Multifunctional Nanostructures for Magnetoelectrics and Spintronics Applications

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Research Theme

- The Objective of the Project is to design and develop nano-structured multi-functional materials for next generation microelectronic devices by combining magnetic, electrical, and/or mechanical properties.

We chose to investigate magnetoelectric and spintronic materials since these can perform more than one task at low power, faster speed, and lead towards the device miniaturization

Spintronics

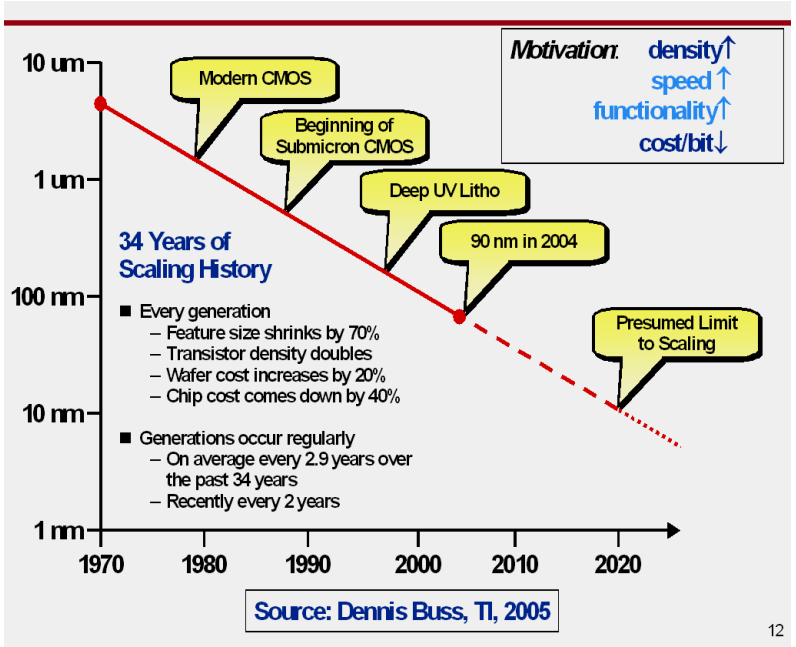
- ***The new class of electron devices based on charges and spins of the electrons***

- ***Enhancement of multifunctionality of devices, i.e. processing and data storage in the same chip***

- ***Spin can be easily manipulated by externally applied electric/magnetic field***

- ***Higher spin relaxation time and long coherence length keep the spin state unchanged compared to the charge state***

- ***Spin flipping is faster process and it consumes less energy***



Moore's law

SPINTRONICS REQUIREMENTS

- Source of spin Polarized carriers
- Efficient spin injection
- Slow spin relaxation
- Reliable spin detection

Source of spin polarized carriers:

- **Ferromagnets, Magnetic Semiconductors** e.g. EuO**, Dilute Magnetic Semiconductor (DMS),** etc

Efficient spin injection:

- **Low resistance to avoid scattering at the interface**
- **Low lattice mismatch & defect free interface to enhance spin injection**

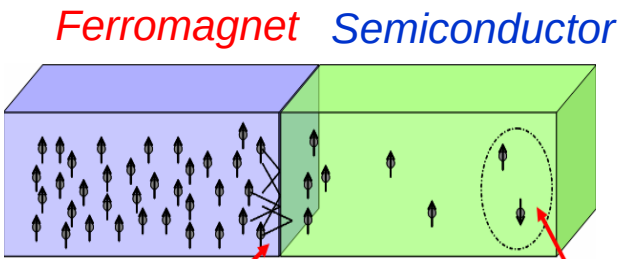
Slow spin relaxation:

- **Long spin coherence time (e.g. ~ 100 ns in semiconductor) due to low spin-orbit interactions**

Spintronics – *Problems and Challenges*

Transfer of Spin polarized carriers from FM to Semiconductor: ~ 1.0%

- ✓ **Large difference in the *conductivities* between *FM* and *semiconductor* ($\gamma \approx \sigma_S/\sigma_M << 1$); severely inhibits spin injection**



- ✓ **Interface defects caused by lattice mismatch limiting the spin injection efficiency**
- ✓ **Magnetic atoms diffuse to semiconductor (close to interface); electrons scatter between the two different spin channels, degrading the injected spin polarization**

❖ **For Sufficient spin injection the conductivity and lattice should be closely matched or the contact interface is 100% spin polarized**

➢ Semiconductors (e.g. DMS) that Exhibit net Spin Polarization are ideal for spin injection!"

- ✓ **Low lattice mismatch**
- ✓ **Defects free/epitaxial interface growth is possible**
- ✓ **Comparable conductivity**

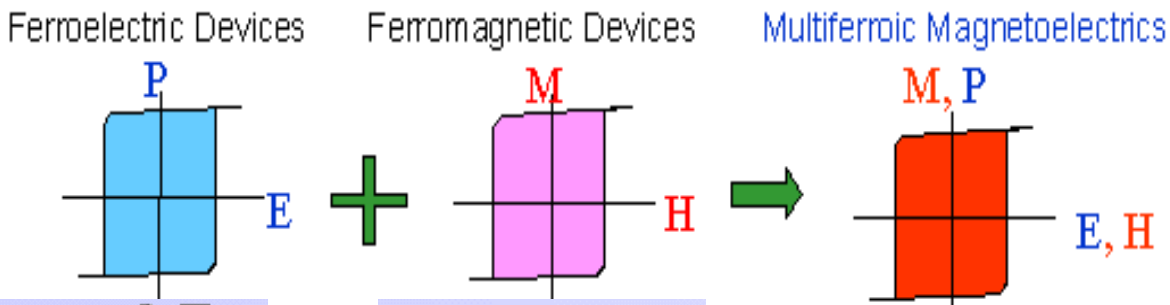
➢ Tunnel barriers at the interface between FM/semiconductor can also transfer net polarized spin to the semconductor"

Potential applications of Spintronic Nanostructures

- Fast Read-head due to giant magneto-resistance (GMR) and tunneling magneto-resistance (TMR)
- Spin valves
- Spin transistors
- Spin LED
- Sensors
- MRAM (NVRAM)
- Quantum computing (Qbit)

Magnetoelectrics

Magnetoelectrics are essentially multiferroics with coupling between magnetic and electrical order parameters. **Technological interest** is enhanced due to an additional degree of freedom, i.e. switching of magnetic bits by electric field and vice versa by virtue of ME coupling..



$$P_i = \epsilon_0 \chi^e_{ij} E_j$$

$$M_i = \chi^m_{ij} H_j$$

$$P_i = \epsilon_0 \chi^e_{ij} E_j + \frac{1}{c} \alpha_{ij} H_j$$

$$M_i = \chi^m_{ij} H_j + \frac{1}{\mu_o c} \alpha_{ji} E_j$$

Problems and Challenges:

- Only a few single-phase materials exist in nature
- Weak coupling between electric field and magnetic order parameters
- Designing multilayer nano-structures for enhancing ME couplings.

Spalding et. al., Science Vol 309, 391-392 (2005)

Potential applications of Multiferroic Nanostructures

- Multi-state memory (NVRAM) devices
- Electric field controlled ferromagnetic resonance devices
- Magnetic field induced changes in electric polarization – magnetic sensor
- Actuators and transducers (NEMS)- magnetic/electric control gives additional degree of freedom
- Dual tunability for microwave (FAME) devices resulting in efficient transfer of power
- As negative index materials (NIM)
- In spintronic devices

Summary of the Progress Report

(September 2008- June 2009)

- *Spintronics*: Dilute Magnetic Semiconductors $Zn_{1-x}TM_xO$, TM=Co, Cu
  ZnO composite fibers and nanoribbons
  Metal silicides: micro- and nano-rods

- *Natural Multiferroic:* $BiFeO_3$, doped $BiFeO_3$
- *New single phase room temperature multiferroic:*

  $PbFe_{0.667}W_{0.333}O_3 : PbZr_{0.53}Ti_{0.47}O_3$ (20:80)

- *Artificially engineered magnetoelectric multilayer nanostructures:*

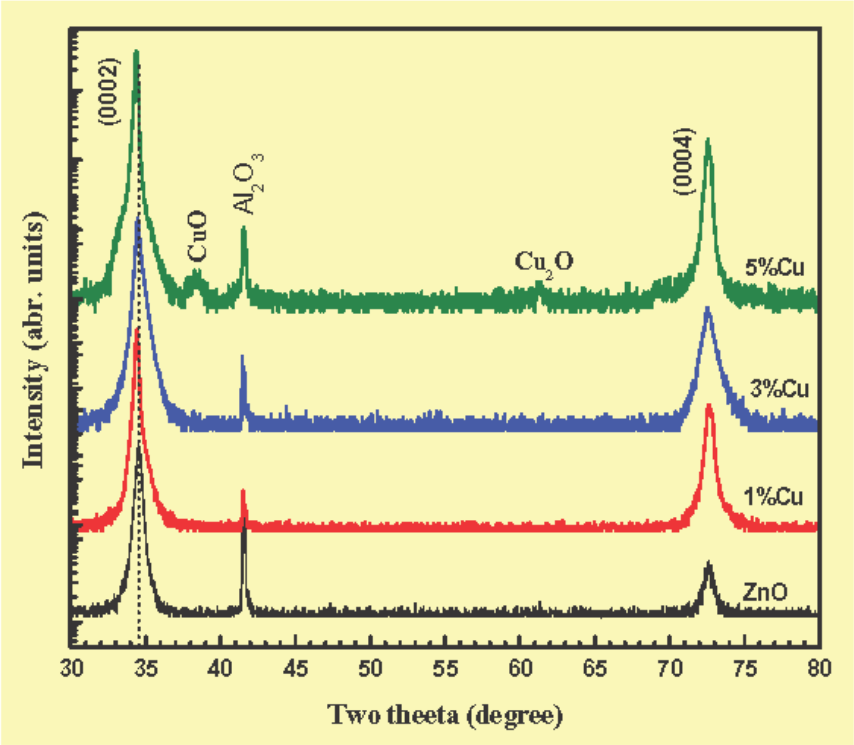
  $PbZr_{0.53}Ti_{0.47}O_3/CoFe_2O_4$
  $Ba_{1-x}Sr_xTiO_3$ (BSTO)/ $La_{2/3}Sr_{1/3}MnO_3$ (LSMO)
  PZT/PFW superlattices

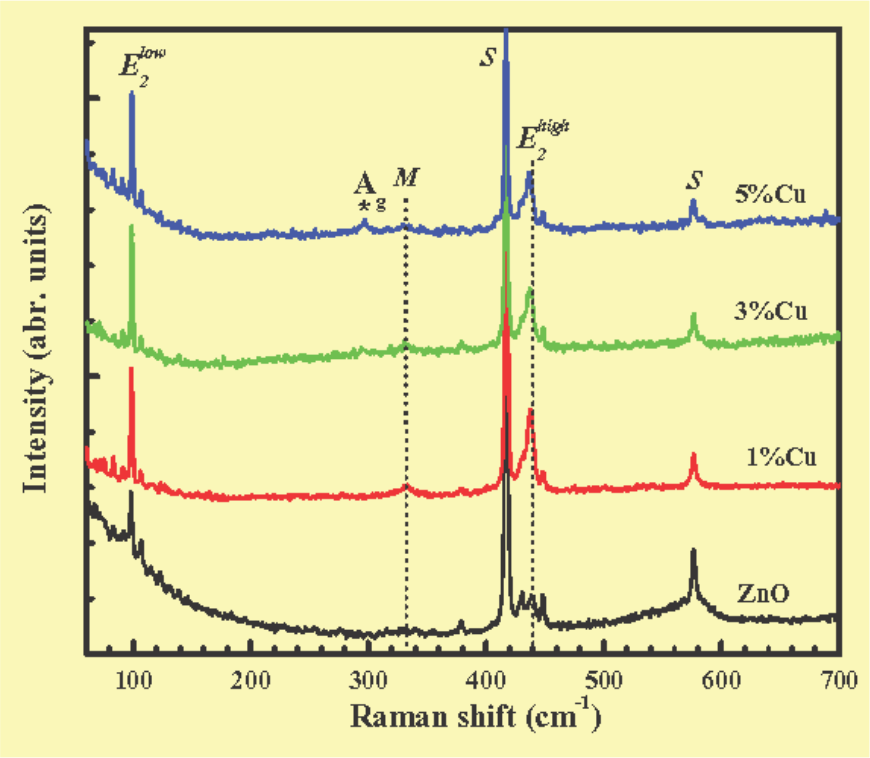
Importance of ZnO for Optoelectronics and Spintronics Devices

- Wide bandgap (3.3 EV); highly transparent (~90%); a potential TCO
- High excitonic binding energy (60 meV) and small excitonic Bohr radius (~ 1.8 nm), may give RT excitonic lasing at low threshold
- Suitable for Blue/Green and UV Light Emitting Diode (LED) fabrications
- Schottky Junction as a UV detector
- Magnetic impurity doped ZnO is promising DMS for Spintronics applications; like, spin-LED, Magnetic bipolar transistors, spin-FET, etc.

❖ **We have successfully synthesized single phase thin films of Cu (≤ 3%) and Co (≤ 10%) doped ZnO by pulse laser deposition (PLD) technique**

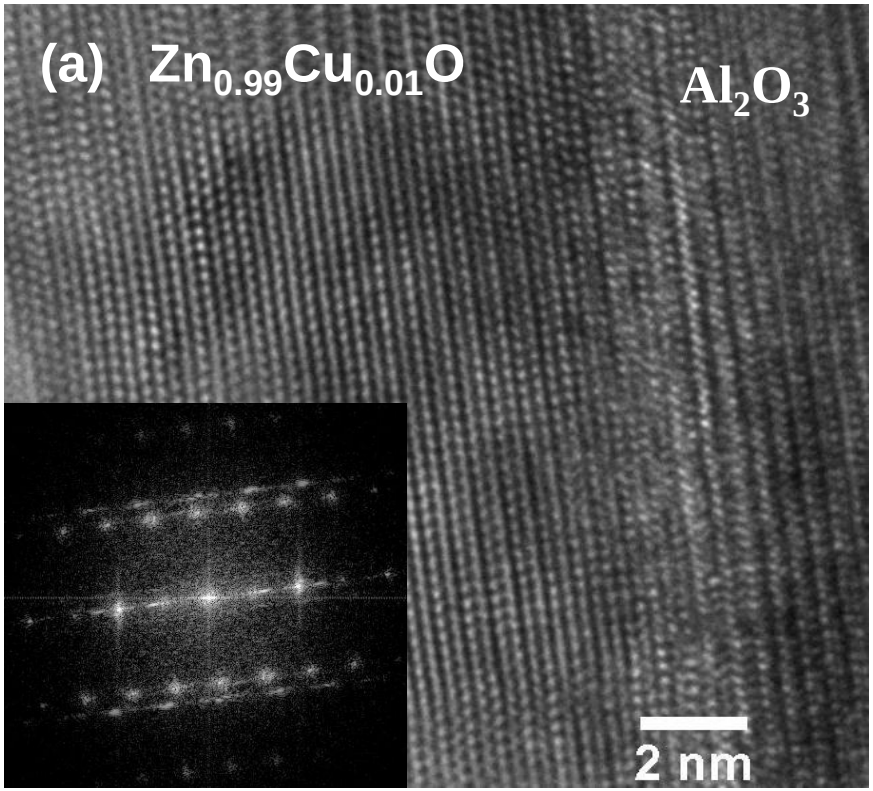
Structural properties of ZnCuO thin films

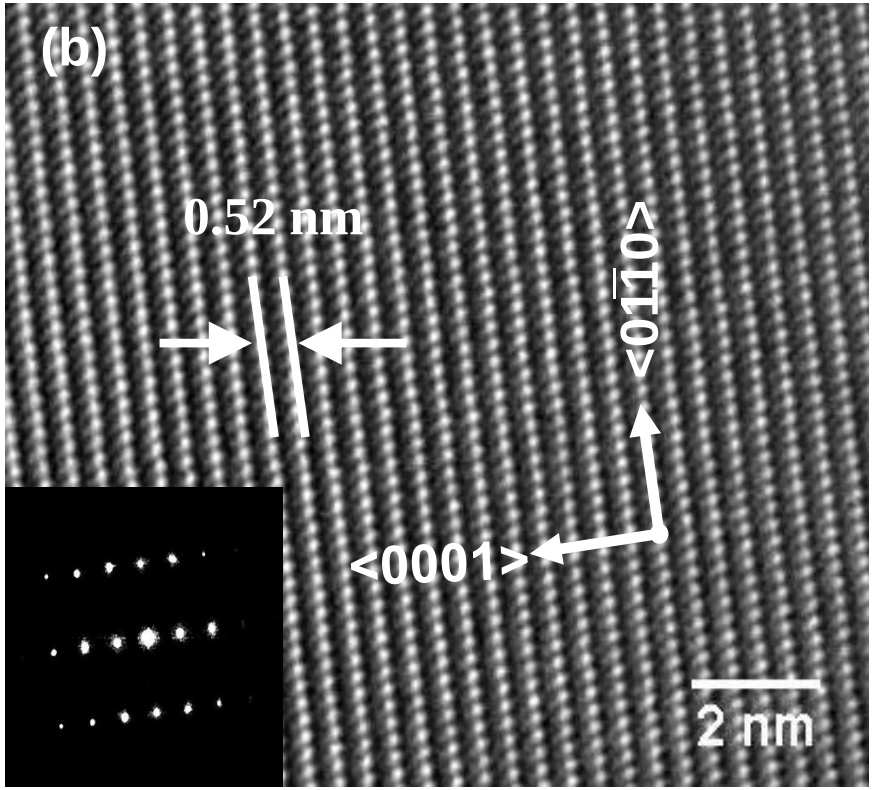




- *Cu related secondary phase detected in 5% Cu doped ZnO thin film in both XRD and Raman measurements*

Cross-sectional HRTEM of 1% Cu doped ZnO thin film

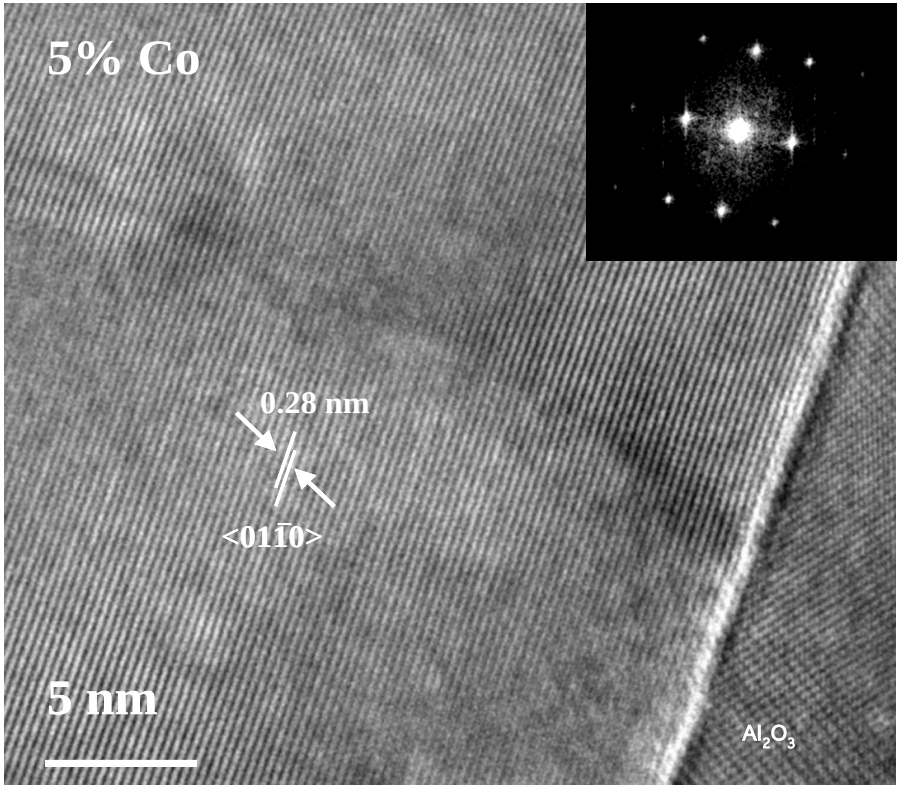


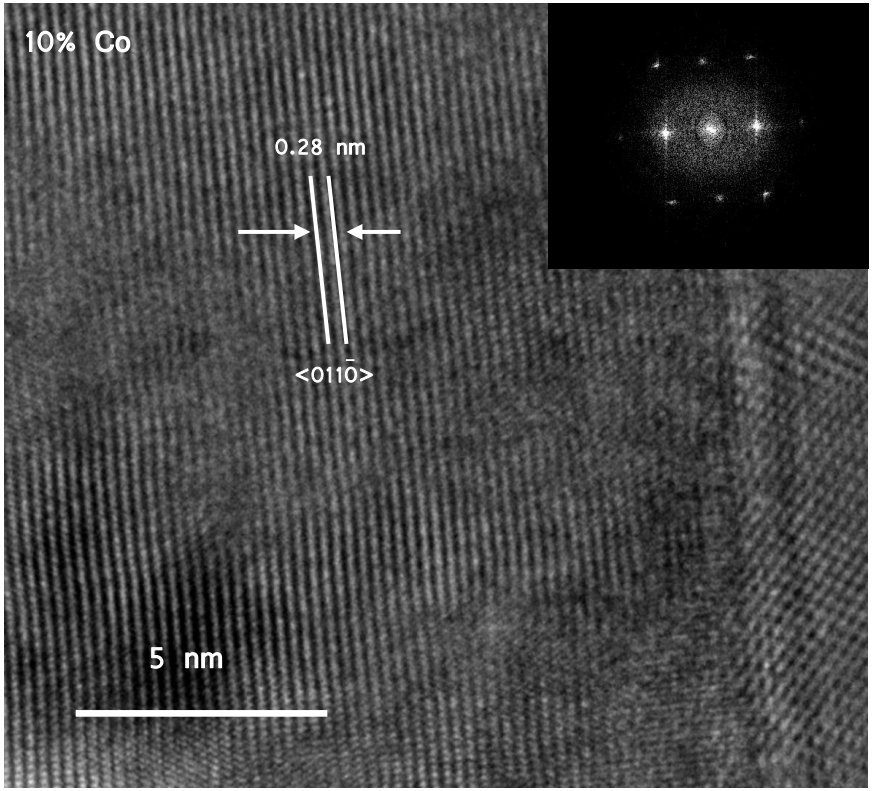


- **The interface of the $Al_2O_3/Zn_{0.99}Cu_{0.01}O$ is compositionally sharp and without any interfacial reaction and inter-diffusion**

