Raman scattering in sulphide glasses

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Abstract. Raman spectra of two ternary glasses of composition $Ge_5As_{37}S_{58}$ and $As_4Ge_{30}S_{66}$ have been investigated. An influence of addition of third element on the spectra of binary glasses has been studied by comparison with spectra of two binary glasses of composition $Ge_{33}S_{67}$ and $As_{40}S_{60}$. Glass structure and phase separation effects are discussed.

Keywords: Raman scattering, chalcogenide glasses.

1. Introduction

Investigations of non-crystalline solids occupy one of the leading places in modern solid state physics. High research interest paid to these materials is caused by a number of their inherent properties (an opportunity to tailor continuously the composition and physical properties, effective production and treatment, stability in various media, etc.) which provide many opportunities for their practical applications. Studying of non-crystalline solid state is also of great importance from the viewpoint of the fundamental science. Chalcogenide vitreous semiconductors are very interesting materials of this class. Beside the mentioned physical properties inherent to glassy state, they have also many specific properties such as transparency in the infrared region of spectrum, a variety of photoinduced phenomena and high nonlinear optical properties, which made them very perspective in such practical applications as telecommunications, sensors, optical data storage, etc. Investigation of structure of these materials and it's relation to the composition and physical properties is a key for effective application. Raman scattering is one of the commonly used ways to investigate the structure of the glassy state. In this paper, we present the results of Raman spectroscopic studies concerning two ternary chalcogenide glasses of composition $Ge_5As_{37}S_{58}$ and $As_4Ge_{30}S_{66}$ and comparison with binary glasses $As_{40}S_{60}$ and $Ge_{33}S_{67}$.

2. Experimental

Glasses of compositions $As_{40}S_{60}$, $Ge_5As_{37}S_{58}$, $Ge_{33}S_{67}$ and $As_4Ge_{30}S_{66}$ were synthesized by direct melting of initial high purity elements in evacuated silica ampoules. $Ge_{33}S_{67}$ and $As_4Ge_{30}S_{66}$ glasses were held at 750 °C for 5 h and then melted at 800 – 970 °C for 10 – 12 h. $As_{40}S_{60}$ and $Ge_5As_{37}S_{58}$, glasses were melted at 650 – 800 °C for 8 – 24 h. After synthesis, the ampoules with melts were quenched in cold water. Raman spectra were investigated using IR Fourier spectrophotometer Bruker IFS55 Equinox with FRA-106 attachment. Nd-YAG laser light with the wavelength 1.064 μm was used for excitation.

3. Results and discussion

Raman spectra of binary glasses $As_{40}S_{60}$ and $Ge_{33}S_{67}$ are presented in Figs 1a and 1b, respectively. The spectrum of $As_{40}S_{60}$ glass consists of the main band centered at 344 cm^{-1} and a broad band in the lower frequency region (50 – 250 cm^{-1}). There is also a weak band at 497 cm^{-1}. The spectrum of $Ge_{33}S_{67}$ glass contains the main peak at 344 cm^{-1} with the shoulder at 372 cm^{-1}, which is usually referred to as A_1^c "companion" mode. Also, there is the distinguished peak at 436 cm^{-1} and weak band at 488 cm^{-1}. In the lower frequency region (50 – 250 cm^{-1}), there is a broad band with features at 85, 117, 154, 208 cm^{-1}.

The Raman spectrum of $As_4Ge_{30}S_{66}$ glass is presented in Fig. 2a. The higher frequency region (300 – 600 cm^{-1}) contains the broad band with two maxima near 346 and 435 cm^{-1}. This band can be deconvoluted into four Gaussian bands centered at 346, 375, 403 and 435 cm^{-1}, as shown in Fig. 1. There is also a weak band at 495 cm^{-1} in this region.

The lower frequency part of the spectrum (50 – 300 cm^{-1}) also can be deconvoluted into Gaussian bands centered at 88, 114, 152, 186, 210 and 246 cm^{-1} (see Fig. 2).

