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Constriction effect in the nearly constant loss of alkali metaphosphate glasses

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We report measurements of the dielectric loss in a series of monovalent metaphosphate glasses at cryogenic temperatures. An analysis of the scaling properties of the dielectric response reveals a nonionic contribution to the loss present only in glasses for which the conduction cation is constricted by the oxide network. As a result, our effort to examine recent conflicting reports for the cation mass dependence of the nearly constant loss in ion-conducting, disordered materials has been obfuscated. Instead, it is shown how this nonionic contribution may explain additional conflicting observations for the nearly constant loss reported over the last 10 years.

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I. INTRODUCTION

The demand for increased energy storage in a smaller package has motivated substantial research into solid-state electrolytes. Part of this research has focused upon disordered materials such as ion-conducting glasses and polymers. In these materials, conduction involves the thermally activated, long-range diffusion of the ion through a disordered matrix. The conduction process is nontrivial and is further complicated by the presence of interactions between the migrating ions. These interactions are thought to cause correlated motion[1,2] of the ions at short times which are evident in the distinctive features of the frequency-dependent ac conductivity of many ion-conducting materials. For many materials, the ac conductivity can be approximated[3–8] as

$$\sigma(f) \approx \sigma_o[1 + (f/f_o)^n] + Af. \tag{1}$$

In this expression, the first term is commonly referred to as the Jonscher power law (JPL) regime.[3] Here, the conductivity is characterized by a thermally activated dc conductivity (σ_o), observed at low frequencies, that crosses smoothly into an approximately power law frequency dependence (with $n \approx 0.5$ to 0.7) at higher frequencies.

Past studies[6–8] of this JPL regime have shown its adherence to specific scaling procedures. In many instances the conductivity and its complex counterpart, the dielectric permittivity (ε'), can be scaled to collapse to a common set of master curves described by

$$\frac{\sigma(f)}{\sigma_o} = F_1(f/f_o), \tag{2}$$

and

$$\frac{\varepsilon'(f)}{\Delta\varepsilon} = F_2(f/f_o), \tag{3}$$

where $f_o \propto \sigma_o T/\varepsilon_o \Delta\varepsilon$. $\Delta\varepsilon$ is the strength of the dielectric response associated with ion relaxation and ε_o is the permittivity of free space. The ac conductivity is essentially a Fourier transform of the time dependence of the ions' mean-squared displacement.[9] Thus, scaling of the frequency-dependent conductivity implies an ionic motion that is fundamentally unchanged by temperature, merely shifted by a thermally activated time scale.

This scaling is also quite universal.[3,10] In many cases,[6,10] glasses of different chemical composition show ac conductivity that can be collapsed onto a global master curve, often with $n \approx 2/3$. However, there are exceptions.[11–14] For example, in a series of alkali metaphosphate glasses a common master curve could not be obtained. There it was observed[13] that the JPL exponent decreased abruptly from a value of approximately 2/3 for Li and Na metaphosphate glasses to about 0.54 for the larger-sized alkali ions. This transition was shown to result from how the larger cations are more "constricted" by the surrounding oxide network in comparison to their small ion counterparts.

The second term in Eq. (1) above is commonly referred to as the nearly constant loss (NCL).[4,15,16] This descriptor follows from the formal relationship between the conductivity and the imaginary part of the dielectric permittivity, ε''. Since $\sigma(f) = 2\pi f \varepsilon_o \varepsilon''(f)$, a linear frequency-dependent conductivity necessarily implies a frequency-independent dielectric loss. Although the NCL has been investigated by several groups in the past,[15–20] it has received far less attention than the JPL feature, and a consensus regarding even the simplest properties of the NCL has not yet been established. For example, the temperature dependence of the NCL has been variously reported to be either weak,[15] weakly Arrhenius,[18] weakly exponential,[19] or weakly power law.[20] Furthermore, the frequency dependence has in some instances been observed[18,21] to be superlinear ($Af^{1.3}$). A recent review of the NCL properties is provided by Ngai.[16]

