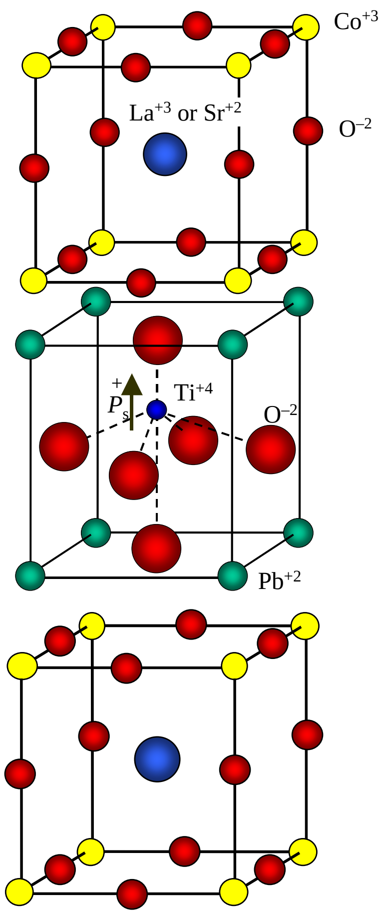
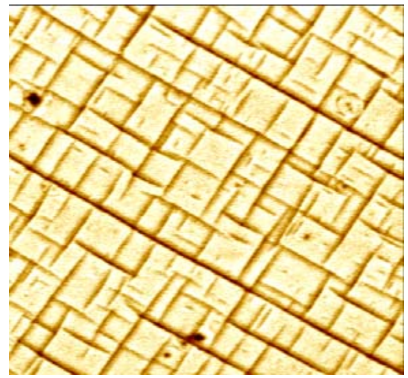
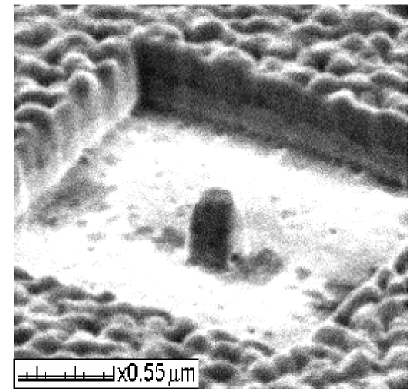
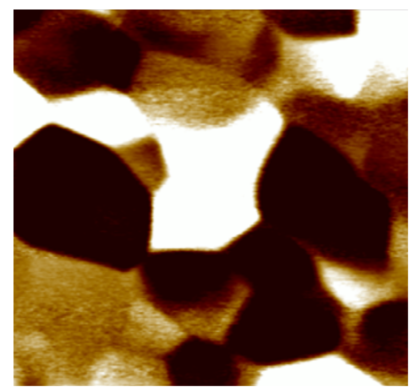
Science and Technology of Complex Oxides









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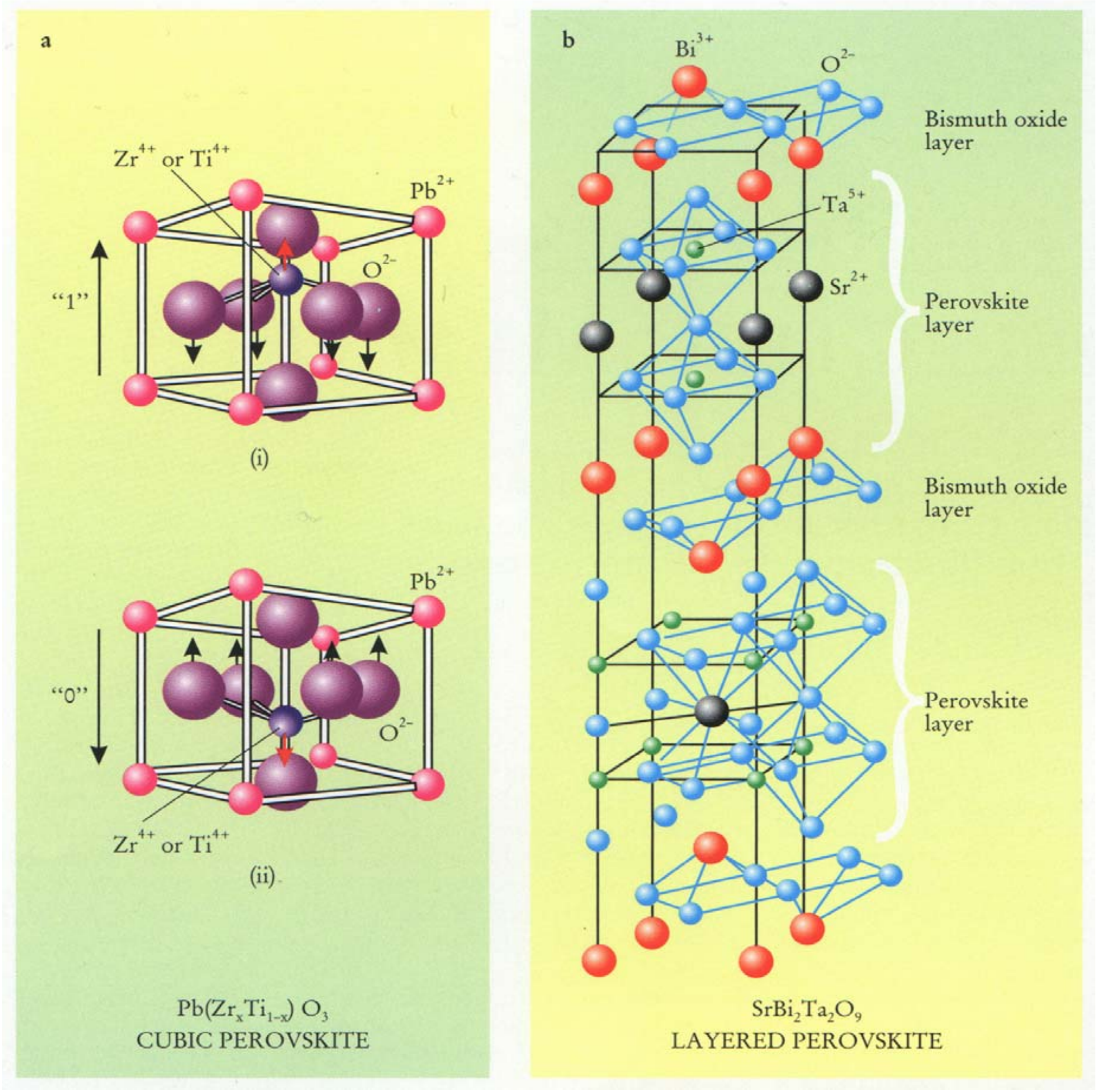
Outline

- Introduction and Motivation
- The World Of Crystalline Oxides on Semiconductors
- Specific Examples
  - Ferroelectric Oxides
  - CMR Oxides ; DMS Oxides
  - Self-assembled magnetic nanostructures
  - Multiferroic Oxides and Nanostructures
- Summary : Challenges and Opportunities

Complex Oxides : Crystal Structure

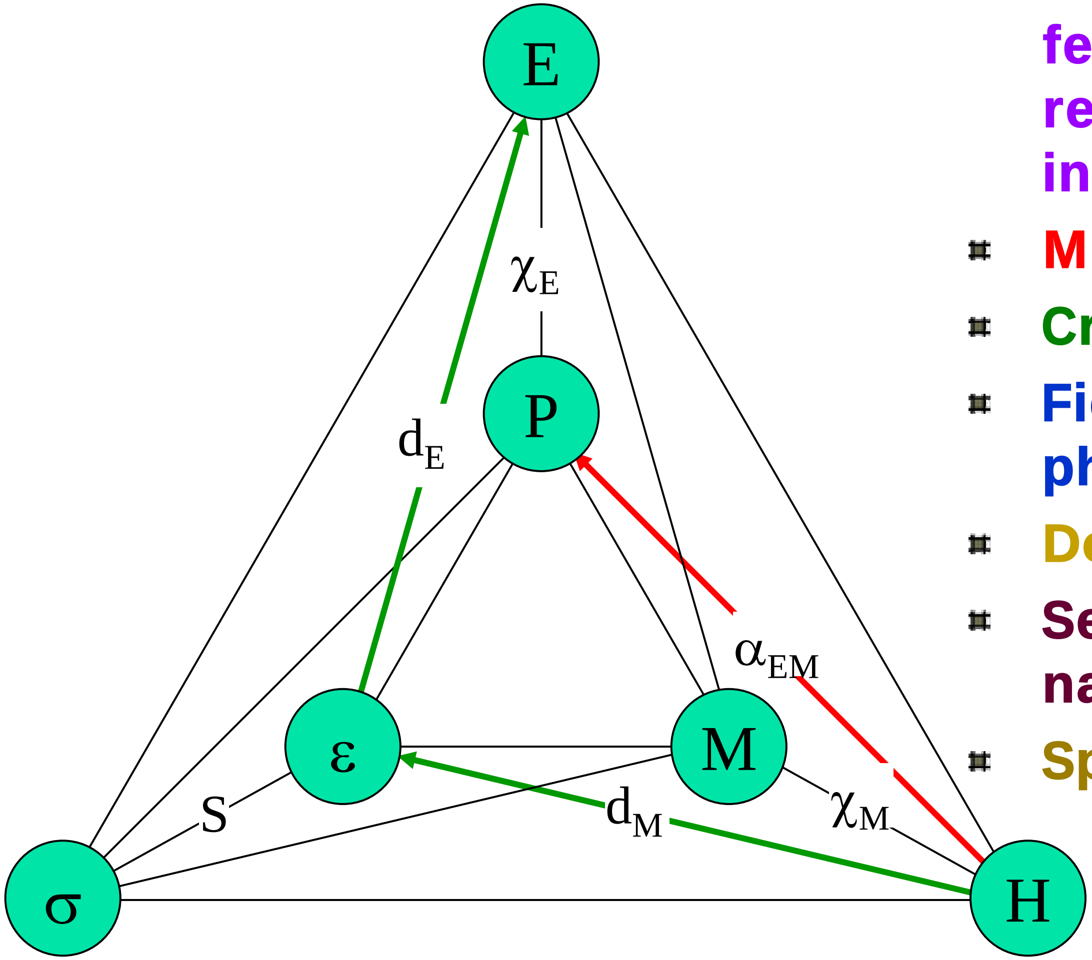


Functional Oxides

- High ε_r Insulators ($SrTiO_3$) $\rho \approx 1\times10^{13}$ Ω·cm
  $\varepsilon_r = 20{,}000$ (4 K)
- Low ε_r Insulators ($LaAlO_3$) $\varepsilon_r = 25$ (300 K)
- Conductors (Sr_2RuO_4) $\rho_{a,b} \approx 1\times10^{-5}$ Ω·cm (77 K)
- Superconductors ($YBa_2Cu_3O_{7-\delta}$) $\rho \approx 0$
- Ferroelectrics ($PbTiO_3$) $P_r = 80\ \mu C/cm^2$
- Semiconductors
  (doped $SrTiO_3$) $\mu = 22{,}000\ cm^2/V{\cdot}s$ (2 K)
- Ferrimagnets ($PrFeO_3$) $M_s = 0.04\ \mu_B$
- Ferromagnets ($SrRuO_3$) $M_s = 1.4\ \mu_B$
- Antiferromagnets ($PrNiO_3$)
- Colossal Magnetoresistance ($(La,Sr)MnO_3$)
  $\Delta R/R_H > 10^4$ (6 T)
- High Thermal Conductivity ($LaCoO_3$)
- Catalysts ($La(Ti,Cu)O_3$)

All Perovskite-Related with *a,b* ≈ 3.8-3.9 Å

Areas of Research

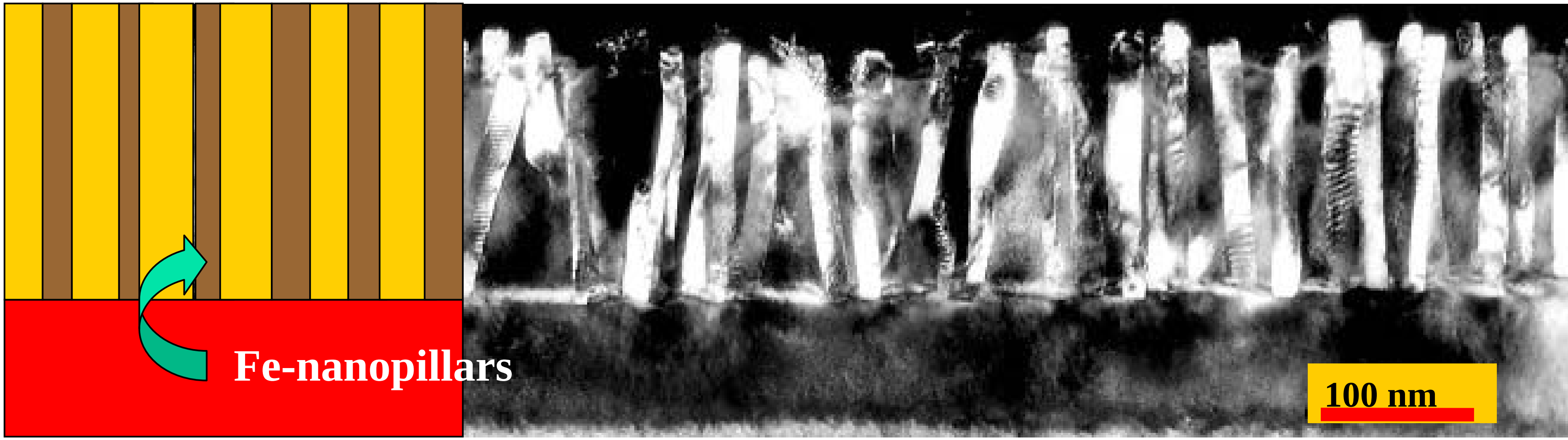


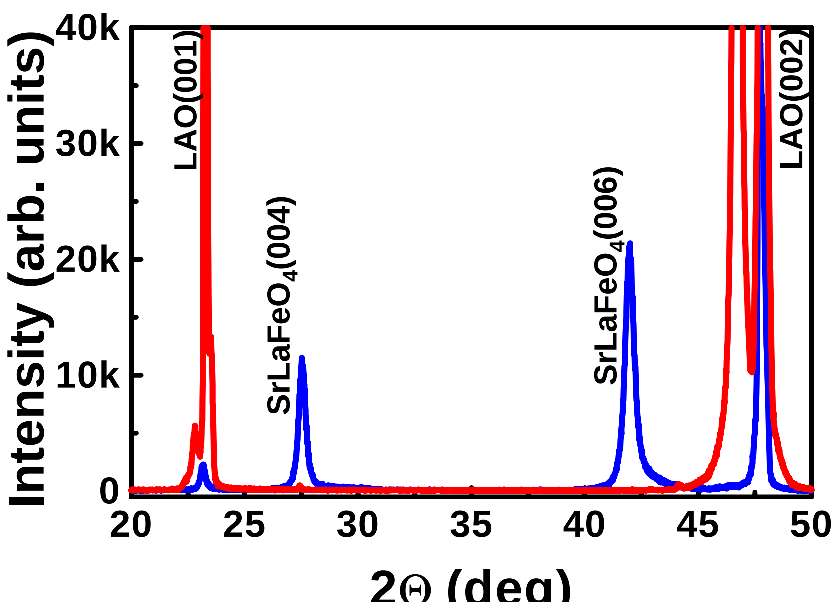
- FERAM's ; Domain dynamics in ferroelectrics: switching and relaxation ; finite size effects ; integration on Si ; reliability
- Multiferroic Oxides :$BiFeO_3$ on Si
- Crystalline Oxides on Si
- Field effects and electronic phase separation in CMR/Si
- Doped Insulators : Oxide DMS
- Self-assembled magnetic oxide nanostructures
- Spin-polarized Intermetallics

