Structural investigation of functional oxides using compositional spreads

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Functional Oxides

Topics addressed in this symposium will include, but not be limited to:

- **Multiferroics**
- **Artificially layered materials, including strain effects**
- **Ferroelectric and dielectric oxides**
- **Piezoelectric/electrostrictive oxides for MEMS, acoustic wave devices, sensors, and actuators**
- **Magnetic and electro-optic oxides**
- **Superconducting oxides, particularly in hybrid heterostructures**
- **Semiconducting oxides**
- **Electric field effect on functional and multifunctional oxides**
- **Multifunctional oxides on silicon and compound semiconductors (e.g., for novel devices)**

Functional Oxides (cont.)

• Search for optimal or novel properties in multi-parameters space of *composition* and *processing* variables

• Most studies are for *thin films* (epitaxial films) because of device-oriented applications

• Many parameters - MANY specimens

• *Combinatorial approach* of using one or more-dimensional compositional thin film spreads

• Different deposition methods for producing compositional spreads

• Large number of tools with localized probes are available for structural and physical properties measurements

Functional Oxides (cont.)

Difficulties:

• Complex process of synthesis of compositional spreads involving interdiffusion, thus reproducibility problem

• In many systems the properties are highly sensitive to crystallographic details and defects

• Limited ability to detect the crystallographic details, thus limitation in interpretation of composition-property relationship

TEM - imaging of microstructure, interfaces, domains, diffuse scattering, precipitation, ordering, dislocations and other defects

Recent combi projects for studying functional oxides

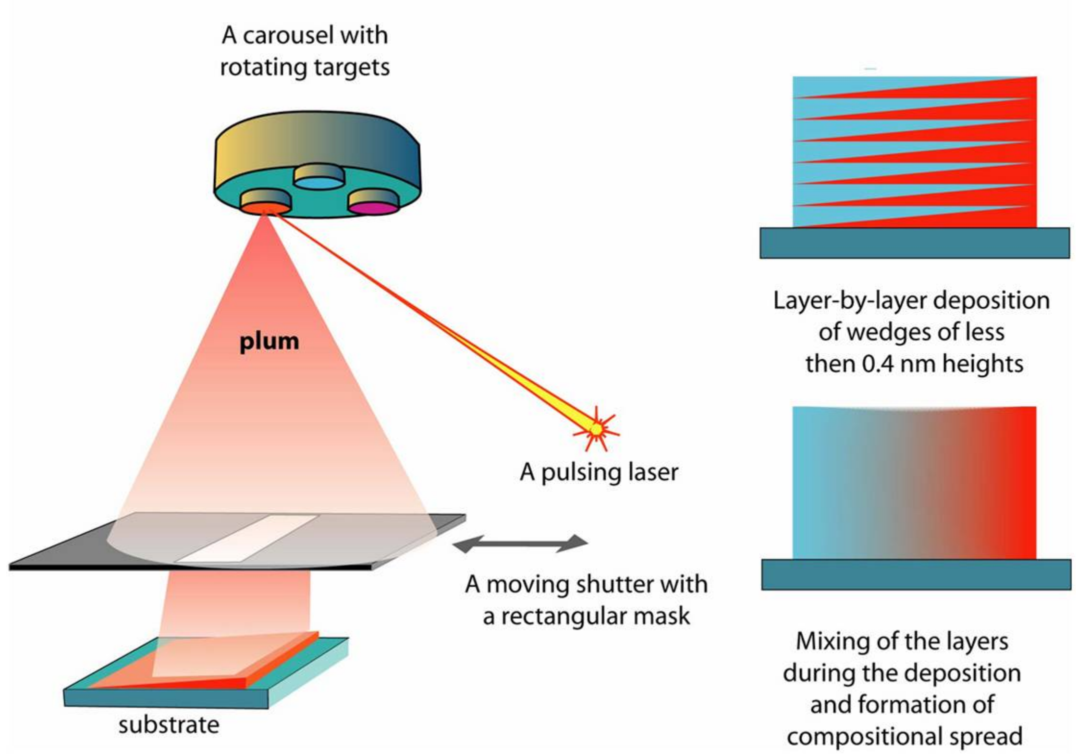
- **$BaTiO_3$ - $SrTiO_3$** on a $SrTiO_3$ substrate.
  High dielectric material for microwave and storage applications

- **ZnO-MgO** on a sapphire substrate.
  The effect of MgO on a band gap of ZnO semiconductor.

- **$LaMnO_3$ - $CaMnO_3$** on $SrTiO_3$ and $LaAlO_3$ substrates.
  CMR material, constructing magnetic diagrams

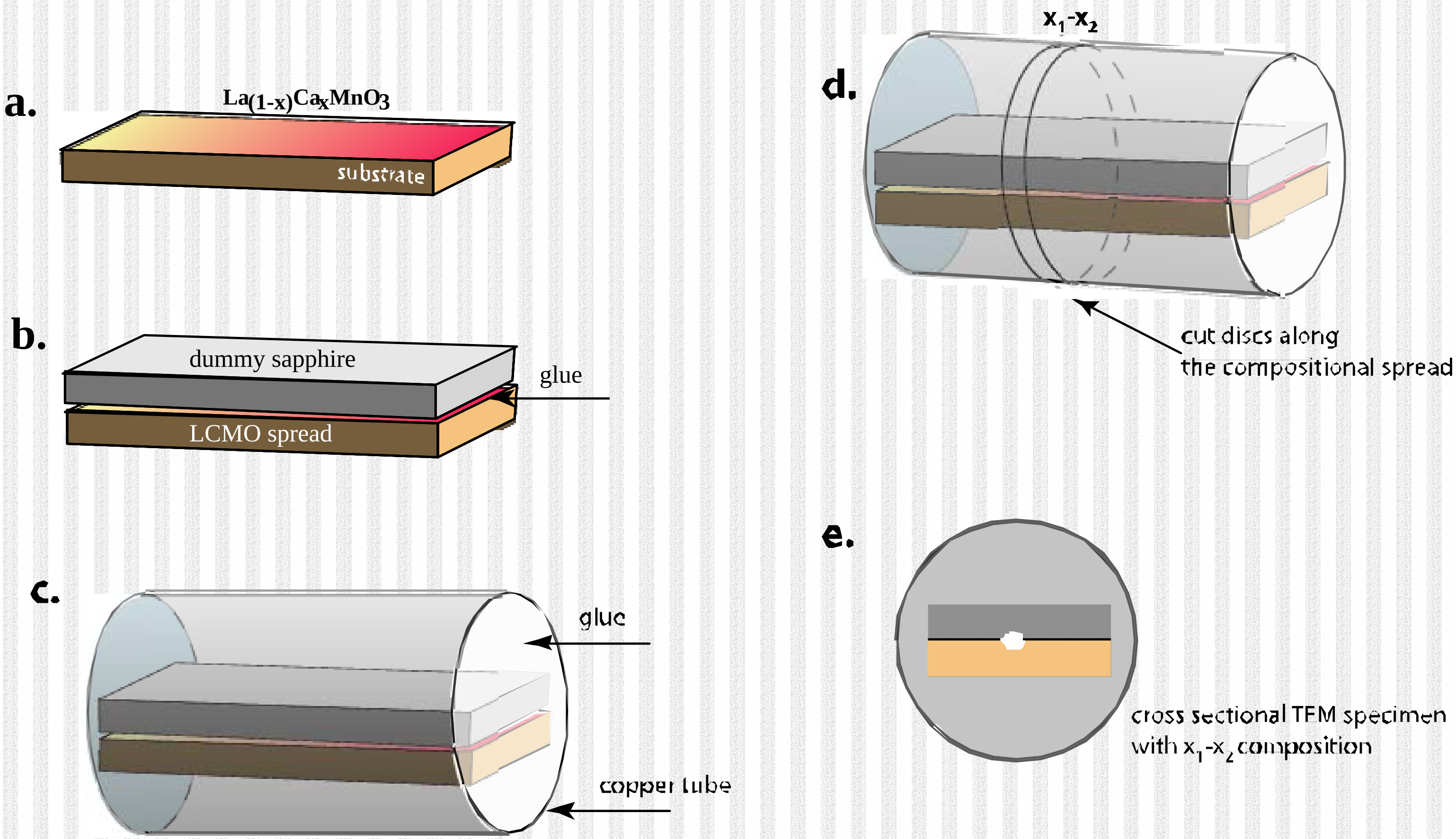
- **$BaTiO_3$-$CoFe_2O_4$** and **$PbTiO_3$-$CoFe_2O_4$** on a MgO substrate.
  Multiferroic material - ferroelectric/ferromagnetic

