

## Distinguishing Two Contributions to the Nearly Constant Loss in Ion-Conducting Glasses

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(Received 18 April 2002; published 18 October 2002)

In an effort to understand the origins of the nearly constant loss in disordered materials, we report dielectric studies of a series of sodium germanate glasses,  $(\text{Na}_2\text{O})_x(\text{GeO}_2)_{1-x}$  for  $x = 0, 0.003, 0.01, 0.03,$  and  $0.1$  at temperatures between  $85$  and  $700$  K. Analysis of the conductivity scaling for these glasses demonstrates the existence of two contributions in the near constant loss; one due to mobile cations that conforms to the same scaling properties found for ion hopping at high temperatures and the other due to the glass network which dominates at low temperatures and low ion densities.

DOI: 10.1103/PhysRevLett.89.195901

PACS numbers: 66.30.Hs, 61.43.Fs, 66.10.Ed, 66.30.Dn

Ion-conducting materials play a prominent role in numerous solid electrolyte applications including batteries and chemical sensors [1,2]. Despite their technological significance, a complete understanding of the ionic transport process is still missing [3]. The challenge is to understand ion motion as a mass transport process that is intimately influenced by the nature of the matrix through which the ions move as well as interactions between the ions themselves. For many years now, the primary source of experimental information regarding the ion kinetics has been derived from frequency-dependent dielectric spectroscopy. Measurements of the ac conductivity and permittivity not only provide for an evaluation of the steady state (dc) transport, but also reflect at higher frequencies the transient dielectric response resulting from localized displacements of the ions [4,5].

A significant feature of the ac conductivity is its remarkably universal frequency dependence [4,6]. For almost all thermally activated hopping processes, involving both ions and electrons and both crystalline and amorphous matrices, the ac conductivity can be well approximated [7–9] as

$$\sigma(f) \approx \sigma_0[1 + (f/f_0)^n] + Af. \quad (1)$$

This frequency dependence corresponds [10] to specific regimes of temporal evolution of the ions' mean square displacement,  $\langle r^2(t) \rangle$ , and covers an enormous range in ion dynamics from the nearly vibrational motion at short times to random diffusion (with dc conductivity,  $\sigma_0$ ) at long times. Furthermore, scaling properties of the ac conductivity have recently revealed the remarkable nature of this hopping process in that the pattern of evolution of  $\langle r^2(t) \rangle$  from shortest times to longest times is largely insensitive to the details of the network through which the hopping charges pass [11]. Such insensitivity is reminiscent of critical phenomena [12].

It is customary in the literature to separate the ac conductivity into two regimes. The first regime, corresponding to the first term in Eq. (1), is commonly referred to as the “Jonscher power law” (JPL) in reference to early

studies by Jonscher [4,6], who demonstrated that the occurrence of power-law-like dispersion is a very common feature of numerous ion-containing materials both crystalline and noncrystalline. The second term in Eq. (1) indicates a second regime of ac conductivity wherein the dielectric loss [ $\epsilon''(f) = \sigma(f)/2\pi f\epsilon_0$ ] is approximately frequency independent. For this reason, this second term is commonly referred to as the “nearly constant loss” (NCL) [8,13].

Current interpretations of Eq. (1) largely agree as to the physical significance of the JPL regime. This frequency-dependent behavior is believed to result from ion hopping within the disordered network and can be mapped back [10] to a corresponding temporal pattern of the ions'  $\langle r^2(t) \rangle$  which includes both correlated and random hopping.

Interpretations of the NCL regime remain more speculative. The NCL has been studied with regards to its temperature and frequency dependence, using both dielectric and NMR spectroscopies [8,13,14], and the findings indicate that, unlike the JPL, the ac conductivity associated with the NCL exhibits a high degree of linearity in frequency and is only weakly dependent upon temperature. Furthermore, the NCL appears endemic to many materials including those which do not possess free mobile charges [15]. Thus one interpretation of the NCL is that it is fundamentally distinct from the JPL motion and may be the result of some form of polarization process occurring in the network [16,17]. In this context, the NCL might even be regarded as a manifestation of the sub- $T_g$  relaxation commonly seen in glassy materials below the glass transition [18,19]. Alternatively, the NCL may be the result of low energy displacements of many cations which collectively behave in the manner of a transition over an asymmetric double well potential (ADWP), as proposed by Kanert and co-workers [14,20]. Such “two level system” scenarios have been advanced to account for many of the anomalous thermodynamic properties seen in glasses at very low temperatures [21,22].