Summary of Research Facilities

- Thin film processing : PLD, CVD, Sputtering, solgel
- Laser MBE of complex oxides ; Crystalline Oxides on Si
- Device processing in a dedicated clean room
- Scanning force microscopy : Piezoforce microscopy of FERAMS ; nanoscale domain dynamics using AFM ; MFM ; TUNA ;
- Switching dynamics using AFM ; high speed measurements
- FE, transport, interface, pyroelectric studies
- Insitu studies using synchrotron : Advanced Light Source
- TEM studies : NCEM

Nanostructures through Spontaneous Phase Decomposition : Formation of Fe nanowires



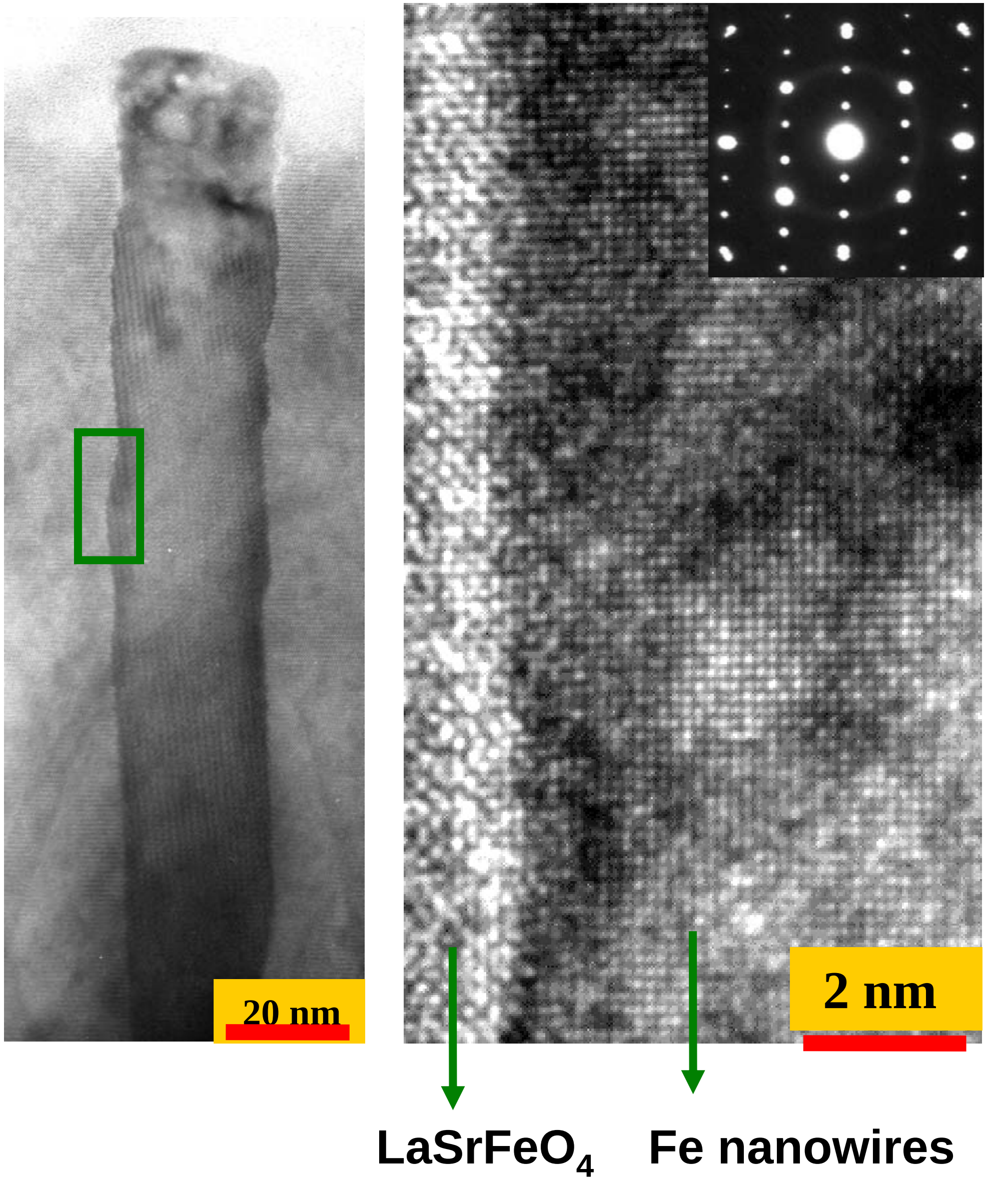


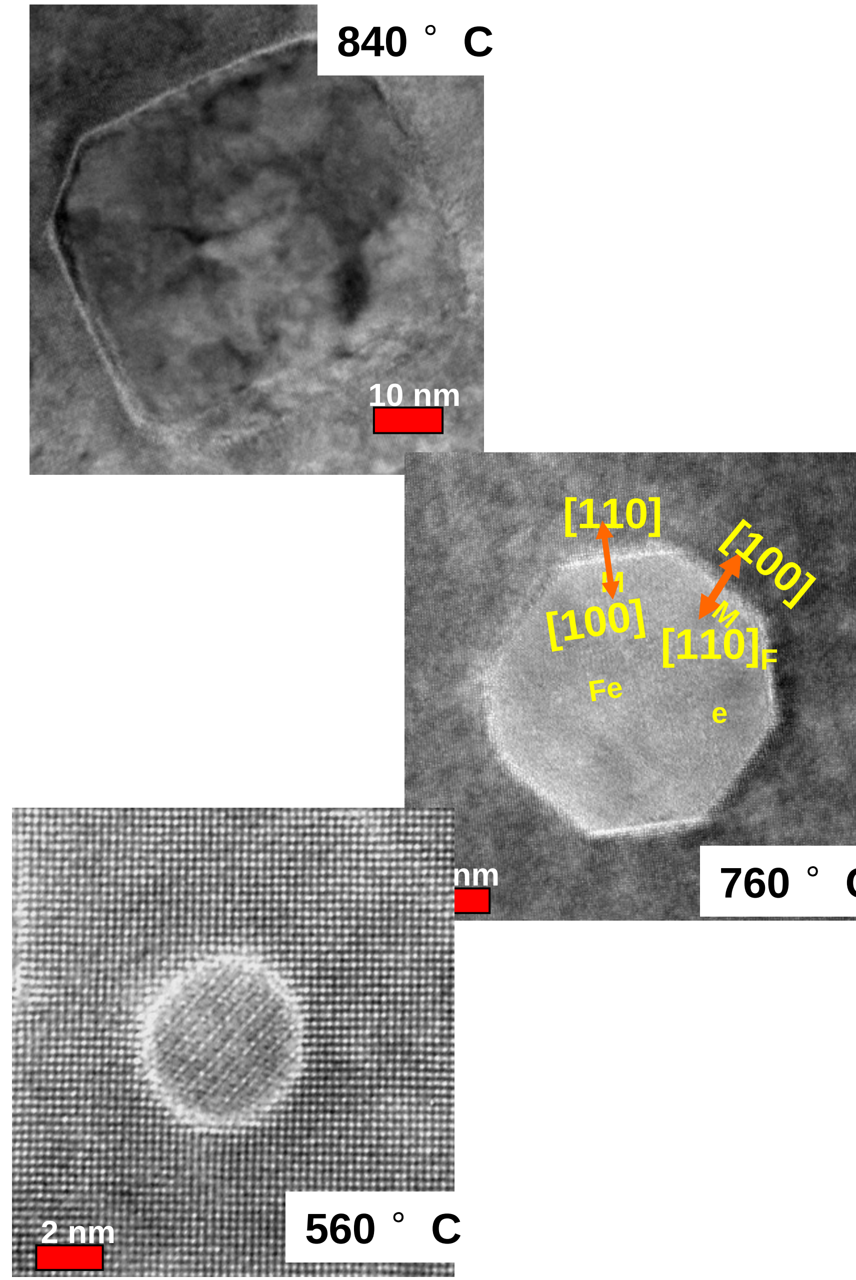
$$LaSrFe_2O_6 \longrightarrow LaSrFeO_4 + FeO_2 - O_x$$

$$\xrightarrow{\text{Vacuum}} LaSrFeO_4 + Fe \longrightarrow \frac{\text{Pillars}}{\text{Matrix}} \cong 0.1226$$