Deposition of compositional spread films

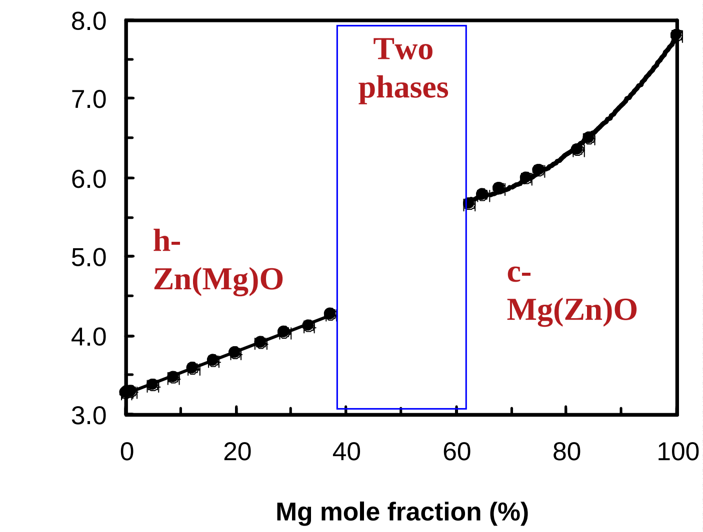


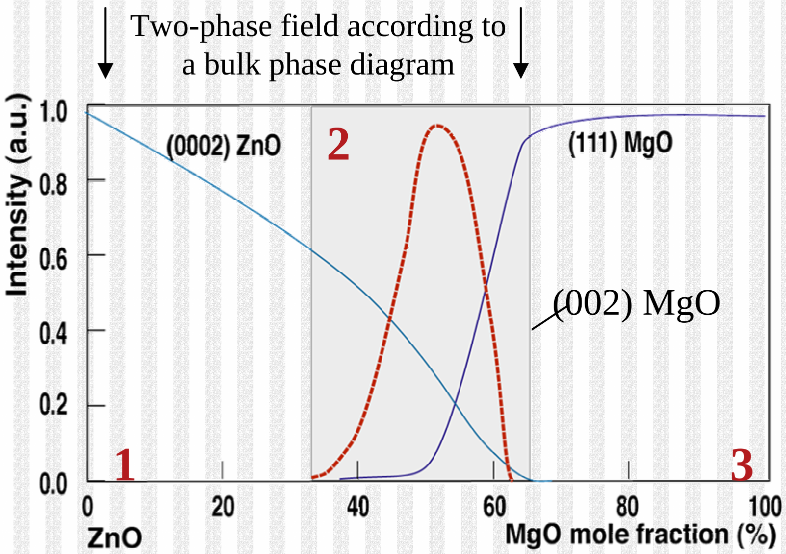
- Combinatorial pulsed laser deposition system of UMD
- Atomic layer-by-layer deposition controlled by a moving shutter
- Substrates at >600 ˚C in 10^{-4} Torr of oxygen

Preparation of the TEM specimens from a compositional spread



$Zn_{1-x}Mg_xO$ spread

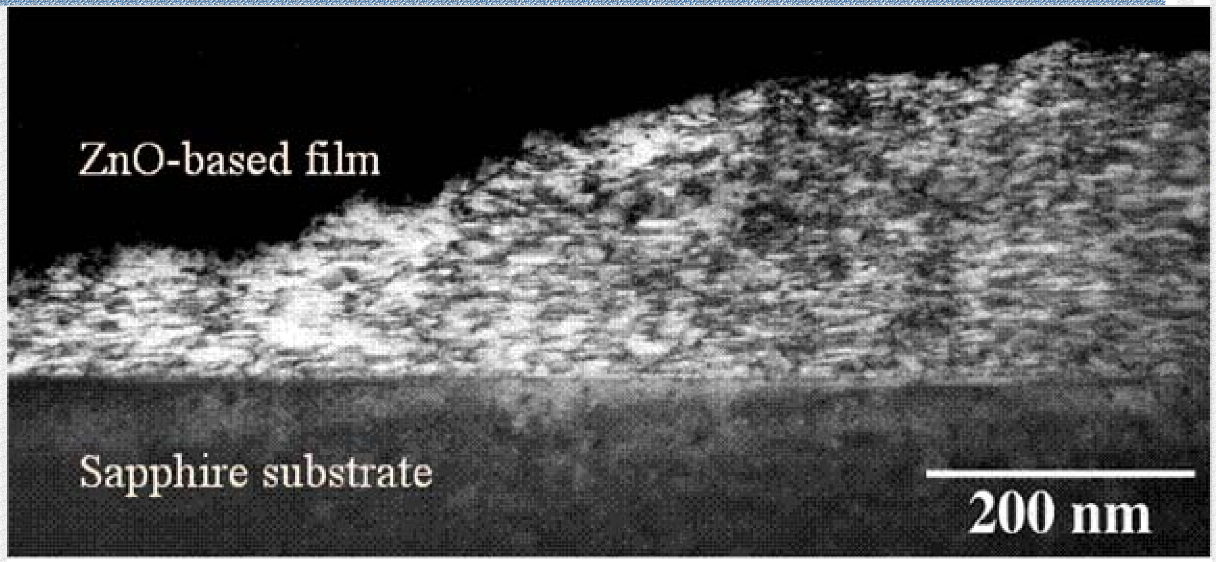


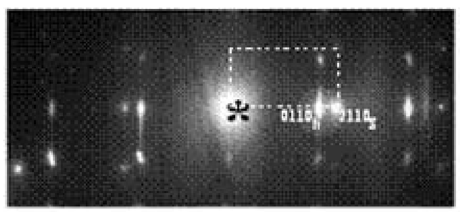


Composition tuned $Mg_xZn_{1-x}O$ band gap and the corresponding phases.

