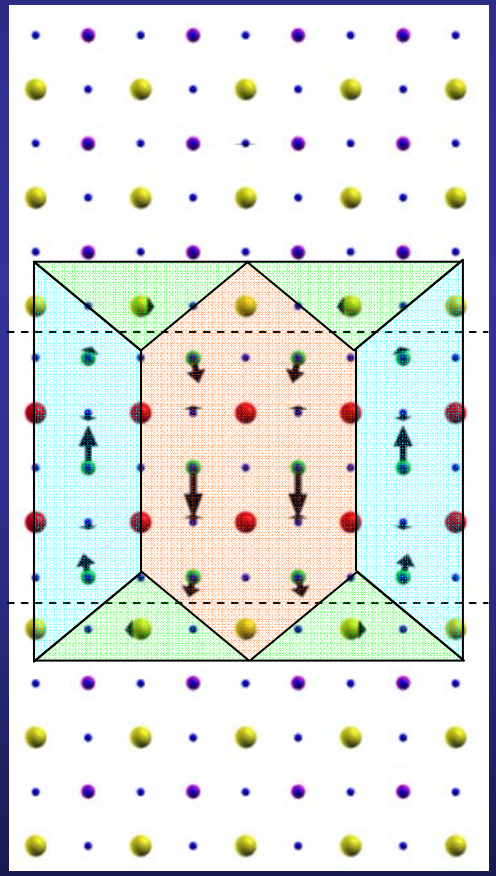
Full first-principles simulations on 180º stripe domains in realistic ferroelectric capacitors



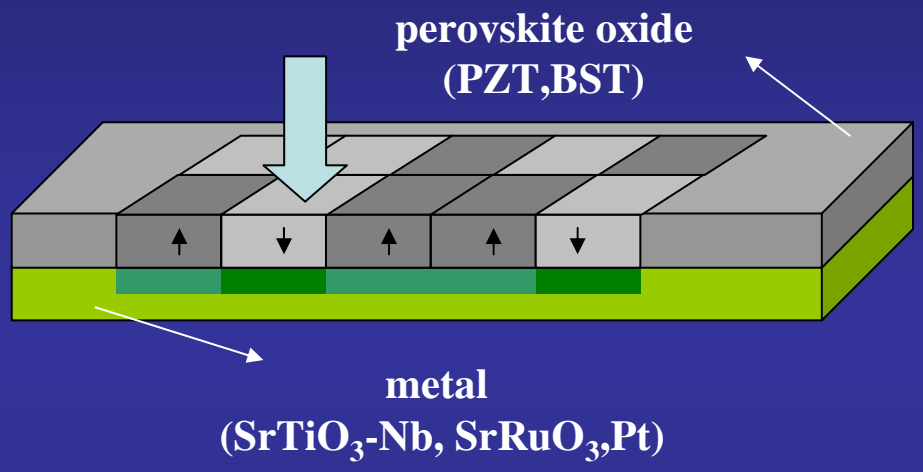
Pablo Aguado-Puente

Javier Junquera

UNIVERSIDAD DE CANTABRIA

CITIMAC

Technological applications: ABO_3 perovskites oxides, promising candidates for NV-FRAM

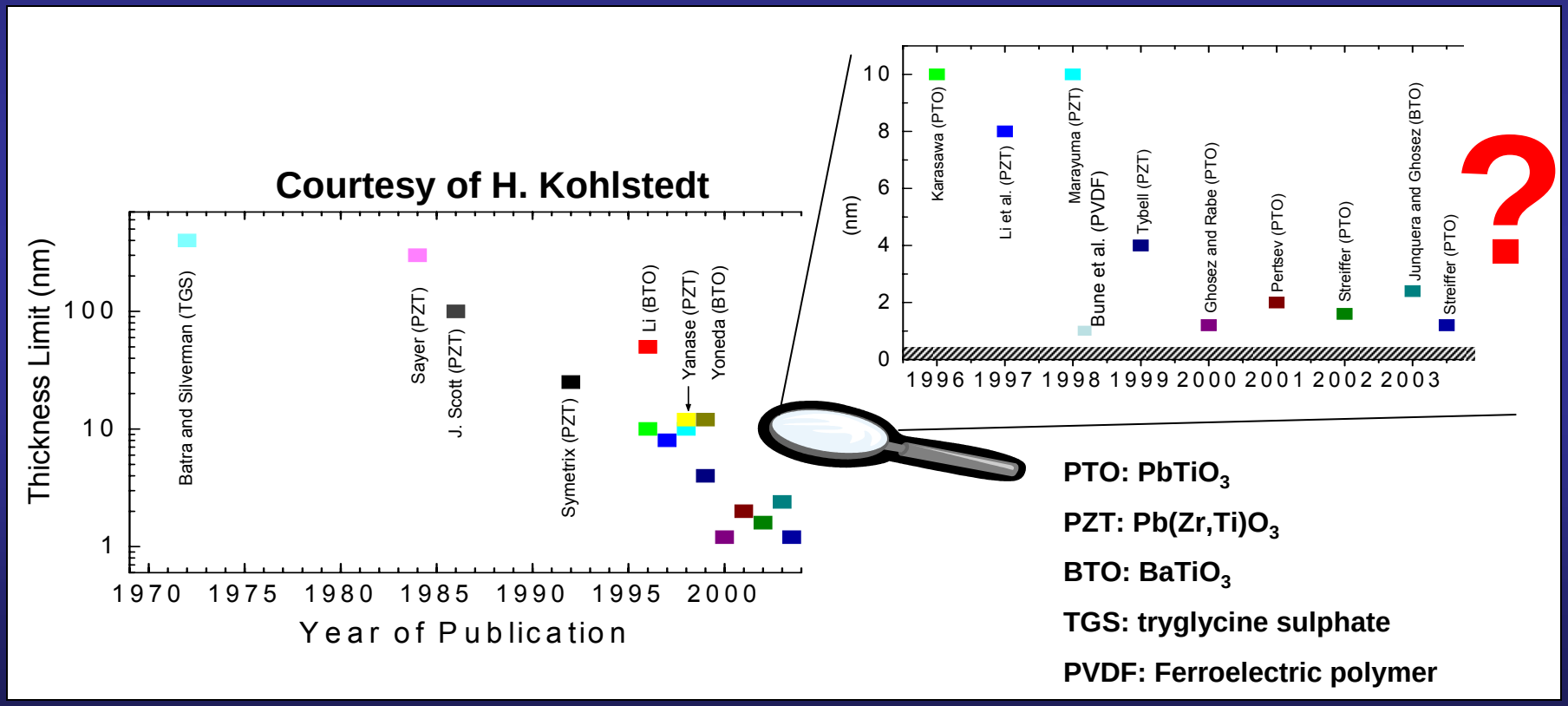


The use as a NV-FRAM depends on the existence of a polar ground state …

… is there a fundamental limit?

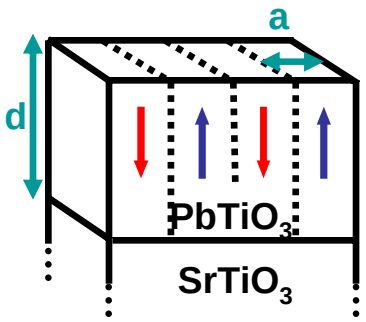
Fundamental motivation: what's the most stable phase for epitaxial ferroelectric ultrathin films?

- Long time question.
- Hot field.



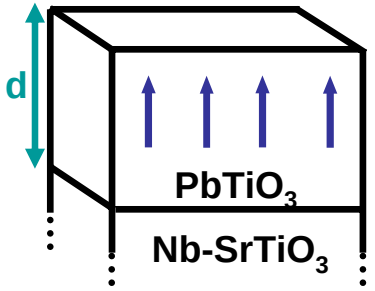
Ph. Ghosez and J. Junquera, *First-Principles Modeling of Ferroelectric Oxide Nanostructures*, *Handbook of Theoretical and Computational Nanotechnology*, Vol. 9, Chap. 13, 623-728 (2006) (http://xxx.lanl.gov/pdf/cond-mat/0605299) and references therein.

