Study of As$_2$Se$_3$ and As$_2$Se$_2$Te glass structure by neutron- and X-ray diffraction methods

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Abstract. Neutron and high-energy X-ray diffraction measurements have been performed on As$_{80}$Se$_{60}$ and As$_{80}$Se$_{50}$Te$_{10}$ glasses. Both the traditional Fourier transformation technique and the reverse Monte Carlo (RMC) simulation of the experimental data have been applied to model the 3-dimensional atomic configurations. From the analysis of the partial atomic correlation functions and structure factors the first and second neighbour distances, coordination numbers and bond-angle distributions were calculated. It is established that substitution of Se by Te does not change the basic glassy network structure. For the As-Se bonding is revealed that the first neighbour distance is at 2.42 Å, the average coordination numbers are CN$_{As-Se}$=2.6±0.1 and CN$_{Se-As}$=1.8±0.1 atoms and the three-atom-bond angle for <Se-As-Se>, <As-Se-As> configurations is 95°, the same value within limit of error, as obtained from RMC calculations.

1. Introduction
Chalcogenide glasses are perspective materials for practical application in optoelectronics as high-speed optical elements, for applications such as data processing devices, electronic switches, and optical memories. In general, they are transparent from the visible or near-infrared regions. Among these glasses the As$_2$Se$_3$ and Te–As–Se compositions are perspective materials for manufacturing optical fibers because of their low phonon energy, good transparency, low optical losses and good thermal and chemical stability. The physical–chemical properties and exploitation possibilities of chalcogenide glasses are usually treated in dependence on their atomic structure [1–5]. The structure of chalcogenide glasses has been the subject of some debate for many years. The absence of translational symmetry in As-Se and Te–As–Se glasses suggests that particles are randomly arranged around each atom. Since there is no universal approach for revealing the glass structure, one can obtain a consistent picture of the glass structure only by combining several investigation techniques.
In this work we focus on the atomic-scale structural characterization of As₄₀Se₆₀ and As₄₀Se₅₀Te₁₀ chalcogenide glasses using neutron- and X-ray diffraction methods. Structure modeling by RMC simulation was also applied.

2. Experimental Details

2.1. Sample preparation
The glassy samples As₄₀Se₆₀ and As₄₀Se₅₀Te₁₀ were synthesized by the conventional melt-quenching method from 5N purity elements. The syntheses were performed in evacuated quartz ampoules (10⁻³ Pa) using a rotary furnace. The specimens were heated up to 950°C, kept at this temperature for 24 h meanwhile the furnace was rotated for homogeneous melting. The ampoules were quenched in air.

2.2. Neutron and X-ray diffraction measurements
Neutron diffraction measurements were carried out by combining the data measured in the 2-axis 'PSD' diffractometer (λ₀=1.068 Å) [1] at the 10 MW Budapest research reactor and by the time-of-flight 'HIPPO' instrument [2] at the LANSCE pulsed neutron source. For both experiments, the powder specimens of about 3-4 g were filled in cylindrical vanadium sample holder of 8 mm and 10 mm diameter, respectively. The neutron structure factors, S(Q)s were revealed in a broad momentum transfer range, Q=0.45-30 Å⁻¹, which made possible high r-space resolution analysis (Ar=2π/Qmax≈0.2 Å).

The high-energy X-ray diffraction measurements were performed at the BW5 experimental station [3] at Desy/Hamburg using 109.5 keV radiation energy (λ₀=0.113 Å). The powdered samples were filled into quartz capillary of 2 mm in diameter (wall thickness of ~0.02 mm). The amplitudes of the small intensity physical oscillations at the relatively high Q-values were obtained with good statistic of about 1%, and the X-ray S(Q)s were revealed in the Q=0.5-19 Å⁻¹ momentum transfer range.

