

**Correlations between the amplitude of the susceptibility and the loss peak frequency in a doped ceramic ferroelectric**

Recently a many-body co-operative model of interacting dipoles was proposed to describe relaxation loss peaks in dielectric materials [1]. From this approach Hill and Dissado [2] derived a set of relationships between the frequency of maximum loss,  $\omega_p$ , and the amplitude,  $A$ , of the dielectric susceptibility as a function of temperature. The specific case considered was that of a system undergoing an alignment transition at a critical temperature,  $T_c$ , equivalent to the Curie temperature in a ferroelectric transition. Two specific regions of behaviour were established

$$A \propto \omega_p^n \quad T \leq T_c \quad (1)$$

and

$$A \propto \omega_p^{-(1-n)} \quad T \approx T_c \quad (2)$$

where  $n$  is the exponent of the universal dielectric relation  $\chi(\omega) \propto (i\omega)^{(n-1)}$  proposed by Jonscher [3, 4]. Hill and Dissado [2] have verified Equation 2 using the measurements of Gesi [5, 6] on  $\text{AgNa}(\text{NO}_2)_2$ . On plotting  $\log(A)$  against  $\log(\omega_p)$  over a temperature range close to the ferroelectric transition temperature Gesi's results exhibited two parallel lines with gradient  $(n-1)$ . As the available experimental temperature range was limited to the region of  $T_c$ , Equation 1 was only indicated on the plot by a slight curvature and was not established.

Experimental data for two ferroelectric tran-

sitions is presented here which clearly shows both regions of behaviour and establishes Equations 1 and 2 above and below  $T_c$ . It is believed that this is the first time that both relationships have been identified in the same system.

For most ferroelectrics the dispersion in the real part of the susceptibility, and the associated loss peak, appear in the GHz region of the frequency domain. The specimens of doped ceramic ferroelectric material examined here show a secondary dispersion in the frequency range  $10^4$  to  $10^{-4}$  Hz. The secondary dispersion is driven by the strong ferroelectric transition and exhibits exactly similar temperature behaviour. The samples are solid solutions of  $\text{PbZrO}_3$ ,  $\text{PbTiO}_3$  and  $\text{Pb}_2\text{FeNbO}_6$  and contain different amounts of uranium as dopant. The uranium has the effect of increasing the d.c. conductivity. Sample 1 contained about 0.6 molar % of uranium and Sample 2 about 0.4 molar %. Slightly different methods of preparation gave an order of magnitude difference in the grain size, as determined by etching and optical microscope examination. For Sample 1 the grain size was about  $24 \mu\text{m}$ , whereas for Sample 2 it was about  $2.5 \mu\text{m}$ .

Dielectric measurements on the specimens were carried out in a non-inductive furnace over the temperature range 295 to 640 K, using a frequency response analyser with computer control [7], the frequency range being  $10^4$  to  $10^{-4}$  Hz. Fig. 1 shows the real part of the susceptibility obtained for the two samples. The high level of d.c. conductivity masks the loss components and

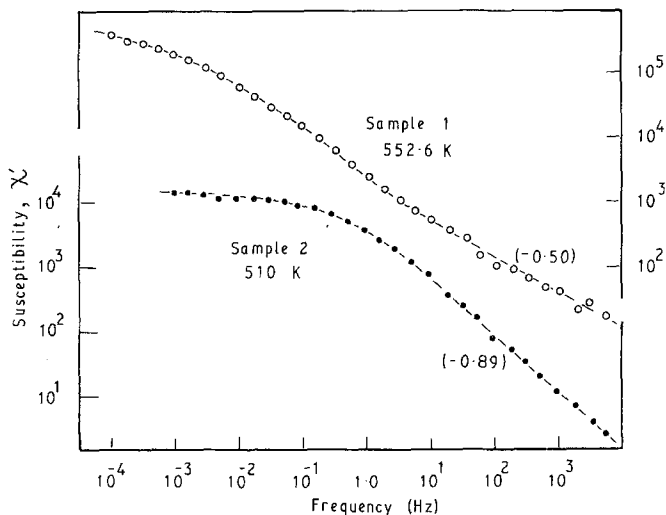


Figure 1 Log/log plots of the real part of the susceptibility as a function of frequency for Samples 1 and 2 at the temperatures indicated. The fractions in brackets are the gradients of the plots for frequencies greater than the peak loss frequency.

