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FORMATION OF COMPLEX STRUCTURAL UNITS AND STRUCTURE OF As-S-Se-Te-I GLASSES

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The dependence between the composition and structure of glasses was studied in the As-S-Se-Te-I system along the half double cut As_2S_3-$AsSe_{0.5}Te_{0.5}I$. Bulk samples were prepared from the high-purity elementary components by vacuum sealing the appropriate quantities in quartz ampoules. The method of cascade heating, isothermal holding at selected temperatures and melt annealing in the air were used as a process of obtaining investigated samples. The far-infrared and Raman spectra of chalcogenides were recorded for various compositions and discussed in terms of the structural units involved. On the basis of spectral data it was established that the structure of glasses alloys $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ is determined by the structure of the binary As_2X_3 and ternary AsXI (X=S, Se or Te) glass-forming compounds.

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1. Introduction

The structure, its formation, as well as the electron transfer properties of amorphous systems are still unsolved subjects, both from the theoretical and experimental point of view. Due to the isotropy, their structural variability and their broad range of existence, amorphous systems can be modelled taking into account the models valid for crystalline bodies and specifics of liquid state.

Instead of oxygen, chalcogenide glasses contain other elements from group VI of the periodic table; namely sulphur, selenium and tellurium as glass-forming anions. Most chalcogenide glasses transmit from approximately 1 μm to infrared wavelengths longer than oxide or fluoride glasses. Glasses containing heavier anions transmit to longer wavelengths. Sulphide glasses are transparent up to 12 μm, selenide glasses up to 15 μm and telluride glasses transmit to 20 μm [1]. Sulphur and selenium can form glass without other elements. The glass-forming ability of tellurides is poorer than that of sulphides and selenides. Glasses made from S and Se consist of irregularly arranged chains and 8-membered rings [2].

Several descriptions of the structure of glass have been developed [3] since Goldschmidt's, but one appears to be dominant only one model, namely the model of Zachariasen and Warren. Goldschmidt noted that in simple oxides glass-forming ability and the radius ratio were correlated: glass-forming ability was associated with a ratio of 0.2-0.4. This, in ionic solids, is associated with tetrahedral distribution of four anions around each cation, which implicates that glasses have structures like those oxides containing tetrahedral polyhedra.

The quality, applicative characteristics and many important physical properties and especially structural characteristics of the binary systems As–S, As–Se and As–Te [4], become richer after introducing two or even three chalcogenide elements into the system. In addition, introducing halogen

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elements in the material leads to the changes in structure, i.e. the chain-structure transforms into space-defined or layer-chain structure.

It has been demonstrated that IR and Raman spectroscopy can be effectively used to study the structure of non-crystalline materials. Namely, the analyses of oscillatory spectra (spectra of IR absorption and reflection, and combinational scattering) of these materials provide valuable information about the types of bonds and structure on the atomic level.

As is known, in accordance with selection rules, only a small number of modes in crystalline materials give contribution to discrete lines in the spectra. In contrast to that, all oscillatory modes of amorphous bodies can become optically active due to violation of the selection rules, caused by the disorder of the material [5].

Considering significant characteristics of the ternary system As–S–Se, As–S–Te, As–Se–Te [6–8] and also results that are related to specific characteristics of chalcogenides and halides, samples of the $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_{x.}$ type were synthesized using cascade heating method. The far-infrared and Raman spectra of those chalcogenides were recorded and discussed in terms of the structural units present.

2. Experimental

The synthesis of complex glasses of the type $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$, for x = 0, 5, 10, 15, 20, 25, 30, 35, 50, 70, 90 and 100 mol% was carried out starting from high-purity elements and employing the regime illustrated in Fig. 1 [9]. The amorphous character of the obtained samples was confirmed by the methods of x-ray diffraction and polarization microscopy.

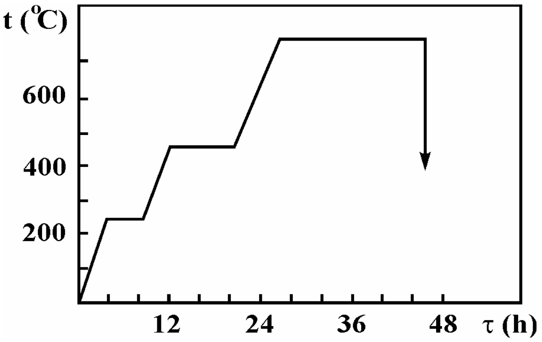

Fig. 1. Diagram of the process for obtaining $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ glasses.

Reflection spectra in the IR range from 2.5 to 20 μm were taken (KBr pellet) on a Perkin Elmer Infracord spectrometer.

