Exotic Polar States
Rewriting What is Possible in Ferroelectrics

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International School of Oxide Electronics | Cargèse, France | July 1, 2019

Selected References

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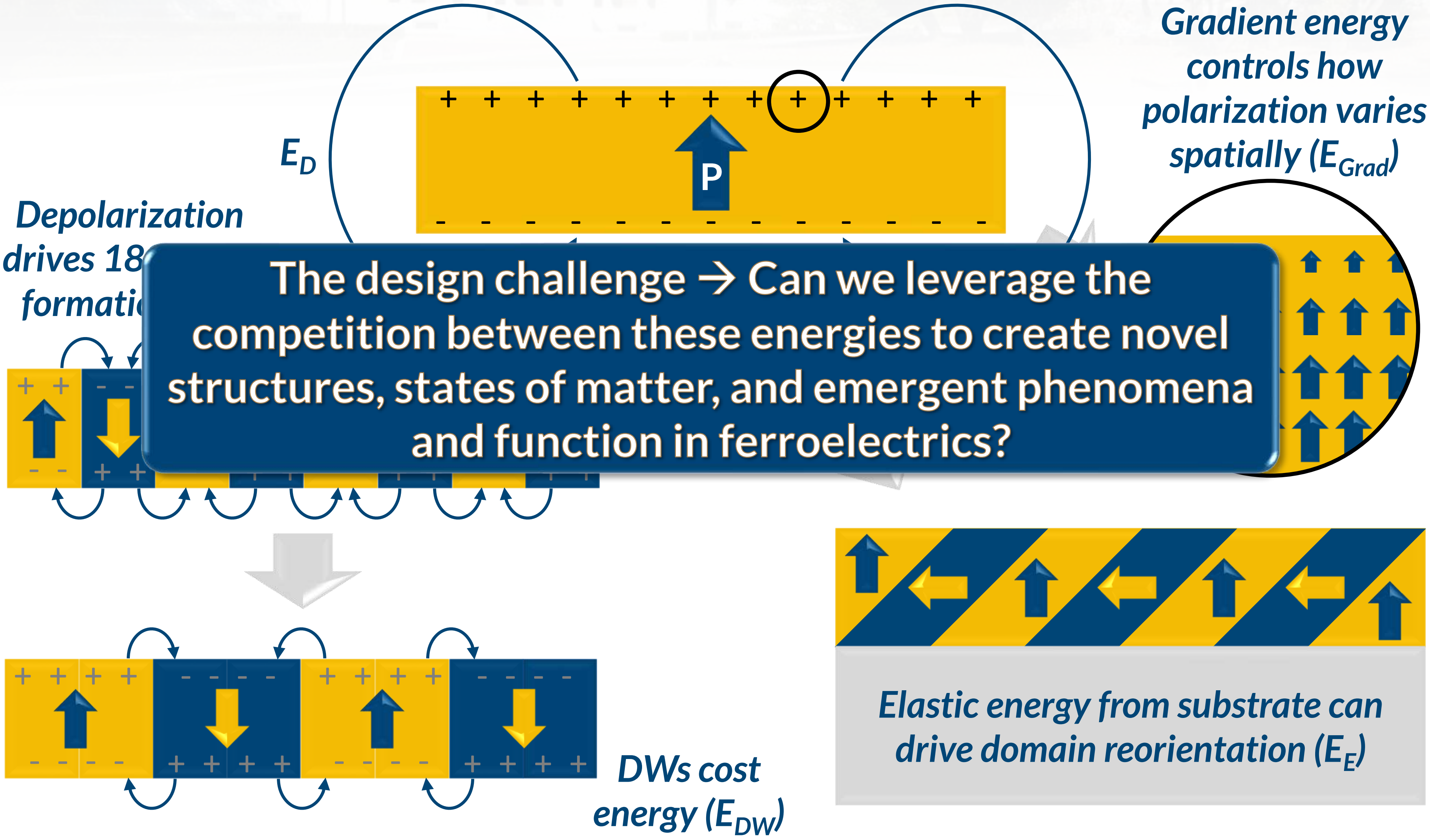
Disclaimer: This topic is a rich one! There is not time cover all of it in detail, some great work is thus not included here. No offense is meant, just a result of the time limits! For those new to the field, know there is more beyond these slides to explore…

Energies in Ferroelectrics

$$E_{Total} = E_P + E_D + E_{DW} + E_{Grad} + E_E$$



Gradient energy controls how polarization varies spatially (E_{Grad})

Depolarization drives 18

formati

The design challenge → Can we leverage the competition between these energies to create novel structures, states of matter, and emergent phenomena and function in ferroelectrics?

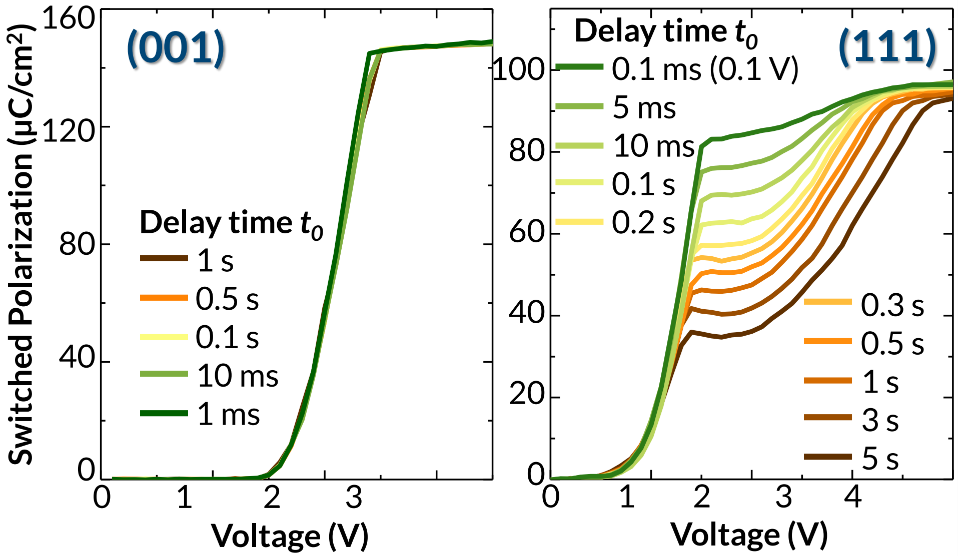
DWs cost energy (E_{DW})

Elastic energy from substrate can drive domain reorientation (E_E)

Emergent Ferroelectric Phenomena

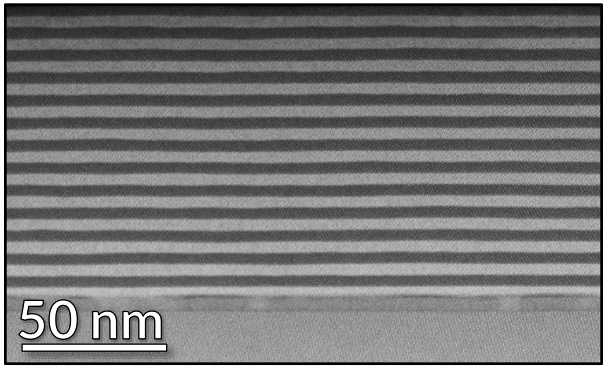
How can "next-generation" growth and epitaxy enable emergent *phenomena* and *function*?

