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Extension of the Landau theory for hysteretic electric dynamics in ferroelectric ceramics

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Abstract In this paper, a macroscopic differential model for the nonlinear dynamics of the electric field in ferroelectric ceramics is developed on the basis of polarization switching theory. In a one-dimensional description, dynamics with hysteresis caused by polarization switching is modelled by using the Landau theory of phase transitions for single-crystal cases. For ferroelectric ceramics, the orientation of the principal axis of grains is assumed to have a certain distribution. The overall dynamics is determined by making a weighted combination of the dynamics of each grain. The weight function for the combination is taken phenomenologically based on experimental observations. It is shown that experimental hysteresis can be reproduced by the macroscopic differential model precisely.

Keywords Hysteresis · Polarization switching · Polycrystals · Landau theory · Macroscopic model

1 Introduction

Ferroelectric ceramics are widely used in many engineering applications due to their capability of converting energy among thermal, mechanic, and electric types. As in many cases, the dynamics of the material (and devices made from it) can be described by using simple linear constitutive laws when the external loading is confined in a rather small range [1, 2]. In fact, the dynamics of the ferroelectric materials is inherently nonlinear when subject to larger loadings where several physical fields are coupled together. In many cases, the applied electric field may induce polarization switching in the material and thus introduce memory effect (hysteresis) into the nonlinear dynamics. Therefore, it is essential for engineering application developments to construct suitable mathematical models for the nonlinear dynamics and hysteresis based on a better understanding about the mechanism of nonlinearity and hysteresis [3, 4].

In modelling the nonlinear coupled dynamics in the ferroelectric material and devices, it is indicated by experimental observations that, in most of cases, the nonlinear dynamics of the electrical field has a major contribution to its hysteretic behaviour, and this nonlinearity will cause nonlinear dynamics in the thermal and mechanical dynamics due to complicated coupling effects among various field components. In order to construct a macroscopic model for the full dynamics of the material in engineering applications, it is essential to capture the hysteretic dynamics in the electric field by using a simple model [3, 4].

It is known experimentally that the polarization and orientation switchings are complex processes with multiscale dynamics embedded in. The switching process involves nucleation, growth kinetics, relaxation effects, grain size effects, local and non-local effects, and many other effects. Construction of a single comprehensive model aiming at capturing all the related features at various scales is almost impossible due to the

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complexity of the physics. On the other side, it is not necessary to use such a model for the purpose of engineering applications since the major concern for engineering applications is related to macroscopic nonlinear and hysteretic dynamics. Although, the dynamics involved in nucleation and growth at the microscale is important for the macroscopic dynamics of the material, it can be safely ignored in the current discussion since it takes place at a much smaller scale compared to typical engineering application scales.

In this paper, a macroscopic differential model for the nonlinear dynamics of the electric field in ferroelectric ceramics is developed on the basis of polarization switching theory. A one-dimensional structure is considered for simplicity. Hysteretic dynamics for single-crystal cases is modelled by using the Landau theory for the first-order phase transitions. The essence of the model is to associate polarization orientations with local minima of a non-convex potential function, and the hysteretic dynamics of the material is then modelled by simulating the dynamics of system state switchings among the local minima. For polycrystals, the single-crystal model is extended by assuming that various polarization grains, each has a different principal-axis orientation, exist in the considered ceramics, and their principal axis orientations follow a certain distribution. The hysteretic dynamics in each grain is then modelled as a single crystal case. The overall dynamics is determined by making a weighted combination of the dynamics of all polarization grains. The weight function employed is taken as a phenomenological function of the angle between the principal axis in the considered grain and the applied electric field, which can be identified by using experimental data. The resulting model is formulated as set of nonlinear differential equations. Numerical experiments are carried out and comparison between model results with reported experimental counterparts indicates that the hysteretic dynamics are well captured by the model.

2 Landau theory for polarization switching

It is well understood nowadays that hysteresis behaviour in ferroelectric materials is a consequence of orientation switching of polarization dipoles upon its exposure to external fields. In a one-dimensional description, assuming that the material temperature is always below the Curie temperature, the polarization orientation is parallel to the principal axis (directed along or opposite to the principal direction). Switching between these two orientations will always be a 180° degree switching [3, 4]. In order to approximate the effects of the 90° degree switching in a higher-dimensional case, another orientation is introduced in the current one-dimensional description as sketched in Fig. 1, namely the upward-polarization orientation P_o [5].

