Structural study of AsS₂–Ag glasses over a wide concentration range

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Abstract

(As_{0.33}S_{0.67})_{100-x}Ag_x (0 ≤ x ≤ 28) bulk glasses showing micro-phase separation in a wide concentration range have been studied by X-ray diffraction, neutron diffraction and extended X-ray absorption fine structure measurements. The AsAgS₂ composition, which forms a homogeneous glass, is modeled with the reverse Monte-Carlo simulation technique. It is established that Ag prefers the environment of S; Ag–As bonding cannot be observed. Similarly to the AsAgS₂ crystalline modifications smithite and trechmannite, the main structural units of the glass are AsS₃ pyramids. The covalent network of As and S atoms becomes fragmented in the glassy AsAgS₂ unlike in the glassy AsS₂. The environment of Ag atoms in the AsAgS₂ glass differs from that in the crystalline state. In average, each Ag atom has four nearest neighbors, three of them being S and one being Ag.

Keywords: chalcogenides; glasses; phase separation; structure; density

1. Introduction

Amorphous As–S chalcogenides with additions of Ag are of considerable interest due to their ionic conductivity, photo-induced Ag diffusion, polarity-dependent switching and memory effect [1-8]. Similar to As–S binary alloys, Ag-containing arsenic sulphides show a very good glass-forming ability over a wide concentration range [1]. Depending on the composition, the glasses produced by

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quenching As–S–Ag melts in air are either homogeneous or inhomogeneous [1, 9-12]. The micro-phase separation in the As–S–Ag glasses is due to the liquid-liquid immiscibility in the As–Ag–S ternary system [13,14]. Two extended miscibility gaps are situated on the As–S side of the As–Ag–S ternary diagram. They are separated by a narrow single-liquid region along the As_2S_3 – Ag_2S tie line.

Most of the previous studies on the As–S–Ag glasses have been carried out for compositions along the As_2S_3 –Ag and As_2S_3 – Ag_2S tie lines. Ohta explained the variation of the physical properties of these glasses upon addition of either Ag or Ag_2S by the breaking of As–S–As links and the formation of Ag–S and As–As bonds [15]. Mastelaro et al [16] did not consider As–As bonding in the $(\text{As}_2\text{S}_3)_{100-x}(\text{Ag}_2\text{S})_x$ ternary glasses in their extended X-ray absorption fine structure (EXAFS) study. They found that each As atom is coordinated by three S atoms ($r_{\text{AsS}} = 2.25\text{--}2.27 \text{ \AA}$) and Ag is coordinated by two S atoms ($r_{\text{AgS}} = 2.46\text{--}2.48 \text{ \AA}$) at any Ag concentration. Penfold and Salmon [17] studied the structure of $\text{As}_{37.6}\text{S}_{58.4}\text{Ag}_4$ and $\text{As}_{25}\text{S}_{50}\text{Ag}_{25}$ glasses and confirmed that As is three-fold coordinated by S atoms both for low and high concentration of Ag. On the other hand they found that the coordination number of Ag varies: it is fourfold coordinated in the $\text{As}_{37.6}\text{S}_{58.4}\text{Ag}_4$ glass and threefold coordinated in the AsAgS_2 glass. Also, they reported on Ag–Ag bonding with an interatomic distance of about $2.97 \text{ \AA}$, but neither As–As nor Ag–As bonds were identified. Bychkov and Price [18] separated As–S, Ag–S and Ag–Ag peaks by fitting a radial distribution function for the AsAgS_2 glass by three Gaussian curves.

Recently [4,7,11,12] attention has also been paid to the chalcogenide glasses along the AsS_2 –Ag line, which goes through the miscibility gap. It was established that the electrical conductivity of the glasses increases significantly with increasing Ag concentration and the Ag^+ ions are the main charge carriers. $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ bulk glasses with Ag content between 4 and 20 at.% were found to be phase-separated on the micrometer scale. In the present work, we investigate the atomic structure of $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ ($0 \leq x \leq 28$) bulk glasses by X-ray diffraction (XRD), neutron diffraction (ND) and extended X-ray absorption fine structure spectroscopy. The structure of a homogeneous bulk glass AsAgS_2 is modeled with the reverse Monte-Carlo simulation technique [19]. The local atomic arrangement of the AsAgS_2 glass is compared with the crystalline structures of the AsAgS_2 compound.

