Structure and Phase Transitions in Multiferroics: The Case of $BiFeO_3$

Phil Lightfoot, EastCHEM, University of St Andrews

Structure and Phase Transitions in Multiferroics: The Case of $BiFeO_3$

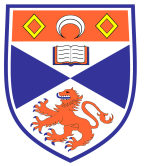
With thanks to:

Dr Donna Arnold

Dr Finlay Morrison
Dr Richard Goff
Ms Alex Gibbs
Dr Kevin Knight (ISIS)

Prof. Jim Scott (Cambridge)
Dr Simon Redfern(Cambridge)
Dr Gustau Catalan(Cambridge)

EPSRC, STFC



$BiFeO_3$

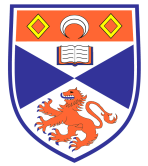
Perhaps the most studied multiferroic?*

Ferroelectric T_C ~ 820 ℃, magnetic T_N ~ 360 ℃

Three suggested (structural) phase transitions above RT:

1. At T_C: α (ferroelectric) to β (paraelectric)
2. Region 925 – 933 °C: β (insulator) to γ (metallic?)
3. Near 185 °C: 'Polomska' transition

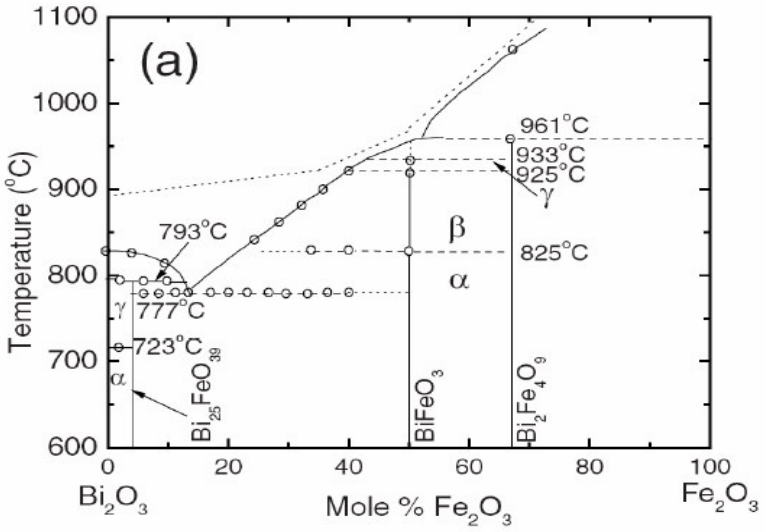
*Catalan and Scott, Adv. Mater. *In press*.



Structural nature of these transitions??

Challenges:

1. $BiFeO_3$ is metastable above 700 °C
2. X-rays can barely 'see' O atoms in the presence of Bi
3. Several previous studies have therefore 'failed'



Solution:

Powder neutron diffraction (HRPD-ISIS)

Palai et al., PRB, 2008, 77,014110

$BiFeO_3$ ferroelectric phase transition

COMMUNICATION

ADVANCED MATERIALS

DOI: 10.1002/adma.200800218

The Ferroic Phase Transitions of $BiFeO_3$**

By *Sverre M. Selbach, Thomas Tybell, Mari-Ann Einarsrud,* and *Tor Grande**

Multiferroics[1] have rapidly gained increasing attention due to a wide range of potential applications[2] in microelectronic and spintronic devices, and the possibility of controlling magnetic order by electric fields,[3] or vice versa,[4] through magnetoelectric coupling.[5] $BiFeO_3$ is termed a multiferroic material due to coexistence of ferroelasticity, antiferromagnetism, and ferroelectricity.[6–8] A large spontaneous polarization[9–11] P_S of 88–100 μC cm^{-2} and a high T_C of 830 °C makes

structure of the high temperature paraelectric phase is centrosymmetric $R\bar{3}c$. The ferroelectric transition is first order and accompanied by discontinuous volume and abrupt changes in atomic positions. A continuous lattice anomaly is associated with the second order magnetic phase transition at T_N. Electrical conductivity anomalies associated with both phase transitions are observed. The present findings provide a basis for fundamental insight to the multiferroic properties.

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Atomic displacements in $BiFeO_3$ as a function of temperature: neutron diffraction study

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Accepted 15 May 2007

The parameters of the crystal structure of $BiFeO_3$, described within the space group $R3c$, have been determined by high-resolution neutron powder diffraction for temperatures from 293 to 923 K. It was found that there is a local minimum for the rhombohedral angle α_{rh}, near the Néel temperature $T_N \simeq 640$ K, a gradual rotation of the FeO_6 octahedra and an increase of the Fe—O—Fe angle. The displacement of the Bi^{3+} ions from the FeO_6 octahedra which influence the electric polarization decreases with temperature. One of the Bi—Fe distances also has a local maximum near T_N. The atomic vibrations of Bi^{3+} and O^{2-} ions show a significant anisotropy.

