Carrier Concentrations and Relaxation Spectroscopy: New Information from Scaling Properties of Conductivity Spectra in Ionically Conducting Glasses

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A new kind of scaling analysis for the conductivity spectra of glasses without any arbitrary parameters is presented. By applying this method to sodium borate glasses of different compositions, we find strong indications for the existence of a universal ionic relaxation process as well as for a strong electrolyte behavior. Our results enable us to show that the often used electric modulus formalism is misleading when relaxation mechanisms on a microscopic level are concerned. A more meaningful discussion can be based on the log-log dependence of the conductivity on frequency. [S0031-9007(97)02613-6]

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In this paper, we present new insights into ion transport in glasses resulting from the scaling properties of the conductivity spectra at frequencies up to 4 MHz. We show that our scaling method provides answers to two problems which are being widely discussed; see [1–3] for a general review of this field.

The first problem is the separation of the respective influences of number density and mobility on the ionic conductivity [4,5]. Ion conducting glasses may be considered as strong electrolytes where most if not all of the cations are mobile [6–9] or as weak electrolytes where the fraction of mobile ions is some function of temperature and composition [10–17]. A decision as to which description is more appropriate requires a proper solution of the separation problem.

The second problem concerns how the ionic relaxation mechanism depends on the total ionic concentration. Contradictory results have been reported in the literature. Generally speaking, application of the complex electric modulus, $\hat{M}$, formalism results in a pronounced concentration dependence of the relaxational characteristics, while such a dependence has not been found in analyses of the complex conductivity $\hat{\sigma}$.

These observations are now receiving much attention since they impact strongly on the assessment of theoretical approaches to charge transport in glasses and to relaxations occurring across the whole field of solid state ionics [18–24].

Angell, Moynihan, Ngai, Martin, and others [2,25–31] have been using the modulus formalism. They show that for a given glass the shape of the M'' ($= \mathrm{Im}\,\hat{M}$) spectra does not depend on temperature. Therefore, appropriate scaling results in a master curve suggesting that the ionic relaxation mechanism is temperature independent. As noted above, the width and shape of the M'' master curves do, however, change with glass composition in the sense that the modulus spectra always become narrower with decreasing ionic concentration. Consequently, it has been concluded that the relaxation mechanism depends on the total ionic concentration in glass.

On the other hand, Kahnt [32] shows that the shape of the conductivity spectra taken below a few megahertz depends neither on temperature nor on glass composition. In his scaling analysis, he utilizes the dc conductivity σ_{dc} and the inverse Cole-Cole parameter $1/\tau$ as scaling parameters for the conductivity and the frequency axis, respectively. Other authors take the frequency of the M'' maximum [31] or the frequency defined by $\sigma_{\mathrm{dc}}/[\epsilon_0\epsilon'(\infty)]$ [33] as scaling parameters for the frequency axis. Here, ϵ_0 and $\epsilon'(\infty)$ are the permittivity of free space and the high-frequency value of the dielectric function, respectively. A disadvantage of these scaling methods for $\sigma'(\nu)$ is, however, that the choice of the parameters is somewhat arbitrary.

We will show in this paper that master plots of the frequency dependent conductivity can easily be generated without the need of such arbitrary parameters, fitting procedures, or phenomenological theory.

Conductivity spectra have been taken of a wide range of inorganic glasses, including fast ionic conductors, and also of supercooled ionic melts of simple composition. In all cases, we have found the same pattern of behavior [34]. In this Letter, we will restrict the discussion to low-frequency conductivity spectra of sodium borate glasses with different sodium ion concentrations.

Glasses of general composition $x\mathrm{Na_2O}\cdot(1-x)\mathrm{B_2O_3}$ were prepared by heating dry mixtures of $\mathrm{Na_2CO_3}$ and $\mathrm{B_2O_3}$ in a platinum crucible under an atmosphere of air. The melts were held at 980 °C for one hour. They were then poured into a graphite mold and held inside the furnace for another ten minutes. After cooling to room temperature the samples were annealed 20 K below their respective glass transition temperatures for twelve hours. The glass transition temperatures were obtained from standard differential scanning calorimetry (DSC) measurements applying a heating rate of 10 K/min. The samples were then ground to their requisite sizes and the surfaces were polished. Gold electrodes were evaporated onto the sample surfaces. The frequency dependent electrical conductivity was measured in the frequency range from 5 Hz to 4 MHz using the LF impedance analyzer HP 4192A.