3. Results and discussion
Figure 1 shows the neutron S(Q) and the total reduced atomic correlation functions, G(r), calculated by Fourier transformation:

\[ G(r) = \frac{2}{\pi} \int_{0}^{Q_{\text{max}}} Q[S(Q) - 1]M(Q)\sin(Qr)\,dQ, \]

where Qmax = 30 Å⁻¹ is the integration limit, and M(Q) is a modification function to reduce the artificial oscillations caused by the finite Qmax truncation (see [4] for more details). The overall character of the S(Q)s is very similar for the studied glasses suggesting a strong similarity of the basic network structure. A small prepeak appears at Q = 1.3 Å⁻¹, which can be interpreted as the existence of intermediate range ordering. The first sharp peak appears at r₁=2.42±0.01 Å in G(r) for both the As₄₀Se₆₀ and As₄₀Se₅₀Te₁₀ compositions, which corresponds to the As-Se atom pairs. A small but significant peak appears for the ternary glass at ≈2.7 Å, which corresponds to the Te-As and/or Te-Se atomic pair distances. The second coordination sphere shows up a strong peak centered at r₂=3.7±0.05 Å. The three-atom-bond angle between As-Se-As and Se-As-Se atoms is estimated from the equation Θ=2sin⁻¹(r₁/2r₁) [5, 6], which gives a value of ΘAs-Se-As ≈ Se-As-Se = 99±3°.

For the data treatment reverse Monte Carlo (RMC) simulation [7] of the diffraction experimental data was applied to get structural information about possible atomic configurations. As a RMC starting model a disordered atomic configuration was built up with a simulation box containing 10 000 atoms. In the RMC simulation procedure for the As₄₀Se₆₀ and As₄₀Se₅₀Te₁₀ glasses the atom densities of 0.03 and 0.035 atoms/cm³ and half-box lengths of 34.668 and 32.931 Å, respectively, were taken. Two types of constraints were used, namely the minimum interatomic distances between atom pairs (cut-off distances) and connectivity constraints.

In order to check the quality of the experimental data, the neutron and X-ray diffraction datasets
were modeled, both separately and simultaneously by the RMC method.

The constituent elements (As, Se, Te) possess rather similar neutron \( b_{\text{As}} = 6.58 \text{ fm} \), \( b_{\text{Se}} = 7.97 \text{ fm} \), \( b_{\text{Te}} = 5.8 \text{ fm} \) [8] and X-ray scattering amplitudes and interatomic distances. Consequently, the atomic correlation functions overlap, which makes difficult to separate the atomic positions. Using reasonable cut-off distances and connectivity constraints in the RMC simulation procedure, we obtained very good agreement between the experimental and the calculated \( S(Q) \) curves, as it is illustrated in figure 2. The cut-off distances were taken from the total G(r) functions (figure 1) as follows: 2.2 Å for As-Se, 2.45 Å for As-Te and for Se-Te, 3.1 Å for As-As, for Se-Se and for Te-Te.

![Figure 1](image1.png)

**Figure 1.** Experimental neutron total structure factor (a) and atomic reduced correlation function (b) for As\(_{40}\)Se\(_{60}\) (full square) and As\(_{40}\)Se\(_{50}\)Te\(_{10}\) (open square) glasses.

![Figure 2](image2.png)

**Figure 2.** Neutron (a and c) and X-ray (b and d) RMC models (solid line) and experimental structure factors (open circles) for As\(_{40}\)Se\(_{60}\) and As\(_{40}\)Se\(_{50}\)Te\(_{10}\) glasses.
In the first approach of the RMC modelling we consider only the possible heteropolar bonds, since homopolar bonds are probably absent. We have applied connectivity constraints for As atoms to be surrounded by three Se neighbours, and for Se atoms to be surrounded by two Se neighbours, as reported in many papers [5, 6, 9-15].

