CONGRESO INTERNACIONAL DEL VIDRIO
INTERNATIONAL CONGRESS ON GLASS
INTERNATIONALER GLASKONGRESS
CONGRÈS INTERNATIONAL DU VERRE

VOL. 4

Glass properties - Propriétés du verre - Glaseigenschaften
Glass composites - Verres composites - Glasverbunde

INFRARED STRUCTURAL STUDIES OF SILVER ION CONDUCTING GLASSES xAgI.(1-x)(Ag$_2$O.nB$_2$O$_3$)

E.I.KAMITSOS, J.A.KAPOUTSIS, G.D.CHRYSSIKOS and A.P.PATSIS

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vas.Constantinou Ave., Athens 116 35, GREECE

ABSTRACT

The structure of AgI-containing borate glasses has been investigated by infrared reflectance spectroscopy. The analysis of the spectra has revealed the presence of AgI "microdomains" , which influence the structure of the borate host matrix in a manner and extent which depend on the AgI content and the Ag$_2$O/B$_2$O$_3$ ratio.

INTRODUCTION

Fast ionic conducting glasses have attracted a wide interest for the fundamental study of mass transport , as well as for applications in electrochemical devices. AgI-containing glasses are of special interest due to their exceptionally high ionic conductivity at room temperature. The system xAgI.(1-x)(Ag$_2$O.nB$_2$O$_3$) has received particular attention because its high conductivity is accompanied by relatively high glass transition temperatures. However, despite the great number of studies devoted to this model system the mechanism of ionic conduction remains quite controversial. Thus, different models have been reported for the state of silver iodide and its interactions with the glass host matrix in this and in similar AgI-containing glasses.

Two main groups of models for the role of AgI can be distinguished. One proposes the organization of silver iodide in "microdomains" within the borate matrix (1-6). It is thought that the movement of silver ions is facilitated by the formation of conduction pathways along the AgI domains. The second model views AgI as highly dispersed in interstices controlled by oxygens of the borate network (7-9). A broad distribution of barrier heights is proposed and the enhancement of ionic conductivity is accounted for by a dynamic coupling of the ion motion with the disorder modes of the borate network. A direct implication of the first model involves the existence of at least two different coordination environments for silver ions, i.e. one provided by I$^-$ anions and the other formed primarily by oxygen atoms (1-6). According to the second model both iodide and oxygen atoms participate to the coordination sphere of the silver ion (7-9).

The existing diversity of view points suggests that further work is required for a better understanding of the structure and the ion conduction mechanism in fast ionic conducting glasses

containing AgI. We report in this work preliminary results of an infrared reflectance investigation of the structure of glasses in the system $xAgI.(1-x)(Ag_2O.nB_2O_3)$. These results are discussed in light of the models proposed for these and similar ionic glasses.

EXPERIMENTAL

Glasses in the system $xAgI.(1-x)(Ag_2O.nB_2O_3)$ were prepared for n=3 (triborate), n=2 (diborate), n=1 (metaborate) and n=0.5 (pyroborate), by using stoichiometric amounts of reagent grade powders of anhydrous AgI, Ag_2O and B_2O_3. The well mixed batches (2-3 g) were melted in platinum crucibles at 700-1000 °C for about 30 min, depending on composition. Splat quenching between two copper blocks yielded glass specimens of good surfaces, and they were used for infrared measurements without further treatment. Infrared reflectance spectra were recorded on a Bruker 113v spectrometer which was properly equipped to provide a continuous coverage in the range 30-4000 cm^{-1}. Absorption coefficient spectra reported in this work were calculated from the reflectance data through the Kramers-Kronig inversion technique (10).

RESULTS AND DISCUSSION

The Influence of AgI on the Borate Network Structure

Typical infrared spectra for glasses in the diborate (n=2) family are presented in Figure 1. The spectrum of the binary glass (x=0) resembles those of lithium- and sodium- diborate glasses (10). It is characterized by strong absorptions centered at ca 1350 cm^{-1} (B-O asymmetric stretching of boron-oxygen triangles) , 990 cm^{-1} (B-O asymmetric stretching of boron-oxygen tetrahedra) and 620-800 cm^{-1} (deformation modes of borate network segments) (10). The low frequency part of the spectrum (below 300 cm^{-1}) shows the presence of an asymmetric absorption profile, peaking at ca 140 cm^{-1}. This band can be attributed to the rattling motion of Ag^+ ions in their suitable anionic environments, in analogy with the behaviour of alkali ions in borate glasses (11). This part of the spectrum will be discussed in more details in the next section.