PRL 99, 227602 (2007) PHYSICAL REVIEW LETTERS week ending 30 NOVEMBER 2007

Finite-Temperature Properties of Multiferroic $BiFeO_3$

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[2]*Mads Clausen Institute for Product Innovation, University of Southern Denmark, Alsion 2, DK-6400 Sønderborg, Denmark*
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(Received 5 July 2007; published 30 November 2007)

An effective Hamiltonian scheme is developed to study finite-temperature properties of multiferroic $BiFeO_3$. This approach reproduces very well (i) the symmetry of the ground state, (ii) the Néel and Curie temperatures, and (iii) the intrinsic magnetoelectric coefficients (that are very weak). This scheme also predicts (a) an overlooked phase above $T_C \simeq 1100$ K that is associated with antiferrodistortive motions, as consistent with our additional x-ray diffractions, (b) improperlike dielectric features above T_C, and (c) that the ferroelectric transition is of first order with no group-subgroup relation between the paraelectric and polar phases.

PHYSICAL REVIEW B 77, 014110 (2008)

β phase and γ-β metal-insulator transition in multiferroic $BiFeO_3$

R. Palai,[1] R. S. Katiyar,[1] H. Schmid,[2] P. Tissot,[2] S. J. Clark,[3] J. Robertson,[4] S. A. T. Redfern,[5] G. Catalan,[5] and J. F. Scott[5]

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We report on extensive experimental studies on thin film, single crystal, and ceramics of multiferroic bismuth ferrite $BiFeO_3$ using differential thermal analysis, high-temperature polarized light microscopy, high-temperature and polarized Raman spectroscopy, high-temperature x-ray diffraction, dc conductivity, optical absorption and reflectivity, and domain imaging, and show that epitaxial (001) thin films of $BiFeO_3$ are clearly monoclinic at room temperature, in agreement with recent synchrotron studies but in disagreement with all other earlier reported results. We report an orthorhombic order-disorder β phase between 820 and 925

PHYSICAL REVIEW B 78, 134108 (2008)

Phase stability and structural temperature dependence in powdered multiferroic $BiFeO_3$

R. Haumont,[1] Igor A. Kornev,[2,*] S. Lisenkov,[2] L. Bellaiche,[2] J. Kreisel,[3] and B. Dkhil[4]

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[2]*Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA*
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We report a temperature-dependent investigation of the multiferroic perovskite bismuth ferrite $BiFeO_3$ (BFO) by using x-ray powder diffraction together with differential scanning calorimetry measurements. Our results provide evidence that the paraelectric phase above T_c=820 °C is not cubic but distorted and can be well refined in a monoclinic $P2_1/m$ space group. An equivalent structure can be reconstructed based on the $C2/m$ monoclinic space group and by assuming two types of bismuth sites. The marked change of the cell volume at T_c provides evidence for the first-order nature of the $R3c$-to-$P2_1/m$ transition. The high-temperature $P2_1/m$ phase is centrosymmetric and characterized by (i) strong oxygen octahedra tilting along the b axis; (ii) the occurrence of antiferroelectric displacements of the Fe cations; and (iii) an interesting lamellar structure characterized by two different types of BiO_{12} cages. The temperature-induced lamellar structure suggests a significant electronic rearrangement in terms of chemical bonding, which in turn might condition anisotropic electronic properties. The occurrence of a lamellar structure provides also an understanding of why BFO decomposes suddenly at higher temperatures. Finally, an anomaly in the evolution of the cell parameters at T_N underlines the spin-lattice coupling in proximity of the magnetic transition.

