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Glass formation and optical properties of the glasses in the Ag_2S–HgS–GeS_2 system

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Using the melt-quenching method, the glass-formation region was investigated in the quasi-ternary system Ag_2S–HgS–GeS_2. The minimum content of the glass-forming element GeS_2 is 45 mol.%. Characteristic temperatures were determined for the glassy alloys and optical absorption spectra of the glasses were recorded. It was established that the optical bandgap energy varies from 1.7 to 2.3 eV.

Chalcogenide glasses / Quasi-ternary systems / Absorption spectra

Introduction

Complex chalcogenide semiconductor glasses (CSGs) are widely used in many industries [1]. They have found application as materials for lenses, prisms, filters for IR optics. CSGs that combine large transparency regions with high values of refraction indexes may be used in acousto-optic devices for the modulation of laser radiation. In microelectronics, they are materials for high-resolution photo-, electrono- and X-ray resistors. CSGs are also used in silver-free photography, video recording, holography etc.

Germanium chalcogenide-based glasses are commonly used due to their transparency in the visible and near-IR spectrum regions [2]. The largest transparency window in the visible part of the spectrum among them belongs to germanium disulfide.

The glasses of the Ag_2S–HgS–GeS_2 system deserve particular interest because of the possible high ionic conductivity due to the mobility of Ag^+ ions. During the investigation of the electric conductivity of binary glasses Ag_2S–GeS_2 the authors of [3-5] showed that the conductivity at room temperature increases from $6.7 \cdot 10^{-5}$ to $1.35 \cdot 10^{-3}$ $\Omega^{-1} \cdot cm^{-1}$ as the Ag_2S content increases from 30 to 55 mol.%, with the ion activation energy gradually decreasing from 0.355 to 0.325 eV. Robinel *et al.* [6] report that such glasses have very high ionic conductivity measurable by the electrochemical semipermeable method. In some ternary Ag- and Ge-containing chalcogenide glasses the conductivity is almost entirely due to ionic transport, with an ionic transport number close to unity. Kawamoto *et al.* [7,8] investigated Ag_2S–GeS–GeS_2 glasses and reported a significant increase in conductivity from $8 \cdot 10^{-15}$ to $3.5 \cdot 10^{-4}$ $\Omega^{-1} \cdot cm^{-1}$ at room temperature and a large decrease of the activation energy from 0.677 to 0.341 eV with increasing Ag_2S content.

The phase equilibria in the Ag_2S–HgS–GeS_2 system were detailed by Parasyuk *et al.* [9]. In the quasi-binary boundary system Ag_2S–GeS_2, the existence of three compounds, Ag_8GeS_6, $Ag_{10}Ge_3S_{11}$ and Ag_2GeS_3, was confirmed at 670 K. The earlier reported $HgGe_2S_5$ compound was not observed in the HgS–GeS_2 system; only a compound at the composition Hg_4GeS_6 was found. Four quaternary compounds were identified in the system. The Ag_2HgGeS_4, $Ag_4HgGe_2S_7$, and $Ag_2Hg_3GeS_6$ compounds form in the Ag_2GeS_3–HgS section at the component ratios 1:1, 2:1, and 1:3, respectively. The fourth quaternary phase has a homogeneity range in the Ag_8GeS_6–Hg_4GeS_6 section of 22–31 mol.% Hg_4GeS_6.

In this work we investigate the glass-formation region in the Ag_2S–HgS–GeS_2 system. Prior studies of the quasi-binary system Ag_2S–GeS_2 [10,11] indicate that the glass-formation region extends from 45 to 100 mol.% GeS_2. The investigation of the quasi-binary

Table 1 Composition of the glassy alloys of the quasi-ternary system Ag_2S–HgS–GeS_2, the quenching temperature (T_q), and characteristic temperatures of the glasses (T_g – glass-transition temperature, T_c – crystallization temperature, T_m – melting point, T_{gr} – reduced glass-formation temperature).

