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High-frequency dielectric properties of Mg–Al–Si, Ca–Al–Si and Y–Al–Si oxynitride glasses

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Recently developed coaxial line techniques [1] have been used to determine, at room temperature, the values of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constants for some Mg–Al–Si, Ca–Al–Si and Y–Al–Si oxynitride glasses over the frequency range 500 MHz to 5 GHz. The frequency dependencies of ϵ' and ϵ'' are consistent with the universal law of dielectric response in that $(\epsilon' - \epsilon_\infty) \propto \omega^{(n-1)}$ and $\epsilon'' \propto \omega^{(n-1)}$ for all glass compositions; the high experimental value of the exponent ($n = 1.0 \pm 0.1$) suggests the limiting form of lattice loss [2] situation. In this frequency range, as previously reported [3] at longer wavelengths, the addition of nitrogen increases the dielectric constant, (ϵ'); in both the oxide and oxynitride glasses ϵ' is also influenced by the cation, being increased with cation type in the order magnesium, yttrium, calcium as at lower frequencies.

1. Introduction

In 1981 Thorp and Kenmuir [4] reported initial measurements on the dielectric properties of Ca–Al–Si and Mg–Al–Si oxynitride glasses. Room temperature measurements of the dielectric constant and loss factor, using bridge techniques from 500 Hz to 10 kHz, showed that for each particular composition the data fitted well with the universal dielectric response law. It was also found that the addition of nitrogen in the glasses increase ϵ' and furthermore that changing from magnesium to calcium increased ϵ' in either the pure oxide or oxynitride glasses. Recently, these investigations have been extended by Kenmuir *et al.* [3] to new oxynitride glass systems. Low-frequency bridge techniques were again used to determine the room temperature values of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant and also the conductivity (σ) 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 Hz to 10 kHz the frequency dependencies of ϵ' and ϵ'' are consistent with the universal law of dielectric response, $(\epsilon' - \epsilon_\infty) \propto \omega^{n-1}$ and $\sigma(\omega) \propto \omega^n$. For all compositions examined the experimental value of n was found to be $n = 1.0 \pm 0.1$. In all four systems the addition of nitrogen increased the dielectric constant (ϵ') while, at each concentration of nitrogen (including the oxide glasses) ϵ' increased with cation type in the order magnesium, yttrium, calcium, neodymium. Measurements on the same group of glasses have now been made in the 500 MHz to 5 GHz range in order to establish whether the trends of behaviour found at the lower frequencies were maintained in the higher frequency regions. These measurements were facilitated by the development of precision coaxial line techniques [1] which were themselves initiated by the need encountered in earlier work on doped magnesium oxide for greater precision in the dielectric constant measurements with low loss materials.

2. Experimental procedure

2.1. Glass compositions

The compositions of the glasses examined, all of which were prepared by the Crystallography

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

Sample	Composition (at%)							% oxygen replaced by nitrogen (R)	ϵ_∞
	Mg	Ca	Y	Si	Al	O	N		
1	17.0	–	–	17.0	6.0	60.0	0	0	2.46
2	17.0	–	–	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
4	–	17.0	–	17.0	6.0	60.0	0	0	2.59
5	–	17.2	–	17.2	6.4	55.1	4.1	8.1	2.73
6	–	17.2	–	17.2	6.5	54.2	4.9	9.8	2.77
7	–	17.3	–	17.3	6.5	53.1	5.8	11.5	2.80
8	–	17.4	–	17.4	6.6	51.0	7.6	14.8	2.84
9	–	–	11.8	17.8	6.8	63.6	0	0	2.76
10	–	–	12.3	18.5	7.1	54.2	7.9	14.8	3.05

Laboratory, University of Newcastle upon Tyne [5], are given in Table I. The compositions were varied systematically and each of the three cation systems (magnesium, calcium and yttrium) 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 (R) is given in Table I for each of the oxynitride compositions. The proportions of other elements were held constant, and the same system was followed between the different cation series, which therefore contained equal chemical equivalents of either magnesium, calcium or yttrium. The ratio of (total positive valence)/(total negative valences) did not vary with either nitrogen concentration or cation type, and was equal to one for all the materials investigated. Table I also includes the limiting high-frequency dielectric constant, ϵ_∞, deduced from optical refractive index measurements [5].

