# The dielectric behaviour of Mg–Al–Si, Ca–Al–Si, Y–Al–Si and Nd–Al–Si oxynitride glasses

S. V. J. KENMUIR, J. S. THORP, B. L. J. KULESZA
*Department of Applied Physics and Electronics, University of Durham, Durham, UK*

Bridge techniques have been used to determine the room temperature values of the real ($\epsilon'$) and imaginary ($\epsilon''$) parts of the dielectric constant and also the conductivity ($\sigma$) for some Y–Al–Si and Nd–Al–Si oxynitride glasses and for further compositions in the Mg–Al–Si and Ca–Al–Si systems. Over the range 500 to 10 kHz the frequency dependencies of $\epsilon'$ and $\sigma$ are in good agreement with the Universal law of dielectric response, $(\epsilon' - \epsilon_\infty) \propto \omega^{(n-1)}$ and $\sigma(\omega) \propto \omega^n$, giving $n = 1.0 \pm 0.1$ for all compositions examined. In all four systems the addition of nitrogen increased the dielectric constant ($\epsilon'$) while, at each concentration of nitrogen (including the oxide glasses) $\epsilon'$ increased with cation type in the order magnesium, ytrrium, calcium, neodymium.

## 1. Introduction

There is, at present, considerable interest in the preparation and properties of oxynitride glasses [1–3] because new glass systems can be envisaged whose physical properties may be enhanced since some of the oxygen has been replaced by nitrogen. In a recent letter [3] the authors reported initial measurements of the dielectric properties of two such systems, calcium–aluminium–silicon and magnesium–aluminium–silicon glasses. Room temperature measurements of the real ($\epsilon'$) and imaginary ($\epsilon''$) parts of the dielectric constant were made over a frequency range from $10^3$ to $10^4$ Hz using bridge techniques. These showed that for each particular composition the data fitted well with the Universal dielectric response law [4–6] giving a value of $n$ (for all compositions) of $n = 0.99 \pm 0.02$. It was also found that, at any frequency in the range examined, the addition of nitrogen increased $\epsilon'$ for both the magnesium and calcium glasses and furthermore that changing from magnesium to calcium increased $\epsilon'$ in either the pure oxide or oxynitride systems. The investigations have now been extended to cover two new oxynitride glass systems, namely yttrium–aluminium–silicon and neodymium–aluminium–silicon, together with further compositions in both the magnesium–aluminium–silicon and calcium–aluminium–silicon glasses so as to obtain a more comprehensive picture of the effects of nitrogen addition on the dielectric behaviour of the glasses.

## 2. Experimental

### 2.1. Glass compositions

The compositions of the glasses examined, all of which were prepared at the Crystallography Laboratory, University of Newcastle-upon-Tyne [3, 7, 8], are given in Table I. It can be seen from this that the compositions were varied systematically. Each of the four cation systems (magnesium, calcium, yttrium and neodymium) included an oxide glass without nitrogen. The oxynitrides of the system were formed by substituting chemical equivalents of nitrogen for proportions of the oxygen of the oxide glass. The percentage of oxygen replaced in this way is given in Table I for each oxynitride composition. Proportions of other elements were held constant, although the decrease in the total number of atoms caused by the substitution of two nitrogen atoms for three oxygen atoms naturally increased the numerical values of their concentrations when expressed in at %. The same system was followed between the different cation series, which therefore contained

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TABLE I Compositions of the Mg–Al–Si, Ca–Al–Si, Y–Al–Si and Nd–Al–Si oxynitride glasses examined

