Institute for Materials Research
FACULTY OF ENGINEERING
UNIVERSITY OF LEEDS

INTERPLAY OF INTERNAL STRESS, EXTERNAL STRESS AND TEMPERATURE ON MAGNETIC ORDERING IN $BiFeO_3$ – $PbTiO_3$

Tim Comyn

Acknowledgements

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Ferroelectricity

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A material must:

(a) Possess a spontaneous polarisation

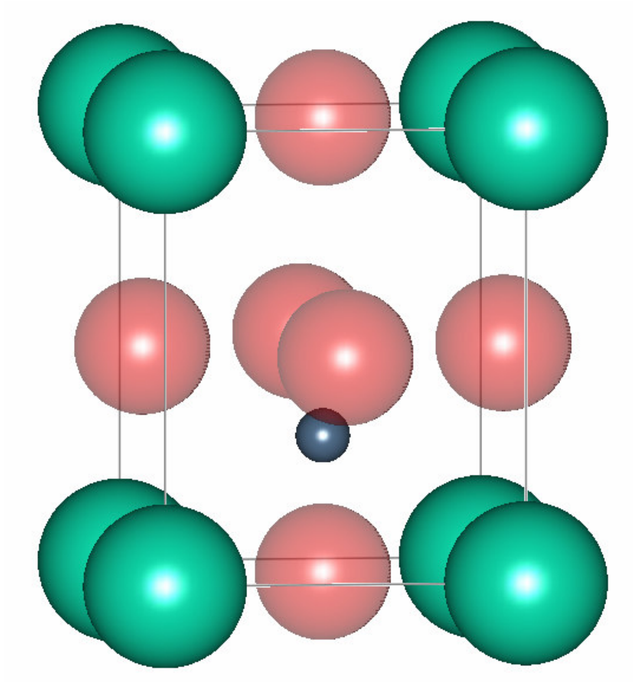
(b) This polarisation must be reversible

Example:

Lead titanate

$PbTiO_3$

Tetragonal perovskite



"Ferro" comes from analogy to ferromagnetism – has nothing to do with iron

Piezoelectricity

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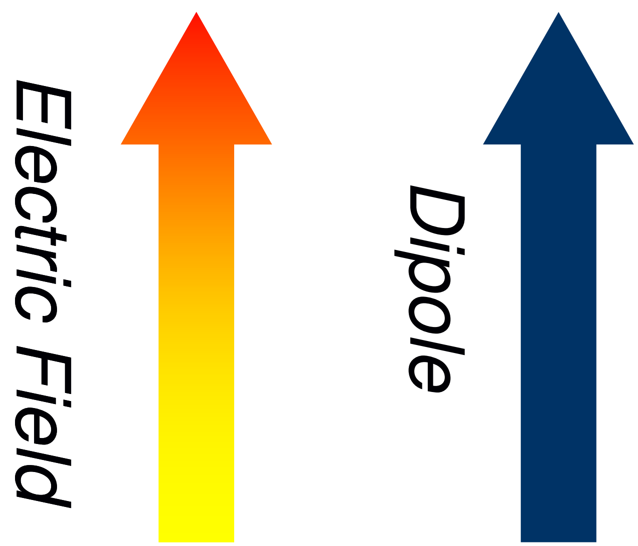
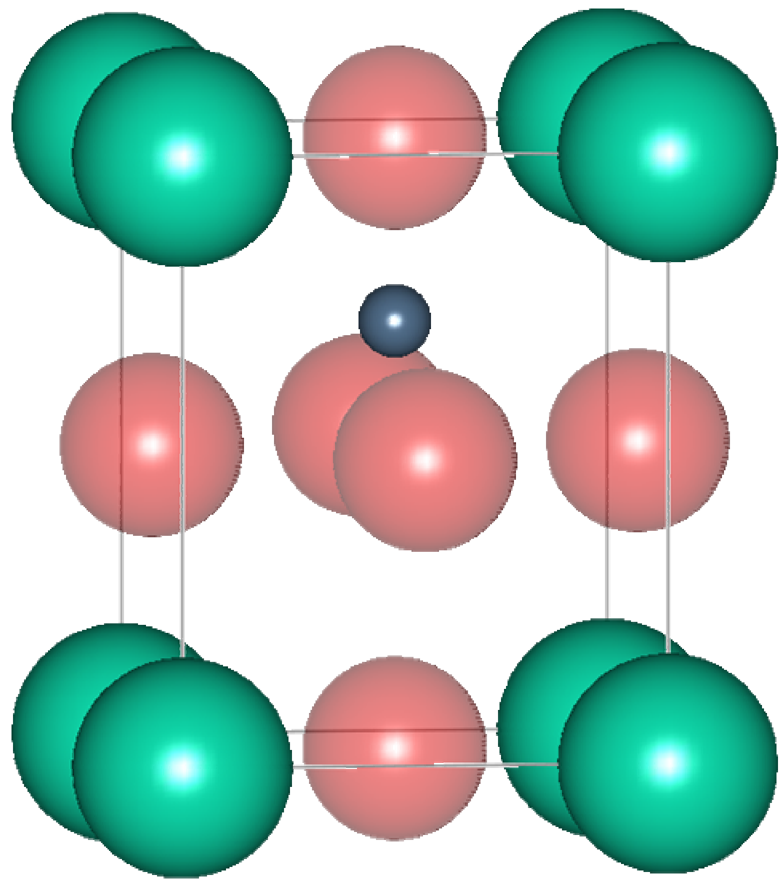
Ferroelectric unit cell is polar

- Electric field couples with dipole
- This coupling induces strain





PZT – Lead Zirconium Titanate

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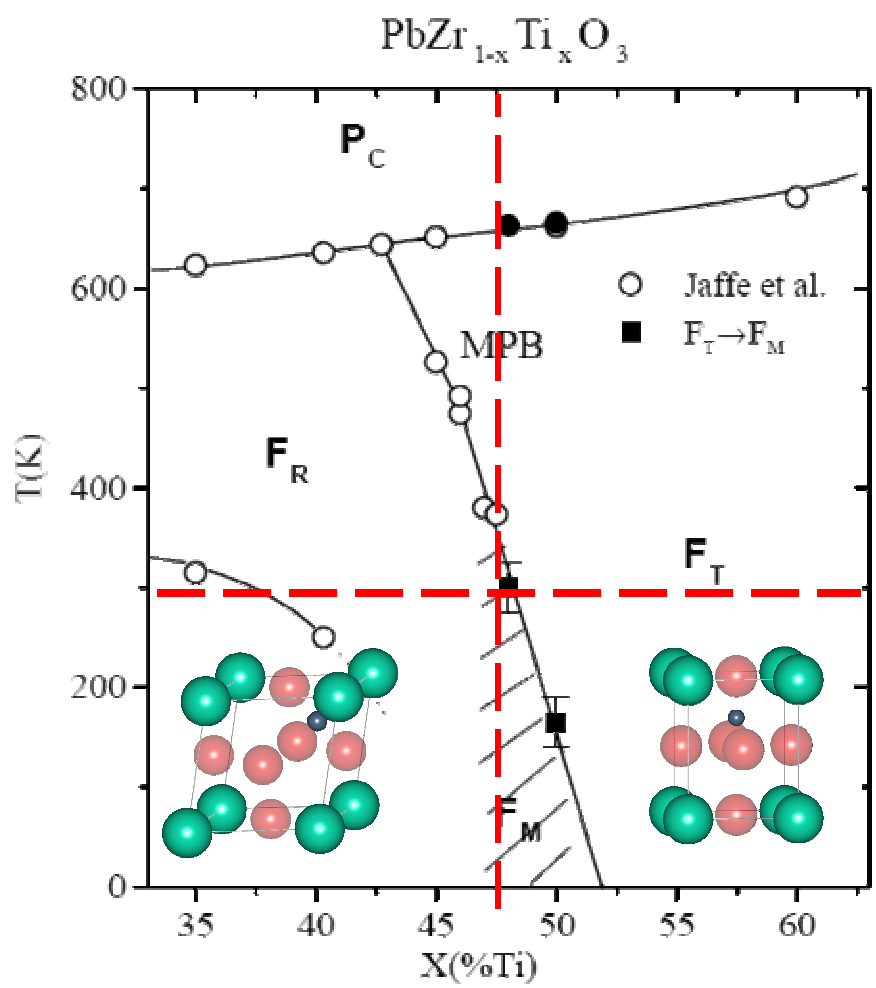
The mainstay piezoelectric material

- $PbZrO_3 – PbTiO_3$

Two pseudo-cubic perovskite phases coexist at around 50:50

At this point we observe enhancement in:

- Piezo activity
- Permittivity



PZT – why so good?