Reflection spectra in the far-infrared region were recorded on a BOMEM DA 8 instrument at room temperature. Samples were prepared in the form of plates, 1 to 1.5 mm thick. Raman spectra were recorded on a SPEX (Model 1401, Ind. Inc., Meteuchen, New Jersey) instrument, using Ar-ion laser (Model CR-3 supergraphite, Coherent Radiation Lab., PaloAlto, CA) as a source of electromagnetic radiation.

For excitation of Raman shifts use was made of two wavelengths – blue line at 488 nm and green line at 524.5 nm. The angle between the incident radiation and the detector was 90°.

3. Results and discussion

In Fig. 2 are presented the transparency spectra recorded in the mid-infrared region for the samples with x = 5, 15, 25, 35 and 100 mol % $(AsSe_{0.5}Te_{0.5}I)$ of the glasses $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$. As can be seen, there is a wide region of relatively high transparency, whereby the absorption maxima at about 3450 cm^{-1} and 1600 cm^{-1} are due to the experimental technique and not to the structure of the glasses themselves. Namely, both maxima appear as a consequence of the presence of water in the KBr used (the first is due to the absorption of the H—O—H bond and the other suggests the presence of OH groups) [10]. In view of the fact that vibration energies corresponding to the possible bonds of components of the materials are in the far-infrared region [11], such a transparency pattern is expectable in this energy interval.

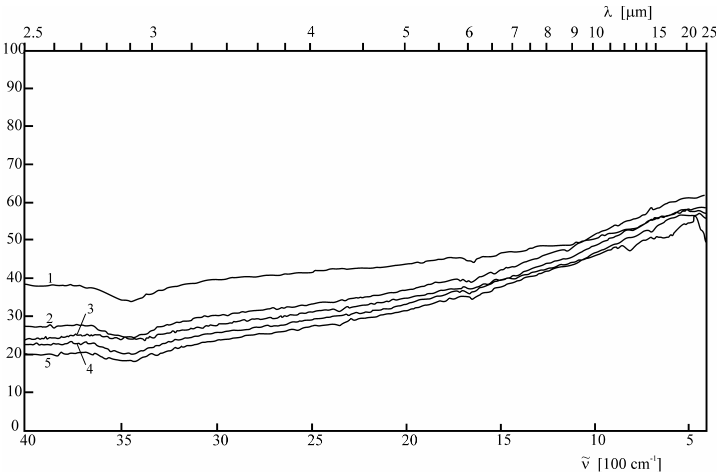

Fig. 2. IR spectra (*KBr pellet*) of the glasses of the type $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$:
1) x=5; 2) x=15; 3) x=25; 4) x=35; 5) x=100.

Fig. 3 shows the relative intensities as a function of Raman shifts for two samples that are representative of the investigated series of glasses (curves A and B), together with the results obtained for the amorphous AsSI (curve C) [12], glassy Se (curve D) [13] and As_2S_3 (curve E) [12].

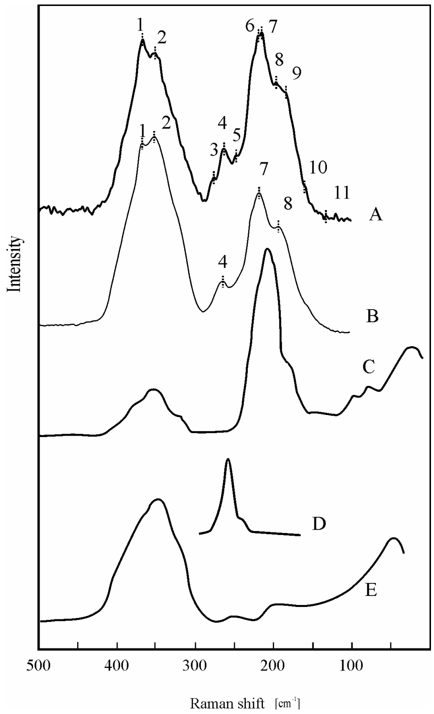

Fig. 3. Raman spectra of the glasses: A) $(As_2S_3)_{70}(AsSe_{0.5}Te_{0.5}I)_{30}$;
B) $(As_2S_3)_{80}(AsSe_{0.5}Te_{0.5}I)_{20}$; C) AsSI [12]; D) Se [13]; E) As_2S_3 [12].

The strong maxima at about 365 cm^{-1} (peak 1 in Fig. 3) are due to oscillation of the As–S bonds occurring in the structural unit AsSI, whereas the maximum at about 350 cm^{1} (peak 2) belongs to the symmetric valence oscillations of the As–S bond in the trigonal pyramids AsS_3 forming the structural units As_2S_3 [12].

The well-defined band in the range of 260–275 cm^{-1} (peaks 3 and 4) is most probably a consequence of the oscillations of bonds in amorphous Se, which may partly appear as free in the glass matrix [14-16]. As a rule, this appears in the spectra of amorphous As_2Se_3 and in the spectra of the majority of complex glasses in which one can expect the presence of structural units of this type.

