Simulations on the electromechanical poling of ferroelectric ceramics

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Abstract

Based on the two-step-switching model, the process of electromechanical poling of a ferroelectric ceramics is simulated. A difference of the remnant polarizations between two poling protocols (mechanical stress is applied before and after the application of poling field) is found from our simulations, which is also observed in experiment. An explanation is given to illustrate why the remnant polarization for the case that mechanical stress is loaded after the application of electric field is larger than the case that mechanical stress is loaded before the application of electric field. Our simulation results supply a proof for the validity of the two-step-switching model in the electromechanical poling of polycrystalline ferroelectric ceramics.

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I. INTRODUCTION

Ceramic Lead-zirconate-titanate\[\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3\] is one of the technologically most important polar oxide materials. It may be used for ferroelectric random access memories, high-storage dynamic RAM capacitors, sensors and actuators in smart structures. Most of these applications require a high remnant polarization, and an external load is applied on the unpolable ceramics to acquire a large polarization in the poling direction\(^1\). On poling, the domains in the ceramics reorient themselves to give a polarization closer to the poling direction. Domain switching and rotation in PZT ceramics can be triggered by either a mechanical stress or an electric field. As is well known, a strong electric field polarizes the ceramics by aligning the polarization of the domains as closely as possible with the electric field. For a strong applied compressive stress paralleling to the polarization, the domain will be rotated to make the polarization as close as possible to 90\(^0\) from the direction of the applied stress. If the external electric and mechanical loads acted on the domain at the same time, a criterion for domain switching was first proposed by Hwang\(^2\) on the basis of the total work done by electric and mechanical loads for switching the domain as the driving force, which is expressed by

\[
\sigma_{ij}\Delta e_{ij}^s + E_i\Delta P^s_i \geq 2P_sE_c,
\]

(1)

where \(E_i\) and \(\sigma_{ij}\) are the components of the applied electric field and stress, respectively, \(P^s_i\) and \(e_{ij}^s\) are the components of the spontaneous polarization and spontaneous strain, respectively. However, Hwang’s criterion cannot explain the dependence of the mechanical stress on coercive electric field, and the dependence of electric field on coercive mechanical stress, and there is no energetic difference between 90\(^0\) domain-switching and 180\(^0\) domain-switching. Last year, a new criterion for domain-switching under the application of both electric and mechanical loads in ferroelectric materials was proposed\(^3,4\), in which the 180\(^0\) domain switching is replaced by two successive 90\(^0\) switchings. It is found that this two-step switching criterion can model the hysteresis loops and butterfly-shape curves of ferroelectric materials and accurately predict the coercive electric fields under different applied mechanical stresses. In most experimental and theoretical studies, the uniaxial compressive stress and the applied electric field are loaded in the same direction\(^1,5\). Recently, the electromechanical poling of a ferroelectric PZT rod is reported\(^6\). The set-up is shown in Fig. 1.
The commercial PZT PIC 151 sample is placed inside a high pressure polyethylene tube which transfers axial compressive stress into uniform radial compressive stress. It is shown that the application of mechanical stress perpendicular to the electric poling direction drastically improves the ferro- and piezoelectric properties, and decreases the magnitude of electric field required for poling. They clearly observe a path dependence of the polarization buildup. The remnant polarization and the piezoelectric coefficient of the ceramics will be different if the mechanical stress is applied before and after the application of electric field. And the energetic approach mentioned above could not give an explanation on this path dependent poling result. In this paper, we employ the two successive $90^\circ$ switchings model to simulate the poling behavior of ferroelectric ceramics under a radial pressures, as shown in Fig. 1. It is found from our simulations that a larger remnant polarization is obtained under the case that the mechanical load is applied after the electric load, and this supply a new evidence for the validity of the two successive $90^\circ$ switchings model in explanation of domain switching behavior of the ferroelectric ceramics under the electromechanical load.

