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## Obtaining and optical properties of the glasses of the GeS<sub>2</sub>–HgS system

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**Abstract.** The glassy alloys of the GeS<sub>2</sub>–HgS system in the range of 0–50 mol. % HgS were obtained by the melt quenching technique. Their Raman spectra were investigated. The dependence of the particularities of the light scattering bands on the chemical composition was analyzed.

**Keywords:** chalcogenide glasses, Raman spectra, structure of glasses.

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### 1. Introduction

Chalcogenide glassy semiconductors (CGS), with their unique properties, belong to an important class of materials that are perspective for optical devices due to high transparency in the visible and near- and mid-IR spectral regions. In particular, CGSs are heavily used for the production of optical elements for IR devices, high-resolution, silver-free photographic media, xerography materials, photosensitive layers for vidicon tubes. CGSs are characterized by inexpensive material costs which is a decisive factor in the mass production [1-3].

The subject of this investigation is a systematic study of the dependence of the physical and the structural properties of the GeS<sub>2</sub>–HgS glasses on the chemical composition, namely the investigation of its effect on the Raman spectra of the glasses.

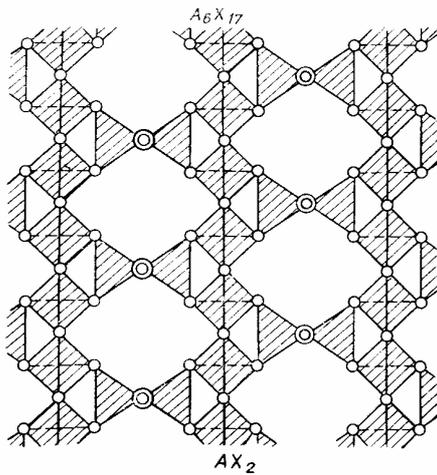
### 2. Experimental

The glasses were synthesized from very high-purity germanium (99.9999 wt. %) and sulfur (99.999 wt. %) and previously synthesized mercury sulfide (99.999 wt. %). The proportionally weighed substances (total mass 4 g) were placed into a specially designed container made of thin-wall (0.7 mm) quartz, from which the air was evacuated to the remaining pressure of 10<sup>-2</sup> Pa. To decrease the loss of material to the melt sputtering and to the condensation of the gaseous phase on the container walls during quenching, top part of the container was isolated by the asbestos cord. The glasses were synthe-

sized in two stages. At the first stage the ampoules with the charge were heated in the oxygas burner flame to complete bonding of the elemental sulfur. Then the ampoules were placed in a single-temperature furnace and heated to the temperature of 250–300 K above the melting point of the alloy on the stable part of the phase diagram. After the exposure to the maximum temperature for 8-10 hours with periodic vibration the alloys were quenched into 25 % aqueous NaCl at the room temperature. The use of this quenching routine allowed us to obtain alloys with 0–50 mol. % HgS in the glassy state. The glassy state was examined by X-ray and microstructure analysis. Obtained glasses are transparent in the visible light (GeS<sub>2</sub>-rich compositions) and vary from yellow (GeS<sub>2</sub>) to black (50 mol. % HgS) color. Raman spectra of the glasses were investigated using an automated set-up based on a DFS-24 spectrometer. The Raman spectra were excited by the argon laser radiation ( $\lambda = 514.5$  nm). The spectra were recorded by a cooled FEP-136 photoelectron multiplier working in the photon count mode. The experiment geometry was set to the reflection mode. Optical resolution was 1.9 cm<sup>-1</sup>.

### 3. Results

It was proved in [4-6] that the 3D structural network of the glassy GeS<sub>2</sub>, like the crystalline  $\alpha$ -GeS<sub>2</sub> which is presented in Fig. 1, consists of the tetrahedral structural units [GeS<sub>4</sub>] that are connected by the corners and the edges to form a quasi-3D network.



**Fig. 1.** Section of a  $\alpha$ -GeS<sub>2</sub> layer where the equal numbers of the GeS<sub>4</sub> tetrahedra are linked by four corners or by two corners and one edge (double circles represent the common edges perpendicular to the figure plane) [7].

