Combinatorial Investigation of Multiferroic Materials

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University of Maryland

Outline

- Combinatorial discovery of lead-free morphotropic phase boundary

- E-field induced transition at the $Bi_{1-x}Sm_xFeO_3$ morphotropic phase boundary

- Microwave microscope as a multifunctional screening tool

- Reversible switching of magnetic easy-axis in $Co/BiFeO_3$

Acknowledgement

Daisuke Kan
A. Varatharajan
C. J. Long
J. Lee
University of Maryland

V. Nagarajan
C.-J. Cheng
Univ. New South Wales

P. Maksymovich
S. Kalinin
A. Borisevich
ORNL

Lucia Palova
K. M. Rabe
Rutgers University

S. E. Lofland
Rowan University

funded by NSF MRSEC, ARO MURI

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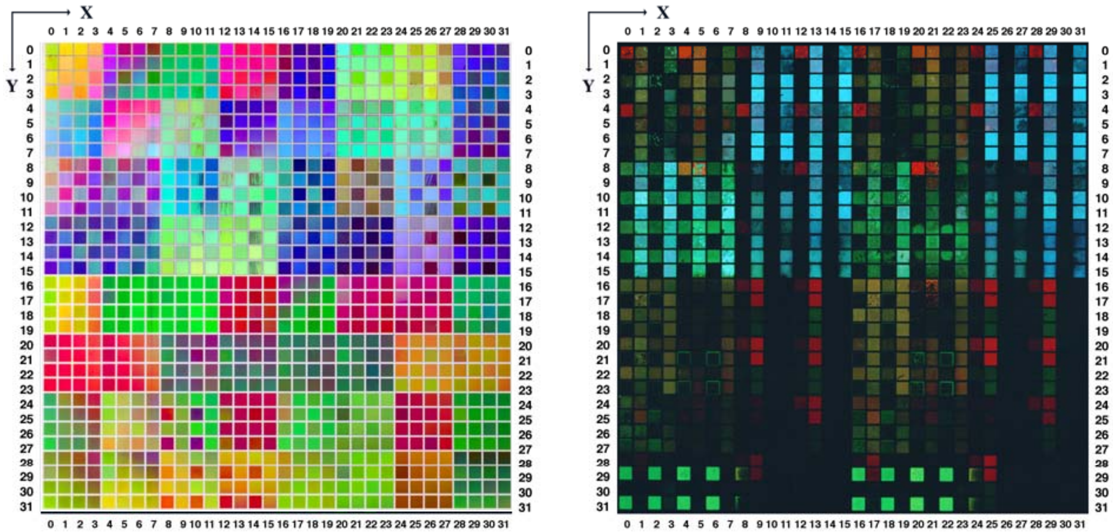
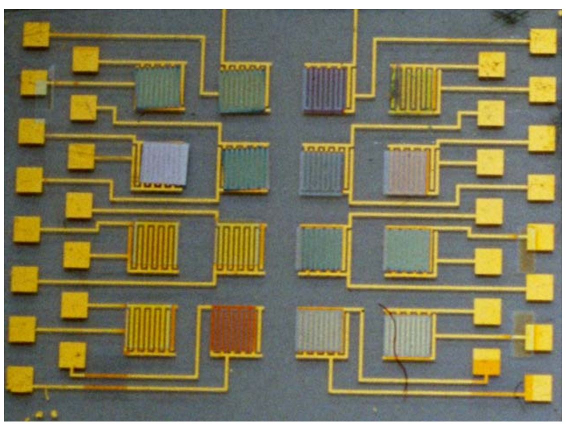
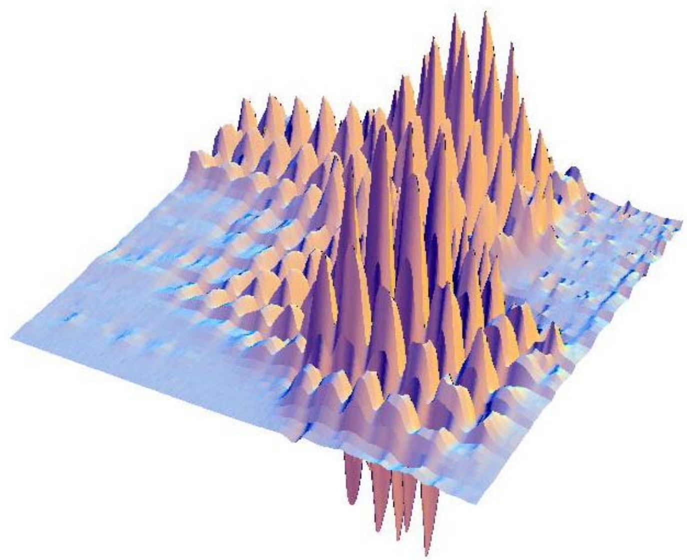
Combinatorial Libraries of Inorganic Materials



Luminescent materials libraries, Science 279, 1712 (1998)

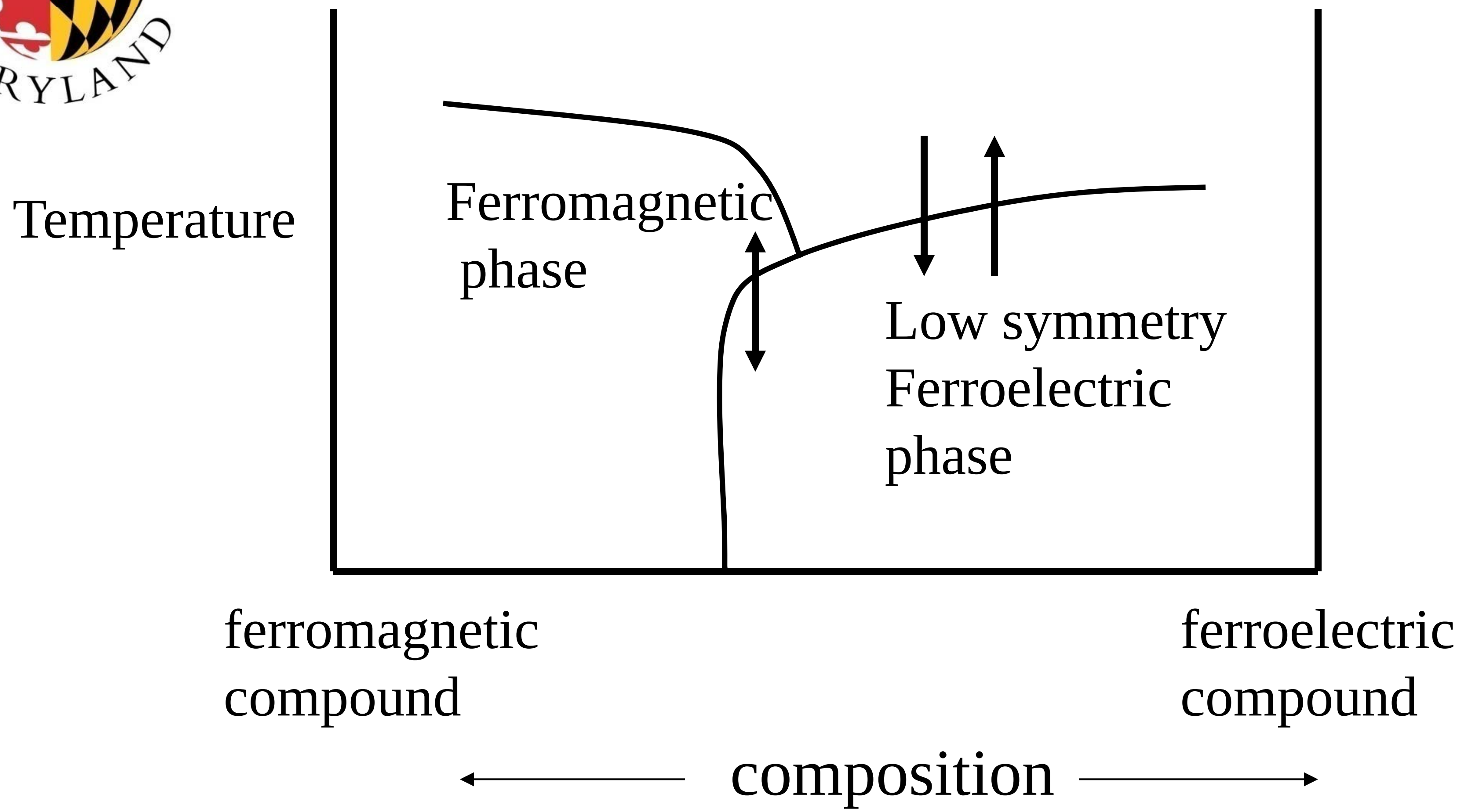


Semiconductor gas sensor library, “electronic nose”, Appl. Phys. Lett. 83, 1255 (2003)



Magnetic shape memory alloy library, Nature Materials 2, 180 (2003)

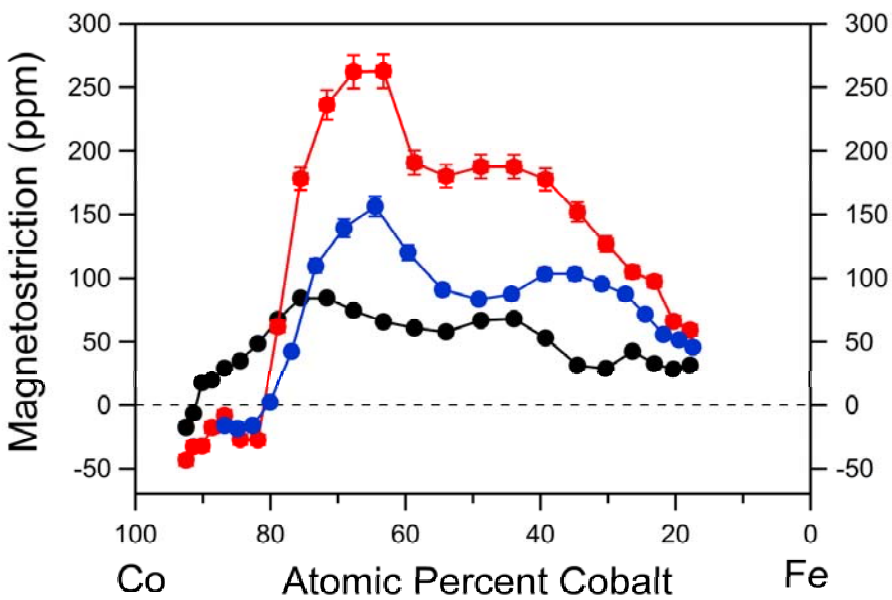
Exploration of Materials on the Brink

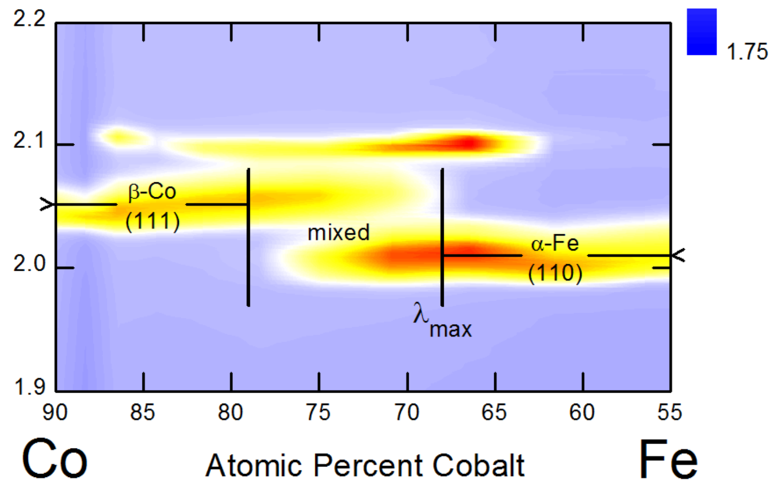


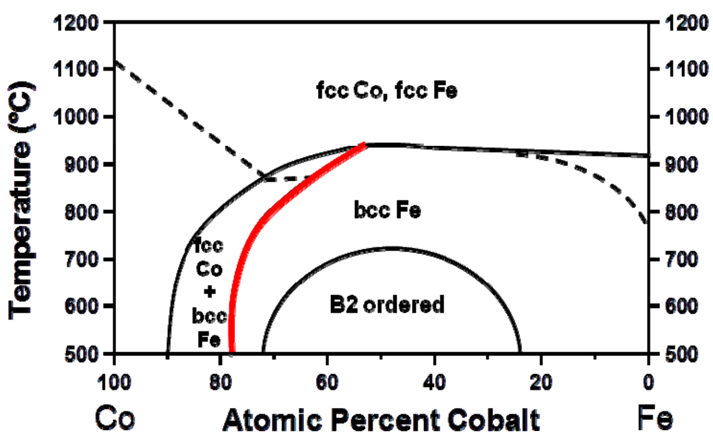
Shape memory alloys, piezoelectric materials, multiferroic materials, magnetostrictive materials, etc.

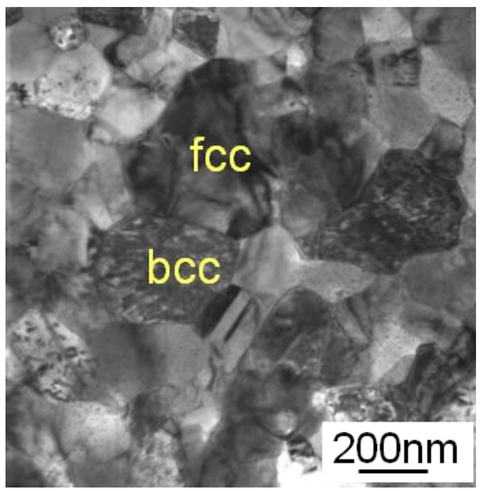
Morphotropic phase boundary in metallic alloys:

Giant magnetostriction in CoFe thin films at structural boundary







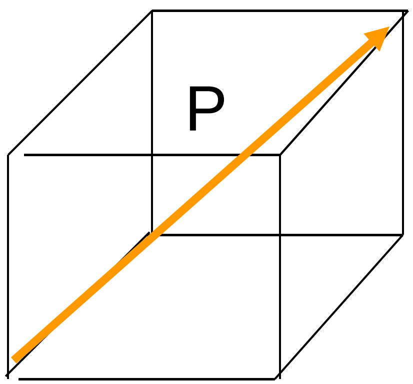


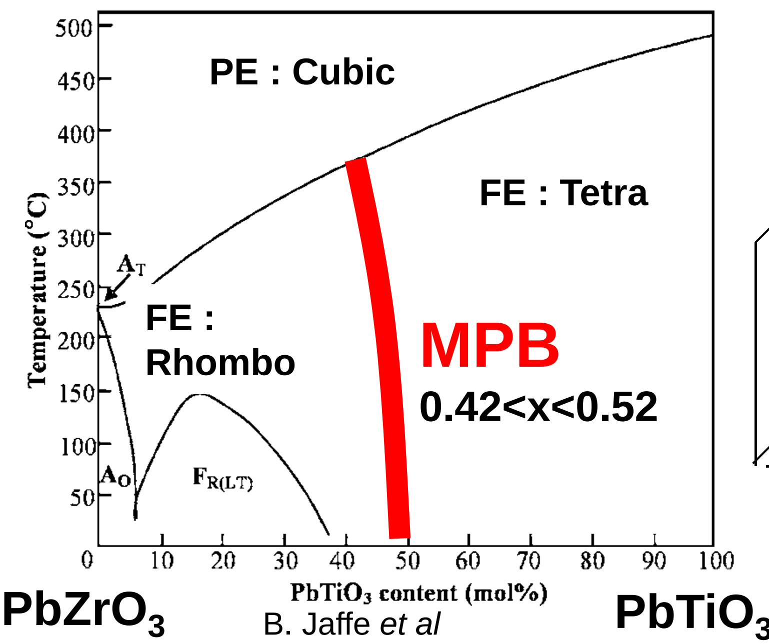
to appear in Nature Communications (2011)

Morphotropic Phase Boundary (MPB)

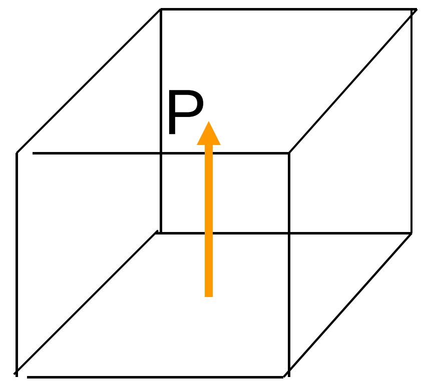
$Pb(Zr_xTi_{1-x})O_3$

Rhombo





Tetragonal



Can we find a similar system in other ferroelectrics?

