90-degree polarization switching in BaTiO3 crystals without domain wall motion

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90-degree polarization switching in $BaTiO_3$ crystals without domain wall motion

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We report 90° polarization switching in a $BaTiO_3$ crystal without domain wall (DW) motion by prefabricating samples with interlocking domains via compression. During electric re-poling of the depoled and aged crystals, 90° domain nucleation still exists, but 90° DW motion is inhibited by the strong constraints from surrounding domains, leading to DW-free 90° polarization switching. The measured coercive field of 500 V/mm for the DW-free 90° switching is close to the intrinsic values and much larger than that of 80 V/mm via 90° DW motion. Compared to the rather difficult domain-free 180° polarization switching in ultrathin films, 90° DW-free switching is easier.
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Polarization switching in ferroelectrics is a very complicated process. Unlike some other condensed matter systems, polarization reversal is almost never the result of homogeneous nucleation, and processes such as spinodal decomposition do not occur. Instead, the dynamics usually occurs through inhomogeneous domain nucleation, typically at the electrode-dielectric interfaces but also at pre-existing domain walls (DWs) or defects, followed by domain wall movements.[1–8] The clearest proof of this is the PFM (piezoresponse force microscopy) switching images on a 100 ns time scale shown recently by Gruverman *et al.*[9]

Such domain-wall dominated switching is not the only possible mechanism for polarization switching. The Landau-Devonshire (LD) theory has indicated[10,11] that simultaneous reversal of all local dipoles is also possible; but the calculated intrinsic coercive field E_{IC} is typically 2-3 orders higher than the measured coercive field E_C for domain-wall driven processes, which is sometimes called Landauer's paradox[3] (although that paradox mostly only implies that nucleation is inhomogeneous). It therefore becomes requisite to suppress domain-wall switching processes in some way if the intrinsic polarization switching is to be reached. However, the experimental studies of intrinsic switching are somewhat controversial. It had been reported that in ultrathin Langmuir–Blodgett polymer films, E_C can reach the intrinsic value of E_{IC}.[12] This statement had been questioned on different grounds,[13–15] and now it is probably favored that the measured large E_C is due to the presence of a conductive nonferroelectric layer at the film-electrode interface ("dead layer").[15] Recently, Highland *et al.*[16] realized domain-free polarization switching in a 4.9 nm thick $PbTiO_3$ film by applying chemical potential. Later, they found that a stable nonpolar phase can exist between the positive and negative polar states when varying the external chemical potential,[17] which is quite different from the LD polarization switching via an applied electric field. Therefore, evidence of intrinsic switching in ultrathin films is still yet to be completely accepted.

Perhaps, the simplest way to generate domain-free switching is to utilize the fact that it is faster than domain-wall motion. The fastest domain wall driven switching recorded is 220 ps in lead titanate zirconate (PZT) thin films.[18–21] In comparison, the theoretical extrapolated limit for intrinsic switching has been estimated as about 1 ps.[22,23] Hence, one approach is to apply a large voltage (say 100 V) across a very thin film (say 50 nm) with a sub nanosecond rise-time voltage source. The main problem is that whereas very high fields can be obtained very quickly, the typical breakdown field of the best ferroelectric oxide is approximately 1 GV/m (Ref. 24), and this is intrinsic.[25]

In present study, we develop a special method to reach DW-free polarization switching (following the early notion raised by Little[2] in 1950s, here the DW motion merely denotes the sideways growth of 90° DW. The forward growth of 90° wedge domains is regarded as the nucleation process). We prefabricated interlocking 90° domain patterns in a $BaTiO_3$ crystal cube by prolonged uniaxial compression depoling. During electric re-poling of the depoled crystal, the 90° domain wall motion is inhibited by constraints from surrounding domains, which leads to DW-free 90° switching. The measured coercive field of 500 V/mm for the DW-free 90° switching is much larger than that of 80 V/mm for switching via DW motion. Moreover, it can be close to the intrinsic values based on the LD theory taking stress into account. The obtained DW-free 90° polarization switching in this work could be very helpful in fast and accurate actuation applications.

Enlightened by that possible intrinsic 180° polarization switching can only be realized in ultrathin ferroelectric films in which the domain nucleation is inhibited,[8,12,16,21,22,25–27] to realize possible domain-free 90° polarization switching, one should also take measures to inhibit new 90° domain nucleation and/or domain wall movements. Since 90° domain wall movement is always accompanied by large strains,

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we can inhibit it using a special solution not applicable for 180° switching, i.e., by suppressing the switching strain. Our candidate material is the prototypical perovskite-structure ferroelectrics, $BaTiO_3$, in it normally the 90° domain walls are highly constrained and often viewed as immobile unless they are curved or tilted.[28] Furthermore, since the mechanical constraint between domains is even larger in three-dimensional crystals,[29,30] we adopt a large $BaTiO_3$ crystal cube ($5 \times 5 \times 5$ mm^3) as the specimen.