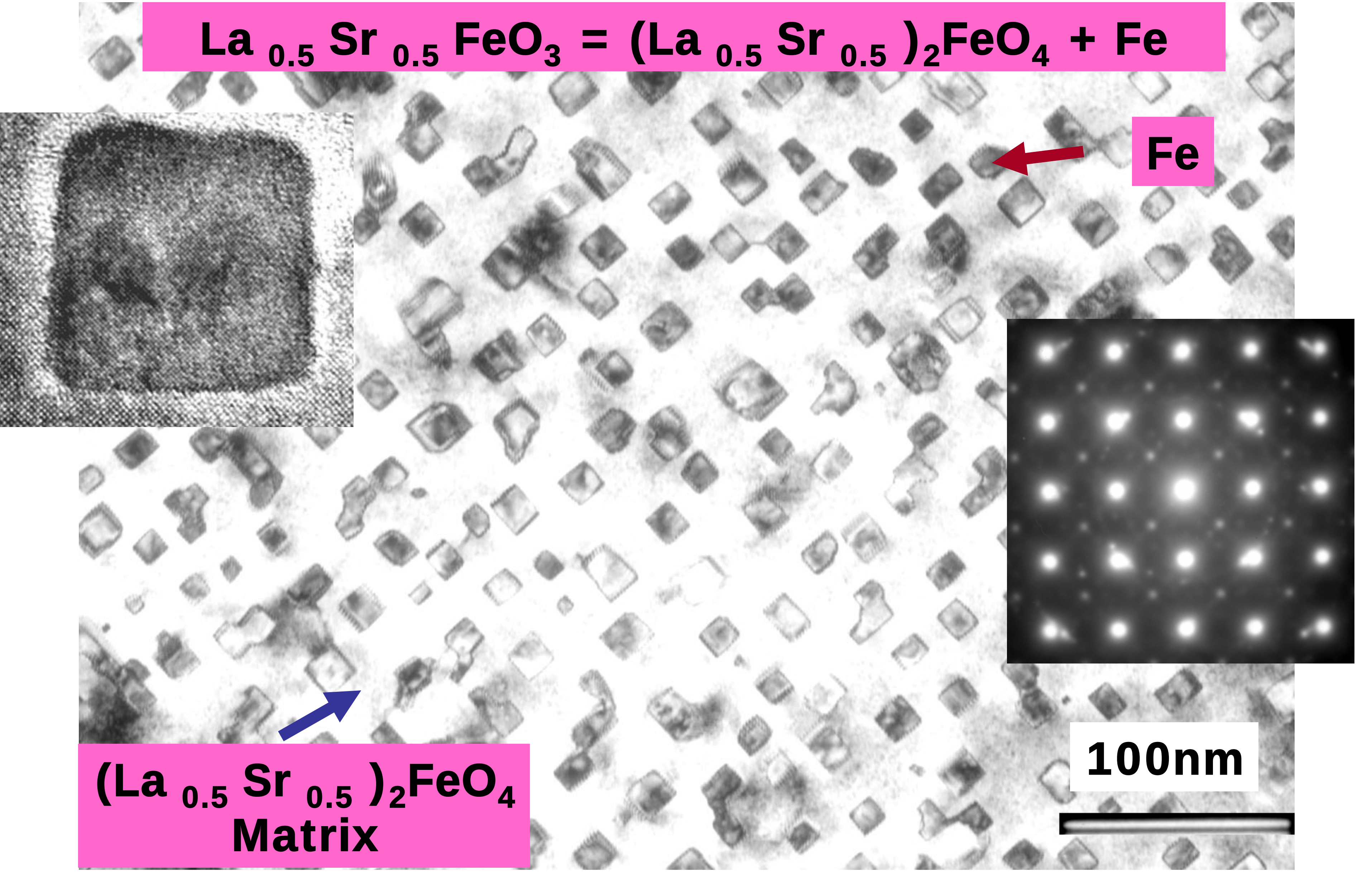
Experimental data: ≅ 13%

Epitaxial Fe nanowires

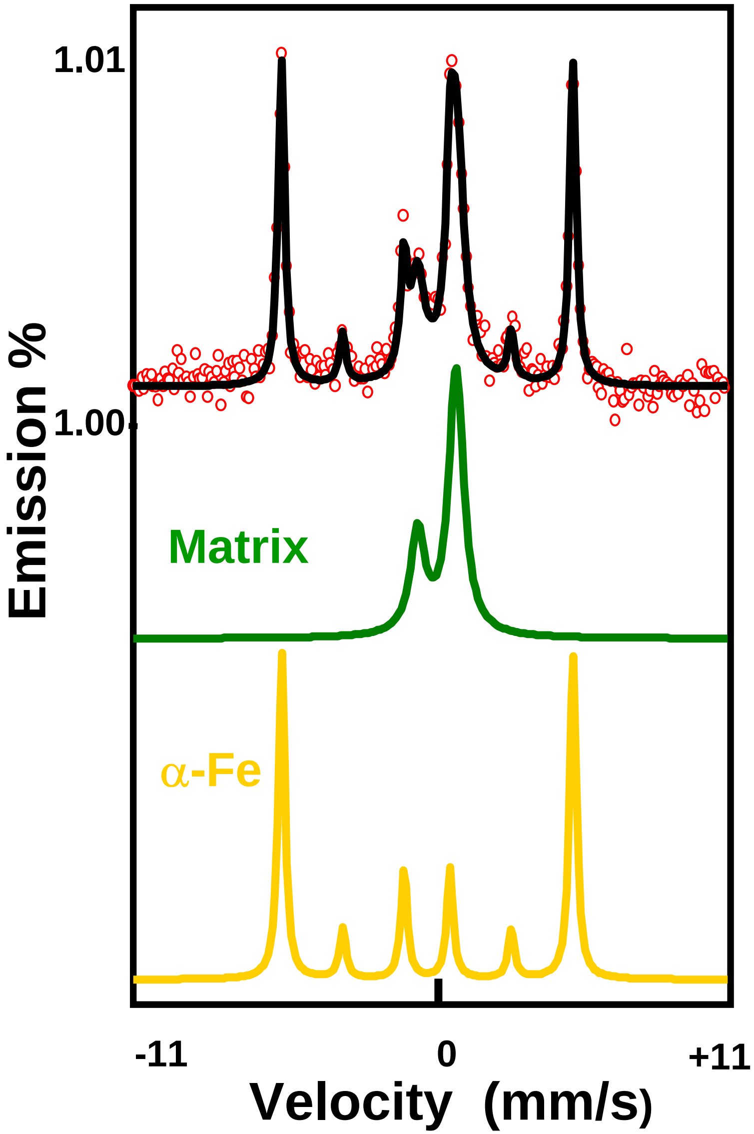


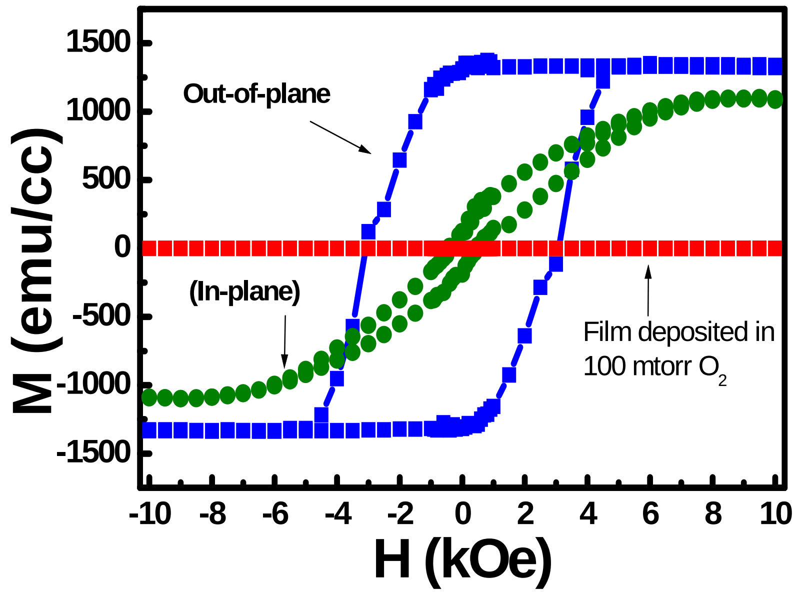


Epitaxial Fe nanowires : Long range order ?



Magnetic Properties of Fe-nanopillars





Vacuum deposited films : Strong ferromagnetism

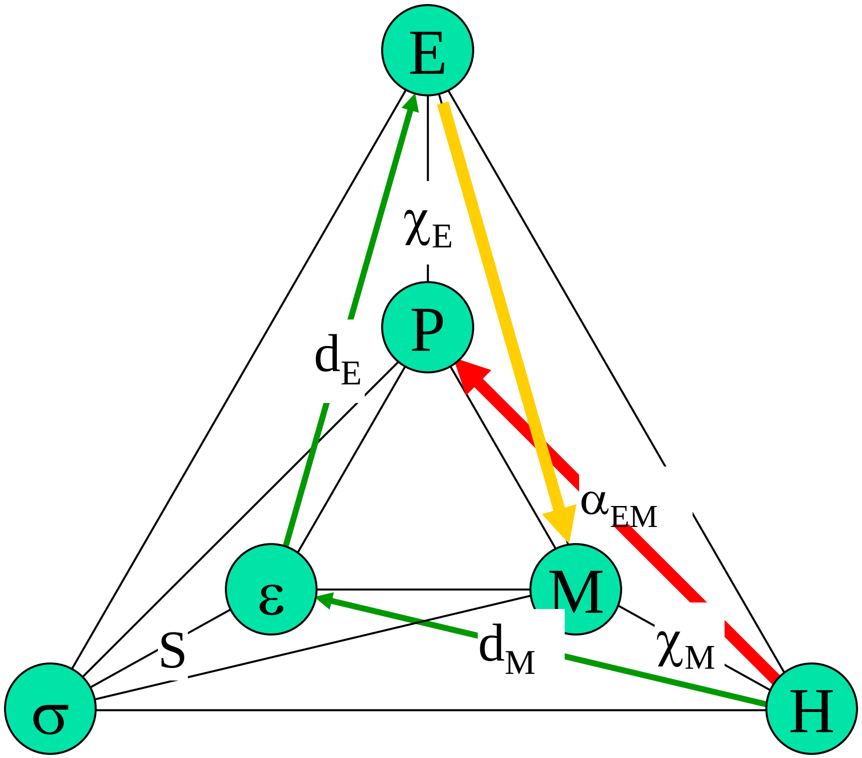
Films deposited in Oxygen : Antiferromagnetic

Mossbauer : shows coexistence of Ferromagnetic Fe and paramagnetic matrix

Control of order among nanowires

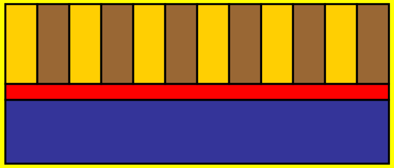
Magnetotransport is critical

Multifunctional Complex Oxide Heterostructures



Single Phase

Heterostructures/ Superlattices



Vertical heterostructures

Magnetism
Magnetostriction
Magnetooptics
Magnetotransport

Ferroelectricity
Piezoelectricity
Electrooptics

Coupling of order parameters
Large cross-susceptibilities

Energy Conversion / Transduction
Field tunable Photonic Bandgap Structures
Information Storage
Radiation Sensing
Energy Storage Systems

Structure of Bulk $BiFeO_3$

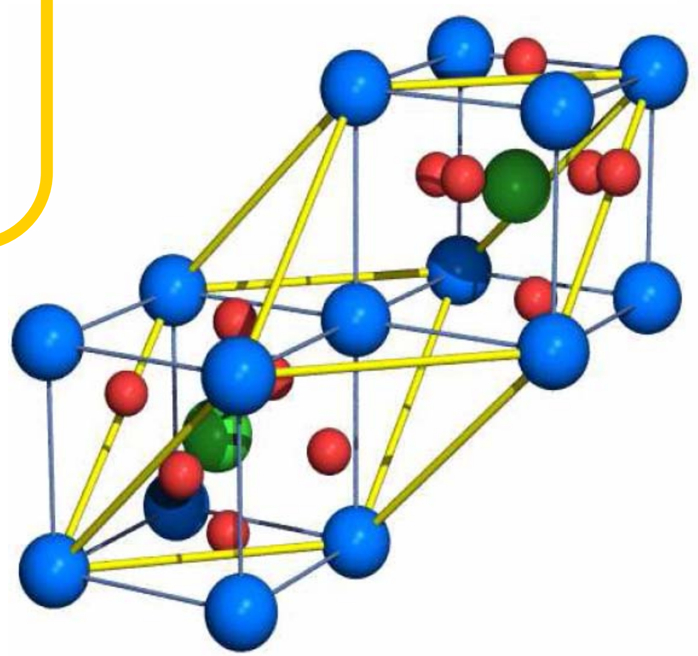
a=3.965Å, α =89.46°

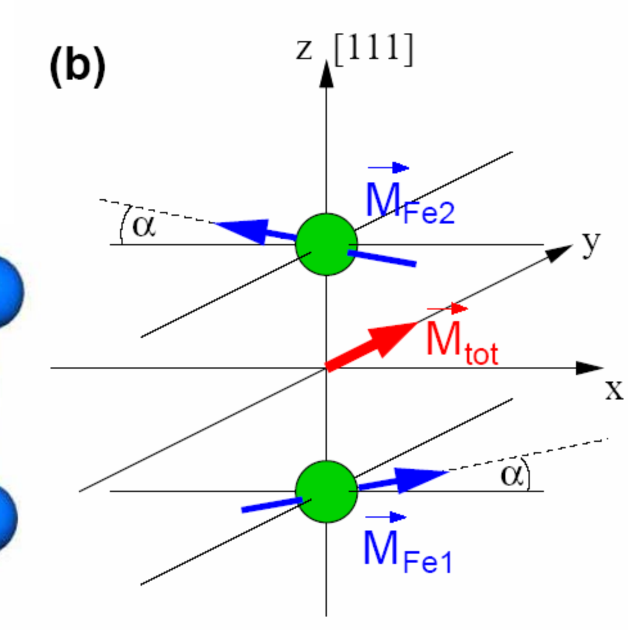
T_N=643 ~ 673K

T_C=1118 ~1123K

Ps=3.5μC/cm²

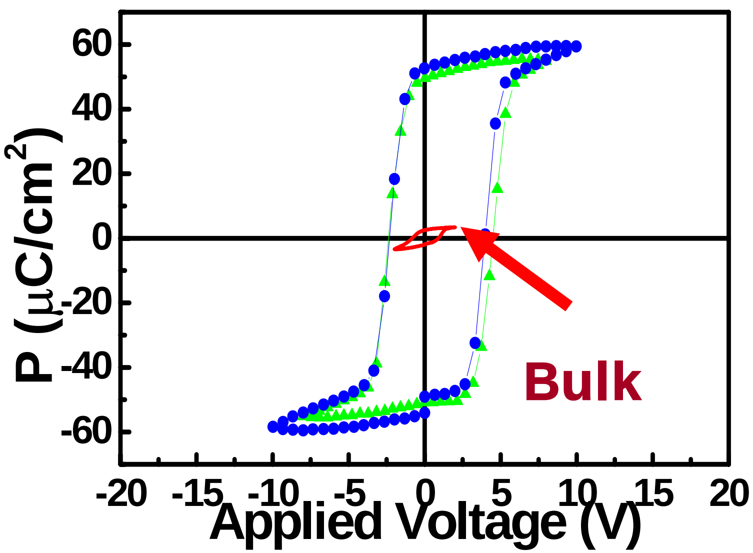
(100)??



