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A temperature-dependent study on the polarization-free straining of barium titanate single crystals

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Abstract
Previous studies by the authors have shown that, when subjected to combined uniaxial stress and electric field at room temperature, a (001)-oriented barium titanate ($BaTiO_3$) single crystal may display incomplete switching characteristics and a severe disproportion of slope gradients at zero electric field for its polarization and strain hysteresis curves. It is proposed that the likely causes for the observed 'decoupling' of switching strain and switching polarization at room temperature are the cooperative operation of multiple 90° switching systems, by which 'polarization-free' strain changes could be induced, and the presence of depolarization fields generated from the unshielded boundaries and/or incompatible domains within the crystal. In the present study, the evolution of polarization and strain hystereses of $BaTiO_3$ single crystals under various electromechanical loading combinations are investigated again at 55 °C. When compared to the hysteresis measurements at room temperature, the degree of discrepancy between the slope gradients at zero electric field for the polarization and strain hysteresis curves measured at 55 °C is significantly reduced. This is due to the increase in domain wall mobility at a higher temperature, lowering the extent of incomplete switching at maximum electric field. At 55 °C, domains with 180° relative orientation are less likely to exist at maximum electric field; hence, the critical prerequisite for polarization-free straining is no longer available. The experimental data obtained in the present study are expected to assist the development of reliable constitutive models for single-crystal ferroelectrics.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

There have been determined efforts to develop large strain actuation in ferroelectric single crystals either via phase transition or via domain switching [1–6]. 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 uniaxial loading of 1.78 MPa compressive stress and ± 1 MV m^{-1} cyclic electric field [4]. Similar switching studies by the authors have also shown a maximum strain of about 0.45% when the $BaTiO_3$ crystal was subjected to a specific electromechanical loading condition [5, 6]. An interesting phenomenon has been identified after carefully examining the existing hysteresis data, all obtained at room temperature, on $BaTiO_3$ single crystals—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 [4–6]. Here, the phrase 'disproportion of slope gradients' means that the two quantities defined by the rate of change of polarization with respect to the electric field and the rate of change of strain with respect to the electric field do not remain in a constant ratio. The discovered disproportion

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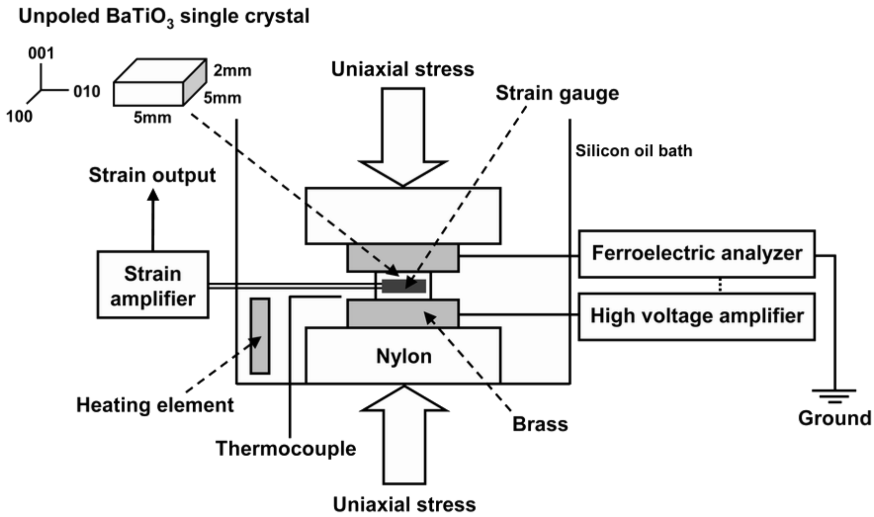

Figure 1. Schematic of the combined uniaxial electromechanical loading apparatus.

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 ferroelectric crystals that switching-induced strains are accompanied by changes in polarization [7–11]. To explain such decoupling behavior, the authors have proposed a mechanism which involves the cooperative operation of multiple 90° switching systems [5, 6]. In order to exhibit a sizable change in strain without a significant change in polarization, multiple 90° switching systems must exist and operate together in the ferroelectric 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 would produce a switching strain without any change in polarization.

