

SCALING BEHAVIOR IN THE CONDUCTIVITY OF ALKALI OXIDE GLASSES

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Although the frequency dependent conductivity, $\sigma(\omega)$, of ion-containing glasses displays power law dispersion ($\sigma(\omega) \approx \omega^n$) that can usually be described by a master curve, several findings have suggested that this scaling fails at low temperatures as indicated by a temperature dependence of the scaling exponent, n . We investigate this behavior in the frequency range between 1 Hz and 10^6 Hz for a different materials including alkali metaphosphate glasses and a polymer.

We identify two distinct regimes of conductive behavior, σ_{\perp} and σ_{\parallel} . The first, σ_{\perp} , is strongly temperature dependent and appears to obey a master curve representation. The second, σ_{\parallel} , exhibits only a weak temperature dependence with a roughly linear frequency dependence. A strong depression of σ_{\perp} occurs for the mixed alkali case, but σ_{\parallel} is unaffected and occurs at roughly the same location in all the alkali compositions studied. We propose that σ_{\parallel} does not arise from cation motion, but rather originates from a second mechanism likely involving small distortions of the underlying glassy matrix. This assignment of σ_{\parallel} is further supported by the roughly universal location of σ_{\parallel} , to within an order of magnitude, of a variety of materials, including a polymer electrolyte and a doped crystal. Since $\sigma_{\perp}(T)$ and $\sigma_{\parallel}(T \approx \text{const.})$ are viewed as separate phenomena, the temperature dependence of the scaling exponent is shown to result merely from a superposition of these two contributions and does not indicate any intrinsic failure of the scaling property of σ_{\perp} .

KEYWORDS: glasses, oxides, electrical conductivity, low temperature, frequency dependent, constant loss

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1. Introduction

Non-Debye relaxation is a common feature in disordered materials and is observed by a wide variety of dynamical probes. One example occurs in the conductivity of ion-containing glasses which quite generally exhibit a power law dispersion of the form,

$$\sigma = \sigma_0 \left\{ 1 + (\omega/\omega_D)^n \right\} \quad (1)$$

where the d.c. conductivity, σ_0 , and characteristic rate, ω_D , typically display Arrhenius temperature dependences. A wide variety of materials exhibit this behavior as was first noted by Jonscher[1] who in comparing the dispersion of many materials concluded that the exponent, n , was roughly universal and confined to a range of $n \approx 0.7 \pm 0.2$. The dispersion, commonly referred to as the "universal dynamic response", is often attributed to the non-exponentiality of ionic relaxation[2] and shows up not only in the electrical conductivity but in other probes of ion motion such as the frequency dependence of the minimum spin-lattice relaxation time, T_1 , measured by nuclear magnetic resonance (NMR) techniques[3,4].

The conductivity given by Eq. (1) has a particularly useful feature in that when n is constant, say independent of temperature, then a double logarithmic plot of $\sigma(\omega)$ can be shifted by σ_0 and ω_D along the ordinate and abscissa, respectively, so as to collapse all the data onto a common master curve, $f(x) = 1 + x^n$. This property highlights the separation of the ion dynamics into one part due to "scales" which merely reflects the thermodynamics and another part, the single scaling curve, $f(x)$, which conveys the fundamental nature of ion motion irrespective of changes in the thermodynamic fields. Indeed if Jonscher's

assertion is correct, the universality of the exponent n necessarily implies that the ion dynamics in all these different materials is fundamentally identical.

However, there is sufficient evidence that the scaling exponent, n , is not constant, but depends upon temperature. Many have observed that the high frequency portion of $\sigma(\omega)$ becomes increasingly more steep as lower temperatures are approached. This trend was well illustrated by Lee et.al.[5] who found that the power law exponent of several glasses became unity at low temperatures, well in advance of zero Kelvin. Furthermore, at these lower temperatures, the conductivity behaves quite differently from that seen at higher temperatures and has been referred to as "Type II" dispersion[6] approximately described by

$$\sigma_{||} \approx BT\omega \quad (2)$$

where the temperature dependence here is much weaker than the Arrhenius dependence seen at higher temperatures.

Quite naturally the contrasting dispersive and temperature dependent features of this second regime suggest that ion dynamics at low temperatures might be controlled by a new mechanism. One proposal which has gained much acceptance is that $\sigma_{||}$ results from the dynamics inherent in a two level system or so-called asymmetric double well potential (ADWP)[2]. Motion of ions in such potential wells can produce a linear frequency dependent conductivity at sufficiently low temperatures, consistent with Eq. (2).