The sulfur atoms bridge the tetrahedra; their mean coordination number equals 2. As a result of the described structuring of the components, four bands can be singled out in the Raman spectrum of the glassy GeS<sub>2</sub> sample in the wavelength range 250–550 nm [4]:

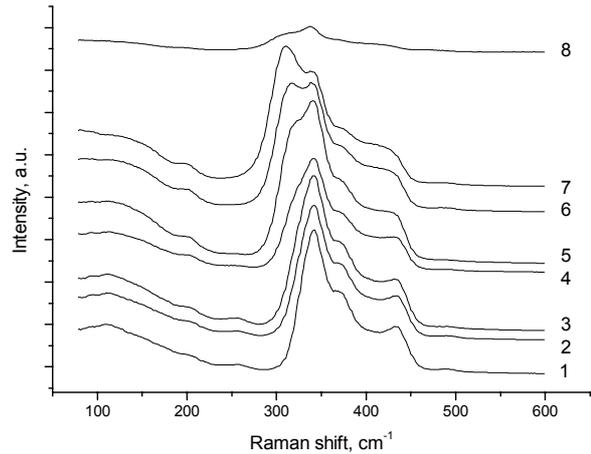
1.  $\nu = 340 \text{ cm}^{-1}$  – strongly polarization-sensitive, caused by the symmetrical vibration mode  $\nu_1$  ( $A_1$ , molecular mode) of the tetrahedral groups [GeS<sub>4</sub>].

2.  $\nu = 370 \text{ cm}^{-1}$  – caused by the vibrations of the edge-linked [GeS<sub>4</sub>] tetrahedra (companion  $A_1^c$  mode).

3.  $\nu = 400 \text{ cm}^{-1}$  – caused by the antisymmetrical vibration mode  $\nu_3$  ( $F_2$ ). This band is absent from the Raman spectrum of the crystalline GeS<sub>2</sub>. One can see its presence in the graph as a high-frequency shoulder that distorts a symmetrical band at  $\nu = 340 \text{ cm}^{-1}$ . This band appears in the Raman spectra due to the interaction of the structural units GeS<sub>4</sub> between themselves.

4.  $\nu = 435 \text{ cm}^{-1}$  – caused by the vibrations of the S<sub>3</sub>Ge–S–GeS<sub>3</sub> unit.

The analysis of the parameters of the scattering spectra of the glassy alloys of the HgS–GeS<sub>2</sub> system shows that the frequency position and the half-width of the scattering bands typical of the glass of GeS<sub>2</sub> composition are practically unchanged but their intensity decreases with the decrease of the GeS<sub>2</sub> content (Fig. 2). Also, an additional scattering band at  $\nu = 312 \dots 331 \text{ cm}^{-1}$  appears upon the introduction of HgS to the alloy composition. The intensity of this band increases with  $x$ , its position shifts to lower frequencies. A possible assumption that this band is caused by the groupings typical of the crystalline HgS phase is invalidated by the known fact that the scattering bands of various HgS modifications lie in the frequency range of 150–270  $\text{cm}^{-1}$  [2]. When the HgS content increases to  $x = 0.5$ , the Raman spectrum is split into six bands with the appearance of a new scattering band at  $\nu = 460 \text{ cm}^{-1}$ .



**Fig. 2.** The Raman spectra of the glasses of the  $(\text{GeS})_{1-x} - (\text{HgS})_x$  system: 1 –  $x = 0$ ; 2 –  $x = 0.05$ ; 3 –  $x = 0.10$ ; 4 –  $x = 0.15$ ; 5 –  $x = 0.25$ ; 6 –  $x = 0.30$ ; 7 –  $x = 0.40$ ; 8 –  $x = 0.50$ .

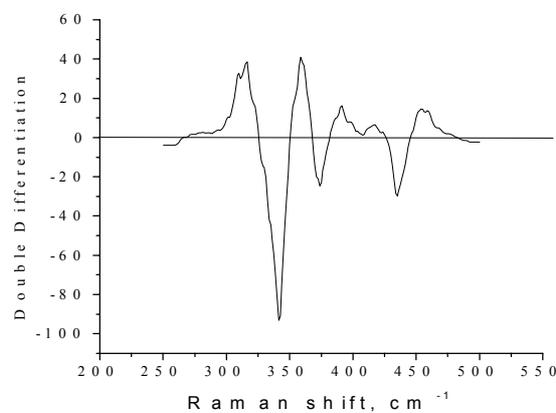
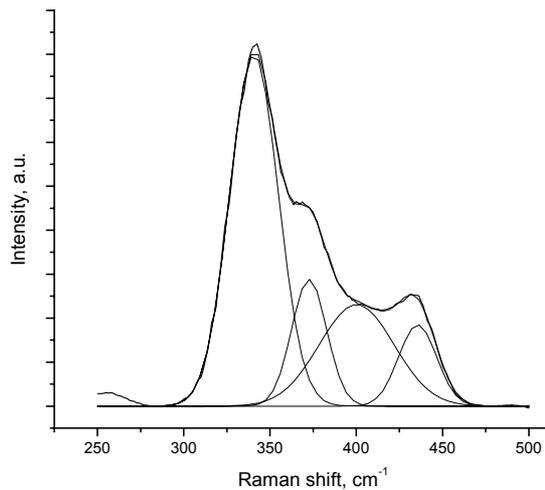
The increase of  $x$  from 0 to 0.50 leads to only minor changes in the Raman spectra displayed as a shift of the scattering band to lower frequencies (some 30  $\text{cm}^{-1}$ ). This is because the contributions of the different modes to the Raman spectra are very difficult to separate (the vibration frequencies are close, whereas the bands are quite wide).