Look for: Piezo/ferro/dielectric properties enhancement
Symmetry changing transition: vertical boundary
Nanodomains/lower symmetry phase

Searching for interesting boundaries

A-site substitutions with rare-earth (RE) element

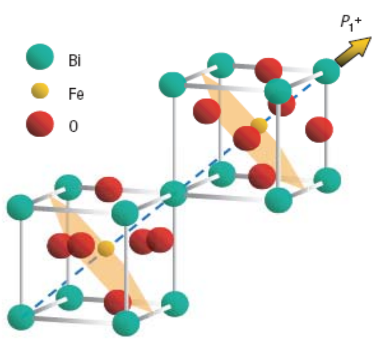
$BiFeO_3$ (BFO)

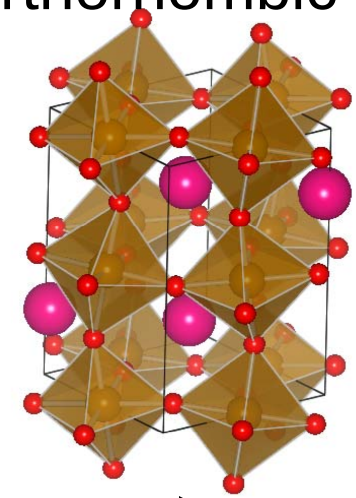
Ferroelectric
Rhombohedral

(Bi,RE)FeO_3
??

(RE)FeO_3
RE = Sm,Gd,Dy

Paraelectric
Orthorhombic

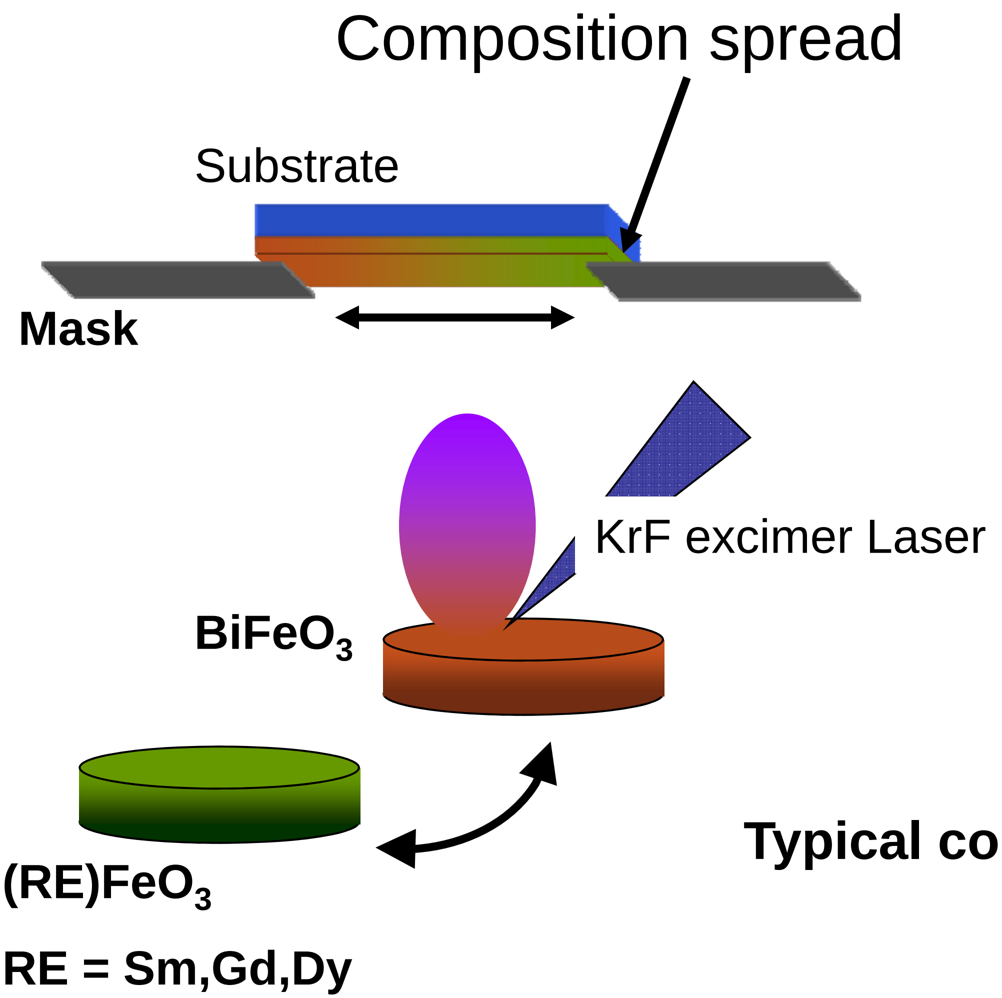


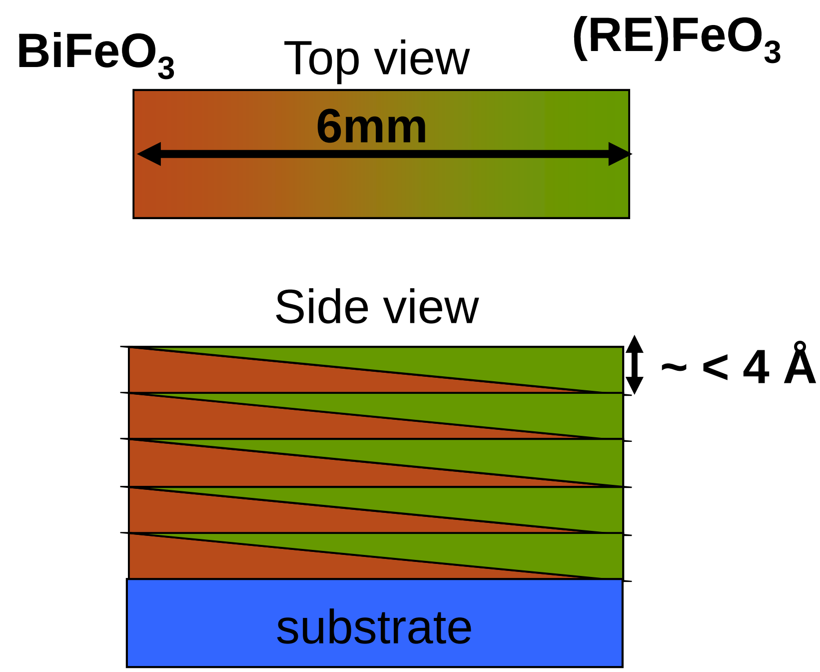


RE substitution concentration

What happens when the transition takes places?

Epitaxial composition spread of perovskite oxides



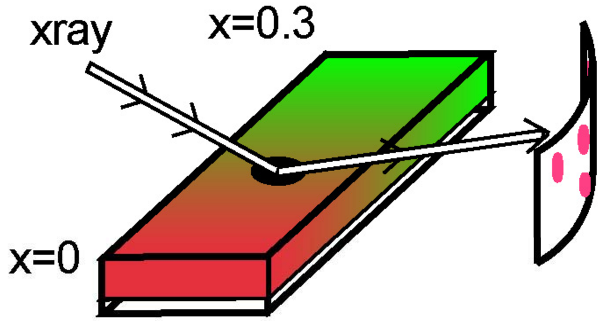


Typical conditions

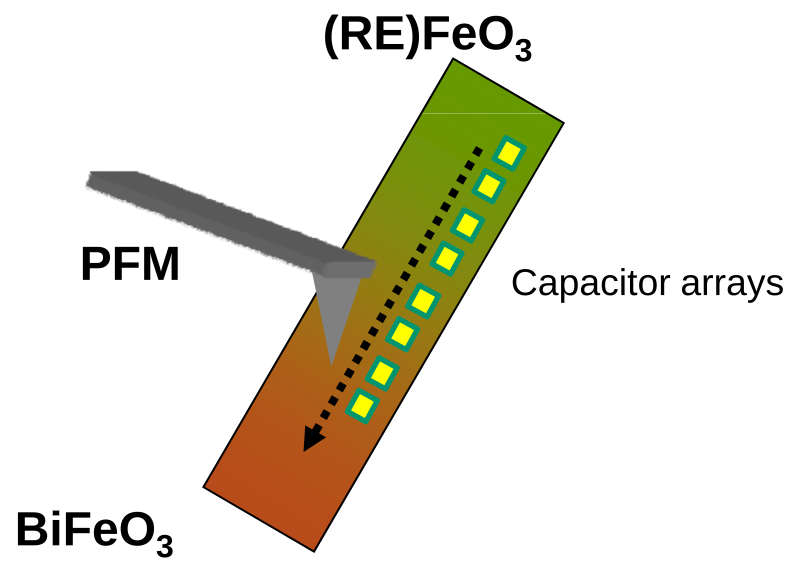
- **Temperature 600 ºC**
- **Oxygen pressure 25 mTorr**
- **Thickness 200 - 400 nm**
- **Substrate $SrTiO_3$(100)**

Rapid characterization of composition spreads

X-ray diffraction (XRD)



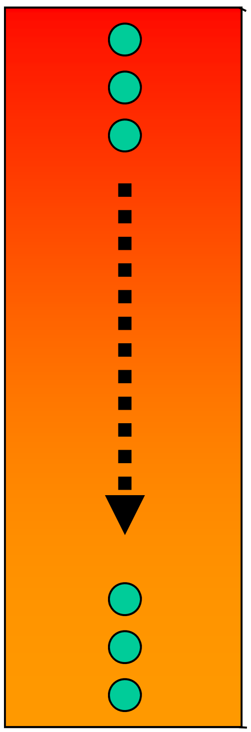
Polarization vs Electric field loop (PE)
Piezo electric force microscope (PFM)



characterized as a function of composition (or position)
XRD, P-E (ε-E) loops, PFM, MFM….

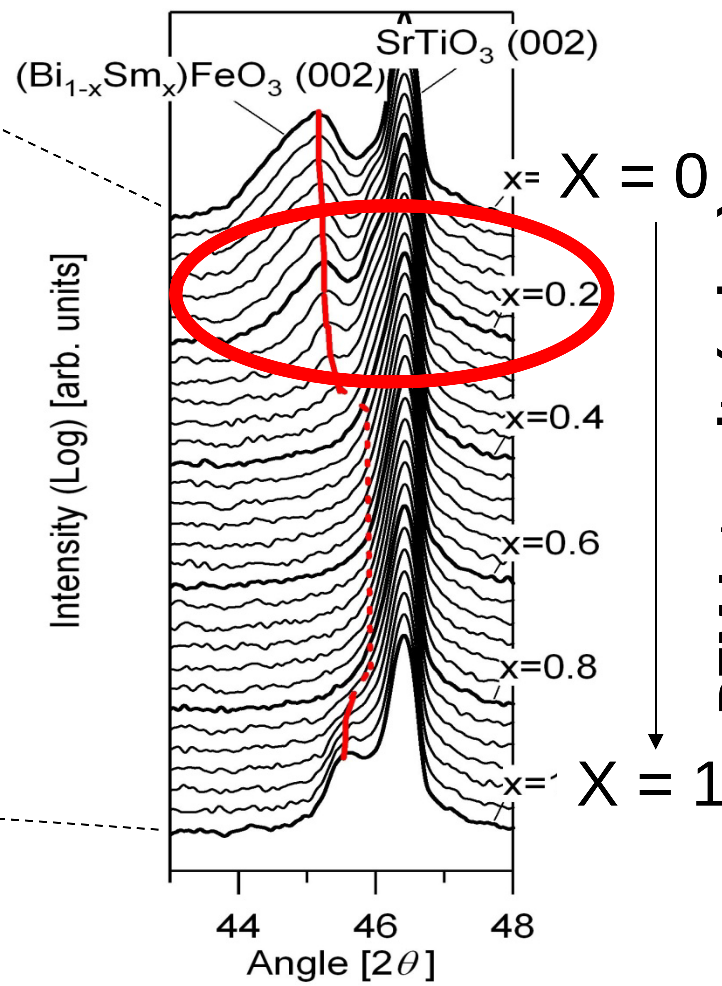
X-ray diffraction of $Bi_{1-x}Sm_xFeO_3$ composition spread on $SrTiO_3$

