Silver environment and covalent network rearrangement in GeS$_3$–Ag glasses

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Received 2 January 2013, in final form 27 March 2013
Published 18 October 2013
Online at stacks.iop.org/JPhysCM/25/454210

Abstract

The structure of Ag-doped GeS$_3$ glasses (0, 15, 20, 25 at.% Ag) was investigated by diffraction techniques and extended x-ray absorption fine structure measurements. Structural models were obtained by fitting the experimental datasets simultaneously by the reverse Monte Carlo simulation technique. It is observed that Ge has mostly S neighbours in GeS$_3$, but Ge–Ge bonds appear already at 15% Ag content. Sulfur has $\sim$2 S/Ge neighbours over the whole concentration range, while the S–Ag coordination number increases with increasing Ag content. Ag–Ag pairs can already be found at 15% Ag. The Ag–S mean coordination number changes from 2.17 ± 0.2 to 2.86 ± 0.2 between 15% and 25% Ag content. Unlike the As–S network in AsS$_2$–25Ag glass, the Ge–S network is not fragmented upon Ag-doping of GeS$_3$ glass.

(Some figures may appear in colour only in the online journal)

1. Introduction

Memristive switching [1] has attracted a great deal of attention in view of the development of advanced nonvolatile memories. There exist several concepts of resistance-change memory, for example, electric switching in chalcogenide glasses [2], resistive switching in transition-metal oxides [3, 4], and resistance change in solid electrolytes [3–8]. The first concept utilizes amorphous-to-crystalline phase change, while the second one uses valency change of transition-metal oxide upon an applied electrical pulse. The third concept is based on nanoscale ionic transport and electrochemical formation or removal of nanoscale conductive pathways in a solid-electrolyte matrix depending on the polarity of electrodes. Devices utilizing this phenomenon are called electrochemical metallization cells (EMC) or conductive bridge memories (CBM).

Different candidate materials for the application in the EMC cells are under investigation at present [3–13]. Among them are Ge–Se or Ge–S chalcogenide glasses as the solid electrolyte containing Ag or Cu as the active metal [5–7]. In comparison to the Ge–Se–Ag glasses, Ag-doped Ge–S glasses are able to withstand much higher temperatures, which is essential for providing long-term resistance-switching functionality. Therefore, they appear to be better candidates for EMC memory applications. To optimize their functionality it is important to understand the structure of Ge–S–Ag glasses. In this paper we present the results of a study on GeS$_3$–Ag glasses with 0, 15, 20, 25 at.% Ag. Atomic level structural models are generated by fitting diffraction and extended x-ray absorption fine structure (EXAFS) datasets with the reverse Monte Carlo (RMC) simulation technique [14–16]. This method offers a frame for combining experimental structural information with physical/chemical knowledge (e.g. density, preferred coordination numbers) available a priori. The validity of various structural models can also be tested. This approach has already been applied to several closely
Figure 1. (a) Comparison of raw and backtransformed EXAFS $k^3 \chi(k)$ curves (GeS$_3$–25Ag, Ge K-edge); (b) module of the Fourier transform of $k^3 \chi(k)$ and the window used for back-transformation.

Table 1. Mass density and number density of the GeS$_3$–Ag glasses investigated. Accuracy of the mass density is about 0.15%.

| Composition    | GeS$_3$ | GeS$_3$–15Ag | GeS$_3$–20Ag | GeS$_3$–25Ag |
|----------------|---------|--------------|--------------|--------------|
| Density (g cm$^{-3}$) | 2.588   | 3.628        | 4.031        | 4.347        |
| Number density (atom Å$^{-3}$) | 0.03692 | 0.041968     | 0.043864     | 0.044654     |

Table 2. Minimum interatomic distances (in Å) used in the reverse Monte Carlo simulation runs.

| Atomic pair | Ge–Ge | Ge–S | Ge–Ag | S–S | S–Ag | Ag–Ag |
|-------------|-------|------|-------|-----|------|-------|
| Composition |       |      |       |     |      |       |
| GeS$_3$     | 3.1   | 2.0  | —     | 1.95| —    | 2.2   |
| GeS$_3$–Ag  | 2.35  | 2.0  | 3.15  | 1.95| 2.2  | 2.85  |

related systems such as AsS$_2$–Ag [17] and As$_2$S$_3$–Ag [18], GeSe$_3$–Ag [19] and Ge–Se–In glasses [20].