On the other hand, several hopping models [23,24] for the ionic motion predict a frequency-dependent conductivity due to ionic motion that increases continuously with increasing frequency to a linear dependence that is indistinguishable from the behavior indicated by Eq. (1). Thus an alternative interpretation of the NCL is that separation of the ac conductivity in Eq. (1) into two parts is purely empirical and that the entire expression should be replaced by a single dielectric response due to hopping ions that evolves continuously from the frequency-independent  $\sigma_0$  at low frequencies to a linear frequency-dependent conductivity at high frequencies.

Discerning which of these two competing interpretations of the NCL is correct (if either) is a difficult task. However, a new aid for distinguishing ion motion from that of other polarization processes is the recent realization that the ac conductivity due to ion hopping appears to conform to specific scaling laws [25–27]. The ac conductivity can be scaled,

$$\sigma(f)/\sigma_0 = F_1(x); \quad x = f/f_0. \quad (2)$$

A corresponding scaling of the permittivity,  $[\varepsilon'(f) - \varepsilon_\infty]/\Delta\varepsilon = F_2(x)$ , is also possible [28] where  $\varepsilon_\infty$  is the limiting high frequency dielectric constant that includes all faster polarizing processes present in the medium and  $\Delta\varepsilon = \varepsilon'(0) - \varepsilon_\infty$  is the magnitude increase of the dielectric constant associated with the microscopic ion hopping process [29]. These two scaling laws are connected by the Kramer-Kronig transforms with the result that

$$f_0 \propto \sigma_0/\varepsilon_0\Delta\varepsilon, \quad (3)$$

where  $\varepsilon_0 = 8.854 \times 10^{-12}$  F/m is the permittivity of free space.

For varying ion concentration, a unique concentration dependence of  $\Delta\varepsilon T$  occurs leading to nontrivial collapse of  $\sigma(f)$  spectra to a common master curve [28]. This concentration dependence is a signature of the ionic motion and can be used to distinguish ionic contributions in the NCL from other, nonionic contributions.

In a recent Letter, Roling and co-workers [30] employed the scaling properties of  $\sigma(f)$  to demonstrate that for  $T > 173$  K, the NCL of a series of Na-germanate glasses conformed to the same scaling as that of the JPL seen at higher temperatures. They concluded that the NCL at temperatures above 173 K is the result of the same ionic dynamics that drives the JPL behavior. The study, however, did not extend to temperatures lower than 173 K, and Roling was cautious to note that others [13,20] have observed distinct features in the ac conductivity of similar low concentration Li-germanate glasses near 100 K that would clearly violate the scaling.

In this study, we have applied scaling to a similar series of Na-germanate glasses. However, our study extends to lower temperatures and to lower ion concentrations to

include the unmodified  $\text{GeO}_2$  glass. Although we find good agreement with the findings of Roling and co-workers in that the ac conductivity of the modified glasses conform to scaling at temperature above ambient, our low temperature results indicate that this scaling begins to fail for the lowest ion-containing samples. We demonstrate that this failure is not the result of any change in ion dynamics but rather is the direct result of the existence of *two separate and distinct contributions* to the NCL present in these materials. The one, dominant at high temperatures and ion concentrations, obeys the scaling and is thus a continuous extension of the JPL response due to hopping ions into NCL regime. The other is found in  $\text{GeO}_2$  (ion-free network) and is proposed to arise from network polarizations of an unknown origin, but which may correspond to sub- $T_g$  relaxations of the network or to the ADWP [13,20–22] dynamics often proposed to explain certain anomalous low temperature properties of glasses.

