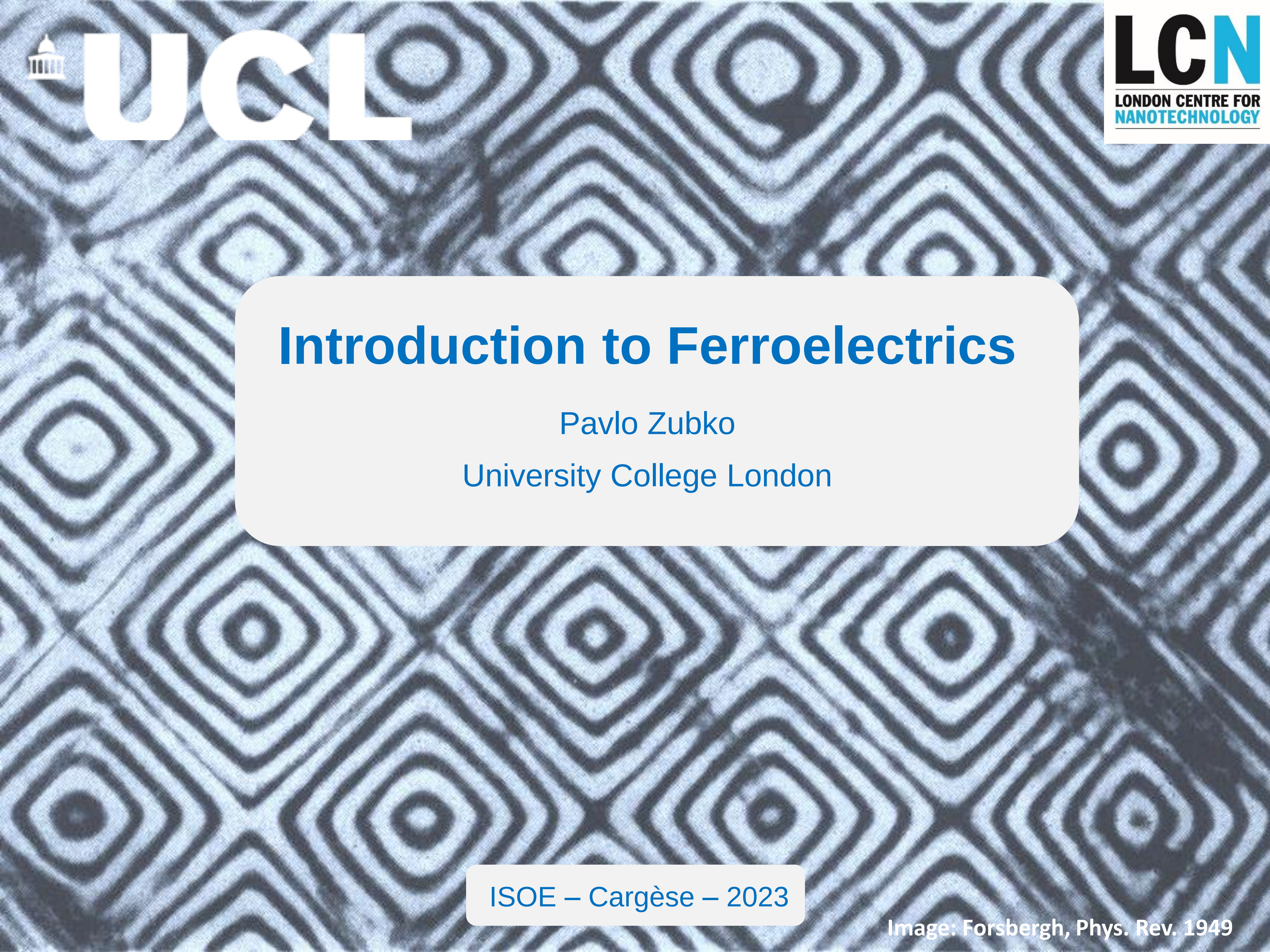


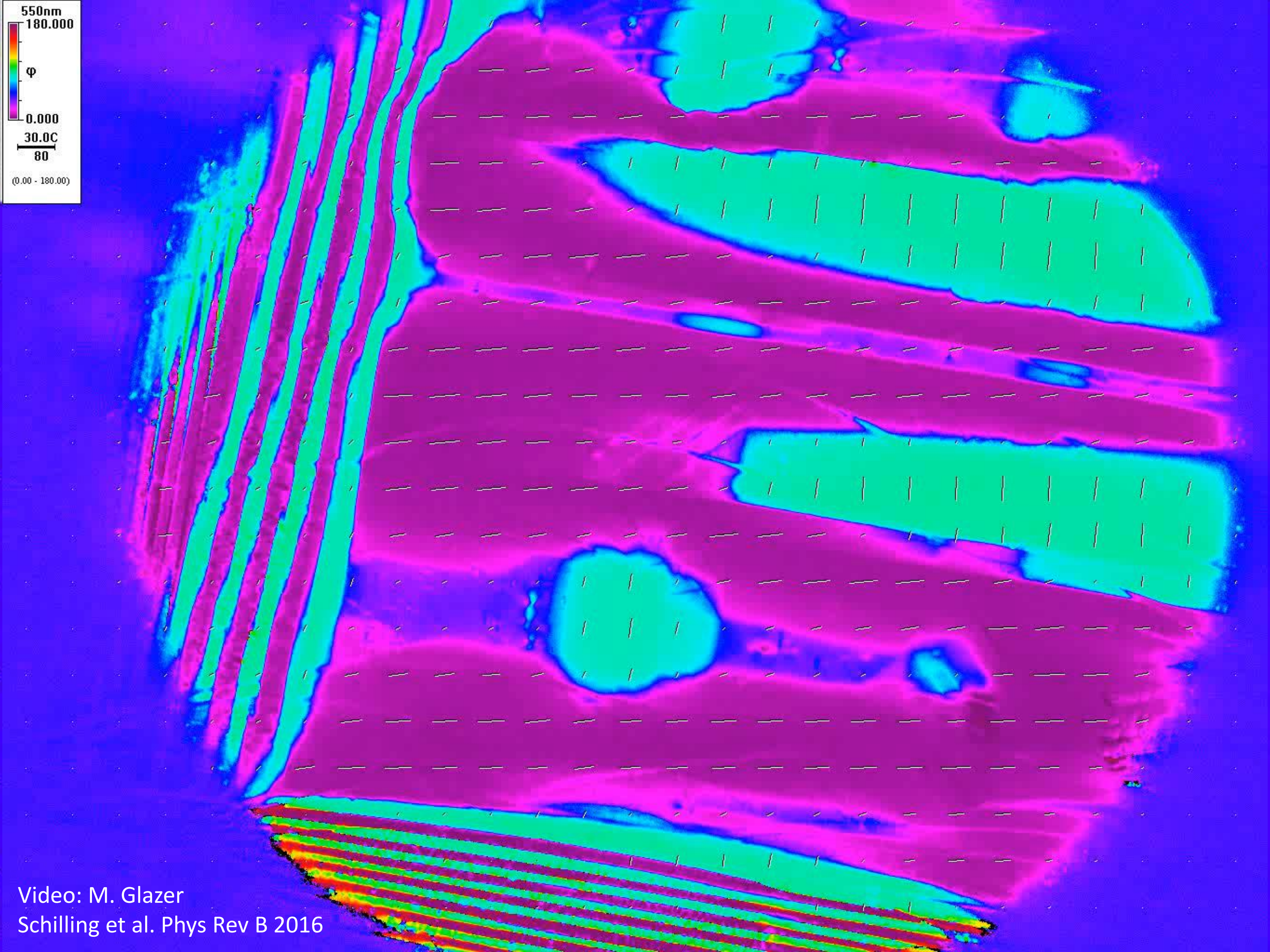
Introduction to Ferroelectrics

Pavlo Zubko

University College London

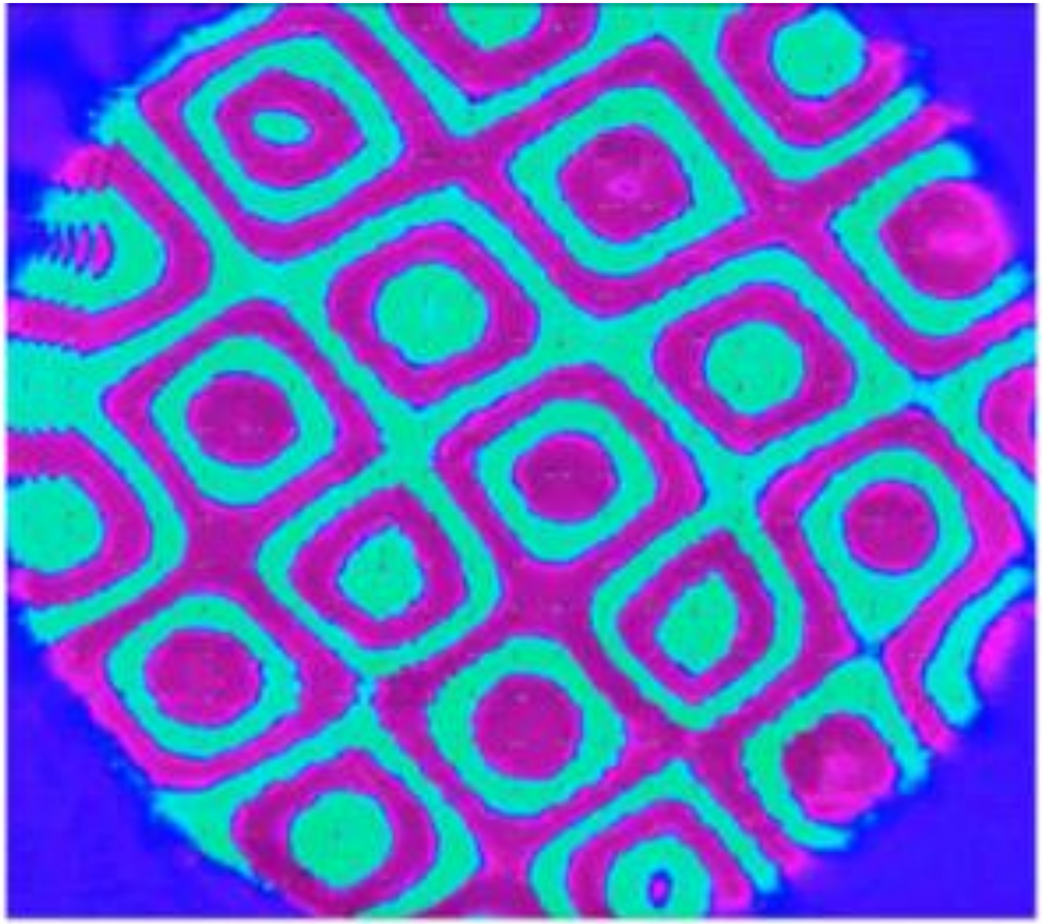
ISOE – Cargèse – 2023

Image: Forsbergh, Phys. Rev. 1949



Video: M. Glazer
Schilling et al. Phys Rev B 2016

Forsbergh patterns in $BaTiO_3$



Schilling et al. Phys Rev B 2016

Forsbergh (Phys. Rev. 1949)

Discovery of ferroelectricity

PIEZOELECTRIC AND ALLIED PHENOMENA IN ROCHELLE SALT.

BY JOSEPH VALASEK.

(AKA potassium sodium tartrate tetrahydrate, $KNaC_4H_4O_6.4H_2O$)

Joseph Valasek in 1922.

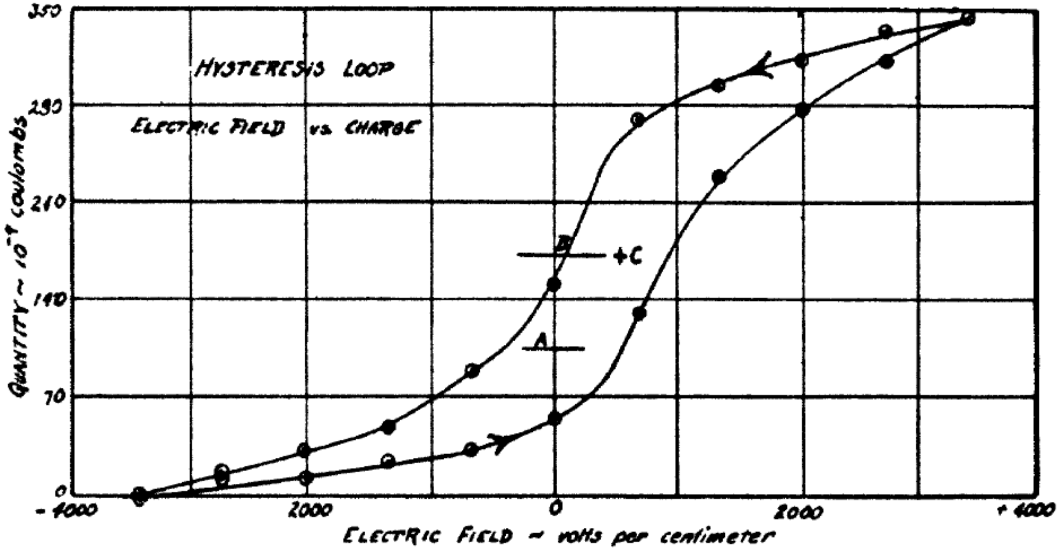
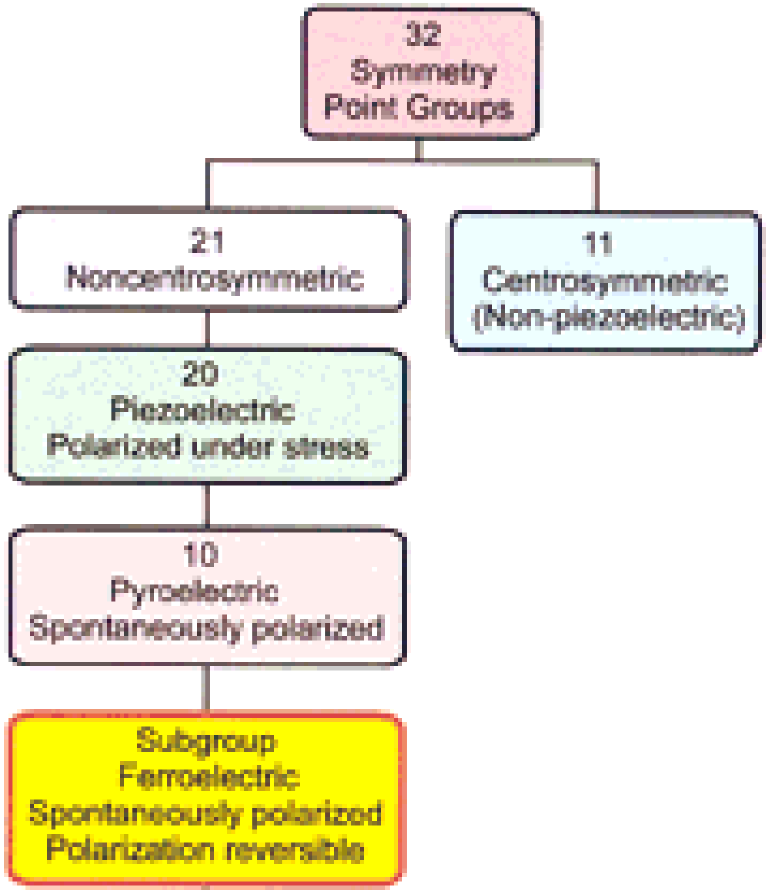


Fig. 4.

Physical Review 1921

Ferroelectrics named after ferromagnets (not because they contain Fe…but there are some, e.g. $BiFeO_3$)

Basic definitions and crystallography



Haertling J. Am. Cer. Soc. 1999

Ferroelectrics:

1) Possess spontaneous polarisation

(restricted by symmetry to pyroelectric point groups)

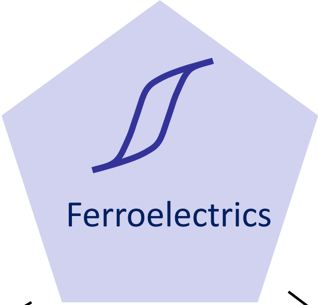
+

2) Polarisation must be switchable by applied field (below breakdown field)

(practical restriction)

- All ferroelectrics are piezoelectric & pyroelectric

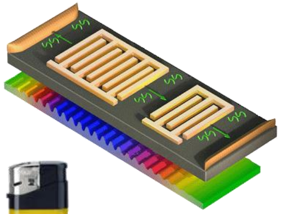
Properties & applications



Ferroelectrics

Piezoelectric

Transducers, actuators, SAW, MEMS

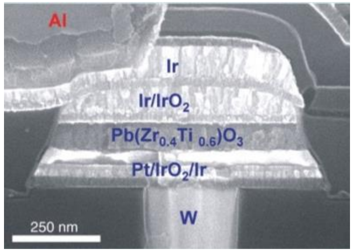


Pyroelectric

IR imaging

Switchable polarisation

Non-volatile RAM

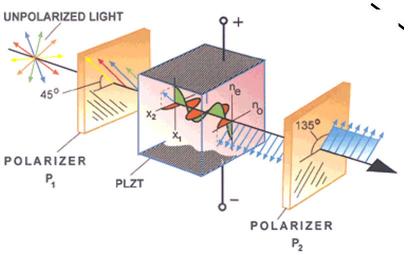


High dielectric constants

Multilayer capacitors

Nonlinear optical properties

Frequency doubling, electro-optical modulators



crystals – ceramics – thin films

A few examples of ferroelectrics

Rochelle salt

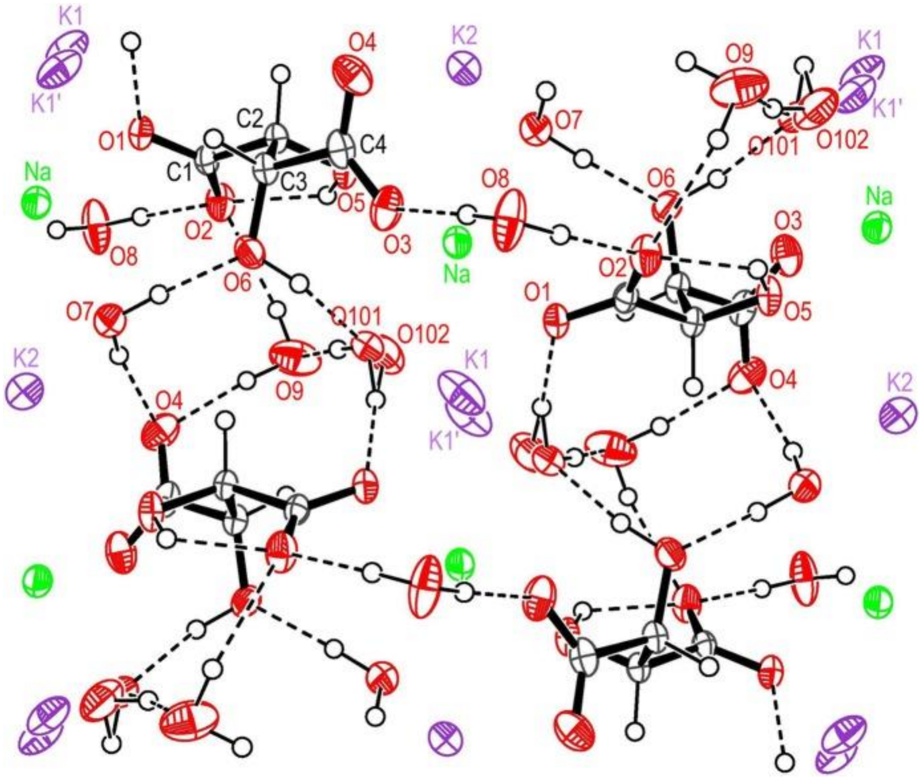


Image: Mo et al. IUCrJ 2015

Wide range of crystal structures from very complex to very simple

- KH_2PO_4 (KDP),
- $(NH_2CH_2COOH)_3H_2SO_4$ (TGS)
- P(VDF-TrFE)
- $NaNO_2$
- HCl, HBr
- and many, MANY others

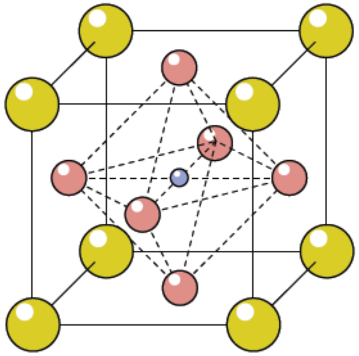
<ins>Oxides</ins>

Perovskites

- $BaTiO_3$, $PbTiO_3$, $KNbO_3$, $BiFeO_3$, Pb(Zr,Ti)O_3 (PZT)…

Other oxides:

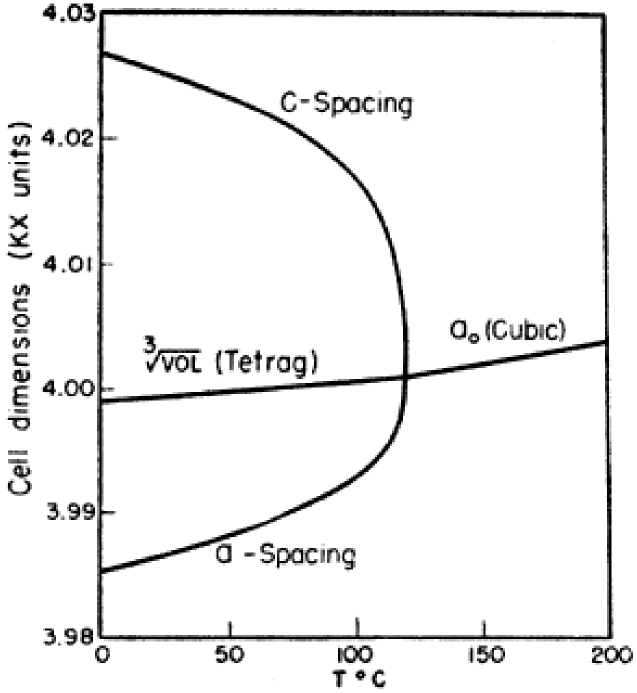
- $LiNbO_3$, $LiTaO_3$, $SrBi_2Ta_2O_9$ (SBT), $Bi_4Ti_3O_{12}$, HfO_2 …



$BaTiO_3$
(1944)

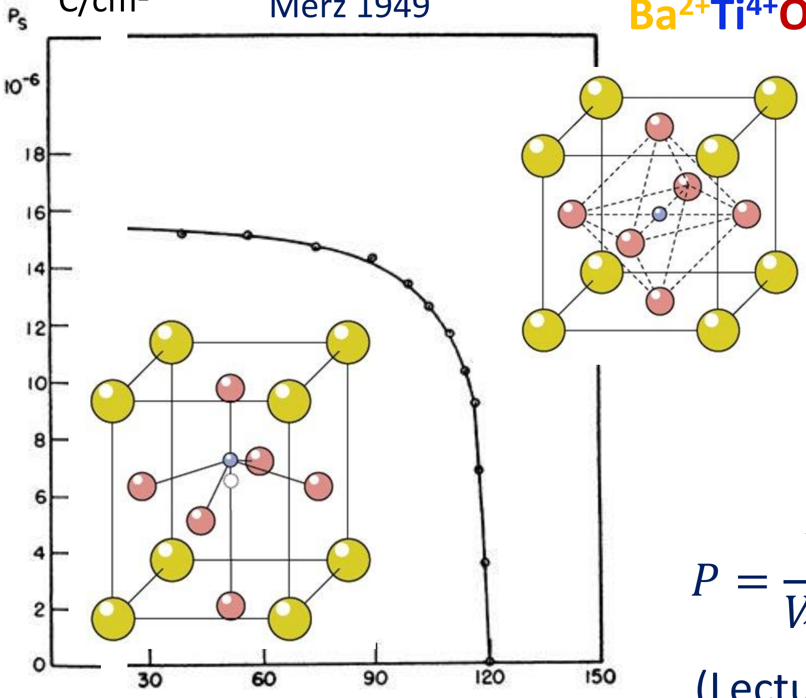
Structural phase transition in BaTiO$_3$

Megaw 1947



C/cm^2 Merz 1949

Ba^{2+}Ti^{4+}O$_3$$^{2-}$



$$P = \frac{1}{V_{uc}} Z^* u$$

(Lecture by Karin Rabe!)