For the convenience of the following discussion, we denote the rightward orientation of the polarization as $P+$ while the leftward one as P_-. Hysteresis and related nonlinear dynamics of the electric field in the ferroelectric materials can be modelled by studying the dynamics of the switching between these three polarization orientations (phase transitions).

According to the Landau theory, the essential element in the modelling of phase transition dynamics is a free-energy function which is capable of characterizing different phases. For the current problem, the polarization orientation switching can be treated as a phase transition problem, in which each polarization orientation is treated as one phase. Since there are three polarization orientations involved (P_+, P_- and P_o), it is necessary to construct the free-energy function such that it has three local minima, each minimum is associated with one polarization orientation. By taking into account the symmetry property of the polarization orientations in ferroelectric materials, it is clear that a 6^{th}-order polynomial of the order parameter with only even order terms is suitable for the purpose [5, 6]. Since only the electric field is considered here, the Helmholtz free-energy function can be constructed similar to the Landau free-energy function at a given temperature [5]:

$$\Psi(P) = \frac{a_2}{2}P^2 + \frac{a_4}{4}P^4 + \frac{a_6}{6}P^6. \tag{1}$$

where a_2, a_4, and a_6 are material constants need to be determined by using experimental data, and P is the polarization which is chosen as the only order parameter for the current problem.

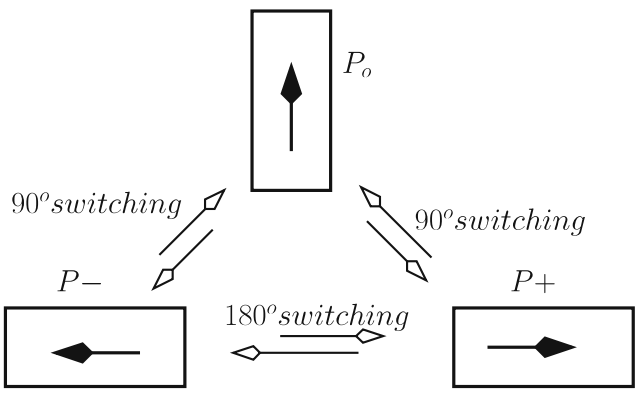

Fig. 1 Sketch of one-dimensional polarization switchings in ferroelectric materials