Early studies of the NCL proposed that the phenomenon might be related to the sort of low-energy, two-level system excitations that successfully accounted for anomalous thermodynamic properties of glasses at low temperatures.[22,23] The NCL was likewise proposed to result from low-energy excursions of collective groups of atoms (ions and network constituents) over an energy barrier in an asymmetric double-well potential (ADWP) configuration.[17,24] The resulting motion gives rise to a frequency-independent dielectric loss that is virtually temperature independent. Owing in part to this significantly weaker temperature dependence, many believe[15–17] that the NCL is fundamentally different in origin from the sort of ionic displacements which produce the JPL behavior.

In contrast, some of the current, viable models[1,2] for the JPL also predict a NCL behavior in the limit of increasing

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frequency. These models imply that no additional mechanism (like the ADWP) is required to account for the NCL. An obvious test of whether the NCL is merely an extension of the JPL phenomenon to higher frequencies is to ascertain to what extent the NCL conforms to the scaling in Eq. (2). A few recent studies[25–27] have explored this idea. Roling[25] found for several glasses that the NCL could be scaled together with the JPL, at least to the 173 K limit of their measurements. However, they also conceded that the scaling may fail below this temperature. Indeed, Jain has observed[28] anomalous features in the loss of a 0.23 Li_2O-99.77 GeO_2 glass below 100 K that could not be related to JPL, and Nowick[29] has observed unusual contributions to the loss in Gd-doped crystalline CeO_2 near 150 K. In our own study[26] of sodium germanate glasses of varying ion concentration, we observed a NCL which conformed to JPL scaling down to temperatures of about 80 K, provided a nonionic contribution, stemming from the oxide network, was first removed.[26]

Recently, Ngai has proposed[16] that the NCL is associated with the quasivibrational motion of cations in an anharmonic cage potential. An inverse dependence of the NCL upon the cation mass is predicted, and was recently reported by Rivera[30] for a series of alkali borate glasses. However, a subsequent investigation by Murugavel and Roling[27] of aluminosilicates and aluminogermanates found no evidence of such a mass dependence. Instead, a correlation was seen between the NCL at 173 K and the room temperature dc conductivity, again suggesting that the NCL is ultimately connected back to the same fundamental ion motion that produces the JPL behavior.

In this present paper, we report results of a study of the NCL in the series of alkali metaphosphate glasses. We find that our NCL scales with the JPL feature up to a point. For the glasses with Li and Na, the scaling is complete to the low-temperature limit of our measurement (about 80 K) and shows a NCL that decreases monotonically with decreasing temperature. However, for the larger-sized cations (K, Cs, and Tl) the NCL increases with decreasing temperature over a range of temperatures and exhibits a maximum at temperatures of about 140 K. This loss peak is seen *only* for the large cations which were previously described as “constricted” in the metaphosphate network. The loss peak itself does not conform to the JPL scaling and so appears to represent a polarization process not directly associated with the ion motion. As a result of this additional contribution, the NCL exhibits a diversity of frequency- and temperature dependences which do not permit broad generalizations to be drawn regarding either its cation mass dependence nor its correlation to the room temperature dc conductivity.

II. EXPERIMENT

Details of the sample preparation have been published previously.[12] The samples are in the shape of disks about 1 mm thick onto which a set of concentric metallic contacts have been coated. Measurements of the diameter of the contacts and the sample thickness were used to determine the cell constant (the capacitance of an equivalent unfilled parallel plate capacitor). By this means our reported loss (absolute value) is accurate to within 5%. Measurements of the capacitance and conductance were achieved using a precision capacitance bridge (GenRad 1615) together with a modern lock-in amplifier (Standford Research Systems 830). Accurate measurements could be obtained for frequencies between 500 Hz and 50 kHz, and the temperature was controlled to ±0.3 K using a home-built liquid nitrogen cryostat. Data were obtained sequentially from lowest temperatures (about 80 K) up to ambient. Raman scattering was performed at Sandia National Labs using an argon ion laser (514.5 nm at approximately 200 mW) and a Spex 1877 Triplemate spectrometer with a typical resolution of about 2 cm^{-1}.