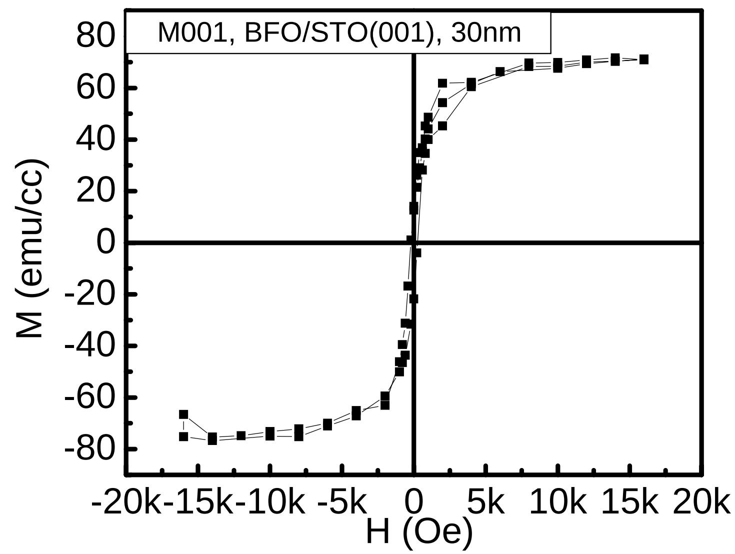


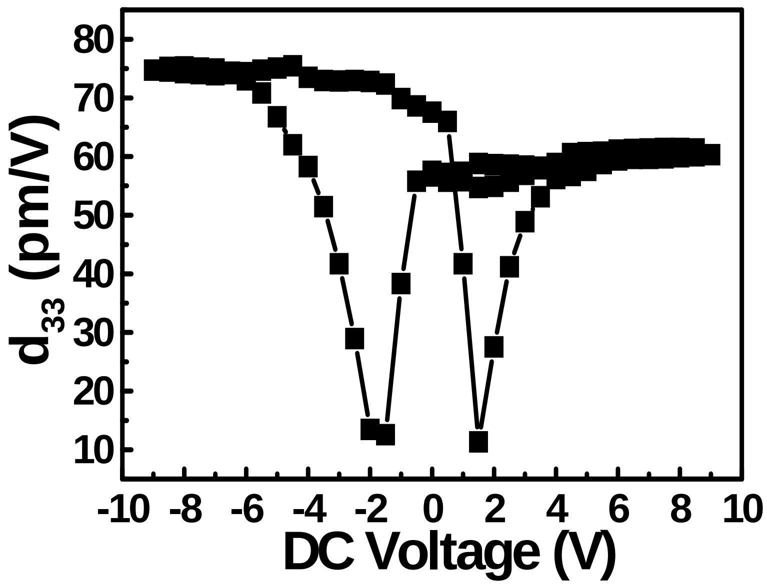
- **Rhombohedral, R3c**
- **Rotation of octahedra about [111] ; displacement of Fe**
- **Canted, spiral G-type, AFM order : no effective moment in low field**
- **Small magnetization in bulk : 8-10 emu/cc in a field of ~180T**
- **Ferroelectricity in bulk : unusually low P ??**

Magnetism and Ferroelectricity
Epitaxial / $BiFeO_3$ / $SrRuO_3$ on STO and STO/Si



Measured at 15kHz





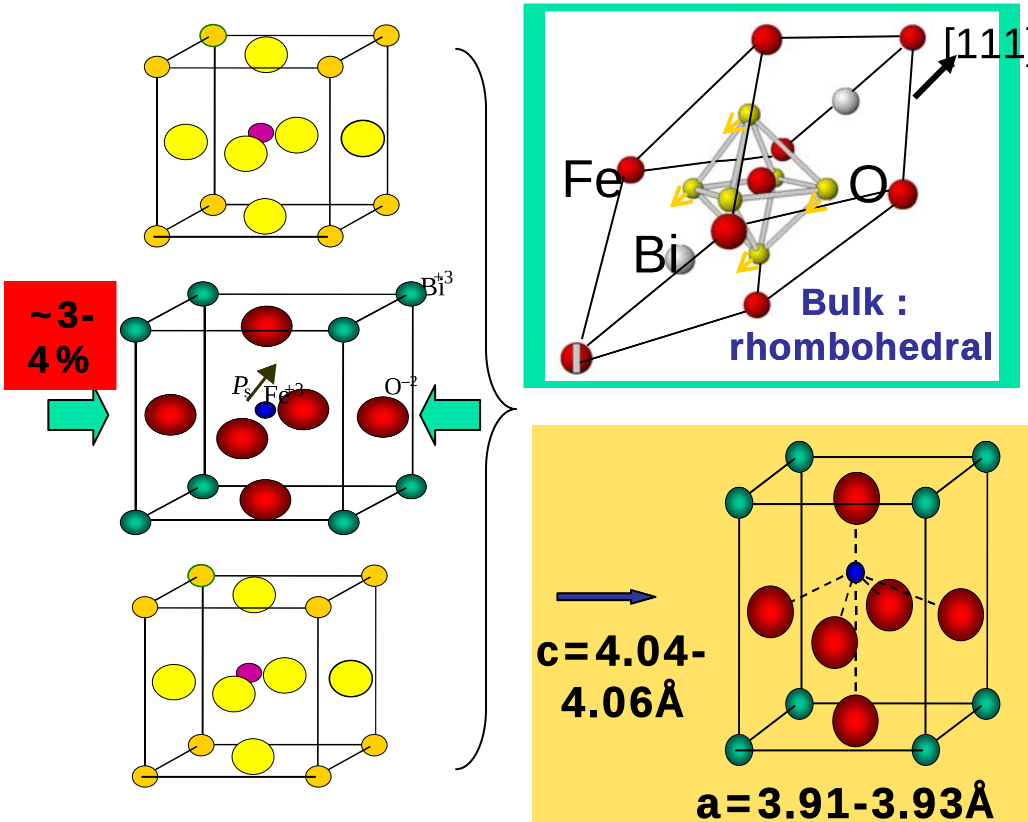
Bulk : G-type antiferromagnet ; low P(maybe due to processing ??)

Thin Films : Large P ; measurable magnetic moment

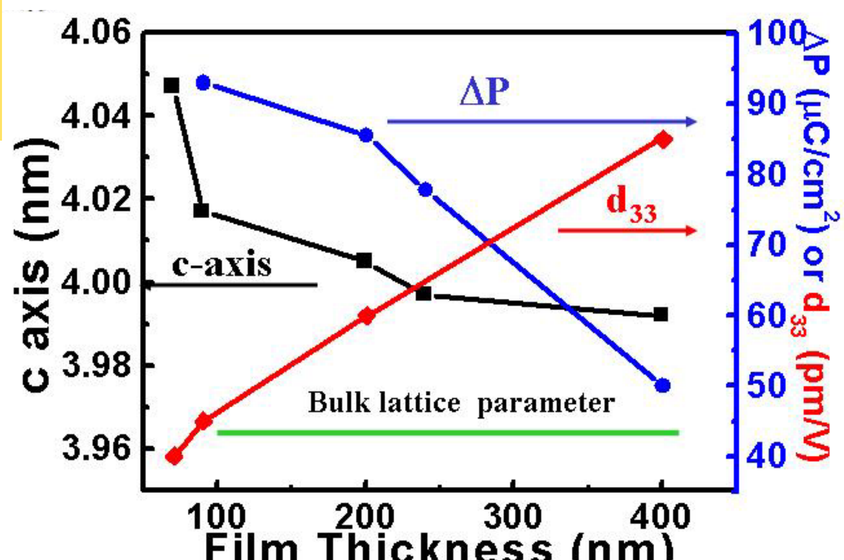
Origin of Magnetism ?

Coupling of order parameters (PFM/MFM ; Optics, microwave)

Heteroepitaxial $BiFeO_3$ on (100) STO



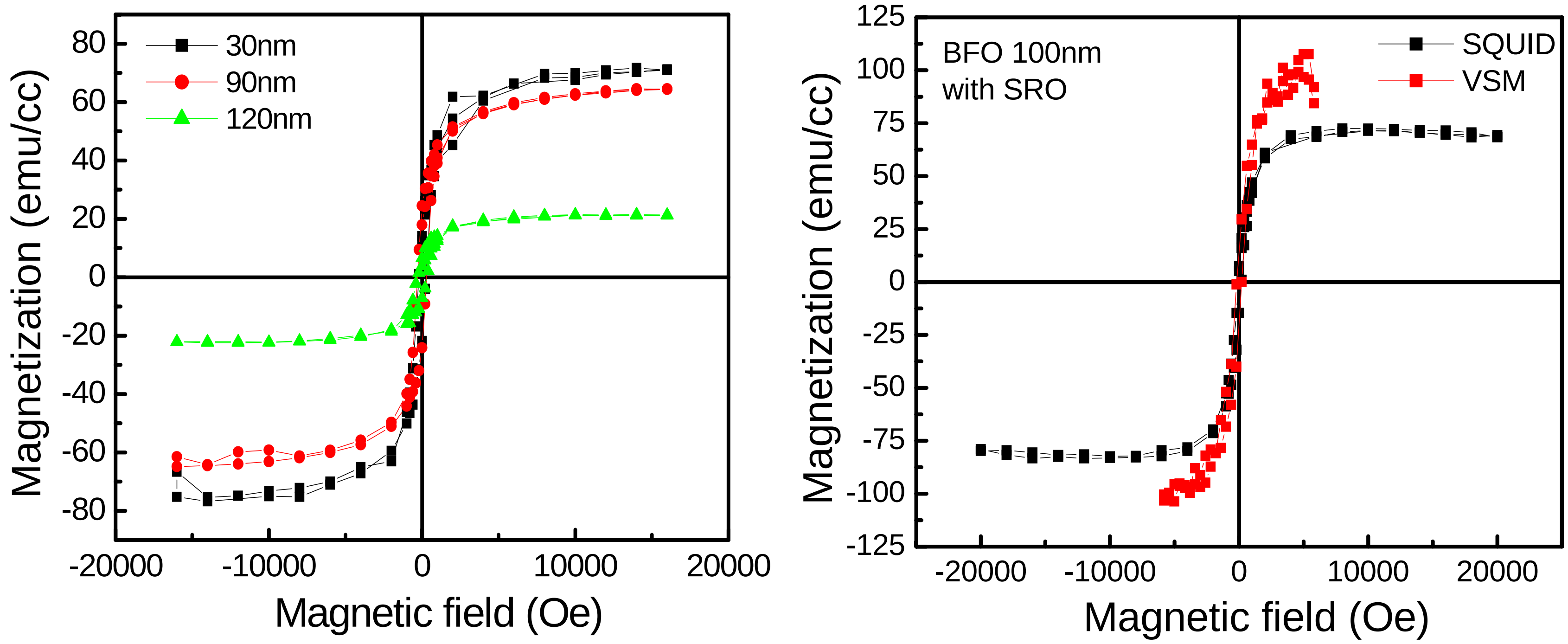
P, M ??



On (100) STO :

- tetragonal distortion + rhombohedral structure = monoclinic symmetry
- "monoclinicity" depends on film thickness

Magnetic Properties of Thin Film $BiFeO_3$ on (100) STO



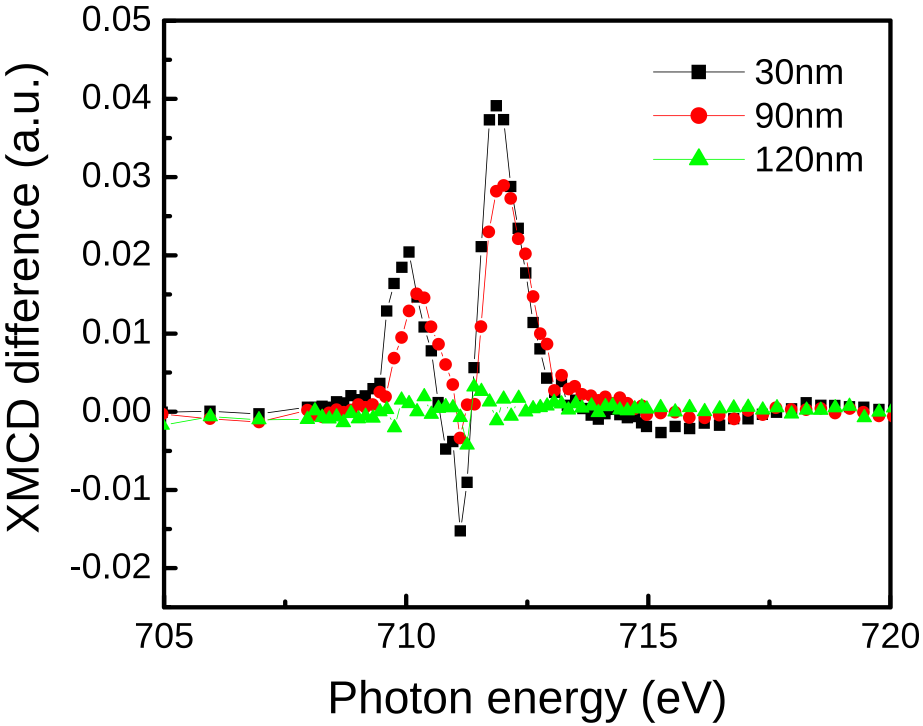
X-ray analysis does not show any macro-size second phase

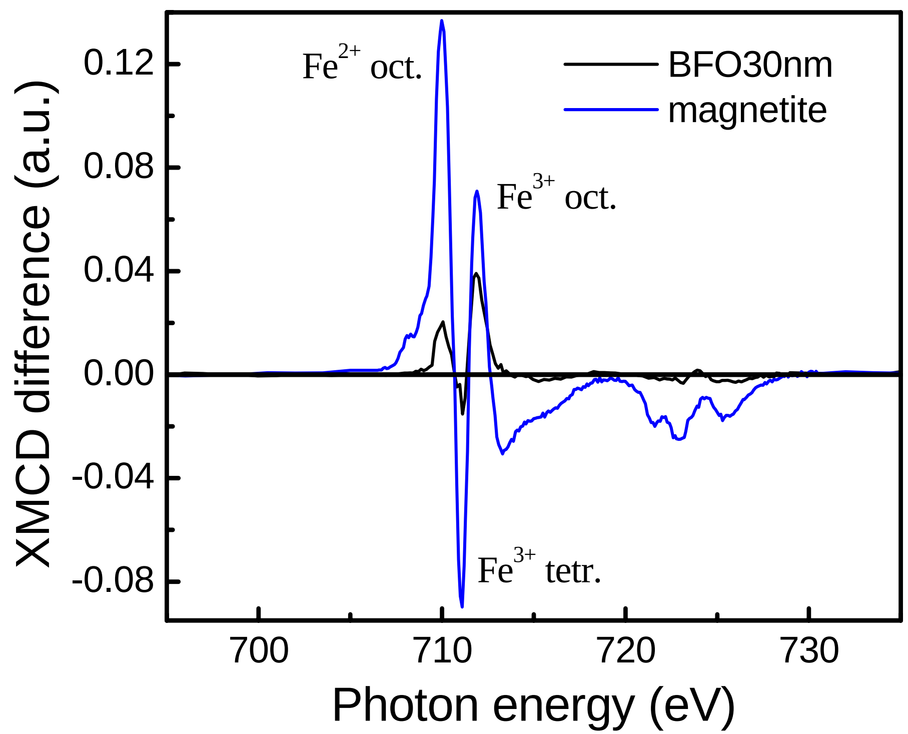
AFM, TEM : no second phase

RBS indicates Bi/Fe ratio ~1

Possible role of oxygen related defects ?