Nevertheless, the $n=n(T)$ behavior appears to be ubiquitous and suggests that the scaling properties of $\sigma(\omega)$ observed at high temperatures fail at lower temperatures. Interestingly, however, this temperature-dependent dispersion is only observed in $\sigma(\omega)$. NMR measurements which probe the dynamics of ions in the glass also reveal a corresponding power law dispersion of the form,

$$T_1 \approx \omega^{-2-n_{\text{NMR}}} \quad (3)$$

However, unlike the situation for $\sigma(\omega)$, the dispersion of T_1 , given by the exponent n_{NMR} is temperature *independent*. Thus, in principal, $T_1(\omega)$ at different temperatures can be collapsed onto a single scaling curve[7]. Both $\sigma(\omega)$ and $T_1(\omega)$ result from cation displacements, and in the most naive approach[8] the two exponents, n and n_{NMR} , should be equivalent. The apparent differences between n and n_{NMR} have most recently been rationalized in terms of differences in the specific correlation functions from which $\sigma(\omega)$ and $T_1(\omega)$ arise[9]. The conductivity reflects simply a particle-particle correlation, while $T_1(\omega)$ is influenced at short distances by a pair-pair correlation resulting from the magnetic dipole interaction of cation pairs. In connection with this, recent Monte Carlo simulations[4,7] of a Coulombic interacting gas of cations, have successfully reproduced the qualitative features of n approaching unity while n_{NMR} remains constant.

In the present work, we examine the low temperature conductivity of a series of alkali metaphosphate glasses including two mixed-alkali compositions. We provide evidence that the $n=n(T)$ behavior observed is a consequence of the superposition of two (unrelated) contributions to the conductivity, the second (σ_{II}) dominating at low temperatures. The mixed alkali compositions further reveal that this second process most likely results from motions of the phosphate matrix. This second contribution is also shown to be remarkably similar for a wide diversity of materials characterised by widely varying cation environments and densities, and again supports the contention that it is a mechanism distinctly separate from cation dynamics. As a consequence of these results, there is no direct indication that the exponent, n_I , associated with the Type I process involving cation dynamics and that is constant at high temperatures, ever ceases

to remain constant. This finding has profound ramifications for recent efforts aimed at relating the dispersive behavior of different cation probes such as electrical and NMR.

2. Experimental Procedures

Reagent grade materials were used to produce the following metaphosphate glasses: LiPO_3 , NaPO_3 , $25\text{Na}/25\text{Li}/50\text{PO}_3$, and $25\text{Cs}/25\text{Li}/50\text{PO}_3$. Each glass was cast into an ingot, then sectioned to 1 mm thick by 20 mm square impedance samples. Samples were annealed and then coated with an approximately 1 cm diameter circle of silver paint. Impedance measurements were performed using a Schlumberger 1260 impedance analyzer over the frequency range from 1 Hz to 1 MHz at several temperatures below the glass transition. Further experimental details have been presented previously[10].

3. Results

The frequency dependence of the conductivity for LiPO_3 is shown in Fig. 1 for several temperatures. The other three glass compositions, NaPO_3 , $25\text{Na}/25\text{Li}/50\text{PO}_3$, and $25\text{Cs}/25\text{Li}/50\text{PO}_3$, also exhibit similar features. In the figure, both the frequency independent (d.c. conduction) process and the frequency dependent (power law) behavior are visible at high temperatures. With decreasing temperature, σ_0 becomes immeasurably small and the slope, $\log(\sigma)/\log(\omega)$, increases. The increase of n with decreasing temperature is more clearly illustrated in Fig. 2 where the d.c. contribution has been subtracted. At high temperatures, n is roughly constant at a value of $n (= n_1) \approx 0.67$. With decreasing temperature below about 285 K, n increases and attains a value of approximately unity at temperatures just below 200 K. Similar results were

obtained for all four glasses, except that the two mixed alkali cases exhibited a slightly lower value of the high temperature exponent, $n_H \approx 0.61$. Otherwise all four show an approach of n to unity and results of $n(T)$ are displayed in Fig. 3b.

These $n(T)$ trends are now compared with the activated behavior of σ_{ac} , here arbitrarily defined at 10^5 Hz by $\sigma_{ac} = \sigma(10^5 \text{ Hz}) - \sigma_0$. As displayed in Fig. 3a, all four glasses show similar temperature trends in that σ_{ac} is reasonably Arrhenius at high temperature, but becomes weakly temperature dependent or nearly constant at lower temperatures. The only distinction is in the high temperature regimes where the activation energy of the two mixed alkali glasses are larger in comparison with the single alkali glasses. This increase in activation energy is obviously a reflection of the well documented "mixed-alkali effect" (MAE)[11,12] which strongly suppresses cation conduction.

4. Discussion

One key observation from Figs. 3a,3b is the distinctive correlation of $n(T)$ to $\sigma_{ac}(T)$. In fact, three specific regimes of σ_{ac} and n can be identified. The first occurs at high temperature where σ_{ac} is Arrhenius and $n = n_H$ and is constant. The second regime is at low temperatures where σ_{ac} is not particularly temperature dependent and $n \approx 1$ and again is constant. The last regime separates the other two and is characterised by continuous variation in both n and E_{ac} . Hence the evolution of $n(T)$ in Fig. 3b is neither smooth nor monotonic, but instead appears characteristic of a crossover between two separate regimes of constant n behavior.

