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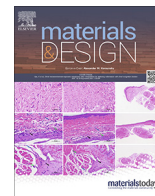
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# Unexpected role of metal halides in a chalcogenide glass network

Rayan Zaiter<sup>a</sup>, Mohammad Kassem<sup>a</sup>, Daniele Fontanari<sup>a</sup>, Anton Sokolov<sup>a</sup>, Takeshi Usuki<sup>b</sup>, Maria Bokova<sup>a</sup>, Alex C. Hannon<sup>c</sup>, Chris J. Benmore<sup>d</sup>, Fabrice Cousin<sup>e</sup>, Ilya Ozheredov<sup>f</sup>, Eugene Bychkov<sup>a,\*</sup>

<sup>a</sup> Université du Littoral Côte d'Opale, 59140 Dunkerque, France

<sup>b</sup> Faculty of Science, Yamagata University, Yamagata 990-8560, Japan

<sup>c</sup> ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK

<sup>d</sup> X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, United States

<sup>e</sup> Laboratoire Léon Brillouin, 91191 Gif sur Yvette, France

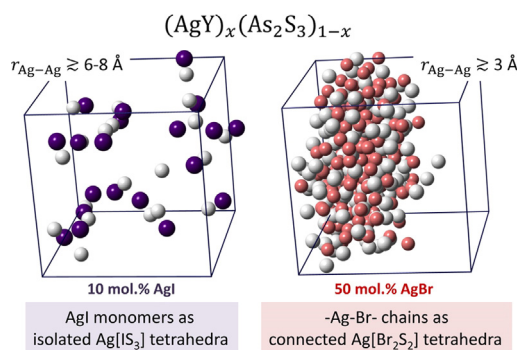
<sup>f</sup> Lomonosov Moscow State University, 119991 Moscow, Russian Federation



## HIGHLIGHTS

- Silver halides in  $\text{AgY-As}_2\text{S}_3$  ( $\text{Y} = \text{Br, I}$ ) glasses behave as unconventional modifiers.
- Formation of terminal sulfur with AgY additions is accompanied by increasing fraction of As-As homopolar bonds for 16% of arsenic species.
- AgY monomers are distributed randomly in AgY-poor glasses ( $\lesssim 2\text{--}3$  at.% Ag)
- Edge- and corner-sharing  $\text{Ag}[\text{Br}_2\text{S}_2]$  tetrahedra are forming preferential conduction pathways in AgBr-rich glasses ( $\gtrsim 10$  at.% Ag)

## GRAPHICAL ABSTRACT



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## ABSTRACT

Chalcogenide glasses containing light alkali and Group 11 (Cu, Ag) halides MY ( $\text{Y} = \text{Cl, Br, I}$ ) exhibit high ionic conductivity while their heavy alkali counterparts show promising properties for optical applications. The structural role of metal halides in chalcogenide glass networks remains either essentially unknown (alkali halides) or controversial (CuY, AgY). In addition, possible structural changes as a function of MY content have not been reported. Using pulsed neutron diffraction, high-energy X-ray scattering, Raman spectroscopy and FPMD modeling, we show unexpected role of silver halides as unconventional modifiers taking two contrasting glass compositions:  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  (critical percolation domain) and  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  (modifier-controlled region) as an example. The latter alloy seems to be a promising precursor for thermoelectric applications. The deep insight into the glass structure on the short- and intermediate-range scale, including an enhanced chemical disorder, enables a rational design of these functional materials.

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## 1. Introduction

Chalcogenide glasses containing alkali and Group 11 (Cu, Ag) halides MY ( $\text{Y} = \text{Cl, Br, I}$ ) are promising materials for various appli-

\* Corresponding author.

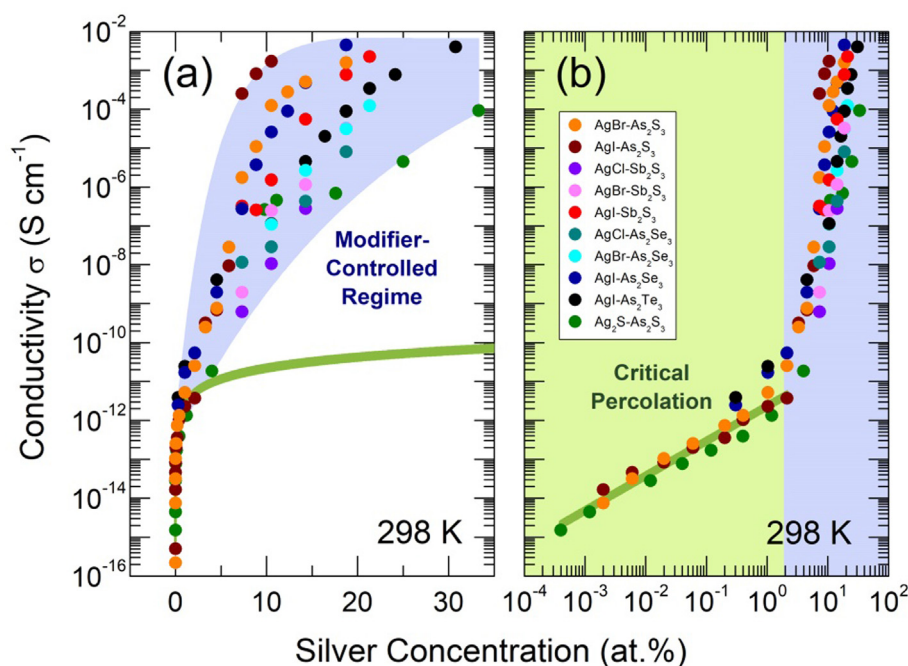
E-mail address: [bychkov@univ-littoral.fr](mailto:bychkov@univ-littoral.fr) (E. Bychkov).

cations. The light alkali and AgY/CuY vitreous chalcogenide alloys exhibit high ionic conductivity [1–4] while their heavy alkali counterparts show excellent optical properties, see for example, [5,6] and references therein. The structural role of metal halides in chalcogenide glass networks remains either essentially unknown (alkali halides) or controversial (CuY, AgY). In addition, possible structural changes as a function of MY content have not been reported. A common point of view related to silver halide glasses consists in considering AgY additions as *chemically inert* dopant salts providing network expansion and additional free volume for fast ion transport associated with a large size of the halide anion [7]. A widely discussed problem was related to anion distribution in glasses with two contrasting hypotheses: (a) clustering of silver halide rich domains of  $\alpha$ -AgI type or (b) a statistical distribution within disordered network [8]. Comparing three silver halides, AgCl, AgBr and AgI, and the resulting glass-forming ability, we have observed that silver bromide and iodide behave more or less similarly, and the glass-forming limits are nearly identical with a slight improvement for AgI. AgCl-As<sub>2</sub>X<sub>3</sub> (X = S, Se) and AgCl-Sb<sub>2</sub>S<sub>3</sub> glasses are less stable and the limiting AgCl concentration is lower compared to bromide and iodide counterparts. It looks like chloride species are destabilizing the glass network but this observation will need additional studies.

The network expansion with a cubic scaling relation between the conductivity enhancement and the resulting free volume,  $\sigma(x)/\sigma(0) \propto [(V_m(x) - V_m(0))/V_m(x)]^3$ , where  $\sigma(x)$  and  $V_m(x)$  are the conductivity and molar volume of the doped glass with a AgY molar fraction  $x$ , cannot be applied to AgY-containing chalcogenide glasses [9]. In case of pseudo-binary (AgY)<sub>x</sub>(As<sub>2</sub>X<sub>3</sub>)<sub>1-x</sub> vitreous alloys, where X = S, Se, or Te, alloying with AgY even decreases the molar volume  $V_m(x)$  with increasing  $x$  for X = Cl and Br, or  $V_m(x)$  remains invariant for AgI-As<sub>2</sub>S<sub>3</sub> glasses [10]. Nevertheless, the ionic conductivity  $\sigma_i(y)$  of the AgY – As<sub>2</sub>S<sub>3</sub> glasses increases by 13 orders of magnitude over 5 orders of magnitude in the silver content  $y$  [10], confirming two drastically different ion transport regimes in silver halide thioarsenate glasses, Fig. 1.

The ionic conductivity in the critical percolation domain,  $20 \text{ ppm} < y \leq 2 \text{ at.}\% \text{ Ag}$ , follows a power-law dependence,  $\sigma_i(y, T) \propto y^{T_0/T}$ , where the critical temperature  $T_0$  is related to the connectivity of the glassy host and the average coordination number  $\langle n_0 \rangle$  [2]. Moreover, Fig. 1 shows that  $\sigma_i(y, T)$  is chemically invariant in the critical percolation domain. Three silver thioarsenate glass families, AgY- and Ag<sub>2</sub>S-As<sub>2</sub>S<sub>3</sub>, reveal identical ionic conductivity within experimental uncertainty over three orders of magnitude in the silver content  $y$ . The ionic conductivity in the percolation domain should be sensitive to the stoichiometry of the host glassy matrix, affecting the average coordination number  $\langle n_0 \rangle$  [2]. However, slight deviations in the As content will not change significantly  $\langle n_0 \rangle$  and therefore  $\sigma_i(y, T)$ . The ionic conductivity diverges in the modifier-controlled region,  $y > 7\text{--}10 \text{ at.}\% \text{ Ag}$ , and the difference in  $\sigma_i(y)$  between AgI- and Ag<sub>2</sub>S-As<sub>2</sub>S<sub>3</sub> glasses approaches 4 orders of magnitude. The critical percolation and modifier-controlled regimes of the ion transport in glasses are related to random vs. non-random distribution of mobile cations in the glass network, confirmed by small-angle neutron scattering, neutron and high-energy X-ray diffraction [2,15,16] and recent first-principles molecular dynamics (FPMD) modeling for silver thioarsenate and thiogermanate glasses [4].