2. Experimental details

$(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ bulk glasses ($x = 0, 4, 8, 12, 16, 20, 24, 25, 28$ at.%) were prepared from high purity (99.999%) Ag, As and S. Proper quantities of the constituent elements were put in silica ampoules, which were then evacuated to a residual pressure $\approx 10^{-4} \text{ Pa}$ and sealed. To avoid oxide formation arsenic was purified by sublimation just before weighing. The alloys were molten in a rocking furnace, kept for 24 hours at a high temperature ($\text{As}_{33}\text{S}_{67}$ composition – at 923 K; ternary alloys – at 1223 K) and quenched in air. The glassy samples were annealed for three hours near the respective glass transition temperature. They were kept under inert atmosphere of N_2 after breaking the synthesis ampoules. The mass density of the glasses was determined with the accuracy of 0.15% using

the Archimedean method by weighting samples in air and in toluene. The density values are listed in Table 1 and are plotted as a function of Ag content in Fig. 1.

X-ray diffraction experiments were performed at the BW5 beamline at HASYLAB (DESY, Hamburg, Germany). The measurements of glass pieces of about 2 mm thickness were carried out in transmission geometry. The energy of the incident beam was 100 keV and the beam size was 1×2 mm². The scattered intensity was recorded by a Ge solid-state detector. The raw data were corrected for background, absorption, polarization, detector dead-time and variations in detector solid angle [20]. The neutron diffraction experiments were carried out with the 7C2 diffractometer at the Léon Brillouin Laboratory (CEA-Saclay, France). The glassy samples were ground and filled into thin walled (0.1 mm) vanadium containers of 7 mm diameter. The measured diffraction data were corrected for detector efficiency, empty instrument background, scattering from the sample holder, multiple scattering, and absorption. The Ag and As *K*-absorption edge EXAFS measurements were carried out at the X1 experimental station at HASYLAB in transmission mode. The samples were finely ground, mixed with cellulose and pressed into tablets. The sample quantity in the tablets was adjusted for the composition of the sample and to the selected edge to achieve an approximate transmission of $1/e$. EXAFS spectra were obtained with steps of 0.03 Å above the absorption edge. The measuring time was *k*-weighted during the collection of the signal. The X-ray absorption cross sections $\mu(E)$ were converted to $\chi(k)$ by standard procedures of data reduction using the program Viper [21].

3. Experimental results

The experimental structure factors $S(Q)$ measured by XRD and the As and Ag *K*-edge back Fourier-transformed EXAFS spectra of the $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ bulk glasses are plotted in Fig. 2 (the data for some compositions are not shown for clarity of the presentation). The total XRD pair distribution functions $g(r)$ are presented in Fig. 3. The Fourier transformation of the $S(Q)$ s has been performed with the number densities ρ calculated from the measured mass density (Table 1).

It is noteworthy that the EXAFS spectra of the $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ glasses at both the As and Ag absorption edges exhibit a rather weak composition dependence. This suggests small changes of the local atomic arrangement around As and Ag atoms over the whole concentration range studied. In opposite, significant changes are observed with increasing Ag concentration for the structure factors as well as for the pair distribution functions. The structure factor of the binary $\text{As}_{33}\text{S}_{67}$ composition is characterized by pronounced oscillations extending over the whole *Q*-range measured in the present work. There is an intensive first sharp diffraction peak (FSDP) at about 1.26 Å^{-1} whose intensity decreases rapidly with increasing Ag content (Fig. 4). The height of the next two peaks on the $S(Q)$ (at $Q = 2.16 \text{ Å}^{-1}$ and $Q = 3.86 \text{ Å}^{-1}$ in glassy $\text{As}_{33}\text{S}_{67}$) changes in the opposite way (decreasing/increasing) by addition of Ag. The intensity of the oscillations for the *Q*-values larger than $\sim 10 \text{ Å}^{-1}$ drops fast and becomes negligibly small at 25 and 28 at.% Ag. Also the FSDP almost disappears for these

compositions. It is interesting that the $S(Q)$ parameters obtained from the XRD measurements vary practically linearly with composition, similar to the composition variation of the mass density (Fig. 1, Fig. 4).