Our second key observation in Figs. 3a,3b concerns the influence of the MAE upon these two (low and high temperature) regimes. As is seen in Fig. 3a, the activation energy of the two mixed alkali glasses is much larger than that of either of the two single alkali glasses. Hence the conduction of cations in the

mixed glasses is drastically impeded. This MAE however, shows up only in the high temperature process[13,14], since at low temperatures σ_{ac} is virtually the same ($\sigma_{ac} \approx 2 \times 10^{-7}$) for all four glasses.

We take this second observation as evidence that the low temperature process cannot be directly associated with the dynamics of the cations but instead results from some, presently unspecified, (anionic) motion of the host matrix. Consequently, the net conductivity that we observe results from the superposition of two separate contributions; $\sigma_1(\omega)$ due to cation displacements and given by Eq. (1) with n fixed at n_1 , and $\sigma_{II}(\omega)$ due to matrix motions and given by Eq. (2). Due to the strong Arrhenius dependence of σ_1 , it naturally dominates at high temperatures. By the same reasoning, this cation contribution also becomes vanishingly small at low temperatures allowing σ_{II} to eventually dominate the measured conductivity.

We interpret the temperature dependence of the exponent n as merely a result of the increasing dependence, as viewed within a given spectrometer window, of σ_{II} to the total conductivity with decreasing temperature. $n(T)$ appears different for all four glasses only because the specific temperature dependence of σ_1 differs for each glass. In principle n should evolve identically when viewed in terms of the relative approach of $\sigma(\omega)$ to that of the matrix $\sigma_{II}(\omega)$. We can test this by attempting to scale $n(T)$ of all four glasses to a common curve. In Fig. 4 we plot the exponent n (normalized so as to extend from zero to one in all four cases) against the ratio of σ_{II} at 10^5 Hz to σ_{ac} , and observe a reasonably good collapse of all four data sets to a single common dependence. Also included are measurements on the ionic glassformer $0.4Ca(NO_3)_2-0.6KNO_3$ which can also be collapsed to this same curve. Furthermore, the collapsed data conform well to the line which we obtained by least squares fitting

a single power law to a synthetic data set numerically formed by summing together two power laws, $\sigma_1 \approx \omega^n$ and $\sigma_{II} \approx \omega$.

In an effort to better understand the nature of the σ_{II} mechanism we have compiled in Fig. 5 σ_{II} data from systems including not only the present phosphate glasses, but also a doped crystal and a polymer. Despite its weak temperature dependence, σ_{II} is found in roughly the same range, namely $\sigma_{II} \approx 10^{-12} \chi(\omega/2\pi)$, to within a decade for all these different materials. This remarkably similar behavior is contrasted by the dissimilar cation concentrations involved and again supports the notion that σ_{II} is a reasonably universal feature which is not derived from the cation dynamics. It also suggests that the mechanism responsible for σ_{II} is quite common and roughly independent of any long range details of the matrix. In many respects, σ_{II} appears to be what others often refer to in condensed matter as "1/f" or "flicker" noise; a phenomenon found in a vast number of situations[15].

Lastly, we consider the polymer case in more detail. In Fig. 6a are results of $\sigma(\omega)$ at various temperatures above and below T_g of poly(propylene glycol) (MW \approx 4000) (PPG4000) into which a small amount of LiClO_4 was dissolved. The ratio of ether oxygens of PPG4000 to lithium cations is about 300. The spectra are complicated by the presence of dipolar relaxation processes[16] (α - and α' -relaxations) but at high temperatures a d.c. conduction is apparent and at low temperatures $\sigma(\omega)$ approaches a roughly linear slope (i.e., σ_{II}). This is to be contrasted with $\sigma(\omega)$ of neat PPG4000 shown in Fig. 6b. In this situation the absence of free cation carriers is clearly marked by the absence of a d.c. conductivity, yet despite the absence of charge carriers, essentially the same σ_{II} is observed at low temperatures! Indeed σ_{II} remains virtually unaffected even up to high concentrations of 16 ether oxygen per Li cation. It appears then that σ_{II} cannot be attributed to cation motion in this case and instead must reside in

features of the matrix dynamics which in turn are reasonably similar in most materials.

Since it now appears that $n(T)$ does not result from any intrinsic changes in cation dynamics, it would be profitable to review the issues of NMR and conductivity dispersion anew. Our findings suggest that the dispersion exponent of cation motion, n_1 , is in fact constant at all temperatures. This clearly conflicts with the simulation results of Bunde and co-workers[4,7] who observed n increase with decreasing temperature. This temperature-dependent conductivity dispersion is predicted by their simulations of a Coulombically interacting ion gas in a disordered matrix. However, the same model produces no temperature dependence of the NMR dispersion, in accord with experiment. Our results here suggest that $n(T)$ is only an artifact associated with the interference of a separate mechanism, and is not a direct result of changes in cation dynamics. Indeed the constant nature of n_1 suggests that the NMR and conductivity dispersions might be more directly related than previously thought.

5. Conclusions

In summary, we have presented here several pieces of evidence which support the proposal that low temperature, linear frequency dependent conductivity in disordered material is caused not by the direct motion of cations, but more likely by distortions of the host matrix in which these cations reside. As a consequence, the often observed increase in the dispersion exponent to unity at low temperatures does not necessarily imply that there is a change in the physical characteristics of the cation relaxation. Hence recent models aimed at explaining the rise in n as resulting from cation motions may be misdirected and should be re-examined.

