

Antiferroelectric-like Switching inside Ferroelastic Domain Walls

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Ferroelastic materials (materials with switchable spontaneous strain) can be centrosymmetric, but their domain walls are always polar, as their internal strain gradients cause flexoelectricity. This flexoelectric polarization of the walls is not switchable by voltage, because reversing their polarity would require switching the spontaneous strain of the adjacent domains, annihilating the domain wall in the process. However, polarization can also arise from biquadratic coupling between polar and nonpolar order parameters (e.g., octahedral tilts in perovskites). Being quadratic, such coupling is independent of the sign of the polarization and thus allows switching between $+P$ and $-P$. In this Letter, we seek to answer the question of whether the polarization of domain walls in an archetypal ferroelastic perovskite (CaTiO_3) is switchable, as per biquadratic coupling, or nonswitchable due to unipolar flexoelectricity. Using molecular dynamics calculations, we find that high electric fields gradually suppress tilts, broaden the ferroelastic domain walls, and eventually enable the onset of switchable polarization. Such switching can happen also in the bulk of the crystal, but the critical field is markedly lower in the domain walls, which are thus independently switchable. We also find that the polarization switching is antiferroelectric-like, with a double hysteresis loop. The analysis suggests that double-hysteresis switching can also occur in other ferroelastic perovskites.

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Ferroic domain walls (DWs) have their own functional properties [1–4]. Examples include free-electron gas confinement [5,6], DW magnetism [7,8], conductivity [9–11], and photovoltaic effects [12,13]. In ferroelastics, DWs have been shown to display polarization [14–19], superconductivity [20,21], or magnetism [22–25], in stark contrast to the domains, which are only defined by having a mechanically switchable spontaneous strain [26]. External fields can also change a domain configuration and thus cause changes in the DW distribution, with concomitant changes in the volume-averaged polarization [18]. Such change in polarization, however, is due to the DW motion rather than a change in the internal polarization of the wall; switching the internal polarization of individual ferroelastic DWs remains an unfulfilled challenge.

The emergence of DW properties stems from their structural deviations with respect to the parent bulk phase [27,28]. The structural causes of DW polarization in ferroelastic materials can be multiple, but a ubiquitous one is flexoelectricity: by linking two domains of opposite spontaneous strain, ferroelastic DWs necessarily possess an internal strain gradient, roughly equal to the difference in spontaneous strain of the domains divided by the domain wall thickness; such a strain gradient induces polarization via flexoelectricity [29,30]. For the archetypal ferroelastic perovskite calcium titanate (CaTiO_3 , the eponymous perovskite mineral), the polarization of the twin DWs has been established [27,31], but the hope of using twin walls as memory devices by switching their dipoles with a voltage has never been realized. The reason is that switching requires two or more stable polar configurations, whereas linear effects such as flexoelectricity (linear coupling between strain gradient and polarization) are unipolar.

However, flexoelectricity is not the only possible source of polarization. Crystals in general, and perovskites in particular, may possess more than one structural order parameter (e.g., octahedral tilts, spontaneous strain, polarization), and these can couple to each other and their gradients linearly or quadratically depending on symmetry constraints. The biquadratic Houchmandzadeh-Lajzerowicz-Salje term, $\lambda Q_1^2 P^2$ [32], where P is the

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polarization, Q is a structural order parameter and λ is the coupling coefficient, is allowed in any symmetry (including even magnetic symmetry [33]), and therefore can always be present. Moreover, since the polarization term is squared, $+P$ and $-P$ have the same energy, the energy cost of switching between them is symmetric.

