# *Ultrafast Structural Probes in Nanoscience and Electronics*

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# *The Importance of Being Fast*

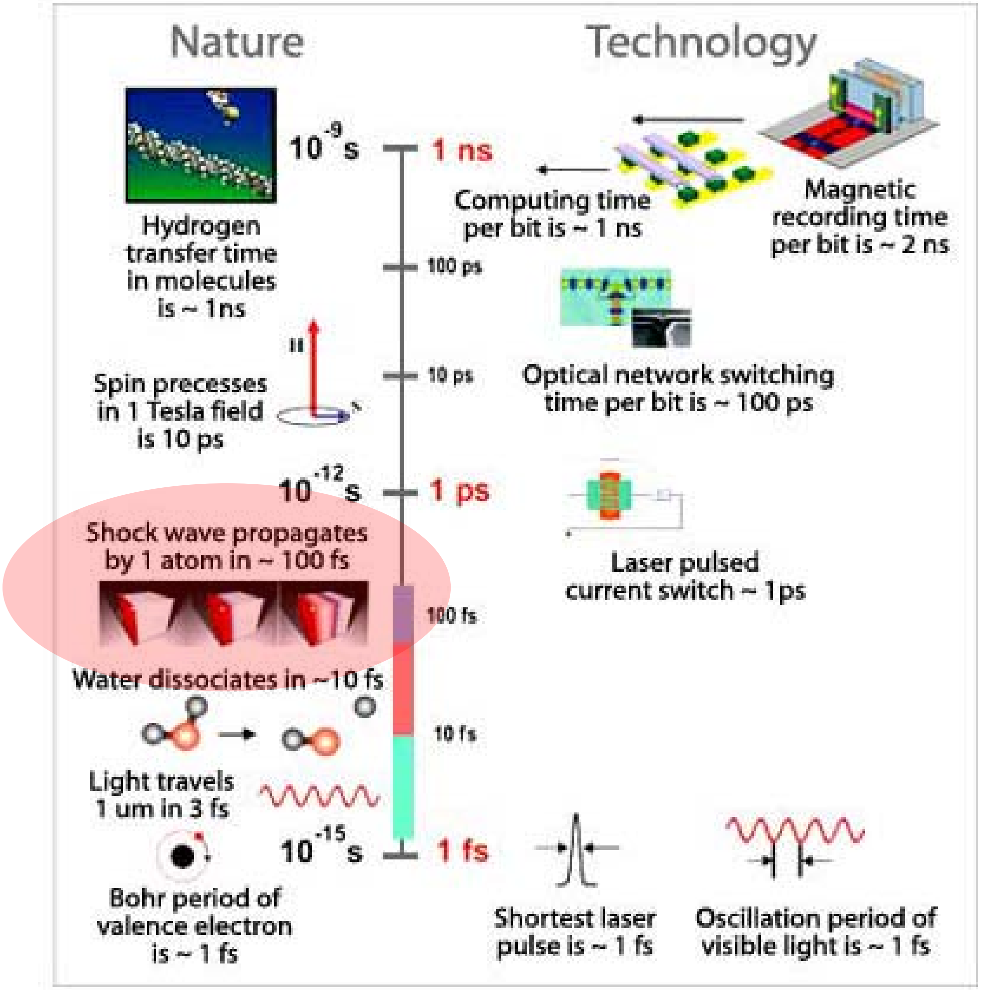
Time scale of structural dynamics of ferroelectrics is several km/s.

⇩

At 1 km/s a perturbation propagates 1 μm in 1 ns.

⇩

Need submicron and sub-nanosecond resolutions in time and space.




SLAC / Stanford

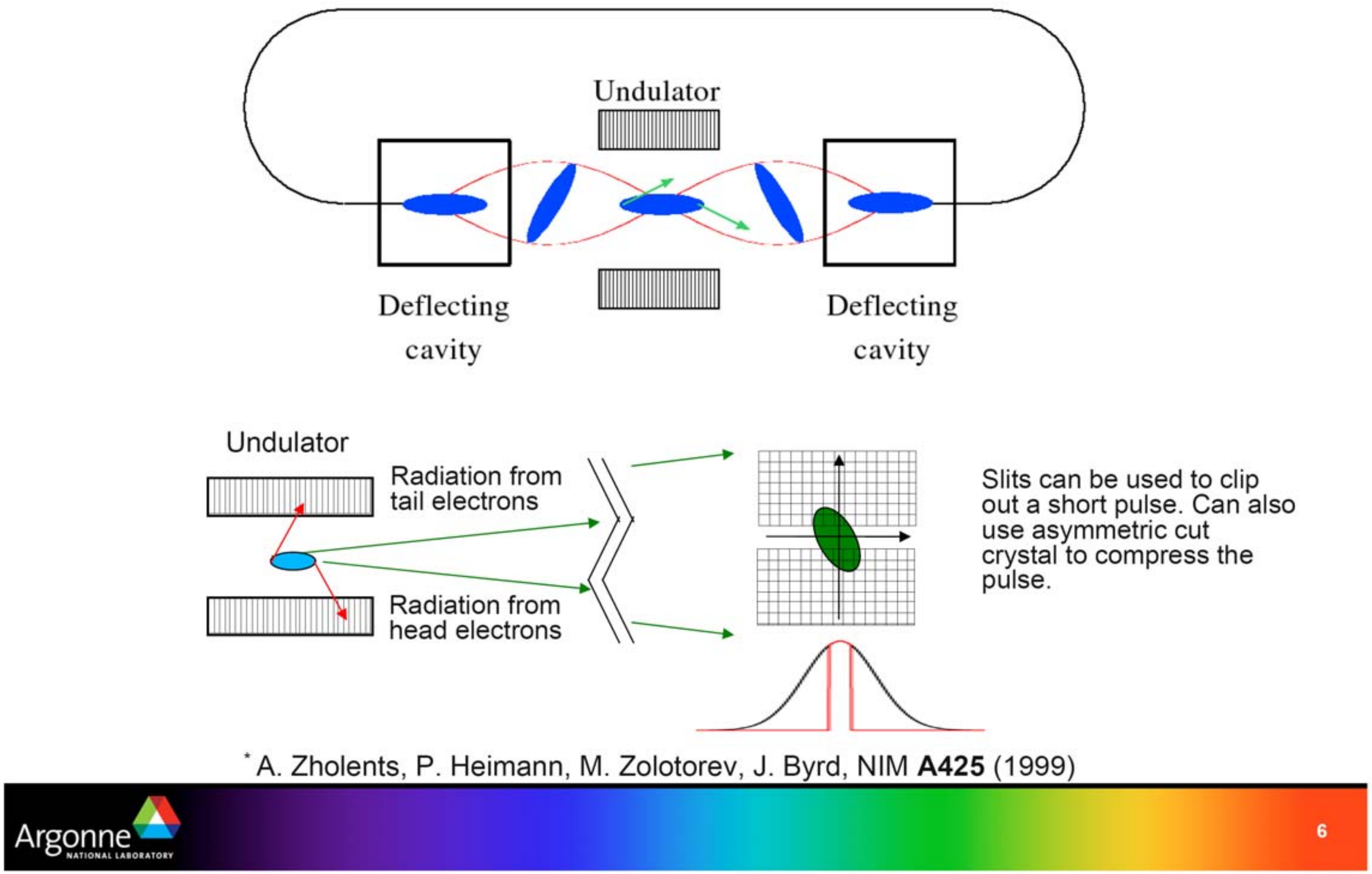
# *Dynamics in Solids are Often Coupled With Lattice Distortion*

- Switching in ferromagnets and ferroelectrics.
- Structural and electronic phase transitions.
- Sliding charge density waves.
- Phase transitions driven by biaxial strain.

# *It's Hard to Probe Phenomena that are Both Small and Fast*

| Technique | Spatial Res. | Time Res. | Structural Sensitivity (strain, CDW, etc.) (ΔQ/Q resolution) | Sensitive to Magnetism? (Ferro- and/or Antiferromagnetic) | Element Specific? | Requires Applied Fields? |
|---|---|---|---|---|---|---|
| Scanning Probe (including STM, AFM, MFM, BEEM, etc.) | < 1 Å | 100 μs (but can be coupled with THz or visible radiation) | Some. (1%) | Limited, F. and A. with broad limitations, often including reduced resolution. | Indirectly, via density of states in STM. | MFM requires **H**, STM and piezoresponse AFM large **E**. |
| Transmission Electron Microscopy (TEM, STEM, etc.) | 1 Å | 1 μs (?) | Yes. (0.1%) | Yes, F. with reduced resolution. | Yes, via Z-contrast, EELS, etc. | No. |
| Optical Microscopy | > 200 nm | 5 fs | Indirect, via Raman, birefringence. (~1%) | Yes, F. and A. | Limited (via Raman) | No. |
| Soft X-ray Microscopy | 20 nm | < 100 ps | No. | Yes, F. and A. | Yes. | No. |
| **Hard X-ray Microdiffraction** | **100 nm** | **< 100 ps** | **Yes. ($10^{-5}$)** | **Yes, F. and A.** | **Yes, via resonant scattering.** | **No.** |

# *Synchrotrons Can Go Faster!*

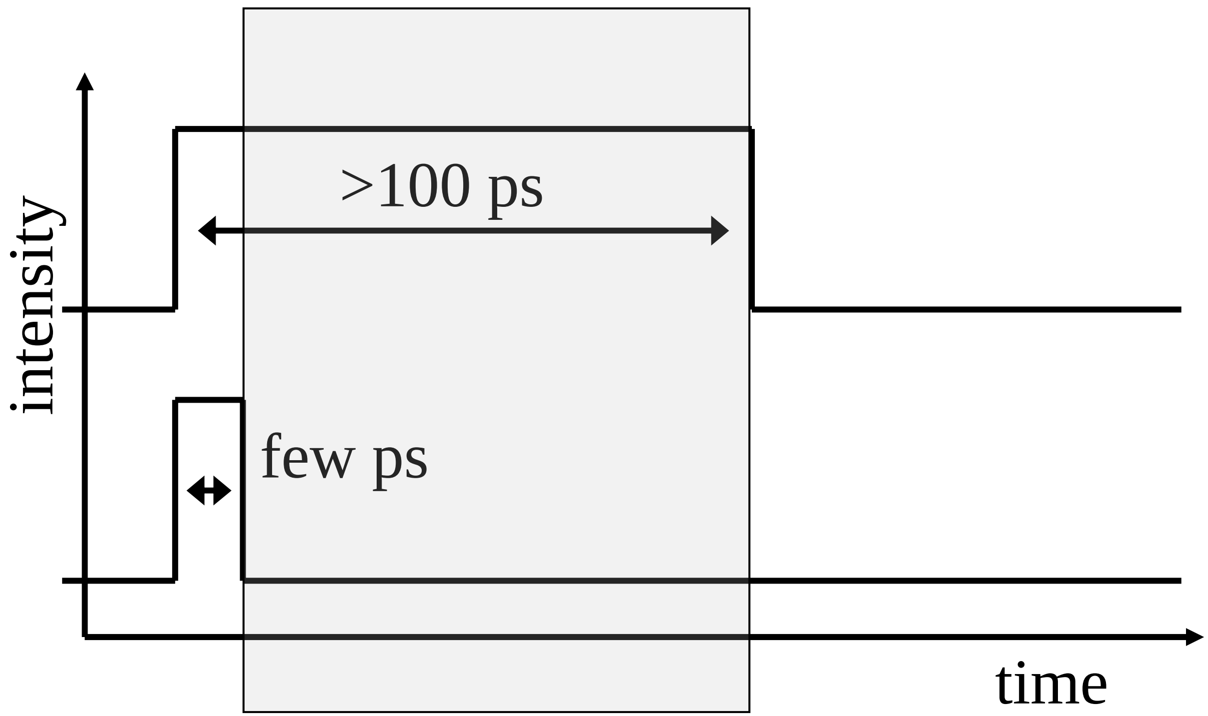



**1 ps x-ray pulses!**

G. Srajer, APS

How does piezoelectricity really work?