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FIGURE CAPTIONS

- Fig. 1 $\sigma(\omega)$ of LiPO_3 measured at 336, 316, 295, 279, 267, 253, 240, 203, and 133 K. The line with unity slope identifies Type II dispersion seen at low temperatures.
- Fig. 2 The a.c. 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.
- Fig. 3 (a) Arrhenius plot of σ_{ac} showing the low temperature approach to a limiting value. (b) Corresponding plot of the dispersion exponent showing the simultaneous crossover from Type I to Type II behavior. Also displayed are the differing high temperature exponents for the single ($n_1 = 0.67$) and mixed ($n_1 = 0.61$) alkali cases.
- Fig. 4 Scaling plot of the normalized exponent n versus the fraction of $\sigma_{||}$ contributing to σ_{ac} showing the common crossover behavior of all four metaphosphate glasses. Also included is the ionic glassformer $0.4\text{Ca}(\text{NO}_3)_2\text{-}0.6\text{KNO}_3$. The solid line is a predicted variation described in the text.
- Fig. 5 Compilation of available $\sigma_{||}$ for a variety of differing materials including (A) a doped crystal[13] (55K to 300K), (D) a polymer (130K to 180K), and several ionic glassformers (B[5] (4K to 220K), C (130K to 250K), E (250K)).

Fig. 6 a) Conductivity of PPG4000 with a low concentration of LiClO_4 added. With decreasing temperature, σ_0 , α -relaxation, and $\sigma_{||}$ are sequentially observed. b) Conductivity of neat PPG4000 showing absence of σ_0 , presence of two relaxations (α , and α'), and $\sigma_{||}$ virtually unchanged from above.

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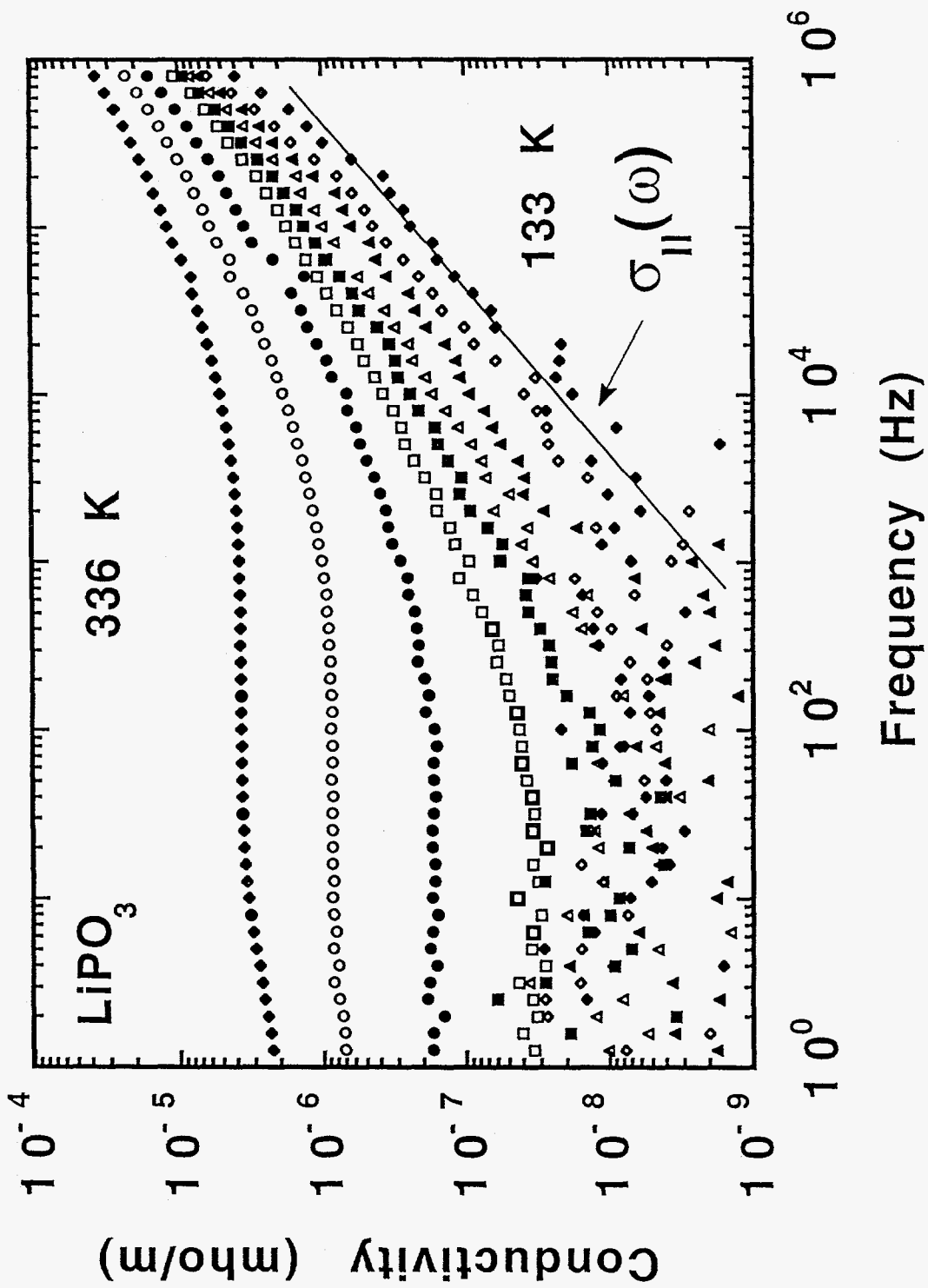


