

Structure of bulk glassy As_2Se_3 and As_2S_3

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The structure of bulk glassy As_2Se_3 has been investigated by X-ray diffraction. The structure was compared with that of bulk glass As_2S_3 measured in the same conditions. Similarities and differences have been pointed out.

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1. Introduction

The chalcogenide glasses are important materials for optoelectronics [1-39]. Many applications are related to the use in fiber optics, optical devices, smart memories, filters, etc. [40-51]. Binary and especially ternary compositions can be tailored in order to exhibit the best properties for every application [52-75]. Although the thin amorphous chalcogenide films are broadly used for devices, bulk glassy samples are important both for the fundamental investigation of the particularities of the phenomena in the disordered state and for special applications.

The structure at the atomic scale is one of the most important problems in the physics of amorphous materials in general and non-crystalline chalcogenide materials in particular. The short-range order in a given solid (SRO) is related to the chemical bonding. Therefore, a deep similarity does exist between the SRO in crystalline and in non-crystalline state of the same material composition. The medium range order (MRO) or intermediate range order (IRO) is defined by the correlation between the positions of the atoms in the range 0.5 – 1.0 nm, in excess of those expected for an ideal Zachariasen-type continuous random network characterized by a random dihedral angle distribution.

It is very unlikely that a detailed physical theory will succeed to relate all macroscopic properties of a glass with atomic processes, without providing practical means for defining the atomic scale geometry and bonding.

The signature of MRO in covalently bonded glasses (and especially in low dimensional glasses, as e.g. chalcogenides, pnictides, etc.) is the first sharp diffraction peak (FSDP) or pre-peak in the X-ray diffraction pattern $I(Q)$. The intensity, half-width, and position of this peak on the scale of the scattering vector, Q , are characteristic for every material. The FSDP of a non-crystalline solid exhibits high sensitivity against temperature, pressure, light and nuclear particle irradiation [76, 26].

The FSDP is situated at low Q values (1.0-1.5 $\text{\AA}^{-1}$) and arises probably from correlation at the distances of 4.5

– 6.0 $\text{\AA}$ rather from simple nearest or next nearest neighbors.

In this paper we report our results of X-ray diffraction investigation of As_2Se_3 bulk amorphous sample and compare the results with those obtained from the investigation of bulk As_2S_3 sample.

2. Experimental

Very pure As_2Se_3 ingot were prepared by Prof. M. F. Churbanov et al. in the Institute of Ultra pure Compounds of the Russian Academy of Sciences, Nizhni-Novgorod (Russia) and kindly offered to us. Pure As_2S_3 glassy ingot was prepared in Center of Optoelectronics Kishinau, Moldova, and kindly offered to us by Prof. M. S. Iovu.

The investigation of the glassy samples have been made by X-ray diffraction using a TUR M-62 diffractometer provided with copper target tube and proportional counter for X-ray quanta detection. The following conditions were kept constant for both types of samples: arsenic selenide and arsenic sulphide.

- X-ray emitted radiation: wavelength = 0.154178 nm;

- Scattering angle range: $0.5 \div 74.5^\circ$ (theta);

- Angular step: 0.25° (theta);

- Measuring time per angular position: 100 s.

The X-ray diffraction factors were corrected for air scattering effect and Compton scattering. Thereafter, using special computing programs, the Fourier transforms of the diffraction curves have been calculated and the coordination spheres of both materials have been determined.

The careful investigation of the first sharp diffraction peak, allowed for characterization of the medium range order in the structure.

3. Results

3.1 As_2Se_3

The X-ray scattering factor of the As_2Se_3 glassy ingot is presented in Fig. 1. The curve exhibits a first narrow

diffraction peak (FSDP), followed by several large maxima characteristic for the scattering in non-crystalline materials.

In order to carry out the Fourier transformation of the diffraction curve, we have calculated the independent scattering curve for the atomic composition of the sample. The independent scattering curve is represented on the Fig. 1 (the smooth curve without maxima).

