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Modeling large reversible electric-field-induced strain in ferroelectric materials using 90° orientation switching

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Reversible large electric-field-induced strain caused by reversible orientation switchings in $BaTiO_3$ is modeled using the Landau's theory of phase transition. A triple well free energy function is constructed. Each of its minima is associated with one of the polarization orientations involved. Nonlinear constitutive laws accounting for reversible orientation switchings and electrostriction effects are obtained by using thermodynamic equilibrium conditions. Hysteretic dynamics of one-dimensional structures is described by coupled nonlinear differential equations. Double hysteretic loops in the electric and mechanic fields are both successfully modeled. Giant reversible electrostriction is modeled as a consequence of reversible orientation switchings via electro-mechanical couplings. Comparisons with experimental results reported in literatures are presented.

large electrostriction, reversible switchings, double hysteresis, differential model

1 Introduction

Electro-mechanical materials are widely used for electro-mechanical sensing and actuation in many engineering applications due to their capability of converting energy between mechanical and electrical forms. In particular, piezoelectric lead zirconate titanate (PZT), which is a solid solution of lead titanate and lead zirconate, is probably the most widely used piezoelectric material. The current popularity of the PZT materials can be explained by the fact that its constitutive relations can be approximated precisely by linear equations when it operates with a rather weak field. However, the piezoelectric effects of the PZT materials are generally very small (less than 0.1% generally). Albeit the electric-field-induced strain (electro-strain) can be increased by applying a stronger electric field, the increment is still very small, and the constitutive relations will become nonlinear and hysteresis will occur and become more and more remarkable, which means that the mechanical configuration will not be restored when the applied electric field returns to zero[1−3]. Another drawback of the PZT materials is that the application of PZT now causes much environmental concern due to the harmful lead component. In order to enhance the performance of the sensors and actuators and make it environment friendly, smart materials having larger strain responses to the electric inputs whilst less environmental destruction are sought[3,4].

For the sake of obtaining larger electro-strain using environment friendly materials, the increase of the electro-strain of non-lead electro-mechanical materials has been the subject of the recent research efforts, in particular for the ferroelectric materials with perovskite

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structures[3,4] such as $BaTiO_3$ (barium titanate materials). It was reported recently that a quite large electrostrictive strain response can be obtained by inducing polarization switchings in single crystals barium titanate, and the theoretical analysis on this topic was followed and verified by experimental observations[5−7]. Unfortunately, the orientation switchings reported there is inherently irreversible due to the fact that all involved polarization orientations are energetically equivalent. Therefore, there is no driving force to re-establish the initial configuration when the applied external electric field returns to zero. Consequently, the related electro-strain will also have a remanence when the applied field returns to zero. These irreversible orientation switchings and electro-strain response limit the usefulness of the materials for sensing and actuating purposes. Recently, it was reported by Ren's group that the orientation switchings in the barium titanate can be adjusted to be reversible via introducing point defect into material on purpose[8−11], which makes the material capable of producing a large recoverable electro-strain and potentially very useful for sensing and actuating.

For the application developments related to the reversible orientation switchings and electro-mechanical response, a suitable model which is able to account for the hysteretic dynamics and capture the electro-mechanical coupling on macroscale becomes essential. At the same time, it is always desired that the model for the dynamics of the materials should be formulated in a differential form, since most of the smart devices are embedded in overall systems as a sub-system or components. From a practical point of view, a differential model for the smart devices will make analysis and control of the overall systems very convenient by utilizing the well established control theory and optimization methods.

In the current paper, a phenomenological model for the reversible orientation switchings and the induced large electro-strain in barium titanate is constructed by using the Landau theory for the orientation switchings. The reversible orientation switchings and electro-strain in the materials are attributed to the 90° orientation switchings. A triple well free energy function is constructed to characterize the three polarization orientations in the one-dimensional description. Each of its local minima is associated with one of the involved polarization orientations. Constitutive laws of the materials are obtained by using the thermodynamic equilibrium conditions. Governing equations for the dynamic behavior of the materials are formulated by assuming that the system states will keep trying to achieve its local equilibriums with certain relaxation effects, and the driving force of the evolution of the system states is the negative gradient of the free energy. Numerical simulations of the dynamics of the materials are performed and presented. Comparisons with experimental results reported in literatures show that the double hysteresis loops in the *E*-*P* and *E*-ε curves are both successfully modeled. The reversible large electro-strain is obtained as a consequence of the reversible orientation switchings via electro-mechanical coupling.

