Ferroelectricity in Pb$_{1+\delta}$ZrO$_3$ Thin Films

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INTRODUCTION

The antiferroelectric perovskite PbZrO$_3$ is regarded as a promising candidate for applications in energy storage,1 bulk, PbZrO$_3$ is able to undergo an electric-field-induced, first-order phase transition from a nonpolar ground state to a metastable polar state, as manifested by a double-hysteresis loop.6,7 This antiferroelectric behavior arises from structural distortions and complex lattice dynamics, namely cooperative antiparallel displacements of the lead ions and antiferrodistortive octahedral rotations, and is manifested as nearly energy-degenerate centrosymmetric, antiferroelectric and noncentrosymmetric, ferroelectric states.8–12 Because of the small free energy difference between the phases, the system is highly susceptible to perturbations including electric fields, point defects,13,14 lattice distortions,15,16 and electrostatic boundary conditions,17–19 which can tip the balance of the ground state energy competition.

Thus, it is important to understand the effect of these perturbations to better control and engineer PbZrO$_3$ for future applications and to synthesize the material in a controllable way such that the desired properties are achieved. In the past decades, although various routes, such as chemical substitution,20–24 epitaxial strain,25–28 and size effects,29–31 have been studied to modify and control the ground state of PbZrO$_3$, the impact of cation nonstoichiometry has rarely been explored. There is growing evidence that cation nonstoichiometry can play a significant role in the evolution of material properties as has been highlighted in, for example, SrTiO$_3$,30,31 BaTiO$_3$,31 and BiFeO$_3$.31 This is particularly important in perovskite systems where the polarization and lattice modes are strongly coupled, and, thus, local nonstoichiometry and lattice imperfection can distort the structure and drive the material...
Figure 1. (a) X-ray $\theta$–$2\theta$ line scans reveal high-quality (120)$_C$-oriented, 50 nm thick Pb$_{1+\delta}$ZrO$_3$ ($\delta = 0, 0.1$, and 0.2) films on 10 nm SrRuO$_3$/DyScO$_3$ (110) substrates. Reciprocal space mapping studies about the 332$_C$ and 440$_C$ (280$_C$)-diffraction conditions of the substrate and film, respectively, for the (b) PbZrO$_3$, (c) Pb$_{1.1}$ZrO$_3$, and (d) Pb$_{1.2}$ZrO$_3$ heterostructures reveal nearly completely relaxed epitaxial Pb$_{1+\delta}$ZrO$_3$ films with similar lattice parameters. Rutherford backscattering spectrometry studies reveal film chemistries of (e) PbZrO$_3$, (f) Pb$_{1.1}$ZrO$_3$, and (g) Pb$_{1.2}$ZrO$_3$ for growth from targets of the same chemistries.

into exotic ground states. For instance, in nonstoichiometric Sr$_{1-\delta}$TiO$_3$ thin films, local Sr-deficiency is thought to perturb the lattice and give rise to relaxor-like behavior. It has also been reported that in ferroelectric BaTiO$_3$ thin films, local lattice imperfection and aligned defect dipoles can induce dramatic changes in the ferroelectric-to-paraelectric phase transition temperature. Thus, the effect of cation nonstoichiometry, where local cation excess or deficiency and lattice distortions are expected, could have a significant impact on antiferroelectric PbZrO$_3$ where multiple lattice instabilities are involved in determining the final ground state. Additionally, in PbZrO$_3$ previous work has already found that the system is prone to antisite defects (i.e., lead ions replacing zirconium ions). This tendency for antisite defects, and the fact that to acquire high-quality lead-based compounds excess lead is typically added to the precursors to compensate for the evaporation of lead at high temperature, motivates the need for a systematic study of the impact of cation nonstoichiometry on the properties of PbZrO$_3$.

