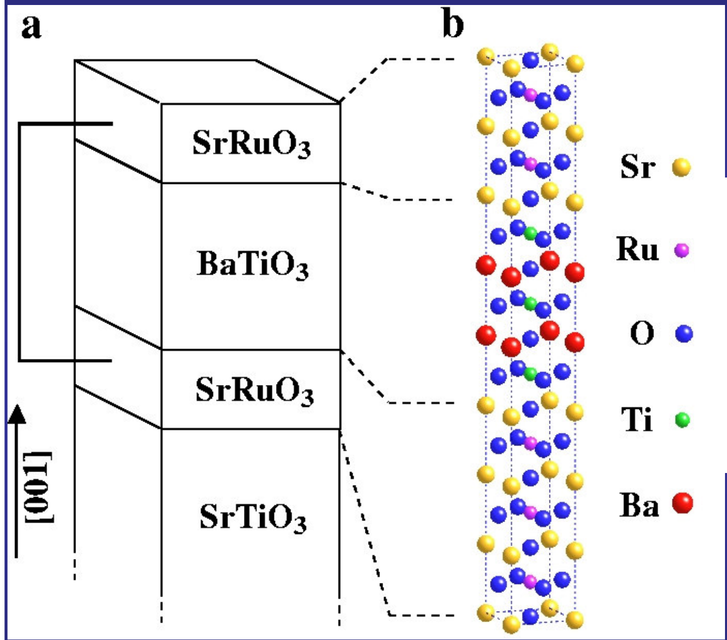
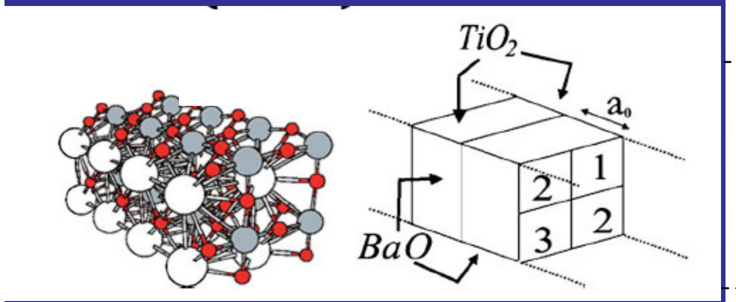
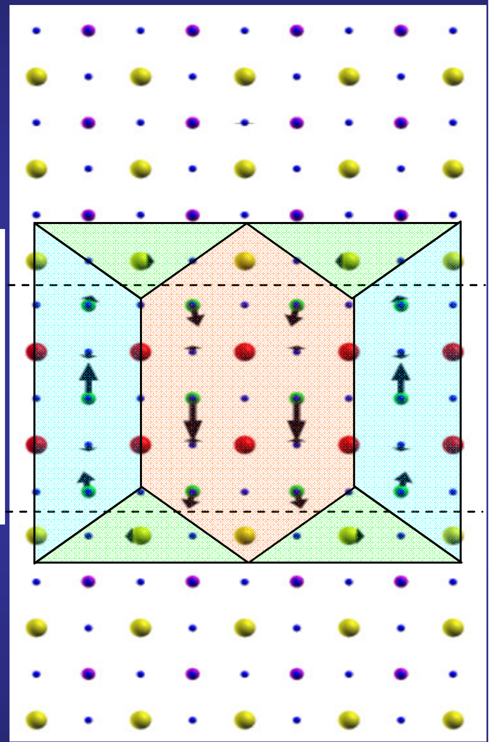
First-principles modeling of ferroelectric oxide nanostructures







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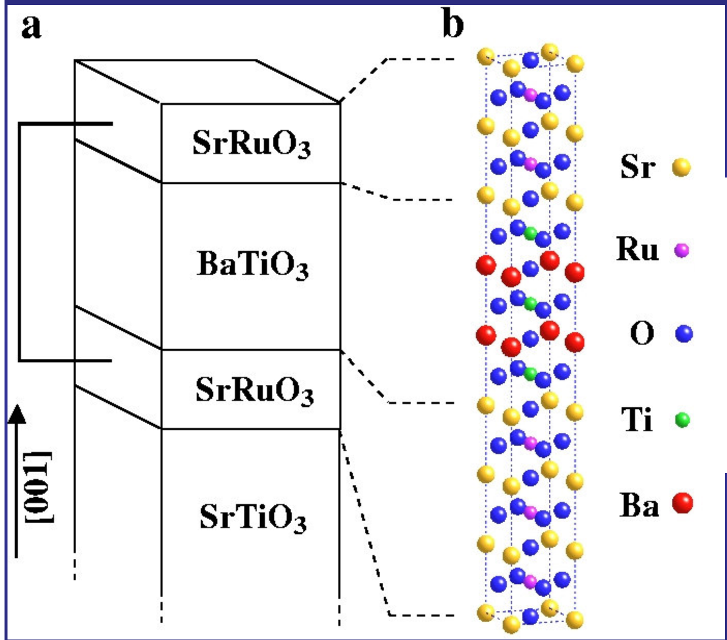
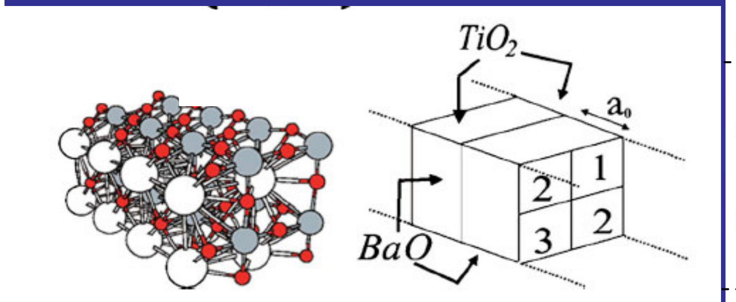
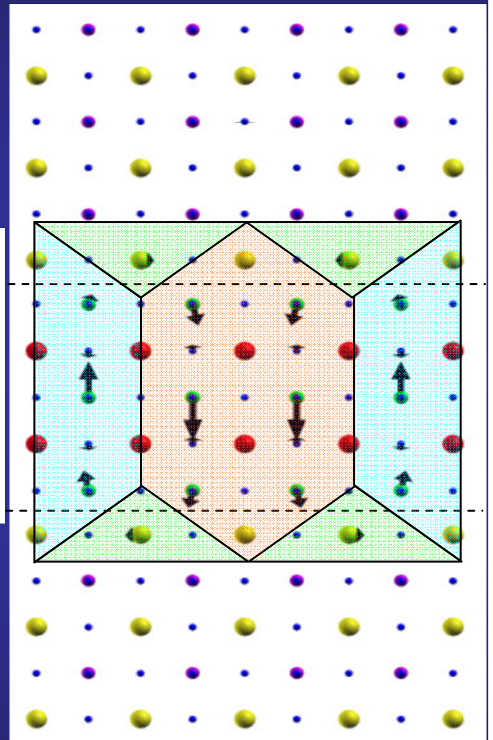
First-principles modeling of ferroelectric oxide nanostructures







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Transition metal oxide compounds

Simple structures with different phase transitions

Insulating

Semi-conducting

OXIDES

Metallic

Superconducting

Transition metal oxide compounds

Simple structures with different fundamental properties

Ferroelectricity

High T_c superconductivity

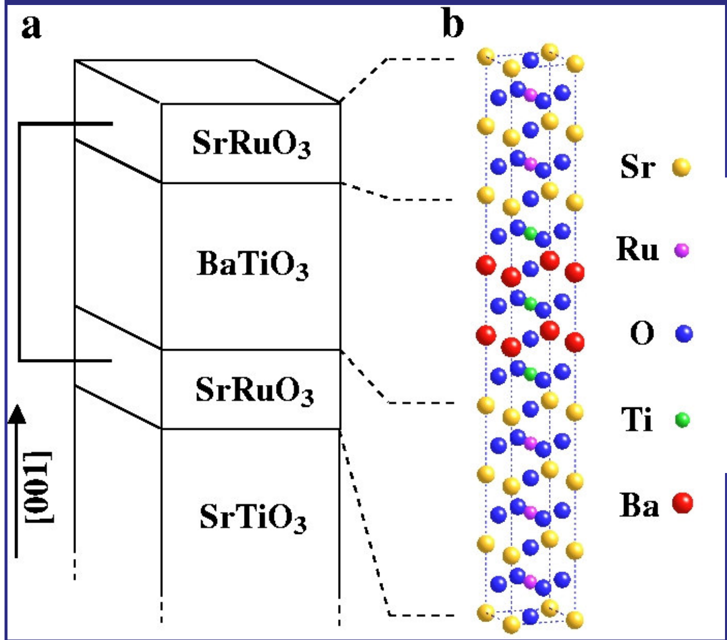
Ferromagnetism

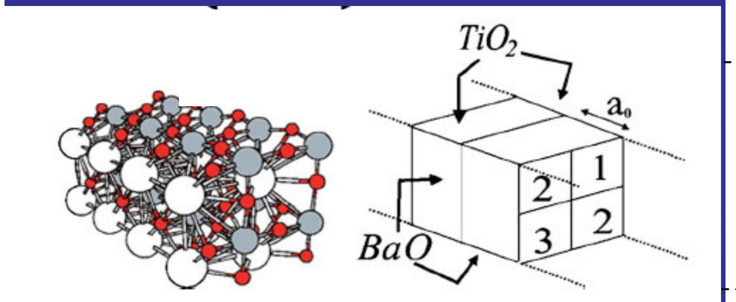
OXIDES

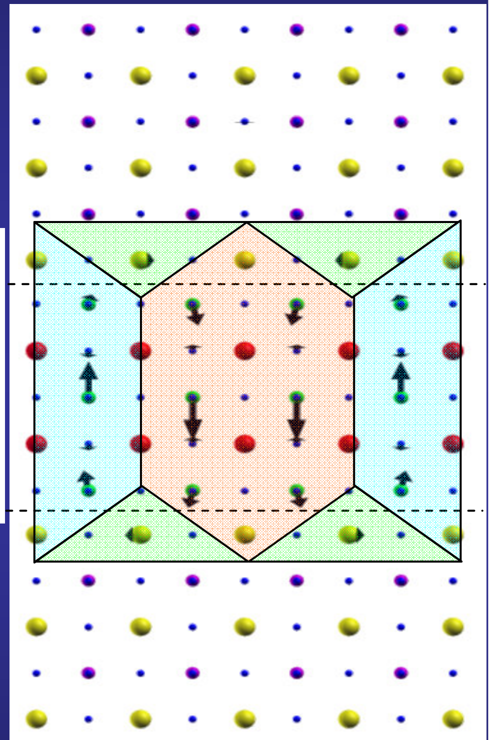
Colossal magnetoresistance

Multiferroics

First-principles modeling of ferroelectric oxide nanostructures







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Atomically precise methods for preparing thin films and multilayer structures

Methods

Pulsed Laser Deposition (PLD)

Molecular Beam Epitaxy (MBE)

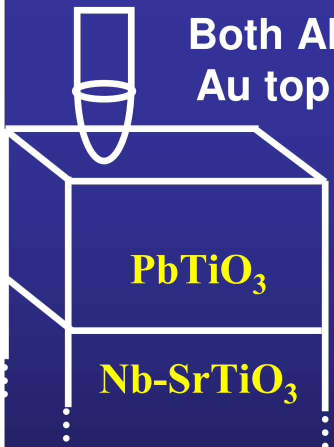
Off-axis rf magnetron sputtering

$\Rightarrow$

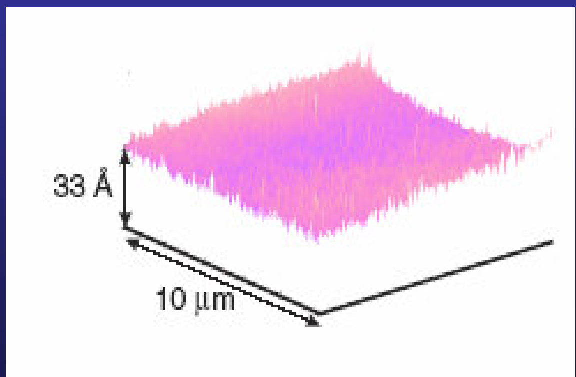
Control at the atomic level

Crystalline and surface quality ≈ semiconductor heterostructures

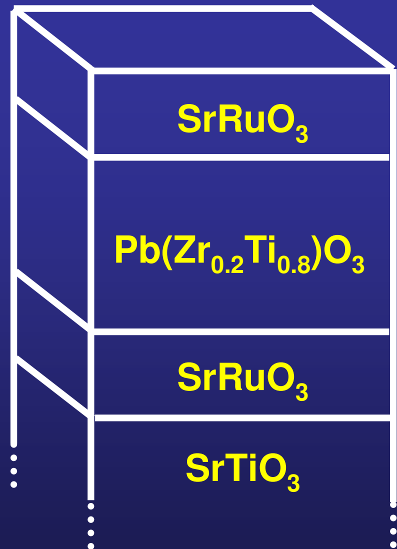
Both AFM tip and Au top electrode



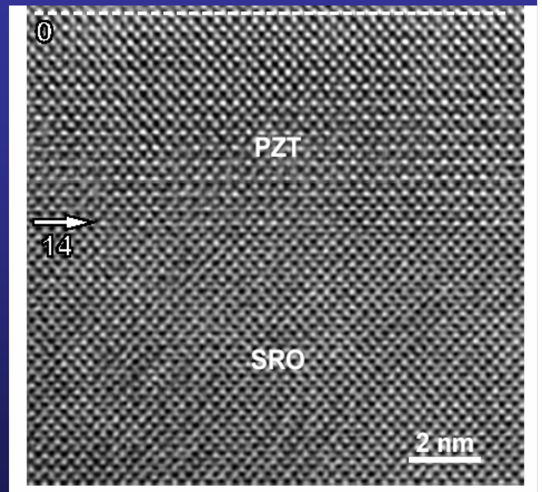
AFM



C. Lichtensteiger *et al.*, Phys. Rev. Lett. 94, 047603 (2005)



HRTEM



V. Nagarajan, J. Junquera *et al.*, J. Appl. Phys. 100, 051609 (2006)

Accurate characterization methods

Methods

X-ray scattering

- analysis of satellites
- COBRA

High resolution Transmission Electron Microscopy (HRTEM)

Reflection High-energy Electron Diffraction (RHEED)

Atomic Force Microscopy (AFM)

Piezoelectric Force Microscopy (PFM)

Photoemission based photoelectron diffraction (XPD)

PUND Hysteresis loops

…

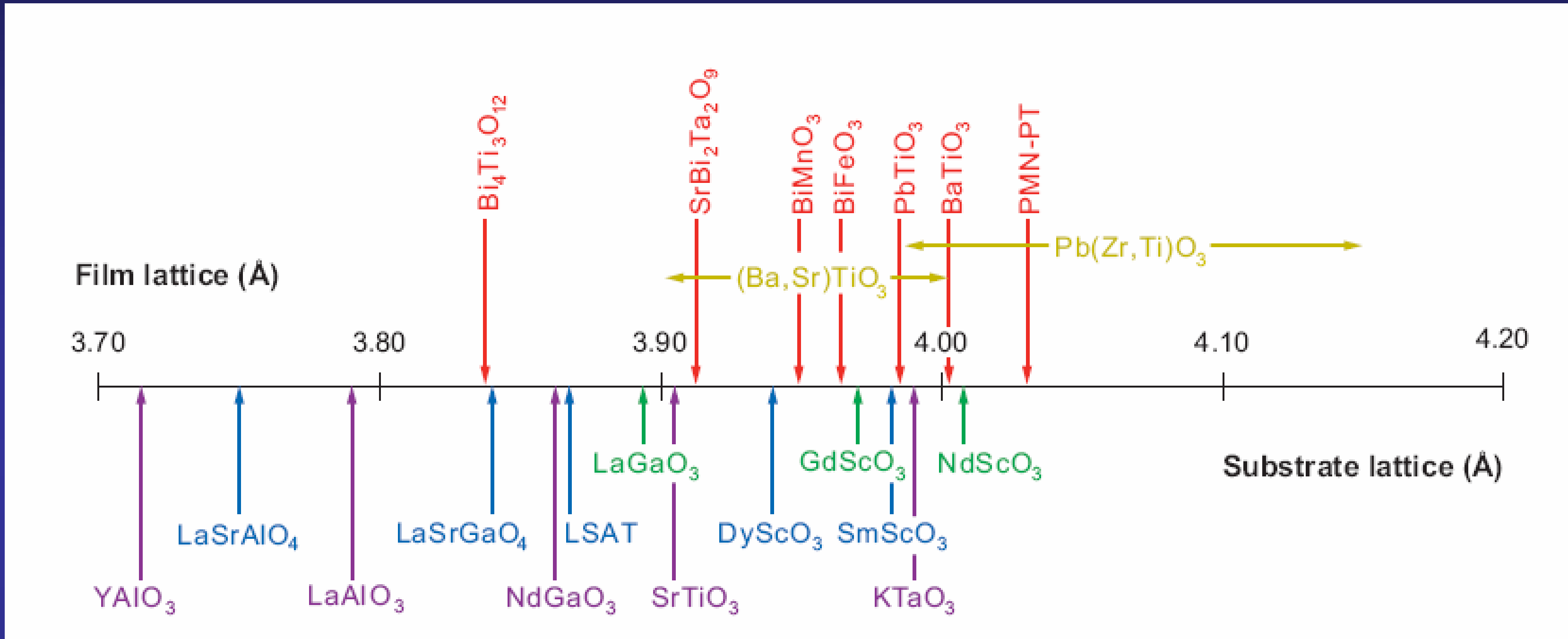
Results

High (atomic) resolution

Local proofs of:

- atomic structure
- piezoelectric properties
- ferroelectric properties

Many oxides have similar lattice constants allowing for a good match at the interfaces



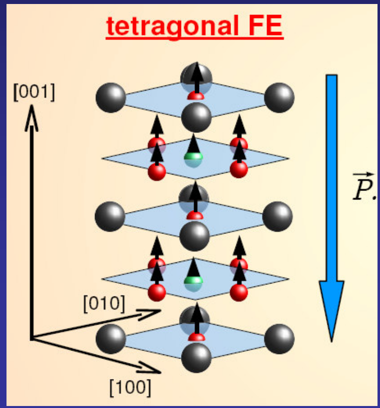
D. G. Schlom *et al.*, Annu. Rev. Mater. Res. 37, 589 (2007)

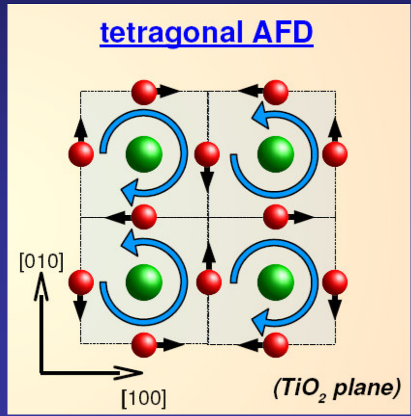
What would happen if we could mix materials with different properties?

Potential for novel behaviour

Some surprises at the interfaces between two oxides

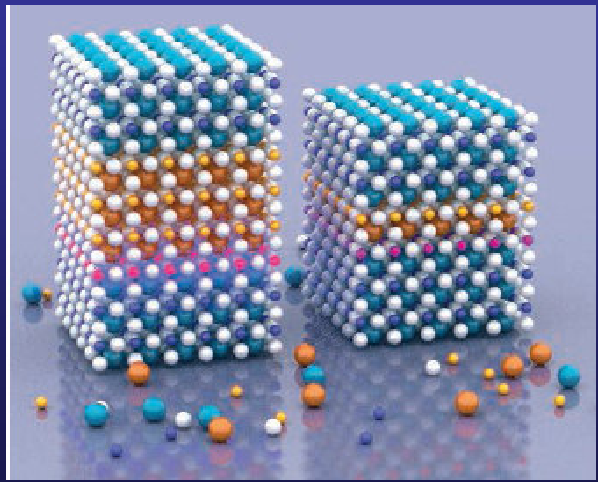
New type of ferroelectricity in $PbTiO_3/SrTiO_3$ superlattices





E. Bousquet *et al.*, Nature (in press)

The interface between two good insulators ($LaAlO_3$ and $SrTiO_3$) is metallic



A. Ohtomo and H. Y. Hwang, Nature 427, 423 (2004)

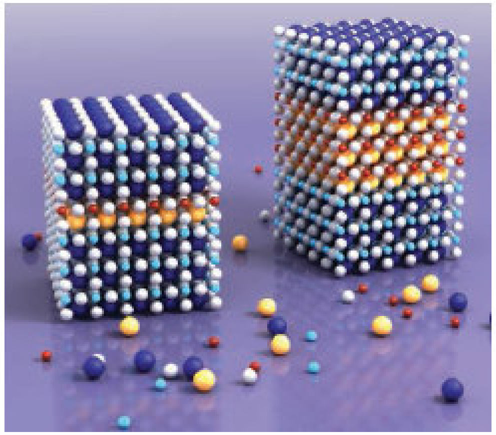
Recent discoveries on transition metal oxides: one of the "top tens" scientific breakthroughs of 2007

Breakthrough of the Year

5 BEYOND SILICON? Sixty years ago, semiconductors were a scientific curiosity. Then researchers tried putting one type of semiconductor up against another, and suddenly we had diodes, transistors, microprocessors, and the whole electronic age. Startling results this year may herald a similar burst of discoveries at the interfaces of a different class of materials: transition metal oxides.

Transition metal oxides first made headlines in 1986 with the Nobel Prize–winning discovery of high-temperature superconductors. Since then, solid-state physicists keep finding unexpected properties in these materials—including colossal magnetoresistance, in which small changes in applied magnetic fields cause huge changes in electrical resistance. But the fun should really start when one oxide rubs shoulders with another.

If different oxide crystals are grown in layers with sharp interfaces, the effect of one crystal structure on another can shift the positions of atoms at the interface, alter the population of electrons, and even change how



Tunable sandwich. In lanthanum aluminate sandwiched between layers of strontium titanate, a thick middle layer (*right*) produces conduction at the lower interface; a thin one does not.

Science, 318, 1846 (2007)

The field is still in an incipient stage, comparable to that of semiconductors 60 years ago

PERSPECTIVES

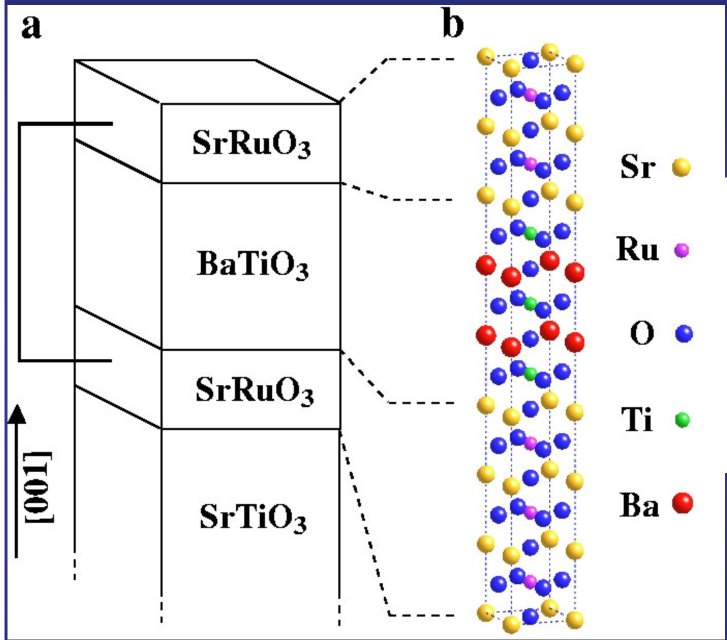
PHYSICS

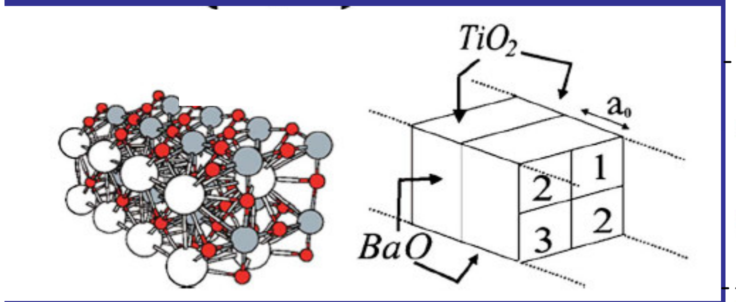
When Oxides Meet Face to Face

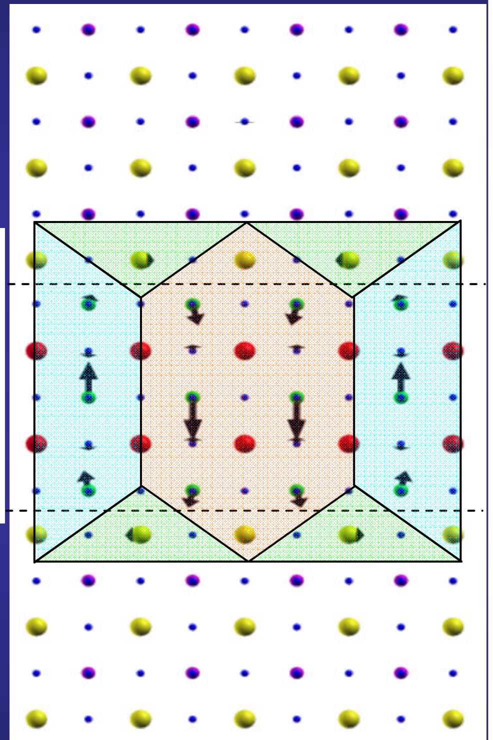
Elbio Dagotto

Despite recent activity, the field of oxide interfaces remains virtually unexplored. What might happen if we could mix materials with vastly different properties such as ferromagnets, antiferromagnets, superconductors, ferroelectrics, multiferroics, geometrically frustrated spin systems, heavy fermions, and others? Considering this enormous number of

First-principles modeling of ferroelectric oxide nanostructures







Javier Junquera

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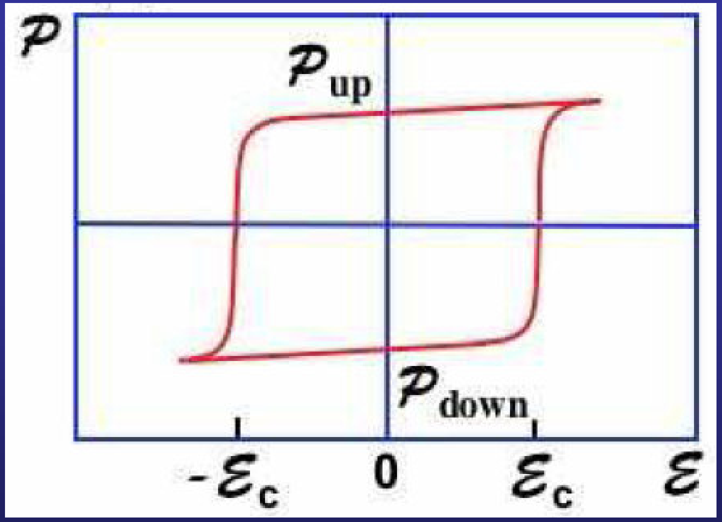
Ferroelectricity: Basic definitions

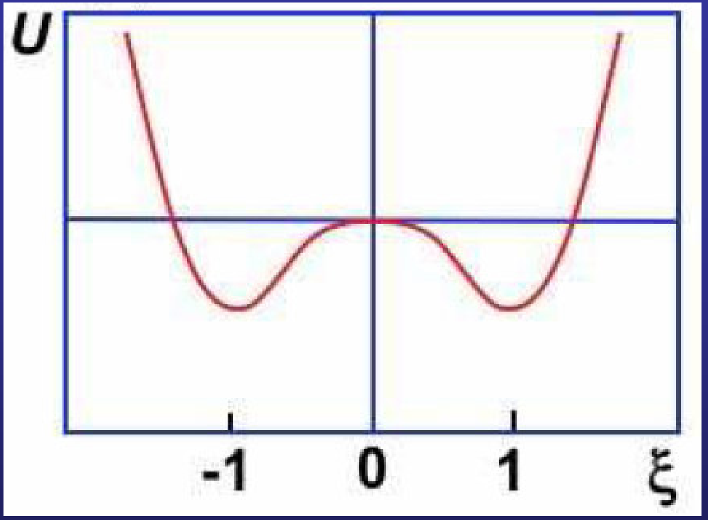
Existence of two or more states with a non-zero polarization in the absence of an electric field

Can be shifted from one to another of these states by the application of an electric field

