Complex Oxides

Gustau Catalan
ICREA and ICN2, Barcelona

INSTITUCIÓ CATALANA DE RECERCA I ESTUDIS AVANÇATS

Institut Català de Nanociència i Nanotecnologia

EXCELENCIA SEVERO OCHOA

European Research Council
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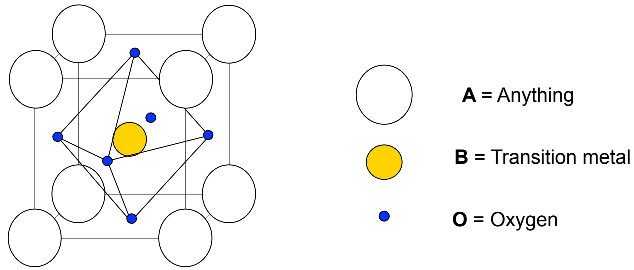
Outline

- Perovskite oxides: a simple structure with a complex soul...
- Metal-insulator transition in nickelates.
- Ferroelectrics: basic properties and applications.
- Strain Engineering.
- Domain walls.
- Flexoelectricity.

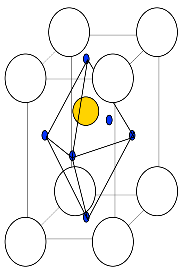
Perovskite oxides



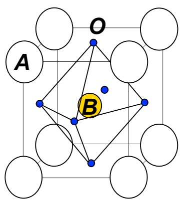
- (Relatively) simple structure, yet extremely versatile.
- Strong interaction between oxygen p-orbital and transition metal d-orbital.
- Maaaany different compositions with same structure yet different properties.
- Very sensitive to strain: suitable for strain engineering.

Goldschsmidt tolerance factor

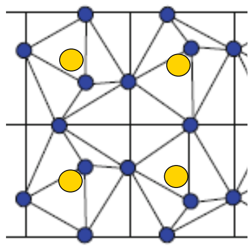
$$t = d_{A-O} / \sqrt{2}\, d_{B-O}$$



t>1
Ferroelectrics



t=1
$SrTiO_3$



t<1
Everything else

Note #1: to estimate *t*, you can use the ionic radii from: R. D. Shannon, Acta Cryst. (1976). A32, 751
Note #2: this paper has >37000 citations!

Notable perovskites

Ferroelectrics and piezoelectrics
$BaTiO_3$, $PbTiO_3$, $Pb(Zr,Ti)O_3$, $Pb(Mg,Nb,Ti)O_3$, $Pb(Zn,Nb,Ti)O_3$ (world's best piezo)

Multiferroics
$TbMnO_3$, $BiFeO_3$ (room temperature multiferroic)

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

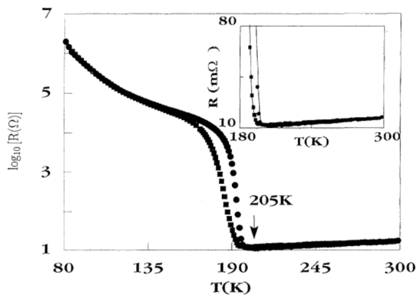
High temperature superconductors:
$YBa2Cu_3O_{7-\delta}$ (high temperature superconductors)

"Mott materials"
$RENiO_3$ (tunable metal-insulator transition)

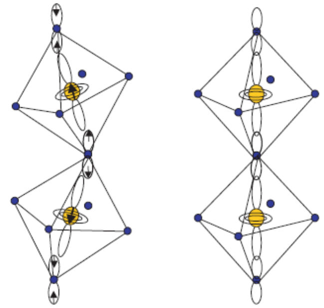
The drossophila of perovskites
$SrTiO_{3-\delta}$ (from quantum paraelectric to superconductor and everything in between)

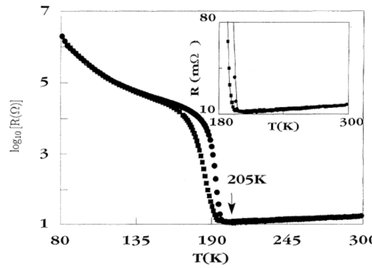
Funky interfaces
$LaAlO_3$ (insulator) on $SrTiO_3$ (insulator) = (super)conducting interface.

Nickelates



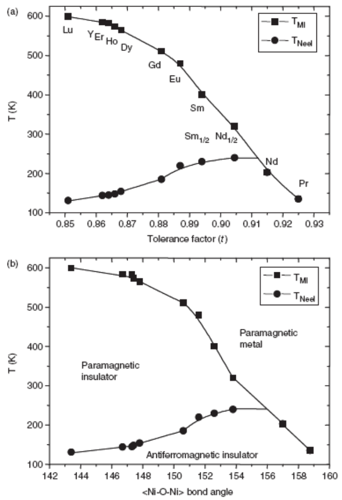
Octahedral rotations in perovskite nickelates

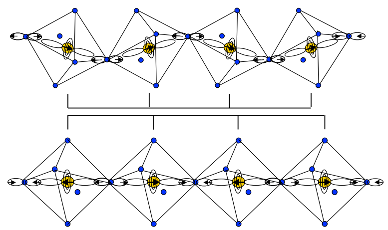




Metal-insulator tranistion in rare-earth nickelates ($RENiO_3$)

Phase Diagram of Nickelates





As t increases, bond becomes straighter, thus:

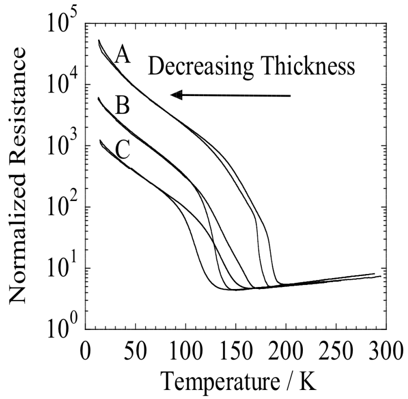
1) Stronger magnetic eschange interaction and higher T_{Neel}
2) Stronger orbital overlap and therefore higher stability of metallic state, hence lower T_{MI}.

Note: in the metallic state, magnetic electron is delocalized and thus magnetic ordering disappears above T_{MI}.

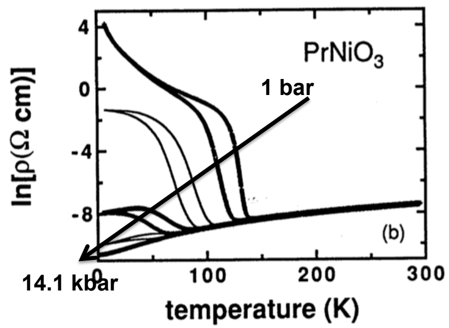
Catalan, *Phase Transitions*, (2008)

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Effect of epitaxial strain



Catalan *et al.*, J. Appl. Phys. 87, 606 (2000)



P.C. Canfield *et al.*, *Physical Review B*, (1993)

Stress under AFM tip

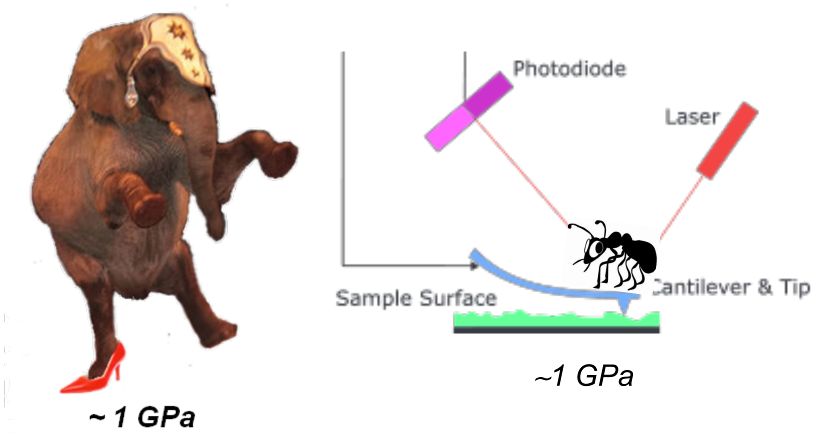
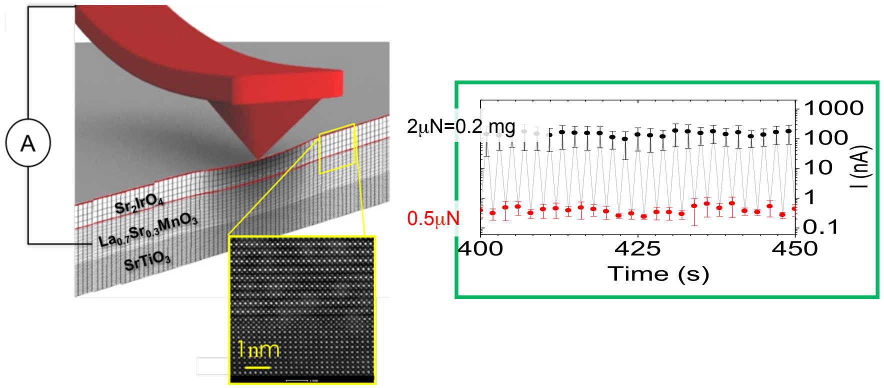


