ISOE, Corsica 2019

Introduction to (oxide) ferroelectrics

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Institut Català de Nanociència i Nanotecnologia



European Research Council

IMPORTANT DISCLAIMER

NOT all ferroelectrics are perovskites, or even oxides.

In this talk we will use perovskite ferroelectrics as a useful introduction, but Some of the things that we will say about perovskites are <u>not</u> true for all ferroelectrics.

Outline

1. Ferroelectrics: basic principles and applications.

2. Measurements: experimental artifacts.

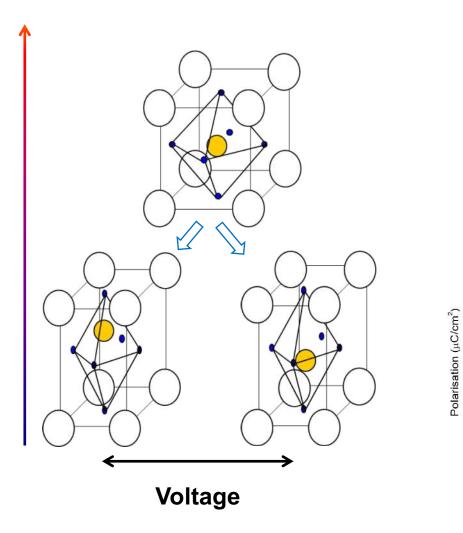
3. Landau theory & strain engineering.

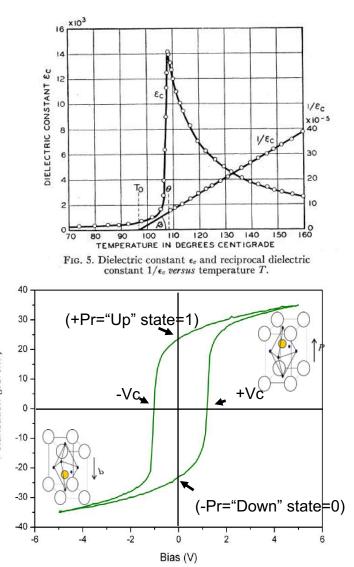
4. Trending topics.

Before we start...

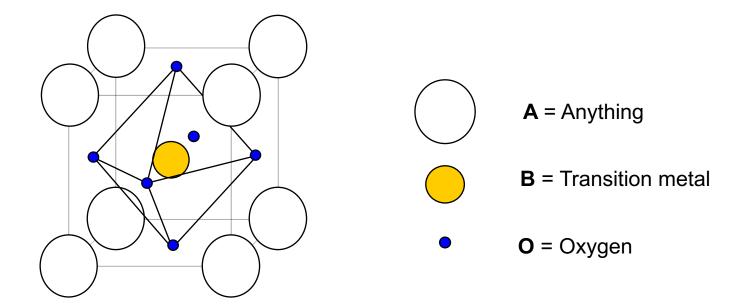
FERROELECTRICS

Temperature





Why perovskite oxides?



- (Relatively) simple structure.
- Strong interaction between oxygen p-orbital and transition metal d-orbital.
- Many different compositions with same structure but very different properties.
- <u>Very</u> sensitive to strain: suitable for strain engineering.

Notable perovskites...

Ferroelectrics and piezoelectrics

BaTiO₃, PbTiO₃, Pb(Zr,Ti)O₃, Pb(Mg,Nb,Ti)O₃, Pb(Zn,Nb,Ti)O₃ (world's best piezos)

Multiferroics TbMnO₃, BiFeO₃ (first room temperature multiferroic)

Colossal magnetoressistance manganites (La,Sr)MnO₃, (La,Ca)MnO₃ (highest magnetoresistance of any material)

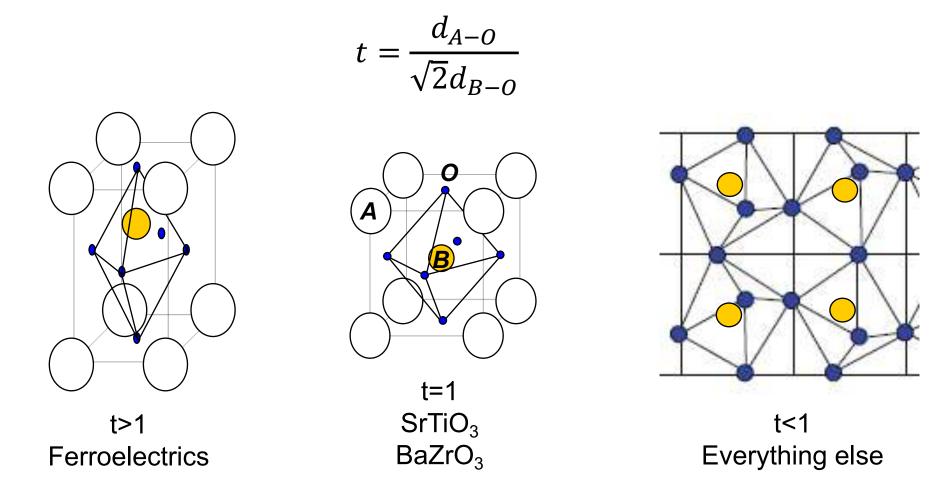
High temperature superconductors: YBa2Cu₃O_{7- δ} (high temperature superconductors)

"Mott materials" RENiO₃ (tunable metal-insulator transition)

The drossophila of perovskites $SrTiO_{3-\delta}$ (from quantum paraelectric to superconductor and everything in between)

Funky interfaces LaAlO₃ (insulator) on SrTiO₃ (insulator) = (super)conducting interface.

Perovskite geometry: Goldschmidt tolerance factor



Note #1: to estimate t, use the ionic radii from: R. D. Shannon, Acta Cryst. (1976). A32, 751

Note #2: this paper has almost 50 000 citations!

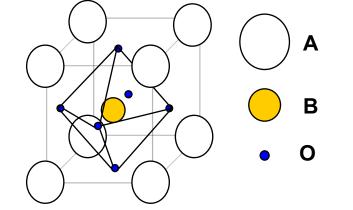
Chemistry of perovskite ferroelectricity

Two classic chemical mechanisms for a polarized perovskite unit cell:

1. The p-orbital of oxygen hybridizes with the d-orbital of the transition metal in B-site. Easiest when there are no electrons in the d-orbital (to minimize Coulombic repulsion). Thus, d_0 . Examples: Ti⁺⁴ (but not Ti⁺³), Zr⁺⁴, Nb⁺⁵ or Ta⁺⁵.

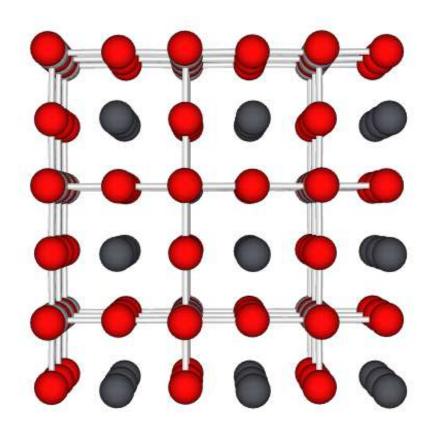
2. The last occupied orbital of A-site is an s-orbital with two electrons (aka "lone pair"). Spherical symmetry of s-orbital makes it easy for these electrons to move in any direction. Examples: Bi⁺³, Pb⁺², Li⁺¹.

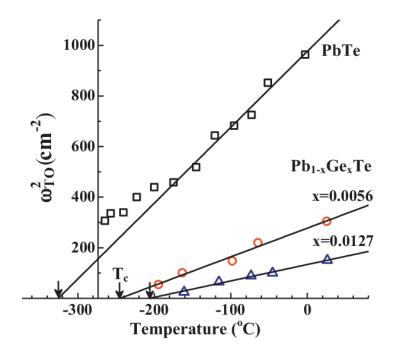
<u>Final consideration: the unit cell has to be charge-neutral!</u> In ABO₃ there are 3 oxygens with total negative charge=-6. Thus, the total charge of A+B=+6



	(+1) (+5)	+2 +4	+3 +3
A site	Li	Pb, Ba, Sn	Bi
B site	Nb, Ta	Ti, Zr	Fe, Mn?

Ferroelectricity as a frozen phonon

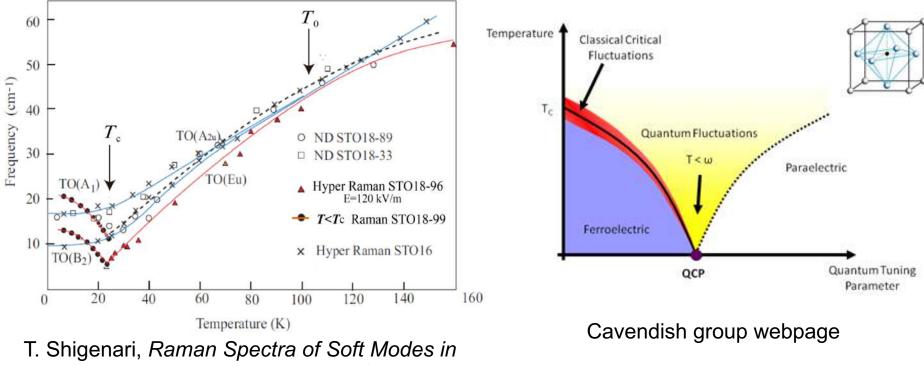




S. Lee et al, J. Am . Ceram. Soc. 2012

Note: quantum paraelectrics

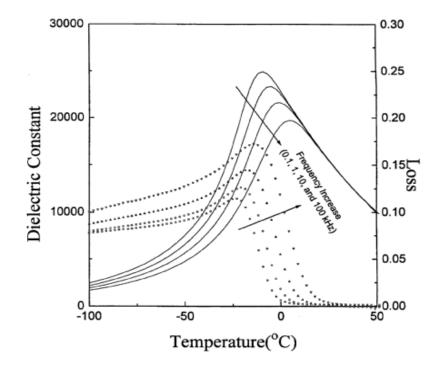
In SrTiO3, the ferroelectric phonon freezing temperature is so low that quantum fluctuations prevent it from actually freezing. It stays paraelectric: "quantum paraelectric"

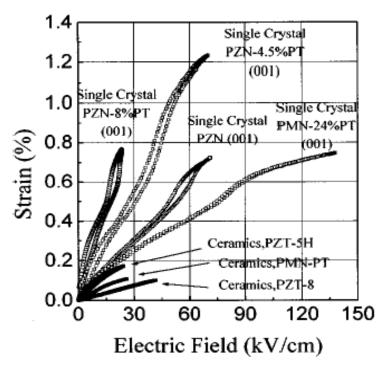


Ferroelectric Crystals, DOI: 10.5772/60613

If you substitute O16 for O18, the phonon becomes "heavier" and freezes at higher temperature, so $SrTiO_3$ actually becomes ferroelectric.