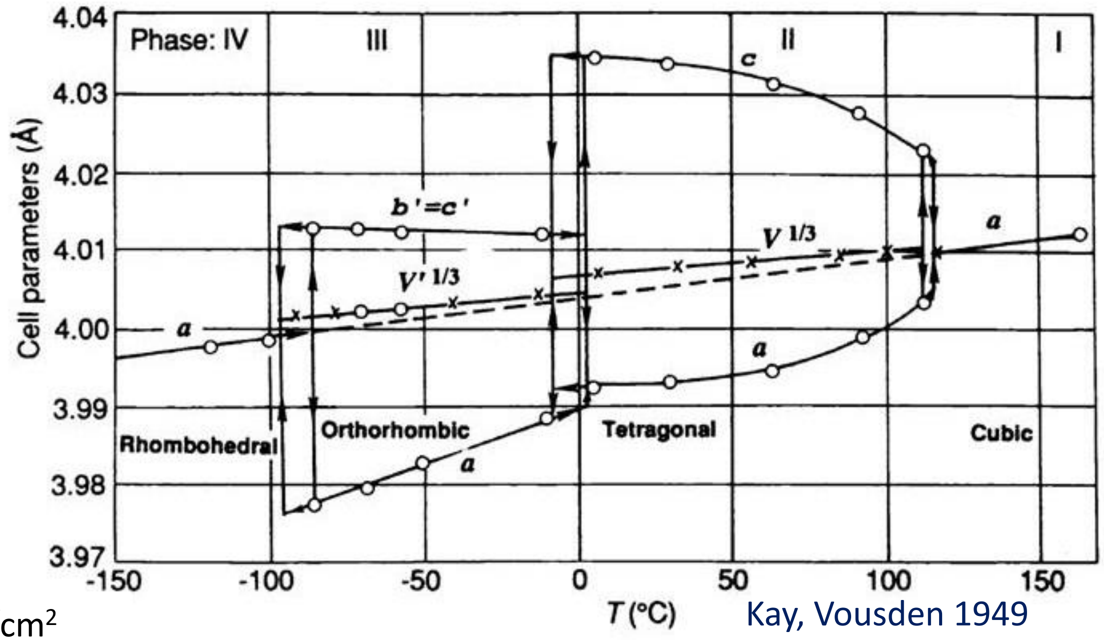
Phase transition:

$T > T_C$ - cubic, centrosymmetric

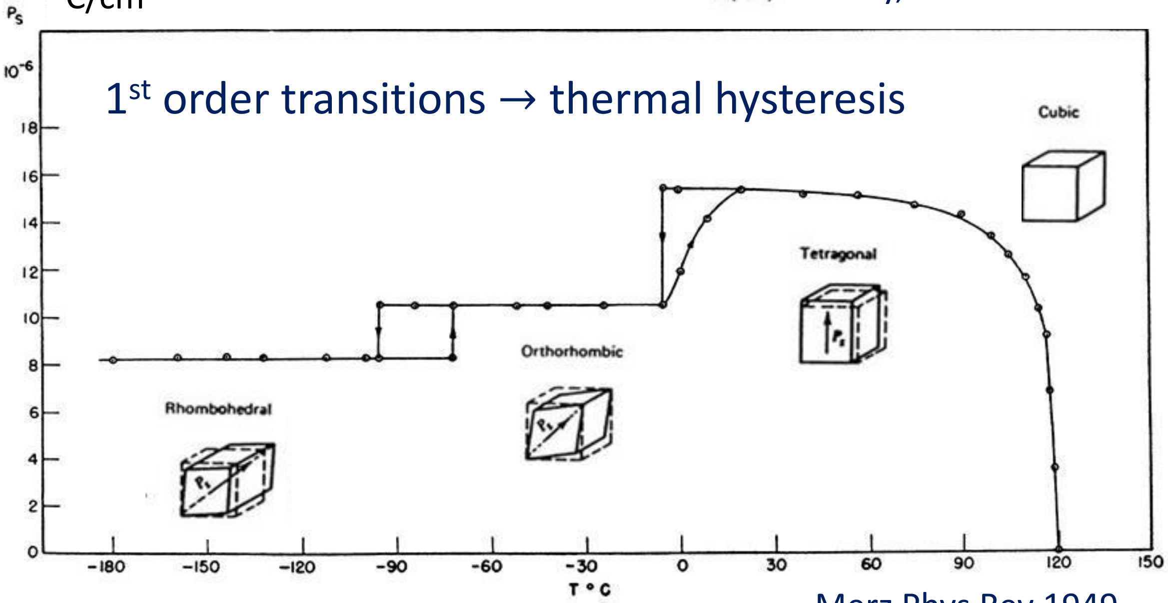
$T < T_C$ - tetragonal, polar

Cooperative alignment of dipoles → macroscopic polarisation

Hold on…there are more!



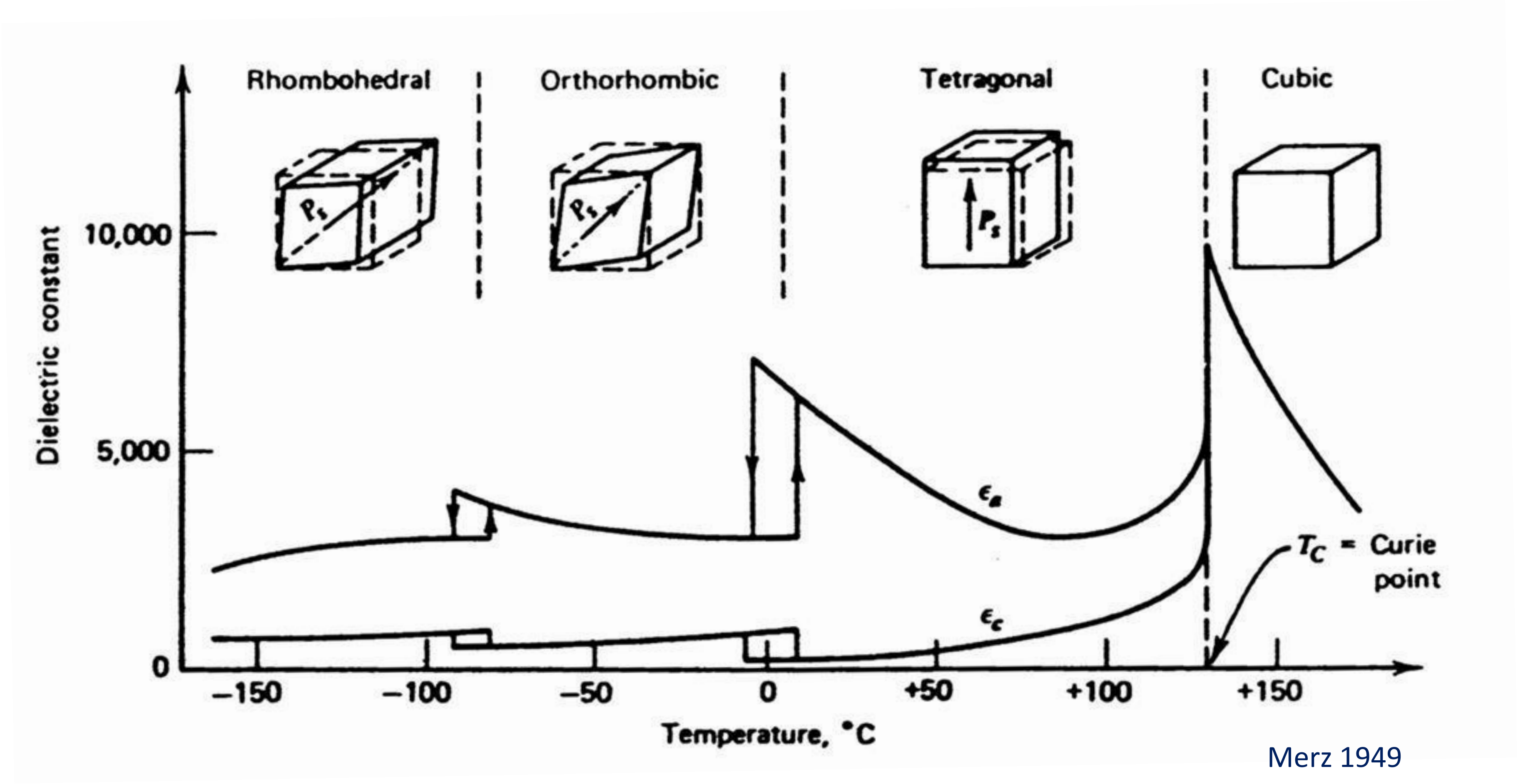
Kay, Vousden 1949



1st order transitions → thermal hysteresis

Merz Phys Rev 1949

Massive dielectric response!



Merz 1949

Huge dielectric constants! Especially near T_C

$BaTiO_3$-based dielectrics used in multilayer capacitors

Phenomenology

Landau theory

- based on symmetry considerations
- provides no microscopic insight…but…
- links different macroscopic properties through thermodynamics

Landau anzatz: expand free energy in powers of order parameter(s).

Primary OP = P (proper ferroelectrics)

$$F = \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 + \cdots - EP$$

Allowed terms constrained by symmetry (free energy must describe ferro- and para- phase)

Landau – Devonshire

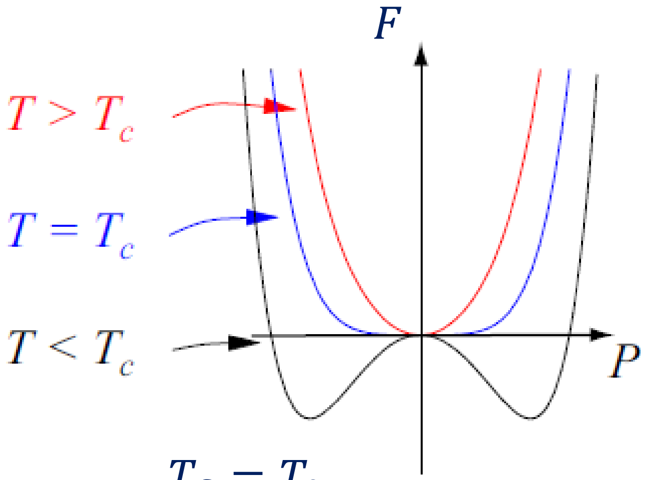
Phenomenology: 2nd order transitions

Simplest potential describing a phase transition

$$F = \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 - EP$$

Assume:

- $\alpha = \alpha_0(T - T_0)$
- $\beta > 0$ & temp. independent (last term in expansion must be positive for stability)



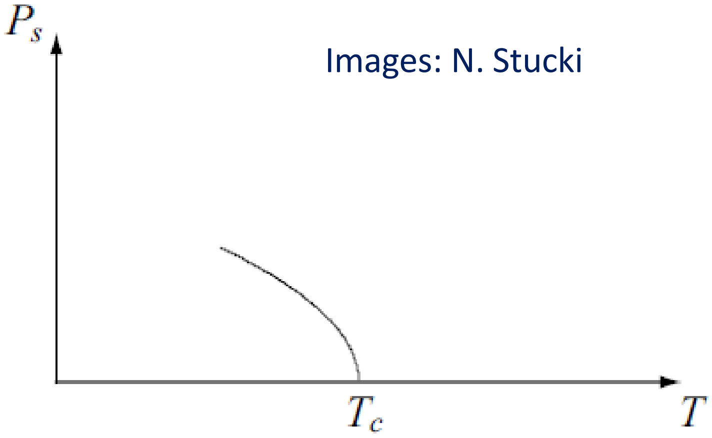
$T_C = T_0$

In zero field, equilibrium when $\frac{\partial F}{\partial P} = 0$

$$\frac{\partial F}{\partial P} = \alpha P + \beta P^3 = 0$$

→ spontaneous polarisation P_s

$$P_s^2 = -\frac{\alpha}{\beta} = \frac{\alpha_0(T_0 - T)}{\beta}$$



Images: N. Stucki

2nd order PT – OP changes continuously

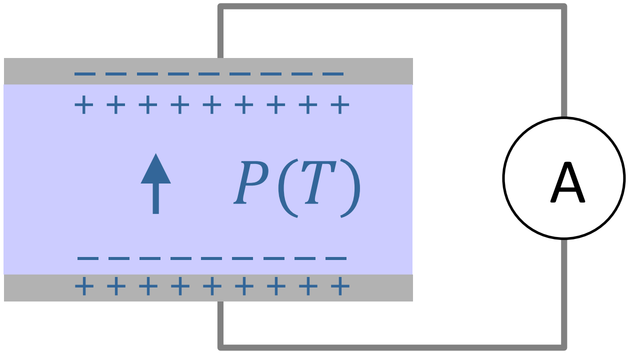
Phenomenology: pyroelectricity

Pyroelectricity

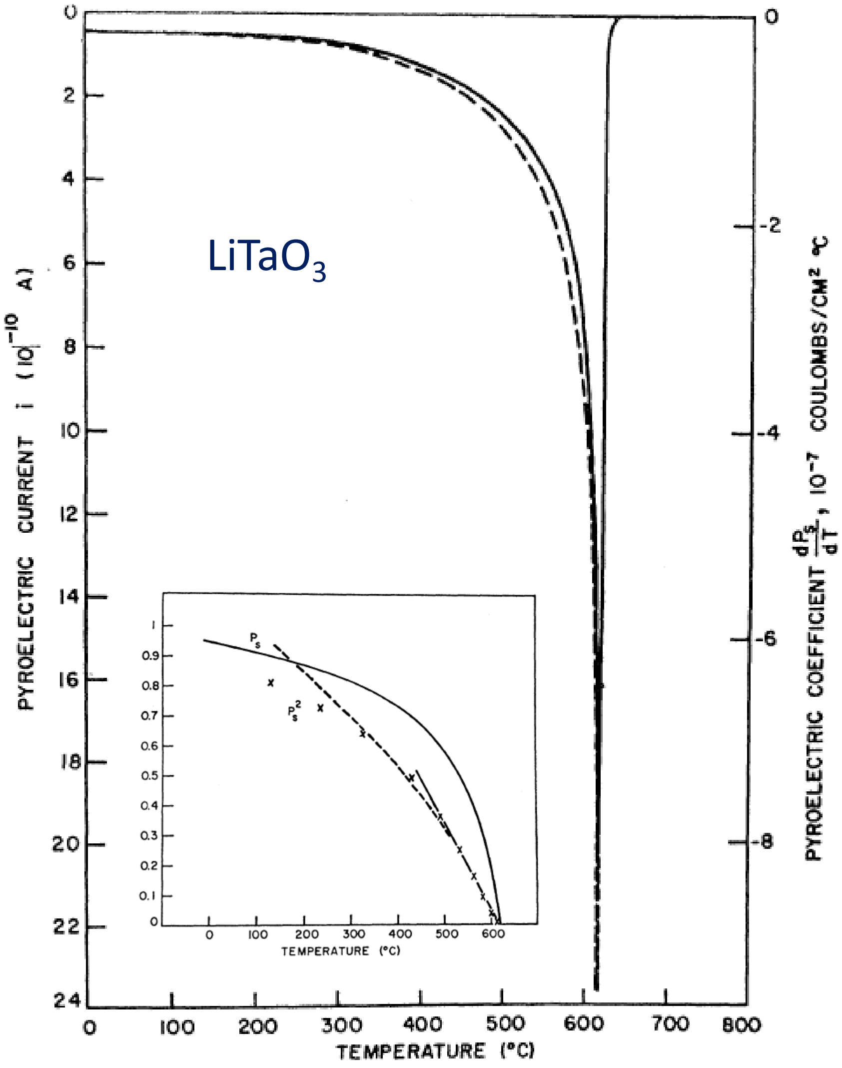
$$\pi = \frac{dP}{dT}$$

Change T, measure short circuit pyroelectric current

$$j = \frac{dD}{dt} = \frac{dP}{dt}$$



$$D = P + \epsilon_0 E = P \quad (E = 0)$$



Glass, Phys. Rev. 1968

Phenomenology: homogeneous switching

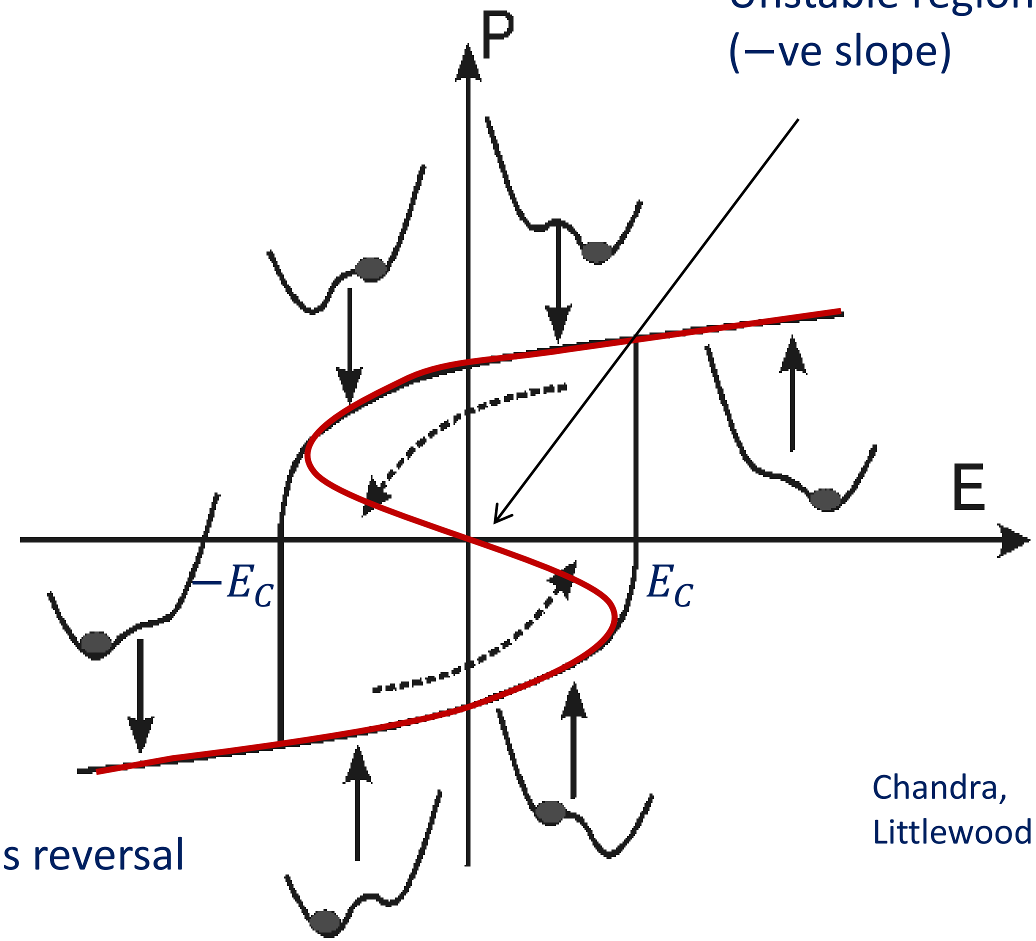
$$F = \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 - EP$$

In electric field, $\frac{\partial F}{\partial P} = 0$ gives

$$\alpha P + \beta P^3 - E = 0$$

→ Ferroelectric hysteresis

→ Intrinsic coercive field E_C



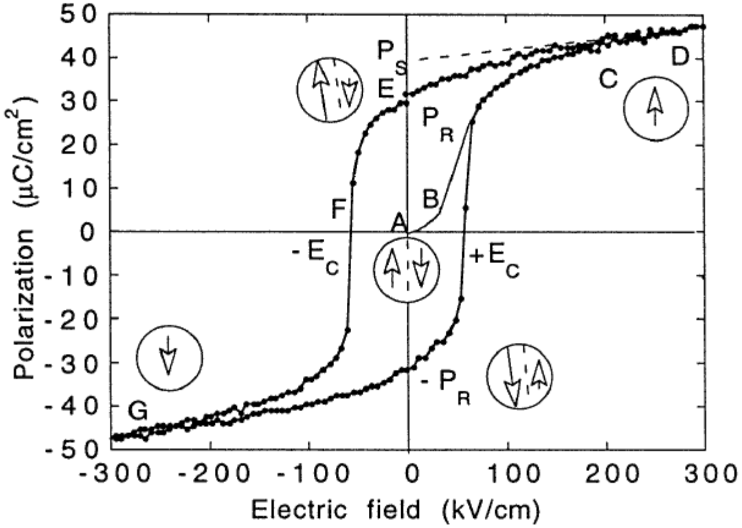
Chandra, Littlewood

Intrinsic coercive field (homogeneous reversal of polarisation)≫ experimental E_C

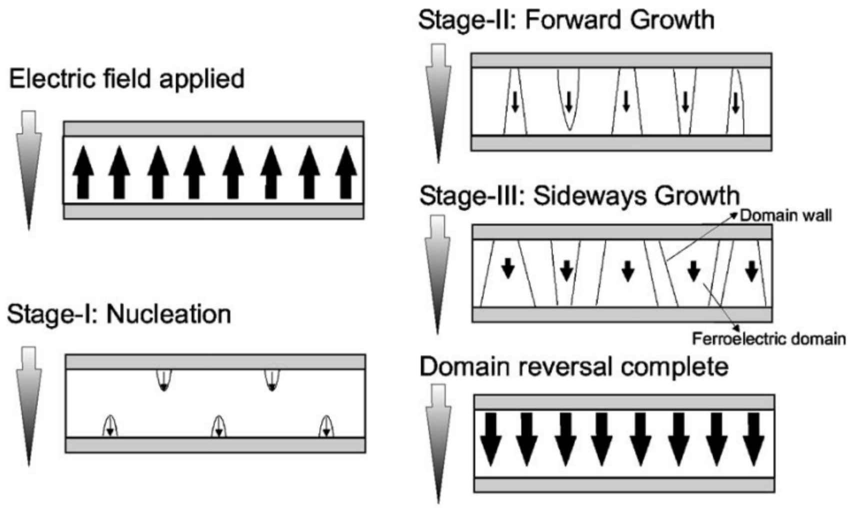
→ In practice switching is domain mediated and the intrinsic coercive field is not observed

Polarisation switching

Switching proceeds via domain nucleation and growth



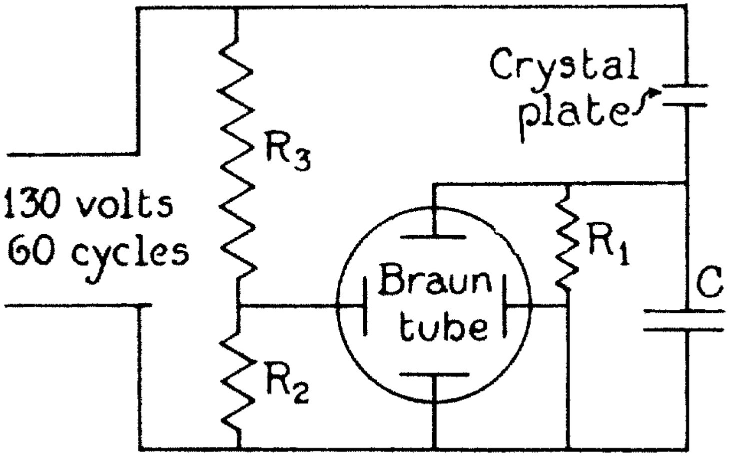
Damjanovic, Rep. Prog. Phys. 1998



Dawber et al. Rev. Mod. Phys. (2005)