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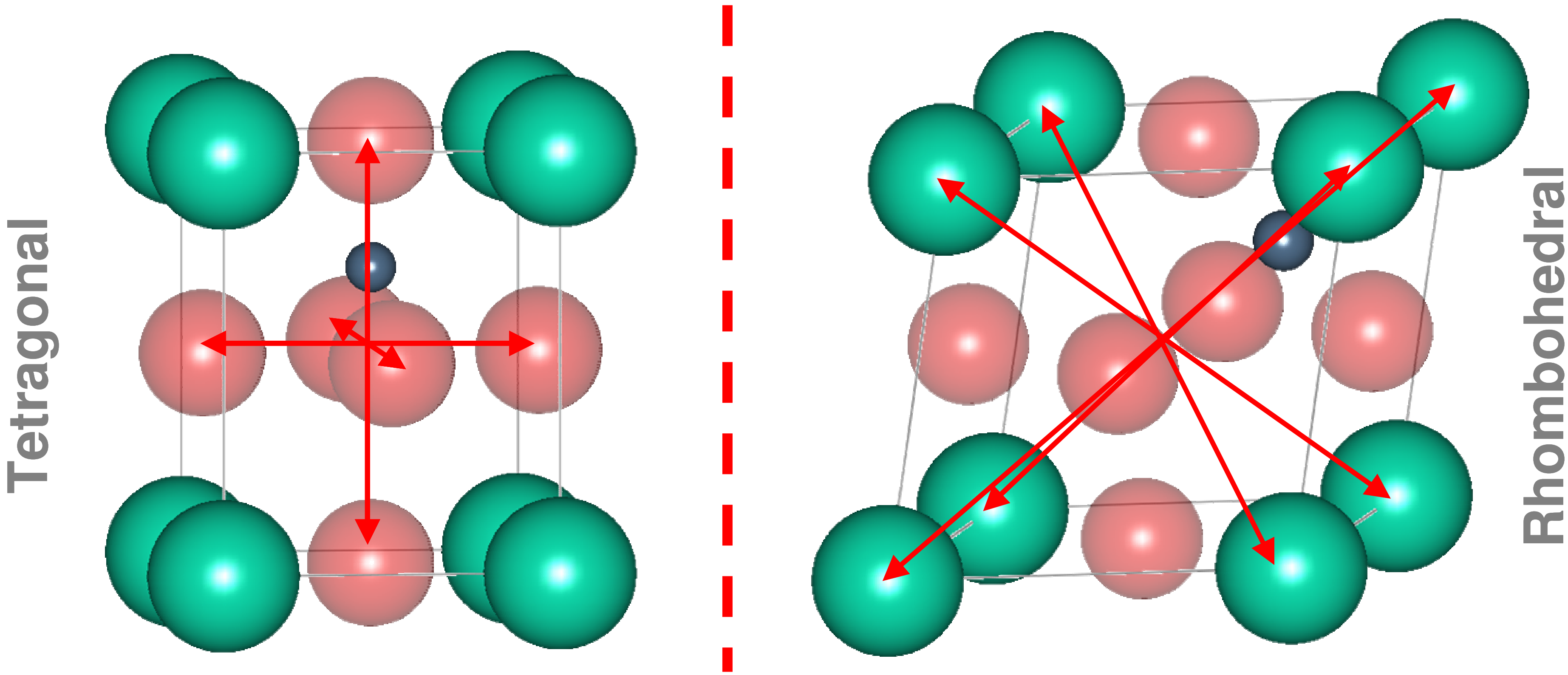
Driven by crystallography : coexistence leads to instability



6 Polar Directions 8

TOTAL = 14

$BiFeO_3$ – A room temperature multiferroic material

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T_N = <u>640 K</u>

G-type antiferromagnetic with spiral ordering

Ferroelectric $T_C \approx$ <u>1100 K</u>

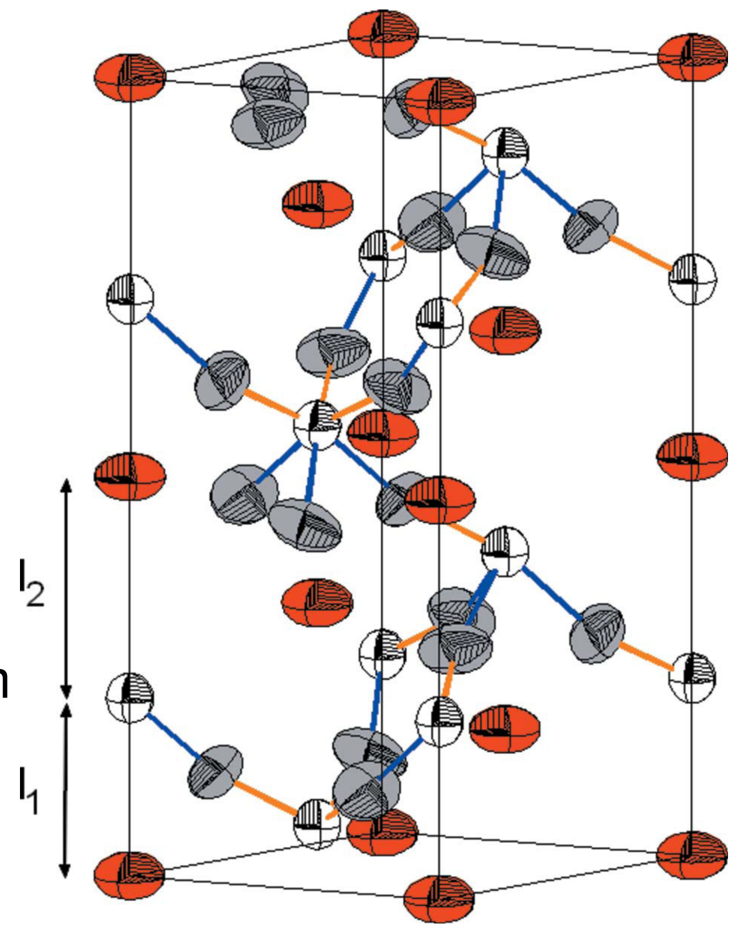
Problem 1:

Electrical conduction – Fe^{2+}/Fe^{3+}

Max drive field in bulk at RT 1-2 kV / mm

Problem 2:

Nightmare to make; competing non-perovskite $Bi_2Fe_4O_9$ ever present



$BiFeO_3 – PbTiO_3$

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S. A. Fedulov,
Soviet Physics – Solid State,
6(2), 375,1964

Properties of $BiFeO_3$-$PbTiO_3$

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Huge increase in electrical resistivity –

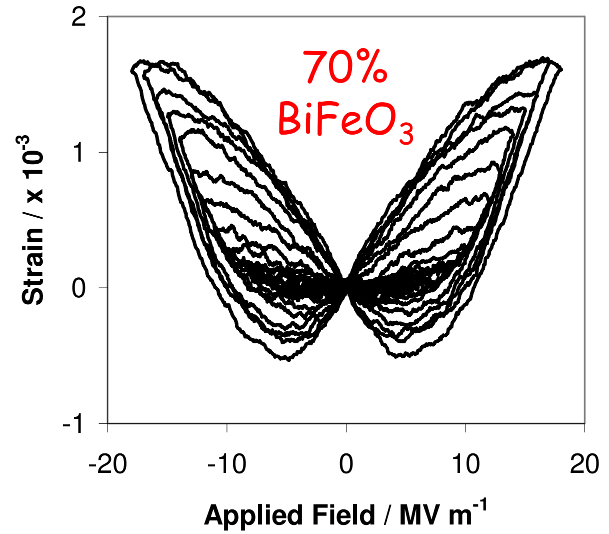
80% $BiFeO_3$ can be driven to 23000 V / mm at room temperature !!!

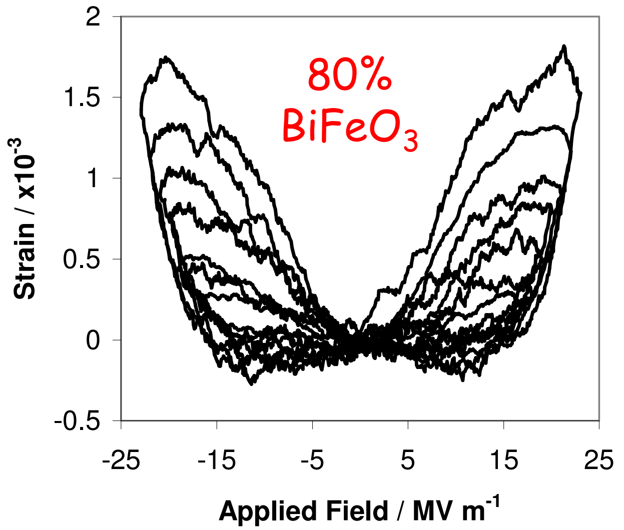
Strongly ferroelectric and piezoelectric – strains of ≈ 0.2 % can be developed

