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Abstract
We report results of an extensive study of the structural relaxation occurring in mixed alkali metaphosphate liquids obtained by photon correlation spectroscopy. Values for the glass transition temperature, the fragility index, and the heterogeneity parameter (also known as the Kohlrausch exponent) are extracted from the measurements and are all shown to exhibit a mixed alkali effect wherein nonlinear variations with mixing occur. The depression in the glass transition temperature is shown to be the direct result of mechanical relaxations, present in the solid, which prematurely loosen the glass structure. A minimum in the fragility index is believed to be an artifact of the resulting depression of the glass transition temperature.

There has been considerable discussion in the glass community [1–5] regarding the peculiar behavior occurring in alkali-modified oxide glasses when approximately half of the alkali ions of a given species (say Li) are replaced by that of another (say Na). As a function of the mixing of these two alkali species, a so-called 'mixed alkali effect' (MAE) is observed wherein many properties are seen to vary in a nonlinear manner. An extreme example is that of the dc conductivity associated with the ion diffusion through the oxide network. In some cases, mixing of the two cations reduces the conductivity by several orders of magnitude in comparison to either single alkali composition itself [2]. In addition, new mechanical relaxations develop as a direct byproduct of the mixing [1]. These new mechanical modes signal the onset of additional energy barriers associated with ion hopping [3].

Current theoretical interpretations [4–7] for the MAE suggest it arises from a site mismatch mechanism. The oxide network which forms the local environment surrounding the cation adjusts itself to relieve local stress and accommodate the specific cation (say, A or B). As a result, the site itself takes on a specific identity; it is either an 'A-site' or a 'B-site'. In either single alkali case, if an ion leaves its site to move to another site no adjustment of the oxide network is required because all sites are equivalent and are preconfigured for their specific residents. However, in the mixed alkali situation, the movement of an A cation into a B-site (or vice versa) will necessitate an additional energy requirement associated with the reconfiguration of the site. This energy penalty shows itself by the new mechanical relaxation peak and by the increase in the activation energy for dc conduction.

Interestingly, the MAE is not altogether limited to the solid state. Some have noted that a mixing of alkali ions has a pronounced effect on the liquid-to-solid transformation producing a nonlinear reduction in the glass transition temperature in comparison with either single alkali glass [4]. An example is shown in figure 1 for a series of mixed $LiPO_3$ and $NaPO_3$ glasses. In his review, Ingram [4] puzzled over the 'contrary direction' of this MAE phenomenon in which the 'mixing of cations leads ... both to a loosening of the structure and, at the same time, to the immobilization of the cations'. So while current theories of the MAE appear to explain phenomena occurring in the solid, it is not clear how their relevance translates into the *liquid* state above T_g.

Traditionally, the glass transition temperature is defined by a viscoelastic timescale of roughly 100 s [8, 9]. The liquid state is that for which structural relaxation occurs on any shorter time. For glass-forming liquids the structural relaxation has two important characteristics. Firstly, the decay of the structure, as conveyed through (non-equilibrium) volume relaxation studies or (equilibrium) measurements of the dynamic structure factor, $S_q(t)$, exhibits a non-exponential dependence on time of the form:

$$S_q(t) = f_q \exp\{-(t/\tau)^\beta\}. \qquad (1)$$

Here, q is the scattering wavevector whose inverse represents the spatial range of density fluctuations being probed [10]. The
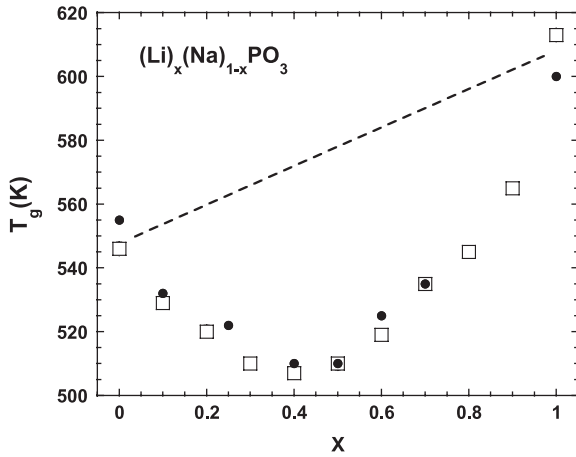
Figure 1. Variation of the glass transition temperature for $(Li)_x(Na)_{1-x}PO_3$ glasses. Solid circles are calorimetric data from [23] and open squares are from the present study. The dashed line indicates the compositional dependence anticipated for the glass transition temperature based only upon the average field strength of the cation.