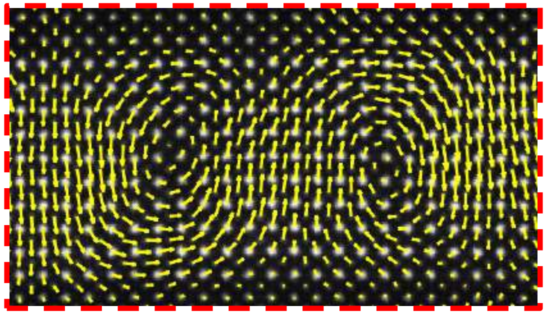
Film Orientation and Elastic Frustration



Beyond Binary & Neuromophic Function → Multi-state Switching and Stable Intermediate States

Superlattices and Artificial Heterostructures





Novel Polarization Profiles & Function → Vortices, Phase Competition, Chirality, Skyrmions

Neuromorphic Function

Arithmetic Calculation

Logic Calculation

Perfect Memory

Digital Computation vs. the Brain

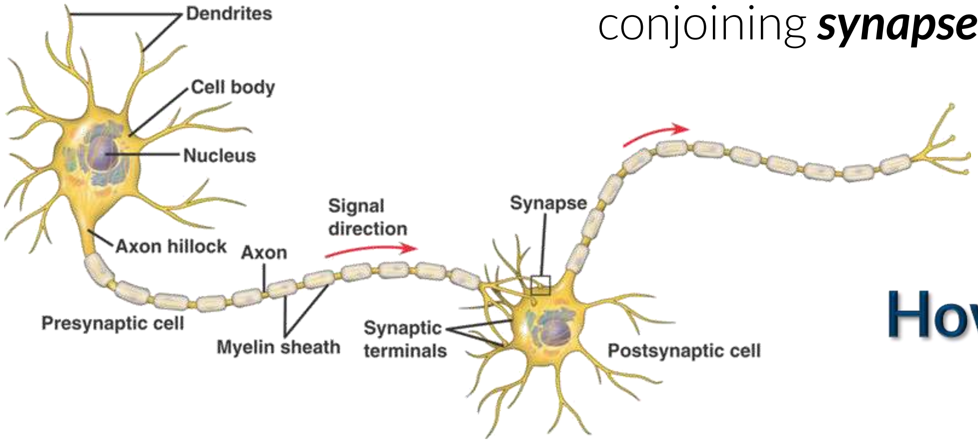
- Modern computers → "0s" and "1s" to complete logic operations, store data, etc.
- Brain → does not use binary logic/address-able memory, or perform binary arithmetic
- Information → represented as statistical approximations/estimations, not exact values
- Brain is non-deterministic, cannot replay instruction sequences error-free

Generalization

Fault Tolerance

Pattern Recognition

Neuron → electrochemical pulses transmitted from adjacent neurons to alter the weight of conjoining ***synapse***



Requirements for adaptive electronic components:
Multistate behavior • Sensitivity • Threshold behavior • Fault tolerance • Nonvolatility • Insensitivity to noise • Low energy • Compatibility

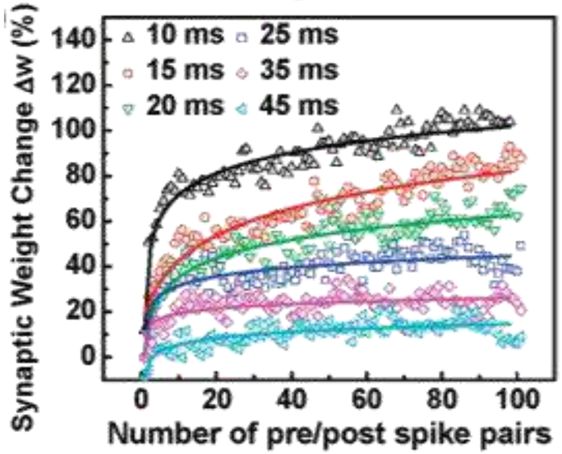
How do we create these functions in a single material?

Emulating Neuromorphic Function

Neuromorphic Engineering: Develop solid-state materials that can mimic neuron function to enable brain-like computing

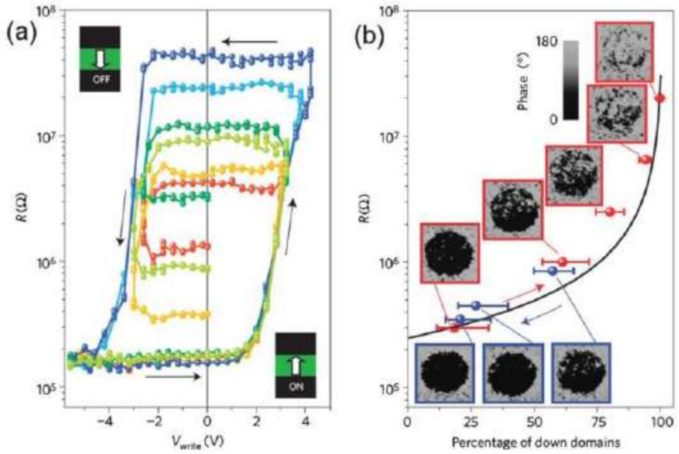
- **State-of-the-art**: Adapt natural internal states including **resistance**, ***polarization***, ***magnetization***,…

Phase-change Materials



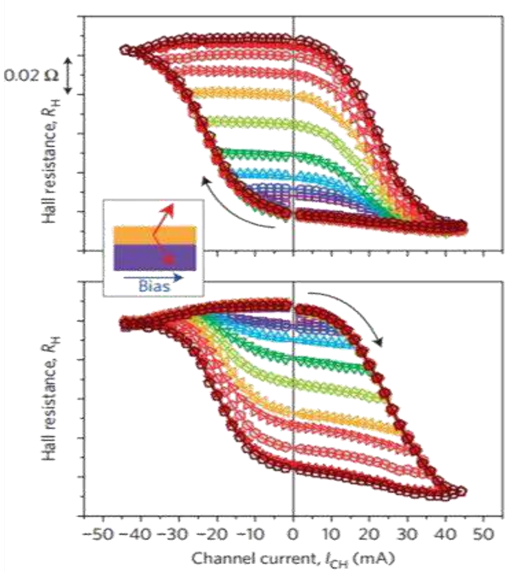
Kuzum *et al. Nano Lett.* **12**, 2179 (2012)

Ferroelectricity



Chanthbouala *et al. Nature Mater.* **11**, 860 (2012)

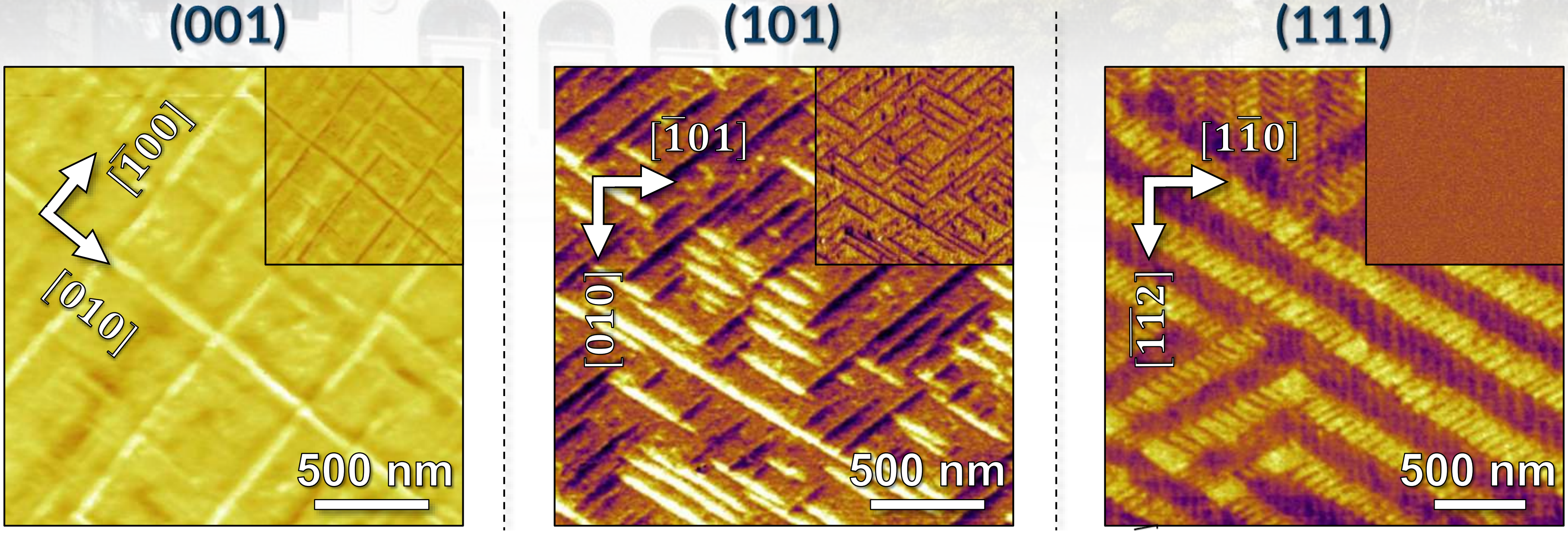
Ferromagnetism



Fukami *et al. Nature Mater.* **15**, 535 (2016)

