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STRUCTURE OF AgI-Ag₂O-B₂O₃ GLASSES BY INFRARED SPECTROSCOPY

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ABSTRACT

Superionic glasses in the system $x\text{AgI} \cdot (1-x)[\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3]$ were prepared from AgNO_3 , AgI and B_2O_3 and studied by infrared reflectance spectroscopy to investigate the structure of the borate network and the nature of sites hosting silver ions. The analysis of the mid-infrared spectra showed that the network building units are $\text{B}\emptyset_3$ and $\text{B}\emptyset_2\text{O}^-$ triangles, as well as $\text{B}\emptyset_4^-$ tetrahedra (\emptyset =oxygen atom bridging two boron centres). The fractions of these units were obtained by spectral deconvolution and were found to be related to the glass transition temperature, T_g . In particular, it was shown that upon addition of AgI the equilibrium $\text{B}\emptyset_4^- \rightleftharpoons \text{B}\emptyset_2\text{O}^-$ shifts to the left, while T_g decreases. This result illustrates the influence of AgI on the short range structure of the borate network by lowering the temperature at which the structure of the supercooled liquid is frozen into the glassy state. The analysis of the far-infrared profiles of glasses in the diborate system indicates the formation of mixed oxyiodide sites for silver ions, whereas glasses with higher $\text{Ag}_2\text{O}/\text{B}_2\text{O}_3$ ratios are known to contain Ag^+ ions in oxide and iodide sites. The findings of this work are discussed in relation to results of other structure-sensitive techniques and models proposed for the structure of AgI-containing superionic glasses.

INTRODUCTION

Among the variety of glasses classified as superionic, particular attention has been devoted to the $x\text{AgI} \cdot (1-x)[\text{Ag}_2\text{O} \cdot n\text{B}_2\text{O}_3]$ ternary system, since its high conductivity (up to 10^{-2} Scm^{-1} at room temperature) is accompanied by relatively high glass transition temperatures and a wide glass forming region. As a consequence, glasses in this system have been studied extensively by different experimental techniques including NMR [1], X-ray and neutron diffraction [2-4], EXAFS and Raman spectroscopy [5, 6] and infrared reflectance and transmittance spectroscopy [1, 7, 8].

However, the conduction mechanism operating in these glasses remains debatable, since there is no consensus on the existence or not of a distinct AgI phase in the glass. Thus, it has been proposed that AgI is randomly dispersed in the host matrix [2-5], or aggregated in AgI microdomains of a disordered nature [6-8]. Theoretical models predict that the ionic conduction takes place either in a structurally inhomogeneous [9] or in a homogeneous glass matrix [4, 10]. Furthermore, the influence of AgI on the borate glass network, i.e. the $\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ matrix, is not fully understood. Neutron scattering [4], NMR [1], X-ray [3, 4] and infrared [1, 8] studies concluded that AgI addition induces no modification to the binary network, while other infrared spectroscopic data [7] suggested that AgI affects the local range order of the borate network in a rather systematic way.

In view of the above, the present work aims at a better understanding of the structure of these glasses and at the elucidation of the existing controversies. Along these lines, a series of $x\text{AgI} \cdot (1-x)[\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3]$ glasses has been prepared and studied by infrared reflectance spectroscopy. Appropriate analysis of the measured spectra in the mid-IR range can yield information on the glass structure and its dependence on AgI content. In addition, the complementary analysis of the far-IR spectra reveals the nature of the sites hosting Ag^+ cations and provides useful information related to the various proposed models of the conduction mechanism.

Finally, the effect of the glass preparation method is discussed, since different results have been reported depending on the way Ag_2O is incorporated into the glass melt. Thus, a previous IR specular reflectance study of $x\text{AgI} \cdot (1-x)[\text{Ag}_2\text{O} \cdot n\text{B}_2\text{O}_3]$ glasses ($n=3, 2, 1, 0.5$), which were prepared using pure Ag_2O as starting material, revealed a systematic change of the network structure upon AgI addition [7].

On the other hand, an analogous IR transmittance study of $x\text{AgI} \cdot (1-x)[\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3]$ glasses prepared from AgNO_3 concluded that the network structure remained unmodified as the AgI content varied [8]. In the present work the glasses studied were prepared by using AgNO_3 as the source of Ag_2O .

