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The dielectric properties of certain ZnO-Al_2O_3-SiO_2 glass-ceramics

P. W. McMILLAN, G. PARTRIDGE
Nelson Research Centre, General Electric Co Ltd, Beaconhill, Weston Road, Stafford, UK

An original study has been made of the influence of additions of alkaline-earth metal oxides (CaO, SrO, BaO) at the expense of ZnO on the dielectric properties of certain ZnO-Al_2O_3-SiO_2 glass-ceramics. Tests were carried out at 20° C at frequencies of 10^5 to 10^{10} Hz and at temperatures up to 400° C at a frequency of 9.37×10^9 Hz. X-ray diffraction analysis showed that the major crystalline phase in all cases was Zn_2SiO_4 and this was little changed in proportions or lattice parameters by the additions. Some changes in secondary crystal phases were noted but no positive identification of crystals containing Ca^{2+}, Sr^{2+} or Ba^{2+} was made. It is concluded that the alkaline-earth metal ions are essentially contained in the residual glassy phase and that the major contribution to the dielectric losses is by the residual glassy phase. Increase in the BaO content causes a loss peak to move to lower frequencies (in the range $> 10^{10}$ to 10^8 Hz) and this is believed to be partly due to the BaO additions rendering the network of the residual glassy phase more open, and partly due to the heavy mass of the Ba^{2+} ions. A similar effect was not observed for additions of CaO and SrO. Furthermore, it appears that the alkaline-earth metal oxide additions are restricting deformation of the network of the residual glassy phase.

1. Introduction

For insulating materials that are to be used in electronic applications it is necessary, in addition to the need for generally good electrical properties, that the dielectric losses and the temperature coefficients of dielectric constant of the materials should be as low as possible. Glass-ceramics are potentially useful in electronic applications because of their generally good dielectric properties and glass-ceramics which also possess good mechanical and thermal properties can be prepared. In addition glass-ceramics can readily be formed to desired shapes and can be made with controlled linear thermal expansions closely matched to those of a variety of metals, thus enabling vacuum-seals to be made.

In selecting a glass-ceramic which would be expected to possess the required dielectric properties perhaps the most important criterion is that the glass-ceramic shall be substantially alkali-free. It has been demonstrated that the presence of alkali ions in glass-ceramics, as in other materials such as conventional glasses and ceramics, leads to degradation of the dielectric properties.

The present paper is primarily concerned with the dielectric properties of zinc-alumino-silicate glass-ceramics, particularly at X-band frequencies (about 10^{10} Hz), and the influence of the additions of proportions of alkaline-earth metal oxides on the dielectric properties. This type of glass-ceramic was selected for study since previous work had demonstrated their potentially good dielectric properties and the materials were relatively easy to melt and shape.

2. Preparation of the glass-ceramics

Glass-ceramics of the ZnO-Al_2O_3-SiO_2 type incorporating the variations in composition given in Table I were prepared, the various alkaline-earth metal oxides being added at the expense of ZnO. The raw materials used in their preparation were of at least "Analar" purity and were carefully weighed out and thoroughly mixed prior to melting, The glasses were melted initially in high alumina crucibles at a temperature in the region of 1500° C for a period of approximately 2 h. The glasses were then cast onto cold iron plates and the cast pieces broken up. Each glass was remelted in a 2% rhodium/platinum crucible for

TABLE I Variation in the constituents and percentage of alkaline-earth oxide added to the ZnO-Al_2O_3-SiO_2 glass-ceramics

Glass-ceramic	Mol % alkaline-earth metal oxide		
	BaO	SrO	CaO
A	—	—	—
B	3.0	—	—
C	5.1	—	—
D	7.8	—	—
E	10.6	—	—
F	—	2.5	—
G	—	3.6	—
H	—	5.1	—
I	—	7.8	—
J	—	—	2.5
K	—	—	4.5
L	—	—	6.5

Glass-ceramics M and N are Li_2O-Al_2O_3-SiO_2 compositions.

a period of approximately 15 h at the appropriate melting temperature after which the glass was completely refined and ready for shaping.

The molten glass was cast from the rhodium/platinum crucible into preheated iron moulds to form cylindrical blanks which were annealed at temperatures in the region of 600° C. The blanks were heat-treated to convert the glasses to micro-crystalline glass-ceramics. The required samples for dielectric testing were cut and ground from the cylindrical glass-ceramic blanks.