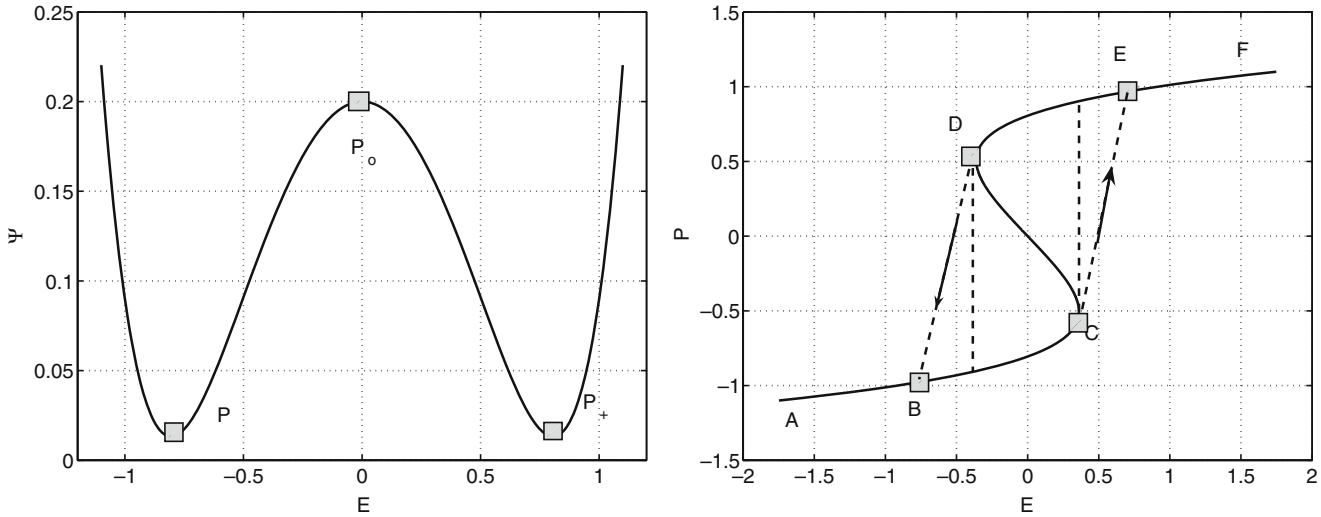

Fig. 2 The schematic plot of a free-energy function Ψ with two local minima (*left*). The resultant $E - P$ relationship revealing hysteresis (*right*)

Using the above free-energy function, the three different polarization orientations can be characterized by its three local minima, provided suitable values for the parameters. To clarify the discussion, one example of the free-energy function (non-dimensionalized) is plotted in Fig. 2 (left) with the following parameter values, $a_2 = -1$, $a_4 = 0.846$, $a_6 = 1.07$.

The plots evidently show that there are two local minima in the free-energy function, corresponding to the P_+ (right rectangle) and P_- (left rectangle), respectively. The two orientations are symmetrical (with regard to the center). It is also clear that in this case only P_+ and P_- are stable and the local maximum P_o is unstable. It indicates that orientation switching can only take place between P_+ and P_o. If a_2 is increased to a certain value, P_o will also become a local minimum and thus locally stable. In this case, a 90° switching is also modelled.

3 Governing equations

For the construction of a differential model at the macroscale, the relationship between the polarization and the applied electric field is sought as a differential equation. For engineering applications, the whole device made from ferroelectric materials is normally treated as a homogeneous one, hence microstructures and related dynamics are averaged out. The governing equations for the entire material (devices) is then the same in the considered domain (independent on the location). Therefore the governing equation for a single lattice can be used as the macroscopic governing equation for the material. To formulate the dynamic equation for a single lattice, the relaxational Time-Dependent Ginzburg-Landau (TDGL) theory at mesoscale is employed [5, 7].

Using the Helmholtz free energy function, the governing equation for the polarization P can be formulated as follows:

$$\frac{dP}{dt} = -\gamma \frac{\partial \Psi(P)}{\partial P} + r, \tag{2}$$

where γ is a coefficient accounting for dissipation effects in the polarization dynamics, r represents disturbances (including external input) to the system [5, 7]. For the current problem, the input is the applied electric field E, so the dynamical process of polarization can be described by the following equation, according to the TDGL theory:

$$\tau \frac{dD}{dt} = a_2 D + a_4 D^3 + a_6 D^5 - E. \tag{3}$$

where $\tau = -1/\gamma$ can be regarded as relaxation coefficient, and P is replaced by the electric displacement D due to the fact that D is very close to P in most cases (for high relative-permitivity materials) [5].

If the loading E is kept at a constant value for a long time (or is sufficiently slow), the system will achieve its equilibrium state which is given by the following relation (setting $\frac{dD}{dt} = 0$):

$$E = a_2 D + a_4 D^3 + a_6 D^5. \tag{4}$$

It can be easily illustrated that hysteresis is embedded in the dynamics given by Eq. 3. As indicated by the $E-D$ relation sketched in Fig. 2 (right), when the applied field E is increased from negative to positive values, the equilibrium curve will be the curve ABC. Point C is a turning point because CD is not a stable branch. Therefore the system will jump to another stable branch EF favored by the applied field. Ideally the jump will follow the vertical line (dashed vertical line start from C) but in reality there are always friction- and dissipation-mechanisms which make the line non-vertical and non-straight (i.e., a smooth curve with a changing slope). Here it is sketched as a straight line CE for illustrative purposes. The slope depends on frictions and many other factors. When the loading direction is reversed, a jump DB is present starting from another turning point D also with a changing slope. Point B does not coincide with C, neither does E with D. This yields the hysteresis behaviour.

