Section 1. Structure

Review: the structure of simple phosphate glasses

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Abstract

Recent developments of phosphate glasses for a variety of technological applications, from rare-earth ion hosts for solid state lasers to low temperature sealing glasses, have led to renewed interest in understanding the structures of these unusual materials. In this review, spectroscopic and diffraction studies of simple phosphate glasses, including v-P2O5 and binary phosphate compositions, are described. Special attention is given to the structures of anhydrous ultra-phosphate glasses, which have received close attention from the glass community only in the past six years. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Phosphate glasses with low dispersion and relatively high refractive indices (compared with silicate-based optical glasses) were developed for achromatic optical elements about 100 yr ago by Schott and co-workers. Subsequent interest in alkaline earth phosphate glasses stemmed from their high transparency for ultraviolet (UV) light, again when compared with silicate glasses. However, the poor chemical durability of these early optical glasses limited their applications and (temporarily) discouraged their further development. (See [1] for a description of these early studies and citations to them.)

In the 1950s, interest in amorphous alkali phosphates was stimulated by their use in a variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing and pigment manufacturing [2]. By studying such materials, Van Wazer [2] established the foundations for much of our present understanding of the nature of phosphate glasses. About the same time, Kordes and co-workers [3,4] re-examined the alkaline earth phosphate glasses, including UV-transmitting compositions, and noted some ‘anomalous’ trends in properties which they suggested showed a compositional-dependence for the coordination number of metal cations like Zn$^{2+}$.

The advent of solid state lasers in the 1960s heralded a new era of phosphate glass research. Certain compositions have large rare-earth stimulated emission cross-sections and low thermo-optical coefficients (compared with silicate glasses) and are the materials of choice, particularly for high power laser applications [5]. (Campbell and Suratwala review the development of Nd-doped phosphate laser glasses elsewhere in this volume [6].)

More recently, phosphate glasses have been developed for a variety of specialty applications. Alkali aluminophosphate compositions have glass transition temperatures under 400°C and thermal...
expansion coefficients greater than $150 \times 10^{-7}/^\circ\text{C}$ and so are used for specialty hermetic seals [7]. Zinc phosphate compositions are chemically durable, have processing temperatures under 400°C and can be co-formed with high temperature polymers to produce unusual organic/inorganic composites [8]. The chemical durability and low processing temperature of iron phosphate glasses have led to their development as nuclear waste hosts [9]. Biocompatible phosphate glasses and glass-ceramics have medical applications [10] and amorphous lithium phosphate [11] and phosphorus oxynitride glasses [12] have fast ion conductivity that make them useful as solid state electrolytes.

The properties that make phosphate glasses candidates for so many different applications are related to their molecular-level structures. There have been many excellent reviews of structural studies on phosphate glasses, including those of Van Wazer [2], Abe [13] and Martin [14]. Since Martin’s 1991 review, a great deal of new structural information about phosphate glasses has been reported. For the first time, the structures of anhydrous ultraphosphate compositions have been determined, as have the structures of polyphosphate compositions with very low (<40 mol%) $\text{P}_2\text{O}_5$ contents. New structural probes, including solid state nuclear magnetic resonance (NMR) spectroscopy, X-ray absorption spectroscopy (XAS), and neutron diffraction analyses, have provided unprecedented detail about the bonding arrangements in glasses, from simple alkali and alkaline earth phosphates, through more complex and technologically useful, multicomponent glasses. These more recent studies, particularly those published since 1991, will be emphasized in this review.

2. Background

The basic building blocks of crystalline and amorphous phosphates are the P-tetrahedra that result from the formation of sp$^3$ hybrid orbitals by the P outer electrons ($3s^23p^3$). The fifth electron is promoted to a 3d orbital where strong $\pi$-bonding molecular orbitals are formed with oxygen 2p electrons (see, e.g., [15,16]). These tetrahedra link through covalent bridging oxygens to form various phosphate anions. The tetrahedra are classified using the $Q'$ terminology [17], where 'i' represents the number of bridging oxygens per tetrahedron (shown schematically in Fig. 1). The networks of phosphate glasses can be classified by the oxygen-to-phosphorus ratio, which sets the number of tetrahedral linkages, through bridging oxygens, between neighboring P-tetrahedra [2].

Zachariasen [18] identified vitreous $\text{P}_2\text{O}_5$ as one of the prototypical ‘random network’ glass formers. Indeed, recent diffraction studies of $\nu$-$\text{P}_2\text{O}_5$, described below, are consistent with the Zachariasen description of an open, distorted network of $Q^3$ tetrahedra. Hägg [19], however, challenged Zachariasen’s idea that glass forming tendency relied upon the development of a random, three-dimensional network, using the metaphosphate composition as an example of glass formation in which a large one-dimensional ‘molecular’ group (based on $Q^2$ tetrahedra) inhibits crystallization. The chromatography studies of Van Wazer [2] and others since have reinforced the utility of the description of phosphate glass structures in terms of distributions of molecular species such as those proposed by Hägg.

These two descriptions of glass structure are not incompatible; both predict local bonding similarities in glasses and crystals of identical composition. (That is, a metaphosphate glass and crystal will both have structures based on linkages of $Q^2$ tetrahedra.) More importantly for the present review, these two models also illustrate the need to describe ‘glass structure’ at different length scales. Having information about the local bond arrangements of the glass forming (or modifying) polyhedra will not necessarily complete the description of a glass structure. That short-range information (generally defined by the immediate

![Fig. 1. Phosphate tetrahedral sites that can exist in phosphate glasses.](image-url)
coordination environment of an ion; e.g., see [20]) must also be coupled with longer range information, including how those polyhedra are linked to form larger structures, whether ordered or disordered, before a proper structural description is available. The studies reviewed below describe both the short-range and longer-range structures of phosphate glasses.

Phosphate glasses can be made with a range of structures, from a cross-linked network of \( \text{Q}^3 \) tetrahedra (vitreous \( \text{P}_2\text{O}_5 \)) to polymer-like metaphosphate chains of \( \text{Q}^2 \) tetrahedra to glasses based on small pyro- (\( \text{Q}^1 \)) and orthophosphate (\( \text{Q}^0 \)) anions, depending on the \([\text{O}]/[\text{P}]\) ratio as set by glass composition. This review is likewise organized in this order.

3. Vitreous \( \text{P}_2\text{O}_5 \) (\([\text{O}]/[\text{P}] = 2.5\))

There are a number of polymorphs of crystalline \( \text{P}_2\text{O}_5 \), including a hexagonal form (I) based on discrete \( \text{P}_4\text{O}_{10} \) molecules [21], and two orthorhombic forms (II [22] and III [23]) based on helices of \([\text{PO}_4]\) tetrahedra, each sharing three corners. The tetrahedra in each polymorph are linked to three other tetrahedra through bridging (P–O–P) oxygens. The fourth bond is to a terminal oxygen P’ and is significantly shorter than the others, a consequence of its enhanced \( \pi \)-bond character, as confirmed by recent ab initio calculations [24]. Table 1 lists the average lengths for bridging (BO) and terminal (TO) P–O bonds for the different \( \text{P}_2\text{O}_5 \) polymorphs.

Until recently, little detailed information about the structure of vitreous \( \text{P}_2\text{O}_5 \) was available. \( \text{P}_2\text{O}_5 \) is hygroscopic and volatile. Anhydrous glasses must be prepared using dry-box handling procedures from crystalline \( \text{P}_2\text{O}_5 \) (purified by vacuum-sublimation) that is then typically melted in sealed silica ampoules (see [25] for details).

Recent neutron diffraction studies [26,27] confirm that \( \text{Q}^3 \) P-tetrahedra are the basic building blocks of v-\( \text{P}_2\text{O}_5 \). Fig. 2 (from Ref. [26]) shows the real-space correlation function, \( T(r) \), of v-\( \text{P}_2\text{O}_5 \). There are two P–O contributions to \( T(r) \) near 1.5 Å and the second is three times more intense than the first, consistent with their assignment to P–TO and P–BO bonds, respectively [26]. Table 1 compares bond lengths determined from neutron diffraction studies of v-\( \text{P}_2\text{O}_5 \) with those from diffraction studies of the three crystalline polymorphs. In general, the P–TO bond lengths are shorter and the P–BO bond lengths are longer in the glass than in the different crystalline polymorphs.

Longer-range information about how the \( \text{Q}^3 \) tetrahedra are linked can also be obtained from diffraction studies. The neutron scattering factor, \( S(Q) \), from v-\( \text{P}_2\text{O}_5 \) and several \( x\text{Na}_2\text{O}(1-x)\text{P}_2\text{O}_5 \) glasses are shown in Fig. 3 [27]. Of interest are the two peaks at smaller \( S(Q) \) from the v-\( \text{P}_2\text{O}_5 \) structure factor, identified by the arrows at \( Q \approx 1.30 \) and 2.12 Å\(^{-1}\). These peaks represent intermediate range order in the P–O network corresponding to periodicities of 4.8 and 3.0 Å, respectively, similar to the intermolecular distances in crystalline \( \text{P}_4\text{O}_{10} \) (H–\( \text{P}_2\text{O}_5 \) (I)). Suzuya et al. [27] contend that orientation correlations of \( \text{P}_4\text{O}_{10} \) molecular units in the glass account for these features in the scattering factor. Hoppe et al. note that the distribution of O–O distances in v-\( \text{P}_2\text{O}_5 \) (centered at 2.5 Å, Fig. 2) cannot be explained exclusively by the presence of \( \text{P}_4\text{O}_{10} \) molecular units. On the other hand, based on a similar double maximum in the X-ray scattering factor from Mg-ultraphosphate glasses, Walter et al. [28] proposed that the structure of O’–\( \text{P}_2\text{O}_5 \) (III) was a better model.