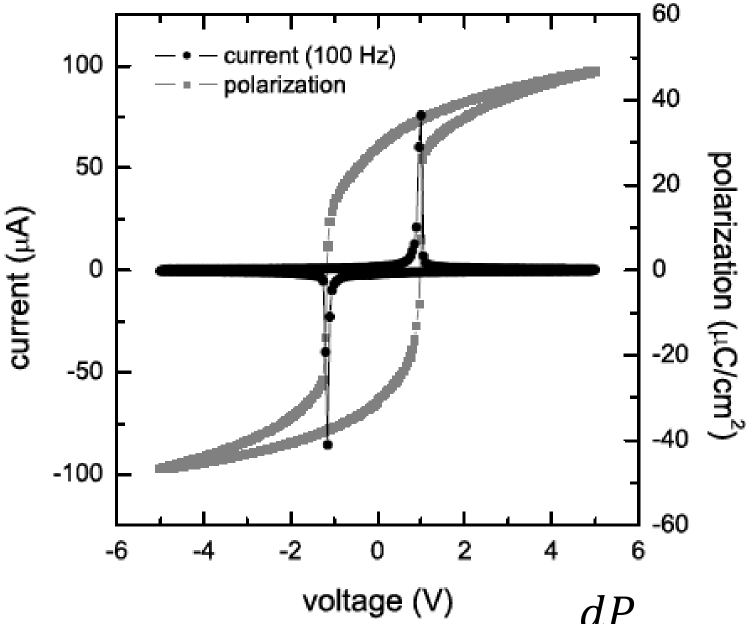
Switching is usually inhomogeneous (nucleation at predetermined sites)

Measuring polarisation reversal

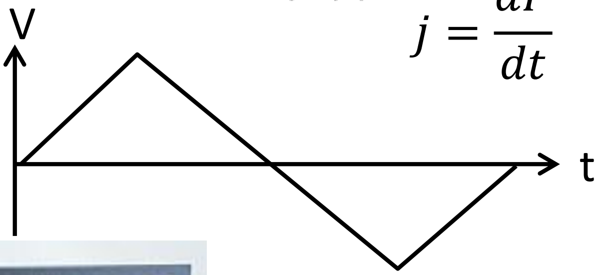


Sawyer-Tower method

Sawyer, Tower, Phys. Rev. 35, 269 (1930)

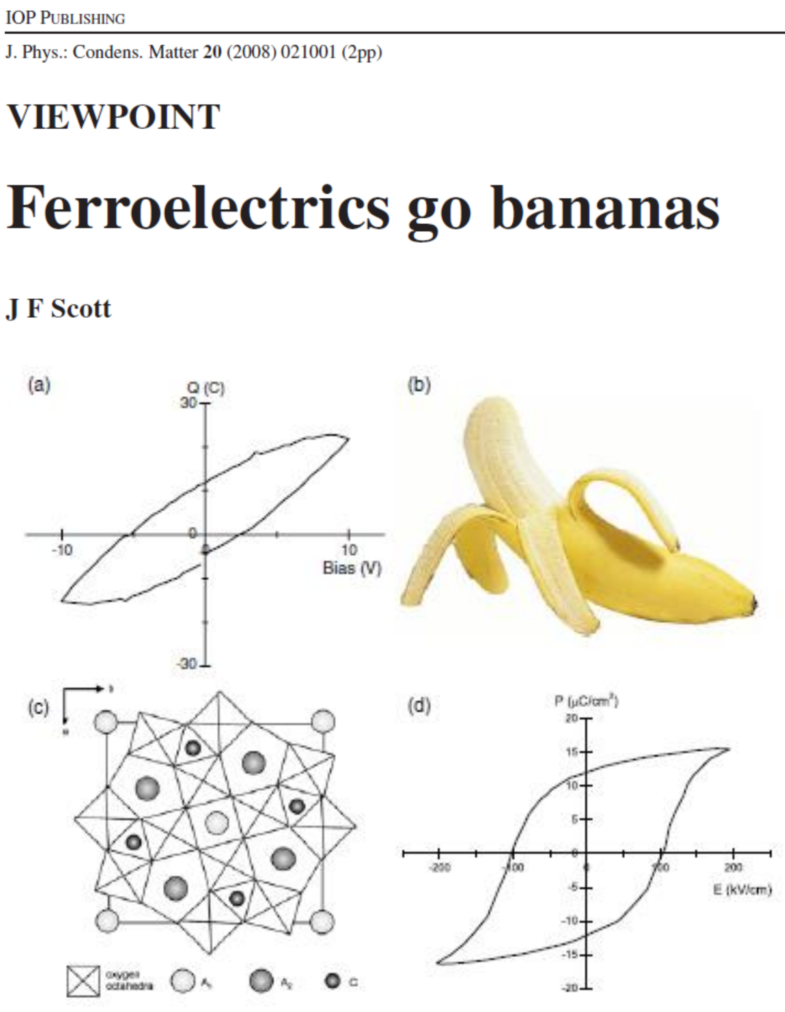


$$j = \frac{dP}{dt}$$



Commercial testers

Beware of bananas!



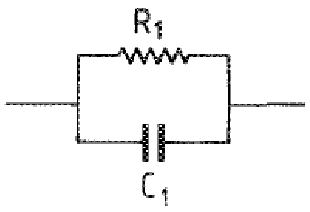
IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 021001 (2pp) doi:10.1088/0953-8984/20/02/021001

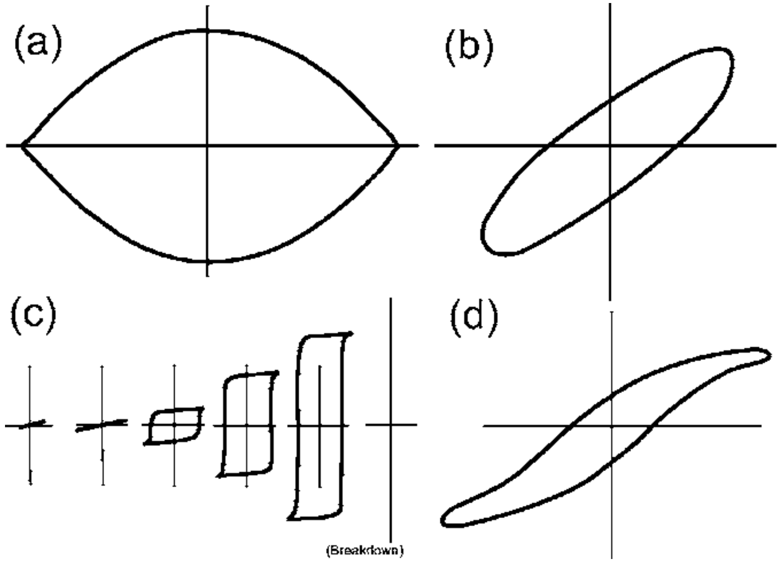
VIEWPOINT

Ferroelectrics go bananas

J F Scott



$$j = \frac{dP}{dt} + \sigma_{dc} E$$



Common hysteresis artifacts:

(a) dead short

(b) linear lossy dielectric,

(c) saturated amplifier

(d) nonlinear lossy dielectric.

Dawber et al. Rev. Mod. Phys. (2005)

Measuring remnant polarisation

(Positive-Up-Negative-Down)

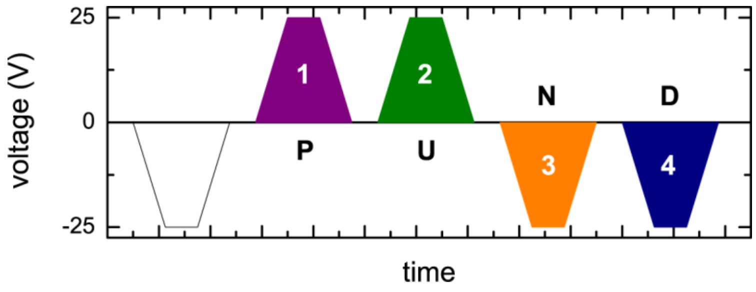


Image: N. Stucki

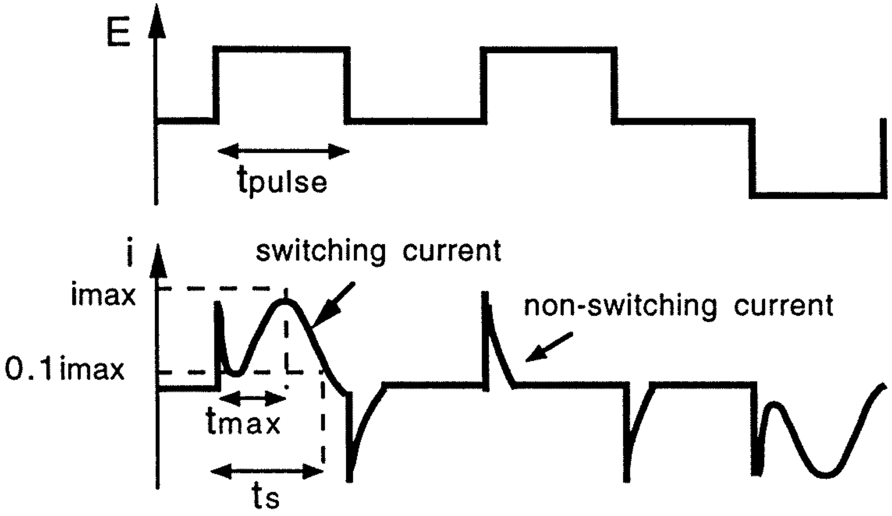
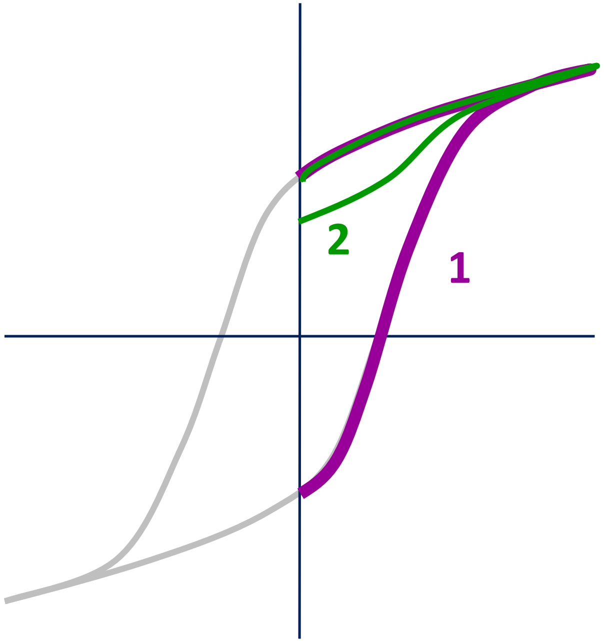


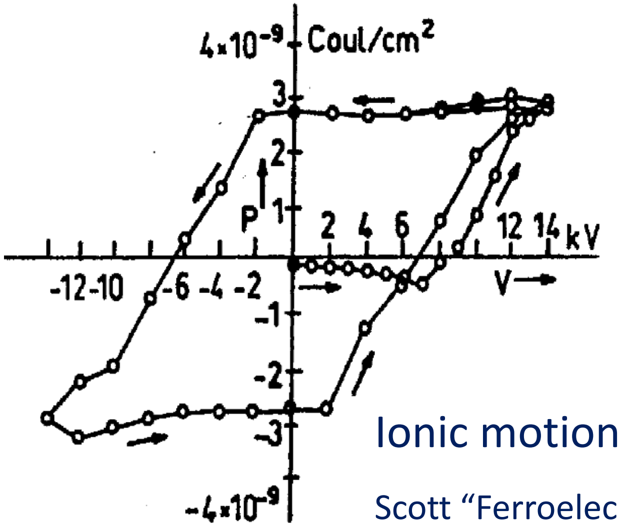
Image: Damjanovic, Rep. Prog. Phys. 1998



- Look at switching current
- Frequency dependence
- PUND

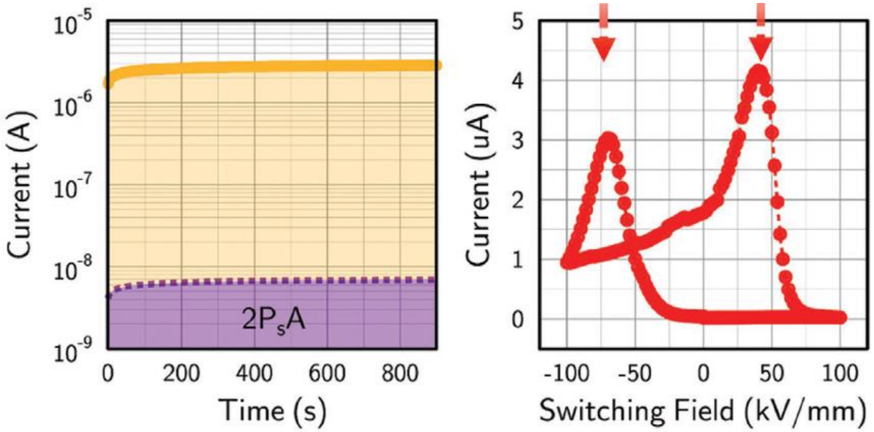
Note: only measure **changes** in polarisation

More subtle artefacts



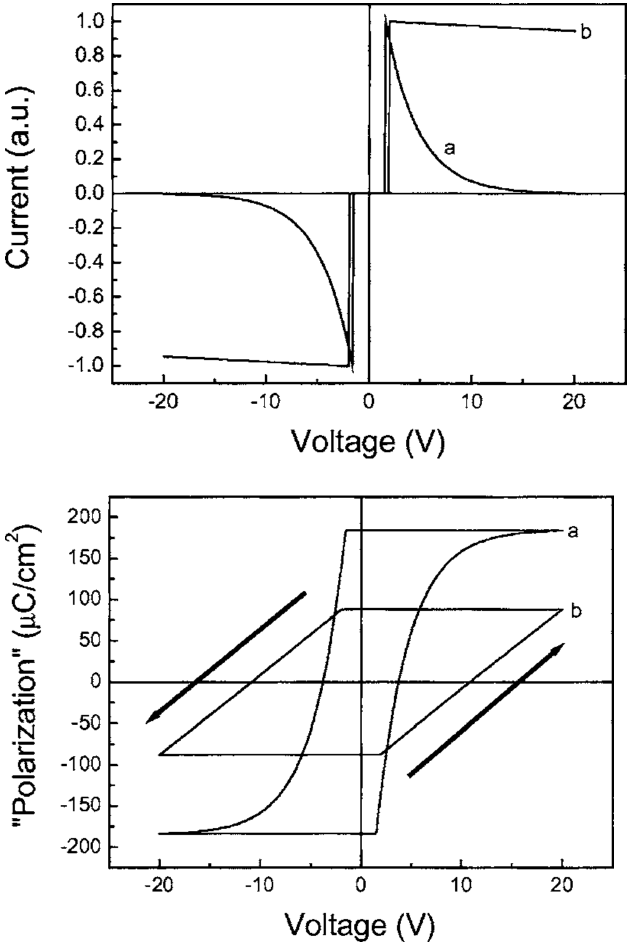
Ionic motion (electrets)

Scott “Ferroelectric Memories”



Domain wall conductivity

McClusky et al. Adv. Func. Mater. 2020



Emission from traps, back to back Schottky diodes

Pintilie & Alexe, APL 2005

Phenomenology: dielectric response

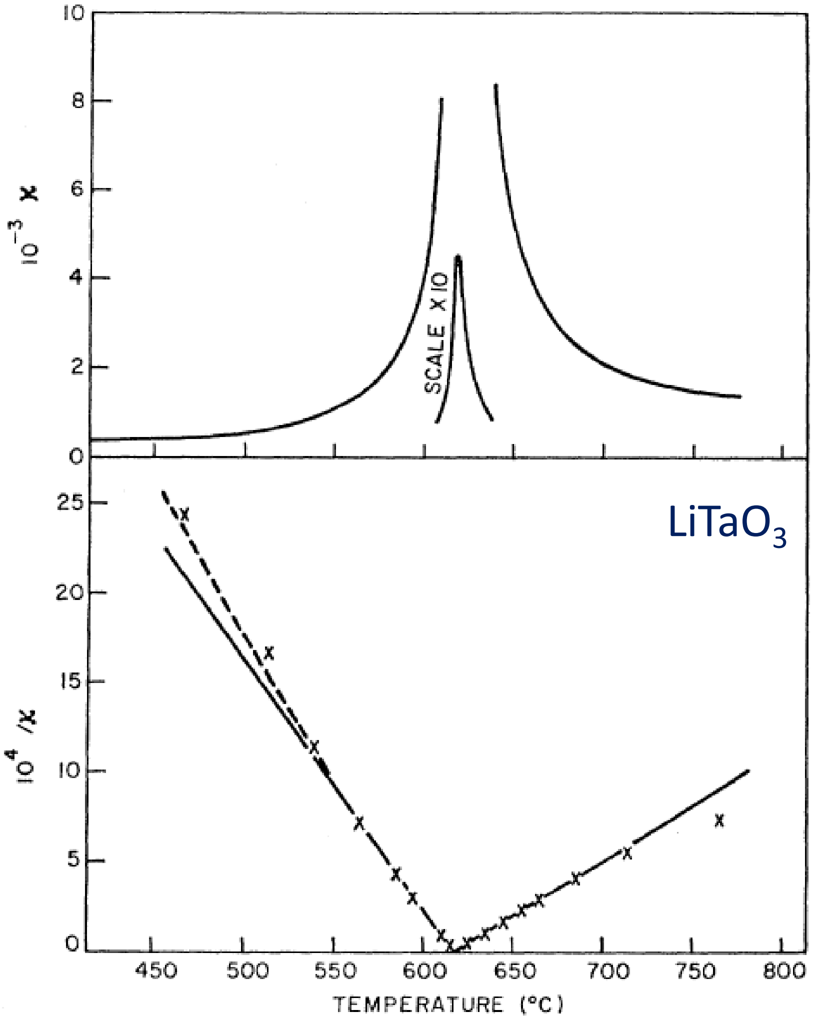
$$\chi\epsilon_0 = \frac{\partial P}{\partial E}$$

$$E = \alpha P + \beta P^3$$

$$(\chi\epsilon_0)^{-1} = \alpha + 3\beta P^2$$

$$= \begin{cases} \alpha & T > T_0 \\ -2\alpha & T < T_0 \end{cases}$$

$$\chi \propto \frac{1}{T - T_0}$$ Curie-Weiss



$LiTaO_3$

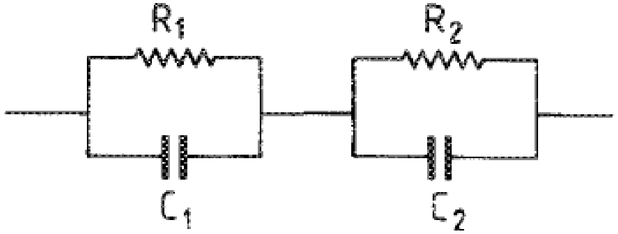
Glass, Phys. Rev. 1968

Dielectric constant diverges at 2nd order PT

Maxwell-Wagner effects

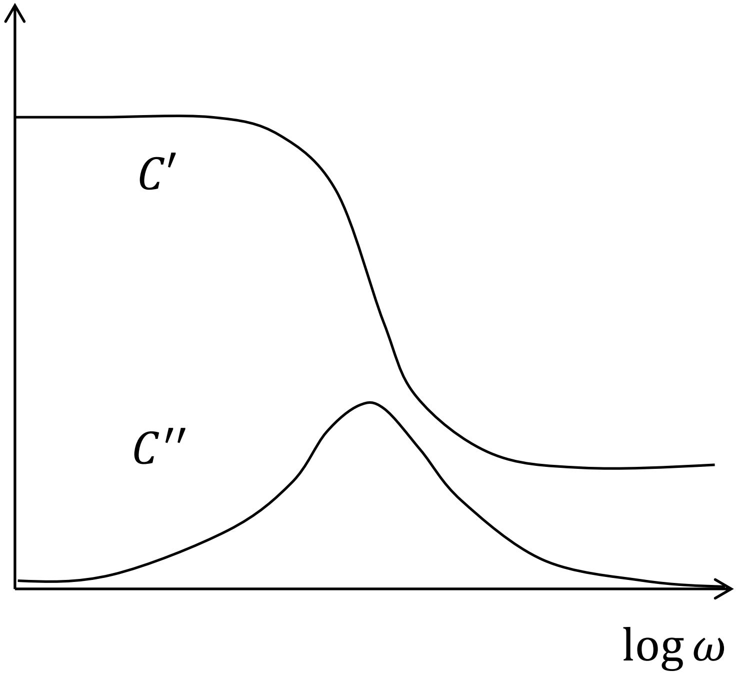
Often have a two (or more) component system, e.g. bulk + grain boundaries + metal/dielectric interface, Schottky barrier capacitance, etc…

Different C_i, R_i have different temperature dependences that combine to give a complex, frequency dependent dielectric response



$$Z(\omega) = Z' - iZ'' = \left(\frac{1}{R_1} + i\omega C_1\right)^{-1} + \left(\frac{1}{R_1} + i\omega C_1\right)^{-1}$$

$$C(\omega) = C' - iC'' \equiv \frac{1}{i\omega Z}$$

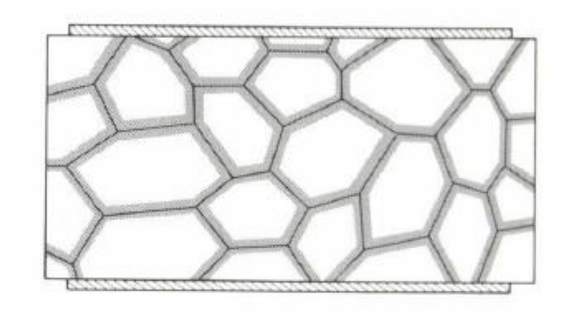


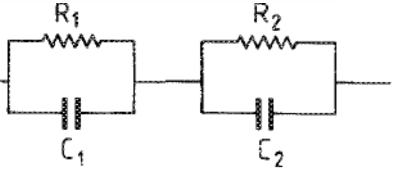
Relaxations also due to space charge, domain wall motion etc.

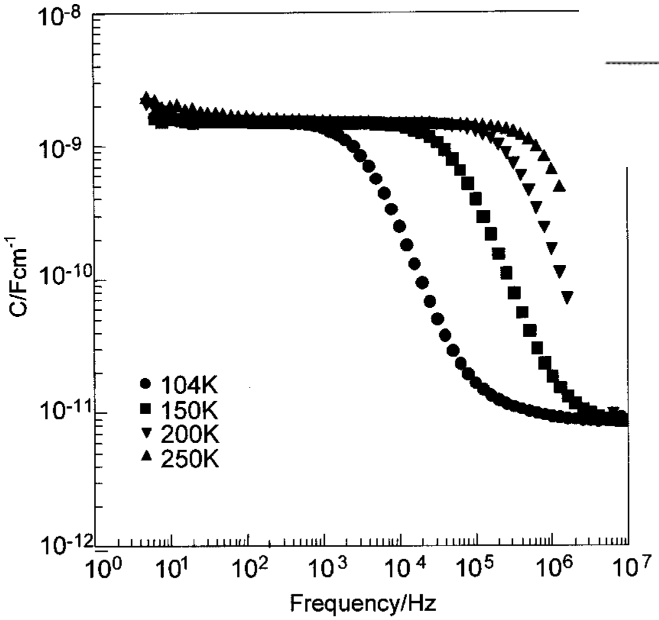
Always measure the frequency dependence!