In the present study, the evolution of polarization and strain hystereses of $BaTiO_3$ single crystals under various electromechanical loading combinations are investigated at 55 °C. From the hysteresis measurements, the correlation between the rate of change of polarization with respect to the electric field and the rate of change of strain with respect to the electric field is studied. At 55 °C, which is just below half the ferroelectric–paraelectric Curie temperature of $BaTiO_3$ (i.e. $T_c \approx$ 120–130 °C), it is expected that, while the stability and magnitude of the ferroelectric dipoles are maintained, the switching behaviors and the level of polarization saturation of $BaTiO_3$ single crystals will be noticeably different to those at room temperature due to additional thermal energy. The current investigation is designed to further examine the notion of cooperative operation of multiple 90° switching systems within the $BaTiO_3$ single crystal by manipulating the critical prerequisites of such a notion.

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 $BaTiO_3$ single crystals measuring 5 mm × 5 mm × 2 mm at room temperature and 55 °C. 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 figure 1 was developed for the simultaneous application 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 ($\pm$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 to the 5 mm × 2 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 heatable silicon oil bath to prevent breakdown arcing. Heating of the oil bath was provided by a digitally controlled resistive heating element suspended within the oil. The temperatures of different regions of the oil bath were monitored by thermocouples.

3. Results and discussion

3.1. Hysteresis behaviors at room temperature

Figures 2(a) and (b) show, respectively, the stable room temperature polarization and strain hysteresis curves for the 5 mm × 5 mm × 2 mm unpoled (001)-oriented $BaTiO_3$ 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 $\pm$1.25 MV m^{-1}. Some of

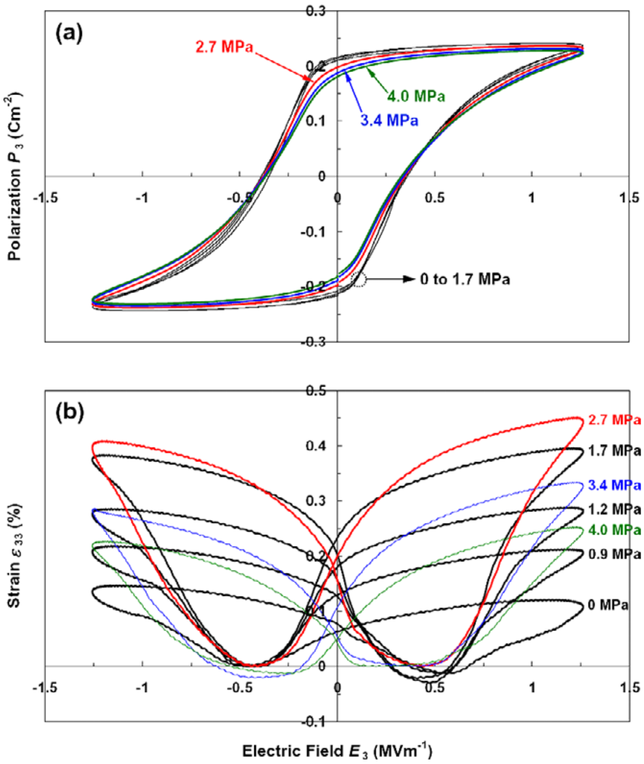

Figure 2. (a) Polarization versus electric field and (b) strain versus electric field hysteresis curves for unpoled (001)-oriented $BaTiO_3$ single crystals measured at room temperature and various constant compressive stresses.

the room temperature hysteresis data have been previously presented and discussed [5, 6]. At room temperature and under purely electrical loading, the crystal exhibits a remanent polarization (P_r) of 0.21 C m^{-2}, a coercive field (E_c) of 0.35 MV m^{-1} and a total electrostrain ($\varepsilon_{33,\mathrm{total}}$) of about 0.14% in the 33 direction. It is evident from figure 2(b) that, with increasing compressive stress, $\varepsilon_{33,\mathrm{total}}$ 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, $\varepsilon_{33,\mathrm{total}}$ is quickly reduced and the butterfly-shaped strain hysteresis becomes squashed and broadened. This hysteresis behavior suggests that, at room temperature and 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 $\varepsilon_{33,\mathrm{total}}$ 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. The maximum apparent d_{33} is achieved at 2.7 MPa. Further increase of stress leads to a gradual decrease in the apparent d_{33}.