Alloy	Composition, mol.%			T_q, K	T_g, K	T_c, K	T_m, K	T_{gr}
	Ag_2S	HgS	GeS_2					
6	6.7	13.3	80	1200	613	663	1049	0.58
8	15	15	70	1200	607	658	1028	0.59
9	10	20	70	1150	584	736	1011	0.58
10	27	13	60	1200	565	671	969	0.58
11	20	20	60	1200	558	665, 698	961	0.58
12	13	27	60	1150	565	683, 695, 736	875	0.65
13	33.3	16.7	50	1200	558	655	873	0.64
14	25	25	50	1200	545	617, 629, 711	877	0.62
15	16.7	33.3	50	1150	549	595, 623, 718	873	0.63
17	5	25	70	1150	577	745	998	0.58
19	9	41	50	1040	505	631, 711	851	0.59
20	33	7	60	1200	565	677	974	0.58
21	41	9	50	1200	569	658	851	0.69
22	37	18	45	1200	545	605, 625, 665	877	0.62
23	27.5	27.5	45	1200	533	575, 614, 714	887	0.60
26	50	5	45	1200	571	657	956	0.60

system HgS–GeS_2 revealed a large region of existence of glasses from 50 to 100 mol.% GeS_2 [12].

Experimental

Glassy alloys of the quasi-ternary system Ag_2S–HgS–GeS_2 were synthesized by the melt quenching method from high-purity elements (at least 99.99 wt.% of the principal component) and preliminarily synthesized mercury sulfide (99.999 wt.%). 3 g batches were placed in quartz ampoules, which were evacuated to ~10^{-1} Pa, soldered and heated in an oxygen-gas burner flame until complete bonding of the elementary sulfur. Then they were heated in a shaft-type furnace to 1070-1220 K at a rate of 50 K/h, depending on the composition, without intermediate exposure. The alloys were held at the maximum temperature for 4 h and cooled to room temperature over 2 days. Thus-synthesized alloys were repacked into specially designed thin-wall (0.8 mm) quartz ampoules, which were evacuated, and heated to the maximum synthesis temperature at a rate of 40-50 K/h. Since the liquidus of the quasi-ternary system is not known, the selection of the maximum synthesis temperature was based on data on the binary systems HgS–GeS_2 and Ag_2S–GeS_2. The temperature was selected depending on the sample composition in such a way that it would generally exceed the liquidus temperature by 250-300 K (see Table 1). The samples were exposed to this temperature for 10 h to achieve melt homogeneity and then quenched into a saturated aqueous sodium chloride solution. The cooling rate during quenching was estimated at ≥200 K/s. The glasses obtained this way exhibit a characteristic luster. Their color varies from yellow-orange for high GeS_2 content to red and further to black for a GeS_2 content of 60 mol.% or less.

The glasses were studied by X-ray phase analysis (DRON 4-13 diffractometer, CuK_α radiation) to determine the glass-formation region, and by differential thermal analysis (Paulik-Paulik-Erdey derivatograph) to determine the characteristic temperatures of the glassy alloys. Optical properties of the glasses were studied in the 400-1100 nm wavelength range using a CM-2203 spectrofluorimeter.

Results and discussion

The majority of the samples synthesized for the investigation of the glass formation in the Ag_2S–HgS–GeS_2 system are located on five rays (Fig. 1).

The presence of a good glass-forming element (GeS_2), a significant general decrease of the liquidus temperature in the bounding quasi-binary systems [13,14], together with a high degree of covalent bonding in the compounds of the quasi-ternary system, are the major factors favoring the existence of a large glass-formation region in the Ag_2S–HgS–GeS_2 system. The glass-formation region covers the entire concentration triangle for GeS_2 concentrations over 50 mol.%.

Typical powder diffraction patterns of the samples are shown in Fig. 2 for 50 mol.% GeS_2 concentration.

