An X-Ray RDF Study on the Glass $50AgI–25Ag_2O–25MoO_3$

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A structural investigation using an X-ray RDF (radial distribution function) technique was carried out for a glass of composition $50AgI–25Ag_2O–25MoO_3$ (in mole% units). Results indicated the presence of strong Ag–I interactions at $r_{Ag–I}=287$ pm and the average number of iodine atoms around an Ag atom, $n_{Ag–I}$ was 0.77. Two Ag–O interactions characterized by $r_{Ag–O}=197$ pm, $n_{Ag–O}=1.8$ and $r_{Ag–O}=234$ pm, $n_{Ag–O}=2.6$ were also observed. The structural parameters of the glass former MoO_3 were given as $r_{Mo–O}=198$ pm and $n_{Mo–O}=5.5$. The results showed that AgI was dispersed in the glassy matrix.

The constituent MoO_3 is not a facile glass former according to the well known Zachariasen's rule.[1,5] However, glass formation in the tricomponent $AgI–Ag_2O–MoO_3$ system has been reported by a normal cooling process.[1,2] Studies on conductivities, transport and thermal properties on the system have been done extensively so far.[1,2] The conductivity of glasses in the system lay in the range 10^{-5}—10^{-2} S cm^{-1} at room temperature. IR spectra showed that the coordination of oxygen atoms to molybdenum(VI) is 4 and glasses with the mole ratio $Ag_2O/MoO_3=1$ or those in the pseudobinary system $AgI–Ag_2MoO_4$ contained discrete ions of Ag^+, I^-, and MoO_4^{2-}. On the basis of IR spectra strong partial covalency has also been proved to be present between some of the Ag^+ and MoO_4^{2-} ions, which makes these Ag^+ ions less mobile and there is another kind of Ag^+ ions surrounded by I^- ions which are more mobile.[3,4] Our earlier work on $60AgI–20Ag_2O–20MoO_3$ glass showed six-coordination of oxygen atoms around Mo(VI) and strong interaction of silver atoms with network oxygen atoms. These conclusions are at variance with those based on results of above mentioned IR results, namely, tetrahedral coordination of oxygen atoms around molybdenum. With this in mind, we have chosen to study another molybdate glass with a different composition to check our earlier results on $60AgI–20Ag_2O–20MoO_3$ glass.

Experimental

Sample Preparation. The method of preparation of the glass is the same as reported previously for the glass $60AgI–20Ag_2O–20MoO_3$ (mole% units).[5] A circular glass plate, yellowish in colour of about 2.5 cm in diameter and 0.3 mm in thickness was used for the diffraction study. The amorphous nature of the sample was verified by means of X-ray diffraction. The density and conductivity of the glass was found to be 6.09 g cm^{-3} and 6.0×10^{-4} S cm^{-1}, respectively.

X-Ray Diffraction Measurement. X-Ray diffraction measurements on this glass were carried out with a Philips Vertical θ–2θ diffractometer using a proportional counter with pulse height analyzer and discriminator in a thermostated room (25±1°C). The Mo $K\alpha$ radiation ($\lambda=$ 71.07 pm) was used. The available scattering angle 2θ in the experiment was from 2° to 150°. The procedures for data collection and data reduction were the same as those reported earlier.[5,6]

Analysis of Intensity Data. Intensities measured were corrected for background and absorption and then normalized to 1° divergence and 1° scattering slit combination. These intensities were further corrected for polarization and then scaled to absolute intensities. The reduced intensities $i(s)$ were obtained after subtracting intensities of independent atomic scattering and incoherent scattering from the experimental intensities:

$$i(s) = K\cdot I(s) - \sum_{j=1}^{\mathrm{NATOM}} n_j[\{f_j(s)+\Delta f_j'(s)+\Delta f_j''(s)\}^2 + \phi(s)\cdot I_j^{\mathrm{incoh}}] \quad (1)$$

where $s=(4\pi/\lambda)\sin\theta$, $I(s)$ the observed intensity corrected for polarization, $\phi(s)$ the fraction of the incoherent scattering which reached the counter and I_j^{incoh} the incoherent scattering intensity for atom j.

