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VIBRATIONAL SPECTRA AND STRUCTURAL STUDIES OF Hg-As-S GLASSES

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Structural interpretation of Raman and IR spectra, and X-ray diffraction study give evidence to the fact that the adding of mercury into binary glass-forming system causes the formation of α–HgS and β–As_4S_4 at $C_{\mathrm{Hg}} > 2$ at.%. Slow quenching of the melt of $HgAsS_2$ compound results in the separation of α–HgS and β–As_4S_4. In the chain-like model of a–As_2S_3 structure, the addition of Hg atoms results in the increase of chain dimensions from 1.42 to 1.8 nm.

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1. *Introduction*

In a binary As-S system, the composition As_2S_3 exists in crystalline (c) and in amorphous (a) form [1]. In layered c-As_2S_3, each arsenic atom is bonded with three sulphur atoms, forming a pyramid with arsenic atom at the apex. In each layer, the atoms are arranged in the order S–As–S–As and form a spiral which produces a chain due to the translation parallel to the spiral axis. Such spiral chains are parallel one to another and to the c-axis [2–4]. The results of several diffraction measurements confirm the presence of the short-range crystalline order in amorphous a-As_2S_3 [3,5–7]. On this base, a new type of order was defined: the medium-range order (MRO), known as the intermediate-range range order (IRO) [8–11]. There is also evidence that the medium-range order of this glass involves neighbouring pyramids of AsS_3 and their shared atom of sulphur [11]. The vibrational spectra of the system of interconnected clusters based on $AsS_{3/2}$ structural units (s.u.) in the region of valence vibrations is similar to that of bulk glass a-$As_{22}S_{78}$ [12]. In the chain-like approximation, the average correlation length of clusters (MRO) in a-As_2S_3 is 1.42 nm [12].

The introduction of additives into the As-S system causes the variation in some important physical characteristics [2,13]. This allows one to improve the properties of materials which are important for their application in coherent optoelectronics and laser-technology devices [14]. Among the chalcogenide materials with bivalency additives, the glasses of the Hg-As-S system are of particular importance. In this system, a ternary $HgAsS_2$ compoud, a natural mineral halchaite, is known [15]. Since structural peculiarities of Hg-As-S glasses have not been properly studied yet, the investigation of the vibrational spectra of these materials is of special interest.

We present the studies of the changes in far infrared (IR) and Raman spectra, edge absorption and sound velocity of glasses of the Hg-As-S system of compositions close to As_2S_3.

2. Experimental

The Raman spectra of the glasses were taken with the spectrophotometer DFS-24. The velocity of ultrasound was measured by the echo method. The absorption edge was estimated from the transmission and reflection data for samples up to 5 cm in size. The multiple reflections were also taken into account. Far IR spectra were taken using a FIS-3 spectrophotometer. The glasses were synthetized using the methods similar to those described in Ref. 4. For the X-ray diffraction analysis of powder of the glasses, the widespead method was used. The dimensions of chain-like fragments (L) were calculated using the relation [17]:

$$L = \frac{I}{2\,c\,\omega_B}\sqrt{E/\rho}\,,$$

where E is the calculated value of the Young's modulus, ρ the measured density of the glass, ω_B the low-frequency maximum in the Raman spectra and c is the velocity of light.

3. Results and discussion

We have started the structural interpretation of vibrational spectra od Hg-As-S glasses by considering the spectrum of a-As_2S_3 (Fig. 1, curve 1). The profile of the 250 – 400 cm^{-1} absorption envelope of this glass suggests the existence of three main component bands at 310, 342 and 380 cm^{-1}. In the first approximation, the assignement of these bands can be made on the basis of the molecular model proposed in Ref. 20 for the interpretation of the vibrational spectra of glasses of type As_2X_3 (X = S, Se, Te). This model considers the modes of vibrationally decoupled AsX_3 pyramid and As-X-As "water-like" bridging bonds. Thus, in terms of the molecular model, the stronger band at 310 cm^{-1} is assigned to the asymmetric mode

ν_3(E) of AsS_3 pyramidal s.u., while the one at 342 cm^{-1} to the symmetric stretching mode $\nu_1(A_1)$ s.u. The high frequency component at 380 cm^{-1} is attributed to the asymmetric stretching vibration of the As-S-As bridges. These assignements are consistent with the Raman spectrum of a-As_2S_3, which shows strong scattering at ν_1(A)= 342 cm^{-1}, weaker feature at ν_3(E)= 310 cm^{-1} and a shoulder at 375 cm^{-1} [20].

