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ATOMIC STRUCTURE OF $As_{34}Se_{51}Ag_{15}$ GLASS

I. Kaban*, W. Hoyer, T. Petkova[a], P. Petkov[b], B. Beuneu[c], A. Schöps[d], M.A. Webb[d]

Institute of Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany
[a] Institute of Electrochemistry and Energy Systems, G. Bonchev Str. Bl.10, 1113 Sofia, Bulgaria
[b] University of Chemical Technology and Metallurgy, Department of Physics, 8Kl Ohridsky Blvd., 1756 Sofia, Bulgaria
[c] Laboratoire Léon Brillouin CEA-SACLAY, 91191 Gif sur Yvette Cedex France
[d] Hamburger Synchrotronstrahlungslabor HASYLAB am Deutschen Elektronen-Synchrotron DESY Notkestrasse 85, D-22603 Hamburg, Germany

Amorphous $As_{34}Se_{51}Ag_{15}$ has been studied with high energy X-ray diffraction, neutron diffraction and extended X-ray absorption spectroscopy. The experimental results were modelled simultaneously with the reverse Monte Carlo simulation method. Combination of data from three measurement techniques allowed the separation of partial pair correlation functions and estimation of the corresponding coordination numbers.

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1. Introduction

Glassy semiconductor As_2Se_3 becomes ionic conductor upon doping with Ag [1,2]. Other physical properties also change remarkably with addition of Ag and variation of its concentration in $(As_{0.4}Se_{0.6})_{100-x}Ag_x$ ternary glasses [1-3]. Atomic structure of ternary and quaternary chalcogenide glasses is not so well studied as their physical properties. The structural study of multicomponent alloys is always a nontrivial task 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 may still not be 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 [4-6] that the reverse Monte Carlo simulation technique (RMC) [7] 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 [8, 9].

In the present work, we study $As_{34}Se_{51}Ag_{15}$ glass 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.

* Corresponding author: ivan.kaban@physik.tu-chemnitz.de

2. Experimental details

The $As_{34}Se_{51}Ag_{15}$ glass was prepared in evacuated (~10^{-3} Pa) and sealed quartz ampoules by a conventional synthesis in a rotary furnace. At the first stage, binary As_2Se_3 was synthesised from high purity (99.999%) As and Se. Then, the proper quantity of As_2Se_3 was mixed with Ag (99.99%) and heated. The molten alloy was kept at 1200 K and stirred for 2 h. Finally, it was quenched in ice-water.

The EXAFS measurements were carried out at Ag and Se K-edges at the beam line X [11] 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 the step 0.5 eV in the vicinity of the absorption edge. The measuring time was *k*-weighted during the collection of the signal.

The neutron diffraction experiment was carried out at the 7C2 diffractometer (LLB, France). The $As_{34}Se_{51}Ag_{15}$ sample was 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 [12, 13].

3. RMC-modelling

For the details of the reverse Monte-Carlo simulation method we refer to two recent papers [14, 15]. Calculations in the present work were performed with a new version of the RMC code [16]. The simulation box contained 12000 atoms. The number density 0.0403 A^{-3} for $As_{34}Se_{51}Ag_{15}$ glass used throughout the simulation runs was calculated from the mass density 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 [17].

Simulations of the atomic structure have been started with the following cut off distances: As–As: 3.1 Å, As–Se: 2.1 Å, As–Ag: 3.1 Å, Se–Se: 3.1 Å, Se–Ag: 2.4 Å, Ag–Ag: 2.7 Å. Later some of these distances were varied to check the effect of the corresponding bond on the quality of the fits.

4. Results and discussion

In a previous structural study [4] it was assumed that there are no As–Ag bonds in $As_{40}Se_{40}Ag_{20}$ and $(AsSe)_{65}(AgI)_{35}$. A thorough investigation of the present data suggests that the situation may be different for $As_{34}Se_{51}Ag_{15}$. The fit of the Ag K-edge EXAFS measurement improved when the Ag–As cut off distance was decreased to 2.5. Fits obtained by the simultaneous modelling of the four independent measurements (with low Ag–As cut off distance) are shown in Fig. 1. The general agreement between model curves and experimental data is excellent.

