

Piezoelectricity and ferroelectric cluster size in relaxor ferroelectrics

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The dipole configuration and electromechanical behaviors of dipole-disorder induced relaxor ferroelectrics (RFs) are investigated using a phenomenological model. In comparison to normal ferroelectric lattice, the RF lattice shows spatially inhomogeneous cluster configuration but no breaking of the dipole orientation symmetry is identified. A clean relationship between the piezoelectric response and the characteristic size of the ferroelectric clusters is established, which predicts a broad peak of the piezoelectric coefficient in response to the dipole disorder degree.

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The enhanced electromechanical performance of some relaxor ferroelectrics (RFs) has been a research focus in the last ten years;^{1,2} however, its origin remains not yet completely understood. Since the morphotropic boundary (MPB) was identified in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) and other important lead-based piezoelectric solid solutions, the high piezoelectricity was explained via the polarization rotation mechanism,^{3,4} where the key point is that polarization vector P can rotate freely within the mirror plane of monoclinic (MO) phase instead of being confined along a particular symmetry axis, as well believed in rhombohedral (RH) or tetragonal (TE) phase.⁵ Recently, this understanding was questioned by Glazer *et al.*,⁶ who argued from their electron diffraction analysis that no MPB exists, because both the RH and TE phases are really MO phase although they exhibit different correlation lengths of ferroelectric (FE) orders. This picture obtained confirmation from a series of experiments.^{7,8}

On the other hand, macroscopic piezoelectricity in Nd-doped PZT was observed at temperature (T) above the point at which the dielectric permittivity is maximized, and this effect was ascribed to the existence of dipole nano regions and their correlation.⁹ These works allow us to consider the relationship between piezoelectricity and characteristic size of the FE clusters regardless of the details of the microscopic symmetry, and this issue has not been addressed so far. It is widely accepted that relaxor ferroelectric (RF) lattice is facilitated with nanosized FE clusters embedded in the paraelectric (PE) matrix.¹⁰ These nanosized FE clusters may be implemented by disordering a normal FE lattice of long-range dipole order, i.e., by dipole disorder. In this letter, we start from a phenomenological model for FE lattice, which can evolve into RFs by dipole disorder.¹¹ By investigating the FE cluster patterns and their sizes in such a RF lattice, we develop the relationship between the piezoelectric response and the characteristic size of the FE clusters, and predict that an optimized cluster size favors an enhanced piezoelectric effect.

In order to construct a RF lattice with dipole disorder, we start from the well known Ginzburg-Landau-Devonshire theory and the free energy functional F for a FE lattice with local dipole $\mathbf{P}(\mathbf{r})$ and displacement $\mathbf{u}(\mathbf{r})$ at site \mathbf{r} is¹²

$$F[\mathbf{P}(\mathbf{r}), \mathbf{u}(\mathbf{r})] = \int (f_{\text{ld}} + f_g + f_u + f_{\text{es}} + f_E) d\mathbf{r}, \quad (1)$$

where f_{ld} , f_g , f_u , f_{es} , and f_E are the Landau potential, gradient energy, elastic energy, electrostrictive interaction, and static electric energy, respectively. This model is a coarse-grained semimacroscopic one and $\mathbf{P}(\mathbf{r})$ should be considered as an average of local dipoles over a number of sites. For a $2d$ square lattice in x - y plane with periodic boundary conditions, the Landau potential is

$$f_{\text{ld}}(\mathbf{P}(\mathbf{r})) = A_1(P_x^2 + P_y^2) + A_{11}(P_x^4 + P_y^4) + A_{12}P_x^2P_y^2 + A_{111}(P_x^6 + P_y^6) + A_{112}(P_x^4P_y^2 + P_y^4P_x^2), \quad (2)$$

where A_{11} , A_{12} , A_{111} , and A_{112} are the coefficients independent of T and $A_1 < 0$ and $A_{11} > 0$ are required for first-order FE transitions. The dipole disorder is introduced by imposing fluctuations to coefficient A_1 via the following scheme:

$$A_1(r) = A_{10}(T - T_c) + c(r) + \sum_R c(r+R)R^{-a}, \quad (3)$$

where R represents the sites neighboring site r , $T_c = 3.0$ is the critical point, and $c(r) = 0$ or $c(r) \in [(-b_M, 0)U(0, b_M)]$ labels to the perfect order regions or dipole disorder ones, respectively, with b_M the strength of disorder imposed to the lattice. Exponent a refers to the effect of dipole disorder on sites $r+R$ other than site r itself, and we choose $a=2$ in this work. For the present simulation, we choose $T=1.0 < T_c$. The degree of dipole disorder is measured by C , the percentage of sites with $c(r) \neq 0$, while C_p scales the ratio of sites with $c(r) > 0$.