2 The 180° and 90° orientation switchings

It has been well understood nowadays that the physical essence of the unique properties of the ferroelectric materials is the polarizations and orientation switchings. To clarify this, we confine our discussion here by the perovskite-type materials in the one-dimensional case. We also assume that the temperature of the material considered here is far below its Cure temperature such that there is no stable cubic structure and only tetragonal structures exist. In its one-dimensional analog, there are only two polarization orientations involved, as sketched by the two horizontally oriented rectangles in Figure 1(a). The switching between the two horizontal rectangles is

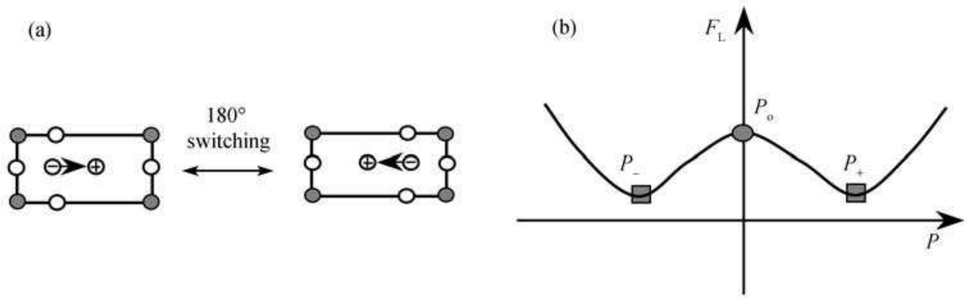

Figure 1 (a) The sketch of 180° orientation switchings in ferroelectric materials with only two orientations; (b) the Landau free energy function has two stable local minima (rectangles).

associated with the 180° orientation switchings. According to the Landau theory of phase transition, the modeling of the orientation switchings in the case with only 180° switchings can be performed by constructing a non-convex free energy function with two local minima, as sketched in Figure 1(b). Each of the local minima is associated with one of the two stable orientations (denoted as P_+ and P_- and marked as shaded rectangles in (b)), such that the orientation switchings induced in the materials can be modeled by investigating the transition of the system states from one local minimum to another.

As sketched in Figure 1(b), the system states will keep approaching to one of the two local equilibriums whenever it is perturbed. The two stable orientations are symmetric and energetically equivalent and the system states can be transformed from one equilibrium to another only when the applied electric field is strong enough to overcome the energy barrier between them, requiring 180° orientation switchings. The 180° switchings will be inherently irreversible since there will be no driving forces for the recovery when there are no external electric or mechanical loadings. It is also clear from the sketch in Figure 1 that when the electric field returns to zero, the polarization will not be zero since the system cannot stay at point P_o due to the fact that it is unstable and therefore not sustainable. This fact means that there will be a remanence in the polarization due to the single hysteretic nature caused by the 180° orientation switchings. Consequently, the electro-strain certainly will be irreversible too[11,12].

By utilizing point-defect-mediated orientation switchings, it was reported that a metastable 90° orientation may be induced in the ferroelectric materials such that the 90° switching can be induced either by stress or electric field, and more importantly, it is reversible[8,12]. Thus, a reversible electro-strain is obtained via electro-mechanical coupling. In order to model the reversible orientation switchings and the related electro-strain, a vertical orientation is introduced into the one-dimensional model as sketched in Figure 2(a), denoted by the vertical rectangle. Hence, there are three orientations involved, which can be characterized by the three local minima via associating each polarization orientation with one of the local equilibriums. As sketched in Figure 2(b), the vertical orientation is characterized by P_o, while the two horizontal orientations are characterized by P_- and P_+, respectively. The introduced vertical orientation is globally stable while the two horizontal orientations become metastable in this case, with a higher free energy than the vertical orientations (as sketched in Figure 2(b)). The vertical orientation has no polarization contributions in the horizontal direction since it is perpendicular. Because P_o is located in the middle of P_+ and P_-, and has a lower energy than the horizontal orientations, all the transitions between the two horizontal orientations (P_+ and P_-) will be trapped by the vertical orientation. Therefore, we assume that there are only 90° switchings ($P_o \Leftrightarrow P_+$ and $P_o \Leftrightarrow P_-$) and all the 180° switchings are performed via two consecutive 90° switchings (horizontal to vertical and vertical to horizontal). Since the 90° orientation has no contribution to the horizontal polarization and it is globally stable, the polarization will return to zero when there are no external loadings. The mechanism here is very similar to the phase transitions in the thermoelastic material, as indicated in refs. [11, 17, 18].

