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The dielectric response of doped semiconducting glasses

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Measurements are reported of the dielectric properties of two semiconducting glasses of composition $SiO_2 \cdot Na_2O$ with admixtures of Sb_2O_5 and SnO_2, covering a wide range of temperatures and a range of six decades of frequency 10^{-2} to 10^4 Hz. Both glasses show a gradual evolution of growing low frequency dispersion (LFD) with increasing temperature, with both the real and imaginary components of the complex susceptibility following a power law of the type ω^{n-1}, with $n \ll 1$ at the lowest frequencies. There are also clear indications of reversible phase transitions taking place which manifest themselves by changes in the spectral shape of the dielectric response.

1. Introduction

The dielectric properties of carrier-dominated solids in which the dielectric response is strongly affected by limited motions of hopping charge carriers of ionic or electronic nature are not well understood [1, 2] and the present investigation was intended to advance our knowledge in this respect. The materials under study consist of a silica base with the following wt % composition: $69SiO_2$, $9.2Al_2O_3$, $9.3CaO$, $7.6ZnO$, $2.5K_2O$ and $1.8Na_2O$, with the addition of a dopant consisting of SnO with 5 wt % of Sb_2O_5, the percentage of the dopant being 15% in glass J15 and 22% in J22. The initial powdered components were mixed mechanically and fired at 1550° C for 2 h.

The resulting glass has been found to consist of a glassy matrix in which particles of SnO_2 of 0.3 μm mean diameter have crystallized in clusters [3, 4]. Measurements of d.c. electrical conductivity σ_0 as function of temperature reveal two different activated processes, above 500 K the activation energy is given as 1.26 eV (although our own interpretation of the published data suggests a value of 0.8 eV) and has been associated with ionic conduction, possibly by sodium ions, while at lower temperatures the activation energy is 0.4 eV and is associated with electronic processes [3].

Our dielectric measurements were carried out on a specially adapted frequency response analyser [5] using either a cryostat or a furnace. Disc-shaped samples had flat faces ground and polished, sample diameter was 10 mm and thickness 1 mm, evaporated gold electrodes had a diameter of 7.5 mm.

Our presentation of dielectric data follows the pattern adopted by the Chelsea Dielectrics Group [2] of plotting logarithmically the real and imaginary components of the complex capacitance $C'(\omega) - C''(\omega)$ against the circular frequency $f = \omega/2\pi$, with a view to accommodating the strong dispersion exhibited by these materials and bringing out the prevailing power law dependence of the effective complex susceptibility

$$C'(\omega) - C_\infty = \tan(n\pi/2)\,[C''(\omega) - G_0/\omega] \propto \omega^{n-1} \qquad (1)$$

where C_∞ is the high-frequency limit of the capacitance, G_0 is the d.c. conductance and the exponent n falls in the range $0 < n < 1$. In view of the high values of the d.c. conductivity in our sample, the loss component, denoted for brevity as $C''(\omega)$ in the following, was calculated by the Kramers–Kronig transformation from $C'(\omega)$ [2].

2. Experimental details

Fig. 1 shows a display of dielectric responses of the less heavily doped glass J15 shown as pairs of $C'(\omega)$ and $C''(\omega)$ data for each temperature, with vertical shifts to avoid confusion. Starting at 77 K, the response corresponds to a loss peak with a high-frequency slope $N - 1$ deviating markedly from the classical Debye shape, and with a saturation at the highest frequency of the real part, corresponding to C_∞. There is a sign of a second loss peak at the lower frequencies but nothing firm can be said about this feature since the K–K transformation may not be very reliable in view of the relatively slight dispersion of $C'(\omega)$ involved at this temperature. As the temperature increases to 273 K the structure of the loss peak becomes more clearly pronounced and the loss peak moves slightly to higher frequencies – the activation energy between 173 and 341 K corresponds to approximately 0.07 eV. This loss peak is therefore most likely of electronic origin.