In this spirit, we explore the effects of cation stoichiometry on antiferroelectric–ferroelectric phase stability, structural distortions, and field-dependent polarization behavior of Pb$_{1+\delta}$ZrO$_3$ thin films. In this work, 50 nm thick Pb$_{1+\delta}$ZrO$_3$ ($\delta = 0, 0.1, 0.2$) thin films were synthesized via pulsed-laser deposition on 10 nm thick SrRuO$_3$-buffered DyScO$_3$ (110) substrates using lead-excess, lead zirconate ceramic targets of the same compositions. Single-phase Pb$_{1+\delta}$ZrO$_3$ thin films with negligible differences in lattice parameters are revealed by X-ray diffraction despite Rutherford backscattering spectrometry (RBS) studies revealing large cation nonstoichiometry and heterostructures with nominal chemistries of PbZrO$_3$, Pb$_{1.1}$ZrO$_3$, and Pb$_{1.2}$ZrO$_3$. Electrical characterization reveals that PbZrO$_3$ and Pb$_{1+\delta}$ZrO$_3$ heterostructures remain antiferroelectric, display double-hysteresis loops, and exhibit dielectric anomalies at $\sim$290 °C, while Pb$_{1.2}$ZrO$_3$ heterostructures exhibit single-hysteresis loops, indicative of ferroelectric response, with a broader dielectric response peaked at $\sim$260 °C. Synchrotron-based X-ray reciprocal space mapping (RSM) studies further confirm the change in ordering with film chemistry wherein Pb$_{1+\delta}$ZrO$_3$ and Pb$_{1.2}$ZrO$_3$. Functional theory (DFT) calculations suggest that antisite PbZr defects are the favorable point defects in lead-excess PbZrO$_3$ such defects have a smaller formation energy than in the antiferroelectric PbZrO$_3$. That said, it is important to note that PbZrO$_3$ and Pb$_{1+\delta}$ZrO$_3$ heterostructures for growth from targets of the same chemistries.
J/cm² and 5 Hz, respectively. All films were grown in an on-axis geometry with a target-to-substrate distance of 5.2 cm. Following growth, the films were cooled to room temperature at a rate of 10 °C/min. in a static oxygen pressure of 700 Torr. The film chemistry was probed ex situ using RBS (incident ion energy 3040 keV, incident angle 22.5°, exit angle β = 25.35°, and scattering angle θ = 168°), and the spectra were fitted using the RBS analysis software SIMNRA.

**X-ray Diffraction Studies.** A high-resolution X-ray diffractometer (Panalytical, X’ Pert MRD) was used to perform line scans and preliminary RSM studies. Synchrotron X-ray RSM studies were conducted at the Advanced Photon Source, Argonne National Laboratory, Sector 33-BM using the Pilatus 100 K detector.

**Electrical Characterization.** Symmetric capacitor structures were fabricated on SiO₂ substrates using an MgO hard-mask process. Deposition of top electrodes was done at 500 °C and in a dynamic oxygen pressure of 100 mTorr to avoid significant lead loss. Other than temperature, the same growth conditions were used for the top SrRuO₃ growth as for the bottom electrodes. Ferroelectric polarization hysteresis loops were measured using a Precision Multifrequency Tester (Radiant Technologies), and dielectric and loss tangent measurements were performed using an E4890 LCR meter (Agilent/Keysight).

**First-Principles Calculations.** DFT calculations are performed within a revised generalized gradient approximation of Perdew–Burke–Ernzerhof (PBEsol) with VASP. The calculations use a plane-wave basis and an energy cutoff of 500 eV, gamma-centered k-point grid, and projected augmented wave pseudopotentials with 14, 12, and 6 valence electrons for Pb, Zr, and O, respectively, from the VASP library. Structural relaxations are performed until atomic forces are <0.01 eV/Å. Antisite defects are simulated in supercells containing 32 formula units with 5 atoms/formula unit. We consider Pb/Zr ratios of 33:31, 34:30, and 35:29, corresponding to Pb₁⁺ZrO₃ with δ = 0.06, 0.13, and 0.21, respectively. The formation energy of a Pb₂⁺ antisite is computed by replacing a zirconium atom with a lead atom and fully relaxing the atomic coordinates and lattice constants. The formation energy of stoichiometric PbZrO₃ is given by $E_F^{PbZrO_3} = E_{PbO} + E_{ZrO_2} - E_{PbZr - Def}$, where $E_{PbO}$, $E_{ZrO_2}$, and $E_{PbZr - Def}$ correspond to the total energies of PbZrO₃, PbO, and ZrO₂, respectively. The antisite formation energy is given by $E_{Pb_{def}} = E_{Pb_{def}} - E_{PbO} - E_{ZrO_2} + E_{PbZr - Def}$, where $E_{Pb_{def}}$ is the total energy of a supercell containing one Pb₂⁺-antisite defect, and corresponds to the total energy of PbO₂. In addition, the formation energies of Pb, Zr, and O vacancies at relevant charge states, as well as lead and zirconium antisites, as a function of Fermi energy are computed. Charged defects are simulated by adding or removing electrons in the supercell and by adding a compensating uniform background charge. In this case, we assume oxygen-rich growth conditions and the corresponding chemical potentials. Polarization calculations are performed from Berry phases using the modern theory of polarization, as implemented in VASP. Further details of the calculations are in the Supporting Information.

