

# Strain engineering of multiferroic phase transitions and order parameters in $\text{BiFeO}_3$

Manuel Bibes<sup>1</sup>

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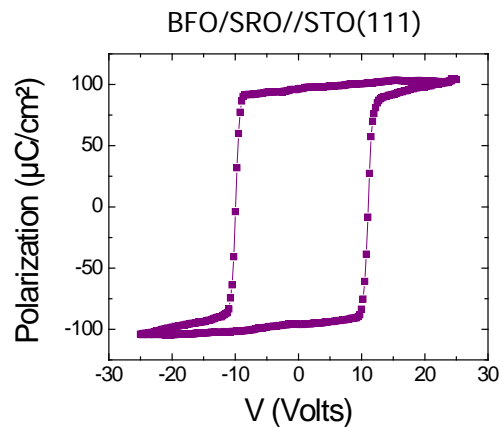
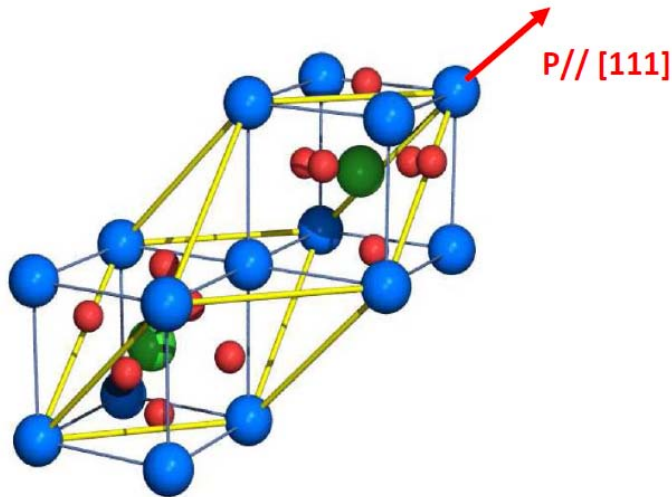
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# Bulk BiFeO<sub>3</sub> : ferroic properties

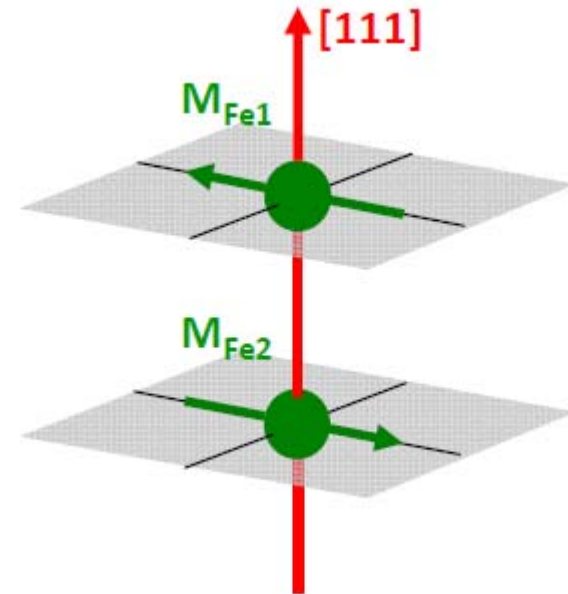
## Ferroelectric properties

- ⊙ P in bulk : 100  $\mu\text{C}/\text{cm}^2$  D. Lebeugle et al, APL 91, 022907 (2007)
- ⊙ T<sub>c</sub> = 1100K

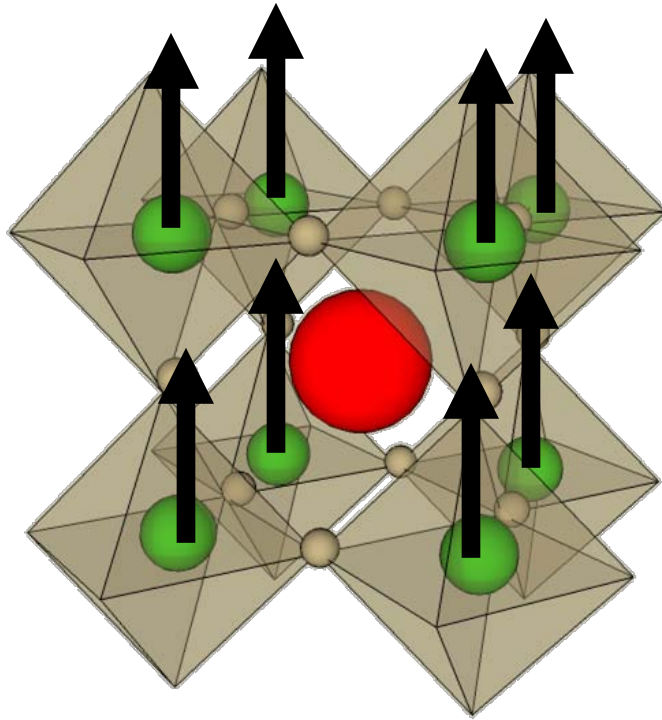


## Magnetic properties

- ⊙ G-type Antiferromagnetic with T<sub>N</sub>=640K
  - ⊙ Canted spins (weak FM) and incommensurate cycloidal modulation
  - ⊙ In bulk, M < 0.01  $\mu_B/\text{Fe}$
- P. Fisher et al., J. Phys. C, 13, 1931 (1980)

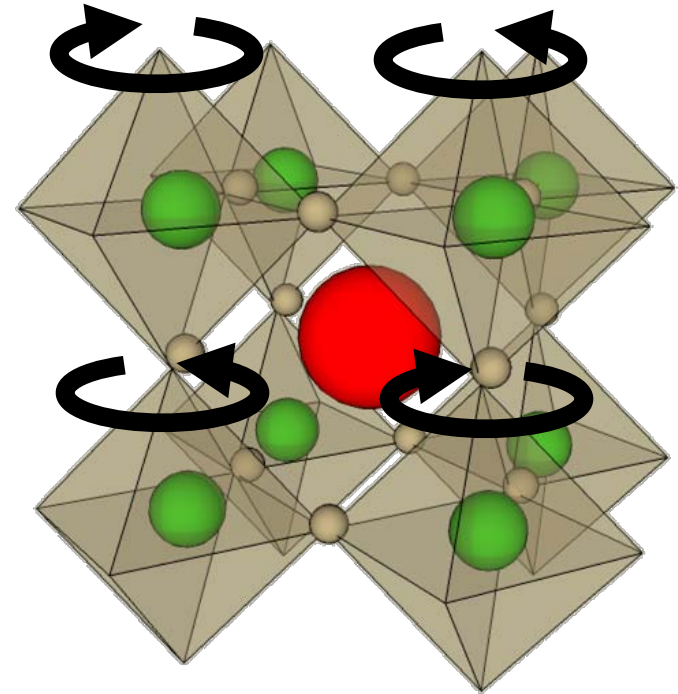


## Polar shift



Responsible for ferroelectricity like in BaTiO<sub>3</sub>

## Oxygen octaedra tilts/rotations

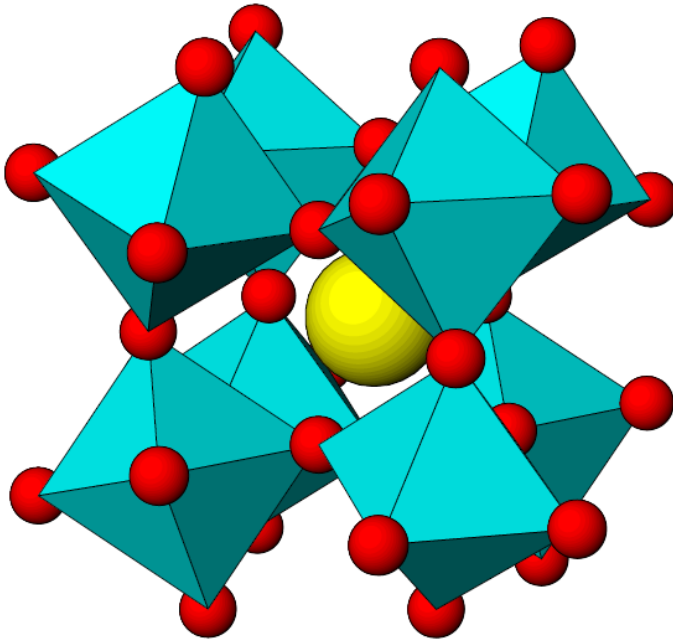


Usually not compatible with ferroelectricity as in SrTiO<sub>3</sub> at low T or in orthoferrites