The radial distribution function (RDF) $D(r)$ was deduced from the Fourier transform of the $s\cdot i(s)$ function.

$$D(r) = 4\pi r^2\rho_o + \frac{2r}{\pi}\int_0^{s_{\max}} s\cdot i(s)\cdot M(s)\sin(sr)\mathrm{d}s \quad (2)$$

where ρ_o denotes the average scattering density of the system in electron units and $M(s)$ the modification function.

$$M(s) = \frac{\sum_i n_i[(f_i(0)+\Delta f_i'(0))^2+(\Delta f_i''(0))^2]}{\sum_i n_i[(f_i(s)+\Delta f_i'(s))^2+(\Delta f_i''(s))^2]}\exp(-k\cdot s^2) \quad (3)$$

The correlation function $G(r)=D(r)/4\pi r^2\rho_o$ is obtained from $D(r)$. The programs KURVLR[7] and NLPLSQ[8] were used for performing all calculations with respect to one silver atom chosen as the stoichiometric unit. Plausible literature values of the main interactions in the glasses were inserted as the initial values of the bond parameters and they were refined by the least-squares (LSQ) method. When a reasonable convergence was reached, parameters of the three bonds, Ag–O (short), Ag–O (long), and Ag–I were further refined at the additional 2 cycles of LSQ. The results are summarized in Table 1.

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Table 1. Mean Distance r, Temperature Factor b, and Frequency Factor n for the Interactions in the AgI–Ag_2O–MoO_3 Glasses

Atom pair	60AgI–20Ag_2O–20MoO_3			50AgI–25Ag_2O–25MoO_3		
(A–B)	r/pm	b/pm^2	n	r/pm	b/pm^2	n
		glass b			glass a	
Mo–O	210.0	20	5.7	198.0	3	5.5
Ag–O[a]	188.9(1)	25(1)	1.60(2)	197.0(1)	5(1)	1.78(1)
Ag–O[a]	226.1(2)	20(1)	1.34(2)	234.3(1)	7(1)	2.61(1)
Ag–I[a]	286.6(1)	166(0)	1.47(1)	287.1(1)	213(1)	0.77(1)
Mo–I	248.0	20	1.2	—	—	—
Mo–I	358.0	89	0.3	—	—	—
Mo–Ag	—	—	—	359.0	73	1.0
Ag–Ag	330.0	20	0.2	335.0	154	0.4
Mo–Mo	357.0	54	1.5	—	—	—
Mo–Mo	387.0	20	1.0	394.0	151	3.1
I–I	425.0	72	0.3	437.0	81	0.3
O–O	266.0	20	8.7	265.0	13	11.7
O–O	318.0	26	13.1	317.0	65	5.3
O–O	—	—	—	466.0	7	7.9
		$^*R$=0.23			R=0.17	

$$^*R^2 = \frac{\Sigma w(s)[s\cdot i(s)_{\mathrm{calcd}} - s\cdot i(s)_{\mathrm{exp}}]^2}{\Sigma w(s)[s\cdot i(s)_{\mathrm{exp}}]^2}$$

a) Standard deviations are given in parentheses only for those parameters which were refined during the last 2 cycles of refinement.

