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Dielectric nonlinearity of relaxor ferroelectric ceramics at low alternating-current-drive amplitudes

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Abstract. The dielectric nonlinear response of $(PbMg_{1/3}Nb_{2/3}O_3)_{0.9}(PbTiO_3)_{0.1}$ (0.9PMN–0.1PT) relaxor ceramics was investigated under different ac-drive voltages. It was observed that: (i) the dielectric permittivity is independent of the ac-field amplitude at high temperatures; (ii) with increasing ac-drive amplitude, the permittivity maximum increases, and the temperature of the maximum shifts to lower temperature; (iii) the nonlinear effect is weakened when the measurement frequency increases. The influence of increasing ac-drive amplitude was found to be similar to that of decreasing frequency. It is believed that the dielectric nonlinearities of relaxors at low drive amplitudes can be explained by the phase transition theory of the ergodic space undergoing a succession of shrinkages. A Monte Carlo simulation was performed on the flips of micro-polarizations at low ac-drive amplitudes to verify the theory.

1. Introduction

Since $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) was first synthesized by Smolenski and Agranovuskaya in the late 1950s [1], a series of relaxor ferroelectrics (relaxors) with complex perovskite structure whose dielectric and ferroelectric properties are rather different from those of normal ferroelectrics have been studied. For the lead-based relaxor ferroelectrics, the dielectric permittivity is unusually high, the sintering temperature is rather low, and the temperature coefficient of capacitance is quite small due to the diffuse phase transition (DPT), which leads to their successful application as multi-layered capacitors (MLC) [2]. In addition, the field-induced piezoelectric effect of relaxors is strong, and the pulse-echo response of a transducer can be controlled by a bias voltage. So the relaxors are suited to use in actuators, medical diagnostic transducers, etc [3, 4]. Recently, the observation of the highly excellent electromechanical properties of some single crystals of relaxors (for example, the PMN–PT solid solution) has aroused great interest in the investigation, development, and application of this kind of material [5].

In actual applications, components and devices made from relaxors usually work under dc-bias or ac-drive voltages. So the performances of these materials under external fields always attract great interest. In recent years, some works have focused on the dielectric nonlinear response under various ac-drive voltages. Apart from the strong applications

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background, these works can also provide some clues as to the polarization mechanism of relaxors in theory. Although several possible models have been proposed, the nature of the dielectric response of relaxors, especially PMN, remains unclear [6]. Experiments such as high-resolution transmission electron microscopy (HTEM) have confirmed a main feature of the PMN structure: a great number of nanoscaled ordered microregions, probably nonstoichiometric, are embedded randomly in the disordered matrix [7, 8]. The assumption made in the superparaelectric model that the ordered microregions are just the centres of polar microregions [9] needs further testing in experiments, although theoretical calculations based on this assumption can explain the particularly large permittivity of PMN [10].

For normal ferroelectrics such as $BaTiO_3$, the nature of the dielectric nonlinearity at different ac-drive amplitudes has been universally accepted, i.e., the nonlinearity is caused by the movement of domain walls among the ferroelectric domains with different polarization directions. For relaxor ferroelectrics, as opposed to normal ferroelectrics, no macro-phase transition takes place across the Curie region, and no ferroelectric domain with micrometric dimensions appears. Under the usual conditions, the nanoscaled polar microregions in relaxors do not grow into ferroelectric domains even if the temperature is much lower than T_{max} (the temperature at which the permittivity reaches a maximum). Therefore, it is extremely interesting to investigate the connections between the dielectric nonlinear response and the polar microregions.

