

Antiferroelectric like state in $\text{BiFeO}_3/\text{LaFeO}_3$ superlattices

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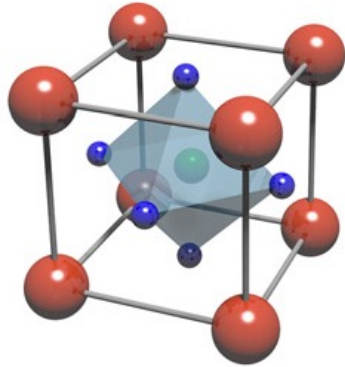


- 1. Introduction**
- 2. Structural investigation and phase transition of (001) oriented BFO/LFO superlattices**
- 3. Room temperature investigation of (111) oriented BFO/LFO superlattices**
- 4. Conclusions**



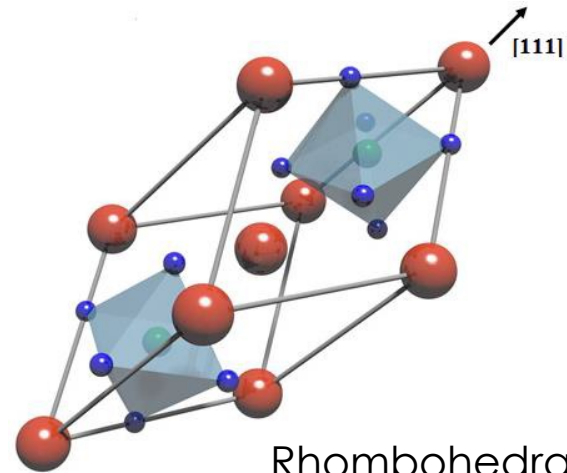
Introduction : BiFeO₃

The multiferroic BiFeO₃



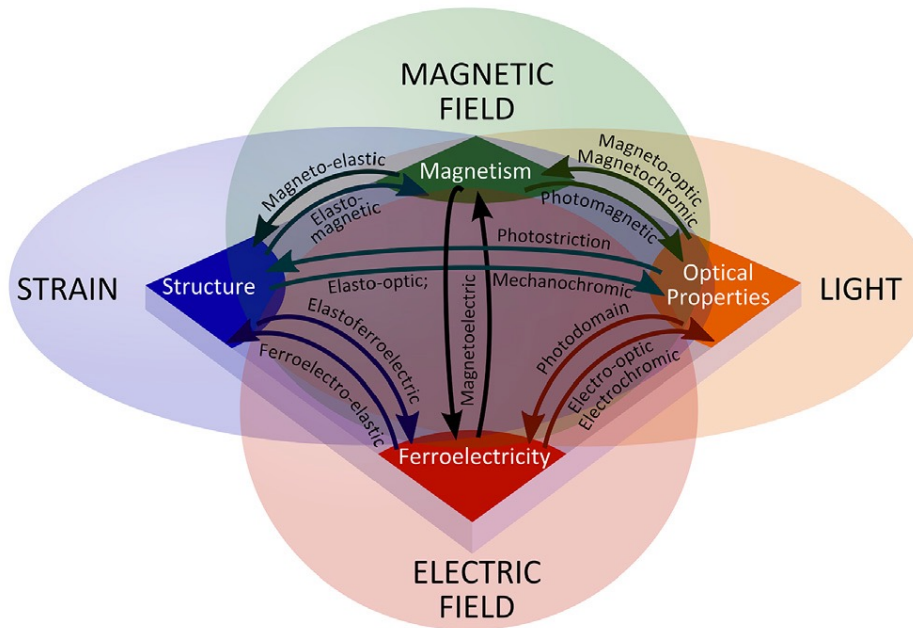
$T_C = 1100\text{K}$
 $P \approx 100 \mu\text{C}/\text{cm}^2$

$T_N = 640\text{K}$ AFM
type G



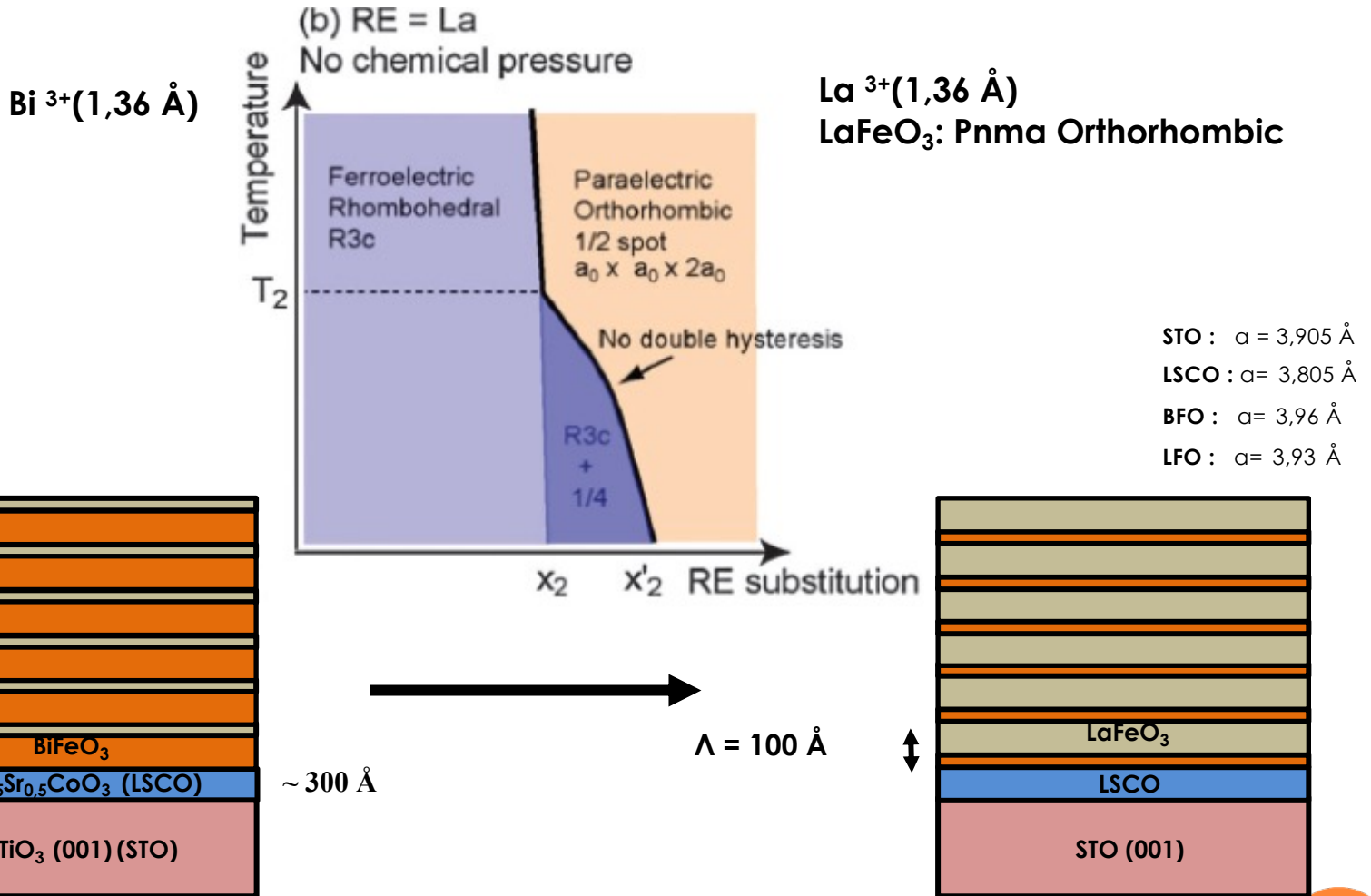
$a_{pc} = 3,96 \text{Å}$

Rhombohedral structure
R3c





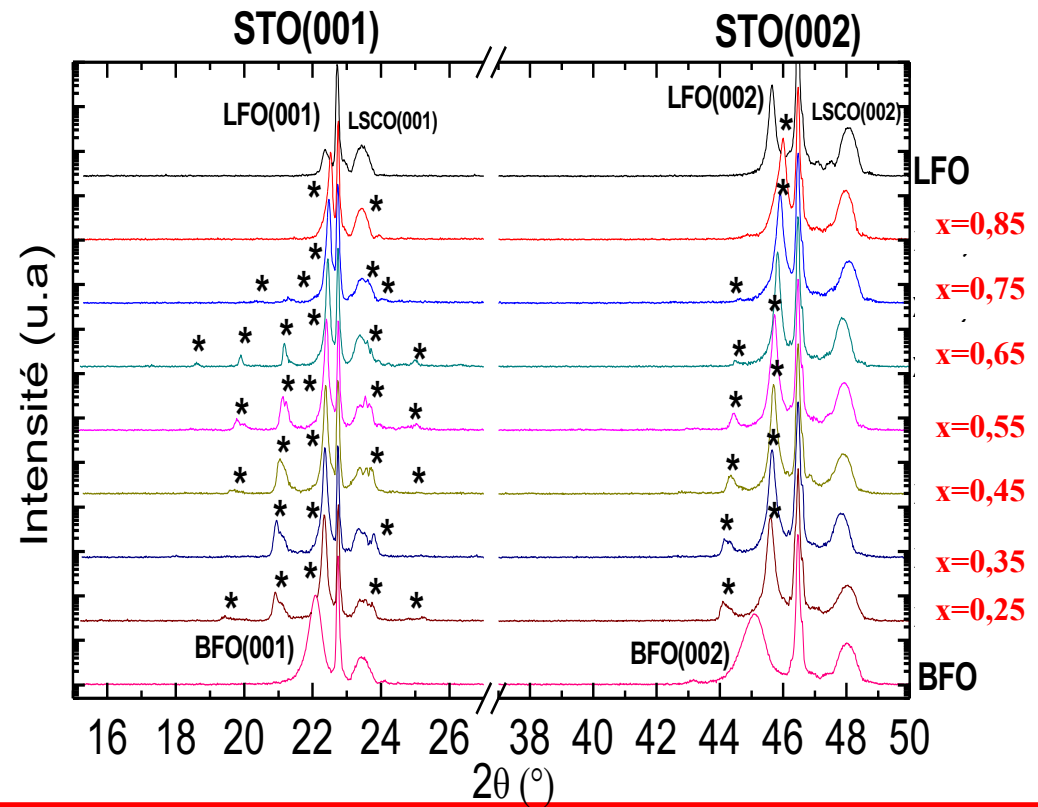
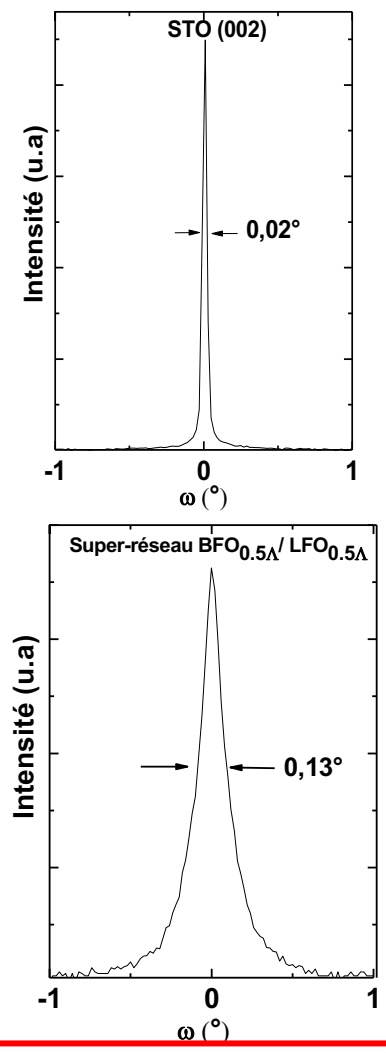
MPB: R3c+antiferroelectric like (PbZrO_3)+signatures of incommensurate structures