- **The film is nearly single crystalline, defects free, and absence of any secondary phase**

Cross-sectional HRTEM of $Zn_{1-x}Co_xO$ thin films

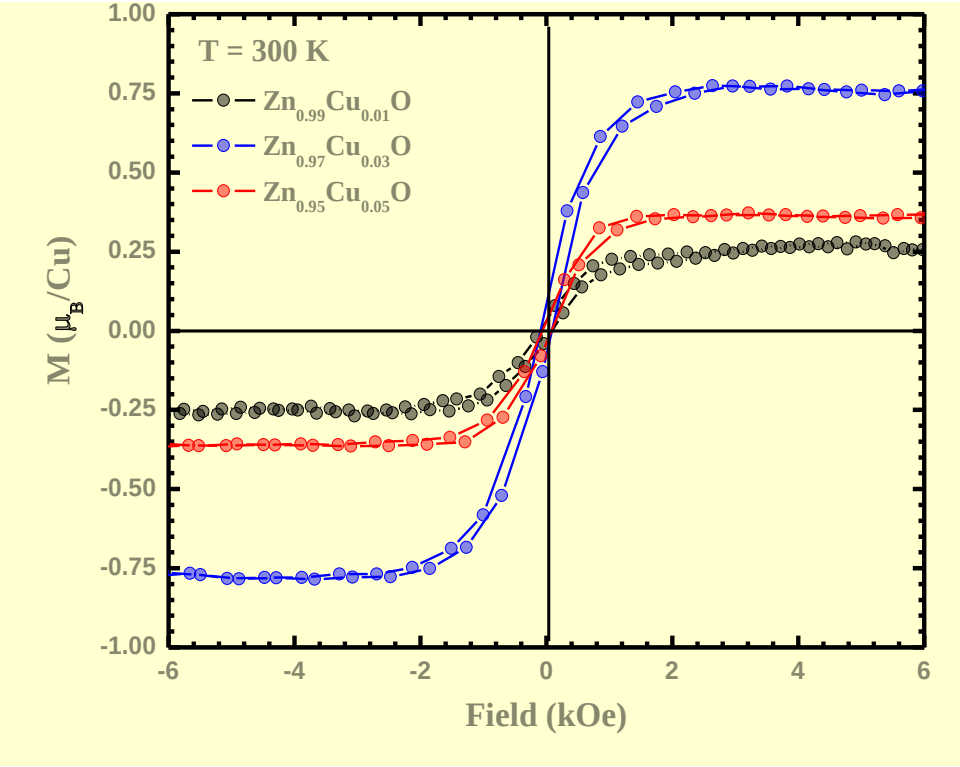


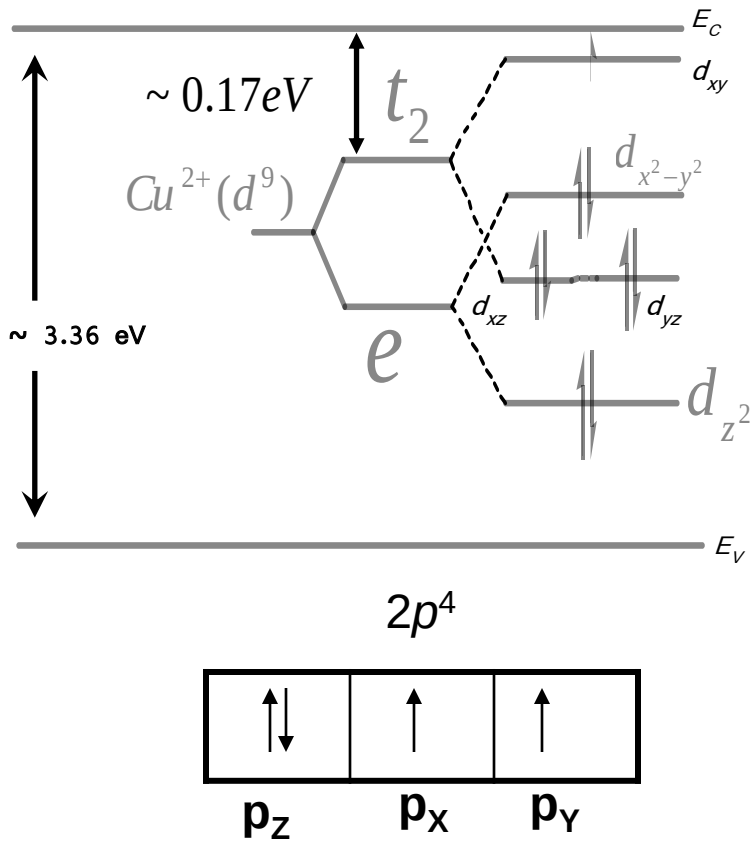


- Cross-sectional HRTEM micrograph of 5 and 10% Co doped ZnO thin film; inset shows the FFT of the selected area of the film

- Single crystalline and defects free

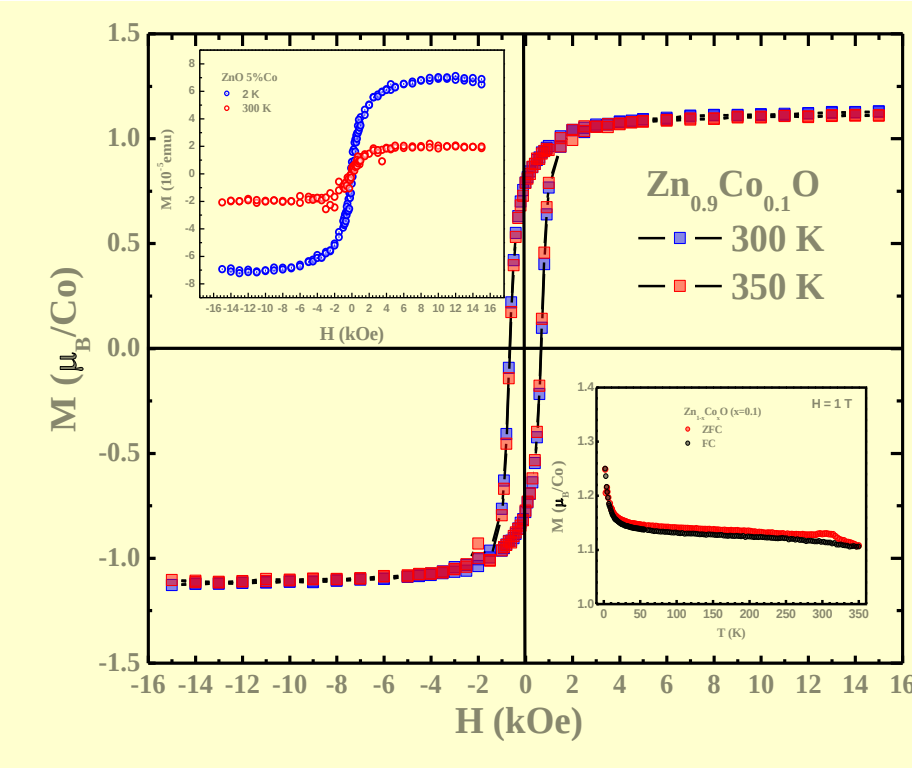
Magnetic properties of $Zn_{1-x}Cu_xO$ thin films (VSM)

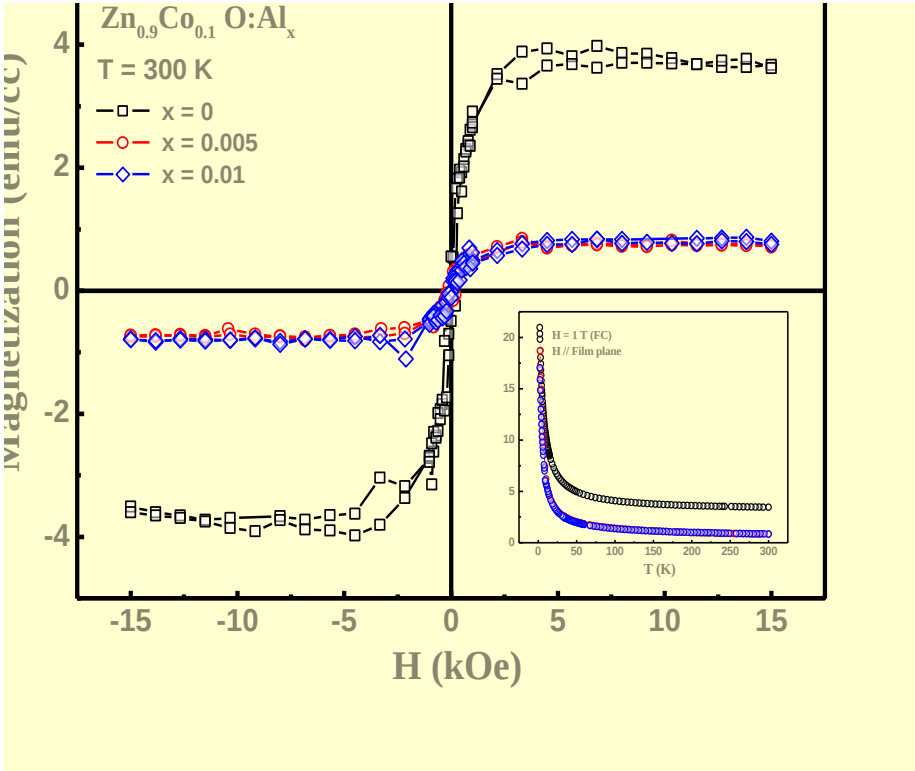




❖ ***p-d* orbital mixing (p_x or p_y of O-atom and unpaired d-electron of Cu^{2+}) in ZnCuO system may give ferromagnetic exchange interaction**

Magnetic properties of $Zn_{1-x}Co_xO$ thin films

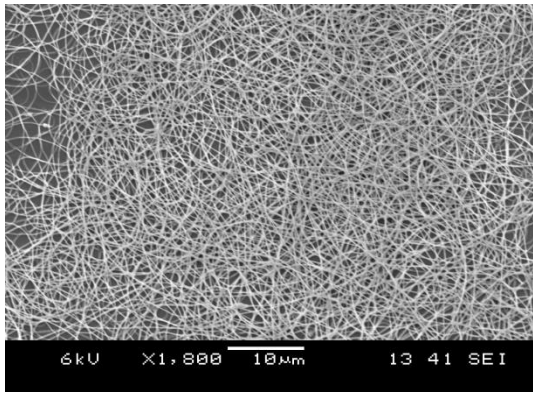


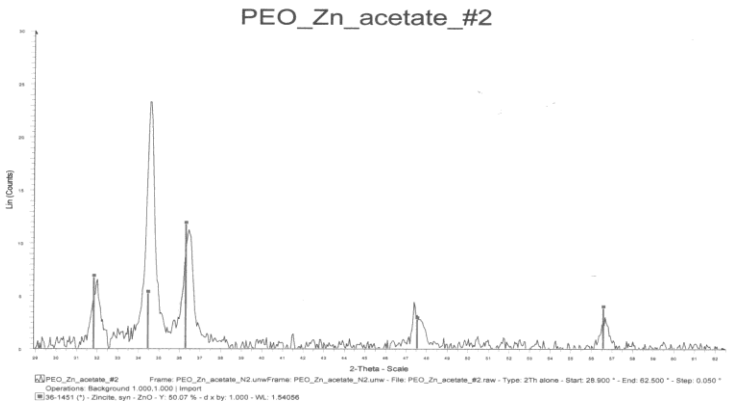


- Room temperature ferromagnetism was observed in Co doped ZnO thin films
- Additional carrier concentration (by Al doping) reduced the Ms value
- Resistivity droped by 5 orders of magnitude (~ 0.02 Ω-cm) and carrier concentrations increased by 4 order of magnitude (~ $10^{19}/cm^3$) due to Al doping

Growth of Nano-structured Fibers by Electro-spinning

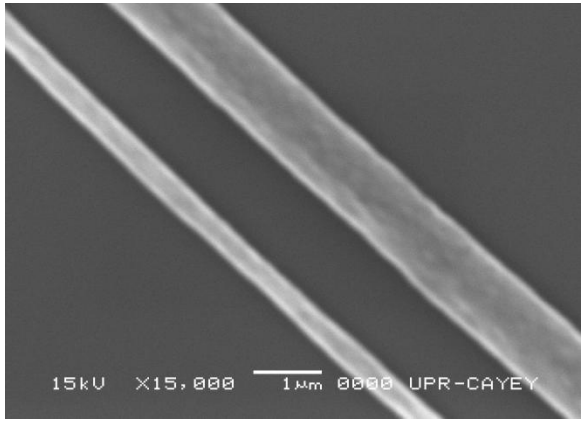
ZnO

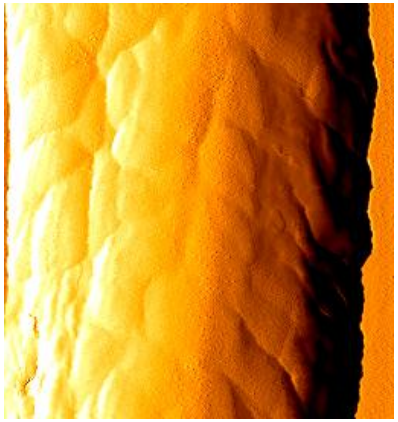




1) Synthesis of ZnO nano-structured fibers

ZnO [13% Fe]

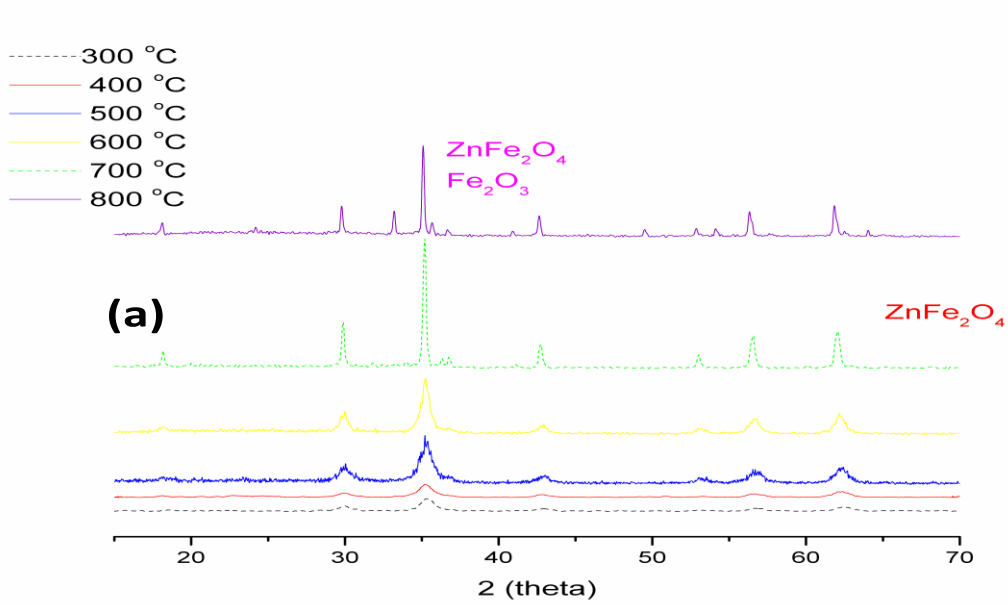


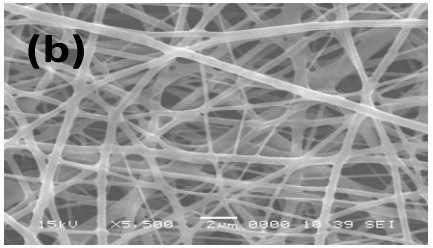


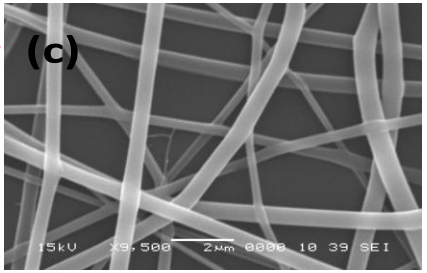
ZnO [13% Fe]
MFM-Phase

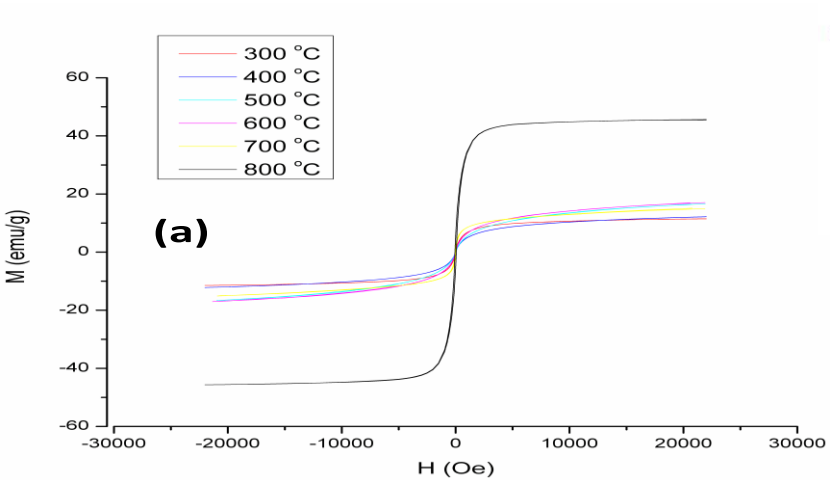
2) Doping of the fibers with transition metals

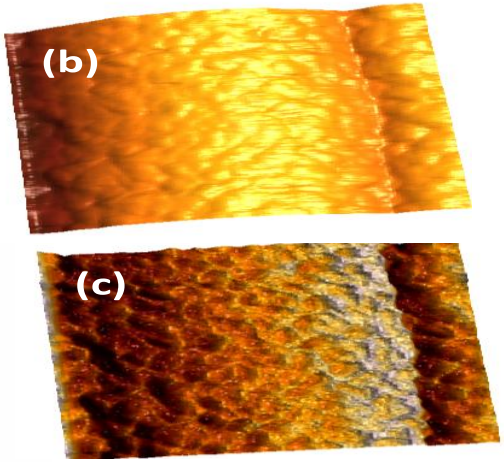
$ZnFe_2O_4$ spinel composite fibers and ribbons











Transition metal silicides

Transition metal silicides are promising semiconducting materials for spintronics applications due to small mismatch with Si that allows defect free interfaces. Magnetic response has been predicted at reduced dimesionality.