Phases according to scanning x-ray diffraction.

$Zn_{1-x}Mg_xO$ spread, region 1



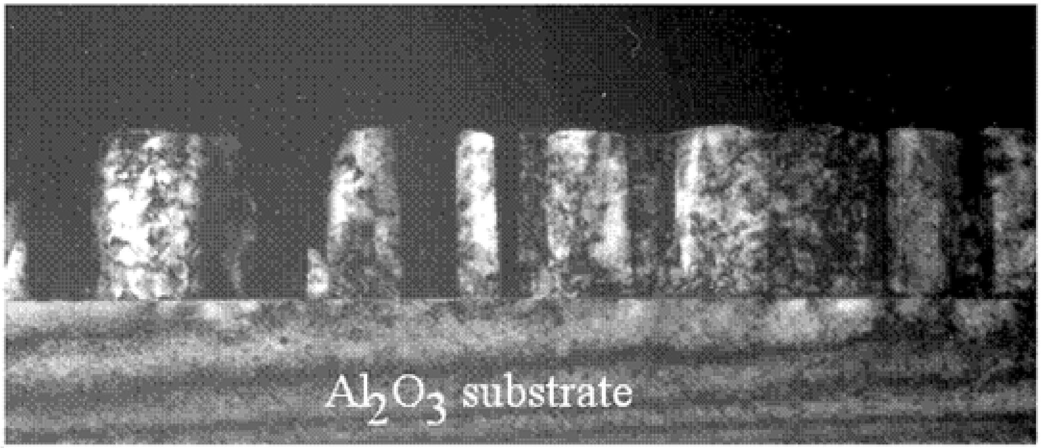


ZA=$[01\bar{1}0]_S$

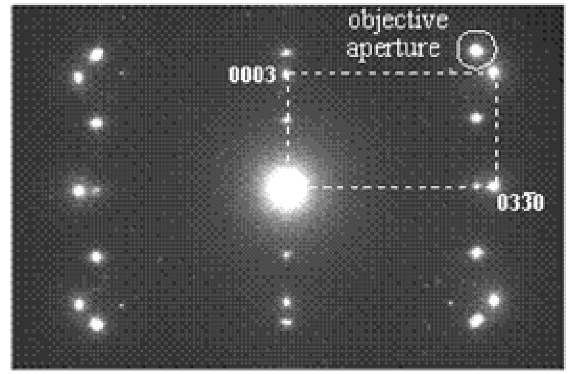
A ZnO-based phase with a high density of extended planar defects.

Orientation relationship: $(0001)_S$ //$(0001)_{ZnO}$; $[2\underline{1}\underline{1}0]_S$ //$[01\underline{1}0]_{ZnO}$

$Zn_{1-x}Mg_xO$ spread, region 3

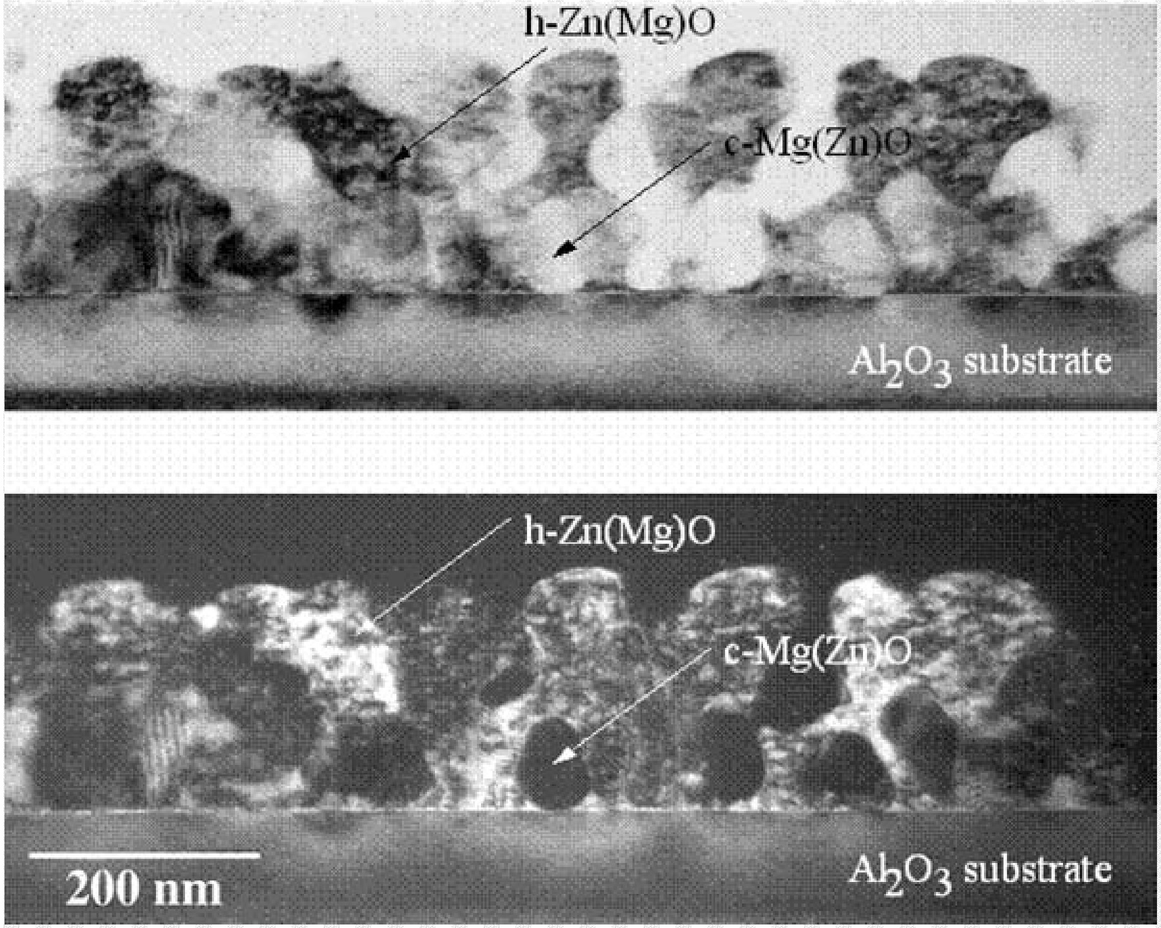


Dark field image of one of the twin variants.



