# Order-Disorder Phase Transition and Dielectric Mechanism in Relaxor Ferroelectrics<sup>\*</sup>

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Abstract: An overview is presented on the order-disorder structural transitions and the dielectric mechanism in the complex-perovskite type relaxor ferroelectrics, i.e., the relaxors. Emphasis is put on the theoretical understanding of the structural transitions, the macroscopic dielectric properties, and the relationship between them. The influences of the composition, the temperature, and the atomic interactions on the order-disorder microstructures can be well understood in the cluster-variation-method calculations. The criterion drawn from theoretical analysis is successful in predicting the order-disorder structure of relaxors. Among various physical models about relaxors, the dipole glassy model that described the dielectric response as the thermally activated flips of the local spontaneous polarization under random interactions is discussed in details. The Monte Carlo simulation results of this model are consistent with the linear and nonlinear experiments of relaxors.

Key words: order-disorder transition; relaxor ferroelectrics; complex perovskite

# Introduction

Since Pb(Mg1/3Nb2/3)O3(PMN) was first synthesized by Smolenski and Agranovuskava in the late 1950s<sup>[1]</sup>, a series of relaxor ferroelectrics 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, which lead to their successful application as multi-layered capacitors (MLC). 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 be used in actuators, medical diagnostic transducers, etc. Recently, the observation of the highly excellent electromechanical properties of some single crystals of relaxors [for example, the (1-x) Pb $(Mg^{1/3}Nb^{2/3}) - O_{3-x}$  PbT iO<sub>3</sub>(PMN-PT) solid solution] has aroused great interest in the investigation, development, and application of this kind of material<sup>[2]</sup>.

The dielectric behaviors of the relaxor ferroelectrics with complex perovskite structure are different from those of normal ferroelectrics. Relaxor ferroelectrics experience no macroscopic phase transition at zero electric field. The ferroelectric phase can be induced by an external electric field at low temperatures, which has been studied by Liu et al.<sup>[3]</sup> with eight-potential-well order-disorder ferroelectric model. In Fig. 1(a) is illustrated first the behavior in a rather perfect single crystal of normal ferroelectrics which goes through an abrupt second order phase transition into the ferroelectric phase. Above the Curie temperature  $T_{\circ}$ , the permittivity follows a Curie-Weiss law  $\epsilon' = C (T - T_c)^{-1}$ . At  $T_c$  there is an abrupt but continuous onset of spontaneous polarization which evolves into the domain structure of the ferroelectric form. In the relaxor ferroelectrics, three features of the dielectric response are qualitatively different. The transition

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is clearly diffuse and rounded (which is called as Diffuse Phase Transition, DPT), but the response is now markedly dispersive below  $T_m$  (the temperature at which the dielectric permittivity reaches its maximum), and  $T_m$  is a function of frequency (Fig. 1(b)). The response under weak field above  $T_m$  no longer obeys the Curie-Weiss law. In the polarization the root-mean-square (RMS) value persists to a temperature ( $T_D$ ) of 200 to 300 °C above  $T_m$ , but the mean polarization  $\overline{P}$ decays to zero at a temperature  $T_f$  which is well below  $T_m$ .



Fig. 1 Types of ferroelectric phase transitions: (a) Simple proper ferroelectric: sharp second order phase change in highly perfect single crystal; (b) Relaxor ferroelectric defining  $T_{\rm m}(\omega)$ ,  $T_{\rm D}$ , and  $T_{\rm f}$ 

Smolenski and Agranovuskaya<sup>[1]</sup> originally proposed that the DPT was caused by the chemical inhomogeneity arising from the B-site cation disorder in complex perovskite relaxors. However, with the development of microscopic techniques, especially as the transmission electron microscopy (TEM) and the high resolution electron microscope (HREM) were used, many compounds previously accepted as disorder were found to be ordered on nanoscale. Randall et al.<sup>[4]</sup> summarized the experimental results and pointed out that complex perovskites possessing nanoscale ordered microregions are relaxor ferroelectrics, while those disordered (< 2 nm) or ordered with long coherency (> 100 nm) are normal ferroelectrics or antiferroelectrics. It seems that the nanoscale ordering is closely related to the relaxor behaviors. This knowledge about complex perovskites greatly supports the study of the order-disorder structural phase transition and the dielectric mechanism in these materials.

# **1** Order–Disorder Phase Transition

In 1980, Setter and Cross indicated that B-site cations in  $Pb(Sc_{\frac{1}{2}}^{1}Ta_{\frac{1}{2}})O_{3}(PST)$ , Sc and Ta, were partly ordered and formed an FCC superlattice<sup>[5,6]</sup>. The ordering degree varied with annealing time and had great influence on DPT characteristics. By using the HREM in conjunction with selected-area electron diffraction, Krause et al.<sup>[7]</sup> found that there existed 2-5 nm superlattice microregions in Pb  $(Mg_{\frac{1}{3}}Nb_{\frac{2}{3}})$  O<sup>3</sup> in which  $Mg^{2+}$  and  $Nb^{5+}$  were ordered in alternating {111} planes with the 1 .1 composition. Such a nonstoichimetric structure was later confirmed by Chen et al.<sup>[8]</sup> This  $\frac{1}{2}$ {111}type ordering (Fig. 2 (a)) is most commonly observed in complex perovskites. Meanwhile, other kinds of ordered structure have also been reported. Randall et al.<sup>[9]</sup> observed the  $\frac{1}{2}$ {110} superlattice reflections in PMN, PST, (PbLa)  $(ZrTi) O_3(PLZT)$ ,  $(Ba_{1-x}Pb_x)TiO_3$ , etc. Fang et al.<sup>[10]</sup> provided a clear lattice image of this kind of superstructure in PLZT via HREM. V Pb<sup>2+</sup> and La<sup>3+</sup> are assumed to occupy the corner and the bodycentered positions (Fig. 2). What is more interesting is that the  $\frac{1}{2}$  { 111 },  $\frac{1}{2}$  { 110 } and  $\frac{1}{2}$  {100} superlattice reflections were found to exist