It should be mentioned here that the dipole disorder may be introduced via schemes other than the present one. The essential point of this work is the relationship between the piezoelectricity and the characteristic size of the FE clusters in a typical RF lattice with nano-sized FE clusters embedded in the PE matrix, while the physical soundness of the scheme to generate the dipole disorder is not of special significance. Given the RF lattice with FE clusters randomly embedded in the PE matrix, one may denote the two-point correlation function of $P(r)$ by $\rho(R)$, which writes $\rho(R) = \langle \mathbf{P}(\mathbf{r}) \cdot \mathbf{P}(\mathbf{r}+\mathbf{R}) \rangle$, where the bracket $\langle \rangle$ represents averaging over the whole lattice. As well known, by excluding the harmonic contribution, $\rho(R)$ decays exponentially with increas-

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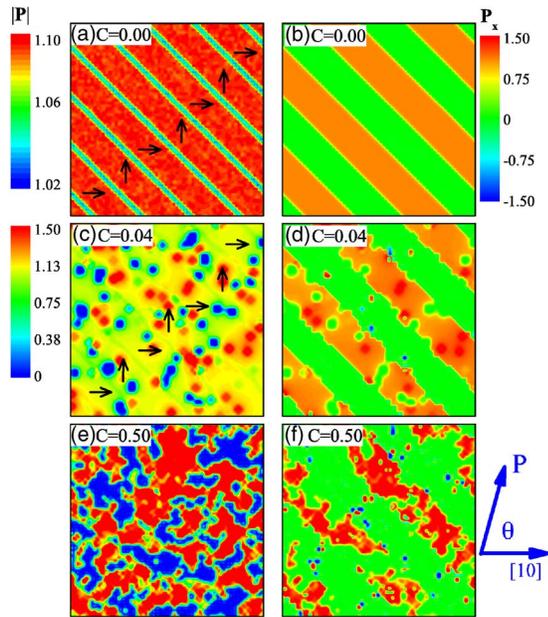


FIG. 1. (Color online) Simulated local dipole pattern at $T=1.0$, where the colors represent magnitude $|P(r)|$ (left column) and the $[10]$ -component $P_x(r)$ (right column) for lattices with different C , separately.

ing R , i.e., $\rho(R) \sim \exp(-R/L_{\text{FE}})$, where L_{FE} is the characteristic size of the FE clusters.¹³ Therefore, one has

$$L_{\text{FE}} = \int R\rho(R)dR / \int \rho(R)dR, \quad (4)$$

which can be used to evaluate L_{FE} , the characteristic size of the FE clusters, noting that the interval for the integration is $[0, L/2]$ in practical calculation, where L is the lattice dimension.

The coupled set of time-dependent Ginzburg-Landau (TDGL) equation is employed to simulate the temporal evolution of local $P(r)$ and $u(r)$,

$$\partial P_i(\mathbf{r}, t) / \partial t = -L_P \delta F / \delta P_i(\mathbf{r}, t),$$

$$\partial u_i(\mathbf{r}, t) / \partial t = -L_u \delta F / \delta u_i(\mathbf{r}, t) \quad (i = x, y), \quad (5)$$

where L_P and L_u are the evolution kinetic coefficients for P and u , respectively. The calculation is performed via Euler algorithm by a finite difference scheme for spatial and time derivatives in the $L \times L$ lattice, with lattice spacing $\Delta L=1.0$ and time step $\Delta t=0.001$ for numerical stability. The details of other energy terms and coefficients, which are chosen to simulate the FE phase of TE structure, with spontaneous polar (SP) axis along $\langle 10 \rangle$, could be found in our previous work.¹² From the lattice initialized by employing the scheme reported earlier,¹⁴ the SP at $T=0$ and external electric field $E=0$ is obtained. Then the set of TDGL equation is solved by quasistatically varying T and E , in order to simulate the effect of T and E . The data presented below are taken after a sufficiently long time of evolution of the lattice towards the equilibrium configurations.

