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Phase equilibria, glass formation and optical properties of glasses in the Ag_2S–$B^{IV}S_2$–$C^{V}{}_2S_3$ systems (B^{IV}–Ge, Sn; C^{V}–As, Sb)

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Phase equilibria of the quasi-ternary systems Ag_2S–$B^{IV}S_2$–$C^{V}{}_2S_3$ (B^{IV}– Ge, Sn; C^{V}–As, Sb) were investigated using phase analysis based on XRD. Isothermal sections at 500 Kand glass formation regions in the respective systems were determined. The quasi-binary sections GeS_2–As_2S_3 and GeS_2–Sb_2S_3 of the studied systems exhibit glass formation in the entire concentration range. Large glass formation regions were also found at the Ag_2S–GeS_2 (0–55 mol.% Ag_2S) and Ag_2S–As_2S_3 (0–75 mol.% Ag_2S) sections. As the starting compounds As_2S_3, GeS_2 and Sb_2S_3 are in the glassy state, they act as the glass-forming agents in the quasi-ternary systems. Glass formation regions in the tin-containing systems are significantly smaller than the analogous germanium-containing ones which is due to metal nature resulting in the change from tetrahedral to octahedral surrounding. Glassy materials may possess interesting optical properties, therefore optical absorption spectra at 300 K were measured. Bandgap energy E_g of the glasses of the quasi-binary system GeS_2–As_2S_3 was estimated from the data on the spectral distribution of the absorption coefficient at the fundamental absorption edge. It was found that the addition of As_2S_3 to germanium (IV) sulfide results in shifting the absorption edge to higher energies.

Keywords: quasi-ternary system, phase equilibria, glass formation, optical bandgap energy

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Introduction

Chalcogenide semiconductor glasses obtained by rapid quenching of the melts are widely used in modern photonics and optoelectronics, for instance, in numerous civilian, medical and military applications, including fiber IR sources, high-power laser technology, optical amplifiers, switches, scanning microscopy, chemical sensors, information recording etc. The uniqueness of such glasses is explained by excellent optical properties [1,2] and high sensitivity to external factors (light radiation, temperature, ionizing radiation, electromagnetic fields, etc.) [3-5], which in combination with the relatively low cost of the technological process creates attractive conditions for developers of various devices.

Investigation of phase equilibria in the Ag_2Se–$Ge(Sn)Se_2$–$As(Sb)_2Se_3$ systems is reported in [6,7].The quasi-ternary system Ag_2Se–$SnSe_2$–As_2Se_3 features at 520 K the existence of a quaternary compound $Ag_2SnAs_6Se_{12}$ (S.G. R–3m, a = 0.38118 nm, c = 3.9724 nm). Based on the above information, the objective of the work is the study of the phase equilibria in similar sulfur-containing systems Ag_2S–$B^{IV}S_2$–$C^{V}{}_2S_3$ (B^{IV}–Ge, Sn; C^{V}–As, Sb) at 500 K, determination of the glass formation regions and investigation of the optical absorption spectra of glasses.

I. Experimental

1.1. Characteristics of starting compounds and synthesis methods

Phase equilibria in the quasi-ternary systems Ag_2S–$B^{IV}S_2$–$C^{V}{}_2S_3$, where B^{IV}–Ge, Sn; C^{V}–As, Sb, were studied on 140 samples. The starting components for the synthesis of alloys of the studied systems were pre-synthesized binary compound As_2S_3 and elemental silver (99.99 wt.%), germanium (99.9999 wt.%), tin (99.999 wt.%), antimony (99.998 wt.%) and sulfur (99.997 wt.%) used in stoichiometric quantities. The starting materials were weighed with an accuracy of $5{\cdot}10^{-5}$ g at VLA-200 analytical scales. The prepared batches of pure components were placed in quartz ampoules (60-80 mm long, 8-10 mm in diameter) that were evacuated to $1.33{\cdot}10^{-2}$ Pa and sealed. To avoid sublimation of volatile components formed during the synthesis reaction, the upper end of the ampoule was heated to 70 K above the temperature of the synthesis zone.

