Supplementary Publication

Atomic displacements at and order of all phase transitions in multiferroic $YMnO_3$ and $BaTiO_3$

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Abstract

Coordinate analysis of the multiple phase transitions in hexagonal $YMnO_3$ leads to the prediction of a previously unknown aristotype phase, with resulting phase-transition sequence: $P6_3'cm'$(*e.g.*) ↔ $P6_3cm$ ↔ $P6_3/mcm$ ↔ $P6_3/mmc$ ↔ $P6/mmm$. Below the Néel temperature $T_N \approx 75$ K, the structure is antiferromagnetic with magnetic symmetry not yet determined. Above T_N, the $P6_3cm$ phase is ferroelectric with Curie temperature $T_C \approx 1105$ K. The nonpolar paramagnetic phase stable between T_C and ~1360 K transforms to a second nonpolar paramagnetic phase stable to ~1600 K, with unit cell volume one-third that below 1360 K. The predicted aristotype phase at the highest-temperature is nonpolar and paramagnetic, with unit cell volume reduced by a further factor of 2. Coordinate analysis of the three well known phase transitions undergone by tetragonal $BaTiO_3$, with space group sequence $R3m$ ↔ $Amm2$ ↔ $P4mm$ ↔ $Pm\bar{3}m$, provides a basis for deriving the aristotype phase in $YMnO_3$. Landau theory allows the I ↔ II, III ↔ IV and IV ↔ V phase transitions in $YMnO_3$, as also the I ↔ II phase transition in $BaTiO_3$, to be continuous; all four, however, unambiguously exhibit first-order characteristics. The origin of phase transitions, permitted by theory to be second order, that are first order instead have not yet been thoroughly investigated; several are briefly considered.

Contents

$BaTiO_3$ atomic coordinate thermal dependence based on: Kwei *et al.* (1993)

Kim *et al.* (2004)

Aoyagi *et al.* (2002)

Buttner & Maslen (1992)

Jiang *et al.* (1988)

Harada *et al.* (1988)

Shirane *et al.* (1957)

Hewat. (1957)

Schildkamp *et al.* (1981)

Hayward *et al.* (1981)

Atomic coordinate thermal dependence of $BaTiO_3$ over the thermal range 350 to 15 K through space groups *P*4*mm* (phase II),[1] *Amm*2 (phase III) and *R*3*m* (phase IV) (Kwei *et al*., 1993).

$Pm\bar{3}m$ to *P*4*mm*, 350 – 280 K

Table S1. Atomic coordinates of $BaTiO_3$ in phase II at 350 K (Kwei *et al*., 1993) and those of phase I in supergroup $Pm\bar{3}m$ together with their corresponding Δx, Δy, Δz differences, also the thermal/static u_{33} displacements of phase II in Å. Lattice constants for a_{III} transformed as below.

a = 3.9956(5), c = 4.0354(5) Å. $z^* = z + 0.0042$.

	Wyckoff position *P*4*mm*	$Pm\bar{3}m$	x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\zeta_{II-I}$	$u_{Eq.}$†
Ba	1(*a*)	1(*a*)	0	0	0.	0.0042	0	0	0	0	0	0.017	0.02	0.06
Ti	1(*b*)	1(*b*)	½	½	0.5195(11)	0.5237	½	½	½	0	0	0.096	0.10	0.08
O1	1(*b*)	3(*c*)‡	½	½	-0.0251(7)	-0.0209	½	½	0	0	0	-0.084	0.08	-0.04
O2	2(*c*)		½	0	0.4890(10)	0.4932	½	0	½	0	0	-0.027	0.03	0.09

‡ ½,½,0 and ½,0, ½ are equivalent in $Pm\bar{3}m$

† With $U_{eq} = \frac{1}{3}(u^2)$ and $u_{eq} = (3\ U_{eq})^{½}$ throughout.

Table S2. Atomic coordinates of $BaTiO_3$ in phase II at 320 K (Kwei *et al*., 1993), see also Table S1.

a = 3.9938(3), c = 4.0361(3) Å. $z^* = z + 0.0028$.