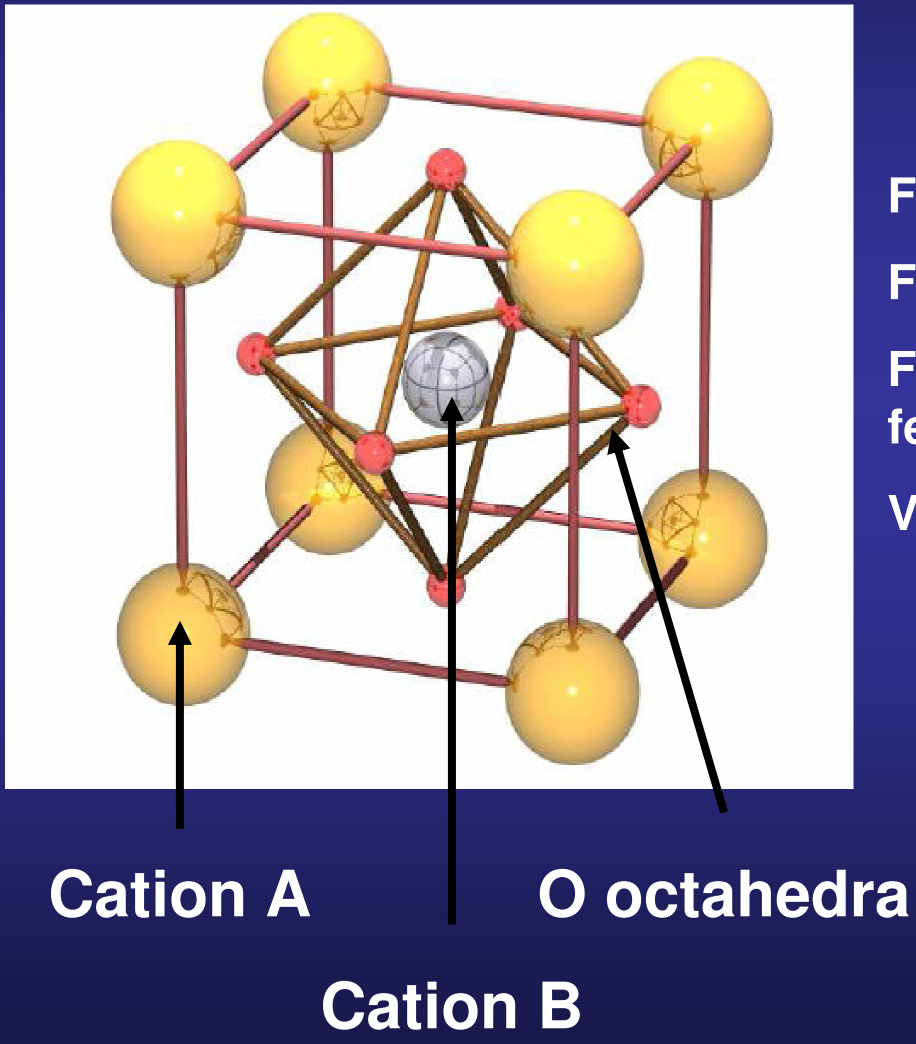
Hysteresis loop



Double well energy



Perovskite oxides ABO_3: prototypes of ferroelectric materiales



$BaTiO_3$

First ferroelectric without hydrogen bonds

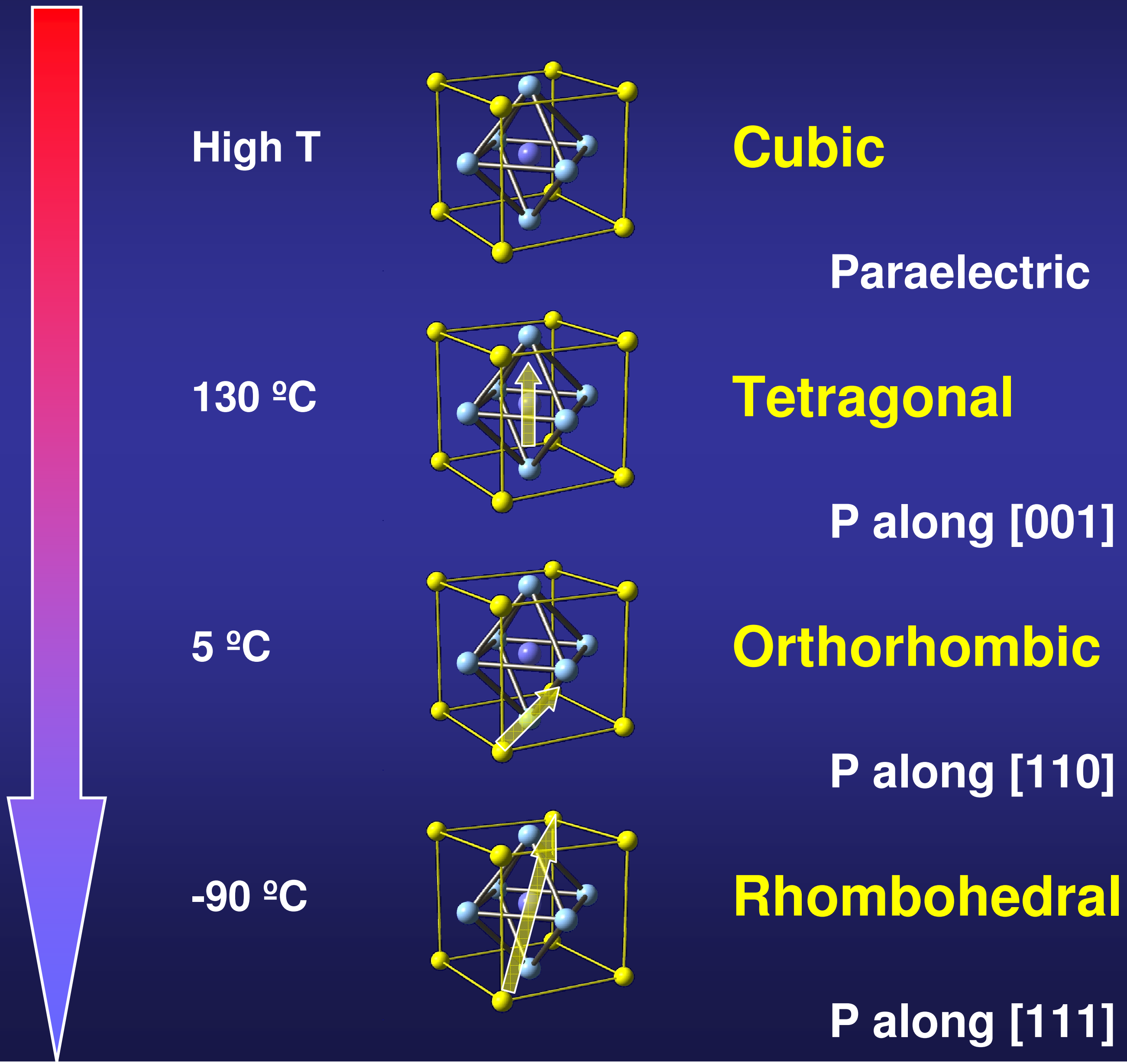
First ferroelectric with a paraelectric phase

First ferroelectric with more than one ferroelectric phase

Very simple (5 atoms per unit cell)

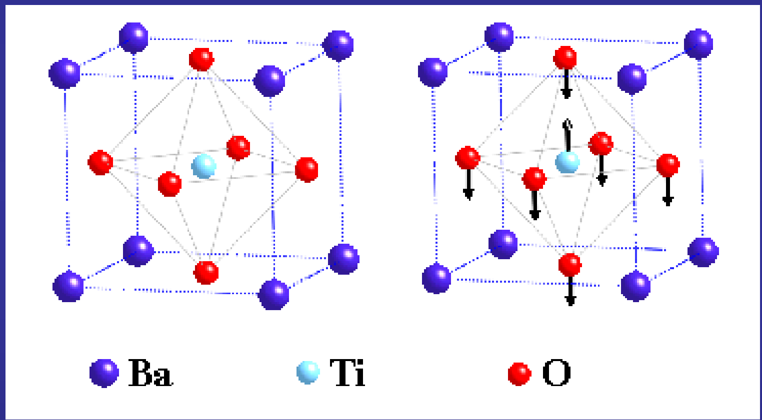
$\Rightarrow$ lot of theoretical models

Phase transitions of $BaTiO_3$ as a function of the temperature

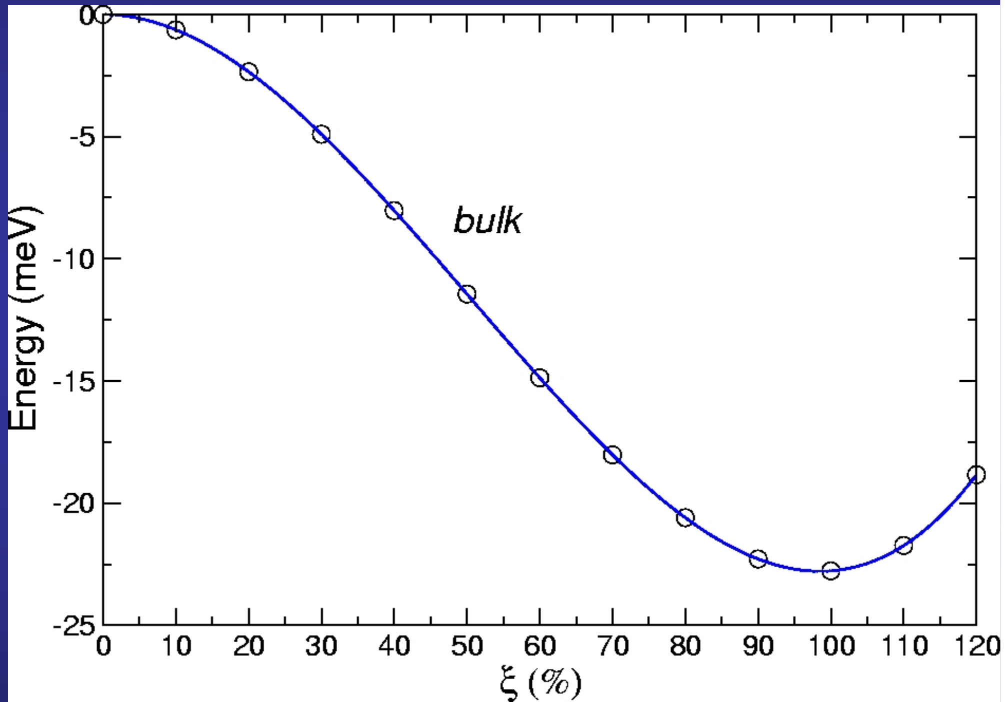


Phase transitions from cubic to tetragonal, pattern of cooperative polar atomic displacements

Paraelectric **Up**

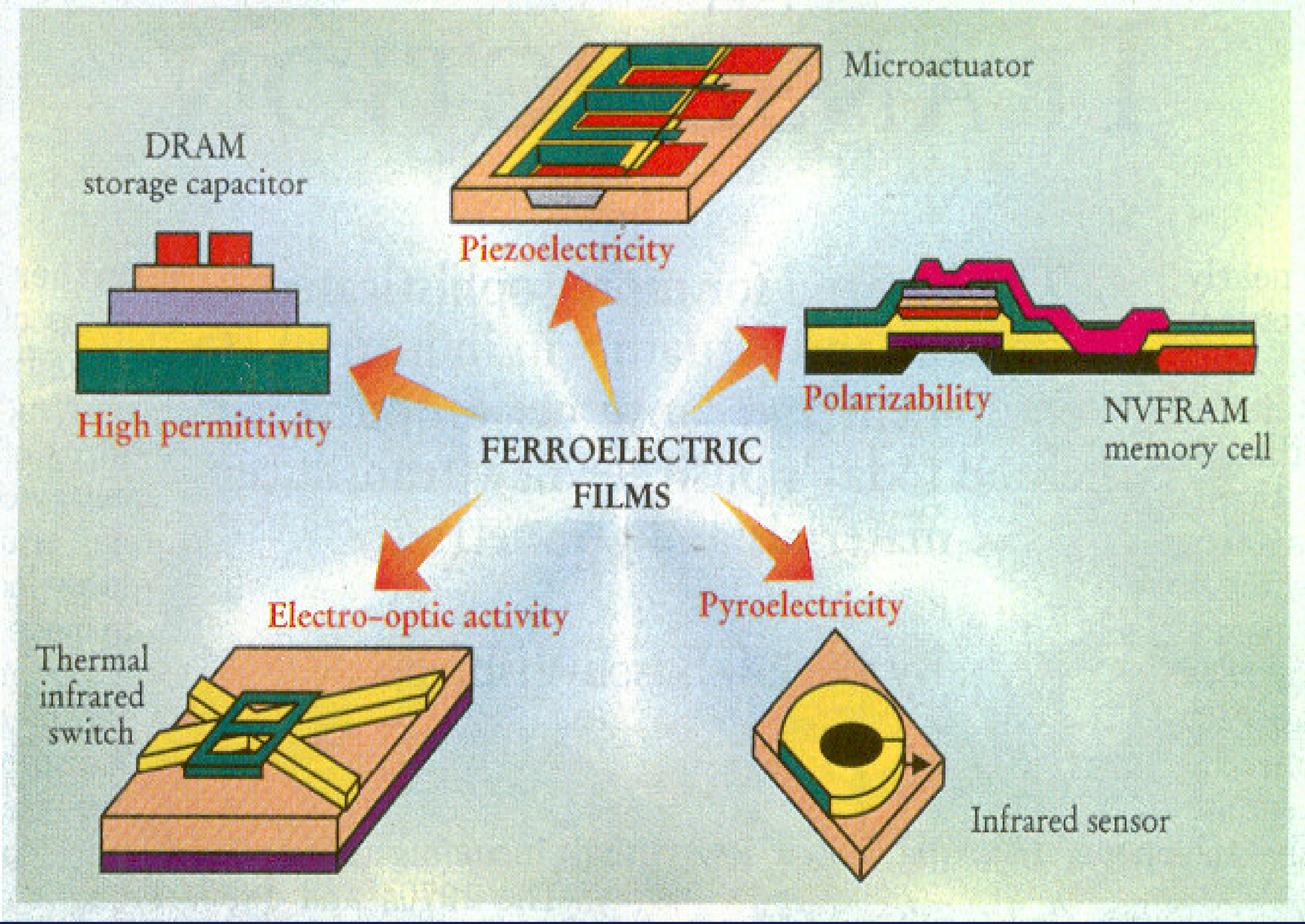


$\xi = 0$ $\xi = 1$



Continuum evolution of ξ

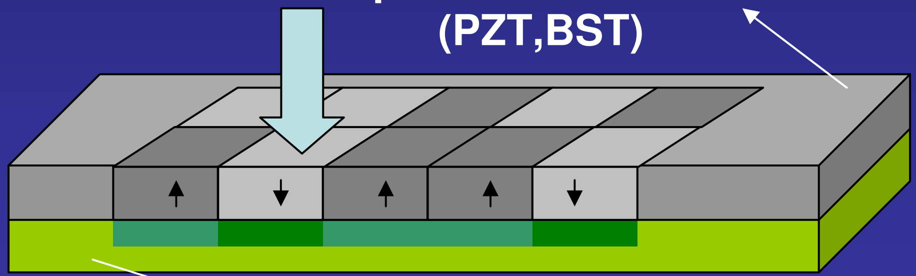
Technological applications: ABO_3 perovskites oxides as multifunctional materials



O. Auciello *et al.*, Physics Today July 1998, 22-27

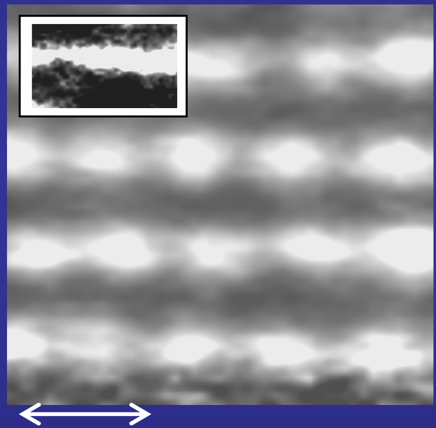
Many applications depend on the stability of films with a switchable polarization along the film normal

NV-FRAM



28 Gbit/cm^2

Line width < 20nm



100 nm

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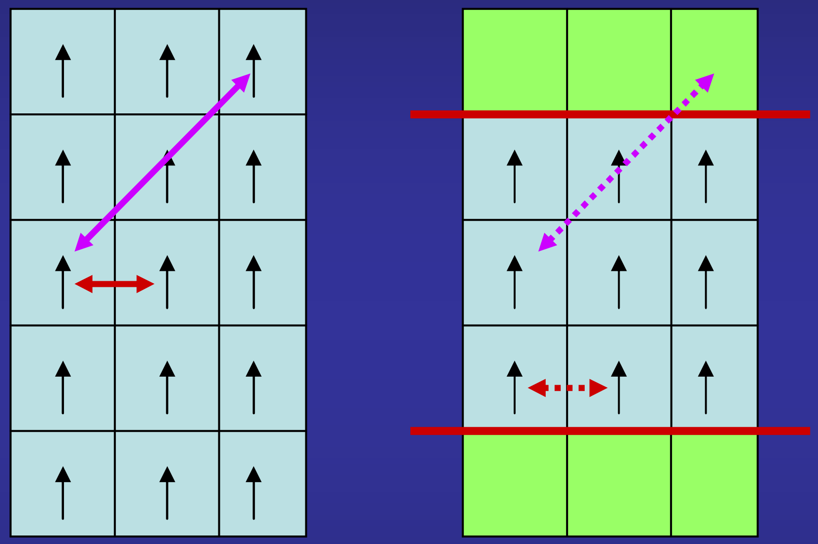
… is there a fundamental limit?

Ferroelectricity is a collective effect with delicate balance between short and long range interactions

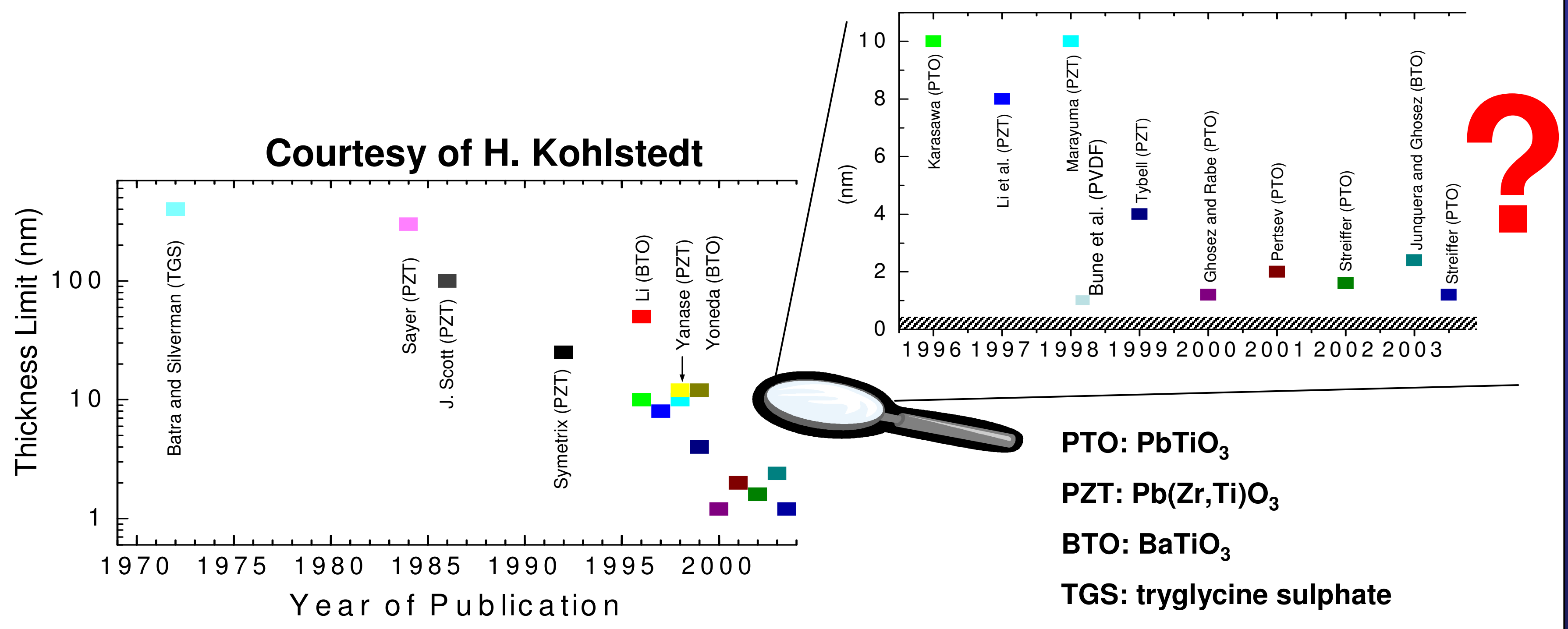


Both interactions strongly affected in small particles and thin films

Finite size effect: a subtle problem

Fundamental motivation: what's the most stable phase for epitaxial ferroelectric ultrathin films?

- **Long time question.**
- **Hot field.**



PTO: $PbTiO_3$

PZT: $Pb(Zr,Ti)O_3$

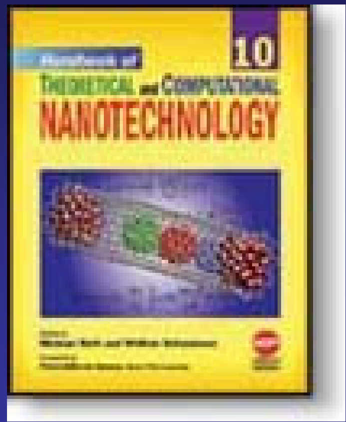
BTO: $BaTiO_3$

TGS: tryglycine sulphate

PVDF: Ferroelectric polymer

A few unit cells might be ferroelectric!

Recent reviews on state-of-the-art on size effects in ferroelectric nanostructures



Ph. Ghosez and J. Junquera, *First-Principles Modeling of Ferroelectric Oxide Nanostructures*, *Handbook of Theoretical and Computational Nanotechnology*, Vol. 9, Chap. 13, 623-728 (2006)

(http://xxx.lanl.gov/pdf/cond-mat/0605299)

First-principles study of ferroelectric oxide epitaxial thin films and superlattices: role of the mechanical and electrical boundary conditions

Javier Junquera

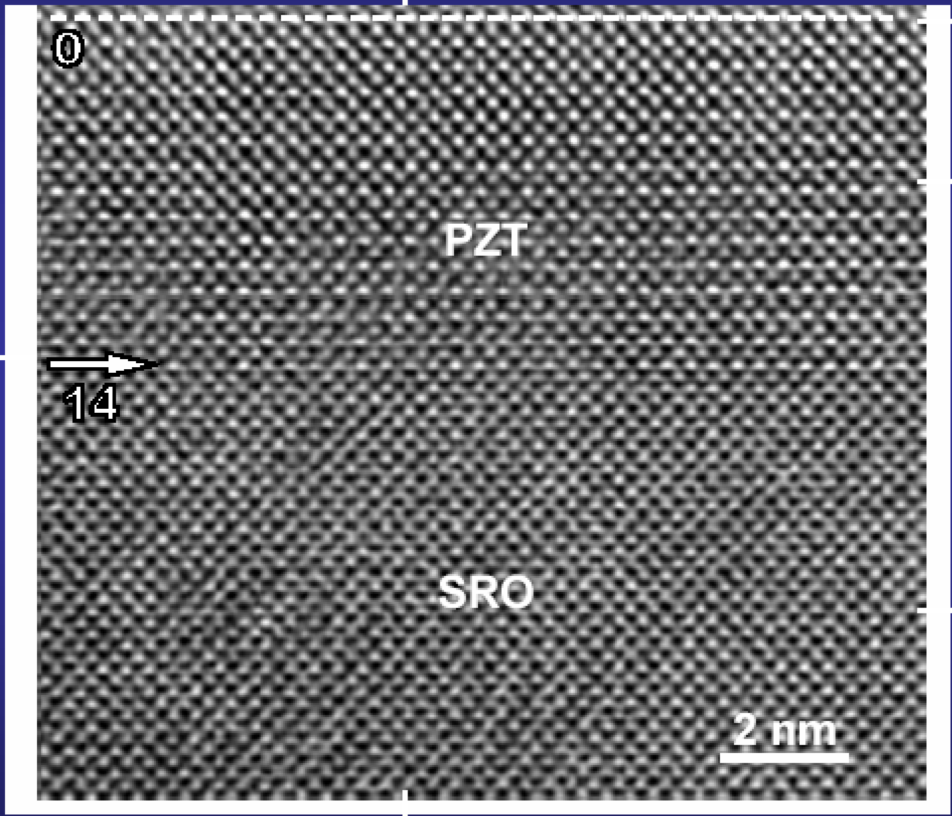
Departamento de Ciencias de la Tierra y Física de la Materia Condensada, Universidad de Cantabria, Avda. de los Castros s/n, E-39005 Santander, Spain

Philippe Ghosez

Physique Théorique des Matériaux, Université de Liège, B-4000 Sart Tilman, Belgium

arXiv:0711.4201v1 [cond-mat.mtrl-sci] 27 Nov 2007

Many effects might alter the delicate balance between long and short range forces



Chemistry

Electrostatic

Surface

Defects

(vacancies, misfit dislocations…)

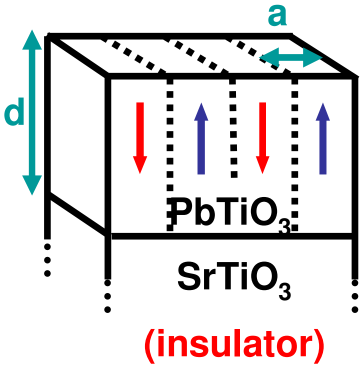
Finite conductivity

Mechanical

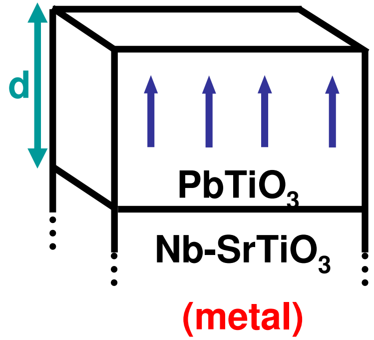
Experimental measurements,

global result

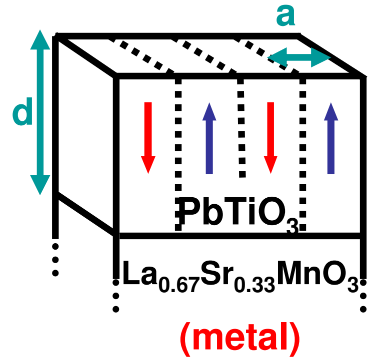
Experimentally: small changes in boundary conditions, great changes in stable state



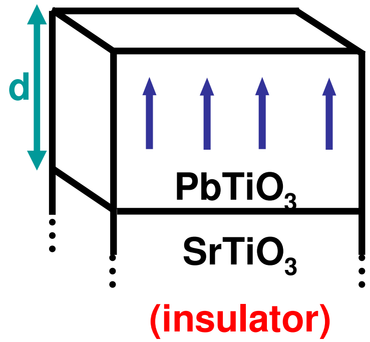
D. D. Fong et al. (2004)
S. K. Streiffer et al. (2002)



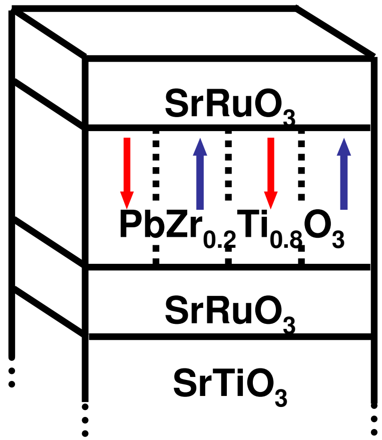
C. Lichtensteiger et al. (2005)
A. T. J. van Helvoort et al. (2005)