# The Opportunity




New opportunity to see phenomena at timescales between 100 ps and 1 ps or frequencies up to 1 THz.

***This is an important regime because the dynamics of small systems are just beginning to be exploited.***

# *Outline*

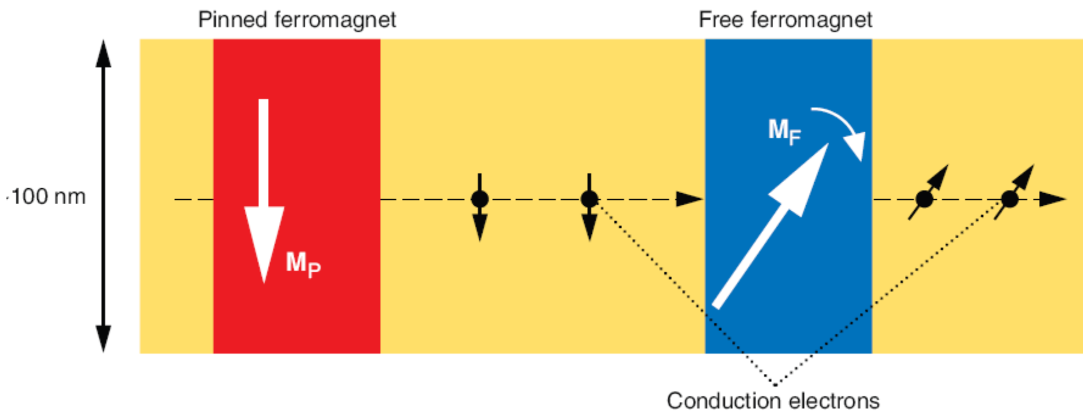
- **Three “straw-man” areas:**
  - Nanomagnetism/spintronics
  - Nanomechanical systems
  - Dynamics of electrically driven materials

- **Our work: Dynamics in complex oxides (extreme conditions, short times, coupling of ferroelectricity with magnetism)**

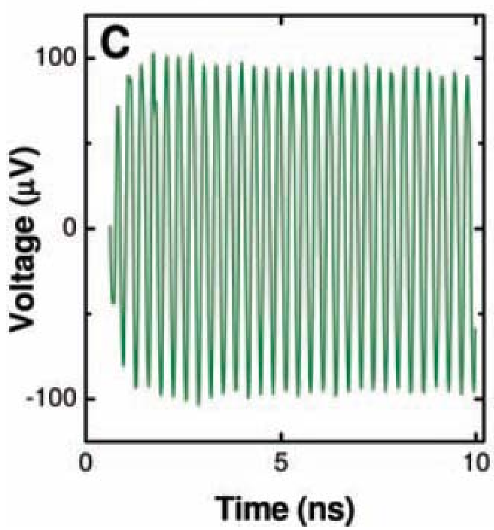
- **(I am optimistic about count rates, detectors, synchronization, making and contacting samples, discovering scattering geometries and mechanisms, etc.) It seems like all of these things are solvable problems, especially by 2013!)**

# 1. Nanomagnetism and Spintronics

Coherent Magnetic Oscillations due to Spin Transfer Torque




Perspective by Covington, Science **307**, 215 (2005).

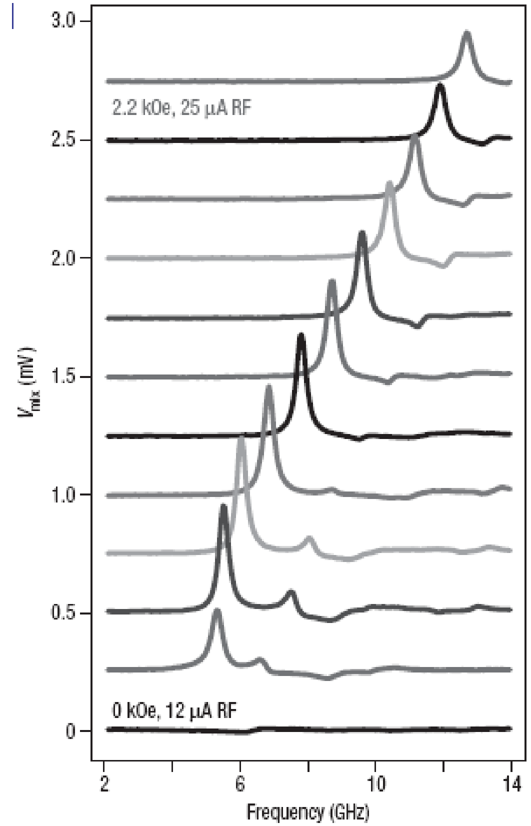



Krivorotov *et al.*, Science **307**, 228 (2005).

Dynamics are relatively slow now, but only beginning to be explored.

# *What is the Timescale of this Effect?*

- Coherent Oscillation of the Magnetic Moment of the Free Layer
- Frequency depends on size and driving current
- Resonance frequencies can exceed 10 GHz, even in relatively large devices




Sankey, *et al*., Nature Physics **4**, 67 (2008).

# *What can be Learned?*

- What are the magnetic structures of the pinned and free layers? (Perhaps this is a soft x-ray problem…)

- How is the structure of this system evolving?

- How can even more functional materials be integrated with this precision in control of the dynamics?

# *Spintronics with Complex Materials*

- Exchange Bias in Complex Oxide Systems

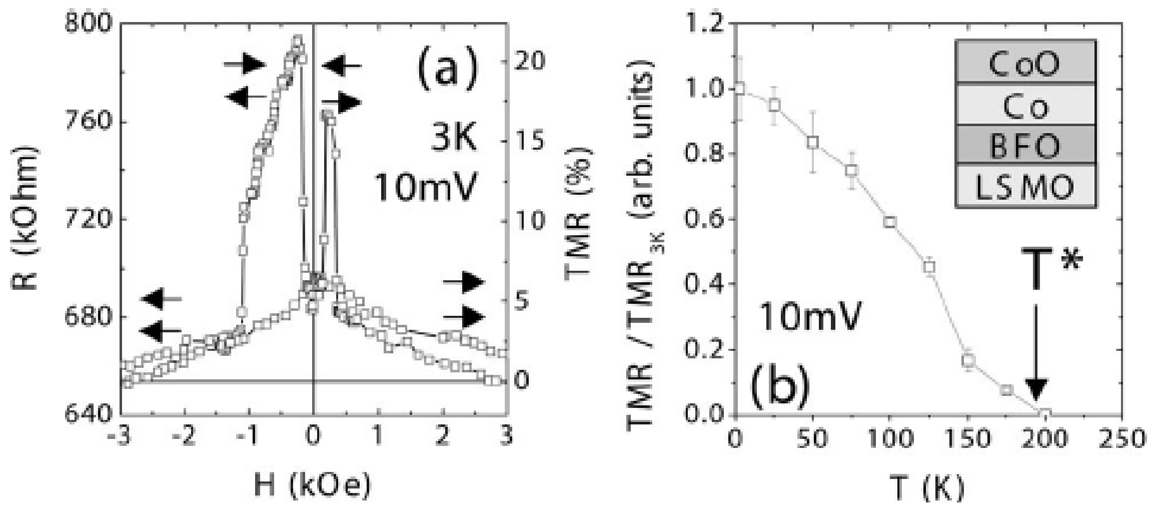


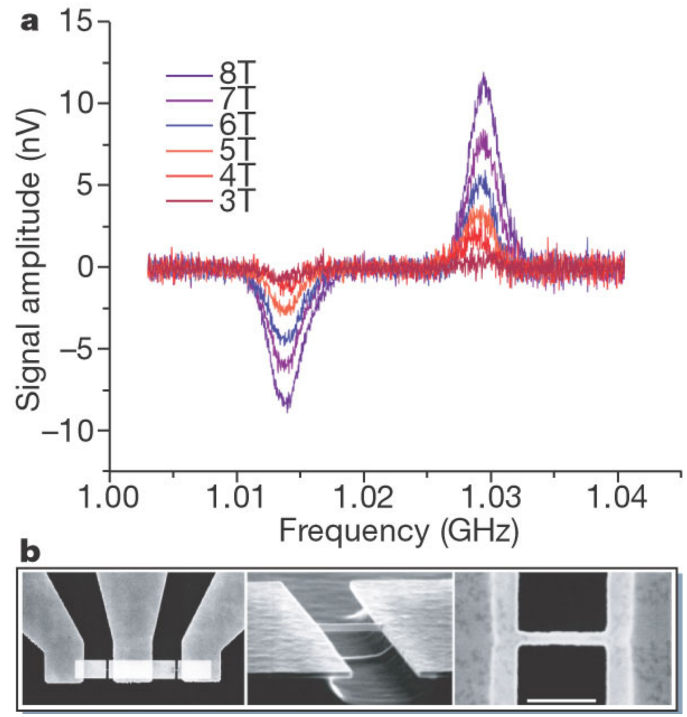

FIG. 2. (a) *R*(*H*) curve of a Au/CoO/Co/BFO/LSMO//STO (001) junction. The arrows show the magnetic states of each layer for the different resistance states. (b) Evolution of the TMR with T.