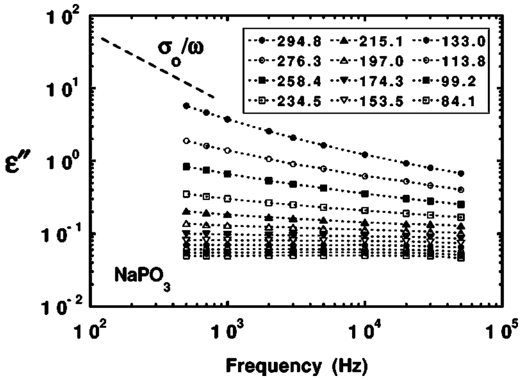

FIG. 1. The dielectric loss in $NaPO_3$ glass collected at 12 temperatures (in K). Dotted lines are only a guide for the eye. The straight dashed line in the upper left-hand corner shows the approach at low frequencies to a slope of −1 that corresponds to dc conduction.

III. RESULTS

Figure 1 shows an example of our measured loss for the $NaPO_3$ glass. At high temperatures, one finds significant frequency dependence of the loss. Here, the loss is dominated by the JPL regime. With increasing temperature, the loss eventually assumes an approximately inverse dependence upon frequency corresponding to the dc conduction of Na ions. With decreasing temperature, this frequency dependence disappears. At temperatures below approximately 190 K, the slope in Fig. 1 becomes less than 0.05 and at this point one could accurately describe this as nearly constant loss behavior.

What we observe in Fig. 1 are actually snapshots, taken in a narrow (2 decade) frequency window, of a more extensive ionic response (spanning tens of decades) which is being displaced toward lower frequencies with decreasing temperature. As a result of our limited frequency range we are unable to observe the entire dielectric response at a fixed frequency. This is a common dilemma that has been encountered by many researchers in the past. When a broad dielectric relaxation process cannot be seen in its entirety at a given temperature, it often can be reconstituted by shifting each snapshot so as to overlap it with the previous snapshot. The success of such a procedure is evidence that the relaxation process exhibits what is referred to by some[31] as “time-

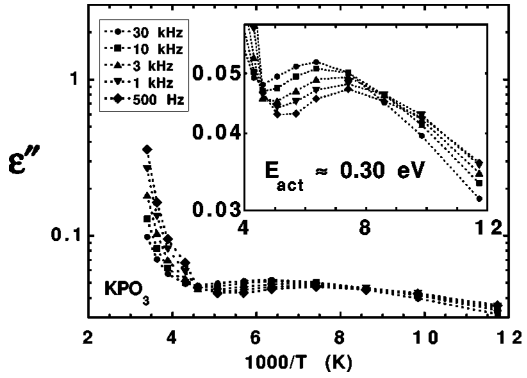

FIG. 2. The dielectric loss in KPO_3 glass at fixed frequency as a function of the inverse temperature. The inset shows an enlargement of the NCL region that exhibits a loss maximum with an effective activation energy of 0.30(±0.04)eV.

temperature superposition" (TTS). Time-temperature superposition implies that the relaxation process under investigation possesses a frequency dependence that is not distorted by temperature. Rather, the frequency dependence is preserved and the entire relaxation simply shifts in response to temperature dependent (often Arrhenius) changes of the characteristic relaxation rate ($f_o \propto e^{-E/kT}$).

