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Journal of Non-Crystalline Solids 353 (2007) 729–732
JOURNAL OF NON-CRYSTALLINE SOLIDS
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Structure of chalcogenide glasses by neutron diffraction

G.J. Cuello [a,*], A.A. Piarristeguy [b], A. Fernández-Martínez [a], M. Fontana [c], A. Pradel [b]

[a] *Institut Laue Langevin, 6 rue Jules Horowitz, BP 156, F-38042 Grenoble, France*
[b] *LPMC-CNRS, Université Montpellier II, Place E. Bataillon, F-34095 Montpellier, France*
[c] *Lab. de Sólidos Amorfos, Fac. de Ingeniería, UBA. Paseo Colón 850, 1063 Buenos Aires, Argentina*

Available online 26 February 2007

Abstract

The purpose of this work is to study the change in the structure of the Ge–Se network upon doping with Ag. We report here a neutron diffraction study on two glasses of the system $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ with different silver contents ($x = 15$ and 25 at.%) and for two different temperatures (10 and 300 K). The total structure factor $S(Q)$ for the two samples has been measured by neutron diffraction using the two-axis diffractometer dedicated to structural studies of amorphous materials, D4, at the Institut Laue Langevin. We have derived the corresponding radial distribution functions for each sample and each temperature, which gives us an insight about the composition and temperature dependence of the correlation distances and coordination numbers in the short-range. Our results are compatible with the presence of both $GeSe_{4/2}$ tetrahedra and Se–Se bonds. The Ag atoms are linked to Se in a triangular environment. Numerical simulations allowing the identification of the main peaks in the total pair correlation functions have complemented the neutron diffraction measurements.

PACS: 61.12; 61.43

Keywords: Neutron diffraction/scattering; Fast ionic conduction; Modelling and simulation; Short-range order

1. Introduction

Silver-containing chalcogenide glasses have been extensively studied in the last decades. Of particular interest are their electrical conductivity that changes by several orders of magnitude upon silver doping. For example the conductivity of $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses suddenly changes by seven orders of magnitude for $x \sim 10$ at.% [1–3]. It was recently shown by field effect-scanning electron microscopy and electrostatic field microscopy that the change occurred in these phase-separated glasses when the silver-rich phase starts connecting [4]. However, the mechanism of diffusion throughout the glassy matrix is still not well understood. Structural investigation might help in getting a better insight to answer these questions.

This work is focused on the structure of two glasses within the fast ionic conduction region, *i.e.* $Ag_{15}(Ge_{0.25}Se_{0.75})_{85}$ and $Ag_{25}(Ge_{0.25}Se_{0.75})_{75}$, at two different temperatures. Neutron diffraction and MD simulations have been combined in order to have an insight of the short-range order in these glasses.

2. Experimental details

2.1. Synthesis

Two $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ samples with $x = 15$ and 25 at.% (hereafter named Ag15 and Ag25, respectively) were prepared with $4N$ elements ($4N = 99.99\%$). In all cases, 12 g of materials were synthesized by placing the powdered elements in stoichiometric proportions in a cylindrical quartz ampoule. The ampoules were evacuated to a pressure of $\sim 10^{-5}$ mbar and sealed. After synthesis and homogenization for 7 h at $T \sim 1200$ K in a furnace, the ampoules were

* Corresponding author. Tel.: +33 476 207697; fax: +33 476 207648.
E-mail address: cuello@ill.fr (G.J. Cuello).

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doi:10.1016/j.jnoncrysol.2006.12.036

quenched in an ice + water mixture to obtain the glassy materials.

2.2. Neutron characterization

Neutron diffraction experiments were carried out on D4 instrument at the Institut Laue Langevin (Grenoble, France) [5]. A monochromatic beam of 0.5 Å was produced by reflection in a Cu 220 crystal. Low- and room-temperature experiments were performed using a standard orange cryostat.

For the experiment, the samples were placed in cylindrical vanadium containers of 8 mm (outer diameter) and 0.1 mm thick. The beam size was 13 mm width and 50 mm height. Diffraction spectra for both samples were registered at 10 and 300 K. The required ancillary measurements, *i.e.* vanadium rod (8 mm in diameter), empty cryostat/furnace, empty cell and boron carbide plate with the same dimensions than the sample, were also carried out.

Further to measurements, raw diffraction data underwent the usual corrections; the background was first subtracted and the standard absorption, multiple scattering and inelasticity corrections were then performed using the CORRECT code [6].

2.3. Modelling

MD simulations were carried out with the Density Functional Theory (DFT) based code, Vienna Ab-initio Simulation Package (VASP) [7,8]. The Perdew–Burke–Enzerhof variation of the General Gradient Approximation to DFT was chosen to calculate the atomic ground state energy with VASP.

