Pergamon

Mechanics Research Communications, Vol. 26, No. 4, pp. 407–414, 1999

0093-6413/99/$–see front matter

PII S0093-6413(99)00041-5

TIME DEPENDENCE OF EFFECTIVE PROPERTIES OF POLYCRYSTALLINE FERROELECTRIC CERAMICS

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(Received 15 June 1998; accepted for print 20 June 1999)

ABSTRACT: In this paper, based on Merz[7] experimental results and classical nucleation theory, a micromechanics statistical model is proposed to describe the relation between the special microstructure-level evolution phenomena-domain switching and macro-response. The polycrystalline ferroelectric ceramics treated as a composition of switched domain and unswitched domain, the approaches of Eshelby's equivalent inclusion and Mori-Tanaka's mean field theory are used to analyze and predict its effective electroelastic properties. The model can incorporate the effects of time dependence of domain switching and shape of individual crystalline. To the $BaTiO_3$ polycrystalline ceramics, the analytical results are in good agreement with the experimental results.

1. INTRODUCTION

Recently the ferroelectric ceramics have such good characteristics of piezoelectricity and pyroelecticity that they have been increasingly used to design various application instructments, such as ultra-precise displacement transducers and actuators used in smart structures[1]. As is all known, $BaTiO_3$ and PZT *et al* commonly applied in the area of technology and engineering, have a tetragonal structure at room temperature, in which exhibits spontaneous polarization and strain. In a stable configuration, each crystallite is divided into a number of microscopic regions in which the polar direction differ from each other by either 180^0 or approximately 90^0. These regions are called the ferroelectric domain and the interface is referred to the 80^0 or 90^0 domain wall respectively. Application of an electric field can make new nucleation formed or domain wall moved so as to switch the polar of a domain by either 180^0 or approximately 90^0, called 180^0 or 90^0 domain (polarization) switching. As a consequence of domain switching, the polarization of individual crystal is reoriented to be approximated to the electric field direction in order to minimize the energy of body[2],[3]. An electrical field can make both 180° and 90° domain switching, but a mechanical field only causes 90° domain switching. Domain switching is well known to cause nonlinear behavior of ferroelectric ceramics[4],[5],[6]. Then, it is necessary and important to lay bare the relation between the domain structure evolution of ferroelectric and external field. Merz[7], Wieder[8] and Fatuzzo[9] had done some experiments to reveal the relation between the microstructure changes and macroscopic response under the application of electric field and found an analytical expression for the switching time of ferroelectric ceramics. Marks *et al*[10] and Redin *et al*[11] studied the distribution of polarization of single crystal and calculated the average polarization of ferroelectric ceramics in terms of the crystal structure and microstructure evolution. Hwang *et al*[12] established a one-dimension model to investigate the polarization switching and obtained many curves which fitted well the experimental results in term of the critical energy value for domain switching. Loge and Suo[13] described the ferroelectric domain evolution by the theory of nonequilibrium thermodynamics and variation principle. Chen *et al*[14] and Huo and Jiang[15] assumed the ferroelectric was consisted of six-type domains to reveal the process of domain switching inside the ferroelectric crystal. Their work mostly regarded the domain switching as one-dimension evolution. On the other hand, many papers[16],[17],[18],[19] had used micromechanical method to analyze and predict the effective electroelastic properties of ferroelectric/piezoeletric, which can't consider the effect of the inherent microstructural change of domain switching under the application of external field on macroscopic properties. In this paper, according that domain switching is mainly a process of nucleation, we developed a micromechanical statistical model to describe the evolution of domain switching under applied external field and then predicted the effective electroelastic of polycrystalline ferroelectric ceramic by the mean field approach.