- Focus on ***ferroelectrics***…
  - **Challenges**: Dominated by stochastic processes → how do we achieve deterministically controllable multi-states in ferroelectrics?
  - **Goal**: Evolve beyond stochasticity and explore potential for tunable, multi-state polarization via control of switching kinetics and elastic frustration

Orientation & Domains: $PbZr_{0.2}Ti_{0.8}O_3$



- Orientation provides a knob by which we can control the domain structure of materials
- All samples possess 90° domain walls → controlled structures
- Advantage of thin films → direct observation and quantification of domain structure features

Volume fraction of minority domains

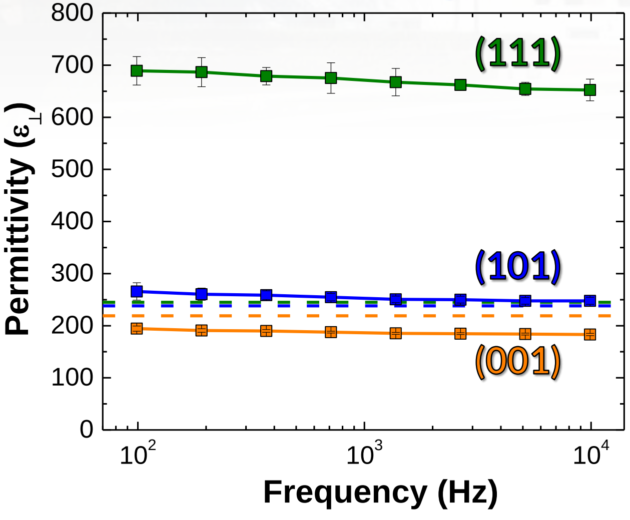
Line density of domain walls

Orientation	λ (µm^{-1})	ϕ (%)
(001)	8.91	15.3
(101)	16.3	19.9
(111)	48.9	33.3

Xu *et al.*, *Nature Commun.* 5, 3120 (2014)

Exotic Low-/High-Field Effects

Stationary (Frozen) Permittivity

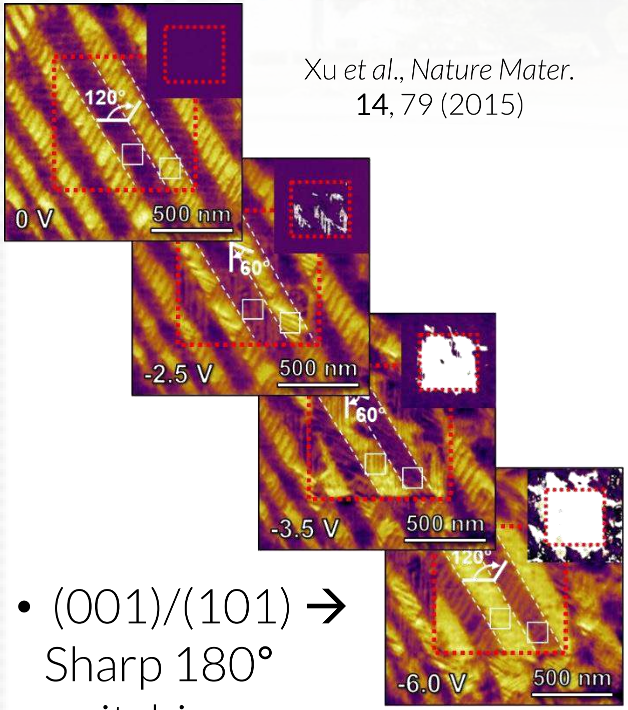


Xu *et al.*, *Nature Commun.* 5, 3120 (2014)

- Response of the volume of the ferroelectric material within the finite width of the domain walls (non-motional)

ε_{dw} ≈ 1,500-19,000 (for 1-10 nm) → 6-78x ε_b

Multi-Step Polarization Reversal

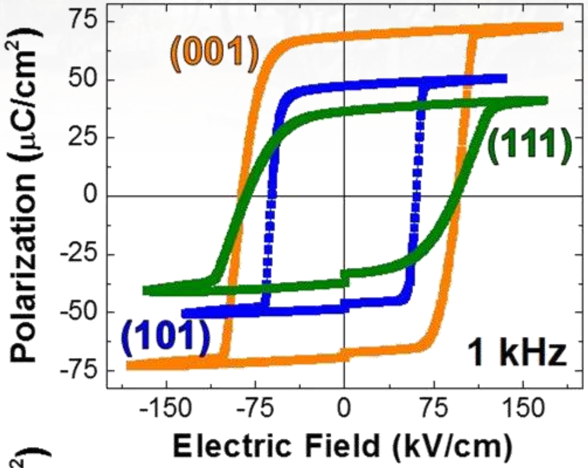


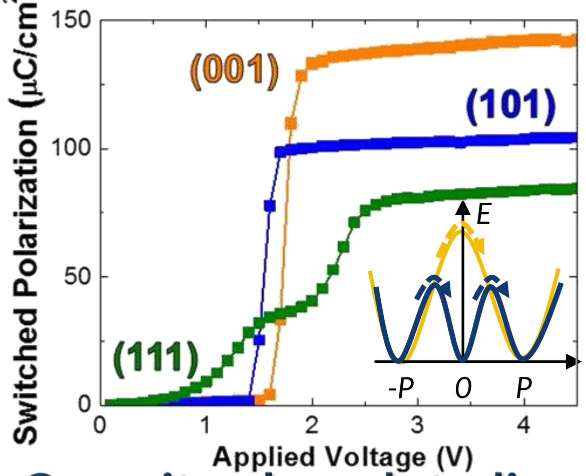
Xu *et al.*, *Nature Mater.* 14, 79 (2015)

- (001)/(101) → Sharp 180° switching process
- (111) → Broad switching, 90° switching events that match models

Observation of multi-step 90° switching process → intermediate states?