The relatively poorly-defined peak at about 248 cm^{-1} (peak 5) suggests the presence of oscillations of the As–S bonds in the bipyramids of $AsS_{3/2}$, and the strong peak at 220 cm^{-1} (peak 6) is a consequence of the asymmetric oscillations of the ν_3 mode in the $AsSe_{3/2}$ pyramids. The band at 215 cm^{-1}, i.e. at 218 cm^{-1} (peak 7) is due to stretching vibrations of the bonded atoms of As and I in the structural units AsI_3 [17]. Its high intensity is probably due to the fact that the As–I bond is realized not only in the mentioned compound but also in AsSeI.

The interaction of As and Te corresponds in these spectra to the frequency at about 195 cm^{-1} (peak 8), which is characteristic of the oscillations of the As–Te bond realized in the compound As_2Te_3. The relatively high intensity of this maximum most probably indicates also the oscillations of the S–S bond. It should be mentioned that in the case of identification of the maxima that are due to the S–S or Se–Se bonds, as is the case here, it is supposed that there exist oscillations of the two-atom bridges –S–S– and –Se–Se–, through which the pyramidal structural units $AsS_{3/2}$ (or $AsSe_{3/2}$) are bonded in the glass network [17].

Table 1. Raman spectra results of the glasses $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$.

No. maximum	maximum position: [cm^{-1}]		bond oscillation
	x=30	x=20	
1	365.5	367.5	oscillations of the bonds As—S in AsSI
2	350.0	352.0	symmetric valence oscillations of the bonds As—S in the trigonal AsS_3 pyramids
3	277.0		oscillations of the bonds Se—Se
4	262.5	263.5	
5	248.0		oscillations of the bonds As—S in the $AsS_{3/2}$ bipyramids
6	220.0		asymmetric oscillations of the mode ν_3 in the $AsSe_{3/2}$ pyramids
7	215.0	218.0	stretching vibrations of the bond between As and I atoms in the structural unit AsI_3
8	195.0	193.0	oscillations of the bonds As—Te in As_2Te_3 and of the bonds S—S
9	182.5		deformation oscillations of the bonds As—Se—As in As_2Se_3
10	160.0		deformation oscillations of the molecules As_4S_4
11	132.0		oscillations of Se atoms in the Se_n chains

The peak at about 182 cm^{-1} (peak 9) is characteristic of the deformation oscillations of the As–Se–As bond from the compound As_2Se_3, and the peak at 160 cm^{-1} (peak 10) of deformation oscillations of the As_4S_4 molecule.

The low-intensity maximum at about 130 cm^{-1} (peak 11) may be ascribed to oscillations of the Se atom bound into Se_n chains (characteristic of the oscillation mode E).

In Table 1 are given characteristic values of frequencies with indication of the appropriate bond for the glasses with x = 30 and x = 20.

The decrease of the maximum 1 in comparison with peak 2 when passing from $(As_2S_3)_{70}(AsSe_{0.5}Te_{0.5}I)_{30}$ to $(As_2S_3)_{80}(AsSe_{0.5}Te_{0.5}I)_{20}$, is accompanied by a decrease of the population of iodine, i.e. of the corresponding structural units AsSI and AsSeI.

By comparing experimental results of the Raman shifts for the investigated glasses (curves A and B) with the literature data it can be concluded the following: the peak on experimental curves (4) that corresponds to oscillations of the Se–Se bonds (curve D) is more pronounced for the glasses with x = 30 (curve A). This is a logical consequence of a higher population of the structural unit $AsSe_{0.5}Te_{0.5}I$, i.e. of the larger number of these bonds compared to the glass with x = 20 (curve B). Also, for the glass with x = 30 (curve A) the experimental peak (7), corresponding to oscillations of the bonds with iodine (curve C), is more pronounced. This points to more diversified forms of iodine-containing molecules, i.e. of structural units of the chain (AsSI, AsSeI) or discrete (AsI_3) forms in the materials with higher contents of $AsSe_{0.5}Te_{0.5}I$.

The peak on experimental curves (2) corresponding to oscillations of the As–S bond in the trigonal pyramids forming spatially layered structure of the unit As_2S_3 (curve E) is more pronounced for the glasses with x = 20 (curve B), which is expectable in view of the higher population of this structural unit in the glass $(As_2S_3)_{80}(AsSe_{0.5}Te_{0.5}I)_{20}$.

