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# Fourier Raman spectroscopy studies of the $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$ glasses

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**Abstract.** The present paper is concerned with the investigations of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses with the help of Fourier Raman spectroscopy. The results of Raman spectroscopy investigations indicate increased presence of non-stoichiometric  $\text{Se}_n$ ,  $\text{As}_4\text{S}_4$  fragments for intermediate compositions of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses, which in combination with composition dependencies of molar volume, previous results on investigations of optical and thermal properties of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  can be explained by the small deviation from the statistical one under the isovalent substitution of Se on S in  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses with the composition change.

**Keywords:**  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses, Raman spectra.

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## 1. Introduction

Intermediate compositions of glasses from  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  composition cross-section with the help of Raman spectroscopy practically were not studied, the investigations mainly were carried out by IR spectroscopy [1-4]. We know only one investigation concerning the Raman spectroscopy of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses [5]. In supposition, that the behavior of the vibration spectra of glasses and amorphous films can be described on the base of the models formulated for the crystalline pseudo-binary solid solutions [6], the two-mode behavior of the IR and Raman spectra is predicted for  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  compositions [2]. The experimental investigations have shown, that indeed for the bands evolution as for IR and as well for Raman spectra of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses the two-mode behavior [1-5] is characteristic, similar to that observed for  $\text{CdS}_x\text{Se}_{1-x}$  solid solutions [6].

In the IR-reflectance spectra of  $(\text{As}_2\text{S}_3)_{1-y}(\text{As}_2\text{Se}_3)_y$  glasses the characteristic vibrations bands of As-S ( $310\text{ cm}^{-1}$ ) and As-Se ( $220\text{ cm}^{-1}$ ) are present which relate to the antisymmetric vibrations  $\nu_3(E)$  of  $\text{AsX}_{3/2}$  structural units [1, 3-4, 7-8]. For both bands oscillator strength linearly depends on the mole content of the component. If the content of selenium in  $(\text{As}_2\text{S}_3)_{1-y}(\text{As}_2\text{Se}_3)_y$  glasses is increased the band position shift to the high-frequency

side of the spectrum [2, 3-4]. It was noted in [3] that the additional structures which can be related to the Se-S, Se-Se and S-S bonds were not observed. In Raman spectra vibrations bands of  $\text{As}_2\text{S}_3$  ( $345\text{ cm}^{-1}$ ) and  $\text{As}_2\text{Se}_3$  ( $227\text{ cm}^{-1}$ ) which relate to the symmetric vibrations  $\nu_1(E)$  of  $\text{AsX}_{3/2}$  structural units are dominant [2, 8]. Besides the main  $\text{AsX}_{3/2}$  structural units structure of  $\text{As}_2\text{X}_3$  glasses also includes  $\text{As}_4\text{X}_4$  and  $\text{X}_n$  units [7,8]. On the base of the mentioned above data of IR-spectra investigations of  $(\text{As}_2\text{S}_3)_{1-y}(\text{As}_2\text{Se}_3)_y$  glasses it was supposed in [1] that the pyramidal molecules are preserved for all compositions and that the statistical substitution for the atoms in the two-fold coordinated atomic sites of the chalcogens takes place. This contradicts our results obtained during investigations of optical and thermal properties of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  ( $x = 0, 20, 30, 40, 60$ ) [9] which gave indication of the small deviation from the statistical one for the substitution of Se atoms by S in the investigated compositional range. In present study we tried to find evidence of such deviation from statistical substitution with the help of Raman spectroscopy.

## 2. Experiment

The bulk materials ( $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$ ,  $x = 0; 20; 40, 60$ ) were prepared by the direct synthesis from 5N purity elements

in evacuated quartz ampoules at 700–750 °C for 8–24 hrs. After synthesis, the ampoules were quenched in water at a temperature of  $\approx 15$  °C, which is equivalent to a cooling rate of the order of  $10 \text{ Ks}^{-1}$ . The Raman spectroscopy investigations were carried out by using Fourier Transformation BRUKER IFS55 IR spectrophotometer with a FRA 106 accessory. The laser irradiation on the wavelength  $1,06 \mu\text{m}$  (having an output power 90 mW during measurement of glasses) was used for the excitation of the Raman spectra. In our case, this wavelength value was very essential because irradiation of samples in this range causes no detectable photostructural transformations within the scale of 100 scans for glasses. The resolution of the Raman spectrometer was  $1 \text{ cm}^{-1}$ . Backscattering geometry was used. Spectra were reduced according to Shuker-Gammon procedure [10] and were normalized on area.

