Unexpected Phase Transition Sequence in the Ferroelectric Bi4Ti3O12

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**Table S1** Crystallographic models derived from the I4/mmm parent structure by action of each significant tilt mode or selected combinations.

**Table S2** Constraints applied to the ‘simplified’ B1a1 model discussed in the text, such that all atoms except O1/O1’ confirm to the ideal B2eb model.

**Figure S1:** Temperature dependence of β angle for the monoclinic phase below Tc.

**Figure S2.** Crystal structures of the P4/mbm and Cmce models for the intermediate phase at 685 °C, with atomic numbering for the P4/mbm phase, and highlighting the differing X2+ modes and the M1+ modes for the P4/mbm model.

**Figure S3.** Rietveld plots, B1a1 ‘constrained’ model at 20 °C

**Figure S4.** Rietveld plots, B1a1 ‘constrained’ model at 655 °C

**Figure S5.** Rietveld plots, P4/mbm model at 685 °C

**Figure S6.** Rietveld plots, I4/mmm model (+ Bi2Ti2O7 impurity) at 1000 °C

**Separate Files:**

1. ISODISTORT output for refined B1a1 models (‘constrained’ and ‘independent’) at 20 °C (Isodistort_B1a1_RT_78v; Isodistort_B1a1_RT_101v) and refined P4/mbm model (68 variables) at 685 °C (Isodistort_P4mbm_685C_68v).

2. CIF files for B1a1 (constrained) model at 20 °C (B1a1_RT_78v) and 655 °C (B1a1_655C_78v).

3. CIF files for comparative refined models at 685 °C (Table 1): P4/mbm, 68 variables (P4mbm_685C), Cmce (Cmce_685C) P42/ncm (P42ncm_685C) and P4/nbm, (P4nbm_685C).

4. CIF files for idealized models described in Table 4 (Cmce_X2+, P4mbm_X2+, P4mbm_X2+_M1+).

5. CIF file for I4/mmm model at 1000 °C, with impurity phase included (I4mmm_1000C).
Table S1 Crystallographic models derived from the I4/mmm parent structure by action of each significant tilt mode or selected combinations.

| Mode   | OPD   | Space group | basis       | origin | s,i | k-active       |
|--------|-------|-------------|-------------|--------|-----|----------------|
| X₃⁺    | (a,a) | P4₂/ncm     | (1,1,0)     | (0,0,0)| 4.4 | (1/2,1/2,0), (1/2,1/2,1) |
| X₃⁺    | (o,a) | Cmce        | (1,1,0)     | (0,0,0)| 2.4 | (1/2,1/2,1)    |
| ⁵X₃⁺   | (a,b) | Pccn        | (1,1,0)     | (0,0,0)| 4.8 | (1/2,1/2,0), (1/2,1/2,1) |
| X¹⁻    | (a,a) | P4/nbm      | (1,1,0)     | (0,1/2,0)| 4.4 | (1/2,1/2,0), (1/2,1/2,1) |
| X¹⁻    | (0,a) | Ccce        | (0,0,1)     | (0,1/2,0)| 2.4 | (1/2,1/2,1)    |
| ⁵X¹⁻   | (a,b) | Pbnn        | (1,1,0)     | (0,1/2,0)| 4.8 | (1/2,1/2,0), (1/2,1/2,1) |
| X₂⁺    | (a,a) | P4/nbm      | (1,1,0)     | (1/2,1/2,0)| 4.4 | (1/2,1/2,0), (1/2,1/2,1) |
| X₂⁺    | (0,a) | Cmce        | (0,0,1)     | (0,0,0)| 2.4 | (1/2,1/2,1)    |
| ⁵X₂⁺   | (a,b) | Pbnn        | (1,1,0)     | (0,0,0)| 4.8 | (1/2,1/2,0), (1/2,1/2,1) |
| ⁵⁵X₂⁺/X¹⁻ | (0;a|b;0) | Pcca | (-1,1,0)   | (1/4,1/4,1/4)| 4.8 | (1/2,1/2,0), (1/2,1/2,1) |
| ⁵⁵X₂⁺/X₃⁺ | (0;a|b;0) | Pbca | (-1,1,0) | (0,0,0)| 4.8 | (1/2,1/2,0), (1/2,1/2,1) |
These lower symmetry models were not considered.