A consequence of this TTS is that it establishes an isomorphic correspondence between data plotted on logarithmic frequency scale for fixed temperature with the same data plotted on a linear $1/T$ scale for fixed frequencies. This approach has been used by many researchers in the past, and we shall employ it here. In Fig. 2, we present our data for the KPO_3 glass as a function of inverse temperature measured at five frequencies. At high temperatures, the loss is dominated by the JPL regime and shows substantial temperature dependence. But, at temperatures below about 200 K, the temperature dependence becomes weak by comparison. In Fig. 2 we observe an unusual feature. Between approximately 200 and 80 K the loss actually passes through a maximum. This loss peak is more evident in the inset of Fig. 2, where the temperature of the maximum is found to increase with increasing frequency. The peak position displays a temperature dependence with an effective activation energy of only 0.30(±0.04) eV.

A similar loss peak was observed in both the $CsPO_3$ and $TlPO_3$ samples. In Fig. 3 the loss at 3 kHz is plotted against inverse temperature for all the glasses examined in the present study. While three of the glasses (KPO_3, $CsPO_3$, and $TlPO_3$) exhibit a similar loss peak, the other two glasses ($LiPO_3$ and $NaPO_3$) do not exhibit a loss peak, but rather decrease monotonically with decreasing temperature.

From Fig 3, we immediately draw two important conclusions. First, we conclude that there appears to be a constriction effect for the NCL. Namely, it is only the large-sized cations (K, Cs, Tl) that produce a peak in the loss below 200 K. In our previous studies[13] of the JPL, these same large cations exhibited a significantly smaller JPL exponent which was proposed to result from how these cations are more constricted by the oxide network than the smaller cations. Second, our plan to examine proposed[16] mass dependence of the NCL has run into a quandary. Rivera[30] reported a NCL in alkali triborate glasses that varied as $m^{-1/3}$ regardless of the temperature chosen. Murugavel and Roling,[27], however, saw no such mass dependence for aluminosilicates and aluminogermanates at 173 K. In Fig. 3 we see that the mass dependence of the NCL is quite sensitive to the temperature chosen and so we cannot ascribe any definitive mass dependence to the NCL we measure.

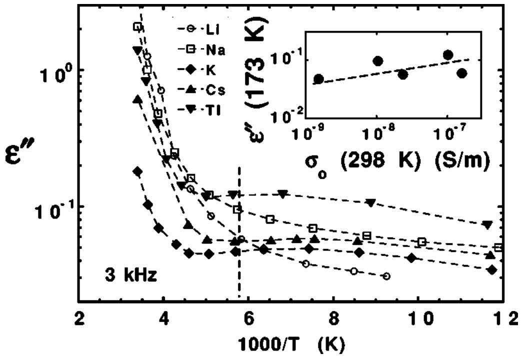

FIG. 3. The dielectric loss at 3 kHz as a function of inverse temperature for all the monovalent metaphosphate glasses examined. The vertical dashed line locates 173 K. The inset explores the proposed correlation (Ref. 27) between the dielectric loss at 173 K and the room temperature dc conductivity.

While Murugavel and Roling[27] did not observe a mass dependence, they did report a correlation between the NCL and the room temperature dc conductivity. In their study, the NCL was characterized by a frequency scale, f_{NCL}, defined by a fit of $\sigma(f)=(f/f_{NCL})^{0.95}$ conducted for their lowest temperature of 173 K. A correlation was found between this frequency (inversely proportional to the value of ε'' at this temperature) and the dc conductivity at 298 K. Specifically, f_{NCL} increased with decreasing dc conductivity. The correlation was improved when f_{NCL} was further scaled by $\Delta\varepsilon T$ to compensate for differences in the ion concentration. The dc conductivity of our alkali metaphosphate glasses is reported in Fig. 4. From this we have determined the dc conductivity at 298 K, and in the inset of Fig. 3 we have tested the correlation observed by Murugavel and Roling[27] by plotting the loss at 173 K versus the dc conductivity at 298 K. The values of