The changes of the shape of the total structure factors are reflected in the respective XRD total pair distribution functions (Fig. 3). The peak of the $g(r)$ functions at $r = 2.26$ Å reflects the As–S bonding. This value (2.26 Å) agrees with the As–S distance in glassy As_2S_3 [22] as well as with the sum of covalent radii of As and S [23]. The intensity of this peak decreases monotonically with increasing Ag concentration. At the same time, a shoulder on the right-hand side of the first peak on $g(r)$ at about 2.5–2.6 Å appears and develops into a main peak for the alloy with 28 at.% Ag. This distance corresponds to the sum of the covalent radii of Ag and S (2.50–2.58 Å [23]). These findings can be interpreted as a decrease of the number of As–S bonds and formation of Ag–S bonds when Ag is alloyed with AsS_2 . As it has been mentioned, some previous studies reported also on the formation of As–As bonding [15] and Ag–Ag bonding [17,18]. Due to an averaged character of the information provided by the total pair distribution functions, a method to extract the partial pair distribution functions should be applied. In the present work, we use the reverse Monte Carlo simulation technique [19,24–26], which enables construction of large three-dimensional structural models compatible with a set of available experimental information (XRD, ND and EXAFS data in our case). Partial pair distribution functions, most probable interatomic distances and coordination numbers can be extracted from a model atomic configuration. Scanning electron microscopy (SEM) and Raman studies of $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ bulk glasses [11] showed that the alloys with x from 4 up to 24 at.% Ag and with $x = 28$ were micro-phase separated. On the other hand, the alloy AsAgS_2 ($x = 25$) was homogeneous. Therefore, we selected the AsAgS_2 glass for the RMC modeling in the present work.

4. RMC modeling and discussion

The details of RMC and its application to chalcogenide glasses can be found elsewhere [19,24–26]. The atomic structure of AsAgS_2 glass has been modeled with the RMC++ code [24]. The simulation box contained 16000 atoms. A number density $\rho = 0.0454$ Å⁻³ was used for the simulations. The backscattering factors needed to obtain the model EXAFS curves from the partial pair distribution functions were calculated by the FEFF8.4 program [27]. The fits obtained by simultaneous modeling of the XRD, ND and EXAFS data for the AsAgS_2 glass are compared with the experimental data in Fig. 5. The partial pair distribution functions $g_{ij}(r)$ extracted from the final configuration box are presented in Fig. 6. The corresponding mean nearest neighbor distances r_{ij} and coordination numbers N_{ij} are given in Table 2. The uncertainty of r_{ij} is around ± 0.02 Å. The uncertainty of N_{ij} is usually around 0.3–0.5.

Several simulation runs were carried out to check whether As–As, As–Ag or Ag–Ag bonds exist in glassy AsAgS_2 . As–S and Ag–S bonds were allowed in all runs. It was found that the R-factors decreased by 10–30% upon introducing Ag–Ag bonding. The mean Ag–Ag distance 2.92 ± 0.03 Å

found for glassy AsAgS_2 agrees very well with the Ag–Ag bond length obtained for other chalcogenide glasses containing silver [28,29]. Further improvement of the fits was observed when As–As bonds were also allowed. However, the As–As peak position was at about 2.3 Å. This distance is obviously too short for the As–As bond, which is usually around 2.40–2.46 Å in glassy chalcogenides [28,30]. If the As–As peak was pushed up to 2.4 Å by increasing the corresponding cut-off, the quality of the fits became remarkably worse. As–Ag bonding was also tested, but the quality of the fits did not improve. Hence our findings suggest that the chemical short-range order in the AsAgS_2 glass is characterized by the three bonds: As–S, Ag–S and Ag–Ag.

