Phase Transitions in Relaxor Ferroelectrics

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Abstract

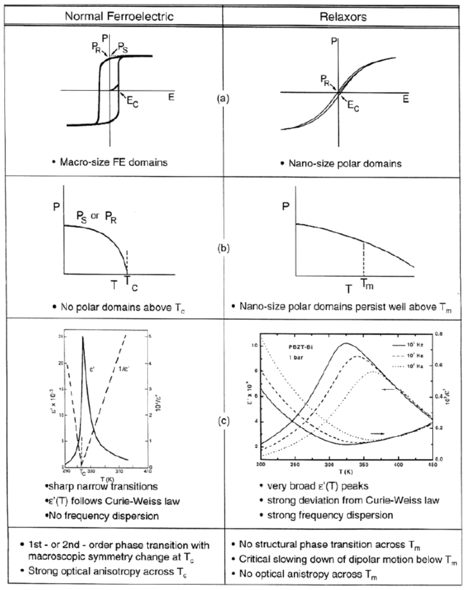
This paper covers the properties of relaxor ferroelectrics and considers the transition from the paraelectric state to the relaxor state comparing experimental data with the spherical random-bond random-field model (SRBRF). It found that this model predicts and is experimental verifies a glassy state at the transition temperature for $E < E_c$ and a ferroelectric state with quench random fields for $E > E_c$. In addition, a critical phase transition in the tungsten bronze family of relaxor ferroelectrics and a crossover from random field Ising model behave to 3d Ising model behavior.

1 Introduction

Ferroelectrics have recently seen a resurgent of interest due particularly to the discovery of such materials with large dielectric susceptibility. In particular, relaxor ferroelectrics have found applications in industry with optical applications such as phase conjugate mirrors, piezoelectric sensors and actuators [5]. The ferroelectric nature of the materials considered in this paper arises from the competition between order-disorder due to the structural composition, and this in turn can lead to dramatic static and dynamical properties in the material [1]. The strong relaxor ferroelectrics can be categorized into two structural families: perovskites with complex composition and bronze tungsten structure [2]. This field of research is very rich with open questions . Therefore I will like to give an overview of the system and focus on one just on these questions. Due to the chemical disorder and lattice defects then there exist dipoles and these dipoles can polarize the region around them forming nano/microdomains [1]. In the relaxor there is a distinct transition from high temperature with polar nanodomains to a state that exhibits relaxor behavior. The nature of the transition and composition of the relaxor state are debated. In this paper the transition of a representative material from both of the families of will be considered, PMN from the perovskites and SBN from the bronze tungsten family.

2 Ferroelectric versus Relaxor Ferroelectrics

A useful starting place to understand the qualitative features of relaxors is to contrast them with the normal ferroelectrics which are better understood. The distinction between ferroelectrics (FE) and relaxor ferroelectrics (RFE) can be distinguished by three qualitatively different features in the temperature dependence of the dielectric susceptibility, as shown in Figure 1. Firstly, in normal ferroelectrics the real part dielectric susceptibility, χ'(T) shows a Curie-Weiss law behavior at the transition temperature T_c, whereas in the relaxors at the transition temperature the peak does have a divergence but it is broad and rounded. This rounded peak position at T_m, marks the dynamic freezing temperature or glass like transition [1]. Secondly, there is a strong frequency dependence in the peak position, T_m of



Normal Ferroelectric		Relaxors
• Macro-size FE domains	(a)	• Nano-size polar domains
• No polar domains above T_c	(b)	• Nano-size polar domains persist well above T_m
•sharp narrow transitions •ε'(T) follows Curie-Weiss law •No frequency dispersion	(c)	• very broad ε'(T) peaks • strong deviation from Curie-Weiss law • strong frequency dispersion
• 1st - or 2nd - order phase transition with macroscopic symmetry change at T_c • Strong optical anisotropy across T_c		• No structural phase transition across T_m • Critical slowing down of dipolar motion below T_m • No optical anistropy across T_m

Figure 1: Contrast between normal ferroelectrics and relaxor ferroelectrics [1]

χ'(T). Lastly, the polarization in FE goes to zero at T_c and in the relaxors the polarization extends well beyond T_m [3]. The fact that there is zero polarization at T_c shows that polar nanodomains vanish whereas in the relaxor the nanodomains persist well beyond the glassy transition temperature [1].