In order to characterize the three phases involved in the current model, the free-energy function is chosen as the sixth-order polynomial given in Eq. 4 such that it has three local minimum and satisfy symmetry requirements [8]. Such a choice is purely due to its mathematical convenience for the analysis, which certainly not unique. In some cases, a sixth order polynomial will introduce numerical difficulties and other unnecessary restrictions. In practice, it can be conveniently replaced by a piecewise non-convex spline having the same number of local minima and the required symmetry [8].

4 Multiple domain model

Different from the single crystal cases, the principal axis of polarization orientations is not uniform in ferroelectric ceramics. There are many grains in the material. In each grain, orientation switching can only be induced in the direction parallel to the principal axis, as sketched in Fig. 3 but the principal axes in different grains are different. Therefore the same applied electric field on the bulk material will induce different dynamics of orientation switching in different grains.

Let us consider a grain in which the principal axis has an angle of θ ($\theta \in [0, \pi/2]$ is representative with the symmetry properties required) with the direction of the applied electric field. If one assume that only the field component parallel to the principal axis can induce orientation switching (is effective for polarization switching), the polarization dynamics along the considered principal axis can be modelled by using Eq. 3:

$$\tau \frac{dD_\theta}{dt} = a_2 D_\theta + a_4 D_\theta^3 + a_6 D_\theta^5 - E\cos\theta, \tag{5}$$

where the function $\cos\theta \in [0, 1]$ is to model the effective electric field for the orientation switching along the considered principal axis direction. It is actually a projection from the applied electric field E to the principal axis. The effect of $\cos\theta$ is that, for a certain applied electric field E on the considered ferroelectric ceramics, orientations along some principal axis (θ is close to zero) will be switched earlier since the effective field along the principal axis is stronger. There might be some orientations which will not be switched at all if θ is close to or equal to $\pi/2$ since the effective field is very small. The distribution θ varies with materials.

The polarization in the considered grain induced by polarization switching has its contribution to the overall polarization in the direction of the applied electric field. Again, the contribution should be projected from D_θ

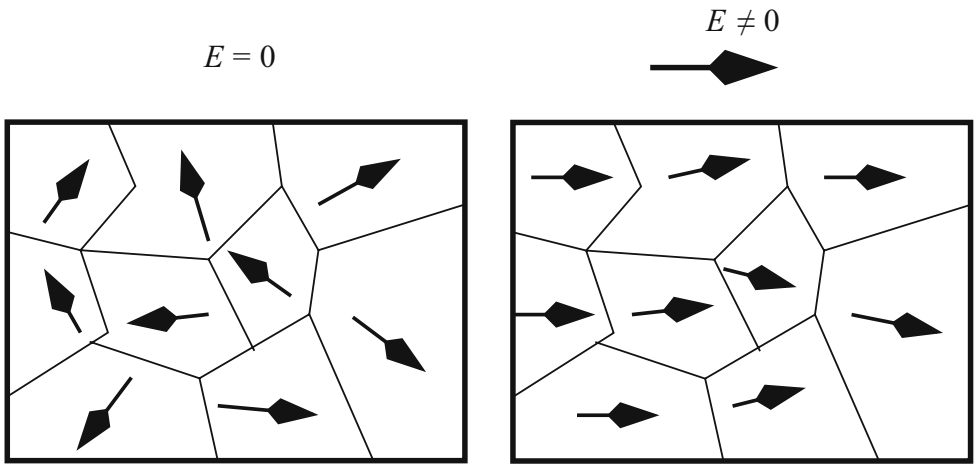

Fig. 3 Sketch of polarization switching in ferroceramics

to the direction of the applied electric field due to the angle θ, which can be expressed as $D_\theta \cos\theta$. In order to average the contributions from the grains with different orientations, it is assumed that there is a grain orientation distribution in the considered material, by which the volume ratio of grains with a specific θ can be specified as function $\beta(\theta)$. This orientation distribution measures the amount (by ratio) of grains whose principal axis has a angle θ with the applied electric field. By using the grain orientation distribution, the overall dynamics of the material can be formulated as a weighted combination of dynamics in different grains as follows:

$$D = \int_0^{\pi/2} D_\theta \cos\theta \beta(\theta) d\theta = \int_0^{\pi/2} D_\theta \lambda_\theta d\theta, \tag{6}$$

where $\lambda_\theta = \cos\theta\beta(\theta)$ is the effective weight function accounting for the contribution of the electric displacement from the grains with θ to the overall electric displacement. It is a function of θ and independent on time and the applied field.

