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# Influence of glass structure on the ac conductivity of alkali phosphate glasses

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## Abstract

The conductivity dispersion in several alkali phosphate glasses is examined as the glass structure changes from an interconnected ‘mesh’ network to one of phosphate chains cross-linked by alkali ions. For metaphosphate glasses the dispersion varies in response to the size of the mobile ion relative to the mean spacing between phosphate chains. Preliminary work on ultraphosphate glasses suggests this ‘constriction’ effect largely disappears as the chain structure is replaced by a mesh structure. However, some puzzling changes in the conductivity dispersion with respect to alkali ion size remain. It is suggested that these changes may be related to a ‘re-polymerization’ mechanism thought to occur in phosphate glasses.

## 1. Introduction

A large class of materials, referred to as solid-state ionics, owe their technological importance to the motion of mobile charges (via hopping) through a solid matrix. These materials include both ion-conducting crystals and glasses which find application in solid fuel cells and chemical sensors among other devices [1]. The path to understanding the motion of ions through the surrounding matrix lies principally in understanding the microscopic origins of the peculiar time dependence of the ions’ mean square displacement,  $\langle r^2(t) \rangle$ . This  $\langle r^2(t) \rangle$  arises partly from the hopping motion of the ions and produces [2] a contribution to the measured ac conductivity of the material. This ac conductivity displays a frequency dependent dispersion of the approximate form [3, 4]

$$\sigma(f) \approx \sigma_o(1 + (f/f_o)^n) + Af. \quad (1)$$

The dc conductivity, evident at low frequencies, corresponds to random ‘uncorrelated’ ion hopping for which  $\langle r^2(t) \rangle$  increases in proportion to time in the manner of a random walk. At higher frequencies, this random motion is supplanted by ion motion that is ever increasingly ‘correlated’ [5] and for which  $\langle r^2(t) \rangle$  displays sub-diffusive time dependence.

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Although the expression given above for  $\sigma(f)$  is only approximate [6], the actual frequency dependence of the ac conductivity often preserves its shape and conforms to scaling [7–11] in the sense that individual  $\sigma(f)$  spectra can be combined to form a ‘master curve’ given as

$$\frac{\sigma(f)}{\sigma_o} = F_1(f/f_o). \quad (2)$$

Such scaling is possible for a given ion conductor for  $\sigma(f)$  spectra obtained at different temperatures, even above and below the glass transition temperature [11], and often for  $\sigma(f)$  obtained from a series of different ionic glasses of varying ion concentration [7, 8, 10]. Since the frequency dependence of the ac conductivity is related in an isomorphic manner to the time dependence of  $\langle r^2(t) \rangle$ , this scaling consequently implies a corresponding scaling of  $\langle r^2(t) \rangle$  in the form [2]

$$\frac{\langle r^2(t) \rangle}{\xi^2} = G_1(t/t_o), \quad (3)$$

where  $\xi^2$  corresponds approximately to the  $\langle r^2(t) \rangle$  attained at  $t \approx t_o = 1/f_o$ . This necessarily means that the inherent pattern of correlated ion motion is often preserved in cases where the ion concentration is varied or in ionic melts (e.g. calcium potassium nitrate) when a liquid to glass transition is crossed [11]. In both these examples, structural changes occur that result in significant changes in such properties as the density, glass transition temperature and response of the material to an applied stress. Yet, these changes do not appear to disturb the correlated motion of the ions in any *inherent* fashion (since the shape of the dispersion is conserved).

While many ionic materials show tremendous tenacity in that the dispersion is impervious to changes in the glass structure, there are some instances where compositional changes do cause systematic variations in the conductivity dispersion. The present study focuses on these ‘exceptions’ which deviate from scaling in an effort to help elucidate the origins of the correlated motion in ion conducting glasses.

