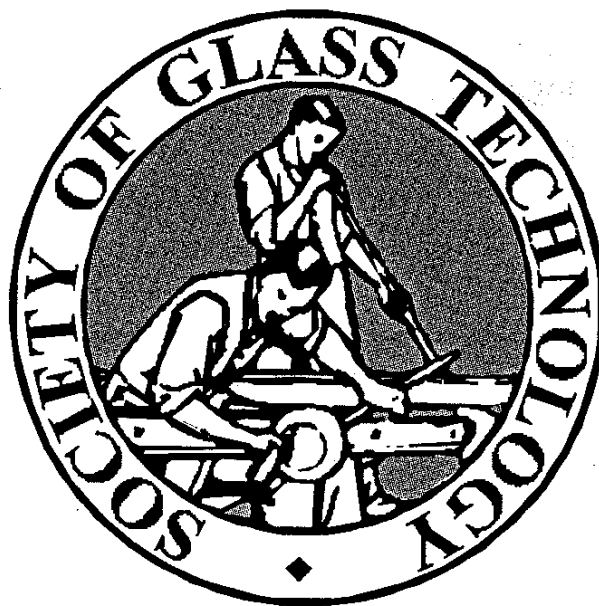


BORATE GLASSES, CRYSTALS & MELTS

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AN XPS STUDY OF THE CHEMICAL STRUCTURE OF AgI–Ag₂O–B₂O₃ GLASSES

H. JAIN

*Materials Science and Engineering Dept., Lehigh University,
Bethlehem, PA 18015, USA*

A. C. MILLER

*Zettlemoyer Center for Surface Studies, Lehigh University,
Bethlehem, PA 18015, USA*

E. I. KAMITSOS & J.A. KAPOUTSIS

National Hellenic Research Foundation, Athens 11635, Greece

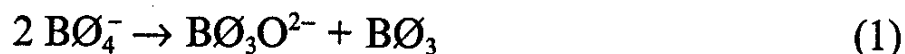
The chemical structure of six glasses within the $x\text{AgI}:(1-x)[\text{Ag}_2\text{O}:n\text{B}_2\text{O}_3]$ system, and polycrystalline AgI has been determined using high resolution x-ray photoelectron spectroscopy. The O 1s spectra reveal a new kind of oxygen atom with charge density lower than that on bridging oxygens. These low charge density oxygens (LCDO) are believed to result from a predominantly covalent bonding with Ag. The concentration of LCDO increases with the initial addition of Ag₂O to B₂O₃, or AgI to Ag₂O:B₂O₃ glasses. For $n=1$, with increasing x , Ag and I approach the chemical state of crystalline AgI. There is no obvious indication of distinct AgI microdomain formation at low AgI content.

1. INTRODUCTION

Among the various halogenated borate glasses, the structure of silver iodoborates has been investigated most because of their potential application as a solid electrolyte [e.g. 1-11]. In these studies much attention has been given to the structural significance of AgI, since it is the high conductivity component in the AgI–Ag₂O–B₂O₃ system. In this regard two conflicting views are prevalent in the literature: (A) AgI maintains its identity within the glass structure forming microdomains or clusters such that fast conduction of Ag⁺ ions occurs along these regions [8,12-16]. Then silver ions must have at least two different environments, although a greater variety of silver coordinations is possible. For example, Minami *et al.* [9] have proposed three environments of silver ions corresponding to (i) bonding with a non-bridging oxygen (NBO) in BO₃ groups, (ii) bonding only to I and (iii) bonding to BO₄ groups. Further, a fourth kind of

environment is proposed corresponding to two intermediate size structural units, and different ion conduction rates are assumed for the silver atoms in the various environments [3]. The recent far infrared results show two energetically different Ag sites in a silver borate glass and a third kind of site is introduced with the addition of AgI [6]. (B) AgI is uniformly dispersed in the glass network so that all silver ions perceive an average uniform environment. Then the conductivity is enhanced because the average environment in AgI containing glass provides a lower energy barrier for ion migration.

