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Abstract

The structures of $x\text{AgI} + (1-x)\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses, where $0.2 < x < 0.6$, have been investigated using mid- and far-infrared spectroscopy. The mid-IR spectra revealed that in those glasses prepared using AgNO_3 as the starting material for Ag_2O , the $\text{BO}-4/\text{BO}_3$ ratio is constant with increasing amounts of AgI as would be expected from the proposed behavior of AgI in these glasses. However, a survey of the literature revealed those glasses prepared from pure Ag_2O show a strong linear dependence of the $\text{BO}-4/\text{BO}_3$ ratio on AgI content. Most probably, in those glasses prepared with Ag_2O the $\text{Ag}_2\text{O}/\text{B}_2\text{O}_3$ ratio changes with AgI content due to the decomposition of Ag_2O during melting. This different behavior is associated with AgNO_3 decomposing to Ag_2O with heating followed by incorporation into the glassy network. For Ag_2O used directly, it is proposed that it decomposes to Ag metal and $\text{O}_2(\text{gas})$ with heating before it can be incorporated into the borate network. This latter behavior decreases with increasing AgI in the batch composition because AgI lowers the liquidus temperature of the melt considerably. The far-IR analysis of the AgI-doped silver diborate glasses suggests that there are three coordination environments for the Ag^+ ions; one with iodide anions and the other two with oxygen ions. It is proposed that the separate oxygen coordination environments for the Ag^+ ions arise from one with bridging oxygens of $\text{BO}-4$ units, and the other with nonbridging oxygens on $\text{BO}-3$ units. Furthermore, it is proposed that the Ag^+ ions in the iodide-ion environments progressively agglomerate into disordered regions of AgI, but do not form structures similar to $\alpha\text{-AgI}$. These results appear to support the conduction pathway or "microdomain" model for ionic conduction in $x\text{AgI} + (1-x)\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses where the pathways are built up from disordered structures of AgI.

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Mid-IR and far-IR investigation of AgI-doped silver diborate glasses

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The structures of $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glasses, where $0.2 \leq x \leq 0.6$, have been investigated using mid- and far-infrared spectroscopy. The mid-IR spectra revealed that in those glasses prepared using AgNO_3 as the starting material for Ag_2O , the $\text{BO}_4^-/\text{BO}_3^-$ ratio is constant with increasing amounts of AgI as would be expected from the proposed behavior of AgI in these glasses. However, a survey of the literature revealed those glasses prepared from pure Ag_2O show a strong linear dependence of the $\text{BO}_4^-/\text{BO}_3^-$ ratio on AgI content. Most probably, in those glasses prepared with Ag_2O the $\text{Ag}_2\text{O}/\text{B}_2\text{O}_3$ ratio changes with AgI content due to the decomposition of Ag_2O during melting. This different behavior is associated with AgNO_3 decomposing to Ag_2O with heating followed by incorporation into the glassy network. For Ag_2O used directly, it is proposed that it decomposes to Ag metal and $\text{O}_2(\text{gas})$ with heating before it can be incorporated into the borate network. This latter behavior decreases with increasing AgI in the batch composition because AgI lowers the liquidus temperature of the melt considerably. The far-IR analysis of the AgI-doped silver diborate glasses suggests that there are three coordination environments for the Ag^+ ions; one with iodide anions and the other two with oxygen ions. It is proposed that the separate oxygen coordination environments for the Ag^+ ions arise from one with bridging oxygens of BO_4^- units, and the other with nonbridging oxygens on BO_3^- units. Furthermore, it is proposed that the Ag^+ ions in the iodide-ion environments progressively agglomerate into disordered regions of AgI, but do not form structures similar to α -AgI. These results appear to support the conduction pathway or "microdomain" model for ionic conduction in $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glasses where the pathways are built up from disordered structures of AgI.

INTRODUCTION

In the past decade, it has been shown that "superionic" materials can be formed in the compositions $z(\text{MX})+(1-z)(\text{M}_2\text{O}+n\text{M}'_x\text{O}_y)$, where M is a metal, X is a halide, and $\text{M}'_x\text{O}_y$ is a Lewis acid such as B_2O_3 , P_2O_5 , MoO_3 , etc. These materials have been labeled "superionic" because of their high conductivities at room temperature ($\approx 10^{-2} \Omega^{-1} \text{cm}^{-1}$) as compared to most other materials (e.g., $\sigma_{\text{soda-lime glass}} = 3 \times 10^{-13} \Omega^{-1} \text{cm}^{-1}$). While most of these superionic materials are oxysalts, in systems where the Lewis acid is a network glass former, e.g., B_2O_3 , superionic glasses can also be formed. The formation of network glassy solid electrolytes is advantageous because, unlike their polycrystalline oxysalt counterparts, network glassy superionic materials can be doped with a number of metal halides (AgI, NaCl, LiI, etc.) over wide composition ranges, they are easy to prepare, and bulk shapes can be formed. Moreover, because transport properties are similar in ionic vitreous systems, the superionic systems can be used as a model for ionic conductivity in many glass systems.

Chiodelli *et al.*¹ were the first to demonstrate the superionic behavior of glasses in the $\text{AgI}+\text{Ag}_2\text{O}+\text{B}_2\text{O}_3$ system, finding the borate system to be among the best vitreous silver ion conductors. Not surprisingly, the maximum conductivity in the pseudobinary $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3$ glass system is realized at the AgI-rich end of the glass-forming region, $x\text{AgI} \sim 0.6-0.8$. It is understood that the movement of the Ag^+ ions within the glassy matrix is responsible for the ionic conductivity; however, the arrangement of the Ag^+ ions in relation to the backbone of the glassy network and the mode of conduction for the Ag^+ cations is still widely debated.²

Within the $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glassy matrix, the

Ag^+ ions can either be coordinated with an iodide anion, an oxygen anion, or with both. However, the fast diffusion of the Ag^+ ions complicates the structural assignment of their coordination. Furthermore, it has been suggested that the temperature dependence of the ionic conductivity suggests different structural arrangements of the Ag^+ ions as a function of temperature.³ To elucidate the structural role of Ag^+ ions in these glasses, researchers have used many structural probes. From these studies, several theories have been proposed to describe the coordination of Ag^+ ions in these glasses.

