Isostructural Phase Transition in $BiFeO_3$ Solid Solutions

Dhananjai Pandey
School of Materials Science and Technology
Institute of Technology ,Banaras Hindu University, Varanasi

Email: dpandey_bhu@yahoo.co.in

PhD Students:Anar Singh, Shuvrajyoti Bhattacharjee,BHU

Neutron Scattering: Anatoliy Senyshyn and H Fuess
SXRD: Y Kuroiwa, C Moriyoshi, K Taji
M(T) data: R K Kotnala, V Pandey

PLAN

- Ferroic Order Parameters and Their Coupling in Multiferroics
- Contra-indication of Ferroelectricity and Magnetism: Novel Mechanisms of Ferroelectricity
- Signatures of Magnetoelectric Coupling in Dielectric Studies in $BiFeO_3$ Solid Solutions
- Evidence for Isostructural Phase Transition in $BiFeO_3$ Solid Solutions (Magnetoelectric Coupling , unusual tetragonality, critical point, large NTE)

Primary Ferroics

Ferroelectrics (FE): Spontaneous polarization ($\overrightarrow{P}$) in the absence of electric field ($\overrightarrow{E}$)

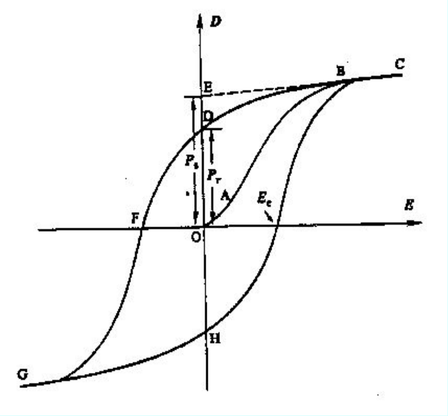
Ferromagentics (FM): Spontaneous magnetization ($\overrightarrow{M}$) in the absence of magnetic field ($\overrightarrow{H}$)

Ferroelastics (FS): Spontaneous strain (e) in the absence of stress (σ)

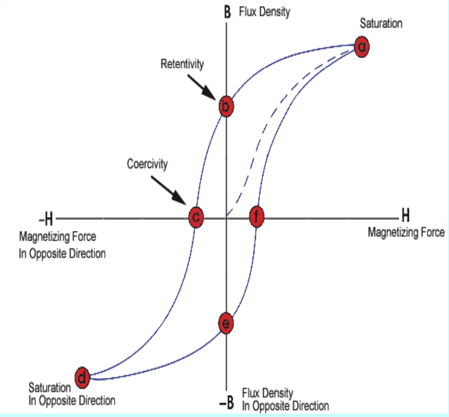
Antiferromagnetics and Antiferroelectrics are also considered as (Anti-) Ferroics

Switchable spontaneous P/M/e by E/H/σ

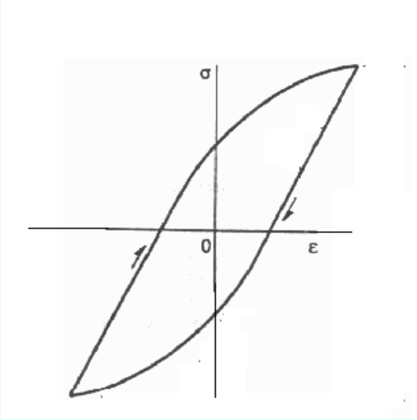
Ferroelectricity
Spontaneous polarization



Ferromagnetism
Spontaneous magnetization



Ferroelasticity
Spontaneous strain



Magnetoelectric Effect (ME) in Multiferroics

Coupling of primary order parameters (P & M) in Multiferroics

Free energy of magnetoelectric materials

$$-F(E_i, H_j) = 1/2\varepsilon_0\varepsilon_{ij}E_iE_j + 1/2\mu_0\mu_{ij}H_iH_j + \alpha_{ij}E_iH_j + (1/2)\beta_{ijk}E_iH_jH_k + (1/2)\gamma_{ijk}E_iE_jH_k$$

electric polarization: $P(H) = - dF / dE$

magnetization: $M(E) = - dF / dH$

- Linear magnetoelectric effect: $P_i = \alpha_{ij} H_j$; $M_j = \alpha_{ij} E_j$
- Higher order couplings for $\beta \neq 0, \gamma \neq 0$

Potential Technological applications

Novel sensors and actuators

New Four State Logic System

Information storage technology (write electrically and read magnetically)

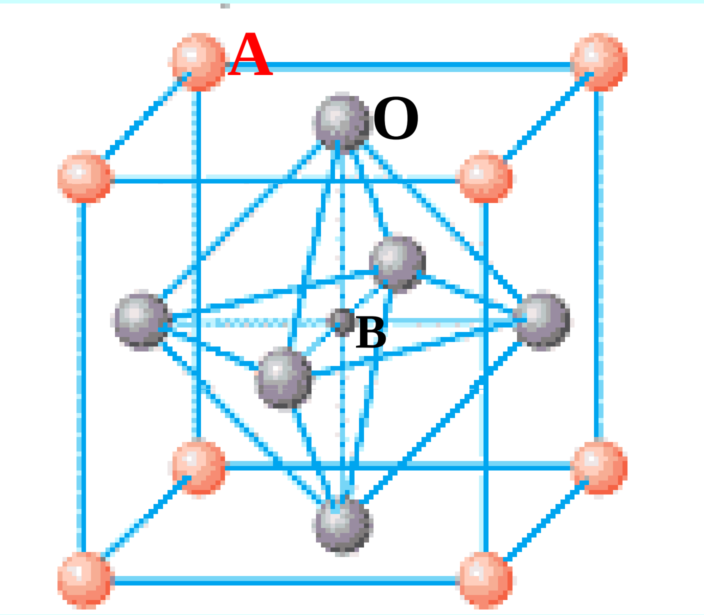
ABO_3 Perovskite Structure

“d^0 vs d^n paradox”

Ferroelectricity
$PbTiO_3$,$BaTiO_3$ & other Perovskites :

$3d^0$ of Ti^{4+} & 2p of O^{2-} hybridize

Magnetism
Partially filled d band



Novel Mechanisms of Inversion Symmetry Breaking in Multiferroics ((A)FM+FE)

1. Lone pair stereochemistry of A site atom for FE and d electrons of B atom for FM/AFM in ABO_3, eg. $BiMnO_3$, $BiFeO_3$ (Hill, J Phys Chem B (2000))

2. Geometric ferroelectricity: Structural instability in magnetic compounds, eg. $YMnO_3$, $InMnO_3$ (hexagonal)

   (Van Aken et al, Nature Mat. 3, 164 (2004)).

3. Magnetic Ferroelectrics: Spin spiral as a source of electric polarization in magnetic compounds, eg. $TbMnO_3$, $DyMnO_3$ (Kimura et al, Nature ,2003),

   $CaMn_7O_{12}$ (Johnson et al PRL 2012)
4. Charge ordering

$BiFeO_3$: The only RT Multiferroic

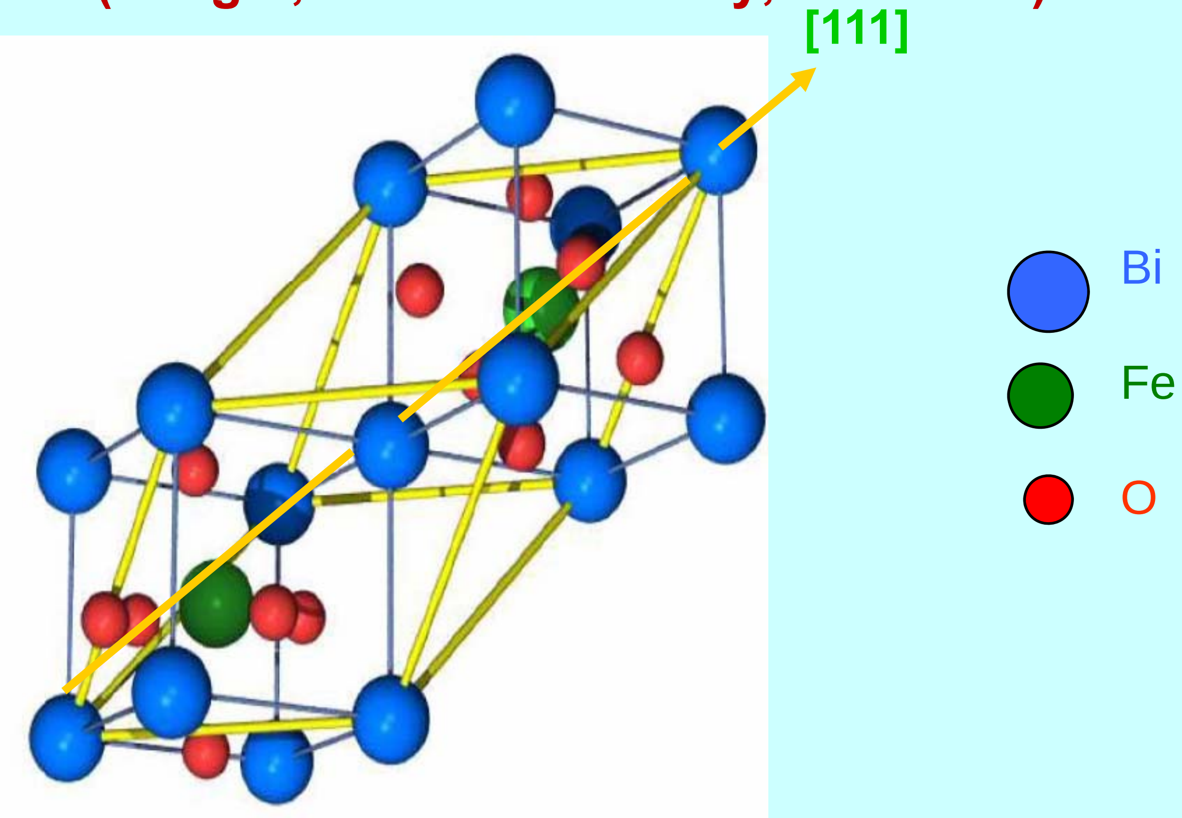
Multiferroic with the highest ordering temperatures

Ferroelectric T_C= 1103K

Antiferromagnetic T_N= 643K

Structure of BiFeO$_3$

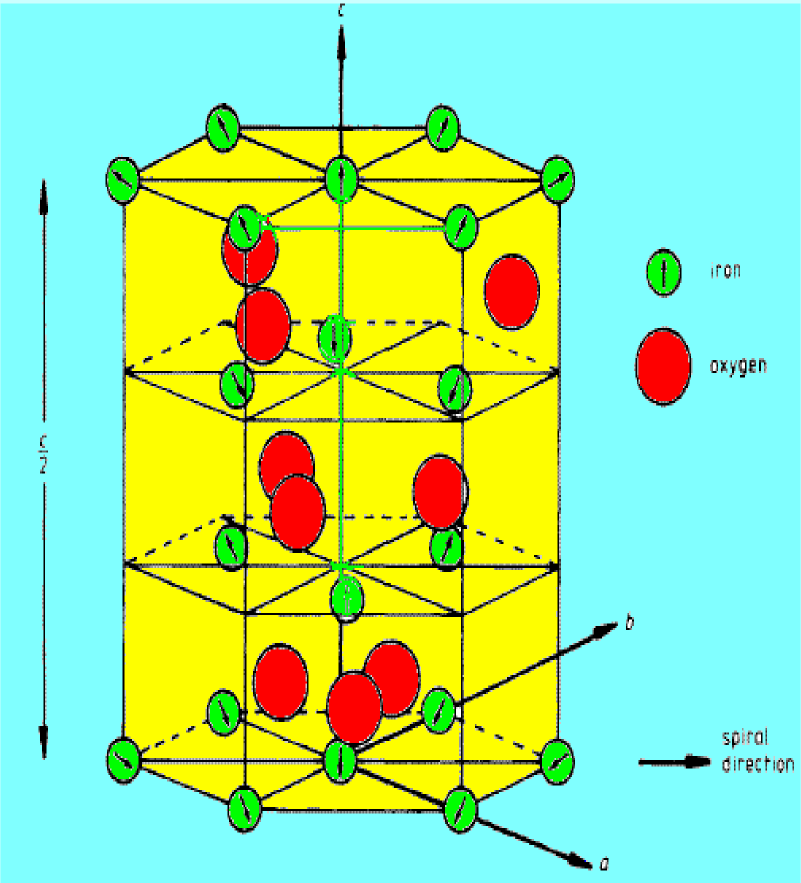
- R3c space group.
- The cations are displaced along the [111] direction relative to the anions.
- Anti-phase rotated neighbouring oxygen octahedra about [111] due to an antiferrodistortive transition involving R (q = 1/2 1/2 1/2) point phonon.
- Trigger type transition (Singh , Patel and Pandey, APL 2010)



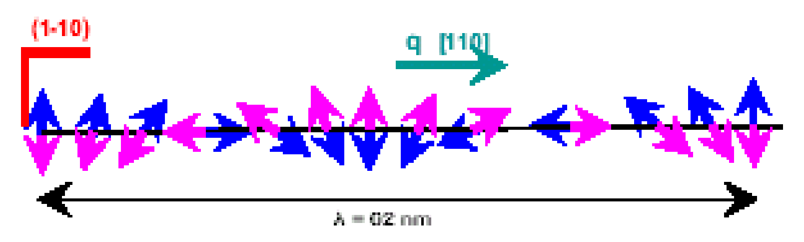
A. J. Jacobson and B. E. F. Fender, J. Phys. C 8,844 (1975)

Magnetic structure of $BiFeO_3$

Ferromagnetically coupled Fe moments within the (111) plane and antiferromagnetic coupling between adjacent planes : G-type antiferromagnetic ordering (wrt the perovskite cell).



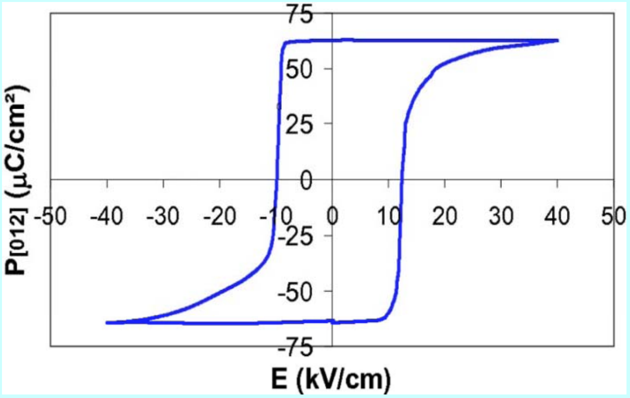
- Plane of spin orientation is (1-10)
- Incommensurate modulated spin structu
- Long period wavelength ~620 A
- Propagation vector q is along [110]
- Inhibits the linear magnetolelectric effect



I. Sosnowaska et al., J. Phys. C 15,4835 (1982)

$BiFeO_3$ Single Crystal

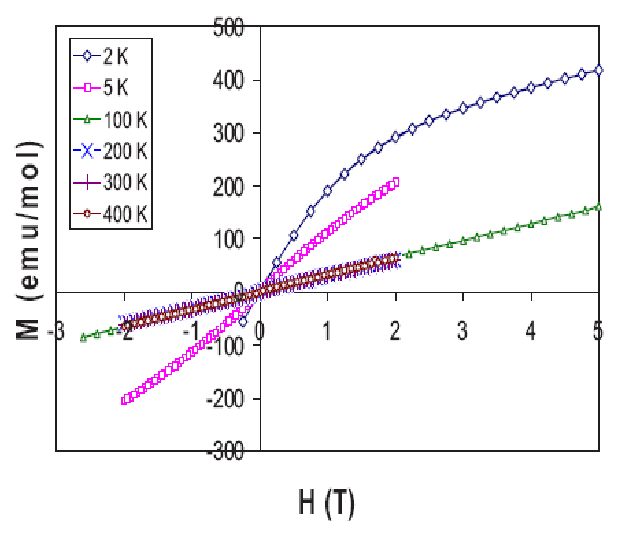
Ferroelectric hysteresis (P-E) loop



Remnant polarization
$P_{r\ [012]}$~60 to 100 μC/cm²
Coercive field ~12 kV/cm

(D.Lebeugle et al., Appl. Phys. Lett. 91, 022907 2007)