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<td><strong>Average bond lengths for ( \text{P}_2\text{O}_5 ) polymorphs (adapted from Refs. [26,27])</strong></td>
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for v-P\textsubscript{2}O\textsubscript{5}. They propose that the glass is made up of corrugated sheets of six-member rings of Q\textsuperscript{3} tetrahedra. The two peaks in the structure factor are then ascribed to distances between (effectively) aligned P=O bonds within the rings (shorter) and between the sheets (longer). Hoppe et al. discuss the diffraction studies of v-P\textsubscript{2}O\textsubscript{5} and other phosphate glasses elsewhere in this volume [29].

Some of the details about the Q\textsuperscript{3} tetrahedra in v-P\textsubscript{2}O\textsubscript{5} can also be obtained by various spectroscopic techniques. Vibrational spectroscopy has long been used to investigate the short-range structures of phosphate glass. Galeener and Mikkelsen [30] reported the first Raman spectra from anhydrous v-P\textsubscript{2}O\textsubscript{5}. By comparing those spectra with ones collected from various gas phases, they were able to confirm the tetrahedral structure of the phosphate building blocks and in so doing, associated the \(~1390\text{ cm}^{-1}\) Raman peak (discussed below) with the short P–O bond. Galeener’s assignments were confirmed by the infrared and Raman spectra calculated from an ab initio study of phosphate clusters [31] and in more recent Raman studies of v-P\textsubscript{2}O\textsubscript{5} and series of alkali [32,33] and Zn-ultraphosphate glasses [34]. From the latter study [34], Fig. 4 shows the Raman (top) and infrared (bottom) spectra collected from v-P\textsubscript{2}O\textsubscript{5} and from O’–P\textsubscript{2}O\textsubscript{5} (III). The Raman spectra are dominated by bands near 1380 cm\textsuperscript{-1}, due to P–TO stretching modes, and at 630 cm\textsuperscript{-1}, due to symmetric P–O–P stretching modes. The intense IR absorption band, centered near 970 cm\textsuperscript{-1} is assigned to asymmetric P–O–P stretching modes. This IR spectrum is similar to that reported by Hudgens and Martin [25] for anhydrous v-P\textsubscript{2}O\textsubscript{5}. Meyer notes that the shift to greater wavenumbers for the P–TO band is due to a shorter P–TO bond length in v-P\textsubscript{2}O\textsubscript{5} compared to O’–P\textsubscript{2}O\textsubscript{5}. This difference agrees with the diffraction results shown in Table 1, and led Meyer to the conclusion that the crystalline structure of O’–
P\textsubscript{2}O\textsubscript{5} is not similar to the extended range structure of v-P\textsubscript{2}O\textsubscript{5}. Meyer rules out H–P\textsubscript{2}O\textsubscript{5} (I) as a proper structural model because it is the low temperature polymorph, and so considered unlikely because of the high temperature for glass processing.
Solid state $^{31}$P nuclear magnetic resonance (NMR) spectroscopy also provides information about the local structure of phosphate glasses [35]. Grimmer and Wolf [36] collected $^{31}$P NMR spectra from the three crystalline $\text{P}_2\text{O}_5$ polymorphs and from $\nu$-$\text{P}_2\text{O}_5$. For each sample, they found axial symmetric tetrahedra with large shielding tensors ($D_{d}$) due primarily to very shielded ($\Delta$$\delta$) to $-240$ to $-260$ ppm) $\sigma_{33}$ tensor elements. For axial symmetry, $\sigma_{33}$ lies along or near the P–TO bond, consistent with the expected greater shielding associated with the localized electron density. Hudgens [37] examined a drier $\nu$-$\text{P}_2\text{O}_5$ sample and reports a $^{31}$P isotropic chemical shift, relative to H$_3$PO$_4$, of $-54.2$ ppm, vs. $-38.1$ ppm reported by Grimmer and Wolf – and drew similar conclusions, despite a greater degree of deviation from axial symmetry.

In summary, the basic building block for the structure of $\text{P}_2\text{O}_5$ glass is the $Q^3$ tetrahedron, possessing three covalent bridging oxygen bonds to neighboring tetrahedra, and one short (P–TO) bond to a terminal oxygen. These tetrahedra are linked to form a three-dimensional network that appears to possess some similarities to the structure of $\text{P}_4\text{O}_{10}$ molecules found in crystalline $\text{H}_2\text{P}_2\text{O}_5$ (phase I), although there remains uncertainties as to the details of such extended range ordering. That the density of $\nu$-$\text{P}_2\text{O}_5$ is intermediate to those of the H- and O-forms of crystalline $\text{P}_2\text{O}_5$ (Table 1) indicates that the glass likely contains longer-range structural similarities to both forms.

4. Binary phosphate glasses

The addition of a modifying oxide to $\nu$-$\text{P}_2\text{O}_5$ results in the creation of non-bridging oxygens at the expense of bridging oxygens. The resulting depolymerization of the phosphate network with the addition, e.g., of alkali oxide, $\text{R}_2\text{O}$, can be described by the pseudo-reaction [2]

$$2Q^a + \text{R}_2\text{O} \rightarrow 2Q^{a-1}. \quad (1)$$

For binary $x\text{R}_2\text{O}$ (or R’O) ($1-x$)$\text{P}_2\text{O}_5$ glasses, the concentrations of $Q^i$ tetrahedra (Fig. 1) 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 [2]

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

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

Anhydrous ultraphosphate glasses must also be prepared in sealed ampoules because of the hygroscopicity and volatility of $\text{P}_2\text{O}_5$. Because of preparation difficulties, detailed spectroscopic information about ultraphosphate structures has only recently been obtained, as described below. The reactivity of $Q^3$ sites to water limits the technological usefulness of ultraphosphate glasses even though they possess UV edges at wavelengths shorter than found for silicate glasses [38].

*Metaphosphate glasses* ($x = 0.50$) have networks based entirely on $Q^2$ tetrahedra that form chains and rings. The chains and rings are linked by more ionic bonds between various metal cations and the non-bridging oxygens. Because of the difficulty in obtaining an exact stoichiometry, these compositions are usually more accurately described as long-chained polyphosphates (see
below). The term ‘metaphosphate’ is reserved for cyclic anions of the exact (PO₄)ₙ composition [39]. However, the convention is to label compositions with \( x \approx 0.50 \) ‘metaphosphate glass’ and that convention will be followed here.

**Polyphosphate glasses** (\( x > 0.50 \)) have networks based on Q² chains terminated by Q¹ tetrahedra (one bridging and three non-bridging oxygens per tetrahedron). The average chain length becomes progressively shorter as the [O]/[P] ratio increases. At \([O]/[P] = 3.5\) (the pyrophosphate stoichiometry, \( x = 0.67 \)), the network structure is dominated by phosphate dimers, two Q¹ tetrahedra linked by a common bridging oxygen. Glasses for which \([O]/[P] > 3.5\) contain isolated Q⁰ (orthophosphate units) tetrahedra. Between the metaphosphate \((x = 0.50)\) and pyrophosphate \((x = 0.67)\) boundaries, the fraction of Q¹ and Q² tetrahedra are given by [2]

\[
f(Q^1) = \frac{2x - 1}{1 - x}, \quad f(Q^2) = \frac{2 - 3x}{1 - x}.
\]

Between the pyrophosphate \((x = 0.67)\) and orthophosphate \((x = 0.75)\) boundaries, the fraction of Q⁰ and Q¹ tetrahedra are given by

\[
f(Q^0) = \frac{3x - 2}{1 - x}, \quad f(Q^1) = \frac{3 - 4x}{1 - x}.
\]

Much research has been done on the structure and properties of metaphosphate and polyphosphate glasses and details can be found in a number of review papers (e.g., [13, 14, 40]). Glass formation in binary \( xR_2O \) (or \( OR' \)) \((1-x)P_2O_5\) systems (where \( R_2O \) is an alkali oxide and \( R' \) is an alkaline earth oxide) is typically limited to \( x < 0.55–0.60 \) (mole fraction) for conventional melt processing. Rapid quenching techniques have yielded Li-phosphate glasses with \( x \) as large as 0.70 \((O)/[P] \approx 3.67\), having structures based on Q¹ and Q⁰ tetrahedra [41]. Pyrophosphate glasses based on a variety of low-coordinated (coordination number \( \leq 6 \)) metal oxides, including SnO, ZnO, CdO, PbO and Fe₂O₃, can be made by conventional melt techniques [42]. These latter glasses are analogous to the silicate ‘invert glasses’, stable compositions with \([O]/[Si] > 3\) [43]. Such glasses do not have a continuous random network of glass-forming polyhedra, at least as described by Zachariasen [18]. Instead, the glass structure consists of isolated tetrahedra and small molecular fragments linked through their non-bridging oxygens by larger, smaller valence (‘non-glass forming’) cations.

For binary glasses, the bridging-to-terminal oxygen ratio, for \( 0 \leq x \leq 0.75 \), depends on composition according to

\[
BO/TO = 0.5(3 - 4x).
\]

As will be shown below, the predictions represented by Eqs. (1)–(3) can be tested using probes such as solid state \(^{31}\)P magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and chromatography, to provide quantitative descriptions of the phosphate glass network structures.

