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# X-Ray diffraction and Raman spectra of $As_4S_3Se_3$-Sn glasses

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The XRD measurements showed that the Sn atoms introduced in $As_4S_3Se_3$-Sn glasses (Sn=0÷10 %) don't change essentially the shape of the first sharp diffraction peak (FSDP) of the X-ray diffraction patterns, the intensity and the position of the FSDP non-monotoniously depend on the Sn concentration. Raman spectroscopy is an efficient method for obtaining information on the local structure of the disordered material, especially when the composition is varied. In this paper the Raman spectra of $As_4S_3Se_3$-Sn glasses are presented. The Raman spectra consist of two broad bands located at around $\nu$=236 $cm^{-1}$ and $\nu$=341 $cm^{-1}$, which corresponds to the symmetric stretching vibration modes of $AsSe_{3/2}$ and $AsS_{3/2}$ pyramids, respectively. Tin impurities didn't change the shape of Raman spectra, but shift the both bands to low frequency region.

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*Keywords:* Chalcogenide glasses, X-ray diffraction, Amorphous thin films, Raman spectra

## 1. Introduction

Ghalcogenide glassy $As_2S_3$, $As_2Se_3$ and $As_2S_3$-$As_2Se_3$ are promising candidates for optoelectronic applications due to high chemical stability, high transmission in the IR region (up to 12 μm), high refractive index ($n\approx2.4\div2.8$), and low phonon energy. The noncrystalline semiconductors preserve a *short range order (SRO)* in a range of 0.3-0.5 nm and are characterized by the existence of a correlation in the first atomic coordination sphere. In the case of dominantly covalently bounded amorphous solids, SRO is described by local coordination polygons, e.g., pyramidal $AsS_3$ ($AsSe_3$) in $As_2S_3$ ($As_2Se_3$). In many amorphous semiconductors, such as chalcogenide glasses, this order is shown at longer distances, the so-called *medium range order (MRO)* which extends up to a range of 0.5-1.0 nm [1]. Optical investigation such as infrared reflectance and Raman spectroscopy are efficient tools for obtaining information on the local structure of the disordered material, especially when the composition is varied [2,3]. It was shown that doping of chalcogenide glasses with metal impurities shift the main bands to the high frequency region and lead to the appearance of the additional vibration bands in the low frequency spectral range [3,4]. Some experimental results on the Raman spectroscopy studies of the $As_{40}S_{60-x}Se_x$ glasses are discussed in [5]. The Raman investigations revealed some increased of the non-stoichiometric $Se_n$ and $As_4S_4$ fragments for the intermediate compositions which are explained by the isovalent substitution of Se on S atoms in $As_{40}S_{60-x}Se_x$ glasses with the composition change. The investigations of $As_{40}S_{60-x}Se_x$ films doped with Ag and Cu show the shift of the main bands to the high frequency region of the Raman spectra, and lead to the appearance of the additional scattering bands in the low frequency spectral range [6]. It was suggested that these features in the Raman spectra of photo-doped with Ag and Cu amorphous films are consistent with the supposition concerning normal covalent and coordinative bond formation between metal additives and chalcogenide atoms. Some results on the Raman spectra of $As_4S_3Se_3$-Sn glasses were reported in [7]. It was shown that the tin impurities in the host glass shift the position of the vibration modes situated at $\nu$=236 $cm^{-1}$ and $\nu$=341 $cm^{-1}$ to lower frequencies, and increase the full width at half maximum (FWHM) values. In the present paper we report the experimental results on X-ray diffraction experiments and Raman spectra of $As_4S_3Se_3$-Sn glasses.