Addition of AgI to the silver-diborate glass appears to systematically effect the infrared response. Specifically, the increase of the relative intensity of the band at ca 990 cm^{-1} is evident upon increasing the AgI content (Fig.1). This trend clearly suggests an increase of the fraction of borate arrangements containing $B\varnothing_4^-$ tetrahedra, relative to those containing boron-oxygen triangles. To quantify this effect we have obtained the area under the absorption envelopes 800-1180 cm^{-1}, denoted by $<A_4>$, and 1180-1550 cm^{-1}, denoted by $<A_3>$. The ratio of the areas, $<A_4>/<A_3>$, is shown in Figure 2 as a function of AgI content. While the infrared spectra of glasses in the other families will be presented and discussed in detail elsewhere (12), we include in the same figure the relevant results for glasses in the n = 3, 1, 0.5 systems for the purpose of comparison.

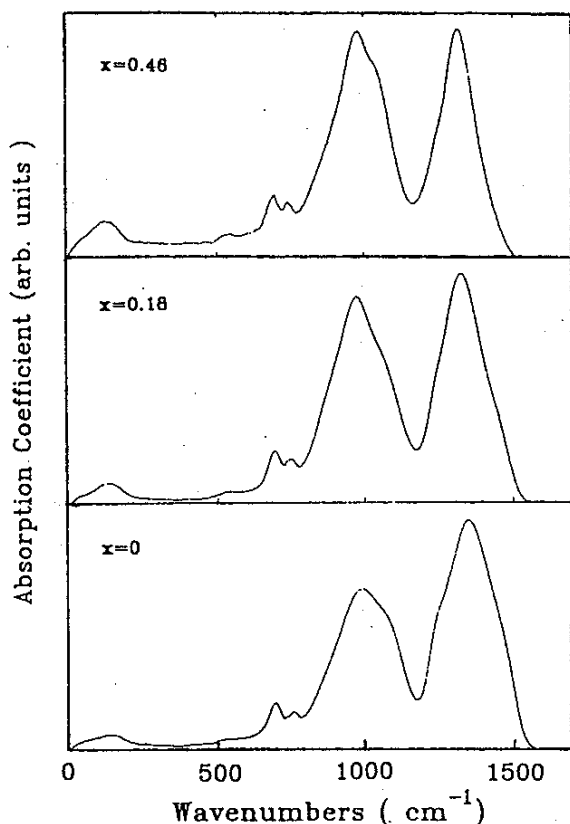It is quite evident from Figure 2 that the ratio $<A_4>/<A_3>$ depends on the glass content

Figure 1. Infrared absorption spectra of $xAgl.(1-x)(Ag_2O.2B_2O_3)$ glasses.
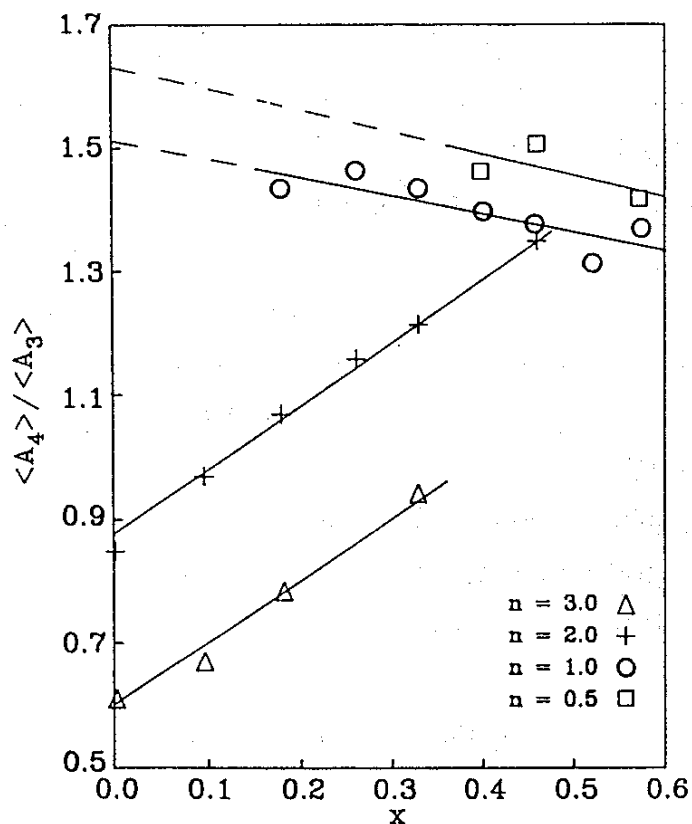
Figure 2. Composition dependence of the infrared relative areas $<A_4>/<A_3>$ of $xAgl.(1-x)(Ag_2O.nB_2O_3)$ glasses

