Strong Reciprocal Interaction between Polarization and Surface Stoichiometry in Oxide Ferroelectrics

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ABSTRACT: We present a systematic evaluation of the effects of polarization switchability on surface structure and stoichiometry in BaTiO3 and PbTiO3 ferroelectric oxides. We show that charge passivation, mostly by ionic surface reconstructions, is the driving force for the stability of the surfaces, which suggests that varying the substrate polarization offers a new mechanism for controlling surface reconstructions in polar systems and inducing highly nonstoichiometric structures. Conversely, for thin-films the chemical environment can drive polarization switching via induced compositional changes on the surface. We find that the value of the oxygen partial pressure for the positive-to-negative polar transition is in good agreement with the recent experimental value for thin-film PbTiO3. For BaTiO3, we show that it is harder for oxygen control to drive polar transition because it is more difficult to reduce. This study opens up the possibility of real-time control of structure and composition of oxide surfaces.

KEYWORDS: Surface reconstructions, ferroelectric oxides, surface charge compensation, BaTiO3 surface, PbTiO3 surface, thin films

Ferroelectricity (FE) is characterized by coordinated ionic displacements from nominal high-symmetry lattice sites that cause a macroscopic electric polarization. Consequently, electric charge appears at the surfaces or interfaces due to the polar discontinuity. This produces an electrostatic surface instability that is similar to the situation of polar surfaces. Stabilization can be achieved by charge passivation of electronic or ionic origin. In the first case, the surface electronic structure is modified, perhaps leading to metallic surfaces. In the second case, the surface stoichiometry is altered from that of the bulk. Both cases lead to surfaces that are very different from the bulk or from the nonpolar terminations. The surface conductivity and catalytic chemistry of these surfaces are of prime interest for practical as well as fundamental purposes.

The reorientable polarization of FE oxides holds the promise for immense control of surface composition and properties. The interest in FE perovskites has been continuously increasing over the past decade due to their widespread use in a wide range of applications including catalysis, sensing devices, actuators, high-storage capacitors and nonvolatile memories. BaTiO3 (BTO) and PbTiO3 (PTO) of the ABO3 perovskite family, perhaps the most prominent and well studied FE oxides, have divalent A-cations (Ba2+ and Pb2+) and tetravalent B-cations (Ti4+). There are only a few studies of reconstructions on FE surfaces despite their practical importance in many applications. Adsorption studies of molecules on FE surfaces have shown unambiguously that the positive-polar (P+) and negative-polar (P−) surfaces interact differently with molecules and thus it can be anticipated that the stability of different surface compositions on FE surfaces would be highly polarization-dependent. Indeed, this was found the case in LiNbO3 which has an intrinsically polar (0001) termination and is ferroelectric. The equilibrium stoichiometry on the P+ surface contains more oxygen than on the P− surface at similar chemical conditions.

Received: September 11, 2014
Published: October 16, 2014
To date, the systematic changes of surface composition with FE polarization have not been explored. In this Letter, we demonstrate the paradigm of polarization-controlled surface composition and structure. Because we are primarily interested in the effect of the polarization component perpendicular to the surface, we select the tetragonal phases of BTO and PTO for study. We use a thermodynamic approach in conjunction with density functional theory (DFT) energies to map out the stability regions of various surface compositions under different experimental boundary conditions. The tetragonal phases of BTO and PTO, both belonging to the perovskite family and sharing similar properties, are expected to have similar surface phase diagrams. We find that this is generally true, but there are several notable differences between them that stem from the stronger FE polarization of PTO compared to BTO, as well as from the greater reducibility and oxidizability of Pb compared to Ba. The current study highlights the significant and systematic impact that polarization can have on the reconstruction of polar surfaces, especially with structural and compositional changes beyond the formation of oxygen vacancies. We provide the general principles of how ionic nonstoichiometry enables compensation for bound polarization vacancies. We include a large variety of surface compositions and reconstructions including \( (1 \times 1) \), \( (2 \times 2) \), \( (2 \times 1) \), and \( (3 \times 1) \) in addition to the \( (1 \times 1) \) bulk-like terminations. We have also included a small set of \( (2 \times 2) \) reconstructions to reproduce previous results for PE BTO. For each reconstruction, we examined BaO/PbO and TiO\(_2\) terminations, as well as surface compositions that have adatoms (cations or oxygen), vacancies (cations or oxygen), and adlayers (BaO/PbO, TiO, or TiO\(_2\)).