| Sample | Composition (at %) | | | | | | | | % oxygen replaced by nitrogen | $\epsilon_\infty$ | $\sigma$ $10^{-12}$ $ohm^{-1}$ $cm^{-1}$ (1600 Hz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mg | Ca | Y | Nd | Si | Al | O | N | | | |
| (1) | 17.0 | – | – | – | 17.0 | 6.0 | 60.0 | – | – | 2.46 | 12.0 |
| (2) | 17.2 | – | – | – | 17.2 | 6.4 | 55.1 | 4.1 | 8.1 | 2.62 | |
| (3) | 17.4 | – | – | – | 17.4 | 6.6 | 51.0 | 7.6 | 14.8 | 2.71 | 22.7 |
| (4) | – | 17.0 | – | – | 17.0 | 6.0 | 60.0 | – | – | 2.59 | 12.8 |
| (5) | – | 17.2 | – | – | 17.2 | 6.4 | 55.1 | 4.1 | 8.1 | 2.73 | 15.8 |
| (6) | – | 17.2 | – | – | 17.2 | 6.5 | 54.2 | 4.9 | 9.8 | 2.77 | 15.6 |
| (7) | – | 17.3 | – | – | 17.3 | 6.5 | 53.1 | 5.8 | 11.5 | 2.80 | 16.9 |
| (8) | – | 17.4 | – | – | 17.4 | 6.6 | 51.0 | 7.6 | 14.8 | 2.84 | 16.6 |
| (9) | – | – | 11.8 | – | 17.8 | 6.8 | 63.6 | – | – | 2.76 | 11.4 |
| (10) | – | – | 12.3 | – | 18.5 | 7.1 | 54.2 | 7.9 | 14.8 | 3.05 | 11.0 |
| (11) | – | – | – | 11.8 | 17.8 | 6.8 | 63.6 | – | – | 2.90 | |
| (12) | – | – | – | 12.1 | 18.2 | 7.0 | 58.4 | 4.3 | 8.1 | 3.14 | 14.5 |
| (13) | – | – | – | 12.4 | 18.6 | 7.1 | 53.1 | 8.8 | 16.5 | 3.29 | |

equal chemical equivalents of either magnesium calcium, yttrium or neodymium. The ratio of (total positive valences)/(total negative valences) did not vary with either nitrogen concentration or cation type, and was equal to one for all the materials investigated.

## 2.2. Measurement techniques

The real ($\epsilon'$) and imaginary ($\epsilon''$) parts of the dielectric constant and the conductivity ($\sigma$) were obtained from measurements made at room temperature over the frequency range 500 Hz to 10 kHz, respectively, using bridge techniques and correction procedures similar to those described by Thorp and Rad [9, 10]. Disc shaped specimens of 1 cm diameter and 0.05 cm thickness were cut from the bulk glasses and polished to finishes of 0.25 $\mu$m. Circular gold electrodes slightly smaller in diameter than the specimen were evaporated onto the polished faces to provide good electrical contact to a well defined area of the disc. The width of the outer ring not covered by gold was chosen to reduce surface conduction over the edges of the disc to acceptable levels. Appropriate edge effect corrections were applied [9, 11]. Care was taken to establish conditions such that $\epsilon'$ and $\sigma$ remained constant when the ring was widened further, indicating that surface leakage was negligible compared to bulk conduction. All the measurements were carried out under an applied field of 130 V $cm^{-1}$ peak-to-peak. Tests at higher voltages proved that $\epsilon'$ and $\sigma$ showed no dependence on field up to 1.3 kV $cm^{-1}$ peak-to-peak.

## 3. Results

The variations of $\log(\epsilon' - \epsilon_\infty)$ with $\log(f)$ for the different compositions are given in Fig. 1. The values of $\epsilon_\infty$ were calculated from the optical refractive index measurements of Drew [7, 8] and are included in Table I. Each composition showed a linear variation. The slopes of the plots were independent of composition and had the value $0.99 \pm 0.02$ for all specimens. At any given frequency the value of $\epsilon'$ depended markedly on composition, increasing as nitrogen concentration increased and varying with cation type. It is useful to refer to the loss behaviour in two alternative ways. In the first place, in order to facilitate comparison with previously published data on oxynitride glasses [3, 12, 13] it is convenient to use conductivites.