Origin of Magnetism : Heteroepitaxy & Defect Chemistry Probing through XAS / XMCD





Key Points

Existence of Fe^{+2} (XPS, XMCD)

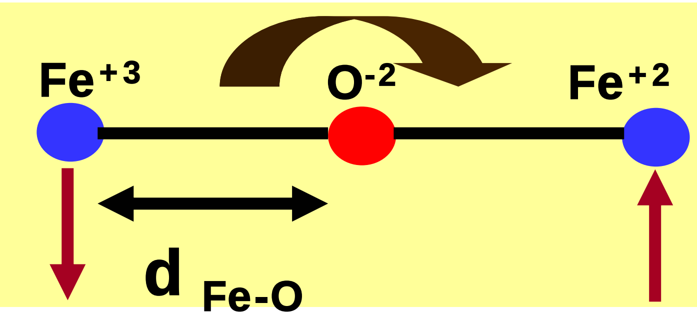
Moment is ~15% of Fe3O4

Site occupancy is different from Fe3O4

Fe+3 in tetrahedral site : Puzzling??

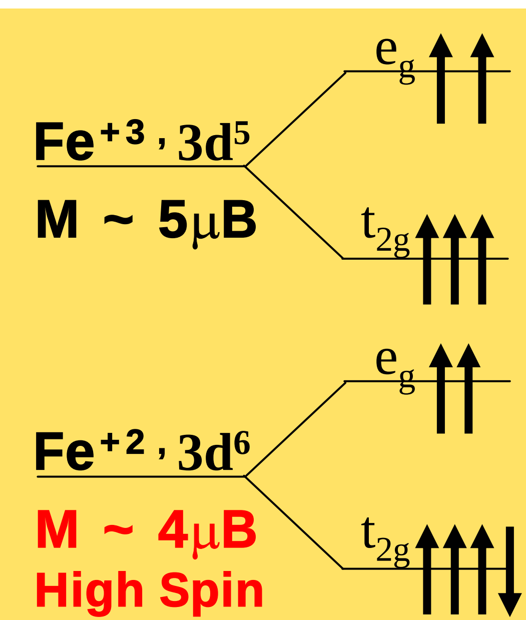
Need better understanding and modeling of MCD data

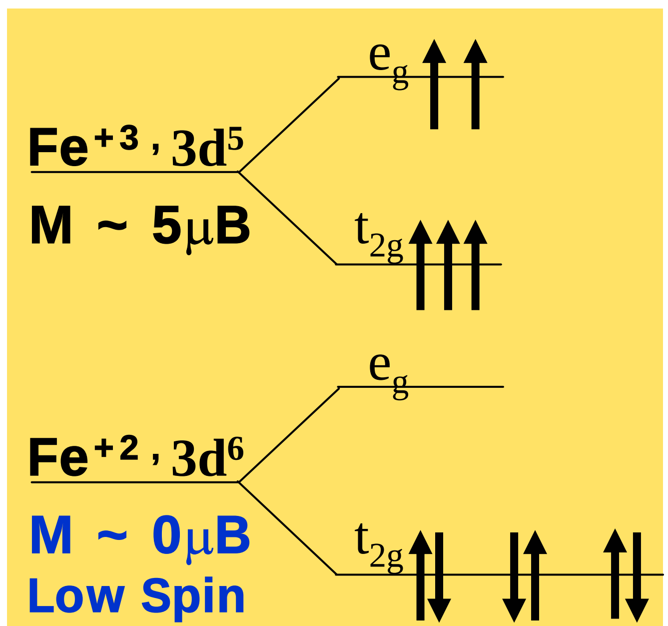
Possible Origins of Magnetism

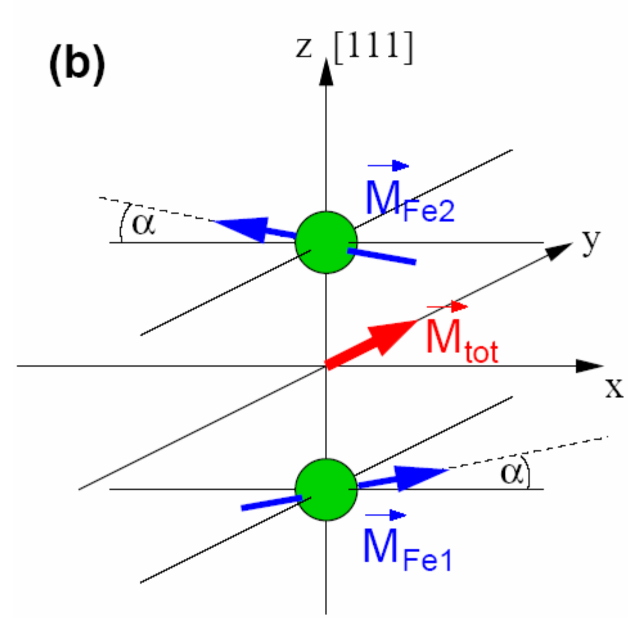


Antiferromagnetic Super-exchange

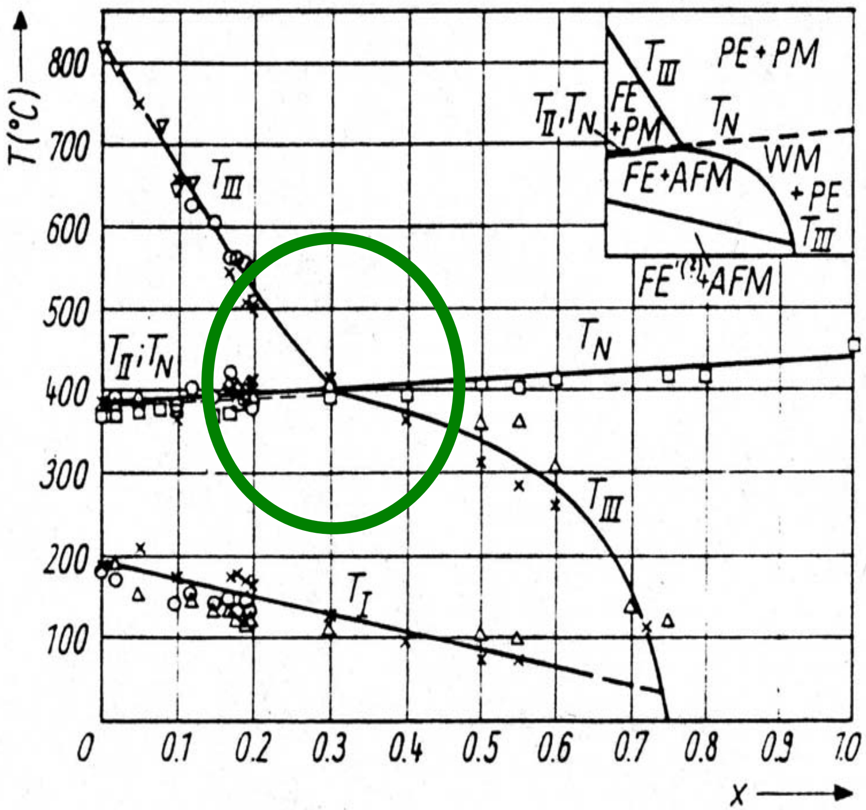
- Need to understand Fe-O defect chemistry under heteroepitaxial constraints
- Electronic structure of Fe+3/Fe+2 under Heteroepitaxial stresses
- Spin canting effects under combined oxygen defect-electronic structure effects







