Modifier Coordination and Phosphate Glass Networks

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Abstract

The addition of up to approximately 16 mole% Cs_2O to vitreous P_2O_5 reduces the glass transition temperature (T_g) by 150 K, whereas further additions up to 50 mole% produce little additional change in T_g . ^{31}P magic angle spinning nuclear magnetic resonance spectra indicate that the phosphate network is progressively depolymerized over the entire range of compositions. The property trend is explained by a transition in the Cs^+ coordination environment, from isolated Cs-polyhedra below ~16 mole% Cs_2O to a corner-sharing Cs-polyhedral sub-structure in the glasses with greater Cs_2O contents. This 'modifier transition' does not occur in Al-phosphate glasses. ^{27}Al MAS NMR spectra indicate that the average Al coordination number decreases with increasing Al_2O_3 content to avoid the formation of Al-O-Al bonds in these binary phosphate glasses.

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1. Introduction

The basic building blocks of crystalline and amorphous phosphates are the P-tetrahedra. These tetrahedra link through covalent bridging oxygens to form various phosphate anions. The tetrahedra are classified using the Q^i terminology [1], where 'i' represents the number of bridging oxygens per tetrahedron. The networks of phosphate glasses can be classified by the oxygen-to-phosphorus ratio, which sets the number of linkages through bridging oxygens to neighboring P-tetrahedra. Thus, metaphosphate ($O/P=3$) and polyphosphate ($O/P>3$) glasses have structures that are based on chain-like phosphate anions that are themselves interconnected through terminal oxygens by ionic bonds with modifying cations. Q^2 tetrahedra form the links within the chains and Q^1 tetrahedra terminate the chains. The chain length of the average phosphate anion decreases with increasing O/P .

Ultraphosphate ($O/P<3$) glasses have networks that are cross-linked by Q^3 tetrahedra. The addition of an alkali or alkaline earth oxide depolymerizes the three-dimensional P_2O_5 network as Q^2 sites replace Q^3 sites. The effect that these structural modifications have on the properties of ultraphosphate glasses is unusual. **Figure 1** shows the densities reported for binary Li- and Na-ultraphosphate glasses [2,3]; both systems exhibit density minima near 20 mole% alkali oxide. These minima do not correspond to coordination changes of the network forming cation, as are the cases for binary alkali borate and alkali germanate glasses.

Kordes identified a number of other phosphate glass-forming systems, including $BeO-P_2O_5$, $MgO-P_2O_5$ and $ZnO-P_2O_5$, as 'anomalous' because they have unusual discontinuities in composition-property dependence (i.e., refractive index and molar

volume) at the metaphosphate composition [4]. This dependence was originally explained by a coordination change of the modifying cation [4,5], but subsequent spectroscopic and diffraction studies generally failed to support this model. (For example, see reference [6] for references to studies of the ZnO-P₂O₅ glasses and reference [7] for a review of the MgO-P₂O₅ glasses.) Okura et al. [8] proposed that the anomaly in the properties of the MgO phosphate glass forming system was related to the transition from a metaphosphate glass structure dominated by tetrametaphosphate rings to one based on pyrophosphate dimers, although there appears not to be supporting spectroscopic evidence for glass structures dominated by tetrametaphosphate rings.

Hoppe and co-workers elucidated the role that modifier coordination plays in determining the properties and structures of phosphate glasses in his diffraction studies of binary ultraphosphate glasses [9,10,11]. They noted that the composition at which a packing density minimum was reached in binary alkaline earth phosphates depended on the coordination number of the modifying divalent cation: ~50 mole% MgO (CN~4), ~33 mole% CaO (CN~6), and ~25 mole% BaO (CN~8). The latter two compositions are ultraphosphates. Structural studies of crystalline ultraphosphates (e.g., [12,13]) indicate that the local coordination environment of the modifying cations includes terminal oxygens from both Q² and Q³ tetrahedra. Hoppe et al. recognized that similar bonding arrangements were likely present in the ultraphosphate glasses and proposed that the structure (and properties) of ultraphosphate glasses would be dependent on the number of terminal oxygens available to coordinate the modifier ions (Me^{v+}, where v is the ion valence). Such cations will have a preferred coordination number (CN_{Me}) similar to that