At the temperature of 341 K the low-frequency response becomes dominated by a strongly dispersive dependence of both the real and the imaginary parts of capacitance corresponding to the power law,

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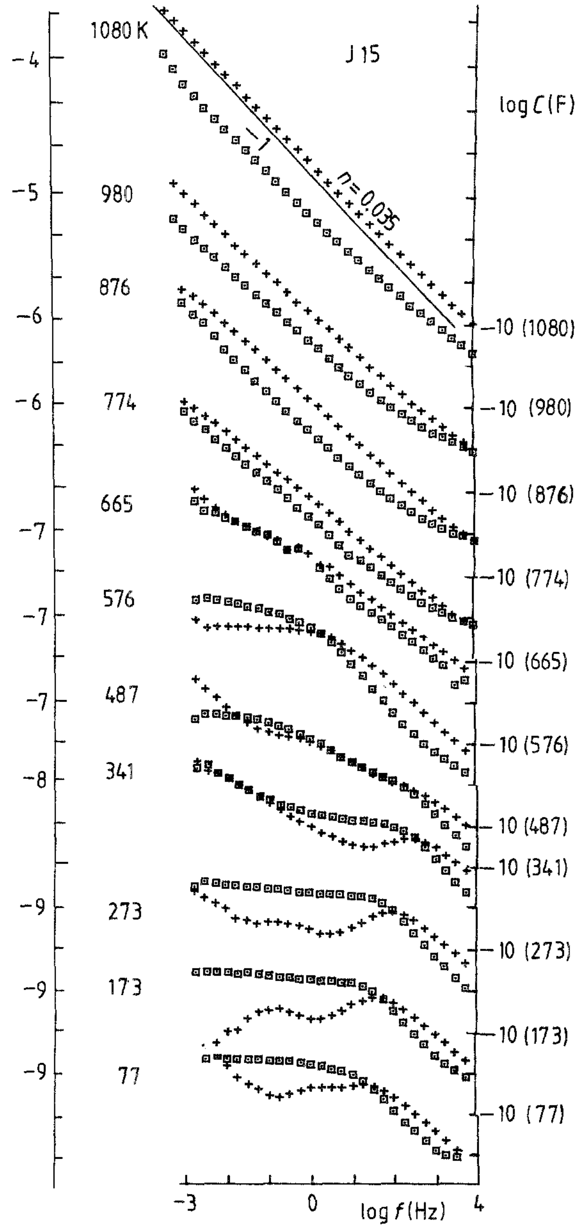

Figure 1 The frequency dependence of the real (□) and imaginary (+) components of the complex capacitance of a sample of J15 glass, plotted as pairs of curves displaced with respect to one another for clarity. The 10^{-10} F marker is shown on the right hand side, with the corresponding temperature to which it refers. The loss data are obtained by Kramers–Kronig transformation from the real part to eliminate the dominant effect of d.c. conductivity.

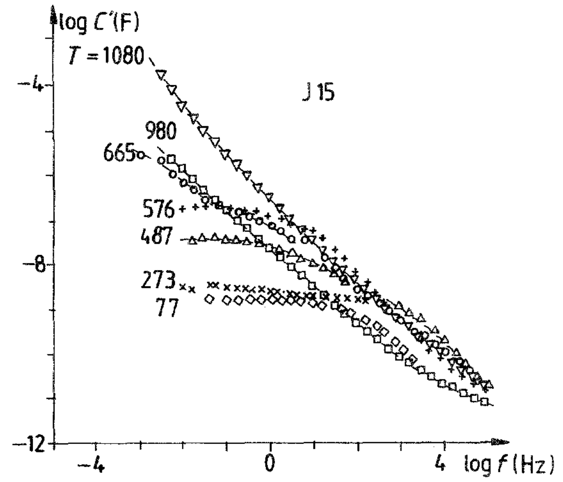

Figure 2 Selected data for the real part of capacitance from Fig. 1, plotted on common ordinate scale to show their relative disposition. The crossing over of the high-frequency data should be noted, indicating that rising temperature causes an actual reduction of the capacitance as a consequence of the disappearance of some loss process. No normalization in the conventional sense appears to be possible in this case.