The intensity of the bands that correspond to the scattering by the groupings of the glassy GeS<sub>2</sub> decreases with the  $x$  increase; the intensity of these bands is proportional to the number of the tetrahedra, i.e. to the amount of the Ge atoms. This amount decreases with  $x$  which leads to the decrease of the scattering intensity.

A detailed analysis of the experimentally obtained Raman spectra in the frequency range of 250–500  $\text{cm}^{-1}$  required their split into separate scattering bands as shown, for instance, in Fig. 3. It is shown in Fig. 3a that the spectrum of the glass of GeS<sub>2</sub> composition ( $x = 0$ ) consists of four bands. At the same time, the spectra of the glasses of the  $(\text{GeS}_2)_{1-x} - (\text{HgS})_x$  system at  $x > 0$  reveal five bands as shown in Fig. 4a, for  $x = 0.15$ . This means that an additional scattering band not typical of the GeS<sub>2</sub> glass appears in the Raman spectra at  $x > 0$ .

Indeed, the fact that the Raman spectrum of glass of GeS<sub>2</sub> composition consists of four Gaussian components is confirmed by the results of double differentiation of the original spectrum that produces four negative minima shown in Fig. 3b. Meanwhile, the Raman spectra of the glasses of the  $(\text{GeS}_2)_{1-x} - (\text{HgS})_x$  composition at  $0 < x \leq 0.4$  split into five Gaussian components as confirmed by five negative minima of the second derivative of the experimental spectrum (Fig. 4b).

The spectrum of the  $(\text{GeS}_2)_{1-x} - (\text{HgS})_x$  glass at  $x = 0.5$  can be split into six bands as shown in Fig. 5a; this is confirmed by six negative minima of the second derivative of the experimental spectrum (Fig. 5b).

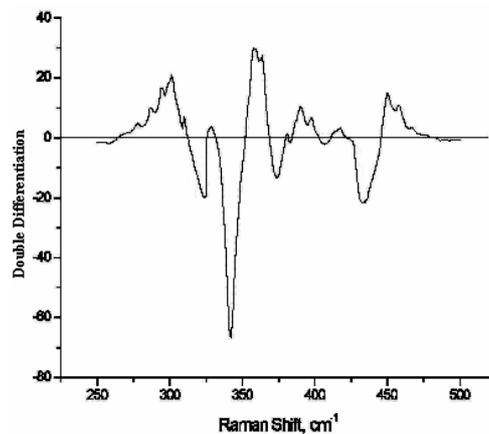
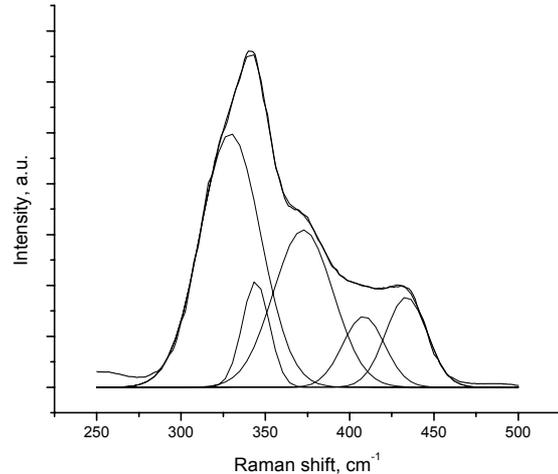


**Fig. 3.** The Raman spectrum of the  $\text{GeS}_2$  glass and its split into the Gaussian components (a) and the second derivative of the spectrum (b).

The results of the analysis of the experimental Raman spectra are given in Table where the scattering band frequencies, their half-width and the integral intensities in arbitrary units are listed.