All the above observations are in agreement with the known fact that the introduction of arsenic into amorphous chalcogens (S, Se and Te) causes polymerisation of macromolecular chains and rings, yielding chain-layered, i.e. trigonal-pyramidal, structural forms. With the glassy As_2S_3, structural units involved are the pyramidal molecules AsS_3, bound by the bridging S atoms. With As_2Se_3, there is a layered arrangement of the atoms. Each layer consists of strips and each strip consists of five rows of atoms. The structure of As_2Se_3 may be described via trigonal pyramids bound into layers or chains and the layers are bound by van der Waals forces. Glassy As_2Te_3 has a layered structure consisting of atomic columns involving six infinite arrays of Te atoms and four As atoms. One half of the arsenic atoms is found on the outer side of the column and each of them is bound to three Te atoms. The other half of arsenic atoms are inside the columns and each As atom of this group is in an almost regular octahedral surroundings of six Te atoms. The introduction of iodine into arsenic compounds with chalcogens yields formation of structural units in the form of AsSeI and AsSI chains and discrete AsI_3.

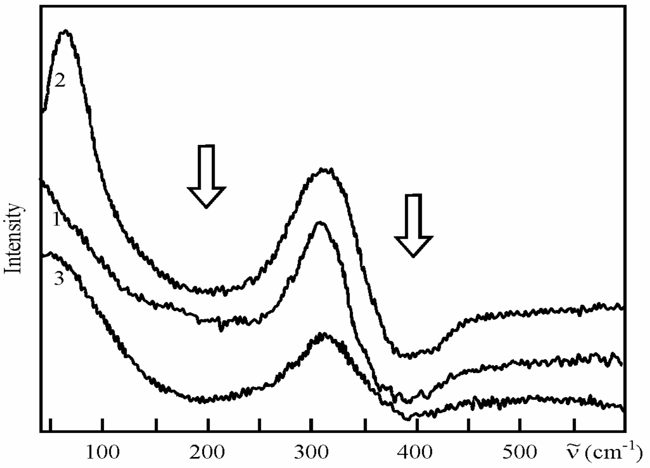

Fig. 4. Reflection spectra recorded in far-infrared region for the glasses $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$: 1) x=5; 2) x=10; 3) x=20.

In Fig. 4 are presented the spectra recorded in the far-infrared region. Of the two broad absorption bands the first at 160-250 cm^{-1} corresponds to the peaks 7-9 in the Raman spectra, i.e. to stretching of the As–I bonds in the compounds AsI_3, AsSI and AsSeI, to oscillations of the bonds As–Te, S–S and As–Se–As. The other broad absorption band from 320 to 410 cm^{-1} corresponds to the peaks 1 and 2 in the Raman spectrum, i.e. to oscillations of the As–S bonds in AsSI and trigonal pyramids AsS_3.

4. Conclusion

The introduction of $AsSe_{0.5}Te_{0.5}I$ into the basic matrix of the glass As_2S_3 results in significant changes of structure.

On the basis of Raman and far-infrared spectra recorded in the interval to 500 cm^{-1}, it was possible to confirm, in a direct or indirect way, the existence of the structural units As_2S_3, As_2Se_3, As_2Te_3, AsI_3, AsSI and AsSeI in the glass matrix. Besides, the Raman spectra pointed to the presence of the excess sulphur (i.e. selenium) atoms, bonded in the form of chains.

The maxima of the Raman spectra clearly indicate oscillations of the bonds existing in the postulated structural units. Thus, the detected maxima stand for oscillations of the bonds As–S (in AsSI); As–S (in trigonal pyramids AsS_3); Se–Se (in amorphous Se, which may partly appear as free in the glass network); As–S (in the bipyramids $AsS_{3/2}$); As–I (in the structural units AsI_3 and As–Se–I); As–Te (in As_2Te_3); oscillations of the two-atom –S–S–, i.e. –Se–Se– bridges (connecting the pyramidal structural units $AsS_{3/2}$ or $AsSe_{3/2}$ in the glass lattice); deformation oscillations As–Se–As (in As_2Se_3).

By comparing the experimental results obtained for Raman shifts in the spectra of the investigated glasses with the corresponding literature data it can be seen that the peaks of the experimental curves corresponding to oscillations of the Se–Se bonds and the bonds with iodine are more pronounced in the case of samples with a higher content of the structural unit $AsSe_{0.5}Te_{0.5}I$ in its composition. Also, it is evident that the experimental peak corresponding to oscillations of the As–S bond in the trigonal pyramids that form a layered structure of the As_2S_3 unit are more pronounced with the glasses with a higher content of As_2S_3. This suggests a more diversified involvement of iodine-containing molecules, i.e. of the structural elements of the chain (AsSI, AsSeI) or discrete (AsI_3) forms, with the materials with a higher content of $AsSe_{0.5}Te_{0.5}I$. The absorption bands in the spectra recorded in the far-infrared region at room temperature correspond to the peaks in the Raman spectra, i.e. to oscillations of the bonds in the postulated structural units.

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