Some simulated local $P(r)$ configurations are shown in Fig. 1, where the colors represent the magnitude $|P(r)|$ (left column) and the x component $P_x(r)$ (right column). To clarify the effect of the dipole disorder, the normal ferroelectric (NF) lattice with $C=0$ is shown in Figs. 1(a) and 1(b), where the perfect twin-domain structure (α -FE phase with

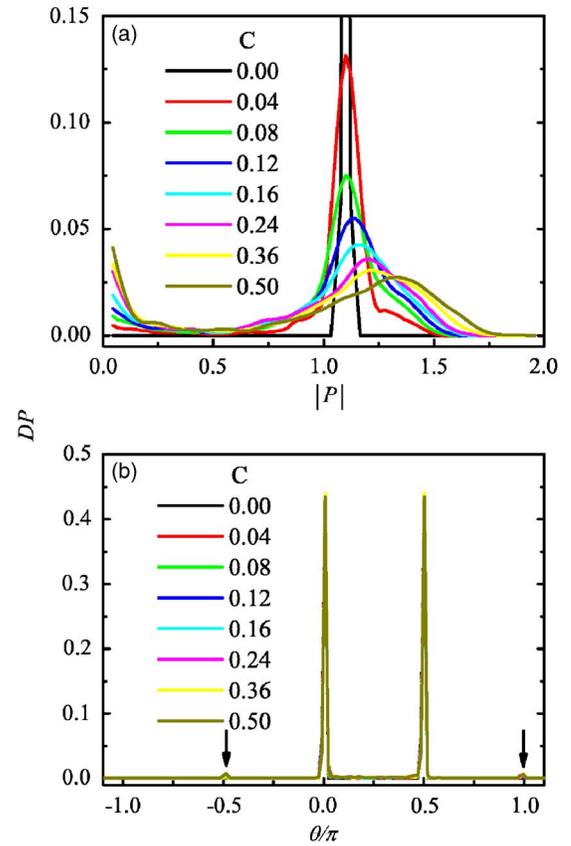


FIG. 2. (Color online) Distribution function DP of the local dipoles in terms of (a) magnitude $|P|$ and (b) angle θ for lattices with different C .

either $P_x \sim 1.1$ or $P_y \sim 1.1$) is demonstrated. It is revealed that $|P(r)|$ is spatially homogenous, i.e., $|P(r)| \approx P_\alpha = 1.1$ for all lattice sites except those within the cluster boundaries, where P_α is the saturated value at $C=0$. By slightly introducing the dipole disorder ($C=0.04$), the homogeneous α -FE phase is broken. For those sites with $c(r) > 0$, the FE order is suppressed and $|P(r)| \approx 0$ identifies the disorder-induced small-sized PE regions. On the other hand, for those sites with $c(r) < 0$, the FE order is enhanced and the disorder-induced FE regions with $|P(r)| \approx P_\beta > P_\alpha$, which will be denoted as β -FE phase hereafter, are generated. The PE phase and β -FE phase are embedded in the α -FE phase [Fig. 1(c)]. The striplike pattern for the FE order is maintained, as given in Fig. 1(d).

When more dipole disorder is introduced (e.g., $C=0.5$), one observes the formation of typical RF lattice: the islands of PE and β -FE phases are well developed, leading to highly dispersed and small α -FE clusters in coexistence with the PE and β -FE phases, as demonstrated by the highly contrasted pattern shown in Fig. 1(e). In correspondence, $P_x(r)$, as shown in Fig. 1(f), is characterized by irregular β -FE clusters smaller in size than those for $C=0.04$.

