JOURNAL OF MATERIALS SCIENCE 23 (1988) 707–712

The temperature dependences of permittivity and a.c. conductivity in Ca–Al–Si oxynitride glasses

J. S. THORP*, S. V. J. KENMUIR*, D. EVANS‡
*School of Engineering and Applied Science and ‡Department of Physics, University of Durham, Durham, DH1 3LE, UK

N. E. RAD
Department of Electrical Engineering, University of Tabriz, Iran

The temperature dependence of the permittivity and conductivity of a Ca–Al–Si oxynitride glass has been measured between 200 and 500° C at frequencies covering the range 0.5 to 10 kHz. A d.c. component of the conductivity has been extracted which has an activation energy of 1.6 ± 0.2 eV for the associated charge carriers, and the remaining dielectric conductivity is shown to vary with frequency in a manner consistent with the presence of loss peaks, the loss-peak frequency having a thermal activation of 0.9 ± 0.1 eV. Below and above the resonant loss frequencies, the dielectric loss shows power-law behaviour. Comparisons are presented with other results on oxynitride and normal oxide glass and with silicon nitride.

1. Introduction

In previous publications the room-temperature dielectric behaviour of a series of oxynitride glasses (including Mg–Al–Si, Ca–Al–Si, Y–Al–Si and Nd–Al–Si compositions) has been discussed both for medium frequencies in the range 500 Hz to 10 kHz [1] and in the higher-frequency range of 500 MHz to 5 GHz [2]. The combined results showed that the almost frequency-independent behaviour of permittivity (ε') and dielectric loss (ε'') was consistent with the universal law of dielectric response. Analysis showed that, for all these glass compositions, the data could be fitted well to the relations $(\varepsilon' - \varepsilon_\infty) \propto \omega^{(n-1)}$ and $\varepsilon'' \propto \omega^{(n-1)}$ with a value of the exponent n of 1.0 ± 0.1, suggesting a situation corresponding to the limiting form of lattice loss [3]. For the Ca–Al–Si oxynitride glasses the values of permittivity were about 10.2 and of $\tan\delta$ about 1.8×10^{-3}, increasing slightly as the percentage of oxygen replaced by nitrogen was increased. However, from the point of view of potential applications of oxynitride glasses (for example, as r.f. window or radome materials) it is also important to know how the dielectric properties vary with temperature so that an assessment of the material's characteristics under different environmental or operational conditions can be made. Here we report an investigation of the temperature dependences of the permittivity and dielectric loss for Ca–Al–Si oxynitride glasses; the measurements extended over a temperature range from 200 to 500° C using a frequency coverage of 500 Hz to 10 kHz, and clear evidence of "loss peak" behaviour [4] has been obtained.

2. Experimental procedure

The calcium oxynitride glass samples investigated were prepared and supplied by the Crystallography Laboratory, Wolfson Centre for High Strength Materials, University of Newcastle upon Tyne. Their compositions (at %) were Ca 17.2, Si 17.2, Al 6.5, O 54.2 and N 4.9. This corresponds to an oxynitride glass in which, compared to the equivalent $CaO–Al_2O_3–SiO_2$ oxide glass, about 9.8% of the oxygen had been replaced by nitrogen; it was one of the compositions examined in our earlier work at room temperature. Details of the preparative methods employed have been given by Drew [5] and by Jack *et al.* [6]. These oxynitride glasses were made by starting with mixtures of powders of the appropriate components (usually using silicon nitride as the starting nitride); pellets were then formed which, after being introduced into either a high-alumina or boron nitride crucible, were fired at 1700° C in a tungsten resistance furnace. Despite restrictions imposed by the dimensions of the hot zone of the furnace it was possible to obtain bulk samples of about 1 cm diameter and up to 1 cm thick. Specimens 0.5 mm thick were cut from the bulk material with a diamond-wheel cutting machine. Care was taken to make the large surfaces, which were polished with diamond paste to a 0.25 μm finish, flat and parallel. Circular gold electrodes 6 mm in diameter were evaporated on to the flat surfaces and platinum wires were cemented to the gold with platinum paste.