simultaneously in (PbCa)  $TiO_3^{[11, 12]}$ .

From crystal chemical arguments, Setter and Cross<sup>[5]</sup> have summarized five rules to determine whether the ordering could be formed, which were stated as follows:

(1) Structure: In order to reduce the energy for ordering, a simple structure is preferred. The perovskite of the form  $A(B'B'')O_3$  is considerably a simpler form and is therefore prefered.

(2) Cation ratio: The same argument of simplicity to reduce ordering energy would suggest a cation ratio of B' to B" is  $1 \cdot 1$ .

(3) Charge of B-site ions: Large difference in valence between B' and B" results in a very strong tendency to ordering.

(4) B-site ion size: Materials with large size difference between B-cations are driven strongly



Fig. 2 Ordered structures observed in complex perovskites: (a) The 1/2{111}-type ordered structure; (b) The 1/2{100}-type ordered structure; (c) The 1/2{110}-0.25-type ordered structure; (d) The 1/2{110}-0.50-type ordered structure; (e) The 1/2{110}-0.75-type ordered structure

towards ordering by electric forces.

(5) A-site ion size: Reducing the size of Asite cation enhances the elastic drive towards ordering on the B-sites.

Some theoretical work has been done on the order-disorder transition in  $A(B'B')O_3 \operatorname{crystals}^{[13]}$ . The order-disorder transition in  $A(B'_xB''_{1-x})O_3$  and  $(A'_xA''_{1-x})BO_3$  is modelled as the order-disorder transition of a two-component system  $C'_xC''_{1-x}$  on a simple cubic Bravais lattice considering the fact that A site and B site in ABO<sub>3</sub> form simple cubic lattices. The influences of the other sites are included in the effective-interaction parameter. Using the cluster variation method (CVM) with pair approximation, the phase diagram of the order-disorder transition in A (B'B'') O<sub>3</sub> complex perovskites has been obtained (shown in Fig. 3).

A criterion of ordering was drawn as:

•  $\epsilon' T F_0 < 2.0$ , M = 1, ordered;

• 2.  $0 < \epsilon' T F_0 < 5.0$ , 0 < M < 1, partially ordered;

•  $\epsilon' T F_0 > 5.0$ , M = 0, disordered,

where M is the ordering parameter,  $k_{\rm B}T/J$  is the reduced temperature and J is the effective interaction energy parameter. Considering the nearest-neighbor electrostatic interaction between ions, the reduced temperature was obtained as

$$\frac{k_{\rm B}T}{J} = \epsilon' T F_0 \tag{1}$$

where  $\epsilon'$  is the dielectric constant of the crystal and  $F_0$  was defined as the ordering structure factor. In A(B'B')O<sub>3</sub>, it has been deduced that

$$F_0 = \frac{4\pi\epsilon_0 kr}{\Delta q^2 + 4\Delta q(\Delta r/r)}$$
(2)

where q is the average valence,  $2\Delta q$  and  $\Delta r$  are respectively the charge and the radius difference between the two kinds of B-cations. It is obvious that large differences in valence, large size difference between B-cations and reducing r are favorable for the atomic ordering, which is consistent with the rules (3), (4), and (5) given by Setter<sup>[5]</sup>. The theoretical predictions of the order-disorder structure of nineteen typical A (B'B')O<sub>3</sub> compounds were given and compared with experiments by Zhang et al.<sup>[13]</sup>, which were listed in Table 1. The theoretical work are rather consistent with experimental results except the case of Pb ( $Yb_{1/2}^{2+}Ta_{1/2}^{6+}$ ) O<sub>3</sub> (PYT), which was theoretically predicted to form ordered structure. Two years after the prediction was given, Yasuda et al.<sup>[14]</sup> experimentally observed the ordered PYT and thus confirmed the theoretical prediction.

The stability of various ordered structures in complex perovskites has been investigated by Gui et al. [15] using the eight-point cluster variation method. They introduce two parameters  $u = J_2/J_1$ and  $v = J_3/J_1$ , where  $J_1$ ,  $J_2$ , and  $J_3$  are, respectively, the nearest-, next-nearest- and thirdneighbor effective interaction parameters. The under various effective results interaction conditions are depicted in Fig. 4. It can be seen that the nearest-neighbor interaction favors the formation of the  $\frac{1}{2}$  {111}-type ordered structure, while the  $\frac{1}{2}$  { 110} + type ordered structures result

from the next-nearest interaction.