The structural interpretation of fast ion conduction in the system $x\text{AgI}:(1-x)[\text{Ag}_2\text{O}:n\text{B}_2\text{O}_3]$ becomes considerably more complex when one considers also the glass network. One set of spectroscopic data including NMR [2], Raman [7,8] and neutron scattering [14] indicate that the borate network is not affected by the introduction of AgI. The latter simply occupies and expands the interstitial space without significantly affecting the network. On the contrary, infrared investigations show significant changes in the borate network [6,9,10], which should indirectly influence the silver ion migration. In particular, for $n=1$ AgI promotes the following structural transformation



where \emptyset represents a bridging oxygen (BO). Thus, there are several diverse and, in some ways, contradictory views of the glass structure which should be important for Ag conduction in the glasses of interest. However, so far no attempt has been made to characterize the chemical structure of silver borate glasses by x-ray photoelectron spectroscopy (XPS). In this paper we present a preliminary analysis of our high resolution XPS results on $x\text{AgI}:(1-x)[\text{Ag}_2\text{O}:\text{B}_2\text{O}_3]$ glasses. Considering that the chemical structure strongly influences both the transport and dielectric properties of a glass [18,19], such information should be useful for establishing a structural basis of conductivity in silver based fast ion conducting glasses.

2. EXPERIMENTAL

The glasses were prepared by mixing and then melting in a platinum crucible appropriate amounts of Ag_2O , B_2O_3 and AgI powders at 700-1000°C depending on the composition. The homogenized clear melt was then splat quenched between two polished copper blocks, which resulted in glass specimens with a good surface. The specimens were stored in the dark to prevent any light induced changes. The XPS spectra were obtained using a Scienta spectrometer (ESCA-300) with monochromatic Al $K\alpha$ X-rays (1486.6 eV). To avoid surface contamination, the sample was fractured in situ in a vacuum better than 4.0×10^{-9} Torr. The surface was flooded with ≈ 2 eV electrons to minimize the surface charging of our electrically insulating samples. Data analysis was conducted with the ESCA-300 software package using a Voigt function and Shirley background subtraction [20]. The B 1s and O 1s peaks for B_2O_3 glass inherently show a small asymmetry [25]. Therefore, these spectra for all the present glasses were analyzed with the same asymmetry parameter (0.11 and 0.12, respectively).

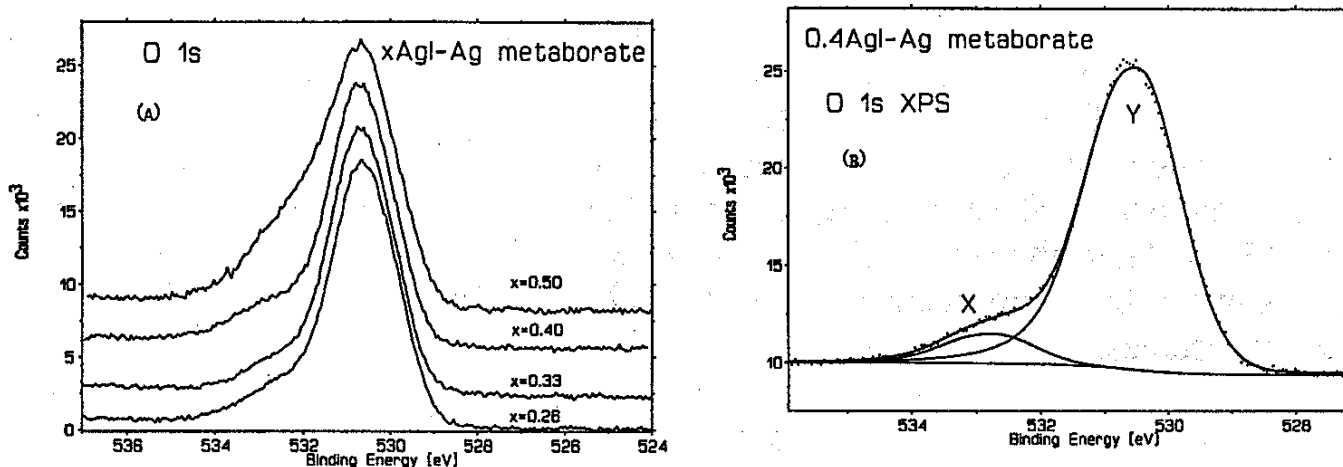


Fig. 1. O 1s x-ray photoelectron spectra for $x\text{AgI}:(1-x)[\text{Ag}_2\text{O}:\text{B}_2\text{O}_3]$ glasses. (a) Comparison of the spectra for $x=0.26-0.50$. (b) Decomposition of the spectrum for $x=0.40$ into two components.