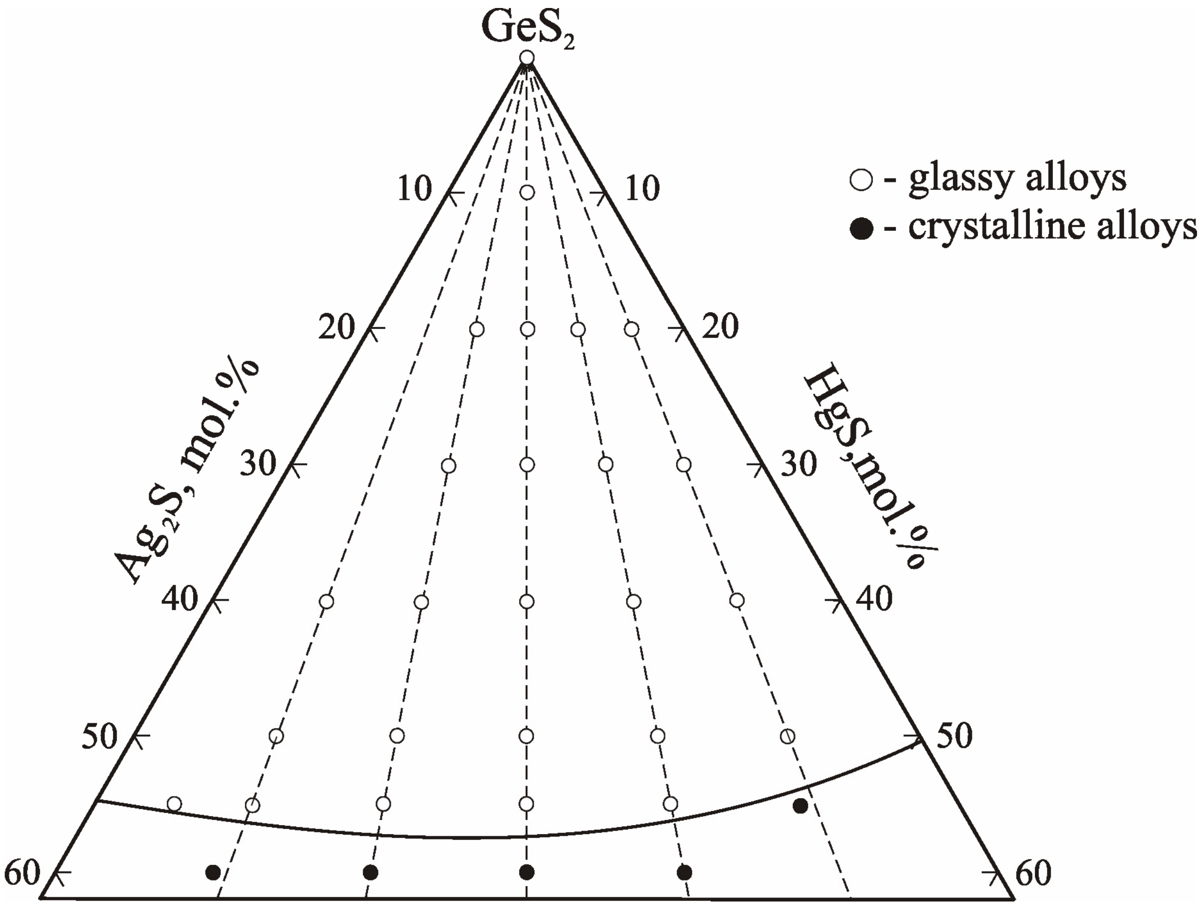

Fig. 1 The glass-formation region in the Ag_2S–HgS–GeS_2 system.

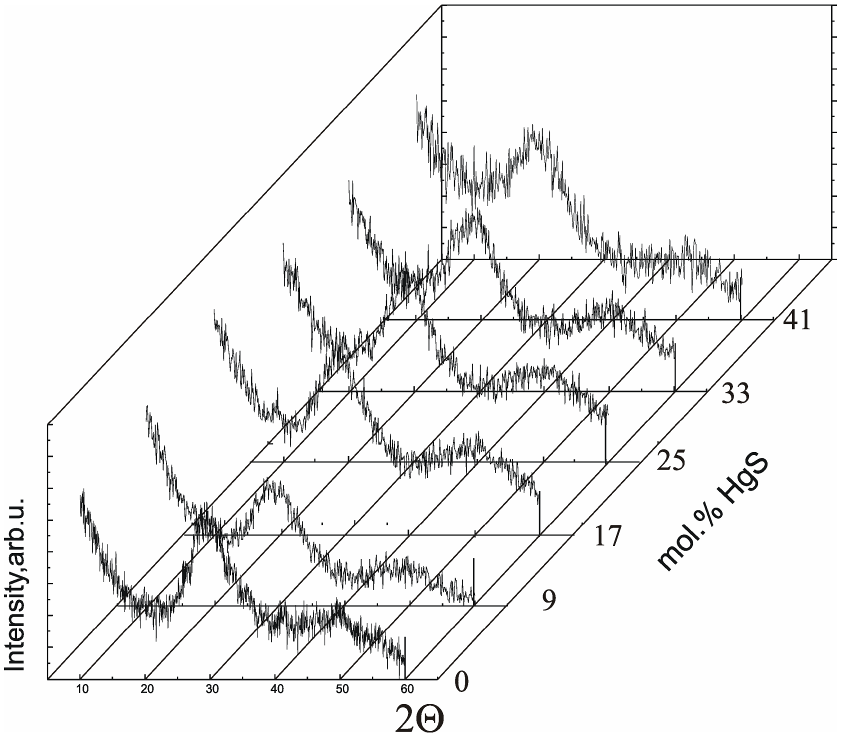

Fig. 2 Diffraction patterns of the samples with 50 mol.% GeS_2 content.