The low-frequency dielectric properties of PMN at different ac-drive voltages were first reported by Bokov and Mylnikova in the early 1960s [11]. But there was little work reported on this subject until the 1990s. In the last decade, with the wide application of PMN-type relaxors and the increasing interest in the polarization mechanism of relaxors, research into nonlinearity became emphasized again. Experiments showed that T_{max} shifts to lower temperature with increasing ac-drive amplitude for PMN [12, 13]. And the case of PLZT with relaxor behaviour is similar [14, 15]. The curves for the permittivity at various voltages are similar to those for the frequency dispersion in relaxors. Glazounov *et al* [12] showed that the nonlinear behaviour was controlled by the domain wall motion rather than the reorientation of polar clusters (i.e., the superparaelectric approach [16]). However, they did not explain either the types of domain present nor the process of domain wall motion. Colla *et al* [17] investigated the experiments on PMN–PT single crystals and pointed out that the nonlinearity mechanism is related to the drive amplitude: a glass-like dynamics of the polarization freezing process is dominant at low voltages; at intermediate voltages, movements and reconstructions of the boundaries of polar nanodomains take place; at higher voltages, the interactions between polar regions cause the formation of normal micron-sized domains and the movement of domain walls.

In this paper, the nonlinear dielectric response of 0.9PMN–0.1PT ceramics at various ac-drive amplitudes and frequencies is studied. The experimental results are qualitatively explained by the phase transition theory of the ergodic space undergoing a succession of shrinkages, and a Monte Carlo simulation was conducted to verify the theory.

2. Experimental procedure

0.9PMN–0.1PT powder was prepared by the columbite precursor method [18]. The four starting materials were analytically pure PbO, Nb_2O_5, TiO_2, and $(MgCO_2)_4{\cdot}Mg(OH)_2{\cdot}6H_2O$. $MgNb_2O_6$ was synthesized from the $(MgCO_2)_4{\cdot}Mg(OH)_2{\cdot}6H_2O$ and Nb_2O_5 at 1000 °C. $MgNb_2O_6$, PbO, and TiO_2 powders were mixed and calcined at 870 °C for 2 h. Then the PMN–PT powders obtained were pressed into pellets ($\varnothing 10 \times (1$–$2)$ mm) at 100 MPa, and sintered in a PbO-rich atmosphere for 2 h at 1200 °C. The specimens were analysed by the x-ray diffraction technique on a diffractometer (Rigaku D/max-RA) using Cu Kα radiation,

and a pure perovskite structure was confirmed. Finally, the specimens were polished to 0.4 mm and electroded with silver paste. The dielectric permittivity was measured using an HP4284 LCR meter over the frequency range 1–100 kHz at the heating rate 3 K min^{-1}. The amplitudes of the ac measuring fields were 0.05, 0.25, 0.40, and 0.50 kV cm^{-1}.

3. Results and discussion

The usual amplitude of the ac signal used to measure the dielectric permittivity of relaxors is 0.01 kV cm^{-1} [12]. The results obtained correspond to the slope of the hysteresis loop, $\partial P/\partial E$, at the starting point. Because the amplitude is small enough to fall in the linear-response region, $\partial P/\partial E$ is constant, which represents the real part of the dielectric permittivity ε', i.e., the ε'-value is independent of the amplitude of the external field. However, as the ac-field amplitude is increased, it ceases to be appropriate to ignore the nonlinear terms.

Figures 1–3 show the changes in the dielectric permittivity measured at various amplitudes when the ac-field frequency is 1 kHz, 10 kHz, and 100 kHz, respectively. From the figures one can note the following features:

(1) when the measuring frequency is fixed, the dielectric permittivity remains constant for various ac-drive amplitudes at high temperatures, while it increases with increasing ac amplitude at low temperatures;
(2) with increasing amplitude, the dielectric permittivity maximum, ε'_m, increases and shifts to lower temperature;
(3) the diffusion behaviour is more evident at larger ac amplitude;
(4) the dielectric nonlinear effect is weakened at higher frequencies.

Figure 4 shows the dielectric permittivity at various frequencies when the amplitude is fixed as 0.05 kV cm^{-1}. (The curves for $E = 0.25$, 0.4, and 0.5 kV cm^{-1} are omitted since they are similar to those in figure 4.) It is noted that increasing amplitude has the same effect on the permittivity as decreasing frequency.