in Ag_2O, which dictates the structure of the borate host matrix, as well as in Agl additive. These results manifest quite convincingly that the borate glass network structure is affected not only by Ag_2O but also by Agl additions. For a constant n value, that is for a fixed Ag_2O/B_2O_3 ratio, the addition of Agl should not affect the total negative charge on the borate network. Thus, any change in the $<A_4>/<A_3>$ ratio Agl should originate from a redistribution of the negative charge on the borate matrix, induced by the presence of Agl. For relatively low Ag_2O contents, i.e. triborate and diborate systems, it seems that the presence of Agl favours the creation of $B\Phi_4^-$ tetrahedra. We suggest that this is effected by the transformation of boron-oxygen triangles containing one non-bridging oxygen ($B\Phi_2O^-$, Φ=bridging oxygen atom) into their isomeric $B\Phi_4^-$ tetrahedra. Addition of Agl to glasses of higher Ag_2O content (n = 1, 0.5), appears to slightly decrease the $<A_4>/<A_3>$ ratio (Fig.2). This suggests the destruction of $B\Phi_4^-$ tetrahedra, probably in favour of boron triangles with two non-bridging oxygen atoms ($B\Phi O_2^{2-}$, pyroborates) and boron triangles with all bridging oxygens ($B\Phi_3$).

The effect of Agl on the structure assumed by the borate matrix can be understood by considering the Lewis base properties of I^- and the various negatively charged borate groups. It is known that I^- is a soft base (13), while the hardness of the borate network polyhedra increases in the order $B\Phi_2O^- < B\Phi_4^- < B\Phi O_2^{2-}$ (14). Thus, in the presence of the soft I^- base the average hardness of the borate base properties increases, probably via polarization effects mediated by the soft Lewis

Ag^+ acid. We have shown that at $n=3$ and $n=2$ $B\Phi_2O^-$ and $B\Phi_4^-$ species coexist in the binary glass, thus in the presence of AgI the soft $B\Phi_2O^-$ base transforms into the harder one $B\Phi_4^-$. Binary silver borate glasses with $n=1$ and $n=0.5$ cannot be prepared. However, careful consideration of the spectra of the ternary glasses shows the presence of $B\Phi_4^-$ and $B\Phi O_2^{2-}$ species (12); justifying the dependence of the $<A_4>/<A_3>$ ratio on the AgI content.

The results of this section concerning the behaviour of the $<A_4>/<A_3>$ ratio are in agreement with the earlier study of Minami et al (1) for $n=2$, but not for $n=1$ and $n=0.5$. Previous Raman studies of similar AgI-containing borate glasses led to the conclusion that there is no effect of AgI on the borate structure (15). It is noted though that in these studies the part of the Raman spectrum between 1300 and 1600 cm^{-1}, which is particularly sensitive to borate groups containing non-bridging oxygens (16) was not investigated. This fact may provide an explanation for the conclusions reached on the basis of the lower frequency Raman spectrum alone (15).

