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Structure of the dielectric spectrum of relaxor ferroelectrics

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Abstract

Wide range dielectric response (10–10^{14}Hz) of three relaxor ferroelectrics: PMN, PLZT and PST is analyzed. The common features are: low phonon contribution to the high static permittivity; dielectric relaxation in a wide frequency range; widening of the relaxation times distribution with decreasing temperature down to the freezing temperature T_f, where extrapolated divergence of the mean relaxation time takes place; change of dielectric behaviour at the Burns temperature T_B. Dynamics of polar nanoclusters, which appear below T_B, is considered to be responsible for the relaxor behaviour. It enables us to define the general structure of the dielectric spectrum of relaxor ferroelectrics. Only above T_B the fundamental dielectric contribution is due to polar phonons. Below T_B the contributions caused by polar clusters dynamics prevail: both dipole reversal of polar cluster and fluctuations of their boundaries contribute to the dielectric response. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Wide range dielectric response of any material is defined by several polarization mechanisms contributing to the static dielectric permittivity. The sum of the dielectric contributions, with account of their temperature dependences, represents the structure of the dielectric spectrum. To define the structure, dielectric measurements in a wide frequency range, including the dispersion regions of all the polarization mechanisms, are required. Concerning relaxor ferroelectrics characterized by both slow dynamical processes and highly polarizable crystal lattice, the measurements from very low to infrared (IR) frequencies is as a rule necessary.

Dielectric properties of relaxor ferroelectrics were broadly investigated, especially in the case of model relaxors lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and lanthanum doped lead zirconate titanate $(Pb_{1-x}La_x)(Zr_{0.65}Ti_{0.35})O_3$ (PLZT). However, the dielectric measurements were performed mainly only in the standard low frequency range of 10–10^6 Hz where only a small part of the very wide dispersion range could be revealed. Besides our own investigations, only a few wide range studies of the typical relaxors including microwave (MW) range are known to the authors.[1] Our recent studies[2–4] of relaxor PLZT 8/65/35 ($x=0.08$) and PLZT 9.5/65/35 ($x=0.095$) and ferroelectric with some relaxor features B-site ordered $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST-O) ceramics as well as more earlier studies of the PMN crystals[5–7] provide the full dielectric response from 10^2 to 10^{11} Hz (PMN) or even to 10^{14} Hz (PST-O and PLZT). Here we used the results as basic experimental data for determining the general structure of the dielectric spectrum of relaxor ferroelectrics.

2. Common features of the dielectric spectra

Generally, the dielectric spectra of PLZT, PMN and PST-O are similar to each other. Temperature and frequency dependences of the real (ε') and imaginary parts (ε'') of complex dielectric permittivity of PLZT 9.5/65/35 and PMN (Figs. 1 and 2) are typical for relaxors. Low frequency permittivity is very high and a well pronounced diffuse $\varepsilon'(T)$ maximum is observed at T_m. Phonon contribution is much lower than $\varepsilon'(T_m)$. Dielectric dispersion takes place in the whole investigated frequency range and in a broad temperature region both below and above T_m. The peaks of $\varepsilon'(T)$ and $\varepsilon''(T)$ move

