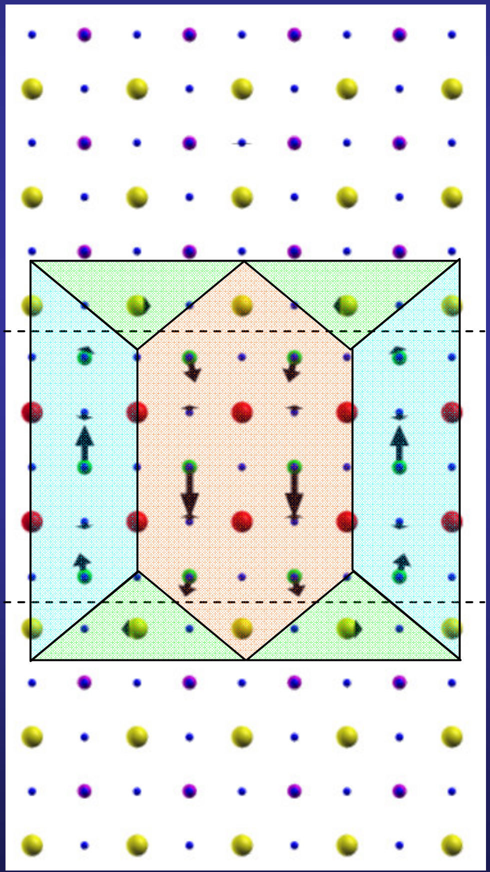
Ferromagnetic like closure domains in ferroelectric ultrathin films



Pablo Aguado-Puente

Javier Junquera

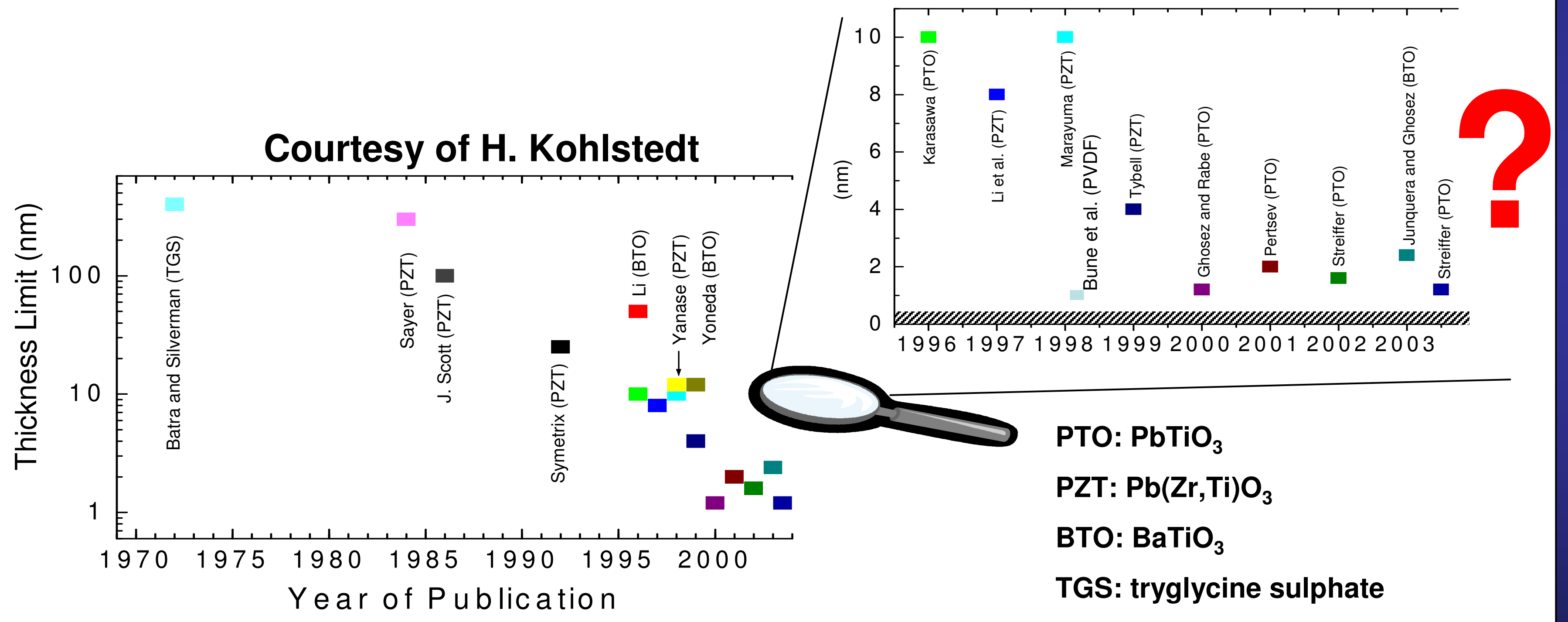
UNIVERSIDAD DE CANTABRIA

CITIMAC

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

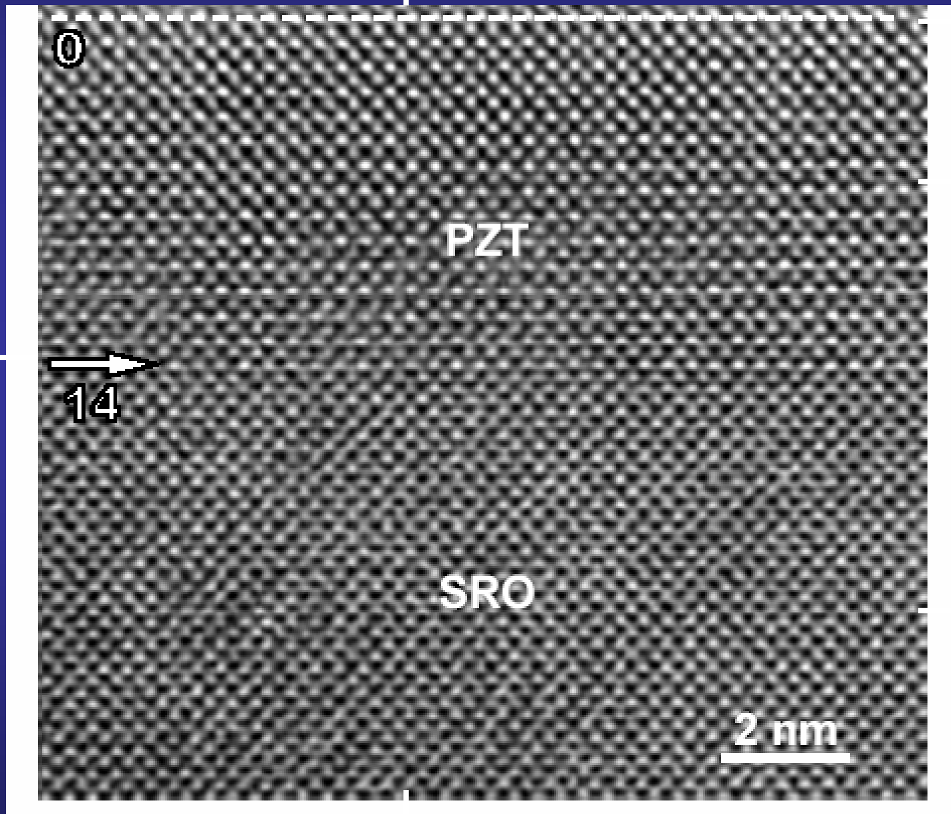
PVDF: Ferroelectric polymer

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)

and references therein.

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



Chemistry

Surface

Defects

(vacancies, misfit dislocations…)

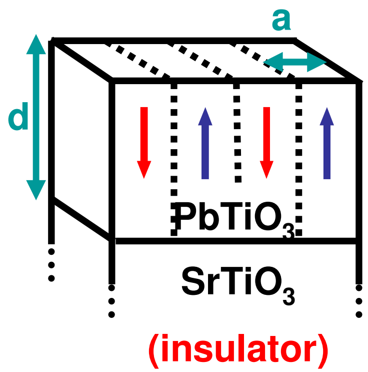
Finite conductivity

Mechanical

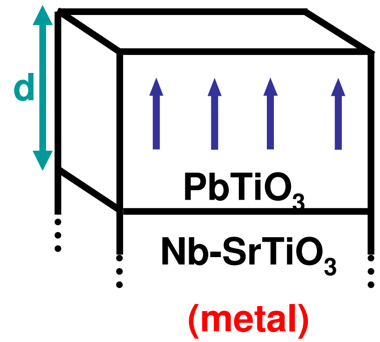
Electrostatic

Experimental measurements, global result

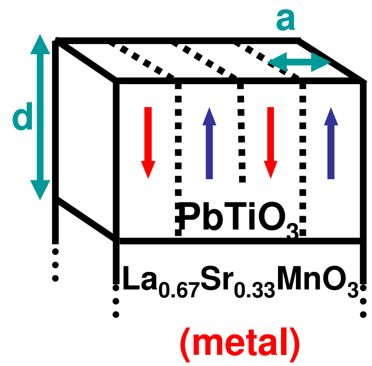
Experimentally: small changes in boundary conditions, great changes in stable state



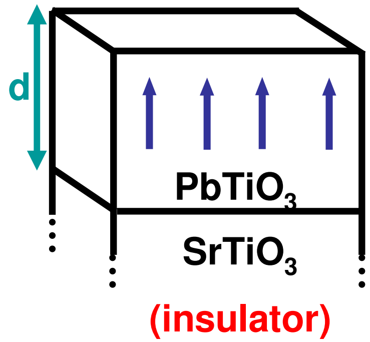
D. D. Fong et al. (2004)
S. K. Streiffer et al. (2002)



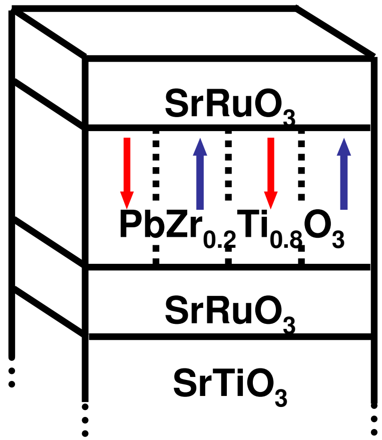
C. Lichtensteiger et al. (2005)
A. T. J. van Helvoort et al. (2005)



C. Lichtensteiger et al. (2007)

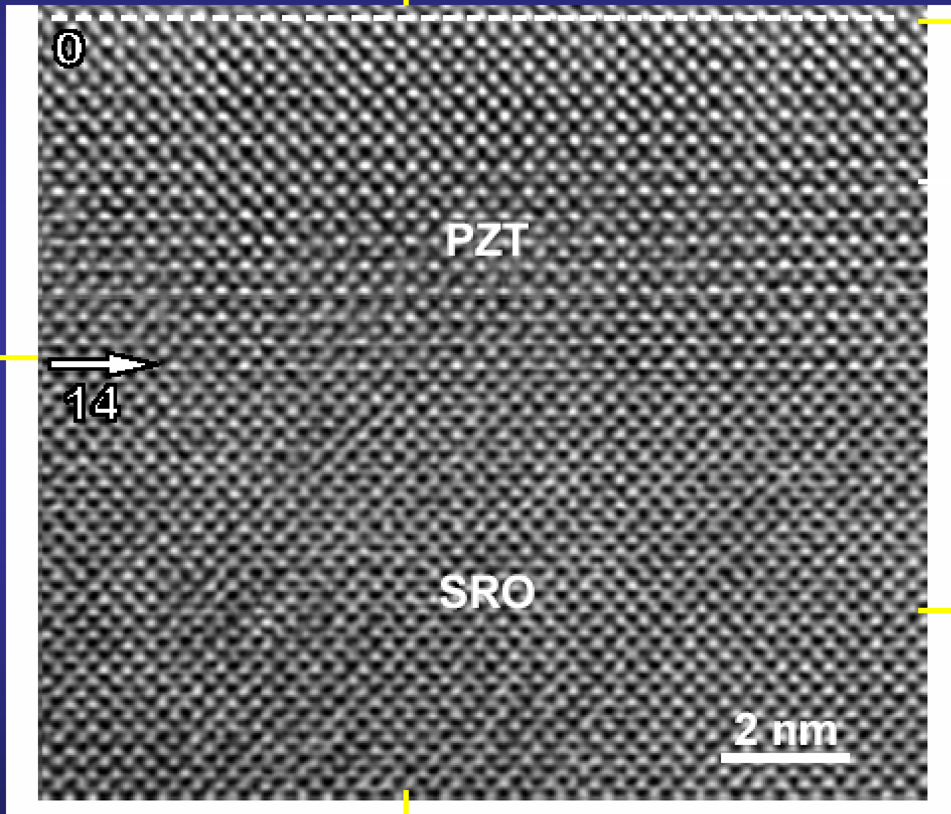


D. D. Fong et al. (2005)



V. Nagarajan et al. (2006)

First-principles calculations allow to isolate their respective influence



Surface

Defects

(vacancies, misfit dislocations…)