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



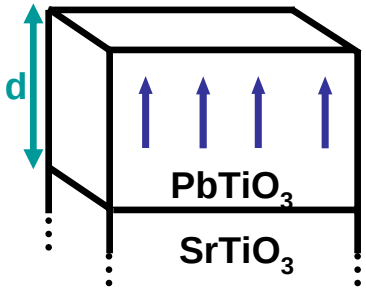
(insulator)

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



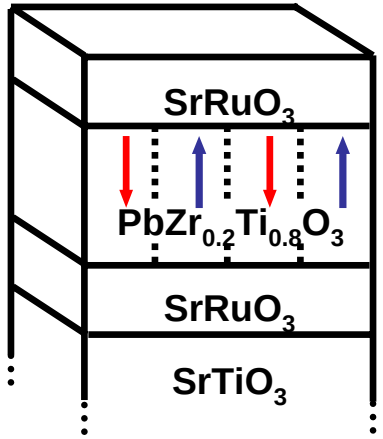
(metal)

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



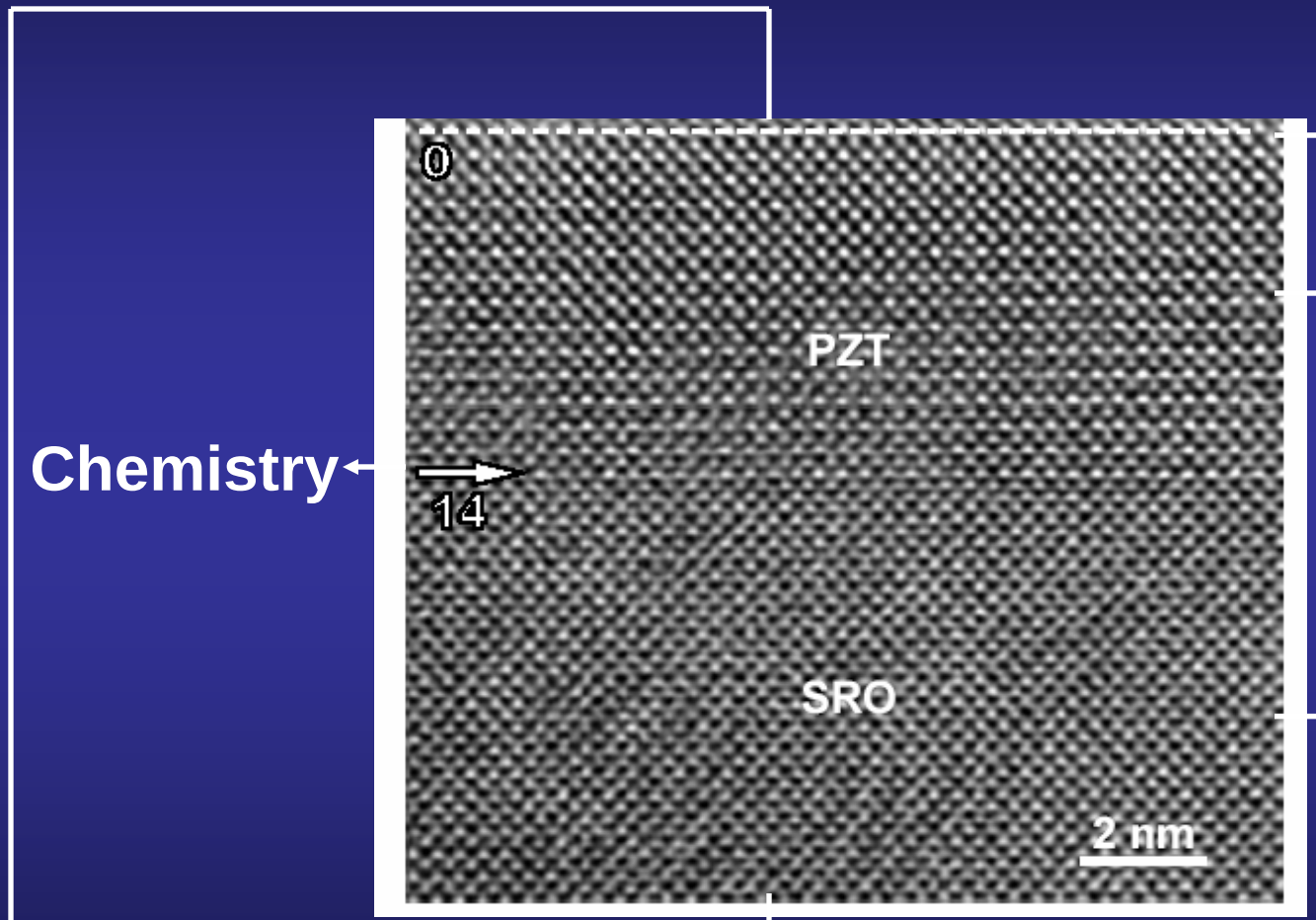
(insulator)

D. D. Fong et al. (2005)



V. Nagarajan et al. (2006)

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



Surface

Defects

(vacancies, misfit dislocations…)

Finite conductivity

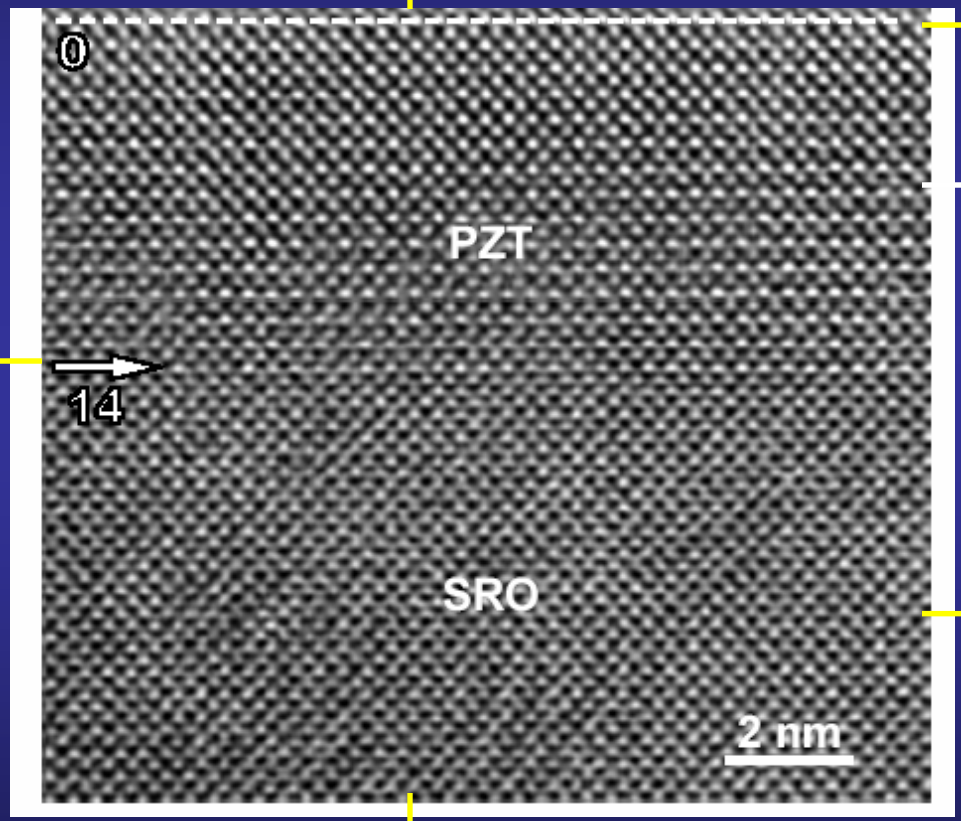
Mechanical

Chemistry

Electrostatic

Experimental measures, global result

First-principles calculations allow to isolate their respective influence



Surface

Defects

(vacancies, misfit dislocations…)