Magnetization curve versus applied magnetic field

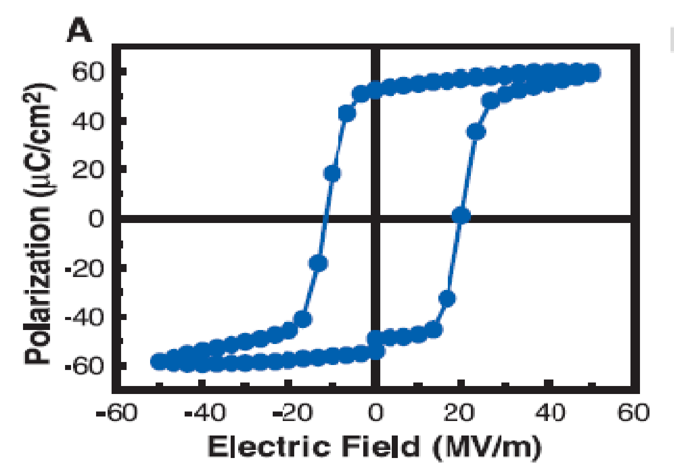


Magnetic field perpendicular to (012) plane at different temperatures

D.Lebeugle et al., PRB 2007

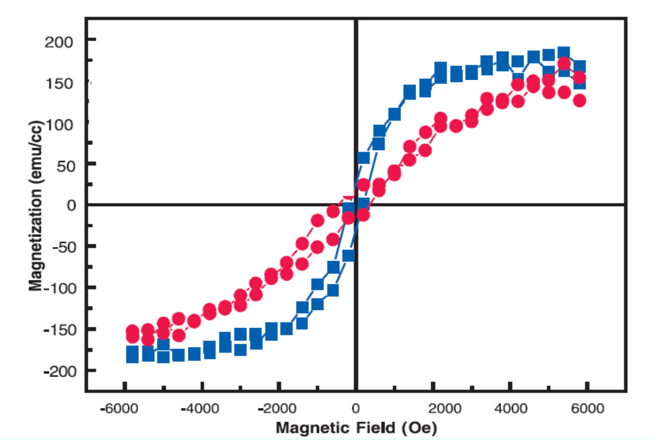
Epitaxial $BiFeO_3$ Multiferroic Thin Film

Ferroelectric hysteresis loop measured at 15 kHz for 200 nm thick film:



Remnant Polarization ~ 55μC/cm^2)

Magnetic hystersis (M-H) loop for a 70nm BFO film: Spin spiral melting



Saturation magnetization ~150emu/cm^3
(controversial result)

Coercive field ~200Oe

Linear magnetoelectric (ME) effect was reported: **Melting of spin spiral**

J. Wang et al., Science 299, 1719 (2003)

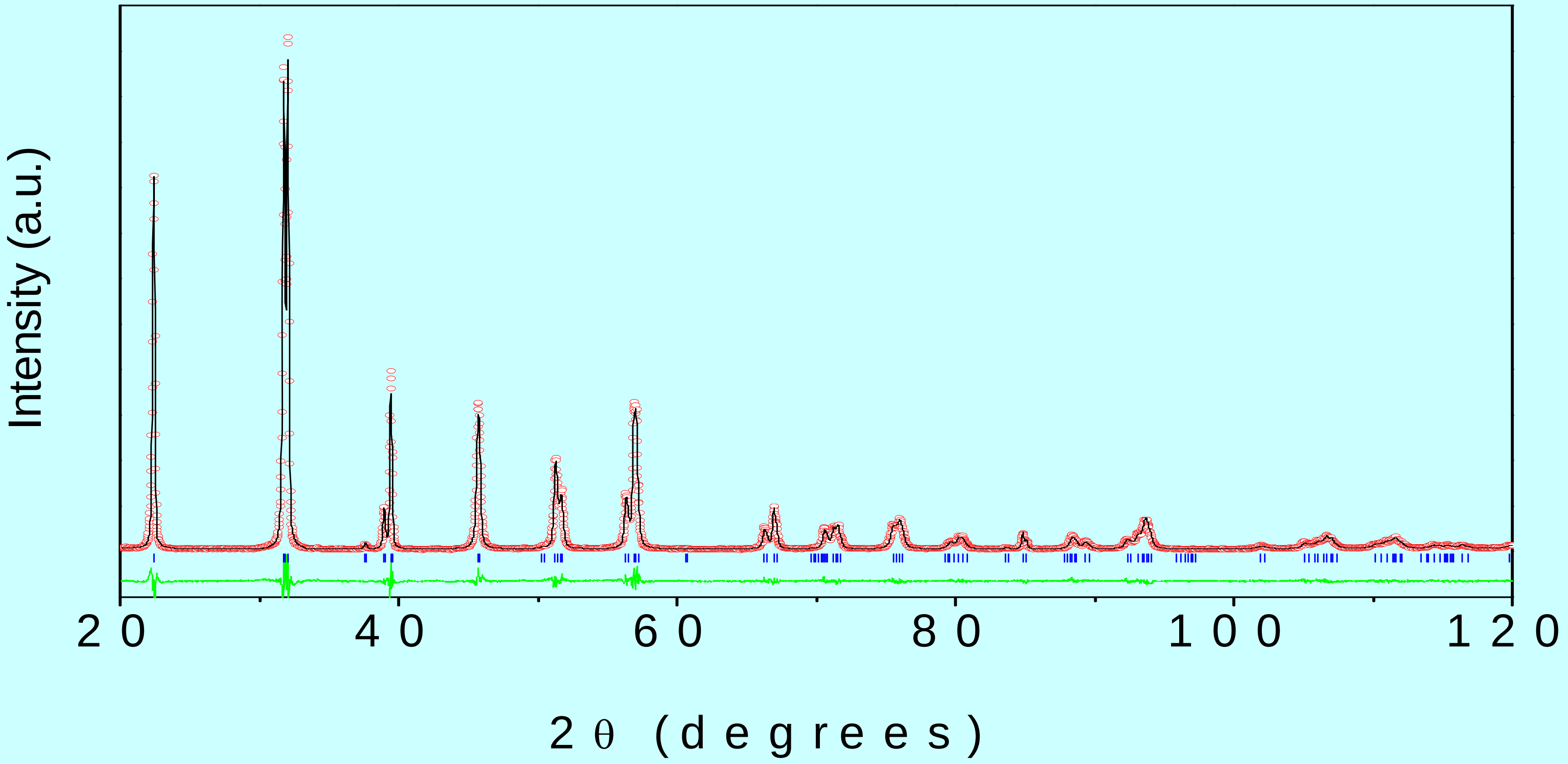
Magnetoelectric Coupling of Intrinsic Multiferroic Origin in 0.9BiFO$_3$-0.1BaTiO$_3$

Anar Singh

Can disorder in the magnetic sublattice suppress the spatial modulation of the spins and release the latent magnetisation?

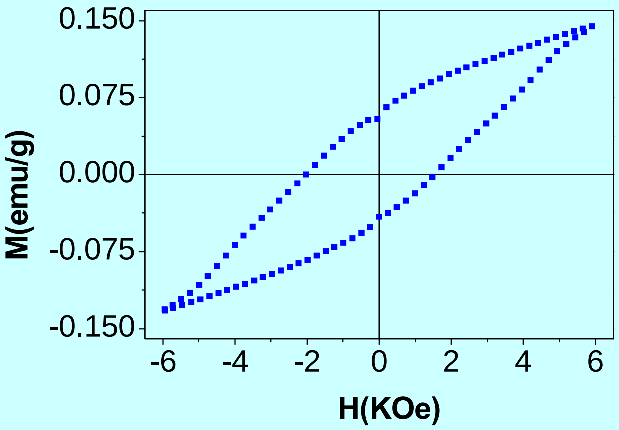
Physical Review Letters 101,247602 (2008)

Rietveld fit for $0.9BiFeO_3$-$0.1BaTiO_3$ using R3c space group



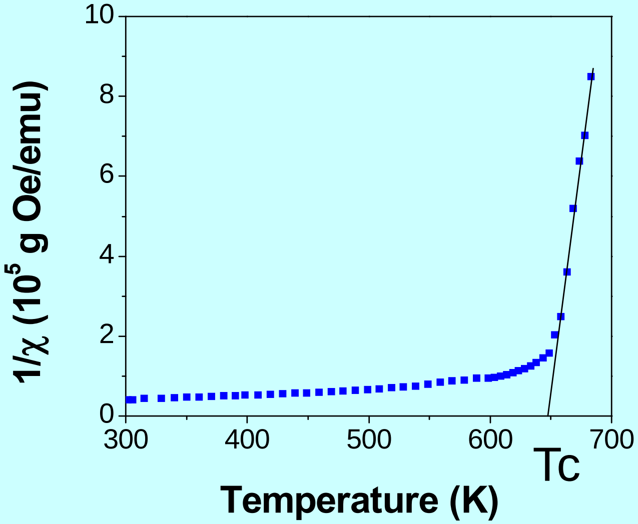
Magnetic study

Magnetic hystersis (M-H) loop



- ***Weak ferromagnetism unlike pure*** $BiFeO_3$
- ***Spin spiral ordering may be suppressed***

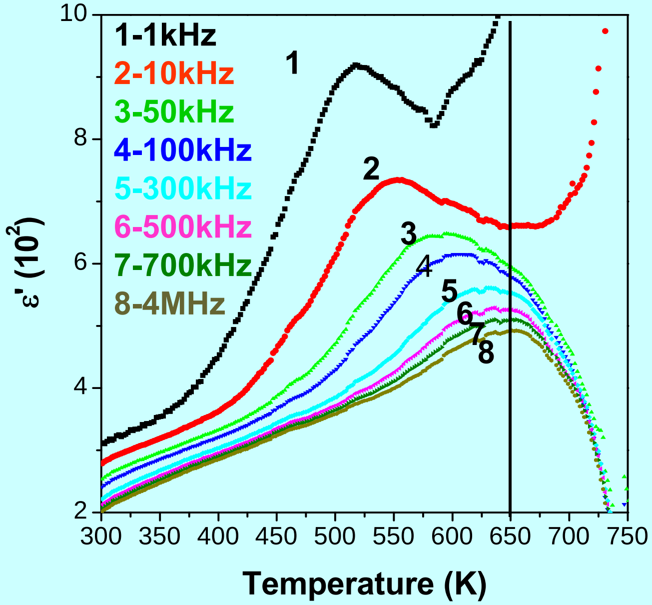
Inverse of magnetic susceptibility vs. temperature



Magnetic transition temperature
$T_c = 648\ K$

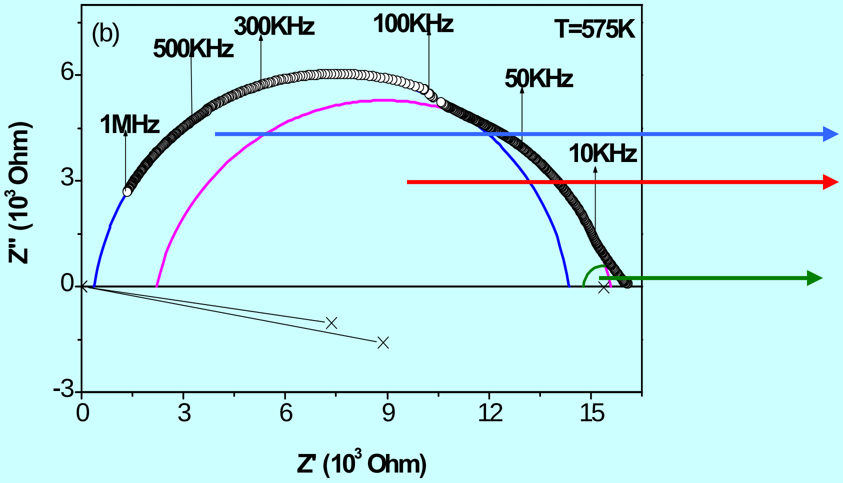
Singh et al , Phys. Rev. Lett. 101, 247602 (2008)

Dielectric study: Magnetoelectric coupling ?



For frequencies > 300 kHz

- **$T^{/}_{m}$ nearly coincides with the magnetic transition temperature T_C ~648 K**
- **Grain (intrinsic) contribution linked with magnetoelectric coupling**



Grain

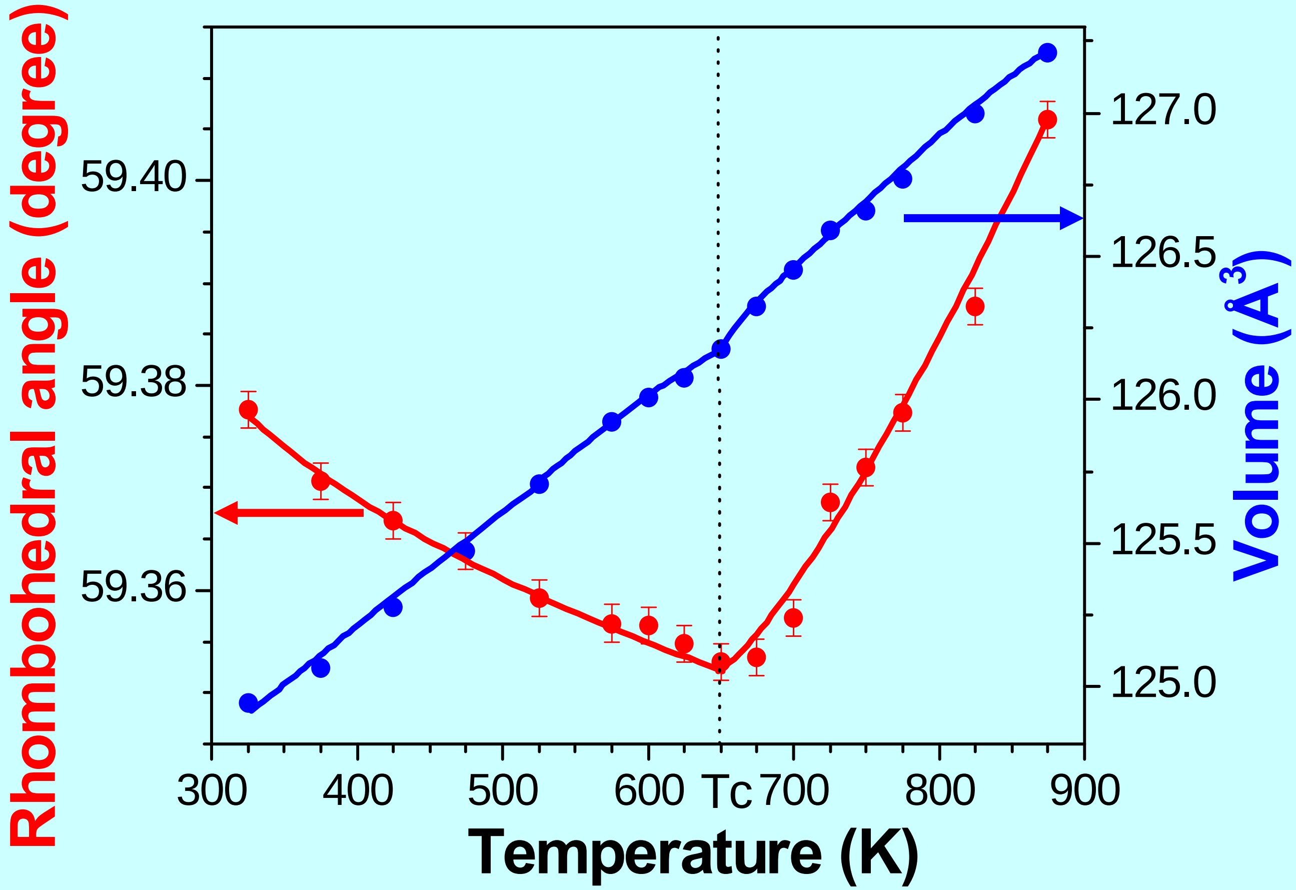
Grain boundary

Electrode-grain interface

Singh et al, Phys. Rev. Lett. 101, 247602 (2008)

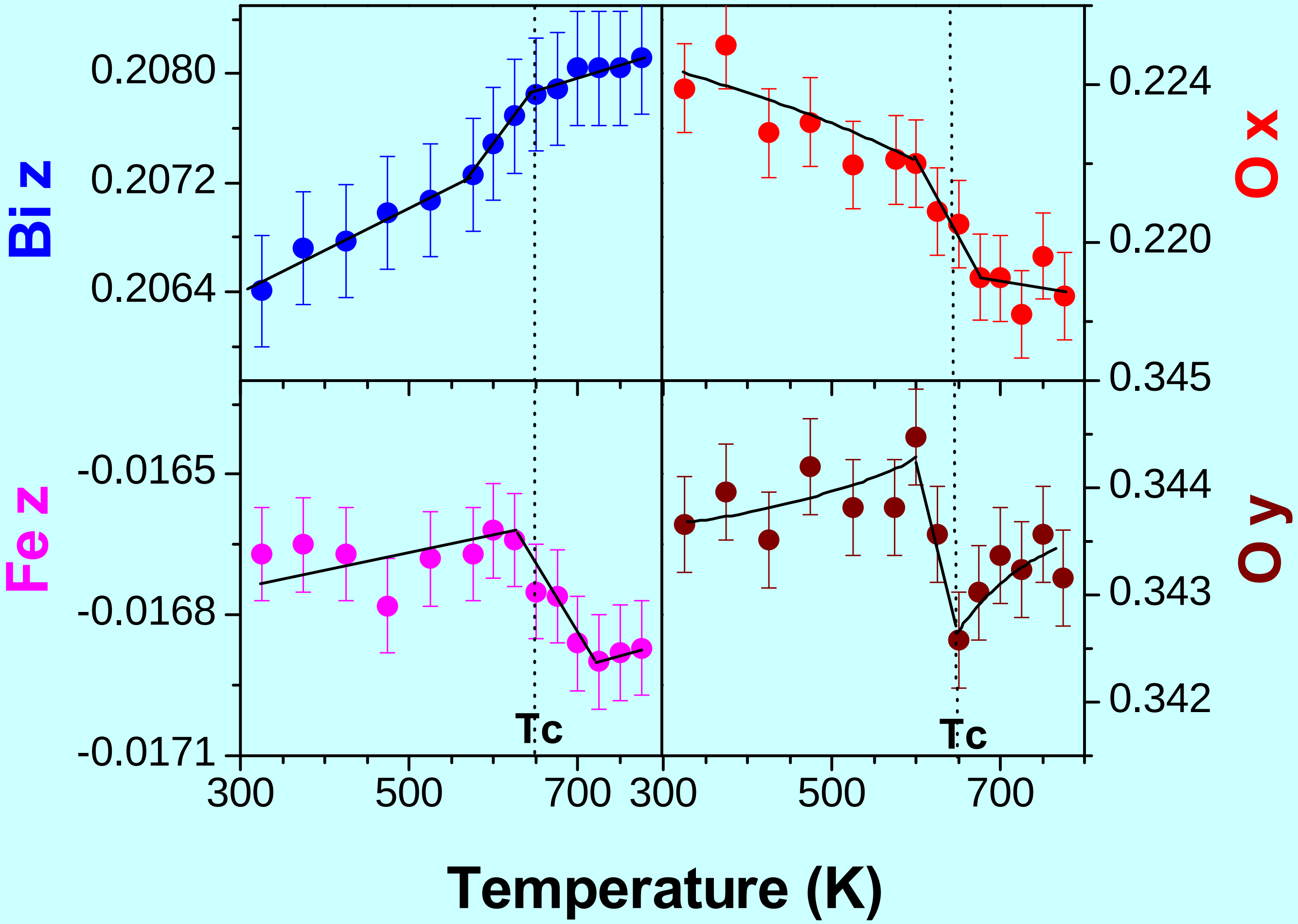
Magneto-elastic coupling in BF-0.10BT

- Rhombohedral distortion angle
- Unit cell volume



Singh et al.,Phys. Rev. Lett. 101, 247602 (2008)