Figure courtesy of J. Kreisel

Giant piezoresistance by tip pressure

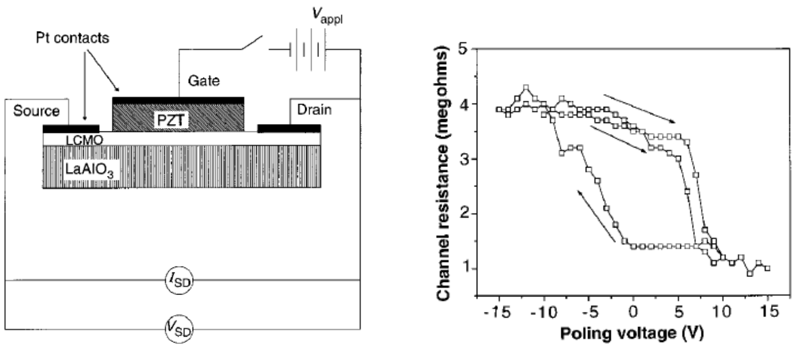


Nanoscale

Giant reversible nanoscale piezoresistance at room temperature in Sr_2IrO_4 thin films†

Neus Domingo,*[a] Laura López-Mir,[a,b] Markos Paradinas,[b] Vaclav Holy,[c] Jakuv Železný,[c,d] Di Yi,[e] Siriyara J. Suresha,[f] Jian Liu,[f,g] Claudy Rayan Serrao,[e] Ramamoorthy Ramesh,[e,f,g] Carmen Ocal,[b] Xavi Marti*[a,d,h] and Gustau Catalan*[a,i]

Field field effect devices

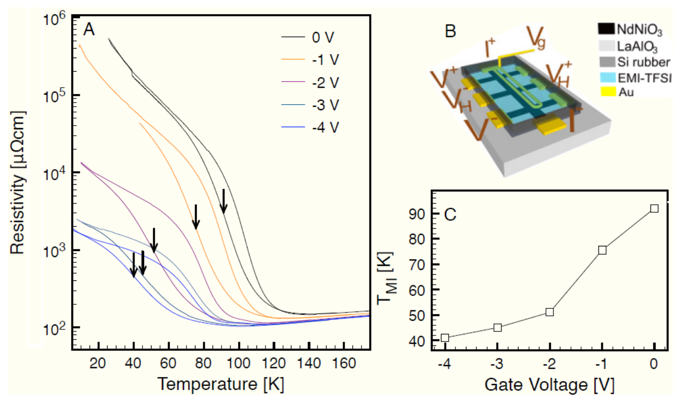


Mathews, Science 1997

Important size consideration: the change in resistance will be inversely proportional to the thickness of the channel. **Ultra-thin films are best**.

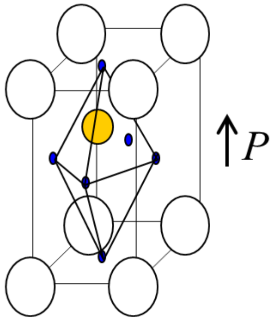
Metal-Insulator transistor

Voltage tuning of metal-insulator transition can be used in field-effect transistors

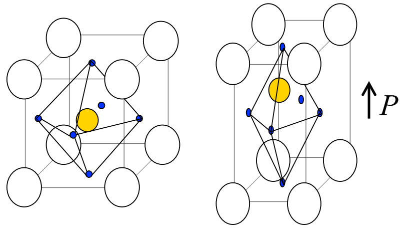


Scherwitzl et al, Avanced Materials 2010

Ferroelectrics



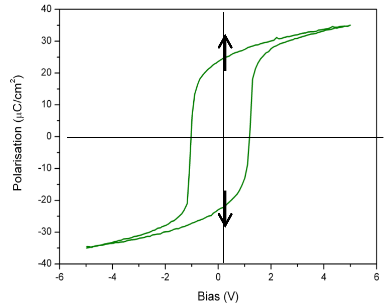
Perovskite ferroelectrics



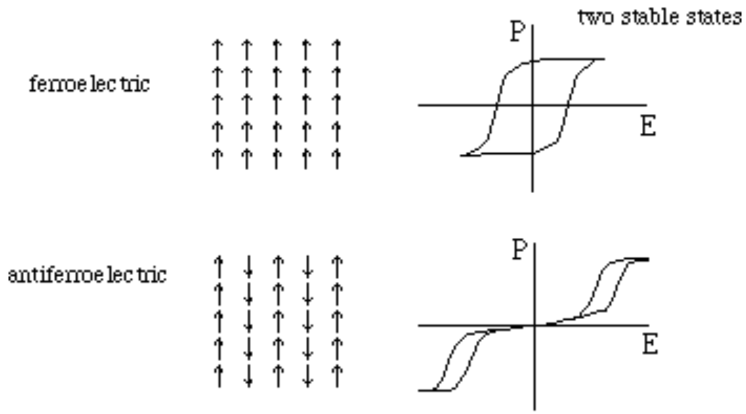
A = Ba, Sr, Pb, Bi

B = Zr,Ti

O = oxygen



Antiferroelectrics



FERROELECTRIC MEMORIES

- Coercive field, E_C:

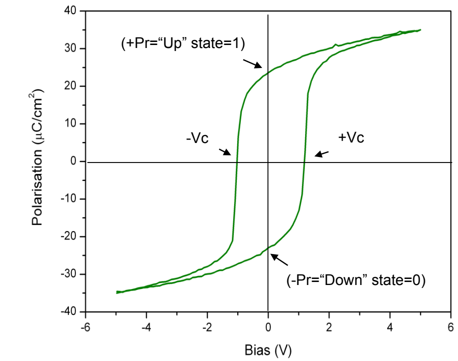
E_C = 10 – 100 kV/cm

- Coercive Voltage V_C, for 1mm

V_C = 1000 – 10000V…**huge!**

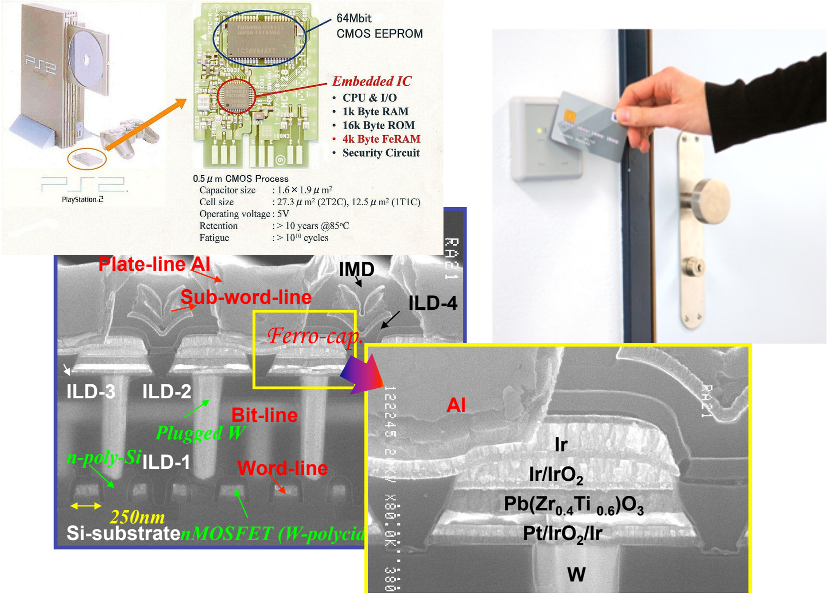
- Coercive voltage V_C, for 1μm

V_C = 1 – 10V…**tiny!**

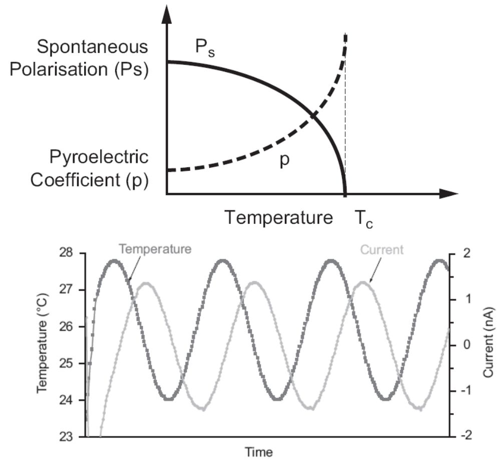


Thin Films (t < 1 μm) suitable for ferroelectric memories.

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)

Capacitors

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

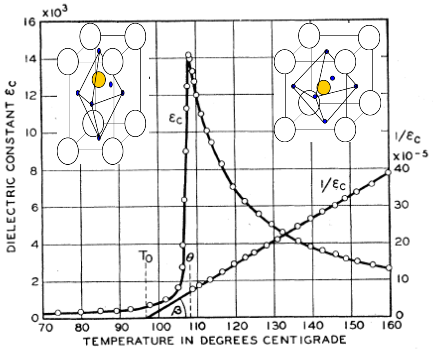


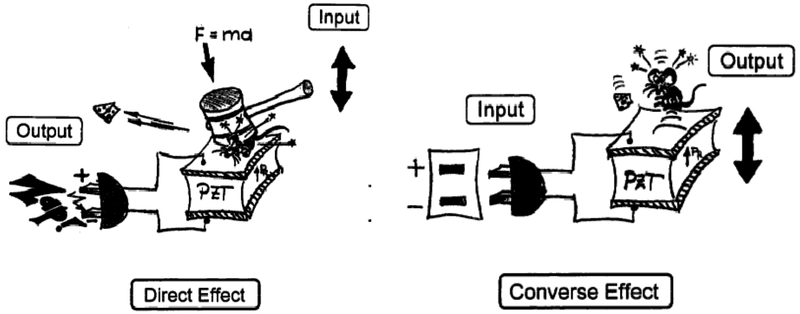
FIG. 5. Dielectric constant ϵ_c and reciprocal dielectric constant $1/\epsilon_c$ *versus* temperature T.