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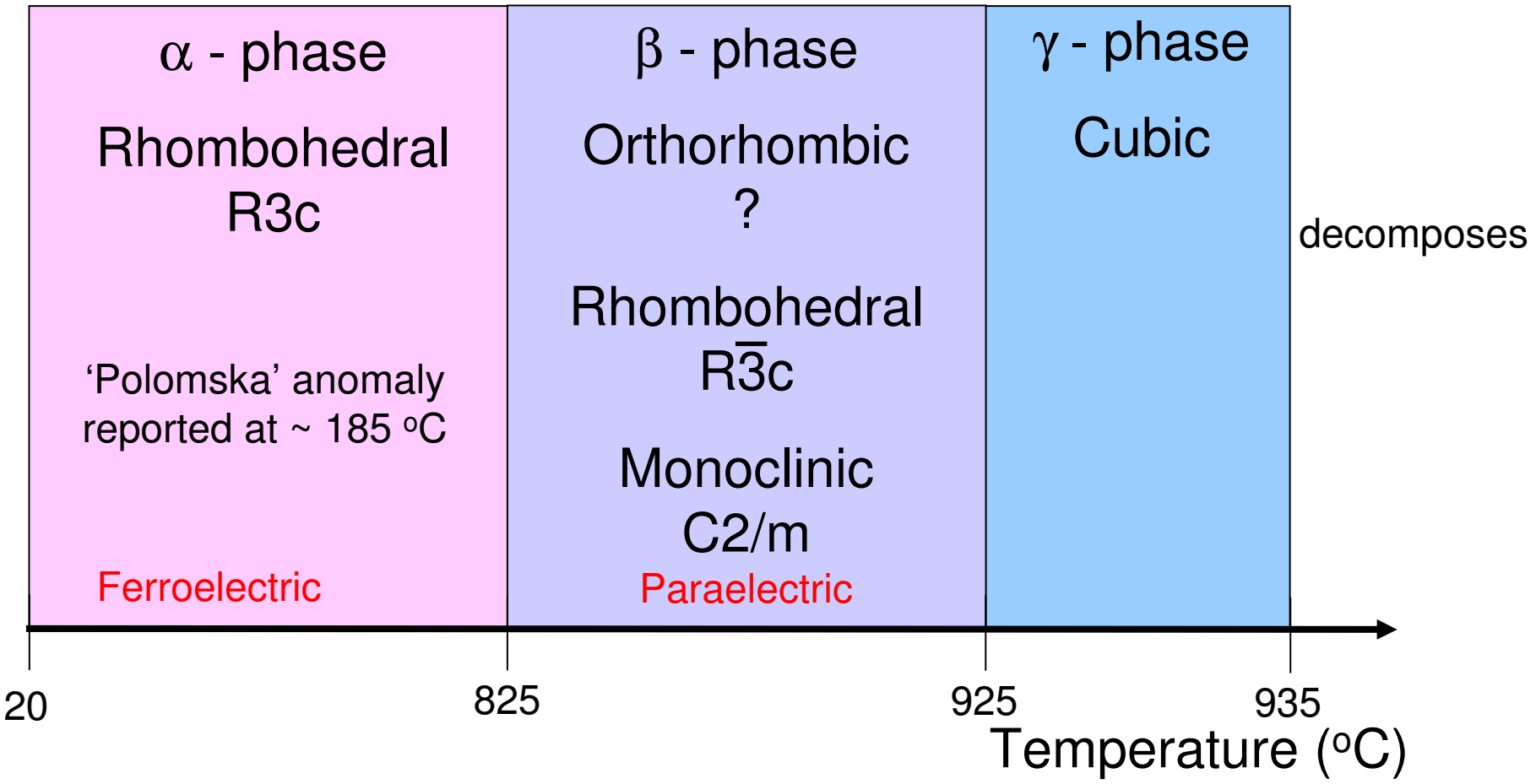
The $\alpha - \beta$ and $\beta - \gamma$ transitions

Recent studies (2007 – 08):

1. PND: RT – 700 °C – retains RT structure (R3c – paraelectric). Sample degrades at high T
2. PXRD: RT - 900 °C – suggests R3c – R-3c transition at T_C
3. Theoretical: suggests R3c – I4/mcm- Pm-3m (PXRD suggests C2/m not I4/mcm!)
4. PXRD – $P2_1/m$ or C2/m above T_C
5. Raman, XRD, conductivity etc: R3c – orth(?) – cubic (M-I transition $\gamma - \beta$)

The $\alpha - \beta$ and $\beta - \gamma$ transitions



Our PND experiments (HRPD at ISIS):

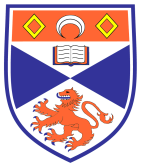
(Sample preparation): elimination of $Bi_2Fe_4O_9$

1. Sept 08 – to study the $\alpha - \beta$ transition (what happens at T_C?)

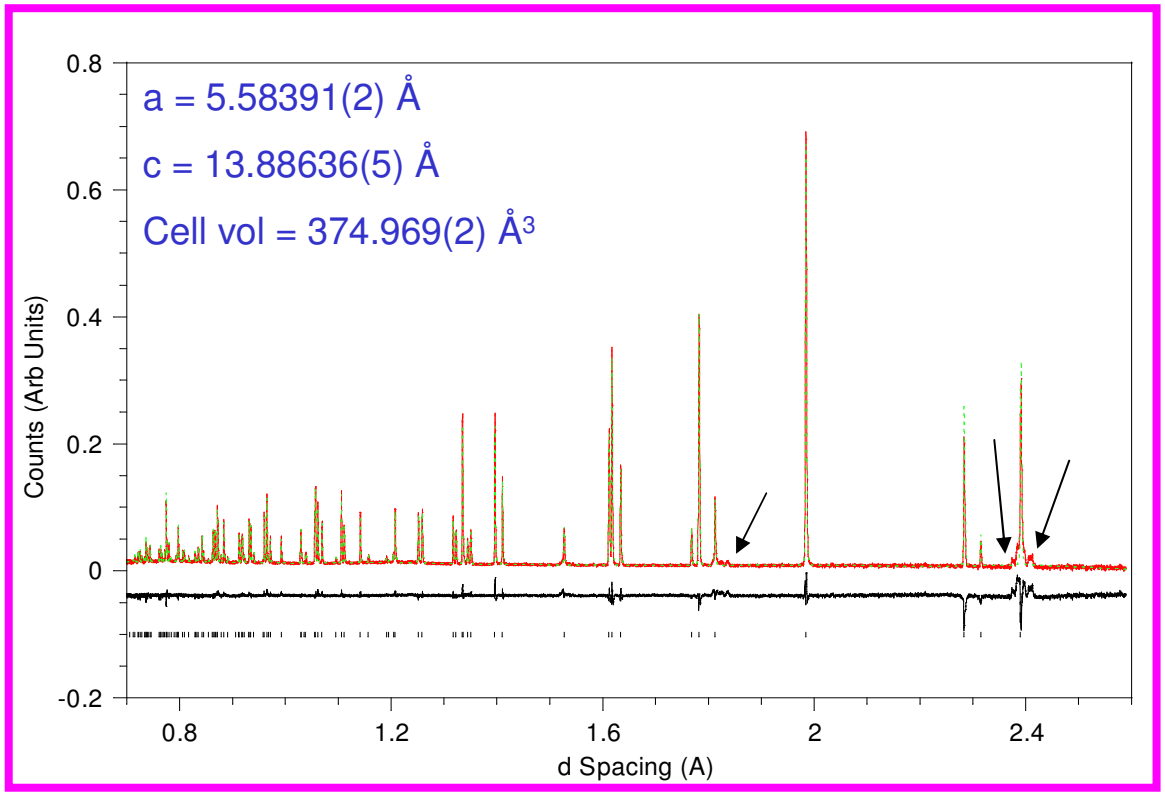
V can / Sealed quartz tube RT – 900 °C; 20 min – 1hr runs

