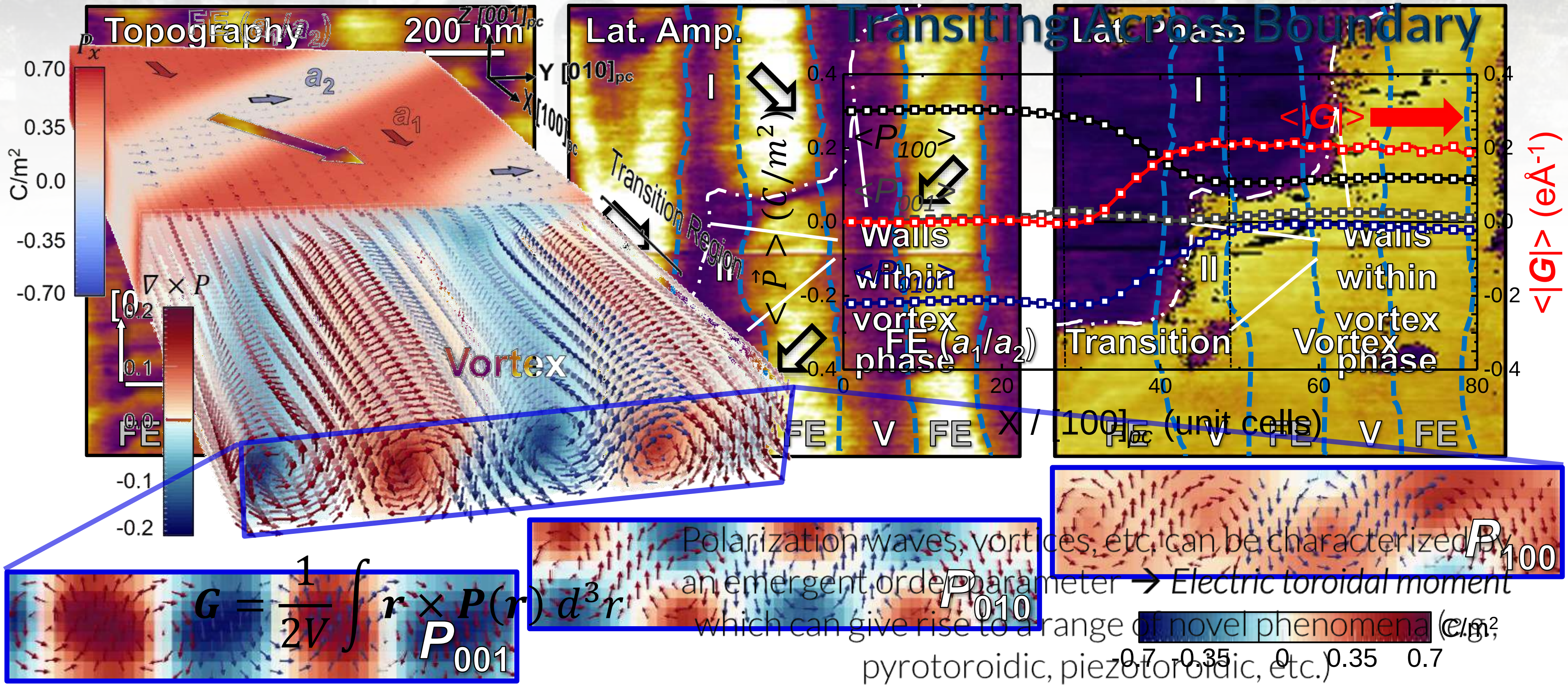
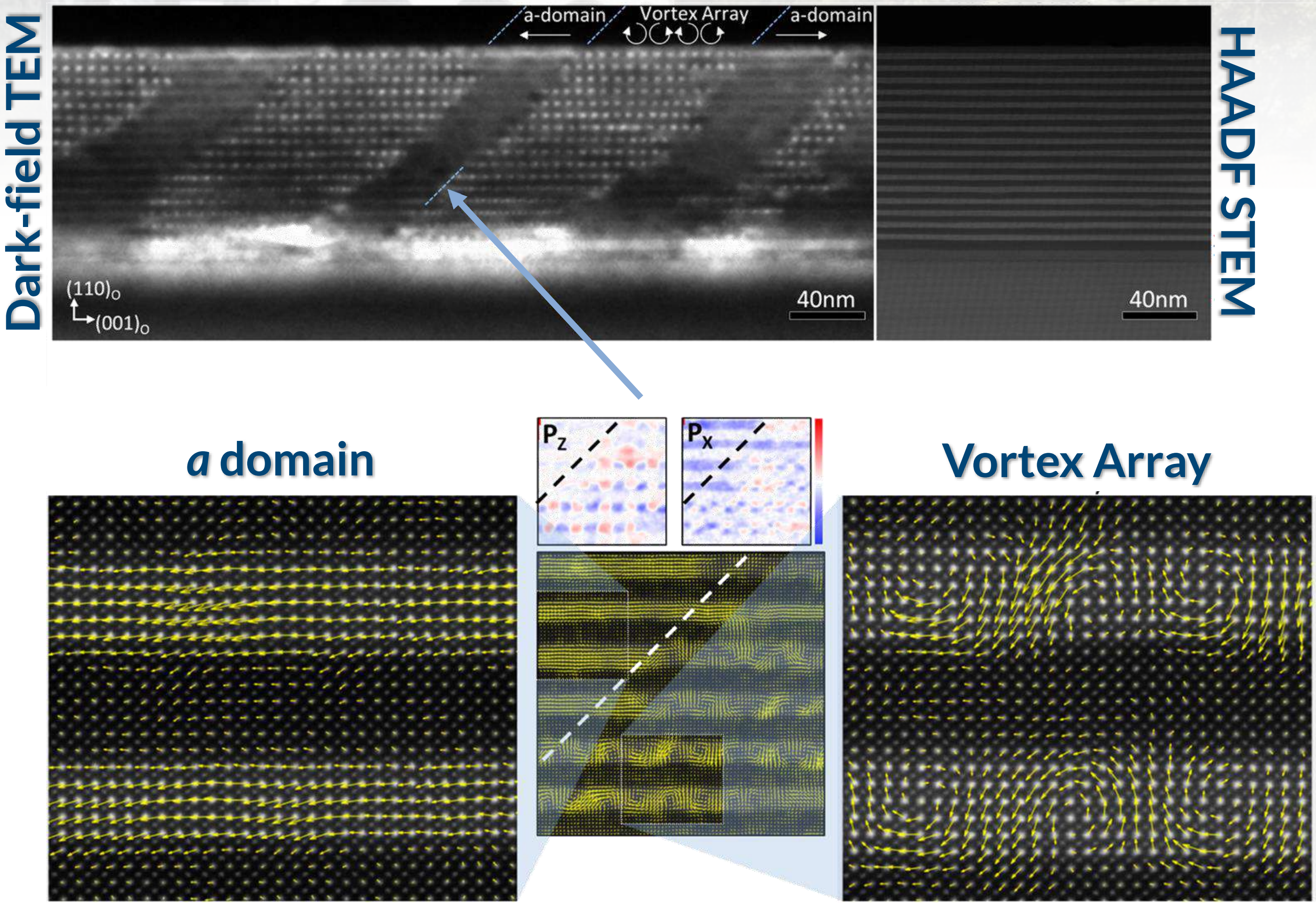
Emergent Toroidal Order