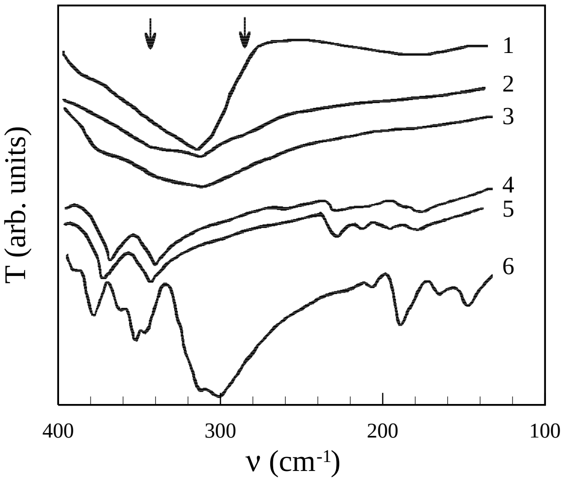

Fig. 1. Far infrared spectra of Hg-As-S *glasses: 1* – a-As_2S_3, *2* – $Hg_5As_{38}S_{57}$, *3* – $Hg_{10}As_{36}S_{54}$, *4* – $Hg_5As_{50}S_{45}$, *5* – $As_{50}S_{50}$, *6* – c-As_2S_3. *The arrows indicate the positions of bands in IR spectrum of* α-HgS.

If adding 5 or 10 at.% of Hg into a-As_2S_3, new shoulders near 340 and 290 cm^{-1} appear in IR spectra of the ternary glasses (Fig. 1, curves 2 and 3). In Ref. 21, it was reported that the corresponding strongest bands of α-HgS are at 345 and 284 cm^{-1} [21] (in Figs. 1 and 3, the arrows indicate the positions of bands in IR spectrum of α-HgS). Such peculiarities are not revealed in the Raman spectra because the frequencies of the main bands of Raman spectra of α-HgS are close to the vibration band ν_1(a) of $AsS_{3/2}$ s.u. [20]. But at $C_{\mathrm{Hg}} = 5$ at.%, in Raman spectra of ternary glass (Fig. 1, curve 1), the bands typical of β-As_4S_4 (at 182, 222 and 360 cm^{-1}) [18] begin to appear (Fig. 2, curve 2). When $C_{\mathrm{Hg}} = 7$ at.%, the latter three typical bands of β-As_4S_4 are clearly observed in Raman spectra of ternary glass (Fig. 2, curve 1). Similar situation in transformation Raman spectra was observed in Ref. 17 after adding a small (1 – 5 at.%) content of Ge into As_2S_3.

These typical bands of β-As_4S_4 are clearly seen in the IR spectrum of materials whose composition is corresponding to $HgAsS_2$ compound (Fig. 3, curve 1).

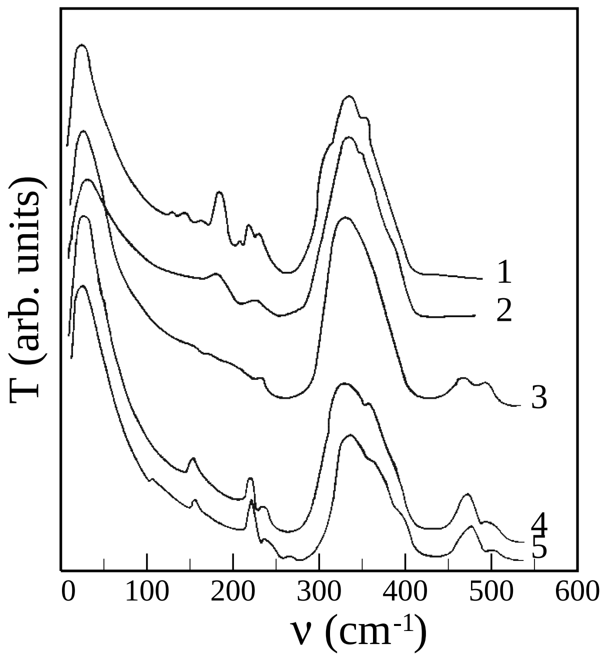

Fig. 2. Raman spectra of Hg-As-S *glasses: 1* – $Hg_7As_{40}S_{53}$, *2* – $Hg_5As_{38}S_{57}$, *3* – $Hg_{2.4}As_{29.2}S_{68.4}$, *4* – $Hg_2As_{29.6}S_{68.4}$, *5* – $Hg_4As_{22.2}S_{73.8}$.

