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DEFECT STABILIZED PERIODIC AMPLITUDE MODULATIONS IN FERROELECTRICS

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Theoretical analysis shows that the total free energy of a ferroelectric system with free boundary conditions increases with the number of the inhomogeneous regions, such as domain walls and other modulated structures. However, charged defects could lower the total energy of a ferroelectric system by interacting with charge density fluctuations in inhomogeneous regions. We discuss a special kind of inhomogeneous microstructure in a lanthanum doped lead titanate, the amplitude modulations, which can be stabilized by aliovalent dopants.

KEY WORDS: Defects, precursor, modulations, ferroelectrics, doping

1 INTRODUCTION

There are many known microstructures in ferroic systems, such as twinbands, microtwinning, tweed, etc., particularly in many proper and improper ferroelastic systems (Tanner, Pelton and Gronsky, 1982; Clapp, Rifkin and Tanner, 1988; Osjima, Sugiyama and Fujima, 1988) including high T_c-superconductors (Schmahl *et al.*, 1989). In many cases, complex microstructure originate from localized stress or strain due to defect doping (Cao and Krumhansl, 1990; Falk, 1982; Salje, 1990).

These microstructures not only fascinate scientists but also control the physical properties of ferroic materials. They have a strong dependence on the nature and number of defects in the system. In some cases, an intrinsic excitation of the system is the driving force for the ordering of the defects and these ordered defects play the role of pinning centers to stabilize the intrinsic excitations of the system which otherwise will be unstable or metastable.

Recently a new type of spatial amplitude modulations was reported in a lanthanum doped lead titanate solid solution system, $Pb_{1-ay}La_yTiO_3$, as shown in Figure 1 (Randall, Rossetti and Cao, 1994; Rossetti, Cao and Randall, 1994). Figures 1(a)–(d) are the bright-field image of the microstructures for La content of 1%, 5%, 10%, and 25%. One can see that a modulation is developing with the lanthanum content and it is most pronounced in Figure 1(c) where clear modulations are shown inside each of the domains. Through the change of the image conditions it is found that the modulations are not microtwinning; instead, they are amplitude modulations with the polarization directions