In order to write the equation in a differential form, the above model is re-formulated as the following by taking the derivatives of D with respect to time:

$$\frac{dD}{dt} = \int_0^{\pi/2} \frac{dD_\theta}{dt} \lambda_\theta d\theta, \tag{7}$$

which is continuous in θ. For the sake of convenience of engineering applications, the integral can be approximated by using the Gaussian quadrature as the following:

$$\frac{dD}{dt} = \sum_{k=1}^{N} w_k \lambda_k \frac{dD_k}{dt} = \sum_{k=1}^{N} W_k \frac{dD_k}{dt}, \tag{8}$$

where w_k is the kth weight coefficient for the Gaussian quadrature formulation which approximates the integral operator, N is the number of quadrature points, λ_k is λ_θ valued at the k^{th} quadrature point, and D_k is D_θ valued at the k^{th} quadrature point. Since w_k is already known (given by the quadrature formulation), it can be easily merged with the weight function into a new one W_k.

If one assume that the relaxation effects in all the grains are the same as τ, the overall differential model can be formulated as:

$$\tau \frac{dD_k}{dt} = a_2 D_k + a_4 D_k^3 + a_6 D_k^5 - E\cos\theta_k, \quad k = 1, 2, \cdots, N, \tag{9}$$

$$D = \sum_{k=1}^{N} W_k D_k. \tag{10}$$

where θ_k is θ valued at the k^{th} quadrature point. A closer look at Eq. 9 shows that, there is no need to simulation N equations simultaneously, since they all have the same coefficients, except that the loading is changing as $E\cos\theta_k$. This fact indicates that one can obtain the output D_k for all the k with one simulation followed by certain transformations.

The remaining task for the modelling is to identify the coefficients τ, a_2, a_4, a_6 and to construct the weight function W_k from experimental data. The estimation process itself is a challenging task due to the complexity of the dynamics caused by nonlinearity and bifurcations. Only primitive estimation results will be presented in the next section, while detailed information for the estimation tasks will be reported elsewhere.

5 Numerical experiments

To demonstrate the capability of the proposed model, hysteresis caused by the polarization switching in PZT-5 is modelled and compared with experimental measurements. Experimental $E - D$ relations for the material are found from [3] and re-plotted for comparison purposes. The validation of the model is done by checking the closeness of the model results using estimated parameters to the experimental data.

The estimation is done in two steps. The first step is to estimate the coefficients τ, a_2, a_4 and a_6. Theoretically, it has to be estimated by using several sets of dynamic experimental data performed with various loading rates on a single crystal sample. The second step is to simulate the outputs D_k by using the estimated τ, a_2, a_4 and a_6 values, and fit it to the experimental data to determine the weight coefficients W_k. Due to lacking of dynamical experimental data with different loading rates, here the estimation of τ is ignored and it is artificially set zero, which is based on the assumption that the loading rate is sufficiently slow such that the system will be always in its equilibrium states (no relaxation effects are taken into account for switchings in single crystal).

For the estimation of a_2, a_4 and a_6, the numerical strategy chosen is to formulate the parameter estimation problem as a nonlinear optimization problem as the following [5]:

$$\min_{a_2, a_4, a_6} G = \sum_{i=1}^{M} \left(\tilde{D}_i - D_i\right)^2 \tag{11}$$

where M is the number of experimental data samples, $\tilde{D}_i$ experimental values of D at the i^{th} time instant,