	Wyckoff position *P*4*mm*	$Pm\bar{3}m$	x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\zeta_{II-I}$	$u_{Eq.}$
Ba	1(*a*)	1(*a*)	0	0	0.	0.0028	0	0	0	0	0	0.011	0.01	0.06
Ti	1(*b*)	1(*b*)	½	½	0.5215(7)	0.5243	½	½	½	0	0	0.098	0.10	0.06
O1	1(*b*)	3(*c*)	½	½	-0.0233(5)	-0.0205	½	½	0	0	0	-0.083	0.08	-0.04
O2	2(*c*)		½	0	0.4905(5)	0.4933	½	0	½	0	0	-0.027	0.03	0.09

[1] Kwei *et al.* (1993) consistently refer to the space group of ferroelectric tetragonal $BaTiO_3$ as (nonpolar) *P*4/*mmm* but present their results in a form consistent with atoms Ti, O1 and O2 occupying locations corresponding to 1(*b*) or 2(*c*) in polar *P*4*mm*, the well-substantiated phase II polar space group.

Table S3. Atomic coordinates of $BaTiO_3$ in phase II at 300 K (Kwei *et al*., 1993), see also Table S1.

$a = 3.9910(3)$, $c = 4.0352(3)$ Å. $z^* = z + 0.0031$.

	Wyckoff *P*4*mm*	position $Pm\bar{3}m$	x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\xi_{II-I}$	$u_{Eq.}$
Ba	1(*a*)	1(*a*)	0	0	0.	0.0031	0	0	0	0	0	0.013	0.01	0.06
Ti	1(*b*)	1(*b*)	½	½	0.5224(6)	0.5255	½	½	½	0	0	0.103	0.10	0.07
O1	1(*b*)		½	½	-0.0244(4)	-0.0213	½	½	0	0	0	-0.086	0.09	-0.07
		3(*c*)												
O2	2(*c*)		½	0	0.4895(5)	0.4926	½	0	½	0	0	-0.030	0.03	0.09

Table S4. Atomic coordinates of $BaTiO_3$ in phase II at 290 K (Kwei *et al*., 1993), see also Table S1.

$a = 3.9925(5)$, $c = 4.0365(5)$ Å. $z^* = z + 0.0036$.

	Wyckoff *P*4*mm*	position $Pm\bar{3}m$	x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\xi_{II-I}$	$u_{Eq.}$
Ba	1(*a*)	1(*a*)	0	0	0.	0.0036	0	0	0	0	0	0.015	0.02	0.06
Ti	1(*b*)	1(*b*)	½	½	0.5215(10)	0.5251	½	½	½	0	0	0.101	0.10	0.06
O1	1(*b*)		½	½	-0.0253(6)	-0.0217	½	½	0	0	0	-0.087	0.09	-0.05
		3(*c*)												
O2	2(*c*)		½	0	0.4895(9)	0.4931	½	0	½	0	0	-0.028	0.03	0.09

Table S5. Atomic coordinates of $BaTiO_3$ in phase II at 280 K (Kwei *et al*., 1993), see also Table S1.

$a = 3.9970(5)$, $c = 4.0314(6)$ Å $z^* = z + 0.0045$.

	Wyckoff *P*4*mm*	position $Pm\bar{3}m$	x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\xi_{II-I}$	$u_{Eq.}$
Ba	1(*a*)	1(*a*)	0	0	0	0.0045	0	0	0	0	0	0.018	0.02	0.05
Ti	1(*b*)	1(*b*)	½	½	0.5203(10)	0.5248	½	½	½	0	0	0.100	0.10	0.08
O1	1(*b*)		½	½	-0.0258(6)	-0.0214	½	½	0	0	0	-0.086	0.09	-0.04
		3(*c*)												
O2	2(*c*)		½	0	0.4877(10)	0.4922	½	0	½	0	0	-0.031	0.03	0.09

