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1998 J. Phys.: Condens. Matter 10 L297

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## LETTER TO THE EDITOR

**The dielectric relaxation relationship of PMN–PT ceramics**

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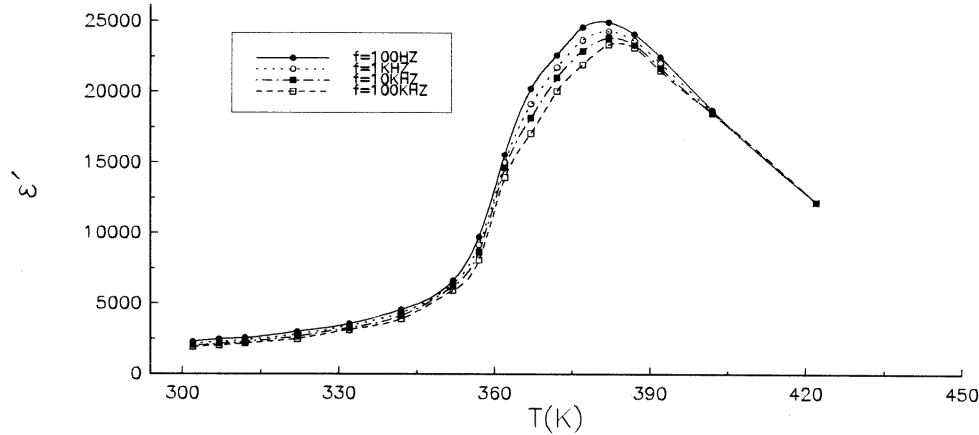
Received 26 November 1997, in final form 5 March 1998

**Abstract.** A simple dielectric relaxation relationship,  $\varepsilon'' = A_0 e^{-\omega/\omega_0} \varepsilon''_{\text{glass}} + \varepsilon''_{\text{Debye}}$ , describes the high- and low-frequency dielectric relaxation in PMN–PT relaxor ferroelectrics. It fits the experimental data closely. Debye relaxation arises from superparaelectric clusters; the correlation of clusters leads to dipole-induced regions, which give rise to the glassy behaviour of the system. Their relationship and the changes that they undergo with changing temperature are discussed.

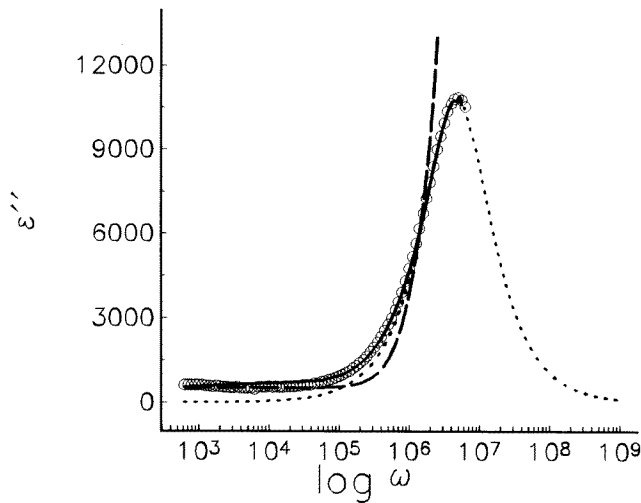
Lead magnesium niobate (PMN) is the classic relaxor ferroelectric. It easily forms a solid solution with lead titanate (PT), and the relaxor behaviour persists up to the morphotropic phase boundary for a composition containing 40 at.% PT [1]. Relaxor ferroelectrics are characterized by diffuse phase transitions (DPT). Research into relaxation characteristics is believed to have provided a basic physical understanding of ferroelectrics exhibiting DPT [2]. The obvious feature of their relaxation is that at high and low frequency they show different relaxation behaviours. The high-frequency behaviour is typical Debye relaxation (DR). The low-frequency behaviour shows a wide spectrum of relaxation times; it has been suggested that this is polar glassy relaxation (GR) [3]. Using DR to analyse the low-frequency data [4, 5] would not give a meaningful result, because the broad distribution of relaxation times is simplified as simple deviation from DR. GR with a broad spectrum of relaxation times cannot be fitted to the high-frequency DR [6]. Researchers have had to study them separately. This cannot provide an entirely clear description, and does not give the relationship of the various processes and regions. In this letter, we try to improve on this situation. We will suggest a simple dielectric relaxation relationship, which agrees closely with the high- and low-frequency experimental data.

