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Operation of multiple 90° switching systems in barium titanate single crystals under electromechanical loading

J. Shieh[a] and J. H. Yeh
Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

Y. C. Shu and J. H. Yen
Institute of Applied Mechanics, National Taiwan University, Taipei 106, Taiwan

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Hysteresis evolution of a $5 \times 5 \times 2$ mm^3 barium titanate single crystal during a combined electromechanical loading sequence reveals incomplete switching characteristics and a considerable disproportion of slope gradients at zero electric field for the measured polarization and strain hysteresis curves. A likely cause for the disproportion of gradients is the cooperative operation of multiple 90° switching systems by which "polarization-free" strain changes are induced. In addition, a theoretical study indicates that the presence of depolarization fields generated from the unshielded boundaries and/or incompatible domains within the crystal can have a substantial influence on the polarization measurement in the loading direction. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2766658]

Various attempts have been carried out to develop large strain actuation in ferroelectric single crystals either via phase transition or via domain switching.[1–3] One of the most notable examples is the endeavor by Burcsu *et al.* in which the 90°-switching-induced strain of barium titanate ($BaTiO_3$) single crystals under combined electrical and mechanical loadings was examined, and a strain of nearly 0.8% was observed under a combined loading of 1.78 MPa compressive stress and 1 MV m^{-1} electric field.[3] An important discovery is made after carefully examining the hysteresis data of the work of Burcsu *et al.*—a severe disproportion of slope gradients at zero electric field for the measured polarization and strain hysteresis curves is apparent, especially at high compressive stresses. Here, the phrase "disproportion of slope gradients" means that the two quantities defined by the rate of change of polarization with respect to electric field and the rate of change of strain with respect to electric field do not remain in a constant ratio. The discovered disproportion characteristic would imply a "decoupling" between switching strain and switching polarization within the $BaTiO_3$ single crystals. This seems to be in contradiction to the common understanding of ferroelectrics that switching-induced strain is accompanied by changes in polarization.[4–6] The current investigation is therefore conducted to study such a discrepancy, focusing on providing possible explanations and mechanisms.

A series of polarization and strain hysteresis measurements under combined uniaxial electrical and mechanical loadings were performed on an unpoled (001)-oriented cuboidal $BaTiO_3$ single crystal measuring $5 \times 5 \times 2$ mm^3. The crystal was obtained from MTI Co., CA. The electromechanical loading fixture and measuring apparatuses for the hysteresis measurements were identical to the ones reported in the authors' previous works.[7,8] The loading direction was in the 2 mm thickness direction. Figures 1 and 2 show, respectively, the stable polarization (P_3) versus electric field (E_3) and the corresponding strain (ε_{33}) versus electric field (E_3) hysteresis curves for the $BaTiO_3$ single crystal measured at various compressive stresses ranging from 0 to 2.7 MPa. The electrical part of the applied loading has an amplitude of ±1.25 MV m^{-1} and a frequency of 0.2 Hz. It is evident from Fig. 2 that with increasing compressive stress, the total electrostrain increases significantly. This is mainly due to the enhancement of 90° domain switching by additional compressive stress (i.e., stress-activated ferroelastic switching). Although measured with an entirely different loading setup to the one employed by Burcsu *et al.*,[3] the polarization and strain hystereses obtained in the present study also display a considerable disproportion of slope gradients at zero electric field.

It is assumed that the maximum possible variations in polarization and strain through 90° switching for the $BaTiO_3$ single crystal, allowed by crystallography, are its theoretical