Dielectric constant of $BaTiO_3$

Market > $\$10^9$/year
Price ~ 0.1 cents each
$>10^{12}$ made each year. You own many.

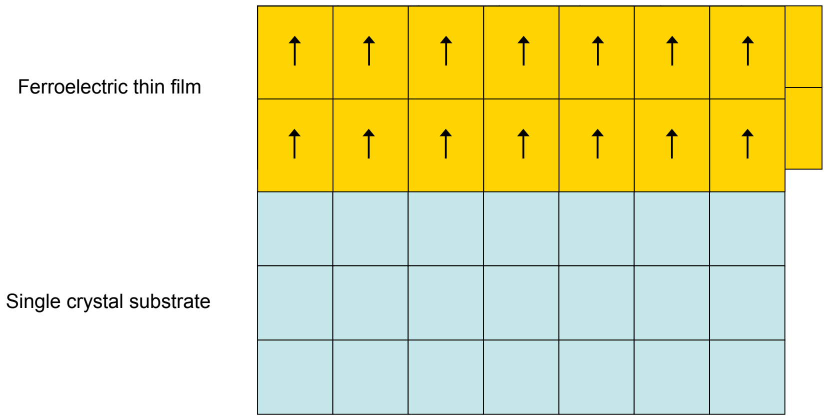
Piezoelectricity

Direct: sensors **Converse: actuators**

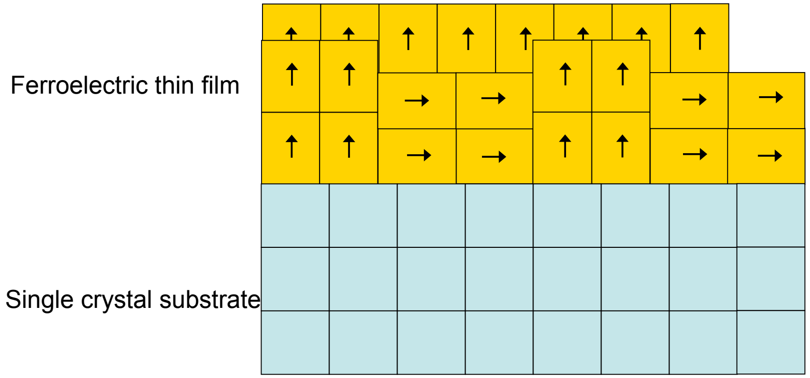


Used in many important applications such as ultrasound scans, inkjet printers, sonar…

Strain engineering in ferroelectric thin films

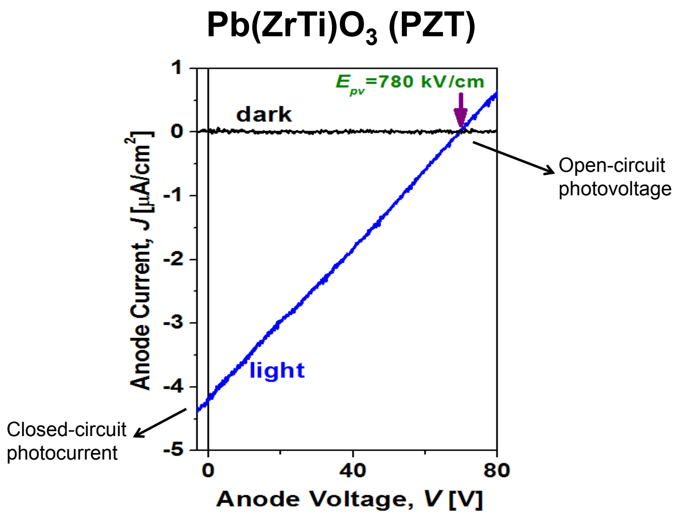


Strain relaxation via twinning

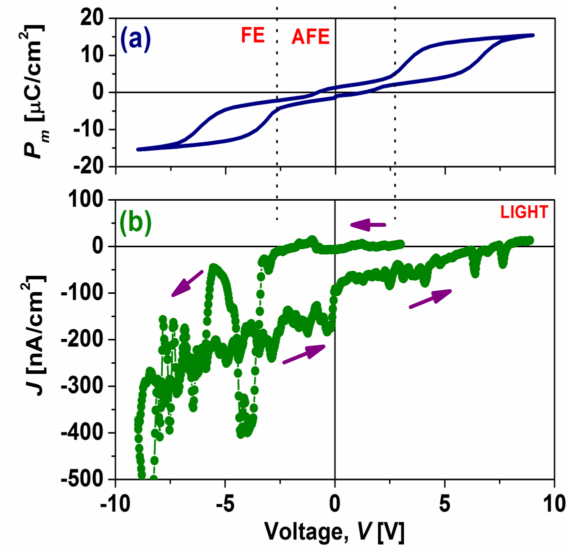


Polarization oriented alternatively along tetragonal *out* and *in-plane* directions in order to reduce elastic energy.

Ferroelectrics show larger-than-bandgap photovoltages

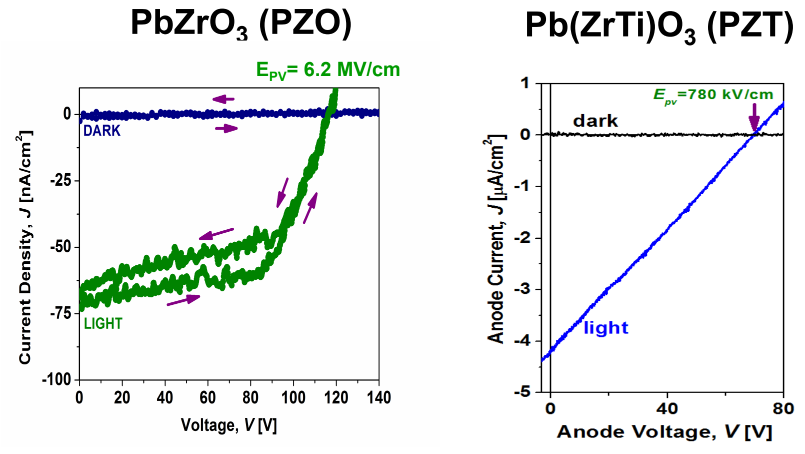


photovoltaic antiferroelectrics



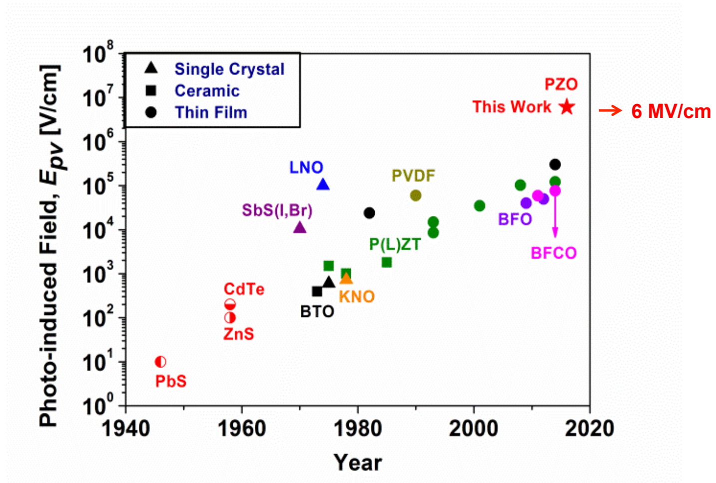
A. Perez-Tomas, M. Lira-Cantu, G. Catalan; Adv. Mat. 16, 9644 (2016)

Antiferroelectric and ferroelectric PV



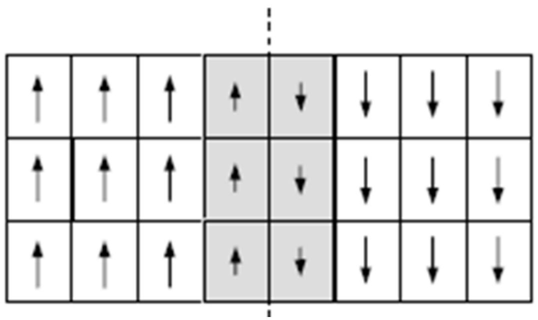
- **Photoelectric field = Shift current (intrinsic) / photoconductivity (extrinsic)**
- **Maximum photoelectric field = P/ε**

Large photoelectric fields

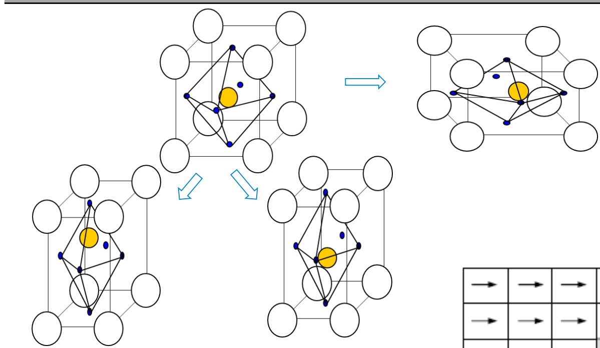


A. Perez-Tomas et al; Adv. Mat. 16, 9644 (2016)

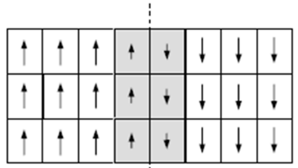
Domains and domain walls



Ferroelectric domains and domain walls

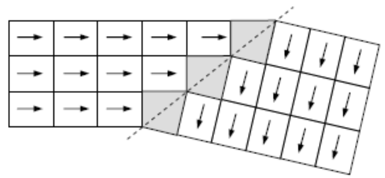


180º domain wall



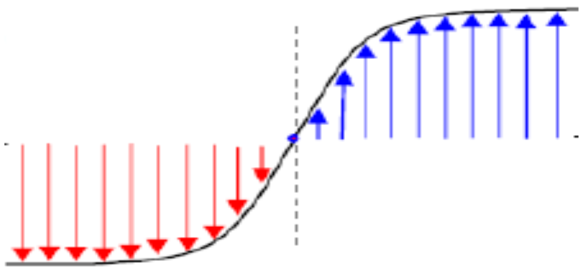
The middle of the ferroelectric wall has P=0. It resembles the paraphase.