C. Lichtensteiger et al. (2007)

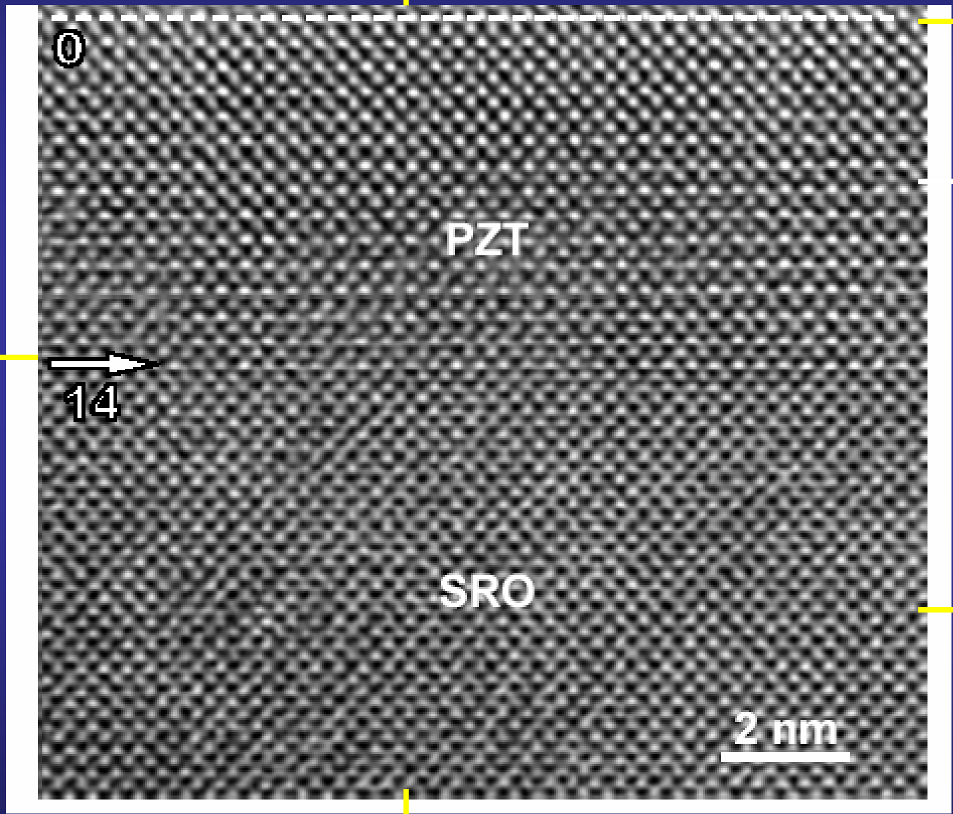


D. D. Fong et al. (2005)



V. Nagarajan et al. (2006)

First-principles calculations allow to isolate their respective influence



Surface

Defects

(vacancies, misfit dislocations…)

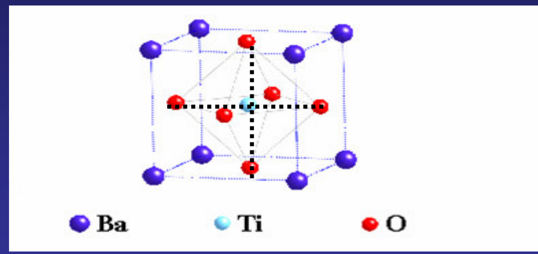
Finite conductivity

Mechanical

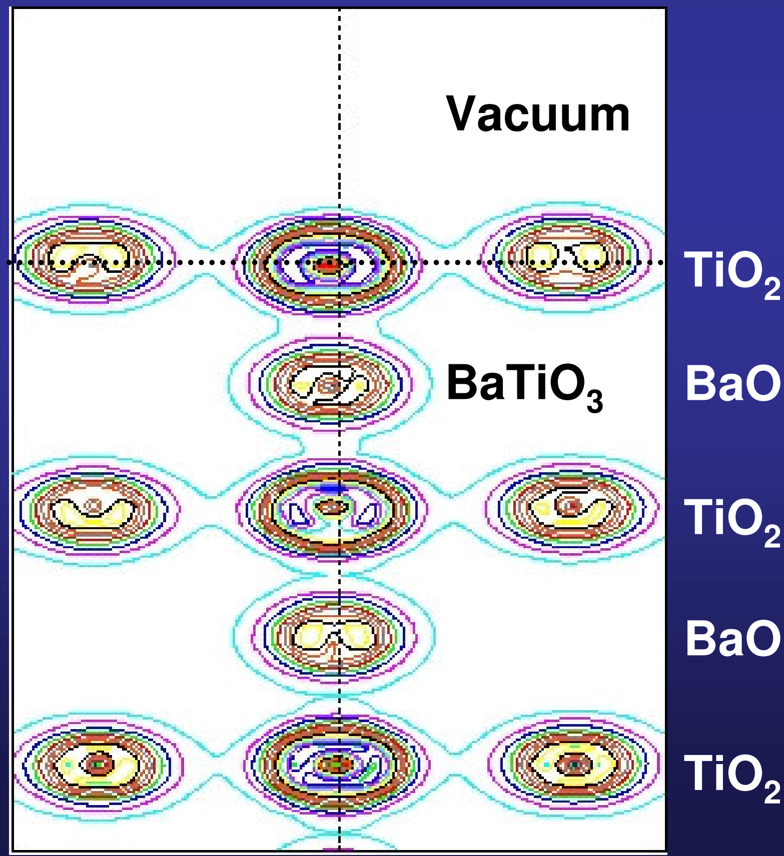
Chemistry

Electrostatic

Surface effects
Some questions that might be answered *ab-initio*



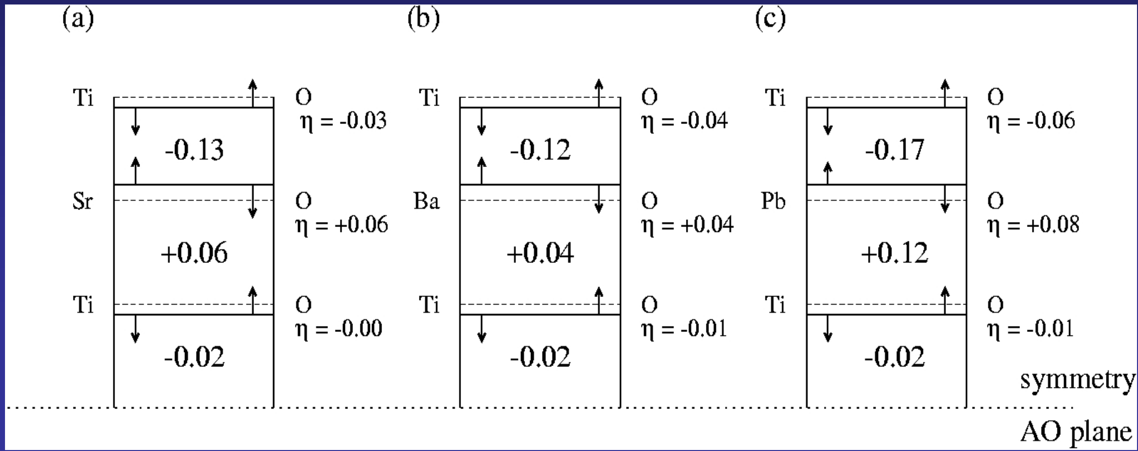
- Missing of Ti 3d-O 2p hybridization
- Intrinsic degradation of the polarization?
- Coupling of the polarization with surface-induced relaxations and reconstructions
- Influence of surface termination



The presence of a surface induces atomic relaxations

(001) TiO_2-terminated

$SrTiO_3$ $BaTiO_3$ $PbTiO_3$



Paraelectric structure

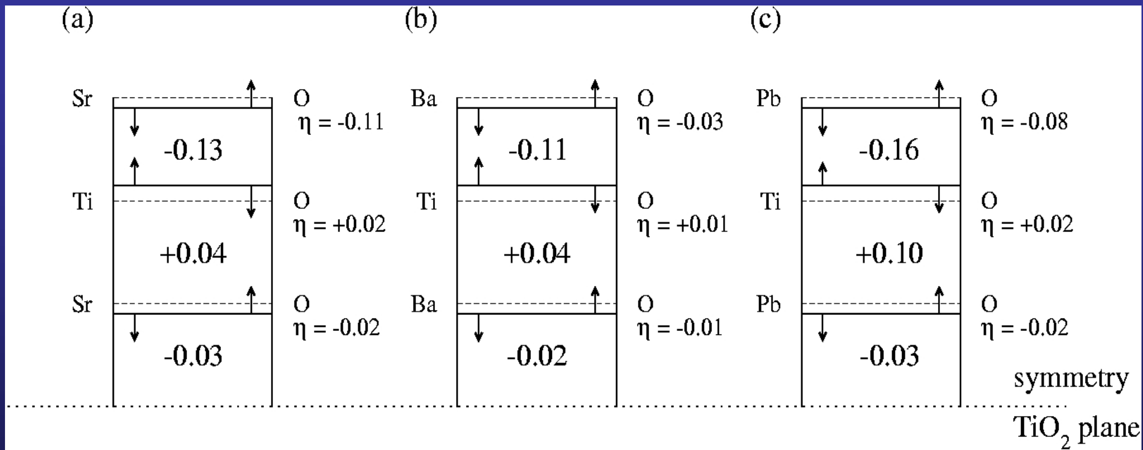
Cubic

Theoretical in-plane lattice param.

(1×1) surface reconstruction

Units in Å

(001) AO-terminated



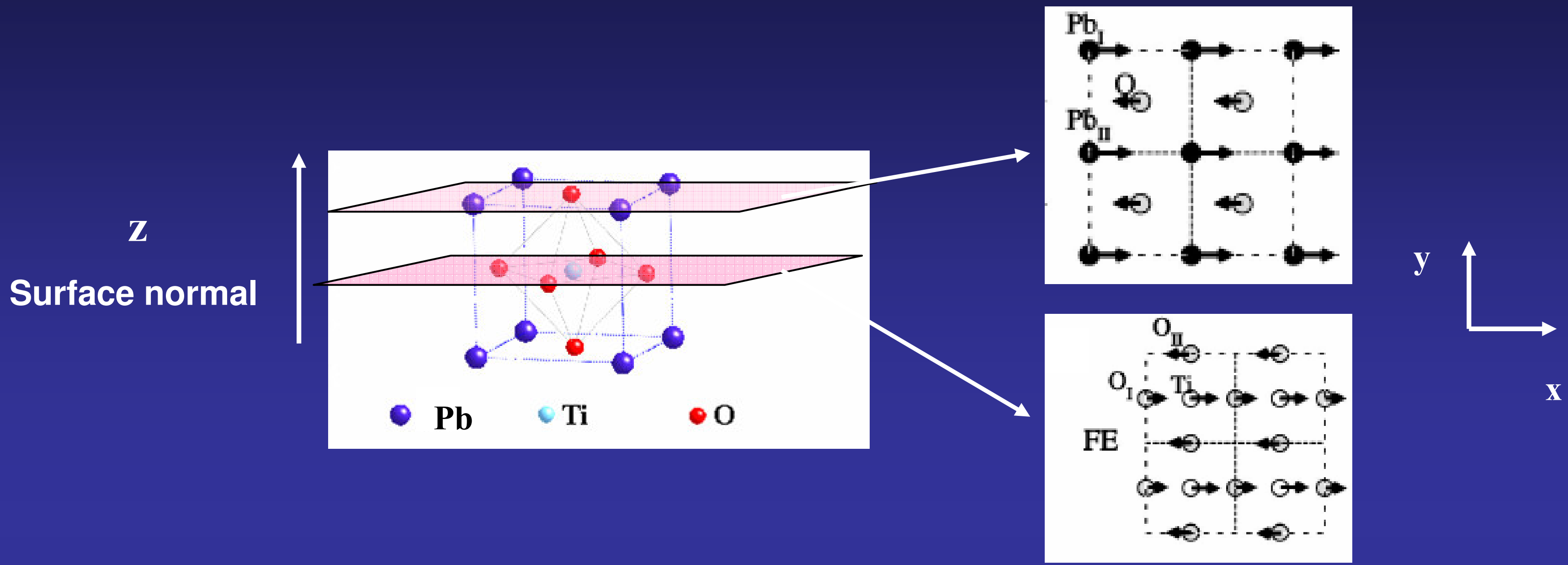
- •Largest relaxations: surface atoms
- •Surface layer contracts inwards
- •Rumpling of the layers gives rise to ionic surface dipole
- •Oscillating relaxation pattern
- •Relaxation energy (100 meV) >> bulk ferroelectric well (30-50 meV)

J. Padilla and D. Vanderbilt, Surface Science 418, 64 (1998)

J. Padilla and D. Vanderbilt, Phys. Rev. B 56, 1625 (1997)

B. Meyer *et al.*, Faraday Discussions 114, 395 (1999)

Coupling of the surface with in-plane polarization



Small influence of surface relaxation on in-plane ferroelectricity

	$BaTiO_3$	$PbTiO_3$	$SrTiO_3$
TiO_2-terminated	Slightly $\uparrow$	Slightly $\downarrow$	
AO-terminated	Slightly $\downarrow$	Slightly $\uparrow$	Very modest (likely destroyed by T)

J. Padilla and D. Vanderbilt, Surface Science 418, 64 (1998)

J. Padilla and D. Vanderbilt, Phys. Rev. B 56, 1625 (1997)

B. Meyer *et al.*, Faraday Discussions 114, 395 (1999)

Surface might induced reconstructions to saturate dangling bonds

(001) $PbTiO_3$

c(2×2) reconstructions in PbO-terminated

substantial enhancement of the AFD distorsion

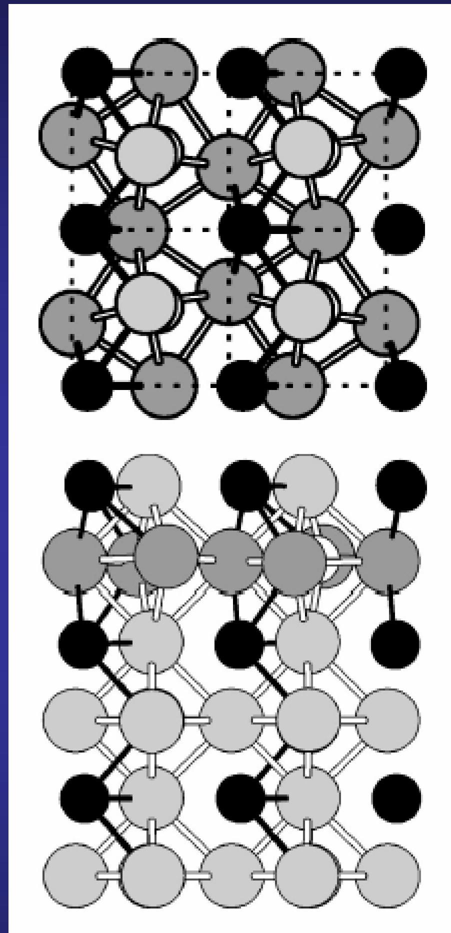
Driving force: shorter PbO bonds

⇓

Not observed neither in TiO_2 termination
nor $BaTiO_3$ surface

A. Munkholm *et al*., Phys. Rev. Lett. 88, 016101 (2002)

C. Bungaro and K. M. Rabe, Phys. Rev. B 71, 035420 (2005)



(001) $SrTiO_3$

Experimentally: (2×1) reconstruction

N. Erdman *et al.* Nature 419, 55 (2002)

Theoretically: (1×1) reconstruction

K. Johnston *et al*., Phys. Rev. B 70, 085415 (2004)

Mechanical effects
Some questions that might be answered *ab-initio*

• Strong coupling of homogeneous and inhomogeneous strain with P

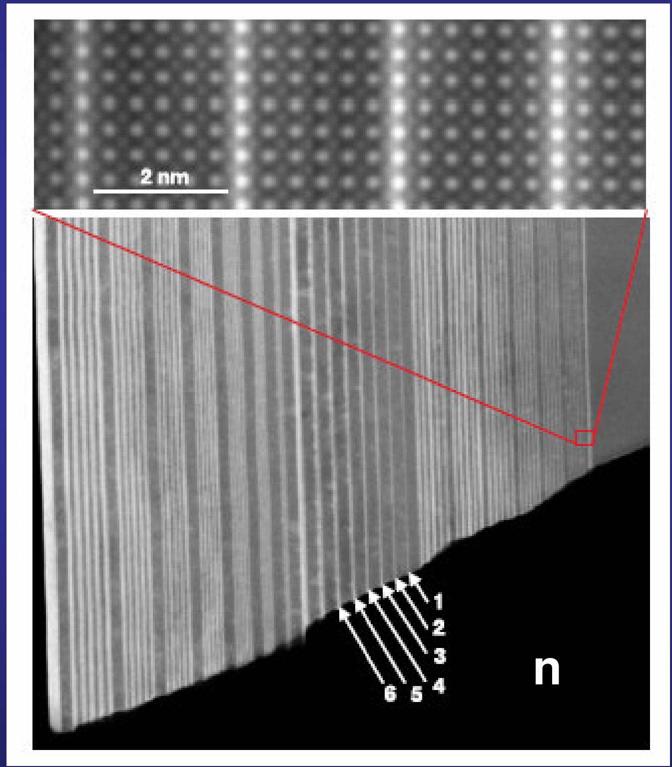
• Strain engineering

- tune specific properties by choosing substrate
- appearance of new phases

• Role of misfit dislocation

$SrTiO_3/LaTiO_3$

(5×n)



n=1

Ohtomo, Nature 419, 378 (2002)

Recent reviews on strain effects in epitaxial ferroelectric oxides

Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Current Opinion in Solid State and Materials Science 9 (2005) 122–127
Current Opinion in **Solid State & Materials Science**

Theoretical investigations of epitaxial strain effects in ferroelectric oxide thin films and superlattices

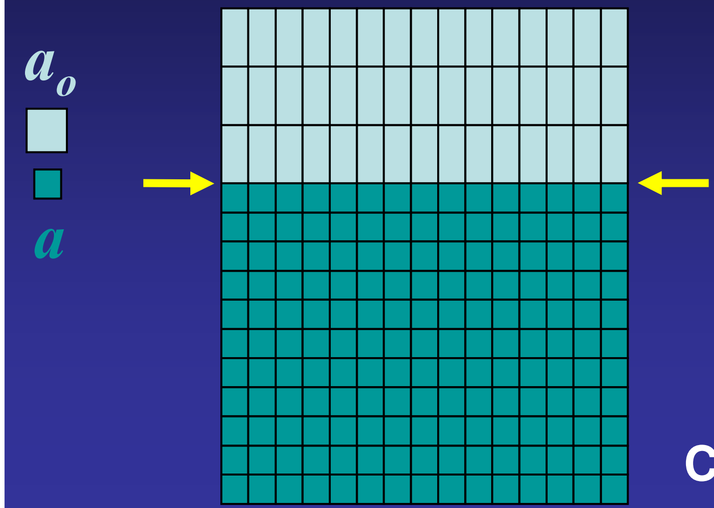
Karin M. Rabe *

Strain Tuning of Ferroelectric Thin Films*

Darrell G. Schlom,[1,†] Long-Qing Chen,[2] Chang-Beom Eom,[3] Karin M. Rabe,[4] Stephen K. Streiffer,[5] and Jean-Marc Triscone[6]

Annu. Rev. Mater. Res. 2007. 37:589–626

Strain imposed by the substrate affects the properties of ferroelectric materials



misfit strain

$u_m = (a - a_o)/a_o$

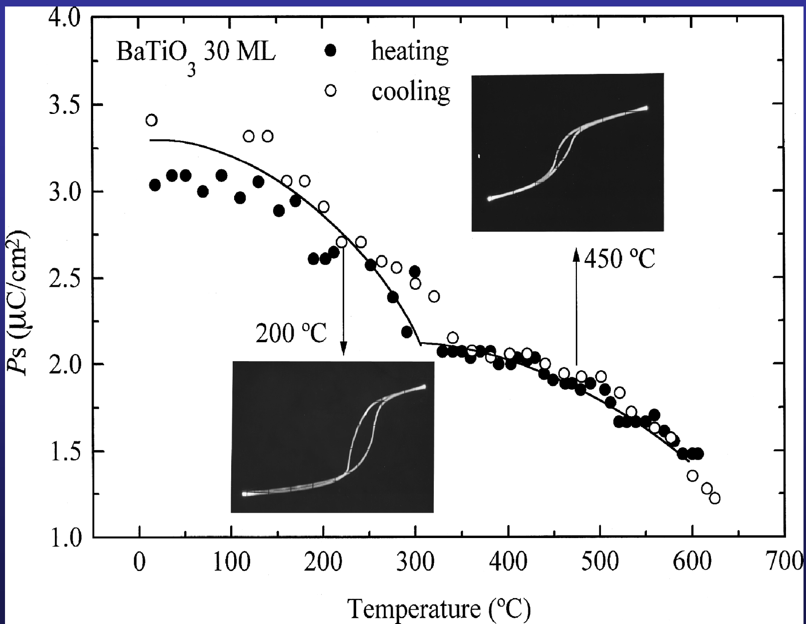
Example:

$BaTiO_3$ $a_o = 4.00$ Å

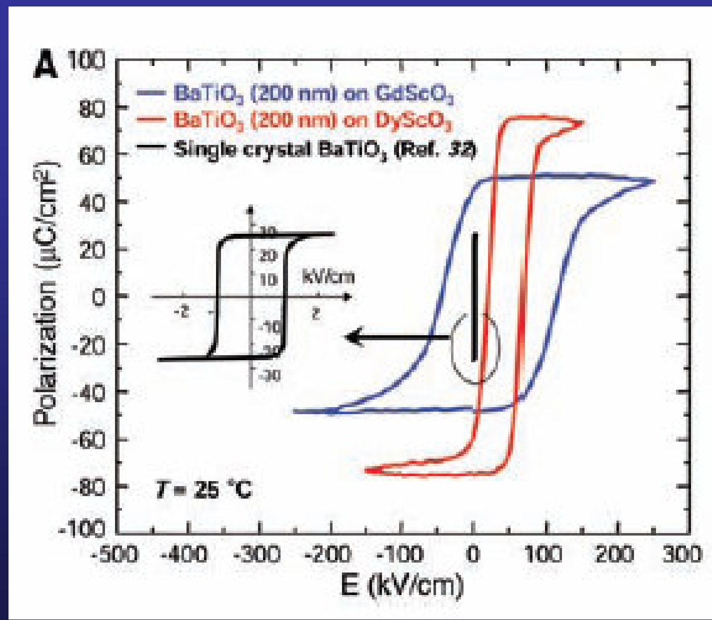
$SrTiO_3$ $a = 3.91$ Å

$u_m = -22.5 \times 10^{-3}$

Courtesy of O. Diéguez



Yoneda *et al.*, J. Appl. Phys. 83, 2458 (1998)



K. J. Choi *et al.*, Science 306, 1005 (2004)

Pertsev *et al*. mapping the equilibrium structure as a function of T and strain

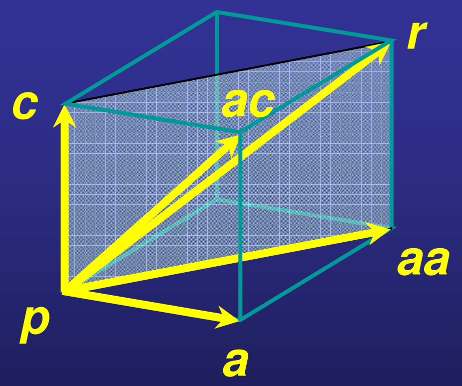
- The free energy is written as a function of polarization and strain.
- Temperature incorporated via a linear dependence of some expansion coefficients
- Infinite solid (no interface nor surface) subject to homogeneous strain
- Parameters are taken from experiments near bulk FE transition
- The most stable phase is found by minimizing the free energy

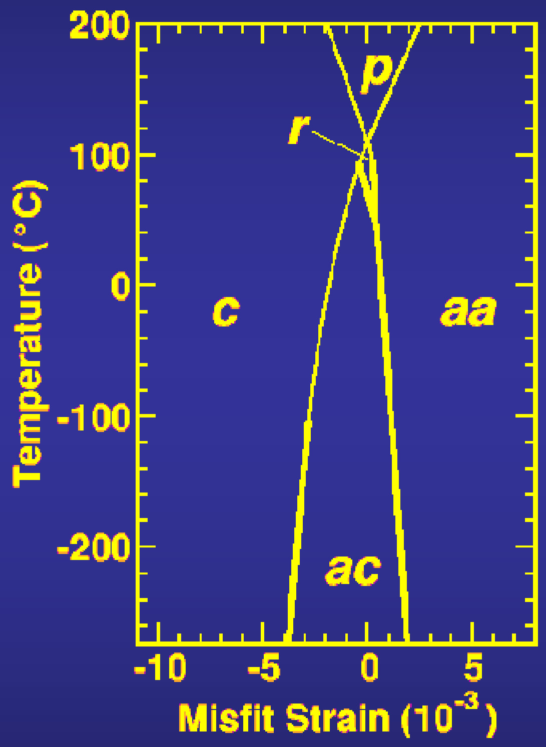
$$\begin{aligned}\tilde{G} \quad = \quad & a_1^*(P_1^2+P_2^2)+a_3^*P_3^2+a_{11}^*(P_1^4+P_2^4)+a_{12}^*P_1^2P_2^2 \\ & +a_{13}^*(P_1^2P_3^2+P_2^2P_3^2)+a_{33}^*P_3^4+a_{111}(P_1^6+P_2^6+P_3^6)+a_{123}P_1^2P_2^2P_3^2 \\ & +a_{112}[P_1^4(P_2^2+P_3^2)+P_2^4(P_3^2+P_1^2)+P_3^4(P_1^2+P_2^2)]+u_m^2/(s_{11}+s_{12})\end{aligned}$$

$$a_1^* = a_1^*(T,u_m);\ a_3^* = a_3^*(T,u_m);\ a_{11}^* = a_{11}^*(T);\ a_{33}^* = a_{33}^*(T);\ a_{123} = a_{123}(T)$$

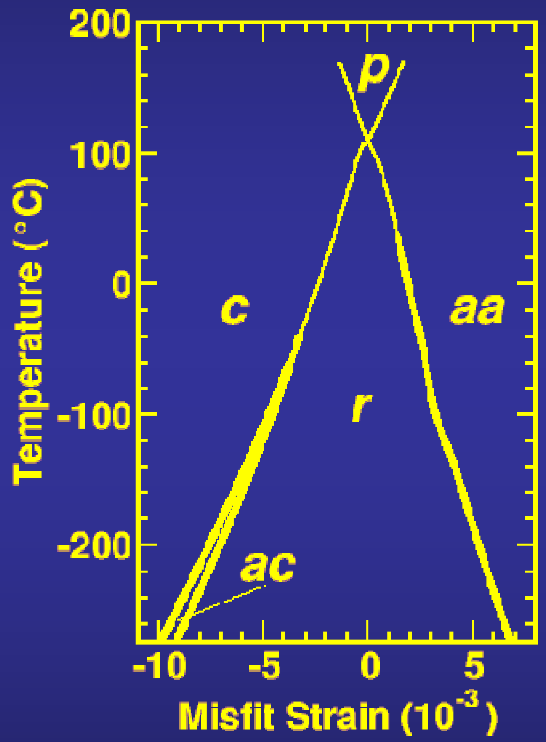
N. A. Pertsev, A. G. Zembilgotov, A. K. Tagantsev Phys. Rev. Lett. 80, 1988 (1998)

Pertsev *et al.* obtained a semiempirical phase diagram for epitaxial $BaTiO_3$





Parameters:
PRL 80, 1988 (1998)

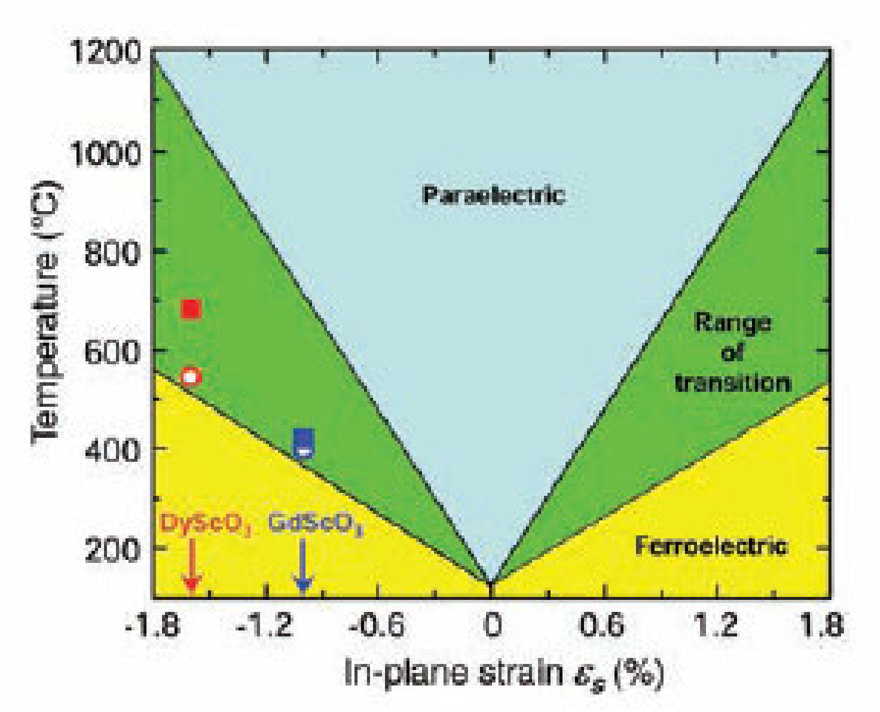


Parameters:
PRB 64, 214103 (2001)