When the room temperature conductivity data (σ_{RT}) of the AgI doped silver diborate glasses is extrapolated to $x\text{AgI}=1$, the σ_{RT} is found to be $\sim 10^{-2} (\Omega \text{cm})^{-1}$, very close to the σ_{RT} value for α -AgI ($\sigma_{\text{RT}}=5 \times 10^{-2} (\Omega \text{cm})^{-1}$, extrapolated from 200 °C), a high temperature (147 °C) superionic polymorph of AgI.⁴ This extrapolation would suggest ordered α -AgI domains form within the glassy matrix and grow and/or multiply as AgI is added. According to this structural model, when the metal halide dopant is changed to one that does not have a superionic crystalline phase (e.g., AgBr), the glass should not exhibit superionic behavior. However, Chiodelli *et al.*⁵ found that when I^- is exchanged for Br^- or Cl^- there are no dramatic changes in σ_{RT} signifying no α -AgI microdomains form in these glasses. Extended x-ray-absorption fine structure (EXAFS),³ ¹⁰⁹Ag NMR,⁶ and x-ray diffraction⁷ all support the absence of an ordered AgI phase resembling α -AgI. Raman spectroscopy results, on the other hand,⁸ suggest the existence of such α -AgI domains, especially at higher AgI concentrations. While the probability of the existence of α -AgI microdomains is questionable, there does exist a great deal of evidence supporting the presence of *disordered* AgI "microdomains." In this type of structure, ionic conduction is facilitated by the formation of conduction

TABLE I. The as-batched compositions of $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glasses prepared in this study. Also shown are the percent weight losses per unit mass of AgNO_3 beyond that expected for each composition.

mol % AgI	Weight			Weight loss (%)
	Weight AgI (g)	AgNO ₃ (g)	Weight B ₂ O ₃ (g)	
20	1.107	6.411	2.627	1.51
30	1.899	6.411	2.627	1.54
40	2.531	5.495	2.252	1.57
50	6.282	4.545	1.863	1.61
60	5.969	5.495	2.252	2.82

pathways along these AgI domains. However, there also exists an equal volume of data in support of AgI being dispersed in the interstices of the diborate network.⁹ Here, the disorder modes of the borate network are proposed to dynamically couple with the ion motion, thus enhancing ionic conduction. Structurally, the difference between the two models is the Ag⁺ cation environment. In the microdomain model, the Ag⁺ cations exist in two coordination environments, one related to the iodide anion and the other with oxygen ions (bridging or non-bridging oxygens). In the latter model, the Ag⁺ cations all share a common coordination with iodide anions and oxygen atoms.

In this study we report one of the first far-IR absorbance studies of AgI-doped silver diborate glasses. Far-IR analysis has proven to be a valuable method for differentiating cation coordination environments in glassy systems.¹⁰ In this way, if different coordination environments exist for Ag⁺ cations, the far-IR spectra should reveal multiple absorptions. In this study, the mid-IR spectra were also recorded and it was observed that the structures of these glasses are highly starting and material processing dependent and this behavior will also be reported.

EXPERIMENT

Seven $x\text{AgI}+(1-x)\text{AgI}\cdot 2\text{B}_2\text{O}_3$ glasses were prepared in the range $0 \leq x \leq 0.6$. The glasses were prepared from AgI (prepared in our laboratory from NaI and AgNO₃), AgNO₃ (Spectrum Chemical Mfg. Corp., Lot No. GD161) and B₂O₃ (99.9%, Alfa Products, Lot No. 1281) according to the following reaction:



Batches were calculated to yield 5–7 grams of glass. The raw materials were weighed on an electronic balance to ± 0.001 g, thoroughly ground in a porcelain mortar and pestle, then loaded into a 50 ml porcelain crucible.

The glass charge was first heated in a hood over a Meeker burner until the NO_x gas had dissipated, as determined by weight loss measurements. Next, the charge was placed into a Lindberg box furnace for 10–15 min at 750–900 °C, depending on composition. The glasses were then cooled to room temperature and weight loss measurements were made to check the glass composition. Table I shows the as-batched compositions of the AgI-doped diborate glasses along with the weight loss measurements. The glasses were reheated on

TABLE II. The densities and glass transition temperatures (Tg's) of $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glasses prepared in this study.

mol % AgI	Density (g/cm ³) ± 0.02	Tg (°C) ± 5 °C
10	4.30	410
20	4.50	403
30	4.57	395
40	4.75	384
50	4.86	370
60	5.01	350

a Bunsen flame until a fluid liquid developed. Using Pyrex tubing, thin films (~ 10 – 100 μm) were blown from the melt for far-IR and mid-IR spectra. The remaining liquid was poured into a stainless steel mold and allowed to cool to room temperature forming glass disks for density and glass transition temperature (Tg) measurements. To prevent photo-decomposition and hydrolysis of the glasses, all samples were stored in a darkened desiccator.

Densities of the glasses were measured using the Archimedes method in absolute ethanol (95%). An electronic balance (± 0.001 g) was used for the density measurements.