EXPERIMENTAL

Stoichiometric amounts of reagent grade AgI, AgNO_3 and B_2O_3 were mixed and heated in Pt crucibles at 650°C until the NO_x gas had dissipated. Then, the mixture was melted at $850\text{--}950^\circ\text{C}$ for 25–30 min depending on composition. Splat quenching the melt between two polished copper blocks yielded bulk samples with flat surfaces appropriate for specular reflectance measurements. Clear glasses were obtained in the composition range $0 \leq x \leq 0.65$.

Infrared reflectance spectra were measured at room temperature in a quasi-normal incidence mode (11°) on a Fourier-transform vacuum spectrometer (Bruker 113v); properly equipped with sources, detectors and beamsplitters to allow a continuous coverage in the $25\text{--}5000\text{ cm}^{-1}$ range. Absorption coefficient spectra were calculated through a Kramers-Kronig analysis of the reflectance data.

RESULTS

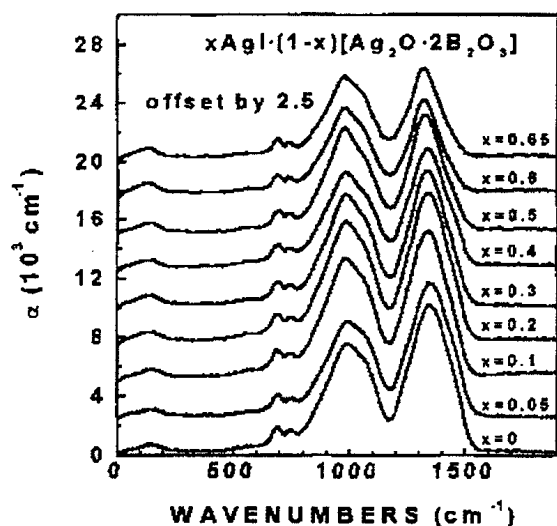


Figure 1. Infrared absorption coefficient spectra of $x\text{AgI} \cdot (1-x)[\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3]$ glasses.

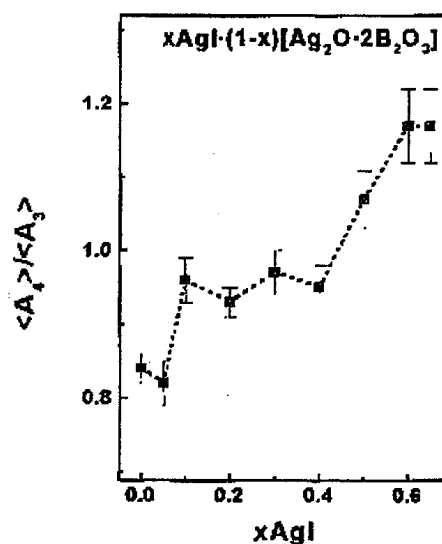


Figure 2. Composition dependence of the $\langle A_4 \rangle / \langle A_3 \rangle$ ratio.

The infrared absorption coefficient spectra, α , of $x\text{AgI} \cdot (1-x)[\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3]$ glasses are shown in Fig. 1 as a function of AgI content. Three strong absorption bands can be distinguished in the mid-IR region, centered at ca. 1350 cm^{-1} (B-O and B-O⁻ asymmetric stretching of BO_3 and $\text{B}\text{O}_2\text{O}^-$ units), 985 cm^{-1} (B-O asymmetric stretching of BO_4^- units), and $630\text{--}750\text{ cm}^{-1}$ (deformation modes of the borate network) [11].

The similarity of the spectral curves indicates that the appearance of new structural units upon AgI addition should be excluded. However, it is noted that AgI induces a change in the relative intensities of the bands at ca. 1350 cm^{-1} and 985 cm^{-1} in favour of the latter, and a shift to lower frequencies accompanied by narrowing of the 1350 cm^{-1} band. The observed trends suggest the occurrence of structural rearrangements between the BO_3 , $\text{B}\text{O}_2\text{O}^-$ triangles and BO_4^- tetrahedra of the borate network.