### 4.1. Ultraphosphate glasses \((2.5 \leq [O]/[P] < 3.0)\)

The hygroscopic nature of ultraphosphate glasses must be taken into account when analyzing structure and property trends. Binary sodium ultraphosphate glasses prepared in open crucibles will absorb water; e.g., over 20 mol% \( H_2O \) is present as P–OH bonds in a glass with the nominal composition 25 mol% \( Na_2O \) and 75 mol% \( P_2O_5 \) [44]. Water is an additional structural modifier that depolymerizes the ultraphosphate network (Eq. (1)) beyond that expected from the nominal alkali-to-phosphorus ratio. Fig. 5 compares the densities of Na-ultraphosphate glasses prepared by conventional open crucible techniques [45, 46] with those prepared using anhydrous raw materials melted in sealed ampoules [37]. Although some of the density differences between the series might be ascribed to fictive temperature effects due to the different preparation conditions, the density trends for the two series differ markedly. Anhydrous Na-ultraphosphate glasses have a minimum in density, near 20 mol% \( Na_2O \) that does not occur when glasses are prepared in open crucibles. (Bartenev [47] reported a minimum in the speed of
ultrasound in Na-ultraphosphate glasses near 25 mol% Na₂O and related this to an analogous minimum in density.) The densities (and glass transition temperatures) of anhydrous Li-ultraphosphate glasses have similar compositional dependencies [25].

Care must also be taken when analyzing anhydrous ultraphosphate glasses prepared using sealed ampoule techniques. Meyer et al. [48] have shown that 30 s of exposure to ambient air is enough to degrade the IR reflectance spectra from (originally) anhydrous v-P₂O₅. The hydration of alkaline earth ultraphosphates is slower, but still evident.

4.1.1. Phosphate site distributions in ultraphosphate glasses

The evolution of the cross-linked Q³ network of P₂O₅ to the chain-like Q² network of a metaphosphate glass can be readily seen in the ³¹P NMR spectra collected from the series of Na-phosphate glasses shown in Fig. 6 [35]. The different Qᵗ tetrahedra have isotropic ³¹P NMR chemical shift peaks that are separated by ca. 20 ppm (inset to Fig. 6). Peaks due to Q⁰ (isotropic chemical shift at ~-51 ppm), Q² (~-22 ppm), and Q¹ (0 ppm) tetrahedra are evident in the various spectra. The decrease in shielding (less negative chemical shift) with decreasing polymerization (fewer bridging oxygens per tetrahedron) is due to the increased ionicity of the non-bridging oxygen bonds [44]. The chemical shifts of the individual peaks are also sensitive to the glass composition. Each peak becomes less shielded with increasing Na₂O content. Similar changes in isotropic chemical shifts have been noted in other NMR studies of binary phosphate glasses [35] and indicate a redistribution of electron density among tetrahedra with changing bridging to non-bridging oxygen ratios. One-dimensional ³¹P NMR studies have been reported for a variety of anhydrous binary ultraphosphate glass systems [32,37,49,50] and for ultraphosphate glasses that contain significant (>5 mol%) amounts of structural water [44,51].
Such spectra can be used to test the site-distribution models outlined above. Fig. 7 shows the tetrahedral site distributions from a number of $^{31}$P NMR studies of different ultraphosphate glasses. The solid lines are the predicted distributions from Eqs. (2a) and (2b).

Also shown in Fig. 7 are the $Q^3$ site fractions (shown as asterisks) determined from Na-ultraphosphate glasses melted in open crucibles [44], plotted against their analyzed Na$_2$O content. These glasses contain large amounts of water (5–20 mol%) which also depolymerize the phosphate network by forming P–OH bonds and so reducing the $Q^3$ fraction to much less than that expected from the Na$_2$O-content alone. That is, bridging oxygens associated with $Q^3$ tetrahedra react with H$_2$O to form $Q^2$ tetrahedra with P–OH bonds. Mercier et al. [51] show that $^1$H–$^{31}$P cross polarization NMR spectroscopy can distinguish between $Q^2$ tetrahedra with and without P–OH bonds in a series of ‘wet’ Zn-ultraphosphate glasses. Wenslow and Mueller [52] report a similar study of water-containing (near) metaphosphate glass that reveals $Q^1$ sites with and without hydroxyl bonds and that identifies both intra-and intermolecular hydrogen bonding. This ‘structurally complex’ incorporation of water supports the conclusions drawn from earlier IR and $^1$H NMR analyses [53]. Eqs. (2a) and (2b) are consistent with the measured Q-distributions when ‘x’ is defined as (R$_2$O + H$_2$O) [44]. In this way, P–OH bonds will affect ultraphosphate glass properties, such as the density data in Fig. 5. The presence of P–OH bonds likely explains the smaller than expected $Q^3/Q^2$ ratios reported in a $^{31}$P NMR study of Zn- and Pb-ultraphosphate glasses [54]. Those glasses were prepared in open crucibles with water-producing raw materials such as NaH$_2$PO$_4$·H$_2$O.

The spectra in Fig. 6 indicate that only $Q^2$ and $Q^1$ tetrahedra are present in the ultraphosphate range; this is typical for ultraphosphate glasses and indicates that no site disproportionation of the type

$$2Q^2 \leftrightarrow Q^1 + Q^3 \quad (4)$$

occurs in these glasses. The absence of $Q^1$ sites implies that the pseudo-reaction indicated by Eq. (4) would have an equilibrium constant $k_{Q^2} = 0$, in agreement with Van Wazer’s predictions for ultraphosphate glasses [2]. (There has been one report for $Q^2$ disproportionation ($k_{Q^2} > 0$) in a Ca-metaphosphate composition [55].) Site disproportionation is important for the structures of polyphosphate glasses, as described below.

Neutron and X-ray diffraction studies of Ca- and Zn-ultraphosphate glasses indicate that the average P–TO and P–BO bond lengths increase with increasing metal oxide (MeO) contents [26,66]. The mean P–O bond length does not change within experimental errors in the same series because the fraction of shorter P–TO bonds increases (Fig. 8 [26]). These studies could not resolve different P–TO bond lengths from $Q^2$ and $Q^3$ tetrahedra coexisting in ultraphosphate glasses. This latter observation is not surprising since Hoppe’s survey of diffraction studies of ultraphosphate crystals indicates that such a difference would be on the order of 0.01 Å [56], too small to be evident in the broad diffraction peaks from glasses.
There has been some controversy about the different oxygen species in phosphate glasses, particularly as it relates to the relevance of distinguishing ‘double bonded’ oxygens from ‘non-bridging’ oxygens [14]. For example, a $Q^2$ tetrahedron is often represented as possessing one $P=O$ and one $P-O-R^+$ terminal oxygen bond, the implication being that the double bond is shorter because of the localization of the fifth valence electron from $P^{5+}$. This description was supported by an early X-ray photoelectron study [57] in which the O1s spectra from various phosphate glasses were decomposed into three components, representing distinct $P=O$, $P-O-R^+$ and $P-O-P$ species.

Subsequent diffraction studies of metaphosphate glasses [58,59] challenge this assumption, revealing instead that the two $P-TO$ bonds on a $Q^2$ tetrahedron are indistinguishable. Ab initio molecular orbital calculations indicate that the negative charge associated with the fifth valence electron of $P^{5+}$ is almost equally delocalized over each non-bridging oxygen on the $Q^2$ tetrahedron [24,60]. Given these recent results, the proper way to decompose the O1s spectra from simple phosphate glasses then seems to be the two-peak fit, first proposed by Gresch et al. [61].

Examples of the O1s spectra collected from anhydrous sodium ultraphosphate glasses [32] are shown in Fig. 9 (left). The greater binding energy
peak is due to bridging oxygens (P–BO) and the other binding energy peak is due to terminal oxygens (P–TO) on the phosphate tetrahedra. Note that the separation between the two binding energies decreases, from 2.56 eV for v-P$_2$O$_5$, to 1.90 eV for Na-metaphosphate glass. This trend is consistent with the ab initio molecular orbital predictions of Uchino and Ogata [24]. Fig. 9 (right) shows the bridging-to-terminal oxygen ratio, determined by decomposing the O1s spectra, in comparison to those calculated from the Q$^-d$ distributions (Fig. 7) from $^3$P NMR spectra and to the predicted ratio from Eq. (3). Similar results were obtained in other XPS studies of binary phosphate glasses [61–64].

The progression from a cross-linked Q$^3$ network, to chain-like Q$^2$ structures, to depolymerized Q$^1$/Q$^0$ glasses with increasing [O]/[P] ratio can be monitored by a variety of other spectroscopic probes. For example, Fig. 10 shows Raman spectra collected from several Li-ultraphosphate [32] and polyphosphate [65] glasses. The anhydrous ultraphosphate glasses were prepared using sealed ampoule techniques and the polyphosphate glasses were quenched to avoid crystallization. Bands in the 1000–1400 cm$^{-1}$ range are due to the symmetric and asymmetric stretching modes of P–non-bridging (or terminal) bonds, whereas bands in the 620–820 cm$^{-1}$ range are due to the symmetric and asymmetric stretching modes of bridging oxygens. Note that the frequency of the dominant ‘non-bridging’ stretching mode decreases from 1390 cm$^{-1}$ ($x = 0$, symmetric P=O stretch on Q$^3$ tetrahedra), to 1180 cm$^{-1}$ ($x = 0.50$, symmetric PO$_2$ stretch on Q$^3$ tetrahedra), to 1050 cm$^{-1}$ ($x = 0.67$, symmetric PO$_3$ stretch on Q$^3$ tetrahedra) and 950 cm$^{-1}$ ($x = 0.70$, symmetric PO$_4$ stretch on Q$^0$ tetrahedra) with increasing [O]/[P] ratio. This decrease in frequency shows the progressive depolymerization of the phosphate network, as well as the increase in the average bond length of P–non-bridging oxygens. This latter observation is consistent with neutron and X-ray diffraction studies of ultraphosphate glasses (e.g., [66]) discussed above and can be explained by a decrease in the average $\pi$-bond character of the P–TO bond [24]. Raman spectra have also been reported for series of anhydrous Na- [32,33], Ca- [67] and Zn-ultraphosphate glasses [34]. Infrared spectroscopy can also provide useful, complementary information about the network structures of anhydrous ultraphosphate glasses, as reported for series of binary Li- [25] and Zn-phosphate [34] compositions.