Temperature Dependence of Atomic Positions
(Isostructural Phase Transition)

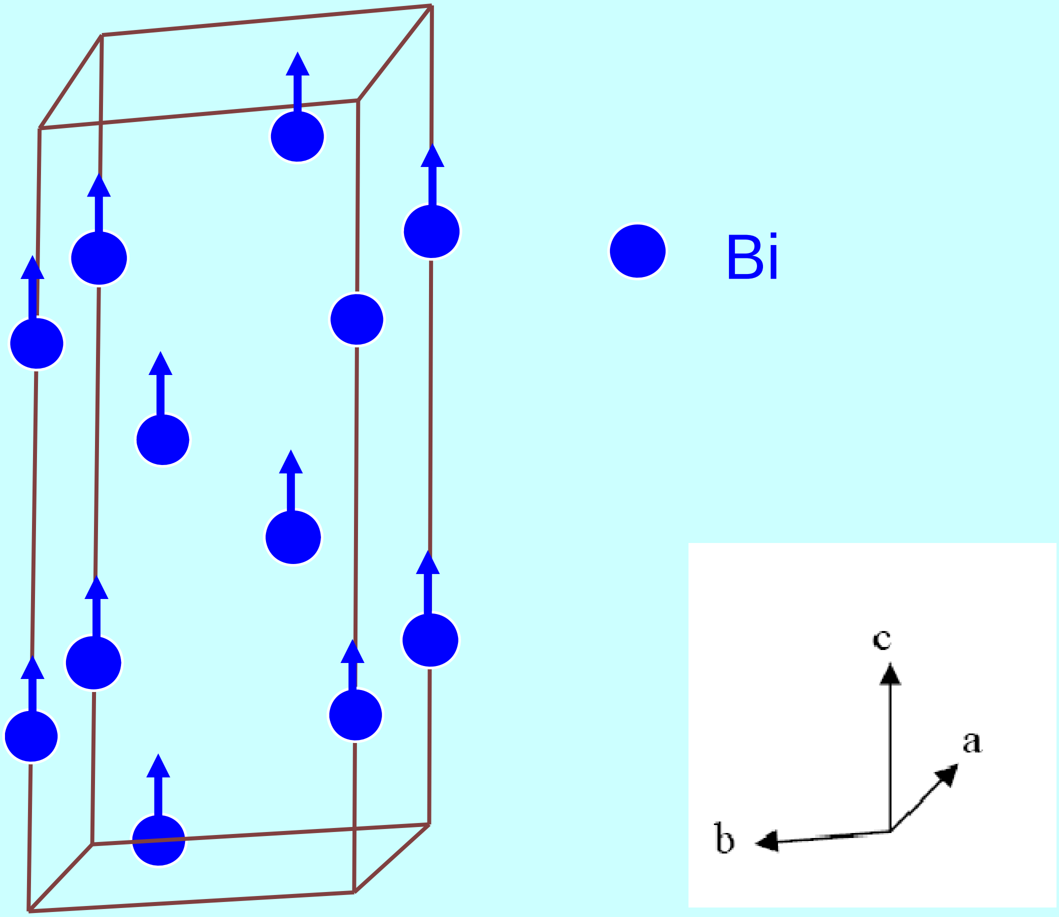


In the magnetic phase:

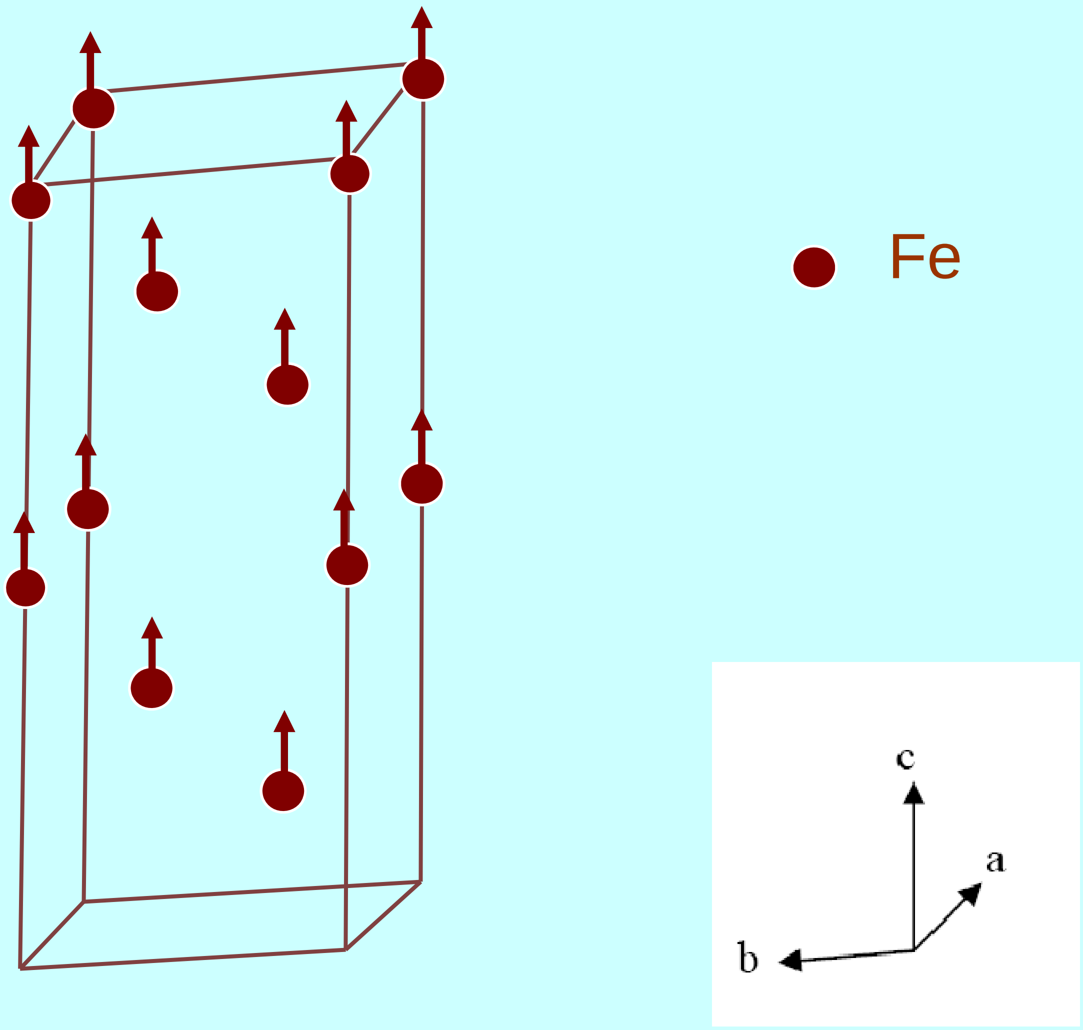
ΔZ_{Bi} (i.e. $Z_{300\ K}$-$Z_{700\ K}$)~ 0.038 Å

Singh et al , Phys. Rev. Lett. 101, 247602 (2008)

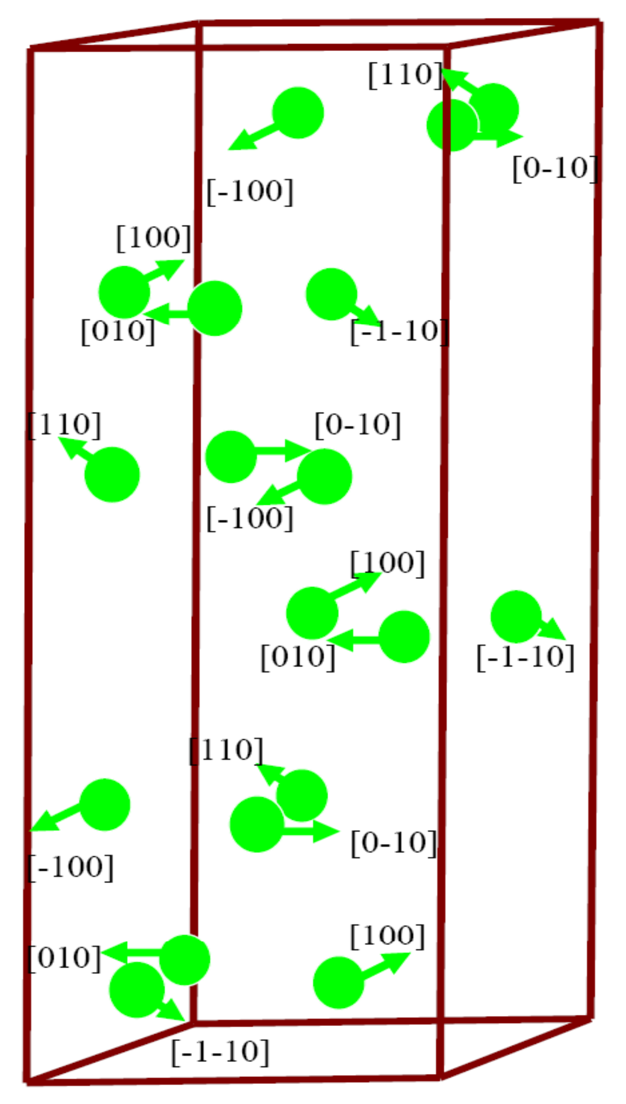
Atomic displacements of IR(1) mode for Bi



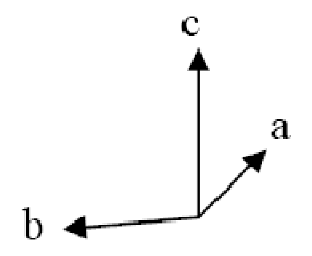
Atomic displacements of IR(1) mode for Fe



Atomic displacements of IR(1) mode for O



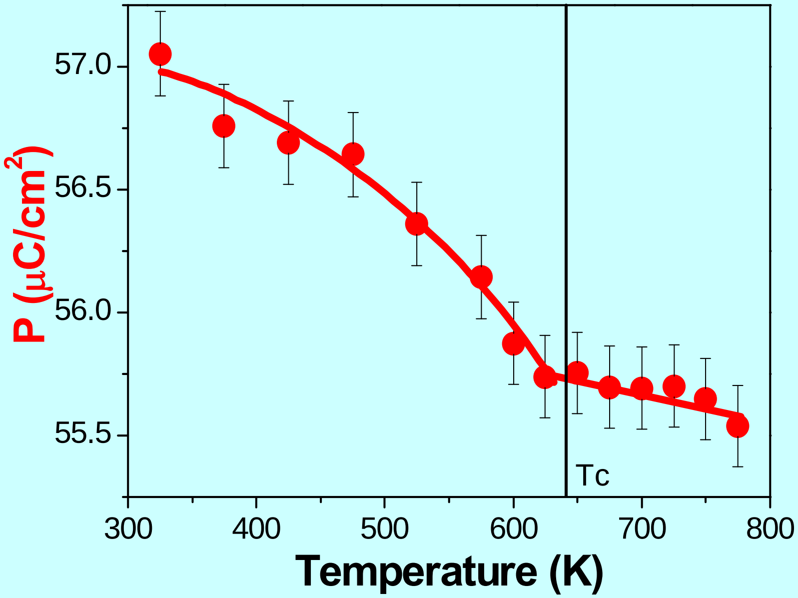
● O



Temperature dependence of ionic polarization (P)

$$P_{ionic} = \frac{\sum_{i}^{natom} Z_i d_i}{V}$$

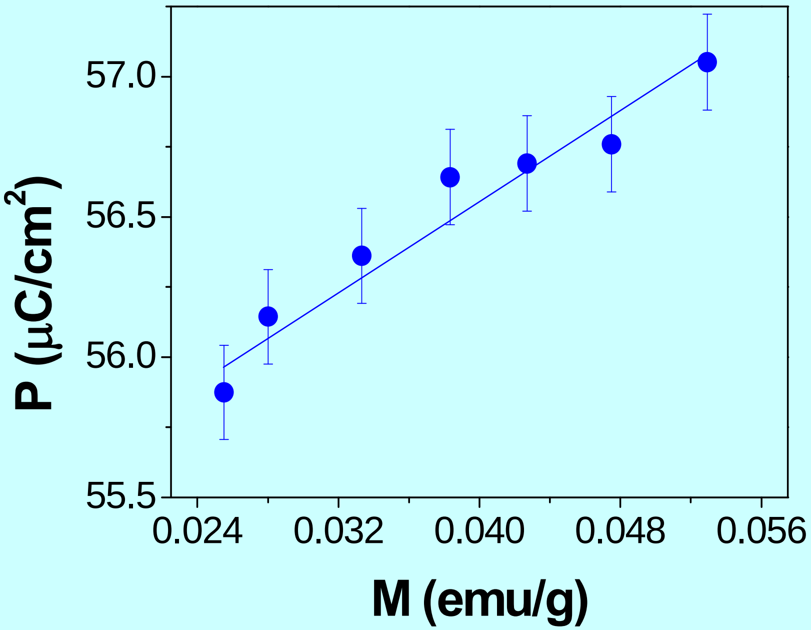
Z_i: nominal charge of ith atom
d_i: shift of ith atom
V: volume of the cell



Singh et al, Phys. Rev. Lett. 101, 247602 (2008)

Evidence for linear magnetoelectric coupling

- P scales linearly with M
- Suggests suppression of the magnetic spiral order?