3. Dielectric testing

3.1. Dielectric testing at X-band frequencies

Dielectric testing of the glass-ceramics at the X-band frequency of 9.37 GHz was carried out using a shorted waveguide technique on samples 22.85 mm diameter by three-quarters wavelength thick. Corrections were applied for the length of waveguide between the probe in the standing wave indicator and the short-circuit plate in the sample holder. Measurements were taken at temperatures up to 400°C. The accuracy of measurement using this equipment was estimated at better than $\pm 1\%$ on the dielectric constant and $\pm 2 \times 10^{-4}$ on loss angle.

3.2. Dielectric testing at frequencies of 10^9 Hz and 3×10^9 Hz

Dielectric testing of selected materials at frequencies of 10^9 and 3×10^9 Hz was carried out using a resonant cavity technique on samples 38.1 mm long × 5 mm diameter. The accuracy of measurement using this equipment was estimated at about $\pm 5\%$ on the dielectric constant and $\pm 5\%$ on loss angle.

3.3. Dielectric testing at frequencies in the range 10^5 to 10^8 Hz

Dielectric testing of the glass-ceramics at frequencies in the range 10^5 to 10^8 Hz was carried out using a Marconi Circuit Magnification Meter on samples 25 mm diameter × 2 mm thick. The samples were provided with cold silver electrodes and connecting links to the test set were provided by metal strips soldered to the electrodes. The accuracy of measurement using this equipment was estimated at about $\pm 5\%$ on the dielectric constant and $\pm 5\%$ on loss angle.

4. Results of the dielectric tests

The results obtained on the various aspects of dielectric testing which have been carried out are illustrated in Figs. 1 to 6 and summarized in Table II.

4.1. Measurements at 9.37 GHz

4.1.1. Substitution of ZnO by BaO

The influence of the substitution of BaO for ZnO on the dielectric properties at 9.37 GHz is shown in Fig. 1. The first addition of 3.0 mol % BaO decreased the room temperature dielectric constant and increased the loss angle of the material. Further addition of BaO increased the room temperature dielectric constant and decreased the loss angle. The temperature-coefficient of dielectric constant decreased as the BaO content increased to about 8 mol % as in glass-ceramic D with no further reduction for the addition of more BaO. The temperature-coefficient of loss angle was reduced markedly for BaO contents in the range 5 to 11 mol % as in glass-ceramics C, D and E which had loss angles less than 10×10^{-4} over the temperature range 20 to 400°.

4.1.2. Substitution of ZnO by SrO

The influence of the substitution of SrO for ZnO on dielectric properties at 9.37 GHz is shown in Fig. 2. The first addition of 2.5 mol% SrO at the expense of ZnO markedly decreased the room temperature dielectric constant of the material and also its temperature coefficient of dielectric constant (glass-ceramics A and F). Further increase in the SrO content caused the room

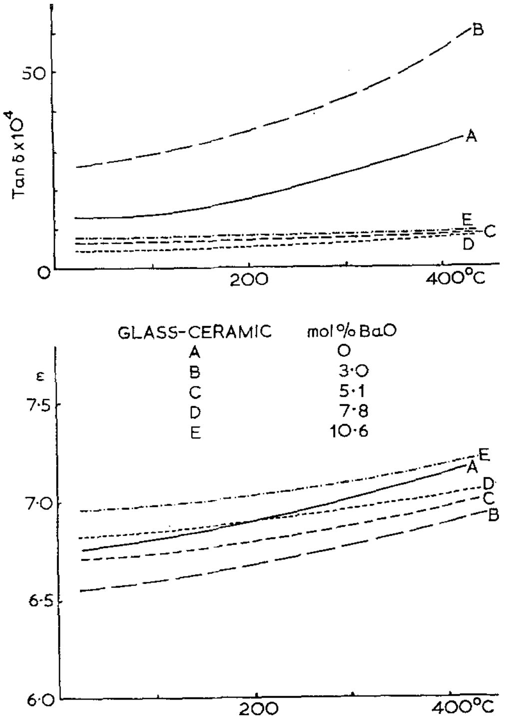

Figure 1 Dielectric properties versus temperature for glass-ceramics A to E, measured at a frequency of 9.37 GHz.