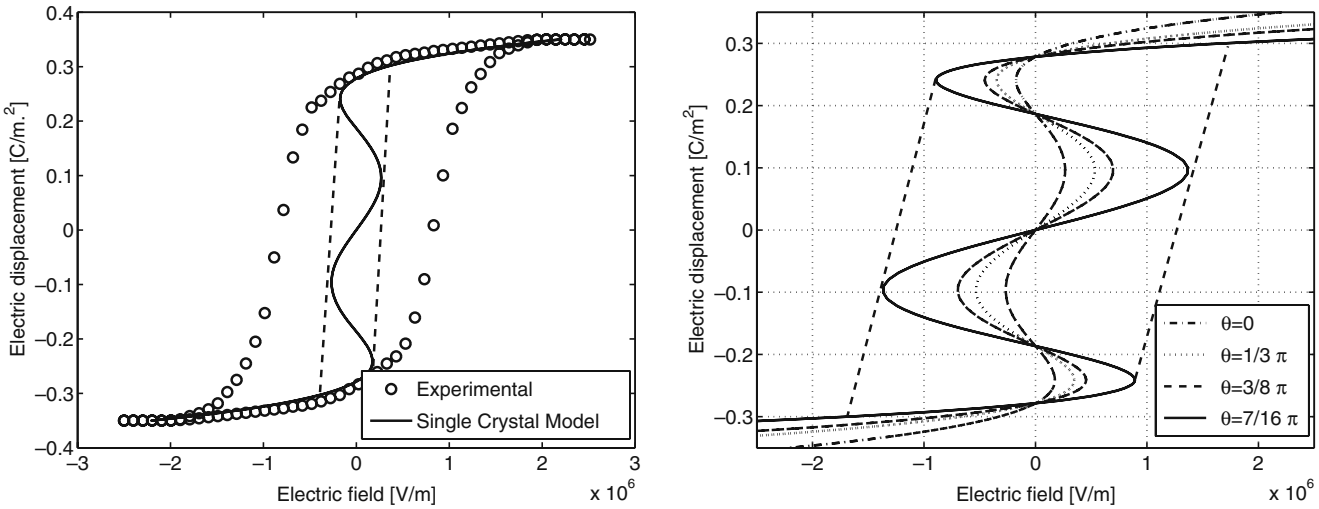

Fig. 4 Single-crystal models by using the Landau theory, (**a**) Hysteresis loop with $\theta = 0$, (**b**) Hyseresis loops with different grain orientations

while D_i are the simulated values at the i^{th} time instant. By using the given experimental data, the estimated values for the three coefficients are the following:

$$a_2 = -4.2951 \times 10^6, \quad a_2 = 1.7889 \times 10^8,$$
$$a_6 = -1.5928 \times 10^9, \tag{12}$$

Using the above values, one can easily simulate all the D_k as functions of t and E by using Eq. 9, which are all hysteresis loops with different shapes. For the sake of clarification, the predicted hysteresis loops for the grain with $\theta = 0$ is plotted in the left in Fig. 4 together with the experimental data, and other hysteresis loops associate the angle of $\theta = 0, \pi/3, 3\pi/8, 7\pi/16$ are plotted in the right of Fig. 4. The full loop is only sketched for one of them ($\theta = 7\pi/16$) by using dashed line in order to make illustration clearer. Similar closed loops for other θ can be easily obtained by inserting lines following the same way as being done in Fig. 2.

By fitting the weighted combination of all the hysteresis loops to the experimental data, all the weight coefficients W_k can be identified by using Eq. 10. W_k can be regarded as the continuous weight function valued the kth quadrature point. It is a function of θ. The estimated profile is plotted in Fig. 5, which is interpolated from the discrete values W_k.

Using the estimated parameter values and weight coefficients, the closeness of the modelled hysteresis loop to the experimental one is sketched in Fig. 6 (solid lines). In the simulation, 50 quadrature points are used,