Maxwell-Wagner effects

Mechanism for Internal Barrier Layer Capacitors (IBLC)



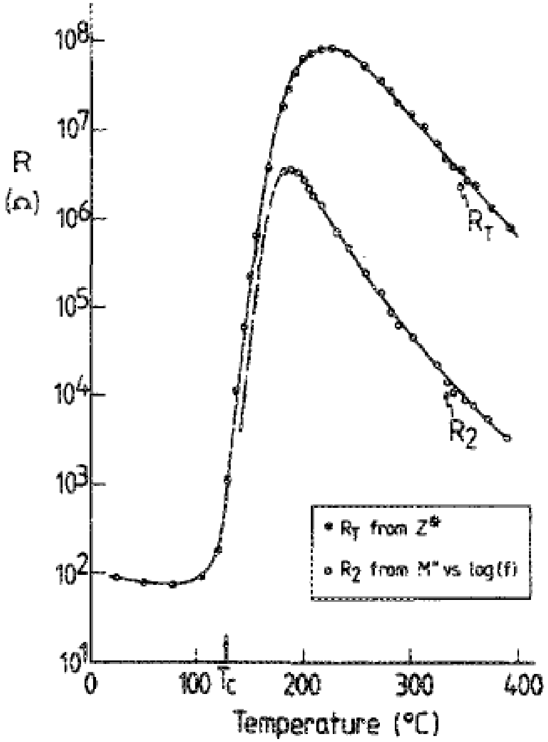




'giant dielectric constant' of $CaCu_3Ti_4O_{12}$

Sinclair et al. APL 2002

Internal barrier structure important for PTCR $BaTiO_3$ ceramics



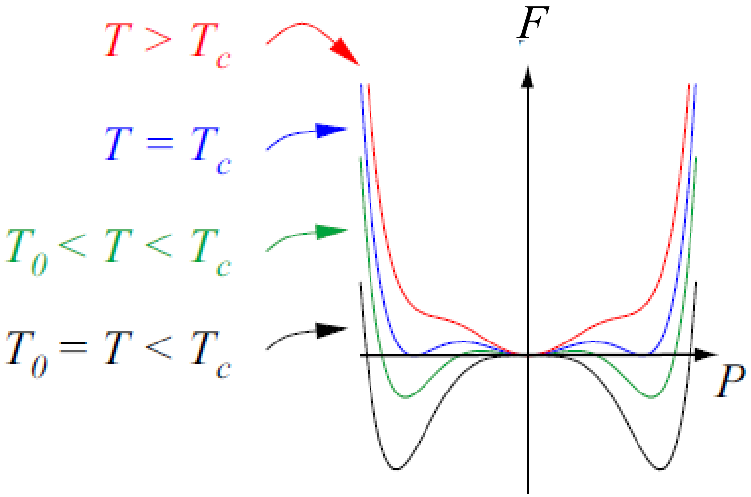
Sinclair & West JAP 1989

Phenomenology – 1st order transitions

If $\beta < 0$, need to include P^6 term.

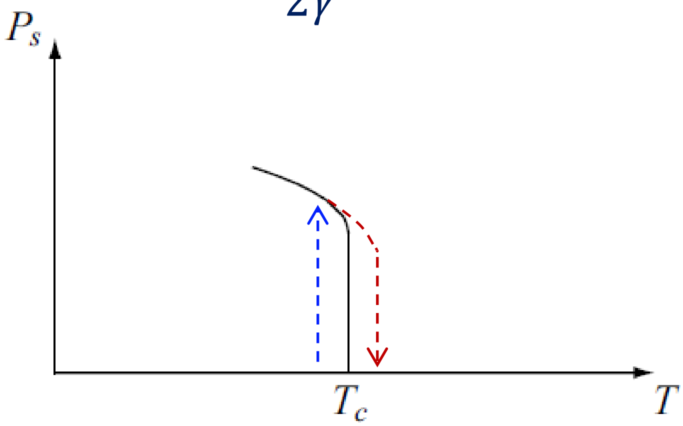
$$F = \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6$$

$$T_C = T_0 + \frac{3}{16}\frac{\beta^2}{\alpha_0\gamma} \qquad T_C \neq T_0$$

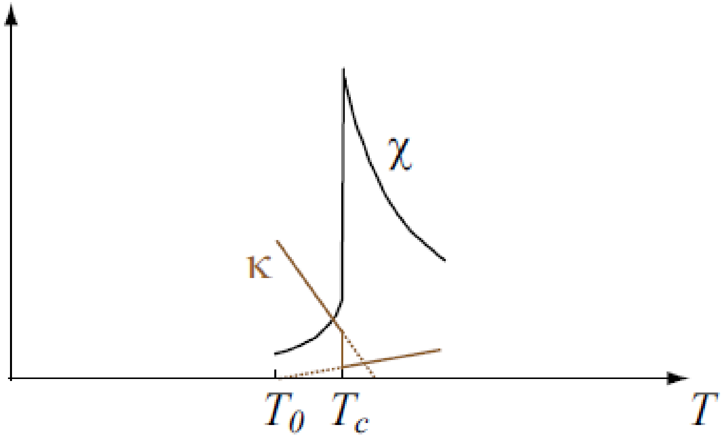


Images: N. Stucki

$$P_S^2 = \frac{-\beta + \sqrt{\beta^2 + 4\gamma\alpha_0(T - T_0)}}{2\gamma} \neq 0 \text{ at } T_C$$



Discontinuous order parameter
→ thermal hysteresis



No divergence

Many ferroelectrics are weakly first order in bulk (e.g. $PbTiO_3$, $BaTiO_3$)

Displacive vs. order-disorder

Ferroelectric phase transitions often classified as being displacive or order-disorder:

- Displacive – symmetry change results from displacement of atoms with respect to the more symmetric phase

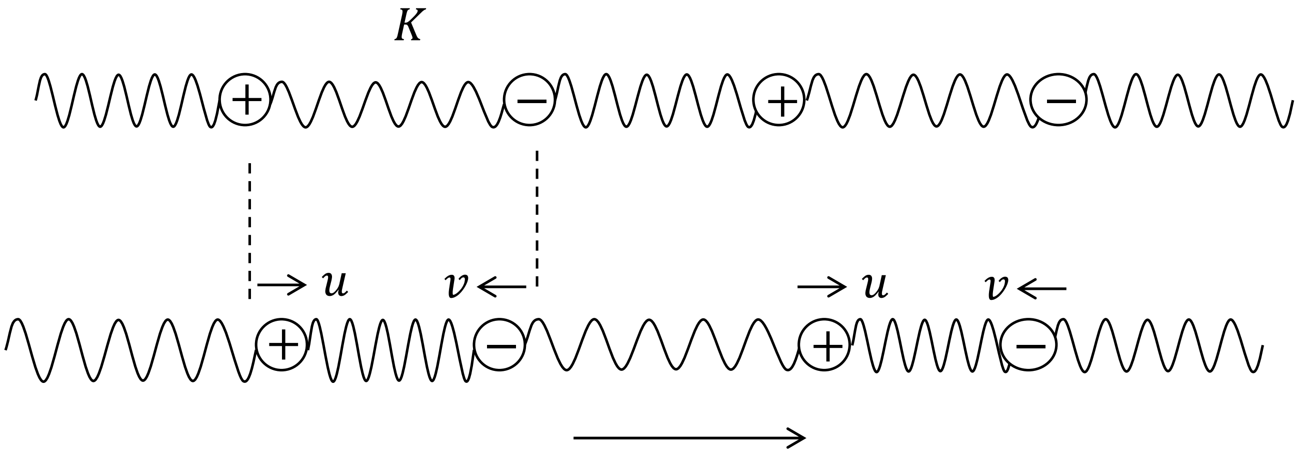
- Order-disorder – symmetry change at transition results from redistribution of atoms over equiprobable positions

Generally, phase transitions have both displacive and order-disorder character

Soft mode picture of displacive transitions

Cochran 1960

Toy model:



$q = 0$

$P \propto \xi$ $\xi = u - v$

$q = 0$ ionic displacements

→ $P \propto \xi$

→ local field $E_{loc} \propto P \propto \xi$

→ force $= C\xi$

$$m\ddot{\xi} = -K\xi + C\xi$$

Short range

long range dipole-dipole interactions

$$\omega^2 = \frac{K - C}{m}$$

(TO phonon)

Soft mode picture of displacive transitions

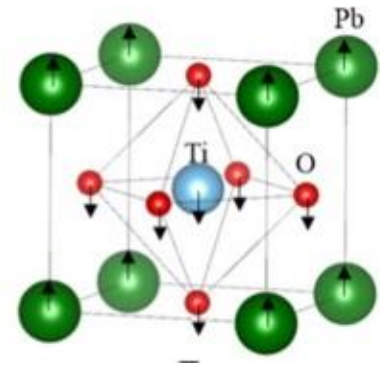
$\omega^2 \propto (T - T_0)$ Mode softens!

Below T_C freeze new equilibrium structure with finite ξ

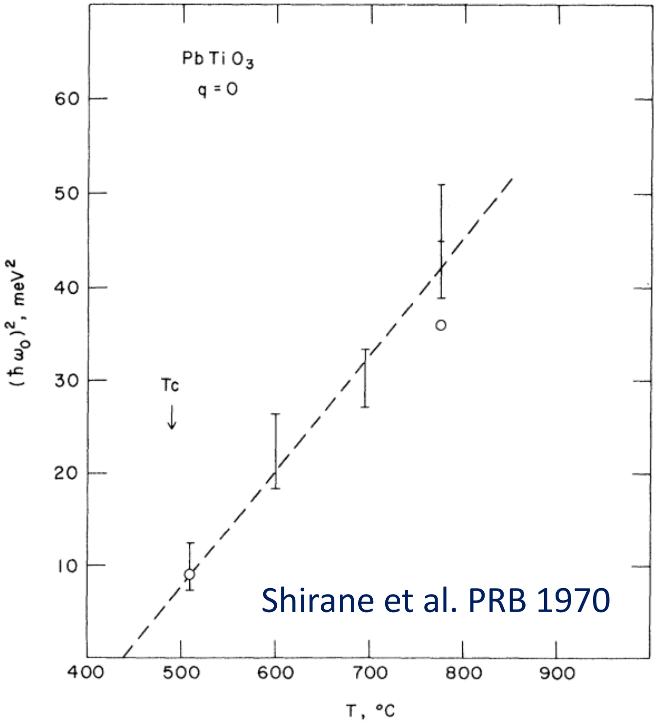
Lyddanne-Sachs-Teller relation

$$\frac{\epsilon(0)}{\epsilon(\infty)} = \frac{\omega_L^2}{\omega_T^2} \propto \frac{1}{T - T_0}$$

Displacive transition in $PbTiO_3$

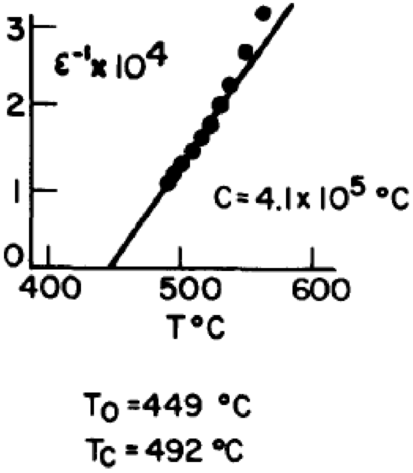


$$P = \frac{Z^*}{V}\xi_{FE}$$



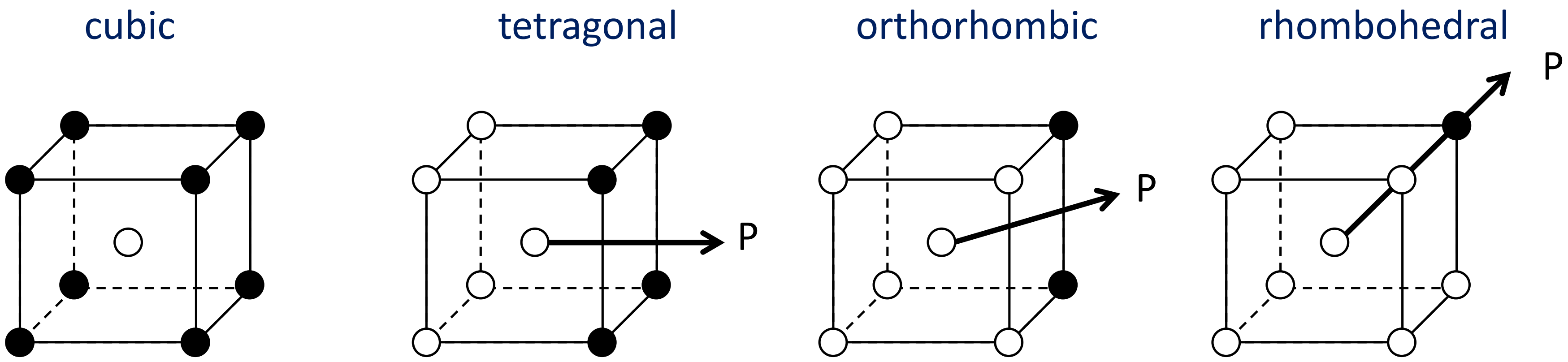
Shirane et al. PRB 1970

Remeika & Glass (1970)

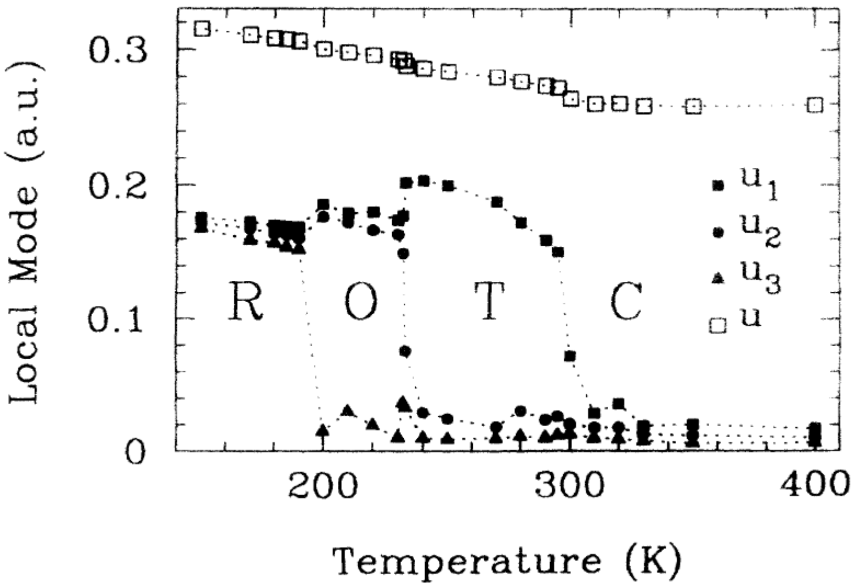


Order-disorder transitions

e.g. eight-site model for $BaTiO_3$



Comes Acta Cryst. 1970



Zhong, Vanderbilt, Rabe, PRL 1994

Generally, both displacive and order-disorder character present

The elastic dielectric – coupling to strain

$$F = \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \cdots + \frac{1}{2}C\eta^2 - g\eta P^2 - \eta\sigma - EP$$

$P \to P_i$ polarisation vector
$C \to C_{ijkl}$ elastic compliance tensor
$\eta \to \eta_{ij}$ strain tensor
$g \to g_{ijkl}$ electrostrictive coefficients
$\sigma \to \sigma_{ij}$ stress tensor

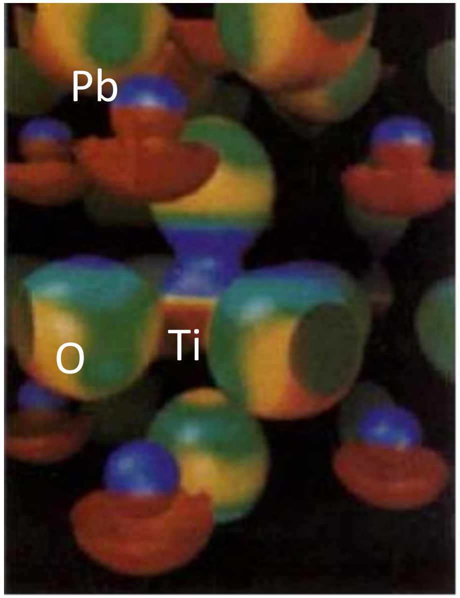
In equilibrium $\frac{\partial F}{\partial P} = 0, \frac{\partial F}{\partial \eta} = 0$

$$C\eta - gP^2 - \sigma = 0$$

Free crystal, fix $\sigma = 0$ → $\eta = \frac{gP^2}{C}$

Spontaneous strain along *P*

Coupling to strain especially strong in $PbTiO_3$ due to polarisability of the lone pair on Pb



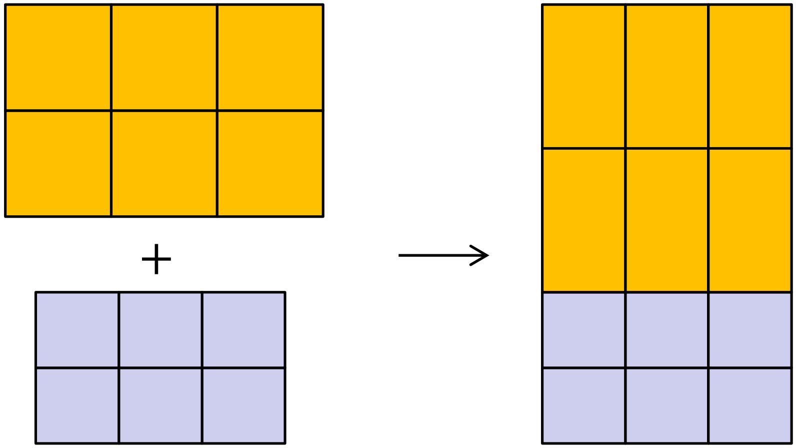
Cohen Nature 1992

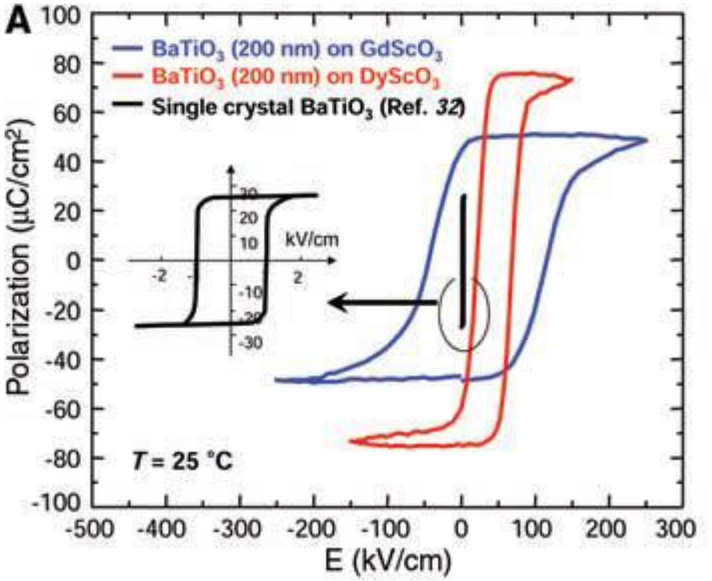
Using Landau theory for predictions

$$F = \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \dots + \frac{g^2}{2C}P^4 - \frac{g^2}{C}P^4 = \frac{\alpha}{2}P^2 + \left(\frac{\beta}{4} - \frac{g^2}{2C}\right)P^4 + \cdots$$

Spontaneous strain renormalizes P^4 coefficient! Can lead to change in the order of PT

If instead we fix η (clamped crystal) – renormalize P^2 coefficient – change T_C!



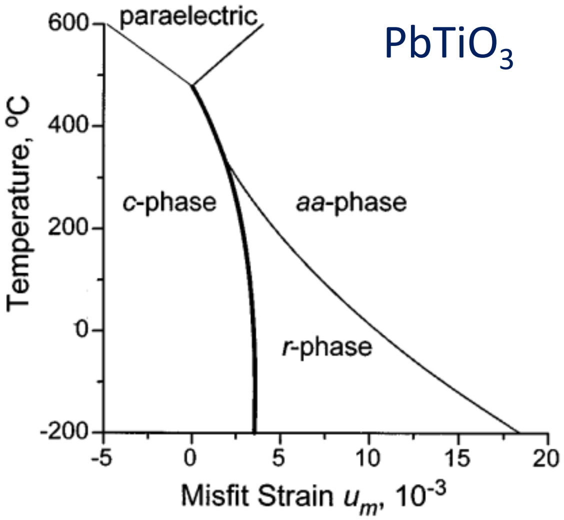


Choi et al. Science 2004

BASIS FOR STRAIN ENGINEERING!

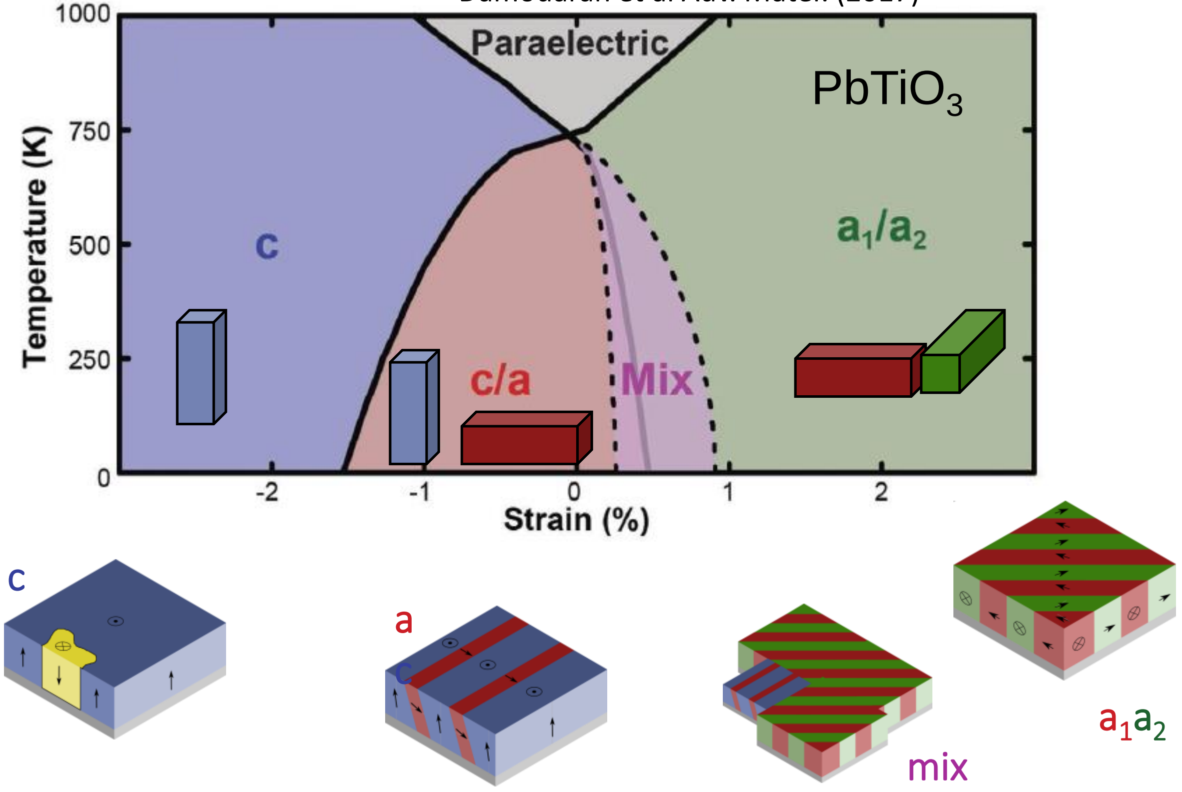
Strain engineering

New phases unavailable in bulk!