$BiFeO_3$
Rhombohedral
Bi^{+3}: 1.38 Å

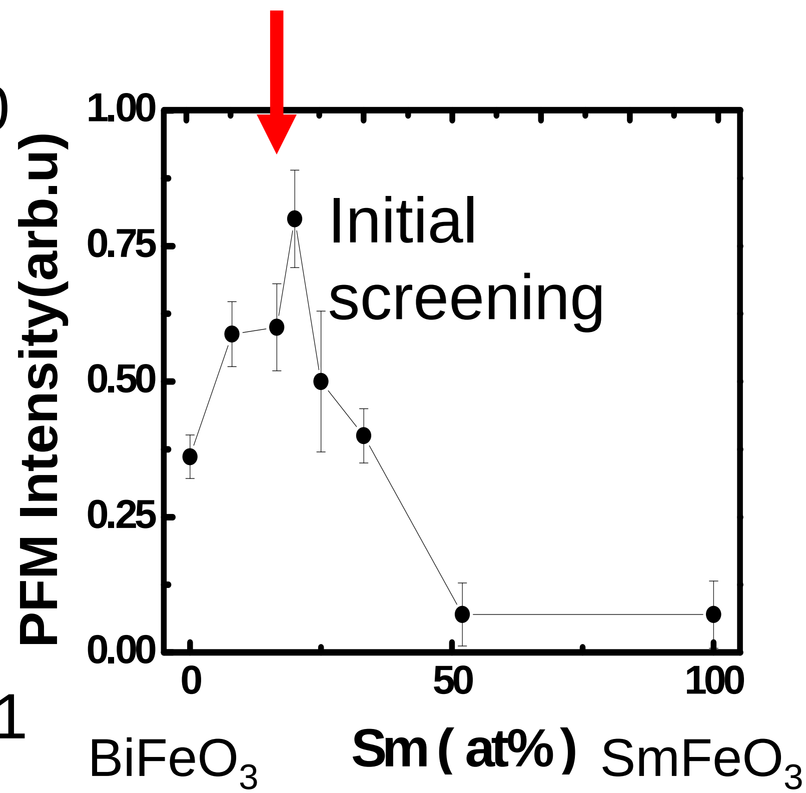


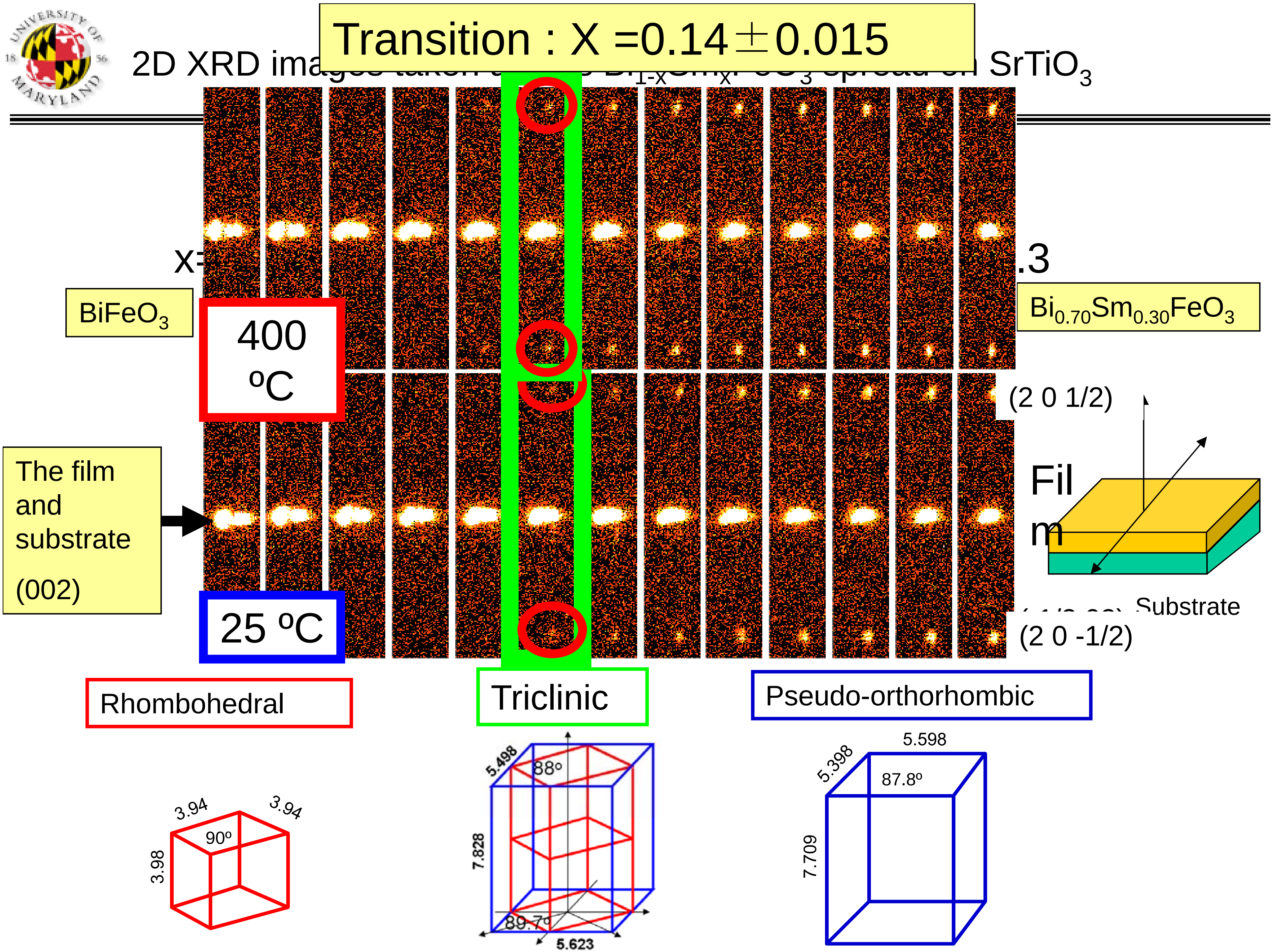
$SmFeO_3$
Orthorhombic
Sm^{+3}: 1.24 Å

$Bi_{1-x}Sm_xFeO_3$



Sm : 10 ~ 20 (at%)

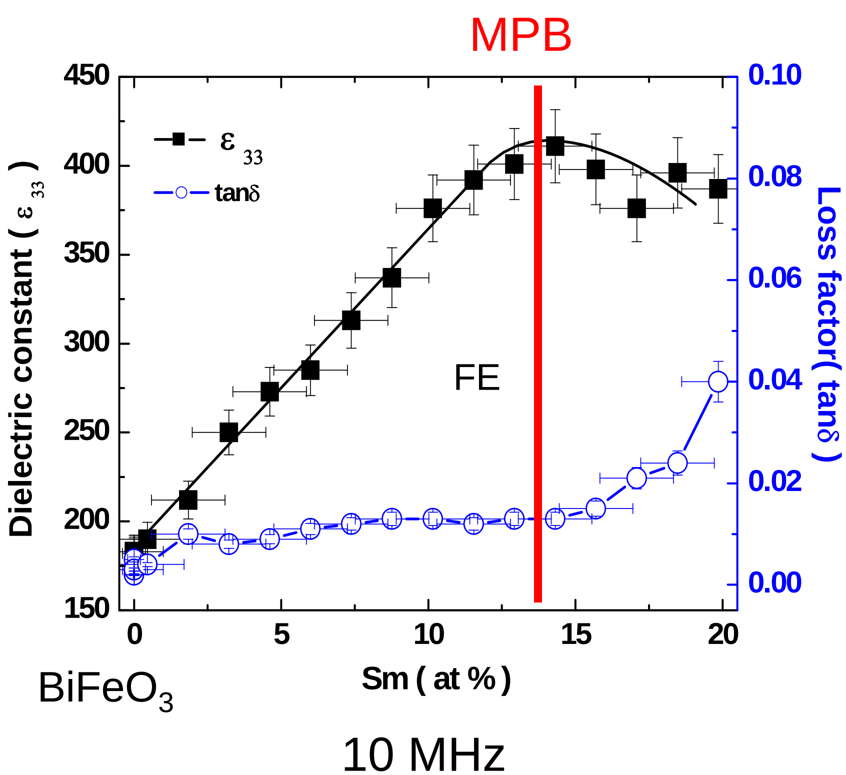


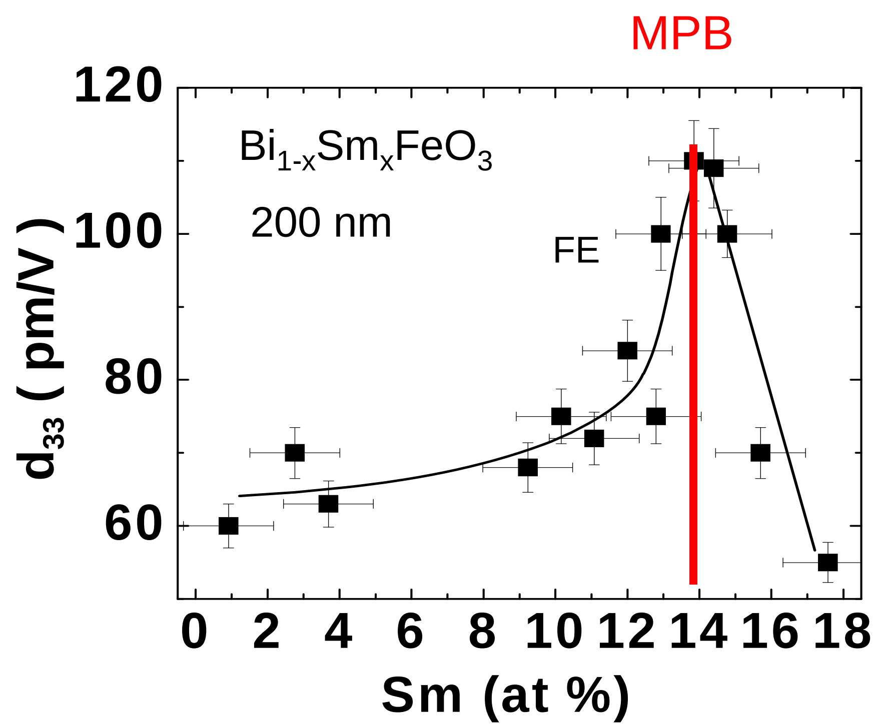

Transition : X =0.14±0.015
2D XRD ima
SrTiO3
x=
.3
BiFeO3
Bi0.70Sm0.30FeO3
400 ºC
25 ºC
The film and substrate
(002)
(2 0 1/2)
(2 0 -1/2)
Fil
m
Substrate
Rhombohedral
Triclinic
Pseudo-orthorhombic
3.94
3.94
3.98
90º
5.498
88º
7.828
89.7º
5.623
5.598
5.398
87.8º
7.709

Dielectric constant and d_{33} enhanced at MPB in $(Bi,Sm)FeO_3$

- Dielectric constant peaks at 14% Sm
- Loss tangent at this composition is relatively low (~0.01)

- d_{33} continuously increases peaking at 14% Sm to about 110 pm/V.

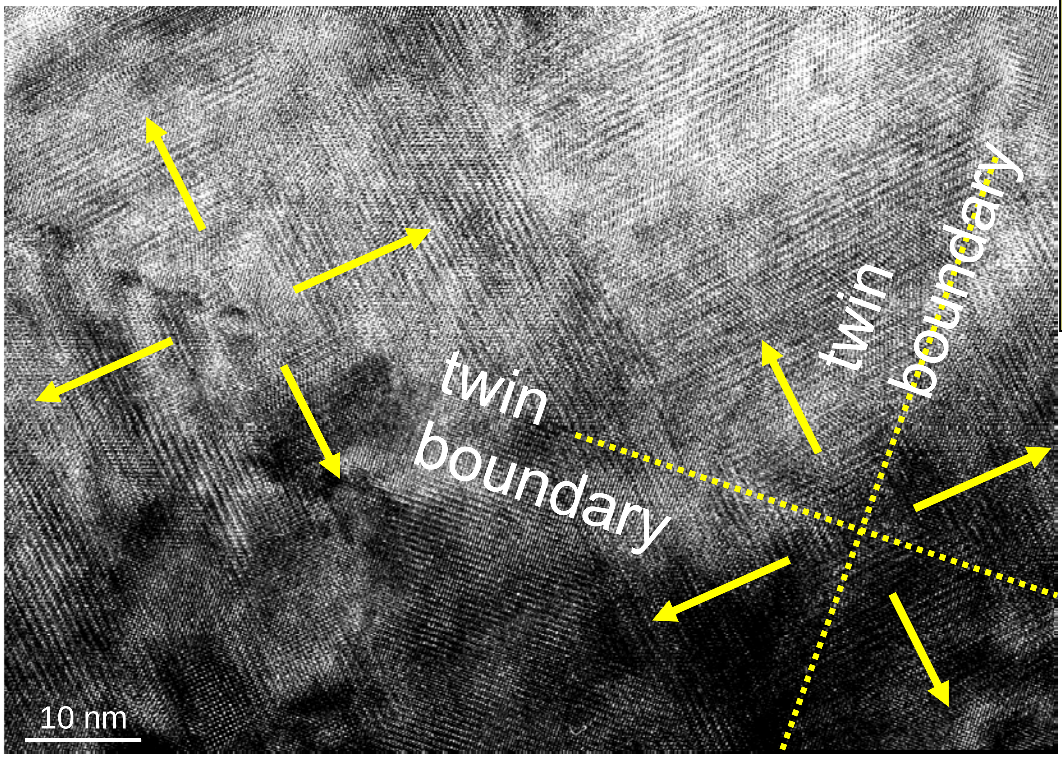




Applied Physics Letters **92**, 202904 (2008)

Planar TEM image of MPB : $Bi_{0.86}Sm_{0.14}FeO_3$

Nano domains with twin boundaries are observed at MPB



Typical domain size at MPB : 20 - 50nm,

Away from MPB : ~ 500nm

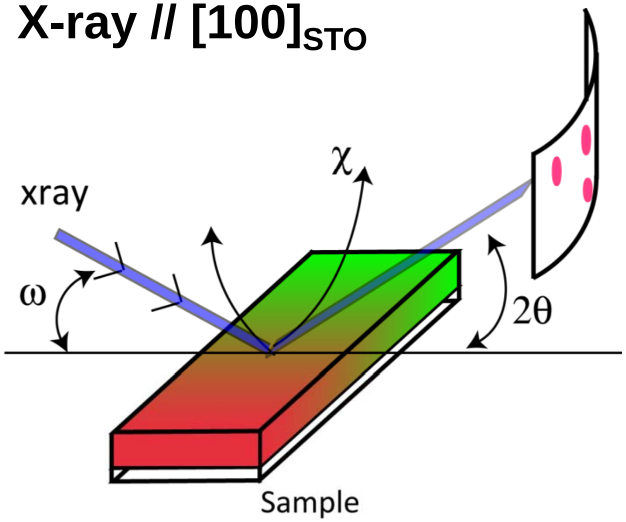
PZT at MPB shows similar nano domains

Phys. Rev. B**80**, 01409 (2009)

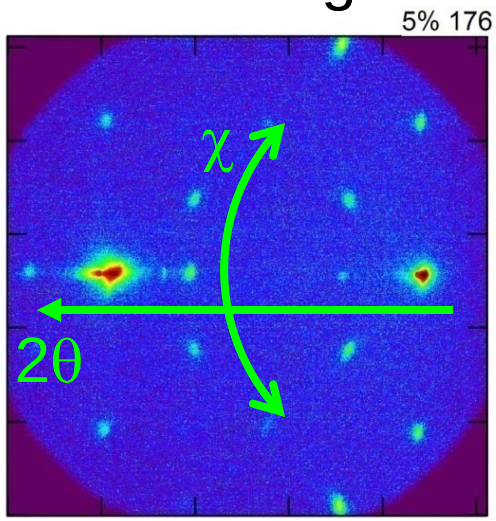
- **Piezo/ferro/dielectric properties enhancement**
- **Symmetry changing transition: vertical boundary**
- **Nanodomains/lower symmetry phase**

2D XRD mapping of

2D XRD recorded in 2θ-χ plane
X-ray // $[100]_{STO}$

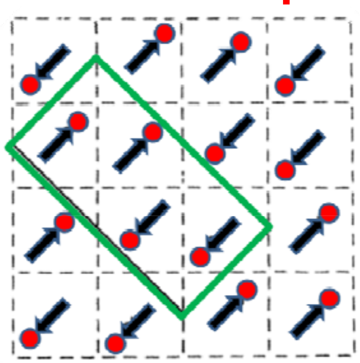


2d XRD image



1/4{011} spot

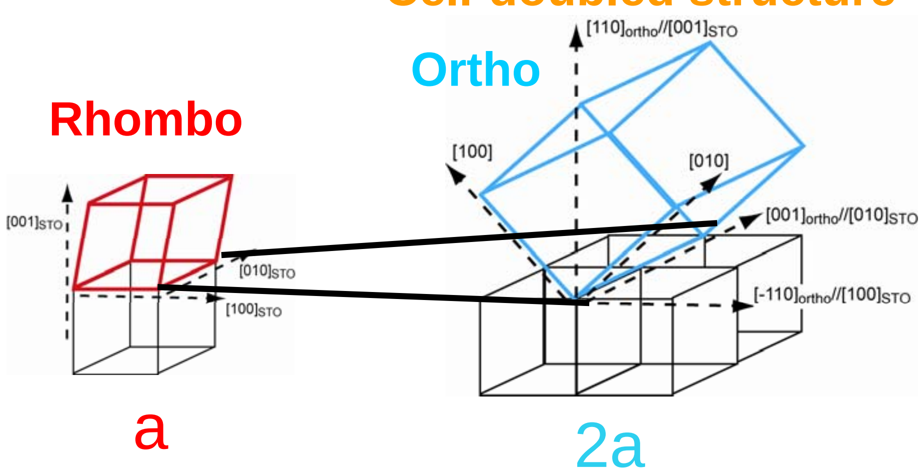
Anti-parallel cation displacements



($PbZrO_3$ like AFE)