**RESULTS AND DISCUSSION**

In stoichiometric PbZrO₃, the room temperature Pham ground state structure is related to the high-temperature cubic Pm₃m perovskite structure by the combined distortion of two lattice modes: the antipolar displacement of the lead atoms (Σ mode) and the antiferrodistortive oxygen octahedral rotations (R mode). These collective distortions lower the symmetry of the cubic lattice and lead to an orthorhombic unit cell with lattice parameters $a = 5.882$ Å, $b = 8.228$ Å, and $c = 11.783$ Å. X-ray line-scans indicate that the films are (120)ₜ-oriented (i.e., the film [120]ₜ is parallel to the substrate normal [110]₀, where “O” denotes orthorhombic indices) for all three target chemistries (Figure 1a). Further examination of the X-ray line scans (Supporting Information, Figure S2) and RSMs (Figures 1b–d) for all three heterostructure variants reveals that all Pb₁₊ZrO₃ films are single phase and exhibit essentially identical lattice parameters regardless of the target chemistry. Note that the coexistence of 90° structural domains in PbZrO₃, which has been observed previously, should correspond to the...
440°, 280°, and 260° diffraction peaks in the RSM scans. Despite no clear separation between these peaks in the laboratory-based RSM studies, later synchrotron-based studies show both are present but likely unresolved due to the small lattice distortion in PbZrO3. Additionally, the three heterostructure variants have essentially equal crystalline quality as indicated by the presence of strong Laue fringes and nearly identical rocking-curve full-width-at-half-maximum (fwhm ≈ 0.025°) values (Supporting Information, Figures S2b–d). Initial analysis of the structural data suggests that all three heterostructure variants, despite being grown from different target compositions, have the same structure. Studies of the film chemistry using RBS (Figures 1e–g) reveal that the resulting films are in fact stoichiometric replications of the targets with nominal chemistries of PbZrO3, Pb1.1ZrO3, and Pb1.2ZrO3. The latter implies that at least 20% lead excess can be accommodated in the lattice without a significant change in the lattice or deterioration of the film crystallinity. Such a finding is, at face value, intriguing and suggests a need for careful analysis of PbZrO3 materials produced from lead-rich starting chemistries since basic structural characterization may not directly reflect these variations.

In turn, before exploring a more thorough analysis of the defect structures of these films, we first examine how the cation nonstoichiometry in Pb1.1ZrO3 affects the electrical properties. Polarization—electric field hysteresis loops and dielectric permittivity as a function of frequency and temperature were measured for the three different Pb1+δZrO3 heterostructure variants (Figure 2). For the PbZrO3 (Figure 2a) and Pb1.1ZrO3 (Figure 2b) heterostructures, double-hysteresis loops (here shown for frequencies from 0.1 to 10 kHz), typical for an antiferroelectric, are observed for both stoichiometries with a saturated polarization of ~50 μC/cm² and similar switching field values (380 and 390 kV/cm, respectively). Studies of the Pb1.1ZrO3 heterostructures (Figure 2c), however, reveal the presence of a single-hysteresis loop indicative of ferroelectric-like response. The coercive field for the ferroelectric-like Pb1.1ZrO3 heterostructures is ~100 kV/cm, and the saturation polarization is ~40 μC/cm², slightly smaller than the antiferroelectric samples. Different from antiferroelectric PbZrO3 where the remnant polarization is close to zero at zero field, the Pb1.2ZrO3 heterostructures exhibit a remnant polarization of ~10 μC/cm². Further study of the dielectric permittivity as a function of temperature reveals that both the antiferroelectric PbZrO3 and Pb1.1ZrO3 heterostructures (Figures 2d,e) exhibit a relatively sharp anomaly at ~290 °C and that the loss tangent remains low for frequencies ranging from 0.5 to 100 kHz. Similar studies of the ferroelectric-like Pb1.2ZrO3 heterostructures (Figure 2f) reveal considerably broadened temperature dependence of the permittivity (which gradually peaks around ~260 °C) and essentially flat loss tangent at all temperatures measured (except at the highest temperatures, likely due to increased conduction of the sample). Furthermore, no obvious changes in the frequency dispersion of the dielectric permittivity or permittivity peak shifts as a function of frequency were observed for all heterostructures across the temperature range studied.