Finite conductivity

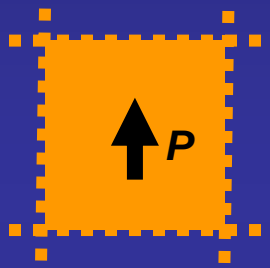
Mechanical

Chemistry

Electrostatic

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

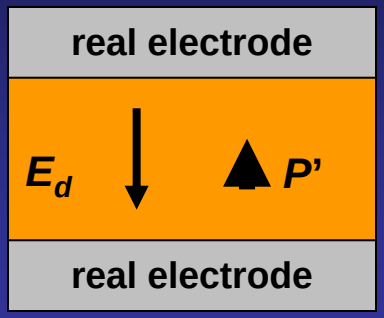
bulk

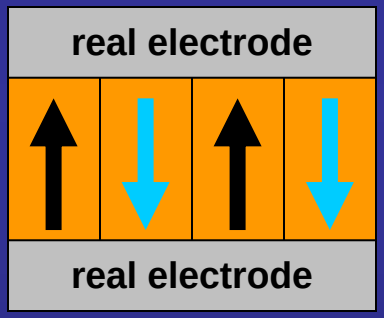


- Uniform reduction of the polarization
  Junquera and Ghosez, (2003)
  Umeno et al. (2006)

- **Break down into domains**

Present work

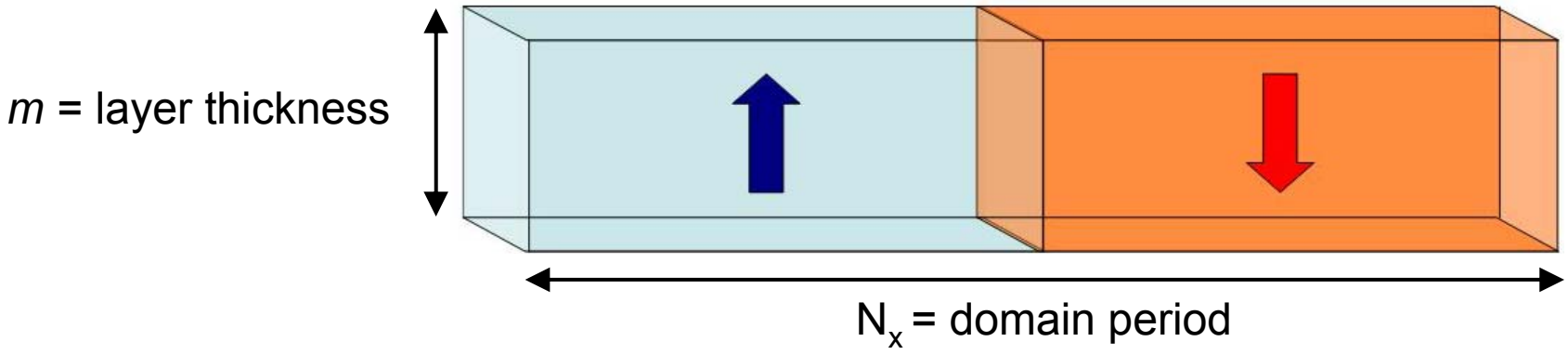




- Full first-principles simulation using siesta
- Explicitly included electrodes.

Ferroelectric layer: fundamental parameters of the simulations

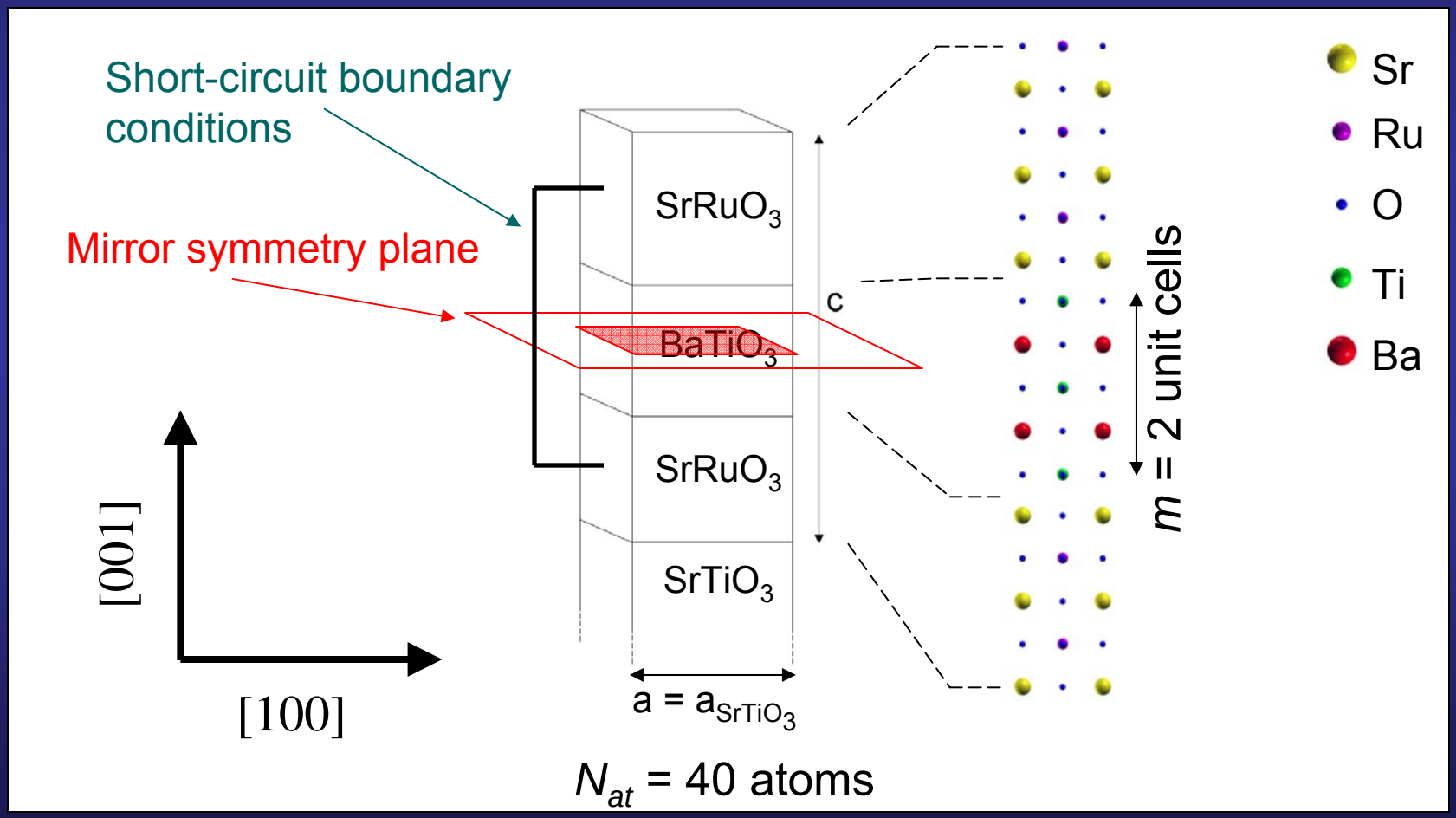
FE layer: N_x repetitions in [100] direction and *m* cells in [001] direction



- N_x from 2 to 8 cells
- *m* from 2 to 4 cells
- FE layer made of $BaTiO_3$.
- Domain wall in BaO and TiO_2

