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Two Contributions to the ac Conductivity of Alkali Oxide Glasses

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Although the frequency dependent conductivity of ion-containing glasses often displays scale invariant power law dispersion at high temperatures, the exponent increases to unity at lower temperatures. We report measurements of the conductivity of a series of alkali metaphosphate glasses including a mixed alkali composition and demonstrate that this temperature dependence results from the superposition of two power law dispersions originating from *separate mechanism*, and does not indicate any intrinsic change in scaling of the process which dominates at high temperatures.

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Systems that exhibit scale invariant behavior lend themselves to simplified and often universal explanation. The frequency dependent conductivity that arises from ion motion in disordered materials also appears to exhibit scaling behavior and can generally be described by a power law of the form

$$\frac{\sigma_I(\omega)}{\sigma_0} = f(\omega/\omega_c), \quad f(x) = 1 + x^n. \quad (1)$$

We say that $\sigma_I(\omega)$ exhibits “scaling behavior” in the sense that, when n is constant, $\sigma_I(\omega)$ collected at different temperatures can be scaled by the dc conductivity σ_0 and some characteristic frequency scale ω_c , so as to collapse upon the single curve $f(x)$. The subscript I has been introduced following the convention of Elliott [1] to distinguish this type I dispersion from that discussed later.

In 1977, Jonscher [2] conducted a survey of available literature for a wide variety of disordered materials including ion-conducting glasses and amorphous semiconductors. In that study, the dispersive behavior was found to be remarkably similar for all these materials with n rather narrowly distributed around 0.7 ± 0.2 . This finding led to the description of Eq. (1) as the “universal dynamic response” [3].

Physically, $\sigma_I(\omega)$ arises from the motion of ions through a comparatively fixed matrix [4–6]. The motion is discrete and involves activated hopping of the ions over energy barriers that separate adjacent sites. In alkali oxide glasses, such as LiPO_3 , nonbridging oxygens (NBO's) serve as negatively charged sites about which the cations preferentially associate. Long range displacements lead to a dc conductivity exhibiting an Arrhenius temperature dependence with an activation energy E_{dc} .

At higher frequencies, short range displacements of the ion are thought to be coupled to the ionic environment. Interionic interactions become important, and the short range hopping is often viewed as highly correlated motion in which the ion performs several reiterated forward-backward hops before completing any successful forward displacement [3,7]. The power law dispersion is then a consequence of this reiterative hopping and occurs down to a frequency ω_c below which successful hops

can be completed. Hence σ_0 and ω_c are directly related and one finds from Eq. (1) that the dispersive portion of $\sigma_I(\omega)$, $\sigma_0(\omega/\omega_c)^n$, exhibits a lower activation energy $E_{ac} = (1 - n)E_{dc}$.

An excellent demonstration of the scaling and *universal* nature of ion conduction has been provided by Kahnt [8]. Kahnt showed that measurements of $\sigma(\omega)$ for a wide variety of dissimilar glasses at different temperatures collapsed upon a common scaling curve, with n about 0.67, once appropriately scaled by σ_0 and ω_c .

However, a growing body of evidence suggests that the scaling with $n \approx 0.7$ occurs only at high temperatures and that at low temperatures the power law exponent is approximately unity [9]. This was demonstrated in a recent Letter by Lee, Liu, and Nowick [10] who observed temperature dependence of the power law exponent in a series of alkali silicate glasses. Over a range of high temperatures, they observed n with a constant value of about 0.60, but as the temperature was lowered, n increased, eventually reaching unity as a limiting value well in advance of zero kelvin. The high temperature (constant n) region conforms well with $\sigma_I(\omega)$ but it is evident that n evolves to a second dispersive regime (type II) characterized by a weak temperature dependence and a roughly linear dependence on frequency [1,11],

$$\sigma_{II}(\omega) \approx B\omega^1. \quad (2)$$

Presently, it is unclear what leads to type II dispersion. Ngai, Strom, and Kannert [12] have noted interesting correlations with low temperature NMR results and have suggested that the dispersion reflects ion motion associated with traversing a double well potential whose energy difference is small. Recent Monte Carlo simulations by Maass *et al.* [13] for a Coulombic-interacting lattice gas exhibited a temperature dependent n , with n rising steadily toward unity with decreasing temperature. This continuous evolution of n is, however, qualitatively different from the rather abrupt rise seen by Lee, Liu, and Nowick. In contrast, Elliott has recently proposed that $\sigma_{II}(\omega)$ is not directly connected with ion motion at all, but instead is a separate phenomenon associated with the motion of counterions (e.g., NBO's) in the host matrix [1].