❑ Superlattice approach for investigating structural interaction between BiFeO_3 and LaFeO_3

BFO_{(1-x)Λ}/LFO_{xΛ} superlattices grown on STO buffered with LSCO

X-ray diffraction in $\theta/2\theta$ geometry

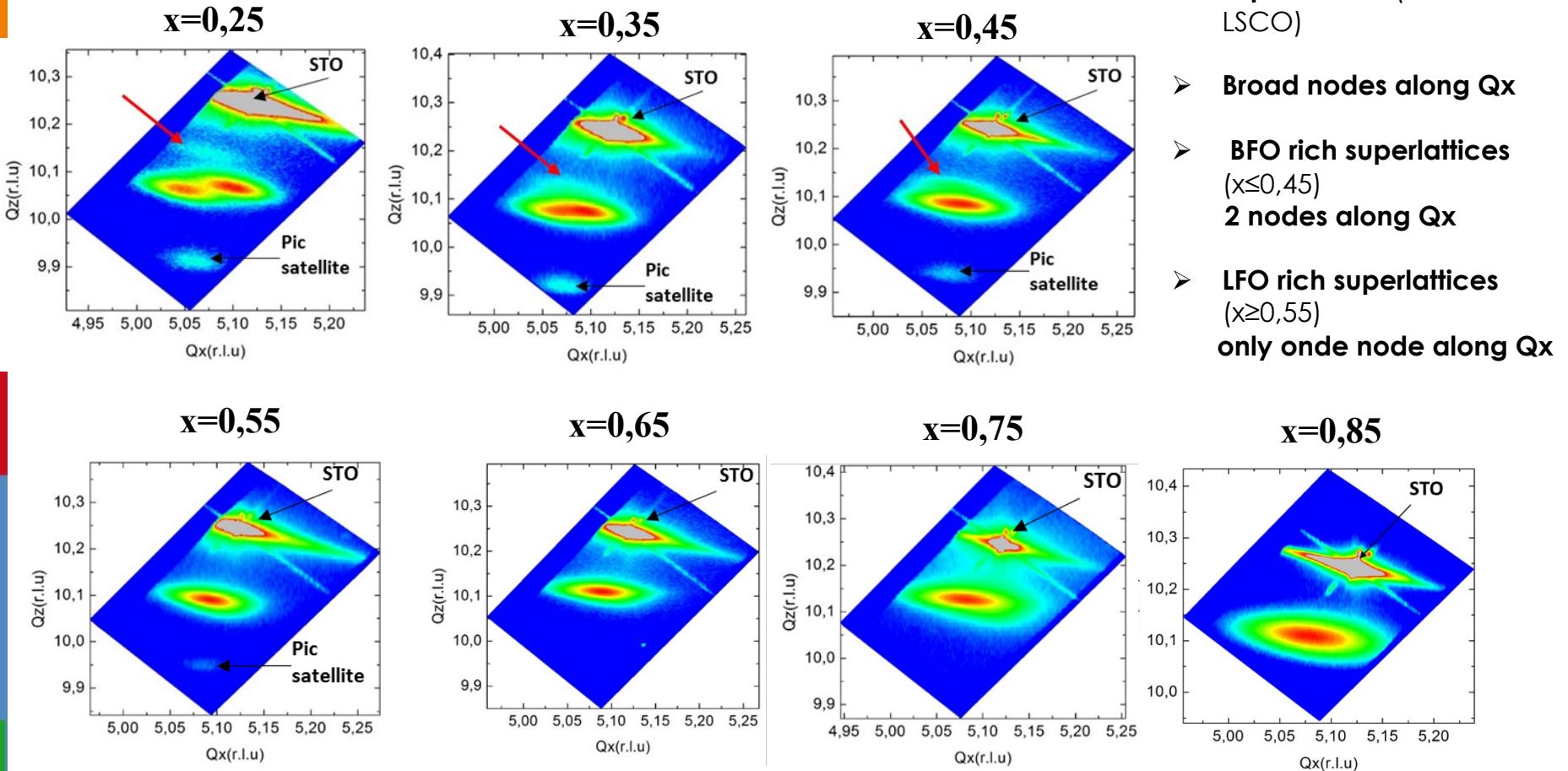


➤ Satellite peaks: Chemical modulation along the growth direction

➤ No parasitic phases

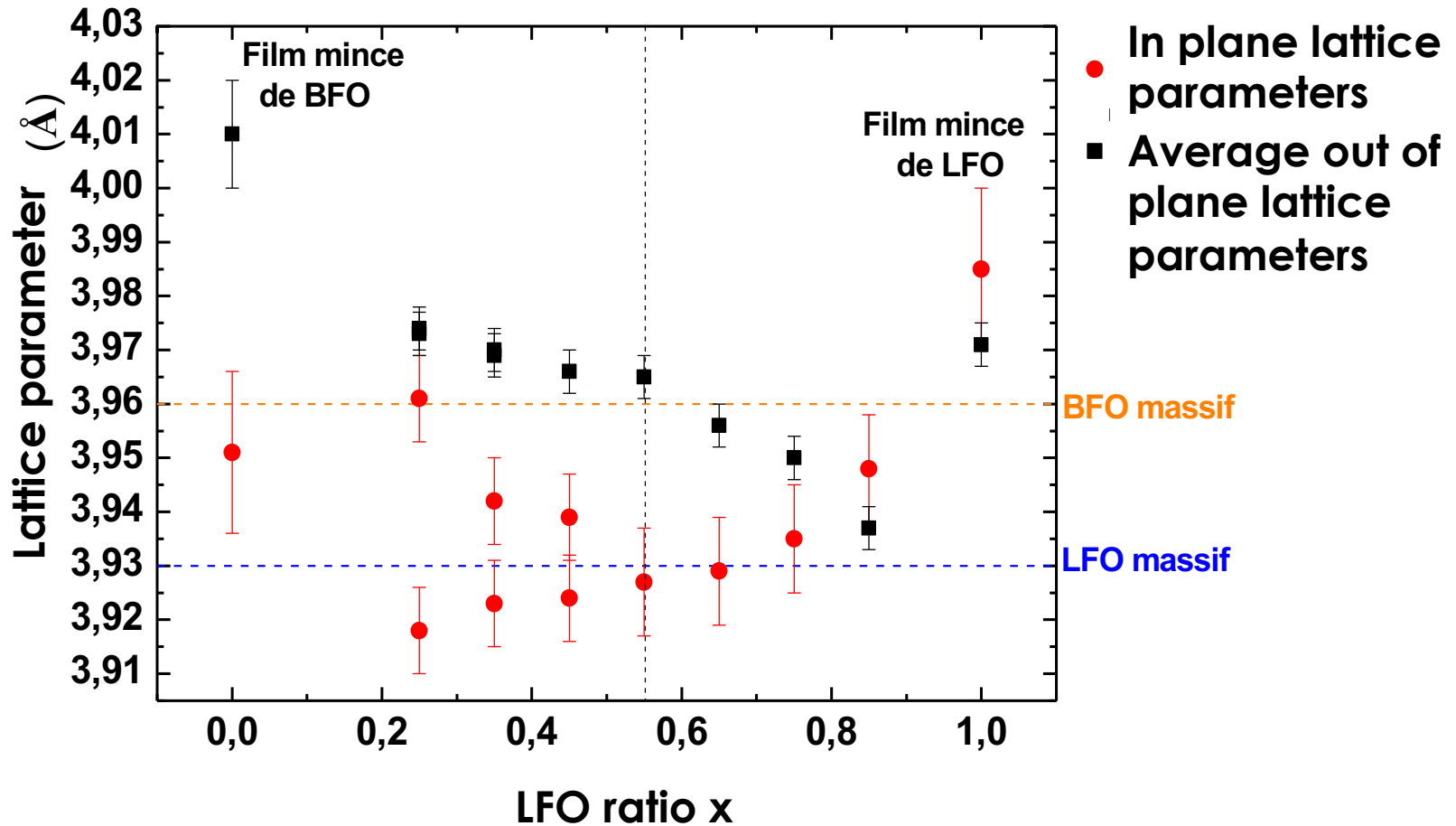
➤ Good quality of the orientation

(204) Reciprocal space mapping

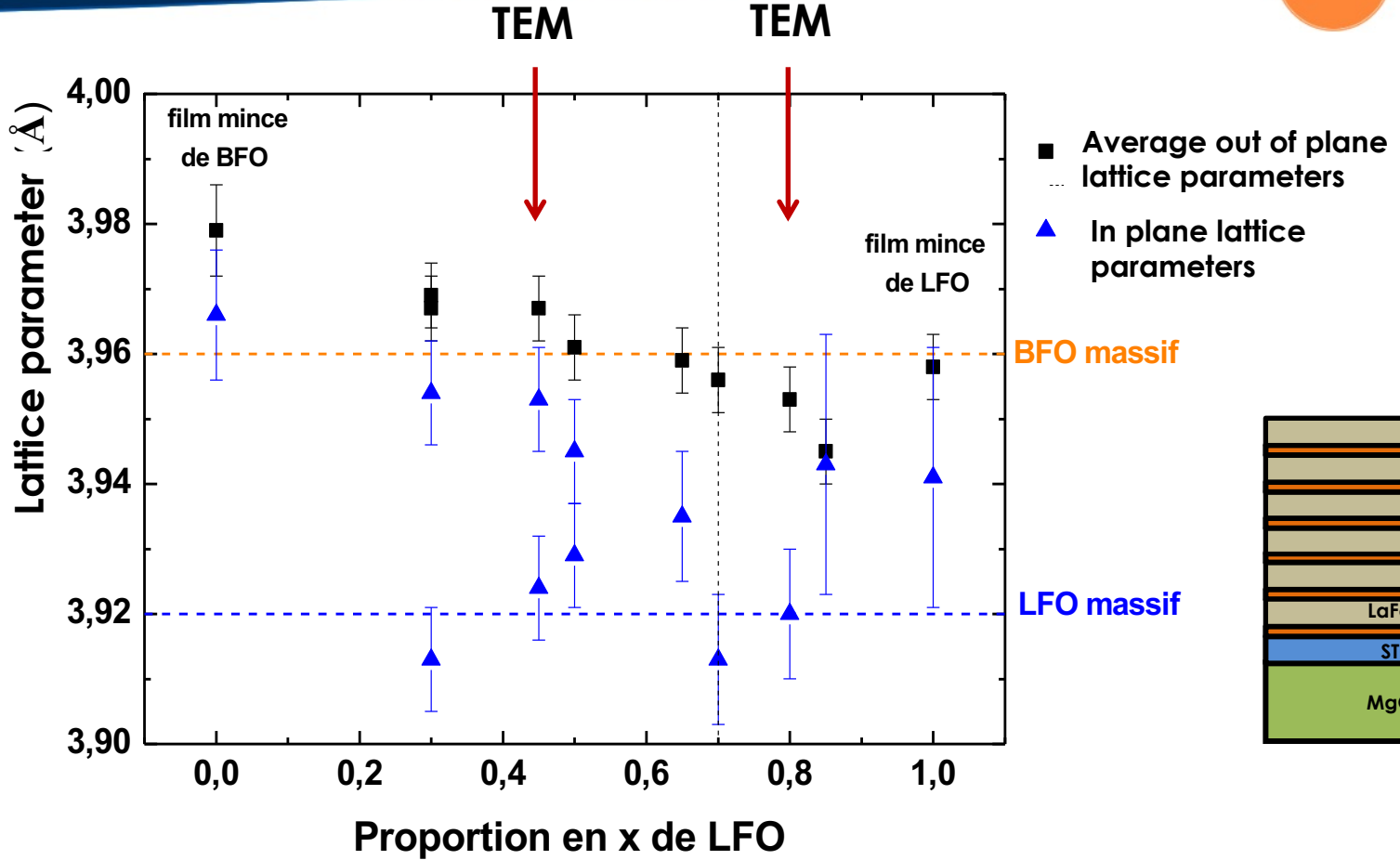


- In plane relaxation of the superlattices (coherent LSCO)
- Broad nodes along Qx
- BFO rich superlattices ($x \leq 0,45$)
2 nodes along Qx
- LFO rich superlattices ($x \geq 0,55$)
only one node along Qx

- Same results for (024) reciprocal space mapping