The proposed scenario to realize DW-free 90° polarization switching is illustrated in Fig. 1, where the single-domain state (hereafter, the upward domain is referred as "+c" domain and the perpendicular domains are referred as "a-domains") of the completely poled $BaTiO_3$ crystal in Fig. 1(c) is set as the starting point. The poled crystal is first mechanically depoled by a large uniaxial compression to get an interlocking, multiple a-domain state, as shown in Fig. 1(a). Then an electric field is applied to drive 90° polarization switching from Figs. 1(a)–1(c). As partial 90° switching from a-domain to +c-domain will be strongly constrained by the surrounding a-domains, conventional 90° polarization switching through domain nucleation and DW movements from Fig. 1(a) → Fig. 1(b) → Fig. 1(c) is rather difficult. Meanwhile, the four types of a-domains are energetically identical, and they are expected to switch to the +c-domain simultaneously, thus, leading to polarization switching without DW motion.

We then conducted this testing scenario to realize the possible DW-free 90° polarization switching. The $BaTiO_3$ samples were first poled using an electric/mechanical poling method,[31] and then the *D-E* hysteresis loop and butterfly loop of one sample were tested (see Fig. S2 of the supplementary material[32]). The remnant polarization after poling is 25.5 μC/cm^2, very close to the saturated value of 26 μC/cm^2, indicating that the poled sample is nearly the single-domain state. Compression depolarization testing was then conducted, during which both the strain and polarization were measured (see Fig. S4 of the supplementary material[32]), and results show that a compressive stress of 15 MPa is sufficient to depole the sample completely to the multiple a-domain state as in Fig. 1(a).

After compression depolarization, the re-poling testing was done under a 0.2 Hz unipolar triangle-waveform electric field of 800 V/mm. Here, two types of depoled $BaTiO_3$ samples were used: (I) The sample was re-poled just after the compression depolarization (without maintaining stress); (II) During compression depoling, the maximum stress of 15 MPa was held for 48 h; then the re-poling started after the compression was removed. Fig. 2 shows the polarization and strain responses of these two types samples during electric re-poling. In Sample I, 90° polarization switching occurs at about 80 V/mm and advances quickly with the applied field. The polarization saturates at 26 μC/cm^2 under 200 V/mm, while the strain cannot be saturated until 400 V/mm. Obviously in Sample I, 90° polarization switching is accomplished via DW motion, i.e., in a path similar to that from Fig. 1(a) → Fig. 1(b) → Fig. 1(c), although the actual domain structures may be more complicated than that in Fig. 1(a).

In comparison, in Sample II during electric re-poling, both the polarization and strain remain zero below 200 V/mm, indicating no polarization switching occurs in this period. From 200 V/mm to slightly below 500 V/mm, the polarization and strain increase almost linearly with the electric field, resulting in a polarization of about 1.5 μC/cm^2 and a strain of about 0.05%. The rather small polarization and strain responses may indicate that 90° domain nucleation can still occur at this period, but the 90° domain walls can hardly move because of the strong constraints. When the field reaches 500 V/mm, both the polarization and strain undergo a large jump. The polarization jumps to the saturated values of 27 μC/cm^2 (of which 26 μC/cm^2 is switching polarization), and the strain jumps to 0.99%, approaching the corresponding saturated value of 1.0%. With further increase in electric field, both the polarization and strain remain constant, i.e., they had saturated after the jump, indicating that all the polarization switching had been accomplished at 500 V/mm.

The time-dependent polarization and strain near the coercive field are plotted in the insets of Fig. 2 to show the detailed switching process. The strain acquisition rate is 50 kHz, whereas the polarization recording rate is only 100 Hz, limited by the ferroelectric analyzer. The polarization switching time is less than 10 ms, but it should be larger than 3 ms, as determined by the current limit of 2 mA of the ferroelectric analyzer. In comparison, the strain switching process is much faster with the duration of only 0.5 ms.

