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ON THE NATURE OF BULK ELECTRICAL RELAXATION IN SILICATE GLASSES

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Three sodium and mixed-alkali silicate glasses were studied to separate bulk relaxation processes from those due to electrode blocking. Conductance, G, and capacitance, C, were measured as a function of frequency over a wide range of temperature. Electrode effects were separated by their dependence on the type of electrode and sample thickness. We found no evidence for a bulk relaxation loss peak but the residual bulk process took the form of the well-known "universal" behavior involving power-law dependence of both G and C, with a fractional exponent, s, close to 0.6. The corresponding relaxation time has precisely the same activation energy as the dc conductivity. By extending the measurements to low temperatures, we find that s becomes equal to unity at the lower temperatures.

INTRODUCTION

It has often been suggested that a bulk relaxation process, which takes the form of a dielectric loss peak and has the same activation energy as the dc conductivity, is present in most glasses. (Tomozawa, 1977; Namikawa, 1975; Ingram, 1987) In a previous study of lithium borate glasses (Lee et al., 1990), however, we observed a relaxation peak by both dielectric loss and thermally stimulated depolarization, but showed that it was due to electrode blocking effects. The only bulk relaxation process observed was the Jonscher-type "universal" power-law behavior (Jonscher, 1983). In the present work, we have examined three silicate glasses in a similar way, through measurements of the conductance, G, and capacitance, C, as a function of frequency. By extending the measurements to lower-than-usual temperatures, we were able to examine the Jonscher-type behavior in greater detail than was previously possible.

EXPERIMENTAL METHODS

Three silicate glasses were studied: $Na_2O{\cdot}3SiO_2$, $Na_2O{\cdot}4SiO_2$ and a mixed alkali $(NaCs)_2O{\cdot}3SiO_2$. The glasses were prepared by mixing and melting appropriate amounts of SiO_2 and alkali nitrate powders in a platinum crucible at 1575 C until the melt became bubble free. The melt was cast as glass into a stainless steel mold. Finally, the glass pieces were annealed at 540 C for 3 h and slowly cooled to eliminate any residual stresses.

Samples of $\sim 1 \times 1 \times 0{\cdot}1$ cm^3 were used for the electrical measurements. Sample surfaces were polished and cleaned, after which either silver paint or sputtered silver electrodes were applied. In all cases guarded electrodes were employed to eliminate surface conduction. Conductance, G, and capacitance, C, were measured with an automated ac bridge (Andeen Associates, model CGA-83) over the frequency range 10 Hz to 100 kHz. The usual temperature range of measurement was from 20-200 C, but in some cases measurements were made down to 55 K by employing a liquid-nitrogen cryostat.

RESULTS AND DISCUSSION

The three silicate glasses studied showed very similar behavior, which we illustrate for the Na trisilicate glass in Figs. 1 and 2. The measurements for this glass were carried out with both painted and sputtered electrodes. Figure 1 shows the G(f) data obtained with the painted electrode over the temperature range from 97 to 381 K. At the lowest temperatures G(f) shows only a power-law dependence on frequency f. At higher temperatures G, or the ac conductivity, σ, may be represented by the well-known expression for the "universal" behavior (Jonscher, 1983):

$$\sigma(\omega) = \sigma_0 + A\omega^s \qquad (1)$$

where ω is the angular frequency, σ_0 is the dc conductivity and s is the exponent $(0 \leq s \leq 1)$.

