FIXIT

Ferroelectricity and ferroelectric materials

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History: 1920-2020: 100-year anniversary

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editorial

A century of ferroelectricity

Ferroelectricity was experimentally discovered one hundred years ago, spurring research on its fundamental properties and potential applications.

1920 – 2020: 100th anniversary

Ferroelectricity was first discovered by Joseph Valasek **in 1920** in Rochelle salt

($KNaC_4H_4O_6.4H_2O$ = potassium sodium tartrate)

Phys. Rev. 15, 537(1920)

Rochelle salt under polarized light, showing evidence of different ferroelectric domains. Credit: Sciencephotos/Alamy Stock Photo

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History

It is interesting to note that ferroelectricity was discovered well after other phenomena such as pyroelectricity, piezoelectricity…

- **Pyroelectricity** first observed in Tourmaline (Theophrastus ˜300 BC, Aepinus 1756)
- **Piezoelectricity** discovered in 1880 by the Curie brothers
- **Pockels effect** (anomalous dielectric response - E.O. effect) in 1893 in Rochelle Salt
- **Ferroelectricity**: term coined by E. Schrödinger in 1912

first discovered by J. Valasek **in 1920** in Rochelle salt ($KNaC_4H_4O_6.4H_2O$ = potassium sodium tartrate)

Phys. Rev. 15, 537(1920); *Phys. Rev*. 17, 475 (1921)

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History

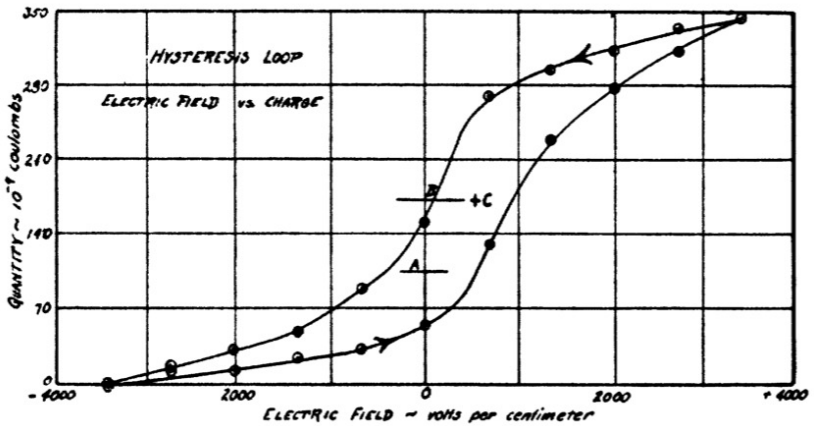
First discovered by J. Valasek in 1920 in Rochelle salt ($KNaC_4H_4O_6.4H_2O$ = potassium sodium tartrate tetrahydrate)

Phys. Rev. 15, 537(1920)

Permanent polarization and hysteretic switching are observed

Phys. Rev. 17, 475 (1921)

T=0° C



Joseph Valasek, 1922

University Minesota

"…is due to a hysteresis in P analogous to magnetic hysteresis. This would suggest a parrallelism between the behavior of Rochelle salt as a dielectric and steel, for example, as a ferromagnetic substance."

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About Rochelle salt $KNaC_4H_4O_6 \bullet 4H_2O$

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Elie Seignette, a pharmacist in La Rochelle,
synthesized Rochelle salt (or Seignette salt)
in ~1665 (“sel polychreste”)

It was used for its mild medicinal purgative properties

Now: - food additive (E337)
- antioxidant and pH regulation

How did Seignette prepare this potassium sodium tartrate salt ?

→ It is a natural salt of potassium hydrogen tartrate that is found at the bottom of Bordeaux wine bottles + soda

The first ferroelectric to be discovered (in 1920) is a byproduct of Bordeaux wine !

Ferroelectricity was also called “Seignette electricity”

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What is a ferroelectric?

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What is a ferroelectric?

- A ferroelectric possesses, along at least one direction, a spontaneous macroscopic dipole moment i.e. non-zero spontaneous electric polarization in the absence of an applied electric field

  $\boldsymbol{P_S \neq 0}$ **when** $\boldsymbol{E = 0}$

- The polarization can be switched in the opposite direction by application of an electric field

  Switchable polar state: $+\overrightarrow{P_S}$ **and** $-\overrightarrow{P_S}$ **by application of** $\overrightarrow{E_{ext}}$

- There is a **phase transition at a temperature T_c above which the phase is paraelectric (Ps = 0)**

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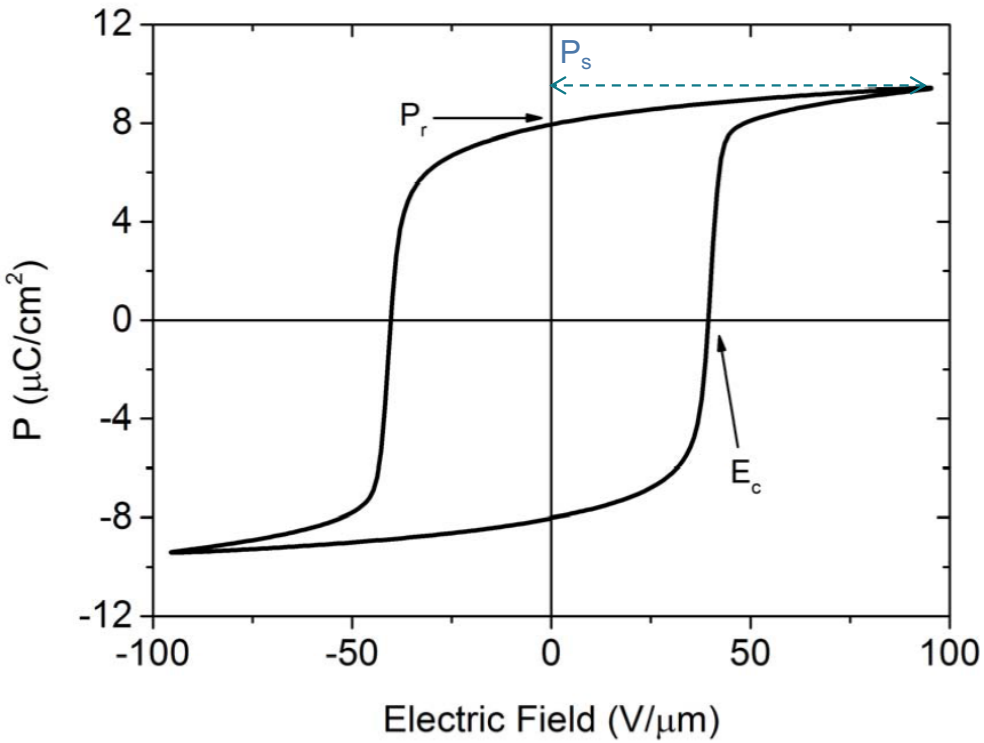
What is a ferroelectric?

Ferroelectric hysteresis

P_s: spontaneous polarization

P_r: remanent polarization

E_c: coercive field



Adapted from **DOI:** 10.1109/TRANSDUCERS.2015.7181322

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Ferroelectrics and crystallography

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- Ferroelectric crystal structures are **non-centrosymmetric.** The point group does not possess the *inversion operation.*

  Otherwise, by Neumann's principle, P_s would vanish.

Note: Neumann's principle, or principle of symmetry, states that, if a crystal is invariant with respect to certain symmetry operations, any of its physical properties must also be invariant with respect to the same symmetry operations, or otherwise stated, the symmetry operations of any physical property of a crystal must include the symmetry operations of the point group of the crystal. (https://dictionary.iucr.org/Neumann%27s_principle)

- To support a non-zero P_S, **the point group of the crystal must be polar**

Polar point group: Those point groups for which every symmetry operation leaves more than one common point unmoved are known as the polar point groups (http://pd.chem.ucl.ac.uk/pdnn/symm2/polar1.htm)
In a point group, the unmoved points will constitute a line, a plane, or all of space.

- A polar direction is one for which there is no symmetry operation that makes one end of the direction equivalent to the other.

Note: a point group can be non-centrosymmetric but non-polar (e.g. point group 32, the point group of alpha-quartz)

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Ferroelectrics and crystallography

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- There are 10 polar point groups, which all of them have a „built in“ unique polar direction. These are the only one that can support a spontaneous polarization.
- All crystals belonging to these 10 crystal classes (corresponding to the 10 polar point) are **pyroelectrics.**

Crystal System	Polar Point Groups	
Triclinic	1	
Monoclinic	2	*m*
Orthorhombic	*mm*2	
Tetragonal	4	4*mm*
Trigonal	3	3*m*
Hexagonal	6	6*mm*
Cubic	(None)	

http://pd.chem.ucl.ac.uk/pdnn/symm2/polar1.htm

- All ferroelectrics are pyroelectrics
- But all pyroelectrics are not ferroelectrics: when the electric polarization of a pyroelectric crystal can not be switched , it is by definition not a ferroelectric.

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Ferroelectric compounds

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Ferroelectric compounds

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- 1920: **Rochelle salt (**synthesized by Elie Seignette
- 1933: **Potassium dihydrogen phosphate** (KDP) by Paul Scherrer and Georg Busch
  KH_2PO_4 „ Eine neue seignette-elektrische Substanz“ (1935)

} Fragile and water soluble materials → Limited applications

In the early 1940‘s, intensive search for high dielectric materials

- 1945-1946: **$BaTiO_3$** first inorganic ferroelectric discovered (first ferroelectric that did not contain H-bonds)

(6) A. Von Hippel, R.G. Breckenridge, F.G. Chesley, and L. Tisza, Ind. Eng. Chem. 38 1097 (1946).

(7) B. Wul and J.M. Goldman, C.R. Acad. Sci. URSS 51 21 (1946).

Ferroelectrics, 1987, Vol. 74, pp. 267–284

https://ieee-uffc.org/wp-content/uploads/2016/11/cross_newnham.pdf

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Ferroelectric compounds

Table V. Period of Proliferation

1949 to 1960	20 Perovskite compounds	WO_3 to $Pb_3MgNb_2O_9$	Matthias (Refs. 43–45) Smolenskii (Refs. 46–48)
1949	$LiNbO_3$ family		Matthias (Ref. 49)
1951	$LiTlC_4H_4O_6 \cdot H_2O$		Matthias (Ref. 50)
1952	$Cd_2Nb_2O_7$ pyrochlore family		Cook, Jaffe (Ref. 51)
1953	$PbNb_2O_6$ tungsten bronze		Goodman (Ref. 52)
1955	G.A.S.H. family		Holden (Ref. 53)
1956	$Sn(NH_2)_2$ thiourea		Soloman (Ref. 54)
1956	TGS family		Matthias (Ref. 55)
1956	$(NH_4)_2SO_4$ family		Matthias (Ref. 56)
1956	Colemanite		Goldsmith (Ref. 57)
1956	$(NH_4)_2Cd_2(SO_4)_3$ family		Jona, Pepinsky (Ref. 58)
1957	Alums		Jona (Ref. 59)
1957	Dicalcium strontium propionate		Matthias (Ref. 60)
1957	Boracite family		Le Corre (Ref. 61)
1958	$(NH_4)HSO_4$		Pepinsky (Ref. 62)
1958	$NaNO_2$ family		Sawada (Ref. 63)
1958	KNO_3		Sawada (Ref. 64)
1959	$LiH_3(SeO_3)_2$ family		Pepinsky (Ref. 65)
1959	$(NH_4)NaSO_4$)		Pepinsky (Ref. 66)
1960	$N(CH_3)_4 \cdot HgCl_3$ family		Fatuzzo, Merz (Ref. 67)
1960	$K_4Fe(CN)_6 \cdot 3H_2O$ family		Waku (Ref. 68)
1962	SbSI family		Fatuzzo (Ref. 69)
1963	$YMnO_3$ family		Bertaut (Ref. 70)

$PbTiO_3$
$Pb_{1-x}Zr_xTiO_3$ (PZT)

2008: HfO_2 compounds – Breakthrough discovery for integration

https://ieee-uffc.org/wp-content/uploads/2016/11/cross_newnham.pdf

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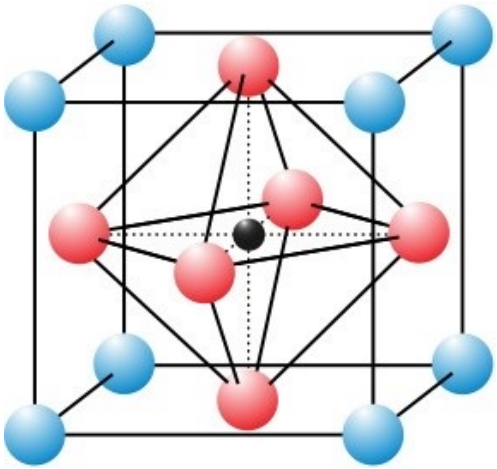
Perovskite ferroelectrics

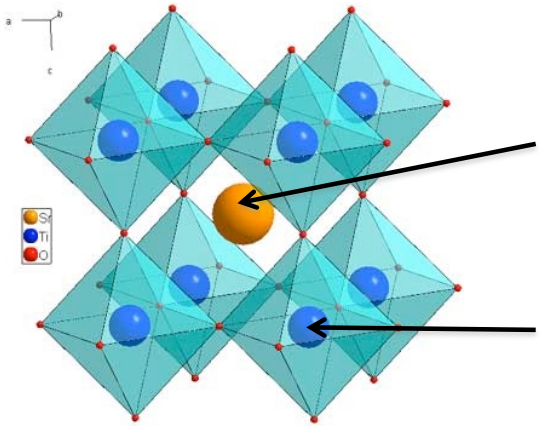
Perovskite structure ABX_3: cubic structure

X=Oxygen **ABO_3** (e.g. **$CaTiO_3$**) Space group Pm3m

ABX_3



One formula unit/unit cell



B site atom inside oxygen octahedra
Transition metal oxide (at RT) such as Ti, Mn, Cu (polarization, magnetic character…)

A site atom in-between oxygen octahedra
Alkali metal, alkaline earth metal, rare earth

3D oxygen octagedra network sharing corners

https://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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Perovskite ferroelectrics

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Perovskite structure

The original perovskite compound is **$CaTiO_3$.**

However, it was later found that $CaTiO_3$ is not cubic but orthorombic!

Discovered by:

Gustav Rose
1798 - 1873

Named after:

Lev Perovski
1792 - 1856

In $CaTiO_3$, Ca is slightly too small for 12 coordination with O . In order to reduce the size of the cavity, **the octahedra rotates and the unit cell becomes orthorhombic**

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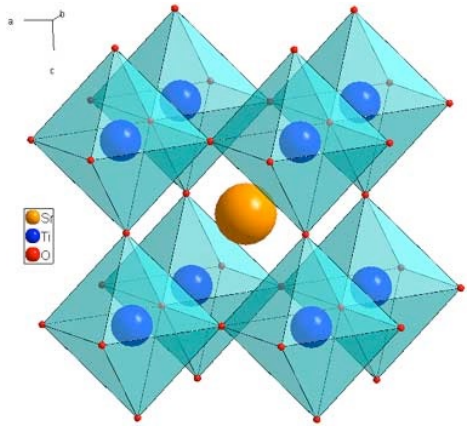
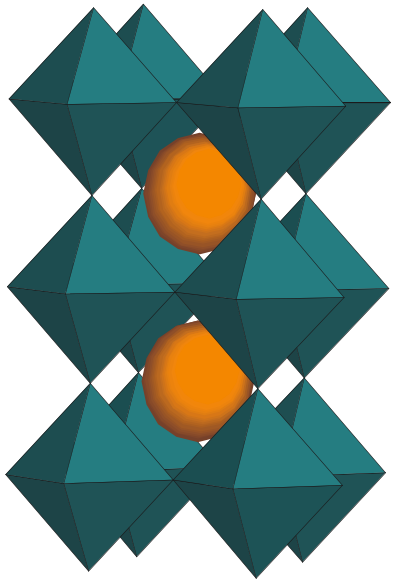
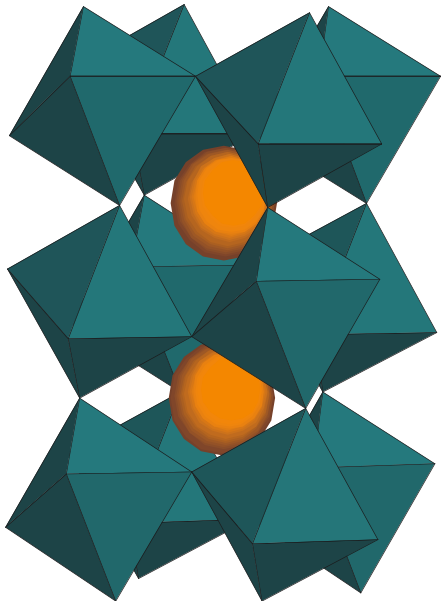
Perovskite ferroelectrics

Perovskite structure





Cubic unit cell



Orthorhombic unit cell

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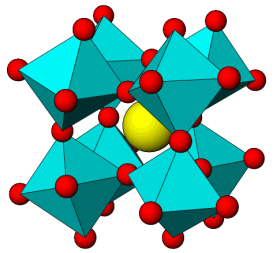
Perovskite ferroelectrics

Perovskite structure ABO_3



A large variety of possible distortions ot the cubic cell (which becomes “pseudo-cubic“)

- Possible tilt of the octahedra, depending on the size of the cation A
- Possible Jahn-Teller distortion
- Possible B cation displacement (ferroelectricity)

Playing with chemical substitution for a given compound often give rise to multiple different structures and, in turn, to different physical properties

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Perovskite structure compounds

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Perovskites exhibit a large variety of properties, among them are:

Dielectric
Piezoelectric
Pyroelectric
Ferroelectric
Semiconductive
Superconductive
Magnetic
Colossla magnetoresistive
Multiferroic
Charge ordering
Thermoelectrics
Photoelectric
…

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Perovskite ferroelectrics: $BaTiO_3$

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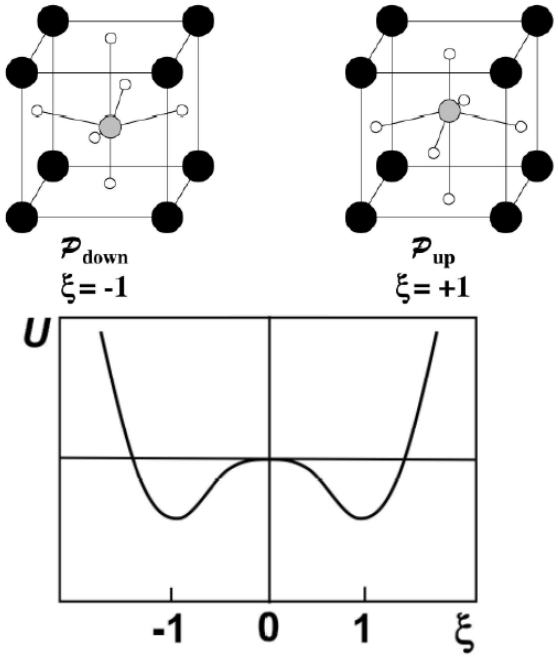
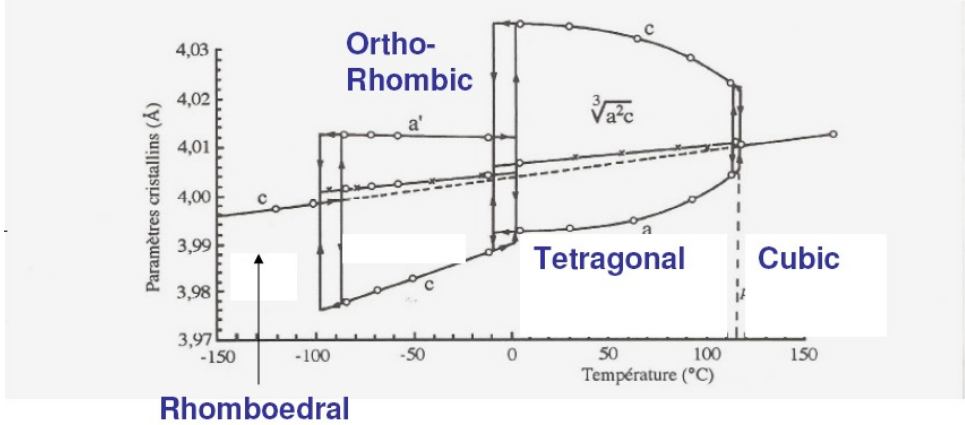
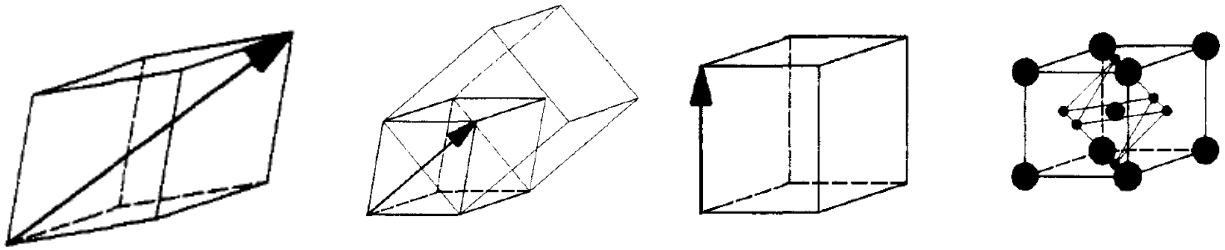


$T_c \sim 120℃$

Kay and Vousden, Phil. Mag. 40, 1019 (1943)





G.H. Kwei et al., J. Phys. Chem. 97, 2368 (1993)

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Perovskite ferroelectrics: $BaTiO_3$

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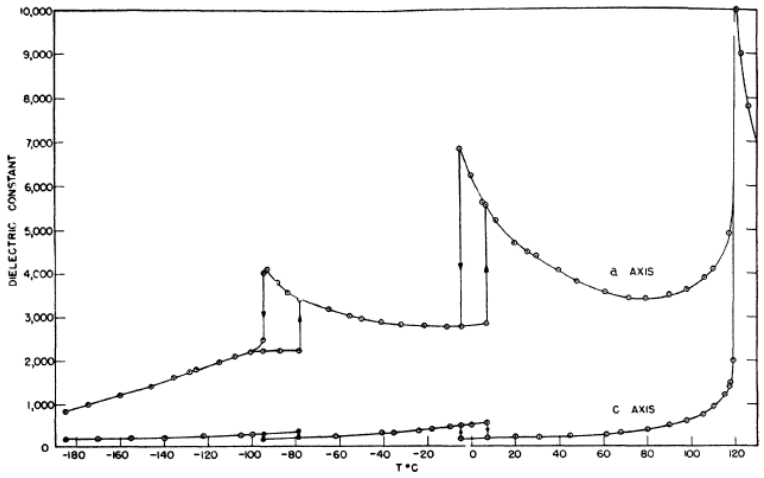
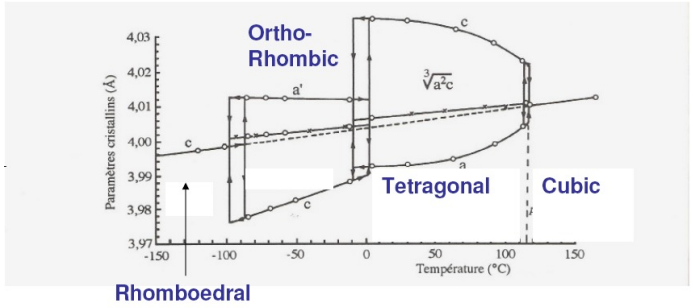
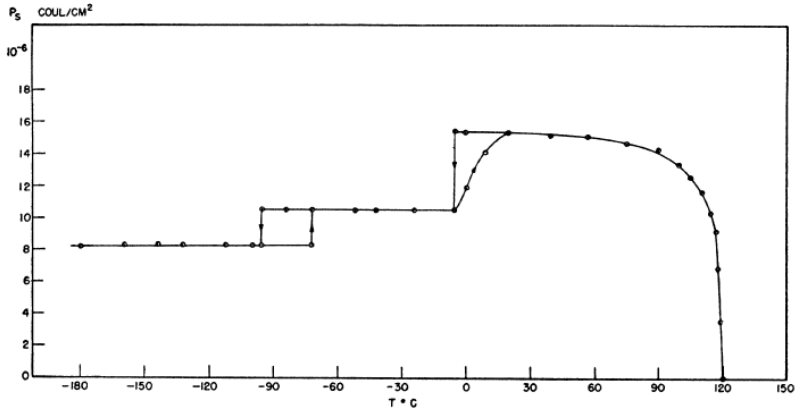
Dielectric constants as a function of temperature





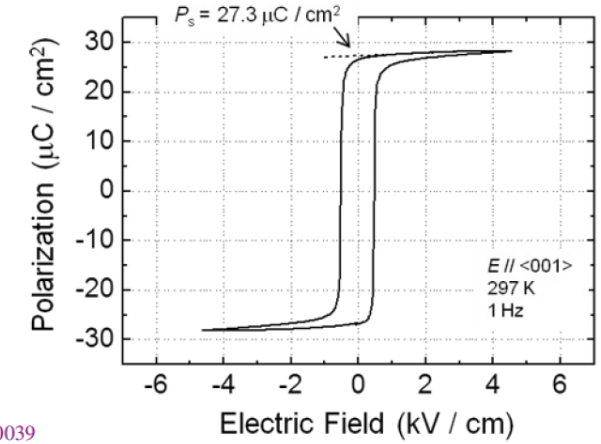
Kay and Vousden, Phil. Mag. 40, 1019 (1943)

Spontaneous polarization P_S as a function of temperature



W.J. Merz, Phys. Rev. 76, 1221 (1949)

P_s~ 26-27 μC/cm²



R. Imura *et al.*, 10.1142/S2010135X14500039

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Perovskite ferroelectrics: $BaTiO_3$

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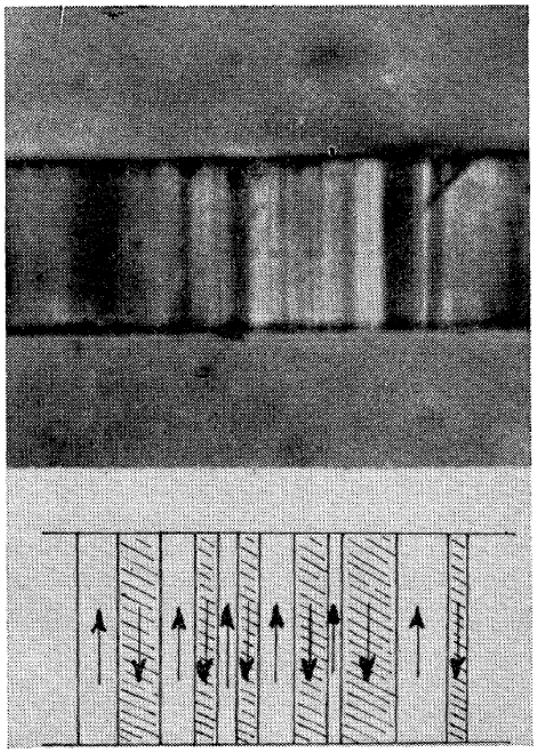
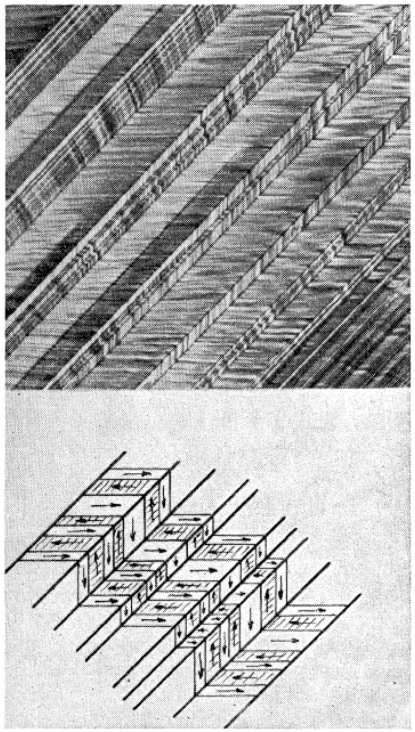
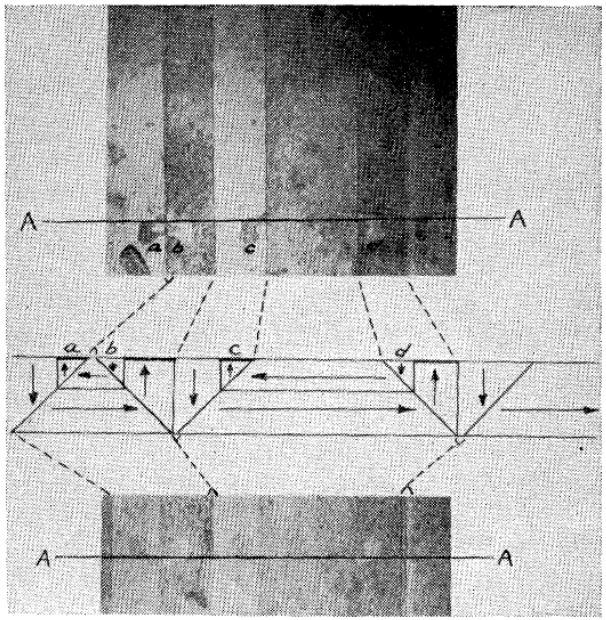
Domains imaged on etched $BaTiO_3$ single crystals







J.A. Hooton and W.J. Merz, Phys. Rev. 98, 409 (1955)

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Perovskite ferroelectrics

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	T_c(K)	P_S (μC/cm^2)
$BaTiO_3$	393	27
$PbTiO_3$	768	60 [1]
$KNbO_3$	708 [2]	30
$LaTiO_3$	1773 [3]	5 [3, 4]
$LiNbO_3$	1476 [5]	78 [5]
BiFeO3	1083 [6]	6.1 [7]

[1] Nishino, Ryutaro, et al. "Evolution of ferroelectricity in ultrathin $PbTiO_3$ films as revealed by electric double layer gating." *Scientific reports* 10.1 (2020): 1-8.