Antagonist degrees of freedom

**In BiFeO<sub>3</sub> both instabilities coexist at room temperature**

Coexistence of both polar shifts and oxygen octaedra rotations

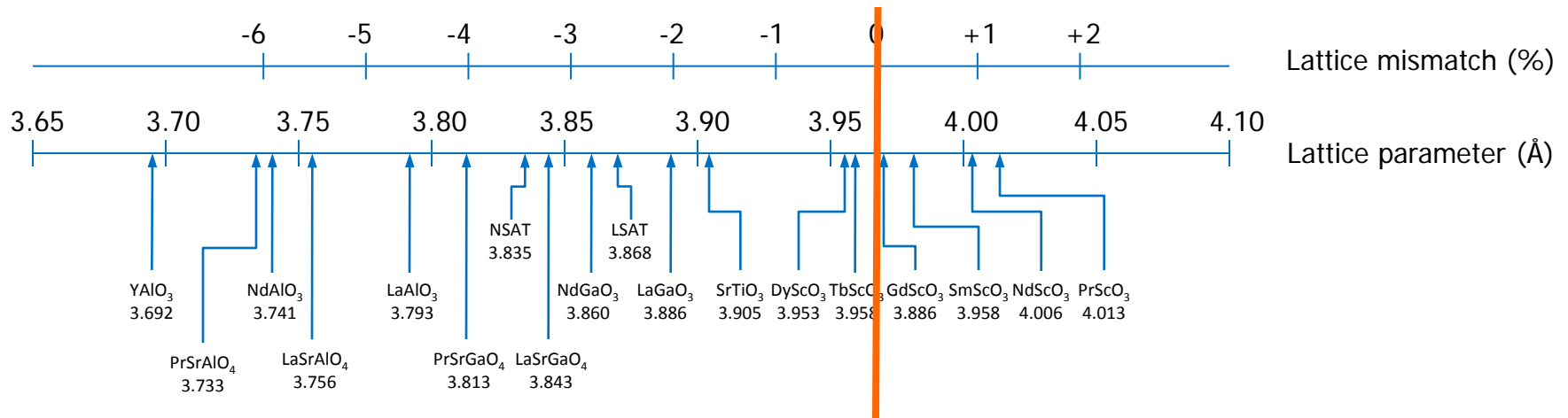


Polarization along  $[111]$   
Octaedra tilt  $[\bar{a}^- \bar{a}^- \bar{a}^-]$

Is it possible to manipulate both structural instabilities to **tune the multiferroic properties** ?  
Or **create readily new ferroic / multiferroic phases** ?

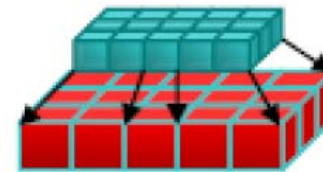
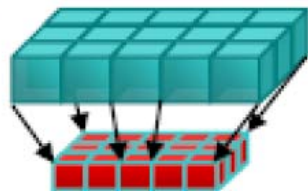
Use epitaxial strain : **strain engineering**

## Mismatch with commercial substrates

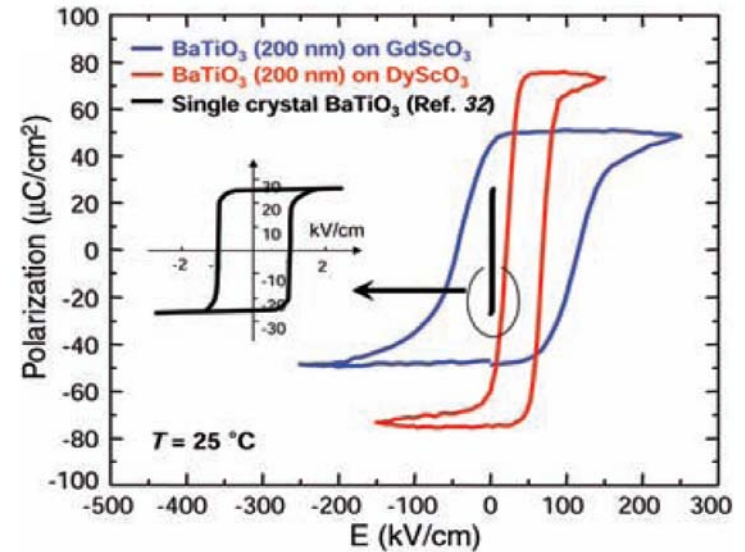
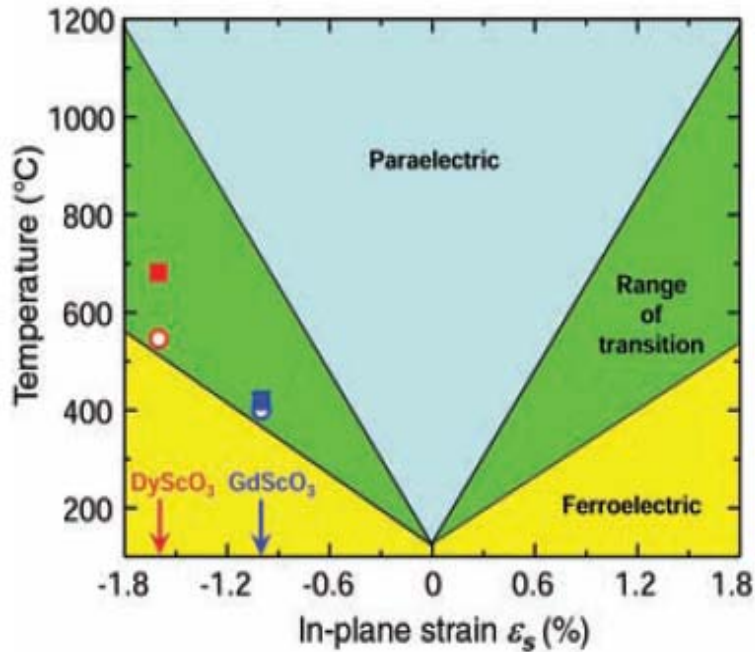


← **BiFeO<sub>3</sub>** →

Compressive strain
Tensile strain



## Prototypical example : BaTiO<sub>3</sub>



Choi et al., Science 306, 1005 (2004)

- ⊙ Strong predicted increase of ferroelectric Curie temperature and polarization with both compressive and tensile strain
- ⊙ Experimentally observed for compressive strain (P out of plane)

# BiFeO<sub>3</sub> thin film growth



Growth from Bi<sub>1.15</sub>FeO<sub>3</sub> targets

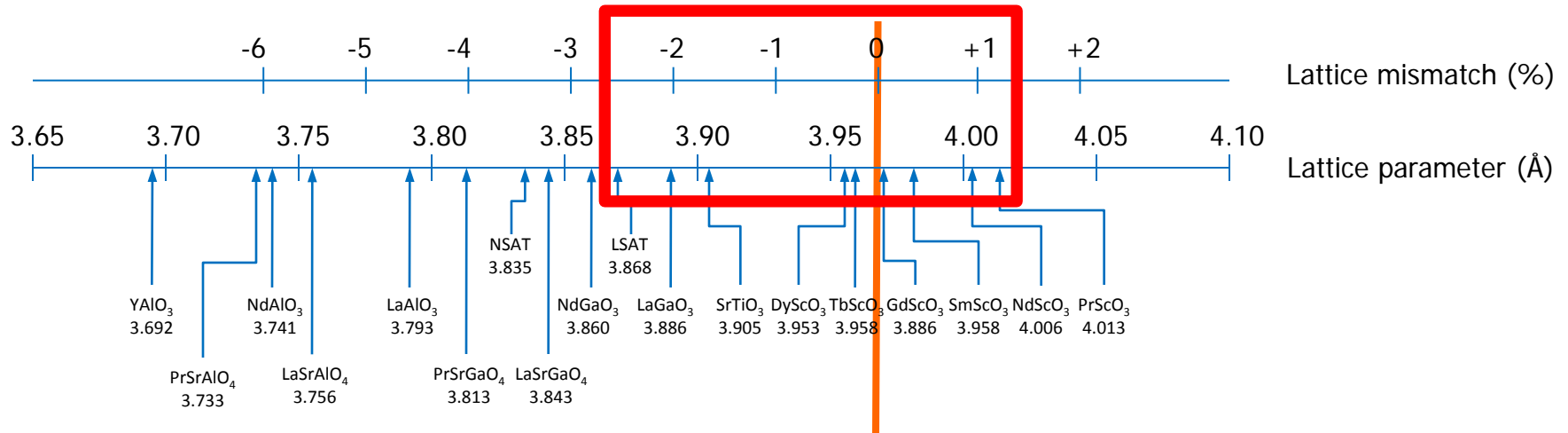
T<sub>dep</sub> : 580°C

PO<sub>2</sub> : ~10<sup>-2</sup> mbar

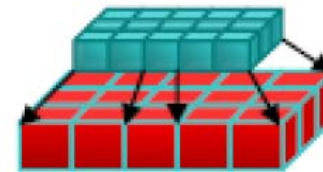
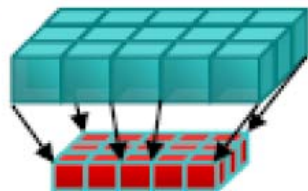
f : 2.5Hz