In many ferroelastic perovskites, octahedral tilts are anticorrelated with ferroelectric polarization [34], and this anticorrelation can be described by positive biquadratic coupling; if the tilt is the primary order parameter, a positive sign of the coupling requires the polarization to go to zero to minimize the free energy [32,33]. Conversely, when tilts are cancelled (as happens inside antiferrodistortive antiphase boundaries) the hitherto suppressed order parameter—the polarization—can emerge [35]. In Morozovska's work [36], the combined effects of flexoelectricity and biquadratic coupling were considered under the framework of Landau-Ginzburg-Devonshire theory and thought to be responsible for the emergence of ferroelectric polarization at ferroelastic walls in nonferroelectric SrTiO_3 . In SrTiO_3 , however, the spontaneous strain is small and thus the domain wall flexoelectricity is also small. Moreover, the symmetry of the ferroelastic phase of SrTiO_3 (space group $I4/mcm$) is such that some octahedral tilts are spontaneously cancelled inside its twin walls [36], enabling the emergence of biquadratic polarization. Yet even in such favorable conditions, the switchability of domain wall polarization has not yet been established, nor has it been for any other ferroelastic [37].

A critical question thus emerges: Given the competition between switchable (biquadratic) and nonswitchable (flexoelectric) couplings, can the polarization of ferroelastic DWs be switched by voltage? To answer this question, we have calculated the effect of applying electric fields to the ferroelastic DWs of the orthorhombic $Pnma$ phase of CaTiO_3 . Using molecular dynamics simulations (details and a correct prediction of the bulk phase diagram of CaTiO_3 are provided in the End Matter section), we determine that individual polar twin walls in CaTiO_3 can indeed be switched by electric field, but with a catch: the switching is not ferroelectric-like, with a single hysteresis loop between two polar states, but antiferroelectric-like, with a double hysteresis between three states: a flexoelectrically biased ground state at low fields, and two states with larger polarizations of opposite sign under high fields. We moreover observe that, as the field increases, domain walls broaden and can act as nuclei of a bulk phase transition to a polar phase.

The calculated structure of ferroelastic DWs oriented along the (110) plane of orthorhombic CaTiO_3 at room temperature ($T = 300$ K) is shown in Fig. 1. Their geometry and orientation are depicted in Fig. 1(a). Two ferroelastic DWs are included in the calculation [Fig. 1(b)]. The calculated twin angle is ca. 0.52° , somewhat smaller than the bulk experimental value ($\sim 0.6^\circ$) [16], but larger than the

near-surface value ($\sim 0.4^\circ$) [38], as surface relaxation by image forces tends to lower spontaneous strain [39,40]. The calculated polar vectors and octahedral tilts along the x , y , and z axes are shown in Figs. 1(c)–1(h). Our simulated polar textures at the DWs resemble the experimental ones [16] [inset in Fig. 1(b)]. The main polar components lie inside the twin wall plane along the y direction, which is the direction of maximum transverse strain gradient and thus maximum flexoelectricity. The dipole components along the y direction for concave (valleylike) and convex (ridge-like) twin junctions are antiparallel [Figs. 1(c) and 1(d)], consistent with the opposite signs of the strain gradients. This pairwise, gradient-driven antiparallel polarization of ferroelastic DWs is different from (and more general than) the depolarization-driven antipolar order of individual 180° walls in some hyperferroelectrics [41]. The local polarization density $\vec{P}_j$ of each unit cell in our simulations was calculated using $\vec{P}_j = (1/V) \sum_i (1/\omega_i) q_i \vec{r}_i$, where V is the volume of the unit cell, q_i and $\vec{r}_i$ are the charge and displacement with respect to the centrosymmetric configuration of atom i . Each Ti-centered unit cell contains one Ti atom surrounded by eight Ca atoms and six O atoms shared with ω_i neighboring cells ($\omega_{\text{Ca}} = 8, \omega_{\text{O}} = 2$). The maximum polarization density inside individual DWs in our simulation was calculated to be ca. $2.4 \mu\text{C}/\text{cm}^2$, in the same range as reported by Van Aert *et al.* [16].

We now look at the effect of an external electric field on polarization. The first thing to notice is that, although bulk CaTiO_3 is not ferroelectric, a sufficiently large electric field can induce a phase transition to a polar phase with suppressed octahedral tilts (Fig. 2). The double-hysteresis switching behavior of monodomain CaTiO_3 already indicates that the energy balance between a tilt-dominated phase with suppressed polarization and a tilt-suppressed phase with emerging polarization can be changed by a sufficiently large electric field. With this in mind, we turn our attention to the DWs.