In order to formulate the orientation switchings and electro-mechanical couplings on the basis of the Landau theory for the phase transformations, the free energy function is constructed as a polynomial retaining the 6th order term of the order parameter (the polarization). It may have three local minima with suitable coefficients,

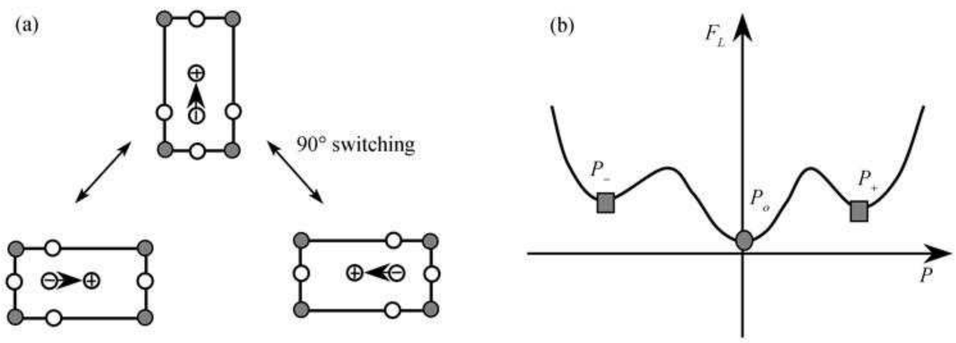

Figure 2 (a) The sketch of 90° switchings in ferroelectric materials; (b) the Landau free energy function has three local minima.

which can be used to characterize the three polarization orientations involved in the current problem, as sketched in Figure 2(b). The Helmholtz free energy function ψ for the ferroelectric materials can be constructed in the following form[12−14]:

$$\psi\left(P,\varepsilon\right)=\frac{a_2}{2}P^2+\frac{a_4}{4}P^4+\frac{a_6}{6}P^6+\frac{k}{2}\varepsilon^2+\frac{b}{2}\varepsilon P^2, \quad (1)$$

where ε and P are the strain and polarization (being the only order parameter in the one-dimensional case), respectively. The constants a_2, a_4, a_6, k, and b are material constants. The Landau free energy function (for the current problem it is the electric potential energy) used in (1) has the following form:

$$F_L\left(P\right)=\frac{a_2}{2}P^2+\frac{a_4}{4}P^4+\frac{a_6}{6}P^6. \quad (2)$$

Piezoelectric effects are ignored in the above representation in order to highlight the discussion about the electrostriction effects. Thermal contributions to the free energy are also excluded here since the thermal dynamics is not in the focus of the current paper. The coefficient a_2 can be chosen linearly dependent on the material temperature for the modeling of temperature-dependent characteristics when needed. It has been verified that, provided with suitable parameter values, the Landau free energy function used in eq. (2) may have three local equilibriums due to the 6th order nonlinearity, as sketched in Figure 2.

3 Differential model

In order to construct a thermodynamically consistent differential model for the dynamics of the reversible orientation switchings and the electro-strain response, the constitutive laws for the materials can be derived by utilizing the thermodynamic equilibrium conditions as follows:

$$E=\frac{\partial\psi}{\partial P},\quad \sigma=\frac{\partial\psi}{\partial\varepsilon}, \quad (3)$$

which gives the following two nonlinear algebraic equations:

$$E=a_2P+a_4P^3+a_6P^5+b\varepsilon P,\quad \sigma=k\varepsilon+bP^2, \quad (4)$$

where E is the electric field and σ is the stress.