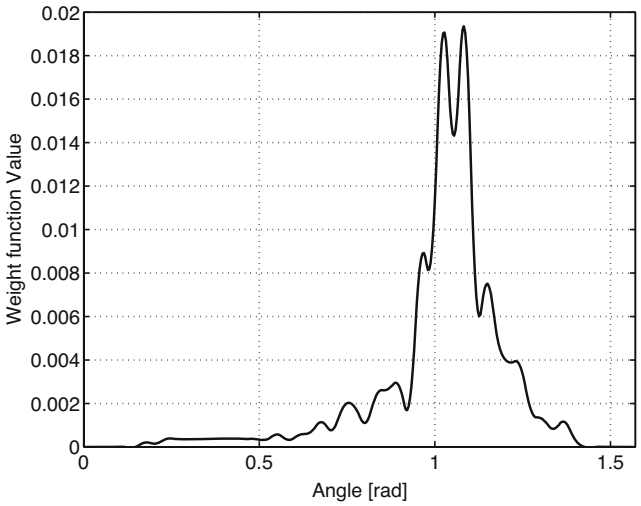

Fig. 5 Weight function profile of the combination for the overall dynamics

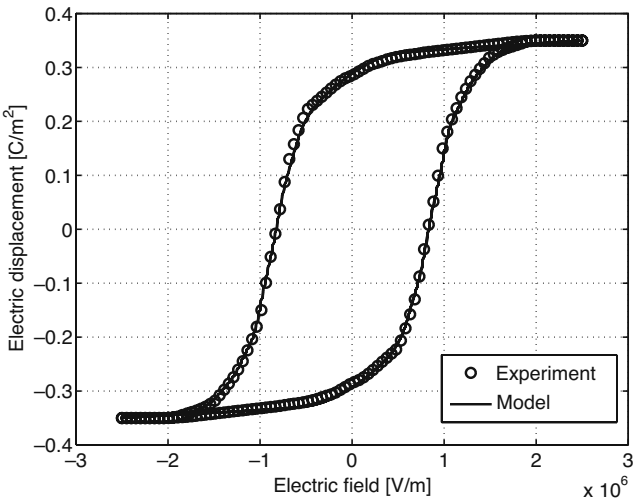

Fig. 6 Comparison of the simulated $E - D$ curve in ferroelectric ceramics between experimental and simulated results

thus 50 nonlinear differential equations are included. In the figure, experimental data are plotted as circles for comparison purpose. It is shown that the experimental measured $E - D$ curve including hysteresis loops is precisely captured by the model constructed in this paper including the relaxation of polarization switchings in polycrystals as mentioned in [5, 8].

The comparison indicates clearly that the experimental results could be captured precisely by the constructed model. It is easy to understand that for different hysteretic behaviour in different materials, two things need to be adjusted. One is the single-crystal model determined by the crystal structure in the material. Another one is the weight function determined by the distribution of the various grain orientations. Beneficially, the current model is formulated as ordinary differential equations, which is very convenient for many engineering applications such as analysis and control. The rate-dependency is naturally enclosed in the model due to the differentiation operation in time domain.

6 Conclusion and discussion

In the current paper, the hysteretic dynamics of ferroelectric ceramics is modelled by a set of nonlinear differential equations. The hysteretic dynamics of single crystals is first described by a single differential equation using the Landau theory for the first-order phase transition. In polycrystals cases, the model is extended by assuming that the overall dynamics is a mixture of dynamics in each grain. Comparison of model results with experiments shows that hysteretic dynamics can be precisely captured by the proposed model.

References

1. G.S. Kino, *Acoustic Waves, Devices, Imaging & Analog Signal Processing* (Prentice-Hall Inc., New Jersey, 1987)
2. M. Willatzen, Ultrasound transducer modeling: general theory and applications to ultrasound reciprocal systems. IEEE Trans. UFFC **48**, 100–112 (2001)
3. M. Kamlah, Ferroelectric and ferroelastic piezoceramics - modeling of electromechanical hysteresis phenomena. Contin. Mech. Thermodyn. **13**, 219–268 (2001)
4. D.A. Hall, Review nonlinearity in piezoelectric ceramics. J. Mater. Sci. **36**(19), 4575–4601 (2001)
5. L.X. Wang, M. Willatzen, Modelling of nonlinear response for reciprocal transducers involving polarization switching. IEEE Trans. UFFC **54**(1), 177–189 (2007)
6. F. Falk, Model free energy, mechanics, and thermomechanics of shape memory alloys. Acta Metall. **28**, 1773–1780 (1980)
7. T. Lookman, S. Shenoy, D. Rasmussen, A. Saxena, A. Bishop, Ferroelastic dynamics and strain compatibility. Phys. Rev. B **67**, 024114 (2003)
8. R.C. Smith, *Smart Material Systems: Model Development* (SIAM, Philadelphia, 2005)