2. A STATISTICAL MODEL FOR DOMAIN SWITCHING

According to the characteristic of the domain structure evolution, it is efficient to use Kolmogorov-Avrami(K-A) statistical theory to describe the process of domain switching during the action of external field. During the theory description of evolution process of domain, it is essential and necessary to know the four factors: the probability of nucleation, the initial size of the domain, the nucleus growth velocity and the dimensionality of domain motion. Many papers[7],[8],[9] had studied the switching time of $BaTiO_3$ and postulated two mechanisms for the switching. The first mechanism is that when the electric field is reversed the formation of new domains is called nucleation. The second mechanism is called as domain wall motion that describes the growth of small new domain. Based on these postulations, Merz[7] had done many experiments and made a conclusion that domain switching is mostly a nucleation problem under the action of external mechanical or electrical field. Thus, we can obtain an expression that fitted well the experimental results[7],[8],[9] as follows:

The probability of new domain nucleation formation is:

$$P = P_0 \exp[-\frac{\alpha}{E}] \tag{1}$$

Then the switching time t_s versus applied field E can be obtained:

$$\frac{1}{t_s} = \frac{1}{t_\infty}\exp[-\frac{\alpha}{E}] \tag{2}$$

$$t_\infty = b(d - d') \tag{3}$$

where t_∞ is the switching time for an infinite field strength E and α is a constant, which depends on temperature and size of the crystallite. For $BaTiO_3$ ceramics, $b=25.2\times10^{-6}$ s/cm, $d'=3.5\times10^{-3}$ cm, for $d> 5\times10^{-3}$ cm. P_0 is the probability of domain switching for an infinite electric field strength E. The constant α is 470 *kV/m*.

Based on the characteristics of microstructure-level evolution and macrostructure changes, the ferroelectric ceramics can be regarded as a composition of many crystallites with different polar direction as Fig. 1. Here each grain can be treated as an effective domain by taking the vector sum of the spontaneous polarization intensities of all the domains inside it to be the effective polarization of individual crystal. The polarization direction of individual grain for the unpoled ferroelectric shown in Fig. 1(a) are randomly distributed with spatially distributed function $f(\theta)=\sin(\theta)/4\pi$, so the unpoled ferroelectric ceramics are isotropic and non-piezoelectric materials. But after poled, the polar direction of single crystallite would switch to be paralleled to the electric field direction, shown in Fig. 1(b). Then we can take the process of domain switching as polar direction of individual crystal switching, which is conjugated by mixed unswitched or new-switched grains. Based on Eqs. (2), (3), the angle velocity of polar direction switching can be given as:

$$\omega = \omega_\infty \exp[-\frac{\alpha}{E}] \tag{4}$$

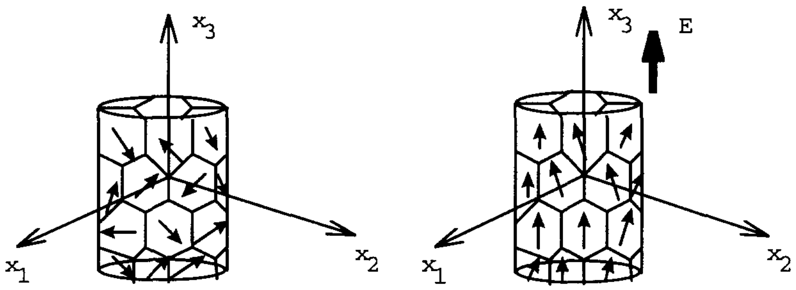
$$\omega_\infty = \frac{\pi}{t_\infty} = \frac{\pi}{b(d-d')} \tag{5}$$

Then, the volume fraction of switched crystal at some time t can be obtained as:

$$V_f(E,t) = \int_0^{2\pi} d\varphi \int_0^{\omega t} f(\theta) d\theta s \qquad (t < t_\infty \exp[\frac{\alpha}{E}]) \tag{6a}$$

$$V_f(E,t) = 1 \qquad (t > t_\infty \exp[\frac{\alpha}{E}]) \tag{6b}$$

These equations also are suitable for the case of stress-induced domain switching. When ferroelectric ceramics are subjected to external stress field, we can transfer the applied stress into electric field through the constitutive equation and assume that the ferroelectric ceramics are subjected to this imaginary electric field.