Space group *P*4*mm* to *Amm*2, 270 – 190 K

Table S6. Atomic coordinates of $BaTiO_3$ in phase III at 270 K (Kwei *et al*., 1993) transformed to match the orientation of phase II with hypothetical coordinates for phase II in space group *P*4*mm* averaged over *y*- and *z*′-values. Differences in supergroup *y* and/or *z* coordinates from ½ or ¼, as averaged from Tables S1-5 with respect to ~4.03 Å length axes, are increased by the factor √2 in evaluating $\Delta x_{III\text{-}II}$, $\Delta y_{III\text{-}II}$ and $\Delta z_{III\text{-}II}$. Kwei *et al*.s' (1993) thermal/static u_{Eq} displacements in Å are also given. Lattice constants for a_{III} transformed as below.

a = 3.9874(3), b = 5.6751(5), c = 5.6901(5) Å. $z^* = z$ - 0.0037.

	Wyckoff position *Amm*2†	*P*4*mm*	x_{III}	y_{III}	z_{III}	z'_{III}	x_{II}	y_{II}	z_{II}	$\Delta x_{III\text{-}II}$	$\Delta y_{III\text{-}II}$	$\Delta z_{III\text{-}II}$	$\Delta\xi_{III\text{-}II}$	$u_{Eq.}$
Ba	2(*a*)	1(*a*),1(*b*)	0	0	0.	-0.0037	0	0	0	0	0	-0.021	0.02	0.04
Ti	2(*b*)	2(*c*)	½	0	0.5169(6)	0.5133	½	0	0.5297	0	0	-0.093	0.09	0.06
O1	2(*a*)	2(*c*)	0	0	0.4910(8)	0.4874	0	0	0.4649	0	0	0.128	0.13	0.07
O2	4(*e*)	4(*f*)	½	0.2560(4)	0.2360(5)	0.2324	½	0.2583	0.2347	0	0.000	-0.013	0.01	0.06

† The *b* and *c* axes of the*P*4*mm* unit cell are rotated 45ºabout the 4-fold axis to form the orthorhombic cell in *Amm*2 with $b_{orth} \approx c_{orth} \approx \sqrt{2}.a_{tetr}$, doubling the cell volume.

Table S7. Atomic coordinates of $BaTiO_3$ in phase III at 250 K (Kwei *et al*., 1993), see also Table S6.

a = 3.9855(5), b = 5.6738(8), c = 5.6903(8) Å. $z^* = z$ - 0.0024.

	Wyckoff position *Amm*2†	*P*4*mm*	x_{III}	y_{III}	z_{III}	z'_{III}	x_{II}	y_{II}	z_{II}	$\Delta x_{III\text{-}II}$†	$\Delta y_{III\text{-}II}$	$\Delta z_{III\text{-}II}$	$\Delta\xi_{III\text{-}II}$	$u_{Eq.}$
Ba	2(*a*)	1(*a*),1(*b*)	0	0	0.	-0.0024	0	0	0	0	0	-0.014	0.01	0.03
Ti	2(*b*)	2(*c*)	½	0	0.5124(13)	0.5100	½	0	0.5297	0	0	-0.112	0.11	0.08
O1	2(*a*)	2(*c*)	0	0	0.4910(12)	0.4886	0	0	0.4649	0	0	0.135	0.14	0.08
O2	4(*e*)	4(*f*)	½	0.2567(6)	0.2354(8)	0.2330	½	0.2559	0.2347	0	0.005	-0.010	0.01	0.06

Table S8. Atomic coordinates of $BaTiO_3$ in phase III at 230 K (Kwei *et al*., 1993), see also Table S6.

a = 3.9841(3), b = 5.6741(5), c = 5.6916(5) Å. $z^* = z + 0.0012$.

	Wyckoff position *Amm*2	*P*4*mm*	x_{III}	y_{III}	z_{III}	z'_{III}	x_{II}	y_{II}	z_{II}	Δx_{III-II}†	Δy_{III-II}	Δz_{III-II}	$\Delta\xi_{III-II}$	$u_{Eq.}$
Ba	2(*a*)	1(*a*),1(*b*)	0	0	0.	0.0012	0	0	0	0	0	0.007	0.01	0.00
Ti	2(*b*)	2(*c*)	½	0	0.5079(8)	0.5091	½	0	0.5297	0	0	-0.117	0.12	0.09
O1	2(*a*)	2(*c*)	0	0	0.4854(6)	0.4866	0	0	0.4649	0	0	0.124	0.12	0.07
O2	4(*e*)	4(*f*)	½	0.2544(3)	0.2311(4)	0.2323	½	0.2559	0.2347	0	-0.009	-0.014	0.01	0.06

Table S9. Atomic coordinates of $BaTiO_3$ in phase III at 210 K (Kwei *et al*., 1993), see also Table S6.

a = 3.9806(5), b = 5.6710(8), c = 5.6904(8) Å. $z^* = z - 0.0018$.