3. RESULTS

To obtain a complete picture of the changes in bonding of the various elements, the x-ray photoelectron spectra have been obtained for the Ag 3d, B 1s, O 1s and I 3d electrons in four $x\text{AgI}:(1-x)[\text{Ag}_2\text{O}:n\text{B}_2\text{O}_3]$ glasses with $n=1$. For comparison, spectra for the binary $\text{Ag}_2\text{O}:2\text{B}_2\text{O}_3$ ($x=0$, $n=2$) and $\text{Ag}_2\text{O}:9\text{B}_2\text{O}_3$ ($x=0$, $n=9$) glasses were also obtained. The silver diborate glass is the one which could be prepared with the highest Ag_2O content without adding AgI. Compared to binary silver borate glasses, the AgI containing glass surfaces showed relatively little charging. Nevertheless, we could not be completely sure that a sample remained at the ground potential. Therefore, all the binding energies (b.e.) reported here are referenced (somewhat arbitrarily) to B 1s as being at 191.0 eV. We have chosen B 1s as an internal reference because generally cation energy levels do not shift much with composition. Furthermore, at least for the metaborate series the B/O ratio remains fixed and no variation is observed in the full width at half maximum (FWHM, D) of the B 1s peak.

The O 1s spectrum shows the strongest variation with the addition of AgI, as shown in Fig. 1. At least two peaks are required to describe it, indicating two distinguishable chemical environments of the oxygen atoms. Therefore, each O 1s spectrum is fitted with two components: a peak 'X' at high b.e. and a peak 'Y' at low b.e. as shown, for example, in Fig. 1(b) for the $0.4\text{AgI}:0.6[\text{Ag}_2\text{O}:\text{B}_2\text{O}_3]$ glass. The dots are actual data points and the upper solid curve is the best fit to data. The following procedure was adopted for curve fitting: since the spectrum shows strong asymmetry on the high binding energy side, the dominant peak is selected to parallel the height and slope of the spectrum on the low binding energy side. Then a second peak is added with its maximum corresponding to that of the shoulder on the high binding energy side. With these two peaks as initial input, the ESCA-300 computer program obtained the two component peaks with the best least-square fit to the experimental data. The fitting procedure is initially constrained to assign the same value of D for both the components. Subsequently D for the two components was made independent. For the case of $x=0.4$ and 0.5 , the high b.e. shoulder is sufficiently strong for unambiguously determining its approximate position and

height. For the case of $x=0.26$ and 0.33 , the shoulder location is not obvious. Then the peak position of the shoulder for the $x=0.4$ glass was used as the initial peak position input. The results of the deconvolution of the O 1s spectra are listed in Table 1, which includes the binding energy, FWHM and % area (%A) of the two component peaks. The error in b.e. from the curve fitting procedure is estimated to be ± 0.1 eV. Then the b.e. of the X and Y peaks remains nearly independent of composition. By comparison the %A of the X component increases with increasing x or decreasing n .

In contrast to the O 1s spectrum, the Ag 3d and I 3d spectra are nearly symmetric and can be described reasonably well by single peaks as characterized by the parameters given in Table 1 (Ag 3d spectrum for $n=9$, as an exception, consists of two peaks). At the same time D for these two peaks is significantly larger for the present glasses than for crystalline AgI, particularly for the Ag 3d peak. Further, D for both the peaks decreases appreciably with increasing x (Table 1). In general, given the relatively large scatter in data, the B 1s spectra can be described approximately by a single peak with the small asymmetry found for B_2O_3 glass [25], but with a D much larger than for the Ag and I peaks.