Fig. 1

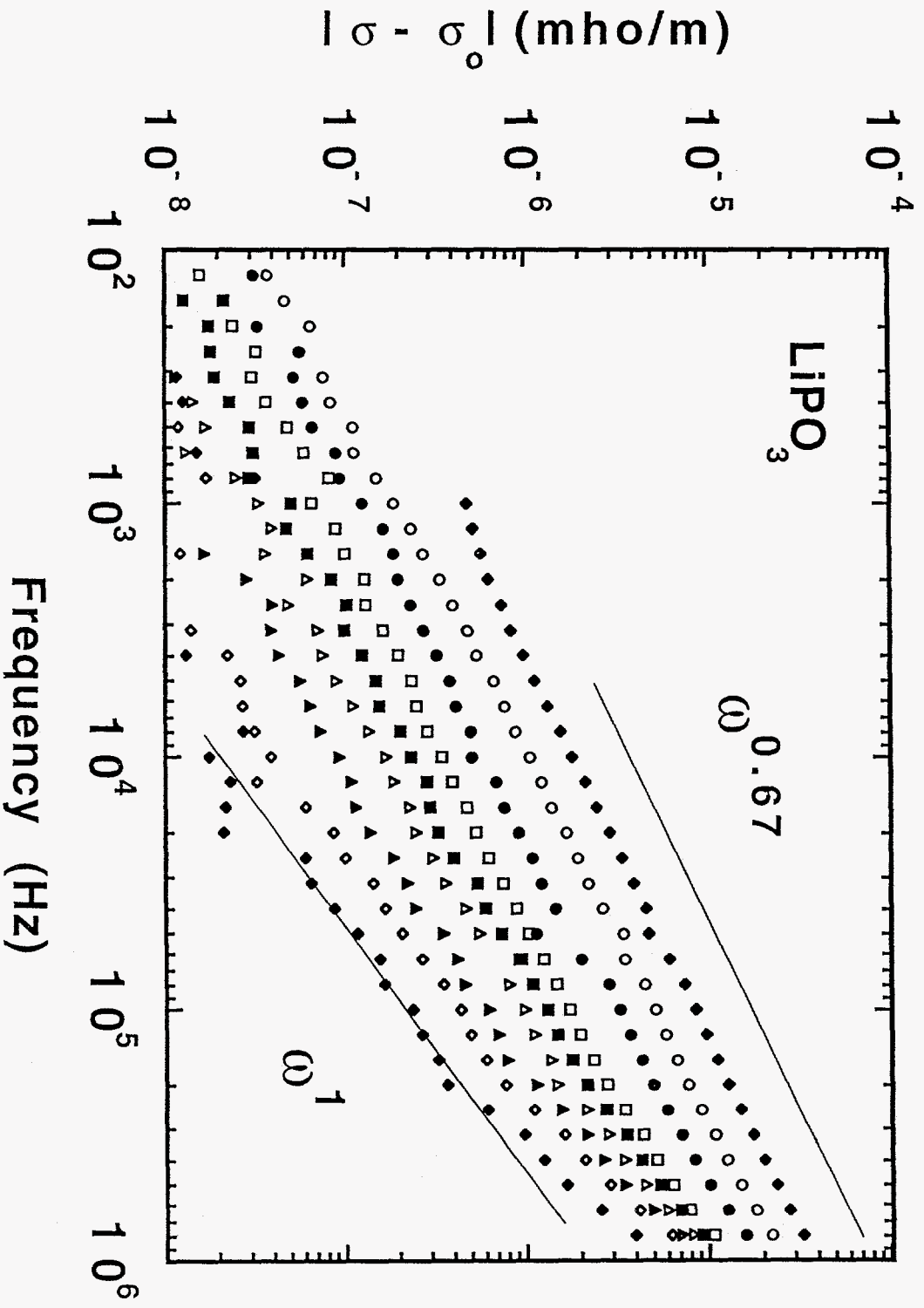


Fig. 2