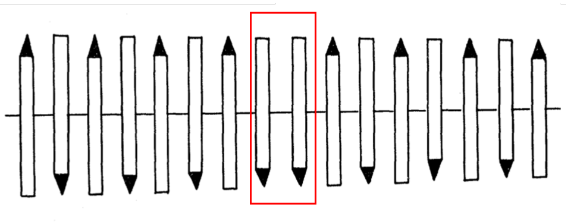
90º domain wall



“A ferroelastic wall is always piezoelectric” (Vaclav Janovec *dixit*)

Domain walls are different

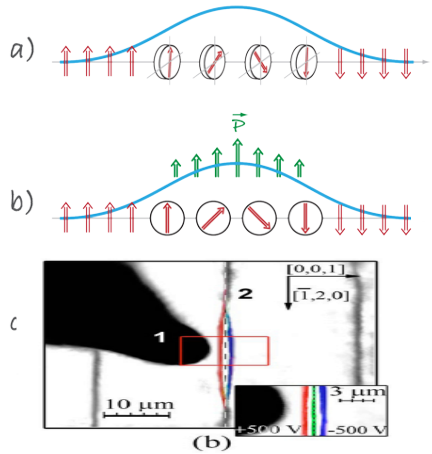




DW chirality has consequences

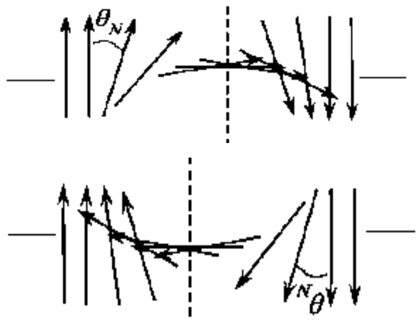
Neel walls in ferromagnetic insulators are ferroelectric

D. Khomskii, Physics 2, 20 (2009)

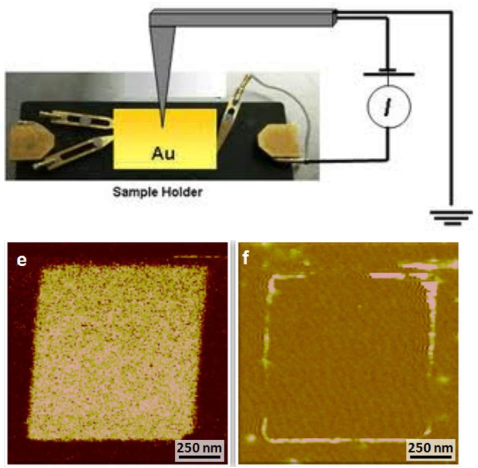


Logginov et al, Appl. Phys. Lett. 93, 182510 (2008).

DW Chirality adds an additional, switchable, degree of freedom inside the wall (see also "walls within walls, by E. Salje).

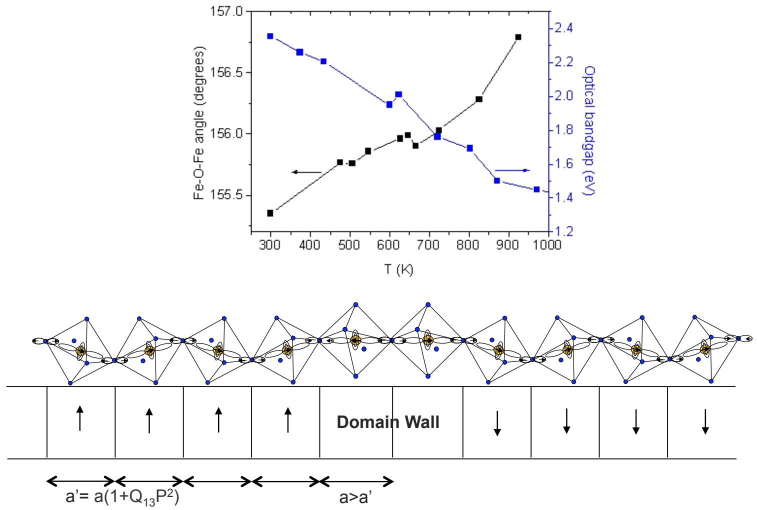


Testing domain walls: conducting tip AFM or STM



conductivity in multiferroic domain walls of $BiFeO_3$
Seidel et al Nat. Mat. 2009

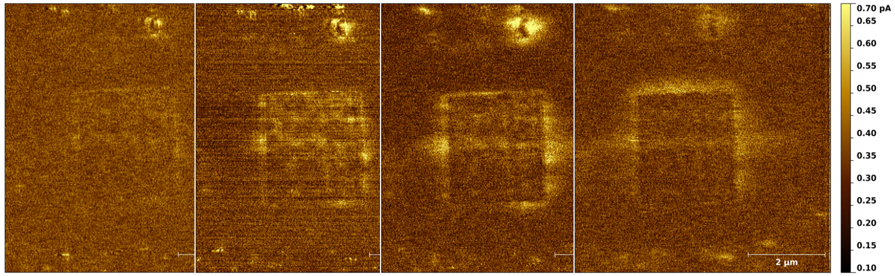
Intrinsic origin of wall conductivity?

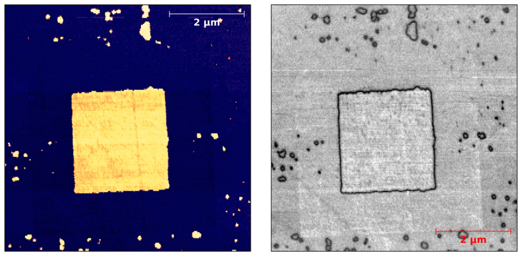


The enhanced conductivity of domain walls is consistent with local bond straightening

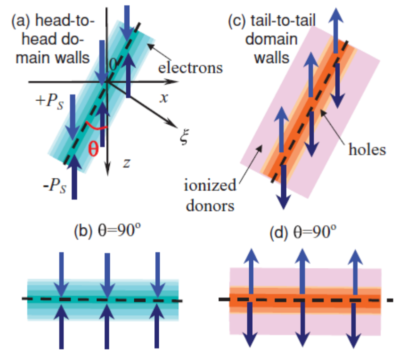
Catalan, Ferroelectrics 2010

Extrinsic origin: ionic difussion/vacancy accumulation?

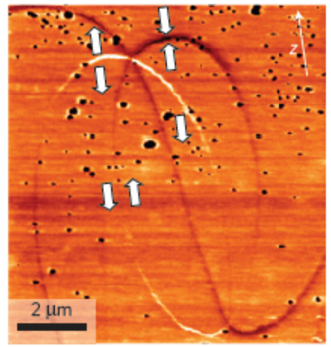




“Polar catastrophe at in DW’s”