The main goal of the present contribution is to unravel a previously unknown structural role of silver halides in pseudo-binary AgY-As<sub>2</sub>S<sub>3</sub> glasses belonging to the critical percolation domain, (AgI)<sub>0.1</sub>(As<sub>2</sub>S<sub>3</sub>)<sub>0.9</sub> ( $y = 2.13 \text{ at.}\% \text{ Ag}$ ), and modifier-controlled region, (AgBr)<sub>0.5</sub>(As<sub>2</sub>S<sub>3</sub>)<sub>0.5</sub> ( $y = 14.29 \text{ at.}\% \text{ Ag}$ ), using Raman spectroscopy, diffraction techniques and FPMD. The latter alloy also seems to be a promising precursor for thermoelectric applications [17–19], starting from the first patent to recently calculated super-high thermoelectric figure of merit  $ZT \approx 7$  for similar metal halides and chalcogenides. A deep insight into the structure will be crucial for improving design of new thermoelectric amorphous materials, including printed thermoelectric sheets [20], as well as phase-change memories [21,22], materials for energy storage [23,24], photodetection [25] and spintronics [26].



**Fig. 1.** Room-temperature ionic conductivity isotherms of AgY-As<sub>2</sub>S<sub>3</sub> (Y = Br, I), AgY-As<sub>2</sub>X<sub>3</sub> (Y = Cl, Br, I; X = Se, Te), AgY-Sb<sub>2</sub>S<sub>3</sub> (Y = Cl, Br, I), and Ag<sub>2</sub>S-As<sub>2</sub>S<sub>3</sub> glasses [10–14]; (a) linear concentration scale, (b) a log–log plot. The bold green solid line shows chemically-invariant power-law composition dependence of  $\sigma_{298}(y)$  for three families of silver thioarsenate glasses in the critical percolation domain. The modifier-controlled region is highlighted in light blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 2. Methods

### 2.1. Glass synthesis

The  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  and  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  glasses were prepared from silver bromide and silver iodide respectively, with arsenic sulfide precursors via conventional high-temperature synthesis. The various components in the required proportion were sealed under vacuum ( $10^{-6}$  mbar) in silica tubes, heated up to 850 °C for 24 h before quenching in icy salt water.

### 2.2. Glass homogeneity characterization

A JEOL JSM-7100F thermal field emission scanning electron microscope equipped with EDX Bruker QUANTAX 800 spectrometers was used to check the sample uniformity. The PAXY small-angle neutron scattering instrument (Laboratoire Léon Brillouin, France) was used for mesoscopic (10–1000 Å) structural studies using different neutron wavelengths and sample-to-detector distances: 5 Å/1.5 m, 5 Å/3.5 m, 8.5 Å/5 m, and 15 Å/6.7 m. The velocity selector of the PAXY instrument yielded  $\Delta\lambda/\lambda = 0.11$  for the used wavelengths.

### 2.3. Raman spectroscopy measurements

Raman spectra were collected at room temperature using a Lab-Ram HR spectrometer (Jobin Yvon Horiba Group); in most cases a long working distance microscope objective (50×, 0.50NA) was applied. Raman scattering was excited by a 785 nm solid-state laser and recorded in the 80–850  $\text{cm}^{-1}$  spectral range. To avoid crystallization of the glassy samples, the laser power was chosen between 150  $\mu\text{W}$  and 1.5 mW, and the acquisition time was 100 to 300 s. Two to three spectra were registered for each sample at different positions to verify the sample homogeneity and the absence of photo-induced phenomena. At least, two samples of each composition were studied to check the reproducibility of the data. Some characteristic Raman spectra showing the effect of the laser power and glass reproducibility are given in [Supplementary material, Figures S1 and S2](#).

### 2.4. Diffraction measurements

The  $\text{AgY-As}_2\text{S}_3$  glasses were measured using time-of-flight neutron diffraction at the ISIS spallation neutron source (Rutherford-Appleton Laboratory, UK). The GEM diffractometer at ISIS provides diffraction data over an extended range in reciprocal space up to 50  $\text{\AA}^{-1}$ , leading to a high resolution in real space. The neutron diffraction data were corrected for background and container scattering, self-attenuation, multiple scattering, and inelasticity (Placzek) effects to obtain the total neutron structure factor  $S_N(Q)$  [27].

High-energy X-ray diffraction measurements were conducted at the 6-ID-D beamline of the Advanced Photon Source (Argonne National Laboratory, USA). The X-ray energy was 100 keV, providing data at  $Q$  values up to 30  $\text{\AA}^{-1}$ . A 2D setup was used for data collection with a Perkin Elmer model 1621 X-ray area detector. The two-dimensional diffraction patterns were reduced using the Fit2D software [28]. The measured background intensity was subtracted, and corrections were made for the different detector geometries and efficiencies, sample self-attenuation, and Compton-scattering using standard procedures [29] giving the X-ray total structure factor  $S_X(Q)$ .

### 2.5. First-principles molecular dynamics modeling

The Born-Oppenheimer molecular dynamics calculations were performed with the CP2K package [30] using the generalized gradi-

ent approximation and the PBEsol exchange–correlation functional [31]. Basically, the employed FPMD technique was similar to that used in previously published reports on similar glass systems [32–34]. Randomly generated initial configurations of 940 atoms,  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ , and 1050 atoms,  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , were optimized using RMC++ code [35] to obtain a good agreement with neutron and high-energy X-ray diffraction results. The cubic box sizes were chosen to match the experimental number density. Further optimization was carried out using DFT with the consecutive basis sets SZV, DZVP and TZVP. We should note that in the RMC optimization we only used coordination number constraints since the DFT optimization at 0 K decreases the total energy of the system substantially, also changing the electronic structure.

The FPMD simulations included sample annealing above the glass transition temperature, 56 ps at 500 K for  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  and 32 ps at 450 K for  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , using a Nosé–Hoover thermostat chain controlling the temperature [36,37] and the final modeling over 50 ps or 38 ps at 300 K for the two systems, respectively. Further FPMD details can be found in [Supplementary material](#), including [Figures S3 and S4](#), and elsewhere [38–40].

## 3. Results and discussions

### 3.1. Glass homogeneity

Similarly to  $\text{Ag}_2\text{S-As}_2\text{S}_3$  glasses [14,16,41,42], the  $(\text{AgY})_x(\text{As}_2\text{S}_3)_{1-x}$  vitreous alloys are homogeneous at low silver content,  $x \lesssim 0.1$ –0.2 (2–4 at.% Ag), and phase-separated above this limit [10]. However, in contrast to homogeneous silver-rich thioarsenate glasses at  $y \gtrsim 20$  at.% Ag, the AgY-rich thioarsenate compositions do not reach the second homogeneous glass domain and remain phase-separated at the limit of the glass-forming range,  $y_{\text{max}} = 14.3$  at.% Ag ( $x = 0.5$ ).

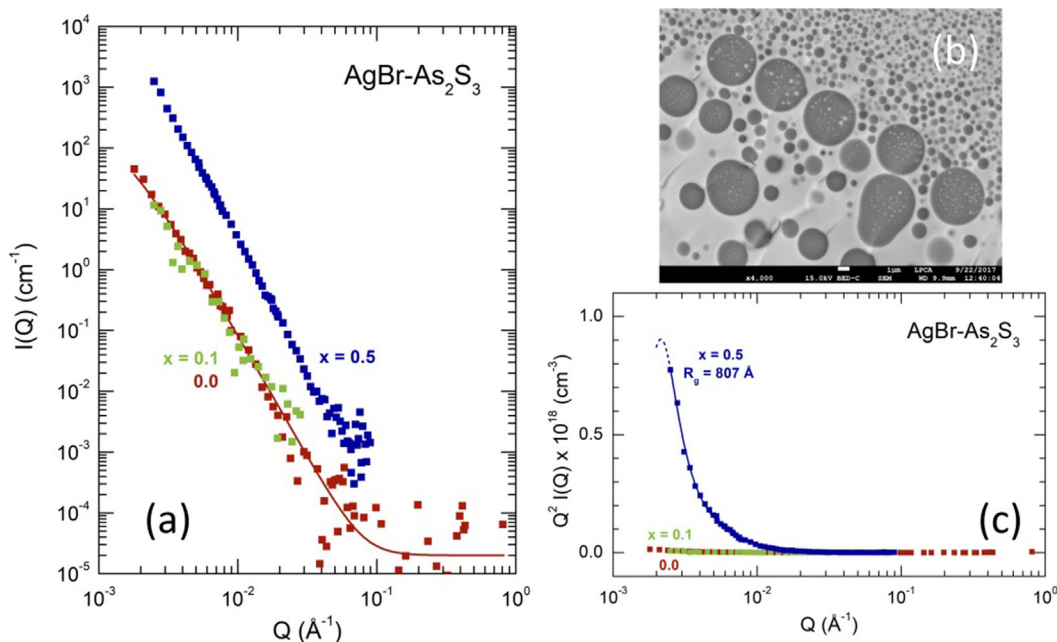
The small-angle neutron scattering (SANS) data for glassy  $g\text{-As}_2\text{S}_3$ ,  $(\text{AgBr})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  and  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  are shown in [Fig. 2\(a\)](#). The corrected and normalized SANS intensity  $I(Q)$  is very similar for homogeneous  $g\text{-As}_2\text{S}_3$  and  $(\text{AgBr})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  alloys. These homogeneous chalcogenide glasses exhibit weak small-angle signal,  $I(Q) \approx 10^{-4} \text{ cm}^{-1}$  at  $Q \approx 0.05 \text{ \AA}^{-1}$ , related to density fluctuations, which are often described by the Debye-Bueche (DB) model [43], the solid line in [Fig. 2\(a\)](#), see [Supplementary material](#) for further details. Similar  $I(Q)$ 's were reported for different homogeneous chalcogenide glasses [16,44,45], and the density fluctuations reveal a characteristic DB length scale  $\xi \approx 200 \text{ \AA}$ .