Tg measurements were made on a Perkin-Elmer DSC-4 (Perkin-Elmer Corporation, Norwalk, CT) scanning calorimeter using glass samples of 25–35 mg (± 0.01 mg) weighed on a Perkin-Elmer AD-2Z microbalance and hermetically sealed in aluminum sample pans. The DSC-4 head, baseline pans, and each glass sample were given thermal histories of cooling at 20 °C/min through the glass transition region and scans were made at 20 °C/min over the appropriate ranges to determine the Tg for each glass composition. All Tg's reported are onset Tg's.

Far-IR spectra were obtained on a BioRad FTS-60V FT-IR (BioRad-Digilab, Cambridge, MA) spectrometer using blown glass films. Spectra were obtained between 0 and 900 cm^{-1} under vacuum using a 12.5 μm beam splitter from 512 scans at 2 cm^{-1} resolution. There is zero intensity through the 12.5 μm beam splitter at >700 , ~ 530 , ~ 260 , and <25 cm^{-1} . Experimentally, there is not enough intensity through the beam splitter below ~ 50 cm^{-1} for accurate measurements; therefore, analysis of the far-IR spectra were limited to >50 cm^{-1} . Deconvolution of the far-IR spectra were performed using standard nonlinear least-squares fits using commercially available software (Peakfit). Mid-IR spectra were obtained on a Bio-Rad FTS-40 FT-IR spectrometer using blown thin films of the glass samples. Spectra were collected in a dry air atmosphere between 400 and 4400 cm^{-1} using 64 scans at 2 cm^{-1} resolution.

RESULTS

All glasses were observed to be homogeneous except at $x=0$, the silver diborate composition, where metallic Ag precipitated from the melt;¹¹ and for this reason, this glass was not further studied. Table II and Figs. 1 and 2 show the Tg and density compositional trends, respectively, of the AgI-doped silver diborate superionic glasses as a function of AgI content. As reported previously,⁴ the glass transition temperature decreases with increasing AgI content. The higher

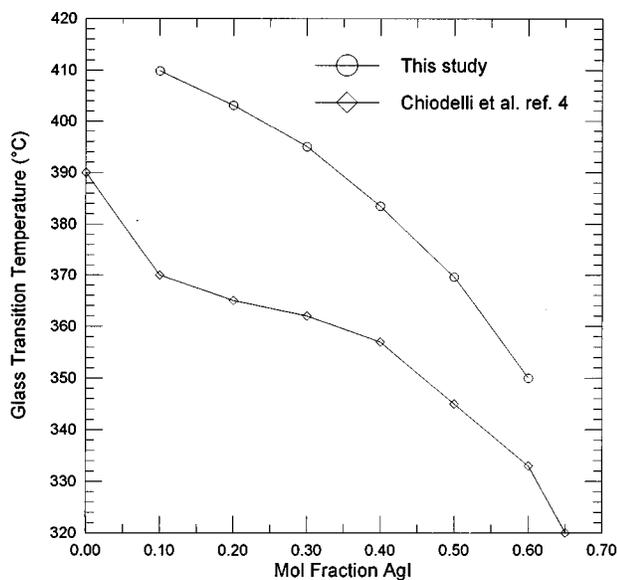


FIG. 1. The glass transition temperatures of glasses in the series $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ from the present study (circles) and from Chiodelli *et al.* (Ref. 4) (diamonds).

T_g 's found in this study may be due to different thermal histories between the sets of samples. The densities increase with the addition of AgI. Again, the difference in densities between glasses in this study and those by Chiodelli *et al.*⁴ is most probably due to thermal history differences between the sets of samples.

The mid-IR absorbance spectra obtained in this study are shown in Fig. 3. The peaks centered between 1200–1500 cm^{-1} represent the asymmetric stretching of B-O bonds in BO_3 triangles, those between 800–1200 cm^{-1} represent the asymmetric stretching of B-O bonds in BO_4^- tetrahedra, and

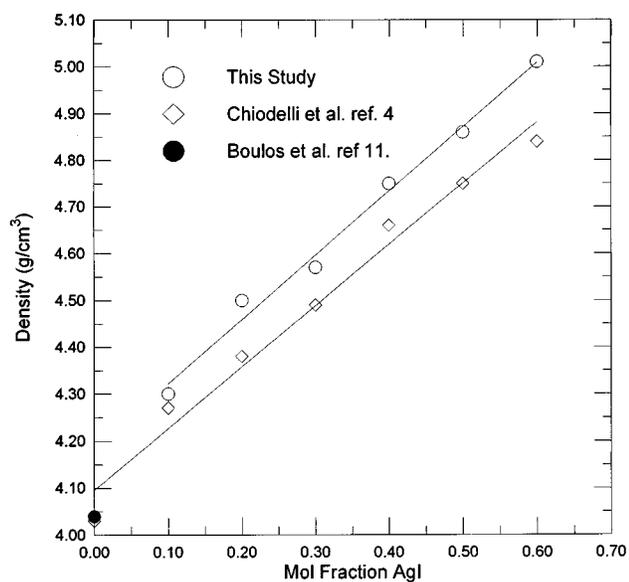


FIG. 2. The densities of glasses in the series $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ from the present study (open circles) from Chiodelli *et al.* (Ref. 4) (open diamonds) and Boulos *et al.* (Ref. 11) (solid circles). The solid lines indicate the best-fit linear regression of the data.