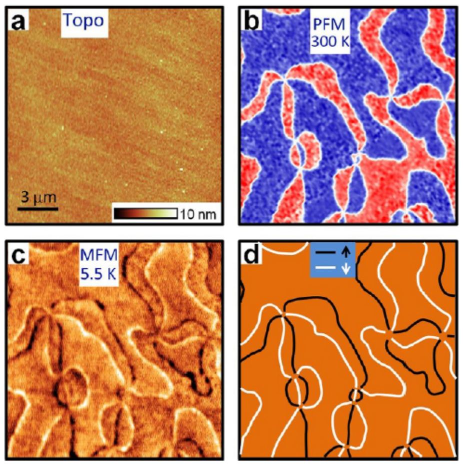


Eliseev et al, PRB 2011



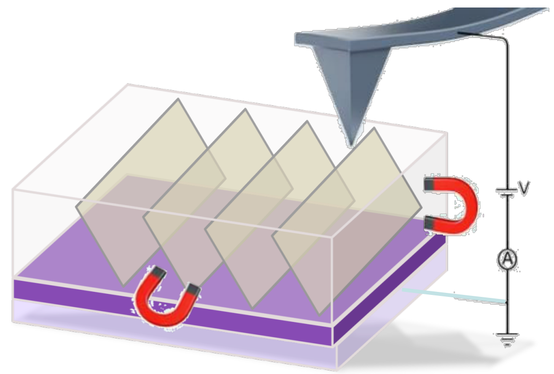
Meier et al, Nat. Mat. 2012

Magnetization inside ferroelectric domain walls



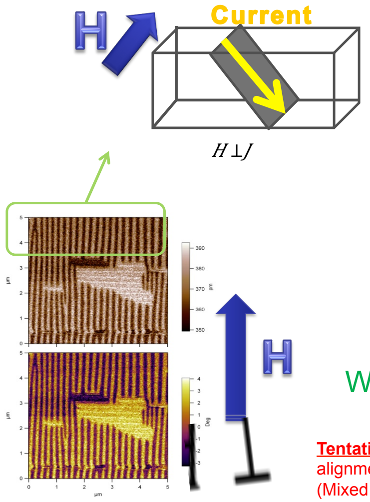
Geng et al, Nano Letters 12, 6055, 2012

DW magnetoresistance

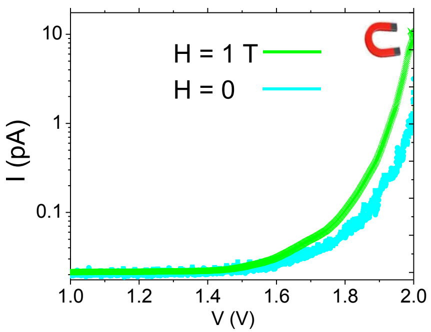


Beatriz Noheda, Saeedeh Farokhipoor (Groningen)
Neus Domingo (ICN2)

MAGNETORESISTANCE @ 71º DW



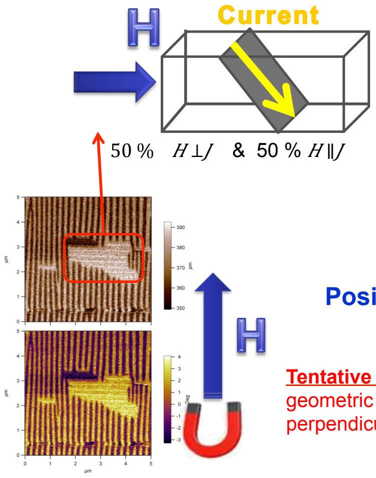
Magnetic ordering along DW favours conductivity

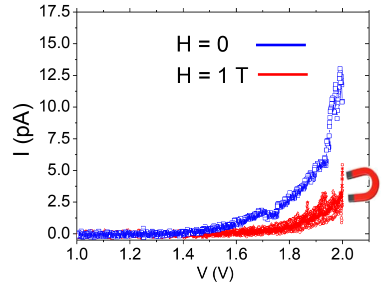


Weakly **negative** magnetoresistance

Tentative explanation: increased hopping probability due to parallel alignment of spins, similar to MR in mixed-valence manganites? (Mixed valence would be consistent with existence of oxygen vacancies at the wall)

MAGNETORESISTANCE @ 71º DW



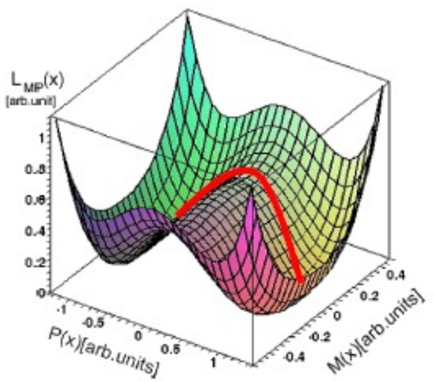


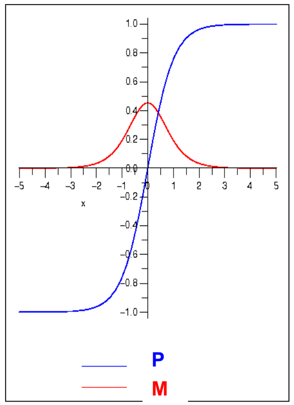
Positive Magnetoresistance of up to 300%

Tentative explanation:
geometric MR = Hall-effect carrier localization due to B perpendicular to plane of DW

Order parameter coupling

$$\Delta G = \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{a}{2}M^2 + \frac{b}{4}M^4 + \gamma P^2 M^2 \qquad G_M = \left(\frac{a}{2} + \frac{\gamma}{2}P^2\right)M^2 + \frac{b}{4}M^4$$





Daraktchiev et al, PRB 2010

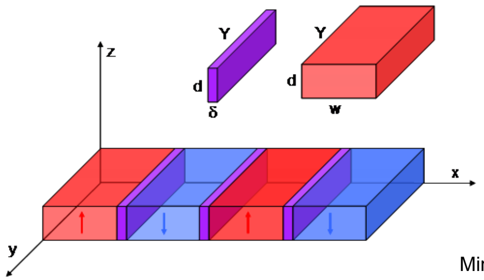
Kittel's law and its consequences

$$E(domains) = Uw \qquad E(walls) = \sigma \frac{d}{w}$$

$d \rightarrow$ depth ∝ size of DW's

$w \rightarrow$ 1/w ∝ concentration of DW's

σ: Energy density of DW



Total energy density

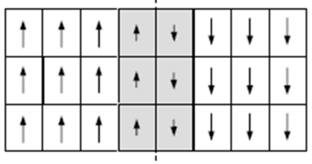
$$E = Uw + \sigma \frac{d}{w}$$

Minimizing E with respect to the domain size *w:*

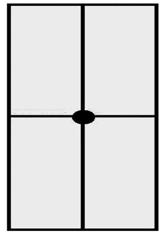
$$\boxed{w = \sqrt{\frac{\sigma}{U}d}}$$

Landau&Lifshitz, Sov. Phys. Utz. 1935;
Kittel, Phys. Rev. 1946

Domain walls are the tasty stuff inside the sandwich



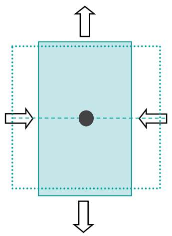
FLEXOELECTRICITY

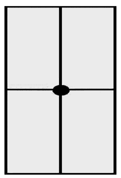


Flexoelectricity

- **Electric polarization** induced by **strain gradients**

$$\boxed{P_i = f_{ijkl} \frac{\partial \varepsilon_{kl}}{\partial x_j}}$$

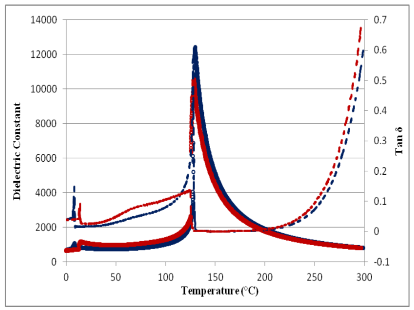




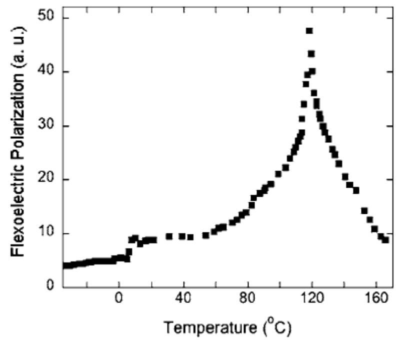
First theoretical prediction: Kogan, Sov. Phys. JETP 1964

Flexoelectricity is proportional to permittivity

BaTiO3 permittivity



BaTiO3 Flexoelectricity

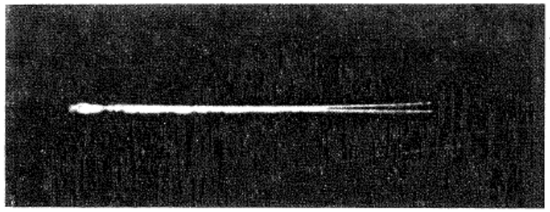


Ma and Cross, APL 2006

The best flexoelectrics will tend to also be ferroelectric

Converse (or inverse) Flexoelectricity

If bending induces polarization, polarization MUST induce bending.