Equation 1 with the value of the exponent $n \cong 0.5$ which is normally associated with diffusive processes [2, 6]. The 487 K data are broadly speaking similar except that the "diffusive" component effectively swamps the loss peak. We note, however, that the classical diffusive model need not be considered as the only explanation of the power law response with $n = \frac{1}{2}$, but it may correspond instead to a particular case of the "universal" law, Equation 1 and may be the result of many-body interactions which can give rise to any value of the exponent between 0 and 1 [7, 8].

A qualitative difference becomes evident at 576 K in that the entire spectral response changes shape to the extent that it cannot be derived from the response at lower temperatures by simple displacements vertically and horizontally of the type used in the familiar normalization processes which derive a "master curve" for the spectral response [7]:

$$C(\omega, T) = A(T)\, F(\omega/\omega_p) \qquad (2)$$

where $\omega_p(T)$ is a temperature-dependent characteristic frequency, $F(\omega/\omega_p)$ is a generalized spectral shape function of the reduced frequency variable and $A(T)$ is an amplitude factor. So long as the spectral function remains invariant with respect to temperature, it is possible to assert that the dielectrically active species, dipoles or hopping charges, as the case may be, are moving in a medium which is characterized by certain interactions determined, among other factors, by the structural arrangement of the lattice. A change of the spectral function implies, on the other hand, that the system has undergone some structural transformation. Dielectric measurements represent a very sensitive means of detecting such transformations, even when they may not yet be detectable by other physical measurements [9–11].

With the temperature increasing beyond 576 K we note the trend to complete disappearance of the residual loss peak, which is still discernible at 665 K. At the highest temperature of 1080 K the power law shows an exponent $n = 1 - 0.035$ which corresponds to the ratio of the real to imaginary parts from Equation 1 of 18. This is seen to be followed by the data over seven decades of frequency.

A different aspect of the temperature dependence is shown in Fig. 2 which gives a number of data for the real part only, $C'(\omega)$, on the same co-ordinate axes. The low-temperature data form clearly one set, the high temperature data another set, with the intermediate temperatures giving a gradual transition from one set to the other. One of the noteworthy features is the relative positions of the 980 K data with respect to the 77 K data at high frequencies, suggesting the complete disappearance of the loss process dominating the low-temperature data. This is so because we are dealing here with the real part $C'(\omega)$ which would not decrease in amplitude if the loss peak simply