From these measurements, we can conclude that cation nonstoichiometry can dramatically change the electrical properties of Pb1+δZrO3 such that antiferroelectricity is no longer manifested in the Pb1.2ZrO3 heterostructures. We further propose that the electrical behavior of the Pb1.2ZrO3 heterostructures is indicative of true ferroelectricity, not spurious effects arising from leakage or otherwise. This is consistent with current–voltage studies (Supporting Information, Figure S3a) as well as the low loss tangent (as a function of frequency; Supporting Information, Figure S3b) at room temperature for all three heterostructure variants which shows that the samples are quite insulating and should have minimal leakage-related contributions to the ferroelectric hysteresis loops. Also, the ferroelectric nature of the Pb1.2ZrO3 heterostructures is further supported by frequency-dependent hysteresis loops at room temperature (a wider range of frequencies, from 0.0001 to 100 kHz, is provided; Supporting Information, Figure S3c) which show that the coercive field increases systemically with frequency and that polarization saturates to the same level, with the same profile, indicating that the effects likely arise from switched polarization. Current hysteresis loops also exhibit a single switching peak at low fields and remain essentially constant above the saturation field, again indicating the ferroelectric nature of the Pb1.2ZrO3 heterostructures (Supporting Information, Figure S3d). Furthermore, the nature of the temperature- and frequency-dependent dielectric response of the Pb1.2ZrO3 heterostructures suggests a homogeneous bulk response, instead of inhomogeneously polarized nanoregions where strong frequency-dependent dispersion in dielectric permittivity would be expected in the low-temperature regime. Taken together, the data suggest that the Pb1.1ZrO3 heterostructures are intrinsically ferroelectric, which implies that the structure of the film must be different from the antiferroelectric PbZrO3 and Pb1.1ZrO3 heterostructures.

To confirm this point, synchrotron-based X-ray RSM studies were performed. In antiferroelectric PbZrO3, the frozen Σ mode that gives rise to the antiparallel displacement of the lead atoms also gives rise to $\frac{28}{12}$ (1, 0, 0) quarter-order diffraction peaks, in a pseudocubic unit cell where a is the pseudocubic unit cell lattice constant. Such diffraction peaks would not be observed in a ferroelectric phase. In turn, RSM studies about the DyScO3 332−δ diffraction condition were undertaken (Figures 3a–c). These RSM studies reveal a number of interesting points. First, the scans show evidence of a predominantly relaxed film, but with a small fraction of coherently strained material. Both the relaxed and strained peaks (labeled as “R” and “S”, respectively) can be observed for all heterostructures. This finding is consistent with the growth mode observed by RHEED (Supporting Information, Figure S1). Briefly, the RHEED analysis reveals a Stranski–Krastanov-like growth mode wherein the film relaxes and transitions from 2D to 3D growth after 2–3 unit cells as evidenced by 2–3 oscillations of the RHEED intensity followed by an intensity drop and corresponding transition from streaks to dots in the diffraction pattern. The strained layer observed by the strain in the RHEED intensity follows by an intensity drop and corresponding transition from streaks to dots. The strained layer observed by the synchrotron-based X-ray RSM likely corresponds to those initial 2–3 unit cells. Second, the scans showed marked variations in the intensity of the quarter-order diffraction peaks. The main Pb1.44ZrO3 diffraction conditions are indexed as 440°, 280°, while the quarter-order Bragg diffraction conditions from the antiparallel displaced lead atoms are indexed as 450°. Examination of the RSMs for the PbZrO3 and Pb1.1ZrO3 heterostructures reveals the presence of both the main and quarter-order diffraction peaks, clearly revealing antiferroelectric order and the coexistence of 90° antiferroelectric domains (Figures 3a,b). Similar examination of the RSMs for the Pb1.2ZrO3 heterostructures, however, reveals considerably different structural response.
Pb1.2ZrO3 heterostructures exhibit a peak 2 orders of magnitude reduced intensity of the quarter-order Bragg peaks (Figure 3c). Plotting the dominant 450°-diffraction condition intensity, normalized with respect to the substrate intensities, further reveals that for both the PbZrO3 and Pb1.1ZrO3 heterostructures a sharp Bragg peak can be observed and that the Pb1.2ZrO3 heterostructures, while diffused patterns along the [101]pc are observed for the Pb1.1ZrO3 heterostructures. (d) 450°-diffraction peak intensity normalized with respect to the substrate along the L-direction reveals strong Bragg diffraction for antiferroelectric PbZrO3 and Pb1.1ZrO3 heterostructures but 2 orders of magnitude lower intensity in the ferroelectric-like Pb1.2ZrO3 heterostructures.