Film thickness ~70 nm

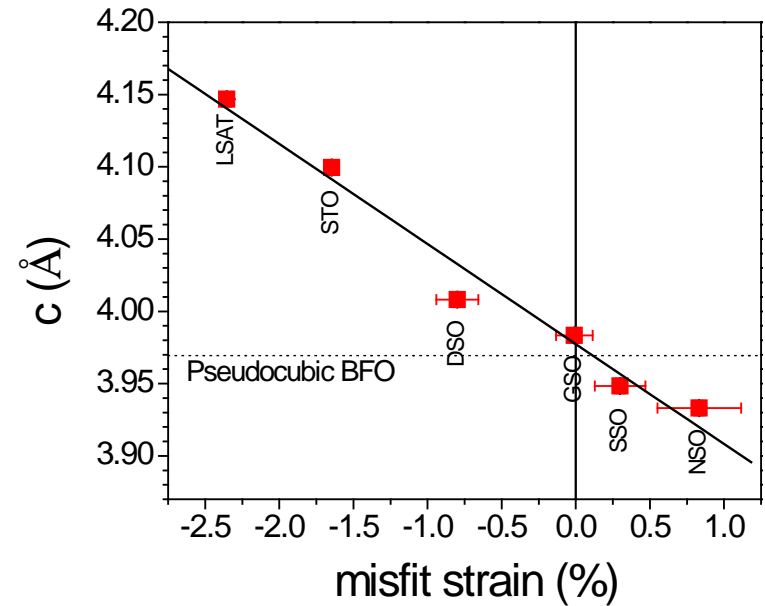
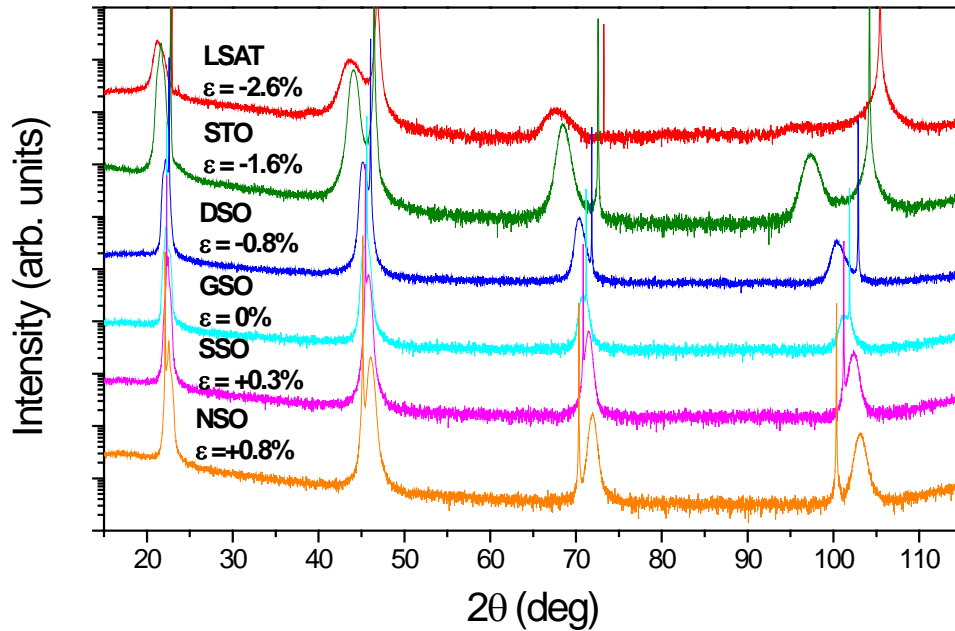
## Mismatch with commercial substrates



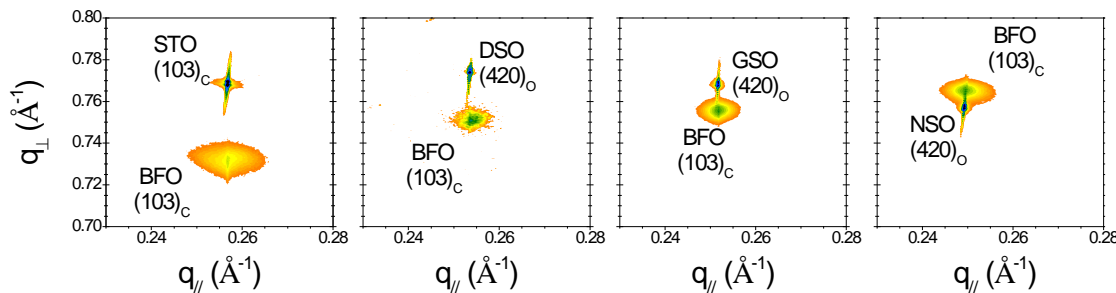
← **Compressive strain** **BiFeO<sub>3</sub>** **Tensile strain** →



## Structural properties



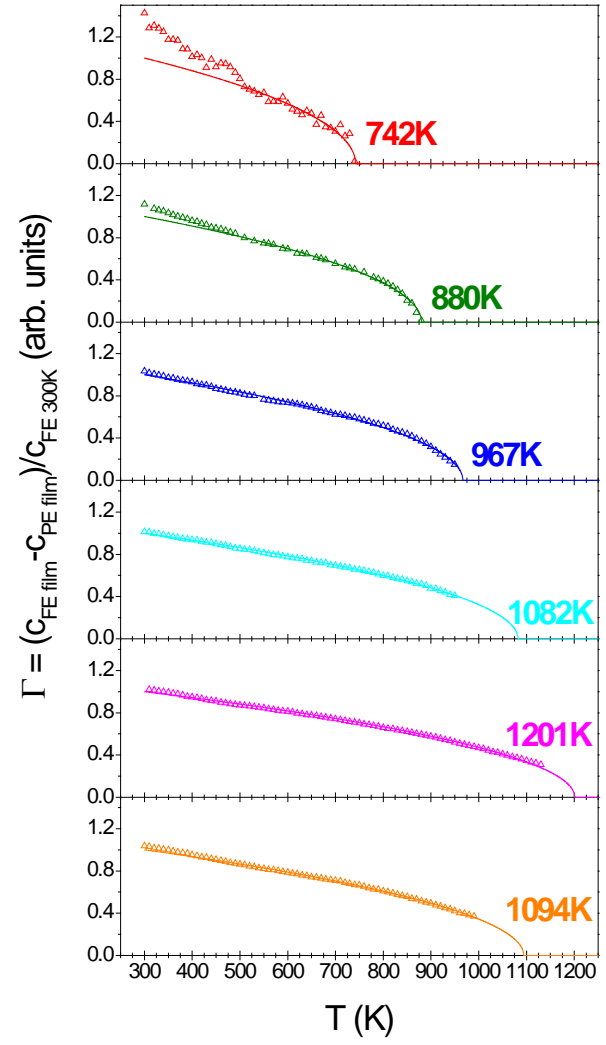
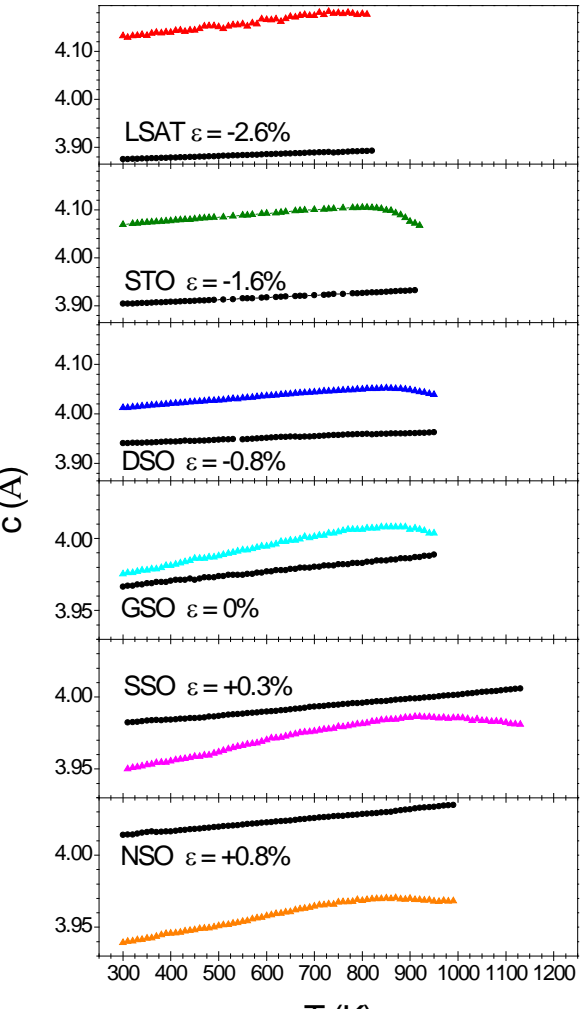
Infante, MB et al., PRL 105, 057601 (2010)



- Single phase fully strained BFO films with monoclinic symmetry (most likely Cc)
- Substrates impose strain and tune c/a ratio