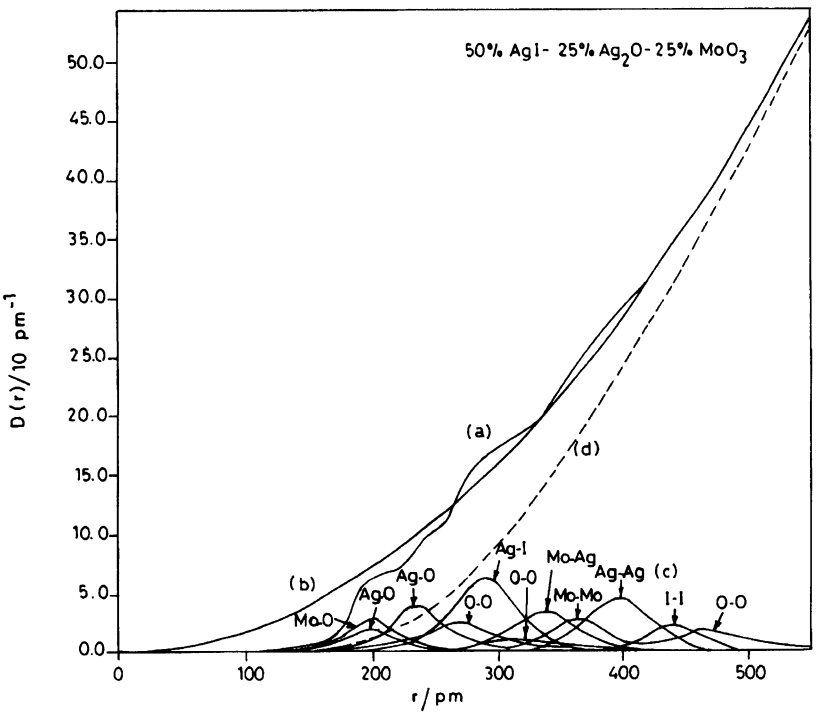

Fig. 1. Radial distribution curve, $D(r)$. (a) $D(r)$ corrected for Fourier ripples. (b) $4\pi r^2\rho_o$. (c) Individual theoretical peak shapes for atom pairs. (d) Curve (a)–curve (c).

Figures 1 and 2 show the radial distribution function $D(r)$ corrected for Fourier ripples and the correlation function $G(r)$ as a function of r, respectively. In the former, a strong peak at 285 pm and a medium peak at 230 pm were assigned to Ag–I and Ag–O interactions, respectively.[5,6] The Mo–O[9] and short Ag–O[5] distances were assumed to be 197 pm as initial values to be refined in the course of the least-squares procedure. Other interactions, namely, Ag–Ag, Mo–Ag, Mo–Mo, and I–I in the range of 300—500 pm were quoted from reported values in crystalline Ag_2O,[21] Ag_2MoO_4,[10] MoO_3 glass,[9] and similar AgI based glasses.[5,6] They were fixed at the last two LSQ cycles. The Hamilton R-factor fi-

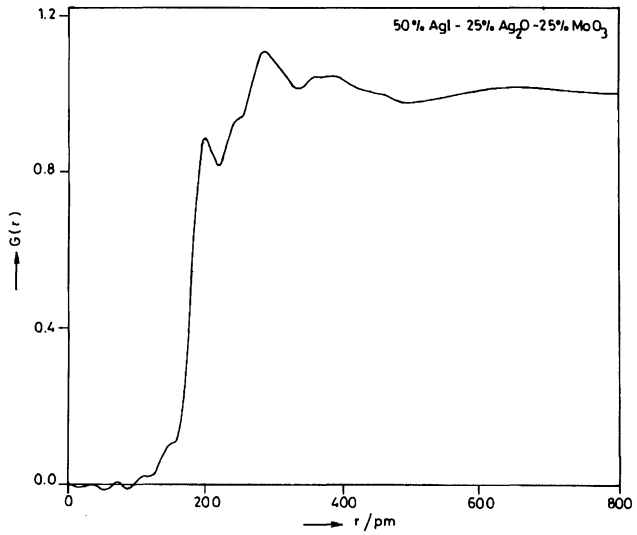

Fig. 2. A plot of correlation function $G(r)$ vs. r.

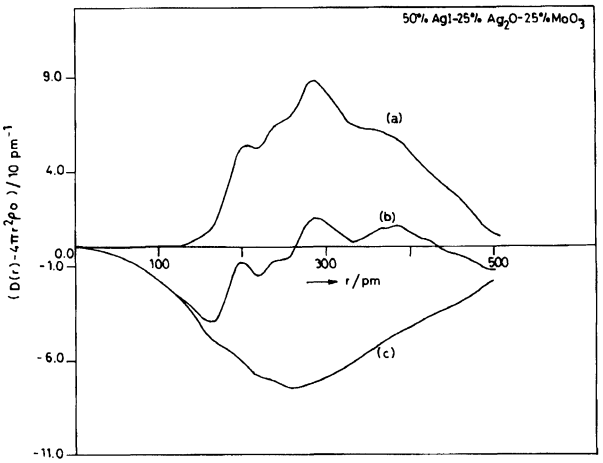

Fig. 3. Differential radial distribution curve $\Delta D(r)$. (a) Theoretical peak shape. (b) $D(r)-4\pi r^2\rho_o$. (c) Residual curve after subtraction of the theoretical peak shape from the $D(r)-4\pi r^2\rho_o$ curve vs. r.

nally converged to $R=0.17$ over the examined range of 0.03 to 0.17 pm^{-1}. Individual peak-shapes calculated from the structure parameters finally obtained and listed in Table 1 are drawn in Fig. 1.