- Lateral PFM → 180° in-plane polarization change within vortex
- Phase-field → replicates coexistence
  - FE → Electric toroidal moment (G) = 0, in-plane $P \neq 0$
  - Transition → ~20 UC, *P* rotation (Bloch-/Néel-like wall in FM), G increases
  - Vortex → G saturates to 0.2 e•$Å^{-1}$, arises from the continuous rotation of *P*, emergence of axial polarization component → **Electric toroidal phase**

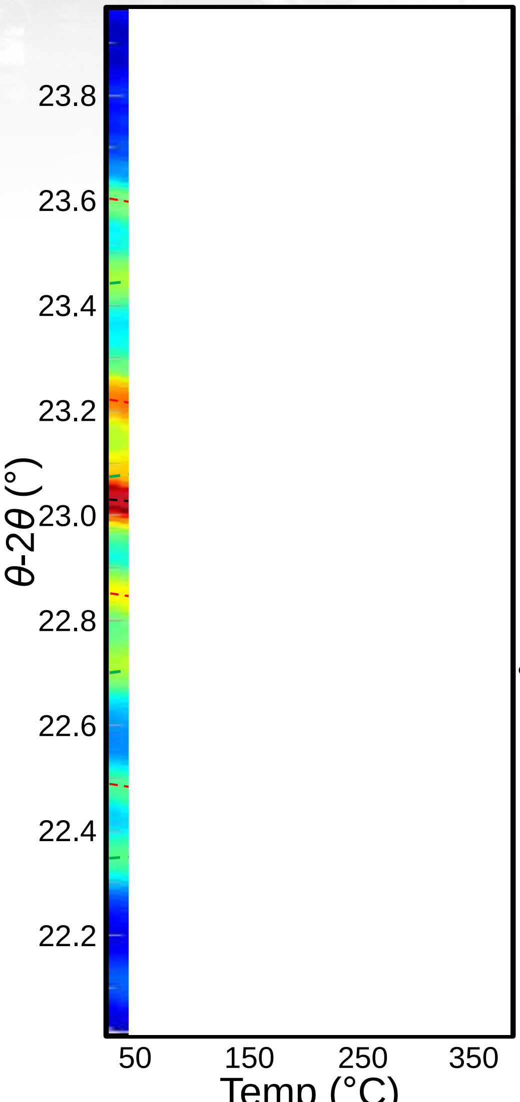
Coexistence of Phases

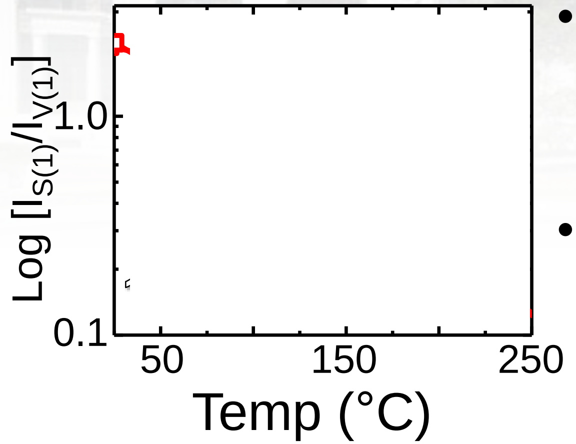