The glasses investigated in the present study are  $(\text{Na}_2\text{O})_x(\text{GeO}_2)_{1-x}$  with  $x = 0.1, 0.03, 0.01, 0.003$ , and the unmodified  $\text{GeO}_2$ . Details of the glass synthesis and dielectric measurements have been published previously [31]. Measurements above ambient were performed using an automated impedance analyzer. Measurements below ambient temperature required additional precision and were obtained using a capacitance bridge (GenRad 1615A).

Figure 1 shows scaling of the  $\sigma(f)$  spectra obtained for all four modified glasses at temperatures above ambient. This scaling was performed in the following sequence. First, data sets for which  $\sigma_0$  was visible within the available frequency window of the analyzer (ca. 1 Hz to 1 MHz) were scaled using  $\sigma_0$  as obtained directly from

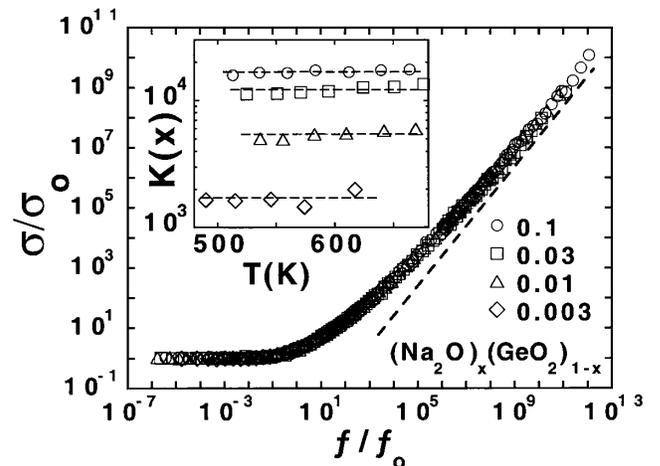


FIG. 1. Scaling plot of ac conductivity spectra obtained from  $(\text{Na}_2\text{O})_x(\text{GeO}_2)_{1-x}$  glasses at temperatures from ambient to 700 K. The dashed line of unit slope indicates the approach to NCL at high frequencies. Inset shows the concentration-dependent factor  $K(x)$  that results from scaling.

the data and  $f_0$  via the JPL as  $\sigma(f_0) = 2\sigma_0$ . Values of  $\sigma_0$  and  $f_0$ , so obtained, were used to determine the concentration-dependent constant  $K(x) = \sigma_0 T / f_0 \epsilon_0$  that is proportional to  $\Delta\epsilon T$  in the scaling ansatz [see Eq. (3)]. These values, displayed in the inset of Fig. 1, are reasonably temperature independent and can be approximated by the average value,  $\bar{K}(x)$ , indicated by the dashed lines in the figure. Additional spectra, including spectra obtained down to ambient temperature, for which  $\sigma_0$  could not be observed were then added to the scaling plot by obtaining  $\sigma_0$  through an extrapolation of  $\sigma_0 T = B \times \exp(-E/kT)$  and then  $f_0$  from  $f_0 = \sigma_0 T / \bar{K}(x) \epsilon_0$ .

Figure 1 demonstrates remarkable adherence of  $\sigma(f)$  to scaling over several decades in both  $\sigma$  and  $f$  (as well as 1.5 decade variation in ion density) that incorporates the NCL regime. In full agreement with Roling [30], we too conclude that, at these above-ambient temperatures, the NCL conforms to the same scaling as the JPL regime and so must originate from the same ion hopping processes.

We now follow the scaling to lower temperatures near and below 100 K. The extrapolation of  $\sigma_0 T$  becomes increasingly unreliable with decreasing temperature, and so we have chosen an alternative route for examining the scaling. The ac conductivity scaling in Eq. (2) can be rewritten as an equivalent scaling expression for the dielectric loss,  $\epsilon''(f)/\Delta\epsilon = F_3(x) \propto (1/2\pi x)F_1(x)$ . Since  $\Delta\epsilon T$  is proportional to the concentration-dependent constant  $\bar{K}(x)$ , this necessarily implies that the quantity  $\epsilon'' T$  in regions where  $\epsilon''(f)$  is nearly frequency independent should be a function of only the concentration and should appear vertically shifted with varying ion density regardless of the temperature dependence.