H. Bea *et al*., Appl. Phys. Lett. **89**, 242114 (2006).

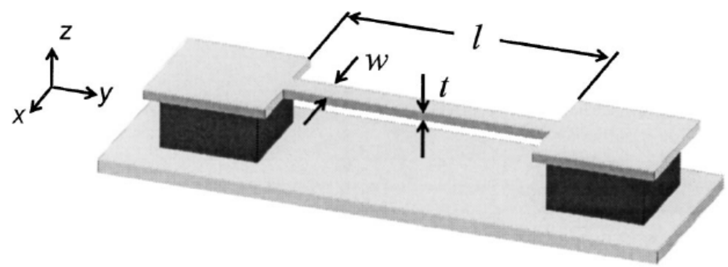
***$BiFeO_3$ is ferroelectric, so now expect dynamics in the structure and the magnetism – and coupling between them.***

# 2. Nanoelectromechanical Systems

- NEMS frequencies have been at the level of 1 GHz+ for several years.
- Fundamental limits depend on mechanics, materials, fabrication
- Predictions based on mechanical models.




Huang *et al*., Nature **421**, 496 (2003).

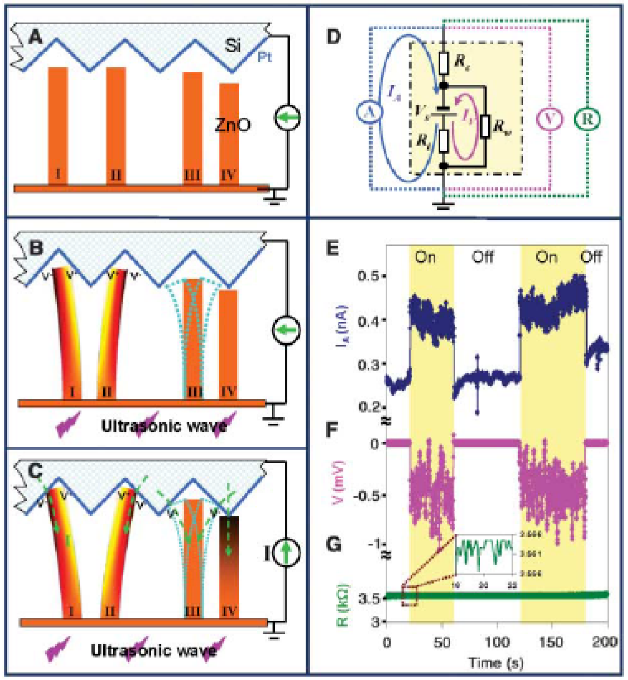



Ekinci *et al*., J. Appl. Phys **95**, 2682 (2004).

# *Electronics based on NEMS*

- Sensors, oscillators, single electron transistors.
- One more: Piezoelectric Energy Harvesting

Wang *et al*., Science **316**, 102 (2007).



# *What can be Learned?*

- Present understanding is all based on modeling. Predict resonant frequencies, $Q$, etc. What are these things really?
- Short timescales expose fundamental materials properties. Materials can be SiC, Si, C nanotubes, graphene, diamond.
- How can functional materials be integrated?

# 3. Electrostatically Driven Materials

REVIEWS OF MODERN PHYSICS, VOLUME 78, OCTOBER–DECEMBER 2006

## Electrostatic modification of novel materials

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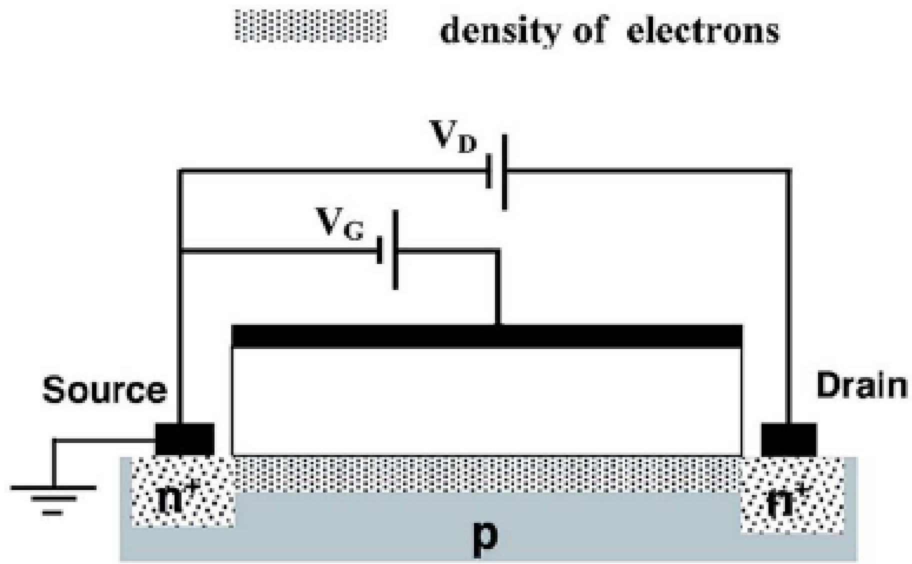
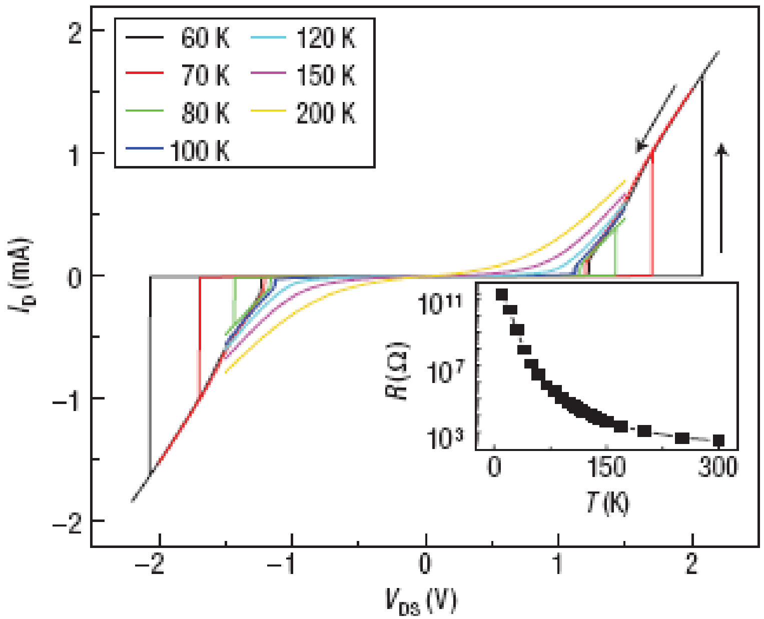
(Published 10 November 2006)




Ahn *et al.*, Rev. Mod. Phys. **78**, 1185 (2006)

# *Switching in Magnetite ($Fe_3O_4$)*

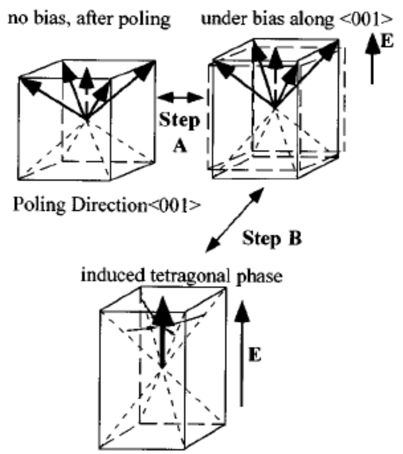
- Electrostatic modification pushes $Fe_3O_4$ across the Verwey transition.
- Signature in conduction because this is a metal-insulator transistor.




Lee *et al.*, Nature Mat. 7, 130 (2007)

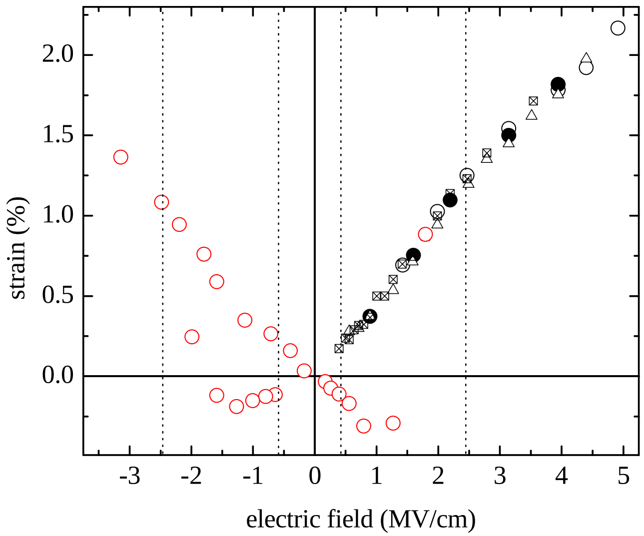
# Ferroelectric Phase Transitions in High Electric Fields