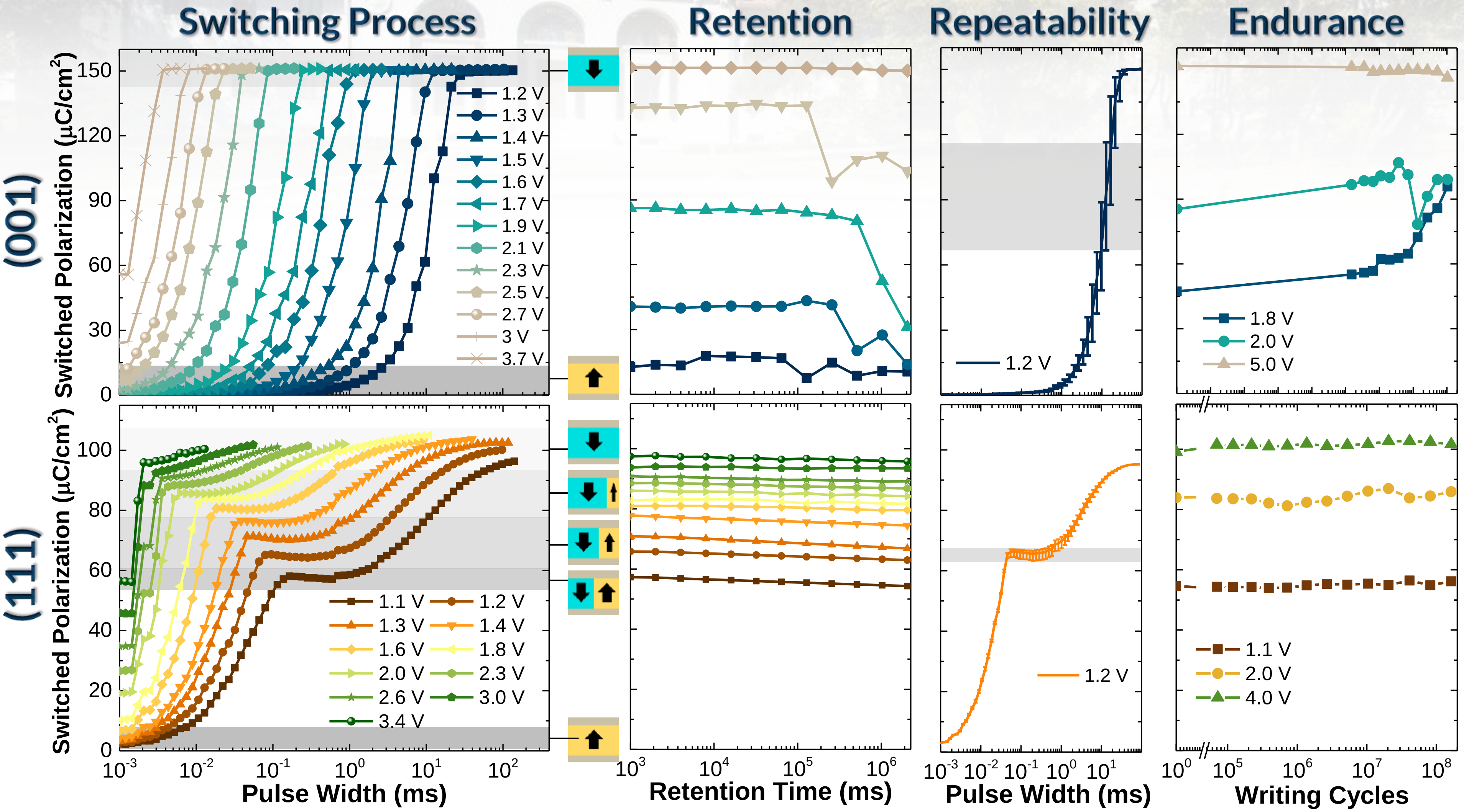
Indications of Intermediate States





Capacitor-based studies suggest potential for intermediate states…

Probing the Switching Behavior



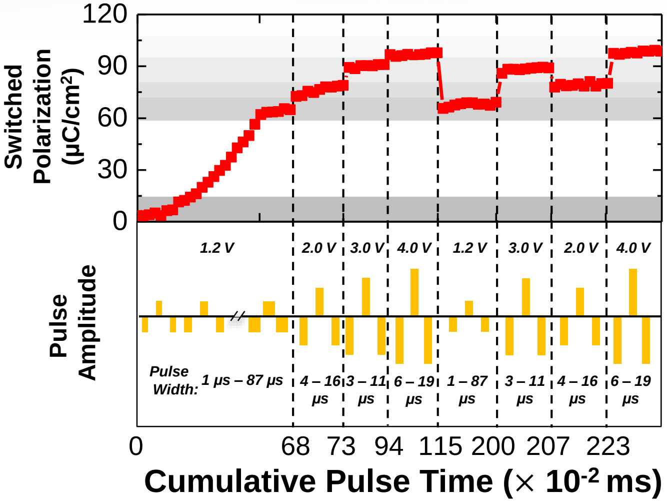
- (001) → Poor state selection, stability, repeatability, endurance → States unstable
- (111) → Good deterministic state selection, stability (<10% *P* loss over 8 hr.), repeatability (< 5% variation), endurance → Robust, defined states which are stable

Xu *et al.* *Nature Commun.* 10, 1282 (2019)

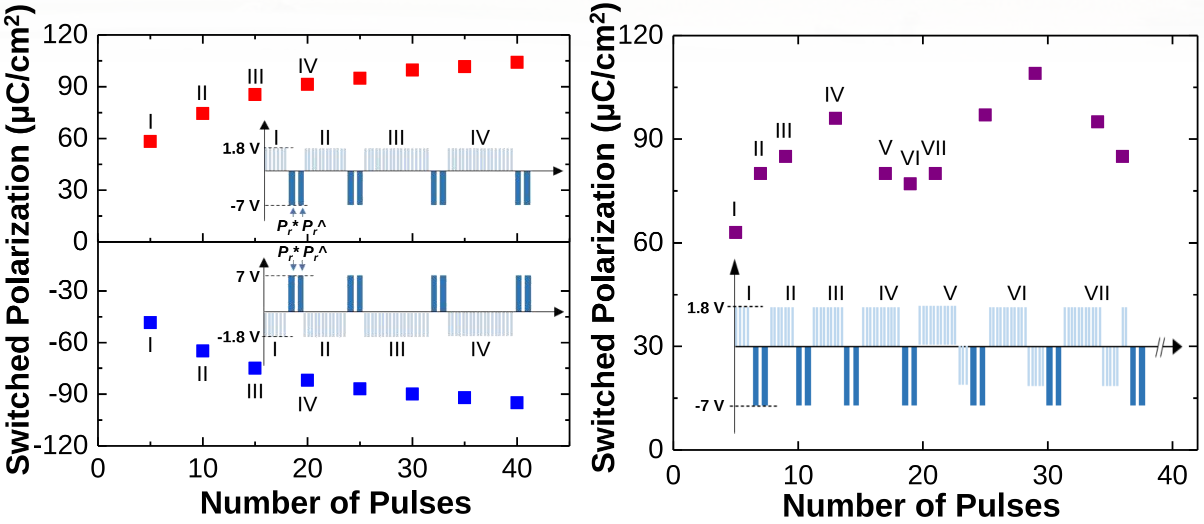
Exploring the (111)-Oriented Films

- **(111) films show: Deterministic access to precise & distinguishable states, retention, repeatability, endurance to repeated modification…**

Arbitrary State Access



Spike-time-dependent Plasticity



In (111)-oriented films it is possible to achieve…

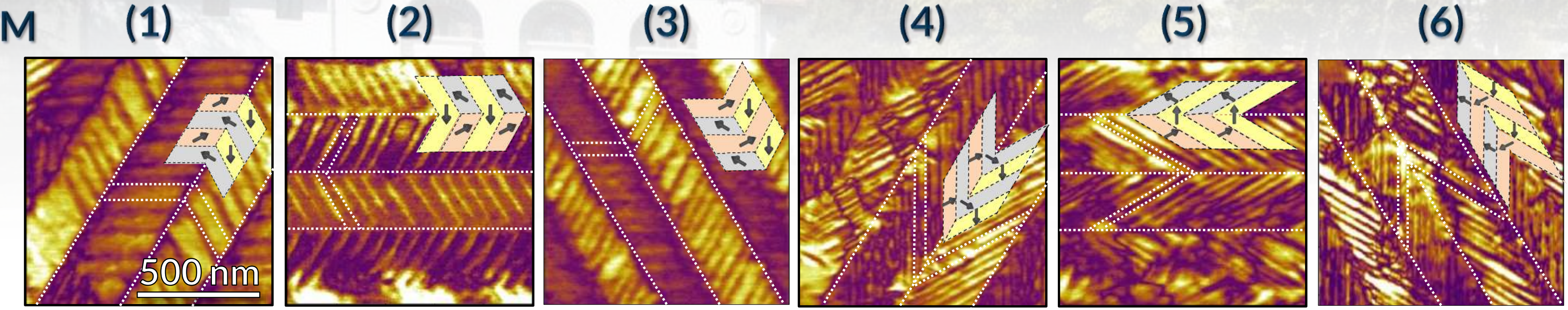
- Effects difficult to accomplish in classical bi-stable switching
- Deterministic, tunable multi-state polarizations and critical functions required for potential neuromorphic applications

The question is: What enables this type of response?