While the normal ferroelectric has a hysteresis loop that at zero field retains large polarization, in the relaxor this zero field polarization is significantly smaller owing to the fact that the the nanodomains being randomly distributed. It is possible to create a large polarization when there is a sufficiently large external electric field, but once the field is removed polarization returns to being small owing to the randomness of the domains [1]. Finally it is should be noted that in FEs there is a macroscopic structural change at T_c and this occurs in RFEs [1]. Due the these qualitatively different features then one should not expect the transitions in FEs to be the same mechanism in RFEs. Now that the essential differences between normal ferroelectrics and relaxors have been overviewed, in the interest of space I would go review the transition at from above T_m to below T_m.

3 PMN

One of the most extensively studied relaxor ferroelectrics is $PbMg_{1/3}Nb_{2/3}O_3$ (PMN). To probe the transition from a glassy state to the long range ferroelectric ordered state several different experimental techniques have been used. Those included pyroelectric measurements, NMR, dielectric spectroscopy and neutron scattering. First, we begin by looking at the high temperature and the nature of the phase there . At very high temperature the thermal fluctuations are so strong that there are no well-defined dipole in the sample [1]. As the temperature reduced polar nanodomains begin to form at a temperature T_d, the Burns temperature [1]. This is the analogue of the freezing of the spin fluctuations in a magnetic system. The evidence for the formation of polar nanodomains was done by measuring the refractive index n as a function of temperature. Normal (weak) perovskite relaxors show deviation from the Curie-Weiss law but at a much lower temperature than was seen in PMN. This was interpreted that there exist polar nanodomains at up to T_d, upon which they are destroyed and normal Curie-Weiss behavior is obeyed. Evidence for polar nanodomains well above T_m is also seen in measurements of the dielectric susceptibility, as see in figure 2. The departure from Curie-Weiss behavior become more severe as T decreases from the fact that the nanodomains increase in correlations and size [1].

3.1 Diffuse Transition

Now that we know that polar nanodomains come into existence at T_d, the question is what role do the domains play in describing the relaxor behavior and the apparent glassy nature of the material below T_m? It is generally agreed that disorder/randomness plays a crucial role in the transition from the paraelectric state to the glassy transition. The nature of the diffuse transition of the relaxor ferroelectric in zero electric is still much debated. This is due to contradictory experimental results. The question to be answered is whether the relaxor behavior is due to a basically glass state with polar nanodomains interacting randomly in the presence of random fields [7]. Or is the relaxor basically a FE with macroscopic domain broken up into nanodomains subject to quenched random fields, in which the random field interaction causes a smearing out of the FE transitions and lead to relaxor behavior [1]? While there is no general agreement on nature of state,

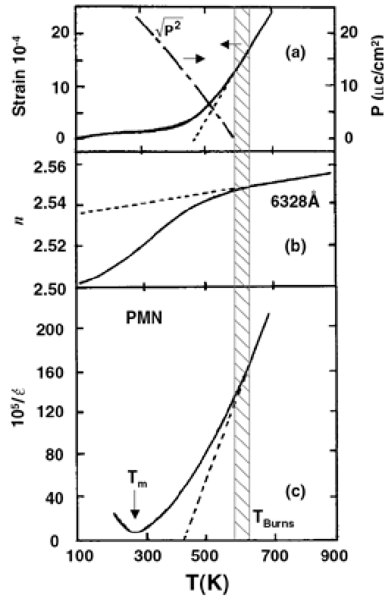


Figure 2: Deviations from linearity at T_d measured by the index of refraction and reciprocal dielectric constant [1]

most of the evidence is in favor to the glassy state behavior [1].