# Influence of strain on ferroic transition temperatures : $T_C$

## X-ray diffraction vs temperature



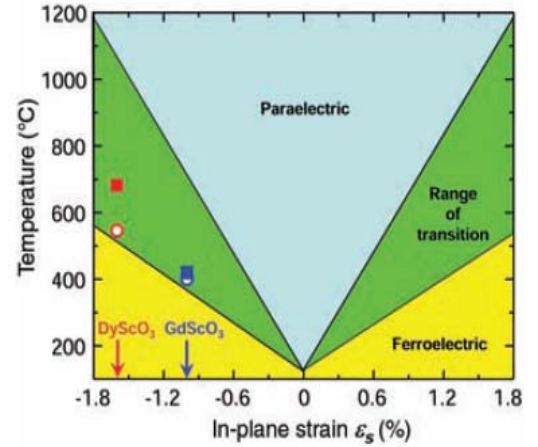
$$\Gamma(T) = (c_{FE\ film}(T) - c_{PE\ film}(T)) / c_{FE\ film}(300K)$$

$$c_{PE\ film}(T) = a_{PE\ bulk}(T) [1 + 2v_{film} / (v_{film} - 1) \cdot (a_{subst}(T) / a_{PE\ bulk}(T) - 1)]$$

$$\Gamma(T) = A + B \cdot (T_C - T)^{1/2}$$

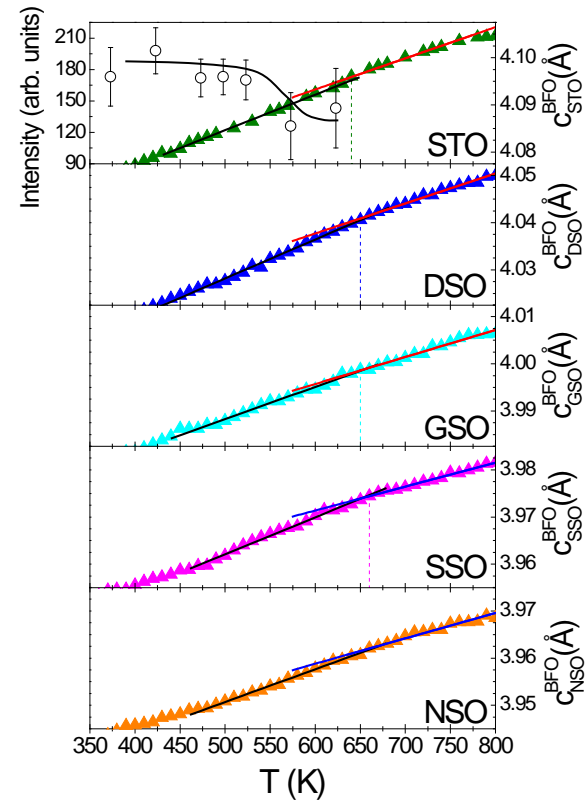
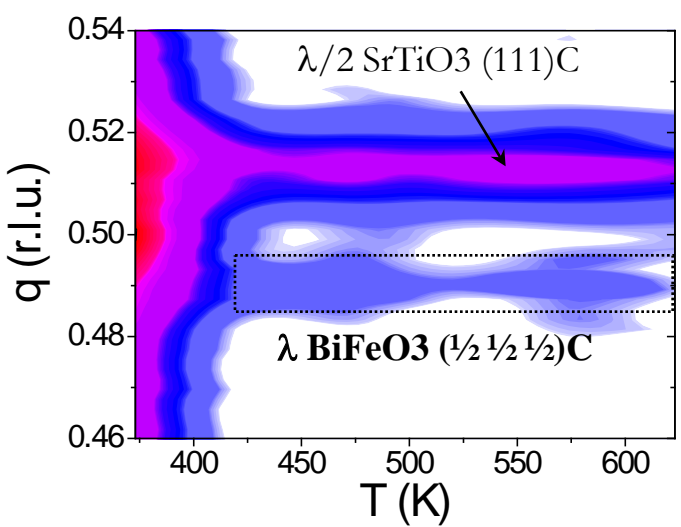
⊙ Ferroelectric  $T_C$  **decreases** with increasing compressive strain

⊙ **Completely antagonist behaviour** compared to  $BaTiO_3$

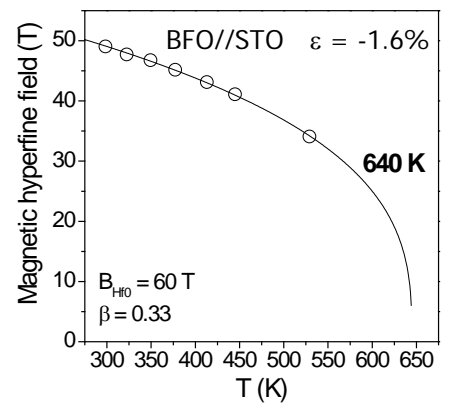
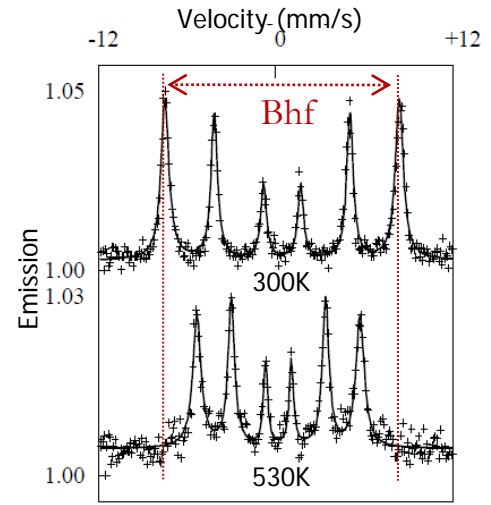