a

b
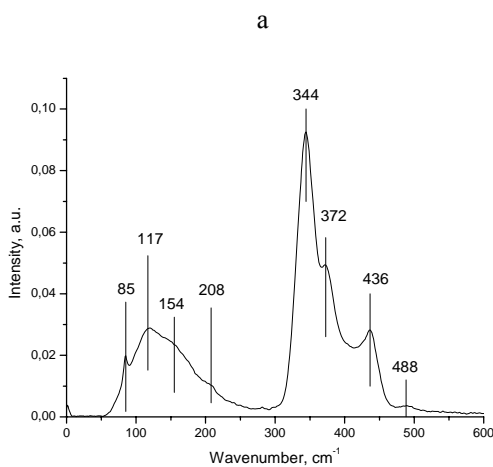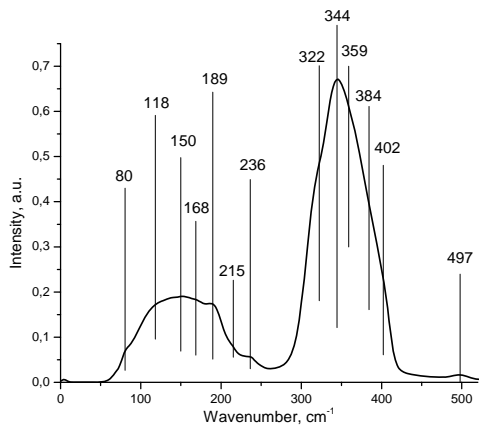
**Fig. 1.** Raman spectra of binary glasses $As_{40}S_{60}$ (a) and $Ge_{33}S_{67}$ (b).

In Fig. 2b, the Raman spectrum of $Ge_5As_{37}S_{58}$ glass is presented. There is a broad band centered near 343 cm^{-1} in the higher frequency region (260 – 500 cm^{-1}). Deconvolution of this band leads to five Gaussian-shaped lines (see Fig. 2) with the maxima at 320, 167, 189, 214 and 237 cm^{-1}. There is also a weak band at 496 cm^{-1}.

In the lower frequency region (60 – 260 cm^{-1}) there is a broad band which has local peculiarities at 150, 167, 189, 214 and 237 cm^{-1}.

The most intensive band in the spectrum of $Ge_{33}S_{67}$ glass is located at 344 cm^{-1}. In the case of $As_4Ge_{30}S_{66}$ glass, it is shifted towards 346 cm^{-1}. This band has been previously observed in binary glasses of Ge–S system either of stoichiometric or non-stoichiometric composition [1-5]. The peak at 346 cm^{-1}, as usually accepted, corresponds to the A_1 symmetric stretching vibrations in the main structural units of the glass – $Ge(S_{1/2})_4$ tetrahedra, and in the case of ternary

$As_4Ge_{30}S_{66}$ system, it also contains a contribution from symmetrical vibrations of $As(S_{1/2})_3$ pyramidal units [6]. Two other bands – A_1^c companion mode at 375 cm^{-1}, and the band near 435 cm^{-1} have been also observed in Ge_xS_{1-x} glasses of different compositions, but their origin still remains controversial.

Authors of the paper [7] associated the band 375 cm^{-1} with the presence of medium range order structures in these glasses. A model was assumed, according to which, glassy $Ge(S, Se)_2$, as opposed to SiO_2, are formed not by a three-dimensional random network, but have rather layer-like structure consisted of medium-range order regions. The typical scale of these structures is about 10 to 20 Å.

a

b
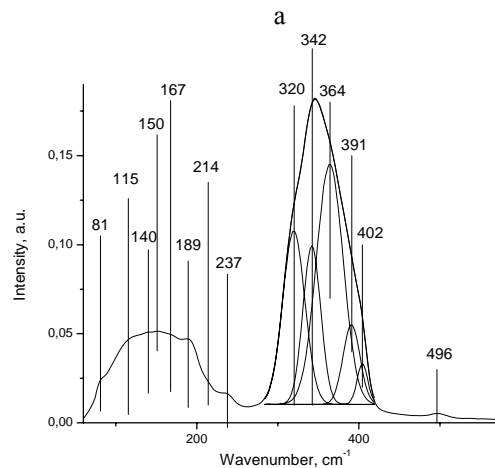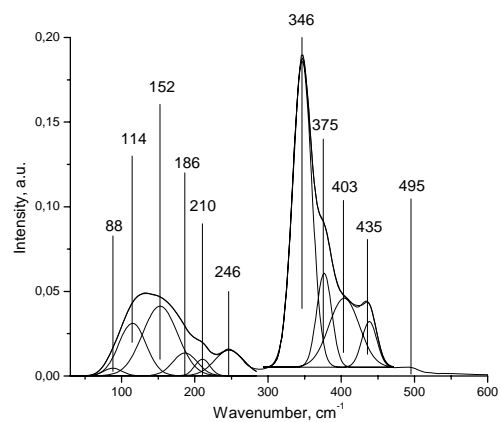
Fig. 2. Raman spectra of ternary glasses $Ge_{30}As_4S_{66}$ (a) and $Ge_5As_{37}S_{58}$ (b).