The samples used in this study were PMN ceramics containing 20 at.% PT (PMN–20PT). They were prepared by a sol–gel technique [7]. Disks were pressed from PMN–20PT powders under a pressure of 100 MPa, and then sintered at 1000 °C for 1 h, to produce dense PMN–20PT ceramics. Figure 1 shows the real part of the dielectric constant ( $\varepsilon'$ ) for the PMN–20PT ceramics; this was measured using an HP4192A LCR. These curves demonstrate typical relaxor behaviour, with the magnitude of the dielectric constant decreasing with increasing frequency and the maximum shifting to higher temperature. Figure 2 shows the frequency dependence of the imaginary part of the dielectric constant ( $\varepsilon''$ ) measured over the frequency range  $10^2$ – $10^7$  Hz at the Curie temperature  $T_m = 378$  K.

In an ideal Debye medium, the dipoles are free to rotate individually, and there is no interaction between them. A modified Debye relationship has been proposed for a relaxor



**Figure 1.** The real part of the dielectric constant ( $\epsilon'$ ) as a function of temperature for measurement frequencies of 0.1, 1, 10 and 100 kHz.



**Figure 2.** The frequency dependence of the imaginary part of the dielectric constant ( $\epsilon''$ ) at  $T_m = 378$  K (open circles: experimental data; dotted line: the curve calculated from the DR; dashed line: the curve calculated from the GR, equation (6); solid line: the curve calculated from the new relationship, equation (7)).

with more realistic dipoles [8]:

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau_0)^{(1-h)}} \quad (1)$$

where  $\epsilon_\infty$  is the high-frequency value of the dielectric constant and  $\epsilon_s$  its low-frequency limit. The parameter  $h$  indicates the degree of deviation from the standard Debye relation, and  $0 \leq h \leq 1$ . When  $h = 0$  it becomes the standard Debye relation.  $\tau_0$  is the most probable relaxation time. The dotted line in figure 2 shows the curve calculated from the Debye relation, equation (1). In the high-frequency region, it closely fits the experimental data.

Now, let us consider the relaxation in between the measured dielectric response and the dielectric relaxation spectrum. The dielectric constant could be represented as a superposition of Debye relaxors with different relaxation times  $\tau$ , and the probability distribution  $G(\tau, T)$  of relaxation times can be supposed to be slowly varying in  $\ln \tau$  [9–11]:

$$\varepsilon(T) = \varepsilon_0(T) \int_0^\infty \frac{d(\ln \tau)}{1 - i\omega\tau} G(\tau, T) \quad (2)$$

where  $\varepsilon_0(T)$  is the very-low-frequency limit of  $\varepsilon$ . Consequently, the imaginary part,  $\varepsilon''$ , can be written as

$$\varepsilon'' = \varepsilon_0(T) \int_0^\infty G(\tau, T) \frac{d(\omega\tau)}{1 + \omega^2\tau^2} \quad (3)$$

for the case of a broad spectrum, when

$$\tau_{\min} \leq 1/\omega \leq \tau_{\max} \quad (4)$$

For a broad spectrum  $G(\tau, T)$ , the important contribution to the integral comes from the region where  $\omega\tau = 1$  ( $\tau = 1/\omega$ ) [10, 11].  $\varepsilon''$  can then be approximately represented as

$$\varepsilon''(\omega, T) \cong (\pi/2)\varepsilon_0(T)G(1/\omega, T). \quad (5)$$

Thus, the dielectric loss spectrum gives direct information about the distribution of relaxation times  $G(\tau, T)$ . At the same time, one can also obtain an important relationship between the real and imaginary parts of the dielectric constant under the condition that the spectrum is broad [12]:

$$\varepsilon'' = (-\pi/2) \partial\varepsilon'(\omega)/\partial(\ln \omega). \quad (6)$$

This relationship has been proved to be a fundamental characteristic of glassy states that have a broad spectrum of relaxation times [6, 10, 11].