Far-Infared Investigation of the Localized Silver Ion Vibration

As shown in Figure 1 addition of AgI to the binary glass affects the far-infrared spectrum as well; in particular a change of the far-infrared absorption profile with x is effected. This is also shown in the far infrared spectra of glasses in the metaborate ($n=1$) and pyroborate ($n=0.5$) families, as depicted in Figure 3, in an expanded frequency range. The measured profiles are quite broad and asymmetric, denoting the presence of a number of component bands. Thus, we have analyzed these spectra by utilizing deconvolution techniques already applied to binary and ternary alkali borate glasses (10,11,16). It was found that a consideration of at least three component bands was necessary to simulate the spectra of the AgI-containing glasses (Fig.3), while those of the binary $Ag_2O.nB_2O_3$ glasses could be described by two component bands, in agreement with the results obtained for alkali borate glasses (10,11).

Figure 3. Deconvoluted far-infrared spectra of $xAgI.(1-x)(Ag_2O.nB_2O_3)$ glasses for $n=1$ and $n=0.5$.

Of particular interest is the band at ca 100 cm^{-1} which appears to increase in relative intensity with increasing AgI content compared to the bands at ca 50 and 175 cm^{-1}. The area of the band at ca 100 cm^{-1}, denoted by $<A_{Ag-I}>$, has been measured and is plotted vs x in Figure 4 for
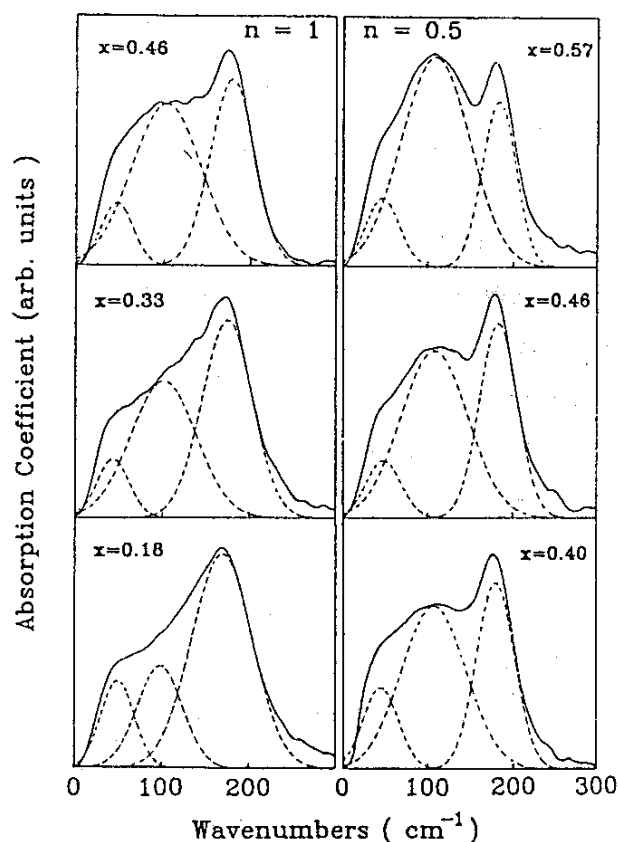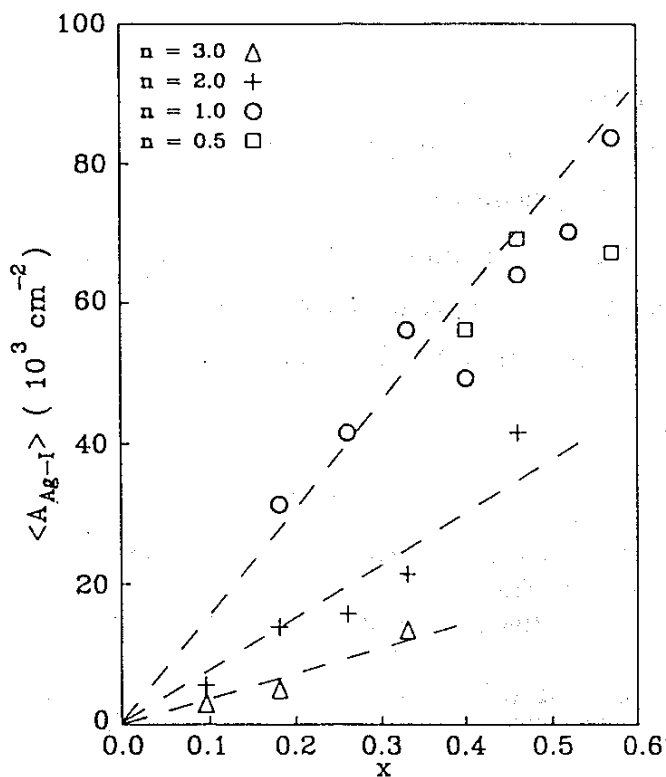
Figure 4. Composition dependence of the area of the $\underline{ca}$ 100 cm^{-1} band of $xAgI.(1-x)(Ag_2O.nB_2O_3)$ glasses.
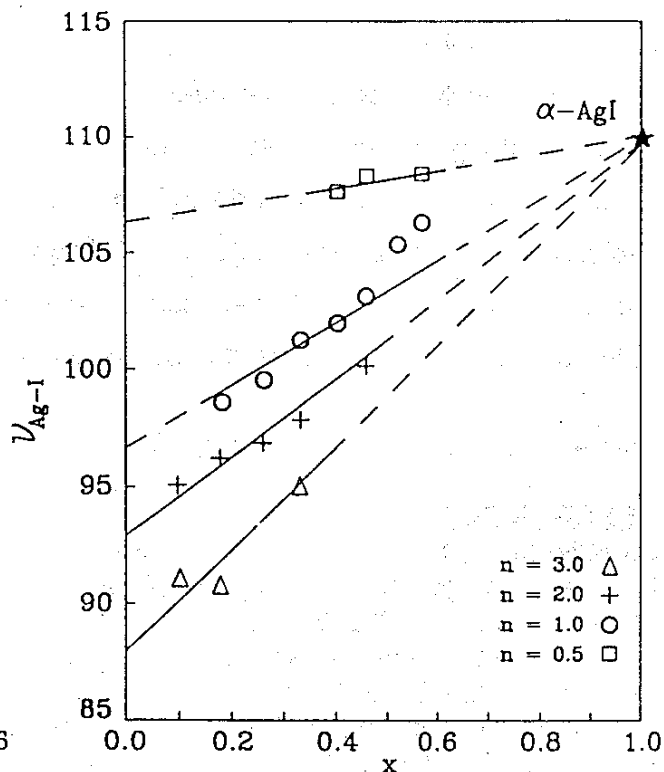
Figure 5. Ag^+ motion frequency in AgI "domains" in $xAgI.(1-x)(Ag_2O.nB_2O_3)$ glasses