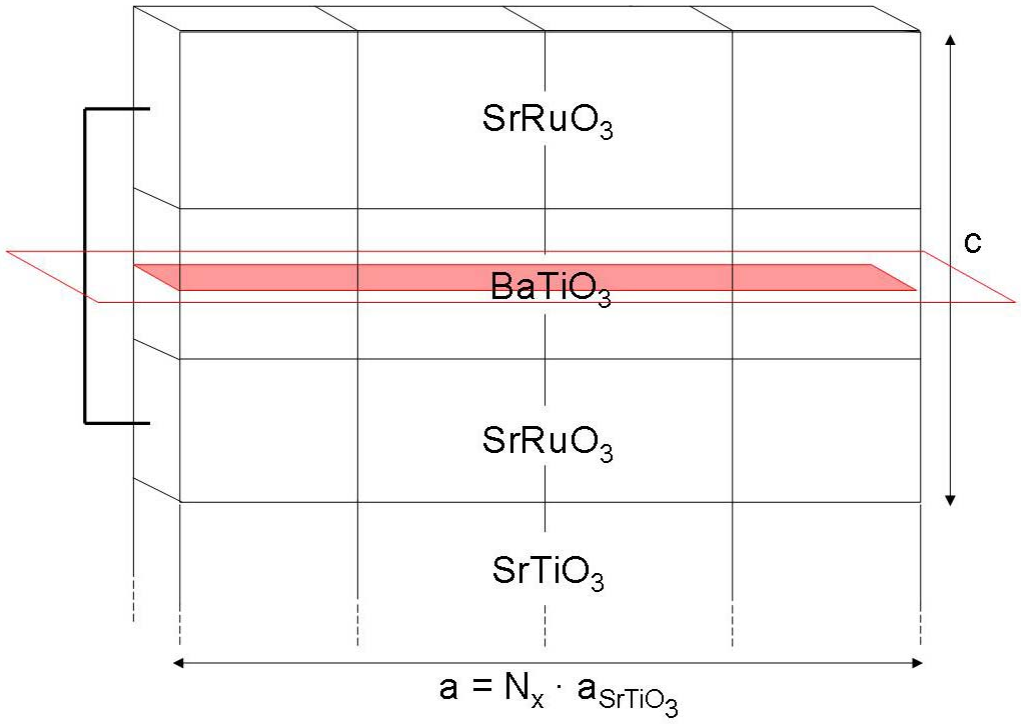
Building the cell: the paraelectric unit cell

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



Building the cell: replicating the paraelectric structure

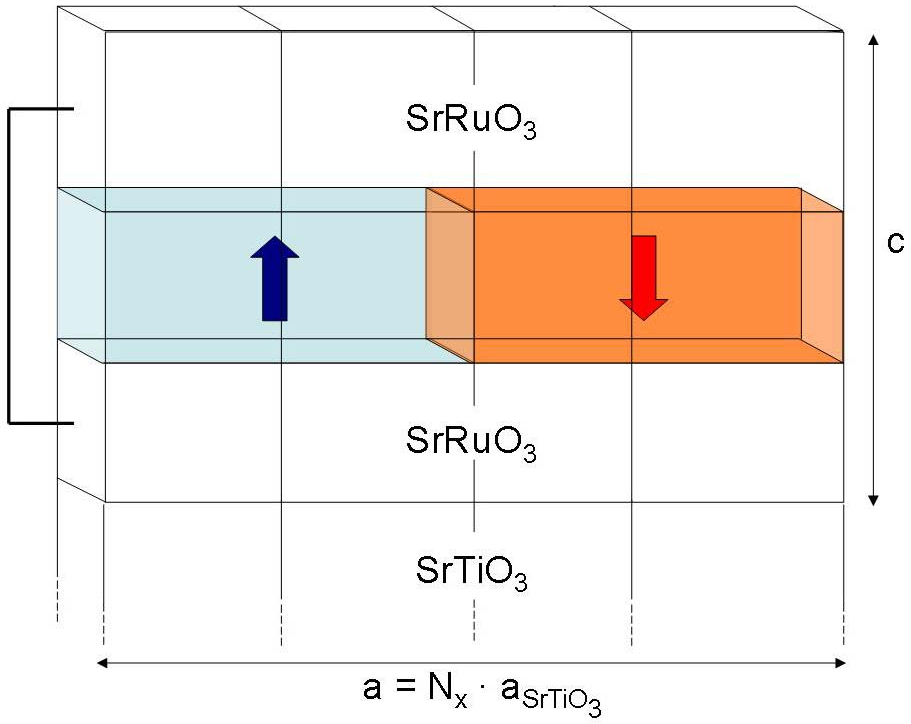
- N_x repetitions in [100] direction.
- The energies of these cells as references.



$N_{at} = N_x \cdot 40$ 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.