Finite conductivity

Mechanical

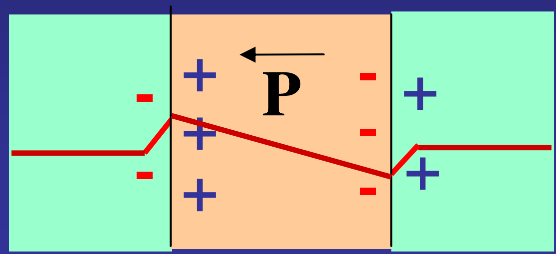
Chemistry

Electrostatic

Residual depolarizing field increases electrostatic energy and opposes to a polarization

Real electrodes

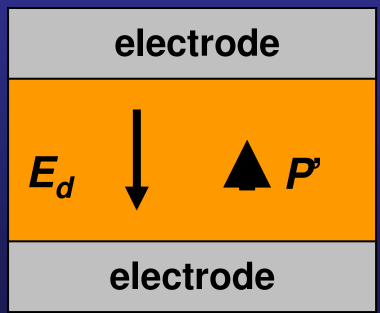
imperfect screening



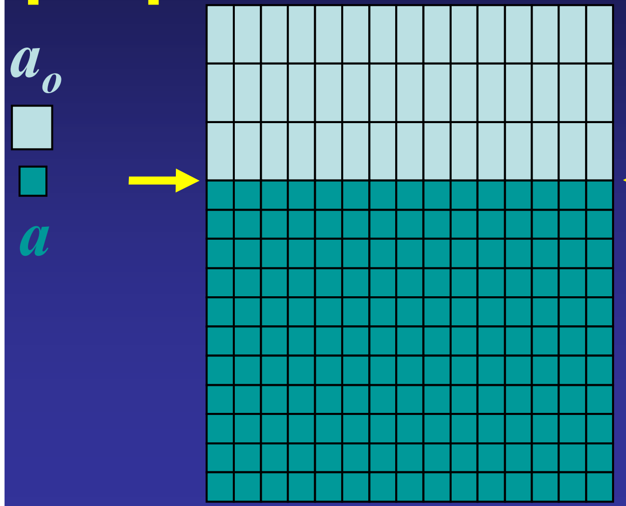
$$\mathcal{E}_d = -4\pi.[2.\lambda_{eff}/d]\cdot \mathbf{P}$$

Screening by free charges

(electrodes or adsorbates)



Strain imposed by the substrate affects the properties of ferroelectric materials



misfit strain

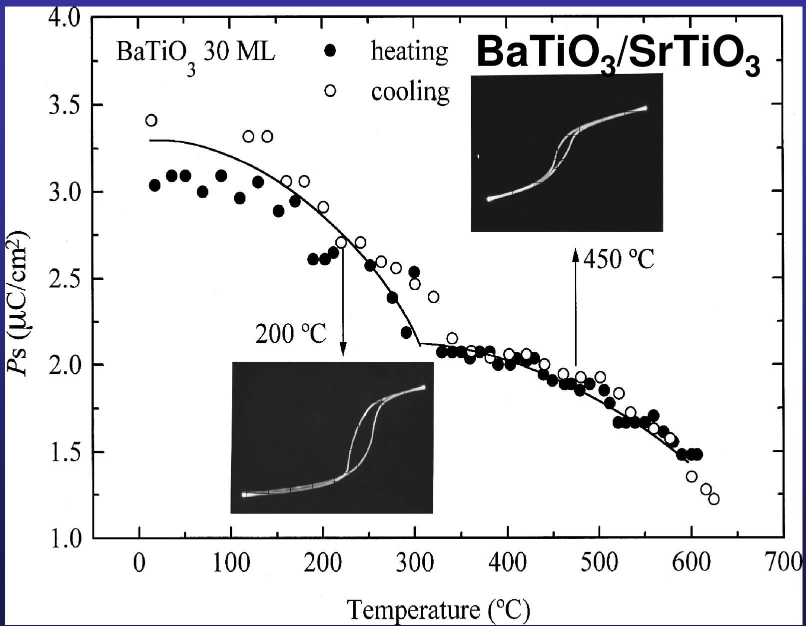
$u_m = (a - a_o)/a_o$

Courtesy of O. Diéguez

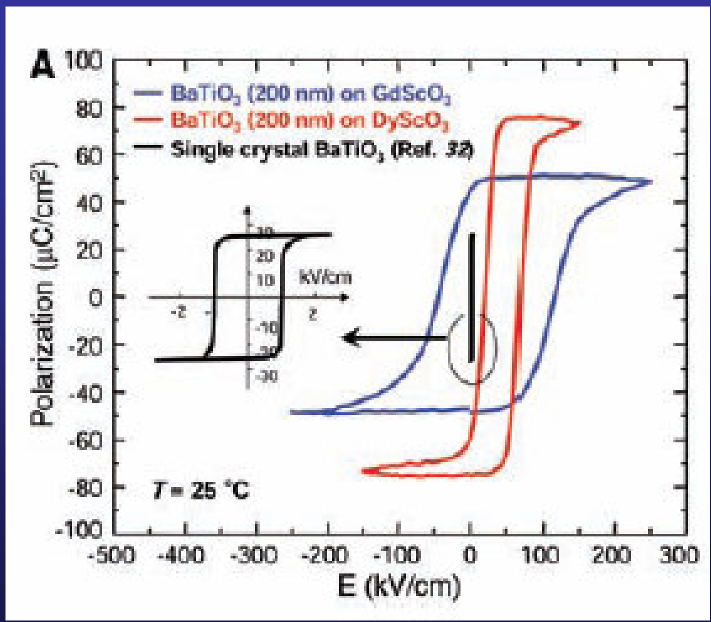
Typical picture:

Compressive strain ⇒ tetragonal *c*

Tensile strain ⇒ orthorrombic *aa*

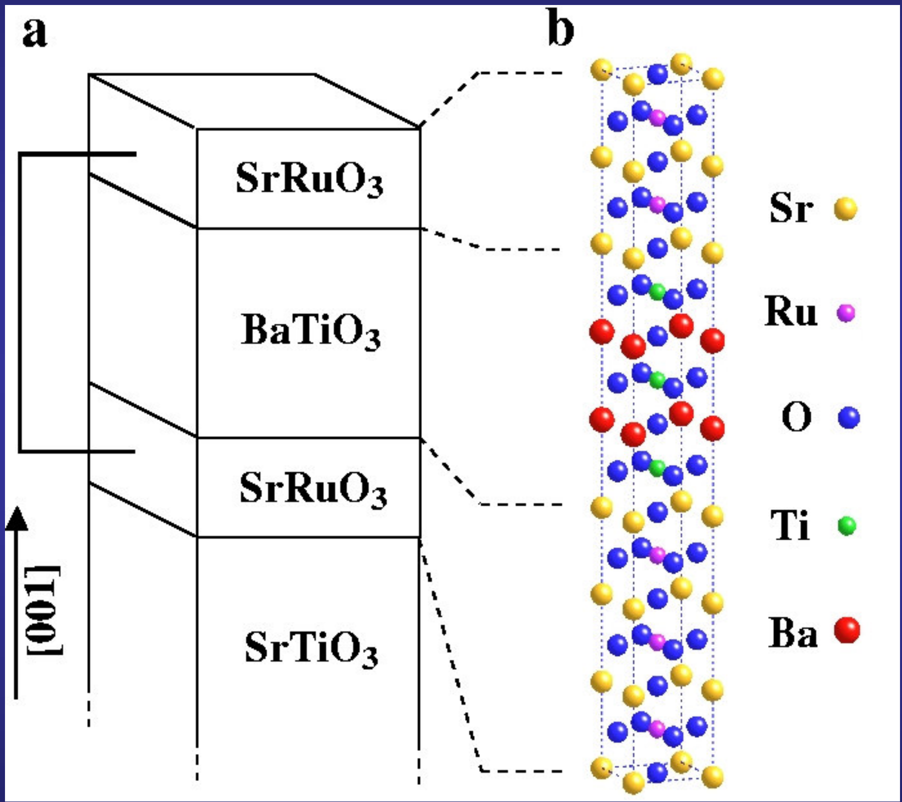


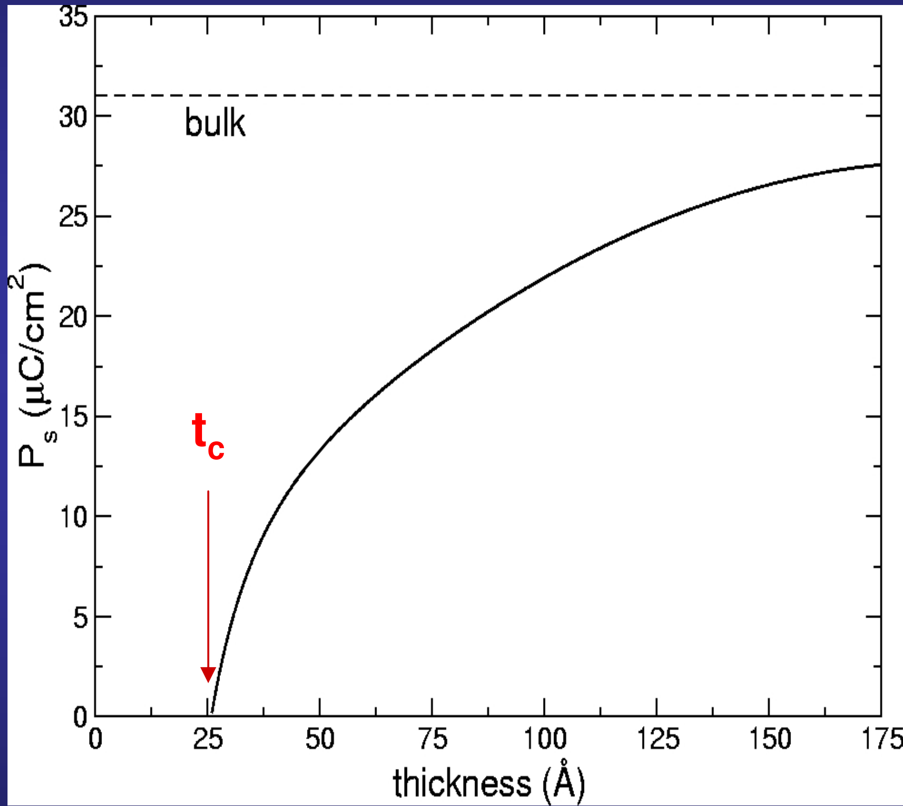
Yoneda *et al.*, J. Appl. Phys. 83, 2458 (1998)



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

Simulations of ferroelectric nanocapacitors from first-principles





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

Many DFT first-principles computations on size effects in *monodomain* 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]

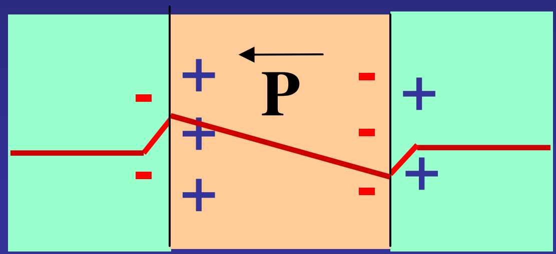
Many DFT first-principles computations on size effects in *monodomain* ferroelectric ultrathin films

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

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

Real electrodes

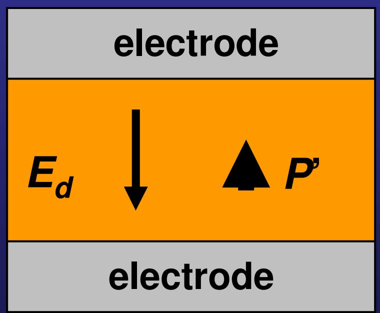
imperfect screening



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

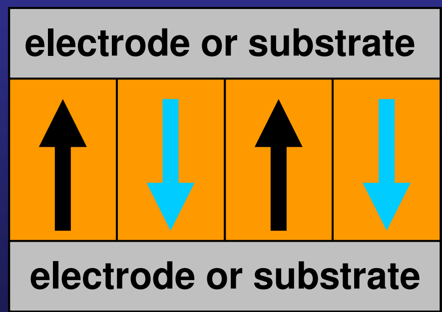
Screening by free charges

(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?