glasses in the four families investigated. A quite linear dependence of $<A_{Ag\text{-}I}>$ on the AgI content has been obtained, suggesting that this band should originate from Ag^+ rattling motions in an iodide environment. It is noted that a band at ca 110 cm^{-1} has also been measured in the Raman spectra of AgI containing glasses (17), as well as in the far-infrared spectrum of the $0.5AgI.0.5AgPO_3$ glass (18). The other two bands at ca 50 and 175 cm^{-1} are attributed to Ag^+-oxygen vibrations in two different distributions of oxygen site environments (12).

While the intensity of the band at ca 100 cm^{-1} increases with AgI content, of equal interest is also its frequency variation with x and n. This frequency, as obtained by deconvolution, is plotted in Figure 5, where it is marked by $v_{Ag\text{-}I}$. It is observed that for glasses of the same AgI mole fraction (x), the Ag-I frequency increases upon decreasing n, i.e upon increasing the modification of the borate network. For glasses in the same family (constant n) $v_{Ag\text{-}I}$ increases with AgI content and extrapolates to the value of the corresponding Ag^+ ion motion in α-AgI (19).

We interpret the far-infrared results as demonstrating the presence of AgI "microdomains", or "pseudophases", with a structure different than that of α-AgI. This structure is distorted by the interaction with the borate matrix, changes continuously with AgI content and eventually tends towards the structure of α-AgI at very high AgI contents. Silver ions are also present in two oxygen environments, controlled by the borate matrix. These environments are also affected by the presence of AgI, and such effects will be discussed in more details elsewhere (12).

CONCLUSIONS

The analysis of the mid-infrared spectra of AgI-containing borate glasses has shown the influence of AgI on the borate network structure. The extent and manner of this influence is a function of both AgI content and Ag_2O/B_2O_3 ratio. The far-infrared spectra have demonstrated the evolution of a third band with intensity scaling with the AgI content and frequency extrapolating to that of α-AgI (110 cm^{-1}). These results were interpreted as indicating the development of AgI "microdomains", with a distorted structure due to interactions with the borate matrix.