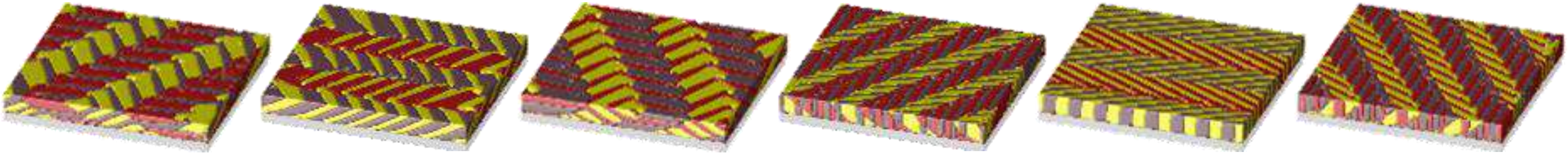
Xu *et al*. *Nature Commun.* 10, 1282 (2019)

Manifold of Degenerate Structures

PFM

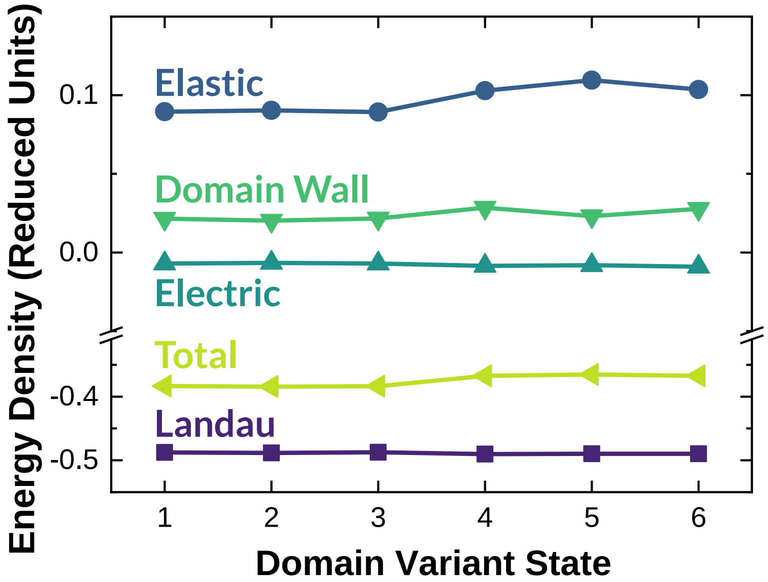


Phase-field simulations



J. Wang, Z. Hong, L.-Q. Chen, Penn State

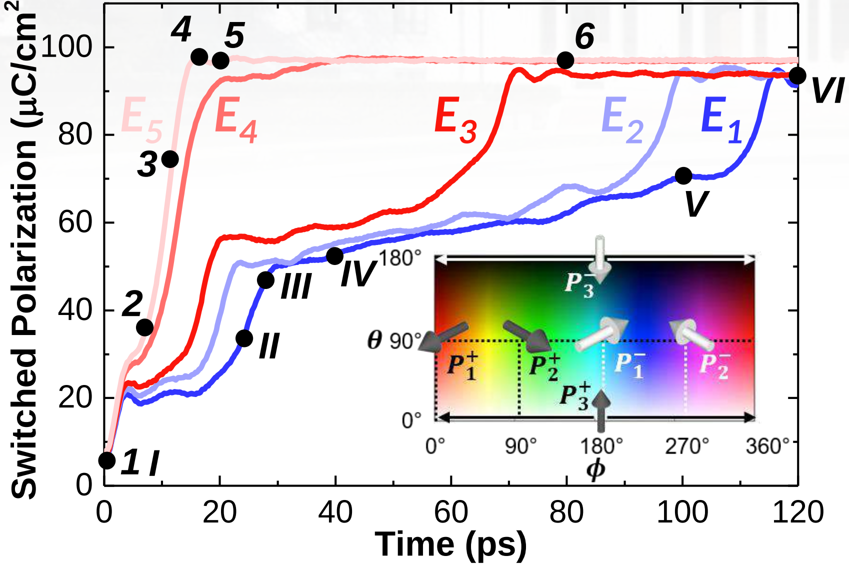
- (111) PZT → *P* can point in 6 directions
- PFM → Poling results in multiple unique, but related ordered domain structures
- Phase-field modeling → Confirms creation of varied domain structures
- Energies → All structures have nearly identical energies → Manifold degeneracy of available domain structures



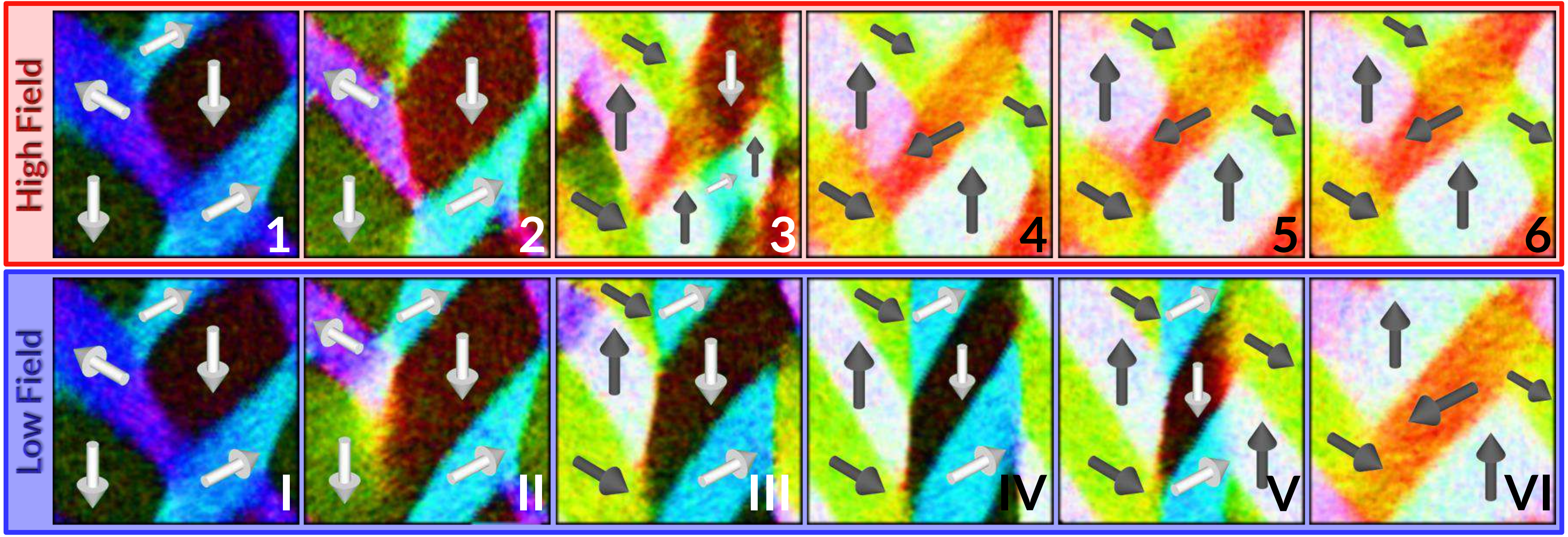
Xu *et al.* *Nature Commun.* 10, 1282 (2019)

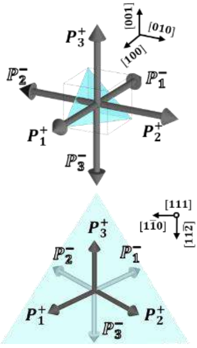
Understanding the Switching Process

S. Liu (ARL) & A. Rappe (UPenn), MD Simulations



- **High-field/Bi-polar switching** → Coordinated 90° switching events; domains unchanged
- **Low-field/multi-state switching** → Two 90° switching events, intermed. state w/ new configuration (half ↑/↓), fraction of the ↓-poled band is reduced with further *E*
- **Take home → 90° switching favored, two kinetically-distinct pathways, competition of which gives multi-states**