# Influence of strain on ferroic transition temperatures : $T_N$

## Neutron and X-ray diffraction

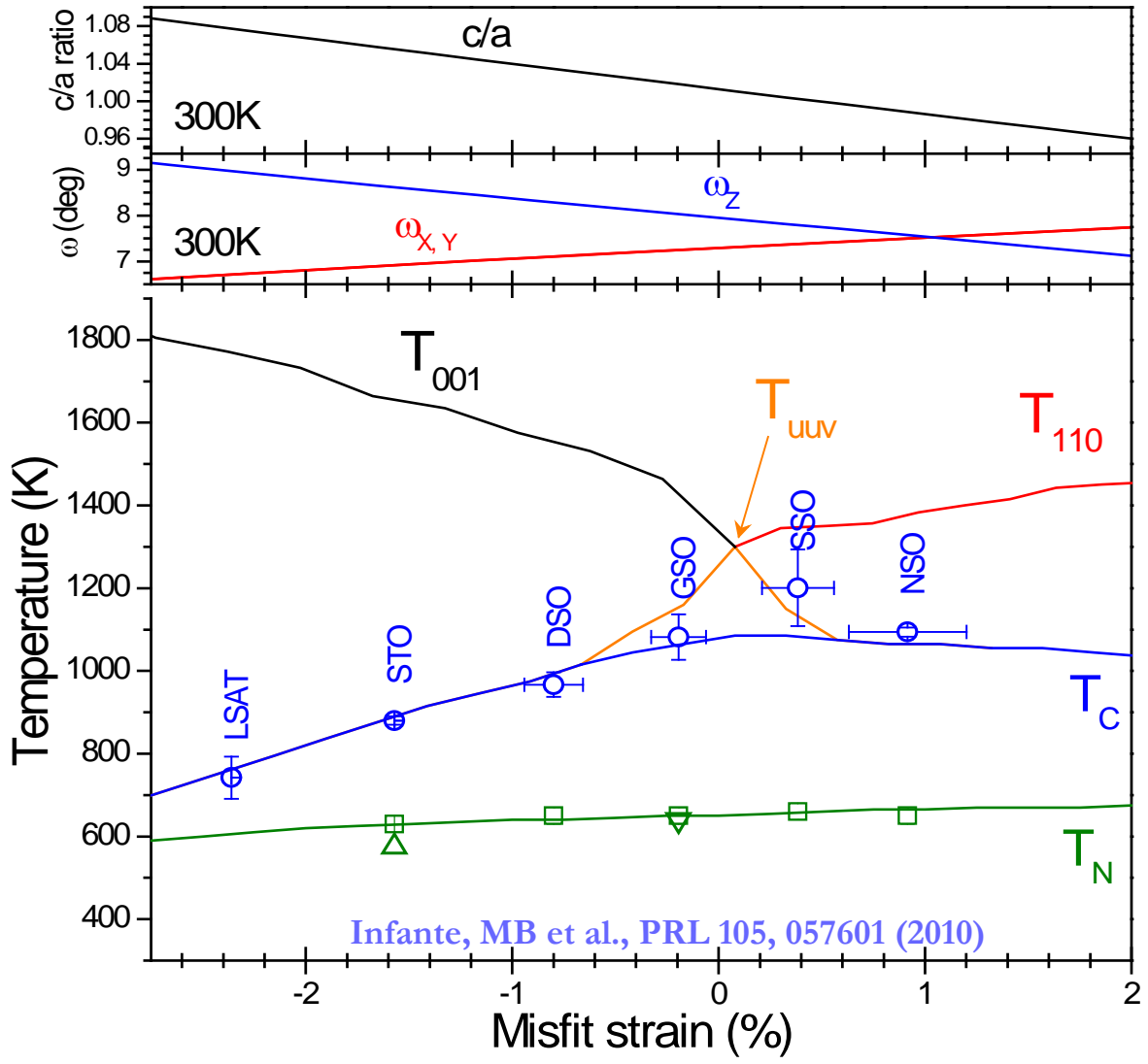


## Mössbauer spectroscopy



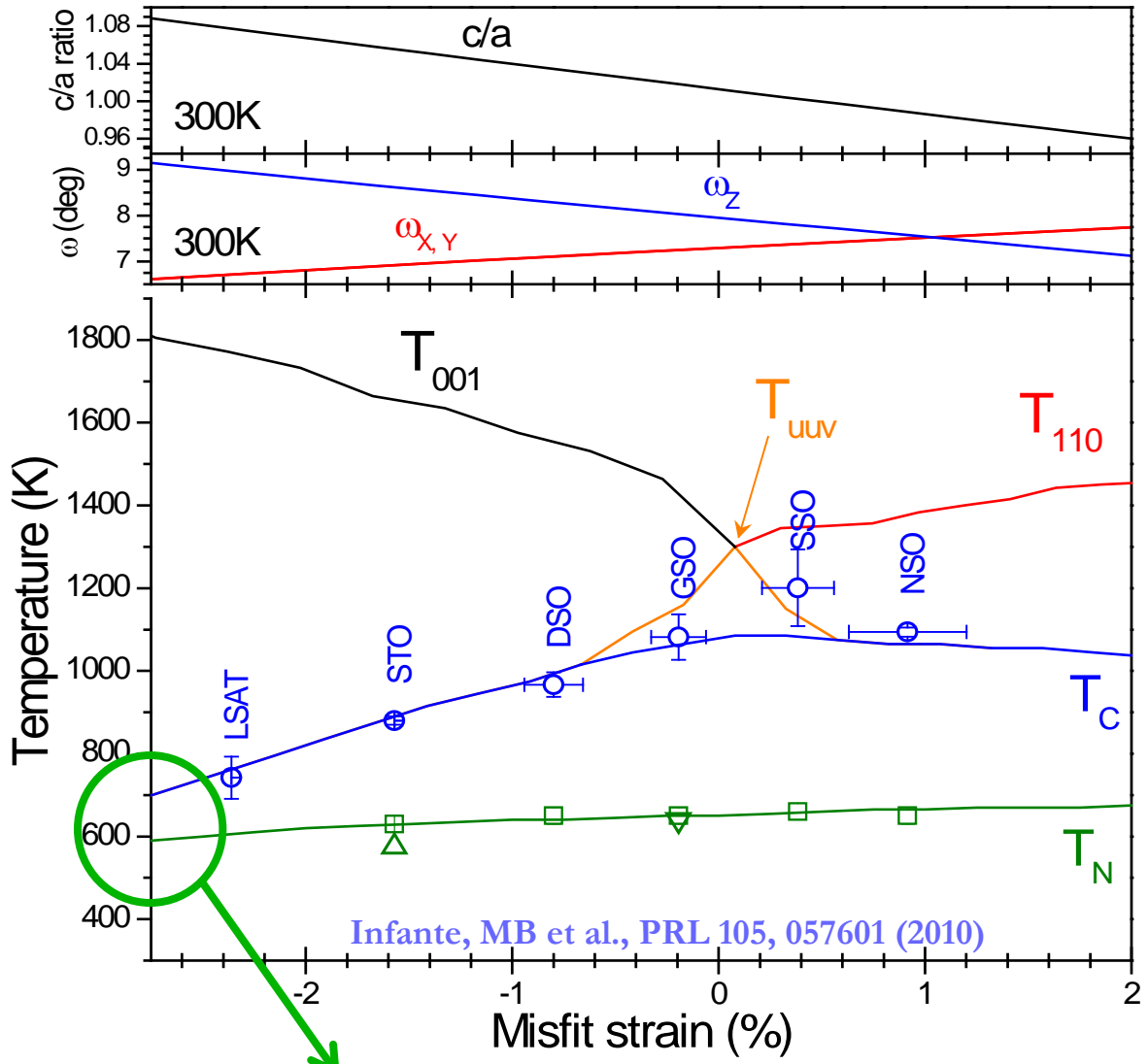
⊙ All samples show antiferromagnetic transition close to the bulk  $T_N$  of 640K

# Strain-temperature phase diagram : effective Hamiltonien calculations



**Key role of tilts to capture the physics of BiFeO<sub>3</sub> thin films**

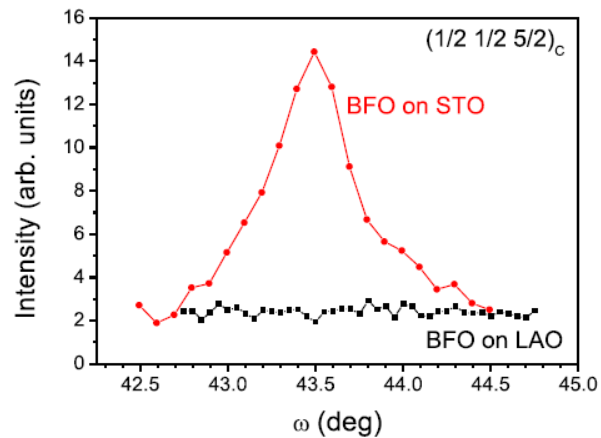
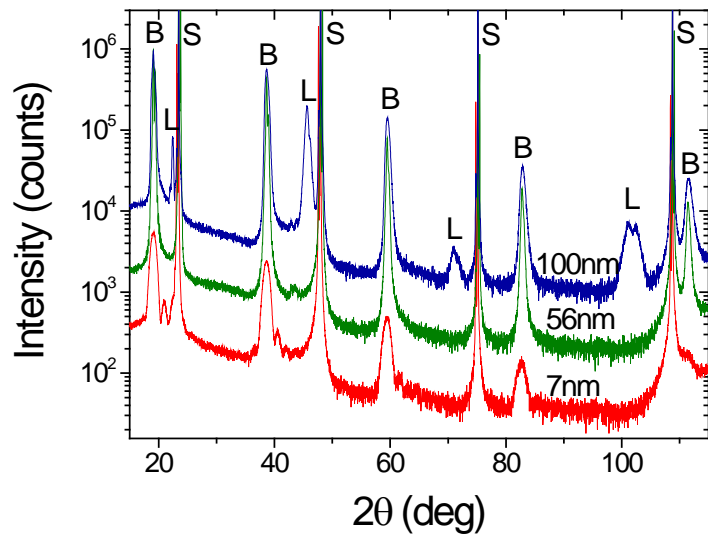
# Strain-temperature phase diagram : effective Hamiltonien calculations



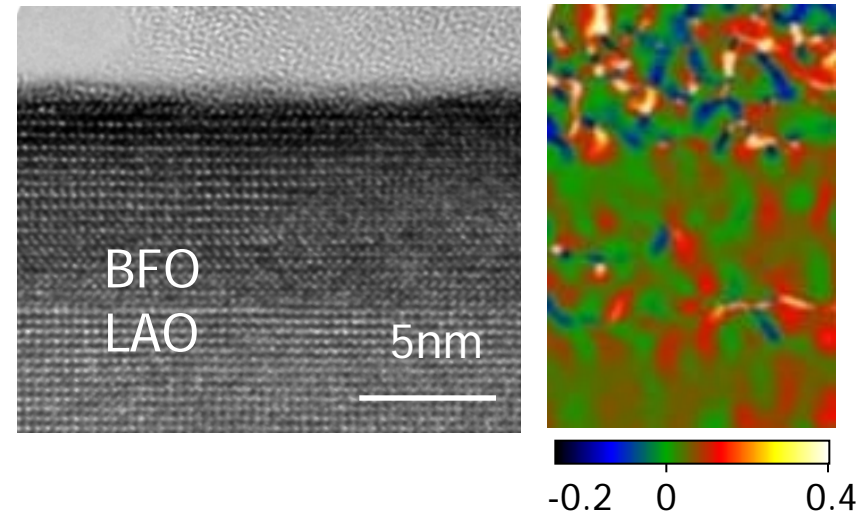
At about 3 to 3.5% compressive strain,  $T_N$  and  $T_C$  should meet  
Enhanced magnetoelectric coupling



## X-ray diffraction



## Transmission electron microscopy

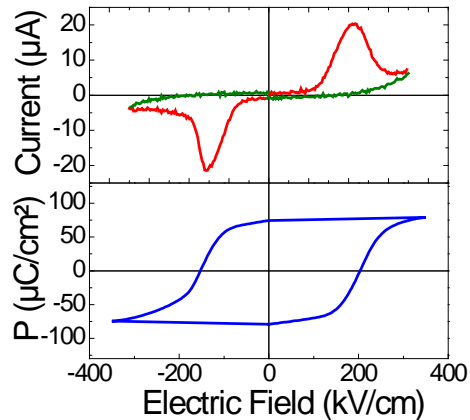
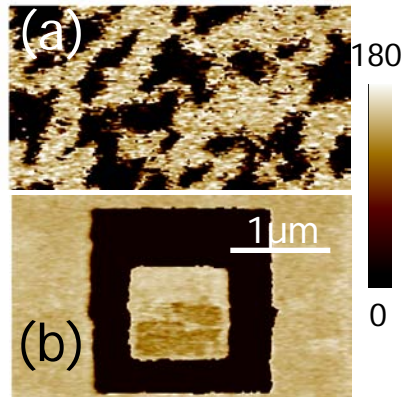