The plots of $\log(\sigma)$ against $\log(f)$ shown in Fig. 2 are also linear with the same slope for all compositions, in this case $1.0 \pm 0.1$. Again, the value of $\sigma$ at any frequency in the range depended on both nitrogen concentration and cation type, although the variation of $\sigma$ with composition was different from that of $\epsilon'$. The observed power law dependence of $\epsilon'$ and $\sigma$ on frequency is in good agreement with the Universal law of dielectric response in solids [4–6] in that

$$(\epsilon' - \epsilon_\infty) \propto \omega^{n-1}$$

and

$$\sigma(\omega) \propto \omega^n$$

For each composition the values of $n$ found from Figs. 1 and 2 agree within experimental error. The fact that the same value of $n$ was found for all the specimens suggests that, at room temperature in this frequency range, dielectric polarization and a.c. conductivity in all the compositions examined result from the same hopping mechanism, and

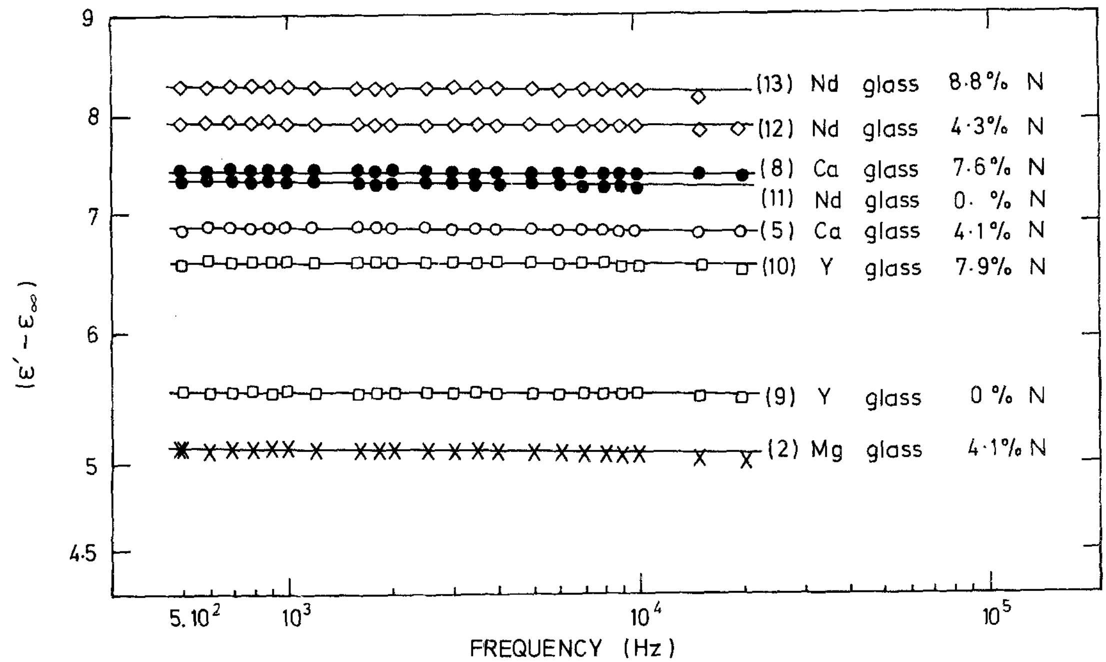


*Figure 1* Dependence of ($\epsilon' - \epsilon_\infty$) on frequency and composition.

that this mechanism is not changed by the substitution of nitrogen. On the other hand a more direct appreciation of the nature of the dependence of loss on frequency is obtained by direct plotting of $\epsilon''$ and $f$. This plot is given in Fig. 3 and shows that over the frequency range covered, the loss for each particular composition is almost independent of frequency.

The nature of the dependence of dielectric behaviour on nitrogen becomes more apparent when the dielectric constant and dielectric loss ($\tan \delta$) are plotted against nitrogen concentration at a single frequency for all the compositions examined, including those reported in detail in reference [1]. Fig. 4 shows the variation of the dielectric constant with nitrogen concentration at