Substraction of the theoretical peak-shape from $\Delta D(r)$ shown in Fig. 3 resulted in a smooth background curve (Fig. 3c) in the range $r=0$ to 500 pm. The fit between theoretical and experimental $s\cdot i(s)$ curves (Fig. 4) proved that the interactions proposed in our study were highly representative of the short-range atomic order in the glass.

Discussion

The molybdenum(VI) ion generally exhibits four and six coordinations of oxygen atoms around it. In Ag_2MoO_4,[10] K_2MoO_4,[11] and $PbMoO_4$,[12] the tetrahedral arrangement of oxygen atoms around Mo(VI) was found as isolated MoO_4^{2-} as in the potassium and ammonium compounds and interconnected with Ag as in Ag_2MoO_4. The Mo–O distance in these compounds varies between 174 pm and 183 pm. In $Bi_2(MoO_4)_3$,[13] MoO_5 polyhedra are paired to form Mo_2O_8 by sharing the edges. Consequently, the variation in the Mo–O distance (169—230 pm) is large. The octahedral coordination has been found in crystalline MoO_3[14] with the Mo–O distance ranging between 180 and 235 pm. Recent X-ray RDF studies also showed octahedral coordination around Mo(VI) in amorphous thin films of MoO_3 with $r_{Mo-O}=195$ pm.[9] In the glassy state, Mo(VI) adopts both four and six coordinations of oxygen atoms as reported in spectroscopic and structural studies of multicomponent glasses containing molybdenum atoms.[15,16] In general, Mo(VI) takes octahedral and tetrahedral configurations. Five coordinated Mo(VI) crystalline compounds have rarely been reported, though an infrared work on glasses with thirteen different compositions in the TeO_2–MoO_3 system showed MoO_6 octahedra for high MoO_3 contents and MoO_5 units for low MoO_3 contents.[17] This is the only instance of the five coordinated Mo(VI) found in glasses so far. No explanation for the formation of the rare five coordinated MoO_5 units has been given by the authors, however. X-ray RDF studies on $45TeO_2$–$55MoO_3$ and $66.7TeO_2$–$33.3MoO_3$ glasses[17] reported coordination numbers of 6.41 and 5.48, respectively, around an Mo atom. Since the systems contain two glass formers of TeO_2 and MoO_3, steric requirements, perhaps force Mo atoms to accept the five coordination structure around it. From Table 1, we see the average Mo–O distance to be 198 pm and the average coordination of oxygen atoms around Mo, n_{Mo-O} to be 5.5. The Mo–O distance in $60AgI$–$20Ag_2O$–$20MoO_3$[5] (glass b) is slightly longer, which is expected with its slightly higher n_{Mo-O}. In spite of the O/Mo molar ratio in glasses a and b to be four, and thus, a favorable four coordination structure of Mo(VI) with oxygen atoms begin expected, the values n_{Mo-O} of 5.5 and r_{Mo-O} of 198 pm suggest the formation of octahedral MoO_6 units in the glasses, though a small fraction of the four-fold arrangement of oxygen atoms around Mo(VI) may not be ruled out. In crystalline MoO_3, adjacent octahedra present in a single layer share edges and octahedra between the layers share corners. The edge sharing Mo–Mo distance is 343 pm and corner-sharing distances are 373 pm and 397 pm.[14] The Mo–Mo distance of 394 pm reported here agrees with the corner sharing values reported earlier by other workers as well as ours and also in amorphous thin films of MoO_3, (392 pm).[9] It is unlikely that the neighboring MoO_3 octahedra share edges, since the Ag atom in the role of the glass modifier occupies positions around oxygen atoms in the network. Short and long Mo–Mo distances are observed in glass b with a total n_{Mo-O} of 2.5 whereas in glass a only a single Mo–Mo distance is observed with higher n_{Mo-Mo} and longer r_{Mo-Mo} than glass b. Since both the glasses have the same modifier to glass former ratio, the reason for this