- ⊙ BFO unit cell is **strongly elongated out of plane**
- ⊙  $c=4.62 \text{ \AA}$  ; giant  $c/a = 1.23$
- ⊙ Symmetry is NOT tetragonal, possibly monoclinic
- ⊙ **No tilts**

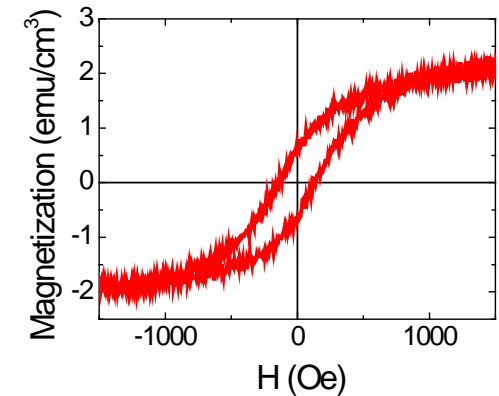
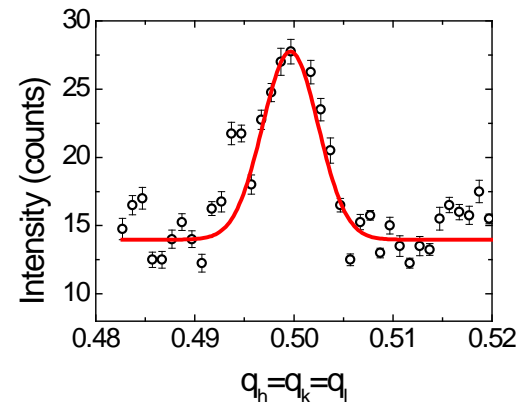
**New « T » phase of BiFeO<sub>3</sub> !!!**

Béa, MB et al., PRL 102, 217603 (2009)  
Dupé, MB et al., PRB 81, 144128 (2010)

## Ferroelectric properties

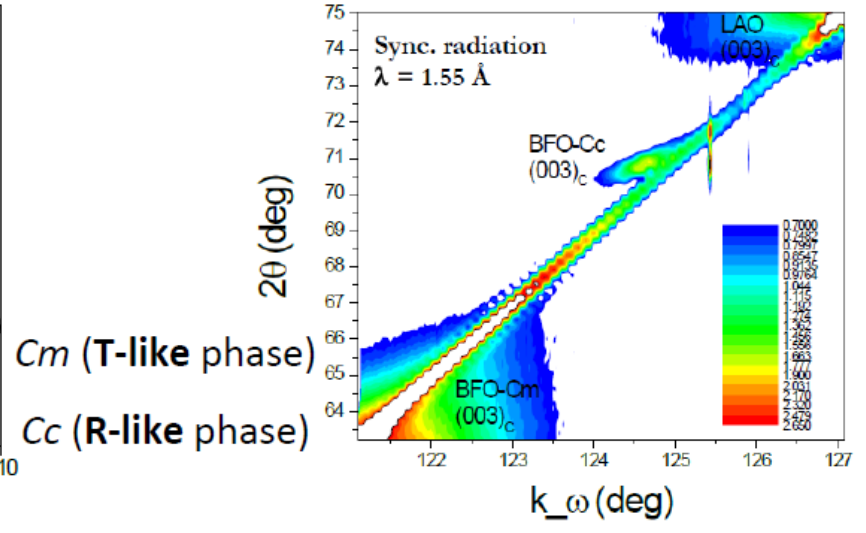
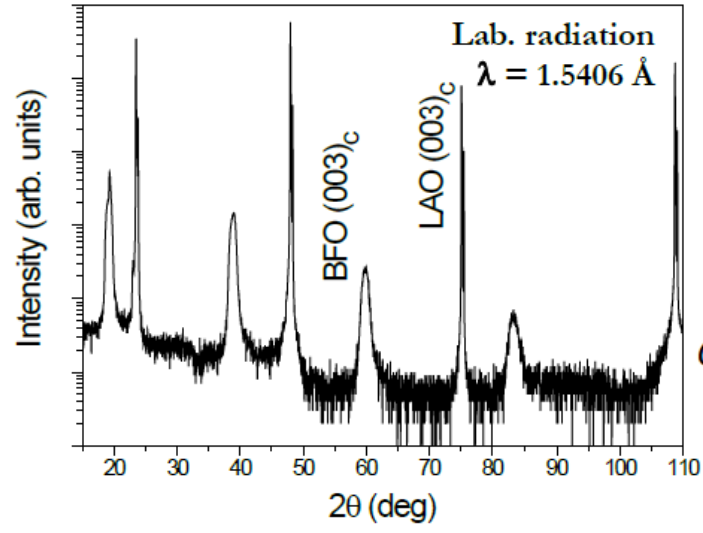


## Magnetic properties



- ⊙ PFM indicates samples are ferroelectric with finite in-plane component : confirms not tetragonal space group
- ⊙ Polarization is comparable with bulk
- ⊙ Neutron diffraction indicates G-type order
- ⊙ Magnetization is weak as for weakly strained samples
- ➔ Despite the giant structural change, room temperature properties rather similar to those of bulk BFO...

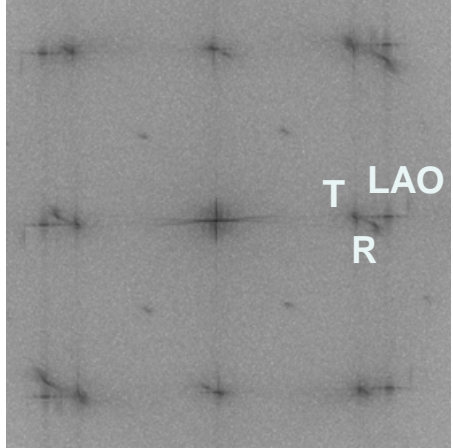
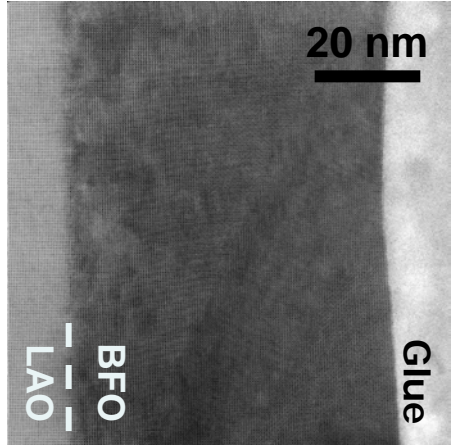
# BiFeO<sub>3</sub> films on LaAlO<sub>3</sub> : phase coexistence



Cm (T-like phase)  
Cc (R-like phase)

T phase

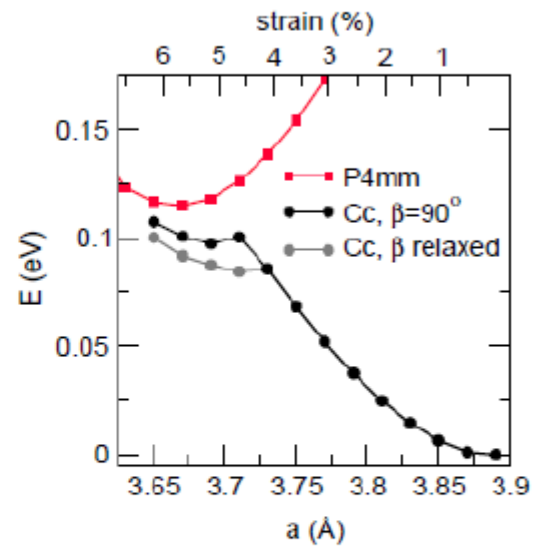
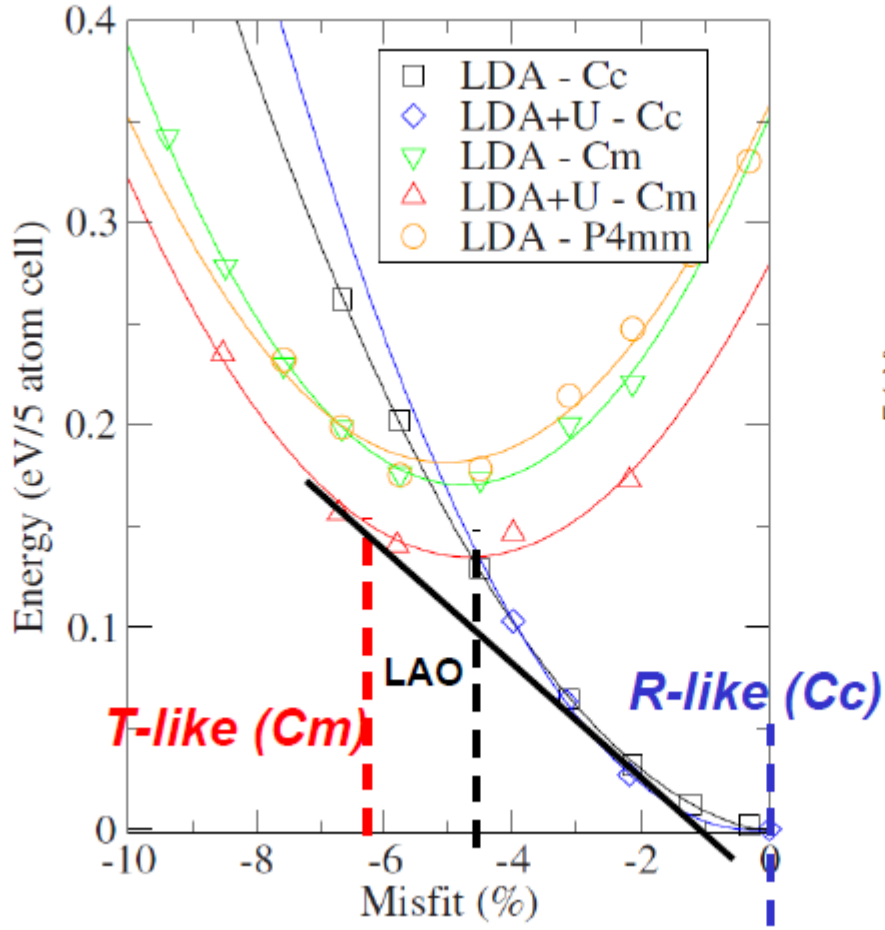
R phase