Authors of [3] investigated evolution of Raman spectra with temperature. They observed two stage crystallization of glassy GeS_2. It was found that the A_1^c mode is present in spectra during the rise of temperature

and remains after the transition to 3D-crystalline state (at ~750 ºC), and also it is present at temperatures higher than 850 ºC as a shoulder (when the transition to the 2D-crystalline state occurs). After slow cooling down to room temperature, material retains 2D-crystalline structure that also has the A_1^c mode in its spectrum. Therefore, by analogy with the 2D-crystalline state, the A_1^c mode in glassy GeS_2 was ascribed to symmetrical vibrations of sulphur bridge atoms in edge-shared tetrahedra.

Authors of [5] provided comparison of Raman spectra of glassy GeS_2 obtained under different quenching temperatures and cooling rates. A conclusion has been drawn that A_1^c mode together with 433 cm^{-1} band can be ascribed to vibrations in edge-shared tetrahedra. In paper [3], 433 cm^{-1} band was ascribed to the stretching vibrations of S–S bonds that were either present separately in glass matrix or bond together with tetrahedral elements. This opinion is supported by the authors of [8]. They stated that the 434 cm^{-1} band that was observed by them in germanium sulphide films, corresponds to the vibrations of S–S bonds interconnecting $Ge(S_{1/2})_4$ tetrahedra. Authors of [3] claims that the presence of such bonds in stoichiometric glass indicates the presence of homopolar Ge–Ge bonds. The band at 260 cm^{-1}, the intensity of which was growing up with the increase of Ge concentration was ascribed to the presence of these bonds. The authors, however, didn't explain why the intensity of 433 cm^{-1} band (along with A_1^c band) decreases with increasing of the sulphur content.

Authors of [5] don't support the assumption about the presence of homopolar bonds in glassy GeS_2. The bands at 200, 237 and 256 cm^{-1} which were observed in samples of glassy GeS_2 obtained at different synthesis conditions, were ascribed to the vibrations in three-fold coordinated structures consisted of Ge and S atoms, for instance, to the vibrations in crystalline nanophase c-GeS. As mentioned in [5], c-GeS nanoparticles with sizes about 7–12 Å may exist in the glass structure, or, depending on the synthesis conditions, may form larger c-GeS particles within the matrix of glassy GeS_2.

In the paper [4], the band near 440 cm^{-1} that was observed in glasses of nearly stoichiometric compositions Ge_xS_{1-x}, was ascribed to the F_2 mode of tetrahedra $Ge(S_{1/2})_4$. In paper [9], the structure of $As_4Ge_{30}S_{66}$ glass was investigated by means of X-ray diffraction. By comparison of experimental results with those of numerical simulation, a conclusion was drawn that the structure of glass is given by inhomogeneous network with regions expressing a quasi-layer type stacking interlinked with regions of random network where the amount of homopolar bonds is kept minimum.

The 495 cm^{-1} band observed in the spectrum of $As_4Ge_{30}S_{66}$ is characteristic for the presence of S–S bonds. Presence of these bonds implies the existence of edge-shared $Ge(S_{1/2})_4$ tetrahedra in the structural backbone of the glass, which must lead to the appearance of redundant S atoms.

The 246 cm^{-1} band was observed earlier in the $Ge_xA_{40-x}S_{60}$ glass spectra [10]. When x = 0, a weak band near 231 cm^{-1} was observed, which was growing and shifting towards the higher frequencies with increasing x until 245 cm^{-1} when x = 36. This feature was related by authors with increasing amount of homopolar Ge–Ge bonds compared to As–As. As claimed in [10], homopolar Ge–Ge bonds are located in $Ge–S_{4-n}Ge_n$ tetrahedra and/or in $Ge_2S_{6/2}$ ethane-like clusters.

Similar peculiarity was observed in [11] during the investigation of series of compounds $(Ge_2S_3)_x(As_2S_3)_{1-x}$ where 0<x<1. When x>0.5, the broad band centered at 250 cm^{-1} appeared and began to increase. As stated in [11], this band corresponds to the vibrations in ethane-like Ge_2S_6 nanophase that segregates from GeS_2. According to the results of calculations provided in [5], ethane-like nanophase possesses the intensive peak at 250 cm^{-1} and also several bands near 400 cm^{-1}. In the decomposition of the main peak in the $As_4Ge_{30}S_{66}$ spectrum (see Fig. 2), there is a broad band centered at 403 cm^{-1}. Therefore, bands at 246 and 403 cm^{-1} can be ascribed to the vibrations in ethane-like nanophase Ge_2S_6.