	Wyckoff position *Amm*2	*P*4*mm*	x_{III}	y_{III}	z_{III}	z'_{III}	x_{II}	y_{II}	z_{II}	Δx_{III-II}†	Δy_{III-II}	Δz_{III-II}	$\Delta\xi_{III-II}$	$u_{Eq.}$
Ba	2(*a*)	1(*a*),1(*b*)	0	0	0.	-0.0018	0	0	0	0	0	-0.010	0.01	0.03
Ti	2(*b*)	2(*c*)	½	0	0.5143(10)	0.5125	½	0	0.5297	0	0	-0.098	0.10	0.07
O1	2(*a*)	2(*c*)	0	0	0.4890(13)	0.4872	0	0	0.4649	0	0	0.127	0.13	0.07
O2	4(*e*)	4(*f*)	½	0.2561(6)	0.2333(7)	0.2315	½	0.2559	0.2347	0	0.001	-0.018	0.02	0.06
					1.2366	1.2294			1.2293			0.001		

Table S10. Atomic coordinates of $BaTiO_3$ in phase III at 190 K (Kwei *et al*., 1993), see also Table S6.

a = 3.9828(3), b = 5.6745(5), c = 5.6916(5) Å. $z^* = z - 0.0028$.

	Wyckoff position *Amm*2	*P*4*mm*	x_{III}	y_{III}	z_{III}	z'_{III}	x_{II}	y_{II}	z_{II}	Δx_{III-II}†	Δy_{III-II}	Δz_{III-II}	$\Delta\xi_{III-II}$	$u_{Eq.}$
Ba	2(*a*)	1(*a*),1(*b*)	0	0	0	-0.0028	0	0	0	0	0	-0.016	0.02	0.03
Ti	2(*b*)	2(*c*)	½	0	0.5170(5)	0.5142	½	0	0.5297	0	0	-0.088	0.09	0.05
O1	2(*a*)	2(*c*)	0	0	0.4890(6)	0.4862	0	0	0.4649	0	0	0.121	0.12	0.07
O2	4(*e*)	4(*f*)	½	0.2561(3)	0.2343(4)	0.2315	½	0.2559	0.2347	0	0.001	-0.018	0.02	0.05

Phase transition from rhombohedral phase IV (*R*3*m*) to orthorhombic phase III (*Amm*2)

$BaTiO_3$ phase III undergoes a transition from *Amm*2 to *R*3*m* in phase IV at $T \approx 183$ K. The axial lengths in phase IV reportely vary less than 0.0022 Å, the interaxial angles less than 0.0019°, between 15 and 180 K (Kwei *et al*., 1993) hence the unit cell of phase IV closely approximates that of phase I. Since the unit cell volume in space group *R*3*m* is about half that in space group *Amm*2, comparison of coordinates in phases III and IV (space groups *P*4*mm* and *R*3*m* are subgroups of $Pm\bar{3}m$, but *Amm*2 is not a supergroup of *R*3*m*) requires their modification. Those reported in phase IV have an expanded unit cell of dimensions $\sim a\sqrt{2} \times a\sqrt{2} \times a_{polar}$ with Ba at 0, 0, 0; Ti at ½, 0, ½ $+\Delta z_{Ti}$, O1 at 0, 0, ½ $+\Delta z_O$ and O2 at ½, ¼ + Δy_O, ¼ + Δz_O for Δ_{Ti} and Δ_O values as reported in Tables S11-19. Values for the variable y_I and z_I coordinates listed for *Amm*2 are averaged over those reported in Tables S6 - S10 to give coordinates that are directly comparable with those in the orthorhombic phase.