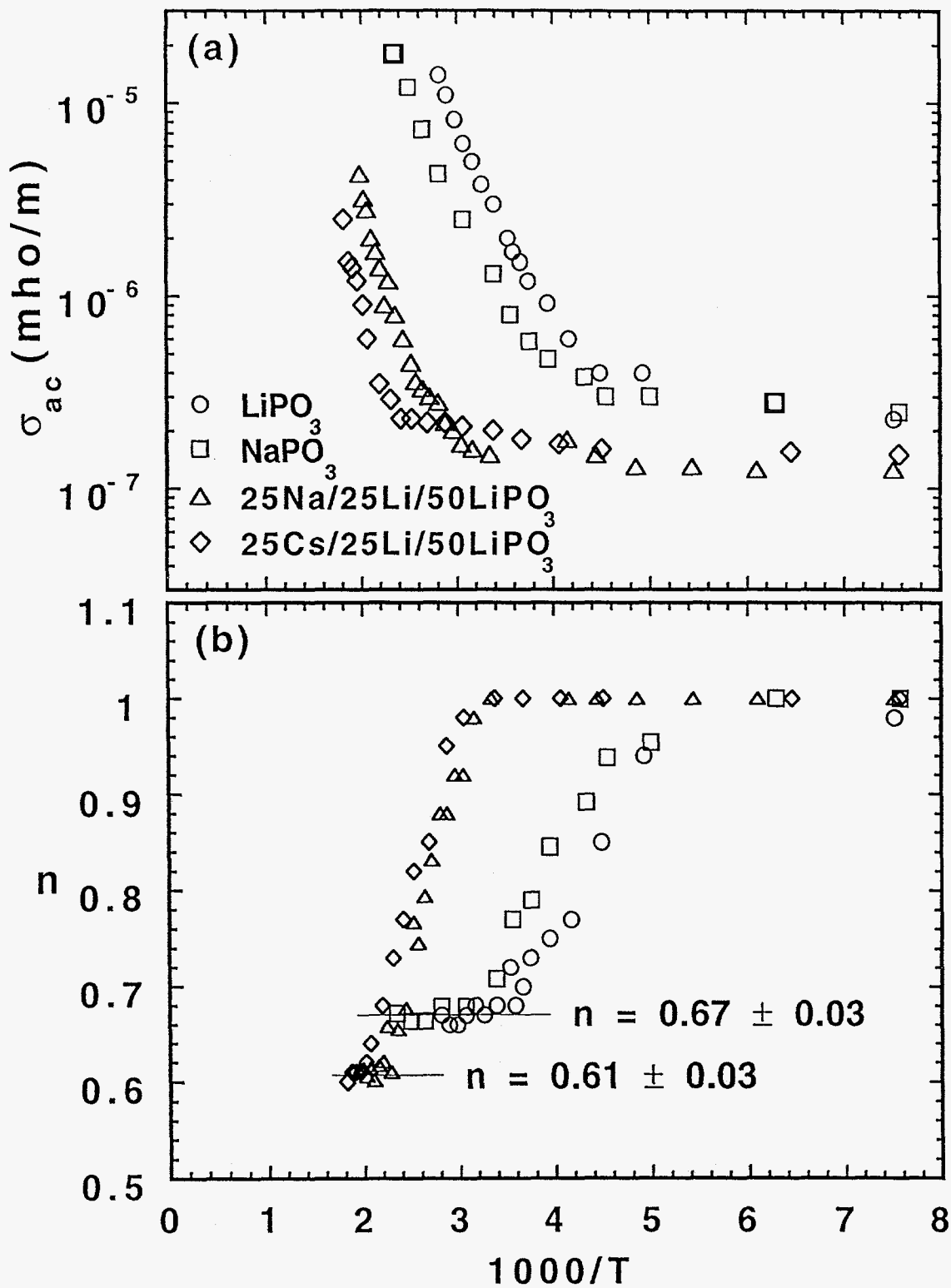


Fig. 3