Thus an important issue arises. Does the $n(T)$ behavior, as seen by Lee, Liu, and Nowick indicate an intrinsic change in *ion motion* such that the scaling function in Eq. (1), $f(x)$, changes; or is $n(T)$ merely a consequence of the observed $\sigma(\omega)$ crossover from ion motion described by $\sigma_I(\omega)$ dominating at high temperatures to an unrelated *separate process* described by $\sigma_{II}(\omega)$ dominating at low temperatures? It is imperative to determine which is the case since scaling is an obvious simplification in the theoretical description of physical phenomena.

In this Letter we investigate these two regimes of dispersive behavior for a series of alkali metaphosphate glasses including a mixed alkali composition. While dramatic changes in $\sigma_I(\omega)$ accompany the mixing of ions, $\sigma_{II}(\omega)$ is seen to be only modestly affected. We propose then that $\sigma_{II}(\omega)$ is a process separate from $\sigma_I(\omega)$ and likely related to the motion of counterions in the metaphosphate substructure. We show that the crossover between these two regimes, while occurring over different temperature intervals in each of the glasses studied, occurs identically over a single interval of σ_0 . In this sense the temperature dependence of n results from a crossover where $\sigma_I(\omega)$ dominates at high temperatures but decreases at lower temperatures to uncover a separate and essentially temperature independent $\sigma_{II}(\omega)$.

Samples of LiPO_3 , NaPO_3 , and the mixed alkali glass, $25\text{Li}/25\text{Na}/50\text{PO}_3$, were prepared from reagent grade materials. Measurements of the conductivity of each were performed using a commercial impedance analyzer over the frequency range from 1 to 10^6 Hz. Additional details of our experimental procedures are described elsewhere [14].

Results for LiPO_3 are shown in Fig. 1. Aside from electrode polarization effects [15] present at low frequen-

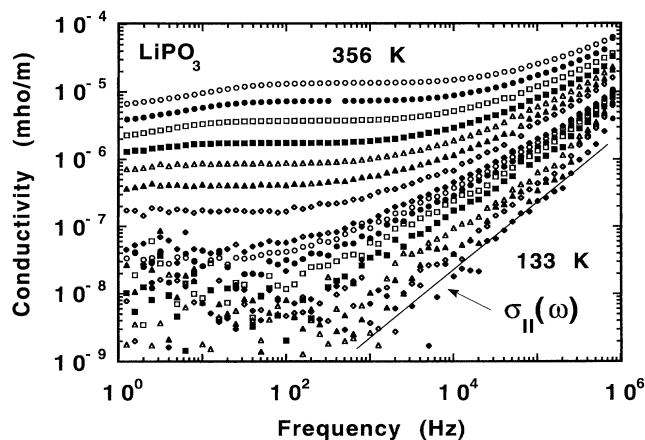


FIG. 1. $\sigma(\omega)$ of LiPO_3 measured at 356, 346, 336, 326, 316, 307, 295, 283, 279, 273, 267, 253, 240, 223, 203, and 133 K. The line with unity slope identifies type II dispersion seen at low temperatures.

cies for our highest temperatures and a slight excess loss at frequencies above 5×10^5 Hz due to stray impedances in the coaxial leads used, the data at high temperatures display type I dispersion consistent with Eq. (1).

The dispersive portion is analyzed by subtraction of the dc conductivity as shown in the double logarithmic plot in Fig. 2(a). At temperatures above about 290 K, we obtain from the slope $n = 0.67 \pm 0.03$. Below this temperature, the slope begins to increase, rising to a value of approximately unity found at the lowest temperatures in qualitative agreement with the results of Lee, Liu, and Nowick for alkali silicates. Similar trends were found for NaPO_3 and for the mixed alkali, except that as seen in Fig. 2(b); the mixed alkali system exhibited type I dispersion with a reduced exponent, $n = 0.61 \pm 0.03$. The error estimate here reflects error in determining the slope at each temperature. So while the difference in n seen between the single and mixed alkali systems may appear to be just within the overlap of the error bars, the scatter in n [see Fig. 3(b)] concentrates at about 0.67