In order to re-formulate the model into a differential form, the system states are assumed to continuously achieve its thermodynamic equilibrium states with certain relaxation effects. Therefore, the dynamics of transformation process of the system states from one of its local equilibriums to another can be expressed by the following kinetic equations for each particle in the considered material:

$$\frac{\mathrm{d}}{\mathrm{d}t}P=-\delta_p\frac{\partial\psi}{\partial P}+r_p,\quad \frac{\mathrm{d}}{\mathrm{d}t}\varepsilon=-\delta_\varepsilon\frac{\partial\psi}{\partial\varepsilon}+r_\varepsilon, \quad (5)$$

where δ_p and δ_ε are the coefficients accounting for the relaxation effects in the electric and mechanical fields, respectively. The above equations basically say that the system will keep evolving in such a way that its total free energy will be gradually minimized. This idea is consistent with the time dependent Ginzburg-Landau theory[14,15]. In (5), r_p and r_ε are the disturbances to the electric and mechanic fields, respectively. Here it is worth noting that the major interest of the current paper is not to investigate the orientation switchings on the mesoscopic scale and the related domain wall movements, but to model the macroscale reversible behavior of the material. Therefore, one can simply assume that the polarization and strain are both uniform in the considered material, and r_p and r_ε can be simply set to the external loadings multiplied by the relaxation coefficients, which are $r_p=\delta_p E$ and $r_\varepsilon=\delta_\varepsilon\sigma$.

By substituting the Helmholtz free energy function given in eq. (1) into eq. (5), the dynamic equations for the evolution can be recast into the following form:

$$\begin{aligned}\tau_p\frac{\mathrm{d}P}{\mathrm{d}t}&=a_2P+a_4P^3+a_6P^5+b\varepsilon P-E,\\ \tau_\varepsilon\frac{\mathrm{d}\varepsilon}{\mathrm{d}t}&=k\varepsilon+bP^2-\sigma,\end{aligned} \quad (6)$$

where the definitions of τ_p and τ_ε are obvious by comparing eq. (6) with eq. (5). τ_p and τ_ε here act as the time constants of the relaxation processes in the electric and mechanic fields, respectively. If τ_p and τ_ε are both very small such that the relaxation effects can be safely ignored, one can immediately obtain the constitutive laws given in eq. (4) by setting the time derivative terms to zero in the above equations.

In many ferroelectric materials, it can be assumed that the mechanical field will achieve its equilibrium state much faster than the electric field[15,16]. In other words, τ_ε is much smaller than τ_p, such that the relaxation effects related to τ_ε and the dynamical behavior of the material can be ignored, and the evolution equation can be simplified to

$$\tau_p\frac{\mathrm{d}P}{\mathrm{d}t}=a_2P+a_4P^3+a_6P^5+b\varepsilon P-E,\ k\varepsilon+bP^2=\sigma, \quad (7)$$

which is a system of differential algebraic equations. It will be illustrated in the following sections that the model given by eq. (7) is capable of modeling the double hysteresis loops related to the reversible orientation switchings and the electro-strain response. The mechanic and electric fields are coupled intrinsically in the above differential model.

4 Double hysteresis loops

To illustrate that the proposed model is capable of modeling the reversible orientation switchings, an example of the *E*-*P* relation given by the first equation in eq. (7) is plotted in Figure 3 as the solid curve. It is assumed here that the strain has a very small contribution to the polarization *P* and can be ignored in the first equation in eq. (7) (when there is no external stress applied). At the same time, for a qualitative analysis of the hysteresis structures, the time derivative term can be temporarily ignored. Therefore the constitutive relation can be simplified as

$$E = a_2 P + a_4 P^3 + a_6 P^5. \quad (8)$$

The parameter values used for the plot are roughly estimated from the experimental curve given in ref. [11] as follows: a_2=−0.225, a_4=0.00143, and a_6=−2.578×10^{-6}. Here, *E*, *P*, ε are all non-dimensionalized. The scales used for non-dimensionalization is 10^6 V/m for *E*, 10^{-2} C/m^2 for *P*, and percentage for ε, respectively.

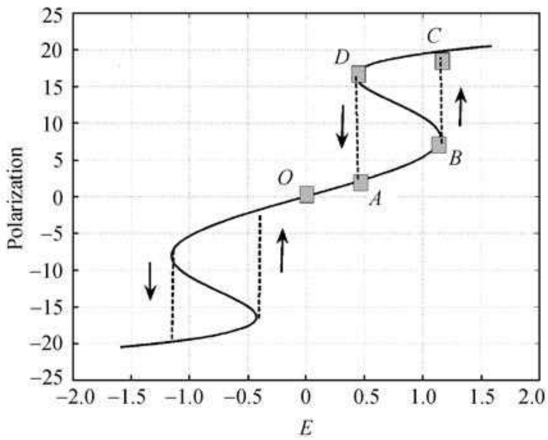

Figure 3 Double hysteresis loops and recoverable orientation switchings in the ferroelectric materials due to a non-convext *E*-*P* relation.