Tuning Phase Transitions



$BiFeO_3$

$LaFeO_3$

FUTURE DIRECTIONS

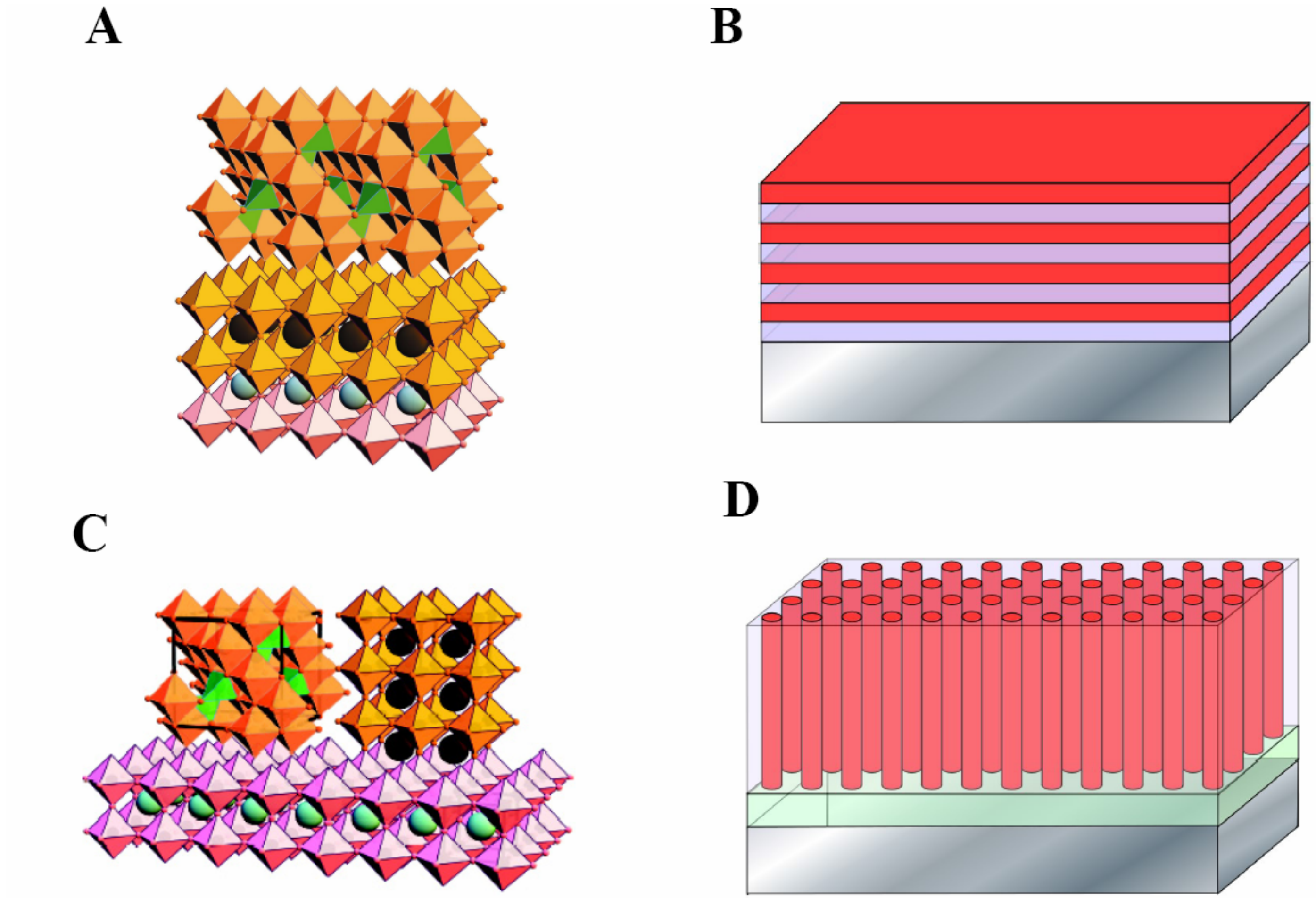
Magnetism in BFO: Fe+2/Fe+3

(Bi, RE)(Fe,Cr)O3 : enhance magnetism

LaBiFeO : enhance coupling thru phase transitions

Need interplay between experiment and theory : KEY

Perovskite-Spinel Multifunctional Heterostructures

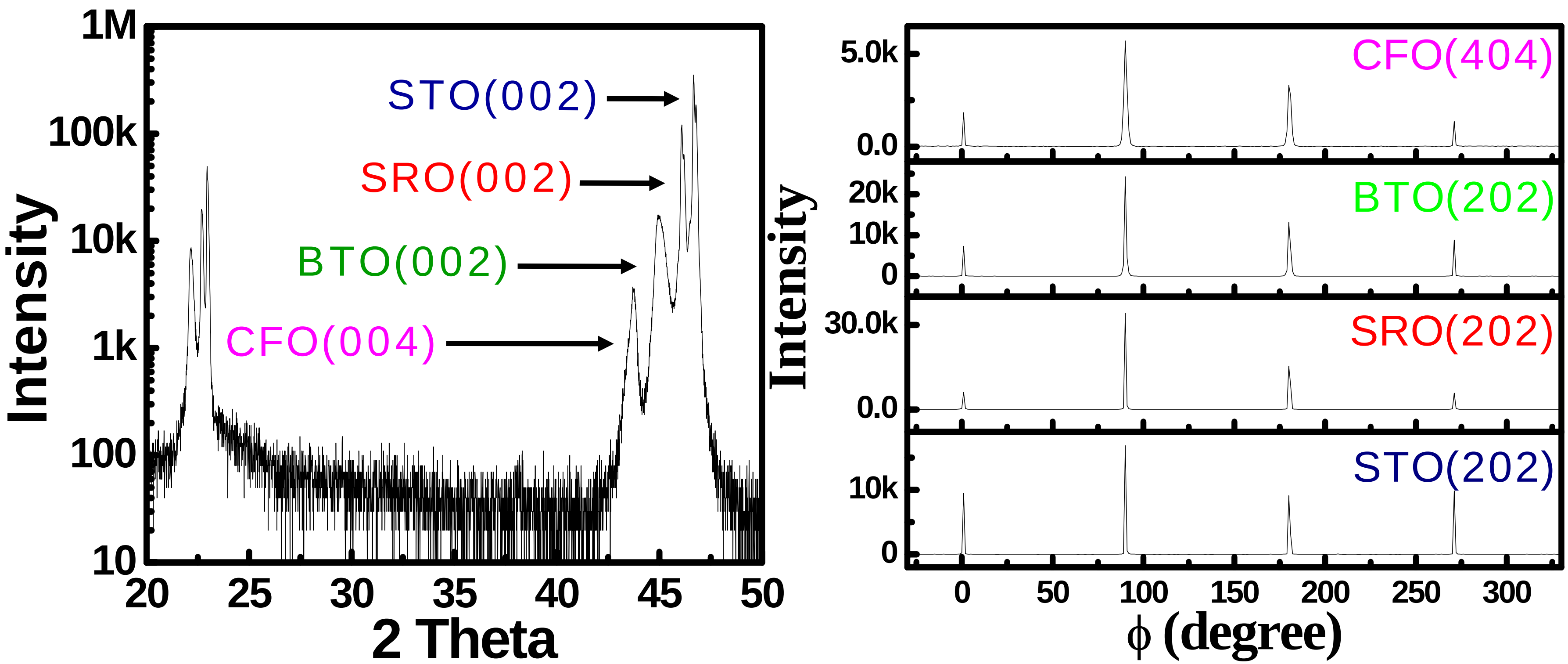


Spinel (CoFe2O4)
a ~ 8Å
Ferrimagnet with
Large Magnetostriction

Perovskite BaTiO3
a ~ 4Å
Ferroelectric / Piezoelectric
Landau Parameters known

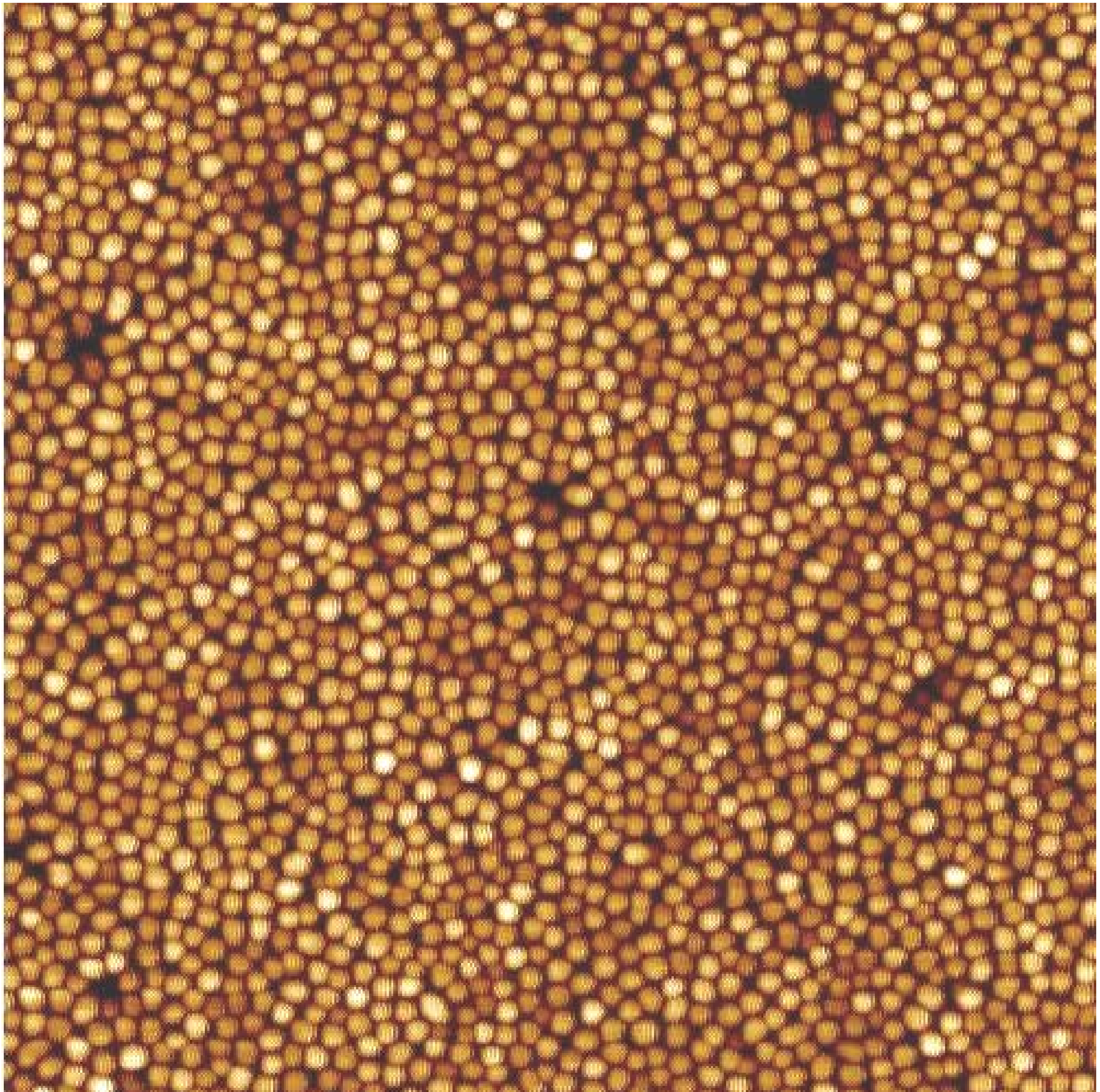
Coherent interface :
enhance coupling
Elastic Interactions :
ordered structures

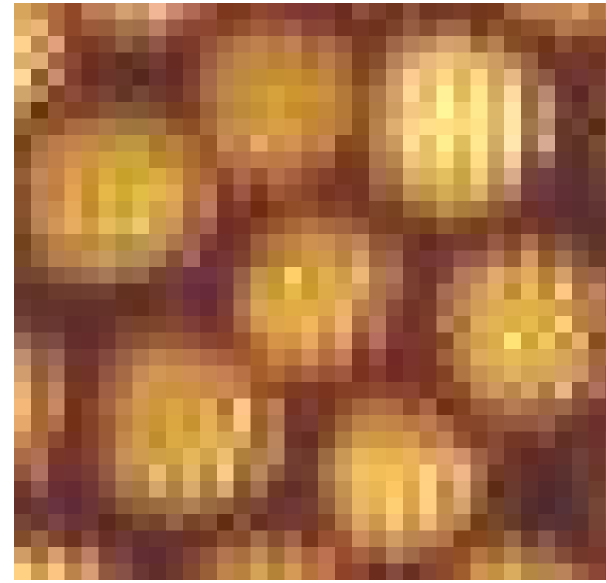
Self-assembled $CoFe_2O_4/BaTiO_3$ Nanostructures

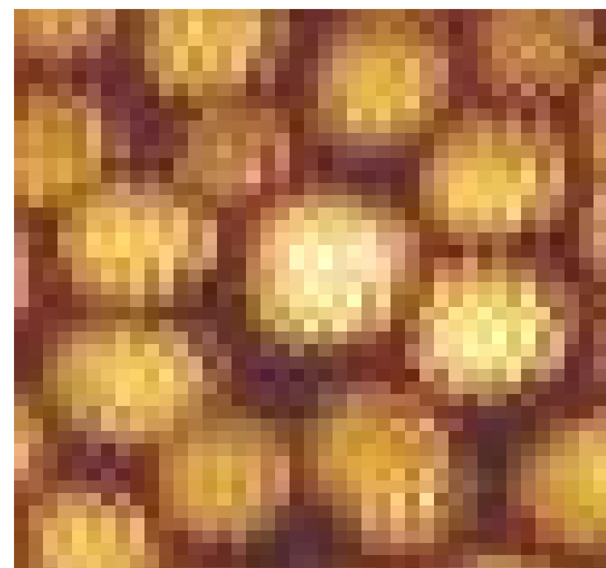


- XRD studies show phase separation of CFO and BTO
- Both phases are heteroepitaxial.

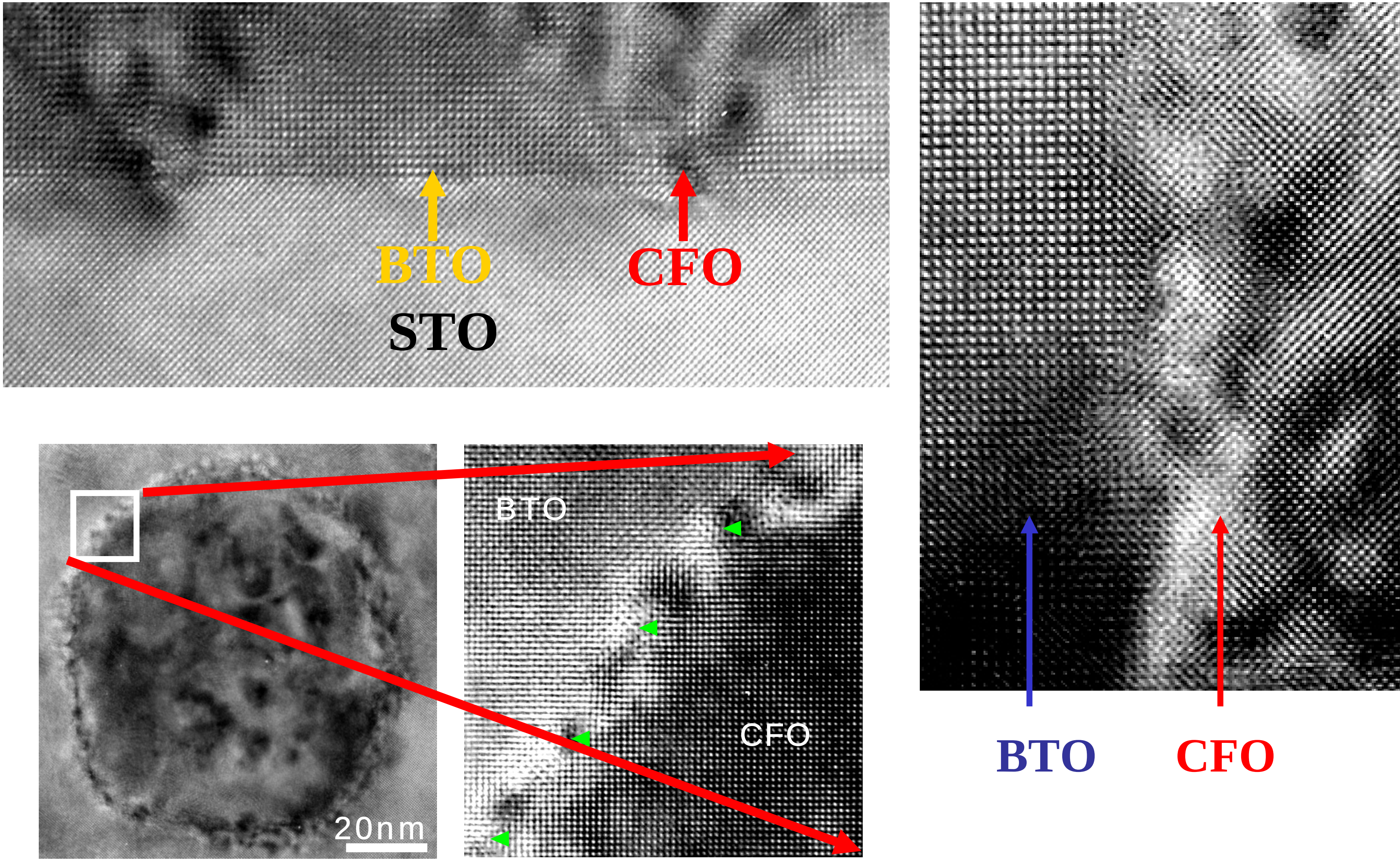
Vertically aligned $CoFe_2O_4$ / $BaTiO_3$ heterostructures