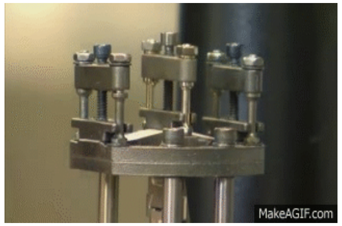


Bursian&Zaikovskii, Sov. Phys. Solid State 1968

$$R^{-1} = \mu E \cdot \frac{12(1-\nu^2)}{Gd^2} = \mu V \cdot \frac{12(1-\nu^2)}{Gd^3}$$

Measuring Flexoelectricity

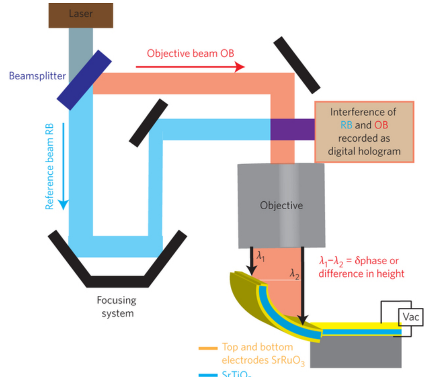
Direct flexoelectricity



$$P_i = \mu_{ijkl} \frac{\partial \varepsilon_{kl}}{\partial x_j}$$

Theory: Kogan, Sov. Phys. JETP 1964

Inverse flexoelectricity

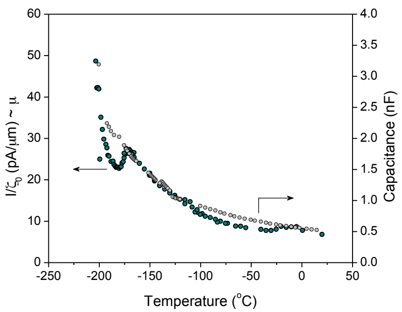


$$R^{-1} = \mu E \cdot \frac{12(1-\nu^2)}{Gd^2} = \mu V \cdot \frac{12(1-\nu^2)}{Gd^3}$$

ExperimentBursian&Zaikovskii, Sov. Phys. Solid State 1968

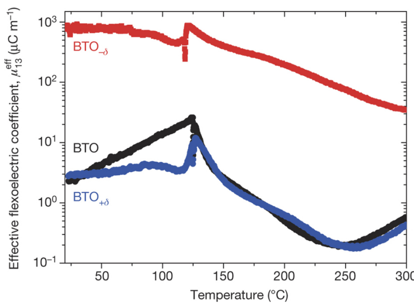
Flexoelectricity really is universal

SrTiO3 (cubic, insulator)



Zubko, Catalan et al, Phys. Rev. Lett. 2007

BaTiO3-δ (semiconductor)



Narvaez, Vasquez, Catalan, Nature 2016

Flexoelectric effects grow as sample size decreases

Equation of state: $$\boldsymbol{E} + \boldsymbol{f}\frac{\partial \boldsymbol{s}}{\partial \boldsymbol{z}} = \boldsymbol{aP} + \boldsymbol{bP}^3$$

$$\boldsymbol{f} \approx 1 - 10\,V$$

$$\frac{\partial s}{\partial z} \approx \frac{\Delta s}{\Delta z} \approx \frac{1\%}{1-1000\ nm} = 10^4 - 10^7\ m^{-1}$$

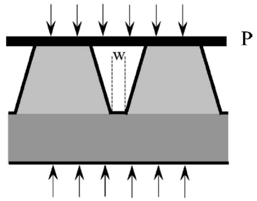
$$E_{flexo} \approx 10^2 - 10^6\ V\ cm^{-1}$$

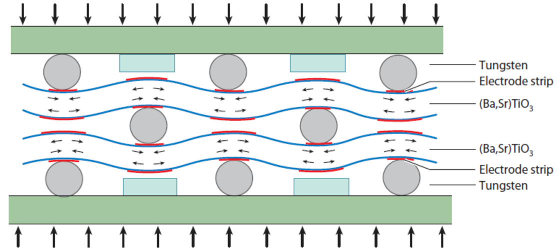
…So, you can use strain gradients to manipulate ferroelectric polarization

What can we do with it?

- Piezoelecric-like sensors
- Piezoelectric-like actuators
- Novel functionalities that are not possible by piezoelectricity or flexoelectricity alone

Electromechanical transducers with non-piezoelectrics





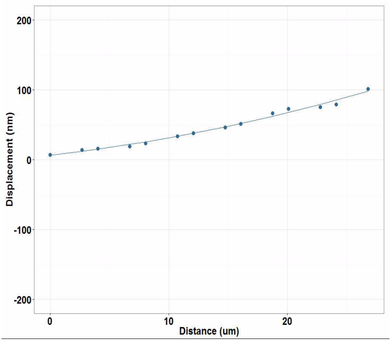
Zhu et al, APL **89**, 192904 (2006)

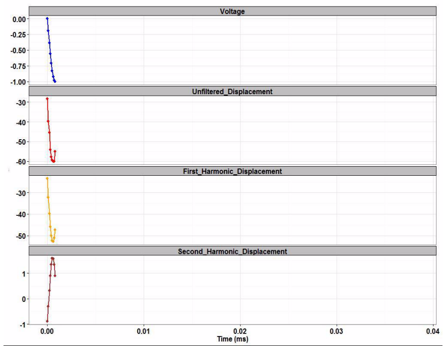
Chu et al, J. Appl. Phys. 106, 104109 (2009)

Voltage-induced bending

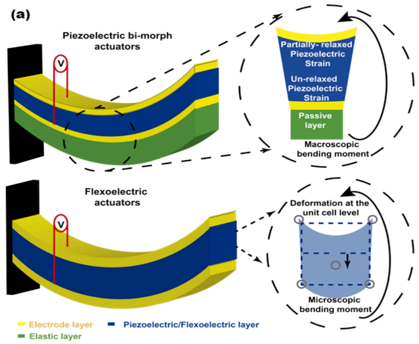
Bursian&Zaikovskii, Sov. Phys. Solid State 1968

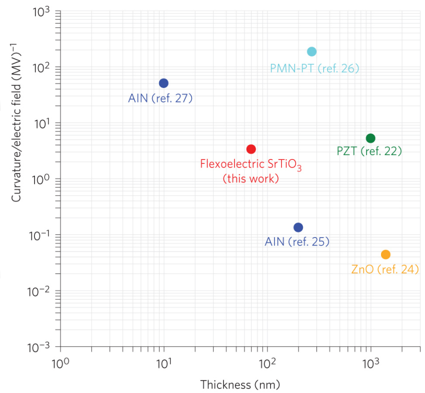
$$R^{-1} = \mu E \cdot \frac{12(1-\nu^2)}{Gd^2} = \mu V \cdot \frac{12(1-\nu^2)}{Gd^3}$$





MEMS actuators based on inverse flexo

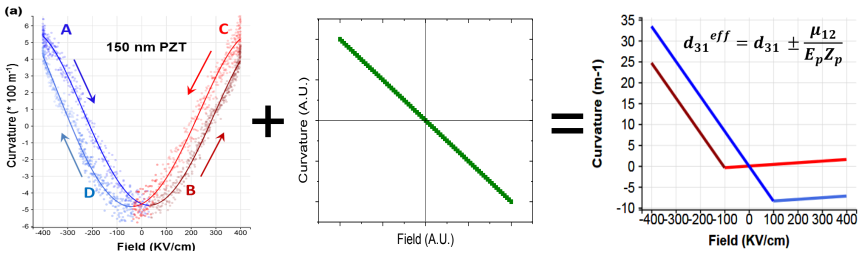


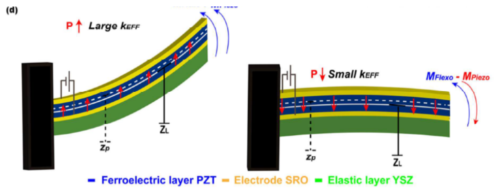


U. Bhaskar et al., Nature Nanotech. 11, 263–266 (2016)

Flexoelectric “strain diode”

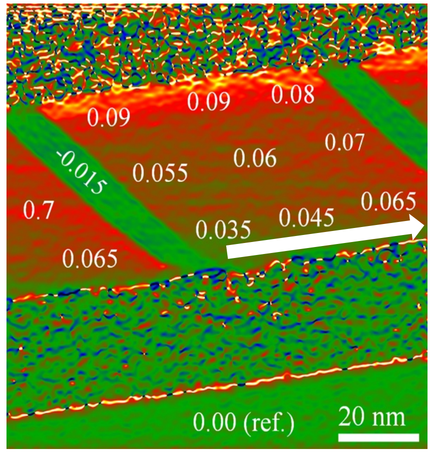
https://umeshkbhaskar.shinyapps.io/pzt_app/





U. Bhaskar *et al.*, Nanoscale 8, 1293 (2016)

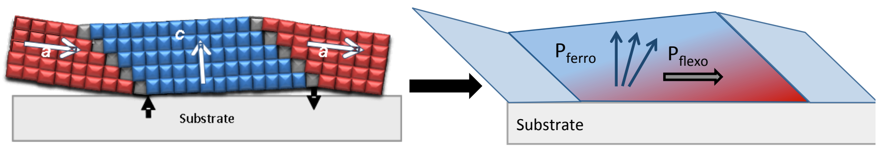
“Strain gradient engineering”



There is a **lateral** as well as well as a **vertical** gradient of tetragonality

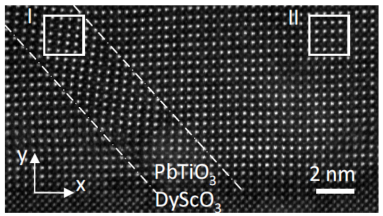
Catalan et al, Nat. Mat. 2011

Polar rotation by strain gradient

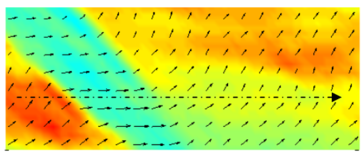


- **Large stresses accumulate at the corners of domains.**
- **This results in lateral strain gradients and thus lateral flexoelectric polarization.**
- **When lateral flexoelectricity is added onto vertical ferroelectricity, the total polarization is tilted.**

a)

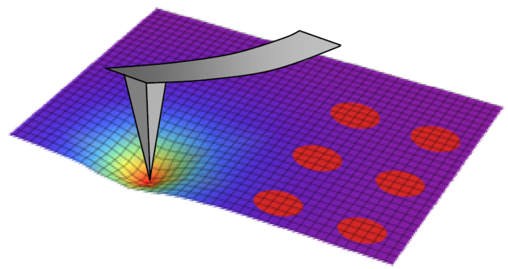


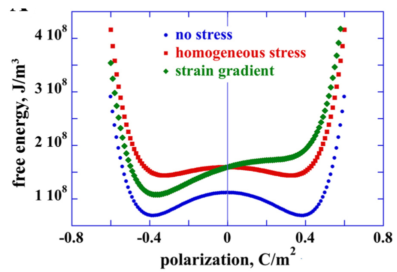
b)

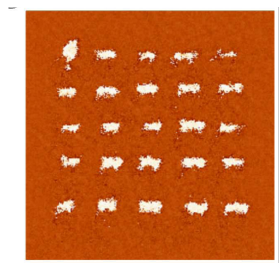


Catalan et al., Nat. Mat. 2011

Flexoelectric switching (aka “mechanical writing of ferroelectric memories”)







Lu et al, Science 2012

Can we also read polarization mechanically?