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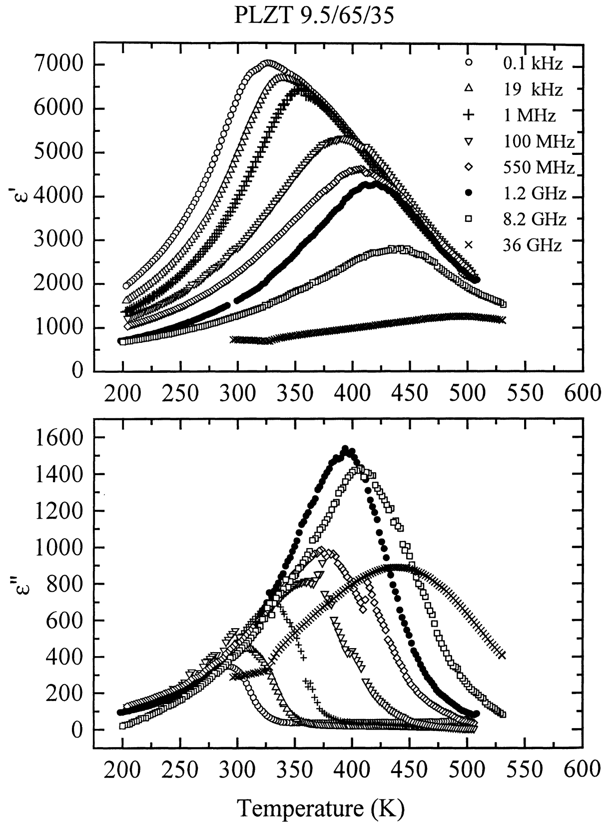
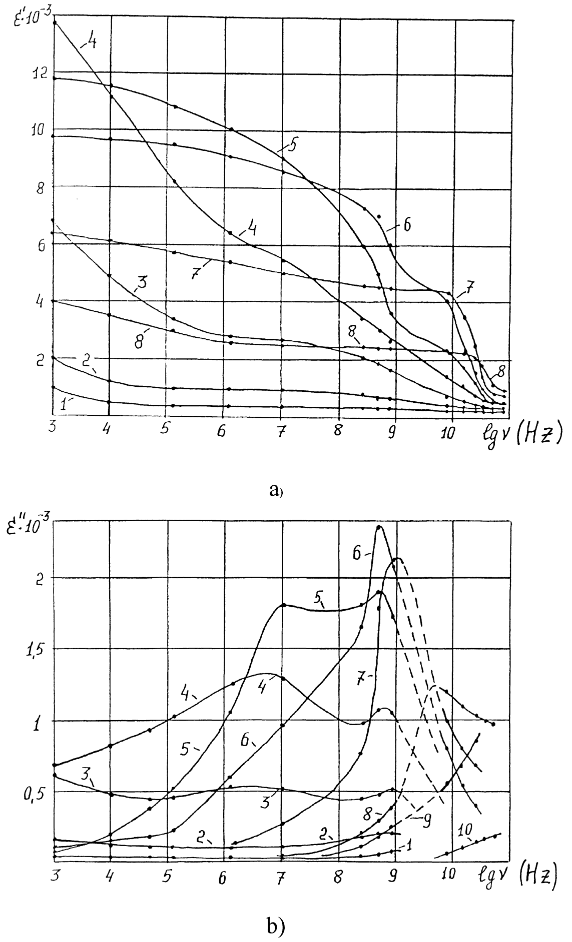


Fig. 1. Temperature dependences of permittivity (ε') and loss (ε'') of PLZT 9.5/65/35 ceramics at various frequencies.

towards higher temperatures with the increasing frequency. Permittivity remains of the order of 1000 even in the millimetre wave range and losses are also very high ($\tan\delta \geqslant 1$) at MW. This indicates that the main dielectric dispersion occurs in the MW range. The dispersion is of complex polydispersive type and corresponds to the relaxation models with a broad relaxation time distribution. Near T_m the dispersion begins at low frequencies, but at higher temperatures the dispersion occurs in the higher frequency range of 10^7–10^{11} Hz. While PLZT ceramics possess only one diffused dispersion region below phonon frequencies, in PMN and PST-O two regions can be distinguished at the temperatures near and below T_m.

Distribution of the relaxation times widens with the decreasing temperature until $T_f < T_m$, where extrapolated divergence of the mean relaxation time (τ_0) takes place. In the case of PLZT we have estimated temperature behaviour not only of τ_0, but also of the upper (τ_1) and lower (τ_2) limits of the relaxation times distribution (Fig. 3) within the model of the uniform distribution of relaxation times.[2] The lower limit τ_2 is nearly temperature independent. Both τ_1 and τ_0 fit well to the Vogel–Fulcher law and Vögel–Fulcher freezing temperature $T_{VF} = 230$ K can be treated as the ideal freezing temperature ($T_{VF} < T_f$), reflecting the collective nature of the freezing process.[2] In our considerations we will not pay attention to the difference between T_{VF} and T_f.



a)

b)

Fig. 2. Wide range dielectric spectra of PMN crystals at various temperatures: (a) permittivity ε' vs. frequency (in Hz). T, K: 1 — 140, 2 — 200, 3 — 240, 4 — 270, 5 — 290, 6 — 320, 7 — 360, 8 — 400. (b) Loss ε'' vs. frequency (in Hz). T, K: 1 — 140, 2 — 200, 3 — 240, 4 — 270, 5 — 290, 6 — 300, 7 — 320, 8 — 360, 9 — 400, 10 — 500.

At temperatures far above T_m ($T > 650$ K for PMN, $T > 620$ K for PLZT, $T > 500$ K for PST-O) all the dispersion processes merge into the overdamped soft phonon response. These temperatures correspond to the Burns temperatures T_B where the polar clusters begin to appear on cooling.[8] MW ε' (T) deviates from the Curie–Weiss law below T_B and (at least in the case of PMN) obeys this law above T_B. So, we can conclude that the change of dielectric behaviour of relaxors at T_B, are evidently caused by the polar clusters appearance. This is also supported by the MW $\tan\delta$ (T) maximum in PMN near 650 K (Fig. 4).

3. Dynamics of polar nanoclusters and the general structure of the dielectric spectrum

Dynamics of the polar nanoclusters, which appear below T_B, is considered to be responsible for the relaxor behaviour.