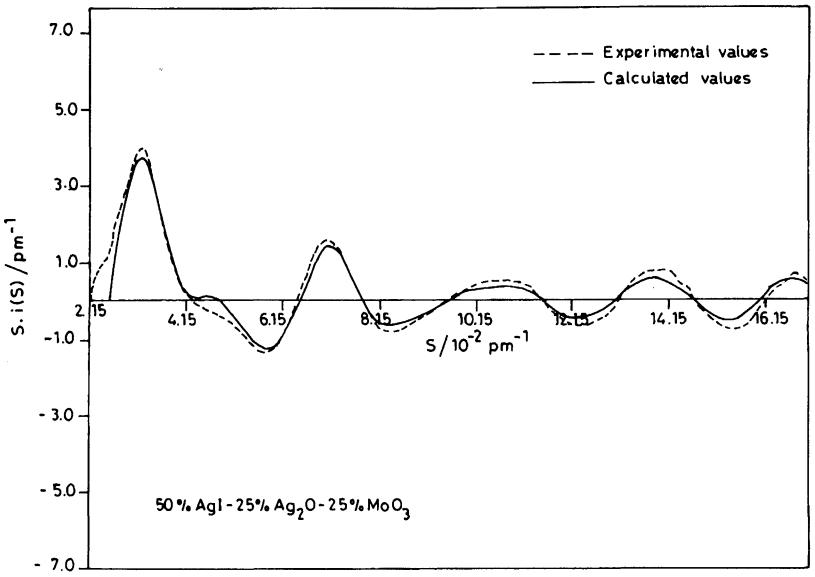

Fig. 4. Comparison between $s \cdot i(s)_{calcd}$ and $s \cdot i(s)_{exp}$.

result is not clear. Probably the higher iodide content in glass b compared to glass a is responsible for this.

The Mo–I distances in Mo_6I_{12}[18] have been reported to lie in the range 268—280 pm, where Mo is in the oxidation state (II). Since Mo atoms in the glass are in a higher oxidation state than (II) and the first shell around Mo atoms is constructed by oxygen atoms, the Mo–I interaction in the glass may appear around 270 pm. However, a recent EXAFS study at I L_3-edge on $(AgI)_x$–$(Ag_2O \cdot 4B_2O_3)_{1-x}$ (x=0.1—0.5) showed an I–O distance of 450 pm and no short I–I distance has been found.[19] Therefore, the 359 pm distance has been assigned to the Mo–Ag interaction in glass a and not to Mo–I, as reported earlier for glass b, since this would involve an I–O interaction shorter than the reported value of 450 pm. The interaction occurring at 248 pm in the previously reported glass b, which has been designated as an Mo–I interaction may be incorrect from the viewpoint of the recent I L_3-edge EXAFS.[19]

Short and long Ag–O distances have been found at 197 and 234 pm, respectively, and they can be compared, respectively, with 189 and 226 pm reported in our earlier work on glass b and in many AgI based superionic glasses.[5,6] EXAFS results on glass b at the Ag K edge show the difference in length of the short and long Ag–O interactions to be 38 pm, which is what is observed in glasses a and b. The shorter Ag–O distance at 197 pm indicates a strong Ag–O bond and the longer distance is indicative of a weak Ag–O interaction. Due to the excess oxygen atoms coming from the modifier Ag_2O, many of the Mo–O–Mo linkages connecting neighbouring MoO_6 octahedra in the network are broken, and thus, terminal Mo=O bonds are created.[5,17] The oxygen atom at terminal with a negative charge attracts Ag atoms and may form strong Ag–O interactions at 197 pm. The weak Ag–O interaction at 234 pm arises from the Ag atoms interacting with the bridging oxygen atoms of the network. Since our results indicate (as explained below) that AgI in the glass does not exhibit the form as has been found in crystalline AgI, many of the Ag atoms from Ag_2O move towards iodide ions due to the high affinity of Ag^+ ions to I^- ions. Thus, only a fraction of Ag atoms in Ag_2O may form the Ag–O bonds of 230 pm length. The iodine content increases form glass a to b, but the molar ratio of the modifier/glass former remains unchanged. A smaller number of silver atoms in glass b than that of glass a are available for the interaction with the network oxygen atoms and this causes the shortening of both short and long Ag–O bonds and the decrease in n_{Ag-O} for both interactions. The Ag–O distance in Ag_2MoO_4 is 242 pm, which is much longer than that found in the glasses, since an Ag atom in Ag_2MoO_4 is surrounded by six oxygen atoms in the octahedral arrangement. These Ag^+ ions, which interact weakly with the network oxygen atoms, may have a high mobility and contribute to the large conductivity in the glasses.