- (113) reciprocal space mapping: a single reflection
- ✗ Exclusion of the monoclinic or rhombohedral structure



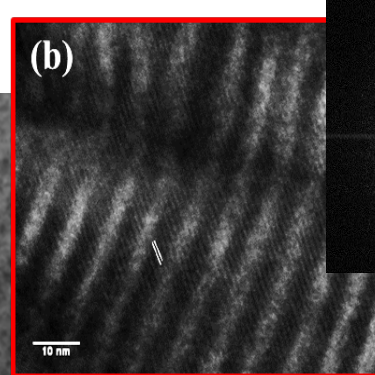
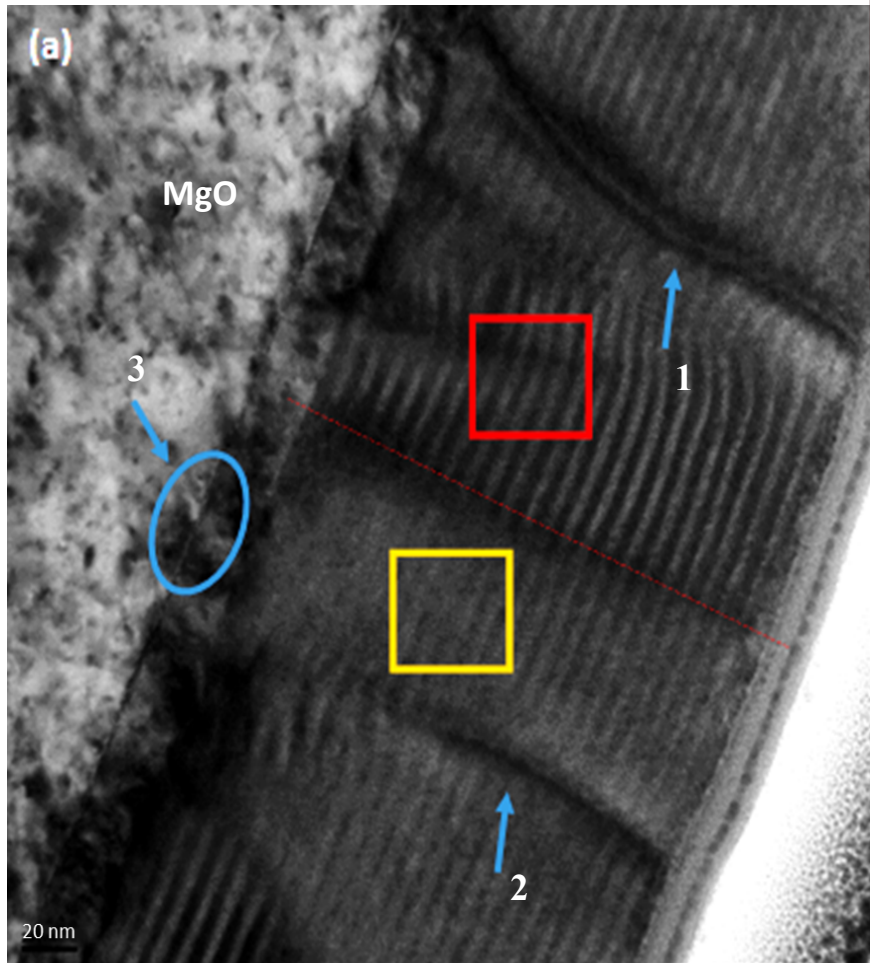
➤ Change of structure at about $x=0,55$



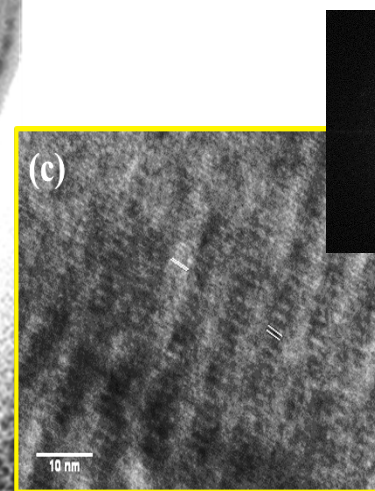
- Similar structural evolution:
2 nodes for the rich BFO superlattices ($x \leq 0,65$)
1 node for the rich LFO superlattices ($x \geq 0,7$)

Room temperature structural investigation by TEM

x=0,45



- Lamellar structure at 45° in BFO layers
- (1,15 nm periodicity)
- FFT : Modulation along [011]_{pc}



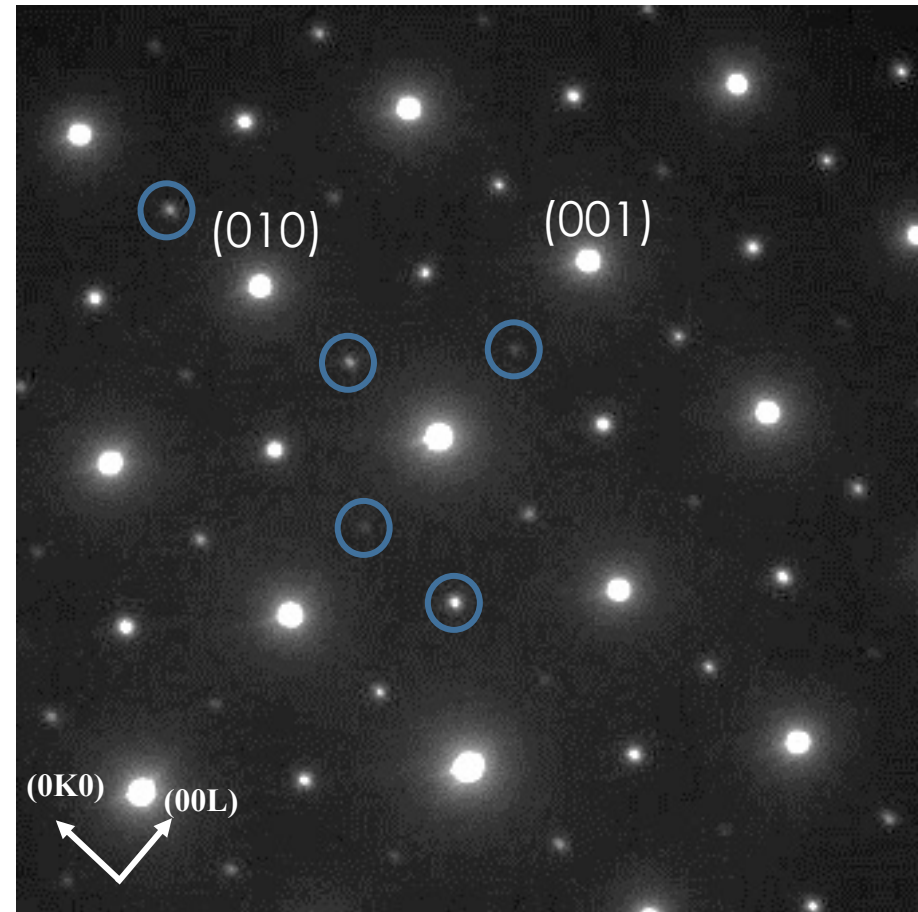
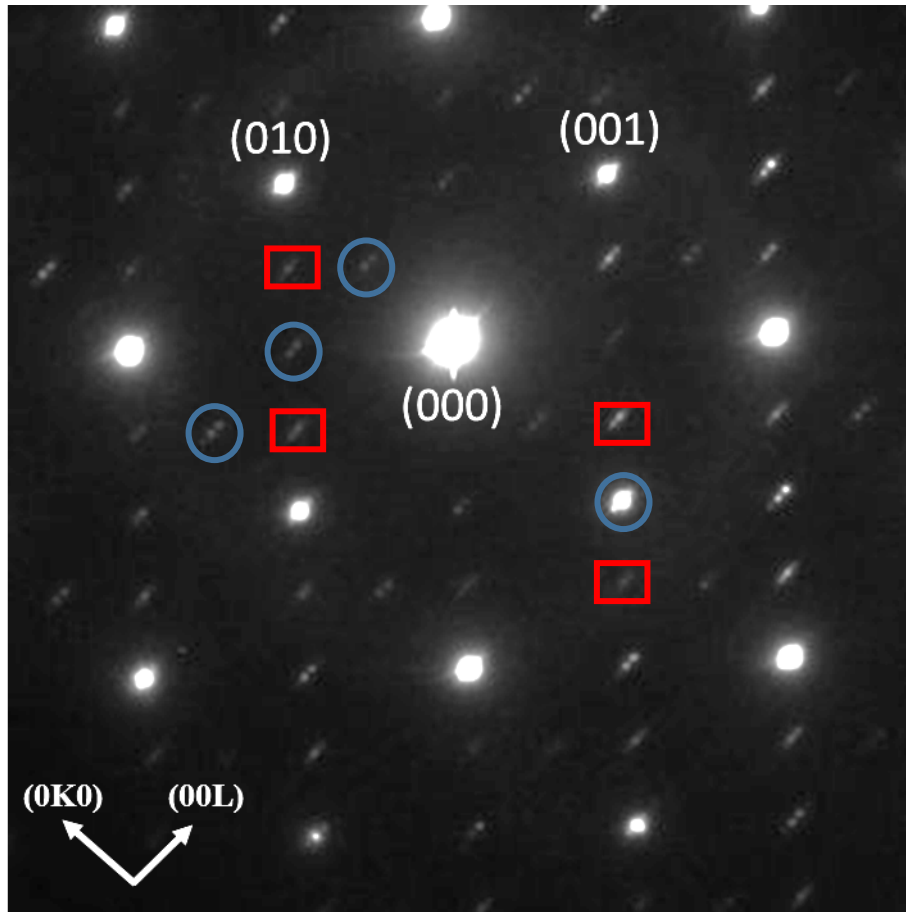
- Vertical lamellar structure in BFO layers (1,6 nm periodicity) and LFO (0,8 nm periodicity)
- FFT : Modulation along [010]_{pc}