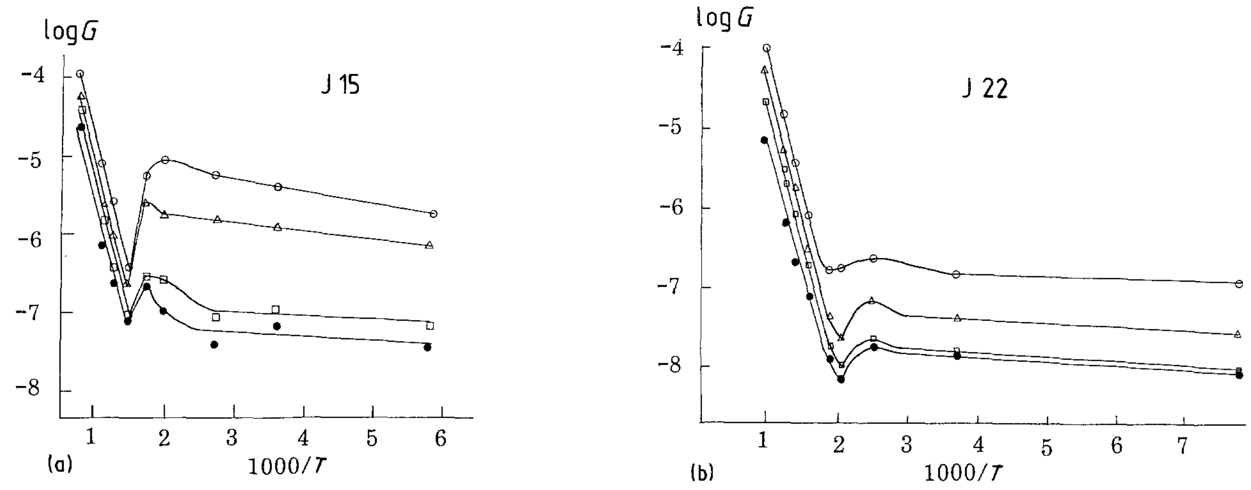

Figure 3 The activation energy plot of the frequency conductance against reciprocal temperature. The anomaly of the transition region should be noted, corresponding to the change of the shape of the dielectric response shown in Fig. 2. (a) J15 glass, (b) J22 glass. (○) 10^5 Hz, (△) 10^3 Hz, (□) 10^1 Hz and (●) 10^{-1} Hz.

moved at higher temperatures to higher frequencies [2]. Instead, the evidence presented here suggests the complete disappearance of the low-temperature process.

We thus conclude that the glass under study goes through a phase transformation between the low and high temperatures which gives rise to a completely different dielectric response.

Confirmation of this phase transition can be seen in the plots of the activation energy of conductivity, shown in Fig. 3 where the conductance $G(\omega) = \omega C''(\omega)$ is plotted against the reciprocal temperature for several spot frequencies. The high-temperature data are dominated by d.c. conduction and they show a high activation energy of 0.8 eV above 500 K, which is in agreement with the results of [3], as evaluated by us above. The lower temperature data are dominated by dielectric loss and show the corresponding frequency dependence. The important evidence from our point of view is the pronounced dip in the activation plots around 700 K, which corresponds broadly to the transition from one set of dielectric response spectra to the other. A similar behaviour was reported in [3].

Returning to Fig. 1, we conclude that the low-temperature modification favours strictly localized motions of charges – most likely electrons, in view of the low activation energy – giving rise to loss peaks [2]. At the higher temperatures the behaviour corresponds to low frequency dispersion (LFD) which is characterized by the power law behaviour of Equation 1 but with the exponent n much smaller than unity and is associated with extended motions of charge carriers with limitations at contacts and at internal barriers [1, 2]. In our case the exponent is changing gradually with temperature, which manifests itself by the visibly changing ratio $C''(\omega)/C'(\omega)$, in accordance with Equation 1. At 665 K both the low-temperature and high-temperature processes appear to coexist.

A fundamental question arises regarding the nature of the strong LFD visible at high temperatures. The activation energy between 980 K and 1080 K amounts to 2 to 3 eV, according to the frequency chosen, suggesting that we are dealing with an ionic process. The dispersion covers seven powers of ten of amplitude within our measurement range and there is no sign of saturation, the capacitance at 0.01 Hz corresponding to 1 F m^{-2}. We shall return to this question later in this paper.

Turning now to the more heavily doped glass J22, Fig. 4 gives the display of data corresponding to various temperatures and a somewhat similar pattern repeats itself as in Fig. 1 for the J15 glass. At low temperatures the "dipole-like" loss peaks are clearly visible and they become superseded by LFD behaviour above 490 K. This strongly dispersive behaviour evolves gradually with rising temperature, through an almost pure single power law at 665 K, into a pronounced "diffusive" tail at the lowest frequencies between 750 and 960 K, only to revert to nearly simple LFD at 1060 K. Fig. 5 shows the display of $C'(\omega)$ only on a common scale, where the gradual evolution of the form of the response is clearly seen, with a similar decrease of capacitance at high frequencies with rising temperature as seen in Fig. 2. The temperature dependence of conductance is also shown in Fig. 3 and its appearance is similar to J15. The curve shown beyond the chain-dotted line in Fig. 5 represents a normalization of the higher-temperature data from 490 to 960 K, leading to a single activation energy of 0.73 eV. There are minor deviations at high and low frequencies, but the overall behaviour is clearly normalizable, but the 1066 K data do not fit at all into the same pattern as the lower temperature data.

The conclusion here is that there is a transition in the properties between 273 and 490 K, and apparently again above 960 K, although in this material the evolution proceeds in a normalizable fashion, at least over certain temperature ranges, unlike in the case of the J15 glass where no normalization was possible.