2.2. Measurement methods

The measurements were made using coaxial line methods in which a disc-shaped sample is fitted in a coaxial holder terminated by either a short-circuit, a matched termination or a resonance circuit; the details of these techniques have been described recently by Kulesza *et al.* [1]. For these measurements circular samples of about 6.5 mm diameter and 0.5 mm thick were cut from the bulk oxynitride glasses using conventional diamond cutting methods and polished with diamond paste to 0.25 μm finishes. The coaxial line with short-circuit termination proved most suitable for the determination of ϵ' in the frequency range 500 MHz to 5 GHz while the coaxial line resonance method was found to be preferable for ϵ'' determination. The matched termination method gave reliable answers only below about 1 GHz and was more suitable for the lower dielectric constant compositions. Above 5 GHz the voltage standing wave ratio (VSWR) measured by the coaxial line resonance method becomes very high, thus effectively setting an upper frequency limit of about 5 GHz for the loss measurements on these glasses. All the data were obtained at room temperature.

3. Results

The variations of $\log(\epsilon' - \epsilon_\infty)$ with $\log(f)$ for the different compositions are given in Fig. 1. The values of ϵ_∞ were calculated from the optical refractive index data given by Drew [5] and are included for reference purposes in Table I. Each composition showed a linear variation. The slopes of the plots were independent of composition and have the value $1.0 + 0.1$ for all specimens. (It may be noted here that, since there are likely to be some other loss processes between the microwave and optical regions, the optical refractive index may not be the relevant value for the purpose of the present investigation.) At any given frequency the value of ϵ' depended markedly on composition, increasing as nitrogen concentration increased and varying with cation type. The corresponding loss (ϵ'') behaviour is shown in Fig. 2 and this shows that over the extended frequency range from 0.5 to 9 GHz the loss for each particular composition is almost independent of frequency. The observed power law dependences of both ϵ' and ϵ'' on frequency are consistent with the universal dielectric response law in solids [6–8] in that $(\epsilon' - \epsilon_\infty) \propto \omega^{n-1}$ and $\epsilon'' \propto \omega^{n-1}$. For each composition the values of n found from Figs. 1 and 2 agree within