The first temperature stops for 24 h at 670 K ensured the interaction of free sulfur with the formation of the respective sulfides, the next stop for 24 hat 700 K ensured complete binding of sulfur. The final interaction of the initial components was achieved by slow heating (~20 K/h) to 1170 K with exposure at this temperature for 48 h. Cooling to the temperature of homogenizing annealing at 500 K was held at the rate of 10-20 K/h. Annealing was performed for 500 h, after which the ampoules were quenched into 25% sodium chloride solution. Obtained alloys were dark gray with a metallic luster.

The synthesis of the glassy samples was performed similarly to that of polycrystalline alloys. The maximum synthesis temperature was 1170 K. The samples were kept at this temperature for 10 h, after which the ampoules with alloys were quenched into 25% sodium chloride solution with crushed ice. To prevent splashing of the melt during quenching, as well as to reduce losses on the condensation of the vapor phase on the walls of the ampoules, they were thermostated with asbestos cord.

1.2. X-ray phase analysis

X-ray phase analysis of the synthesized samples was performed based on the results recorded at a DRON 4-13 diffractometer (CuKα radiation, 2θrange 10–90°, scan step 0.05°, 5 s exposure in each point). Calculations and indexing of powder diffraction patterns were performed using Full-Prof software [8]. The diffraction patterns of glassy samples showed a broad diffuse band typical of amorphous substances, an "amorphous halo" which indicates the absence of long-range order in the structure of the alloy [9].

1.3. Investigation of optical properties

Measurements of absorption spectra were performed at room temperature 297 K at a standard factory set-up which consisted of an MDR-208 monochromator and silicon-based photodetectors. Parallel-plane samples of ~0.1 mm thickness with optical quality polished surfaces were prepared. The bandgap energy was estimated from the spectral distribution of the absorption coefficient of the compounds. The absorption coefficient was calculated from the transmission spectra in the region of the intrinsic absorption edge by [10].

II. 2. Results and discussion

2.1. Isothermal sections of the quasi-ternary systems Ag_2S–$Ge(Sn)S_2$–$As(Sb)_2S_3$ at 500 K

Experimental studies of the Ag_2S–$B^{IV}S_2$–$C^{V}{}_2S_3$ systems (B^{IV}–Ge, Sn; C^{V}–As, Sb) found no new ternary and quaternary phases, and the extent of solid solution ranges of binary and ternary compounds at this temperature is negligible. Preliminary analysis of the samples showed that all samples at 500 K are in the solid state as the section lies below the ternary eutectic.

Using literature data on Ag_2S–$B^{IV}S_2$, $B^{IV}S_2$–$C^{V}{}_2S_3$, Ag_2S–$C^{V}{}_2S_3$ systems (where B^{IV}–Ge, Sn; C^{V}–As, Sb) and own studies of 140 samples by X-ray phase analysis method, isothermal sections of the quasi-ternary systems Ag_2S–$Ge(Sn)S_2$–As_2S_3 and Ag_2S–$Ge(Sn)S_2$–Sb_2S_3 were plotted (Fig. 1).The Ag_2S–$Ge(Sn)S_2$ sections feature the crystallization of compounds with different composition, $Ag_{10}Ge_3S_{11}$, Ag_2GeS_3, Ag_2SnS_3, $Ag_2Sn_2S_5$, which results in the change of thermodynamic equilibria in the quasi-ternary systems.

2.2. Glass formation in the Ag_2S–$Ge(Sn)S_2$–$As(Sb)_2S_3$ systems

Investigation of the glass formation regions in the quasi-ternary systems Ag_2S–$B^{IV}S_2$–$C^{V}{}_2S_3$ (B^{IV}–Ge, Sn; C^{V}–As, Sb) was performed under the above conditions (Fig. 2).

It was determined that all samples at the GeS_2–$As(Sb)_2S_3$ sections are glassy. The samples in the quasi-binary systems Ag_2S–As_2S_3 and Ag_2S–GeS_2 were also glassy up to 75 mol.% and 55 mol.% Ag_2S, respectively. It was found that glasses are not formed in the Ag_2S–Sb_2S_3 system under the selected quenching conditions. Obtained results correlate well with the literature data [11].

Two glass formation regions were observed in the Ag_2S–SnS_2–Sb_2S_3 system. One extends from 15 to 25 mol.% Sb_2S_3 and includes up to 8 mol.% Ag_2S, the other has the content of 65–85 mol.% Sb_2S_3, with the maximum Ag_2S content that can be introduced into glass of 3 mol.%. The glass formation region at the SnS_2–As_2S_3 section of the quasi-ternary system Ag_2S–SnS_2–As_2S_3 extends from 78 to 100 mol.%As_2S_3.

