

NEUTRON DIFFRACTION STUDY OF As_40Se_60 , $\text{As}_40\text{Se}_30\text{S}_30$, $\text{As}_40\text{Se}_30\text{Te}_30$ CHALCOGENIDE GLASSES

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The partial, total and average coordination number of atoms and, their neighbor distributions have been determined by the neutron diffraction method and application of the Reverse Monte Carlo modeling for experimental data in As_40Se_60 , $\text{As}_40\text{Se}_30\text{S}_30$ and $\text{As}_40\text{Se}_30\text{Te}_30$ chalcogenide glasses. The total coordination number of the arsenic and chalcogen atoms is 3 and 2 for all compounds. The average coordination number is 2.4, i.e. the 8-N rule is performed and main structural element is AsSe_3 type pyramids, where depending on the chemical composition Se atom is replaced by S or Te atoms. It has been established the change of the optical gap by variation of the chemical composition.

Keywords: amorphous, chalcogenide glass, neutron scattering

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INTRODUCTION

The structure of chalcogenide glasses are characterized by short range order (SRO) determined by the coordination number, bond lengths and angle of the bond [1]. In addition, there is a certain order in the arrangement of structural elements on a nanometer scale - i.e. medium range order (MRO).

The purpose of this paper is to study the local structure and optical properties of chalcogenide glasses, with compositions As_40Se_60 , $\text{As}_40\text{Se}_30\text{Te}_30$ and $\text{As}_40\text{Se}_30\text{S}_30$. For the study were applied neutron diffraction measurements and optical results. In this study we have used the software package RMC++ [2] while applying of Reverse Monte Carlo simulation (RMC) to experimental results for obtaining the atomic structural parameters.

EXPERIMENTAL DETAILS

The glassy bulk samples with compositions of As_40Se_60 , $\text{As}_40\text{Se}_30\text{Te}_30$ and $\text{As}_40\text{Se}_30\text{S}_30$ was powdered in order to prepare specimens for the neutron diffraction. Neutron diffraction (ND) data have been obtained on the 2-axis 'PSD' monochromatic neutron diffractometer (wavelength was $\lambda_0=1.068$ Å; $Q=0.45-9.8$ Å⁻¹) at the 10 MW Budapest Research Reactor [3], with thermal neutrons.

RESULTS AND THEIR DISCUSSION

Fig. 1a shows that all curves of the $S(Q)$ dependence in the interval $1.2 \div 1.3$ Å⁻¹ exhibit the first sharp diffraction maximum (FSDP). Fig. 1b shows FSDP curves in which the amplitude, shape and position of the maximum undergo a change depending on the chemical composition of the material. It can be seen that FSDP is weakly expressed for $\text{As}_40\text{Se}_30\text{Te}_30$ the composition than other compositions, which is evidence of higher disorder. In Fig. 2 the corresponding total pair distribution functions, $G_{\text{total}}(r)$, calculated by the RMC simulation from the experimental values of structure factors, are presented. The

diffraction result of chalcogenide samples has been attributed to the influence of MRO, and this is called first sharp peak (FSDP) or a pre-peak in the structure factor.

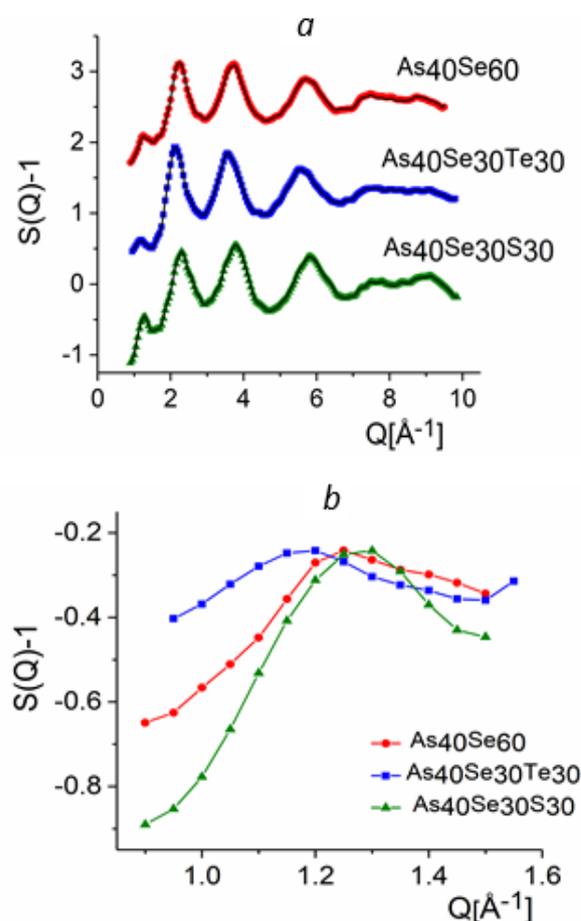


Fig. 1 Neutron diffraction structure factor, $S(Q)$ of glassy series: experimental data (color marks) and RMC simulation (solid line) (a) and the first sharp diffraction peak (FSDP) curves for As_40Se_60 (circle), $\text{As}_40\text{Se}_30\text{Te}_30$ (squares) and $\text{As}_40\text{Se}_30\text{S}_30$ (triangles) glassy series(b).

