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# Dielectric field dependence of doped silica glass–ceramics

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The dielectric properties of two heavily doped silica glass–ceramics are reported in the frequency range $10^{-2}$ to $10^5$ Hz with field, both d.c. and a.c., as variable. The response of the dielectric loss peaks in both systems was found to be field dependent with two separate behaviours, a d.c. conductance-dominated imaginary component corresponding to electronic injection at the electrodes, and a capacitive component corresponding to a dipolar loss-peak process. It was found that there is a general relationship between loss-peak response and applied field that holds for both loss-peak systems. At the highest fields, one of the materials is seen to undergo a phase transition.

## 1. Introduction

The interest in the properties of semiconducting glass–ceramics, materials used as glazes to coat high-tension pin-and-cap insulation blocks [1, 2, 3] has led to the study of the low-frequency ($10^{-3}$ to $10^5$ Hz) dielectric properties of these glasses [4]. The glasses consist of a silica base with modifiers ($Al_2O_3$, CaO, ZnO, $K_2O$ and $Na_2O$) to which different weight percentages of semiconducting tin oxide–antimony oxide ($SnO_2$ with 5 wt % $Sb_2O_5$) have been added. Electron micrographs [3] show that the $SnO_2$–$SbO_5$ comes out of solution as semiconducting crystallite clusters within the glassy silica matrix.

Work on the dielectric properties of two of the doped glasses, with 15 and 22 wt % added dopants (to be called J-15 and J-22, respectively) [4] has revealed the presence of two distinct dielectric processes in each glass, the loss-peak and the anomalous low-frequency dispersive (LFD) [5, 6] processes. Measurements with respect to temperature reveal the collapse of the low-temperature loss-peak system and their replacement by the low-frequency dispersive behaviour for temperatures above 500 K [4]. This is indicative of a phase transition taking place in the glass around this temperature, and is supported by activation energy considerations [2, 4].

Electric field measurements on these two heavily doped glasses are reported here. It will be shown that the materials show non-linear effects at fields (both a.c. and d.c.) as low as $3.3\,kV\,m^{-1}$. These non-linear effects manifest themselves in two separate components, a d.c. conductance and a loss-peak response. It will be seen that there is a general relationship for the loss-peak behaviour with field which holds for the loss-peaks of both materials. One material, the J-15 glass, also manifests memory effects. Furthermore, this same glass undergoes a transition at the highest fields, where the loss-peak response collapses and is replaced by an LFD response.

## 2. Results

The presentation of the results follows the pattern used by the Chelsea Dielectrics Group, that is the plotting of the results in the form of log(capacitance), log(conductance) against log(frequency). The measurements were carried out using the minicomputer-controlled Solartron 1174 and 1191 Frequency Response Analysers [7]. For the results at high a.c. voltages, a General Radio 1605 Bridge was used.

Fig. 1 shows the effect of applied a.c. signal on the response of the glasses, showing the capacitative and conductive components of the dielectric response for the J-15 system in the range 0 to $42\,kV\,m^{-1}$. Looking at the capacitative component first, it can be seen that the material is field-dependent for fields as low as $3.3\,kV\,m^{-1}$, the capacitance decreasing with increases in a.c. voltage. These decreases are practically negligible at $10^5$ Hz, but become greater as the frequency decreases. The highest field results cannot be measured at the lowest frequencies due to the loading of the bridge.

The effect of field on the conductance, however, shows the opposite effect, with increases in field causing increases in conductance, even at the lowest fields. As with the capacitative component, the lowest frequencies show the largest changes. The gradient in this case decreases with increasing field, eventually becoming practically zero at low frequencies, an indication that this effect is due to a growing direct-current contribution (there is no equivalent dispersion of slope $-1$ in the capacitative part). The J-22 glass shows the same behaviour for a.c. field as the J-15 glass.