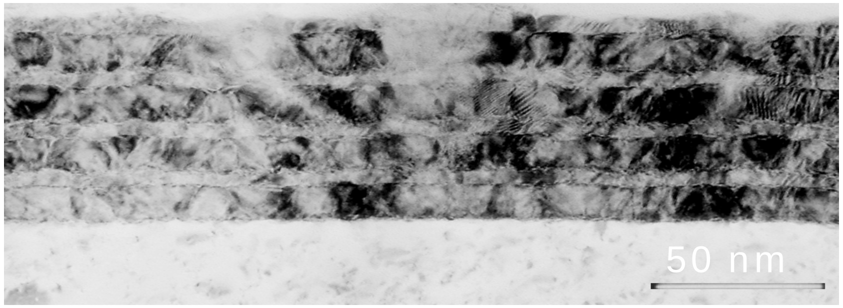


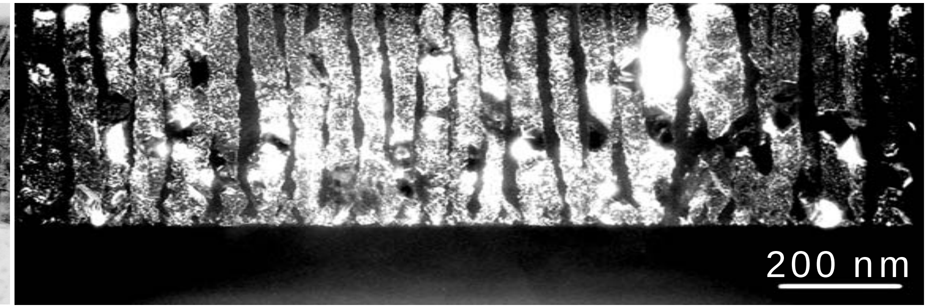


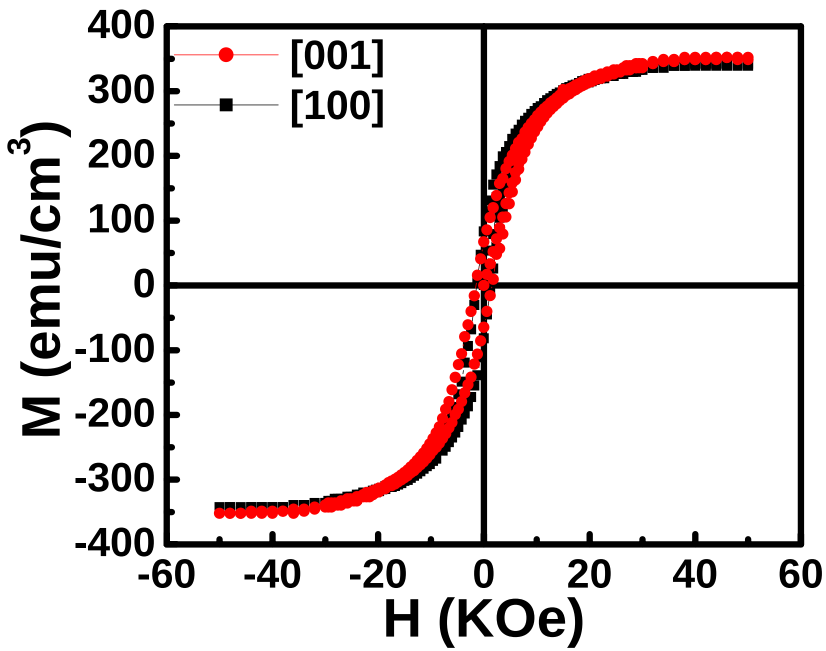
3-D Heteroepitaxy

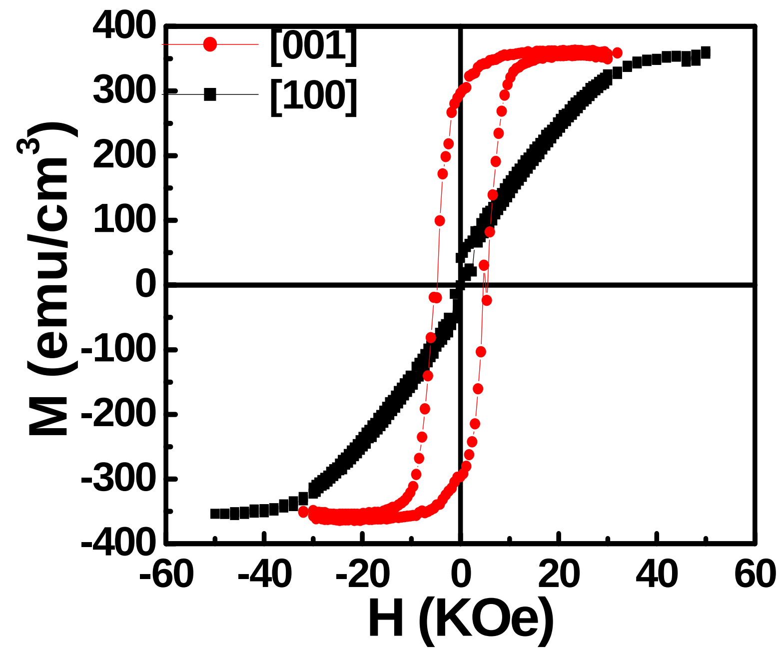


Magnetic Properties









Anisotropy Field: ~35 KOe

Bulk CFO M_s 350 ~ 400 emu/cm^3

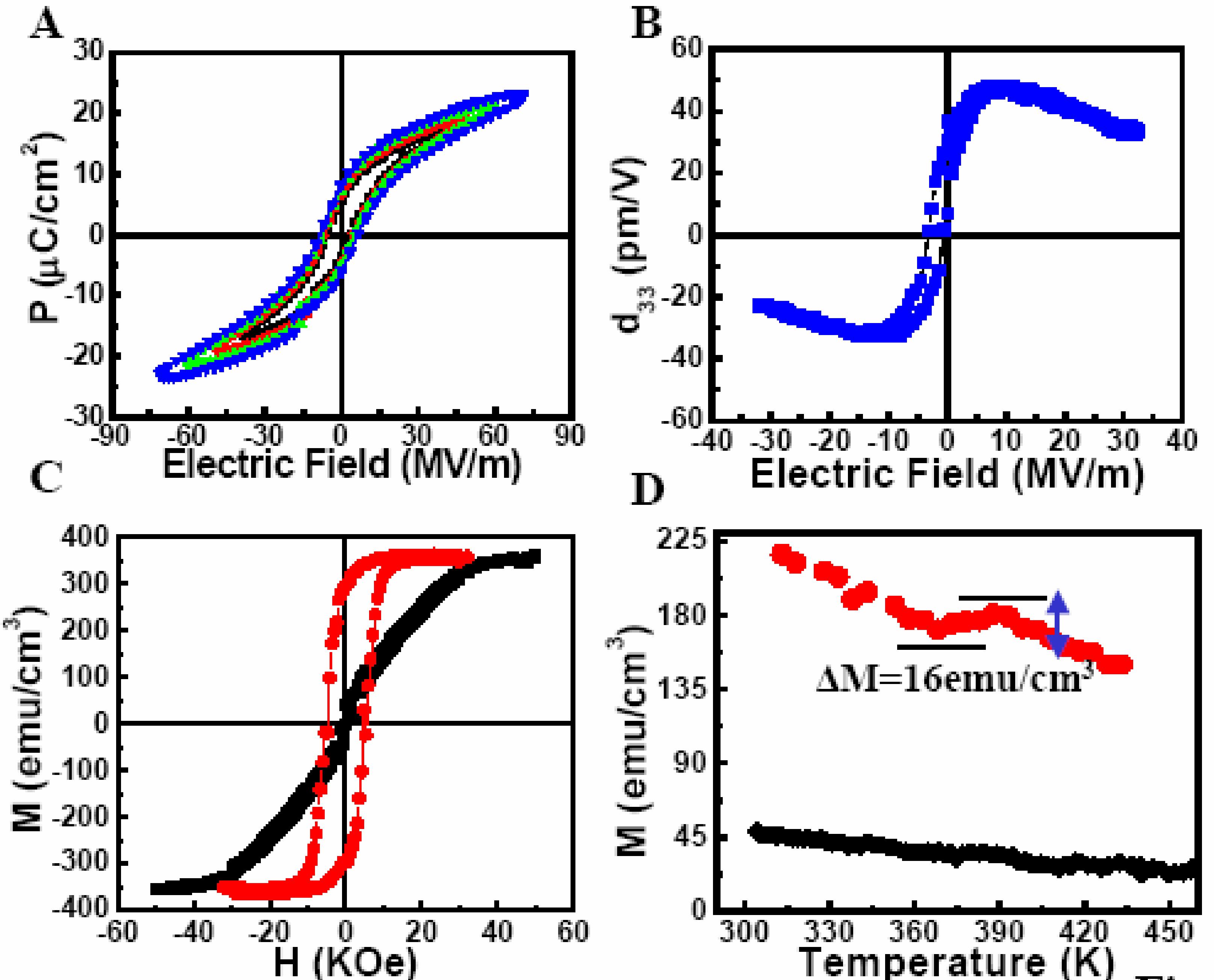
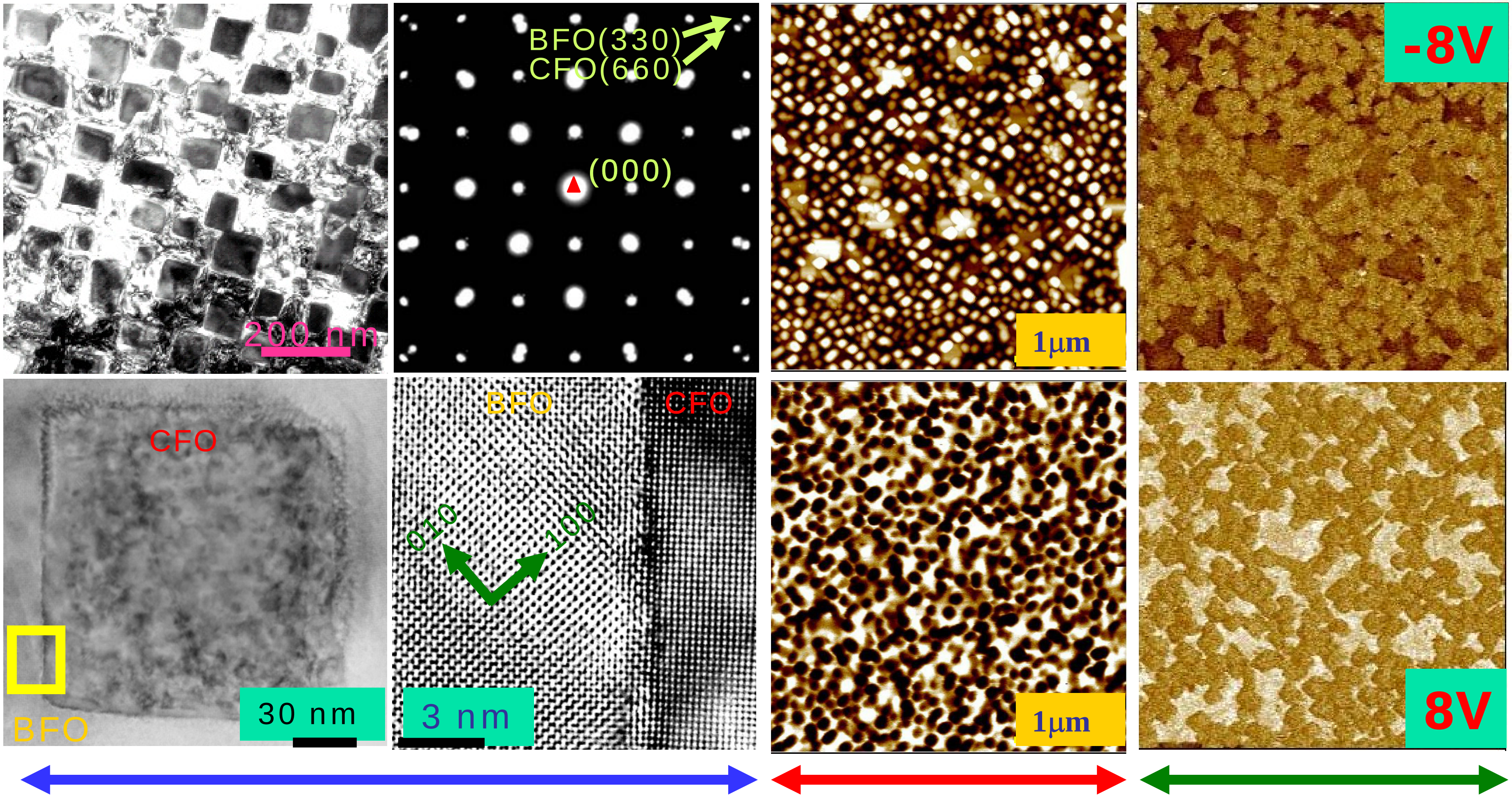

A
P (μC/cm2)
Electric Field (MV/m)
B
d33 (pm/V)
Electric Field (MV/m)
C
M (emu/cm3)
H (KOe)
D
M (emu/cm3)
ΔM=16emu/cm3
Temperature (K)