The MD runs started from a randomly distributed model with the appropriate densities for the amorphous systems (0.03695 and 0.03901 atoms/Å^3 [9] for the Ag15 and Ag25, respectively). A first step of thermalization was done at 2400 K using the compass force-field, before starting the DFT calculations. A second thermalization at 1400 K was performed with VASP, followed by a quenching down to 400 K during 7 ps, and a third thermalization at 400 K during 4 ps. The MD time step was 2 fs.

3. Results

Fig. 1 shows the normalized structure factors for the Ag15 sample at the two different temperatures (10 and 300 K). On the whole the shapes of the two curves are very similar with only some changes in the intensity of the main features. The same observation is true for the Ag25 glass. Fig. 2 shows the normalized structure factors for the two glassy samples Ag15 and Ag25 at $T = 10$ K. Here also the main features are similar. However, one can note a marked decrease in the first sharp diffraction peak at 1 Å^{-1} when the silver amount increases as usual in oxide and chalcogenide glasses. Also while the second peak does not change from one sample to the other, the next ones

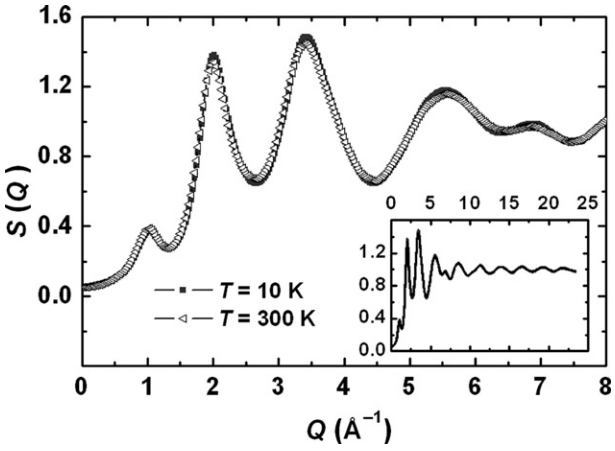

Fig. 1. Structure factors $S(Q)$, measured at $T = 10$ and 300 K for $Ag_{15}(Ge_{0.25}Se_{0.75})_{85}$ glasses. The inset shows the whole Q-range accessible in the neutron diffraction experiment.

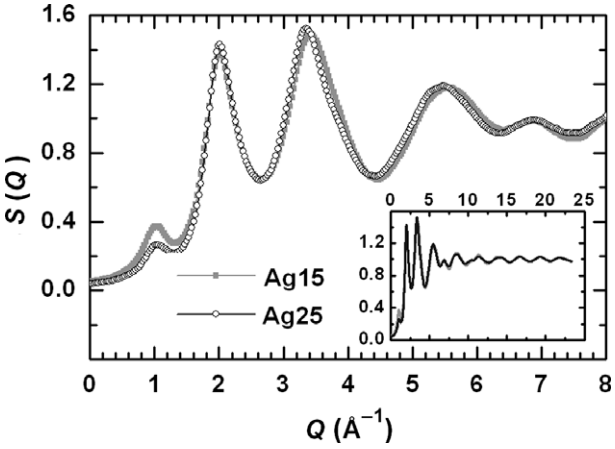

Fig. 2. Structure factors $S(Q)$ for glasses $Ag_{15}(Ge_{0.25}Se_{0.75})_{85}$ and $Ag_{25}(Ge_{0.25}Se_{0.75})_{75}$ at $T = 10$ K. The inset shows the whole Q-range accessible in the neutron diffraction experiment.

shift to lower Q values when the silver content increases. Similar trends for the structure factors were observed at 300 K.

Fig. 3 depicts the simulated structure factor for the Ag15 glass along with that derived from neutron data. The simulations produced slightly different peak positions and widths than experiments. Such a difference is due to the use of a soft pseudo potential for Se with cut-off energy of 211 eV (the only one available at hand). It affected the coordination in which Se was present by overestimating the correlation distances by about 4%. The width of the peaks in the low-Q range of the simulation data are affected by the effect of a small simulation box. This is the main reason for the differences between experimental and simulated widths of the pre-peak and first sharp diffraction peak. However, since the simulations were fairly well reproducing the trends in the experimental curves, the resulting atomistic model was used for the partial pair correlation functions, $g_{ij}(r)$ for the two studied chalcogenide glasses.

