/Pt–Rh

thermocouple. The heating rate was equal to about 10 K/min, with cooling in inertial mode.

Optical transparent measurements were performed at ambient temperature using MDR-208 monochromator with the wavelength determined error $\lambda = \pm 0.1$ nm. The

samples were cut as parallel-plane plates of ~ 0.1 mm thickness with high optical quality surfaces obtained by mechanical polishing.

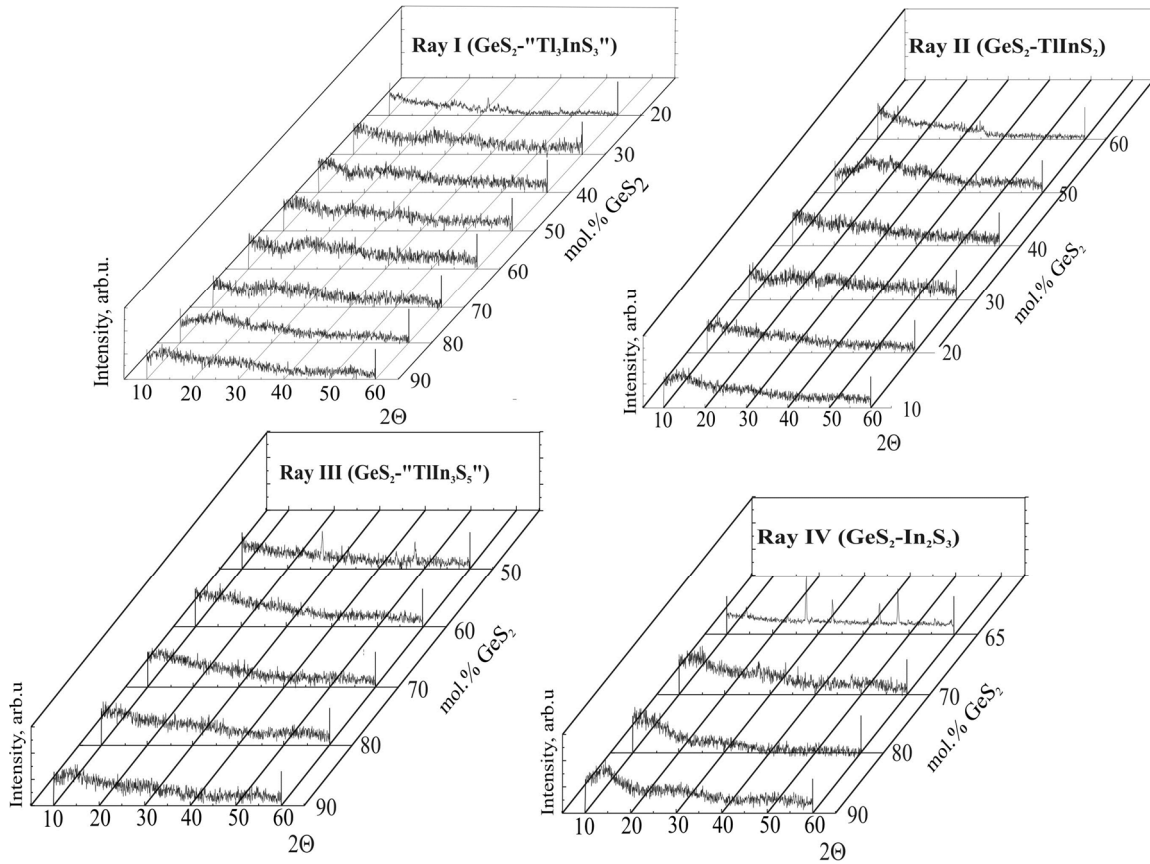


Fig. 1. XRD diffraction patterns of the $\text{Tl}_2\text{S}-\text{In}_2\text{S}_3-\text{GeS}_2$ glasses along the rays: I – $\text{GeS}_2-\text{Tl}_3\text{InS}_3$, II – $\text{GeS}_2-\text{TlInS}_2$, III – $\text{GeS}_2-\text{TlIn}_3\text{S}_5$, IV – $\text{GeS}_2-\text{In}_2\text{S}_3$ (compositions are given in the coordinates of the quasi-ternary system).