(YES…)

Mechanical consequences of flexoelectricity…

Cost of deforming a ferroelectric has elastic and electrical components.

$$U = \frac{1}{2}kx^2 + \frac{1}{2}\chi P^2$$

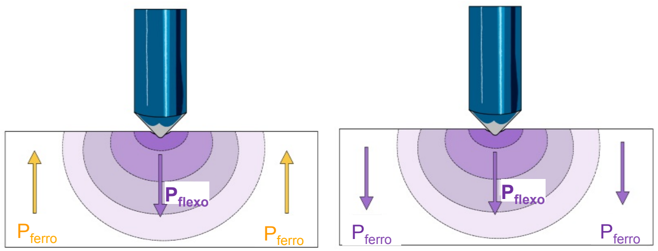
Both are quadratic and thus symmetric with respect to space inversion **in the absence of flexoelectricity**.

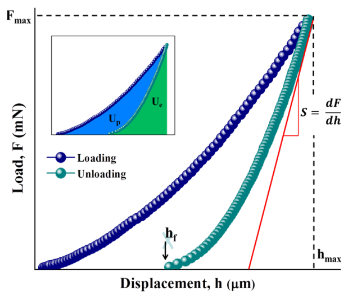
BUT, when there is both flexoelectricity and ferroelectricity:

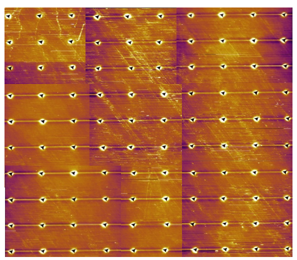
$$P = P_{flexo} \pm P_{piezo}$$

The energy cost of denting a ferroelectric is asymmetric

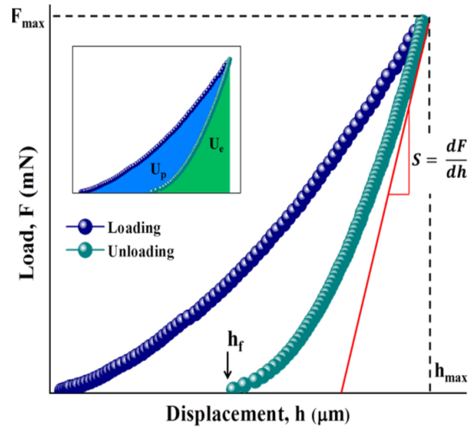
Nanoindentation in Lithium Niobate



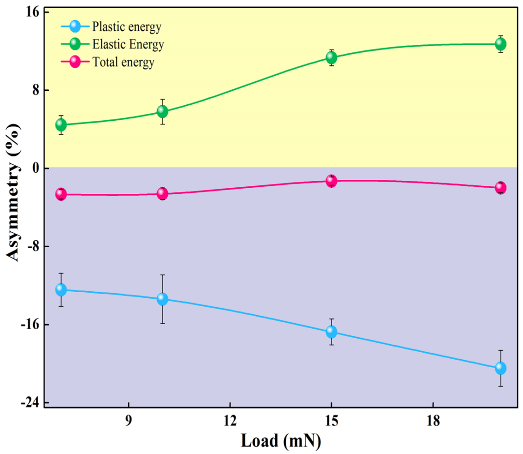




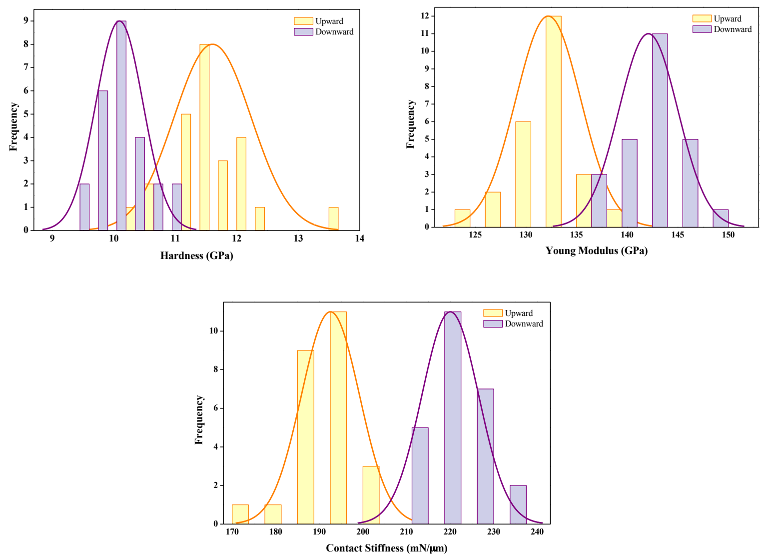
Plastic and elastic energy from indentation



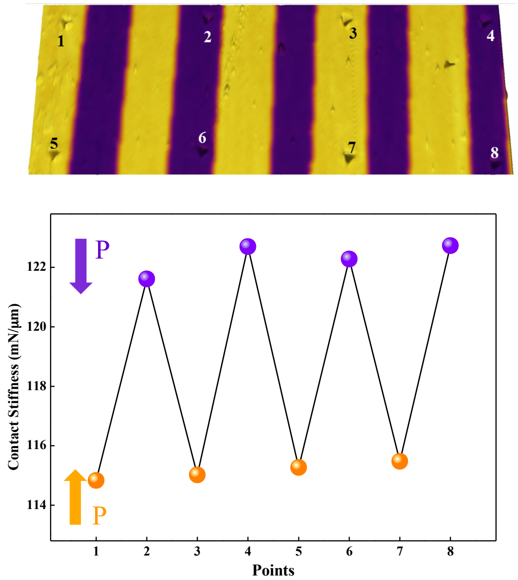
Both plastic and elastic properties are sensitive



All mechanical properties are polarity-sensitive

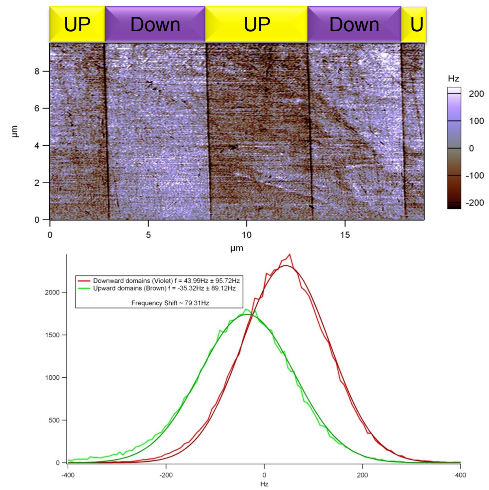


Reading polarization "by touch"



Can we do it non-destructively?

Yes: we can "tickle" the domains using the tip of an AFM and monitor the resonance frequency. Higher resonance frequency=higher stiffness.



Summary…

- **Perovskite oxides share a common structure but can have a very wide variety of behaviours, often showing the most exotic and dramatic examples of funky functional properties.**

Examples: room temperature multiferroics, high temperature superconductors, colossal magnetoresistance…

- **Small distortions of the structure result in big changes in properties.**

Example: metal-insulator transition in nickelates.

- **Strain, whether epitaxial, hydrostatic or uniaxial (tip-induced) can be used very effectively to modify oxide properties.**

Example: Strain engineering in ferroelectrics, uniaxial piezoresistance in iridates.

- **Of all the functional oxides, ferroelectrics stand out as being particularly multifunctional**.

Examples: piezoelectrics, pyroelectrics, capacitors, photovoltaics….

- **Domain walls are funky, mobile, 2-D, topologically protected material nanostructures embedded in the host lattice.**

Examples: conductive walls in insulating ferroics, magnetic walls in non-magnetic materials.