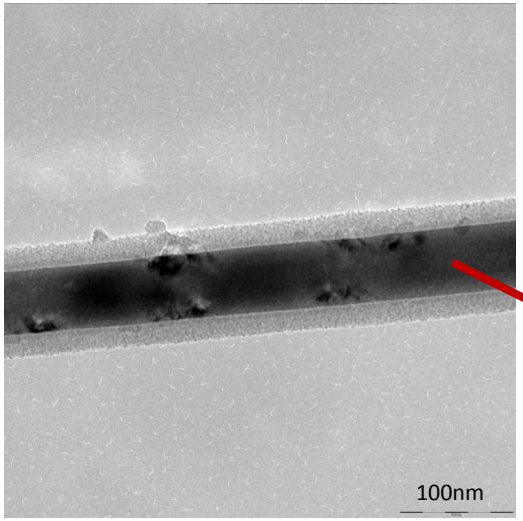
- **Following Nanostructures were synthesized by CVT :**
  - Cobalt Silicide
  - Chromium, Iron, Manganese alloy silicide

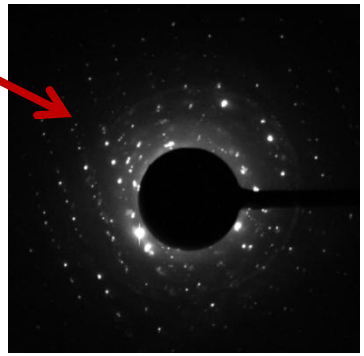
CoSi:

•Grows as nanowires with diameter ~50nm and several microns in length.

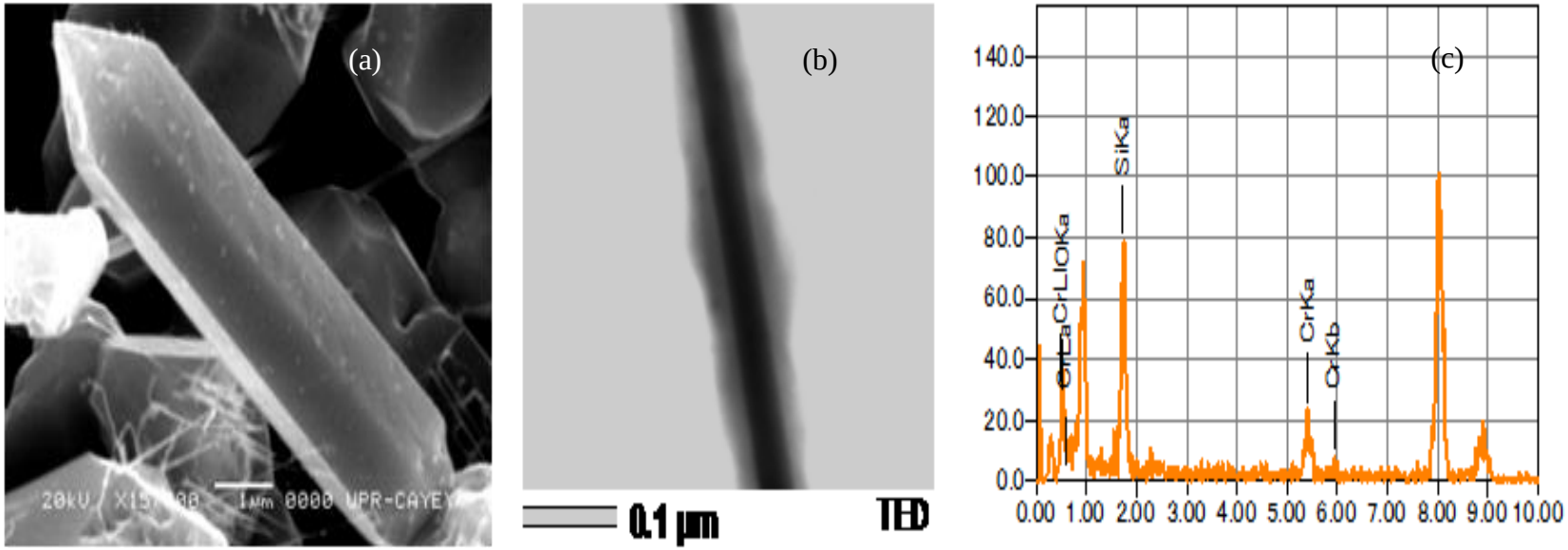
•EDS showed $Co_{x=1}Si_{y=1}$

•Nanowires were single crystals with a core shell structure. The shell was made of amorphous silica.





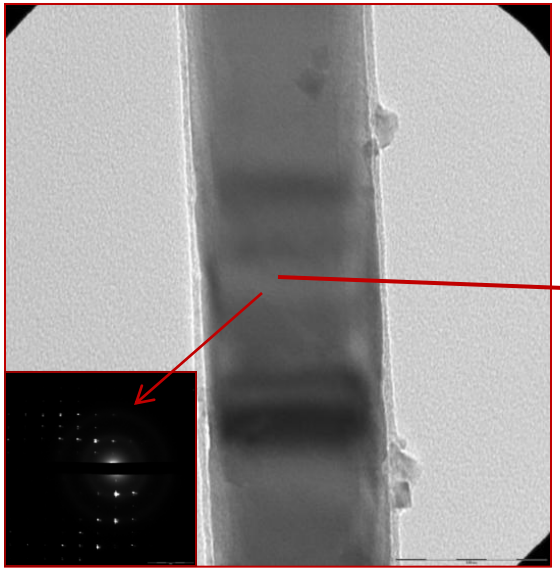
Transition metal silicide ($CrSi_2$) micro- and nano-rods and wires by CVT

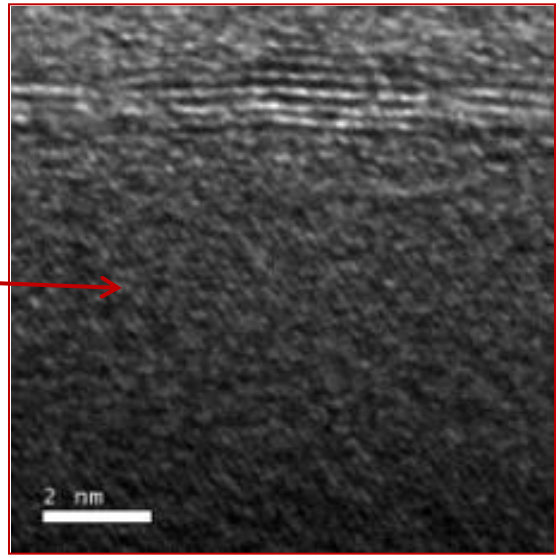


(a) SEM image of a $CrSi_2$ microwire,
(b) STEM image of a nanowire covered with SiO_2 ,
(c) EDS spectrum

Alloy silicide $Cr_xFe_yMn_{1-x-y}Si$:

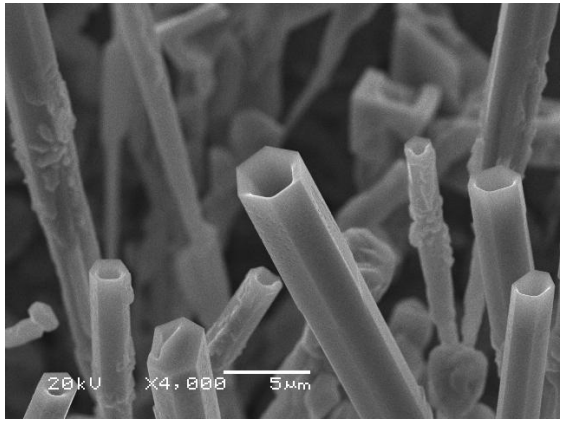
- EDS shows that x=0.50, y=0.48
- Material grows as nanowire and microtube crystalline structures

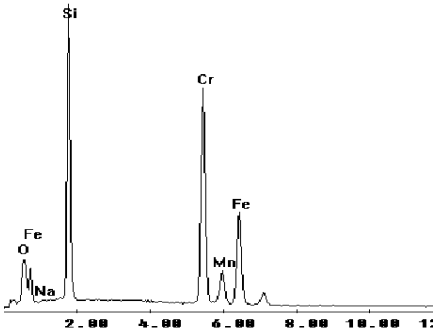


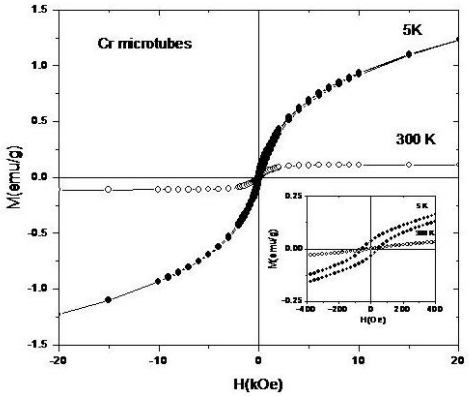


Single crystal nanowires

Single crystal microtubes







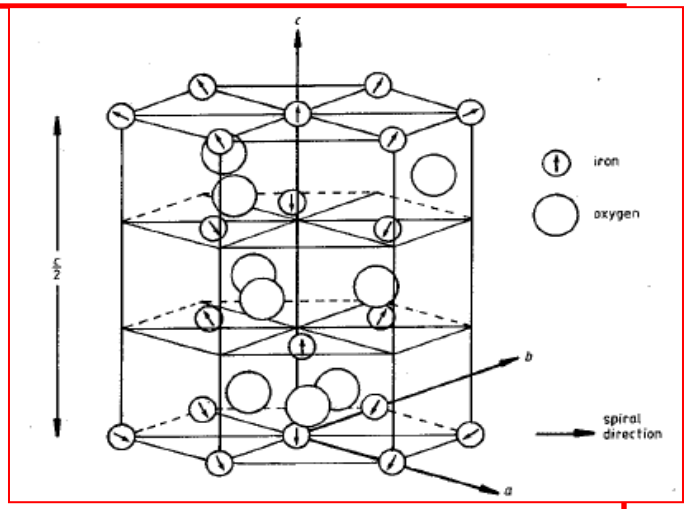
Magnetoelectric Multiferroic $BiFeO_3$

- Structure: Rhombohedral
- Space group: R3c

(a = 5.58Å, α = 89.5° ; (NOT 59.5°!!))

- $P_s \| [111] = 6.1\ \mu C/cm^2$
- $P_s \| [001] = 3.5\ \mu C/cm^2$

(Teague et al SSC, 8, 1073,1970)

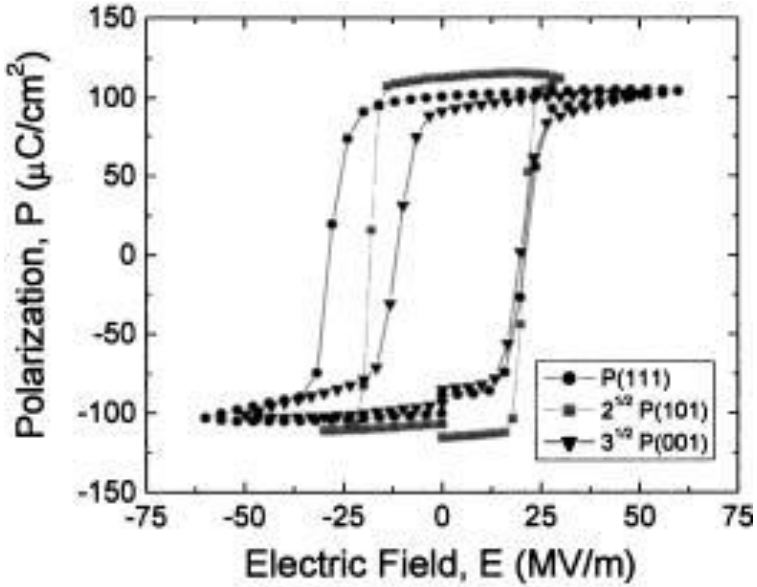


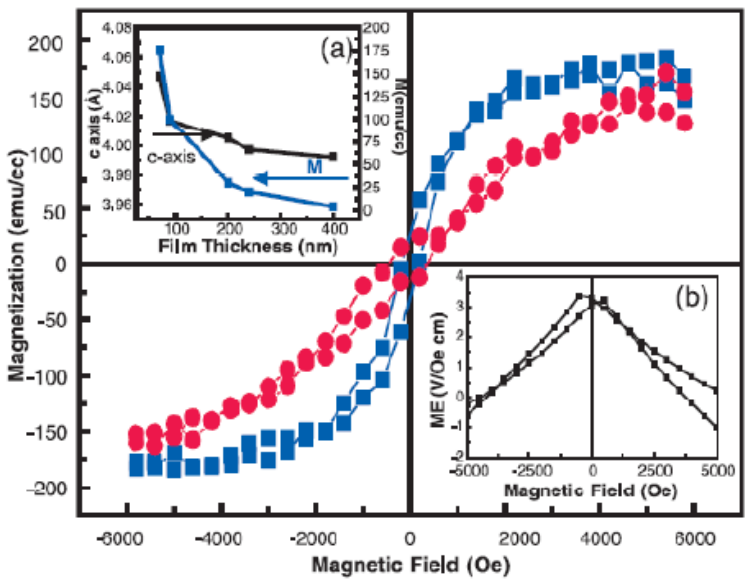
- FE-PE @T_c ~ 820 °C

- AFM-PM @ T_N ~ 370 °C with G-type antiferromagnetic ordering (weak ferromagnetism which is observed due to spin canting)

- Room Temperatrure Magnetoelectric Multiferroic !

Epitaxial $BiFeO_3$ thin films on STO





Li et al. APL, 84, 5261 (2005)

Wang et at Science, 299,1719, (2003)

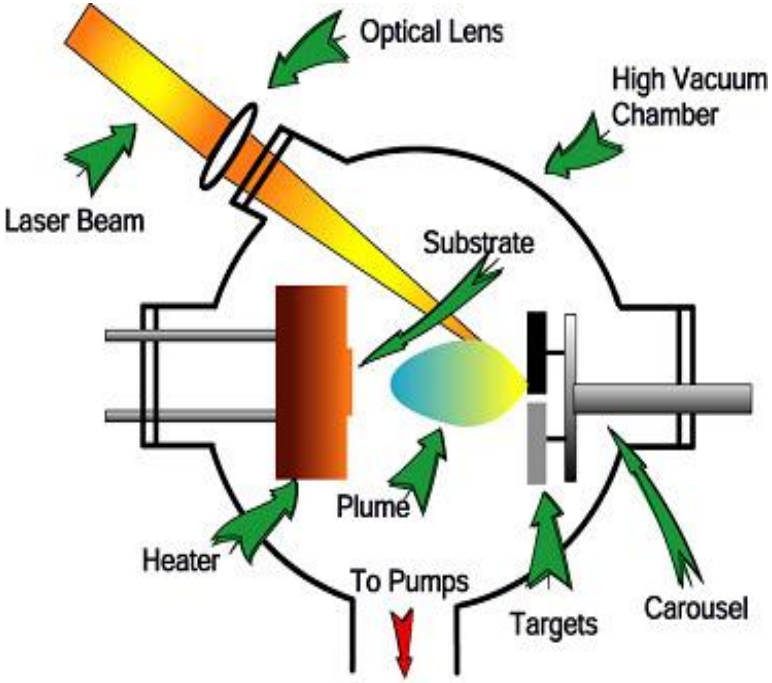
- Ps∥[111]= 80 ~ 90 μ C/cm^2
- Ps∥[001]= 50 ~ 60 μ C/cm^2
- Enhanced Magnetism (~ 150 emu/cc) due to spin canting

Advantage: High polarization (compared to the best known FEs, PZT, PLZT, BSTO)

Disadvantage: High Leakage current !

PLD grown BFO thin films

Target preparation: Conventional ceramic processing



Deposition Parameters:

Substrates: (001), (111) $SrTiO_3$,

Substrate temperature: 400°C

Oxygen pressure: 10 mTorr

Laser fluence: 250 mJ

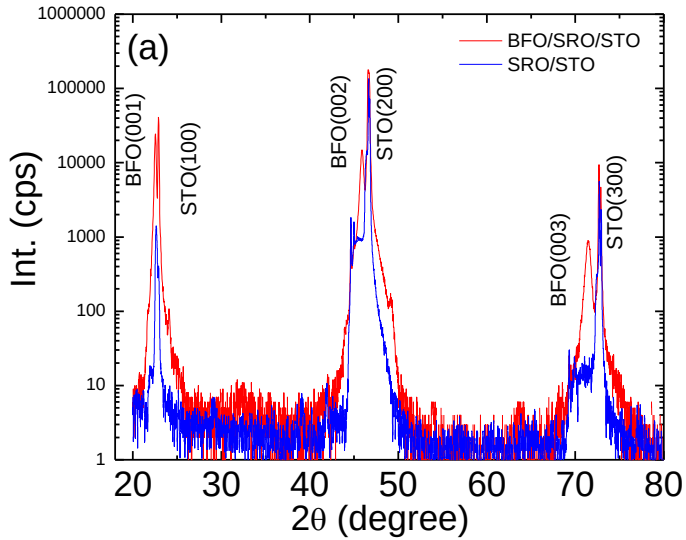
Repetition rate: 10Hz

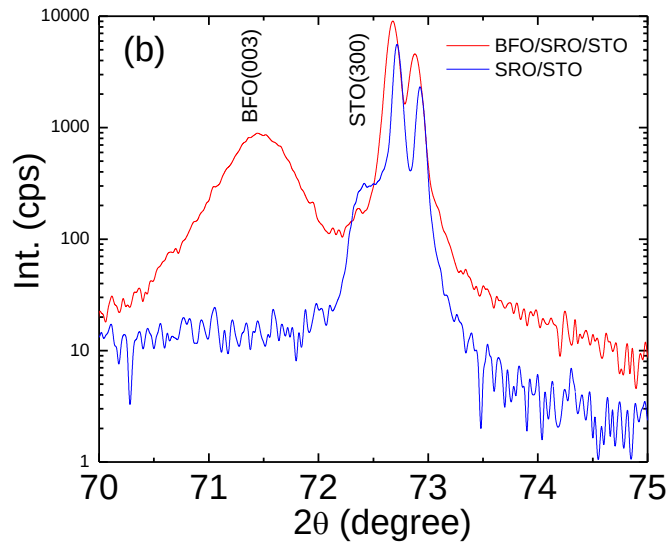
Substrate-Target distance: 5 cm

Rapid thermal annealing (RTA) in air at 650°C for 150 s

X-ray Diffraction of BFO/STO (001) thin films

(300 nm thick)