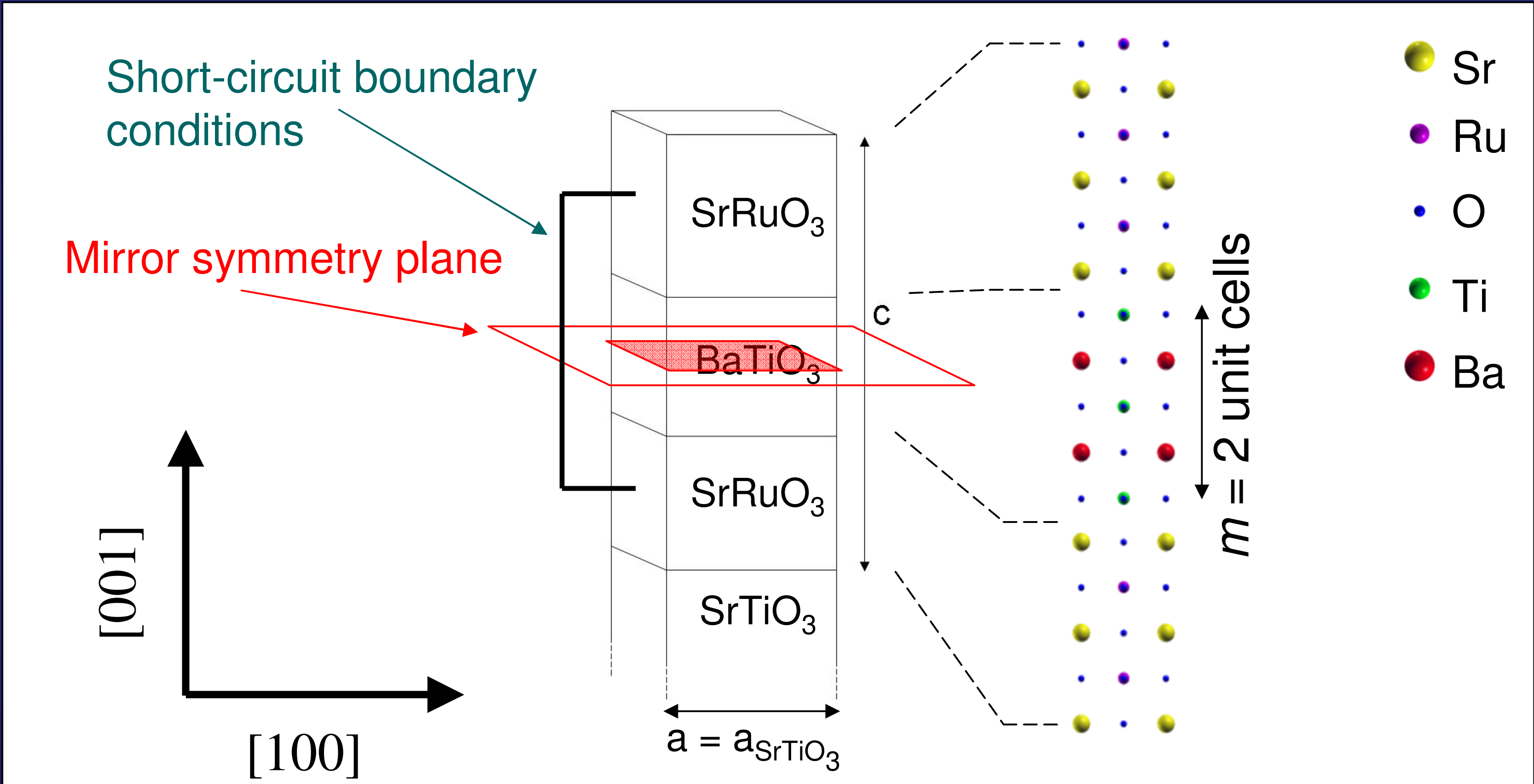
"It is not certain yet whether this instability in a single-domain ground state results in paraelectricity or in many small domains"

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: the paraelectric unit cell

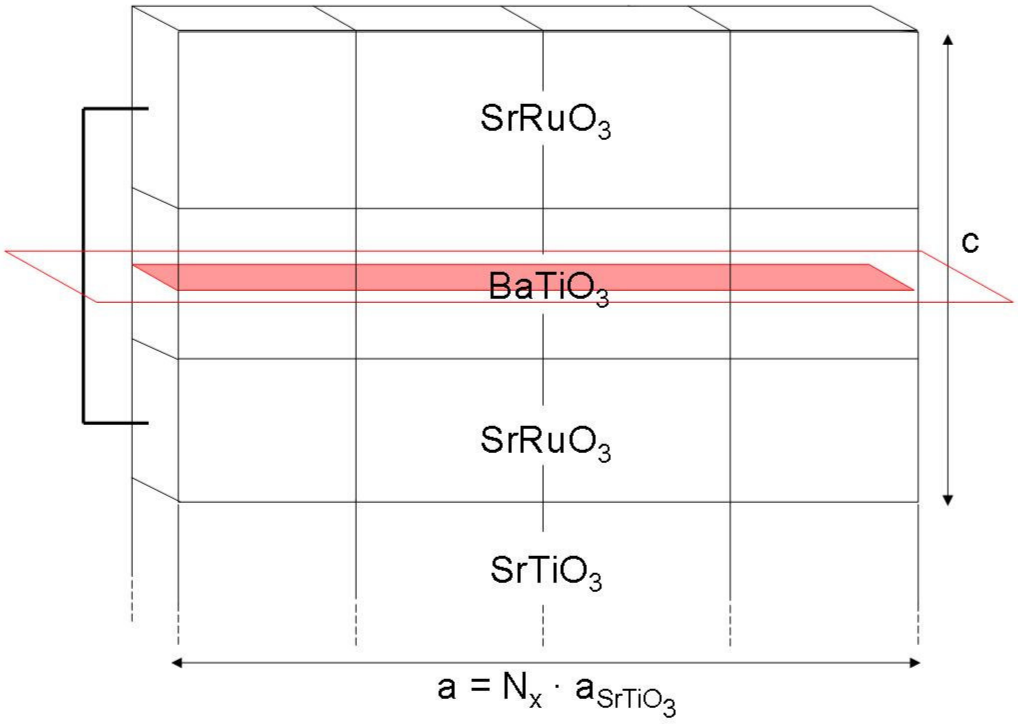
- Building the reference cell following the scheme of Junquera and Ghosez (2003).



N_{at} = 40 atoms

Building the cell: replicating the paraelectric structure

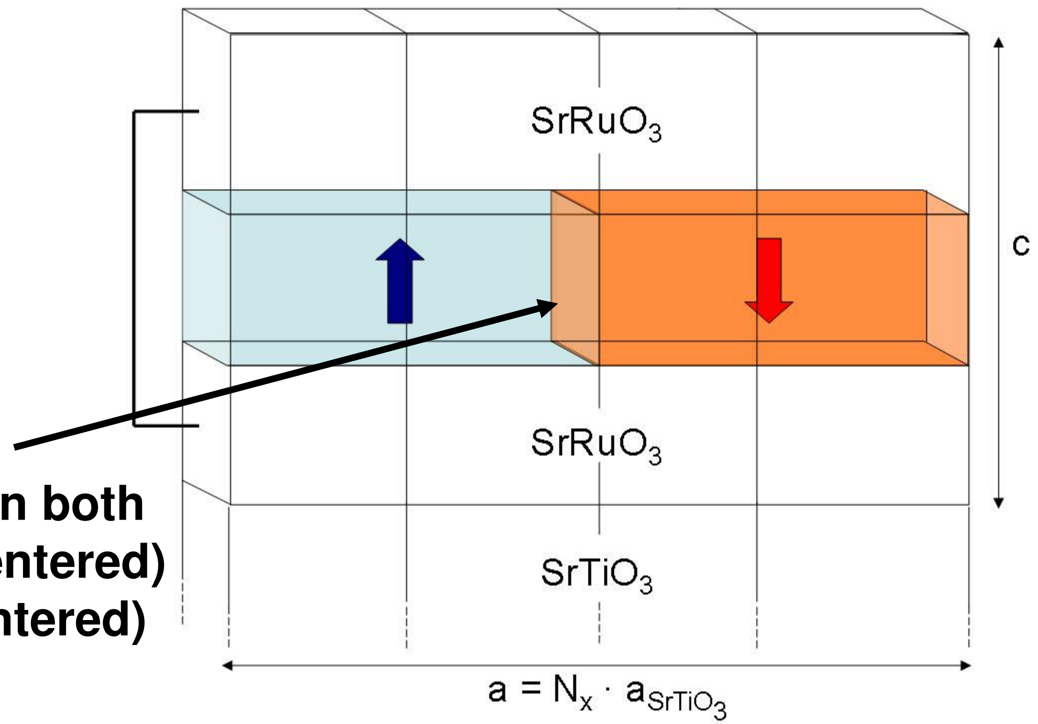
- N_x repetitions in [100] direction.
- The energies of these cells as references.



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

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.



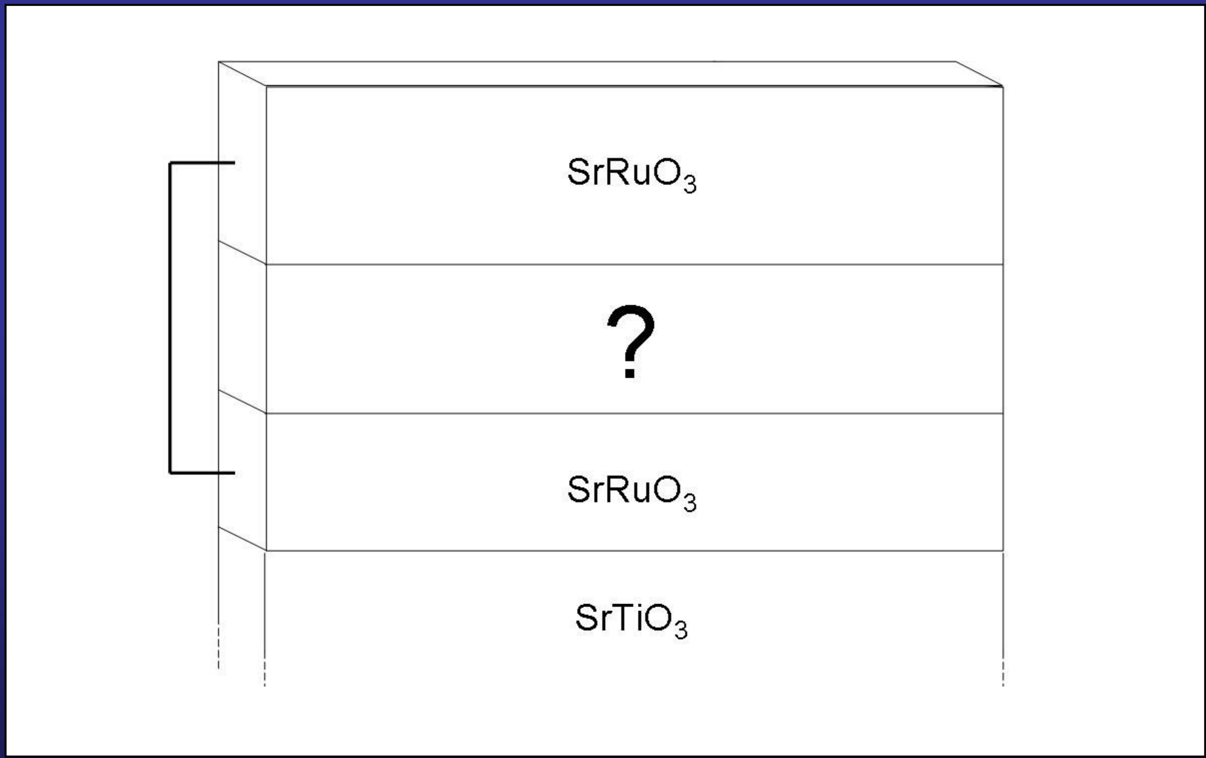
Twinning on both
BaO (Ba-centered)
TiO_2 (Ti-centered)