Courtesy of O. Diéguez

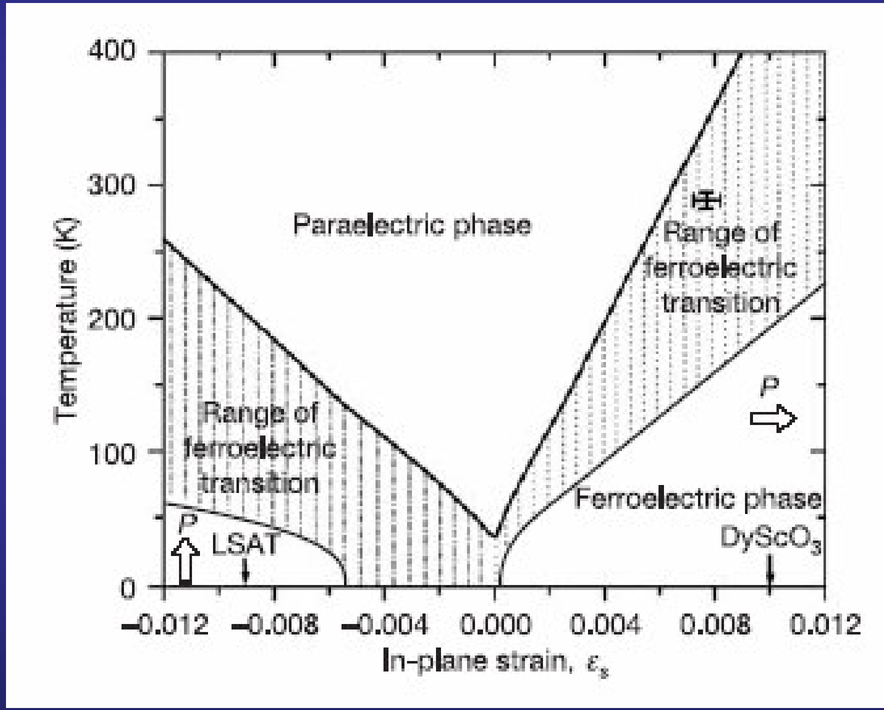
The scattering in the reported parameters produces "range of transitions" rather than clean boundaries

$BaTiO_3$



K. J. Choi *et al.*, Science 306, 1005 (2004)

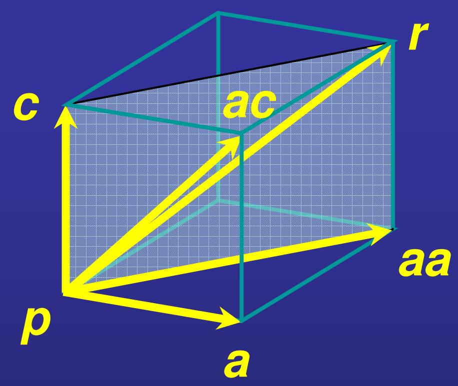
$SrTiO_3$

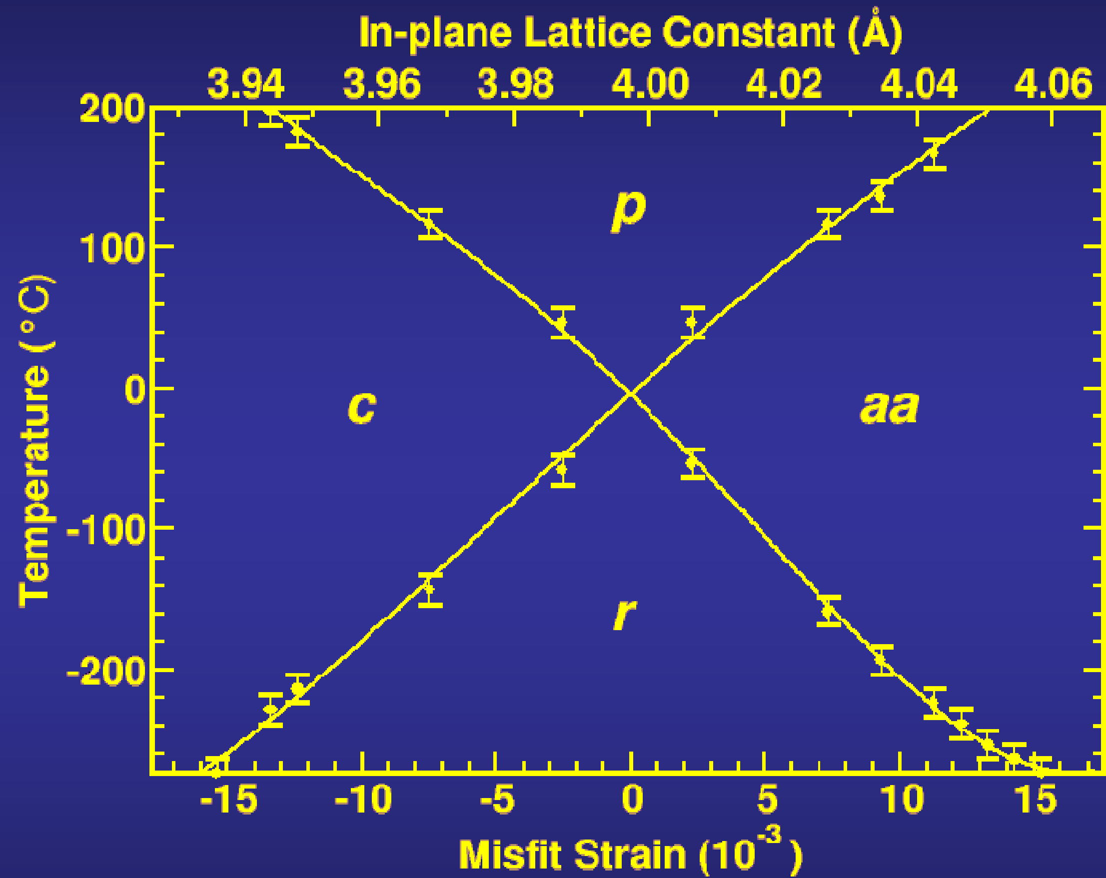


J. H. Haeni *et al.*, Nature 430, 758 (2004)

First-principles phase diagram for epitaxial $BaTiO_3$ resolve earlier discrepancy

No *ac* phase



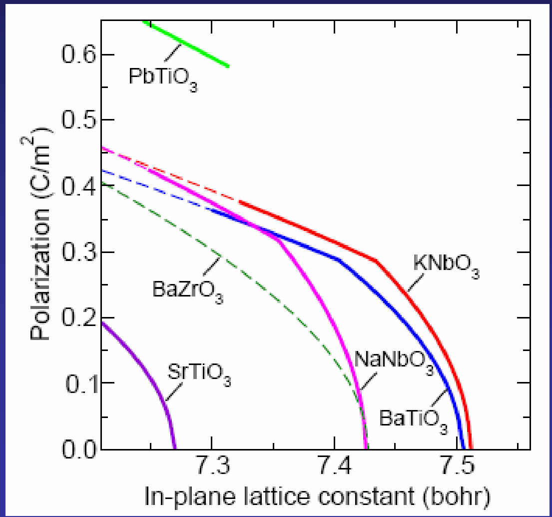


O. Diéguez *et al.*, Phys. Rev. B 69, 212101 (2004)

B. Lai *et al.*, Appl. Phys. Lett. 86, 132904 (2005)

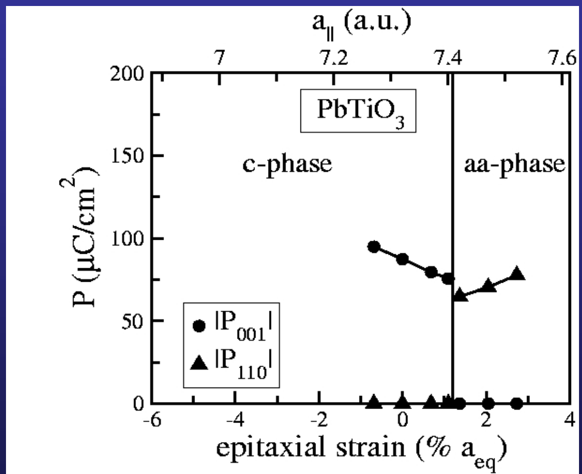
Courtesy of O. Diéguez

Other perovskites epitaxially grown on a cubic substrate theoretically explored



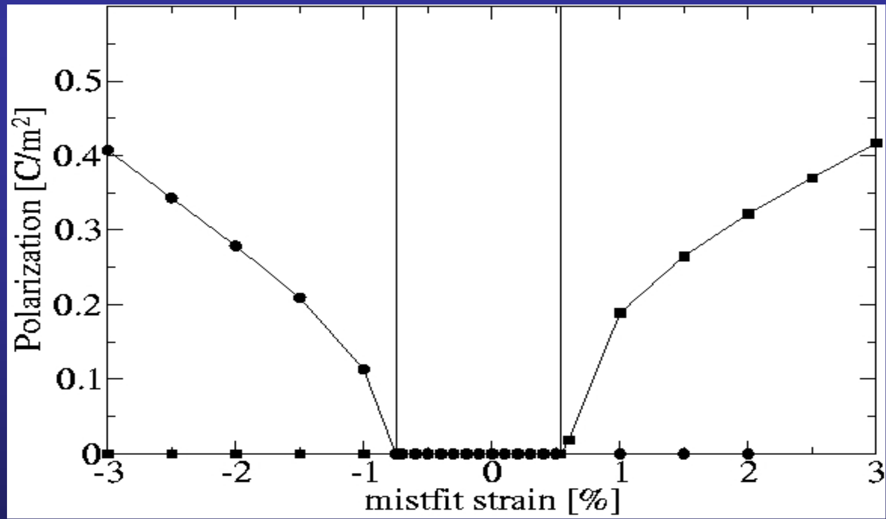
O. Diéguez et al., Phys. Rev. B 72, 144101 (2005)

PbTiO$_3$



C. Bungaro *et al.*, PRB 69, 212101 (2004)

SrTiO$_3$



A. Antons *et al.*, PRB 71, 024102 (2005)

Kim et al., Appl. Phys. Lett. 85, 5649 (2004)

T. Schimizu, Solid State Commun. 102, 523 (1997)

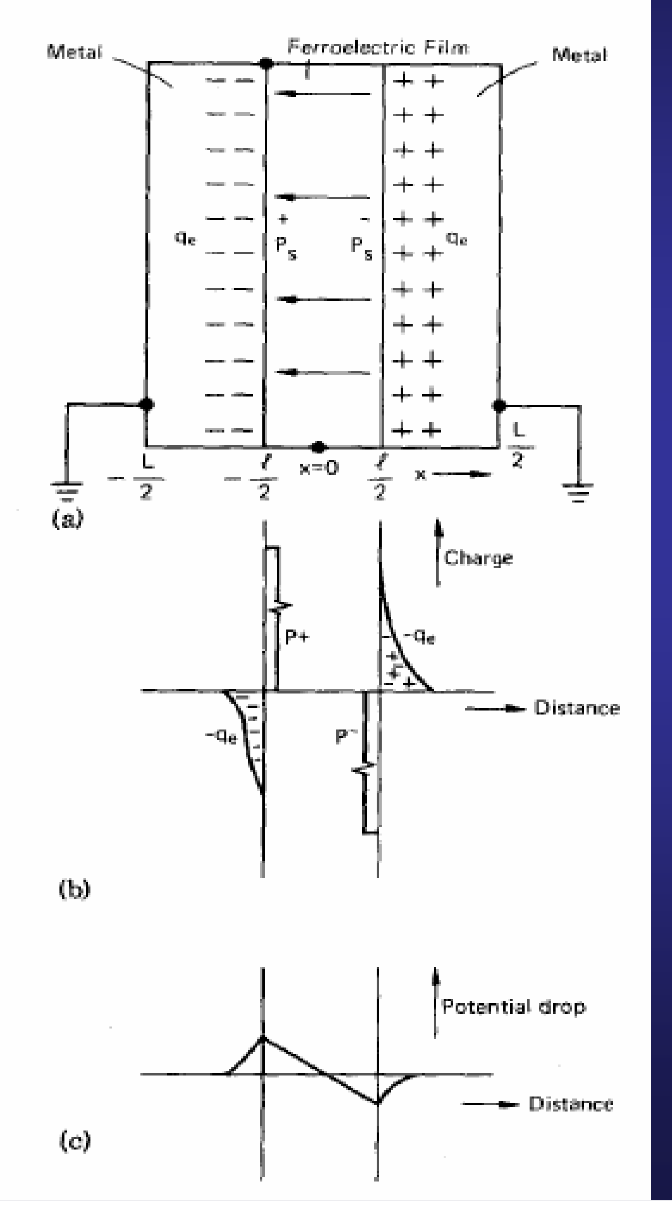
Electrostatic effects
Some questions that might be answered *ab-initio*

- **Finite depolarizing field**
  - **- imperfect screening**
  - **- polarization gradient**
  - **- dead layer at the interface**

couples with the polarization.

- **Dependence of**
  - **- density of free carriers**
  - **- metal/ferroelectric interface**
  - **- partial screening inside the ferroelectric**

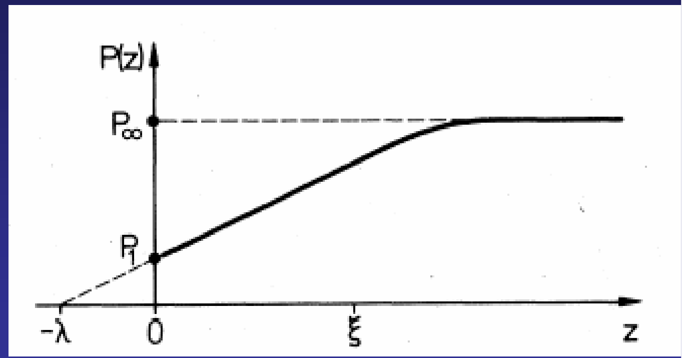
on the screening mechanism?



R. R. Mehta et al.,
J. Appl. Phys. 44, 3379 (1973)

Different mechanisms for the appearance of a depolarizing field

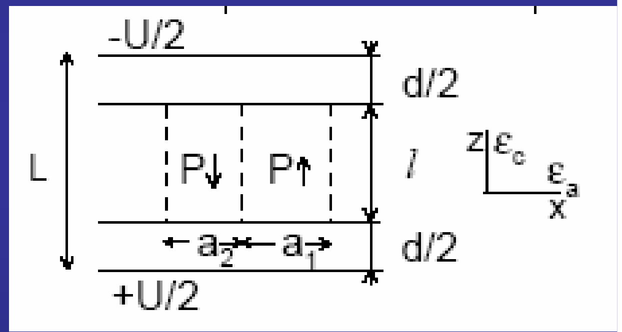
• Inhomogeneity of the polarization distribution



K. Kretschmer and K. Binder, Phys. Rev. B 20, 1065 (1979)

M. D. Glinchuk et al., Physica B 322, 356 (2002)

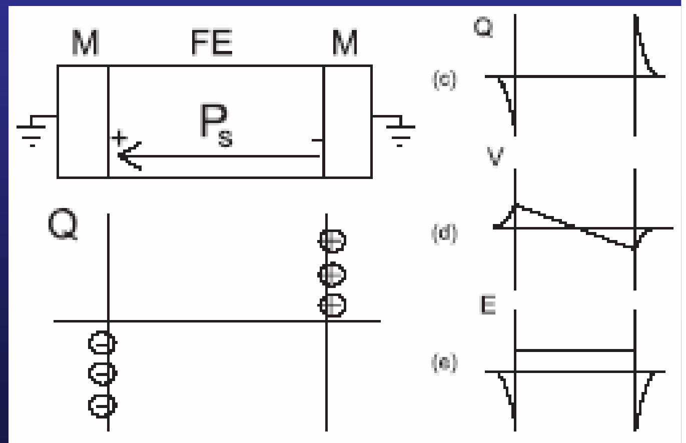
• Existence of a dead layer at the ferroelectric/electrode interface



A. M. Bratkovsky and A. P. Levanyuk, Phys. Rev. Lett. 84, 3177 (2000)

A. M. Bratkovsky and A. P. Levanyuk, Phys. Rev. B 63, 132103 (2001)

• Incomplete screening by real metallic electrode



I. P. Batra *et al.*, J. Vac. Sci. Technol. 10, 687 (1973)

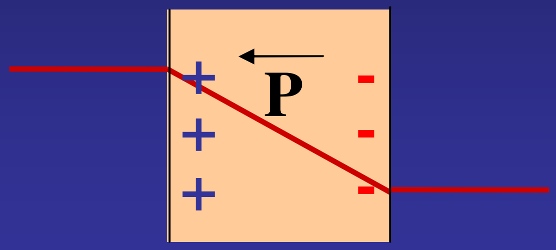
J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)

M. Dawber *et al.*, J. Phys.: Condens. Matter 15, 393 (2003)

Imperfect screening by real metallic electrodes produces a depolarizing field

Vacuum

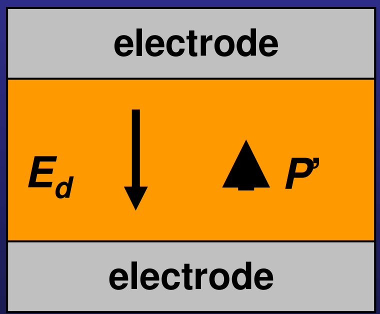
no screening



$$\mathcal{E}_d = - 4 \pi P$$

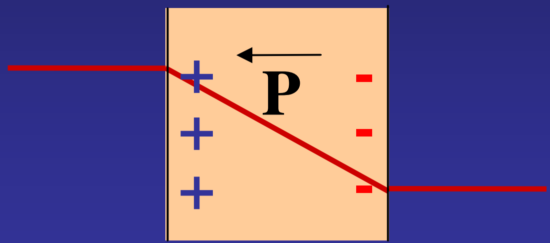
Screening by free charges

(electrodes or adsorbates)

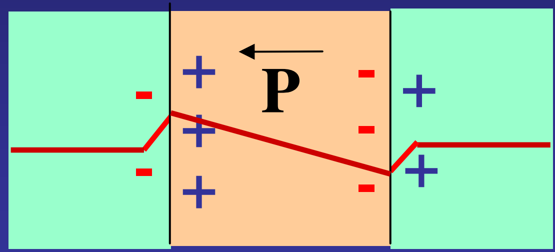


Imperfect screening by real metallic electrodes produces a depolarizing field

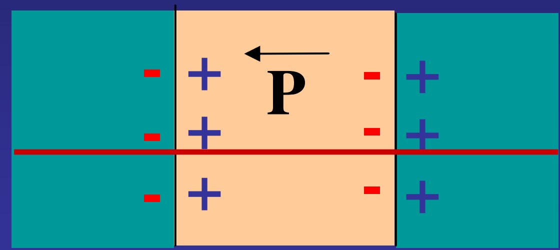
Vacuum	Real electrodes	Ideal electrodes
no screening	imperfect screening	perfect screening



$$\mathcal{E}_d = -4\pi P$$



$$\mathcal{E}_d = -4\pi\alpha P$$



$$\mathcal{E}_d = 0$$

Depolarizing field $\mathcal{E}_d$:

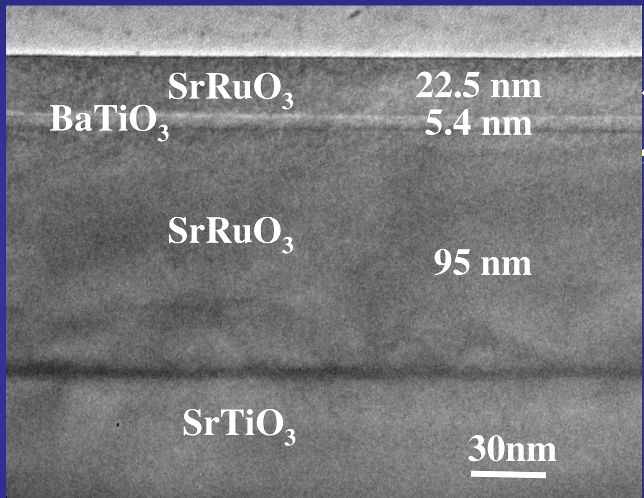
$$\mathcal{E}_d = -2\,\Delta V / d \qquad \Delta V = 4\pi\,\sigma_{pol}\,\lambda_{eff} \qquad \sigma_{pol} = \mathbf{P}\cdot\mathbf{n}$$

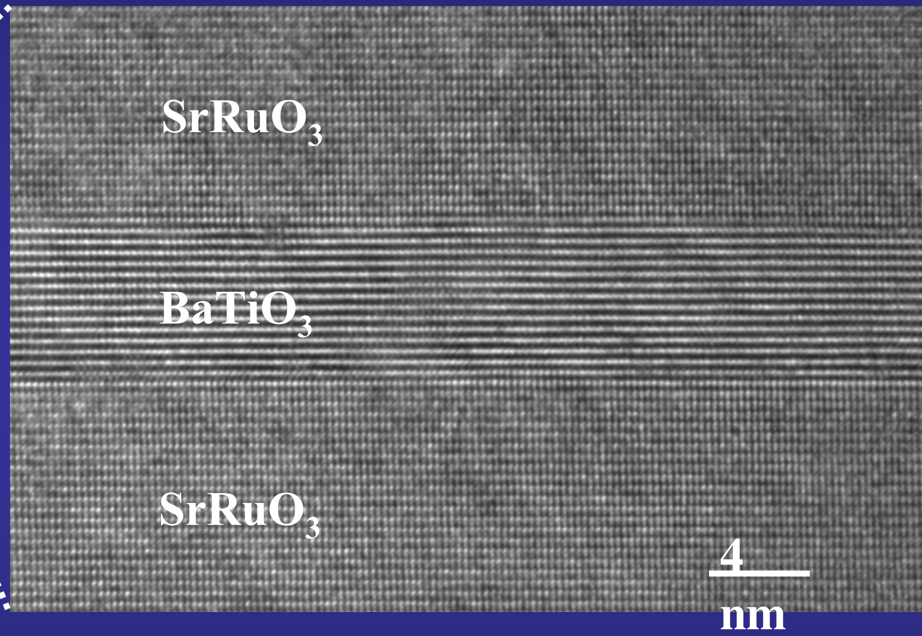
$$\mathcal{E}_d = -4\pi \cdot \underbrace{[\,2\,.\,\lambda_{eff}\,/\,d\,]}_{\alpha} \cdot \mathbf{P}$$

depends on:

- the metal and interface chemistry: screening length λ_{eff}
- the ferroelectric: the spontaneous polarization $\mathbf{P}$
- the film thickness d

High-resolution TEM of a typical ferroelectric capacitor





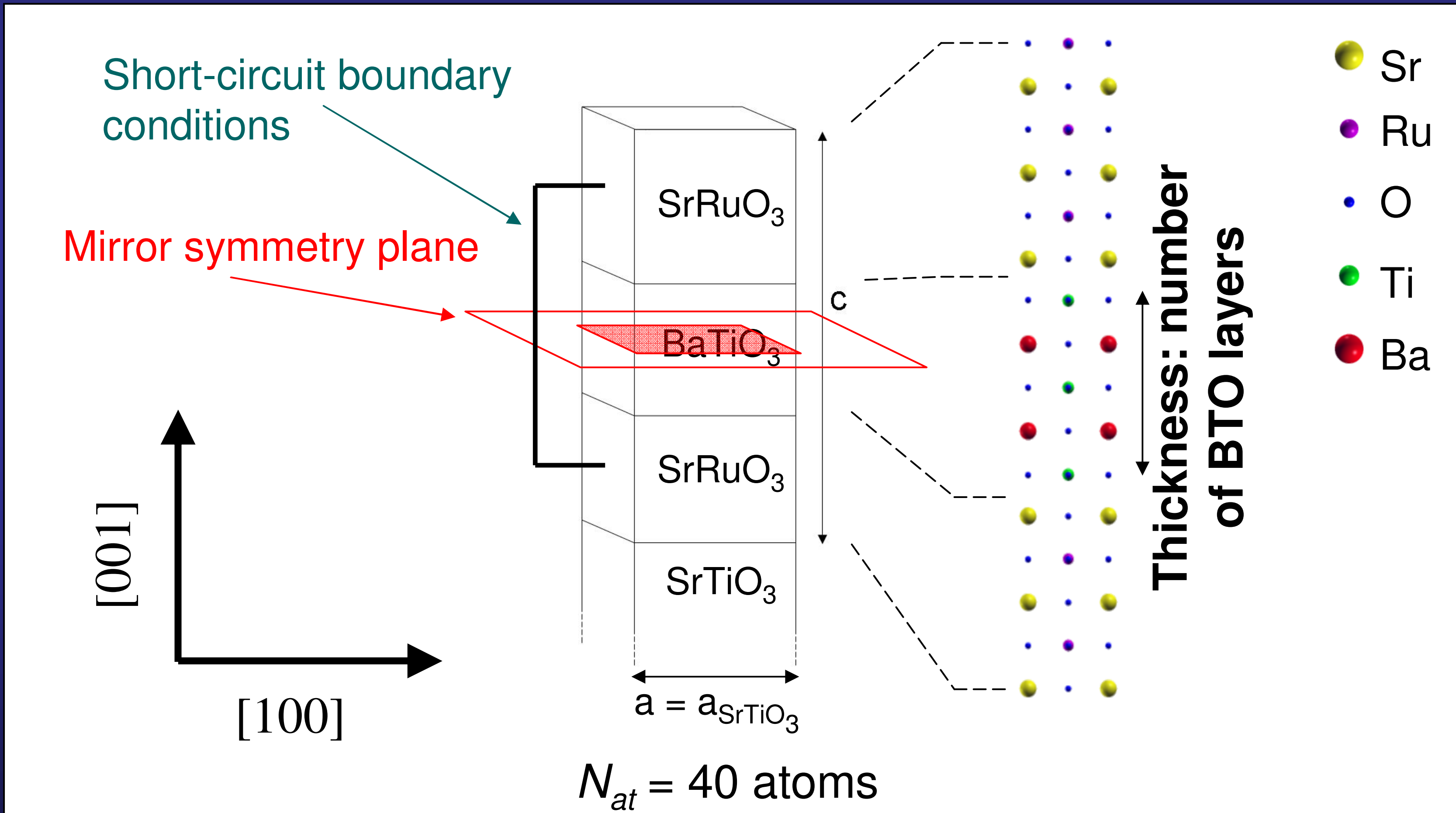
13 unit cells $BaTiO_3$ grown by MBE

J. Rodriguez Contreras, C. Jia, H. Kohlstedt, D. G. Schlom

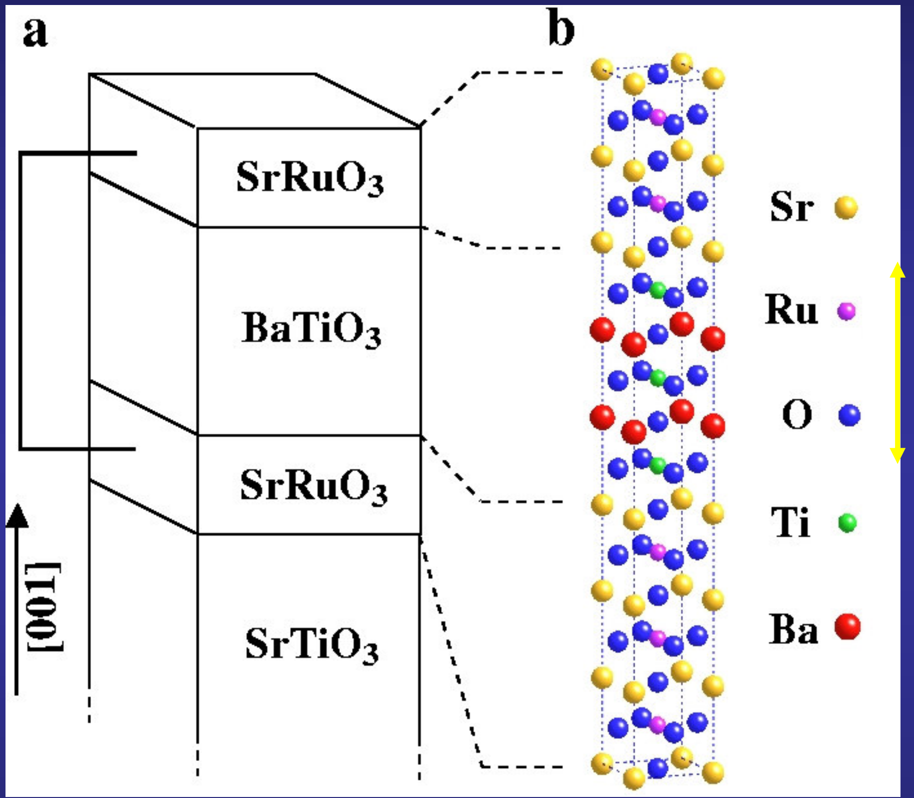
Forschungszentrum Jülich

Institut für Festkörperforschung – Elektrokeramische Materialien

Simulations of ferroelectric nanocapacitors from first-principles: Building the paraelectric unit cell