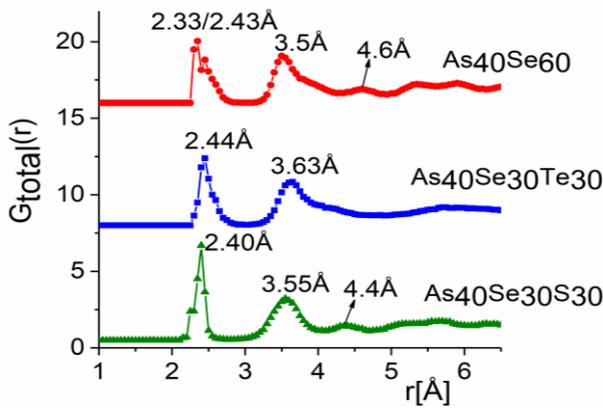


Fig. 2 Total pair correlation function obtained from the RMC modeling of $As_{40}Se_{60}$, $As_{40}Se_{30}Te_{30}$ and $As_{40}Se_{30}S_{30}$ compositions

The positions of the observed maxima on the graphs of $G_{total}(r)$ correspond to the radii of the coordination spheres. As a result, application of Reverse Monte Carlo simulation (RMC) are determined the partial structural factors, $S_{ij}(Q)$ and partial pair correlation functions, $g_{ij}(r)$. The results obtained show that, the FSDP intensity depends on the atomic number of chalcogen and also indicate the decisive role of the Se-Se correlation in the formation of MRO area. In Table 1 are summarized the short-range order parameters, i.e. “the partial coordination numbers” N_{ij} , i.e. the average number of j atoms around i atom, average number of neighbors, total coordination number, average coordination number. As can be seen, the coordination number of homopolar bonds in all the compositions is appreciably high both are between the arsenic atoms and between the chalcogenide atoms.

Table 1

Sample	Central	Neighbor				Total	Average coordination number	Calculated by the rule 8-N
		As	Se	S	Te			
$As_{40}Se_{60}$	As	0.67	2.36	-	-	3.03	2.42	2.4
	Se	1.57	0.45	-	-	2.02		
$As_{40}Se_{30}Te_{30}$	As	0.36	1.35	-	1.30	3.01	2.41	2.4
	Se	1.80	0.10	-	0.15	2.05		
	Te	1.73	0.15	-	0.10	1.98		
$As_{40}Se_{30}S_{30}$	As	0.73	1.18	1.09	-	3	2.42	2.4
	Se	1.57	0.2	0.3	-	2.07		
	S	1.45	0.3	0.25	-	2		

Table 2

Sample	Packing density	V_a cm ³ /mol	δ	ρ g/cm ³	d (Å)	L (Å)	Q_0 (Å)	ΔQ (Å)	D (Å)	Area	Amplitude
$As_{40}Se_{60}$	3.57	16.85	-0.0075	4.59	5.04	13.95	1.25	0.45	4.396	0.3954	0.23
$As_{40}Se_{30}Te_{30}$	3.36	17.91	-0.0102	5.13	5.23	12.56	1.20	0.50	4.579	0.2580	0.15
$As_{40}Se_{30}S_{30}$	2.74	15.03	-0.0118	3.86	4.83	15.70	1.30	0.40	4.226	0.6295	0.36

The parameters FSDP determined according to Fig. 1b, the position (Q_0) and full width of half maximum FWHM (ΔQ), the amplitude (Å) and area of peak are shown in Table 2.

As can be seen from the figure and the table, the numerical values of the amplitude (Å) and the maximum area decrease, and FWHM (ΔQ) is increasing, according to order $As_{40}Se_{30}S_{30}$, $As_{40}Se_{60}$, $As_{40}Se_{30}Te_{30}$, which shows the increasing degree of disorder with such series. Using the FSDP parameters, the microstructure parameters are determined by the formula

$$d = 2\pi/Q_0 \quad \text{and} \quad L = 2\pi/\Delta Q_0 \quad (1)$$

Where, the parameter d is related to the structural unit size corresponding to FSDP [4, 5]. Also, this parameter is called the quasi-periodic atomic density fluctuations, can be determined using the position of FSDP (Q_0) [5, 6] L (the structural correlation length) is determined using the width of FSDP. The microstructure parameters calculated by the equations (1) are also presented in Table 2. In case of