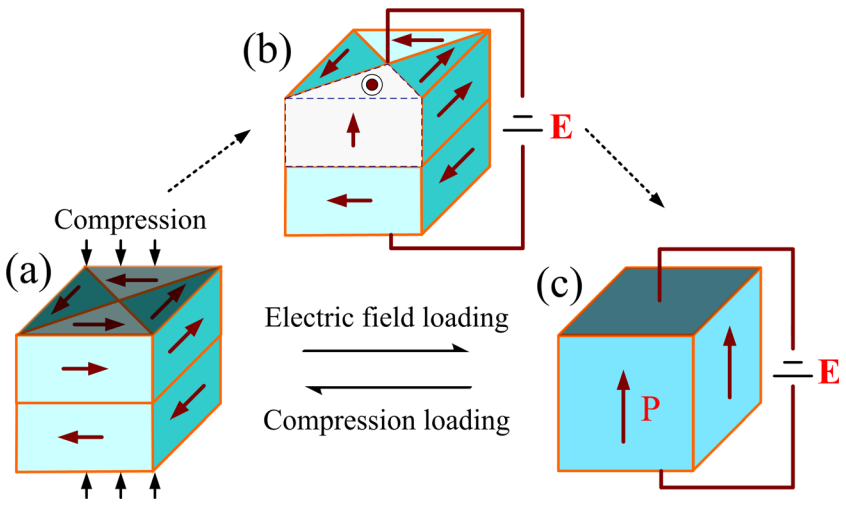

FIG. 1. Schematic of DW-free 90° polarization switching from (a) → (c) and conventional 90° polarization switching from (a) → (b) → (c) via domain wall movement in a $BaTiO_3$ crystal during electric stressing. Polar directions are denoted by bold arrows.

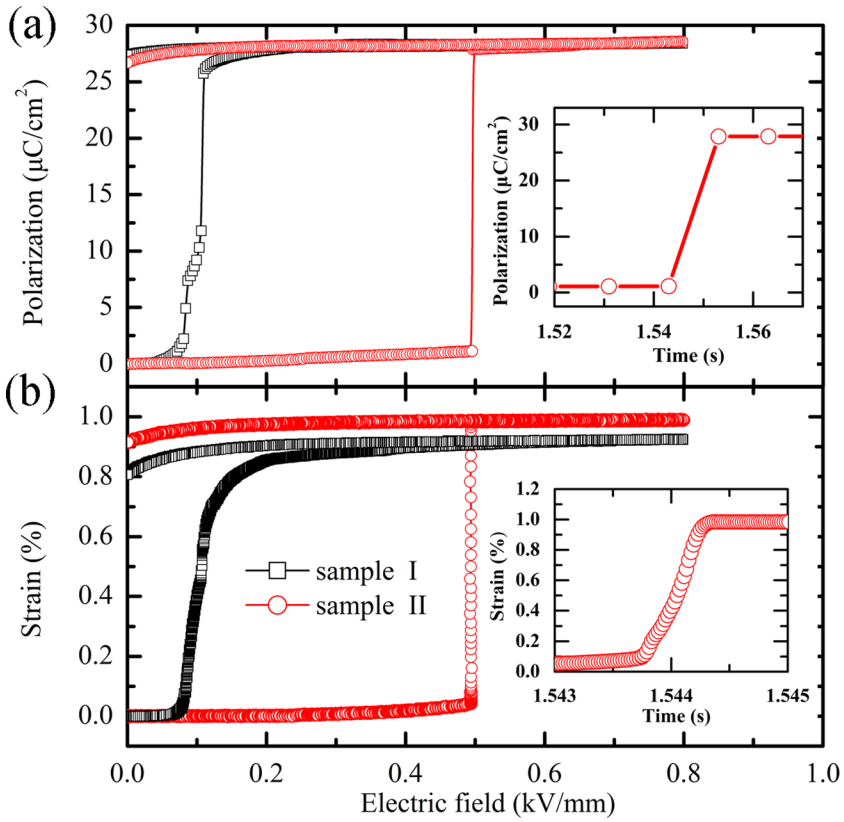

FIG. 2. Polarizations (a) and longitudinal strains (b) of two types of mechanically depoled $BaTiO_3$ crystals during electric re-poling. Insets are the time-dependent polarization and strain of Sample II near the coercive field to show the detailed switching process.

From Fig. 2, it can be seen that the 90° polarization switching in Sample II is almost a homogeneous process, quite different from the typical 90° switching processes via DW motion. Moreover, the repeatability of the sudden 90° domain switching in Type II samples is very good. Fig. S5 in the supplementary material[32] shows the polarization and strain responses of another Type II sample under bipolar electric field loading. The curves also show sudden 90° domain switching at about 500 V/mm during the first cycle electric loading.