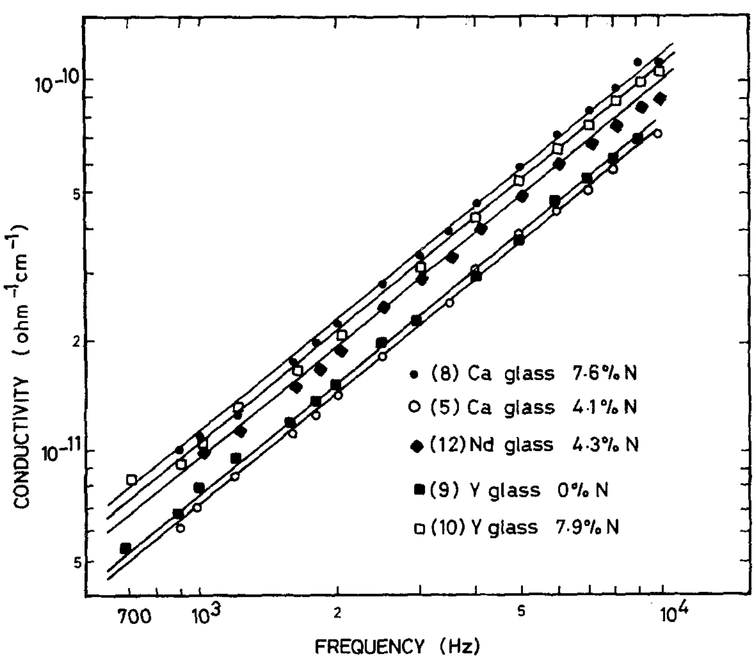


*Figure 2* Dependence of conductivity on frequency and composition.

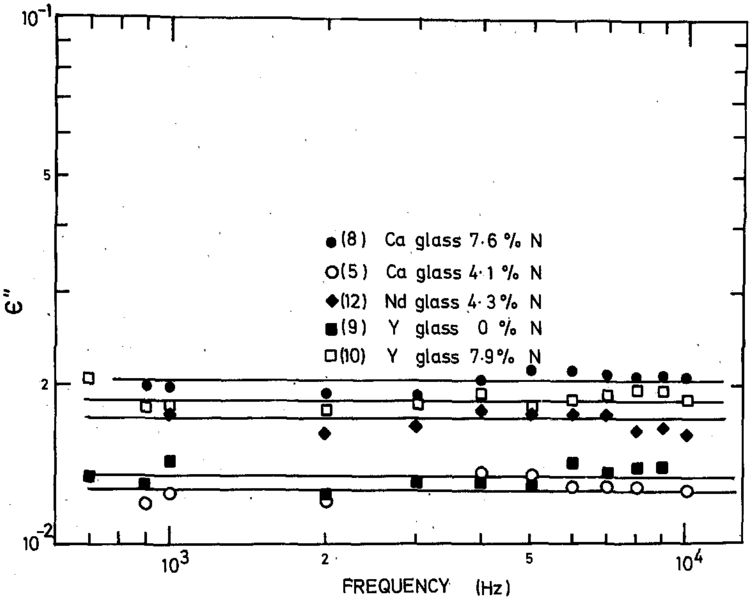


*Figure 3* Variation of $\epsilon''$ with frequency.

a frequency of 1600 Hz ($\omega \simeq 10$ kHz). Fig. 5 shows the variation of dielectric loss with nitrogen concentration at 1600 Hz. Values of conductivity at this frequency are given in Table I. In order to provide a more consistent comparison of the nitrogen dependence of different cation systems, nitrogen concentration has been expressed as the percentage of the oxygen of the appropriate oxide glass for which nitrogen has been substituted.

## 4. Discussion

Values of the dielectric constant ranged from 6.8 for the magnesium oxide glass to 11.6 for a neodymium oxynitride containing 8.8 at % nitrogen. The dielectric constant increased with increasing nitrogen concentration for each glass system, and substitution of the same proportion of nitrogen produced increases ($\Delta\epsilon'$) of similar magnitude. A comparison of $\Delta\epsilon'$ for 14.8% substitution is given in Table II. At each concentration of nitrogen, and for the oxide glasses, the dielectric constant increased with cation type in the order magnesium, yttrium, calcium, neodymium.