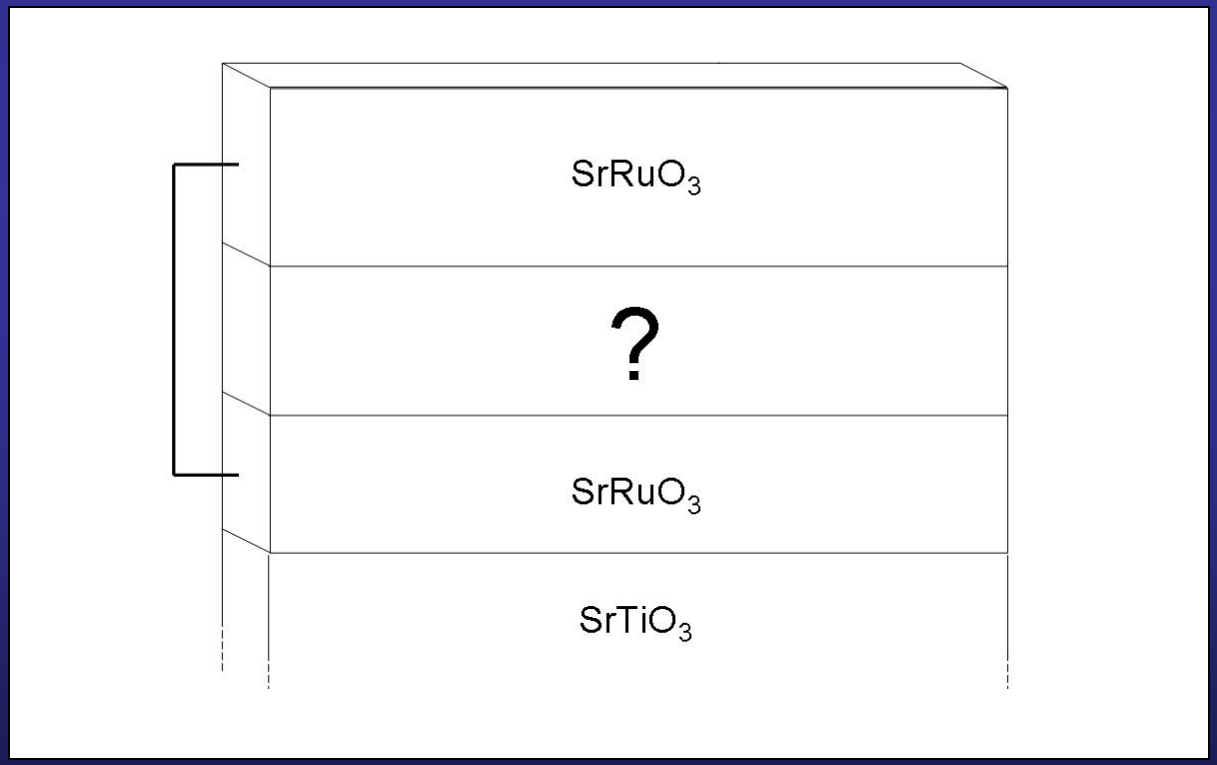


$N_{at} = N_x \cdot 40$ atoms

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

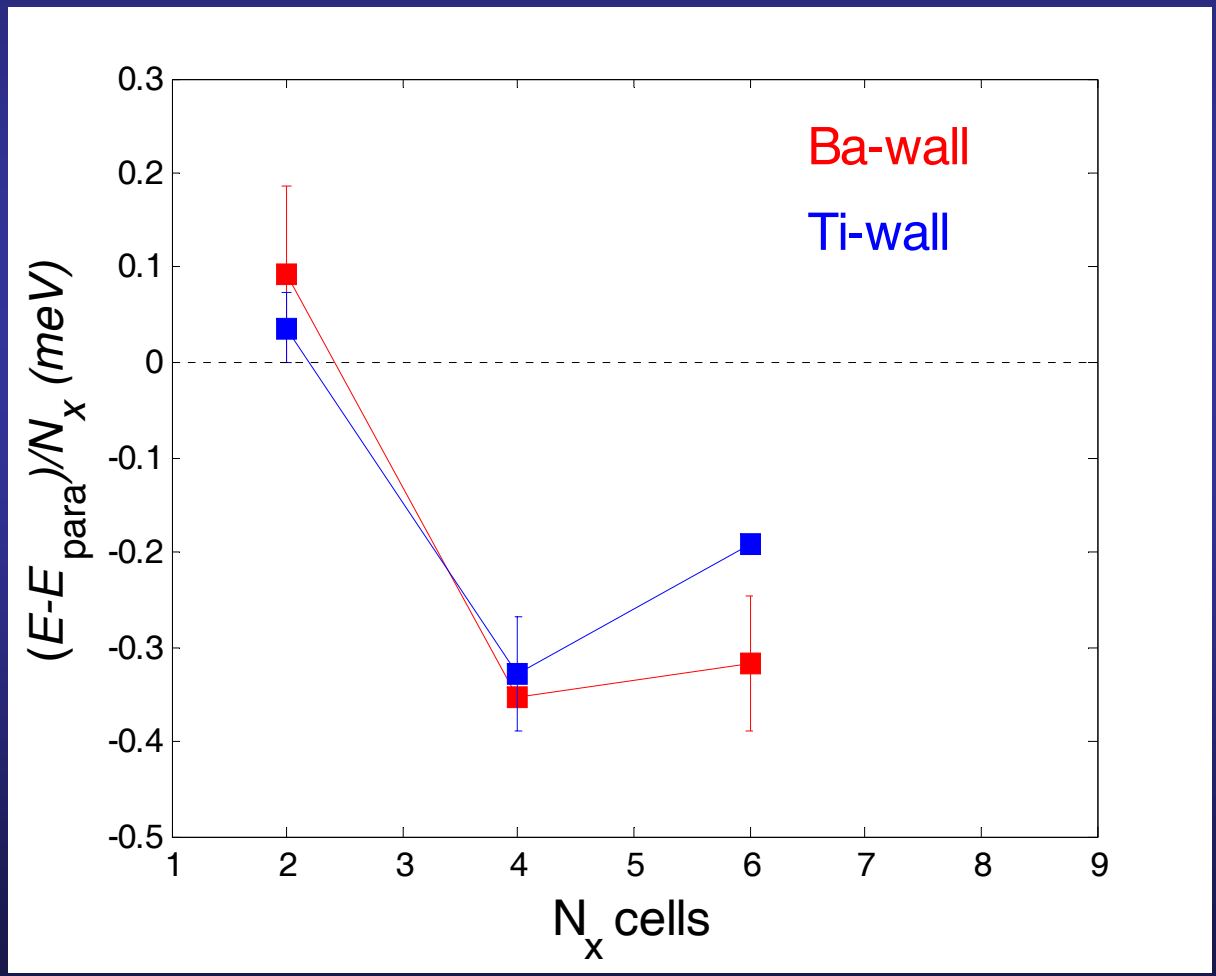
Forces smaller than 0.01 eV/Å

No constraints impossed on the atomic positions



Results: multidomain phases more stable than paraelectric structure for $N_x > 4$

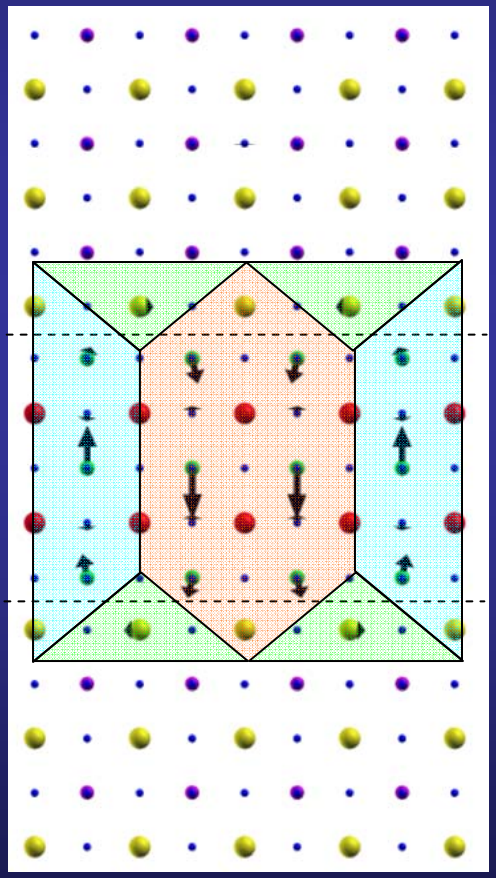
2-unit-cells thick $BaTiO_3$ layer

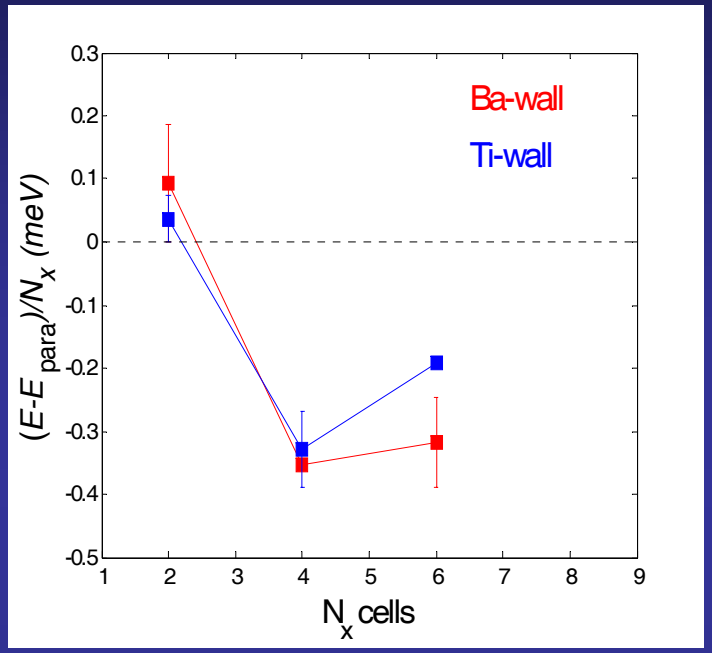


Results: multidomain phases more stable than paraelectric structure for $N_x > 4$