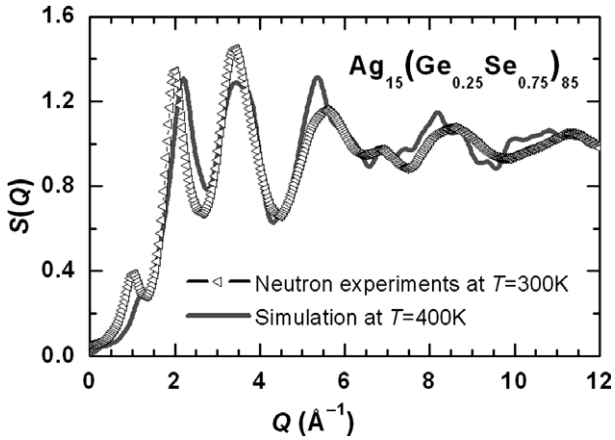

Fig. 3. Simulated structure factor $S(Q)$ for Ag15 sample at $T = 400$ K compared to neutron experiments at $T = 300$ K.

It was mainly used to interpret the experimental total pair correlation functions $g(r)$.

The total pair correlation functions were obtained by a Fourier transformation of the structure factors. The radial distribution function $\mathrm{RDF}(r) = 4\pi r^2 \rho g(r)$, where ρ is the density of the samples, was used for obtaining the correlation distances r and coordination numbers N in the system using the standard procedure [10]. In this purpose the different peaks were fitted using Gaussians. Simulation data helped us in identifying the peaks that could be attributed to the different coordination pairs. Fig. 4 shows the radial distribution function for the Ag15 sample at 10 K and the Gaussian peaks corresponding to the correlations observed below 3.5 Å. According to simulation, the first peak had contributions from both Ge–Se and Se–Se pairs. A coordination number $N_{\mathrm{GeSe}} = 4$ was assumed for Ge–Se which is in agreement with the generally accepted assumption that Ge is mainly present in a $GeSe_{4/2}$ tetrahedral environment (four half-Se atom at each corner of the tetrahedron) in Ge–Se glasses with at.% Ge $\leqslant 33$. Such an assumption helped us in calculating the $N_{\mathrm{Se-Se}}$ coordination number. The next two peaks at about 2.38 Å and 3 Å were attributed to Ag–Se and Ag–Ag correlations, respectively. Data obtained for both samples and both temperatures are given in Table 1.

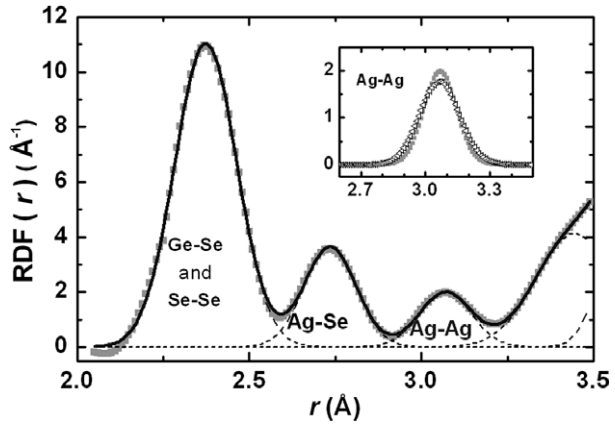

Fig. 4. Peak fitting in the radial distribution function RDF(r) for Ag15 sample at $T = 10$ K. The Gaussian functions are depicted by dotted lines, the total fitted function by solid line and the experimental data by symbols. The inset shows the changes with temperature for the Ag–Ag correlation (open and full symbols for 300 and 10 K, respectively).

4. Discussion

The structure factors $S(Q)$ and radial distribution functions RDF(r) for both samples, Ag15 and Ag25, and both temperatures, 10 and 300 K, showed the same main features. Our data are in good agreement with those obtained at 10 K by Dejus et al. who studied an $Ag_{25}(Ge_{0.25}Se_{0.75})_{75}$ glass by neutron diffraction with isotopic substitution [11]. The differences can be attributed to the different instrumental resolution for both experiments.

The first peak of the total pair correlation function (Fig. 4) was attributed to the superposition of the correlation Ge–Se and Se–Se. Dejus et al. [11] did not include any Se–Se correlation in the analysis. Our choice was based upon both our simulation data and those by Tafen et al. [12] who studied two $Ag_{10}(Ge_{0.25}Se_{0.75})_{90}$ and $Ag_{15}(Ge_{0.25}Se_{0.75})_{85}$ glasses using the FIREBOLD code. Owing to the ratio Ge/Se in both glasses, such correlations are expected if one accepts for the germanium the model of a $GeSe_{4/2}$ coordination polyhedron. A correlation distance for Ge–Se at 2.37–2.38 Å is in agreement with such a model since the average bond length of Ge and Se is 2.36 Å in the $GeSe_2$ crystal structure [13].