Most complex-perovskite type relaxors have very high dielectric constants  $(10^3 - 10^4)$ . This means that the screening effect in the crystal is so strong that the nearest-neighbor approximation is valid in most complex perovskites. It may be the reason that the  $\frac{1}{2}$  { 111}-type ordered structure is most commonly observed in this kind of materials. Furthermore, while  $\frac{1}{2}$  { 111}-type order-disorder phase transition takes place, a nonstoichiometric ordering structure could be formed if the composition in complex perovskites deviates from 0.5. The nonstoichiometric ordering causes the

| rable 1 - rataineters of some typical A(D D) 03 compounds       |                   |               |                     |                          |                                   |   |                  |                   |
|---|-------------------|---------------|---------------------|--------------------------|-----------------------------------|---|------------------|-------------------|
| Com pounds  | $\epsilon_{ m m}$ | <i>T</i> ₀/ ℃ | $F_{\rm s}/\rm kHz$ | Dielectric<br>properties | F <sub>0</sub> / 10 <sup>-5</sup> | $\epsilon_{\mathrm{m}} \bullet T_{\mathrm{c}} \bullet F_{\mathrm{0}}$ | Theo.<br>results | Ex p.<br>result s |
| $Pb(Co_{1/2}^{2+}W_{1/2}^{6+})O_3$                              | 150               | 20            | 450                 | AFE FE                   | 0. 55                             | 0.2   | 0                | 0                 |
| Pb( $M n_{2'3}^{3+} W_{1/3}^{6+}$ ) O <sub>3</sub>              | 200               | 410           | 200                 |                          | 0. 98                             | 1.3   | 0                | 0                 |
| Pb( $Mg_{1/2}^{2+}W_{1/2}^{6+})O_3$                             | 115               | 38            | 1. 0                | A FE                     | 0.56                              | 0.2   | 0                | 0                 |
| $Pb(Zn_{1/2}^{2+}T e_{1/2}^{6+}) O_3$                           | 60                | 55            | 1. 0                | A FE                     | 0.56                              | 0.1   | 0                | 0                 |
| $Pb(Cd_{1/2}^{2+}Te_{1/2}^{6+})O_3$                             | 140               | 295           | 1. 0                | A FE                     | 0. 51                             | 0.4   | 0                | 0                 |
| ${ m Pb}({ m Mg}_{1/2}^{2_{+}}{ m Te}_{1/2}^{6_{+}}){ m O}_{3}$ | 350               | - 80          | 1. 0                | A FE                     | 0. 57                             | 0.4   | 0                | 0                 |
| $Pb(Ca_{1/2}^{2+}Te_{1/2}^{6+})O_3$                             | 200               | 320           | 1. 0                | AFE                      | 0. 51                             | 0.6   | 0                | 0                 |
| $Pb(Cd_{1/2}^{2+}Te_{1/2}^{6+})O_3$                             | 50                | 290           | 1. 0                | AFE                      | 0. 52                             | 0.1   | 0                | 0                 |
| $Pb(Ca_{1/2}^{2+}Te_{1/2}^{6+})O_3$                             | 170               | 280           | 1. 0                | A FE                     | 0. 52                             | 0.2   | 0                | 0                 |
| Pb(Y $b_{1/2}^{2+}Ta_{1/2}^{6+})O_3$                            | 100               | 7             | 500                 |                          | 2. 12                             | 0.6   | 0                | D                 |
| Pb $(In_{V2}^{3+}Nb_{V2}^{5+})O_{3}$                            | 550               | 120           | 500                 |                          | 2. 13                             | 4.7   | D                | D                 |
| $Pb(Ho_{1/2}^{3+}Nb_{1/2}^{5+})O_3$                             | 480               | 230           | 500                 |                          | 2.06                              | 5.0   | D                | D                 |
| $Pb(Lu_{1/2}^{3+}Nb_{1/2}^{5+})O_3$                             | 350               | 260           | 500                 |                          | 2. 16                             | 4.0   | Р                | D                 |
| $Pb(Mg_{1/2}^{2+}Te_{1/2}^{6+})O_3$                             | 4 0 0 0           | - 173         | 1. 0                | FE                       | 0. 58                             | 2.3   | 0                | 0                 |
| $Pb(Fe_{1/2}^{3+}Ta_{1/2}^{5+})O_3$                             | 3 600             | - 43          | 200                 | $\mathbf{FE}$            | 2. 31                             | > 5.0   | D                | D                 |
| $Pb(Sc_{1/2}^{3+}Nb_{1/2}^{5+})O_3$                             | 4 900             | 80            |                     | FE                       | 2. 18                             | > 5.0   | D                | D,P               |
| $Pb(Fe_{1/2}^{3+}Nb_{1/2}^{5+})O_3$                             | 12 000            | 390           | 10                  | FΕ                       | 2. 29                             | > 5.0   | D                | D,P               |
| $Pb(Mg_{1/2}^{2+}Nb_{1/2}^{5+})O_3$                             | 18 000            | - 25          | 0. 1                | $\mathbf{FE}$            | 1.06                              | > 5.0   | D                | D,P               |
| Pb( $Zn_{1/2}^{2+}Nb_{1/2}^{5+})O_3$                            | 2 000             | - 130         | 1. 0                | FE                       | 1. 05                             | > 5.0   | D                | D,P               |

Table 1 Parameters of some typical  $A(B'B'') O_3$  compounds

O, D, and P in the last two columns represent Ordered, Disordered, and Partly Ordered<sup>[13]</sup>, respectively.