The extent of the glass formation regions in the tin-containing systems is smaller compared to similar germanium-containing systems which is related to the increase of the metallic component of the chemical bonding from germanium disulfide to tin disulfide.

2.3. Optical properties

Spectral dependences of the light absorption coefficient of the glasses of the GeS_2–As_2S_3 system on the photon energy in the hν region 1.6–2.4 eV are plotted in Fig. 3. The optical absorption coefficient was estimated using thevalue of the reflection coefficient R at room temperature. The variation of R with the temperature change from 100 to 300 K was considered negligible, taking into account the data of [12].

The bandgap energy Eg was estimated from the spectral distribution of the absorption coefficient in the absorption edge region by the energy of light quanta for which α=300 cm^{-1}. The dependence of Eg on the composition of the glassy alloys is shown in Table1.

The value of the bandgap energy Eg for the studied glasses does not change significantly in the range of 2.27–2.32 eV. In our opinion, this is due to the fact that both binary compounds GeS_2 and As_2S_3 are glass-forming reagents. Additionally, Ge^{4+} and As^{3+} have close values of ionic radii of 0.53 and 0.47 Å, respectively. A consequence of the site disorder of the position of atoms in non-crystalline materials is the formation of the tails of the density of states at the edge of permitted energy bands which results in the exponential dependence of the absorption coefficient. Such exponential dependence α(hν) is observed from the high-energy part of the spectrum indicating the adherence to Urbach's rule which

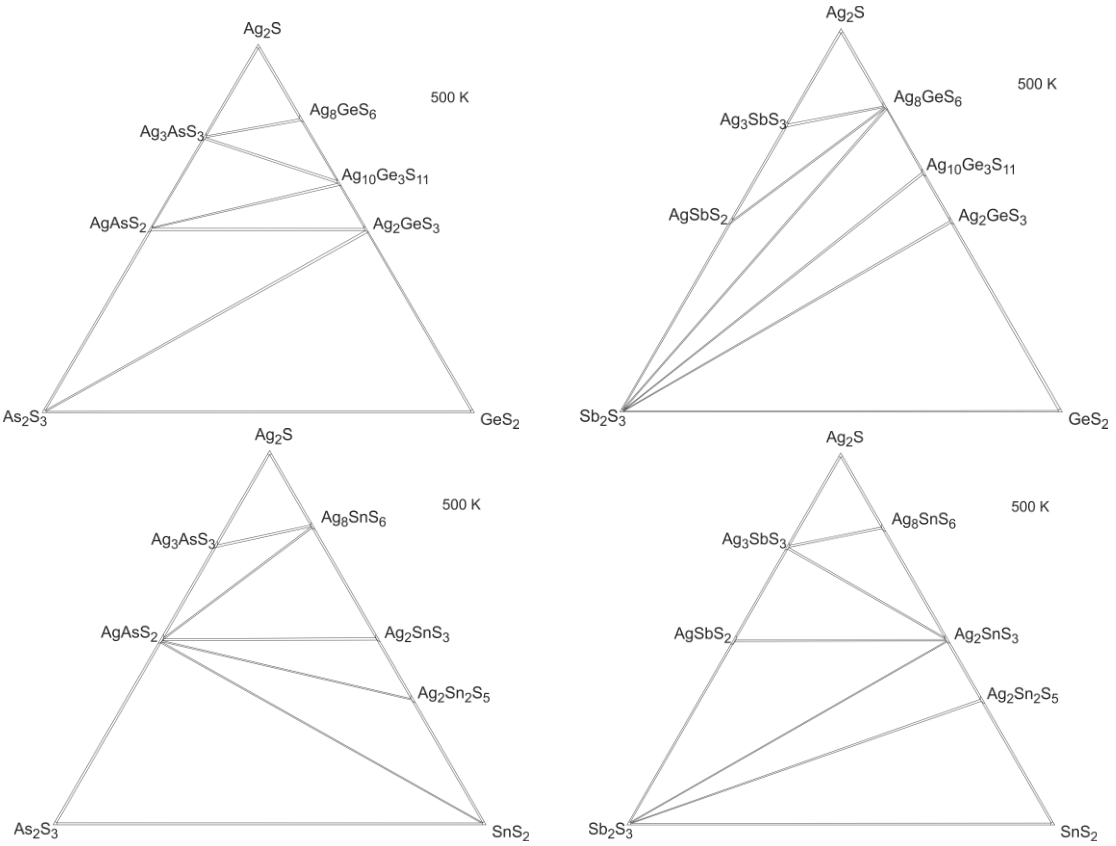

Fig. 1. Phase equilibria in the $Ag_2S–Ge(Sn)S_2–As(Sb)_2S_3$ systems at 500 K.