The energies of the different surface terminations are analyzed using a thermodynamic framework.\(^1\) The surface Gibbs free energy \( \Omega \) for the \( i \)th termination can be written as

\[
\Omega^i = \phi^i + \Gamma^i_{Ba/Pb} \Delta \mu^i_{Ba/Pb} + \Gamma^i_O \Delta \mu^i_O
\]

where \( \phi^i = [\Delta E - n_i^i \cdot \mu_{bulk}^{PTO/BTO}] / A^i \) and \( \Gamma^i_O = -(n_O^i - 3n_p^i) / A^i \) are all intrinsic properties for each surface termination that are independent of the chemical environment.\(^1\) \( \Delta E \) is the DFT total energy computed with respect to the fixed base of the slab (i.e., Pt + BTO/PTO layers that are fixed during the structural optimization), \( n_{Ba/Pb} \), \( n_p \), and \( n_O \) denote the number of Ba/Pb, Ti, and O atoms excluding those in the fixed base.
\( \Delta \mu_{Ba/Pb} \) and \( \Delta \mu_{O} \) are chemical potentials measured with respect to the standard states at 0 K, and \( A' \) is the surface area.

**Results and Discussion.** The BTO and PTO phase diagrams in Figure 1 show a rich proliferation of surface reconstructions with a variety of stoichiometries. The range of chemical potentials for which the surfaces are in equilibrium with the corresponding bulk phase and with no precipitation of secondary phases is also drawn. The surface compositions found can be grouped into three categories, namely (i) BaO/PbO-DL termi-

\[ \text{BaO} / \text{PbO} \text{-derived} \] (Ba/PbO double layer (DL), BaO/PbO, BaO-

\[ \text{(VO)} \]; (ii) TiO\text{2-DL}, TiO\text{2}-

\[ \text{TiO}_5 \text{O}_{12}/3 \] and (iii) Ti-rich (TiO\text{2}-Ti\text{5}O\text{5}/3). The range of

\[ \mu_{Ba/Pb} \text{ and } \mu_{O} \] is the surface

\[ \text{of subsurface O atoms while also forming bonds with the O} \]

\[ \text{of O₄ hollow sites previously occupied by Pb, see Figure 2d. This reconstruction is similar to forming a partially reduced TiO₂ double layer (discussed below) where instead the overlayer is composed of PbO_{1/2} \text{ (or PbO-O1/2). This striking similarity is not surprising if put in the context of the ability of PbO₂ to form similar structures as TiO₂ (for example rutile).} \]

**TiO₂-DL-Derived Surfaces.** The TiO₂-DL and its partially reduced forms have been extensively studied on the SrTiO\text{3}(001) surface. The (2 \times 2) TiO₂-DL, see Figure

\[ \text{2e, which is the most stable among the investigated TiO₂-DL structures, has its edge-shared TiO₅ polyhedra arranged in rows along the [110] direction. The reduced forms of TiO₂-DL such as } 3 \times 1 \text{ TiO}_2\text{TiO}_5/3 \text{ (see Figure 2f) preserve these edge-

\[ \text{shared TiO}_5 \text{ units. However, some corner-shared TiO}_5 \text{ polyhedra are also now present (see O-sharing in } ^{5}\text{Ti-}

\[ \text{and } ^{6}\text{Ti-centered polyhedra in Figure 2f). Unlike in the TiO₂-DL structures, excess TiO on TiO₂ terminations prefers the Ti adatoms to be in O₄ hollow sites with the O atom directly on top of Ti, maximizing the Ti coordination (maintaining a 5-fold coordination) despite the very low O concentration on the surface relative to Ti, see Figure 2g,h. This type of reconstruction has been thoroughly investigated recently by Morales et al.} \]