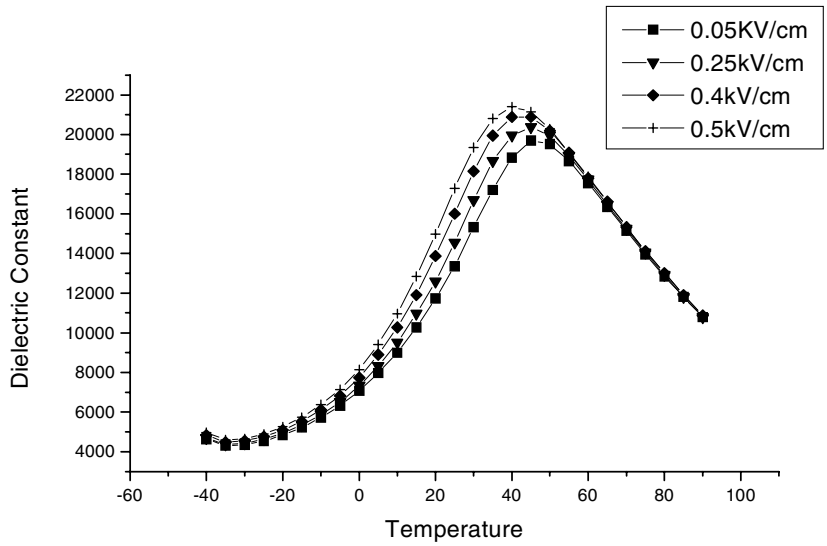

Figure 1. The dielectric permittivity of 0.9PMN–0.1PT as functions of temperature at various amplitudes when the frequency is fixed as 1 kHz.

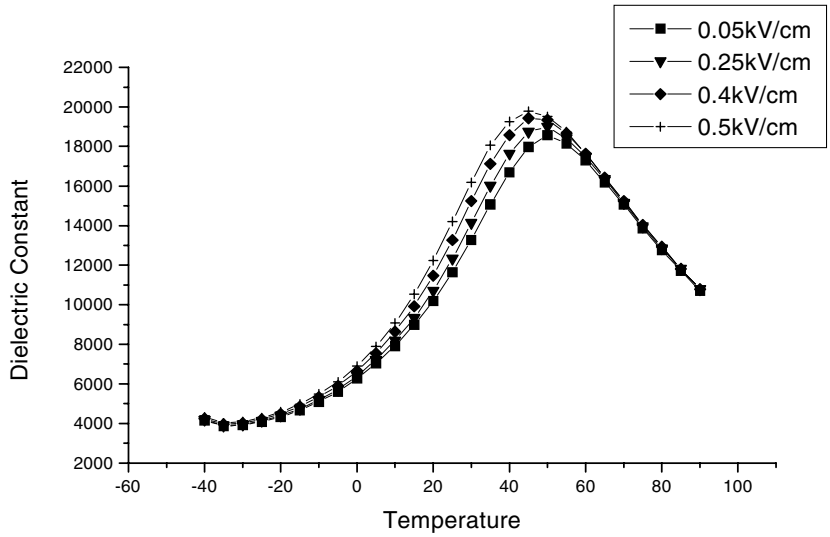

Figure 2. The dielectric permittivity of 0.9PMN–0.1PT as functions of temperature at various amplitudes when the frequency is fixed as 10 kHz.