As seen from the plot, the double hysteresis loops observed in the electric field in the ferroelectric materials can be modeled by the above constitutive laws, due to the non-convex nature of the curve given by eq. (8). When the applied field *E* is increased from zero to positive values, the constitutive curve will be the curve *AB*. Point *B* is a turning point, because *BD* is not a stable branch (it corresponds to a decrease in energy when the applied field increases). Therefore the system will jump to another stable branch *DC* favored by the applied field, as indicated by the arrow in the plot. Here, the jump is briefly sketched as a straight dash line *BC* for simplicity. When the loading direction is reversed, another jump *DA* is presented, starting from another turning point *D*. Neither point *A* coincides with *B* nor point *C* coincides with *D*. This yields the hysteresis loops, which can be sketched by the cycle *ABCD*. These jump phenomena are associated with the 90° orientation switchings between the vertical orientation and the two horizontal orientations. When the electric field is decreased from point *O*, another pair of 90° orientation switchings will be induced and there will be another hysteresis loop, as sketched in the bottom-left area of the plot.

The recovery of the orientation switchings in the ferroelectric materials can be explained easily by utilizing the non-convex constitutive relation. Point *O* in Figure 3 is associated with the system state where the applied electric field (external loading) is zero. The constitutive relation is a one-to-one relation in the adjacent area of *O*, which ensures that the polarization induced in the material will be zero whenever the applied electric field returns to zero. Thus the electro-strain response will be also zero according to the electro-mechanical coupling when there is no stress applied. On the other side, since the 90° orientation switchings can be induced in the material, the materials still have a rather large polarization and electro-strain upon the applied field.

5 Reversible electro-strain response

On the basis of the modeling of the reversible orientation switchings, it is straightforward to model the reversible electro-strain by utilizing the electro-mechanical coupling mechanism. For the discussion here, the second constitutive relation given in eq. (7) is taken for the analysis. Assuming that there is no external stress applied (σ=0), one can easily see that the induced strain in the material upon exposure to the electric field is proportional to the square of polarization. The induced strain can be simply approximated by the representation

$$\varepsilon = -\frac{b}{k} P^2, \ \tau_p \frac{\mathrm{d}P}{\mathrm{d}t} = a_2 P + a_4 P^3 + a_6 P^5 - E, \quad (9)$$

in which the strain contribution to the polarization is ignored again (the $b\varepsilon P$ term). The coupling between the electric and mechanic fields now becomes a single direction coupling and the strain ε becomes a function that depends on the polarization P, and in turn, on the applied field E. Based on the above simplification, the electro-strain can be easily plotted as a function of E.

Since the polarization P is a nonlinear function of the applied electric field, and has double hysteresis loops in the E-P curve as sketched in Figure 3, one can expect that there will be also double hysteresis loops in the E-ε curve. To illustrate the electro-strain response, a simple plot of eq. (8) with b/k=−1 is presented in Figure 4 by using the E-P curve plotted in Figure 3. As predicted above, there are two hysteresis loops that occur in the curve, as indicated by the dashed lines accompanied by the arrows. It is also clear that the electro-strain will be zero whenever the applied electric field returns to zero, which means that the electro-strain is reversible.

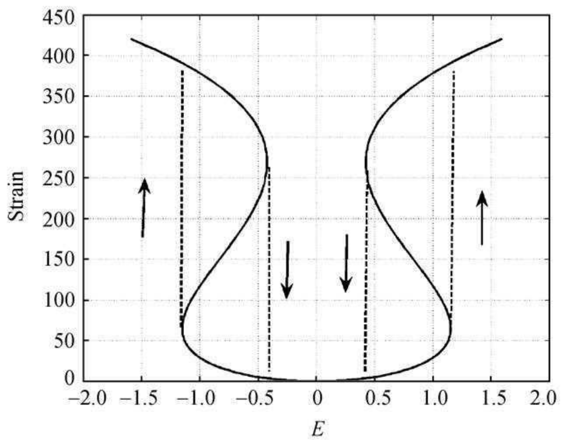

Figure 4 Sketch of large reversible electro-strain induced by reversible 90° orientation switchings in the ferroelectric materials.

It is worth while to note that in real materials subject to electric field E, σ will not be zero even when there is no external stress applied, which means that there will be always a shift in the E-ε curve given by eq. (9), and the shape of the curve will also be changed.