The effect of d.c. bias on the response can be seen in Figs 2 and 3 for the J-22 and J-15 glasses, respectively. It can be seen in Fig. 2 that the capacitative component of the loss peak for the J-22 glass decreases with applied field. The conductive component, which has zero gradient at low frequencies, increases with

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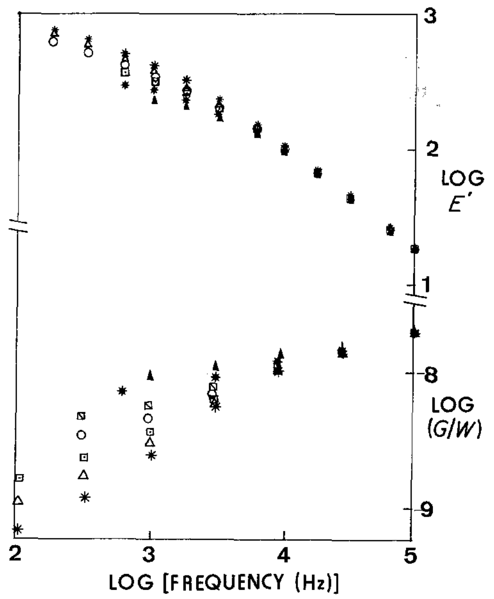


*Figure 1* The frequency dielectric response, the real ($E'$) and imaginary ($G/W$) parts of the complex capacitance, as a function of a.c. field for J-15 glass. Field values (✱) 0, (△) 3.3, (□) 6.6, (○) 10, (⊡) 20, (✱) 33, (▲) 42 kV m$^{-1}$.

increasing applied d.c. bias, the whole frequency spectrum becoming dominated by d.c. conductance at high fields.

In the case of the d.c. bias results for the J-15 glass (Fig. 3), the method of bias application was changed. In this case (to be called "quasi-d.c.") a potential d.c. bias was applied to the sample for one hour, the sample shorted, and the dielectric response then measured. This method allowed for far higher voltages to be applied to the material, albeit under different conditions. As the system was measured after the removal of the bias, there was no d.c. conductance contribution to these high fields.

Fig. 3 shows the capacitative response of this J-15 glass. It can be seen that the sample has memory effects, as the capacitative response is changed before and after the application of a bias. As in the case of the a.c. response, the capacitance decreases with applied bias at low frequencies, while the high capacitative response is unchanged before and after the application of a bias. As in the case of the a.c. response, the capacitance decreases with applied bias at low frequencies, while the high-frequency portion of the response remains practically constant, with a gradient of ~0.9.

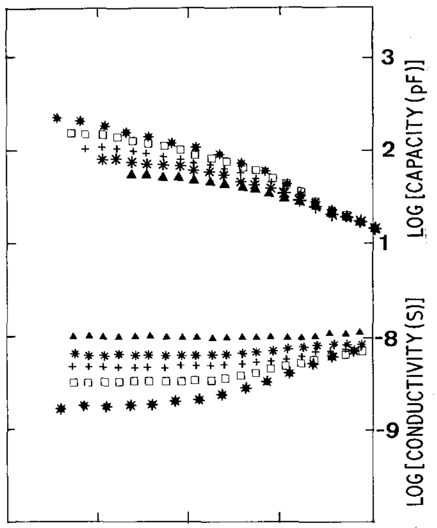


*Figure 2* The frequency dielectric response as a function of d.c. field for J-22 glass. Field values (✱) 0 and 10, (□) 25, (+) 37, (✱) 57, (▲) 84.5 kV m$^{-1}$.

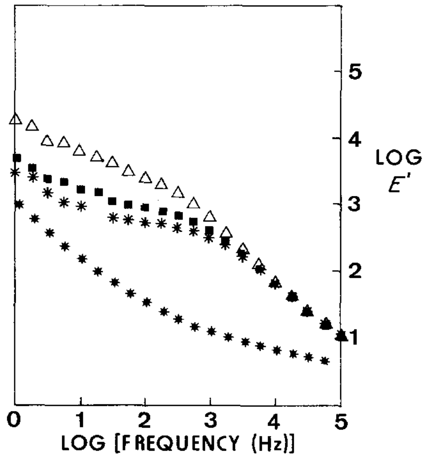


*Figure 3* The frequency dielectric response as a function of "quasi-d.c." field for J-22 glass. Field values (△) 0, (■) 30, (✱) 90, (✱) 1500 kV m$^{-1}$.