Measurements of  $\epsilon'(f)$  and  $\epsilon''(f)$  were performed at approximately ten frequencies between 500 Hz and 70 kHz using a high precision capacitance bridge. An example of  $\epsilon''(f)$  for  $x = 0.03$  is provided in Fig. 2 and

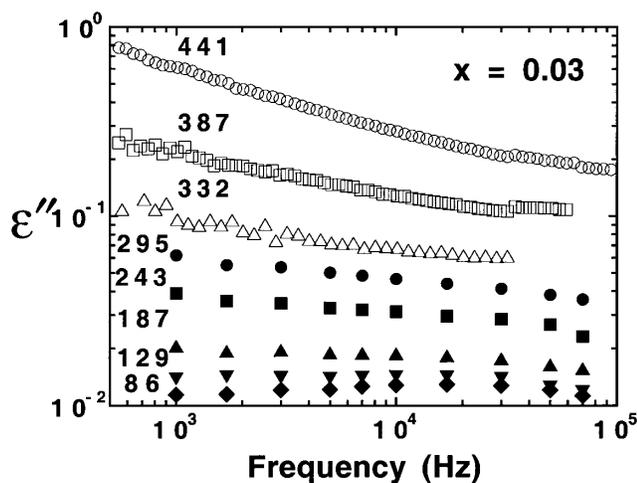


FIG. 2. Dielectric loss for  $x = 0.03$  at selected temperatures (in Kelvin) obtained with the impedance analyzer (open) and the capacitance bridge (solid).

indicates a frequency-independent loss at temperatures below about 200 K. A critical feature of this study was the inclusion of similar measurements performed on the “ion-free,” unmodified  $\text{GeO}_2$  glass. In Fig. 3 we plot  $\epsilon'' T$  (at a median frequency of 3 kHz) against temperature for all the glasses. For each of the modified glasses, we observed a steady decrease in  $\epsilon'' T$  with decreasing temperature. However, the measured  $\epsilon'' T$  do not conform to scaling since their relative spacing decreases with decreasing temperature.

The unmodified  $\text{GeO}_2$  glass also displayed a measurable loss. This loss represents inherent polarization processes present in the bare network without the added mobile alkali cations. Indeed, the temperature dependence of  $\epsilon'' T$  we observe here for  $\text{GeO}_2$  is similar to that observed by Jain [13] for  $0.23(\text{Li}_2\text{O})99.77(\text{GeO}_2)$  in that a minimum in  $\epsilon''$  is observed in roughly the same temperature range.

The simplest explanation for the scaling failure shown in Fig. 3 is that it is caused by an additional, nonionic, contribution to the total measured dielectric loss. Since none of the modified glasses contain large amounts of added alkali, a simple subtraction of  $\epsilon'' T$  of  $\text{GeO}_2$  from  $\epsilon'' T$  of each modified glass composition should offer a reasonable approximation of the value of  $\epsilon'' T$  due to only the presence of mobile cations. This subtraction was performed and the results are included in Fig. 3. As can be seen in the figure, this ionic contribution  $\epsilon''_{\text{ion}} T$  now displays a similar temperature dependence for all compositions with each composition shifted by a temperature-independent but concentration-dependent factor. In Fig. 4 we compare this shift with the value of  $\bar{K}(x)$  required for scaling ac conductivity spectra at above-ambient temperatures. Both  $\epsilon''_{\text{ion}} T$  and  $\epsilon'' T$  taken from Fig. 3 at two temperatures are plotted against