Relaxor ferroelerics



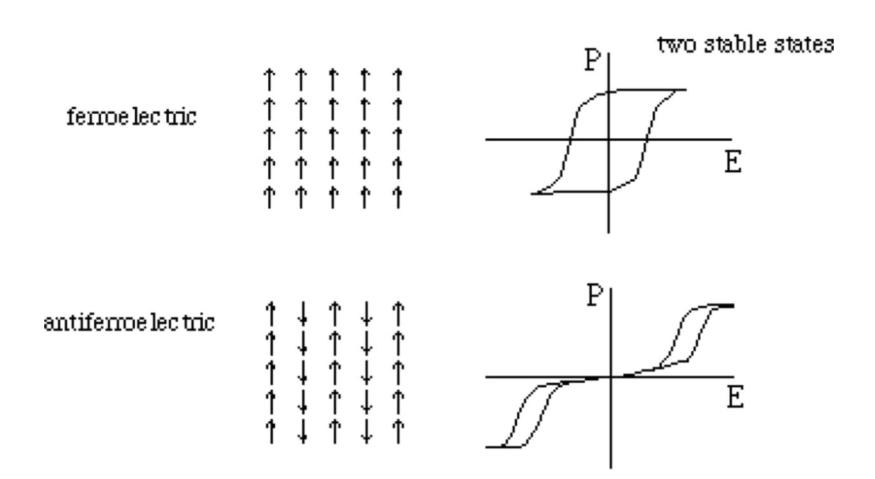


S.E. Park, T.R. Shrout, J.Appl.Phys 82, 1804 (1997)

- Very high dielectric constant with weaker T-dependence tan ferroelectrics (socalled "difuse phase transition").
- Notice the strong frequency dependence
 of permittivity.

Highest electromechanical responses (piezoelectricity, electrostriction) of any ceramic material.

Antiferroelectrics

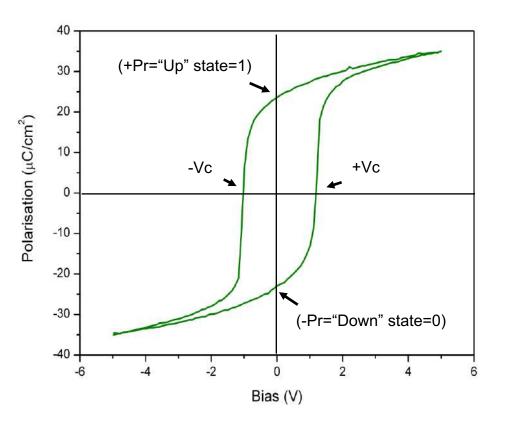


Applications

- Ferroelectric memories
- Capacitors
- Pyrelectric sensors
- Piezolectric transducers
- "Futuristic" applications...

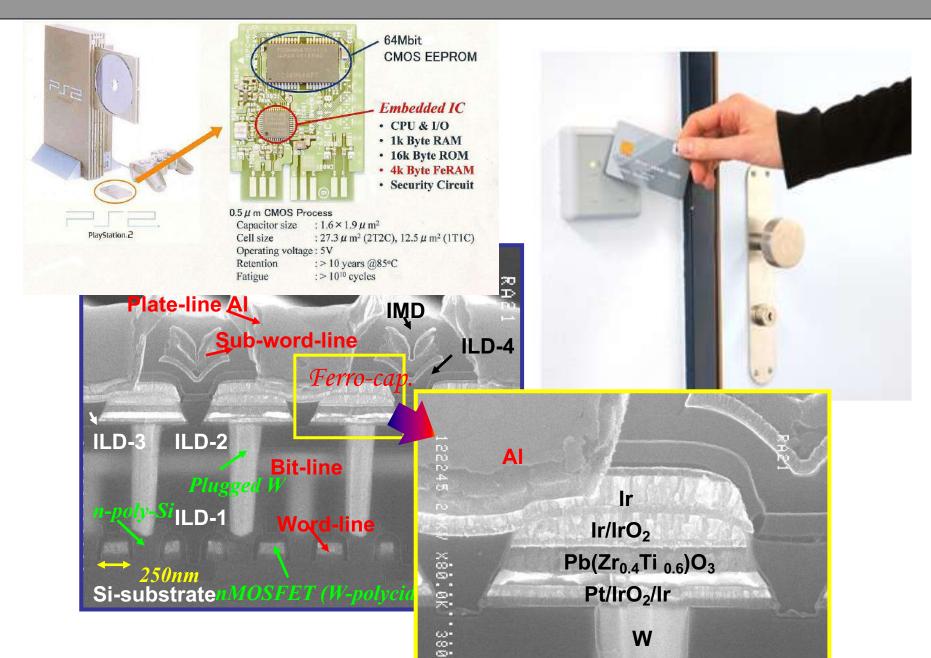
FERROELECTRIC MEMORIES

- Coercive field, E_c : $E_c = 10 - 100 \text{ kV/cm}$
- Coercive Voltage V_c , for 1mm $V_c = 1000 - 10000V...huge!$
- Coercive voltage V_c , for $1\mu m$ $V_c = 1 - 10V...tiny!$

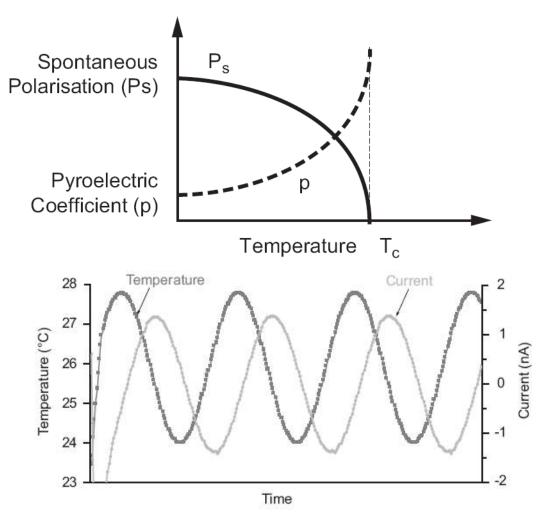


Thin Films (t < 1 μ m) suitable for ferroelectric memories.

Memories



Pyroelectricity



Sensitivity to temperature makes it useful for thermal detectors, infrared cameras and pyroelectric voltage generators

R.W. Whatmore, "Polar Oxides: Properties, Characterisation and Imaging" Wiley (2005)

Pyroelectric devices

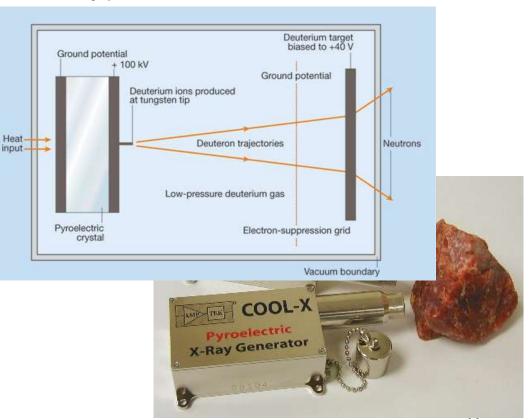
 Applications range from heat sensors to x-ray and neutron emission via pyroelectric voltage



Observation of nuclear fusion driven by a pyroelectric crystal

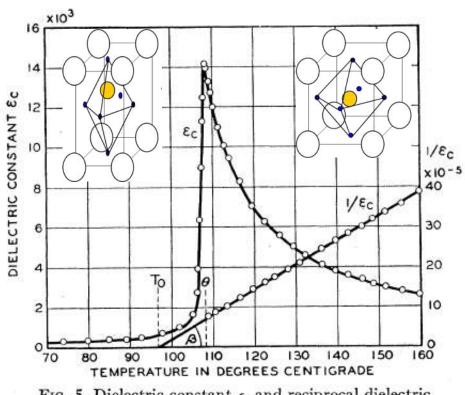
B. Naranjo¹, J.K. Gimzewski^{2,3} & S. Putterman^{1,3}

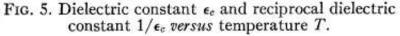
(Nature 2005)



Capacitors

Capacitance:
$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$
 Thin film = Big capacitance



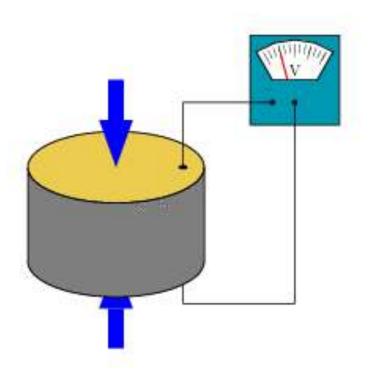


Dielectric constant of BaTiO₃



Market > \$10⁹/year Price ~ 0.1 cents each >10¹² made each year. You own many.