At the highest field, however, the response changes dramatically, with the collapse of the loss-peak system and the appearance of a low-frequency dispersion behaviour, with its characteristic low frequency–high gradient, high frequency–low gradient slopes [5]. This high-voltage anomaly will be discussed later. It should be remarked that the collapse of the loss-peak response is reversible. It suffices to leave the sample shorted for 24 h for the response to return to its pre-bias response; this is true for all bias results in Fig. 3.

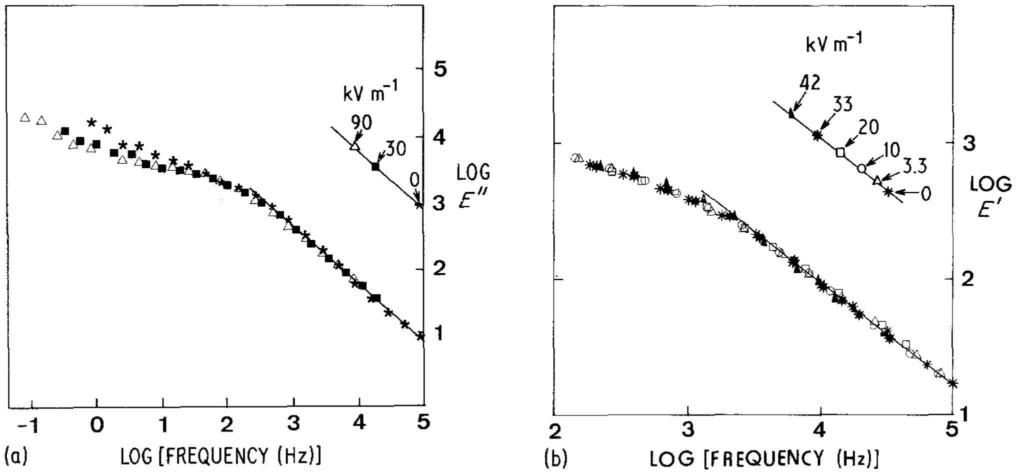
## 3. Discussion

In the preceding section it has been seen that the high-field behaviour shows two quite separate trends in the capacitative and conductive components. The conductive part is dominated by a direct-current component which increases with increasing field. The capacitance part, which has no d.c. conductivity contribution and thus represents only the loss-peak response, shows the opposite behaviour. This decrease in amplitude of the capacitance can be quite substantial – for the J-22 glass of Fig. 2, the capacitance drops by almost half a decade.

With respect to the quasi-d.c. bias results of Fig. 3, three points should be noted:

1. The capacitative component decrease is seen even after the removal of the field. This indicates that the material has memory properties. This memory response reverts back to its pre-stress behaviour if short circuited and left for 24 h.

2. There is no difference in d.c. conductance before and after application of the bias, which indicates that the d.c. conductance contribution is not related to the dipolar process, but comes directly from the application of a bias. This suggests that the increases seen in the other bias-dependence results reported above



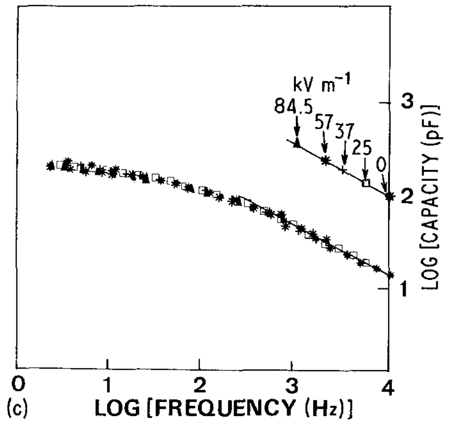


*Figure 4* Normalization of data. (a) J-15 "quasi-d.c." field, (b) J-15 a.c. field, (c) J-22 d.c. field. Straight-line slopes (a) 0.9, (b) 0.75, (c) 0.55.

arise due to electronic injection, caused by field-induced effects at the electrodes.