As regards the dielectric loss behaviour several

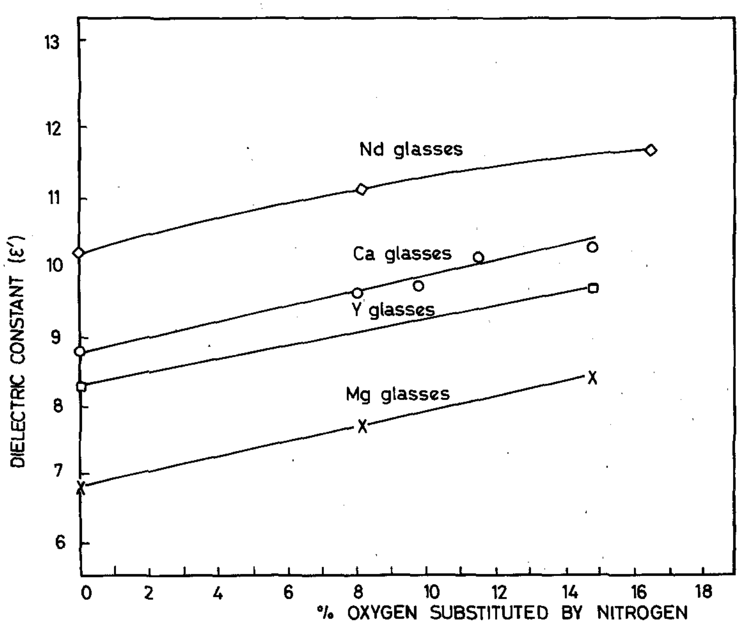


*Figure 4* The variation of dielectric constant ($\epsilon'$) with nitrogen concentration for magnesium, calcium, yttrium and neodymium glasses (1600 Hz).

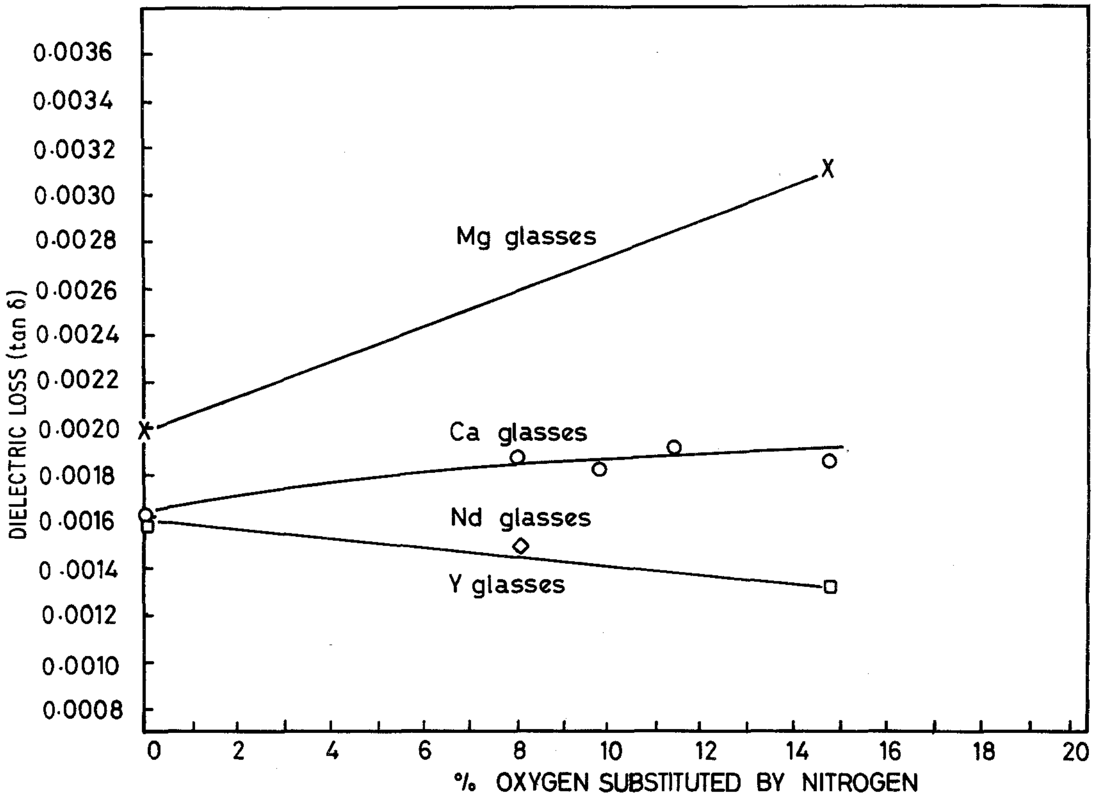


*Figure 5* The variation of dielectric loss (tan $\delta$) with nitrogen concentration for magnesium, calcium, yttrium and neodymium glasses (1600 Hz).