Table S11. Atomic coordinates of $BaTiO_3$ in phase IV at 180 K (Kwei *et al*., 1993), transformed to the orientation of phase III. Values of z_{III} in *Amm*2 are the average of all five determinations in Kwei *et al*.'s Table III. See introductory material to phase IV → phase III transition above.

$a = 4.0043(3)$, $b = 5.6629(4)$, $c = 5.6629(4)$ Å. $z^* = z + 0.0032$.

	Wyckoff position *R*3*m* cell *ca.*4×5.67×5.67†	Wyckoff position *Amm*2 4×5.67×5.67†	x_{IV}†	y_{IV}	z_{IV}	z'_{IV}	x_{III}††	y_{III}	z_{III}	$\Delta x_{IV\text{-}III}$†	$\Delta y_{IV\text{-}III}$	$\Delta z_{IV\text{-}III}$	$\Delta\xi_{IV\text{-}III}$	$u_{Eq.}$
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0021	0	0	0.0000	0	0	0.012	0.01	neg.
Ti	2×1(*a*)	2(*b*)	0.4870(5)	-0.0092(5)	0.4908(5)	0.4929	½	0	0.5137	-0.052	0.052	-0.118	0.14	0.06
O1	3(*b*)	2(*a*)	0.0189(3)	0.0065(5)	0.5065(5)	0.5086	0	0	0.4891	0.076	0.037	0.110	0.14	0.05
O2	3(*b*)	4(*e*)	0.5189(3)	0.2565(5)	0.2565(5)	0.2586	½	0.2559	0.2594	0.076	0.003	-0.004	0.08	0.05

† $BaTiO_3$ in space group *Amm*2 has unit cell lengths 3.9828×5.6745×5.6916 Å at 190 K, hence the atomic coordinates in *R*3*m* for Ba, Ti, O1 and O2 are transformed from the given rhombohedral cell *x,y,z* with $a \approx$ 4.0036 Å by rotating 45º about a nominal *a*-axis to a cell with volume comparable to that in *Amm*2 with the four given atoms respectively at 0,0,0; ½+Δz, $\Delta x/\sqrt{2}$, ½+$\Delta y/\sqrt{2}$; Δz, $\Delta x/\sqrt{2}$, $\Delta y/\sqrt{2}$ and ½+Δz, ¼+$\Delta x/\sqrt{2}$, ¼+$\Delta y/\sqrt{2}$ with respect to the coordinates as given. The $\sqrt{2}$ factors are required by the change in cell size.

†† Averaged *xyz* values from Tables S6-10.

Table S12. Atomic coordinates of $BaTiO_3$ in phase IV at 170 K (Kwei *et al*., 1993), transformed to the orientation of phase III. Values of z_{III} in *Amm*2 are the average of all five determinations in Kwei *et al*.'s Table III. See also introductory material to phase IV → phase III transition.

a = 4.0041(3), b = 5.6627(4), c = 5.6627(4) Å. $z^* = z$ - 0.0026.

	Wyckoff position *R*3*m* cell 4×5.67×5.67††	*ca. Amm*2 4×5.67×5.67†	x_{IV}†	y_{IV}	z_{IV}	z'_{IV}	x_{III}††	y_{III}	z_{III}	Δx_{IV-III}†	Δy_{IV-III}	Δz_{IV-III}	$\Delta\xi_{IV-III}$	$u_{Eq.}$
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0026	0	0	0.0000	0	0	0.015	0.02	neg.
Ti	2×1(*a*)	2(*b*)	0.4860(3)	-0.0099(4)	0.4901(4)	0.4927	½	0	0.5137	-0.056	-0.056	-0.119	0.14	0.05
O1	3(*b*)	2(*a*)	0.0185(2)	0.0059(4)	0.5059(4)	0.5085	0	0	0.4891	0.074	0.033	0.110	0.14	0.05
O2	3(*b*)	4(*e*)	0.5185(2)	0.2559(4)	0.2559(4)	0.2585	½	0.2559	0.2594	0.074	0.0	-0.005	0.07	0.05

†, †† See footnotes to Table S11.