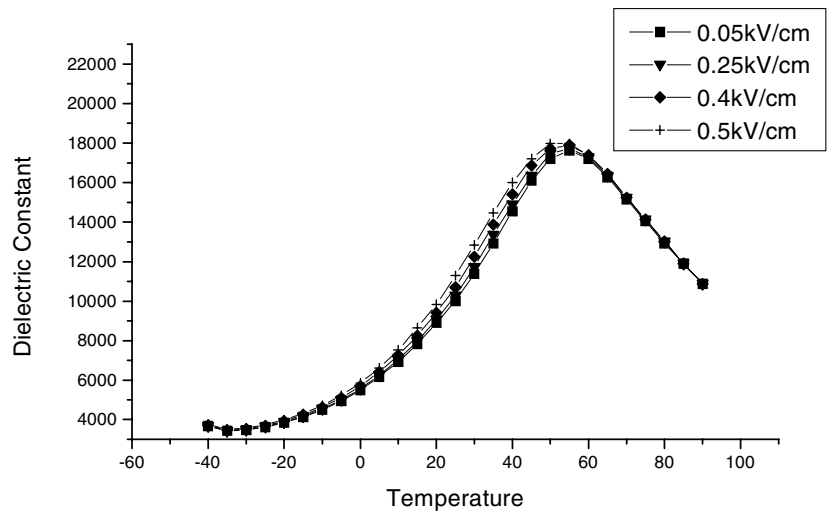

Figure 3. The dielectric permittivity of 0.9PMN–0.1PT as functions of temperature at various amplitudes when the frequency is fixed as 100 kHz.

It can be seen from the results above that the effect of the ac-field amplitude on the permittivity maximum ε'_m is obvious. The relation between ε'_m and the amplitude is depicted in figure 5. A linear law is found in the range of amplitude and frequency under study, which is consistent with the results for single crystals [16]. With increasing frequency, the effect of the amplitude on ε'_m is weakened. By extrapolating the curves in figure 5 to zero field, we can obtain the real part of the permittivity maximum without nonlinear effects.

Table 1 gives the variation of ε'_m when the amplitude increases from 0.05 kV cm^{-1} to 0.5 kV cm^{-1}. It shows that ε'_m increases by 7.4% at 1 kHz (which is the frequency in usual

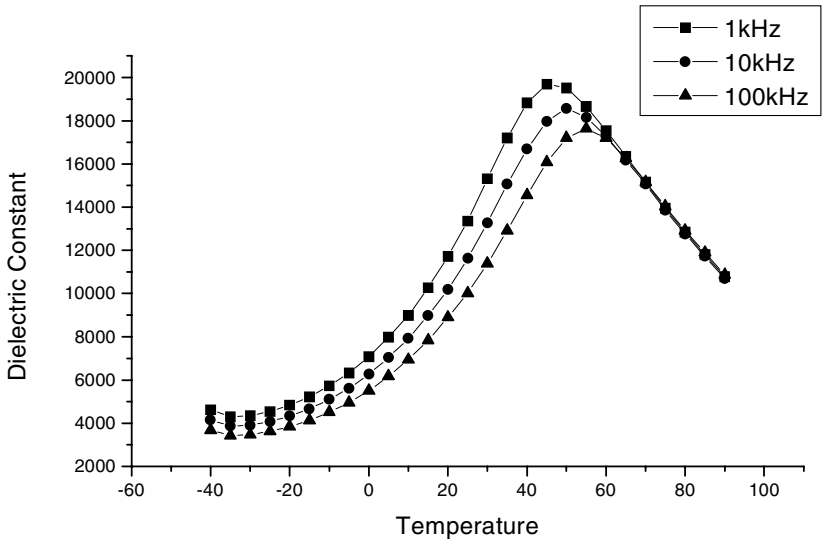

Figure 4. The dielectric permittivity of 0.9PMN–0.1PT as functions of temperature at various frequencies when the amplitude is fixed as 0.05 kV cm^{-1}.