[2] Rani, Jyoti, et al. "Mo^{6+} modified $(K_{0.5}Na_{0.5})NbO_3$ lead free ceramics: structural, electrical and optical properties." *Journal of Materials Science & Technology* 30.5 (2014): 459-465.

[3] Herrera, G., J. Jiménez-Mier, and E. Chavira. "Layered-structural monoclinic–orthorhombic perovskite $La_2Ti_2O_7$ to orthorhombic $LaTiO_3$ phase transition and their microstructure characterization." *Materials characterization* 89 (2014): 13-22.

[4] Nanamatsu, S., et al. "A new ferroelectric: La2Ti2O7." *Ferroelectrics* 8.1 (1974): 511-513.

[5] Ganesamoorthy, S., et al. "A comparative study on the domain switching characteristics of near stoichiometric lithium niobate and lithium tantalate single crystals." *Materials Science and Engineering: B* 120.1-3 (2005): 125-129.

[6] Shvartsman, V. V., et al. "Large bulk polarization and regular domain structure in ceramic Bi FeO_3." *Applied physics letters* 90.17 (2007): 172115.

[7] Kadomtseva, A. M., et al. "Phase transitions in multiferroic $BiFeO_3$ crystals, thin-layers, and ceramics: enduring potential for a single phase, room-temperature magnetoelectric 'holy grail'." *Phase Transitions* 79.12 (2006): 1019-1042.

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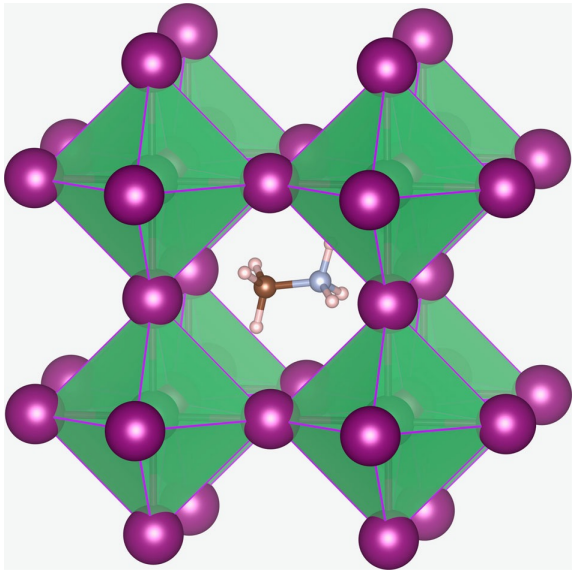
Perovskite ferroelectrics

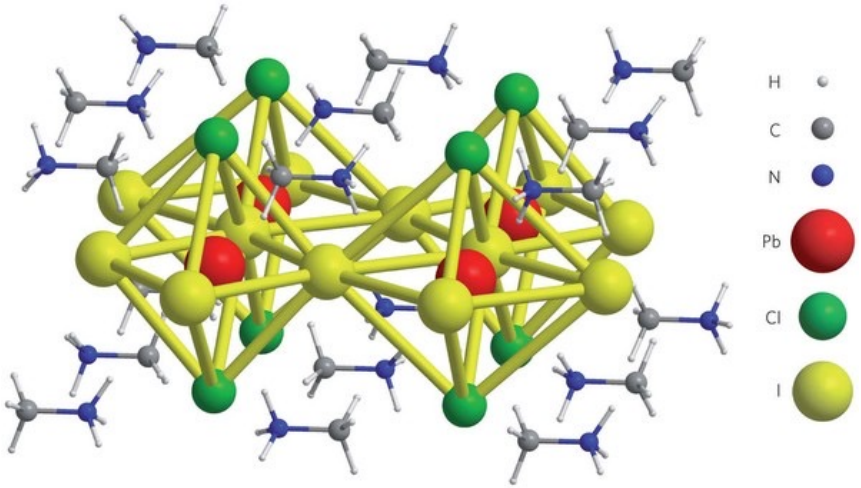
Organic / Inorganic Perovskite

Photovoltaics

ABX_3



$CH_3NH_3PbI_3$



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Hybrid perovskite ferroelectrics

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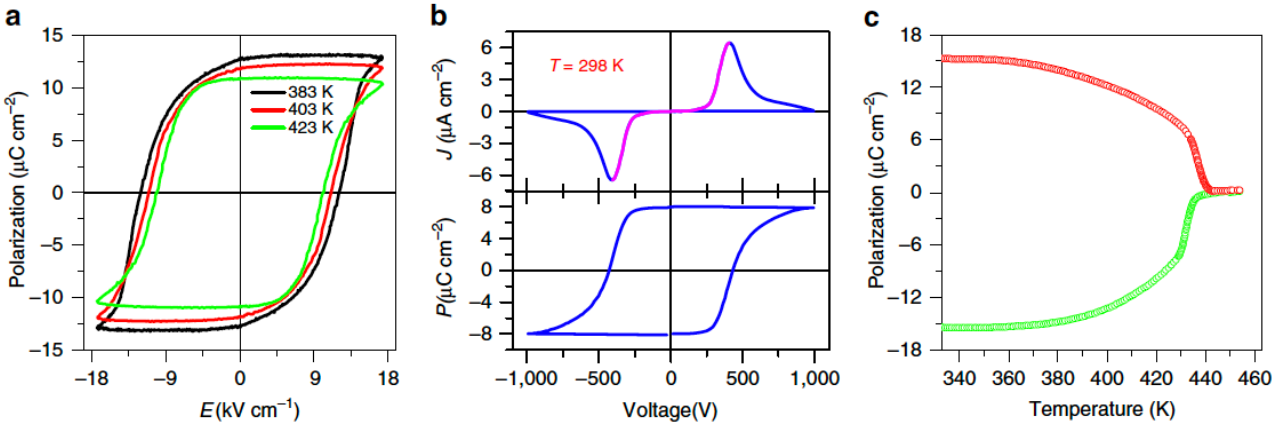
$(benzylammonium)_2PbCl_4$



P_s = 13 μC/cm^2 and Curie temperature T_c = 438K

W.Q. Liao et al, Nat. Comm. 6, 7338 (2015)

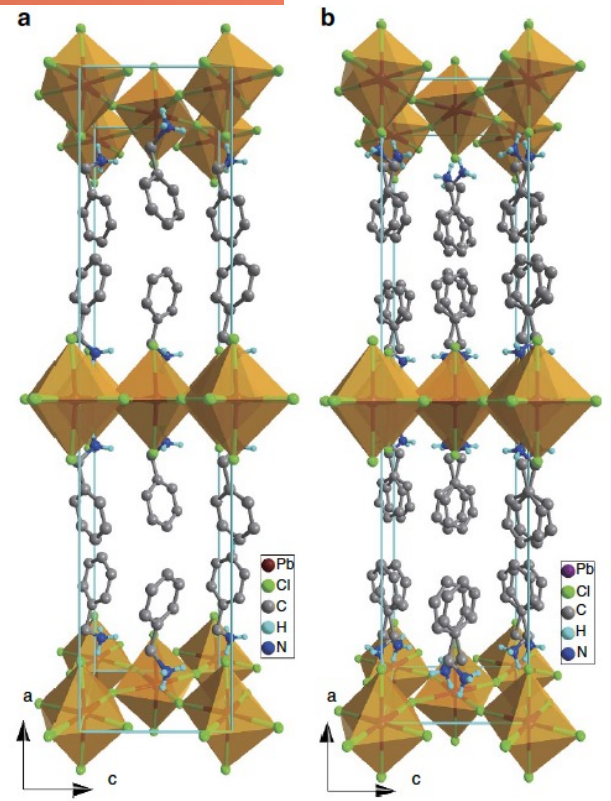


Figure 1 | Comparison of the crystal structures between the para-electric and ferroelectric phases. (**a**) Perspective view of **1** at 293K. (**b**) Perspective view of **1** at 453K. Hydrogen atoms bonded to the C atoms were omitted for clarity.

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Hybrid perovskite ferroelectrics

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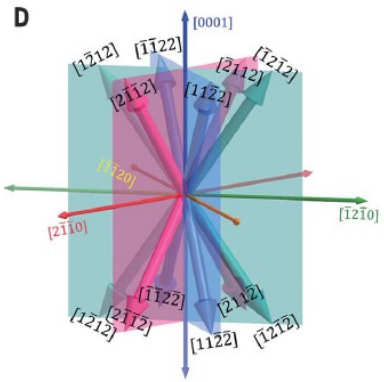
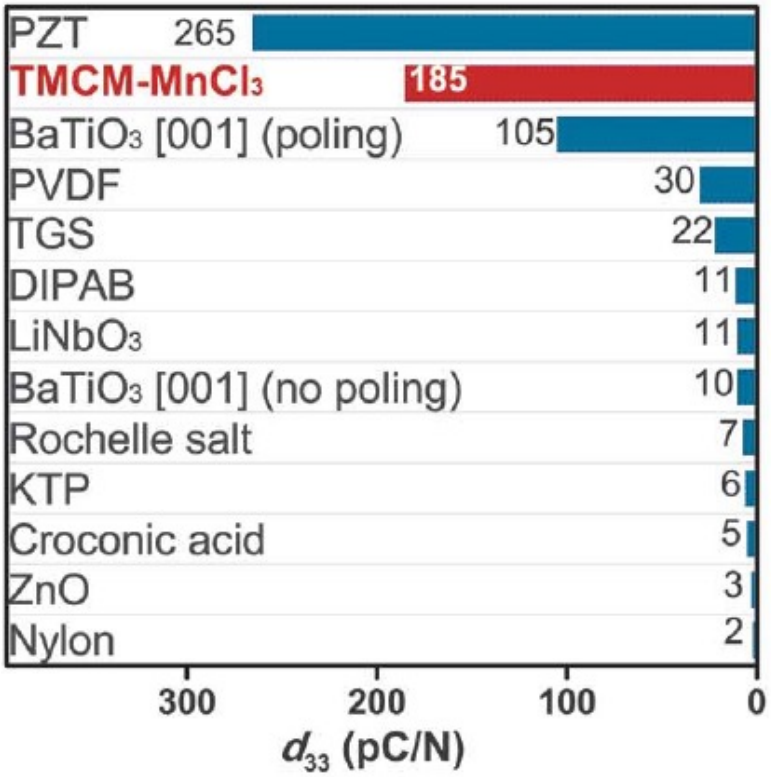
PIEZOELECTRICS

An organic-inorganic perovskite ferroelectric with large piezoelectric response

Yu-Meng You,[1*†] Wei-Qian Zhang,[1] Qionghua Zhou,[3] Xianghong Hu,[1] Zheming Wang,[4] Song Gao,[4*] Kunlun Yang,[5] Jun-Ming Liu,[5] Jiangyu Li,[5,6*] Yanfa Yan,[2*] Ren-Gen Xiong[1*]

Science **357**, 306–309 (2017)





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Perovskite ferroelectrics

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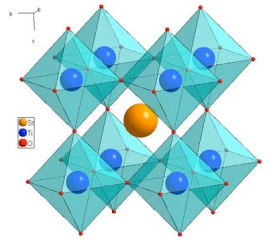
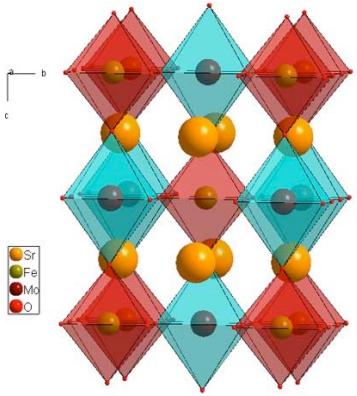
Perovskite (ABO_3: $CaTiO_3$)



Double Perovskite

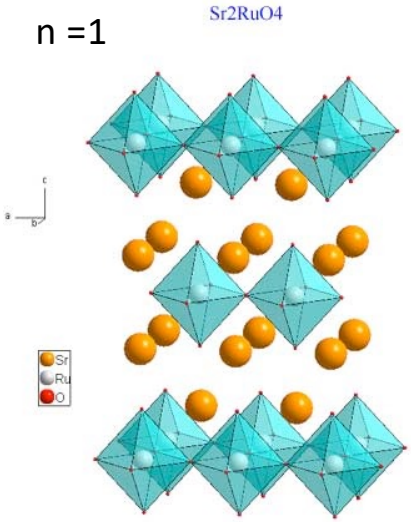


Ex: $CaMnTi_2O_6$

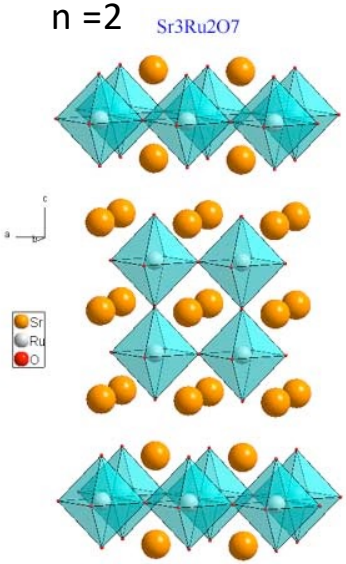
Layered Perovskites:

Ruddlesden-Popper phases $A_{(n+1)}B_{(n)}O_{(3n+1)}$

n =1



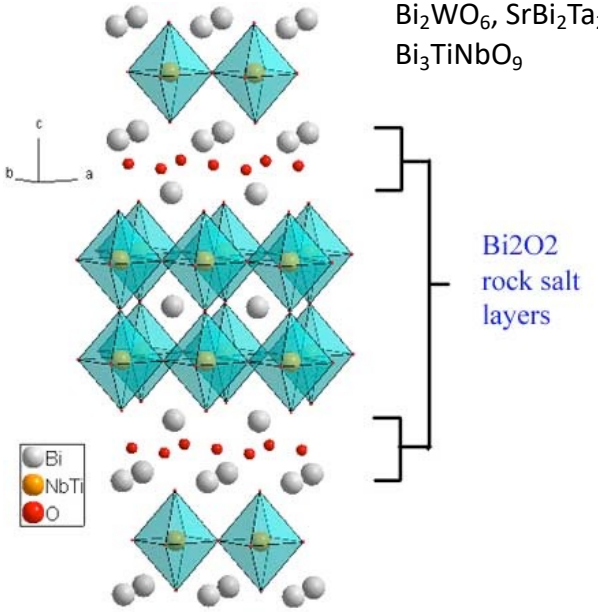
n =2



Ex: $Ca_3Ti_2O_7$, $Li_2CaTa_2O_7$ (hybrid improper ferroelectrics
See - N.A. Benedek, C.J. Fennie, PRL 106, 107204 (2011))

Aurrivillius phases $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$

Bi_2WO_6, $SrBi_2Ta_2O_9$
Bi_3TiNbO_9



Ex: $PbBi_2Nb_2O_9$, $SrBi_2Ta_2O_9$, $SrBi_2Nb_2O_9$

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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Hexagonal manganites

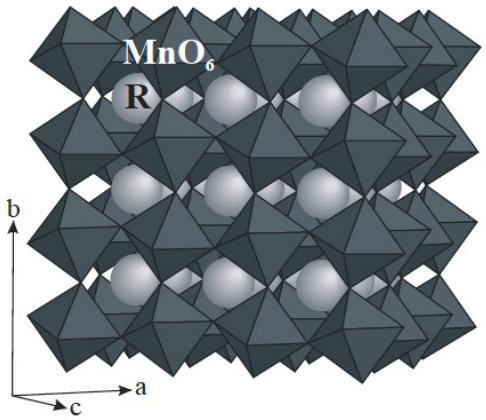
FIXIT

$RMnO_3$: "perovskite structure" (Pnma)

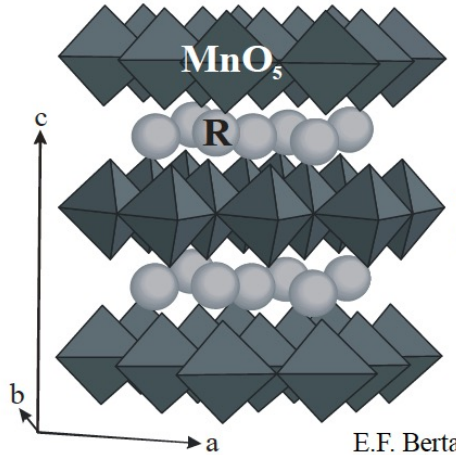
$RMnO_3$: hexagonal structure

Ce	Pr	Nd	*Pm*	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La									Y				

perovskite



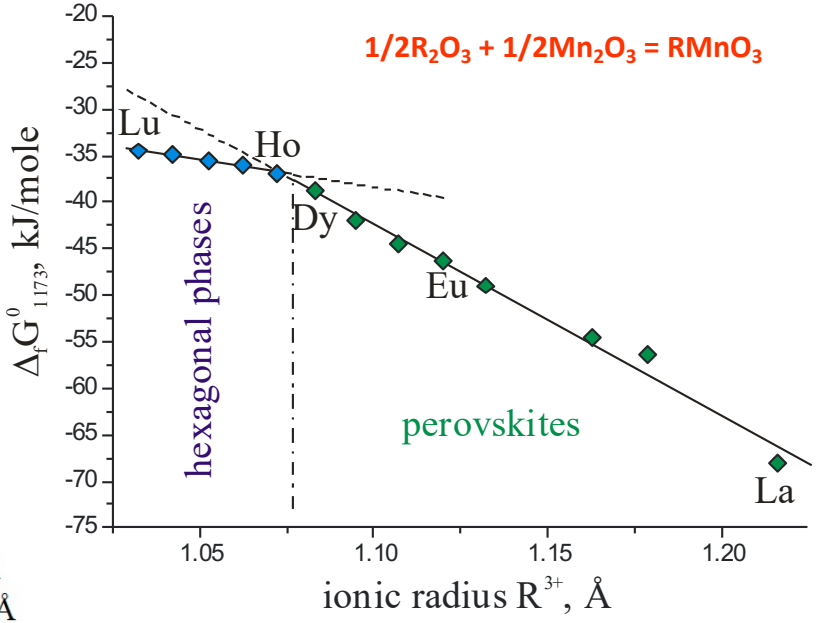
hexagonal



a ~ 6.14 Å
c ~ 11.41 Å

E.F. Bertaut *et al.* ~1963

$1/2R_2O_3 + 1/2Mn_2O_3 = RMnO_3$



T. Atsumi, T. Oghushi, N. Kamegashira
J. of Alloys and Compounds 238 (1996) 35

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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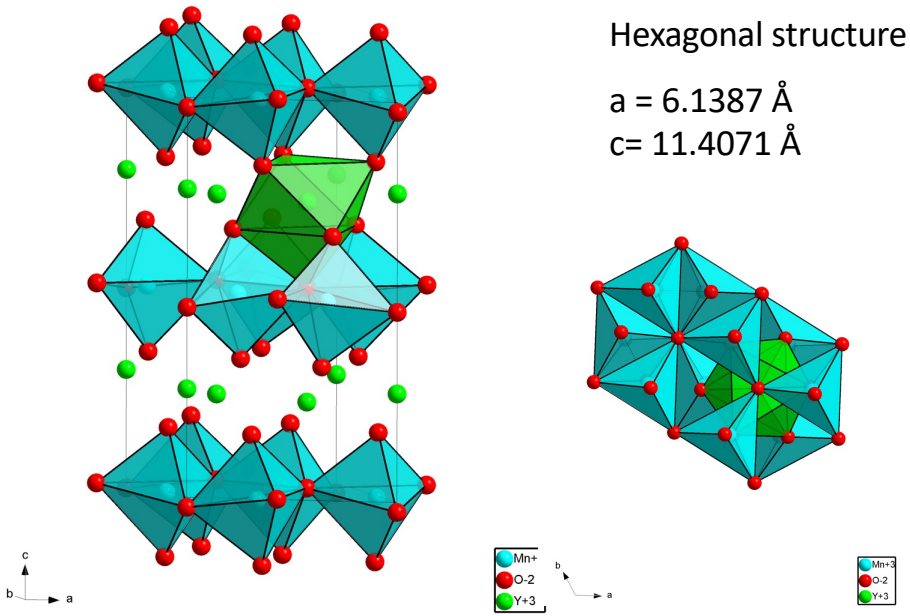
Hexagonal manganites

FIXIT



Hexagonal structure $P6_3cm$

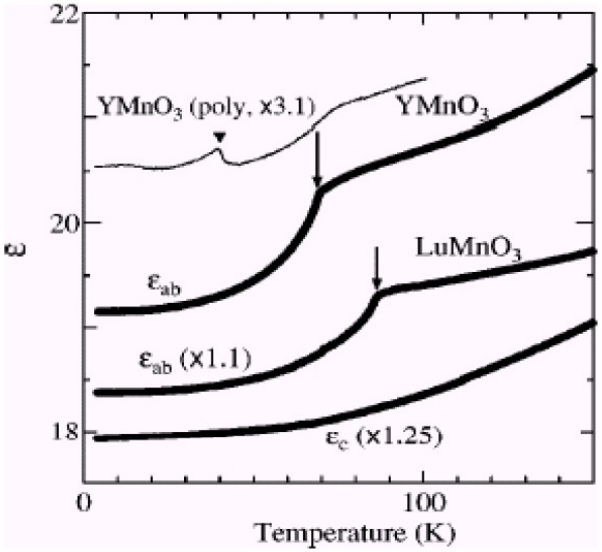
a = 6.1387 Å
c= 11.4071 Å

Van Aken *et al.*, Acta Crystallographica C 57, 230 (2001)

- **Ferroelectric** (T_c ~ 800 - 1000 K)

  polarisation **along c axis** with P_S ~ 5.5 µC/cm^2
  improper ferroelectric

- **Antiferromagnetic** (T_N ~ 70 - 100 K)



Katsufuji et al., PRB 64, 104419 (2001)

Huang et al., PRB 56, 2623 (1997)

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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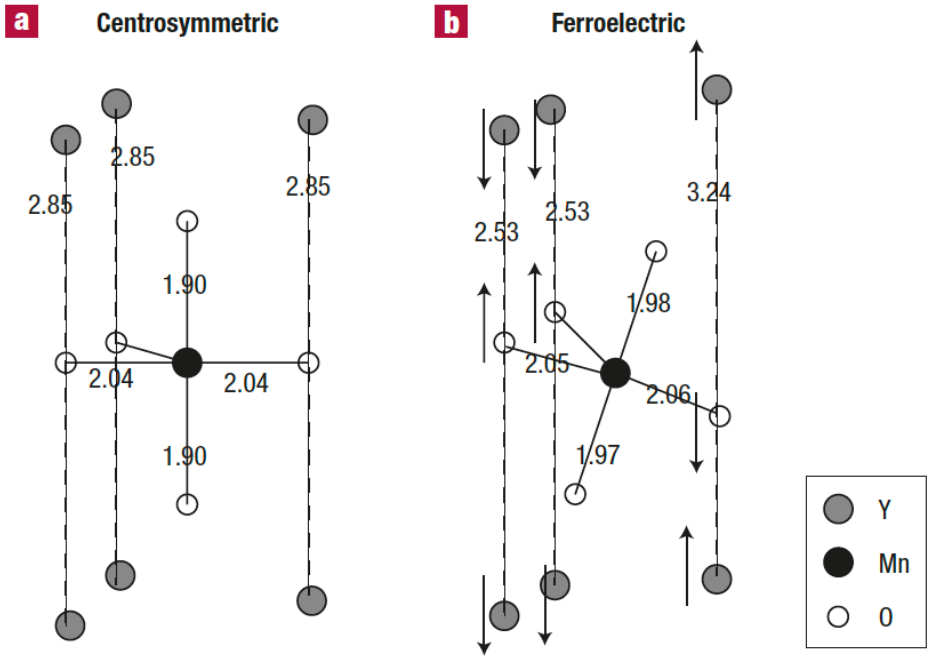
Hexagonal manganites

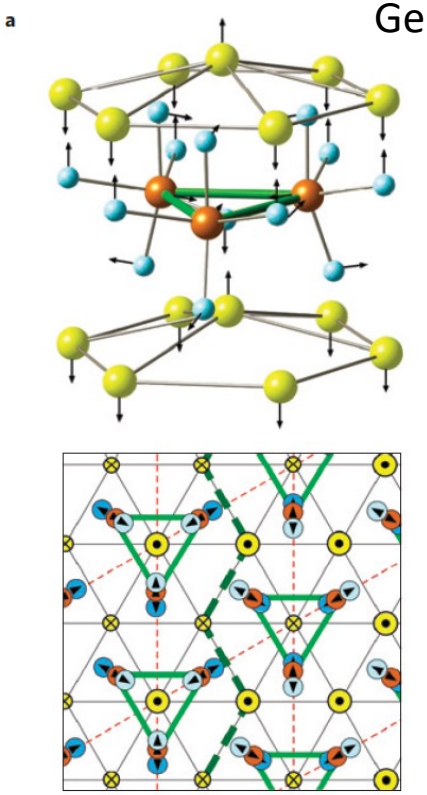
FIXIT



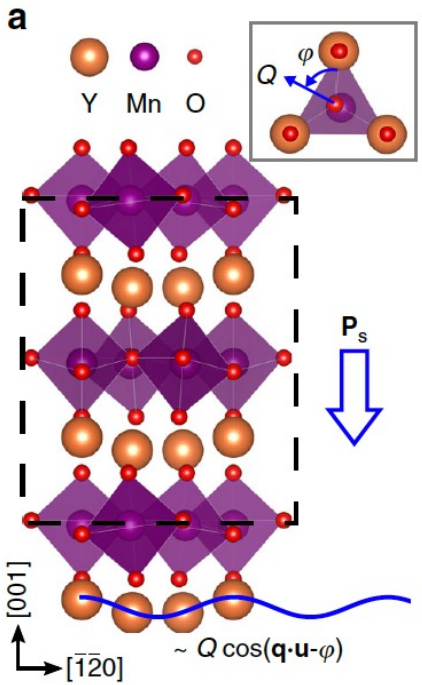
centrosymmetric (a) and ferroelectric structures (b)

Van A., Bas B., et al. , *Nature materials* 3, 164 (2004).