Table S13. Atomic coordinates of $BaTiO_3$ in phase IV at 150 K (Kwei *et al*., 1993), transformed to the orientation of phase III. Values of z_{III} in *Amm*2 are the average of all five determinations in Kwei *et al*.'s Table III. See also introductory material to phase IV → phase III transition.

a = 4.0057(3), b = 5.6649(6), c = 5.6649(6) Å. $z^* = z$ + 0.0022.

	Wyckoff position *R*3*m* cell 4×5.67×5.67†	*ca. Amm*2 4×5.67×5.67†	x_{IV}†	y_{IV}	z_{IV}	z'_{IV}	x_{III}††	y_{III}	z_{III}	Δx_{IV-III}†	Δy_{IV-III}	Δz_{IV-III}	$\Delta\xi_{IV-III}$	$u_{Eq.}$
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0022	0	0	0.0000	0	0	0.012	0.01	neg.
Ti	2×1(*a*)	2(*b*)	0.4864(6)	-0.0096(6)	0.4904(6)	0.4926	½	0	0.5137	-0.054	0.054	-0.119	0.14	0.06
O1	3(*b*)	2(*a*)	0.0181(4)	0.0066(6)	0.5066(6)	0.5088	0	0	0.4891	0.072	0.059	0.112	0.15	0.05
O2	3(*b*)	4(*e*)	0.5181(4)	0.2566(6)	0.2566(6)	0.2588	½	0.2559	0.2594	0.072	0.004	-0.004	0.07	0.05

†, †† See footnotes to Table S11.

Table S14. Atomic coordinates of $BaTiO_3$ in phase IV at 130 K (Kwei *et al*., 1993), transformed to the orientation of phase III. Values of z_{II} in *Amm*2 are the average of all five determinations in Kwei *et al*.'s Table III. See also introductory material to phase IV→ phase III transition.

a = 4.0036(3), b = 5.6623(3), c = 5.6623(3) Å. $z^* = z + 0.0020$.

	Wyckoff position *R*3*m* cell *ca.*	Wyckoff position *Amm*2 4×5.67×5.67†	x_{IV}†	y_{IV}	z_{IV}	z'_{IV}	x_{III}††	y_{III}	z_{III}	Δx_{IV-III}†	Δy_{IV-III}	Δz_{IV-III}	$\Delta\xi_{IV-III}$	$u_{Eq.}$
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0020	0	0	0.0000	0	0	0.011	0.04	neg.
Ti	2×1(*a*)	2(*b*)	0.4853(4)	-0.0104(4)	0.4896(4)	0.4916	½	0	0.5137	-0.059	0.059	-0.125	0.22	0.04
O1	3(*b*)	2(*a*)	0.0185(2)	0.0059(4)	0.5086(4)	0.5106	0	0	0.4891	0.074	0.033	0.122	0.12	0.05
O2	3(*b*)	4(*e*)	0.5185(2)	0.2559(4)	0.2559(4)	0.2579	½	0.2559	0.2594	0.074	0	-0.008	0.14	0.05

†, †† See footnotes to Table S11.

Table S15. Atomic coordinates of $BaTiO_3$ in phase IV at 100 K (Kwei *et al*., 1993), transformed to the orientation of phase III. Values of z_{II} in *Amm*2 are the average of all five determinations in Kwei *et al*.'s Table III. See also introductory material to phase IV → phase III transition.

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a = 4.0042(4), b = 5.6628(6), c = 5.6628(6) Å. $z^* = z + 0.0010$.