Measurements were made over the frequency range 500 Hz to 10 kHz at temperatures up to 500° C by suspending the specimens inside a vertical furnace and measuring their conduction and capacitance on a Wayne Kerr B 224 bridge. The furnace arrangement is shown in Fig. 1. The specimen was suspended from platinum wires threaded through a silica tube and

0022–2461/88 $03.00 + .12

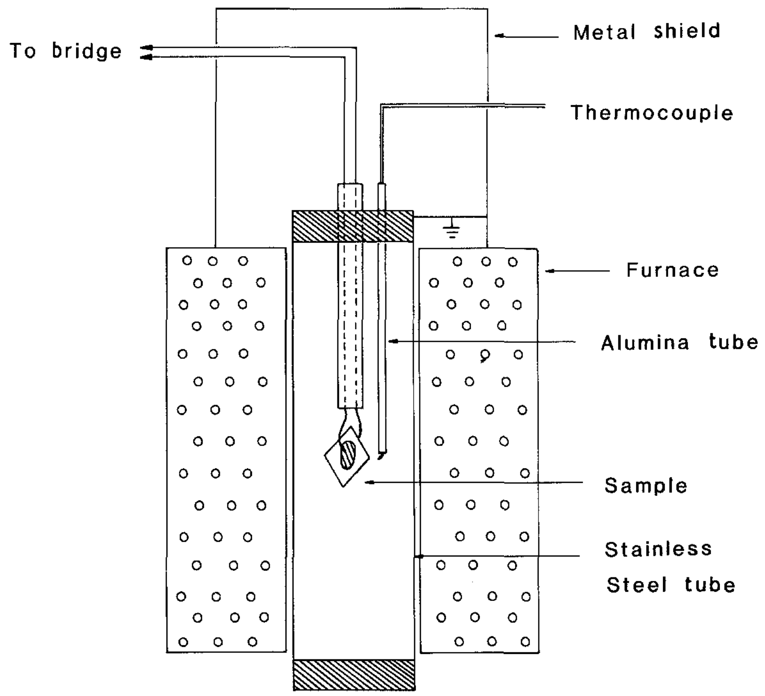

Figure 1 Schematic arrangement for measuring ε′ and ε″ at high temperatures

leading to the bridge connections. A thermocouple monitored the temperature near the specimen. A steel furnace tube was used, earthed to provide electromagnetic screening of the specimen area. The top of the furnace was also shielded and all leads entering the shielded area were screened. The furnace heating current and controller were switched off while each measurement was being made. A water-cooled collar at the top of the furnace tube kept the region outside the tube at room temperature, providing a constant ambient temperature for connections and equipment. An inert atmosphere of argon was maintained in the specimen area. The maximum temperature of 500° C was chosen to be well below the glass transition temperature, reported by Drew [5] to be about 800° C, in order that structural changes in the material should not occur within the range of measurement. Two other possible causes of change in the specimen at high temperatures are the diffusion of electrode material into the specimen and reaction with the surrounding atmosphere. The use of gold electrodes and operation below 500° C should prevent the first and the inert argon atmosphere the second, but as these oxynitride glasses were new materials no previous data on diffusion rates were available. As a check, therefore, after the measurements at each of the selected temperatures in the range, the specimen was returned to room temperature and the values of capacitance and conductance measured at a few frequencies; no measurable change in the room-temperature values was observed. Full details of the measurements and the derivation of permittivity (ε′), dielectric loss (ε″) and tan δ have been given by Kenmuir [7].

3. Results

The permittivity ε′, measured for temperatures between 212 and 500° C, is shown as a function of frequency in Fig. 2. There is little variation observed, ε′ increasing by about 15% at 500 Hz and by about 10% at 10 kHz over the full temperature range.

Fig. 3 gives the variation of conductivity σ, for fixed frequency f, between 600 Hz and 10 kHz, as a function of reciprocal absolute temperature ($1/T$). Here there is considerable variation, σ falling by about two orders of magnitude as temperature and frequency are changed from high to low values. The functional dependence is structured in the middle T range, showing features which could be the result of loss peaks but complicated by decreased frequency dependence at the higher temperatures. This is shown clearly in Fig. 4, where the conductivities are given as a function of frequency at fixed temperatures. Above 400° C the variation of σ with f is seen to get less as the