In Fig. 1 we present the frequency dependent conductivity (expressed as product $\sigma' T$) of the glass $0.3\ \mathrm{Na_2O} \cdot 0.7\ \mathrm{B_2O_3}$ at different temperatures. Data below 372 K are not included in the figure because of increasing scatter at low frequencies owing to the high resistance of the sample. Otherwise, at low frequencies, the conductivity is constant. This is the dc conductivity of the glass, σ_{dc}, which is found to obey an Arrhenius law

$$\sigma_{\mathrm{dc}} T \propto \exp[-E_A^{\mathrm{dc}}/k_B T]. \tag{1}$$

This behavior is observed at all compositions, see Fig. 2, and can be used to extrapolate σ_{dc} to lower temperatures. As expected, the activation energy E_A^{dc} increases with decreasing sodium oxide content [22,35]. The compositional range was limited at low values of x by the increasing value of E_A^{dc} and at high values of x by the ability of the system to form glasses.

Let us return to Fig. 1. The crossover frequency from the dc behavior to the dispersive conductivity, ν^*, increases with temperature. Defining this frequency by

$$\sigma'(\nu^*) = 2\sigma_{\mathrm{dc}}, \tag{2}$$

we find that ν^* is thermally activated with the same energy as $\sigma_{\mathrm{dc}} T$. Therefore, connecting the crossover frequencies in Fig. 1, we obtain a straight line with a slope of one.

We have begun the detailed analysis by shifting the conductivity isotherms along the straight line of slope one, i.e. by scaling both axes with the factor $\sigma_{\mathrm{dc}} T$. The resulting scaling plot is shown in Fig. 3 with all isotherms falling onto one master curve. Obviously, the time-temperature superposition principle is fulfilled suggesting a temperature independent relaxation mechanism.

The validity of this scaling relationship seems, however, not to be restricted to ion conducting glasses, but has also been found in the case of amorphous semiconductors [36].

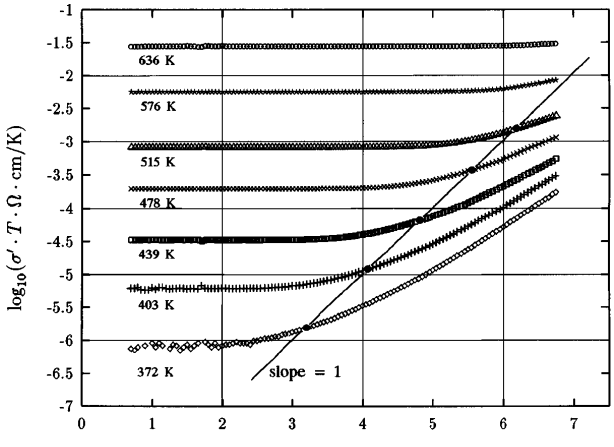

FIG. 1. Frequency dependent conductivity of the glass $0.3\ \mathrm{Na_2O} \cdot 0.7\ \mathrm{B_2O_3}$ at different temperatures.

Let us now consider the scaling properties of glasses of different sodium oxide content x. For any given value of x, the conductivity isotherms are found to fall onto one master curve. As shown in Fig. 4, these individual curves are, however, shifted to higher values of $\nu/(\sigma_{\mathrm{dc}} T)$ as x decreases.