The phase-separated  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  glass, [Fig. 2\(b\)](#), exhibits by a factor of 100 higher SANS intensity  $I(Q)$  below  $Q < 0.1 \text{ \AA}^{-1}$ , roughly following the Porod law,  $I(Q) \propto Q^{-4}$  [46]. Nevertheless, the exact shape of  $I(Q)$  is more complicated with positive and negative deviations from the Porod slope  $n = \partial \log I(Q) / \partial \log Q = -4$ . The accessible  $Q$ -range ( $Q_{\text{min}} \approx 2 \times 10^{-3} \text{ \AA}^{-1}$ ) does not enable following further evolution, most probably a Guinier regime [46],  $n = -2$ , at lower  $Q$ . The Kratky plot,  $Q^2 I(Q)$  vs.  $Q$ , [Fig. 2\(c\)](#), is often used to estimate a typical size of mesoscopic particles if the Guinier approximation is valid [46,47]. In this case, the function  $Q^2 I(Q)$  plotted versus the scattering vector  $Q$  shows a maximum. The position of this maximum,  $Q_{\text{max}}$ , and the Guinier radius of gyration  $R_g$  are related,  $Q_{\text{max}} = \sqrt{3}/R_g$ . Here again, the limited  $Q$ -range does not allow to observe a clear maximum. Nevertheless, a rough estimation of  $R_g = 800 \pm 200 \text{ \AA}$  is consistent with the smallest particles observed by SEM, the upper right corner of [Fig. 2\(b\)](#).

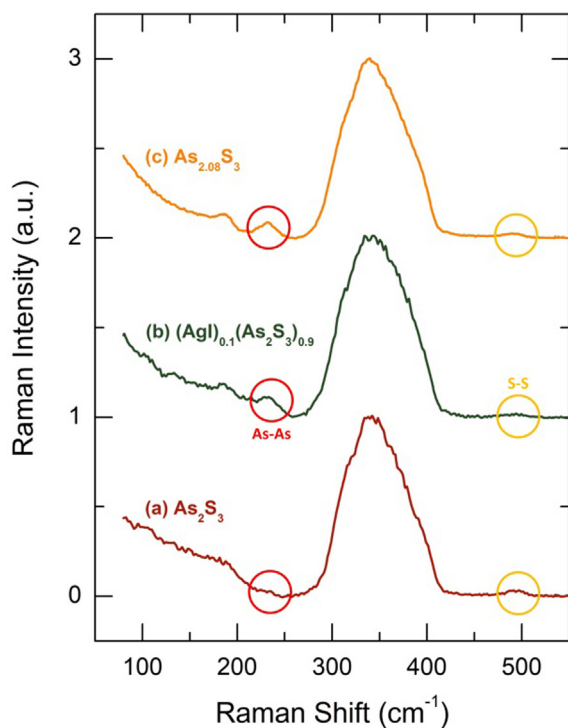
### 3.2. Raman spectra

Typical Raman spectra of the  $\text{AgY-As}_2\text{S}_3$  glasses and related references are shown in [Figs. 3 and 4](#). The spectral shape of  $(\text{AgI})_{0.1}(-$



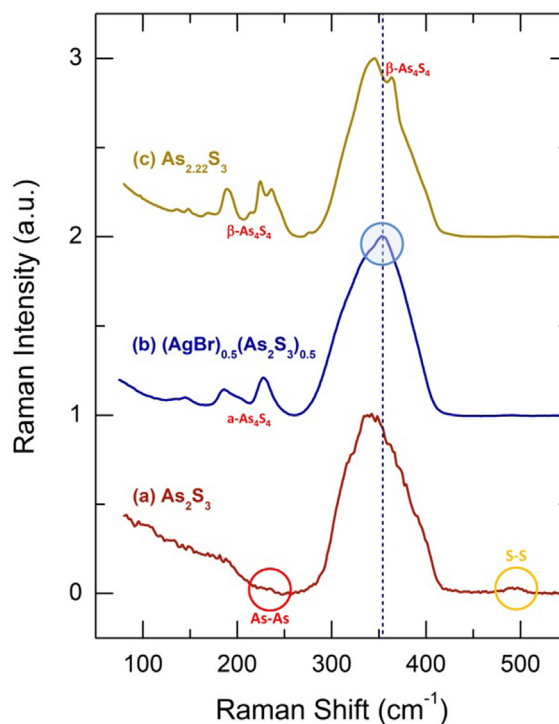


**Fig. 2.** Homogeneity of  $(\text{AgBr})_x(\text{As}_2\text{S}_3)_{1-x}$  glasses, where  $x = 0, 0.1$  and  $0.5$ : (a) corrected and normalized small-angle scattering function  $I(Q)$ ; (b) a SEM image of glassy  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ ; (c) the Kratky plots,  $Q^2 I(Q)$  vs.  $Q$ , for  $\text{AgBr}-\text{As}_2\text{S}_3$  glasses. The solid brown line in (a) represents a Debye-Bueche fit for  $g\text{-As}_2\text{S}_3$  with a typical size of DB density fluctuations  $\xi \approx 200$  Å. The solid blue line in (c) shows estimation of the Guinier radius of gyration  $R_g$  using a Voigt function. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Raman spectra of glassy (a)  $\text{As}_2\text{S}_3$ , (b)  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  and (c) As-enriched  $\text{As}_{2.08}\text{S}_3 = \text{As}_{0.41}\text{S}_{0.59}$ . The As-As stretching at  $230\text{ cm}^{-1}$  and S-S stretching at  $490\text{ cm}^{-1}$  are emphasized by red and yellow circles, respectively. See corresponding text for further details. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\text{As}_2\text{S}_3)_{0.9}$  is mostly similar to that in glassy  $\text{As}_2\text{S}_3$ . A broad unresolved feature, centered at  $\approx 340\text{ cm}^{-1}$  and corresponding symmetric and asymmetric As-S stretching [48–50], appears essentially intact while both high-frequency ( $\approx 490\text{ cm}^{-1}$ ) and low-frequency ( $\omega < 250\text{ cm}^{-1}$ ) modes exhibit characteristic changes.



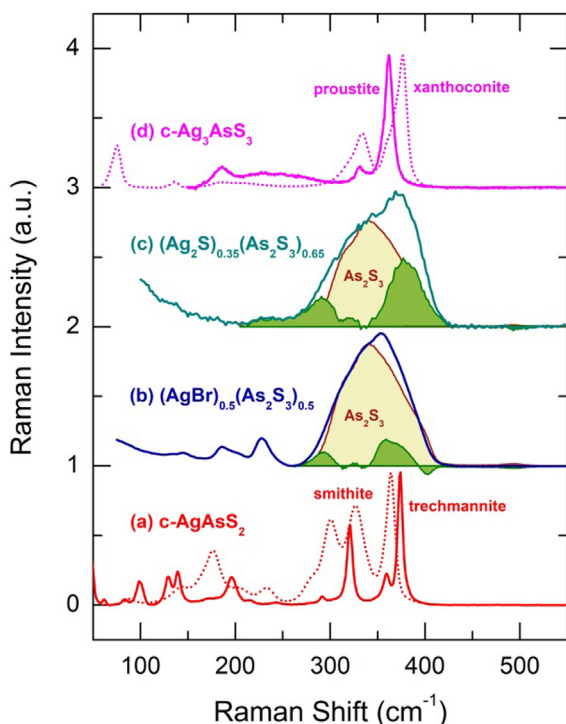
**Fig. 4.** Raman spectra of glassy (a)  $\text{As}_2\text{S}_3$ , (b)  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , (c) glassy-crystalline  $\text{As}_{2.22}\text{S}_3 \cong \text{As}_{0.43}\text{S}_{0.57}$ . Raman features of  $\beta\text{-As}_4\text{S}_4$  and  $\alpha\text{-As}_4\text{S}_4$  can be identified for  $\text{As}_{2.22}\text{S}_3$  and  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , respectively, in addition to a distinct feature at  $354\text{ cm}^{-1}$  for glassy  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , blue circle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The two features are related to chemical disorder in stoichiometric  $g\text{-As}_2\text{S}_3$  [45,51–54], corresponding to S-S and As-As stretching, respectively. Adding silver iodide, one observes a decrease of S-S dimers with a corresponding increase of As-As homopolar

bonds, similar to that in As-enriched nearly stoichiometric glassy  $\text{As}_{2.08}\text{S}_3$ , Fig. 3(c). The observed increase in intensity of the  $230\text{ cm}^{-1}$  peak, emphasized by a red circle in Fig. 3, is accompanied by a second low-frequency feature at  $\approx 180\text{ cm}^{-1}$ , probably indicating the appearance of  $\text{As}_4\text{S}_4$  monomeric cages in the glass network [51,54]. The increasing population of As-As bonds is amplified on further silver halide additions, Fig. 4. Glassy  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  shows a distinct signature of amorphous  $\text{As}_4\text{S}_4$  [55] in contrast to nanocrystallites of high- $T$  realgar polymorph  $\beta\text{-As}_4\text{S}_4$  [51] in glassy/crystalline  $\text{As}_{2.22}\text{S}_3$ .

The  $\text{AgBr}$ -rich glass also shows a new spectroscopic feature at  $354\text{ cm}^{-1}$  emphasized by a blue circle in Fig. 4(b) and absent in  $g\text{-As}_2\text{S}_3$  and As-rich sulfide glasses. This emerging peak appears to be similar to that reported earlier for  $\text{Ag}_2\text{S-As}_2\text{S}_3$  glasses with increasing silver sulfide content. Fig. 5 shows the Raman spectra of  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  and  $(\text{Ag}_2\text{S})_{0.35}(\text{As}_2\text{S}_3)_{0.65}$  glasses in comparison with crystalline silver thioarsenate compounds  $\text{AgAsS}_2$  and  $\text{Ag}_3\text{-AsS}_3$ . In addition, a scaled spectroscopic envelope for  $g\text{-As}_2\text{S}_3$  was subtracted from the spectra of glasses revealing changes in the spectra with increasing  $\text{AgBr}$  or  $\text{Ag}_2\text{S}$  content.