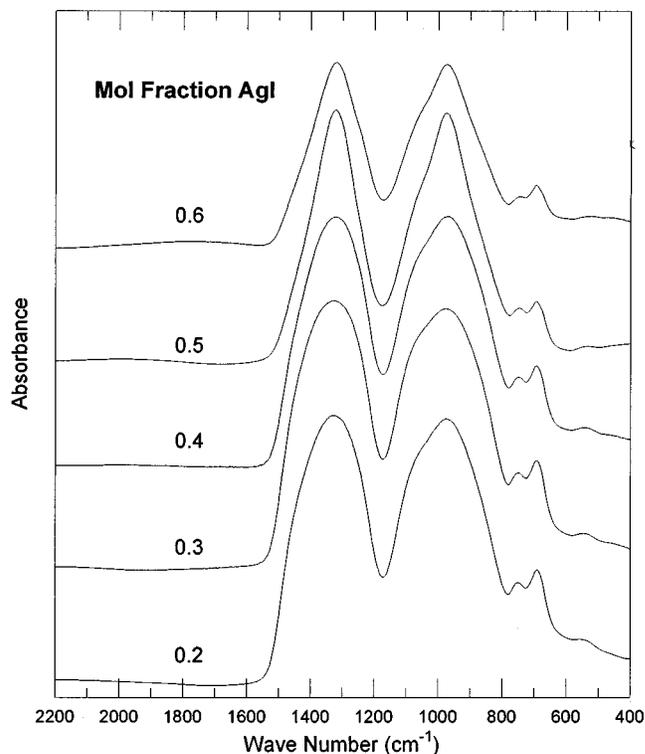


FIG. 3. The mid-IR absorbance spectra of glasses in the series $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ showing the addition of AgI does not change the relative intensities or peak positions of the peaks and the narrowing of the FWHM with increasing AgI content. The spectra have been offset in order to improve clarity.

the remaining absorbance modes between 620 and 800 cm^{-1} arise from the deformation modes of borate network structures.¹² The systematic addition of AgI does not affect the relative peak intensities of these modes in the mid-IR absorbance spectrum, nor are the peak positions changed as will be discussed further below. However, the full width at half maximums (FWHM's) of the BO_3 and BO_4^- absorption modes decrease systematically with increasing AgI content.

The far-IR absorbance spectra obtained in this study are shown in Fig. 4. The far-IR spectra show a set of broad, asymmetrically shaped modes centered at $\sim 135 \text{ cm}^{-1}$. These absorbance modes are ascribed to the “rattling motion” of Ag^+ cations in their local coordination environment. The profile of these absorbance modes become increasingly asymmetric with the center moving to lower wave numbers as AgI is added ($\sim 110 \text{ cm}^{-1}$ at 0.6 AgI).

DISCUSSION

Mid-IR spectra

It is well known that B_2O_3 consists of interconnected, planar rings of three-coordinated borons. With the addition of Ag_2O , BO_3 units are converted into BO_4^- units without the creation of nonbridging oxygens. The Ag^+ ions charge balance the negatively charged BO_4^- units.¹³ The fraction of BO_4^- units created follows the $x/1-x$ law, where x is the mole fraction of metal oxide.¹⁴ At the diborate composition, $\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$, ^{11}B NMR (Ref. 14) shows a departure from the $x/1-x$ law indicating nonbridging oxygens (NBO's) are

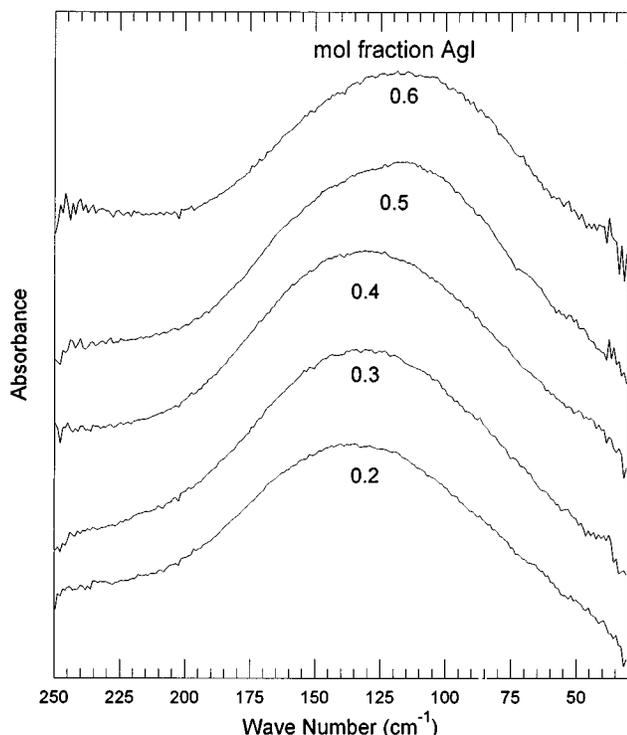


FIG. 4. The far-IR absorbance spectra of glasses in the series $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$. The spectra have been offset in order to improve clarity.

formed on the BO_3 units. The Ag^+ ions can now either be ionically bonded to NBO^- s or BO_4^- units. EXAFS (Ref. 15) studies confirm there are two coordinations for Ag^+ ions in silver diborate glass, one with a bond distance of $\sim 2.25 \text{ \AA}$ with a coordination of ~ 2 (charge balance of an BO_4^- group) and one with a bond distance of $\sim 2 \text{ \AA}$ with a coordination of ~ 1 (ionic bond with an NBO). Furthermore, the EXAFS studies suggest the Ag^+ ions coordinated with BO_4^- units are not randomly dispersed in the interstices of the borate glass network, but rather have a high degree of local order,³ similar to the linear O-Ag-O units present in $c\text{-Ag}_2\text{O}$, but bent at an angle of $\sim 64^\circ$. This result indicates either the Ag^+ is coordinated with two oxygens on the edge of the same BO_4^- tetrahedra or the Ag^+ is bridging between two BO_4^- tetrahedra. A more recent EXAFS study¹⁶ indicates the latter is true, i.e., the Ag^+ ion bridges between different BO_4^- units within the glass matrix.