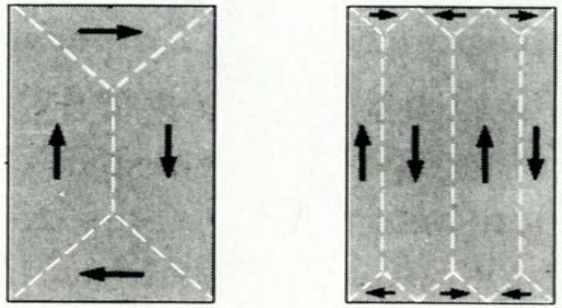
$N_x = 4$

BaO domain walls





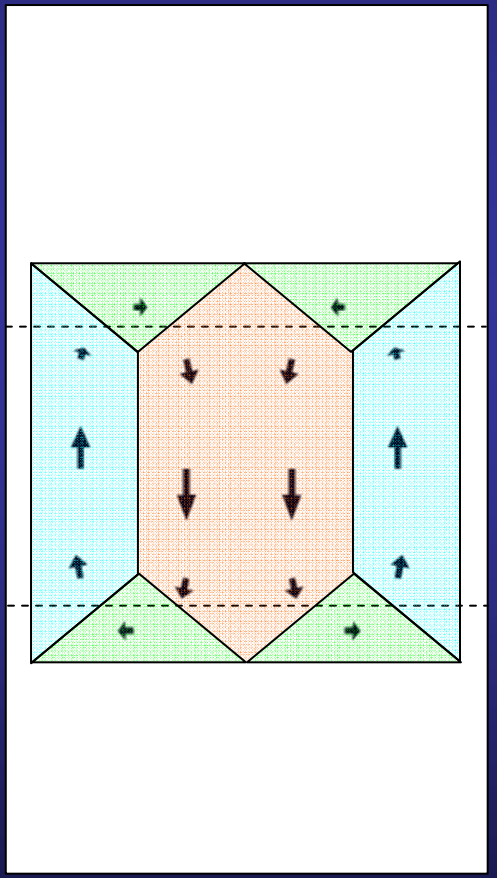
Ferromagnetic domains



C. Kittel (1971)

$N_x = 4$

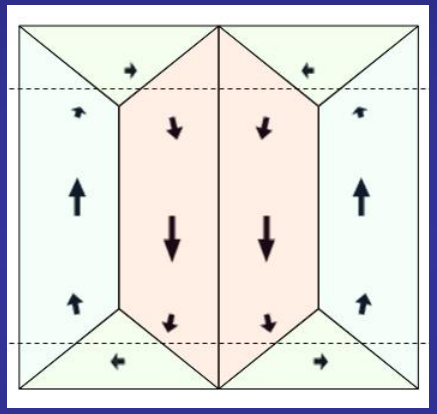
BaO domain walls



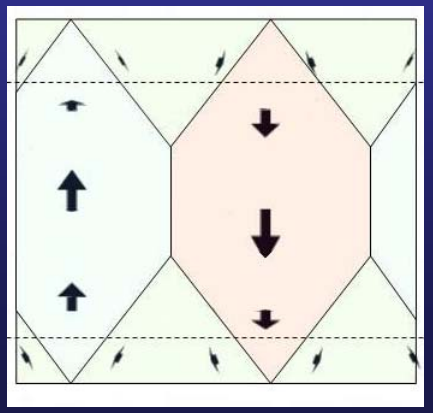
Results: multidomain phases more stable than paraelectric structure for $N_x > 4$

N_x=4

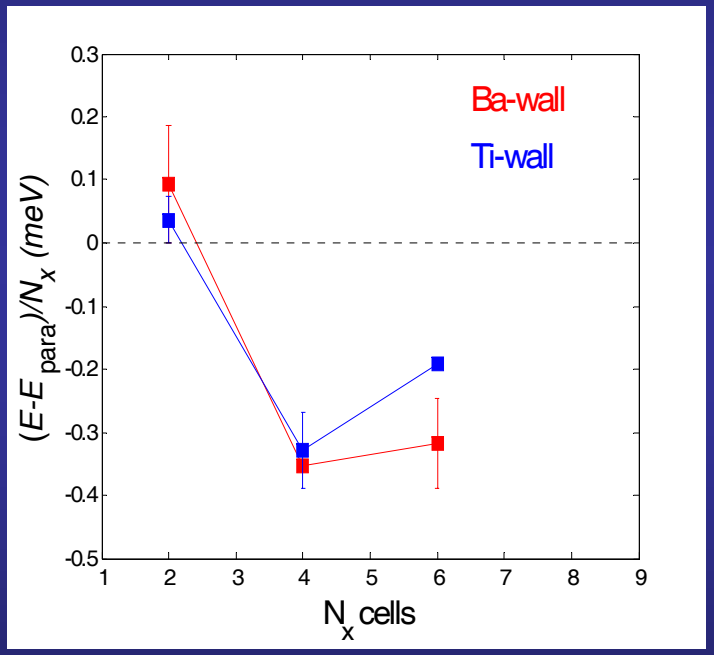
BaO wall



TiO_2 wall

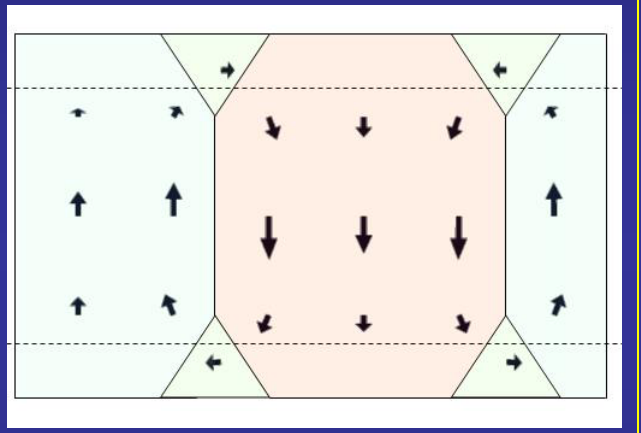


2-unit-cells thick $BaTiO_3$ layer

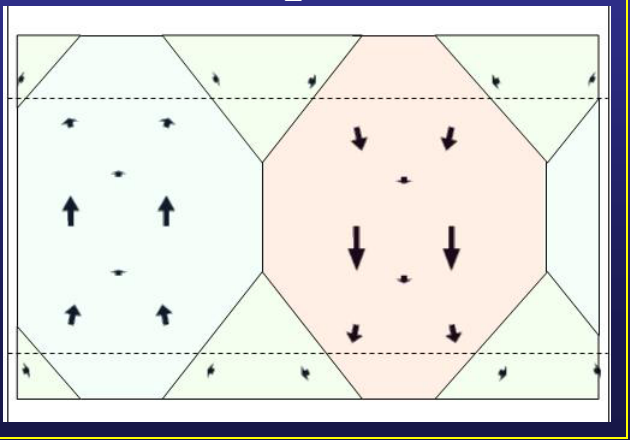


N_x=6

BaO wall



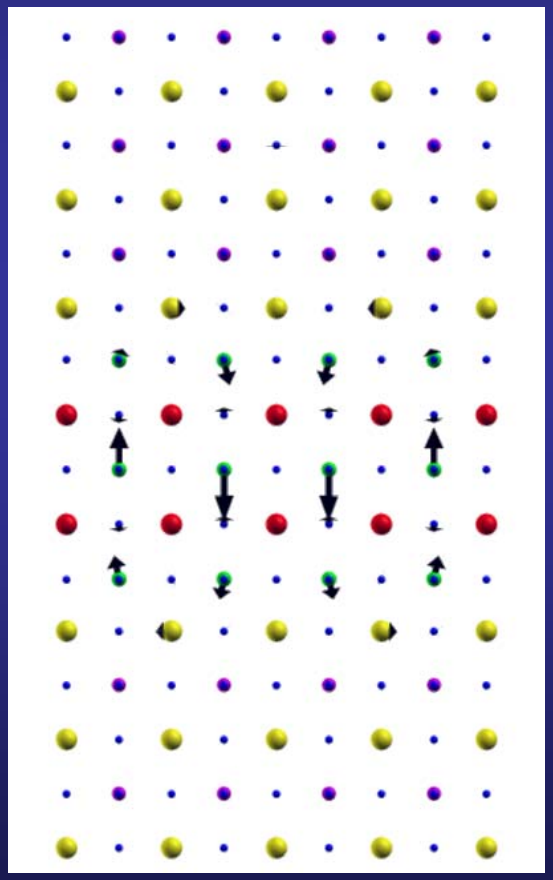
TiO_2 wall



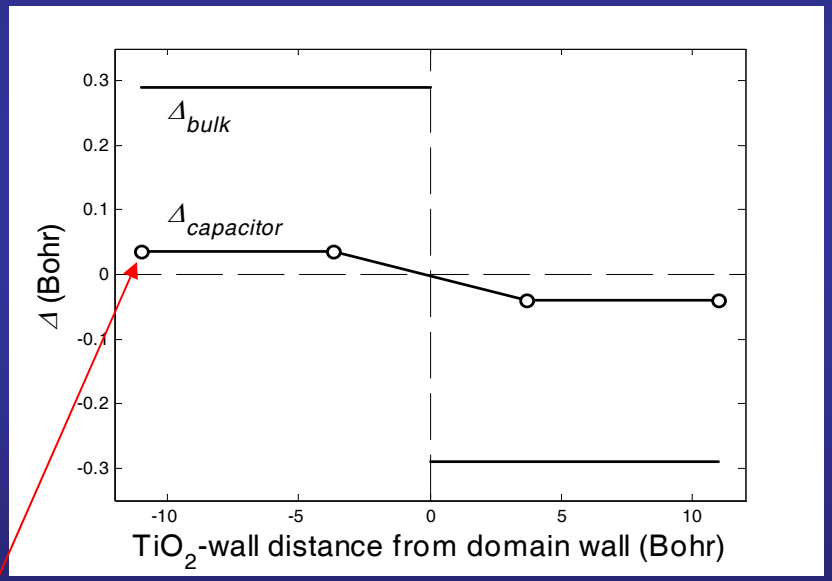
Resulting phases show in-plane displacements and small polarization

