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Low-frequency dielectric response of $PbMg_{1/3}Nb_{2/3}O_3$

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Abstract. An investigation was carried out on both the linear and non-linear parts of the complex dielectric susceptibility in the frequency and temperature ranges 10^{-3}–10^3 Hz and 100–450 K, respectively. The analysis of the imaginary part of the dielectric susceptibility has revealed the existence of a broad spectrum of relaxation times in the above temperature range. The temperature dependence of the most probable frequency of the spectrum was obtained. For temperatures $T \leqslant 230$ K this frequency tends to some temperature-independent constant value. Comparison of these results with the neutron scattering data has shown that in the same temperature region ($T \sim 230$ K) spatial scale stabilization of the ferroelectric fluctuations takes place. The third harmonic of the non-linear permittivity components undergoes critical divergency at $T \sim 230$ K.

1. Introduction

In recent years there has been a considerable amount of interest in the investigation of so-called ferroelectrics with diffuse phase transitions (DPT) (relaxor ferroelectrics). Lead magnoniobate $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) can be considered as a model crystal for investigations of such systems. However, in spite of the fact that a number of papers concerned with the studies of PMN have been published (see Smolensky *et al* 1981, Krainik *et al* 1989, Dorogovtsev and Yushin 1990, Cross 1987 and the references therein) the nature of DPT is not yet clear. It has been suggested that some of the peculiar low temperature properties of PMN could be explained by the transition to the dipole glass state (Dorogovtsev and Yushin 1990, Vakhrushev *et al* 1989, 1990). To clarify this problem it seems to be important to study the dielectric properties of PMN in the low- and ultra-low-frequency regions in order to obtain information about the probability distribution of the relaxation times and to obtain the dynamic scaling function. It is also important to investigate the non-linear susceptibility and, in particular, to look for its critical divergency. Several papers devoted to the investigation of the dielectric properties of PMN (Krainik *et al* 1989, Nadolinskaya *et al* 1987) were not detailed enough and no results concerned with the scaling law were obtained. As far as the authors are aware, up to now there are no data concerned with the non-linear susceptibility of PMN. Consequently, we have performed a systematic study of the dielectric properties of PMN in the frequency range 10^{-3}–10^3 Hz over a broad temperature region.

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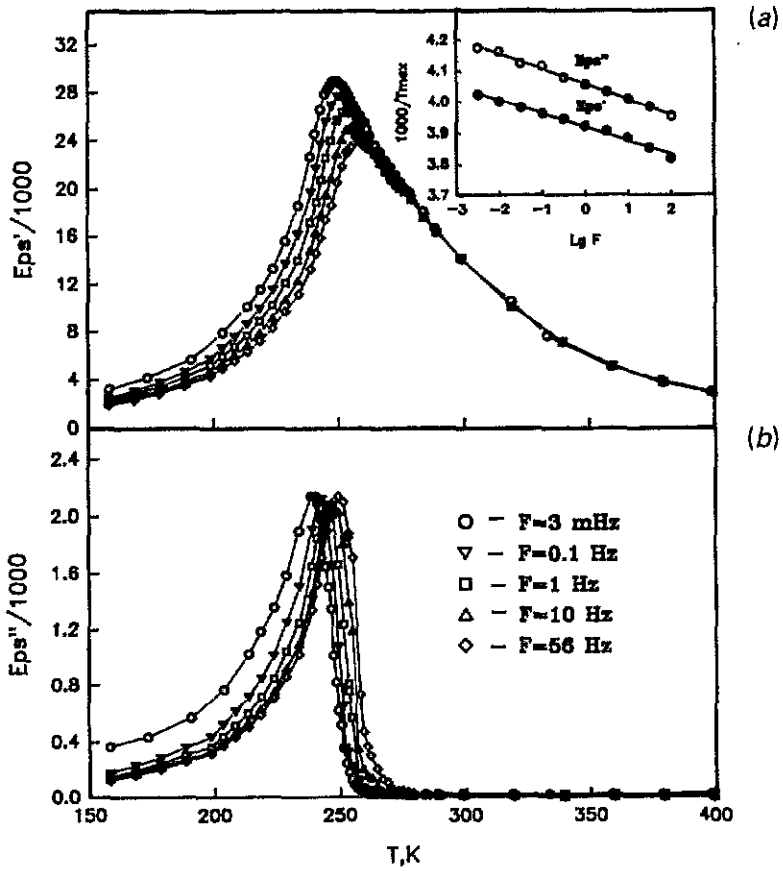