3. It can be strikingly seen that between 90 kV m$^{-1}$ and 1.5 MV m$^{-1}$ there is a dramatic change in the dielectric properties of this J-15 glass. Here, the dielectric loss-peak response vanishes entirely, to be replaced by the low-frequency dispersive response. The fact that the capacitance spectrum at 1.5 MV m$^{-1}$ lies below that at 90 kV m$^{-1}$ indicates that the loss peak has not moved to higher frequencies, but has disappeared completely. This type of effect has already been seen in the J-15 and J-22 materials with respect to temperature [4], where it has been found that at temperatures above 500 K the loss peak response is replaced by a low-frequency dispersion. This has been interpreted as a phase transition, and is supported by activation energy considerations [2, 4]. The results discussed above indicate that there is also a voltage-driven phase transition taking place in the glass.

Returning to the capacitative response to field in general, the most noteworthy aspect of these results can be seen on carrying out a normalization of the capacitance with respect to field. The method of normalization involves the fitting of each datum set to a master curve [8]. The shift in amplitude and frequency required for this fitting at each applied field gives the locus of normalizing points, and this is shown to the right of the master curve for each set of normalized data points in Figs 4a, b and c. The figures reveal that for each loss process, the gradient of this locus of normalizing points describes a straight line which runs parallel to the high-frequency gradient (to be called $(1 - n)$) of the loss peak. For the J-15 d.c. case (Fig. 4a), the locus and $(1 - n)$ have a gradient of 0.9. The J-15 a.c. normalization (Fig. 4b) has a gradient 0.75, and the J-22 d.c. has 0.55 as the gradient of the locus and $(1 - n)$. The difference between the $(1 - n)$ gradient of Figs 4a and b is due to a time-relaxation of the loss process – the results of Fig. 4b were obtained 6 months after those of Fig. 4a.

The fact that the locus of points runs parallel to this $(1 - n)$ slope regaredless of the magnitude of $(1 - n)$ means that one can describe the behaviour of the loss peak response to field by the relationship

$$A(\chi) \propto \omega_p^{-(1-n)} \qquad (1)$$

where $A(\chi)$ is the amplitude and $\omega_p$ the frequency of the peak of the loss.

The type of behaviour of Equation 1 is illustrated in Fig. 5, for a system whose imaginary part of the dielectric response is not masked by d.c. conductance. It can be seen that the loss peak appears to slip down the $(1 - n)$ side of the loss peak. As there is no shift in this high $(1 - n)$ frequency region with respect to field, the response can be regarded as having a high-frequency portion which is field-invariant.

This can be more clearly seen if the behaviour is transformed into the time domain. Fig. 6 shows the transformation of a loss-peak response into the time domain. The effect of increasing temperature, shown in Fig. 6b, is to increase the magnitude of the current and decrease the relaxation time. The effect of the field results reported above is seen in Fig. 6c. It can clearly be seen that the short-time (i.e. high-frequency) response to field is invariant. The response at long times (i.e. low-frequency), however, can be seen to shift to shorter times.

The fact that the high-frequency part of the loss peak appears to be field-independent, while the peak itself and the low-frequency portion show marked field dependence, suggests that the response of the loss peak is in fact made up of more than one separate component. Taking the normal activated temperature dependence [4] of these and most dielectric materials [9], along with the field response shown above, these

