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Hysteresis behaviors of barium titanate single crystals based on the operation of multiple 90° switching systems

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ABSTRACT

Large strain actuation in barium titanate (BaTiO₃) single crystals subjected to combined uniaxial stress and electric field is examined. A maximum strain of about 0.45% is measured under a combined loading of 2.7 MPa compressive stress and ± 1.25 MV m⁻¹ cyclic electric field. Above 2.7 MPa, the crystal does not cycle fully between the in-plane and out-of-plane polarized states due to large compressive stress, and consequently, a considerable reduction in actuation strain is apparent. The hysteresis evolution of the crystal under combined electromechanical loading 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 slope gradients is the cooperative operation of multiple 90° switching systems by which "polarization-free" strain changes are induced. An *in situ* domain observation study reveals the formation of bubble-like micro-domains prior to the macroscopic 90° switching of the crystal bulk. The presence of these bubble-like "switching weak points" indicates that regions within the BaTiO₃ single crystal do not necessarily switch 90° at the same time, and hence, in a way, supports the existence of multiple 90° switching systems. Results obtained in the present study are expected to assist the development of reliable constitutive models for single crystal ferroelectrics.

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1. Introduction

Among all ferroelectric materials, single crystal ferroelectrics have received extensive attentions recently due to their ability to provide a high degree of polarization domain alignment with electrical poling, which could in turn give rise to superb piezoelectric characteristics. Various attempts have been carried out to develop large strain actuation in ferroelectric single crystals either via composition development or via domain switching [1-4]. Park and Shrout [1] introduced a single crystal relaxor ferroelectric PZN-PT (a solid solution of lead zirconate niobate and lead titanate) which possesses an electrostrictive strain up to 1.7% with very little hysteresis. Ren [2] demonstrated that the symmetry conforming property of point defects can give rise to large reversible electrostrains (up to 0.75%) in thermally aged barium titanate (BaTiO₃) single crystals. Burcsu et al. [3] examined the 90°-switching-induced strain of BaTiO₃ single crystals under combined electrical and mechanical loadings, and observed nearly 0.8% strain at 1.78 MPa compressive stress together with 1 MV m⁻¹ electric field. Large strain changes in ferroelectric crystals caused by

domain switching are typically induced through angles other than 180° [5,6]. It is therefore essential to investigate factors which might influence the effective operation of non-180° switchings. By doing so, the achievable strain by an electrical, mechanical, or electromechanical loading could potentially be gauged accurately. In the present study, the straining and switching characteristics of BaTiO₃ single crystals are investigated. This is achieved through examining their hystereses in the electric polarization (*P*) vs. electric field (*E*) and strain (ε) vs. electric field (*E*) responses. The effect of constant bias stress on the hysteresis behavior is also examined. From the hysteresis measurements, the correlation between the rate of change of polarization with respect to electric field and the rate of change of strain with respect to electric field is studied to get a picture of the competition between different switching systems.

2. Experimental procedure

A series of polarization and strain hysteresis measurements under combined uniaxial electrical and mechanical loadings were performed on unpoled (001)-oriented cuboidal BaTiO₃ single crystals measuring 5 mm × 5 mm × 2 mm. The crystals were obtained from MTI Co., CA, USA. Conductive silver paints were used to produce electrodes on the 5 mm × 5 mm surfaces. A loading fixture shown in Fig. 1 was developed for the simultaneous application

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Fig. 1. Schematic of the combined uniaxial electromechanical loading apparatus.