2. Experimental details

2.1. Sample preparation

Four glasses of the composition (GeS$_3$)$_{100-x}$Ag$_x$ with $x = 0$, 15, 20, 25 at.% were prepared from 5N purity elements. The components of total mass of 10 g were inserted into the quartz ampoules, which were then evacuated to a pressure of $10^{-3}$ Pa, sealed, and placed in a rocking furnace. The glasses were synthetized at the well defined heating profile with a maximum temperature of 1000°C kept for 12 h. The ampoules were quenched in iced water and then these ampoules were annealed for 3 h at 50 K below the respective glass transition temperature.

The mass density of the glasses was determined with an accuracy of 0.15% by dual weighing by the standard Archimedean method at room temperature. The measured values are given in table 1.

2.2. Experiments

Neutron diffraction measurements were carried out at the 7C2 diffractometer of Laboratoire Léon Brillouin (Saclay, France). Powder samples were filled into vanadium sample holders with 0.1 mm wall thickness and 6 mm diameter. The wavelength of incident radiation was 0.72 Å. Raw data were corrected for background scattering and detector cell efficiency and normalized following standard procedures. Ge and Ag K-edge EXAFS spectra were recorded at beamline X1 of Hasylab, Hamburg. Measurements were carried out in transmission mode. Powder samples were mixed with cellulose and pressed into tablets. The transmission of the tablets was around $1/e$ at the measured absorption edge. Intensities before and after the samples were recorded with ionization chambers filled with Ar and Kr with pressures depending on the energy of the edge. The x-ray absorption cross sections $\mu(E)$ were converted to $\chi(k)$ by the program Viper [21].

X-ray diffraction data were taken at the BW5 high energy x-ray diffractometer [22] (Hasylab). The energy of incident radiation was 100.0 keV ($\lambda = 0.124$ Å). Raw data were corrected for background scattering, detector deadtime, and Compton scattering [23].

3. Reverse Monte Carlo simulation

Large scale structural models (12 000 atoms) were obtained by fitting simultaneously diffraction and EXAFS datasets. Simulations were carried out with the rmcppm code [16]. Number densities used in the models were calculated from the experimental mass densities (table 1). Minimum interatomic distances (cut offs) are listed in table 2. Backscattering amplitudes and phases needed to transform partial pair correlation functions to model $\chi(k)$ curves [24] were obtained by the feff programme [25]. The EXAFS data
were Fourier-filtered before being fitted by RMC. Raw and back transformed $k^3 \chi(k)$ curves are compared in figure 1(a). Figure 1(b) displays the module of the Fourier transformation of $k^3 \chi(k)$ of GeS$_3$–Ag Ge K-edge data. The window used for back-transformation is also shown. It can be observed that the contribution of next nearest neighbour shells is rather low. The same holds for the Ag EXAFS data (figure 2). Besides, minimum interatomic distances, coordination constraints were also used: each Ge atom was forced to have four neighbours (either S or S/Ge, see below) and each S atom had at most two Ge neighbours. Artificially low coordination numbers for Ag and S atoms (0 or 1 neighbours) were also eliminated.

4. Results and discussion

4.1. GeS$_3$ glass

A structural model of glassy GeS$_3$ was obtained by fitting simultaneously ND, XRD and Ge K-edge EXAFS datasets. As this composition is sulfur-rich, Ge–Ge bonding was forbidden while S–S bonding was allowed during the simulation. For this composition only, the coordination number of sulfur was constrained to 2.

Experimental curves and fits are compared in figure 3 while partial pair correlation functions are shown in figure 4. The Ge–S distance is 2.23 Å which agrees well with Ge–S bond lengths (2.20–2.23 Å) found in GeS$_2$ [26] and in Ge–In–S, Ge–In–S–AgI and Na$_2$S–GeS$_2$ glasses [27–29]. The S–S distance is 2.06 Å, which is close to the value found in amorphous sulfur [30].