Fig. 3 Phase diagram of the order-disorder transition in A (B'B") O<sub>3</sub> complex perovskite crystals in the space of the ordering parameter M and the reduced temperature  $k_BT/J^{[13]}$ 



Fig. 4 Maximal order parameter  $(M_{\text{max}})$  of the  $\frac{1}{2}$  {111} -type (dashed) and  $\frac{1}{2}$  {110} -type (solid) ordered structures as functions of u when v = 0 at  $k_BT/J_1 = 3.0^{15}$ 

charge imbalance in the ordered domains, hence, the static electric energy increases with the growth of ordered domains. When the decrease of the free energy is compensated by the increase of the static electric energy, the growth of the ordered domains stops. So the space charge caused by the nonstoichimetric ordering is the main reason for the formation of nanoscale-ordered microregions in systems like PMN. Wu et al. [16] estimated the equilibrium size of the ordered microregions in PMN using a configurational thermodynamic approach. Considering the charge-imbalance effect, they constructed the Helmholtz free-energy function, in terms of the domain size. Their calculational results indicated that the equilibrium size of the ordered microregions was in the nanometer-size range, which agreed fairly well with the experimental observation. Recently, Jang et al.<sup>[17]</sup> suggests that the dispersion entropy term associtated with the formation/dispersion of the ordered microregions and the diffuse characteristic in the spatial distribution of the counter-charged ions around a given negatively charged ordered microregion also play a significant role in determining the equilibrium ordered microregion size. When ordering of  $Pb^{2+}$  and  $V_{Pb^{2+}}$  takes place on an A-site lattice, the charge imbalance may play a more important role in determining the crystal structure. The  $\frac{1}{2}$ {110}-type-ordered structure is perferred because the system has the smallest charge imbalance. The coexisting of three kinds of ordered structure in (Pb<sub>x</sub>Ca<sub>1-x</sub>) TiO<sub>3</sub> is believed to be caused by the fluctuation of effective ionic interactions. The CVM calculations suggest that different kinds of ordered structure may appear when the values of the effective interactions vary from one case to another.

Liu et al.<sup>[18]</sup> also conducted a CVM calculation to investigate the order-disorder transitions in complex perovskites. Without making any assumption on the form of the effective interaction parameter, J(R), they modeled  $(1 - x) A(B_c' B_{1-c}')$  $O_{3-x}AB''O_3$  as a three-component system (1-x) $(B_c'B_{1-c}'') \cdot xB'''$  on a simple cubic Bravais lattice. c is equal to 1/3 for 1.2 perovskites such as BMN-BZ, and equal to 1/2 for  $1 \cdot 1$  perovskites such as PST-PT. The driving mechanism responsible for the ordering is mainly the electrostatic interaction. In the case of c = 1/2, they introduced  $\sigma(\mathbf{R}) = -1$ , 0, or + 1 if **R** is occupied by B', B''' or B''; in the case of c = 1/3, they introduced  $\sigma(\mathbf{R}) = -2$ , 0, or + 1 for B', B''' or B''. The electrostatic energy between a pair of cations at R and R' can be reduced to

$$E_{\text{dec}}(\sigma, \sigma', \boldsymbol{R}, \boldsymbol{R}') = W(\boldsymbol{R} - \boldsymbol{R}')\sigma(\boldsymbol{R})\sigma'(\boldsymbol{R}')$$
(3)

The energy of the system with a certain configuration  $\{\sigma(\mathbf{R})\}$  can be expressed as

$$E(\{\sigma(\boldsymbol{R})\}) = E_0 + \frac{1}{2} \sum_{\boldsymbol{R}, \boldsymbol{R}'} W(\boldsymbol{R} - \boldsymbol{R}') \sigma(\boldsymbol{R}) \sigma'(\boldsymbol{R}')$$
(4)

where  $E \circ$  is a constant independent of  $\{\sigma(\mathbf{R})\}$ . Neglecting  $E \circ$ , the average energy is

$$E = \sum_{\{\sigma(\boldsymbol{R})\}} E(\{\sigma(\boldsymbol{R})\}) P(\{\sigma(\boldsymbol{R})\}) = \frac{1}{2} \sum_{\boldsymbol{R}, \boldsymbol{R}' \sigma, \sigma'} W(\boldsymbol{R} - \boldsymbol{R}') \sigma(\boldsymbol{R}) \sigma'(\boldsymbol{R}') X_{\sigma\sigma'}(\boldsymbol{R}, \boldsymbol{R}')$$
(5)

where  $P(\{\sigma(\mathbf{R})\})$  is the statistic probability of the configuration  $\{\sigma(\mathbf{R})\}$ , and  $X\sigma\sigma(\mathbf{R}, \mathbf{R}')$  is the pair occupation probability.

When the atomic interaction is long range, it is difficult to directly handle Eq. (5) with CVM since a large cluster should be used to contain the long range interaction. Therefore, some approximation should be made.