One of the models recently proposed for relaxors is the spherical random bond random field model (SRBRF). In experiments conducted with quadrapole perturbed NMR and measurements on the nonlinear susceptilbility it is suggested that the experimental results could fit into this model's framework [6]. The ^{93}Nb NMR lineshape and the probability distribution of the polarization was shown to be Gaussian at all temperatures, which means that the order parameter should be a variable length continuous vector field rather than fixed length field like in dipolar glasses [6]. The vector field is associated with the reorientable polar clusters but subject to a constraint on the square of the total polarization [6]. The Hamiltonian describing these clusters is given by

$$H = -\frac{1}{2}\sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j - \sum_i \vec{h}_i \cdot \vec{S}_i - g\sum_i \vec{E}_i \cdot \vec{S}_i \qquad (1)$$

where J_{ij} is the random bond interaction, $\vec{h}_i$ is the random local electric field, and the last term is the effective local field, with local field factor g [6]. The order parameter $\vec{S}_i$ is proportional to the dipole moment at the i^{th} site in that cluster and it is discrete with finite number of orientations. The order parameter is subject to the constraint that

$$\sum_i \vec{S}_i^2 = 3N \tag{2}$$

where N is the number of polar clusters. It is assumed, like in dipolar glasses, that the random bonds are infinitely ranged with a Gaussian probability distribution, and to simplify the calculations it is assumed that the components of $\vec{S}_i$ vary continously [6]. This model is what is know as the spherical random bond random field model.

3.2 Experimental Test of SRBRF

Next we would like to verify that this model does indeed capture the features of the transition correctly. Bobnar et. al. conducted experiment on single crystal PMN with a dc electric field as well as in zero field, measuring the temperature dependence of the dielectric nonlinearity to test the nature of the transition. Because the PMN has centrosymmetrical cubic symmetry, the polarization can be written as a power series as

$$P = (\epsilon_1 - 1)E - \epsilon_3 E + \ldots, \tag{3}$$

where P is the polarization and E is the electric field [7]. This relationship can be inverted to give $E = a_1 P + a_3 P^3 + \ldots$, where $a_1 = 1/(\epsilon_1 - 1)$ and $a_3 = \epsilon_3/(\epsilon_1 - 1)^4 \approx \epsilon_3/\epsilon_1^4$ [7]. The dielectric nonlinearity is a_3. The dielectric nonlinearity test the proposed question because for the scaling theory of the second order transition predicts that a_3 should go to zero at a ferroelectric transition whereas for dipolar glasses it should diverge at the freezing transition [7] as observed [7]. The disagreement comes about because from measurements of the real part dielectric permittivity ϵ' as a function of a dc electric field [7]. The quantity $\hat{a}_3 = [\epsilon'(E = 0) - \epsilon'(E)]/3E^2\epsilon_s^4$ with ϵ_s being the static dielectric constant, show that $\hat{a}_3$ decreases with decreasing temperature above the freezing temperature, which is consistent with the ferroelectric domain break up model, and in contradiction with SRBRF [7]. Reasons for the conflicting results are that the measurements have been taken in different parts of the $E - T$ phase diagram, and cooling the relaxor in a field greater than the critical field E_c will cause ferroelectric order to be formed [7].

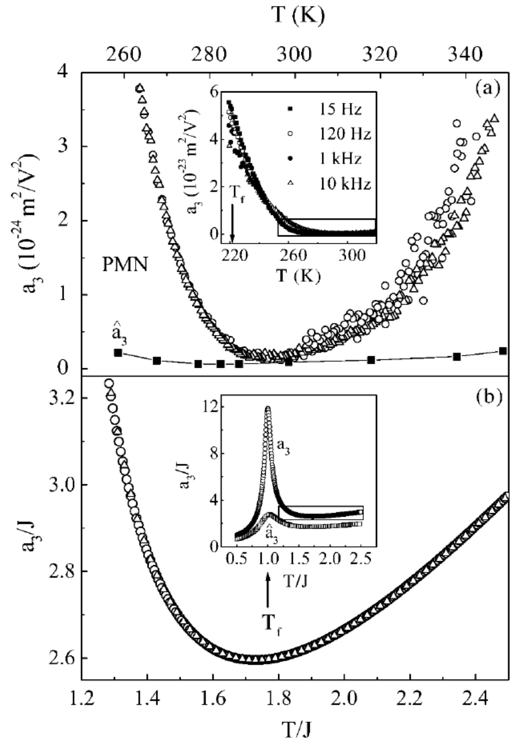


Figure 3: (a) The dielectric nonlinearities a_3, $\hat{a}_3$, in PMN. Open circles are in $E_{dc} = 0$, open triangles $E_{dc} = 1.5kV/cm$. Solid squares show scanned range $0 < E_{dc} < 3kV/cm$ for $\hat{a}_3$. (b) Temperature dependence of a_3 based on SRBRF model, with open circles at $E = 0$ and open triangles at $E = 0.85E_c$ [7]