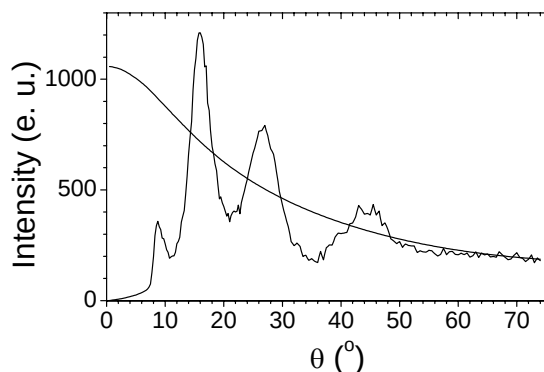


Fig. 1. The X-ray diffracted intensity as a function of the scattering angle, compared with the calculated independent scattering curve for the bulk glassy As_2Se_3 ingot.

Fig. 2 shows the results got after computer processing of the X-ray scattering curve. The so-called reduced curve represents the intensity curve $i(Q)$ where Q is the scattering vector $4\pi\sin\theta/\lambda$.

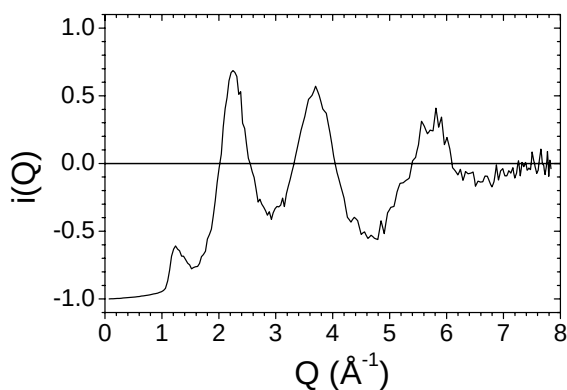


Fig. 2. The reduced X-ray scattering intensity on the glassy As_2Se_3 ingot, $Q=4\pi\sin(\theta)/\lambda$.

The curve of the Fig. 2 is the last step to the Fourier transformation procedure, because this curve can be easily transformed in order to obtain the reduced radial distribution curve (DRDF) and the radial distribution curve (RDF) that allows for the direct determination of the positions of the atomic coordination spheres in the glassy materials, and the coordination number in the first two spheres. These data represent the maximum information, which can be extracted from the diffraction curves measured on non-crystalline materials.

The differential RDF and the RDF curves are presented in Fig. 3 and 4.

Careful measuring of the positions and areas under the main peaks allows for getting important data on the structure at the atomic scale in the glassy ingot of As_2Se_3 .

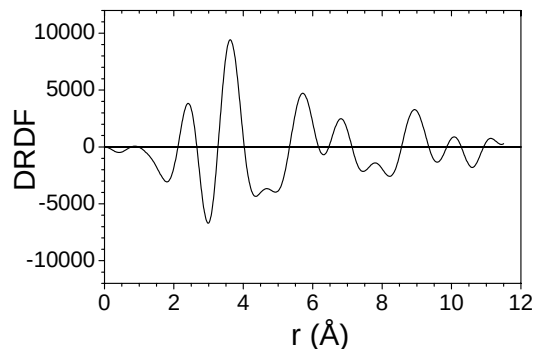


Fig. 3. The differential radial distribution function for the glassy As_2Se_3 ingot.

The first coordination spheres of a central atom in the structure of As_2Se_3 are the following:

First coordination spheres (first order neighbour position): $r_1=2.414 \text{ \AA}$

Second coordination sphere (second order neighbour position): $r_2=3.625 \text{ \AA}$

The areas under the first two peaks of RDF are: $2856.7 \text{ e}^2/\text{\AA}^3$ and $9433.1 \text{ e}^2/\text{\AA}^3$, respectively.

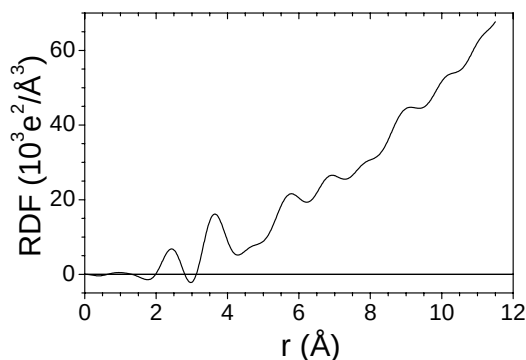


Fig. 4. The radial distribution function of glassy As_2Se_3 ingot.

3.2 As_2S_3

We have determined the structure of a pure amorphous As_2S_3 ingot, starting from the X-ray diffraction data recorded in the same conditions as above.

The X-ray diffraction pattern is given in Fig. 5. The final radial distribution function is represented in Fig. 6.