Fascinating mechanical properties –

Primitive unit cell volumes v.different (few %) for R3c and P4mm phases

Fabrication far more simple than $BiFeO_3$





Forms

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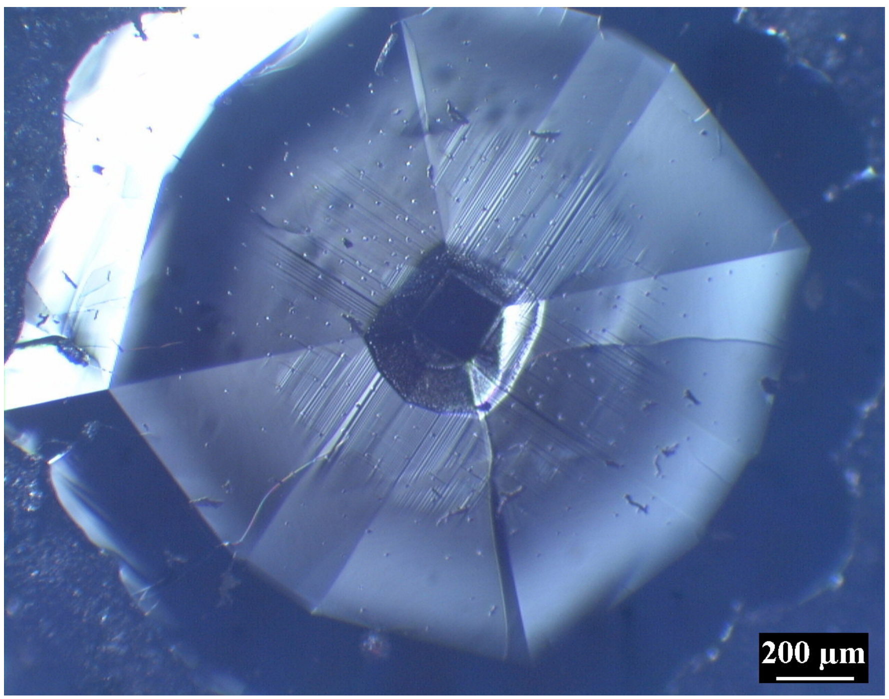
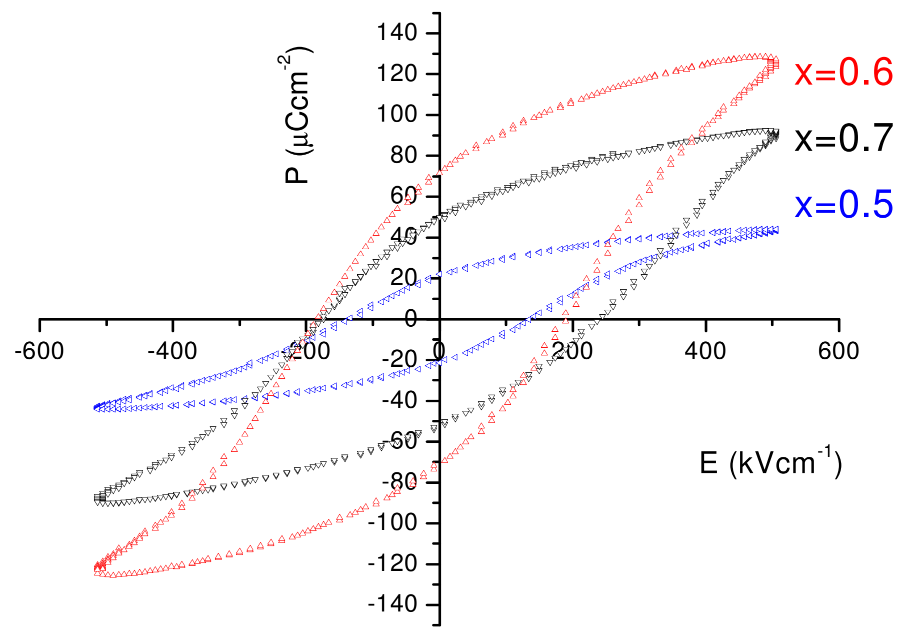
Can be made in dense poly-crystalline form (reported here), or

Single crystals (not poss. in PZT!!!)



Tim Burnett

Thin films



Mikael Khan

Doping

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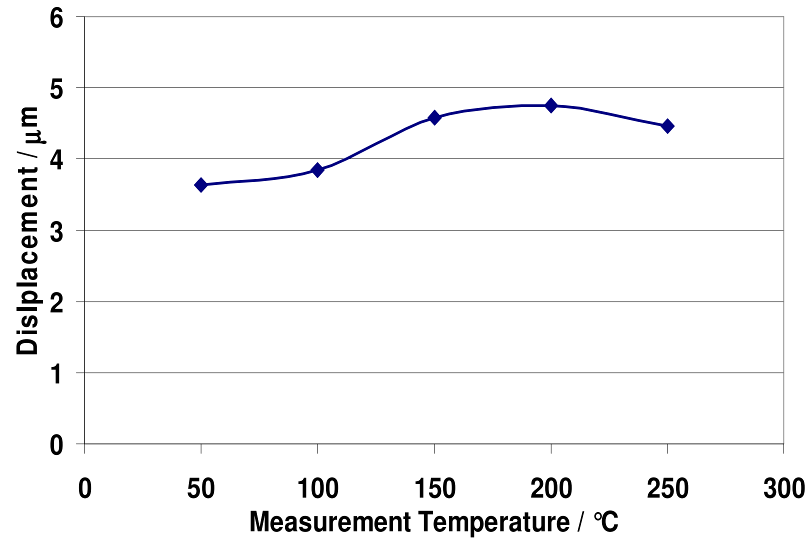
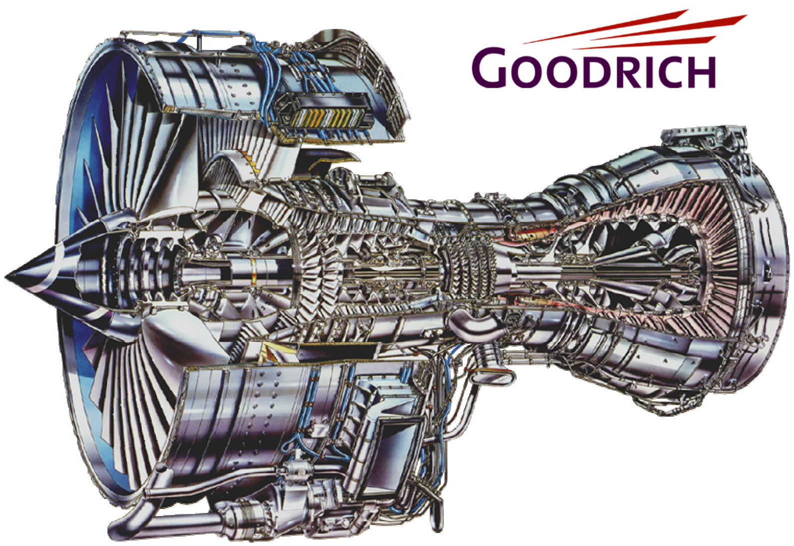
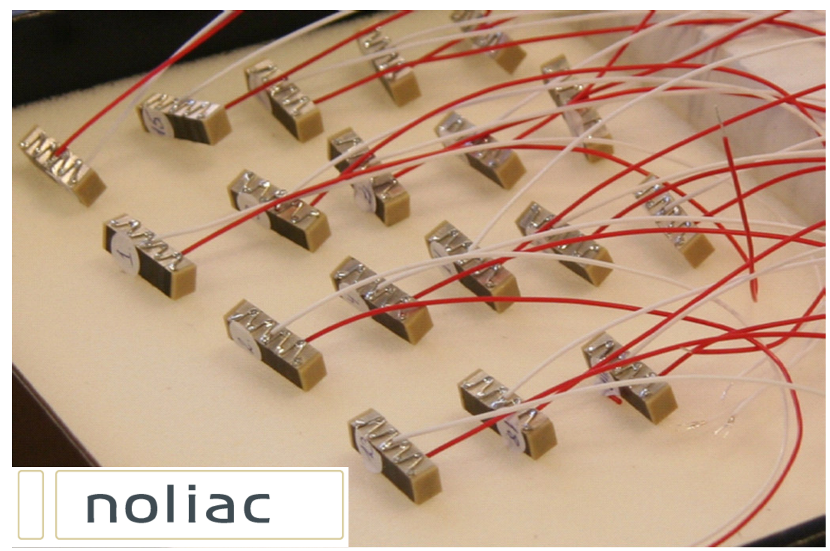
Dramatic change in properties with low levels of doping

- With 3% La doping, high temperature piezoelectric materials developed and manufactured for aero-engines
- Magnetic ordering in these materials confirmed at room temperature







High temperature piezoelectrics

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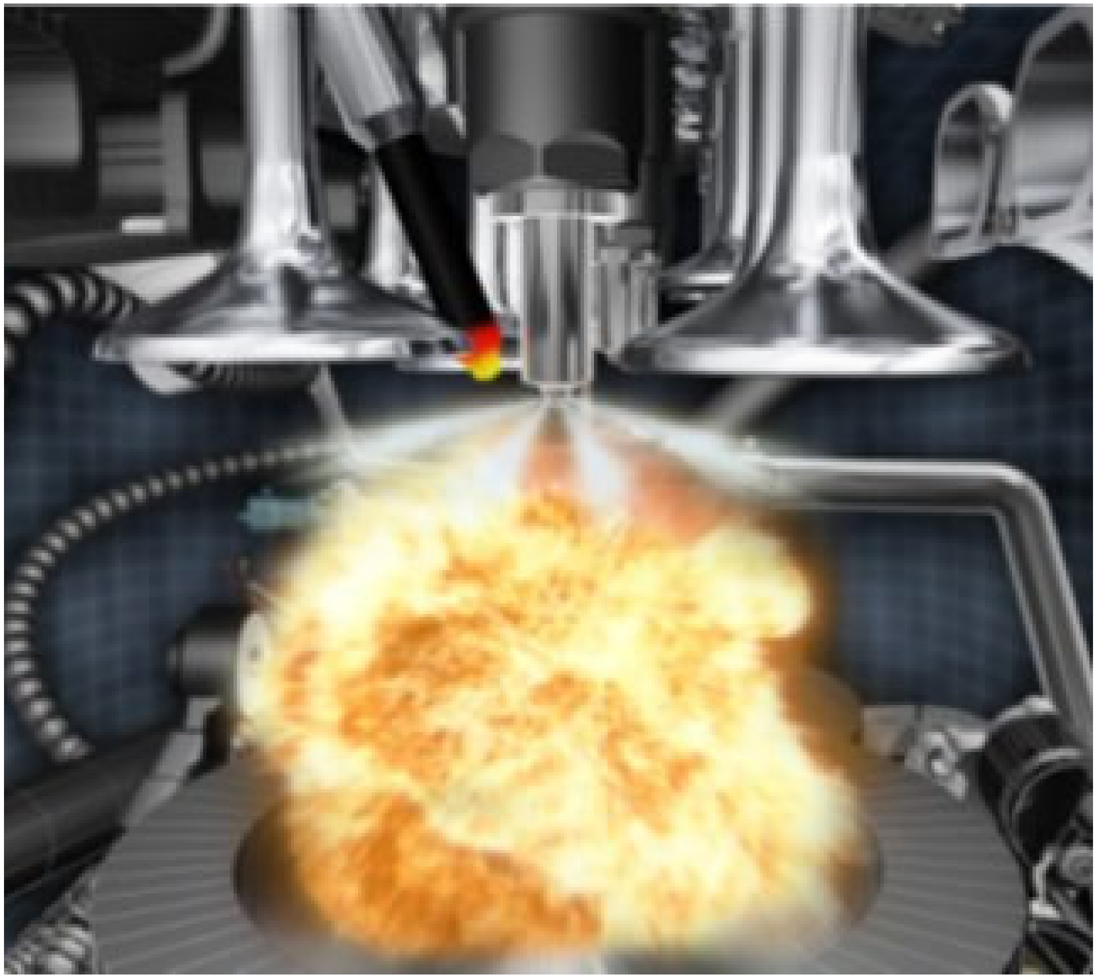
Direct Fuel injection - *Huge recent Euro effort*