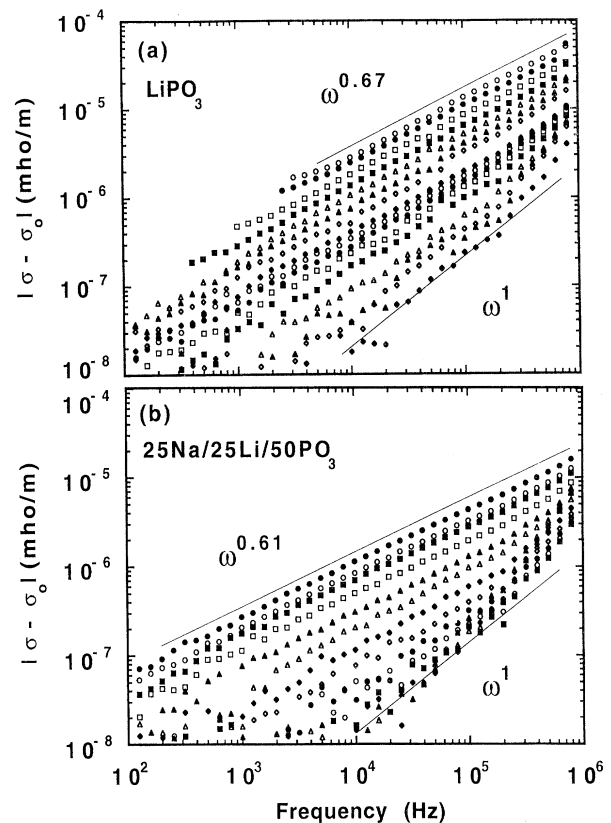


FIG. 2. (a) The ac portion of $\sigma(\omega)$ of LiPO_3 from Fig. 1 showing type I dispersion with $n = 0.67$ at high temperatures and type II dispersion at low temperatures. (b) The ac portion of $\sigma(\omega)$ for the mixed alkali glass measured at 504, 494, 486, 476, 455, 446, 410, 389, 369, 348, 328, 299, 241, 184, and 133 K showing type I dispersion with $n = 0.61$.

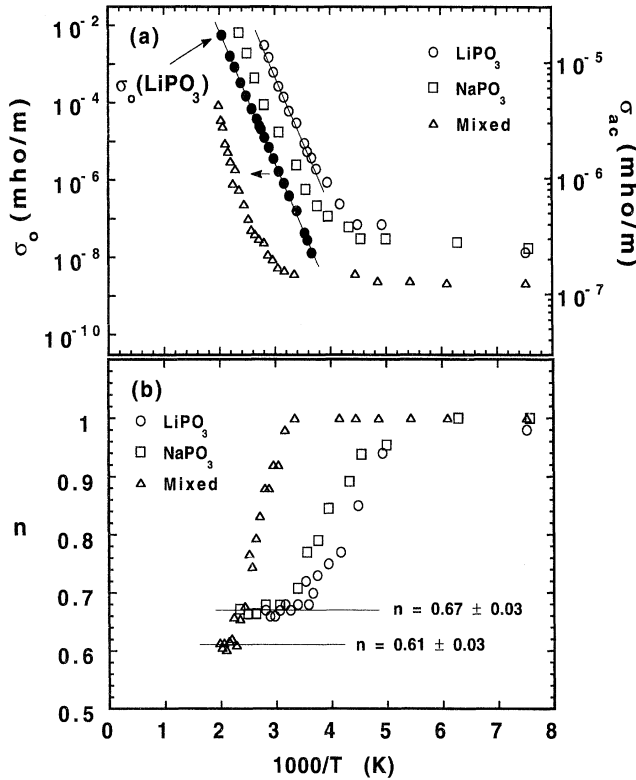


FIG. 3. (a) Arrhenius plot of σ_{ac} showing the low temperature approach to a limiting value. The dc conductivity of LiPO_3 is included to indicate that $E_{ac}/E_{dc} = 1 - n$. (b) Corresponding plot of the dispersion exponent showing the simultaneous crossover from type I to type II behavior.

and 0.61, respectively. Thus a decrease in the exponent occurs for the mixed alkali case and demonstrates that interionic interactions are a determining factor controlling the dispersive behavior. The result further suggests that the mixed alkali system represents a different class of universality [16].

In Fig. 3(a), we consider the activated nature of the observed dispersive component by plotting the temperature dependence of the ac conductivity as arbitrarily defined by $\sigma_{ac} = \sigma(10^5 \text{ Hz}) - \sigma_0$. Also included for comparison in the figure, but depicted on a 3-to-1 scale, is σ_0 of LiPO_3 . The solid lines included in the figure are parallel and indicate confirmation of the additional relationship, namely, $E_{ac}/E_{dc} = 1 - n (= 0.33)$. A similar confirmation holds for NaPO_3 and as well for the mixed alkali case but with $E_{ac}/E_{dc} = 0.4$ for the latter.

In all three systems, the high temperature Arrhenius trend in σ_{ac} fails at lower temperatures and either approaches a constant limiting value or becomes substantially less temperature dependent. An important finding, seen in Fig. 3(b), is that this transition of $\sigma_{ac}(T)$ occurs *simultaneously* with the transition of n from its high temperature constant value to that of unity.

Interestingly, Fig. 3(a) indicates that all three glasses approach nearly the same low temperature value of $\sigma_{ac} \approx 2 \times 10^{-7}$ mho/m, to within about a factor of 2. This occurs despite the several orders of magnitude decrease in σ_0 that occurs for the mixed alkali case in comparison to that of either single alkali glass. This "mixed alkali effect" is well documented [17] and causes nearly a doubling of the dc activation energy and a substantial downward shift of σ_{ac} as seen in Fig. 3(a). In spite of this, the low temperature limit of σ_{ac} is only modestly lowered in the mixed alkali case.