1st observation of toroidal and ferroic order co-existence

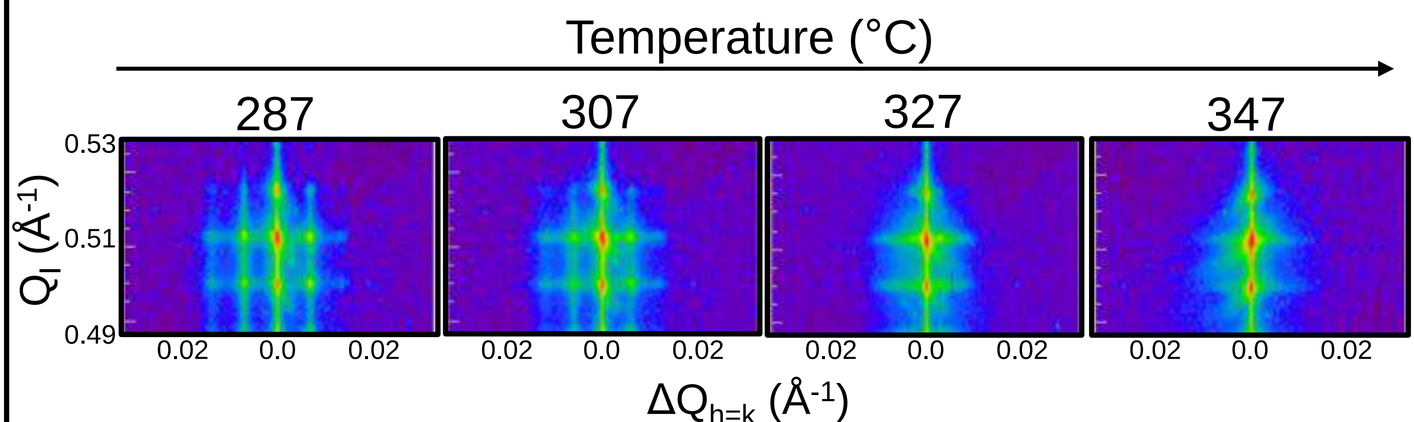
Damodaran *et al. Nature Mater.* **16**, 1003 (2017)

Phase Competition and Evolution: Temp.





- *First-order phase transition* from toroidal to ferroelectric a_1/a_2 phase at ~175°C
- Satellites from a_1/a_2 periodicity about 022-diffraction condition vanish at ~327°C → FE to paraelectric transition



Phase evolution upon cooling:

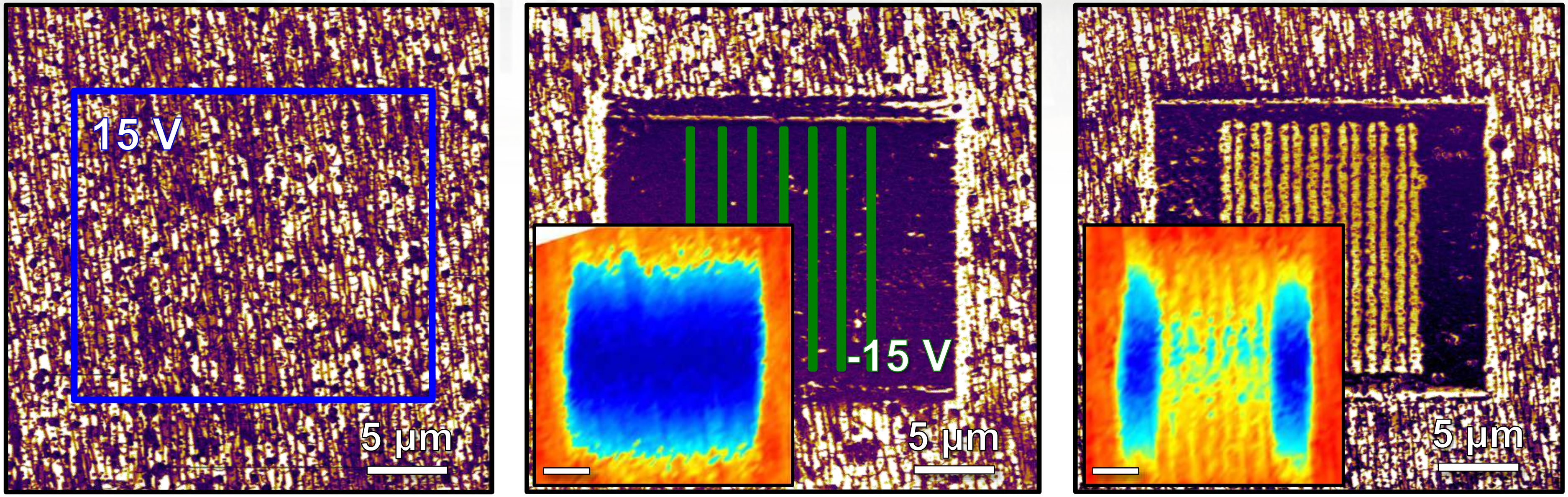
PE → FE (a_1/a_2) → FE (a_1/a_2) + vortex (toroidal)