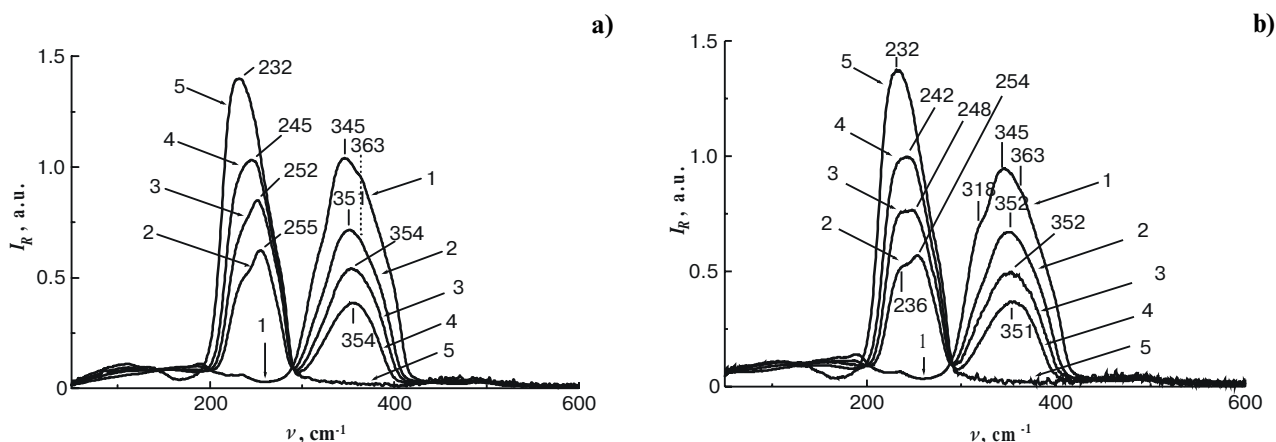
### 3. Results and discussion

Results of our investigations of Raman spectra for  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses are presented in Fig. 1 (a – VV, b – VH configurations) [9, 11–15]. For the evolution of the Raman bands of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses with the composition (as for VV, as well for -VH configuration) the two mode behavior is characteristic. Next peculiarity is the shift of the maxima frequency positions of the main Raman bands to the high-frequency side. In the case of VV-configuration in the region of the main  $345 \text{ cm}^{-1}$  band, which is characteristic for  $\text{As}_{40}\text{S}_{60}$  the position of the main maximum is gradually shifted from  $345$  ( $\text{As}_{40}\text{S}_{60}$ ) up to  $354 \text{ cm}^{-1}$  ( $\text{As}_{40}\text{S}_{20}\text{Se}_{40}$ ). In the region of the main  $232 \text{ cm}^{-1}$  band characteristic for  $\text{As}_{40}\text{Se}_{60}$  changes are of more complex nature because in this region the peaks near  $224$  and  $234 \text{ cm}^{-1}$  are present and together with other small features characteristic for  $\text{As}_{40}\text{S}_{60}$  glass and the structure became more complex – for the glasses of  $\text{As}_{40}\text{S}_{40}\text{Se}_{20}$  composition the shoulder near  $232 \text{ cm}^{-1}$  and peak at  $255 \text{ cm}^{-1}$  are clearly seen.

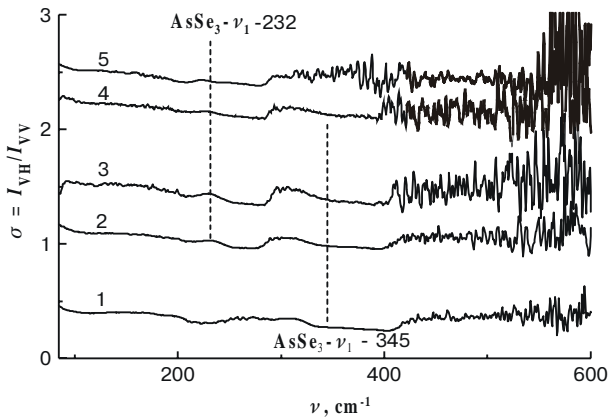
Similar picture is characteristic for the evolution of spectra in VH-configuration. For the case of HV-polarization we have the different feature from the case observed in [5] where maximum was at  $315 \text{ cm}^{-1}$  and practically was not shifted with the change of Se content, in our data the position of the main maximum near  $345 \text{ cm}^{-1}$  ( $\text{As}_{40}\text{S}_{60}$ ) with the increase of the Se content was shifted up to  $352 \text{ cm}^{-1}$  ( $\text{As}_{40}\text{S}_{20}\text{Se}_{40}$ ). Also in the case of VH-configuration the peculiarities near  $248$ – $254 \text{ cm}^{-1}$  were clearly observed, in difference from the data in [5].

The origin of  $255 \text{ cm}^{-1}$  band we explain by the increased presence for the intermediate compositions of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses of the  $\text{Se}_n$  chains among other non-stoichiometric fragments (see Fig.1). Their presence can be connected with the existence of the small deviation from the statistical one under the isovalent substitution of Se on S in  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses [2] and single crystals [8] with the composition change. As a result of such deviation the quantity of the sulphur deficient (as compared with  $\text{AsS}_{3/2}$ ) non-stoichiometric structural units which are characteristic for  $\text{As}_4\text{S}_4$  is increased, which leads with the increase of the Se content in  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses to the gradual shift of band maximum in the ( $300$ – $400 \text{ cm}^{-1}$ ) region which is characteristic for the vibrations of the  $\text{As}_{40}\text{S}_{60}$  structural units to the side of higher frequencies due to increased relative intensity of  $363 \text{ cm}^{-1}$  band related to the vibrations of the  $\text{As}_4\text{S}_4$  structural units (see Fig. 1).