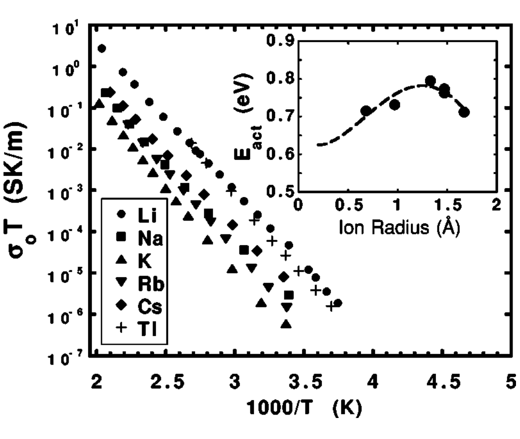

FIG. 4. An Arrhenius plot of the quantity $\sigma_{\mathrm{o}}T$ for monovalent metaphosphate glasses. The inset shows how the corresponding activation energy varies with ion radius.

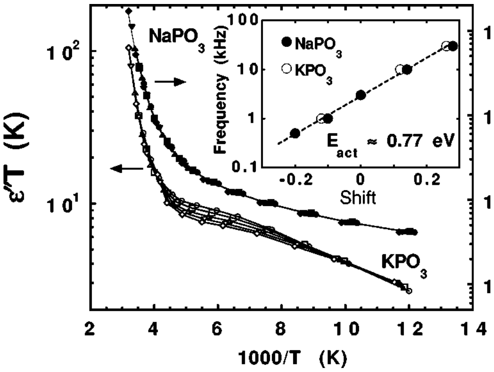

FIG. 5. The quantity $\varepsilon''T$ for both $NaPO_3$ and KPO_3 glasses at 3 kHz together with the same at four other frequencies (500 Hz, 1 kHz, 10 kHz, and 30 kHz) shifted horizontally so as to coincide at high temperatures. The required shifting is indicated in the inset and corresponds to an effective activation energy of 0.77(±0.03)eV.

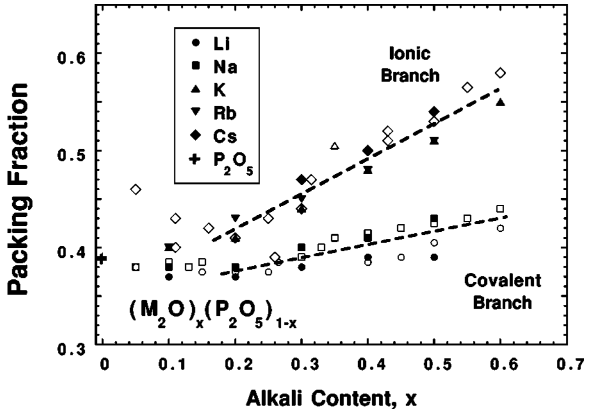

FIG. 6. Values of the atomic packing fraction for monovalent phosphate glasses as a function of increasing ion content. Open symbols are taken from Giri (Ref. 32). Solid symbols have been added from our own previous work (Ref. 33). The dashed lines indicate the two types of glass structure discussed by Giri (Ref. 32).

$\Delta\varepsilon T$ for our glasses are nearly identical (about 3700±500 K) and so this additional correction has been omitted. Since our loss is inversely related to the quantity f_{NCL}, we would anticipate ε'' to decrease with decreasing dc conductivity. This decrease is not overwhelmingly apparent in the inset, although the data do scatter about a line whose slope corresponds to the slope of the correlation reported by Murugavel and Roling.[27]

The reason for the absence of a sharply resolved correlation is likely the presence of a loss peak in our measurements coupled with the arbitrary choice of 173 K for characterizing the NCL and 298 K for characterizing the dc conductivity. Like the mass dependence discussed previously, this correlation is also sensitive to the temperature chosen for evaluating the NCL. Nevertheless, others have found that the NCL does correlate with the dc conductivity in the sense that scaling of the JPL often extends to the NCL region. Thus, let us try an alternative approach to examine how the NCL might be related to the JPL.