From the RMC modelling we revealed the partial correlation functions ($g(r)$), the coordination number ($CN$) and bond angle ($\theta$) distributions with a fairly good reproducibility for the studied glasses. Figures 3-5 compare the results obtained for As-Se, As-As and Se-Se network former atom pairs. In general, the curves are almost the same for the two compositions. This suggests that substituting Te for Se atoms does not change the basic network structure within the limit of experimental error and modelling procedure. The As-Se correlation (figure 3a) shows a rather sharp first neighbour distance at 2.42±0.02 Å. The corresponding average coordination numbers are $CN_{AsSe}=2.6\pm0.1$ atoms and $CN_{SeAs}=1.8\pm0.1$ atoms (figure 4). These values are somewhat less than the expected (constrained) 3 and 2 atomic neighbours, which may be a consequence of a slight distortion from the ideal AsSe$_3$ trigonal pyramid units reported in the literature. From the RMC calculations for the three-atom-bond angle $\theta_{AsSeAs,SeAsSe}=95\pm5^\circ$ is obtained (figure 5), which is in accordance with the value calculated from the $G(r)$'s distances, as discussed above. These results are in good agreement with reference [5] and are somewhat less than that reported in references [12, 14, 15]. The error of the actual structural parameters is calculated from the data obtained from different RMC runs.

The observed 2nd neighbour distance at 3.7 Å and 3rd neighbour distance at 5.6 Å for the As-Se bonds are an evidence for medium range correlation in the glassy structure. For the As-As bonds the characteristic distance is at 3.7 Å, while for Se-Se at somewhat shorter distance of 3.65 Å (figures 3b and 3c, respectively).

![Figure 3](image1.png)

**Figure 3.** Partial atomic correlation functions obtained from the RMC modelling of As-Se (a), As-As (b) and Se-Se (c) atom pairs for As$_{40}$Se$_{60}$ (full circles) and As$_{40}$Se$_{60}$Te$_{10}$ (open circles) glasses.

![Figure 4](image2.png)

**Figure 4.** Coordination number distribution for As$_{40}$Se$_{60}$ (filled) and As$_{40}$Se$_{60}$Te$_{10}$ (crossed) glasses from RMC modelling of As-Se (a) and Se-As (b) atom pairs.
The partial atomic correlation functions of the possible Te-containing chemical bonds revealed from the RMC modelling are presented in figure 6. Relatively low intensity first neighbour peak appears at 2.50 Å in the As-Te and Se-Te pair correlation functions, indicating a random substitution of Se atoms by Te atoms. It should be noted, that both the position and peak intensity depend on the constraints applied in the RMC modelling. For unconstrained case, the $g_{\text{AsTe}}(r)$ and $g_{\text{SeTe}}(r)$ fully overlap with $g_{\text{AsSe}}(r)$, while in the constrained RMC calculation $g_{\text{AsTe}}(r)$ is shifted to higher distances. The intense peak at 3.5-3.6 Å for all three As-Te, Se-Te and Te-Te partial atomic pair correlations is an evidence of second neighbour distance of these bonds.

![Figure 5](image1.png)

**Figure 5.** Three-atom-bond angle distribution from RMC modelling for As$_{40}$Se$_{60}$ (full circles) and As$_{40}$Se$_{50}$Te$_{10}$ (open circles) glasses: a) Se-As-Se b) As-Se-As

![Figure 6](image2.png)

**Figure 6.** Partial atomic correlation functions, obtained from the RMC modelling of As-Te (a), Se-Te (b) and Te-Te (c) atom pairs for As$_{40}$Se$_{50}$Te$_{10}$ composition.

### 4. Conclusions
We have performed neutron and X-ray diffraction measurements and reverse Monte Carlo modelling on As$_{40}$Se$_{60}$ and As$_{40}$Se$_{50}$Te$_{10}$ glasses. A 3-dimensional structure model has been devised which is consistent with the experimental data. The partial atomic correlation functions, coordination number distributions and three-atom-bond angle distributions have been obtained. Our main findings are the following:
- addition of Te to the binary glass does not change the basic glassy network structure;
- for As-Se first neighbour distance 2.42 Å is revealed;
- the average coordination numbers of As and Se atoms are established, according to which As atoms are surrounded by 2.6±0.1 Se atoms, while Se atoms - by 1.8±0.1 As atoms;
- RMC calculation reveals an angle of 95° for the average three-atom-bond angle of <Se-As-Se> and <As-Se-As>.
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