found in the appropriate crystalline phases. For glasses with the stoichiometry $x\text{Me}_{2/v}\text{O} \cdot (1-x)\text{P}_2\text{O}_5$, the number of terminal oxygens available per modifying ion is

$$M_{\text{TO}} = v(1/x) \quad (1)$$

Hoppe et al. predict that there are two structurally-distinct compositional ranges: when $M_{\text{TO}} > \text{CN}_{\text{Me}}$ (region I) and when $M_{\text{TO}} < \text{CN}_{\text{Me}}$ (region II). For region I, sufficient individual terminal oxygens are available for coordination with each Me^{v+} ion and so these ions can exist as isolated coordination polyhedra within the phosphate network; viz., there are no Me-O-Me bonds (**Figure 2**, left). In region II, there are not enough individual terminal oxygens to satisfy the coordination environments of every Me^{v+} ion, and so these ions must share the available TO's by forming Me-O-Me linkages. As a result, in region II Me^{v+} coordination polyhedra share corners and edges and act as bridges between neighboring Q^2 polyhedra (**Figure 2**, right).

The transition in modifier bonding, from isolated polyhedra to a modifier substructure with shared polyhedral corners, coincides with changes in macroscopic properties, like the density data shown in **Figure 1**. Diffraction studies indicate that lithium ions in metaphosphate crystals [14] and glasses [15] are tetrahedrally coordinated. A recent ^6Li nuclear magnetic resonance (NMR) study of Li-ultraphosphate glasses reached a similar conclusion: the average CN for Li is in the range of 4 to 5 [16]. Diffraction studies of NaPO_3 glass indicate that the coordination number of Na^+ is about 5 [17,18]. Using these coordination numbers for CN_{Me} , from equation 1 the transition from region I to region II will occur at 20 to 25 mole% for Li and Na ultraphosphate glasses, the compositional range of the density minima observed in **Figure 1**. In glasses with less than ~20 mole% Li_2O or Na_2O , isolated alkali polyhedra such as those shown in

Figure 2 (left) are present. Because there is an excess of Q^3 terminal oxygens, these alkali ions likely are bonded to the terminal oxygens on a single Q^2 -tetrahedron, and less-strongly bonded to neighboring Q^3 -tetrahedra through the terminal P=O bonds. Density decreases (**Figure 1**) as the Q^3 network expands to accommodate the alkali polyhedra. Above ~20 mole% Me_2O , $M_{TO} < CN_{Me}$ and so neighboring alkali polyhedra must share the terminal oxygens on Q^2 tetrahedra (**Figure 2**, right). Density increases as more Me-polyhedra share corners and edges and the alkali polyhedra act as bridges between neighboring Q^2 and Q^3 tetrahedra.

The modifier substructure that forms in region II is a hallmark of the 'modified random network' (MRN) model for glass structure, introduced by Greaves to describe silicate glasses [19]. The nanosegregation of modifiers has obvious consequences for the bulk properties of oxide glasses [20]. For phosphate glasses, the 'extra' terminal oxygen associated with each P-tetrahedron makes it possible for simple phosphate compositions to be model systems for characterizing the consequences of the development of 'MRN' structures, as at the transition from region I to region II compositions (**Figure 2**).

A similar analysis provides an explanation for the 'anomalous' glasses identified by Kordes. Be^{2+} , Mg^{2+} , and Zn^{2+} are each small enough to exist in tetrahedral coordination. From equation (1), the transition from isolated divalent tetrahedral modifiers to a corner-sharing modifier sub-structure will occur at 50 mole% MeO, the 'anomalous' composition.

In the present study, we will use these ideas to relate structure to the properties of two very different series of phosphate glasses. Information about the effects of a large modifying cation on the transition from isolated modifying polyhedra to the corner-

sharing modifier sub-structure will be obtained from the $x\text{Cs}_2\text{O}-(1-x)\text{P}_2\text{O}_5$ glasses series. The $x\text{Al}_2\text{O}_3-(1-x)\text{P}_2\text{O}_5$ glasses, on the other hand, represent a series where modifier coordination number changes to avoid that transition.