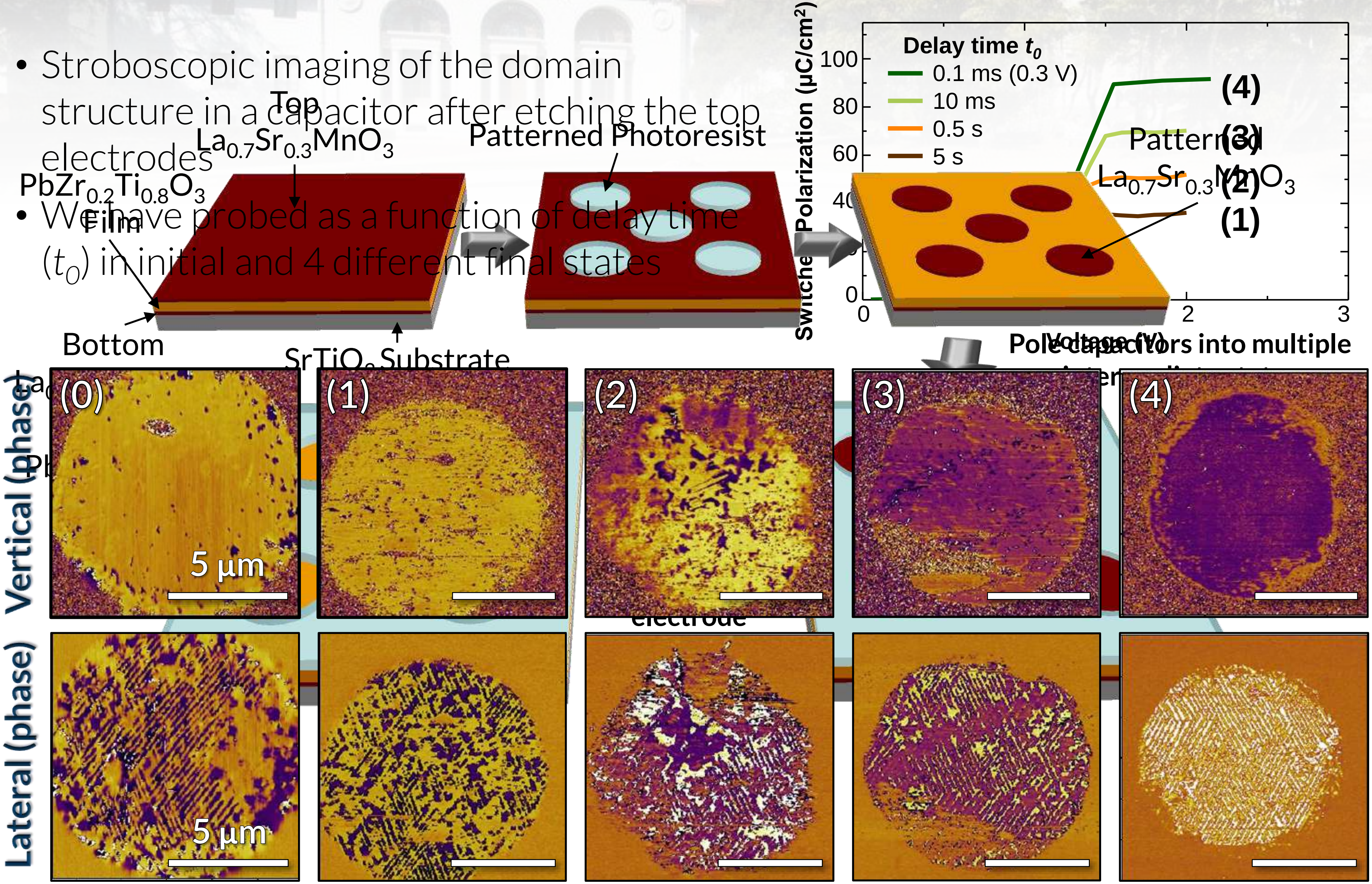




Xu *et al*. *Nature Commun*. **10**, 1282 (2019)

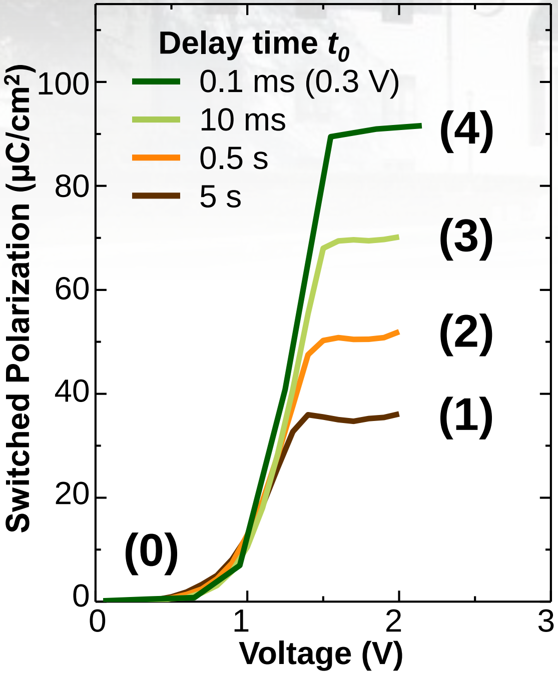
Mechanism for Intermediate States

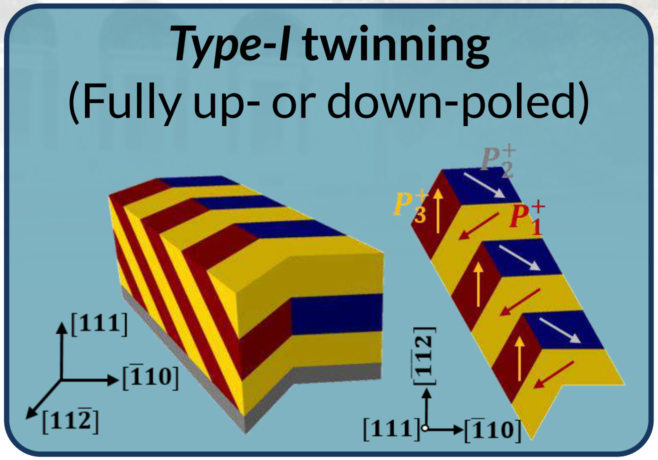
- Stroboscopic imaging of the domain structure in a capacitor after etching the top electrodes
- We have probed as a function of delay time (t_0) in initial and 4 different final states



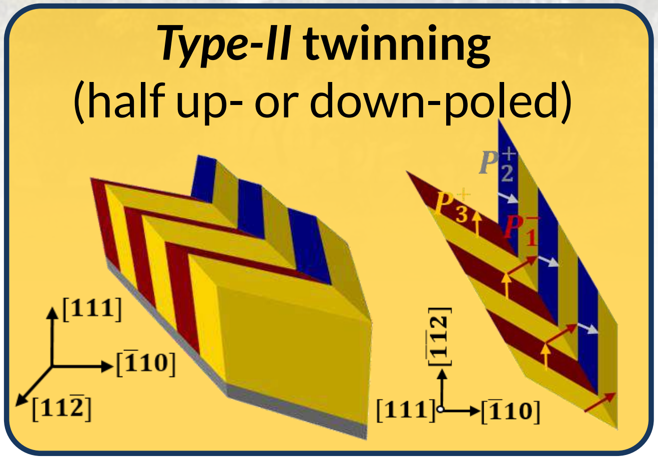
Xu *et al*. *Nature Commun.* 10, 1282 (2019)

Mechanism for Intermediate States





***Type-I* twinning**
(Fully up- or down-poled)



***Type-II* twinning**
(half up- or down-poled)

Xu *et al.*, *Nature Mater.* **14**, 79 (2015)

- Prior work → two domain structure configurations are possible in this system
- These configurations mediate multi-state function

Kinetically and elastically "frustrated" domain switching and configurations in (111)-oriented films enables…