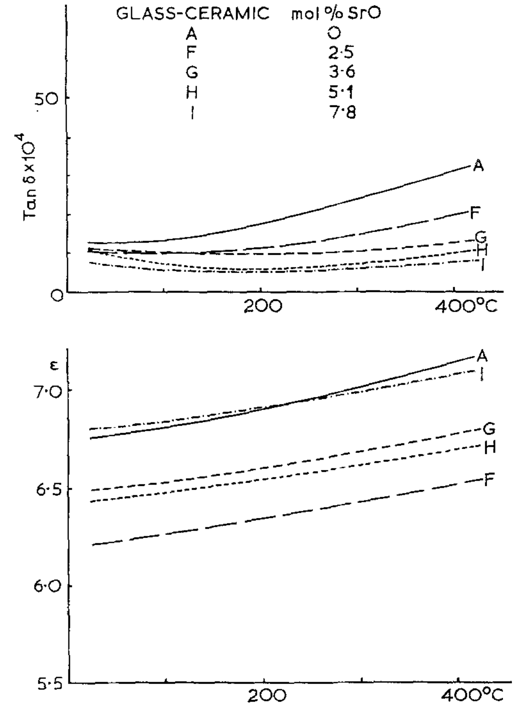

Figure 2 Dielectric properties versus temperature for glass-ceramics A and F to I, measured at a frequency of 9.37 GHz.

temperature dielectric constant to increase but had only a minor effect on the temperature-coefficient of dielectric constant. Increase in the SrO content reduced the room-temperature loss angle only slightly but had a marked effect on the temperature-coefficient of loss angle, this latter parameter being decreased as the SrO content increased.

4.1.3. Substitution of ZnO by CaO

The influence of the substitution of CaO for ZnO on dielectric properties at 9.37 GHz is shown in Fig. 3. The first addition of 2.5 mol % CaO markedly decreased the room-temperature dielectric constant of the material and also decreased the temperature-coefficient of dielectric constant (glass-ceramics A and J). Further increase in the CaO content caused both the room-temperature dielectric constant and the temperature-coefficient of dielectric constant to increase. The first addition of CaO (2.5 mol %) had little effect on the room-temperature loss angle but increased markedly the temperature-coefficient of loss angle. Further increase in the CaO content increased the room-temperature loss angle but decreased the temperature-coefficient of loss angle. For glass-ceramic L the loss angle decreased noticeably with rise in temperature up to a temperature of about 300° after which the loss angle rose with increase in temperature.

4.1.4. Tests on Li_2O-Al_2O_3-SiO_2 materials

For comparison, the dielectric properties of two Li_2O-Al_2O_3-SiO_2 glass-ceramics (glass-ceramics M and N) have been measured at a frequency of 9.37 GHz. These materials show much higher losses than the ZnO-Al_2O_3-SiO_2 materials (glass-ceramics A to L) and the influence of temperature on their dielectric properties is shown in Fig. 4. The loss-angle curves showed marked minima at temperatures in the region of 200°C. The temperature-coefficients of dielectric constant of these materials are appreciably higher than those of the ZnO-Al_2O_3-SiO_2 materials (see Table II).

4.2 Measurements at various frequencies at 20°C

The results of the dielectric measurements over the frequency range 5×10^4 to 9.37×10^9 Hz

TABLE II Dielectric properties of the glass-ceramics at 9.37 GHz

Glass-ceramic	Dielectric constant, Σ		Temperature coefficient of Σ, 20 to 400°C ppm	Loss angle tan δ × 10^4		Inflection temperature °C	Activation energy above inflection temp. k cals.
	at 20°C	at 400°C		at 20°C	at 400°C		
A	6.76	7.14	148	13	31	133	1.71
B	6.56	6.90	136	27	55	234	1.79
C	6.72	6.97	98	7	9	344	2.05
D	6.83	7.03	77	5	8	253	1.83
E	6.97	7.18	79	8	9	376	1.71
F	6.22	6.51	123	11	20	173	1.68
G	6.49	6.77	113	11	13	289	1.77
H	6.43	6.68	102	11	10	201	1.74
I	6.80	7.07	104	8	7	292	1.81
J	6.23	6.54	131	12	53	145	3.05
K	6.37	6.74	144	21	40	198	2.01
L	6.85	7.13	177	35	30	337	1.71
M	5.66	6.09	200	110	210	284	8.60
N	5.93	6.41	213	117	123	312	8.45