$N_x = 4$

BaO domain walls



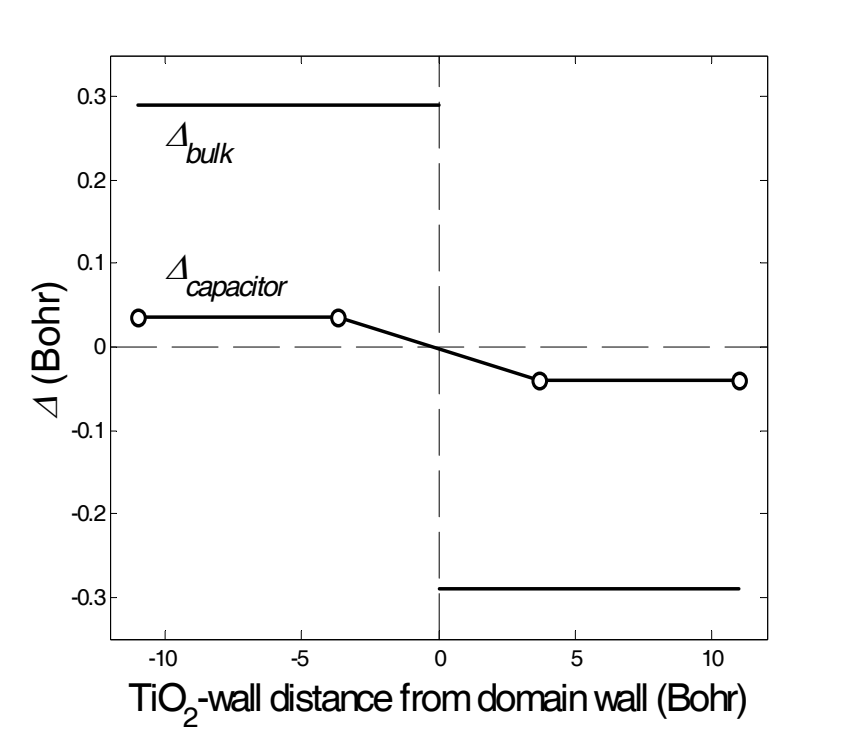
Small polarization inside the domains.



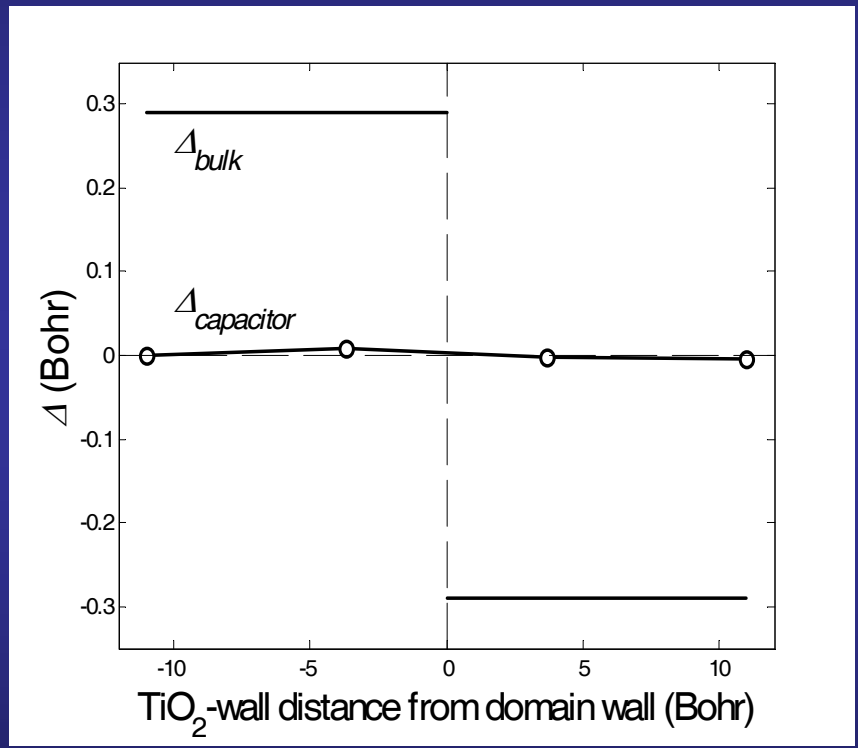
About 1/10 of bulk soft-mode polarization

In-plane displacements are essential to get polarization domains

In-plane displacements: ON



In-plane displacements: OFF



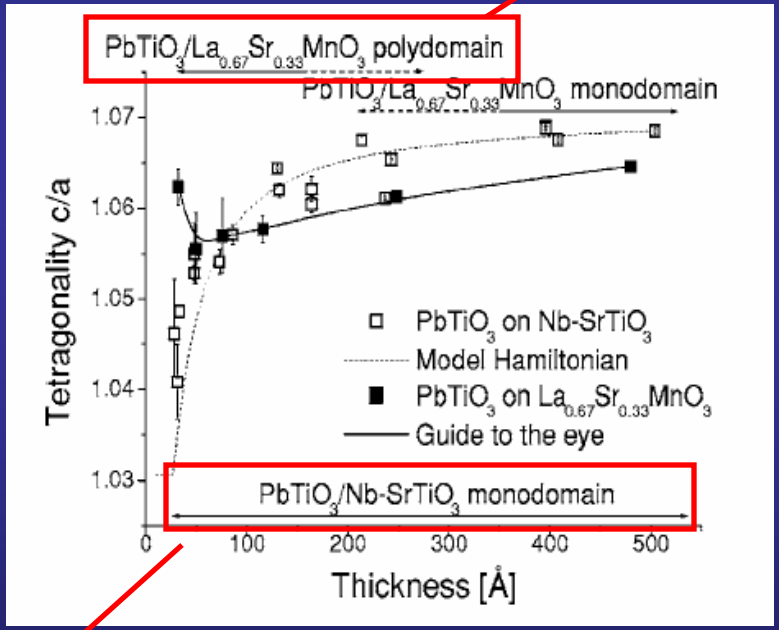
When in-plane coordinates are fixed, structure goes back to the paraelectric phase

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

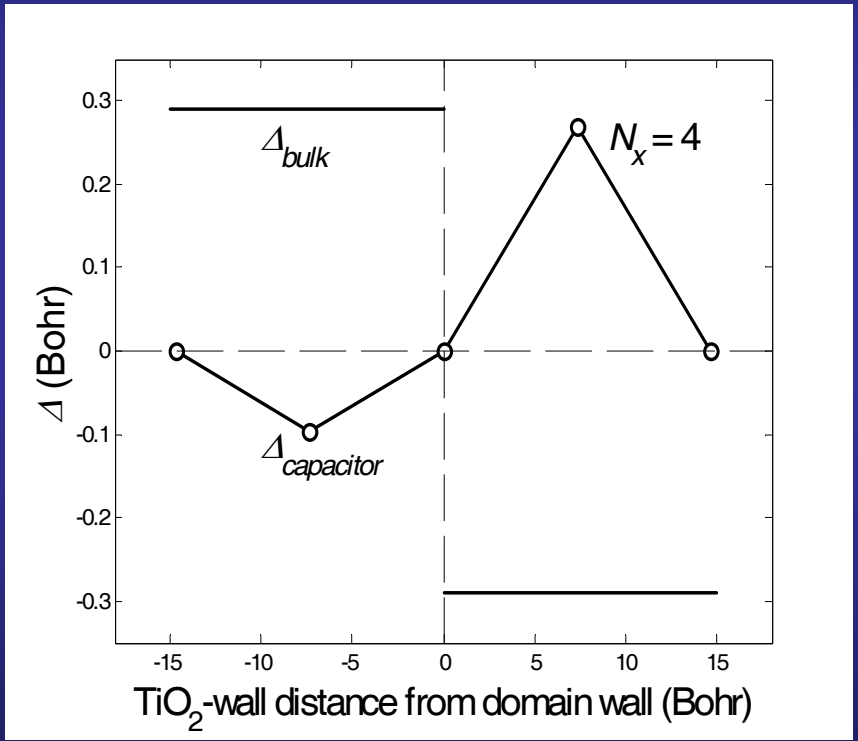
Ferroelectricity and Tetragonality in Ultrathin $PbTiO_3$ Films