Figure 3. Synchrotron-based X-ray reciprocal space mapping studies about the around 332°-diffraction condition of the DyScO3 substrate for the (a) PbZrO3, (b) Pb1.1ZrO3, and (c) Pb1.2ZrO3 heterostructures. Data is plotted in reciprocal HKL vector space with respect to the DyScO3 orthorhombic lattice such that [0 0 1] is the in-plane axis and [H K 0] is the out-of-plane axis. Relaxed and strained peaks from the Pb1.1ZrO3 are labeled as “R” and “S”, respectively. Quarter-order Bragg peaks (450° and 290°c) are observed for the PbZrO3 and Pb1.1ZrO3 heterostructures, while diffused patterns along the [101]pc are observed for the Pb1.2ZrO3 heterostructures. (d) 450°-diffraction peak intensity normalized with respect to the substrate along the L-direction reveals strong Bragg diffraction for antiferroelectric PbZrO3 and Pb1.1ZrO3 heterostructures but 2 orders of magnitude lower intensity in the ferroelectric-like Pb1.2ZrO3 heterostructures.

Figure 4. (a) Formation energies at T = 0 K of stoichiometric PbZrO3, zirconium vacancies (VZr), and antisite defects (PbZr) in the Pbam PbZrO3 lattice. Stoichiometric PbZrO3 is suggested to be metastable at low temperature while antisite defect formation in PbZrO3 lattice is unavoidable. (b) The energy difference between R3c and Pbam phases in nonstoichiometric Pb1.1ZrO3 is small and remains <1 meV across the range of compositions probed herein. (c) Antisite defects (PbZr) can form in both Pbam and R3c Pb1.1ZrO3 films, while such defects are more favored in the R3c phase as suggested by the lower defect formation energy across the entire doping range.
more energetically favorable than creating stoichiometric PbZrO₃. These results are consistent with previously reported defect studies on PbZrO₃. In addition, examination of the Born effective charge shows that the valence state of the lead ions increases from +3.2 to +4.8 when they are located at the lead antisite (Supporting Information, Table S2), which indicates that lead is in a higher valence state on the zirconium site; in this manner, the system achieves charge neutrality in the system without the need to introduce additional point defects or charge carriers, consistent with our experimental findings that all three lead-excess samples remain electrically insulating. Also, the transition to a higher valence state for the lead-antisite defect is accompanied by a decrease in ionic radius (the Shannon–Prewitt ionic radii for Pb³⁺, Pb⁴⁺, and Zr⁴⁺ in sixfold coordination are 1.19, 0.775, and 0.72 Å) such that very little lattice distortion is expected for the system including significant lead-antisite defects. Directly probing such a small concentration of point defects is, however, difficult. In the absence of direct probes, one qualitative approach utilizes X-ray absorption near edge spectroscopy (XANES) at lead L-edge. Such studies revealed that the local coordination environment for lead ions in Pb₁₋ₓZrO₃ heterostructures has changed with respect to antiferroelectric PbZrO₃ and Pb₀.₅ZrO₃ (Supporting Information, Figure S6). Again, the small concentration of lead antisites prohibits quantification of the changes, but it does further suggest that some fraction of the lead ions in the system is occupying B-sites as antisite defects.

With this understanding of the nature of defects in the system, we proceed to examine their effect on the relative stability of the antiferroelectric and ferroelectric phases. To do this, we consider the relative energy stability of several polar structures with respect to the orthorhombic Pb₀.₅ZrO₃ ground state. The competing polar structures of PbZrO₃ are obtained by freezing in the unstable zone-center polar mode along different crystallographic directions, in combination with different oxygen octahedral patterns. In agreement with previous results, the first-principles calculations show that the lowest energy structures correspond to the orthorhombic Pb₀.₅ZrO₃ and rhombohedral R₃c structures (Supporting Information, Table S3). These results confirm the Pb₀.₅ZrO₃ structure as the lowest-energy antiferroelectric phase and suggest that the nearly energetically degenerate R₃c polar structure most likely corresponds to the field-induced ferroelectric phase observed here for PbZrO₃. We find a small volume difference between Pb₅₀.₅ZrO₃ and R₃c of +0.5%. The computed macroscopic polarization is found to be 59 μC/cm², in good agreement with the saturated polarization for pristine PbZrO₃.