The first coordination spheres of a central atom in the structure of As_2S_3 are the following:

First coordination spheres (first order neighbour position): $r_1=2.306 \text{ \AA}$.

Second coordination sphere (second order neighbour position): $r_2=3.475 \text{ \AA}$.

The areas under the first two peaks of RDF are: $1285.8 \text{ e}^2/\text{\AA}^3$ and $3394.8 \text{ e}^2/\text{\AA}^3$, respectively.

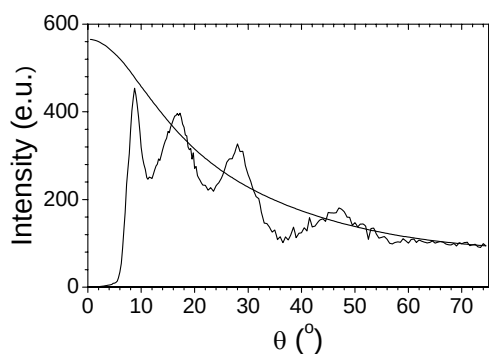


Fig. 5. The X-ray diffracted intensity as a function of the scattering angle, compared with the calculated independent scattering curve for the bulk glassy As_2S_3 ingot.

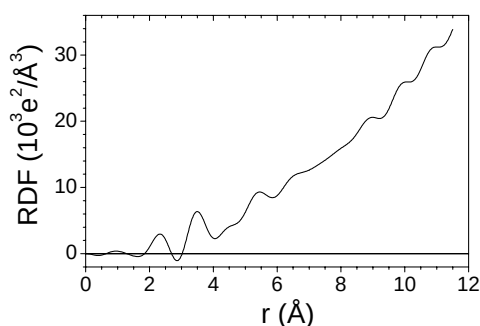


Fig. 6. The radial distribution function of glassy As_2S_3 ingot.

4. Discussion

In the systems As-S and As-Se the best studied are the compounds As_2S_3 and As_2Se_3 . In the crystalline state both compounds are isostructural with monoclinic lattice (space group C_{2h}^5 - $P_{21/b}$).

The standard structure of As_2S_3 (orpiment) is shown in Fig. 7. The unit cell has four molecules. The structure consists of extended layers of interconnected 12 atoms rings. This configuration was proved to be the densest packing possible for the chalcogen atoms linked with arsenic. Every arsenic atom has five valence electrons. Three electrons are used for valence bonds with three neighbouring chalcogens and the other two electrons form non-bonding orbitals. The chalcogen has six valence electrons: two are used for bonding with arsenic and the other four electrons form two non-bonding orbitals. As a result, the arsenic atoms show strong covalent bonds with three chalcogens and the chalcogen with three arsenic atoms. The valence state of arsenic is a hybrid state between $s+3p$ and sp^3 . The difference of electronegativity between arsenic and chalcogens atoms corresponds to the maximum value of the bond ionicity of $\sim 6\%$. Due to the difference in the hybridization of the arsenic electrons, the bonds with chalcogens are not equivalent from the point of view of strength. Therefore, after the Gordy rule [77], the distances between the arsenic atom and the bonded neighbors will be also not equivalents.

Between As_2S_3 or As_2Se_3 layers act Van der Waals forces with a minor covalent component. The minimum

interlayer distance ($4.785 \text{ \AA}$) exceeds considerably the distance between the first neighbours within the layer. The arsenic chalcogenides could be considered as molecular crystals where the molecules are extended to infinite in two spatial directions. The interaction forces between layers are hundred times weaker than the binding forces within the layers. Currently the structure is viewed as an interlinking of As-S₃ or As-Se₃ 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. The bond angle in the pyramid is 99° . The angle on sulphur is also 99° . As opposite to As_2S_3 , in As_2Se_3 there exist two kinds of pyramids with different distances to the first order neighbors and different valence angles on arsenic.

