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Phase Coexistence of Ferroelectric Vortices and Classical a_1/a_2 Domains in $\text{PbTiO}_3/\text{SrTiO}_3$ Superlattices.

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Ferroic order topological defects are of considerable interest as field controllable, low dimension regions exhibiting non-bulk properties. Recently, arrays of ferroelectric vortices were reported in ferroelectric / paraelectric superlattices of $\text{PbTiO}_3/\text{SrTiO}_3$, exhibiting large but significantly non-collinear polarization [1]. The reduced symmetry forecasts non-bulk properties and emergent phenomena such as recently reported axial polarization [2] resulting in emergent chirality [3]. Large field-coupling parameters often exist at phase boundaries where additional phases (or polarization configurations) are available both as end-states and as lower energy transition pathways. Phase-field simulations predict such a degeneracy with classical in-plane a-domain configurations from scaling of superlattice period for the vortex structure in the $[\text{PbTiO}_3(m_{\text{u.c.}})/\text{SrTiO}_3(n_{\text{u.c.}})]/\text{DyScO}_3$ system to approximately $m=n\sim 10$ u.c. [4]. Figure 1 depicts such a simulated phase boundary for an $m=n=16$ u.c. system, exhibiting an axial vortex component coupling to the adjoining a-domain. This phase coexistence and coupling has been experimentally observed, forming a striped superstructure capable of reversible electric-field switching and concomitant large changes piezoelectric and non-linear optical properties [2]. The present work is the microscopic companion to that macroscale study, revealing the nanoscale structure of the mixed phase vortex/a-domain system.

Ferroelectric vortices are stabilized by competition between electrostatic and elastic energies resulting from the depolarization fields at the insulating SrTiO_3 interfaces and epitaxial constraint to DyScO_3 , respectively. Under biaxial constraint, short period superlattice layers ($m=n\leq 10$) energetically favor the more homogeneous in-plane $[100]_{\text{psuedocubic}}$ polarizations (a-domains), where the energetic cost of modulating the $[001]_{\text{pc}}$ axis polarization grows too large. Thin TEM cross sections of the superlattice, such as in Fig. 2, relax into uniaxial constrained systems, stabilizing the vortex phase within periods as low as $m=n=6$ u.c. Figure 1 depicts the phase coexistence of vortices and a-domains within an $m=n=8$ u.c. superlattice using dark-field TEM. As in the macroscale case, the phases separate into roughly periodic blocks of a-domain and vortices, although the uniaxial strain produces a single $[010]_{\text{pc}}$ vortex axis and $[100]_{\text{pc}}$ a-domain axis. The domain boundaries form on $[101]_{\text{pc}}$ planes, reminiscent of classic a-domain / c-domain boundaries, requiring the offsetting of a clockwise-anticlockwise pair with each superlattice period while maintaining the inter-layer alignment of rotation direction.

Atomic resolution STEM reveals that the a-domain / vortex boundary is narrow, the transition accomplished by large $[001]$ offset of the final vortex “core,” merging the in-plane component of the vortex with the a-domain polarization. In a similar manner, the overall vortex regions exhibit net in-plane

polarization due to corrugated [001] vortex core offsets. The direction of this net polarization aligns with the in-plane direction of the adjoining a-domain in a similar manner as the axial component of biaxially constraint. [5]

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 [5] Authors acknowledge support by the U.S Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract number DE-AC05-00OR22725 (CTN), DE-AC02-05CH11231 (AKY,CTN), DE-SC0012375 (ARD), and FG02-07ER46417 (L-QC), the army research office under grant W911NF-14-1-0104 (ARD), NSF-MRSEC grant number DMR-1420620 (ZH) and NSF-MWN grant number DMR-1210588 (ZH), and NSF-MRSEC grant number DMR-1420620 (SLH). R.R. and L.W.M. acknowledge support from the Gordon and Betty Moore Foundation's EPIQS Initiative, under grant GBMF5307.

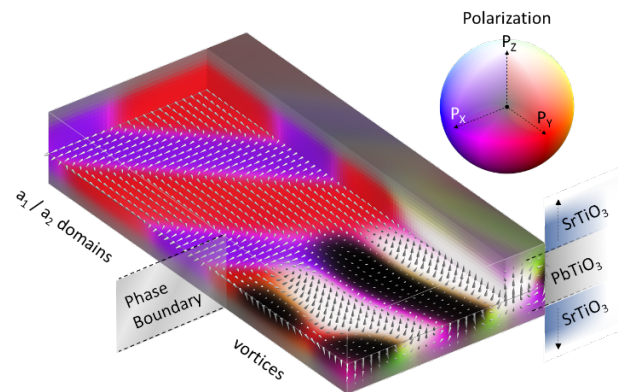


Figure 1. Colorized phase field model of the a-domain / vortex boundary for one of the PbTiO₃ layers within a PbTiO₃(16u.c.)/SrTiO₃(16u.c.) superlattice. A net axial polarization is predicted for the vortex region matching the sign of the P_Y component of the neighboring a₁/a₂ domains.

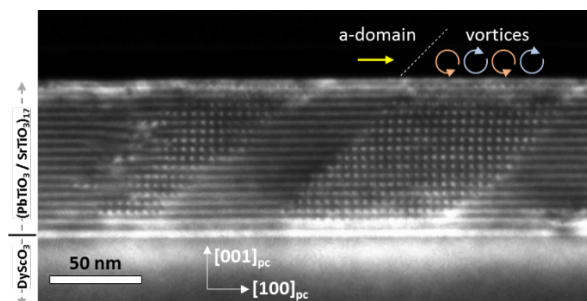


Figure 2. Dark field TEM image showing ferroelectric vortices and a-domain coexistence in a PbTiO₃ (8u.c.) / SrTiO₃ (8u.c.) superlattice. Image formed from the $[00\bar{4}]_{pc}$ reflection.