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The influence of obtaining and heat treatment conditions on the structure of As_2S_3-SbSI system

V.M. Rubish[1], L. Bih[2], O.A. Mykaylo[3], O.V. Gorina[1], V.M. Maryan[1], S.M. Gasinets[1], A.M. Solomon[4], P. Lazor[5], S.O. Kostyukevych[6]

[1]*Uzhgorod Scientific-Technological Center of the Institute for Information Recording, NAS of Ukraine, 4, Zamkovi Skhody str., 88000 Uzhhorod, Ukraine, e-mail: center.uzh@gmail.com*

[2]*UFR-PCMI: ceramiques et verres, FST-Errachidia, 52000, B.P. 509, Boutalamine, Errachidia, Morocco*

[3]*Institute of Solid State Physics & Chemistry, Uzhhorod National University, 36, Pidgirna str., 88000 Uzhhorod, Ukraine*

[4]*Institute of Electron Physics, NAS of Ukraine, 21, Universitetska str., 88017 Uzhhorod, Ukraine*

[5]*Institute of Earth Science, Uppsala University, S-752 36 Uppsala, Sweden*

[6]*V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 03028 Kyiv, Ukraine*

Abstract. $(As_2S_3)_{100-x}(SbSI)_x$ (x = 80 and 90) glasses were prepared by cooling homogenized melts from 720…750 K in cold water. Their structure and structural changes under heat treatment of glasses are confirmed by studies of micro-Raman scattering and X-ray diffraction. In the matrix of these glasses, we observed SbSI nanocrystalline inclusions. It has been shown that the sizes of crystalline inclusions are dependent on the heat treatment regimes.

Keywords: chalcogenide glasses, ferroelectrics, Raman spectra, X-ray diffraction, structure, nanocrystal.

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1. Introduction

The interest to the studies of glass materials based on antimony sulfoiodide (SbSI) that is the typical representative of the class of $A^{V}B^{VI}C^{VII}$ ferroelectric semiconductors and possesses excellent dielectric, photo-, pyro-, piezo-electric and pyro-optic properties [1] is caused by the possibility of using it as a basic material for production of nonvolatile memory devices, ferroelectric glass ceramics with preset parameters, pyro- and piezo-electric detectors, actuators [2 - 4].

It was shown that in the matrix of SbSI glass [5] and in the matrix of $(As_2S_3)_{100-x}(SbSI)_x$, $(As_2Se_3)_{100-x}(SbSI)_x$, $(GeS_2)_{100-x}(SbSI)_x$ glasses [6-11] at the certain thermal treatment temperature and duration regimes one could obtain crystallites of a targeted size and orientation, possessing ferroelectric properties. There is also a report on the fabrication of SbSI crystal inclusions in the matrix of As_2S_3-SbSI [12, 13] and GeS_2-SbSI [14] glasses under laser beam treatment.

However, obtaining glassy SbSI and $(As_2S_3)_{100-x}(SbSI)_x$, $(As_2Se_3)_{100-x}(SbSI)_x$, $(GeS_2)_{100-x}(SbSI)_x$ glasses with $x \geq 80$ encounters considerable technological difficulties due to the high crystallization ability of its melts [11, 12]. For example, SbSI can be obtained in the glass form only in a hard quenching regime at the melt cooling rates within the range 200…300 K/s and in the small amounts (1…2 g) [5, 15]. The structure and physical properties of glasses can be modified in different ways: variations of a ratio of the starting components; preparation of the glasses at the different regimes of synthesis (homogenization temperatures of the melts and melt cooling rates); physical treatments (annealing, optical irradiation, etc.) [16, 17].

Earlier we have detected the amorphous nature of the structure of $(As_2S_3)_{100-x}(SbSI)_x$ (x = 80, 90) glasses that were prepared by cooling the melts at homogenization temperatures 850 to 870 K in cold water [8, 9]. The reason lies in too high cooling rates of melts that suppress the nucleation processes in cooled melts.

In this paper, we focused our attention at the influence of glass preparation conditions and heat treatment on formation of SbSI crystals in the matrix of $(As_2S_3)_{20}(SbSI)_{80}$ and $(As_2S_3)_{10}(SbSI)_{90}$ glasses.

2. Experimental

$(As_2S_3)_{100-x}(SbSI)_x$ (x = 80 and 90) glasses were prepared using the vacuum melting method (~0.01 Pa) of the relevant mixture of As_2S_3 and SbSI components, preliminary synthesized from high-purity elemental substances. Glassy As_2S_3 was obtained by cooling a homogenized (for 48 h) melt from 780 K in air. Polycrystalline SbSI was obtained by slow cooling the homogenized (for 72 h) melt from 900 K to room temperature. $(As_2S_3)_{100-x}(SbSI)_x$ melts were homogenized at 720…750 K for 24 h. The melts were periodically stirred. Cooling the melts was carried out in cold water.