Comparisons of Raman (and infrared) spectra from ultraphosphate glasses prepared by different techniques illustrate the depolymerizing effects of water on the phosphate network. Fig. 11 shows Raman spectra from glasses with the same nominal composition (mol%) of 25Na$_2$O·75P$_2$O$_5$. The top spectrum is from an anhydrous glass prepared in a sealed ampoule [32] and the bottom spectrum is from a glass prepared and handled in a dry box [68]. The relative intensity of the v(P=O)$_{\text{sym}}$ peak (near 1370 cm$^{-1}$) from the anhydrous glass is greater than from the ‘wet’ glass, indicating that the former structure is more cross-linked; i.e., has
a greater Q³-content. A comparison of the relative intensities of these bands with those reported for a series of anhydrous \( x \text{Na}_2\text{O}(1-x)\text{P}_2\text{O}_5 \) [32] indicates that the spectrum of the 'wet' 25Na₂O·75P₂O₅ glass in Fig. 11 is more like that from a glass with 35–40 mol% modifier content. It is likely, therefore, that this glass possesses ~20 mol% water, as has been measured elsewhere for this composition [44,46], despite the reported precautions taken in preparation and handling of the glass.

Similar precautions are warranted when analyzing the spectra of other ultraphosphate glasses prepared by open crucible techniques, including recent infrared studies of Na- [69] and Pb-ultraphosphate glasses [70] and an early Raman study of a K-ultraphosphate glass [71].

4.1.2. Network linkages in ultraphosphate glasses

An arrow in Fig. 10 indicates the presence of an additional band on the high frequency shoulder of the \( v(\text{PO}_2)_{\text{sym}} \) band in the Raman spectrum of the anhydrous 30Li₂O·70P₂O₅ glass. Similar bands can be seen in the Raman spectra of anhydrous Na-ultraphosphate glasses with 30–40 mol% Na₂O [32,33] but not in the spectrum of a 'wet' 40 mol% ultraphosphate glass [68]. The band amplitude is temperature dependent, disappearing when the glass is heated to a liquid, and reappearing when the liquid is cooled to a temperature near \( T_g \) [32,33]. These observations indicate that the band is associated with strained Q² sites that apparently react in the presence of water and relax when the glass is heated above \( T_g \).

The frequency of a number of vibrational modes changes with composition. Fig. 12 shows that the position of the \( v(\text{P}==\text{O}) \) band in the Raman spectra of Li- and Na-ultraphosphate glasses (Fig. 10) decreases in frequency with increasing alkali content [33]. (Note in Fig. 10 that the \( v(\text{P}==\text{O}) \) peak becomes indistinguishable from the \( v(\text{PO}_2)_{\text{sym}} \) band when Li₂O > 40 mol%). This decrease is particularly evident when R₂O exceeds about 20 mol%, The decreasing frequency indicates that the P=O bond on Q³ tetrahedra becomes longer, particularly when R₂O > 20 mol% [33], because of \( \pi \)-bond delocalization. Similar decreases at 20 mol% Li₂O occur to the frequency of the P=O IR absorption band [25] and there are changes in the shielding of the \(^{31}\text{P}\) chemical shift tensor elements from several Li-ultraphosphate...
glasses [49] that are consistent with this explanation.

The change in frequency of the $v(P=O)$ band indicates a possible change in the longer-range (beyond a local P-tetrahedron) ultraphosphate network structure at 20 mol\% $R_2O$. Such structural modifications are indicated in the neutron scattering factors from the Na-ultraphosphate glasses shown in Fig. 3. Note that the two intermediate-range order peaks of $vP_2O_5$ at $Q = 1.30 \text{ Å}^{-1}$ and 2.12 Å$^{-1}$ (indicated by arrows in Fig. 3) are replaced by a single peak ($Q = 1.60 \text{ Å}^{-1}$) for the 20 mol\% Na$_2$O glass, corresponding to a peak at 1.16 Å$^{-1}$ for the 50 mol\% Na$_2$O sample, implying order on an extended length scale (5.8 Å) presumably associated with metaphosphate chains. Walter and co-workers [28,72] have reported similar compositionally dependent changes in the X-ray scattering factors from alkaline earth ultraphosphate glasses. They propose that ultraphosphate glasses with up to 20 mol\% modifying oxides retain the ‘quasi-layer’ structure of $vP_2O_5$, with isolated modifier ions occupying positions between the corrugated sheets of $Q^3$ rings. Above about 20 mol\% modifying oxide, these $Q^3$ layers are consumed as $Q^2$ tetrahedra are converted to $Q^2$ tetrahedra.

Recent inelastic neutron scattering studies of Na-ultraphosphate glasses indicate changes in the phonon density of states (PDOS) that are consistent with the description of the evolution of a 3D $P_2O_5$ network to corner-shared $PO_4$ chains with increasing Na$_2$O content [73]. The breadth of the PDOS was greatest at 20 mol\% Na$_2$O, indicating larger distributions of P–O–P and O–Na–O coordination environments. A narrower PDOS at the metaphosphate composition was related to the appearance of extended-range order in the static structure factor (viz., Fig. 3 [27]).

There has been speculation that the way that the $Q^2$ and $Q^3$ tetrahedra are arranged may be responsible for these indicated changes in ‘extended-range’ order [25,33,49,56]. As discussed earlier, the concentrations of different tetrahedra depend on composition according to the simple depolymerization model described by Eqs. (1)–(2b). There are, however, several different ways in which these tetrahedra could be linked to form the phosphate network, including: (a) randomly distributed linkages; (b) chemically ordered linkages; and (c) phase separated structures. $Q^1$–$Q^2$ linkages are preferred in the ‘chemically ordered’ network; the fraction of $Q^1$–$Q^2$ linkages will equal one at 37.5 mol\% $R_2O$ (or $R'O$) [66]. There are virtually no $Q^3$–$Q^3$ linkages in a phase-separated network. For the ‘random distribution’ network, the number of $Q^3$–$Q^2$ linkages can be determined from a simple binomial expansion to calculate probabilities [49].

There are a number of alkaline earth ultraphosphate crystals with the stoichiometry $R'O$·$2P_2O_5$ that possess chemically ordered structures dominated by $Q^3$–$Q^2$ linkages. The similarities between the vibrational spectra of these crystals and the respective glasses led Meyer and co-workers to conclude that the structures of ultraphosphate glasses were best described as a combination of chemically ordered substructures similar to the appropriate, equilibrium crystalline phases [34,67,74,75]. In this model, a Zn-ultraphosphate glass with a composition $0 \leq ZnO \leq 33.3$ mol\% will have a structure based on a combination of chemically ordered substructures similar to crystalline $P_2O_5$ and ZnP$_4$O$_{11}$ [34]. A Zn-ultraphosphate glass with a composition $33.3 \leq ZnO \leq 50$ mol\% will have a structure based on a combination of chemically ordered substructures similar to crystalline ZnP$_4$O$_{11}$ and Zn(PO$_3$)$_2$. Likewise, the glasses in the Ca-ultraphosphate series should have phosphate network structures based on the combinations of the substructures of appropriate intermediate phases [67].
An advantage of the DQ technique over the RFDR type of experiment is the poorer resolution of the latter due in part to magnetization transfer from a third (or more) spins [78].

Fig. 13 (from Ref. [79]) shows a $^{31}$P 2D DQ spectrum from a $35\text{Na}_2\text{O} \cdot 65\text{P}_2\text{O}_5$ (mol%) glass. The connectivities between $Q^n$ and $Q^{n'}$ tetrahedra are indicated by $n-n'$. Signal intensity along the indicated diagonal represents homonuclear (2–2 and 3–3) connections and off-diagonal intensity represents heteronuclear (2–3 and 3–2) connections. Feike et al. suggest that the −23 ppm chemical shift for the 2–2 auto-peak indicates that $Q^2–Q^2$ linkages are present in this glass, either in the form of 3-membered rings or in chains with at least four $Q^2$ tetrahedra. Trimetaphosphate rings were presumed to be present in alkali ultraphosphate glasses, based on the hydrolytic degradation of $Q^3$ sites [80]. Similar moieties have been proposed [33] to explain the high frequency $\nu(\text{PO}_2)_{\text{sym}}$ Raman band (Fig. 10) discussed above. Elsewhere in this volume, Liang et al. [81] describe molecular dynamics simulations of ultraphosphate glass structures which possess rings of varying sizes and they suggest that the property minima in alkali ultraphosphate glasses (e.g., Fig. 5) may be related to the variations in the distributions of these rings.