REFERENCES
(1) MINAMI T., SHIMIZU T. and TANAKA M. J.Non-Cryst.Solids: Structure and ionic conduction in the ternary systems $AgX-Ag_2O-B_2O_3$. 9+10(1983) 577-584.
(2) SCHIRALDI A., PEZZATI E. and BALDINI P. J.Phys.Chem.: Thermoelectric power of the high ionic conductivity glasses $AgI.Ag_2O.B_2O_3$. 89(1985) 1528-1531.
(3) CARINI G., CUTRONI M., FEDERICO M., GALLI G. and TRIPODO G. Phys.Rev.B: Acoustic properties and diffusion in superionic glasses. 30(1984) 7212-7224.
(4) DALBA G., FORNASINI P., FONTANA A., ROCCA F. and BURATTINI E. Solid State Ionics: EXAFS structural studies on $(AgI)_x(Ag_2O.4B_2O_3)_{1-x}$ glasses. 28-30(1988) 713-716.
(5) MERCIER R., TACHEZ M., MALUGANI J.P. and ROUSELOT C. Materials Chemistry and Physics: Microstructure of silver superionic glasses. 23(1989) 13-27.
(6) BORJESSON L. and HOWELLS W.S. Solid State Ionics: Intermediate range structural ordering in AgI doped superionic glasses: a neutron diffraction study. 40-41(1990) 702-704.
(7) CHIODELLI G., MAGISTRIS A., VILLA M. and BJORKSTRAM J. J.Non-Cryst.Solids: Short range order and glass transition in $AgI-Ag_2O-B_2O_3$ vitreous electrolytes. 51(1982) 143-159.
(8) LICHERI G., MUSINU A., PASCHINA G., PICCALUGA G., PINNA G. and MAGISTRIS A. J.Chem.Phys: Coordination of Ag^+ ions in $AgI-Ag_2O-B_2O_3$ glasses by X-ray diffraction. 85(1986) 500-506.
(9) CHUNG S.H., JEFFREY K.R., STEVENS J.R. and BORJESSON L. Phys.Rev.B: Dynamics of silver ions in $(AgI)_x.(Ag_2O.nB_2O_3)_{1-x}$ glasses: A ^{109}Ag magnetic resonance study. 41(1990) 6154-6164.
(10) KAMITSOS E.I., PATSIS A.P., KARAKASSIDES M.A. and CHRYSSIKOS G.D. J.Non-Cryst.Solids: Infrared reflectance spectra of lithium borate glasses. 126(1990) 52-67.
(11) KAMITSOS E.I., KARAKASSIDES M.A. and CHRYSSIKOS G.D. J.Phys.Chem: Cation-Network interactions in binary alkali metal borate glasses.A far-infrared study. 91(1987) 5807-5813.
(12) KAMITSOS E.I. et al. in preparation.
(13) PEARSON R.G. J.Chem.Educ.: Hard and Soft acids and bases. 45(1968) 581-648.
(14) KAMITSOS E.I. J.Phys.Chem.: Modifying role of alkali-metal cations in borate glass networks. 93(1989) 1604-1611 and references therein.
(15) CARINI G., CUTRONI M., FONTANA A., MARIOTTO G. and ROCCA P. Phys.Rev.B: Inelastic light scattering in superionic glasses $(AgI)_x(Ag_2O.nB_2O_3)_{1-x}$. 29(1984) 3567-3572.
(16) CHRYSSIKOS G.D., KAMITSOS E.I. and KARAKASSIDES M.A. Phys.Chem.Glasses: Far-infrared and Raman studies of Sodium ion conducting glasses. 36(1989) 243-250.
(17) FONTANA A. and ROCCA F. Phys.Rev.B: Concentration dependence of Raman scattering in superionic glasses $(AgI)_x(Ag_2O.B_2O_3)_{1-x}$. 36(1987) 9279-9282.
(18) ANGELL C.A. Chem.Rev.: Dynamic processes in ionic glasses. 90(1990) 523-542.
(19) ALBEN R. and BURNS G. Phys.Rev.B: Lattice dynamics of the superionic conductor AgI. 16(1977) 3746-3752.