Geometrically-driven ferroelectricity



T. Choi et al., Nat. Mater. 9, 253 (2010)



From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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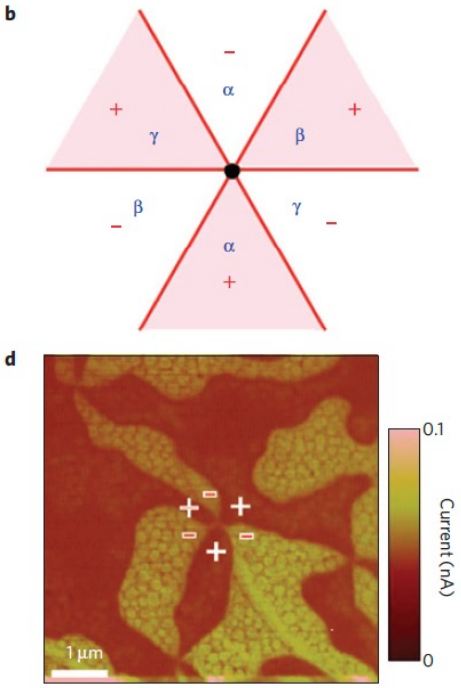
Hexagonal manganites

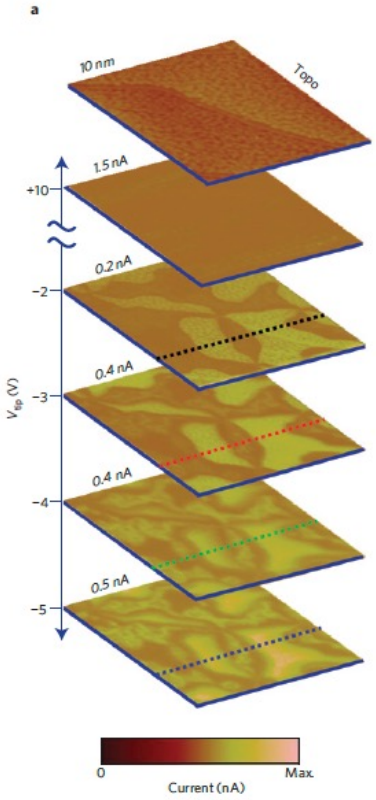
FIXIT

Peculiar domain configuration

6 domains with vortex line at center

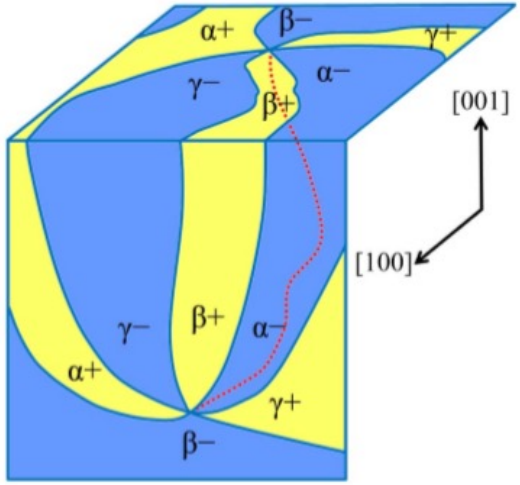


Change of domain configuration with applied voltage



T. Choi et al., Nat. Mater. 9, 253 (2010)

Vortex-antivortex structure (V-AV)



Zhang, Qinghua, et al., *Scientific reports* 3 (2013): 2741

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

Funded by the European Union

T. Atsumi, T. Oghushi, N. Kamegashira
Journal of Alloys and Compounds 238 (1996) 35

Hexagonal rare earth manganites

FIXIT

Material	Space group	Crystal structure	Magnetic ordering	Electrical ordering	T_N or T_M (K)	T_C (K)
$YMnO_3$	$P6_3cm$	Hexagonal	AFM	FE	70–80	914
$YbMnO_3$	$P6_3cm$	Hexagonal	AFM	FE	87	983–993
$HoMnO_3$	$P6_3cm$	Hexagonal	AFM	FE	72 ~49	875
$TmMnO_3$	$P6_3cm$	Hexagonal	AFM	FE	86	>573

Critical Reviews in Solid State and Materials Sciences 34, 179 (2009

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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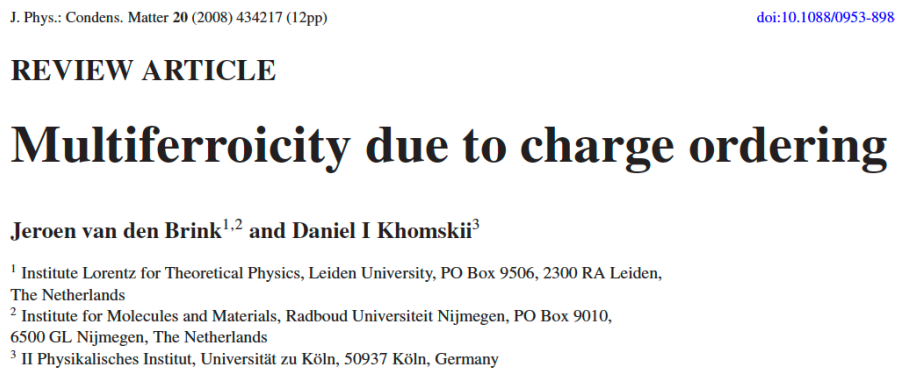
Improper ferroelectrics in magnetic systems

FIXIT

Type-II multiferroics ferroelectricity occurs only in the magnetically ordered state: **ferroelectricity sets in at the same temperature as a certain type of magnetic ordering and is driven by it.**

- $TbMnO_3$ (perovskite structure)
- $Ni_3V_2O_8$
- $MnWO_4$
- Ca_3CoMnO_6
- RMn_2O_5 , where R is a rare earth ion
- …



J. Phys.: Condens. Matter **20** (2008) 434217 (12pp) doi:10.1088/0953-898

REVIEW ARTICLE

Multiferroicity due to charge ordering

Jeroen van den Brink[1,2] and Daniel I Khomskii[3]

[1] Institute Lorentz for Theoretical Physics, Leiden University, PO Box 9506, 2300 RA Leiden, The Netherlands
[2] Institute for Molecules and Materials, Radboud Universiteit Nijmegen, PO Box 9010, 6500 GL Nijmegen, The Netherlands
[3] II Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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Many more…

FIXIT

Material	Space group	Crystal structure	Magnetic ordering	Electrical ordering	T_N or T_M (K)	T_C (K)
$YMnO_3$	$P6_3cm$	Hexagonal	AFM	FE	70–80	914
$YbMnO_3$	$P6_3cm$	Hexagonal	AFM	FE	87	983–993
$HoMnO_3$	$P6_3cm$	Hexagonal	AFM	FE	72 ~49	875
$TmMnO_3$	$P6_3cm$	Hexagonal	AFM	FE	86	>573 348
$TbMnO_3$	$Pbnm$	Orthorombic	AFM	FE	41	28
$DyMnO_3$	$Pbnm$	Orthorombic	AFM	FE	~40	~19
$LaMnO_3$	$Pbnm$	Orthorombic	AFM		140	
$BiMnO_3$	$C2$	Monoclinic	FM	AFE	105	723
$BiFeO_3$	$R3c$	Rhombohedral	AFM	FE	643	1,100
$BiCrO_3$	$C2/c$	Monoclinic	AFM	AFE	109	420
$HoMn_2O_5$	$Pbam$	Orthorombic	AFM	FE	~45	~39
$ErMn_2O_5$	$Pbam$	Orthorombic	AFM	FE	~45	~39
$TmMn_2O_5$	$Pbam$	Orthorombic	AFM	FE	~45	~36
$TbMn_2O_5$	$Pbam$	Orthorombic	AFM	FE	~45	~38
$DyMn_2O_5$	$Pbam$	Orthorombic	AFM	FE	~42	~38
YMn_2O_5	$Pbam$	Orthorombic	AFM	FE	~45	~41

N. Izymskaya et al., Critical Reviews in Solid State and Materials Sciences 34, 179 (2009

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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the European Union

HfO_2-based compounds

Ferroelectricity in HfO_2 discovered in 2008 (first published in 2011)

APPLIED PHYSICS LETTERS **99**, 102903 (2011)

Ferroelectricity in hafnium oxide thin films

T. S. Böscke,[1,a),b)] J. Müller,[2] D. Bräuhaus,[3] U. Schröder,[4,b)] and U. Böttger[3]
[1]*Löberwallgraben 2, 99096 Erfurt, Germany*
[2]*Fraunhofer CNT, 01099 Dresden, Germany*
[3]*RWTH Aachen, Institut für Werkstoffe der Elektrotechnik, 52062 Aachen, Germany*
[4]*Namlab gGmbH, 01187 Dresden, Germany*

APPLIED PHYSICS LETTERS **99**, 112904 (2011)

Phase transitions in ferroelectric silicon doped hafnium oxide

T. S. Böscke,[1,2,a),b)] St. Teichert,[3,b)] D. Bräuhaus,[4] J. Müller,[5] U. Schröder,[2,b)] U. Böttger,[4] and T. Mikolajick[2,6]
[1]*Löberwallgraben 2, 99096 Erfurt, Germany*
[2]*Namlab gGmbH, 01187 Dresden, Germany*
[3]*UAS Jena, Department of SciTec, 07745 Jena, Germany*
[4]*RWTH Aachen, Institut für Werkstoffe der Elektrotechnik, 52062 Aachen, Germany*
[5]*Fraunhofer Center Nanoelectronic Technologies (CNT), 01099 Dresden, Germany*
[6]*Department of Nanoelectronic Materials, University of Technology Dresden, 01062 Dresden, Germany*

APPLIED PHYSICS LETTERS **99**, 112901 (2011)

Ferroelectric $Zr_{0.5}Hf_{0.5}O_2$ thin films for nonvolatile memory applications

J. Müller,[1,a)] T. S. Böscke,[2,b)] D. Bräuhaus,[3] U. Schröder,[4,b)] U. Böttger,[3] J. Sundqvist,[1,b)] P. Kücher,[1] T. Mikolajick,[4,5] and L. Frey[6]

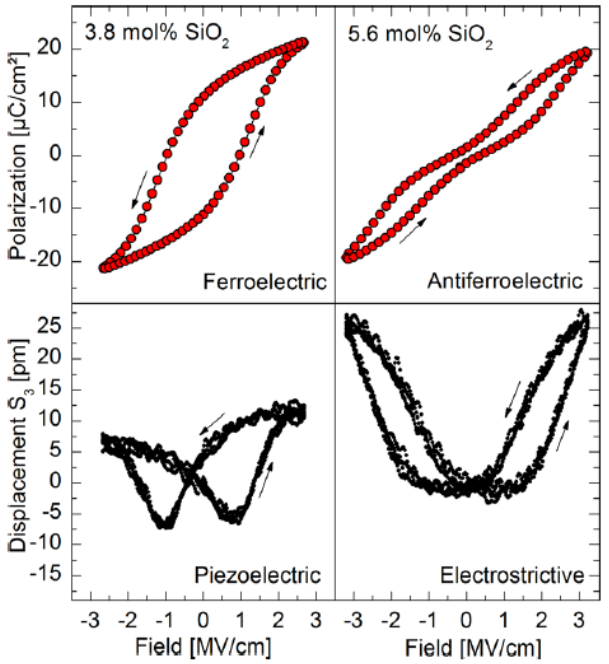
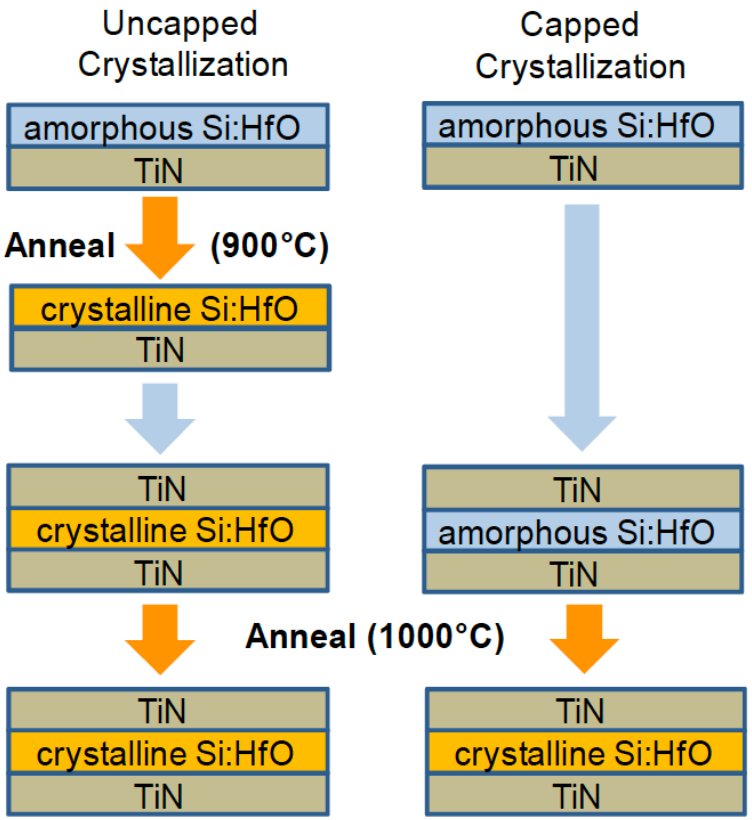


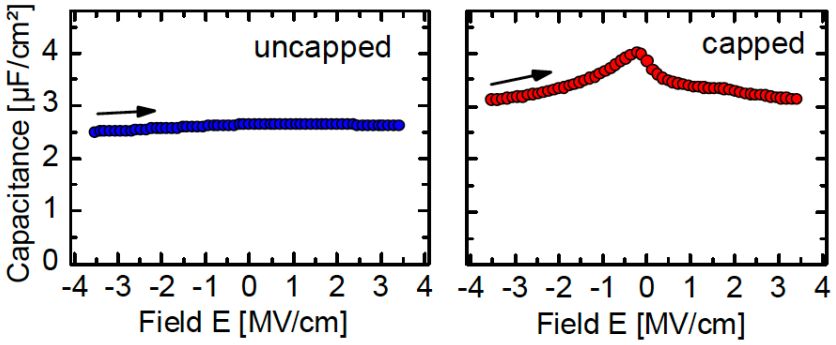
FIG. 3. (Color online) Polarization (top row) and piezoelectric displacement (bottom row) measurement of MIM capacitor samples with ferroelectric (left column) and antiferroelectric (right column) Si:HfO_2 insulators.

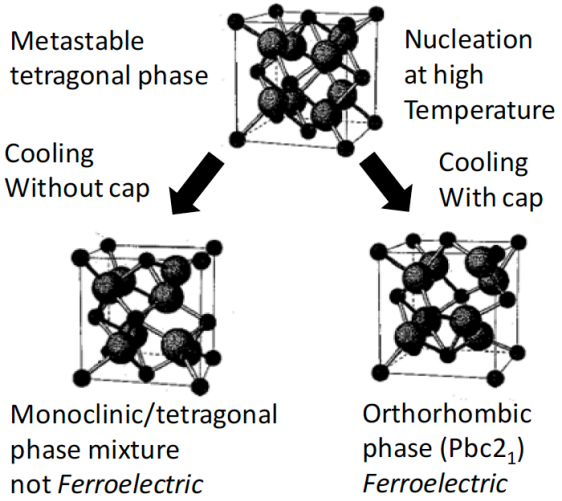
From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

Funded by the European Union

HfO_2-based compounds







T. S. Böscke et al., IEDM (2011)

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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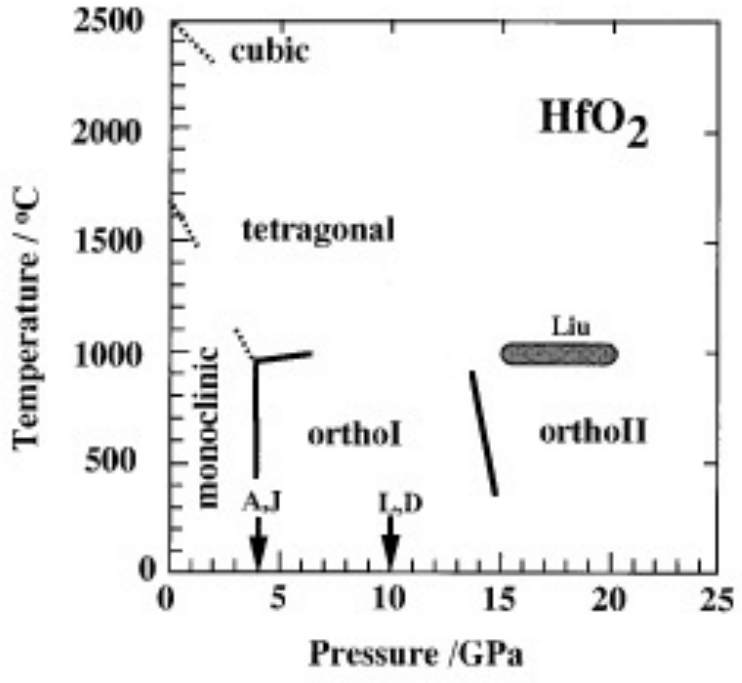
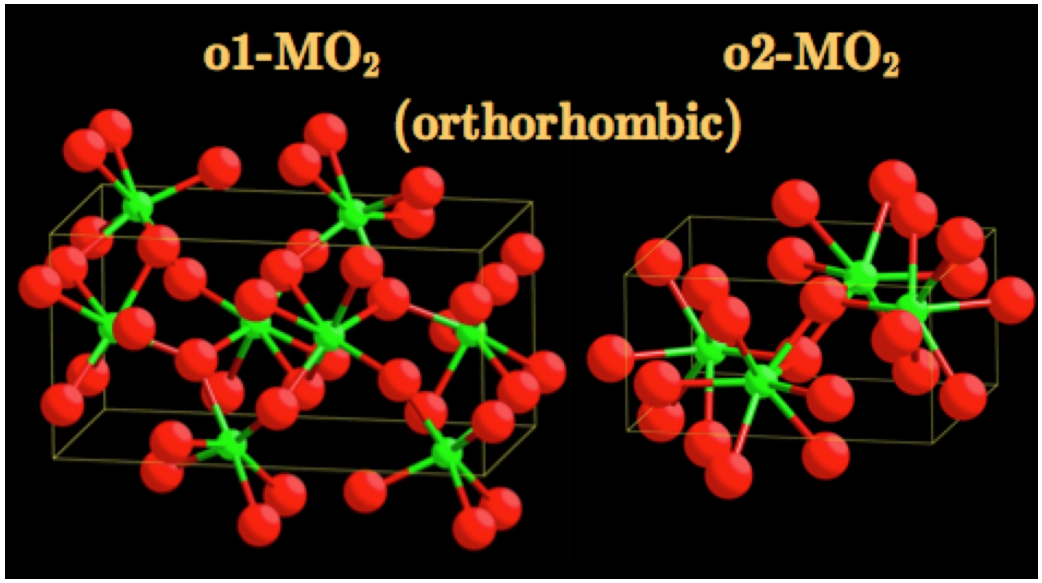
HfO_2-based compounds



O. Ohtaka *et al.*, J. Am. Cer. Soc. 84(6), 1369 (2001)



From G.M. Rignanese, Louvain

Orthorhombic	Orthorhombic
Space group Pbca	Space group Pnam (cotunnite)
Hf 7-fold coordinated	Hf 9-fold coordinated
O_I 3-fold coordinated	O_I 4-fold coordinated
O_{II} 4-fold coordinated	O_{II} 5-fold coordinated

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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HfO_2-based compounds

FIXIT

Non-centrosymmetric $Pca2_1$ orthorhombic III phase is ferroelectric

Stress/strain play a major role in the stabilization of this polar structure of HfO_2.

The polar phase has been stabilized for a large variety of solid solution combination („dopant“) HfO_2 (Zr, Si, Al, Gd, Y, Sr, La…)

$HfO_2(ZrO_2)$ system is the most studied one, with a composition close to $Hf_{0.5}Zr_{0.5}O2$

E.H. Kisi, J. Am. Ceram. Soc., 81 [3] 741–45 (1998)

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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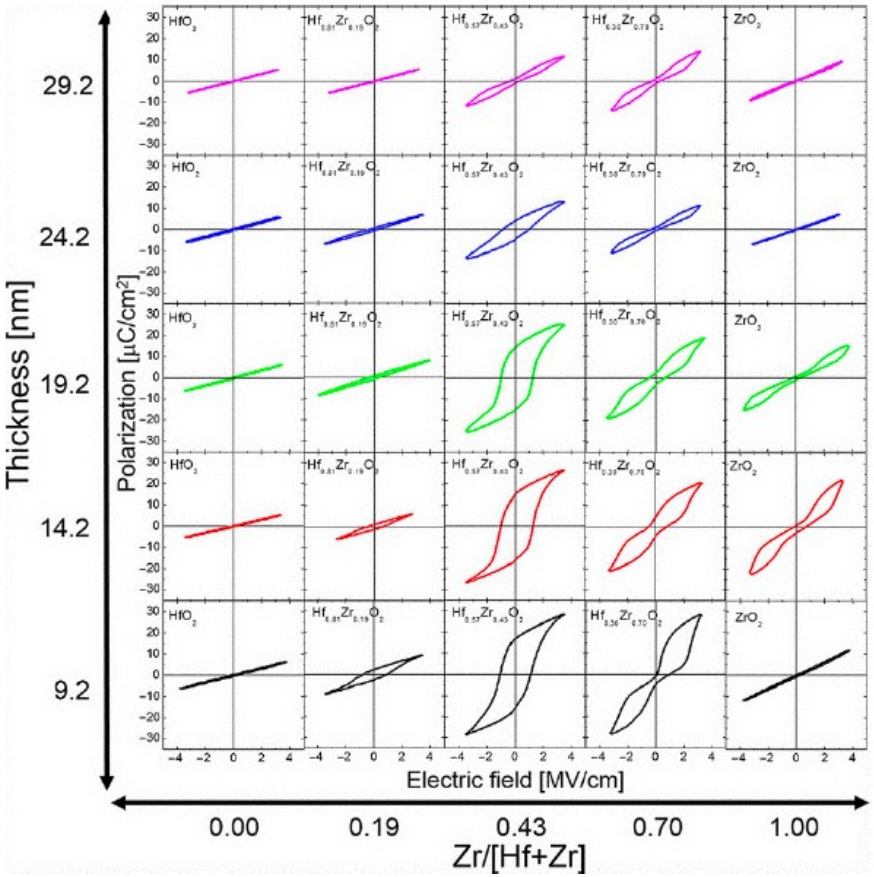
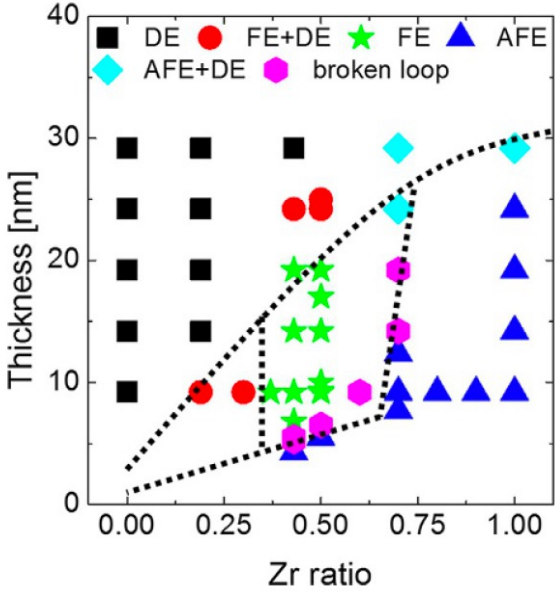
HfO_2-based compounds

Dependence of ferroelectricity on composition and thickness



$HfO_2(ZrO_2)$ system



Narrow range of optimized properties

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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HfO_2-based compounds

Non-centrosymmetric $Pca2_1$ orthorhombic III phase is ferroelectric

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$HfO_2(ZrO_2)$ system is the most studied one, with a composition close to $Hf_{0.5}Zr_{0.5}O2$

A major difference with previously described compounds: these polycrystalline films require „wake-up“ to reach full polarization

Fully CMOS compatible, no need for epitaxial films (films are polycrystalline with ˜10-20 nm size grains)

E.H. Kisi, J. Am. Ceram. Soc., 81 [3] 741–45 (1998)

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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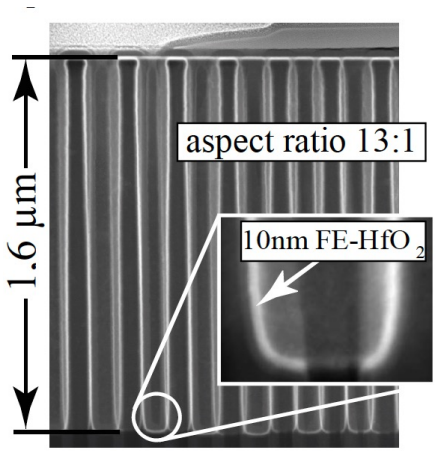
HfO_2-based compounds

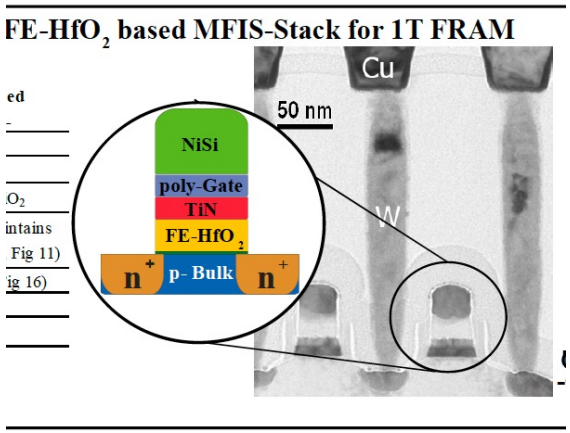
FIXIT

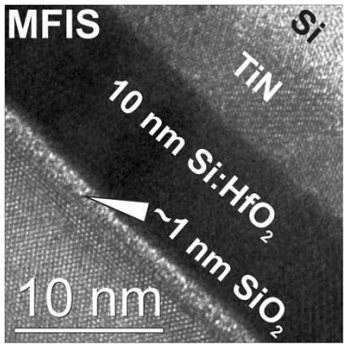
- **Fully CMOS compatible**

	SBT FeFET	PZT FeFET	This work
Gate Stack	Pt/SBT/HfAlO	Al/PZT/Dy_2O_3	TiN/HfSiO/SiO_2
FE/IF Thickness	400 nm/10 nm	250 nm/20 nm	**8.5 nm/1.2 nm (5.5 nm/1.2 nm)**
Thermal budget	800°C	700°C	1000°C
Memory Window	400 mV	800 mV	1000 mV
10y Memory Window	250 mV	?	650 mV
Programming Voltage	-6V/+6V	-8V/8V	-3V/4V

Figure 12 Comparison of FE-HfSiO based field effect transistors to, in our knowledge, the best previously published devices based on conventional ferroelectrics SBT and PZT [3].







Ferroelectric Hafnium Oxide: A CMOS-compatible and highly scalable approach to future ferroelectric memories

J. Müller, T.S. Böscke[e], S. Müller[a], E. Yurchuk[a], P. Polakowski, J. Paul, D. Martin[a], T. Schenk[a], K. Khullar[a], A. Kersch[d], W. Weinreich, S. Riedel, K. Seidel, A. Kumar[f], T.M. Arruda[f], S.V. Kalinin[f], T. Schlösser[c], R. Boschke[c], R. van Bentum[c], U. Schröder[a], T. Mikolajick[a,b]
Fraunhofer IPMS-CNT, [a]NaMLab gGMBH, [b]IHM TU-Dresden, [c]GLOBALFOUNDRIES, Dresden, Germany,
[d]FH-München, München, Germany, [e]Bosch Solar Energy, Erfurt, Germany, [f]ORNL, Oak Ridge, TN, U.S.A.
Email: johannes.mueller@ieee.org

(2013)

T. S. Böscke et al., IEDM (2011)

J. Muller et al, IEEE EDL (2012)

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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HfO_2-based compounds

FIXIT

nature materials

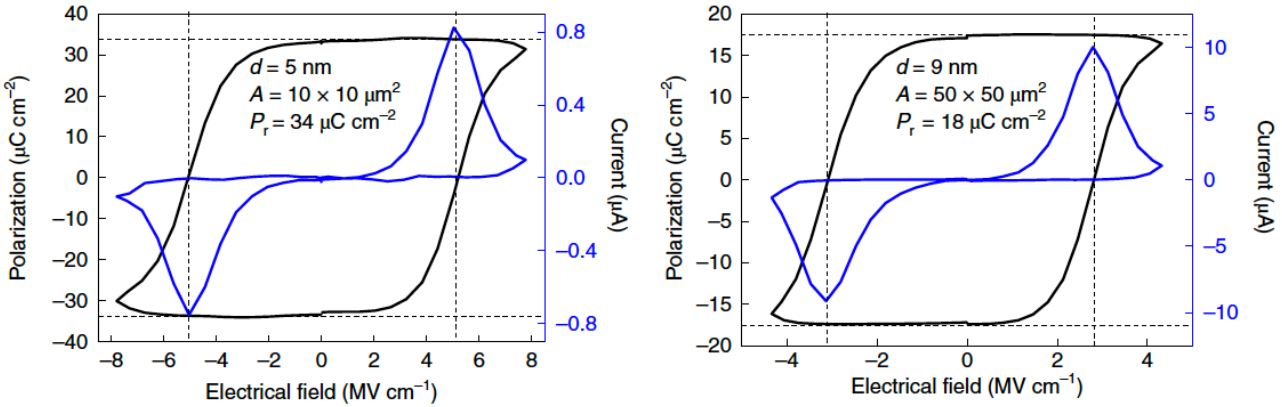
ARTICLES

https://doi.org/10.1038/s41563-018-0196-0

A rhombohedral ferroelectric phase in epitaxially strained $Hf_{0.5}Zr_{0.5}O_2$ thin films

Yingfen Wei[1], Pavan Nukala[1,2], Mart Salverda[1], Sylvia Matzen[3], Hong Jian Zhao[4], Jamo Momand[1], Arnoud S. Everhardt[1], Guillaume Agnus[3], Graeme R. Blake[1], Philippe Lecoeur[3], Bart J. Kooi[1], Jorge Íñiguez[4], Brahim Dkhil[2] and Beatriz Noheda[1*]

$Hf_{0.5}Zr_{0.5}O_2$ thin films on $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$



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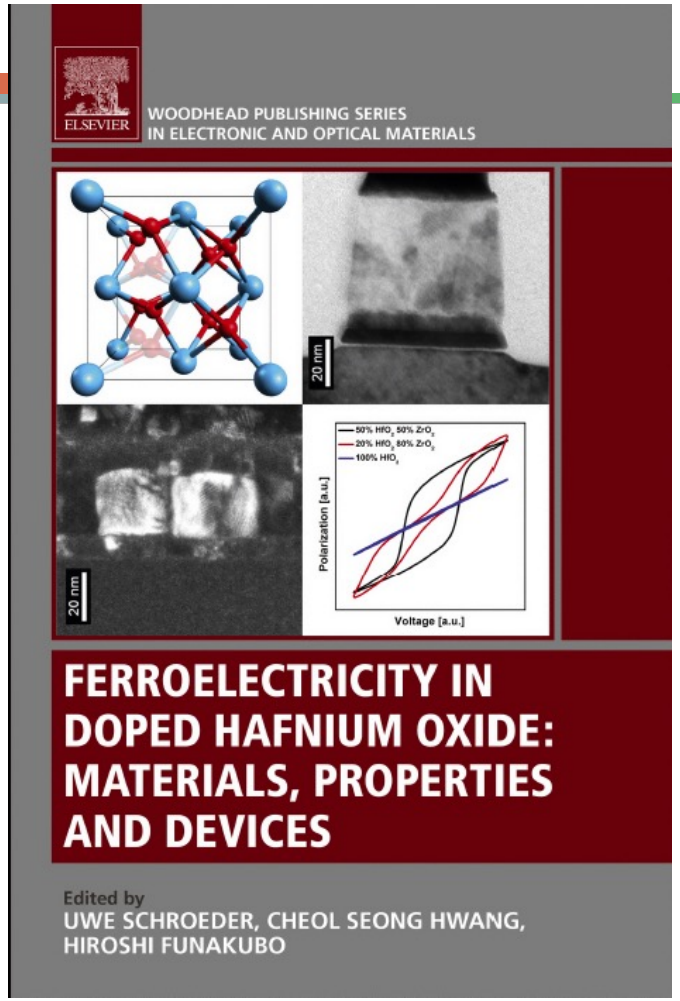
HfO_2-based compounds