The conclusion by Feike et al. that $Q^2–Q^2$ and $Q^1–Q^3$ linkages are present in this $35\text{Na}_2\text{O} \cdot 65\text{P}_2\text{O}_5$ glass differs from that drawn in earlier 2D $^{31}$P RFDR NMR. Those earlier studies found only heteronuclear linkages in a similar glass and led to the conclusion that the ‘chemically ordered’ model best described the linkages that make up an alkali ultraphosphate glass network [76,77]. Alam and Brow [49,82] used 2D $^{31}$P RFDR NMR to determine the relative concentrations of $Q^n–Q^{n'}$ linkages for a series of Li-ultraphosphate glasses and those results are summarized in Fig. 14. The solid lines are the expected populations of linkages based on a random distribution model and are in good agreement with the measured connectivity concentrations. The ‘chemically ordered’ model predicts much greater numbers of $Q^3–Q^2$ and $Q^2–Q^3$ linkages and the ‘phase separation’ model predicts fewer $Q^3–Q^2$ and $Q^2–Q^3$ linkages than are found experimentally.

4.1.3. Modifier bonding in ultraphosphate glasses

There seems to be little connection between the ratio of $P$-tetrahedra (Fig. 7) or their distribution (Fig. 14), and the significant property minima that have been reported near 20 mol% alkali oxide (e.g., Fig. 5). The local bonding arrangements of the tetrahedra do change near 20 mol% however, as indicated by the $\nu(\text{P} \equiv \text{O})$ frequency shifts shown in Fig. 12.

Hoppe [56] presented a structural model that is based on the coordination environments of the modifier cations to explain packing densities in alkaline earth and zinc ultraphosphate glasses. (That model – and supporting diffraction experiments – is also discussed in Hoppe’s article elsewhere in this volume [29].) Structural studies of crystalline ultraphosphates (e.g., [83,84]) indicate that the local coordination environment of the modifying cations includes terminal oxygens from both $Q^2$ and $Q^3$ tetrahedra. Hoppe 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 coordination numbers (CNMe) similar to those found in the appropriate crystalline phases. For glasses with the stoichiometry $x$Me$_2$/O $(1-x)$P$_2$O$_5$, the number of terminal oxygens per modifying ion is

$$M_{TO} = v(1/x).$$  \hspace{1cm} (5)$$

Hoppe noted that there will be two structurally different compositional ranges: when $M_{TO} > CN_{Me}$ (region I) and when $M_{TO} < CN_{Me}$ (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 (Fig. 15, 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 TOs. As a result, in region II Me$^{v+}$ coordination polyhedra share corners and edges and act as bridges between neighboring Q$^2$ polyhedra (Fig. 15, right).

Consider first the single valent ions. Diffraction studies indicate that lithium ions in metaphosphate crystals [85] and glasses [86] are tetrahedrally coordinated. A recent $^6$Li NMR study of Li-ultraphosphate glasses reached a similar conclusion, that the average CN for Li is in the range of 4–5 [87]. Diffraction studies of NaPO$_3$ glass indicate that the coordination number of Na$^{+}$ is about 5 [88,89]. Using these coordination numbers for CNMe, from Eq. (5) the transition from region I to region II is calculated to occur at 20–25 mol% for Li and Na ultraphosphate glasses. This analysis then provides an explanation for the minima in properties (viz., Fig. 5) and for the spectral changes such as those shown in Fig. 12. In glasses with less than ~20 mol% Li$_2$O or Na$_2$O, isolated alkali polyhedra such as those shown in Fig. 15 (left) form. 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 (Fig. 5) as the Q$^3$ network expands to accommodate the alkali polyhedra. $T_g$ decreases [25,33] because the fraction of bridging oxygens is decreasing (Eq. (3)) as Q$^2$ tetrahedra replace Q$^3$ tetrahedra. Above ~20 mol% Me$_2$O, M$_{TO} < CN_{Me}$ and so neighboring alkali polyhedra must share the terminal oxygens on Q$^2$ tetrahedra (Fig. 15, right). Density increases as more Me-polyhedra share corners and edges. In addition, the bonds between alkali ions and neighboring Q$^3$ tetrahedra are strengthened, as indicated by the lengthening of the Q$^3$ P–O bond (Fig. 12). Thus, the alkali polyhedra act as bridges between neighboring Q$^2$ and Q$^3$ tetrahedra, strengthening

![Graph showing connectivity distributions](image)

**Fig. 14.** Connectivity distributions obtained from $^{31}$P RFDR analyses of a series of $x$Li$_2$O$(1-x)$P$_2$O$_5$ glasses. The solid lines are the expected connections based on a random distribution model [49].
the network (and so increasing $T_g$) even as P–O–P bonds are replaced by P–O–Me bonds as the alkali concentration increases.

In this volume, Prabakar et al. [90] describe a $^{23}$Na $→$ $^{31}$P cross-polarization (CP) NMR experiment that is consistent with this modifier structural model. The CP time constant ($T_{cp}$) for magnetization transfer between neighboring Na and Q$^2$-P nuclei is longer for a 20Na$_2$O·80P$_2$O$_5$ glass than for either a $\sim$44Na$_2$O·56P$_2$O$_5$ or a 50Na$_2$O·50P$_2$O$_5$ glass. This observation indicates that the number of sodium ions associated with an average Q$^2$ site in the 20Na$_2$O glass is less than that found for the glasses with greater Na$_2$O contents, as would be expected if TOs in the latter glasses were coordinated to more than one sodium ion. In the same study, Prabakar et al. report a correlation between Na nuclei and Q$^3$-P nuclei in the 20Na$_2$O·80P$_2$O$_5$ glass, indicating that the P–O bond likely participates in the alkali coordination environment, as indicated in Fig. 15.

When divalent or trivalent ions are incorporated into an ultraphosphate network, their charge requirements dictate that at least two Q$^2$ tetrahedra are present in their immediate coordination sphere. As a result, ‘restructuring’ through Q$^2$–Me$^{2+}$–Q$^2$ bridges will occur in region I, even though the Me$^{2+}$-polyhedra can remain isolated as long as M$_{TO}$ > CN$_{Me}$ [56]. When M$_{TO}$ < CN$_{Me}$, the Me$^{2+}$-polyhedra again begin sharing corners and edges, with resulting changes in property trends. One prediction of Eq. (5) is that the transition from region I to region II will depend on the coordination number of the Me$^{2+}$ ion and this effect in fact has been reported. Minima in ultraphosphate glass packing densities, in the transition from region I to region II, occur at $\sim$50 mol% MgO (CN $\sim$ 4), $\sim$33 mol% CaO (CN $\sim$ 6), and $\sim$25 mol% BaO (CN $\sim$ 8) [56,91]. There are corresponding changes in the X-ray diffraction structure factors that are consistent with the formation of more compact structures of Me-polyhedra sharing corners and edges [72].

There are differences in the vibrational spectra of Ca- and Zn-ultraphosphate glasses that are related to the expected coordination effects of the different modifiers on the phosphate network. Fig. 16 compares the Raman spectra collected from binary ultraphosphate glasses with 30 mol% Li$_2$O, Na$_2$O (both from [33]), CaO [67] and ZnO [34]. Of particular interest is the presence of separate bands due to the υ(P=O) and υ(PO$_2$)$_{asym}$ modes in the spectrum from the Zn-ultraphosphate (and, to a lesser extent, the Li-ultraphosphate), whereas these two modes are indistinguishable in the spectra from the Ca- and the Na-ultraphosphate glasses. The smaller Zn$^{2+}$ ion apparently does not form bonds to terminal oxygens P=O on the remaining Q$^3$ tetrahedra which are as strong as those of larger Ca$^{2+}$ and Na$^+$ ions, and so does not affect the frequency of the P=O band to nearly the degree found for the other modifying ions.

The frequencies of the υ(PO$_2$)$_{sym}$ and υ(PO$_2$)$_{asym}$ peaks in Fig. 16 are cation dependent, increasing
in frequency as the field strength of the modifying cation increases (in the order \( \text{Na}^+ < \text{Li}^+ < \text{Ca}^{2+} < \text{Zn}^{2+} \)), consistent with previous studies of metaphosphate glasses [92]. The full-width at half maximum (FWHM) of the \( \nu(\text{PO}_2)_{\text{sym}} \) band also increases with increasing cation field strength (from about 22 cm\(^{-1} \) for the 30Na\(_2\)O glass to about 52 cm\(^{-1} \) for the 30ZnO glass), indicating an increase in the degree of disorder that may be due to changes in the distributions of the Q\(^2\) P–O bond lengths and bond angles. Again, these observations are consistent with previous spectroscopic studies of metaphosphate glasses [93].

Finally, there are neutron and X-ray diffraction studies which show that the coordination numbers of divalent ions in ultraphosphate glasses are larger in region I (when \( \text{M} \text{TO} > \text{CNMe} \)) than in region II [56,66,91,94]. For example, the coordination number of Zn changes from approximately six at 33 mol\% ZnO to four at 50 mol\% ZnO [66]). The availability of ‘excess’ terminal oxygens in this range is consistent with the larger coordination numbers. Inflections in packing density trends have been correlated with the changes in coordination number [56].

The modifier substructure that forms in region II is a hallmark of the ‘modified random network’ (MRN) theory for glass structure, introduced by Greaves to describe the structure of modified silicate glasses [95]. The apparent segregation of modifiers has obvious consequences for the properties of oxide glasses [96]. For phosphate glasses, the ‘extra’ terminal oxygen associated with each P-tetrahedron makes it possible for simple phosphate compositions to be model systems for illustrating the consequences of the development of ‘MRN’ structures, such as at the transition from region I to region II compositions (Fig. 15).