**Ti/Pb-Rich Surfaces.** The Ti adatom on the Ti-rich TiO₂ surfaces prefers to sit on an O₄ hollow site, a 4-fold coordination site. Increasing Ti coverage on the surface draws the O of the TiO₂ more out of plane, which further reduces the

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Figure 2. Ball-and-stick models for important surfaces that are affected by bulk polarization: (a) (1 \times 1) BaO/PbO and (b) TiO₂. Top and side views for (c) 3 \times 1 \text{ BaO-O}_{1/2}, (d) (2 \times 2) \text{ PbO-O}_{1/2}, (e) (2 \times 2) TiO₂ double-layer, (f) 3 \times 1 \text{ TiO}_2\text{TiO}_5/3 \text{, (g) } 3 \times 1 \text{ TiO}_2\text{TiO}_5/3 \text{, (h) } 2 \times 1 \text{ TiO}_2\text{TiO}_5/3 \text{, (i) } 3 \times 1 \text{ TiO}_2\text{-TiO}_5/3 \text{ and (j) } 2 \times 1 \text{ TiO}_2\text{-Pb}_{1/2}. \]
TiO$_2$ layer (see Figure 2). Analogous to this system are the Pb-rich TiO$_2$ terminations found in PTO. A Pb adatom adsorbs at the same site on a TiO$_2$ surface, although situated more out-of-plane than a Ti adatom, owing to its larger ionic radius (see Figure 2j). Similar Ba-rich surfaces are not stable owing to the strong stability of BaO compared to PbO as we will discuss below.

PE BTO and PTO surfaces have distinctly different phase diagrams, as seen by comparing Figure 1b,e. The PE BTO phase diagram is in excellent agreement with previous theoretical and experimental studies. For PE PTO, the oxidized $c(2 \times 2)$ TiO$_2$-DL and the $c(2 \times 2)$ PbO termination are the most stable at high (800–1000 K) and room temperature, respectively. This is consistent with previous $T = 0$ DFT calculations which concluded that only PbO and not TiO$_2$ surface is stable for thin film PTO with an in-plane polarization. A number of experimental studies are available for PTO as well.

It has been found that epitaxial PTO thin-films grown on STO substrate exhibited a $c(2 \times 2)$ surface reconstruction in a wide range of temperature 875–1025 K, and with different oxygen partial pressure $P_O$ conditions. For very low PbO pressures, for example, $P_{PbO} = 4 \times 10^{-10}$ bar at 1000 K, this study found the surface to reconstruct into a disordered ($1 \times 6$) superstructure that is more TiO$_2$-rich than the $c(2 \times 2)$ phase. We show in Figure 1e the region corresponding to the oxygen theoretical and experimental studies. For PE PTO, the phase diagram is in excellent agreement with previous diagrams, as seen by comparing Figure 1b,e. The PE BTO microscopic domains composed of more than one TiO$_2$ reconstruction exhibits short-range order, prominently showing in Figure 1, and more information is given in Supporting Information Table S4. In the PE case, and polarization can also induce highly polarized regions as arising from the formation of defects on the disordered ($1 \times 6$) phase found in PTO for very low $P_{PbO}$ in ref 22 is similarly composed of multiple TiO$_2$ overlayers.

We now examine how FE polarization influences the surface phase diagram. Most of the PE surface reconstructions are also found in the phase diagrams of the FE surfaces but under different ranges of chemical potential. In fact, the FE polarization can stabilize or eliminate surface reconstructions with stoichiometry similar to the most stable reconstructions in the PE case, and polarization can also induce highly nonstoichiometric structures. This is explained schematically in Figure 1, and more information is given in Supporting Information Table S4.