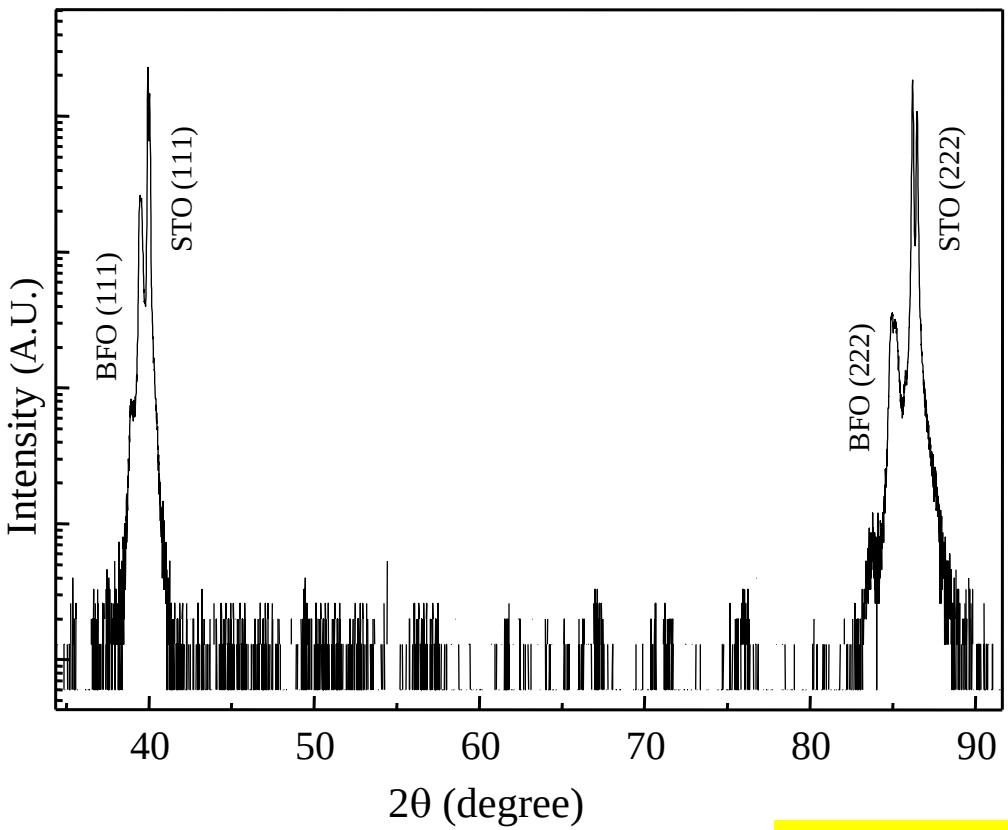


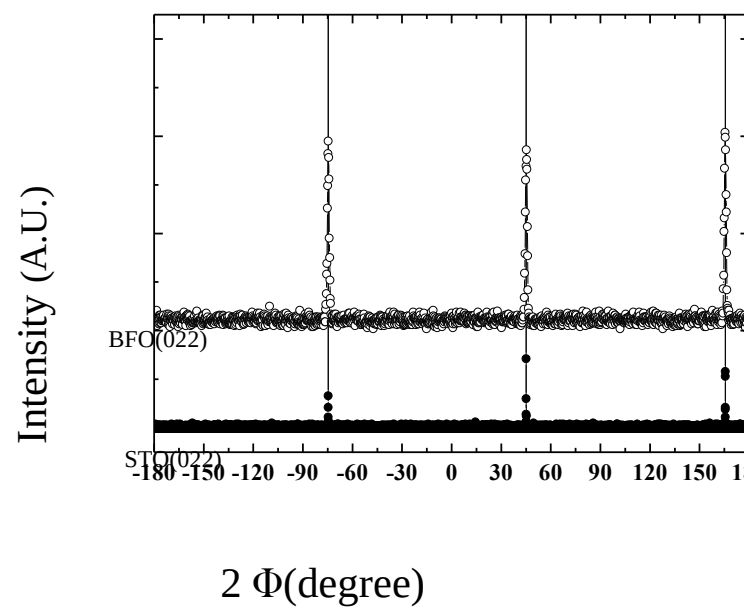
XRD patterns show that the films are *c*-axis oriented with high degree of crystallinity. The c-axis length was 3.95Å

Rhombohedral, a = 5.58Å, Tetragonal c = 4.0Å

BFO/STO (111) Thin Films grown by PLD

Theta-2theta XRD pattern and Φ scan



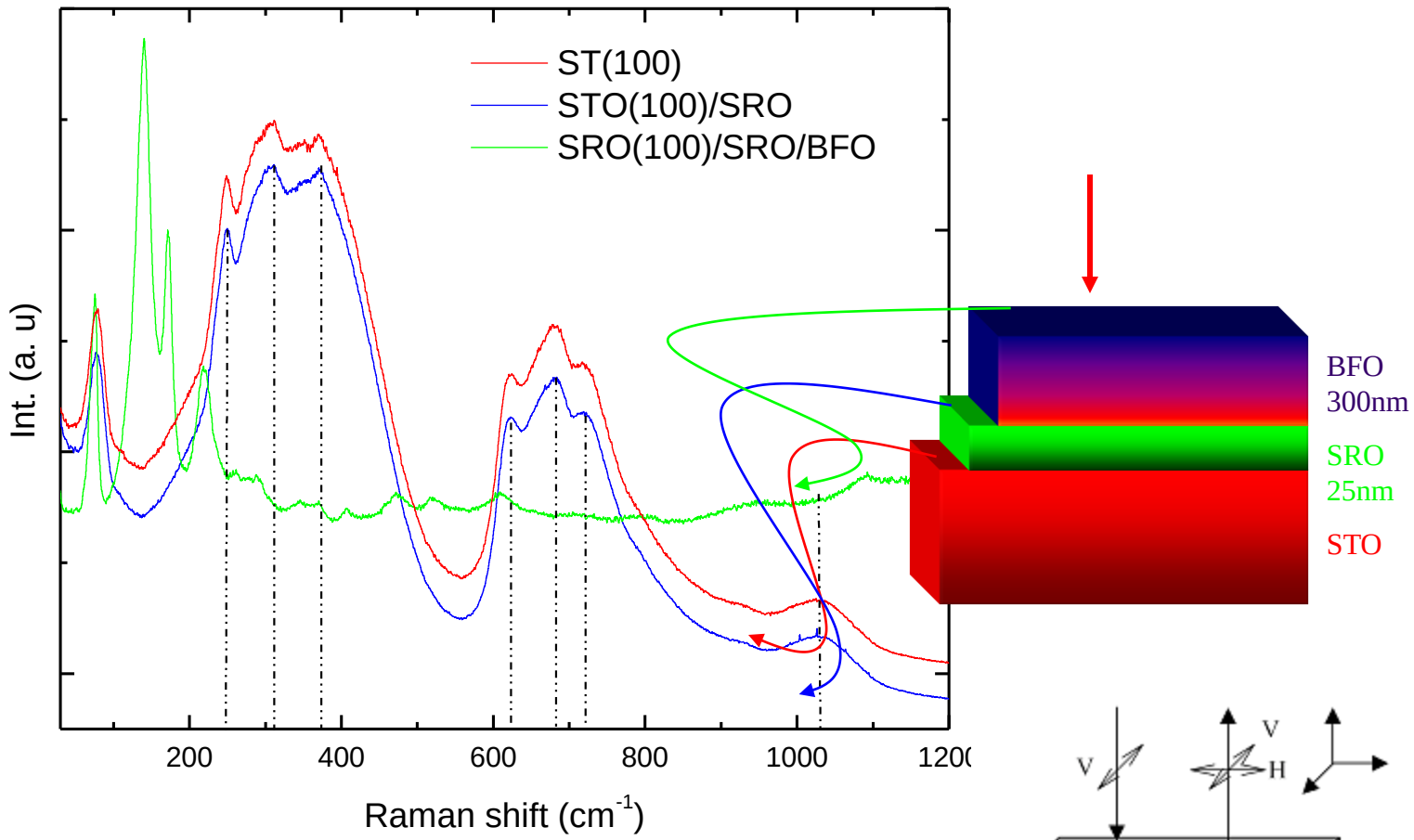


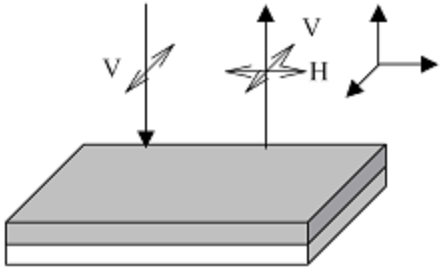
- Successfully obtained a highly (111)-oriented BFO thin film

- presence of 3-fold symmetry along [111] direction
- 'cube-on-cube' epitaxial growth

Figure:1

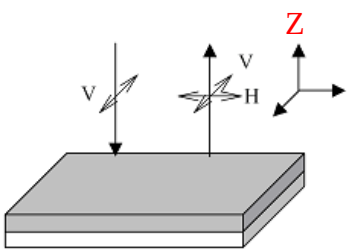
Raman Spectra of STO(100)/SRO/BFO(001) thin films

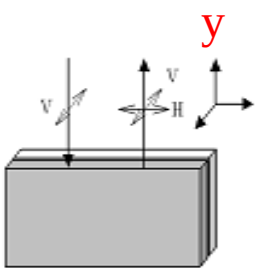




NO Raman contribution from bottom electrode (SRO) and STO substrate!!

Optical Vibrations in $BiFeO_3$

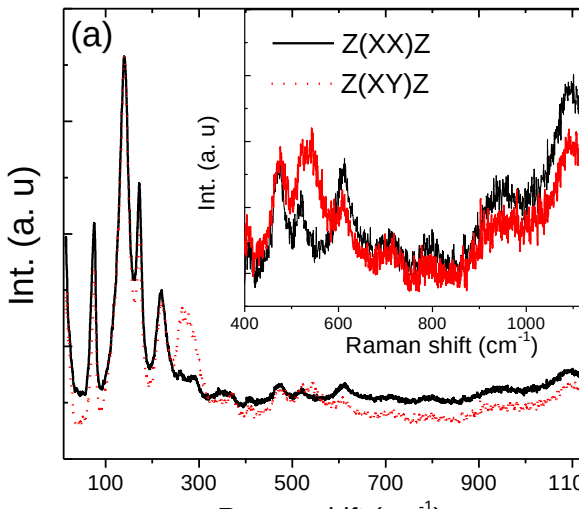




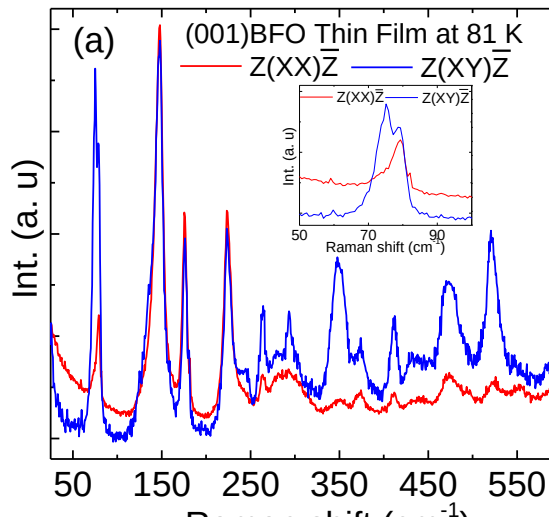
Scattering Geometry	**Raman Active Modes**		
	Rhombohedral, R3c **(C_{3v}) , Z=2**	Tetragonal, P4mm *(C_{4v})*	Monoclinic, Bb (Cs)
Normal Modes	*$4A_1$ + 9E*	*$3A_1$ + 1 B_1 + 4E*	*13A' + 14 A"*
Z(XX)Z' (VV)	**$4A_1$ + 9E**	**$3A_1$ + 1 B_1**	**13A'**
Z(XY)Z' (VH)	**9E**	**No modes**	**13A'**
Y(ZZ)Y' **(VV)**	***$4A_1$***	***$3A_1$***	***13A'***
Y(ZX)Y' **(VH)**	***9E***	***4E***	***14A"***

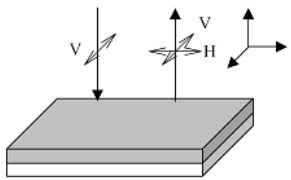
Polarized Raman Scattering of BFO(001) thin film (300 nm)

@RT



@ 81K





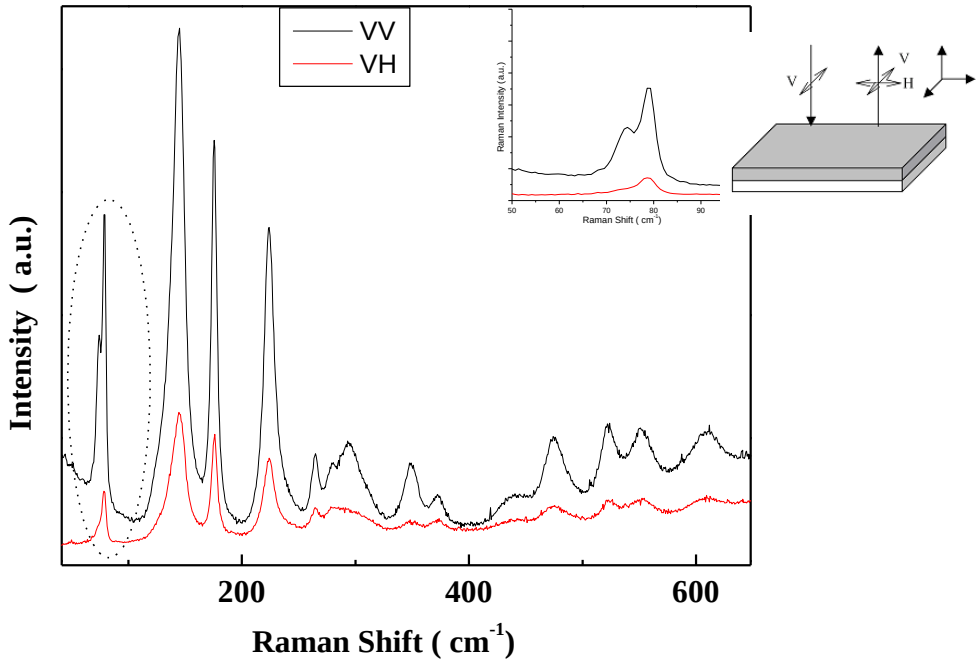
Stronger peaks were seen@ 74, 140, 172, 219 cm^{-1}, while weaker peaks @ 261, 370, 406, 478, 529, 609, 808, 946, 1093 cm^{-1}

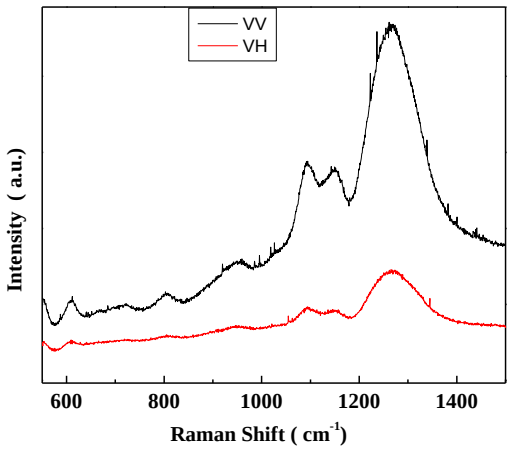
Polarized Raman spectra do NOT follow the selection rules for either Rhombohedral or Tetragonal structure.

It showed Monoclinic structure, that agrees with the Synchrotron X-ray studies of (001) BFO thin films. *Xu et al. APL 86, 182905 (2005).*

Raman Scattering from (111)BFO/STO thin films at 80 K

[For rhombohedral symmetry R3c (C_{3v}) , $\Gamma = 4A_1+9E$]

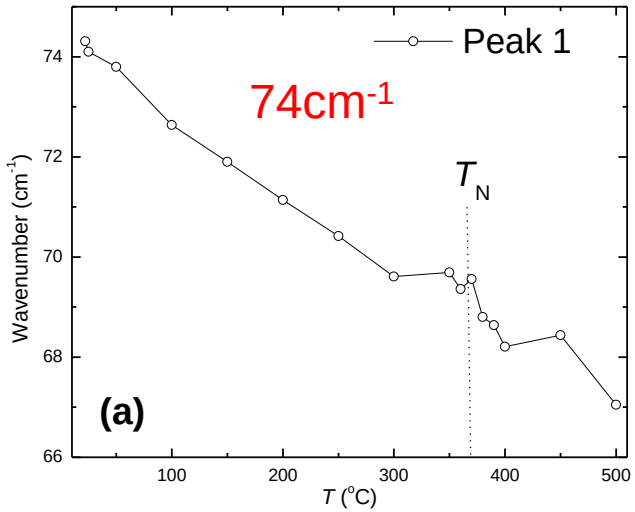


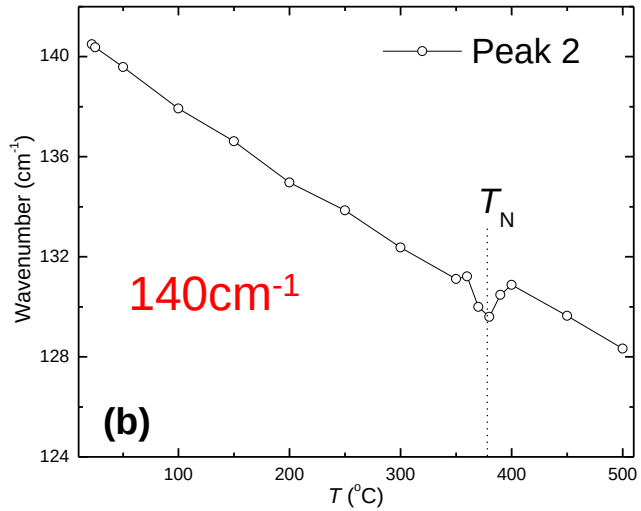


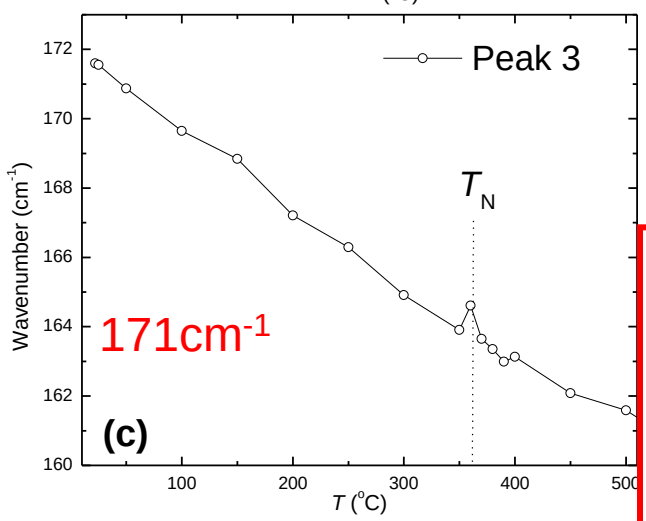
❖The polarized Raman spectra of (111) BFO thin films are compatible with R_{3c} symmetry selection rules.

❖Second order Raman modes were observed at 611, 803, 947, 1093, 1148, 1264 cm^{-1}

Phonon Anomalies near 370°C (T_N) in (001) BFO film







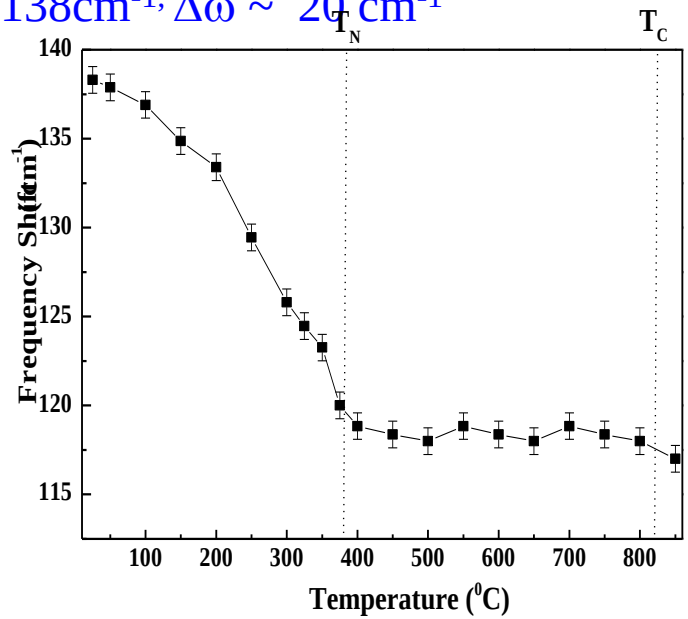
Phonon anomalies (< 2%) were observed near T_N (370 °C)

Hard-Mode Raman Spectroscopy (HMRS): Any change in structural and/or physical properties will lead to variation in phonon characteristics (frequency, FWHM, and intensity)

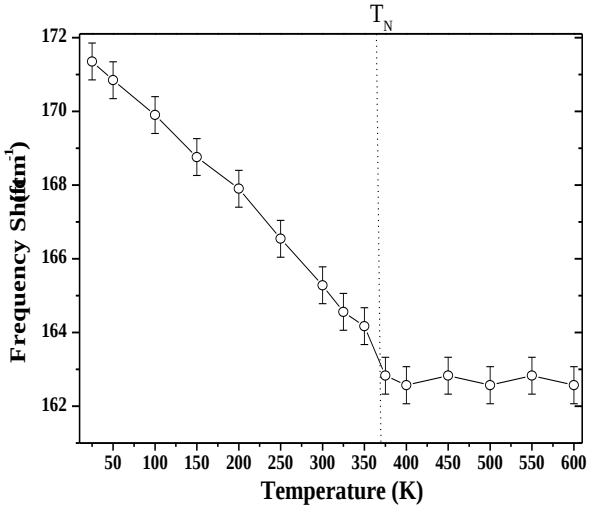
E.K.H Salji, *Phase Transition*, 37, 83 (1992); E.K.H. Salji and U. Bismayer, *Phsae Transition*, 63, 1, (1997)