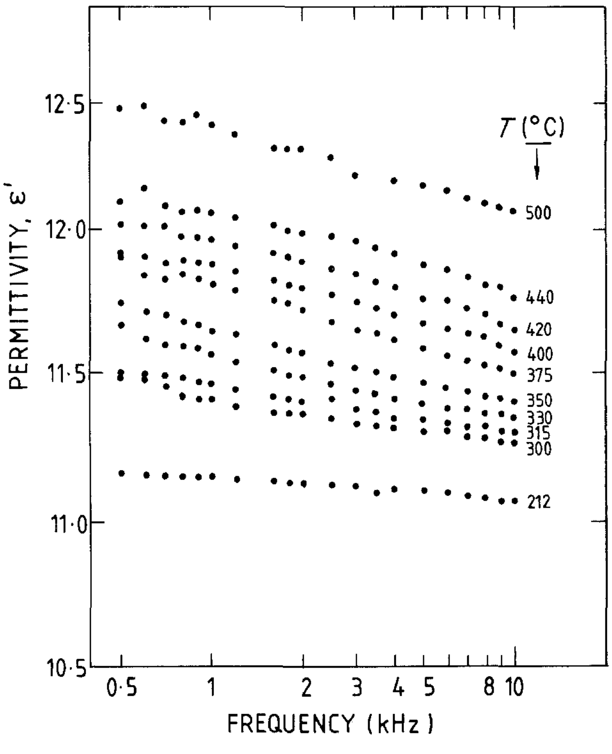

Figure 2 Variation of permittivity ε′ with frequency at different temperatures.

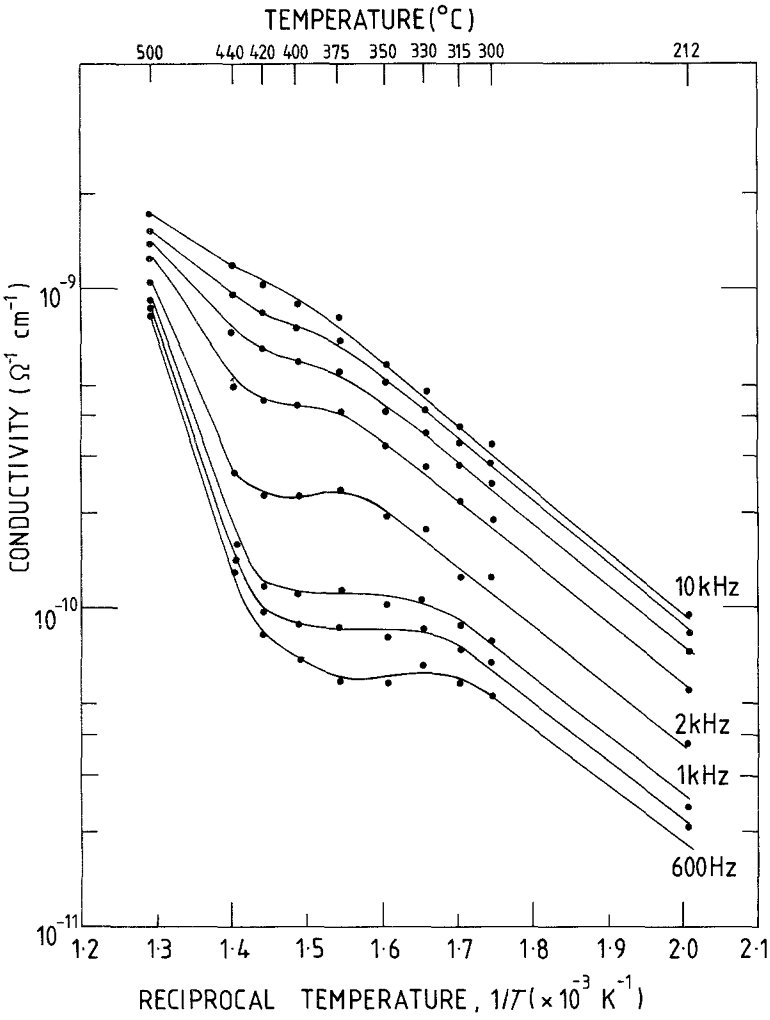

Figure 3 Measured conductivity with temperature for a range of frequencies.