FIXIT



From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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Ferroelectrics and phase transitions
Thermodynamic description

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Ferroelectrics and phase transitions
Thermodynamic description

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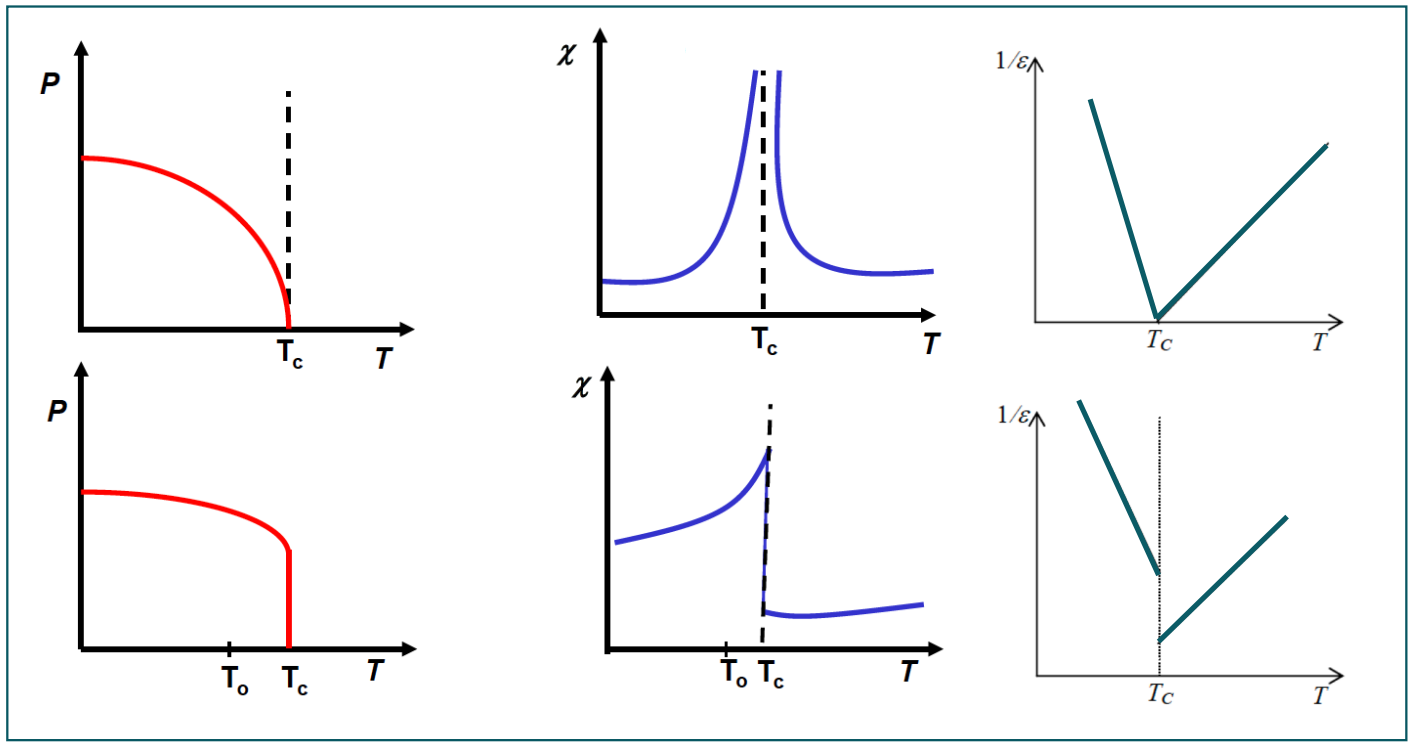
There is a **phase transition at a temperature T_c above which the phase is paraelectric (Ps = 0).**



Second-order phase transition

First-order phase transition

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Thermodynamic description

Phenomenological or macroscopic theory (treat the material as a continuum without considering the underlying atomic structure)

The stable phase of a system is the one that minimizes its **Gibbs free energy G**

For a ferroelectric system: $G = U - TS - \eta\sigma - ED = H - TS$

Phase transition arises from the competition between the different terms that can evolve with P or T

For a system with free mechanical boundary conditions (no stress applied: $\sigma = 0$ - constant volume V of the system) and no external field applied (E = 0), the quantity to be minimized becomes the **Helmholtz free energy F**:

$$F = U - TS$$

where U is the internal energy, T is the temperature and S is the entropy

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Thermodynamic description: Landau-Ginzburg-Devonshire phenomenological theory

FIXIT

There is no polarization (P=0) in the non-polar state and there is a polarization P below a transition temperature T_c.

For (proper) ferroelectrics, the polarization P is taken as the order parameter (or the displacement)

Note: for improper ferroelectrics (such as $YMnO_3$), P is not the order parameter!

- **Second-order phase transition:** there is a **continuous change in the order parameter**, from zero in the non-polar state to a non-zero value in the polar state.
- **First-order phase transition**: there is a discontinuous jump in the order parameter from zero in the non-polar state to a finite value at the transition temperature

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Thermodynamic description: Landau-Ginzburg-Devonshire phenomenological theory

FIXIT

Following the **Landau-Ginzburg-Devonshire theory**, the free energy F of a ferroelectric material can be described as a Taylor expansion in terms of the order parameter, which is taken to be the **polarization P**

$$F\ (T) = F_0 + \frac{1}{2}A(T)\ P^2 + \frac{1}{4}BP^4 + \frac{1}{6}C\ P^6 + \ \ldots$$

at constant volume V

Second-order phase transition (B> 0)

Hypothesis:

- The expansion around the high symmetry phase remains valid above and below the phase transition temperature (T_c), the polarization varies continuously across T_c (and thus takes small values close below T_c)
- The expression must be invariant under symmetry operations of both phases – since the paraelectric phase possesses a center of symmetry → no even terms in the expansion
- B and C are constant, C >0 – only A is not a constant

For a given temperature, the spontaneous polarization values in the paraelectric (Ps =0) and in the ferroelectric phases are the ones **that minimizes the free energy F**.

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Landau-Ginzburg-Devonshire phenomenological theory

FIXIT

Second-order phase transition (B> 0)

$$F\ (T) = F_0 + \frac{1}{2}A\ P^2 + \frac{1}{4}BP^4 + \frac{1}{6}C\ P^6 + \ \ldots$$

- **When T > T_c** , the system is in the paraelectric phase, F should have its minimum value for P = **Ps = 0**

  → the free energy F(P) exhibits a single well as a function of P with a minimum at P=Ps =0, i.e. A must be positive → **A(T) >0**

- **When T < T_c** , the system is in the ferroelectric phase and the minimum of F should be for **non zero values of Ps** (finite value)

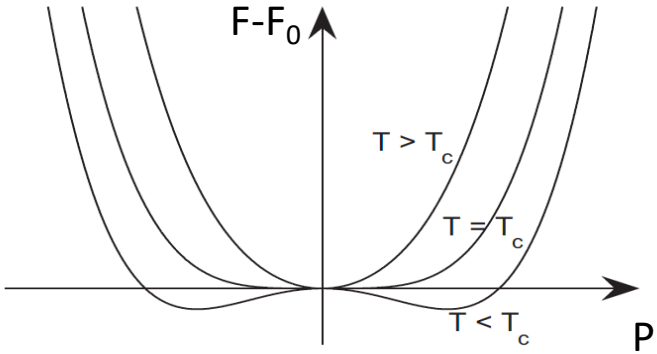
  → The free energy F(P) exhibits a double well as a function of P, i.e. A must be negative → **A(T) < 0**

- **When T = T_c** , when passing the transition, the A coefficient (supposed to be continuous) should pass through zero and change sign

  → **$A(T_c) = 0$**

  Hence, A can be written as $\mathbf{A = \alpha\ (T - T_c)}$ with α >0

F(P) is of the following form:



Note: For P_S = 0 to represent a minimum of the free energy (and a stable state) at T=T_c, B must be positive (or zero)

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Landau-Ginzburg-Devonshire phenomenological theory

FIXIT

Second-order phase transition (B> 0)

$$F(P,T) = F_0 + \frac{1}{2} A(T) P^2 + \frac{1}{4} B P^4 + \frac{1}{6} C P^6$$

B being assumed to be non-zero, the higher order (in P^6) term can be neglected: $F = F_0 + \frac{1}{2} A P^2 + \frac{1}{4} B P^4$ $A = \alpha (T - T_c)$ $B > 0$

T < T_c **The stable spontaneous polarization P_S states are the ones that minimizes F**

$$\frac{\partial F}{\partial P} = A P_S + B P_S^3 = 0 \quad \text{and} \quad \frac{\partial^2 F}{\partial P^2} = A + 3 B P_S^2 > 0 \Rightarrow P_S^2(T) = -\frac{A}{B} = \frac{\alpha(T_c - T)}{B}$$

$$\boldsymbol{P_S(T) = \pm\sqrt{\frac{\alpha}{B}}\sqrt{(T_c - T)}}$$

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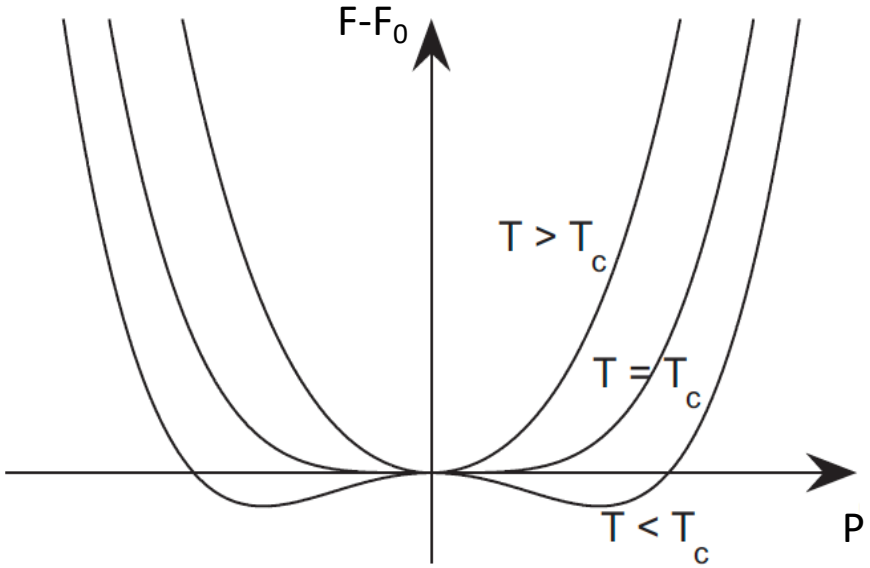
Landau-Ginzburg-Devonshire phenomenological theory

FIXIT

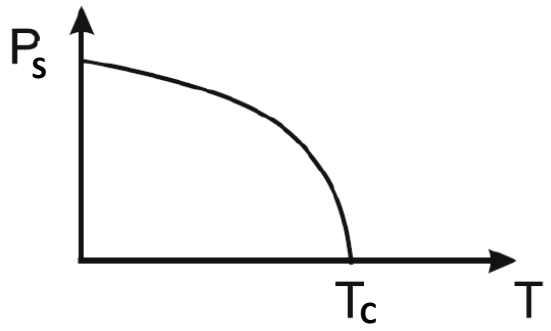
Second-order phase transition (B> 0)

$$F = \frac{1}{2}\,\alpha\,(T - T_c)\,P^2 + \frac{1}{4}B\,P^4 \qquad \alpha > 0$$



$P_S = 0$ for T≥ Tc

$$\boldsymbol{P_S(T) = \pm\sqrt{\frac{\alpha}{B}}\,\sqrt{(T_c - T)}}$$ for T≤ Tc



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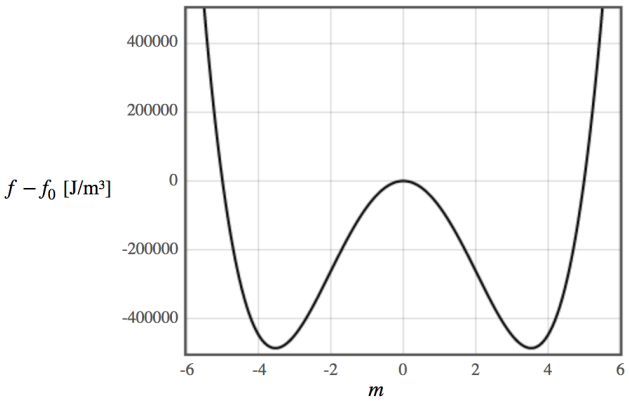
Landau-Ginzburg-Devonshire phenomenological theory

FIXIT

Second-order phase transition ($B > 0$)

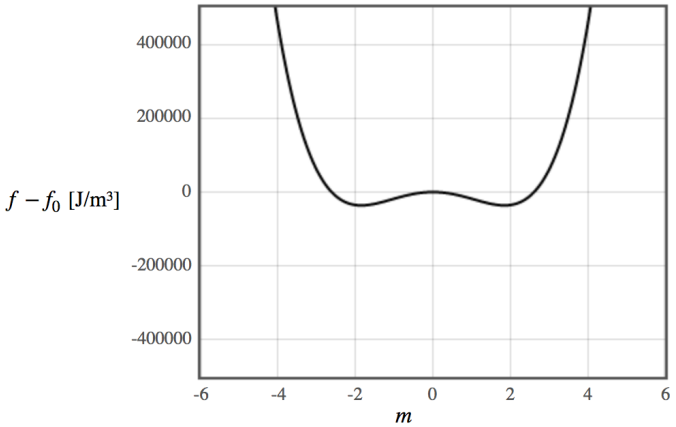
T_c for $BaTiO_3$ is ~120°C

$BaTiO_3$ T = 340 K



α_0 = 1406.8
β = 6167
T = 340
T_c = 395
$f_0(T)$ = -109.39*T*T+25184*T*(log(
submit

$BaTiO_3$ T = 380 K



α_0 = 1406.8
β = 6167
T = 380
T_c = 395
$f_0(T)$ = -109.39*T*T+25184*T*(log(
submit

m is the order parameter

https://lampx.tugraz.at/~hadley/ss2/landau/second_order.php

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Landau-Ginzburg-Devonshire phenomenological theory

FIXIT

First-order phase transition ($B < 0$)

$$F = F_0 + \frac{1}{2} A P^2 + \frac{1}{4} B P^4 + \frac{1}{6} C P^6 \qquad A = \gamma (T - T_c)$$

There is discontinuous jump of P from 0 to a finite value. This can happen if **B is negative** and then, **for stability, C must be positive**.

The spontaneous polarization P_S at T is the one that minimizes F

$$\frac{\partial F}{\partial P} = A P_S + B P_S^3 + C P_S^5 = 0 \quad \Rightarrow \quad A + B P_S^2 + C P_S^4 = 0$$

and $$\frac{\partial^2 F}{\partial P^2} = A + 3 B P_S^2 + 5 C P_S^4 > 0$$

also $$F(T = T_c) - F_0 = 0 = \frac{1}{2} A P_S^2 + \frac{1}{4} B P_S^4 + \frac{1}{6} C P_S^6$$

Solutions: not so easy as for second order phase transitions

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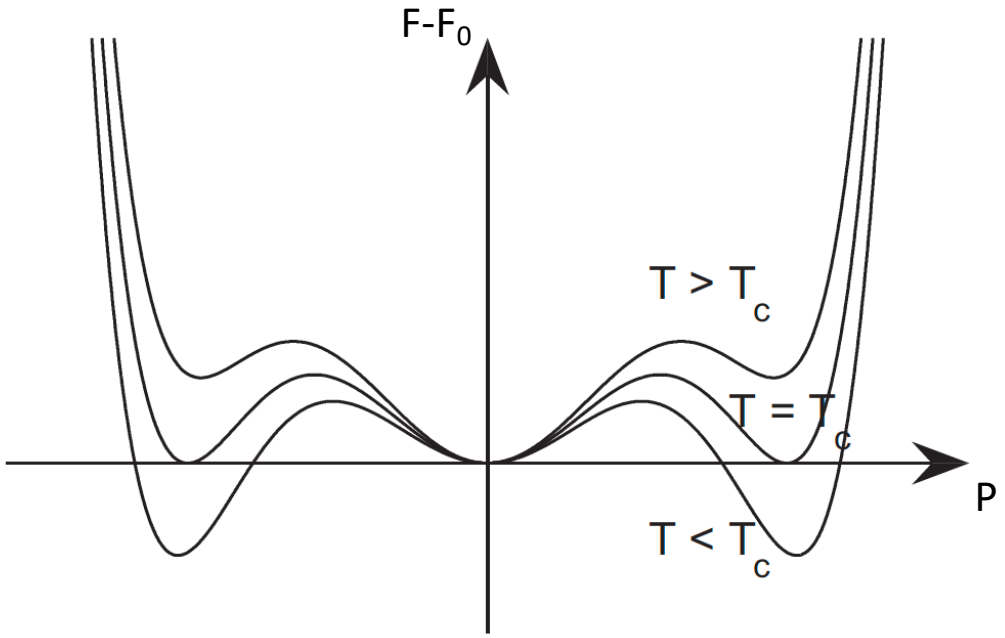
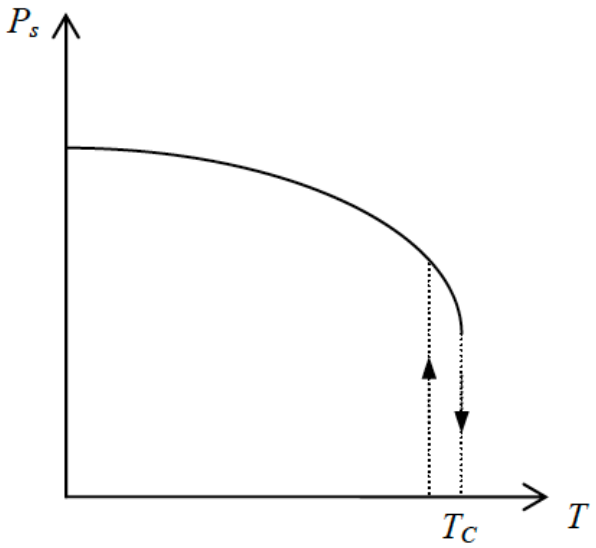
Landau-Ginzburg-Devonshire phenomenological theory

FIXIT

First-order phase transition (B< 0)





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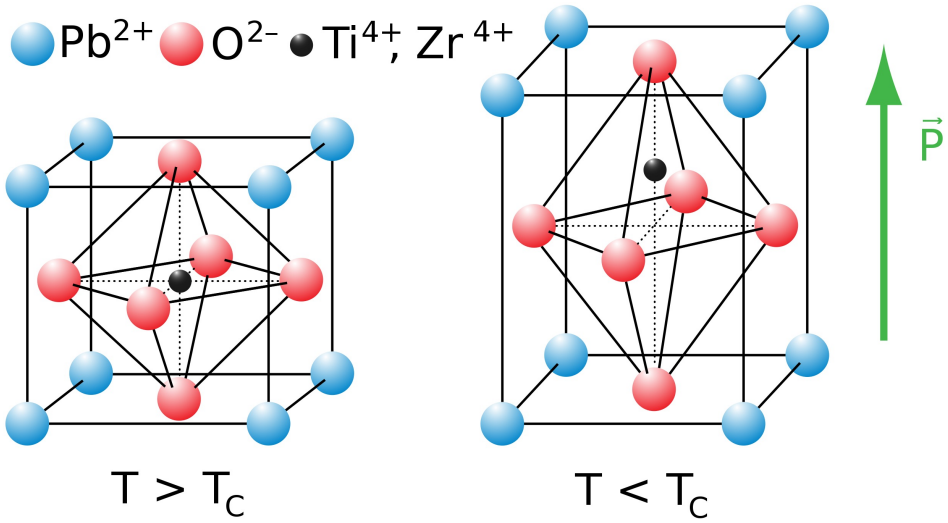
Microscopic approach for the ferroelectricity of perovskite compounds

FIXIT

With the discovery of ferroelectricity in $BaTiO_3$ (1945) and in other perovskite compounds, the theory of the microscopic origin of ferroelectricity had to be completely revised (it was by then believed that H-bonds were required - the ferroelectricity in the previously known ferroelectrics, Rochelle salt and KDP, was thought to be an order–disorder phenomenon associated with the hydrogen bonds).

The atomistic origin of ferroelectricity in ABO_3 perovskites involves the movements of ions in the unit cell.



By Pinin - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=11103109

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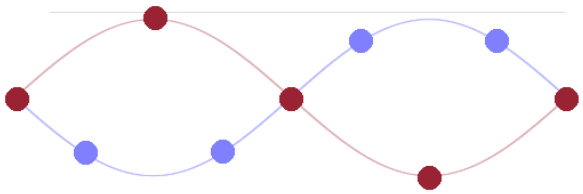
Microscopic approach for the ferroelectricity of perovskite compounds

The “soft mode” model for ferroelectricity

W. Cochran, Adv. Phys., Crystal stability and the theory of ferroelectricity, 9, 387 (1960)

“The phenomenon of ferroelectricity in pseudo-cubic crystals is discussed in terms of the normal modes of vibration. It is shown that the parameters which determine the lattice vibrations of a diatomic ionic crystal may be chosen in such a way that the crystal will exhibit ferroelectric properties, and that **ferroelectric or anti-ferroelectric transitions may be regarded as the result of an instability of the crystal for a certain normal mode of vibration**. The theory is extended to apply to other cubic crystals, including barium titanate, and the concepts of ‘ionic polarizability’ and ‘a polarizability catastrophe’ are discussed in terms of lattice dynamics.“

Softening of the lowest energy transverse optical (TO) phonon mode(s) i.e. lattice mode vibrations involving ions soften and lead to the displacive instability



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Microscopic approach for the ferroelectricity of perovskite compounds

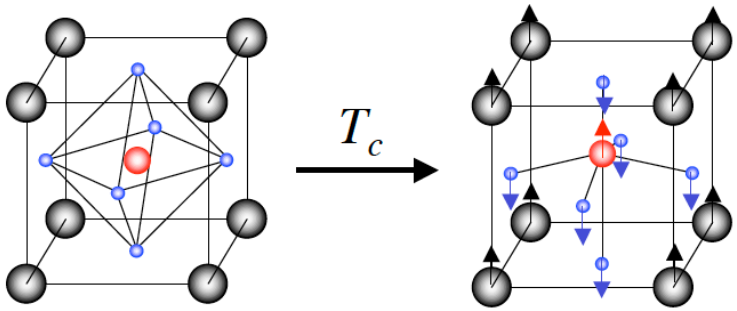
FIXIT

The “soft mode” model for ferroelectricity

- The soft mode is a transverse optic mode and is at the center of the Brillouin zone
- The frequency of the mode goes to zero to freeze in static off-centre displacements of atoms, which gives rise to the ferroelectric polarization. Atoms stay off-centre because the restoring force fails to bring the atoms back to the equilibrium positions due to “softening” of the spring constants.
- Soft mode model accounts for **displacive phase transitions**

Cooperative off-centre displacements of atoms

Competition between short range forces (B cation /nearest neighbors) **and the long range Coulomb** (dipole-dipole) interaction in the compound.



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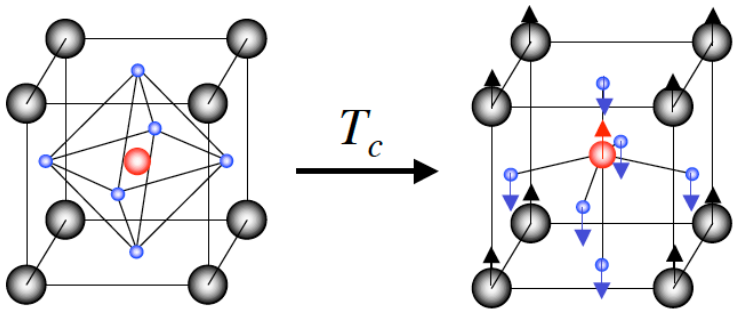
Microscopic approach for the ferroelectricity of perovskite compounds

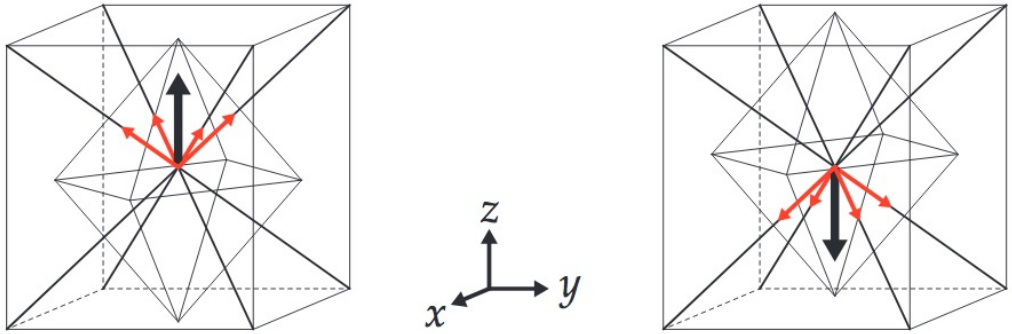
FIXIT

The “soft mode” model for ferroelectricity

$BaTiO_3$



Displacement along the <111> directions of the cubic perovskite



In the tetragonal phase, P is along <001>

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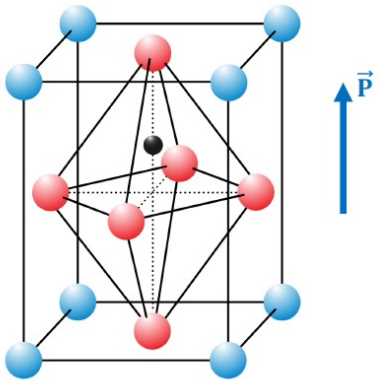
Domains in ferroelectrics

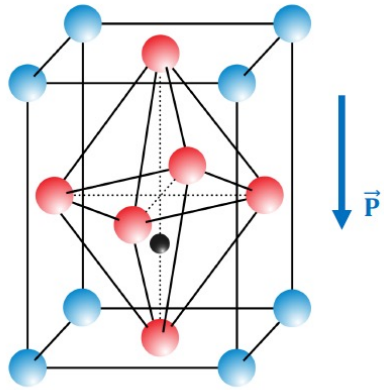
FIXIT

At least two polarization orientations are stable and can be switched between each other by application of an electric field.

These polarizations are equivalent in energy and therefore may occur equally upon cooling from the high symmetry phase (paraelectric) to the ferroelectric phase

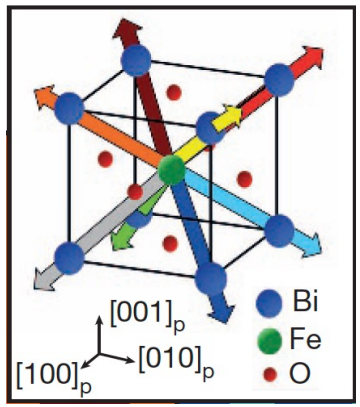
→Domains will form





From a cubic to a tetragonal phase ($BaTiO_3$): polarization along the 2 equivalent directions <001> of the crystal →Domains of opposite directions (**180° domains)**

From a cubic to a rhomboedral phase : polar order along the 8 equivalent directions <111> of the crystal
→ Domains with diagonal long axes that are **71 °, 109 °**, and **180 °** apart.