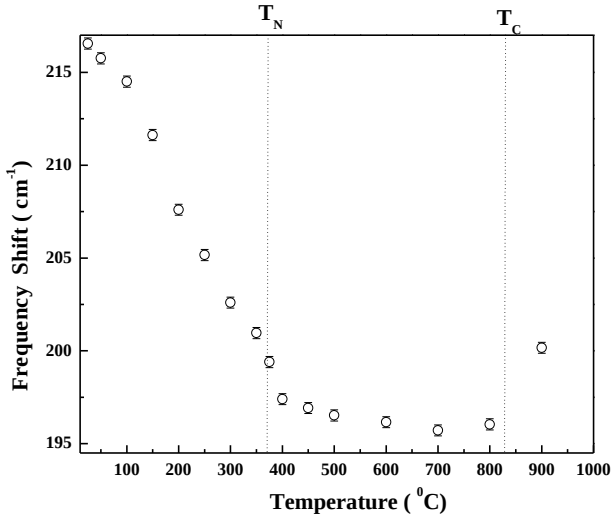
Frequency shifts of three prominent A_1 Raman modes in (111) $BiFeO_3$ thin films near T_N

(For 138cm^{-1}, $\Delta\omega \sim$ 20 cm^{-1}



(For 171cm^{-1}, $\Delta\omega \sim$ 12 cm^{-1}

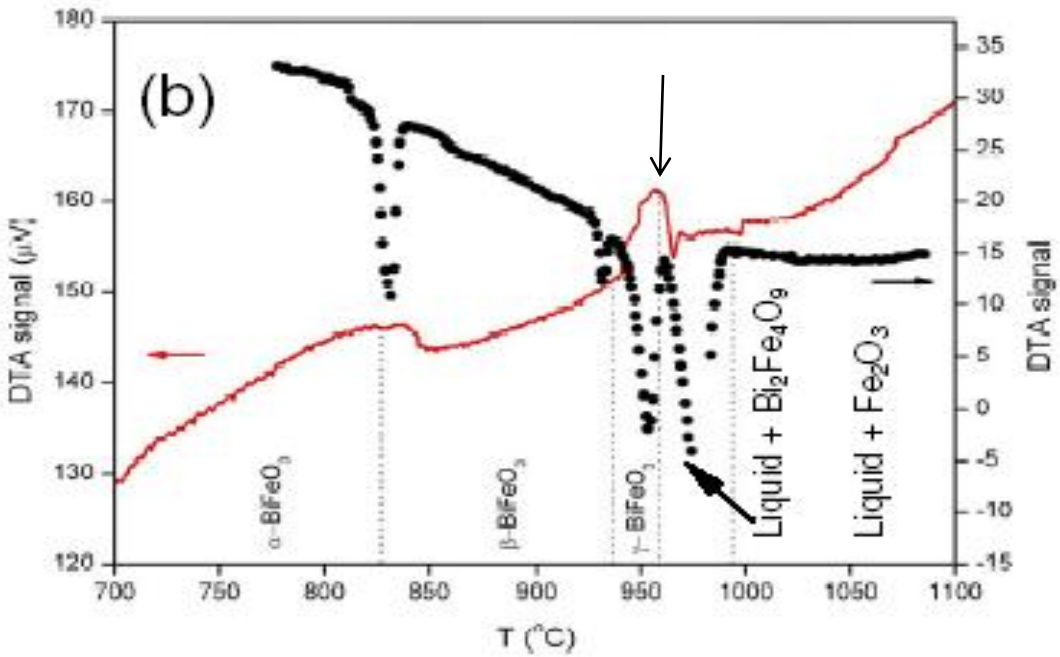




(For 216 cm^{-1}, $\Delta\omega \sim$ 16 cm^{-1})

Anomalous frequency shifts may be associated with the spin lattice coupling that ceases to exist above T_N.

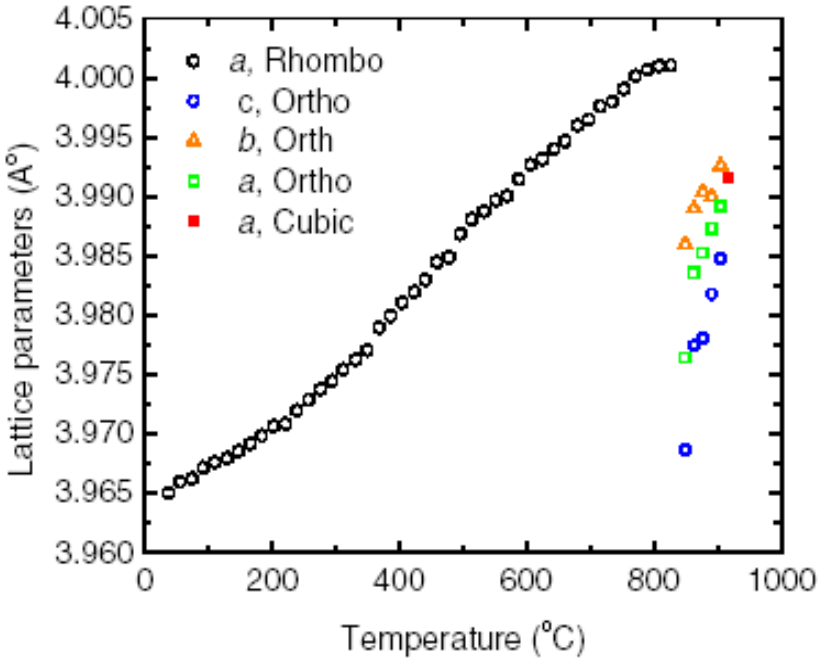
Differential Thermal Analysis (DTA) of $BiFeO_3$



The DTA peaks were reversible below down arrow on cooling.
Up to T_C (820 ^{0}C) = α phase with rhombohedral structure,
820 ^{0}C ~ 930 ^{0}C = β phase with orthorhombic structure
~930 ^{0}C ~ 950 ^{0}C = γ phase with cubic structure

Palai, Katiyar, Scott, …. PRB 77, 014110 (2008)

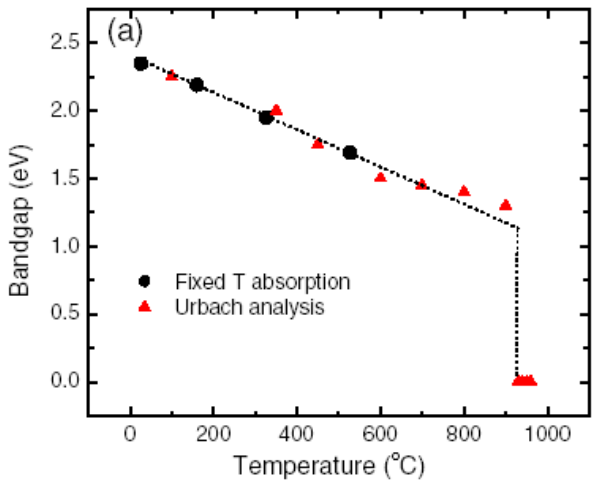
High temperature XRD studies

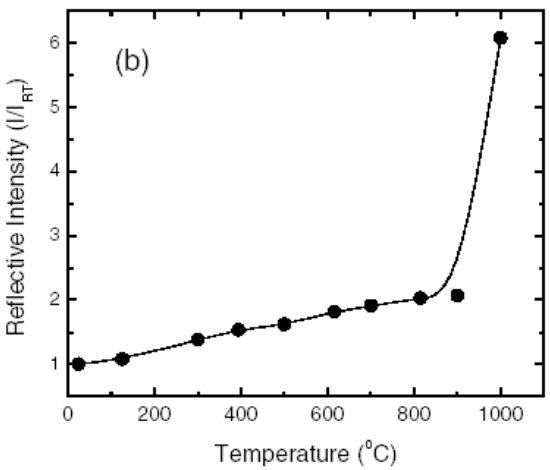


Lattice parameter of $BiFeO_3$

At 825◦C, the lattice constant *a* = 4.0011 °A splits into a triplet (open circles, squares, and triangles), which combines again at ~ 925(± 5)◦C in the cubic phase (solid square), where *a* = 3.9916 °A.

Bandgap energy of $BiFeO_3$ from RT to its melting point



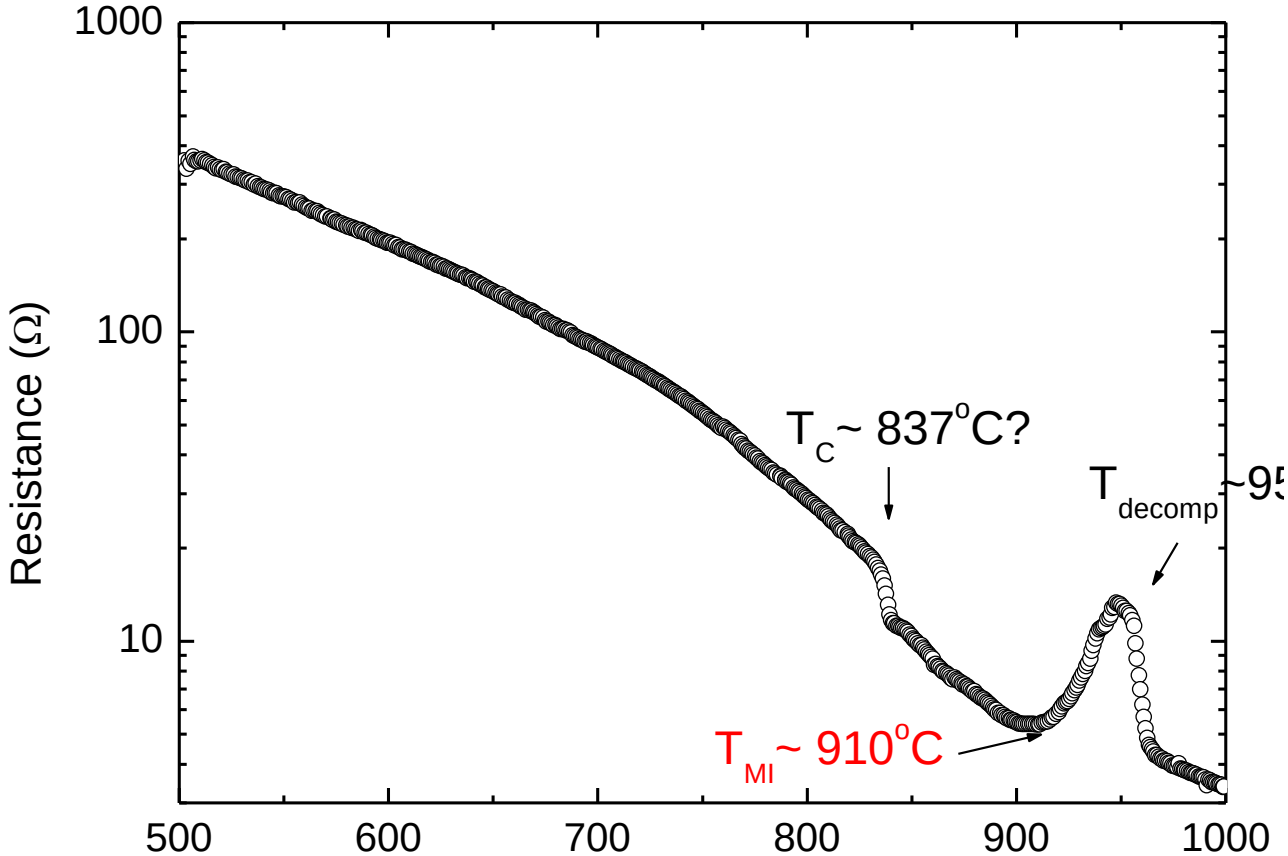


❖The bandgap data were obtained by conventional absorption spectroscopy between RT and 1000 ^{0}C for a fixed wavelength (632.8 nm) by slowly varying temperature and using the Urbach Equation to relate it to the bandgap: $E_g(T)$: $\log a(T) = (E - E_g)/E_g + constant$.

The data show a linear decrease from ~ 2.5 eV at RT to ~1.5 eV at 820 K, followed by a discontinuous drop at the beta-gamma transition to near zero (metallic).

❖The reflectivety measurements showed a sudden increase in reflectivity above 900 ^{o}C (metallic behavior ?)

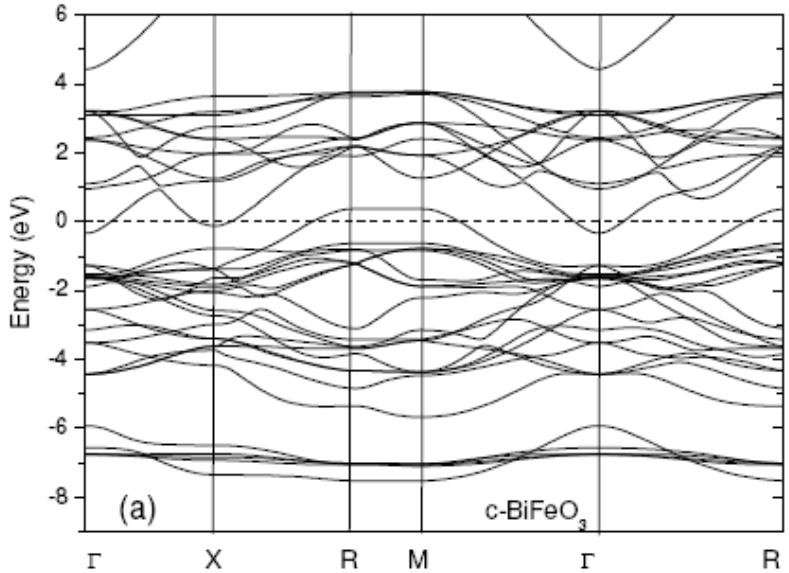
Resistance of BFO vs. Temperature

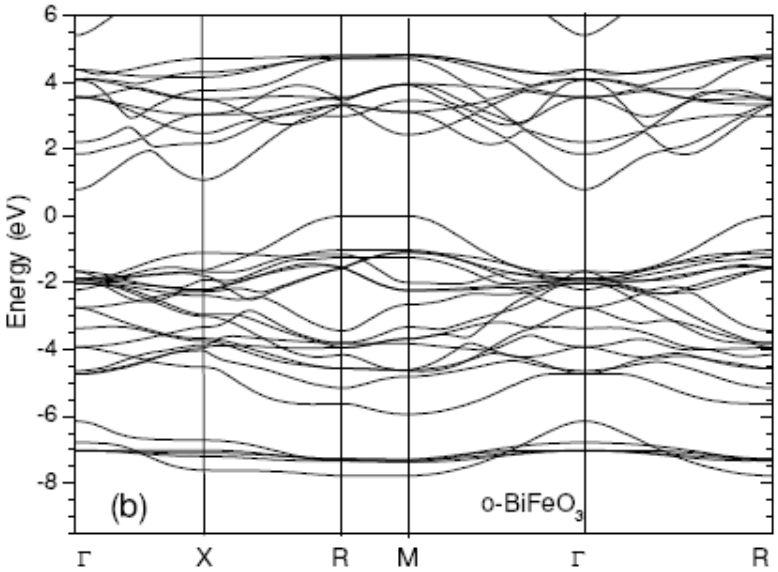


Temperature vs. Resistance measurements show a Metal-Insulator Transition above 910 (cubic phase).

RT metallic phase at ~47GPa already reported by Gavriliuk et. al. JETP Lett. 82, 224 (2005).

Bandstructure Model: Screened Exchange (SX) Model (Not Local Density Approximation (LDA)!):

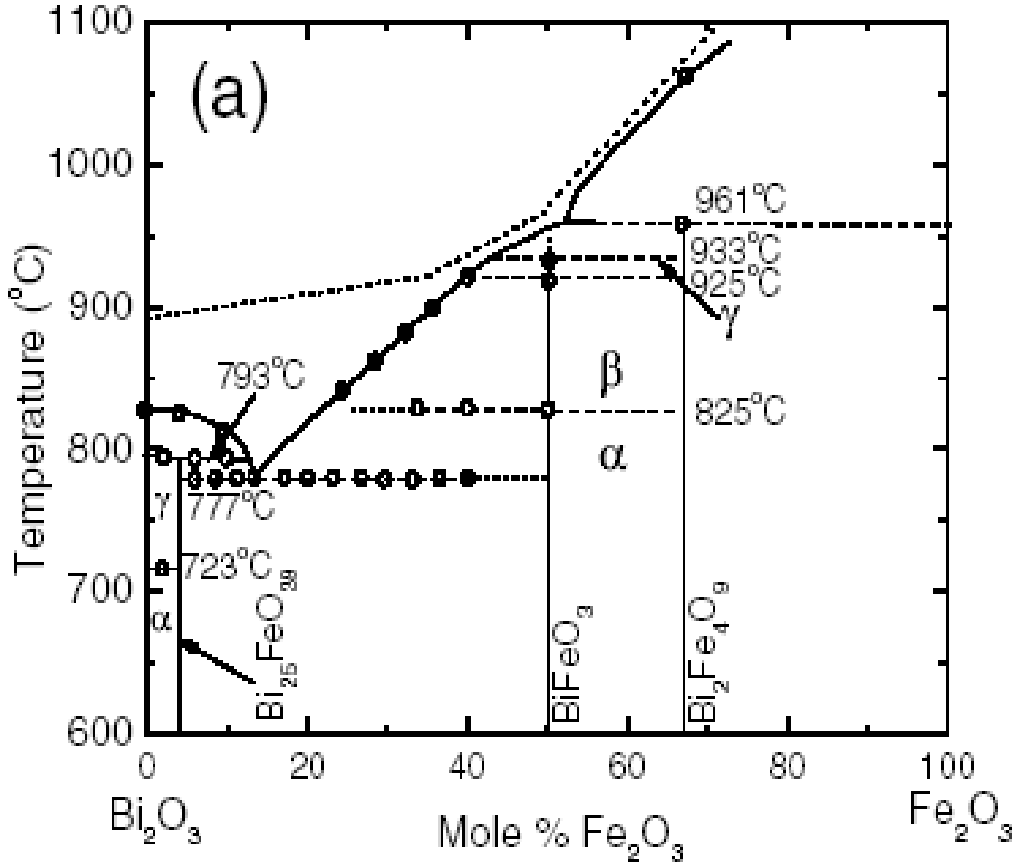




Is Cubic phase metallic ?

Palai, Katiyar, Scott, Robertson, … PRB 77, 14110, 2008

Phase diagram of $BiFeO_3$



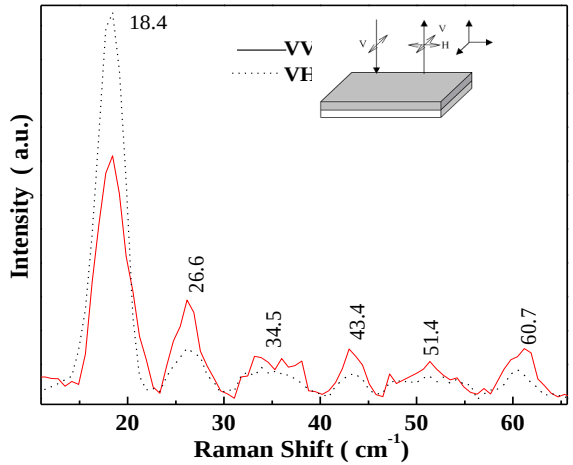
This is a modified phase diagram based on DTA, high temperature XRD, single crystal domains, Raman studies, and unconventional band gap measurements.

α phase (rhombohedral)

β phase (orthorhombic)

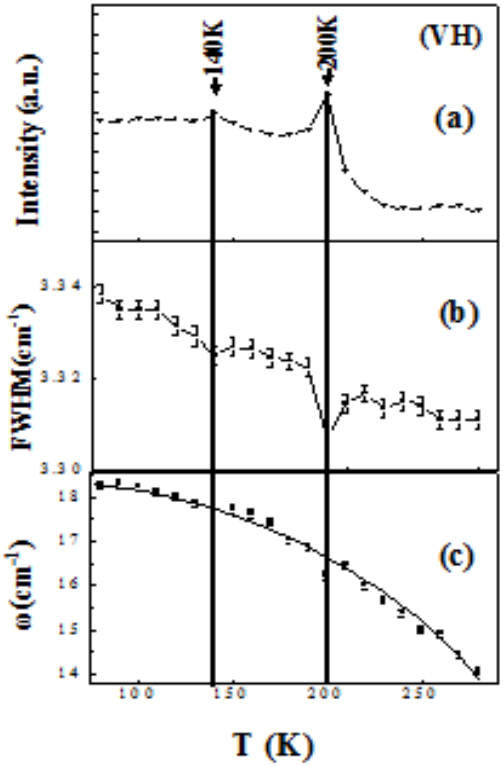
γ phase (cubic) – metallic ?