Simulations of ferroelectric nanocapacitors from first-principles



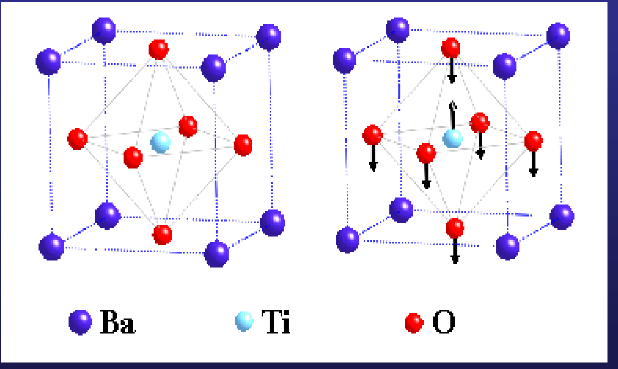
J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)

Thickness:

m number of BTO cells

Polarization control:

ξ percentage bulk soft mode



ξ=0 ξ=1

The depolarizing field is directly proportional to the induced polarization

- **Charge density *changes* for $\xi \neq 0$:**

Complex pattern of charge at the interface

Beyond simple Thomas-Fermi screening (with screening length λ)

- **Electrostatic potential *changes* (electrons + ions) for $\xi \neq 0$:**

Potential drop at the interface:

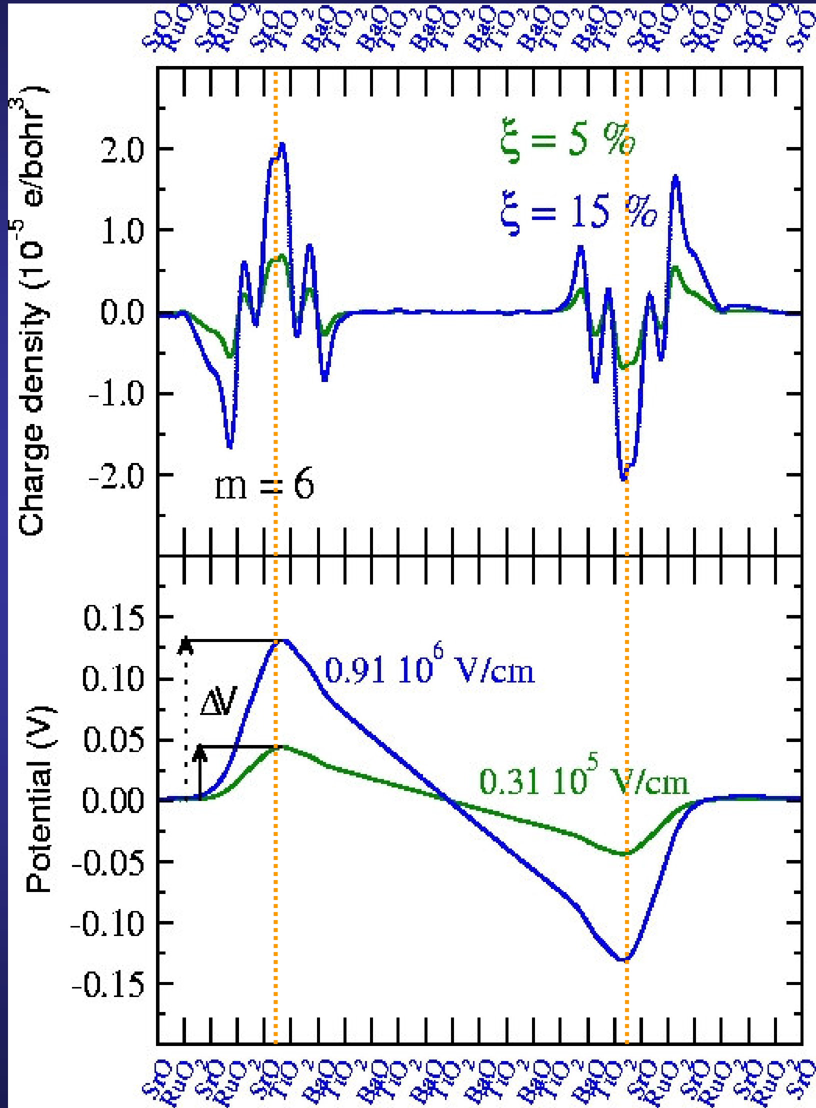
ΔV ***linear*** **with** $\sigma_{pol} = P \cdot n$

Effective screening length :

$$\Delta V = 4\pi \lambda_{eff} \,.\, \sigma_{pol} \qquad (\lambda_{eff} \sim 0.23 \text{ Å})$$

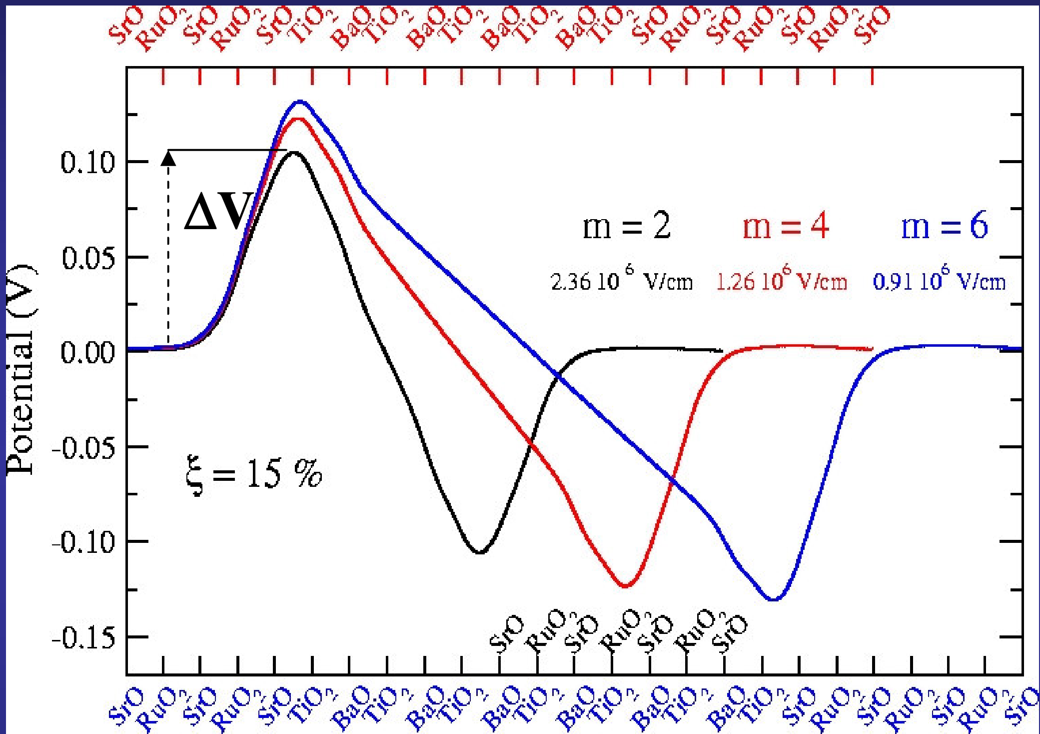
Depolarizing field :

$$\mathcal{E}_d = -2 \,.\, \Delta V \,/\, (m \,.\, a_{cell})$$



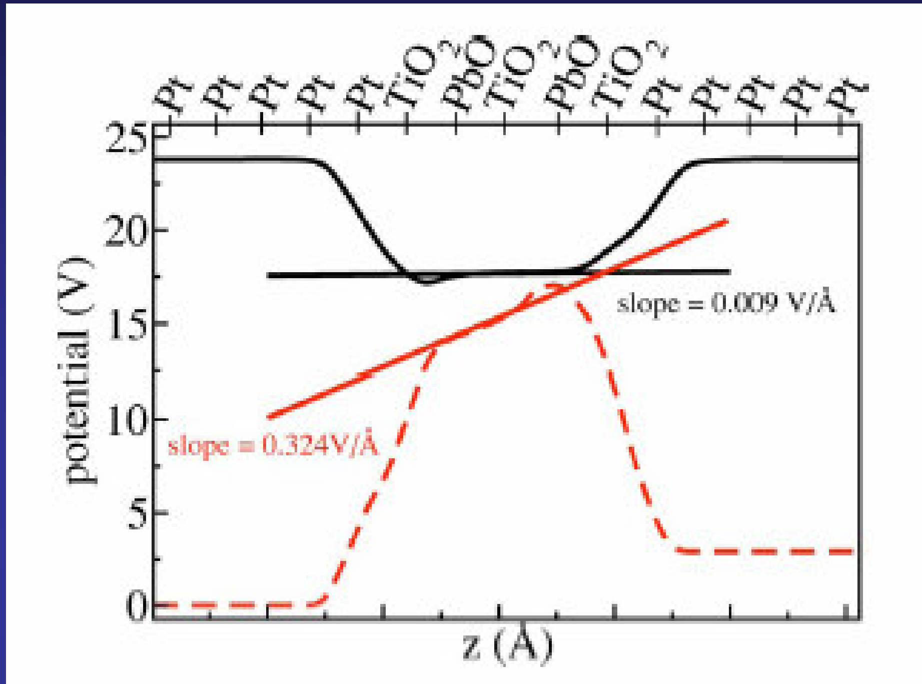
J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)

The depolarizing field is inversely proportional to the thickness



- **Depolarizing field $\mathcal{E}_d$ evolves with thickness *m* :** $\mathcal{E}_d = -2 \, . \, \Delta V / (m \, . \, a_{cell})$
- **Potential drop ΔV :** $\Delta V = 4 \pi \lambda_{eff} \, . \, \sigma_{pol}$

The depolarizing field depends on the interface

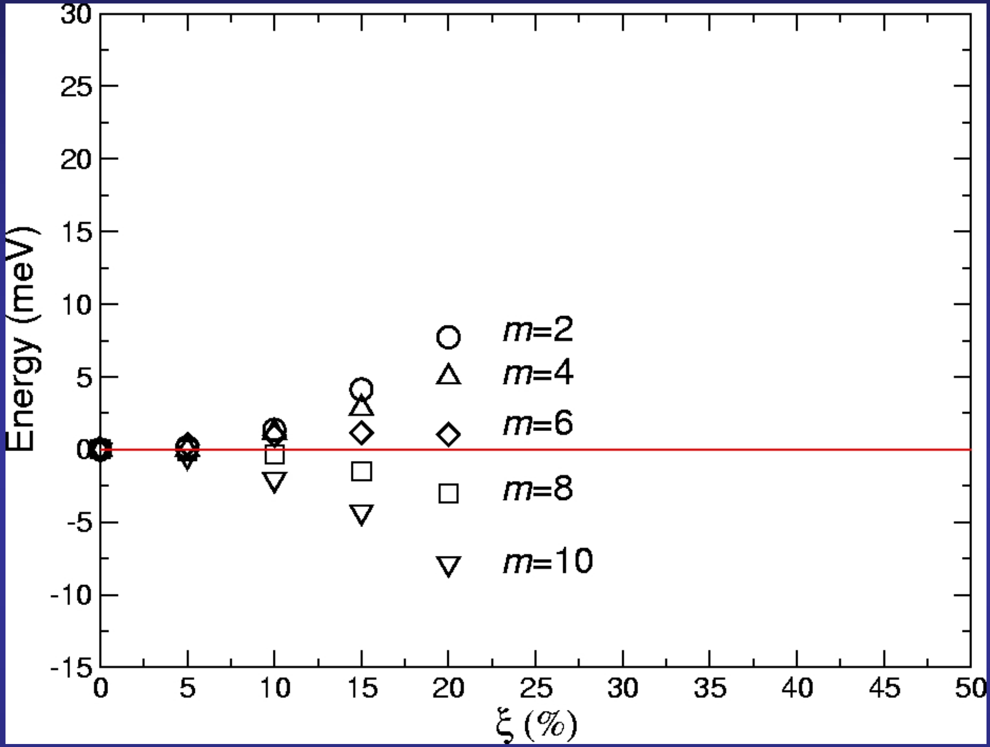


Na Sai *et al.,* Phys. Rev. B 72, 020101 (2005)

$SrRuO_3$ / $BaTiO_3$
$SrRuO_3$ / $PbTiO_3$ } **Incomplete screening**

Pt / $PbTiO_3$
Pt / $BaTiO_3$ } **“Perfect” screening**

Existence of a critical thickness in monodomain films
DFT results



Critical thickness for *m* ≈ 6

Smaller t_c if relaxation of all the atoms is allowed

J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)

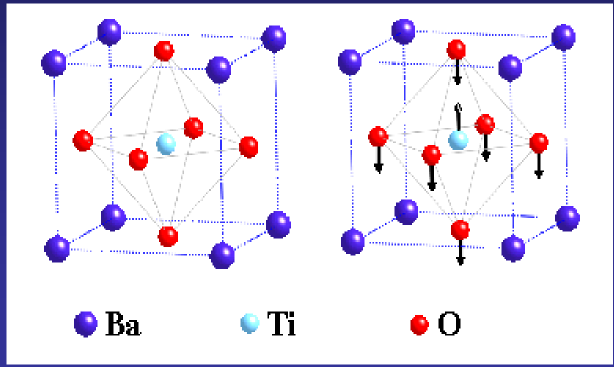
m = 2 : full atomic relaxation starting from a *ferroelectric* state
➔ the structure went back to the *paraelectric* state

Existence of a critical thickness in monodomain films
Electrostatic model

Bulk:

$$U = A\,\xi^2 + B\,\xi^4$$

$\xi = 0$



$\xi = 1$

Thin film:

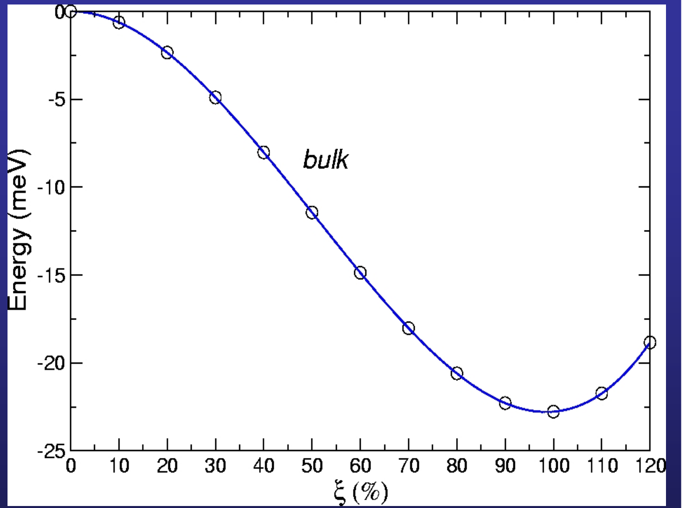
$$E = U - \mathcal{E}_d \cdot P$$

U ≈ *bulk* double-well energy

$$P = Z_T^{*} \cdot \xi / \Omega_o + \chi^{\infty} \cdot \mathcal{E}_d$$

$$\mathcal{E}_d \approx 2.\Delta V / (m\,.a_{cell})$$

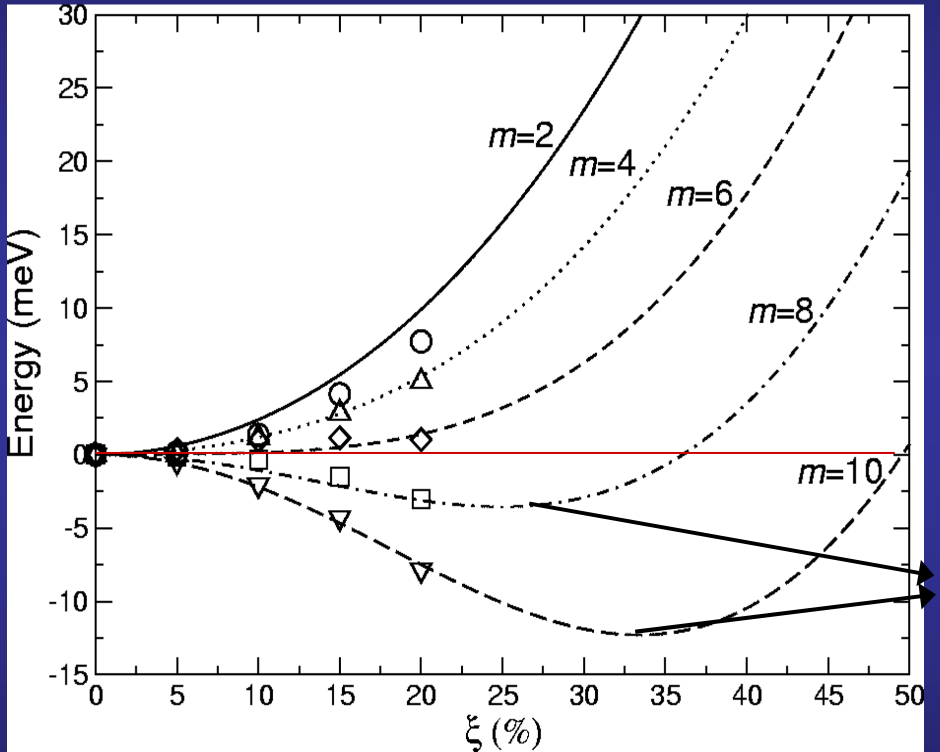
U



ξ

Existence of a critical thickness in monodomain films DFT versus model results

$$E = U - \mathcal{E}_d \cdot P$$



Minima below bulk (ξ = 1)

P_s deduced from ξ_{min}

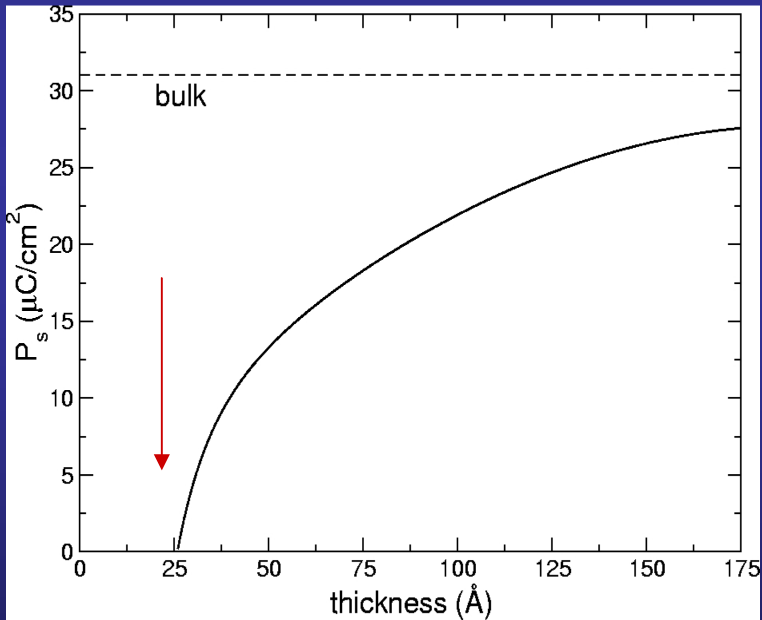
J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)

Behavior can be explained by ***electrostatic*** effects.
The ***chemistry*** of the interface buried in λ_{eff}.

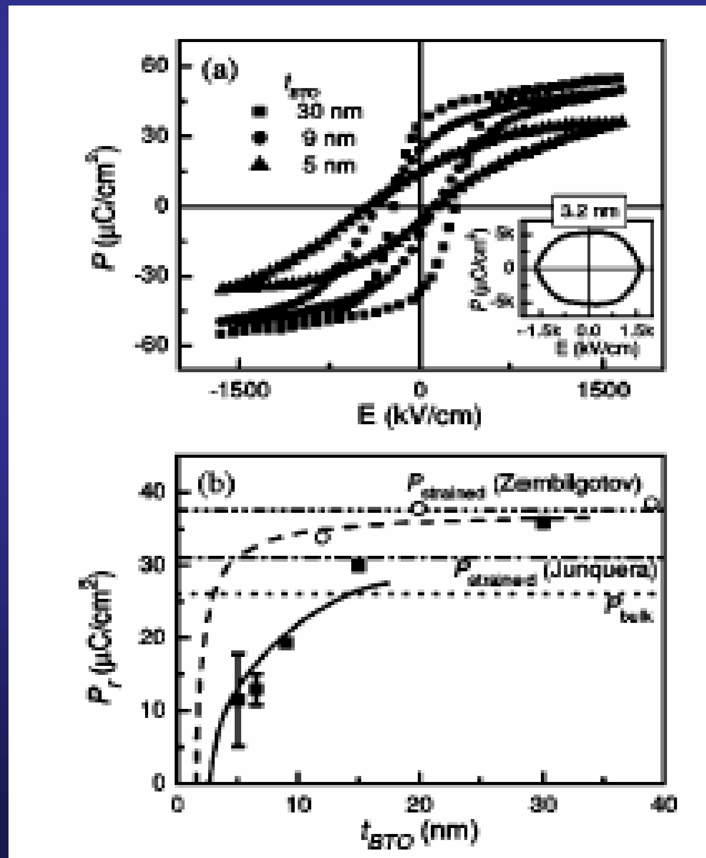
Twofold effect of the depolarizing field in monodomain films

$$\mathcal{E}_d = -4\pi\alpha P \qquad E = U - \mathcal{E}_d \cdot P$$

- Below the critical thickness: suppression of the ferroelectricity
- Above the critical thickness: reduction of spontaneous polarization



J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)



Y. S. Kim et al., Appl. Phys. Lett. 86, 102907 (2005)

Many DFT first-principles computations on size effects in ferroelectric ultrathin films

PHYSICAL REVIEW B **72**, 020101(R) (2005)

Ferroelectricity in ultrathin perovskite films

Na Sai, Alexie M. Kolpak, and Andrew M. Rappe

PRL **96**, 107603 (2006) PHYSICAL REVIEW LETTERS week ending 17 MARCH 2006

Ionic Polarizability of Conductive Metal Oxides and Critical Thickness for Ferroelectricity in $BaTiO_3$

G. Gerra,[1,*] A. K. Tagantsev,[1] N. Setter,[1] and K. Parlinski[2]

PHYSICAL REVIEW B **74**, 060101(R) (2006)

***Ab initio* study of the critical thickness for ferroelectricity in ultrathin $Pt/PbTiO_3/Pt$ films**

Yoshitaka Umeno,[1,2] Bernd Meyer,[3] Christian Elsässer,[4,1] and Peter Gumbsch[1,4]

Interface Effect on Ferroelectricity at the Nanoscale

Chun-Gang Duan,[†,‡,§] Renat F. Sabirianov,[‡,§] Wai-Ning Mei,[‡,§] Sitaram S. Jaswal,[†,§] and Evgeny Y. Tsymbal[*,†,§]

NANO LETTERS
2006
Vol. 6, No. 3
483−487

PRL **96**, 127601 (2006) PHYSICAL REVIEW LETTERS week ending 31 MARCH 2006

Stabilization of Monodomain Polarization in Ultrathin $PbTiO_3$ Films

D. D. Fong,[1] A. M. Kolpak,[2] J. A. Eastman,[1] S. K. Streiffer,[1] P. H. Fuoss,[1] G. B. Stephenson,[1] Carol Thompson,[3] D. M. Kim,[4] K. J. Choi,[4] C. B. Eom,[4] I. Grinberg,[2] and A. M. Rappe[2]

Many DFT first-principles computations on size effects in ferroelectric ultrathin films

Reference	Heterostructure	Method	Functional	Interface	$a_{\parallel}$	t_c
Junquera *et al.* [56]	$SrRuO_3/BaTiO_3/SrRuO_3$	NAO	LDA (CA)	SrO-TiO_2	3.874 Å ($a^{th}_{SrTiO_3}$)	6
Junquera *et al.*	$SrRuO_3/PbTiO_3/SrRuO_3$	NAO	LDA (CA)	SrO-TiO_2	3.874 Å ($a^{th}_{SrTiO_3}$)	6
Gerra *et al.* [63]	$SrRuO_3/BaTiO_3/SrRuO_3$	PW	GGA (PW91)	SrO-TiO_2	3.94 Å ($a^{th}_{SrTiO_3}$)	3
Umeno *et al.* [89]	$Pt/PbTiO_3/Pt$	MBPP	LDA (CA)	Pt-PbO	3.845 Å ($a^{th}_{SrTiO_3}$)	4
				Pt-TiO_2		6
			GGA (PW91)	Pt-PbO	3.905 Å ($a^{exp}_{PbTiO_3}$)	No
				Pt-TiO_2		No
Duan *et al.* [86]	$SrRuO_3/KNbO_3/SrRuO_3$	PW	LDA (CA)	SrO-NbO_2	3.905 Å ($a^{exp}_{SrTiO_3}$)	4
	$Pt/KNbO_3/Pt$			Pt-NbO_2		2
Na Sai *et al.* [64,90]	$SrRuO_3/BaTiO_3/SrRuO_3$	PW	GGA	SrO-TiO_2	3.991 Å ($a^{exp}_{BaTiO_3}$)	> 4
				RuO_2-BaO		> 4
	$Pt/BaTiO_3/Pt$			Pt-TiO_2		> 4
				Pt-BaO		> 4
	$SrRuO_3/PbTiO_3/SrRuO_3$			SrO-TiO_2	3.905 Å ($a^{exp}_{PbTiO_3}$)	No
				RuO_2-PbO		No
	$Pt/PbTiO_3/Pt$			Pt-TiO_2		No
				Pt-PbO		No
D. D. Fong *et al.* [47]	$SrRuO_3/PbTiO_3$/vacuum	PW	GGA	SrO-TiO_2	$a^{th}_{PbTiO_3}$	> 3
	$SrRuO_3/PbTiO_3$/OH, O or H					< 3
	$SrRuO_3/PbTiO_3/CO_2$					~ 3
	$SrRuO_3/PbTiO_3/H_2O$					> 3

Be careful with the functional used…
GGA overestimates tetragonality and double-well depth in bulk $PbTiO_3$

	Cubic phase		Tetragonal phase						
	a	E_{gap}	a	c/a	$u_z(\text{Ti})$	$u_z(\text{O}_1)$	$u_z(\text{O}_3)$	E_{gap}	ΔE
LDA, MBPP	3.880	1.55	3.853	1.050	0.5312	0.0923	0.6012	1.62	−0.053
LDA, PAW	3.894	1.48	3.867	1.043	0.5334	0.0883	0.6018		−0.056
LDA[a]	3.894		3.858	1.051					
PW91, MBPP	3.957	1.69	3.827	1.247	0.5571	0.1938	0.6670	2.04	−0.196
PW91, PAW	3.969	1.61	3.841	1.233	0.5559	0.1859	0.6660		−0.192
PBE, MBPP	3.962	1.69	3.836	1.244	0.5579	0.1949	0.6675	2.05	−0.208
PBE[a]	3.971		3.857	1.230					
Expt. (298 K)[b]	3.969		3.905	1.064	0.539	0.114	0.617	3.5	

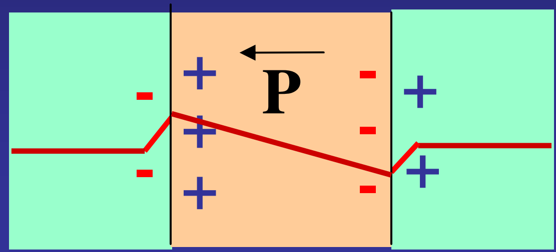
…responsible for the absence of critical thickness in $PbTiO_3$ nanocapacitors?

Y. Umeno et al., Phys. Rev. B 74 060101 (2006)

Until today, monodomain studies, goal of this work: multidomain simulations

Real electrodes

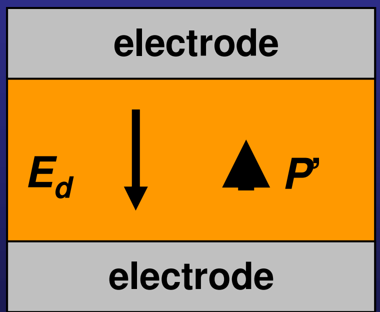
imperfect screening



$$\mathcal{E}_d = -4\pi . [\, 2\, .\, \lambda_{eff} / d\,] \cdot \mathbf{P}$$

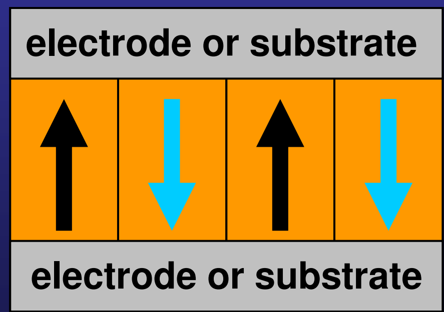
Screening by free charges

(electrodes or adsorbates)



Formation of domains

(no net charge at surface)



Goal of this work

Main questions addressed in this work

- Is the phase transition as a function of thickness from…

  homogeneous polarization to paraelectric?

  homogeneous polarization to inhomogeneous polarization?