## 2. Background

### 2.1. Dimensionality

Several years ago a survey [12] of  $\sigma(f)$  data available from the literature was conducted from which estimates of the power law exponent ( $n$ ) of the ac conductivity given in equation (1) were obtained and compared. It was observed that for many of the traditional alkali oxide glasses, the exponent was narrowly distributed near  $n = 2/3$ . Indeed, none of the materials surveyed possessed  $n$  greater than 0.7. The exceptions to this  $n = 2/3$  result were the so-called ‘mixed-alkali’ (MA) glasses, in which roughly half the alkali ions (e.g.  $\text{Li}^+$ ) are replaced by ions of another species (e.g.  $\text{Na}^+$ ), and the glasses in which halide anions had been introduced. The survey also included ion-conducting crystals like  $\beta\text{-Al}_2\text{O}_3$  in which ion motion is constrained to two-dimensional conduction planes and Hollandite where the ion motion is constrained to one-dimensional channels. For these crystalline ion conductors the exponents were approximately  $n = 0.6$  and  $0.3$ , respectively.

These trends in the power law exponent naturally indicate that the correlated ion motion is in some way influenced by the dimensionality of the conduction pathways. In fact, it was proposed that traditional oxide glasses, with  $n = 2/3$ , possessed some maximal dimensionality of conduction space associated with a random disordered network, and that the exponent decreased with decreasing dimensionality, as was indicated by the behaviour of the two- and one-dimensional conducting crystals. The suppressed exponents seen for MA glasses and halide-doped glasses were also thought to reflect a reduction of the dimensionality of the

conduction pathways over that present in single-alkali and undoped oxide glasses. In these instances, the reduced dimensionality is thought to arise from a separation of the original contingent of conduction pathways into percolated subsets [13, 14] that are either ‘preferred’ or ‘unfavoured’.

Since this survey, it has become clear that the  $\langle r^2(t) \rangle$  corresponding to correlated motion is a *localized* process in which the cation moves no further than a few ångströms from its initial position [12, 15]. As a consequence, the concept of dimensionality of the conduction pathways has been replaced by the notion of a ‘coordination of the local conduction space’ (CLCS) which better reflects the localized nature of the motion. This CLCS can be envisioned as the average number of ‘doorways’ that are available in the immediate vicinity of a mobile ion.

## 2.2. Constriction

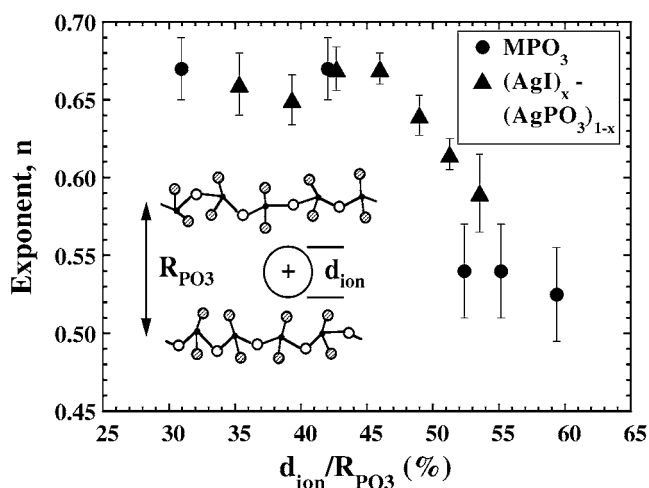
Further support for the proposal that the correlated motion is sensitive to the CLCS comes from a recent study [16] of alkali metaphosphate and AgI-doped  $\text{AgPO}_3$  glasses which reported an ion ‘constriction’ effect. In the AgI-doped glass, the addition of the halide anion (which is incorporated between long  $(\text{PO}_3)_n$  chains) serves to increase free volume and open the conduction pathways to better accommodate the  $\text{Ag}^+$  ion [17]. As a result, the  $\text{PO}_3$  chains of the metaphosphate network are spread apart [18] by the halide anion resulting in a maximal CLCS for the  $\text{Ag}^+$  ion associated with a disordered network. This causes the exponent to increase systematically from  $n \approx 0.60$  found for  $\text{AgPO}_3$  to  $n \approx 2/3$  for AgI contents of 30 mol% and above [16].