Pertsev et al. PRL 1998

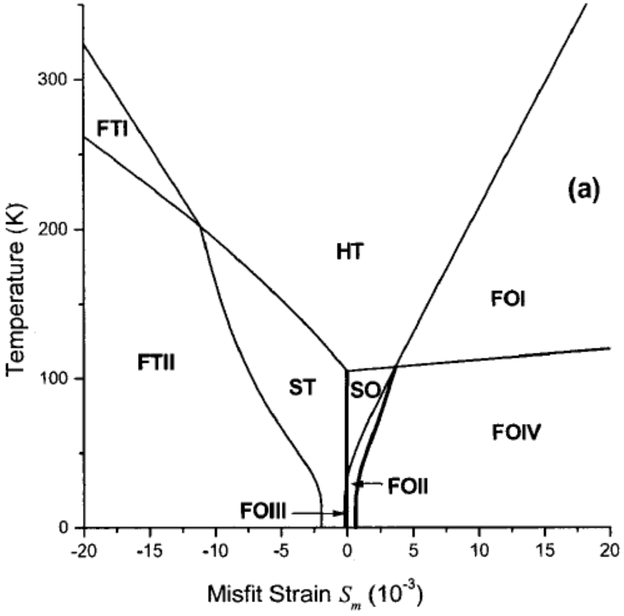
Damodaran et al Adv. Mater. (2017)



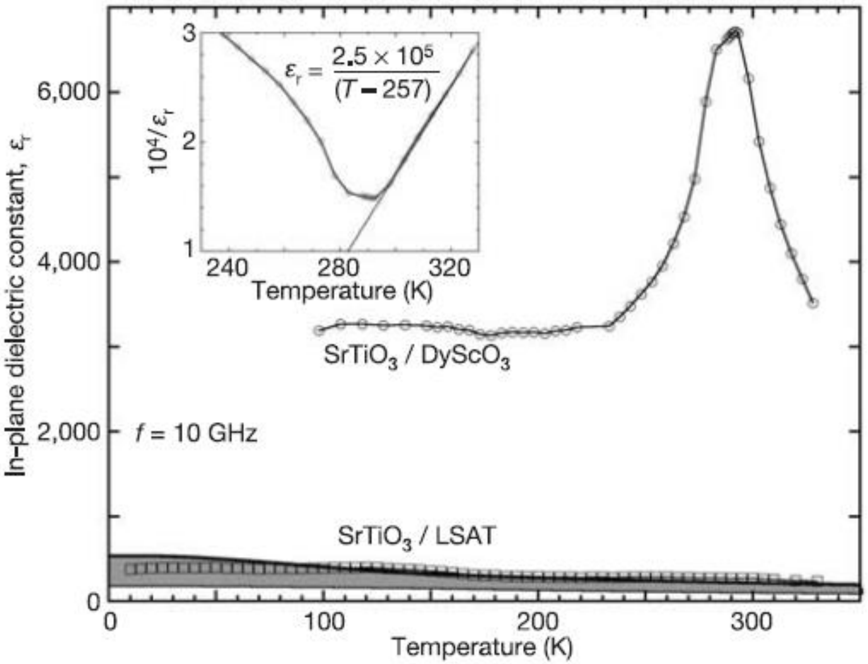
Koukhar et al. PRB 2001

See also review by Schlom et al. Annu. Rev. Mat. Res. 2007

Strain-induced ferroelectricity in $SrTiO_3$

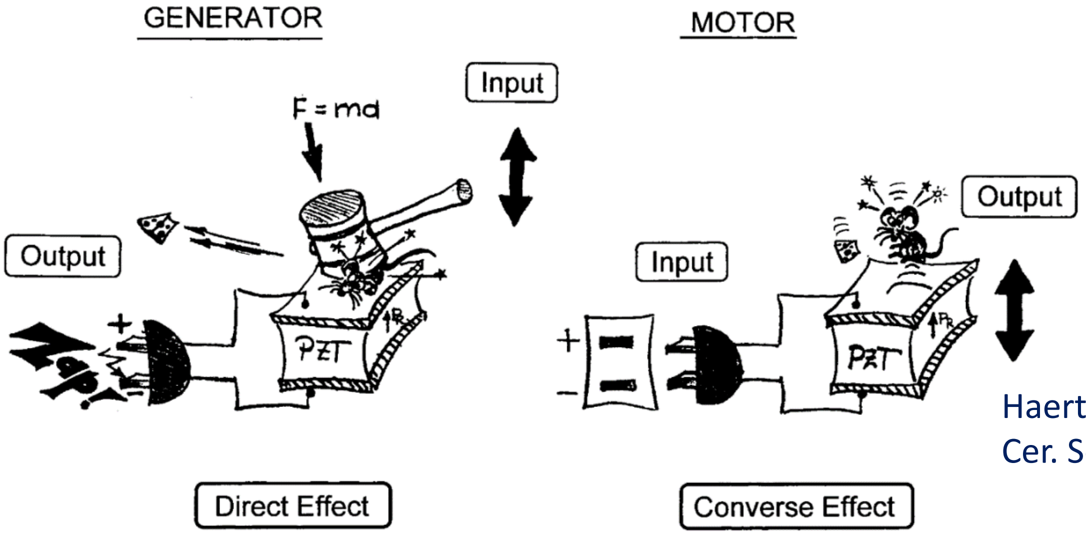


Pertsev et al. PRB 2000



Haeni et al. Nature 2004

The elastic dielectric – piezoresponse



Haertling J. Am. Cer. Soc. 1999

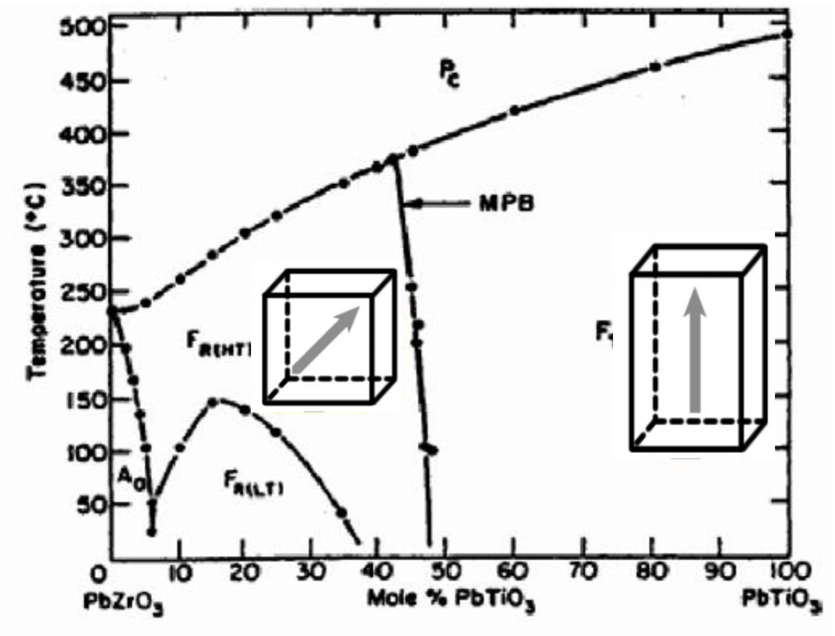
$$D = d\sigma \qquad \eta = dE$$

Linear electromechanical coupling

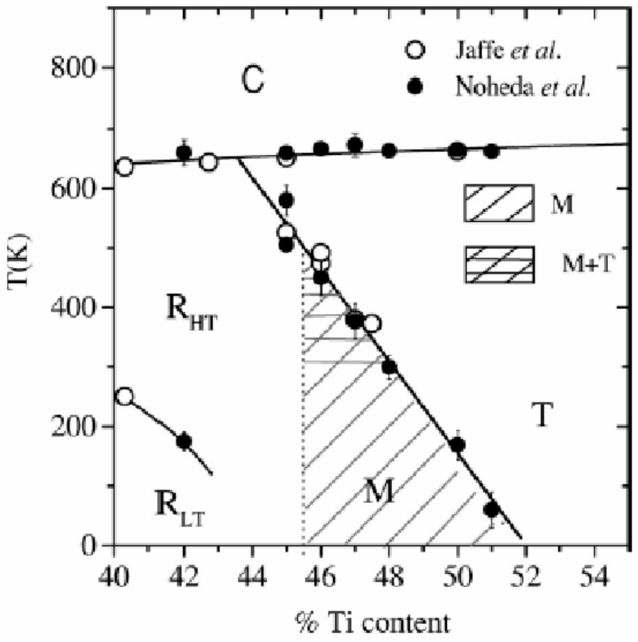
$$d = \frac{\partial \eta}{\partial E} = \frac{\partial \eta}{\partial P}\frac{\partial P}{\partial E} = \left(-\frac{2gP}{C}\right)\chi\epsilon_0$$

$PbZr_{1-x}Ti_xO_3$ (PZT)

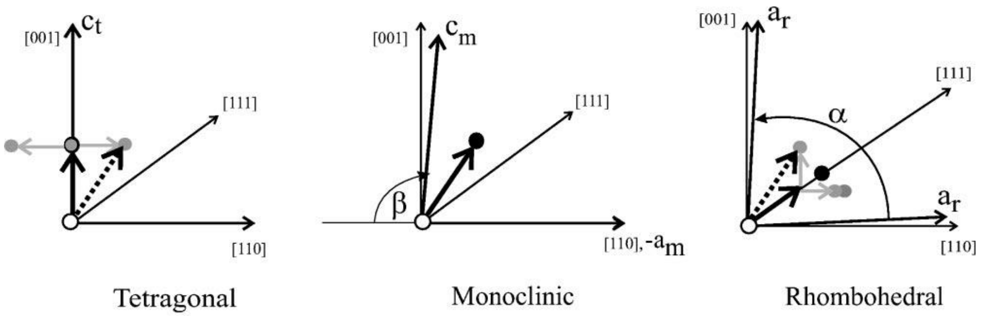
Noheda PRB 2000



Jaffe 1971



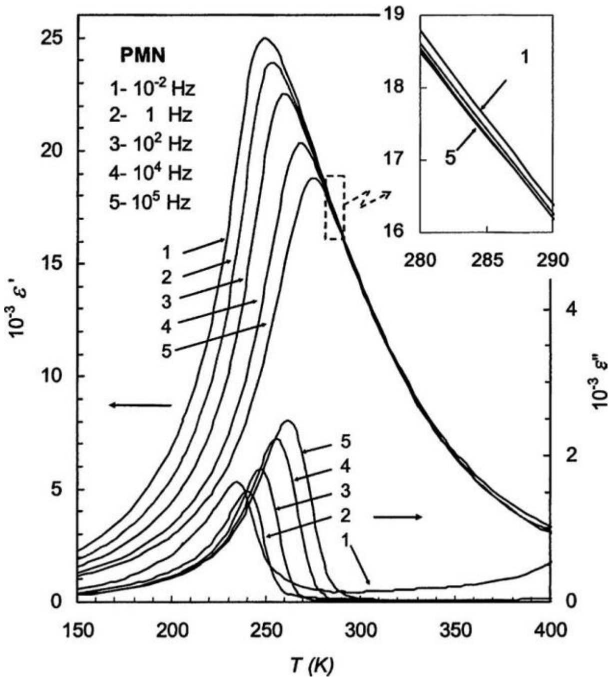
Dielectric and piezoelectric properties enhanced at morphotropic phase boundary (MPB)



Intermediate monoclinic phase (M) facilitates polarisation rotation → large piezoresponse

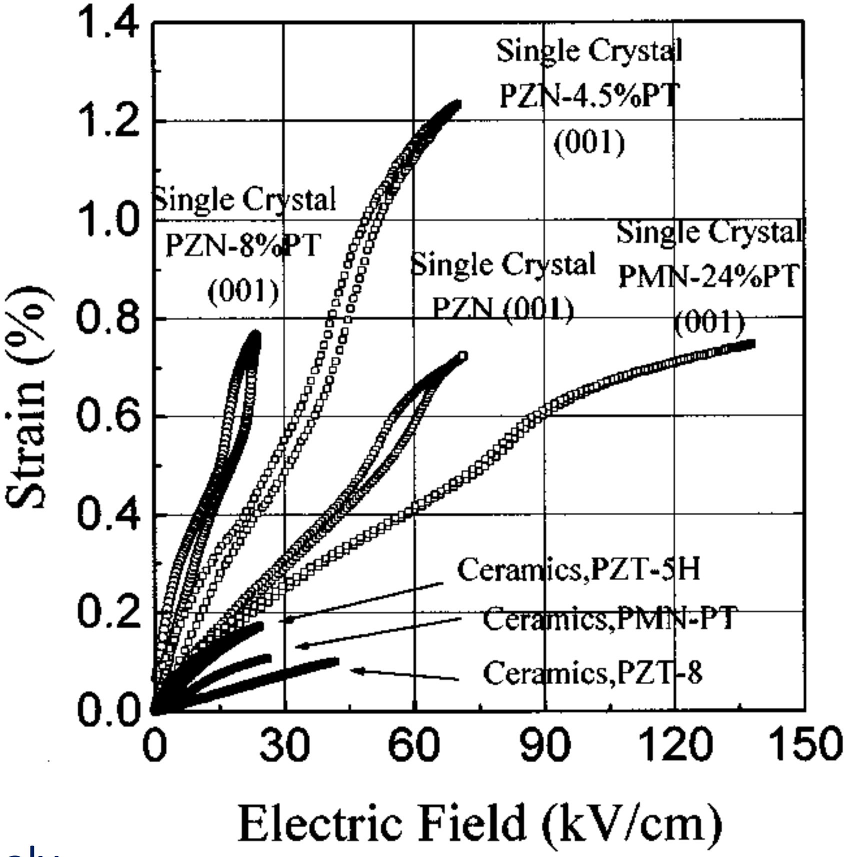
Pb-based relaxors

Bokov, Ye – J. Mater. Sci. 2006



PMN = $Pb(Mg_{1/3}Nb_{2/3})O3$

Park & Shrout – JAP 1997



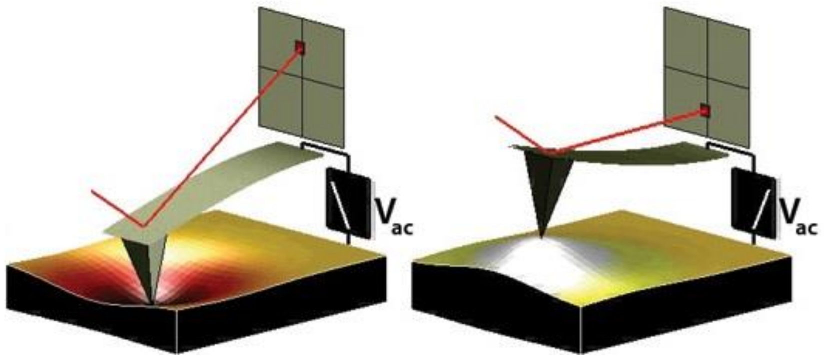
- Broad, frequency dependent dielectric anomaly
- No macroscopic structural phase transition
- Compositional disorder
- Mobile polar nanoregions (PNRs) that freeze below T_f or transition to ferroelectric state at T_C

- Giant electromechanical response!

See lecture by Brahim Dkhil

Piezoresponse Force Microscopy

Exploit piezoresponse to probe ferroelectricity and ferroelectric domains using AFM

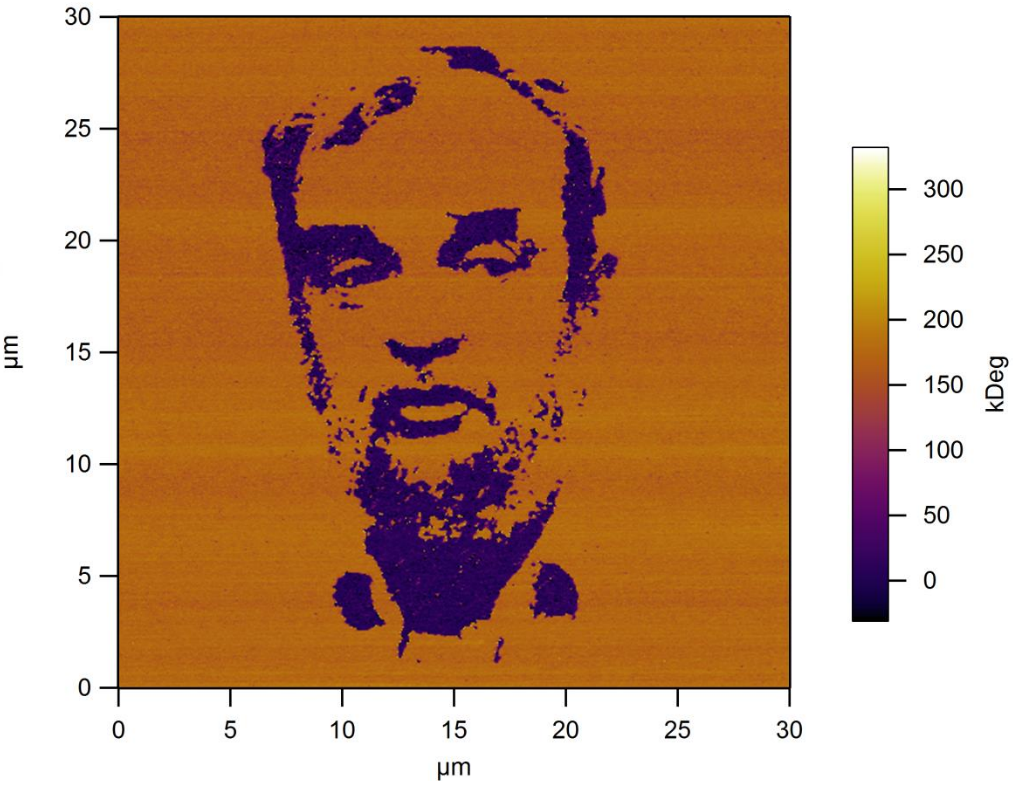


Imaging:

- Apply voltage between tip and sample
- Sample expands or contracts piezoelectrically depending on local direction of P

Writing:

- Apply large enough voltage to switch P



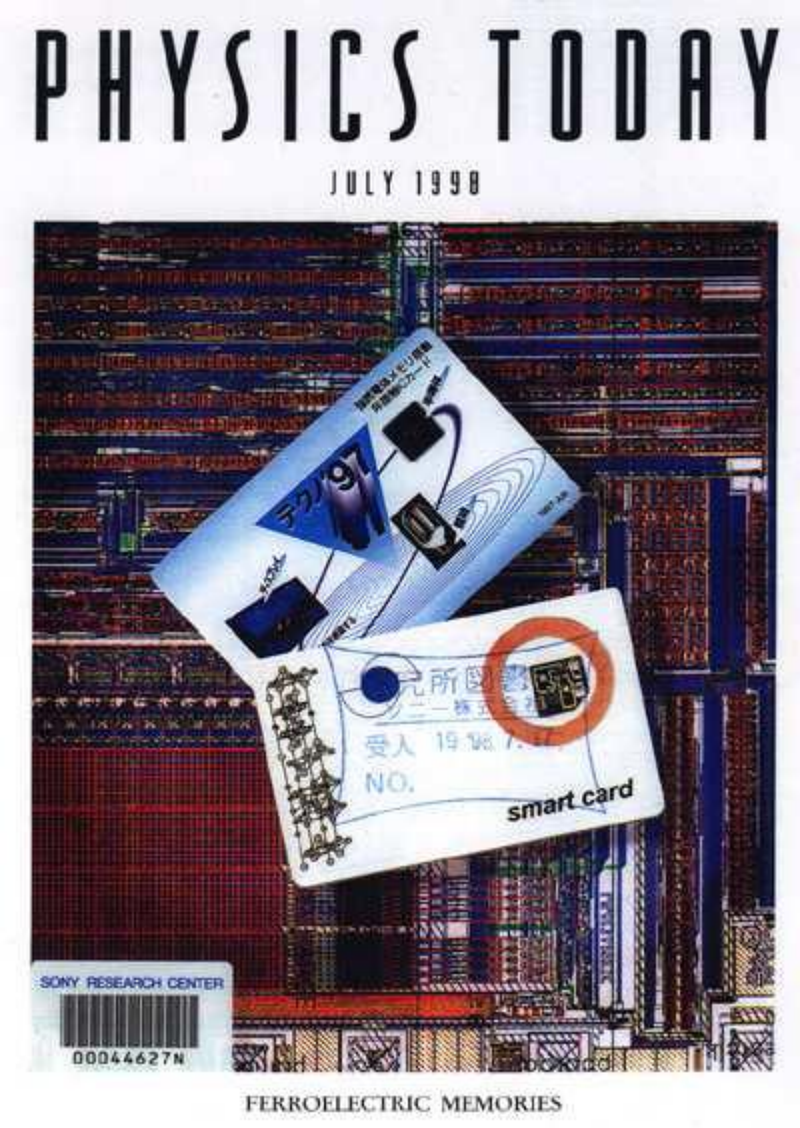
PFM microportrait of Jim Scott
Canvas: $BiFeO_3$ thin film

Ferroelectric thin films

- Finally enabled *ferroelectricity* to be exploited
  - FeRAM
  - Fe tunnel junctions
  - FeFET

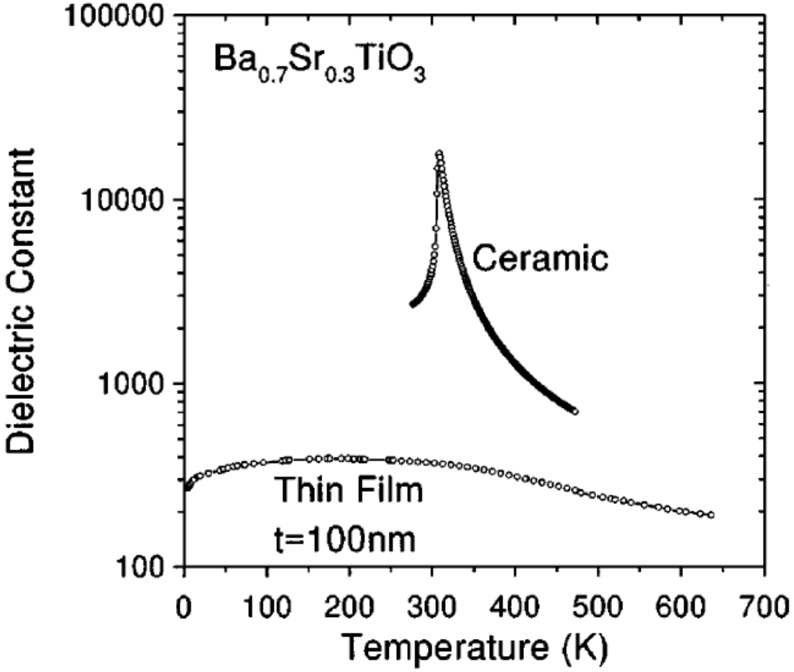
- Must consider the properties of the whole system (M-F-M or M-F-S)

- Properties can be dominated by the interface rather than the ferroelectric itself



Ferroelectric thin films

Shaw APL 75, 2129 (1999)



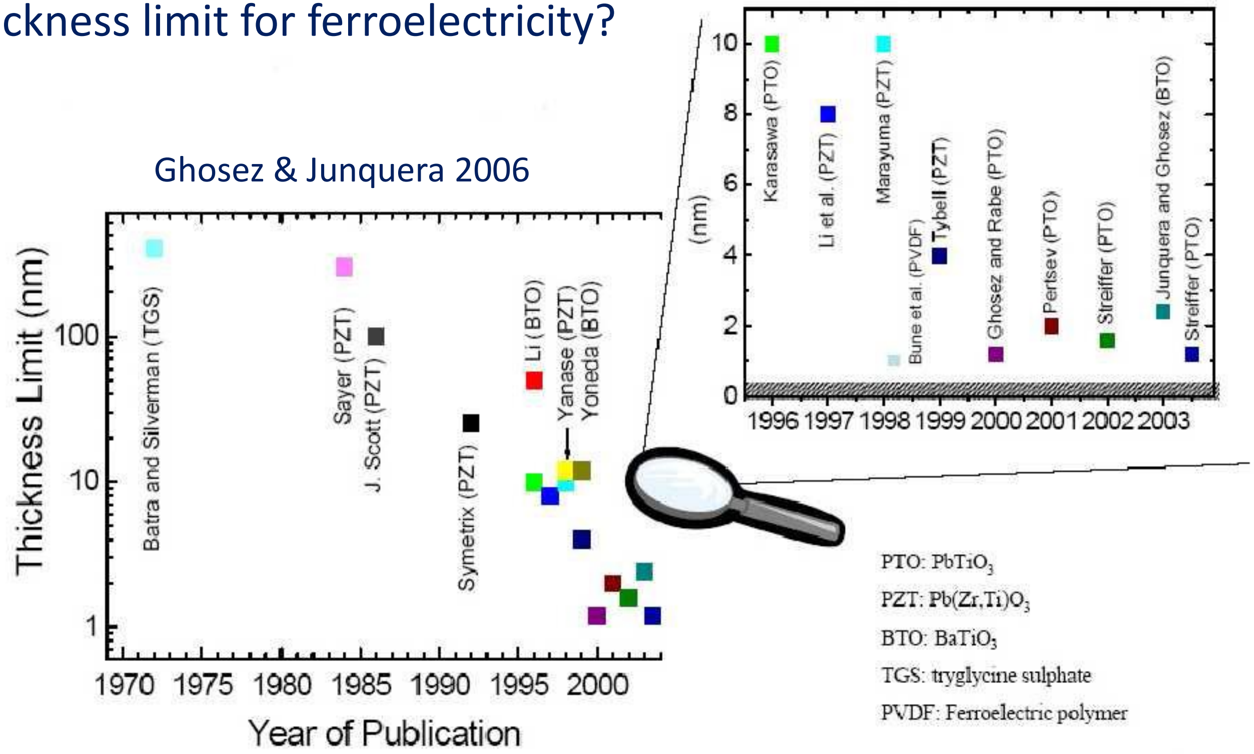
Thin films tend to have:

- smeared out transition
- reduced dielectric constants
- reduced/less stable polarisation

Ferroelectric thin films

What is the thickness limit for ferroelectricity?