Piezoelectricity



Direct piezoelectricity: sensors. Converse piezoelectricity: actuators.

Examples: sonar, ultrasound scanners, accelerometers, inkjet printers, resonanc filters...

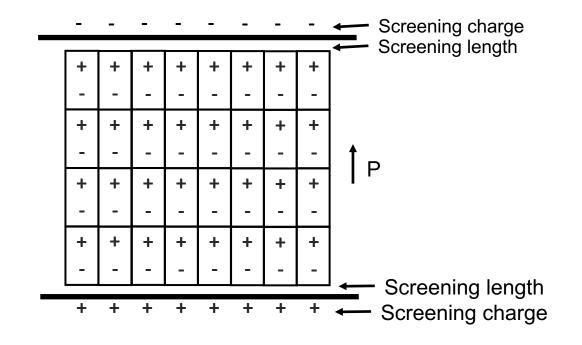
NOT YET COMMERCIAL applications of FE

- Field-effect transistors
- Electrocalorics
- Photovoltaics
- Energy storage
- Magnetoelectric multiferroics

Two dirty secrets of real ferroelectrics

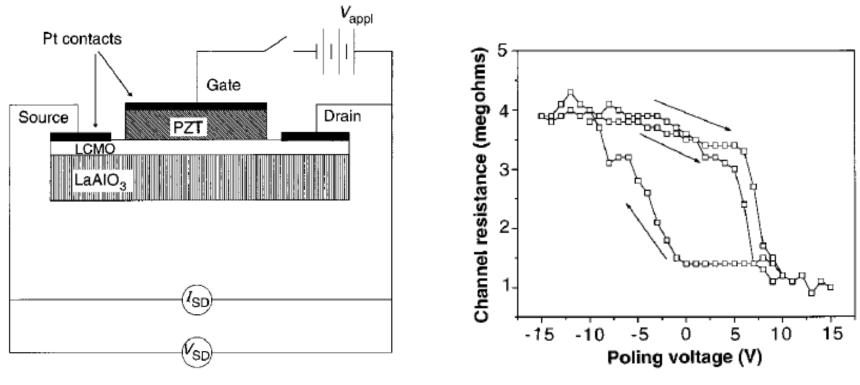
1. They are NOT insulators but wide bandgap semiconductors. (2.5-2.7 eV for BFO; 3.5-4 eV for PZT or BTO).

2. Depolarizing fields are all but inevitable.



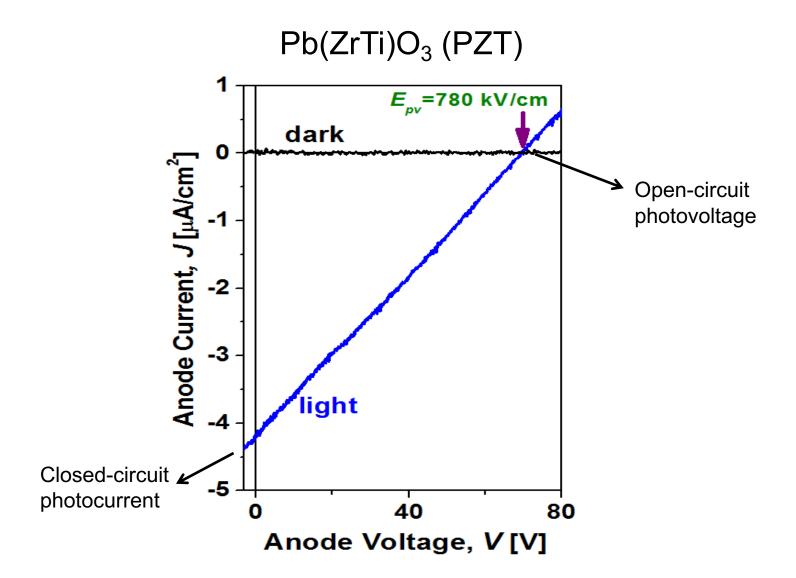
Field field effect transistor+memory

Use the depolarizing field emanating from the ferroelectric gate to modulate the charge density (and thus the conductivity) in the channel.



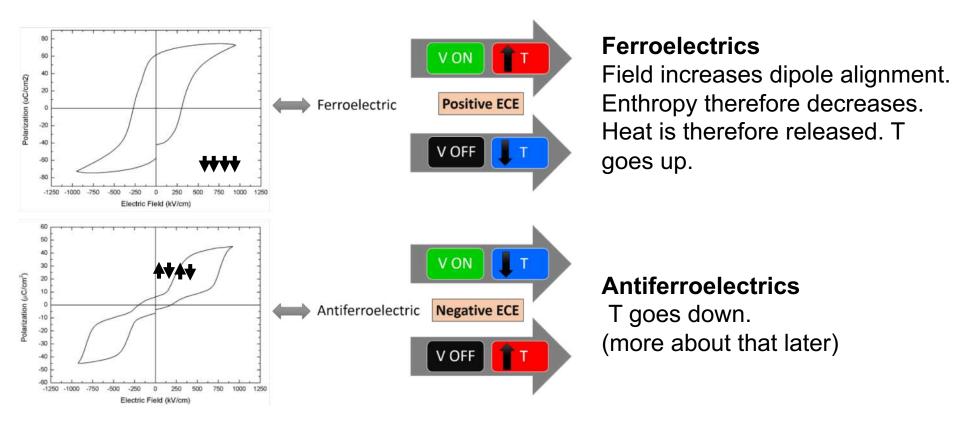
Mathews, Science 1997

Ferroelectrics and larger-than-bandgap photovoltages



The internal asymmetry of the crystal structure can separate photo-excited carriers

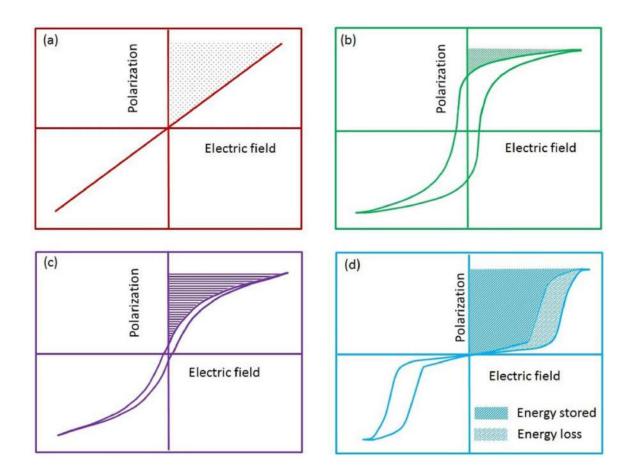
Electrocaloric effect of FE and AFE



We use the field-induced change in enthropy to absorbe or release heat.

Energy storage in antiferroelectrics

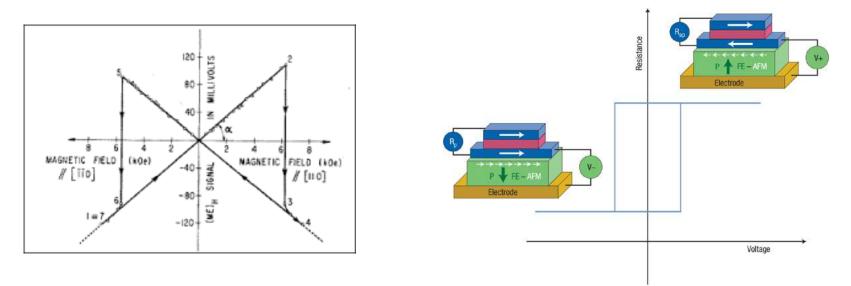
Work required to charge a capacitor $U=\int EdP$



Chauhan et al, Materials 2015

Multiferroics

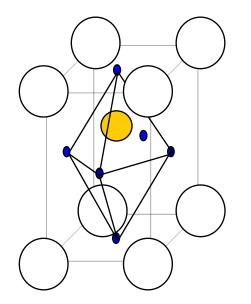
- MULTIFERROIC=Material with two or more ferroic order parameters (e.g. ferroelectric+ferroelasic, ferroelectric+ferromagnetic).
- MAGNETOELECTRIC MULTIFERROIC=material that is symultaneously magnetic and ferroelectric, and where those two orders are coupled.
- If coupling is strong, we can write electrically (and voltage scales down with thickness) while reading magnetically (readout is non-destructive).



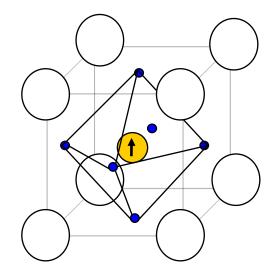
E. Ascher et al, Journal of Applied Physics, 1966.

Bibes&Barthelemy, Nat. Materials 2008

Why are perovskite multiferroics rare?