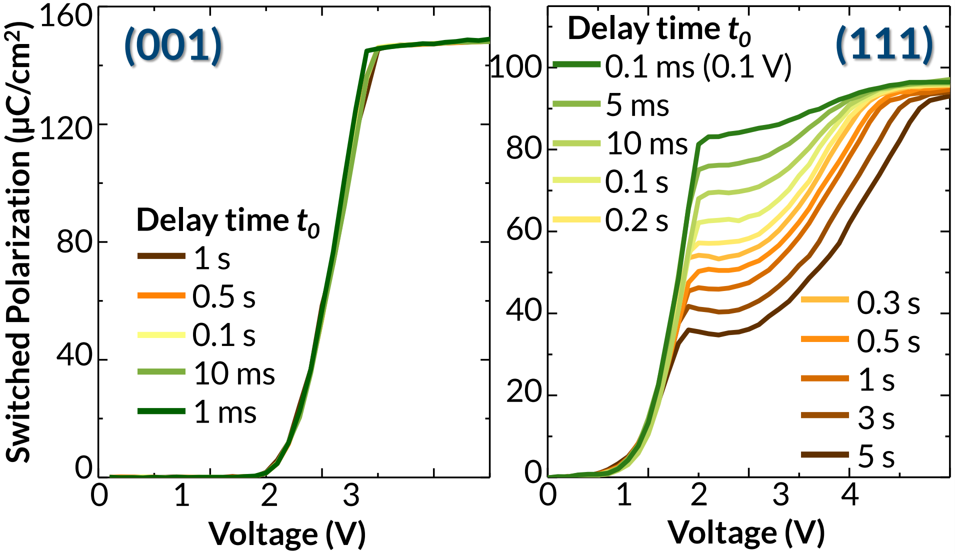
- **Beyond binary function → Presence of 3 stable states, produces a huge number of configurational states**
- **Beyond stochasticity → Elastic constraints provide for "quantized" switching and stability (no back-switching)**
- **Function commensurate with needs of neuromorphic effects**

Xu *et al*. *Nature Commun*. **10**, 1282 (2019)

Emergent Ferroelectric Phenomena

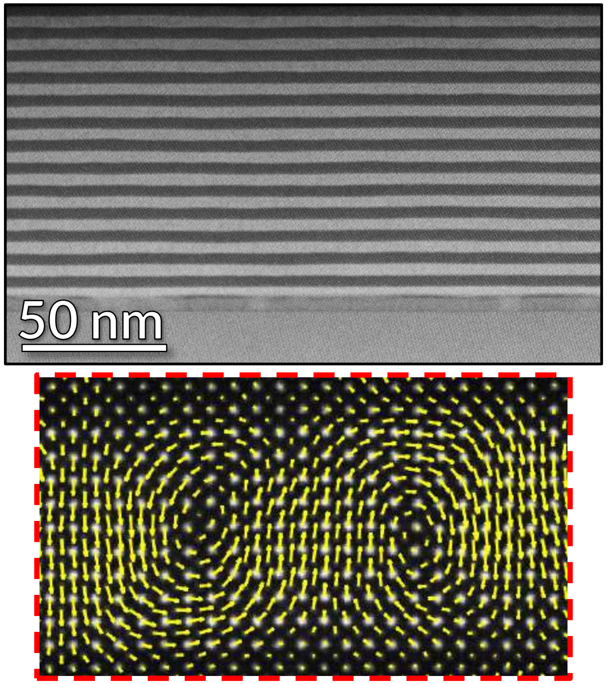
How can "next-generation" growth and epitaxy enable emergent *phenomena* and *function*?

Film Orientation and Elastic Frustration



Beyond Binary & Neuromophic Function → Multi-state Switching and Stable Intermediate States

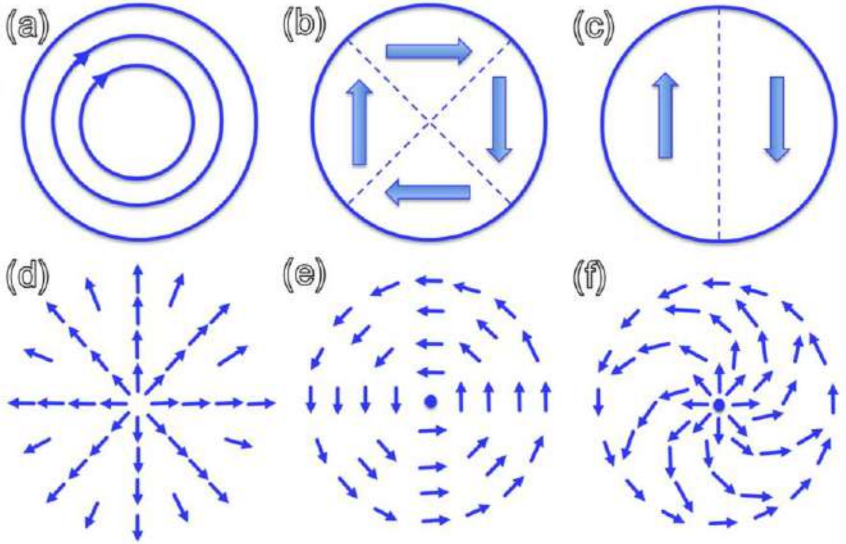
Superlattices and Artificial Heterostructures



Novel Polarization Profiles & Function → Vortices, Phase Competition, Chirality, Skyrmions

Lessons from Magnetism

- Recall…Ferroic materials have a tendency to form domains as a means to reduce the depolarization/demagnetization fields that occur at surfaces
- Uniform domains with aligned *P*/*M* are most common → Interest in potential for more exotic, smoothly varying dipole topologies to form in both FE and FM
- Magnets…
  - Vortex-like states are well documented
  - 1940s → Depending on the *exchange interaction* and *anisotropy* energies, different patterns are possible
  - **Ring-** or **vortex-like** → *Exchange interactions* dominate over *anisotropy* (a)
  - **Flux-closure** → *Anisotropy* energy dominates (b, c)
  - These are common in "small" magnets
  - Experimental observations of flux-closure domains, vortices abound
  - Complex topological patterns (d, e, f) can develop → Depends on relative strength of exchange/anisotropy/demagnetization energies



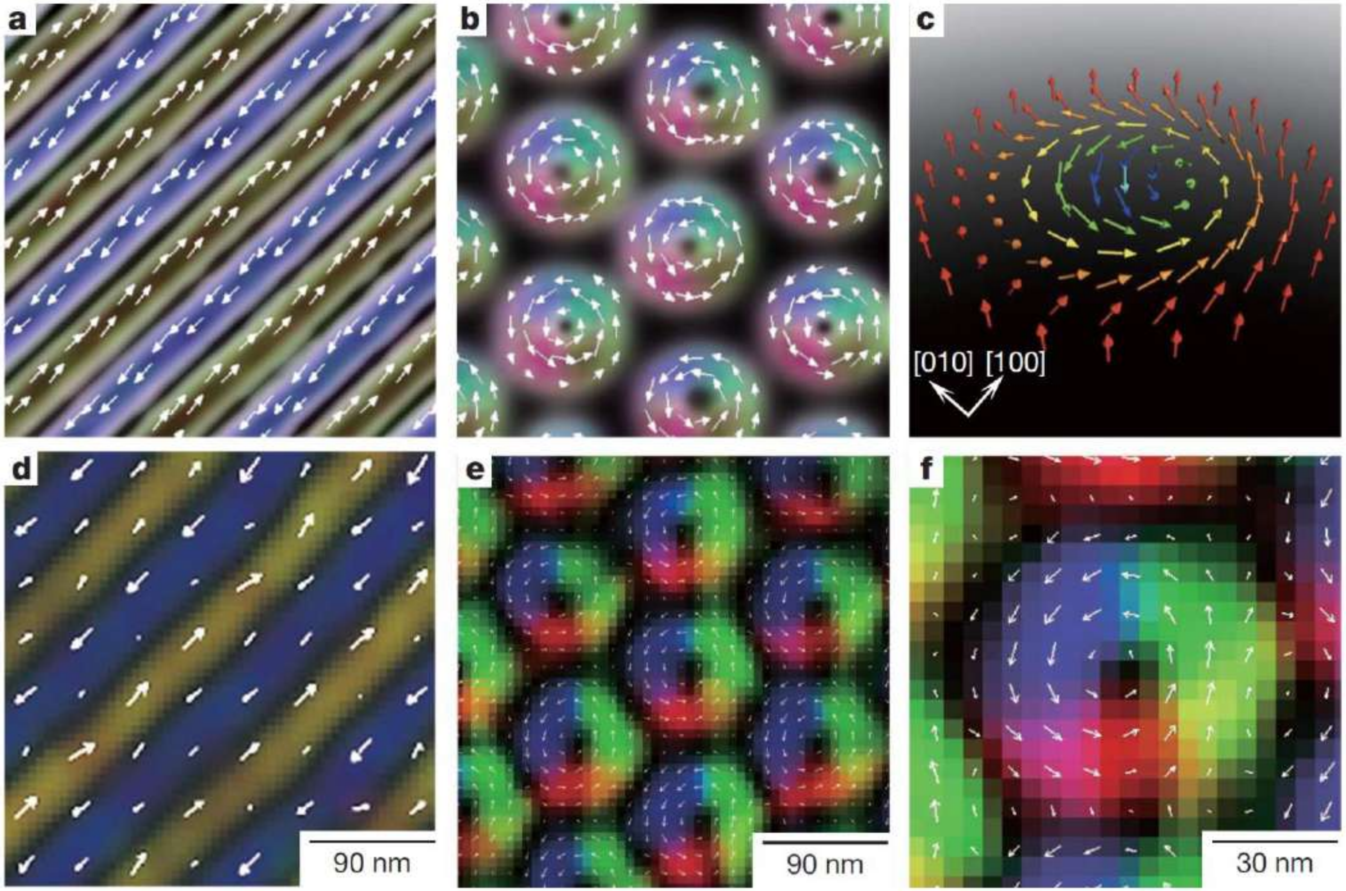
Kittel, *Rev Mod. Phys.* **21**, 541 (1949); Das *et al.*, *APL Mater.* **6**, 100901 (2018)