x=0,45

SAED [100] zone axis

x=0,8

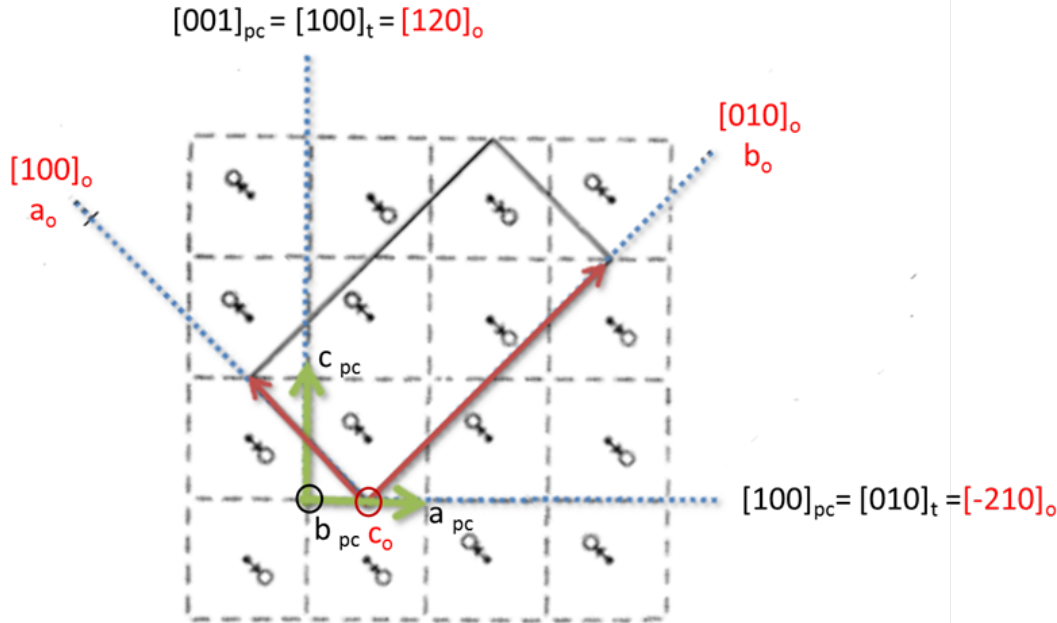


- presence PbZrO₃ like reflections $\frac{1}{4}(011)$
- Presence of Pnma like reflections $\frac{1}{2}(010)$

- no PbZrO₃ like reflections $\frac{1}{4}(011)$
- Presence of Pnma like reflections $\frac{1}{2}(010)$



Orientation of the PbZrO₃ orthorhombic unit cell (a⁻a⁻c⁰) and relation with the pseudo-cubic unit cell



▪ Pbam

$$\begin{aligned} a_o &= \sqrt{2}a_c \\ b_o &= 2\sqrt{2}a_c \\ c_o &= 2a_c \\ a^-a^-c^0 \end{aligned}$$

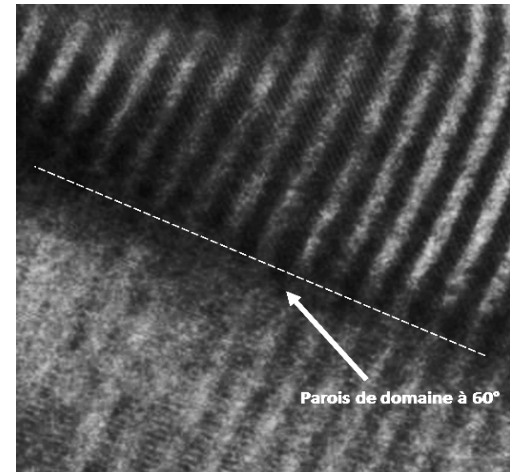
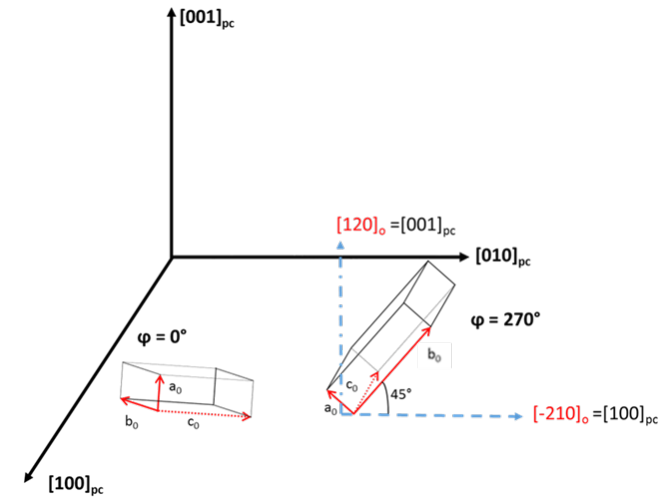
PbZrO₃

▪ Pnma AFE

$$\begin{aligned} a_o &= \sqrt{2}a_c \\ b_o &= 2\sqrt{2}a_c \\ c_o &= 4a_c \\ a^-a^-c^+ / a^-a^-c^- \end{aligned}$$

Mundy et al., arXiv preprint arXiv:1812.09615,

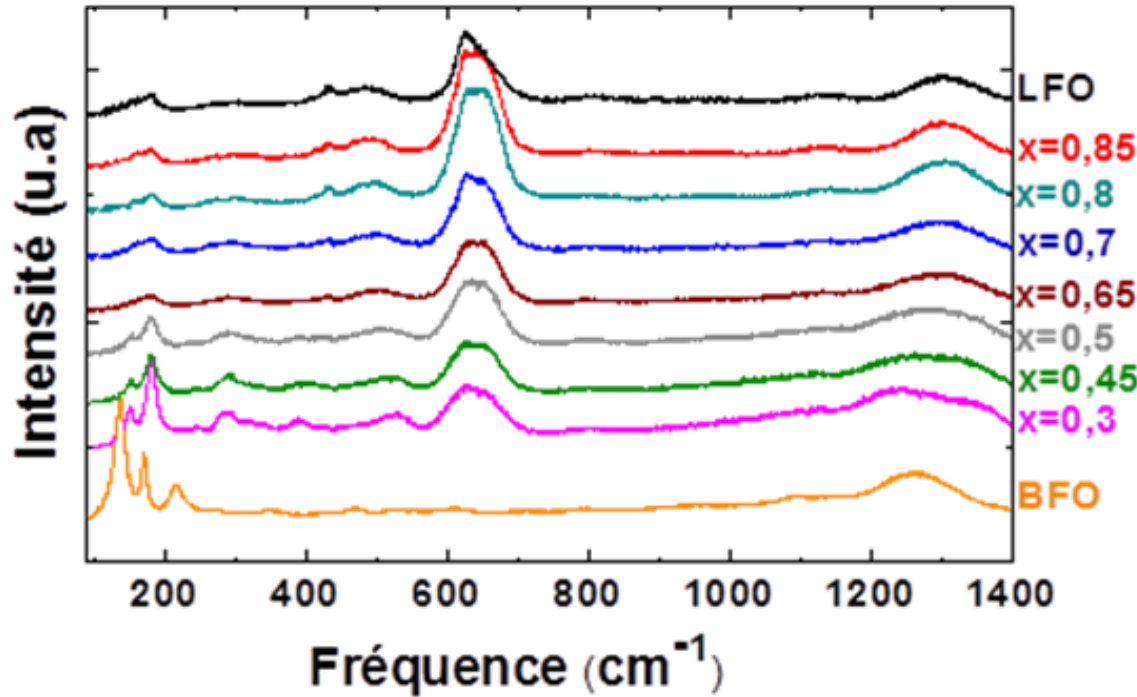
4 possible domains



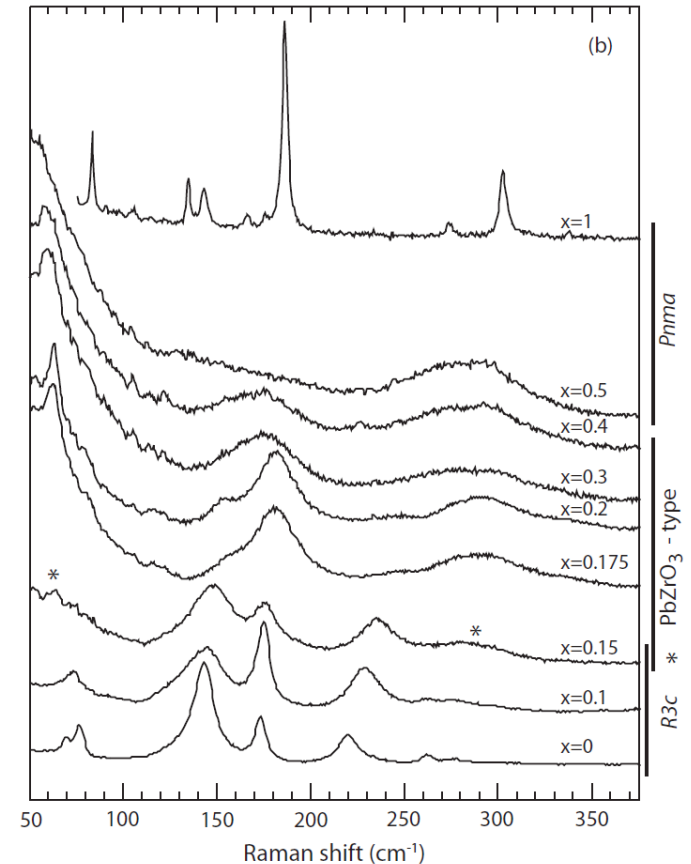
Raman spectroscopy

Parallel polarisation

$Z(XX)\bar{Z}$



Raman spectra of the solid solution: $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$



