Ab initio phase diagram of BaTiO$_3$ under epitaxial strain revisited

Anna Grünbohm,$^{1,2}$ Madhura Marathe,$^2$ and Claude Ederer$^2$

$^1$Faculty of Physics and Center for Nanointegration, CeNiDE, University of Duisburg-Essen, 47048 Duisburg, Germany
$^2$Materials Theory, ETH Zürich, 8093 Zürich, Switzerland

We revisit the phase diagram of BaTiO$_3$ under biaxial strain using a first principles-based effective Hamiltonian approach. We show that, in addition to the tetragonal ($c$), quasi-rhombohedral ($r$), and quasi-orthorhombic (aa) ferroelectric phases, that have been discussed previously, there are temperature and strain regions, in particular under tensile strain, where the system decomposes into multi-domain structures. In such cases, the strained system, at least on a local level, recovers the same phase sequence as the unclamped bulk material. Furthermore, we extend these results from the case of “uniform” biaxial strain to the situation where the two in-plane lattice constants are strained differently and show that similar considerations apply in this case.

The optimization of ferroelectric materials by epitaxial growth and interface-mediated strain is nowadays a well-established and highly successful method. However, the experimental determination of strain-temperature phase diagrams is quite challenging, since only specific strain values, corresponding to the given lattice mismatch with a specific substrate, can be investigated. Therefore, the theoretical modeling of strain-dependent phase diagrams is highly relevant.

An important case is the prototypical ferroelectric BaTiO$_3$ (BTO), which, in its free bulk form, exhibits one paraelectric and three different ferroelectric structures as function of temperature and thus gives rise to a rich strain dependence. Different levels of sophistication have been used to model/calculcate the strain-dependent phase diagram of BTO, however, leading in part to conflicting results. First, various calculations based on Ginzburg-Landau-Devonshire theory have been performed, yielding qualitatively consistent phase diagrams as long as only mono-domain phases are taken into account. Once multi-domain consistent phase diagrams as long as only mono-domain phases are taken into account. Once multi-domain consistent phase diagrams as long as only mono-domain phases are taken into account. Once multi-domain consistent phase diagrams as long as only mono-domain phases are taken into account. 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and out-of-plane components, for different values of the epitaxial strain ($\eta_a = \eta_b$). It can be seen that for zero strain both in-plane and out-of-plane components of $P$ appear at the same temperature, while under compressive strain the appearance of the out-of-plane (in-plane) components are shifted to higher (lower) temperatures, and vice versa under tensile strain. This is in agreement with Refs. 13 and 16. However, we also observe that the temperature dependence of the in-plane polarization under tensile strain exhibits an unusual “kink-like” feature at a (strain-dependent) temperature $T_S$, somewhat below the overall critical temperature $T_C$.

Further inspection of the local soft mode configurations reveals that in the temperature range between $T_C$ and $T_S$ the system exhibits a multi-domain state, with average in-plane polarization along [110], but local in-plane polarization along [100] and [010], separated by 90° domain walls parallel to (110) (see Fig. 2(a)). Below $T_S$, the system adopts a mono-domain state with both local and global in-plane polarization along [110]. The formation of a multi-domain state under tensile strain allows the material to essentially recover the same phase sequence as in the free (unclamped) case, at least on a local level. At temperatures immediately below $T_C$, the tetragonal ferroelectric phase with polarization along (100) has the lowest free energy in the unclamped case. However, a corresponding mono-domain state is strongly disfavored by the elastic boundary conditions introduced through the epitaxial constraint. Thus, by forming the observed multi-domain state, the system can lower its overall free energy by achieving (100) polarization locally, at the cost of introducing energetically unfavorable domain walls. Therefore, the epitaxial constraint $\eta_a = \eta_b > 0$ promotes in-plane polarization with an equal volume fraction of [100] and [010] domains. However, for cell sizes below 20×20×20, the energy penalty for forming domain walls exceeds the gain in free energy within the (100)-polarized domains, and consequently the multi-domain phase has been overlooked in previous ab initio simulations employing smaller simulation cells. Under further cooling, the (110)-polarized phase becomes more favorable, cf. Ref. 34 for the unclamped material, and thus a transition into a corresponding mono-domain state, which is also compatible with the epitaxial constraint under tensile strain, occurs at $T_S$.

For local (100) polarization, only 180° domain walls and 90° walls parallel to {110} are possible by symmetry. The latter type is indeed observed in our simulations (see Fig. 2(a)), whereas 180° domain walls do not relax any elastic energy and are thus not favorable in the present case. The polarization across the 90° domain wall can be separated into the nearly constant polarization perpendicular to the wall ($P_{\perp}$) and the polarization parallel to the wall ($P_{\|}$), which approximately follows a tanh-profile:

$$P_{\|}(x) = P_{0,\|} \tanh \left[ \frac{x_N}{4\pi d_{DW}} \sin \left( \frac{4\pi}{x_N}(x - x_0) \right) \right], \quad (1)$$

with $d_{DW}$ half of the domain wall width, $x_0$ center of one wall, $P_{0,\|}$ polarization in the domain center, $x_N$ width of the fit region, and 4 the number of domains in the simulation cell (a minimum of 4 domains is necessary to match the domain profile at the periodic boundaries of the simulation cell). For $T = 400$ K and 0.75% tensile strain, the fit shown in Fig. 2(b) yields a domain wall width of about 5 nm, in good agreement with literature.