SAED pattern showing MgO cubic phase in the following OR with a substrate: $(111)//(0001)_S$ and $[1\bar{1}0]//[2\bar{1}\bar{1}0]_S$.
Two twin variants are present.

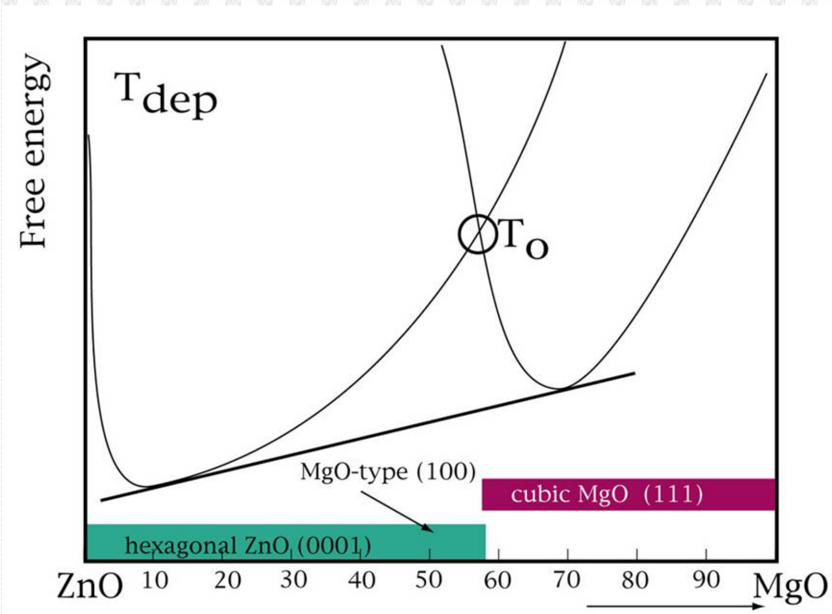
$Zn_{1-x}Mg_xO$ spread, region 2

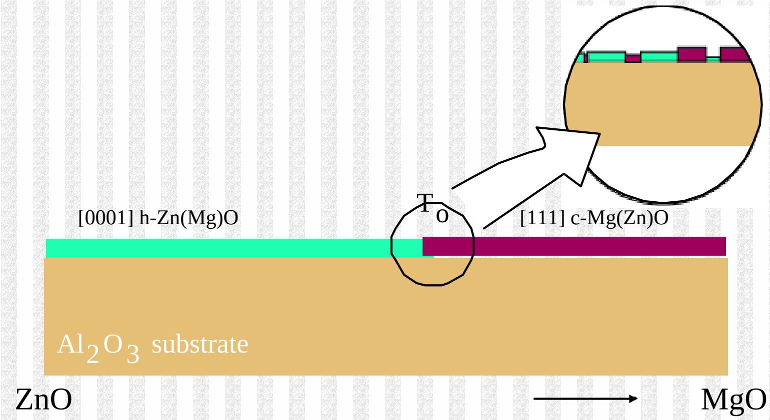


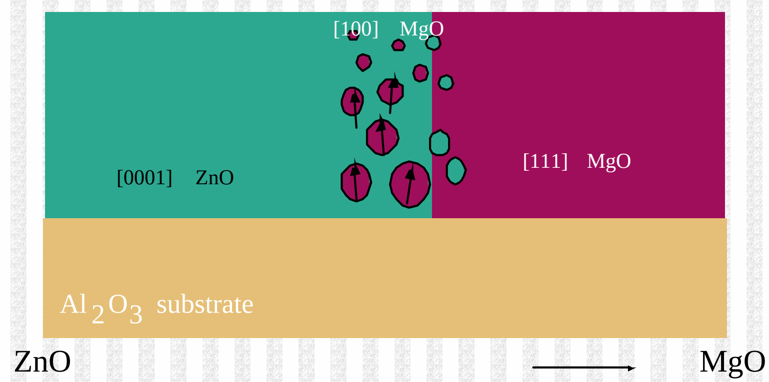
$(0001)_S //(0001)_{h-(Zn,Mg)O}//(100)_{c-(Mg,Zn)O}$;

$[2\bar{1}\bar{1}0]_S //[01\bar{1}0]_{h-(Zn,Mg)O}//[110]_{c-(Mg,Zn)O}$

$Zn_{1-x}Mg_xO$ spread, formation of region 2





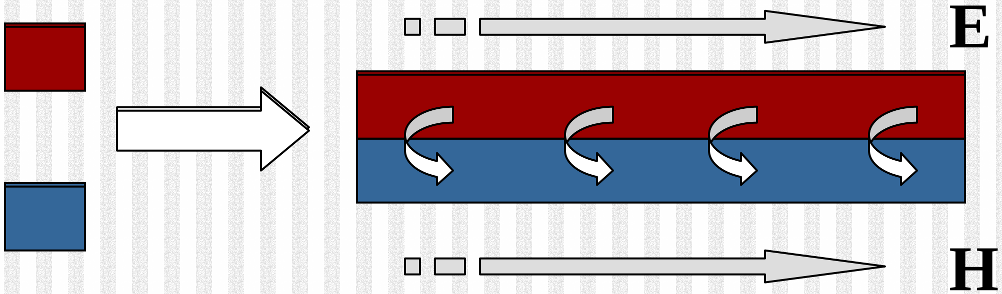


Ferroelectric/ferromagnetic $PbTiO_3$-$CoFe_2O_4$

Concept of multiferroic magneto-electric composites:

Piezoelectric, $\varepsilon_{jk}=d_{ijk}E_i$; E_i - electric field; ε_{jk} - strain ($PbTiO_3$)

Piezomagnetic, $M_i = q_{ijk}\sigma_{jk}$; M_i - magnetic moment; σ_{jk} - stress ($CoFe_2O_4$)



$\varepsilon_{jk} = s_{ijkl}\sigma_{kl}$

s_{ijkl} - effective elastic compliance,

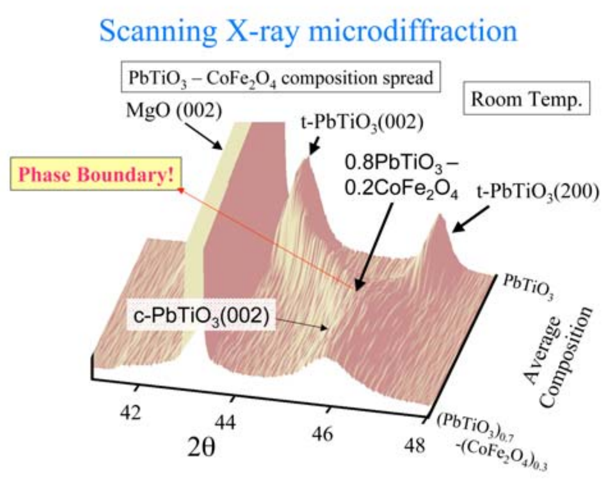
$s_{ijkl}(s_1, s_2, \alpha, \text{shape})$