smallness of the Kohlrausch exponent, β, is a measure of the degree of non-exponentiality. This exponent is also referred to as the heterogeneity parameter, since non-exponential relaxation can be equivalently viewed as the collective response of numerous microscopic relaxations occurring with a distribution of relaxation times [11].

A second characteristic of the dynamics of glass-forming liquids is the non-Arrhenius temperature dependence for the structural relaxation time (τ in equation (1)). This temperature dependence is often approximated by

$$\tau = \tau_o \exp\left\{\frac{DT_o}{T - T_o}\right\}. \tag{2}$$

Both of these features, the non-exponential and the non-Arrhenius behavior, have been shown to vary in a somewhat predictable manner with respect to the chemical structure of the glass-former. Generally, the oxide glasses in which the structure arises from a three-dimensional network of covalent bonds, tend to exhibit nearly exponential and nearly Arrhenius behavior [12]. For this reason, these glass-forming liquids are classified [13] as 'strong'. By comparison, the many molecular liquids whose structure arises from weaker van der Waals interactions tend to exhibit the greatest deviations from exponential and Arrhenius behavior. These latter liquids are classified as 'fragile'. It is customary to introduce a fragility index [12],

$$m = \left.\frac{d\log_{10}(\tau)}{d(T_g/T)}\right|_{T \to T_g}, \tag{3}$$

which characterizes the level of fragility.

Ionic relaxation occurs both in the solid and in the liquid state. The timescale for ionic relaxation is typically defined [14] by the Maxwell timescale comprising a ratio of the dc conductivity (σ_o) to the high frequency permittivity ($\varepsilon_o\varepsilon_\infty$):

$$\tau_\sigma = \frac{\sigma_o}{\varepsilon_o\varepsilon_\infty}, \tag{4}$$

where ε_o is the permittivity of free space. At very high temperatures, this ionic relaxation time is nearly equivalent to that of the structural relaxation. However, as the liquid cools the two relaxations begin to 'decouple' in the sense that the ionic relaxation occurs more rapidly than that of the surrounding oxide network [14, 15]. At the glass transition this decoupling becomes complete; the network is formally frozen and yet the ions continue to diffuse within the network. It is customary to classify the degree of decoupling by a 'decoupling ratio' [15] which characterizes the amount by which these two timescales have separated at T_g.

The theoretical picture behind the MAE involves a mechanism in which ions migrate into and out of well-defined sites in the oxide network of the glass. In the solid, where macroscopic structural relaxation vanishes and the ionic motion is fully decoupled, this mechanism is sharply defined. However, above T_g the return of macroscopic structural relaxation and the recoupling of ionic motions to that relaxation will necessarily degrade the MAE mechanism. To what extent the MAE persists into the liquid state remains to be determined.

To date, few of any studies have been devoted to examining the MAE in the liquid state far above T_g. We recently reported preliminary results of a dynamic light scattering study of the viscoelastic response of alkali metaphosphate melts including one mixed alkali composition [16]. Here we report extended measurements, canvassing the entire compositional range of mixing ratios for Li and Na cations. A MAE is found in the transition temperature, the heterogeneity parameter, and, to a lesser degree, in the fragility index. These compositional variations are explained within the framework of current theoretical interpretations of the MAE.

1. Experimental details

Samples of $LiPO_3$ and $NaPO_3$ were obtained by combining $NH_4H_2PO_4$ (Sigma Aldrich) with either Li_2CO_3 (Fisher) or Na_2CO_3 (Sigma Aldrich). This mixture was heated in a Pyrex beaker to about 550 °C to allow the reaction to take place. It was then cooled to obtain the crystalline form of the (single) alkali metaphosphate and ground into a fine powder. Mixed alkali samples were batched from these two stock powders.