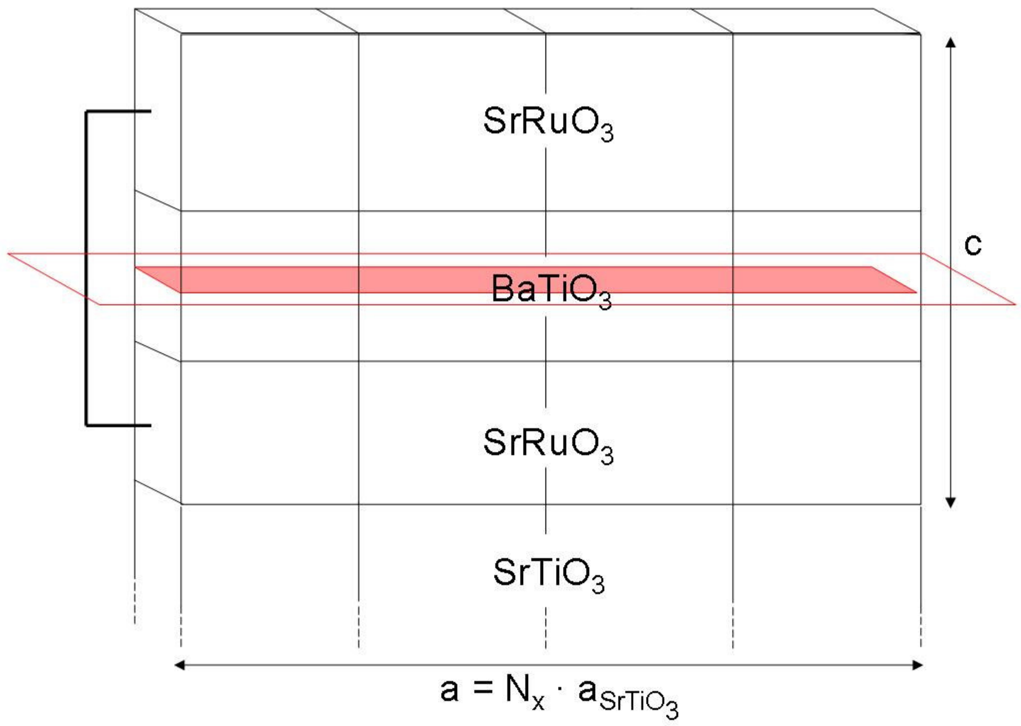
"It is not certain yet whether this instability in a single-domain ground state results in paraelectricity or in many small domains"

J. F. Scott, J. Phys.: Condens. Matter 18, R361 (2006)

- If the second is true, do the domains have a defined structure?

Building the cell: replicating the paraelectric structure

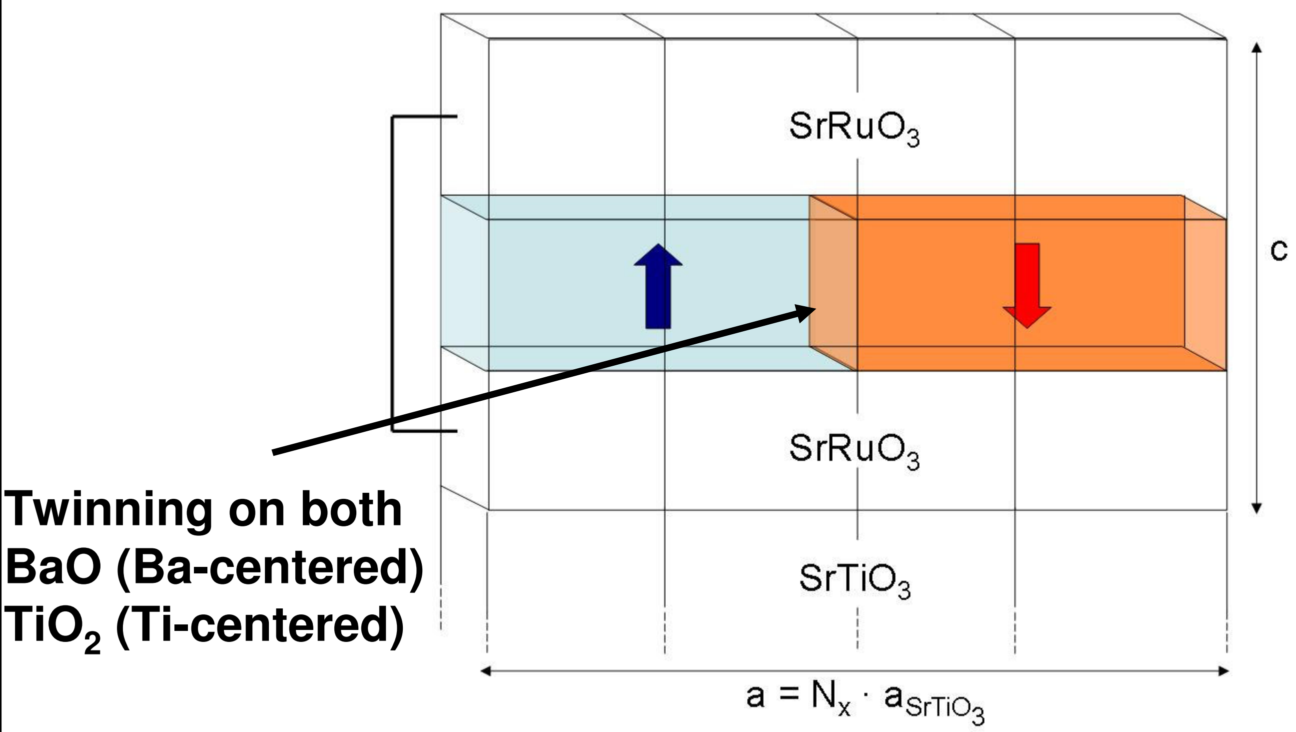
- N_x repetitions in [100] direction.
- The energies of these cells as references.



$$N_{at} = \mathrm{N_x} \cdot 40 \text{ atoms}$$

Building the cell: inducing a polarization by hand

- Chosing a domain wall.
- Inducing a polarization by hand in the FE layer displacing the atoms a percentage of the bulk soft mode.

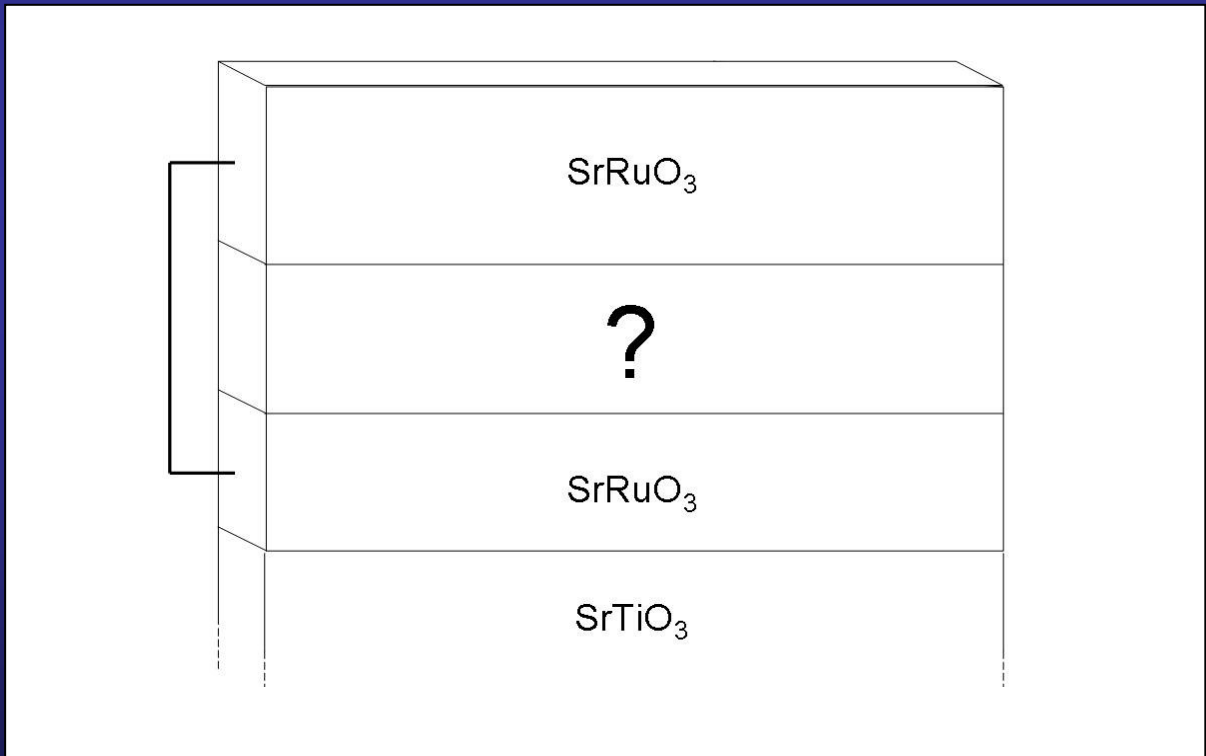


$$N_{at} = N_x \cdot 40 \text{ atoms}$$

Relaxing all the atomic coordinates, both in the ferroelectric layer and the electrodes

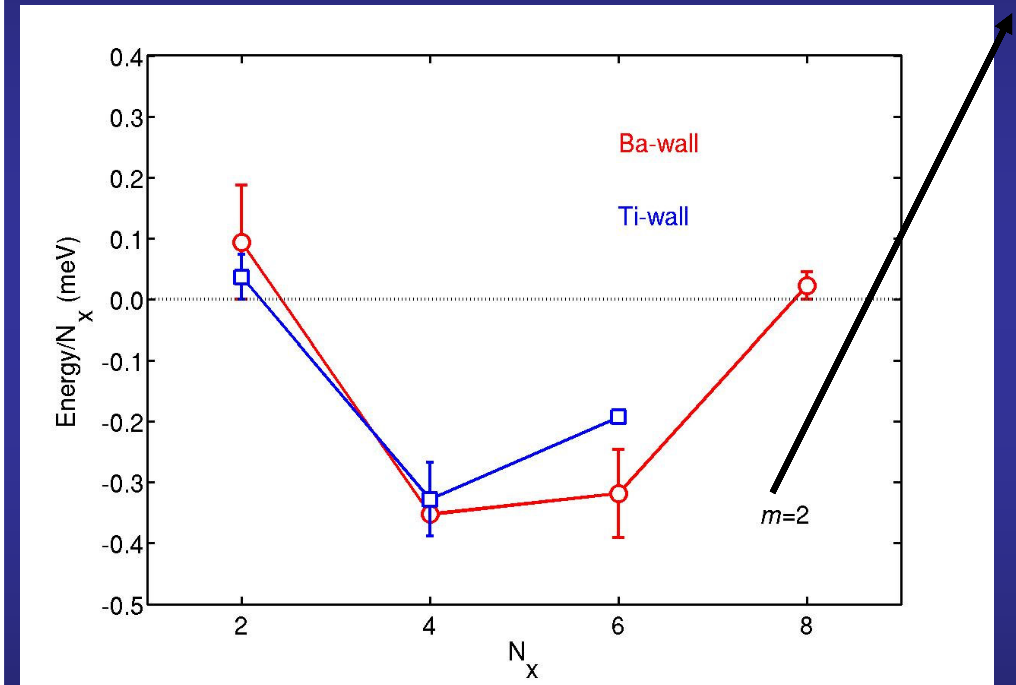
Forces smaller than 0.01 eV/Å

No constraints impossed on the atomic positions



Polydomain phases more stable than paraelectric structure for $2 < N_x < 8$

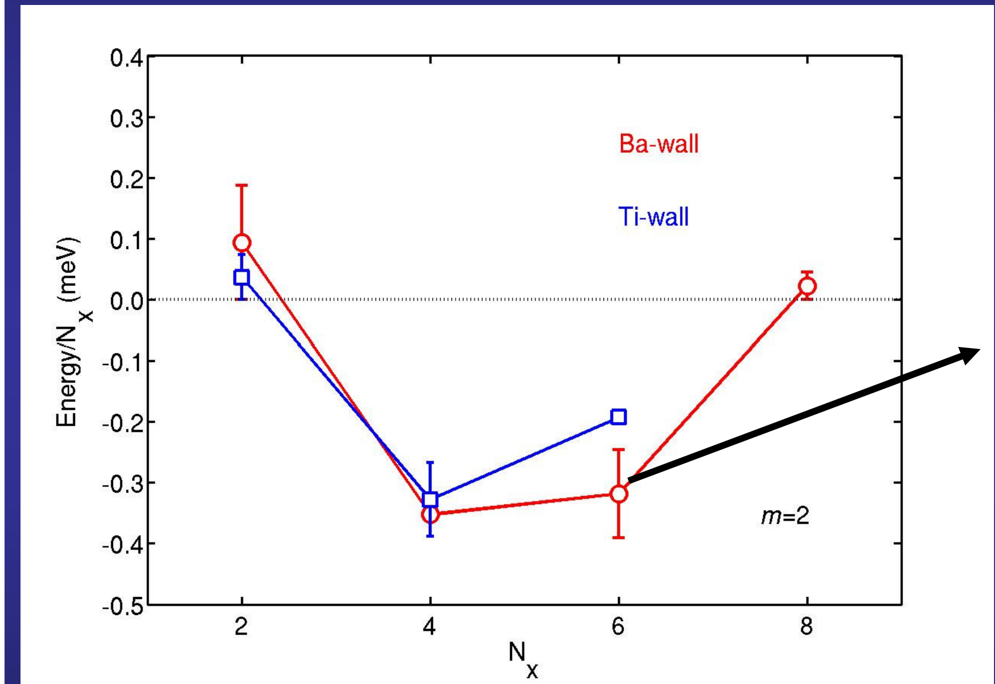
2-unit-cells thick $BaTiO_3$ layer



Polar domains stabilized below critical thickness for the monodomain configuration

Polydomain phases more stable than paraelectric structure for $2 < N_x < 8$

2-unit-cells thick $BaTiO_3$ layer



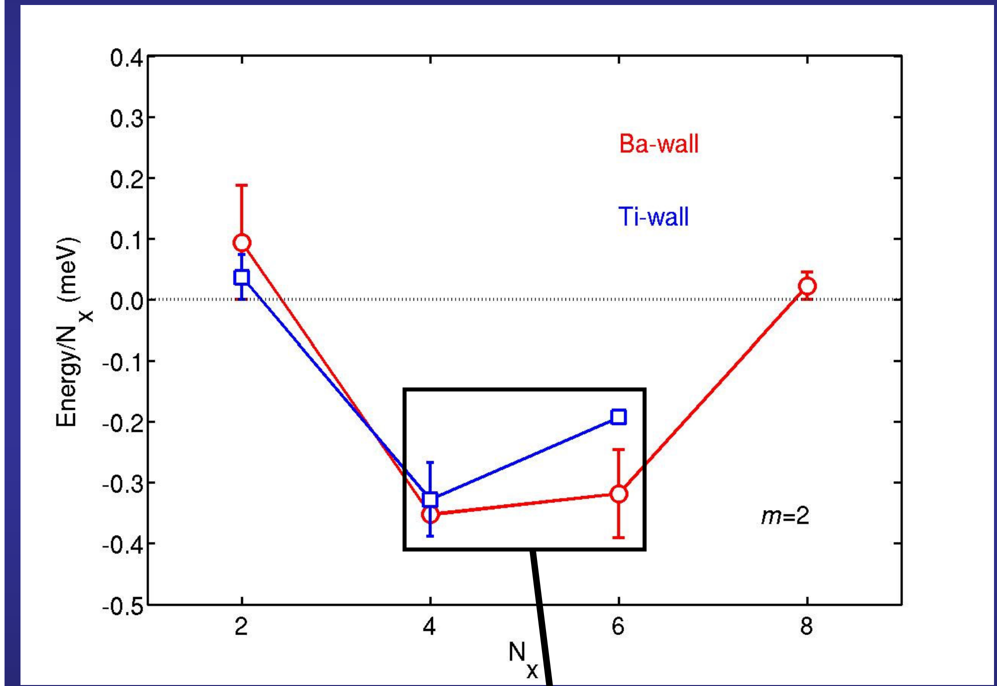
Polar **domains stabilized below critical thickness** for the **monodomain** configuration

As 180º domains in bulk,

Ba centered domain wall preferred

Polydomain phases more stable than paraelectric structure for $2 < N_x < 8$

2-unit-cells thick $BaTiO_3$ layer



Polar domains stabilized below critical thickness for the monodomain configuration

As 180º domains in bulk,

Ba centered domain wall preferred

No energy difference between $N_x = 4$ and $N_x = 6$

Both of them might be equally present in an sample

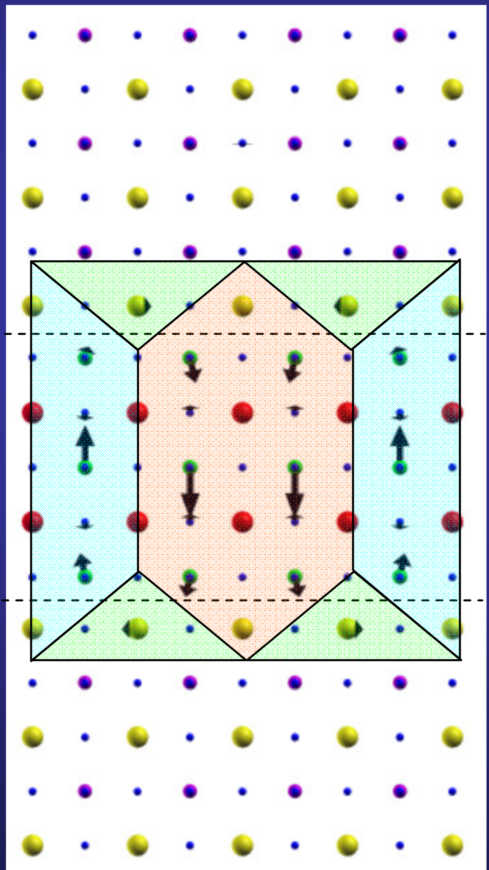
(α and β phases in $PbTiO_3/SrTiO_3$ interfaces?)

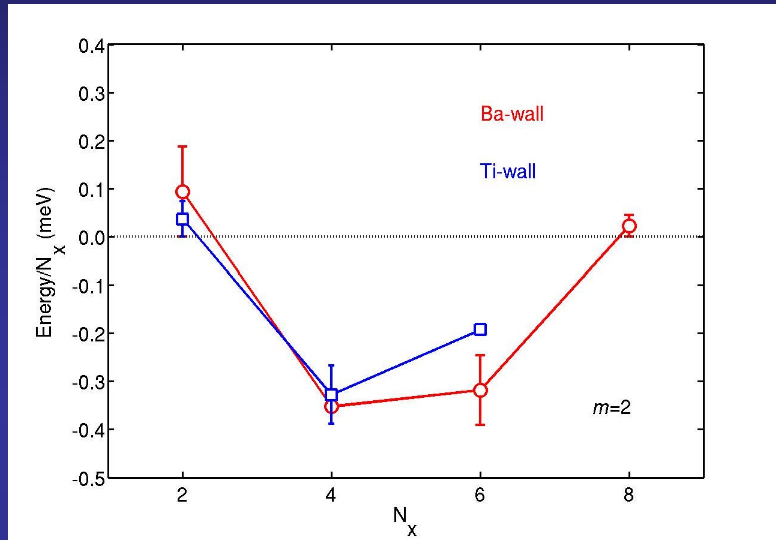
D. D. Fong *et al.*, Science 304, 1650 (2004)

Polydomain phases adopt the form of a "domain of closure", common in ferromagnets

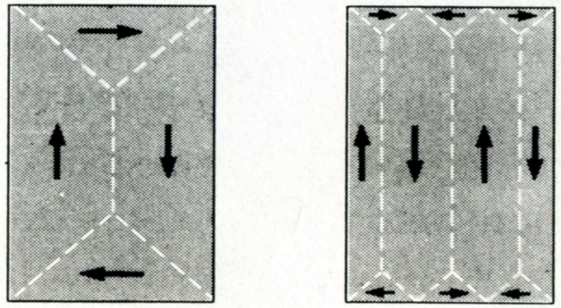
$N_x = 4$

BaO domain walls





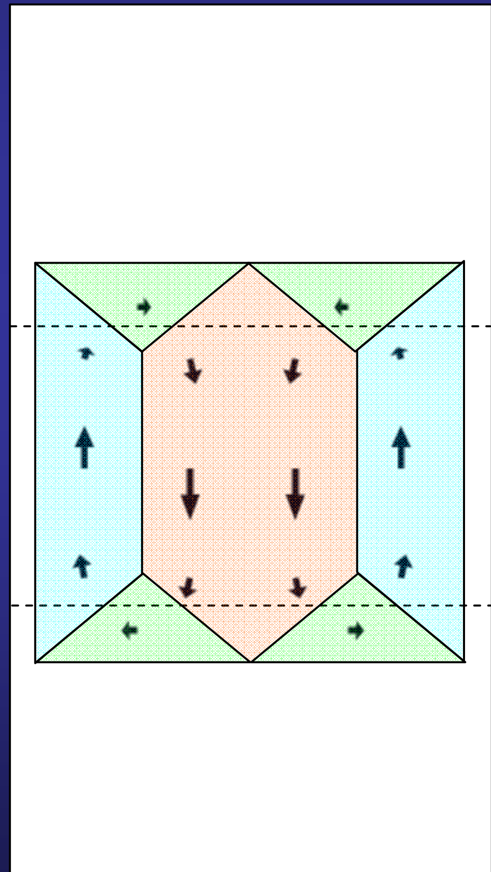
Ferromagnetic domains



C. Kittel (1946)

$N_x = 4$

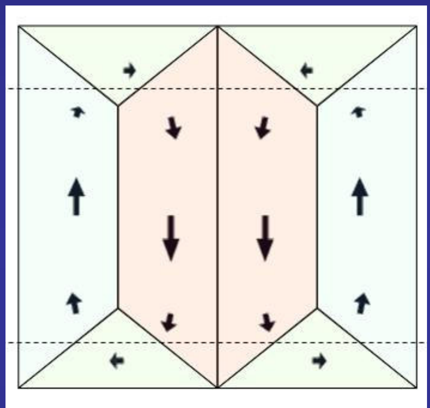
BaO domain walls



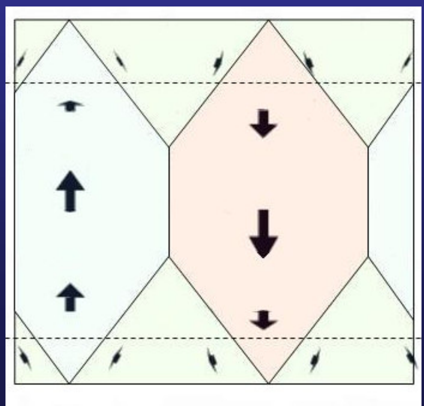
Polydomain phases adopt the form of a "domain of closure", common in ferromagnets

N_x=4

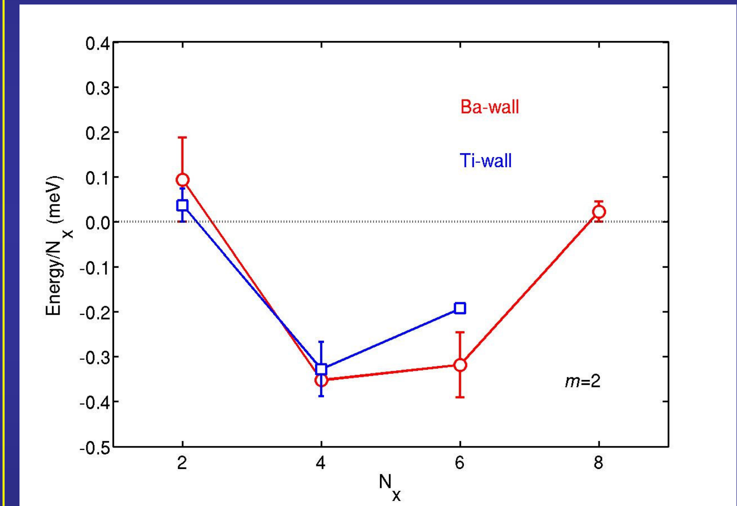
BaO wall



TiO_2 wall

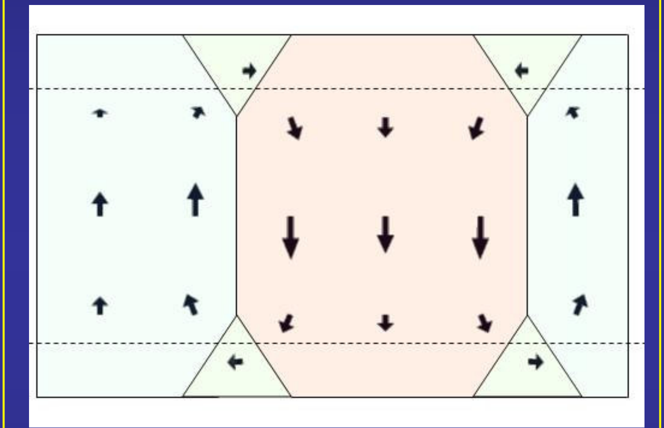


2-unit-cells thick $BaTiO_3$ layer

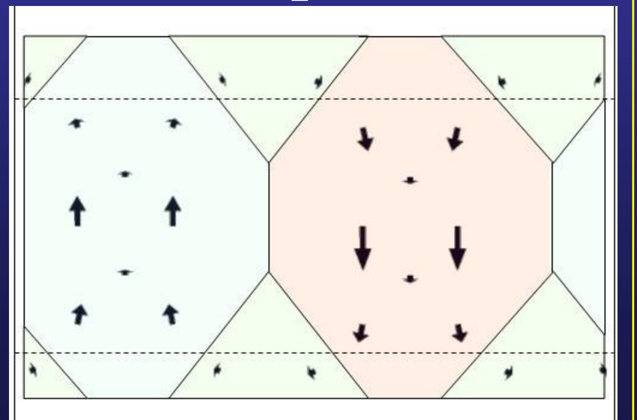


N_x=6

BaO wall



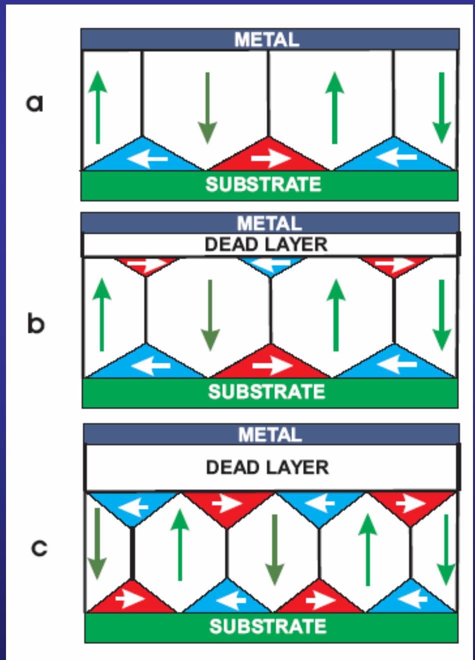
TiO_2 wall



Domains of closure recently predicted using a model hamiltonian approach

48 Å thick $PbZr_{0.4}Ti_{0.6}O_3$ thin films

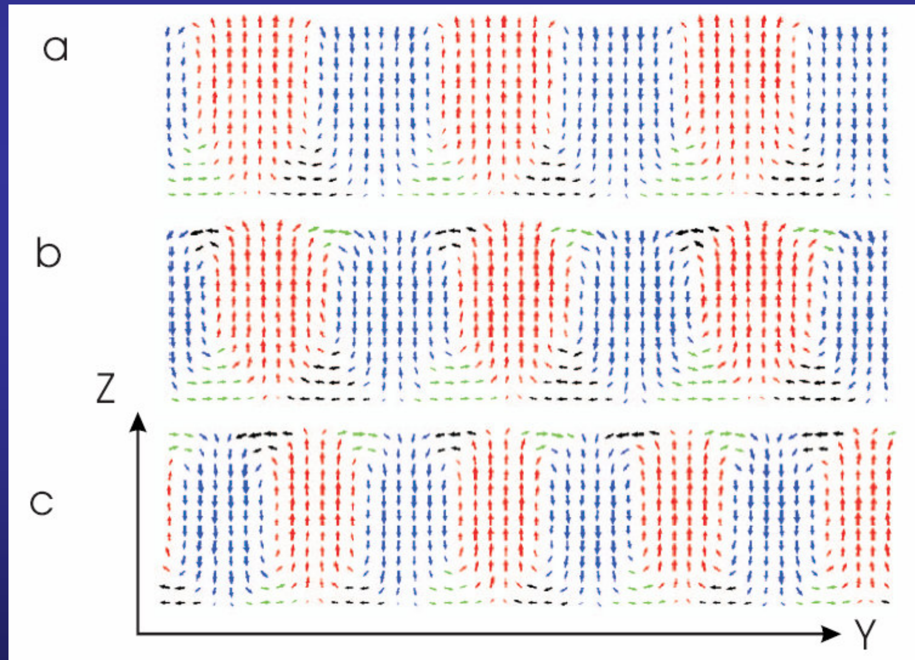
sandwiched with a nongrounded metallic plate (top) and a non-conductive substrate (bottom)



d = 0

d = 0.3 a

d = 0.5 a



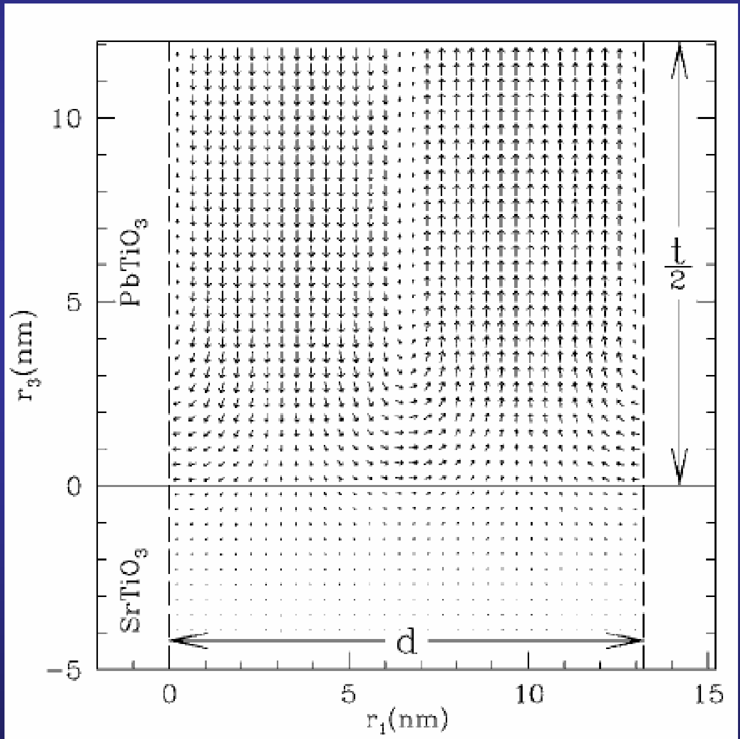
Dead layer thickness

S. Prosandeev and L. Bellaiche, Phys. Rev. B 75, 172109 (2007)

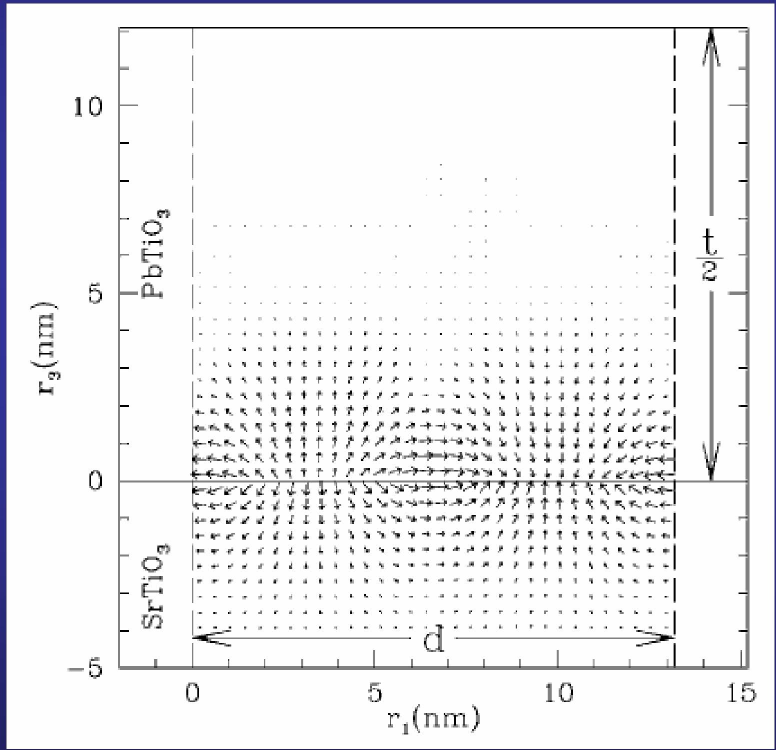
Domains of closure recently predicted using a phenomenological thermodynamic potential