Figure 1. The temperature dependencies of real (*a*) and imaginary (*b*) parts of the dielectric permittivity of PMN measured at different frequencies. The inset represents the frequency dependencies of ε' and ε'' maxima.

2. Experimental details

We used plate-like samples having sizes of about $5 \times 5 \times 1\,\text{mm}^3$ cut from the PMN single crystal, perpendicular to the [100] direction, with Al electrodes sputtered on the preliminary polished surface. All measurements were carried out with a computer-controlled measuring system (Vakhrushev *et al* 1991), operating in the frequency domain mode. Both linear and non-linear susceptibilities were measured in the frequency region 10^{-3}–10^{3} Hz with a measuring field of $30\,\text{V cm}^{-1}$. As will be shown later, for PMN this field can be considered 'weak'. All measurements were performed on samples preliminarily annealed at 500 K.

3. Results and discussion

Figure 1 shows the temperature dependencies of the real and imaginary components of the dielectric permittivity measured at different frequencies. One can see that both $\varepsilon'(T)$

and $\varepsilon''(T)$ maxima are shifted toward the lower temperatures as the measuring frequency is decreased, and that a strong dispersion of ε' and ε'' exists in the low temperature part of both dependencies. Such behaviour is well known for frequencies down to 0.1 Hz. (Nadolinskaya *et al* 1987). By analogy with spin glasses, such behaviour of the dynamic susceptibility in disordered ferroelectrics was supposed to be concerned with the existence of the broad spectrum of relaxation times (Ginzburg 1989). As for spin glasses in the investigated frequency range, the positions of both ε' and ε'' maxima (figure 1(*a*)) could be described by the Arrhenius law

$$\omega = \omega_0 \exp(-Ea/kT). \tag{1}$$

However, also like spin glasses (Ginzburg 1989), the values of both $\lg(\omega_0) = 104$ and $E_a/k = 26\,000$ K obtained from the experimental data have no physical sense.

Now, let us consider the relaxation between a measured dielectric susceptibility and the dielectric relaxation spectrum. The dielectric susceptibility could be represented as a superposition of Debye relaxators with different characteristic times τ

$$\chi^*(T) = \chi_0(T) \int_0^\infty \frac{\mathrm{d}(\ln \tau)}{1 - \mathrm{j}\omega\tau} g(\tau, T) \tag{2}$$

where $g(1/\omega, T)$ is the temperature dependent distribution of the relaxation times. Consequently, the imaginary part of ε^* could be written as

$$\chi''(\omega, T) = \chi_0(T) \int_0^\infty g(\tau, T) \frac{\mathrm{d}(\omega\tau)}{1 + \omega^2\tau^2} \tag{3}$$

and in the case of a broad spectrum, when

$$\tau_{\min} \leqslant 1/\omega \leqslant \tau_{\max} \tag{4}$$

ε'' could be approximately represented as (Courtens 1986)

$$\chi''(\omega, T) \cong (\pi/2)\chi_0(T) g(1/\omega, T). \tag{5}$$

Thus, the spectrum of dielectric loss gives direct information about $g(1/\omega, T)$. In the limit of the broad spectrum (4), one can also obtain an important simple relation between real and imaginary parts of the susceptibility (Ginzburg 1989, Lindgren *et al* 1981)

$$\chi'' = (\pi/2)\, \partial\chi'(\omega)/\partial(\ln \omega). \tag{6}$$

We used our experimental data to verify satisfactorily (6) and, consequently, the validity of assumption (4), about the large width of spectrum. The results obtained are shown in figure 2. One can easily see that at all temperatures a good agreement between the directly measured values of ε'' and those calculated from the dispersion of ε', using (6), exists. This led us to conclude that the spectrum $g(1/\omega, T)$ is extremely broad not only at low temperatures but up to the highest measured temperatures.