In addition, the polarization is strongly coupled to piezoelectricity (strain) in perovskite ferroelectrics

Catalan *et al*, Rev. Mod. Phys, 84, 119 (2012)

J.T. Heron et al., Nature 516, 370 (2014)

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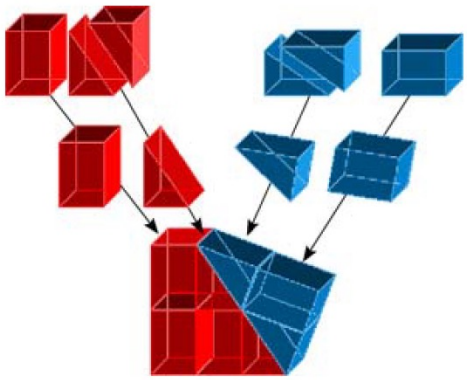
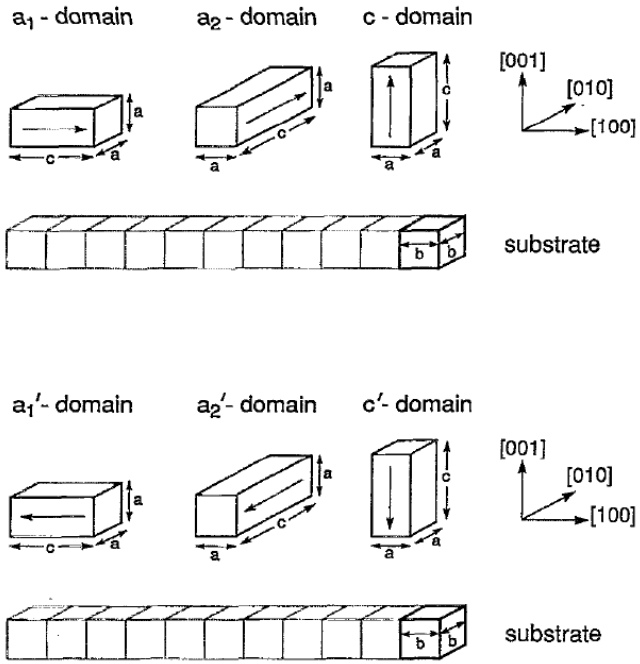
Domains in ferroelectrics

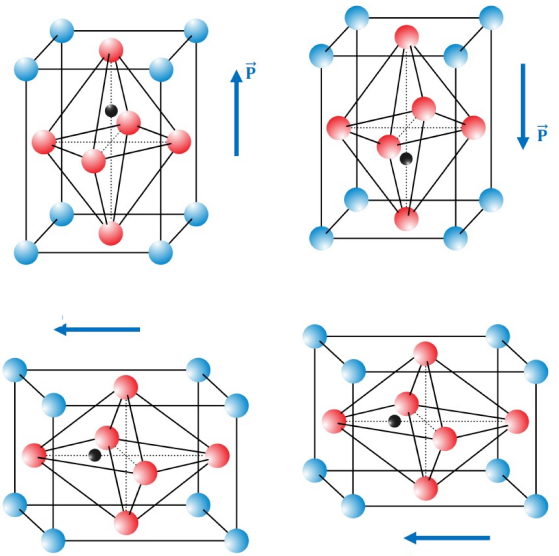
FIXIT

In addition, the polarization is strongly coupled to piezoelectricity (strain) in perovskite ferroelectrics

→ Twinning will lead to the presence of domains perpendicular to each others







P.-E. Janolin, J Mater Sci (2009) 44:5025–5048

Catalan *et al*, Rev. Mod. Phys, 84, 119 (2012)

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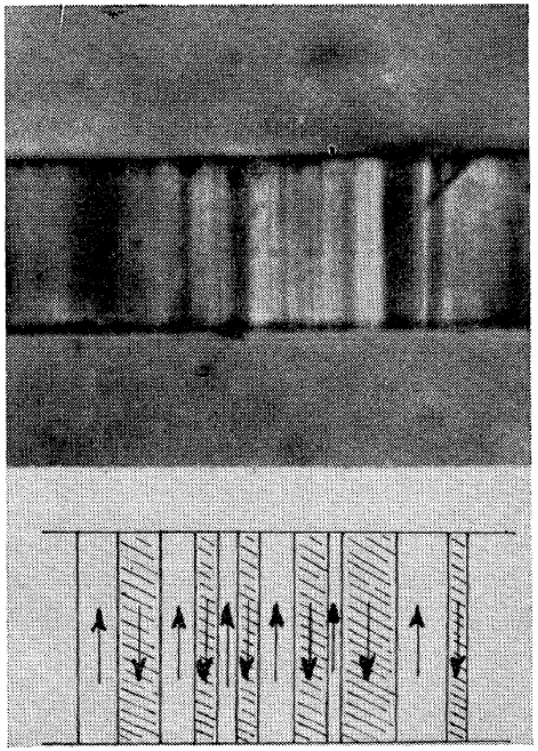
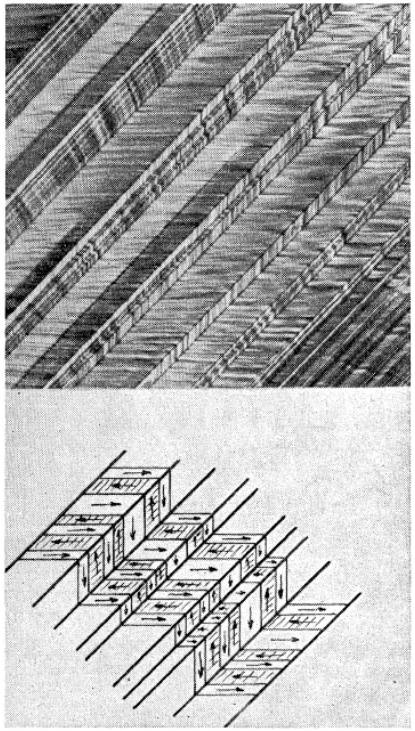
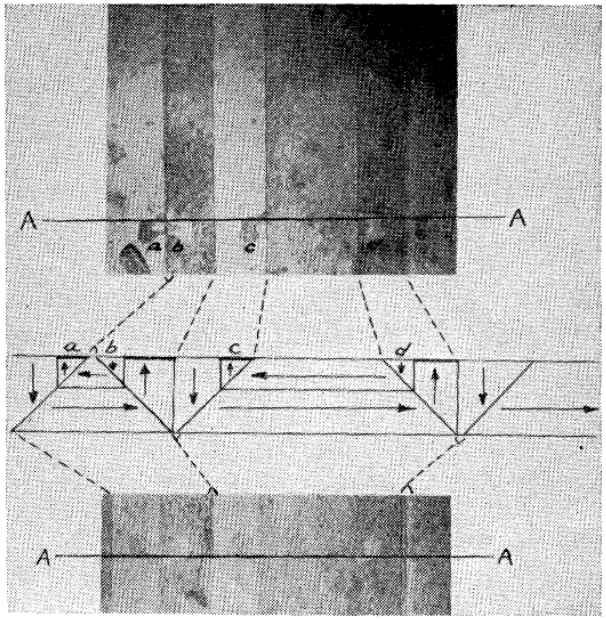
Perovskite ferroelectrics: $BaTiO_3$

FIXIT

Domains imaged on etched $BaTiO_3$ single crystals







It was observed that ferroelectric domains in BaTiOs crystals are always so arranged that there is no build-up of a space charge on the domain walls.

J.A. Hooton and W.J. Merz, Phys. Rev. 98, 409 (1955)

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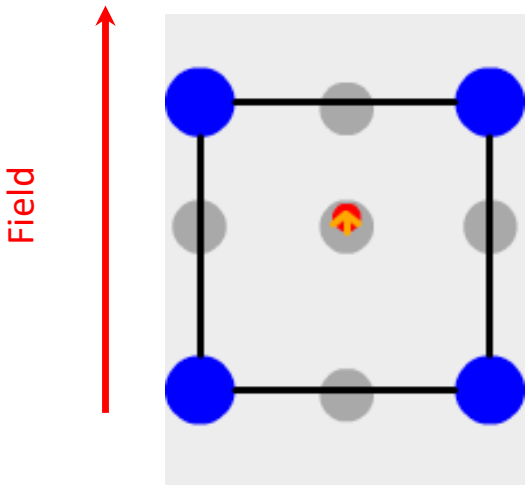
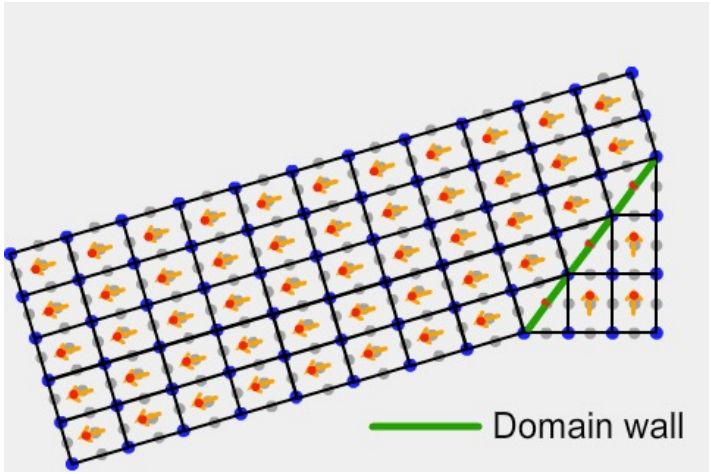
Domains contribution to the ferroelectricity – Intrinsic and Extrinsic Piezoelectricity

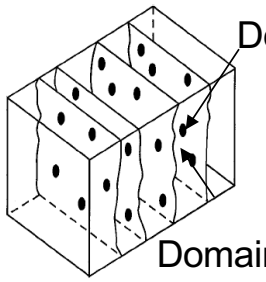
FIXIT

Intrinsic – deformation of lattice



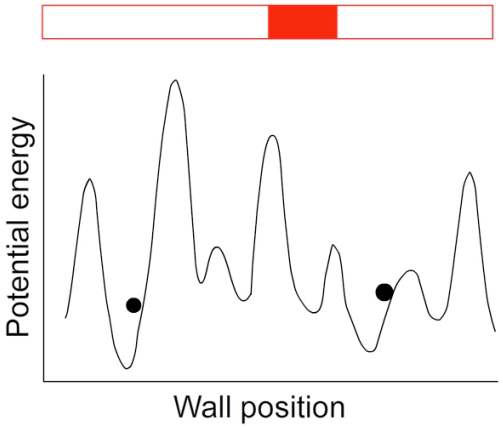
Extrinsic – domain wall or phase boundary motion





Defect: pinning center

D. Damjanovic, *NATO Science Series 3. High Technology* **76** (2000) 123



Courtesy Prof. S. Trolier-McKinstry

DW motion:

- Contributes to the RT permittivity of capacitors
- Provides up to 75% of the piezoelectric response of soft piezoelectric ceramics
- Controls aging of properties
- Governs the dynamics and the stability of stored domain states, as well as the ability to reset the state

Funded by the European Union

PennState

Ferroelectrics thin films:

Domains, domain walls

Strain and size effects

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the European Union

Ferroelectrics thin films:

FIXIT

(r)evolution in the past 20 years

- **Unit cell control of the growth of thin films and of their interfaces**
- **First principle calculation**
- **New probes (scanning probe microscopy, advanced microscopy methods…)**
- **AI and big data analysis**

➡ **<u>Better understanding and engineering of properties:</u>**

- Size effects
- Strain effects (role of substrate, buffer…)
- Coupling at interfaces / new phenomena at interfaces
- Domain structure and dynamics
- Role of boundary conditions (mechanical, electrical…)

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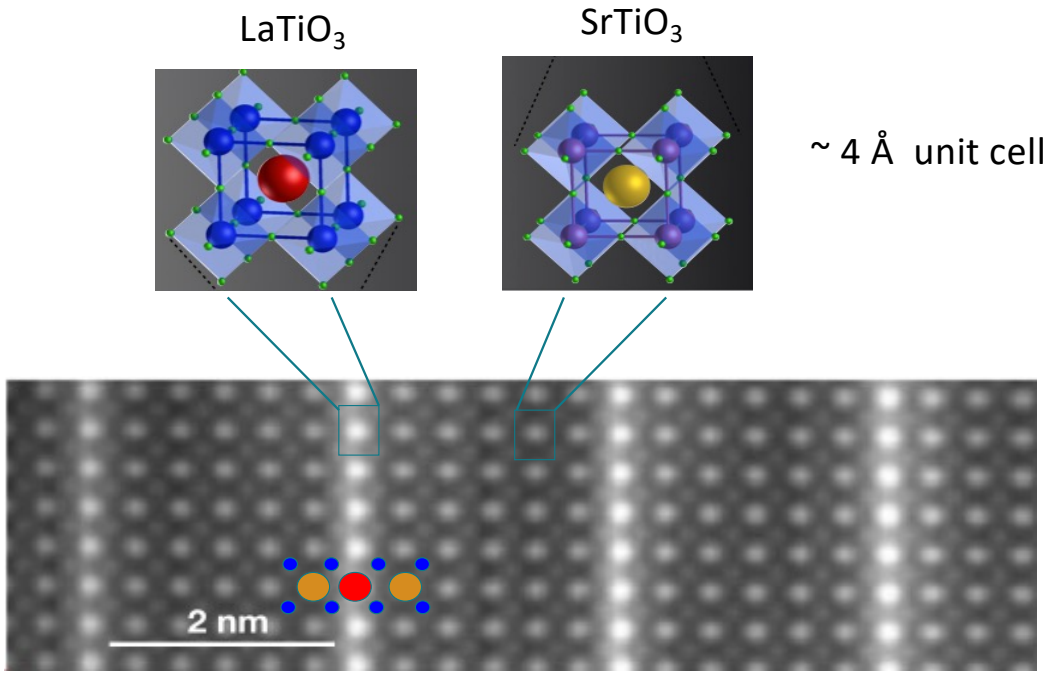
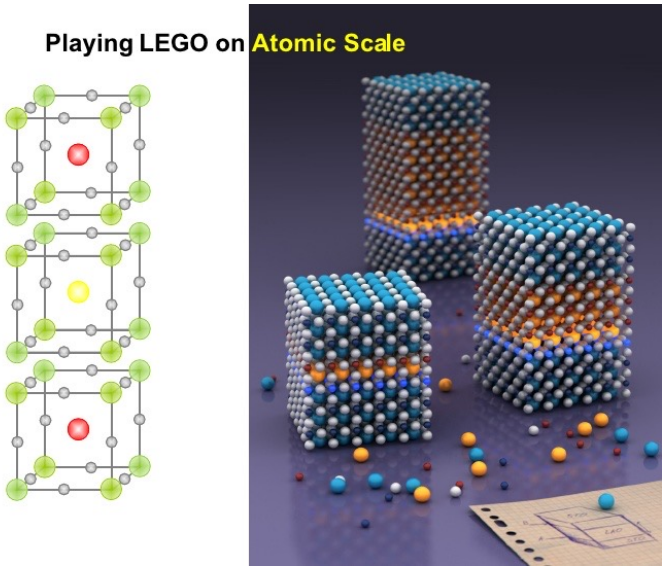
Epitaxy of ferroelectrics

FIXIT

Huge progress since the 2000‘s in the epitaxy of oxides with control of the growth at the unit cell



~ 4 Å unit cell



Ohtomo *et al.* Nature (2002)

$LaTiO_3/SrTiO_3$ superlattice
(inserting one plane of La-O in $SrO-TiO_2$)

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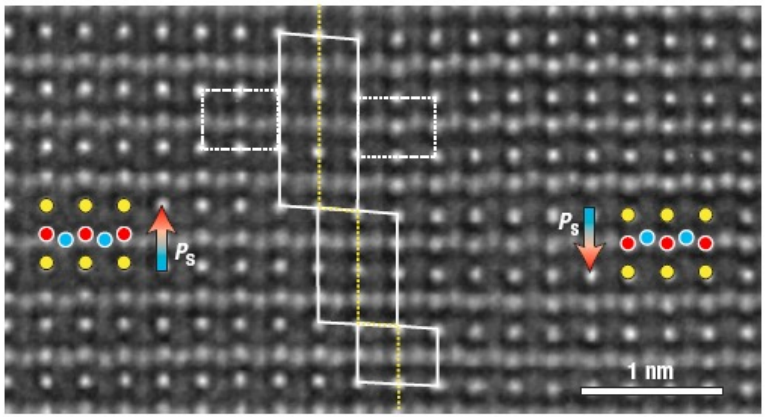
Structural characterization of ferroelectrics

FIXIT

Progress in microscopes and analytic tools (Cs-corrected microscopes…)

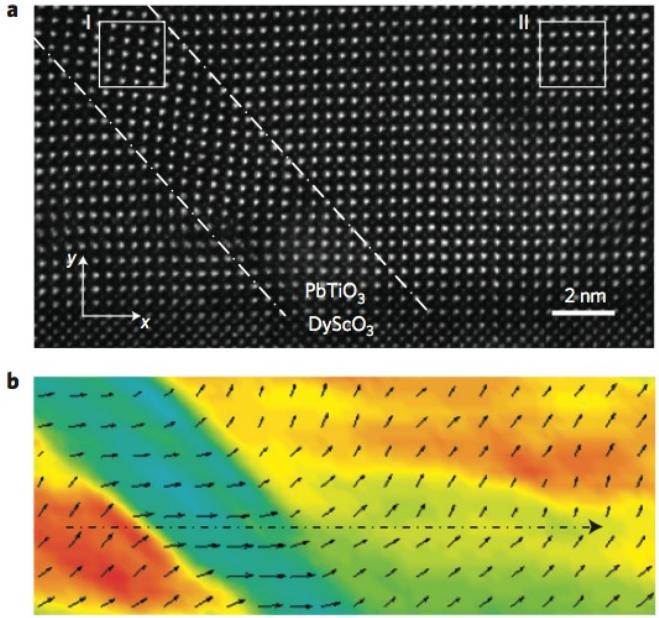
- **Geometrical phase analysis , electron holography –> strain**
- **Imaging of the atomic positions of atomic columns using HAADF-STEM**
- **4D STEM methods**

$Pb(Zr,Ti)O_3$ on $SrTiO_3$



C.-L. Jia *et al*, Nature Materials 7, 57 (2008)

Mapping of the polarization



G. Catalan *et al., Nat. Mater. (2011)*

Funded by
the European Union

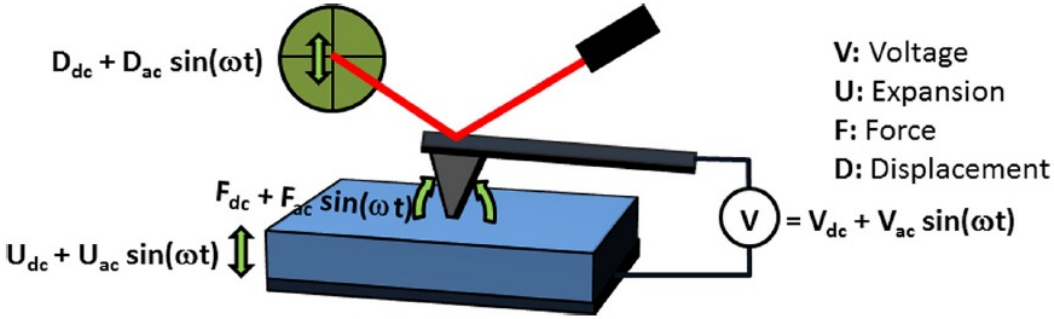
Piezoelectric force microscopy (PFM)

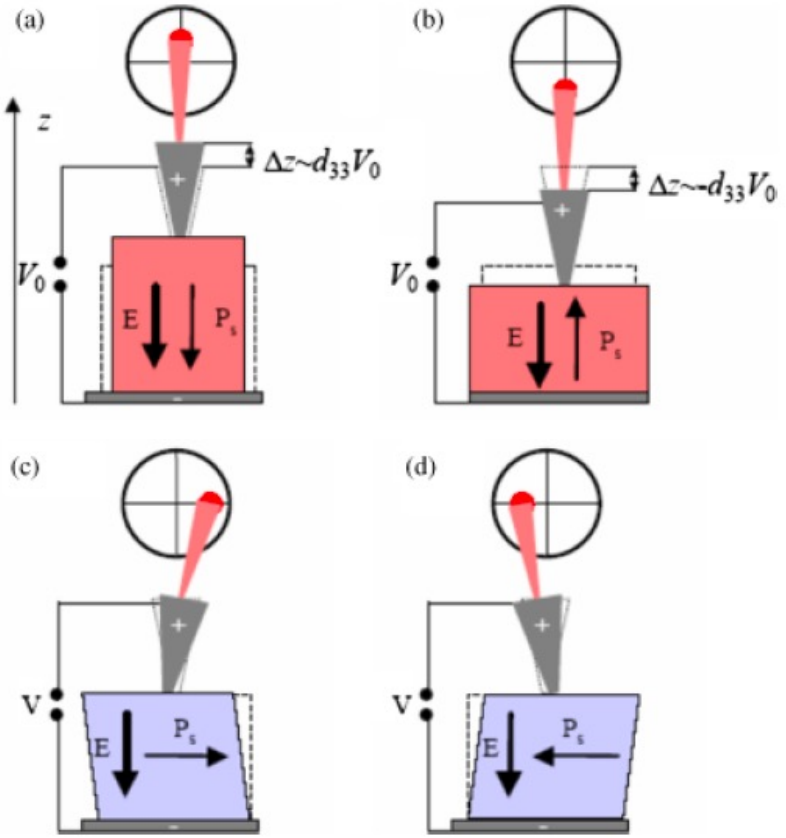
FIXIT

A ferroelectric material is piezoelectric – hence it deforms under an applied electric field

Application of a small a.c. periodic electric bias (via the tip) and detection (via the tip as well) of the cantilever mechanical motion due to the piezoelectric strain generated in the ferroelectric sample.

The cantilever motion can be a vertical displacement, torsion or bending.





A. Gruverman et al., Ferroelectrics 184, 11 (1996)
S. V. Kalinin, B. J. Rodriguez, S. Jesse, J. Shin, A. P. Baddorf, P. Gupta, H. Jain, D. B. Williams, and A. Gruverman, Vector Piezoresponse Force Microscopy, Microsc. Microanal. 12, 206–220 (2006)
A. Gruverman, M. Alexe and D. Meier, Nat. Comm.10, 1661 (2019)
Owoong Kwon, Daehee Seol, Huimin Qiao, and Yunseok Kim, Recent Progress in the Nanoscale Evaluation of Piezoelectric and Ferroelectric Properties via Scanning Probe Microscopy, Adv. Sci. , 1901391 (2020)
N. Balke et al., J. Am. Ceram. Soc., 92 [8] 1629–1647 (2009)
R.K. Vasudevan et al., Appl. Phys. Rev. 4, 021302 (2017)

Funded by
the European Union

Piezoelectric force microscopy (PFM)

FIXIT

A ferroelectric material is piezoelectric – hence it deforms under an applied electric field

Application of a small a.c. periodic electric bias (via the tip) and detection (via the tip as well) of the cantilever mechanical motion due to the piezoelectric strain generated in the ferroelectric sample.

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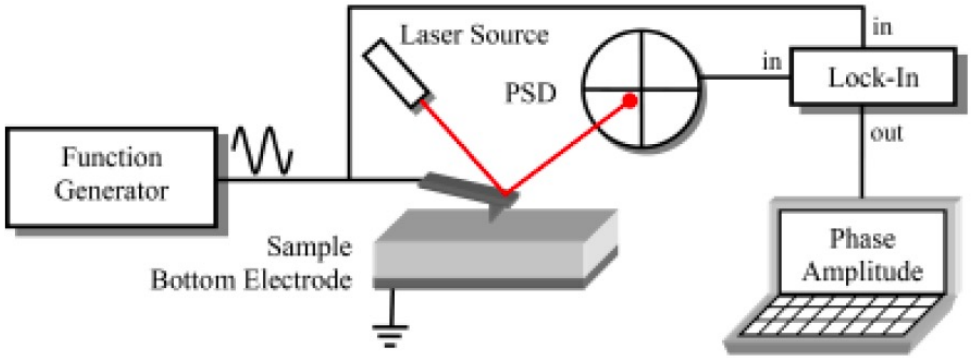

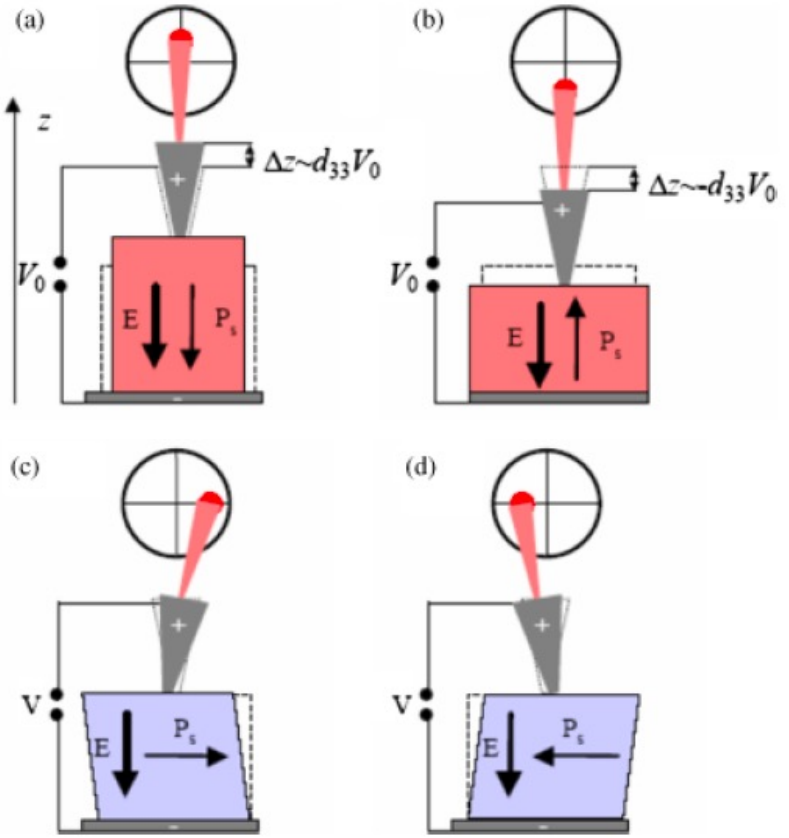

N. Balke et al., J. Am. Ceram. Soc., 92 [8] 1629–1647 (2009)

R.K. Vasudevan et al., Appl. Phys. Rev. 4, 021302 (2017)

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Piezoelectric force microscopy (PFM)

FIXIT

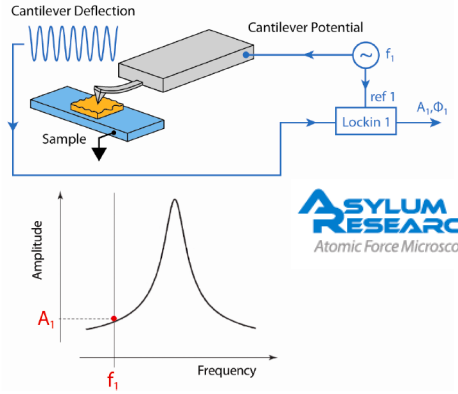
Single frequency PFM:

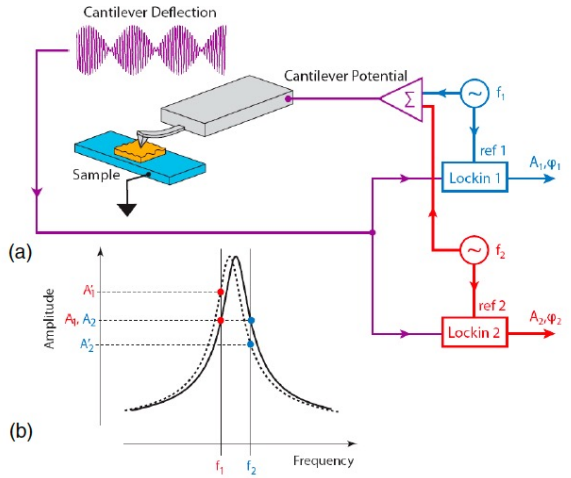
The excitation frequency is maintained constant during imaging: amplitude and phase of the cantilever response are determined using a lock-in amplifier.