A molecular dynamics simulation of the twinning angle and polarization of a CaTiO_3 supercell with two twin walls is shown in Fig. 3. The polarization is plotted as a function of the electric field. Before applying the electric field, there is no polarization in the bulk, and only a small flexoelectric polarization in the wall. Applying an electric field along the positive y direction dielectrically polarizes the crystal structures both of the domain and the DW, but the higher dielectric constant of the wall (bigger slope of P as a function of electric field) causes its polarization to increase faster. Concomitant with this increase in dielectric polarization, the difference in spontaneous strain between the domains decreases, signified by a decrease in the twinning angle [color map in Fig. 3(b)] and a gradual broadening of the DWs. These events decrease flexoelectricity—which, to remind, is roughly equal to the spontaneous strain divided by the DW width. At a critical field of ~ 27 MV/cm, the

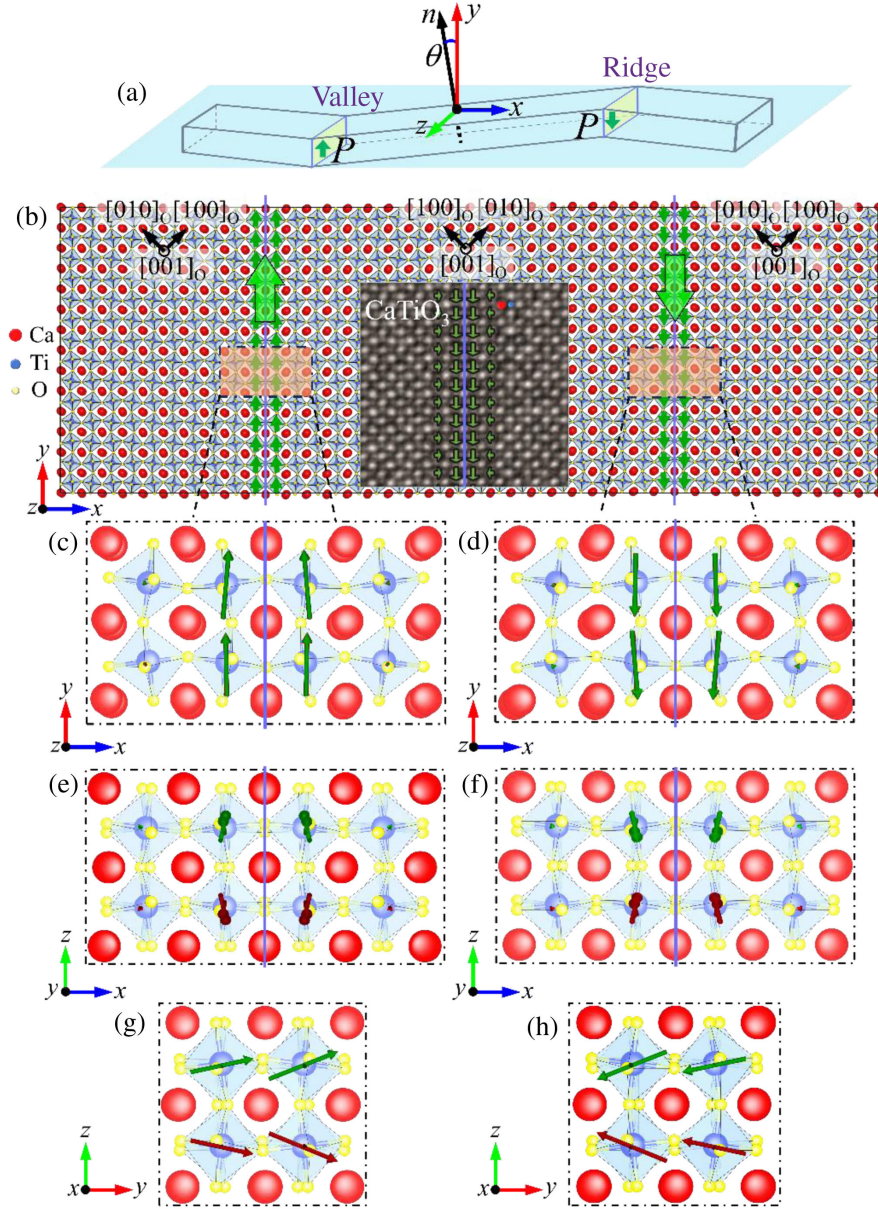


FIG. 1. Structural and polar properties of (110)-type DWs in orthorhombic CaTiO_3 at room temperature ($T = 300$ K). (a) Sketch of the geometry and orientation of a (110) DW pair in the room-temperature orthorhombic phase of CaTiO_3 . The twinning angle θ is defined as the angle between the normal direction of the sample surface and the y axis. (b) is the sandwich model consisting of two parallel DWs with antiparallel DW polar vectors (green arrows). The calculated ferroelastic twinning angle and maximum polarization inside the DWs are ca. 0.52° and $2.4 \mu\text{C}/\text{cm}^2$. The inset in (b) shows the polar displacements inside the DW obtained by transmission electron microscopy [16]. Local depictions of the DW polarizations inside the x - y , x - z , and y - z (twin wall plane) planes were shown in (c)–(h). Green and red arrows are the polar vectors of odd and even layers along z direction. Small polarization tilts exist inside x - y and x - z planes, while relatively large tilts have been found inside the twin wall (y - z). The overall polarization vectors of the nearest walls cancel out due to the conservation of global inversion symmetry. The polar vector arrows are amplified by a factor of 150 for clarity.