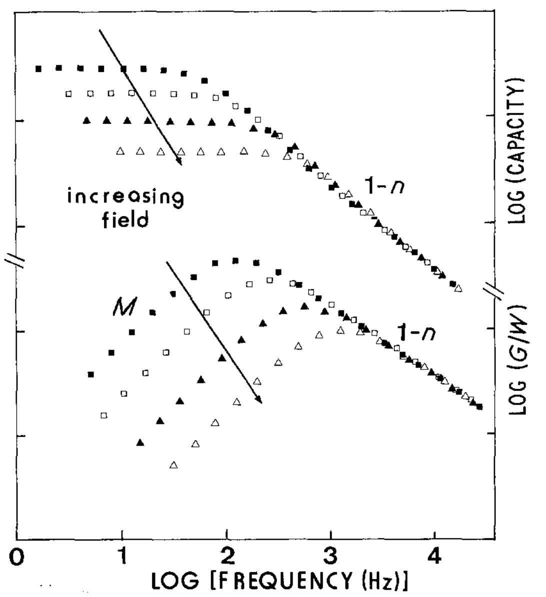


*Figure 5* Representation of the dielectric response as a function of field for an ideal loss-peak system.

glasses can be regarded as having the following behaviour.

| | |
|---|---|
| Low-frequency $m$-gradient region | $f(T, E)$ |
| Peak-frequency region | $f(T, E)$ |
| High-frequency $(1 - n)$-gradient region | $f(T)$ only |

This type of high-field response is not predicted from any of the current dielectric theories. One theory that does predict the relationship of Equation 1 is the many-body approach of Dissado and Hill [10], developed for ferroelectric materials. In this approach, they predict the behaviour of Equation 1 as a function of temperature, in the region of a phase transition. This relationship has been seen in ferroelectric substances [11]. The theory has since been extended to cover imperfect crystals [12], although the response discussed above is not a prediction for materials other than ferroelectrics.

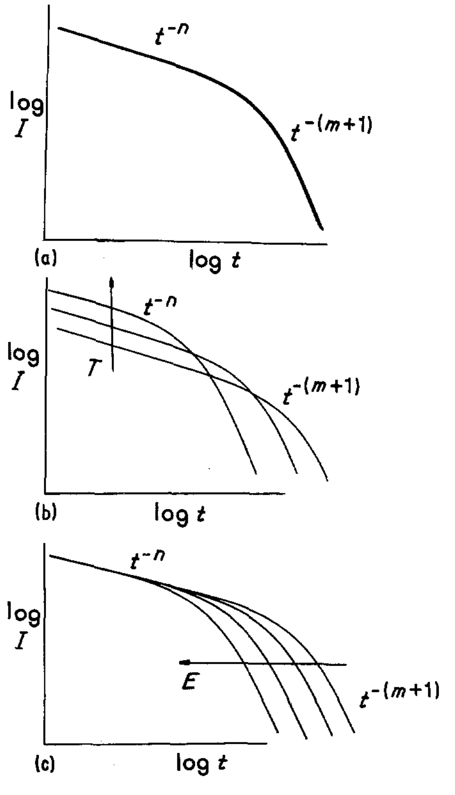


*Figure 6* (a) Transformation of a loss-peak response into the time domain. (b) Time-domain response as a function of temperature. (c) Time-domain response as a function of field.

One point that is perhaps relevant for the discussion of these results in the light of the aforementioned many-body theory is that in both temperature results [2, 4] and quasi-d.c. results (Fig. 3) a dielectric phase transition is seen to be taking place in the material. It is possible then that Equation 1 applies to materials in which such type of transition or ordering, either structural or electrical, takes place.

## 4. Conclusions

Two heavily doped glass–ceramics showing nonlinear behaviour were examined with both a.c. and d.c. voltages as variables. There were found to be two separate components to these high-field effects, a d.c. conduction which increases with increasing field, and the loss-peak response, seen in the real part, which moves to lower amplitudes and higher frequencies with increases in field. The loss peaks in both systems were found to obey a specific relationship related to the gradient of the high-frequency side of the loss peak. From this relationship, it can be stated that the high-frequency side of the loss peak is independent of high-field effects, supporting the view that the loss-peak response is made up of more than one independent component. Finally, it was found that at the highest fields there is a collapse of the loss-peak response and its replacement by a low-frequency dispersion, indicating that a phase transition occurs in the material, a view supported by results on the dielectric measurements as a function of temperature.

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