Structure study of chalcogenide glasses from high Q-range neutron diffraction experiment and RMC modelling

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Abstract. A neutron diffraction structure study has been performed on newly synthesized Ge20As20Se50Te10 and Ge27As13Se50Te10 chalcogenide glasses. Oscillations in the structure factor, S(Q) have been measured with good sign-to-noise up to 35 Å⁻¹. The reverse Monte Carlo simulation was used to model the 3-dimensional atomic configuration. The partial atomic correlation functions and structure factors have been revealed. Several first and second neighbour distances, and coordination numbers have been calculated. We have established that several first neighbour atomic distances are overlapping at two characteristic distances, namely the Ge-Ge, Ge-Se and As-Se are centred at 2.42 Å, while the Ge-Te, As-Te and Se-Te are centred at 2.60 Å.

1. Introduction
Chalcogenide glasses are transparent in the infrared region and exhibit high third order non-linear optical properties [1,2]. Thus, they are very attractive as high-speed optical elements for application such as data processing devices, electronic switches, and optical memories. Among such materials is the quaternary Ge-As-Se-Te telluride system, which is in the focus of our interest. Here we present our neutron diffraction experiments on Ge20As20Se50Te10 and Ge27As13Se50Te10 compositions, and preliminary results revealed by reverse Monte Carlo modelling characterising the short range structure.

2. Experimental details

2.1. Sample preparation
The glassy samples Ge20Sb20S50Te10 and Ge27Sb13S50Te10 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 rotating the furnace for homogeneous melting. The ampoules were quenched in air.

2.2. Neutron diffraction experiments
Neutron diffraction measurements have been performed in a relatively broad momentum transfer range, combining the data measured by the 2-axis 'PSD' monochromatic neutron diffractometer (λ₀=1.068 Å; Q=0.45-9.8 Å⁻¹) [3] at the 10 MW Budapest research reactor and by the time-of-flight 'HIPPO' instrument at the LANSCE pulsed neutron source Q=0.9-50 Å⁻¹ [4]. The ND patterns have shown that the specimens are fully amorphous. The structure factor, S(Q) was obtained with a good signal-to-noise ratio up to Q_max=35 Å⁻¹ (see figure 1), which made possible high-resolution r-space analyses. The S(Q)'s for the two compositions are fairly similar to each other, however, several fine
details are somewhat different, i.e. the position of the first peak at around 1 Å⁻¹ (called also pre-peak), or the oscillations in the 6-8 Å⁻¹ Q-range.

Figure 1. Experimental structure factors for the Ge²⁰As²⁰Se⁵⁰Te¹⁰ (blue cross) and Ge²⁷As¹³Se⁵⁰Te¹⁰ (orange circle) glasses.

3. Data evaluation – Reverse Monte Carlo modelling

The S(Q) data displayed in figure 1 have been simulated by the RMC method [5]. For the RMC starting model a disordered atomic configuration was built up with a simulation box containing 10 000 atoms, \( \rho_0 = 0.033/0.036 \) atom density and half-box lengths of 33.5/32.6 Å for Ge²⁰As²⁰Se⁵⁰Te¹⁰/Ge²⁷As¹³Se⁵⁰Te¹⁰ specimens, respectively. The RMC modelling was performed in two main steps. As a first step, the MCGR method was applied [6] with the aim to lighten the atomic motions in the RMC calculations. MCGR is a 1-dimensional version of RMC to produce a total atomic pair correlation function, \( g(r) \), by allowing atomic movements to minimize the difference between calculated and experimental structure factors and, contains some fine corrections for the background as well. The MCGR data were used as input experimental data for the RMC modelling. In the RMC simulation procedure several runs have been performed with different interatomic cut-off distances used as constraints and, the corresponding results have been carefully analysed. Because of the several overlapping first neighbour distributions, we decreased the number of \( g_i(r) \) by applying further constraints, supposing that no Se-Se, Ge-As, As-As and Te-Te bonds are present. In a first approach this is feasible, because of the small probability of being first neighbours. We have revealed that with the following cut-off atomic neighbour distances the results proved to be highly stable: Ge-Ge: 2.2/2.2 Å, Ge-Se: 2.18/2.17 Å, Ge-Te: 2.5/2.55 Å, As-Se: 2.17/2.19 Å, As-Te: 2.58/2.56 Å and Se-Te: 2.5/2.56 Å, for Ge²⁰As²⁰Se⁵⁰Te¹⁰/Ge²⁷As¹³Se⁵⁰Te¹⁰, respectively.