of uniaxial compressive stress and electric field. The loading fixture consisted of brass plates, providing electrical contact to the electrode surfaces of the crystal, and nylon spacers to insulate the crystal from the mechanical load frame. The upper brass plate was connected to ground via a ferroelectric analyzer (Model TF2000, aixACCT, Germany) for charge measurement. The lower brass plate was connected to a high voltage amplifier (Model 20/20C, Trek, USA) which supplied the electrical loading (± 1.25 MV m⁻¹ at 0.2 Hz; sinusoidal waveform). Mechanical loading (stress up to 4.0 MPa) was applied using a universal test frame (Model HT-9102, Hung-Ta, Taiwan). Miniature strain gauges (Model FBX-04-11-005LE, TML, Japan) were attached onto the $5 \text{ mm} \times 2 \text{ mm}$ faces of the crystal to measure strain changes in the loading direction. A thin coat of epoxy resin was applied to the exposed surface of the strain gauges to afford extra insulation against electrical breakdown. The entire loading fixture was supported in a silicon oil bath to prevent breakdown arcing, and all tests were carried out at temperatures in the range of 20−25 °C.

3. Results and discussion

3.1. Hysteresis behaviors

Fig. 2a and b shows, respectively, the stable polarization and strain hysteresis curves for the $5 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$ unpoled (001)-oriented BaTiO₃ single crystal measured at various compressive stresses ranging from 0 to 4.0 MPa. The applied cyclic electric field has a frequency of 0.2 Hz and an amplitude of ± 1.25 MV m⁻¹. At zero compressive stress, the crystal exhibits a remanent polarization (P_r) of 21.0 μ C cm⁻², a coercive field (E_c) of 0.35 MV m⁻¹, and a total electrostrain ($\varepsilon_{33,total}$) of about 0.14% in the 33-direction. It is evident from Fig. 2b that with increasing compressive stress, $\varepsilon_{33,total}$ increases significantly and eventually reaches a maximum value of 0.45% at 2.7 MPa. As the compressive stress increases to levels higher than 2.7 MPa, $\varepsilon_{33,total}$ is quickly reduced and the classic butterfly-shaped strain hysteresis becomes squashed and broadened. This hysteresis behavior suggests that at stresses higher than 2.7 MPa, polarization switching is happened over a wider range of electric field and high strain actuation is harder to achieve even with an applied electric field much higher than the coercive field. A similar trend to $\varepsilon_{33,total}$ is also observed for the apparent piezoelectric charge coefficient (d_{33}) , obtained from the slope gradient of the strain hysteresis curve at zero electric field. Maximum apparent d_{33} is achieved at 2.7 MPa of compressive stress. Further increase of stress leads to a gradual decrease in the apparent d_{33} .

The measured polarization hystereses shown in Fig. 2a also display stress-dependent characteristics. At zero or low stress levels (≤ 1.7 MPa), a $P_{\rm r}$ of about 21.0 μ C cm⁻² is measured, which is lower than the theoretical spontaneous polarization ($P_{\rm s}$) value of 26.0 μ C cm⁻² for BaTiO₃ [5,7]. This is most likely due to the incomplete switching of polarization during the loading cycle. In other words, the unpoled 5 mm \times 5 mm \times 2 mm BaTiO₃ single crystal tested in the present study is unable to produce one single polarization domain at 1.25 MV m⁻¹. This inability is also evident from



Fig. 2. Measured (a) polarization vs. electric field and (b) strain vs. electric field hysteresis curves for unpoled (001)-oriented BaTiO₃ single crystal at various constant compressive stresses.

the relatively large measured E_c value (0.35 MV m⁻¹), and from the considerable deviation of the *P*–*E* hysteresis from the classic boxy rectangular shape typically expected for single crystal ferroelectrics. It is evident from Fig. 2a that as the compressive stress is increased above 1.7 MPa, the corners of the *P*–*E* hysteresis become rounded, both the saturation and remanent polarizations start to decrease, and switching is completed over a wider range of electric field. The measured *P*_r value at 4.0 MPa is approximately 15% smaller than the *P*_r value at zero stress.