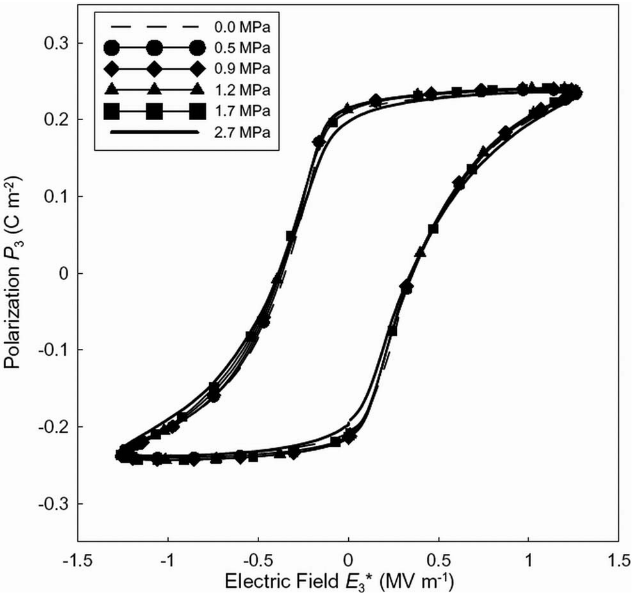

FIG. 1. Measured polarization vs electric field hysteresis curves for (001)-oriented $BaTiO_3$ single crystal at various constant compressive stresses.

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[a] Author to whom correspondence should be addressed; electronic mail: jayshieh@ntu.edu.tw

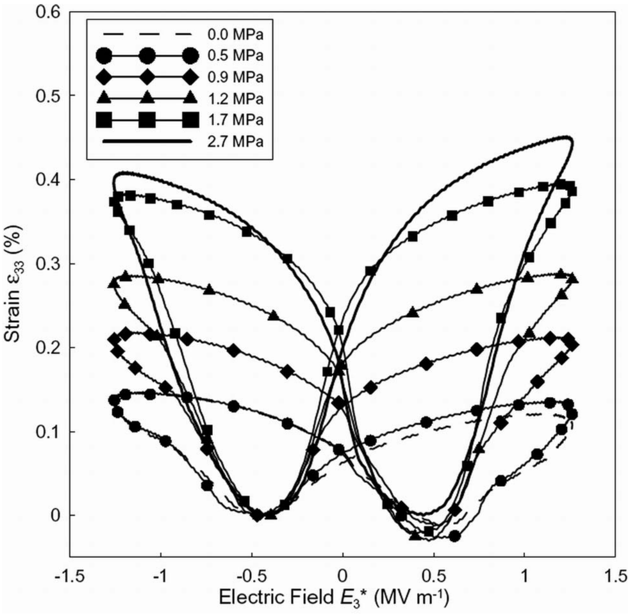

FIG. 2. Measured strain vs electric field hysteresis curves for (001)-oriented $BaTiO_3$ single crystal at various constant compressive stresses.

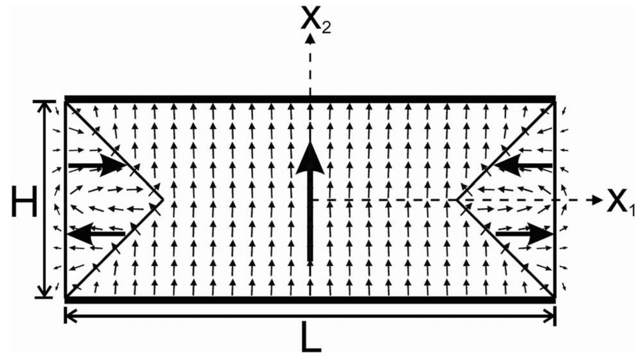

FIG. 3. Compatible domain pattern in a 5×2 mm^2 $BaTiO_3$ single crystal [the heavy arrows denote the polarizations, while the small arrows denote the directions of electric displacement vector (**D**)].