2. Experimental Procedure

Anhydrous Cs-ultraphosphate glasses were prepared using similar procedures to those developed by Hudgens and Martin [3]. Cs-metaphosphate glass (50 mole% Cs_2O) was first prepared from the appropriate mixture of reagent-grade Cs_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ that was calcined in platinum crucibles at 500°C for one hour and melted at 900°C for one hour while bubbling with dry oxygen. The bubbler tube was then raised to provide an oxygen cover for the melt and the temperature was reduced to 800°C and the melt held for about thirty minutes until bubbles were eliminated. The melts were quenched between steel plates. This glass was then ground to a coarse powder in a drybox and mixed with P_2O_5 powder that had first been purified by vacuum sublimation. The mixtures were sealed in a silica ampoule, which was then slowly heated to 900°C and held for four hours. The ampoules were removed from the furnace and immediately placed into a drybox to prevent exposure of the glasses to the ambient. Glass compositions were calculated from the Q^2/Q^3 ratios determined by ^{31}P NMR analyses, described below. The compositions were verified for some of the samples by a combination of inductively coupled plasma mass spectrometry (ICP-MS) and ICP emission spectrometry (ICP-ES). Duplicates were run and average analyses are reported; the estimated uncertainty is $\pm 5\%$ relative. Glass transition temperatures were determined using differential scanning calorimetry on samples sealed in aluminum pans and analyzed

under nitrogen. Analyses were done at heating rates of 10°C/minute after first quenching the sample in the calorimeter at -10°C/minute from well above T_g to eliminate fictive temperature effects. Most glasses contained small bubbles, precluding an adequate measure of density.

Na-ultraphosphate glasses were prepared in a similar fashion, using mixtures of NaPO_3 glass and P_2O_5 . These samples are discussed in detail elsewhere [21]. Glass transition temperatures from these glasses were measured as described above.

$x\text{Al}_2\text{O}_3-(1-x)\text{P}_2\text{O}_5$ glasses were prepared by melting mixtures of reagent grade $\text{Al}(\text{PO}_3)_3$ and AlPO_4 in covered alumina crucibles in air at 1500°C for less than one hour. Glasses were quenched onto steel plates and annealed near 750°C. Glass compositions were analyzed by ICP-ES. P_2O_5 -loss occurred from every melt prepared for this study, as reported elsewhere [22].

^{31}P magic angle spinning (MAS) NMR spectra were collected using a Bruker AMX400 spectrometer at a frequency of 162.0 MHz, using a 4 mm MAS broadband probe. The spectra were obtained using a 12.5 kHz spinning speed, a 3.0 μs $\pi/2$ pulse, a 60 sec recycle delay, a 81.97 kHz spectral width, 2 K complex points and 16 averages. ^{31}P chemical shift values are reported with respect to external phosphoric acid ($\delta=0$ ppm). The relative site concentrations were obtained from simulation of the entire spinning sideband manifold.

The ^{27}Al MAS NMR spectra were collected at 94.7 MHz at MAS frequencies of 8 kHz, using 2.0 μs pulses and 1 s recycle times. These pulse widths were 1/3 of the 90° pulse width for a 1M AlCl_3 solution ($\delta=0$ ppm) used to reference the ^{27}Al peak positions. The reported ^{27}Al peak positions are peak maxima, uncorrected for second order

quadrupolar effects, and are not the true isotropic chemical shifts. Relative site concentrations are taken to be the respective areas of the Gaussian curves used to reproduce each spectrum using a best-fit algorithm; the uncertainty associated with these fits is ~10%.

3. Results

3.1 *Cs-phosphate glasses*

The glass transition temperatures for the Cs-phosphate glasses are shown in **Figure 3** and are compared with those determined from Na-ultraphosphate glasses. (The T_g 's from our Na-ultraphosphate glasses are generally within ± 5 K of those reported by Hudgens [2].) For both series, T_g decreases upon the initial addition of alkali oxide. For the Cs-ultraphosphates, T_g reaches a minimum of ~470 K near 16 mole% Cs_2O where it remains independent of further Cs_2O additions. T_g reaches a minimum of ~490 K near 20 mole% Na_2O , then increases with further Na_2O additions. This latter behavior is similar to the reported compositional dependencies of Li- and Na-ultraphosphate glasses and mirrors the density data shown in **Figure 1** [2,3].

Figure 4 shows several of the ^{31}P MAS NMR spectra collected from the Cs-phosphate glasses. These spectra are similar to those collected from other alkali ultraphosphate glasses [23] and are interpreted in the same way. The central isotropic resonance near -45 ppm is due to Q^3 tetrahedra and the peak centered near -20 ppm is due to Q^2 tetrahedra. Increasing the Cs_2O content increases the relative intensity of the -20 ppm peak, indicating an increase in the relative concentration of Q^2 tetrahedra.