As mentioned in Section 1, large strain changes in ferroelectric crystals caused by domain switching are typically induced through angles other than 180° [5,6]. At zero compressive stress, the BaTiO₃ single crystal cycles between the two out-of-plane polarized states (i.e., 180° domains perpendicular to the top and bottom electrodes) by going rapidly through the in-plane polarized state (i.e., a domain parallel to the electrodes) "sandwiched" in between the two outof-plane states. Therefore, there is little strain detected at zero compressive stress, and hence the relatively flat strain hysteresis curve. As the compressive stress is increased, the loading path begins to go through the in-plane 90° polarized state at a slower rate. This is because that the 90° domain state is enhanced through the means of ferroelastic switching (i.e., stress-activated switching). Consequently, the actuation strain rises due to the development of 90° switching. The amount of actuation strain continues to increase with increasing stress and reaches its peak value at 2.7 MPa. Above this stress level, the domains do not cycle fully between the in-plane and out-of-plane polarized states due to large compressive stress. At this point, the crystal experiences a large physical constraint and therefore a considerable reduction in actuation strain is apparent; e.g., at 4.0 MPa, $\varepsilon_{33,total}$ decreases to about 0.25% only. At large compressive stresses, the incomplete (partial) polarization switching to the out-of-plane polarized states also causes a decrease in both the saturation and remanent polarizations, as clearly shown in Fig. 2a.

3.2. Multiple 90° switching systems

An important discovery is made after carefully examining the hysteresis data shown in Fig. 2-a significant 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 BaTiO₃ single crystal. This seems to be in contradiction to the common understanding of ferroelectrics that switching-induced strain is accompanied by changes in polarization [5,6]. It is interesting to notice that although adopting a totally different electromechanical loading setup, the hysteresis measurements by Burcsu et al. [3] on BaTiO₃ single crystals also display a severe disproportion of slope gradients at zero electric field. Fig. 3 shows the hysteresis curves measured by Burcsu et al. [3] at compressive stresses of 1.07 and 1.78 MPa.

Theoretically, the maximum possible variations in polarization and strain through 90° switching for the BaTiO₃ single crystal, allowed by crystallography, are $P_s = 26.0 \,\mu\text{C}\,\text{cm}^{-2}$ and $\varepsilon_{\text{max}} = 0.011$, respectively [7–9]. The percentages of polarization and strain changes from maximum to zero electric field at selected stress levels for the BaTiO₃ crystals tested in the present and Burcsu et al.'s [3] studies are calculated and listed in Table 1. Stress-activated 90° switching typically gives rise to a change in both strain and polarization. However, Figs. 2 and 3 and Table 1 all suggest that at high



Fig. 3. Burcsu et al.'s hysteresis measurements on BaTiO₃ single crystal at compressive stresses of 1.07 and 1.78 MPa [3].

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 "polarizationfree" 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. 2a do not have the classic boxy rectangular shape typically expected for ferroelectric single crystals. Furthermore, they exhibit high coercivity and lower saturation level than the theoretical value. These are strong indications that the single crystal used in the present study possesses 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.

A simple calculation is conducted to verify the above argument. Let C_1 and C_2 denote, respectively, the volume fraction of outof-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 $(1 - C_1 - C_2)$. In terms of C_1 and 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 $23.5 \,\mu\text{C}\,\text{cm}^{-2}$ (see Fig. 2a) which is about 90% of the theoretical maximum 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

Table 1

Polarization and strain changes (in percentages) from maximum to zero electric field at selected stress levels for the BaTiO₃ single crystals tested in the present and Burcsu et al.'s [3] studies.

BaTiO ₃ crystal	Compressive stress σ^*_{33} (MPa)	$(P_3^{E=0} - P_3^{E_{\max}})/P_s \times 100\%$	$(\varepsilon_{33}^{E=0} - \varepsilon_{33}^{E_{\max}})/\varepsilon_{\max} \times 100\%$
Present study	2.7	16.04	25.54
	1.7	10.27	15.28
Burcsu et al.	1.78	24.23	61.10
	1.07	8.92	43.16

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 polarizationfree straining is in operation. This estimation is in good agreement with the experimental data which show a 9.5% difference (see Table 1).