The vitreous  $(\text{Ag}_2\text{S})_{0.35}(\text{As}_2\text{S}_3)_{0.65}$  composition is on the border between phase-separated and homogeneous glasses in the  $\text{Ag}_2\text{S-As}_2\text{S}_3$  system [42] and exhibits the Raman spectrum which is similar to those published previously [57,58]. In addition, the silver content in the two thioarsenate glasses is comparable: 14.3 at.% for  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  and 16.3 at.% for  $(\text{Ag}_2\text{S})_{0.35}(\text{As}_2\text{S}_3)_{0.65}$ . Fig. 5 reveals that both the entire and difference Raman spectra of these glasses are rather similar. Moreover, the difference spectra are reminiscent of the Raman spectra for crystalline  $\text{AgAsS}_2$  and  $\text{Ag}_3\text{-AsS}_3$  polymorphs: smithite [56] and trechmannite (this work),



**Fig. 5.** Raman spectra of silver-containing glasses and  $\text{Ag}_2\text{S-As}_2\text{S}_3$  crystalline references: (a)  $\text{AgAsS}_2$  crystals, the solid red line corresponds to trechmannite (this work), the dotted red line to smithite [56]; (b)  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  glass; (c)  $(\text{Ag}_2\text{S})_{0.35}(\text{As}_2\text{S}_3)_{0.65}$  glass; (d)  $\text{Ag}_3\text{AsS}_3$  crystals, the solid magenta line corresponds to proustitite (this work), the dotted magenta line to xanthoconite [56]. The scaled spectroscopic envelope of vitreous  $\text{As}_2\text{S}_3$  used for glass subtraction is highlighted in light yellow; the silver-related difference spectrum is highlighted in green. See text for further details. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

proustitite (this work) and xanthoconite [56], respectively. Consequently, the broad high-frequency feature,  $350\text{ cm}^{-1} \lesssim \omega \lesssim 400\text{ cm}^{-1}$ , seems to be related to As-S stretching in either  $\text{As}_2\text{S}_3$  rings, present in the crystalline structure of  $\text{AgAsS}_2$  [59,60], or isolated  $\text{AsS}_3$  pyramidal units, characteristic of the  $\text{Ag}_3\text{AsS}_3$  lattice [61,62].

### 3.3. Neutron and X-ray diffraction data

Weighted average structure factors  $S(Q)$  were derived from the measured scattering cross section per atom  $d\sigma/d\Omega$  through the relation:

$$\frac{d\sigma}{d\Omega} = \left| \sum_{\alpha} c_{\alpha} \bar{b}_{\alpha} \right|^2 [S(Q) - 1] + \sum_{\alpha} c_{\alpha} \bar{b}_{\alpha}^{-2} \quad (1)$$

in the case of neutron scattering, where  $c_{\alpha}$ ,  $\bar{b}_{\alpha}$ , and  $\bar{b}_{\alpha}^{-2}$  are, respectively, the atomic concentration, the average of the neutron-nucleus scattering length, and the mean square scattering length of element  $\alpha$ . In the X-ray case,  $\bar{b}_{\alpha}$  in Eq. (1) is replaced by  $f_{\alpha}(Q)$ , the atomic scattering factor of element  $\alpha$ , which is  $Q$ -dependent.

The average structure factor  $S(Q)$  of a polyatomic system can be decomposed into Faber-Ziman partial structure factors  $S_{\alpha\beta}(Q)$  for  $(\alpha, \beta)$ -atomic pairs.

$$S(Q) = \sum_{\alpha, \beta} w_{\alpha\beta} S_{\alpha\beta}(Q) \quad (2)$$

and the neutron weighting factors are defined as

$$w_{\alpha\beta}^N = (2 - \delta_{\alpha\beta}) \frac{c_{\alpha} \bar{b}_{\alpha} c_{\beta} \bar{b}_{\beta}}{\left| \sum_{\alpha} c_{\alpha} \bar{b}_{\alpha} \right|^2} \quad (3)$$

where  $\delta_{\alpha\beta}$  is the Kronecker delta function. Likewise, in the X-ray case, the average neutron coherent scattering lengths are replaced by  $Q$ -dependent atomic scattering factors.

Typical neutron  $S_N(Q)$  and X-ray  $S_X(Q)$  structure factors for the  $\text{AgY-As}_2\text{S}_3$  glasses and  $g\text{-As}_2\text{S}_3$  are shown in Figs. 6 and 7, respectively. The  $\text{AgI}$ -poor glass reveals similar diffraction pattern to vitreous arsenic sulfide with distinct first sharp diffraction peak (FSDP) at  $Q_0 \approx 1.2\text{ \AA}^{-1}$  and the most intense second principal peak (PP2) at  $Q_2 \approx 3.9\text{ \AA}^{-1}$ . In contrast, both  $S_N(Q)$  and  $S_X(Q)$  for silver-rich glassy  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  show a strongly reduced FSDP, the most intense principal peak (PP) at  $Q_1 \approx 2.3\text{ \AA}^{-1}$ , and some indications of the enhanced small-angle scattering below  $0.5\text{ \AA}^{-1}$ . Similar trends were observed earlier for  $\text{Ag}_2\text{S-As}_2\text{S}_3$  glasses [15], except small-angle scattering at low  $Q$  for silver-rich glasses, and indicate significant changes in intermediate-range ordering as well as the network contraction with increasing  $\text{Ag}_2\text{S}$  or  $\text{AgY}$  content.

To extract the parameters of the FSDP, a Voigt function was used to approximate the background underneath it, allowing the FSDP to be isolated and fitted, see Figure S5 in Supplementary material and related references. The isolated FSDPs are shown in Fig. 8, and the fitting parameters are collected in Table 1. The FSDP position  $Q_0$  remains essentially invariant both in neutron and X-ray data,  $Q_0 = 1.23 \pm 0.03\text{ \AA}^{-1}$ , while the FSDP area  $A_0$  is smaller for X-rays. The last trend is simply related to different As-As neutron and X-ray weightings,  $w_{\text{As-As}}^N$  and  $w_{\text{As-As}}^X(Q)$ , since the FSDP mostly reflects periodicity of the glass-forming species at the intermediate-range scale confirmed by neutron diffraction with isotopic substitution [63] and anomalous X-ray scattering [64]. Table 1 shows that the weighted FSDP areas are comparable,  $A_0^N/w_{\text{As-As}}^N \cong A_0^X/w_{\text{As-As}}^X(Q)$ , and confirms changes in the intermediate-range ordering for vitreous  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  compared to  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  and  $\text{As}_2\text{S}_3$  glasses.

The neutron  $T_N(r)$  and X-ray  $T_X(r)$  total correlation functions were derived through the usual Fourier transform,

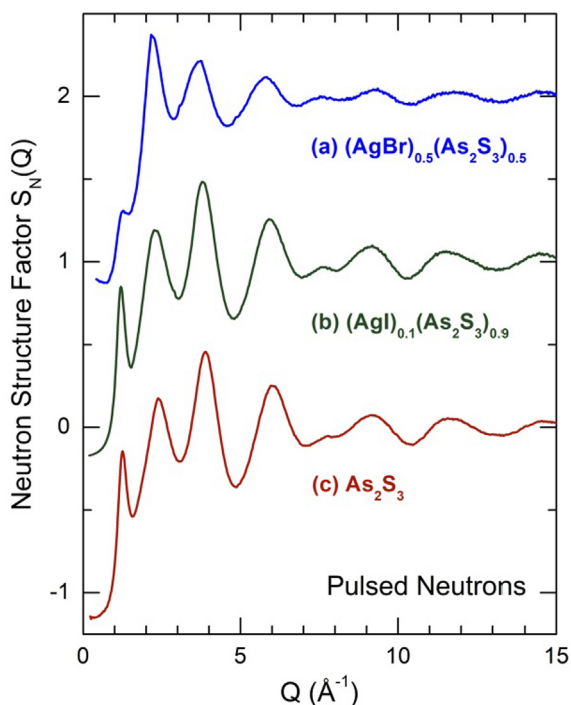


Fig. 6. Neutron structure factors  $S_N(Q)$  of (a)  $(AgBr)_{0.5}(As_2S_3)_{0.5}$ , (b)  $(AgI)_{0.1}(As_2S_3)_{0.9}$ , and (c)  $As_2S_3$  glasses over a limited  $Q$ -range.

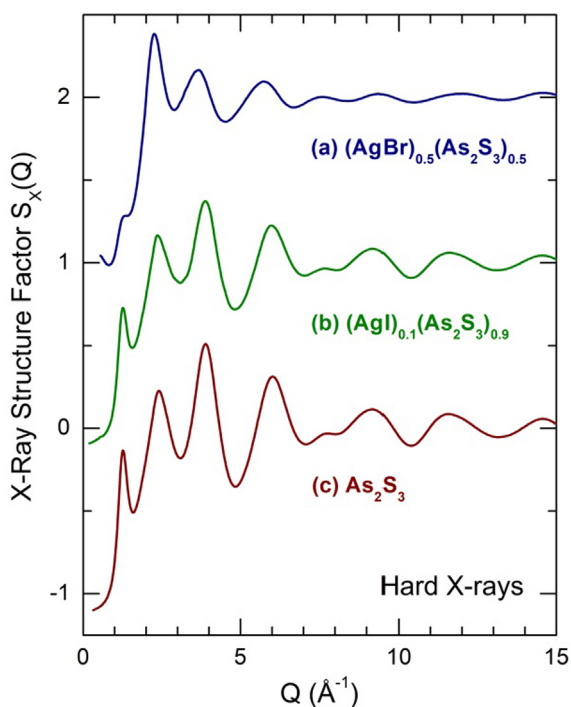


Fig. 7. X-ray structure factors  $S_X(Q)$  of (a)  $(AgBr)_{0.5}(As_2S_3)_{0.5}$ , (b)  $(AgI)_{0.1}(As_2S_3)_{0.9}$ , and (c)  $As_2S_3$  glasses over a limited  $Q$ -range.

$$T(r) = 4\pi\rho_0r + \frac{2}{\pi} \int_0^{Q_{max}} Q[S(Q) - 1] \sin(Qr)M(Q)dQ \quad (4)$$

where  $\rho_0$  is the atomic number density, and  $M(Q)$  is the Lorch modification function.