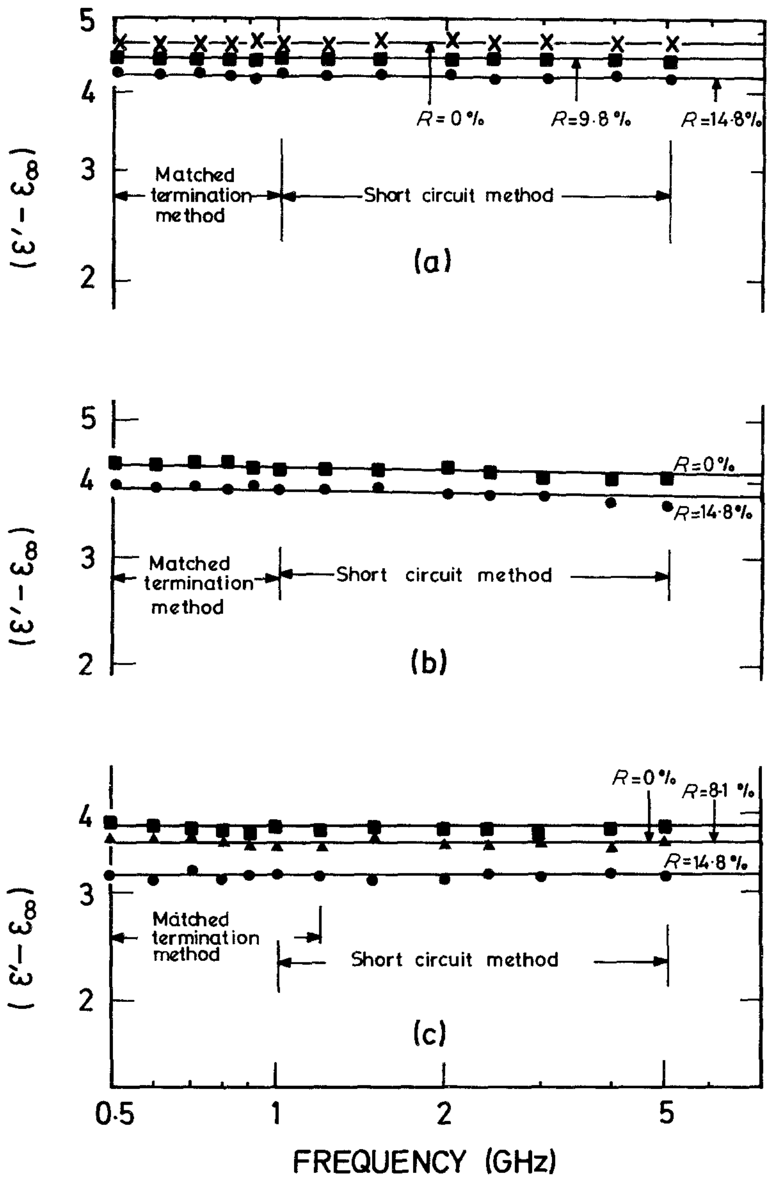

Figure 1 Variation of reduced dielectric constant ($\epsilon - \epsilon_\infty$) with frequency; (a) calcium glasses, (b) yttrium glasses, (c) magnesium glasses.

experimental error and the observation of the same value of n for all the specimens suggests that, at room temperature in this extended frequency range, the dielectric polarization and loss in all the compositions examined results from the same mechanism, and that this mechanism has not been changed by the substitution of nitrogen for oxygen.

The nature of the changes in dielectric behaviour caused by the substitution of nitrogen for oxygen becomes more apparent when the dielectric constant (ϵ') and $\tan\delta$ values are plotted against the nitrogen concentration at a single frequency for all the compositions examined. In order to provide a more consistent comparison of the nitrogen dependence of different cation systems, the nitrogen concentration has been expressed as a percentage of the oxygen of the appropriate oxide glass for which nitrogen has been substituted ($R\%$). Fig. 3 shows the variation of dielectric constant (ϵ') with nitrogen concentration at a frequency of 1 GHz ($\omega \simeq 6.3 \times 10^9$). Fig. 4 shows the corresponding variation of $\tan\delta$ with nitrogen concentration at 1 GHz and the