DW undergoes a hysteretic transition to a phase with higher polarization (“B”). After switching, the wall is broader but remains distinct from the domain all the way up to 40 MV/cm, whereupon new polar nuclei appear inside the domains (“C”) and eventually coalesce so that the entire crystal switches into the polar phase (“F”). Applying the electric field along the negative y direction,

the dipoles do the same in reverse. Thus, by applying electric fields smaller than the bulk critical field, an antiferroelectric-like double-hysteresis loop [red curve in Fig. 3(a)] is generated in the DW without altering the bulk domain structure.

Since the hysteresis loops of the walls are saturated at a lower critical field than the bulk phase transition, the walls

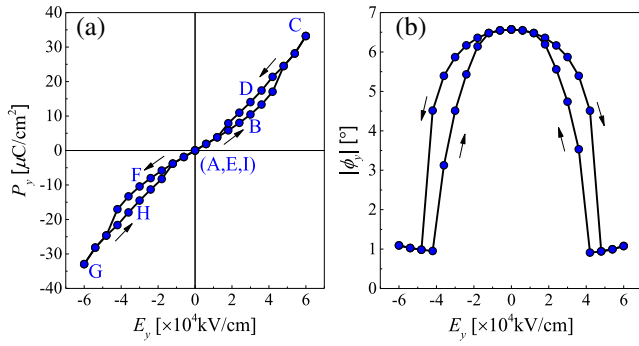


FIG. 2. (a) Polarization along the y axis (P_y), and (b) octahedral tilts around the y axis (ϕ_y) of bulk CaTiO_3 , as a function of electric field along the y axis. A field-induced double-hysteretic transition to a phase with increased polarization and suppressed octahedral tilts is observed.

can be switched independently. However, if the domains are sufficiently small, the strain field from the DW can penetrate throughout the domain and reduce the difference between the domains and the domain wall. This results in unsaturated loops, with the walls acting *de facto* as nucleation points of the bulk transition and then broadening until they occupy the entire volume. This process is illustrated with calculations for a smaller supercell, shown in the End Matter Fig. 5. This role of DWs as nuclei of a different phase is somewhat reminiscent of the order parameter exchange observed at multiferroic domain walls [42]. The results also suggest that finely twinned crystals (e.g., thin films) may be easier to switch into a polar phase.