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

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

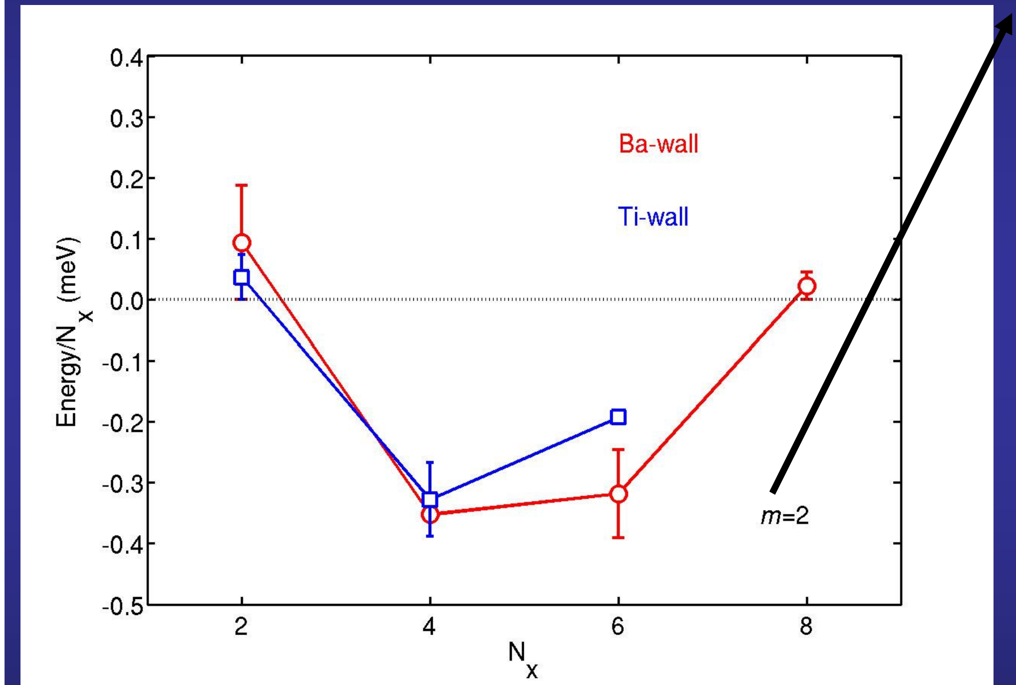
Forces smaller than 0.01 eV/Å

No constraints impossed on the atomic positions



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

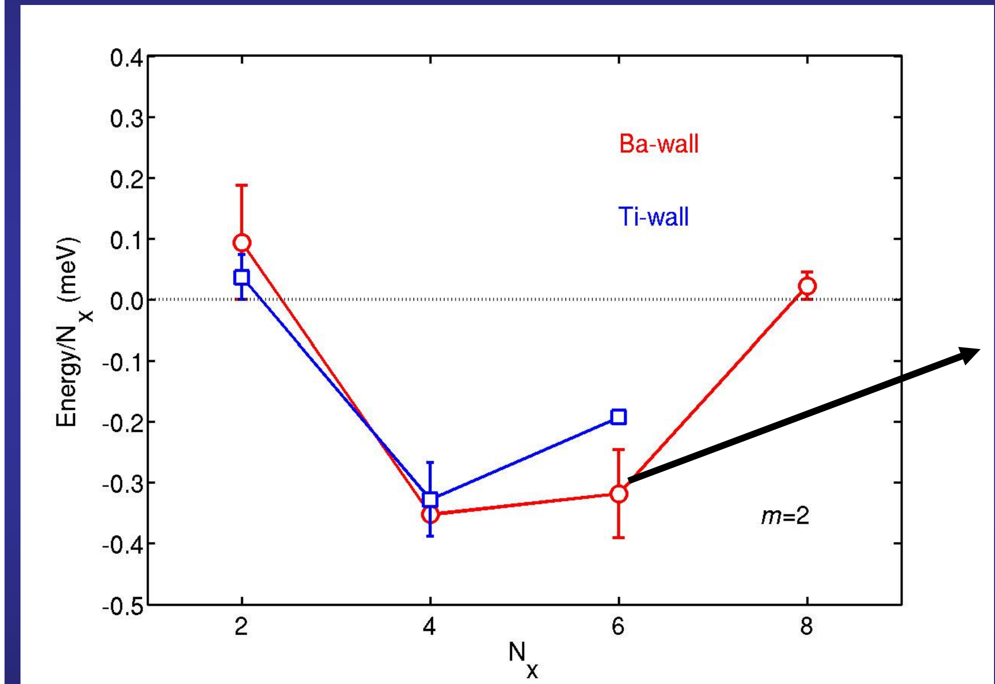
2-unit-cells thick $BaTiO_3$ layer



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



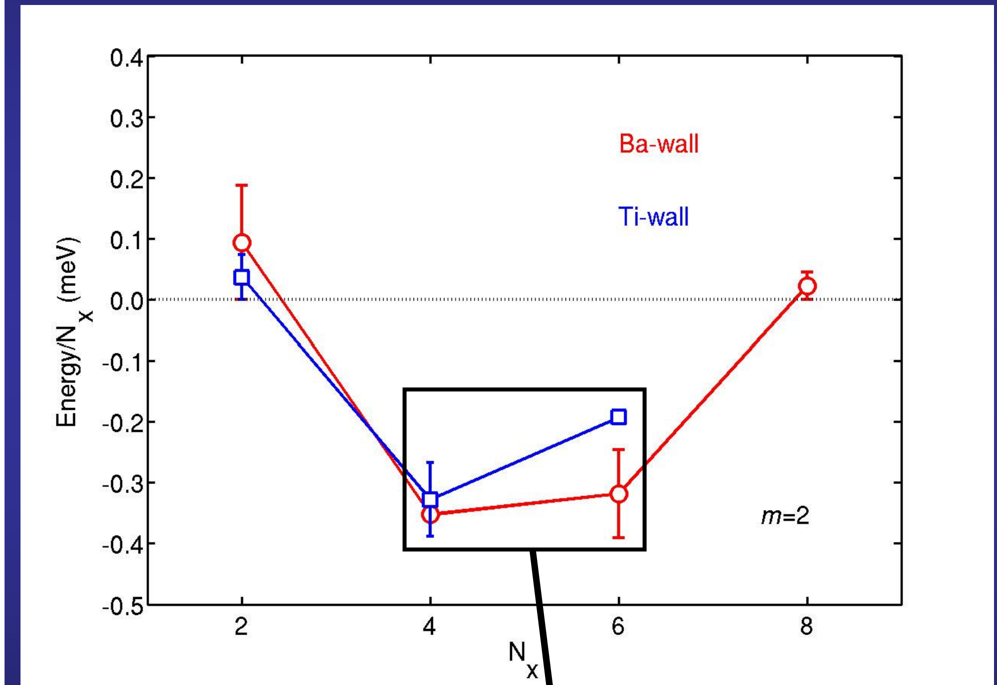
Polar **domains stabilized below critical thickness** for the **monodomain** configuration

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

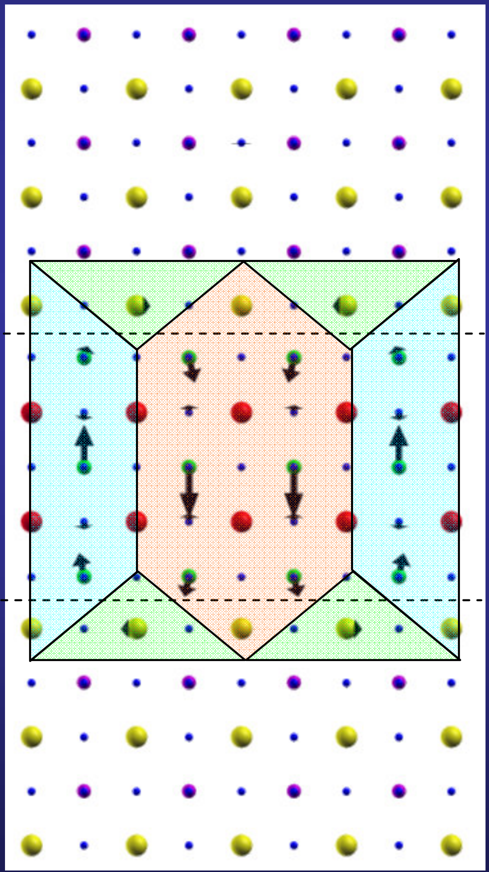
(α and β phases in $PbTiO_3/SrTiO_3$ interfaces?)

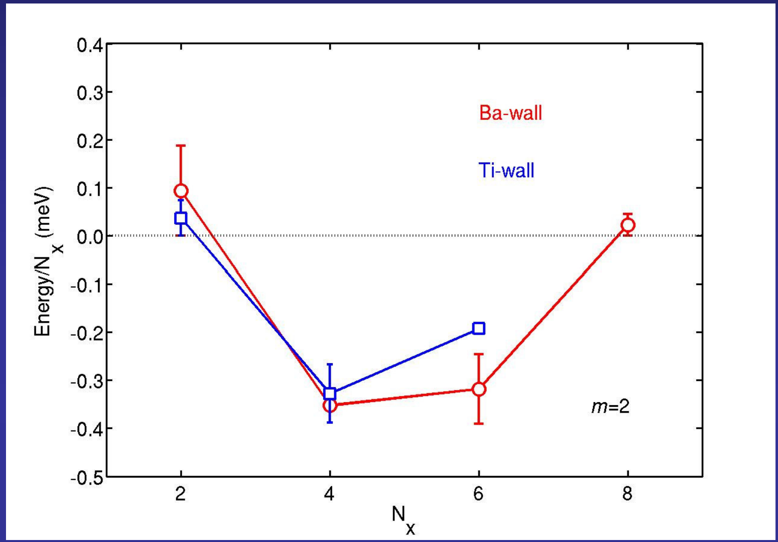
D. D. Fong *et al.*, Science 304, 1650 (2004)

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

$N_x = 4$

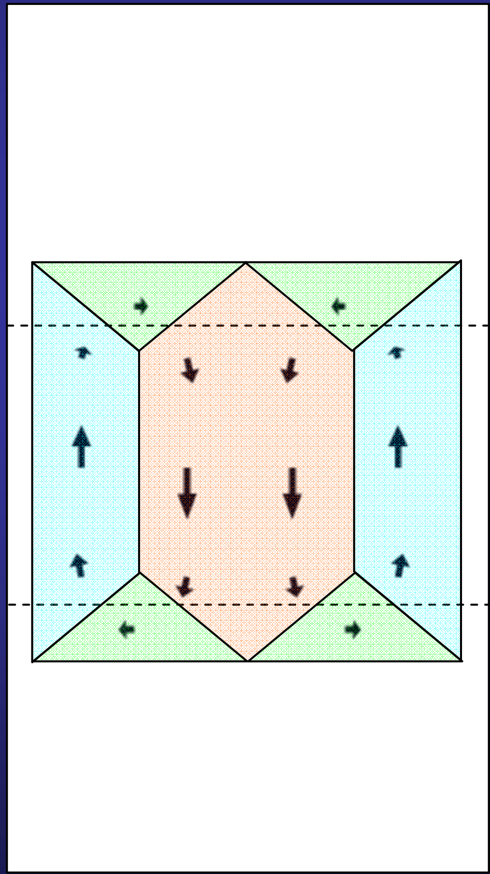
BaO domain walls

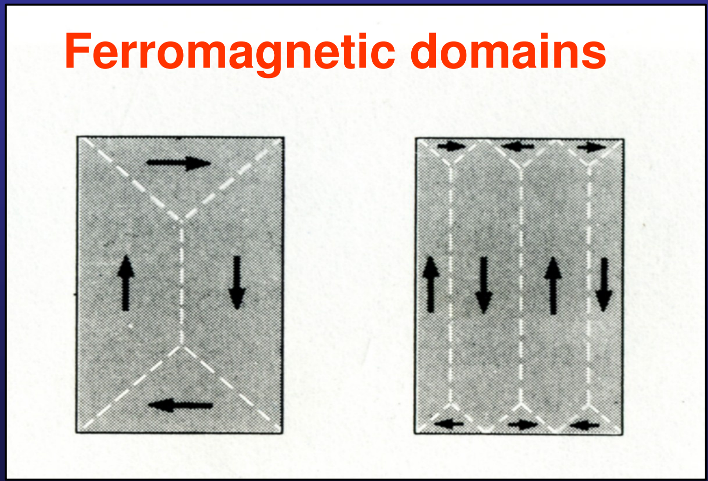




$N_x = 4$

BaO domain walls



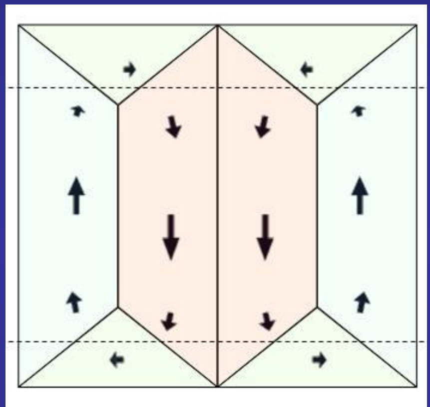


C. Kittel (1946)

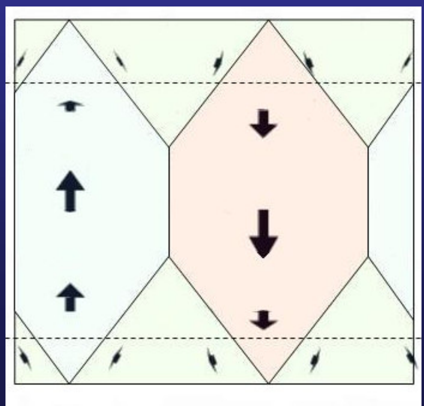
Polydomain phases adopt the form of a "domain of closure", common in ferromagnets