(a) unpoled ferroelectric ceramic (b) poled ferroelectric ceramic

Figure 1. Model showing the unpoled (a) and poled (b) ceramics and individual domain switching under external field.

3. BASIC FORMULATION AND THE ESHELBY-MORI-TANAKA METHOD FOR POLYCRYSTALLINE FERROELECTRIC CERAMICS

3.1 Basic formulation

In order to describe the piezoelectricity and elasticity of ferroelectric or piezoelectric ceramics, there are four types of piezoelectric equations. Based on the notation introduced by Barnett and Lothe[20], the piezoelectric equations can be simplified and expressed as:

$$\Sigma_{ij} = E_{ijmn} Z_{mn} \tag{7a}$$

or

$$Z_{mn} = E_{ijmn} \Sigma_{ij} \tag{7b}$$

where

$$\Sigma_{ij} = \begin{cases} \sigma_{ij} & j = 1,2,3 \\ D_i & j = 4 \end{cases} \tag{8}$$

$$E_{ijmn} = \begin{cases} C_{ijmn} & j,m = 1,2,3 \\ e_{nij} & j = 1,2,3; m = 4 \\ e_{imn} & j = 4, m = 1,2,3 \\ -k_{in} & j,m = 4 \end{cases} \tag{9}$$

$$Z_{mn} = \begin{cases} \varepsilon_{mn} & m = 1,2,3 \\ \phi,_n & m = 4 \end{cases} \tag{10}$$

and Z_{mn} is derived from U_m given by

$$U_m = \begin{cases} u_m & m = 1,2,3 \\ \phi & m = 4 \end{cases} \tag{11}$$

It is noted that the "inverse" of E_{ijmn} is defined as F_{abij}, evidently E_{ijmn} and F_{abij} are diagonally symmetric for common piezoelectric ceramics.

On the other hand, elastic equilibrium requires that the stress σ is divergence free in each crystallite and that the traction remains continuous across grain boundaries. According to Coulomb's law, the dielectric displacement also should be divergence free in those cases, thus:

$$\Sigma_{ij,i} = 0 = \begin{cases} \sigma_{ij,i} = 0 & j = 1,2,3 \\ D_{i,i} = 0 & j = 4 \end{cases} \tag{12}$$

3.2 Eshelby-Mori-Tanaka's method[21] for polycrystalline ferroelectric ceramics

Now based on the presented model on the domain switching and Eshelby's equavilent inclusion theory, we can take the new-switched crystal as the inclusion phase. Then, the average field of matrix with electroelastic moduli E_m can be given by:

$$\Sigma_m = \Sigma^0 + \Sigma^1 = E_m (Z^0 + Z^1) \tag{13}$$

where Z^1, Σ^1 are the disturbed fields due to the inhomogeneous inclusions and their interaction. The volume average field in the inclusion which occupy a region Ω with electroelastic moduli E_{in} can be expressed as:

$$\begin{aligned}\Sigma_{in} = \Sigma^0 + \Sigma^1 + \Sigma^{pt} &= E_{in}(Z^0 + Z^1 + Z^{pt} - Z^*) \\ &= E_m(Z^0 + Z^1 + Z^{pt} - Z^* - Z^{**})\end{aligned} \tag{14}$$

Where, Z^* is the eigenfield of the new-switched crystal, which polarization orientation is purposed to be parallel to the direction of applied electric field, Z^{**} is the fictitious eigenfield: strain and electric field. According to Wang[22]'s three-dimensional solution for an ellipsoidal inclusion in a piezoelectric material, Σ^{pt}, the disturbed field, can be obtained as

$$Z^{pt} = S(Z^* + Z^{**}) \tag{15}$$

where S is the electroelastic Eshelby tensors.