Raman spectra were measured using the micro-Raman spectrometer LABRAM and He – Ne laser (λ = 632.8 nm). Used in these measurement was laser radiation of a low power (P < 3 mW). In this case, the samples were not undergone to photostructural transformations as well as the heating the samples.

X-ray diffraction studies of glassy, crystallized and crystalline materials were carried out on a ДРОН-3 X-ray apparatus (λ = 1.5418 Å).

3. Results and discussion

Raman spectra of $(As_2S_3)_{100-x}(SbSI)_x$ glasses with x = 80 and 90 are shown in Fig. 1 (curves *1* and *7*). The glass spectrum with x = 80 contains broad intense bands with the maxima at 110, 153 and 315 cm^{-1} and a feature (as a shoulder) at 363 cm^{-1} (Fig. 1, curve *7*). The Raman spectrum of x = 90 glass contains similar bands at 111, 155, 313 and 363 cm^{-1} (Fig. 1, curve *1*).

Previously, the Raman spectra of the same compositions for glasses of the As_2S_3-SbSI system have been investigated [9, 18], but they were obtained after quenching the melt from the temperatures of 850…870 K in cold water. In this case, Raman spectra performed in 180-degree geometry using a spectrophotometer DFS-24 and He – Ne laser (λ = 630 nm) at the room temperature. The intense bands at 314…316 and 156...160 cm^{-1} and the weak features at the 206…209, 360…367 and 426...493 cm^{-1} were found in Raman spectra of these glasses. The bands at 156…160 and 206...209 cm^{-1} are due to the vibrations of Sb and I atomic pairs, and As and I ones in the trigonal pyramids of SbI_3 and AsI_3, respectively, while the bands in the region of 314...316 cm^{-1} are responsible for the vibrations of atomic pairs of antimony, arsenic and sulfur in the structural groups of SbS_3 and AsS_3, interconnected via two coordinated sulfur atoms. Note that in As_2S_3 glass a broad band observed at 343 cm^{-1} is related to the symmetric stretching vibrational modes of $AsS_{3/2}$ pyramids (AsS_3 pyramids linked together by As - S - As bonds) [19-21]. In Raman spectra of Sb_2S_3 glass, the intense broad band caused by vibrations of $SbS_{3/2}$ structural groups is observed at 290...293 cm^{-1} [17, 22]. The presence of weak features at 365…367 and 426...493 cm^{-1} indicates an existence in the matrix of As_2S_3-SbSI glasses the certain amount of structural fragments with homopolar bonds As - As and S - S. In Raman spectra of studied glasses, there were not observed the features that could indicate the existence in the matrix of glasses the ternary chain structural units of $SbS_{2/2}I$, which built the crystalline lattice of SbSI [1, 23]. Raman spectra and X-ray powder diffraction patterns of the annealed glasses demonstrated the features that were characteristic for crystalline SbSI [8, 9, 18].

