Structure and Phase Transitions in Multiferroics: The Case of BiFeO$_3$

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Structure and Phase Transitions in Multiferroics: 
The Case of BiFeO$_3$

With thanks to:

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EPSRC, STFC
BiFeO$_3$

Perhaps the most studied multiferroic?*

Ferroelectric $T_C \sim 820$ °C, magnetic $T_N \sim 360$ °C

Three suggested (structural) phase transitions above RT:

1. At $T_C$: $\alpha$ (ferroelectric) to $\beta$ (paraelectric)
2. Region 925 – 933 °C: $\beta$ (insulator) to $\gamma$ (metallic?)
3. Near 185 °C: ‘Polomska’ transition

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

**The Ferroic Phase Transitions of BiFeO$_3$**

By Severe M. Semyanich, Thomas Teyssell, Mari-Anti Hinsen, and Tor Grande

Ferroic materials have rapidly gained increasing attention due to a wide range of potential applications in non-volatile memories, optical devices, and for the possibility of controlling magnetic order by electric fields, or vice versa, through magnetostrictive coupling. BiFeO$_3$ is a ferroic material due to the combined effect of ferroelectricity, antiferromagnetism, and ferromagnetism. A large spontaneous polarization and a high Curie temperature make BiFeO$_3$ a material of interest for fundamental and applied research.

The structure of the high temperature paraelectric phase is tetragonal I4$_1$/amd. The ferroelectric transition is first order and accompanied by discontinuous volume and abrupt changes in atomic positions. A concomitant lattice anomaly is associated with the second order magnetic phase transition at Tc. Electrical conductivity anomalies associated with both phase transitions are observed. The present findings provide a basis for fundamental insight into the ferroic properties.

**Finite-Temperature Properties of Multiferroic BiFeO$_3$**


The parameters of the crystal structure of BiFeO$_3$ described within the space group P4$_2$mm have been determined by high-resolution powder diffraction for temperatures from 293 to 923 K. It was found that there is a first-order transition for the Fe-O-Fe angle near the Neel temperature $T_N$ = 440 K, a gradual rotation of the Fe-O-Fe octahedron angle, and an increase of the Fe-Fe-Fe angle. The displacement of the Bi$_2$O$_2$ octahedron, which influences 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.

**Phase Stability and Structural Temperature Dependence in Powdered Multiferroic BiFeO$_3$**


We report a temperature dependence measurement of the ferroic properties of powdered BiFeO$_3$ by using powder diffraction together with differential scanning calorimetry. Our results provide evidence that the paraelectric phase above $T_N$ = 440 K is the tetragonal I4$_1$/amd space group. This phase is not an order-disorder transition, but is rather a novel structural transition. The Curie-Weiss law provides evidence for the first-order nature of the P4$_2$mm to P4$_2$mm transition. The high-temperature phase is characterized by a tetragonal unit cell with a unit cell parameter of $a = 4.278(2)$ Å and $c = 2.386(2)$ Å, and the unit cell volume is $V = 39.2(3) Å^3$. The experimental results are compared with the calculated results. The optimized cubic lattice constant suggests a significant structural misalignment between the ferroelectric and magnetic phases.
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

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$\alpha$ - phase</th>
<th>$\beta$ - phase</th>
<th>$\gamma$ - phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Rhombohedral R3c</td>
<td>Orthorhombic</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>‘Polomska’ anomaly reported at ~ 185 $^\circ$C</td>
<td>$\text{R3c}$</td>
<td>Decomposes</td>
</tr>
<tr>
<td>825</td>
<td>Ferroelectric</td>
<td>Monoclinic C2/m</td>
<td></td>
</tr>
<tr>
<td>925</td>
<td></td>
<td>Paraelectric</td>
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<tr>
<td>935</td>
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</tbody>
</table>
Our PND experiments (HRPD at ISIS):

(Sample preparation): elimination of $\text{Bi}_2\text{Fe}_4\text{O}_9$

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 $\text{N}_2$; 900 – 960 °C; 5 min runs
BiFeO$_3$ $\alpha$ – phase

$$a = 5.58391(2) \text{ Å}$$
$$c = 13.88636(5) \text{ Å}$$
$$\text{Cell vol} = 374.969(2) \text{ Å}^3$$

R3c
Ferroelectric
$\pm\pm\pm\pm$ tilt

BiFeO$_3$ evolution of the $\alpha$ phase

BiFeO$_3$ ferroelectric phase transition ($\alpha - \beta$)

1$^{\text{st}}$ order transition: phases co-exist at 825 ºC

Trigonal R3c, a\textsuperscript{-}a\textsuperscript{-}a\textsuperscript{-}  
Ferroelectric

Orthorhombic Pbnm, a\textsuperscript{-}a\textsuperscript{-}b\textsuperscript{+}  
Paraelectric

BiFeO$_3$ ferroelectric phase transition ($\alpha - \beta$)

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

Orthorhombic $Pbnm$, $a^-a^-b^+$
Paraelectric
BiFeO$_3$ ferroelectric phase transition ($\alpha - \beta$)

820-830 °C

Trigonal R3c, $a\cdot a\cdot a$  
Ferroelectric

FeO$_6$ octahedron

Orthorhombic Pbnm, $a\cdot a\cdot b^+$  
Paraelectric

‘ilmenite’

‘GdFeO$_3$’


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BiFeO$_3$ $\beta$ – $\gamma$ phase transition

Palai et al. suggest cubic $\gamma$-phase:

Appears ‘cubic’ from PXRD

Our sample decomposes ‘quickly’ to Bi$_2$Fe$_4$O$_9$ under conditions used in Experiment 1 (7% at 835 C, 64% at 870 C)

∴ A ‘quicker’ experiment was carried out to isolate the $\gamma$ phase (metallic, cubic?)
BiFeO$_3$ $\beta - \gamma$ phase transition

Unit cell volume suggests abrupt transition.
BUT Rietveld still suggests orthorhombic

Howard et al., Acta Cryst., 1998, B54, 782
Close inspection of the PND data shows no evidence of the cubic phase - characteristic orthorhombic peaks persist at 945 °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....

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Summary

1. $\alpha - \beta$ phase transition: R3c – Pbnm

2. $\beta - \gamma$ 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!