saturation values, i.e., $P_s=0.26$ C m^{-2} and $\varepsilon_{\max}=0.011$, respectively.[9–11] The percentages of polarization and strain changes from maximum to zero electric field at selected stress levels for the crystal of Burcsu *et al.*[3] and the crystal tested in the present study are calculated and listed in Table I. Stress-activated 90° switching typically gives rise to a change in both strain and polarization. However, Figs. 1 and 2 and Table I suggest that at high stresses, a sizeable change in strain during electric field unloading is accompanied by a relatively small change in polarization. To exhibit such a behavior, multiple 90° switching systems must exist and operate together in the crystal in such a way that "polarization-free" strain changes are produced. Theoretically this is possible if one considers that a 90° switching of an out-of-plane 180° domain wall into an in-plane 180° domain wall produces no change in polarization. The polarization hystereses shown in Fig. 1 possess high coercivity and lower saturation level than the theoretical value. These are strong indications that the single crystal used in the present study exhibits hardening and depolarization characteristics and that switching is incomplete at maximum electric field, possibly leaving some domains with 180° relative orientation. Such an arrangement of domains, if it exists at maximum electric field, would be the prerequisite for subsequent multiple stress-assisted 90° switches during electric field unloading where the overall change in polarization is near zero.

TABLE I. Polarization and strain changes (in percentages) from maximum to zero electric field at selected stress levels for $BaTiO_3$ single crystal of the Burcsu *et al.* (Ref. 3) and the $BaTiO_3$ single crystal tested in the present study.

$BaTiO_3$ crystal	Compressive stress σ_{33}^* (MPa)	$\frac{\lvert P_3^{E=0}-P_3^{E_{\max}}\rvert}{P_s}$	$\frac{\lvert \varepsilon_{33}^{E=0}-\varepsilon_{33}^{E_{\max}}\rvert}{\varepsilon_{\max}}$
Burcsu *et al.*	1.8	24.23%	61.10%
	1.1	8.92%	43.16%
Present study	2.7	16.04%	25.54%
	1.7	10.27%	15.28%

A simple calculation is conducted to verify the above argument. Let C_1 and C_2 denote, respectively, the volume fraction of out-of-plane domains oriented in a direction identical to the applied electric field and in a direction parallel but opposite to the applied electric field. The volume fraction of in-plane domains is therefore equal to $(1-C_1-C_2)$. The polarization and actuation strain in the loading direction are $\langle P_3\rangle = P_s(C_1-C_2)$ and $\langle \varepsilon_{33}\rangle = \varepsilon_{\max}(1-C_1-C_2)$, respectively, where $\langle\cdots\rangle$ denotes the volume average. At 2.7 MPa and maximum electric field, the crystal tested in the present study exhibits a polarization value of 0.235 C m^{-2} (see Fig. 1) which is about 90% of the theoretical saturation value. At this stage of loading, if only out-of-plane 180° domains exist in the crystal, the relationships between C_1 and C_2 can be stated as $C_1+C_2=1$ and $C_1-C_2=0.9$. Hence, $C_1=0.95$ and $C_2=0.05$ can be derived. Assume that 0.05 out of 0.95 C_1 domains and all C_2 domains switch 90° cooperatively to form in-plane 180° domains when the applied electric field decreases from maximum to zero at constant compressive stress; it can then be worked out that the 90° switching of this "cooperative pair" gives rise to zero change in P_3, while a change of magnitude $\varepsilon_{\max}\times 10\%$ is produced in ε_{33}. The above-described calculation indicates a 10% difference in the magnitude of change between polarization and strain during electric field unloading at 2.7 MPa when polarization-free straining is in operation. This estimation is in good agreement with the experimental data which show a 9.5% difference (see Table I).

In contrast, a huge difference in the magnitude of change between polarization and strain (i.e., up to 36%) is observed in the experimental data of Burcsu *et al.* (see Table I), suggesting that the cooperative operation of multiple 90° switching systems is unlikely to be the sole reason for the apparent polarization-free strain changes. Since the $BaTiO_3$ single crystal tested in the present study exhibits hardening characteristics, the influence of depolarization field within the crystal on the distribution of surface charges is studied to see whether it offers additional explanations for the observed hysteresis behaviors.