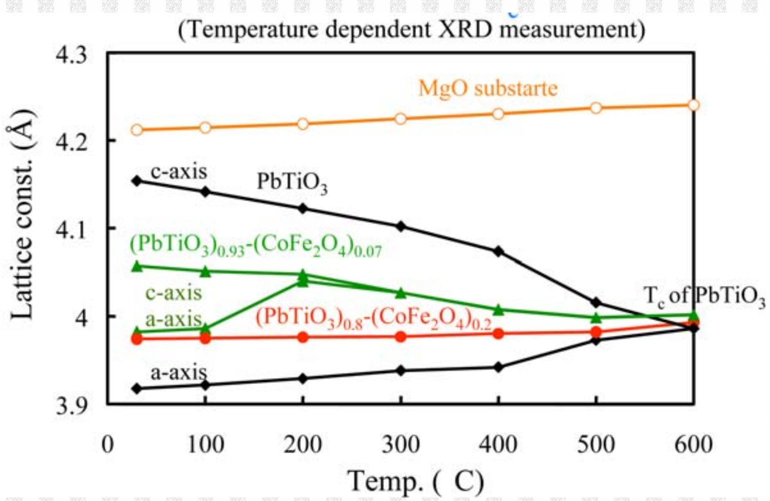
$B_i = q_{ijk}\varepsilon_{jk} + \lambda_{in}E_n + \mu_{in}H_n$