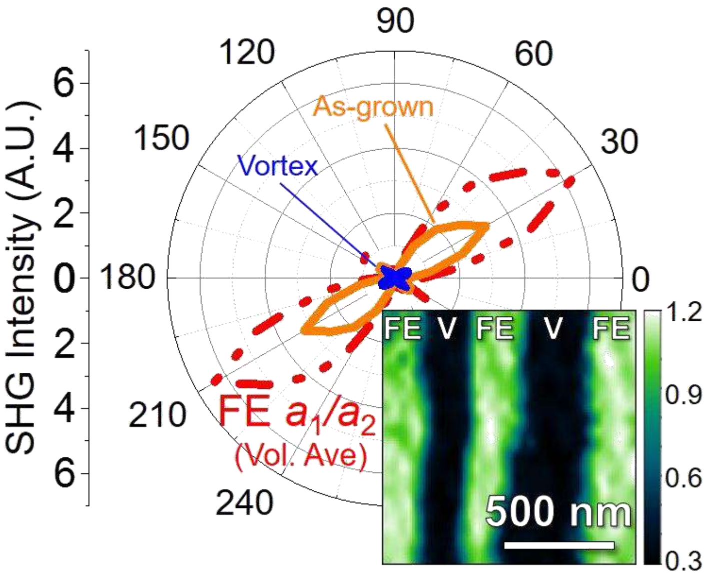
Vortex phase → Exotic, glass-like transition

Damodaran *et al.* *Nature Mater.* **16**, 1003 (2017); Ghosh *et al.* in preparation (2019)

E-Field Control of Toroidal States

As-grown (Mixed Phase) | Poled to Vortex | Poled Back to Mixed Phase





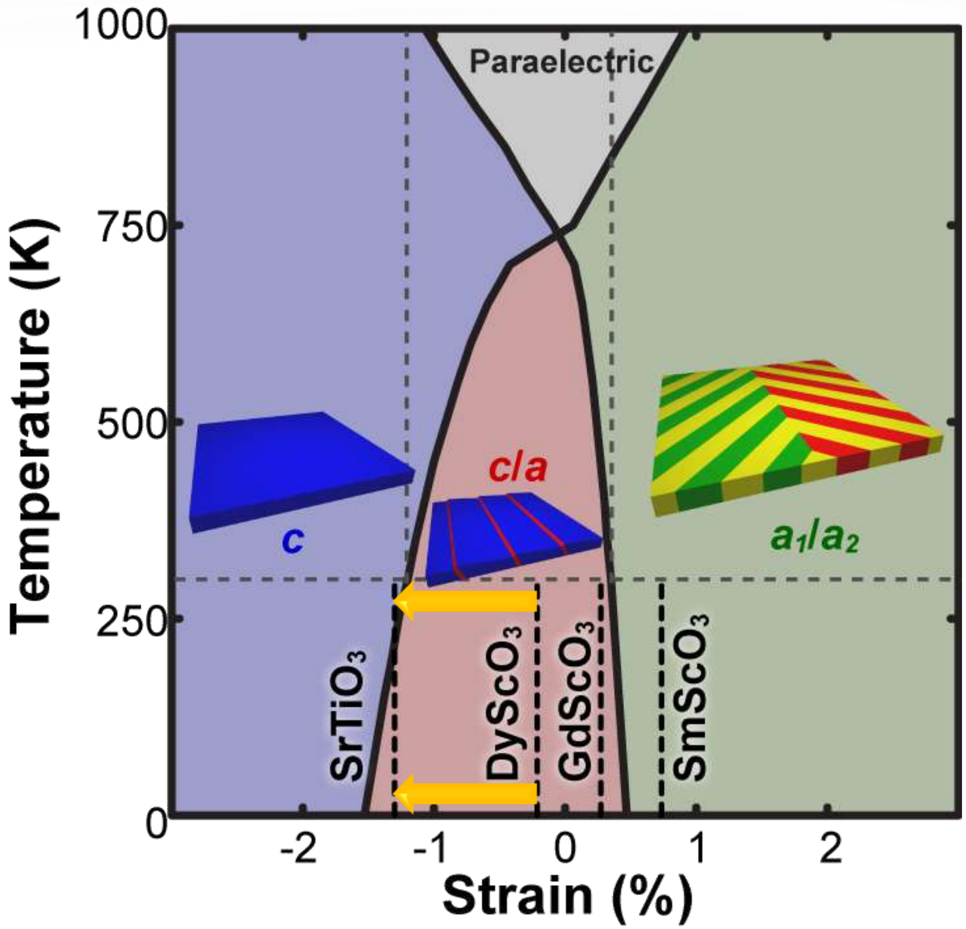
- +15V → Pure vortex
- -15 V → Mixed-phase
- X-ray microdiffraction → confirms reversible switching between phases
- Large changes in properties → Nonlinear optical properties dramatically different

E-field control of toroidal and ferroic order → New cross-coupled function

Damodaran *et al. Nature Mater.* **16**, 1003 (2017)