$1/2\{0,1,0\}_{cubic}$ spot

Cell-doubled structure

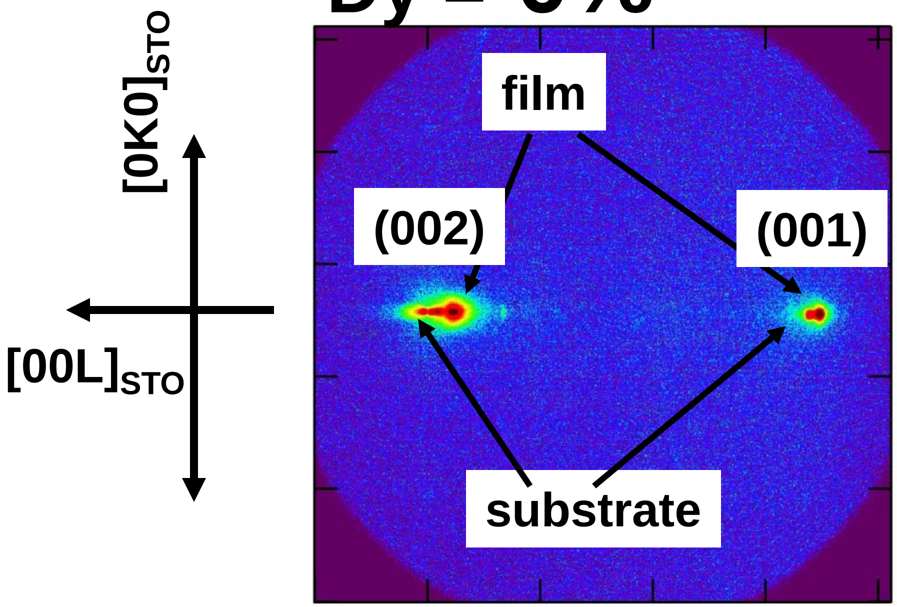


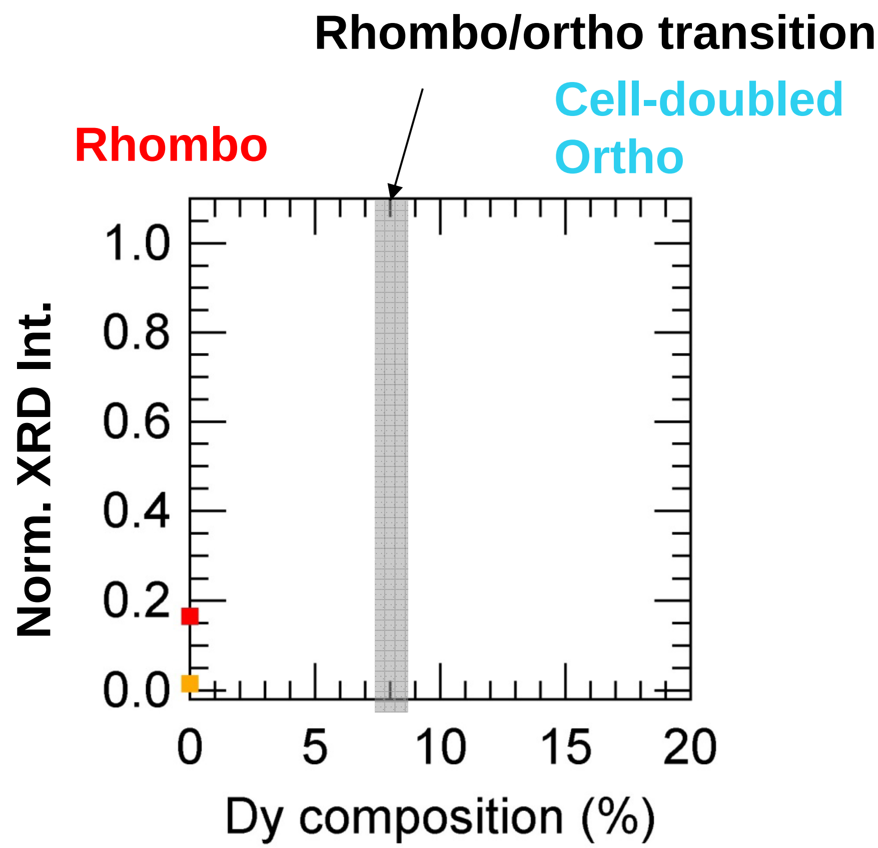
Structural transition of (Bi,Dy)FeO_3 films

2D XRD recorded in 2θ–χ plane

X-ray // $[100]_{STO}$

Dy = 0%





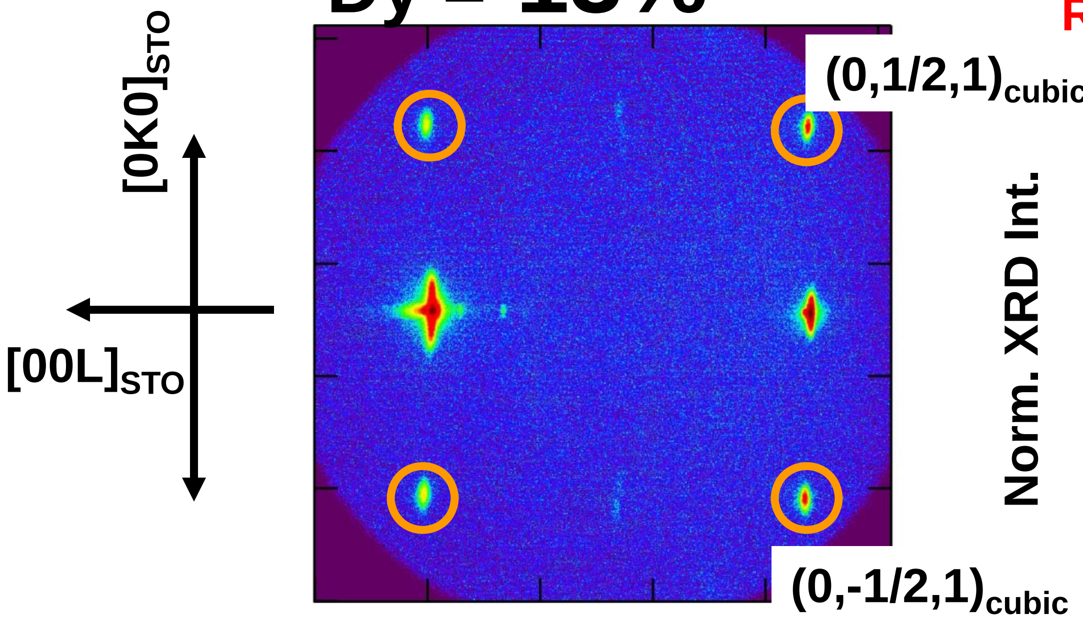
($PbZrO_3$ like AFE)

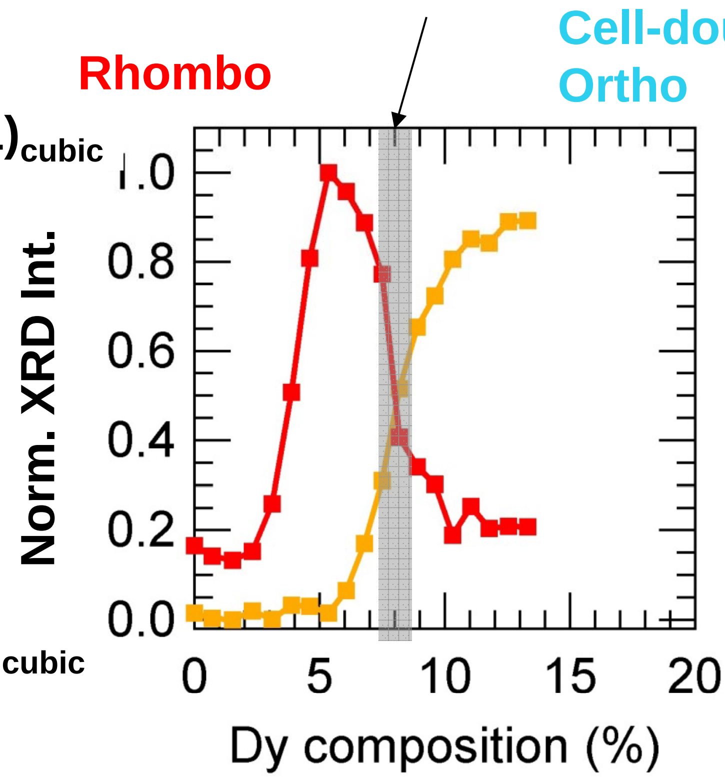
- **1/4{011} spot → Anti-parallel cation displacement**
- **$1/2\{0,1,0\}_{cubic}$ spot → Cell-doubled structure**

Structural transition of (Bi,Dy)FeO_3 films

2D XRD recorded in 2θ–χ plane

Dy = 13%





($PbZrO_3$ like AFE)

■ 1/4{011} spot → Anti-parallel cation displacement

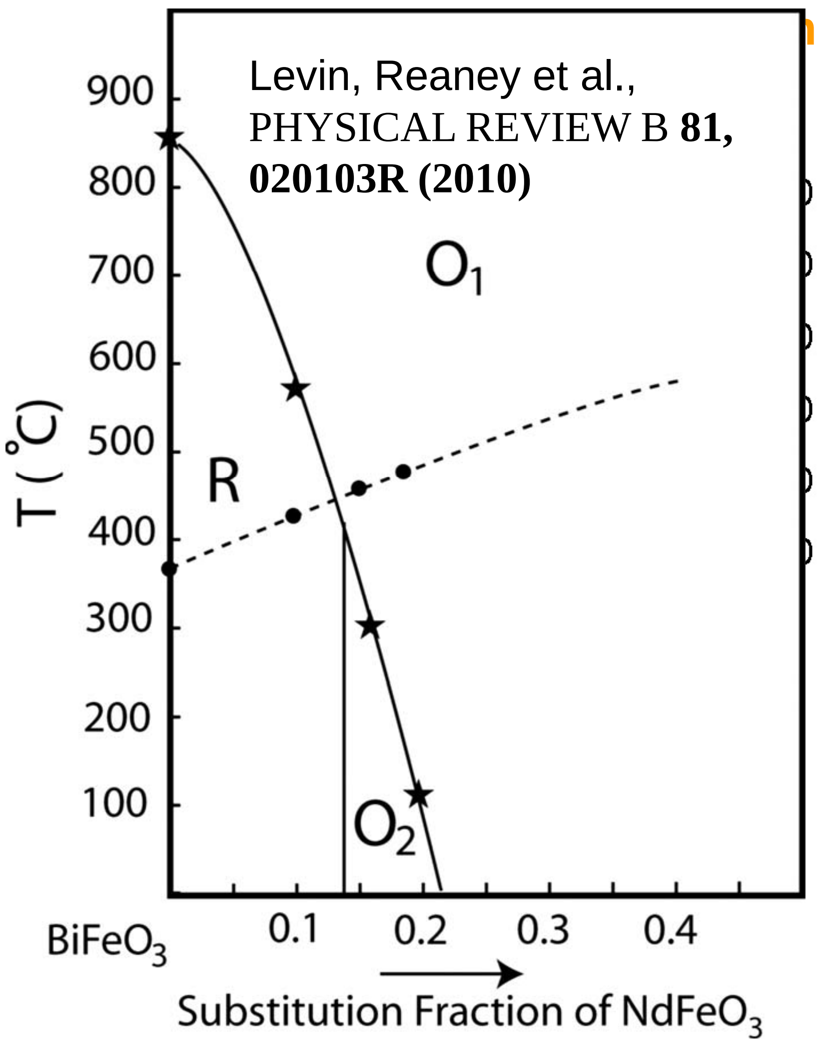
■ 1/2$\{0,1,0\}_{cubic}$ spot → Cell-doubled structure
Orthorhombic phase

Mapping universal phase diagram for RE-substituted $BiFeO_3$

tion displacement

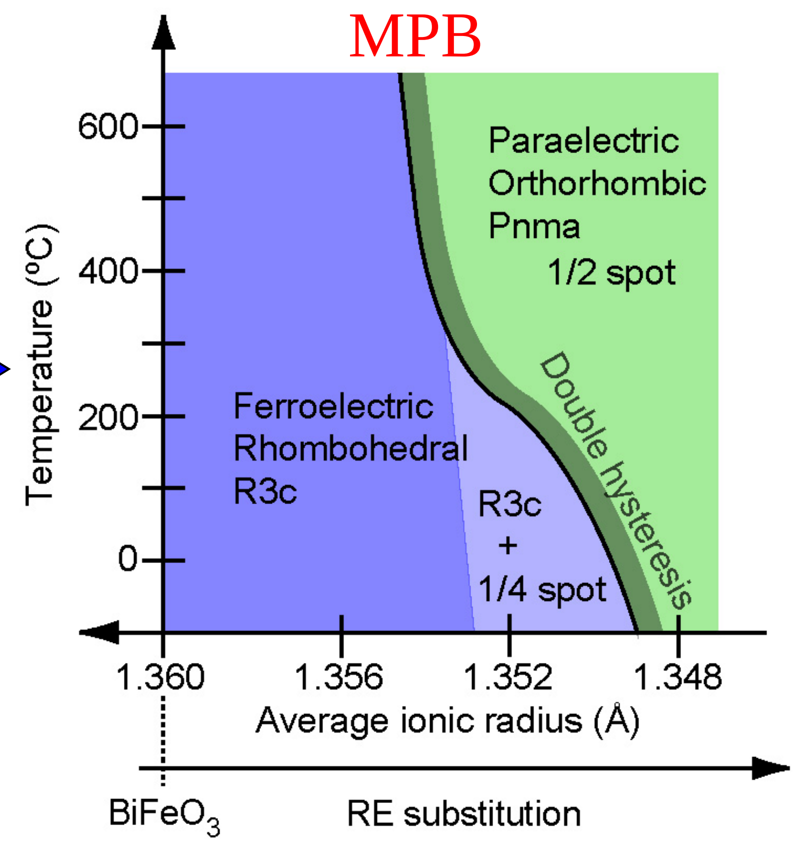
hombic phase

Bulk study: $Bi_{1-x}Nd_xFeO_3$



Levin, Reaney et al., PHYSICAL REVIEW B **81, 020103R (2010)**

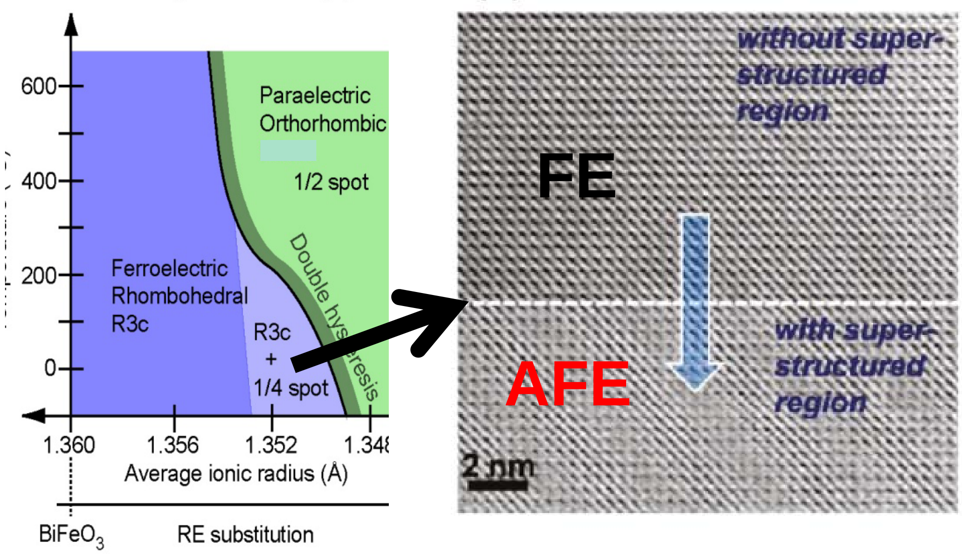
Phase diagram

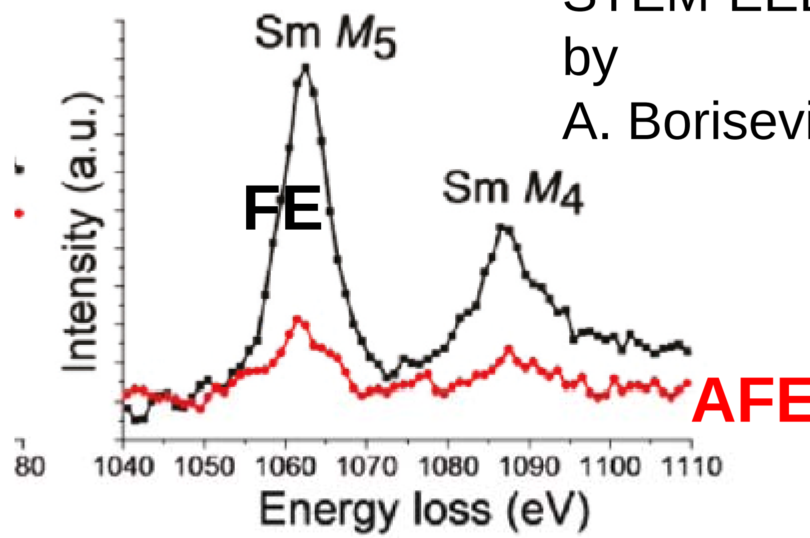


Advanced Functional Materials 20, 1108 (2010)

Chemistry of Antipolar cluster in FE matrix

(Chemistry of Materials 22, 2588 (2010))





STEM-EELS
by
A. Borisevich

Sm deficiency in the cluster!