Let us expand  $X \sigma \sigma'$  (**R**, **R**') in a Fourier transform:

$$X \, \sigma \sigma'(\boldsymbol{R}, \boldsymbol{R}') = \sum_{\boldsymbol{k}, \boldsymbol{k}'} Q \, \sigma \sigma'(\boldsymbol{k}, \boldsymbol{k}') \times$$

$$\exp[i(\boldsymbol{k} \cdot \boldsymbol{R} + \boldsymbol{k}' \cdot \boldsymbol{R}')] \qquad (6)$$

and substitute it into Eq. (5). This yields

$$E = \frac{N}{2} \sum_{\sigma, \sigma', \mathbf{k}} V(\mathbf{k}) \, \sigma \sigma' Q \, \sigma \sigma'(\mathbf{k}, - \mathbf{k})$$
(7)

where  $V(\mathbf{k})$  is the Fourier transform of  $W(\mathbf{R})$ :

$$V(\boldsymbol{k}) = \sum_{\boldsymbol{R}} W(\boldsymbol{R}) \exp(i\boldsymbol{k} \cdot \boldsymbol{R})$$
(8)

For a certain ordered structure, only a few  $Q\omega(\mathbf{k}, -\mathbf{k})$  in Eq. (7) are nonzero under the singleparticle approximation<sup>[19,20]</sup>. Liu et al. assumed that this is still valid in their CVM calculation<sup>[18]</sup>. The assumption is not absurd since for any certain ordered structure only a few superlattices are experimentally observed.

The result of CVM calculation is depicted in Figs. 5 and 6, where the reduced temperature is defined as  $T^* = k_{\rm B}T/|V_{1/2}|$  and the long-range order parameter (LRO) is defined as

$$\eta = |P_i - P_j| \tag{9}$$

which represents the occupation-probability difference between nonequivalent sites. For the  $1/2\{111\}$ -type ordered structure, the ordering transition is of the second order, and  $\eta$  gradually decreases to zero with increasing temperature 0.4 r



Fig. 5 (a) LRO of the  $1/2\{111\}$ -type ordered structure as functions of reduced temperature  $T^* = k_B T/|V_{1/2}|$  at x = 0. 25 and c = 1/3. (b) LRO of the  $1/3\{111\}$ -type ordered structure as functions of reduced temperature at x = 0. 25 and c = 1/3. The reduced temperature is defined as  $T^* = k_B T/|V_{1/3}|^{1.18}$ 

(Fig. 5(a)). For the  $1/3 \{ 111 \}$ -type ordered structure, the ordering transition is of the first order, and  $\eta$  suddenly drops to zero at the transition temperature (Fig. 5(b)).

Figure 6 (a) shows that  $\eta_{B'}$  increases with decreasing x, while  $\eta_{B''}$  and  $\eta_{B'''}$  reach their maxima at about x = 0.25. The appearance of the maximum in LRO is consistent with the



Fig. 6 (a) LRO of the 1/2(111) -type ordered structure as functions of x at  $T^* = 0.5$  and c = 1/3. (b) Reduced free energies of the 1/2(111)-type (solid line) and 1/3(111)-type (dashed line) ordered structures as functions of x when c = 1/3,  $V_{1/2} = -1.4$ ,  $V_{1/3} = -1.0$ , and  $k_B T = 0.6 | V_{1/3} |$ . Inserted graphics is the case of c =1/2. (c) Combined phase diagram when c = 1/3.  $\alpha$ ,  $\beta$ , and  $\gamma$  designate disordered, 1/2 { 111 } -type and 1/3{111}-type ordered phases, respectively.  $V_{1/2} =$ -1.4,  $V_{1/3} = -1.0$ . The reduced temperature is defined as  $T^* = k_B T | V_{1/3} |$ <sup>[18]</sup>

experimental findings in BZT-BZ<sup>[21]</sup> and previous theoretical work<sup>[22]</sup>. The 1/3 {111}-type ordered phase appears at small x range, and the 1/2{111}type phase favors larger x values (Fig. 6(b)), which agrees with results in BMN-BZ<sup>[23]</sup>. The boundary of x values is determined by the crossing of the curves for the 1/2{111}-and 1/3{111}-type ordered phases. The combined phase diagram of the system is shown in Fig. 6(c). The phase region of the 1/3{111}-type ordered phase near x = 0 is located inside the region of the 1/2{111}type ordered phase and the critical temperatures of the order-disorder phase transition  $T_c$  decrease linearly with increasing x.

# 2 Model and Simulation of the Dielectric Mechanism

One of the characteristics of relaxor ferroelectrics is that the mean polarization  $\overline{P}$  decays to zero at a temperature  $T_{\rm f}$  which is well below  $T_{\rm m}$ , but both electron-optic and electronstrictive effects show  $\overline{P^2}$  persists to a that the RMS polarization temperature  $T_{D}$  (Fig. 1 (b)), which is several hundred degrees above  $T_{m}$ . It means that local, randomly oriented polar microregion began to exist below  $T^{\mathbf{D}}$ . Since Randall et al. pointed out that the nanoscale ordering is closely related with the relaxor characteristics, it is widely accepted that presence of the nanoscale ordering the micror egions isresponsible for the relaxor



Fig. 7 (a) Simulated and (b) experimental relation between the frequencies and the peak temperature,  $T_m$ . The straight line represents the *V*-*F* relationship<sup>[33]</sup>

behaviors. It was suggested that the nanoscale ordered microregions act as locations of polar microregions<sup>[24, 25]</sup>. Cross<sup>[25]</sup> pointed out that since the energy barriers to reorientation in any ferroelectrics are linearly related to the volume, at these very fine scales the electrocrystalline anisotropy energy  $\Delta H$  might become comparable to  $k_{\rm B}T$  leading to a super-paraelectric behavior at the higher temperature, which has been confirmed carefully by neutron spectroscopy. A key feature of the dielectric response is the strong dispersion in the weak field permittivity. Studies by Viehland et al.<sup>[26]</sup> have shown that the frequency/temperature  $(\omega, T_m)$  characteristics are nicely described by the Vogel-Fulcher relation (Fig. 7(b)) which suggests a slowing down and freezing into a glass like ensemble of nano-domains. Glassy polarization behavior is also found in relaxor, which means the correlations between polar microregions essential<sup>[27]</sup>.