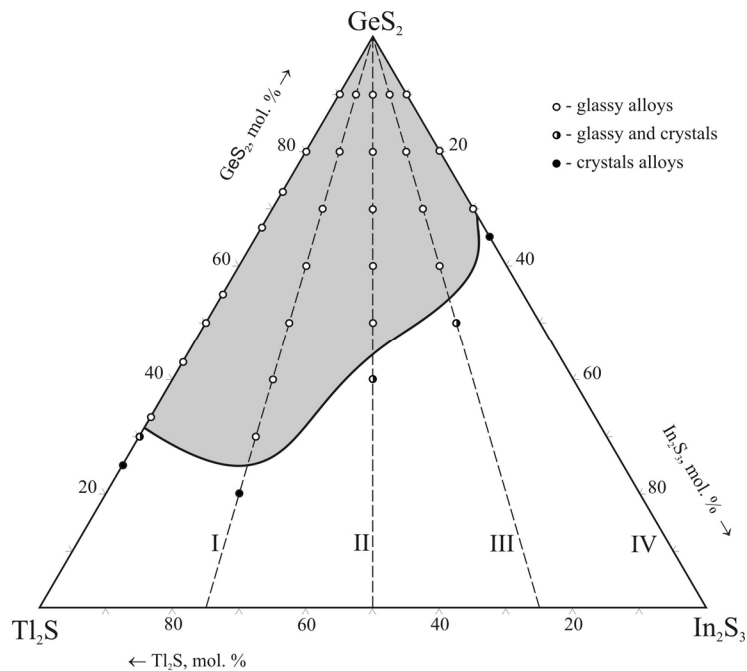


Fig. 2. Glass-formation region (grey area) for the quasi-ternary system $\text{Tl}_2\text{S}-\text{In}_2\text{S}_3-\text{GeS}_2$.

III. Results and discussion

The structure of all of 23 samples possess different composition, were examined by XRD method, which allowed determining glass formation region. The diffraction patterns are shown at Fig. 1 and follow them the glass-formation region (grey area) in the quasi-ternary system Tl₂S–In₂S₃–GeS₂ was determined, see Fig. 2.

The majority of the prepared samples in the Tl₂S–In₂S₃–GeS₂ system are located on five paths that are shown along with the glass-formation region in Fig. 2. All obtained glasses are transparent in the visible

spectrum.

Under the selected quenching conditions, the glassy alloys at the boundary sides contain up to 66.7 mol.% Tl₂S [8] or 30 mol.% In₂S₃. The compositions of the alloys inside the concentration triangle were located on three paths. The range of the glassy alloys along path *I* (GeS₂–‘Tl₃InS₃’ (75 mol.% Tl₂S – 25 mol.% In₂S₃)) is 30 - 100 mol.% GeS₂, along path *II* (GeS₂–TlInS₂ (50 mol.% Tl₂S – 50 mol.% In₂S₃)) is 50 - 100 mol.% GeS₂, and along path *III* (GeS₂–‘TlIn₃S₅’ (25 mol.% Tl₂S – 75 mol.% In₂S₃)) is 60 - 100 mol.% GeS₂.

Typical temperatures of the glasses (glass formation temperature, crystallization and melting point) that were

Table 1

Characteristic temperatures, band gap energy and characteristic energy of the glassy alloys for the quasi-ternary system Tl₂S–In₂S₃–GeS₂.

№	Alloy composition, mol.%			T _g , K	T _c , K	T _m , K	T _{gr}	E _g , eV	Δ ₀ , eV
	Tl ₂ S	In ₂ S ₃	GeS ₂						
Trace I									
1	7.5	2.5	90	476	675. 707	–	–	2.17	0.06
2	15	5	80	511	669	777, 833	0.66	2.18	0.065
3	22.5	7.5	70	483	690. 719	795	0.61	2.10	0.055
4	30	10	60	498	–	835	0.60	2.10	0.06
5	45	15	40	484	580	728	0.66	–	–
Trace II									
6	5	5	90	655	796	951	0.69	2.23	0.055
7	10	10	80	633	757	933	0.68	2.23	0.06
8	15	15	70	626	731	922	0.68	–	–
9	20	20	60	612	739. 755	912	0.67	2.28	0.05
10	25	25	50	580	714	840	0.69	–	–
Trace III									
11	2.5	7.5	90	642	783	1050, 1095	0.61	2.25	0.05
12	5	15	80	638	780	914, 1016	0.69	2.25	0.05
13	7.5	22.5	70	568	733	908	0.63	2.26	0.05
14	10	30	60	590	612. 723	859	0.68	–	–
Trace IV									
15	–	10	90	648	768	1035	0.63	2.12	0.06
16	–	20	80	601	710. 815	997, 1029	0.60	2.17	0.065
17	–	30	70	590	651. 811	1018	0.58	2.22	0.07

Table 2

Chosen set of glass samples for optical investigations of absorption coefficient to evaluate band gap