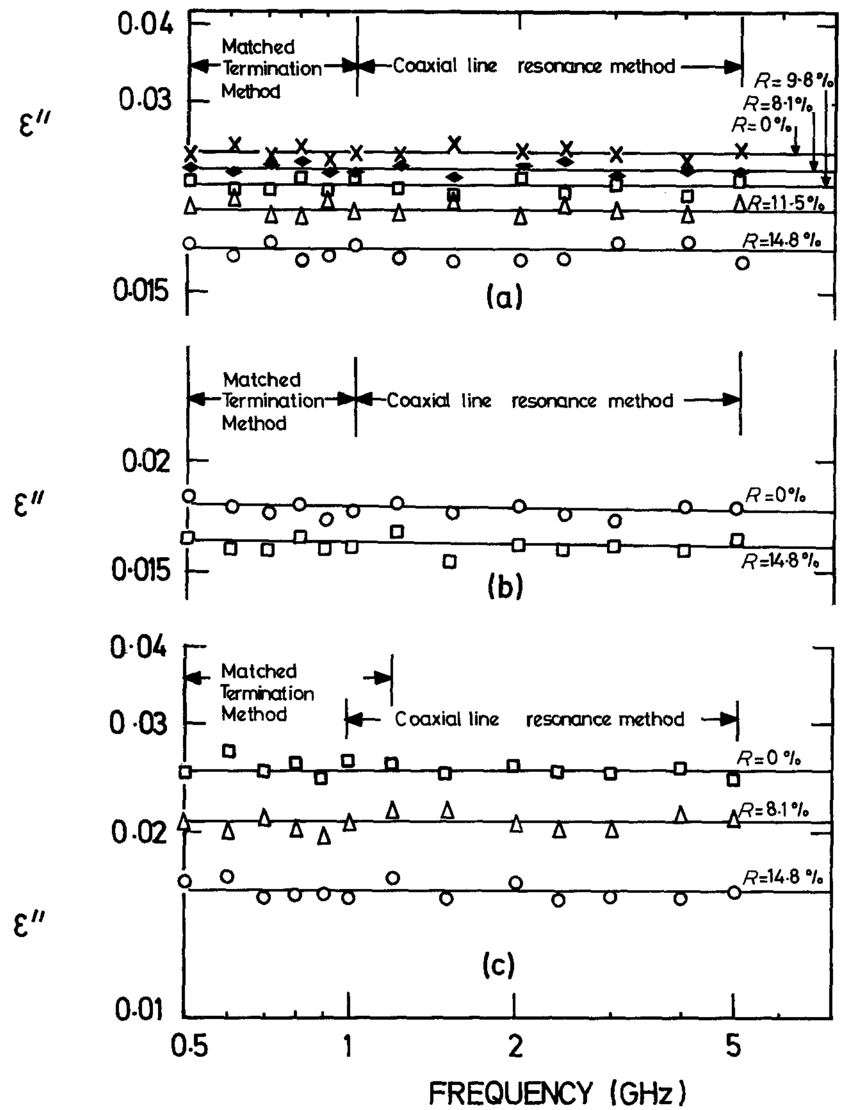

Figure 2 Variation of loss ϵ'' with frequency; (a) calcium glasses, (b) yttrium glasses, (c) magnesium glasses.

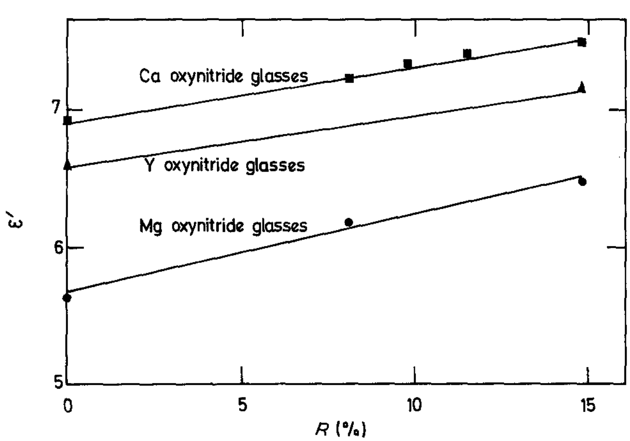

Figure 3 Variation of dielectric constant ϵ' with % oxygen replaced by nitrogen in oxynitride glasses; 1 GHz data.

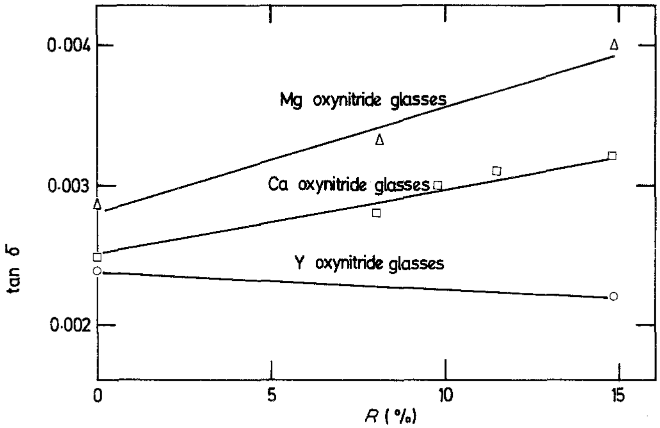

Figure 4 Variation of loss tangent with % oxygen replaced by nitrogen in oxynitride glasses; 1 GHz data.

results obtained for ϵ', ϵ'' and $\tan\delta$ are summarized in Table II.

4. Discussion

Since the present measurements, made over the frequency range 500 MHz to 5 GHz, and the previous observations, made by Thorp *et al.* [3] over the lower frequency region from 500 Hz to 20 kHz, were all taken with the same series of oxynitride glass samples, a unique opportunity exists for assessing the dielectric behaviour over this very extensive frequency range. A number of important features are revealed.

For each individual glass composition the frequency dependencies of both the diselectric constant ϵ' and loss ϵ'' are consistent with the universal law of dielectric response. Taking the results for all the individual compositions collectively reveals that this whole group of rigid ceramics gives dielectric behaviour corresponding to the limiting form of "lattice loss" [2] in which most dipolar processes have been eliminated and frequency independent loss is expected. This is not common though it is interesting to note that similar properties have been reported both for doped magnesium oxide [9], a rigid refractory oxide ceramic and for several sialon materials [10], high frequency refractory ceramics containing oxygen and nitrogen.