Off-centering of central cation often caused by hybridisation of **empty dorbital** (d⁰) with p-orbital of oxygen



Magnetism usually requires exchange interaction between **electron in d-orbital** of central cation and p-orbital of oxygen



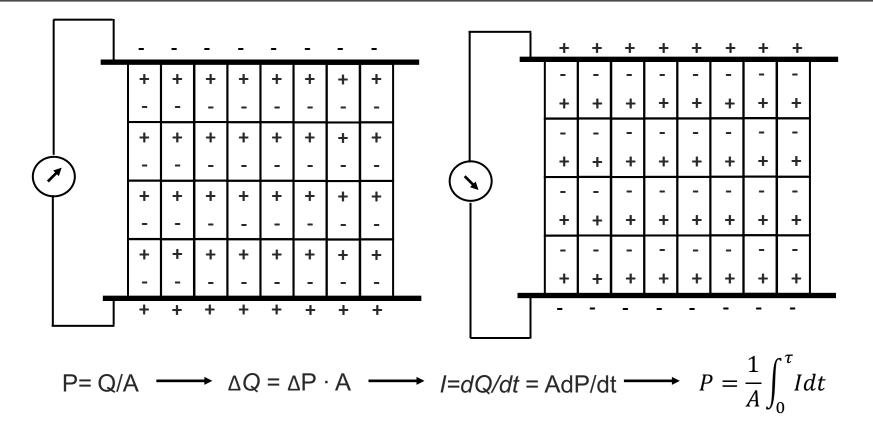
MUTUALLY EXCLUSIVE REQUIREMENTS!

N. A. Hill, J. Phys. Chem. B 104, 6694 (2000).

Part 2

 Experimental characterization of ferroelectrics and multiferroics: basic principle and important artifacts.

What do we actually measure?

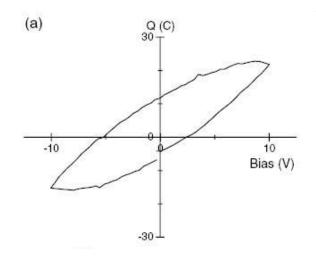


- Polarization, pyroelectricity, permittivity: they are characterized by measurements of **surface charge**.
- In fact, what we measure are CHANGES in surface charge in the form of displacement currents.

Problem: all changes polarization induce currents, but not all currents arise from polarization changes.

Polarization Artefacts

• Artifact number 1: non-ferroelectric hysteresis loops



Origin of bogus loops

Hysteresis loops are in fact **charge vs voltage** loops: $Q = A (2P_r + \sigma E\tau)$, (*A=electrode area, P=polarization, \sigma= sample conductivity and \tau =integration time of hysteresis loop.*

Charge may come from ferroelectric polarization, but it may also have a conductivity (leakage) current contribution in poorly insulating samples (often the case in multiferroics and photovoltaic materials). Sometimes, leakage is the ONLY contribution.

•Schotky contacts back-to-back can give you spurious and very convincing hysteresis loops (Pintilie and Alexe, APL 2005)

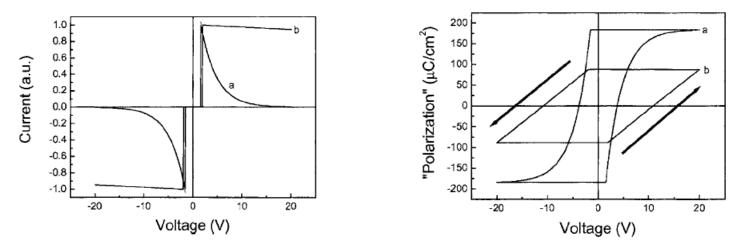
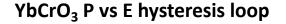


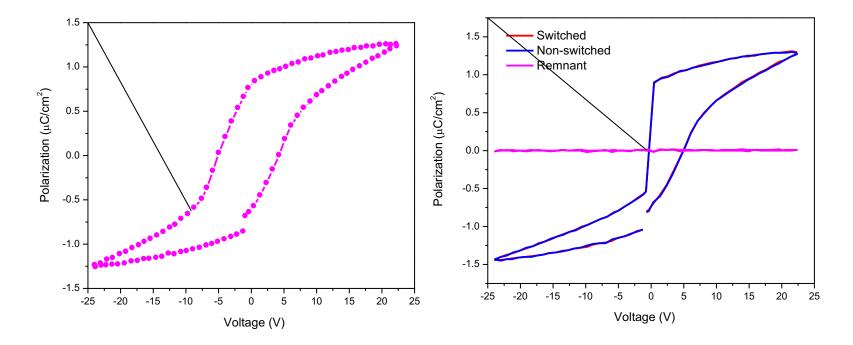
FIG. 2. The voltage dependence of the current due to the carrier emission from the traps. Parameters in Eq. (5) used for simulation were: electrode area $A = 1 \text{ mm}^2$, $N_{T0} = 10^{21} \text{ cm}^{-3}$, $\tau = 0.2 \text{ ms}$. The frequency was 100 Hz for the curve (a) and 10 kHz for (b).

FIG. 3. The hysteresis loop obtained by the numerical integration of the current-voltage dependencies presented in Fig. 2 for two frequencies: (a) 100 Hz and (b) 10 kHz. The arrows show a counterclockwise orientation of the loops, as for a normal ferroelectric hysteresis. The loop (b) was magnified ten times on the polarization axis.

Fake loops can be very realistic!

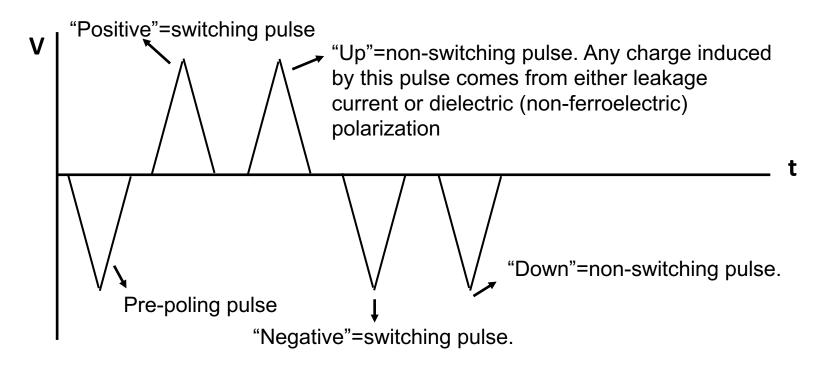


YbCrO₃ PUND measurement



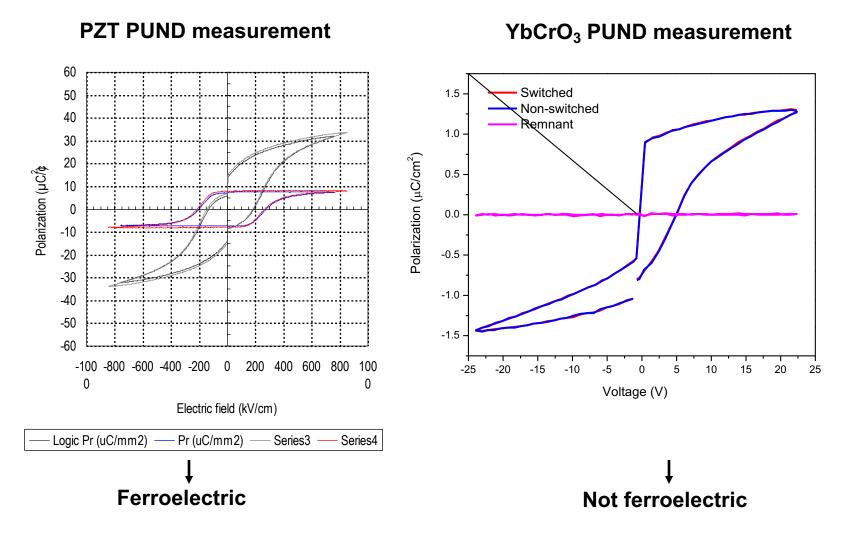
How do to identify fake loops (1)

- Some machines (e.g. Radiant) allow to extract the switching charge from the non-switching one performing so-called PUND measurements.
- **PUND**="Positive-Up, Negative-Down", which stands for the sequence of applied voltage pulses.



Substracting the charge collected in the non-switching pulses from that of the switching ones, one can separate the true ferroelectric polarization

Two examples

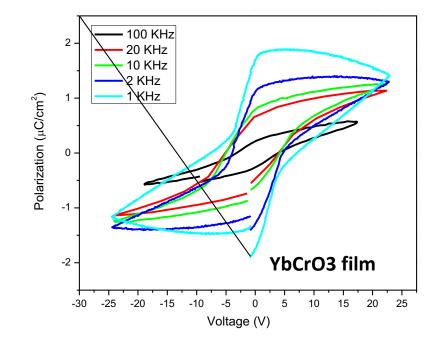


How do to identify fake loops (2)

Examine frequency dependence of hysteresis loops. The integrated charge is:

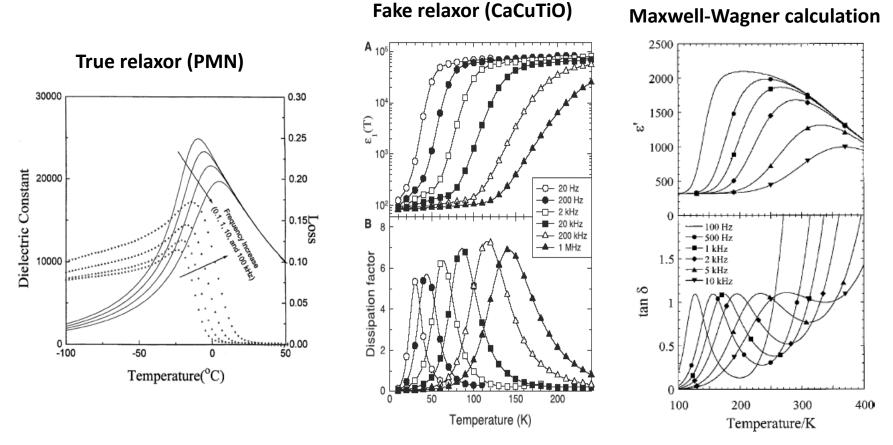
$$Q = A \times \left(2P_r + \int_{\tau} I \, dt\right) = A \times \left(2P_r + \int_{\tau} \frac{\partial I}{\partial V} \frac{\partial V}{\partial t} \, dt\right)$$

Leaked charge grows proportionally to integration time; switched (ferrolelectric) charge does not.