	Wyckoff position *R*3*m* cell *ca.* 4×5.67×5.67†	Wyckoff position *Amm*2 4×5.67×5.67†	x_{IV}†	y_{IV}	z_{IV}	z'_{IV}	x_{III}††	y_{III}	z_{III}	Δx_{IV-III}†	Δy_{IV-III}	Δz_{IV-III}	$\Delta\xi_{IV-III}$	$u_{Eq.}$
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0010	0	0	0.0000	0	0	0.006	0.05	neg.
Ti	2×1(*a*)	2(*b*)	0.4893(5)	-0.0076(5)	0.4924(5)	0.4934	½	0	0.5137	-0.043	-0.043	-0.115	0.21	0.07
O1	3(*b*)	2(*a*)	0.0200(3)	0.0080(7)	0.5080(7)	0.5090	0	0	0.4891	0.080	0.045	0.113	0.21	0.05
O2	3(*b*)	4(*e*)	0.5200(3)	0.2580(7)	0.2580(7)	0.2590	½	0.2559	0.2594	0.080	0.012	-0.002	0.21	0.05

†, †† See footnotes to Table S11.

Table S16. Atomic coordinates of $BaTiO_3$ in phase IV at 70 K (Kwei *et al*., 1993), transformed to the orientation of phase III. Values of z_{II} in *Amm*2 are the average of all five determinations in Kwei *et al*.'s Table III. See also introductory material to phase IV→ phase III transition.

a = 4.0042(4), b = 5.6628(6), c = 5.6628(6) Å. $z^* = z + 0.0028$.

	Wyckoff position *R*3*m* cell 4×5.67×5.67†	position *ca. Amm*2 4×5.67×5.67†	x_{IV}†	y_{IV}	z_{IV}	z'_{IV}	x_{III}††	y_{III}	z_{III}	Δx_{IV-III}†	Δy_{IV-III}	Δz_{IV-III}	$\Delta\xi_{IV-III}$	x_{IV}†
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0028	0	0	0.0000	0	0	0.016	0.05	neg.
Ti	2×1(*a*)	2(*b*)	0.4845(6)	-0.0110(6)	0.4890(6)	0.4918	½	0	0.5137	-0.062	0	-0.124	0.21	0.04
O14	3(*b*)	2(*a*)	0.0175(4)	0.0061(6)	0.5061(6)	0.5089	0	0	0.4891	0.034	0.016	0.112	0.12	0.05
O2	3(*b*)	4(*e*)	0.5175(4)	0.2561(6)	0.2561(6)	0.2589	½	0.2559	0.2594	0.034	0.016	-0.003	0.15	0.05

†, †† See footnotes to Table S11.

Table S17. Atomic coordinates of $BaTiO_3$ in phase IV at 40 K (Kwei *et al*., 1993), transformed to the orientation of phase III. Values of z_{II} in *Amm*2 are the average of all five determinations in Kwei *et al*.'s Table III. See also introductory material to phase IV → phase III transition.

a = 4.0035(4), b = 5.6618(6), c = 5.6618(6)) Å. $z^* = z + 0.0027$.

	Wyckoff position *R*3*m* cell 4×5.67×5.67†	position *ca. Amm*2 4×5.67×5.67†	x_{IV}†	y_{IV}	z_{IV}	z'_{IV}	x_{III}††	y_{III}	z_{III}	Δx_{IV-III}†	Δy_{IV-III}	Δz_{IV-III}	$\Delta\xi_{IV-III}$	$u_{Eq.}$
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0027	0	0	0.0000	0	0	0.015	0.04	neg.
Ti	2×1(*a*)	2(*b*)	0.4847(6)	-0.0109(6)	0.4891(6)	0.4918	½	0	0.5137	-0.046	0	-0.124	0.20	0.05
O1	3(*b*)	2(*a*)	0.0183(4)	0.0062(6)	0.5062(6)	0.5089	0	0	0.4891	0.050	0.016	0.112	0.13	0.04
O2	3(*b*)	4(*e*)	0.5183(4)	0.2562(6)	0.2562(6)	0.2589	½	0.2559	0.2594	0.050	0.016	-0.003	0.16	0.04

†, †† See footnotes to Table S11.

Table S18. Atomic coordinates of $BaTiO_3$ in phase IV at 20 K (Kwei *et al*., 1993), transformed to the orientation of phase III. Values of z_{II} in *Amm*2 are the average of all five determinations in Kwei *et al*.'s Table III. See also introductory material to phase IV→phase III transition.

a = 4.0036(3), b = 5.6619(4), c = 5.6619(4) Å. $z^* = z + 0.0011$.