In figure 3a the measurements of $\hat{a}_3$, a_3 are shown from the single crystal PMN. The measurement of a_3 was made at $E < E_c$ where $E_c = 1.7kV/cm$ and after the sample was annealed. As can be seen from the figure, a_3 at first begins to decrease as T is decreased above T_f the freezing temperature. Then upon further temperature reduction a_3 begins to increase dramatically as T approaches T_f. In addition, $\hat{a}_3$ begins to increase, which is consistent with SRBRF. This suggests that the transition is to a glassy state at zero field and not a ferroelectric state with quenched random fields. Figure 3b. is a plot based on the model for parameters that correspond to the glass phase with mean coupling constant $J_0/J = 0.9$ and $\Delta/J^2 = 0.001$, and $E = 0$

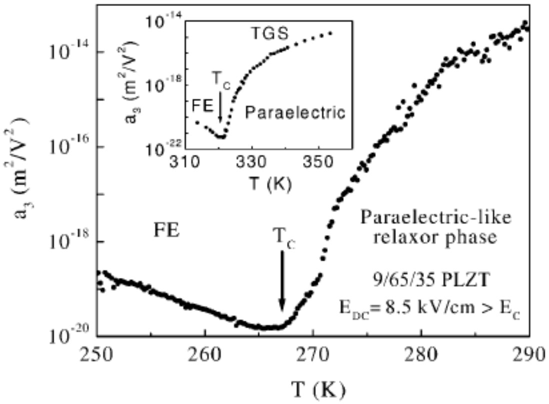


Figure 4: Temperature dependence of a_3 at $E = 8.5kV/cm$ in PLZT at 400 Hz. The monotonic decrease of a_3 is consistent with the prediction of SRBRF [7]

where Δ is the variance in the random fields, h_i, and the open triangles correspond to $E = 0.85E_c$ [7]. In comparsion with figure 3a, the model fits the data quite well. Furthermore, the inset in figure 3b shows (from the model) that $\hat{a}_3$ increases with decreasing temperature to T_f. As T_f is approached, the critical slowing down of the polar nanodomains makes the response of impossible to measure, and thus the behavior of a_3 near T_f cannot be measured [7]. It would be interesting to measure near the peak, and this where other experimental techniques could be used besides the technique in Ref [[7]].

Next we verify that if the experiments are done in a part of the $E - T$ with $E > E_c$ then the relaxor should enter a FE phase with quench RF's. When a_3 is measured in this part diagram, as shown in figure 4. a_3 decreases as T_c is approached which is predicted by the model [7].

In summary we can say that in PMN, above the transition temperature with zero dc electric field, the relaxor goes from the paraelectric state with nanodomains to entering a glassy state where the random interactions between the nanodomains increase and freeze out. Moreover, the $E - T$ phase diagram shows thats if the system starts above E_c and above T_c then the relaxor will enter a FE state with RF's as the temperature decreases to the critical temperature, while below

E_c the relaxor will enter the dipolar glass phase. Furthermore, these phases are in agreement with the SRBRF model proposed.