From the comparison between glasses a and b, we found that r_{Mo-O} and n_{Mo-O} increase as the AgI content increases at a constant ratio of modifier to glass former. The variation of the average r_{Mo-O} bond length comes from the two types of Mo–O linkages in the network, namely the bridging Mo–O–Mo and Mo–O–Ag and the terminal Mo=O bonds. Any increase in r_{Mo-O} may be due to (i) the decrease in the number of Mo=O bonds, (ii) the increase in strength and the consequent decrease in length of the Ag–O bonds, and (iii) the increase in the number of the Mo–O coordination. The lesser the modifier oxygen atoms, the lesser are the Mo=O bonds. Since the modifier to glass former ratio remains unchanged in glasses a and b, (i) is not likely to occur. But as the iodine content increases, the num-

ber of silver atoms available for interactions with the network oxygen atoms decreases, and it results in the increase of the strength of the Ag–O interaction and decrease of r_{Ag-O}. In the Mo–O–Ag linkage the above effect weakens the Mo–O interaction and increases r_{Mo-O} as observed in Table 1. The reason for the slight increase in n_{Mo-O} from glass a to b found in the present work is not clear, since the increase in the iodine content or decrease in the Ag content is not likely to influence the Mo–O coordination number at a constant O/Mo ratio.

The superionic conductivity observed in the glass is due to the movement of Ag^+ ions located at 287 pm from iodide ions, which is highly characteristic of all AgI based superionic glasses. The Ag–Ag distance of 335 pm in glass a and 330 pm in glass b is nearly the same as found in Ag_2O (334 pm). This Ag–Ag interaction is between silver atoms taking part in Ag–O interaction. The shortening of r_{Ag-Ag}, though it is slight, from glass a to b agrees with the shorter Ag–O bonds in the latter than in the former which mediates the Ag–Ag interaction.

The distance r_{I-I} increases with decreasing iodine content as shown in Table 1. The r_{I-I} in superionic α-AgI is 435 pm[22] and in the non-conducting β-AgI it is 454 pm.[23] This indicates that the conductivity varies inversely with r_{I-I}. The same trend is observed between glasses a and b since glass b has higher conductivity than glass a. If all the AgI moieties in the glass exhibit the crystalline AgI structure, n_{I-I} and n_{Ag-I} should have values much bigger than the values observed in the present study, namely 0.3 and 0.77. Such a small n_{I-I} value cannot even be explained in terms of a large spread in r_{I-I} due to dislocation of iodine atoms, since the iodine atoms are not mobile as the silver atoms. This again indicates that AgI is dispersed in the glass and is not present as clusters as seen in crystalline AgI. The O–O distances of 265 and 317 pm in our glass can be compared with similar distances found around six coordinated molybdenum in crystalline MoO_3 wherein the distance between oxygen atoms belonging to the same octahedron is 260 pm and between oxygen atoms belonging to neighbouring octahedra is 325 pm. These values agree with our values given above.

The electrical conductivity (σ) in AgI based glasses is found to vary directly with the AgI content in glass.[1—3] A similar trend is observed in glasses a and b, the σ values at room temperature being 6.0×10^{-4} S cm^{-1} and 8.4×10^{-4} S cm^{-1} for glasses a and b, respectively.[24] To discuss the dependence of σ on the structure in general and on modifier content in particular, we need more structure data on glasses with varying glass former to modifier ratios. From the structure results obtained for glasses a and b, it is not possible to draw any meaningful conclusions about the influence of structure on σ.

Conclusions

The following conclusions are drawn from the present study: a) The Mo–O distance, r_{Mo-O} and the coordination number, n_{Mo-O} found in the present study indicate the presence of octahedral MoO_6 units as the main group and a small amount of tetrahedral MoO_4 arrangement of oxygen atoms around molybdenum atoms. b) The Mo–Mo distance at 394 pm in the glass suggests that the MoO_n (i. e. MoO_6 and MoO_4) polyhedra in the glass share corners. c) The characteristic Ag–I interaction occurs at 287 pm, as in other AgI containing superionic glasses. d) Variations in the structure parameters of Mo–O, Ag–O, Ag–Ag, and I–I interactions with composition are explained in terms of a dispersed AgI model. e) The obtained n_{I-I} and n_{Ag-I} values preclude the presence of a significant amount of crystalline AgI clusters or microdomains in glass.

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