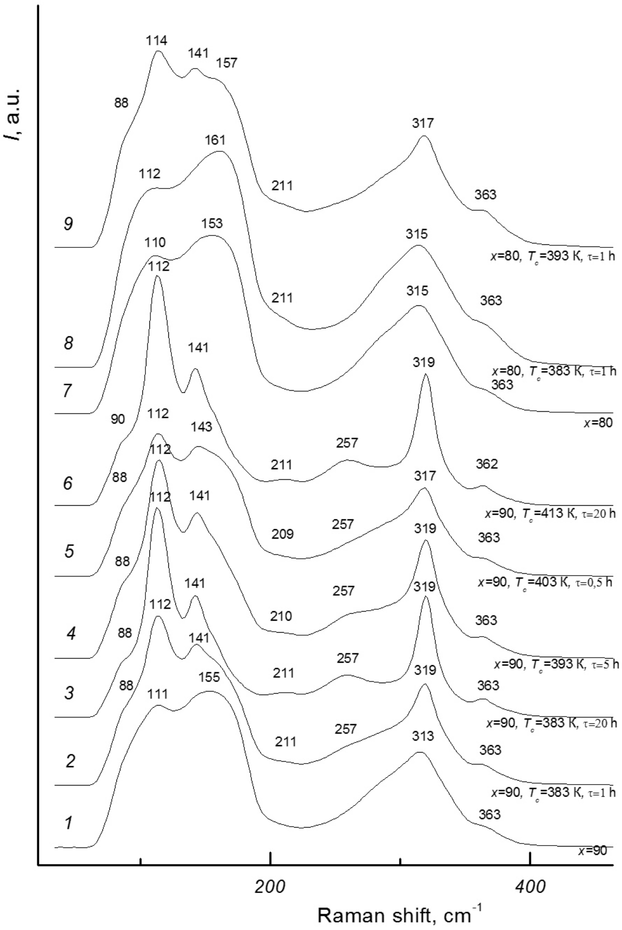

Fig. 1. Raman spectra of as-prepared (*1*, *7*) and crystallized at the different annealing temperatures T_c and times τ (*2–6*, *8*, *9*) $(As_2S_3)_{100-x}(SbSI)_x$ glasses.

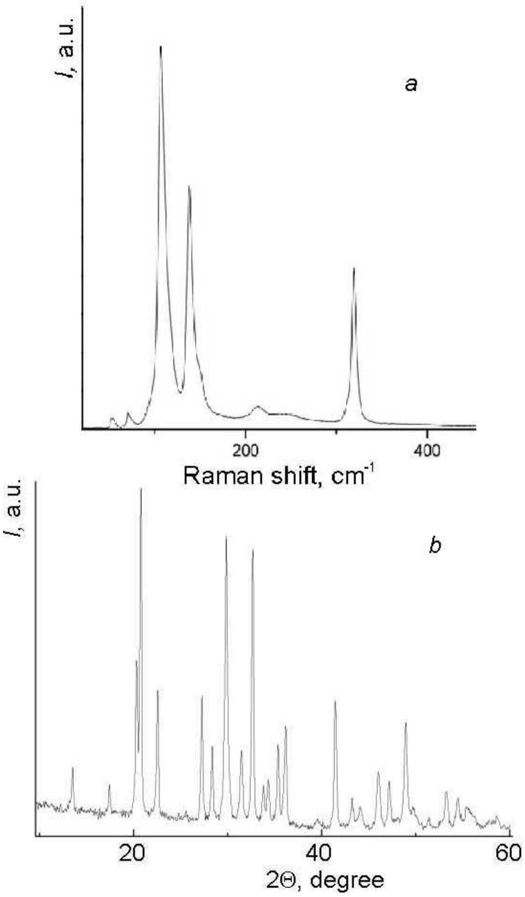

Fig. 2. Raman spectra (*a*) and X-ray powder diffraction pattern (*b*) of polycrystalline SbSI.

As a result of these studies, it was concluded that the glasses of As_2S_3-SbSI system have the nanoheterogeneous structure. The matrix of these glasses is built basically just of binary structural groups of $Sb(As)S_{3/2}$ and $Sb(As)I_3$, also contains small amounts of molecular fragments with homopolar As - As and S - S bonds. The breaking and switching of As - S, Sb - S, As - I, Sb - I chemical bonds in binary structural groups occur when heating in the temperature range of $T_g - T_c$ with simultaneous formation of the triple chain groups $SbS_{2/2}I$, which is characteristic for sulfoiodide antimony crystals.

A comparison of Raman spectra of $(As_2S_3)_{100-x}(SbSI)_x$ (x = 80 and 90) glasses and the data presented in [9, 18] shows that the spectra of glasses, obtained at the melt homogenization temperatures 720…750 K, differ from the Raman spectra for the same composition glasses but obtained at homogenization temperatures 850…870 K by the presence of the additional band with maximum at 111 (x = 90) and 110 ($x = 80$) cm^{-1}. The similar band ($107...110\,\text{cm}^{-1}$) is observed in the Raman spectra of the single crystal [24, 25] and polycrystalline antimony sulfoiodide (Fig. 2a), also in crystallized glasses of the As_2S_3-SbSI system [8, 9, 18]. This fact may testify to the presence of nanocrystalline inclusions of SbSI in the matrix glasses, obtained in less rigid hardening conditions. In the course of cooling the melts from lower homogenization temperatures (700 to 720 K), and, accordingly, at lower cooling rates, it wasn't possible to completely suppress the processes of nucleation and crystal growth. The strong smeared band at $110...111\,\text{cm}^{-1}$ may indicate the existence of nanosize crystals.