Ghosez & Junquera 2006



PTO: $PbTiO_3$

PZT: $Pb(Zr,Ti)O_3$

BTO: $BaTiO_3$

TGS: tryglycine sulphate

PVDF: Ferroelectric polymer

At surfaces

- Change in bonding
- Electrostatic boundary conditions
- Mechanical boundary conditions

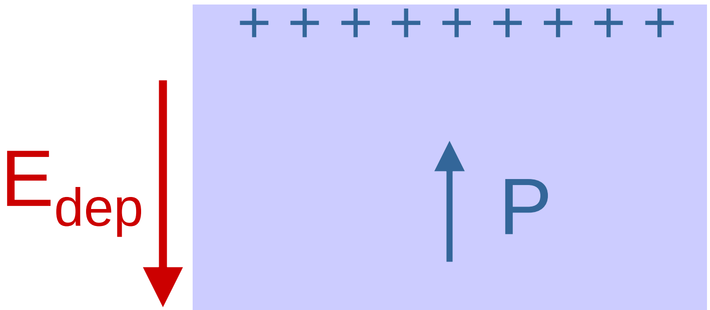
Critical thickness for ferroelectricity has progressively decreased as better quality films have been made

Boundary conditions – very important!

Depolarising field

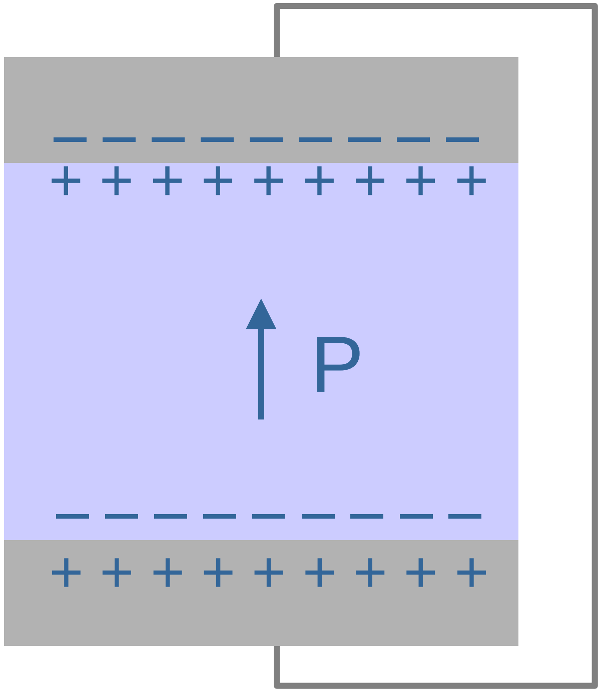
$$D = \epsilon_0 E + P$$

open circuit



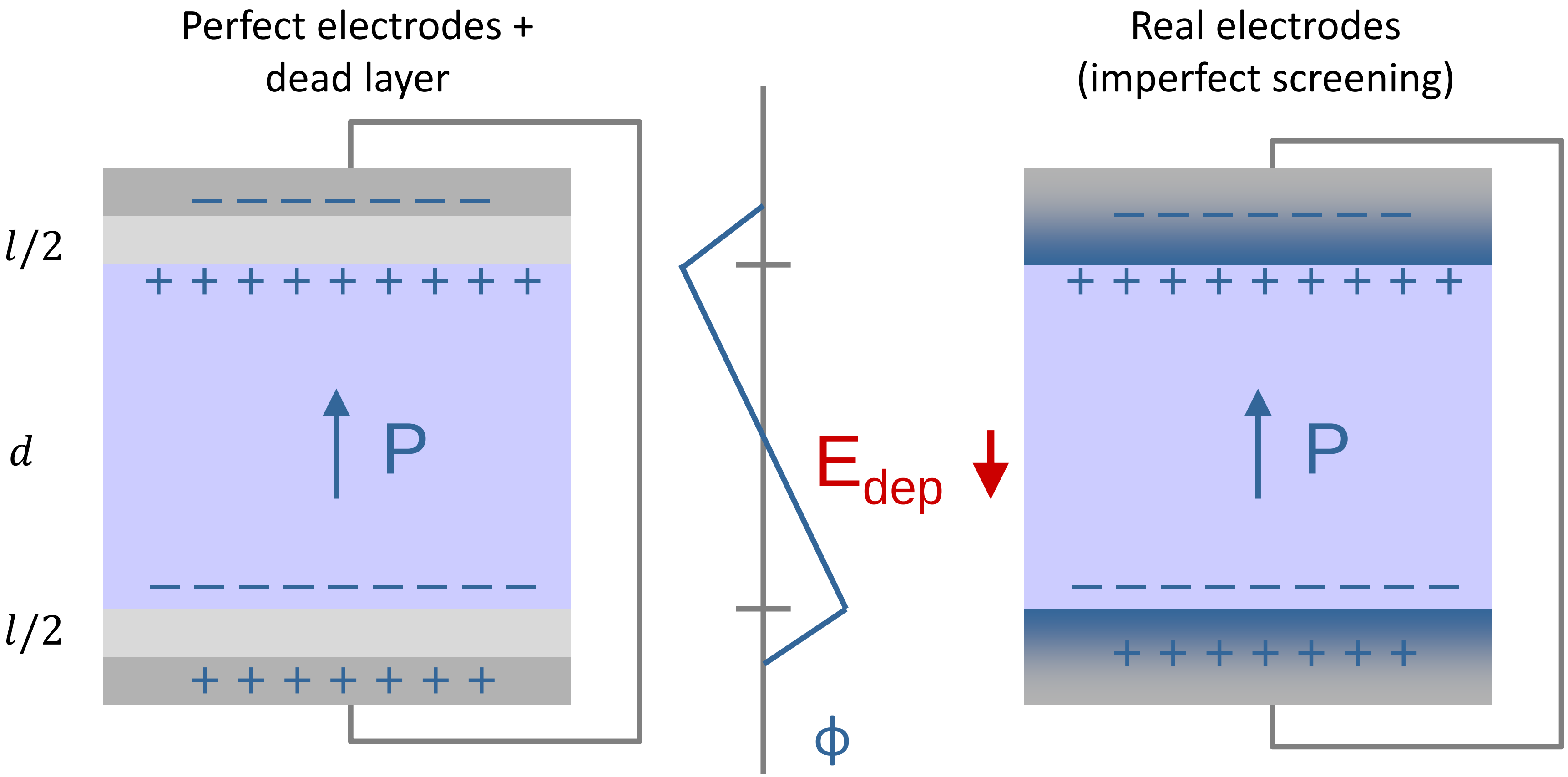
$$D = 0, E = -\frac{P}{\epsilon_0}$$

ideal short circuit



$$E = 0, D = P$$

Depolarising field – imperfect screening



Perfect electrodes +
dead layer

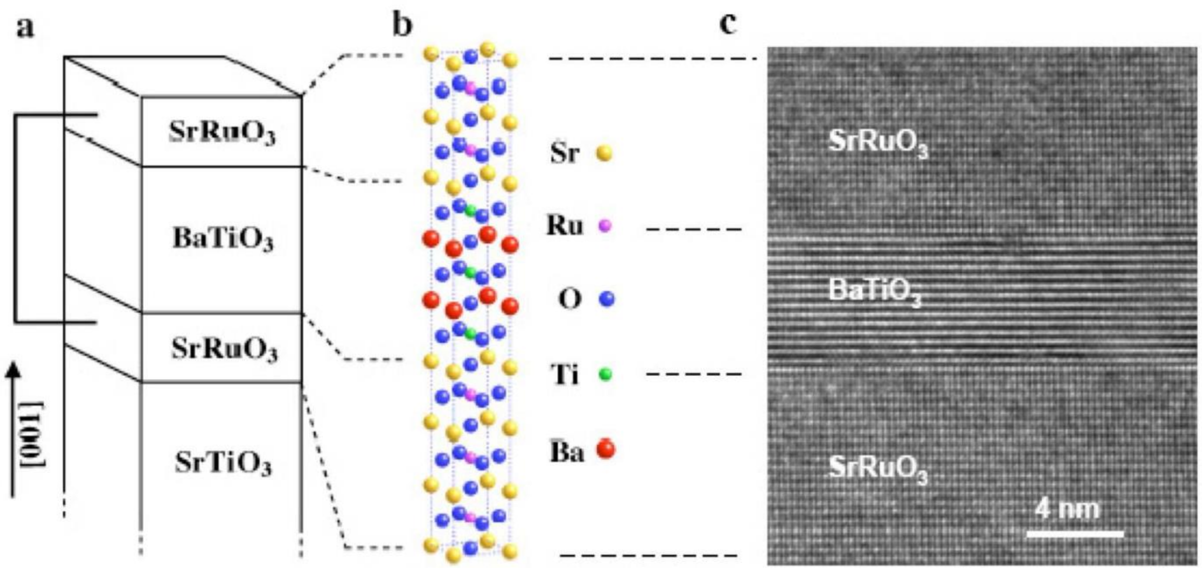
Real electrodes
(imperfect screening)

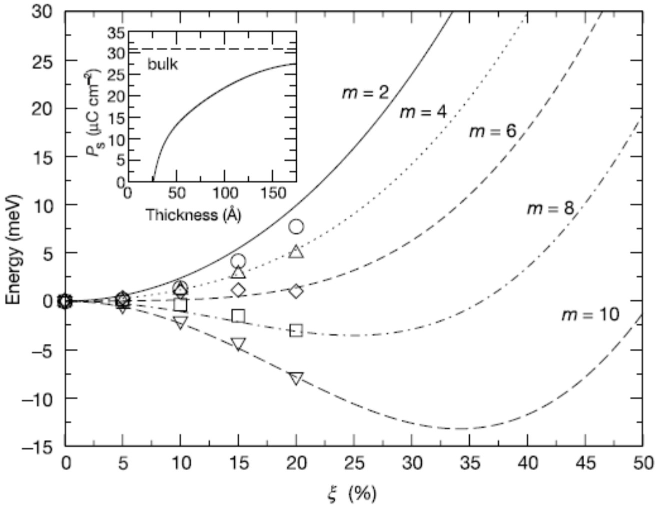
$$D = \epsilon_0 E_f + P_f = \epsilon_d \epsilon_0 E_d$$

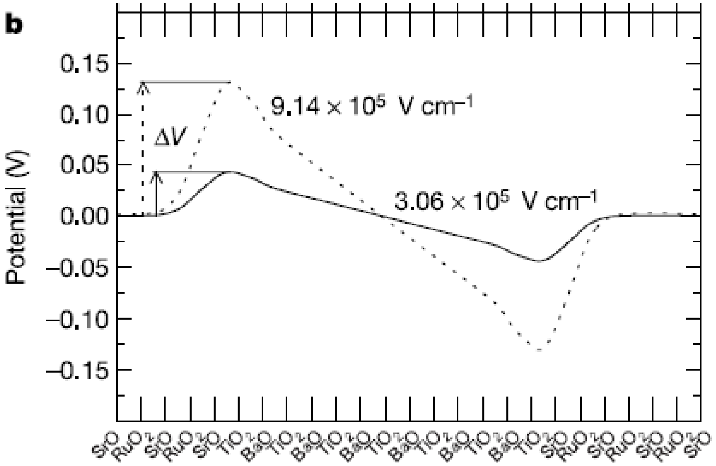
$$\Delta\phi = E_d l + E_f d = 0$$

$$E_f = -\frac{l}{\epsilon_d}\frac{P_f}{\epsilon_0 d} \equiv -\frac{\lambda_{eff}}{d}\frac{P_f}{\epsilon_0}$$

Depolarising field suppresses ferroelectricity





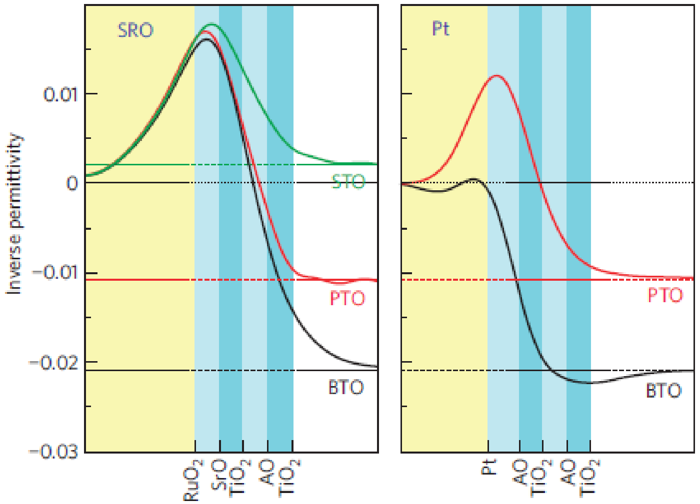


$$\lambda_{eff} \sim 10-20\ \text{pm}$$

Junquera, Ghosez Nature 2003

Surface chemistry matters

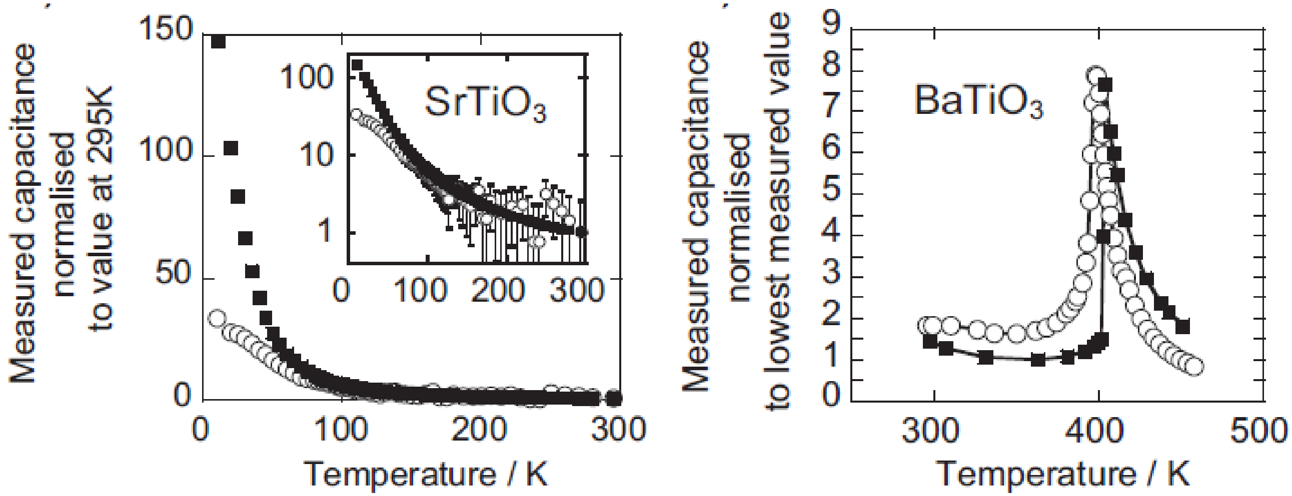
Theory



Stengel et al. Nature Mater. 2009

- For certain metal-ferroelectric combinations, ‘dead layers’ can be avoided
- Ferroelectricity can even be enhanced!

Experiment



Thin lamellae FIB-cut from single crystal

-○-

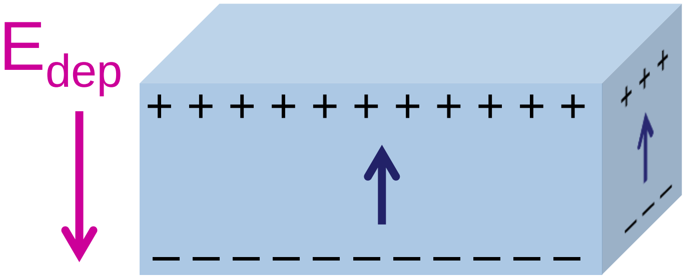
vs

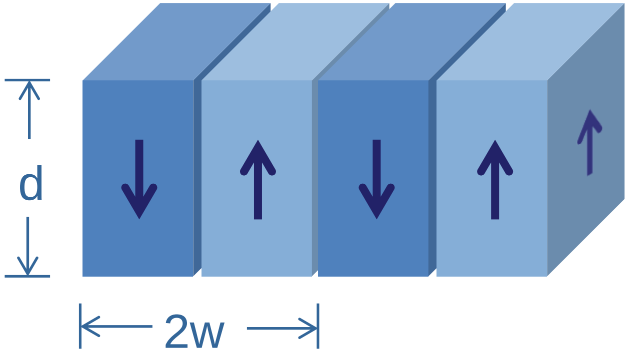
single crystal

-■-

Chang et al. Adv. Mater. 2009

Domain formation

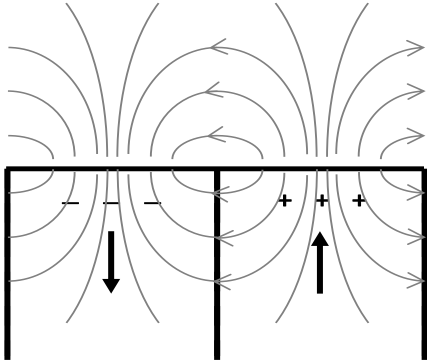




Domain wall energy (σ_{dw}) vs. electric field energy (U)

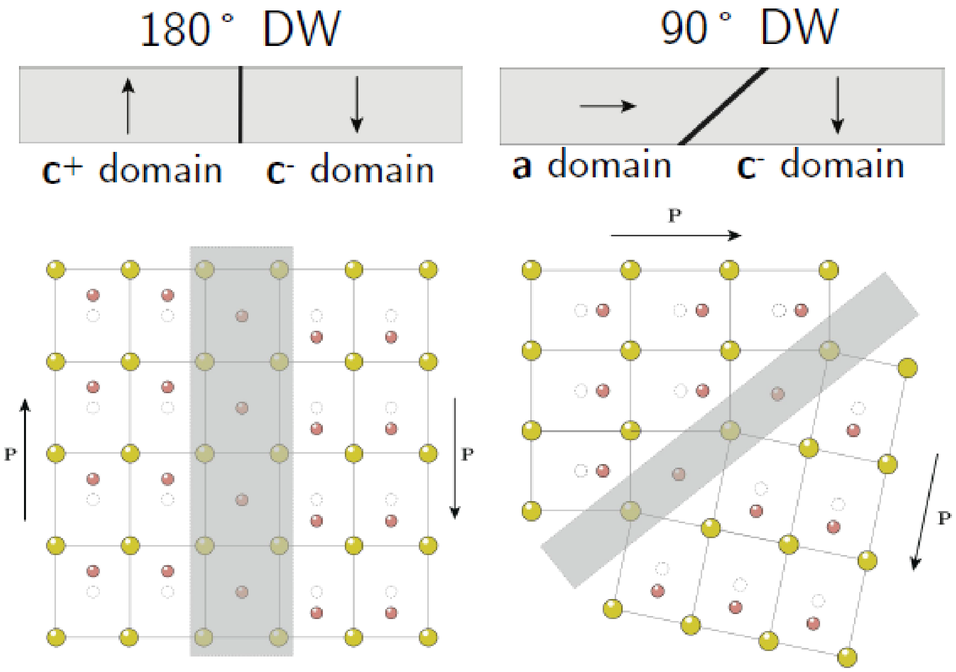
$$\Delta F = \sigma_{dw}\frac{d}{w} + Uw$$

$$w = \sqrt{\frac{\sigma_{dw}}{U} d}$$



Landau-Lifshitz-Kittel law

Domains in tetragonal ferroelectrics



Respond to applied electric fields

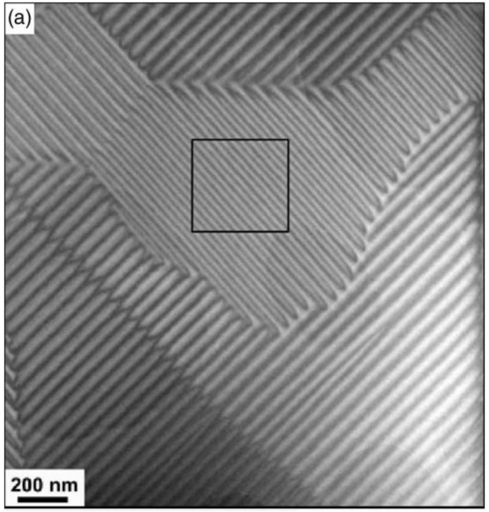
Ferroelastic – respond to electric fields and mechanical stress

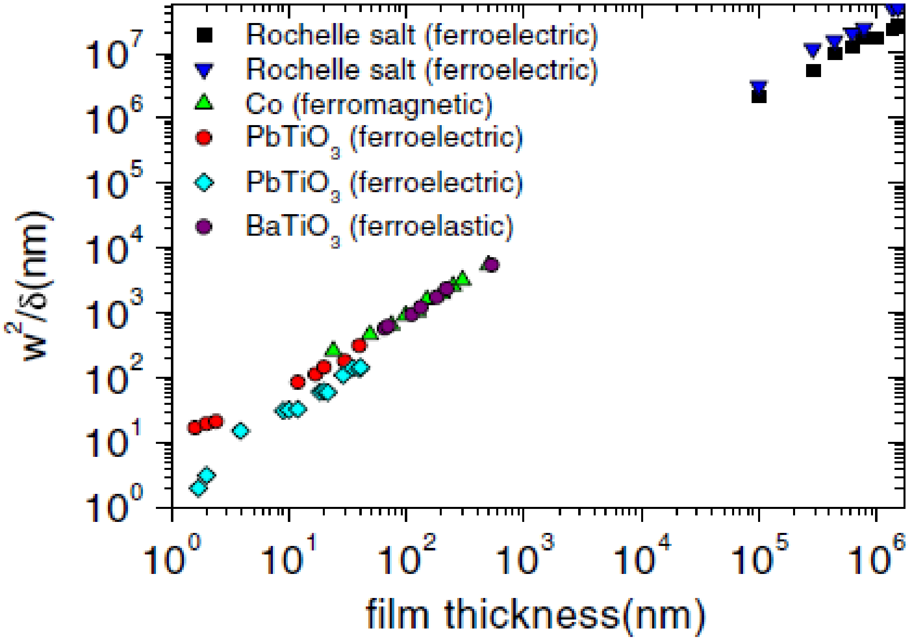
(The $\sqrt{d}$ law also applies to ferroelastic domains)