**A. Electric-field driven structural phase transitions**



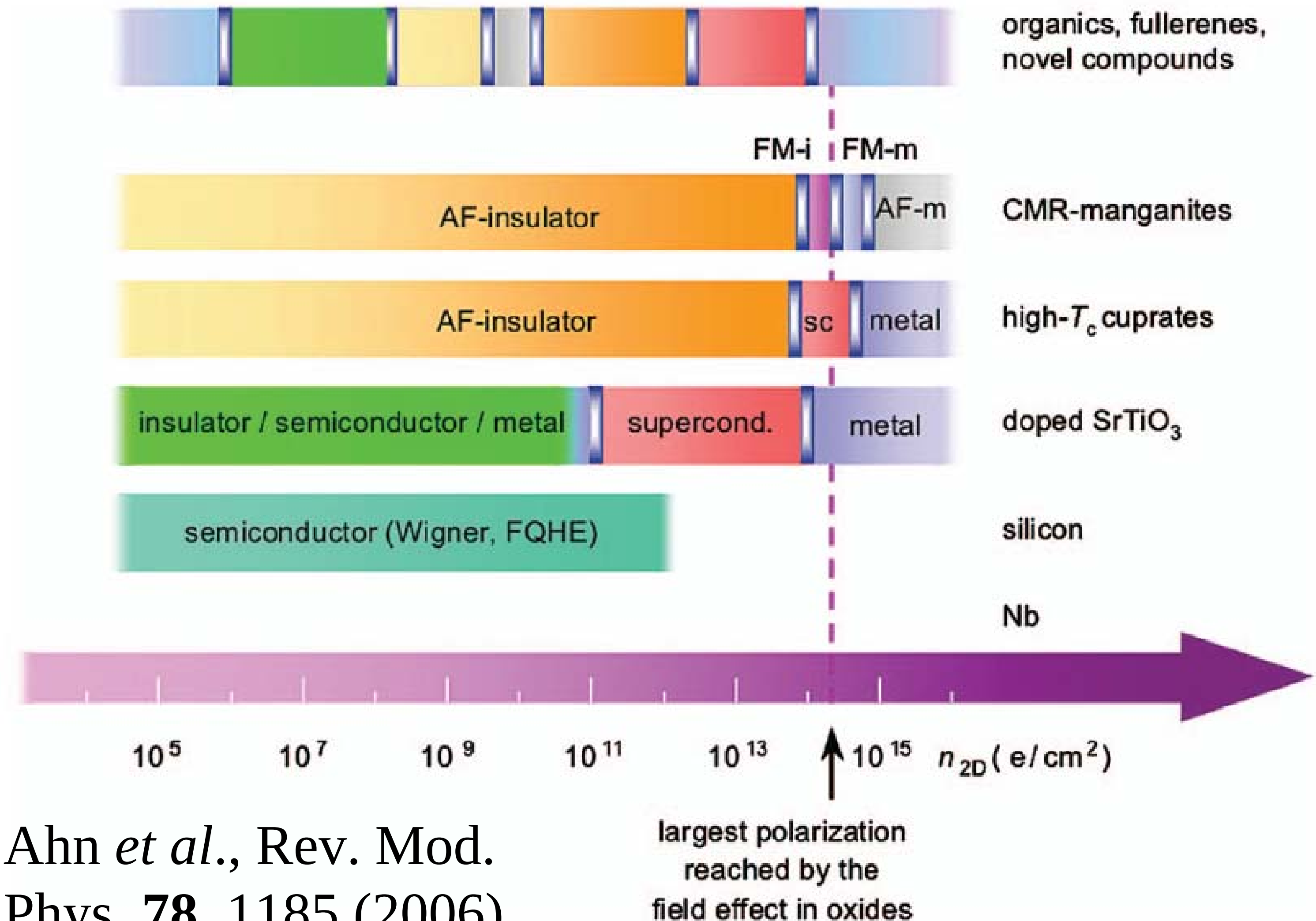

Nucleation mechanism?
Speed of phase transitions?

**B. Polarization switching near the intrinsic coercive electric field**




We're already within a factor of ~2 of some predictions of the intrinsic coercive electric field.

# Applicable to a Wide Range of Systems




Ahn *et al*., Rev. Mod. Phys. **78**, 1185 (2006)

# *What Can be Learned?*

- How fast can these transitions be?
- What other structural transitions can be driven?
- Fundamental physics of these phase transitions have been previously available only by changing T (or doping, or H, etc.). Nothing fast!
- Short pulses go along with high E fields.

# *Outline*

- **Three "straw-man" areas:**
  - Nanomagnetism/spintronics
  - Nanomechanical systems
  - Dynamics of electrically driven materials

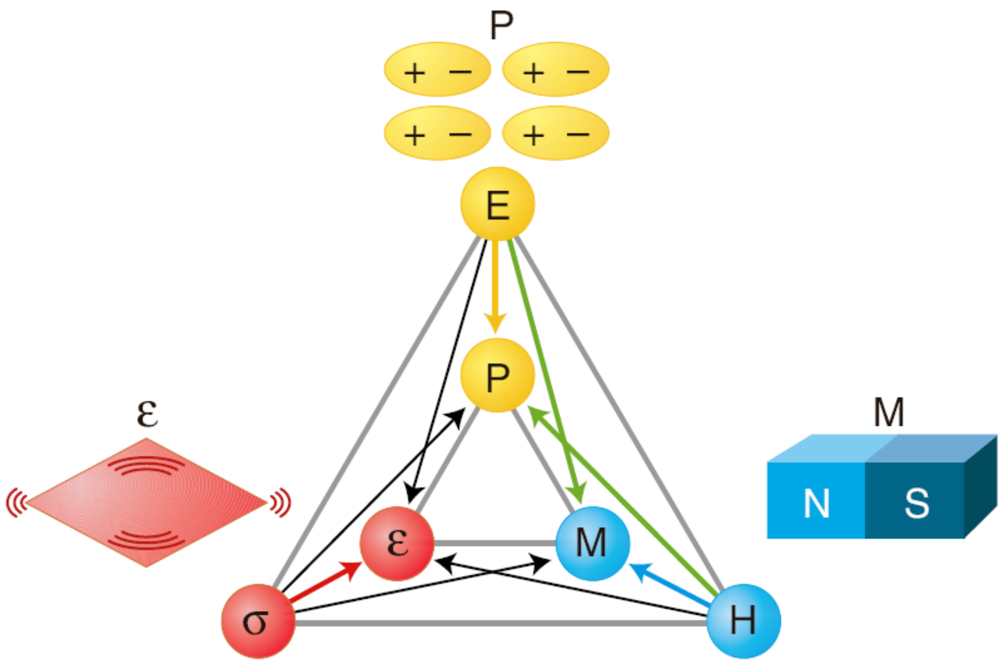
- **Our work: Dynamics in complex oxides (extreme conditions, short times, coupling of ferroelectricity with magnetism)**

- **(I am optimistic about count rates, detectors, synchronization, making and contacting samples, discovering scattering geometries and mechanisms, etc.) It seems like all of these things are solvable problems, especially by 2013!)**

# *Functions of Complex Oxide Materials*

- **Properties:** Superconductivity, ferroelectricity, insulators, conductors, ferromagnetism, antiferromagnetism.
- **Phenomena:** Phase transitions, long-range ordering and disorder, doping, colossal magnetoresistance.
- **Applications:** Power, acoustics, imaging, communications, quantum computing, magnetoresistive sensors, …

# *Properties are Interrelated*




N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).

- Polarization switching in ferroelectrics
- Ferroelectrics in extreme electric fields
- Magnetism and ferroelectricity in multiferroics

**domain dynamics**

*microseconds to nanoseconds*

**elastic and acoustic coupling in multicomponent structures**

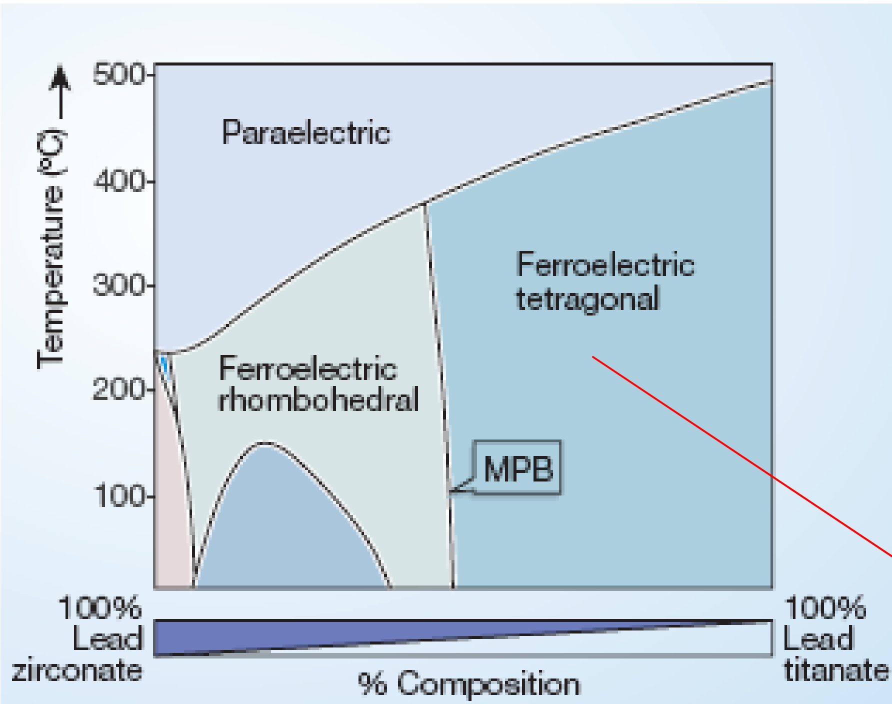
*nanoseconds*

**linear and nonlinear constitutive relations: piezoelectricity, piezomagnetism, elasticity**

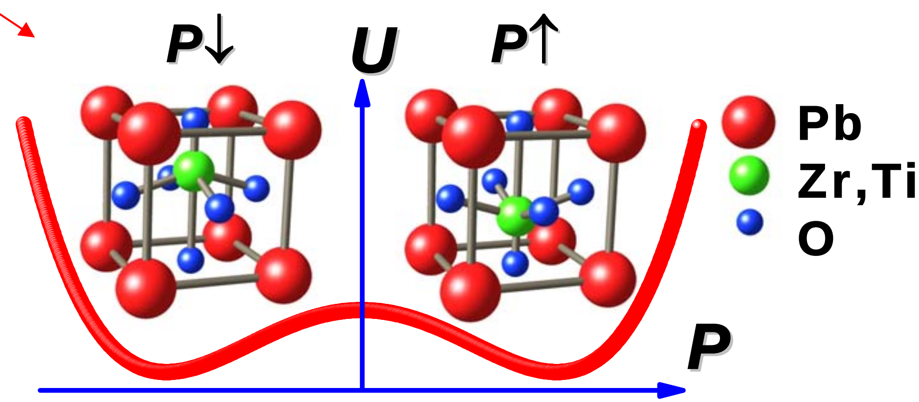
*picoseconds to femtoseconds*

*shorter times*

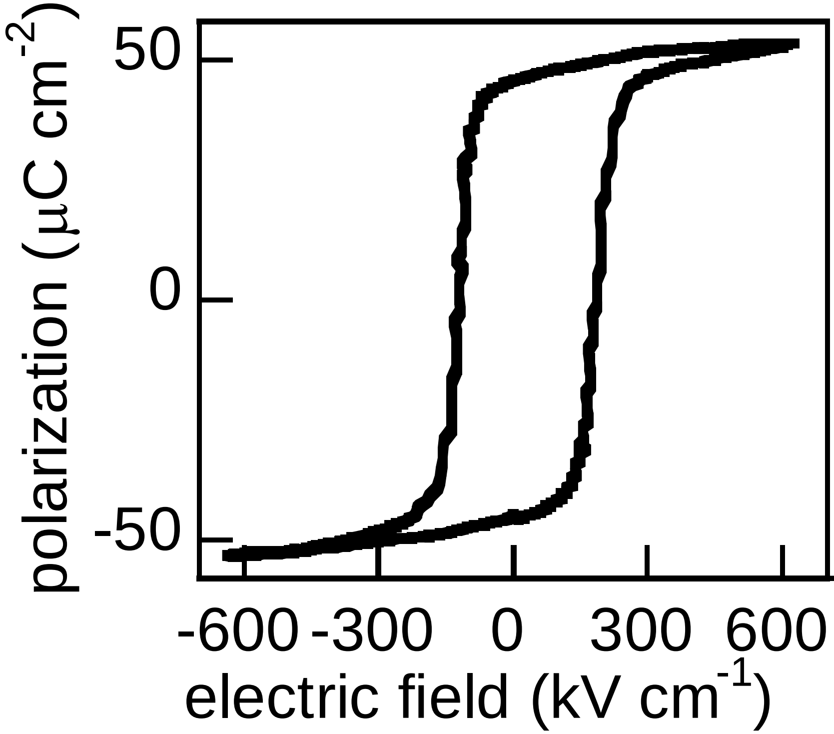
# *Ferroelectricity*




*E. Cross, Nature 432, 24 (2004)*



# *Electric field scales for ferroelectric phenomena*




Up to tens of MV/cm:
High field regimes of
interatomic interactions

< 1 MV/cm: Polarization domain dynamics controls electromechanical and switching properties.