The dashed line in figure 2 shows the result calculated from equation (6). Obviously, it agrees closely with the low-frequency data, but does not fit the high-frequency results which manifest DR with a narrow spectrum of relaxation times. Similar results were given in [6].

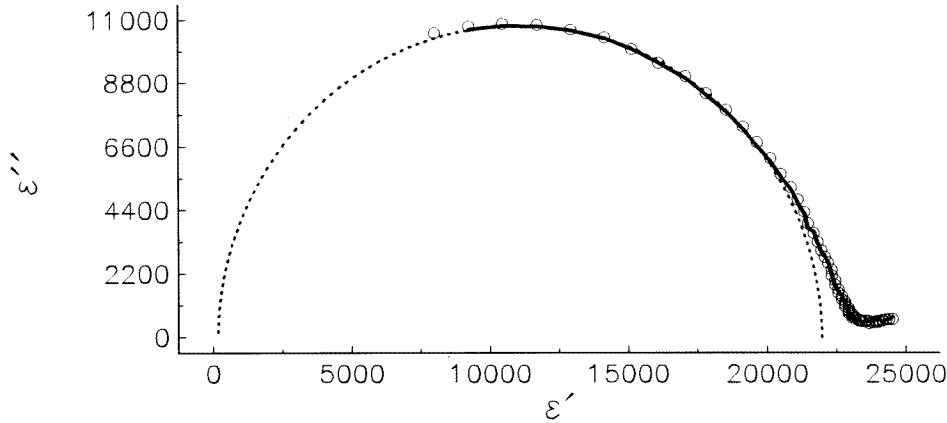
Here we give a new relationship, which describes the low- and high-frequency relaxation completely:

$$\varepsilon'' = A_0 e^{-\omega/\omega_0} \left( -\frac{\pi}{2} \right) \partial\varepsilon'(\omega)/\partial(\ln \omega) + (\varepsilon_s - \varepsilon_\infty) \frac{(\omega\tau_0)^{1-h} \cos([\pi/2]h)}{1 + 2(\omega\tau_0)^{1-h} \sin([\pi/2]h) + (\omega\tau_0)^{2(1-h)}} \quad (7)$$

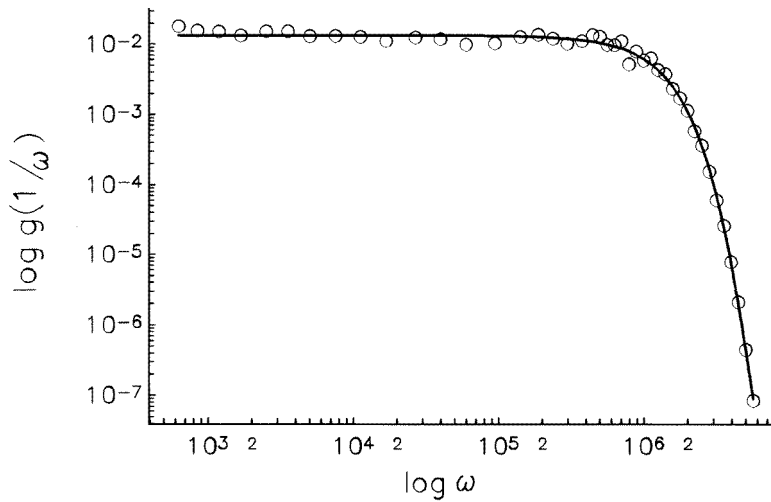
where the second term is the  $\varepsilon''$ -expression from the modified Debye relationship (equation (1)). We recast equation (7) as a simple expression:

$$\varepsilon'' = A_0 e^{-\omega/\omega_0} \varepsilon''_{\text{glass}} + \varepsilon''_{\text{Debye}} \quad (8)$$