$As_{40}Se_{60}$ and $As_{40}Se_{30}Te_{30}$ samples, the value of d increases and L decreases. The growth of d is associated with the increase in atomic radius in some Se, Te chalcogens, while the reduction of L (size of the MRO region) is connected with increasing degree of disorder in the specified row. In Table 2 are presented the numerical values of the compactness of the structure (δ) calculated in accordance with [7], taking into account the atomic density of the elements and the measured density. The smallest value of δ obtained for the composition $As_{40}Se_{60}$ indicates a more perfect structure of the amorphous matrix in this composition. The cluster-void model is proposed by Elliott [8] to explain the nature FSDP. According to this model numerical values of D are computed and the results are presented in Table 2. The results show that value of D is increasing from $As_{40}Se_{30}S_{30}$ to $As_{40}Se_{60}$ and $As_{40}Se_{30}Te_{30}$ compositions. If we consider that the nano-voids are created due to of atoms in themselves, then the growth in their diameter is associated with an increase in the average atomic radius of the indicated compositions. As can be seen from Table 1, the experimentally determined values and

those calculated by the 8-N rule for the coordination number coincide in all compounds, i.e. 8-N rule is satisfied. The optical band gap (E_g) investigated materials undergo a change depending upon the chemical composition. When half of selenium atoms are replaced by sulfur atoms increases the band gap (E_g), determined according Tauc methods [9], but decreases by replacing tellurium atoms. As already mentioned, the substitution part of selenium atoms with sulfur contributes to the improvement of the amorphous matrix, but substitution of Se with tellurium leads to partial destruction of the structure, increasing the degree of disorder. The changes in the values of parameter may occur as a result of changes in the average molar energy of different bonds present in the material and as a result of changes in the degree of disorder of the amorphous matrices. Using the energy of different bonds [10], the average molar energy of bonds is calculated and its values are shown in Table 3, whence it is clear that the participation of sulfur atoms increases and tellurium decreases the value of the E_g parameter.

As seen from Table 3, the values of E_g for the $As_{40}Se_{60}$, $As_{40}Se_{30}S_{30}$ and $As_{40}Se_{30}Te_{30}$ chalcogenide glasses compositions are 1.82, 1.98 and 1.59 eV, respectively. Such a change in the values of E_g depending on the chemical composition can be explained with the assistance of considerations proposed by the authors of [11] considering the values of atomic density in the studied compositions.

Table.3

Film composition	E_g (eV)	Average molar energy of bonds (kcal/mol)
$As_{40}Se_{60}$	1.82	223.6
$As_{40}Se_{30}Te_{30}$	1.59	215
$As_{40}Se_{30}S_{30}$	1.98	238

CONCLUSIONS

The appearance of FSDP in the graphs $-S(Q)$ is due to the emergence of the MRO region and main role in the formation of the MRO region belongs to the Se-Se bonds environment. It has been obtained that, the optical gap strongly depends on the content. This is explained with changes in the degree of disorder and concentration of local defects depending on the chemical composition.

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| <p>[1] <i>J.P. Neufoile, S.C. Moss, S.R. Ovshinsky.</i> Photostructural transformations in amorphous As_2Se_3 and As_2S_3 films. <i>J Non-Cryst Solids.</i> 1973;13:191-223</p> <p>[2] <i>O. Gereben, P. Jovari, L. Temleitner, et al.</i> A new version of the RMC++ Reverse Monte Carlo programme, aimed at investigating the structure of covalent glasses. <i>J Optoelect Adv Materials</i>, 2007, 9, 3021-3027</p> <p>[3] <i>E. Sváb, Gy. Mészáros, F. Deák.</i> Neutron Powder Diffractometer at the Budapest Research Reactor. <i>Mater Sci Forum</i>, 1996, 228, 2247-252</p> <p>[4] <i>W.H. Wei, R.P. Wang, X. Shen, et al.</i> Correlation between Structural and Physical Properties in Ge-Sb-Se Glasses. <i>J Phys Chem C.</i> 2013,117, 16571-16576</p> <p>[5] <i>K. Tanaka.</i> Topological phase transitions in amorphous semiconductors. <i>J Non-Cryst Solids</i>, 1987, 97-98, 391-398</p> | <p>[6] <i>S.R. Elliott.</i> Second sharp diffraction peak in the structure factor of binary covalent network glasses, <i>Phys Rev B.</i> 1995, 51, 8599-8601</p> <p>[7] <i>G.A. Isayeva</i> Ph.D. Dissertation in Physics, Institute of Physics, Baku, 2014</p> <p>[8] <i>T.S. Kavetsky.</i> Modified correlation equation in the FSDP-related void-based model for $As_2S(Se)_3$ chalcogenide glasses. <i>Semiconductors Phys, Quantum Electronics & Optoelectronics</i>, 2013, 16, 136-139</p> <p>[9] <i>D.I. Wood, J. Tauc</i> Weak Absorption Tails in Amorphous Semiconductors. <i>Phys Rev B.</i> 1972, 5, 3144-3151</p> <p>[10] <i>M.A. Popescu,</i> Non-Crystalline Chalcogenides (Solid-State Science and Technology Library, Vol. 8). ed. Springer. ISBN10: 0792366484. 2000</p> <p>[11] <i>M. Kastner,</i> Bonding bands, lone-pair bands, and impurity states in chalcogenide semiconductors. <i>Phys. Rev. Lett.</i> 1972, 28, 355-357</p> |
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