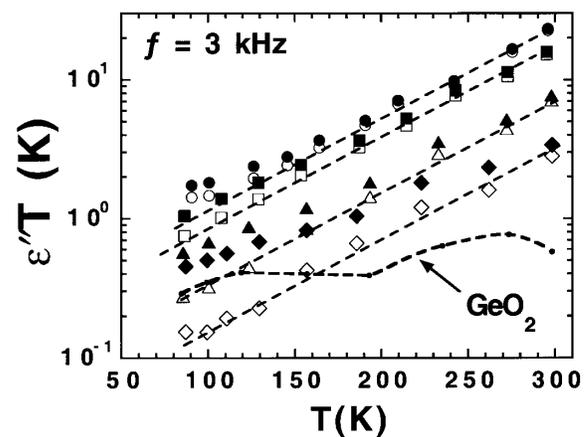


FIG. 3.  $\epsilon'' T$  measured at 3 kHz for a series of Na-germanate glasses at temperatures below ambient. Symbols correspond to key in Fig. 1. Closed symbols are the experimentally observed  $\epsilon'' T$ . Open symbols are the ionic contribution ( $\epsilon''_{\text{ion}} T$ ) obtained after subtraction of  $\epsilon'' T$  of the unmodified glass.

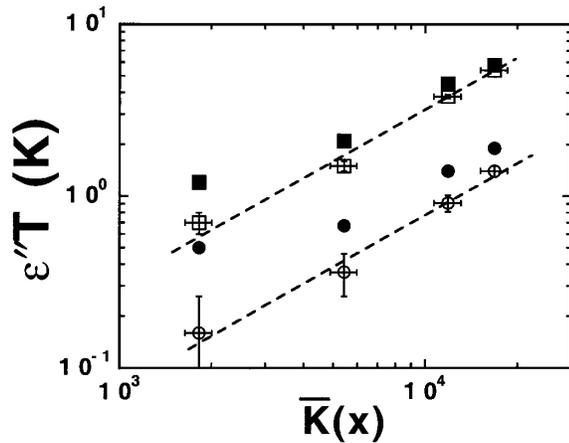


FIG. 4. Comparison of the concentration-dependent JPL scaling factor,  $\bar{K}(x)$ , to the concentration dependence of both the total measured  $\epsilon''T$  (solid) and the ionic contribution  $\epsilon''_{\text{ion}}T$  (Fig. 3) (open) at 100 K (circles) and 200 K (squares). The dashed lines indicate proportionality.

$\bar{K}(x)$ . From the figure we find that when the network contribution ( $\epsilon''_{\text{net}}T$ ) is removed, the remaining loss ( $\epsilon''_{\text{ion}}T$ ) displays the same concentration-dependent shift as that of the JPL scaling [i.e., the shift is proportional to  $\bar{K}(x)$ ]. This ionic contribution to the total NCL conforms to the same scaling and shows no tendency (down to 85 K) to deviate from that scaling.

Figure 3 conveys an important message. There are *two distinct contributions* to the NCL; one that is ionic and the other which is nonionic. Furthermore, once the nonionic contribution is removed, the remaining contribution due to mobile ions conforms to scaling and therefore shares the same origin as the hopping of ions that gives rise to conductivity dispersion in the JPL region near  $f/f_0 = 1$ .

Like Roling [30], we too conclude that in some sense both interpretations of the NCL are correct. There is at high temperatures a NCL that conforms to JPL scaling and therefore must share its origins in the same ion hopping process. At lower temperatures, the scaling appears to fail and the ac conductivity behaves as if ion motions are governed by an altogether new dynamic process.

The new finding here, however, is a clarification of what actually transpires near the 100 K temperature range. We see that the conductivity scaling does not really fail at all, but continues *unabated* to the limit of our current experimental temperature range (85 K). It is only the existence of other (nonionic) contributions in the dielectric response of the material, competing with the ionic response, which give rise to the impression that the ionic process changes. The significant result of the present work is our identification of this extra non-ionic contribution as a polarization process inherent in atoms that comprise the oxide network of the glass.

Special thanks are extended to Professor Gyan P. Johari for the loan of equipment. This work was supported by the U.S. Department of Energy, Division of Basic Energy Science (Grant No. DE-FG03-98ER45696)

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