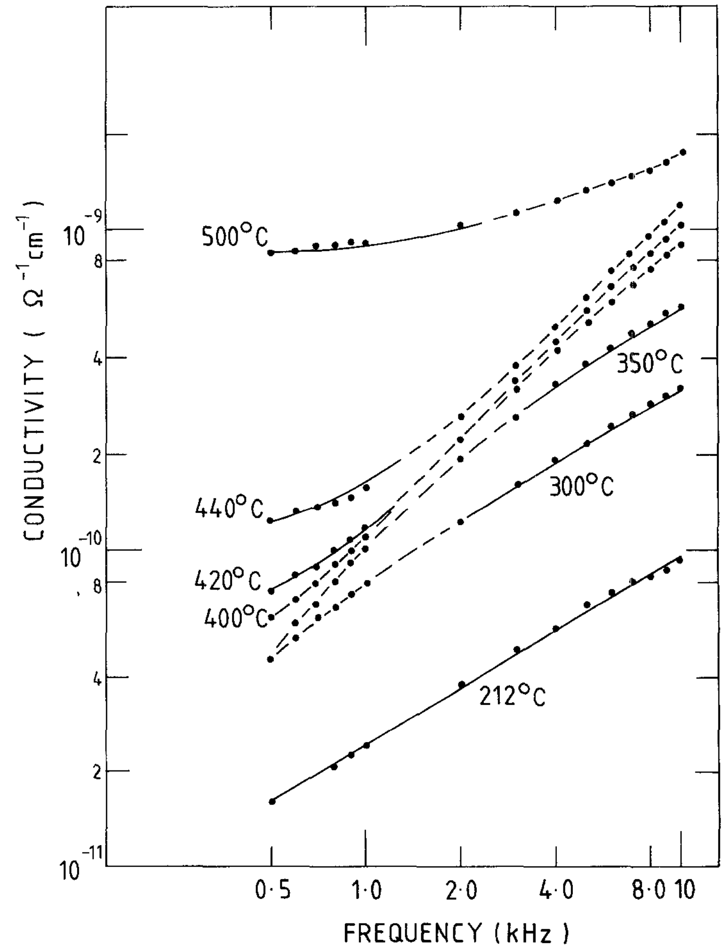

Figure 4 Measured conductivity with frequency for a range of temperatures.

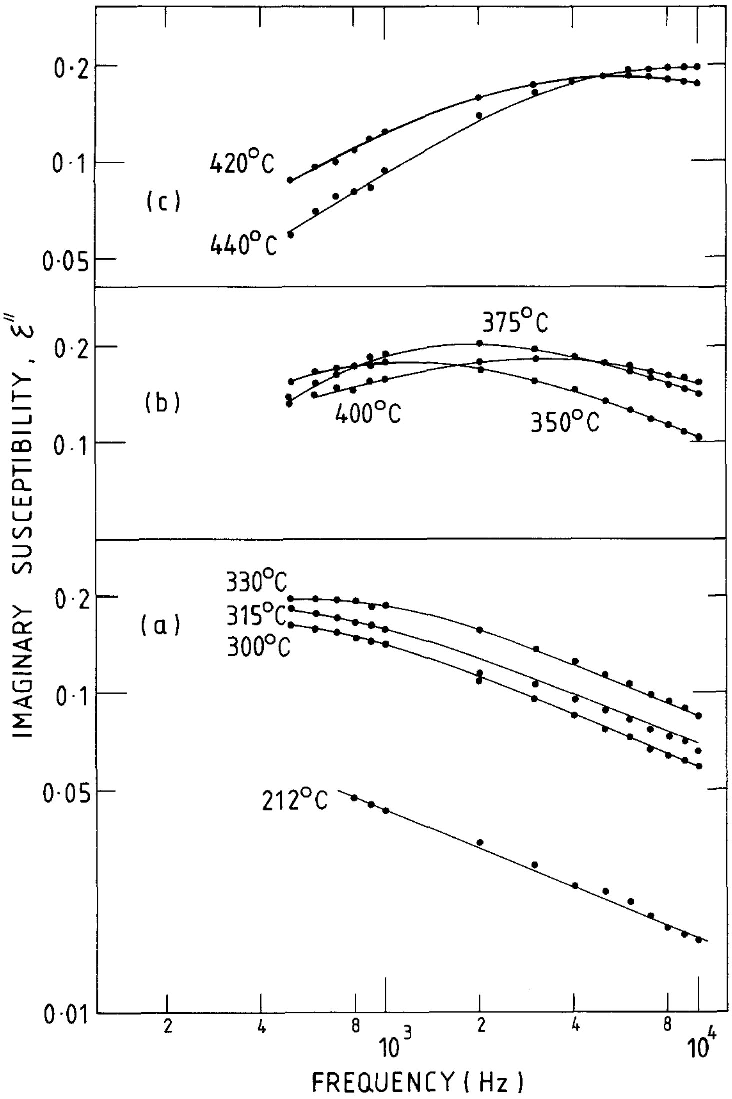

Figure 5 (a–c) Dielectric loss, ε″, with frequency for different ranges of temperature.