In summary, anhydrous ultraphosphate glasses have network structures based on combinations of Q\(^2\) and Q\(^3\) tetrahedra, the concentrations of which can be predicted from Van Wazer’s chemically simple depolymerization model. These tetrahedra appear to be randomly linked, at least in alkali ultraphosphate glasses. In glasses with large P\(_2\)O\(_5\) contents (greater than about 75 mol\%), the phosphate network most resembles that found for v-P\(_2\)O\(_5\). With increasing modifier content, there is a loss of extended-range order associated with v-P\(_2\)O\(_5\), as the fraction of Q\(^2\) tetrahedra increases. The composition at which this transition occurs depends on the coordination number and valence of the modifying cation. Water has a depolymerizing effect on the phosphate network and account must be made for P–OH bonds when describing the structure and properties of these glasses.

4.2. Metaphosphate glasses ([O]/[P] = 3.0)

Metaphosphate and polyphosphate glasses have structures that are based on phosphate anions. The average chain-length \( n_{av} \) of an anion in a polyphosphate glass is given by Van Wazer [2]

\[
n_{av} = 2(1 - x)/(2x - 1).
\]  

Note that when \( x = 0.5 \) (the metaphosphate stoichiometry), \( n \) is \( \infty \). (This conclusion assumes that there are no cyclic anions, the presence of which will reduce the average chain length. In general,
the percentage of cyclic metaphosphate anions, including \((P_3O_9)^3\) and \((P_4O_{12})^4\) is greatest when \(x \approx 0.5\) and decreases with increasing \(x\) [97]. Average chain lengths can be estimated by end group titration techniques (e.g., Ref. [98]) and typical ‘metaphosphate’ glasses have chains with \(n_{av}\) ranging from 40 to 100 P-tetrahedra and terminated by hydroxyl groups [99]. By removing water from alkaline earth metaphosphate liquids, glasses with chain lengths approaching 1000 tetrahedra have been reported [13]. Abe [13] reviews the effects of water on the properties of metaphosphate glasses. Griffith reports that glasses with average chain lengths no greater than 400 tetrahedra are possible by quenching alkali polyphosphate liquids, in contrast to crystallized sodium Kurrol’s salts with chain lengths over 10,000 tetrahedra [100].

The transition from cross-linked ultraphosphate structures to polymer-like metaphosphate structures affects the temperature dependence of viscosities of alkaline phosphate liquids; in general, metaphosphate liquids are more fragile (as defined by Angell, e.g., Ref. [101]) than ultraphosphate liquids [102]. The rheological properties of metaphosphate liquids are more like those of a polymer liquid than a conventional cross-linked oxide glass [103–105]. The motion of intact phosphate chains determines macroscopic phenomena such as viscous flow near \(T_g\) [106]. Chain alignment in metaphosphate fibers can create anisotropic optical and mechanical properties [107–109]. (A recent 2D rotor-synchronized NMR experiment identified partial alignment of phosphate chains along the extrusion direction [110]. Jäger et al. [111] describe these, and newer, experiments elsewhere in this volume.) Consistent with this effect are recent X-ray diffraction studies of NaPO₃ which indicate that upon heating above \(T_g\) the alkali polyhedral environment expands and the phosphate chains remain intact and are more ordered in the liquid than in the glass [112–114].

Diffraction studies of crystalline (linear) metaphosphates indicate that the P-tetrahedral chains have a variety of conformations. In general, larger field strength cations can be correlated with chains with greater conformational periodicities (defined by the number of tetrahedra per repeating chain element) [17]. The chain constitution in a metaphosphate glass is also affected by the modifying cation, as indicated by a variety of spectroscopic studies. For example, the full width at half maximum (FWHM) of the \(^{31}\)P NMR peaks from series of metaphosphate glasses increases with the field strength of the modifying cation, indicating an increase in the distribution of P–O bond lengths and bond angles [35,115]. A similar trend was reported in the breadth of P–O bond lengths from a neutron diffraction study of several metaphosphate glasses [125]. Luminescence studies of Eu-doped metaphosphate glasses confirm the increase in the degree of disorder with increasing modifier field strength [116].

The phosphate chains are linked through bonds between terminal oxygens and the modifying cations, as shown schematically in Fig. 15 (right). Raman band broadening, frequency shifts, and a decrease in the ratio of the amplitudes of the \(v(PO_2)_{sym}\) (~1180 cm⁻¹) and \(v(POP)\) (~690 cm⁻¹) Raman bands (Fig. 17), as well as an increase in the amplitude ratio of depolarized vs. polarized spectra, indicate that the modifier-TO bond becomes increasingly covalent as the field strength of the modifier increases [117–120,130]. The resulting increase in the rigidity of the metaphosphate network is consistent with a concomitant increase in the glass transition temperature [121]. Thus, the properties of metaphosphate glasses are less dependent on the nature of the P–O–P bonds that form phosphate chains than on the P–O–Me inter-chain bonding.

A narrow (5–6 cm⁻¹) band is present on the low frequency side (~630 cm⁻¹) of the \(v(POP)\) band in the Raman spectra of Cs-, Rb- and K-metaphosphate glasses and melts [122] that is not present in the spectra of the metaphosphate glasses shown in Fig. 17. This narrow band increases in intensity as the size of the modifying cation increases and is assigned to a stretching mode of ordered phosphate chain segments with P–O–P bond angles of 180° [122].

Uchino and Yoko, in this volume [123], describe alkali metaphosphate clusters simulated by ab initio calculations and they note the important role played by the alkali ions in cross-linking and distorting neighboring metaphosphate...
clusters. From simulations of the vibrational spectra of their clusters, they correlate low frequency (<100 cm\(^{-1}\)) bands with rotational motions of Q\(^2\)-tetrahedra and suggest that it is the thermal excitation of such modes that is responsible for the structural rearrangements at the glass–liquid transition. Larger field strength cations increase structural rigidity, increasing the temperature required to activate the rotational motions, and so increasing \(T_g\). (The low frequency rotational modes modeled by Uchino and Yoko may be related to slower, sub-\(T_g\) relaxation processes, decoupled from faster viscous modes, in mixed alkali metaphosphate glasses described by Rufflé et al. [124].)

Neutron diffraction studies indicate a decrease in the mean P–O bond length with increasing modifier field strength [125], consistent with the interpretations of the Raman spectral trends described above. Variations in the intermediate range order of metaphosphate glasses have been measured by X-ray scattering [126] and by neutron diffraction [27]; prominent peaks in the structure factor were related to quasi-periodic superstructures, the dimensions of which depend on the modifying cation. Scattering from such structures may involve the electron density differences between the metaphosphate chains and the intervening metal oxide polyhedral configurations [127]. (See [29] for further discussion of these scattering studies.)

The structural environments of modifying cations in metaphosphate glasses have been determined in a variety of diffraction and X-ray absorption spectroscopic measurements. Table 2 summarizes some results. Of interest are the zinc metaphosphate glasses, in which the Zn[IV] ions combine with the Q\(^2\) P sites to form a tetrahedral network which has low temperature vibrational anomalies [128] and an unusually large photoelastic coefficient [129], reminiscent of three-dimensional network glasses such as silica.
Kordes identified a number of phosphate glass-forming systems, including BeO–P₂O₅, MgO–P₂O₅ and ZnO–P₂O₅, as ‘anomalous’ because they have unusual discontinuities in composition-property dependence (i.e., refractive index and molar volume) at the metaphosphate composition [3]. This dependence was originally explained by a coordination change of the modifying cation [3,4], but subsequent spectroscopic and diffraction studies generally failed to identify such a change. (For example, see Ref. [64] for references to studies of the ZnO–P₂O₅ glasses and Ref. [139] for a review of the MgO–P₂O₅ glasses.) Okura et al. [140] 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.

The ‘modifier coordination model’ described in Section 4.1.3 provides a likely explanation for the properties of the anomalous glasses identified by Kordes. Consider that the ‘anomalous’ divalent cations (e.g., Zn²⁺ and Mg²⁺) have coordination numbers of about 4 (Table 2). From Eq. (5), the transition from isolated divalent tetrahedra to corner-sharing tetrahedra will occur at 50 mol% RO; viz., the anomalous composition. The compositions at which the coordination requirements for monovalent and larger divalent cations (e.g., Ca²⁺) exceed the number of available terminal

Table 2
Cation coordination numbers (CN), average metal–oxygen and P–O bond distances reported for metaphosphate glasses