## 2. Experimental

The bulk $As_4S_3Se_3$-Sn (Sn=0÷10.0 %) chalcogenide glasses were prepared from the elements of 6N (As, S, Se, Sn) purity by conventional melt quenching method. The starting components elements $As_4S_3Se_3$ and Sn were mixed in quartz ampoules and then evacuated to pressure of $P\sim10^{-5}$ torr, sealed and heated to temperature $T$=900 °C at the rate of 1 °C/min. The quartz tubes were held at this temperature for 48 hours for the homogenization and then slowly quenched in the furnace. The X-ray diffraction (XRD) measurements were performed on DRON-UM1 diffractometer with $Fe$-$K\alpha$ radiation ($\lambda$=1.93604 Å), with Mn filter by $\theta/2\theta$ scanning method. The Micro-Raman measurements was performed using a Horiba LabRam 800 with an CW excitation working at $\lambda$=633 nm (P=17 mW) and at $\lambda$=532 nm (50 mW), in the spectral range $\nu$=100-2500 cm$^{-1}$. The 800 focal length spectrograph was equipped with two switcheable gratings in the spectral range $\lambda$=200 – 1600 nm. The spectral resolution in the UV region was $\nu$=1.5 cm$^{-1}$, in the VIS region - $\nu$=0.6 cm$^{-1}$, and in the NIR region $\nu$=0.3 cm$^{-1}$.

## 3. Experimental Results and Discussion

Using the X-Ray diffraction method were obtained the diffraction patterns in the range of diffraction angles $2\theta$ from 10$^{o}$ to 80$^{o}$ ($\theta$ is the Bragg angle) for the chalcogenide glasses $As_2S_3$, $As_2Se_3$, $As_4S_3Se_3$, and $As_4S_3Se_3$-Sn.

Fig.1 indicates the angular distribution of X-Ray diffraction intensity for $As_2S_3$, $As_2Se_3$, and $As_4S_3Se_3$ glasses. The position of the first sharp diffraction peak (FSDP) for $As_2S_3$ is $2\theta$=22.47$^{o}$ and increase up to $2\theta$=24.60$^{o}$ for $As_2Se_3$. For the intermediate composition $As_4S_3Se_3$ the maximum of the FSDP is situated at $2\theta$=23.00$^{o}$.

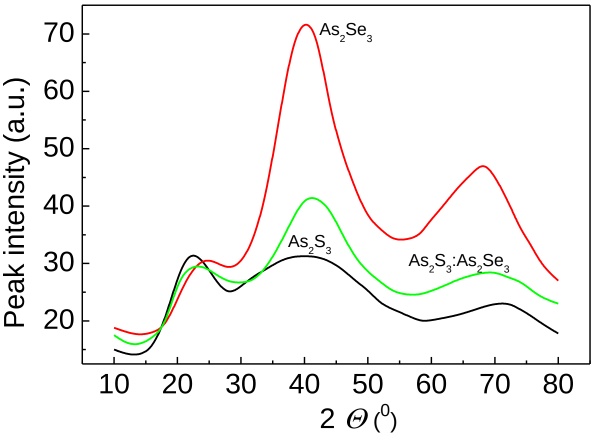


*Fig.1. The X-Ray diffraction patterns for $As_2S_3$, $As_2Se_3$, and $As_4S_3Se_3$ glasses.*

These spectra represent a sum of diffraction patterns of izostructural vitreous $As_2S_3$ and $As_2Se_3$ with three broad lines of diffractograms and which are similar to the unvelope of the rounded lines of the spectra of crystalline $As_2S_3$ and $As_2Se_3$. It can be assume about the microcrystalline state of the investigated glasses – existense of domains with ordered structure with dimensions about 15 – 20 Å. Previously a analogy between the structure of vitreous and crystalline states of $As_2S_3$ was vindicated by short-range order investigations – interatomic distances and coordination numbers – with the add of the radial distribution function [8].

The carefull investigations of the FSDP of viteous $As_2S_3$ and $As_2Se_3$ show that they have a similar structure [1]. According to [1], the first coordination spheres (first order neighbour position) of a central atom in the structure is $r_1$=2.414 Å for $As_2Se_3$, and $r_1$=2.306 Å for $As_2S_3$, respectively. The second coordination spheres (second order neighbour position) of a central atom in the structure is $r_1$=3.625 Å for $As_2Se_3$, and $r_1$=3.475 Å for $As_2S_3$, respectively. It was established that between $As_2S_3$ and $As_2Se_3$ layers act Van der Waals forces with a reduced covalent component. The interaction forces between layers are hundred times weaker than the binding forces between the layers.