Chiodelli *et al.*⁹ showed that silver diborate glasses with ≤ 60 mol % AgI can be formed without decomposition. When $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glasses are prepared using AgNO_3 as a starting material or evacuated and sealed silica tubes are employed, IR,⁴ ^{11}B NMR,¹⁷ Raman,¹⁸ and neutron diffraction¹⁹ studies show that the diborate network is left unmodified with the addition of AgI . We have found from careful analysis of the literature, however, that when glasses are prepared using pure Ag_2O itself, rather than AgNO_3 as the starting material for Ag_2O , the IR spectra²⁰⁻²² reveal a dependence of the $\text{BO}_4^-/\text{BO}_3$ ratio on AgI content. Figure 5 displays the AgI compositional dependence of the ratio of the fractional area under the BO_4^- peak (A_4) and the fractional area under the BO_3 peak (A_3) as calculated from the mid-IR spectra in this study, where the glasses were prepared from

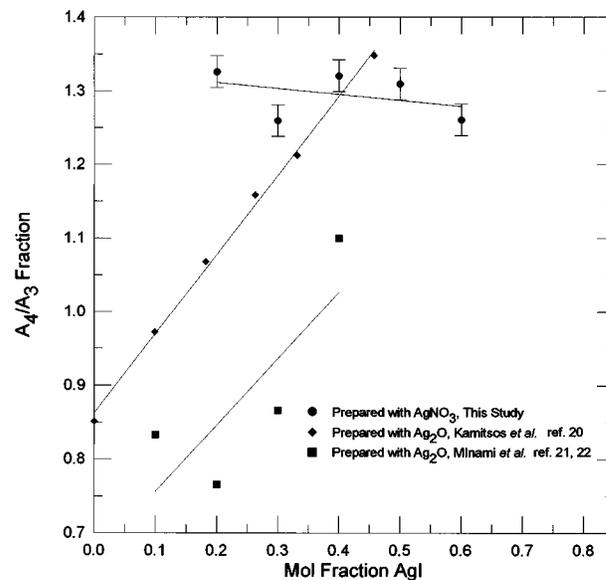


FIG. 5. The dependence of the A_3/A_4 fraction in $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glasses on mole fraction of AgI . Glasses prepared using pure Ag_2O (solid circles) (Refs. 20, 22) show a strong dependence, while those prepared from AgNO_3 (closed diamonds) show little dependence of the A_3/A_4 fraction on AgI content.

AgNO_3 , and the same fraction as calculated from the mid-IR spectra of Kamitsos *et al.*²⁰ and Minami *et al.*^{21,22} where the glasses were prepared from pure Ag_2O . Kamitsos *et al.*²³ have shown that the areas A_4 and A_3 of the absorption peaks arising from the BO_4^- and BO_3 structural groups, respectively, are directly proportional to the numbers of those structural units present in the glassy matrix. In the low AgI content glasses prepared from Ag_2O , the A_4/A_3 ratios are substantially lower than those of glasses prepared from AgNO_3 starting material. As AgI is added, however, the A_4/A_3 ratios of the glasses prepared from Ag_2O increase to the same fraction as the glasses made using AgNO_3 .

A more recent study of Kamitsos *et al.*²⁴ has examined a broader range of $x\text{AgI}+(1-x)\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3$ glasses to include $n=0.5, 1$, and 3 families. They observed an AgI dependence of the A_4/A_3 ratio that depended upon n ; glasses with $n=2$ and 3 showed a strong AgI dependence of A_4/A_3 , while glasses with $n=0.5$ and 1 did not; in fact within error their observed ratios for these glasses were constant with AgI , as would be expected. To understand their data, Kamitsos *et al.*²⁴ proposed a series of chemical equilibria that shifted towards the formation of tetrahedral borons for the higher n glasses, $n=2$ and 3 , and shifted away from the formation of tetrahedral borons for the lower n glasses, $n=0.5$ and 1 .

Although such a chemical restructuring of these glasses is not entirely unlikely, it is without much chemical basis. It is not clear why such a profound restructuring of the glass should result by dissolving such a relatively chemically inert species as AgI into these glasses. In their studies they found that the A_4/A_3 ratios changed by almost a factor of 2.

The differences in the mid-IR spectra and hence glass structure most probably arise due to decomposition of Ag_2O . Ag_2O decomposes at $\sim 230^\circ \text{C}$ to Ag (metal) and O_2 (gas) and

B_2O_3 melts at ~ 450 °C; therefore, when these constituents are heated to a melt (800–900 °C), a large amount of Ag_2O may decompose to Ag(metal) and O_2 (gas) before the Ag_2O is incorporated into the B_2O_3 glass melt. The result is less metal oxide in the glass, hence a lower fraction of BO_4^- units than would be expected from the batch composition. However, as AgI is added to the composition, the melting point of the system (liquidus temperature) is lowered and less Ag_2O will decompose thereby increasing the fraction of N_4 units. Contrary to this behavior of Ag_2O , $AgNO_3$ (mp 212 °C) does not decompose to Ag_2O and NO_x until 444 °C and, therefore, at these temperatures, the Ag_2O can be incorporated into the now melted B_2O_3 before it decomposes. In this case, the BO_4^-/BO_3 ratios are independent of AgI since the Ag_2O fraction is constant with AgI content. Due to the problems with the decomposition of Ag_2O and our findings here, it is prudent to use $AgNO_3$ as a starting material or use a sealed and evacuated tube technique to ensure the correct stoichiometry.

While the fraction of BO_3 and BO_4^- units in the $xAgI+(1-x)Ag_2O \cdot 2B_2O_3$ glasses remains constant, the structural groups in the glass appear to be becoming more ordered with increasing AgI content. Figure 3 shows the FWHM's of the absorbance envelopes related to BO_3 and BO_4^- units decrease with increasing AgI content, this indicates that the distribution of bond angles and bond lengths among the same structural groups is becoming smaller. A consequence of the increased order of the borate network should be an increase in the tendency of the glass to crystallize. Chiodelli *et al.*⁴ report the crystallization exotherms are broader at lower AgI concentrations but become well defined and at lower temperatures for silver diborate glasses with increasing AgI contents, confirming an increase in the ordering of the glassy network.