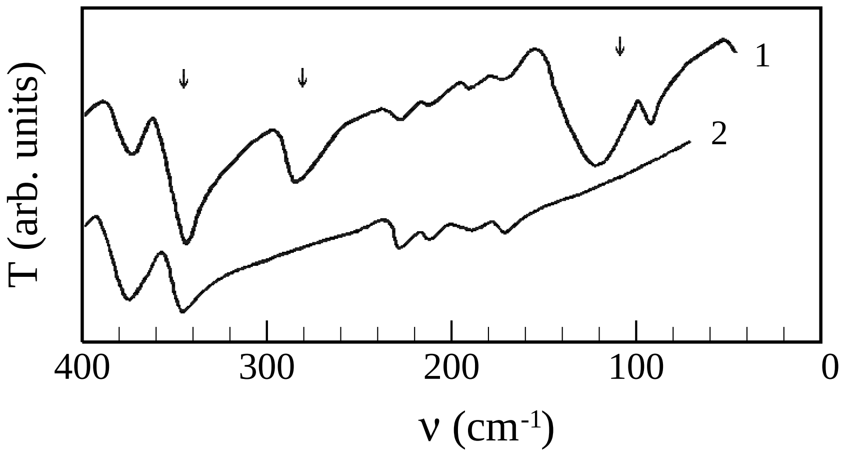

Fig. 3. Far infrared spectra of Hg-As-S_2 *(curve 1) and* $As_{50}S_{50}$ *(curve 2). The arrows indicate the positions of bands in IR spectrum of* α-HgS.

In Ref. 21, the bonding energy of α-HgS was determined from X-ray photoelectron spectra (XPS) of ternary glassy Hg-As-S near As_2S_3 ($C_{Hg} > 2$ at.%). The analysis of XPS spectra of ternary glasses with $C_{\mathrm{Hg}} < 2$ at.% reveals that mercury is present mainly in elementary form.

We have also taken into account data on differential-thermal treatment (DTT) [21] and X-ray diffraction analysis of ternary glasses of corresponding composition but in powder form. In accordance with the diffraction data for ternary glasses ($C_{\mathrm{Hg}} > 2$ at.%), both crystalline phases, β-$\mathrm{As_4S_4}$ and α-Hg-S, appear.

One may suppose that the reaction

$$\mathrm{As_2S_3} + x\ \mathrm{Hg} \rightarrow (1-x)\ \mathrm{As_2S_3} + x\,\alpha\text{-}\mathrm{HgS} + \beta\text{-}\mathrm{As_4S_4}$$

takes place. This is confirmed by the structural data obtained from structural interpretation of vibrational spectra (Figs. 1 and 2), data from X-ray diffraction and XPS spectral analyses [21].

It should be mentioned that according to the far IR spectra and X-ray analysis, the direct synthesis in quartz ampoules of elementary As, S and Hg, whose composition corresponds to $\mathrm{HgAsS_2}$ compound (halchaite) [15] and subsequent quenching of the melt in air (10^{-2} K/s) results in the formation of microheterogeneous mixture of β-$\mathrm{As_4S_4}$ and α-HgS crystals (see Fig. 3).

Thus, the formation of stable glasses in the Hg-As-S system under slow quenching (10^{-2} K/s) takes place on the basis of the $\mathrm{AsS_{3/2}}$ glass-forming s.u. only. The analysis of the change of ultrasound velocity (Fig. 4), and the effect of adding more than 2 at.% of Hg into the binary As-S system, corresponds well to the data on diffraction and X-ray analysis, which show that chalcogen reaction with Hg is energetically more favourable than the one with arsenic. That is why adding more than 2 at.% of metal into the mixture results in the formation of chalcogenides of Hg