N_x=4

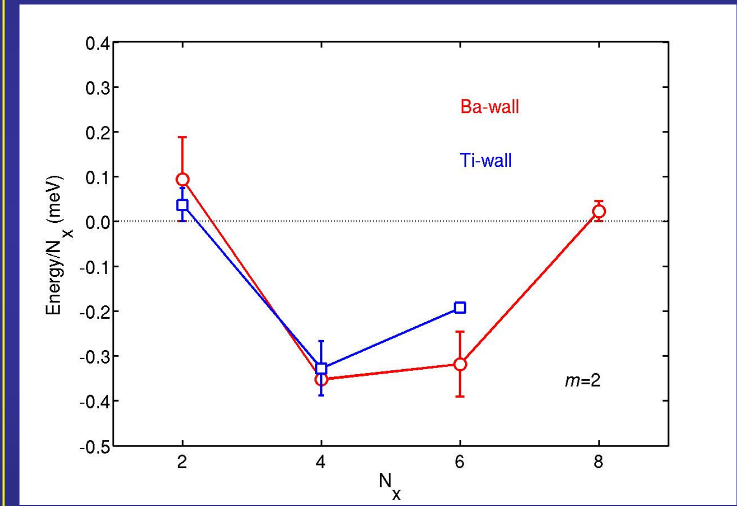
BaO wall



TiO_2 wall

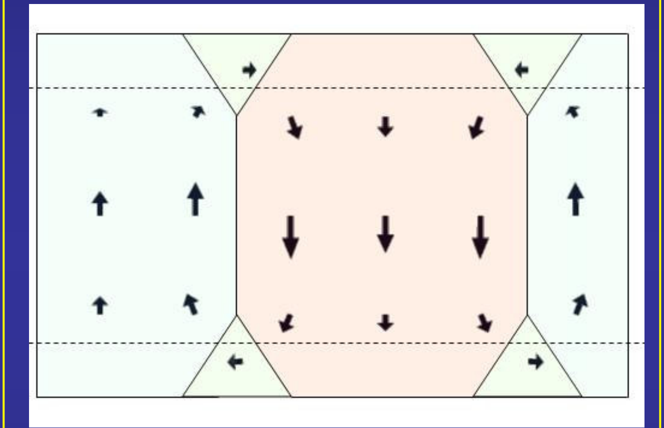


2-unit-cells thick $BaTiO_3$ layer

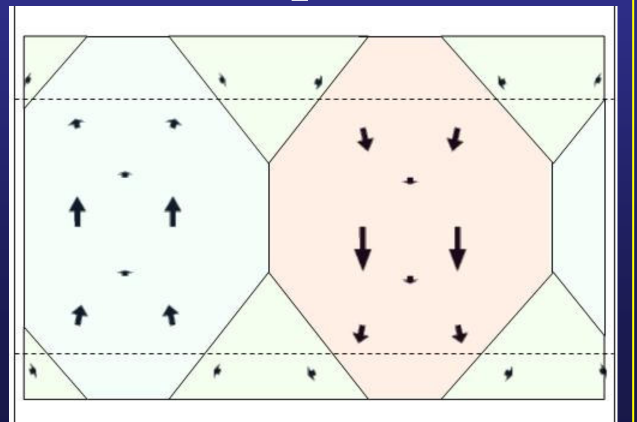


N_x=6

BaO wall



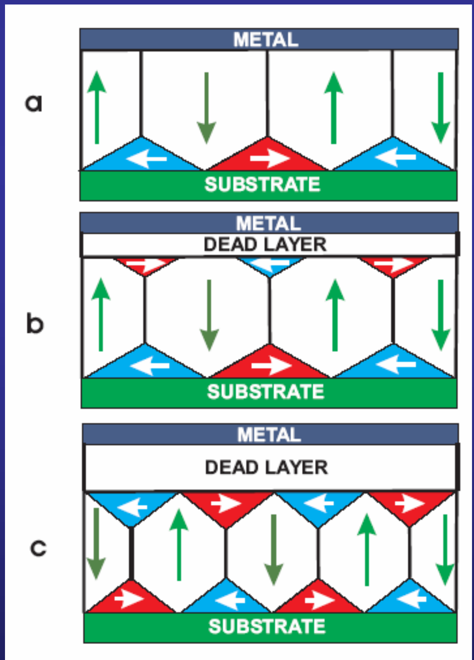
TiO_2 wall



Domains of closure recently predicted using a model hamiltonian approach

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

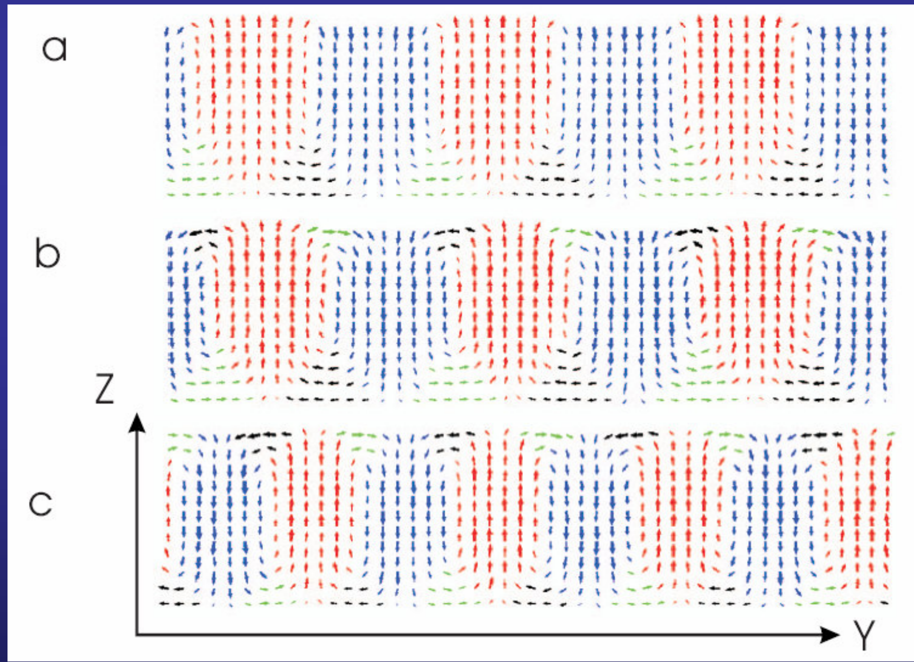
sandwiched with a nongrounded metallic plate (top) and a non-conductive substrate (bottom)



d = 0

d = 0.3 a

d = 0.5 a



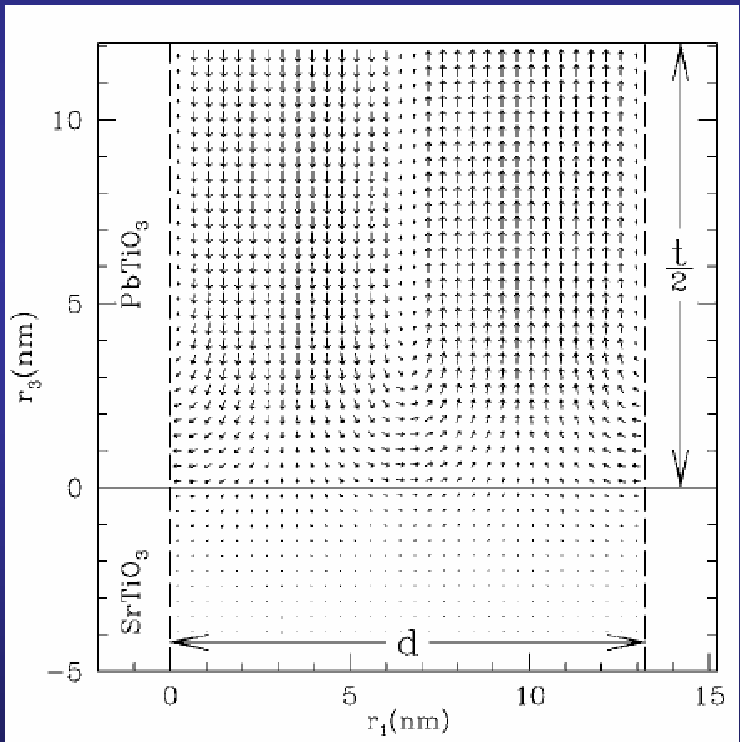
Dead layer thickness

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

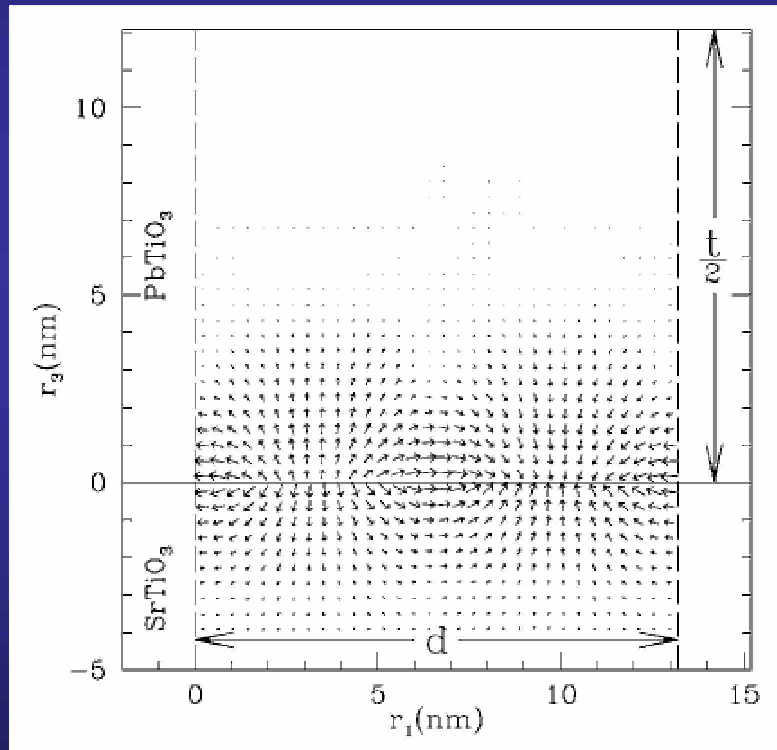
Domains of closure recently predicted using a phenomenological thermodynamic potential

242 Å thick $PbTiO_3$ thin films

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



Polarization distribution

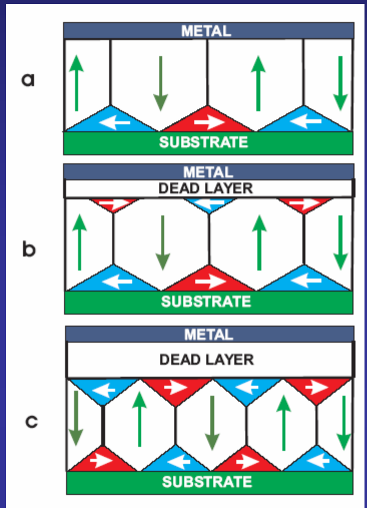


Equilibrium field distribution

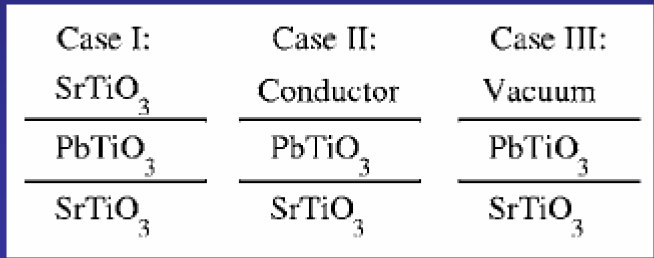
G. B. Stephenson and K. R. Elder, J. Appl. Phys. 100, 051601 (2006)