In Fig. 3, the difference between spectra of $As_4Ge_{30}S_{66}$ and $Ge_{33}S_{67}$ glasses normalized to the intensity of the main peak is shown. The difference spectra clearly reveal the changes made by addition of arsenic to the $Ge_{33}S_{67}$ glass. The abrupt transition from minimum to maximum near 346 cm^{-1} is due to the red shift of the main band. The difference spectrum has maximum near 250 cm^{-1} corresponding to the appearance of this band in the spectrum of $As_4Ge_{30}S_{66}$ glass, and minima at 374 and 438 cm^{-1} due to the softening of corresponding bonds. The former peculiarity can be ascribed to the precipitation of ethane-like nanophase, while the latter to the decrease of the $Ge(S_{1/2})_4$ tetrahedra concentration.

The Raman spectrum of $Ge_5As_{37}S_{58}$ glass (see Fig. 2b) is almost similar to the spectrum of binary $As_{40}S_{60}$ glass. The main broad band in the spectra of $As_{40}S_{60}$ and $Ge_5As_{37}S_{58}$ glasses at 342 cm^{-1} corresponds to the band characteristic for As_xS_{100-x} glasses of different compositions. The bands at 321, 343 and 361 cm^{-1} that are present in the decomposition of main band are typical to the $As_{42}S_{58}$ glass enriched by arsenic as compared to the stoichiometric $As_{40}S_{60}$ glass. The 342 cm^{-1} band, as generally accepted [6, 10, 11], corresponds to the symmetric v_1 vibrations of pyramidal $As(S_{1/2})_3$ units. The band at 361 cm^{-1} corresponds to the intensive mode of crystalline As_4S_4 [6]. The increase in this band intensity is characteristic of As_xS_{1-x} compositions when x>40, that is arsenic enriched as compared to the stoichiometric glass [6, 12]. Numerical calculations provided in [12] allow to ascribe the band at 361 cm^{-1} to the presence of As_4S_4 clusters in material. In the lower frequency region of the $Ge_5As_{37}S_{58}$ spectrum, we can also see the bands observed earlier by the authors of [6] in the $As_{42}S_{58}$ glass, in particular: the bands at 150 (corresponds to the 147 cm^{-1} band), 167, 189, 214 and 237 cm^{-1} (corresponds to the

234 cm^{-1} band). Bands at 150, 167, 189 and 214 cm^{-1} can also be ascribed to the vibrations in As$_4$S$_4$ clusters [6, 11].

The band near 496 cm^{-1} that is characteristic of S-S bonds appears in spectra of glass of either stoichiometric As$_{40}$S$_{60}$ or non-stoichiometric Ge$_5$As$_{37}$S$_{58}$ glass with Ge additive. Thus, presence in the spectrum of As$_{40}$S$_{60}$ glass bands at 361, 150, 167, 189 and 214 cm^{-1} that are characteristic of As$_4$S$_4$ clusters, and the band at 496 cm^{-1}, suggests the non-homogeneity and nanophase separation in stoichiometric glass.

In Fig. 4, the difference between spectra of Ge$_5$As$_{37}$S$_{58}$ and As$_{40}$S$_{60}$ glasses normalized to the intensity of the main peak is shown. As can be seen from Fig. 4, introduction of Ge additives leads to appearance of the minima at 310 and 330 cm^{-1}, which corresponds to the anti-symmetrical and symmetrical vibrations of AsS$_3$ pyramids [6]. The positive peaks near 241, 383 and 408 cm^{-1} can be ascribed to the vibrations in ethane-like clusters that can be formed in glass with addition of Ge.
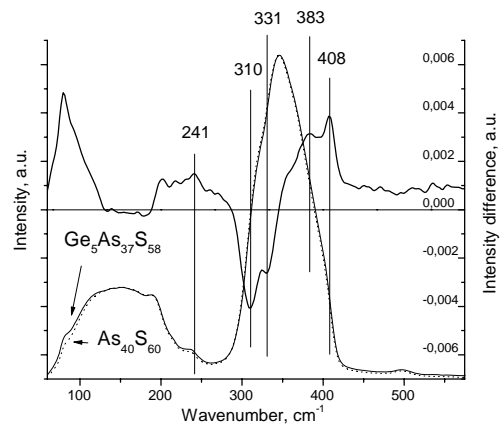