After mixing, the powder sample was placed in a quartz ampoule manufactured from standard wall tubing (8 mm OD). The ampoule was carefully cleaned using a dilute solution of HF followed by repeated rinses with distilled water and flame dried under vacuum. Powder samples were melted in a commercial furnace (Thermolyne) at 900 °C for about 2 h to produce transparent, bubble-free melts.

Following the melting, the ampoule containing the sample was transferred to a preheated optical furnace. The optical furnace consisted of a stainless steel cylinder heated by an external winding of nichrome wire. The temperature of the optical furnace was controlled by a commercial controller (Omega Engineering) to provide less than 0.2 K variation over the duration of the measurements.
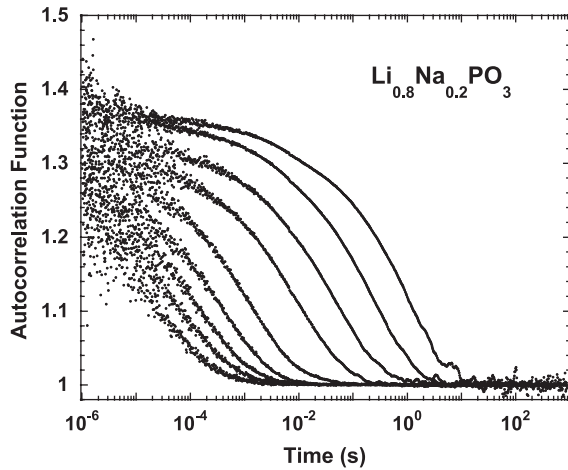
Figure 2. Intensity–intensity autocorrelation functions obtained for $(Li)_{0.8}(Na)_{0.2}PO_3$ liquid at selected temperatures (from left to right): 330.0, 325.0, 320.0, 315.0, 310.0, 300.5, 295.5, 290.5, and 285.6 °C.

Figure 3. Arrhenius plot of the relaxation time obtained from fitting the present measurements of the dynamic structure factor to equation (1).

Photon correlation spectroscopy (PCS) was then performed for a series of fixed temperatures as the liquid was cooled in steps toward T_g. Incident light of 532 nm wavelength from a diode-pumped solid state laser (Coherent Verdi) was focussed into the ampoule. The light scattered at 90° was collected by a lens, focussed onto a 50 μm pinhole and then passed to the active area of a photomultiplier tube (EMI 9863). Photopulses from the PMT were discriminated and digitized and then input into a commercial digital correlator (Correlator.com) which computed the intensity–intensity autocorrelation function for timescales ranging from 0.1 μs to 100's of seconds. This autocorrelation function is then related [10] to the dynamic structure factor as

$$\frac{\langle I(0)I(t)\rangle}{\langle I\rangle^2} = 1 + A_{coh}|S_q(t)|^2, \qquad (5)$$

where A_{coh} is an instrumental 'coherence' factor [17] which could be calibrated ($A_{coh} = 0.71 \pm 0.03$) for a given pinhole arrangement by performing measurements on a standard solution of polystyrene spheres.

An example of the measured autocorrelation function is provided in figure 2 for a metaphosphate liquid containing 80% Li and 20% Na ($x = 0.8$). With decreasing temperature, the decay of the autocorrelation function is progressively shifted to longer times as the liquid becomes more viscous. These autocorrelation spectra were then analyzed by fitting the dynamic structure factor to the stretched exponential (equation (1)) using a commercial data analysis software (Kaleidagraph) to obtain values for the relaxation time (τ), the stretching exponent (β) and the non-ergodic level (f_q).