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

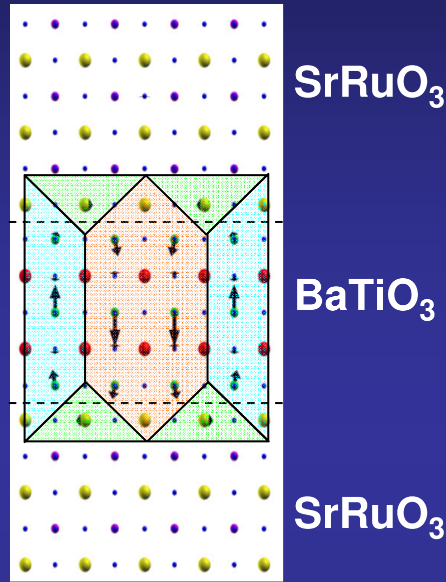
Domains of closure appear even with symmetric metallic electrode



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

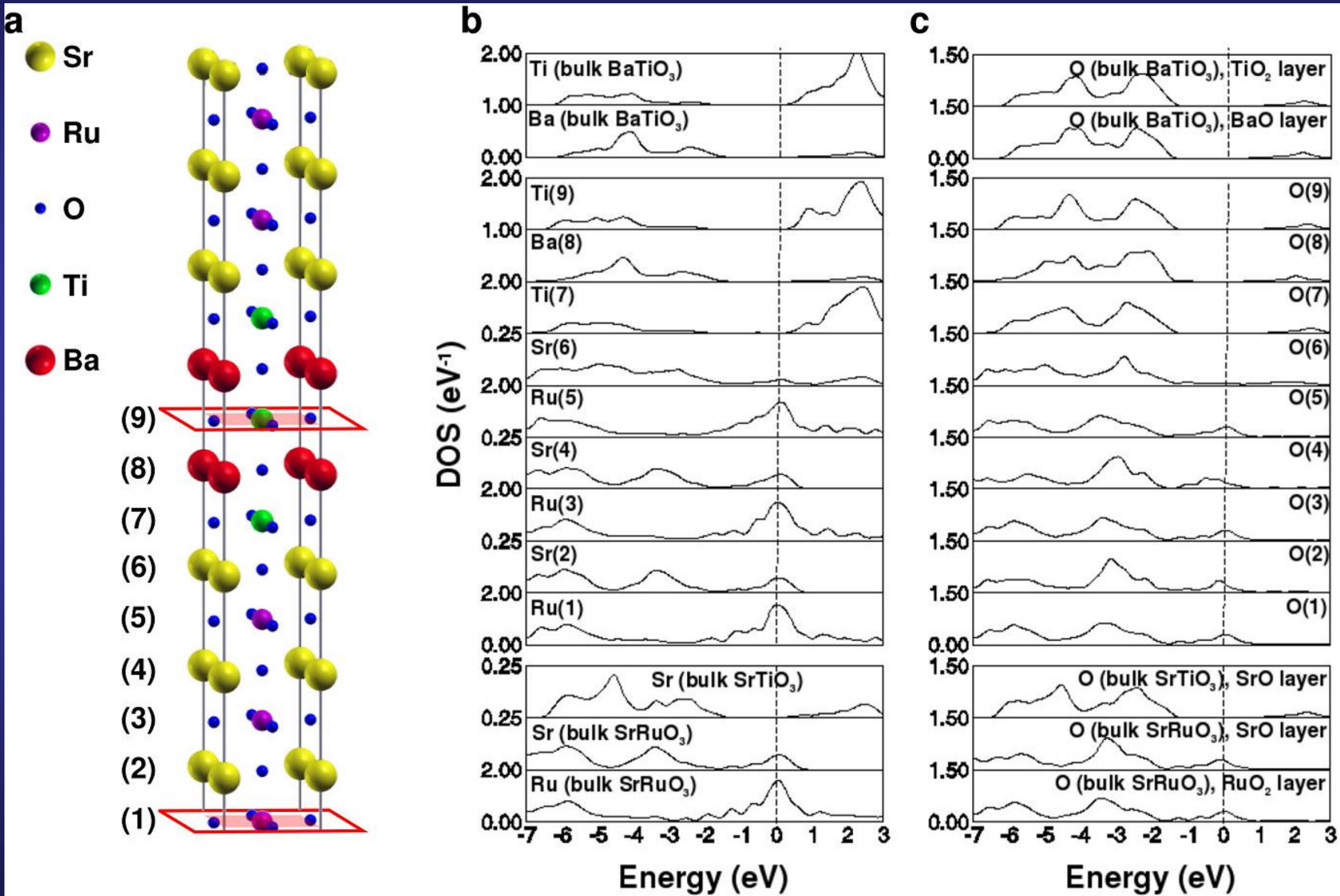
Domains of closure appear even in $BaTiO_3$ ferroelectric capacitors

“$BaTiO_3$ 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)

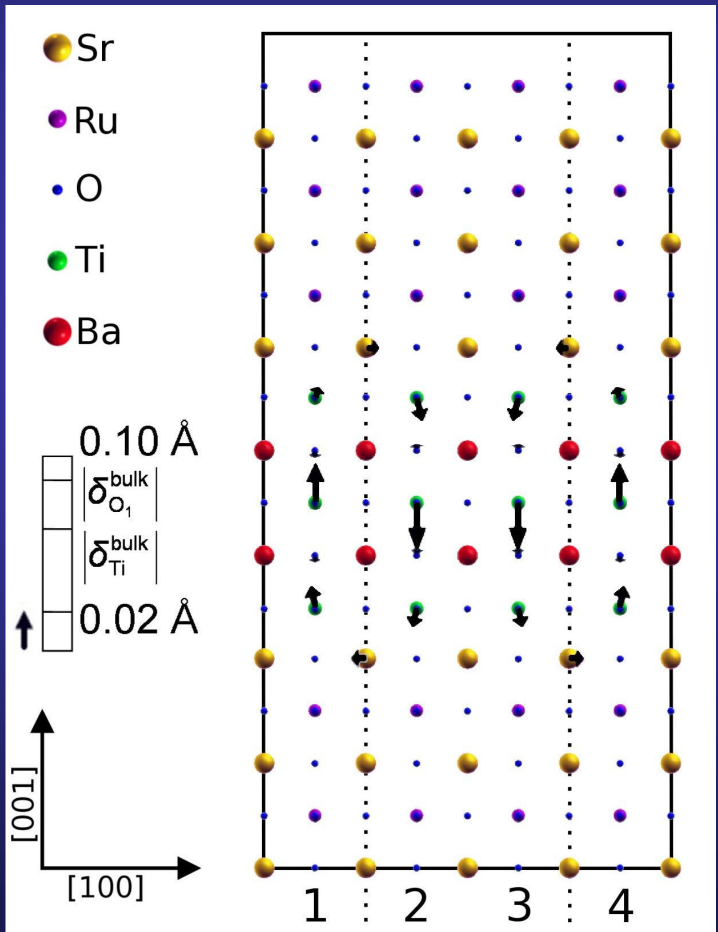
SrO layer at the interface behaves more like $SrTiO_3$ than $SrRuO_3$ $\Rightarrow$ highly polarizable



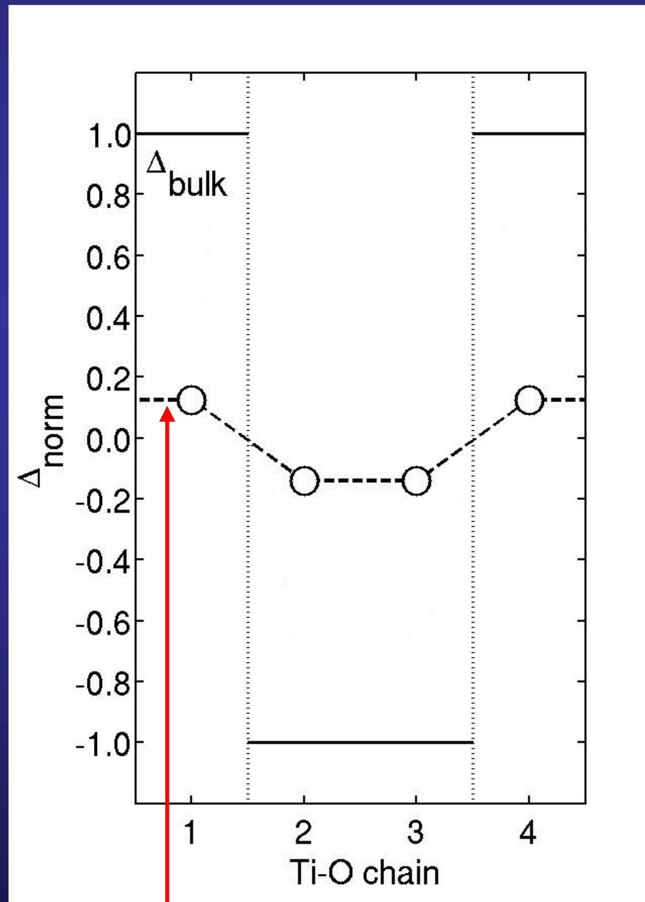
Projected Density of States in the reference paraelectric structure

Resulting phases show in-plane displacements and small polarization

$N_x = 4$ BaO domain walls



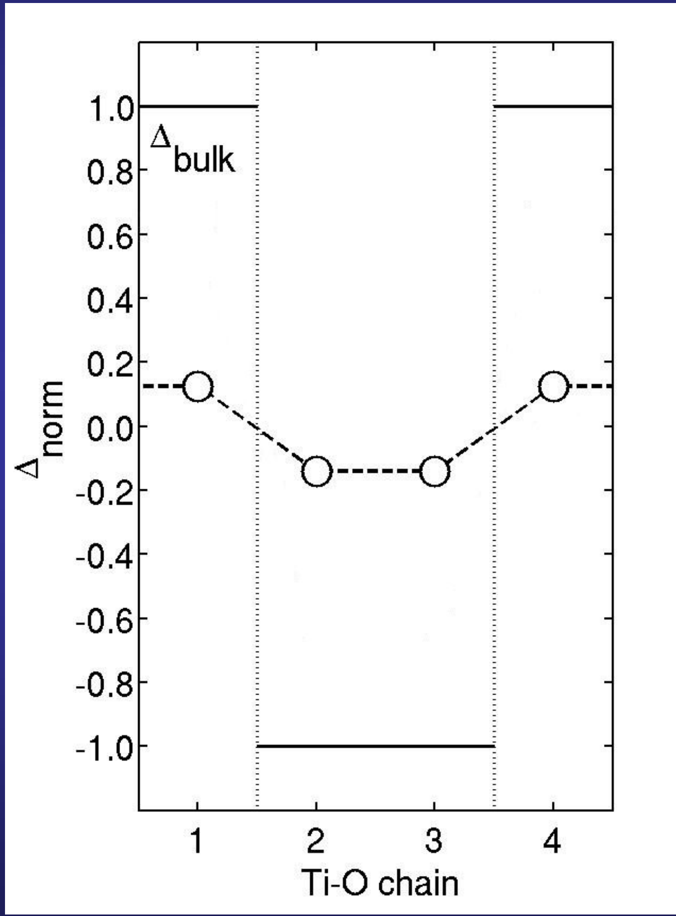
Small polarization inside the domains



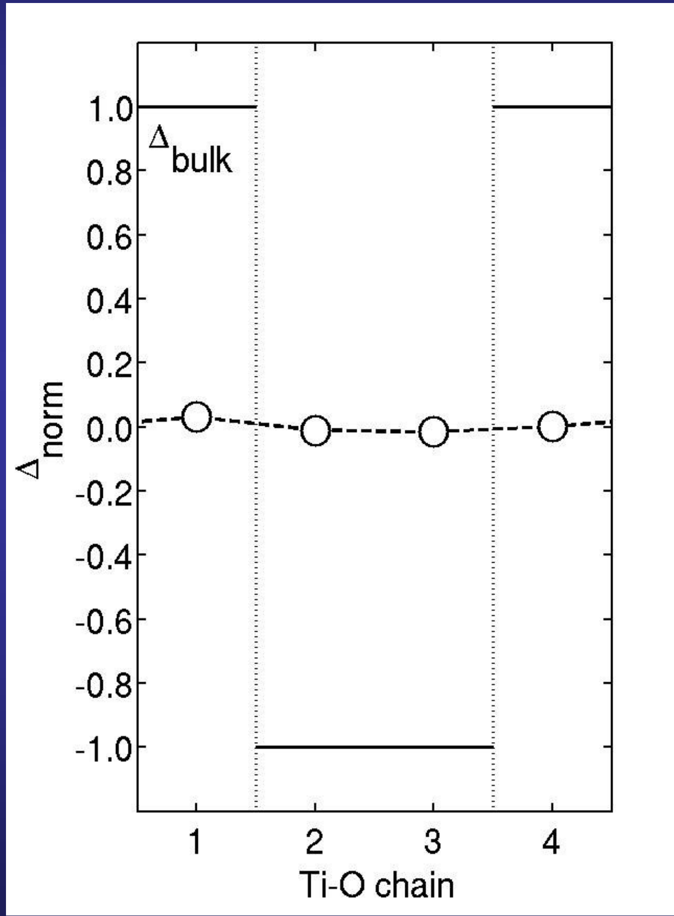
About 1/10 of bulk soft-mode polarization