100s MV/cm:
Bond breaking.

# New Potential to Understand the High-Field Regime

VOLUME 89, NUMBER 11 PHYSICAL REVIEW LETTERS 9 SEPTEMBER 2002

**First-Principles Approach to Insulators in Finite Electric Fields**

Ivo Souza, Jorge Íñiguez, and David Vanderbilt
*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019*
(Received 29 May 2002; published 26 August 2002)

We describe a method for computing the response of an insulator to a static, homogeneous electric field. It consists of iteratively minimizing an electric enthalpy functional expressed in terms of occupied Bloch-like states on a uniform grid of $k$ points. The functional has equivalent local minima below a critical field $\mathcal{E}_c$ that depends inversely on the density of $k$ points; the disappearance of the minima at $\mathcal{E}_c$ signals the onset of Zener breakdown. We illustrate the procedure by computing the piezoelectric and nonlinear dielectric susceptibility tensors of III-V semiconductors.

DOI: 10.1103/PhysRevLett.89.117602 PACS numbers: 77.22.Ch, 42.70.Mp, 78.20.Bh

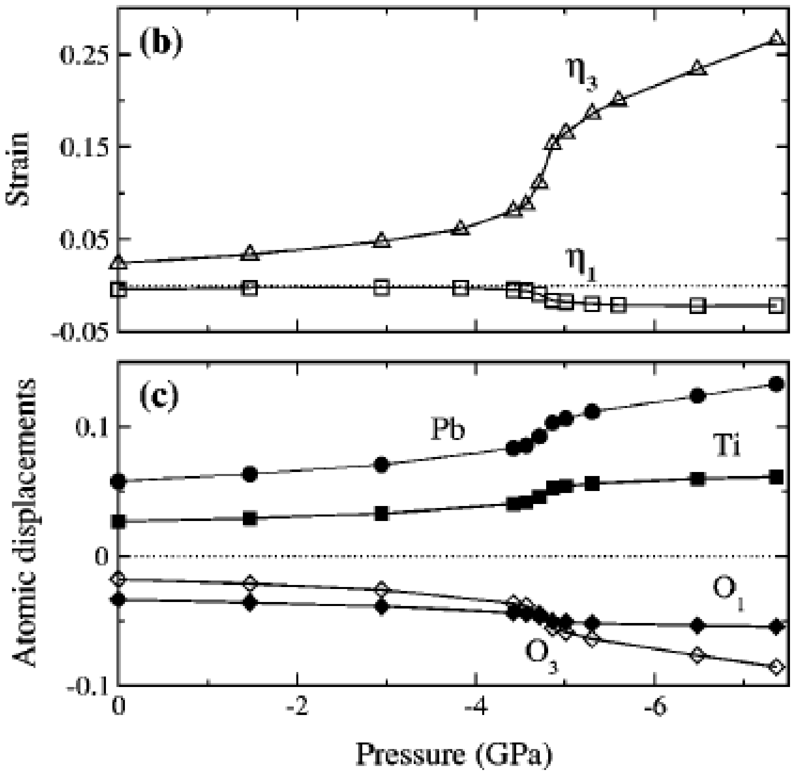
The response of insulators and semiconductors to external electric fields is of fundamental as well as practical interest. It determines their dielectric, piezoelectric, and ferroelectric behavior. Much current technological interest is focused on the use of static fields to tune properties such

Wannier functions [12], which removed the need for supercells; however, the full first-principles implementation [13] was hindered by convergence problems and proved too cumbersome to find widespread use.

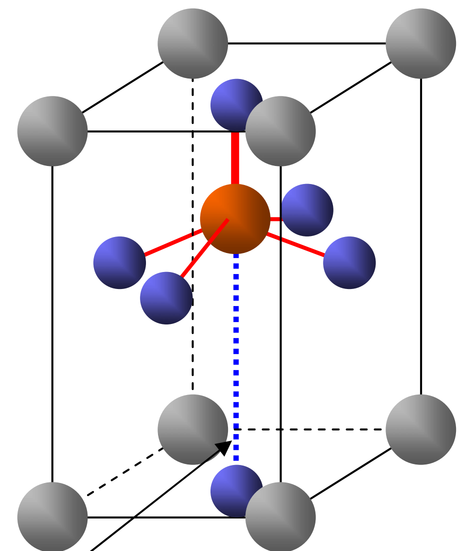
In this Letter we propose an alternative variational ap-

Phys. Rev. Lett. **89**, 117602 (2002).

# *Tetragonality enhancement due to bond elongation*




*S. Tinte, K.M. Rabe, and D. Vanderbilt, Phys. Rev. B* ***68****, 144105 (2003).*

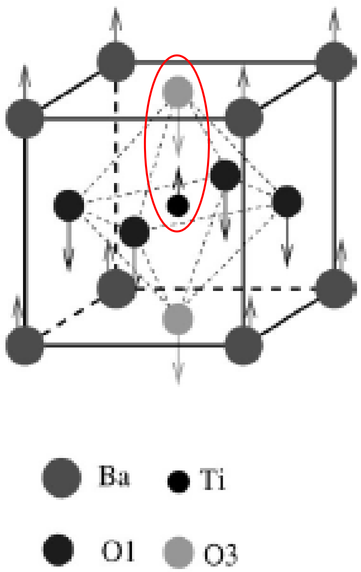


Ti-O bond is predicted to elongate under high negative hydrostatic pressure.

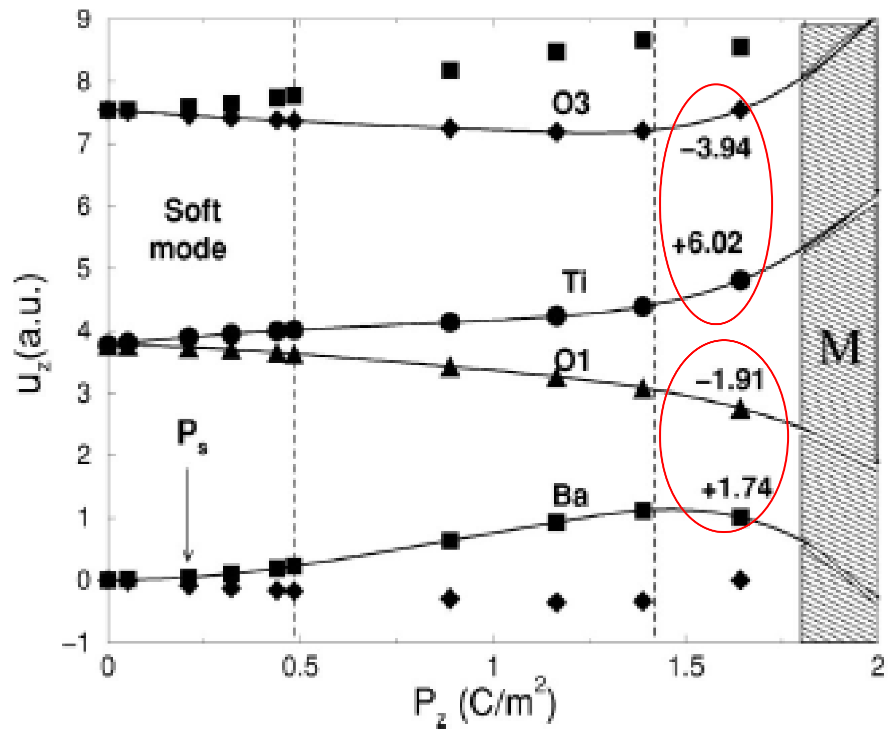
Stronger piezoelectric response is predicted in a ferroelectric that tetragonality increases as a result of the bond elongation.

# Changes in Atomic Interactions at High Fields

$BaTiO_3$




N. Sai, K.M. Rabe, and D. Vanderbilt, Phys. Rev. B **66**, 104108 (2002).



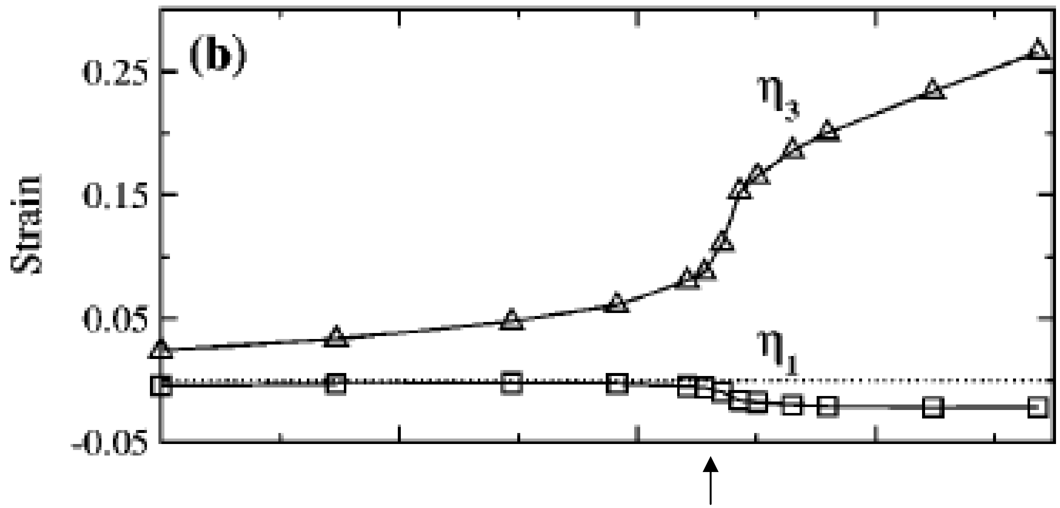

$Ti\text{-}O_3$ and $Ba\text{-}O_1$ pairs move rigidly at high fields

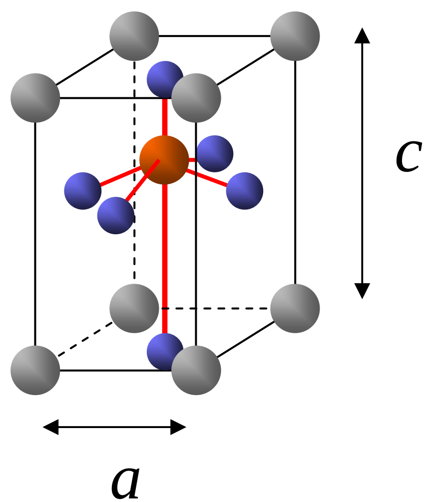
→ Phonon modes get harder, dielectric constant gets smaller