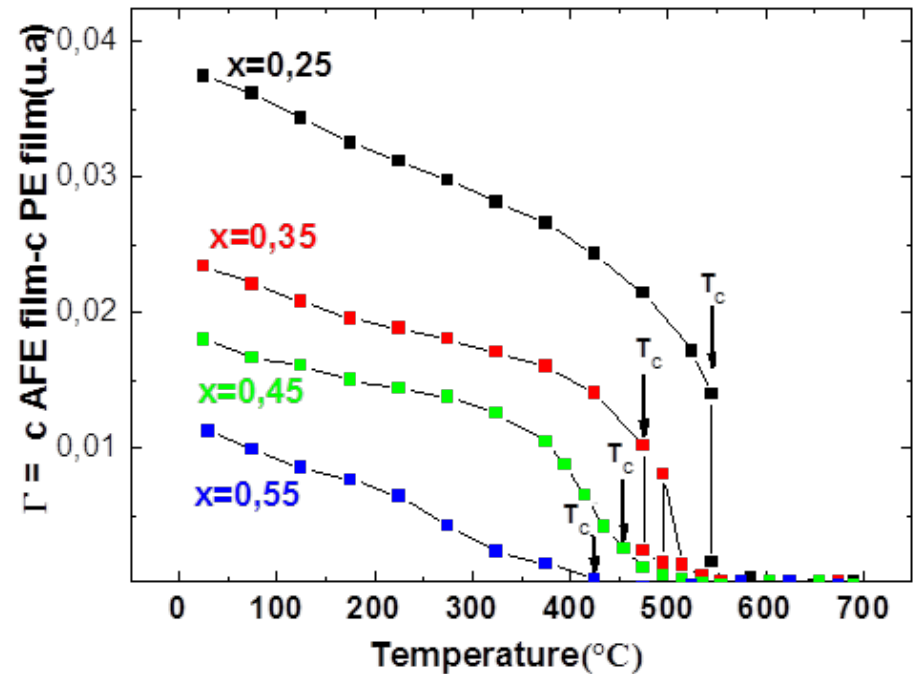
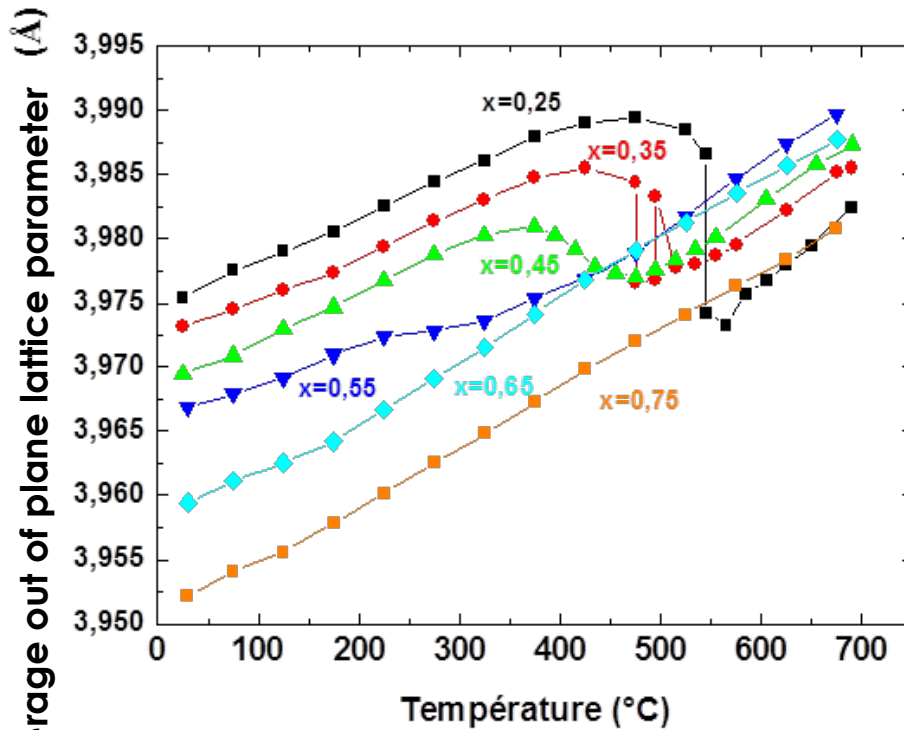
➤ Evolution from PbZrO_3 like to Pnma like structure

PHYSICAL REVIEW B **86**, 184422 (2012)

Johan Bielecki

Temperature dependent XRD investigation

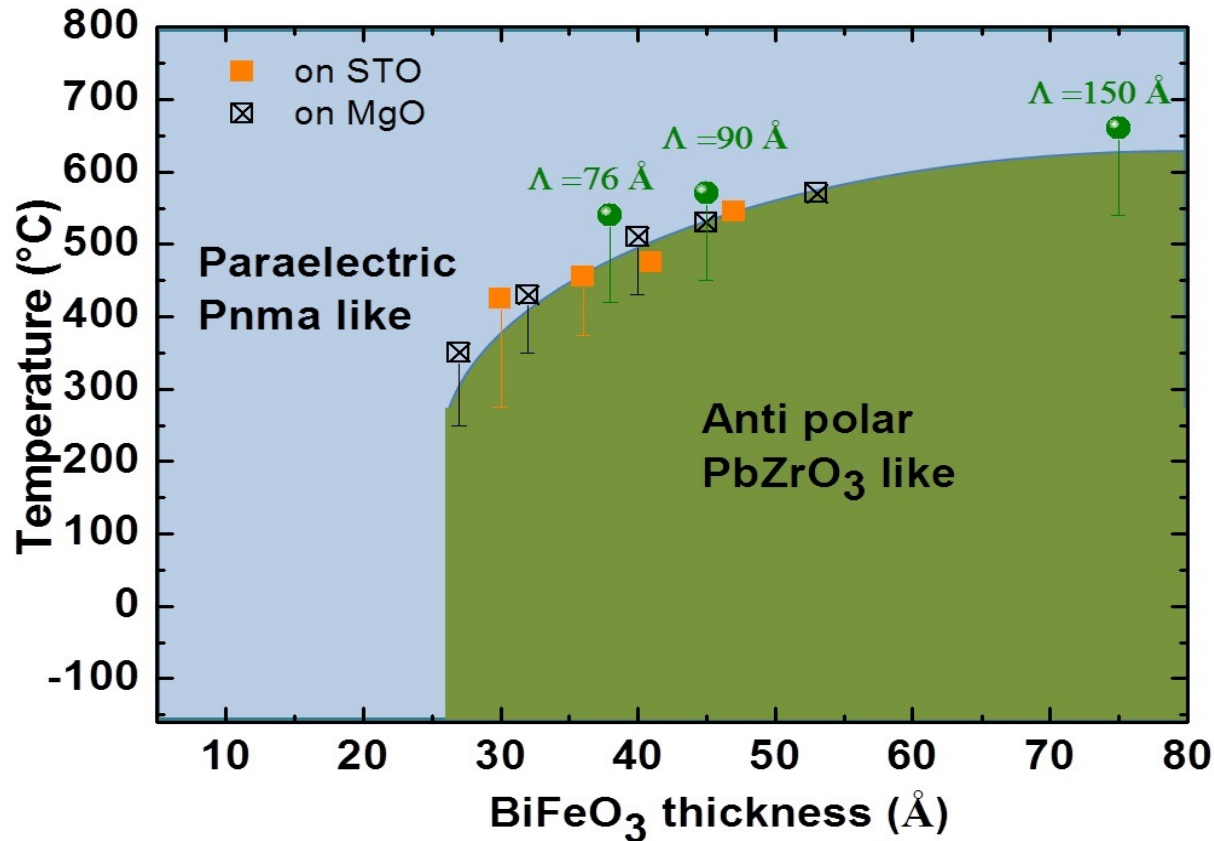
Average lattice parameter versus temperature (on LSCO/STO(001))



Similar results for superlattices on STO/MgO(001)

Structural transition from an antipolar phase to a non polar phase (Pnma)