<table>
<thead>
<tr>
<th>Cation</th>
<th>CN</th>
<th>r_{Me–O} (Å)</th>
<th>Avg. r_{P–O} (Å)</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>4.0</td>
<td>2.02</td>
<td>1.52</td>
<td>XRD</td>
<td>[86]</td>
</tr>
<tr>
<td>Li⁺</td>
<td>4.0 (±0.4)</td>
<td>2.03 (±0.04)</td>
<td></td>
<td>ND</td>
<td>[130]</td>
</tr>
<tr>
<td>Na⁺</td>
<td>5.0 (±0.4)</td>
<td>2.38</td>
<td>1.57</td>
<td>XRD</td>
<td>[94]</td>
</tr>
<tr>
<td>Na⁺</td>
<td>5.7 (±0.4)</td>
<td>2.43 (4)</td>
<td></td>
<td>XRD</td>
<td>[88]</td>
</tr>
<tr>
<td>K⁺</td>
<td>6.7 (5)</td>
<td>2.77 (2)</td>
<td>1.48 (1) TO 1.625 (10) BO</td>
<td>XRD, ND</td>
<td>[59]</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>5.0 (±0.6)</td>
<td>2.9 (±0.1)</td>
<td></td>
<td>ND</td>
<td>[130]</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>3.4 (3)</td>
<td>2.362 (5)</td>
<td>1.590 (3)</td>
<td>XRD</td>
<td>[132]</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>4.0</td>
<td>2.06</td>
<td>1.53</td>
<td>XRD</td>
<td>[132]</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>4.9</td>
<td>2.33</td>
<td>1.52</td>
<td>XRD</td>
<td>[132]</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>7.0 (±0.4)</td>
<td>2.39</td>
<td></td>
<td>XRD</td>
<td>[88]</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>8.0</td>
<td>2.79</td>
<td>1.56</td>
<td>XRD</td>
<td>[94]</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>3.7 (3)</td>
<td>1.94 (1)</td>
<td></td>
<td>EXAFS</td>
<td>[134]</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>4.0 (2)</td>
<td>1.95 (1)</td>
<td>1.53 (1)</td>
<td>XRD</td>
<td>[134]</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>4.7 (4)</td>
<td>1.996 (5)</td>
<td>1.558 (3)</td>
<td>XRD</td>
<td>[131]</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>3.9 (4)</td>
<td>1.939 (3)</td>
<td>1.50 (1) TO 1.60 (1) BO</td>
<td>XRD</td>
<td>[54]</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>5.0 (4)</td>
<td>2.484 (5)</td>
<td>1.593 (3)</td>
<td>XRD</td>
<td>[131]</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>5.2 (6)</td>
<td>2.47 (2)</td>
<td>1.49 (1) TO 1.59 (1) BO</td>
<td>ND</td>
<td>[125]</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>8 (±1)</td>
<td>2.47</td>
<td></td>
<td>EXAFS</td>
<td>[135]</td>
</tr>
<tr>
<td>La³⁺</td>
<td>7.1 (5)</td>
<td>2.458 (15)</td>
<td>1.484 (5) TO 1.604 (5) BO</td>
<td>ND,XRD</td>
<td>[136]</td>
</tr>
<tr>
<td>La³⁺</td>
<td>7.3 (±1.2)</td>
<td>2.42 (±0.03)</td>
<td></td>
<td>EXAFS</td>
<td>[137]</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>10.4 (±2.7)</td>
<td>2.35 (±0.010)</td>
<td></td>
<td>EXAFS</td>
<td>[138]</td>
</tr>
<tr>
<td>Sm³⁺</td>
<td>6.9 (±0.3)</td>
<td>2.31 (±0.01)</td>
<td></td>
<td>EXAFS</td>
<td>[137]</td>
</tr>
<tr>
<td>Eu³⁺</td>
<td>7.6 (±0.2)</td>
<td>2.28 (±0.002)</td>
<td></td>
<td>EXAFS</td>
<td>[138]</td>
</tr>
<tr>
<td>Eu³⁺</td>
<td>6.2 (±0.3)</td>
<td>2.31 (±0.01)</td>
<td></td>
<td>EXAFS</td>
<td>[137]</td>
</tr>
<tr>
<td>Gd³⁺</td>
<td>5.7 (±0.3)</td>
<td>2.27 (±0.002)</td>
<td></td>
<td>EXAFS</td>
<td>[138]</td>
</tr>
<tr>
<td>Gd³⁺</td>
<td>5.0 (±0.4)</td>
<td>2.28 (±0.01)</td>
<td></td>
<td>EXAFS</td>
<td>[137]</td>
</tr>
<tr>
<td>Tb³⁺</td>
<td>8.0 (±0.2)</td>
<td>2.25 (±0.002)</td>
<td></td>
<td>EXAFS</td>
<td>[138]</td>
</tr>
<tr>
<td>Ho³⁺</td>
<td>7.0 (±0.1)</td>
<td>2.20 (±0.001)</td>
<td></td>
<td>EXAFS</td>
<td>[138]</td>
</tr>
</tbody>
</table>

The P–O distances are averages, unless otherwise indicated. Limit errors, from original references, are in parentheses.
oxygens are in the ultraphosphate range and hence those metaphosphate glasses do not have the anomalous properties. Hoppe et al. [136] used a similar analysis to explain the correlation of La–O–La bonds in a diffraction study of a La-metaphosphate glass. La\(^{3+}\) has a coordination number of about 7, which exceeds the number of available terminal oxygens in that composition (Eq. (5)), necessitating the corner sharing by neighboring La-polyhedra.

4.3. Polyphosphate glasses ([O]/[P] > 3.0)

A variety of spectroscopic techniques detect changes in the average chain length (or, by extension, to the [O]/[P] ratio) for polyphosphate glasses. These include \(^{31}\)P NMR chemical shifts [44,141], P2p/P2s electron binding energies from XPS experiments [61], and P L-edge and K-edge energies from X-ray absorption spectroscopy [142]. Such studies indicate a decrease in the average \(\pi\)-bond character of a P–O bond with increasing modifier content [24] and can account for variations in optical basicity as measured by fluorescence and absorption spectroscopy of phosphate glasses doped with optically active ions [143–146]. The evolution of extended range order, from that associated with a 3D cross-linked ultraphosphate network to metaphosphate chains to pyrophosphate dimers with increasing modifier content has been measured by neutron diffraction and inelastic scattering [73].

The distribution of chain lengths in polyphosphate glasses is best determined by chromatographic analyses of solutions of dissolved glasses e.g., [147,148]. Such techniques can quantitatively detect phosphate anions with chain lengths up to 30 tetrahedra [149]. Anion distributions were quantitatively explained by Van Wazer [2], using an approach originally developed by Flory [150] to describe the distributions of polymer molecular weights. Reorganization of phosphate anions in a liquid depends on disproportionation reactions of the type

\[
2(P_nO_{3n+1})^{-(n+2)} \leftrightarrow (P_{n+1}O_{3n+4})^{-(n+3)} + (P_{n-1}O_{3n-2})^{-(n+1)} \quad (7a)
\]

and these reactions will have equilibrium constants defined by

\[
k_n = \frac{([P_{n+1}O_{3n+4}]^{-(n+3)}) \left([P_{n-1}O_{3n-2}]^{-(n+1)}\right)}{\left([P_nO_{3n+1}]^{-(n+2)}\right)^2}.
\]

The distribution of chain lengths, at constant \([O]/[P]\), depends on the type of modifying cation and such analyses can be related to various glass properties. Fig. 18 (left) shows chromatographs obtained from three different polyphosphate glasses [151]. The Na-glass has the narrowest distribution of P-ions and the Al-glass has the broadest distribution. As seen in Fig. 18 (right), the latter liquids have larger equilibrium constants for the disproportionation reactions (Eqs. (7a) and (7b)); these reactions appear to shift to the right as the field strength of the modifying cation increases. The more complicated phosphate structures that result from the larger anion distributions can be correlated with ease of glass formation [147,151]. A similar cation sensitivity for ‘structural complexity’ was noted above for the metaphosphate glasses. (Sales reviews chromatographic studies of polyphosphate glasses elsewhere in this volume [152].)

Anionic distributions in polyphosphate glasses can also be described using the tetrahedral-sensitive spectroscopic techniques discussed above. The advantage is that information can be obtained about the phosphate anions without first dissolving the glass, as must be done for chromatographic analyses. For example, Fig. 19 (left) shows the \(^{31}\)P NMR spectrum collected from a 67ZnO:33P\(_2\)O\(_5\) glass [64]. Based on stoichiometry, only Q\(^1\) sites should be present, but the spectrum indicates detectable concentrations of Q\(^2\) and Q\(^0\) sites that result from Q\(^1\) site disproportionation reactions that occur during the reorganization of the glass liquid

\[
2Q^1 \leftrightarrow Q^2 + Q^0.
\]

Fig. 19 (right) shows the quantitative distributions of tetrahedra from a series of \(x\)ZnO(1–\(x\))P\(_2\)O\(_5\) glasses. The open symbols are tetrahedral distributions determined from high-performance liquid chromatography [153] and the closed symbols are
the results from a $^{31}$P NMR study [64]. By treating the disproportionation reaction (8) as an equilibrium reaction and assuming constant activity coefficients for each site, the NMR results indicate that $k_1 = 0.028 \pm 0.018$. One consequence of this analysis is that $k_n$ depends not only on the field strength of the modifying cation (Fig. 19, right) but also on the liquid temperature [147], and so it is possible to modify the constitution of the phosphate network by varying the melt conditions.

Montagne et al. [154] used NMR to observe similar site disproportionation reactions in polyphosphate glasses when ZnO is added to NaPO$_3$. Tatsumisago et al. [65] used Raman spectroscopy to study the same in Li-polyphosphate glasses. Efimov [155] used infrared spectroscopy to study the structures of alkali zinc pyrophosphate glasses and concluded that the $Q^2$ tetrahedra in Eq. (8) are incorporated into (P$_2$O$_3$)$^{3-}$ metaphosphate rings, particularly in the zinc-rich compositions.
An interesting feature of Zn-pyrophosphate glass is that the addition of an alkali oxide (replacing ZnO) increases its aqueous corrosion resistance [156]. This improvement in durability has been correlated with a concomitant decrease in the fraction of more easily hydrolyzed Q^2 sites [156]; viz., replacing ZnO with an alkali oxide shifts the disproportionation reaction (8) to the left to yield a more durable glass. This change in structure is seen in the Raman spectra from a series of Zn-phosphate glasses (adapted from [64]). The solid lines in the distribution figure represent predicted tetrahedral distributions based on Eqs. (2c)-(2f), whereas the dashed lines account for Q^1 disproportionation, according to Eqs. (7a) and (7b). Open symbols are tetrahedral concentrations reported in a high-performance liquid chromatography study of similar glasses [153].