where  $A_0$  and  $\omega_0$  are constants. This relationship shows the GR behaviour decreasing with increasing frequency in an exponential decay. When the frequency reaches  $\omega_0$ , the glassy behaviour has almost disappeared, and the DR behaviour begins to take the main role.  $\omega_0$  is the rate of exponential decay, or it can be described as the high-frequency limit for glassy behaviour in a relaxor ferroelectric system. The solid line calculated from equation (7) shown in figure 2 shows close agreement with the experimental data (open circles). The Argand (Cole–Cole) diagram for PMN–20PT is given for  $T = 378$  K (figure 3), where the parameters are  $A_0 = 1.074$ ,  $\omega_0 = 360\,436$  Hz,  $h = 0.007$ ,  $\tau_0 = 2.1 \times 10^{-7}$  s,  $\varepsilon_\infty = 21\,982.9$ ,  $\varepsilon_s = 171.6$ .



**Figure 3.** The Argand diagram for  $T = 378$  K (open circles: experimental data; dotted line: the Cole-Cole circle calculated from the DR; solid line: the curve calculated from the new relationship, equation (7)).

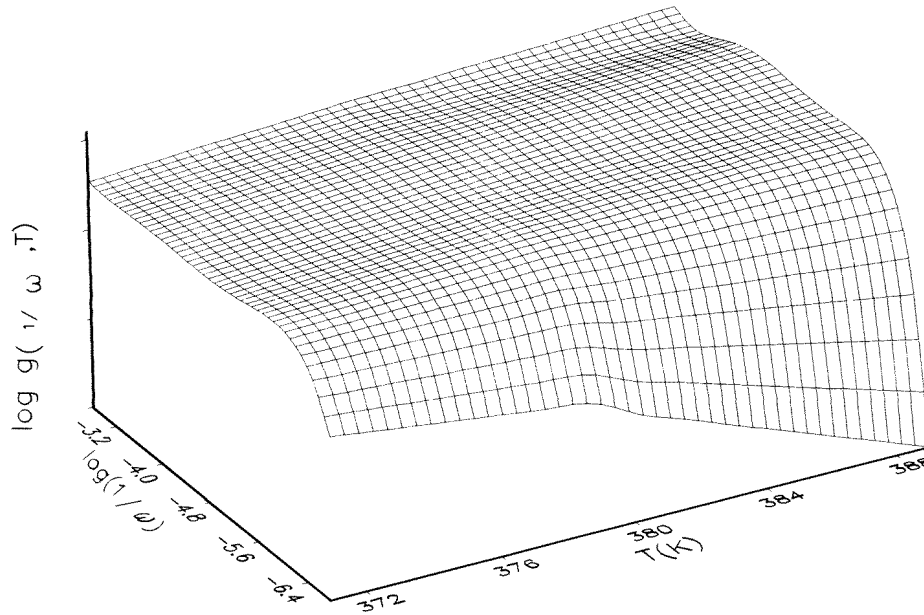


**Figure 4.** The distribution function  $g(\tau)$  of GR times for  $T = 378$  K.

Viehland *et al* [13, 14] gave a distribution of relaxation times  $G(\tau, T)$  of the global effect of  $\varepsilon''$  calculated according to equation (5). But the influence of the relatively sharp distribution of DR times makes equation (5) unreliable. Here we discuss the polar glassy state of the low-frequency range, including its exponential decay factor, of course (we use the notation  $g(\tau, T)$  in order to distinguish this distribution from the global distribution  $G(\tau, T)$  of the GR and DR times):

$$\varepsilon'' = A_0 e^{-\omega/\omega_0} \left( -\frac{\pi}{2} \right) \partial \varepsilon'(\omega) / \partial (\ln \omega) \cong \left( \frac{\pi}{2} \right) \varepsilon_0(T) g(1/\omega, T). \quad (9)$$

The isothermal cross section of  $g(1/\omega)$  as a function of  $\omega$  for PMN-20PT is shown in figure 4 for the temperature  $T = 378$  K.  $\varepsilon_0(T)$  is the value of  $\varepsilon'(\omega, T)$  when the frequency



**Figure 5.** The distribution function  $g(\tau, T)$  of GR times as a function of the relaxation times  $\tau = 1/\omega$  and temperature  $T$  near the Curie temperature  $T_m$ .