A potential issue with performing PCS near a solidifying transition like the glass transition or a sol–gel transition, is the eventual development of a non-fluctuating component present in the scattered light due to the onset of non-ergodic behavior [18]. In gels, this static scattering arises from the formation of the percolated gel network and special 'ensemble-averaging' techniques [19–21] are required in order to obtain a true, ensemble-averaged measure of $S_q(t)$. However, in the
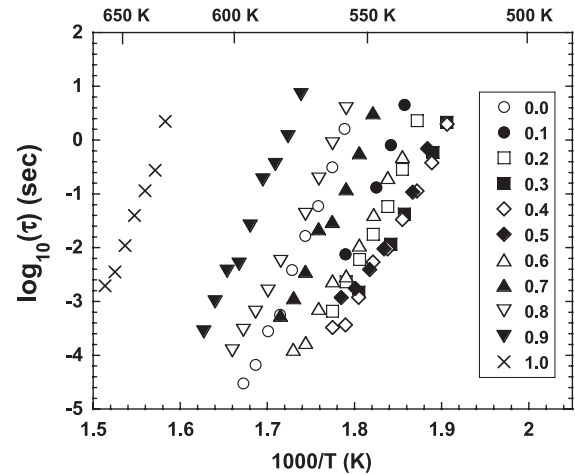
present study, measurements are limited to temperatures above the glass transition where a previous investigation [22] has demonstrated that the system is fully ergodic and that time- and ensemble-averaged measures of $S_q(t)$ are equivalent.

2. Results

Our measured relaxation times (τ) as obtained from fitting to equation (1) are shown in figure 3. The data are plotted in an Arrhenius fashion using an inverse temperature scale and it can be seen that there is only a modest variation of the activation energy with composition. However, there is considerable variation of the temperature at which the glass transition occurs with mixing of the two cations. By extrapolating the data in figure 3 just an additional decade to reach the glass transition relaxation time of 100 s, we can obtain an estimate of the T_g of our samples. These T_g are included in figure 1 and are seen to agree well with the calorimetric values obtained from the literature [23]. This agreement in T_g attests to the compositional integrity of our samples and suggests they are largely free of water.

Using the T_g values obtained as described above, a fragility plot can now be constructed. This plot of $\log(\tau)$ against inverse temperature (scaled to T_g) is presented in figure 4. There one sees a modest variation in the fragility (given by the slopes of the curves) ranging from $m \approx 56$ to $m \approx 82$. Actual values of the fragility index estimated from the slopes of the curves in figure 4 are plotted together in figure 5 as a function of the mixing ratio. Also included are values that were observed in our previous study [16]. Although there is not a definite systematic trend, the overall pattern indicates the fragility index is generally smaller for the mixed alkali samples as opposed to either single alkali glass.

Lastly, we examine the compositional variation of the heterogeneity parameter (β) which is also derived from fitting of equation (1) to our correlation spectra. For all samples except $NaPO_3$ (i.e., $x = 0$), no discernable temperature dependence of the heterogeneity parameter could be found.
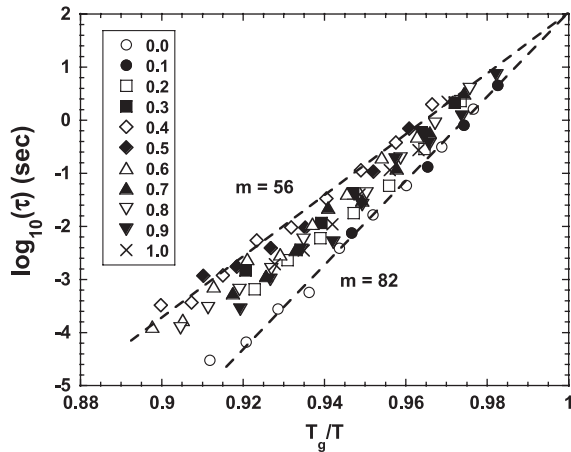
Figure 4. Fragility plot based upon the data presented in figure 3. The dashed lines indicate the extremes of the fragility index.
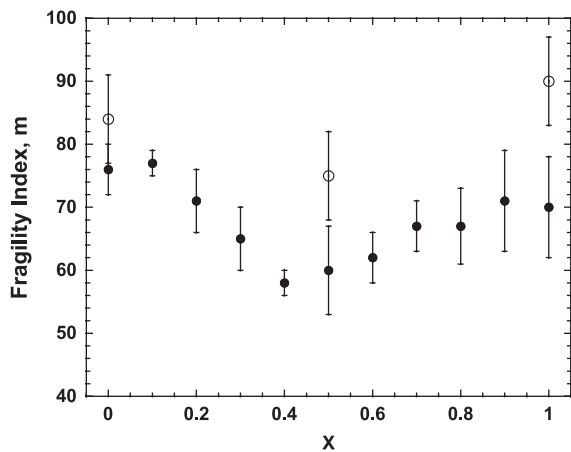

Figure 5. Variation of the fragility index with mixing ratio. Solid circles are from the present study. Open circles are values measured in a preliminary study [16].