According the [1], the structure of the glasses represent as an interliking of As-$S_3$ and As-$Se_3$ pyramids that forms rings with 6 units. The arsenic atoms are situated at the top of the pyramid, while the chalcogen atoms form the basis. As was shown, the crystalline semiconductors are characterized by long-range order (LRO), i.e. there is a good correlation between the position in the network, of the each two atoms, that can't be said about the non-crystalline semiconductors [9,10]. For non-crystalline semiconductors, there is only short-range order (SRO), which belongs to the individual atoms in the first coordination sphere. As in chalcogenide glasses range order can be extended to several interatomic distances, the new concept of the average order was introduced (MRO).

The Sn concentration in the mixted glasses $As_4S_3Se_3$-Sn essentially don't change the shape of the FSDP of the X-ray diffraction patterns (Fig.2).

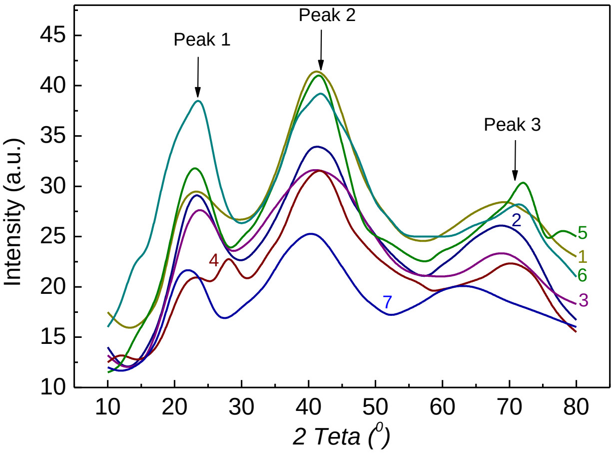


*Fig.2. The X-Ray diffraction patterns for $As_4S_3Se_3$-Sn glasses (Sn=1-0, 2-1.0, 3-2.0, 4-4.0, 5-6.0, 6-7.0, and 7-10.0.*

In general, the diffraction patterns of the $As_4S_3Se_3$-Sn glasses are similar and form three wide lines, the maxima of which correspond to the interlayer distances $d$~4.8 – 2.8

– 1.7 Å. As in the case of $As_2Se_3$:$Sn_x$ [10], the angular position of the FSDP in the $As_4S_3Se_3$-Sn slightly depend on the Sn concentration. The three diffraction peaks of chalcogenide glass $As_4S_3Se_3$-Sn are situated at $2\theta$~22÷24°, $2\theta$~40÷42°, and $2\theta$~62÷70°, respectively.

Fig. 3 represents the Raman spectra of bulk $As_2S_3$ (1), $As_2Se_3$ (2), and $As_4S_3Se_3$ (3) chalcogenide glasses. The Raman spectra of $As_4S_3Se_3$ glasses (curve 3) consist of two broad bands located at around $\nu$=236 $cm^{-1}$ and $\nu$=341 $cm^{-1}$, which corresponds to the main vibration modes of vitreous $As_2Se_3$ and $As_2S_3$ (curves 1 and 2), and are attributed to the symmetric stretching vibration modes of $AsSe_{3/2}$ and $AsS_{3/2}$ pyramids, respectively [3,4].

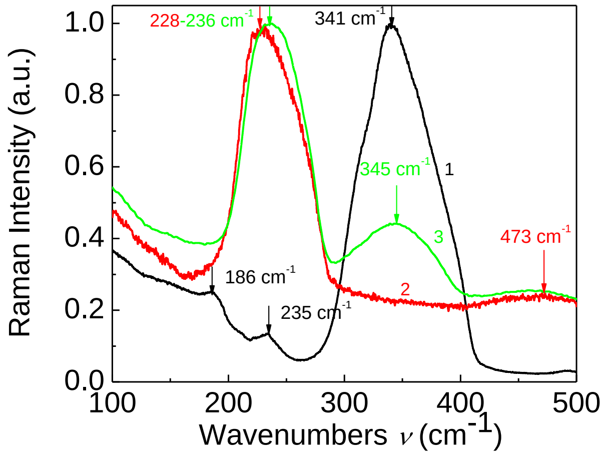


*Fig.3. The Raman spectra of bulk $As_2S_3$ (1), $As_2Se_3$ (2), and $As_4S_3Se_3$ (3) chalcogenide glasses.*