The calculation of the integrated absorption of the infrared envelopes between 780 and 1180 cm^{-1} , $\langle A_4 \rangle$, and between 1180 and 1570 cm^{-1} , $\langle A_3 \rangle$, permits the quantification of the structural changes induced by AgI addition. The dependence of the $\langle A_4 \rangle / \langle A_3 \rangle$ ratio on AgI content is reported in Fig. 2 and shows quite convincingly that this ratio is affected by the AgI content. This result illustrates the subtle but clear influence of AgI on the borate network structure of the binary glass.

DISCUSSION

The network structure and the role of AgI

As noted above, addition of AgI to the binary glassy matrix does not cause the appearance of new structural units. Thus, the network structure of $x\text{AgI} \cdot (1-x)[\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3]$ glasses is similar to that of

$\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glass, i.e. contains BO_3 and $\text{B}\text{O}_2\text{O}^-$ triangles and BO_4^- tetrahedra [12]. Denoting the corresponding fractions of these units by X_3 , X_3^- and X_4 , respectively, mass and charge balance require that:

$$X_3 + X_3^- + X_4 = 1 \quad (1)$$

$$X_3^- + X_4 = 0.5 \quad (2)$$

These equations result in $X_3=0.5$, i.e. the fraction of the BO_3 units is constant.

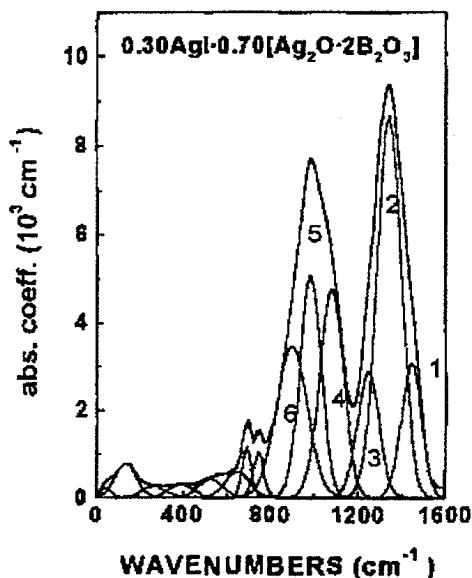


Figure 3. Deconvolution of the infrared spectrum of the $x=0.3$ glass.

The evaluation of the X_3^- and X_4 fractions requires deconvolution of the absorption coefficient spectra into component bands. It was found that the characteristic range of the stretching vibrational modes of the borate network ($800\text{-}1600\text{ cm}^{-1}$) is best fitted with six Gaussian components; three of them are in the range of boron triangles ($1430\text{-}1450\text{ cm}^{-1}$, $1325\text{-}1350\text{ cm}^{-1}$, $1220\text{-}1245\text{ cm}^{-1}$), while the remaining bands are in the range of boron tetrahedra ($1070\text{-}1085\text{ cm}^{-1}$, $980\text{-}995\text{ cm}^{-1}$ and $890\text{-}905\text{ cm}^{-1}$). A typical example of deconvolution is shown in Fig.3 for $x=0.3$.

In order to assign these component bands to specific units, a preliminary group theory approach was made. The BO_3 unit (D_{3h} symmetry) exhibits six normal modes of vibration: $\Gamma_{D_{3h}} = A_1'(R) + 2E'(IR, R) + A_2''(IR)$ with R and IR denoting Raman and infrared activity, respectively. Thus, the BO asymmetric stretching mode active in the infrared has E' symmetry. The six normal modes of vibration of the $\text{B}\text{O}_2\text{O}^-$ unit with C_{2v} symmetry are distributed as follows: $\Gamma_{C_{2v}} = 3A_1(IR, R) + B_1(IR, R) + 2B_2(IR, R)$, with two of these modes (A_1 , B_2) corresponding to IR active asymmetric stretching boron-oxygen vibrations. Thus, creation of a non-bridging oxygen in BO_3 triangles causes the splitting of the E' mode into two components of symmetry A_1 and B_2 and the weak activation in the infrared of the symmetric stretching mode, A_1 . Indeed, crystalline $\text{Li}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ which consists of diborate units, and thus contains only the BO_3 unit besides the BO_4^- tetrahedra, presents a very strong infrared feature at ca. 1390 cm^{-1} , while crystalline $\alpha\text{-Li}_2\text{O}\cdot \text{B}_2\text{O}_3$ consisting of metaborate chains of $\text{B}\text{O}_2\text{O}^-$ units exhibits two strong IR bands at ca. 1445 and 1260 cm^{-1} and a shoulder at ca. 1510 cm^{-1} [11]. On these grounds, it seems reasonable to attribute the $1325\text{-}1350\text{ cm}^{-1}$ band to the BO asymmetric stretching vibration of BO_3 units (band 2 in Fig.3), while the two remaining bands at $1220\text{-}1245\text{ cm}^{-1}$ and $1430\text{-}1450\text{ cm}^{-1}$ (bands 3 and 1 in Fig.3) can be assigned to the asymmetric stretching vibrations of $\text{B}\text{O}_2\text{O}^-$ units with C_{2v} symmetry. For the analysis presented in this work it is not essential to assign in details the bands in the spectral range of tetrahedra ($800\text{-}1200\text{ cm}^{-1}$, bands 4, 5 and 6 in Fig.3).