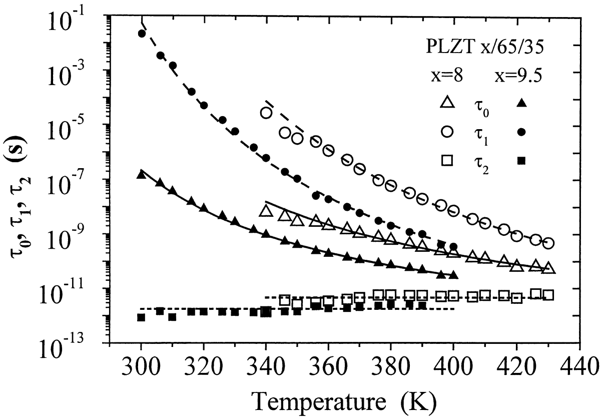


Fig. 3. Temperature variation of the mean, upper and lower relaxation times of PLZT ceramics, estimated from the model of uniform relaxation times distribution.

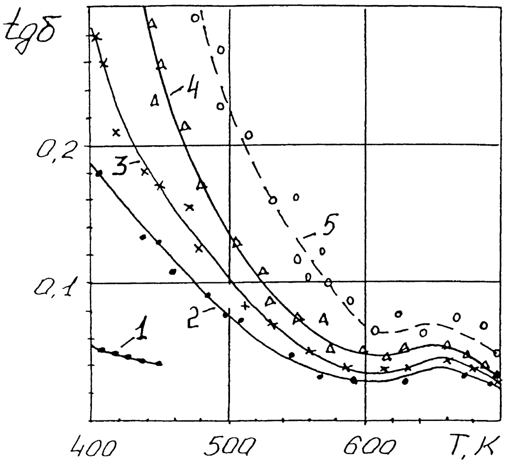


Fig. 4. Temperature dependences of the loss factor $(\tan\delta)$ of PMN crystals at various frequencies in the microwave range. Frequency, GHz: 1 — 0.8, 2 — 7.9, 3 — 17, 4 — 25.4, 5 — 54.

Paraelectric soft mode behaviour, which we suppose to take place above T_B, is suppressed (modified) by the appearance of polar nanoclusters below T_B. The phonon dynamics above T_B is similar to that in displacive ferroelectrics in the paraelectric phase far above T_C. Consequently the phonon contribution to the permittivity is dominant and determines the Curie–Weiss behaviour above T_B. Below T_B the local ferroelectric soft mode within individual polar clusters[2] determines the phonon contribution, however, it is no more dominant. Its temperature dependence should be characterized by a maximum at T_B (Fig. 5).

Both dipole reversal (switching) of polar clusters and fluctuations of polar cluster boundaries should contribute to the dielectric response below T_B. Presumably, the MW dispersion close to T_B is due to the cluster dipole flipping.[9] The distribution of the relaxation times is determined by the size distribution of the polar regions and should be dependent on temperature. The lower limit τ_2 is associated with the smallest polar regions having the volume of a few crystalline unit cells. It is nearly temperature independent.[2] The upper limit τ_1 is associated with the largest polar regions. It is strongly dependent on the temperature because the mean volume and dipole moment of polar regions increase with the decreasing temperature. The interactions among regions cause freezing of the local dipole moments when approaching T_f.[9] The volume fluctuations of the polar regions (i.e. cluster boundary vibrations)[10] is the leading contribution at lower temperatures when the reversal of the polar regions is effectively frozen-out.

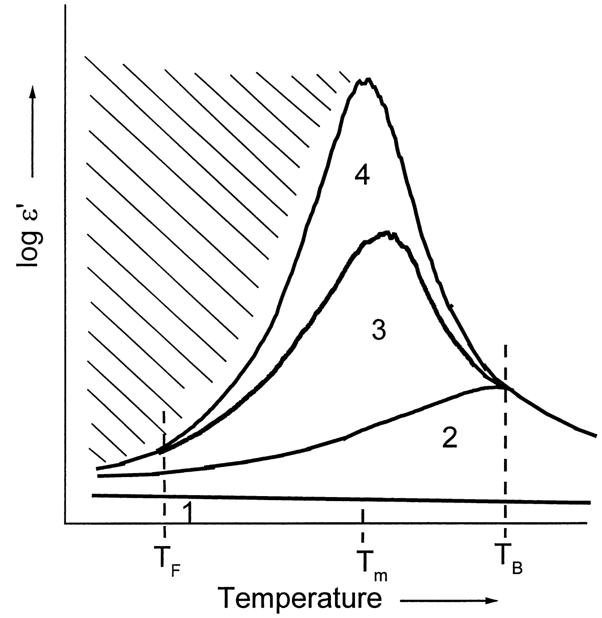


Fig. 5. Structure of the dielectric spectrum of relaxor ferroelectrics. The main dielectric contributions are caused by: 1 — optical polarization mechanism; 2 — phonon polarization mechanism; 3 — fluctuations of the polar cluster boundaries; 4 — polar clusters reversal. The dashed region corresponds to the contribution of infra low frequency processes.