Deep Drilling

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Sensing and actuation at temperatures > 200 °C

Rapid response, less complexity

Hitting a chert seam with a diamond head costs £250k

Applications – aeroengines

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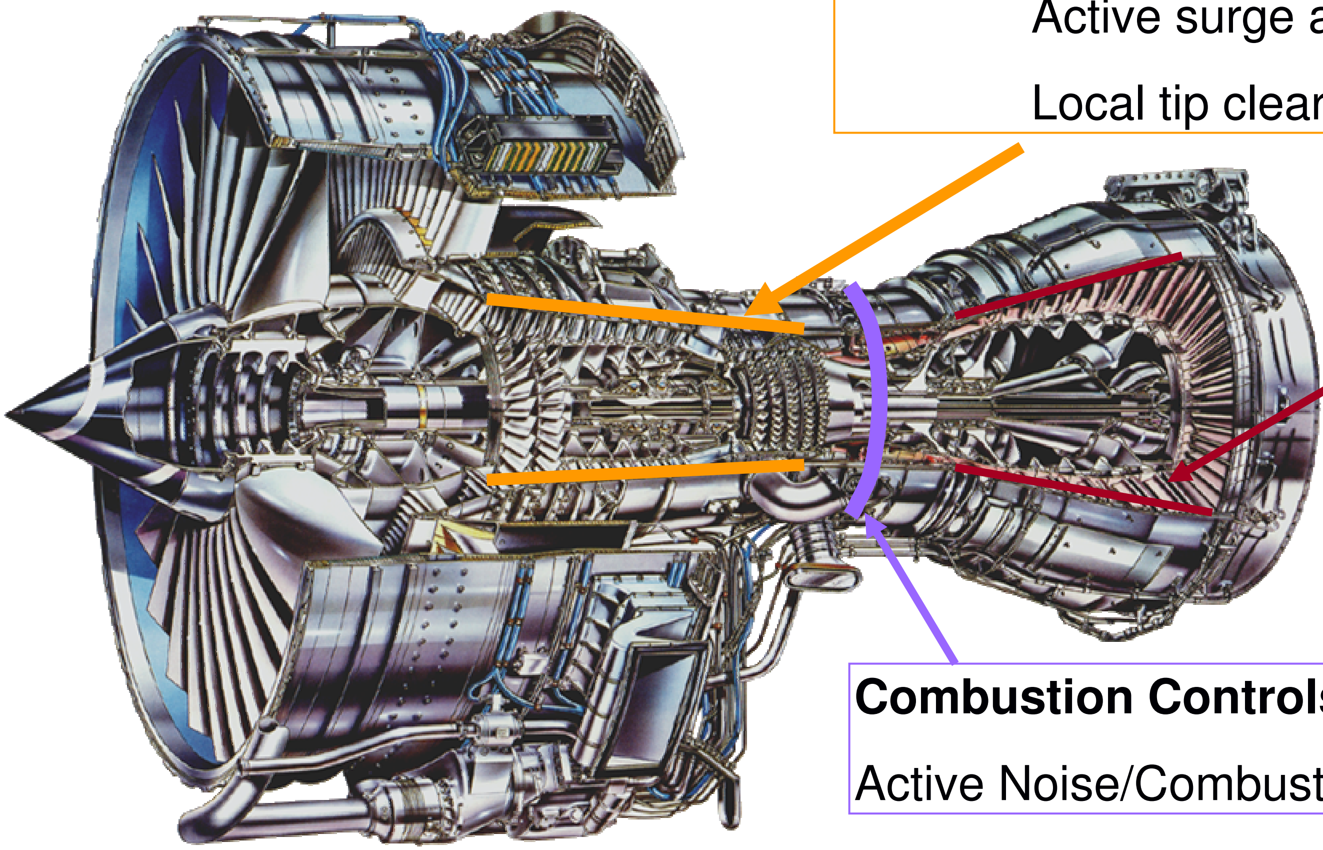
GOODRICH



Compressor controls –

Local VIGV actuation
(Variable inlet guide valve)

Active surge air injection

Local tip clearance actuators

Turbine controls

Cooling air control

Tip clearance actuators

Combustion Controls

Active Noise/Combustion controls

Magnetic Properties

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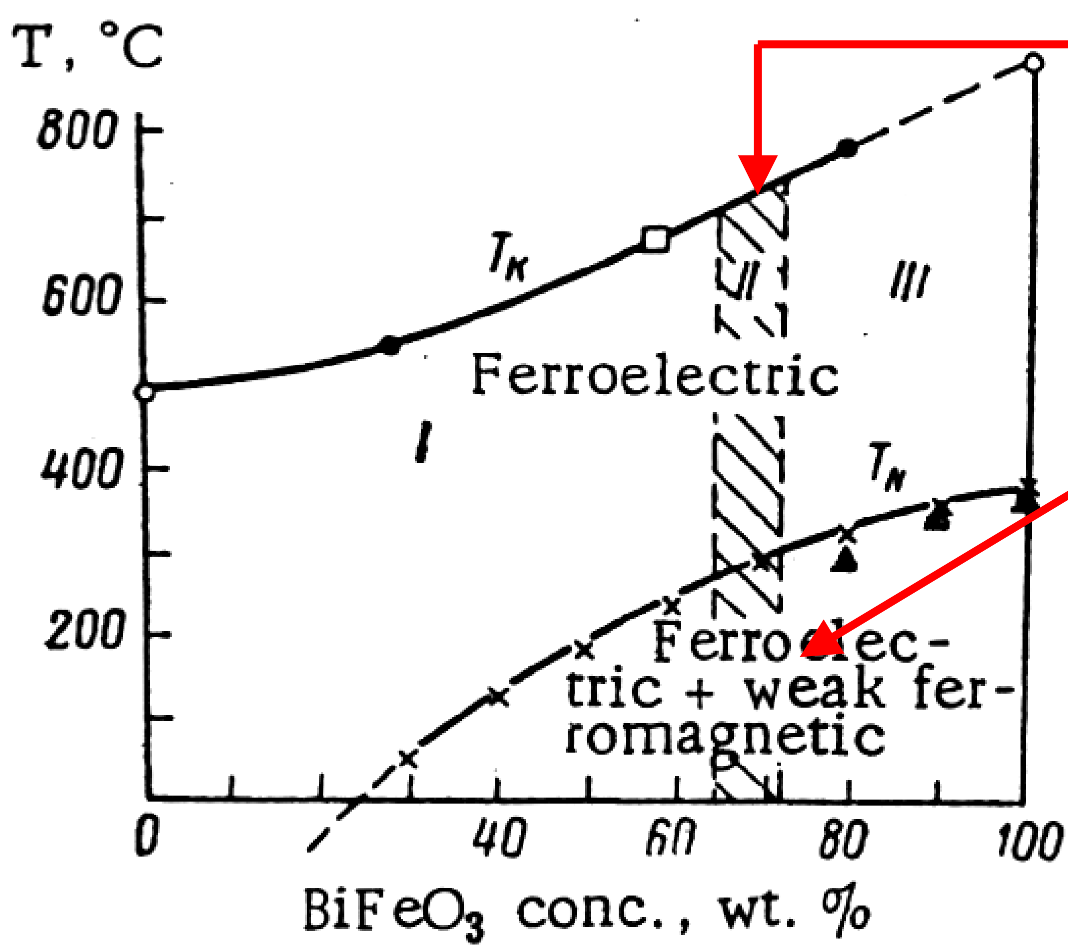

T_C = 630 °C

~ 300 > PZT

Magnetic ordering

S. A. Fedulov,
Soviet Physics – Solid State,
6(2), 375,1964

Electrical and magnetic properties

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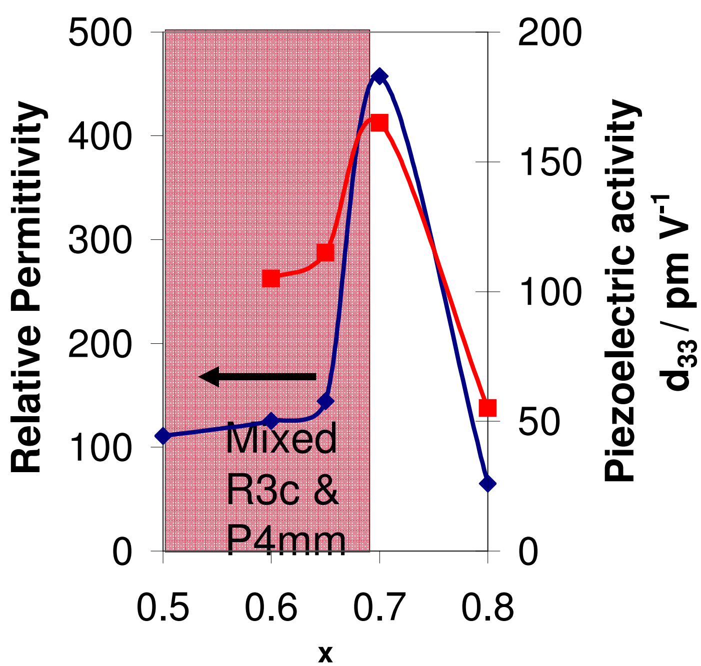
Electrical properties