4 Model of SBN

In the previous section it was shown that there is a transition from a paraelectric state to a glassy state or a paraelectric state to a FE state with RF's. The next question is whether or not this transition is a critical transition described by a critical exponent or a non-critical transition. SBN is in the tungsten-bronze system and is structurally distinct from the perovskites, but it too exhibits relaxor behavior. As previously mentioned, disorder plays a crucial role in the dynamics of relaxors. For uniaxial SBN, the disorder is brought about in two ways. SBN doped with cerium has charge disorder which arises from Ce^{+3} located on Sr^{+2} sites and in addition the tetragonal tungsten bronze-type solid solution structure contains randomly distributed cation vacancies [4]. Also, this system is cut along its crystallographic axis and therefore has only only two easy axes which differ by 180° which make it a uniaxial relaxor[5]. The charge disorder from the ions give random field and the limitation of the domain to two easy direction make the random field Ising model (RFIM) a good candidate to model the system. The RFIM Hamiltonian is given by

$$H = -\frac{1}{2}\sum_{<ij>} J_{ij} S_i S_j - \sum_i h_i S_i \tag{4}$$

where h_i is the random electric field at the i^{th} spin site.

Since this system is ideally the electrical version of ferromagnetic system, eventhough the ferromagnetic variety does not exist because no magnetic monopoles exist, one would expect that the polarization will follow

$$P(T) = P_o(1 - T/T_c)^{\beta}, \tag{5}$$

where β is the critical exponent [5].

As can be seen in the figure, the fit of equation 5 is good well below T_c where one would expect the law to be valid and the fit poor above T_c. As can also be seen from the graph, the exponents in the fully poled sample and the small poled sample are different. For the fully poled sample, $\beta = 0.126 \pm 0.005$ while when it was only partially

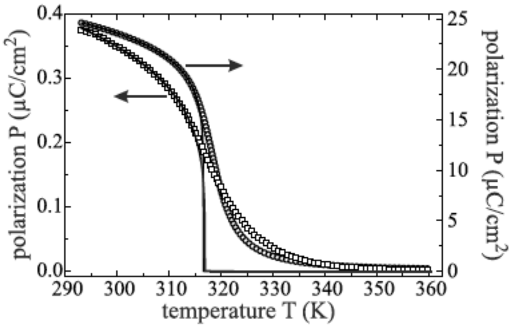


Figure 5: Polarization versus temperature or SBN:Ce of the fully poled sample (circles, right axis) and of the partially poled sample(diamonds, left axis) [5]

poled 1.5% the exponent, $\beta = 0.232 \pm 0.010$ [5]. For intermediate poling β is between these two values [5]. For RFIM system predicts small values $\beta \approx 0$, and for the 3D-Ising model $\beta = 0.325$ [5]. Here we see that when the sample is fully poled the system exhibits a more RFIM like behavior with the exponent being closer to zero. While for low poling the system is closer to that of the 3D-Ising. Also, it is worth noting that the transition temperature is the same for both polings. Equation 5 is obeyed below T_c which means that the relaxor transition is showing criticality. Also, β decreases with increasing poling and hence more domain ordering, but we know that the critical exponent is determined by the long range order and the interactions in the system [5]. However, this should not be totally unexpected since it is not expected that the interaction should remain the same through the transition. The poor fit above T_c can be explain as follows: the FE domains as T_c is approaches from below transform into slowly fluctuating polar clusters and retain the memory of the polarization longer than can be accounted for by equation 5[5].

To summarize, it was shown that this system shows a critical phase transition and therefore can be considered to have FE long range order between local dipoles[5]. And there appears to be a change from RFIM to 3D-Ising depending on the amount of poling as seen from the critical exponent β. This is interesting considering that PMN does not show this type of transition for $E < E_c$ and would be interesting to see if there is criticality for $E > E_c$.

5 Conclusion

In this paper I have covered the defining properties of relaxor ferroelectrics from normal ferroelectrics, describing that they differ in three distinct ways. Then I considered the transition from the paraelectric state to the relaxor state in which it was found that the spherical random-bond random-field model can describe the transition. Where upon comparing with experimental data on the dielectric nonlinearity gave supporting evidence that the SRBRF model describes the transition. Furthermore, the state that is entered below T_f depends on the starting location in the $E - T$ phase diagram. And finally we saw that there is a critical phase transition in the tungsten bronze family of relaxor ferroelectrics. What I have presented here considers only one question concerning the relaxor transition but upon looking through the literauture, one finds that there are many interesting questions that remain, and further research of relaxors will provide an opportunity for a better understanding disorder systems.

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