$D_i = d_{ijk}\varepsilon_{jk} + \lambda_{in}H_n + \kappa_{in}E_n$

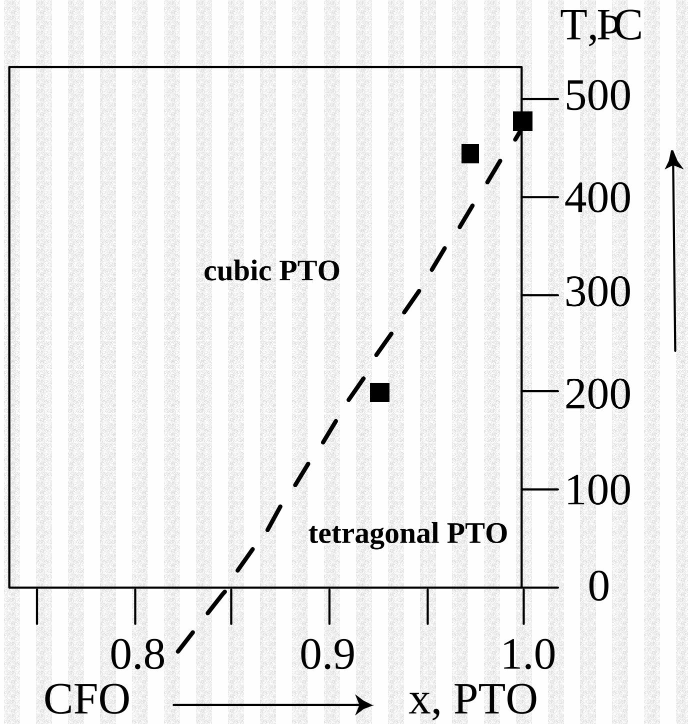
λ_{in} - magnetoelectric coefficient

Ferroelectric/ferromagnetic $PbTiO_3$-$CoFe_2O_4$

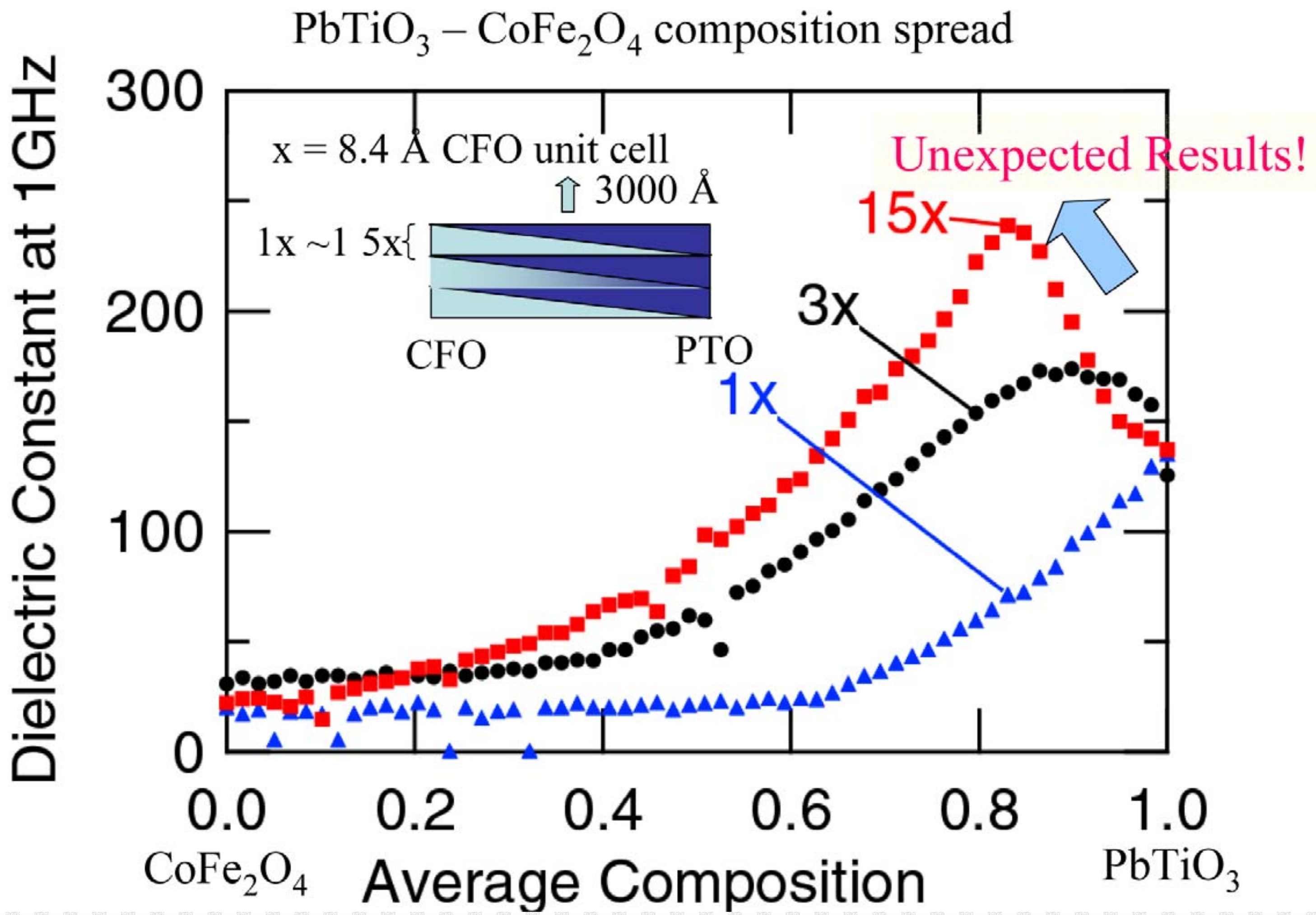




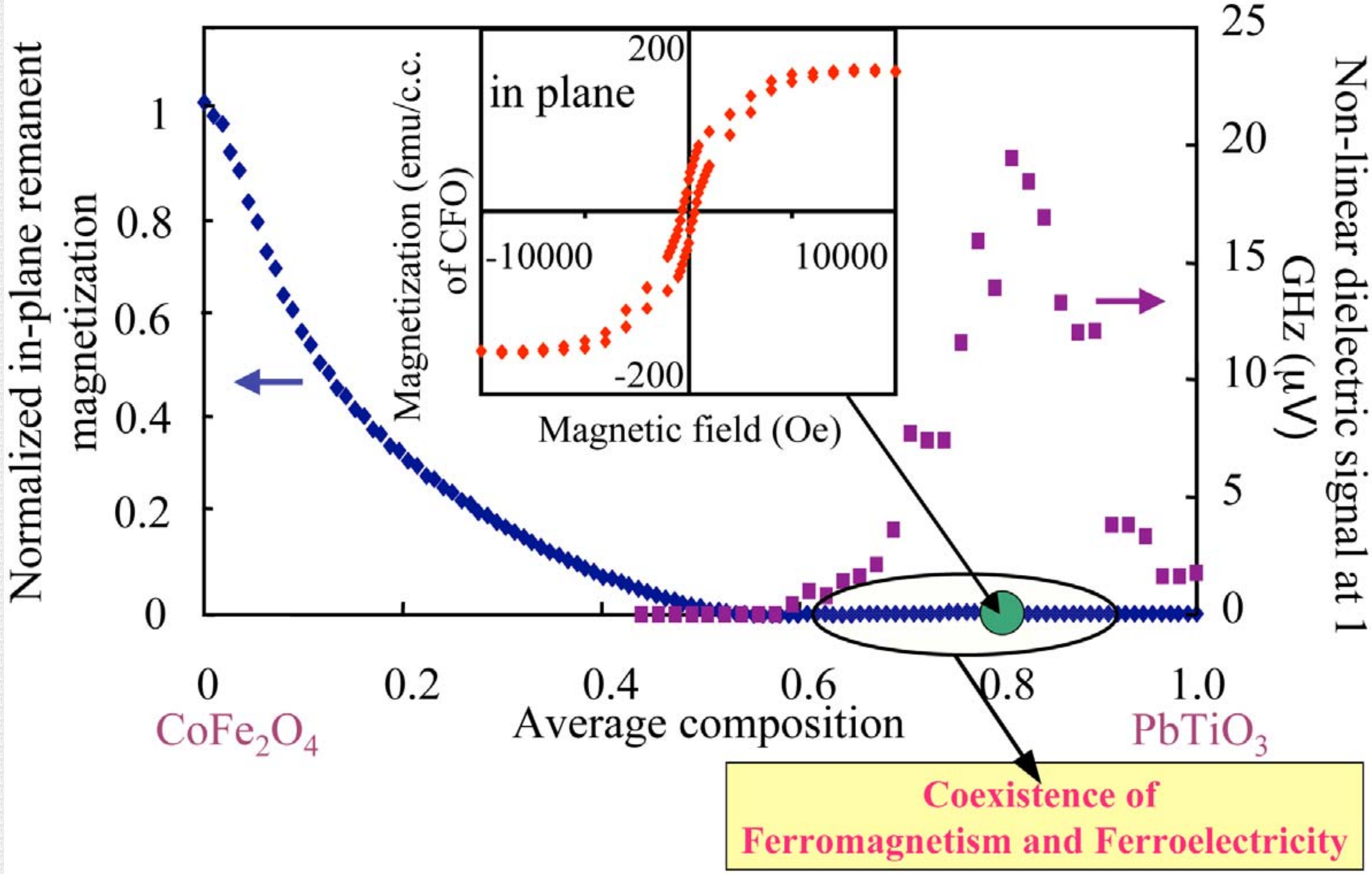
Effect of CFO on
Curie temperature of PTO