Focusing on the Pb₀.₅ZrO₃ and R₃c structures, we next explore the energy evolution as a function of the lead-antisite content by computing the energy difference between the Pb₀.₅ZrO₃ and R₃c structures with \([\text{Pb}] : [\text{Zr}] = 1.00, 1.06, 1.13, \) and 1.20 cation ratios, assuming the appropriate fraction of lead-antisite defects (Figure 4b). Across this range of cation ratios, the calculations reveal that the energy difference between the Pb₀.₅ZrO₃ and R₃c structures remains small, approximately ~1 meV per formula unit, with increasing lead content (purple data, right axis, Figure 4b). While the exact energy difference between the Pb₀.₅ZrO₃ and R₃c structures depends on the choice of functional, we expect similar qualitative results for other functionals. For comparison, the energy difference between the Pb₀.₅ZrO₃ and R₃c structures is found to be ~4 meV per formula unit across the range of cations rations using the local density approximation (LDA). The latter suggests that the structures remain nearly energetically degenerate as the lead content increases and that the ferroelectric order arises due to the energetic cost of defect formation rather than a coherent structural phase transition. To understand this better, we calculated the defect formation energies across the same range of cation ratios for the Pb₀.₅ZrO₃ and R₃c structures. The calculations reveal that as the lead content is increased, the energy gain upon creation of such defects in the R₃c structure is always larger than that for the Pb₀.₅ZrO₃ structure. Thus, we propose that since the energy difference between the Pb₀.₅ZrO₃ and R₃c structures remains small across the entire cation ratio range studied herein, incorporation of lead excess in the form of lead-antisite defects tips the energy balance in favor of the R₃c structure as the cost of producing those defects is smaller in this structure, and this, in turn, gives rise to the ferroelectric order.

CONCLUSION

To summarize, we have studied the effects of cation nonstoichiometry on the evolution of the structure, electrical and dielectric properties, and (anti)ferroelectric order in Pb₁₋ₓZrO₃ thin films. High-quality PbZrO₃, Pb₀.₁ZrO₃, and Pb₀.₂ZrO₃ thin films showing negligible differences in the lattice parameters have been produced. Subsequent studies reveal that the PbZrO₃ and Pb₀.₁ZrO₃ heterostructures exhibit the expected antiferroelectric behavior and structure along with a relatively sharp phase transition at ~290 °C. Pb₀.₁ZrO₃ heterostructures, however, lead to a higher transition temperature (~360 °C). In turn, synchrotron-based RSMs of the Pb₀.₁ZrO₃ heterostructures reveal dramatically suppressed peak intensities for quarter-order Bragg peaks expected for the orthorhombic, antiferroelectric phase—confirming the likely rhombohedral and ferroelectric nature of the nonstoichiometric samples. DFT calculations suggest that excess lead in the system is incorporated in the form of lead antisites, that the cost to form these defects is lower in the rhombohedral phase, and that, since the energy difference between the orthorhombic (antiferroelectric) and rhombohedral (ferroelectric) structures remains small across the entire cation ratio range studied herein, incorporation of lead excess in the form of lead-antisite defects tips the energy balance in favor of the R₃c structure and results in the ferroelectric order. These results reveal the important role of cation stoichiometry in governing the competition between phases in complex materials such as the PbZrO₃ system and provides a potential pathway by which one can control the properties of such materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b02506.

Details concerning the growth of the Pb₁₋ₓZrO₃ thin films; additional structural and electrical characterization of those films; diffuse scattering pattern analysis; details of and additional data from density functional theory calculations; X-ray absorption near edge spectroscopy studies (PDF)
The authors declare no competing financial interest.

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Author Contributions

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Notes

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References

25. Boldyrevá, K.; Pintílie, L.; Lotnyk, A.; Misirlioglu, I. B.; Alexe, M.; Hesse, D. Thickness-Driven Antiferroelectric-to-Ferroelectric Phase Transition of Thin PbZr0.7Ti0.3O3 Layers, in Epitaxial PbZr0.7Ti0.3O3/BaZr0.53Ti0.47O3 Multilayers. Appl. Phys. Lett. 2007, 91 (12), 122915.