4. DISCUSSION

Typical O 1s spectra for alkali silicate glasses consist of a large peak at high b.e. and a small peak at low b.e. corresponding to BOs and NBOs respectively (e.g [21,22] and references therein). The fractional area of the low b.e. peak remains directly proportional to the alkali content. The O 1s spectra of alkali germanate glasses can also be fitted with a large and a small component at high and low b.e. respectively, but in this case the area ratio does not have a

Table 1.
Binding Energy (b.e.), Full Width at Half Maximum (Δ) and Percent Area (%A) of the Various XPS Peaks for the $xAgI:(1-x)[Ag_2O:nB_2O_3]$ Glass System.

Material	O 1s			I 3d _{5/2}		Ag 3d _{5/2}		B 1s	
	b.e.	Δ	%A	b.e.	Δ	b.e.	Δ	b.e.	Δ
$x=0.26, n=2$	530.4	1.82	94	619.7	1.13	368.0	1.08	191.0	1.24
	532.6	1.48	6						
$x=0.33, n=2$	530.5	1.79	96	619.7	1.10	368.1	1.04	191.0	1.21
	532.6	1.16	4						
$x=0.40, n=2$	530.4	1.76	92	619.6	1.07	368.1	1.00	191.0	1.17
	532.7	1.67	8						
$x=0.50, n=2$	530.5	1.97	83	619.4	1.06	368.0	0.95	191.0	1.44
	532.4	1.72	17						
$x=0, n=9$	530.6	2.19	96			366.8	1.60*	191.0	2.02
	532.3	1.97	4			368.5	1.56*		
$x=0, n=2$	530.6	1.76	89			367.3	1.17	191.0	1.38
	532.2	1.61	11						
AgI				620.0	0.93	368.8	0.66		
B_2O_3 [25]	530.6	1.77						191.0	1.68

*Consists of two components with areas 89% and 11%, indicating possible phase separation.

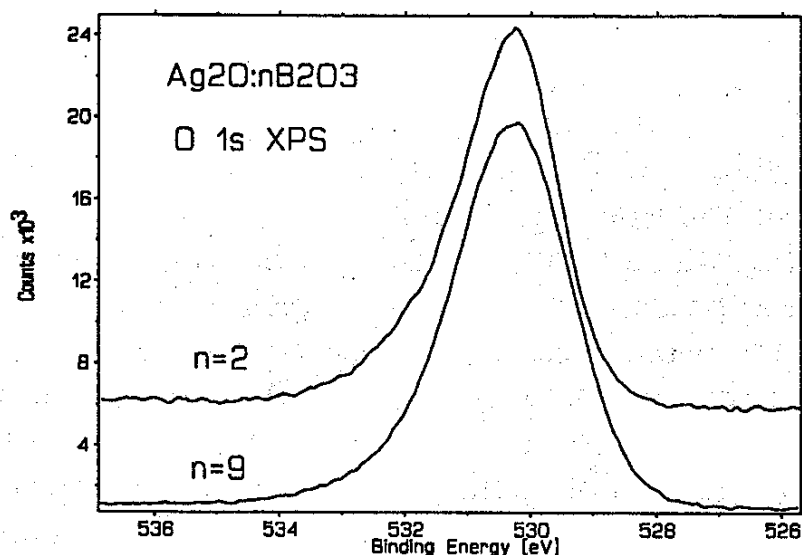


Fig. 2. O 1s x-ray photoelectron spectra for $\text{Ag}_2\text{O}:9\text{B}_2\text{O}_3$ and $\text{Ag}_2\text{O}:2\text{B}_2\text{O}_3$ glasses.

simple relationship with the alkali content because the latter induces $\text{GeO}_4 \rightarrow \text{GeO}_6$ conversion in addition to the formation of NBOs [23,24]. Nonetheless, for both alkali silicate and alkali germanate glasses the dominant BO peak is on the higher b.e. side. By contrast, the dominant O 1s component (Y) for the present silver iodoborate and binary silver borate glasses is at lower b.e. (see Figs 1 and 2; Table 1). Clearly, the structure around O in the present silver borate glasses is significantly different from that in alkali germanate and silicate glasses. The following points may be noted for determining the origin of the two (or possibly more) components of the O 1s spectra in Fig. 1:

(a) The b.e. difference between the peaks X and Y, $\delta_{XY}=1.6-2.3$ eV, is typical of the values reported for the BO and NBO in silicate and germanate glasses [21-24]. Thus it is tempting to assign X to BOs and Y to NBOs, but for the following reasons that will be inappropriate.