We note that the absolute values of the permittivity in the dispersive region are higher by up to two orders of magnitude at the same frequency than in the more lightly doped J15 glass, reaching 10 F m^{-2} at 0.01 Hz with no sign of saturation.

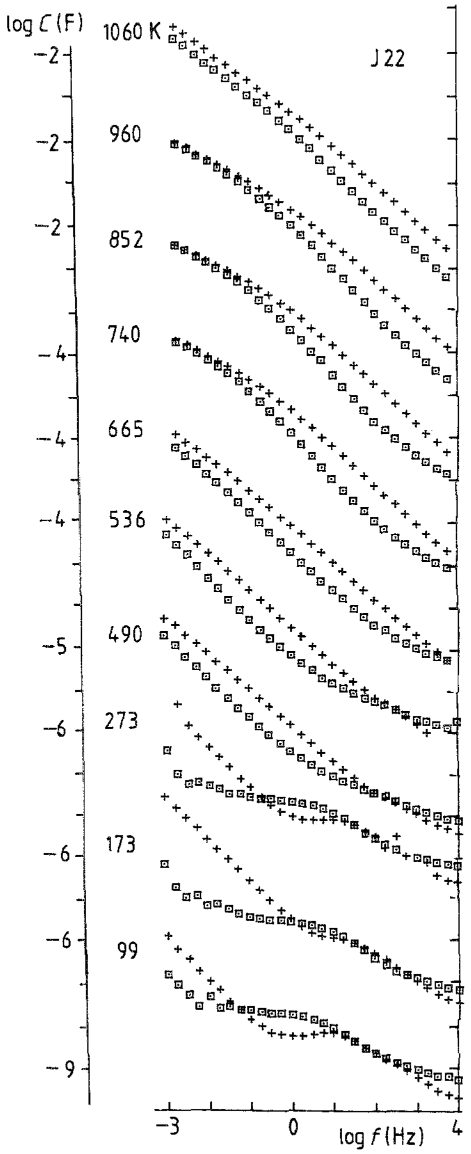

Figure 4 The dielectric response of the J22 glass presented in a similar manner to that in Fig. 1.

3. Interpretation of results

Both glasses show at low temperatures dipole-like peaks of loss which may be traced back to localized electronic hopping between pairs of potential wells – this process is more clearly pronounced in the less heavily doped J15 glass. Both glasses have a strong d.c. component in their loss data and the proper dielectric loss behaviour, $C''(\omega) - G_0/\omega$ is not visible unless Kramers–Kronig transformation is used. The d.c. conductivity activation energy is 0.75 eV and this suggests that there are large numbers of quasi-free carriers moving right across the glass sample with no substantial limitation at the electrodes.

The existence of strong LFD in both glasses requires a detailed discussion. In general, LFD processes may be associated with either volume or interfacial phenomena and in the former case there is a recent theoretical treatment which explains the observed behaviour in terms of an extension of the Dissado and Hill many-body interaction model [8, 12] predicting an almost ω^{-1} behaviour with a limiting dependence on $\omega^{-1/2}$ at very low frequencies. The problem with this interpretation in the present case is the magnitude of the observed capacitance, attaining 10 to 100 F m^{-2} without saturation at the lower frequencies. The charge involved, with 0.1 V, is of the order of 1 C, which corresponds to one electronic charge per surface atom! The resulting field would be so high that breakdown would ensue with any but molecular thickness of the region involved, so that the only reasonable model can be based on the concept of a charge double layer separated by a distance of the order of interatomic spacings. We are therefore led to the conclusion that the low-frequency response in the case of our glass must be determined by interfacial phenomena, although at the present stage we are unable to specify whether these are at the electrodes, or at some internal grain boundaries within the bulk of the material. In the case of our doped glasses there is ample evidence from the scanning electron microscopy studies of phase separation within the bulk material and inter-grain boundaries are not difficult to envisage, as SnO_2-free regions have been seen around the rims of the crystallites [4].