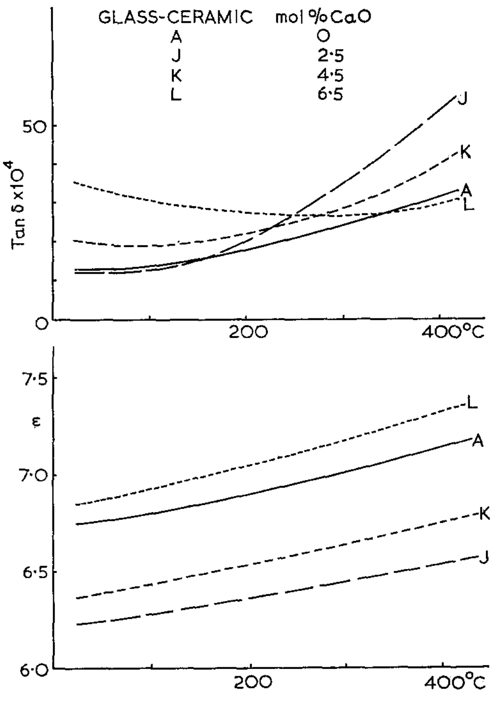

Figure 3 Dielectric properties versus temperature for glass-ceramics A and J to L, measured at a frequency of 9.37 GHz.

for the series of glass-ceramics in which BaO was substituted for ZnO (glass-ceramics A to E) are illustrated in Fig. 5. There appears to be a peak in the curves of loss angle versus $\log_{10}$ frequency and this peak moves to lower frequencies as the BaO content is increased. For these materials there appears to be little significant change in dielectric constant with change of frequency over the range examined.

A similar measurement on one of the Li_2O-Al_2O_3-SiO_2 materials (glass-ceramic M) shows that the loss angle against $\log_{10}$ frequency curve has a marked minimum at a frequency of 5×10^7 Hz (Fig. 6).

5. Crystal phases present in the glass-ceramics

In addition to the dielectric measurements, several of the ZnO-Al_2O_3-SiO_2 glass-ceramics have been examined by X-ray diffraction analysis and by electron microscopy. Table III gives the crystal phases which have been identified. The major crystal phase in all cases was zinc orthosilicate. Variations in the compositions of the materials did not appear to alter the proportions of this phase to any great extent and did not change the lattice dimensions of this phase greatly (within the accuracy of measurements).

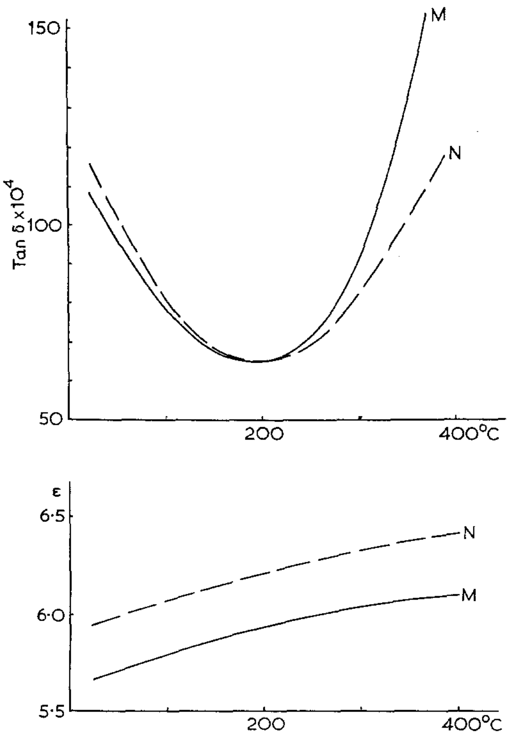

Figure 4 Dielectric properties versus temperature for glass-ceramics M and N, measured at a frequency of 9.37 GHz.

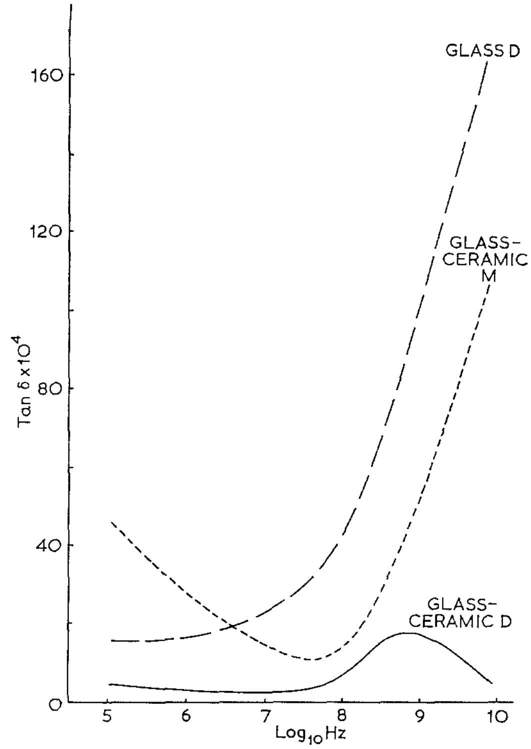

Figure 6 Variation of loss angle with frequency for glass D and glass-ceramics D and M.