temperature increases, until at 500° C there is very little change in σ below 1 kHz. This is suggestive of a charge transport component in σ, which would have to be subtracted to give the dielectric loss contribution. The next section addresses this problem. The continuous lines in Fig. 4 for data above 400° C are calculated from the analysis given below (Section 4.1), and the agreement is seen to be good. The continuous lines at high frequency for data up to 350° C are calculated for a power-law behaviour beyond a loss peak frequency, the parameters used being deduced in Section 4.2.

4. Analysis of conductivity data

4.1. Extraction of constant component

The conductivity data at 420, 440 and 500° C have been fitted below 2 kHz to a form

$$\sigma = \sigma_0 + af^m$$

An inspection of Figs 2 and 3 showed it was unlikely that loss peaks were present for these temperatures at low frequencies. One value of m was used at all three temperatures. The values of m, σ_0 and a which gave the minimum variance, v, over all the data were found. The value of v indicated a measurment error of 10 to 20%, in good agreement with *a priori* estimates. The variation of σ_0 was then fitted to the form

$$\sigma_0 = c_0 \exp(-E_c/kT)$$

where k is the Boltzmann constant and E_c the carrier activation energy. Although only three values of σ_0 were available, they fitted the exponential form with the satisfactorily high regression coefficient of 0.99.

The best-fit values obtained were $m = 1.51$, $a = 1.92 \times 10^{-15}\,\Omega^{-1}\,\text{cm}^{-1}\,\text{Hz}^{-1.51}$, $c_0 = 20.8\,\Omega^{-1}\,\text{cm}^{-1}$ and $E_c = 1.6\,\text{eV}$. Inclusion of the 400° C data and trials with different frequency ranges and values of m gave E_c in the range 1.4 to 1.8 eV, but the values of σ_0 did not vary by more than 15%. The continuous lines in Fig. 4 at low frequency for data above 400° C are calculated from the expression for σ with the values for the constant terms given above. The agreement is seen to be good.

4.2. The dielectric loss behaviour

The value of σ_0 calculated as above was subtracted from the conductivities at all temperatures, and the corresponding value of the imaginary part of the permittivity, ε″, obtained from $\varepsilon'' = (\sigma - \sigma_0)/2\pi f \varepsilon_0$. The values of ε″ as a function of frequency for temperatures up to 440° C are shown in Fig. 5. The value of σ_0 at 500° C was of the same magnitude as the total conductivity measured for most of the frequency range. The subtraction gave values of ε″ fluctuating randomly between 0.11 and 0.23 and therefore, except for noting that the average is reasonable, no deductions