- Careful X-ray and HREM studies reveal coexistence of « R » and « T » phase
- « R » phase is derived from bulk R3c and has Cc symmetry
- « T » phase is super-tetragonal-like and Cm

Infante , MB et al, arXiv:1105.6016  
Zeches et al, Science 2009

# BiFeO<sub>3</sub> films on LaAlO<sub>3</sub> : phase coexistence

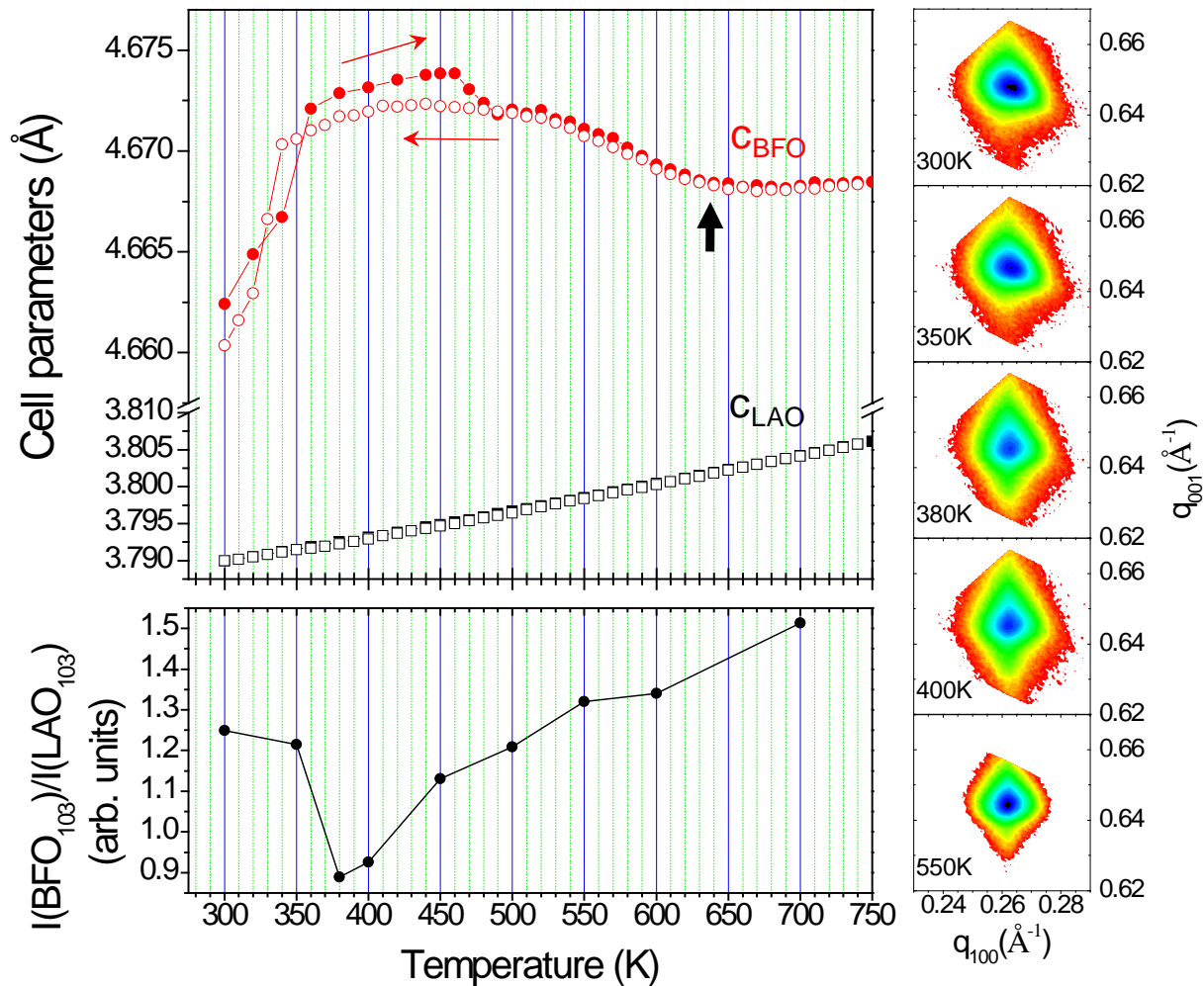


[Hatch, Ederer, Spaldin, PRB10]

Dupé, MB et al., PRB 81, 144128 (2010)  
 Z. Chen et al. (2011), arXiv:1104.4712

⊙ Possible spinodal decomposition between T and R phases for strain levels around -4 and -5% ?

## X-ray diffraction vs temperature

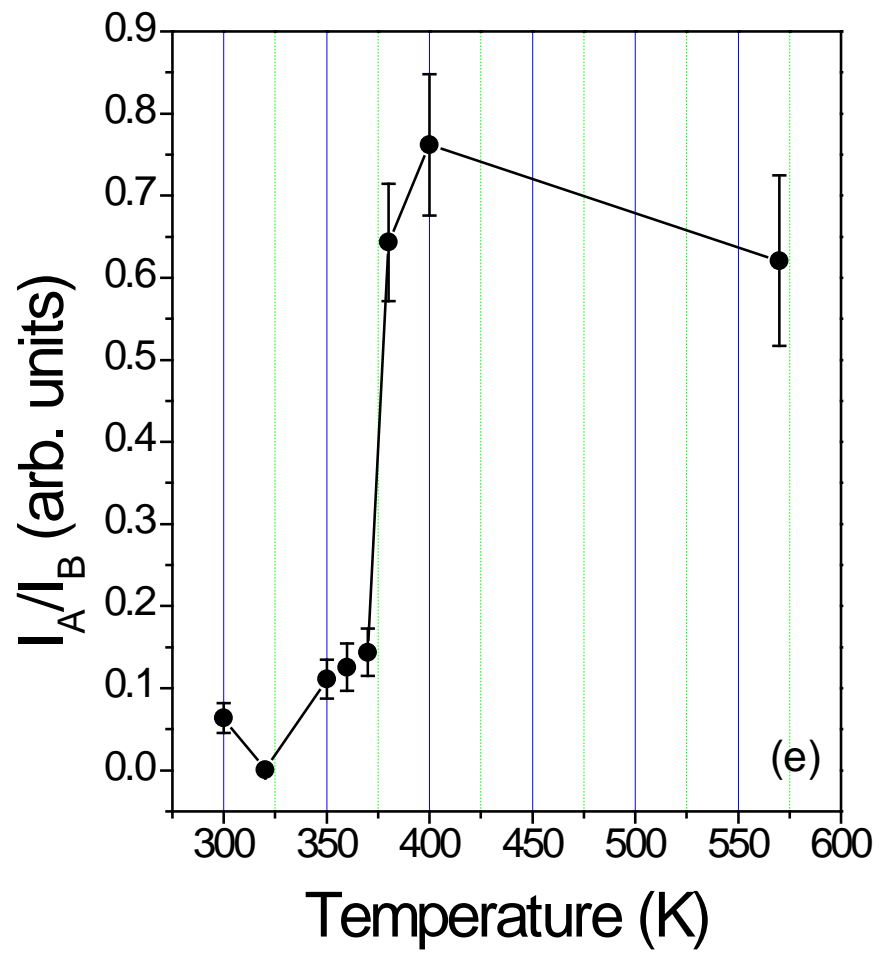
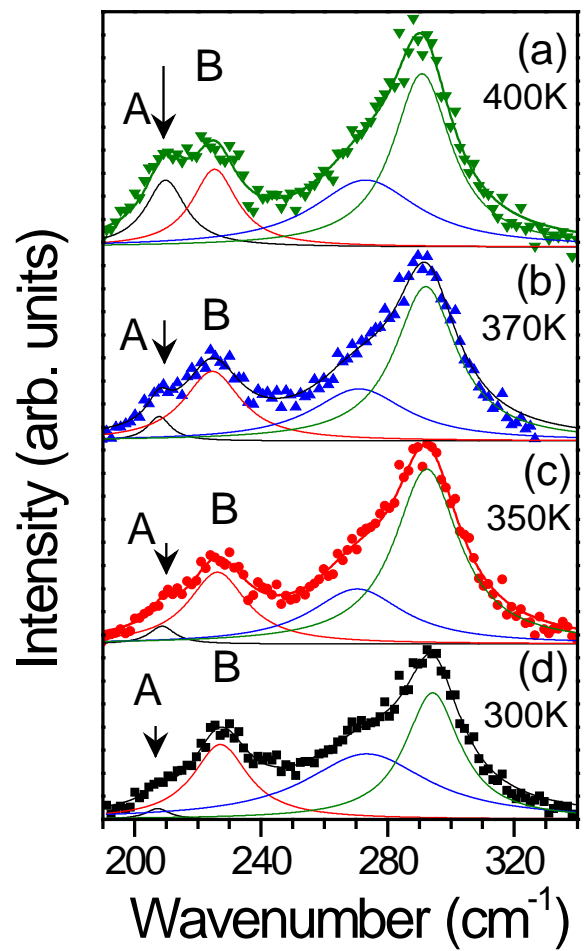