To further illustrate these facts, we present in Fig. 2 the distribution of the local dipoles (DP) in terms of the magnitude $|P|$ and angle θ for different C . For the NF lattice ($C=0$), there is a sharp peak at $|P|=P_\alpha$ and DP=0 for other $|P|$, corresponding to the homogenous α -FE phase. For the lattice with small C , the peak becomes broader at larger C , identifying the inhomogeneous distribution of $|P|$ centered at P_α . The peaks shift to large $|P|$ for the lattices with $C > 0.15$, which means the dominance of the β -FE phase

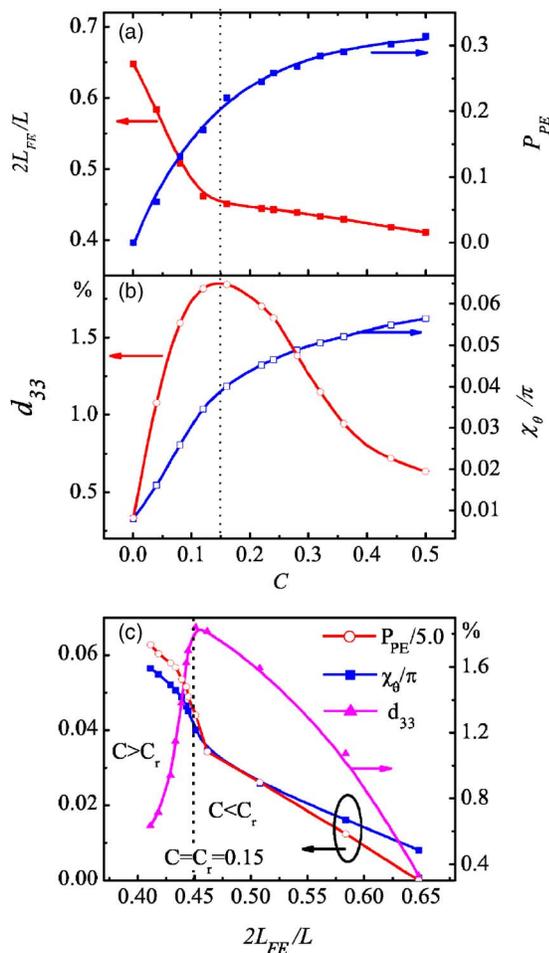


FIG. 3. (Color online) (a) Characteristic cluster size L_{FE} (normalized by $L/2$) and percentage of PE phase, P_{PE} , and (b) rotation ratio χ_θ and longitudinal piezoelectric coefficient d_{33} as a function of C , respectively. (c) Parameters P_{PE} , χ_θ , and d_{33} as functions of $2L_{FE}/L$.

with large magnitude. Meanwhile, the PE phase, which is characteristic by $|P| \approx 0$, increases with increasing C . We plot the percentage of the PE phase, P_{PE} , as a function of C in Fig. 3(a). $P_{PE}=0$ for the normal FE lattice and increases gradually with increasing C , while the β -FE phase increases too. In Fig. 3(a) is also plotted the characteristic size L_{FE} which measures the size of the FE clusters (α -FE and β -FE). There is a distinct inflexion point in the $L_{FE}(C)$ curve at $C=C_r \approx 0.15$, which could be considered as a critical point. With increasing C , L_{FE} decreases sharply for $C < C_r$ and then decays more slowly for $C > C_r$.

On the other hand, different from $DP(|P|)$, distribution function $DP(\theta)$ with respect to θ are much independent of C [Fig. 2(b)]. The sharp peaks at $\theta=0$ and $\theta=\pi/2$ show invisible change even for $C=0.5$, although two very small peaks at $\theta=\pi$ and $\theta=-\pi/2$ could be observed (indicated by arrows). This confirms that the dipole disorder only reduces the size of FE clusters but does not change the dipole orientation configuration, which means that the RF lattice reserves the TE structure locally, same as the normal FE lattice.