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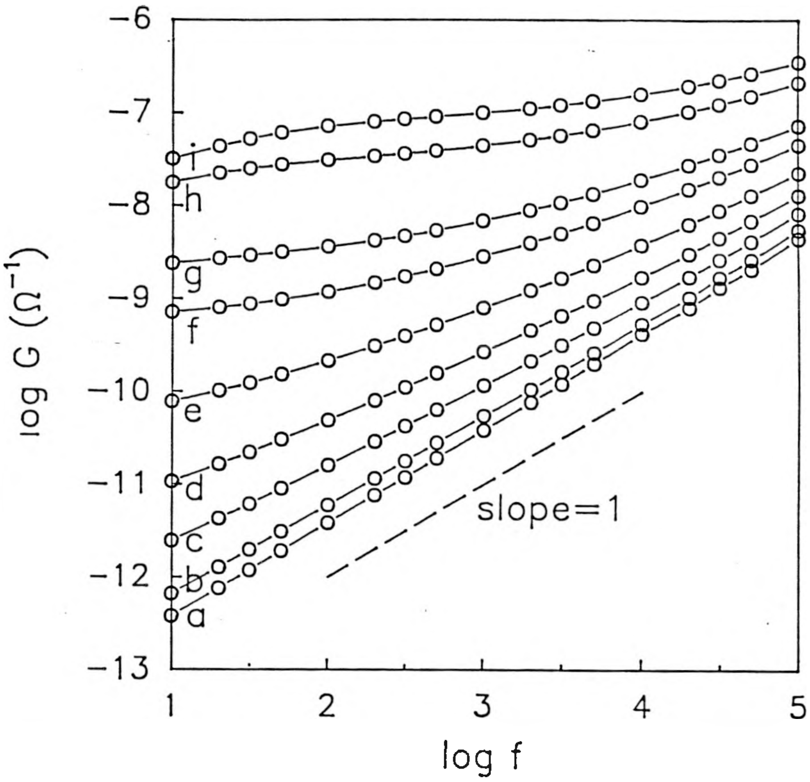

Fig. 1. Variation of conductance, G, with frequency, f, for a Na trisilicate glass with painted electrodes. Curves (a) through (i) are for temperatures: 97, 147, 204, 236, 269, 297, 320, 362 and 381 K, respectively.

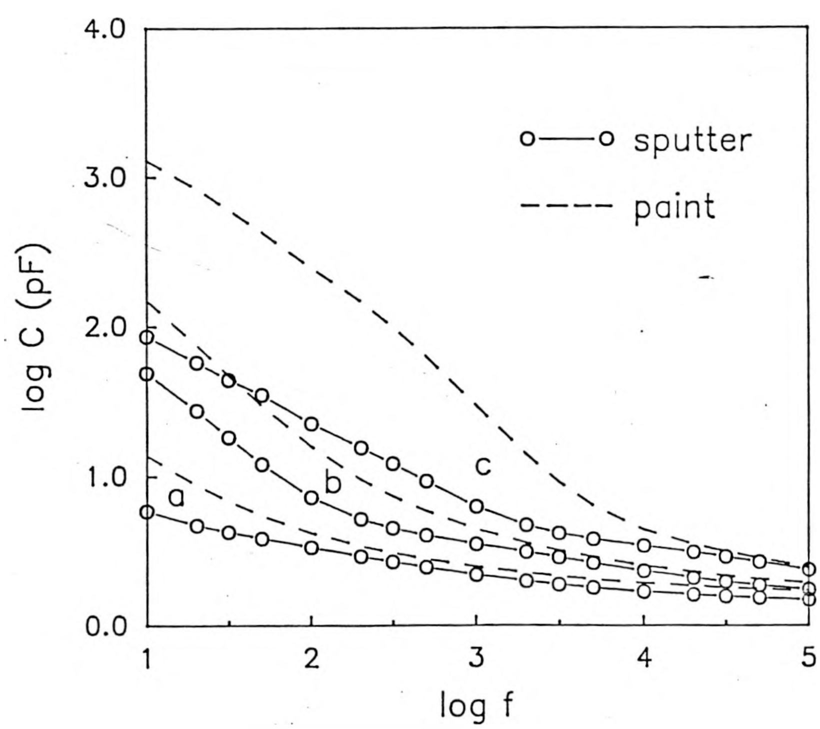

Fig. 2. Variation of capacitance, C, with frequency f, for a Na trisilicate glass with both sputtered (solid curves and points) and painted (dashed curves) electrodes. Curves a, b and c are for temperatures: 319, 362 and 418 K, respectively.

Finally, at the highest temperatures G(f) shows an additional drop at low frequencies which does not appear for the sputtered electrode and is therefore attributed to electrode effects. Some selected data for C(f) that compares the results for painted and sputtered electrodes is given in Fig. 2.