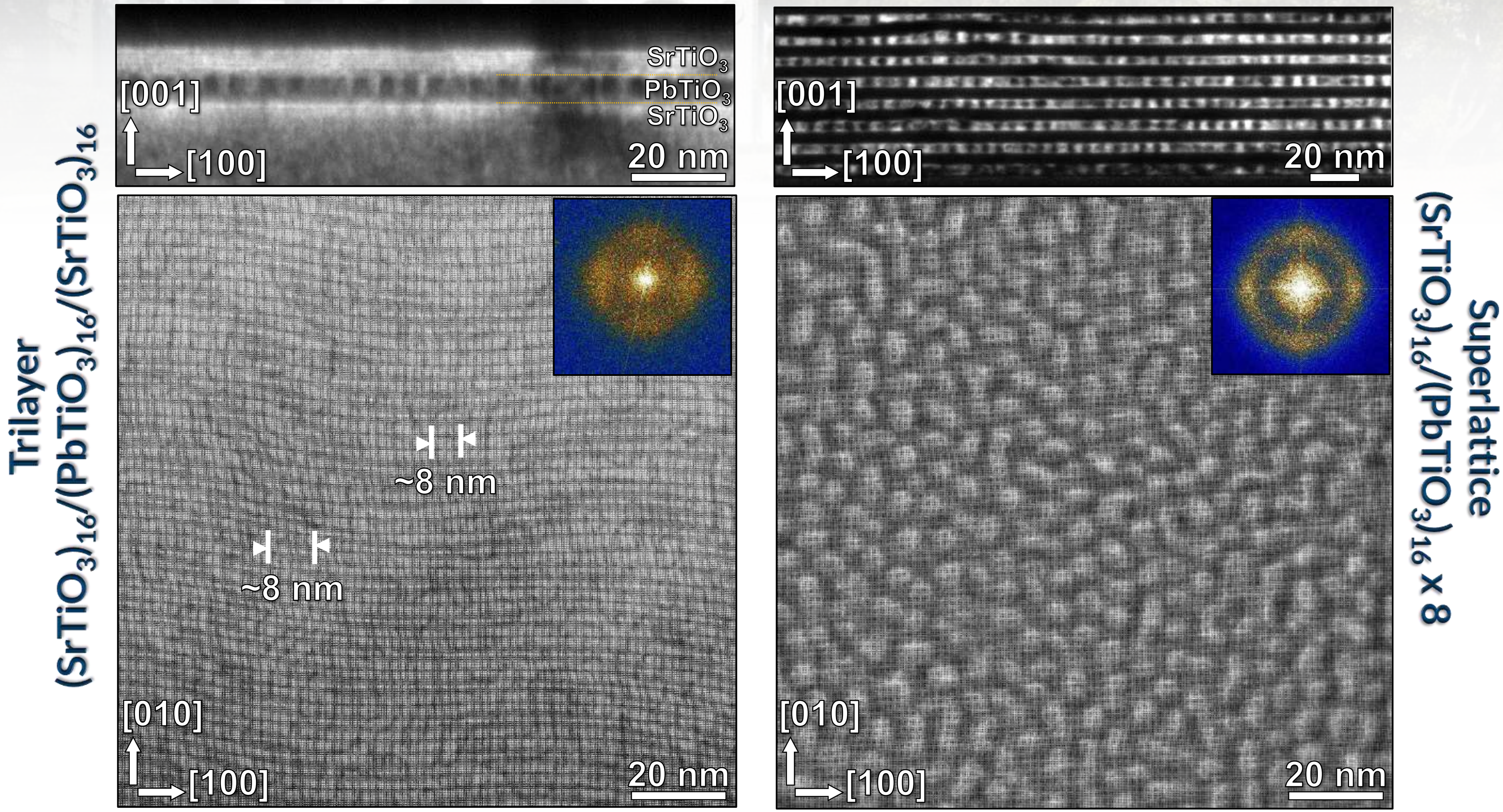
Controlling Emergent Structures

What happens if we change the strain in these superlattice structures? Can strain drive changes in the emergent order?



Das *et al.* *Nature* **568**, 368 (2019)

Controlling Emergent Structures

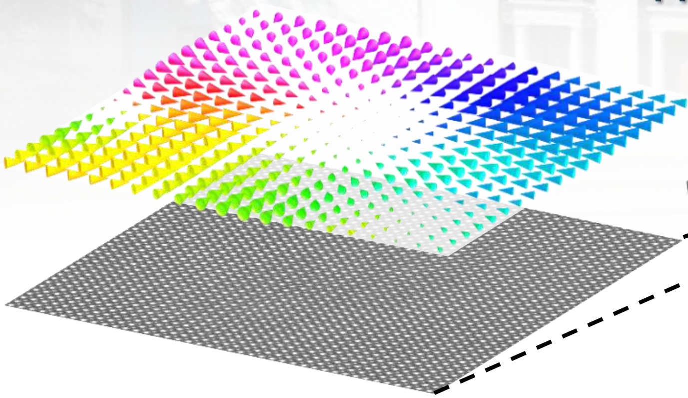


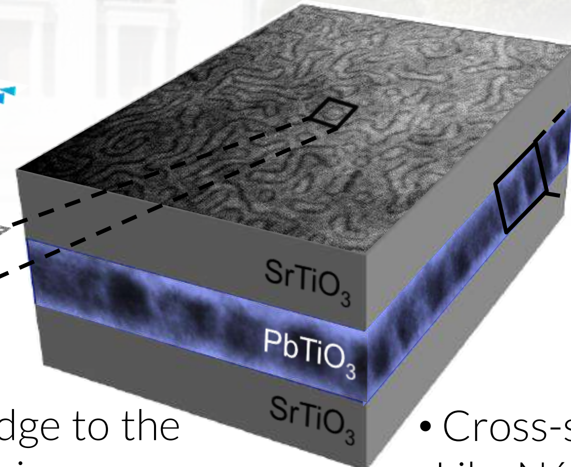
- New polarization morphologies → "Cheetos" and "bubbles", length scale of ~8 nm, suggesting the formation of anti-parallel polar regions

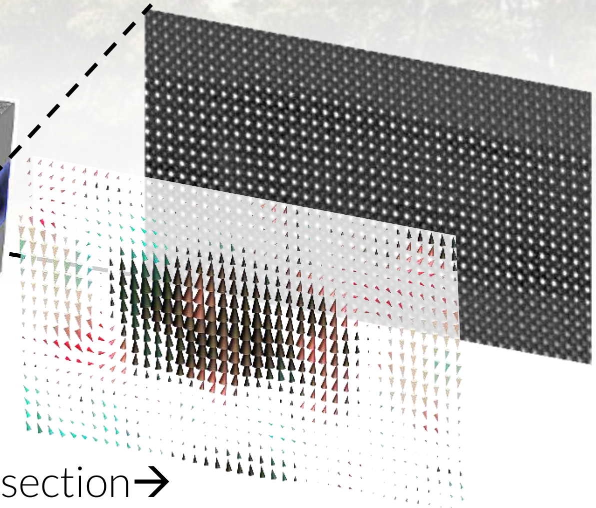
What is the true structure of these new features?