Inhomogeneity due to synthesis ⟶ AFE phase?

Not likely : also observed in bulk
not present at any other compositions
always observed at fixed A-site radius

Intrinsic property ruled by local thermodynamics,
minimization of local polarization leads to RE deficient AFE phase

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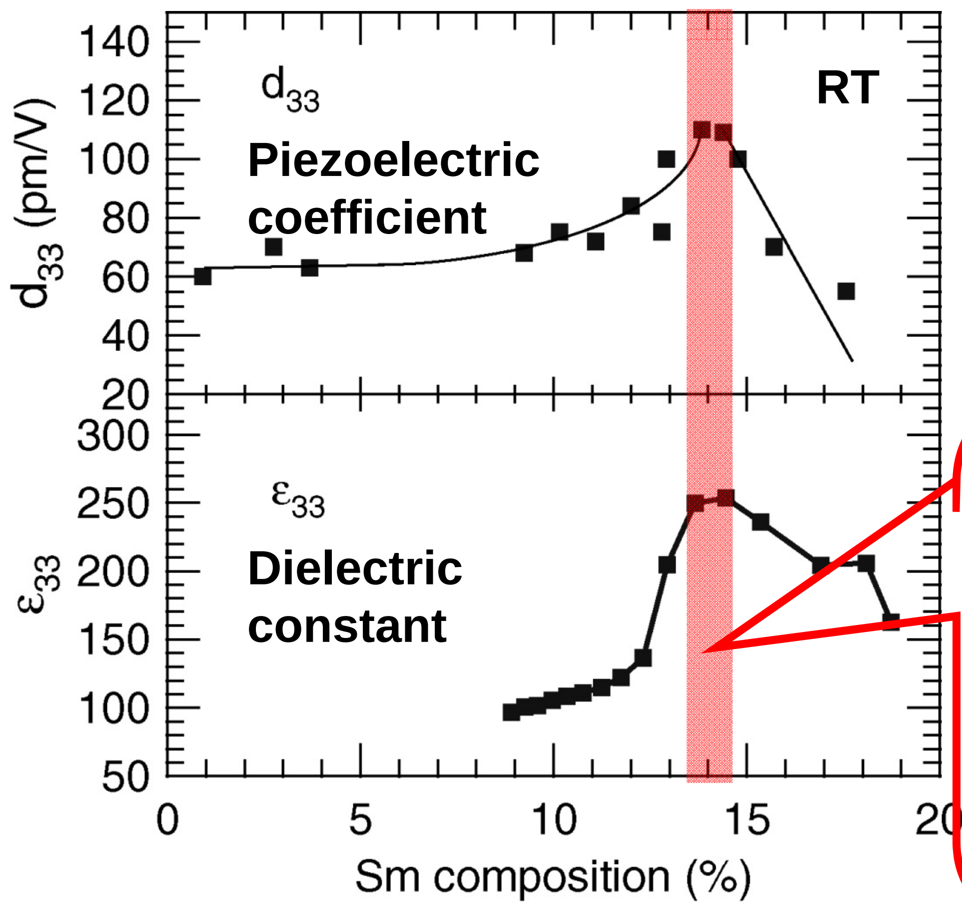
MPB in (Bi,Sm)FeO_3 thin films

S.Fujino, *et al*., APL 92 202904(2008).

Sm 14%

FE/Rhombo **MPB** **PE/Ortho**

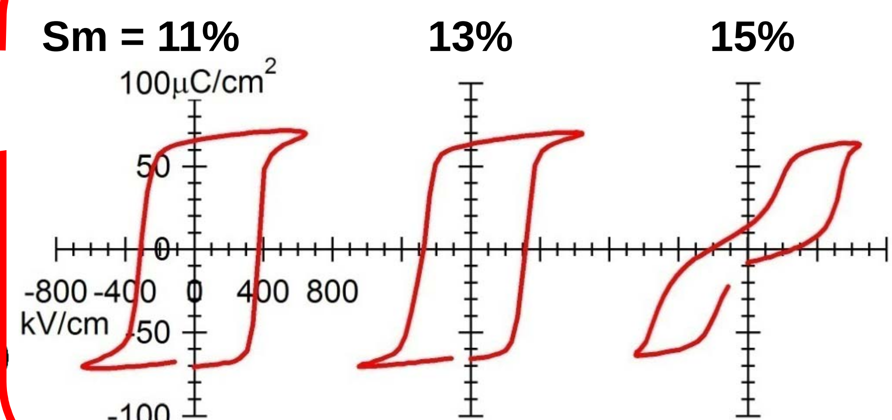


d_{33} at MPB : 110pm/V comparable to PZT

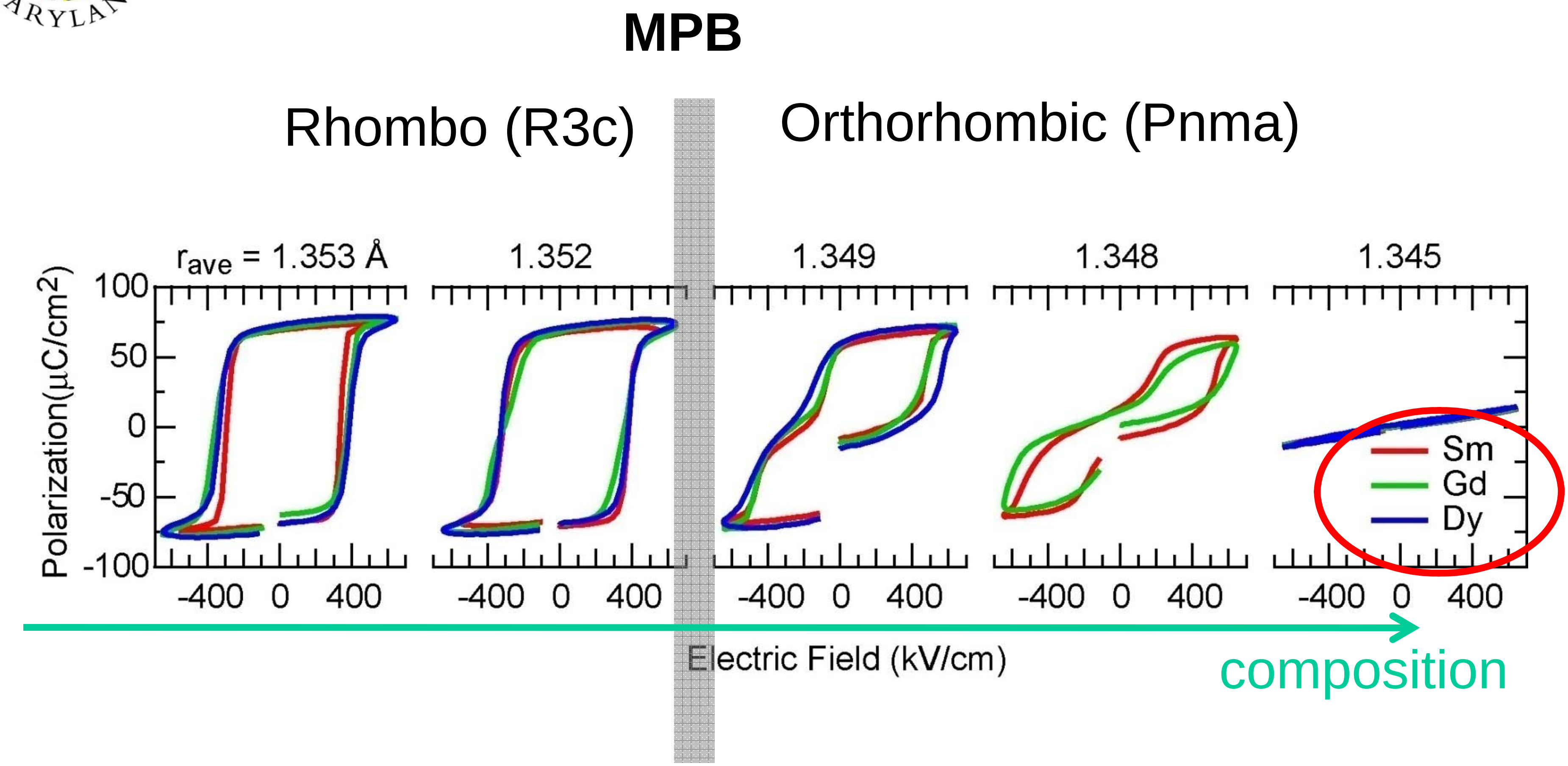
PZT film at MPB d_{33} : 160 pm/V

V. Nagarajan, *et al.,* APL **81**, 4215 (2002).

Evolution in PE across the transition



Universality in PE hysteresis loop evolution



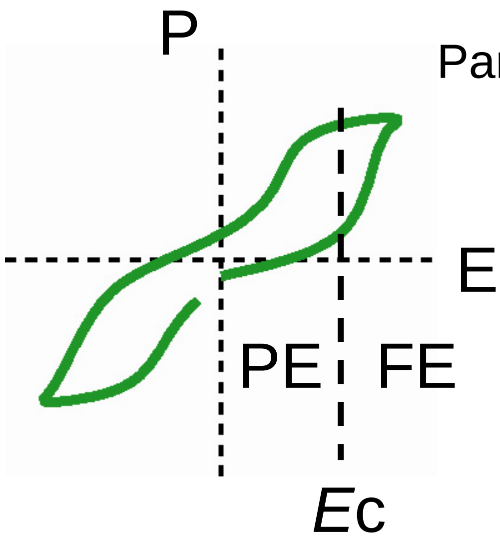
Double hysteresis loop always observed beyond the MPB

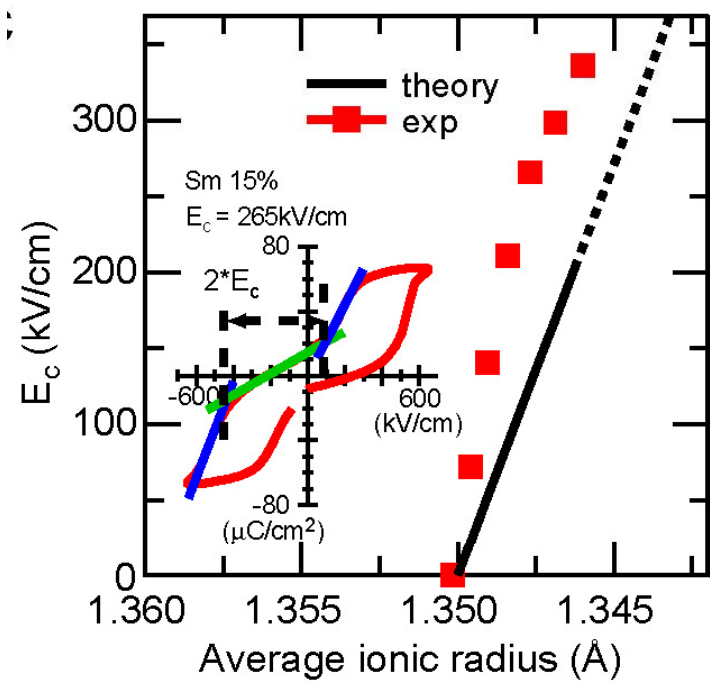
model for double-hysteresis loops

•**Electric-field structural transformation from the non-polar orthorhombic to polar rhombohedral phase** results in the double hysteresis loop at the boundary.

Paraelectric ortho → Polar rhombo

electric field



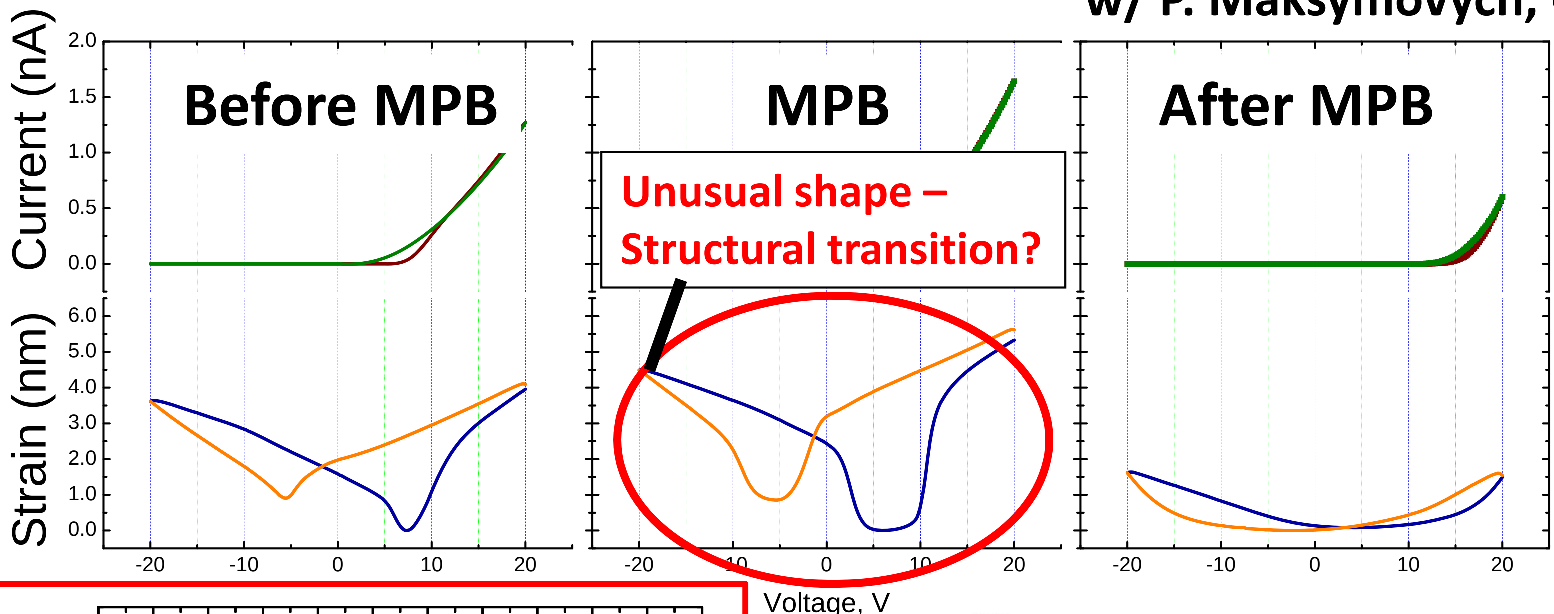


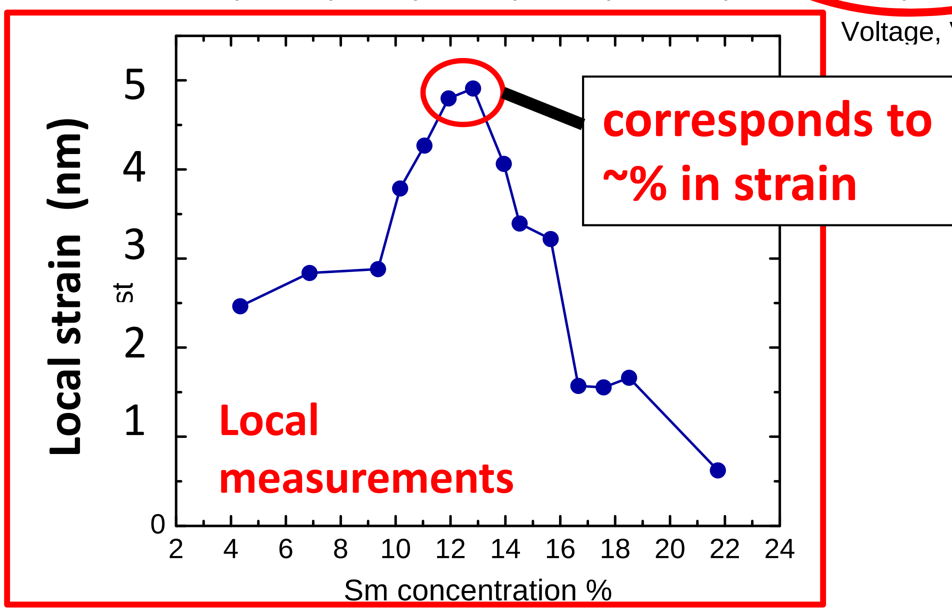
Achievable strain:
750-1000 pm/V

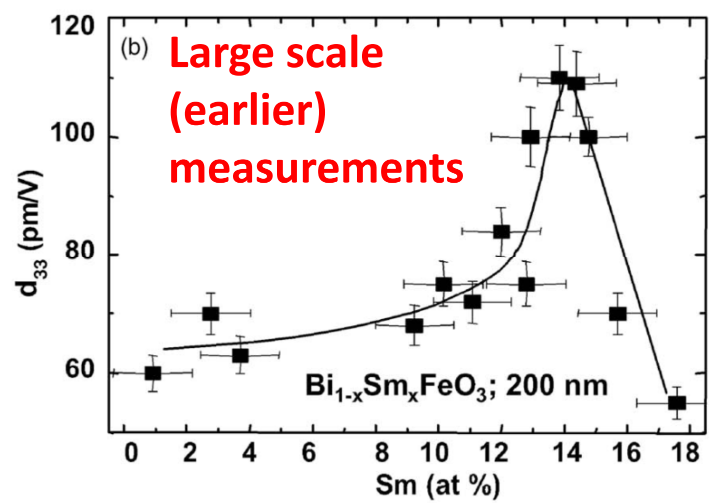
Observed: 110 pm/V
(difference between bulk and thin films)