The analysis of the parameters of separate scattering bands shows that their frequency position and the half-width are typical of the glass of the  $\text{GeS}_2$  composition and are practically unchanged with the composition variation. In its turn, as  $x$  increases, the intensity of the scattering band caused by the symmetric vibration mode  $\nu_1$  ( $350 \text{ cm}^{-1}$ ) decreases. In addition, the increase of  $x$  leads to an appearance of an additional separate scattering band with frequency  $\nu = 320 \text{ cm}^{-1}$ . The intensity of this band increases with  $x$ , and its position shifts to lower-frequency region. This fact is clearly related to the increase of the Hg atom concentration with  $x$ .

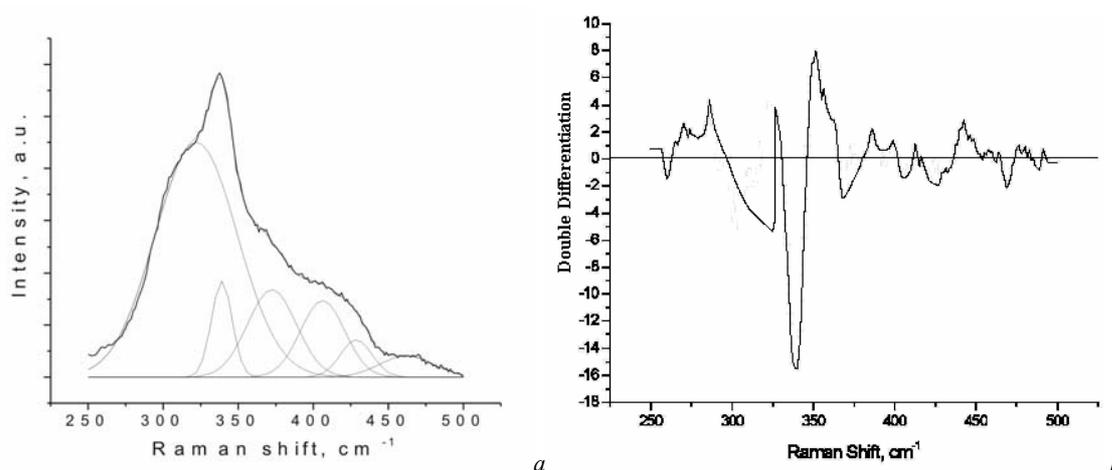
It could be assumed that the existence of HgS clusters is responsible for this band; however, this contradicts the known fact that the scattering bands of various HgS modifications lie in the frequency range of  $150\text{--}270 \text{ cm}^{-1}$  [4].



**Fig. 4.** The Raman spectra of the  $(\text{GeS}_2)_{1-x}\text{-(HgS)}_x$  glass ( $x = 0.15$ ) and its split into the Gaussian components (a) and the second derivative of the spectrum (b).

To elucidate the rules that govern the changes in the Raman spectra with  $x$ , we turn to the stable phase diagram of the HgS– $\text{GeS}_2$  which is the most objective way to determine interrelationship composition–structure–properties. According to the phase diagram, the glass-formation region in this system ( $0 < x < 0.52$ ) corresponds to two liquidus sections, the crystallization of HT- $\text{GeS}_2$  and  $\text{Hg}_4\text{GeS}_6$ , separated by the eutectic at  $x = 0.42$  [8].

According to the pseudo-phase concept introduced by E.A. Porai-Koshits [9] and to the quasi-eutectic theory of V.A. Funtikov [10], the structure of multi-component glasses is constructed with the fragments (structural units) of the stable and the metastable compounds existing in the system. That is, the glassy alloys reflect, to a degree, the character of the component interaction present in the stable phase diagram. However, this “reflection” is accompanied by the loss of the long-range ordering which is typical of the crystalline substances due to the formation of a large number of the nucleation centers and their inability to the consolidation caused by the too-fast increase of the

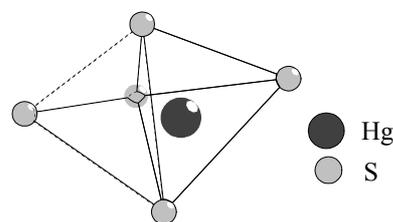


**Fig. 5.** The Raman spectrum of the  $(\text{GeS})_{1-x}-(\text{HgS})_x$  glass ( $x = 0.50$ ) and its split into the Gaussian components (a) and the second derivative of the spectrum (b).

melt viscosity. The structural units of other phases are reflected, probably, only at the level of the preservation of the coordination (hybrid state) of the atoms that form these phases.