Conclusion : Phase diagram



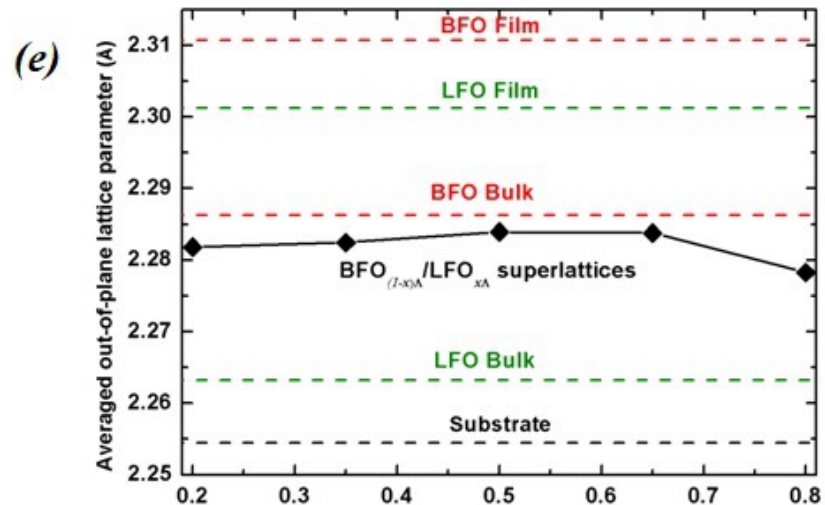
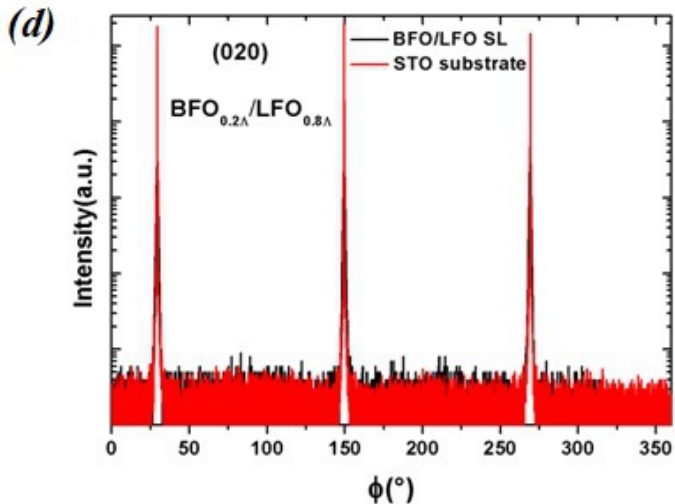
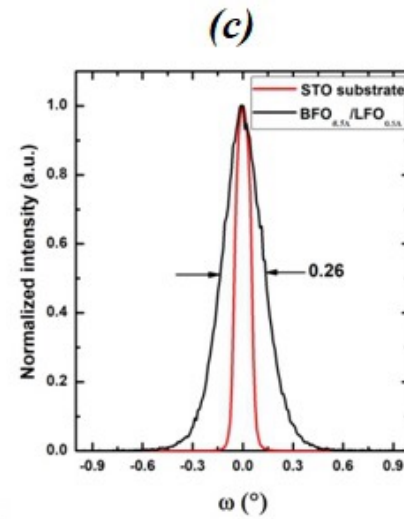
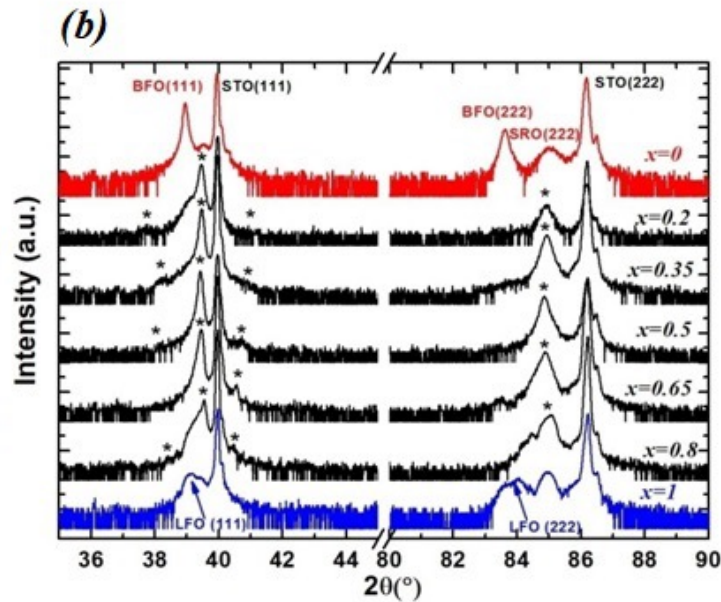
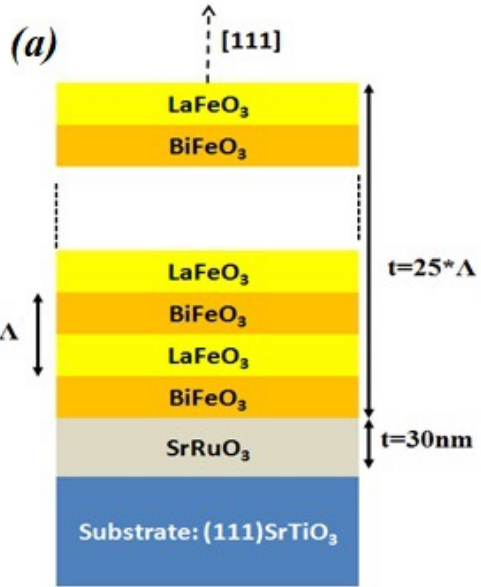
TEM
Raman
DRX

Emergence of an antipolar structure in BFO/LFO superlattices

Interlayer strain and mismatch of oxygen octahedral rotation/tilt system at interfaces ($a^-a^-a^-$ vs $a^-a^-c^0$)

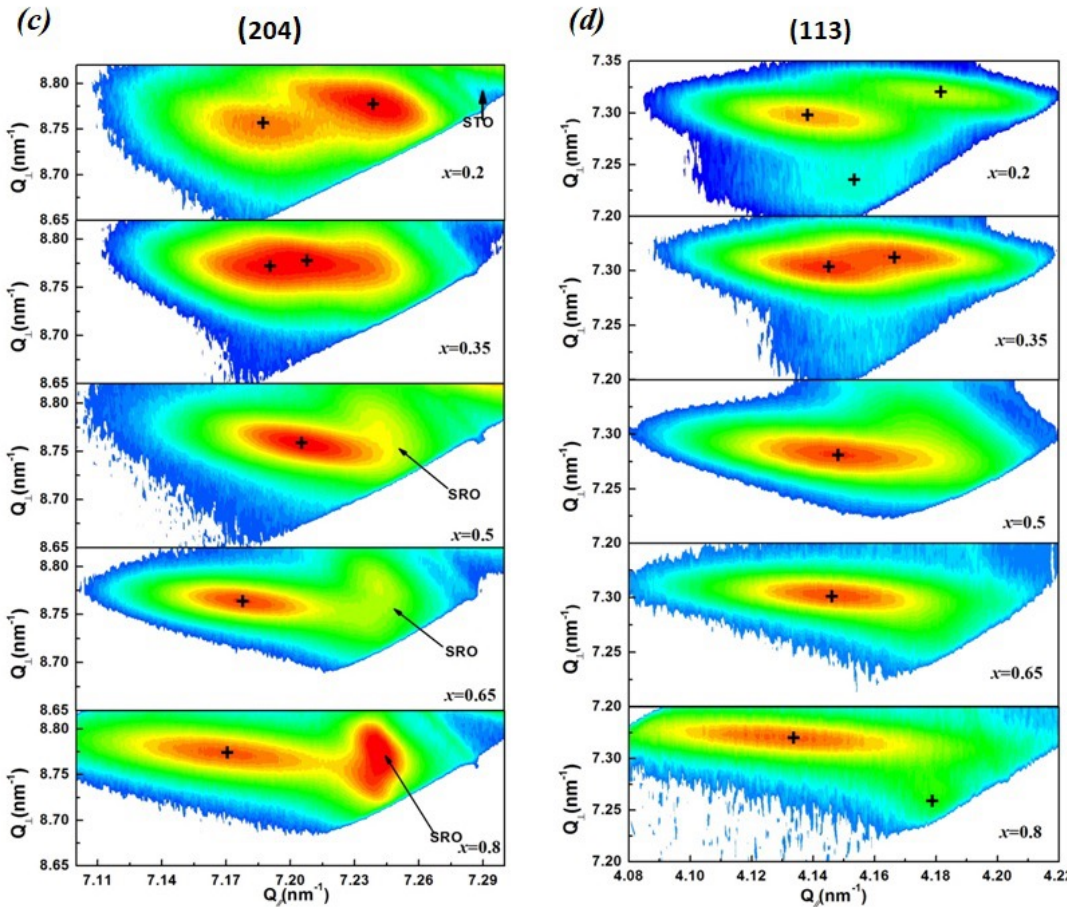
BFO_{(1-x)Λ}/LFO_{xΛ} superlattices grown on (111) STO buffered with SRO

Influence of the crystallographic orientation ((001) vs (111)) on the phase stability



BFO_{(1-x)Λ}/LFO_{xΛ} superlattices grown on (111) STO buffered with SRO

(204) and (113) reciprocal space mapping



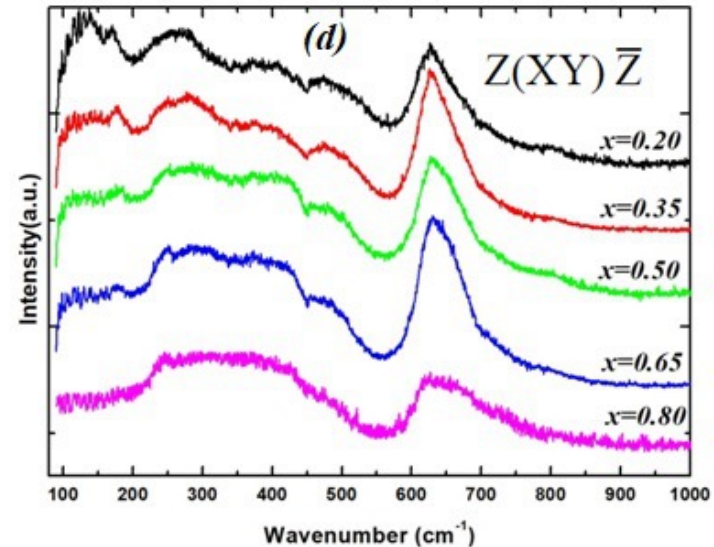
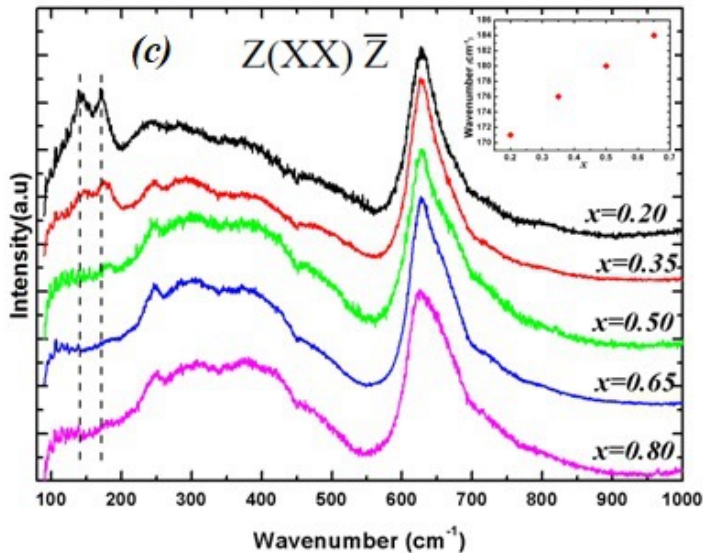
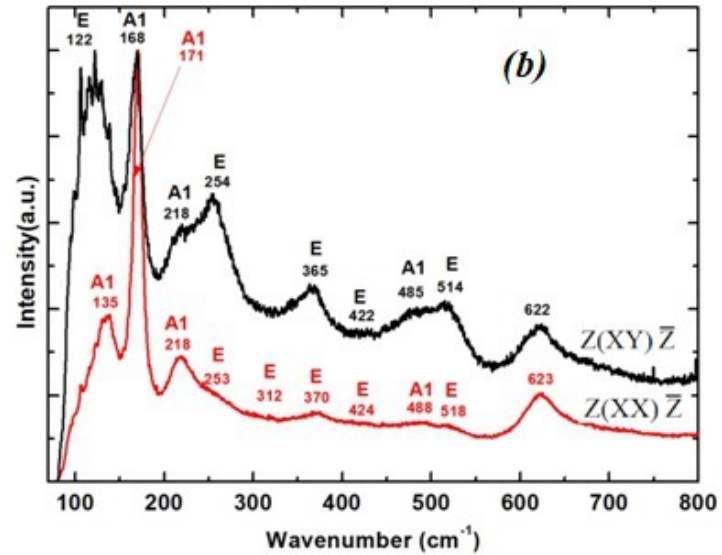
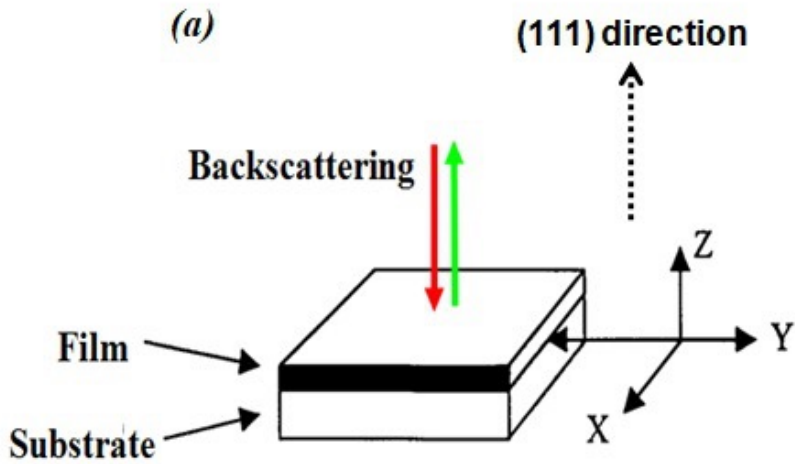
BFO rich superlattices:
rhombohedral or
monoclinic structure?