Singh et al, Phys. Rev. Lett. 101, 247602 (2008)

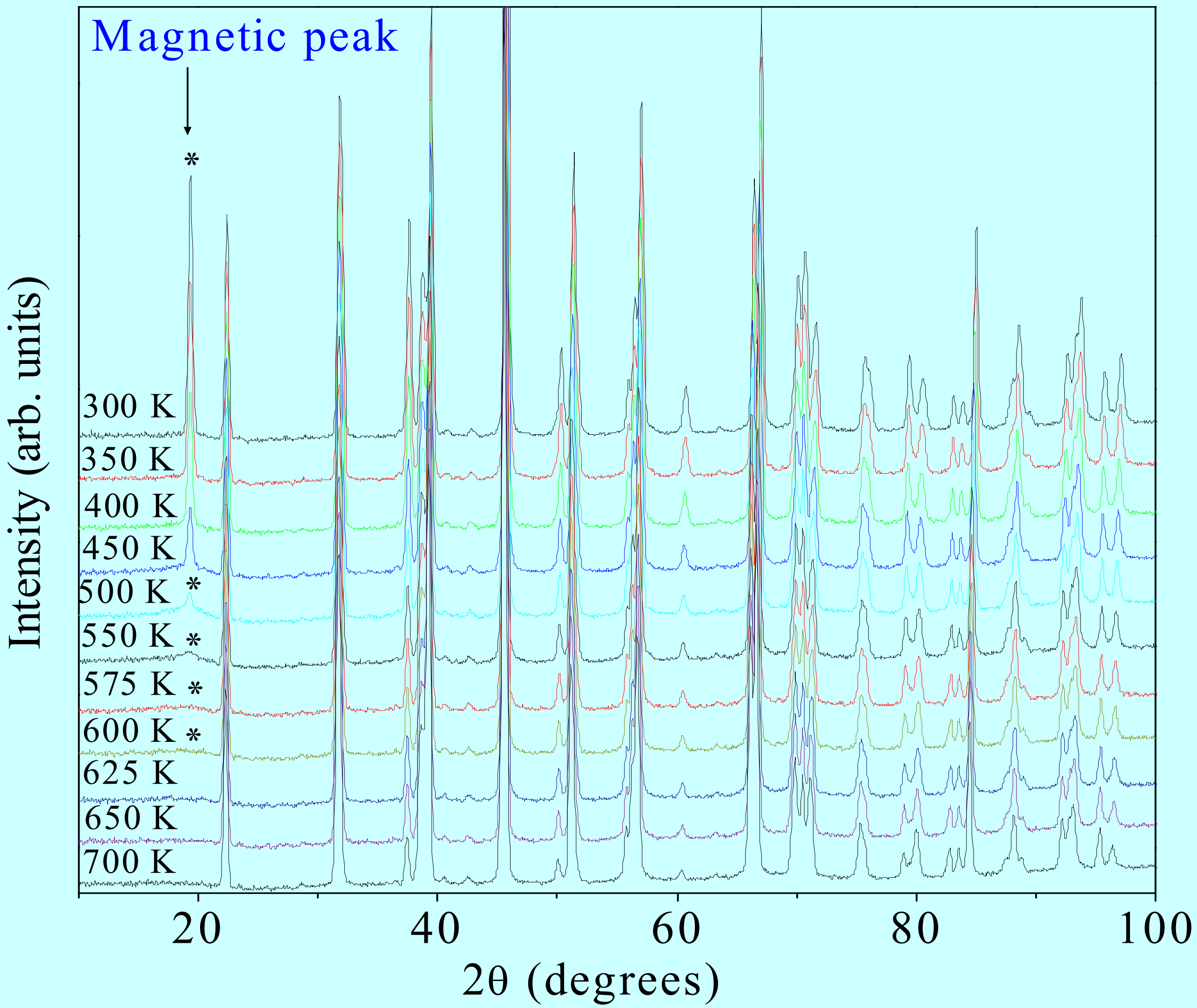
Magnetoelectric Coupling of Intrinsic Multiferroic Origin in 0.8BiFO3-0.2$BaTiO_3$: A Neutron Powder Diffraction Study

Anar Singh et al

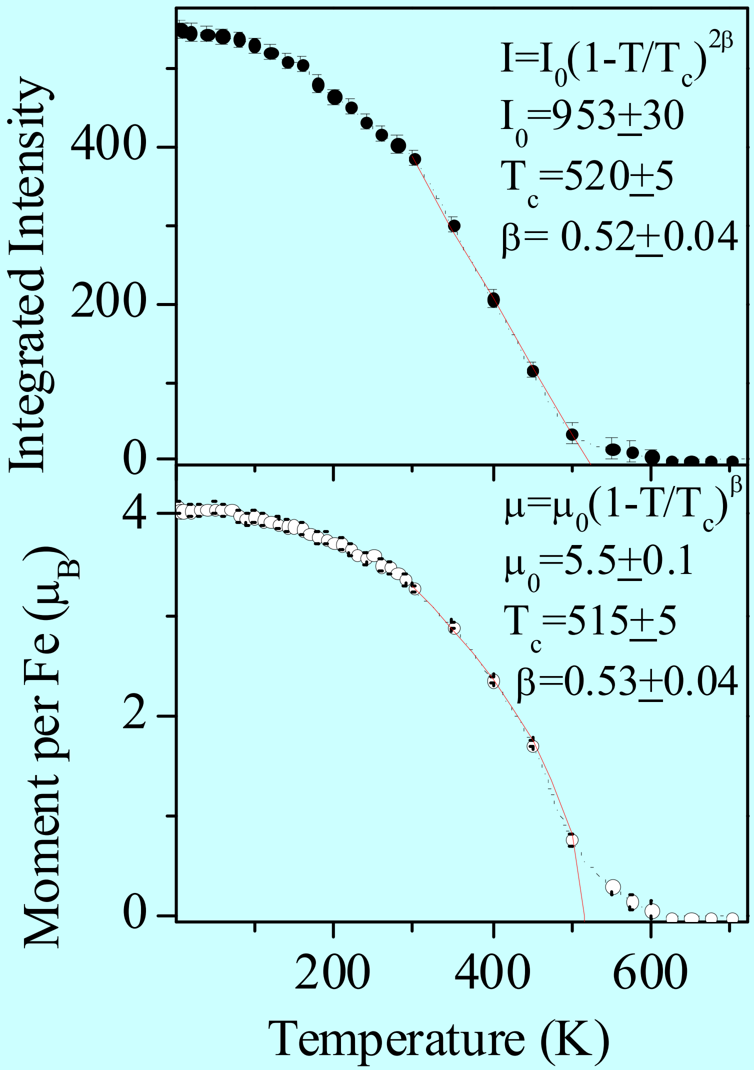
Phys Rev B (2011)

Oxygen positions
Magnetisation

Evolution of Neutron Powder Diffraction Patterns of BF-0.20BT with Temperature

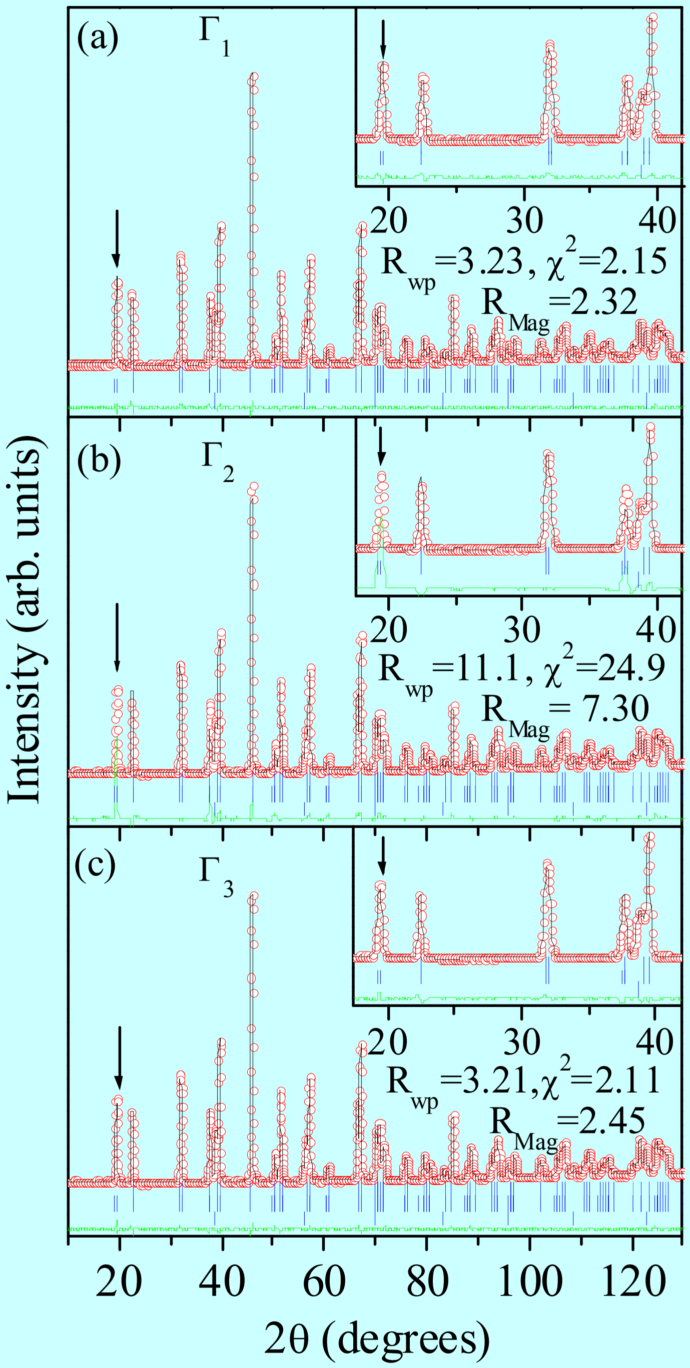


Magnetic Transition Temperature

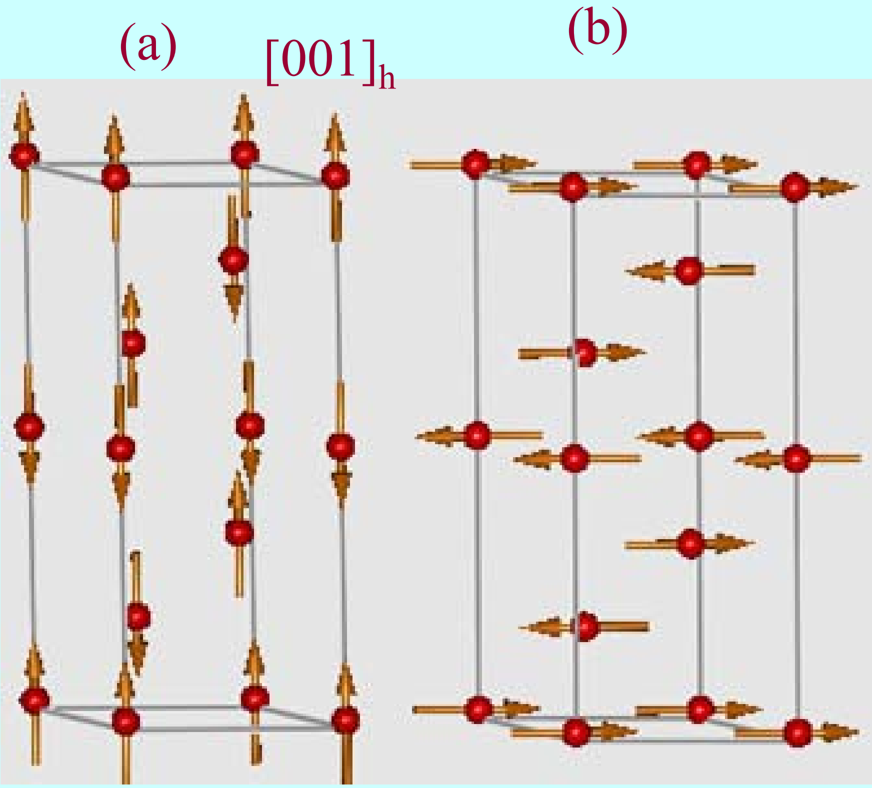


The decomposition of the magnetic representation Γ in terms of irreducible representations Γ_k for the 6a site is as follows :

$$\Gamma(6a/Fe) = 1\Gamma_1^1 + 1\Gamma_2^1 + 2\Gamma_3^2$$



Magnetic Structure of BF-0.2BT



Structural and magnetic parameters for BF-0.2BT pattern at room temp obtained after the Rietveld refinement of the high resolution NPD pattern (FRM II) with wavelength λ=1.54Å corresponding to representation Γ_3

Atom	**x**	**y**	**z**	**B(Å^2)**
Bi/Ba	0	0	0.2905(2)	2.38(5)
Fe/Ti	0	0	0.0154(2)	0.57(4)
O	0.2130(3)	0.3454(3)	0.083333	1.59(4)

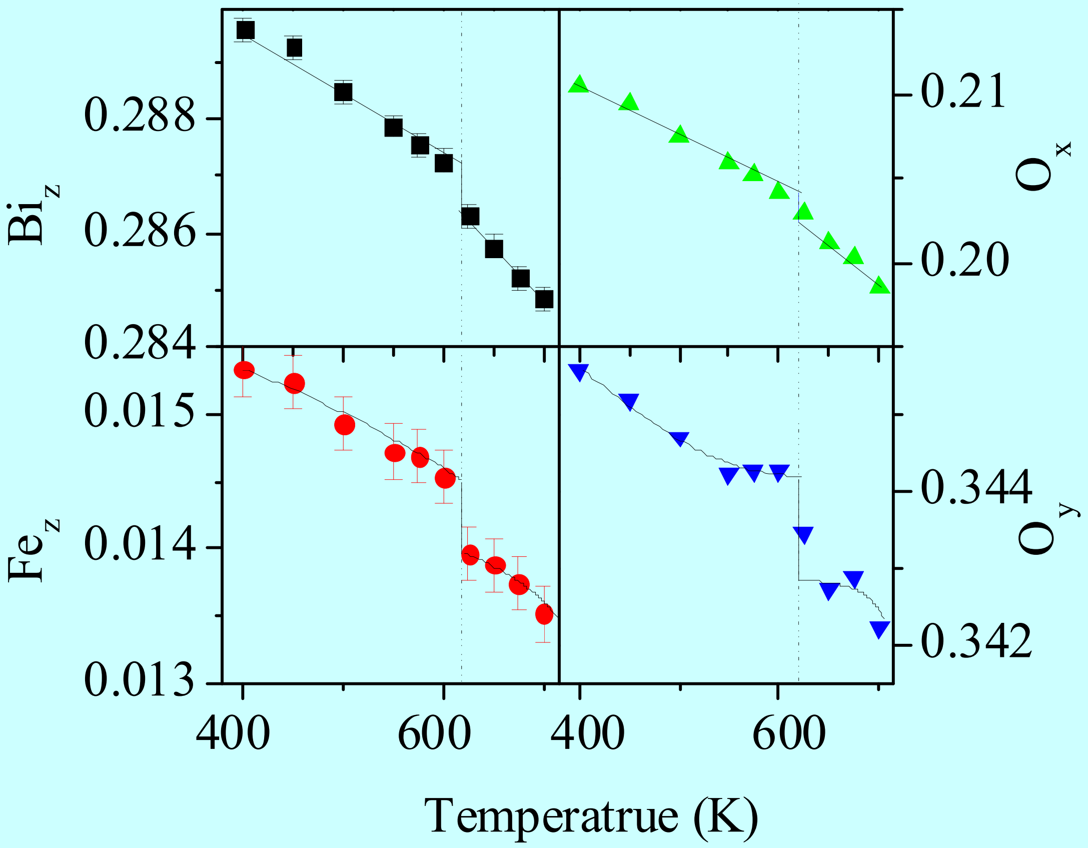
$\beta_{Bi/Ba}$(Å^2):β_{11}= β_{22}= 2β_{12}= 0.0157(3), β_{33}= 0.0029(1)

β_{O}(Å^2): β_{11}= 0.0209(7), β_{22}= 0.0118(5), β_{33}= 0.0021(1)
β_{12}= 0.0077(6), β_{13}= -0.0026(3), β_{23}= -0.0023(2)

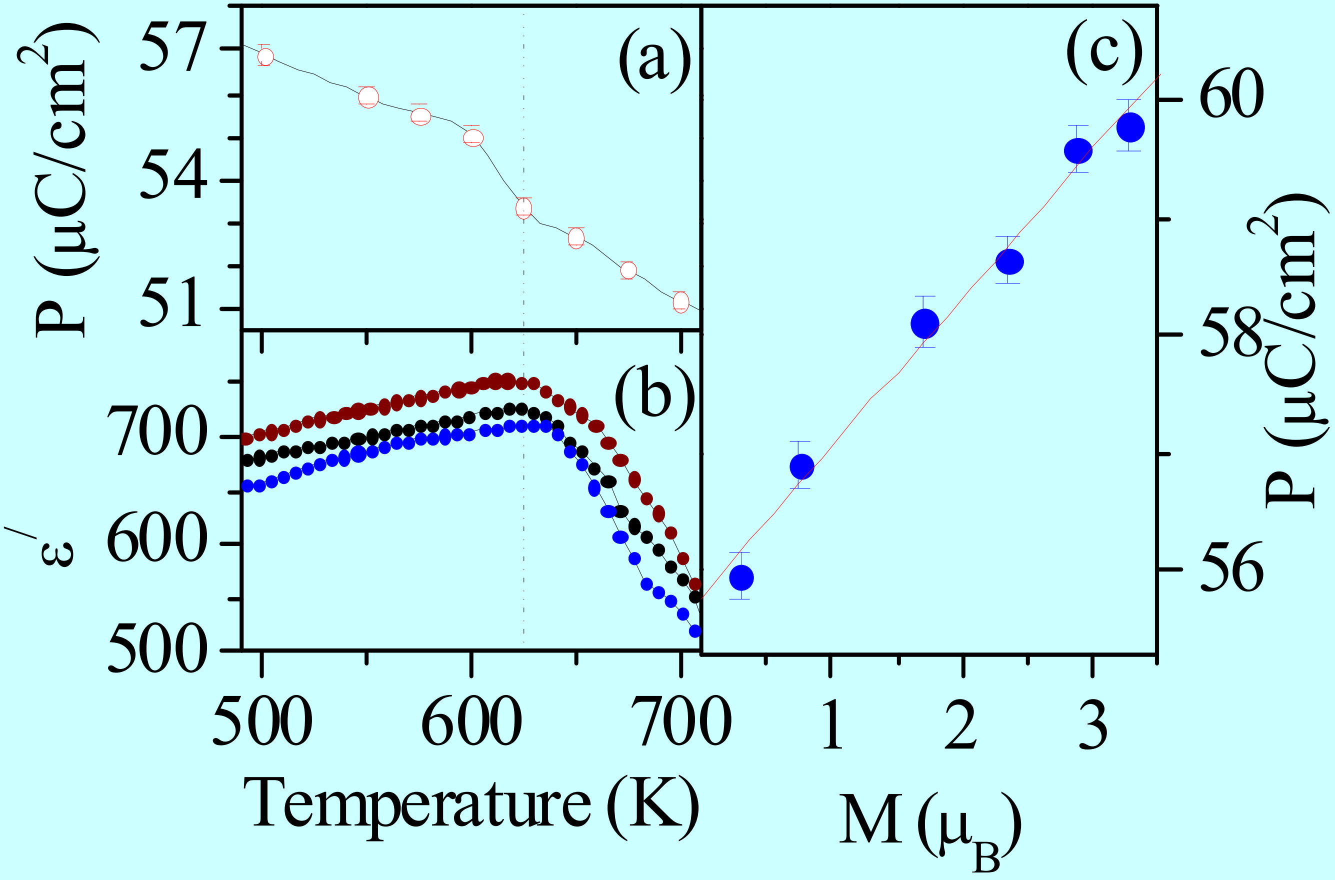
Bi-O1(×3)= 3.340(3)　Bi-O2(×3)= 3.082(2)
Bi-O3(×3)= 2.639(2)　Bi-O4(×3)= 2.358(3)
Fe-O1(×3)= 1.938(2)　Fe-O2(×3)= 2.091(3)

a= 5.60785(2), c= 13.90109(4), γ=120^0, μ_{Fe}=3.27(6)
R_{wp}= 3.21, χ^2= 2.11, R_{Mag}=2.45