From the Kronig-Kramers relations, the real part of the dielectric constant, $\varepsilon'(\omega)$, that accompanies the $\sigma(\omega)$ behavior of Eq. (1) is as follows:

$$\varepsilon'(\omega) - \varepsilon'_\infty \propto \omega^{-(1-s)} \tag{2}$$

where ε'_∞ is the value of ε' at high frequencies. From data such as that in Fig. 2, we see that only this power-law behavior, which occurs at the higher frequencies and lower temperatures, is the same for both the sputtered and painted electrodes. The remaining sharp upturn, in C(f) at low f is much higher for the painted electrode, leading to the conclusion that it is an electrode phenomenon. In the case of the sputtered electrode we considered the possibility that a plateau region before the second turnup at the lowest frequencies might be due to a bulk relaxation. However, previous measurements by Kim and Tomozawa (1976) on this same glass using evaporated electrodes, showed that $\varepsilon'(\omega)$ was thickness dependent in this temperature range, suggesting that it could not be a bulk effect. Thus, we conclude that the only bulk relaxation that we can observe is the "universal" behavior described by Eqs. (1) and (2).

Because some of the present measurements go to quite low temperatures, it is possible to carry out a more extensive analysis of the bulk ac conductivity behavior than usual. First, by analyzing data such as that of Fig. 1, we are able to obtain s(T), the dependence of the exponent s on temperature. The results for the two glasses for which the most extensive temperature range was covered are shown in Fig. 3. It is clear that the curves show three regions. At the higher temperatures, s is a constant (close to 0.6), independent of temperature. In the intermediate temperature range s increases monotonically as T decreases. Finally, at the lowest temperatures, s reaches the value s = 1.

We will deal separately with the first and third of these regions. The region of s = constant (<1) may be regarded as the classical "universal" behavior. In this range, Eq. (1) can be rewritten in a form suggested by Almond and West (1983):

$$\sigma(\omega) = \sigma_0[1 + (\omega\tau)^s] \tag{3}$$

which defines a relaxation time, τ. This form is consistent with the well-known stretched exponential function or KWW function, in the time domain (Williams and Watts, 1970; Jonscher, 1983). By fitting the data to Eq. (3), we have obtained both σ_0 and τ over a wide range of temperature. Table 1 summarizes the data for this region obtained for the three silicate glasses studied here as well as for two Li borate glasses studied earlier (Lee et al., 1990). It is striking that the activation energy E_σ obtained from the dc conductivity and that, E_τ, from the relaxation time are the same to within experimental error ($\pm$ 0·02 eV) in all cases. Also the preexponential τ_0 of the relaxation time is always within an order of magnitude of 10^{-14} sec, suggesting that τ is a true relaxation time and not an artificial quantity.

Almond and West (1983) have argued that the equality of $E_\sigma = E_\tau$ implies that the material in question obeys the strong electrolyte theory in which $E_\sigma = E_m$ where E_m is the migration energy of the ionic carrier. We have also carried out similar studies of certain crystalline materials in which it is well known that weak electrolyte theory applies, i.e. $E_\sigma > E_m$, and yet $E_\sigma = E_\tau$ was found to be strictly obeyed (Lee et al., 1992). Recent theoretical treatments involving correlated motion of ions through many-body interactions predict that Eq. (3) can be obeyed with $E_\sigma = E_\tau$ without requiring strong electrolyte behavior. (See, for example, Funke and Hoppe, 1990).

Finally, the region at the lowest temperatures where s = 1 is of great interest. We have observed such behavior for a number of simple crystalline materials as well as glasses (Lee et al., 1992), and come to the conclusion that $s \rightarrow 1$ at sufficiently low temperatures is a universal phenomenon. (Others, e.g. Cole and Tombari, 1991, have observed such limiting behavior by increasing the frequency rather than lowering the temperature.) A model previously considered for such behavior (Pollak and Pike, 1972) considers a two-level system involving hopping (or tunneling) between two sites that have an energy difference. However, the model is based on the existence of a high degree of disorder in the material. This model may be reconciled with the structure of glasses, but is not applicable to the relatively simple crystalline materials in which s = 1 behavior has been observed (e.g. NaCl doped with 50 ppm Zn^{2+}) (Lee et al., 1992). It is therefore likely that a new model, applicable to both crystals and glasses, will be required.

CONCLUSIONS

1. The only bulk relaxation observed for these silicate glasses is of the Jonscher type.
2. The Jonscher exponent, s(T), shows three regions of behavior, with a constant value ~ 0.6 at higher temperatures, and reaching a constant value of unity in the low-temperature range. This behavior occurs both for glasses and simple crystalline systems.