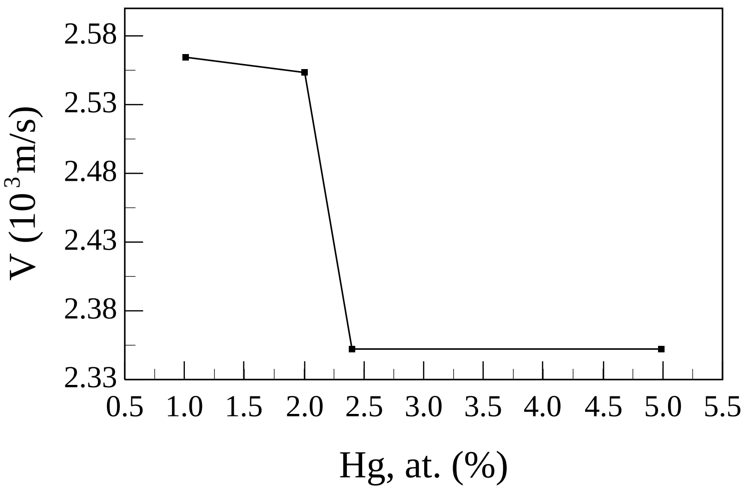

Fig. 4. Concentration dependence of longitudinal sound velocity (V) of Hg-As-S *glasses (points left to right):* $\mathrm{Hg_1As_{39.2}S_{59.8}}$, $\mathrm{Hg_2As_{38.6}S_{59.4}}$, $\mathrm{Hg_{2.4}As_{29.2}S_{68.4}}$, $\mathrm{Hg_5As_{38}S_{57}}$.

with a large ionic component of chemical bond. They form α-HgS when the content of Hg exceeds 2 at.% [21].

Figure 5 shows the influence of Hg on the energy dependence of edge absorption of Hg-As-S glasses in the region of low values of α. For glasses of similar composition to As_2S_3, but with 2 to 5 at.% of Hg, a nonmonotonic shift of the absorption edge to a low-energy region is observed. Besides, with respect to a pure a-As_2S_3 with an increasing Hg content, the increase of the absorption in the region from 10^{-1} to 1.0 cm^{-1} takes place. Such changes of the character of the absorption edge in ternary Hg-As-S glasses may be related to the formation of continuously increasing occurence of Hg-S and As-S bonds, typical for α-HgS and β-As_4S_4 compounds with increasing contents of Hg. The increase of light losses in this low absorption region may be related to the scattering of light by microcrystalline centres of sizes of about 10 nm [10]. A similar situation takes place in the Ag-As-S system where AgS microcrystals are formed [19].

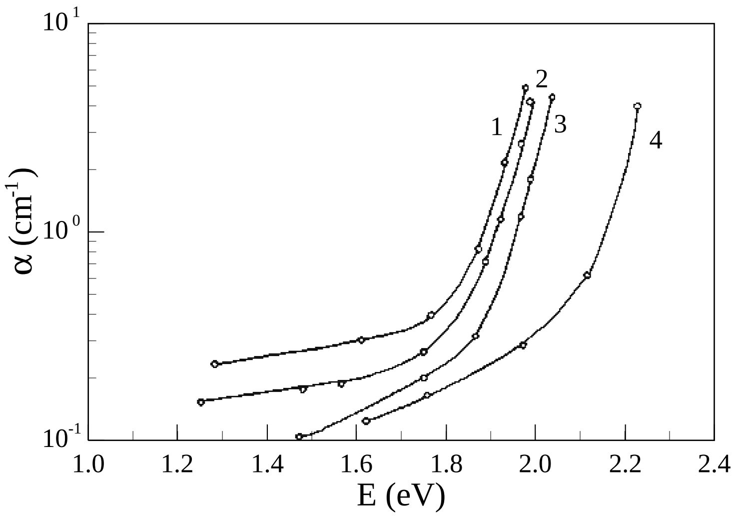

Fig. 5. Dependence of edge absorption on concentration of Hg-As-S *glasses: 1 –* $Hg_5As_{38}S_{57}$, *2 –* $Hg_2As_{39.5}S_{58.5}$, *3 –* a-As_2S_3, *4 –* $Hg_{0.4}As_{22.2}S_{77.4}$.

The shift in Boson maximum from $w_B = 26$ cm^{-1} at $C_{Hg} = 0$ [12] to $w_B = 19$ cm^{-1} at $C_{Hg} = 5$ at.% in Hg-As-S glasses (Fig. 2) is an evidence to the change in the structure compactness [22]. The calculations similar to those described in Ref. 12 show that such changes in the chain-like approximation cause the increse of the length of the chains, which consist of $AsS_{3/2}$ pyramids, from $L = 1.43$ nm (a-As_2S_3 [12]) to $L = 1.89$ nm at $C_{Hg} = 5$ at.%. In the chain-like approximation, the breaking of the structure matrix by the introducing Hg atoms into a-As_2S_3 causes the decrease in the interchain interaction at $C_{Hg} > 2$ at.%.