Consistent with the scaling in Eq. (2) for $\sigma(f)$, one finds an equivalent scaling for the loss

$$\varepsilon''(f) = \Delta\varepsilon F_3(f/f_o). \tag{4}$$

Furthermore, since $\Delta\varepsilon T$ is found to be constant for a given glass of fixed ion concentration,[26,27] the quantity $\varepsilon''T$ should be a function only of the scaled frequency with $f_o \propto \sigma_o T$. Under the assumption of TTS, this function of frequency (on a logarithmic scale) must map into a corresponding function of $1/T$ (on a linear scale). Thus, plots of $\varepsilon''T$ against $1/T$ for different frequencies should appear identical but only shifted horizontally. In Fig. 5 we show $\varepsilon''T$ for both $NaPO_3$ and KPO_3 at 3 kHz. Also plotted are the $\varepsilon''T$ for these glasses at four other frequencies (30 kHz, 10 kHz, 1 kHz, and 500 kHz) that have been shifted along the horizontal axis so as to best coincide with the 3 kHz data in the temperature range above approximately 230 K (corresponding to the JPL regime). The degree of shifting required to perform this collapse is presented in the inset of Fig. 5. The effective activation energy of this shift is 0.77(±0.03) eV and agrees well with the range of activation energies seen for $\sigma_o T$ (see the inset of Fig. 4). Similar results were obtained for the other glasses in our study.

This simple scaling procedure is successful in collapsing $\varepsilon''T$ for both the $LiPO_3$ and $NaPO_3$ glasses. It is also successful in collapsing $\varepsilon''T$ of the larger cation glasses both in the high-temperature (above about 250 K) and the low-temperature (below about 100 K) regimes. Thus, in this sense, the NCL appears to scale with the JPL. However, over a range of temperatures between 100 and 250 K, the collapse is not complete for the large cation glasses. For these glasses, there appears to be a contribution to the dielectric loss which does not scale along with the ionic motion.

IV. DISCUSSION

From our study of alkali metaphosphate glasses, we observe a NCL that is largely correlated to the JPL with both regimes scaling in the same fashion. This correlation is established to the limits of our measurements (roughly 80 K) and is in good agreement with the finding of Murugavel and Roling[27] that extended only to 173 K as well as our earlier study of sodium germanate glasses.[26] This correlation is seen for all the glasses in the alkali series. However, for the large, constricted cations, an *additional contribution* to the NCL appears, possessing an activation energy lower than that for $\sigma_0 T$, which does not correlate with the JPL. The failure of this contribution to scale with the high-temperature dynamics indicates that this new feature is unrelated (or at least not directly related) to the motion of the conducting cations.

The differences between constricted and nonconstricted cations are part of a larger, systematic structural development present in all alkali oxide glasses. Giri and co-workers[32] have recently analyzed density data for all sorts of alkali oxide glasses including silicates, germanates, borates, vanadates, and phosphates to determine the variation of the atomic packing fraction with respect to ion concentration. Their results for the alkali phosphates are reproduced in Fig. 6 together with data from our own work.[33] Two branches of structural development are evident: a lower branch formed by phosphate glasses whose conduction cations are smaller than an oxygen atom, and a higher branch in which the conduction cations are larger than an oxygen atom. It is important to note that this two-branch feature is reproduced for all the oxide glasses. Giri[32] refers to the lower branch as one of "covalent packing," wherein the packing is controlled by the covalent oxide network and depends strongly on the glass former. Here, the structure is limited only by the size of the oxygen atom and the small cations do not efficiently fill the residual space. These glasses have characteristically high conductivity owing in part to the available free volume as well as the smallness of the ion in relation to the size of passageways in the network (doorways) through which the cation must migrate.[34]

The upper branch is referred to as "ionic packing." Here, the packing is dominated by the modifying cation, increases with ion concentration, and is largely independent of the glass former. In the melt, the oxide network adapts to accommodate the large cation and more efficient packing is thus realized. Conventional wisdom would posit that the glasses with ionic packing should possess lower conductivity than their small ion counterparts since the cations are essentially being squeezed into the network. However, while we did observe the lowest conductivity for the KPO_3 glass, we actually observed the conductivity increase with increasing ion size for those cations larger than potassium (see Fig. 4). Indeed, the activation energy for the dc conductivity (actually for $\sigma_0 T$ in Fig. 4) passes through a maximum as a function of the cation radius (see the inset of Fig. 4).