An excitation voltage with frequency near the contact resonance **lead to better sensitivity (amplification effect) BUT** can sometimes lead to large topographic cross-coupling

The amplitude and phase of the local response are a convolution of material response to the external field **and** cantilever response to the material-dependent local force, which cannot be separated unambiguously

Dual AC Resonance Tracking Piezo Force Microscopy





N. Balke et al., J. Am. Ceram. Soc., 92 [8] 1629–1647 (2009)
B.J. Rodriguez et al., Nanotechnology 18, 475504 (2007)

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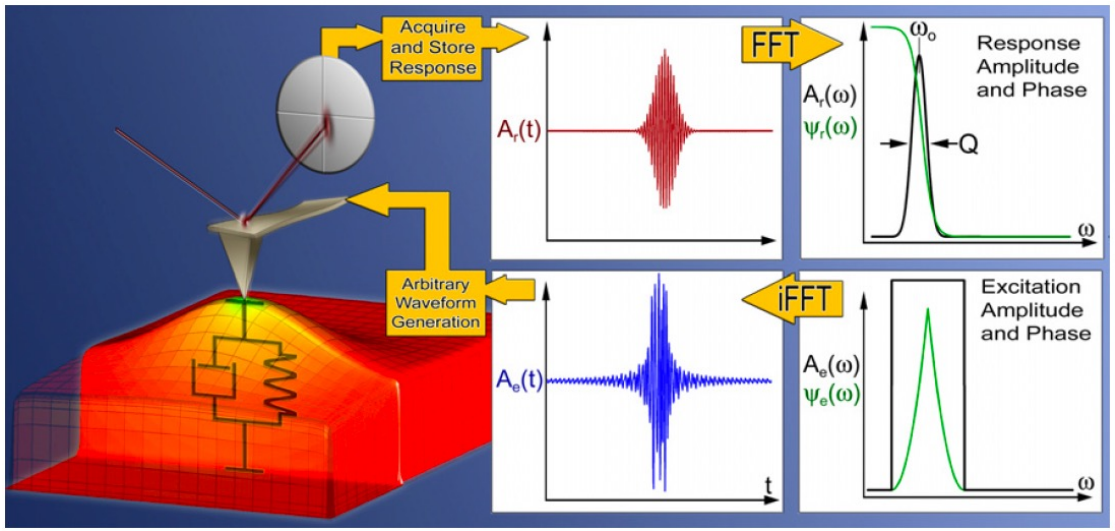
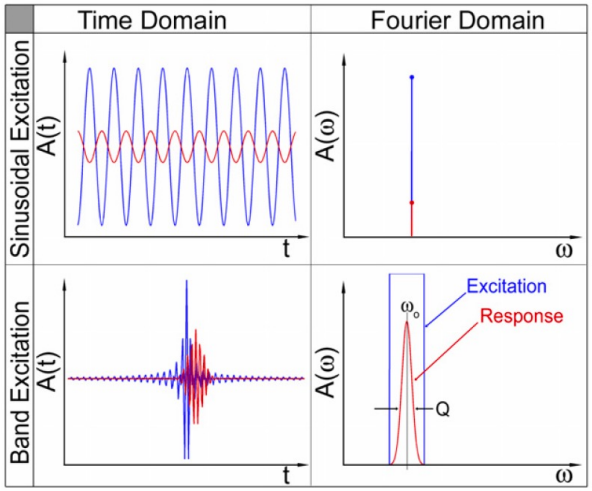
Piezoelectric force microscopy (PFM)

FIXIT

Band excitation PFM

Exciting and monitoring the electromechanical response within a continuous frequency band





Quantitative measurements of the energy dissipation through the determination of the Q-factor of the cantilever-sample system

S. Jesse and S. K. Kalinin, J. Phys. D: Appl. Phys. 44 (2011) 464006 (16pp)

S. Jesse, S. V. Kalinin, R. Proksch,, A. P. Baddorf and B. J. Rodriguez, Nanotechnology 18 (2007) 435503

Funded by the European Union

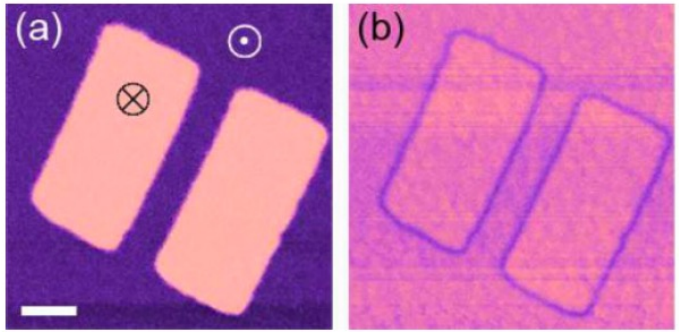
PFM spectroscopy mode

FIXIT

Tetragonal PZT thin film

Vertical PFM phase map

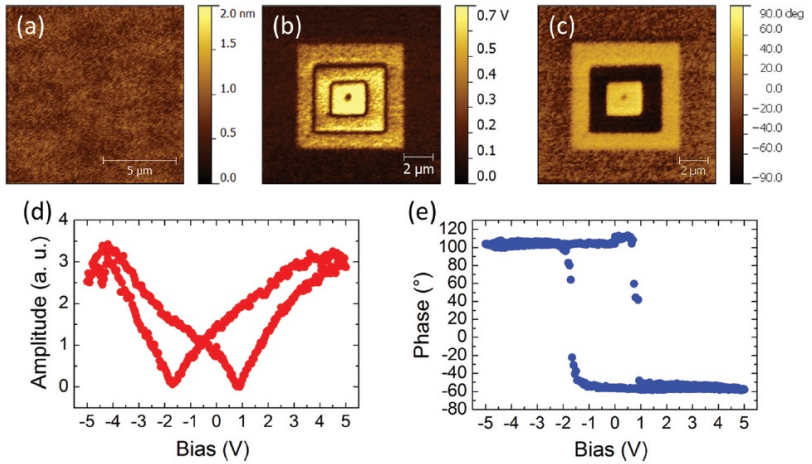
Vertical PFM amplitude map



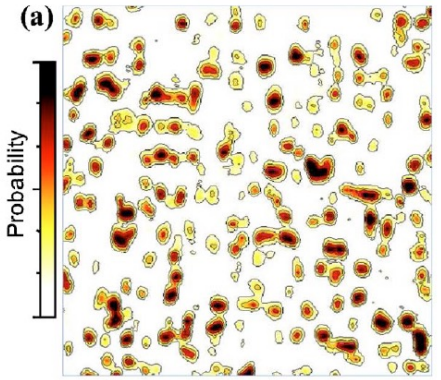
Tetragonal $BaTiO_3$ thin film

VPFM phase map

VPFM amplitude map



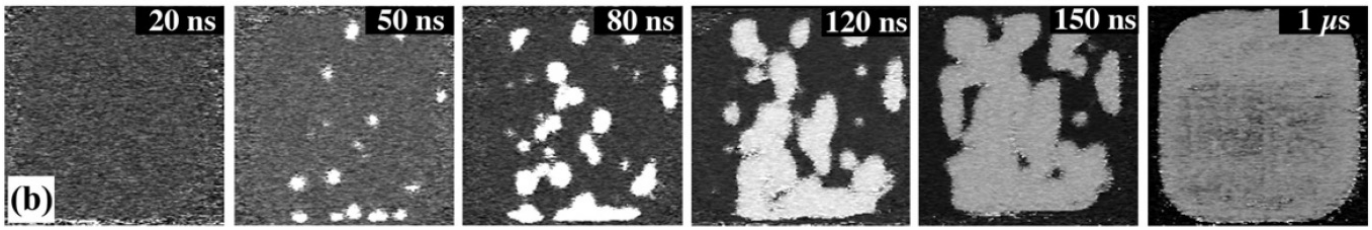
Epitaxial PZT capacitor



Probability of domain nucleation

Epitaxial PZT capacitor

Domain configurations with out-of-plane polarization developing at different stages of polarization reversal



L. Mazet *et al.*, J. Appl. Phys. 116, 214102 (2014)
L. Mazet *et al.*, Sci. Technol. Adv. Mater. 16 (2015) 036005
D. Denning et al., International Materials Reviews 61, 46 (2016)
D.J. Kim et al., Appl. Phys. Lett. 91, 132903 (2007)
A. Gruverman et al., J. Phys.: Condens. Matter 20, 342201 (2008).

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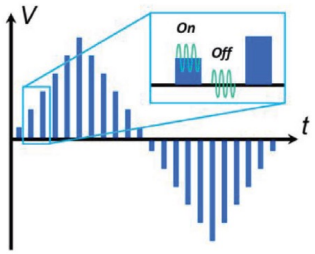
Switching spectroscopy mode (SS-PFM)

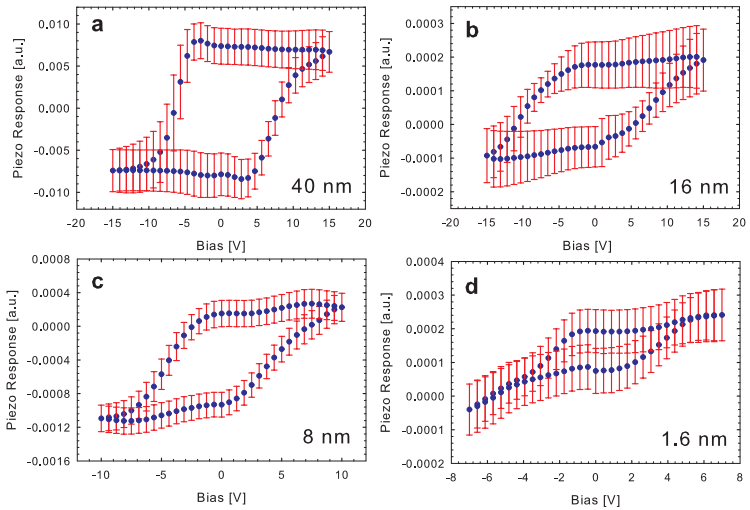
FIXIT

Local measurement of hysteresis loop by PFM

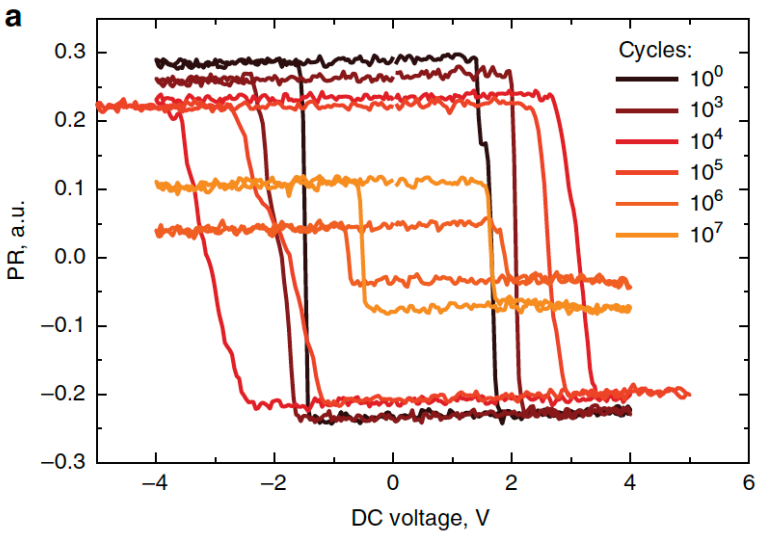
The PFM hysteresis loop is typically measured at a fixed point by applying a pulse-type triangular voltage waveform



Switching of $BaTiO_3$ epitaxial films on Si(001)



Study of fatigues in ferroelectric capacitors



S. Jesse, Appl. Phys. Lett. 88, 062908 (2006)
C. Dubourdieu *et al.*, Nature Nanotechnology (2013)
Anton V. Ievlev et al., Nature Comm. 10, 3064 (2019)

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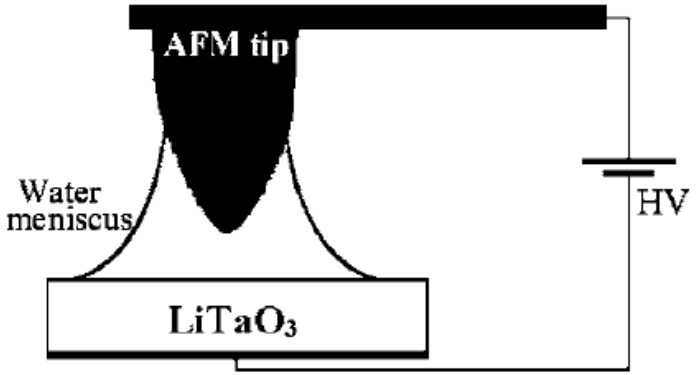
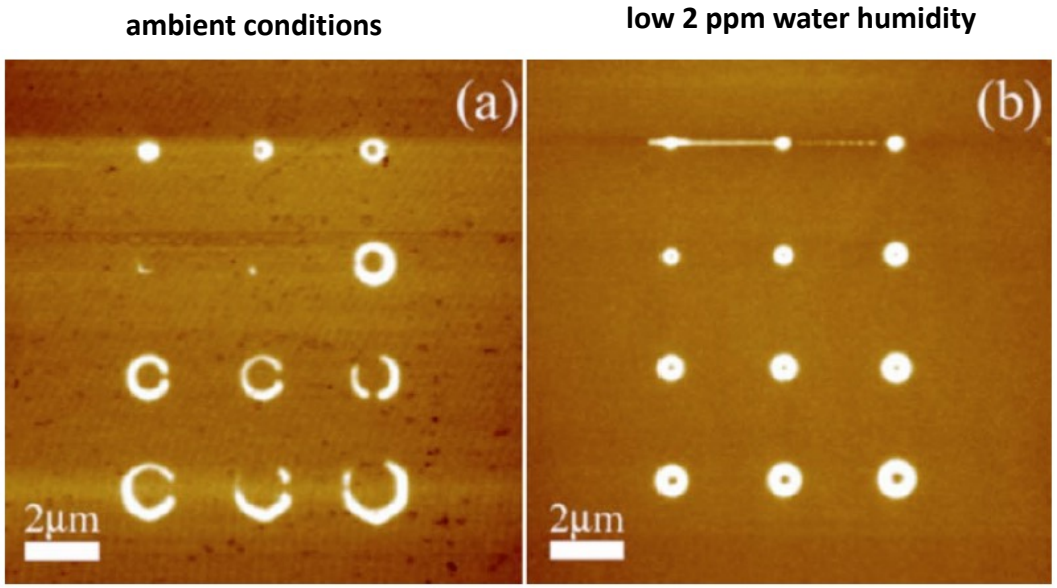
Piezoelectric force microscopy (PFM)

FIXIT

Artefacts

A water meniscus is formed between an AFM tip and sample surface under ambient conditions.





- **Role of humidity in nanoscale domain inversion**

D. Dahan et al., Appl. Phys. Lett. 89, 152902 (2006)

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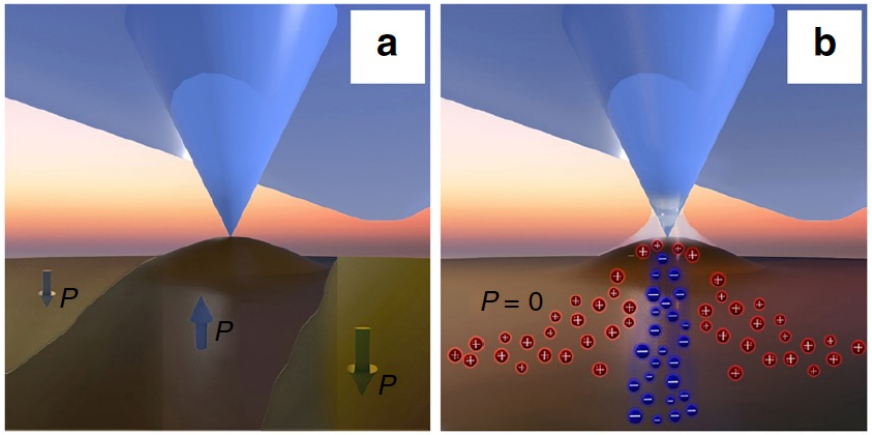
Piezoelectric force microscopy (PFM)

FIXIT

Ferroelectric and non-ferroelectric contributions in PFM

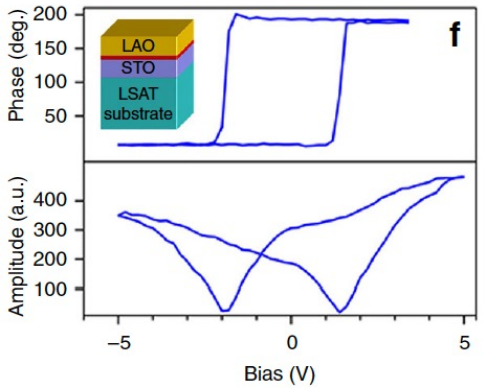


Non ferroelectric thin films may have the same response as the one typical for FE!

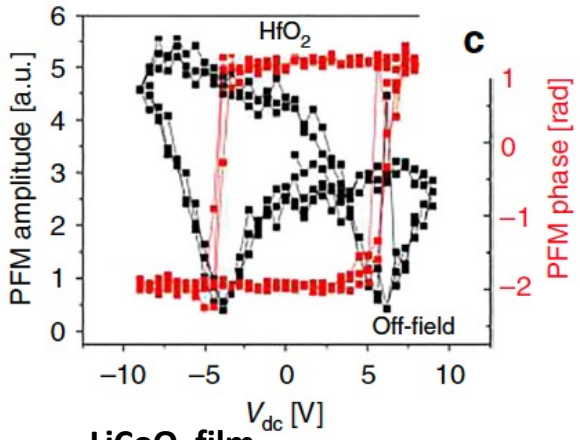
N. Balke et al., Nat. Nano 5, 749 (2010)

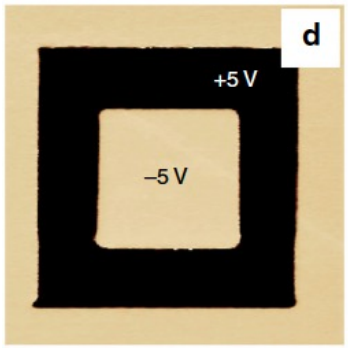
A. Gruverman, M. Alexe and D. Meier, Nat. Comm.10, 1661 (2019)

$LaAlO_3$ thin films

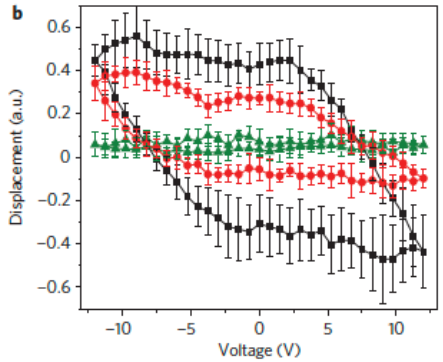


a-HfO_2 thin films





$LiCoO_2$ film



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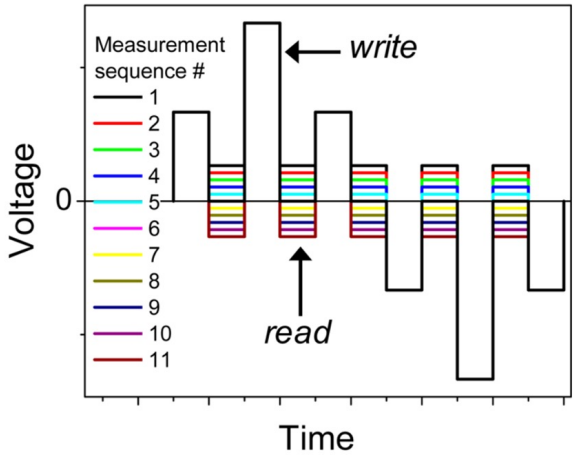
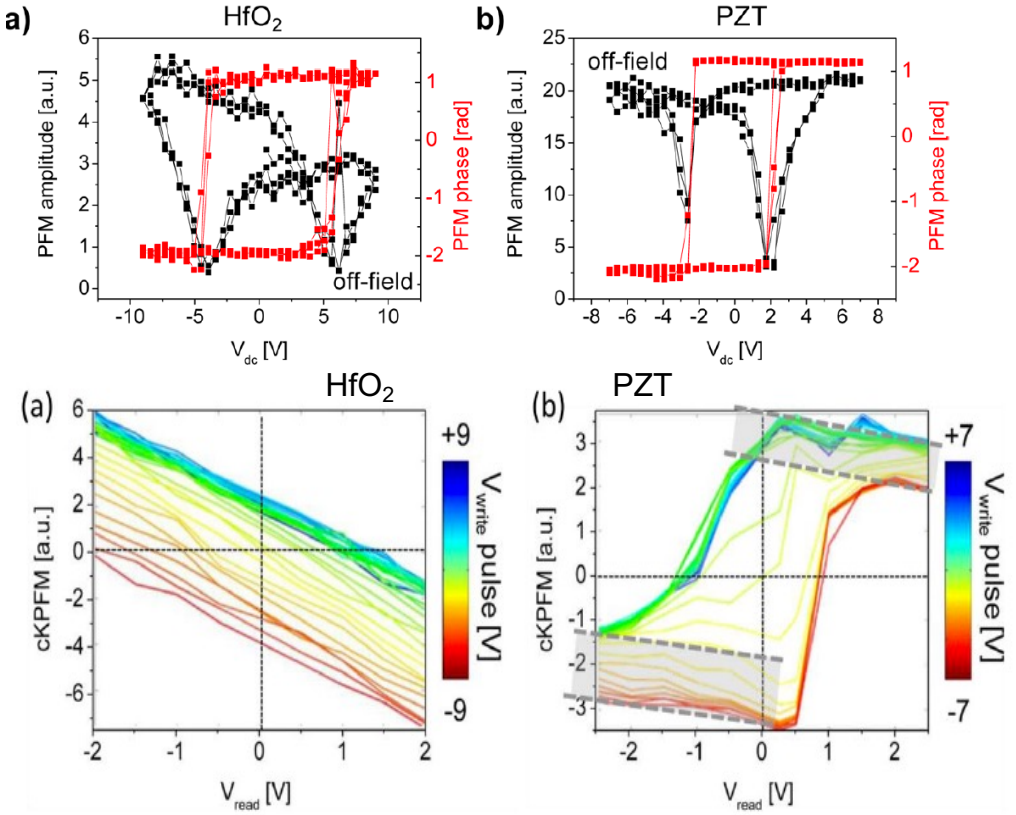
Contact Kelvin Probe Microscopy (cKPFM)

FIXIT

Method developed **to distinguish between FE response and electrostratic force** (charge injection, …)



Opening of a loop for ferroelectric materials while response is linear for dielectrics



N. Balke *et al.,* ACS Nano 8, 10229, 2014
N. Balke *et al*., ACS Nano 9, 6484, 2015

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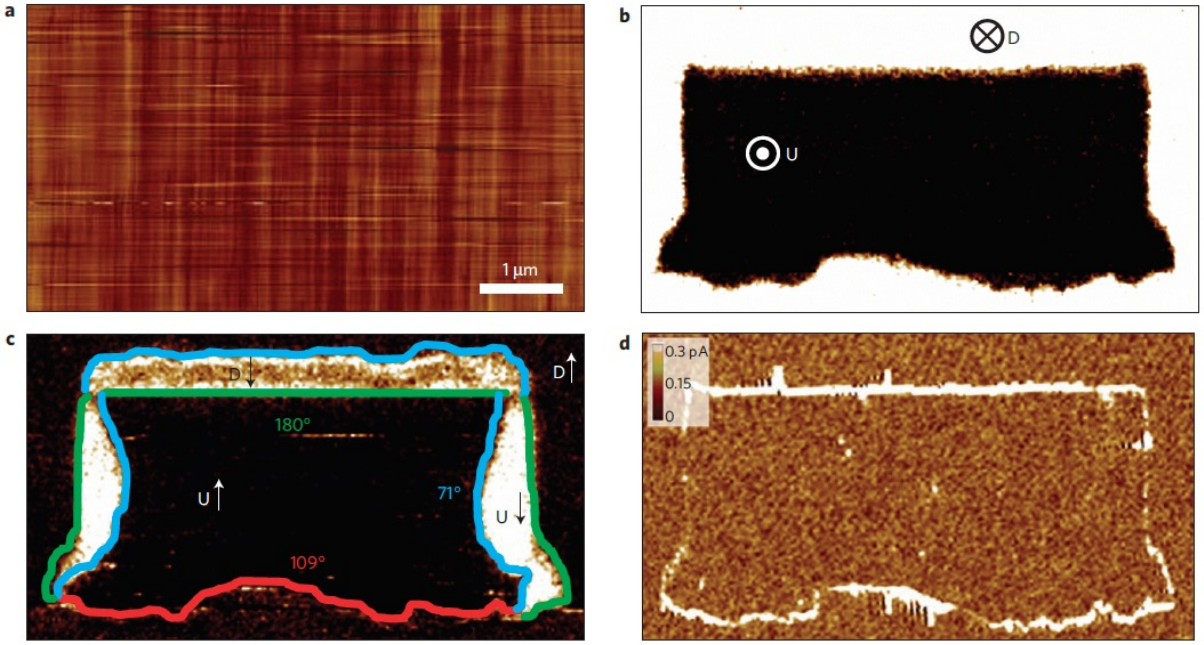
Conductive AFM(CAFM)

FIXIT

Used to test the local electrical properties of a material.

Probing the conductivity of domain walls



J. Seidel et al., Nature Materials 8, 229 (2009)
F. Hui and M. Lanza, Scanning probe microscopy for advanced, Nanoelectronics, Nature Electronics 2, 221 (2019)

Funded by
the European Union

PFM and CAFM: evidence of new phenomena

FIXIT

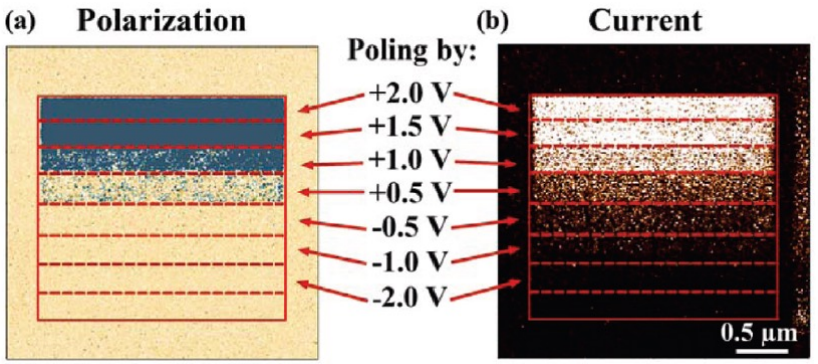
Tunneling Electroresistance Effect in Ferroelectric Tunnel Junctions at the Nanoscale

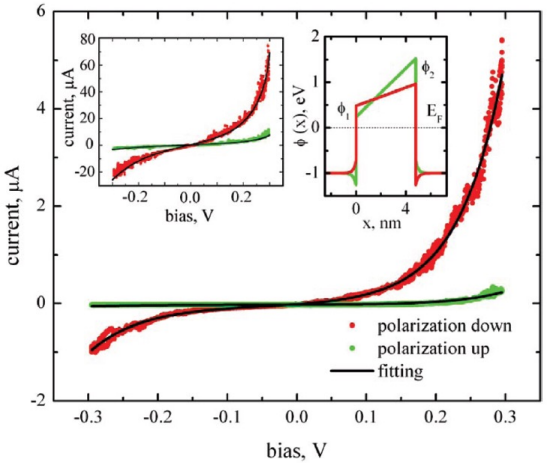
A. Gruverman,*,† D. Wu,‡ H. Lu,† Y. Wang,† H. W. Jang,§ C. M. Folkman,§ M. Ye. Zhuravlev,†,|| D. Felker,§ M. Rzchowski,§ C.-B. Eom,§ and E. Y. Tsymbal†

University of Nebraska, Lincoln, Nebraska 68588, North Carolina State University, Raleigh, North Carolina 27695, University of Wisconsin-Madison, Wisconsin 53706, and Kurnakov Institute for General and Inorganic Chemistry, RAS, Moscow, Russia

NANO LETTERS

2009
Vol. 9, No. 10
3539-3543





A. Gruverman, D. Wu, H. Lu, Y. Wang, H. W. Jang, C. M. FolkmanM. Ye. Zhuravlev, D. Felker, M. Rzchowski, C.-B. Eom, and E. Y. Tsymbal, Tunneling Electroresistance Effect in Ferroelectric Tunnel Junctions at the Nanoscale, Nano Lett.9, 3539 (2009)

V. Garcia, S. Fusil, K. Bouzehouane1, S. Enouz-Vedrenne, N. D. Mathur, A. Barthelemy & M. Bibes, Giant tunnel electroresistance for non-destructive readout of ferroelectric states, Naturee 460, 81 (2009)

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PFM and CAFM: evidence of new phenomena

FIXIT

NANO LETTERS

Letter

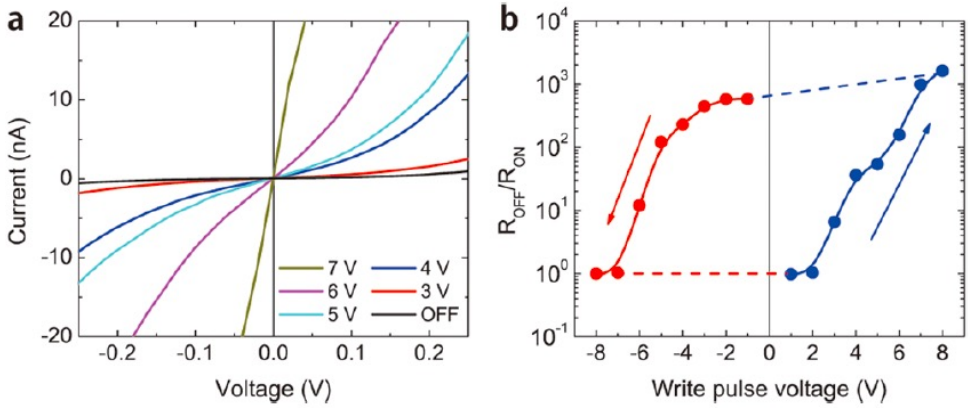
pubs.acs.org/NanoLett

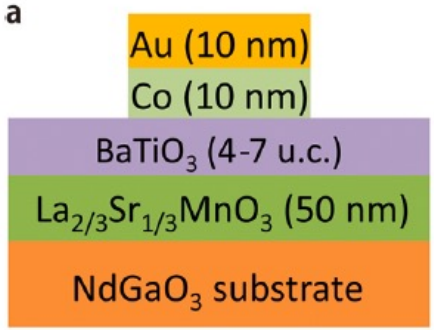
Ferroelectric Tunnel Memristor

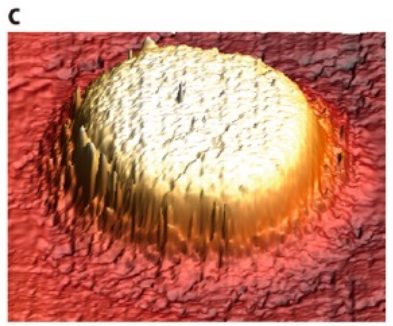
D. J. Kim,[†] H. Lu,[†] S. Ryu,[‡] C.-W. Bark,[‡] C.-B. Eom,[‡] E. Y. Tsymbal,[†] and A. Gruverman*,[†]