The measured polarization hystereses shown in figure 2(a) also display stress-dependent characteristics. At zero or low stress levels ($\leqslant$1.7 MPa), a P_r of about 0.21 C m^{-2} is measured, which is lower than the theoretical spontaneous polarization (P_s) value of 0.26 C m^{-2} for $BaTiO_3$ [11, 12]. This is most likely due to the incomplete switching of polarization during the loading cycle. In other words, at room temperature, the unpoled 5 mm × 5 mm × 2 mm $BaTiO_3$ single crystal is unable to produce one single polarization domain at 1.25 MV m^{-1}. This inability is also evident from 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 figure 2(a) that, as the compressive stress is increased above 1.7 MPa, the corners of the P–E hysteresis near zero electric field become rounded, both the saturation and remanent values in polarization 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.

Large strain changes in ferroelectric crystals caused by domain switching are typically induced through angles other than 180° [7–11]. At zero compressive stress, the $BaTiO_3$ 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 out-of-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 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, $\varepsilon_{33,\mathrm{total}}$ decreases to a low level of about 0.25%. 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 figure 2(a).

3.2. Hysteresis behaviors at 55 °C

Figures 3(a) and (b) show, respectively, the stable polarization and strain hysteresis curves for the 5 mm × 5 mm × 2 mm unpoled (001)-oriented $BaTiO_3$ single crystal measured at 55 °C and various compressive stresses ranging from 0 to 1.5 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 property values of $P_r \approx 0.255$ C m^{-2}, $E_c \approx 0.125$ MV m^{-1} and $\varepsilon_{33,\mathrm{total}} \approx$ 0.17%. In comparison with the room temperature data, the P–E hysteresis measured at 55 °C and under purely electrical loading displays the classic behavior of a soft-switching ferroelectric single crystal. This is demonstrated by the much lower coercivity and higher saturation and remanent values in polarization. An extremely sharp polarization transition at

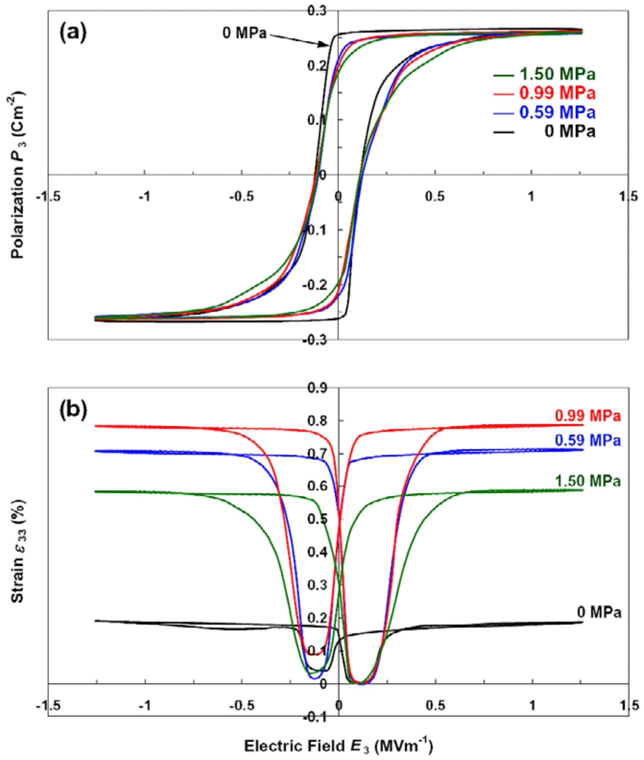

Figure 3. (a) Polarization versus electric field and (b) strain versus electric field hysteresis curves for unpoled (001)-oriented $BaTiO_3$ single crystals measured at 55 °C and various constant compressive stresses.

E_c further confirms the soft-switching quality at 55 °C. The measured P_r value of about 0.255 C m^{-2} is very close to the theoretical P_s value, and the characteristic boxy rectangular hysteresis shape in polarization is easily evident. Although the attributes of the hystereses are considerably different at the two measuring temperatures, the effect of constant bias stress on the hystereses is relatively alike. At 55 °C, $\varepsilon_{33,\text{total}}$ increases significantly with increasing compressive stress and eventually reaches a maximum value close to 0.8% at 0.99 MPa (see figure 3(b)). Notice that the maximum apparent d_{33} is also achieved at 0.99 MPa. It is evident that, at 55 °C, the $BaTiO_3$ single crystal is more susceptible to mechanical loading and consequently a higher $\varepsilon_{33,\text{total}}$ value can be achieved at a lower bias stress due to the higher extent of ferroelastic switching. As the compressive stress is increased above 0.99 MPa, $\varepsilon_{33,\text{total}}$ is quickly reduced because of high blocking force. As discussed in section 3.1, the extent and manner of domain cycling between the in-plane and out-of-plane polarized states decide the magnitude of $\varepsilon_{33,\text{total}}$. The apparent blocking stress (i.e. 1.5 MPa) is smaller than the 90° coercive stress of the present $BaTiO_3$ crystal, which is about 2.95 MPa [9, 10]. This is most likely due to the generation of microcracks under mechanical compression, giving rise to incomplete domain switching.