$\omega$  takes the lowest value, 100 Hz, for which measurements were made [14]. A temperature-dependent relaxation time spectrum near the Curie temperature  $T_m$  is presented in the form of a 3D surface diagram in figure 5. These are not quantitative results, so we do not give the actual values of  $g(1/\omega, T)$  in figure 5.

It is commonly agreed that all relaxors are highly inhomogeneous materials. Smolenski and Agranovskaya [15] originally proposed that underlying the relaxor behaviour was chemical inhomogeneity at cation sites, giving rise to a DPT. Chen *et al* [16] found evidence for short-range chemical order at the nanoscale level using transmission electron microscopy (TEM). Cross [3] proposed that these nanometre-scale clusters are dynamical in nature, with the dipole moment thermally fluctuating between equivalent directions. In the absence of interactions between regions, this model would be analogous to superparamagnetism [17]. It has been suggested that the local polar clusters existing in relaxor ferroelectrics give rise to analogous superparaelectric properties [3]. In an ideal superparaelectric, the clusters are independent, and the dipoles of a cluster can only move individually; the frequency dependence is governed by the Debye relationship. At high temperature  $T > T_m$ , the clusters behave more ideally, and the ferroelectric nature is retained. On the other hand, with decreasing temperature the thermal activation energy for polarization fluctuation increases [13]. The orientation or polarization fluctuation of the dipoles of clusters influences the position of adjacent cations as well as the polarization of adjacent regions, and it has been proved that the correlation length  $\lambda$  increases with decreasing temperature [18]. We believe that this correlation interacts via dipole and dipole-induced reactions with dipoles. This results in polarization-induced regions, in which the dipoles are randomly orientated. Thus it appears that the polar regions grow as the temperature is reduced [2]. Because of the randomness of the orientation of the new growing dipoles, they manifest polar glassy

behaviour. At the same time, the correlation between the superparaelectric clusters becomes stronger, and the degree of DR behaviour is reduced. Equation (8) and figure 2 show this clearly. At the lowest measurement frequency, the glassy behaviour is dipole induced, while at high frequency the Debye response comes from the free dipoles of polar clusters, and for intermediate frequencies it is a superposition of coexisting DR and decayed GR responses.

When the temperature is decreased, the dipole-induced glassy regions become bigger and the correlation length of the superparaelectric clusters becomes longer. The correlation of the clusters restricts the dipole movement. The dipoles of the clusters become randomly oriented in a glassy state, as a result of free-movement DR behaviour. Thus the lower the temperature, the wider the distribution of relaxation times (see figure 5). When the temperature reaches  $T_{rn}$ , the temperature at which the phase transition from the relaxor to the normal ferroelectric state takes place [19], there is a strong global broadening of the relaxation time spectrum. At this temperature, because of the coupling of randomly oriented dipoles with each other and the effect of electrostrictive strain fields, the stability of the high-symmetry structure is destroyed [20]. The configuration of the rhombohedral phase—having lower free energy—now forms. This is the so-called spontaneous transformation from a relaxor to a normal ferroelectric state [19].

The new simple dielectric relaxation relationship  $\varepsilon'' = A_0 e^{-\omega/\omega_0} \varepsilon''_{\text{glass}} + \varepsilon''_{\text{Debye}}$  is in good agreement with the experimentally measured high- and low-frequency values of  $\varepsilon''$ . In relaxor ferroelectrics there are various regions, which exhibit different relaxation responses. Free dipoles of superparaelectric clusters give the peak of DR in the high-frequency stage. Dipole-induced coupling with other dipoles leads to a polar glassy state with a wide spectrum of relaxation times for the low-frequency range, and the GR effect decays exponentially with increasing frequency. The coexistence of these dipoles makes them link up with each other in the intermediate-frequency range in the plot of  $\varepsilon''$  versus  $\omega$  (figure 2). With decreasing temperature, strong coupling of the various dipoles leads to the structural phase transition from the relaxor to the normal ferroelectric state taking place, at the temperature  $T_{rn}$ .

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