We have now shifted the individual curves along the abscissa by introducing an additional scaling factor $f(x)$. Choosing $f(x) = x$, all of them fall onto one "super" master curve; see Fig. 5. This is expressed by the following scaling law:

$$\frac{\sigma'}{\sigma_{\mathrm{dc}}} = F\left(\frac{\nu}{\sigma_{\mathrm{dc}} T}\, x\right). \tag{3}$$

We now take into account that

$$\sigma_{\mathrm{dc}} = N_V q \mu_{\mathrm{dc}}. \tag{4}$$

Here N_V, q, and μ_{dc} are the number density, the charge, and the dc mobility of the charge carriers, respectively. In the sodium borate glasses, the mobile charge carriers are the sodium ions. Therefore, the charge q is independent of composition. Furthermore, assuming that $N_V \propto x$, the scaling law (3) is now rewritten as

$$\frac{\sigma'}{\sigma_{\mathrm{dc}}} = \tilde{F}\left(\frac{\nu}{\mu_{\mathrm{dc}} T}\right). \tag{5}$$

In this equation, the ion dynamics are described by the universal function $\tilde{F}$ which is independent of both temperature and composition. This is a decisive new result. The fact that a super master curve can be produced so easily for sodium borate glasses, just by assuming that $N_V \propto x$, indicates the existence of a universal ionic relaxation process in these glasses. It also indicates that the same proportion of the sodium ions is mobile independent of composition. The latter result is clearly at variance with weak electrolyte models, but is consistent

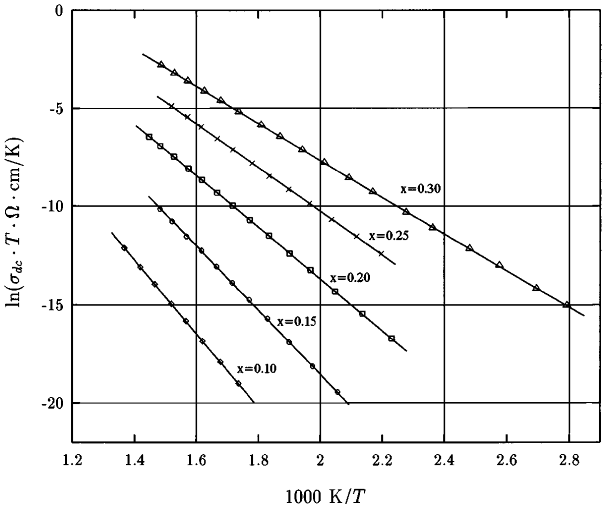

FIG. 2. Arrhenius plot of the dc conductivity of sodium borate glasses of different compositions, $x\ \mathrm{Na_2O} \cdot (1 - x)\ \mathrm{B_2O_3}$.

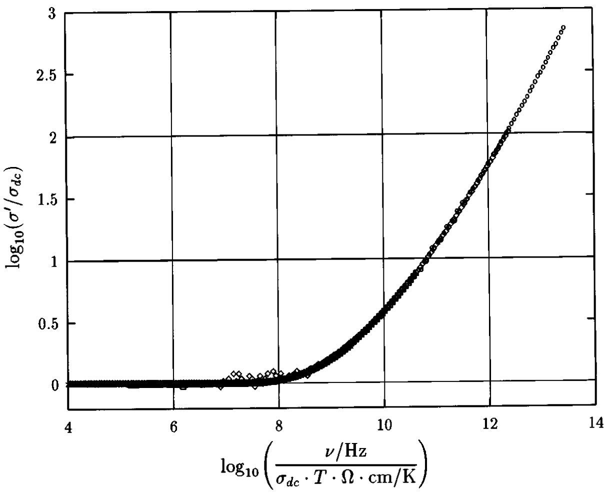

FIG. 3. Master plot of the conductivity data of 0.3 Na_2O · 0.7 B_2O_3.

with a strong electrolyte viewpoint and with conclusions reached earlier by Almond, Duncan, and West [7,8] for other solid electrolyte systems.