Local strain measurements of (Bi,Sm)FeO_3 in high vacuum

w/ P. Maksymovych, ORNL

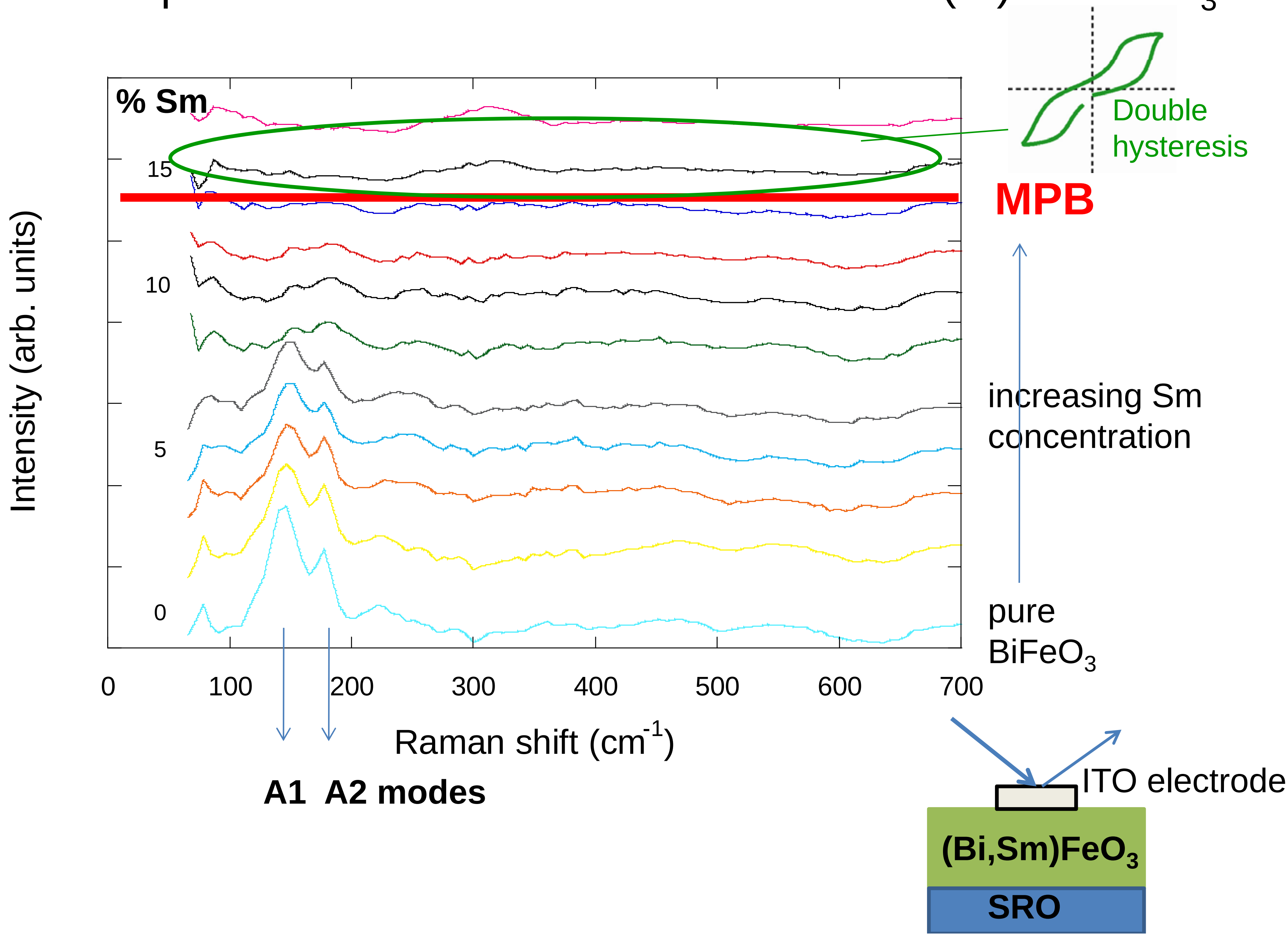




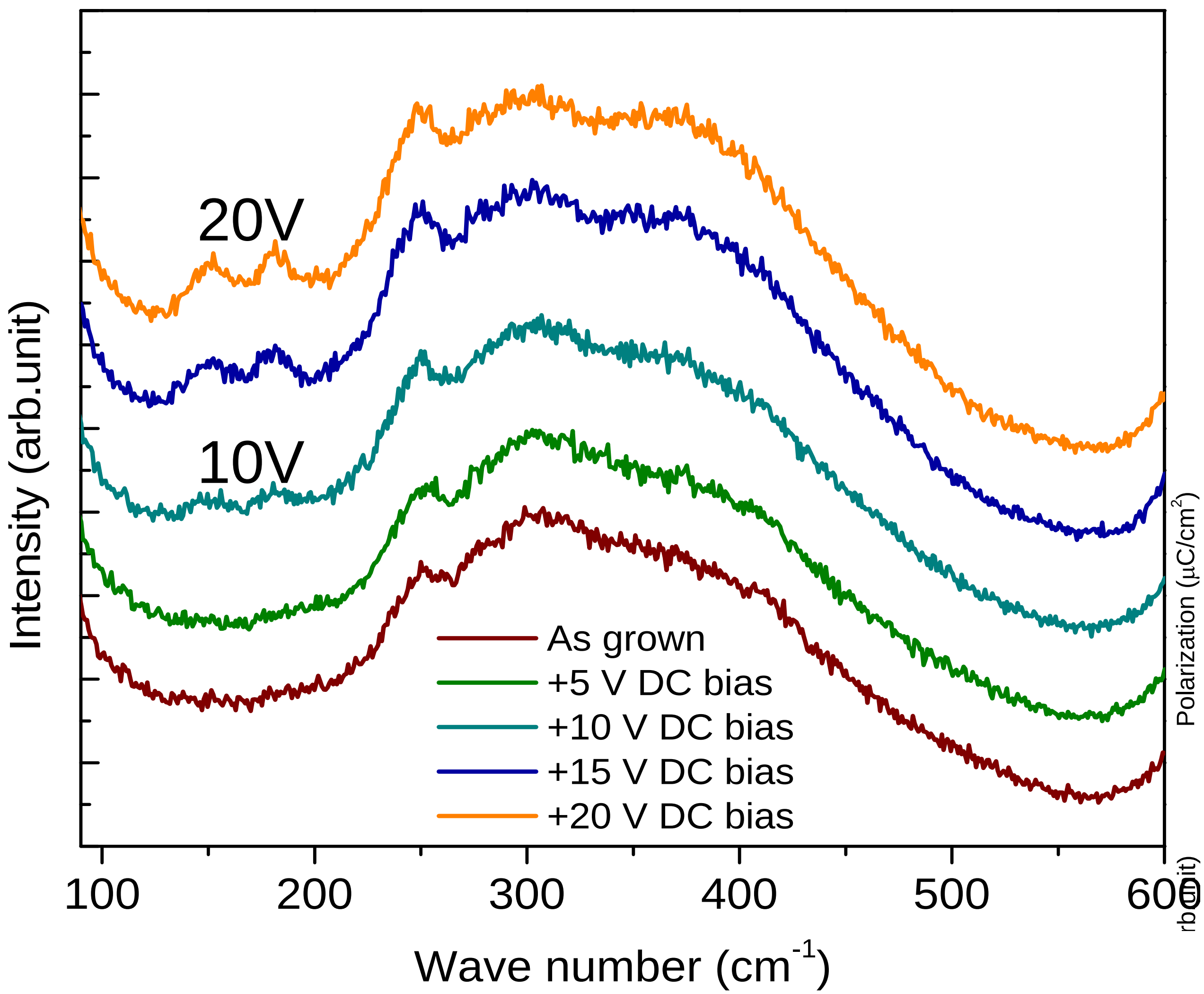


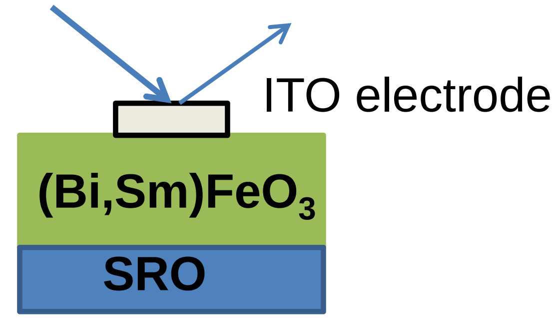
large response and sign of structural transition

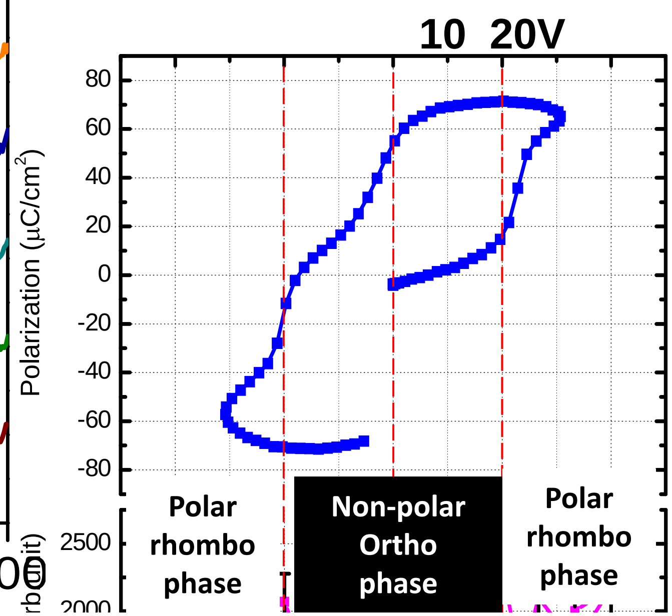
Raman spectra as a function of Sm substitution (%) in $BiFeO_3$



Raman spectrum as a function of voltage ($Bi_{0.85}Sm_{0.15}FeO_3$)



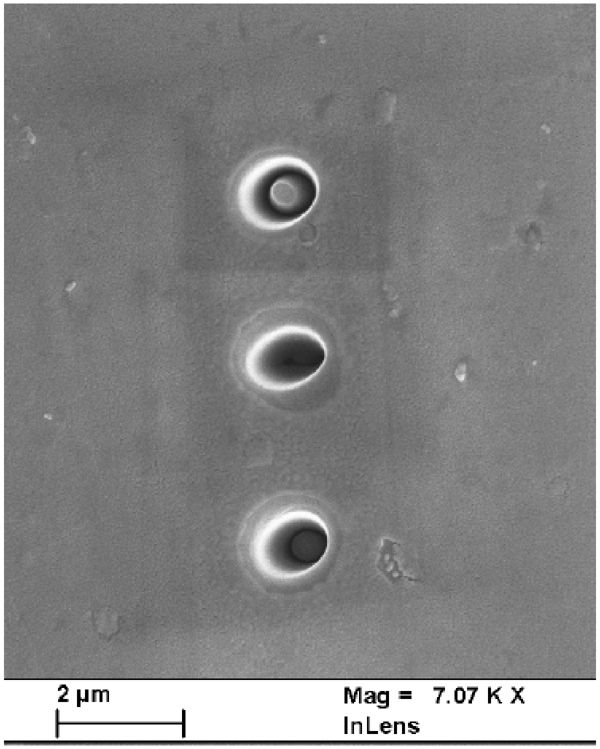




Electric-field induced structural change is confirmed

Theoretically predicted d_{33} ~1000 pm/V at MPB

Can we achieve this? Try fabricating nanopillars:



Top view SEM image of $(Bi,Sm)FeO_3$ film patterned by FIB

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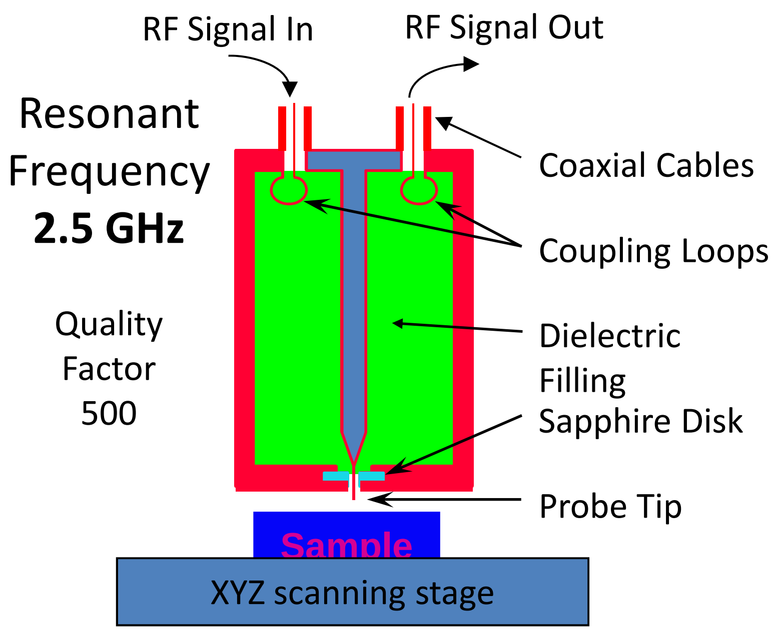
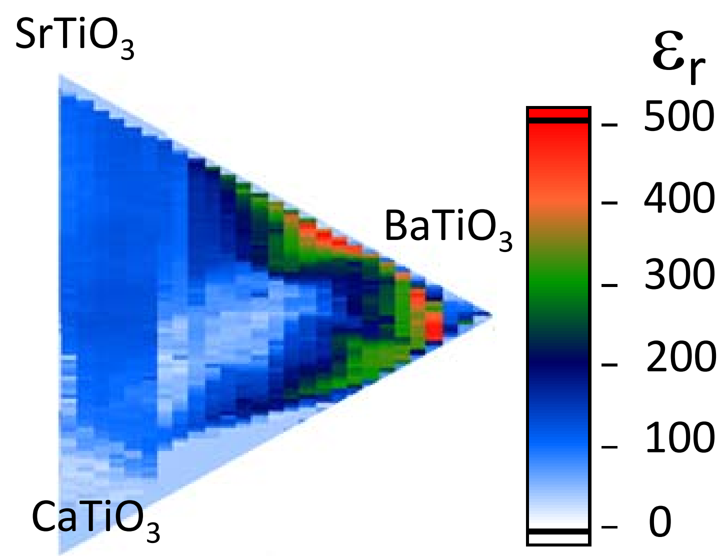
Microwave scanning probe as multifunctional screening tool