Far-IR spectra

Kamitsos *et al.* have reported the far-IR spectra of the undoped silver diborate²⁰ and alkali diborate glasses.²³ They found the far-IR absorbance envelope for the silver diborate glass was best deconvoluted using two Gaussian components. Similarly, the absorptions corresponding to alkali oxide motions in alkali diborate glasses are best deconvoluted using two Gaussian components for the lighter alkali ions (Na, Li). However, three Gaussians are required for the heavier alkalis, Cs and Rb. The added Gaussian used for the heavier alkalis was associated with the alkalis bonded to metaborate rings. The presence of such rings was supported by the presence of a weak absorption mode at 1250 cm^{-1} which has been assigned to the presence of metaborate rings. Inspection of the spectra in Fig. 4 shows no absorbance bands around 1250 cm^{-1} in the mid-IR spectra of $xAgI+(1-x)Ag_2O \cdot 2B_2O_3$ glasses, therefore, the far-IR spectra of the undoped silver diborate glass is expected to consist of two Gaussian components similar to the high frequency, high intensity (ν_H) and low frequency, low intensity (ν_L) components found in the sodium and lithium diborate glasses. The ν_L and ν_H modes are attributed to the presence of two different anionic site environments for the alkali cations.

Kamitsos *et al.*²³ suggest the different environments arise from an inhomogeneous distribution of alkali ions leading to alkali-rich and borate-rich pseudophases. The alkali ions in

the borate rich phase are surrounded by less negative charge density and vibrate at lower frequencies (ν_L) than those cations in the alkali rich pseudophase (ν_H). An alternative explanation for the existence of these two absorbances for alkali ions in alkali borate glasses and Ag^+ ions in $Ag_2O \cdot 2B_2O_3$ glass can be obtained from the EXAFS studies. Dalba *et al.*³ have shown there are two coordinations for the Ag^+ ions in silver diborate glass. One arising from NBO's which will have a higher charge density (discrete negative charge) and hence associated with a stronger bond force constant (ν_H). The other was associated with "network" oxygens which are taken to be the well known and studied tetrahedral boron oxygen sites, BO_4^- . In these sites, the negative charge is fully delocalized over the four equivalent bridging oxygens (BO's), thereby significantly reducing the charge density of this anionic site compared to the discrete NBO site. This site with its larger effective mass, BO_4 , compared to that of an NBO (BO_i) and much smaller charge density would naturally lead to a smaller bond force constant for the silver cation and hence a lower frequency for the cation vibration mode, ν_L . The existence of NBO's in silver diborate glass is consistent with ¹¹B NMR (Ref. 14) results and represents a better explanation of the existence of two Ag^+ coordination environments in the undoped silver diborate glass than does the existence of pseudophases within the glass.

Because the square of the frequency of the vibrational mode of a metal oxide bond is directly proportional to the force constant and inversely proportional to the mass of the metal, the position of the Ag-O absorbance can be estimated. Ag (at. wt. 107.86, $L_{M-O}=2.49\text{ \AA}$) has an atomic weight intermediate between Cs (at. wt. 132.9, $L_{M-O}=3.09\text{ \AA}$) and Rb (a.w. 85.4, $L_{M-O}=2.96\text{ \AA}$) and a metal oxygen bond length (L_{M-O}) shorter than both Cs and Rb. For these reasons, ν_L and ν_H values for Ag^+ are expected to be more similar to those for Rb^+ . As discussed above, in Cs and Rb diborate glasses the metal oxide absorption modes were calculated using three Gaussians centered at 160–187, 109–131, and 49–65 cm^{-1} representing absorptions due to a metaborate unit, ν_H , and ν_L , respectively.²³ Therefore, in Ag diborate glasses ν_H and ν_L components are expected at ~ 130 and 65 cm^{-1} , respectively.

Kamitsos *et al.*²⁰ deconvoluted three Gaussian components at ca. 50, 100, and 175 cm^{-1} in their spectra of the halide doped silver diborates. The Gaussians at 50 and 175 cm^{-1} were assigned to the ν_L and ν_H modes, in close agreement with the above prediction. Their remaining band at 100 cm^{-1} grew in intensity and shifted to higher frequencies with AgI additions. The Raman spectra of AgI-doped silver tetraborate glasses¹⁸ also show the growth of a peak near 100 cm^{-1} with increasing AgI contents. Both authors attribute the mode at 100 cm^{-1} to the motions of Ag^+ ions in I-environments. Their results indicate two (or more) coordination environments for the Ag^+ ions suggesting the presence of "microdomains" of AgI within the glassy matrix.

In this study, the far-IR absorbance envelopes for the Ag^+ motions were best deconvoluted using three Gaussians; the compositional trends of the peak centers are shown in Fig. 6, the lines through the data are linear least-square fits to the data. The Gaussians centered at 65 and 150 cm^{-1} are assigned to the ν_L and ν_H vibrations of the Ag^+ ion in the two