Fig. 4. Difference between spectra of Ge$_5$As$_{37}$S$_{58}$ and As$_{40}$S$_{60}$ glasses normalized to the intensity of the main peak.
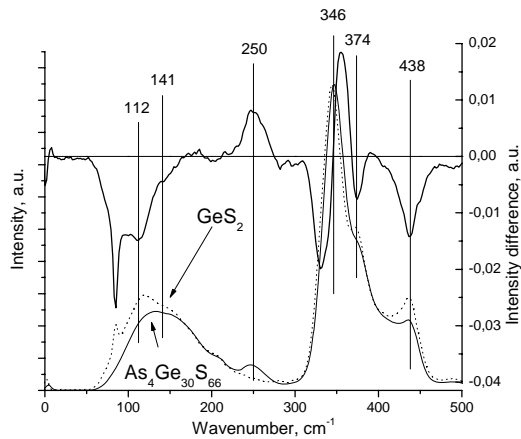
Fig. 3. Difference between spectra of As$_4$Ge$_{30}$S$_{66}$ and Ge$_{33}$S$_{67}$ glasses normalized to the intensity of the main peak.

4. Conclusions

Raman spectra of two ternary glasses with compositions Ge$_5$As$_{37}$S$_{58}$ and As$_4$Ge$_{30}$S$_{66}$ have been investigated. An influence of third element addition on the spectra of binary glasses has been studied by comparison with two binary glasses of composition Ge$_{33}$S$_{67}$ and As$_{40}$S$_{60}$. The observed peaks in Raman spectra are characteristic either to the main elements forming structural backbone of the glasses (tetrahedral Ge(S$_{1/2}$)$_4$ units and pyramidal As(S$_{1/2}$)$_3$ units) or various inclusions (molecular As$_4$S$_4$ clusters and ethane-like nanophase Ge$_2$S$_{6/2}$). Inhomogeneity and nanophase separation can be observed in glasses of either non-stoichiometric or stoichiometric composition.

References

1. X. Feng, W.J. Bresser, P. Boolchand, Direct evidence for stiffness threshold in chalcogenide glasses // *Phys. Rev. Lett.* **78** (23), p. 4422-4425 (1997).
2. Z. Cernosek, J. Holubova, E. Cernoskova, M. Frumar, Homogeneity threshold in sulphur rich Ge–S glasses // *JOAM*, **3**(2), p. 459-462 (2001).
3. [3]. I.P. Kotsalas, C. Raptis, Structural Raman studies of Ge$_x$S$_{1-x}$ chalcogenide glasses // *JOAM*, **3**(3), p. 675-684 (2001).
4. L. Cai, P. Boolchand, Nanoscale phase separation of GeS$_2$ glass // *Phil. Mag.*, **82**(15), p. 1649-1657 (2002).
5. R. Holomb, P. Johansson, V. Mitsa, I. Rosola, Local structure of technologically modified g-GeS$_2$: resonant Raman and absorption edge spectroscopy combined with ab initio calculations // *Phil. Mag.*, **85** (25), p. 2947-2960 (2005).

6. E.F. Venger, A.V. Melnichuk, A.V. Stronski, *Photoinduced Phenomena in Chalcogenide Glassy Semiconductors and Their Practical Application.* Akademperiodika, Kyiv, 2007 (in Russian).

7. P.M. Bridenbaugh, G.P. Espinosa, J.E. Grifiths, et al. // *Phys. Rev. B*, **20**(10), p. 4140 (1979).

8. C.C. Huang, D.W. Hewak, Deposition and characterization of germanium sulphide glass planar waveguides // *Optics Express*, **12** (11), p. 2501-2506 (2004).

9. F. Sava, A. Anghel, I. Kaban, W. Hoyer, M. Popescu, Atomic scale structure of $Ge_{30}As_4S_{66}$ // *JOAM*, 7(4), p. 1971-1975 (2005).

10. E. Vateva, E. Skordeva, Nanoscale arrangement in the $Ge_xAs(Sb)_{40-x}S_{60}$ systems // *JOAM*, **4**(1), p. 3-12 (2002).

11. S. Mamedov, D.G. Georgiev, Tao Qu, P. Boolchand, Evidence for nanoscale phase separation of stressed–rigid glasses // *J. Phys.: Condens. Matter.* **15**, p. S2397-S2411 (2003).

12. R.M. Holomb, V.M. Mitsa, Simulation of Raman spectra of As_xS_{100-x} glasses by the results of ab initio calculations of As_nS_m clusters vibrations // *JOAM*, **6**(4), p. 1177-1184 (2004).