Coaxial Microwave Resonator

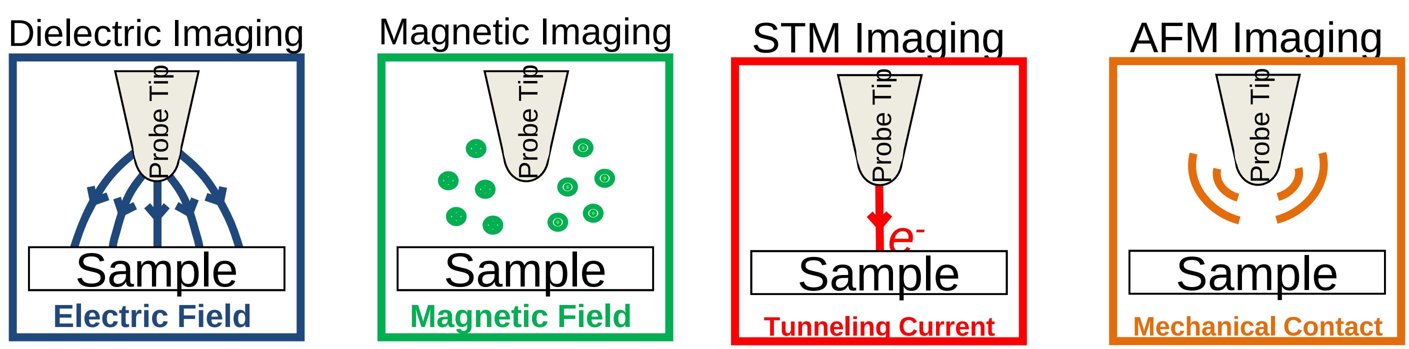


Meas. Sci. Technol. **16,** 248 (2005)

ε mapping of (Ba,Sr,Ca)TiO_3 library



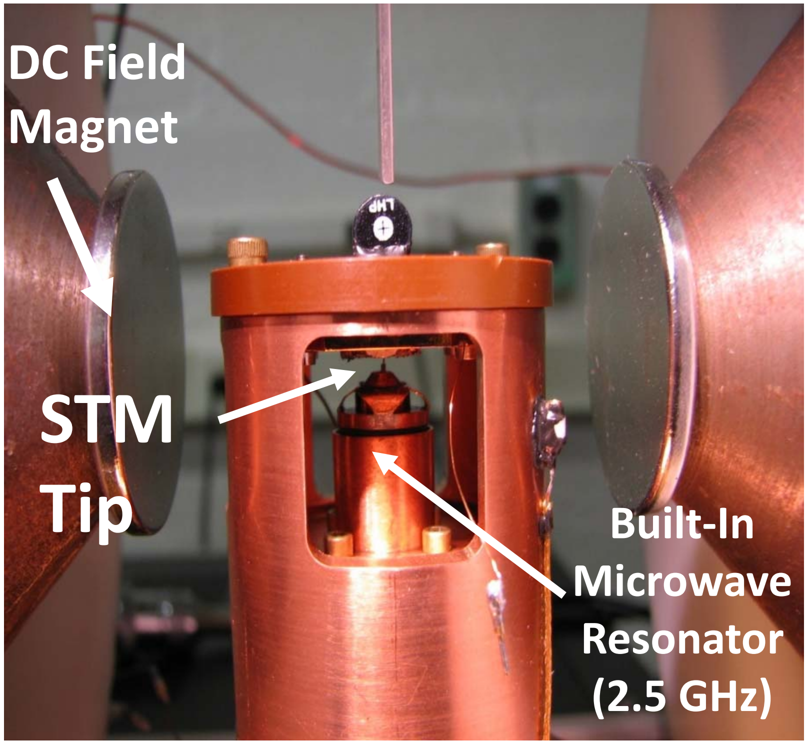
APL, **74**, 1165 (1999)



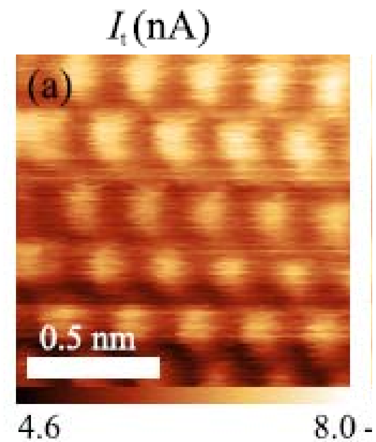
Different modes can be operated simultaneously

Atomic resolution microwave microscope/STM

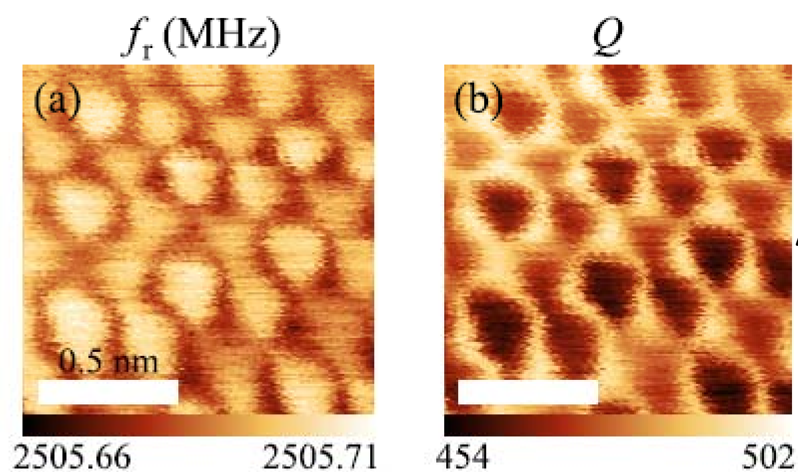
(APL 97, 183111 (2010))



Tunneling current



HOPG

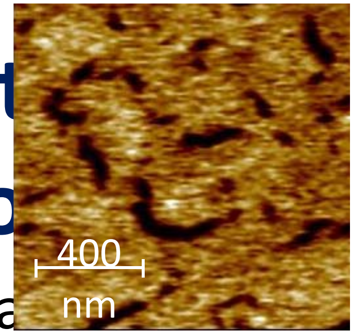


Au(111)

Atomic resolution images obtained with STM disabled –

surface approached using microwave feedback

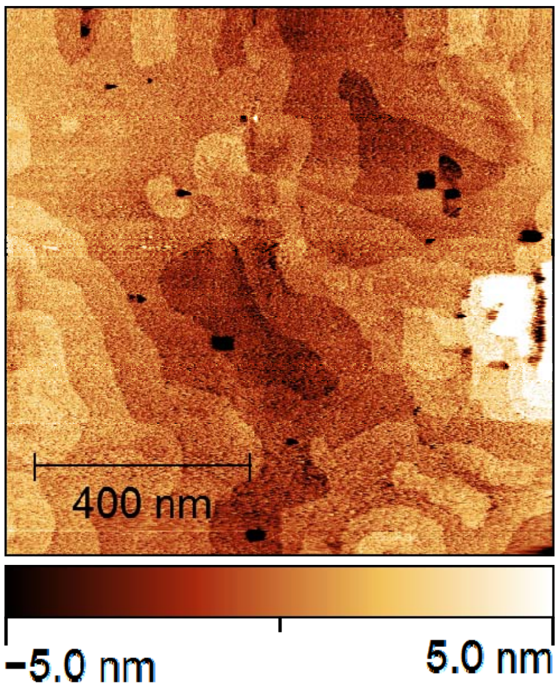
Microwave Response t
Voltage Mo



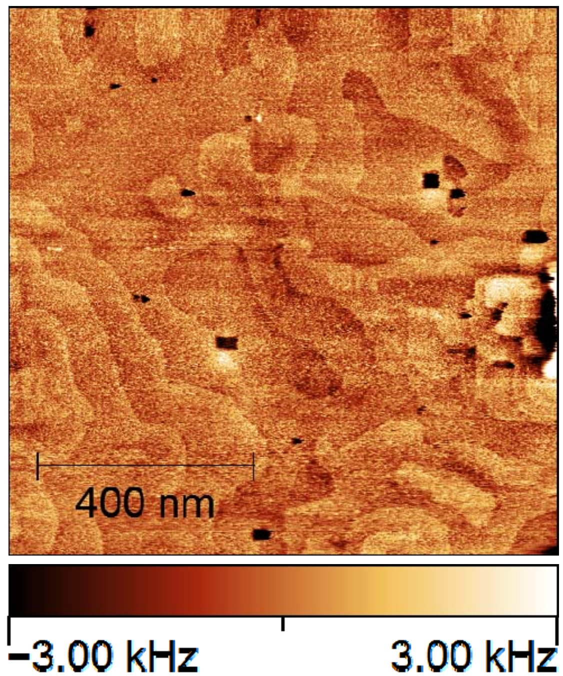
Out-of Plane PFM

Images are acquired simulta

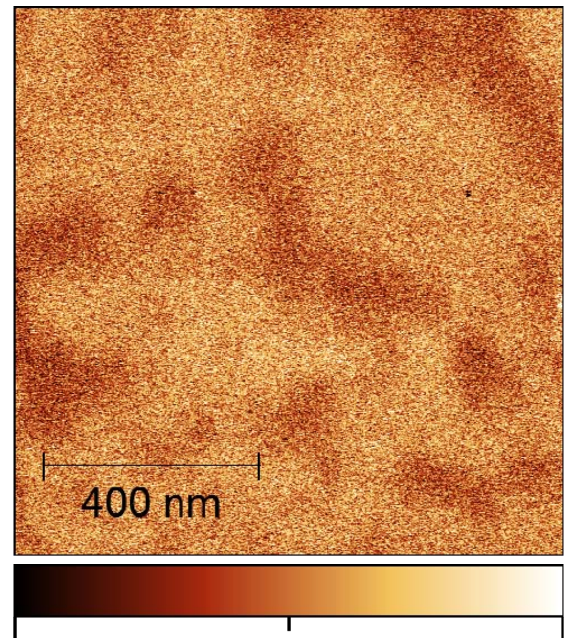
STM Topography



RF Frequency Shift



Lock-in on RF Frequency



Lock-in Signal → **Piezo Response?**
→ **Dielectric Non-linearity?**

Outline

- Combinatorial discovery of lead-free morphotropic phase boundary

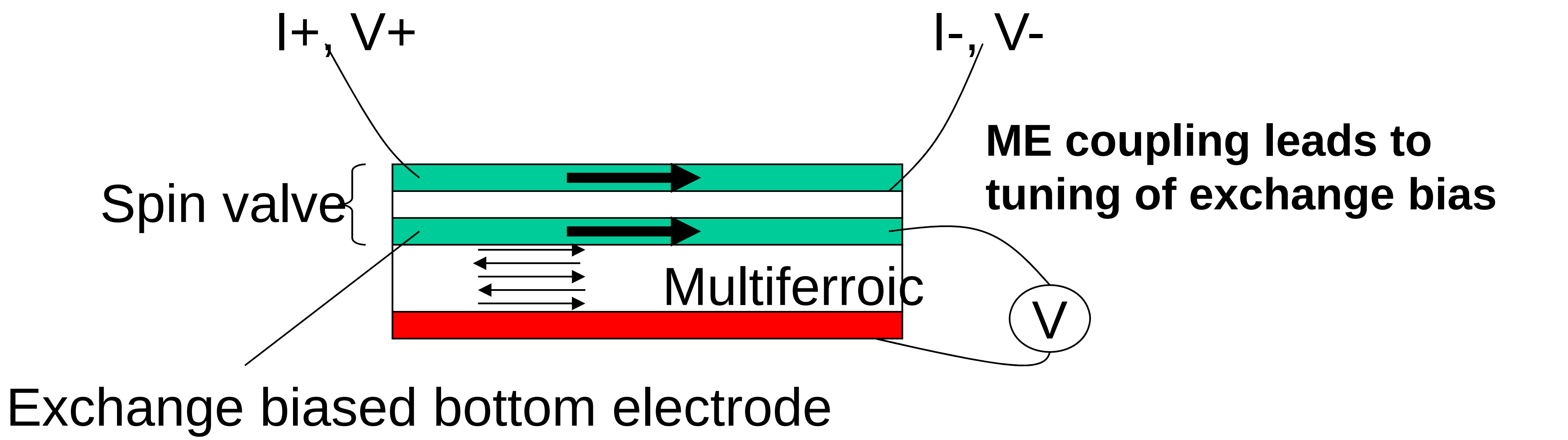
- E-field induced transition at the $Bi_{1-x}Sm_xFeO_3$ morphotropic phase boundary

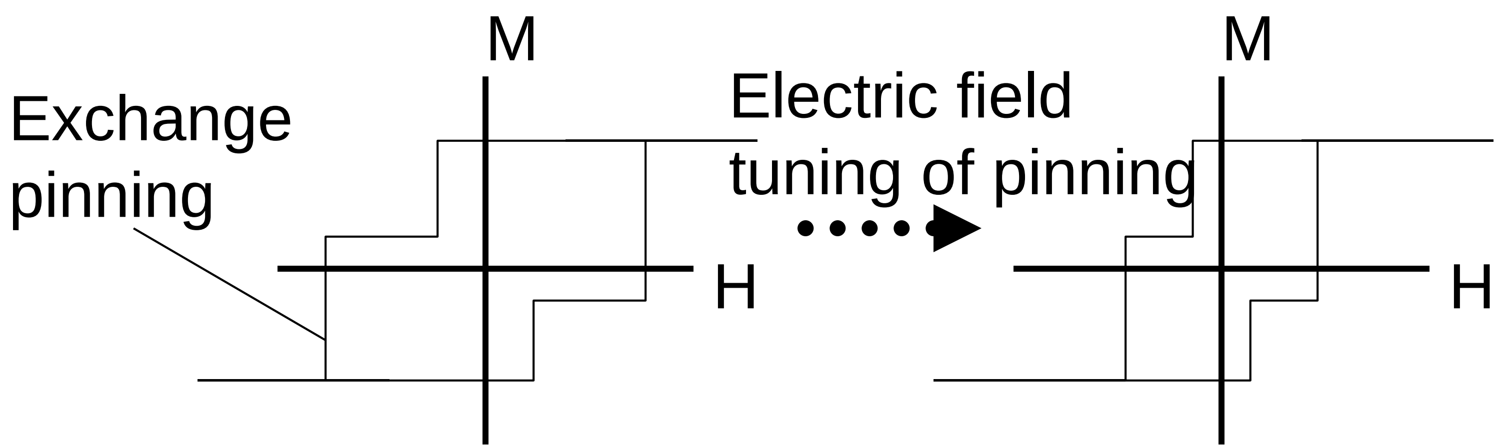
- Microwave microscope as a multifunctional screening tool