For NaPO$_3$, however, the β was observed to monotonically increase with decreasing temperature from a value near 0.2 at highest temperatures to about 0.5 near T_g. To compare these heterogeneity parameters we adopt the protocol used by Boehmer [12] in which only the values of β near T_g, are compared. The results are shown in figure 6 and clearly show a decrease in β upon mixing cations.

3. Discussion

Metaphosphate glasses are comprised of polymeric phosphate chains that are crosslinked by the modifying cation. In a study of the glass transition for the complete series of alkali metaphosphate glasses, Eisenberg [24] demonstrated a direct and systematic dependence of the T_g upon the field strength of the cation. Field strength refers to the ratio of the cation charge to its radius. In that study it was observed that T_g decreased with decreasing field strength. Thus the cohesion of these liquids is determined by how effective the cations are at crosslinking neighboring phosphate chains. Based on this,
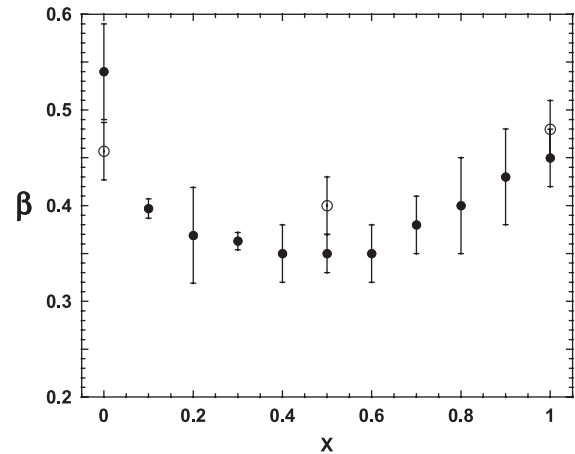

Figure 6. Variation of the heterogeneity parameter near T_g with mixing ratio. Solid circles are from the present study. Open circles are values measured in a preliminary study [16].

one would have anticipated the cohesion (i.e., T_g) to track the average field strength of the cation and thus vary linearly with the mixing ratio as suggested by the dashed line in figure 1. So how then does mixing of two cations result in such dramatic decrease in this cohesion?

Again, current opinion on the MAE has largely settled upon a working model known as the dynamic structure model (DSM) advanced by Bunde and Ingram [6, 7]. A detailed description of the model can be found elsewhere [25]. Here we only emphasize the key elements. Firstly, in a single alkali glass, the cations (say A) reside in sites that are configured to match the coordination requirements of the A cation. As A cations migrate from site to site, this movement occurs without any significant reconfiguration of the site. Likewise for a single alkali glass containing B cations, the sites are preconfigured during glass formation to accommodate the B cation. However, when A and B cations are introduced in similar numbers, there arises a necessity for A cations to move into B-sites and vice versa. Indeed, when the mixing ratio is near 0.5, a percolated pattern of A-sites and B-sites emerges and the cross section for migrations between dissimilar sites is maximum. In these situations, a significant number of site reconfigurations must occur. If a large cation moves into a small site the network must expand, and on average, there will occur a simultaneous migration of a small cation into a large site leading to contraction of the network. Ingram [6] has suggested this process can be thought of as the isochoric relaxation of a 'mechanical dipole' wherein one point in the network expands while a companion location contracts, leaving the net volume unchanged.