The most significant differences between the surfaces of PE and FE slabs can be understood from charge passivation, which is of paramount importance for the stabilization of polar surfaces. To illustrate this, it is useful to regard the different surface terminations as arising from the formation of defects on the stoichiometric surface, which then organize into stable reconstructions. We define neutral reconstructions as those with surface compositions where the layer A/O and Ti/O ratios are 1:1 and 1:2, respectively. Using a simple ionic-charge representation, we can refer to nonstoichiometric surface compositions as positive if the A/O or Ti/O ratios are greater than the neutral ones, and negative if they are smaller than the neutral ratios (with a few exceptions such as O on BaO as discussed below). We illustrate this further for BTO. Starting from the neutral TiO$_2$-DL reconstruction ($Ti/O = 1:2$), abstraction of O from the top layer creates positive reconstructions such as TiO$_2$-TiO$_x$ ($Ti/O = 1:1 + x/2$) 1:2 for all $x < 2$), and in extreme cases this may be accompanied by removal of some TiO$_2$ units as well as O, yielding TiO$_2$-TiO$_{1+x}$ ($Ti/O = (1 + x):(2 + x) > 1:2$ for all $x > 0$) or TiO$_2$-Ti$_x$ ($Ti/O = (1 + x):2 > 1:2$ for all $x > 0$).

The FE polarization decreases the net surface charge of the PE surface for the $P^-$ case, while it increases the charge for the $P^+$ surface. In turn, this coupling creates a mechanism to passivate the polarization charges. This can be seen from a charge partitioning scheme, for example, as provided by Bader charges. For illustration purposes, we consider Bader charges for $3 \times 1$ TiO$_2$-TiO$_{5/3}$ and $3 \times 1$ TiO$_2$-Ti$_{1/3}$ reconstructions shown in Figure 2j (more Bader charge analysis is provided in Supporting Information Table S5). For the PE surface, the net surface charges per unit cell of these two reconstructions are respectively 0.25e and 0.52e, which decrease to 0.10e and 0.43e for $P^-$, and increase to 0.39e and 0.60e for $P^+$.

This shows that on the $P^+$ surface, it is more difficult to abstract O from the surface, and much less desirable to have positive reconstruction. This accordingly shifts the region of stability of the $3 \times 1$ TiO$_2$-TiO$_{5/3}$ and $3 \times 1$ TiO$_2$-Ti$_{1/3}$ as well as other positive reconstructions to a lower $\Delta \mu_O$. The reverse is true for the $P^-$ surface, where the stable regions in the phase diagram for positive reconstructions are shifted to higher $\Delta \mu_O$, an indication for the propensity of the $P^-$ surface to stabilize positive reconstructions. Additional examples include BaO-(V$_0$)$_{1/3}$ for BaO-(V$_0$)$_{1/3}$ that has a broader stability range on P/PTO, and PbO-(V$_0$)$_{1/3}$ for PbO-(V$_0$)$_{1/3}$/STO. Additionally, BaO-(V$_{Ba}$)$_{1/3}$ for BTO, and PbO-(V$_{Pb}$)$_{1/3}$ and PbO-O$_{2/3}$ for PTO have larger stability regions on, or appear exclusively on the $P^+$ surface. See Supporting Information Table S3 for more details.

It is, however, still possible that relatively severe environmental conditions could impose reconstructions that are apparently of the wrong charge type on the FE surfaces. We find that in this case, the polar surface would alleviate the polar instability by localizing a hole or electron around the defect to reduce the effective charge of the surface, as can be seen from inspecting bond lengths or from Bader charge decomposition. One notable example of this is the Ba-O$_2$ surface termination, where the O-adatoms bond to the surface O rather than to the Ba cations. On the PE surface, the O$_2$ bond length is 1.44 Å as in BaO-O$_2$/$_{2/3}$ (see Figure 2c), consistent with the formation of a peroxo-like (O$_2^−$) surface species, thus maintaining a low surface charge (the Bader charge for O$_2^-$ is $+0.4$ e$^-$ while the charge of O atom in $ATiO_3$ is $-1.2e^-$). On the other hand, on the negative surface, the O$_2$ bond length is 1.37 Å indicating the formation of a superoxo-like (O$_2^+$) surface species. The charge of the surface O$_2^+$ is then lowered (−1.12e). This mechanism enables stabilization of the $P^-$ surface despite the presence of high amounts of O, which explains why, in Figure 1c the $3 \times 1$ Ba-O$_2$/$_{2/3}$ (phase # 2, shown in Figure 2c) expands its stability at the expense of the $1 \times 1$ BaO (phase # 4). These show that O on BaO may be regarded as a neutral, negative or positive reconstruction, in response to the bulk polarization. The formation of the surface peroxo and superoxo species is similar to what has been seen before on other oxide surfaces such as LiNbO$_3$, CeO$_2$,$^{25}$ and V$_2$O$_5$. $^{30}$ Interestingly, we find that another mechanism is operative on PTO where the oxygen adatom interacts with the Pb cations rather than the surface O. This is because Pb$^{4+}$ can be oxidized to Pb$^{4+}$, thereby...
stabilizing an additional surface oxo (O\textsuperscript{2−}) group (see Figure 2d for structures).