Some changes in the secondary crystal phases were noted, the most interesting observation from this being that the presence of BaO encourages quartz to form rather than cristobalite. Electron microscopy of these materials reveals a fairly irregular structure to the crystal phases (Fig. 7) the crystals being slightly larger in the more BaO-rich glass-ceramic of the two shown.

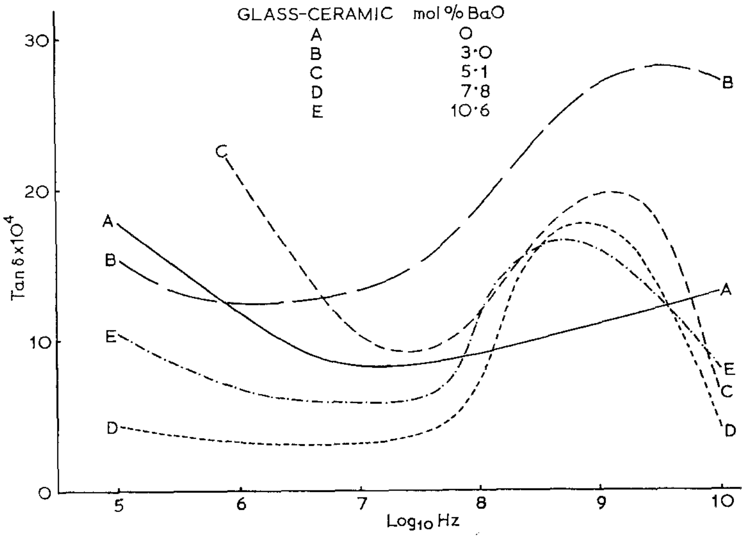

Figure 5 Variation of loss angle with frequency for glass-ceramics A to E.

TABLE III Crystal phases detected in the ZnO-Al_2O_3-SiO_2 glass-ceramics

Glass-ceramic	Major phase	Subsidiary phases
	Zinc orthosilicate	
A	a_0 13.88Å, c_0 9.30Å	$ZnAl_2O_4$, cristobalite
B	a_0 13.86Å, c_0 9.13Å	Not identified
C	a_0 13.86Å, c_0 9.23Å	Quartz
D	a_0 13.86Å, c_0 9.23Å	Quartz
E	a_0 13.81Å, c_0 9.33Å	Quartz
G	a_0 13.83Å, c_0 9.13Å	Cristobalite
I	a_0 13.86Å, c_0 9.25Å	Not identified
L	a_0 13.80Å, c_0 9.35Å	Not identified

N.B. The lattice parameters for zinc orthosilicate, Zn_2SiO_4 are:

a_0 13.94Å
c_0 9.309Å

$BaAl_2Si_2O_8$ possible in many materials.

By comparison the Li_2O-Al_2O_3-SiO_2 glass-ceramics contained a β-spodumene solid solution as the major crystal phase and appear to have a finer crystal structure than the ZnO-Al_2O_3-SiO_2 materials (Fig. 7).

6. Discussion

The dielectric properties of the glass-ceramics examined have proved to be of great interest. It has been shown possible to prepare alkali-free glass-ceramics of the ZnO-RO-Al_2O_3-SiO_2 type (where RO is an alkaline-earth oxide) which exhibit a high stability of dielectric properties with increase in temperature up to 400° C at microwave (X-band) frequencies. However, there are certain features of the results obtained which require explanation.

The dielectric losses of the glass-ceramics are the sum of the losses of the various crystal phases and the loss of the residual glassy phase. As pointed out above the major crystal phase in these materials is zinc orthosilicate and the proportions of this and its crystal parameters in the glass-ceramics do not appear to have been changed much by the alkaline-earth oxide additions. Other crystal phases detected are essentially alkaline-earth free and this suggests that the alkaline-earth oxide content is largely in the residual glassy phase. It has also been shown that the losses in glass D, from which is obtained glass-ceramic D by heat-treatment, are considerably higher at X-band frequencies than the losses in the glass-ceramics (Fig. 6). It is suggested, therefore, that the measured losses are principally the losses occurring in the residual glassy phase and that the losses in the crystal phases represent only a small proportion of the total.