This same influence was also found in a series of alkali metaphosphate glasses of differing alkali ion size (e.g.  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$ ) where  $n = 2/3$  was observed for the  $\text{LiPO}_3$  and  $\text{NaPO}_3$  glasses, but  $n \approx 0.54$  for the glasses containing the larger cations. Here the change in dispersion was again attributed to a collapse of the  $(\text{PO}_3)_n$  chains around the larger cations resulting in reduced CLCS. This collapse is incomplete for the smaller cations. Indeed, the dispersion exponent obtained in both the alkali metaphosphate and AgI-doped  $\text{AgPO}_3$  glasses could be plotted in a combined manner as a function of the cation constriction; namely the ratio of the cation size to the average spacing between phosphate chains. This plot is reproduced in figure 1 and shows that for constrictions below about 50% the collapse of the chains about the cation is insufficient to produce a reduction of CLCS, while above 50% the collapse is sufficient and the exponent is decreased from  $n = 2/3$ .

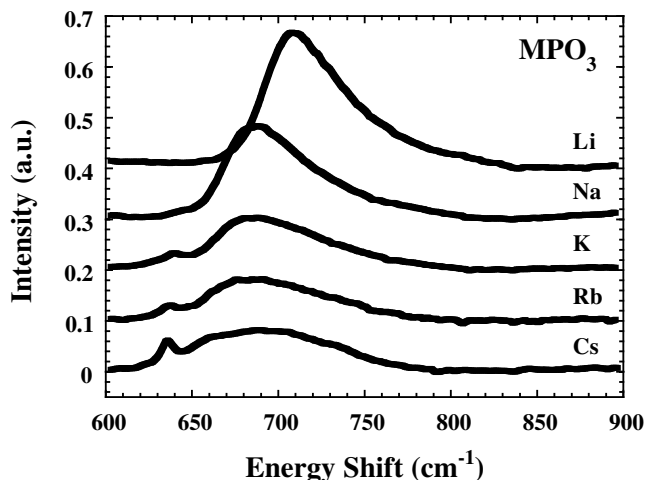
This constriction effect was also supported by measurements of the line width of the far infrared absorption [19] associated with the quasi-vibrational motion of the alkali cation in metaphosphate glasses which displays a corresponding ‘break’ in the vicinity of 50% with narrow modes seen at constrictions below 50%. Additional support is found from Raman scattering spectra of the alkali metaphosphate glasses, shown in figure 2, which show the increasing development of a small sideband (near  $630 \text{ cm}^{-1}$ ) from the P–O–P symmetric stretch mode (near  $680 \text{ cm}^{-1}$ ) with increasing alkali size. This mode has been previously attributed [20] to the presence of neighbouring  $\text{PO}_3$  tetrahedra that are bonded by an approximately  $180^\circ$  angle. Such ‘straightening’ of the  $(\text{PO}_3)_n$  chains is another anticipated result of the ion constriction and would be expected to occur in the vicinity of a large ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) constricted cation.

## 2.3. Topology

While the constriction effect provides a prime example of how the conductivity dispersion can be modified by changes in the CLCS, the effect may be a unique feature of the chain structure of

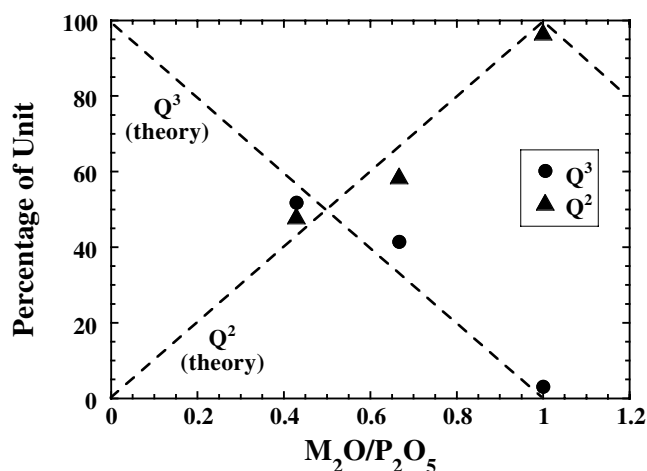


**Figure 1.** Variation of the conductivity exponent  $n$  in  $\text{MPO}_3$  glasses and AgI-doped  $\text{AgPO}_3$  glasses with respect to the constriction as defined by the ratio of the cation diameter,  $d_{\text{ion}}$ , to the mean separation between  $\text{PO}_3$  chains,  $R_{\text{PO}_3}$ .