As one can see, the dynamics of polar nanoclusters generally provides two polarization mechanisms and consequently two dielectric contributions. The first one, caused by the cluster flipping, is present only in the temperature interval between T_B and T_f and is characterized by longer relaxation times. The second one, caused by the boundary fluctuations, is present both above and below T_f. It is characterized by shorter relaxation times and should vanish only at low enough temperatures, as any thermally activated relaxation. Both contributions are present between T_B and T_f and are not always well separated in the frequency domain. At higher temperatures, near T_B when the clusters are small, the mean relaxation time τ_0 of both contributions is close to the lower limit τ_2, so that the two contributions cannot be distinguished and result in one dispersion region.

Summarizing, we can build up the general structure of the dielectric spectrum of relaxor ferroelectrics (Fig. 5). Above T_B the fundamental dielectric contribution is due to polar phonons. Below T_B the phonon contribution slightly decreases on cooling and the contributions caused by polar clusters dynamics prevail. At $T_f < T < T_B$ both dipole reversal of polar cluster and fluctuations of polar cluster boundaries contribute to the dielectric response. Below T_f the reversal process is frozen out, but the contribution of cluster boundary fluctuations remains down to low temperatures, and, of course, the small contribution of the optical polarization mechanism is present in the whole temperature range.

Let us compare the dielectric strengths ($\Delta\varepsilon$) and characteristic frequencies of the contributions. $\Delta\varepsilon < 7$ for the optical contribution. Phonon contribution provides the maximum value of $\Delta\varepsilon \sim 1000$ at T_B. Contributions of the polar cluster flipping and cluster boundary fluctuations together provide the maximum value of $\Delta\varepsilon \sim 10000$ at T_m. With the frequency increase the dielectric contributions will switch off in the following sequence: (1) polar cluster reversal contribution at 10–10^{11} Hz; (2) cluster boundaries fluctuations contribution at 10–10^{11} Hz; (3) phonon contribution at 10^{12}–10^{14} Hz; (4) optical contribution at 10^{15}–10^{17} Hz.

We would like to emphasize that the very long relaxation time processes existing below T_m, especially below T_f in the nonergodic phase, are outside of our consideration. Being exact, the upper line in Fig. 5 corresponds not to the static permittivity, but to the low frequency permittivity at ~10 Hz. Only above T_m can it be considered as a zero frequency limit. Below T_m contributions from infra low frequency processes could exist, strongly depending on the prehistory, experimental conditions, measuring field value, etc. The dashed region in Fig. 5 corresponds to these contributions.

If one compares the structure of the dielectric spectrum of relaxor, displacive and order–disorder ferroelectrics,[7] one can conclude that the dielectric spectrum of relaxor ferroelectrics differs from both the displacive and order–disorder ones. Different dielectric contributions play the dominant role in the phase transition region. The fundamental dielectric contribution in displacive ferroelectrics is caused by the polar soft phonon mode; in order–disorder ferroelectrics it is caused by the polar group ordering. In the case of relaxor ferroelectrics, the contributions caused by polar clusters dynamics prevail.

Let us discuss briefly the nature of the polar nanoclusters. Evidently, the structural disorder is a main reason for the polar clusters appearance. In lead containing relaxor ferroelectrics of the perovskite structure two kinds of the disorder can be considered: compositional (chemical) disorder of B-site (PMN, PST) or both B- and A-site (PLZT), and A-site dynamical disorder, caused by the anharmonic motion of Pb.[11,12] Consequently, two kinds of the clusters could exist: compositionally ordered regions (chemical clusters) and correlated dynamic clusters related to the Pb disorder. The question is: which type of cluster plays the major role in the relaxation phenomena discussed above? We suppose that the latter dominates. This is supported by the absence of MW dielectric dispersion above T_B, where only the dynamical clusters can disappear, but not the chemical ones (because the compositional disorder is still frozen above 650 K). Experiments on PST[4,12] clearly prove this supposition. Polar phonon parameters of the B-site ordered and disordered PST ceramics do not differ strongly, neither do the MW dielectric properties. Ordered and disordered PST show both a step-like anomaly of MW ε' at almost the same temperature and nearly the same high frequency dielectric relaxation at $T < 550$ K. The overdamped mode near 12 cm^{-1} in the paraelectric phase appearing in both B-site ordered and disordered samples is assigned to the hopping of dynamically disordered Pb. Of course, the low frequency cluster dynamics is strongly influenced by the B-site order, which causes that the B-site disordered PST samples reveal much stronger relaxor properties than the B-site ordered samples.

Acknowledgements

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