Landau-Lifshitz-Kittel scaling

Schilling et al. PRB 2006

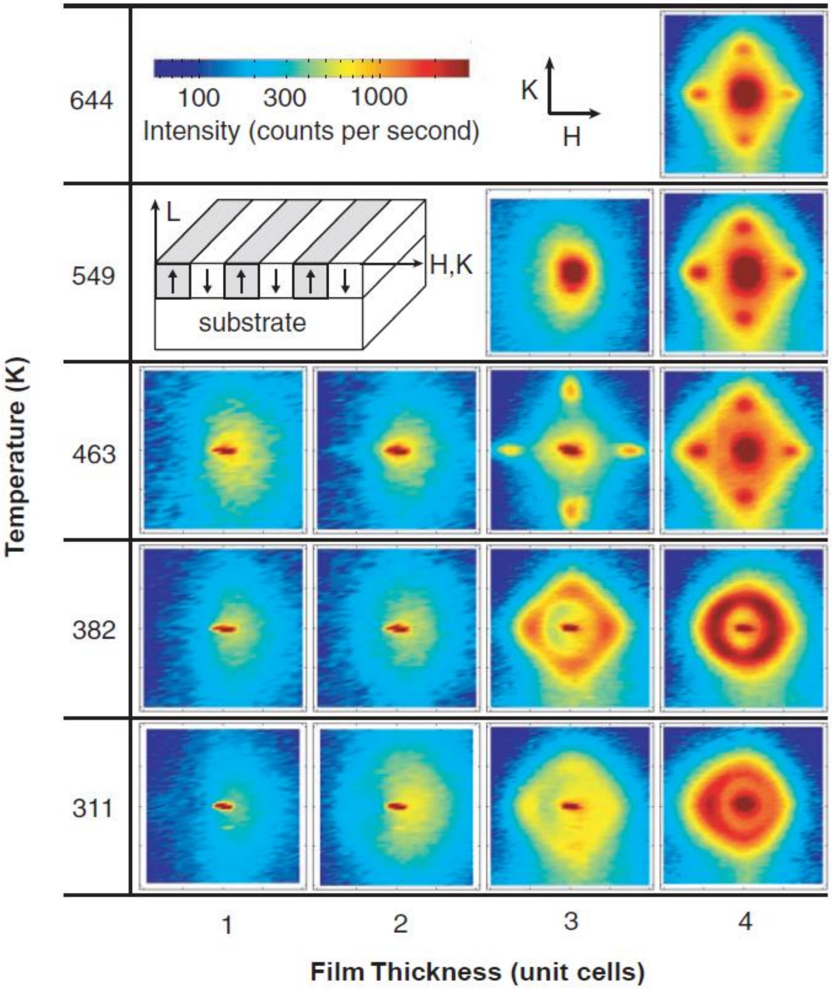
$BaTiO_3$ lamella (90° domains)





Catalan et al. Rev. Mod. Phys. 2012

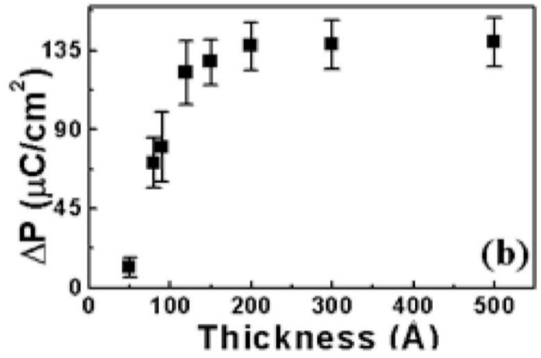
Ultrathin $PbTiO_3$ films (180° domains)

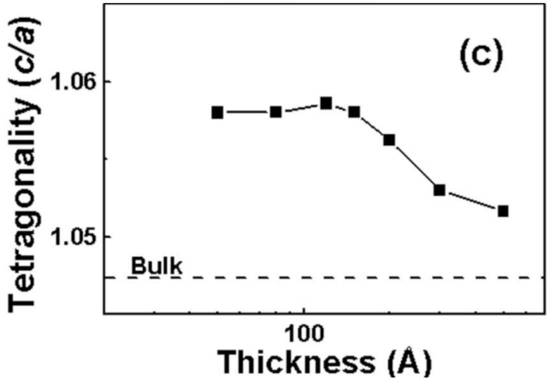


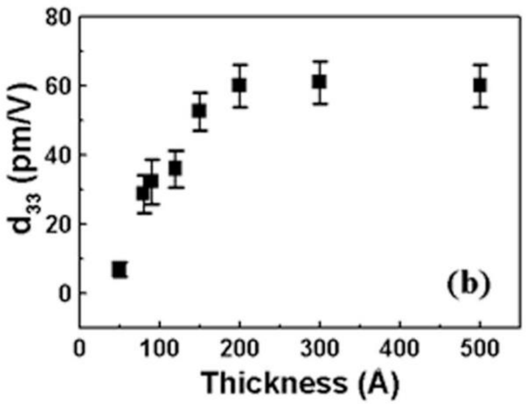
Fong et al. Science 2004

Consequences for properties

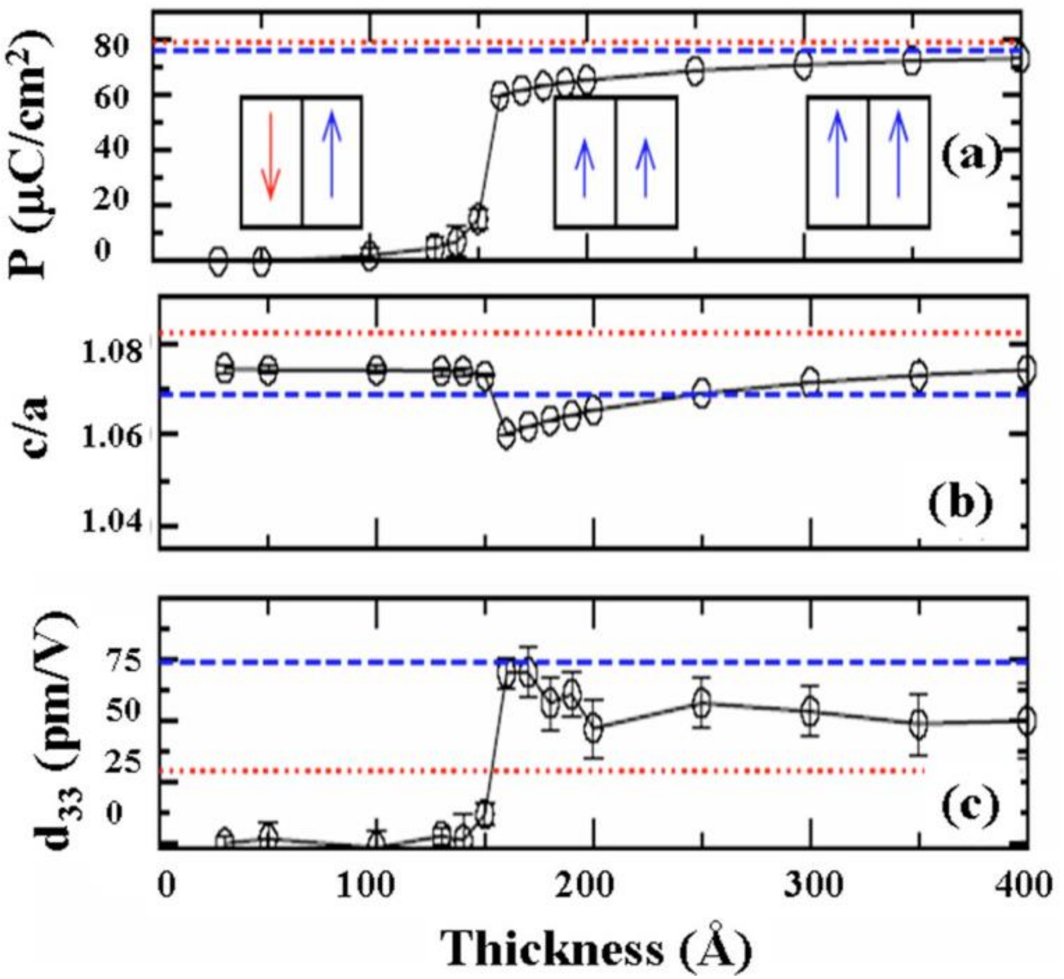
Experiment (PZT capacitors)





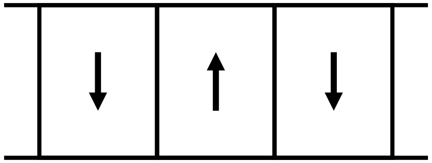


Theory

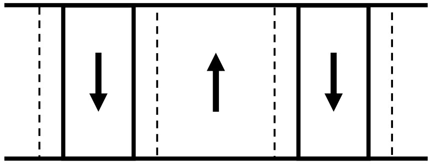


Nagarajan et al. JAP 2006

Enhancement of dielectric response

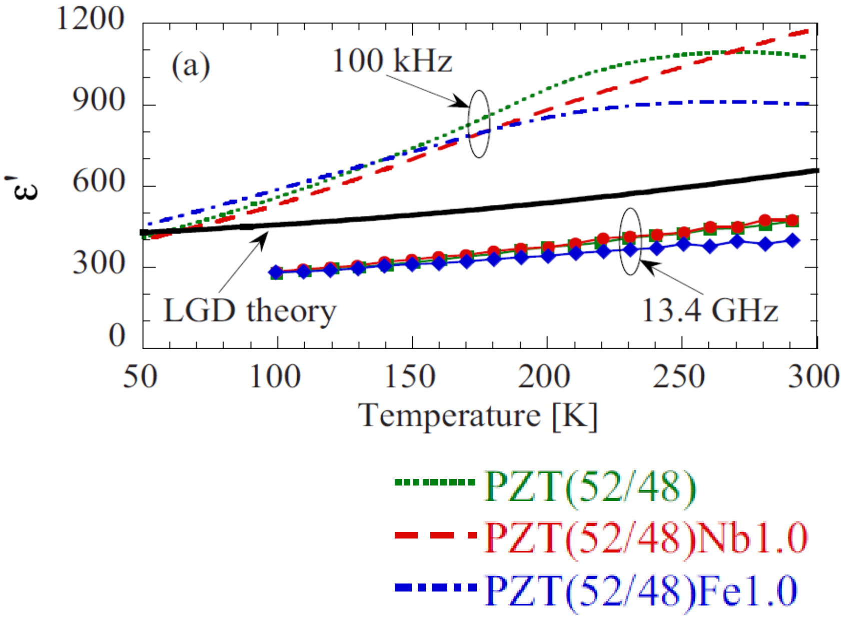


E = 0



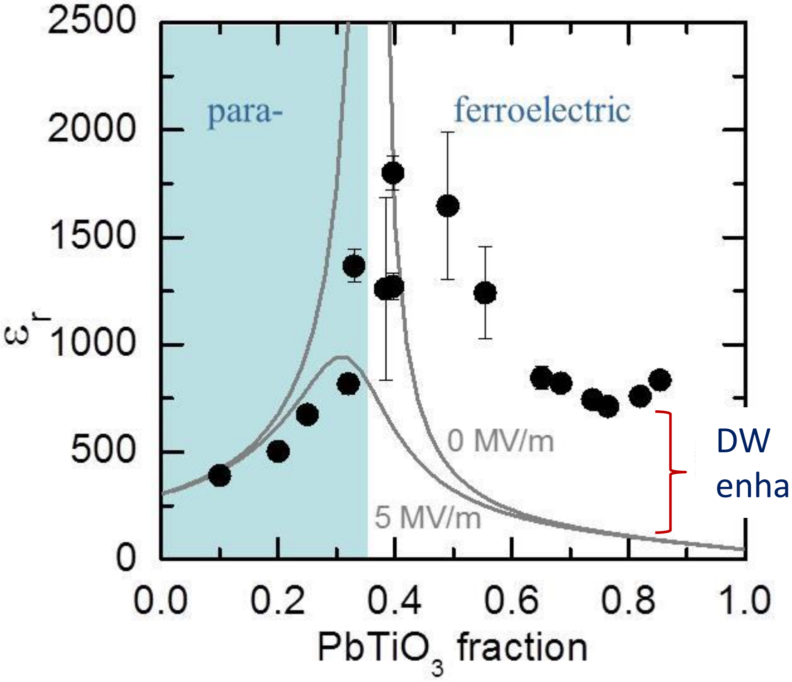
E > 0

PZT ceramics



Lin, Damjanovic – APL 2010

$PbTiO_3$-$SrTiO_3$ superlattices



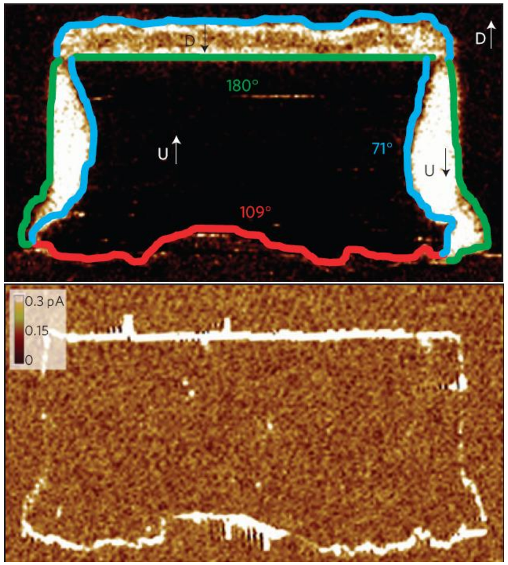
DW enhancement

PRL 104, 187601 (2010)

See also lecture on negative capacitance on Friday

Domain wall functionality

Domain walls break symmetry of the bulk → new properties!



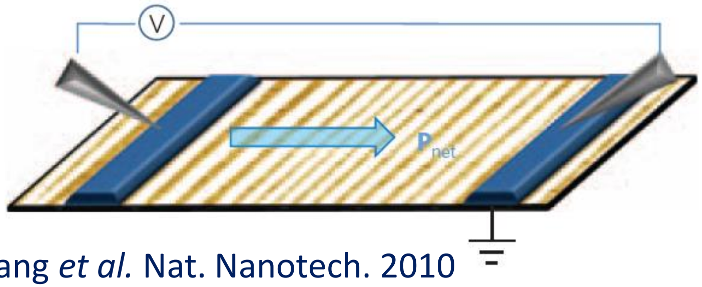
Seidel *et al.* Nat. Mater. 2009

Ferrielectric domain walls in $CaTiO_3$

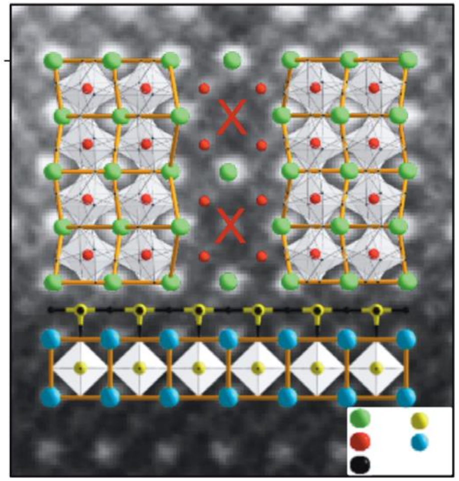
Polar domain walls in $SrTiO_3$

Conducting domain walls in ferroelectrics

Photovoltaic response at domain walls in $BiFeO_3$



Yang *et al.* Nat. Nanotech. 2010



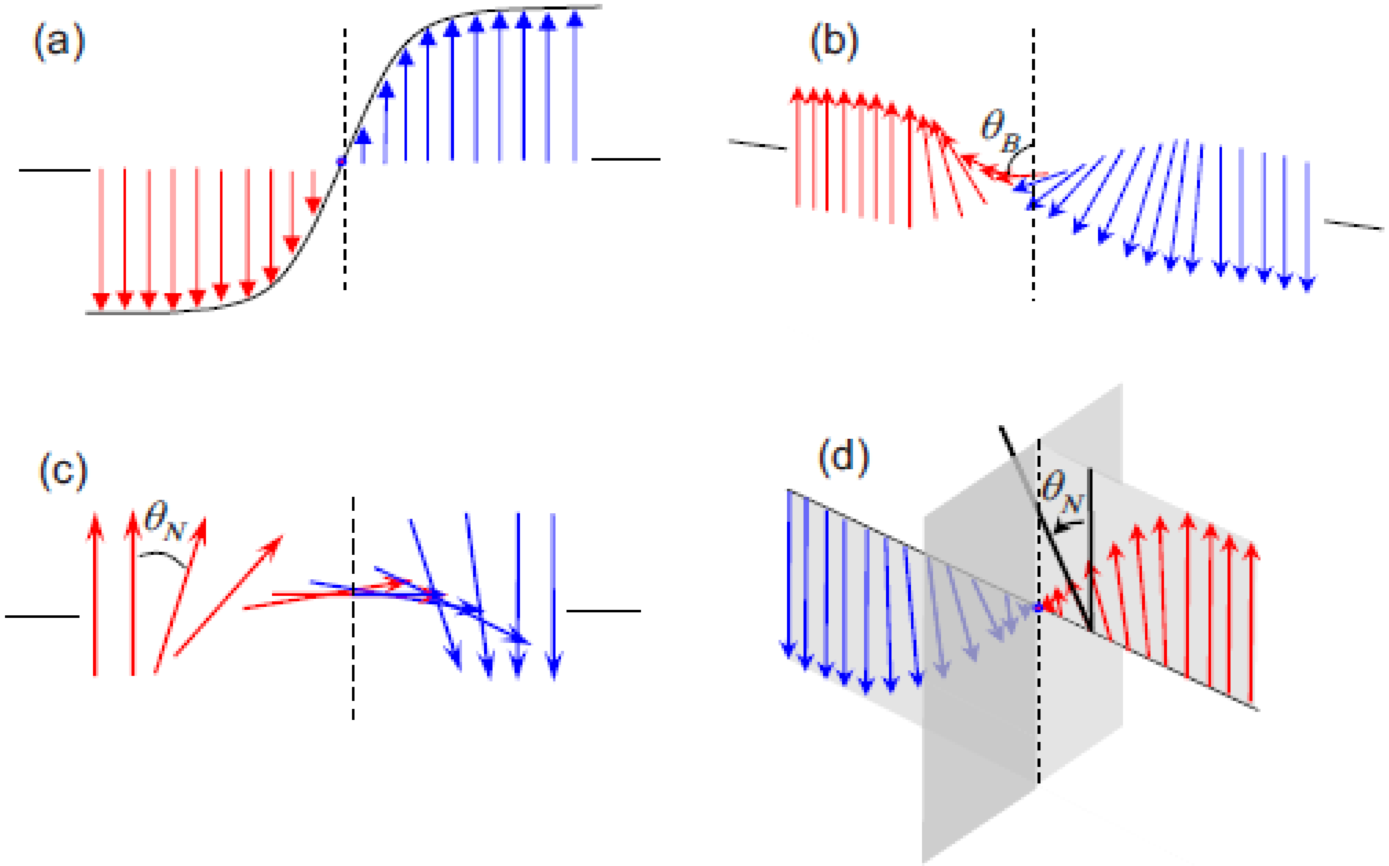
Farokhipoor *et al.* Nature 2015

Superconducting DWs in WO_{3-x}

Magnetism at domain walls

“Domain Wall Nanoelectronics” – Catalan *et al.* Rev. Mod. Phys. 2012

Domain walls – 2D nanoscale objects

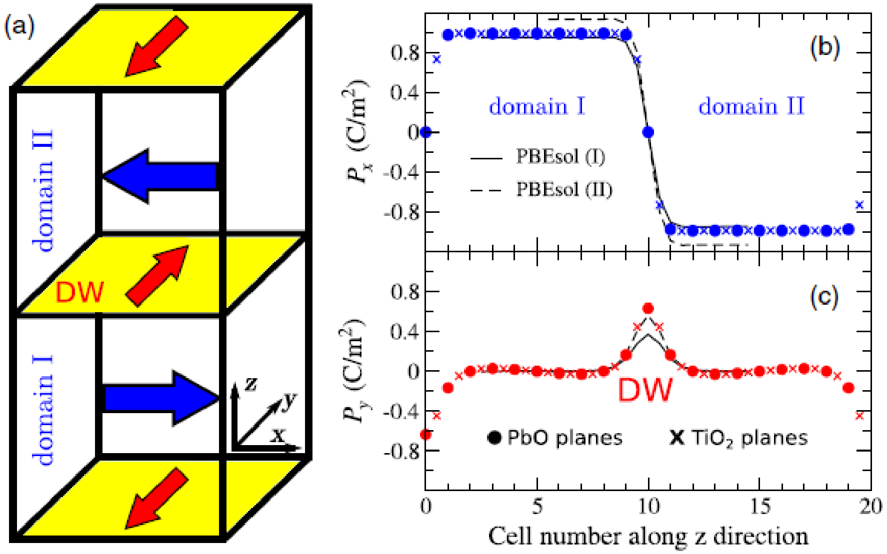


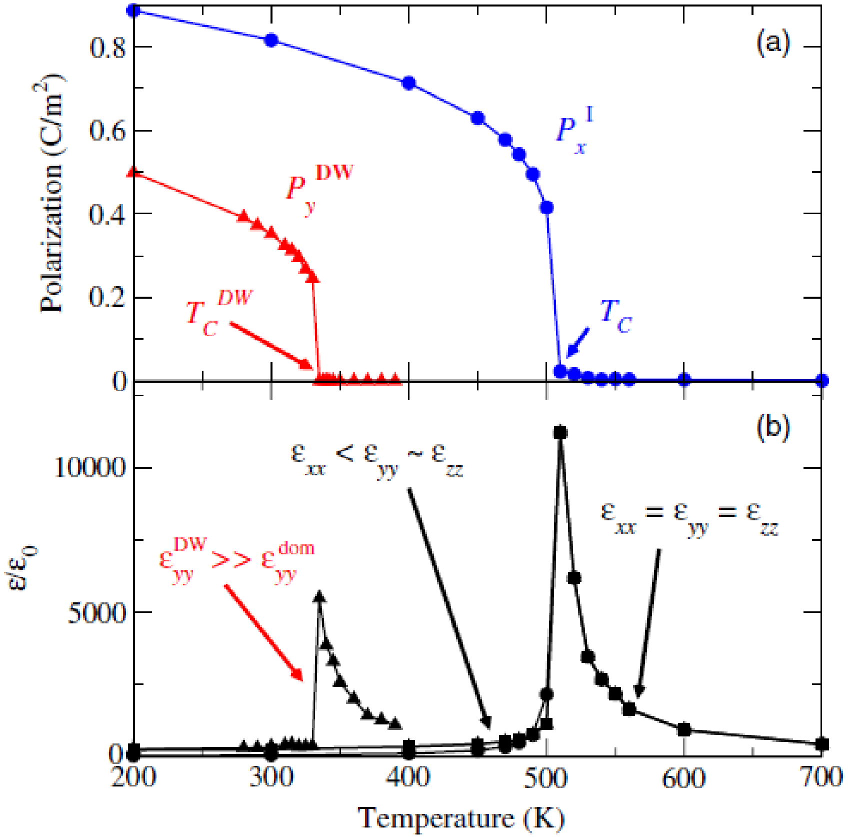
DW structure often not *purely* Ising-like

Lee et al. Phys. Rev. B 2009

(also Stepkova et al. JPCM 2012)

Phase transitions within domain walls



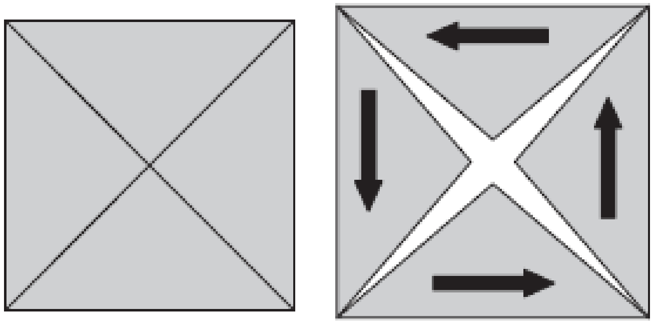


Many interesting theoretical predictions for domain walls and domain structures still to be experimentally explored!