[†]Department of Physics and Astronomy & Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, Nebraska 68588, United States

[‡]Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States







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Ferroelectrics thin films:

Domains, domain walls

Strain and size effects

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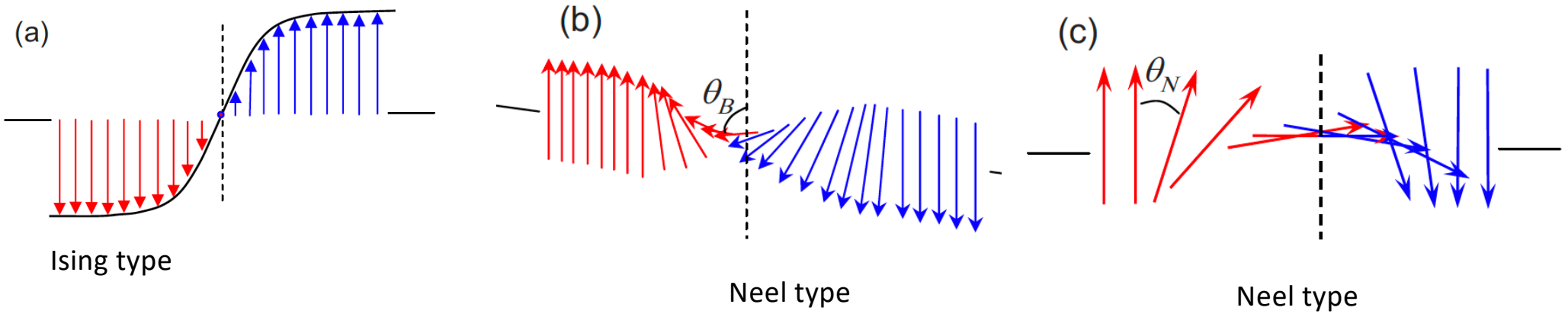
Domains in ferroelectrics

FIXIT



Ising type

Neel type

Neel type

- In ferroelectrics, there is a strong coupling of polarization and strain (piezoelectricity)
- Domains walls were thought to be only of Ising type until ˜15 years ago

- Ferroelectric polarization (direction, amplitude) and domain formation are determined by the boundary conditions which determine the paths to screen the charge and the ability to switch them

D. Lee et al, Phys. Rev. B 80, 060102(R) (2009)

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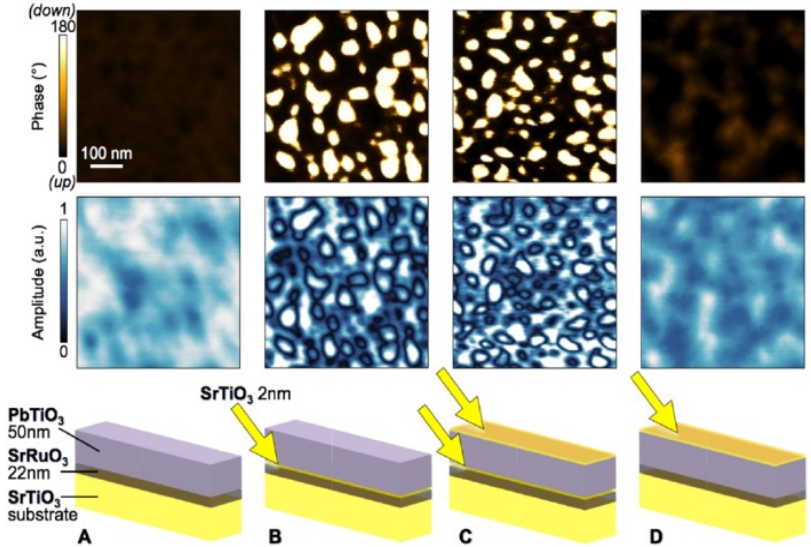
Depolarization field and domains

FIXIT

- **Polarization induces bound charges at surface or interfaces that must be compensated**
- **Ferroelectric polarization (direction, amplitude) and domain formation are determined by the boundary conditions which determine the ability and the paths to screen the charge**

Boundary conditions: **electrical, mechanical, chemical boundary conditions**



Strong change in the domain pattern by inserting a $SrTiO_3$ film on top or below the ferroelectric layer or on both sides of it

Sergei V Kalinin, Yunseok Kim, Dillon D Fong and Anna N Morozovska, Surface-screening mechanisms in ferroelectric thin films and their effect on polarization dynamics and domain structures, Rep. Prog. Phys. 81 (2018) 036502 (74pp)
C. Lichtensteiger *et al*. Nano Letters (2014)

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Depolarization field and domains

FIXIT

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Boundary conditions: **electrical, mechanical, chemical boundary conditions**

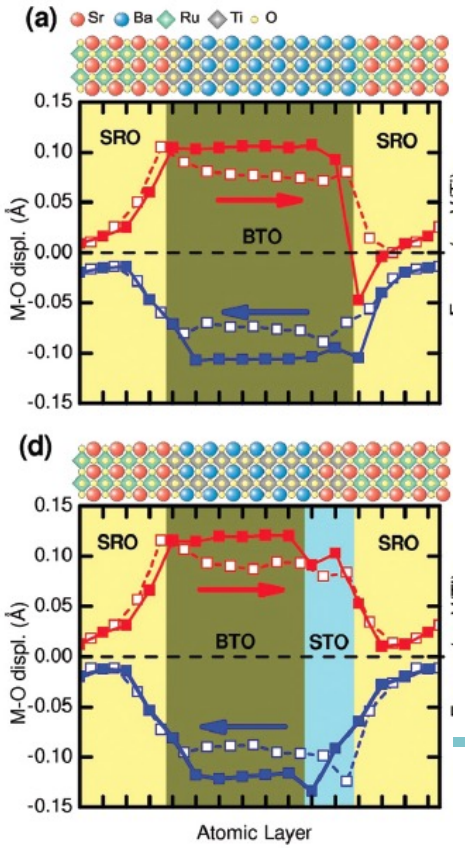
Materials Views
www.MaterialsViews.com

ADVANCED MATERIALS
www.advmat.de

Enhancement of Ferroelectric Polarization Stability by Interface Engineering

2012
Gruverman et al.

Increase of polarization at $BaTiO_3$ interface by insertion of $SrTiO_3$ layer



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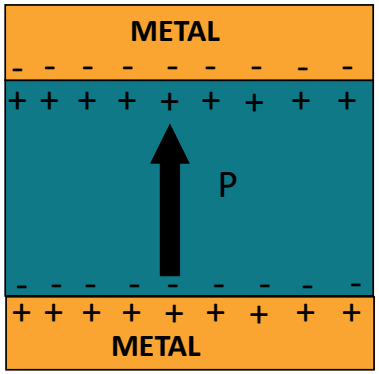
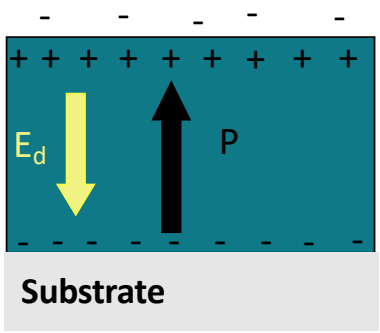
Depolarization field

FIXIT



Perfect screening
(if perfect metal)



Incomplete charge screening at the interface with a semiconductor or an insulator (or a bad metal)

→ **Large effective E_d in thin films**

The thinner the film, the larger the depolarization field

The depolarization field changes

- The magnitude of the polarization
- Transition tenperature
- Coercive field
- Order of the phase transition

PHYSICAL REVIEW B VOLUME 8, NUMBER 7 1 OCTOBER 1973

Phase Transition, Stability, and Depolarization Field in Ferroelectric Thin Films

I. P. Batra, P. Wurfel,* and B. D. Silverman
IBM Research Laboratory, San Jose, California 95193

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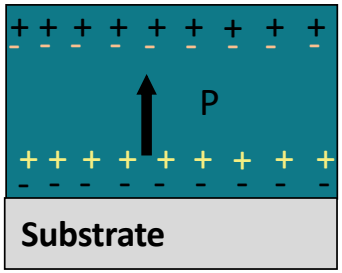
the European Union

Depolarization field

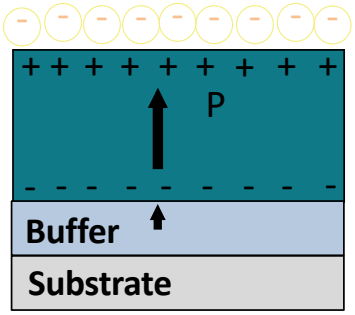
FIXIT

Finite conductivity

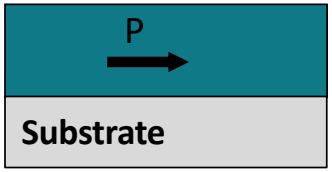


Atmospheric adsorbates

Distortion of lattice for polarization continuity

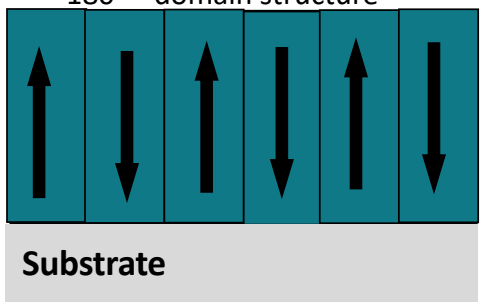


Polarization rotation

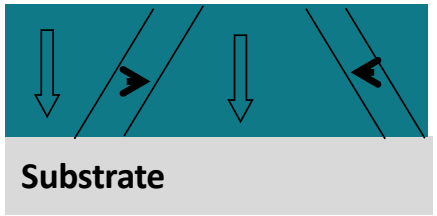


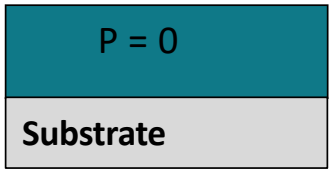
Domain formation

180° domain structure

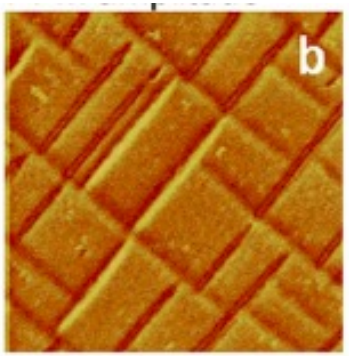


Mixed domain structure





PFM - PZT on $SrTiO_3$:Nb



L. Klein, *et al*, JVST A (2010)

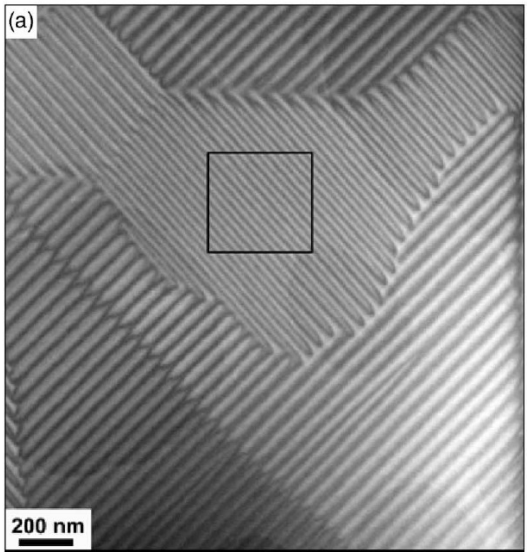
Surface screening of spontaneous polarization (bound charges) in ferroelectrics is typically realized by the mobile charges adsorbed from the ambient in the case of high or normal humidity

Funded by
the European Union

Domains and domain walls

FIXIT

Single crystalline $BaTiO_3$ lamella



The domains are **narrow**, **periodic** and **self-organized**.

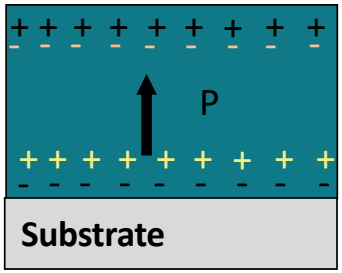
Schilling et al, PRB 2006

Funded by
the European Union

Depolarization field

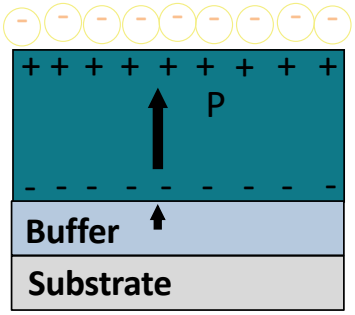
FIXIT

Finite conductivity

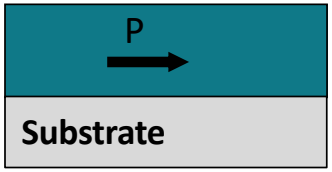


Atmospheric adsorbates

Distortion of lattice for polarization continuity

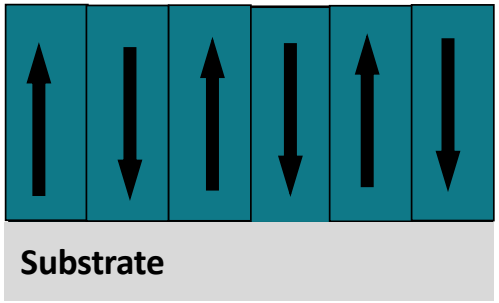


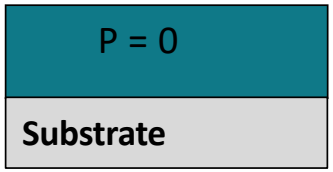
Polarization rotation



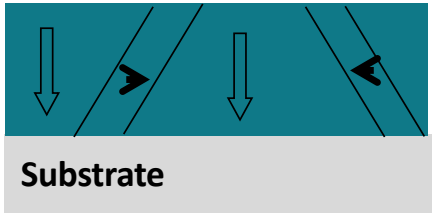
Domain formation

180° domain structure

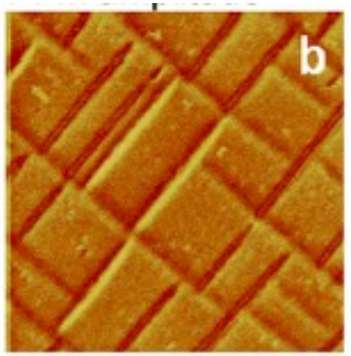




Mixed domain structure



PFM - PZT on SrTiO3:Nb



L. Klein, *et al*, JVST A (2010)

Surface screening of spontaneous polarization (bound charges) in ferroelectrics is typically realized by the mobile charges adsorbed from the ambient in the case of high or normal humidity

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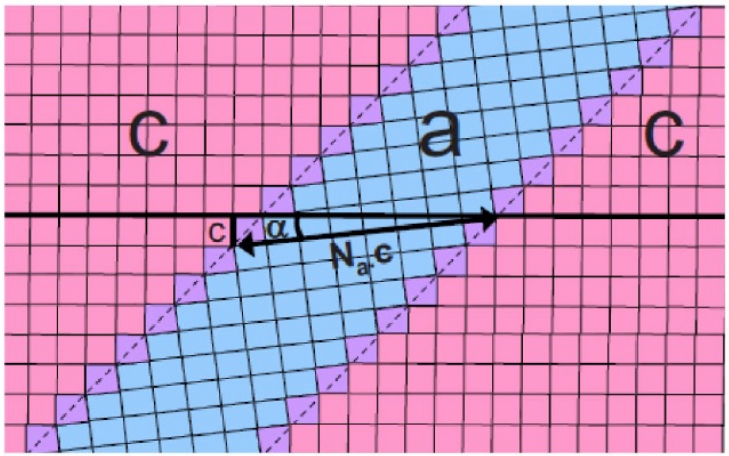
Domains in ferroelectrics

FIXIT

In an epitaxial tetragonal film: domain width depends on substrate (strain)



P.-E. Janolin, J Mater Sci (2009) 44:5025–5048

B. Noheda

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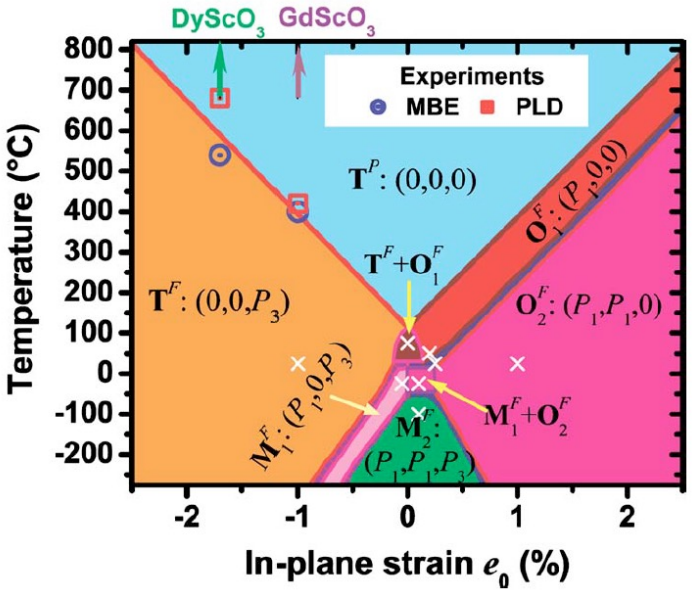
the European Union

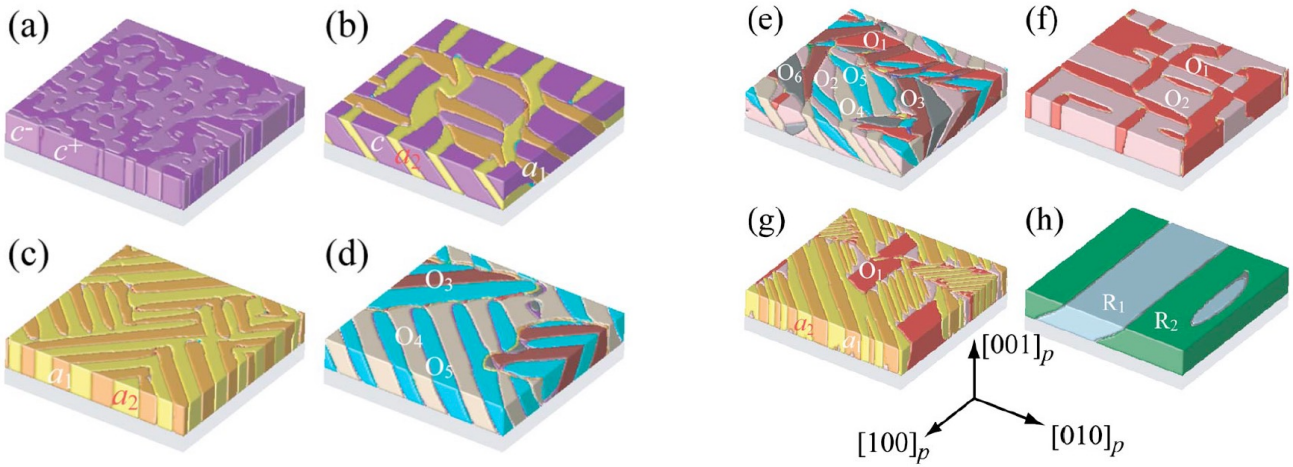
Domains in ferroelectrics

FIXIT

Temperature-strain phase diagram for $BaTiO_3$



Phase field modelling for the conditions shown on the left



- **Rich pattern of possible domain type and configurations**

V. G. Koukhar et al., Phys. Rev. B 64, 214103 (2001)
Y. L. Li and L.Q. Chen, Appl. Phys. Lett. 88, 072905 (2006)

Funded by
the European Union

Ferroelectrics and strain engineering

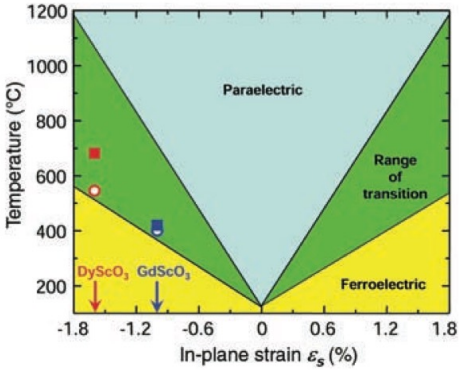
FIXIT

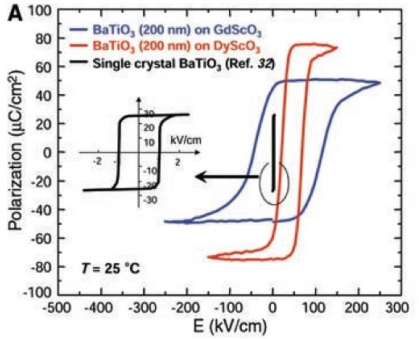
Enhancement of Ferroelectricity in Strained $BaTiO_3$ Thin Films

K. J. Choi,[1] M. Biegalski,[2] Y. L. Li,[2] A. Sharan,[2] J. Schubert,[3] R. Uecker,[4] P. Reiche,[4] Y. B. Chen,[5] X. Q. Pan,[5] V. Gopalan,[2] L.-Q. Chen,[2] D. G. Schlom,[2] C. B. Eom[1]*

Science 306, 1005 (2004)

T_c = 540° C on $DyScO_3$!!
(**compared to 120° C** in bulk crystal

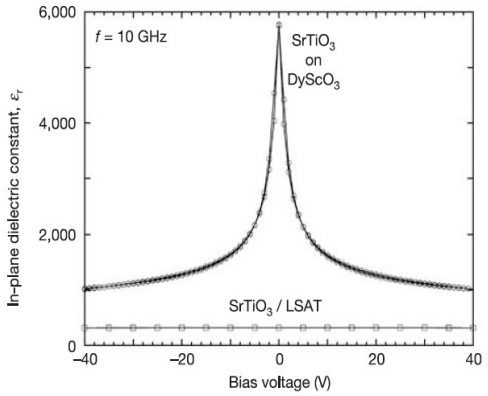




Room-temperature ferroelectricity in strained $SrTiO_3$

J. H. Haeni[1], P. Irvin[2], W. Chang[3], R. Uecker[4], P. Reiche[4], Y. L. Li[1], S. Choudhury[1], W. Tian[5], M. E. Hawley[6], B. Craigo[7], A. K. Tagantsev[8], X. Q. Pan[5], S. K. Streiffer[9], L. Q. Chen[1], S. W. Kirchoefer[3], J. Levy[2] & D. G. Schlom[1]

Nature 430, 758 (2004)

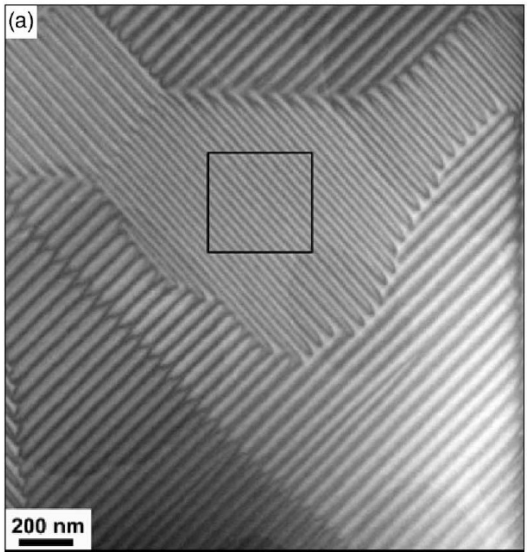


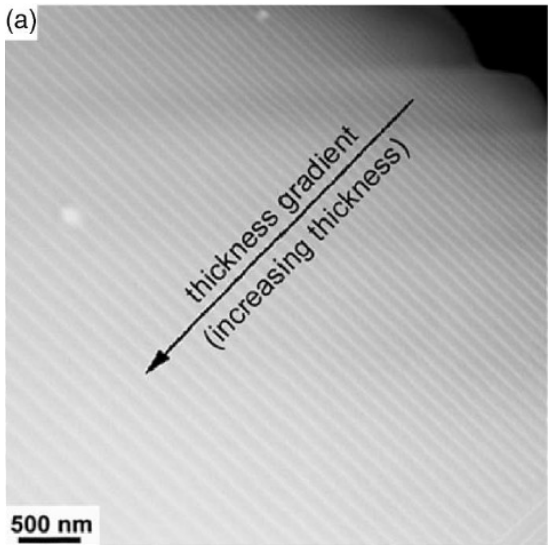
Funded by the European Union

Domains and domain walls

FIXIT

Single crystalline $BaTiO_3$ lamella





The domains periodicity increases towards increasing thickness

Schilling et al, PRB 2006

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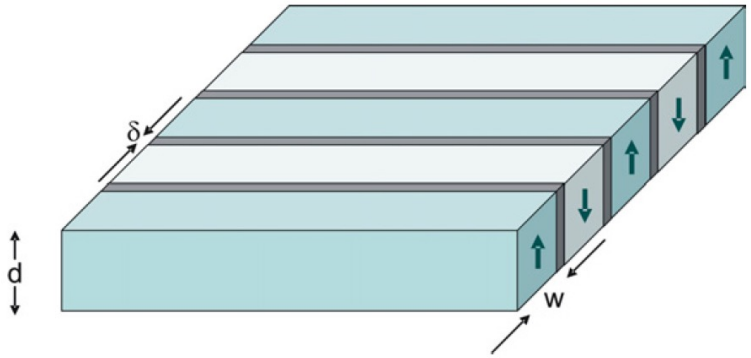
Domain size: Kittel‘s law

FIXIT

Domain size is determined by the competition between the energy of the domains and the energy of the domain walls

Domain energy : E = U. w U is the volume energy density of the domain



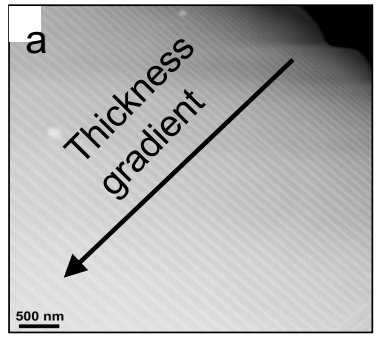
The energy gained by reducing domain size is balanced by the fact that this requires increasing the number of domain walls, which are themselves energetically costly.

Wall energy : E = $\sigma d/w$, σ is the energy density per unit area of the wall

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

$$w \sim \sqrt{d}$$

Open boundary conditions



Schilling *et al*, Phys. Rev. B (2006)

J. F. Scott 2006 J. Phys.: Condens. Matter 18 R361

G. Catalan et al., Rev. Modern Phys.84, 119 (2012)

Landau and Lifshitz (1935)

Kittel (1946)

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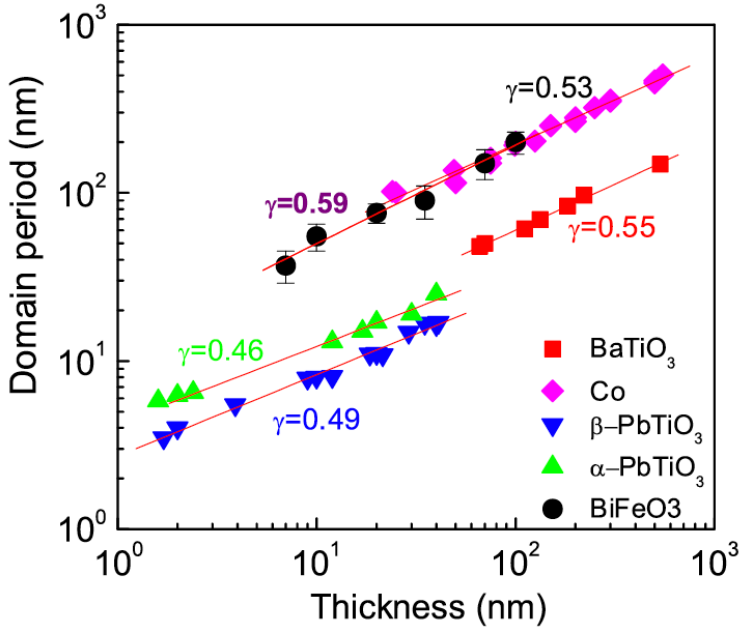
Domains and domain walls

FIXIT



$$w = A\, d^{\gamma}$$

The Kittel's law describe reasonably well the behaviour of ferroelectrics

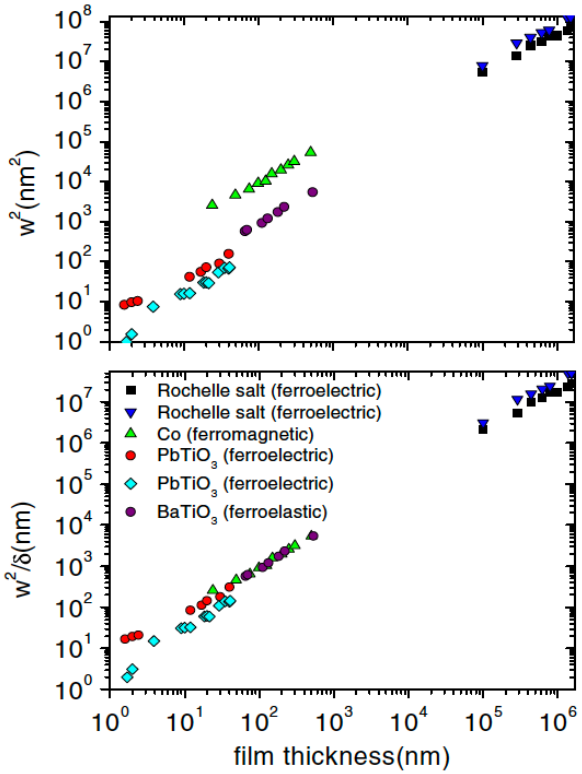
Ferroelectric domains in $BiFeO_3$ are large (similar to magnetic domains)

G. Catalan *et al*, Phys. Rev. Lett. 2008

Funded by
the European Union

Domains and domain walls

FIXIT



Open boundary conditions!

$$\frac{w^2}{d\delta} = G \sim 2.5$$

where G is an a-dimensional parameter

- The domain size of **all ferroics** can be described with a **single universal curve** where domain **wall thickness is the scaling parameter**
- Allows to estimate the wall thickness when domain size is measured (typically, **δ=1-10nm**)
- Conversely, one can use it to determine optimum crystal thickness to stabilize a given domain period

For film thickness d=100nm, *δ/w = 6-20%*

Very thin films can have a considerable fraction of their volume occupied by domain walls, and therefore the functional properties of the films may be affected by those domain walls.