The upshot of the mixing is that the additional energy required for reconfiguring the sites, together with the enhanced cross section for A to B transitions resulting from the percolated pattern of A and B positions, produces a significant reduction in the long range ion migration with a corresponding drop in the measured dc conduction. But according to Ingram and Roling [6], the presence of such a large number of A to B movements implies significant increase of the local expansion and contraction of mechanical dipoles (akin to the rotation of
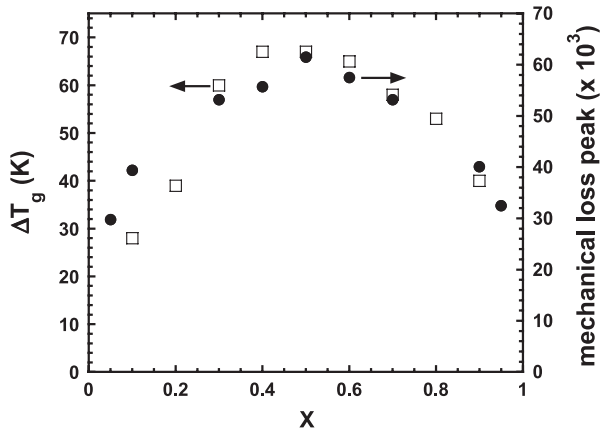
Figure 7. Variation of the glass transition depression (difference of T_g from the dashed line in figure 1) in comparison to the magnitude of the internal friction peak associated with the mixed alkali mechanical loss [26] as a function of the mixing ratio. The direct proportionality indicated by the overlap in these two quantities is evidence that mechanical relaxations are responsible for prematurely loosening the glass structure.

Figure 8. Temperatures at which the specified relaxation time occurs as a function of the mixing ratio. The dashed line illustrates the anticipated linear variation for a relaxation time of 1 μs if the MAE were not present. Inset shows how the strength of the MAE, as measured by the deviation from linearity, is largest near the glass transition but becomes weaker as the relaxation time shortens.

ordinary dipoles) and thus necessitates continual flexing of the oxide network. This isochoric flexing, which is a necessary consequence of the mixing of cations, acts like a laxative, loosening [6] the network and causing premature softening to occur at a lower T_g.

This we believe explains the dip in T_g which we observe. To examine this more carefully, we have subtracted our measured T_g from the linear composition dependence (see dashed line in figure 1) anticipated based only on the crosslinking efficiency that arises from the varying average field strength as one ion is replaced by another. As shown in figure 7, the excess decrease in T_g which results (ΔT_g) is symmetrical and is maximum at the midpoint of mixing.

Furthermore, we can compare this variation of ΔT_g with the magnitude of the mechanical relaxation. Internal friction measurements on several MA metaphosphate glasses were performed by van Ass and Stevels in 1974 [26]. There an additional loss peak was observed to grow in intensity with mixing of cations. The height of this MA peak is a direct measure of the energy loss associated with relaxation of the mechanical dipoles discussed above. The height of the MA internal friction peak is presented in figure 7 and is seen to overlay almost exactly with the data for ΔT_g, thus indicating a direct proportionality between these two quantities. This proportionality is compelling evidence that the mechanical loss associated with mixed cations *is* the source for the depression of the glass transition temperature as conjectured by Ingram and Roling [6].

But what of the fragility dependence? Can the DSM account for the changes in fragility that we observe? Unlike T_g which conveys the bulk cohesion of the liquid, fragility represents differences in how rapidly the cohesion is lost with increasing temperature. Fragile liquids lose this cohesion more rapidly in relation to T_g than do strong glass-formers. In figure 5 we see that mixing has produced a less fragile liquid. This means that while the mixing of cations has loosened the
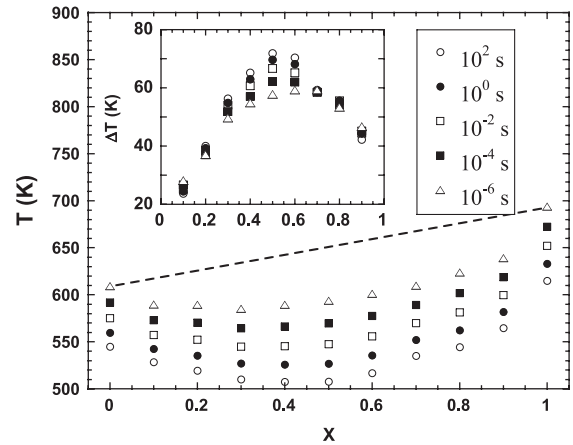
structure to promote softening at a lower temperature, it has also decreased how rapidly that resulting liquid liquifies.