4. *Conclusion*

When one adds more than 2 at.% of mercury to a-As_2S_3, the bands typical for α-HgS begin to separate in the IR spectra of Hg-As-S glasses. One observes the change of the position of the low-frequency maximum and an increase of the absorption coefficient α in the region 10^{-1} to 1.0 cm^{-1} of the absorption edge, and the length of the chains increases from 1.42 nm for As_2S_3 to 1.8 nm for Hg-As-S glasses along the Hg-As_2S_3 and HgS-As_2S_3 sections.

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References

1) H. Rawson, *Inorganic Glass-Forming System, Nonmetalic Solids*, Academic Press, London (1967);
2) A. A. Vaipolin and E. A. Porai-Koshits, Phys. Solid State (Moscow) **5** (1963) 178;
3) N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, Clarendon Press, Oxford (1979);
4) J. P. Mathieu and H. Poulet, Bull. Soc. Fr. Miner. Crystallogr. **93** (1970) 532;
5) R. Zallen, M. L. Slade and A. T. Ward, Phys. Rev. B **3** (1971) 4257;
6) L. Busse, Phys. Rev. B **29** (1984) 3639;
7) D. L. Price, S. Susman and C. Wright, J. Noncryst. Solids **97-98** (1987) 167;
8) J. C. Phillips, J. Noncryst. Solids **43** (1981) 37:
9) G. Lukovsky, J. Noncryst. Solids **97-98** (1987) 155;
10) C. Y. Yang, M. A. Paysler and D. A. Sayers, Phys. Rev. B **36** (1987) 9260;
11) M. A. Paesler and G. J. Pfeifer, J. Noncryst. Solids **137-138** (1991) 967;
12) V. Mitsa and I. Fejsa, J. Mol. Struct. **410-411** (1997) 263;
13) A. R. Hilton and D. I. Hayes, J. Noncryst. Solids **17** (1975) 339;
14) I. Fekeshgazi, K. May, V. Mitsa and A. Vakaruk, NATO ASI Series 3, High Technology **36** (1997) 243;
15) L. Kaplunnic, E. Pobedimskaja and N. Belov, DAN USSR (Moscow) **225** (1975) 561;
16) V. Mitsa, Yu. Babinets, Yu. Gvardionov and I. Yermolovich, J. Noncryst. Solids **137-138** (1991) 959;
17) V. Mitsa, *Vibrational Spectra and Structural Correlation in Non-Oxide Glassy Alloys* (in Russian), Edit. High Educ., Kiev (1992);
18) W. Bues, M. Somer and W. Brockner, Z. Anorg. Allgem. Chem. **499** (1983) 7;
19) A. Vancu, St. Sladaru and R. Grigorovici, in *Proc. 5^{th} Int. Conf. on Amorphous and Liquid Semiconductors*, Garmisch-Partenkirchen, Vol. 1 (1974) p.631;
20) G. Lukovsky, Phys. Rev. B **4** (1971) 1367 and 1945;

21) I. D. Oleksejuk, *Binary and Ternary of Semiconducting Phase in System Me-B^5-C^7* $\{D^7\}$ (in Ukrainian), Edit. Vega, Volin State Univ., Lutsk (1995);

22) M. Ivanda, I. Hartmann and W. Kiefer, Phys. Rev. B **51** (1995) 3.

SPEKTRI VIBRACIJA I PROUČAVANJE STRUKTURE STAKALA Hg-As-S

Objašnjenje strukture na osnovi Ramanovih i infracrvenih spektara i proučavanje difrakcije X zračenja pokazuju da dodavanje Hg u binarni staklasti As-S uzrokuje stvaranje α–HgS i β–As_4S_4 pri $C_{\rm Hg} > 2$ at.%. Sporim kaljenjem taljevine $HgAsS_2$ dolazi do razdvajanja α–HgS i β–As_4S_4. U lančastom modelu strukture a–As_2S_3, dodavanje Hg uzrokuje porast duljine lanaca od 1.42 na 1.8 nm.