242 Å thick $PbTiO_3$ thin films

sandwiched with a nonconducting $SrTiO_3$ electrodes @ 700 K
stripe period 132 Å



Polarization distribution

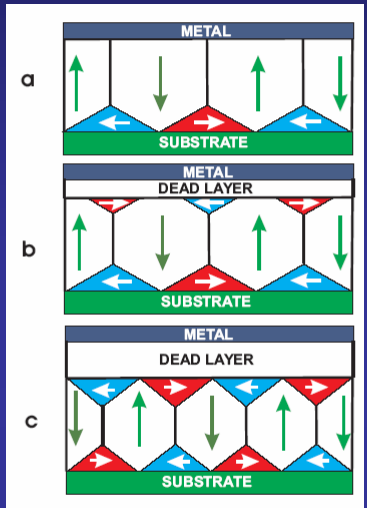


Equilibrium field distribution

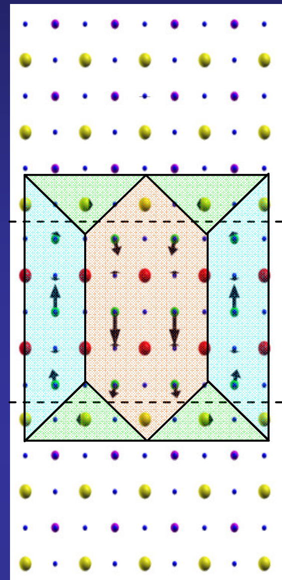
G. B. Stephenson and K. R. Elder, J. Appl. Phys. 100, 051601 (2006)

Full first-principles simulations: the domains of closure structure is more general than expected

Domains of closure appear even with symmetric metallic electrode



Case I:	Case II:	Case III:
$SrTiO_3$	Conductor	Vacuum
$PbTiO_3$	$PbTiO_3$	$PbTiO_3$
$SrTiO_3$	$SrTiO_3$	$SrTiO_3$



$SrRuO_3$

$BaTiO_3$

$SrRuO_3$

S. Prosandeev and L. Bellaiche, Phys. Rev. B 75, 172109 (2007)

G. B. Stephenson and K. R. Elder, J. Appl. Phys. 100, 051601 (2006)

This work

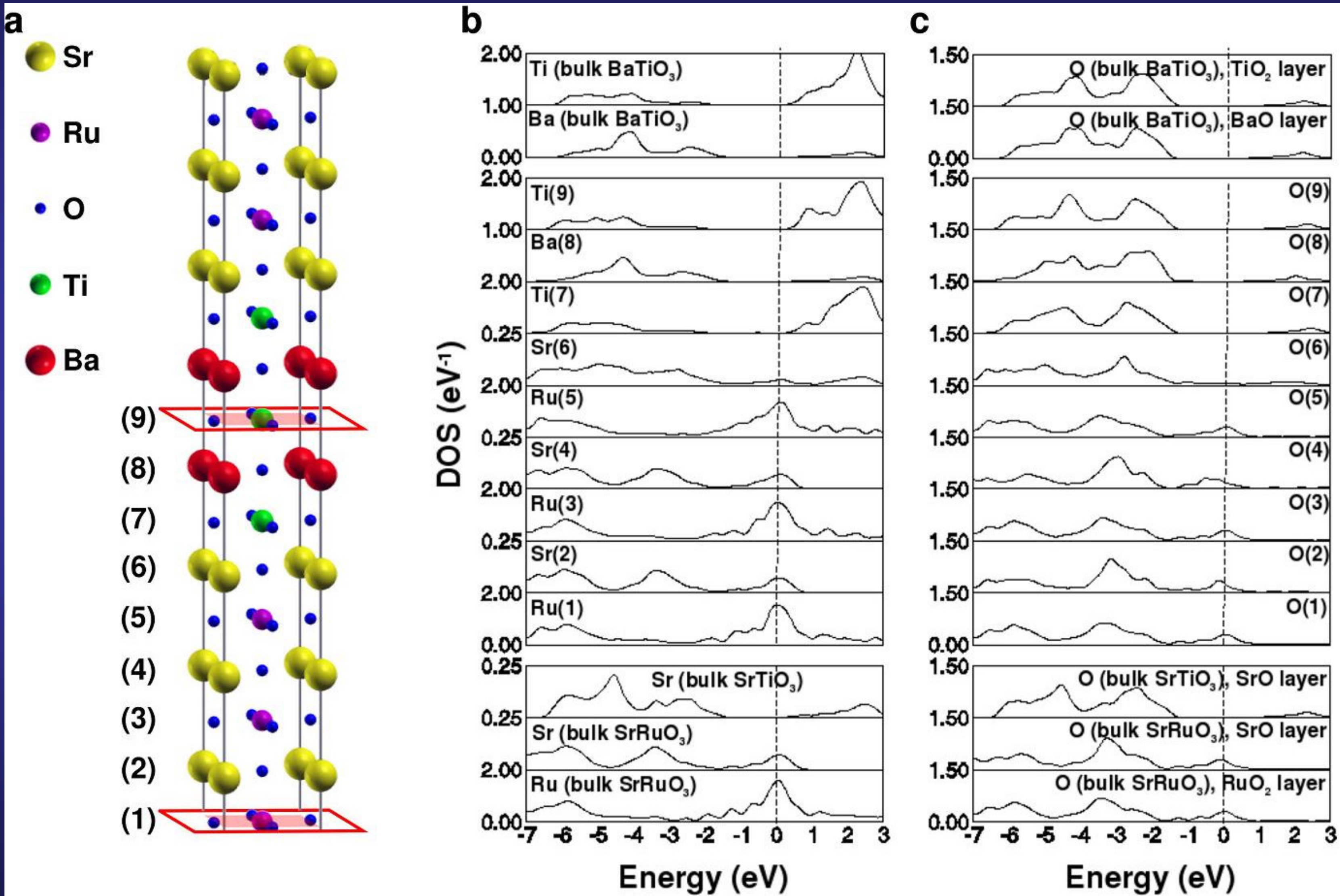
Domains of closure appear even in $BaTiO_3$ ferroelectric capacitors

"$BaTiO_3$ profoundly dislike significantly rotating and in-plane dipole"

"$BaTiO_3$ with the PZT configuration is thermodinamically unstable because it directly transforms into 180 stripe domains after a couple of Monte Carlo sweeps"

B. –K. Lai et al., Phys. Rev. B 75, 085412 (2007)

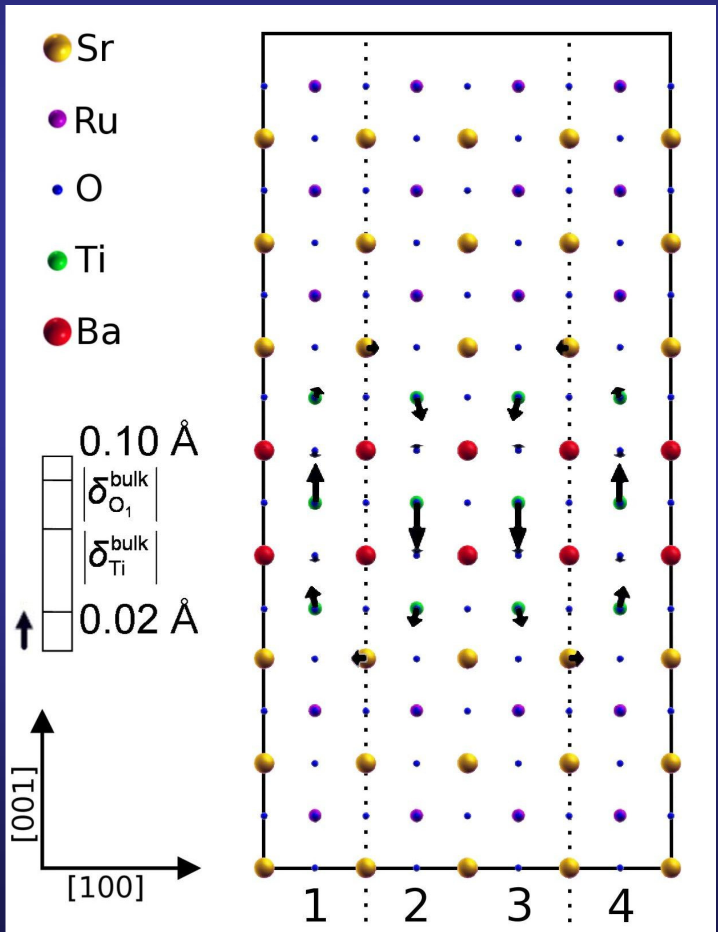
SrO layer at the interface behaves more like $SrTiO_3$ than $SrRuO_3$ $\Rightarrow$ highly polarizable



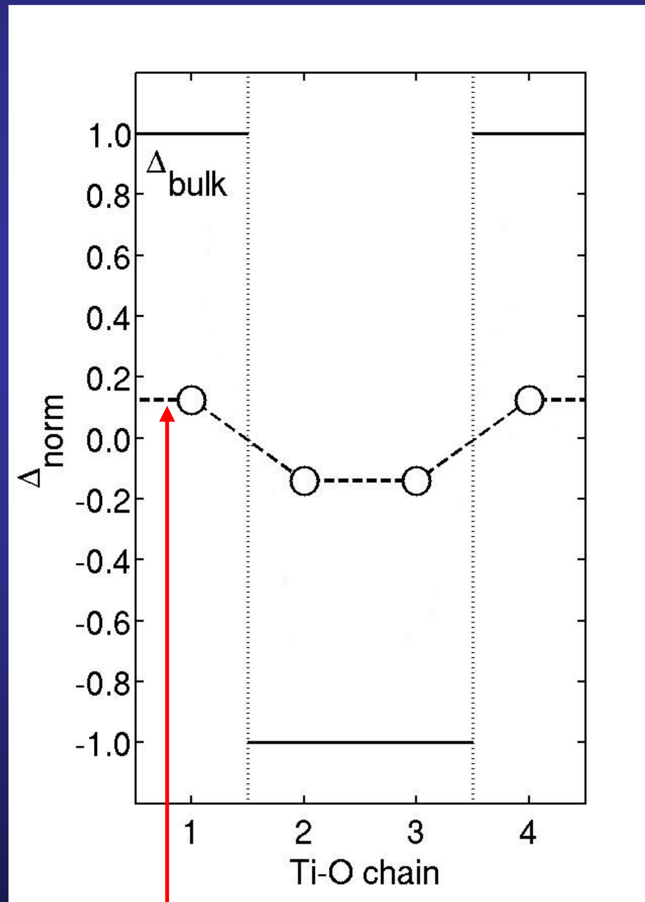
Projected Density of States in the reference paraelectric structure

Resulting phases show in-plane displacements and small polarization

$N_x = 4$
BaO domain walls



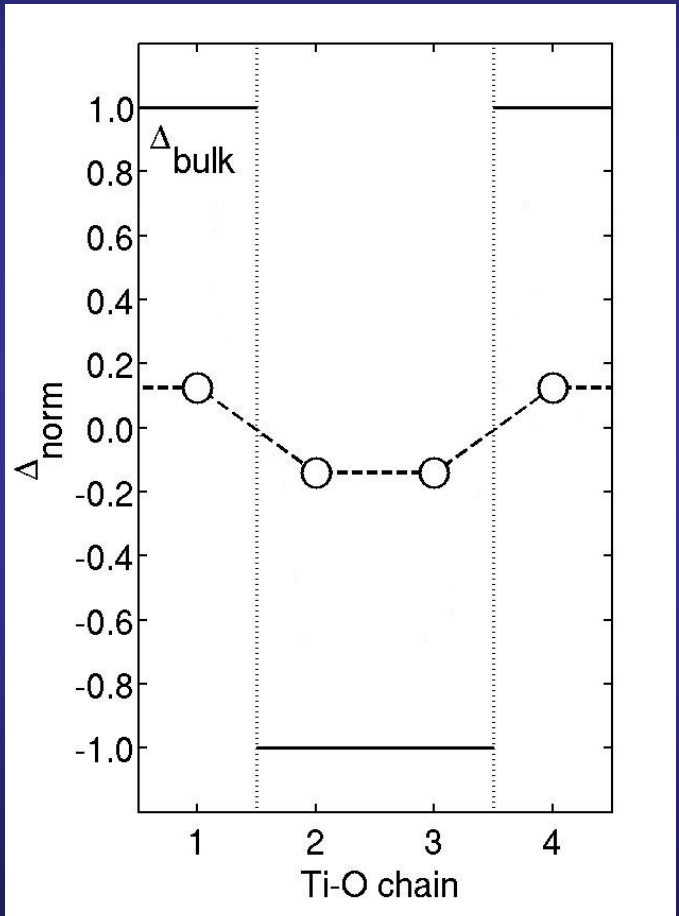
Small polarization inside the domains



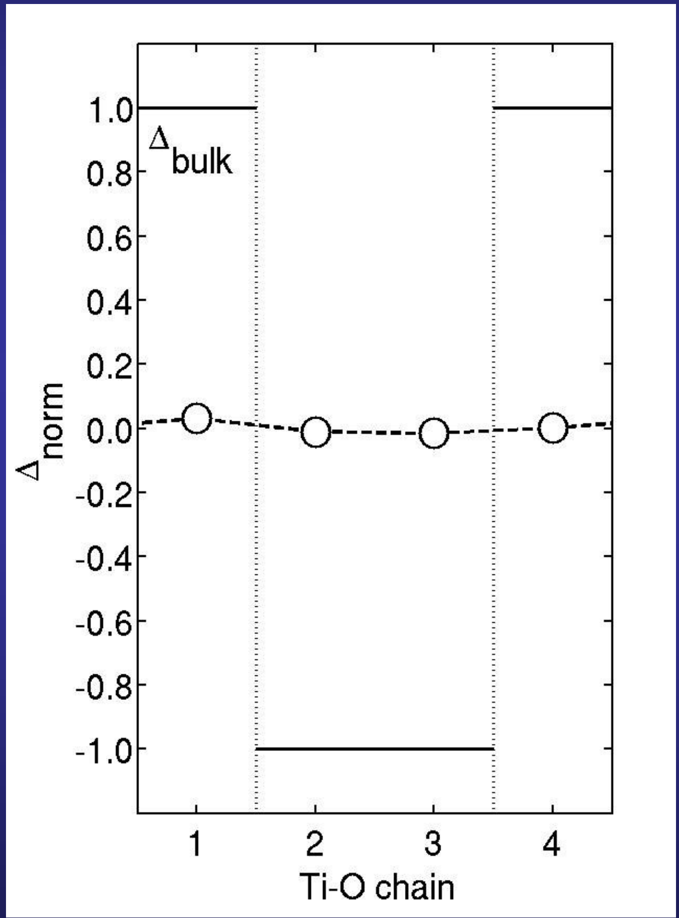
About 1/10 of bulk soft-mode polarization

In-plane displacements are very important to stabilize the domains

In-plane displacements: ON

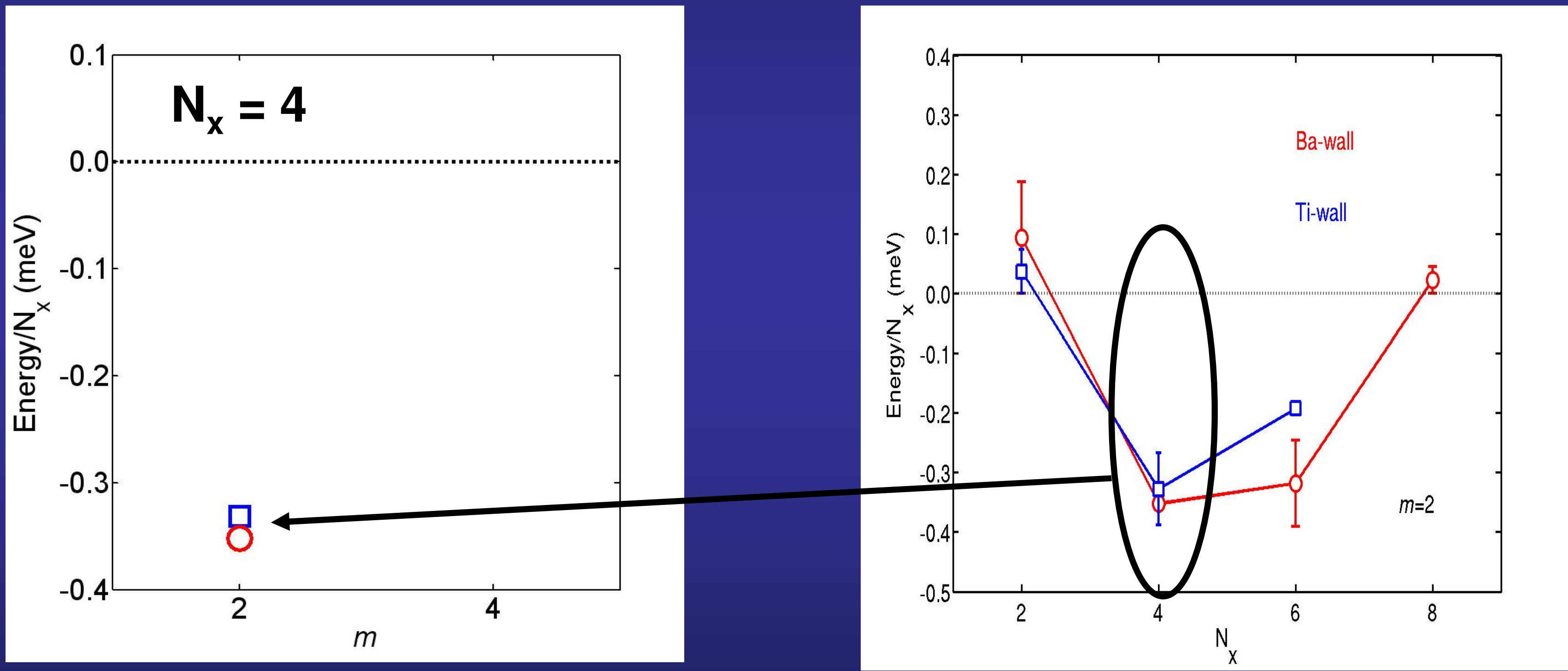


In-plane displacements: OFF

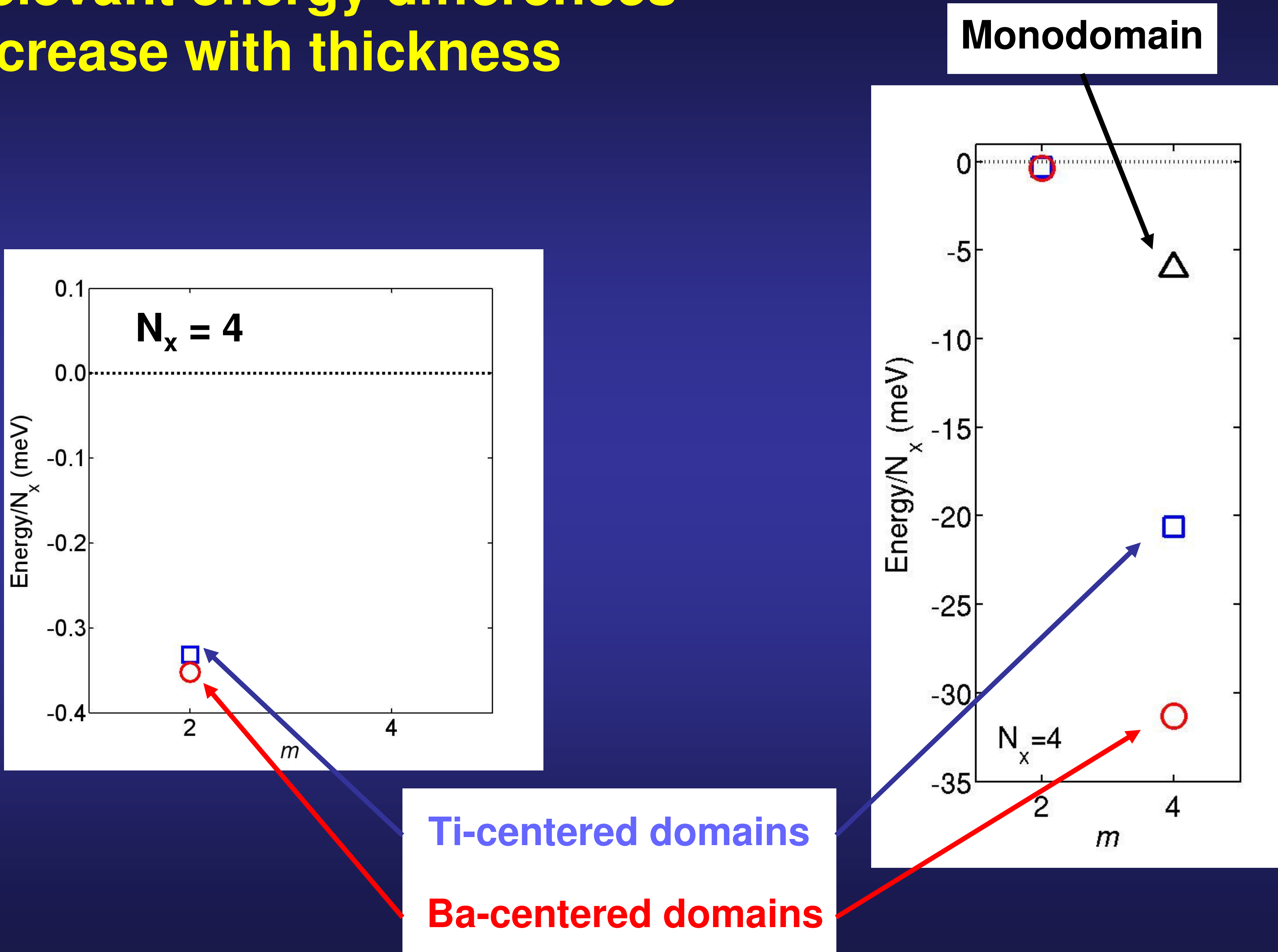


When in-plane coordinates are fixed, structure goes back to the paraelectric phase

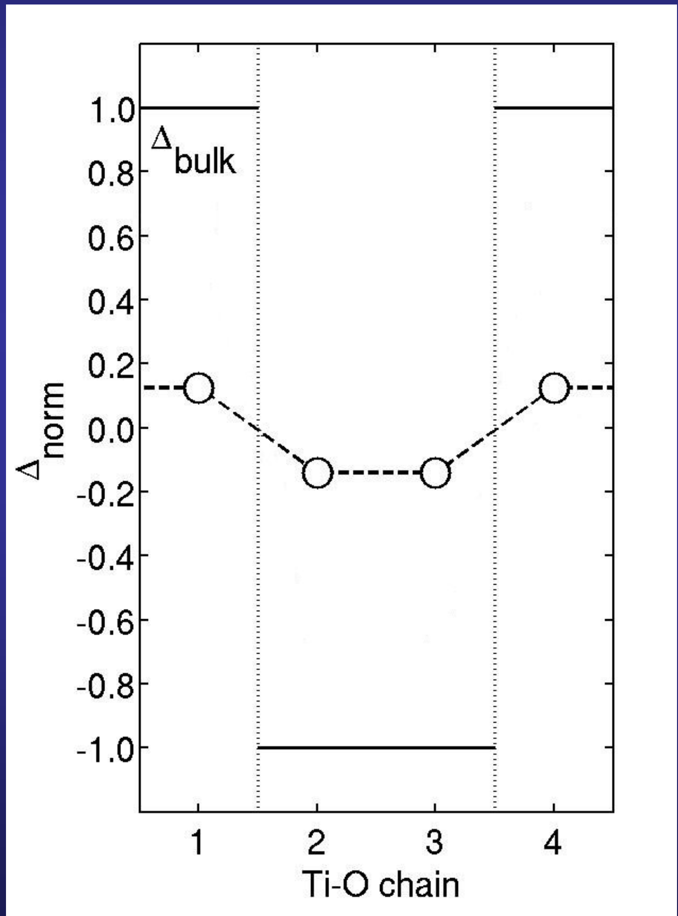
Relevant energy differences very small in the ultrathin m = 2 capacitors