II. MODEL AND SIMULATIONS

The unpolable ferroelectric ceramics is assumed to be made up of many randomly oriented grains, each grain is ferroelectric tetragonal and single domain. The $90^\circ$ switching for the tetragonal symmetry is used as a general representative of the non-$180^\circ$ domain switching in this paper. For a homogeneous ceramics, the Reuss approximation is adopted when the material is subjected to the applied electric field and stress. The orientation of the grain is
described by a global Cartesian coordinate, and a local Cartesian coordinate system is also
set up along with the edges of the tetragonal cell. The orientation of each domain can be
described by three angles $\psi$, $\theta$, and $\varphi$. The orthogonal transformation between the global
coordinate $\vec{x}$ and the local coordinate $\vec{x}'$ has the following form,

$$A = R_z(\psi)R_y(\theta)R_x(\varphi) = \begin{pmatrix}
\cos \theta \cos \psi & \cos \theta \sin \psi & -\sin \theta \\
\sin \varphi \sin \theta \cos \psi - \cos \varphi \sin \psi & \sin \varphi \sin \theta \sin \psi + \cos \varphi \cos \psi & \sin \varphi \cos \theta \\
\cos \varphi \sin \theta \cos \psi + \sin \varphi \sin \psi & \cos \varphi \sin \theta \sin \psi - \sin \varphi \cos \psi & \cos \varphi \cos \theta 
\end{pmatrix},$$

(2)

where $R_z(\psi)$, $R_y(\theta)$, and $R_x(\varphi)$ stand for the rotation along the x-axis, y-axis, and z-
axis of the global coordinate system, respectively. We assume the direction of the grain
polarization is along the direction of $x'_3$ of the grain in the local coordinate system. By
random selecting three angles $\psi$, $\theta$, and $\varphi$ between 0 and $2\pi$ for each grain in the global
coordinate system, we can obtain a random distribution of the polarizations in the ceramics.
The averaged polarization along the $x_3$ direction in the global coordinate system is selected
as the measurable polarization of the ceramics. The ceramic is simulated by a cylindrical
lattice, each lattice site is distributed with a grain. The radial and height of the cylinder
lattice are 15 and 60, respectively.

The main motivation of this paper is to give an explanation on the path dependence elec-
tromechanical poling process mentioned in Ref. 6. In the experiment, two poling protocols
are designed as following: For protocol 1, the poling field is raised on the sample from zero
to a maximum value $E_{max}$ at first, then a radial stress is loaded, and the mechanical stress
is removed after a period of time, then the poling field is turned down from the maximum
value to zero. For protocol 2, the radial stress is loaded on the sample at first, then a poling
field cycle is applied on the sample before the stress is removed. During the above two
protocols, the domain switching is induced either by the electric field or by the combined
electric and mechanical loads. For the first case, i.e., only under an electric load, the $180^0$
switching occurs when the total work done reaches a critical value($E_{180}$) corresponding to
the energy barrier of $180^0$ domains, and the $90^0$ domain switching occurs when the total
work done reaches a critical value($E_{90}$) corresponding to the energy barrier of $90^0$ domains.
If only under the application of electric field, the switching of $180^0$ domain can only be $180^0$
switching, and the switching of $90^0$ domain can only be $90^0$ switching. Mathematically, the
domain switching criterions for $90^0$ and $180^0$ switchings under an electric load can be given
by
\[ E_i \cdot \Delta P_i \geq E_{90}, \]
\[ E_i \cdot \Delta P_i \geq E_{180}. \] (3)

For the second case, i.e., the case that domain-switching is driven by both electric load and mechanical load. A two-step-switching criterion\(^{3,4}\) is used here to simulate the different experimental results between protocol 1 and protocol 2. As referred in Ref. 6, the switching criterion of Eq. (1) cannot obtain the path dependence of the remnant polarization for different poling protocols. The two-step-switching model divides each 180° switching into two successive 90° switchings, and the 90° switching criterion is described as following:

\[ E_i \cdot \Delta P_{s_i}^s + \sigma_{ij} \cdot \Delta e_{s_{ij}}^s \geq E_{90}. \] (4)

In our simulation, the mechanical stress is applied along the radial direction, the electric field is applied along the z-direction in the global coordinate system, we resolve the stress and the spontaneous strain into x-direction and y-direction, and the work done by the stress on each domain \( i \) during the switching process is calculated as the summation \( \sigma_x \Delta e_{s_{ix}}^s + \sigma_y \Delta e_{s_{iy}}^s \).