In the classical ion conduction model by Anderson and Stuart,[34] only two energy barriers are considered in determining the activation energy for ion migration. The first is the Coulomb attraction of the cation to its nonbridging oxygen (NBO) site. This contribution decreases with increasing ion size. The other contribution is the strain energy, which reflects the energy required to distort the local network sufficiently for the cation to pass through. In the Anderson and Stuart model, the size of this doorway is a fixed parameter and the strain energy increases as the ion size exceeds that of the doorway. As a result, the model only predicts a minimum in the activation energy with increasing ion radius. In order to account for the activation energy maximum we observe, we must modify the model to allow for an expanding doorway whose size increases along with the increasing size of the cation. The result[35] of such a simple modification to the Anderson and Stuart model (shown by the dashed curve in the inset of Fig. 4) is capable of accounting for a maximum in the activation energy.

Satisfied that this new contribution to the dielectric loss is not directly associated with the migrating cations, what then is its source? A most likely candidate would seem to be the NBOs that are created when alkali oxide is added to the P_2O_5 network. These negatively charged atoms are bonded to the oxide network and, unlike the cations, are unable to diffuse in any long-range manner through the oxide network. Consequently, they do not contribute to dielectric response in the same manner or to the same extent as the comparatively mobile cations. Nevertheless, they are charges and may be capable of limited local motions (distinct from mere vibrational motion) which could give rise to a dielectric response.

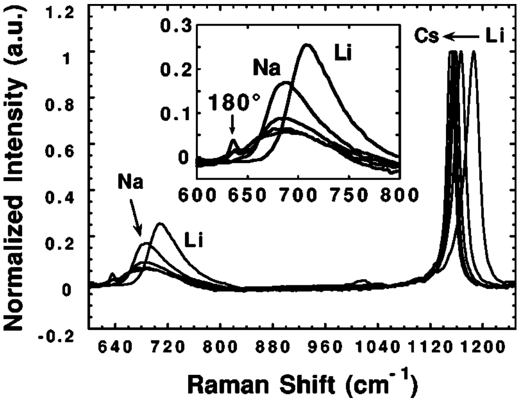

FIG. 7. Raman spectra for the series of alkali metaphosphate glasses. The inset is an enlarged view of the low-frequency band showing the development of a narrow band at 640 cm^{-1} that corresponds to P–O–P bonds with approximately 180° bond angle (Ref. 36).

But, why would this response be more evident in the constricted glasses? Some insight may be obtained by examining what is currently understood regarding changes in the structure of the oxide network which result from addition of the modifying cation.[36] First, in the absence of alkali, P_2O_5 forms an oxide network of PO_4 tetrahedra in which one oxygen atom is a nonbridging, or "terminal oxygen" that is double bonded to the phosphorus atom and the other three oxygen atoms are bridging. As alkali are added, the network is transformed to one consisting of long, polymeric chains of PO_3 units in which two of the oxygen atoms are terminal and two are bridging. Raman scattering studies[36] show that the high-frequency oscillations (≈ 1400 cm^{-1}) of the double-bonded terminal oxygen in amorphous P_2O_5 is replaced by a lower frequency oscillation (≈ 1150 cm^{-1}) in the metaphosphate glass that corresponds to a chemical resonance in which the bonding of the two terminal oxygen atoms is equalized.