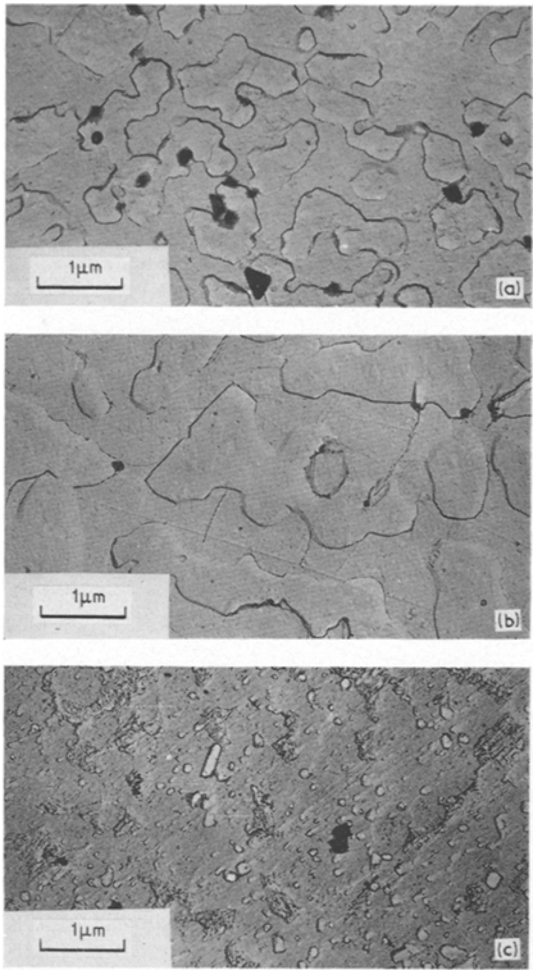

Figure 7 Electron micrographs of the crystal structures in (a) glass-ceramic B, (b) glass-ceramic D and (c) glass-ceramic M.

Stevels [1] regards the apparently complicated variation of loss angle with frequency and with temperature as being more readily understood if the measured loss is regarded as being the sum of four contributions, namely: (*a*) conduction losses (*b*) dipole-relaxation losses, (*c*) ionic-resonance losses, (*d*) deformation losses. These are illustrated in Fig. 8. It is considered to be worthwhile to explain these losses in more detail, as follows:

(*a*) *Conduction losses.* The network modifying

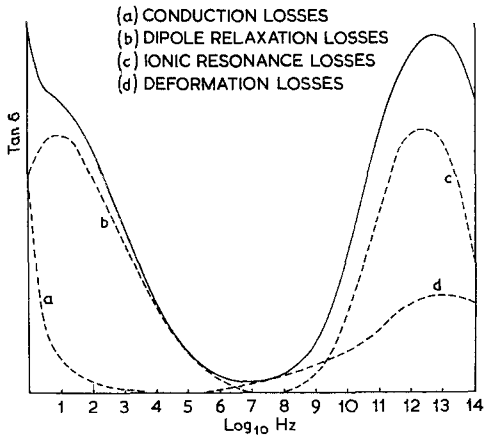

Figure 8 The general shape of tan δ as a function of the frequency at 300 K. After Stevels [1].

ions move through the network under the influence of an electric force and transfer part of the energy obtained from this force to the network in the form of heat. According to Stevels, a better description would be "dc conductivity losses". As a general rule the conduction losses for frequencies higher than 50 Hz are negligible compared with the other losses, although increase in temperature will increase their effect at slightly higher frequencies. For the present discussion, however, where frequencies above 10^5 Hz only are considered, the conduction losses can be ignored.

(*b*) *Dipole-relaxation losses.* These are produced through the mobile ions being able to jump over small distances in the network under the influence of the electric field, so that a number of lower potential barriers can be covered. This involves a polarization of the material which follows the external ac field with a certain relaxation, hence the name of this type of loss. The shape of the dipole relaxation loss curve with frequency is as shown in Fig. 8 (curve b) and this type of loss has some effect at frequencies up to about 10^7 Hz. In the present context the rise in the losses at the lower end of the frequency range covered can be largely attributed to the dipole-relaxation losses.