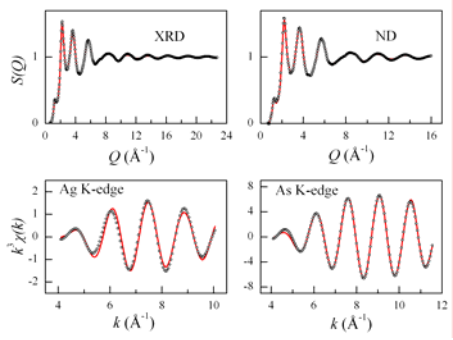

Fig. 1. XRD and ND structure factors, and EXAFS spectra for $As_{34}Se_{51}Ag_{15}$ glass. Circles – measured. Lines – obtained by simultaneous RMC simulation of the experimental XRD, ND and EXAFS data.

It is widely accepted that glassy As_2Se_3 is 'chemically ordered' i.e. it does not contain homopolar (As–As, Se–Se) bonds. If the above premise is true then it is also reasonable to assume that doping with Ag does not lead to the formation of homopolar bonds. In the absence of As–As and Se–Se bonds there are only 4 partial pair correlation functions contributing to the low *r* region ($r < 3.1$ Å). Therefore the separation of partial pair correlation functions (figure 2) and estimation of the corresponding coordination numbers and mean interatomic distances (table 1) can safely be carried out on the base of available experimental information. 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.

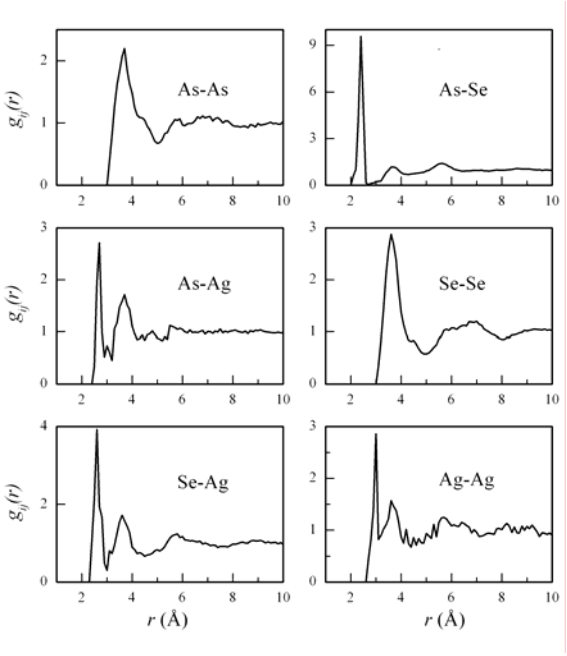

Fig. 2. Partial pair distribution functions for $As_{34}Se_{51}Ag_{15}$ glass obtained by simultaneous RMC simulation of the experimental XRD, ND and EXAFS data.

Table 1. The nearest neighbour distances r_{ij} and coordination numbers N_{ij} for $As_{34}Se_{51}Ag_{15}$ glass.

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 As–Se coordination number 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 an As neighbour The Ag–Ag distance (2.98 Å) agrees with the value found previously in $As_{40}Se_{40}Ag_{20}$ [4].

5. Conclusions

The structure of glassy $As_{34}Se_{51}Ag_{15}$ has been investigated by diffraction techniques and EXAFS. A simultaneous modelling of the measurements by means of the reverse Monte Carlo Simulation technique revealed that the covalent network formed by threefold coordinated As and twofold coordinated Se atoms is not destroyed upon doping of 15 at.% Ag. Ag atoms have in average two Se neighbours and 0.8 As neighbours. The Ag–Ag coordination number is small (~0.4) but Ag–Ag bonding follows clearly from the experimental data.

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