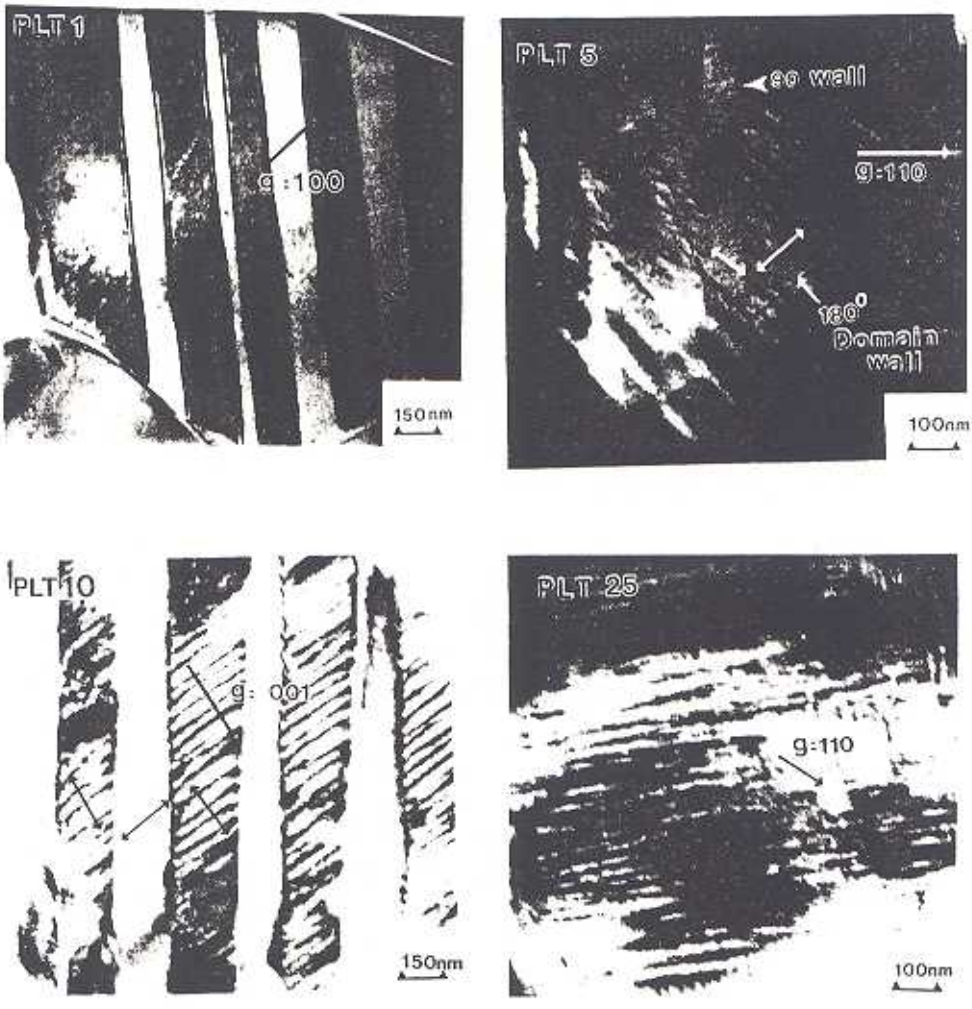

Figure 1 Bright field image of microstructures in a solid solution series $(Pb_{1-3x/2}La_x)TiO_3$. (a) 1% at. La – only the regular domain structure. (b) 5% at. La – some texture inside the domains; (c) 10% at. La – periodic modulations inside the domains; (d) 25% at. La show no regular domains (after Randall, Rossetti and Cao, 1993).

unchanged (Randall, Rossetti and Cao, 1994; Rossetti, Cao and Randall, 1994). In other words, the wave vector of the modulation is oriented in the same direction as that of the polarization.

Obviously, from the sequence of Figure 1, this modulated structure is induced by the lanthanum dopants. This is the result of the interaction between these aliovalent dopants and an inhomogeneous periodic excitations in the system. In what follows, we will derive these intrinsic excitations in a system with a first-order phase transition by using the Landau-Ginzburg theory, and also discuss the mechanism for the formation of the

microstructures shown in Figure 1(c) in terms of defect stabilization of metastable and/or unstable microstructures of a pure system.

2 LANDAU-GINZBURG MODEL

Cao and Cross (1991) have developed a continuum model for the O_h-C_{4v} proper ferroelectric phase transition based on Landau-Ginzburg theory. The free energy density can be written as the following:

$$F(P_i, P_{i,j}, \eta_{kl}) = F_L(P_i) + F_{el}(\eta_{kl}) + F_c(P_i, \eta_{kl}) + F_G(P_{i,j}) \tag{1}$$

where $F_L(P_i)$ is the Landau energy for the polarization,

$$\begin{aligned} F_L(P_i) &= \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^2 + P_2^2 + P_3^2)^2 + \alpha_{12}(P_1^2P_2^2 + P_2^2P_3^2 \\ &\quad + P_1^2P_3^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) + \alpha_{112}[P_1^4(P_2^2 + P_3^2) \\ &\quad + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 + P_2^2)] + \alpha_{123}P_1^2P_2^2P_3^2, \end{aligned} \tag{2}$$

$F_{el}(\eta_{kl})$ is the elastic energy of the system,

$$\begin{aligned} F_{el}(\eta_{kl}) &= \frac{C_{11}}{2}(\eta_{11}^2 + \eta_{22}^2 + \eta_{33}^2) + C_{12}(\eta_{11}\eta_{22} + \eta_{11}\eta_{33} + \eta_{22}\eta_{33}) \\ &\quad + 2C_{44}(\eta_{12}^2 + \eta_{13}^2 + \eta_{23}^2), \end{aligned} \tag{3}$$

$F_c(P_i, \eta_{kl})$ represents the coupling between the primary and the secondary order parameters,

$$\begin{aligned} F_c(P_i, \eta_{kl}) &= -q_{11}(\eta_{11}P_1^2 + \eta_{22}P_2^2 + \eta_{33}P_3^2) - q_{12}[\eta_{11}(P_2^2 + P_3^2) + \eta_{22}(P_1^2 + P_3^2) \\ &\quad + \eta_{33}(P_1^2 + P_2^2)] - 2q_{44}(\eta_{12}P_1P_2 + \eta_{13}P_1P_3 + \eta_{23}P_2P_3), \end{aligned} \tag{4}$$

and $F_G(P_{i,j})$ is the lowest order gradient energy which has the independent invariant form of

$$\begin{aligned} F_G(P_{i,j}) &= \frac{1}{2}g_{11}(P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2) + g_{12}(P_{1,1}P_{2,2} + P_{1,1}P_{3,3} + P_{2,2}P_{3,3}) \\ &\quad + \frac{g_{44}}{2}[(P_{1,2} + P_{2,1})^2 + (P_{1,3} + P_{3,1})^2 + (P_{2,3} + P_{3,2})^2]. \end{aligned} \tag{5}$$