TABLE II Dielectric properties of Mg–Al–Si, Y–Al–Si and Ca–Al–Si oxynitride glasses at 1 GHz

Oxynitride glass systems	% oxygen replaced by nitrogen (R)	ϵ'	ϵ''	$\tan\delta \times 10^3$
Mg	0	5.64	0.016	2.87
	8.1	6.18	0.021	3.32
	14.8	6.48	0.026	4.00
Y	0	6.60	0.017	2.51
	14.8	7.14	0.014	2.00
Ca	0	6.93	0.017	2.48
	8.1	7.22	0.020	2.81
	9.8	7.31	0.022	3.00
	11.5	7.39	0.023	3.10
	14.8	7.49	0.024	3.23

A second point of interest is to note the range of values of ϵ' which can be obtained by compositional changes in the glass system. At the lowest extreme one finds $\epsilon' \simeq 5.6$ at 1 GHz for magnesium oxide glass and at the highest $\epsilon' = 11.6$ at 1 kHz for a neodymium oxynitride glass containing 8.8 at% nitrogen. This wide range suggests potential for the choice of special glasses where dielectric matching is important, e.g. in substrate materials for devices. In the oxide glasses ϵ' is dependent on the cation type and increase in the order magnesium, yttrium, calcium, neodymium while in all the systems the addition of nitrogen increased ϵ'. It should be noted, however, that there are limits to the latter method for increasing ϵ' since, depending on the particular system, the maximum nitrogen solubility lies in the range 10 to 15 at%, the highest nitrogen-containing glasses so far produced [5] being in the Y–Si–Al–O–N system. It would be of interest to compare simpler oxide and nitride systems (e.g. Al_2O_3 and AlN; SiO_2 and Si_3N_4) to find whether there are generalized behaviour rules for nitrogen substitution or whether the effects described above are specific to the oxynitride glasses examined here. A similar increase in ϵ' when 1.5 at% nitrogen was substituted for the same amount of oxygen in an yttrium oxynitride glass has been reported by Loehman [11] and by Leedecke and Loehman [12].

A third feature revealed by a comparison of the measurements in the different frequency ranges relates to the cation order found to give increasing values of the dielectric constant ϵ'. This feature may most easily be demonstrated by reference to the oxide glasses. At low frequencies [3] it can be stated quite definitely that ϵ' increases with change in the cation in the order $Mg < Y < Ca < Nd$; here the differences in ϵ' between compositions are very much greater than any possible experimental errors so that the trend is firmly established. A similar result has now been found at the higher frequencies (between 500 MHz and 5 GHz) and these coaxial line measurements confirm that ϵ' increases in the order $Mg < Y < Ca$.

Some remarks may be made in conclusion regarding the influence of nitrogen substitution on the dielectric loss ϵ''. Unlike the behaviour of the dielectric constant ϵ' the dependence of dielectric loss on nitrogen concentration varied from system to system. The measurements in the lower frequency range showed that an increase in nitrogen concentration produced a relatively large increase in $\tan\delta$ in the magnesium glasses and a smaller though definite increase in the calcium glasses; by contrast a small decrease was observed in the yttrium glasses. The difference in behaviour has been confirmed by the new measurements in the higher frequency range. Substitution of 14.8% oxygen by nitrogen increased $\tan\delta$ by 39% for magnesium glasses, by 22% for calcium glasses and decreased $\tan\delta$ by 16% for yttrium glasses (Fig. 4). These figures may be compared with those of Kenmuir *et al.* [3] where increases of 55% and 13% for magnesium and calcium glasses, and a decrease of 20% yttrium glasses were observed between 500 Hz and 10 kHz for the same increase in nitrogen concentration. It is interesting to note the close similarity between the values obtained in the two frequency ranges and further that the contrast in behaviour between the yttrium glasses and the others has been confirmed. If the changes in dielectric loss are to be attributed to changes in the chemical bonding there seems no obvious reason why the yttrium ion should differ so markedly from both calcium and magnesium. It must be borne in mind, however, that, at the present stage of development of the preparative techniques for making the oxynitride glasses, there may be other impurities present at low levels and that the measured dielectric loss may be determined by these rather than being a direct monitor of the changes in cation–oxygen or cation–nitrogen bonding schemes.

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