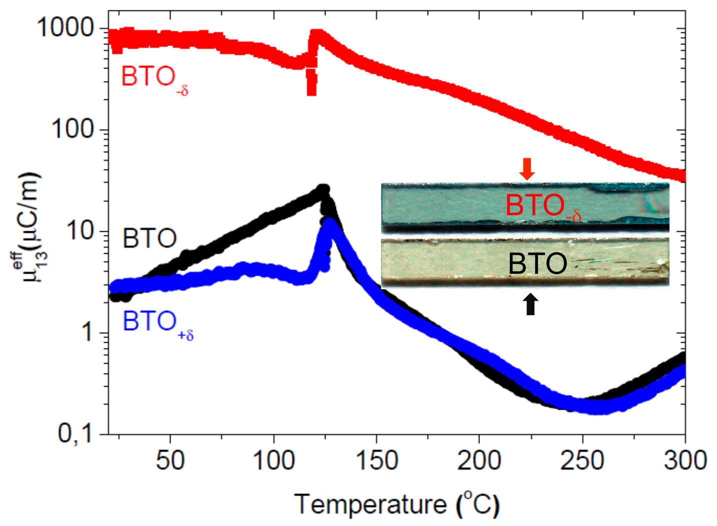
- **Flexoelectricity is a universal property whereby all insulators (and semiconductors) can generate charge when bent or, conversely, bend under voltage.**

Examples: Flexoelectric MEMS actuators, mechanical writing and reading of ferroelectric memories.

Supplementary materials

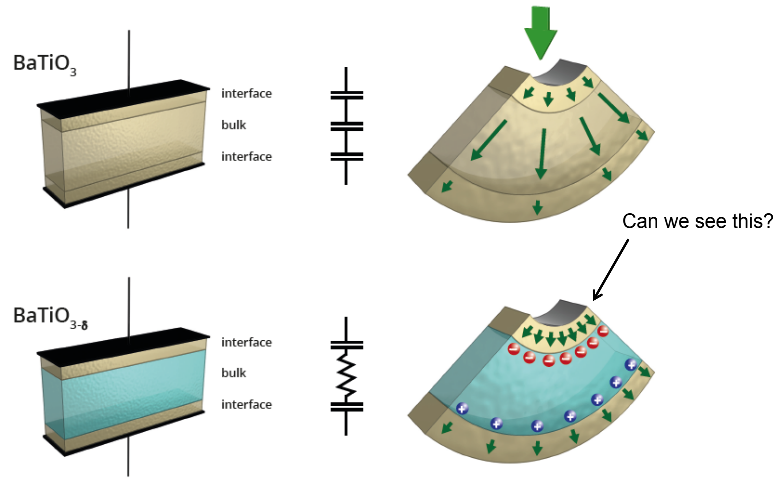
- Colossal flexoelectricity in semiconductors
- Strain gradients in epitaxial films
- Size effects in nickelates

Bonus track: giant flexoelectricity in semiconductors

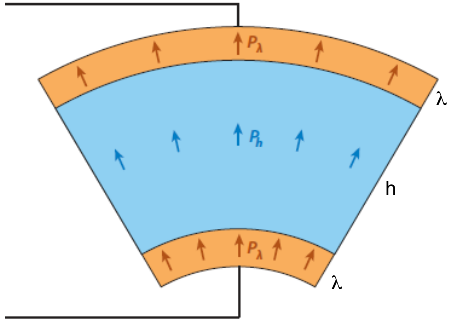


Narvaez, Vasquez & Catalan, DOI: 10.1038/nature19761

Bending polarization in barrier-layer capacitors



BULK+SURFACE

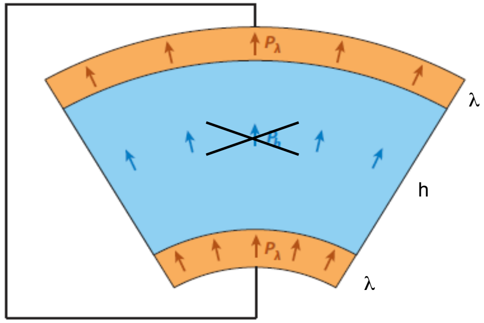


$$\mu_{eff} = e_\lambda \lambda \frac{h\varepsilon_b}{2\lambda\varepsilon_b + h\varepsilon_\lambda}$$

1. Surface piezoelectricity is proportional to surface strain, which for a given curvature is proportional to crystal thickness. Thus, while surface-to-volume ratio decreases with thickness, surface piezoelectricity increases with thickness.
2. Therefore the relative contribution from surfaces is **independent of thickness**.
3. Surface polarization is limited by the depolarization field at the interface with bulk. This, in turn, **depends on the dielectric constant of bulk**.
4. **Conclusion: surface piezoelectricity is qualitatively insistinguishable from bulk flexoelectricity.**

Tagantsev and Yurkov, J. Appl. Phys. 2012
M. Stengel Nat. Coms. 2013

SURFACE PIEZOELECTRICITY

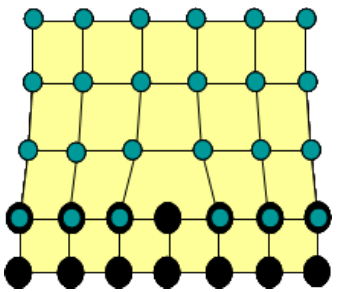


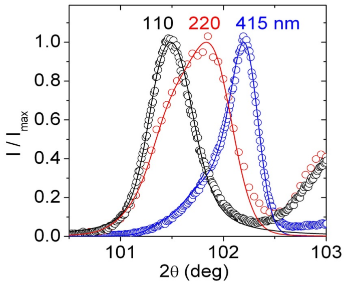
$P = e^{surf}\, h/2\; G$

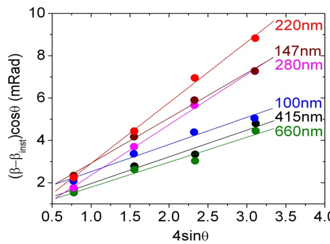
$$\mu_{eff} = e_\lambda \lambda \frac{h\varepsilon_b}{2\lambda\varepsilon_b + h\varepsilon_\lambda} \longrightarrow \mu^{eff} \equiv P/G = e^{surf}\, h/2$$

(G≡Gradient=Curvature and e=piezoelectric constant)

Strain vs strain gradients in ferroelectrics

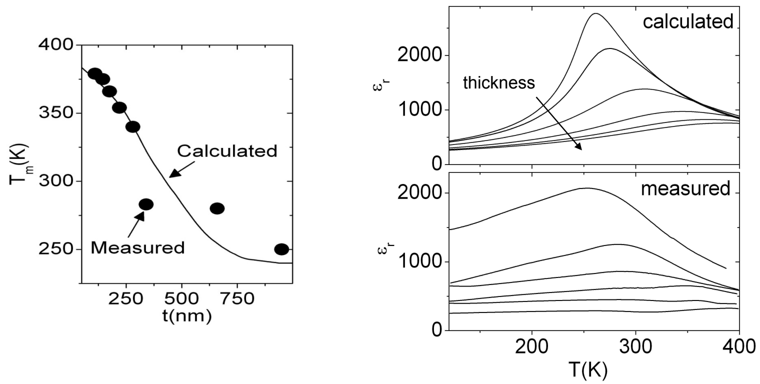






G. Catalan et al. Phys Rev B **72**, 20102 (2005)

Comparison with experiment



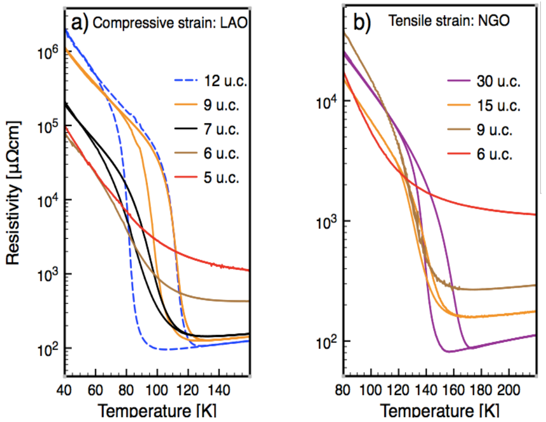
Strain affects the **temperature** of the dielectric peak.

Strain gradient affects the **height** of the dielectric peak.

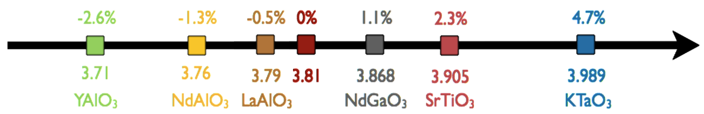
Catalan et al. J. Phys. Cond. Mat 2004 Catalan et al, Phys Rev B 2005

Size effect

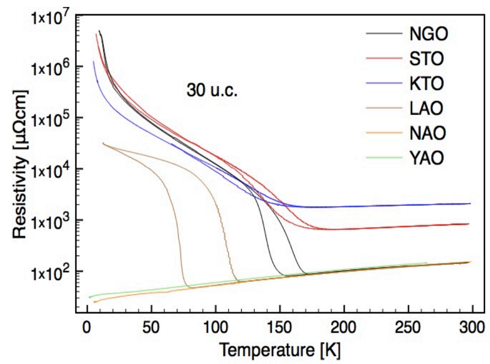
- With decreasing thickness
  - Increase in resistivity in the metallic phase
  - Narrowing of the hysteresis
- Further decrease
  - First to second order transition
  - Insulating behaviour



Strain: different substrates



- Tensile strain
  - Degradation of metallic phase
  - Broadening of MI transition
- ➢ Tensile strain favors oxygen vacancies and Ni^{2+}
- Compressive strain
  - Initial lowering of T_{MI}
  - Complete suppression of MI transition
- ➢ Compressive strain mimics hydrostatic pressure



PFM & C-AFM

RESULTS: Conductivity @ as-grown 71º DW @ $BiFeO_3$/DyScO/STO (001)
(BCN-Groningen collaboration)