Gomez *et al.*, *J. Appl. Phys.* **85**, 6163 (1999); Pulwey *et al.*, *J. Appl. Phys.* **91**, 7995 (2002); Jubert *et al.*, *Europhys. Lett.* **63**, 132 (2003); Hertel *et al.*, *Phys. Rev. B* **72**, 214409 (2005); Shinjo *et al.*, *Science* **289**, 930 (2000); Park *et al.*, *Phys. Rev. B* **67**, 020403 (2003); Nagai *et al.*, *Phys. Rev. B* **78**, 180414 (2008)

Mermin, *Rev. Mod. Phys.* **51**, 591 (1979)
Gregg, *Ferroelectrics* **433**, 74 (2012)

Lessons from Magnetism

- Skyrmions → Topologically stable field configurations with particle-like properties
  - In some cases, like spins point in all directions wrapping a sphere
- Special type of 2D magnetic vortex structures
- Skyrmions happen at the border between paramagnetism and long-range ordered phase (things in competition)



“Zoo” of Magnetic Order

- Numerous topological spin textures in helical magnet $Fe_{0.5}Co_{0.5}Si$

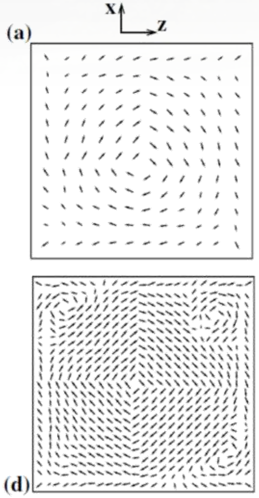
Monte Carlo…
(a) = Helical
(b) = Skyrmion
(c) = 3D pic of Skyrmion

Experimental
(d) = Helical
(e) = Skyrmion
(f) = Skyrmion

Muhlbauer *et al.*, *Science* **323**, 915 (2009); Yu *et al.*, *Nature* **465**, 901 (2010)

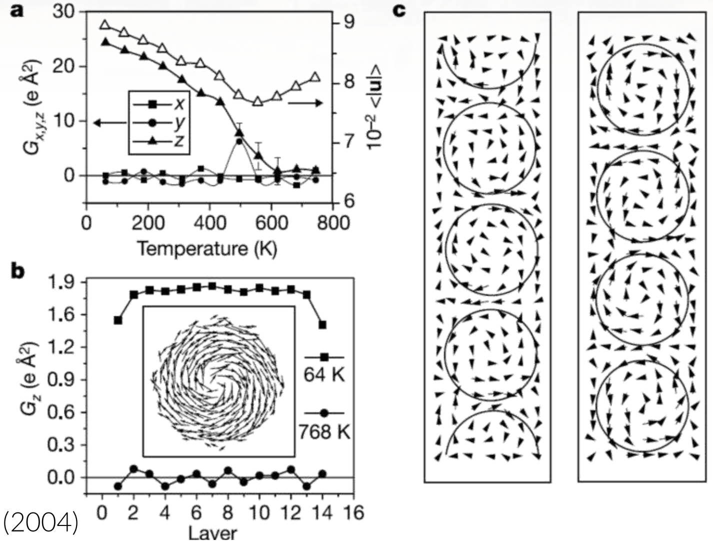
How about FerroELECTRIC Materials?

- Motivated by the observation of exotic magnetic structures, the early 2000s saw the emergence of suggestions of similar effects in ferroelectrics…
- Early work focused on “confined” structures → Nanostructures

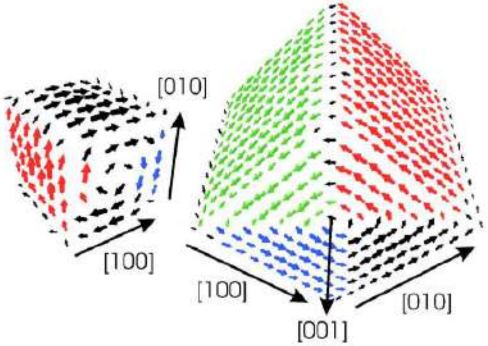


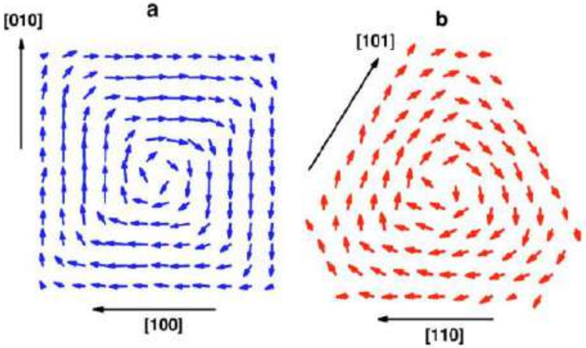
Ab initio studies…

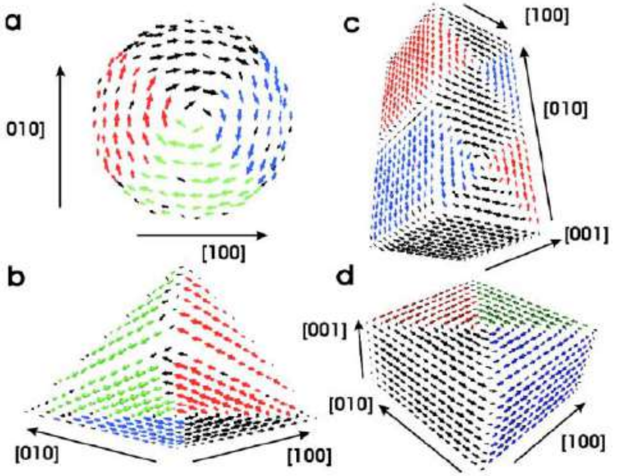
- $BaTiO_3$ “quantum dots” and “wires” → ferroelectric with surrounding non-ferroelectric environment
- $PbZr_{1-x}Ti_xO_3$ nanoscale disks and rods → smoothly rotating structures, “toroidal” moment forming



Fu, Bellaiche, *Phys. Rev. Lett.* **91**, 257601 (2003); Naumov, Bellaiche, Fu., *Nature* **432**, 737 (2004)







A “zoo” for features were predicted → Evolution w/ size, shape, material, and temperature; interactions possible

Prosandeev, Bellaiche, *Phys Rev. B* **75**, 094102 (2007)