Now, returning to (5). Apparently, if one neglects the frequency independent term $(\pi/2)\chi_0(T)$, then $\chi''(\omega, T)$ directly corresponds to the spectral function $g(1/\omega, T)$. In order to compare the shape of the spectrum at different temperatures we represented the experimental dispersion curves $\chi''(\omega, T)$ in coordinates of $\Omega \equiv \lg(\omega/\omega_0)$ and $\chi_{\text{norm}} \equiv \chi''(\omega, T)/\chi''(\omega_0, T)$, where ω_0 is a position of the $\chi(\omega)$ maximum, that is, the most probable relaxation frequency.

The superposition of the normalized dispersion curves, corresponding to the temperature region, where ω_0 is inside the experimental frequency range (10^{-3}–10^3 Hz),

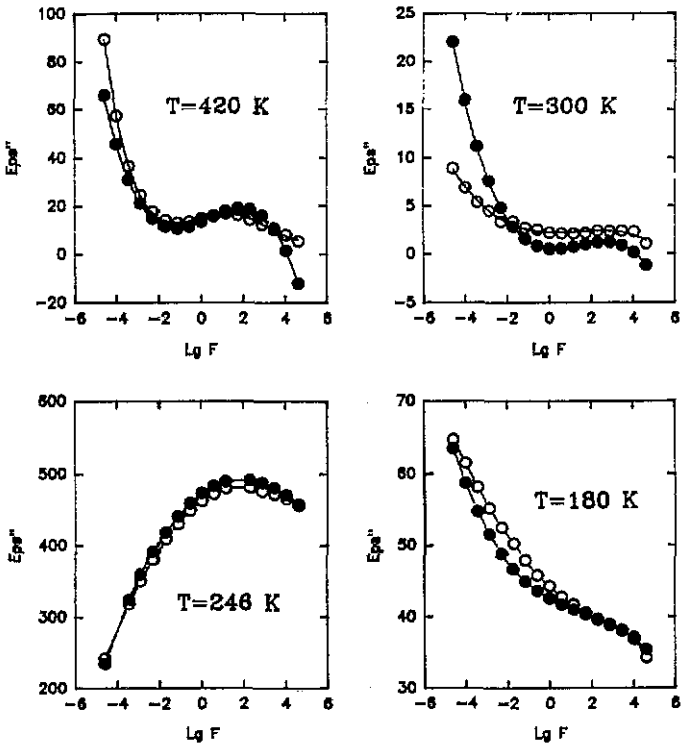

Figure 2. Comparison of the measured imaginary part of the dielectric permittivity of PMN (open circles) with that calculated from (6) (full circles) for different temperatures.

has revealed that the shape of the spectrum does not change with temperature in this region. Next, we fitted the dispersion curves corresponding to the temperatures above and below this region to the part of the 'master curve' already obtained, using ω_0 and $\chi''(\omega_0, T)$ as fitting parameters. Each new added curve coincided with a previously made part of the 'master curve' at a minimum of 80% of the points. As a result of the above procedure we obtained a dielectric loss 'master curve' which, as was noted above, exactly corresponds to the distribution function of the relaxation times. The results are shown in figure 3.