There exists ample experimental evidence for the association of LFD with interfacial phenomena – examples include liquid electrolyte–electrode interfaces, electronic Schottky barriers and contact to ionic semiconductors. We have no theoretical justification

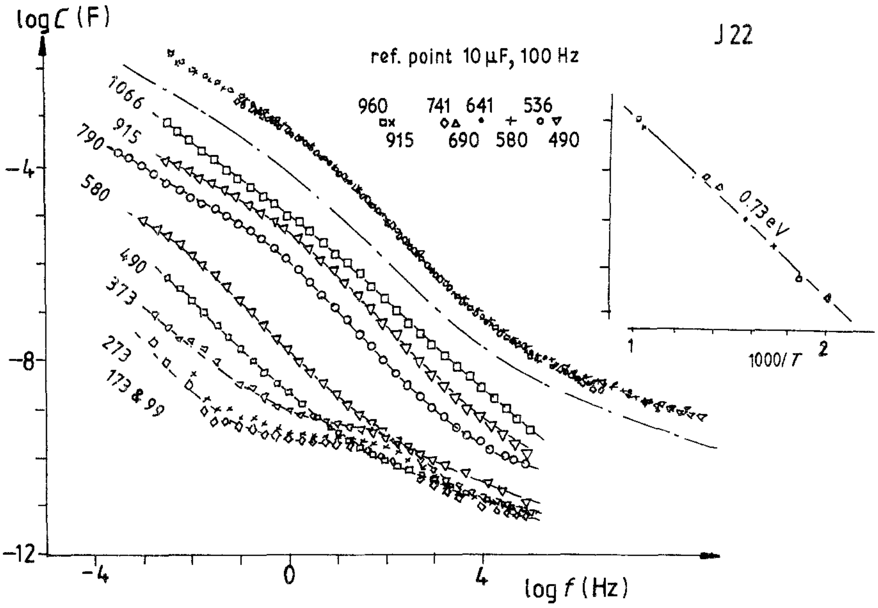

Figure 5 Selected data from Fig. 4 presented on a common scale of ordinates to show their relative dispositions. The curve beyond the chain-dotted line represents the normalization of the data from 490 K upwards, with the exception of the 1066 K data which do not fit at all. The locus of displacement of the representative point is shown and its activation plot shown in the inset gives a single energy of 0.73 eV.

at the present time for this type of power-law behaviour, and it is interesting to note that the corresponding time-domain response to step-function voltage gives a current which is almost independent of time, following a t^{-1} law with a very small exponent n [1, 13]. This type of behaviour has been associated with electrochemical processes at interfaces and there is a close analogy with battery action [1]. The fact that the more heavily doped glass exhibits a stronger dispersion may be understood in terms of the higher densities of available charges in the glass, although it is difficult to account quantitatively for the order of magnitude of the increase with only a few percent difference in the doping concentration.

We are likewise at this stage unable to explain the apparent half-power law at the lowest frequencies in some of the situations, nor is it clear why there are at some temperatures the transitions from $-\frac{1}{2}$ to LFD with nearly -1 logarithmic slope.

Finally, there remains the intriguing question of reversible phase transitions manifesting themselves through the changes of the shape of the dielectric response function. This evidence is in our opinion very strong and it remains to be verified if complementary evidence may be found from other physical measurements, although some suggestion to that effect appears in reference [3]. At the same time it is noteworthy that the dielectric method represents a very sensitive tool for the detection of subtle changes in the interactions between charge carriers or dipoles and the surrounding lattice [9–11].

4. Conclusions

The present investigation has shown the application of dielectric measurement and interpretation techniques to the study of relatively heavily doped semiconducting glasses. The salient point arising from this study is the appearance of reversible "phase transitions" manifesting themselves in important changes of the shape of the dielectric response function which makes the conventional normalization process impossible to perform. This illustrates the power of the dielectric method in situations in which other techniques may be difficult to apply with precision. Another important conclusion from these measurement is the presence of LFD at higher temperatures and at low frequencies – the results reported here should help with a better understanding of the wide class of phenomena which result in LFD and which are at present insufficiently recognized.

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