(*c*) *Ionic-resonance losses.* The ions in the glass, both network formers and modifiers, as well as the oxygen ions, vibrate with a certain frequency round about their positions of equilibrium, and this they will do as a result of the thermal movement. Different ions, of course, resonate with different frequencies, and since the vibrations are always damped, this resonance is accompanied by losses following generally curve (c) in Fig. 8. These losses would normally be expected to show a peak in the region of 10^{12} to 10^{13} Hz but cases have been demonstrated previously where a peak has been observed for loss angles at a much lower frequency. One particular case was for a phosphate glass for which the maximum of the loss angle was at a frequency of 3×10^9 Hz [1]. The phenomenon was believed to be due to this glass having a more open network with fewer bridging oxygen ions, so that the ions were less tightly bound to their surroundings, and the resonance frequencies were shifted to lower values. In addition one of the most important factors affecting the frequency of the ionic-resonance losses is the mass of the ions present. When heavy ions, such as Ba^{2+} ions occur, relatively low resonance frequencies would be expected to be found according to Stevels.

(*d*) *Deformation losses.* These behave in a similar way to the relaxation losses. The deformation losses, however, result from small displacements or deformations of the network of the glass. The maximum value of these losses at room temperature is at frequencies in the region of 10^{13} Hz as shown in Fig. 8, curve (d).

It is clear from the above, and from Fig. 8, that over the major part of the frequency range examined and particularly at X-band frequencies the losses are essentially made up of items (c), the ionic-resonance losses, and (d), the deformation losses, but with the rise in the losses at the lower end of the frequency range covered being largely attributable to the dipole-relaxation losses (b).

If the series of glass-ceramics in which BaO was substituted for ZnO is now considered, the results obtained on the dielectric measurements can be partially explained in similar terms, As was shown above, increase in the BaO content has caused a peak in the losses to move to lower frequencies, this peak occurring at X-band frequencies at a BaO content in the region of 2.5 mol % (Fig. 5). It is now believed that one of the influences of the addition of BaO is to reduce the frequency at which the peak of the ionic-resonance losses occurs, partly owing to the weakening of the network as a result of the introduction of additional non-bridging oxygen ions, and partly because the Ba^{2+} ion is a heavy ion. The effect becomes greater the higher the BaO content without having any significant effect on the consequential crystal phases.

This effect has not been observed for the additions of SrO and CaO oxide to the base glass-ceramic (composition A). It is concluded from this that the Sr^{2+} and Ca^{2+} ions are having a much less disruptive effect on the network of the glassy phase than the Ba^{2+} ions and this can be attributed to the smaller sizes of the Sr^{2+} and Ca^{2+} ions, and also of course to their smaller masses.

A further examination of the variation of loss with temperature at the X-band frequency is possible. Plots of $\log_{10} \tan \delta$ against the reciprocal of absolute temperature are shown in Fig. 9. In all cases the graphs can conveniently be drawn as two straight lines with a marked change of slope occurring at a particular temperature for each glass, although in reality this change of slope is gradual. At temperatures below this inflection point the slopes of the lines are in many cases near to zero. Above the inflection temperature the slope is fairly similar for nearly all the ZnO-Al_2O_3-SiO_2 materials giving activation energies close to 1.8×10^3 cals. Amrhein [2] has suggested that the change of slope of these curves can be explained as follows:

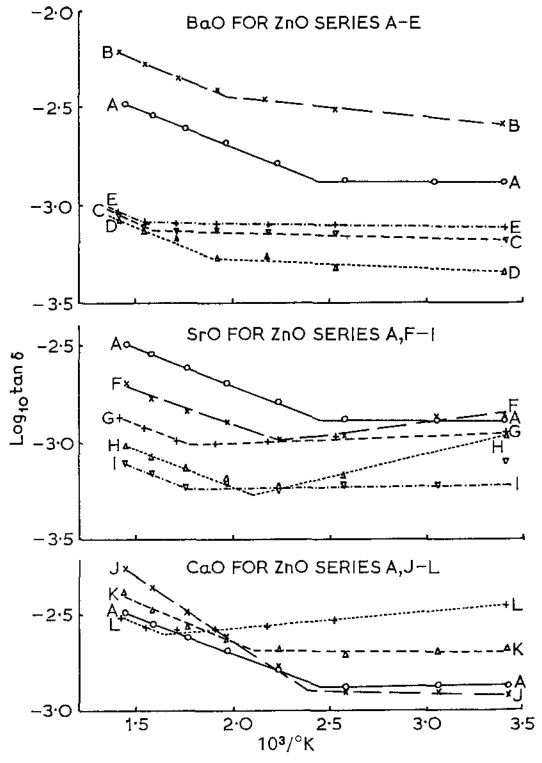

Figure 9 Plots of $\log_{10} \tan \delta$ against the reciprocal of the absolute temperature for the ZnO-Al_2O_3-SiO_2 glass-ceramics, determined at a frequency of 9.37×10^9 Hz.