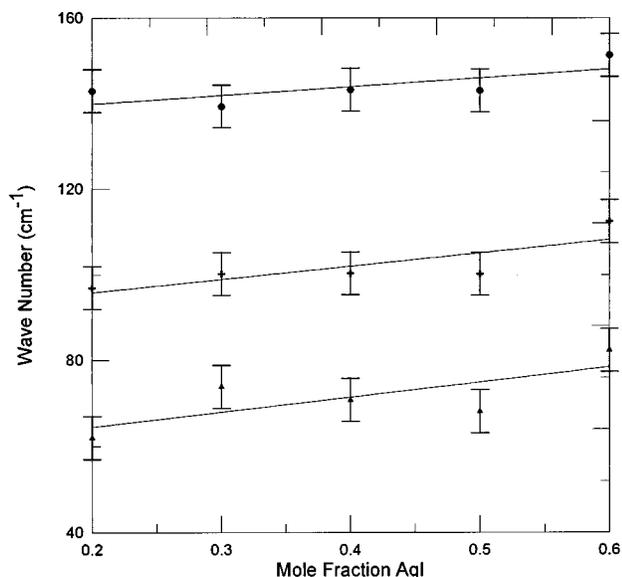


FIG. 6. Dependence of the peak centers of the ν_H (closed circles), AgI (crosses), and ν_L (closed triangles) vibration modes on AgI content. The solid lines represent the best fit linear regression of the data.

oxygen environments, as described above and in agreement with the study by Kamitsos *et al.*²⁰ The band fit was carried out by first deconvoluting the spectra to determine the number and centroids of the constitutive bands. The spectra were then best fit by constraining the number of bands to three and using the centroid of the band as a starting value for the fit. A standard high quality band-fit software, Peak-Fit™ was used in the calculations. The peak positions of the three bands showed systematic composition dependence before and after the band-fit process and for this reason the dependence upon composition is believed to be real.

In these AgI-doped silver diborate glasses it is reasonable to assume that since the mid-IR spectra, shown above, show that AgI does not chemically alter the diborate glass structure, that the two silver-oxygen sites in the diborate glass persist also in the AgI-doped glasses, their fractions simply decrease as the fraction of AgI increases in the glass. The presence of the third band associated with the AgI added to the glass follows from the fact that the charge density and mass of the I^- anion is significantly different from either of the two oxygen sites, BO_4^- and BO^- , respectively, and leading to a markedly different bond force constant hence vibration frequency. Combined with these chemical arguments is the fact that in the fitting process, it was clear that two bands simply could not reproduce the observed far-IR bands within experimental error. Figure 7 shows the deconvoluted components of the 0.2 and 0.6 AgI silver diborate glasses. The Gaussian component centered at 110 cm^{-1} grows in intensity with increasing AgI content while the ν_L and ν_H Gaussians remain in the same relative proportion. Given the proximity of the central Gaussian component to the metal-halide stretch of $\alpha\text{-AgI}$ (114 cm^{-1}) (Ref. 20) and the compositional dependence of its intensity, this vibrational mode is assigned to the Ag-I stretch.

Figure 8 shows the composition dependence of the areas, integrated intensities, of the three far-IR modes as obtained from the deconvolution of the far-IR mode. As seen, the area

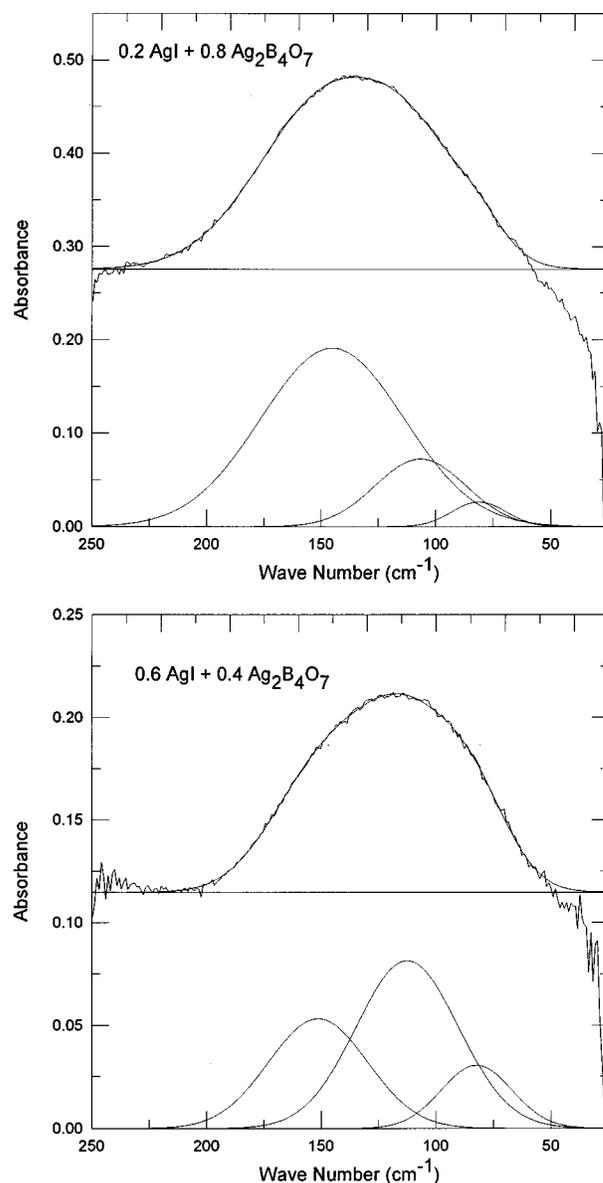


FIG. 7. The far-IR spectra of 0.2 and 0.6 AgI silver diborate glasses showing their deconvoluted Gaussian components. The bands ~ 150 and 75 cm^{-1} represent the vibrations of Ag^+ in oxygen coordination environments. The band centered at $\sim 100\text{ cm}^{-1}$ represents the vibration of an Ag^+ cation in I^- coordination environments. Note the growth in intensity of the 100 cm^{-1} band with increasing AgI content.

of the mode associated with AgI grows steadily with $x\text{AgI}$, where as those for the two oxygen sites steadily decrease. From these spectra it is not clear whether or not the areas of the two oxygen peaks remain constant in ratio as would be expected if there were no interaction at all between the different chemical sites. That is to say, if there were interaction, then cations from the two oxygen sites may well interact with the I^- site to form $O\text{-Ag}^+\text{-I}^-$ linkages. That this latter situation may likely be the case will be seen below when the relative areas of three peaks are compared.