Isostructural Phase Transition in BF-0.20BT



Magnetoelectric Coupling in BF-0.20BT



CONCLUSIONS

- Evidence for Isostructural Phase Transition leading to Magnetoelectric Coupling of Intrinsic Multiferroic Origin in BF-BT

- Key Role of Crystallographic Tools in Revealing this Coupling at the atomic level

Isostructural Phase Transition in (1-x) $BiFeO_3$-(x) $PbTiO_3$

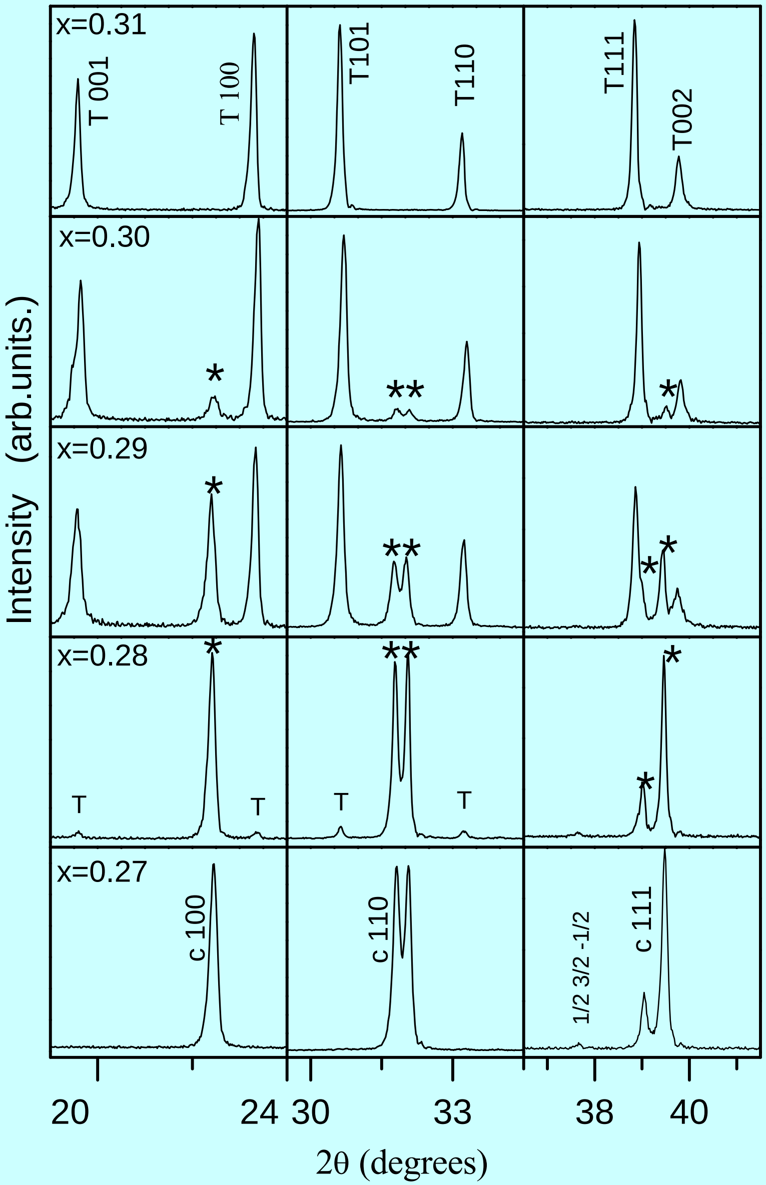
Multiple instabilities (MPB, AFD, Magnetic, Stress- induced transition)

- Unusually large tetragonality (~ 19%)
- Negative Thermal Expansion
- Critical Point

Shuvrajyoti Bhattacharjee

Bhattacharjee, Taji, Moriyoshi, Kuroiwa and Pandey, Phys. Rev. B, **84**,104116 (2011)

Morphotropic Phase Transition

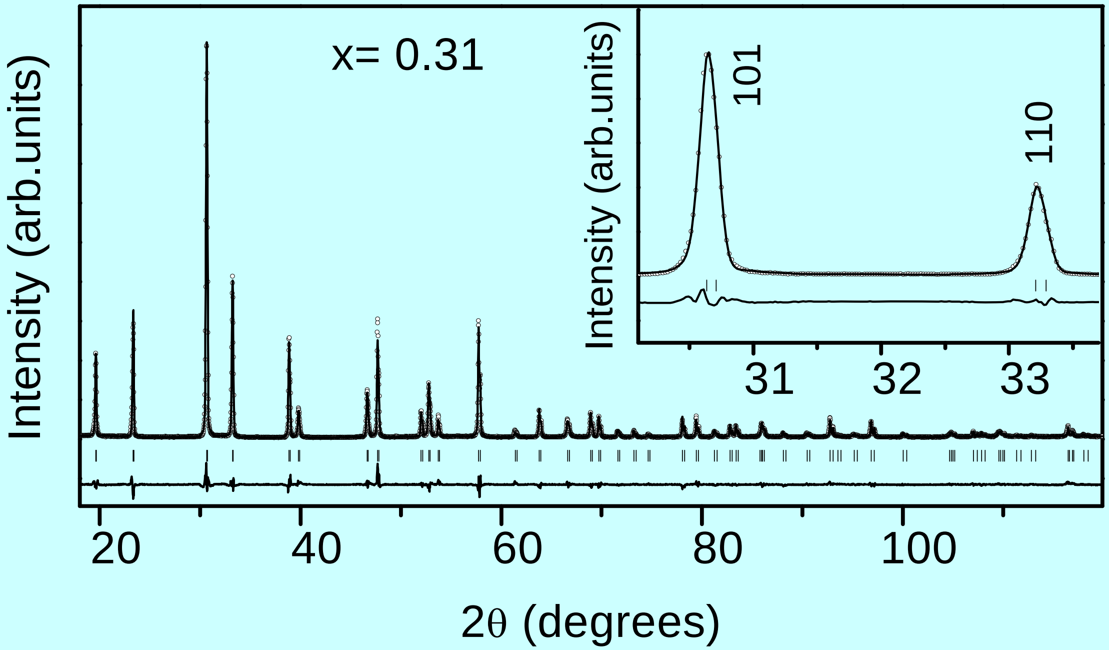


Tetragonal

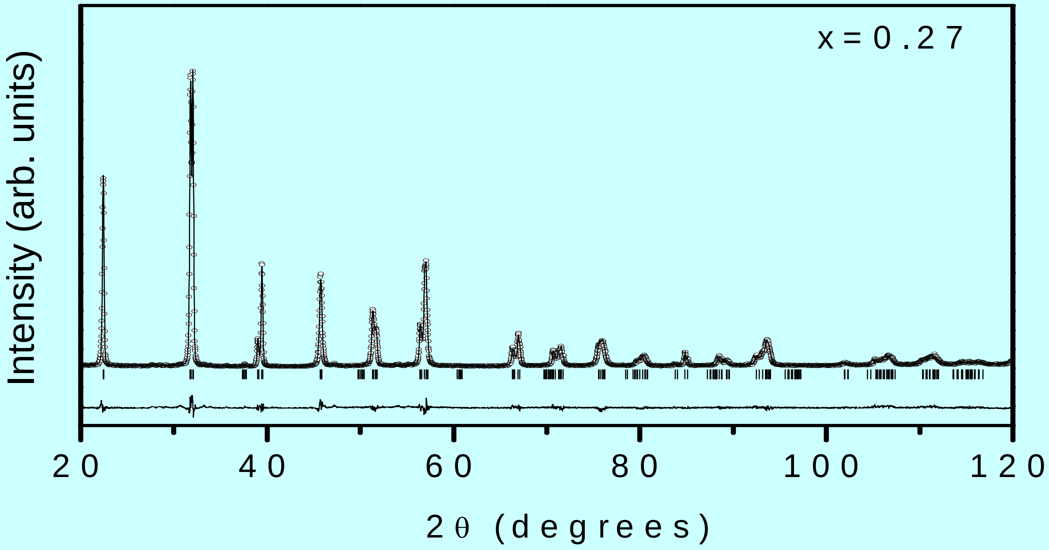
T + M

Monoclinic/Pseudo-rhombohedral

Bhattacharjee, Tripathi and Pandey, Appl.Phys.Lett, 91, 042903(2007)

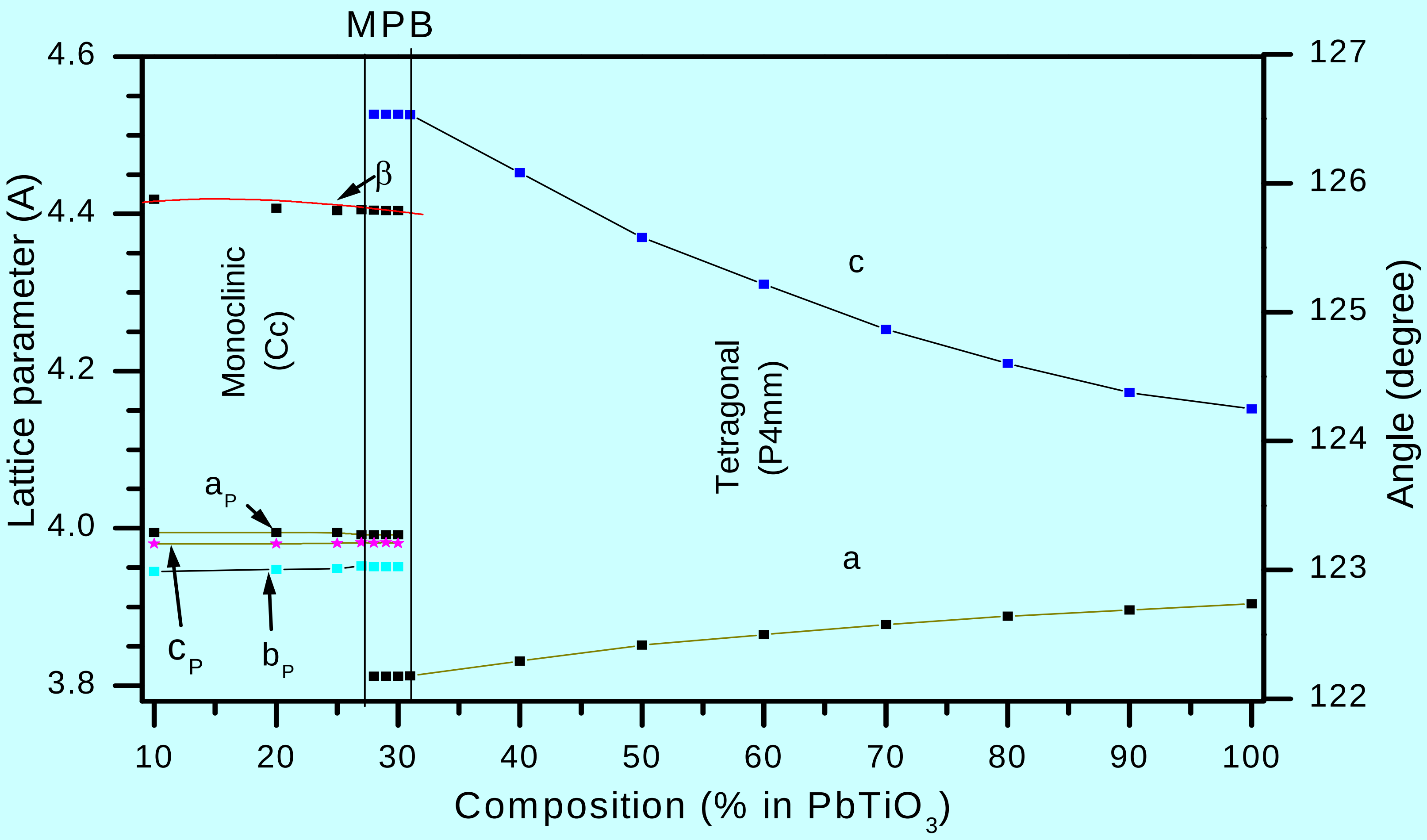


Tetragonal



Monoclinic

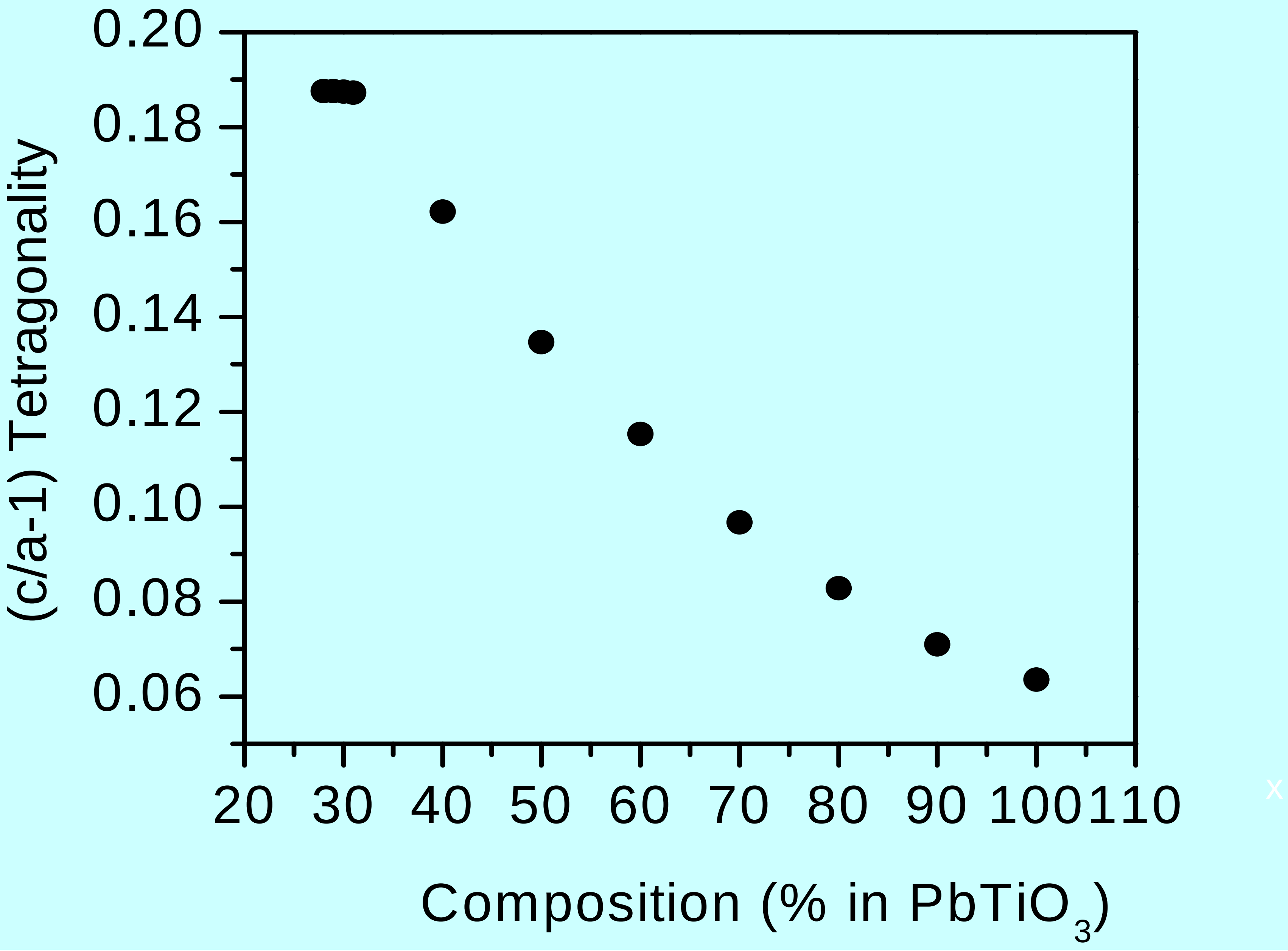
Bhattacharjee, Pandey, Kotnala and Pandey, Appl.Phys.Lett, 97, 262506 (2010)
Bhattacharjee, Tripathi and Pandey, Appl.Phys.Lett, 91, 042903(2007)