A model hamiltonian in which the polar microregions are regarded as point dipoles and relaxors as a system consisting of Ising-like dipoles with randomly distributed interactions has been proposed by Gui et al<sup>[28-30]</sup>. The dynamics of the freezing process is simulated with the Monte Carlo method. The model hamiltonian is expressed as

$$H = -\sum_{i \neq j} \mathcal{J}_{i} \sigma_{i} \sigma_{j} - E_{\text{ext}} \overline{\mu} \sum_{i} \frac{|\mu_{i} \cos \theta_{i}|}{\overline{\mu}} \sigma_{i} (10)$$

where  $\sigma_i$ ,  $\sigma_j = \pm 1$  are dipole spins. When the projection of the *i*-th dipole moment  $\mu_i$  on the direction of the external field  $E_{\text{ext}}$  is positive,  $\sigma_i$ takes value + 1; otherwise,  $\sigma_i$  takes value - 1.  $\theta_i$  is the angle between  $\mu$  and  $E_{\text{ext}}$ , and  $\overline{\mu}$  is the maximal magnitude of the dipole moments.  $\mathcal{J}_{ij}$  is the effective interaction energy between the nearest neighbor dipoles, which is determined by several random variables, such as the volume, the polarization directions of polar microregions, and the distance between them. Then  $\mathcal{J}_{ij}$  in relaxors is a randomly distributed quantity, not like that in normal ferroelectrics  $(\mathcal{J}_{ij} = + \mathcal{J})$  or antiferroelectics  $(\mathcal{J}_{ij} = -\mathcal{J})$ . A Gussian distribution is assumed,

$$P(\mathcal{J}_{ij}) \propto \exp\left[-\frac{\mathcal{J}_{ij}^2}{2(\Delta J)^2}\right]$$
(11)

where  $\Delta J$  is the distribution width determined by the degree of crystal inhomogeneity.

The number of flipping times  $m^i$  for every dipole in a certain observation time  $t_{\rm obs}$  is recorded. The relaxation time of flipping  $\tau^{\rm flip}$  is



Fig. 8 (a) Proportion of the dipoles as a function of the number of flipping times during the observation time at various temperatures (in unit of  $\Delta J/k_{\rm B}$ )<sup>[29]</sup>. (b) Proportion of the frozen dipoles as a function of temperature<sup>[29]</sup>. (c) Remanent polarization as a function of temperature<sup>[28]</sup>

$$\tau_i^{\text{flip}} = \frac{t_{\text{obs}}}{m_i} \tag{12}$$

The distribution of  $\tau^{\text{flip}}$  is reflected by the distribution of the number of flipping times, which is shown in Fig. 8(a) (temperature is in units of  $\Delta J/k_{\text{B}}$ ). At low temperature, there are some dipoles with zero flipping number, i. e., no flipping at all, and they are defined as "frozen dipoles". When the temperature rises, the proportion of frozen dipoles drops (Fig. 8(b)),

and reaches zero at temperature  $T_{\rm f} = 1.5\Delta J/k_{\rm B}$ which is defined as "freezing temperature". The distribution curve reaches its maximum at low flipping frequencies, and drops rapidly with increasing frequency. This indicates that the relaxation time of most dipoles is longer at lower temperature, some of them are comparable with or even longer than  $t_{obs}$ , and these dipoles manifest the frozen properties during the observation time. "Slow dipoles" are defined as the dipoles whose number of flipping times  $m_i \leq m_0$ , which is the criterion of "slow". The frozen dipoles are the special case when  $m_0 = 0$ . The value of  $m_0$  is determined by the time scale used to observe the system, i. e., measuring frequencies. The proportion of slow dipoles  $P_s$  as a function of temperature is depicted in Fig. 9(a) when  $m^{0}=10$ , 20, and 30.

The susceptibility of the dipole system in the complete equilibrium state is  $X^{q} = \frac{1}{T}$ . Deduct the contribution of the slow dipoles and assume that other dipoles have high enough flipping frequencies to reach the equilibrium state. Then the susceptibility of the model system can be expressed as

$$CX = \frac{1 - P_s}{T} \tag{13}$$

where C is a constant independent of temperature. The calculated results are shown in Fig. 9(b). The increasing of m means that only those dipoles with more flipping times can keep up with the switching of the measuring field. Therefore, the bigger the m value is, the higher the measuring frequency is. It can be seen that when measuring frequency increases,  $\chi$  decreases dramatically. The diffuse behavior of susceptibility is affected by the following two factors when system changes from high temperature to low temperature: firstly, the flipping susceptibility of equilibrium dipoles increases; secondly, more and more dipoles become slow and frozen, and can not attend the process of flipping polarization. The competition of the two factors make X(T) reach its maximum at a certain temperature. Since the slowing and freezing of dipoles is a gradual process with the decreasing temperature, the phase transition of complex perovskite relaxor ferroelectrics is diffuse in a wide range of temperature.