Typical  $T_N(r)$  and  $T_X(r)$  functions for  $(AgY)_x(As_2S_3)_{1-x}$  glasses and  $g-As_2S_3$  are shown in Figs. 9 and 10. Increasing the AgY content,

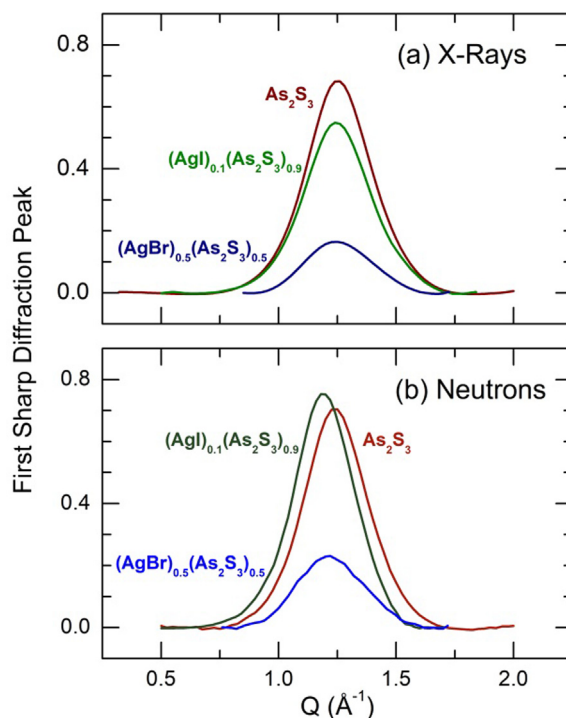


Fig. 8. Isolated FSDPs of AgY- $As_2S_3$  glasses in (a) X-ray and (b) neutron diffraction data.

one observes systematic changes in the real-space functions. The first peak at 2.27 Å, related to As-S first neighbors, decreases, while new high- $r$  features between  $2.5 \text{ Å} \leq r \leq 3.0 \text{ Å}$  emerge and grow with  $x$ . The second neighbor peak at 3.5 Å broadens and a new feature appears at  $\approx 4.1 \text{ Å}$ . Finally, more distant correlations at  $r > 5 \text{ Å}$  are progressively becoming flat indicating disappearance of the intermediate range order, characteristic of  $g-As_2S_3$ , which is also seen in the FSDP systematics.

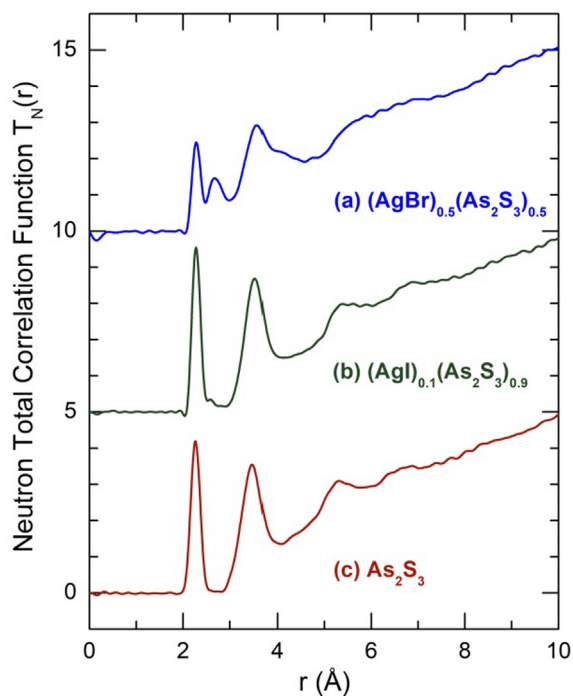
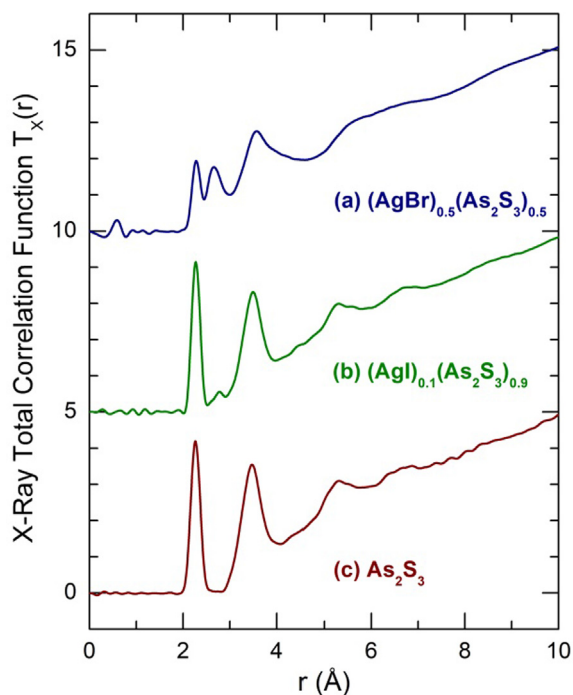
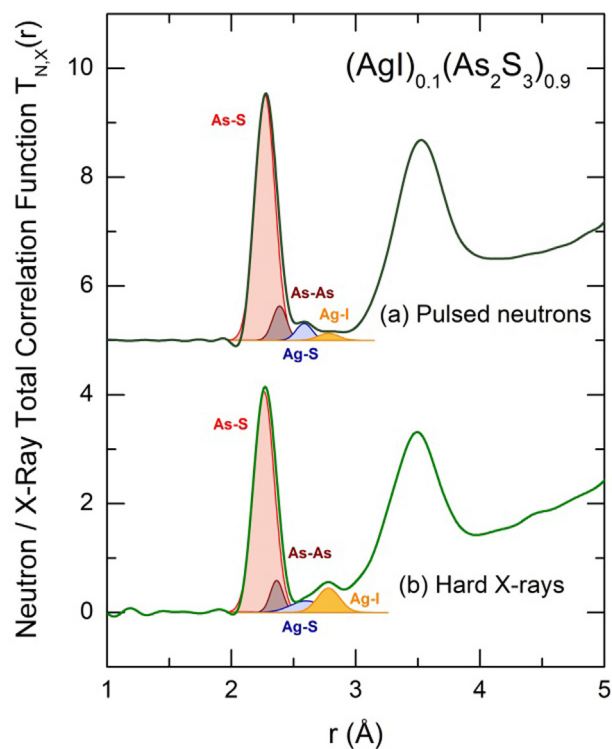
A closer look at the  $T_N(r)$  and  $T_X(r)$  functions for glassy  $(AgI)_{0.1}(As_2S_3)_{0.9}$ , Fig. 11, reveals multiple contributions within the  $2.5 \text{ Å} \leq r \leq 3.0 \text{ Å}$  range. The neutron data shows a distinct feature at 2.6 Å and a shoulder at 2.8 Å, while the  $T_X(r)$  exhibits an opposite trend; a clear feature at 2.8 Å with a shoulder at lower interatomic distances.

The 2.8 Å feature corresponds to Ag-I atomic pairs with interatomic distances,  $2.75 \text{ Å} \leq r_{Ag-I} \leq 2.85 \text{ Å}$ , observed in different crystalline and amorphous solids and liquids [11,65,66]. In addition, a significantly higher amplitude of the 2.8 Å peak in the X-ray data correlates with the Ag-I weightings,  $w_{Ag-I}^N/w_{Ag-I}^X(Q) = 0.248$ , for glassy  $(AgI)_{0.1}(As_2S_3)_{0.9}$ . However, the maximum possible Ag-I coordination appears to be unrealistically low,  $1.0 \leq N_{Ag-I} \leq 1.5$ , for pure iodine local environment of silver. Typically, silver exhibits a tetrahedral local coordination in crystalline iodides. The 2.6 Å feature cannot, in any circumstances, be related to the Ag-I atomic pairs but a possible alternative, Ag-S first neighbors, seems to be plausible, especially taking into account the Raman spectroscopy results. Typical Ag-S interatomic distances,  $2.45 \text{ Å} \leq r_{Ag-S} \leq 2.72 \text{ Å}$ , in sulfide glasses and crystals [15,32,67] are consistent with this hypothesis. In addition, a new class of metal halide coordination polymers,  $MY-A_4X_m$ , where  $M = Cu, Ag; Y = Cl, Br, I; A = P, As; X = S, Se; 3 \leq m \leq 4$  [68–70] is characterized by a mixed tetrahedral local environment of the  $d^{10}$  cation of different stoichiometry:  $1Y + 3X, 2Y + 2X$  or  $3Y + 1X$ , depending on the MY content. The mixed silver environment (1I + 3S) appears to be consistent with the experimental neutron and X-ray results for  $(AgI)_{0.1}(As_2S_3)_{0.9}$ .



**Table 1**FSDP parameters for  $\text{As}_2\text{S}_3$ ,  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ , and  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  glasses in neutron and X-ray diffraction data.