To understand the cause for the observed sudden 90° polarization switching, the domain structures in Sample II were observed by polarized light microscopy using a cut $5 \times 5 \times 0.5$ mm^3 wafer specimen (see Fig. S6 of the supplementary material[32]). A typical domain structure image is shown in Fig. 3 in which two types of multiple "a" domain structures can be clearly seen. One is the stripe domain structure and had been further confirmed to be the two-rank domain pattern (see Fig. S7 of the supplementary material[32]) as shown in Fig. 3(b), which is similar with that observed by Merz.[1] The other is the intersecting domain structure which should be a vortex-like closure domain pattern as shown in Fig. 3(c). The vortex-like domain patterns are mostly in the central area of the wafer specimen, while the stripe patterns are typically near the wafer edges. Note that both types of domain patterns are interlocking and partial 90° switching from a-domain to c-domain will be strongly constrained.

The switching process in Sample II is explained as follows. After prolonged compression, all the "c" domains had been compressed to "a" domains and during electric re-poling, and no *a*-*c* domain wall can serve as "seeds" for domain switching. Therefore, in Sample II, new c-domain nucleation is required for the 90° polarization switching. However, the c-domain nucleation in the large cube sample (Sample II) can only occur at the sample surface (typically from the cathode electrode where free charges can be provided), and nucleation inside the sample is almost impossible because of the rather large mechanical constraint from the surrounding a-domains. If the 90° domain switching in Sample II were accomplished by domain wall motion, then at least one [110] *a*-*c* domain wall had moved sideways by $5\sqrt{2}/2 = 3.54$ mm in 0.5 ms with the average velocity of 7 m/s. While this would obviously be in conflict with the early observations by Little,[2] where the maximum sideways velocity of 90° DW motion at 490 V/mm is less than 0.01 m/s with the wall displacement of only several micron. Therefore, the observed polarization and strain jump in

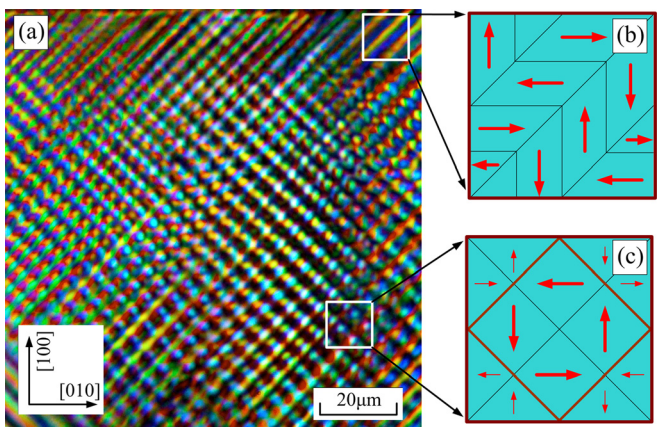

FIG. 3. (a) Typical domain structures by polarized light microscopy in a wafer specimen cut from a mechanically depoled $BaTiO_3$ Sample II; (b) two-rank domain pattern; (c) vortex-like closure domain pattern.

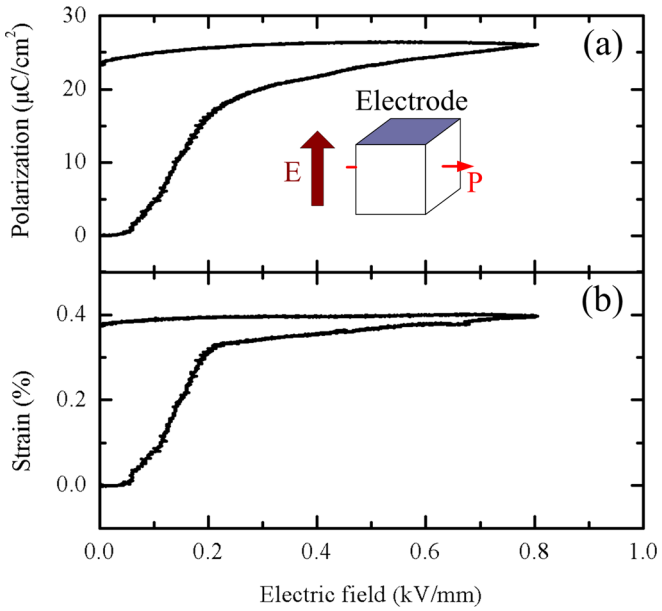

FIG. 4. Polarization (a) and strain (b) responses of a [001] poled BaTiO3 crystal cube under a uni-polar electric field along [100] direction.

Sample II could not possibly be accomplished via DW motion.