Discovery of New Magnetic Phase Transitions in $BiFeO_3$

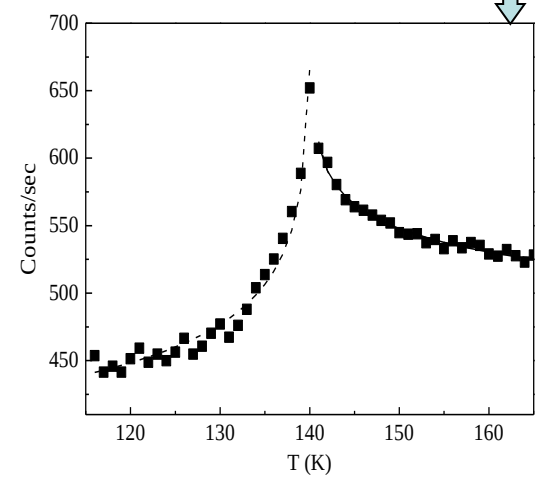


Raman scattering from magnons

❖The diverging cross-sections, FWHM, and the frequency-shifts at ~140K and ~200 K imply spin -reorientation transitions.



The critical exponents are much less than 1 revealing that $BiFeO_3$ has a long range magnetic spin order and it is not of Ising-like.



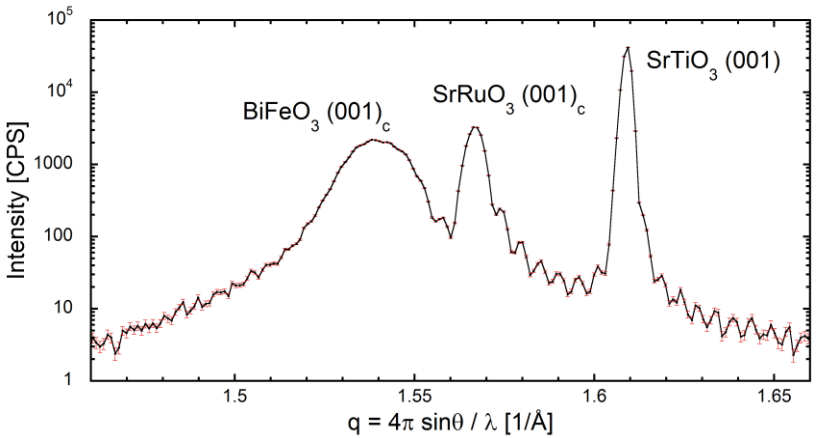
TWO TOP PUBLICATIONS of 2008, RATED by the Editors

1) Manoj K Singh, R S Katiyar, J F Scott, *J. Phys: Condens Matter* **20**, 252203 (2008)
2) J F Scott,Manoj K Singh, R S Katiyar, *J. Phys: Condens Matter* **20,** 322203 (2008)

Prior to the above works the magnetic structure was considered unchanged from ambient temperature to cryogenic temperatures.

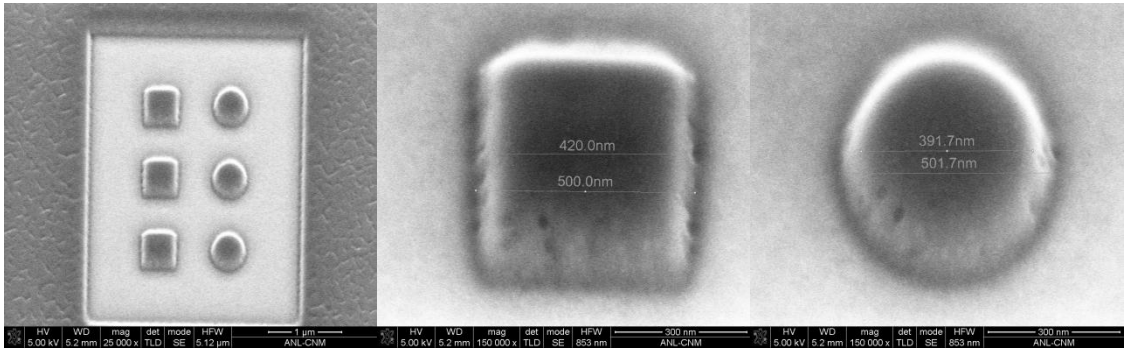
Fabrication of BFO nanocapacitors on /SRO/STO substrates (in collaboration at ANL)

BFO films were grown by off-axis rf magnetron sputtering on epitaxial $SrRuO_3$ (SRO) layers grown on $SrTiO_3$ (STO) (001) oriented single crystal substrates.



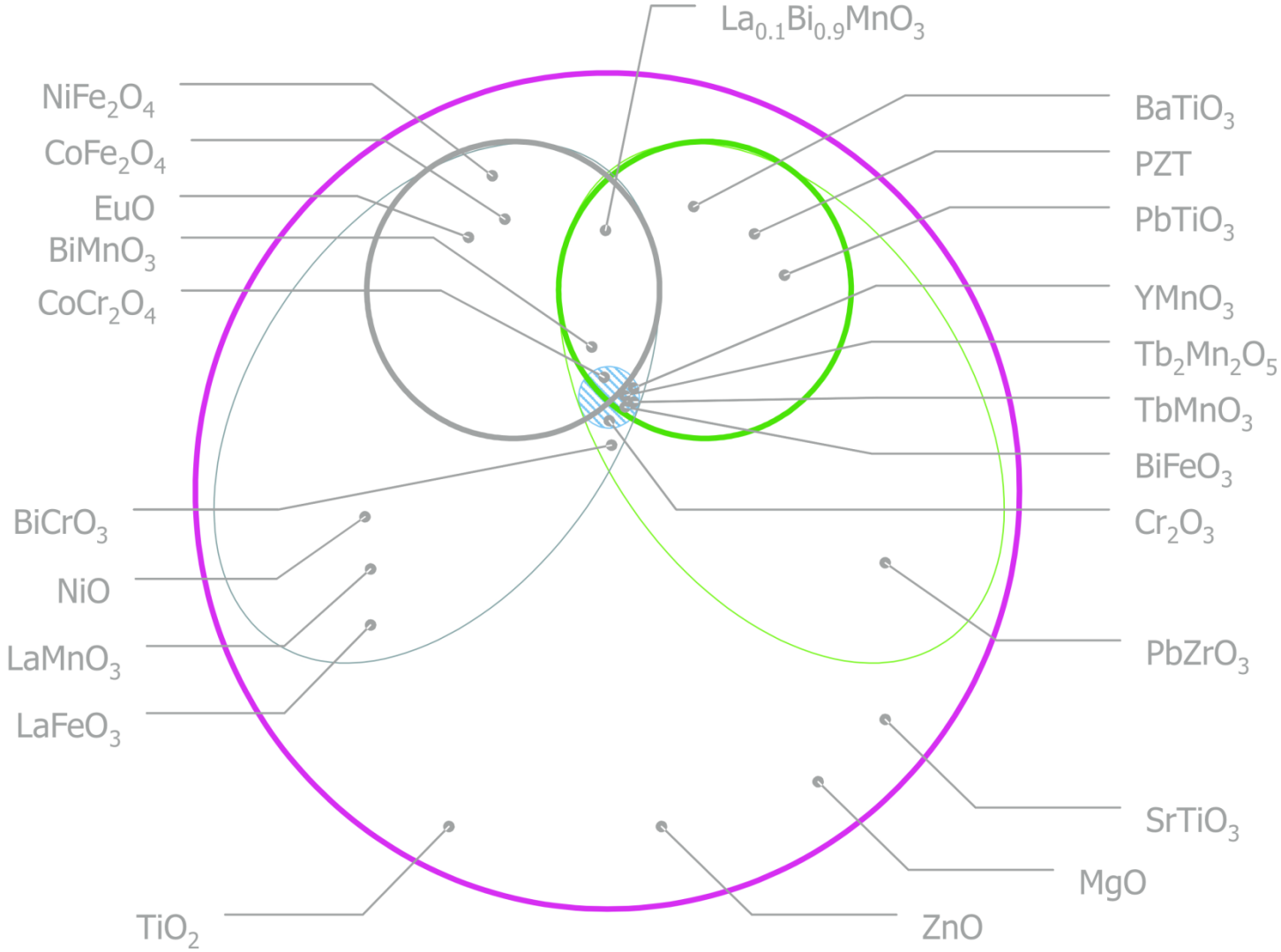
X-ray diffraction shows good crystallinity of The BFO and SRO layers

•Nanocapacitors were patterned using Focused-Ion Beam (FIB). Initial structures include 500x500 nm square and 500nm diameter round capacitors.



BFO/SRO nanostructures fabricated By FIB

Designing multiferroics



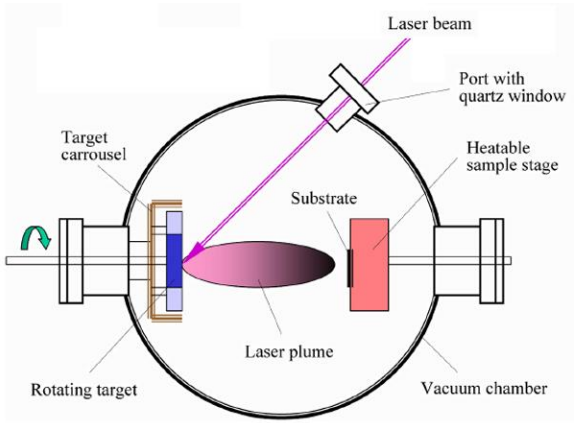
W. Eerenstein, N.D. mathur and J.F. Scott. Nature **442**, 759, (2006)

J.F. Scott , Ashok Kumar, R. Palai., M K Singh ,R.S. Katiyar et al. JACS (In press) (2008)

Designing artificial multiferroic nanostructures

NANOSTRUCTURED THIN FILMS OF $Pb(Zr,Ti)O_3/CoFe_2O_4$ MULTIFERROICS

From two targets
$PbZr_{0.53}Ti_{0.47}O_3$
$CoFe_2O_4$



Parameters for thin film deposition:

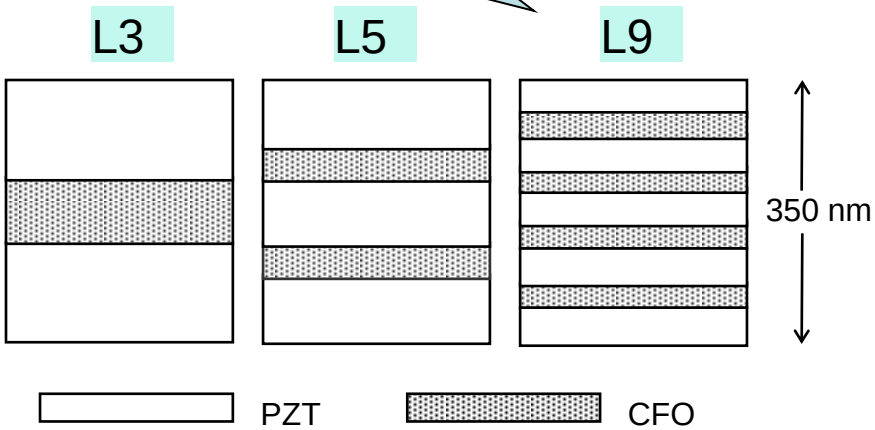
O_2 = 100 mT,

T_s = 400° C

L3 = 135/80/135 nm ,
L5 = 90/40/90/40/90 nm
L9 = 45/20/45/20/45/20/45/20/45 nm

Laser:
λ= 248 nm f=10 Hz, E=250 mJ

Top Electrode:
Platinum (dc Sputtering)



substrate = $Pt/TiO_2/SiO_2/Si$ (polycrystalline)
$LaSr_{0.5}Co_{0.5}O_3$(LSCO)/MgO (textured)
LSCO/STO (textured)

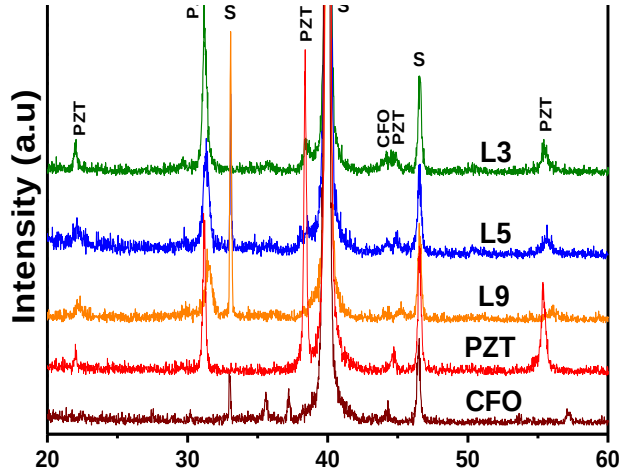
RTA

T_a = 650-700°C x150 s in Air

X- ray Diffraction

Polycrystalline films

$Pt/TiO_2/SiO_2/Si$

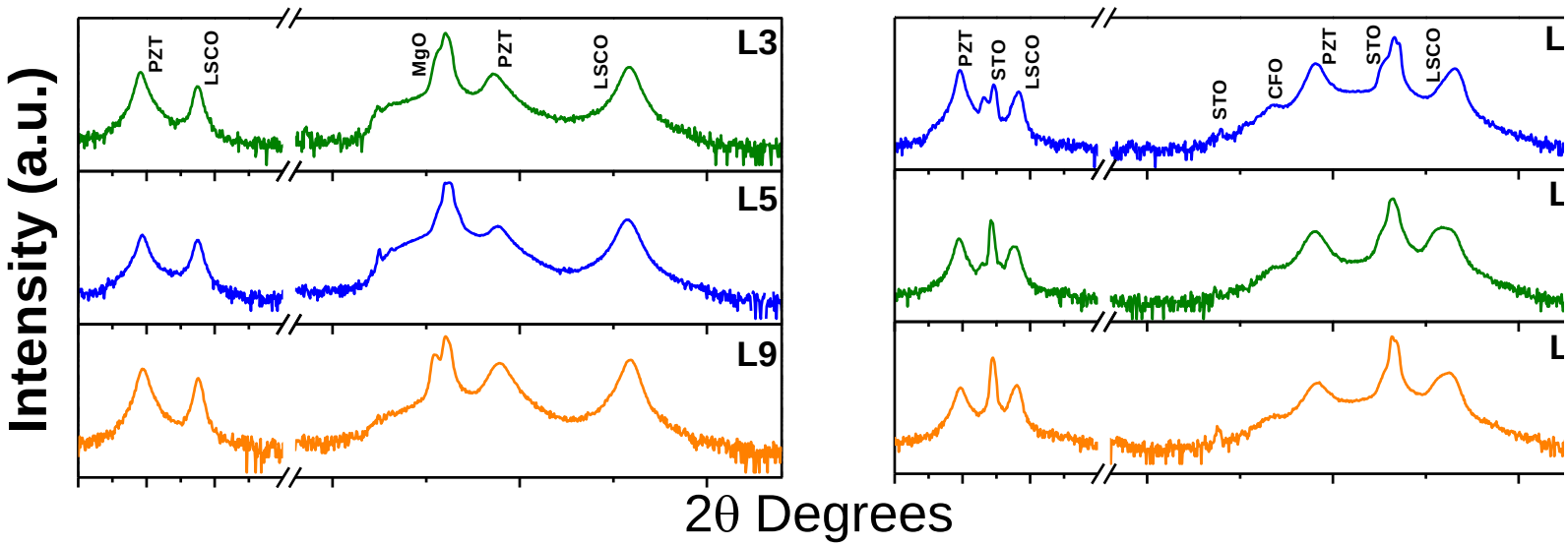


- Perovskite PZT
  Ferroelectric/Piezoelectric
  a = b = 4.036 Å c = 4.146 Å
  T_c = ~600 K
- Spinel CFO
  Ferrimagnetic
  a = b = c = 8.3919 Å
  T_N = ~790 K

Textured Films

MgO

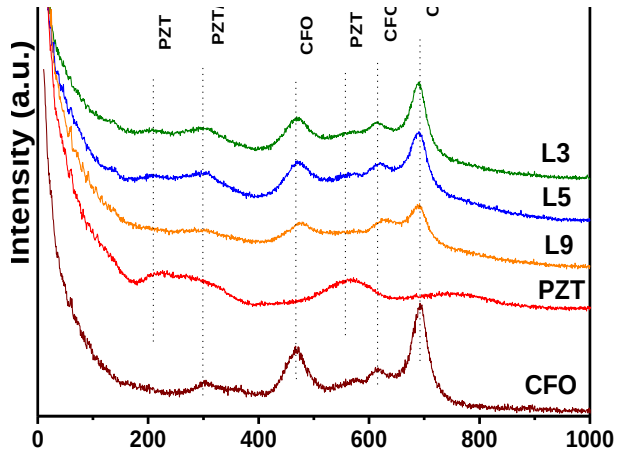
STO



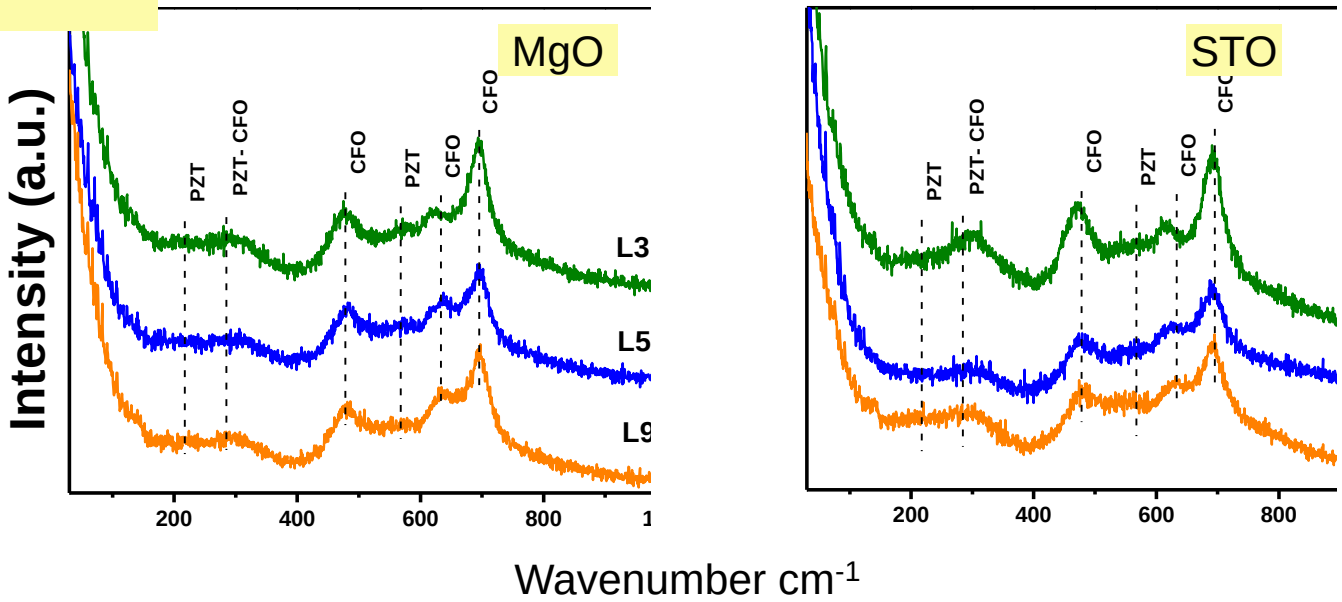
- X-ray patterns of PZT/CFO MLs, indicate that all peaks correspond to PZT and CFO phases without the appearance of any additional peak.