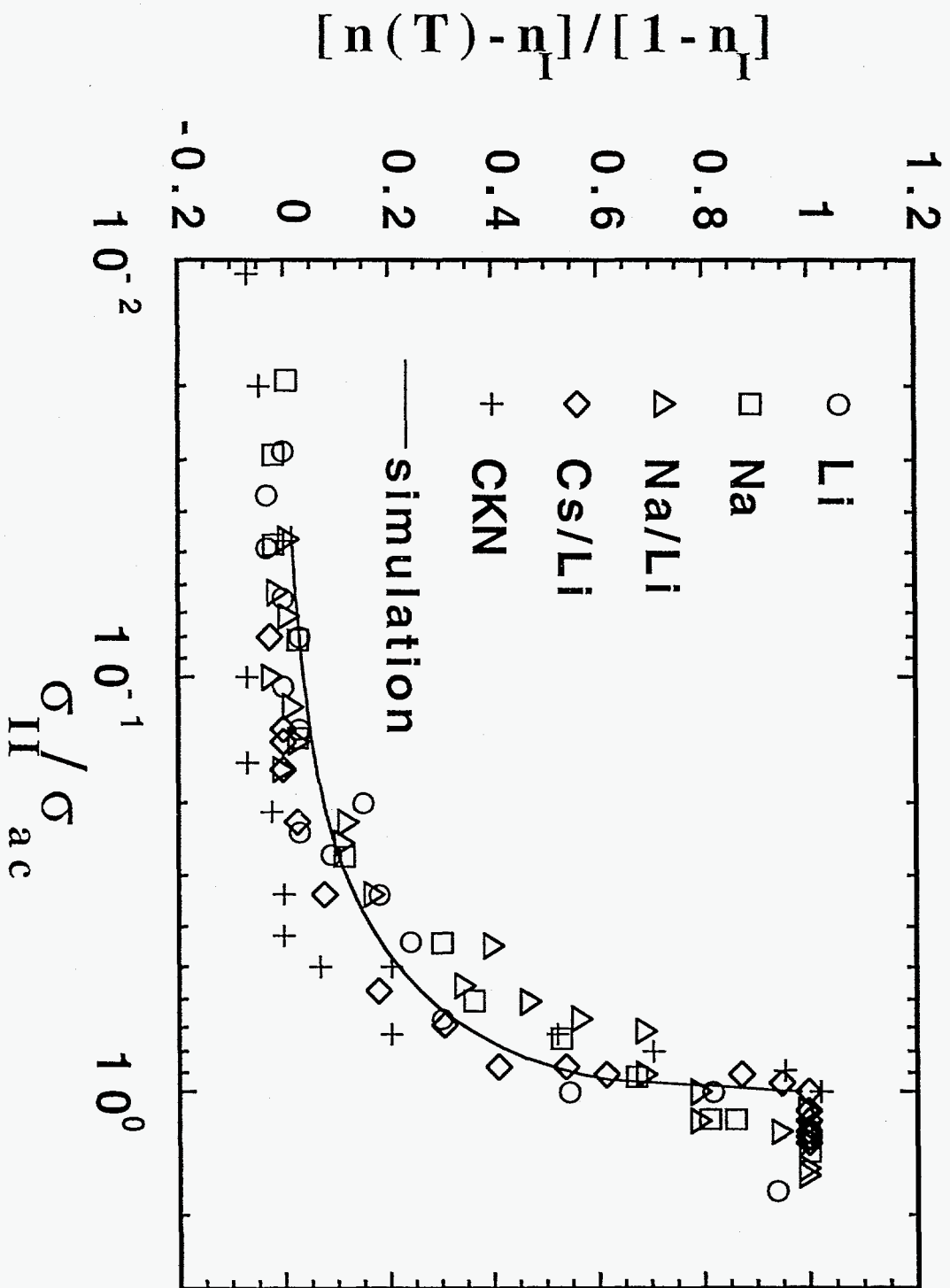


Fig 4

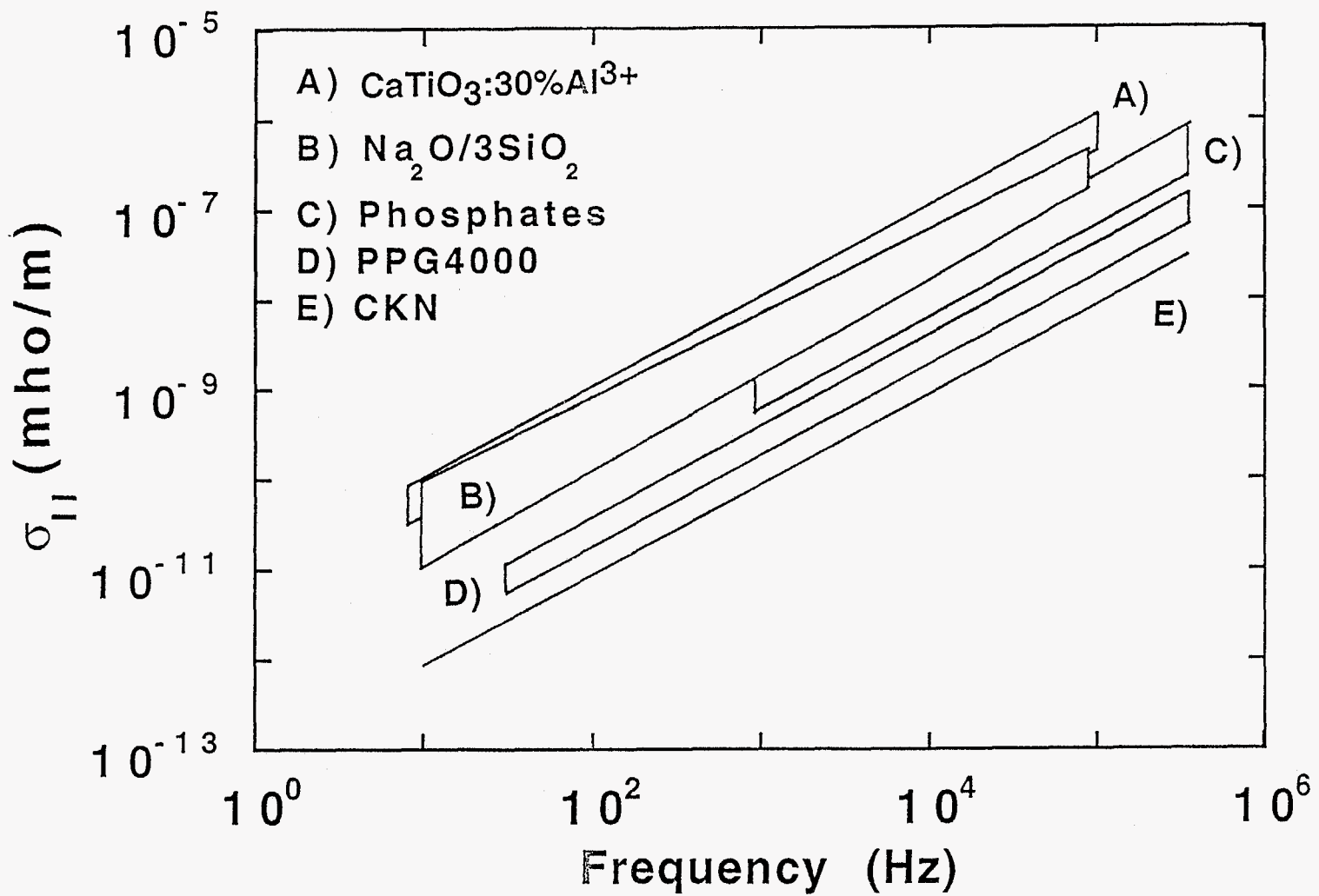