From more than 40 dispersion curves, corresponding to the temperature region 185 K $< T <$ 260 K a smooth enough 'master curve' was obtained to lead us to conclude that the shape of the spectral function is slightly temperature dependent. The cusp, existing on the 'master curve' near $\Omega \cong 4$, could probably be explained by some change in the shape of the spectrum at $T <$ 230 K because this part of the 'master curve' was obtained from the low temperature experimental data. As a result of the fitting procedure the temperature dependencies of ω_0 and $\chi''(\omega_0)$ were obtained. The temperature dependence $\omega_0(T)$ is shown in figure 4(a). As has been already mentioned, in the temperature region 235 K $< T <$ 255 K this dependence can be well described by the Arrhenius law (1). At high temperatures the experimental dependence deviates from (1), but this deviation could be described by the Vogel–Fulcher law, or the modified Arrhenius law (Courtens 1986). However, in the low-temperature region, the experimental data displays anomalous behaviour.

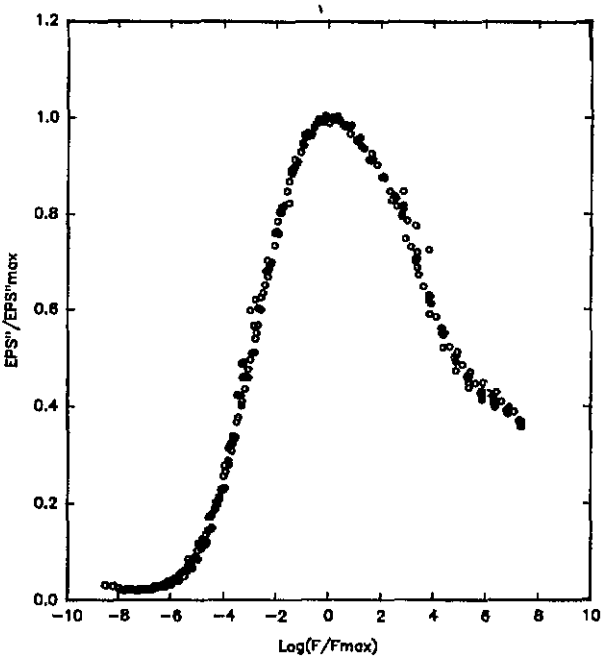

Figure 3. The 'master curve' for dielectric loss data of PMN.

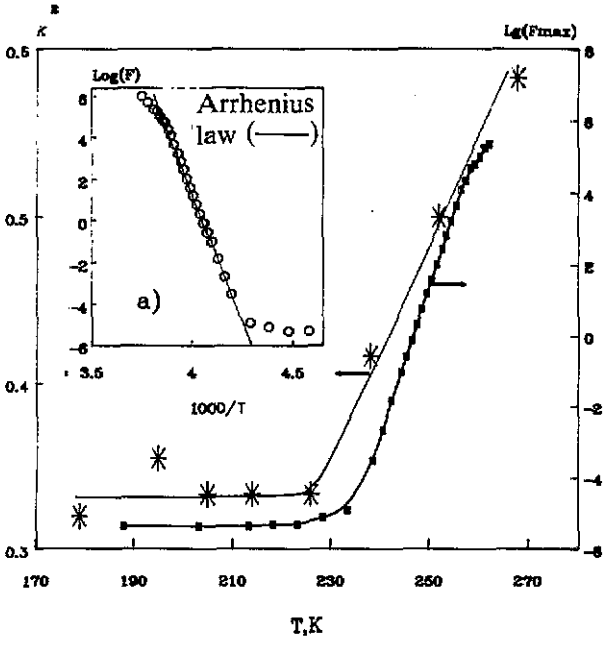

Figure 4. The temperature dependencies of the square inverse correlation radius of ferroelectric fluctuations (stars) and most probable relaxation frequency (full squares) of PMN. The inset shows the deviation from the Arrhenius law.