4.2. GeS$_3$–Ag glasses

The structure of ternary GeS$_3$–Ag alloys was investigated by fitting the four measurements (XRD, ND, and EXAFS at Ge and Ag absorption edges) simultaneously. The quality of the fits is demonstrated in figure 5, while coordination numbers and nearest neighbour distances are summarized in tables 3 and 4. Selected partial pair correlation functions are shown in figure 6.

Previous studies on AsS$_2$–Ag [17], GeSe$_3$–Ag [19] and GeS$_2$–Ag$_2$S [31] glassy systems revealed that Ag prefers S/Se and tries to avoid the network forming cation (As/Ge). Our results show that from this point of view GeS$_3$–Ag alloys behave in a similar way. Ag has, on average, 2.17 ± 0.2 sulfur neighbours in GeS$_3$–15Ag, while it is coordinated by 2.86 ± 0.2 sulfur atoms in GeS$_3$–25Ag. The Ag–S distance is 2.53–2.57 Å, which agrees with the Ag–S bond lengths found in As$_2$S$_3$–Ag$_2$S [32], but it is slightly shorter than the values found in GeS$_2$–Ag$_2$S (2.58 Å [31]) and in GeS$_2$–In$_2$S$_3$–AgI.
glasses (2.60 Å [28]). The deviations may be caused partly by experimental uncertainties, and partly by the composition dependence of the Ag–S interaction. The Ag–Ag distance is around 3.0 Å. A similar value was found in As$_2$S$_3$–Ag$_2$S [32].

On the other hand, a neutron diffraction study on isotopically substituted GeS$_2$–Ag$_2$S gave no clear conclusion: while a peak of $g_{AgAg}(r)$ was reported around 3 Å in the RMC study of Lee et al [33], direct transformation of diffraction datasets gave no evidence of nearest neighbour silver atoms [31]. It needs to be mentioned that the Ag–Ag coordination number (0.73–0.93) does not change significantly in the composition range investigated.

With increasing Ag content, the initially sulfur-rich GeS$_3$–Ag system can turn to a sulfur-deficient state where Ge–Ge bonding may be required to satisfy the four valences of germanium. Test calculations suggest that Ge–Ge bonds can be found already in GeS$_3$–15Ag (figure 7). The Ge–Ge coordination number is around 0.7 ± 0.3, the concentration dependence is not significant.

It is noted that the S–S coordination number is around 1 and on the average each sulfur atom takes part in ∼2 covalent bonds. The existence of S–S bonds was also tested by dedicated runs. It was found that raising the S–S cut off from 1.9 to 2.8 Å only slightly deteriorates the neutron diffraction and Ge K-edge EXAFS fits but drastically influences the fit of Ag K-edge EXAFS data as demonstrated in figure 8. The reason for this change is that the elimination of S–S bonds brings about a forced increase of the Ag–S coordination number. The Ag–S partial pair correlation functions of GeS$_3$–25Ag obtained with and without S–S bonds are compared in figure 9. It can be observed that the elimination of S–S bonds results in a ‘wing’ on the lower side of the main Ag–S peak. The different peak shape causes a qualitatively different decay of the amplitudes of the model $k^3 \chi(k)$ function. The total coordination number of

| Composition  | $N_{GeGe}$ | $N_{GeS}$ | $N_{SS}$ | $N_{SAg}$ | $N_{AgS}$ | $N_{AgAg}$ | $N_S$ | $N_{Ag}$ |
|--------------|------------|-----------|----------|-----------|-----------|-----------|-------|---------|
| GeS$_3$      | —          | 3.90      | 1.30     | 0.86      | —         | —         | —     | —       |
| GeS$_3$–15Ag | 0.64 ± 0.3 | 3.20 ± 0.3| 1.07 ± 0.1| 1.06 ± 0.4| 0.51 ± 0.1| 2.17 ± 0.4| 0.73 ± 0.3| 2.64 ± 0.2| 2.90 ± 0.4|
| GeS$_3$–20Ag | 0.69 ± 0.3 | 3.30 ± 0.3| 1.10 ± 0.1| 0.96 ± 0.4| 0.95 ± 0.1| 2.86 ± 0.4| 0.82 ± 0.3| 3.01 ± 0.2| 3.68 ± 0.4|
| GeS$_3$–25Ag | 0.75 ± 0.3 | 3.25 ± 0.3| 1.08 ± 0.1| 0.95 ± 0.4| 1.27 ± 0.15| 2.86 ± 0.4| 0.93 ± 0.3| 3.30 ± 0.3| 3.79 ± 0.4|