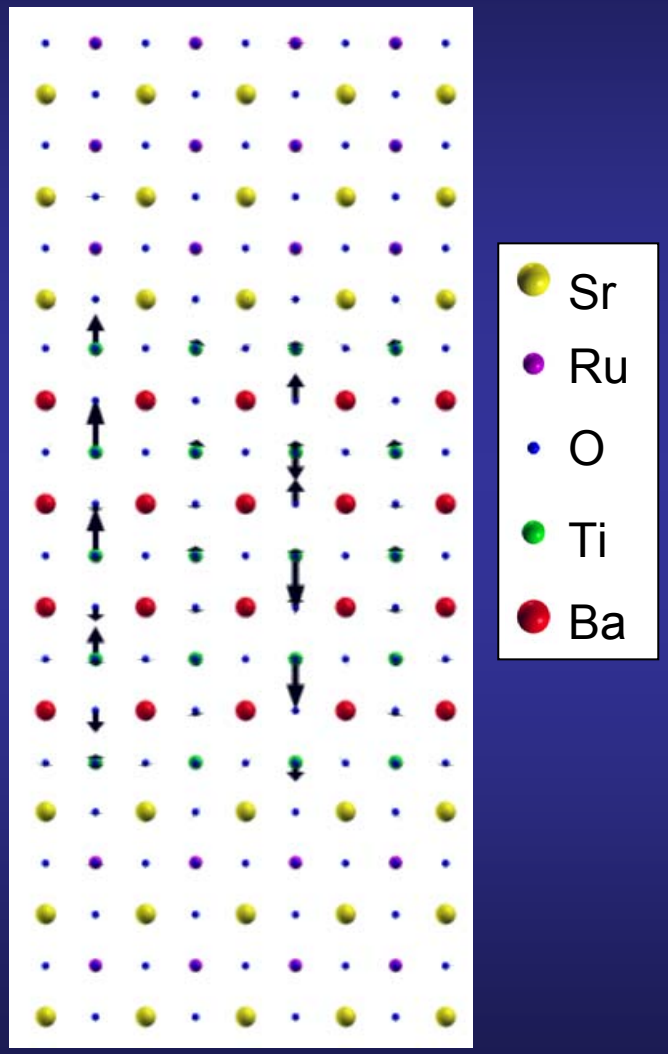
Lichtensteiger, Triscone, Junquera, Ghosez.

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

m = 4, N_x = 4

TiO_2 domain walls

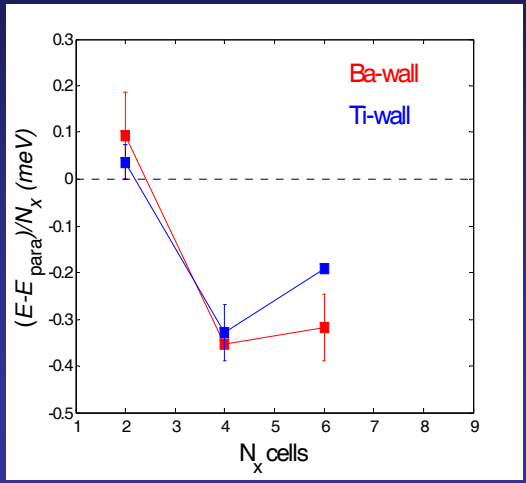




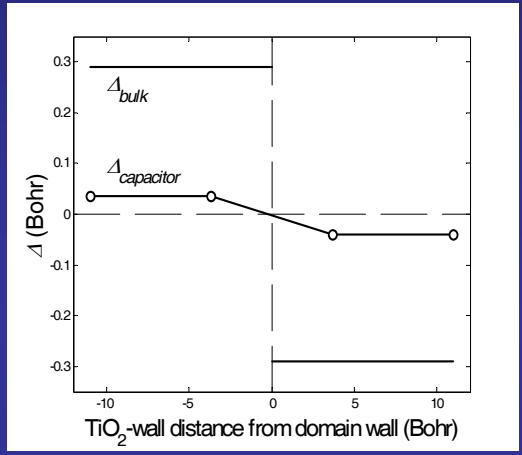
$(E\text{-}E_{para})/N_x$ < -16.6 meV

Displacements 10 times bigger than in the 2-cells thick layer

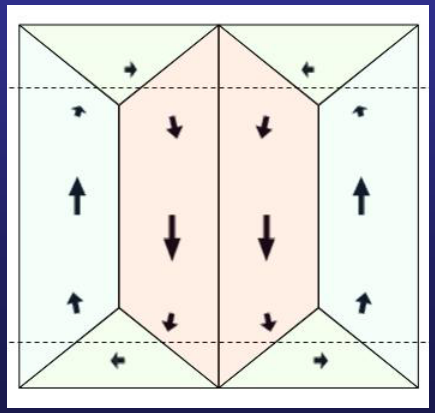
Conclusions



• There are stable multidomain phases in ultrathin FE films.



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



• Closure domains in FE capacitors are predicted.

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

Contact: pablo.aguado@unican.es

javier.junquera@unican.es

More information ...

Method: Computational details

First-principles calculations within
Kohn-Sham Density Functional Theory (DFT)

siesta : **Numerical Atomic Orbital DFT code.**

http://www.uam.es/siesta

J. M. Soler et al., J. Phys. Condens. Matter **14**, 2745 (2002)

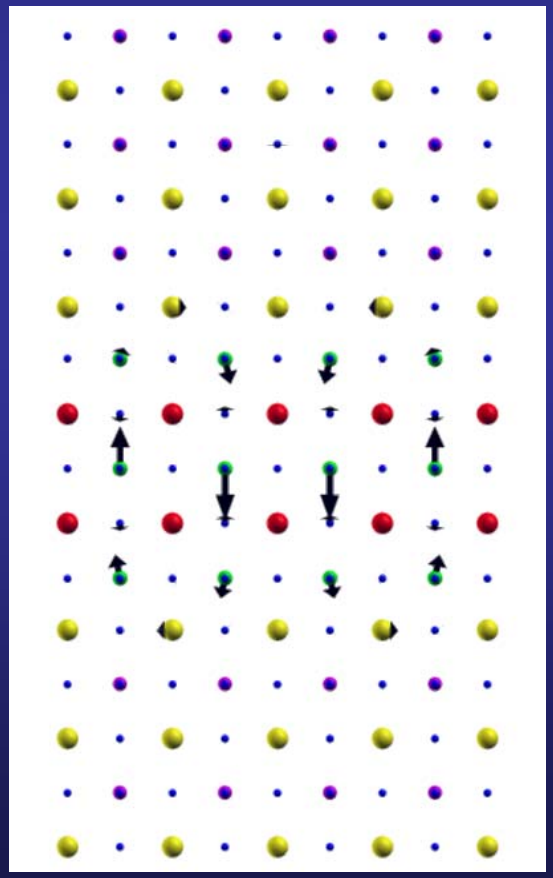
Exchange-correlation functional : LDA, fit to Ceperley-Alder data
Norm conserving pseudopotentials: Ti, Sr, Ba, Ru: semicore in valence

Basis set:
NAO: valence: Double-ζ + Polarization ; semicore: Single-ζ
Real-space grid cutoff : 400 Ry
k-point grid : equivalent to 12x12x12 for simple cubic perovskite
Supercell geometry

Very small energy differences, very accurate simulations needed

$m=2$, $N_x = 4$

BaO domain walls



Structure	Total Energy (eV)
Paraelectric	-138326.083054
Multidomain	-138326.084463

(E-Epara)/Nx = -0.00035 eV