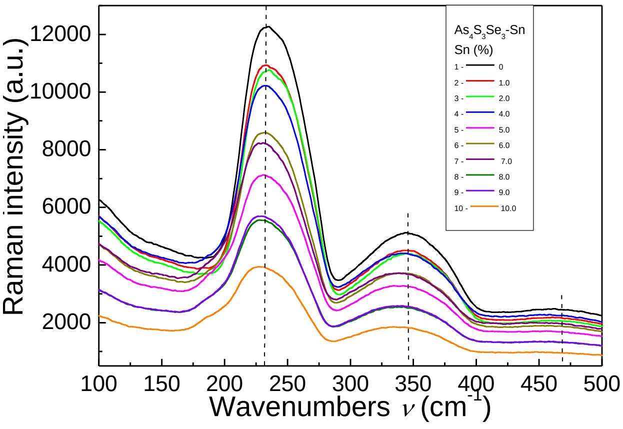


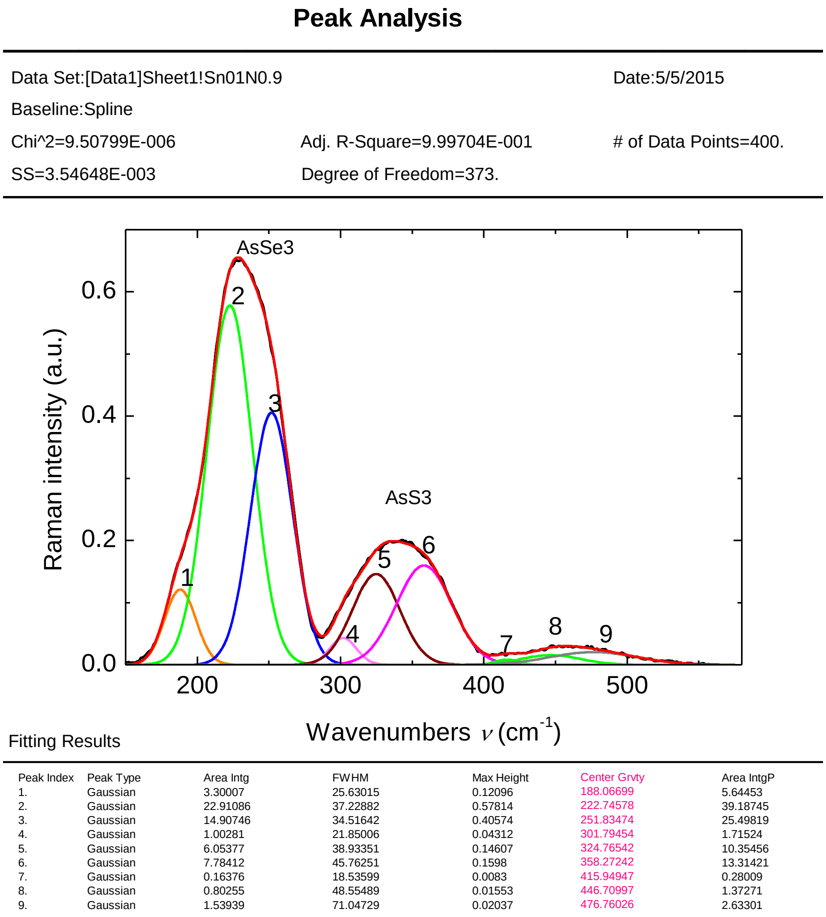
*Fig.4. The Raman spectra of bulk $As_4S_3Se_3$-Sn chalcogenide glasses.*

The normalized Raman spectra of bulk $As_4S_3Se_3$-Sn chalcogenide glasses are presented in Fig.4. For all investigated glasses the Raman spectra contain the vibration bands characteristic for vitreous $As_2Se_3$ and $As_2S_3$. The tin impurities decries the intensity peacs located around $\nu$=236 $cm^{-1}$ and $\nu$=341 $cm^{-1}$, which corresponds to the main vibration modes of vitreous $As_2Se_3$ and $As_2S_3$.

Tin impurities in the host glass shift the main bands situated at $\nu$=236 $cm^{-1}$ and $\nu$=341 $cm^{-1}$ towards the low frequency region of the spectra, and lead to the appearance of new vibration band located at around $\nu$=185 $cm^{-1}$, as was observed in the case of $As_{50}Se_{50}$ doped with 7.5 at.%Sn [3,11].