Fig.3

$BiFeO_3$ / $CoFe_2O_4$ System



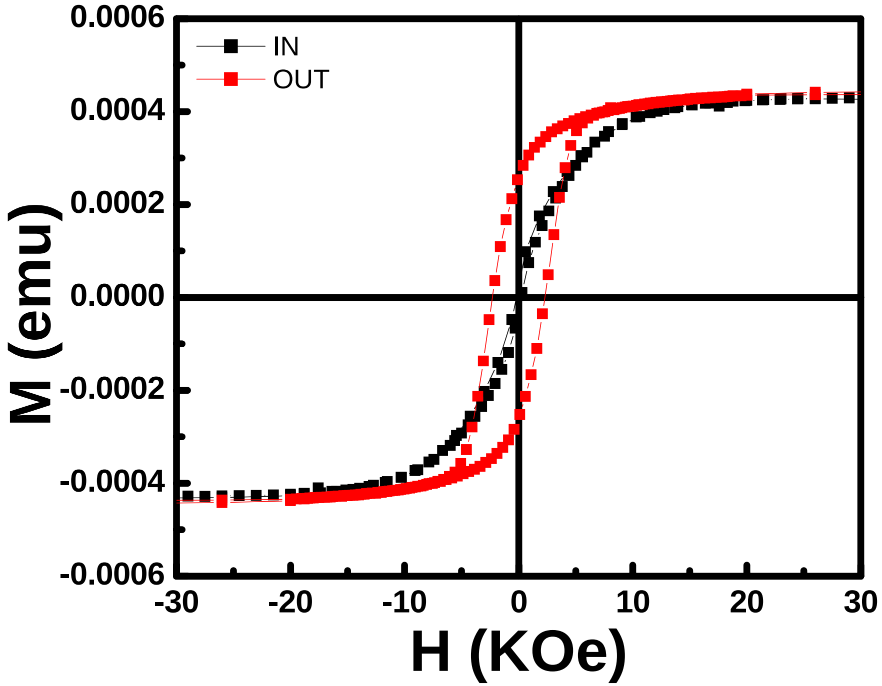
Microstructure and Interfaces

Magnetism

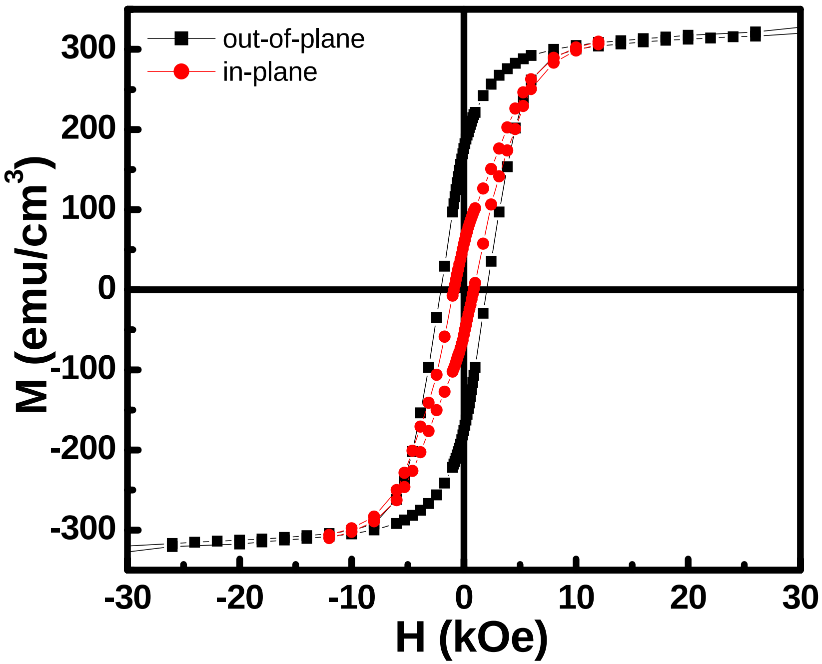
Ferroelectric Switching

Enhancements in Magnetic Anisotropy

$BaTiO_3$ – $NiFe_2O_4$

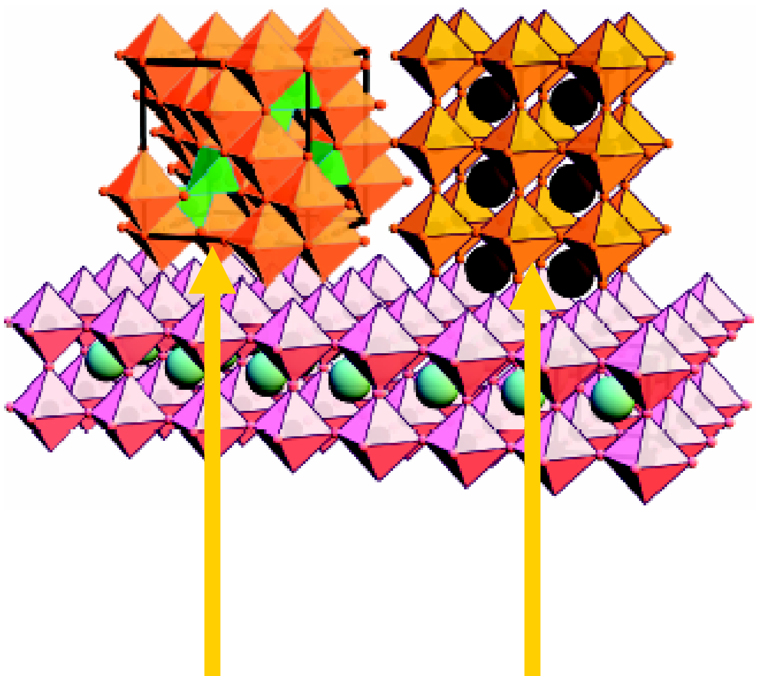


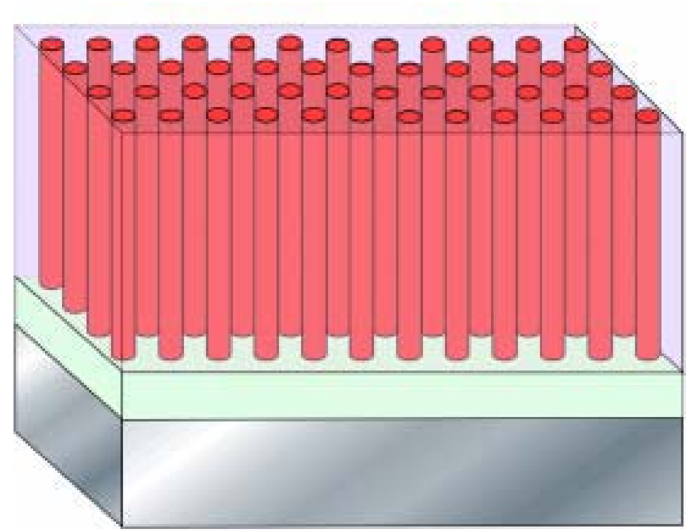
$BiFeO_3$ – $CoFe_2O_4$



Enhancements in anisotropy seem generic to many systems
Enhancements also depend on diameter of nanopillar

Designing Multifunctional Nano-composites : A Generic Approach



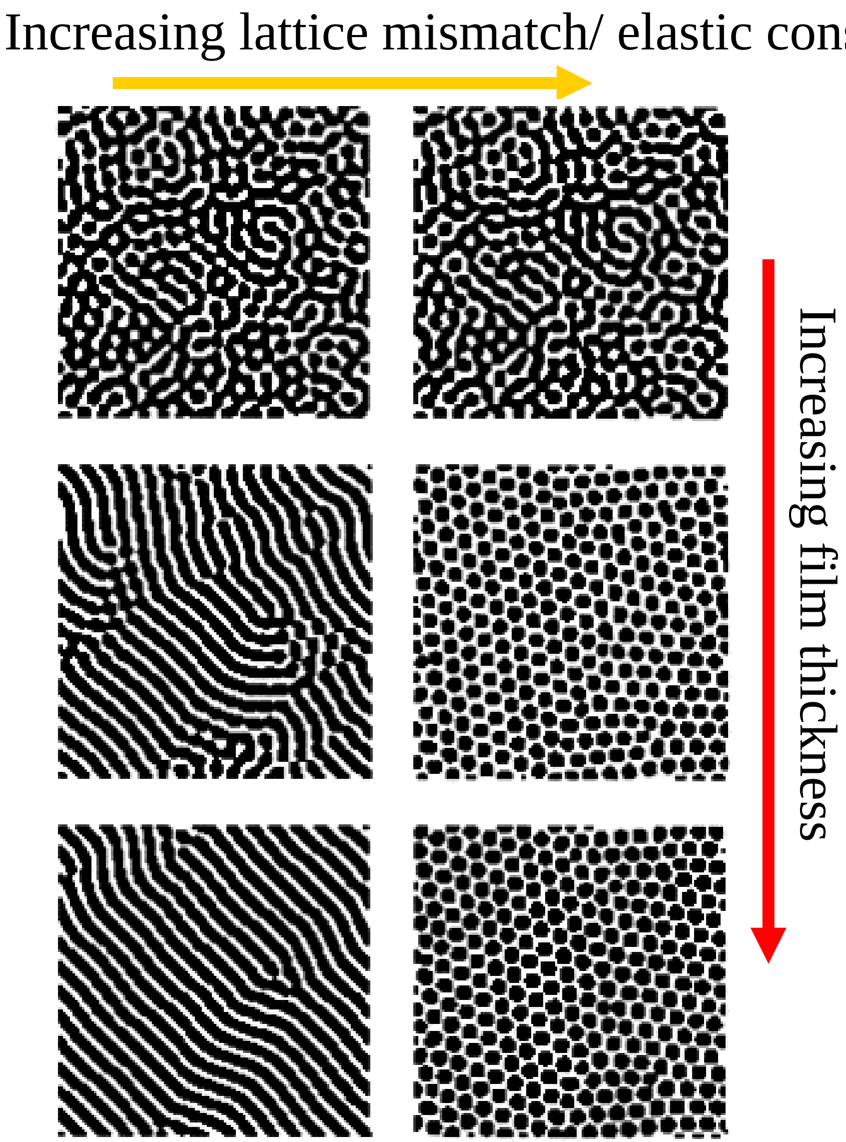


Phase A
Lattice Parameter : a
Line compound : no solubility of B in A

Phase B
Lattice Parameter : n x a
Line compound : no solubility of A in B

- **Coherent interface + Nano-scale : enhance coupling**
- **Self-assembly : ordered nanostructures ; control through heteroepitaxy**
- **Broad Impact**

Challenges : Spontaneous Ordering in Nanostructures
Taking a cue from semiconductors



Theoretically, it is possible to order the second phase!!

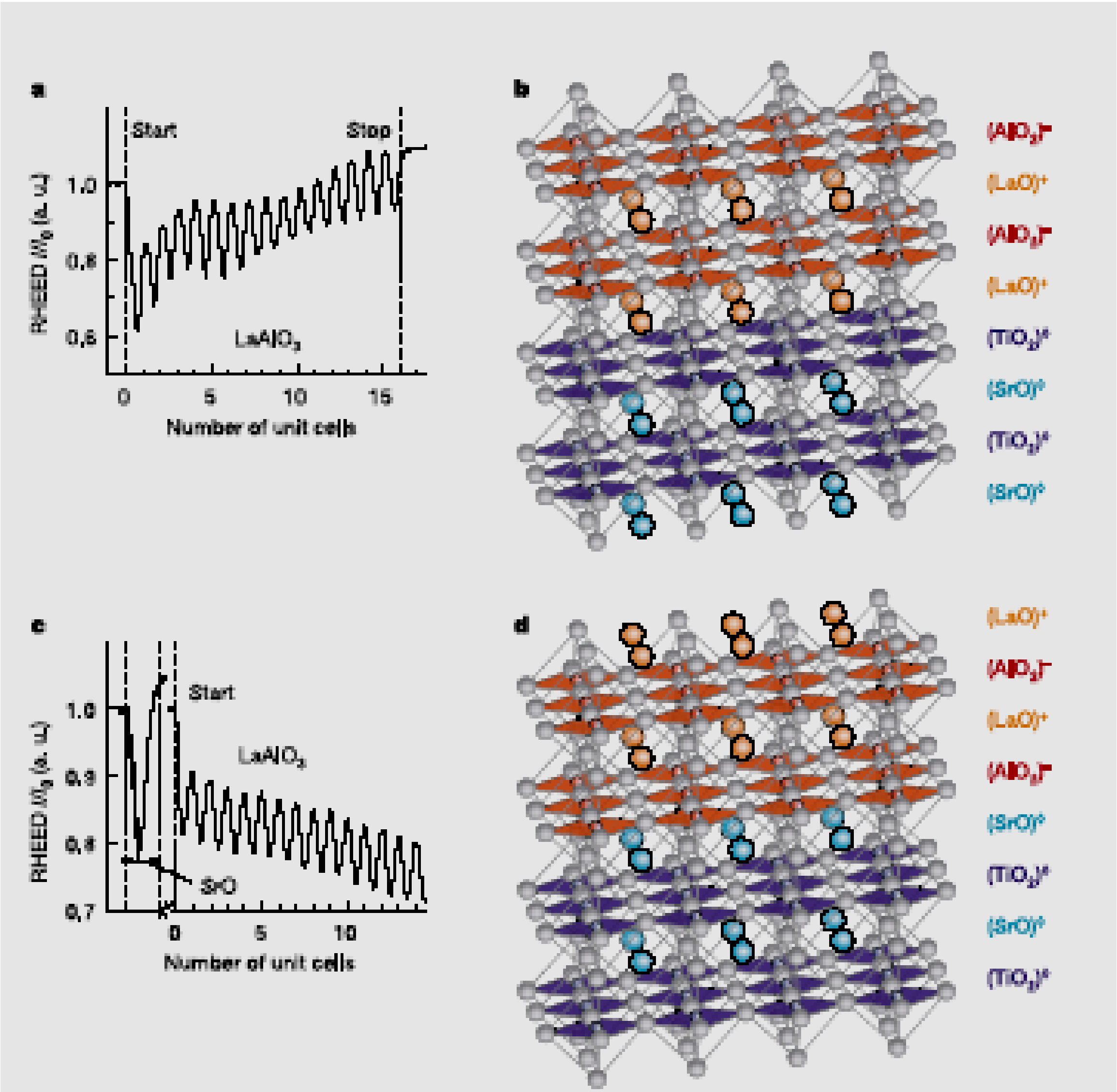
KEY ISSUES
Lattice mismatch effects (substrate/spinel/perovskite)
Understanding growth mechanisms
Crystal structure effects
Need repulsive and attractive interactions

† Leonard and Desai, *Thin Solid Films* 357, p46 (1999) ; Schuhkin and Bimberg, RMP, 1997.

Challenges : Coupling of Order Parameters

1. Enhanced magnetic moments through Ferrimagnetism in Bi(RE)-Fe(Cr)-O3
2. Approaches to probe coupling : Optics ; microwave (e.g. resonance spectroscopy ; Proximal probes; synchrotron studies
3. Magnitude of coupling : Are the coupling coefficients large enough to be technologically valuable ?

NEW DIRECTIONS : Tuned Heteroepitaxy



- **Create New Properties at Interfaces in Complex Oxides**
- **Band vs. Mott Insulators**

•Role of external perturbations and fields

•Possibility of 2-D e-gas ; possibly spin polarized

Summary : Challenges and Opportunities

- **Functional Oxide Heterostructures : An exciting area of basic and applied interdisciplinary research**
- **Ferroelectric Memories : products making their way into the market : interesting dynamics between FRAM's and MRAM's : capturing market share is the key !!**
- **Scanned Probes : Opening up new avenues for spatially resolved nanoscale probing of static and dynamic physical properties**
- **Finite Size Effects : PZT films clearly ferroelectric down to 4nm thickness ; suppression of ferroelectricity begins ~12 nm.**
- **Theory / Experiment Coupling: Very valuable!!**
- **Critical role for in-situ studies : growth studies on the Synchrotron (ALS)**
- **BiFeO3 : lead-free ferroelectric / piezoelectric : very promising for memory / piezo / multifunctional applications**
- **Multi-functional Oxide Heterostructures and Nanostructures : Very exciting new developments ; great area of basic and applied interdisciplinary research**
- **Self-assembly processes : key to getting down to nano-dimensions : can we get nanopillars of FE in a dielectric matrix ? Can we obtain long-range ordered nanostructures??**

Collaborators

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