The polarization of the model system is



Fig. 9 (a) Proportion of dipoles as a function of the temperature (in unit of  $\Delta J/k_B$ ), curve 1, 2, and 3 correspond to  $m_0 = 30$ , 20, and 10, respectively; (b) Susceptibility as a function of the temperature. Curve 1, 2, and 3 correspond to corresponding value of  $P_s$  in (a) <sup>[29]</sup>

$$P = \frac{\int_{t}^{t} d(t) \, dt}{t_{\rm f} - t_{\rm i}} \tag{14}$$

where  $\sigma(t)$  is the space averaged dipole at each Monte Carlo step. The remanent polarization  $P_r$ , i. e.,  $\overline{p}$  in Fig. 1(b), as function of temperature is shown in Fig. 8(c). It can be seen that  $P_r$  collapses near the freezing temperature  $T_{\rm f}=1.5\times \frac{\Delta J}{k_{\rm B}}$ , which agrees with the experiments<sup>[26,31]</sup>.

The dependence of the polarization on the initial state, the thermal and electrical histories are studied. Upon application of a dc external field, the polarization behaviors of slow heating are shown in Fig. 10(a). The results show that at low temperatures, a macroscopic polarization appears in the unpoled sample. The simulation results manifest most of the important features observed in experiments<sup>[27, 32]</sup>. Figure 10 (b) shows the cooling processes started from  $T > T^{r}$ . No macroscopic polarization exists under zero bias.



Fig. 10 Polarization as a function of temperature (in unit of  $\Delta J/k_B$ ). (a) Started from the poled(+) and unpoled( $\blacktriangle$ ) initial states in the slow heating process under the external field  $E = 0.6\Delta J/\bar{\mu}$ . (b) Under external field  $E = 0(\triangle)$  and  $E = 0.2\Delta J/\bar{\mu}(+)$  in the slow cooling process started from a temperature far above  $T_f$ . (c) Under zero bias in the slow cooling process started from various temperatures below  $T_f$  and the poled initial state. The dashed line represents the remanent polarizations shown in Fig. 8(c)<sup>[25]</sup>

The polarization increases with the increasing of the external field. A saturation is observed at  $T < T^{f}$ . When the cooling is started from  $T > T^{f}$ , the processes are not influenced by the initial state. The case is different when the simulation is started from a temperature below  $T^{f}$ . When starting from a poled initial state, the remanent polarization corresponding to the starting temperature is remained through the cooling process except a slight decrease due to the elongation of observation time (shown in Fig. 10(c)). The same behavior has been observed in experiments.

Very recently Duan et al.<sup>[33]</sup> performed the same Monta Carlo simulation as Gui et al. did. Different from Gui's work, they analyzed the simulation result by the fluctuation-dissipation theory. The auto-correlation function of the total magnetization is as follows:

$$C(t) \equiv M(0)M(t) \rangle =$$

$$N \int_{0}^{\infty} d\tau g(\tau, T) \exp(-t/\tau) \qquad (15)$$

where M(t) is the sum of moments of all dipoles at time t, and  $g(\tau, T)$  is the relaxation time distribution. Using the fluctuation dissipation theory, the imaginary part of the dielectric permittivity is expressed by  $g(\tau, T)$ :

$$\epsilon''(\omega) = \frac{\omega}{2T} \int_{0}^{\infty} dt \exp(i\omega) C(t) = \frac{N}{T} \int_{0}^{\infty} \frac{g(\tau, T) \omega \tau d\tau}{1 + (\omega \tau)^{2}}$$
(16)

Using the Kramer-Kroning relation, the real part of dielectric permittivity is as follows:

$$\epsilon' = \frac{N}{T} \int_{0}^{\infty} \frac{g(\tau, T) \,\mathrm{d}\tau}{1 + (\omega \tau)^2} \tag{17}$$

The imaginary parts of permittivity,  $\epsilon''$ , as a function of the temperature are plotted at different measuring frequencies in Fig. 11. With increasing measuring frequencies, the peak value of  $\epsilon''$  increases and the  $T_m$  shifts to high temperature. The relation  $T_m$  and the relaxion times (see Fig. 7 (a)) could be expressed as the Vogel-Fulcher relationship:

$$\omega = \omega_{\rm b} \exp\left[-\frac{E}{k_{\rm B}(T_{\rm m}-T_{\rm 0})}\right] \qquad (18)$$

where the effective energy barrier,  $E \approx 1.95 \Delta J / k_B$ and  $T_0 \approx 0.53 \Delta J / k_B$ . The main features given by Monte Carlo simulation agree very well with the experimental results.



Fig. 11 Simulation results for imaginary part of dielectric permittivity at different frequencies: from bottom to top, 16, 32, 64, and 96. The frequencies are normalized by the inverse of entire observation time<sup>[33]</sup>

The effects of the applied ac field on relaxors are of great interest since they provide some clues of the relaxation mechanism. Glazounov et al.<sup>[34]</sup> observed that the dielectric permittivity of PMN increases with increasing amplitude of the applied ac field. A similarity was also found between the effects of the amplitude and frequency on the permittivity. Dielectric behavior involving only the ac field, i.e.,

$$E_{\text{ext}} = E_0 \exp\left(i2\pi \frac{t}{t^{\text{L}}}\right) \qquad (19)$$

is simulated with Monte Carlo method<sup>[35]</sup>, where t is the real time.  $E_0$  and  $t_{\perp}$  are the amplitude and the period of the ac field, respectively.