At high temperatures, $\sigma_I(\omega)$ exhibits scaling (n constant) with the scale set by σ_0 . If the type II dispersion seen at low temperatures is due to ion motion, as is believed to be responsible for type I dispersion, one would have anticipated that the approach of σ_{ac} to a constant value would likewise reflect the substantial decrease in the scale σ_0 caused by the mixed alkali effect and occur at a value much lower in the mixed alkali case than in the single alkali situation. Instead σ_{ac} approaches nearly the same limit in both situations.

Given the limited influence of ion mixing upon the position of $\sigma_{II}(\omega)$, we propose that type II dispersion represents a process separate from the motion of ions. We further suggest that type II dispersion arises from the limited motion of NBO's in the metaphosphate matrix [1]. Spectroscopic evidence including recent NMR results [18] indicate only nominal changes occurring to the metaphosphate structure upon mixing ions. This then explains the roughly fixed position of $\sigma_{II}(\omega)$ observed in all three glasses.

Hence we interpret the observed temperature dependence of n as a crossover effect which results when the dominance of $\sigma_I(\omega)$ over that of a roughly temperature independent $\sigma_{II}(\omega)$ decreases with decreasing temperature as viewed within a given window of frequency. Such behavior is depicted schematically as an inset to Fig. 4. This decrease of $\sigma_I(\omega)$ is ultimately controlled by the temperature dependence of the scale σ_0 and, since $\sigma_{II}(\omega)$ appears to be roughly the same in all three systems, the slope of $\sigma(\omega) - \sigma_0$ that we observe between 1 and 10^6 Hz should cross over from $n = 0.67$ (0.61) to unity. The crossover appears at different temperatures for the three glasses because $\sigma_0(T)$ differs for each. However, if we instead view the crossover from the standpoint of σ_0 , or equivalently the characteristic frequency scale ω_c , we expect $n(\sigma_0)$ to be the same for all three glasses. In Fig. 4 we plot n versus σ_0 . To complete the plot we have estimated σ_0 at low temperatures from an extrapolation of the observed high temperature Arrhenius behavior. By plotting n in this manner, its variation for all three glasses collapses upon a common curve, as proposed. Furthermore, the crossover from $n = 0.67$ (0.61) to unity occurs over about six decades in σ_0 (or six decades in ω_c) in accordance with the six decades frequency window of our spectrometer.

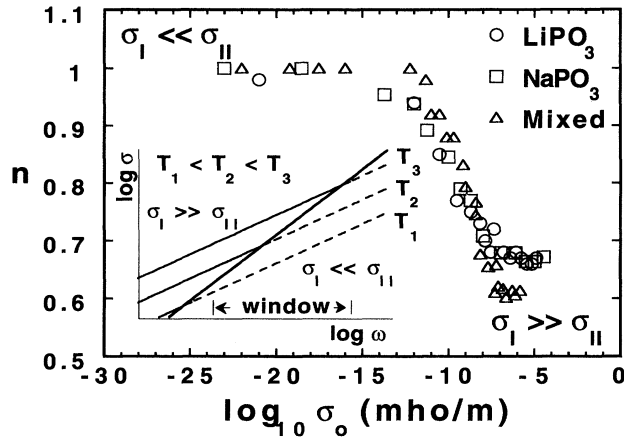


FIG. 4. Plot of n versus σ_0 showing the common crossover behavior of all three glasses. Inset shows schematically how the $n(T)$ behavior arises.

In conclusion, the evidence presented here supports the proposal that $\sigma_{II}(\omega)$ arises from a separate phenomenon unrelated to the ion motion which produces $\sigma_I(\omega)$. There is *no direct indication* that the scaling observed at high temperatures for $\sigma_I(\omega)$, and associated with ion motion, actually changes. Instead the appearance of $n(T)$ is only a result of the increasing significance of the weakly temperature dependent contribution $\sigma_{II}(\omega)$ to the measured $\sigma(\omega)$ that occurs within a given frequency window as $\sigma_I(\omega)$ is pulled past by its strongly temperature dependent scale σ_0 .

The proposition that $\sigma_{II}(\omega)$ is separate from the ionic motion that produces $\sigma_I(\omega)$ is further supported by its roughly fixed location in these metaphosphate materials, which suggests that $\sigma_{II}(\omega)$ is associated with the PO_3 matrix whose structure exhibits only small variations even in the mixed alkali case. In contrast, the mixing of ions not only significantly lowers the dc conductivity but also

results in a shift of the dispersion exponent from 0.67 to 0.61. This shift demonstrates that interionic interactions are an important aspect of $\sigma_I(\omega)$ and that mixing of ions seems to result in a different class of universality.

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