

Local atomic order in $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ and $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$ glasses

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$\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ and $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$ glasses have been studied with high energy X-ray diffraction, neutron diffraction and extended X-ray absorption spectroscopy at various edges. The experimental data have been modelled simultaneously with the reverse Monte Carlo simulation method. Combination of the three independent measurements allowed the separation of the partial pair correlation functions and estimation of the corresponding coordination numbers. Structure modifications induced by different doping elements are established.

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1. Introduction

Scientific interest in amorphous chalcogenides containing noble metal halides originates from their practical application as solid electrolytes in the electrochemical devices. It is known that As-Se glasses become ionic conductors upon doping with AgI [1]. Addition of Ag to As-Se binary increases its electrical conductivity [1,2]. On the other hand, the electrical conductivity changes in a very narrow range in ternary As-Se-I glasses at room temperature [1]. Other physical properties like density, glass transition temperature, crystallization temperature also change in different way in ternary As-Se-Ag and As-Se-I glasses [1,3].

Atomic structure of ternary and quaternary chalcogenide glasses is not as well studied as their physical properties. The structural study of multicomponent alloys is always demanding because of the high number of the partial pair distributions. It is widely accepted that the most efficient direct method of structural investigations is neutron diffraction with isotopic substitution. This tool is, however, in most cases also prohibitively expensive. And even if one of the components is isotopically substituted the additional information is still not sufficient to resolve all partial pair correlation functions. To achieve this rather ambitious goal one has to rely on the results of different experimental techniques (e.g. X-ray diffraction, neutron diffraction and EXAFS). It has been shown in a number of recent studies [4-8] that the reverse Monte Carlo simulation technique (RMC) [9] offers a suitable framework for combining the information content of several datasets. Another useful feature of RMC is that it enables to check whether certain three dimensional structures are compatible with available experimental information [10-14].

Important feature of non-crystalline materials, as e.g. the similarity between amorphous and low- temperature

liquid structure of $\text{Ge}_{15}\text{Te}_{85}$, have been revealed on the basis of RMC modelling [15].

In the present work, we study $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ and $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$ glasses with the X-ray diffraction (XRD), neutron diffraction (ND) and extended X-ray absorption spectroscopy (EXAFS) and model the experimental data simultaneously by means of RMC. The differences in atomic structures in dependence on the doping element are investigated on the base of pair distribution functions obtained by the RMC modelling.

2. Experimental details

The X-ray diffraction experiments were carried out at the BW5 experimental station [16] at HASYLAB (DESY, Hamburg). The samples were filled into thin walled (0.02 mm) quartz capillaries of 2.0 mm in diameter. The energy of the incident beam was 99.8 keV. The size of the incident beam was $1 \times 4 \text{ mm}^2$. Raw data were corrected for background, polarization, detector dead-time and variations in detector solid angle.

The EXAFS measurements were carried out at Ag, As and I K-edges at the beam line X [17] of HASYLAB in transmission mode. The samples were finely ground, mixed with cellulose and pressed into tablets. The sample quantity in the tablets was adjusted to the composition of the sample and to the selected edge. The transmission of the samples was about 1/e. The EXAFS spectra were obtained with a step of 0.5 eV in the vicinity of the absorption edge.

The neutron diffraction experiment was carried out at the 7C2 diffractometer (LLB, France). Samples were filled into thin walled (0.1 mm) vanadium container with 5 mm diameter. Raw data were corrected for detector efficiency, empty instrument background, scattering from the sample holder, multiple scattering and absorption [18,19].

The experimental XRD, ND and EXAFS curves are plotted in Figs. 1 and 2.

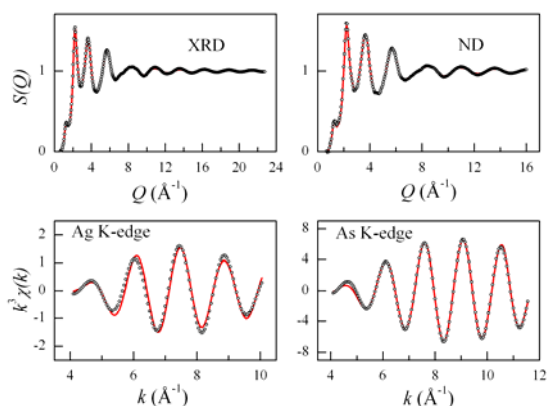


Fig. 1. XRD and ND structure factors, and EXAFS spectra for $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ glass. Circles – measured. Lines – obtained by simultaneous RMC simulation of the experimental XRD, ND and EXAFS data.