To understand how the depolarization field might alter the distribution of free surface charges on the electrodes, a two-dimensional case is considered. Let L and H denote the length and height of the rectangular $BaTiO_3$ single crystal, as shown in Fig. 3. The upper and lower surfaces of the crystal are coated with thin metal electrodes and ΔV^* is the applied voltage across them. The volume average of electric displacement in the direction normal to the electrodes is

$$\langle D_2\rangle = \frac{1}{HL}\int_{-H/2}^{H/2}\int_{-L/2}^{L/2}\left(-\varepsilon_0\frac{\partial V}{\partial x_2}+P_2\right)dx_1dx_2 = \varepsilon_0 E_2^{*} + \langle P_2\rangle, \qquad (1)$$

where ε_0 is the permittivity of free space, V is the electric potential such that the electric field $\mathbf{E}=-\nabla V$, and $E_2^{*}=-\Delta V^{*}/H$ is the external applied field. Assume the crystal is a perfect insulator, which gives $\partial D_1/\partial x_1+\partial D_2/\partial x_2=0$ within the crystal, and from the divergence theorem, the volume average of D_2 can also be expressed as

$$\begin{aligned}\langle D_2\rangle &= \frac{1}{HL}\int_{-H/2}^{H/2}\int_{-L/2}^{L/2}\left\{\frac{\partial}{\partial x_1}(D_1x_2)+\frac{\partial}{\partial x_2}(D_2x_2)\right\}dx_1dx_2\\ &= \langle Q\rangle|_{x_2=-H/2}+\frac{H}{L}\left(\langle x_2D_1\rangle|_{x_1=L/2}-\langle x_2D_1\rangle|_{x_1=-L/2}\right),\end{aligned} \qquad (2)$$

where $\langle Q\rangle|_{x_2=-H/2}$ is the average of free surface charges over the lower electrode and is therefore equal to $-\langle Q\rangle|_{x_2=H/2}$, and $\langle x_2D_1\rangle|_{x_1=x_1^{*}}$ is the weighted flux average across the surface at $x_1=x_1^{*}$; i.e.,

$$\langle Q\rangle|_{x_2=-H/2} = \frac{1}{L}\int_{-L/2}^{L/2} D_2(x_1,-H/2)dx_1, \qquad (3)$$

$$\langle x_2D_1\rangle|_{x_1=x_1^{*}} = \frac{1}{H^2}\int_{-H/2}^{H/2} x_2D_1(x_1^{*},x_2)dx_2. \qquad (4)$$

From Eqs. (1) and (2), it is clear that when the applied field is zero, $\langle P_2\rangle \neq \langle Q\rangle|_{x_2=-H/2}$ unless the aspect ratio H/L is small or the sum of the weighted flux average $\langle x_2D_1\rangle$ evaluated at the unshielded surfaces vanishes. To visualize this, consider a 5×2 mm^2 BaTiO$_3$ crystal with a compatible domain pattern, as shown in Fig. 3. A pronounced reduction in the volume average of P_2 is expected due to the appearance of 90° domains. For this particular case, $\langle D_2\rangle=\langle P_2\rangle=0.8P_s$ when the applied field $E_2^{*}=0$. Moreover, the free surface charge density on the electrodes might not be equal to P_2 due to the depolarization field generated by the surface polarization (immobile) charges on the unscreened boundaries. Indeed, the symmetric domain pattern depicted in Fig. 3 gives $\langle x_2D_1\rangle|_{x_1=L/2}=-\langle x_2D_1\rangle|_{x_1=-L/2}<0$, and as a result, from Eq. (2), $\langle Q\rangle|_{x_2=-H/2}>\langle P_2\rangle$.

From the above-described derivation, it is evident that the experimental polarization data based on charge-on-area measurements might not be able to accurately represent the actual evolution of polarization in the loading direction. This mismatch could be even more significant for noncompatible domain patterns such as 90° wedge nucleation grown during domain switching.[12] The reason being that the depolarization field is created not only from the unshielded boundary surfaces but also from the interior of the ferroelectric specimen.

In summary, the present study shows that the disproportion of slope gradients at zero electric field for the measured polarization and strain hystereses for the bulk BaTiO$_3$ single crystal is likely due to the operation of multiple 90° switching systems and the presence of depolarization fields generated from the unshielded boundaries and/or incompatible domains within the crystal. Further investigations based on *in situ* domain observations throughout the entire electromechanical loading sequence should reveal clearer details.

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