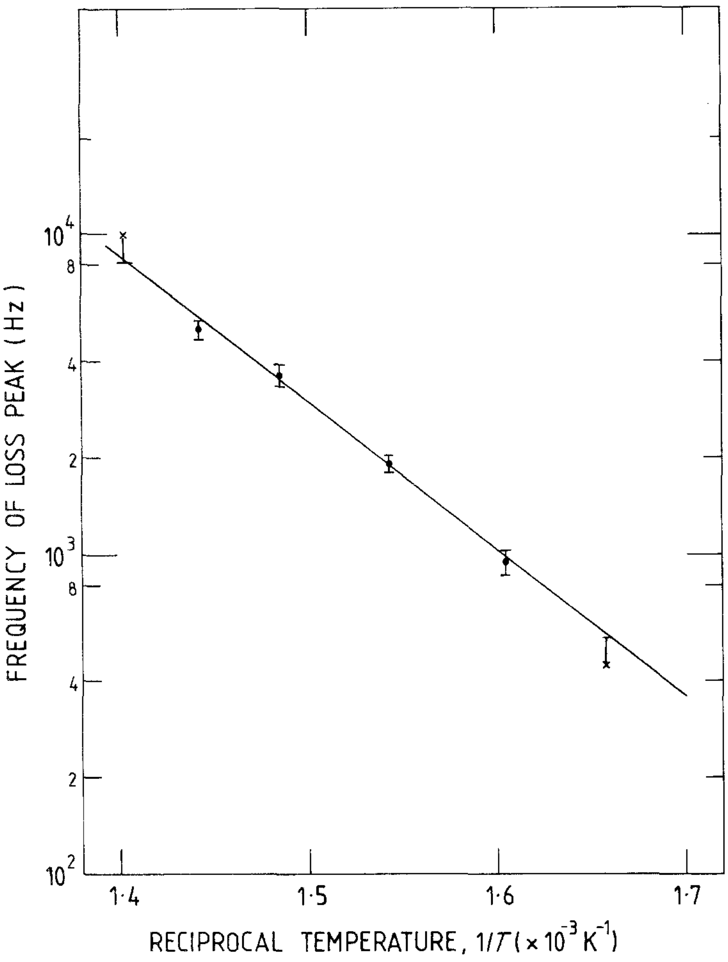

Figure 6 Variation of loss-peak frequency with reciprocal absolute temperature. The end-points are estimated limits and the line is fitted by excluding them.

are made about the frequency dependence of ε'' at this temperature.

Fig. 5a shows the variation of ε'' for temperatures up to 330° C. For most of the frequency range a power-law behaviour is exhibited, with a tendency to flatten off at the lowest values of f, particularly marked at 330° C. The power-law region has been fitted by the relation

$$\varepsilon'' = [a_1 \exp(-E_1/kT)]f^{n-1}$$

and the values $n = 0.6$, $E_1 = 0.33\,\text{eV}$ and $a_1 = 2.12\,\text{Hz}^{0.4}$ obtained. The straight lines shown in Fig. 5a are obtained from the above relation and the continuous lines through the low-temperature data of Fig. 4 calculated thereby.

Fig. 5b shows the temperature region dominated by loss peaks, the 375° C data appearing to give a peak in the middle of the frequency range. The data at the two highest temperatures are shown in Fig. 5c and the low-frequency regions now exhibit the start of a power-law behaviour with positive index. It is clear that the asymptotic behaviour on the low-frequency side of a loss peak lies below the limit of 500 Hz explored in the present work. Some caution therefore has to be expressed regarding the conductivity fitting described in Section 4.1. It was noted there, however, that the determination of σ_0 was insensitive to variations of power index because it dominated the total value of conductivity. We conclude that the precision of σ_0 is adequate and that the low-frequency asymptotic behaviour of the data in Fig. 5c can easily be consistent with a power index of 0.51, which would give 1.51 for the conductivity index as obtained before. The uncertainty in this value is large and it may be that the frequency power indices of the variation of ε'' below and above a loss peak are equal in magnitude at 0.4 and opposite in sign.

4.3. The loss-peak region

The values of ε'' at the loss peaks in Fig. 5 are all within 10% of 0.2 without showing any ordered behaviour with temperature. The fluctuations could easily come from measurement errors, and it may be that for this sample of glass ε'' at a loss peak has a value of about 0.2 independently of temperature.

The frequencies f_p at which the peaks occur show a strong temperature dependence as can be seen in Fig. 6. Using the relation [3, 4]

$$f_p = f_0 \exp(-E_p/kT)$$

the data in Fig. 6 are well fitted with the values $f_0 = 1.77 \times 10^{10}\,\text{Hz}$ and $E_p = 0.9 \pm 0.1\,\text{eV}$.

5. Discussion

There are relatively few previous published data on the loss behaviour of oxynitride glasses although some other physical properties, such as micro-hardness [8], elastic modulus [9] and thermal expansion [10] have been more extensively examined. Two studies of the electrical properties of the Y–Al–Si oxynitride system have however been reported by Leedecke and Loehmann [11] on the glass and by Leohmann [12] on the corresponding glass–ceramics. These authors give values of activation energy obtained from the temperature variations of d.c. conductivity and a.c. loss peak frequency of 1.94 eV and 0.6 eV, respectively. It is interesting to note that in the Ca–Al–Si oxynitride system examined here the effective d.c. activation energy and the a.c. (loss-peak) activation energies were 1.6 ± 0.2 and 0.9 ± 0.1 eV, respectively. Since Leedecke and Loehmann [11] found that, in the Y–Al–Si oxynitride systems, six glasses of slightly different composition all gave similar activation energies it seems likely that the major part of the differences in magnitude of the corresponding activation energies as between the Y–Al–Si and the Ca–Al–Si compositions can be attributed to the change in cation.