P ‖ [001] for Tetragonal ; P ~ ‖ <112> for Monoclinic

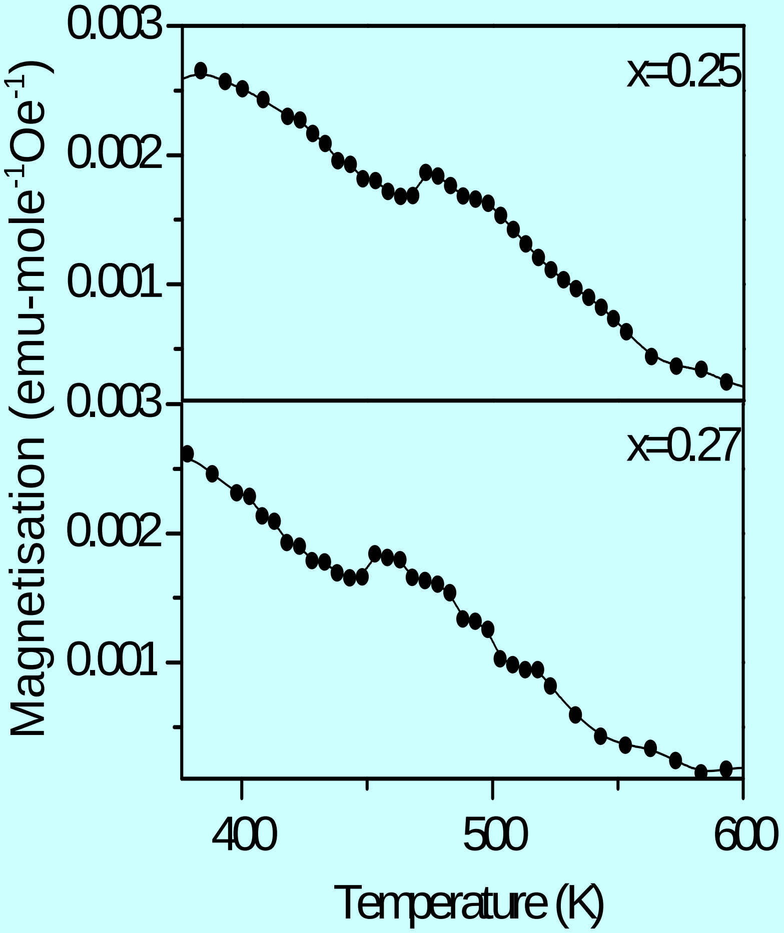
Bhattacharjee and Pandey, J. Appl. Phys. 107,124112 (2010)

Unusually large tetragonality ~ 19%

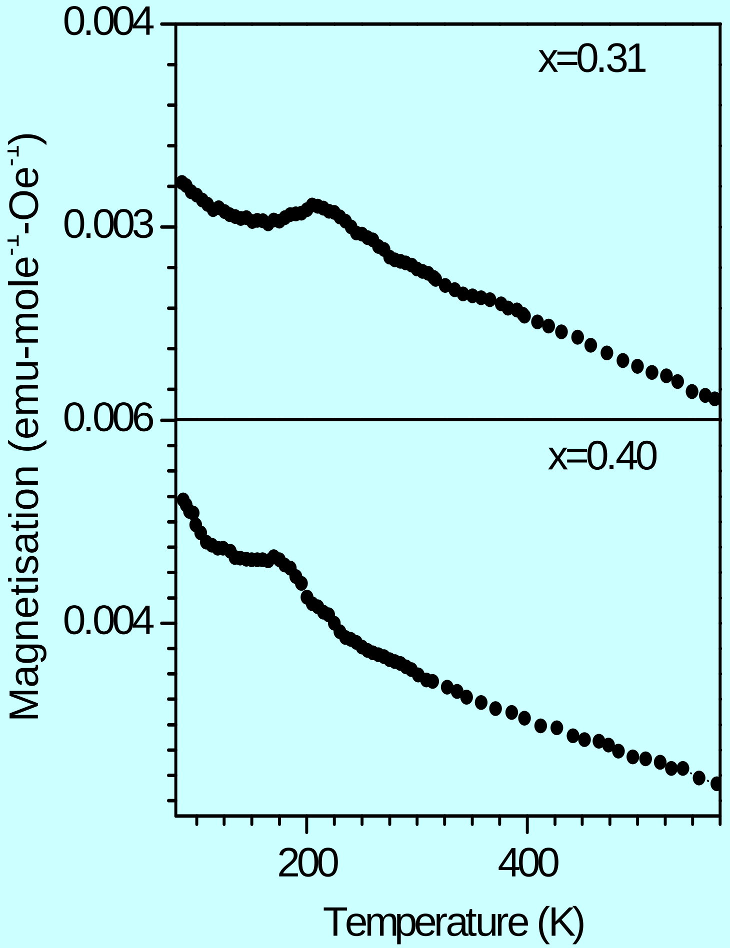


Magnetic Transitions in BF-*x*PT

Monoclinic

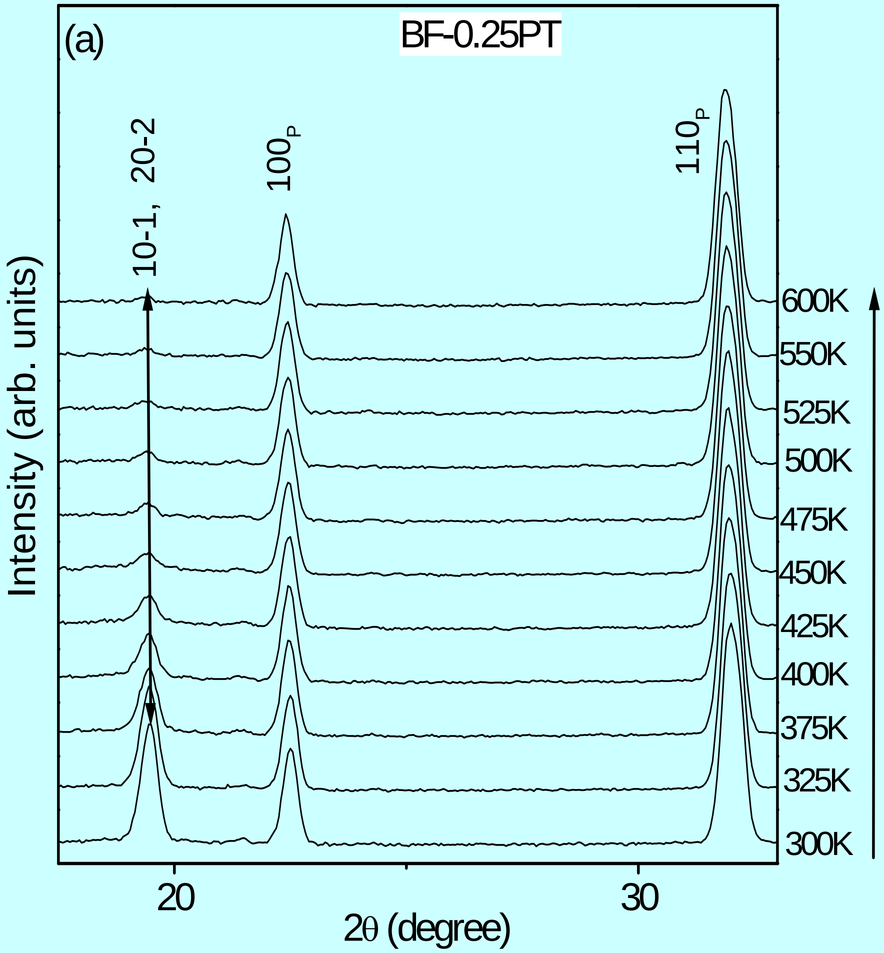


Tetragonal

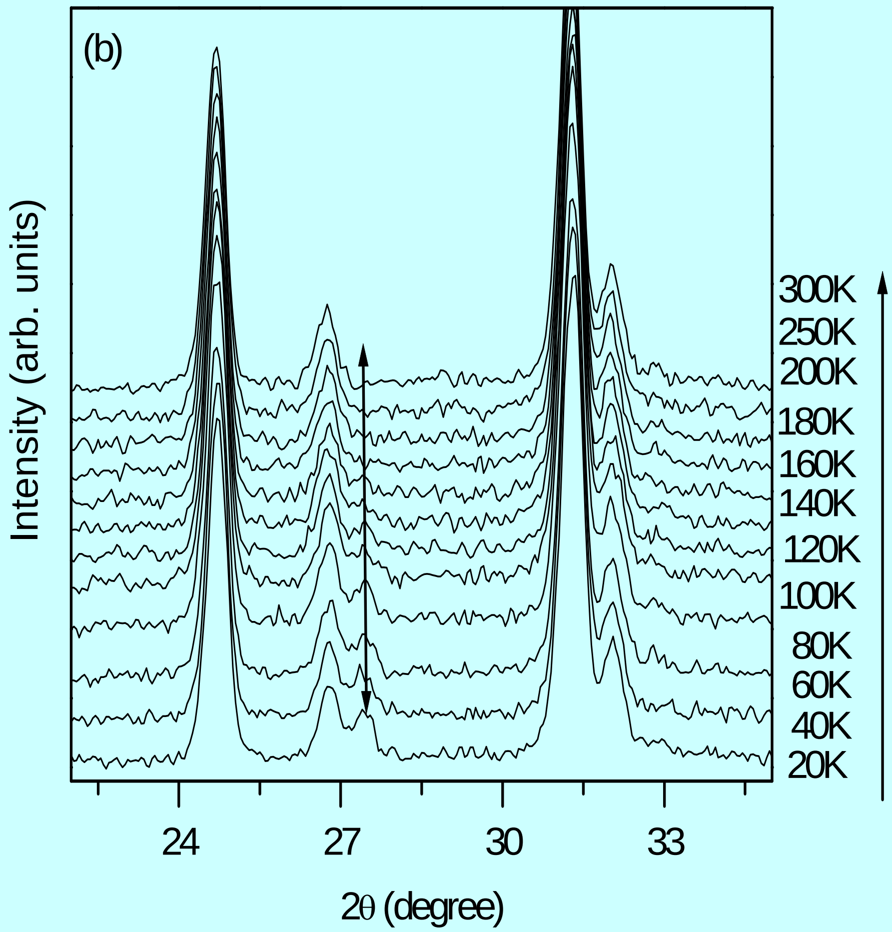


Antiferromagnetic Transition

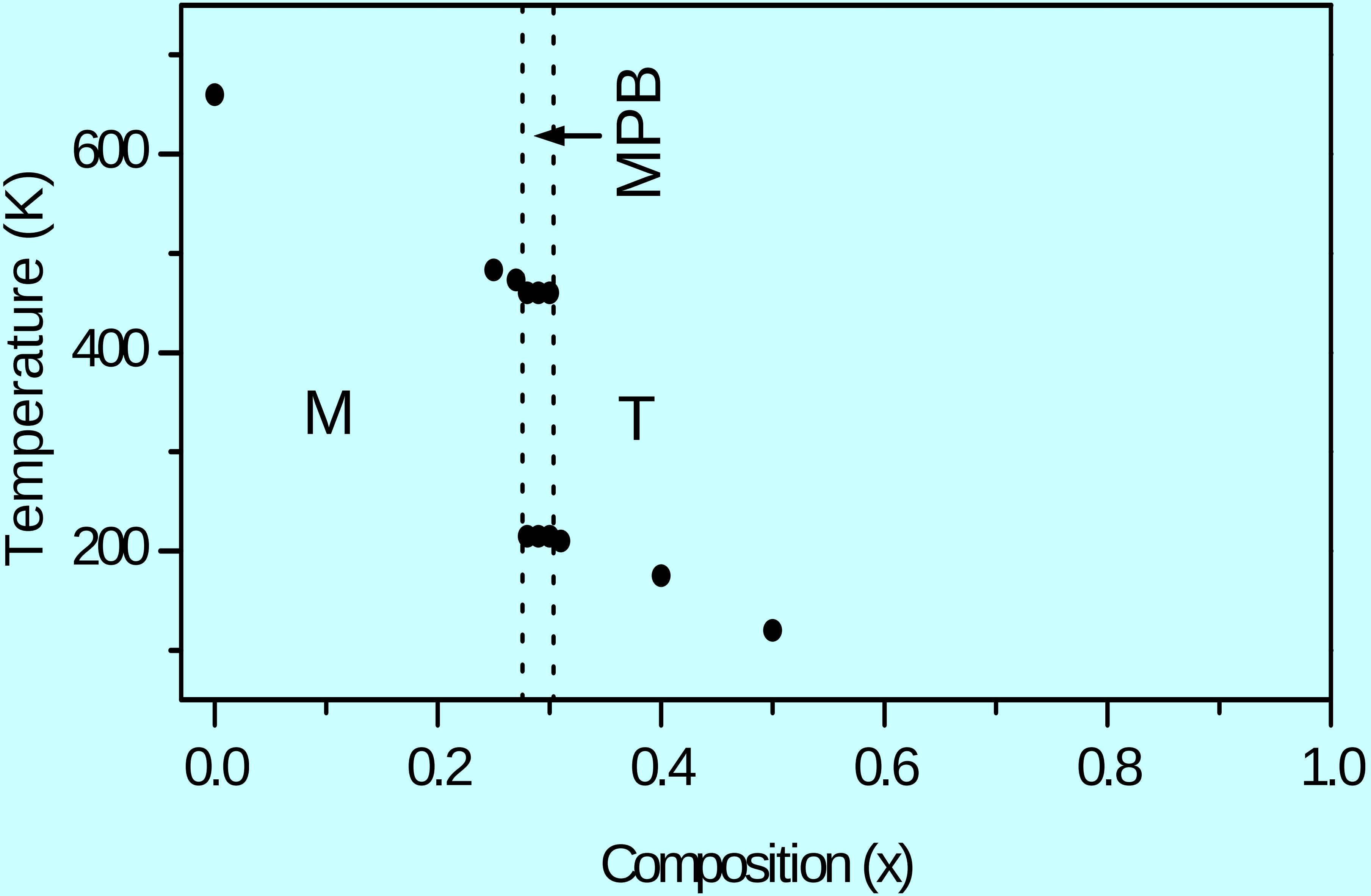
Monoclinic x= 0.25

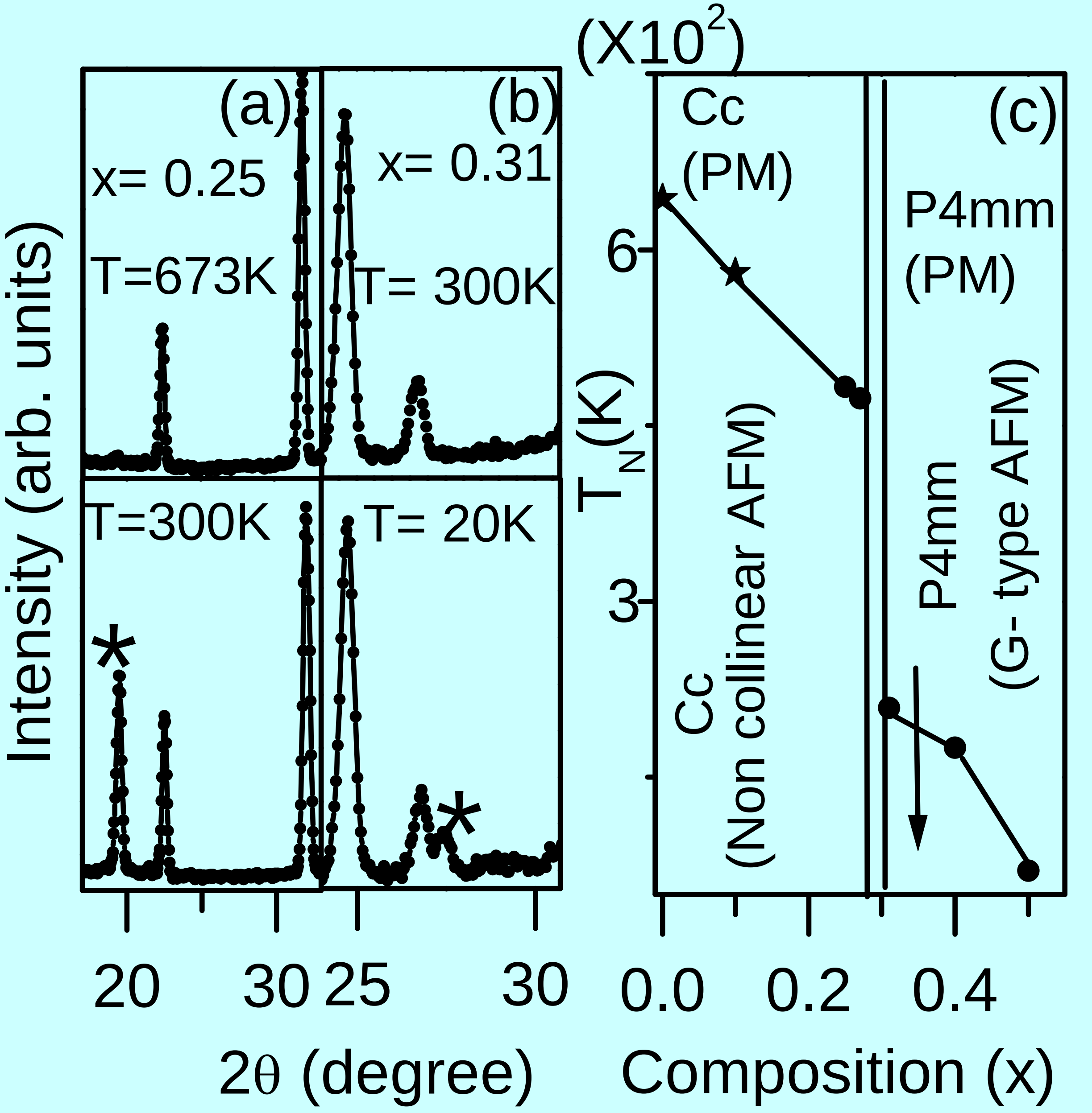


Tetragonal x=0.31



Variation of T_N





Bhattacharjee, Pandey, Kotnala and Pandey, Appl.Phys.Lett, 97, 262506 (2010)