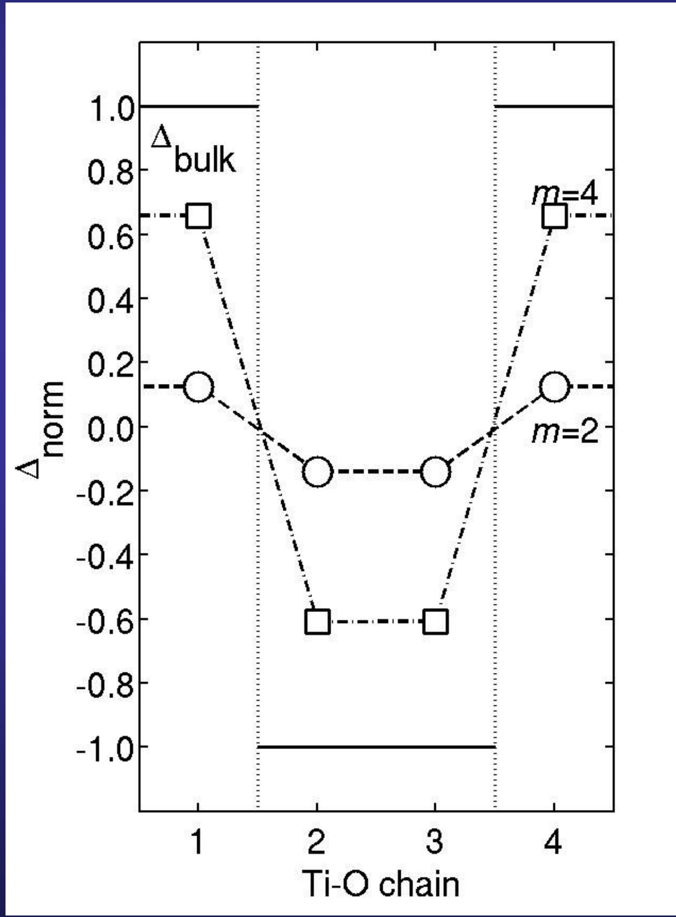
Relevant energy differences increase with thickness



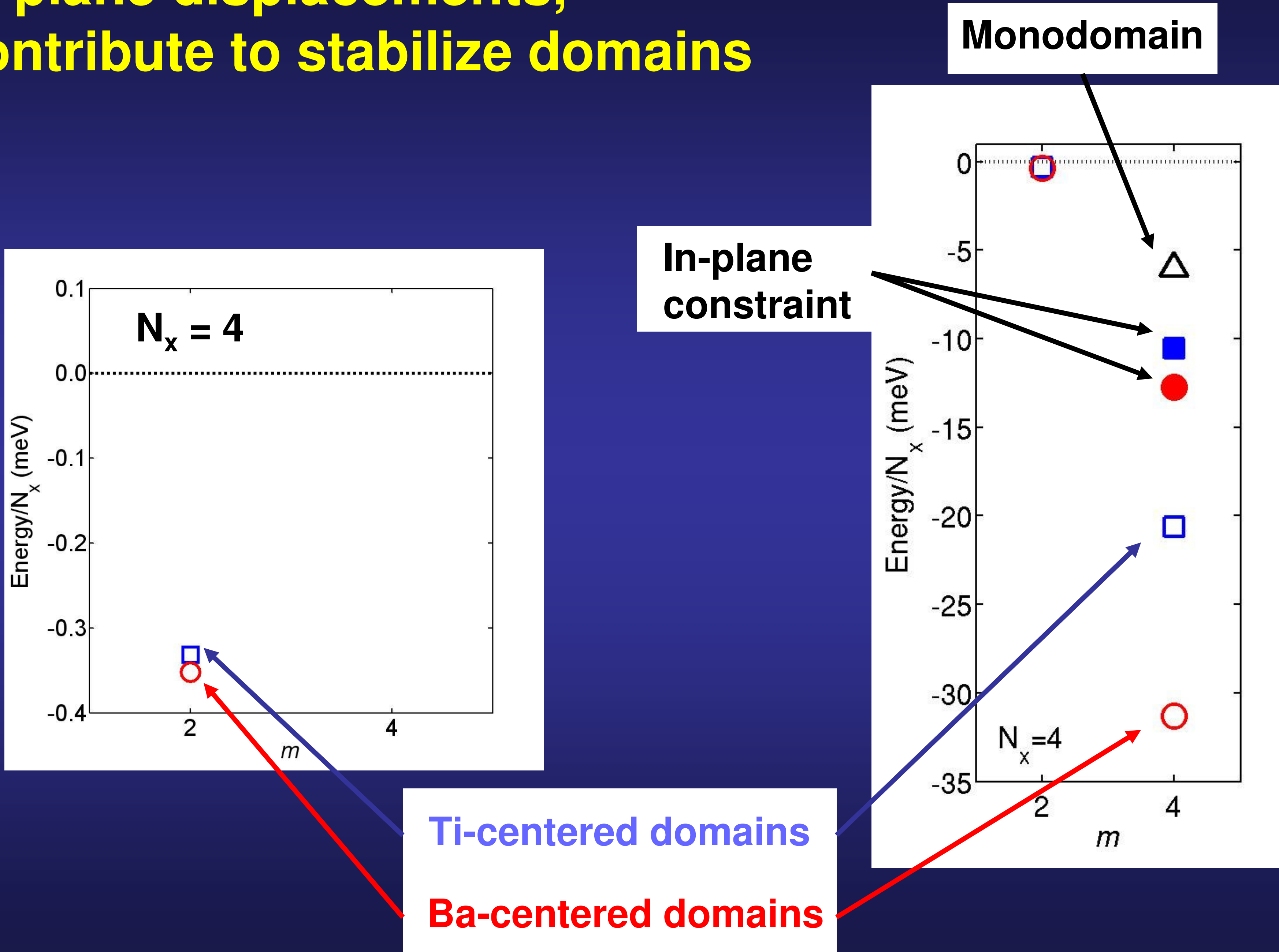
Transition from vortices to standard 180º domains. 4-unit-cell thick layer, great increase in polarization



Transition from vortices to standard 180º domains. 4-unit-cell thick layer, great increase in polarization



In-plane displacements, contribute to stabilize domains

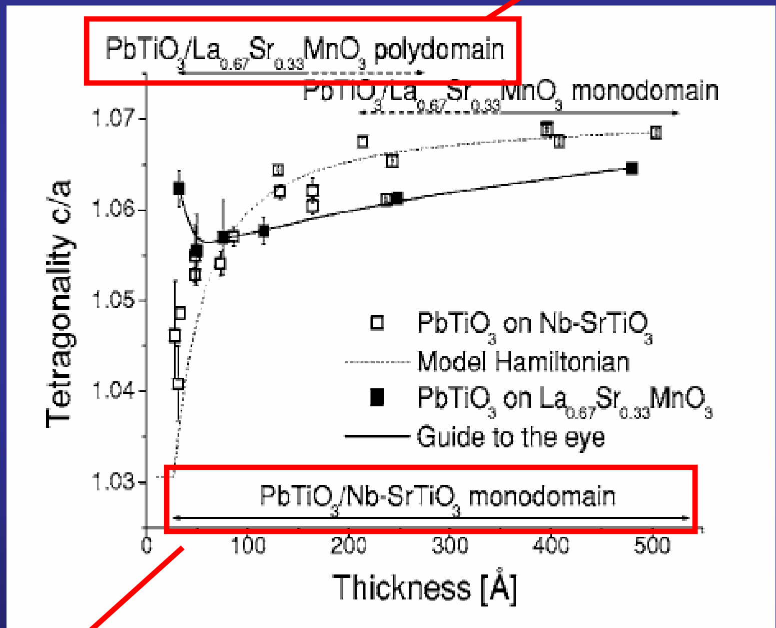


Changing the electrode, the ground state of $PbTiO_3$ changes from monodomain to polydomain

APPLIED PHYSICS LETTERS **90**, 052907 (2007)

Monodomain to polydomain transition in ferroelectric $PbTiO_3$ thin films with $La_{0.67}Sr_{0.33}MnO_3$ electrodes

Lichtensteiger, *et al.*

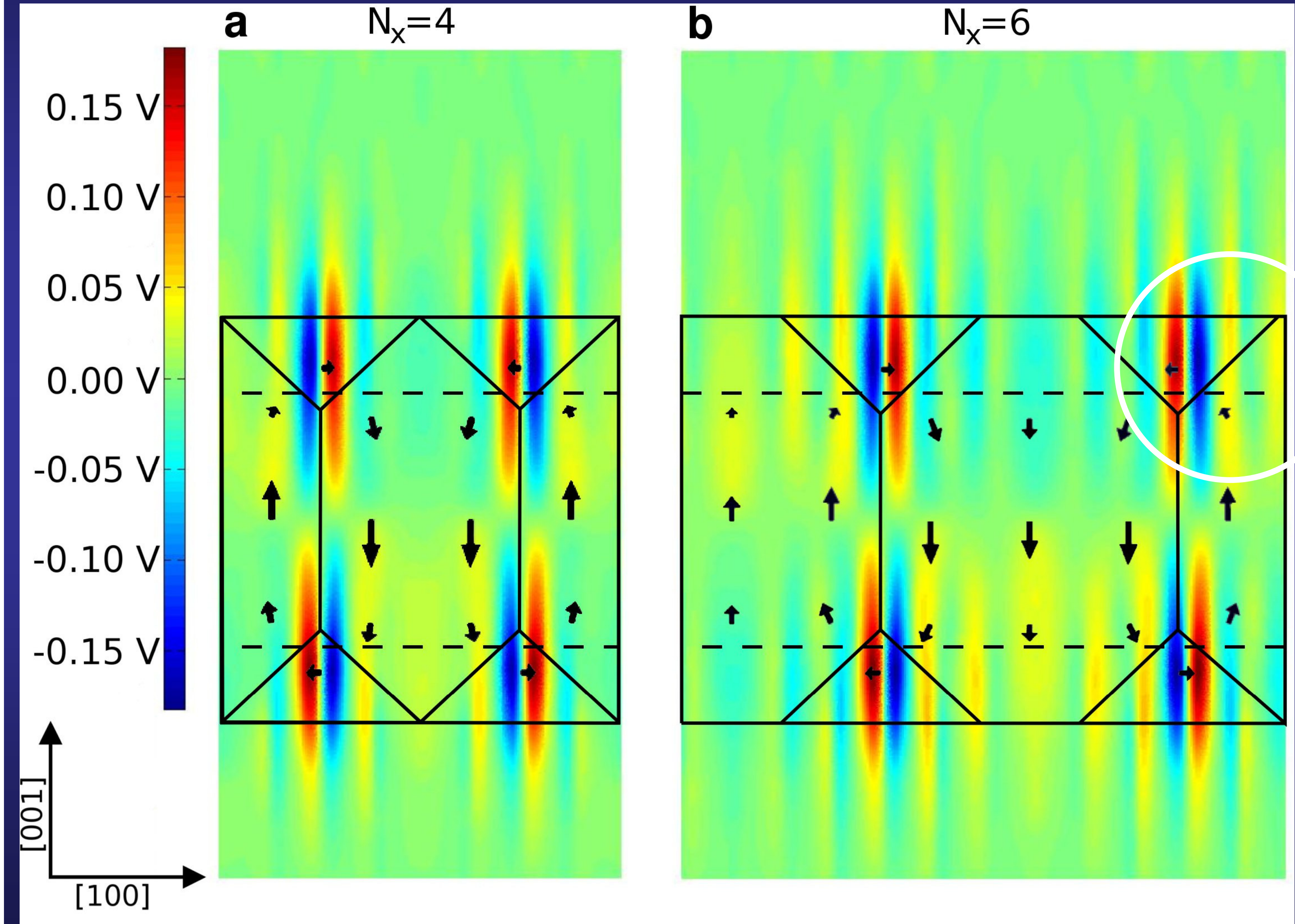


PRL **94**, 047603 (2005) PHYSICAL REVIEW LETTERS week ending 4 FEBRUARY 2005

Ferroelectricity and Tetragonality in Ultrathin $PbTiO_3$ Films

Lichtensteiger, Triscone, Junquera, Ghosez.

Analysis of the electrostatic potential:
large field in *x* at the interface, residual depolarizing field in *z*



Pinning of charged defects at interface?

⇓

role on fatigue?

Two unit cells thick of $BaTiO_3$

Preliminary results on $SrRuO_3/PbTiO_3/SrRuO_3$ $m = 2$, $N_x = 6$ remain paraelectric

Good agreement with experiment

Ferroelectricity in Ultrathin Perovskite Films

Dillon D. Fong,[1] G. Brian Stephenson,[1*] Stephen K. Streiffer,[1] Jeffrey A. Eastman,[1] Orlando Auciello,[1] Paul H. Fuoss,[1] Carol Thompson[2]

At 1

and 2 unit cells, no satellites are observed at any temperature, indicating that the samples remain in the paraelectric phase.

Conclusions

• Many effects affect the delicate balance between short and long range forces in thin films:

Surface

Mechanical (epitaxial strain)

Electrical (depolarizing field)

Chemical

• As a result of the different interactions, wealthy of phase diagrams

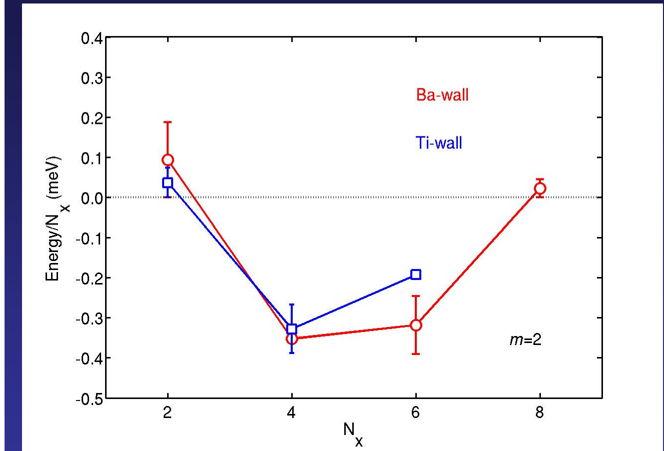
• The question of suppression of ferroelectricity in ultrathin films cannot be answered in general but, instead, must be addressed independently for each individual system.

Slides available at: http://personales.unican.es/junqueraj

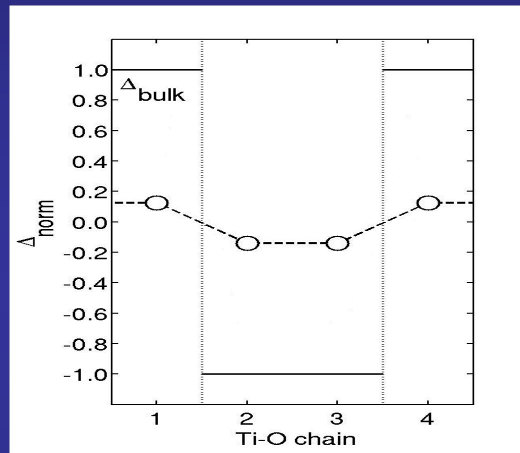
Contact: pablo.aguado@unican.es

javier.junquera@unican.es

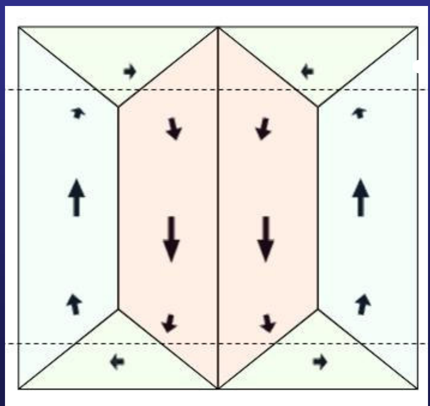
Conclusions



• **Polydomain phases** in ultrathin FE films are stabilized below critical thickness in monodomain configurations.



• The chemical interaction through the interface is an essential factor since it affects the **in-plane mobility** of the atoms.



• Polydomains phases have a structure: **Closure domains**

Slides available at: http://personales.unican.es/junqueraj

Contact: pablo.aguado@unican.es

javier.junquera@unican.es

Preprint available in cond-mat 0710.1515

Many thanks to

Theoretical collaborators

Karin M. Rabe, Morrel H. Cohen

Philippe Ghosez

Alberto García

Experimental collaborators

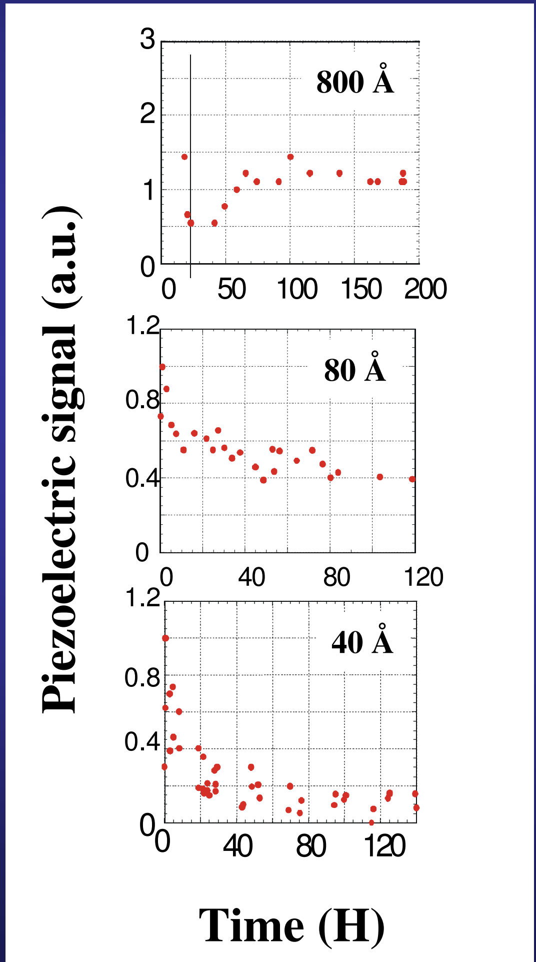
Céline Lichtensteiger, Jean-Marc Triscone

Valanoor Nagarajan, R. Ramesh

More information …

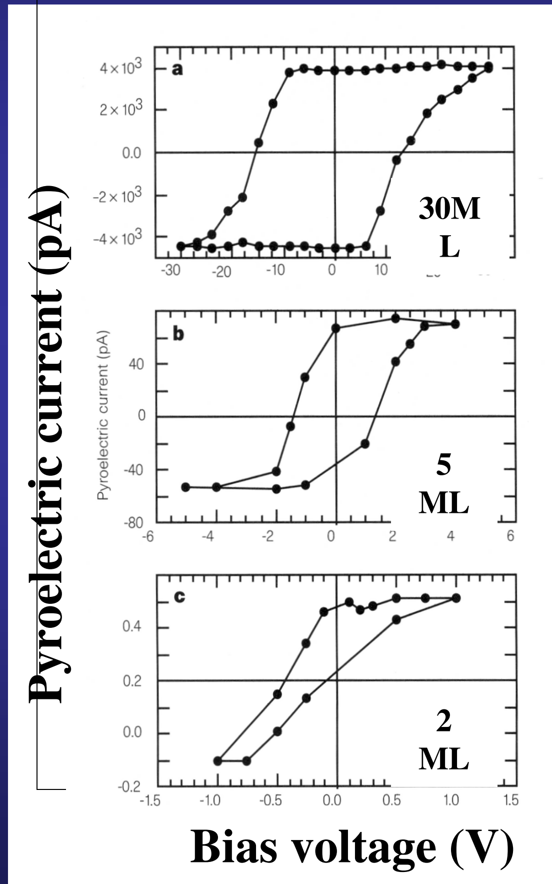
Size effects in ferroelectrics
Two works that challenged the standard viewpoint

10 unit-cells thick
$Pb(Zr_{0.2}Ti_{0.8})O_3$



Th. Tybell, Ch. Ahn and J.-M. Triscone
Appl. Phys. Lett. 75, 856 (1999)

2 monolayers thick
random copolymer

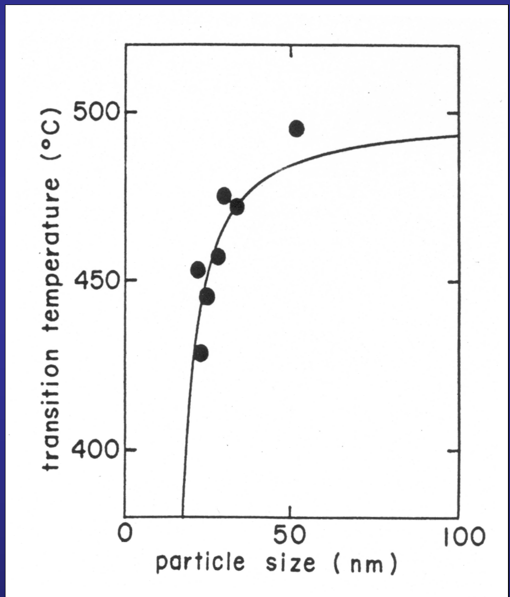


A.V. Bune et al.
Nature 391, 874 (1998)

Size effects in ferroelectrics
Standard view until the end of the nineties

$PbTiO_3$ ultrafine particles

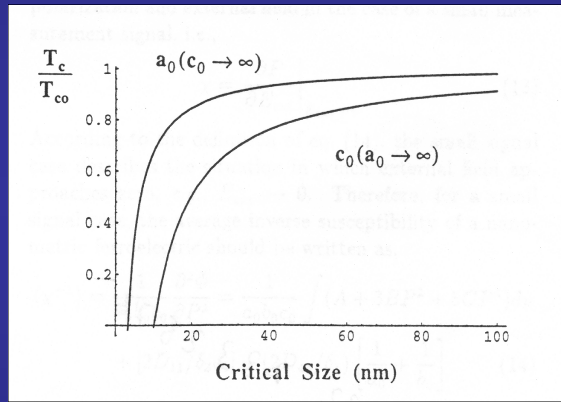
Experiment



K. Ishikawa, K. Yoshikawa, and N. Okada,
Phys. Rev. B 37, 5852 (1988)

ABO_3 ultrathin films

Anisotropic mean-field calculations



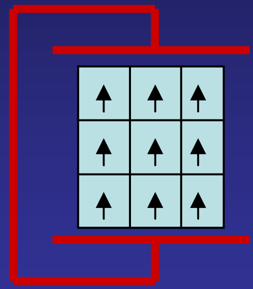
Critical thickness :

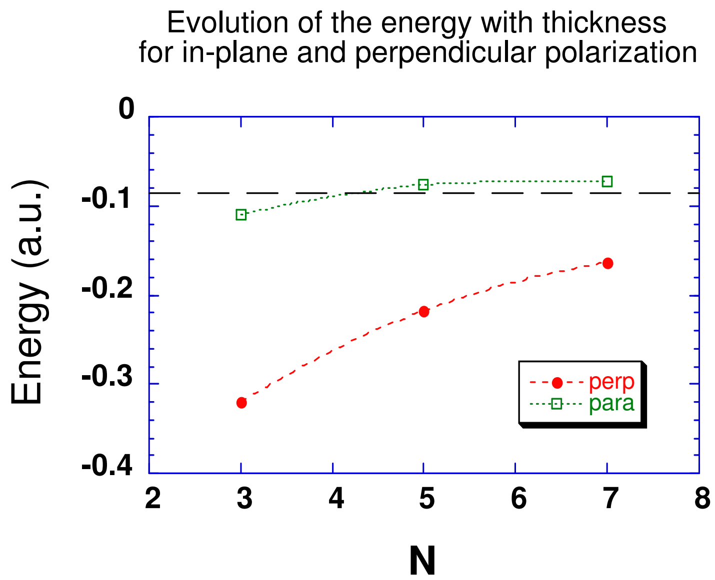
$Pb(Zr_{0.5}Ti_{0.5})O_3$:~ 200Å @ RT
$PbTiO_3$: ~ 80Å @ RT

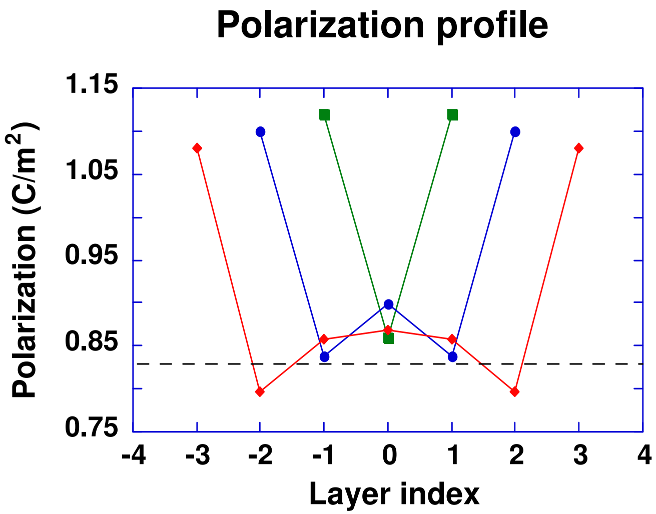
S. Li et al.
Jpn. J. Appl. Phys. 36, 5169 (1997)

First-principles simulations on ferroelectric thin films model Hamiltonian approaches

$PbTiO_3$ free standing slabs under stress free and short-circuit boundary conditions are ferroelectric



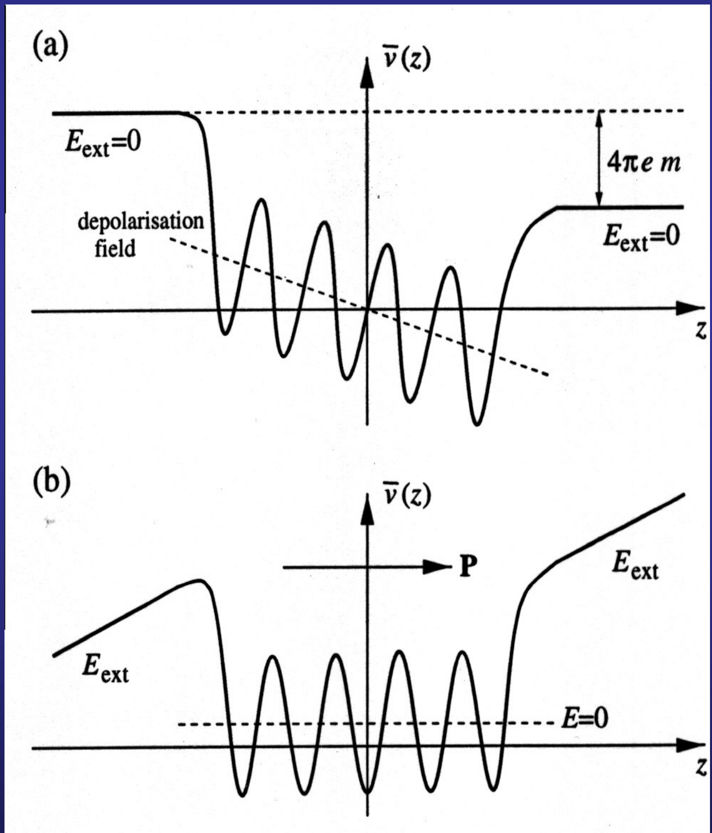


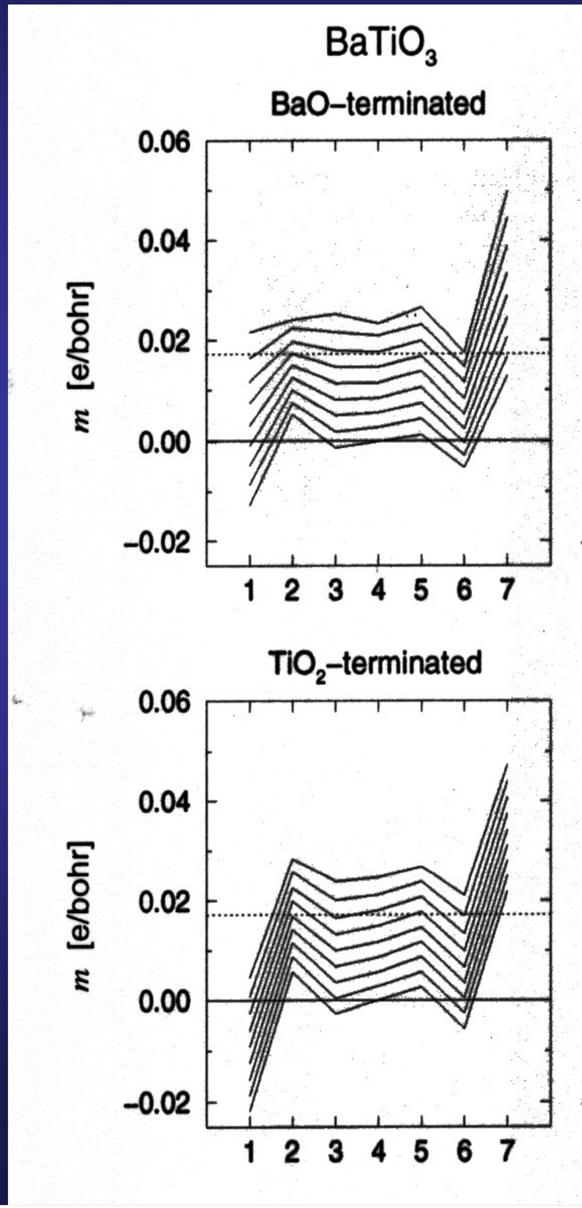


Ph. Ghosez and K. M. Rabe, Appl. Phys. Lett. 76, 2767 (2000)

First-principles simulations on ferroelectric thin films full first-principles simulations

$BaTiO_3$ and $PbTiO_3$ free-standing slabs under external electric fields to screen the depolarizing field





B. Meyer and D. Vanderbilt, Phys. Rev. B 63, 193201 (2001)