The average value of the bond stretching force constant for the interaction between atoms is in As_2Se_3 around 25 % lower than in As_2S_3 . The crystal As_2Se_3 is less covalent than As_2S_3 and this fact leads to the formation of more shifted and more densely packed layers than in As_2S_3 . The lattice constants of the As_2Se_3 crystal are: $a=12.053 \text{ \AA}$, $b=9.890 \text{ \AA}$, $c=4.277 \text{ \AA}$ and $\beta=90^\circ 28'$. The bonding distance As-Se in the helical chains parallel to c-axis are significantly shorter ($2.36 \text{ \AA}$ and $2.37 \text{ \AA}$) than the bonding distance between the chains in the layer. The arsenic trisulphide belongs to the group of compounds that are hardly obtained in the crystalline state. The As_2S_3 has the structure similar to As_2Se_3 , but with slightly modified parameters (the more recent and accurate values are a little bit different from those shown in Fig. 7: $a=11.475 \pm 0.005 \text{ \AA}$, $b=9.577 \pm 0.004 \text{ \AA}$, $c=4.256 \pm 0.002 \text{ \AA}$ and $\beta=90^\circ 23' \pm 5$). The elementary cell contains 4 formula units. The bonding distances As-S are $2.15 \text{ \AA}$, $2.20 \text{ \AA}$ and $2.34 \text{ \AA}$. The mean value is $2.23 \text{ \AA}$.

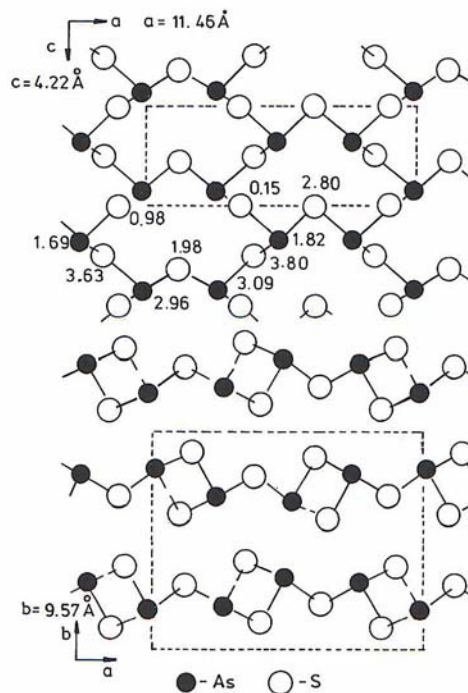


Fig. 7. The crystalline structure of As_2S_3 (orpiment). The packing of the layers along the b axis is also shown. The As_2Se_3 structure has slightly modified parameters.

The first coordination spheres in As_2S_3 in As_2Se_3 are given in the Table 1.

Table 1. Coordination spheres in glassy As_2S_3 and As_2Se_3 .

Sample	r_1 (Å)	r_2 (Å)	r_3 (Å)	r_4 (Å)	r_5 (Å)	r_6 (Å)	r_2/r_1	r_3/r_1	r_4/r_1
As_2S_3	2.306	3.475	4.438	5.380	6.513	7.911	1.507	1.925	2.333
As_2Se_3	2.414	3.625	4.678	5.716	6.815	7.801	1.502	1.938	2.368

As opposite to the crystalline structures of As_2S_3 and As_2Se_3 , the glassy state of these materials show differences. The bonding distance in glassy As_2S_3 is 2.306 Å, with 0.076 Å larger than in crystal. In glassy As_2Se_3 the bonding distance is 2.414 Å, with 0.05 Å larger than in crystal. The dilation of the bonding distance in As_2S_3 and in As_2Se_3 corresponds to 3.14 % and 2.07 %, respectively. This demonstrates weaker interatomic forces in As_2Se_3 compared to As_2S_3 . The ratio r_2/r_1 accounts for the deformation of the basal As-S₃ or As-Se₃ pyramid in the structure, when the crystalline order is lost. In the crystalline As_2S_3 this ratio is 1.521. The glassy As_2S_3 shows a value with 0.92% lower than in crystal. In the crystalline As_2Se_3 the ratio is 1.492, a value quasi-identical to that in crystal. These results show that the basic structural unit, the pyramid As-CH₃, is preserved in As_2Se_3 when the material changes its state from crystalline to glassy one, but in As_2S_3 some deformation occurs. In glassy state both alloys shows identical pyramid geometry.

5. Conclusions

The careful diffraction investigation carried out on two bulk glassy ingots of As_2Se_3 and As_2S_3 allowed for a fine characterization of these binary chalcogenide glasses of high importance in optoelectronics. The atomic scale structure can be understood as a random packing of layered units (probably closed) with similar distortions of the fundamental pyramids: As-S₃ and As-Se₃. The mean coordination in both glasses is 2.4. In As_2Se_3 glass, the geometry of the fundamental pyramid is preserved when the compound transforms from crystalline to glassy state, while in As_2S_3 some deformation occurs.

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