In-plane displacements are very important to stabilize the domains

In-plane displacements: ON

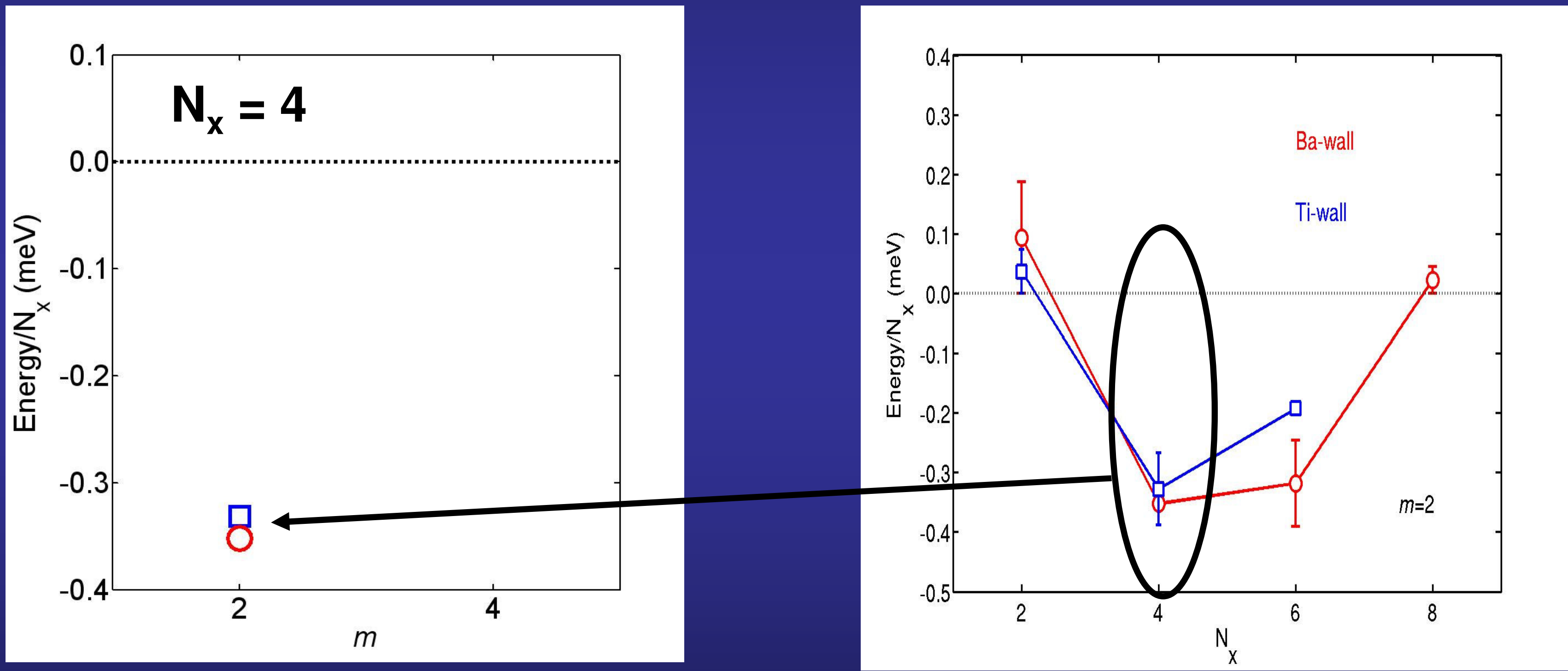


In-plane displacements: OFF

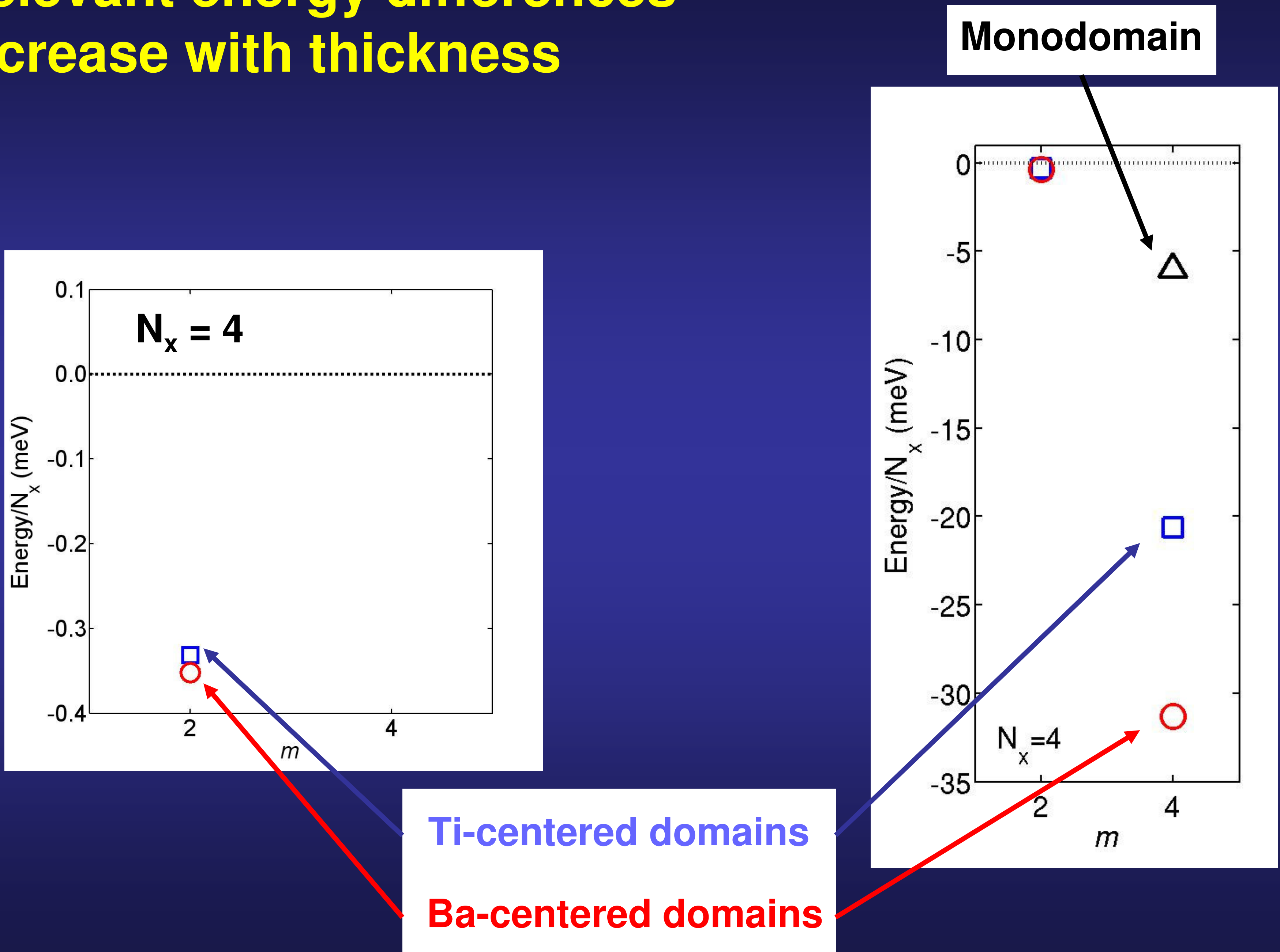


When in-plane coordinates are fixed, structure goes back to the paraelectric phase

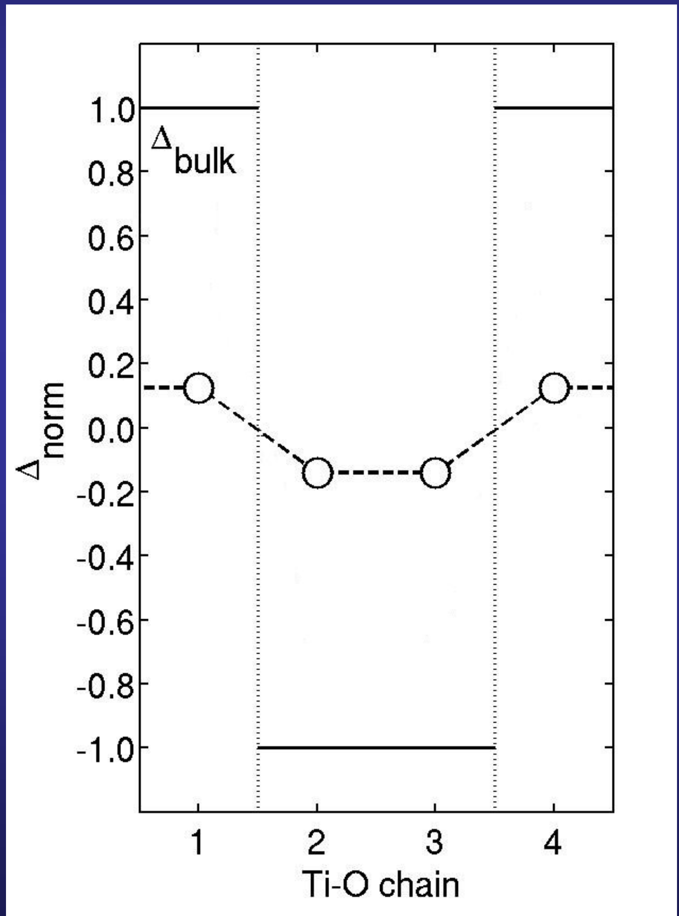
Relevant energy differences very small in the ultrathin m = 2 capacitors



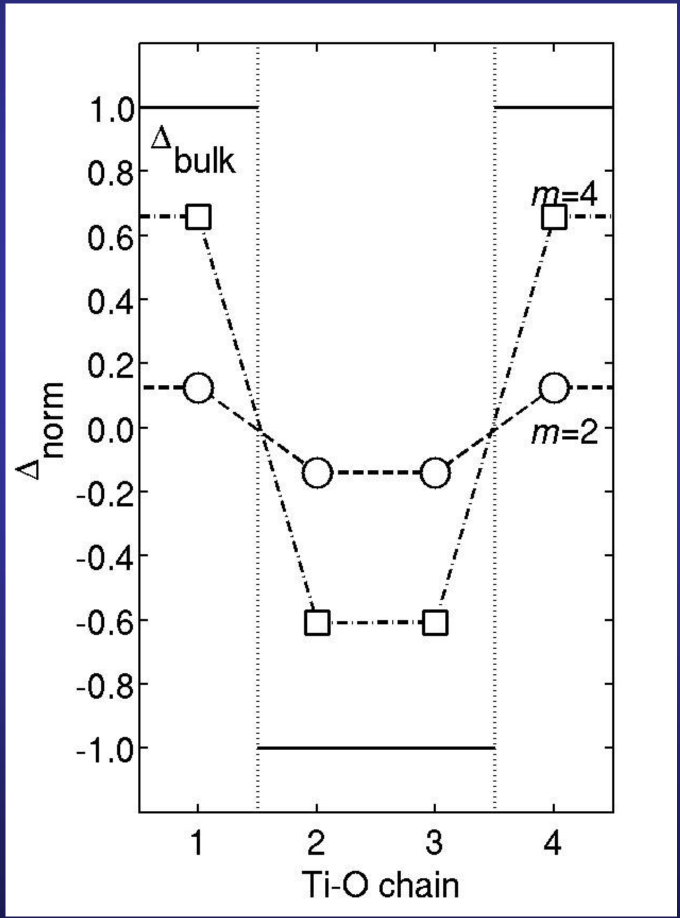
Relevant energy differences increase with thickness