**Figure 2.** Raman scattering spectra for a series of alkali metaphosphate glasses showing the symmetric P–O–P mode. Spectra have been shifted vertically for clarity. The small peak that develops near  $635\text{ cm}^{-1}$  with increasing alkali size is attributed to the presence of P–O–P bonds forming a  $180^\circ$  angle.

the metaphosphate glasses. For example, alkali trisilicate glasses exhibit  $n \approx 2/3$  for both  $\text{Na}^+$  and  $\text{K}^+$  cations [11], suggesting that the constriction effect is absent in trisilicate glasses. Why might this be? Unlike the  $\text{MPO}_3$  glasses, these silicate glasses possess a continuous ‘mesh’ network structure that is randomly punctuated by non-bridging oxygen atoms (NBOs). We propose that this mesh topology might preclude the sort of collapse about the cation that was possible in the case of the chain topology of the metaphosphates. The chain structure of the metaphosphate glasses can be likened to a polymeric fluid in which the long polymer strands are mutually entangled. Locally, these strands can pack close to one another and can effectively



**Figure 3.** Percentage of  $Q^3$  and  $Q^2$  units in ultraphosphate glasses as a function of the  $M_2O/P_2O_5$  ratio. Symbols denote values obtained from the NMR analysis of the potassium ultraphosphate glasses discussed in the text.

collapse around a mobile cation. By comparison, the mesh network is obtained by randomly cross-linking these chains by bridging oxygen (BO) bonds. These covalent bonds may serve to limit the collapse of the network around the cation and thus negate any constriction effect.

Ultra-phosphate glasses, in principle, provide an excellent means to study the effects upon the conductivity dispersion produced by a continuous transformation of the oxide network from one of a mesh structure to one of infinite chains. This transformation is achieved simply by modifying the alkali content. Excellent reviews [21, 22] on the subject of phosphate structure are available and describe the oxide network using the conventional  $Q$ -site notation. In amorphous  $P_2O_5$ , the glass structure is composed of  $PO_4$  tetrahedra in which three of the four oxygen atoms are bonded to neighbouring P atoms and the fourth oxygen is double bonded and unattached to any neighbouring P atom. Such unattached oxygens are referred to as terminal oxygens (TOs). In terms of the  $Q$ -site notation,  $P_2O_5$  is entirely composed of  $Q^3$  units, that is phosphate units with three BO bonds. Addition of the modifier produces a uniform conversion of  $Q^3$  into  $Q^2$  units ( $PO_3$  units that possess two BO bonds) [21]. Evidence suggests [22] that the unbalanced charge of the newly formed NBO is distributed evenly over the two TOs. This conversion is illustrated in figure 3 and continues right up to the metaphosphate composition without any significant formation of  $Q^1$  (single-BO) or  $Q^0$  (unbonded) units. Thus, in the phosphate system, the network topology is directly transformed from mesh to chain with alkali addition.

What do we anticipate will happen to the dispersion exponent as  $P_2O_5$  is added to the alkali metaphosphate glasses and a mesh network replaces the chain topology? For the large cations ( $K^+$ ,  $Rb^+$ ,  $Cs^+$ ) which appeared constricted in the  $MPO_3$  matrix, the addition of  $P_2O_5$  with the formation of oxide cross-links (branches) between chains should expand the structure and remove the constriction. With the constriction removed, the CLCS should increase to that maximal quantity seen in the majority of ion-conducting glasses for which  $n \approx 2/3$ . The small cations ( $Li^+$  and  $Na^+$ ), by contrast, did not appear constricted by the  $MPO_3$  matrix and so already appear to possess a full contingent of doorways and, hence, maximum CLCS. The oxide cross-links added to the matrix by adding  $P_2O_5$  can do nothing more to further increase the CLCS of these small cations. We anticipate then that the dispersion of the small cations will remain fixed at  $n \approx 2/3$  across the entire ultraphosphate range.