These models were used as a confirmatory check on the presence of only the $X_2^+$ mode at 685 °C (above $T_C$). For comparison these models produced $\chi^2$ values of 6.17 and 6.30 (unstable); 76 and 75 variables, for $Pcca$ and $Pbca$ respectively. The best $P4/mnbm$ model gave $\chi^2 = 6.30$ for 72 variables.

Space groups are given in the standard setting, which may result in switching of the axes compared to the $B1a1$ model.

OPD is the Order parameter direction. The parameters $(s,i)$ represent, respectively, the size of the primitive unit cell of the subgroup relative to the parent space group and the index of the subgroup relative to the parent space group. For further details of these and other notations see the ISOTROPY website: stokes.byu.edu/iso/isodistorthelp.php

**Table S2** Constraints applied to the ‘simplified’ $B1a1$ model discussed in the text, such that all atoms except O1/O1’ confirm to the ideal $B2eb$ model.

| Atom 1 | Parameter | Atom 2 | Parameter |
|-------|-----------|-------|-----------|
| Bi1   | x         | Bi1a  | x         |
| Bi1   | y         | Bi1a  | -y        |
| Bi1   | z         | Bi1a  | -z        |
| Bi2   | x         | Bi2a  | x         |
| Bi2   | y         | Bi2a  | -y        |
| Bi2   | z         | Bi2a  | -z        |
| Ti2   | x         | Ti2a  | x         |
| Ti2   | y         | Ti2a  | -y        |
| Ti2   | z         | Ti2a  | -z        |
| O1    | z         | O1a   | -z        |
| O2    | x         | O2a   | x         |
| O2    | y         | O2a   | -y        |
| O2    | z         | O2a   | -z        |
| O3    | x         | O3a   | x         |
| O3    | y         | O3a   | -y        |
Note that the Ti2 y and z coordinates were also constrained to lie on the pseudo 2-fold axis.

\[ \begin{array}{|c|c|c|c|} 
\hline 
O3 & z & O3a & -z \\
\hline 
O4 & x & O4a & x \\
\hline 
O4 & y & O4a & -y \\
\hline 
O4 & z & O4a & -z \\
\hline 
O5 & x & O5a & x \\
\hline 
O5 & y & O5a & -y \\
\hline 
O5 & z & O5a & -z \\
\hline 
O6 & x & O6a & x \\
\hline 
O6 & y & O6a & -y \\
\hline 
O6 & z & O6a & -z \\
\hline 
\end{array} \]

**Figure S1:** Temperature dependence of β angle for the monoclinic phase below Tc.
Figure S2: Crystal structures of the $P4/mbm$ (left) and $Cmce$ (right) models for the intermediate phase at 685 °C, with atomic numbering for the $P4/mbm$ phase, and highlighting the differing $X_2^+$ modes and the $M_1^+$ modes for the $P4/mbm$ model.
Figure S3. Full-range (top left) and expanded Rietveld plots (Bank 1), $B1\alpha1$ ‘constrained’ model at 20 °C.
**Figure S4.** Full-range (top left) and expanded Rietveld plots (Bank 1), $B1\alpha1$ ‘constrained’ model at 655 °C.
Figure S5. Full-range (top left) and expanded Rietveld plots (Bank 1), $P4/mbm$ model at 685 °C.
Figure S6. Full-range (top left) and expanded Rietveld plots (Bank 1), $I4/mmm$ model (+ Bi$_2$Ti$_2$O$_7$ impurity) at 1000 °C.