It was indicated that the rotation and electromechanical behaviors of the small-sized FE clusters associated with the peaks at $\theta=\pi$ and $\theta=-\pi/2$ do not contribute to the piezoelectric effect unless E is high enough so that $E > E_f$, the critical field for the reversal of the disorder-induced FE clusters orientating along $[\bar{1}0]$ or $[0\bar{1}]$.¹² In the present case, E

$\ll E_f$, and then no significant effect of these small sized FE clusters could be possible. The piezoelectric effect is usually ascribed to the rotation of polarization. Therefore, the major contribution to the piezoelectricity comes from the rotation of the FE clusters with $\theta=0$ and $\theta=\pi/2$. This allows us to argue that the piezoelectric behavior is essentially attributed to the spatial correlation of the FE clusters in the RF lattice.

When a small E is applied along one of the polar directions [10], the rotation angle is a linear function of E . We define the rotation ratio χ_θ as the average of term $(d \langle \theta \rangle / dE)$ within $-1.0 < E < 1.0$, and plot it as a function of C in Fig. 3(b). Clearly, χ_θ increases with increasing C . The longitudinal piezoelectric coefficient d_{33} is defined as an average of term $(d\eta^{[10]} / dE^{[10]})$ within $-1.0 < E < 1.0$, where $\eta^{[10]} = \langle Q_{11}P_x^2 + Q_{12}P_y^2 \rangle$ and Q_{11} and Q_{12} are the piezoelectric coefficients and $\langle \rangle$ represents average over the whole lattice. d_{33} shows a broad peak centered at $C=C_r$. It is observed that with increasing C , d_{33} increases for $C < C_r$ and decreases for $C > C_r$. To identify the relationship between the piezoelectric response and the characteristic size of the FE clusters, we plot P_{PE} , χ_θ , and d_{33} as functions of L_{FE} in Fig. 3(c). For $C < C_r$, both χ_θ and d_{33} increase with decreasing L_{FE} , indicating that it is easier to rotate the polarization by E when the FE clusters is smaller and thus introduce higher piezoelectricity. At the critical $L_{FE}=0.45$, corresponding to $C=C_r$, while P_{PE} increases sharply with decreasing L_{FE} . Thus, the local strain induced by the rotation of FE clusters is relaxed due to the existence of the PE phase if $C > C_r$. In other words, for $C > C_r$, the FE clusters cannot respond to external E effectively in the cooperative form in order to facilitate the macroscopic strain, resulting in decreasing d_{33} with C as $C > C_r$. The maximal value of d_{33} is located at $L_{FE}=0.45$, where the FE clusters not only have large rotation ratio but can also respond to external E in the cooperative form. This value of L_{FE} corresponds to the lattice with an optimal dipole disorder degree ($C=C_r$).

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¹S.-E. Park and T. R. Shroud, J. Appl. Phys. **82**, 1804 (1997).

²S. Priya and K. Uchino, Appl. Phys. Lett. **81**, 2430 (2002).

³B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic, London, 1971), 152.

⁴A. K. Singh and D. J. Pandey, Phys. Rev. B **67**, 064102 (2003).

⁵L. Bellaiche, A. Garcia, and D. Vanderbilt, Phys. Rev. Lett. **84**, 5427 (2000).

⁶A. M. Glazer, P. A. Thomas, K. Z. Baba-Kishi, G. K. H. Pang, and C. W. Tai, Phys. Rev. B **70**, 184123 (2004).

⁷R. Haumont, P. Gemeiner, B. Dkhil, J. M. Kiat, and A. Bulou, Phys. Rev. B **73**, 104106 (2006).

⁸A. K. Singh, D. Pandey, and O. Zaharko, J. Appl. Phys. **99**, 0706105 (2006).

⁹I. Franke, K. Roleder, L. Mitoseriu, R. Pitorescu, and Z. Ujma, Phys. Rev. B **73**, 144114 (2006).

¹⁰B. E. Vugmeister and M. D. Glinchuk, Rev. Mod. Phys. **62**, 993 (1990).

¹¹J. B. Keith and D. M. Hatch, J. Appl. Phys. **100**, 033526 (2006).

¹²L.-F. Wang and J.-M. Liu, Appl. Phys. Lett. **90**, 062905 (2007).

¹³J. T. Chayes, L. Chayes, D. S. Fisher, and T. Spencer, Commun. Math. Phys. **120**, 501 (1989).

¹⁴R. Ahluwalia, T. Lookman, A. Saxena, and W. Cao, Phys. Rev. B **72**, 014112 (2005).