features emerge. One of the most significant is that for this whole group of rigid ceramics the exponent $n$ has a value very near to unity and that this corresponds, as shown by Fig. 3, to frequency independent loss. This is the limiting form of dielectric behaviour, referred to as "lattice loss" by Jonscher [14] in which most dipolar processes have been elminated. The other features refer mainly to changes in composition. Unlike the behaviour of the dielectric constant, the dependence of the dielectric loss on nitrogen concentration varied from system to system: an increase in nitrogen concentration produced a relatively large increase in tan $\delta$ in the magnesium glasses, a smaller increase in the calcium glasses,

TABLE II The increases in dielectric constants caused by substitution of 14.8% of oxygen by nitrogen

| Glass system | $\Delta\epsilon'$ | Percentage increase relative to oxide |
|---|---|---|
| Mg–Al–Si | + 1.5 | 21 |
| Y–Al–Si | + 1.3 | 17 |
| Ca–Al–Si | + 1.5 | 15 |
| Nd–Al–Si | + 1.3 | 12 |

and a decrease in the yttrium glasses. Substitution of 14.8% of oxygen by nitrogen increased tan $\delta$ by 55% for magnesium, by 13% for calcium and decreased tan $\delta$ by 20% for the yttrium glass. A neodymium oxynitride glass with 8.1% substitution had a value of tan $\delta$ similar to that of the yttrium glasses. Comparing the oxide glasses, the calcium and yttrium glasses had approximately equal values of tan $\delta$ = 0.0016, while the magnesium glass was higher at 0.002.

The magnesium, calcium and yttrium oxide glasses, at 1600 Hz, had similar values of conductivity (Table I). Nitrogen substitution increased the conductivities of the magnesium and calcium glasses, magnesium more than calcium, and slightly decreased the conductivity of the yttrium glass. A neodymium oxynitride had a conductivity higher than the yttrium glasses but lower than the corresponding calcium and magnesium glasses.

The dielectric behaviour of some yttrium–aluminium–silicon–oxynitride glasses has been investigated by Loehman [12] and Leedecke and Loehman [13]. Two samples similar in composition to sample (10) of Table I had room temperature dielectric constants of 10, in good agreement with the value of 0.6 reported here. Substitution of 1.5 at% of nitrogen for 1.5 at% of the oxygen of a yttrium–aluminium–silicon–oxide glass of composition different to sample (9) increased the room temperature dielectric constant. Room temperature a.c. conductivity and dielectric loss decreased with nitrogen by an extend greater than reported here for samples (9) and (10). However, the variation of conductivity with nitrogen concentration has been shown here to depend on the composition of the glass system; for example substitution of one alkaline earth for the same concentration of another produced a significant change in behaviour. It may be the case that the conductivity variation is also dependent on specific compositions within a glass system, changing with changing concentrations of its elements, and it may be sensitive to different ratios of (total positive valences)/(total negative valences).

It is clear that the substitution of nitrogen into oxide glasses influences dielectric behaviour in a manner which depends on the other constituents of the oxide glass, so that systematic variations of composition are necessary if the effects of the nitrogen are to be distinguished.

Oxynitride glass systems can be prepared in which the increasing dielectric constant is coupled with either increasing, decreasing or approximately constant dielectric loss. This may be of value in optimizing dielectric characteristics for specific applications, particularly as incorporating nitrogen tends to enhance other physical properties: the mobility of alkali ions in the material is reduced, increasing d.c. resistivity and reducing devitrification near electrodes due to electrolysis [15], and oxynitride glasses are harder and more refractory [15–17]. It is interesting to note that in the system containing neodymium (one of the Period 6 elements of the periodic table included in the glass in order to increase the dielectric constant) the oxynitrides have higher dielectric constants than the oxide glass.

Systematic studies of the dielectric behaviour of other oxynitride glasses would be of interest. Systems in which nitrogen substitution has already been achieved include high silica glasses [15], soda-lime–silica, sodium borate and boric acid [18, 19].

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