Second, important structural changes occur as the cation size (and/or valence) is changed. For example, the glass transition temperature of the alkali metaphosphate glass decreases systematically with increasing cation size.[37] This decrease is thought to result from the decreasing field strength of the cation which reduces its ability to crosslink the phosphate chains. In addition to weakening the interchain bonding, the changing cation size also affects properties of the phosphate chain itself. Figure 7 shows the Raman spectra collected for some of our samples, and the results are consistent with other reported findings.[36,38,39] The high-frequency band corresponds to the symmetric stretch of the terminal (PO_2) oxygen, and the lower frequency (≈ 700 cm^{-1}) band to the symmetric stretch of the bridging (P–O–P) oxygen.[38] In both instances the bands shift to lower frequency as the cation size is increased. For the PO_2 band, this decrease has been interpreted as a weakening of the terminal bond due to interaction with the alkali that "leads to an increase in the ionic character"[38] of the bond. Modeling[39] of these vibrational bands shows that the shifts are not merely the result of changes in the effective mass, but rather can only be explained by a weakening of the force constant. For the P–O–P band, the decreased frequency is accompanied by a narrow band observed to form on the low-frequency side (see the inset of Fig. 7 near 640 cm^{-1}). This band corresponds to the vibrations of straightened chain segments with P–O–P bond angles of 180° and suggests that the larger cation causes considerable stretching of the chains in its neighboring environment.[36]

These findings highlight two differing situations of interplay between the cation and the oxide network. For the small cations, the network is composed of reasonably rigid phosphate chains to which the two terminal oxygen are tightly bound. These chains collapse together in a manner that is largely uninfluenced by the presence of the cation. Relative to its size, the small cation experiences an open structure and migrates about without causing substantial displacement of the terminal oxygen. By comparison, the physical size of the large cations limits the extent to which the chains can collapse together and even serves to stretch and weaken the oxide network. Relative to its size, the large cation experiences a more compact conduction space. Moving about within this network, the cation is more apt to contact the nonbridging oxygen atoms. Furthermore, the weakly bound terminal oxygen found in the large cation situation are more likely to display the sort of localized motions that are commonly seen in molecular and polymer glasses and referred to as the “Johari-Goldstein” or “slow-β relaxation.”[40,41] These relaxations typically display activation energies between about 0.2 and 0.4 eV,[42] , in excellent agreement with our observed activation energy (see the inset of Fig. 2). This might explain why the dielectric loss is observable only for the large, constricted cations.

Regardless of its origin, the new loss peak seen in the constricted glasses offers many explanations for previous contradictory reports about properties of the NCL in these disordered materials. For example, one sees in Fig. 3 a variety of temperature dependences which might account for the variety of temperature dependences reported in the literature. Indeed, Jain’s observation[28] of a decreasing conductivity (at fixed frequency) with increasing temperature is not unlike the decrease of the NCL with increasing temperature which occurs in the constricted glasses between approximately 140 and 200 K (see Fig. 3). Furthermore, as seen in the inset of Fig. 2, in our constricted glasses there is a range of temperatures near 200 K where $\varepsilon''(f)$ increases with increasing frequency. This would correspond to a superlinear frequency dependence of the ac conductivity not unlike that reported by some researchers.[18,21]

V. CONCLUSION

We conclude, then, that characterizing the NCL in disordered ion-conducting materials is not a simple matter, as this region of the dielectric response displays a challenging array of features which depends both upon the nature of the cation and its degree of constriction within the oxide network. Growing evidence suggests that much of the NCL is ionic in origin. This ionic contribution is identified by its adherence to the same scaling as the JPL, which indicates that both are part of a single ion relaxation process that is shifted in frequency with changing temperature. However, there is also evidence of nonionic contributions to the NCL, contributions which do not scale with the JPL. Some of these are inherent in the oxide network and become visible whenever the ion concentration is sufficiently reduced.[26] Others appear to be enhanced by the presence of large, constricted cations within the oxide network. In future investigations, scaling should feature as an important tool for properly dissecting the NCL into its respective contributions. In this way its is hoped that a better understanding of ionic motion at all time scales might be achieved.

ACKNOWLEDGMENT

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