2. March 09 – to revisit the $\beta - \gamma$ and 'Polomska' transitions

Open vessel – flowing N_2; 900 – 960 °C; 5 min runs



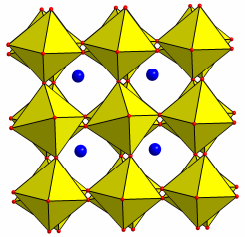
$BiFeO_3$ α – phase



R3c

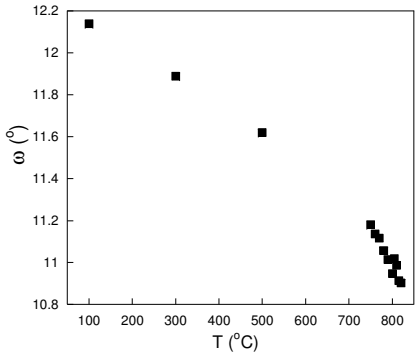
Ferroelectric

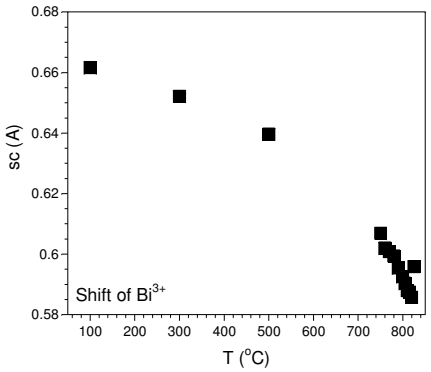
$a^-a^-a^-$ tilt

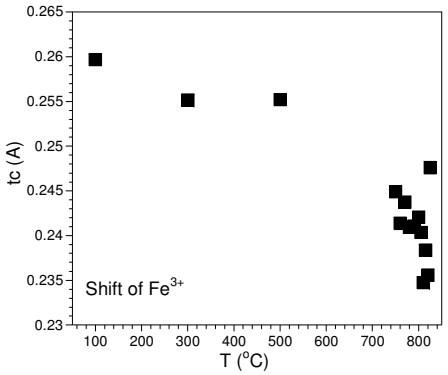


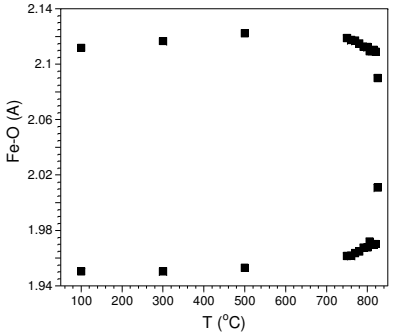
Phys. Rev. Lett., 2009, 102, 027602

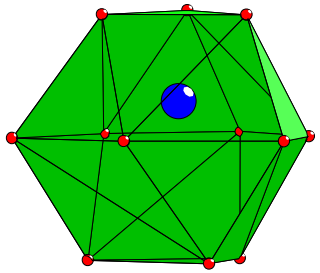
$BiFeO_3$ evolution of the α phase