From the areas of the three Gaussians, the experimental fraction of Ag^+ ions in an I^- coordination environment ($N_{Ag^+I^-}$) can be calculated for each glass composition. As-

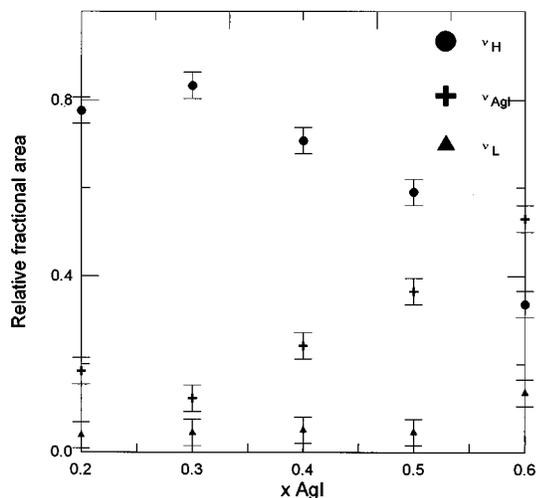


FIG. 8. Dependence of the integrated intensities for the three modes, ν_H (closed circles), ν_{AgI} (crosses), and ν_L (closed triangles), on AgI content, as obtained from the deconvoluted far-IR spectra. The area associated with the AgI mode increases steadily with $xAgI$.

suming no modification of the borate network by AgI and no formation of O-Ag-I bridges, the theoretical $N_{Ag^+I^-}$ can be calculated from Eq. (2),

$$N_{Ag^+I^-} = \frac{x}{[x + 2(1-x)]}, \quad (2)$$

where x is the mole fraction of AgI. Figure 9 shows the experimental $N_{Ag^+I^-}$ follows the theoretical curve, as calculated from Eq. (2), up to 0.5 AgI. At 0.6 AgI $N_{Ag^+I^-}$ calculated from the experimental data is greater than Eq. (2) predicts. Fontana *et al.*²⁵ found similar results in their Raman study of $xAgI + (1-x)Ag_2O \cdot B_2O_3$ glasses. At high AgI contents, these authors found that the integrated intensity of the Ag^+I^- Raman mode is larger than at low AgI content. The authors argue the increased intensity is due to an increase in the connectivity of the AgI regions, possibly facilitating the formation of α -AgI clusters. Similarly, the formation of an ordered network of AgI would increase the IR intensity of the Ag^+I^- mode. In further support of increased ordering of the AgI is the increase in the frequency and intensity of the Ag^+I^- mode with increasing AgI content. Figure 6 shows the Ag^+I^- mode increases from 100 cm^{-1} at 0.2 AgI to 114 cm^{-1} at 0.6 AgI, the same frequency as the α -AgI vibration,²⁰ while Fig. 9 shows that the integrated intensities for the $xAgI=0.5$ and 0.6 glasses lay above that calculated from the composition, the line through the data. Alternatively and as alluded to above, the increased area may well be associated with the interaction of the different Ag^+ sites. Such interaction is not unreasonable due to the high cation fraction in these glasses.

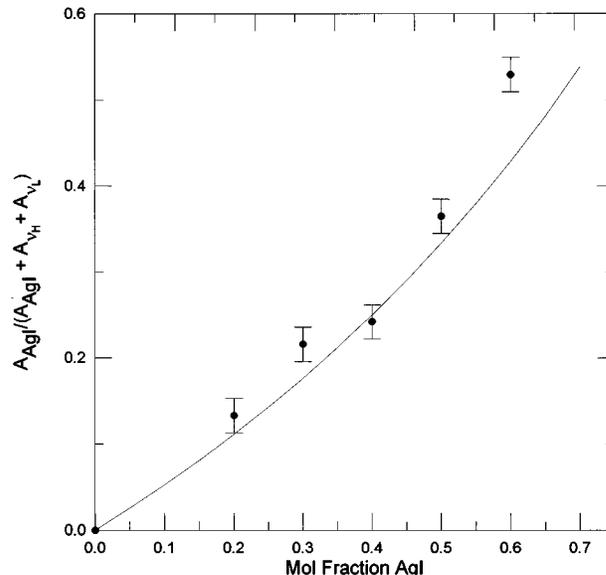


FIG. 9. The fraction of total Ag^+ ions in an I^- coordination environment as calculated from the relative areas of the far-IR modes (closed circles) and as calculated from Eq. (2) (solid line).

CONCLUSIONS

The mid-IR results indicate the addition of AgI to $xAgI + (1-x)Ag_2O \cdot 2B_2O_3$ glasses does not modify the diborate network. In a similar far-IR study, Kamitsos *et al.*²⁰ found a strong dependence of the N_4/N_3 fraction in the diborate network on AgI content; however, the values of the Ag_2O/B_2O_3 ratios in their glasses is questionable due to the use of Ag_2O as a starting material. The mid-IR spectra also indicate the borate structural units are becoming more ordered with increasing AgI.

The results of the far-IR study indicate three coordination environments for Ag^+ ions in $xAgI + (1-x)Ag_2O \cdot 2B_2O_3$ glasses, two with oxygen anions and one with iodides. An analysis of the areas of the deconvoluted absorbance components related to these three coordination environments reveals all the Ag^+ introduced through the incorporation of AgI stays coordinated solely with I^- anions, suggesting the presence of disordered AgI microdomains. At high AgI content, the observed far-IR absorbance is stronger than predicted, suggesting the formation of α -AgI like structures.

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