The physical meaning of the expansion coefficients can be found in the original paper of Cao and Cross (1991), and all the coefficients are assumed to be independent of temperature except α_1.

$$\alpha_1 = \alpha_0(T - T_o). \tag{6}$$

Minimizing the free energy Equation (1) with respect to the polarization and the elastic displacement field give the following solutions for a homogeneous system (Cao and Cross, 1991):

(i) For $T > T_1$,

where

$$T_1 = T_o + \frac{\alpha_{11}'^2}{3\alpha_o\alpha_{11}}, \quad \alpha_{11}' = \alpha_{11} - \frac{\hat{q}_{11}^2}{6\hat{C}_{11}} - \frac{\hat{q}_{22}^2}{3\hat{C}_{22}},$$

and

$$\begin{aligned} \hat{C}_{11} &= C_{11} + 2C_{12}, \\ \hat{C}_{22} &= C_{11} - C_{12}, \\ \hat{q}_{11} &= q_{11} + 2q_{12}, \\ \hat{q}_{22} &= q_{11} - q_{12}, \end{aligned}$$

we have the solution for the cubic phase,

$$P_i = 0, \quad \eta_{ij} = 0, \quad (i, j = 1, 2, 3). \tag{7}$$

(ii) For $T_1 > T > T_c$, where $T_c = T_o + \frac{\alpha_{11}'^2}{4\alpha_o\alpha_{111}}$ is the phase transition temperature, there are two solutions:

(a) $$P_i = 0, \quad \eta_{ij} = 0, \quad (i, j = 1, 2, 3); \tag{8}$$

(b) $$\vec{P} = (\pm P_T, 0, 0), \quad (0, \pm P_T, 0), \quad (0, 0, \pm P_T), \tag{9}$$

with

$$P_T = \sqrt{\frac{-\alpha_{11}' + \sqrt{\alpha_{11}'^2 - 3\alpha_1\alpha_{111}}}{3\alpha_{111}}}, \tag{10}$$

$$\eta_{\parallel} = \frac{P_T^2}{3}\left(\frac{\hat{q}_{11}}{\hat{C}_{11}} + \frac{2\hat{q}_{22}}{\hat{C}_{22}}\right), \tag{11}$$

$$\eta_{\perp} = \frac{P_T^2}{3}\left(\frac{\hat{q}_{11}}{\hat{C}_{11}} - \frac{\hat{q}_{22}}{\hat{C}_{22}}\right), \tag{12}$$

$$\eta_{ij} = 0, (i \neq j), \quad (i, j = 1, 2, 3). \tag{13}$$

Here $\eta_{\parallel}$ and $\eta_{\perp}$ are the normal strain components in the directions parallel and perpendicular to the tetragonal axis in each of the three tetragonal states, respectively, P_T is the amplitude of the spontaneous polarization in the tetragonal phase.

Solution (a) represents a thermodynamically stable cubic phase and (b) indicates that an additional tetragonal metastable phase also exists in this temperature region. This metastable phase can be stabilized to become the ferroelectric phase with further cooling. T_c is the phase transition temperature at which the free energies of the cubic and tetragonal phases are equal.

(iii) For $T_c \geq T > T_o$,

solutions (a) and (b) in (ii) exist, but in this temperature region the tetragonal phase becomes thermodynamically stable and the cubic phase becomes metastable.

(iv) For $T < T_o$,

only the tetragonal phase exists [solution (b) in (ii)].

The interesting temperature region is $T_1 > T > T_o$ in which there are two solutions with one being stable and the other being metastable. When the system has higher energy, a modulation swinging back and forth between the two (local) minima can be excited.

3 INTRINSIC AMPLITUDE MODULATIONS

In the study of martensitic phase transition, Falk (1993) and Barsch and Klumhansl (1988), have derived periodic solutions for the martensite-martensite and martensite-austinite structures. Similarly, we can also derive such periodic solutions for a ferroelectrics system using the Landau-Ginzburg type of model described above (Cao and Cross, 1991).

Considering the nature of the modulation shown in Figure 1(c) the problem may be rendered to quasi-one-dimensional with a space variation only along the polarization direction. Similar to the study of 180° domains (Cao and Cross, 1991) we assume here the following *ansatz* for the polarization and strain,

$$\vec{P} = (0, 0, P_3(x_3)), \tag{14}$$

$$\eta_{ij} = \eta_{ij}(x_3) \tag{15}$$

Note here the space variable is x_3, the same as the polarization direction, while for the 180° domain structure the space variable is perpendicular to the polarization direction (Cao and Cross, 1991).