The spontaneous strain of the tetragonal unit cell has principal values \( e_3 = (c - a_0)/a_0 \) and \( e_1 = e_2 = (a - a_0)/a_0 \), where \( a \) and \( c \) are the lattice parameters of the tetragonal unit cell and \( a_0 \) is the lattice parameter of the cubic cell above the Curie temperature. We assume \( e_1 = e_2 = -\frac{1}{2}e_3 \) with \( e_3 = e_0 \) within the whole paper. From Eq. (4), we can see that the lateral stress will hinder the first 90° switching if the strength of electric field is not strong enough, especially for these grains whose polarizations are almost antiparallel to the external electric field. In order to take the interaction of the grain with its surrounding grains into account, the inclusion model is introduced into our simulation\(^8\). Therefore, the domain switching criterion for the ceramics under both electric load and mechanical load is modified as following:

\[ (E_i + \frac{1}{3\varepsilon}P_{i}^{sm}) \cdot \Delta P_{s_i}^s + (\sigma_{ij} + \frac{2}{3}Y e_{ij}^{sm}) \cdot \Delta e_{s_{ij}}^s \geq E_{90}, \] (5)

and the domain switching criterion in Eq. (3) for the ceramics only under an electric load is changed into

\[ E_i + \frac{1}{3\varepsilon}P_{i}^{sm} \cdot \Delta P_{s_i}^s \geq E_{90}, \]
\[ (E_i + \frac{1}{3\varepsilon}P_{i}^{sm}) \cdot \Delta P_{s_i}^s \geq E_{180}, \] (6)
where $\bar{\varepsilon}$ is the effective dielectric permittivity of the ceramics, $Y$ is the effective modulus of the ceramics, $P_{i}^{sm}$ is the averaged spontaneous polarization of the matrix of grain $i$, and $e_{ij}^{sm}$ the averaged spontaneous strain of the matrix of grain $i$.

We use a cylindrical lattice with radial 15 and height 60 to simulate the cylindrical ceramics sample in the experiment, each lattice site is distributed with a grain. The polarization of the grain is selected randomly by random choosing three angles $\psi$, $\theta$, and $\varphi$ for each grain. So, the averaged total polarization of the sample is zero at initial time. The volume fraction of $90^0$ domain is taken to be 0.1, which can be realized by randomly selecting 10% sites, and do a mark for these polarizations. For $90^0$ domain, only $90^0$ switching can be taken place under an electric load. For $180^0$ domain, only the $180^0$ switching is permitted under an electric load. When the sample is applied by an electric field and a mechanical stress simultaneously, the two-step-switching model is adopted for both the $90^0$ domains and $180^0$ domains. It is assumed that the relax time of domain switching is very short compared with the change of the electric field and mechanical stress. In protocol 1 and protocol 2, when the sample is only under the electric load, the criterion described in Eq. (6) is used to decide whether a $90^0$ switching or a $180^0$ switching is taken place. So, for $180^0$ domain, we can try to reverse the polarization of the grain in the local coordinate system, the direction of the grain polarization will take the new direction when the second formula in Eq. (6) is satisfied, otherwise, the direction of the grain polarization keeps invariant. For $90^0$ domain, there are four possible new directions in the local coordinate system, we can try to re-orientate the polarization to one of the new directions, and if the new direction meets the first criterion described in Eq. (6), then the domain rotates to the new direction, if two or more of the new directions meet the criterion simultaneously, the domain switches to the one that makes the left hand side of the first formula in Eq. (6) the largest. When the sample is under combined electric and mechanical loads, the two-step-switching is simulated as following: the first $90^0$ switching is determined among four possible new directions dependent on whether the condition in Eq. (5) is satisfied. Only the first $90^0$ switching occurs realistically, should we try to decide whether the second $90^0$ switching can occur. The possible test direction for the second $90^0$ switching should be the inverse direction of the grain before the first $90^0$ switching. The simulation process is carried out from a randomly orientated initial state, and then the electric field is increased from zero to 750V/mm with a step length 15V/mm. At each step of the applied
electric field, a scan over all the grains is executed, and the polarization direction of each
grain is simultaneously decided whether to take a new direction to make the ceramics
staying at a low energy state. The total polarization of the ceramics is calculated at each
electric field. After the increasing process, the applied electric field is then decreased from
750V/mm to zero. The parameters for $Pb_{0.99}[Zr_{0.45}Ti_{0.47}(Ni_{0.33}Sb_{0.67})_{0.08}]O_3$ used in our
simulation is taken from Ref. 5,8 and are as following: $P_s = 0.45C/m^2$, $e_0 = 0.0073$,
$E_{90} = 0.13MV/m$, $E_{180} = 2E_{90}$, $\epsilon = 0.80\mu F/m$, $Y = 7.5Gpa$, the effective stress loaded on
the ceramics along x-direction and y-direction is selected as 20Mpa to fit the experiment
data.