Although, both BTO and PTO have similar structural characteristics (with their A cations in the same oxidation state), they show drastic differences in their surface stability, which can be attributed mostly to the significant differences between the affinities of Ba and Pb to oxygen. The PbO-derived surface is more reducible than the BaO-derived one, and Pb is more likely to precipitate out as Pb(s) or vaporize into Pb(g).

This is directly related to the existence of TiO\textsubscript{2}−Pb phases on P\textsuperscript{−}/PTO while a TiO\textsubscript{2}−Ba\textsubscript{x} reconstruction is found to be unstable. Also, PbO-(V\textsubscript{O})\textsubscript{x} is stable at a less negative Δ\textsubscript{μO} compared to BaO-(V\textsubscript{O})\textsubscript{x}. Additionally, PbO is more volatile than BaO or TiO\textsubscript{2} making the formation of the PbO surface less favorable compared to BaO or TiO\textsubscript{2}. Thus, PbO-derived surfaces are found only near the Δ\textsubscript{μPb} = 0 boundary. Moreover, because TiO\textsubscript{2} is also less reducible than PbO, Ti-rich phases are inaccessible in the region where PTO is stable. This means that moderately negative Δ\textsubscript{μO} is enough to reduce Pb\textsuperscript{2+} and destroy the perovskite structure. The most reduced TiO\textsubscript{2}-derived surface that is accessible for PTO is TiO\textsubscript{2}-(TiO)\textsubscript{x} in the P\textsuperscript{−} case. These effects combine to make the stability region of PTO a narrower slice of the phase diagram compared to BTO, and closer to the Δ\textsubscript{μPb} = 0 and Δ\textsubscript{μO} = 0 boundaries.

It is also apparent that the highest accessible non-stoichiometry is higher for PTO than for BTO. For example, compare their respective ΔO\textsubscript{2}-(V\textsubscript{O})\textsubscript{x} or TiO\textsubscript{2}-(TiO)\textsubscript{x} phases where the maximum value of x that is stable for PTO (x = 2/3) than in BTO (x = 1/3). This is consistent with the nature of the charge passivation mechanism. Because PTO has higher polarization than BTO (calculated polarization: 31.89 versus 0.46 C/m\textsuperscript{2}), more charged species on the surface are required to stabilize the surface of FE PTO.

In thin films, surface effects are closely coupled to the substrate polarization,\textsuperscript{11,12,32} and thus it is important to predict the polarization direction that is favored by different surface stoichiometries. Figure 3a,b shows the combined phase diagrams of the P\textsuperscript{−} and P\textsuperscript{+} polarizations for both BTO and PTO. In Figure 3c,d, a region is indicated as P\textsuperscript{−} (P\textsuperscript{+}) if the stable surface compositions have all P\textsuperscript{−} (P\textsuperscript{+}) bulk polarizations and is indicated as P\textsuperscript{−}+P\textsuperscript{+} if the surfaces have both P\textsuperscript{−} and P\textsuperscript{+} stable compositions. However, instead of defining a sharp phase boundary, we consider the surface compositions that are within a small region δ from the lowest energy structure. We chose δ = ±0.1 eV/primitive unit cell as a measure of an average error in the DFT energy differences. As can be seen from Figure 3, oxygen-poor and metal-rich conditions favor P\textsuperscript{−}, while oxygen-rich and metal-poor conditions favor P\textsuperscript{+}. The P\textsuperscript{−} ↔ P\textsuperscript{+} transition can be approximated from the boundaries between surface phases that favor P\textsuperscript{−} and P\textsuperscript{+} within the bulk stability boundary.