Substituting the Equations (14) and (15) into the energy minimization conditions and the elastic compatibility relations (Cao and Cross, 1991) leads to a second-order nonlinear ordinary differential equation for $P(x_3)$,

$$2\alpha_1^+ P_3 + 4\alpha_{11}^+ P_3^3 + 6\alpha_{111} P_3^5 - g_{11} P_{3,33} = 0 \tag{16}$$

with

$$\alpha_1^+ = \alpha_1 - \left[\frac{\hat{C}_{22}}{C_{11}} q_{12}\eta_\perp + \left(q_{11} - \frac{C_{12}}{C_{11}} q_{12}\right)\eta_\parallel\right] \tag{17}$$

$$\alpha_{11}^+ = \alpha_{11} - \frac{q_{12}^2}{2C_{11}}. \tag{18}$$

Equation (16) is equivalent to a one-dimensional model with an effective free energy density of

$$\begin{aligned} f_{\text{eff}} &= \frac{g_{11}}{2}(P_{3,3})^2 + \alpha_1^+ P_3^2 + \alpha_{11}^+ P_3^4 + \alpha_{111} P_3^6 \\ &= \frac{g_{11}}{2}(P_{3,3})^2 + f_L \end{aligned} \tag{19}$$

where f_L is the Landau-like potential as plotted in Figure 2.

Direct integration of Equation (16) leads to the following result:

$$x_3 = \frac{\sqrt{g_{11}}}{2} \int \frac{dP_3}{\sqrt{\alpha_1^+ P_3^2 + \alpha_{11}^+ P_3^4 + \alpha_{111} P_3^6 - f_o}} \tag{20}$$

One can obtain different solutions depending on the value of the integration constant f_o. For the temperature region $T_c < T < T_1$, we are interested in an f_o value in the range of $f_{\min} < f_o < f_{\max}$ as shown in Figure 2. In this case, Equation (20) can be integrated (Gradshteyn and Ryzhik, 1980) and the polarization has the following solution:

$$P_3(x_3) = \frac{\gamma_1}{\sqrt{1 - \left[1 - \frac{\gamma_1^2}{\gamma_2^2}\right] sn^2(x_3/\beta', k)}} \tag{21}$$

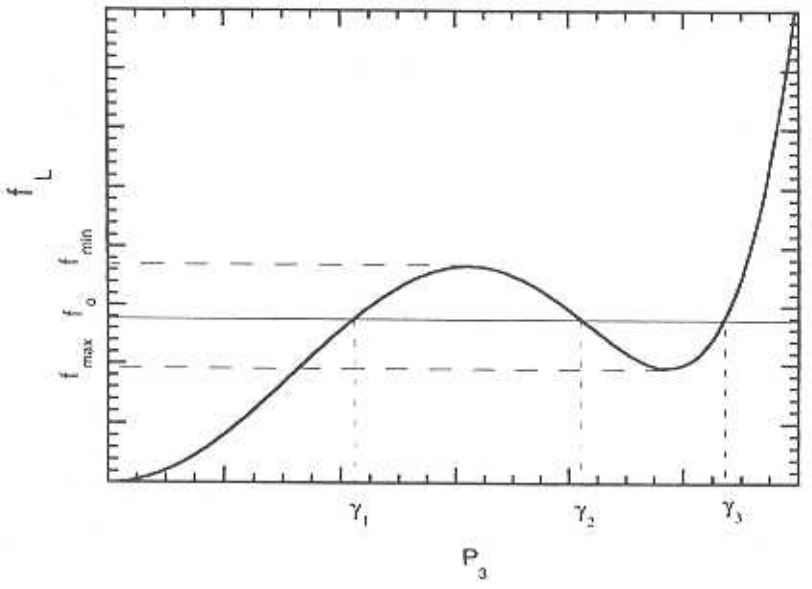

Figure 2 Effective free energy for temperature T with $T_1 > T > T_c$. The modulation reflects a periodic solution for the polarization between the two values γ_1 and γ_2.

and

$$\beta' = \frac{1}{\gamma_2}\sqrt{\frac{g_{11}}{2\alpha_{111}(\gamma_3^2 - \gamma_1^2)}} \tag{22}$$

$$k = \frac{\gamma_3\sqrt{\gamma_2^2 - \gamma_1^2}}{\gamma_2\sqrt{\gamma_3^2 - \gamma_1^2}} \tag{23}$$

where γ_i are the roots of the radicand in the integrand of Equation (20) and $sn(x)$ in Equation (21) is an elliptic sine function. The solution Equation (21) is periodic with a period of

$$x_p = 2\beta' K(k) \tag{24}$$

where $K(k)$ is a complete elliptic integral of the first kind.