III. RESULTS AND DISCUSSIONS

Our simulation results on the polycrystalline ferroelectric ceramics are shown in Fig. 2,
where triangle symbols and circle symbols denote the experiment data in protocol 1 and
protocol 2, respectively, and solid lines and dotted lines stand for our simulation results in
protocol 1 and protocol 2, respectively.

From Fig. 2, we can see that there exists a clear difference of the remnant polarization
between protocol 1 and protocol 2, which cannot be given by Hwang’s switching criterion.
Furthermore, the difference of the remnant polarization between the two protocols will
increase with the increase of radial stress loaded perpendicular to the electric field. The path
dependent remnant polarization is aroused by the first 90° switching of these polarizations
which are almost antiparallel to the electric field. When the radial stress is loaded, the first
90° switching of the above mentioned polarizations are difficult to occur. From Eq. (5), we
can see that the larger the stress is, the more difficult the first 90° switching occurs for these
polarizations whose directions are close to the inverse direction of electric field. If the electric
field is loaded before the application of lateral stress, these polarizations, whose directions
are close to the inverse direction of electric field, are already switched under the action
of electric field when the switching criterion Eq. (6) is satisfied. It is the reason why the
remnant polarizations are different between the two protocols. If only the x-direction lateral
stress in the global coordinate system is loaded for a cubic sample, we can choose a specific
grain, which direction is exactly inverse to the direction of the electric field, to illustrate that
there is no difference in remnant polarization between the two cases that the mechanical stress is applied before and after the application of electric field. The polarization of the above grain will first flip from minus z-direction to y-direction, then flip from y-direction to z-direction, and the stress in this case won’t hinder the switching of the polarizations. As a result, the averaged polarizations along z-axis will be the same for the two protocols. So, the radial stress is also an important factor for the occurrence of the difference of the remnant polarization between the two protocols. The small deviation of our simulation results with the experiment data in Fig. 2 may be resulted from the inclusion model, which does not take the shape of the sample into account. Further investigation is currently in progress to take the neighbor dipole-dipole interactions into account rather than the inclusion model. Despite the simulation being carried out with the assumption that the PZT is tetragonal, the model is still physically justifiable for the rhombohedral material, and the 90\textdegree\ tetragonal switches can provide a reasonable representation of the \(~70\textdegree\) and \(~110\textdegree\) switches in the rhombohedral phase.

In summary, we employ the two-step-switching model to simulate the electromechanical poling behavior of unpolable ferroelectric ceramics. It is found that the application of
mechanical stress perpendicular to the electric poling direction will increase the remnant polarization, especially when the radial mechanical stress is loaded after the application of electric field. An explanation on the path dependence of the polarization buildup is presented.

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Figure Captions

FIG1: Schematic diagram of the electric-mechanical loading system.

FIG2: Polarization of the ferroelectric ceramics as a function of poling field for different protocols. Solid line and dotted line are our simulation results for protocol 1 and protocol 2, respectively. Triangle symbols and circle symbols denote the experimental data\textsuperscript{6} for the two protocols.