The next peak at about 2.71–2.73 Å corresponds to the Ag–Se correlations. A small shift in the peak position from 2.735 Å at $x = 15$ to 2.713 Å at $x = 25$ with increasing Ag was observed. A coordination number of ~2.8 Å was found for both glasses. The Ag–Se correlation distances are somewhat longer than those reported [11]. However, they are in the range of the Ag–Se distances observed for two related crystalline compounds, *i.e.* Ag_2Se and Ag_8GeSe_6. Both crystalline compounds present two phases, a low temperature one and a fast ion conducting high

Table 1
Coordination numbers and bond lengths (in Å) for $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses at $T = 10$ and 300 K

	T (K)	N_{SeSe}	N_{AgSe}	N_{AgAg}	$r_{\mathrm{GeSe\ and\ SeSe}}$	r_{AgSe}	r_{AgAg}
Ag15	10	0.917	2.814	4.254	2.374	2.735	3.070
	300	0.901	2.647	4.665	2.381	2.741	3.066
Ag25	10	0.643	2.892	2.966	2.375	2.713	3.063
	300	0.687	2.647	2.971	2.384	2.724	3.058

temperature one [14–17]. While the Ag atoms are disordered in the fast conducting phases at high temperatures, they are ordered in both low temperature forms. In this case, they have triangular and tetrahedral coordination by Se with distances ranging from 2.62 to 2.86 Å. In the Ag15 and Ag25 glasses they clearly only retain the triangular coordination which is in agreement with Dejus's findings. According to these authors such coordination might be a key in understanding the fast ion motion in these glasses. One can note that a similar coordination by S was also found for Ag in another fast ion conducting glass, *i.e.* Ag_2GeS_3 [18].

The third peak in the total pair correlation function (Fig. 4) was attributed to Ag–Ag correlations. For both samples a correlation distance of 3.06 Å was found. It is in agreement with both the experimental data from Dejus and the correlation distances that can be derived from the structure of the related crystalline phases, Ag_2Se and Ag_8GeSe_6 (2.93–3.6 Å). However, while the coordination number was found to be 4.2 for Ag15 sample it dropped down to 3.0 for the Ag-rich glass Ag25. The number for Ag25 disagrees with that found by Dejus et al. who rather proposed a coordination number of three as the one obtained for Ag15 [11]. However, the authors reported a great difficulty in fitting the peak at 3 Å and had to proceed to a numerical calculation.

If we now look at the effect of the temperature on the structure of the glasses we mainly observe the expected changes due to increased thermal vibrations with a slight increase in length for Ag–Se and Ge–Se bonds. The main changes affect the peak at 3 Å attributed to the correlation Ag–Ag as shown in the inset of Fig. 4 for Ag15 sample. The peak decreases in intensity as a result of its broadening when the temperature increases. It can be explained by the increased diffusion of silver atoms at elevated temperature. Such an increased diffusion can also account for the decrease in coordination number of Ag by Se (refer to Table 1). Dejus et al. have also reported the broadening of peak at 3 Å. In their case, it was a drastic change much larger than the one that we observe. Two facts can explain their results: they work at higher temperature, 100 °C and 170 °C and they report partial crystallization of their sample with appearance of the Ag-rich argyrodite phase. Therefore the Ag–Ag correlations include those occurring in the argyrodite which is a superionic conductor with very high conductivity above room-temperature [19].

5. Conclusions

The structure of ion conducting $Ag_{15}(Ge_{0.25}Se_{0.75})_{85}$ and $Ag_{25}(Ge_{0.25}Se_{0.75})_{75}$ glasses was studied by neutron diffraction and numerical simulations at 10 K and 300 K. Numerical simulations helped us in identifying the contribution of the different correlations to the RDF curves. It showed in particular the presence of both Se–Se and Ge–Se correlations in the first peak of the RDF that was not reported in previous experimental work. The results are consistent with a structure that contains both $GeSe_{4/2}$ tetrahedra and Se–Se bonds. The silver is bonded to Se in a triangular coordination. Changes in the Ag–Ag correlation peak at 3 Å with temperature is in agreement with increased diffusion of silver throughout the glasses, even though much less drastic changes than those reported previously for a similar study of Ag25 glass at higher temperatures were observed. Work is in progress to study the structure of Ag–Ge–Se glasses in the $x < 10$ at.% Ag range where the conductivity decreases by seven orders of magnitude. The results will be shown in a forthcoming publication.

Acknowledgements

We are grateful to Pierre Palleau for his technical support during the diffraction experiments. We thank also Mark Johnson for the helpful advice and discussions.

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