Based on the Mori-Tanaka's mean field theory, the average field of all over the ceramic can be presented by:

$$< \Sigma >= \frac{1}{V}\int_{D-\Omega} \Sigma_m dv + \frac{1}{V}\int_{\Omega} \Sigma_f dv = \Sigma^0 \tag{16}$$

where <·> means the volume average, V is the volume of the overall ceramics.
then :

$$< Z^1 >= -V_f(< Z^{pt} > - < Z^* > - < Z^{**} >)$$

$$< Z^1 >= -V_f(S - I)(< Z^* > - < Z^{**} >) \tag{17}$$

where V_f is the volume fraction of the new switched grains and given by Eq. (6).

Combining Eqs. (13)-(17) leads to

$$Z^{**} = [E_m(S - I) - E_{in}S + V_f(E_{in} - E_m)(S - I)]^{-1}(E_{in} - E_m)[Z^0 + (1 - V_f)(S - I)Z^*] \tag{18}$$

The overall strain and electric field denoted by <Z> can be obtained as the weighted average of the over each phase:

$$\begin{aligned}< Z > &= \frac{1}{V}[\int_{D-\Omega} < Z^0 + Z^1 > dv + \int_{\Omega}(Z^0 + Z^1 + Z^{pt} - Z^*)dv] \\ &= Z^0 + V_f Z^{**}\end{aligned} \tag{19}$$

Thus, substituting Eq. (6) and Eq. (18) into Eq. (19), it is evident that the overall effective electroelastic properties of ferroelectric ceramics are a function of domain switching time t and the magnitude of the external applied field.

4. NUMBERICAL RESULTS AND DISCUSSION

In this section, the time dependence of effective electroelastic properties was predicted and analyzed in accordance with the above statistical model for polycrystalline ferroelectric ceramics. At room temperature, the tetragonal phase of

$BaTiO_3$ has structure constants a=3.992 $\overset{o}{A}$, c=4.035 $\overset{o}{A}$, the spontaneous polarization Ps=0.26C/m^2 and the remanent polarization Pr =0.08 C/m^2. Thus, the eigenstrain and eigenelectric displacement of a single-crystal can be given by:

$$\varepsilon^* = \begin{bmatrix} -0.005 & 0 & 0 \\ 0 & -0.005 & 0 \\ 0 & 0 & 0.01 \end{bmatrix}, \quad D^* = \begin{bmatrix} 0 \\ 0 \\ 0.26 \end{bmatrix}$$

The material constants of $BaTiO_3$ single crystal and ceramic are shown as following Table 1.

Table 1 The elastic, piezoelectric and dielectric coefficients of $BaTiO_3$ at 25°C[1].

	Single crystal	Ceramic
C_{11}^E (GPa)	275	166
C_{33}^E (GPa)	164.8	162
C_{44}^E (GPa)	54.3	43
C_{12}^E (GPa)	178.9	77
C_{13}^E (GPa)	151.6	78
e_{31} (Cm^{-2})	-2.69	-4.4
e_{33} (Cm^{-2})	3.65	18.6
e_{15} (Cm^{-2})	21.3	11.6
k_{11}(×10^{-9} C^{2}N^{-1}m^{-2})	17.4	11.2
k_{33}(×10^{-9} C^{2}N^{-1}m^{-2})	0.96	12.6
d_{31}(×10^{-12} C/N)	-34.5	-79
d_{33}(×10^{-12} C/N)	85.6	191
d_{15}(×10^{-12} C/N)	392	270

In accordance with the electroelastic constants of Table 1 and last section model analysis on the relation between microstructure evolution and macroscopic response, time dependence of the effective electroelastic properties of polycrystalline ferroelectric can be derived. The calculated results under the application of electric field are shown in Fig. 2. From Fig. 2, the electric-induced strain ε_{33} is a function of applied electric field E_3 and time t apparently. Switching time decreases non-linearly with increasing the applied electric field E_3. For a low applied electric field, the switching time is too large to make more domains switched and then can not effect on the macroscopic strain ε_{33} changing in a limit time, so the people can't observe and measure the macroscopic change. But when electric field strength reaches about 10^5 V/m, the value of the strain ε_{33} will become larger at that instant. On the other hand, we can see that the order of coercive electric field for $BaTiO_3$ ceramics is also 10^5 V/m, which is consistent with the experimental result. These results demonstrate that the domain switching is a process of nonequilibrium thermodynamic evolution and time hysteresis of domain switching is the main factor of causing macroscopic non-linearly behavior of ferroelectric ceramics.