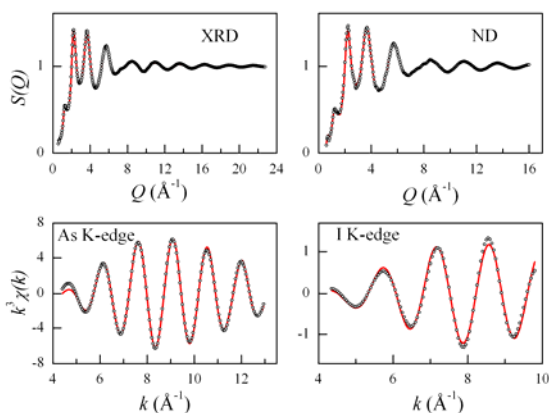


Fig. 2. XRD and ND structure factors, and EXAFS spectra for $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$ glass. Circles – measured. Lines – obtained by simultaneous RMC simulation of the experimental XRD, ND and EXAFS data.

3. RMC-modelling

For the details of the reverse Monte-Carlo simulation method we refer to two recent papers [20,21]. Calculations in the present work were performed with a new version of the RMC code [22]. Simulation boxes contained about 12000 atoms. The number densities, 0.0403 Å^{-3} for $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ and 0.0316 Å^{-3} for $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$, used throughout the simulation runs were calculated from the mass densities given in Ref. 1. The backscattering amplitudes needed to calculate the model EXAFS curves from the pair distribution functions were calculated by the FEFF8.4 program [23].

Simulations of the atomic structure of the two glasses have been started with the following cut off distances: As–As: 3.1 Å, As–Se: 2.1 Å, As–Ag: 3.1 Å, As–I: 2.4 Å, Se–Se: 3.1 Å, Se–I: 2.4 Å, Se–Ag: 2.4 Å, I–I: 3.2 Å, Ag–Ag: 2.7 Å. Later some of these distances were decreased

to check the effect of the corresponding bond on the quality of the fits.

4. Results and discussion

4.1. $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$

In a previous structural study [4] it was assumed that there are no As–Ag bonds in $\text{As}_{40}\text{Se}_{40}\text{Ag}_{20}$ and $(\text{AsSe})_{65}(\text{AgI})_{35}$. A thorough investigation of the present data suggests that it is not so obvious for $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$. There is a small but significant improvement in the fit of the Ag K-edge EXAFS measurement if the Ag–As cut off distance is decreased to 2.5 Å (not shown). Fits obtained by the simultaneous modelling of the four independent measurements (with low Ag–As cut off distance) are shown in figure 1. The general agreement between model curves and experimental data is excellent. In the absence of As–As and Se–Se bonds (it is reasonable to assume that no As–As or Se–Se bonds are created upon adding Ag) there are only 4 partial pair correlation functions contributing to the low r region ($r < 3.1 \text{ Å}$). Therefore the separation of partial pair correlation functions (figure 3) and estimation of the corresponding coordination numbers can safely be carried out on the basis of available experimental information (see Table 1). It should be mentioned at that point that EXAFS possesses a beneficial property: backscattered photoelectrons undergo a phase shift, which depends on the backscattering atom. Due to this effect neighbours with sufficiently different electron numbers can be distinguished even if their mean distance from the absorber is very similar. This way EXAFS can separate correlations that cannot be resolved by diffraction techniques.

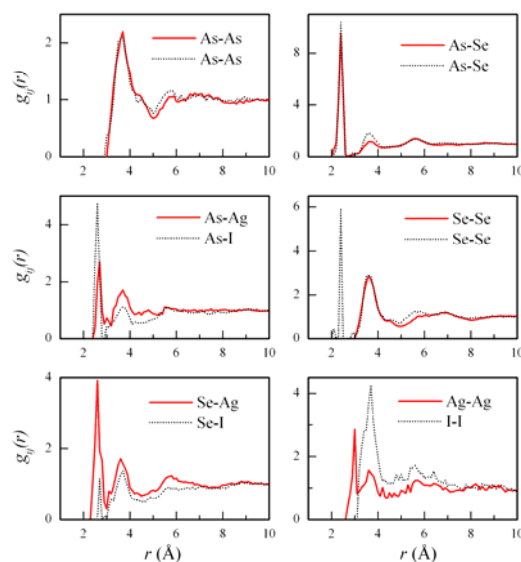


Fig. 3. Partial pair distribution functions for $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ (full line, red) and $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$ (dots, black) glasses obtained by RMC simulations.