AgY	$Q_0^N$ ( $\text{\AA}^{-1}$ )	$A_0^N$	$A_0^N/w_{\text{As-As}}^N$	$Q_0^X$ ( $\text{\AA}^{-1}$ )	$A_0^X$	$A_0^X/w_{\text{As-As}}^X(Q)$
0	1.24(1)	0.250(5)	0.68(2)	1.26(1)	0.242(5)	0.72(2)
10	1.19(1)	0.246(5)	0.75(2)	1.25(1)	0.198(5)	0.71(3)
50	1.22(1)	0.081(5)	0.55(4)	1.25(1)	0.057(5)	0.50(5)

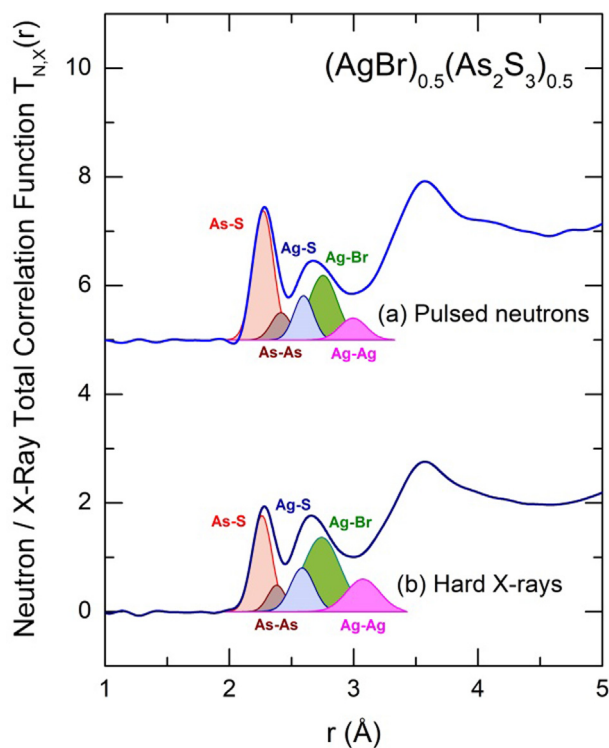
**Fig. 9.** Neutron total correlation functions for (a)  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , (b)  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ , and (c)  $\text{As}_2\text{S}_3$  glasses.**Fig. 10.** X-ray total correlation functions for (a)  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , (b)  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ , and (c)  $\text{As}_2\text{S}_3$  glasses.**Fig. 11.** Fitting the total correlation function for glassy  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ : (a) neutron data, (b) X-ray data. The As-S, As-As, Ag-S and Ag-I atomic pairs are highlighted in red, brown, blue and yellow, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In our fitting, we constrained the coordination numbers to be equal for ND and XRD but the interatomic distances were left to be free. X-rays and neutrons are scattered differently, by electrons and nuclei, respectively. Consequently, the interatomic distances may vary insignificantly even for monoatomic glass or liquid.

The constrained three-peak fitting (As-S, Ag-S and Ag-I first neighbor contributions) shows, however, arsenic overcoordination,  $N_{\text{As-S}} \approx 3.2$ , associated also with a high- $r$  asymmetric broadening of the 2.27 Å peak. Taking into account the increased population of the As-As homopolar bonds, observed in the Raman spectra of the AgY- $\text{As}_2\text{S}_3$  glasses, the additional constraint included trigonal arsenic local coordination,  $N_{\text{As-S}} + N_{\text{As-As}} = 3$ , and the fourth, As-As, contribution. The corresponding fitting results are shown in Figs. 11 and 12; the derived fitting parameters are collected in Table 2.

The four-peak fitting yields consistent results for both neutron and X-ray data, and reveals the increased population of the As-As first neighbors in glassy  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , in agreement with the Raman spectroscopy results, Fig. 4. Table 2 shows that the derived As-As first neighbor distances,  $2.39 \pm 0.04$  Å, are reasonably well agreed with interatomic distances in amorphous arsenic and As-rich sulfide glasses [45,71,72]. The derived Ag-Br interatomic separation is also consistent with diffraction results for AgBr-containing glasses, crystals, and liquids,  $2.67$  Å  $\leq r_{\text{Ag-Br}} \leq 2.89$  Å [73,74]. We should note a different stoichiometry of the mixed sil-





**Fig. 12.** Fitting the total correlation function for glassy  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ : (a) neutron data, (b) X-ray data. The As-S, As-As, Ag-S, Ag-Br, and Ag-Ag atomic pairs are highlighted in red, brown, blue, green, and magenta, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ver local environment in silver-rich  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , consisting of 2S + 2Br first neighbors. The derived stoichiometry follows a usual trend in crystalline  $\text{MY-A}_4\text{X}_m$  with increasing MY content. The MY-poor compounds exhibit the 1Y + 3X stoichiometry while the MY-rich compositions show either 2:2 or 3:1 Y/X ratios [68–70]. Glassy  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  reveals also rather intense peak at  $\approx 3$  Å, which could be related to Ag-Ag short second neighbor contacts, since more intense in the X-ray data. The direct identification and precise coordination of the Ag-Ag second neighbors is hardly possible in a four-component glass without site-sensitive methods as neutron diffraction with isotopic substitution [67,75], anomalous X-ray scattering or low-temperature EXAFS at the Ag K-edge.

### 3.4. First principles molecular dynamics results

The FPMD simulation boxes for  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  and  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  are shown in Figs. 13 and 14. As expected, glassy  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  appears to be homogeneous with rather random

distribution of Ag-I atomic pairs within the simulation box, Fig. 13(b). Surprisingly, silver-rich  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  shows a clear separation into AgBr-rich and AgBr-poor phases although the size of the simulation box ( $29.62 \times 29.62 \times 29.62$  Å<sup>3</sup>) is far below the experimental SANS radius of gyration,  $R_g = 800 \pm 200$  Å. The detailed analysis of the FPMD results will be published elsewhere and some additional results are given in Supplementary material. Here we will limit our discussion to three topics related to (i) silver distribution and connectivity in the critical percolation domain,  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ , and modifier-controlled region,  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ ; (ii) mixed silver and arsenic local environment, and (iii) ring statistics.

The derived FPMD Ag-Ag partial pair-distribution functions  $g_{\text{AgAg}}(r)$  for glassy  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  and  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  are shown in Fig. 15. As expected from Fig. 13(b), the silver-poor glass does not show any direct contact of neighboring AgI units. The shortest Ag-Ag separation distance is centered at  $\approx 6$  Å (16 % of Ag species), and each silver cation has at least one Ag neighbor above  $\approx 8$  Å. The phase-separated silver-rich  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  vitreous alloy exhibits a strongly connected Ag-related subnetwork, clearly visible in Fig. 14. In average, each silver cation has one second neighbor at 3 Å and additionally three neighboring cations at  $\approx 4$  Å, ensuring a heavily correlated  $\text{Ag}^+$  ionic motion, characterized by the Haven ratio  $H_R \approx 0.4$  [13]. Consequently, the main structural difference between the two ion transport regimes, critical percolation vs. modifier-controlled ionic diffusion, related to random or non-random mobile cation distribution [2], is consistent with the FPMD results.

The FPMD simulated Ag- and As-related partial pair-distribution functions, Figs. 16 and 17, confirm mixed silver and arsenic local environment in both silver-poor  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  and silver-rich  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ . Nevertheless, the simulated partial coordination numbers are slightly different from those found experimentally. The difference is more significant for silver-poor glass.

Each silver cation in  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  has in average three sulfur first neighbors but less than one iodine atom,  $N_{\text{Ag-I}} = 0.47$ . In addition, silver also has arsenic nearest neighbors at 2.9 Å,  $N_{\text{Ag-As}} = 0.28$ , thus completing the average total coordination number to nearly tetrahedral local environment,  $N_{\text{Ag-X}} = 3.75$ , where X = I, S and As. We note that Ag-As first neighbors were also found in FPMD simulations of glassy  $\text{AgAsS}_2$  [32]. The remaining iodine species have moved from silver to arsenic,  $N_{\text{I-As}} = 0.53$ , but they are located close to silver at a typical second neighbor distance centered at  $\approx 4$  Å. Low silver and iodine atomic concentrations in  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ , 2.13 at.%, implies negligible effect on arsenic local environment,  $N_{\text{As-I}} = 0.02$  and  $N_{\text{As-Ag}} = 0.01$ . As expected, arsenic has trigonal local coordination with sulfur,  $N_{\text{As-S}} = 2.55$ , and arsenic,  $N_{\text{As-As}} = 0.47$ , first neighbors, Fig. 17(b). The FPMD simulated fraction of As-As homopolar bonds in  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  exceeds therefore the experimental value by a factor of 2. The enhanced

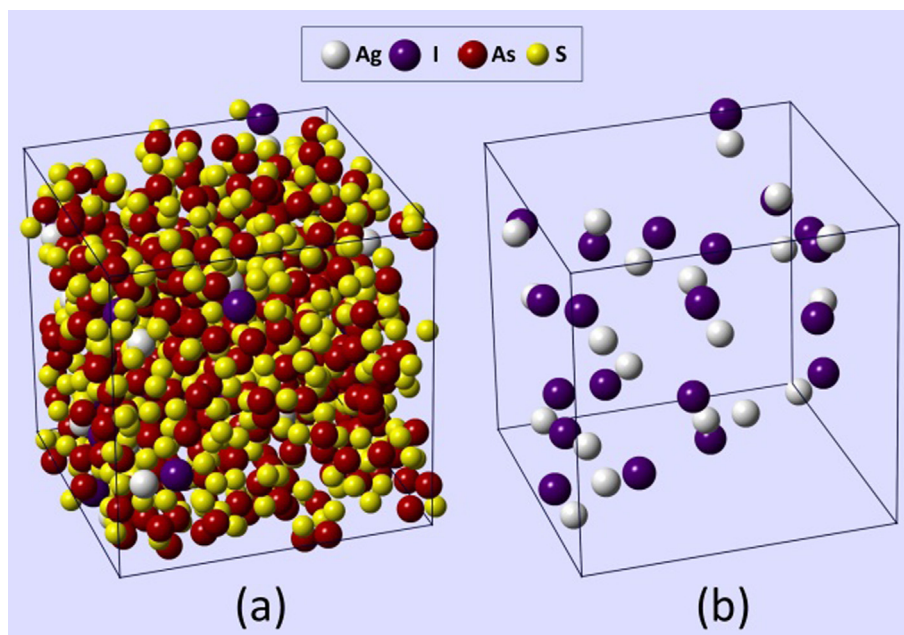
**Table 2**

First neighbor interatomic distances  $r$  and partial coordination numbers  $N_{ij}$  in  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  and  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  glasses..