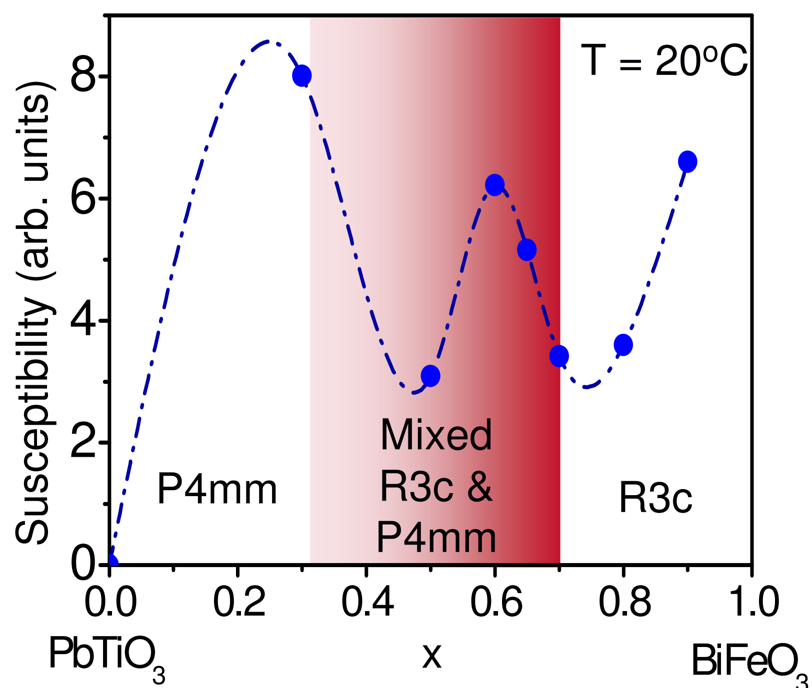
Peak in properties at onset of mixed phase – similar effects observed in other ferroelectric systems



Magnetic properties

3 contributions

- Dilution of Fe with Ti
- Transition from R3c to P4mm ?
- Reduction in T_N



What can neutrons do for us: Practical

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1. We can probe the bulk material without worrying about surface modification and damage through processing – even using synchrotron, this “surface” can comprise many % of the total

2. We are able to study under extreme conditions, such as high isostatic pressure, due to the penetration of the neutrons

Penetration depth:

XRD Cu kα - μm

Synchrotron – mm

Neutrons – cms

What can neutrons do for us: Magnetic

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Neutrons are the <u>only</u> means by which we can explicitly define the magnetic ordering – VSM and susceptibility cannot

What can neutrons do for us: Structural

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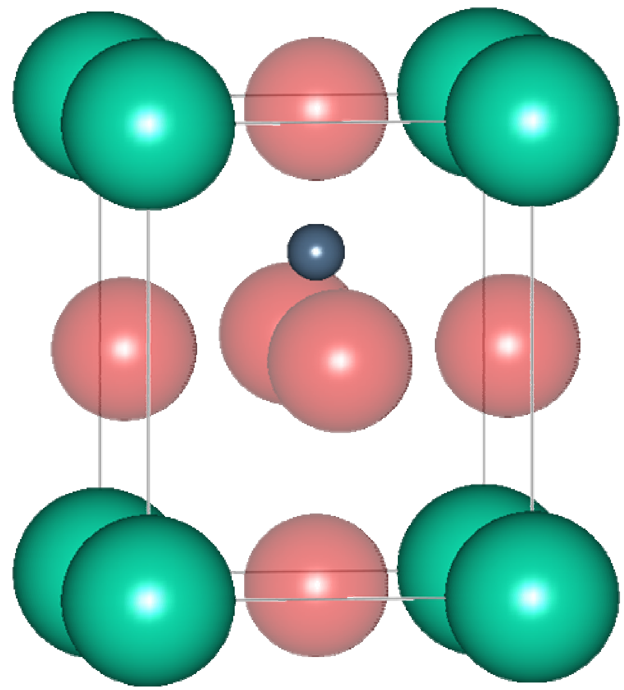
1. The complicated oxygen tilting structure can be revealed; using x-rays, Bi and Pb dominate.

   Electron diffraction required intensive sample preparation which destroys the "bulk" properties

2. Fe and Ti have very different scattering lengths when using neutrons – no differentiation using x-rays or electrons



Why specifically are we using neutrons - <u>contents</u>

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1. Can we explain (or at least reproduce) the observed behaviour shown by susceptibility (VSM and AC) measurements
2. We know that ferroelectricity is inextricably linked to the structure; is the magnetic ordering – can we show a mechanism by which ferroelectricity can couple to the antiferromagnetism – *a room temperature magnetoelectric?*
3. What happens in the mixed phase region?; *the effects of stress*
4. Can we alter the relative phase concentration with hydrostatic pressure (due to the volume difference); can we turn on the magnetism at will

Magnetic Properties

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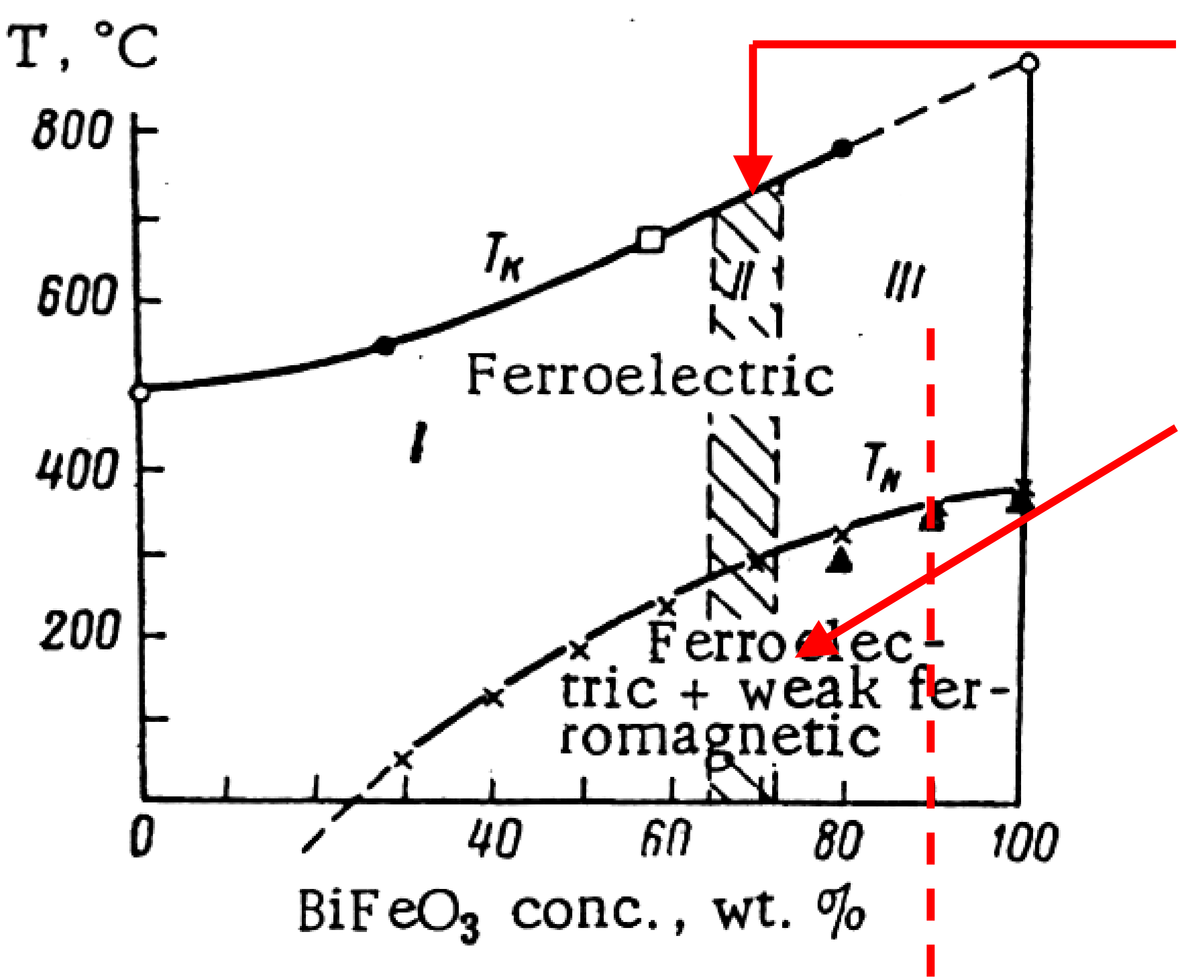

T_C = 630 °C

~ 300 > PZT

Magnetic ordering

S. A. Fedulov,
Soviet Physics – Solid State,
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90% $BiFeO_3$ – effect of temperature
POLARIS (ISIS)