Ferroelectric/ferromagnetic $PbTiO_3$-$CoFe_2O_4$

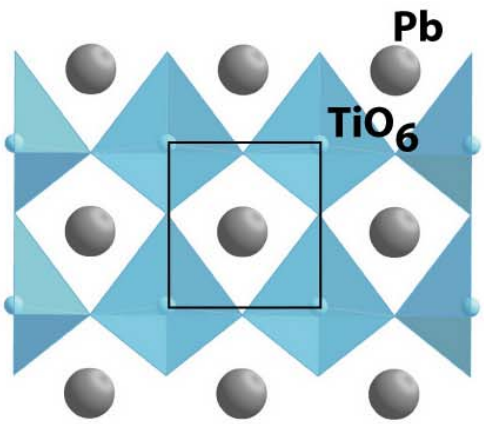


Ferroelectric/ferromagnetic $PbTiO_3$-$CoFe_2O_4$

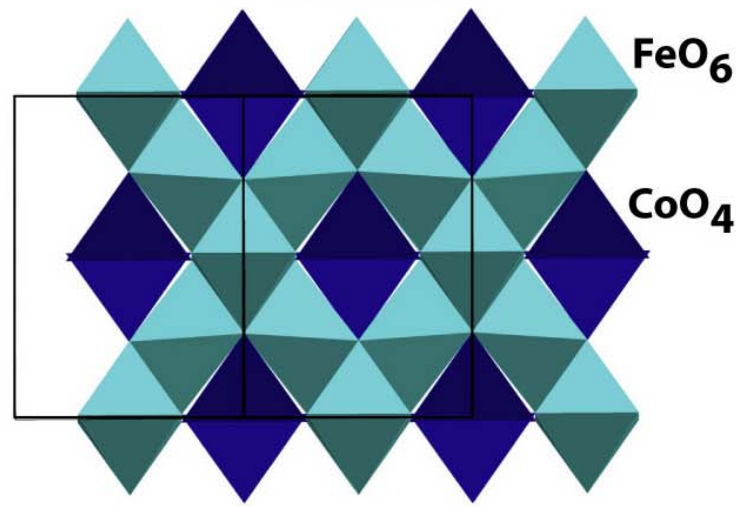


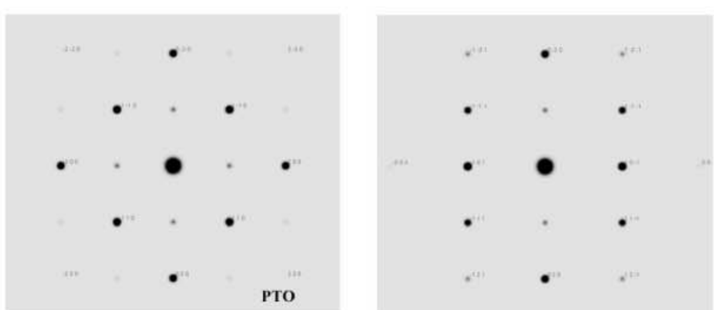
Ferroelectric/ferromagnetic $PbTiO_3$-$CoFe_2O_4$

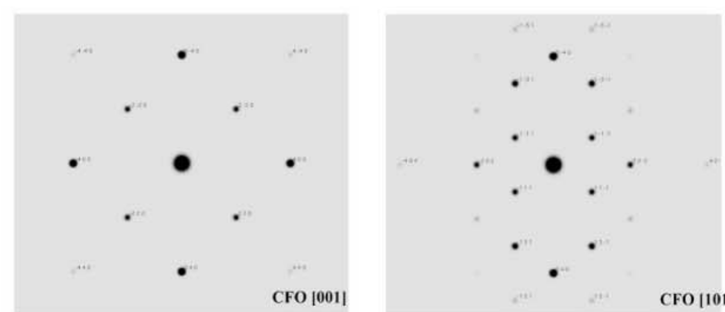
Perovskite $PbTiO_3$
[100] projection
a=0.39 nm; c=0.415 nm