3.2 *Al-phosphate glasses*

Because of the volatility of P_2O_5 during the preparation of the $xAl_2O_3-(1-x)P_2O_5$ glasses, we produced glasses with a limited range of Al_2O_3 contents, from 31.9 to 34.5 mole%. There are, nevertheless, systematic changes in the structures of these glasses. **Figure 5** shows the ^{27}Al MAS NMR spectra collected from several of these glasses. Each spectrum consists of three peaks, centered near +35 ppm, +3 ppm, and -21 ppm. These peaks are assigned to $Al(OP)_4$, $Al(OP)_5$, and $Al(OP)_6$ sites, respectively [24]. The average coordination number (right) decreases with increasing Al_2O_3 content. (Al-CN is calculated from the respective fractional areas of the three peaks in **Figure 5** (left).) This decrease in Al-CN has been used as an explanation for a concomitant decrease in the refractive index and density reported for a series of $xAl_2O_3 (1-x)P_2O_5$ glasses [25].

4. Discussion

4.1 Cs-phosphate glasses

The addition of Cs_2O to P_2O_5 depolymerizes the Q^3 glass network through the formation of Q^2 sites according to the general reaction [26]:

For binary $xR_2O (1-x)P_2O_5$ glasses, the concentrations of Q^i tetrahedra generally follow simple predictions based on the glass composition. In the ultraphosphate region ($0 \leq x \leq 0.5$), the fraction of Q^2 and Q^3 tetrahedra are given by [26]:

$$f(Q^2) = \frac{x}{1-x} \quad (3a)$$

$$f(Q^3) = \frac{1-2x}{1-x} \quad (3b)$$

The compositional dependencies of the glass properties, like T_g (**Figure 3**) are sensitive not only to the number of cross-links through bridging oxygens in the phosphate network but also to changes in how the modifiers are incorporated into that network. For monovalent cations like Cs^+ and Na^+ , the coordination number defines how those modifiers are incorporated. Na^+ has a coordination number of ~ 5 in NaPO_3 glass [17,18] and so, based on equation (1), the transition from isolated to corner-sharing Na-polyhedra should occur at ~ 20 mole% Na_2O . This is the same composition at which minima in density (**Figure 1**) and T_g (**Figure 3**) occur.

Less is known about the coordination environment of Cs^+ ions in phosphate glasses. One X-ray absorption study indicates a Cs-CN of 6 in an aluminophosphate glass [27]. Cs^+ has a larger effective ionic radius ($1.84\text{\AA}$) than Na^+ ($1.16\text{\AA}$) [28] and so will prefer coordination by a larger number of oxygens. If the modifier coordination environment consists only of terminal oxygens, as predicted by Hoppe, et al. [9,10,11], then from equation (1), we expect that the transition from isolated to corner-sharing modifier polyhedra will occur at lower modifier oxide content. There is no distinct minimum in the T_g data in **Figure 3** for the Cs-ultraphosphate glasses. However, the systematic reduction in T_g with Cs_2O additions does not extend to compositions with Cs_2O contents greater than ~ 16 mole%. If this compositional dependence indicates a transition from isolated to corner-sharing Cs-polyhedra, then from equation (1) the Cs coordination number would be ~ 6 .

4.2 Al-phosphate glasses

Equation (1) can be re-written to show the dependence of the number of terminal oxygens per Al^{3+} ion (TO/Al^{3+}) on the mole fraction (x) of Al_2O_3 :