Denoting by A_i the integrated intensity of the i -th component band normalized by the total integrated intensity in the $800\text{-}1600\text{ cm}^{-1}$ spectral range, with i ranging from 1 to 6 in descending order of frequency (Fig.3) and following the assignments made above the fractions X_3^- and X_4 are given by:

$$X_3^- = A_1/\alpha_1 \quad X_3^- = A_3/\alpha_3 \quad X_4 = (A_4 + A_5 + A_6)/\alpha_4 \quad (3)$$

where α_1 and α_3 are the normalized absorption coefficients of the corresponding modes of the $\text{B}\text{O}_2\text{O}^-$ units and α_4 is the normalized absorption coefficient of the BO_4^- tetrahedra. Considering Eqs.(2) and (3) it is obvious that there are five unknown parameters (X_3^- , X_4 , α_1 , α_3 and α_4) and four equations.

Assuming now that α_1 , α_3 and α_4 do not change with AgI addition, we obtain the ratios F_3^j and F_4^j from the deconvolution parameters of the absorption coefficient spectra of two different samples i and j :

$$\frac{(A_1)_i}{(A_1)_j} = \frac{(A_3)_i}{(A_3)_j} = \frac{(X_3^-)_i}{(X_3^-)_j} = F_3^i \quad (4)$$

$$\frac{(A_4 + A_5 + A_6)_i}{(A_4 + A_5 + A_6)_j} = \frac{(X_4)_i}{(X_4)_j} = F_4^i \quad (5)$$

The fractions X_3^- and X_4 for glasses i and j can be obtained now by combining Eqs.(4) and (5) with Eq.(2) (one for each glass composition).

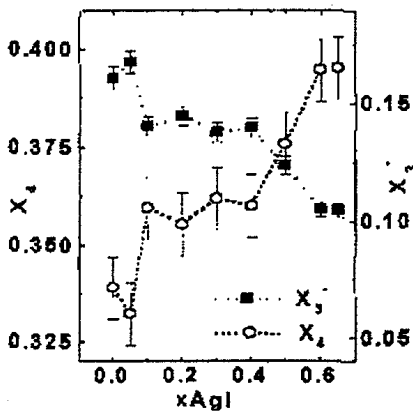


Figure 4. Fractions X_3^- , X_4 as a function of AgI content.

The calculated fractions X_3^- and X_4 are plotted in Fig.4 versus AgI content. The results strongly support the notion of a structural rearrangement in the borate network between the isomeric $B\emptyset_2O^-$ and $B\emptyset_4^-$ units upon adding AgI, as expressed by the following chemical equilibrium:



The data in Fig.4 indicate that addition of AgI to the glass shifts the above equilibrium to the left. This effect can be quantified in terms of the equilibrium constant, K_{eq} , at constant pressure:

$$K_{eq} = \frac{X_3^-}{X_4} \quad (7)$$

It is found that K_{eq} decreases systematically as the AgI content increases. Since the present glasses were prepared under identical quenching conditions, K_{eq} will depend on the fictive temperature at which the structure of the supercooled liquid was "frozen" into the glassy state. Fictive temperatures are not available, but it is was found that the glass transition temperature of these glasses decreases upon addition of AgI [1]. From the change of K_{eq} with T_g we can estimate the enthalpy change for reaction (6) according to:

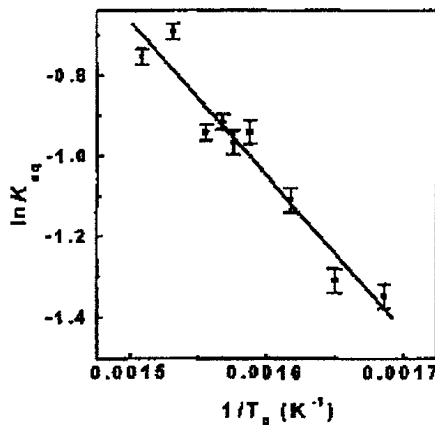


Figure 5. Temperature dependence of K_{eq} of Eq.(6). Solid line is least square fitting of the data.

where ΔH is the enthalpy change, ΔS is the entropy change and R is the gas constant. From the least square fitting of the $\ln K_{eq}$ vs. $1/T_g$ data (Fig. 5) we estimate ΔH to be $\Delta H = (32 \pm 5) \text{ kJ mol}^{-1}$. The value obtained is close to the one reported for a similar equilibrium between silicate species in silicate glasses [13].

These findings are in agreement with previous works on the effects of AgI on the network structure of glasses based on diverse glass formers such as B_2O_3 , P_2O_5 and MoO_3 [7]. Also, the role of CuI in the glasses $x\text{CuI} \cdot (1-x)\text{Cu}_2\text{MoO}_4$ is very similar to that of AgI [14].

The above results show clearly that addition of a relatively inert metal halide salt to an already modified binary glass matrix affects the network structure in a rather indirect way; i.e. it results in a decrease of T_g and presumably in a decrease of the fictive temperature at which the structure of the

supercooled liquid is arrested into the glassy state. This temperature decrease affects directly the value of the constant for the chemical equilibrium that describes the particular oxyanion matrix in the liquid state. The final result is a rearrangement between the structural units which participate in the corresponding chemical equilibrium.

Our findings are consistent with the results of statistical mechanical calculations of Araujo [15] for the fraction of boron tetrahedra (X_4) in alkali borate glasses as a function of temperature and composition. For the same glass composition, Araujo finds that X_4 decreases with increasing temperature, and therefore glasses with different fictive temperatures are expected to result in different structures. In this work, it was found that the decrease in T_D , and most probably in the fictive temperature, causes an increase in X_4 in agreement with the statistical mechanical model.

Concerning the existing controversies for the effect of AgI on the network structure, we note that the NMR results for variations in the fractions of four-coordinated boron atoms, N_4 , as a function of AgI content are of the order of the experimental error (7%) [1]. As shown in Fig.4, the X_4 values obtained in this work vary from 0.34 ($x=0$) to 0.39 ($x=0.65$) with an experimental error estimated to be about 5%. This increase of X_4 by adding AgI ($\approx 15\%$) is well outside our experimental error in determining X_4 .

In a recent infrared transmittance study of $x\text{AgI}\cdot(1-x)[\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3]$ glasses, Hudgens and Martin [8] find that the $\langle A_4 \rangle / \langle A_3 \rangle$ ratio is independent of the AgI content. Considering the relatively large film thickness used ($\sim 10\text{-}100\ \mu\text{m}$) and the large absorption coefficients for the stretching modes of boron-oxygen triangles and tetrahedra this result may have arisen from saturation effects. To the contrary, infrared specular reflectivity data are free from such effects. Indeed, the X_4 value obtained in this study for the binary glass ($x=0$, $X_4=0.34$) is in very good agreement with the NMR result ($N_4=0.35$) reported by Kim & Bray [16].