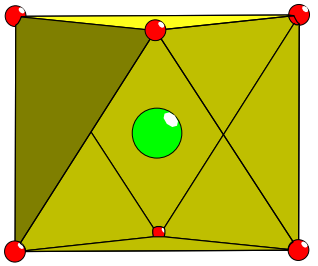












Phys. Rev. Lett., 2009, 102, 027602

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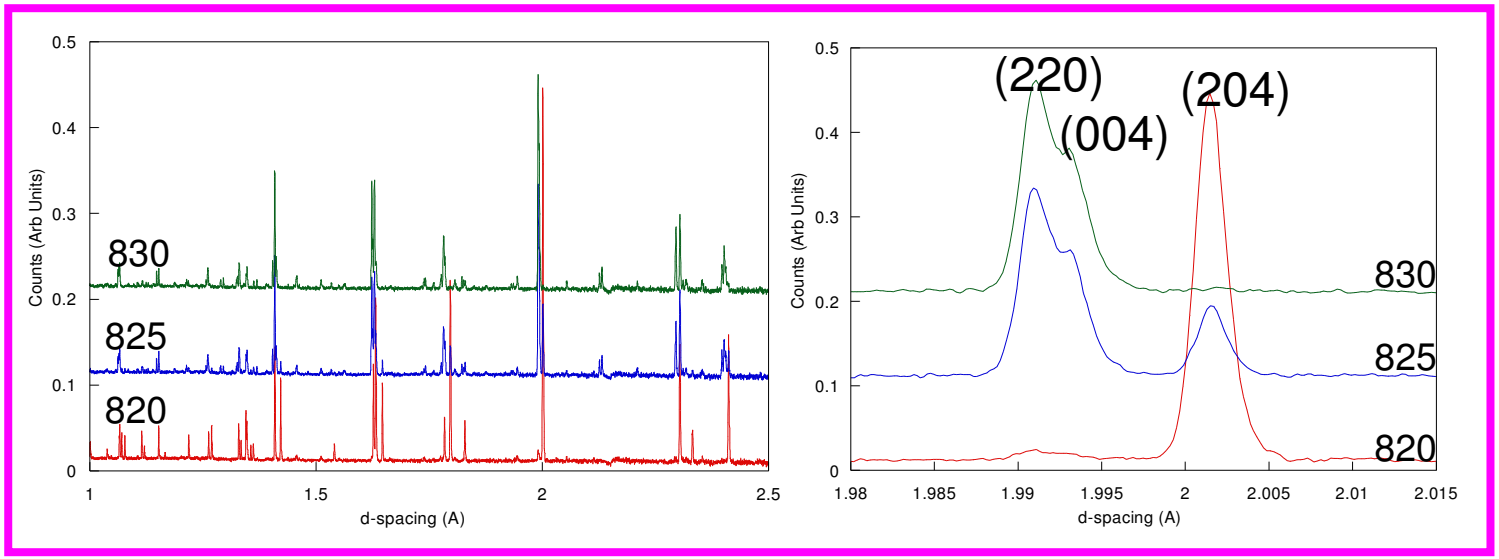
$BiFeO_3$ ferroelectric phase transition ($\alpha - \beta$)



1st order transition: phases co-exist at 825 °C

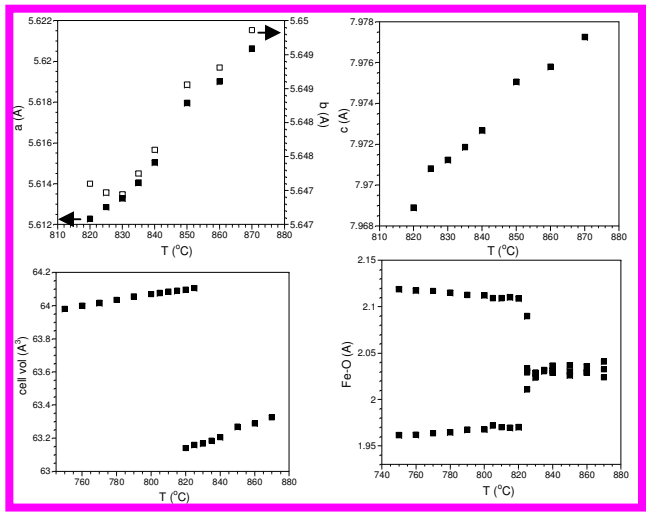
Trigonal R3c, $a^-a^-a^-$
Ferroelectric

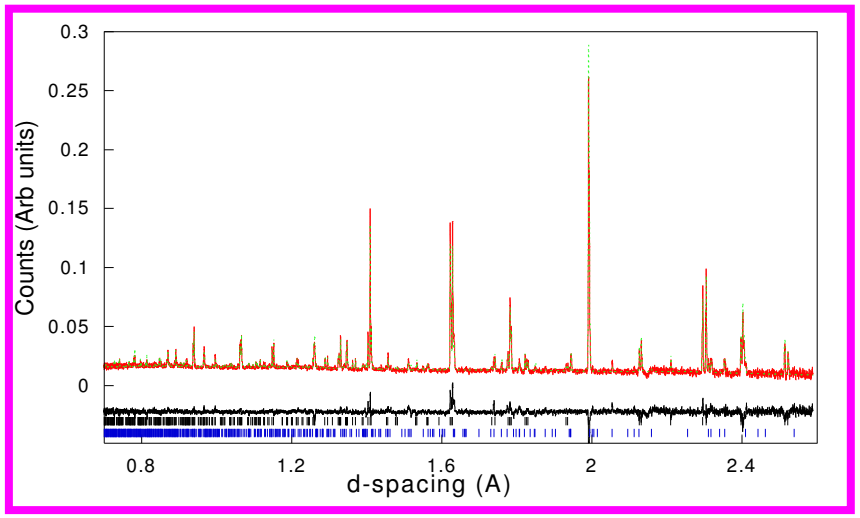
→

Orthorhombic Pbnm, $a^-a^-b^+$
Paraelectric

Phys. Rev. Lett., 2009, 102, 027602

$BiFeO_3$ ferroelectric phase transition (α – β)