Figure 3 is an illustration of the amplitude modulation solution for a special set of parameters in normalized scale. The polarization is normalized in terms of the spontaneous polarization at T_c,

$$P_o = \sqrt{\frac{\alpha_{11}^+}{2\alpha_{111}}} \tag{25}$$

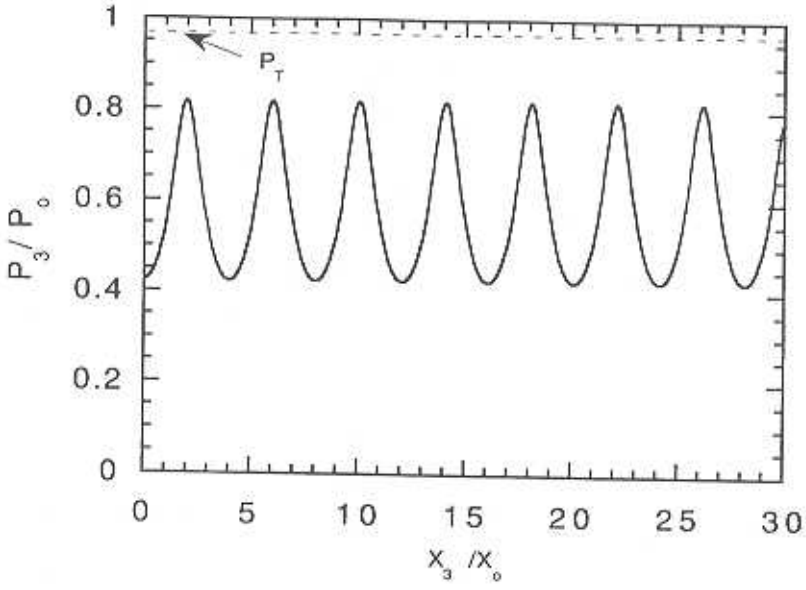

Figure 3 Periodic amplitude modulation along the polarization direction.

while the space variable is normalized by a factor x_o,

$$x_o = \sqrt{\frac{2\alpha_{111} g_{11}}{\alpha_{11}^{+2}}}. \tag{26}$$

The amplitude of the polarization oscillates in space between two values that are less than the polarization value of the fully developed tetragonal phase, P_T, while the direction of the polarization is fixed. The coupling of this polarization to the elastic strain makes the modulation visible to the electron microscopy. The tetragonal strain is proportional to the square of the polarization (Cao and Cross, 1991).

4 INTERACTION BETWEEN THE AMPLITUDE MODULATION AND ALIOVALENT DOPING

As shown in Figure 2, the amplitude modulation solution oscillating between γ_1 and γ_2 has higher energy than both the stable and the metastable states (cubic and tetragonal phases respectively in the case discussed above), but it can be locally stable (in configurational space) once it is excited (Barsch and Krumhansl, 1988). The excitation has two distinct features:

1. It exists only in a limited temperature range, i.e., $T_o < T < T_1$, and hence it may be closely related to the 'precursor' and the 'postcursor' in a first-order transition.

2. The period of the modulation is incommensurate with the lattice and changes continuously with temperature.

However, when aliovalent doping is introduced into the system, the situation will be changed. The existence of inhomogeneous polarization modulation means the presence of a polarization gradient in the system. From electrostatics, there will be charge density fluctuations in space associated with these polarization gradients. These charge density fluctuations will interact with the aliovalent dopants which have excess charge, causing some ordering of these charged defects. On the other hand, the ordering of these defects will pin the modulations so that the period will become commensurate with the underlying lattice and may become temperature independent. In other words, the defect ordering will persist for lower temperatures as a modulation to the tetragonal phase. These facts are consistent with the experimental observations in the lanthanum doped lead titanate shown in Figure 1(c) (Randall, Rossetti and Cao., 1993).

Because the charge density fluctuations are produced at a certain temperature, they have a defined magnitude for specified boundary conditions, and certain amount of defects (>5%) are needed to stabilize the microstructure as indicated in Figure 1.

In conclusion, the amplitude modulation observed in lanthanum doped lead titanate shown in Figure 1 can be understood as the results of defect stabilized intrinsic solitary periodic excitations which exist in systems with a first-order phase transition.

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