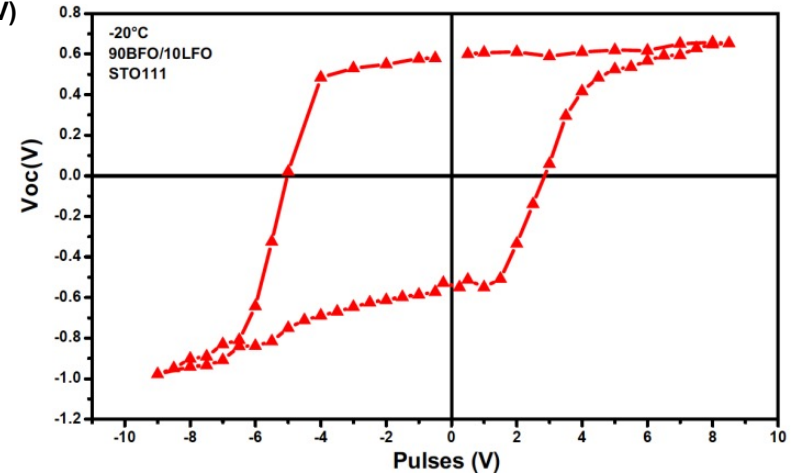
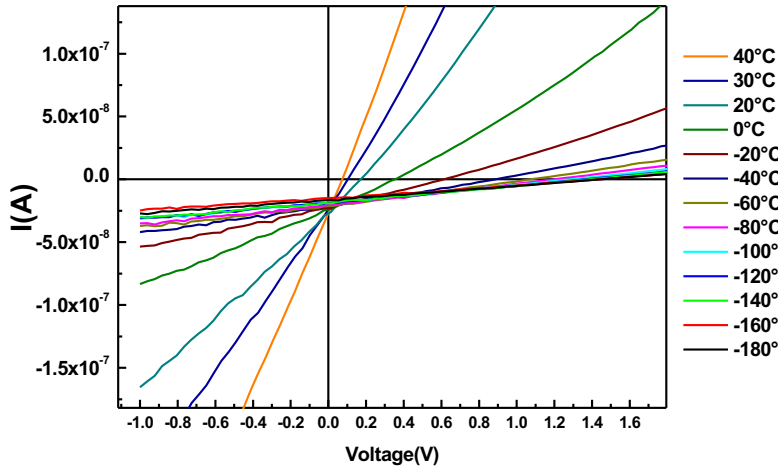
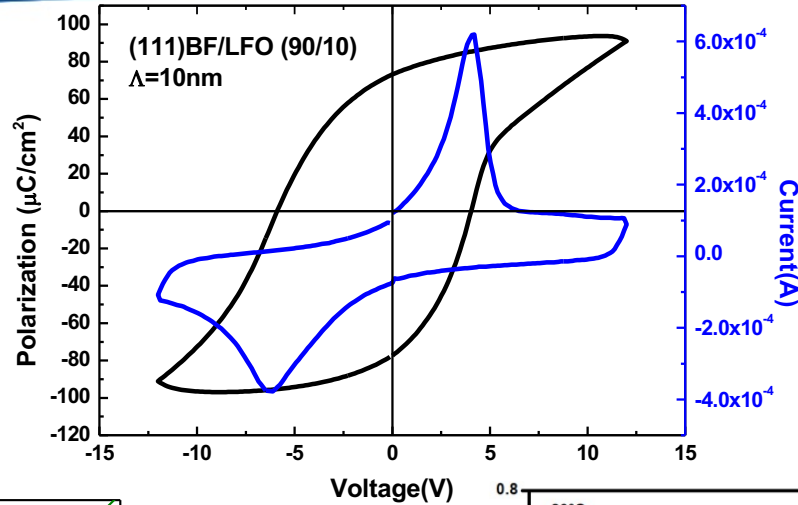
LFO rich superlattices:
orthorhombic structure

Need to check with TEM and explore the effect of temperature

BFO_{(1-x)Λ}/LFO_{xΛ} superlattices grown on (111) STO : Raman spectroscopy



Spectral signature of rhombohedral structure for BFO rich superlattices (phonons at frequencies very close to those observed in R3c thin films)



BFO rich superlattices are ferroelectric : P-E loops and switchable photovoltaic properties

Not observed in LFO rich superlattices and (001) oriented superlattices

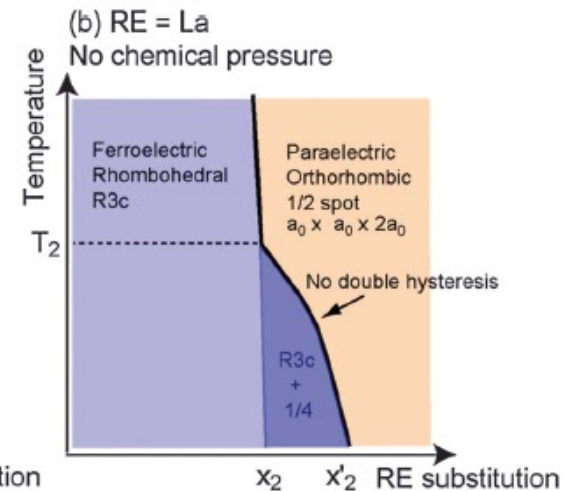
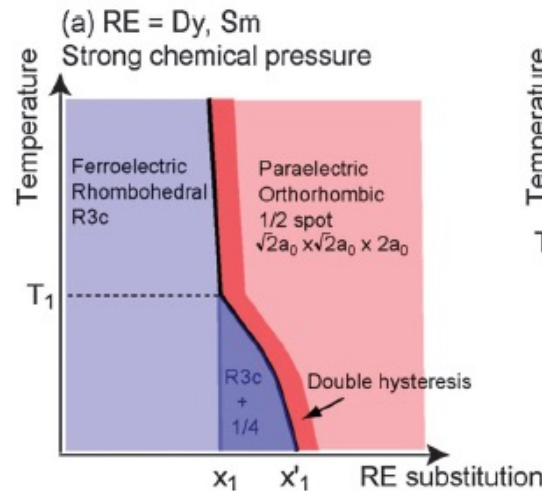
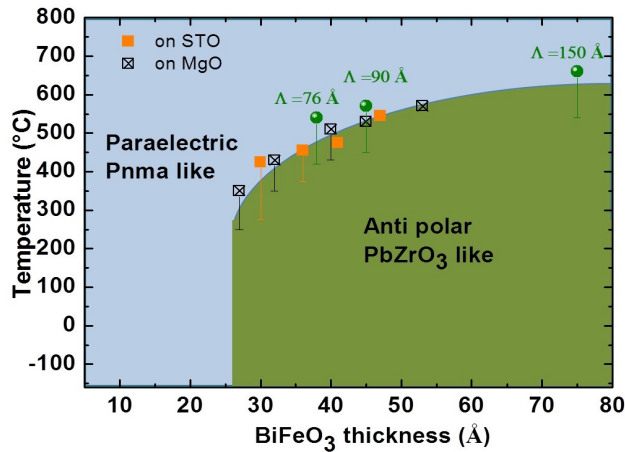
Morphotropic phase boundaries engineering: BFO/ReFeO₃ (Re:La, Nd, Sm, Gd, Dy) (antiferroelectricity, piezoelectricity)

Bi³⁺(1,36 Å) > Sm³⁺(1,28 Å) > Gd³⁺(1,27Å) > Dy³⁺(1,24 Å) > Nd³⁺(1,15 Å)

La³⁺(1,36 Å)

Increase of interlayer strain effect with ReFeO₃ :