⊙ Clear structural transition at ~360K

Infante, MB et al, arXiv:1105.6016

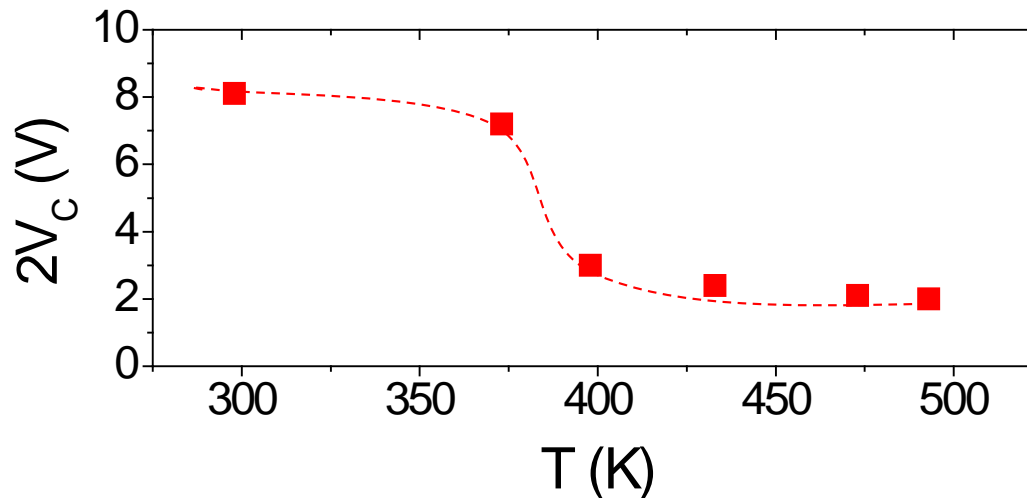
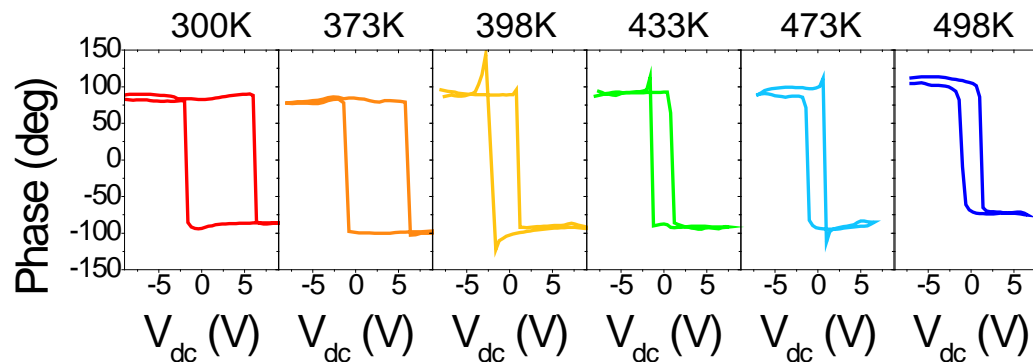
⊙ Change of symmetry, possibly from monoclinic to tetragonal (or at least more tetragonal)

## Raman spectroscopy vs temperature



⊙ Raman confirms phase transition at  $\sim 360 \pm 20$  K

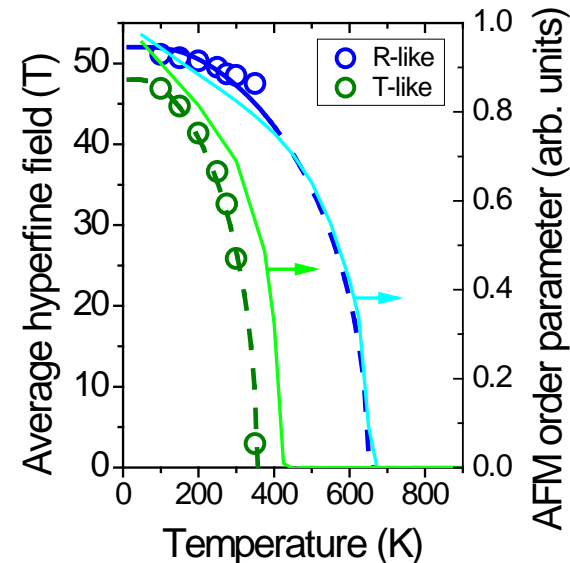
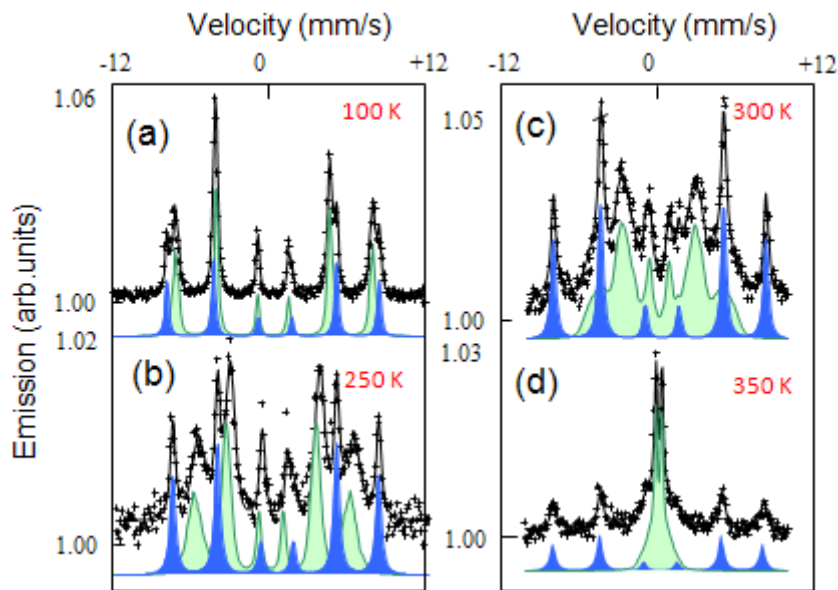
## Piezoresponse vs temperature



- Temperature dependence of coercive voltage suggests a **ferroelectric phase transition at ~370K**
- Below transition, BFO is a standard ferroelectric ; above, non-standard ferroelectricity behaviour

Infante , MB et al, arXiv:1105.6016

## Mössbauer spectroscopy vs temperature



- ⊙ Room temperature spectra confirm phase coexistence of R and T phases
- ⊙ R phase show similar behavior as BFO on STO, with  $T_N \sim 640\text{K}$
- ⊙ **T phase show reduced  $T_N \sim 370\text{K}$**
- ⊙ Monte Carlo simulations show reasonably good agreement for both phases

**Concomitant magnetic and ferroelectric phase transitions close to room temperature**

Infante, MB et al, arXiv:1105.6016

Similar (structural) phase transition also recently found by others : Kreisel et al JPCM 23, 342202 (2011) ; Siemons APEX 4, 095801 (2011)

- ⊙ In BiFeO<sub>3</sub> the competition between polar distortion and oxygen tilts give rise to an anomalous influence of strain of ferroic orders
  - **key role of oxygen tilts**
- ⊙ Strain weakly increases polarization, strongly depresses T<sub>C</sub> and leaves T<sub>N</sub> unchanged
  - at about -3.5% strain T<sub>C</sub> and T<sub>N</sub> should meet : **enhanced ME coupling**
- ⊙ Larger strains give rise to phase coexistence between bulk-derived R phase and **new, super-tetragonal T phase**
- ⊙ T phase has **very different phase diagram**, with still undisclosed physics

Financial support by European Research Council, French ANR program, C-Nano Ile-de-France