Table 2 Optical bandgap E_g and absorption coefficient k in the transparency region of the glassy samples of the quasi-ternary system Ag_2S–HgS–GeS_2.

Alloy	Composition, mol.%			E_g±0.05, eV	k, cm^{-1}
	Ag_2S	HgS	GeS_2		
9	10	20	70	2.06	44–60
10	27	13	60	1.8	60–80
11	20	20	60	2.07	40–53
12	13	27	60	2.07	66–75
13	33.3	16.7	50	1.72	68–85
14	25	25	50	1.92	58–60
15	16.7	33.3	50	2.07	33–47
17	5	25	70	2.27	25–34
19	9	41	50	2.04	28–40
20	33	7	60	2.28	23–34
21	41	9	50	1.87	82–90
26	50	5	45	1.79	40–45

The glass transition temperature (T_g), the crystallization temperature (T_c) and the melting point (T_m) of the crystallized alloy were determined for the glassy alloys. They are presented in Table 1 along with the reduced glass-formation temperature (T_{gr}) calculated from these data.

The glass transition temperature gradually falls with decreasing GeS_2 content. For a steady GeS_2 concentration, it decreases with increasing HgS content. A number of samples, particularly those near the sides of the triangle and those with high GeS_2 content, are characterized by low values of the reduced glass-formation temperature, near the limits of the "two-thirds rule" (i.e., alloys where $T_{gr}\approx0.66$ form glass state easily, whereas alloys with values of $T_{gr}\approx0.60$ or less have a greater tendency to crystallize, at least partially, even upon quenching). On the contrary, for the alloys inside the concentration triangle the T_{gr} values are higher.

Certain alloys from the field of primary crystallization of GeS_2 (Nos. 6–11, 17) exhibit a large difference between the liquidus and solidus temperatures. The large temperature range of crystallization caused complications in obtaining the alloys in the glassy state. This difficulty is indicated also by low values of the reduced glass-formation temperature ($T_{gr}\approx0.58$-0.59). The challenge was usually overcome by increasing the quenching temperature (by 50 K).

The optical absorption spectra of the glassy samples of the Ag_2S–HgS–GeS_2 system were also studied. The dependence of the absorption coefficient on the photon energy for samples with fixed GeS_2 concentration is shown in Fig. 3; the values of the bandgap energy and the absorption coefficient in the transparency region for glasses of various compositions are listed in Table 2. The bandgap is practically the same for samples Nos. 9, 11, 12, 14, 15, 19 (within the experimental error). This is likely related to the fact that these samples lie in the field of primary crystallization of GeS_2. A similar E_g behavior was observed in the study of the optical properties of glasses of the HgS–GeS_2 system [12].

For the glassy samples with 50 mol.% GeS_2 concentration, the bandgap energy increases gradually from 1.72 to 2.07 eV as the HgS content increases from 16.7 to 33.3 mol.%. But in the regions near the sides of the concentration triangle this dependence is broken. While the bandgap energy of sample No. 19 is within the experiment error of that for No. 15, the bandgap energy of sample No. 21 with low HgS content is definitely higher than that of No. 13, despite an expected decrease. We speculate that sample No. 21 falls in the field of primary crystallization of Ag_2GeS_3 (in the stable phase diagram), and that the boundary of this field lies between samples Nos. 21 and 13. It is likely that there is a difference in the structure of these alloys that may explain the different trend of the bandgap energy.

A certain degree of dependence of the absorption coefficient on the sample composition was also observed: the coefficient decreases with increasing HgS concentration. For the glassy samples with 70 mol.% GeS_2 concentration the absorption coefficient in the transparency region decreases from 45 to 25 cm^{-1} for an increase of the HgS content from 20 to 25 mol.%. At the same time, the bandgap energy increases from 2.06 to 2.27 eV.

The patterns described above for the absorption coefficient and the bandgap energy are not observed at all for the 60 mol.% GeS_2 concentration.