Dielectric Artefacts

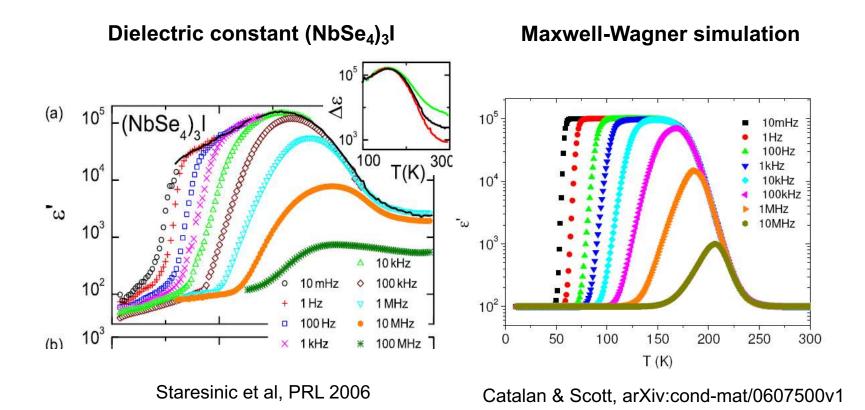
Artefact no 2: the colossal, relaxor-like dielectric constant



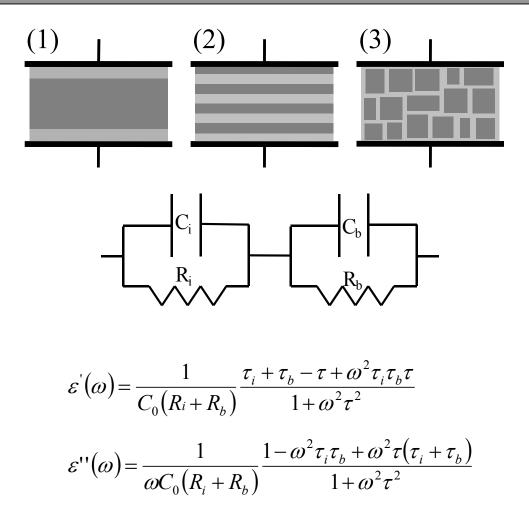
C. C. Homes et al, Science (2001)

Catalan et al, APL (2000)

Example



The Maxwell-Wagner model



The dielectric effectively consists of (at least) two leaky capacitors in series. The time constant of each sub-layer is $\tau_j=R_jC_j$

How does it work?

At high frequencies:

$$\varepsilon'(\omega) = \frac{C_i C_b}{C_0 (C_i + C_b)}$$

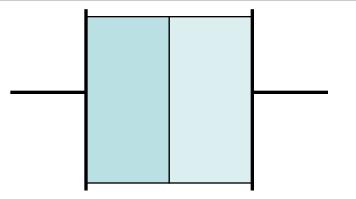
The capacitance is the standard dielectric response of a series capacitor.

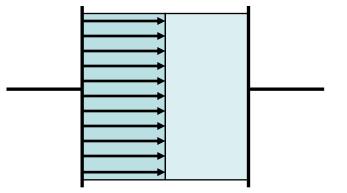
At low frequencies:

$$\varepsilon'(\omega) = \frac{R_i^2 C_i + R_b^2 C_b}{C_0 (R_i + R_b)^2}$$

Current has enough time to flow through the low-resistivity layers.

The thickness of the capacitor is smaller, so capacitance (and apparent dielectric constant) increases at low frequencies and/or at high temperatures.





Catalan & Scott, Nature 2007

"Magnetoresistive magnetocapacitance"

 Change in R means change in time constant τ (=RC) and also change in the lowfrequency capacitance.

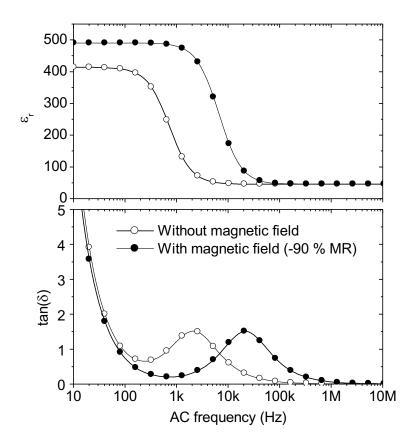
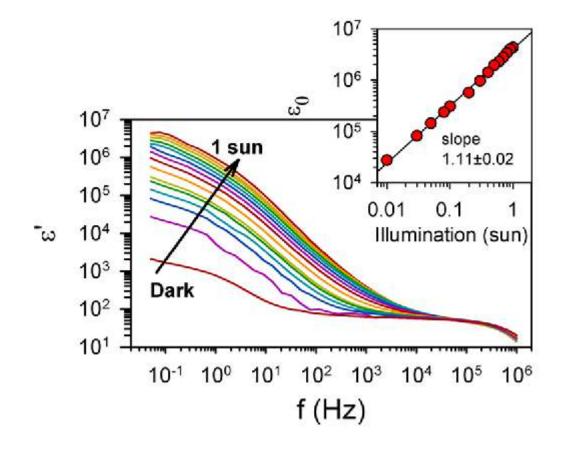


Photo-conductivity will also look like photo-

"Photoinduced giant dielectric constant..."

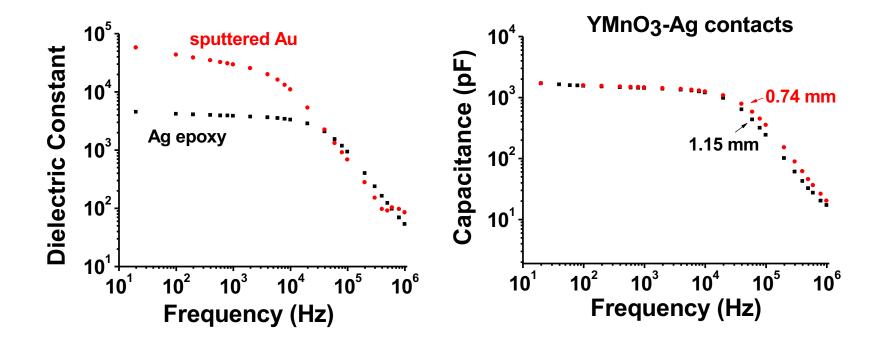


E. J. Juarez-PerezThe journal of physical chemistry letters 2014

Identifying interfacial capacitance

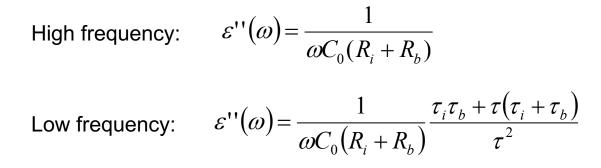
1) Interfacial capacitance depends on the type of electrode

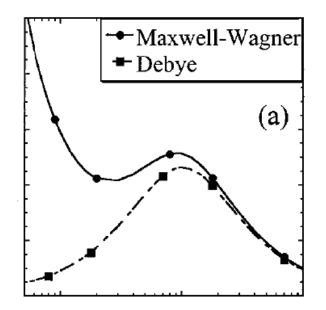
2) Interfacial capacitance is independent of capacitor thickness



Dielectric properties of YMnO3 single crystal multiferroic

Identifying artifacts: dielectric loss

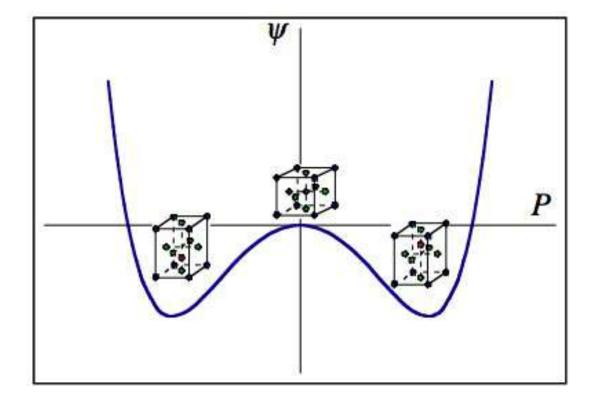




M-W: losses increase with decreasing frequency due to conductivity Relaxors: loses decrease with decreasing frequency

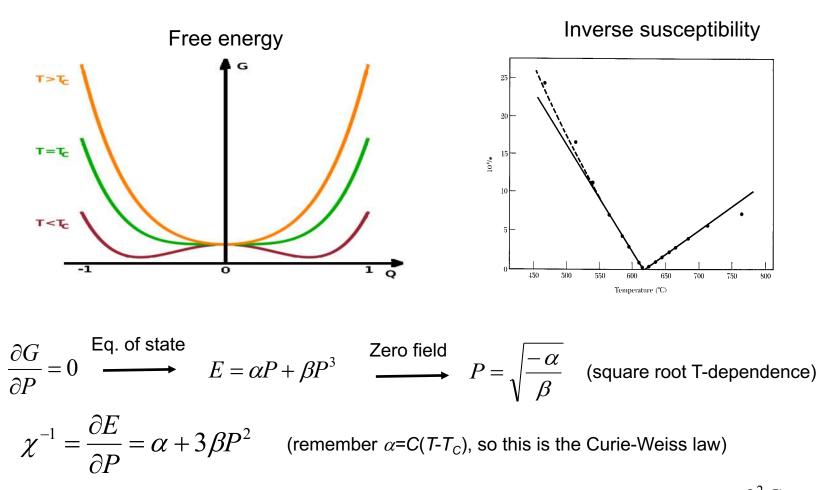
O'Neill et al, APL 2000

Part 3: Landau Theory and Strain Engineering



Landau theory of 2nd order transition

$$G = \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 - E P$$
 (where $\alpha = C(T - T_C)$)