J. F. Scott 2006 J. Phys.: Condens. Matter 18 R361

G. Catalan et al, J. Phys. Cond. Mat. (2007)
G. Catalan et al, J. Mat. Sci. (2009)
De Guerville, et al. Mater. Sci. Eng. B (2005)

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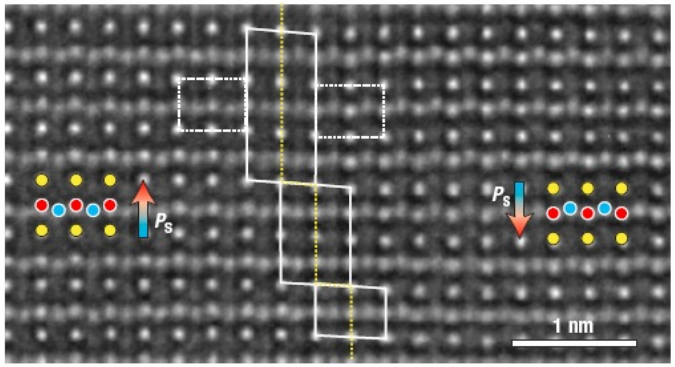
the European Union

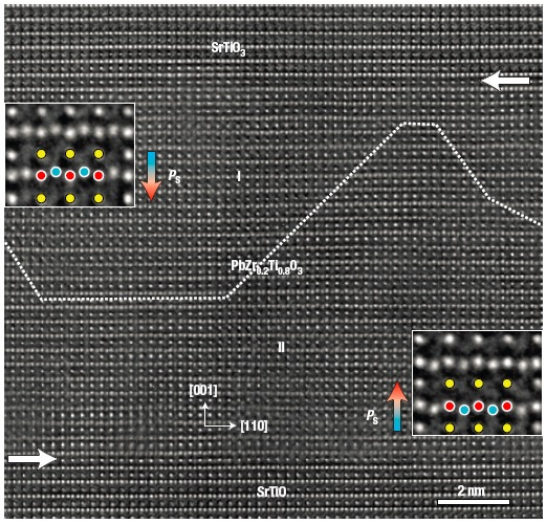
Imaging of domains and domain walls

FIXIT

Domain wall are very thin: few unit cells (abrupt change in polarization)

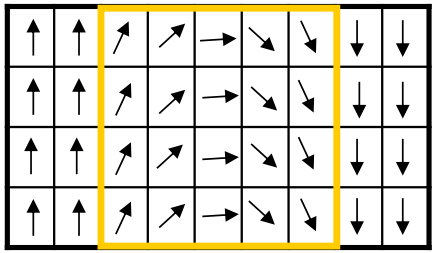


Head-to-head domains→ charged domains

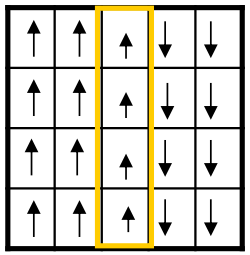


C.-L. Jia *et al*, Nature Materials 7, 57 (2008)

Magnetic domains



Ferroelectric domains



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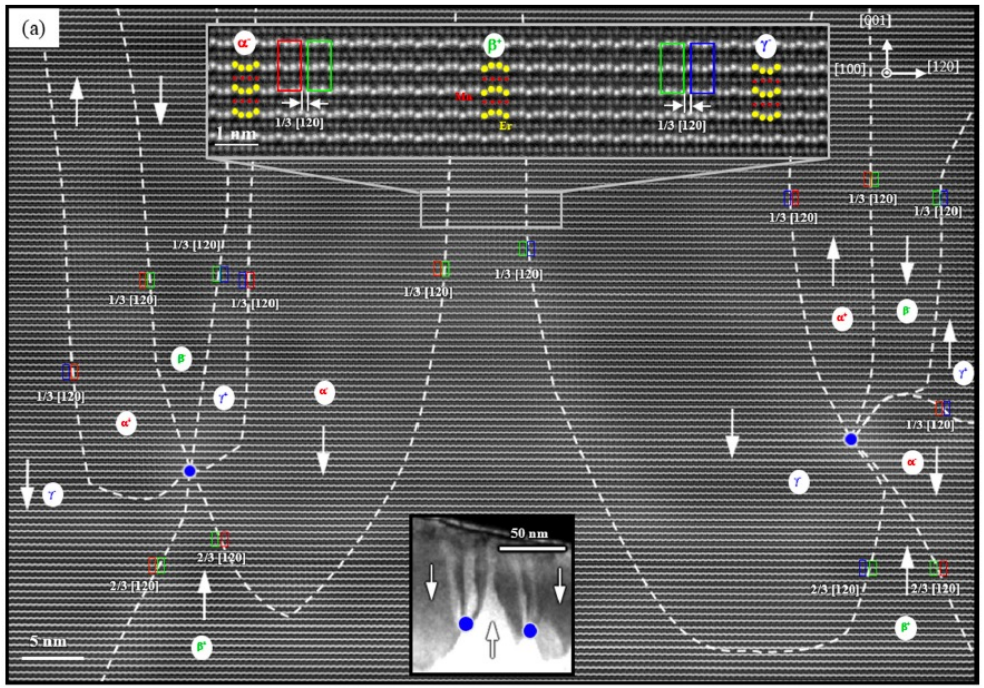
Imaging of domains and domain walls

FIXIT

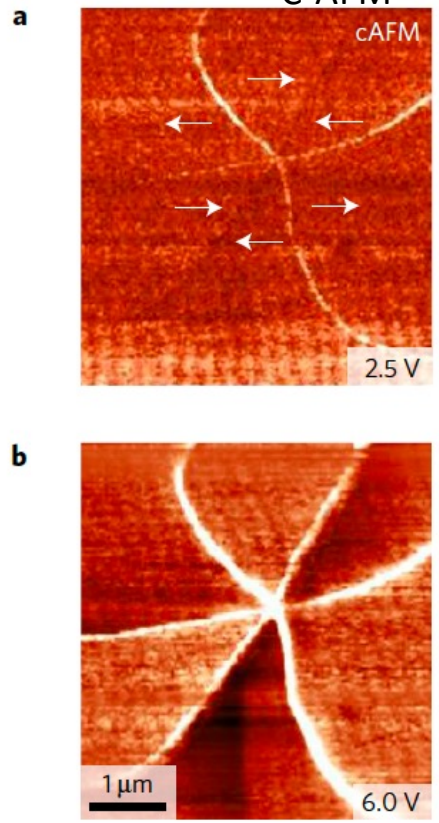
HAADF-STEM
Head-to-head

Hexagonal manganites



M.-G. Han *et al*, Phys. Rev. Mater. 2, 064004 (2018)

C-AFM



J.A. Mundy et al., Nat. Mater. 16, 622 (2017)

From: http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

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T. Atsumi, T. Oghushi, N. Kamegashira
Journal of Alloys and Compounds 238 (1996) 35

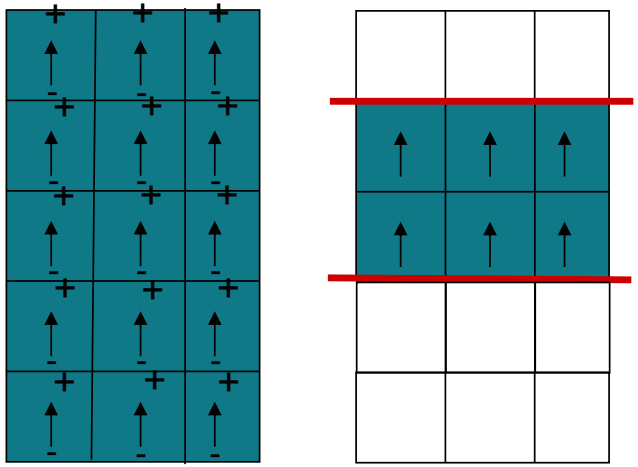
Size: how does it affect ferroelectricity?

FIXIT

Ferroelectricity is a collective effect: balance between short range and dipole-dipole forces

→ expected to be strongly affected by **finite-size effects.**

Ferroelectricity in thin films is closely related to the **boundary conditions** (electrical, mechanical, chemical…)



Questions:

- What is the **critical thickness** for ferroelectricity ?
- Role of the **chemical, electrical and mechanical boundary conditions on ferroelectricity**
(substrate, type of electrodes → screening, depolarization field)

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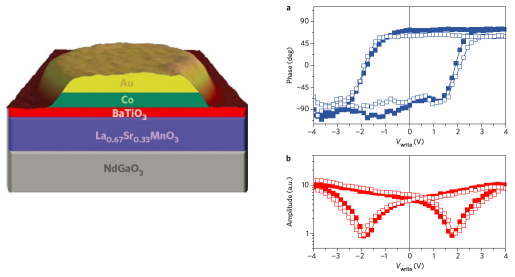
Size effects

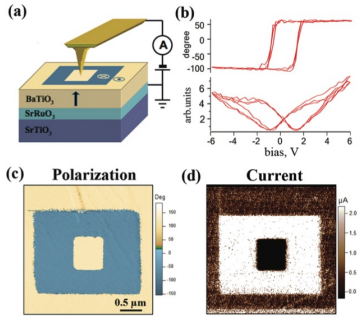
FIXIT

Ferroelectricity in ultrathin films is closely related to the **boundary conditions** (electrical, mechanical…)

$BaTiO_3$ 20 Å (5 ML) on $La_{0.7}Sr_{0.33}MnO_3$ electrode

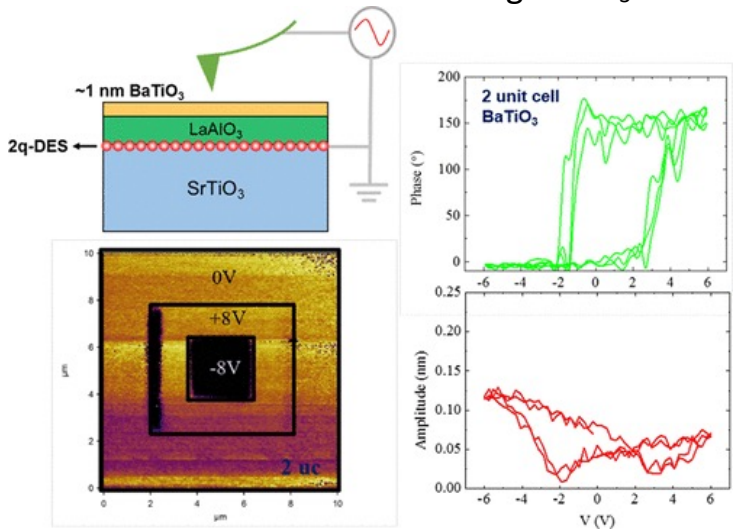


$BaTiO_3$ 6 ML – 24 ML on $SrRuO_3$ electrode



Ferroelectricity down to 2 nm

~1 nm ultrathin Semiconducting $BaTiO_3$ Films



Ferroelectricity down to ~1 nm

V. Garcia *et al*. Nature Materials (2009)
A. Chanthbouala *et al*. Nature Materials (2011)

S.R. Lee et al, Nano Lett. 2019, 19, 4, 2243–2250
A. Gruverman *et al*. Nano Letters (2009)

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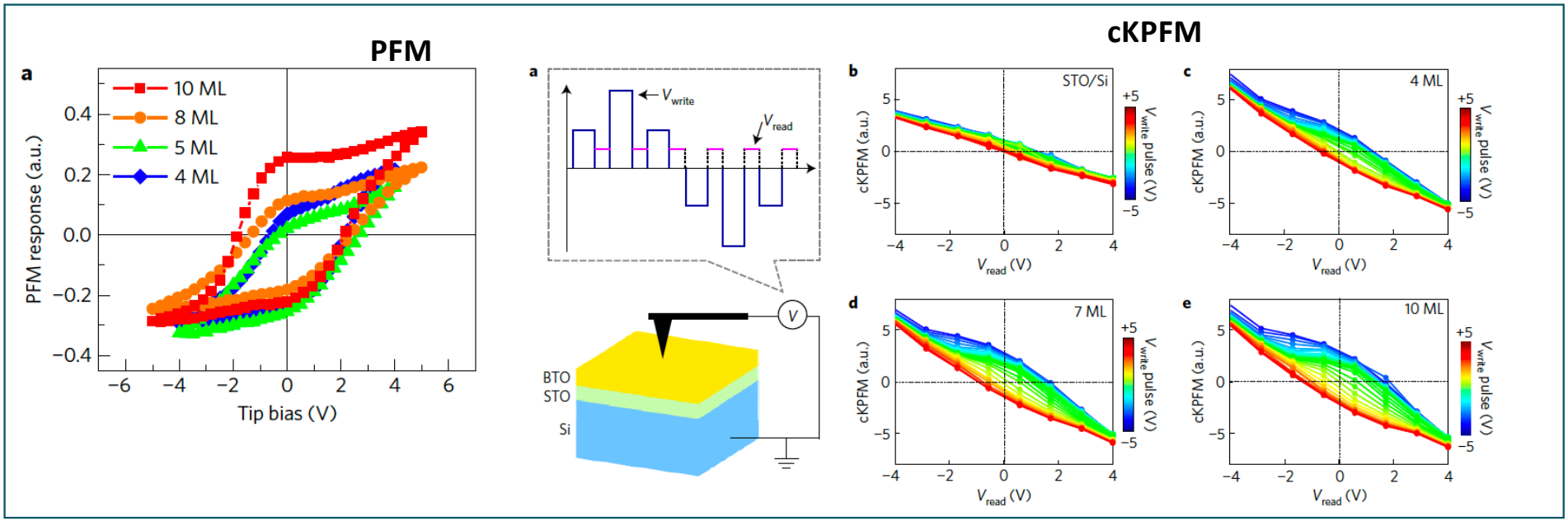
the European Union

Size effects

FIXIT

Ultrathin epitaxial $BaTiO_3$ on epi $SrTiO_3$ on silicon



Ferroelectricity down to 1.6 nm

Mixed ferro-ionic states for ultrathin films

S. M. Yang *et al.*, Nat. Phys. 13, 812 (2017)

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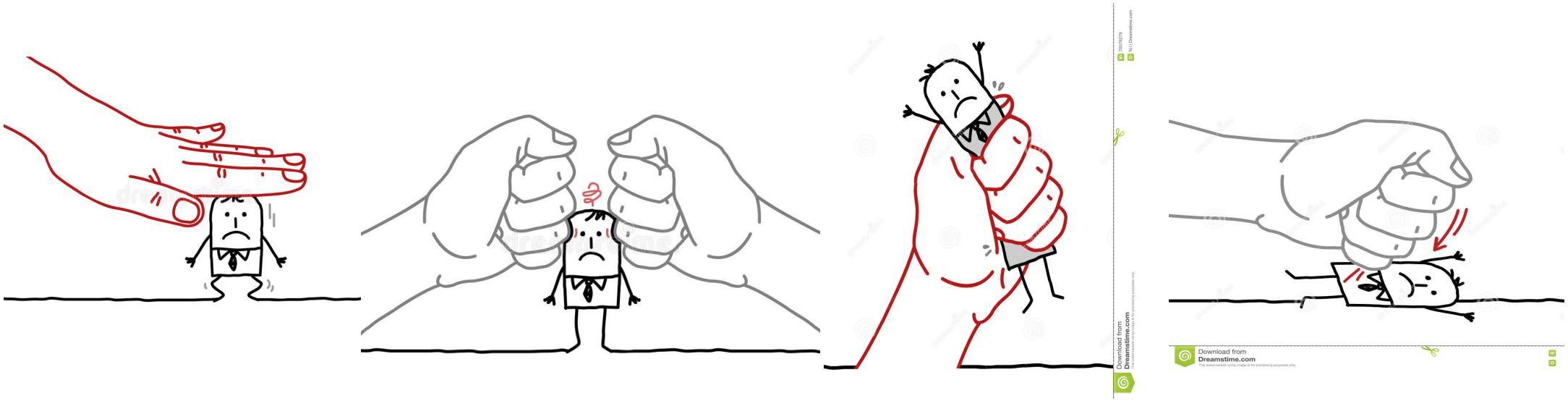
What happen under confinement?

FIXIT

Confinement means small space and usually a lot of stress: one tends to react differently!



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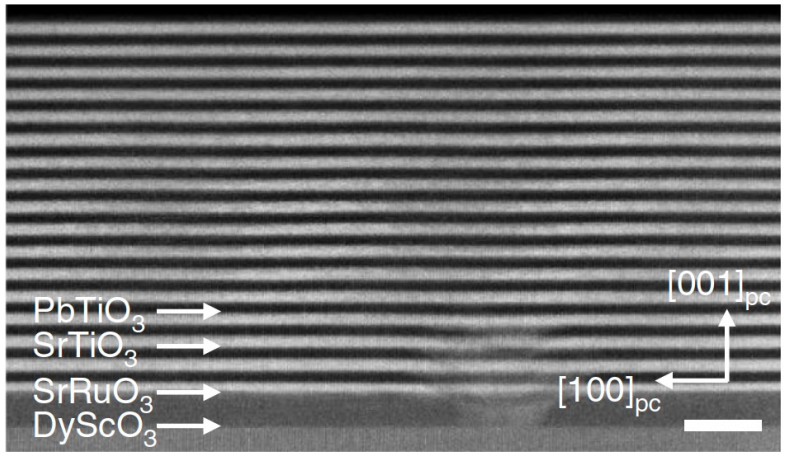
What happen under confinement?

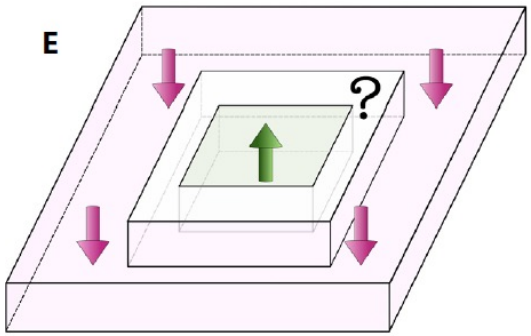
FIXIT

Few nm in size

Ultrathin films in a superlattice



Nanodot embedded in a paraelectric matrix



Domain and domain wall will tend to have similar sizes when domain size decreases down to few nm!
→ Difference between domains and DW may become blurred

The symmetry of domain walls is different from the symmetry of the domains, and hence so are the properties.

→Emerging properties

S. Das et al., Nature (2019)
M.A. Peireira Gonçalves et al., Sci. Adv. (2019)

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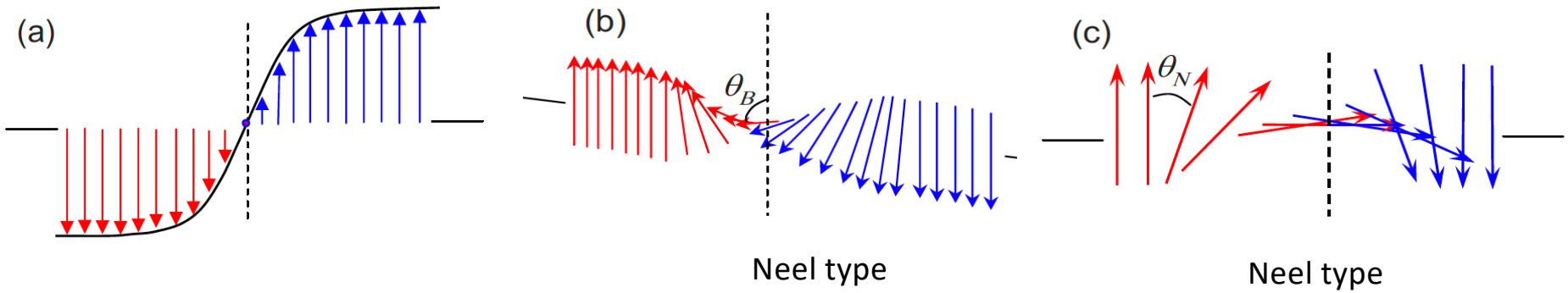
What happen under confinement?

FIXIT



Exotic polar topological textures appear with rotating electric dipoles, similarly to spins in a magnetic material

It was predicted by modelling for several years and experimental hints were there but it was unambiguously proved in 2011 by STEM images

D. Lee et al, Phys. Rev. B 80, 060102(R) (2009)

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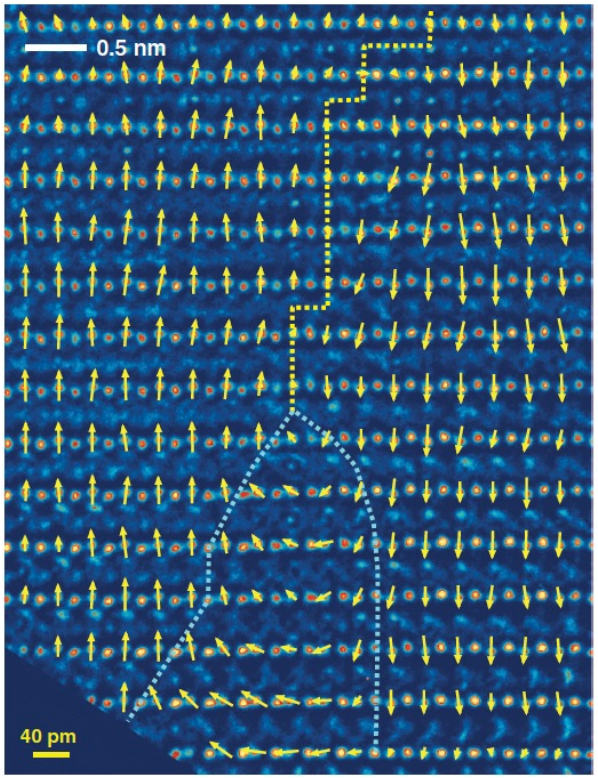
What happen under confinement?

FIXIT

PZT film

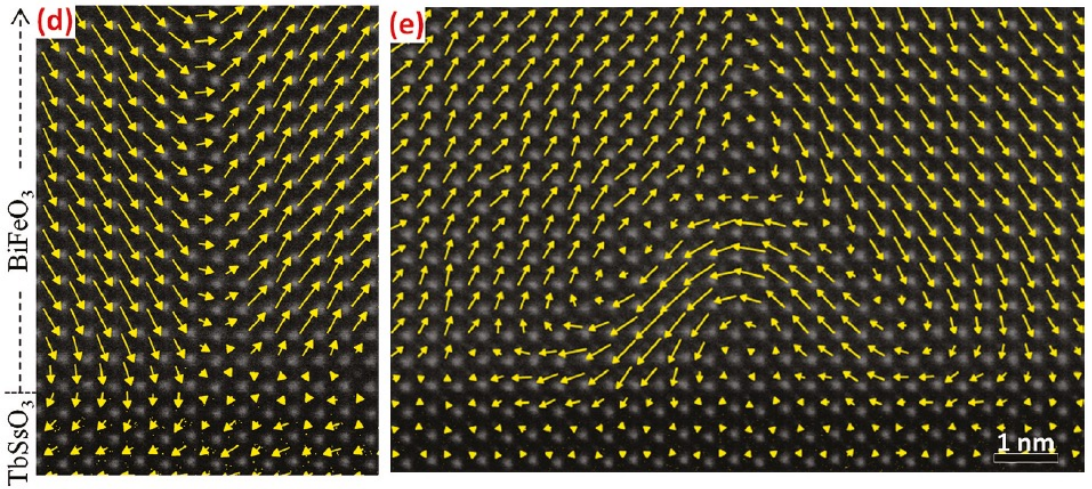
Map of the displacement atomic vectors



Jia et al., Science 331, 1420 (2011)

Continuous rotation of the dipole directions

$BiFeO_3$ film on $TbScO_3$



C.T. Nelson et al., Nano Lett., 11, 828 (2011)

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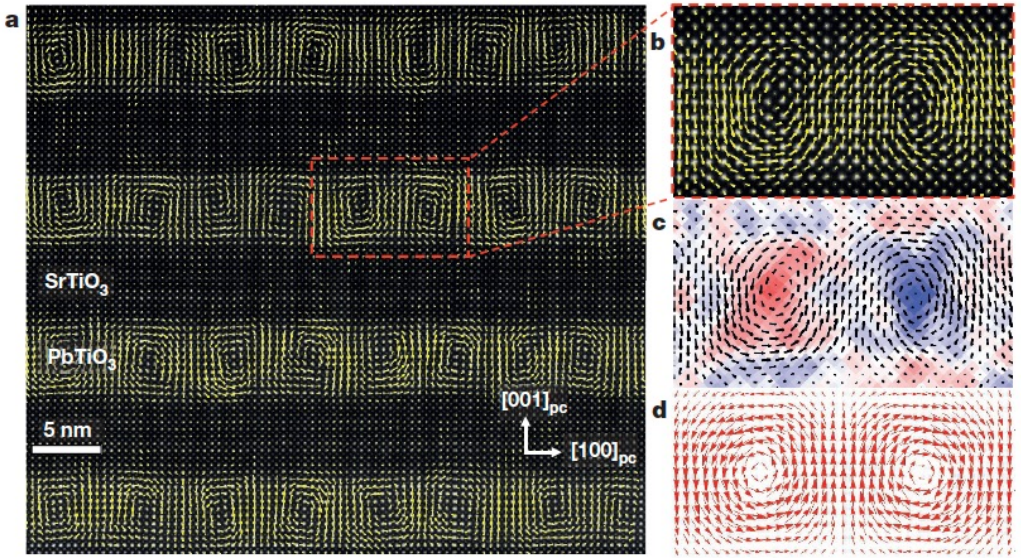
the European Union

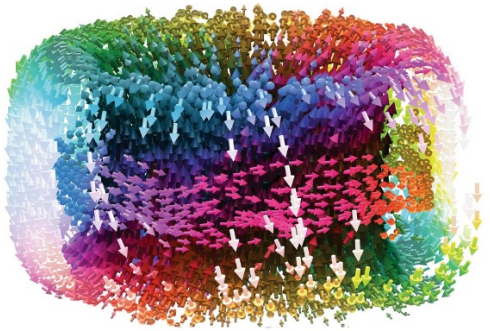
What happen under confinement?

FIXIT

Vortices or skyrmions form in (PZT/$SrTiO_3$)superlattices depending on the thickness

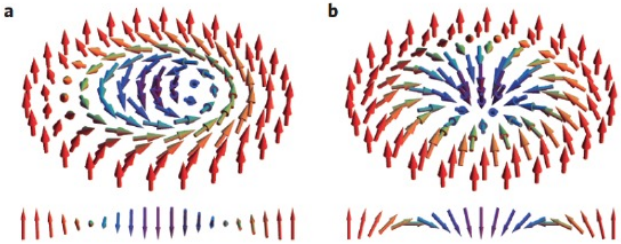


Polar skyrmions



Credit: Xiaoxing Cheng, Pennsylvania State University; C.T. Nelson, Oak Ridge National Laboratory; and Ramamoorthy Ramesh, Berkeley Lab

Magnetic skyrmions



A.K. Yadav et al., Nature (2019)
Nature electronics, 2, 173 (2019)
M.A. Peireira Gonçalves et al., Sci. Adv. (2019)

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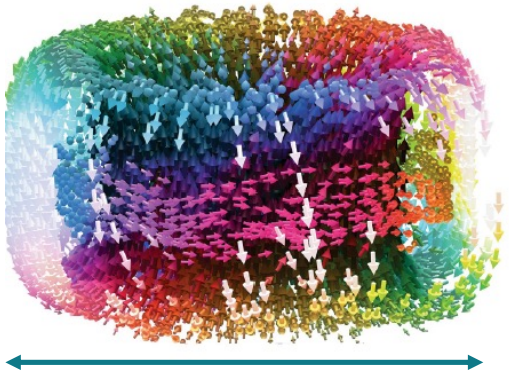
What happen under confinement?

FIXIT



$\sim 10\ nm$

Polar skyrmions/hopfions are chiral textures (topologically protected)

Is it possible to move them under an electrical field or other excitations?

Can we “write“ and „erase“ them at will?

Can such topological textures (or topological defects) be stabilised in ferroelectric HfO_2?

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1920 - 2020: 100-year anniversary

2021… exciting time to work on ferroelectrics!

Thank you for your attention

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