Table 1. Data from Conductivity and Relaxation-time Measurements on Silicate and Borate Glasses

Glass	Temperature range (°C)*	s	E_σ (eV)	E_τ (eV)	$\tau_0(10^{-14}$ sec)
$Na_2O{\cdot}3SiO_2$	20 – 120	0·62	0·67	0·67	5·2
$Na_2O{\cdot}4SiO_2$	60 – 125	0·62	0·70	0·70	2·6
$(NaCs)_2O{\cdot}3SiO_2$	100 – 230	0·60	0·89	0·88	0·1
$Li_2O{\cdot}2B_2O_3$	20 – 100	0·65	0·69	0·66	2·1
$Li_2O{\cdot}3B_2O_3$	80 – 180	0·61	0·84	0·88	0·2

* Temperature range is that in which s = constant.

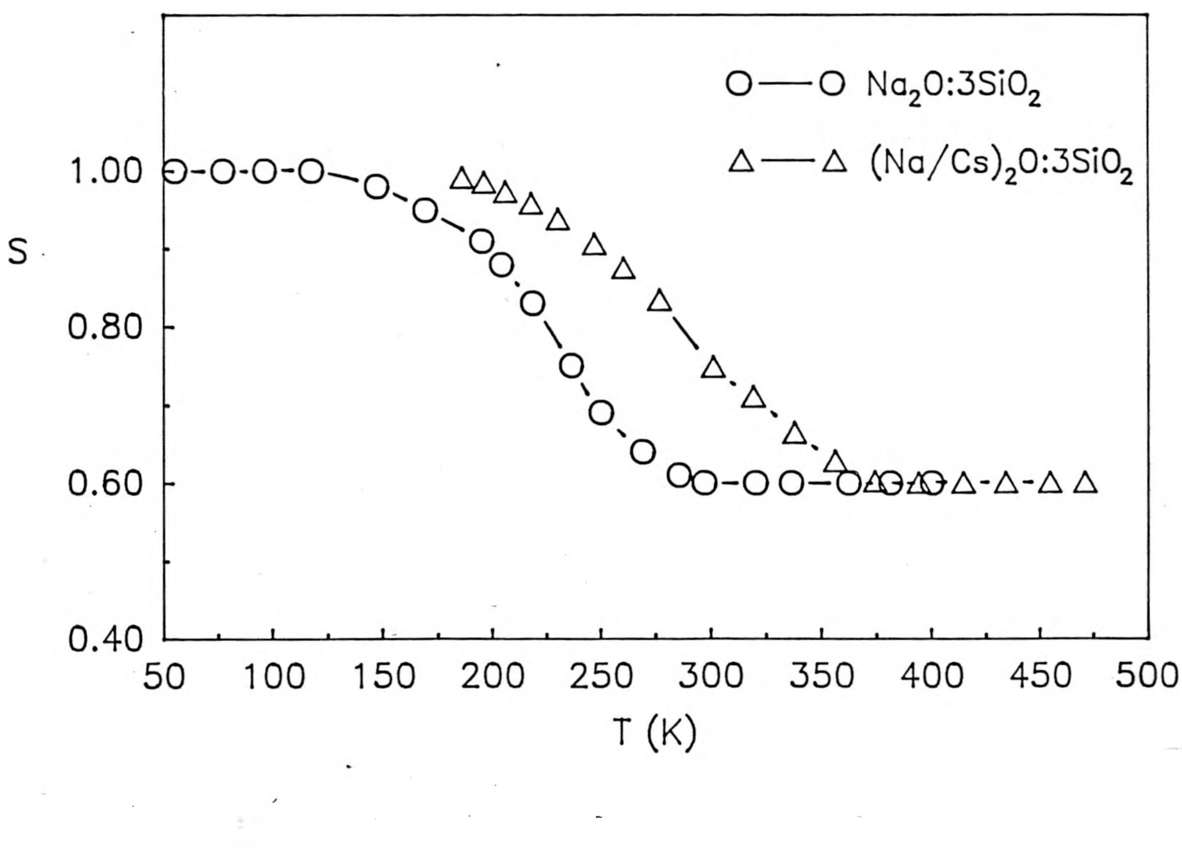

Fig. 3. Dependence of the exponent s on temperature for the sodium and mixed-alkali trisilicate glasses.

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