The final RMC run matched very well the experimental one, as it is illustrated in figure 2.

Figure 2. Structure factors: experimental MCGR data (magenta cross) and RMC modelling (black line). The curves are shifted vertically for clarity.
Several partial atomic correlation functions, $g_{ij}(r)$ and corresponding partial structure factors, $S_{ij}(Q)$ have been revealed from the RMC simulation with a fairly good stability. They are presented in figure 3 and 4 for both compositions. The first neighbour coordination number distributions are shown in figure 5. The 1st and 2nd neighbour interatomic distances and first neighbour coordination numbers are collected in Table 1. The Ge-Ge, Ge-Se and As-Te distribution are fairly similar to each other, both the 1st and 2nd neighbour distances are at the same distance within limit of error, at 2.42±0.02 Å and at 3.78±0.05 Å, respectively. Similarly, the distributions for the Ge-Te, As-Te and Se-Te are fairly similar to each other, the 1st neighbour distance is at 2.60±0.02 Å and the 2nd neighbour distance is at 3.72±0.05 Å.

![Partial Atomic Correlation Functions](image1)

**Figure 3.** The partial atomic correlation functions obtained by RMC simulation, for the Ge$_{20}$As$_{20}$Se$_{50}$Te$_{10}$ (olive cross) and Ge$_{27}$As$_{13}$Se$_{50}$Te$_{10}$ (red circle) glasses.

![Partial Structure Factors](image2)

**Figure 4.** The partial structure factors obtained by RMC simulation, for the Ge$_{20}$As$_{20}$Se$_{50}$Te$_{10}$ (olive cross) and Ge$_{27}$As$_{13}$Se$_{50}$Te$_{10}$ (red circle) glasses.
Table 1. Interatomic distances, $r_{ij}(\text{Å})$ and coordination numbers, $\text{CN}_{ij}$ obtained from RMC simulation. The corresponding intervals are indicated in brackets.

| Atom pairs | $\text{Ge}_{20}\text{As}_{20}\text{Se}_{50}\text{Te}_{10}$ | $\text{Ge}_{27}\text{As}_{13}\text{Se}_{50}\text{Te}_{10}$ |
|------------|---------------------------------|---------------------------------|
|            | Interatomic distances, $r_{ij}(\text{Å})$ | Coordination number, $\text{CN}_{ij}$ | Interatomic distances, $r_{ij}(\text{Å})$ | Coordination number, $\text{CN}_{ij}$ |
|            | $1^{\text{st}}$ ($\pm 0.02$) | $2^{\text{nd}}$ ($\pm 0.05$) | $1^{\text{st}}$ ($\pm 0.02$) | $2^{\text{nd}}$ ($\pm 0.05$) |
| Ge-Ge      | 2.42 3.78 1.08 | 2.43 3.87 1.31 |
| Ge-Se      | 2.43 3.78 2.46 | 2.42 3.86 2.45 |
| Ge-Te      | 2.60 3.70 0.15 | 2.61 3.77 0.19 |
| As-Se      | 2.42 3.80 2.41 | 2.42 3.88 2.40 |
| As-Te      | 2.60 3.70 0.20 | 2.60 3.80 0.31 |
| Se-Te      | 2.61 3.75 0.21 | 2.61 3.73 0.36 |

4. Summary

We have performed a neutron diffraction structural study on newly synthesized 4-component chalcogenide specimens with composition $\text{Ge}_{20}\text{As}_{20}\text{Se}_{50}\text{Te}_{10}$ and $\text{Ge}_{27}\text{As}_{13}\text{Se}_{50}\text{Te}_{10}$. The structure factors have been measured over a broad momentum transfer range, up to 35 Å$^{-1}$, which made available high r-space resolution. RMC simulation was successfully applied to calculate most of the partial atomic pair correlation functions, the partial structure factors and coordination number distributions. Several first and second neighbour distances and coordination numbers have been revealed. We have established that the Ge-Ge, Ge-Se and As-Se are centred at 2.42 Å, and the Ge-Te, As-Te and Se-Te distances are centred at 2.60 Å. Further analyses of the data are in progress.

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5. References

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