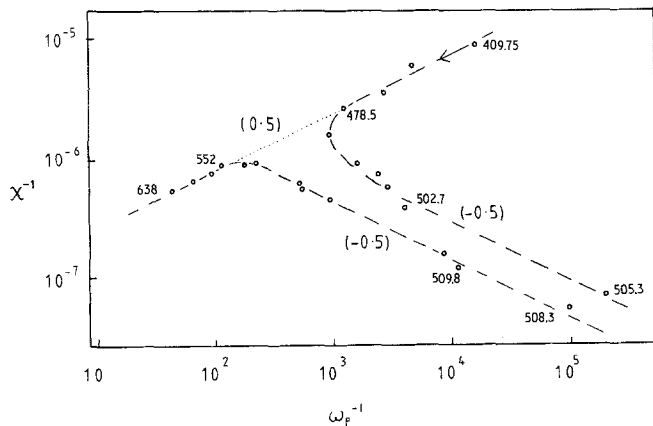


Figure 2 Log/log inverse susceptibility amplitude against inverse peak frequency plot for Sample 1 showing both the activated region of gradient  $n$ , and the transition region of gradient  $(n - 1)$ , with  $n = 0.50$ . The temperatures at which the measurements were made are given in degrees Kelvin.

they could not be recovered without serious inaccuracies. However by using the tracing technique of analysis [8], which produces temperature shift points that are the inverse values of the relative amplitude of the susceptibility and the peak frequency from log/log plots of susceptibility as a function of frequency, plots of  $\log(1/A)$  against  $\log(1/\omega_p)$  were obtained from the real part of the susceptibility. Figs 2 and 3 show these for the two samples. Both diagrams contain essentially the same information and can be divided into two regions for the purpose of discussion. In the first, for which the temperature lies away from the Curie point, the temperature traces are single straight lines with positive gradients of magnitude 0.50 and 0.12 for Samples 1 and 2. From Equation 1 this gives the values of the universal dielectric parameter,  $n$ , as 0.50 and 0.12 for these samples. For temperatures close to the Curie points the traces are still linear but of negative gradients of magnitudes  $-0.50$  and  $-0.88$  which, from Equation 2 are consistent

with the values of  $n$  given above. Both diagrams show the parallel behaviour remarkably well over reasonable ranges of both amplitude and frequency. Furthermore the magnitudes of  $n$  agree with those exhibited in Fig. 1 in which the power law decay at high frequencies is given by  $(n - 1)$ .

It is worth noting that in the vicinity of the Curie point, which is equivalent to  $T_c$ , the frequency  $\omega_p$  tends to zero while the amplitude tends to infinity [2, 9]. The former leads to the conclusion that the closer the system lies to its Curie point the longer it takes to relax after being perturbed. At the Curie temperature the system never completes its relaxation in a finite time and it is therefore extremely difficult to measure in the steady state. Because of this fundamental property it is difficult to obtain a good range of the variables in the transition region with the requisite high degree of accuracy.

As discussed by Dissado and Hill [1, 9] the parameter  $n$  is the magnitude of the correlation of single dipole reorientations. The difference in magnitude of this correlation between the two samples investigated is surprising considering the similarity of the sample compositions. This strongly suggests that the difference is a structural phenomenon, and arises from the different methods of preparation. The sample with the larger value of  $n$  has the larger grain size, and hence could be expected to possess the more correlated structure, both physical and dipolar.