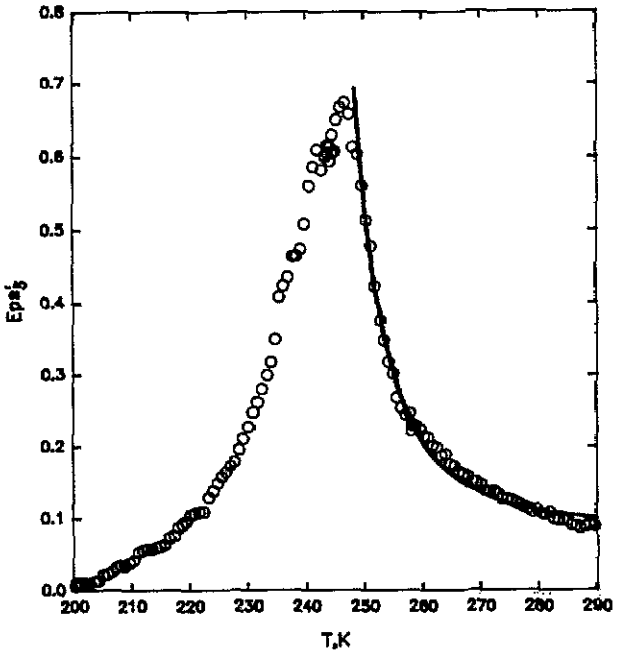

Figure 5. The temperature dependence of the third harmonic of the dielectric permittivity of PMN (open circles) and its approximation by critical dependence (7) (full curve).

Starting at 230 K, ω_0 becomes temperature independent, being of the order of 5×10^{-5} Hz. It is interesting to compare the obtained $\omega_0(T)$ dependence with the temperature dependence of the inverse correlation radius of the ferroelectric fluctuation obtained from the neutron scattering data (Vakhrushev *et al* 1990). Results are shown in figure 4. One can see that at $T < 230$ K both the time and space scales, ω_0 and R_0, correspondingly become temperature independent. As far as we know such phenomena have never been observed before.

In addition to the linear permittivity the non-linear one has also been studied. As one could expect, only odd harmonics of the dynamic response were observed. In figure 5 the temperature dependence of the amplitude of the third harmonic, measured at the main frequency of 1 Hz, is shown. The high-temperature side of this dependence could be described by the critical dependence:

$$\varepsilon_3'(T) = \varepsilon_3^0/(T - 233)^{2.86} \tag{7}$$

with critical temperature equal to 233 K, coinciding with the value of the temperature where both the mean frequency and the correlation radius become temperature independent. The critical exponent value is close to that obtained for the temperature dependence of the third harmonic of susceptibility in spin glasses (Omari *et al* 1983).

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References

Courtens E 1986 *Phys. Rev.* B **33** 2975
Cross L E 1987 *Ferroelectrics* **76** 241
Dorogovtsev S N and Yushin N K 1990 *Ferroelectrics* **112** 18
Ginzburg S L 1989 *Irreversible Phenomena of Spin Glasses* (Moscow: Nauka)
Krainik N N, Markova L A, Zhdanova V V, Sapozhnikova L M and Flerova S A 1989 *Ferroelectrics* **90** 119
Lindgren L, Svedlindh P and Beckman O J 1981 *Magn. Magn. Mater.* **25** 33
Nadolinskaya E G, Krainik N N, Shilnikov A B, Smolensky G A and Vologirova L H 1987 *Sov. Solid State Phys.* **29** 2268 (in Russian)
Omari R, Prejean J J and Souletie J A 1983 *J. Phys.* **44** 1069
Smolensky G A, Bokov V A, Isupov V A, Krainik N N, Pasynkov R E, Sokolov A I and Jushin N K 1981 *Ferroelectrics and Related Materials* (New York: Gordon and Breach)
Vakhrushev S B, Colla E V, Koroleva E Yu and Suramanov R F 1991 Preprint FTI-1505 Leningrad (in Russian)
Vakhrushev S B, Kvytkovsky B E, Nabereznov A A, Okuneva N M and Toperverg B P 1989 *Physica* B **156 & 157** 90
—— 1990 *Ferroelectrics* **90** 173