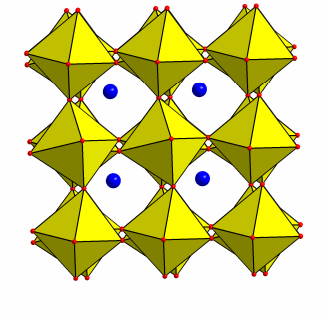


Trigonal R3c, $a^-a^-a^-$
Ferroelectric

→

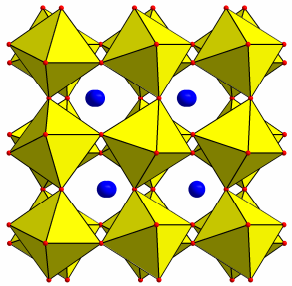
Orthorhombic Pbnm, $a^-a^-b^+$
Paraelectric

$BiFeO_3$ ferroelectric phase transition (α – β)

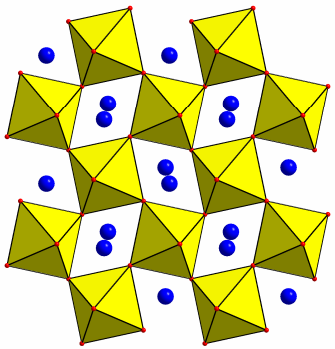


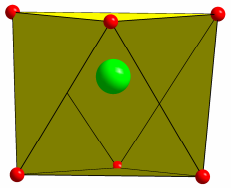
820-830 °C

‘ilmenite’

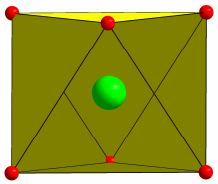


‘$GdFeO_3$’





FeO_6 octahedron



Trigonal R3c, $a^-a^-a^-$
Ferroelectric

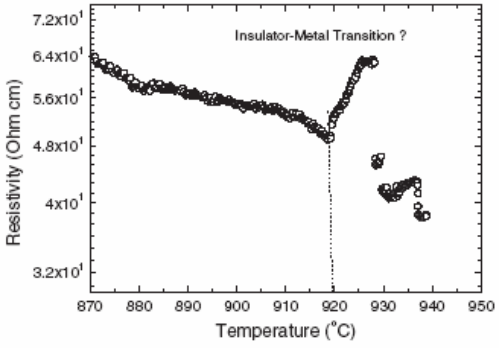
Orthorhombic Pbnm, $a^-a^-b^+$
Paraelectric

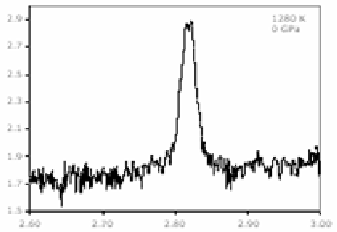
Phys. Rev. Lett., 2009, 102, 027602

$BiFeO_3$ β – γ phase transition

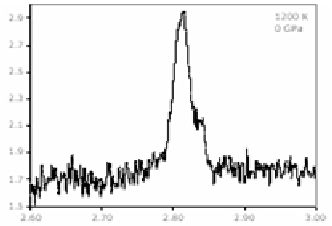
Palai et al. suggest cubic γ-phase:

Appears ‘cubic’ from PXRD

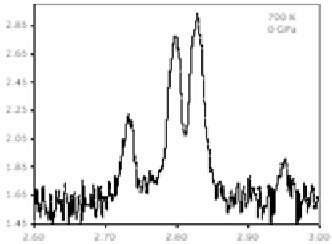




‘Cubic’



Orth



R3c

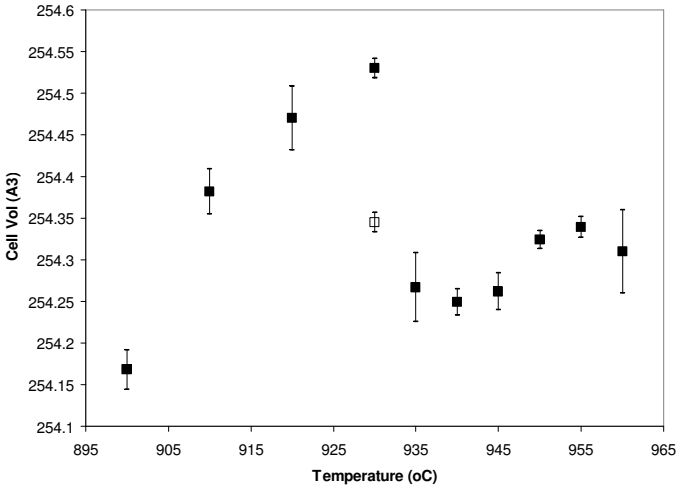
Our sample decomposes ‘quickly’ to $Bi_2Fe_4O_9$ under conditions used in Experiment 1 (7% at 835 C, 64% at 870 C)