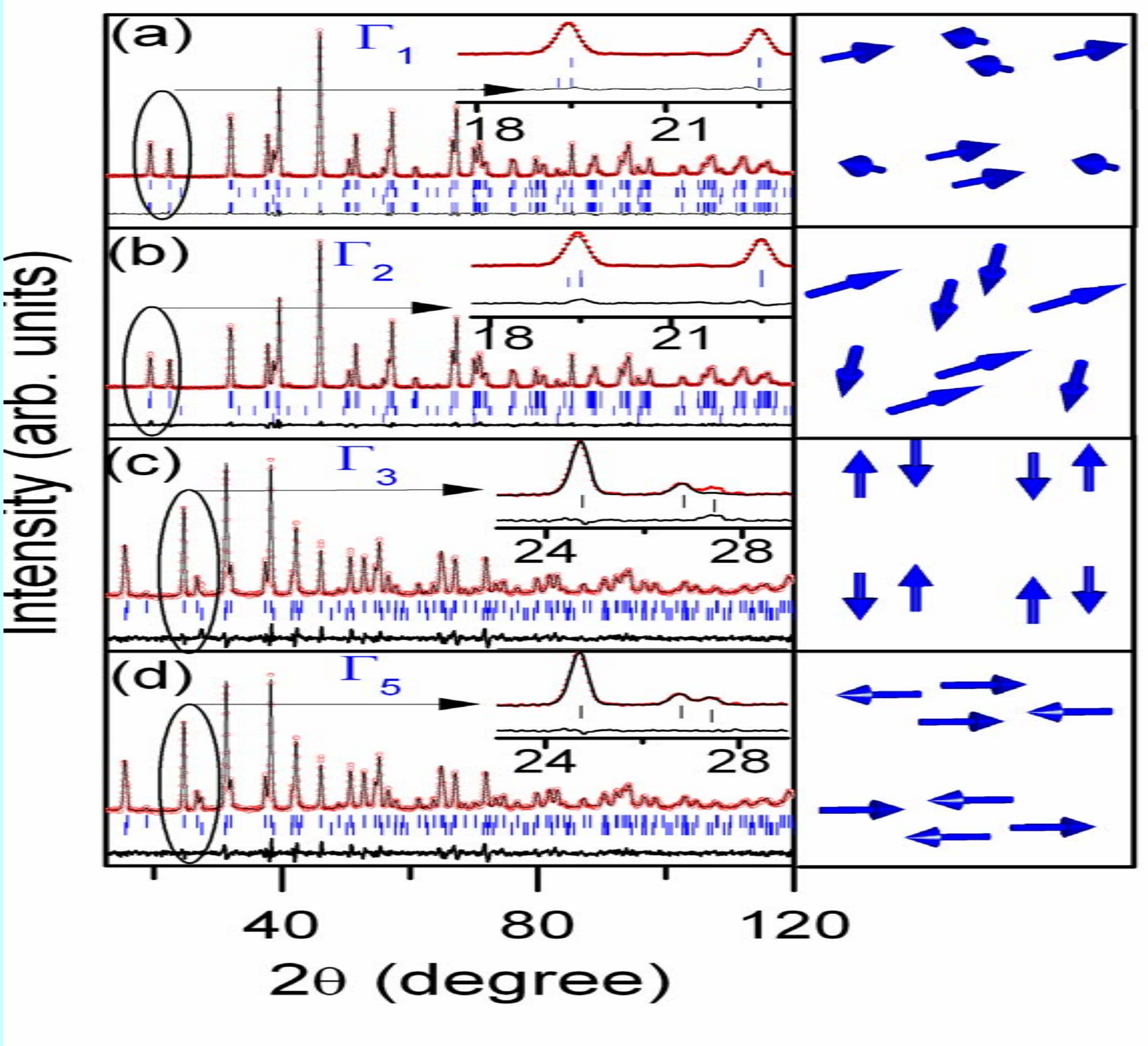
Magnetic Structures : Neutron Diffraction

For Monoclinic (Cc) compositions, Fe^{3+} occupies 4a Wyckoff site

$$\Gamma^{4a} = 3[\Gamma_1 + \Gamma_2]$$

For tetragonal (P4mm) compositions, Fe^{3+} occupies 1b Wyckoff site

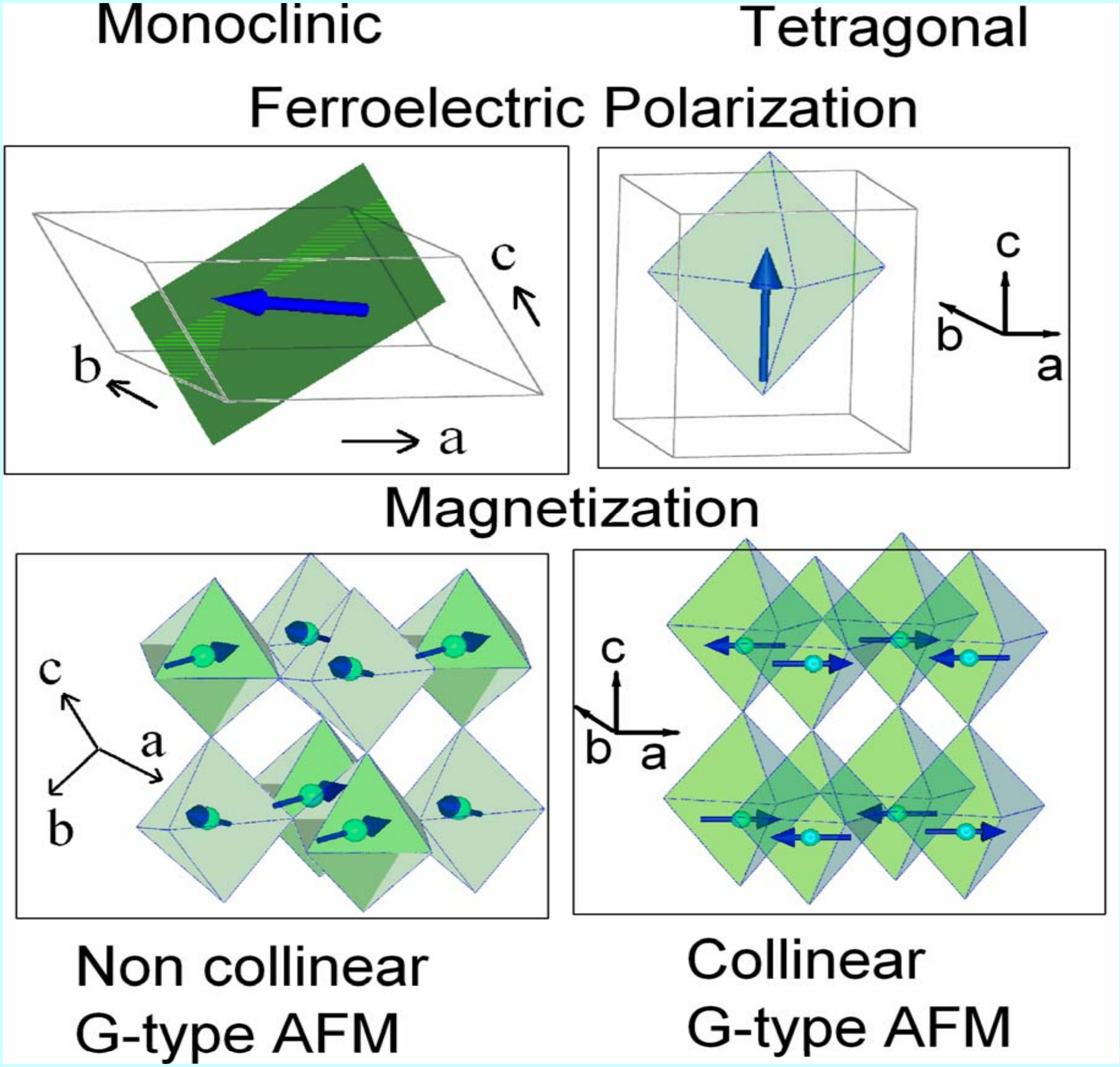
$$\Gamma^{1b} = \Gamma_3 + \Gamma_5$$



x=0.25
Monoclinic

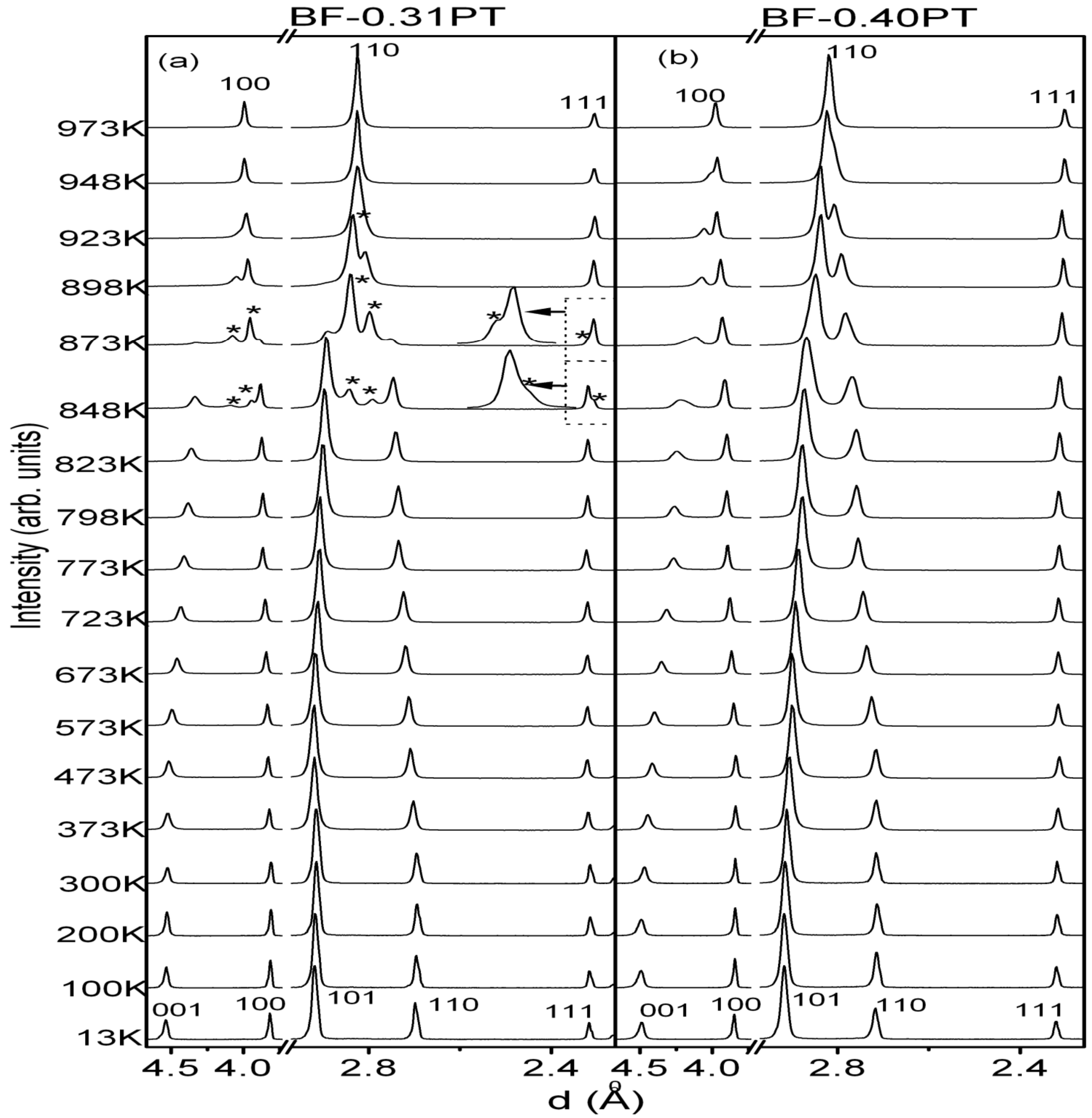
x=0.31
Tetragonal

Bhattacharjee, Senyshyn, Krishna, Fuess and Pandey, Appl.Phys.Lett, 97, 262506 (2010)

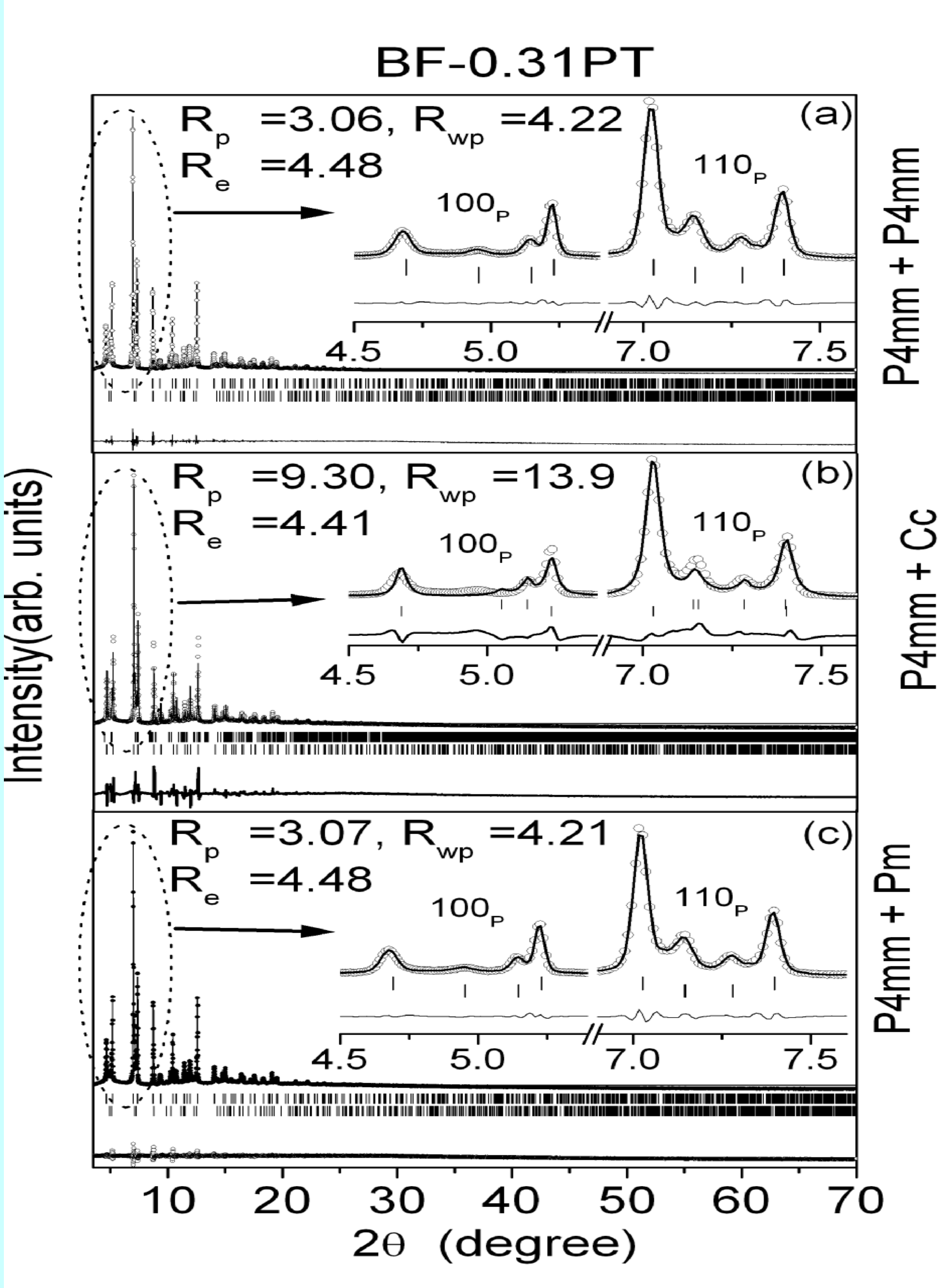


Bhattacharjee, senyshen, Krishna, Fuess and Pandey, Appl.Phys.Lett, 97, 262506 (2010)