- Reversible switching of magnetic easy-axis in $Co/BiFeO_3$

Multiferroic spintronic devices using $BiFeO_3$ thin films

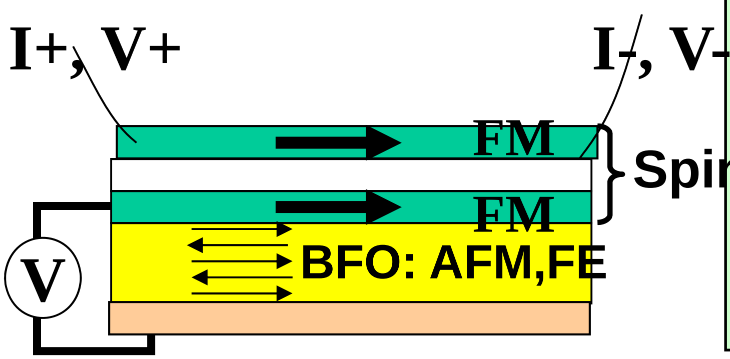
- Electric field control of magnetization,
- Biferroic memory device
- Use AFM for room temperature exchange biasing

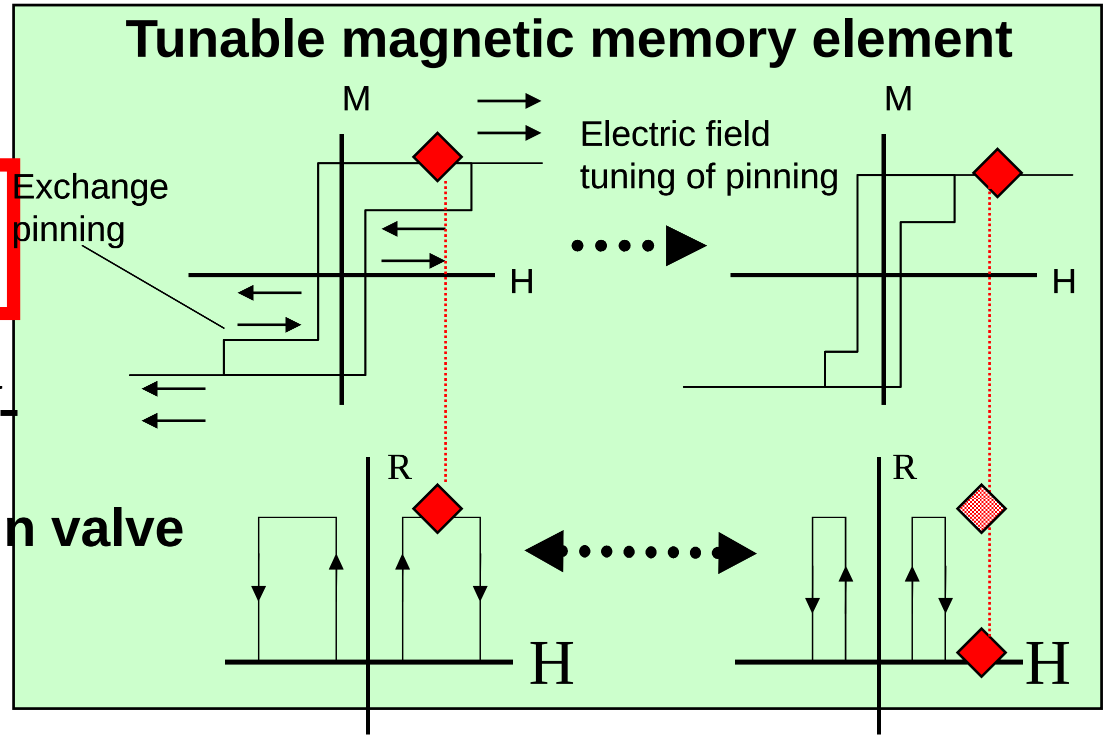


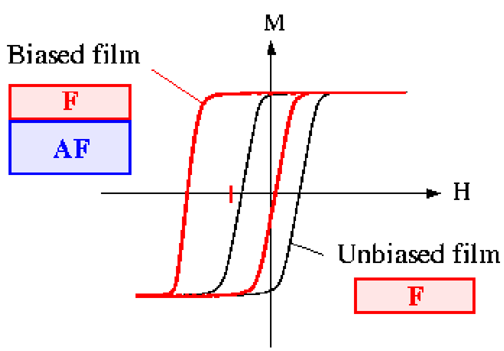


Spin valve + multiferroic

ME coupling leads to tuning of exchange bias







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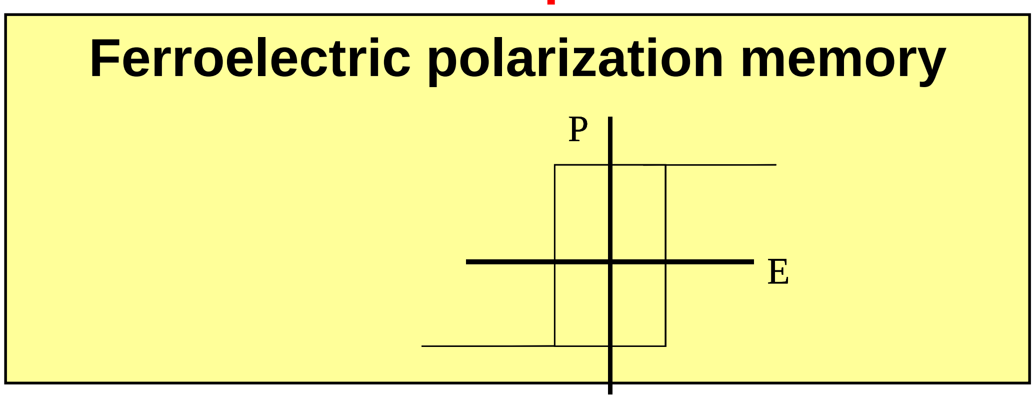
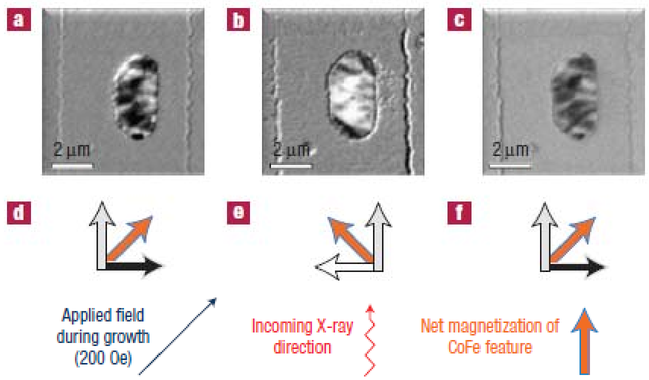


Exchange bias and E-field tuning of magnetism w/ $BiFeO_3$ thin films

Electric-field control of local ferromagnetism using a magnetoelectric multiferroic

nature materials | VOL 7 | JUNE 2008 |

YING-HAO CHU[1,2,3*], LANE W. MARTIN[1,3*†], MIKEL B. HOLCOMB[2,3], MARTIN GAJEK[2], SHU-JEN HAN[4], QING HE[2], NINA BALKE[2], CHAN-HO YANG[2], DONKOUN LEE[4], WEI HU[4], QIAN ZHAN[1,2], PEI-LING YANG[1,2], ARANTXA FRAILE-RODRÍGUEZ[5], ANDREAS SCHOLL[6], SHAN X. WANG[4] AND R. RAMESH[1,2,3]



APPLIED PHYSICS LETTERS **95**, 182503 (2009)

Coengineering of ferroelectric and exchange bias properties in $BiFeO_3$ based heterostructures

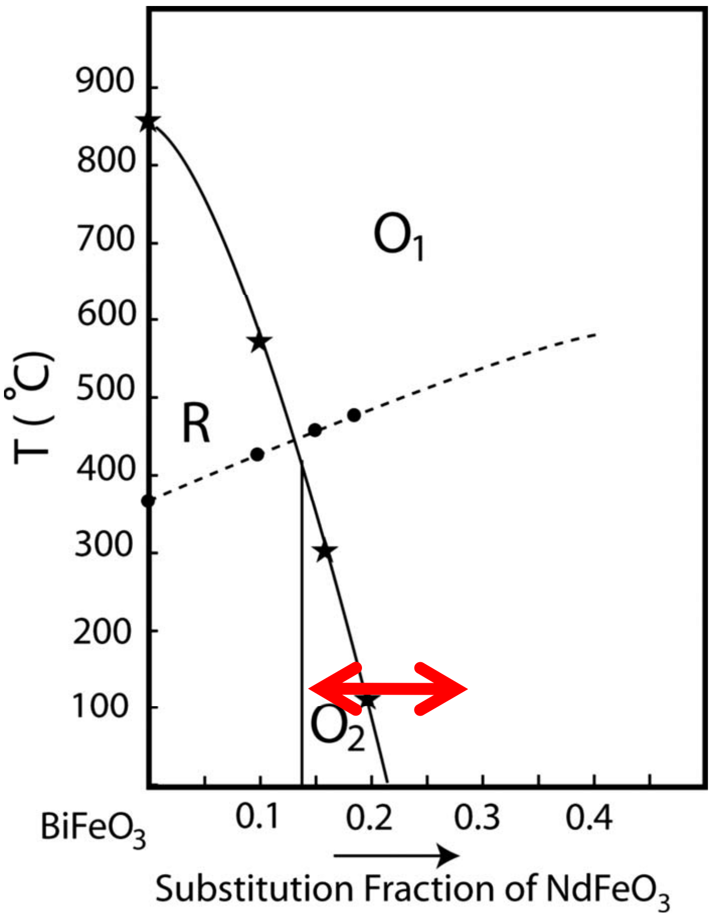
J. Allibe,[1] I. C. Infante,[1] S. Fusil,[1,2] K. Bouzehouane,[1] E. Jacquet,[1] C. Deranlot,[1] M. Bibes,[1,a)] and A. Barthélémy[1,b)]
[1]*Unité Mixte de Physique CNRS/Thales, 1 Av. A. Fresnel, Campus de l'Ecole Polytechnique, 91767 Palaiseau, France and Université Paris-Sud, 91405 Orsay, France*
[2]*Université d'Evry-Val d'Essonne, Bd. F. Mitterrand, 91025 Evry Cedex, France*

Magnetic transition at the structural boundary

PHYSICAL REVIEW B 81, 020103(R) (2010)

Reorientation of magnetic dipoles at the antiferroelectric-paraelectric phase transition of $Bi_{1-x}Nd_xFeO_3$ ($0.15 \leq x \leq 0.25$)

Igor Levin,[1,*,†,§] Sarah Karimi,[2] Virgil Provenzano,[1] Cindi L. Dennis,[1] Hui Wu,[1] Tim P. Comyn,[3] Tim J. Stevenson,[3] Ronald I. Smith,[4] and Ian M. Reaney[2,*,‡,§]



Magnetic transition

\+

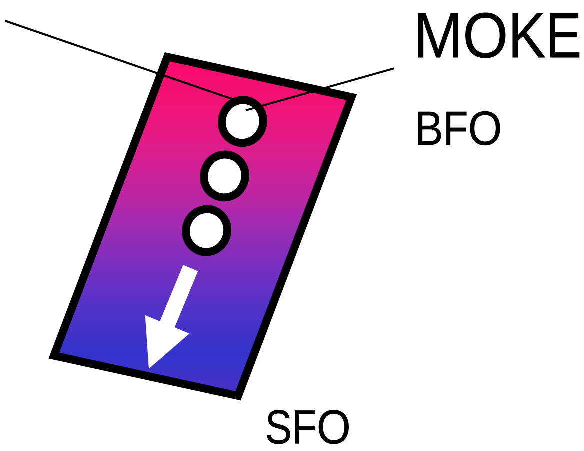
E-field induced transition

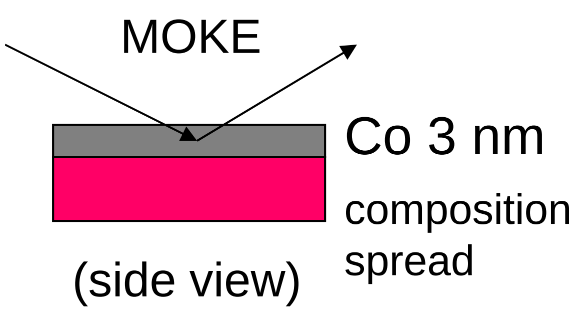
↓

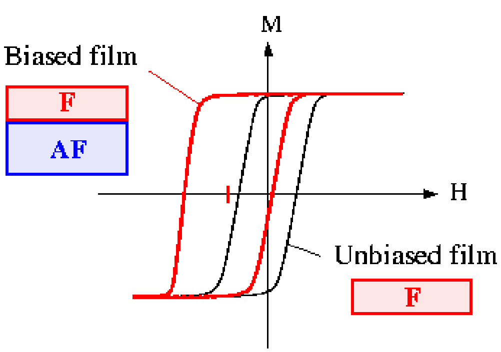
E-field control of magnetism

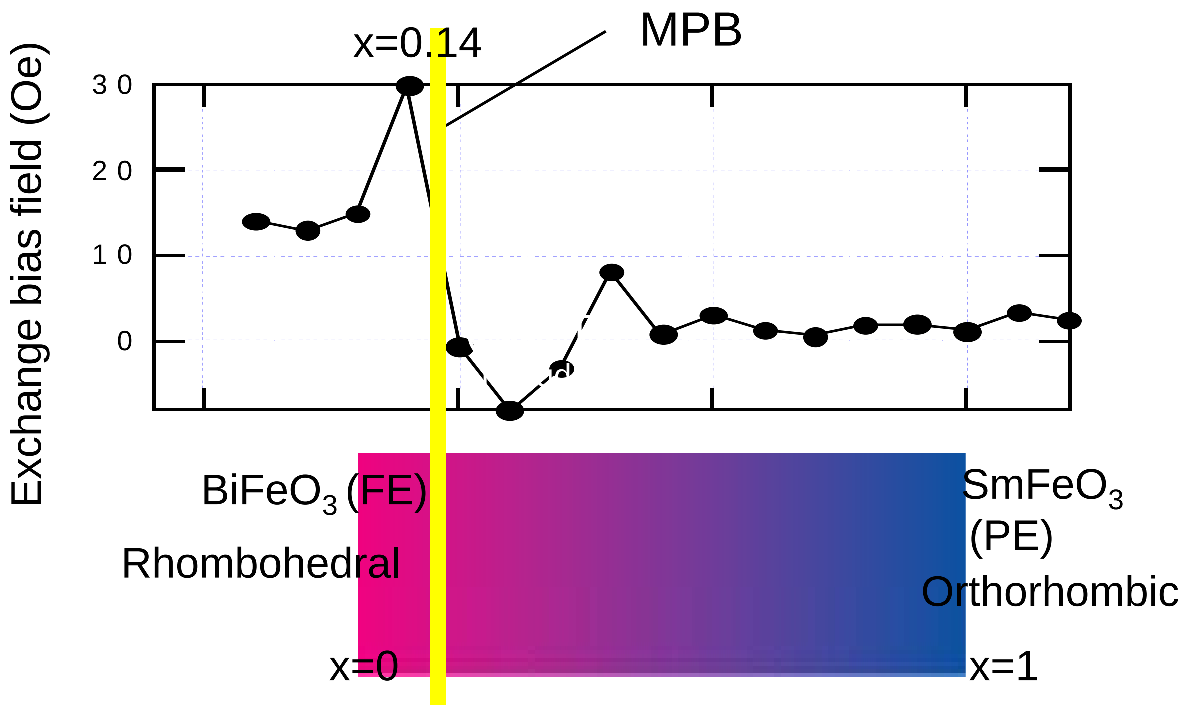
Exchange bias on Co/(Bi,Sm)FeO_3 composition spread

scanning magneto-optical Kerr effect (MOKE) measurement









Abrupt change in exchange bias is observed at the MPB

Electric-field tunable exchange bias?

Summary and more

- Combinatorial approach can be used to look for MPBs and other interesting structural boundaries

- Field-induced transformation explains the double hysteresis and enhancement in d_{33} (value is double that of pure BFO)

- Microwave microscopy is a versatile multifunctional screening tool

- Reversible switching of easy axis of Co coupled to $BiFeO_3$ is achieved, but how are FE and AFM domains coupled?