In this paper, we report dielectric studies of ultraphosphate glasses containing  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$ , which are designed to examine the question posed above and test these anticipated variations of the conductivity dispersion with changing  $\text{P}_2\text{O}_5$  content. We find that the large cations in the constricted  $\text{MPO}_3$  follow the anticipated trend with their dispersion exponent returning to approximately  $n = 2/3$  as the chain structure is replaced by a mesh. However, the small, unconstricted cations do not display the anticipated composition-independent behaviour, but rather display an exponent that decreases from  $n \approx 2/3$  with increasing  $\text{P}_2\text{O}_5$ . This second result is unexpected, but could be a consequence of a unique ‘re-polymerization’ mechanism [23] present in phosphate glasses which promotes enhanced oxygen coordination around the cation. This enhancement might serve to reduce the CLCS of small cations and so account for the anomalous trend seen for the conductivity dispersion.

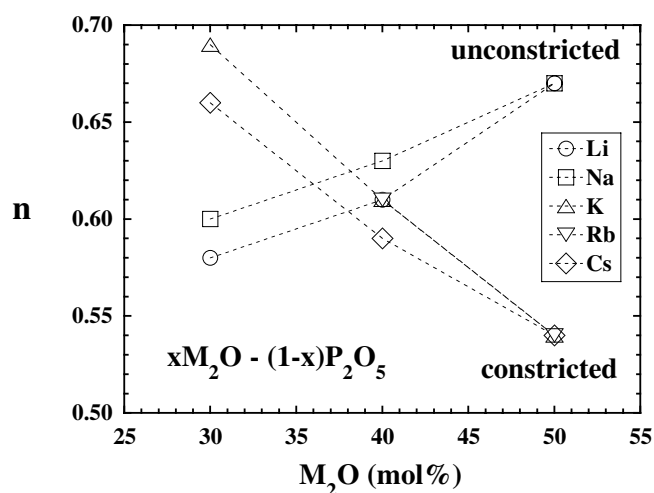
### 3. Experimental details

The synthesis of metaphosphate  $\text{MPO}_3$  glasses has been discussed previously [16] and involved the decomposition of  $\text{MNO}_3$  with ammonium dihydrogen phosphate (ADP) to form anhydrous  $\text{MPO}_3$  crystals. This initial reaction was carried out in a Pyrex beaker at approximately  $300^\circ\text{C}$ . The  $\text{MPO}_3$  crystals were melted at approximately  $900^\circ\text{C}$  in a silica crucible and poured and pressed into glass discs suitable for impedance measurements.

Ultraphosphate glasses are notoriously difficult to produce [21, 22]. Phosphorus pentoxide is both volatile and highly hygroscopic and thus any casual melting approach is likely to yield glasses deficient in  $\text{P}_2\text{O}_5$  and contaminated by water. Even if anhydrous samples can be produced, they must be handled in controlled atmospheres to avoid attack by water. In our study, ultraphosphate glasses were produced by two routes. The first route was essentially that used above to produce the metaphosphates. Namely, alkali nitrate and ADP were decomposed to form a crystalline form of the desired ultraphosphate composition, and this crystal was later re-melted to form the glass. A careful NMR analysis of the K-ultraphosphate glasses produced in this manner indicates that the approach did produce the desired glasses with less than 1% water content, at least for compositions from  $x = 30$  mol% to  $x = 50$  mol% alkali oxide. The fractions of  $Q^3$  and  $Q^2$  units present in these potassium ultraphosphate glasses, as determined from the NMR analysis, are shown in figure 3.

Glasses of alkali oxide content less than 30 mol% could not be produced by the above method and were instead prepared by direct melting of  $\text{MPO}_3$  and  $\text{P}_2\text{O}_5$  in sealed quartz ampoules. This second route to producing ultraphosphate glasses allowed for the production of water free samples with no loss of  $\text{P}_2\text{O}_5$ . Upon cooling, these ampoules would break leaving irregular shaped chunks of quartz and glass from which small samples could be obtained for density measurements. However, since the phosphate glass is closely matched to the index of refraction of quartz and is efficient at bonding to quartz, it was difficult to separate the two glasses to obtain sufficient amounts to re-melt for impedance samples. Invariably, small shards of quartz present in the re-melted material would lead to stresses in the discs that would cause them to shatter on cooling. Consequently, we have been unable to produce impedance samples for compositions below 30 mol%  $\text{M}_2\text{O}$ .