(b). It is reasonable to assume that in B_2O_3 all O atoms form bridges between two B atoms. For this glass, the difference between the B 1s and O 1s peaks, $\delta_{\text{BO}}=339.6$ eV [25]. When silver is added to B_2O_3 , a component grows on the high b.e. side (see Fig. 2), similar to the X peak in Fig. 1. Table 1 indicates that $\delta_{\text{BO(X)}}=341.3$ and 341.2 eV for this component for the binary glasses with $n=9$ and 2 , respectively. On the other hand, for the dominant component $\delta_{\text{BO(Y)}}=339.6$, which is identical to the value for B_2O_3 . Therefore, we should assign the Y peak to BOs similar to those in B_2O_3 .

(c) Since the b.e. of the 'X' peak is larger than that of the 'Y' peak, the former represents O atoms with a smaller electron density. So if the dominant peak 'Y' represents BO, X should represent an O atom with even smaller electron density. To the best of our knowledge the new low charge density oxygen (LCDO) atoms have not been previously observed in the XPS of any alkali containing oxide glass.

Generally, Ag is considered iso-structural to alkali atoms in oxide glasses [26]. That is, silver should be donating its electron to an oxygen atom or polyhedron forming an NBO or inducing a network conversion of the type $\text{GeO}_4 \rightarrow \text{GeO}_6$ or $\text{BO}_3 \rightarrow \text{BO}_4$. In this picture, the addition of a silver atom can only increase

the electron density more or less on a BO. However, the present results show that the addition of silver decreases electron density away from at least an appreciable fraction of the network oxygen atoms. Now if we consider the electronegativity values of O (3.44), B (2.04), Ag (1.93) and the alkali atoms (0.79-0.98) [27], we find that Ag is much more like B than an alkali atom. That is, Ag should be forming a relatively covalent bond just like B. Obviously, this inference must be appropriately modified to reflect the differences in sizes and coordinations of the two atoms. In any case, from electronegativity arguments we may anticipate that at least a fraction of Ag atoms is bonded to O much like B. With the Ag₂O addition the formation of predominantly covalent Ag-O-B linkages appears feasible with lower electron density on O atoms than those in B-O-B linkages. This proposal of a relatively covalent Ag-O bond is consistent with the suggestion of Tarashima *et al.* [28] and the most recent far IR results of Kapoutsis *et al.* [29]. In this connection note that XPS, unlike infrared (IR) spectroscopy, does not directly detect the bond linkages but only the changes in a particular energy level by the changes in chemical environment. The relative fraction of X oxygen atoms, f_x , increases from about 4% to 11% when n decreases from 9 to 2, indicating that indeed the X peak is associated with Ag atoms. Note that for the n=9 and n=2 silver borate glasses Ag/O ratio is 0.0714 and 0.286, respectively. Apparently, more than one Ag atom is needed to produce an LCDO. A simple evaluation of the composition dependence of the X peak, the density of states near the Fermi level and visual observations do not indicate that the LCDO could be a color center produced by x-irradiation. Nonetheless, we are pursuing a systematic investigation to experimentally rule out this possibility or an impurity origin of this peak.

Both the NMR [26] and IR [29] studies show that the addition of up to 25-30 mol% Ag₂O to B₂O₃ is accompanied by BO₃ → BO₄ conversion. For higher mol% Ag₂O, NBOs are presumed to be produced at the expense of BO₄ tetrahedra. However, the XPS spectra do not show a clear evidence of NBOs in any of the present glasses, thus suggesting that either the concentration of NBOs is too small or that their electron density is not sufficiently different from that of BOs. In principle, the Y component can be deconvoluted into a BO and an NBO component, but we have refrained from any deconvolution which is not sufficiently unique and necessary.