Table 4. Nearest neighbour distances (in Å) calculated from the models obtained by reverse Monte Carlo simulation.
sulfur increases from about 2 in GeS$_3$ glass to 3.30 ± 0.4 in GeS$_3$–25Ag glass.

4.3. Comparison of AsS$_2$–25Ag and GeS$_3$–25Ag glasses

Since Ge–S–Ag and As–S–Ag glasses have similar potential applications it may be interesting to compare the environment of silver atoms and the changes of the host covalent matrices induced by alloying. The structure of glassy AsS$_2$–25Ag was investigated by diffraction techniques and EXAFS in a similar way [17]. It was found that the mean Ag–S coordination number is 3.34 ± 0.4, while the Ag–Ag coordination number is 0.78 ± 0.4. On average, the total coordination number of Ag is close to 4. The Ag–S distance is practically the same in the two glasses, but the first peak is more pronounced in AsS$_2$–25Ag (figure 10). The Ag–Ag distance is 2.92 ± 0.03 Å, which is close to the value found in GeS$_3$–25Ag (∼2.96–3.01 Å). The coordination number of As is close to 3 in AsS$_2$–25Ag, and no As–As bonds had to be allowed to get reasonable fits. The S–As coordination number is around 1.5, while the S–S coordination number is not higher than the sensitivity of our approach (∼0.3).
Thus, while Ge–Ge bonds are formed in GeS$_3$–25Ag, AsS$_{3/2}$ units remain intact in AsS$_2$–25Ag. The other important difference between the two glasses is that due to the nonvanishing S–S bonding each sulfur atom participates in $\sim$2 covalent bonds in GeS$_3$–25Ag. The same number is around 1.5 in AsS$_2$–25Ag. It can be concluded that even if the chemical short range order is changed (due to the formation of Ge–Ge bonds) the connectivity of the covalent network of Ge and S atoms is not altered by the addition of Ag.

5. Conclusions

The short range order in GeS$_3$ and GeS$_3$–Ag glasses (15, 20 and 25 at.% Ag) was investigated by neutron and x-ray diffraction as well as EXAFS measurements at the Ge and Ag K-edges. Structural models were obtained by fitting experimental datasets simultaneously with the reverse Monte Carlo simulation technique. It was found that S–S bonding is preserved even in GeS$_3$–25Ag and each S atom takes part in $\sim$2 covalent bonds. The average coordination number of sulfur is 2.64 $\pm$ 0.3 in GeS$_3$–15Ag while it is 3.30 $\pm$ 0.3 in GeS$_3$–25Ag glass. Ge–Ge bonds appear already in the GeS$_3$–15Ag composition; thus the addition of silver changes the chemical short range order of the host GeS$_3$ matrix. On the other hand, as each sulfur atom has $\sim$2 Ge/S neighbours, the connectivity of the covalent network of Ge and S atoms is not altered by the addition of Ag. The average coordination number of Ag is 2.90 $\pm$ 0.3 in GeS$_3$–15Ag glass and 3.79 $\pm$ 0.3 in GeS$_3$–25Ag glass.

Acknowledgments

PJ was supported by OTKA (Hungarian Basic Research Fund) Grant No. 083529. The authors express their thanks to project CZ.1.07/2.3.00/20.00254 ‘Research Team for Advanced Non-crystalline Materials’ realized by the European Social Fund and Ministry of Education, Youth and Sports of The Czech Republic within The Education for Competitiveness Operational Programme for financial support. Financial support from GACR (project number P204/11/0832) is also acknowledged.

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