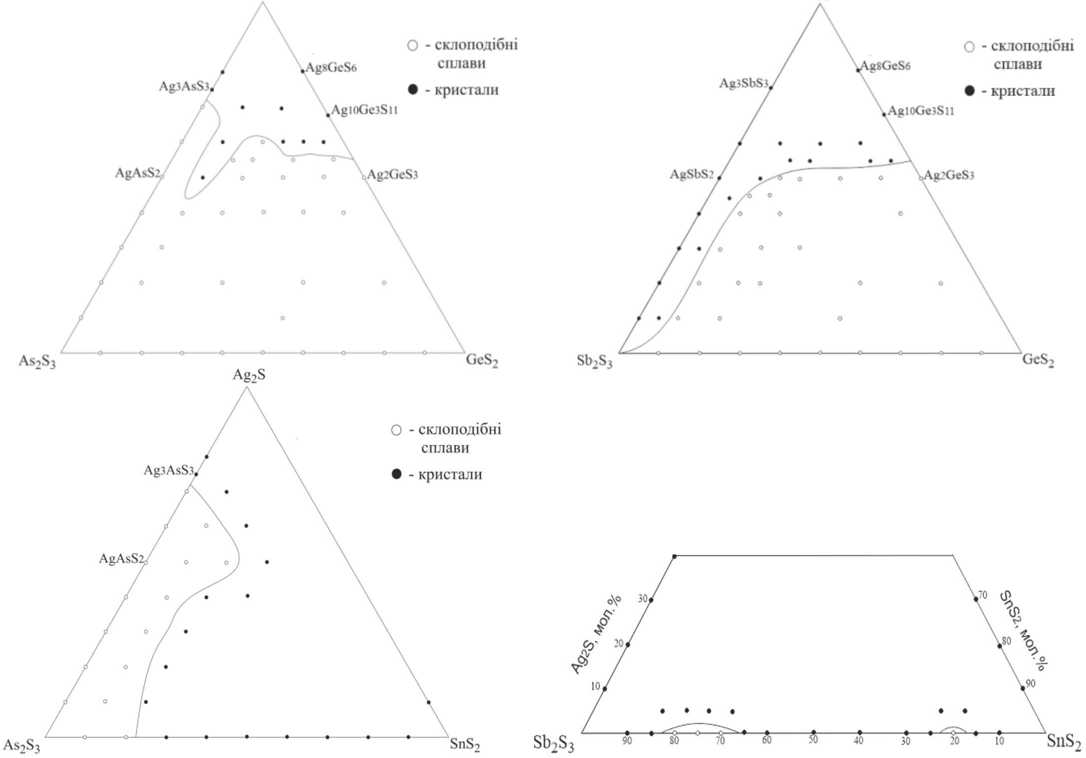

Fig. 2. Glass formation in theAg$_2$S–Ge(Sn)S$_2$–As(Sb)$_2$S$_3$ systems.

