Opportunities in Far-from-Equilibrium Complex Oxide Electronic Materials

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Recent developments in x-ray optics, scattering techniques, and epitaxial growth now make it experimentally possible to probe the properties of complex oxide insulators in regimes which have previously been inaccessible. New studies promise to show how ferroelectricity, electrostriction, crystallographic symmetry, magnetism, and electrical polarization domains evolve in high electric fields and at short times. Opportunities arise from the possibility to understand and exploit the fundamental relationships between strain, magnetic moments, structure, and electrical polarization in these materials. Experiments in this field are guided by a rich set of theoretical predictions under conditions that accurately match experimental conditions. These predictions are possible because a series of advances in theoretical techniques have made it possible to predict the properties of complex oxide materials under non-equilibrium conditions using density functional theory.[1,2]

In the long term, understanding the non-equilibrium properties of complex oxides in high electric fields will lead to the prospect of dynamically tuning the mechanical, optical, and magnetic properties of materials. To do this, requires fundamental effects that – unlike changes in chemical doping – can be reversibly applied under ambient conditions. Such continuous and reversible control of the properties of complex oxides has been demonstrated to date in only few instances, but with severe limitations on the materials involved and on potential applications. The large carrier concentrations induced by a gate electric field in a field-effect transistor, for example, can produce electronic or structural phase transitions - but this approach can be applied only to materials integrated into field-effect transistors.[3] Alternatively, the biaxial strain in epitaxial thin films grown on a piezoelectric substrate can be continuously varied by distorting the substrate, but the magnitude of the variation in strain that can be induced by the bulk substrate is typically limited to on the order of 0.1-1%. Approaches allowing electrical control of properties have thus, to date, achieved far less success than chemical doping – and none of these can be readily generalized. High electric fields and other transient conditions we describe here represent a new complementary reversible method to modify the properties of complex oxides. Three areas are of particular interest in exploiting this emerging capability:

1) High Electric Fields: The time resolution available in x-ray diffraction and scattering experiments makes it possible to apply electric fields to complex oxide ferroelectrics (e.g. $Pb(Zr,Ti)O_3$, as in Fig. 1) that are far in excess of the well-understood regime of fields less than the steady-state breakdown field.[4] One example of the phenomena that are typically negligible at modest fields but which can potentially become relevant at higher fields is electrostriction, a universal property of dielectric materials in which the lattice is elastically distorted in applied electric fields. The origin of this effect lies in the interaction of the induced dipole moment with the applied electric field. Electrostriction leads to a strain ε proportional to the square of the total polarization P. At low fields in dielectrics, where P is proportional to the applied field E, the strain is proportional to E^2. One fundamentally interesting issue is that at higher fields, it is suspected that the polarization induced by the applied field saturates and that the strain is no longer a quadratic function of E. Even with modest polarizations, the strain developed by

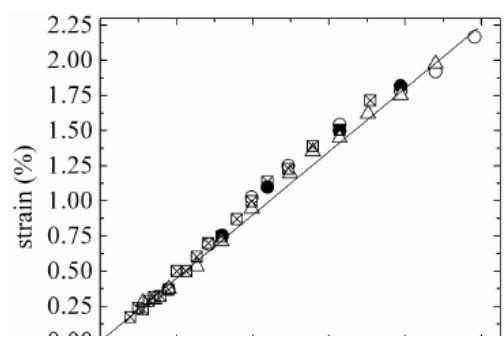

Figure 1 Piezoelectric strain measured at applied electric fields from 0 to 491 MV/m for four ferroelectric capacitors (shown with different symbols). The solid line is the strain predicted by a constant piezoelectric coefficient of 45 pm/V, after ref. 4.

electrostriction in high fields will provide an additional mechanism for producing high strains in dielectric and magnetoelectric materials – a set of phenomena so far which has been limited to piezoelectric materials. One exciting consequence would be the extension of the strain-mediated magnetoelectric effects currently observed in ferroelectric multiferroics to a far wider range of materials.

2) Field-Driven Symmetry Transformations: Large electric fields or large elastic distortions can be sufficient to change the free energy landscape of complex oxides sufficiently that a ground state with a different symmetry becomes stable. For example, rhombohedral to tetragonal phase transitions in bulk materials can be produced by applied fields, and similar transition can be driven in thin films by epitaxial strain.[5] We have found an initial non-linearity of the piezoelectricity ferroelectric dielectric superlattices, suggesting that a similar phenomenon may occur in the symmetry of the dielectric $CaTiO_3$ component.[6] Advances in x-ray scattering will make it possible to detect these transient symmetry changes during and make it possible to design materials in which these transitions produce useful functionalities.

3) Novel Nanodomain Geometries: The ground state domain structure of ferroelectric nanoparticles, films with nm-scale thicknesses, and nm-period superlattices can have complex geometries, including stripes and vortices, that are completely different from bulk domain patterns. X-ray diffraction provides a precise way to study these domains and their dynamics via nanobeam imaging (as in Fig. 2)[7] and via diffuse scattering or coherent scattering. The timescales involved in the dynamics of these domain patterns are short, and are an excellent match for the time resolution of synchrotron radiation-based time-resolved scattering techniques. One important specific example is that striped lateral domain patterns in superlattices are predicted to have unusual domain dynamics. For example, Stephanovich *et al.* predict that domain walls propagate with different velocities in the two different layers of the superlattice such that the polarization in the dielectric layers (e.g. $SrTiO_3$ or $CaTiO_3$) switches at far lower fields than the polarization in the ferroelectric layers (e.g. $BaTiO_3$ or $PbTiO_3$) – completely different than what is observed in the bulk.[8] These predictions have yet to be tested because existing probes cannot separately probe the dynamics of individual layers, something can be done in a straightforward way with x-ray scattering.

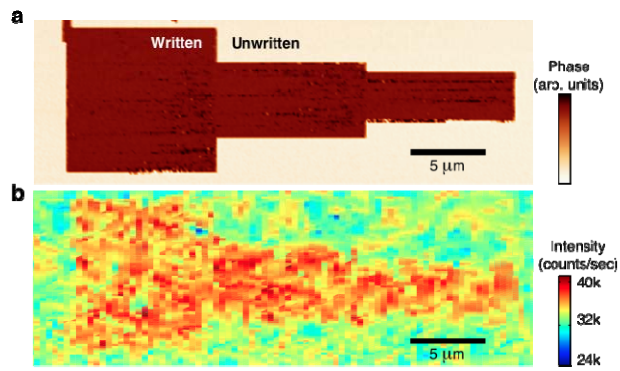

Figure 2 Domains in ferroelectric thin film written by piezoelectric force microscopy (PFM) and imaged using (a) PFM and (b) x-ray nanodiffraction, after ref 7..

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