Considering the obtained results from this viewpoint, we assume that the appearance of the new scattering band at  $\nu \approx 462.2 \text{ cm}^{-1}$  is probably caused by the vibration of the structural units  $[\text{HgS}_4]\text{S}$  that form the structure of the  $\text{Hg}_4\text{GeS}_6$  phase. Presented in Fig. 6, such unit consists of a  $[\text{HgS}_4]$  tetrahedron that is strongly polarized by the presence of another sulfur atom at a distance of 0.34 nm. As a result of the polarization and the shift of the cation to the fifth anion, the symmetry of such an atomic grouping is far from  $T_d$ . Due to the ability to strong deformation, the  $[\text{HgS}_4]\text{S}$  unit is more likely to appear in the glasses as a distorted trigonal bipyramid than a tetrahedron.

The band at  $\nu \approx 462.2 \text{ cm}^{-1}$  recorded for the sample with  $x = 0.5$  is probably caused by the evolution of the structure of the  $\text{Hg}_4\text{GeS}_6$  pseudo-phase and by the appearance of the  $\text{S}[\text{S}_3\text{Hg}]-\text{S}-\text{Hg}[\text{S}_3]\text{S}$  bonding in the beyond-eutectic compositions; however, there was an attempt [11] to explain the band at  $\nu \approx 462.2 \text{ cm}^{-1}$  as a result of the existence of the sulfur rings  $\text{S}_8$ .



**Fig. 6.** A general appearance of the structural unit  $[\text{HgS}_4]\text{S}$ .

**Table.** Parameters of the scattering bands obtained by the split of the Raman spectra of the glasses of the  $(\text{GeS}_2)_{1-x}-(\text{HgS})_x$  system for various  $x$  values.

Scattering band parameters																		
$x$	1			2			3			4			5			6		
	$\nu_1, \text{cm}^{-1}$	$\Gamma_1, \text{cm}^{-1}$	$I_1$	$\nu_2, \text{cm}^{-1}$	$\Gamma_2, \text{cm}^{-1}$	$I_2$	$\nu_3, \text{cm}^{-1}$	$\Gamma_3, \text{cm}^{-1}$	$I_3$	$\nu_4, \text{cm}^{-1}$	$\Gamma_4, \text{cm}^{-1}$	$I_4$	$\nu_5, \text{cm}^{-1}$	$\Gamma_5, \text{cm}^{-1}$	$I_5$	$\nu_6, \text{cm}^{-1}$	$\Gamma_6, \text{cm}^{-1}$	$I_6$
0.00	340.7	28.1	564070	372.7	20.4	147056	400.2	43.3	250764	435.6	22.1	102391						
0.05	344.1	22.4	314455	370.9	24.0	194026	403.4	43.4	243497	436.5	21.7	87454	328.0	26.7	229744			
0.10	344.9	20.5	207679	370.9	25.6	256735	404.6	39.2	263154	436.2	22.7	112501	331.2	32.1	468307			
0.15	344.2	16.6	97962	371.0	35.3	278454	409.9	28.3	109526	435.2	22.6	88272	328.0	34.2	413138			
0.25	343.8	20.0	204833	368.4	35.0	384992	411.6	38.1	256344	435.7	19.8	64674	320.6	33.5	660379			
0.30	343.3	18.7	181153	368.4	34.7	297341	410.2	37.8	207792	434.0	20.5	48394	316.5	34.4	630523			
0.40	343.7	19.2	171389	371.0	34.9	278130	402.9	25.1	88918	426.8	27.8	126655	312.1	37.7	765099			
0.50	339.1	13.7	15913	372.5	32.5	34279	406.2	29.5	27223	428.6	21.1	9484	322.0	54.8	154733	462.2	35.8	9173

#### 4. Conclusions

As a result of the performed investigation, it was established that the Raman spectra of the  $(\text{GeS}_2)_{1-x}(\text{HgS})_x$  glasses depend substantially on their chemical composition. The analysis of the obtained results shows that the spectrum of the  $\text{GeS}_2$  glass consists of four components, the spectra of the glasses of the  $\text{GeS}_2$ -HgS system with  $0 < x < 0.4$  consist of five components, the spectrum with  $x = 0.5$  consists of six components. The appearance of the additional scattering bands is related to the crystal chemical parameters of the phases the primary crystallization of which form the liquidus curve on the stable phase diagram of the  $\text{GeS}_2$ -HgS system in the region of the existence of the glasses.

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