$$\text{TO}/\text{Al}^{3+} = (1+2x)/x \quad (4)$$

This relationship is shown as the solid line in **Figure 6**. If the only terminal oxygens in these $x\text{Al}_2\text{O}_3 \cdot (1-x)\text{P}_2\text{O}_5$ glasses are present as P-O-Al bonds (*viz.*, there are no Q^3 tetrahedra and so no P=O bonds), then TO/Al^{3+} will equal the average Al CN. This relationship is confirmed by the average coordination numbers (from the ^{27}Al NMR spectra) plotted as the closed circles in **Figure 6**. The agreement of the NMR data with the predictions of the 'modifier coordination' model (equation 4) indicates that *isolated* Al-polyhedra must be present in these Al-polyphosphate compositions. That is, the Al-coordination number decreases with increasing O/P ratio to avoid the formation of Al-O-Al bonds from neighboring, corner-sharing Al-polyhedra. Thus, we predict that no 'Al-O-Al sub-structure' will exist in any of our $x\text{Al}_2\text{O}_3 \cdot (1-x)\text{P}_2\text{O}_5$ glasses, in contrast to the $x\text{Cs}_2\text{O} \cdot (1-x)\text{P}_2\text{O}_5$ glasses where we predict that the transition occurs near 16 mole% Cs_2O to form a 'modified random network' that includes Cs-O-Cs bonds.

The effect of composition on the structures of these $x\text{Al}_2\text{O}_3 \cdot (1-x)\text{P}_2\text{O}_5$ glasses also contrasts with the reported structure of $x\text{La}_2\text{O}_3 \cdot (1-x)\text{P}_2\text{O}_5$ glasses. The La^{3+} ion is significantly larger ($1.185\text{\AA}$) than Al^{3+} ($0.67\text{\AA}$) [28] and as a consequence will have a greater coordination number in a binary phosphate glass. A recent x-ray and neutron diffraction study by Hoppe et al. [29] of La-metaphosphate glass (25 mole% La_2O_3) indicates an average La coordination number of about 7 and reveals the presence of La-O-La bonds, as predicted from equation (2). It seems, therefore, that the larger La ion can not exist in the low coordination environments necessary to avoid Me-O-Me linkages and so an 'MRN' forms when the La_2O_3 exceeds ~20 mole%.

5. Concluding Remarks

The 'anomalies' in the properties of binary phosphate glasses, identified by Kordes and others, can be explained by the transition of the modifier bonding from isolated polyhedral units to a sub-structure interconnected through modifier-oxygen-modifier bonds. Hoppe et al. developed this structural model to explain how the properties (valence and coordination) of the modifier ion affect the packing densities of ultraphosphate glasses. We have used the same model here to explain the compositional dependence of T_g for Cs-ultraphosphate glasses. Above the transitional composition, phosphate glass properties are dependent on the numbers of bridging and terminal oxygens (as defined by the relative Q-distributions) as well as the nature of the modifier sub-structure.

We have extended the Hoppe analysis to explain Al coordination changes in binary Al-polyphosphate glasses. In order to retain an aluminophosphate network and avoid Al-O-Al bonds in glasses with increasing Al_2O_3 contents, the Al CN must decrease in response to the reduction in the number of terminal oxygens available to coordinate the individual Al^{3+} ions.

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Figure Captions

- Figure 1:** Densities reported for Li- and Na-ultraphosphate glasses [2,3].
- Figure 2:** Schematic representations of modifier bonding in ultraphosphate glasses when $M_{TO} > CN_{Me}$ (left) and $M_{TO} < CN_{Me}$ (right).
- Figure 3:** Glass transition temperatures from the Cs- and Na-ultraphosphate glasses.
- Figure 4:** ^{31}P MAS NMR spectra collected from several $x\text{Cs}_2\text{O} (1-x)\text{P}_2\text{O}_5$ glasses. The asterisks identify spinning sidebands.
- Figure 5:** ^{27}Al MAS NMR spectra collected from several $x\text{Al}_2\text{O}_3 (1-x)\text{P}_2\text{O}_5$ glasses (left). These spectra were used to calculate an average coordination number (right). The solid line is a linear best fit ($r^2=0.94$).
- Figure 6:** The relationship between terminal oxygen concentration and the composition of $x\text{Al}_2\text{O}_3-(1-x)\text{P}_2\text{O}_5$ glasses, based on equation 4 (solid line). The data points are based on ^{27}Al NMR analyses.

Figure 1: Densities reported for Li- and Na-ultraphosphate glasses [2,3].

Figure 2: Schematic representations of modifier bonding in ultraphosphate glasses when $M_{TO} > CN_{Me}$ (left) and $M_{TO} < CN_{Me}$ (right).

Figure 3: Glass transition temperatures from the Cs- and Na-ultraphosphate glasses.

Figure 4: ^{31}P MAS NMR spectra collected from several $x\text{Cs}_2\text{O}$ ($1-x$) P_2O_5 glasses. The asterisks identify spinning sidebands.

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