Molecular dynamics calculations are based on atomic potentials, but we can use Landau theory to gain further phenomenological insight. For simplicity, we assume scalar order parameters. The minimal free energy expansion for an antiferrodistortive crystal with octahedral tilts (Q , equivalent to ϕ_y in the MD simulations), polarization (P), and strain (u) is

$$F = \underbrace{a(T)Q^2 + bQ^4 + \dots}_{\text{tilts}} + \underbrace{\alpha(T)P^2 + \beta P^4 + \dots}_{\text{polarization}} + \underbrace{cu^2}_{\text{strain}} + \underbrace{\mu u P^2}_{\text{electrostriction}} + \underbrace{\lambda Q^2 P^2}_{\text{biquadratic}} - \underbrace{EP}_{\text{electrostatic}}.$$

Switchable polarization requires a double well in the free energy as a function of P , which in turn requires the coefficient of P^2 to be negative. Biquadratic coupling, however, means there is not one but two terms multiplying P^2 ; specifically, $\alpha(T) + \lambda Q^2$. Thus, even if $\alpha(T)$ is negative (even if CaTiO_3 has a polar phonon instability [43,44]), as long as λQ^2 is positive and has a bigger absolute value, the polar double well (ferroelectricity) will be suppressed. Conversely, since bulk CTO is antiferrodistortive, we know that the two coefficients multiplying Q^2 [that is, $\alpha(T) + \lambda P^2$] must be negative (as mathematically

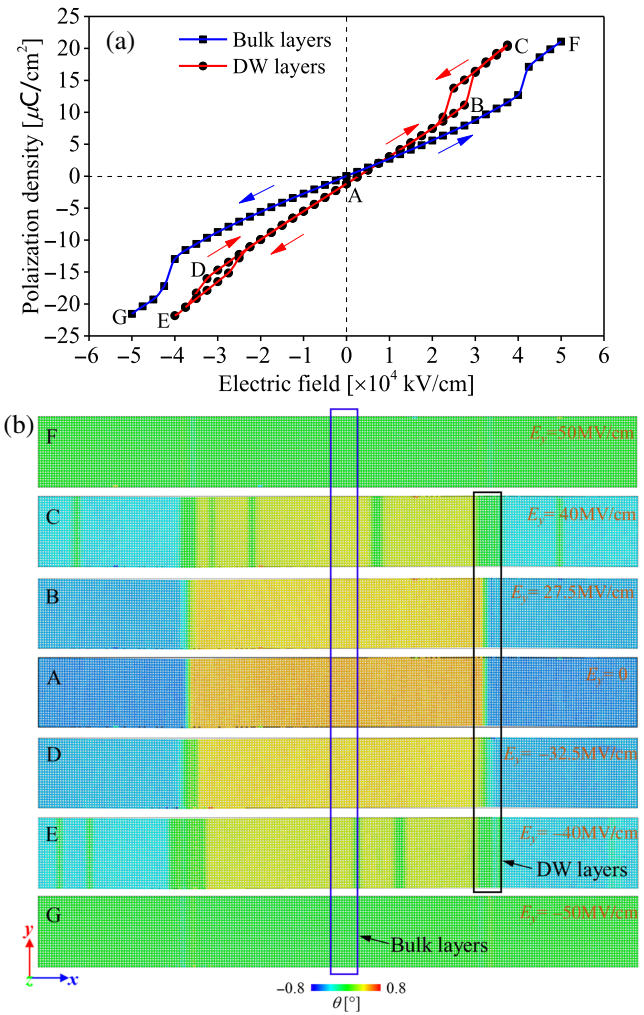


FIG. 3. Domains and domain walls under an electric field. (a) Polarization as a function of electric field in the region marked as DW and “bulk” in (b). (b) Evolution of the ferroelastic twinning angle as a function of electric field. In the middle of the wall and/or in the field-induced polar phase, the twinning angle is zero. It can be observed that, up to panel C (E) corresponding to a field of 40 MV/cm (−40 MV/cm, the DW broadens but does not spread over the entire supercell, i.e., the domains remain unswitched. Moreover, we see that the bulk phase transition does not proceed just by domain wall broadening, but also nucleation of new domains (see green stripes appearing in the middle of the domain in panels C and E). The width of the supercell is 240 formula units (about 96 nm).

required for the existence of a double well as a function of Q). Hence, the absolute value of λP^2 must be smaller than $a(T)$ at room temperature.