Wojdel & Iniguez, PRL 2014

Nanoscale polarization patterns

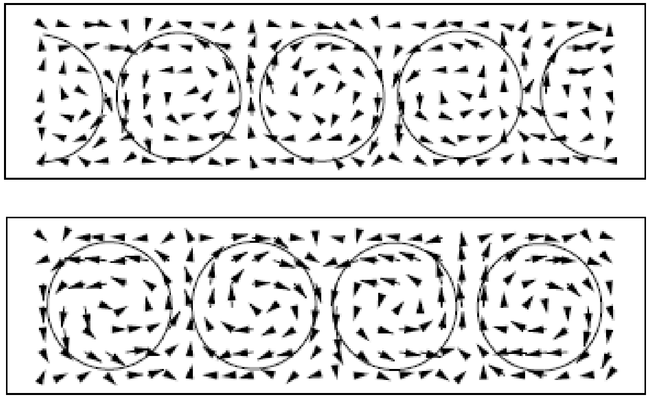
Catalan et al. Rev Mod Phys 2011



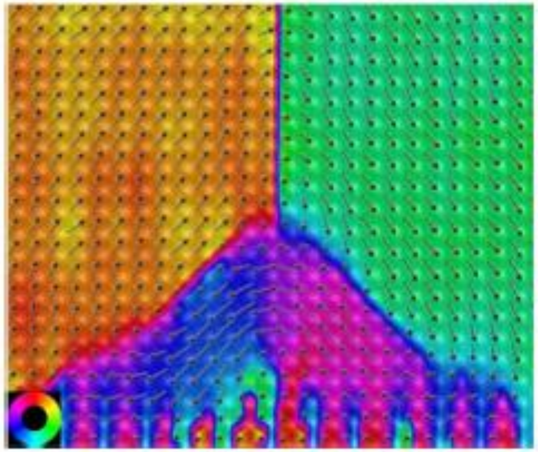
Above T_c Below T_c

Large polarisation-strain coupling – large energy penalty for polarisation rotation in bulk

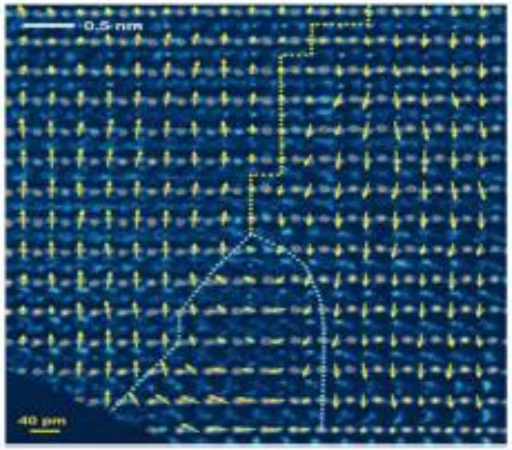
BUT in very thing films & nanostructures can have large local distortions - unusual polarisation structures possible



Naumov & Bellaiche Nature 2004



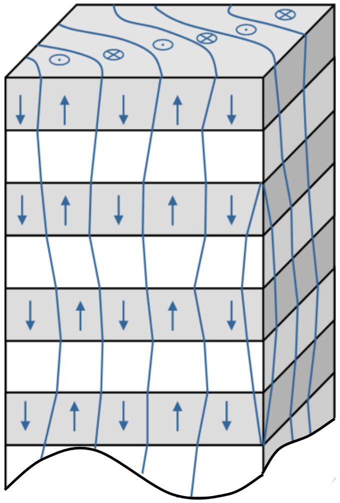
Nelson et al. Nano Letters 2011



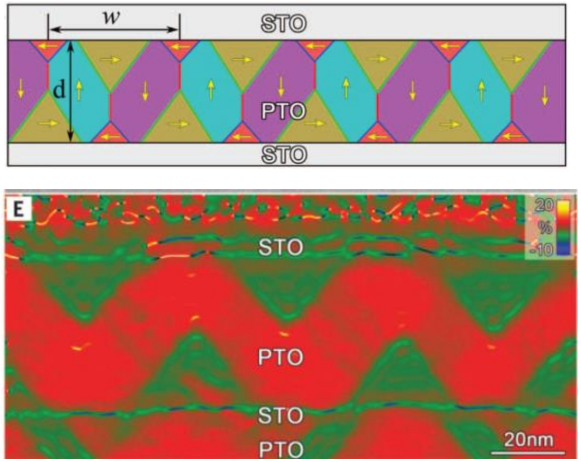
Jia et al. Science 2011

Domains in ferroelectric superlattices

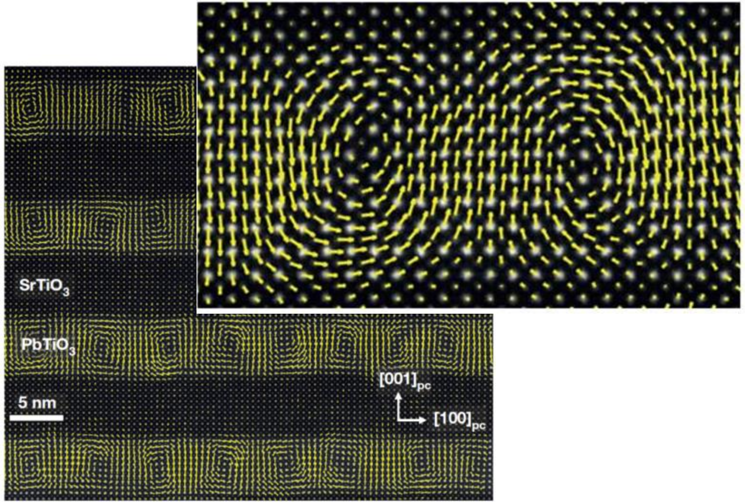
‘Flux-closure domains/vortices’



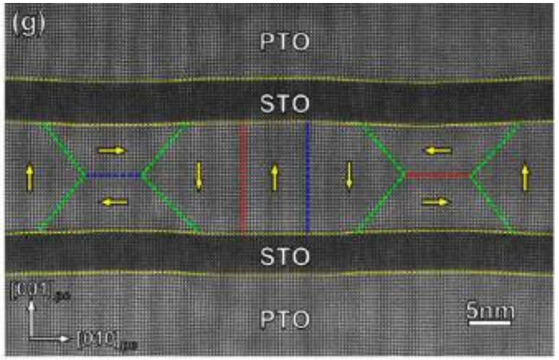
Zubko et al. PRL 2010;
Nano Letters 2012



Tang *et al.*, Science. 2015

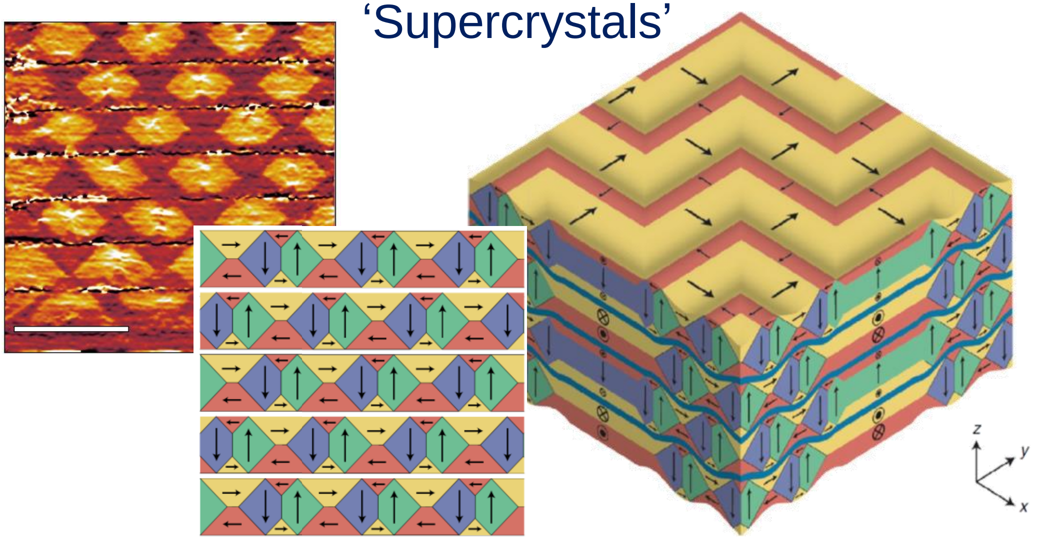


Yadav et al. Nature 2016



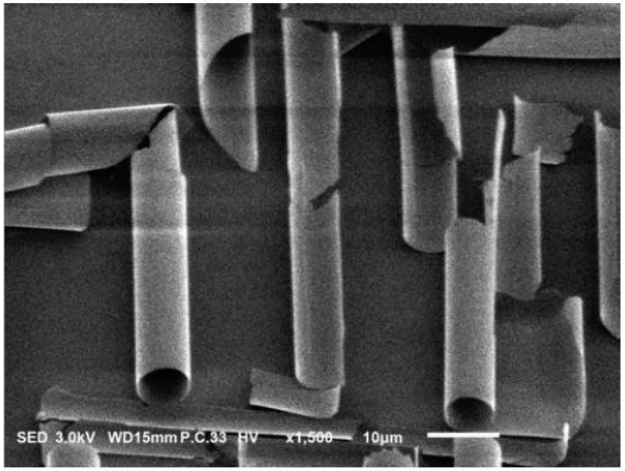
Liu et al. Nano Letters 17, 7258 (2017)

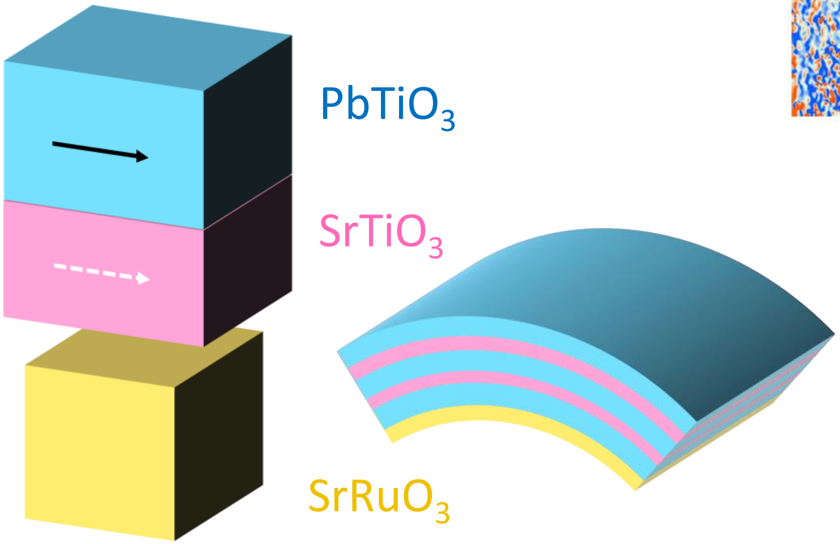
‘Supercrystals’

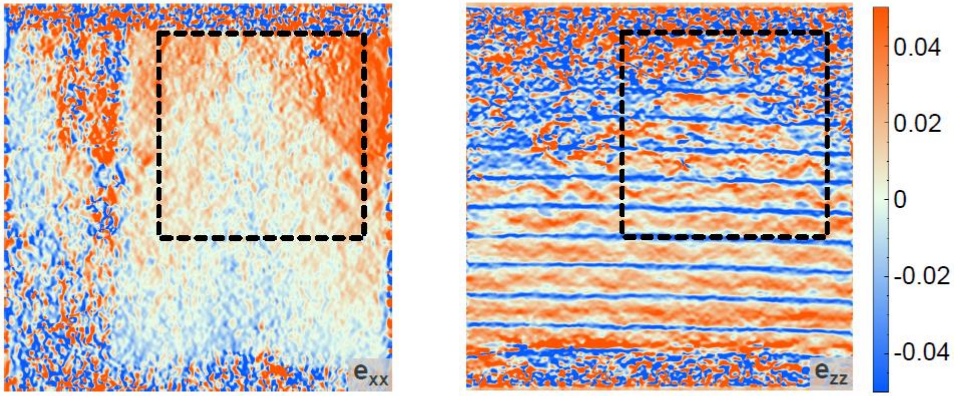


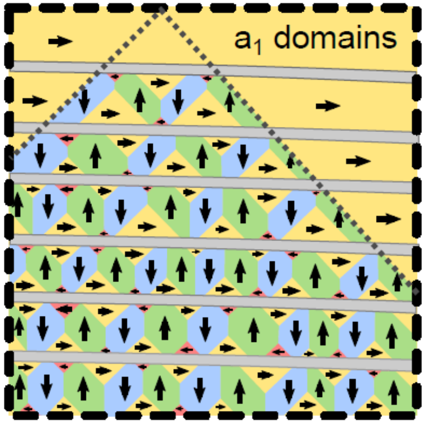
Hadjimichael et al. Nat. Mat. (2021)

Free-standing membranes & nanostructures



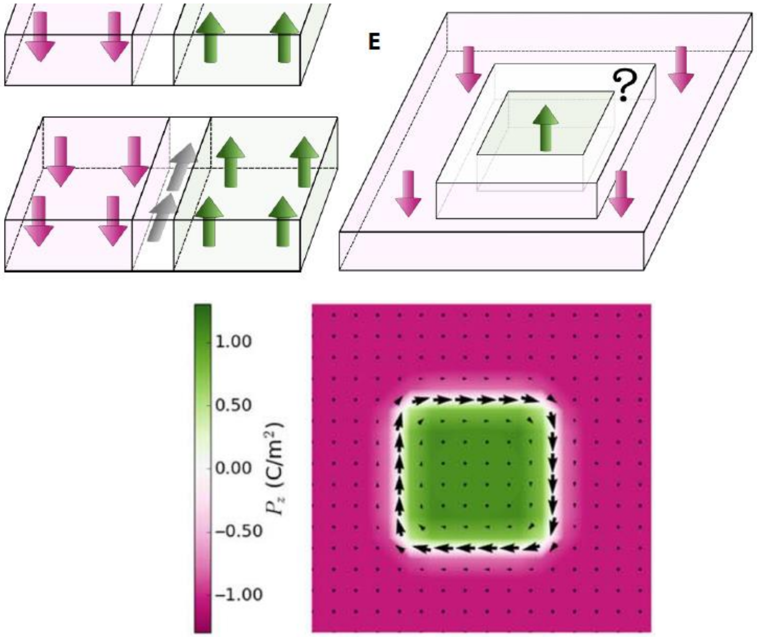




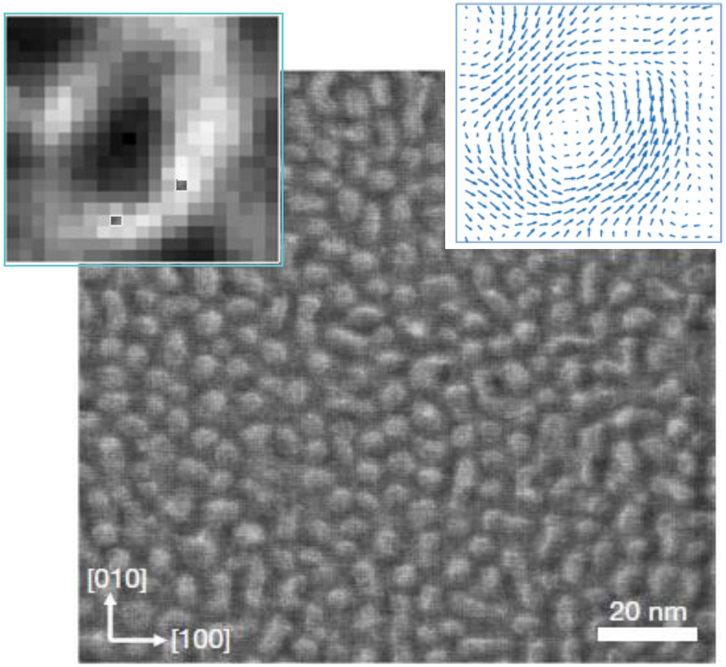


Y. Li et al. Adv. Mater. (2022)

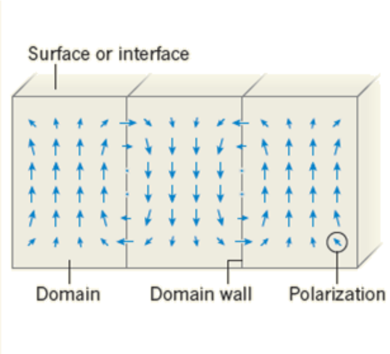
Skyrmion bubbles



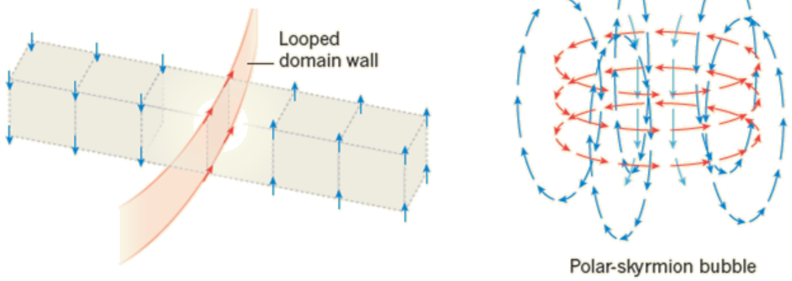
Pereira Goncalves et al. Science Advances 2019

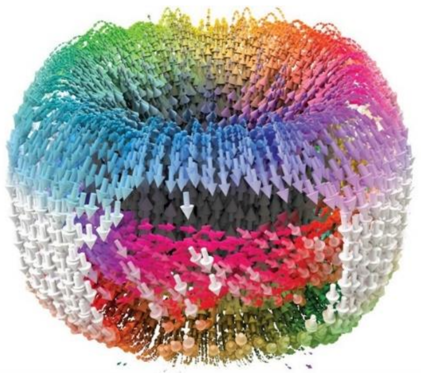


Das et al. Nature 2019



Zubko, Nature N&V (2019)



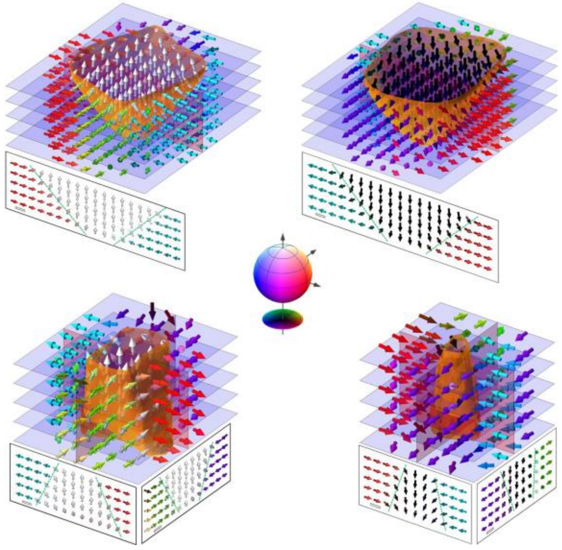


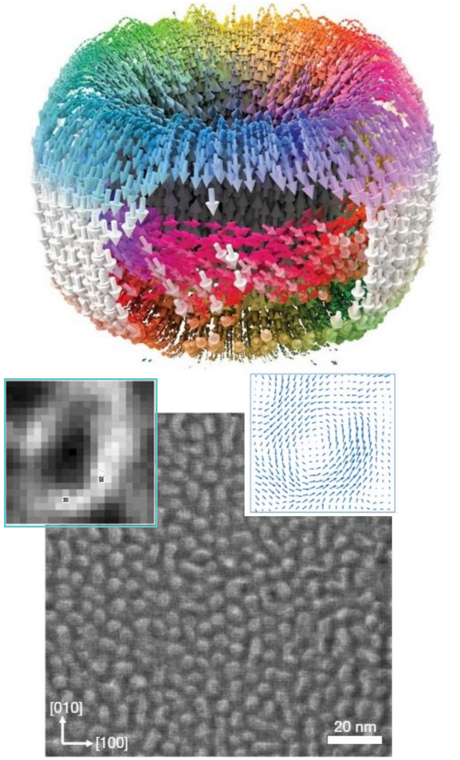
See lecture by Jorge Iñiguez

A zoo of topological objects

Merons

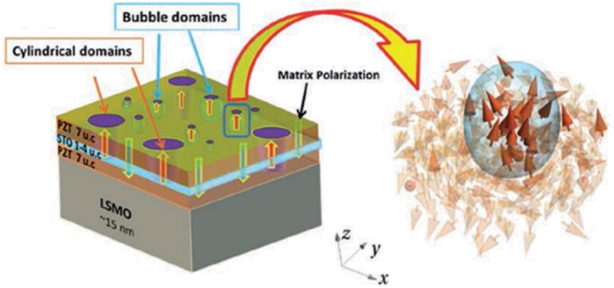
Wang et al. Nat Mat 2020





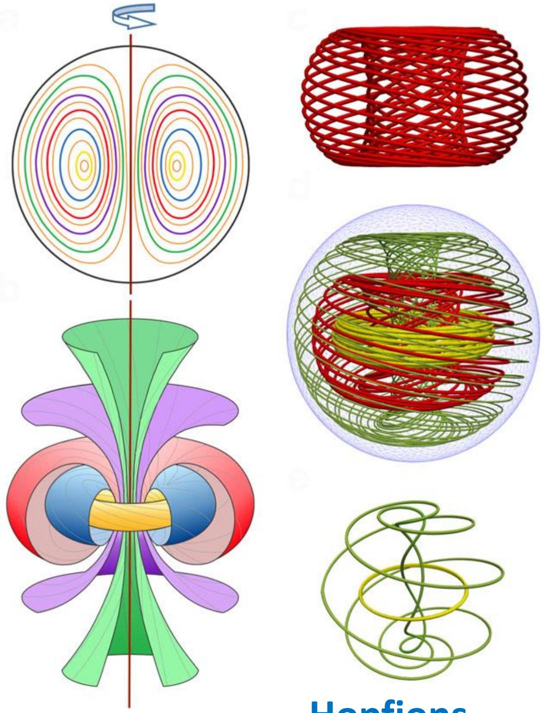
Skyrmion bubbles

Das et al. Nature 2019



Polar bubbles

Zhang et al. Adv Mat 2017
Lichtensteiger et al. Nano Lett 2014



Hopfions

Luk'yanchuk et al. Nat Comms 2020

See lecture by Jorge Iñiguez

A flavour of current activity

- Hafnia ferroelectrics – talk by Beatriz Noheda
- Antiferroelectrics – talk by Karin Rabe
- 2D van der Waals ferroelectrics
- Domain wall functionality
- Strain engineering
- Flexoelectricity – talk by Tae Won Noh
- Ferroelectric photovoltaics
- Negative capacitance – talk on Friday
- Ferroelectric field effect devices & tunnel junctions
- Ferroelectrics for neuromorphic computing – talk by Beatriz Noheda
- Electrocalorics – talk by Emmanuel Defay
- Free-standing films – talk by Mariona Coll
- Multiferroics – talk by Morgan Trassin
- Topology in ferroelectrics – talk by Jorge Iñiguez
- Relaxors – talk by Brahim Dkhil
- Ferroelectric quantum criticality
- Artificially layered ferroelectrics
- ‘Ferroelectric metals’