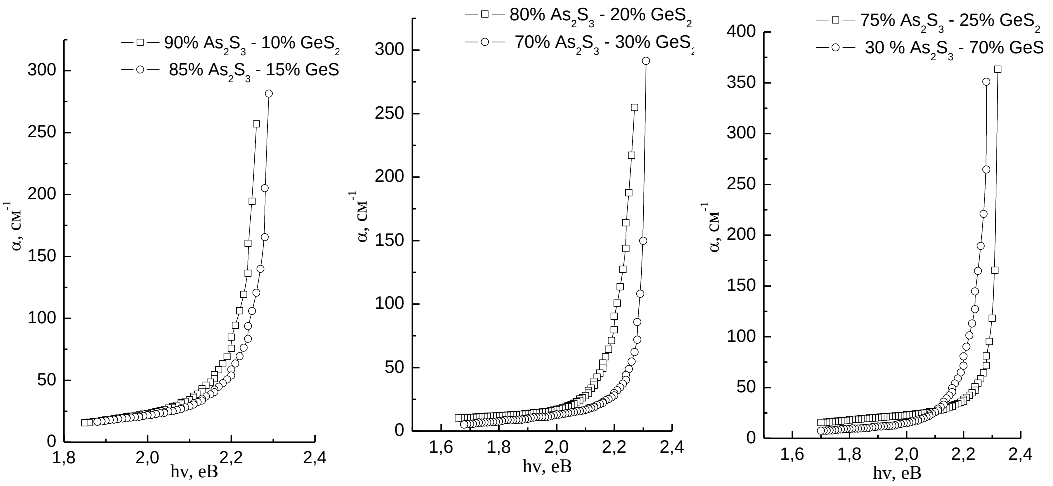

Fig. 3. Edge of the intrinsic absorption band for the glasses of the GeS_2–As_2S_3 system at 300 K.

describes the edge of the fundamental absorption band in disordered systems. The characteristic energy Δ that determines the degree of tailing of the absorption edge was calculated from the energy dependence of the absorption coefficient and the Urbach's rule. The parameter Δ for the studied samples is 0.10–0.20 eV which is consistent with the data of [13, 14].

Table 1.

Optical bandgap energy of the glasses of the GeS_2–As_2S_3 system at 300 K.

Sample composition, mol.%		E_g, eV	Δ, eV
GeS_2	As_2S_3		
10	90	2.27	0. 17
15	85	2.30	0.18
20	80	2.28	0.21
25	75	2.32	0.17
30	70	2.31	0.15
70	30	2.29	0.15

Conclusions

Phase equilibria in the Ag_2S–$B^{IV}S_2$–$C^{V}{}_2S_3$ systems (where B^{IV}–Ge, Sn; C^{V}–As, Sb) at 500 K were determined and presented in the form of isothermal sections of phase diagrams of systems at this temperature. The glass formation regions in the quasi-ternary systems were investigated by X-ray diffraction method. It should be noted that all samples were glassy at the GeS_2–$As(Sb)_2S_3$ sections of the Ag_2S–GeS_2–$As(Sb)_2S_3$ systems. Optical absorption spectra of the glassy alloys were measured. It was determined that the optical band gap varies from 2.27 to 2.32 eV which indicates good prospects of these materials as glassy semiconductors.

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Фазові рівноваги, склоутворення та оптичні властивості стекол у системах Ag_2S–$B^{IV}S_2$–$C^{V}{}_2S_3$ (B^{IV}–Ge, Sn; C^{V}–As, Sb)

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У цій роботі з метою встановлення фазового стану відповідних систем було проведено фазовий аналіз, використовуючи метод Х-променевої дифракції, і на основі отриманих результатів побудовано ізотермічні перерізи та визначено області скло утворення в квазіпотрійних системах Ag_2S–$B^{IV}S_2$–$C^{V}{}_2S_3$ (B^{IV}–Ge, Sn; C^{V}–As, Sb) при 500 К. Важливо зазначити, що по квазібінарних перерізах GeS_2–As_2S_3 та GeS_2–Sb_2S_3 досліджених систем спостерігається склоутворення в повному концентраційному інтервалі. Також існують значні області склоутворення по перерізах Ag_2S–GeS_2 (в межах 0–70 мол.% Ag_2S) та Ag_2S–As_2S_3 (в межах 0–75 мол.% Ag_2S). Оскільки вихідні фази As_2S_3, GeS_2 та Sb_2S_3 перебувають у склоподібному стані, вони виступають склоутворювачами. В станумовмісних системах області склоутворення значно менші порівняно з аналогічними германійвмісними, що пов'язано з природою металу, як наслідок, зміна тетраедричного оточення на октаедричне. Склоподібні матеріали можуть володіти цікавими оптичними властивостями. Тому нами проведено вимірювання спектрів оптичного поглинання за температури 300 К. За даними спектрального розподілу коефіцієнта поглинання в області краю поглинання оцінено ширину енергетичної щілини E_g стекол квазіподвійної системи GeS_2–As_2S_3. Встановлено, що при введенні до германій (IV) сульфіду сполуки As_2S_3 спостерігається зміщення краю поглинання в високоенергетичну область спектра.

Ключові слова: квазіпотрійна система, фазові рівноваги, склоутворення, оптична ширина енергетичної щілини