The vibrations of silver cations in their sites

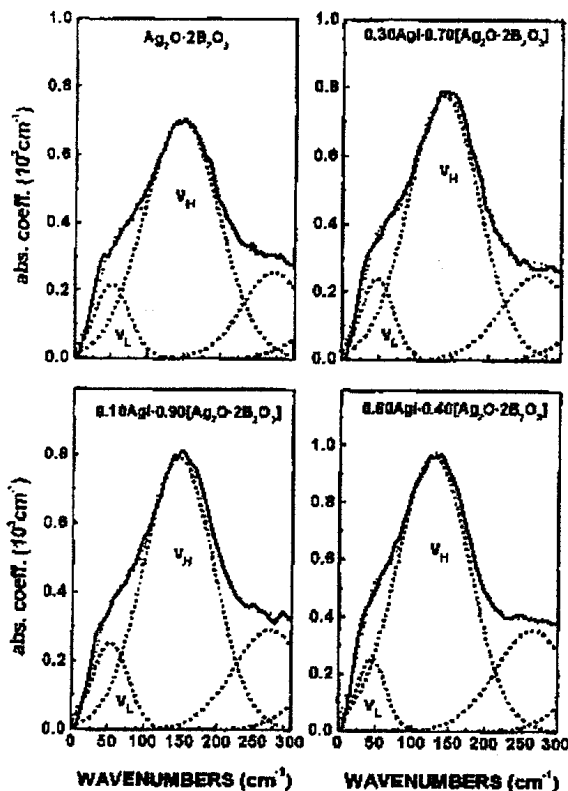


Figure 6. Typical far-IR deconvoluted profiles of $x\text{AgI}\cdot(1-x)[\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3]$ glasses.

Characteristic far-IR profiles are shown in Fig.6 for AgI contents spanning the whole glass forming range. The far-IR spectra of the ternary glasses present no remarkable differences compared to the one of the binary $\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glass. In previous studies such profiles were deconvoluted into Gaussian components and attributed to vibrations of Ag^+ cations in their anionic hosting sites and network vibrational modes [7, 8]. The same deconvolution procedure has been followed in this work. The far-IR spectrum of the $\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glass has been deconvoluted into three component bands centred at $52\ \text{cm}^{-1}$ (v_L), $145\ \text{cm}^{-1}$ (v_H) and $275\ \text{cm}^{-1}$. The last component can be attributed to a borate network mode, while the ones designated by v_L and v_H are attributed to vibrations of Ag^+ ions in two distributions of oxygen-like anionic environments [12]. The spectra of ternary glasses could be also fitted with three Gaussian components; the ones at $40\text{-}50\ \text{cm}^{-1}$ (v_L) and $128\text{-}147\ \text{cm}^{-1}$ (v_H) are assigned to vibrations of Ag^+ ions in mixed oxyiodide sites and the one at ca. $275\ \text{cm}^{-1}$ to a network mode. It was found that v_L and v_H decrease upon increasing AgI content in the glasses, while the frequency of the third component remains practically fixed. The progressive decrease of v_H and v_L with x is attributed to an increase of the effective mass of the vibration caused by the progressive substitution of oxygen by iodide ions.

This far-IR study suggests that AgI is dispersed in the glassy network of $x\text{AgI}\cdot(1-x)[\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3]$ glasses in agreement with the results of neutron and X-ray investigation of the same system [2-4]. It is noted though that our previous investigation of borate glass

families with higher Ag_2O contents, $x\text{AgI}\cdot(1-x)[\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3]$ $n=1, 0.5$, showed the presence of an additional component band in the far-IR at ca. 100 cm^{-1} , which was attributed to vibrations of Ag^+ ions in AgI-like microdomains [7]. Thus, whether or not a separate AgI-like phase is present in $x\text{AgI}\cdot(1-x)[\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3]$ glasses is strongly dependent on the Ag_2O content. In order to further investigate this point, new measurements on $x\text{AgI}\cdot(1-x)[\text{Ag}_2\text{O}\cdot 0.5\text{B}_2\text{O}_3]$ glasses prepared from AgNO_3 are currently in progress. The preliminary results seem to indicate the presence of silver ions in both oxide and iodide sites. A full report of this work will be published later.

CONCLUSIONS

Superionic glasses $x\text{AgI}\cdot(1-x)[\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3]$ have been studied by infrared reflectance spectroscopy to investigate the network structure and its dependence on AgI content, as well as the nature of sites hosting Ag^+ ions. It was found that the network consists of BO_2^- , BO_3^- triangles and BO_4^- tetrahedra. The fractions of BO_4^- and BO_2^- units were found to depend on the AgI content, suggesting that a structural rearrangement occurs between these units. These modifications were correlated with the effect of AgI on the glass transition and fictive temperature at which the supercooled liquid is frozen into the glassy state. It was concluded that the relatively inert AgI influences the network structure in a rather indirect way. The far-IR analysis indicated the presence of mixed oxyiodide sites in this family of AgI-containing diborate glasses.

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