Spinel $CoFe_2O_4$
[110] projection
a=0.839 nm

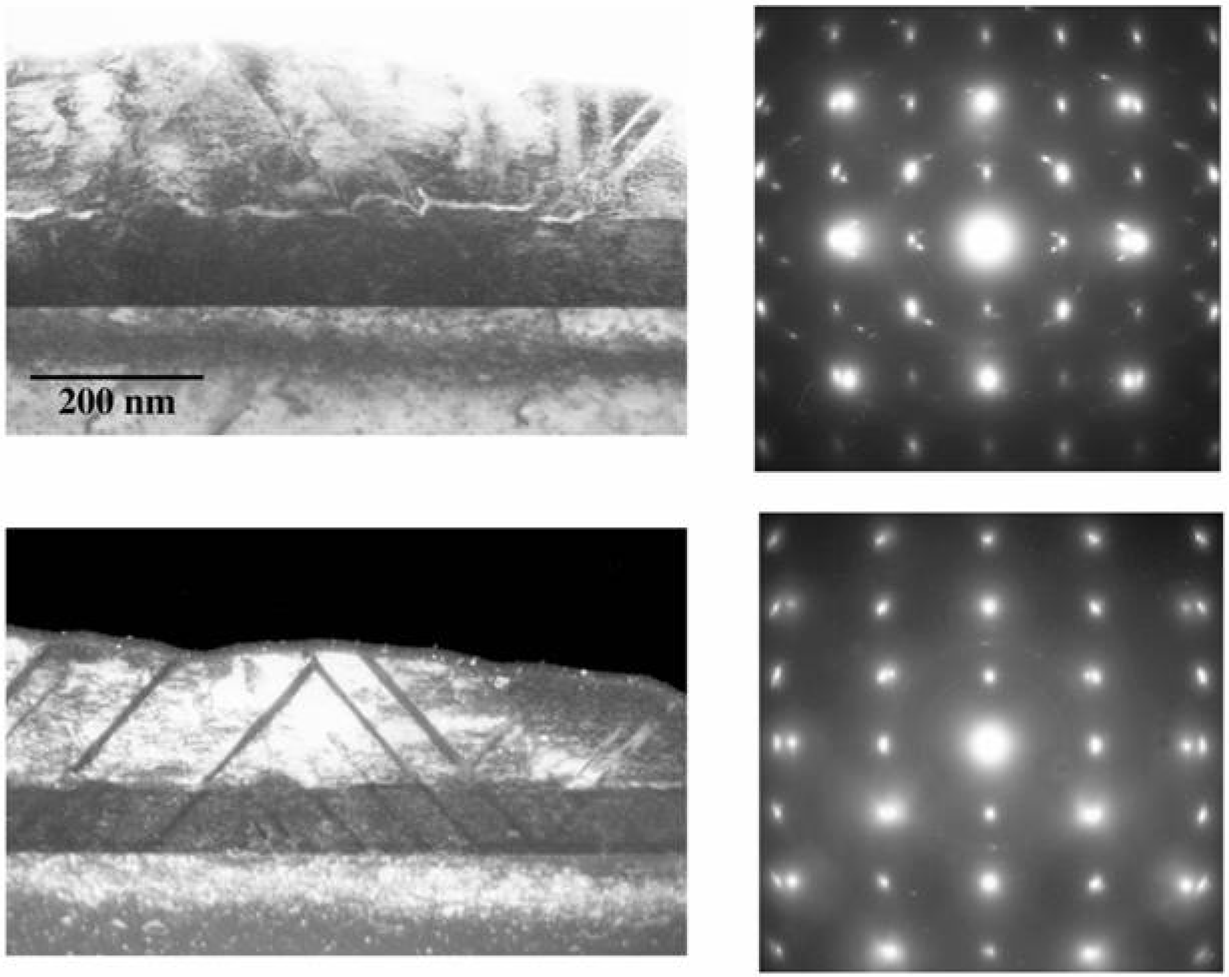






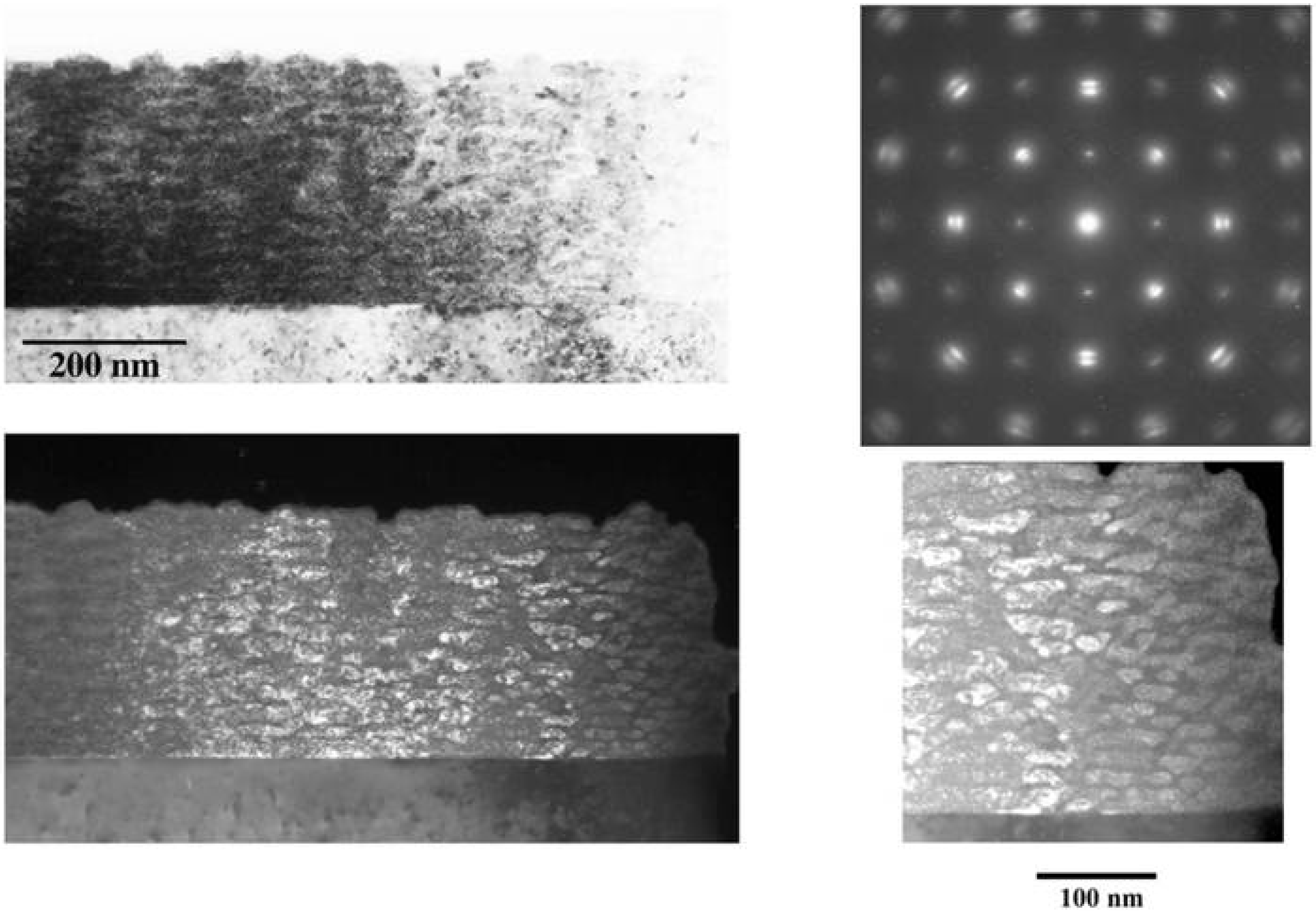
Ferroelectric/ferromagnetic $PbTiO_3$-$CoFe_2O_4$

0.9 PTO



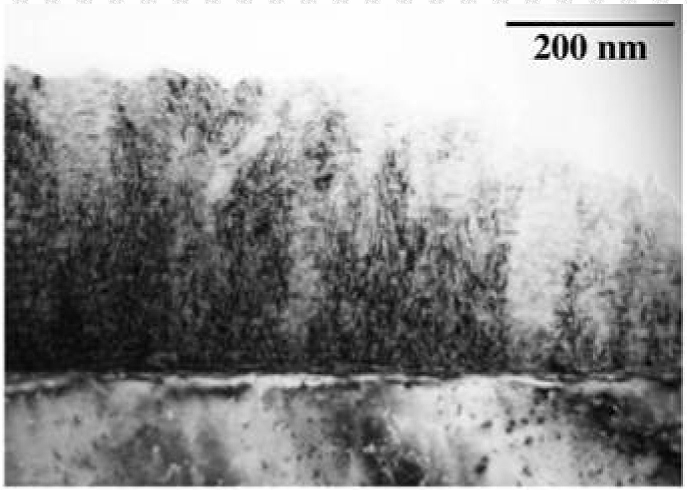
Ferroelectric/ferromagnetic $PbTiO_3$-$CoFe_2O_4$

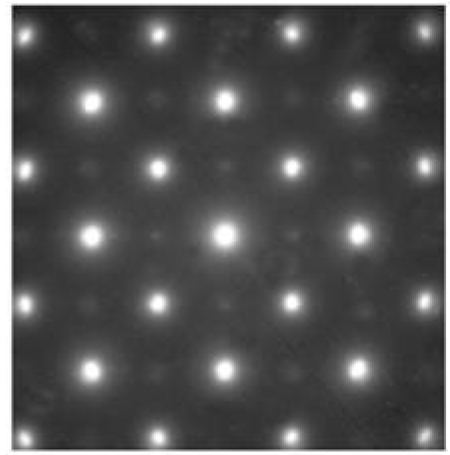
0.8 PTO

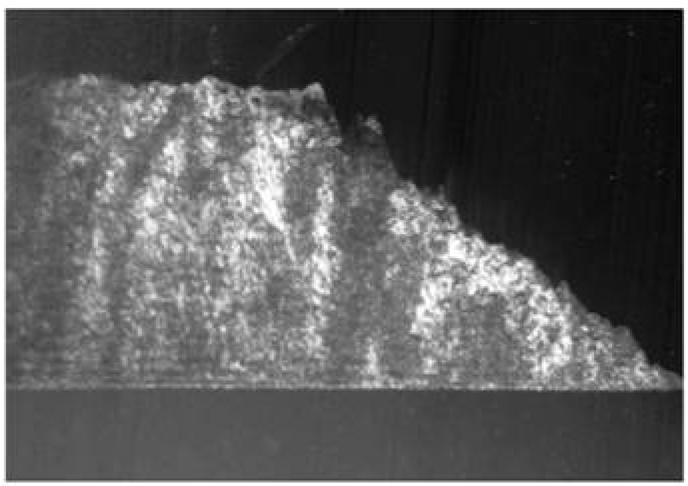


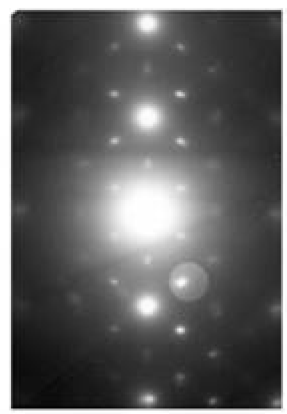
Ferroelectric/ferromagnetic $PbTiO_3$-$CoFe_2O_4$

0.1 PTO









[110]

Ferroelectric/ferromagnetic $PbTiO_3$-$CoFe_2O_4$

0.1 PTO