Impedance measurements were performed using a commercial impedance analyser (Schlumberger 1260). The specimen was maintained in a temperature-controlled cell with a controlled atmosphere. Measurements of the ac conductivity over a range of frequencies between 1 Hz and 1 MHz were obtained at temperatures from ambient to near the softening temperature. These conductivity spectra were analysed using the expression given by equation (1) to obtain the conductivity dispersion exponent.



**Figure 4.** Observed variation of the conductivity exponent in ultraphosphate glasses containing differing alkali cations.

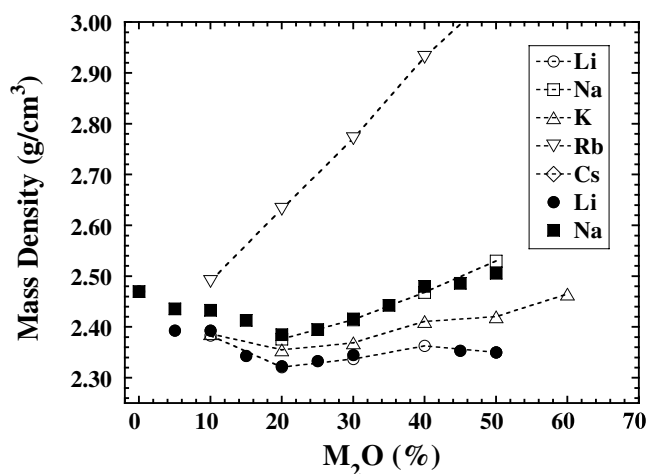
It is well documented that analysis of  $\sigma(f)$  by any empirical expression like equation (1) is afflicted by an inherent ‘window effect’ [6]. Briefly, this means that the power law exponent is only well defined for  $\sigma(f)$  spectra whose characteristic frequency ( $f_o$ ) falls near the centre of the available frequency window. In our analysis, we have been acutely cognizant of this practical limitation, and are careful to only compare  $\sigma(f)$  spectra of similar  $f_o$  when considering compositional variations of the power law exponent.

#### 4. Results

Figure 4 shows the observed variations of the conductivity exponent for the alkali phosphate glasses studied to date. As is evident, the dispersion exponent of the large cations increases to  $n \approx 2/3$  with increasing  $P_2O_5$  content. This is consistent with our prediction that the constriction of these large cations in the  $MPO_3$  glasses resulting from the chain topology would be removed as that structure is replaced by a mesh. The small cations, however, do not display the anticipated composition-independent dispersion. Instead, the conductivity exponent clearly decreases with increasing  $P_2O_5$  content. Within the context of our interpretation of the dispersion and its CLCS dependence, this result is anomalous and would suggest that these small cations somehow experience a decreasing CLCS with increasing  $P_2O_5$ .

In attempting to understand the unexpected trend of the small cation glasses, we first examine the possible effects of unwanted water in the samples. The chief effect of water on the conductivity spectra would likely be an increase in the dc conductivity due to protonic conduction. This would cause the conductivity spectra to exhibit a more acute transition from a dc regime to the dispersion regime and would cause the effective exponent to increase with increasing water content (i.e. increasing  $P_2O_5$ ), just the opposite of what is observed. In addition, the NMR characterization of the potassium ultraphosphates indicates that these glasses (at least down to 30 mol%) do not contain any significant amounts of water and the density measurements shown in figure 5 are in good agreement with the anhydrous glasses produced by Brow [22].





**Figure 5.** The mass density of ultraphosphate glasses containing differing alkali cations. Open symbols are for samples produced in the current study. Closed symbols are the values reported by Brow [22].