At temperatures below the inflection temperature the losses are due to vibrations of the ions in favourable directions and at temperatures above the inflection temperature the losses are due to this vibration together with movement of the network elements.

The influence of the various alkaline-earth ions on the position of the inflection temperature is illustrated in Fig. 10. Increase in the alkaline-earth ion content raises the inflection temperature (within the limits shown in Fig. 10) and this means that increase in the alkaline-earth oxide content is suppressing the losses due to network movement, i.e. the deformation losses of Stevels [1]. This seems reasonable if the normally accepted picture of ions, such as the alkaline earth ions, occupying holes in the network (i.e. interstitially) is considered and clearly as the holes are filled, geometrical considerations indicate that the network, envisaged as a system of ions bonded to one another, is less free to deform. On the other hand, the introduction of additional non-bridging oxygen ions, as pointed out previously, will result in weakening of the bonding within the network, and the resonance losses which are concerned with the vibrations of individual ions, rather than groups of ions, will therefore be increased.

Plots of $\log_{10} \tan \delta$ against the reciprocal of the absolute temperature for the Li_2O-Al_2O_3-SiO_2 glass-ceramics (Fig. 11) show a similar effect to the above. It is clear that the activation energy for loss above the inflection temperature is much higher and the "discontinuity" in the curve more marked than in the case of the ZnO-Al_2O_3-SiO_2

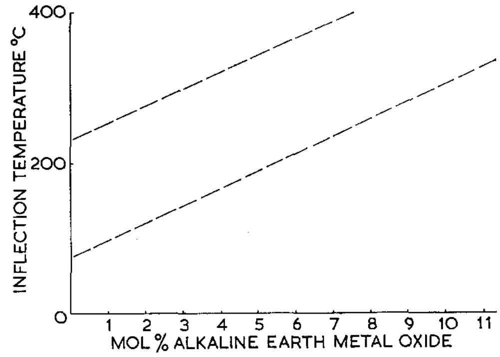

Figure 10 Influence of the mol % alkaline-earth metal oxide on the inflection temperature (from Fig. 9).

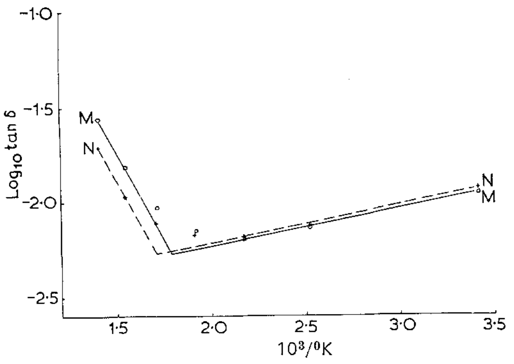

Figure 11 Plot of $\log_{10}\tan\delta$ against the reciprocal of the absolute temperature for the Li_2O-Al_2O_3-SiO_2 glass-ceramics M and N, determined at a frequency of 9.37×10^9 Hz.

glass-ceramics. This means that the network structure of the glassy phase in the Li_2O-Al_2O_3-SiO_2 glass-ceramics is much more tightly bonded than those in the ZnO-Al_2O_3-SiO_2 glass-ceramics tested.

A further point of some interest is that for glass-ceramic D the activation energy of loss (0.2×10^4 cals) derived from Fig. 9 is considerably less than the activation energy for conductivity (2.9×10^4 cals) confirming that the two mechanisms are not related.

7. Conclusions

It is concluded that the dielectric losses in the glass-ceramics examined arise mostly in the residual glassy phase and the crystal phases contribute only a small proportion over the frequency range examined. It has been shown that the addition of alkaline-earth oxides to ZnO-Al_2O_3-SiO_2 glass-ceramics suppresses the network deformation losses at microwave frequencies, the extent of the influence being greater, the higher the proportion of alkaline-earth metal oxide in the glass-ceramics. In addition, the presence of BaO in the materials lowers the frequency at which the peak of the resonance losses occurs, the reduction being greater the higher the proportion of BaO in the material.

The results of this study are of practical significance in that they demonstrate that glass-ceramics possessing the desirable characteristics of good temperature stability of dielectric constant and loss angle at microwave frequencies can be achieved by the inclusion of alkaline-earth oxides in compositions of the ZnO-Al_2O_3-SiO_2 type.

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