Fig. 5

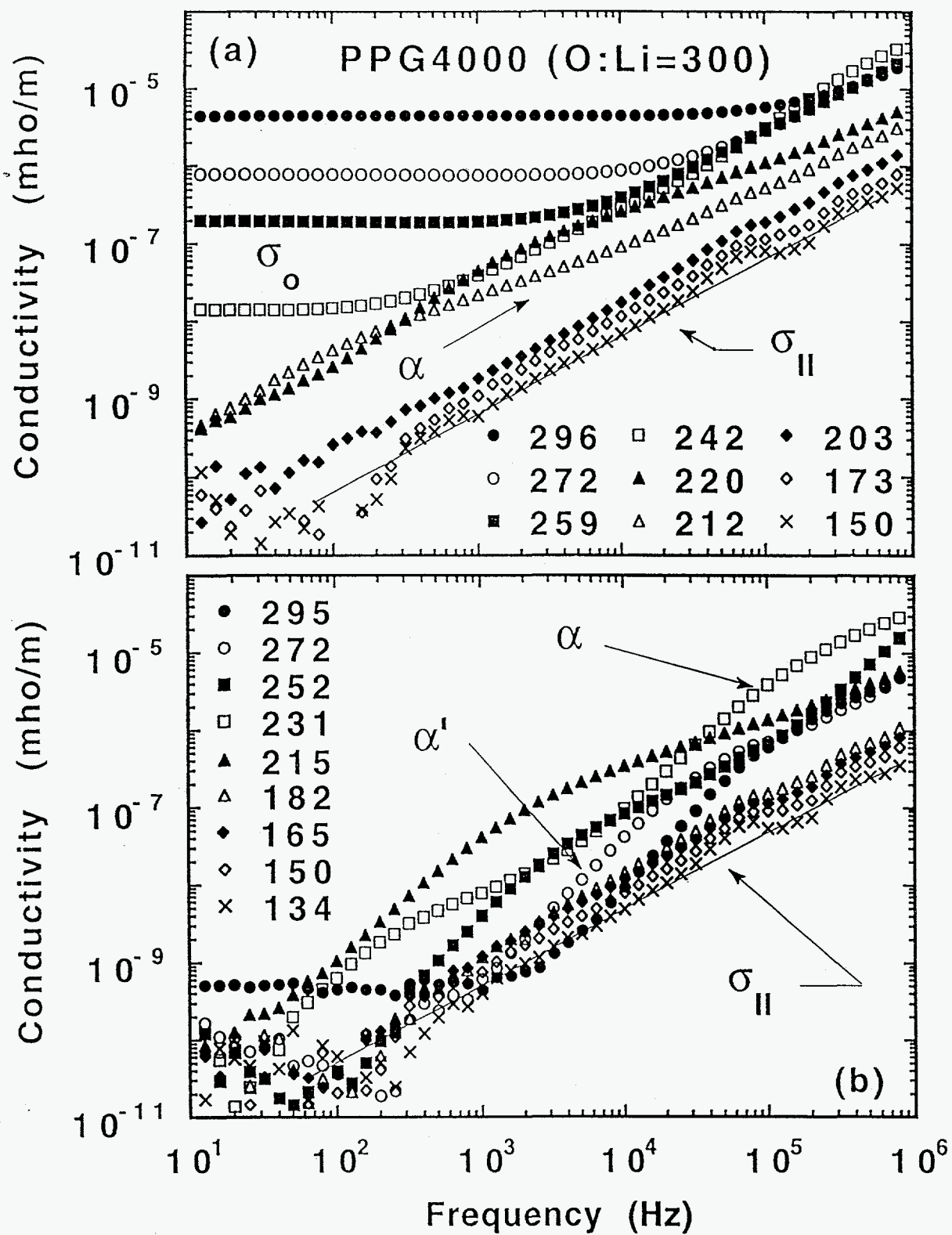


Fig. 6