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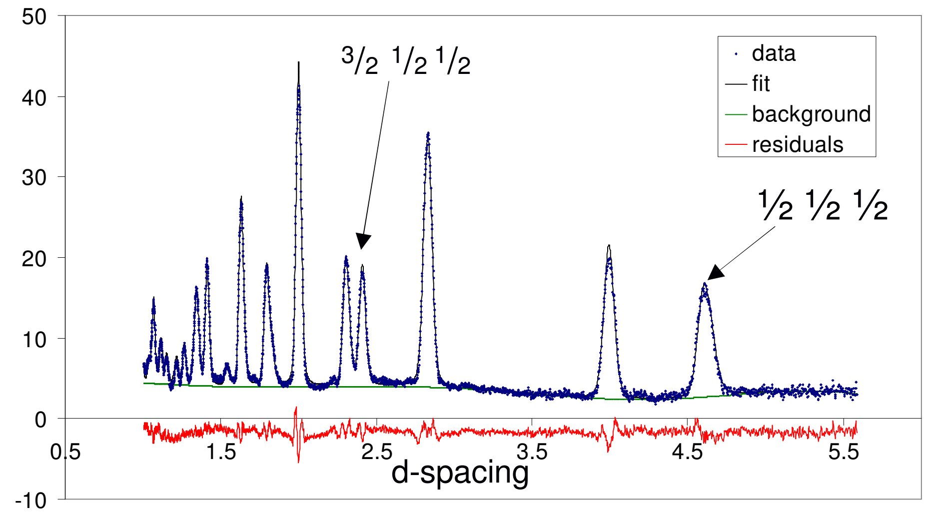
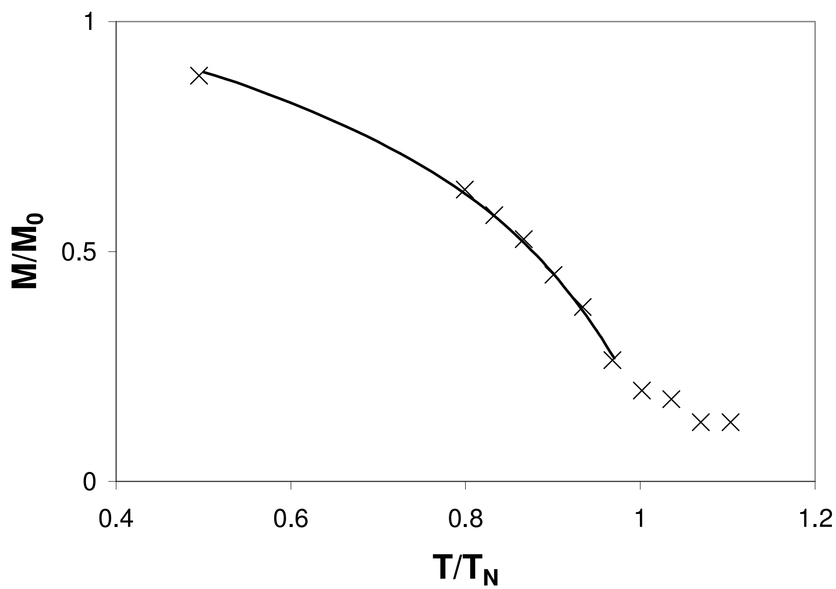
Magnetic order appears to be identical to $BiFeO_3$

but

Magnetic ground state (Fe^{3+}) identical, at 4.34 μ_B

- 10% $PbTiO_3$ has not disrupted ordering
- Concentration of parasitic secondary phases vastly reduced





90% $BiFeO_3$ – structure
POLARIS (ISIS)

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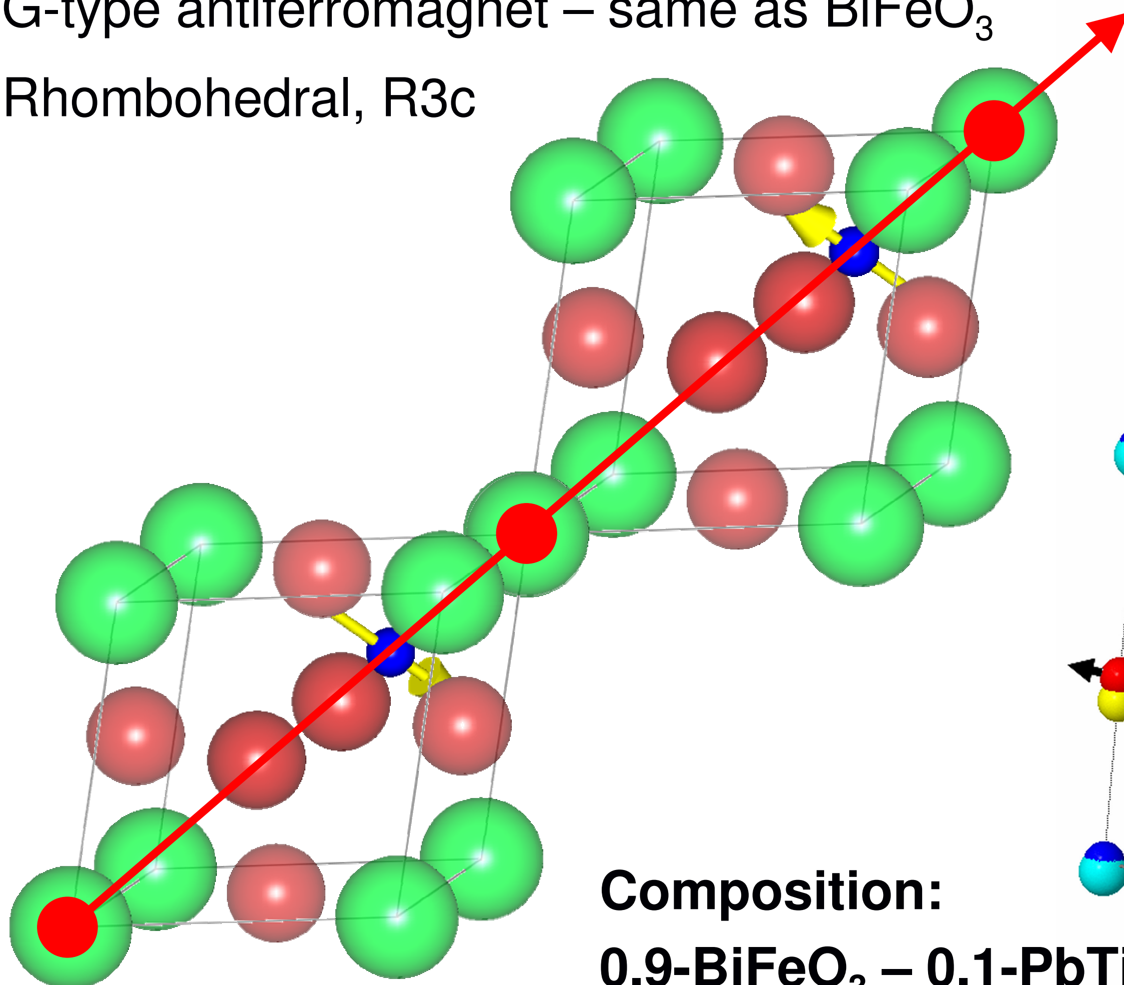
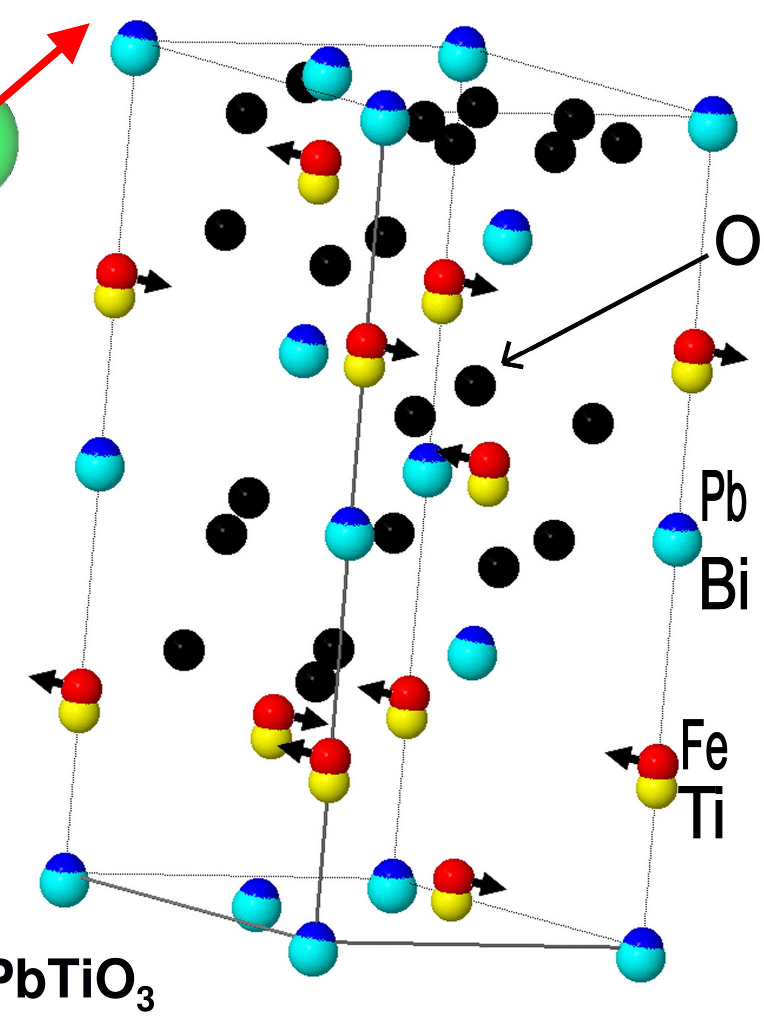
G-type antiferromagnet – same as $BiFeO_3$

Rhombohedral, R3c





Composition:

0.9-$BiFeO_3$ – 0.1-$PbTiO_3$

Analysis of structure

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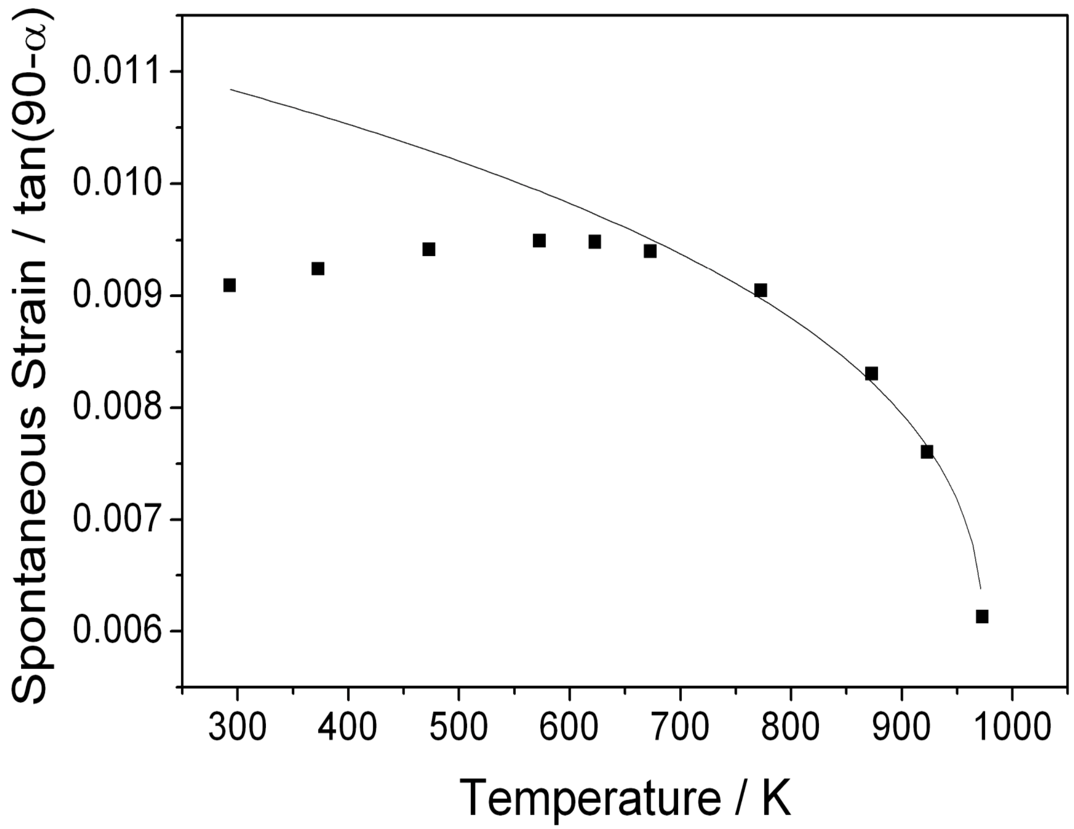
Plot of spontaneous strain (R3c) vs. temperature

- yields maximum at $T_N - 3K$ discrepancy

Is this effect coincidental??

- If not, possible mechanism for magnetoelectricity

Significant deviation from expected behaviour



Mixed phase region

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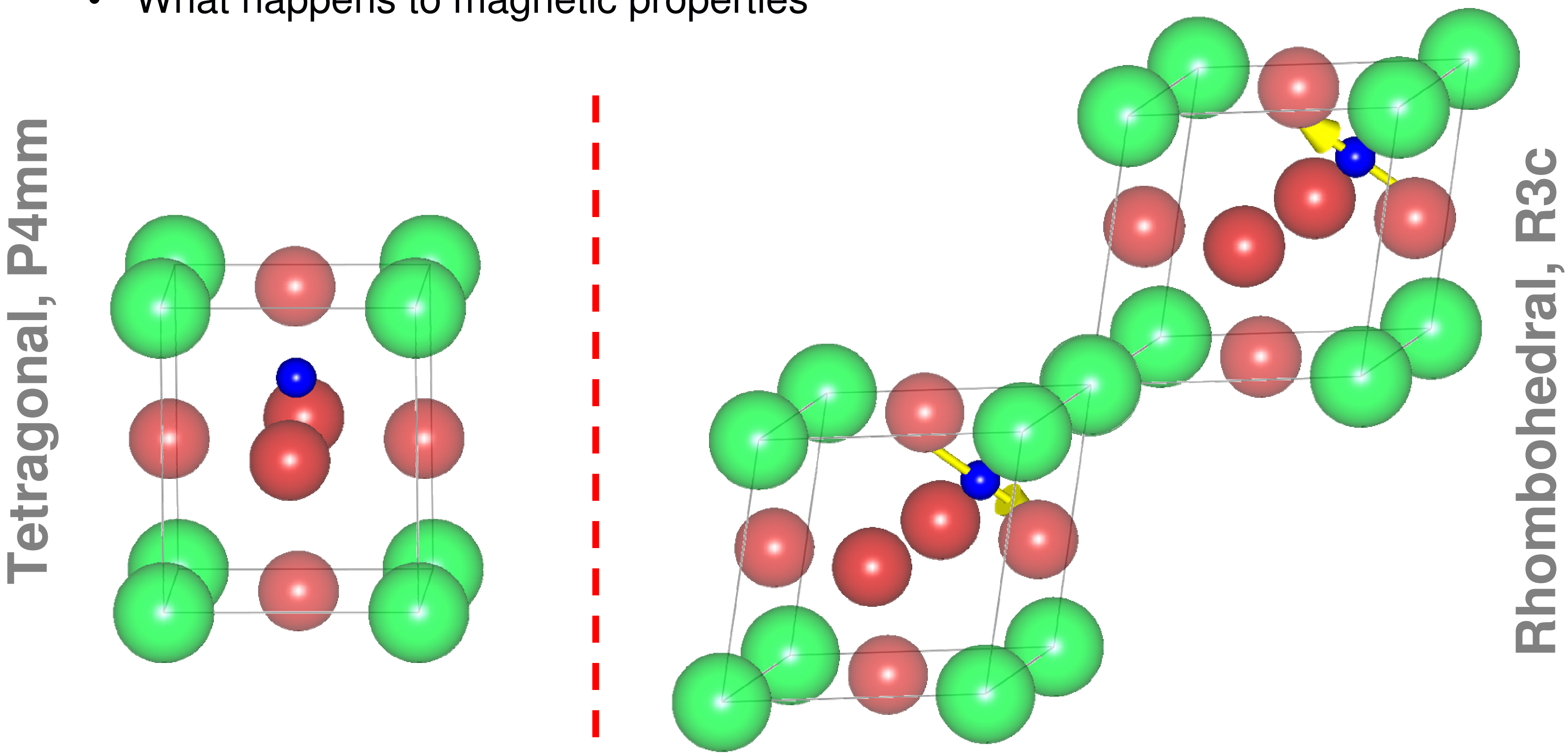
We see enhancement to piezo and dielectric properties

- What happens to magnetic properties



RT moment vs. composition
POLARIS

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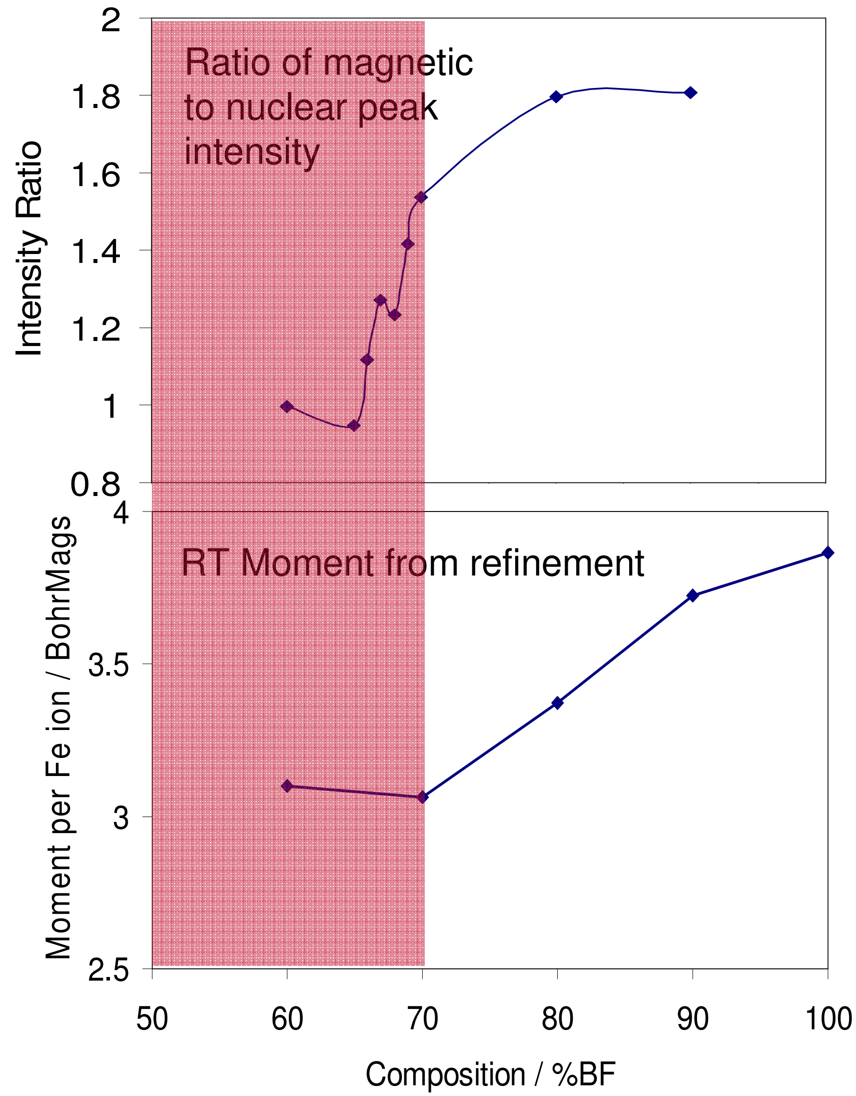
Magnetic moment can be estimated from √(½ ½ ½) peak height or calculated explicitly from refinement – becomes difficult in mixed phase region