A clear signature of the multi-domain state in the temperature range between $T_C$ and $T_S$ can also be seen in various energy contributions, see Fig. 2(c). The modulation of $P_{\|}$ and the elastic mismatch at the domain walls induce an energy penalty in the local mode self energy and the inhomogeneous part of the elastic energy, whereas the coupling energy between local strain and soft mode is reduced if the mono-domain state with $P$ along (110) breaks up into multiple domains with local polarization along (100). We use these anomalies in the different energy contributions to identify $T_C$ and $T_S$ as function of strain and temperature. If no clear jump in energy is visible at $T_C$ (due to the continuous character of this transition under strain), we instead use the lowest temperature with $P = 0$, which, however, gives rise to a large uncertainty of about 20 K.

Fig. 3 (a) illustrates the so-obtained phase diagram of BTO under uniform ($\eta_a = \eta_b$) biaxial strain. In qualitative agreement with previous work, we find two transition lines, $T_C$, corresponding to the appearance of in-plane and out-of-plane polarization, respectively, which cross for zero strain at the transition temperature of the

FIG. 1. (Color online) Calculated temperature-dependent polarization along (a) [110] and (b) [001] for different values of biaxial strain applied in the (001) plane (from −0.85% to +1.75% in steps of 0.1%). Solid (black) line: unstrained case ($\eta = 0$); Dashed (blue) lines: tensile strain; Dash-dotted (red) lines: compressive strain.
free bulk material. An additional transition line, $T_S$, separating multi-domain and single-domain phases is observed, extending from the tensile strain region into the region of small compressive strain. We note that $T_S$ in Fig. 2(a) is still somewhat dependent on the used cell size (e.g. for $\eta = 0.75\%$, $T_S$ is reduced by 35 K when using a 92×92×92 cell, while the domain wall width is fully converged for a 48×48×48 cell).

Below both in-plane and out-of plane $T_C$, we obtain a multi-domain region where the in-plane components of the polarization exhibit the same domain patterns as in the tensile strain region (see e.g. Fig. 2(a)), but with an additional uniform polarization component along c, resulting in 60° domain walls parallel to {110}. Thus, in this region the local and global polarizations are along {110} and {111}, respectively. We note that down to $\eta = -0.45\%$, the imposed strain acts as tensile strain relative to the shorter lattice constant of the tetragonal phase in the free material. For stronger compressive strain, $T_S$ merges with the out-of-plane $T_C$ and no multi-domain states are found.

The case of general biaxial strain (with $\eta_a \neq \eta_b$) is illustrated in Fig. 2 (b)-(g). Under cooling, first a local polarization along $\langle 100 \rangle$ (light, red regions) appears in most regions of the phase diagram, with $P$ pointing towards the longest lattice direction ($a$ or $b$ for $\eta_a$ or $\eta_b > 0$, $c$ for compressive strain). The corresponding out-of-plane $T_C$ decreases linearly with $\eta_a + \eta_b$, while the corresponding in-plane $T_C$ increases linearly with the strain along the polarization direction, but is rather insensitive to the strain in the perpendicular direction. If two directions are under tensile strain, e.g. $b$ and $c$ for $\eta_b = -0.85\%$ and $\eta_b = 0.35\%$, a multi-domain state with local polarization along $\langle 100 \rangle$ and 90° domain walls is more favorable compared to a mono-domain state with polarization along $\langle 110 \rangle$. Thus, both mono- or multi-domain phases with local polarization along $\langle 100 \rangle$ are found below $T_C$.

Under further cooling, local polarization along $\langle 110 \rangle$ (darker, blue) and then along $\langle 111 \rangle$ (black) becomes more favorable, analogously to the case of the free material. In general, the tendency for polarization along a certain direction increases, if the corresponding lattice constants in the clamped case are larger compared to their cubic, tetragonal, or orthorhombic counterparts in the free material. Thus, the transition into the $\langle 110 \rangle$ phases first sets in when both $\eta_a$ and $\eta_b$ are positive and for a combination of large compressive and weak tensile in-plane strains (leading to an elongation along $c$). Again, multi-domain states occur for a broad range of strains and temperatures. For local $\langle 110 \rangle$ polarization, 90°, 60°, and 120° domain walls are in principle possible. As discussed above, only 60° domain walls parallel to $\{110\}$ with local $ac$ and $bc$ polarization are observed for $\eta_a = \eta_b$. For $\eta_a \neq \eta_b$, we find also 90° domain walls parallel to $\{100\}$ with local $ab/\bar{a}b$ or $ab/\bar{a}b$ polarization and vanishing average global polarization along the shorter clamped lattice constant. For local $\langle 111 \rangle$ polarization, no multi-domain states are found for $\eta_a = \eta_b$. For $\eta_a \neq \eta_b$, 109° domain walls parallel to $\{010\}$ and 71° walls parallel to $\{101\}$ are possible and both types are found in our calculations. 71° walls occur for a combination of compressive and tensile strain and the corresponding local $abc/\bar{a}bc$ or $abc/\bar{a}bc$ polarization results in a vanishing global polarization along the compressed lattice constant. 109° walls with local $abc/\bar{a}bc$ or $abc/\bar{a}bc$ polarization, with neither net polarization along the shorter clamped lattice constant nor along $c$, are found for non-uniform tensile in-plane strain.

In summary, we have shown, using ab initio-based molecular dynamics simulations, that the phase diagram of BTO under biaxial strain shows a variety of multi-domain regions. The formation of domains allows the system to recover the same sequence of para- and ferro-
electric phases as in the unstrained bulk material (at least for most combinations of $\eta_a$ and $\eta_b$), while simultaneously fulfilling all epitaxial constraints. Such multi-domain states have not been found in previous ab initio-based studies of strained BTO, due to restrictions in the size of the simulation cells. However, similar multi-domain configurations, have been observed in previous empirical phase-field simulations. Our results thus consolidate to some extent the empirical with the ab initio-based simulations, and provide new insights for future studies and the better interpretation of experimental data in strained BTO films.

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