Fig. 19. \(^{31}\)P MAS NMR spectrum from a 0.67ZnO-0.33P\(_2\)O\(_5\) glass (top) indicating the presence of Q^0, Q^1 and Q^2 tetrahedra and the distributions of tetrahedra (bottom) determined from the NMR spectra from a series of Zn-phosphate glasses (adapted from [64]). The solid lines in the distribution figure represent predicted tetrahedral distributions based on Eqs. (2c)-(2f), whereas the dashed lines account for Q^1 disproportionation, according to Eqs. (7a) and (7b). Open symbols are tetrahedral concentrations reported in a high-performance liquid chromatography study of similar glasses [153].

Fig. 20. Raman spectra collected from \(x\text{Li}_2\text{O}(67-x)\text{ZnO}\) \(3\text{P}_2\text{O}_5\) glasses. (Adapted from Ref. [156].)
with the elimination of bridging P–O–P bonds associated with Q² tetrahedra [158].

Distributions of tetrahedral linkages in polyphosphate glasses have been measured using the multi-dimensional NMR techniques described above. For example, the $^{31}$P double-quantum NMR spectrum of 58Na$_2$O·42P$_2$O$_5$ glass reported by Feike et al. [79] resolves Q²–Q², Q²–Q¹ and Q¹–Q¹ linkages, although the latter might be due to weak dipolar couplings between neighboring Q¹ end-groups. In this volume, Jäger et al. [111] report procedures by which the DQ experiments provide quantitative information about polyphosphate network connectivity. They found that Q² tetrahedra in trimer anions (P$_3$O$_{10}$)$_5^-$ that are bonded to two Q¹ tetrahedra (labeled Q²;11) can be resolved from Q² tetrahedra connected to one Q¹ and one Q² (Q²;22) or from Q² tetrahedra connected to two other Q² (Q²;22). Similar information is provided for the various Q¹;j;k tetrahedra. By determining the relative concentrations of the different Q¹;j;k sites, it will be possible to obtain chain-length distribution information for phosphate glasses similar to that obtained by chromatography but without dissolving the sample [159]. Jäger et al. [111] also raise the possibility that, by determining the relative orientations of the chemical shift tensors, bonding angle data might be obtained in future DQ NMR experiments.

Olsen et al. [160] examined Ag-metaphosphate and Ag-polyphosphate glasses, with and without AgI dopants, using both radio frequency dipole recoupling (RFDR) and $^{31}$P double-quantum experiments. They showed for the former glass that the Q² metaphosphate structure was retained after AgI additions and they could resolve pyrophosphate tetrahedra from Q¹ sites terminating chains in the latter, polyphosphate system. The addition of AgI to AgPO$_3$ appears to ‘open up’ the metaphosphate network [161] without breaking the metaphosphate chains. This effect differs from the effects of the addition of alkali fluorides to alkali metaphosphate glasses, where fluorine replaces bridging oxygens [162], shortening the average polyphosphate chain-length. When LiF is added to LiPO$_3$, fluorine is partitioned between fluorophosphate terminal groups and Li–F fragments [163]. In contrast, the addition of LiCl to LiPO$_3$ leaves the metaphosphate chains unchanged but further separated by the intervening LiCl phase [86], analogous to the effects of AgI additions to AgPO$_3$, described above.

Two-dimensional heteronuclear correlation NMR techniques are now being used to describe modifier bonding in polyphosphate glasses. Mueller and co-workers [90,164] have resolved Na ions near Q² tetrahedra from ones near Q¹ tetrahedra in single and mixed alkali polyphosphate glasses. Such techniques will become increasingly important for the determination of structural organization beyond a local polyhedron.

There are other interesting properties associated with ‘invert’ poly- and pyrophosphate glasses. Glasses in the alkali-modified zinc phosphate system can be prepared with transformation temperatures of 275–375°C, low enough to allow them to be blended with polymers and molded using conventional plastic forming equipment [8]. A related family of glasses is based on the (SnO + ZnO)-pyrophosphate system, under development for low temperature (<200°C), PbO- and alkali-free sealing applications [165]. Properties in this system can be tailored by varying the SnO/ZnO ratio.

The depolymerized Sn-phosphate system has yielded another unusual family of glasses. Tick [166] showed that durable compositions with glass transformation temperatures as low as 100°C could be formed from mixtures of SnO, SnF$_2$, and P$_2$O$_5$, particularly when ([O] + [F]/2)/[P] ~4. The resulting glass networks consist of low coordinated (probably 3 or 4) Sn(O, F) polyhedra linked to isolated or dimer fluorophosphate units in the most durable compositions [167]. The very high thermal expansion coefficients and (too) low glass transformation temperatures probably limit sealing applications for these materials. However, the glasses have been used as chemically stable hosts for low-temperature optically active organic molecules [168].

Orthophosphate compositions from the Li$_2$O–Al$_2$O$_3$–TiO$_2$–P$_2$O$_5$ system have been used to prepare fast-ion conducting glass-ceramics [11] and porous glass-ceramics with membrane, ion exchange and catalytic applications [169]. Such compositions are from the NASICON (Na-superionic conductors) family of orthophosphate
glass forming systems (see [170] for a review of some of these compositions). Other depolymerized titanophosphate glasses have been developed for non-linear optical applications. The hyperpolarizability of Ti-polyhedra increases the non-linear refractive index coefficient \( n_2 \) to make titania-containing glasses useful for photonic devices [171]. Analogous to the Fe-phosphate glasses [172], the titanophosphate glasses possess ‘invert’ networks based on linkages between small \((Q^0, Q^1, Q^2)\) phosphate anions and distorted octahedral titanate species, charge balanced by alkali or alkaline cations [173] and, when crystallized, can form bioactive ortho- and pyrophosphate phases [174].

5. Concluding remarks

New technological applications have spurred much of the recent interest in the structures of simple phosphate glasses. The ultraphosphates are among the simplest compositions but their structures and properties were not properly understood before the recent recognition that special handling procedures are necessary to fabricate anhydrous samples. The anomalous compositional dependencies of glass properties (e.g., Fig. 5) cannot (yet) be adequately explained by changes in the details of the phosphate network structure. There are no P-coordination changes, as found in simple borate and germanate systems, nor do there appear to be any particular relationships between the distributions of tetrahedral linkages and properties. Instead, it appears that the ‘phosphate anomaly’ depends on the modifier sub-structure, with breaks in physical properties associated with compositions that represent a transition from isolated modifier polyhedra to polyhedra linked through non-bridging oxygens on Q\(^2\) tetrahedra. Future spectroscopic and modeling studies that provide details about the modifier bonding environments will provide critical tests for this structural description. New heteronuclear, multi-dimensional NMR experiments will be among the more important of these analyses.

A quantitative understanding of the local environments of oxygen ions in simple phosphate glasses will also provide critical information to test structural models. X-ray photoelectron spectroscopy has provided some quantitative information about the concentrations of different (bridging and non-bridging) oxygen sites, as well as some limited, qualitative information about bond order. Solid state \(^{17}\)O NMR experiments has provided detailed information about oxygen bonding, including bond angles and local coordination environments in silicate-based glasses (e.g., see [175,176]) and similar quantitative information is expected for the phosphate glasses. Among the questions that might be answered by such experiments: Are there differences between the non-bridging oxygens on individual Q\(^2\) and Q\(^1\) tetrahedra? Does the Q\(^3\) double-bonded oxygen \((P\equiv O)\) lengthen at \(x \sim 20\) mol\% alkali oxide, as indicated in the Raman spectra? Do bridging oxygens participate in the local coordination environment of modifying cations, in conflict with the predictions of the ‘modifier coordination’ structural model? How do the P–O–P bond angles change at the transition from isolated to linked alkali polyhedra? What relative level of order exists for bridging and non-bridging oxygens?

Critical experiments that describe in detail the longer-range phosphate network structures will also be important for establishing quantitative structure-property relationships for phosphate glasses. Chromatography experiments provide information about P-anion distributions in polyphosphate compositions, but critical information about chain conformation (including P–O–P bond lengths and angles) that is implied in broad vibrational and NMR spectra is lost in the preparation of liquid chromatography samples, as is network bonding information in ultraphosphate compositions. New solid state multi-dimensional, multiple quantum NMR experiments hold promise for providing that information, particularly for the ultraphosphate compositions that cannot be analyzed by liquid chromatography. These new spectroscopic techniques will also be important for determining the relative importance of rings and chains to the properties of phosphate glasses. For example, does the formation of small, energetic phosphate rings contribute to the ‘phosphate anomaly’? Is the anomaly a consequence of the
entanglement of long phosphate chains with increasing alkali content?

These and other spectroscopic techniques will also be applied to studies of glass liquids to determine structural changes upon heating through the glass transition. Among the questions to be answered are those related to temperature dependencies of ring and chain formation and the relative role of changes in the modifier coordination environment in determining the properties of phosphate liquids. A separate question is whether simple anhydrous ultraphosphate melts have liquid–liquid immiscibility. I am unaware of reports on this topic.

Finally, future spectroscopic studies of the structures of phosphate glasses will benefit from improved structural simulations based on ab initio and molecular dynamics (MD) calculations. Improved molecular orbital descriptions will help decipher subtle spectroscopic information associated with structural changes due to variations in O/P ratios and the nature of modifying cations. Such calculations will also lead to more accurate potentials for $P^{5+}$ ions that will then be used in future MD simulations that should provide important long-range structural information.

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