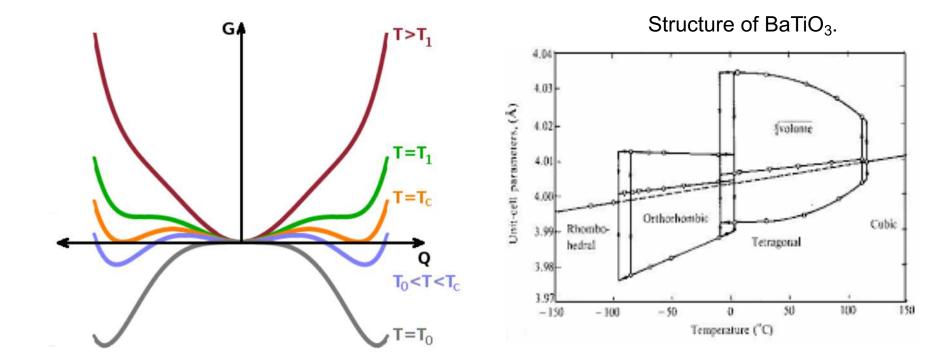


Notice also that the zero-field susceptibility is the curvature of the free energy: $\chi^{-1} = \frac{\partial^2 G}{\partial P^2}$ It can be negative (but unstable)

First order phase transition

$$G = \frac{1}{2}\alpha P^{2} + \frac{1}{4}\beta P^{4} + \frac{1}{6}\gamma P^{6}$$

If β <0, the transition is first order.



Note: most perovskite ferroelectrics are (slightly) first order in bulk The temperature-dependence of their transitions is hysteretic.

Landau theory of strain coupling

$$G = \frac{1}{2} \alpha_{ij} P_i P_j + \frac{1}{4} \beta_{iikl} P_i P_j P_k P_l + (higher order P terms)$$

$$-\frac{1}{2} s_{ijkl} (\sigma_{ik} \sigma_{kl}) - higher order X terms$$

$$-Q_{ijkl} (P_i P_j \sigma_{kl}) - higher order cross - coupling terms$$

- Biaxial in-plane stress: $\sigma_1 = \sigma_2 = \sigma$, $\sigma_{3-6}=0$
- Cubic-tetragonal transition with polarisation out-of-plane only: P_i=P₃

$$G = \frac{1}{2}\alpha P_3^2 + \frac{1}{4}\beta P_3^4 - \frac{1}{2}s_{ij}(\sigma_i\sigma_j) - Q_{j3}\sigma_j P_3^2 - E_3P_3 + \sigma_i\varepsilon_i$$

Minimise with respect to the order parameters:

$$\frac{\partial G}{\partial P_3} = 0 \qquad \frac{\partial G}{\partial \sigma} = 0$$

This yields the equation of state:

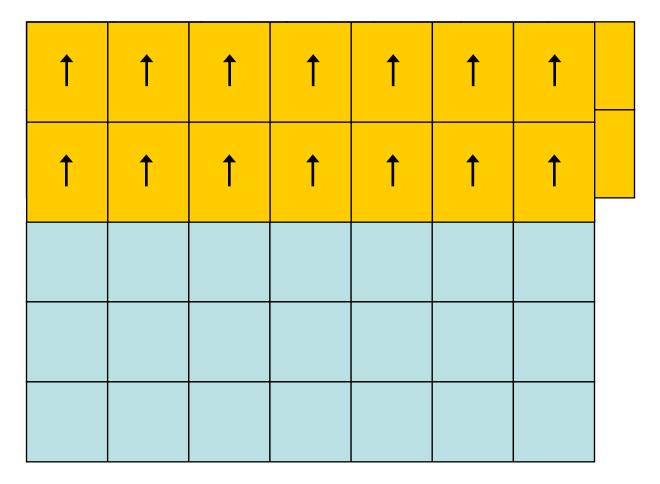
$$E = P\left[\alpha - 2Q_{13}\frac{Y}{1-\nu}\varepsilon\right] + P^3\left[\beta + 2Q_{13}^2\frac{Y}{1-\nu}\right] \quad \text{(where } \alpha = C(T-T_C)\text{)}$$

Strain causes shift in Tc and can change transition from first order (β <0) to second order

Strain engineering in ferroelectric thin films

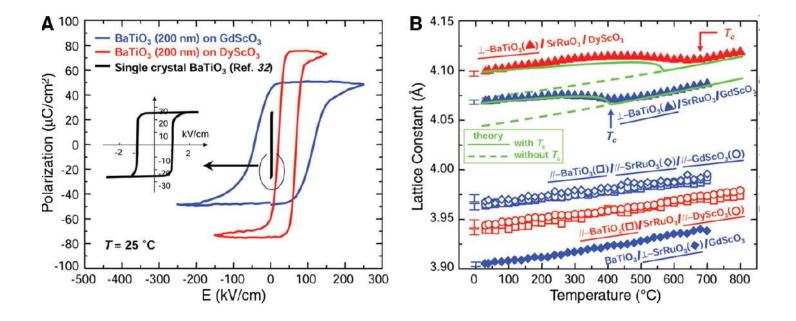
Ferroelectric thin film

Single crystal substrate



Epitaxially constrained ferroelectrics

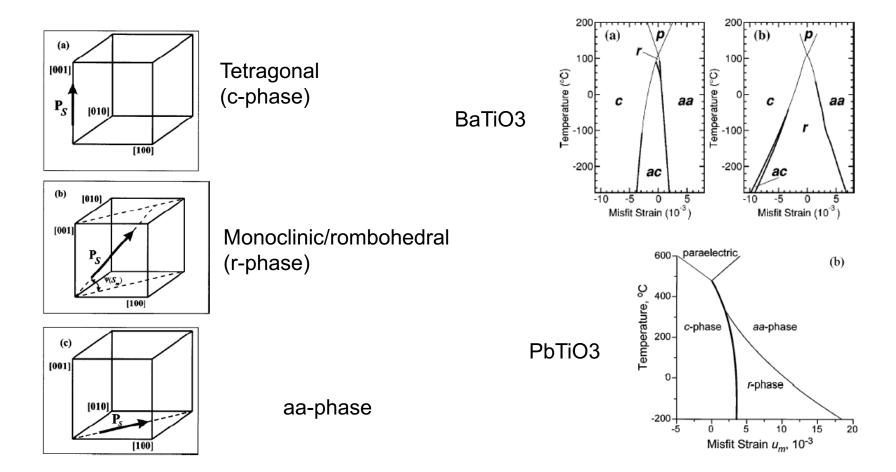
- Modify polarization magnitude
- Modify critical temperature



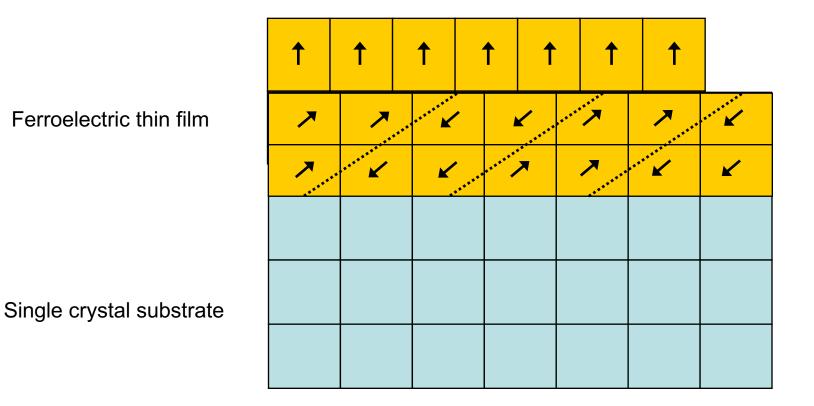
Science 2004

Strain engineering

$$\begin{split} G &= a_1(P_1^2 + P_2^2 + P_3^2) + a_{11}(P_1^4 + P_2^4 + P_3^4) + a_{12}(P_1^2P_2^2 + P_1^2P_3^2 + P_2^2P_3^2) + a_{111}(P_1^6 + P_2^6 + P_3^6) \\ &+ a_{112}[P_1^4(P_2^2 + P_3^2) + P_3^4(P_1^2 + P_2^2) + P_2^4(P_1^2 + P_3^2)] + a_{123}P_1^2P_2^2P_3^2 - \frac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2 + \sigma_3^2) \\ &- s_{12}(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_3\sigma_2) - \frac{1}{2}s_{44}(\sigma_4^2 + \sigma_5^2 + \sigma_6^2) - Q_{11}(\sigma_1P_1^2 + \sigma_2P_2^2 + \sigma_3P_3^2) \\ &- Q_{12}[\sigma_1(P_2^2 + P_3^2) + \sigma_3(P_1^2 + P_2^2) + \sigma_2(P_1^2 + P_3^2)] - Q_{44}(P_2P_3\sigma_4 + P_1P_3\sigma_5 + P_2P_1\sigma_6), \end{split}$$