Sample Nr	Composition
1	7.5% Tl ₂ S- 90% GeS ₂ – 2.5%In ₂ S ₃
2	5.0% Tl ₂ S- 90% GeS ₂ – 5.0%In ₂ S ₃
3	2.5% Tl ₂ S- 90% GeS ₂ – 7.5%In ₂ S ₃
4	15% Tl ₂ S- 80% GeS ₂ – 5.0%In ₂ S ₃
5	10% Tl ₂ S- 80% GeS ₂ – 10%In ₂ S ₃
6	5.0% Tl ₂ S- 80% GeS ₂ – 15%In ₂ S ₃

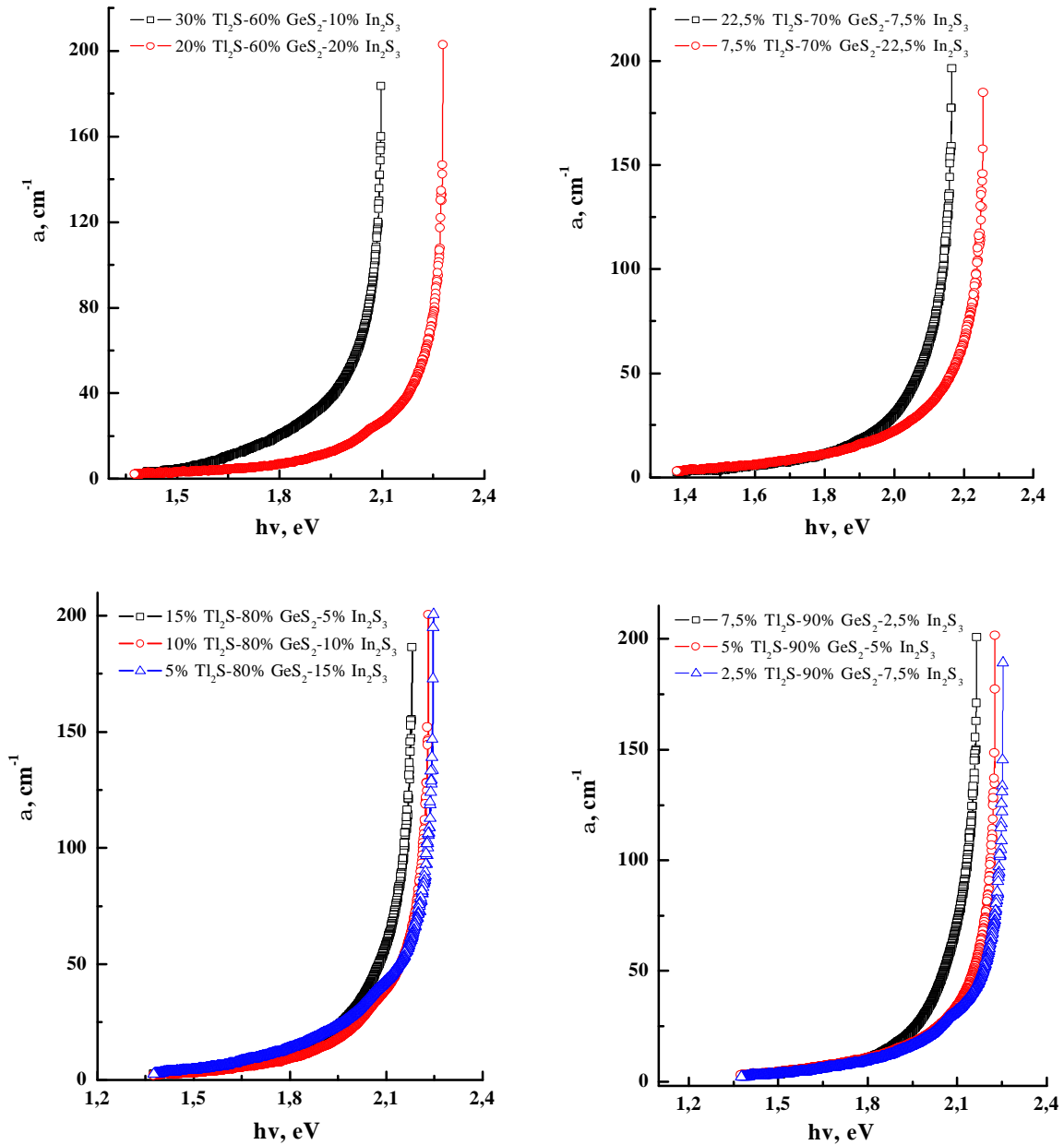


Fig. 3. Dependence of the absorption coefficient on the incident light energy for the glassy alloys $Tl_2S-In_2S_3-GeS_2$ at 300 K.

determined from DTA results are presented in Table 1.