6 Numerical results

To demonstrate the capability of the proposed model, the simulated E-P and E-ε curves are compared with the experimental results reported in ref. [11]. The experiments were performed using the aged Mn-$BaTiO_3$ sample, and the frequency of the electric field was 0.1 Hz. The experimental double hysteresis loops E-P and E-ε were read from Figure 2 in ref. [11], and re-plotted here as dashed lines. It was also used for a rough estimation of the non-convex Landau free energy function and the related constitutive laws. It is worth noting that the parameter estimations using experimental data for the nonlinear dynamics system with bifurcations is a non-trivial task, due to the non-convexity of the constitutive laws which is related to the jump phenomenon among different stable branches. It is also unnecessary to use a high order polynomial to model the constitutive relations. Some detailed discussion with regard to this topic was presented in ref. [13]. Here, for the sake of simplicity of the current discussion, the parameters are not precisely estimated using numerical methods. Instead, the non-convex constitutive relation derived from the Landau free energy function is approximated by piece-wise spline constructed on the basis of a few points from the experimental E-P curve. The time constant is then determined by fitting the numerical E-P curve to the experimental one using a few *error-and-try* iterations. The estimated piece-wise spline for the non-convex E-P relation is plotted in Figure 5, and the estimated time constant is τ_p=0.03, k/b =−1218.39. To fit the simulated E-ε curve to the experimental one, the shift is chosen as 0.04.

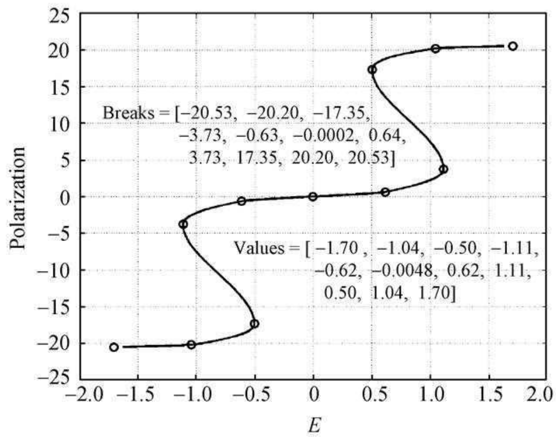

Figure 5 The approximated non-convex E-P constitutive curve by using piece-wise cubic spline (solid line). The nodes used for the approximation are listed in the figure (small cycles).

By using the constitutive E-P relation given in Figure 5, the simulated E-P and E-ε curves are plotted as solid lines in Figures 6 and 7, respectively. For the comparison purpose, their experimental counterparts are also plotted in the same figures as dashed lines. The comparison shows clearly that although the model parame-

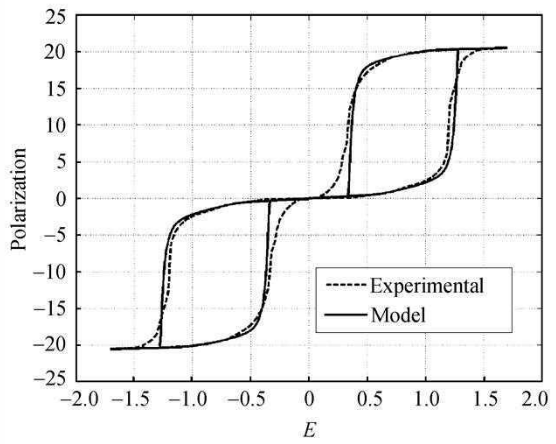

Figure 6 Comparison of the modeled reversible orientation switchings in ferroelectric materials with their experimental counterparts.

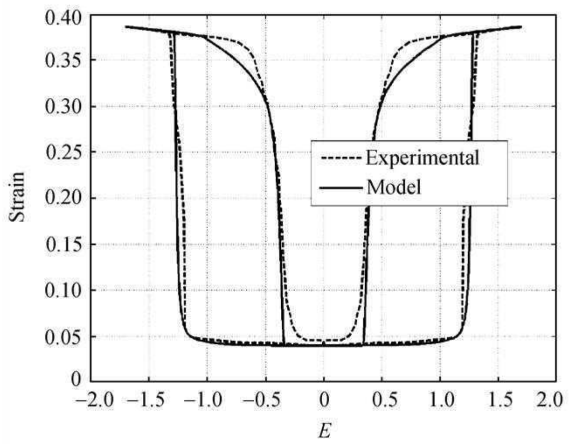

Figure 7 Comparison of the modeled large reversible electro-strain in ferroelectric materials with their experimental counterparts.