Peak analysis using the deconvolution procedure for bulk $As_4S_3Se_3$-Sn chalcogenide glasses show some features at the frequencies $\nu$=188.07, 222.74, 251.83, 301.79, 324.76, 358.27, 415.95, 446.71, 476.76 $cm^{-1}$. (Fig.5). From Raman spectroscopy of glasses $As_{40}S_xSe_{60-x}$ were determined and calculated by Gaussian software based on Density functional theory the frequencies of $AsS_nSe_{3-n}$ clusters [12]. According to this work, the vibrational frequencies around $\nu$=222.74, 251.83, 324.76, 358.27 $cm^{-1}$ can be attributed to the clusters of molecular type $AsSe_3$, $AsSSe_2$, $AsS_2Se$ and $AsS_3$, respectively. According to [12] the shift of main Raman scattering frequency of structural units of $AsS_nSe_{3-n}$ pyramids in the Raman spectroscopy of $As_{40}S_xSe_{60-x}$ glasses can be attributed to the alteration of the nearest neighbor local surroundings with different ratios of S/Se.

The shift of the of the vibration bands situated at $\nu$=236 $cm^{-1}$ and $\nu$=341 $cm^{-1}$ with increasing of tin concentration up to 10.0 %Sn takes a values of $\Delta\nu_1$=7.69 $cm^{-1}$ and $\Delta\nu_2$=10.71 $cm^{-1}$, respectively. At the same time the FWHM peak increase ($\Delta\nu_{FWHM}$=23.42 $cm^{-1}$) with increasing of Sn concentration up to 10.0 %Sn in the glasses.



**Peak Analysis**

Data Set:[Data1]Sheet1!Sn01N0.9 Date:5/5/2015
Baseline:Spline
Chi^2=9.50799E-006 Adj. R-Square=9.99704E-001 # of Data Points=400.
SS=3.54648E-003 Degree of Freedom=373.

Fitting Results

| Peak Index | Peak Type | Area Intg | FWHM | Max Height | Center Grvty | Area IntgP |
|---|---|---|---|---|---|---|
| 1. | Gaussian | 3.30007 | 25.63015 | 0.12096 | 188.06699 | 5.64453 |
| 2. | Gaussian | 22.91086 | 37.22882 | 0.57814 | 222.74578 | 39.18745 |
| 3. | Gaussian | 14.90746 | 34.51642 | 0.40574 | 251.83474 | 25.49819 |
| 4. | Gaussian | 1.00281 | 21.85006 | 0.04312 | 301.79454 | 1.71524 |
| 5. | Gaussian | 6.05377 | 38.93351 | 0.14607 | 324.76542 | 10.35456 |
| 6. | Gaussian | 7.78412 | 45.76251 | 0.1598 | 358.27242 | 13.31421 |
| 7. | Gaussian | 0.16376 | 18.53599 | 0.0083 | 415.94947 | 0.28009 |
| 8. | Gaussian | 0.80255 | 48.55489 | 0.01553 | 446.70997 | 1.37271 |
| 9. | Gaussian | 1.53939 | 71.04729 | 0.02037 | 476.76026 | 2.63301 |

*Fig. 5. Deconvolution of the Raman spectra of bulk $As_4S_3Se_3$-Sn glasses (Sn= 10%).*

## 4. Summary

The XRD measurements showed that the Sn impurities in the $As_4S_3Se_3$-Sn essentially don't change the shape of the first sharp diffraction peak (FSDP) of the X-ray diffraction patterns, the intensity and the position of the FSDP non-monotoniously depend on the Sn concentration. Adding of $As_2Se_3$ in $As_2S_3$ shifts the FSDP towards higher diffraction angles from $2\theta=22.47^o$ for $As_2S_3$ up to $2\theta=24.60^o$ for $As_2Se_3$. The FSDP intensity increases around 5.0÷7.0 % Sn in the $As_4S_3Se_3$-Sn glasses. It was shown that Sn impurity shifts the main Raman spectra main vibration bands in the low frequency region. The maximums situated at around $\nu=236$ $cm^{-1}$ and $\nu=345$ $cm^{-1}$ in the Raman spectra are characteristic for all investigated glass compositions and are attributed to the symmetric stretching vibration modes of $AsSe_{3/2}$ and $AsS_{3/2}$ pyramids, respectively.

## Acknowledgment

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