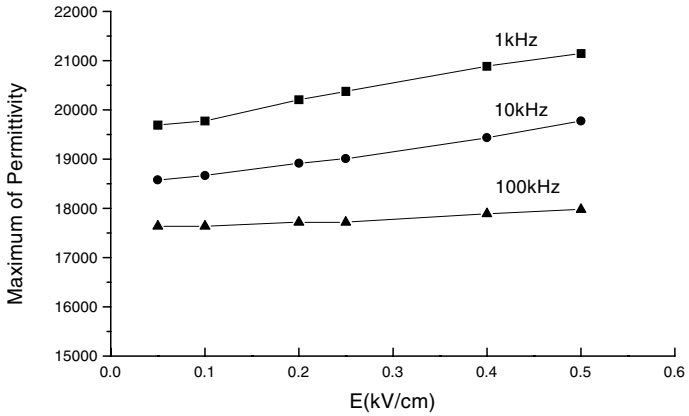

Figure 5. The dielectric permittivity maximum of 0.9PMN–0.1PT at various amplitudes and frequencies.

Table 1. The variation of the dielectric permittivity maximum when the amplitude increases from 0.05 kV cm^{-1} to 0.5 kV cm^{-1}.

Frequency (kHz)	Change of ε_m (%)
1	7.4
10	6.4
100	2.0

measurements). This means that the measured result for the permittivity is affected by the weak-field nonlinearity. As a result, the thickness and the applied voltage of the specimen, i.e., the field strength, should be specified to avoid the influence of the nonlinear effect, so that the results obtained for different experiments are comparable.

It was mentioned in section 1 that different explanations have been advanced for the nonlinear effect in weak fields [12, 17]. Glazounov *et al* [12] opposed the suggestion of a mechanism of reorientation of polar clusters, but they ignored the interactions between polar clusters. Colla *et al* [17] asserted that the glass-like dynamics of the polarization freezing process dominates at low drives. However, the connections between the dynamic process and the nonlinear effect were not explained.

We proposed that the dielectric nonlinearity of relaxor ferroelectrics at low drive amplitudes, as well as the frequency dispersion, can be explained on the basis of a theory of phase transitions of ergodic spaces undergoing a succession of shrinkages [19]. The TEM dark-field image of 0.9PMN–0.1PT proved that there are a great number of nanoscaled ordered microregions embedded in the disordered matrix [9]. At a certain temperature, the homogeneous crystal structure of the ordered microregions causes the cooperative displacement of B-site cations along one of eight $\langle 111 \rangle$-equivalent directions. When the temperature is high enough, the thermal energy, $k_B T$, is much larger than the energy barriers between different directions, which results in the probabilities of displacement along the eight directions being equal, i.e., the system is ergodic. Thus the ordered microregions are nonpolar. However, the environments of the microregions along different directions are not identical, and the spherical symmetry of the ordered microregions breaks down. Therefore the potential wells of different $\langle 111 \rangle$ directions are different, and the B-site ions tend to stay along the direction with the lowest well for more time in the thermal flipping process when the temperature decreases to a certain value. This means that the ordered microregions transform into polar microregions, and dipole behaviour appears. Due to the cooperative displacement of the ordered domain structure, the ions in the same microregion flip as a whole unit under external drives, so the dielectric permittivity of relaxor ferroelectrics is extraordinarily high [10]. The polar microregions are random in magnitude and direction of polarization. Under zero field, $\sum p_i = 0$, while $\sum p_i^2 \neq 0$. When the temperature is much higher than the freezing temperature, the relaxation times of polar microregions are much shorter than the observation time. All the polar microregions flip dynamically with ac drives, so the sum of the polarizations, P, is proportional to the external field, i.e., the dielectric permittivity, $\varepsilon' = \partial P / \partial E$, is independent of the frequency and the amplitude of the external field. In this temperature range, the deviation of the micro-polarization direction from that of the external field caused by thermal fluctuation is weakened with decreasing temperature, and thus the permittivity increases with decreasing temperature. This corresponds to the high-temperature regions in figures 1–4, where no frequency dispersion and nonlinearity are found. The polar microregions can be regarded as independent dipoles. When the temperature decreases further, the electrostatic interactions between dipoles get stronger and stronger. Under an ac drive with a certain frequency, the flip of a dipole is affected by both the external field applied and the internal field generated by other dipoles. Some dipoles cannot keep up with the switching of the measuring field, and become 'slow dipoles'. Some are even frozen along a certain direction, and become 'frozen dipoles'. Thus the phase space displaying ergodicity is undergoing a succession of shrinkages. When the frequency increases, the timescale of the dipole flipping is shortened. More dipoles cannot reach the equilibrium states in the observation time, i.e., the proportion of slow dipoles and frozen dipoles increases. Slow dipoles and frozen dipoles give no or little contribution to the flipping polarization. So the dielectric permittivity decreases, which causes the frequency dispersion in relaxors. When the ac-field amplitude increases, the driving force on the dipoles is enhanced. Slow dipoles and frozen dipoles are forced to flip faster and give more contribution to the flipping polarization. The proportion of slow dipoles and frozen dipoles decreases, and the dielectric permittivity increases; these are the nonlinear effects in relaxors. This is the origin of the special dielectric properties of relaxors (frequency dispersion, nonlinearity, etc).