3.3. In situ domain observation

In order to understand how multiple 90° switching systems might be present within the BaTiO₃ single crystal, an *in situ* domain observation study, in which a poled (001)-oriented BaTiO₃ single crystal measuring $5 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$ is loaded by a unipolar electric field perpendicular to its poling direction, is carried out. The poling direction of the crystal is in the 2-mm direction



Fig. 4. Consecutive optical images of poled BaTiO₃ single crystal during 90° ferroelectric switching with corresponding electric fields (a) E = 0 MV m⁻¹, (b) E = 0.06 MV m⁻¹, (c) E = 0.24 MV m⁻¹, (d) E = 0.25 MV m⁻¹, (e) E = 0.9 MV m⁻¹, and (f) E = 1.5 MV m⁻¹. Some "bubble-like" micro-domains in (b) and (c) are being circled out.

(see Fig. 1 for the orientation and dimensions of the crystal). The applied unipolar electric field is in the 5-mm direction of the crystal and is of triangular waveform with a maximum amplitude of 1.5 MV m^{-1} and a frequency of 0.01 Hz. It is expected that a 90° switching of the crystal's polarization would take place when the first half-cycle of the unipolar electric field (i.e., from 0 to 1.5 MV m^{-1}) is applied. The *in situ* study involves the observation of changes in birefringence patterns on the $5 \text{ mm} \times 5 \text{ mm}$ face of the crystal during electrical loading under a polarized optical microscope.

Fig. 4a-f shows a series of optical images of the poled BaTiO₃ single crystal at different stages of the first half-cycle of the unipolar electric field. It can be seen that macroscopically the crystal switches 90° at about $0.25 \,\text{MV}\,\text{m}^{-1}$ based on the distinct change in image contrast. This value represents the coercive field for 90° switching, which is smaller than that for 180° switching (i.e., $0.35\,MV\,m^{-1}$, shown in Fig. 2a). Abrupt cracking of the crystal at $0.25\,MV\,m^{-1}$ is caused by the large strain associated with non-180 $^\circ$ switching. The size of the cracks increases as the applied electric field increases from 0.25 to 1.5 MV m⁻¹. The birefringence images shown in Fig. 4b and c are obtained prior to the macroscopic 90° switching of the crystal bulk (i.e., <0.25 MV m⁻¹) and reveal the formation of white "bubble-like" dots. Some of these dots are being circled out in Fig. 4b and c to aid the observation. The observed bubble-like dots are believed to be micro-domains which have been switched 90° by electric fields lower than 0.25 MV m⁻¹. One might consider these bubble-like micro-domains as the "switching weak points" within the crystal bulk. The formation of micro-domains within ferroelectric crystals during polarization switching or phase transition has been documented in several existing studies [10–12]. The *in situ* domain observation carried out in the present study indicates that regions within the BaTiO₃ single crystal do not necessarily switch 90° at the same time, and hence, in a way, supports the existence of multiple 90° switching systems. It should be noticed that the birefringence images shown in Fig. 4 do not directly show the cooperative operation of multiple 90° switching systems that is proposed for the polarization-free straining. Further investigations based on *in situ* in-plane and out-of-plane domain observations throughout the entire electromechanical loading sequence (achievable with a transparent electromechanical loading fixture) should

provide clearer details on the pairing or interaction of different 90° switching systems during polarization-free straining.

4. Conclusions

Strain actuation in BaTiO₃ single crystals subjected to combined uniaxial stress and electric field is examined. The enhancement of 90° domain switching by additional compressive stress (i.e., stress-activated ferroelastic switching) results to larger strains. A maximum strain of about 0.45% is measured under a combined loading of 2.7 MPa compressive stress and ± 1.25 MV m⁻¹ cyclic electric field. The BaTiO₃ single crystal used in the present study possesses hardening and depolarization characteristics. Consequently, the observed disproportion of slope gradients at zero electric field for the measured polarization and strain hysteresis curves is likely due to the cooperative operation of multiple 90° switching systems. Further investigations based on *in situ* domain observations throughout the entire electromechanical loading sequence should reveal clearer details.

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