Germanium disulfide is known for its wide transparency region, which decreases upon the addition of various modifiers. However, such a pattern is observed only for samples with low HgS content, i.e. a gradual decrease of the optical density is observed for samples Nos. 20 and 21; 10 and 13; 11 and 14. Samples Nos. 17 and 19 (the closest ray to the side system HgS–GeS_2) exhibit a reversed pattern: the coefficient increases with increasing HgS content,

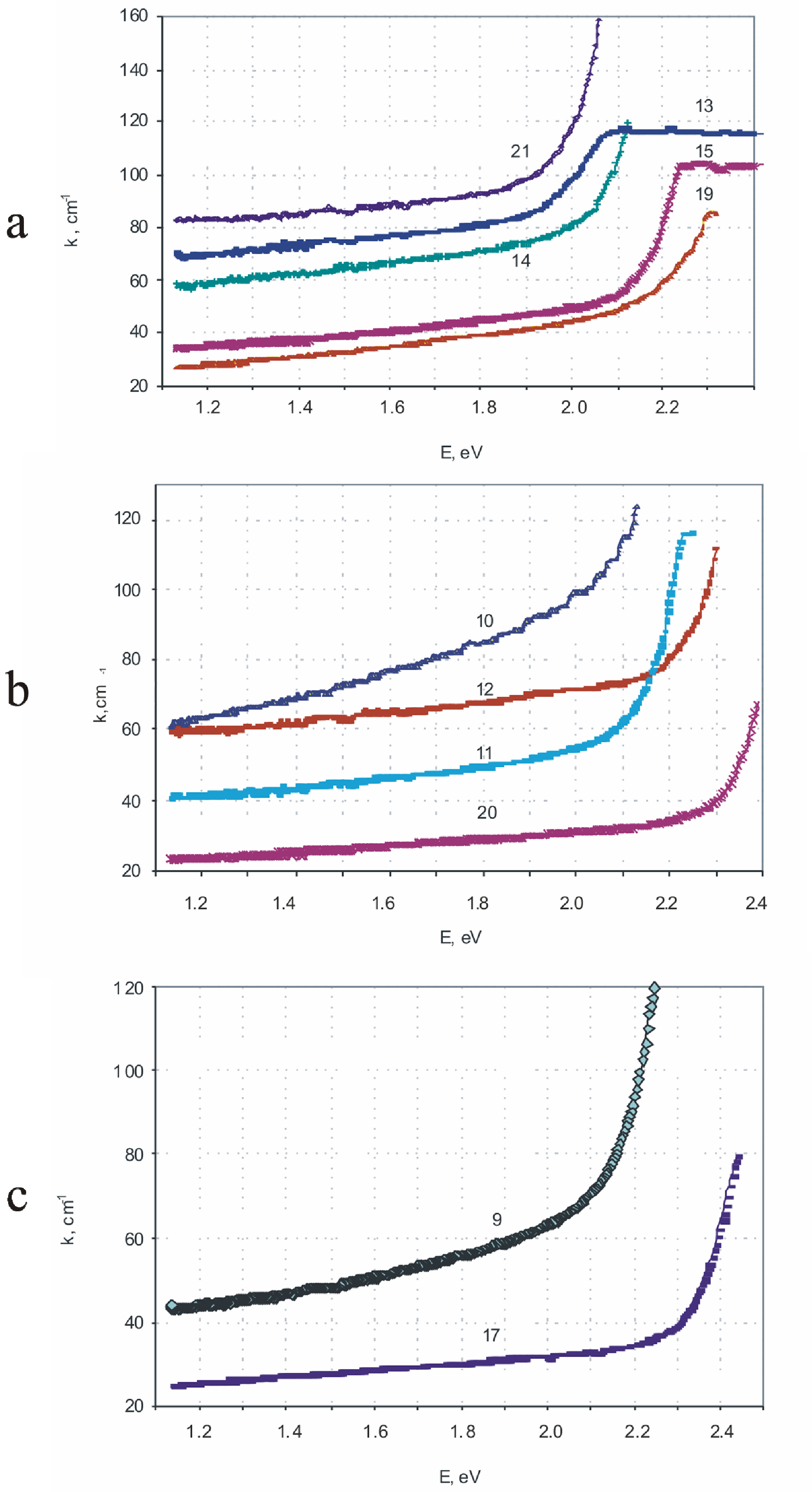

Fig. 3 Absorption spectra of the glassy alloys of the Ag_2S–HgS–GeS_2 system for fixed GeS_2 concentrations: a) 50 mol.%, b) 60 mol.%, c) 70 mol.%.

whereas on the adjacent ray, sample No. 12 (with a medium HgS content) shows the highest optical density. The increase of the optical density along these two rays may be related to the formation of certain groups of defects in the glass-forming matrix.

Conclusions

The existence of a large glass-formation region in the quasi-ternary system Ag_2S–HgS–GeS_2 was established. The characteristic temperatures of the glassy samples were measured, and optical absorption spectra were investigated. The change of the glass-transition temperature T_g of the glasses correlates to the estimated position of the fields of primary crystallization.

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