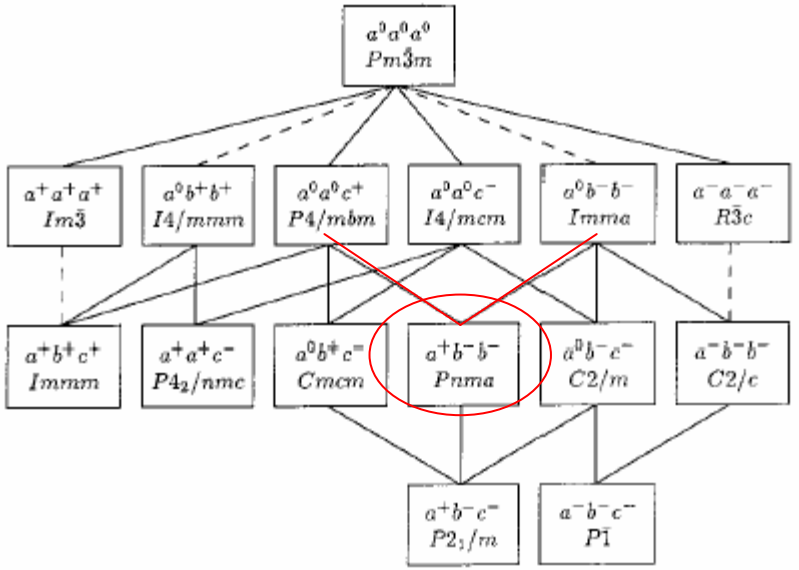
∴ A ‘quicker’ experiment was carried out to isolate the γ phase (metallic, cubic?)

$BiFeO_3$ β – γ phase transition

Unit cell volume suggests abrupt transition.

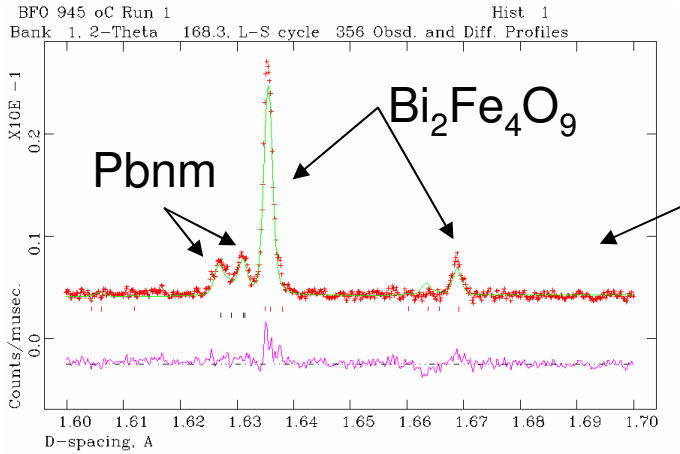
BUT Rietveld still suggests orthorhombic





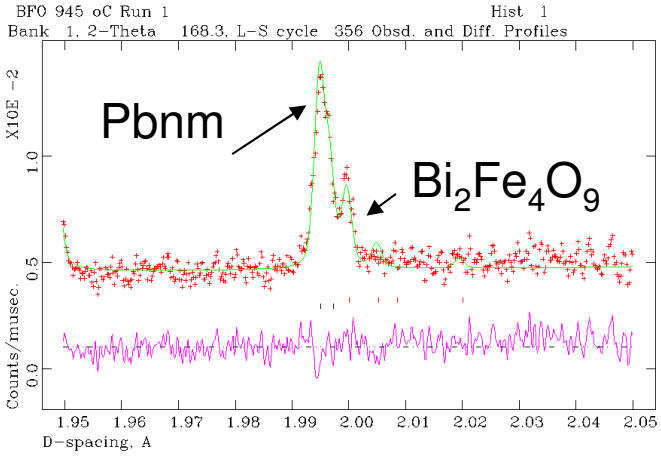
Howard et al., Acta Cryst., 1998, B54, 782