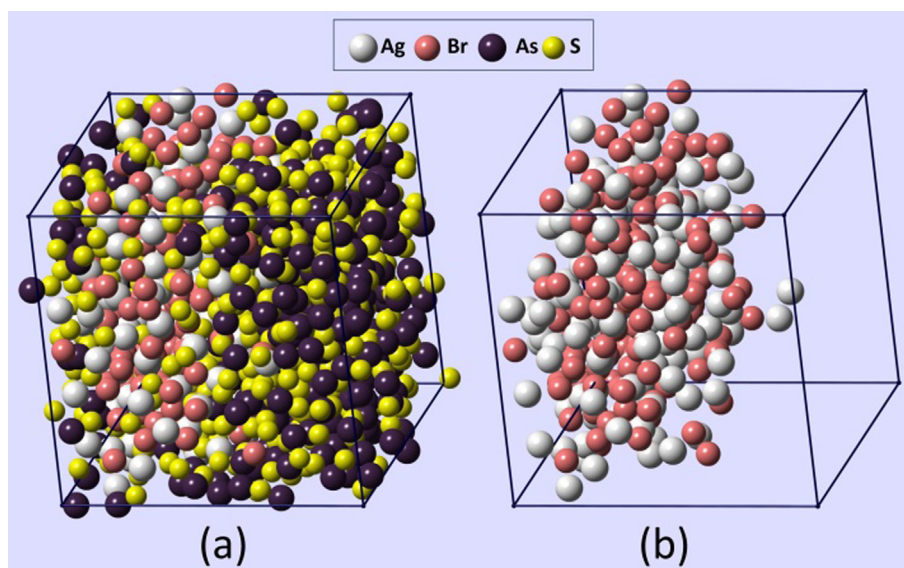
	As-S		As-As		Ag-S		Ag-Y	
	$r$ (Å)	$N_{ij}$	$r$ (Å)	$N_{ij}$	$r$ (Å)	$N_{ij}$	$r$ (Å)	$N_{ij}$
$(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$								
ND	2.27(1)	2.76(5)*	2.39(3)	0.24(5)*	2.58(2)	3.00**	2.78(2)	1.00**
XRD	2.26(1)	2.76(5)*	2.36(3)	0.24(5)*	2.60(2)	3.00**	2.78(2)	1.00**
$(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$								
ND	2.27(1)	2.53(5)*	2.41(3)	0.47(5)*	2.60(2)	2.00**	2.75(2)	2.00**
XRD	2.26(1)	2.53(5)*	2.38(3)	0.47(5)*	2.59(2)	2.00**	2.74(2)	2.00**

\* Trigonal arsenic local coordination was fixed,  $N_{\text{As-S}} + N_{\text{As-As}} = 3$ , and partial  $N_{\text{As-S}}$  and  $N_{\text{As-As}}$  coordination numbers were constrained to be identical in the neutron and X-ray data fitting.

\*\* Tetrahedral silver local coordination was constrained and fixed,  $N_{\text{Ag-S}} + N_{\text{Ag-Y}} = 4$ , and partial  $N_{\text{Ag-S}}$  and  $N_{\text{Ag-Y}}$  coordination numbers were constrained to be identical in the neutron and X-ray data fitting.



**Fig. 13.** Typical snapshot of the FPMD simulation box,  $(29.014)^3 \text{ \AA}^3$ , at 300 K for glassy  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ , containing 20 Ag, 20 I, 360 As, and 540 S atomic species: (a) the entire box, (b) only Ag and I species.



**Fig. 14.** Typical snapshot of the FPMD simulation box,  $(29.62)^3 \text{ \AA}^3$ , at 300 K for glassy  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , containing 150 Ag, 150 Br, 300 As, and 450 S atomic species: (a) the entire box, (b) only Ag and Br species. A clear phase-separation is observed.

chemical disorder in chalcogenide glassy systems seems to be a common feature of FPMD simulations using PBE or PBEsol and requires the use of advanced hybrid functionals, TPSS [76,77], BLYP [78–80] or PBE0 [38–40], to improve the agreement with experiments. Nevertheless, the simulated partial functions reflect reasonably well the diffraction results.

The FPMD simulated silver local environment in  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$  is closer to the derived experimental parameters:  $N_{\text{Ag-S}} = 1.73$  and  $N_{\text{Ag-Br}} = 2.20$  with negligible contribution from arsenic nearest neighbors,  $N_{\text{Ag-As}} = 0.05$ , Fig. 16(a). The trigonal arsenic local coordination consists of sulfur,  $N_{\text{As-S}} = 2.33$ , arsenic,  $N_{\text{As-As}} = 0.51$ , and bromine,  $N_{\text{As-Br}} = 0.13$ , first neighbors. The majority of bromine species are connected to silver, 82 %, in con-

trast to  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ , where the fraction of I-Ag atomic pairs is just 47 %.

The ring statistics in glassy  $\text{As}_2\text{S}_3$ ,  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  and  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , calculated using the R.I.N.G.S. code [81], is shown in Fig. 18. The majority of rings in  $\text{g-As}_2\text{S}_3$  are chemically ordered,  $\text{As}_p\text{S}_q$ , where  $p = q$  and  $p + q$  is the ring size, since the chemical disorder is small,  $[\text{As-As}]/([\text{As-As}] + [\text{As-S}]) = 0.02\text{--}0.03$ . The ring distribution is bimodal with two maxima centered at small,  $3 \leq p + q \leq 6$ , and big,  $14 \leq p + q \leq 36$ , rings. We note a significant fraction of edge-sharing ES- $\text{AsS}_3$  pyramidal units ( $p + q = 4$ ), also reported previously in a small-box FPMD simulation of glassy arsenic sulfide [82]. Surprisingly, the fraction of the 12-membered rings is small even though the  $p + q = 12$  rings are the only elements

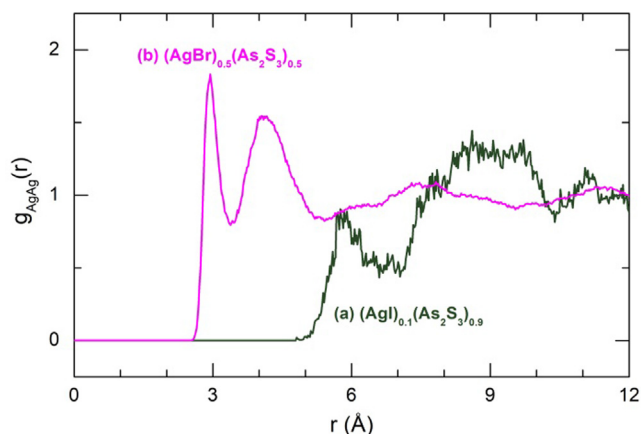


Fig. 15. FPMD Ag-Ag partial pair-distribution function  $g_{AgAg}(r)$  in (a)  $(AgI)_{0.1}(As_2S_3)_{0.9}$  and (b)  $(AgBr)_{0.5}(As_2S_3)_{0.5}$  glasses.

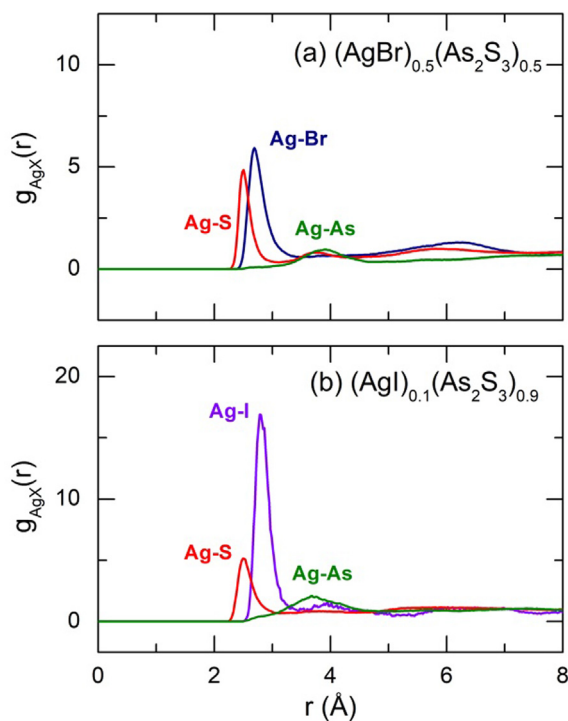


Fig. 16. Ag-related partial pair-distribution functions  $g_{AgX}(r)$  in (a)  $(AgBr)_{0.5}(As_2S_3)_{0.5}$  and (b)  $(AgI)_{0.1}(As_2S_3)_{0.9}$  glasses.

of the intermediate range order in both triclinic and monoclinic polymorphs of  $As_2S_3$  [83,84].