Unfortunately, an Ag₂O:B₂O₃ reference glass could not be prepared without crystallizing the melt. So, if we extrapolate the observed increasing trend of f_x with increasing Ag₂O mol%, we expect the X component to be about 20% of the total O in silver metaborate glass. None of the AgI containing silver metaborate compositions have this high value of f_x . In fact, f_x decreases with decreasing AgI content (the curve fitting error in %A is ±2%). That is, the silver metaborate glass appears to have significantly fewer LCDOs than predicted by the two lower Ag₂O content binary glasses, perhaps because they are being replaced by some other type of BOs in a complex structural unit or NBOs [29].

An important message from the present data is that in contradiction to the assumption that AgI has no influence on the network structure [2,7,8,14], the

O 1s spectrum is significantly influenced by the addition of AgI. The changes from AgI addition in the electron distribution within the network parallel those from the addition of Ag₂O to B₂O₃. In both cases the migration of silver is facilitated by the changes in the network. The previous IR work on the same glasses led to eq. (1) above [29], with the conclusion that AgI destroys B \bar{O}_4^- units. The present results cannot be expressed in the classical simplified picture made of well defined ionic species. Further analysis and modeling of the O 1s spectra are needed to verify the predictions of eq. (1).

As mentioned before, the Ag 3d spectra can be reasonably well described by a single peak. However, the FWHM of the peak is significantly larger than that of Ag in AgI (for which $\Delta=0.66$ eV) but comparable to that for silver diborate (1.17 eV), thus indicating that there is a range of chemical environments of silver. Unfortunately, the Ag 3d XPS line is relatively insensitive to the chemical environment and therefore we are investigating the change in the Ag Auger parameter which is a better indicator of the Ag environment. A close examination of the Ag 3d_{5/2} XPS peak shows a small but significant change with the addition of AgI: the FWHM of this peak decreases slightly. This is an indication of increased homogenization of the average charge distribution around Ag with increasing AgI.

The I 3d_{5/2} spectra show a variation which complements that of Ag 3d_{5/2}. With respect to B 1s there is no change in the b.e. of I 3d_{5/2}, indicating that the I atoms remain unaffected by the rest of the glass structure. Furthermore, the b.e. difference between the Ag and I XPS peaks, d_{Ag-I} , decreases from 251.7 to 251.4 eV as x increases from 0.26 to 0.5, approaching 251.2 observed for the AgI powder. Thus, the charge density difference within the Ag-I bond decreases and it becomes a more covalent bond with the addition of AgI. The same conclusion is found from the increase of the far IR absorption frequencies representing the rattling of Ag atoms in a mostly covalent environment [6,29]. Finally, the I 3d_{5/2} peak also becomes narrower with increasing x, much like the Ag 3d_{5/2} peak, becoming more like the same peak for AgI ($\Delta=0.93$ eV). These observations support the IR observations [10] and suggest the following model: The addition of AgI distinctly modifies the borate network. In particular, the charge distribution in the glass changes much like that which occurs with the initial addition of Ag₂O to B₂O₃. An I atom simply enters as an interstitial without actively affecting the network. Only at high AgI concentration, do the Ag and I atoms become like those in AgI crystal. Therefore, for the same reason, at small x there should not be any microdomains reminiscent of crystalline AgI. There appears to be a gradual conversion of Ag atoms surrounded predominantly by O atoms to those predominantly coordinated by I atoms, ultimately approaching the AgI structure.

5. CONCLUSIONS

The x-ray photoelectron spectroscopy of four silver iodoborate and two silver borate glasses reveals that silver affects the bonding within the glass network differently than do any alkali atoms in silicates, borates or germanates. Most notably, the charge density on a fraction of O atoms decreases with the addition

of Ag₂O or AgI. The observation of these low charge density oxygen (LCDO) appears to be the first one for any oxide glass containing monovalent cations. The observation is opposite to that expected from the formation of NBOs or the usual negatively charged BO₄⁻ tetrahedra. The unusual kind of O bonding in the present glasses is explained in terms of a predominantly covalent bonding of Ag resulting from its high electronegativity, comparable to that of B.

The addition of AgI to silver metaborate glass induces the formation of low electron density O in the structure. With increasing AgI content in the glass, both Ag and I atoms gradually approach the chemical state of crystalline AgI, but there is little support for the existence of AgI microdomains at low AgI content.

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