→ *Piezoelectric response should get weaker at high electric fields*

*E* > 16 MV/cm for $BaTiO_3$ or *E* > 2.5 MV/cm for $PbTiO_3$

# *An estimate of the electric field needed to reach high tetragonality*

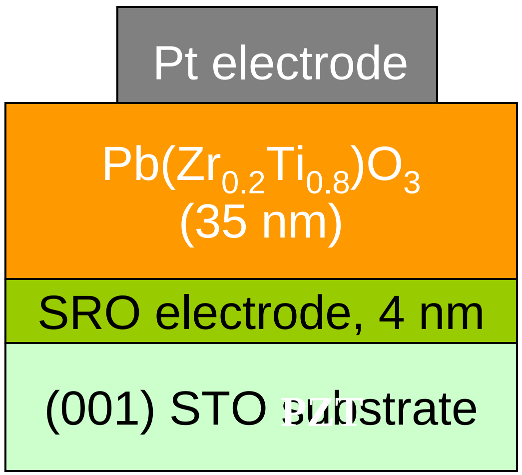


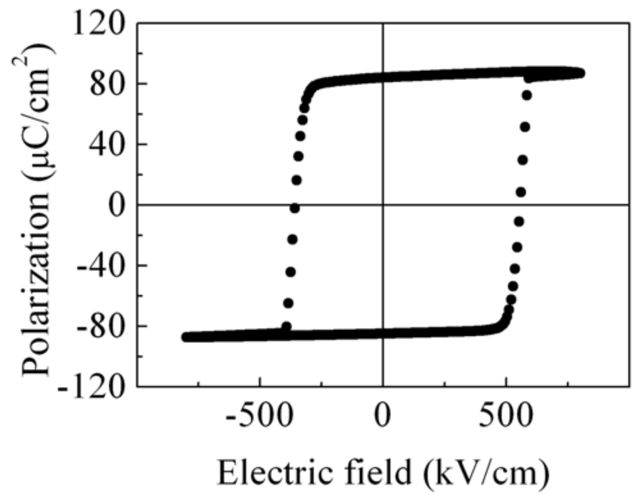

tetragonality $c/a$ ~ 1.1

Assuming $\varepsilon_3 = d_{33} \cdot E_3$ is valid at high fields and
$d_{33} \cong 45$ pm/V for a $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin film
$c/a$ ~ 1.1 can be reached at $E$ ~ 2.5 MV/cm

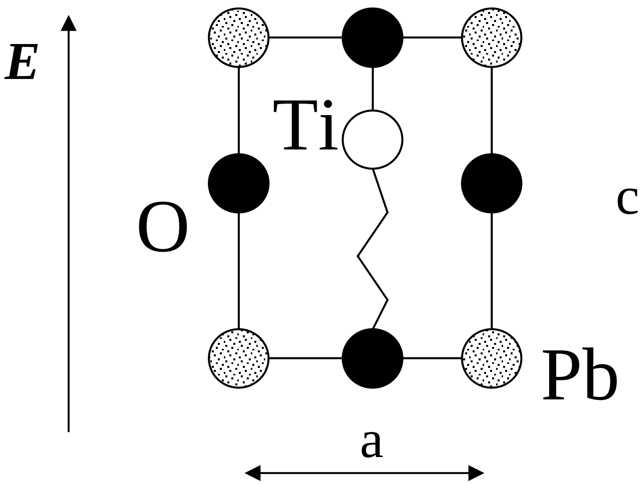
# *Ultrathin epitaxial ferroelectric thin films*

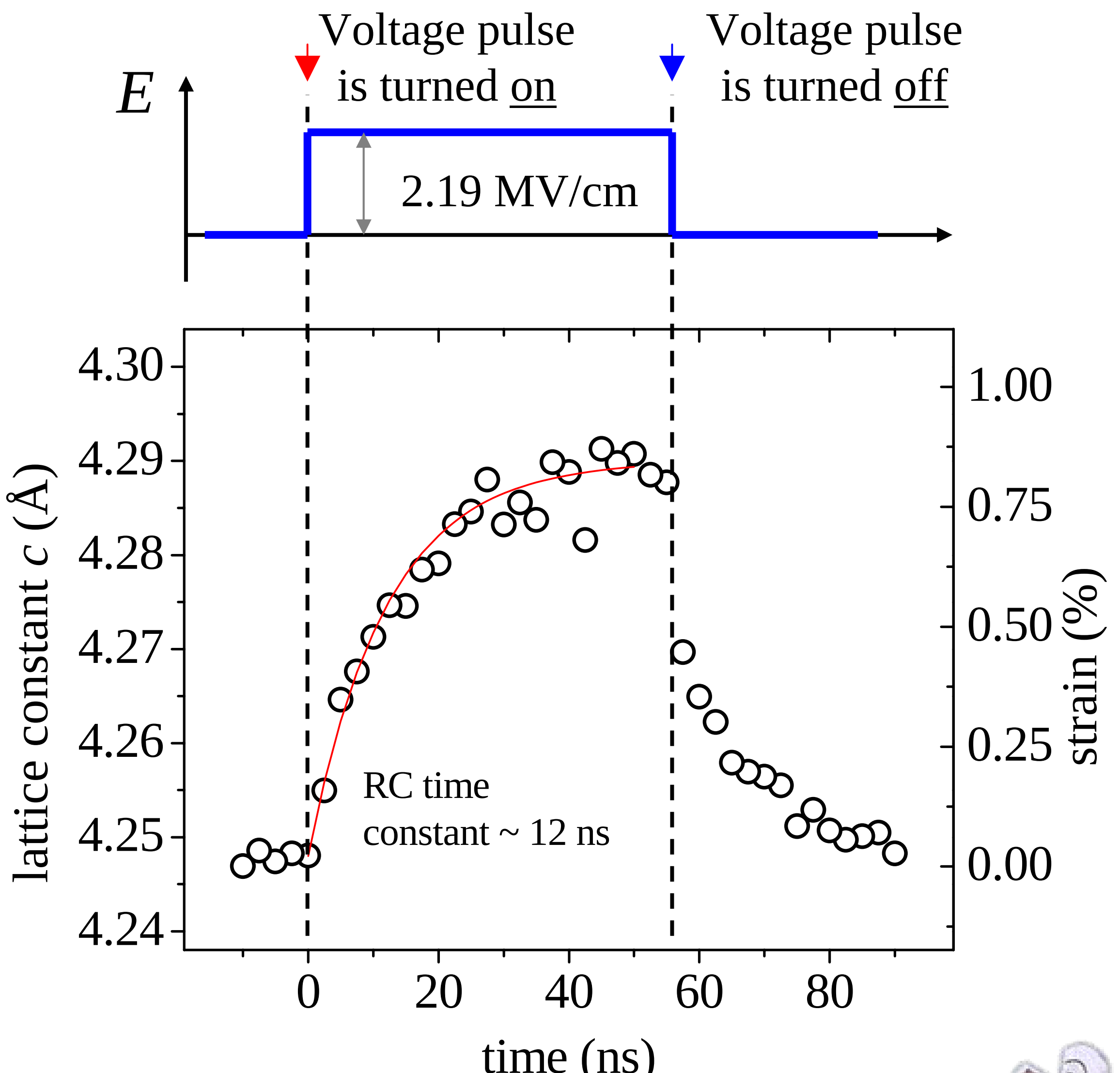



50-μm diameter
ferroelectric capacitors

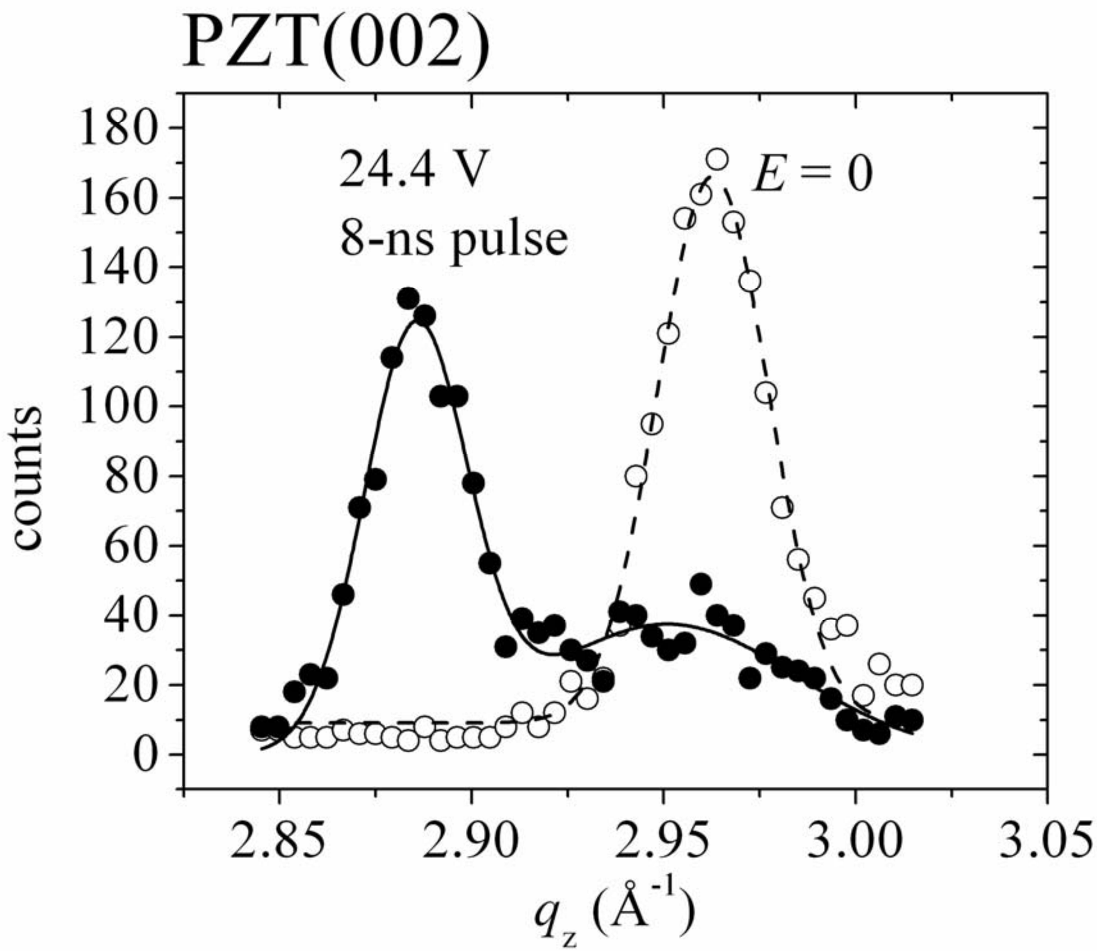


# *Structural Changes in Large Electric Fields*



# *Ultrahigh piezoelectric strain 2.69%*




A. Grigoriev, *et al*., Phys. Rev. Lett. **100** 027604 (2008).

Piezoelectric strain 2.69%
Tetragonality $c/a = 1.117$

# *Piezoelectric strain at high electric fields*

line: $\varepsilon_3 = d_{33} \cdot E_{3,}\ d_{33} \cong 45$ pm/V

Three regimes:

1) $E < 1.8$ MV/cm

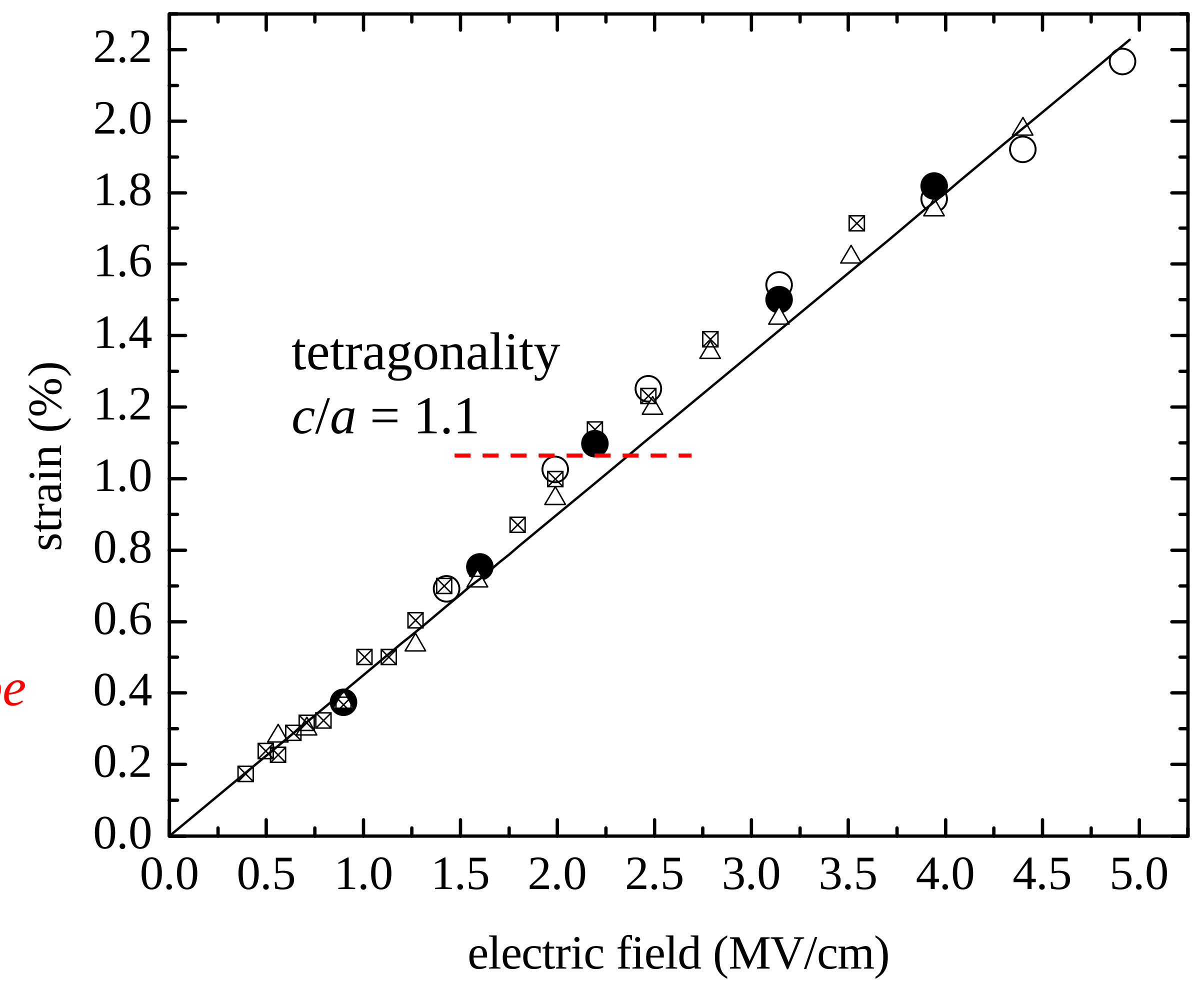
*Exceeds predicted piezoelectric strains.*

2) $E \sim 2$ MV/cm

*Meets predicted bond elongation induced by high tetragonality.*

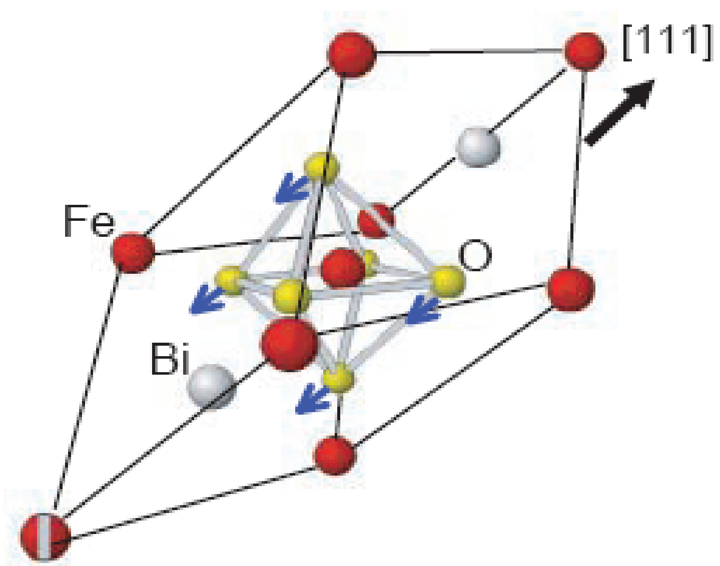
3) $E > 2.5$ MV/cm

*Indicates the system might be approaching the regime of strong repulsive interaction.*

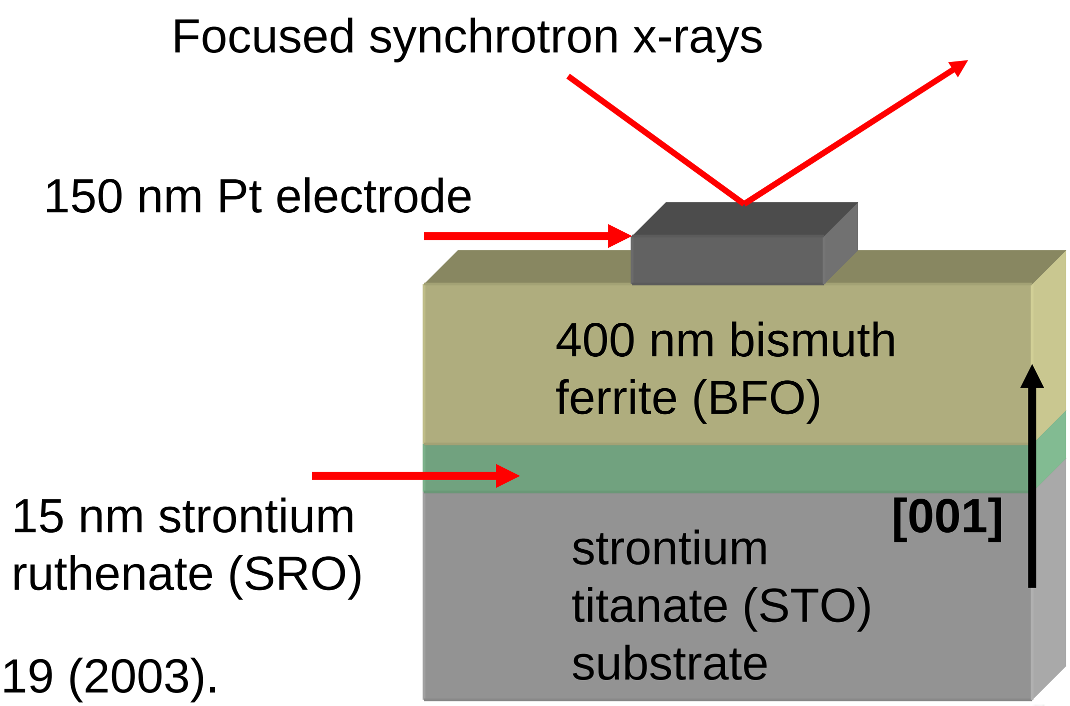


# *$BiFeO_3$ Thin Films*

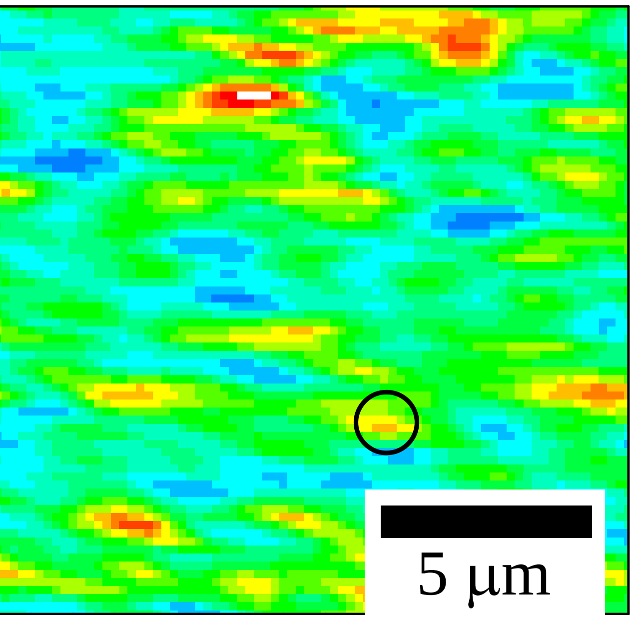
1) In thin films, bismuth ferrite is believed to be rhombohedral. Is it?
2) How many structural variants exist? How do they switch polarization?
3) How does the magnetism change in applied electric fields?




*e.g*. Wang *et al.* Science **299**, 1719 (2003).