Understanding Emergent Structures

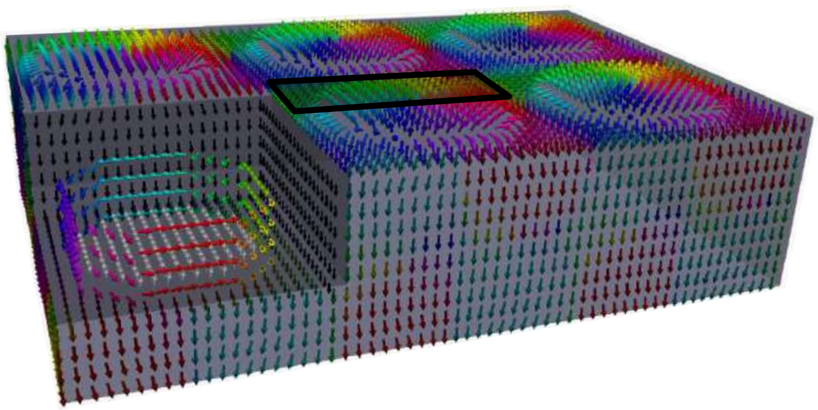
Atomic Polarization Mapping with STEM (NCEM)





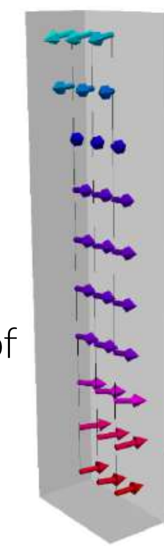


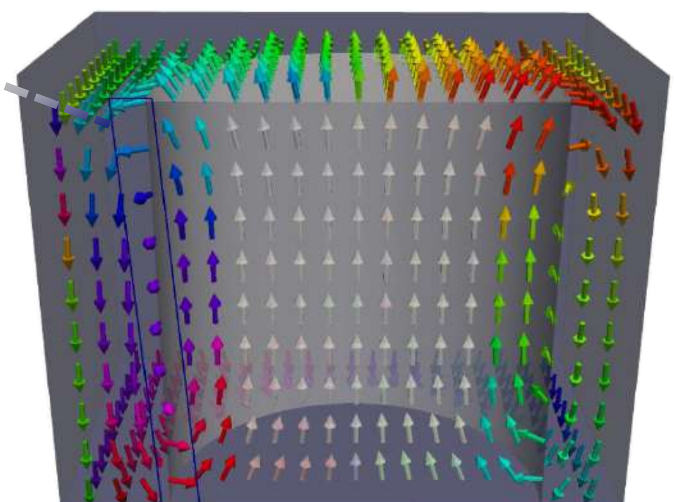
- Plan-view → *P* converging from the edge to the center, reminiscent of hedgehog skyrmion
- Cross-section→ Like Néel skyrmion in FM; diverging and converging hedgehog skyrmion pair



- Second-principles calculations → Confirm formation of polarization structures reminiscent of skyrmions
- Closer look → Bloch-wall structure at mid-plane

Skyrmions → Integer topological number
Are these polarization structures truly skyrmions?