Upon application of an electric field, however, the dielectric polarization increases as $P = \chi E$ (where χ is the dielectric susceptibility and E is the field), so λP^2 grows and eventually $\alpha(T) + \lambda P^2$ can become positive, thus causing the antiferrodistortive double well to disappear, killing the tilts [this anticorrelation between P and Q is observed in Fig. 2(b)]. At the same time, when the

antiferrodistortive tilts (Q) disappear, the polar order parameter is no longer suppressed, because the term λQ^2 becomes zero. Hence the previously biquadratically-suppressed polar double well is restored and P can emerge, as observed [Fig. 2(a)]. The same process happens inside the walls, but their larger internal susceptibility (visible as a higher slope of P vs E) means that the critical value of P for the antiferrodistortive-to-polar transition is reached at a lower field, and thus the walls are switchable without altering the domain structure.

Given the generality of biquadratic coupling, a valid question is whether all ferroelastic walls will behave as antiferroelectrics. We think not. Double hysteresis requires a nonpolar ground state (not counting flexoelectricity). This condition is fulfilled in CaTiO_3 because its octahedral tilts are nonzero around all three axes, which means P is suppressed in all directions, both in the bulk and inside the DWs. In SrTiO_3 , however, some octahedral tilts are cancelled by symmetry inside the DWs [36], so they can be ferroelectric from the get-go. Nevertheless, we note that the antiferroelectric response could be very widespread: the $Pnma$ structure of CaTiO_3 is the most common symmetry among perovskites [45,46]—including magnetic orthoferrites, which also raises the exciting prospect of DWs as voltage-driven magnetoelectric multiferroics.

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Data availability—The data are not publicly available. The data are available from the authors upon reasonable request.

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End Matter

Our molecular dynamics (MD) simulations use empirical potentials developed by Pedone *et al.* [48]. The MD simulations consisted of $40 \times 14 \times 14$ formula units of CaTiO_3 for the small supercell and $240 \times 28 \times 28$ formula units for the large supercell, both with periodic boundary conditions applied in all three directions. The *NPT* ensemble [49,50] (i.e., atomic number N , system pressure P , and temperature T were held constant) was adopted with the system volumes allowed to change freely.