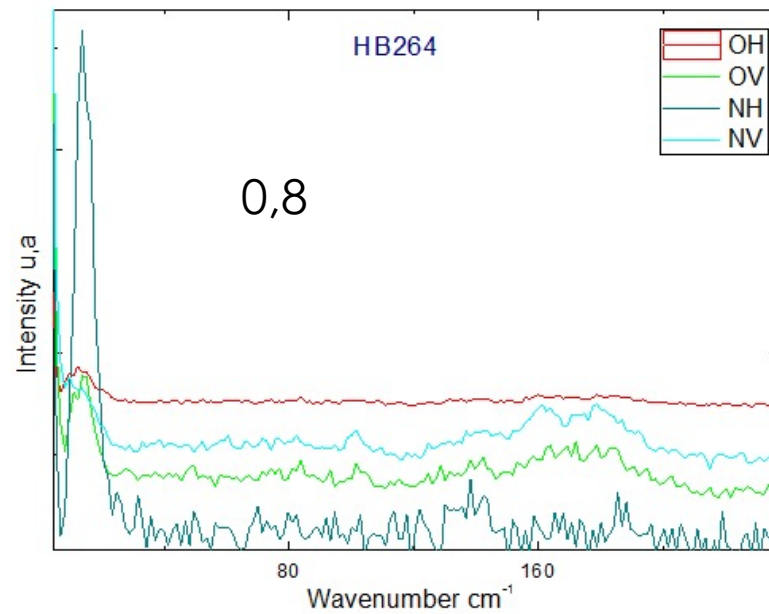
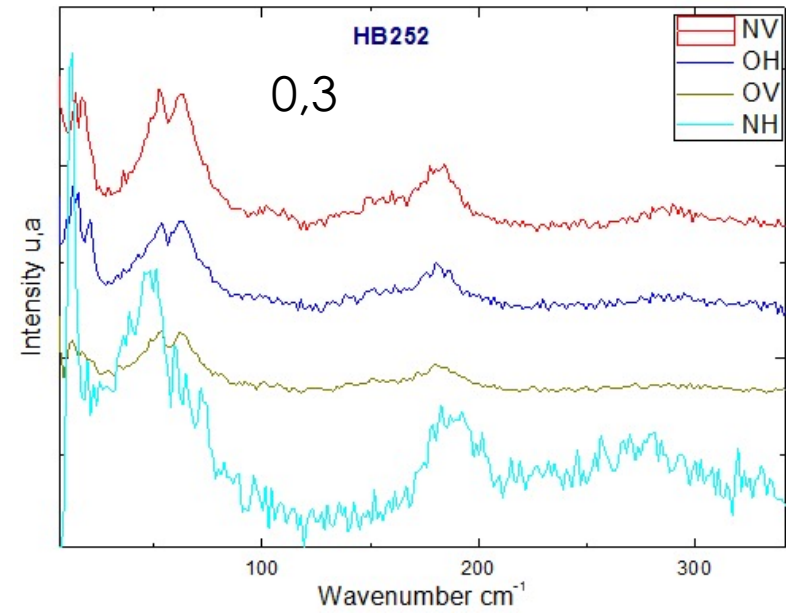
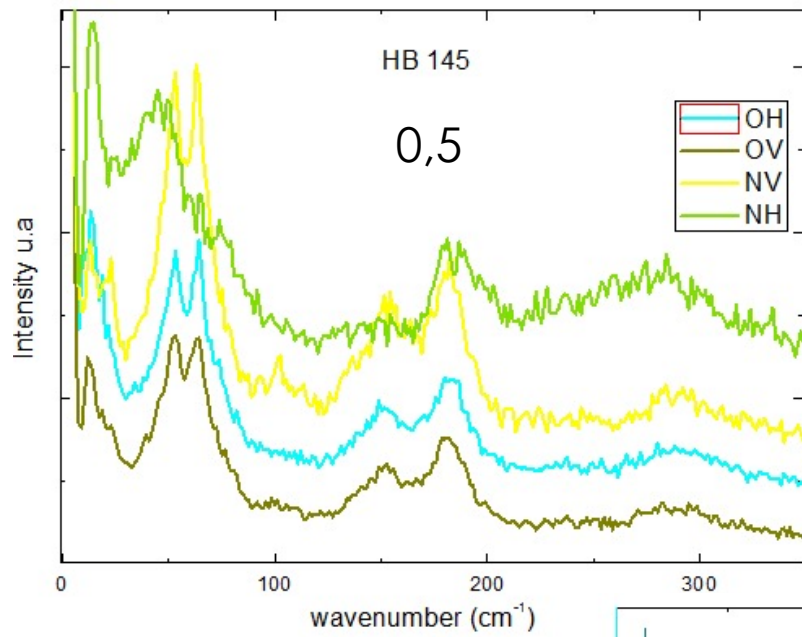
Dichotomy strain effects vs tilt/ rotation mismatch at heterointerfaces ?



Complete the (111) phase diagram and explore other orientations such as (110)



Thank you for your attention



Growth by Pulsed Laser deposition

Pulsed laser deposition

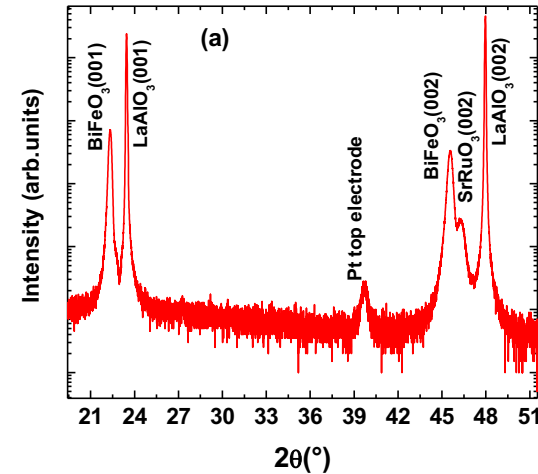


$\text{BiFe}_{0.95}\text{Mn}_{0.05}\text{O}_3$ (280nm) / SrRuO_3 (20nm) / LaAlO_3 (001)

Epitaxial and single phase thin film

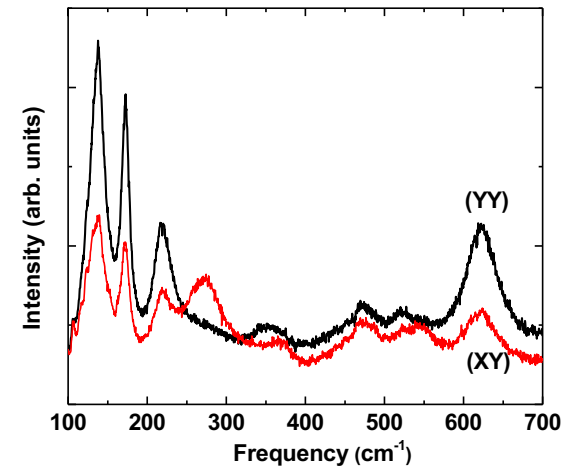
Rhombohedral R3c structure

X-ray diffraction



BFO: $a_{\perp} = 3.98 \text{ \AA}$
SRO $a_{\perp} = 3.93 \text{ \AA}$
LAO: $a_{\perp} = 3.79 \text{ \AA}$

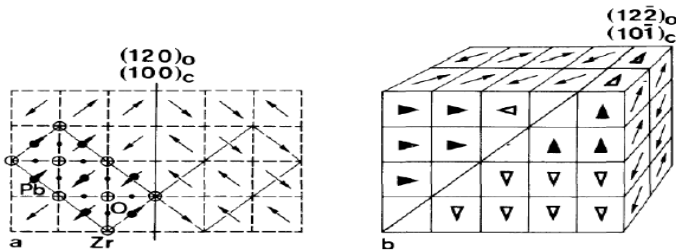
Raman spectroscopy



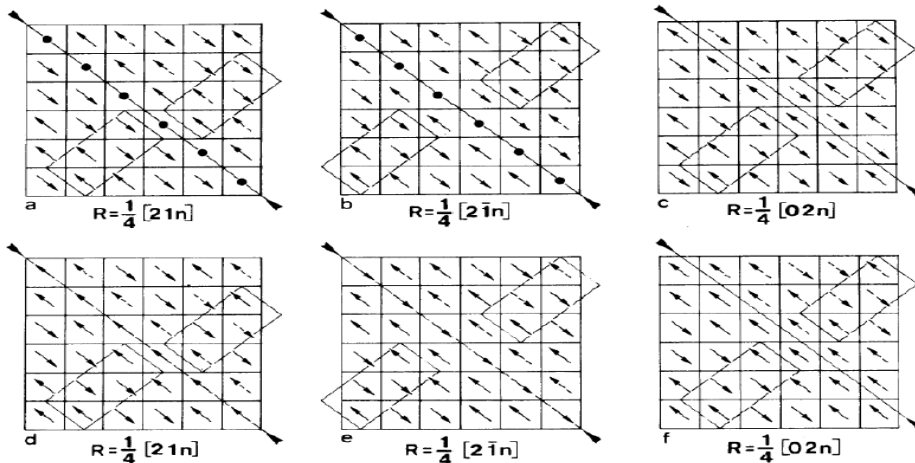
Structure anti polaire et parois de domaines

Structure en domaine à 90° (à gauche)
et à 60° (à droite) et 180° (en dessous)

$x=0,45$ sur MgO



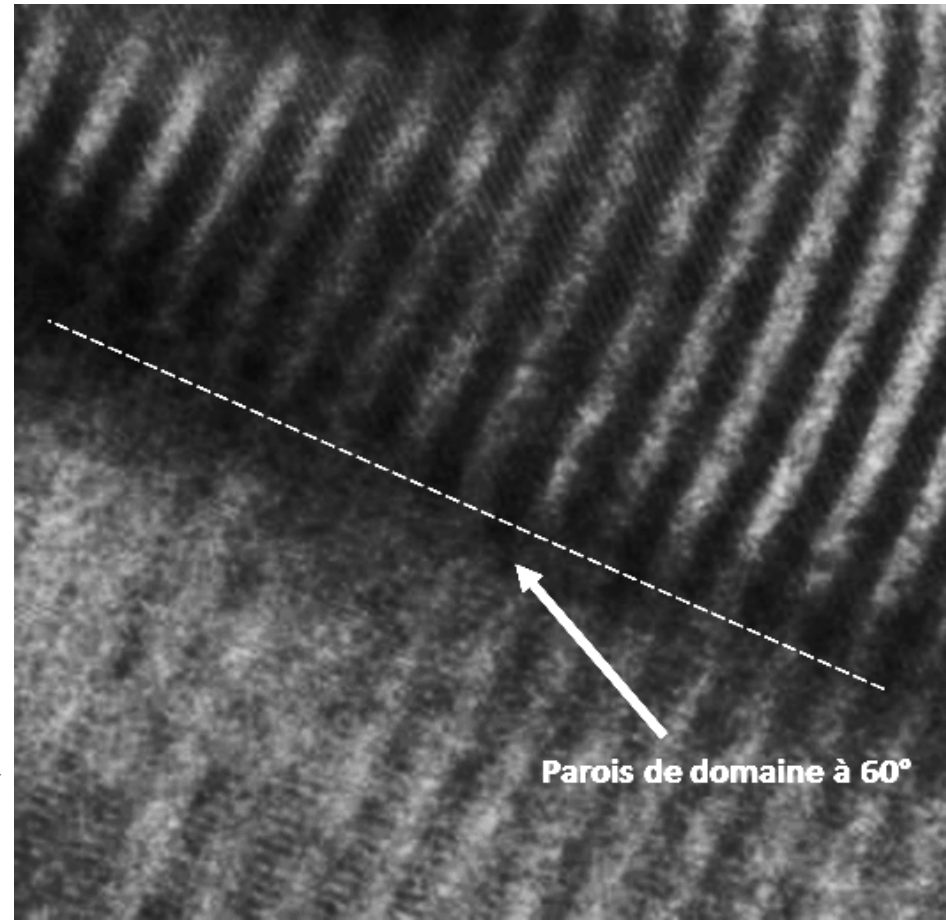
(a)



(b)

Michiyoshi TANAKA

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VOL. 21, No. 2, FEBRUARY, 1982 pp. 291-298



BFO
LFO

Etude en température par DRX

Cartographies dans le réseau réciproque en fonction de la température pour la proportion $x=0,35$ (sur LSCO/STO(001))