It should be emphasized that the external field discussed above is in the range of weak drives (less than 0.6 kV cm^{-1} according to reference [17]). Only at weak drives can nano-scaled dipoles exist, and the long-range interactions between dipoles dominate in the dynamic process. If the external field increased, motions and reconstructions of the boundaries of polar nanodomains would take place. Under strong fields, through interacting with the disordered matrix surroundings, polar nanodomains will switch, coalesce, and grow into the conventional micron-sized ferroelectric domains like those in normal ferroelectrics [17,20]. Then the model discussed above is not appropriate for describing the polarization dynamics.

In order to better understand the dielectric nonlinearity in relaxors and verify the model described above, a Monte Carlo simulation is conducted in the next section to investigate the dynamic flipping process of the polar microregions.

4. Monte Carlo simulation

Gui *et al* [21] have used the Monte Carlo method to simulate the dynamics of the freezing process in relaxor ferroelectrics. In the theory framework of reference [21], the polar micro-regions are modelled as point dipoles. The interaction between two dipoles with moments $\vec{\mu}_i$ and $\vec{\mu}_j$ is expressed as

$$J_{ij} = J_{ji} = -\vec{\mu}_j \cdot \frac{1}{4\pi\varepsilon_0}\left(\frac{3\vec{\mu}_i \cdot \hat{r}_{ij}}{r^3}\hat{r}_{ij} - \frac{\vec{\mu}_i}{r^3}\right)$$
$$= -\frac{1}{4\pi\varepsilon_0}\frac{3\cos\varphi_i\cos\varphi_j - \cos\phi}{r^3}\mu_i\mu_j \tag{1}$$

where $\hat{r}_{ij}$ is the unit vector between the two dipoles. r is the distance between dipoles. φ_i (φ_j) is the angle between $\vec{\mu}_i$ ($\vec{\mu}_j$) and $\hat{r}_{ij}$. ϕ is the angle between $\vec{\mu}_i$ and $\vec{\mu}_j$. The Hamiltonian of the relaxors for dc bias is obtained as

$$H = \frac{1}{2}\sum_{i\neq j} J_{ij} - E\sum_i \mu_i\cos\theta_i \tag{2}$$

where E is the dc field strength. θ_i is the angle between $\vec{E}$ and $\vec{\mu}_i$.

The effective interaction energy, $\tilde{J}_{ij}$, is introduced as

$$\tilde{J}_{ij}\sigma_i\sigma_j = J_{ij}\mu_i\mu_j/2 \tag{3}$$

where $\sigma_i = \pm 1$ is the projection of $\vec{\mu}_i$ on the direction of the external field. Equation (2) can be rewritten as

$$H = -\sum_{i\neq j}\tilde{J}_{ij}\sigma_i\sigma_j - E\overline{\mu}\sum_i \frac{|\mu_i\cos\theta_i|}{\overline{\mu}}\sigma_i \tag{4}$$

where $\overline{\mu}$ is the maximal projection of the dipole moments on the external field.