It is important to note that the frequency axis scales with the product of temperature and the dc mobility of the sodium ions, which by the Nernst-Einstein approximation is proportional to their coefficient of self-diffusion, D. This result bears an interesting implication for the time dependence of functions like the mean square displacement of the mobile ions, $\langle r^2(t)\rangle$. Based on linear response theory [37], we can say that if the frequency dependent conductivity is a function of ν/D, irrespective of temperature and concentration, then at corresponding times, $\langle r^2(t)\rangle$ should be a function of Dt, again irrespective of temperature and concentration. We know that this is indeed correct at long times, when macroscopic diffusion is properly described by $\langle r^2(t)\rangle \propto Dt$. From our present results we conclude that the scaling law $\langle r^2(t)\rangle = f(Dt)$ is also valid at shorter times, when $\langle r^2(t)\rangle$ varies with Dt in a nonlinear fashion [21].

This quantitative treatment as summarized in Eq. (5) has so far been applied only to the sodium borate glass system. In other glasses and also in melts, we find the conductivity isotherms having the same shape. The appropriate values of $f(x)$ may, however, vary from system to system because of differences in chemical stoichiometry and in density. These issues have still to be examined in detail but the outcomes should not affect the arguments presented above.

Finally, we are now able to explain the discrepancy between $M''(\nu)$ and $\sigma'(\nu)$ based analyses. As already suggested by Elliott [38], by Dyre [39], and by Sidebottom *et al.* [40], the electrical modulus formalism is misleading when microscopic relaxation mechanisms are concerned. We now know that the reason is that the number density of the mobile charge carriers is not considered at all in the modulus formalism. The position of the M'' peak on the frequency axis scales in a good approximation with the dc conductivity but certainly not with the dc mobility. The modulus analysis ignores the effect that, for a given conductivity, a lower number density of more mobile charge carriers implies faster ionic relaxation and thus a higher onset frequency of the conductivity dispersion. At very low number densities of mobile charge carriers, the M'' peak therefore occurs in the dc regime, and in shape it approximates to a Debye peak. This does not, of course, imply an entirely frequency independent conductivity. The characteristic dispersion in conductivity is still present [31], but it lies outside the dynamic window of the modulus formalism.

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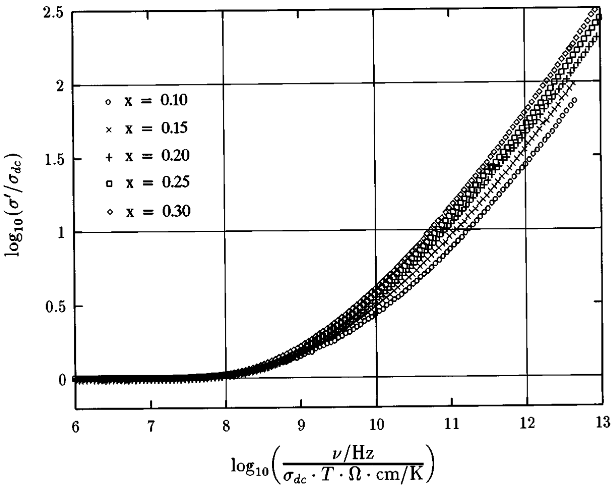

FIG. 4. Conductivity master curves of sodium borate glasses of different compositions, x Na_2O · $(1 - x)$ B_2O_3.

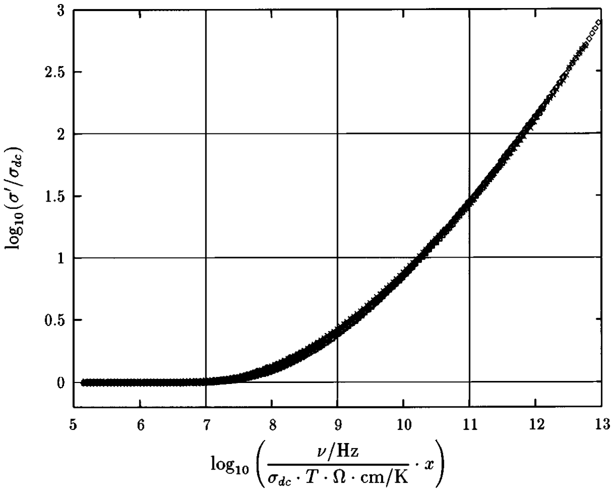

FIG. 5. Conductivity master curves for x Na_2O · $(1 - x)B_2O_3$ glasses where x is included as an additional scaling factor.

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