Table 1. The nearest neighbour distances r_{ij} and coordination numbers N_{ij} for amorphous $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$.

Pairs	As–Se	As–Ag	Se–As	Se–Ag	Ag–As	Ag–Se	Ag–Ag	As–X	Se–X	Ag–X
r_{ij} (Å)	2.41	2.67	2.41	2.60	2.67	2.60	2.98	–	–	–
N_{ij}	3.05	0.34	2.03	0.6	0.77	2.03	0.39	3.39	2.63	3.19

The average coordination number $\langle N \rangle$ in amorphous $(\text{AsSe})_{80}\text{Ag}_{20}$ was found in [4] to be 2.88 ± 0.15 . The As–Se coordination number in glassy $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ is very close to three without any constraint. This result strongly suggests that at the composition investigated Ag does not destroy the covalent network formed by threefold coordinated As and twofold coordinated Se atoms. The Ag–As coordination number is smaller than the Ag–Se one. Along with a longer Ag–As bond it suggests a weaker Ag–As interaction. It should be emphasized, however, that the majority of Ag atoms possess As neighbour in the model generated by RMC. The Ag–Ag distance (2.98 Å) agrees with the value found previously in $\text{As}_{40}\text{Se}_{40}\text{Ag}_{20}$ [4].

Table 2. The nearest neighbour distances r_{ij} and coordination numbers N_{ij} for amorphous $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$.

Pairs	As–Se	As–I	Se–As	Se–Se	Se–I	I–As	I–Se	As–X	Se–X	I–X
r_{ij} (Å)	2.40	2.60	2.40	2.40	2.61	2.60	2.61	–	–	–
N_{ij}	2.38	0.39	1.59	0.74	0.05	0.88	0.17	2.77	2.38	1.05

Each As atom has in average 2.38 ± 0.24 Se neighbours and each Se atom has 1.59 ± 0.16 As atoms. These values are notably less than the coordination numbers of As and Se in binary As_2Se_3 and ternary $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ glasses. The average coordination of I atoms is 1.05 ± 0.1 and the majority of iodine atoms are coordinated by As, $N_{\text{IAs}} = 0.88 \pm 0.09$. Though it is difficult to distinguish between As and Se atoms the Se–I coordination number obtained by the simulation (0.17) is much lower than the As–I one. For this reason it can be concluded that I is connected dominantly to As and tries to avoid Se. The same result has been obtained for amorphous $(\text{AsSe})_{85}\text{I}_{15}$ in Ref. 4. Saitoh et al investigated $\text{As}_{40-x}\text{Se}_{60}\text{I}_x$ ($x \leq 25$) glasses and established that even at such high selenium content I tends to bind As [24].

The average coordination number, $\langle N \rangle$ is about 2.31 in amorphous $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$. It was found in [4] that $\langle N \rangle \approx 2.18$ for $(\text{AsSe})_{85}\text{I}_{15}$ glass. Thus, similarly to $(\text{AsSe})_{85}\text{I}_{15}$, addition of I to As_2Se_3 decreases the connectivity of the matrix.

5. Conclusions

The structure of glassy $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ and $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$ has been investigated by diffraction techniques and EXAFS. Partial pair distribution functions and coordination numbers were obtained by simultaneous modelling of the experimental data.

Results obtained reveal that Ag and I modify the structure of the host matrix (As_2Se_3) in opposite way. Ag

4.2. $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$

The experimental XRD and ND curves and EXAFS data at As and I K-edges for $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$ glass were simulated simultaneously with RMC. Also in this case a very good agreement of the modelled curves with all experimental data has been achieved. The partial pair distribution functions $g_{ij}(r)$ $\text{As}_{34}\text{Se}_{51}\text{I}_{15}$ modelled with RMC are plotted in Fig. 3. The mean interatomic distances r_{ij} and partial coordination numbers N_{ij} estimated from $g_{ij}(r)$ are given in Table 2.

is preferentially (but most likely not exclusively) bonded to Se and does not destroy the host matrix. As a result the average coordination number of As and Se increases upon doping with Ag. On the other hand the vast majority of I atoms are connected to As only, which decreases N_{AsSe} and N_{SeAs} . The twofold coordination of Se can only be maintained by the formation of Se–Se homopolar bonds. The average coordination number decreases if I is added to As_2Se_3 . Taking into account the results of a previous study on $(\text{AsSe})_{85}\text{Ag}_{15}$ and $(\text{AsSe})_{85}\text{I}_{15}$ glasses [4] it can be concluded that such picture is general for As–Se–Ag and As–Se–I ternary glasses.

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