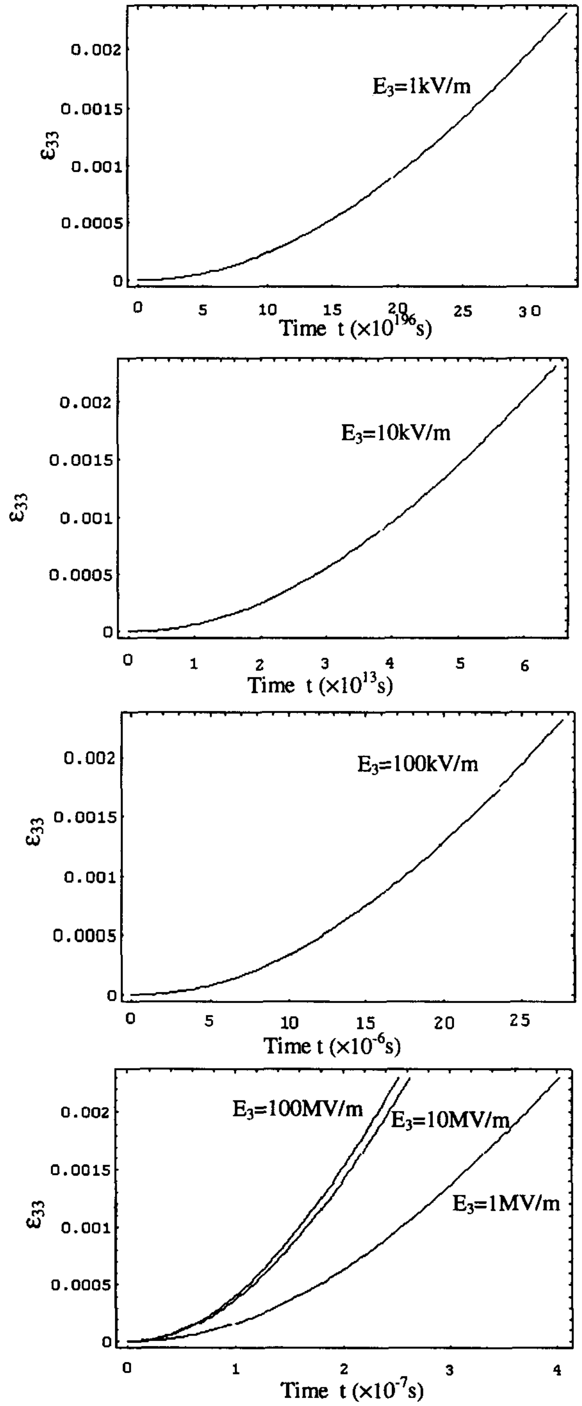


Figure 2. The strain ε_{33} varies with time t under the action of electric field E_3

5. CONCLUSION

Based on the three-dimensional switching model and Wang's solution for piezoelectric matrix containing an ellipsoidal inclusion, time dependence of the effective electroelastic properties of polycrystalline ferroelectric ceramics is calculated by the Eshelby-Mori-Tanaka's mean field approach, which can consider the effect of the grain shape. For sample, the influence of domain evolution and switching time with respect to the applied field on the effective electroelastic properties of a $BaTiO_3$ ceramic is numerically analyzed. The calculated results are in good agreement with the experimental observations.

ACKNOWLEDGMENT:

This work was supported by the National Foundation of China for Excellent Young Investigators.

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