The rings statistics of the glass network changes dramatically on alloying with 10 mol.% of AgI, Fig. 18(b). The fraction of rings with homopolar bonds increases by a factor of 8 consistent with the enhanced chemical disorder in  $(AgI)_{0.1}(As_2S_3)_{0.9}$ . The total number of rings normalized to the size of the simulation box,  $\sum R_c(p+q)$ , remains essentially invariant but the fraction of big rings has decreased substantially. In contrast, the population of small rings has even increased caused by a large number of odd-membered units. Silver-rich  $(AgBr)_{0.5}(As_2S_3)_{0.5}$  exhibits further evolution. The total number of rings has decreased by a factor of 2 both for small and big ring sizes  $p+q$ . The compositional changes in ring statistics and FSDP parameters are similar. The essentially invariant FSDP position  $Q_0(x)$  correlates with the size of the most populated small rings. The FSDP amplitude reflects

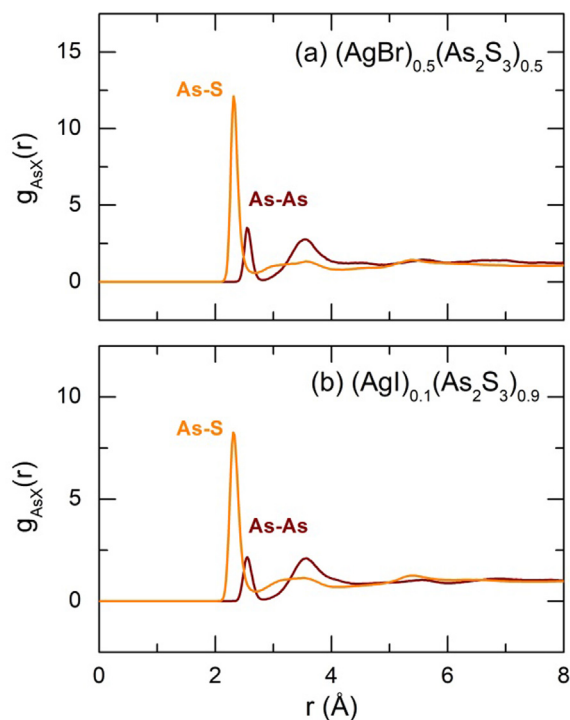


Fig. 17. As-related partial pair-distribution functions  $g_{AsX}(r)$  in (a)  $(AgBr)_{0.5}(As_2S_3)_{0.5}$  and (b)  $(AgI)_{0.1}(As_2S_3)_{0.9}$  glasses.

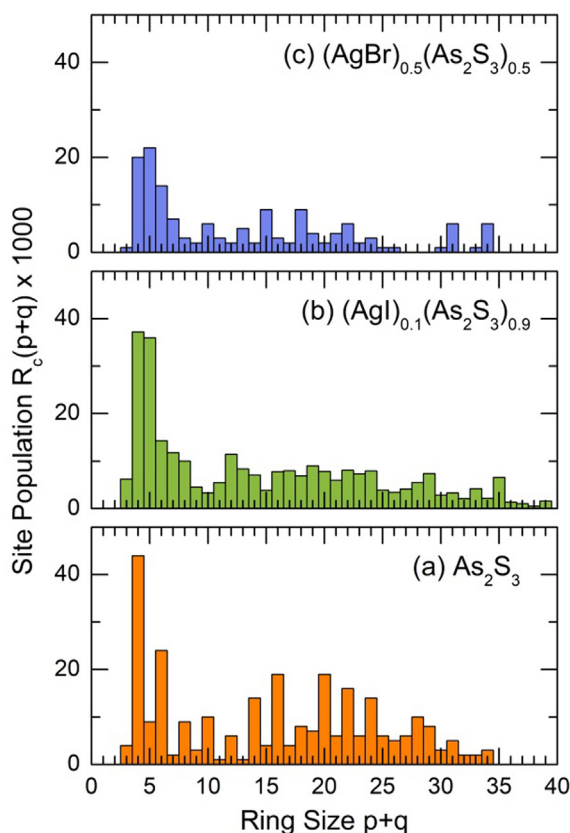


Fig. 18. Ring statistics in glassy (a)  $As_2S_3$ , (b)  $(AgI)_{0.1}(As_2S_3)_{0.9}$ , and (c)  $(AgBr)_{0.5}(As_2S_3)_{0.5}$ .

the population of small rings. In addition, the Raman spectrum of glassy  $(AgBr)_{0.5}(As_2S_3)_{0.5}$  also reveals the presence of small rings in the glass network. We should also note that the ring statistics



and FSDP evolution are similar to those in  $(\text{Na}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$  glasses [85].

### 3.5. Structural role of silver halides in chalcogenide networks

The diffraction and Raman spectroscopy results supported by FPMD modeling show unexpected structural role of silver halides in thioarsenate glass network. In contrast to common point of view considering AgY additions to be chemically inert and mostly providing the network expansion related to a large size of halide anions [7], we observe a different phenomenon. First, silver halides interact with sulfur species of the host network. As a result, the mixed silver environment is formed. Chemical interaction of silver and sulfur has several consequences. (1) The continuous glass network will be broken similarly to that on modifier additions, e.g.  $\text{Ag}_2\text{S}$ . The fragmented network will be characterized by progressively diminished glass transition temperature  $T_g$ , and the composition dependences of  $T_g$  for AgY- and  $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$  glasses really exhibit similar trends [10], Figure S6 (Supplementary material). (2) The network fragmentation will also be accompanied by structural changes on the intermediate-range scale. The compositional changes in the FSDP position and amplitude for the studied AgY- $\text{As}_2\text{S}_3$  glasses, Fig. 8, as well as the Raman spectra of AgY-rich compositions, show a clear similarity compared to silver thioarsenate glasses  $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ . On the other hand, the enhanced chemical disorder in the  $(\text{AgY})_x(\text{As}_2\text{S}_3)_{1-x}$  glasses with increasing  $x$  is a consequence of different chemical nature of silver halides and silver sulfide. The  $\text{Ag}_2\text{S}$  modifier, while transforming the bridging sulfur into the terminal one, compensates the sulfur deficiency releasing its own sulfur species. In case of AgY, this possibility is intrinsically missing leading to a chemical bonding rearrangement and the formation of As-As homopolar bonds. Both the Raman spectra and the diffraction data are consistent with this scenario. Resuming, we suggest that both silver halides and possibly alkali and group 11 halides all behave in a similar manner acting as unconventional modifiers.

### 3.6. Silver distribution as a function of AgY content

Silver distribution and stoichiometry of the mixed silver environment depends on AgY content. The silver-poor glass  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$  belong to the critical percolation domain, which is characterized by a random silver distribution [2,4]. The diffraction data and FPMD modelling confirms a monomeric nature of AgI molecules in the critical percolation region. The shortest Ag-Ag separation distance is centered at  $\approx 6$  Å although a small number of Ag-Ag contacts were observed down to  $\approx 4.5$  Å, see a single count of this type in Figure S7 (Supplementary material) and statistically averaged  $g_{\text{AgAg}}(r)$ , Fig. 15(a). Basically, this indicates the absence of direct Ag-Ag second neighbor contacts and the absence of preferential conduction pathways, ensuring specific ion transport properties and a monotonic decrease of the Haven ratio  $H_R$  from  $H_R = 1$  as a function of reciprocal Ag-Ag distance.

The silver-rich glass,  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , belongs to the modifier-controlled region, characterized by a non-random silver distribution and high ionic conductivity related to preferential conduction pathways. The average 2:2 stoichiometry, i.e., 2 sulfur + 2 Br first neighbors for each Ag cation implies at least Ag-related chains or 2D/3D pathways composed of edge- and corner-sharing ES/CS- $\text{AgBr}_2\text{S}_2$  tetrahedra. The bimodal silver distribution with the first maximum at the Ag-Ag distance of 3 Å and the second one at  $\approx 4$  Å is a characteristic feature of the preferential conduction pathways in silver-rich AgY- $\text{As}_2\text{S}_3$  glasses. The Haven ratio in these glasses is essentially invariant and low, e.g.  $H_R \approx 0.4$ , reflecting strongly correlated ion motion within highly connected conduction

pathways. Similar changes in stoichiometry of the mixed silver or copper environment were reported for crystalline MY –  $\text{A}_4\text{X}_m$  compounds with increasing MY content [68–70].

## 4. Conclusions

Raman spectroscopy, neutron and high-energy X-ray diffraction results supported by FPMD modeling show unexpected and previously unknown structural role of silver halides in two contrasting pseudo-binary systems:  $(\text{AgI})_{0.1}(\text{As}_2\text{S}_3)_{0.9}$ , belonging to the critical percolation domain, and  $(\text{AgBr})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ , from the modifier-controlled region. In a remarkable contrast to a widely accepted point of view suggesting that silver halides are chemically inert dopant salts in a disordered network, providing additional free volume for fast ion migration, we have found that silver halides behave as unconventional modifiers in the AgY- $\text{As}_2\text{S}_3$  glasses. Chemical interactions with sulfur species of the glassy host have usual consequences as fragmentation of the continuous network and the appearance of terminal sulfur. Compared to traditional modifiers as  $\text{Ag}_2\text{S}$ , silver halide additions trigger the enhanced chemical disorder, that is, the As-As homopolar bonds for 16% of arsenic species, related to missing sulfur in AgY. The stoichiometry of the mixed silver environment depends on the silver halide content. In the AgI-poor glass, the main structural motif consists of monomeric AgI entities. The tetrahedral local silver environment of isolated silver sites is completed by sulfur. In the superionic AgBr-rich vitreous alloy, the preferential conduction pathways are formed by highly connected edge- and corner-sharing ES/CS- $\text{AgBr}_2\text{S}_2$  tetrahedra. The observed structural features are consistent with ionic conductivity and tracer diffusion results. A deep insight into the short- and intermediate range order of the last promising thermoelectric materials can also be used to guide the rational design of thermal transport management, improving the figure of merit  $ZT$ .

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2022.110547>.

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