The dielectric susceptibility is defined as

$$X = C \frac{\frac{1}{t^{\text{obs}}} \int_{t_0}^{t_0^{+t_{\text{obs}}}} p(t) \exp\left[i2\pi \frac{t}{t_{\text{L}}}\right] dt}{\langle E_{\text{ext}} \rangle}$$
(20)

where C is a proportional factor which is chosen to be 1. in this contribution, and  $f(\cdot, \cdot)$  denotes the configurational averaging. The susceptibility curves under different ac-field amplitudes  $E_0$  are depicted in Fig. 12 (a) when the measuring frequency is kept as  $t_{\rm L} = 10$  MCS/dipole. From Fig. 12(a) one can list the most essential features of the nonlinear effect: (1) the dielectric susceptibility increases with increasing  $E_0$  at

![](_page_9_Figure_6.jpeg)

Fig. 12 Dielectric susceptibility at various field amplitudes,  $E_0(1-0.5, 2-1.0, 3-1.5, 4-2.0\Delta J/\bar{\mu})$ . (a) The field frequency is kept as  $t_{\rm L}=10$  MCS/ dipole. Inserted graphics is the imaginary part of susceptibility. (b) The field frequency is kept as  $t_{\rm L}=50$  MCS/ dipole<sup>[35]</sup>

temperature  $T < T_{\rm m}$  where the frequency dispersion is observed; (2) increasing  $E_0$  will make the maximum in the temperature dependence of X shift to lower temperatures, which has the similar effect of decreasing frequency (also see Fig. 9(b)). The change of the imaginary part, X'', shows similar features in the simulation. These features agree with the experiments in PMN<sup>[34]</sup> very well. The concepts of "slow dipole" and "fast dipole" can help to understand the increasing of the susceptibility. Slow dipoles are those dipoles which flip too slow to keep up with the changing of the ac field and give no or little contribution to the dielectric susceptibility. At low temperatures, there are large amounts of slow dipoles. When  $E_0$ increases, the driving force on slow dipoles is enhanced. Slow dipoles are forced to flip faster, and consequently contribute more to the dielectric susceptibility  $\chi$  which is consistent with the curves of X as functions of the amplitude  $E_0$  for different temperatures when the measuring frequency is fixed (Fig. 13). Figure 12 (b) demonstrates the field dependence of X at different measuring frequencies and a fixed temperature T =1.  $5\Delta J/k_{\rm B}$ . It shows that the maximum of the curve shifts to lower field amplitude with decreasing measuring frequency. The shapes of curves are similar for different frequencies.

![](_page_9_Figure_10.jpeg)

Fig. 13 Field amplitude ( in units of  $\Delta J/\bar{\mu}$ ) dependence of dielectric susceptibility at a fixed field frequency  $t_{\rm L}$ = 10 MCS/dipole. Curves 1 - 5 correspond to temperatures T= 0. 5, 1. 5, 2. 5, 3. 5, and 4.  $5\Delta J/k_{\rm B}$ , respectively.

The Eq. (20) could be generalized to include the Fourier component at different frequencies rather than that of  $E_{\text{ext}}$ . Figure 14 gives the curve of  $\chi_{2\omega}/\chi$ , where  $\chi_{2\omega}$  is the second-order component of the susceptibility. It can be seen that  $\chi_{2\omega}/\chi$  is larger at lower  $E_{\text{ext}}$  and T.

![](_page_10_Figure_1.jpeg)

Fig. 14 Temperature dependence of  $\chi_{2\omega}/\chi$  at various field amplitudes,  $E_0(1-0.5, 2-1.5\Delta J/\bar{\mu})$ . The field frequency is kept as  $t_L = 10$  MCS/ dipole<sup>[35]</sup>

### **3** Summaries

In this paper, an overview is presented on the order-disorder structural transitions and the dielectric mechanism in the relaxors, which are very important in actual applications due to their excellent dielectric and piezo-electric properties. The special macroscopic properties of relaxors are closely related to the order-disorder microscopic structure The influences of composition, temperature, and atomic interactions on the orderdisorder microstructures can be well understood in CVM calculations. The electrostatic interaction is the main driving force of ordering, and the space charge caused by the nonstoichimetric ordering is the main reason for the formation of the nanoscaleordered microregions in systems. The criterion drawn from theoretical analysis is successful in predicting the order-disorder structure of relaxors. In the aspect of the dielectric mechanism of relaxors, emphasis is put on the introduction of the dipole glassy model that described the dielectric response as the thermally activated flips of the local spontaneous polarization under random interactions. The Monte Carlo simulation results of this model are consistent with the linear and nonlinear experiments of relaxors, which suggests that the model captures the main ingredient of physics, i.e., the randomness and frustration due to competing interactions between the polar microregions are responsible for the special dielectric characteristics of relaxors.

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![](_page_11_Picture_19.jpeg)

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Professor Gu received the awards for Progress in Science and Technology given by the National Education Commission (Ministry of Education, China) in 1989, 1995, 1999, and 2001 and a second class award of 2000 National Prize of Natural Science.

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