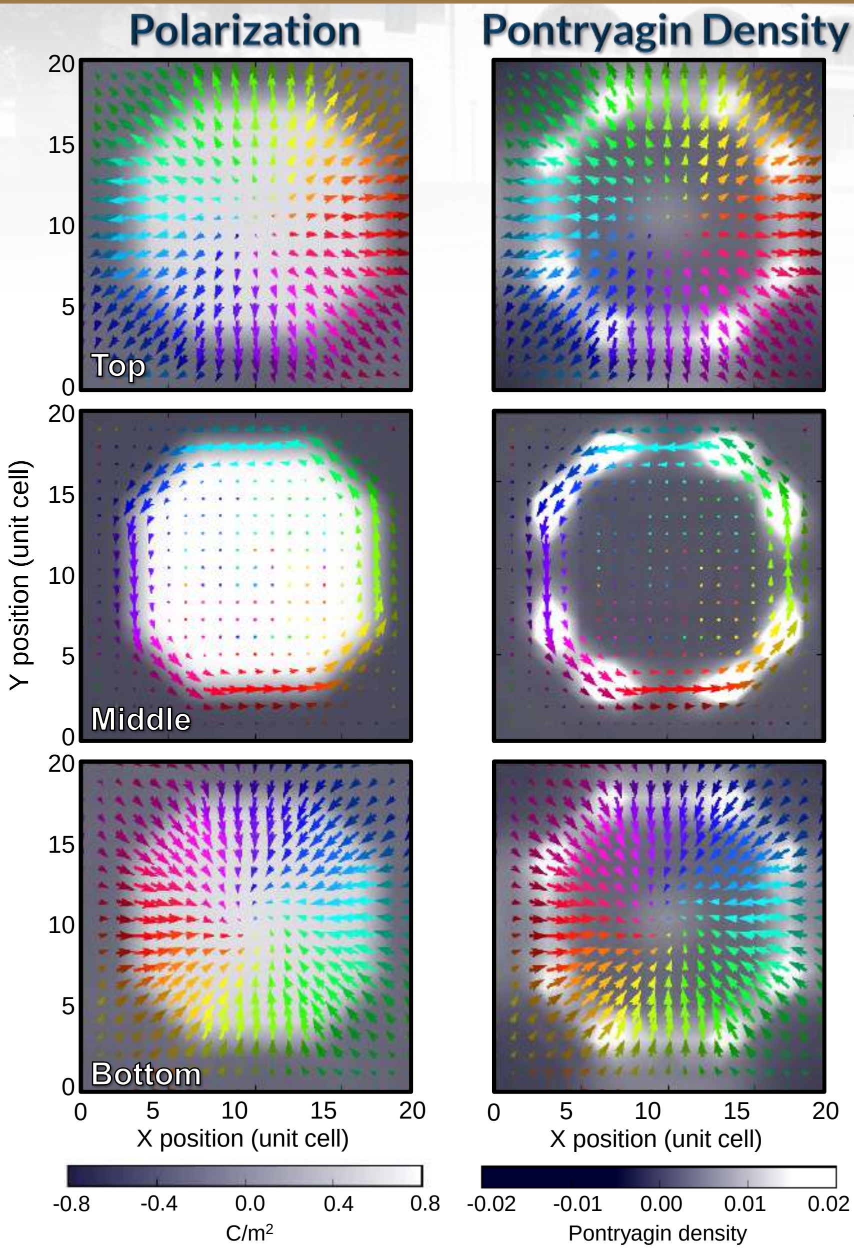




Second Principles – J. Junquera, Univ. de Cantabria

Das *et al.* *Nature* **568**, 368 (2019)

Electric Skyrmions



Second Principles–J. Junquera, Univ. Cantabria

Polarization

- *Top/bottom planes* → Hedgehog-like (Néel) skyrmion; null rotational, +/- divergence
- *Middle plane* → Combed hedgehog (Bloch) skyrmion; IP *P* // domain wall, arises from E_D
- *3D polar skyrmion* → Evolution of 2D skyrmions along the film normal

Topology

- Topological structures can be indexed by a ***skyrmion number***, defined as

N. D. Mermin, *Rev. Mod. Phys.* **51**, 591 (1979)

$$N_{SK} = \frac{1}{4\pi} \iint \vec{u} \cdot \left(\frac{\partial \vec{u}}{\partial x} \times \frac{\partial \vec{u}}{\partial y} \right) dxdy$$

$\vec{u}$ is the normalized local dipole moment; surface integral over corresponding (001)

Integrand = Pontryagin density

- For this system → $N_{SK} = +1$, an integer that is invariant for every plane
- Even the "Cheetos" manifest $N_{SK} = +1$

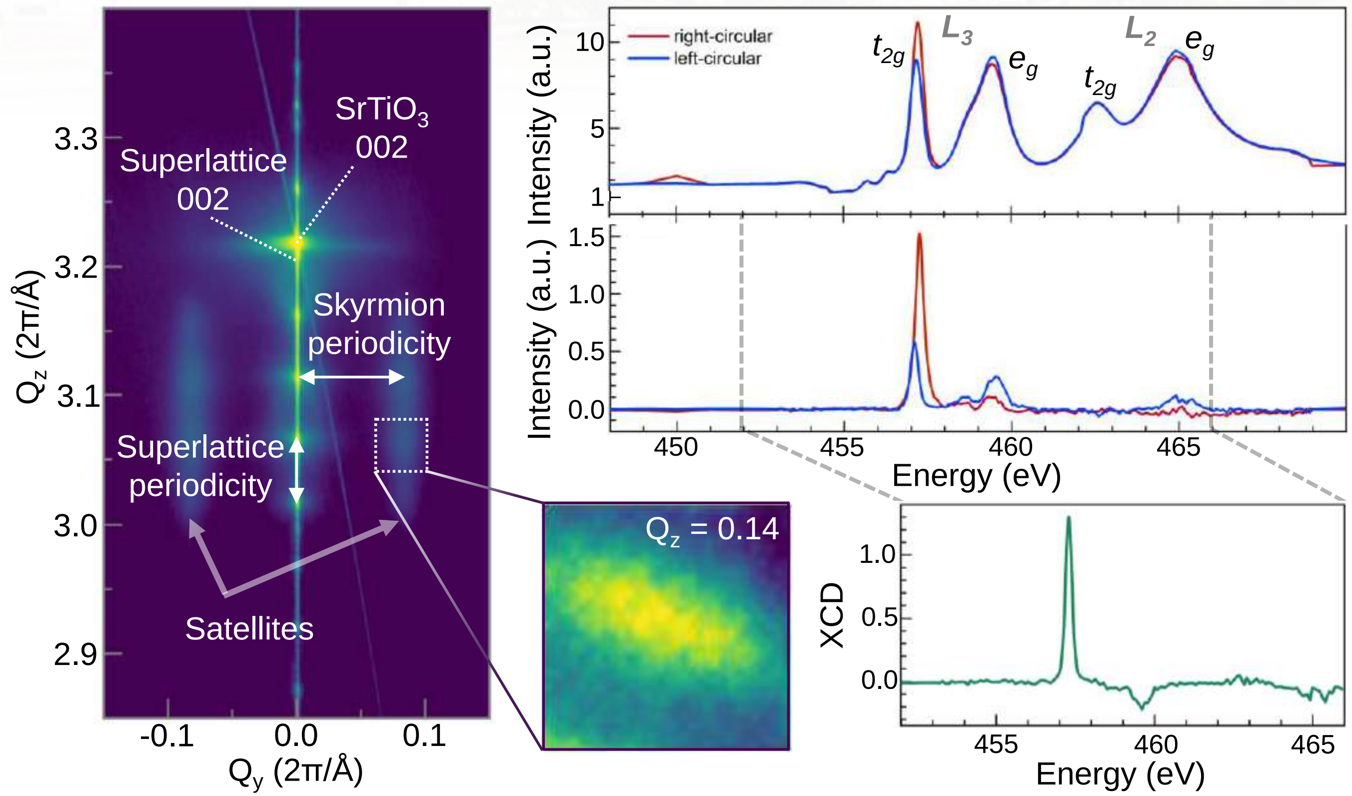
First observation of electric (polar) skyrmion