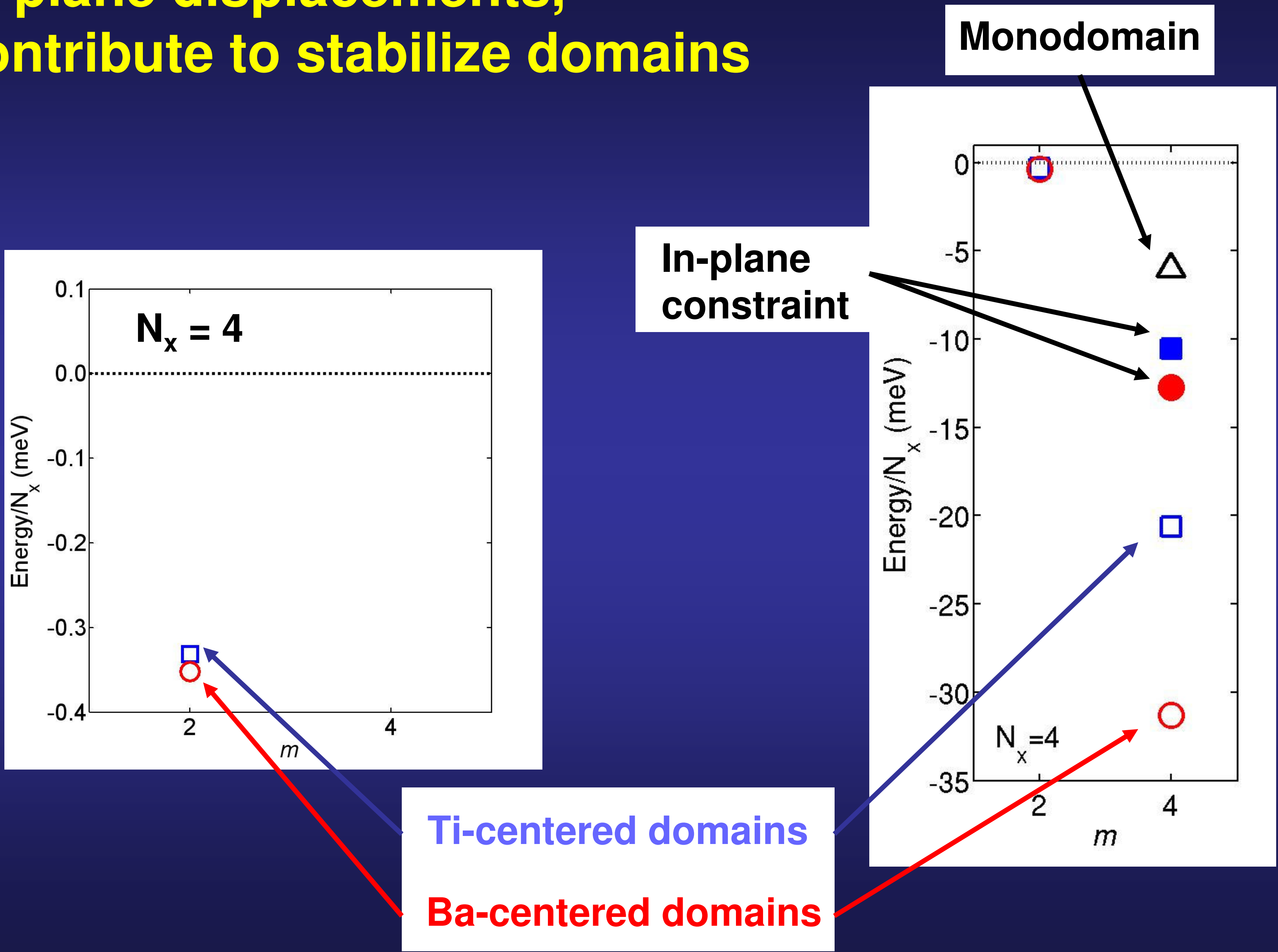
Transition from vortices to standard 180º domains. 4-unit-cell thick layer, great increase in polarization



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



In-plane displacements, contribute to stabilize domains

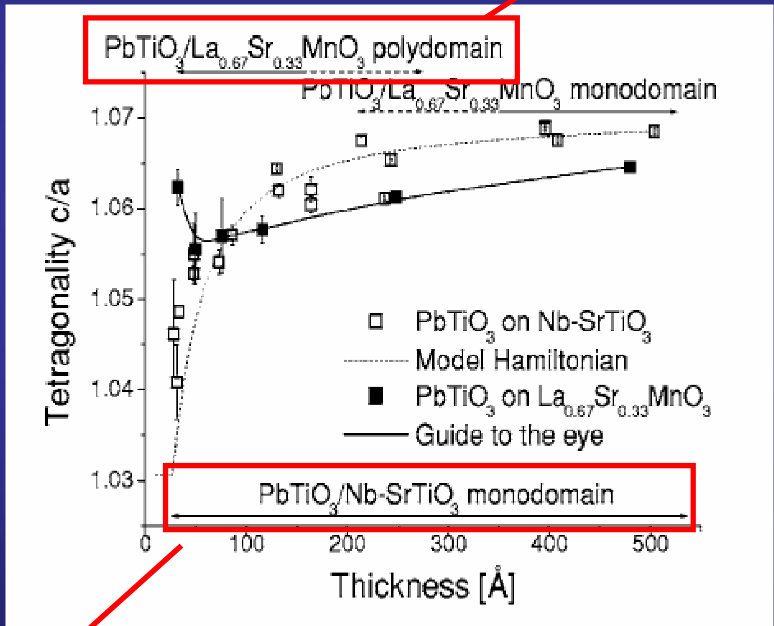


Changing the electrode, the ground state of $PbTiO_3$ changes from monodomain to polydomain

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.*

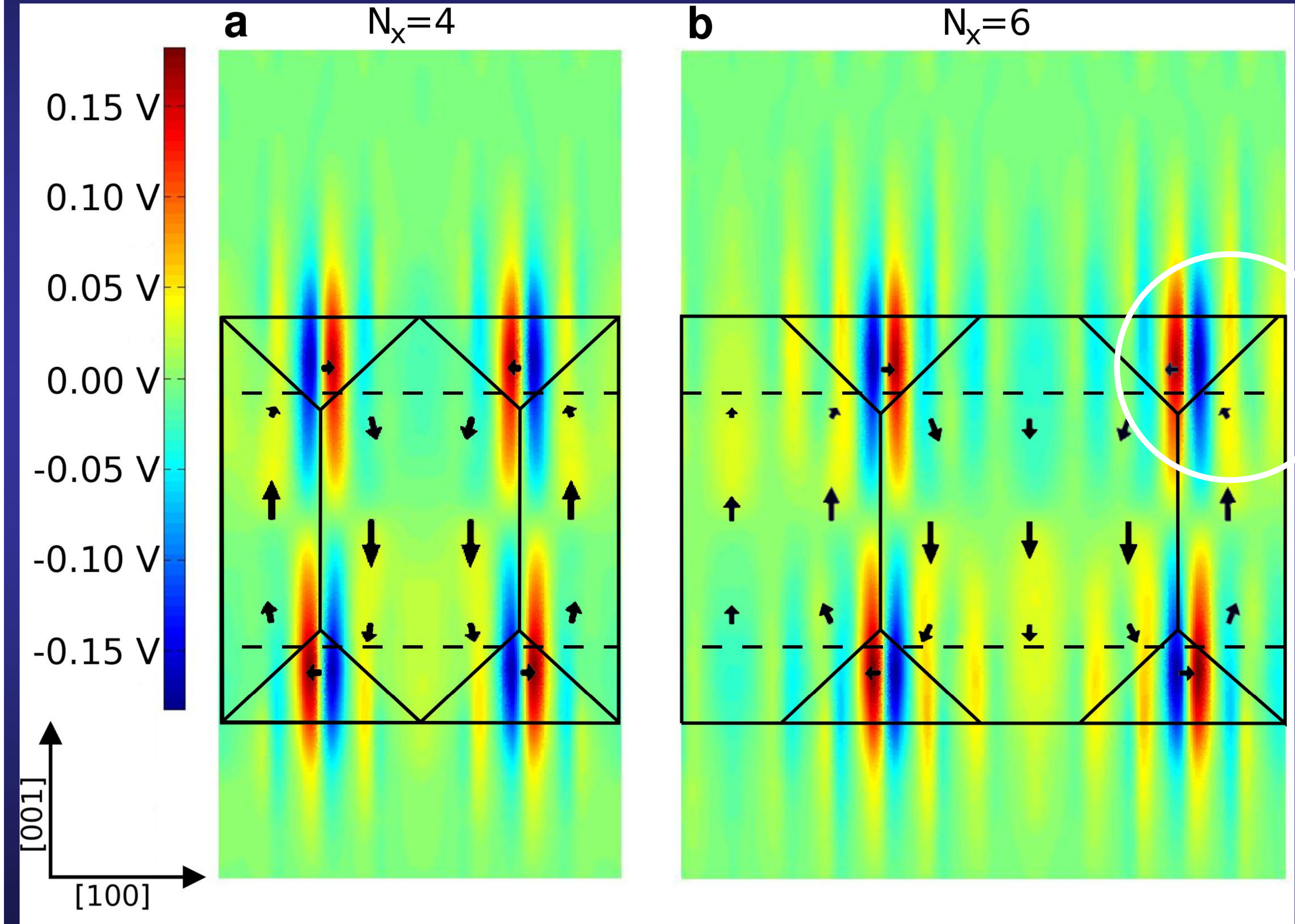


PRL 94, 047603 (2005) PHYSICAL REVIEW LETTERS week ending 4 FEBRUARY 2005

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

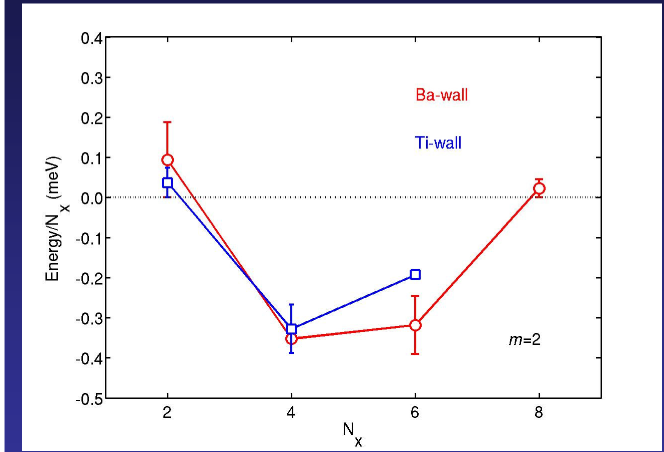
Ferroelectricity in Ultrathin Perovskite Films

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]

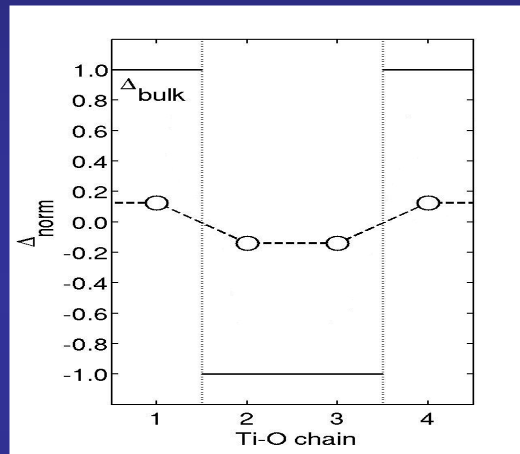
At 1

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

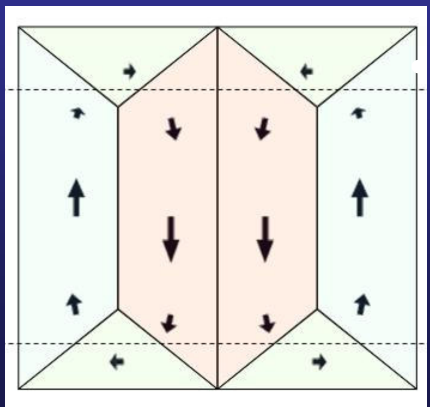
Conclusions



• **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

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Preprint available in cond-mat 0710.1515