It is interesting to compare the local atomic order in the AsAgS_2 glass with the structure of its crystalline counterparts. The AsAgS_2 compound exists in two crystalline modifications: smithite [31] and trechmannite [32]. In both smithite and trechmannite, each As atom is bonded to three S atoms in a trigonal pyramid; three such pyramids form an As_3S_6 molecule by sharing S atoms; the As_3S_6 molecules are connected via Ag atoms. The length of the As–S bonds varies between 2.21 and 2.36 Å in smithite and between 2.21 and 2.30 Å in trechmannite. In both AsAgS_2 crystal modifications, one Ag is coordinated by four S atoms in a distorted tetrahedron. The distortion is larger in smithite where the Ag–S bond length varies from 2.51 to 3.03 Å, while r_{AgS} changes from 2.59 to 2.73 Å in trechmannite. The existence of many nonequivalent bonds is reflected in a series of bands on the infrared (IR) spectrum, as shown for example for smithite by Golovach et al [33]. The IR spectrum of glassy AsAgS_2 is essentially smeared, which has been explained by irregular packing of the AsS_3 structural units [33]. Our study confirms that, similar to smithite and trechmannite, AsS_3 pyramids exist in glassy AsAgS_2 . However, in contrast to the crystalline phases, the As–S bond length is well defined – there is a distinct peak at 2.26 Å on the As–S partial pair distribution function of glassy AsAgS_2 . The environment of Ag atoms in the glass differs from that in the crystalline state. In the glassy state, each Ag atom has about three S nearest neighbors ($N_{\text{AgS}} = 3.34 \pm 0.4$) at an average distance of 2.55 ± 0.02 Å and about one Ag neighbor ($N_{\text{AgAg}} = 0.78 \pm 0.4$) at an average distance of 2.92 ± 0.03 Å. This finding suggests that in the glassy AsAgS_2 silver is predominantly fourfold coordinated but instead of bonding to S atoms - as in the crystalline state - Ag has a Ag neighbor in the glass.

Some selected bond angle distributions in the glassy AsAgS_2 as obtained from the RMC final atomic configuration are shown in Fig. 7. The rather well defined As–S–As bond angle centered at about 103° corresponds to the AsS_3 pyramids. The Ag–S–Ag bond angle distribution is much more diffuse. The main peak is at 95° , but the usual ‘contact peak’ close to 60° can also be found. The latter is due to the first neighbor Ag pairs sharing the same S atom while the second neighbor Ag pairs separated by 3.5–3.8 Å contribute to the main peak. The S–Ag–S bond angle distribution is characterized by a peak at about 82° and a long tail extending to higher angles. The position of the main peak and the small rise close to 180° indicates that in spite of N_{Ag} being close to 4 the local order around Ag is not tetrahedral but slightly reminds of octahedral arrangement.

It has been suggested in [11] that the micro-phase separated $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ glasses with $4 \leq x \leq 20$ consist of Ag-poor (about 3–4 at.% Ag) and AsAgS_2 phases. The Raman spectra of the micro-phase separated $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ glasses were well described by a linear combination of the Raman spectra for the compositions with 4 and 25 at.% Ag [11]. For example, the volume fractions of Ag-poor and Ag-rich phases for the glass with $x = 8$ were determined to be equal to 0.75 and 0.25, and for the glass with $x = 16$ to be equal to 0.4 and 0.6, respectively [11]. We have calculated ND structure factors of these two compositions as a linear combination of the $S(Q)$ s of the glasses with $x = 4$ and $x = 25$. A good agreement has been observed with the weighting coefficients 0.8 and 0.2 for the $(\text{As}_{0.33}\text{S}_{0.67})_{92}\text{Ag}_8$ glass and with 0.35 and 0.65 for the $(\text{As}_{0.33}\text{S}_{0.67})_{84}\text{Ag}_{16}$ glass, as demonstrated in Fig. 8. The difference in the volume fractions between our study and previous work [11] is acceptable taking into account that the Ag-poor phase contains somewhat less than 4 at.% Ag.

On the basis of the Raman scattering results of [11] it can be concluded that the building blocks of Ag-poor phase are AsS_3 pyramids. Ag binds preferentially to excess S atoms and avoids As. It is to be mentioned that in the As_2S_3 –Ag glasses Ag–As bonding was observed [34]. The comparison of As K-edge EXAFS spectra of AsS_2 –Ag glasses (Fig. 2b) suggests that the environment of As atoms is very similar in AsS_2 and AsAgS_2 glasses and AsS_3 pyramids can also be found in the Ag-rich phase. According to [11], S–S bonding decreases with increasing Ag content and vanishes in AsAgS_2 . Thus, S has only As and Ag neighbors in the AsAgS_2 glass. From the stoichiometry it follows that S has on the average 1.5 As neighbors, which means that the covalent network of corner sharing AsS_3 pyramids is fragmented in the AsAgS_2 glass.