Depolarization spectra for Raman spectra of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses are presented in Fig. 2. For the convenience of observation they are shifted on 0.5 in respect to each other. It can be seen from the figure, that in depolarization spectra under the change of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses composition no additional features are observed in comparison the behavior of s characteristic for the stoichiometric compounds  $\text{As}_{40}\text{S}_{60}$  and  $\text{As}_{40}\text{Se}_{60}$ . Depolarization spectra also support the two-mode behavior of the Raman spectra evolution for the glasses from  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  cross-section.



**Fig. 1.** Reduced Raman spectra of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses: 1 –  $\text{As}_{40}\text{S}_{60}$ ; 2 –  $\text{As}_{40}\text{S}_{40}\text{Se}_{20}$ , 3 –  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ , 4 –  $\text{As}_{40}\text{S}_{20}\text{Se}_{40}$ , 5 –  $\text{As}_{40}\text{Se}_{60}$ . a – VV-, b – VH configuration.



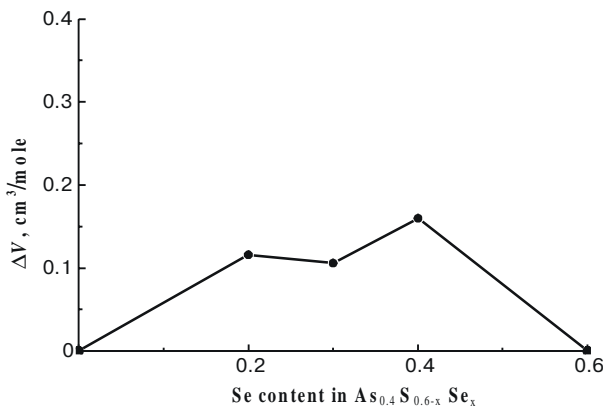
**Fig. 2.** Composition dependencies of depolarization  $\sigma = I_{VH}/I_{VV}$  for Raman spectra of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses: 1 –  $\text{As}_{40}\text{S}_{60}$ ; 2 –  $\text{As}_{40}\text{S}_{40}\text{Se}_{20}$ , 3 –  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ , 4 –  $\text{As}_{40}\text{S}_{20}\text{Se}_{40}$ , 5 –  $\text{As}_{40}\text{Se}_{60}$ .

The composition dependencies of the mole volumes for the glasses of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  compositions presented in [8] and calculated by us (Fig. 3) show small deviation of mole volume composition dependence from the linear one. The mole volume is determined by the relation

$$V = \left( \sum x_i M_i \right) / \rho \quad (1)$$

where  $M_i$  stands for molecular masses of the certain structural units or atomic masses of components,  $x_i$  is their respective content. The compactness  $\delta$ , which is supposed to be more sensitive to the structure of the glass network [16], is calculated according to the formula

$$\delta = \frac{\sum_i \frac{x_i A_i}{\rho_i} - \sum_i \frac{x_i A_i}{\rho}}{\sum_i \frac{x_i A_i}{\rho}} \quad (2)$$



**Fig. 3.** Composition dependence of deviation from linearity  $\Delta V$  of mole volumes for  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses.

where  $x_i$  is an atomic fraction,  $A_i$  – atomic weight,  $\rho_i$  – density of the glass  $i$  component,  $\rho$  – measured glass density. In compactness  $\delta$  composition dependence during the substitution of sulfur by selenium for  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses also exists small deviation from linearity. Deviation of mole volume  $V$  and compactness  $\delta$  composition dependence for  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses from the linearity (additivity) we consider in connection with the deviation in the substitution of sulfur by selenium from the statistical one. Due to such behavior as was said above the number of sulfur deficient (in comparison to the  $\text{AsS}_{3/2}$ ) structural units, which are characteristic for  $\text{As}_4\text{S}_4$  and  $\text{Se}_n$  chains for the intermediate compositions is increased and, consequently, which leads to the slight deviation (small increase due to the presence of chain structure) from the linear one of the mole volume composition dependence. Deviation of mole volume composition dependence for  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses correlates with the little features on the composition dependencies of dispersion energy and optical dielectric constant for exposed or annealed films  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  [9].

## Conclusions

The results of Raman spectroscopy investigations indicate increased presence of non-stoichiometric  $\text{Se}_n$  fragments for intermediate compositions of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses, which in combination with the results of composition dependencies of molar volume, investigations of optical and thermal properties of  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  [9] can be explained by the small deviation from the statistical one under the isovalent substitution of Se on S in  $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$  glasses with the composition change.

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## A.V. Stronski et al.: Fourier Raman spectroscopy studies of the $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$ glasses

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