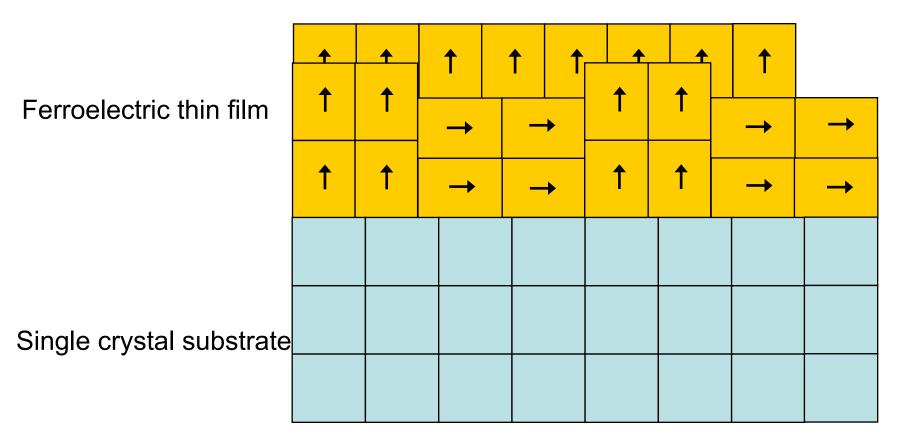


Tensile strain



Polar vector tilted diagonally in order to reduce elastic energy 180° domains appear in order to reduce depolarization energy

Strain relaxation via twinning

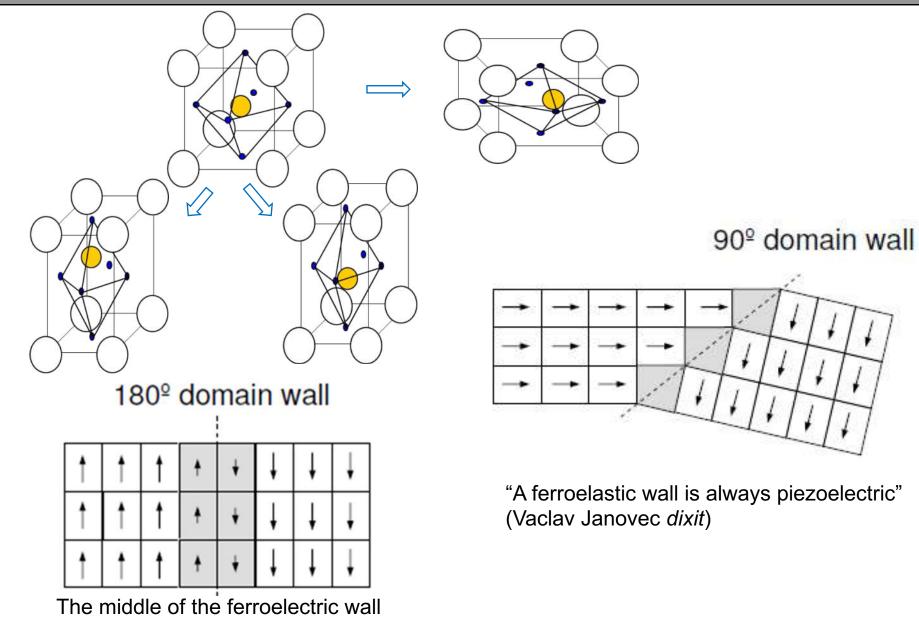


Polarization oriented alternatively along tetragonal *out* and *in-plane* directions in order to reduce elastic energy.

Part 4: (some) trending topics in FE research

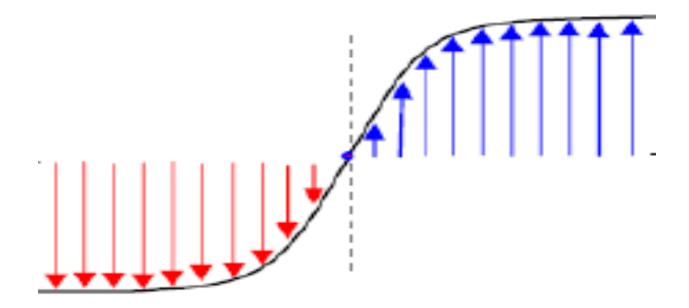
- Domains and domain walls
- Photovoltaics
- Electrocalorics
- Negative capacitance

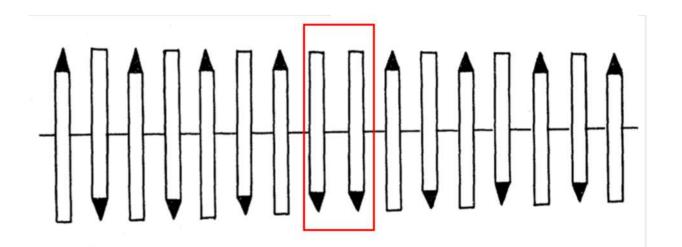
Ferroelectric domains and domain walls



has P=0. It resembles the paraphase.

Domain walls are <u>different</u>

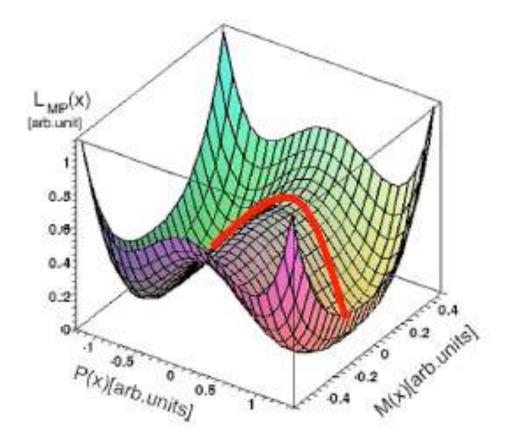


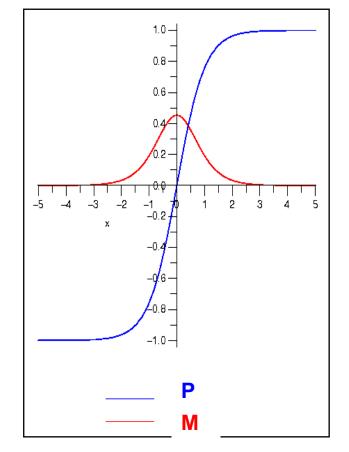


Order parameter coupling

$$\Delta \boldsymbol{G} = \frac{\alpha}{2} \boldsymbol{P}^2 + \frac{\beta}{4} \boldsymbol{P}^4 + \frac{\boldsymbol{a}}{2} \boldsymbol{M}^2 + \frac{\boldsymbol{b}}{4} \boldsymbol{M}^4 + \gamma \boldsymbol{P}^2 \boldsymbol{M}^2$$

$$\boldsymbol{G}_{\boldsymbol{M}} = \left(\frac{\boldsymbol{a}}{2} + \frac{\gamma}{2} \boldsymbol{P}^2\right) \boldsymbol{M}^2 + \frac{\boldsymbol{b}}{4} \boldsymbol{M}^4$$

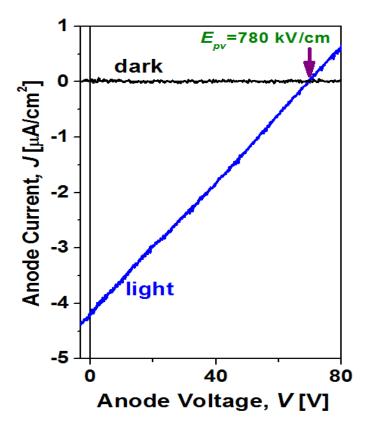




Daraktchiev et al, PRB 2010

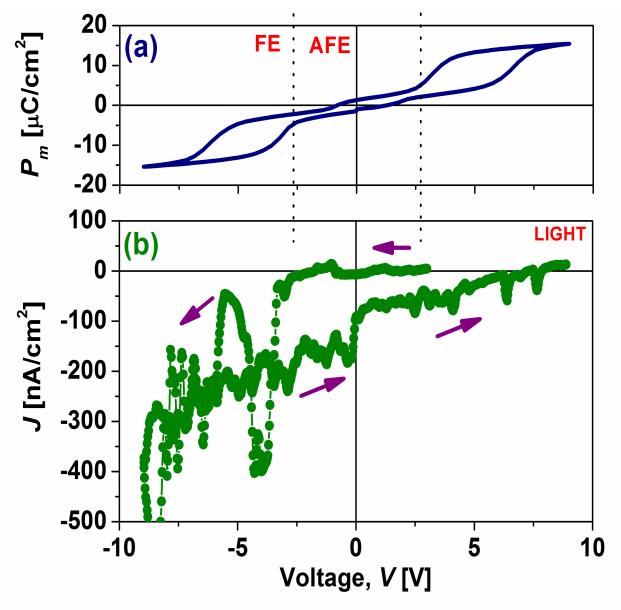
Ferroelectric Photovoltaics

Pb(ZrTi)O₃ (PZT)



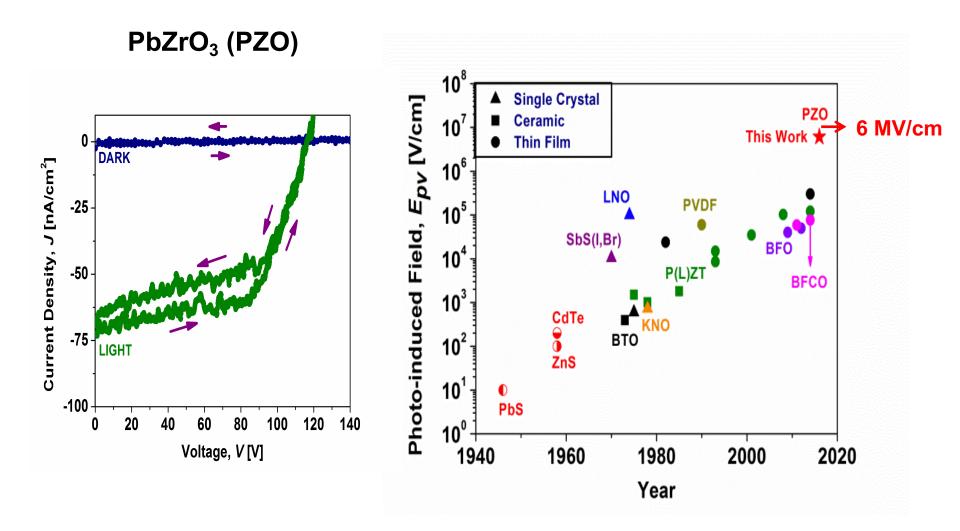
- Photoelectric field = Shift current (intrinsic) / photoconductivity (extrinsic)
- Maximum photoelectric field = P/ε

photovoltaic antiferroelectrics



A. Perez-Tomas, M. Lira-Cantu, G. Catalan; Adv. Mat. 16, 9644 (2016)

photoelectric fields can be huge!