The measured polarization hystereses shown in figure 3(a) also display stress-dependent characteristics. At zero compressive stress, the measured P_r is very close to the theoretical P_s value, suggesting a high level of polarization saturation during switching at 55 °C. A domain structure consisting of only a single domain (or at least very close to a single domain) is therefore possible at maximum electric field. As the compressive stress is applied and increased, the P–E hysteresis is sheared and squashed, its corners near zero electric field become rounded and P_r starts to decrease significantly (e.g. about 27% drop in P_r under 1.5 MPa bias stress). It is evident from figure 3(a) that, under purely electrical loading at 55 °C, the $BaTiO_3$ single crystal exhibits a negligible amount of polarization relaxation, based on the minimal difference between the polarization values at maximum and zero electric fields and the highly linear hysteresis curve detected during electric field unloading. A tiny change in electrostrain (i.e. only piezoelectric strain) is therefore expected, and indeed observed in figure 3(b), during electric field unloading because of the lack of nonlinear variation in polarization (i.e. polarization switching). In contrast, when the constant compressive stress is applied, reorientation of polarization during electric field unloading is promoted. It is clear that the extent of polarization relaxation increases with increasing compressive stress based on the progressive decrease in P_r. Typically, when the difference between the polarization values at maximum and zero electric fields increases, a larger change in electrostrain during electric field unloading is anticipated.

3.3. Multiple 90° switching systems

An important discovery is made after carefully examining the room temperature hysteresis data shown in figure 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. The 'decoupling' between switching strain and switching polarization within the $BaTiO_3$ single crystal at room temperature seems to be in contradiction to the common understanding of ferroelectrics that switching-induced strains are accompanied by changes in polarization [7–11]. It is interesting to notice that, although adopting a totally different electromechanical loading set-up, the hysteresis measurements by Burcsu *et al* [4] on $BaTiO_3$ single crystals also display a severe disproportion of slope gradients at zero electric field. The experiments of Burcsu *et al* [4], though, produce the 'boxy' form of hysteresis in polarization, even at room temperature. This could be a consequence of different defect patterns and dopants in the different $BaTiO_3$ single crystals.

Theoretically, the maximum possible variations in polarization and strain through 90° switching for the $BaTiO_3$ single crystal, allowed by crystallography, are P_s = 0.26 C m^{-2} and ε_{max} = 0.011, respectively [11–14]. The percentages of polarization and strain changes from maximum to zero electric field at selected stress levels for the $BaTiO_3$ crystal tested at room temperature are calculated and listed in table 1. Stress-activated 90° switching typically gives rise to a change in both strain and polarization. However, figure 2 and table 1 suggest that, at room temperature and high stresses, a sizable change in strain during electric field

Table 1. Polarization and strain changes (in percentages) from maximum to zero electric field at selected stress levels for the $BaTiO_3$ single crystals tested at room temperature and 55 °C.

Measuring temp. for hystereses	Compressive stress σ_{33}^* (MPa)	$\frac{\lvert P_3^{E=0} - P_3^{E\max}\rvert}{P_s} \times 100\%$	$\frac{\lvert \varepsilon_{33}^{E=0} - \varepsilon_{33}^{E\max}\rvert}{\varepsilon_{\max}} \times 100\%$
Room temp.	2.7	16.04	25.54
	1.7	10.27	15.28
55 °C	0.99	23.50	26.90
	0.59	20.53	21.91

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 notion is schematically illustrated in figure 4, which shows the joint 90° switching of two domains with 180° relative orientation. The polarization hystereses shown in figure 2(a) do not have the boxy rectangular shape typically expected for soft ferroelectric single crystals. Furthermore, they exhibit high coercivity and lower saturation level than the theoretical value. These are strong indications that, at room temperature, the $BaTiO_3$ single crystal 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 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 $(1 - C_1 - C_2)$. 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 room temperature and the loading condition of 2.7 MPa and maximum electric field, the $BaTiO_3$ single crystal exhibits a polarization value of 0.235 C m^{-2} (see figure 2(a)), 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 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 and room temperature when polarization-free straining is in operation. This estimation is in good agreement with the experimental figure which shows a 9.5% difference (see table 1).