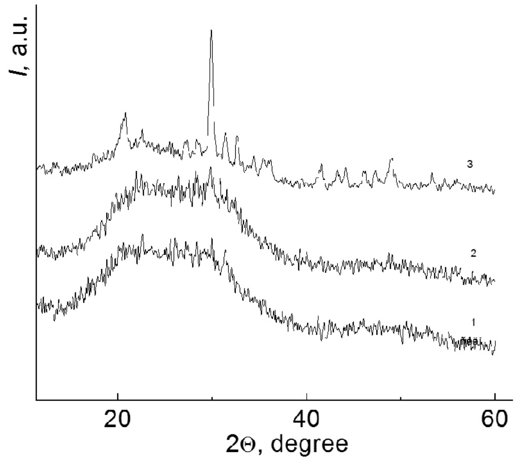

Fig. 3. X-ray powder diffraction patterns of as-prepared (*1*) and crystallized (*2*, *3*) $(As_2S_3)_{20}(SbSI)_{80}$ glasses. The annealing temperature T_a and annealing time τ: *2* – 383 K, 1 h; 3 – 393 K, 1 h.

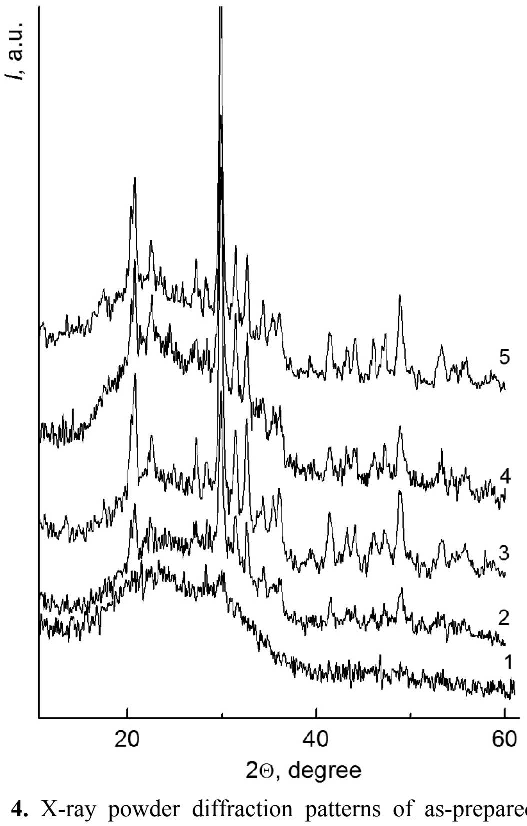

Fig. 4. X-ray powder diffraction patterns of as-prepared (*1*) and annealed (*2* – *5*) $(As_2S_3)_{10}(SbSI)_{90}$ glasses. The annealing temperature T_a and annealing time τ: *2* – 383 K, 1 h; *3* – 383 K, 20 h; *4* – 393 K, 5 h; *5* – 413 K, 20 h.

A confirmation of the presence of nanocrystalline SbSI inclusions in the matrix of glasses obtained from 720 to 750 K could be deduced from the results of X-ray diffraction studies. The X-ray powder diffraction patterns of as-prepared $(As_2S_3)_{20}(SbSI)_{80}$ and $(As_2S_3)_{10}(SbSI)_{90}$ glasses are shown in Fig. 3 (curve *1*) and Fig. 4 (curve *1*). It is clear that they have the weak reflexes, which positions satisfactorily coincide with the positions of intense lines in the diffraction pattern of polycrystalline SbSI (Fig. 2, curve *6*). With increasing the annealing temperature and annealing time, the intensity of reflexes increases (Fig. 3, curves *2* and *3*, Fig. 4, curves 2 - 5), and their half-width decreases. This fact may be considered as the evidence about increasing the size of SbSI crystalline inclusions in the glass matrix.

The Raman spectra of glasses annealed for different times and temperatures contain the intense bands with maxima at 113…114, 141…143 and $315...319\,\mathrm{cm}^{-1}$ (Fig. 1), which clearly indicates the presence of SbSI crystalline inclusions in their matrix. During annealing, the crystallization process is more active and involves diffusion of atoms, and increasing the size of SbSI crystalline inclusions occurs. The evidence of this fact could be the intensity growth of the basic bands in Raman spectra, decrease in their half-widths and their similarity to those obtained for SbSI crystal [24, 25, 27] (see Fig. 1, curves 2 - 6 and bands at 209…211 and $257\,\mathrm{cm}^{-1}$).

4. Conclusions

$(As_2S_3)_{100-x}(SbSI)_x$ glasses were obtained at lower homogenization temperatures and investigated by micro-Raman spectroscopy and X-ray diffraction. The presence of nanocrystalline SbSI inclusions in the glassy matrix was detected. The sizes of SbSI crystalline inclusions increase with annealing temperature and annealing time.

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