Isostructural Tetragonal to Tetragonal Phase Transition in BF-xPT

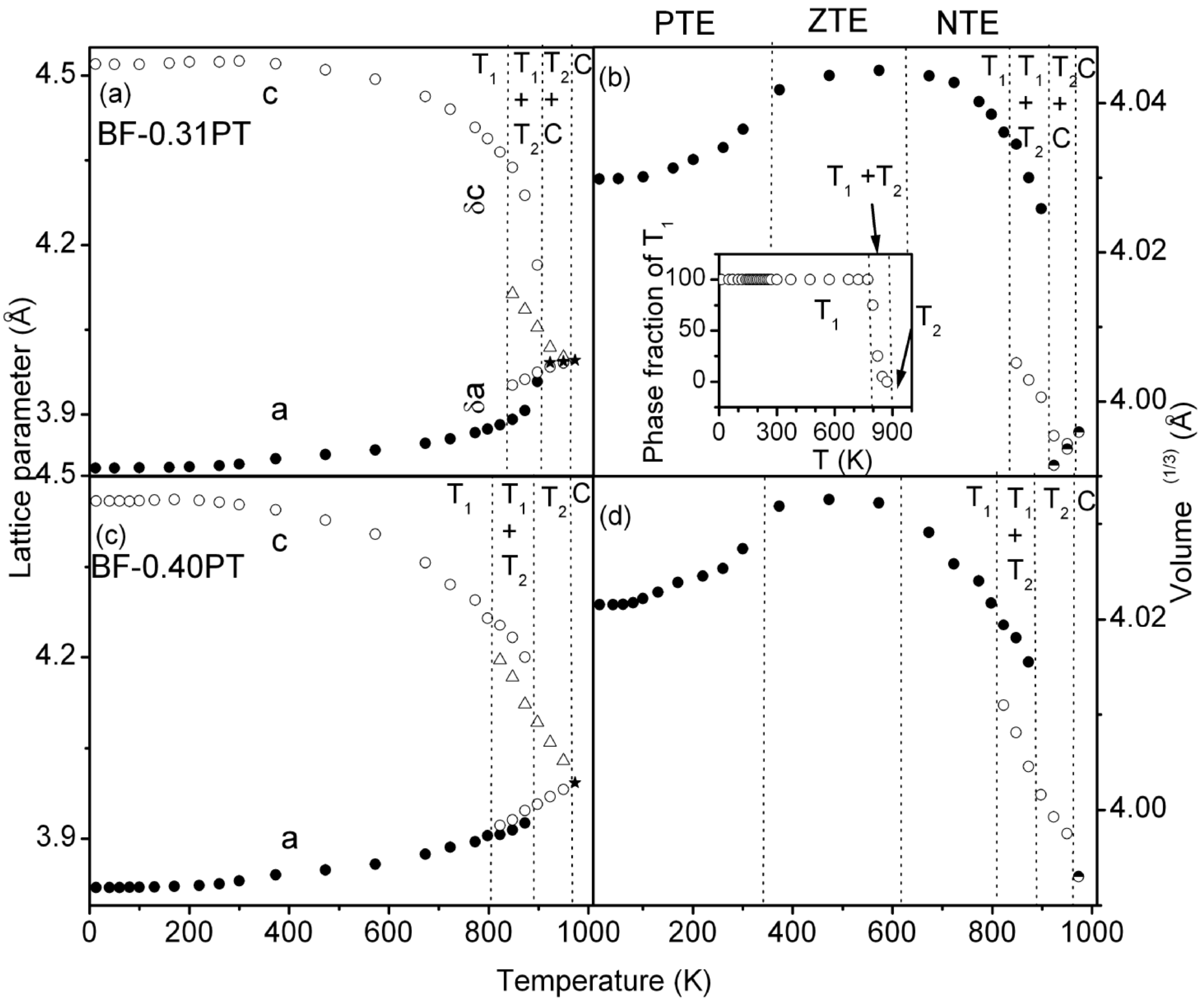


Bhattacharjee, Taji, Moriyoshi, Kuroiwa and Pandey, Phys. Rev. B, **84**,104116 (2010)

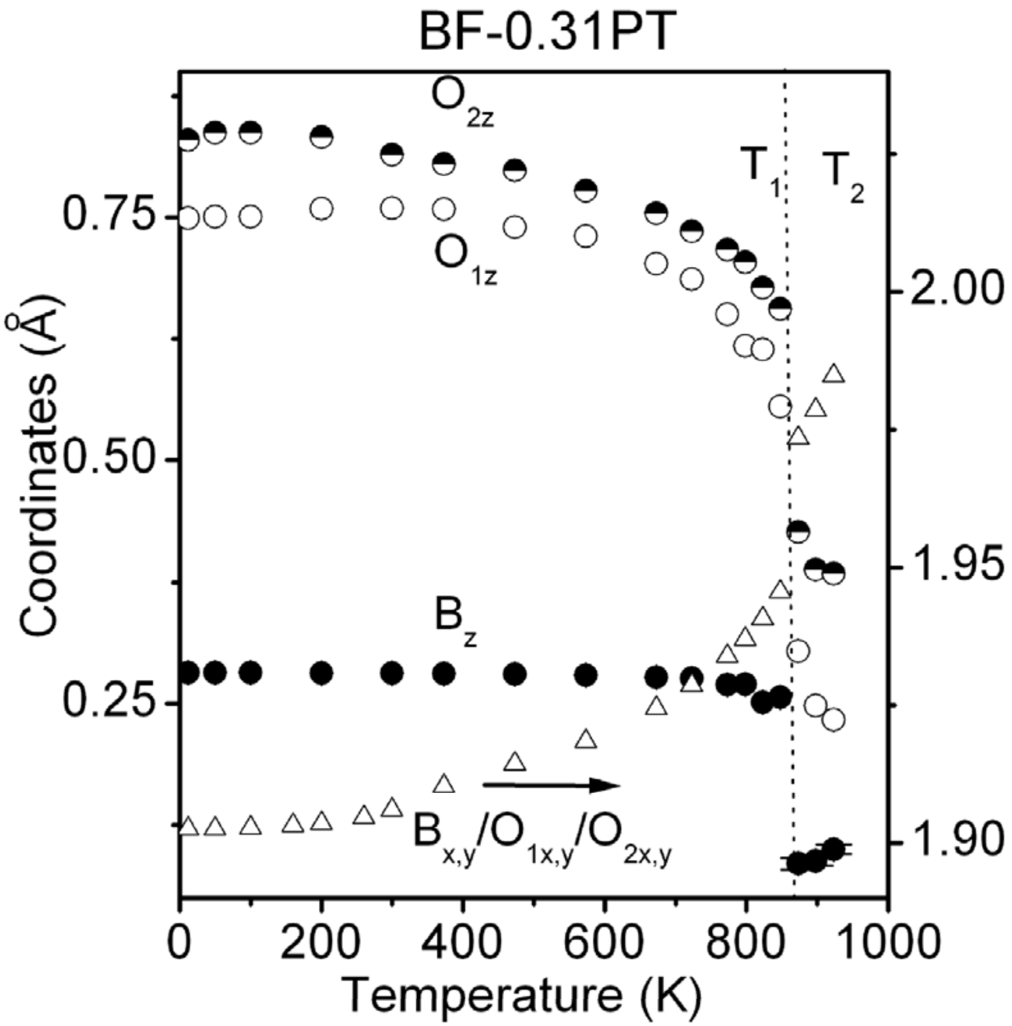


T=848K

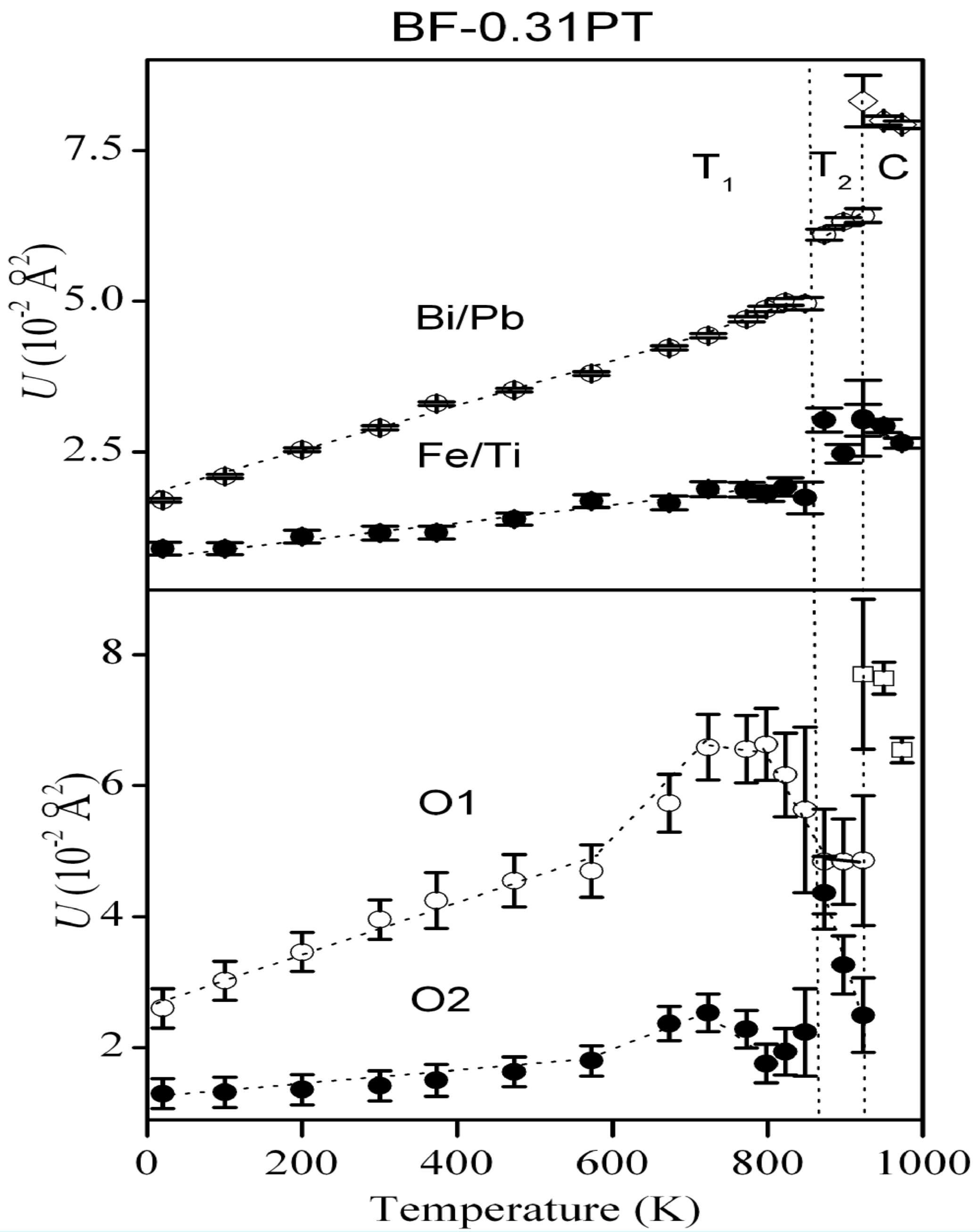
Bhattacharjee, Taji, Moriyoshi, Kuroiwa and Pandey, Phys. Rev. B, **84**,104116 (2011)



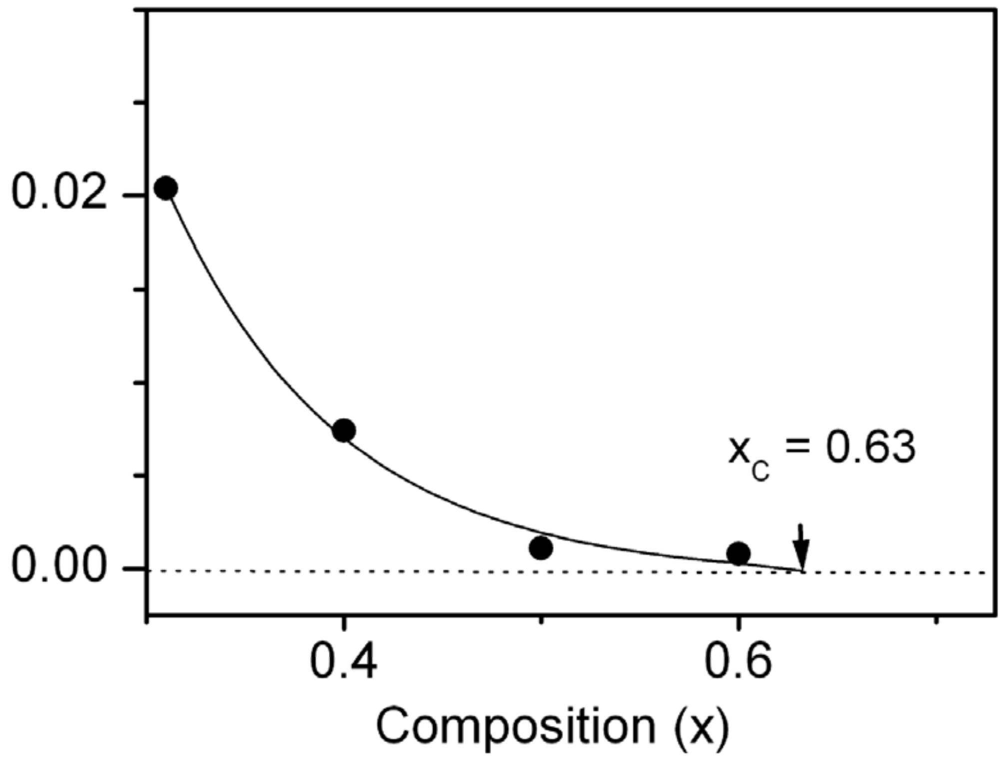
Bhattacharjee, Taji, Moriyoshi, Kuroiwa and Pandey, Phys. Rev. B, **84**,104116 (2011)



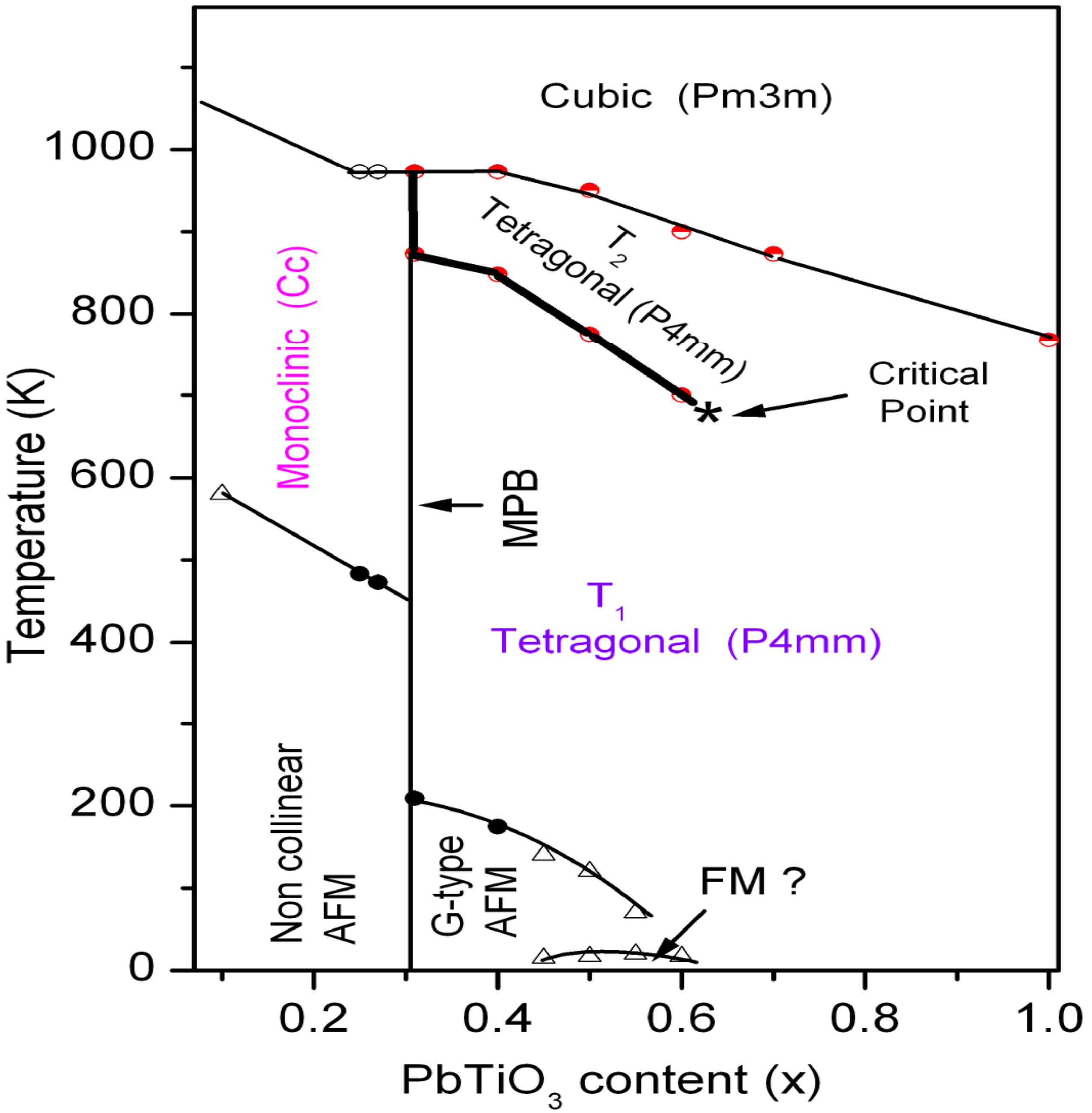
Bhattacharjee, Taji, Moriyoshi, Kuroiwa and Pandey, Phys. Rev. B, **84**,104116 (2011)



Bhattacharjee, Taji, Moriyoshi, Kuroiwa and Pandey, Phys. Rev. B, **84**,104116 (2010)



Bhattacharjee, Taji, Morisoi, Kuriowa and Pandey, Phys. Rev. B, **84**,104116 (2010)



Bhattacharjee, Taji, Moriyoshi, Kuroiwa and Pandey, Phys. Rev. B, **84**,104116 (2010)

Summary

- Evidence for Isostructural Phase Transitions (IPT) in BF-xBT and BF-xPT
- Magnetoelectric coupling arises due to IPT
- Unusually large tetragonality in BF-xPT system is also due to an IPT

Thank You