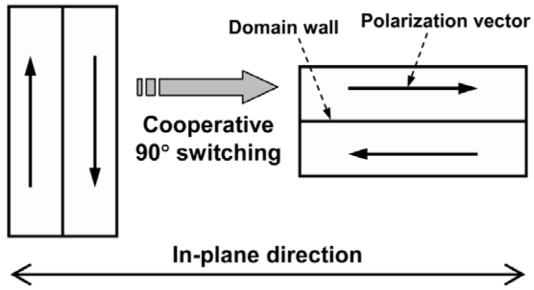

Figure 4. Schematic showing the concept of polarization-free straining achieved by a 90° switching of an out-of-plane 180° domain wall into an in-plane 180° domain wall. (Notice that, for $BaTiO_3$ single crystals, the maximum possible strain through 90° switching, allowed by crystallography, is 0.011.)

In comparison, the percentages of polarization and strain changes from maximum to zero electric field at selected stress levels for the $BaTiO_3$ crystal tested at 55 °C are also calculated and listed in table 1. Experimental data obtained at 55 °C show that, at 0.99 MPa and maximum electric field, the crystal exhibits a polarization value about 2% smaller than the theoretical maximum value (see figure 3(a)), and by adopting the calculation derived in the previous paragraph it is predicted that there should be a 2% difference in the magnitude of change between polarization and strain during electric field unloading. Again, this estimation is reasonably close to the experimental figure which shows a 3.4% difference (see table 1). Both the calculated and experimental figures indicate that, at 55 °C, the switching strain and switching polarization under electromechanical loading is strongly coupled. Hence, the severe disproportion of slope gradients at zero electric field for the measured polarization and strain hysteresis curves, which is clearly observed at room temperature, is no longer evident at 55 °C. The main reason for such a huge difference in switching behaviors at 55 °C and room temperature is the substantial increase in domain wall mobility at a higher temperature. The levels of hardening and depolarization decrease with increasing domain wall mobility and, as a result, the hystereses obtained at 55 °C exhibit high polarization and strain saturations during switching and can be effectively explained using the long-established switching theories which typically couple together the ferroelectric and ferroelastic switchings. At 55 °C, domains with 180° relative orientation are less likely to exist at maximum electric field due to the high level of polarization saturation; hence, the critical prerequisite for polarization-free straining is no longer available. This is why at 55 °C the rate of change of polarization with respect to electric field and the rate of change of strain with respect to electric field very much remain in a constant ratio throughout the entire loading cycle, even at high compressive stresses.

4. Conclusions

Large strain actuation in $BaTiO_3$ single crystals subjected to combined uniaxial stress and electric field is examined at room temperature and 55 °C. The enhancement of 90° domain switching by additional compressive stress (i.e. stress-activated ferroelastic switching) results in larger electrostrains. At room temperature, the $BaTiO_3$ single crystal displays incomplete switching characteristics and a severe disproportion of slope gradients at zero electric field for its polarization and strain hysteresis curves. A likely cause for the observed 'decoupling' of switching strain and switching polarization at room temperature is the cooperative operation of multiple 90° switching systems by which 'polarization-free' strain changes are induced. In comparison, both the experimental and analytical data indicate that, at 55 °C, the switching strain and switching polarization under electromechanical loading is strongly coupled. Hence, the severe disproportion of slope gradients at zero electric field for the measured polarization and strain hysteresis curves, which is clearly observed at room temperature, is no longer evident at 55 °C. The main reason for such a huge difference in switching behaviors at 55 °C and room temperature is the substantial increase in domain wall mobility at a higher temperature. At 55 °C, domains with 180° relative orientation are less likely to exist at maximum electric field; hence, the critical prerequisite for polarization-free straining is no longer available. 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) at different temperatures should provide clearer details on the possible pairing or interaction of different 90° switching systems.

Acknowledgments

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