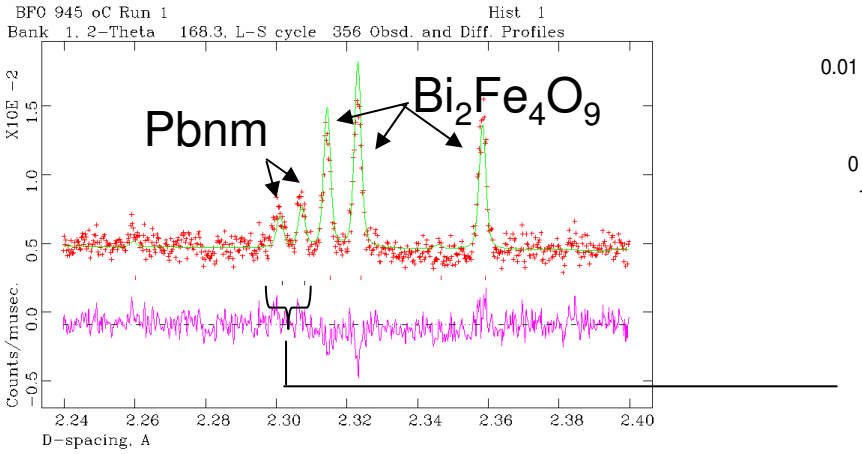
Persistence of ortho phase to HT

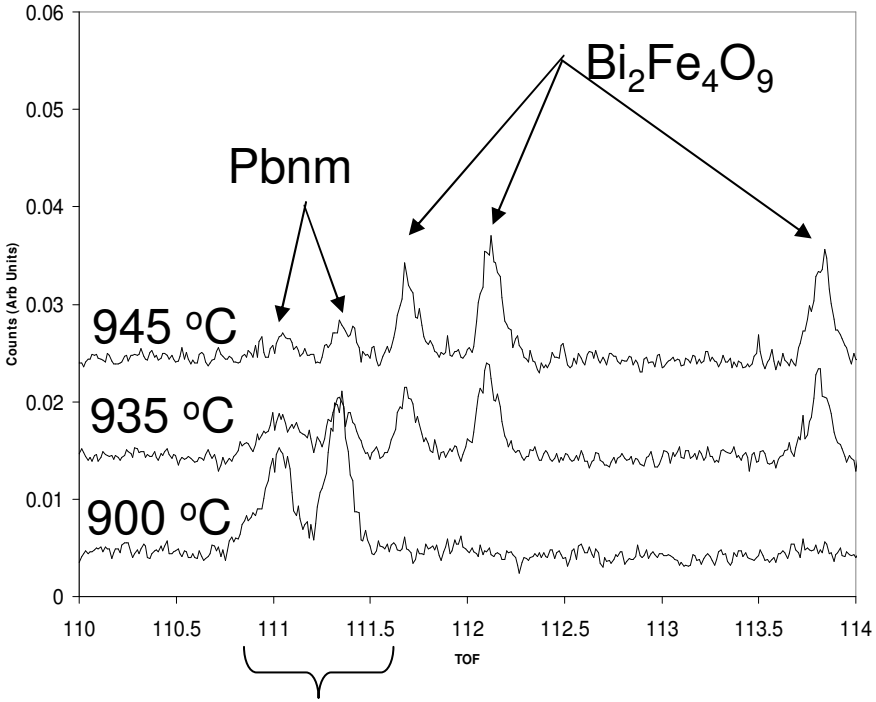


Refinement of 945 ^{o}C data

Close inspection of the PND data shows no evidence of the cubic phase - characteristic orthorhombic peaks persist at 945 ^{o}C

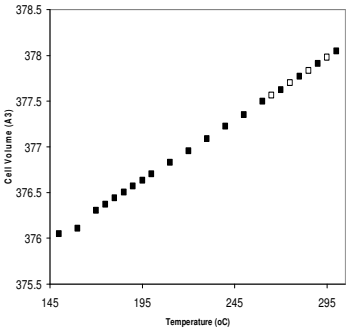




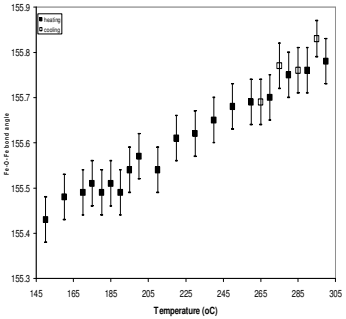


In particular this should be a single peak for cubic or tetragonal symmetry and it clearly remains split

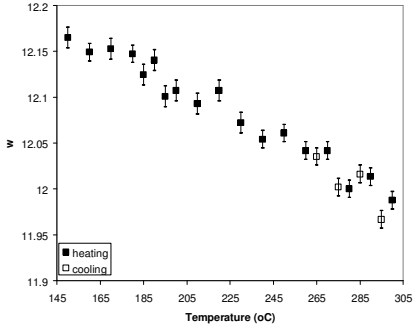
‘Polomska’ transition @ 185 °C



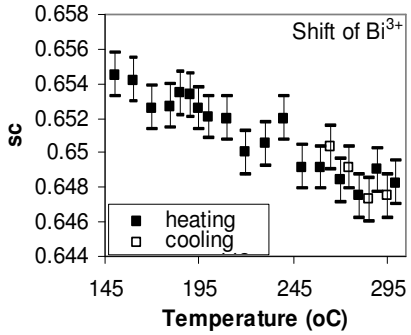
Cell volume



Fe-O-Fe bond angle

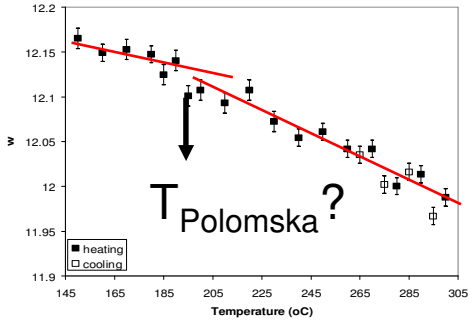


Tilt angle



No obvious anomalies,

BUT….



Summary

1. α – β phase transition : R3c – Pbnm
2. β – γ phase transition: *probably* Pbnm – Pbnm (Imma?)
3. Cubic phase? *might* depend on kinetics, or is actually *orthorhombic*
4. Polomska transition – no observable (?) structural transition (may be magnetic ??)
5. Further phase transitions below RT...
6. WISH diffractometer may clarify (4 and 5).

Thank you for listening!