Raman Spectra

Polycrystalline
$Pt/TiO_2/SiO_2/Si$



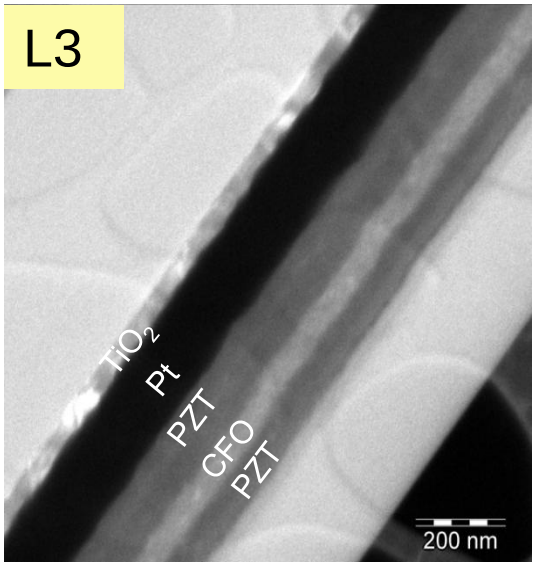
Textured Films



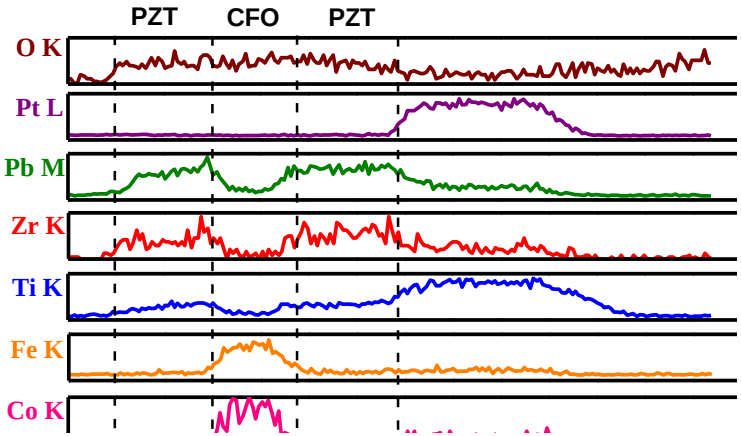
➢ The observation of distinct peaks for PZT and CFO in thin films by XRD and Raman spectroscopy suggest that individual ferroelectric and ferromagnetic phases were retained in the ML structures. No intermediate phase was found.

Microstructure Analysis

L3

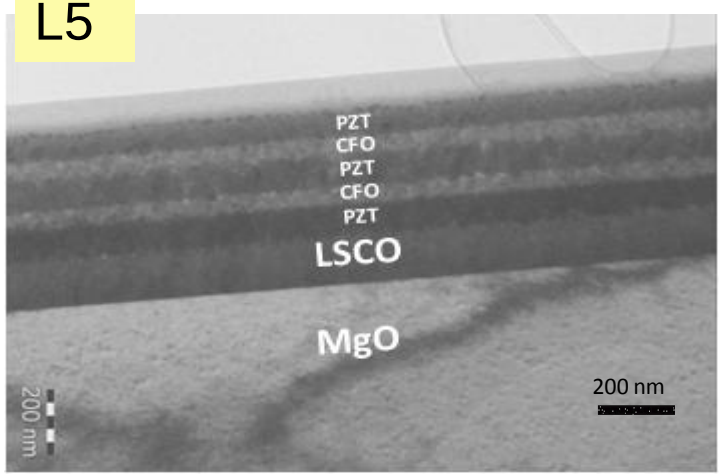


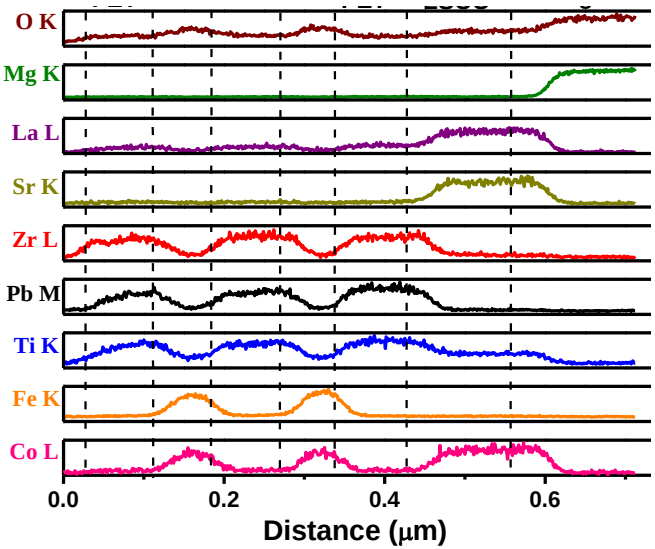
Polycrystalline



Textured Films

L5



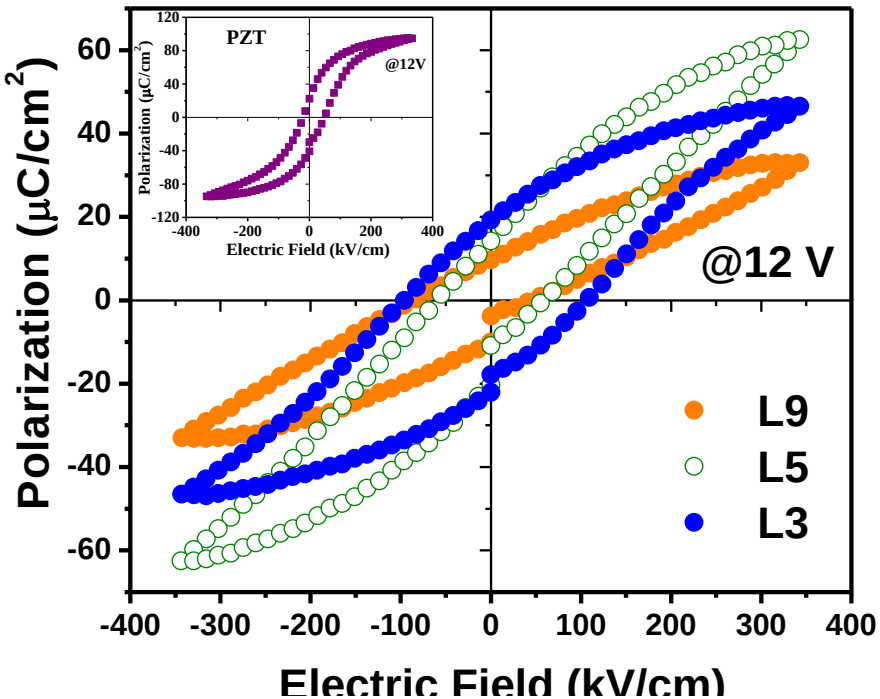


- The STEM line scan data indicate that the as deposited MLs structure were not maintained but partially diffused near interfaces.

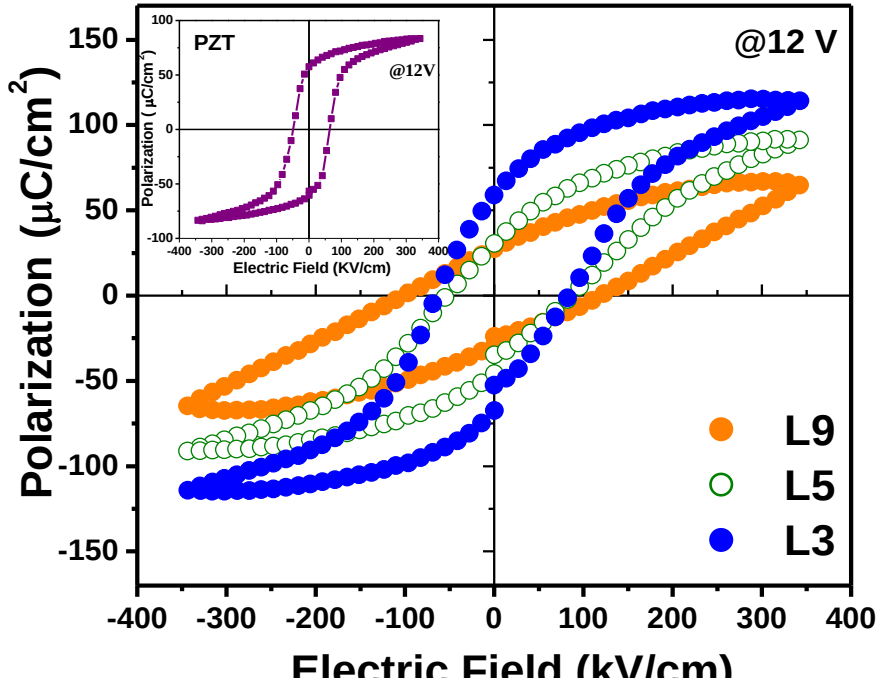
N. Ortega et al. JAP 100, 126105 (2006)

N. Ortega et al. PRB 77, 014111 (2008)

Polycrystalline



Textured Films



- PZT-CFO films showed well-defined but not saturated ferroelectric loop at 12 V

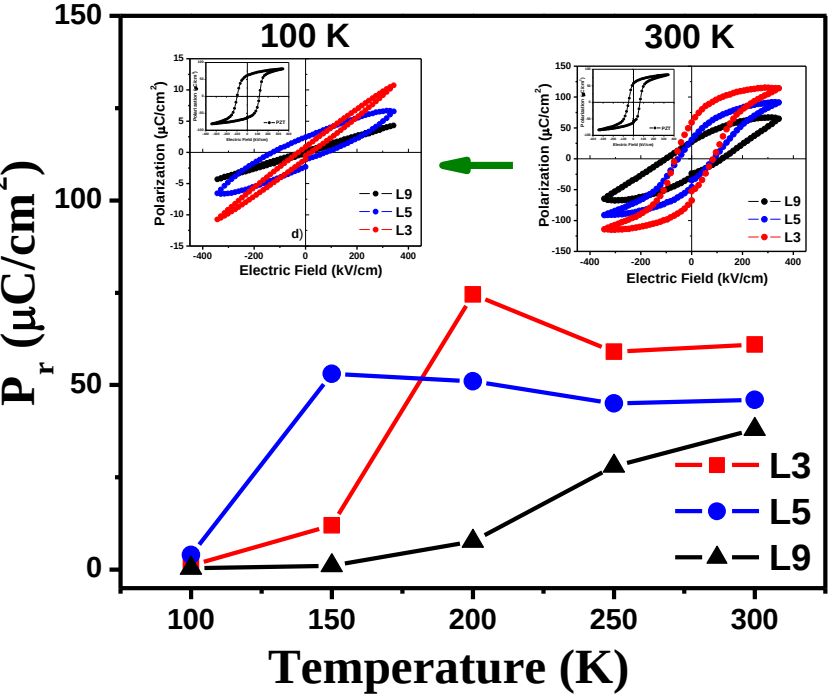
L3: $P_r \rightarrow$ ~ 21 μC/cm^2 and $E_c \rightarrow$ ~ 100 kV/cm
(inset) PZT: $P_r \rightarrow$~ 30 μC/cm^2 $E_c \rightarrow$~ 35 kV/cm

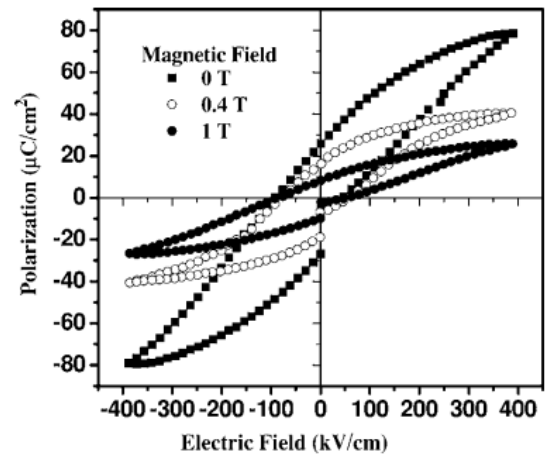
- The textured films exhibited well saturated loop and had larger P_r compared to polycrystalline films.

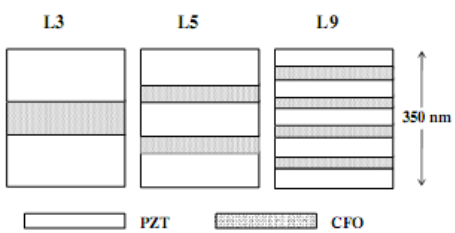
- L3: $P_r \rightarrow$ ~50 μC/cm^2 ; $E_c \rightarrow$ ~ 73.5 kV/cm
PZT: $P_r \rightarrow$~ 60 μC/cm^2 ; $E_c \rightarrow$~ 56 kV/cm
(inset)

- The polarization reduction in ML structures was due to the presence of non-ferroelectric (CFO) regions which also hinder the domain wall motion of the ferroelectric region.

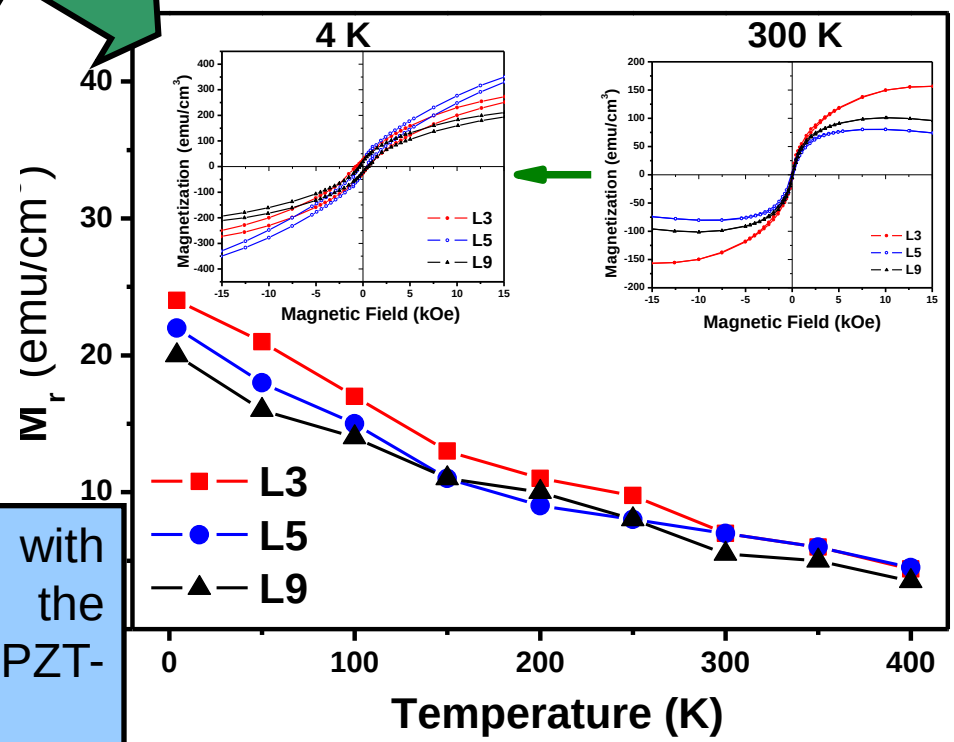
Dynamic temperature dependent magneto-electric coupling in $Pb(Zr,Ti)O_3/CoFe_2O_4$ multilayer nanostructures





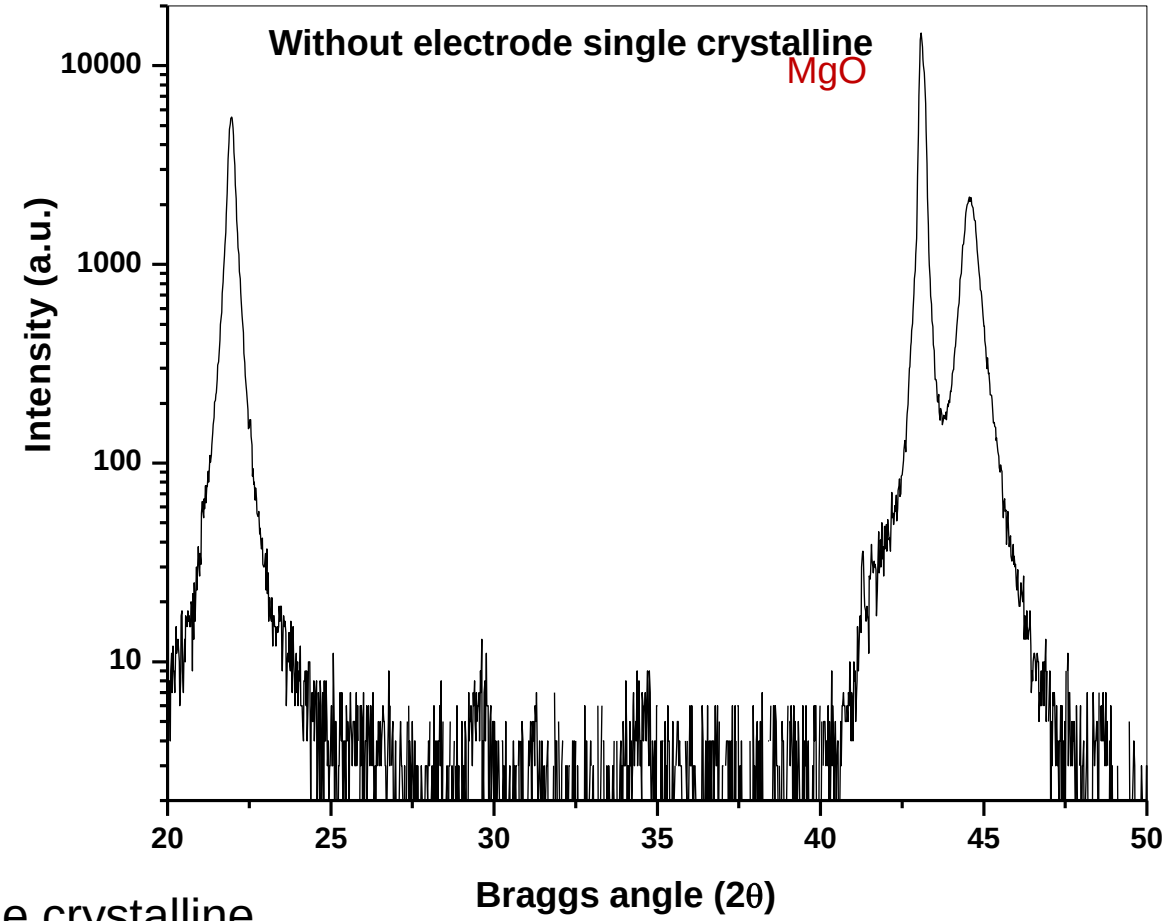


Layered nanostructure



Dynamic decrease in polarization with increase in magnetization suggest the magnetoelctric coupling in multilayers PZT-CFO thin films.