Bearing in mind that the 90° domain nucleation velocity (or the forward velocity of the 90° wedge) is very quick and could reach the sound velocity of ~5000 m/s under a high field (>1.2 kV/mm) in BaTiO3 crystals,[2,33] the observed sudden 90° domain switching in Sample II should be accomplished by successive c-domain nucleation (or forward growth of 90° wedge domains) initializing at the cathode electrode, and no DW motion is involved.

To make a comparison, we also conducted conventional 90° polarization switching in a $5 \times 5 \times 5$ mm^3, [001]-poled $BaTiO_3$ crystal cube by applying electric field along the [100] direction. Both the polarization and strain responses during unipolar electric loading are shown in Fig. 4. The 90° domain switching initiates at only 80 V/mm; it advances quickly with the electric field and slows down at about

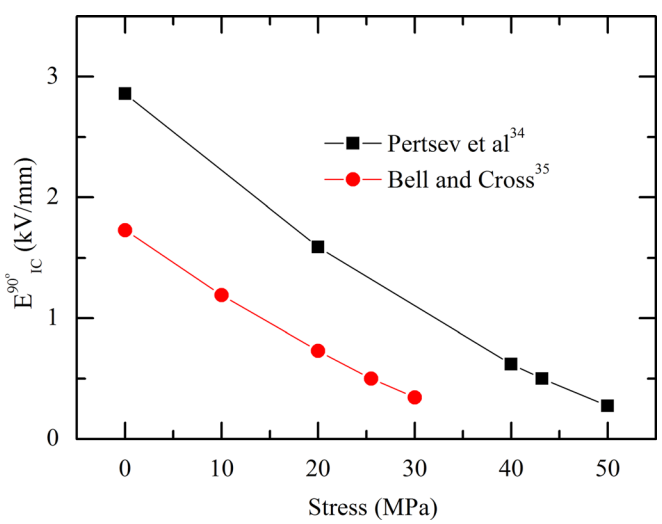

FIG. 5. The calculated theoretical coercive fields for the intrinsic 90° polarization switching with a series of [2-D] compressive stresses using two sets of Landau coefficients from Refs. 34 and 35.

200 V/mm, which is a typical switching process via DW motion.[1–8] Neither the polarization nor the strain can be saturated even at the maximum field of 800 V/mm, indicating the hardening effect in 90° switching accomplished this way. The E_C for this conventional 90° switching is thus determined to be 80 V/mm, which is consistent with that in Sample I and much smaller than that of 500 V/mm for the DW-free 90° switching in Sample II.

For the domain-free 180° polarization switching, the theoretical E_{IC} can be calculated using the LD theory.[10] Unlike 180° switching, the E_{IC} for 90° polarization switching (E^{90}_{IC}) has never been studied, and actually it could also be predicted by the LD theory. However, because debate still exists for the values of the Landau coefficients,[34,35] a unique value of E^{90}_{IC} is unavailable. Meanwhile, it should be noted that after mechanical depoling, the "a" domains illustrated in Fig. 1(a) will be subjected to a two-dimensional [2-D] compressive stress in the a-a plane which will considerably decrease E^{90}_{IC}. Using two sets of typical Landau coefficients from Pertsev *et al.*[34] and Bell and Cross[35] E^{90}_{IC} at room temperature (25 °C) under a series of [2-D] compressive stresses are calculated and shown in Fig. 5. Although the calculated stress-free E^{90}_{IC} of 2.86 kV/mm using the former coefficients[34] and of 1.73 kV/mm using the latter coefficients[35] are both considerably larger than the measured value of 500 V/mm, they can reduce to 500 V/mm when subjected to a [2-D] compressive stress of 43 MPa and 26 MPa, respectively. Since the compressive stresses in a multiple-domain $BaTiO_3$ crystal are typically on the order of several tens of MPa,[36] the measured coercive field for DW-free 90° switching is therefore close to the theoretical values E^{90}_{IC} when corrected for stress.

In summary, we suppress the 90° DW motion by prefabricating interlocking domains in a mechanically depoled $BaTiO_3$ crystal cube and realized DW-free 90° polarization switching during electric re-poling. The measured coercive field of 500 V/mm for such 90° switching is much larger than that of 80 V/mm via 90° DW motion and is close to the intrinsic values predicted by LD theory (which disagree among themselves by ca. 50%) if stress is included. The obtained DW-free 90° polarization switching in this work offers some insight into the long-standing paradox of Landauer regarding homogeneous and inhomogeneous nucleation in the field of ferroelectrics since 1950s.[3]

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