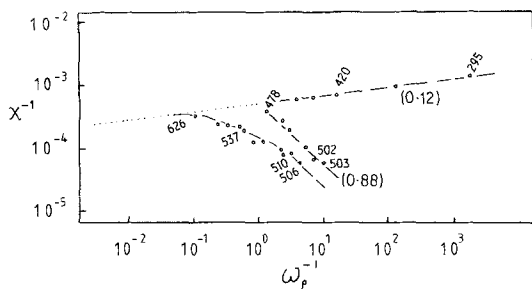


Figure 3 Log/log inverse susceptibility amplitude against inverse peak frequency plot for Sample 2 with  $n = 0.12$  and temperature in degrees Kelvin.

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## References

1. L. A. DISSADO and R. M. HILL, *Nature* **279** (1979) 685.
2. R. M. HILL and L. A. DISSADO, *ibid.* **281** (1979) 286.
3. A. K. JONSCHER, *ibid.* **267** (1977) 673.
4. *Idem*, *Phil Mag.* **B38**, (1978) 587.
5. K. GESI, *Jap. J. Appl. Phys.* **11** (1972) 1745.
6. *Idem*, *Ferroelectrics* **4** (1972) 245.
7. J. PUGH, *Phys. Bull.* **29** (1978) 469.
8. R. M. HILL, *Nature* **275** (1978) 96.
9. L. A. DISSADO and R. M. HILL, *Phil. Mag. B.* **41** (1980) 625.

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## *The effect of substrate temperature on the electrical properties of thin chromium films*

It is generally known that, for films prepared by evaporation, the substrate temperature,  $T_s$ , is one of the most important parameters that influences both crystal properties and electrical properties of grown films. Higher substrate temperature usually leads to (a) larger grain sizes of the crystallites in the films [1] or (b) a greater tendency to form island structures in the films. Although considerable experimental work has been reported on the effect of  $T_s$  on the epitaxial, metallic and semiconductor films [2–4], there is, however, very little work reported on the polycrystalline films [5–7]. In this letter the effect of  $T_s$  on the *in situ* electrical resistivity,  $\rho$ , and the temperature coefficient of resistance, TCR, of evaporated chromium films in the thickness range 100 to 800 Å is reported. The electrical properties of thin chromium films [8] have already been reported.

Chromium of 99.999% purity obtained from Leico Industries, New York, USA, was evaporated from a tungsten helix at a pressure of  $3 \times 10^{-6}$  Torr onto a glass substrate held at different  $T_s$  i.e. 22, 100, 150 and 180°C. The substrate, prior to deposition, was subjected to both ultrasonic and ionic bombardment cleaning. The thickness of the film was monitored during deposition by a quartz crystal monitor. The films were grown at a uniform rate of  $3 \text{ \AA sec}^{-1}$ . A constant current source was

used to maintain a current of 0.1 mA during TCR measurements. The TCR measurements have been performed *in situ* ( $\sim 5 \times 10^{-6}$  Torr) with the standard four-probe technique. During TCR measurements, the resistance of the film was measured after the temperature had equilibrated. The films were heated by a radiant heater at a uniform rate of  $7^\circ \text{C min}^{-1}$  and were cooled at the same rate. The temperature of the film was measured by a chromel–alumel thermocouple held rigidly near the glass substrate. Resistance measurements were carried out both during heating and cooling cycles and were found to be reproducible within an experimental error of about 5%.

The electrical resistivity of thin films can be expressed as [9],

$$\rho = \rho_0 \left[ 1 + \frac{3}{8\lambda} (1 - p) \right] \quad 0.1 < \lambda < 10 \quad (1)$$

where  $\rho$  is the resistivity of the film,  $\rho_0$  is the resistivity of the bulk metal,  $\lambda$  is the ratio of the film thickness,  $t$ , to the electron mean free path,  $l$ , in the bulk and  $p$  is the specularity parameter.

Fig. 1 shows the thickness dependence of the resistivity curves for thin chromium films over the thickness range 100 to 800 Å for four different  $T_s$  values (a) 22°C, (b) 100°C, (c) 150°C and (d) 180°C. It is evident from Fig. 1, that the resistivity is higher for all thicknesses at higher