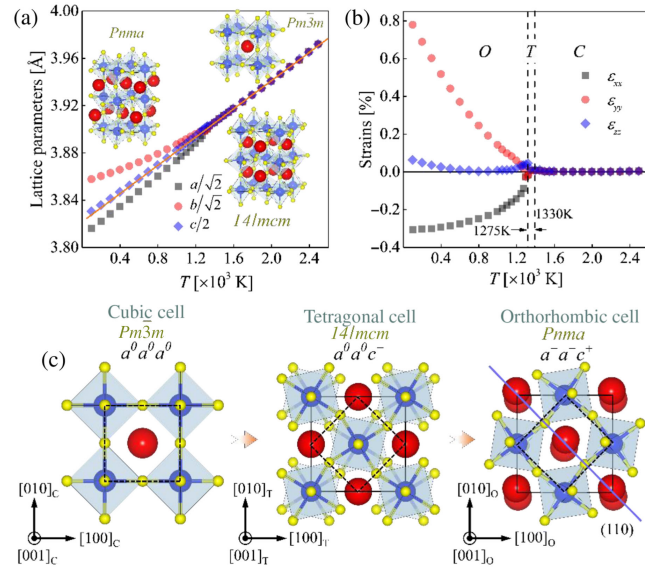


FIG. 4. Phase transitions predicted by the empirical potential. (a) The temperature dependence of scaled lattice constants $a/\sqrt{2}$, $b/\sqrt{2}$, and $c/2$. (b) Strains ϵ_{xx} , ϵ_{yy} , and ϵ_{zz} calculated with respect to the pseudocubic lattice parameters extrapolated from the high temperature cubic phase [red line in (a)]. (c) Crystalline structures of the cubic (space group, $Pm\bar{3}m$), tetragonal (space group, $I4/mcm$), and orthorhombic (space group, $Pnma$) phases. $a^0a^0a^0$, $a^0a^0c^-$, and $a^-a^-c^+$ denote the TiO_6 octahedra tilt models written in Glazer notation [45]. Black dashed rectangles in (c) indicate the reference cubic cell.

We used the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) codes [51], with visualizations by the OVITO software [52]. For each simulation, a first 100 000 steps (100 ps) were performed to allow the structures to relax while another 100 000 steps were followed to obtain the time-averaged domain structures. To calculate the effect of an electric field (E), we add a force $F = qE$ to each charged atom in the system, where q is the charge carried by each ion.

We initially tested the phase transitions described by this potential. The phase transition sequence, along

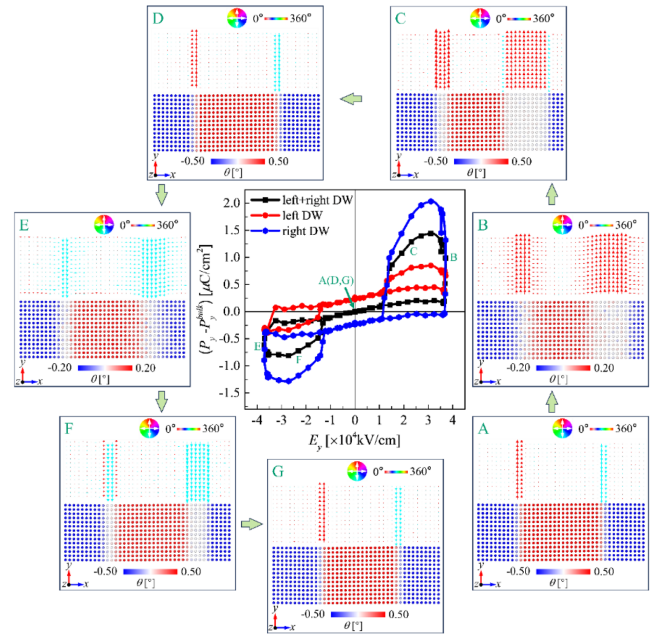


FIG. 5. Antiferroelectriclike double hysteresis loops of polar twin walls in ferroelastic CaTiO_3 at $T = 300$ K. Insets A–G indicate the strain (denoted by the twinning angle θ) and polar configurations under different electric fields. Polarization vectors are amplified by a factor of 1.5 for clarity.

with respective tiltings of the TiO_6 octahedra, is Cubic($Pm\bar{3}m, a^0a^0a^0$) $\rightarrow$ Tetragonal($I4/mcm, a^0a^0c^-$) $\rightarrow$ Orthorhombic($Pnma, a^-a^-c^+$) [Figs. 4(a)–4(c)], and is in accordance with the experimental observations by Carpenter [53,54], Redfern [55], and Ali [56]. The simulated transition temperatures are somewhat lower than the experimental values [48,57], but the phases themselves are correct and stable, so the typical (110)-oriented ferroelastic DW of orthorhombic CaTiO_3 could be further investigated.

For domain wall calculations, besides the large supercell of 940 800 atoms (188 160 formula units) shown in Fig. 3, we also solved a smaller supercell (39 200 atoms) with $6\times$ smaller domains (~ 8 nm vs ~ 48 nm for the central domain). The calculations for the smaller supercell are shown in Fig. 5. The results are qualitatively similar to those of Fig. 3, but with a reduced difference in critical field between domains and domain walls, resulting in unsaturated loops.