5. Conclusions

The mass density as well as the main structural parameters of the $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ bulk glasses change practically linearly with Ag concentration between $x = 0$ and $x = 28$. The structure of the glasses with $4 < x < 25$ is well described by the combination of ND curves of glassy alloys with $x = 4$ and $x = 25$, which correlates with the results of Raman and SEM investigations proving micro-phase separation in the ternary glasses. Micro-phase separated glasses consist of Ag-poor (up to 4 at.% Ag) and AsAgS_2 phases. Reverse Monte Carlo modeling of the AsAgS_2 composition, which forms a homogeneous glass, revealed that AsS_3 pyramids remain the main structural units of the glass similar as for the AsAgS_2 crystalline modifications smithite and trechmannite as well as for the binary As–S glasses. However, unlike in the AsS_2 glass, the covalent network of As and S atoms becomes fragmented in the glassy AsAgS_2 . The environment of Ag atoms in the AsAgS_2 glass differs from that in the crystalline state. In average, each Ag atom has 4 nearest neighbors, three of them being S and one being Ag.

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Table 1. Mass density of $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ glasses measured by the Archimedean method and the number density calculated.

Alloy	Mass density (g/cm ³)	Number density (atoms/Å ³)
$\text{As}_{33}\text{S}_{67}$	2.968 ± 0.005	0.0387
$(\text{As}_{0.33}\text{S}_{0.67})_{96}\text{Ag}_4$	3.235 ± 0.005	0.0400
$(\text{As}_{0.33}\text{S}_{0.67})_{92}\text{Ag}_8$	3.397 ± 0.006	0.0400
$(\text{As}_{0.33}\text{S}_{0.67})_{88}\text{Ag}_{12}$	3.728 ± 0.006	0.0419
$(\text{As}_{0.33}\text{S}_{0.67})_{84}\text{Ag}_{16}$	4.023 ± 0.006	0.0427
$(\text{As}_{0.33}\text{S}_{0.67})_{80}\text{Ag}_{20}$	4.295 ± 0.006	0.0442
$(\text{As}_{0.33}\text{S}_{0.67})_{76}\text{Ag}_{24}$	4.540 ± 0.006	0.0448
$(\text{As}_{0.33}\text{S}_{0.67})_{75}\text{Ag}_{25}$	4.644 ± 0.006	0.0454
$(\text{As}_{0.33}\text{S}_{0.67})_{72}\text{Ag}_{28}$	4.792 ± 0.006	0.0455

Table 2. The nearest neighbor distances r_{ij} (within the first coordination shell) and coordination numbers N_{ij} for amorphous AsAgS_2 . The uncertainty of r_{ij} is 0.02–0.03 Å. The uncertainty of N_{ij} is about 0.4.

Pairs	This work		Ref. [17]	
	r_{ij} (Å)	N_{ij}	r_{ij} (Å)	N_{ij}
As–As	–	0	–	–
As–S	2.26	2.99	2.27	3.0
As–Ag	–	0	–	–
S–As	2.26	1.49	2.27	1.5
S–S	–	0	–	–
S–Ag	2.55	1.67	2.54	1.6–1.65
Ag–As	–	0	–	–
Ag–S	2.55	3.34	2.54	3.2–3.3
Ag–Ag	2.92	0.78	–	–
As–X	–	2.99	–	3.0
S–X	–	3.16	–	3.1–3.15
Ag–X	–	4.12	–	3.2–3.3

Fig. 1. Mass density in the $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ bulk glasses in dependence of Ag content. The experimental uncertainty is comparable with the size of symbols.

Fig. 2. (Color online) Structure factors measured with X-ray diffraction (a); arsenic (b) and silver (c) K -edge back Fourier-transformed EXAFS spectra of the $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ glasses.

Fig. 3. (Color online) Pair distribution functions of the $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ glasses measured by X-ray diffraction.

Fig. 4. (Color online) Intensity of the first, second and third peaks on the XRD total structure factors as a function of Ag content in the $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ bulk glasses. The uncertainty is comparable with the size of symbols.

Fig. 5. (Color online) XRD and ND structure factors, and EXAFS spectra for AsAgS₂ glass: *circles* – measurement; *lines* – obtained by simultaneous RMC simulation of the experimental data.

Fig. 6. Partial pair distribution functions for AsAgS₂ glass obtained by RMC.

Fig. 7. (Color online) As–S–Ag, Ag–S–Ag and S–Ag–S bond angle distribution in AsAgS₂ glass.

Fig. 8. (Color online) Neutron diffraction structure factors for the micro-phase separated $(\text{As}_{0.33}\text{S}_{0.67})_{100-x}\text{Ag}_x$ glasses: *full line* – experiment; *dashed line* – linear combination of the experimental ND structure factors of the glasses with $x = 4$ and $x = 25$.