The glass formation temperature decreases with the increasing GeS_2 content (except for the glasses on trace I) and are ranged within 476 - 655 K. The glassy alloys 1, 3, 9, 14, 16, 17 feature two exothermal crystallization effects. The melting points of the studied glasses lay in the region of 728–1095 K. The DTA results of the alloys along ray IV ($GeS_2-In_2S_3$) agree with the data in [2]. Qualitative analysis of the thermal stability of the glasses was estimated by the calculated reduced glass formation temperature that correlates well the glass formation temperature T_g and the melting point T_m of the glassy alloys ($T_{gr} = T_g/T_m$).

The values of the reduced glass formation temperature listed in Table 1 indicate high affinity of the alloys to glass formation.

IV. Optical Properties

Optical investigations of absorption coefficient to evaluate band gap were performed for chosen set of glass samples (numbers used for optical measurements) Table 2:

Typical spectral dependences of the absorption coefficient of the glassy alloys of the $Tl_2S-In_2S_3-GeS_2$ system with various ratios of Tl_2S , GeS_2 and In_2S_3 at ambient temperature are presented in Figs. 3, 4.

Such drastic enhancement of α for the light with $h\nu > 1.8$ eV confirms a domination of the absorption caused by inter-band transitions with respect to scattering.

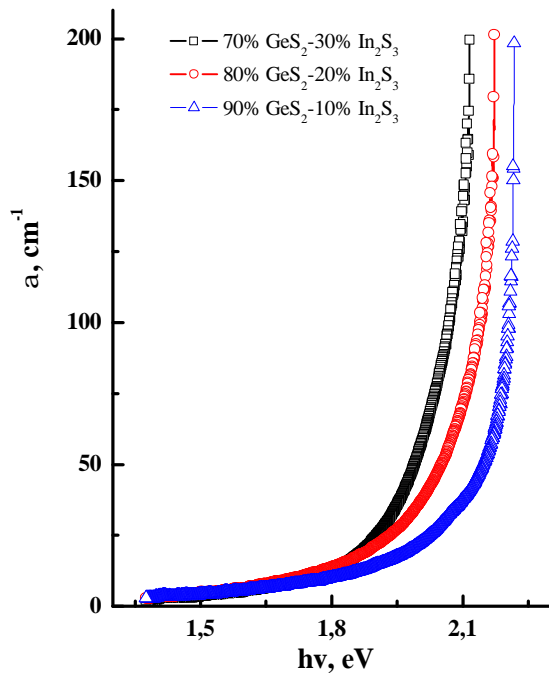


Fig. 4. Spectral dependence of the absorption coefficient near the fundamental energy gap for the glasses of the In₂S₃–GeS₂ system at 300 K.

The approximation of the $\alpha(h\nu)$ plots in the region of $h\nu > 2.1$ eV to linear dependences witnesses the adherence to Urbach's rule which is typical for disordered semiconductors [5]:

$$\alpha(h\nu) \sim \exp\left(-\frac{h(\nu_0 - \nu)}{\Delta_0}\right), \quad (1)$$

where Δ_0 is the characteristic energy with values of $\sim 0.05 - 0.07$ eV and estimates of E_g at the level of $\alpha = 200 \text{ cm}^{-1}$ what is listed in Table 1.

Parameter of Δ_0 is a characteristic energy directly

related to local disorder for determination of the respective absorption edge or to the degree of the crystalline disorder. Thus, according to Urbach's rule, high Δ_0 values mean that the glassy alloys of the Tl₂S–In₂S₃–GeS₂ system present intrinsic defective semiconductors, with electronic structure analogous to disordered systems.

The band gap energy of the glasses of the Tl₂S–In₂S₃–GeS₂ system (Table 1) is varied with the change of the ratio of the modifiers (Tl₂S, In₂S₃).

Conclusions

Glass-formation region in the quasi-ternary system Tl₂S–In₂S₃–GeS₂ was investigated by X-ray phase analysis. The minimum concentration of the glass-forming component GeS₂ is 30 mol.%. Characteristic temperatures of the glasses of the system were determined, and the reduced glass-formation temperature was calculated. Obtained results show high affinity of the alloys to glass formation. Optical absorption of obtained glasses was investigated. It was determined that optical bandgap energy varies from 2.10 to 2.28 eV.

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Скросистема $Tl_2S - In_2S_3 - GeS_2$ як новітні перспективні матеріали для фотоніки

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Встановлено, що мінімальний вміст складоутворюючого компонента GeS_2 дорівнює 30 мол.% (досліджували набір 23 різних сплавів з різним складом). Встановлено взаємозв'язок між структурними властивостями, термічними параметрами (температура скла, температури кристалізації та плавлення) та оптичними спектрами поглинання. Експериментально досліджені температури, енергія розриву смуг та характерна енергія склоподібних сплавів для системи $Tl_2S-In_2S_3-GeS_2$.

Ключові слова: халькогенідні окуляри; оптичні властивості; дифрактограми XRD.