Reference [21] used equation (4) to study the dielectric origins of relaxor ferroelectrics under dc external fields. It is unsuitable for the case of an ac field. However, the polarization mechanisms should be similar for ac and dc fields. Therefore, an ac-field term is introduced:

$$E(t) = E\cos\left(2\pi\frac{t}{t_L}\right) \tag{5}$$

where t_L is the period of the ac field, which corresponds to the frequency. Thus a Hamiltonian similar to equation (4) is obtained:

$$H = -\sum_{i\neq j}\tilde{J}_{ij}\sigma_i\sigma_j - E(t)\overline{\mu}\sum_i \frac{|\mu_i\cos\theta_i|}{\overline{\mu}}\sigma_i. \tag{6}$$

A Gaussian distribution is assumed for $\tilde{J}_{ij}$, i.e.,

$$P(\tilde{J}_{ij}) \propto \exp\left[-\frac{\tilde{J}_{ij}^2}{2(\Delta J)^2}\right] \tag{7}$$

where ΔJ is the distribution width.

There are N dipoles in the system ($N = 16 \times 16 \times 16$). The flipping probability of the ith dipole is defined as

$$W = \frac{1}{e^{\delta H/k_B T} + 1} \tag{8}$$

where δH is the change of energy when the dipole flips from σ_i to $-\sigma_i$. The details of the simulation process can be found in reference [21]. Thus the ac permittivity can be obtained as

$$\chi = C\frac{1}{E}\frac{1}{t_{obs}}\int_{t_0}^{t_0+t_{obs}} p(t)\exp\left(\mathrm{i}\,2\pi\frac{t}{t_L}\right)\mathrm{d}t \tag{9}$$

where $p(t)$ is the average polarization, and C is an arbitrary constant which is chosen to be 1 in this contribution.

In the simulation, an attempt to flip is made for every dipole on the lattice sites in sequence. One Monte Carlo step per dipole (MCS/dipole) consists of $16 \times 16 \times 16$ attempted flips. Figure 6 shows the temperature dependence of the dielectric permittivity at various ac amplitudes when the frequency is fixed as $t_L = 5$ MCS/dipole. It can be seen that the diffusion behaviour is enhanced with increasing amplitude. The simulation results are consistent with experiments as regards the main features, which verifies the polarization mechanism described by the above model. It is noted that the curve $E = 3.0\,\Delta J/\overline{\mu}$ (which corresponds to a stronger field) lies below the other curves at high temperatures. In this case, the corresponding field is perhaps too strong and causes the growth of dipoles, so the weak-field model is not applicable.

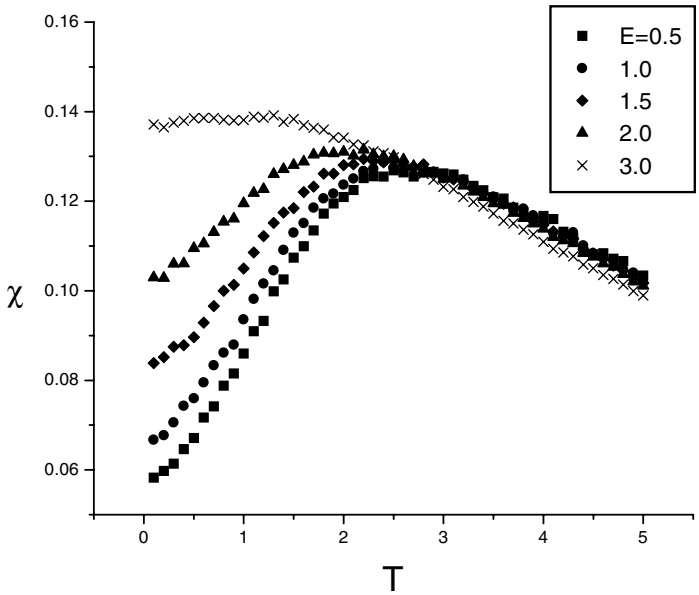

Figure 6. The simulation results for the dielectric permittivity at various amplitudes when $t_L = 5$ MCS/dipole. The temperature is measured in units of $\Delta J/k_B$, and the amplitude in units of $\Delta J/\overline{\mu}$.