The region in the phase diagrams where P\textsuperscript{−} and P\textsuperscript{+} may coexist according to the defined energy window approximates the chemical potential range where the P\textsuperscript{−} ↔ P\textsuperscript{+} transition will occur (see Figure 3c,d). For BTO, the transition takes place at Δ\textsubscript{μO} ≈ −2.75 to −1.5 eV at 300 K, while for PTO the transition happens at Δ\textsubscript{μO} ≈ −1.25 to −1 eV at 300 K and Δ\textsubscript{μO} ≈ −1.25 to −0.75 eV at 700 K. The approximate range of O\textsubscript{2} pressure corresponding to these chemical potentials can be obtained using

\[ \Delta \mu_0(0 \text{ K} \rightarrow T, p_{O_2}) = \Delta \mu_0(0 \text{ K} \rightarrow T, p_{O_2}^0) + \frac{1}{2} kT \ln \left( \frac{P_{O_2}}{P_{O_2}^0} \right) \]

where \( \Delta \mu_0(0 \text{ K} \rightarrow T, p_{O_2}) \) and \( \Delta \mu_0(0 \text{ K} \rightarrow T, p_{O_2}^0) \) are respectively the relative chemical potential of O at temperature T and O\textsubscript{2} partial pressures \( p_{O_2} \) and \( p_{O_2}^0 \), measured with respect to O\textsubscript{2} at 0 K and \( p_{O_2}^0 = 1 \text{ bar} \), and k is the Boltzmann constant.

To some extent, the limited number of sizes of supercells investigated imposes limitations on our ability to predict exact symmetries and sizes of the reconstructions that can be found experimentally. Nevertheless, the investigated wide range of defect concentrations and symmetries are excellent representatives of larger surface reconstructions of similar nonstoichiom-
etry. The uncertainty in the predictive ability of the phase diagrams stemming from the neglect of the small contribution of the vibrational entropy to the total energy of the surface, inherent DFT errors, and possible coexistence due to thermal effects, does not change our findings significantly, as we discuss in the Supporting Information (see Figure S3). We conclude that despite the modest uncertainty, the stable surface phases shown in the phase diagrams are close representatives of the likely stoichiometry and structure in a given environmental condition. Thus, the phase diagrams presented here enable the prediction of compositional phase transitions on the PE and FE BTO (001) and PTO (001) surfaces.

For polar surfaces, where the Curie temperature $T_C$ serves as the upper bound for FE stability, severe reduction of oxygen partial pressure cannot be achieved by thermal means. Nevertheless, surface reduction could be carried out at fixed temperature by using reducing agents (for example, $H_2$) or solid-state coulometric titration with gas-phase $O_2$ as the ambient gas in the sample chamber. Furthermore, for these perovskites their Curie temperatures can be increased and their polarization can be enhanced by imposing an epitaxial strain.

Different avenues to modify the stoichiometry of transition metal oxide surfaces are highly coveted in the field of catalysis. Here we demonstrate the strong interaction between the ferroelectric polarization and surface stoichiometry, which give the surface structure tunable sensitivity to changes in the ambient environment. Specifically, by altering the bulk $P$, the bound charge changes, altering the stability of various nonstoichiometric compositions and reconstructions. The possibility of systematically and reversibly tailoring the surface composition and pattern by accessing a switchable property of the bulk is clearly demonstrated by this investigation.

**ASSOCIATED CONTENT**

Supporting Information

Detailed methodology, convergence tests, validation of the model, tabulated Bader charges, phase coexistence analysis plots, and tabulated surface energies for all the investigated surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

W.A.S. was supported by the Office of Naval Research, under Grant N00014-12-1-1033. J.M.P.M. was supported by the Air Force Office of Scientific Research, Air Force Materiel Command, USAF, under Grant FA9550-10-1-0248. A.M.R. was supported by the DoE Office of Basic Energy Sciences under Grant DE-FG02-07ER15920. Computational support was provided by the High Performance Computing Modernization Program (HPCMO) of the US DoD.

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