On one hand, the drop in *m* could be interpreted as a result of decreased cooperativity in the relaxation. Mixing leads to a segregation of the liquid into A-rich and B-rich regions that do not prefer to intermingle because of the energy mismatch. This in turn could be viewed as a loss in the level of cooperative participation by the ions in relieving local stresses. However, there is a question as to whether the mismatch in energy necessarily persists into the liquid state where the notion of well-defined sites retaining their memory becomes suspect; in the liquid state, the decoupling of ionic and structural relaxations is partly removed.

Instead we would offer another interpretation for the fragility minimum observed. This idea is illustrated in figure 8 where temperatures corresponding to specific relaxation times are plotted as a function of the mixing ratio. At low temperatures, where ion motions are highly decoupled from the network, the action of the mechanical dipoles described by Ingram and Roling [6] promote significant loosening of the structure with a pronounced dip in the glass transition temperature (where $\tau = 100$ s). At higher temperatures, where the relaxation time is faster and the ion motions become more coupled with that of the network, the influence of the mechanical dipole relaxation (whose existence is contingent on the decoupling) is diminished. This can be seen in the inset to figure 8 where the deviation of a given isochronal temperature from the linear variation (e.g., dashed line in figure 8) expected in the absence of a MAE is compared for several relaxation times. The magnitude of this deviation is a measure of the strength of the mechanical dipole effect and, as the inset shows, the effect is diminished at shorter relaxation times as the liquid is heated further above the glass transition.

Looking again at figure 8, one sees that in all cases where the relaxation timescale changes from the fastest times (say 1 μs in the diagram) to the value of 100 s at T_g, the temperature

interval required for this common time change is smaller for the SA glasses than for the MA composition. Since the fragility, as operationally defined in equation (3), is essentially the slope of this time change against temperature interval, it follows from the above discussion that this slope would be smallest for the MA situation. Thus we do not interpret the dip in the fragility index (see figure 5) to be a true reflection of any traditional 'strengthening' of the oxide liquid such as is seen when the connectivity of the oxide network is altered. Indeed, our mixing of cations does nothing to modify the oxide structure; no bridging oxygens are removed nor any phosphate chain length altered. Instead, we believe the dip in m seen here is an artifact of how the fragility index (as operationally defined by equation (3)) is sensitive to the unique depression of the glass transition temperature wrought by the mixed alkali mechanical loss.

Lastly, we consider the compositional variation in the exponent β. Again, in light of the temperature dependence observed for the $x = 0$ glass, we have adopted Boehmer's protocol [12] to compare only the values of β near T_g. As seen in figure 6 the β exponent dips slightly at the MA composition. It changes from roughly 0.45 seen for either SA glass to about 0.35 for the $x = 0.5$ composition.

Here we see no puzzle regarding the dip in β. The smallness of β as long been regarded as a measure of the heterogeneity in the relaxation. Thus, the result of mixing cations is to increase this heterogeneity. This makes sense as mixing of two dissimilar cation species should result in greater diversity of the microscopic level relaxations over that in either SA glass. Although, the simultaneous decrease in β with decrease in fragility contradicts the inverse relationship between these two quantities that was established by Boehmer [12], we believe this is further evidence for our unconventional interpretation of the dip in the fragility index discussed earlier: mixing cations results in greater distributions of relaxation times (a fragile property) and had the mixing not forced the premature loosening of the glass structure, the fragility index would likely have remained unchanged or possibly increased slightly with mixing.

In conclusion, our dynamic light scattering study of the MAE in glass forming alkali metaphosphate liquids has revealed nonlinear variations in all the relevant quantities: the glass transition temperature, the heterogeneity parameter, and the fragility index. A direct comparison of the depression in the glass transition temperature with the evolution of a mixed alkali mechanical loss has demonstrated how the relaxation of mechanical dipoles described by Ingram [6] loosens the glass structure to promote the onset of macroscopic structural relaxation at a lower T_g. Although the MAE seen for the fragility index is opposite to that conventionally anticipated based on the MAE seen in the heterogeneity parameter, this violation occurs as a unique consequence of the additional internal modes of relaxation (in this case the decoupled mechanical relaxation of mixed cations) which act to lower the glass transition point.

Acknowledgment

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