5. Conclusions

The dielectric nonlinear response of 0.9PMN–0.1PT ceramics was revealed over the field range 0.05–0.50 kV cm^{-1}. When the measurement frequency is fixed, the dielectric permittivity is invariant with field amplitude at high temperatures. At low temperatures, the permittivity maximum, ε'_m, increases and shifts to lower temperatures with increasing amplitude. A linear law relating ε'_m and the amplitude was observed at all frequencies and amplitudes in the experiment. The nonlinearity is weakened at higher frequencies. The effect of increasing amplitude is similar to that of decreasing frequency. It was proposed that the nonlinearity of relaxors at low drive amplitudes can be explained in a theory of the phase transition of ergodic space undergoing a succession of shrinkages. A Monte Carlo simulation was conducted to investigate the dynamic flips of polar microregions at low drive amplitudes and verify the proposition.

Acknowledgments

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References

[1] Smolenski G A and Agranovuskaya A I 1959 *Sov. Phys.–Solid State* **1** 1429
[2] Shrout T R and Dougherty J P 1990 *Ceramic Transactions (Ceramic Dielectrics vol 8)* ed H C Ling and M F Yan, (Ohio: Westerville) pp 3–19
[3] Newnham R E and Ruschan G R 1991 *J. Am. Ceram. Soc.* **74** 463
[4] Uchino K 1986 *Am. Ceram. Soc. Bull.* **65** 647
[5] Service R F 1997 *Science* **275** 1878
[6] Glazounov A E and Tagantsev A K 1998 *J. Phys.: Condens. Matter* **10** 8863
[7] Chen J, Chan H M and Harmer M P 1989 *J. Am. Ceram. Soc.* **72** 593
[8] Pan X Q, Kaplan W D, Ruhle M and Newnham R E 1998 *J. Am. Ceram. Soc.* **81** 597
[9] Randall C A, Bhalla A S, Shrout T R and Cross L E 1990 *J. Mater. Res.* **5** 829
[10] Gui H, Gu B L and Zhang X W 1995 *Ferroelectrics* **163** 69
[11] Bokov V A and Mylnikova 1961 *Sov. Phys.–Solid State* **3** 613
[12] Glazounov A E, Tagantsev A K and Bell A J 1996 *Ferroelectrics* **184** 217
[13] Glazounov A E, Tagantsev A K and Bell A J 1996 *Phys. Rev.* B **53** 11 281
[14] Tan Q and Viehland D 1996 *J. Am. Ceram. Soc.* **79** 2747
[15] Tan Q and Viehland D 1996 *Phys. Rev.* B **53** 14 103
[16] Cross L E 1987 *Ferroelectrics* **76** 241
[17] Colla E V, Furman E L, Gupta S M, Yushin N K and Viehland D 1999 *J. Appl. Phys.* **85** 1963
[18] Swartz S L and Shrout T R 1982 *Mater. Res. Bull.* **17** 1245
[19] Zhang X W, Gui H, Liu Z R and Gu B L 1999 *Phys. Lett.* A **251** 219
[20] Liu Xi, Zhou He-Ping, Zhang Xiao-Wen, Han Li and Chen Hao-Min 1999 *J. Inorg. Mater.* **14** 1000 (in Chinese)
[21] Gui H, Gu B L and Zhang X W 1995 *Phys. Rev.* B **52** 3135