Work on oxide glasses has shown that generally the activation energies for d.c. conductivity and loss peaks are equal [13]; a value of 0.9 eV for soda–lime glass may be calculated from data given by Tomozawa [13]. It would thus seem that nitrogenization of glasses may be responsible for increasing the activation energies of the charge carriers of the d.c. conductivity. These comparisons must be made with caution, however; for the soda–lime glass referred to above ε' and ε'' have a variation with frequency which clearly shows the influence of a loss peak. Thus, similar mechanisms are determining both permittivity and dielectric loss in this case. However, for the oxynitride glass reported here ε'' is some two orders of magnitude smaller than ε' which shows no evidence at all of being affected by a resonance loss (see Fig. 2). It would seem that quite different processes are determining the values of ε' and ε'' in this oxynitride glass.

Finally, it is interesting to make a comparison with silicon nitride [14], since this was the component in manufacture that provided the main source of nitrogen (Section 2). Silicon nitride shows loss-peak behaviour in which values of both ε' and ε'' are commensurate, the corresponding activation energy being 1.9 eV, consistent with that for the d.c. conductivity of the glass but about three times the activation energy for loss peaks in the latter. Clearly the creation of a glass which includes silicon nitride has greatly modified its dielectric loss characteristics.

6. Conclusions

Measurements of a.c. conductivity on a Ca–Al–Si glass in which 9.8% of the oxygen was replaced by nitrogen showed a large d.c. component, σ, between 420 and 500° C. Expressed in the form $\sigma_0 = c_0 \exp(-E_c/kT)$, values of $c_0 = 21 \pm 3\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and $E_c = 1.6 \pm 2$ eV have been found. The remaining a.c. conductivity shows a broad loss-peak variation with frequency, f, having a power-law behaviour proportional to $f^{1.51}$ below, and $f^{0.6}$ above the loss-peak frequency f_p. The behaviour of f_p with temperature T has the form $f_0 \exp(-E_p/kT)$ with values of $f_0 = 1.77 \times 10^{10}$ Hz and $E_p = 0.9 \pm 0.1$ eV. These results are similar to other measurements which have been made on oxynitride glasses, but the loss-peak activation energies are not the same as those determining the d.c. conductivity, which is the case for oxide glasses. The permittivity of the oxynitride glass does not show the effect of the dielectric loss and one is led to conclude that a different physical mechanism must be its basis. This is unlike the behaviour of an oxide glass or of silicon nitride, one of the components of the oxynitride glass being measured.

References

1. S. V. KENMUIR, J. S. THORP and B. L. J. KULESZA, *J. Mater. Sci.* **18** (1983) 1725.
2. J. S. THORP, A. B. AHMAD, B. L. J. KULESZA and S. V. J. KENMUIR, *ibid.* **19** (1984) 3211.
3. A. K. JONSCHER, *ibid.* **16** (1981) 2037.
4. L. A. DISSADO and R. M. HILL, *Phil. Mag.* **B41** (1980) 625.
5. R. A. L. DREW, PhD thesis, University of Newcastle upon Tyne (1980).
6. K. H. JACK, D. THOMPSON, S. HAMPSHIRE and R. DREW, private communication (1980).
7. S. V. J. KENMUIR, PhD thesis, University of Durham (1984).
8. K. R. SHILLITO, R. R. WILLS and R. B. BENNETT, *J. Amer. Ceram. Soc.* **61** (1978) 537.
9. D. R. MESSIER and A. BROZ, *ibid.* **65** (1982) C123.
10. G. H. FRISCHAT and C. SCHRIMPF, *ibid.* **63** (1980) 714.
11. C. J. LEEDECKE and R. E. LOEHMANN, *ibid.* **63** (1980) 190.
12. R. E. LOEHMANN, *ibid.* **62** (1978) 491.
13. M. TOMOZAWA, in "Treatise on Materials Science and Technology", Vol. 12, edited by M. Tomozawa and R. H. Doremus. (Academic Press, New York, 1977) p. 283.
14. J. S. THORP, T. G. BUSHELL, D. EVANS and N. E. RAD, *J. Mater. Sci.* **22** (1987) 2641.

Received 12 May
and accepted 22 July 1987