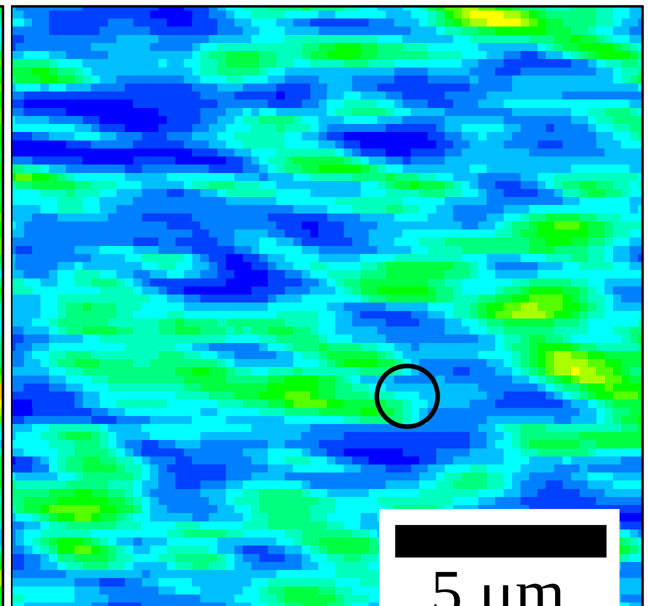


# Polarization Switching in $BiFeO_3$



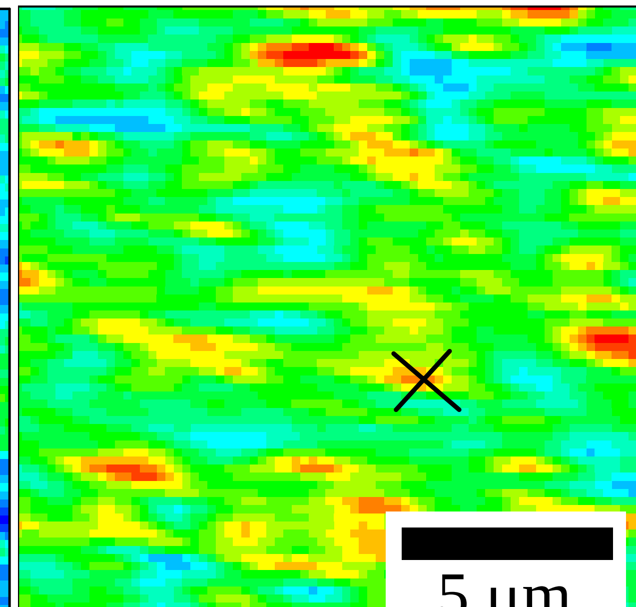

poled with +10 V

*Integrated intensity: 1*




poled with +10 V

*Integrated intensity: 0.76*



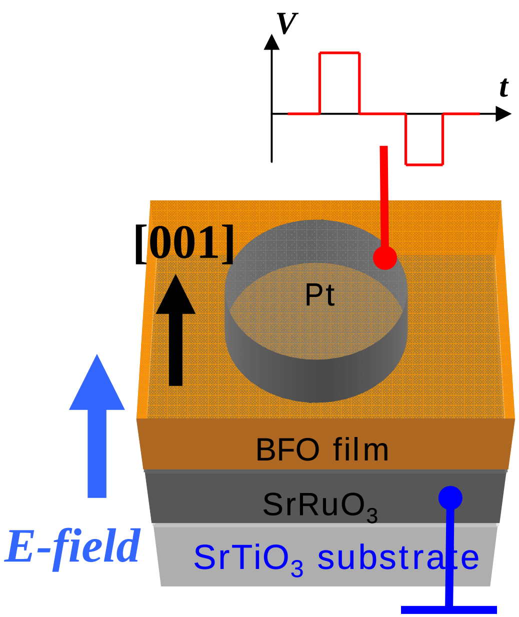

poled with +10 V

*Integrated intensity: 1.1*

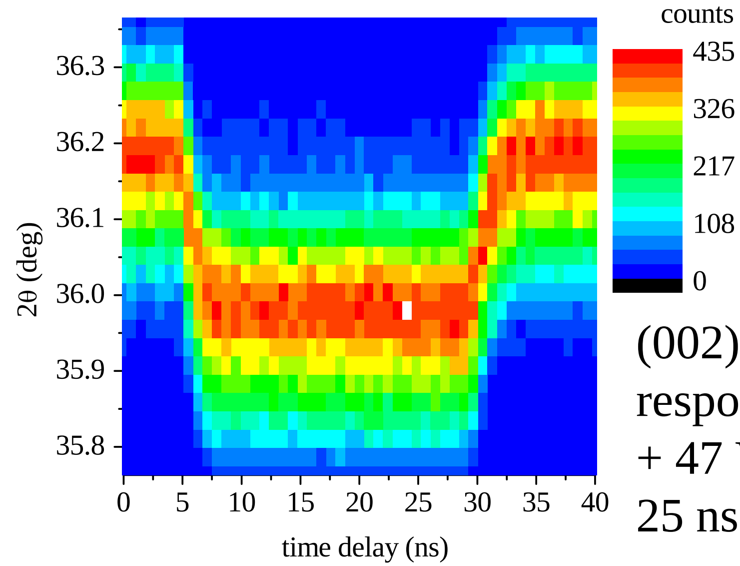
# *Fast piezoelectric response of $BiFeO_3$*

450-nm epitaxial multiferroic film $BiFeO_3$ (BFO)

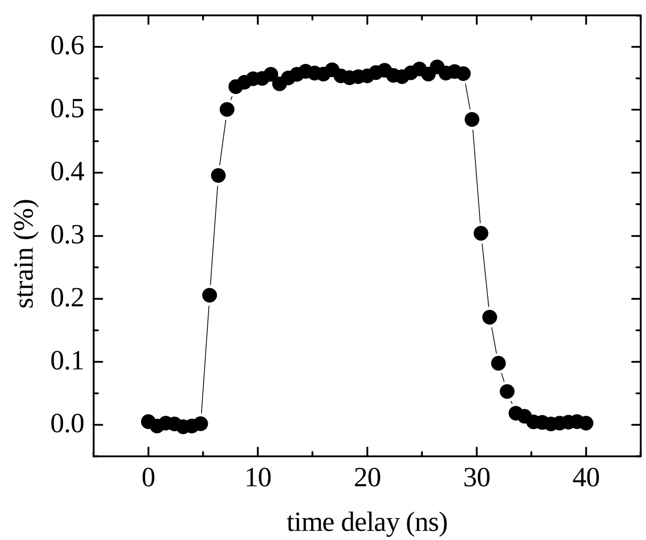
- 100-nm $SrRuO_3$ epitaxial oxide film bottom electrode
- Pt top electrode




**Multiferroic capacitor**

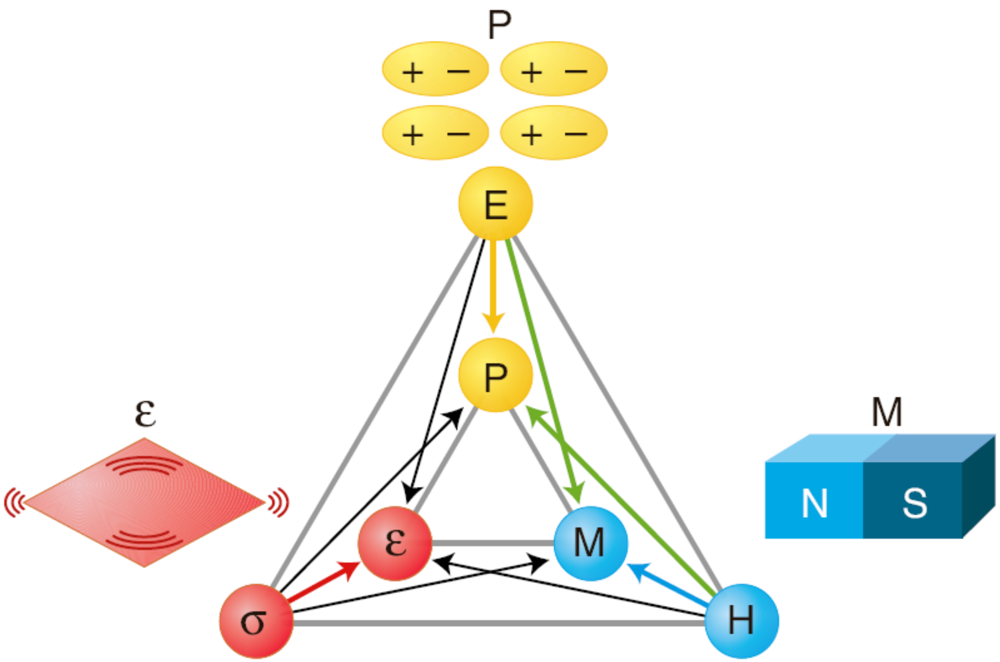



(002) Bragg peak response to + 47 V (1.04 MV/cm) 25 ns square pulse

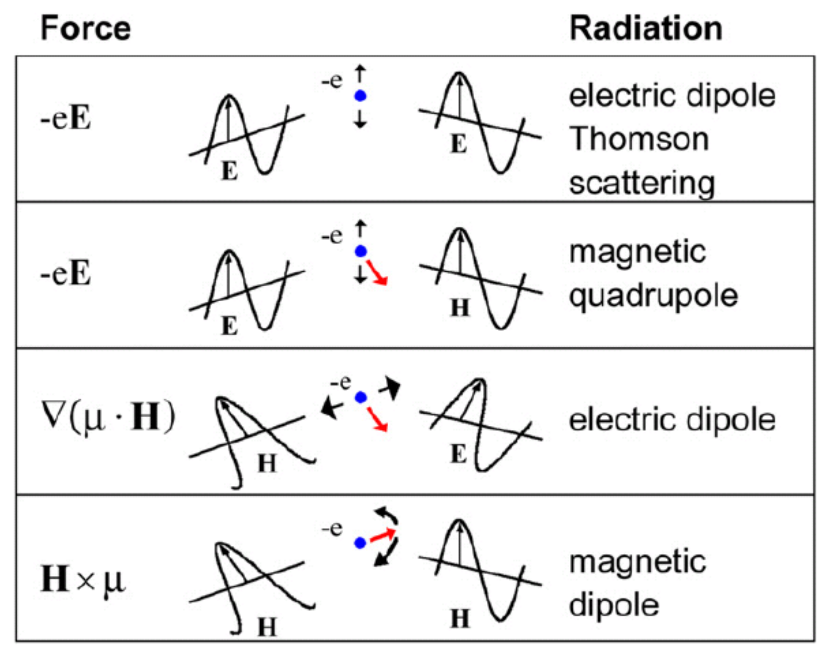



0.55% strain in thin BFO film at E=1.04 MV/cm

# *Dynamics of the "Other" Multiferroic Relationships*




N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).




Non-resonant magnetic x-ray scattering

# Conclusion

- Several important experimental directions in nanoscience
- Experiments can start immediately, but techniques and ideas can be widely applicable