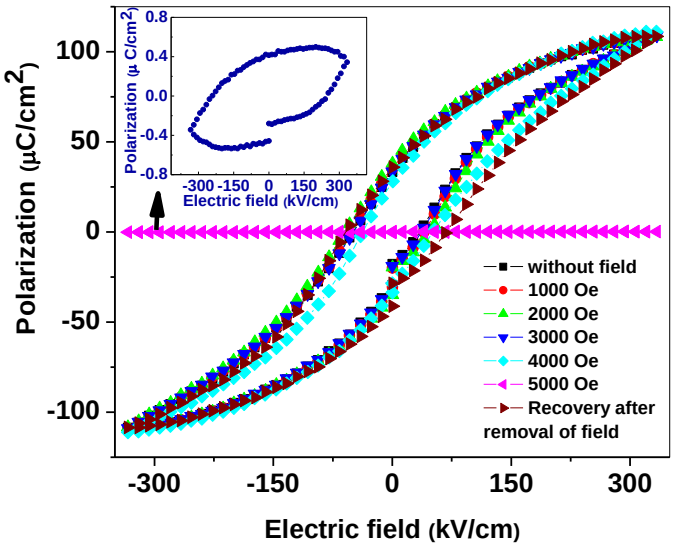
X-ray diffraction patterns of PZT/PFW (80:20) single crystalline thin films on MgO (001)

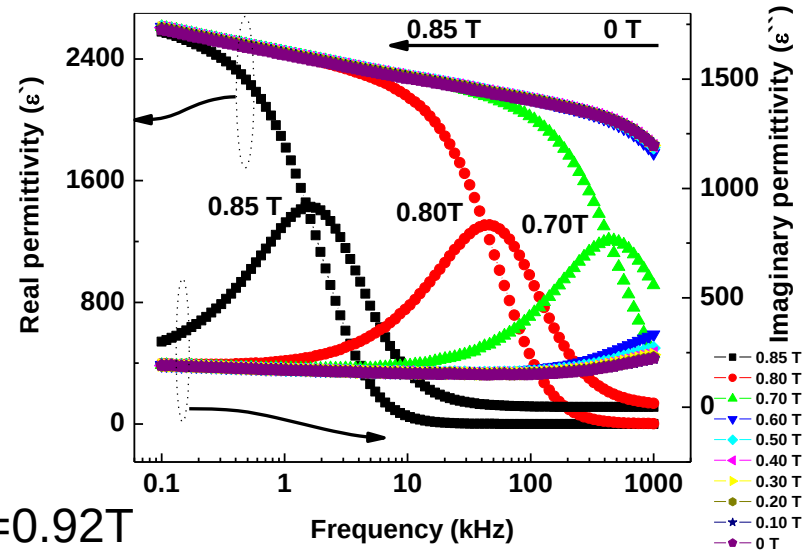


- ✓ Single crystalline
- ✓ Single phase
- ✓ Epitaxial growth along (001) plane of MgO

Discovery of Novel Room temperature Multiferroic with Large Magnetoelectric Magnetic control of large room-temperature polarization

$20\%PbFe_{1/3}W_{2/3}$ $80\%PbZr_{.57}Ti_{.43}O_3$





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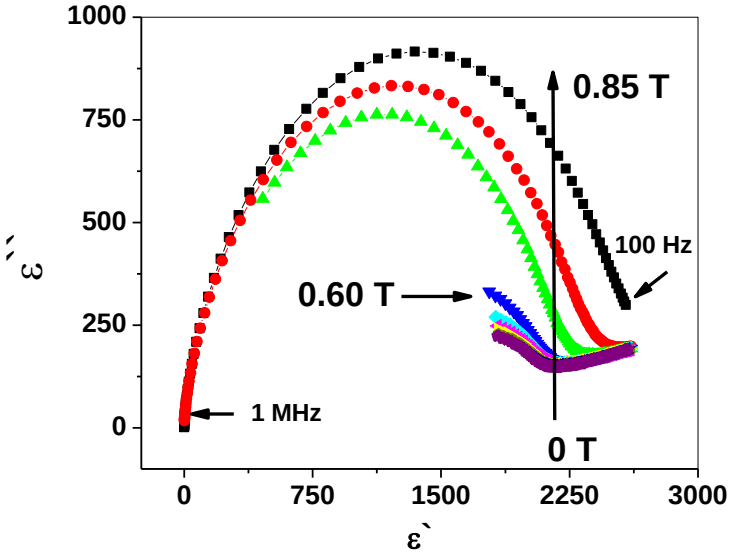
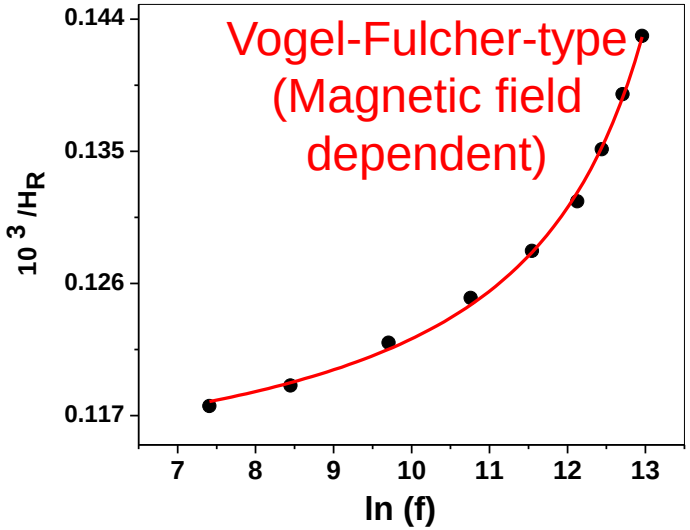
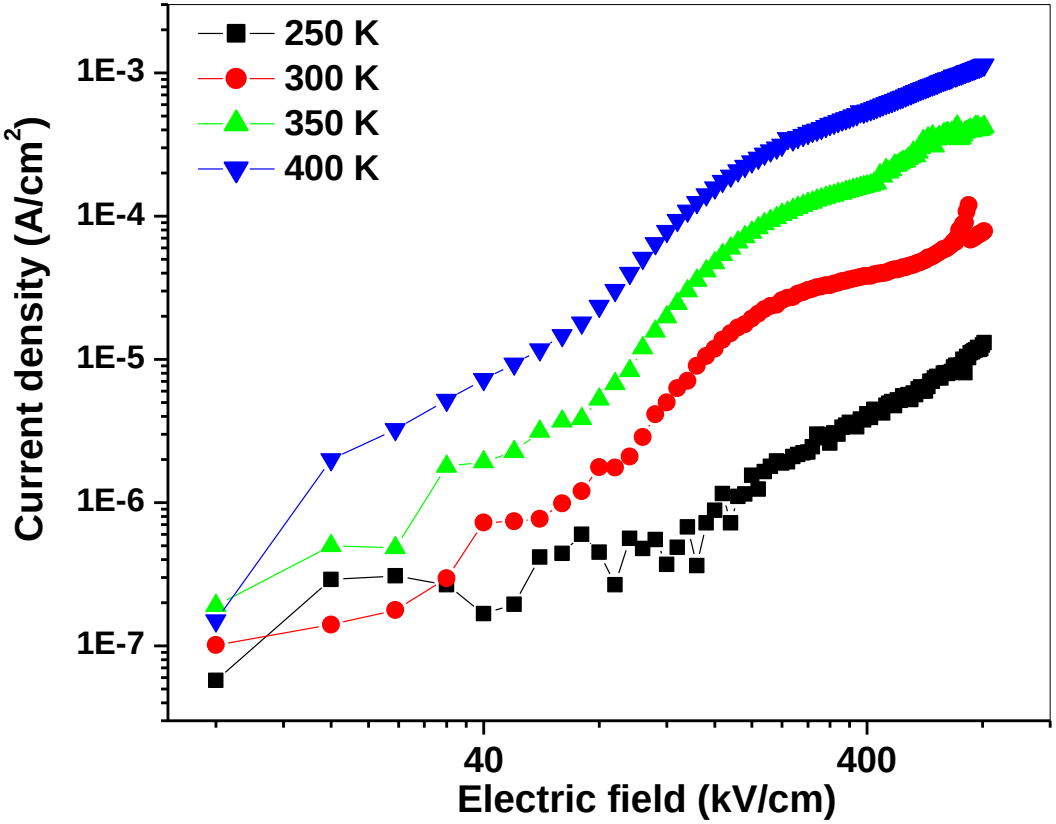


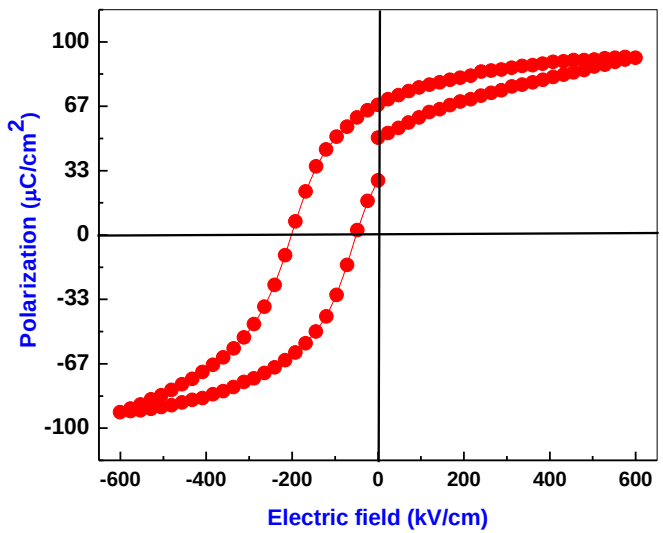


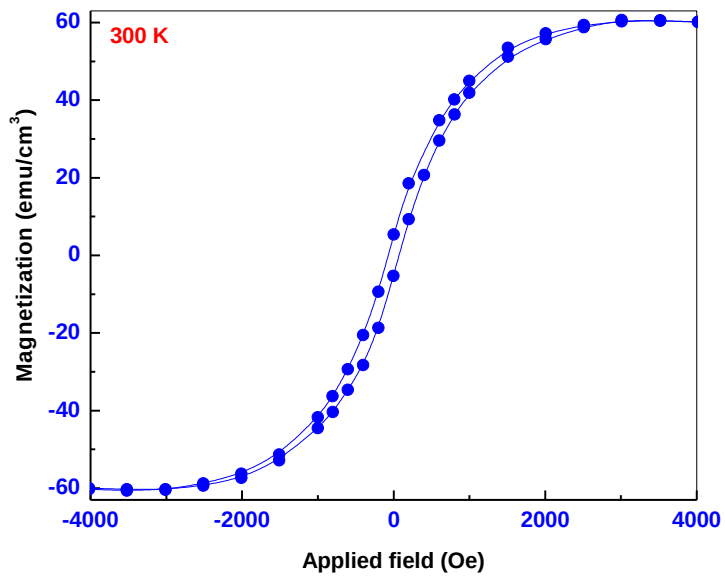
Very low leakage current in PZT/PFW supperlattices

- Low leakage current ~ 1e-5 at 150 kV/cm applied external electric field.
- Very high breakdown field suggesting its utility for high energy density capacitors.
- The current density increased with increase in temperature and applied external electric field.
- The low leakage current remained low even at elevated temperatures

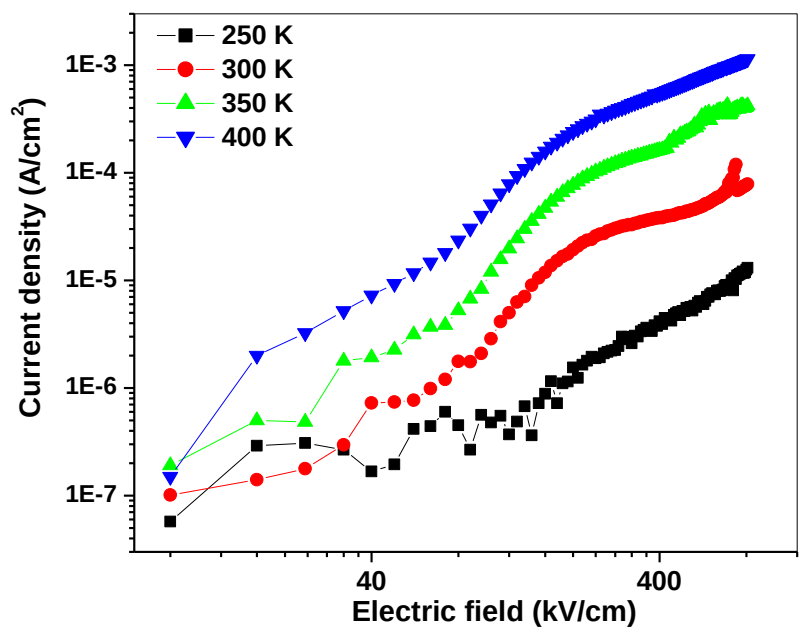


Strain induced effect in PZT/PFW supperlattices



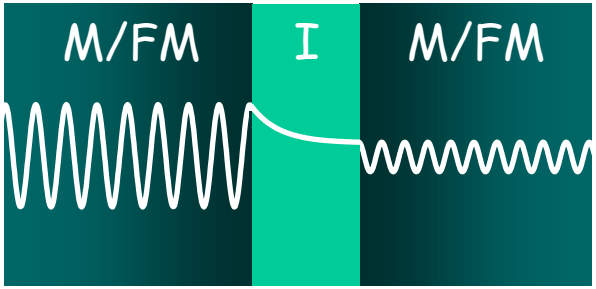


- **Room temperature high remanent polarization almost 40 μC/cm² and ferromagnetism**
- **Very high breakdown field. At 20 V (for 300 nm film) ~ 60-100 MV/m, Very low leakage current**
- **Probably good for multiferroic memory and high energy density capacitors**



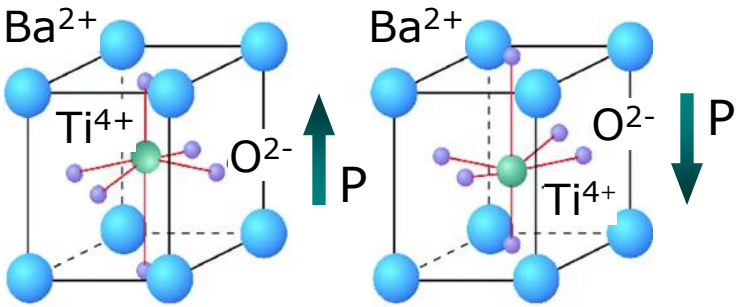
Modeling of Multiferroic Heterostructures

(Magnetic) Tunnel Junction

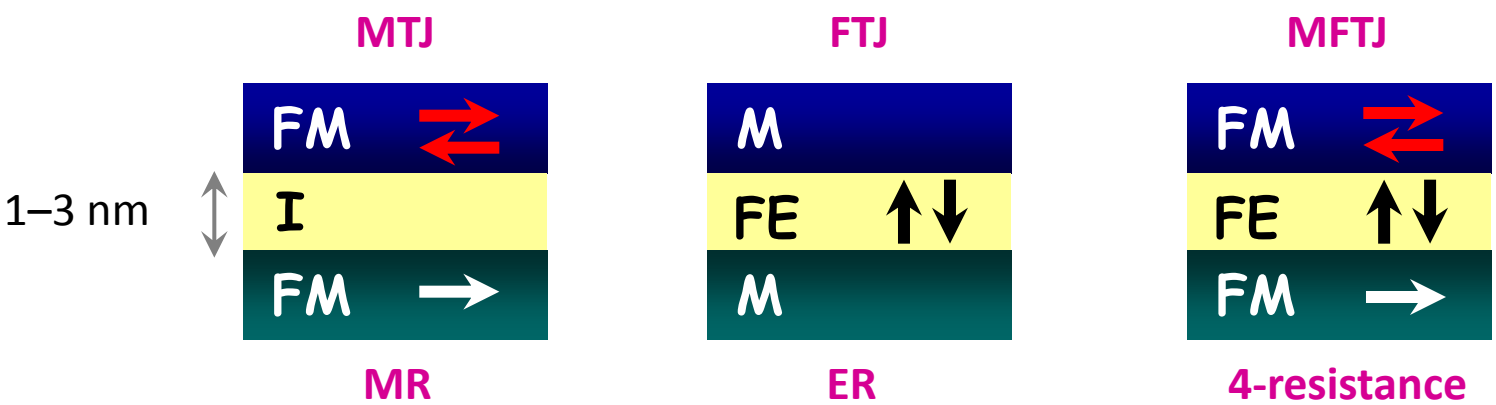


⊗

Thin-Film Ferroelectric



Heterogeneous (Multiferroic) Structures with New Properties



e.g. $SrRuO_3/BaO/BaTiO_3/TiO_2/SrRuO_3$

Tsymbal and Kohlstedt, Science **313**, 181 (2006)
Velev *et al*, Surf. Sci. Rep. **63**, 400 (2008)

Cluster Productivity Summary

(9/08 - 6/09)

Number of Reviewed Publications: 33

Applied Physics Letters: 4
Physical Review B: 3
Journal of Applied Physics: 6
J. Phys: Condes Matter: 2
J. Phys. Applied Physics D: 1
J. Raman Spectroscopy = 2

Number of scientific presentations: 32 + 16(*pending*)

Invited Presentations 4 + 5 (*pending*)

Graduate (Ph.D.)Students: 14

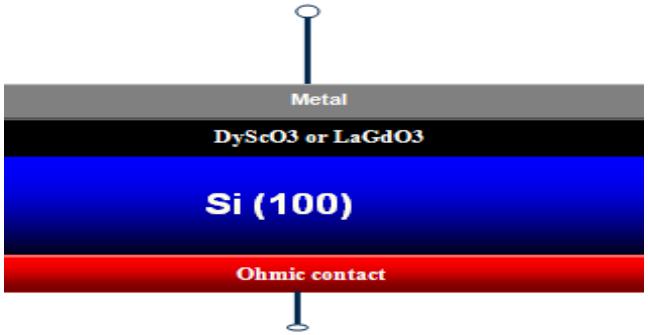
(**2 graduated**, Nora Ortega, K. Samanta)

Summer training for High school students (6) - projects completed

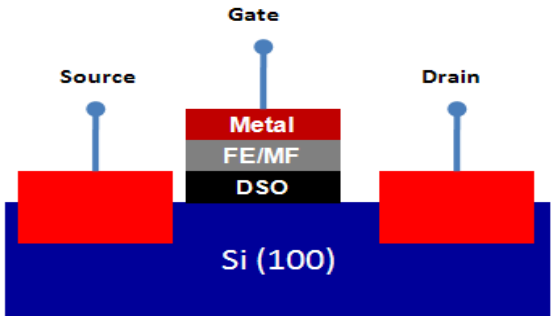
Future Work Plan

- Continue fundamental science work to understand nansocale phenomena in magnetoelectric and spintronic materials and thereby develop new single phase room temperature multifunctional materials.
- Continue synthesizing multiferroic and DMS spintronic materials utilizing sol-gel, CVT, PLD, and RF magnetron sputtering techniques, and characterize them by various characterization tools in order to understand structural, magnetc, electrical, and magnetoelectric properties.
- Develop processes to fabricate $BiFeO_3$ (BFO) nano-capacitors, using metalorganic chemical vapor deposition (MOCVD) and Atomic Layer Deposition (ALD) systems (new chemical route) and nanolithography.
- Study materials properties at the nanoscale, using a unique combination of complementary techniques: Synchrotron X-ray scattering, with the only worldwide x-ray nano-beam operational at the Advanced Photon Source (APS) at ANL, piezoresponse force microscopy (PFM), and high-resolution transmission electron microscopy (HRTEM).

Testbed devices for fabrication at ANL

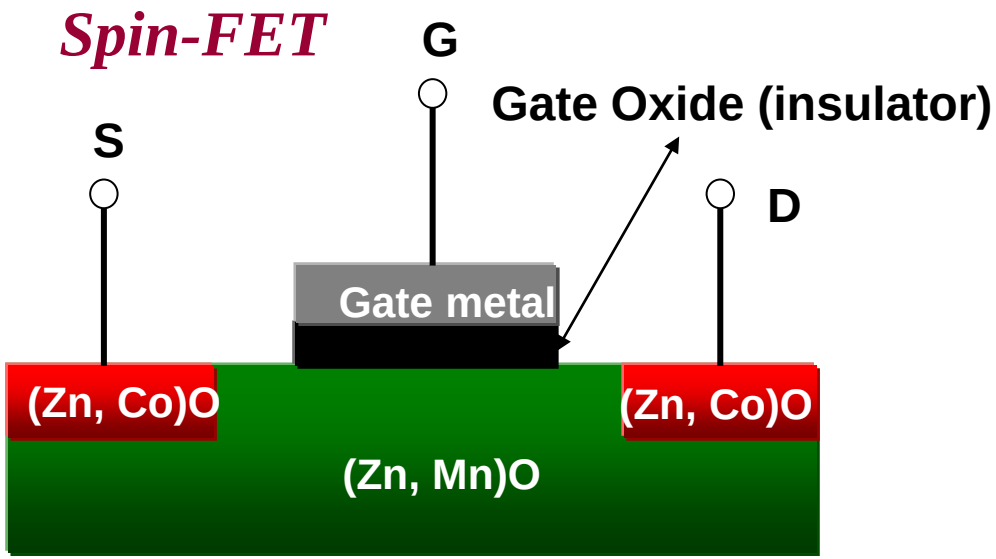


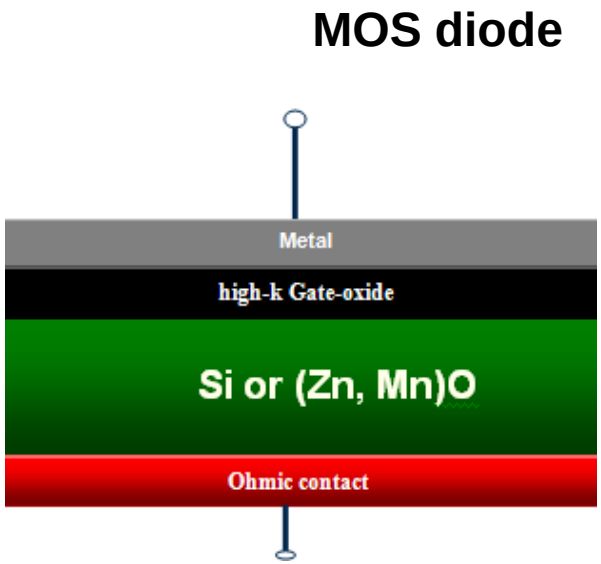
Metal-Oxide-Silicon (MOS) diodes with high-k buffer layers



MOS-FET (Field effect transistor) based high-k buffer layer, ferroelectric and multiferroic material for Si based CMOS process.

Testbed Device Structures for Fabrication at SUNY-BU





- Pure (Zn, Mn)O can be grown as an antiferromagnetic spin-glass insulator
- Negative (-) gate bias brings holes in to the (Zn, Mn)O region
- hole + (Zn, Mn)O is the Ferromagnetic semiconductor
- Ferromagnetic (Zn, Co)O or (Zn,Co,Al)O or other RT FM semiconductor can be used as the Source and Drain
- Highly spin polarized electrons can flow in the (Zn, Mn)O channel region

End of Presentation

For Further Information refer to the Website:

http://www.ifn.upr.edu

http://speclab.upr.edu