Perturbation in mixed phase

- correlates with VSM and AC susceptibility measurements



$BiFeO_3 – PbTiO_3$

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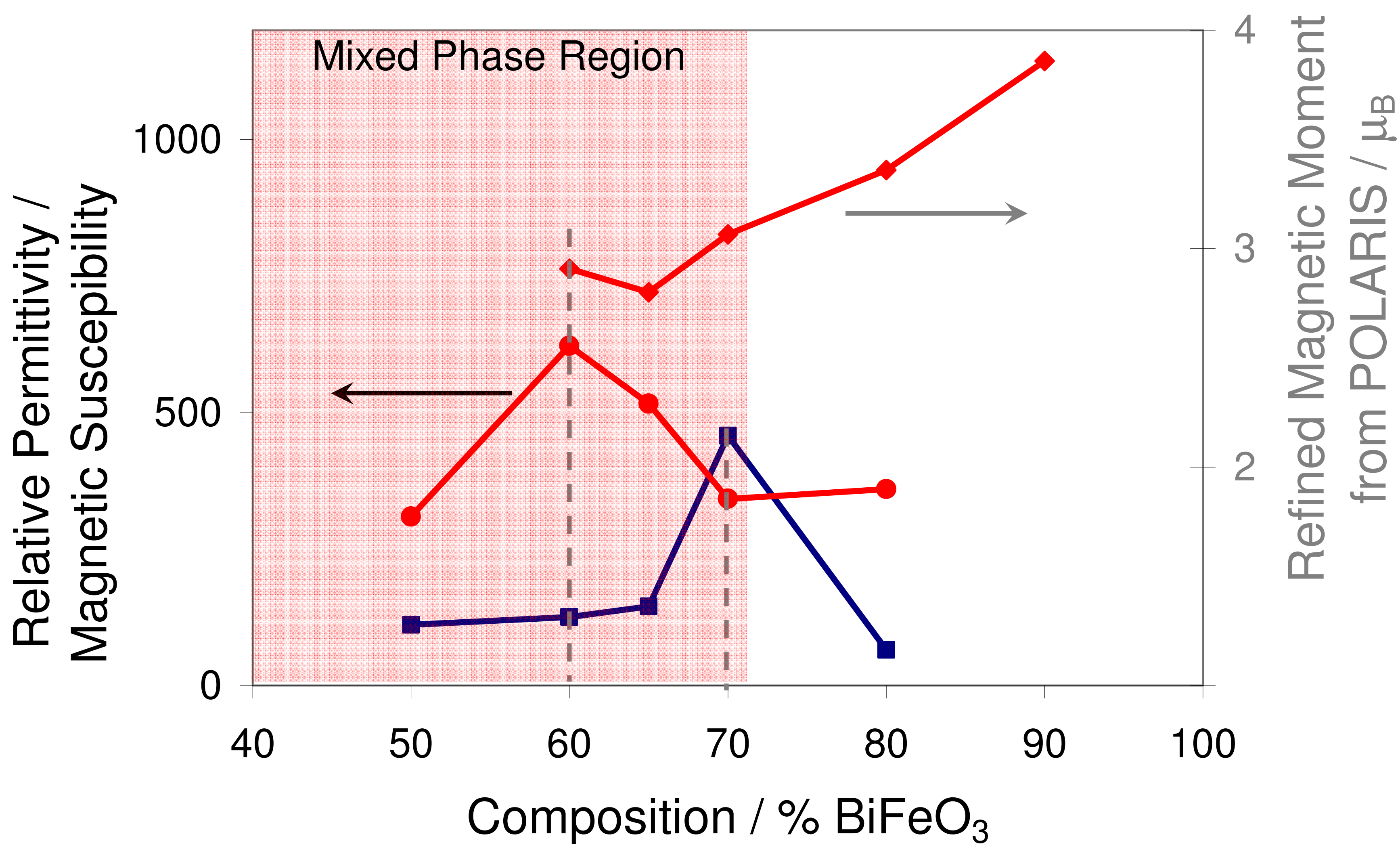

Enormous internal stress

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$BiFeO_3$ – $PbTiO_3$ (BFPT)

- Extremely high microstrain in ceramics

P4mm (Tet) and R3c (Rhom) have significantly different volumes

P4mm 5% > primitive R3c

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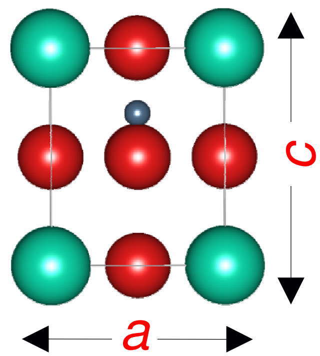
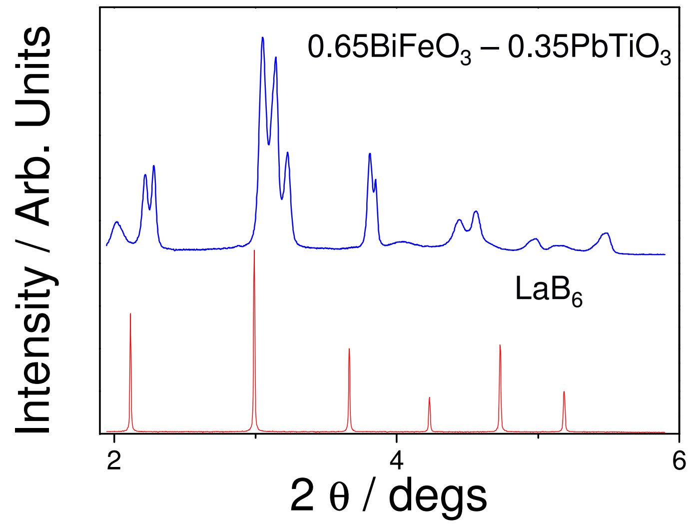
R.T.Smith, J. Appl. Phys. 39(1), 70, 1968



c/a as high as 18.7% reported

Microstrain evident from x-ray broadening



Enormous internal stress

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From FWHM for 001

Av. Strain = 4%

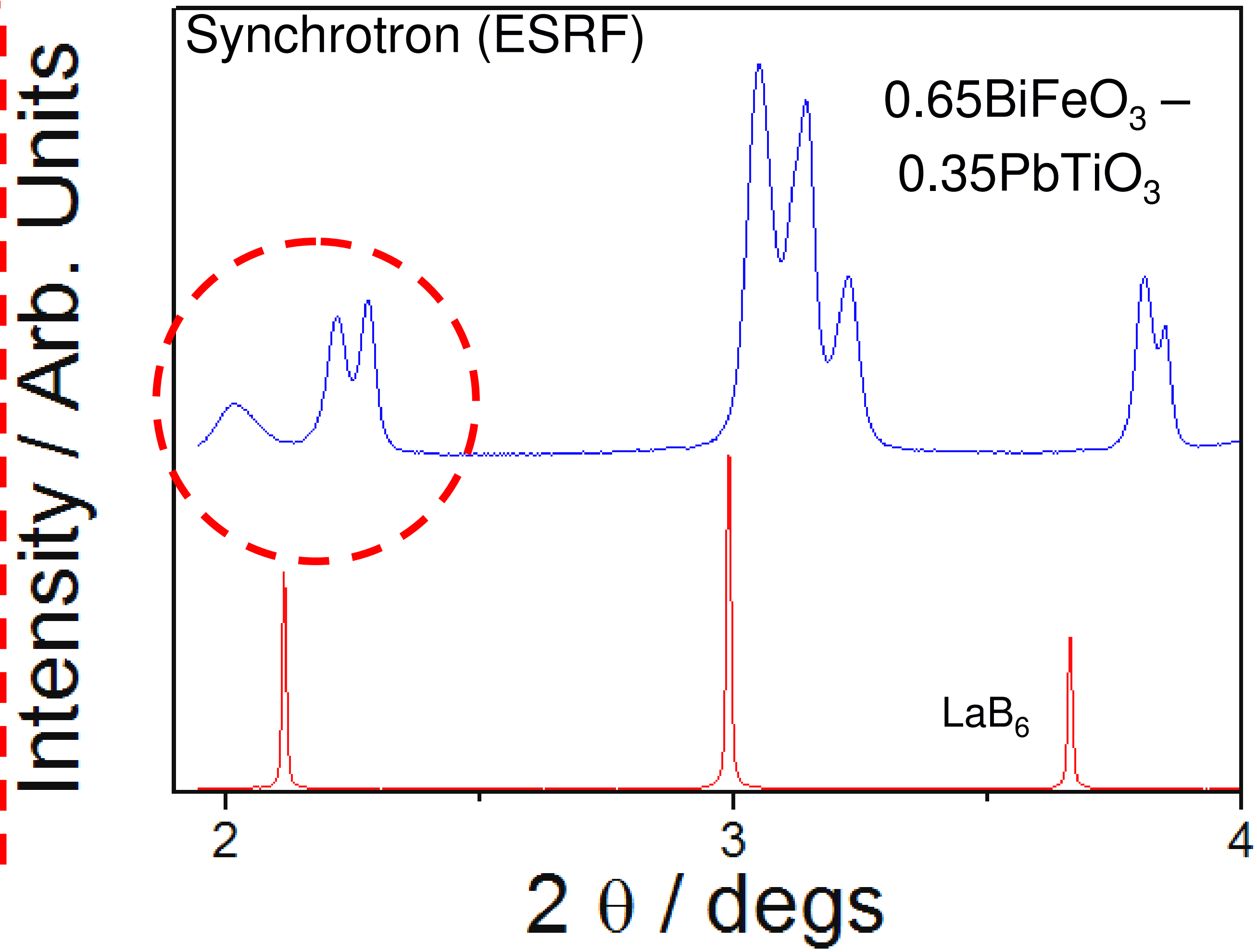
Max. Strain = 8%

Resonance measurements:

YM = 96 GPa

Av. Stress = 3.8 GPa

Max Stress = 7.7 GPa



Effect of internal stress

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Two fabrication methods –0.7-$BiFeO_3$ – 0.3 $PbTiO_3$ *or* BFPT 7030

Sinter 1000℃ 30 mins

↓

300 ℃ / hr. to 700 ℃

↓

20 ℃ / hr. to room temp

↓

SLOW COOL - CERAMIC

Sinter 1000℃ 30 mins

↓

900 ℃ / hr. to room temp

↓

FAST COOL – POWDER