One possible interpretation for the anomalous behaviour of the small cations might be found in the re-polymerization effect (RPE) introduced by Hoppe [23] to account for the observation of a density minimum in divalent ultraphosphate glasses. Brow [22] has used this same RPE to account for both the density and  $T_g$  minimum found in  $\text{Li}^+$  and  $\text{Na}^+$  ultraphosphate glasses. A full description of the RPE can be found in Hoppe's paper [23]. Briefly, the RPE arises in phosphate glasses due to the availability of a large supply of TOs (about 40% in the form of double bonded oxygens or DBOs) even in the unmodified  $\text{P}_2\text{O}_5$  glass. According to Hoppe, the initial addition of  $\text{M}_2\text{O}$  to the  $\text{P}_2\text{O}_5$  network not only causes the rupture of BO bonds (so-called depolymerization), but also causes the density to decrease as  $Q^3$  units in the network expand so as to maximize the oxygen coordination of the alkali cation. Below a certain critical alkali concentration,  $x_c$ , the over-abundance of TOs leads to isolated cations surrounded by an oxygen rich local environment. This effectively increases the cross-linking of the network and acts as a repolymerization process which competes with the traditional bond-breaking depolymerization process that is well known for modifier addition in oxide glasses. Although experimental evidence for these coordination changes is unavailable for the alkali (monovalent) ultraphosphate glasses (due primarily to the difficulty in glass synthesis discussed earlier), it can be found in x-ray diffraction studies of both divalent [24] and trivalent [25] cations in ultraphosphate glasses. In both cases, substantial increases in the oxygen coordination number (CN) occur with decreasing ion concentration.

In the Hoppe model, the critical composition is given by the condition that the number of TOs just matches the 'normal' CN of the particular cation (i.e. that observed in the corresponding crystalline phase). For the monovalent alkali cations this condition implies  $x_c = 1/\text{CN}$  [22]. At concentrations above this critical concentration, the cations are no longer isolated, but occur in groups whose oxygen polyhedra contain shared corners and edges.

How might the RPE account for the compositional dependence of the conductivity dispersion seen in figure 4? We propose that there are two competing mechanisms that influence the CLCS and in turn the dispersion. The first is the topology change discussed earlier wherein the chain structure of  $\text{MPO}_3$  (which permits constriction) is replaced by a mesh structure (where constriction is precluded) causing the CLCS of the cation to increase. The other mechanism

is repolymerization, which acts to enhance the number of oxygens coordinating to the cation, decreasing the bulk density, but increasing the network density in the immediate vicinity of the cation with the result that the cations' CLCS is decreased.

The RPE is more dominant for the small cations for two reasons. First, the small cations are already unconstricted in the chain structure of the  $\text{MPO}_3$  glass network and so already possess a full contingent of doorways. For these small cations, the topology change is irrelevant. Second, since the CN is between three and four for  $\text{Li}^+$  and  $\text{Na}^+$  ions [26, 27], the critical concentration,  $x_c \approx 25\text{--}33$  mol%, occurs relatively close to the  $\text{MPO}_3$  composition and so the RPE becomes dominant even with small increases of  $\text{P}_2\text{O}_5$ . By comparison, the large cations are only weakly influenced by the RPE, since for these cations, with a CN between five and seven [26, 28], the effect only begins to dominate at  $x < x_c \approx 15$  mol%. Instead, these cations initially experience the increase of CLCS due to the topology change and display an increase in the dispersion exponent with increasing  $\text{P}_2\text{O}_5$  content.

If our interpretation of the compositional dependences of  $n$  shown in figure 4 in terms of this competition between topology change and RPE is correct, we anticipate that, like the small cations, the large cations will eventually display a decrease in the dispersion exponent with increasing  $\text{P}_2\text{O}_5$  content somewhere in the range of  $x < 20$  mol%. Currently, we are unable to produce reliable impedance samples at these levels and this will have to await further improvements in our preparation techniques.

## 5. Conclusion

In conclusion, we have examined the conductivity dispersion of a series of alkali ultraphosphate glasses containing both large ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) and small ( $\text{Li}^+$ ,  $\text{Na}^+$ ) cations. We find opposite trends for each, with the large cations displaying an increase of  $n$  with increasing  $\text{P}_2\text{O}_5$  content whereas  $n$  decreases for the small cations. While further investigation and improvements in glass synthesis are needed, we believe the anomalous composition dependences found here may be a consequence of competition between topology change of the phosphate network and a unique RPE present in the ultraphosphate system.

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