A. Perez-Tomas et al; Adv. Mat. 16, 9644 (2016)

Negative electrocaloric effects in AFE

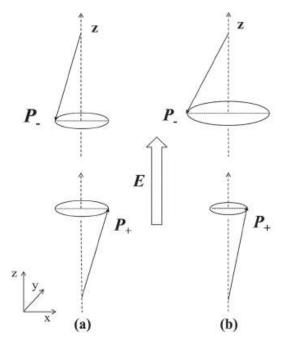
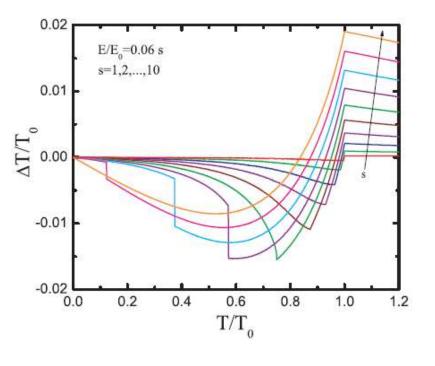
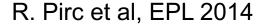


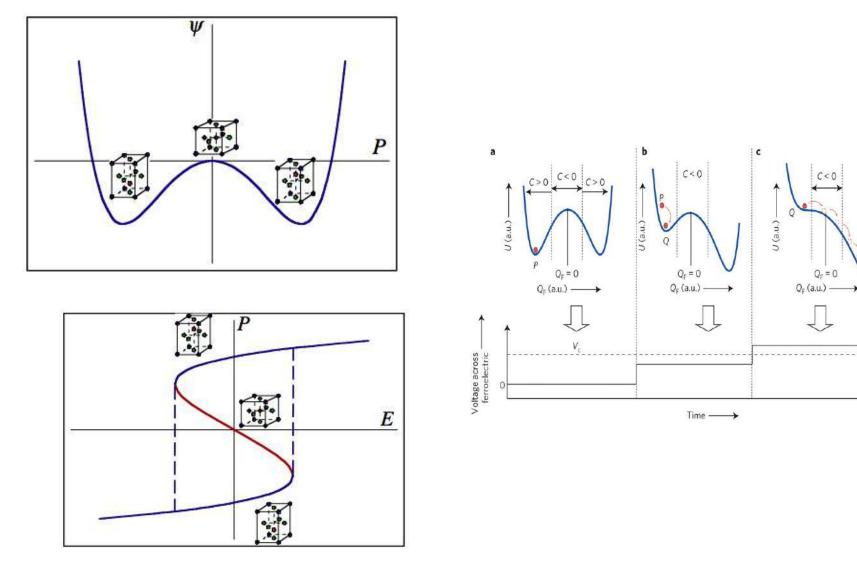
Figure 3. Schematic of a possible mechanism of negative ECE in AFEs: a) without any electric field and b) under a modest electric field.

W. Geng et al, Adv. Mat. 2015





Negative capacitance



Field field effect transistor+memory

NANO LETTERS

Use of Negative Capacitance to Provide Voltage Amplification for Low Power Nanoscale Devices

2008 Vol. 8, No. 2 405-410

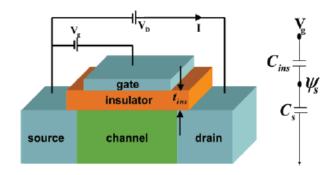
Sayeef Salahuddin* and Supriyo Datta[†]

School of Electrical and Computer Engineering and NSF Center for Computational Nanotechnology (NCN), Purdue University, West Lafayette, Indiana 47907 Received July 24, 2007; Revised Manuscript Received October 3, 2007

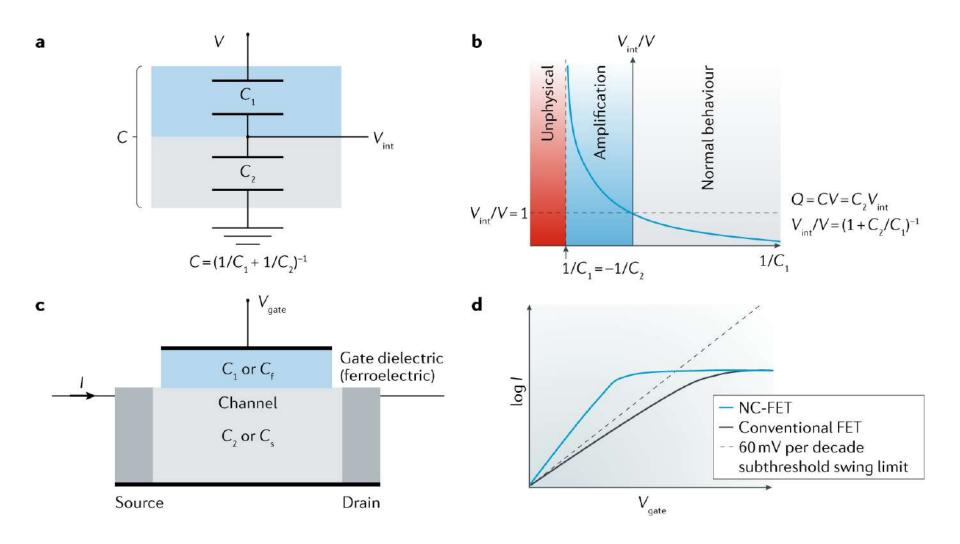
ABSTRACT

It is well-known that conventional field effect transistors (FETs) require a change in the channel potential of at least 60 mV at 300 K to effect a change in the current by a factor of 10, and this minimum subthreshold slope *S* puts a fundamental lower limit on the operating voltage and hence the power dissipation in standard FET-based switches. Here, we suggest that by replacing the standard insulator with a ferroelectric insulator of the right thickness it should be possible to implement a step-up voltage transformer that will amplify the gate voltage thus leading to values of *S* lower than 60 mV/decade and enabling low voltage/low power operation. The voltage transformer action can be understood intuitively as the result of an effective negative capacitance provided by the ferroelectric capacitor that arises from an internal positive feedback that in principle could be obtained from other microscopic mechanisms as well. Unlike other proposals to reduce *S*, this involves no change in the basic physics of the FET and thus does not affect its current drive or impose other restrictions.

It is generally accepted that the ongoing scaling of field effect transistors (FETs, see Figure 1) will be eventually limited by the inability to remove the heat generated in the switching process, ¹⁻⁴ making it very important to find ways to reduce the power dissipated per switching event. It is also clear that the power dissipation would be lowered significantly, if FETs could be operated at lower voltages. A key factor limiting the operating voltage is the subthreshold swing *S*, which is the inverse of the change of current that can be obtained for a unit change in gate voltage, V_g :



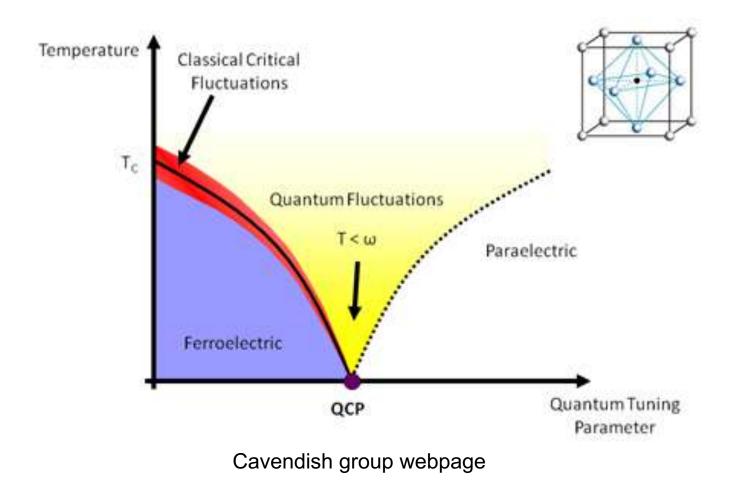
Physics of negative capacitance



Iñiguez et al. Nature Reviews Materials 4, p.243–256 (2019)

Quantum ferroelectricity

What happens when the ferroelectric Tc is close to 0K? How do quantum fluctuations affect ferroelectricity?



Summary / Take home messages

- Ferroelectrics are among the most multi-functional materials: piezoelectricity (sensors and actuators), pyroelectricity (sensors), permittivity (capacitors), electrooptical modulators, resonant filters (SAW, BAW), etc.
- The coupling between polarization and structure is inherent, and can be used both as a functionality (piezoelectricity) or as a way to tune the properties of thin films (strain engineering)
- Ferroelectric characterization is delicate. Artifacts WILL happen!
- At the nanoscale, things get even more complicated. Depolarization fields can cause the appearance of domains, the suppression of ferroelectricity, and (perhaps) the appearance of negative capacitance.