Das *et al.* *Nature* **568**, 368 (2019)

Chiral Electric Skyrmions

Such electric (polar) skyrmions should be chiral…
Can be probed with *resonant soft X-ray diffraction (ALS)*

- Imaginary line along any direction within the middle plane crosses only Bloch domain walls → Local *P* exhibits helical rotation
- Helical *P* texture is virtually identical to the helical *P* configuration in polar vortex arrays
- Probed at satellite peak, Ti $L_{3,2}$ edge



- Strong circular dichroism at the L_3 edge (corresponding to the t_{2g} states) → Chiral structures; consistent with the presence of Bloch domain walls

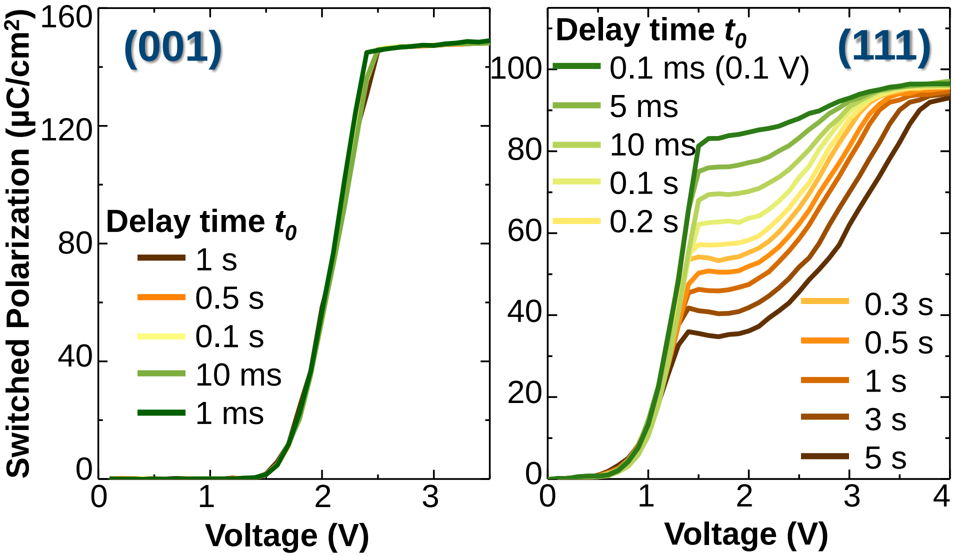
Observation of electric (polar) skyrmions | 3D structure evolves from Néel/Bloch/Néel (top to bottom) | Emergent chiral nature

Das *et al.* *Nature* **568**, 368 (2019)

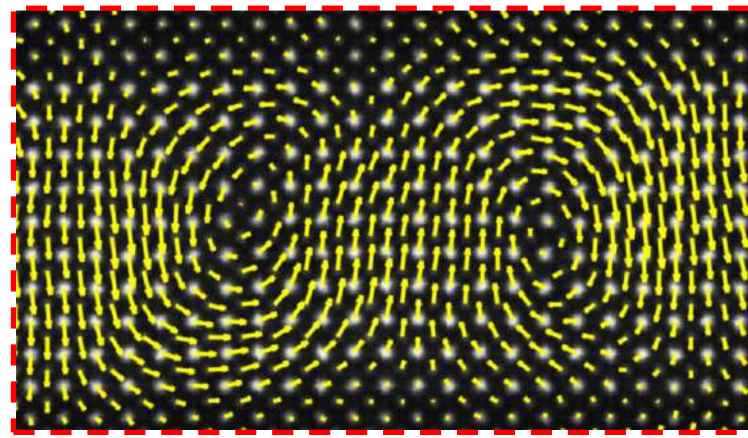
Conclusions and Implications

Accessing emergent phenomena requires novel routes to manipulate and control materials…

Multi-state Switching and Stable Intermediate States



Polar Vortices, Toroidal Order, Phase Competition, Chirality, Electric (polar) Skyrmions



- **(111)-oriented Films** → "Frustration" gives rise to kinetically and elastically-mediated switching, multi-state structures, and the potential for deterministic intermediate states needed for neuromorphic function
- **Superlattices** → Deterministic competition of energies begets novel polarization profiles and emergent properties and function