ters are just roughly estimated, the agreement of the simulated *E-P* and *E-ε* curves with the measured ones is rather satisfactory. The discrepancies between the modeled and measured responses in the electric and mechanic fields are both small, and therefore acceptable for most engineering applications. One can expect that when the model parameters are identified more accurately by using suitable numerical methods, the agreement will be improved further. The above comparison indicates that the essential mechanism of the reversible orientation switchings and reversible electro-strain responses are successfully captured by the proposed model. Furthermore, the model is given by ordinary differential equations and is very convenient for related research applications and developments. Due to its dynamic nature, the rate dependence of the dynamical response of the material can also be modeled by accurately identifying time constants if a group of tests are provided in different loading conditions (frequencies, etc.).

7 Conclusion

We have presented a theoretical model for the reversible orientation switchings and reverisble electric-field-induced strain responses. A globally stable vertical orientation has been introduced into the one-dimensional model, and the reversible orientation switchings have been successfully modeled on the basis of the Landau theory. The double hysteresis loops in the electric and mechanical fields have been both successfully modeled. Model verification has been carried out by comparing model results with their experimental counterparts.

1 Lynch C S. The effect of uniaxial stress on the electromechanical response of 8/65/35 PLZT. Acta Metallurgica, 1996, 44(10), 4137—4148

2 Kamlah M. Ferroelectric and ferroelastic piezoceramics – modeling and electromechanical hysteresis phenomenon. Cont Mech Thermodyn, 2001, 13: 219—268

3 Smith R C. Smart Material Systems: Model Development, Frontiers in Applied Mathematics 32. Philadelphia: SIAM Publishers, 2005

4 Scott J F. Ferroelectric Memories. Berlin: Springer Verlag, 2000

5 Burscu E, Ravichandra G, Bhattacharya K. Large electrostrictive actuation of barium titanate single crystals. J Mech Phy Solid, 2004, l52: 823—846

6 Shilo D, Burcsu E, Ravichandran G, et al. A model for large electrostrictive actuation in ferroelectric single crystals. Int J Solid Struct, 2007, 44: 2053—2065

7 Bhattacharya K, Ravichandran G. Ferroelectric perovskites for electromechanical actuation. Acta Mater, 2003, 51: 5941—5960

8 Ren X, Zhang L X. Electro-shape-memory effects in ferroelectric martensite. Mater Sci Eng A, 2006, 438-440: 1071—1076

9 Zhang L X, Ren X. Electro-shape-memory effect in Mn-doped $BaTiO_3$ single crystals and *in situ* observation of the reversible domain switching. Mater Sci Eng A, 2006, 438-440: 354—359

10 Liu Y, Liu W F, Chen W, et al. Electro-shape-memory effect in Mn-doped $(Pb,Sr)TiO_3$ ceramics. Mater Sci Eng A, 2006, 438-440: 176—180

11 Ren X B. Large electric-field-induced strain in ferroelectric crystals by point-defect-mediatd reversible domain switching. Nature Materials, 2004, 3: 91—94

12 Ahluwalia R, Lookman T, Saxena A, et al. Domain-size dependence of piezoelectric properties of ferroelectrics. Phys Rev B, 2005, 72: 014112

13 Wang L X, Willatzen M. Modeling of nonlinear responses for reciprocal transducers involving polarization switching. IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control, 2007, 54(1): 177—189

14 Shu Y C, Bhattacharya K. Domain patterns and macroscopic behaviour of ferroelectric materials. Philos Mag B, 2001, 8(12): 2021—2054

15 Demjanovic D. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. Rep Prog Phys, 1998, 61: 1267—1324

16 Cross L E. Ferroelectric materials for electromechanical transducer applications. Jpn J Appl Phys (part I), 1998, 34: 2525—2532

17 Wu Y Z, Tao Y M. Simulations on the electromechanical poling of ferroelectric ceramics. J Appl Phy, 2007, 102: 114104

18 Li F X, Fang D N, Lee J J, et al. Effects of compressive stress on the nonlinear electromechanical behavior of ferroelectric ceramics. Sci China Ser E-Tech Sci, 2006, 49(1): 29—37