	Wyckoff *R*3*m* *ca.* 4×5.67×5.67†	position *Amm*2 4×5.67×5.67†	x_{IV}†	y_{IV}	z_{IV}	z'_{IV}	x_{III}††	y_{III}	z_{III}	Δx_{IV-III}†	Δy_{IV-III}	Δz_{IV-III}	$\Delta\xi_{IV-III}$	x_{IV}†
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0011	0	0	0.0000	0	0	0.006	0.05	neg.
Ti	2×1(*a*)	2(*b*)	0.4880(7)	-0.0085(7)	0.4915(7)	0.4926	½	0	0.5137	-0.046	0	-0.119	0.22	0.05
O1	3(*b*)	2(*a*)	0.0195(3)	0.0082(5)	0.5082(5)	0.5092	0	0	0.4891	0.078	0.046	0.114	0.13	0.04
O2	3(*b*)	4(*e*)	0.5195(3)	0.2582(5)	0.2582(5)	0.2592	½	0.2559	0.2594	0.078	0.032	-0.001	0.16	0.04

†, †† See footnotes to Table S11.

Table S19. Atomic coordinates of $BaTiO_3$ in phase IV at 15 K (Kwei *et al*., 1993), transformed to the orientation of phase III. Values of z_{II} in *Amm*2 are the average of all five determinations in Kwei *et al*.'s Table III. See also introductory material to phase IV→ phase III transition.

a = 4.0036(3), b = 5.6619(5), c = 5.6619(5) Å. $z^* = z + 0.0021$.

	Wyckoff *R*3*m* 4×5.67×5.67†	position *Amm*2 4×5.67×5.67†	x_{IV}†	y_{IV}	z_{IV}	z'_{IV}	x_{III}††	y_{III}	z_{III}	Δx_{IV-III}†	Δy_{IV-III}	Δz_{IV-III}	$\Delta\xi_{IV-III}$	$u_{Eq.}$
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0021	0	0	0.0000	0	0	0.012	0.03	neg
Ti	2×1(*a*)	2(*b*)	0.4872(4)	-0.0091(4)	0.4909(4)	0.4930	½	0	0.5137	-0.051	-0.052	-0.117	0.21	0.0
O1	3(*b*)	2(*a*)	0.0193(2)	0.0064(4)	0.5064(4)	0.5085	0	0	0.4891	0.077	0.077	0.109	0.17	0.0
O2	3(*b*)	4(*e*)	0.5193(2)	0.2564(4)	0.2564(4)	0.2585	½	0.2559	0.2594	0.077	0.003	-0.005	0.15	0.0

†, †† See footnotes to Table S11.

Additional structural studies of $BaTiO_3$ as a function of temperature

P4mm (phase II) to *Pm*$\bar{3}$*m* (phase I)

Table S20 Atomic coordinates of ambient $BaTiO_3$ in phase II (Kim *et al.*, 2004). See also introductory material to phase I → phase II transition.

a = 4.0022(1), c = 4.0318(5) Å, *P*4*mm*. $z^* = z - 0.0045$.

	Wyckoff position		x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\xi_{II-I}$	$u_{Eq.}$
	*P*4*mm*	*Pm*$\bar{3}$*m*												
Ba	1(*a*)	1(*b*)	0	0	0	-0.0045	0	0	0	0	0	-0.018	0.02	0.04
Ti	1(*b*)	1(*a*)	½	½	0.537(2)	0.5325	½	½	½	0	0	0.131	0.13	0.05
O1	1(*b*)		½	½	-0.037(4)	-0.0415	½	½	0	0	0	-0.167	0.17	0.03
		3(*d*)												
O2	2(*c*)		½	0	0.518(4)	0.5135	½	0	½	0	0	0.054	0.05	0.08

Table S21. Atomic coordinates of ambient $BaTiO_3$ in phase II (Aoyagi *et al.*, 2002). See also introductory material to phase I → phase II transition.

a = 4.0000(2); c = 4.0240(2) Å. $z^* = = z - 0.0035$.

	Wyckoff position		x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}	Δy_{II-I}	Δz_{II-I}	$\Delta\xi_{II-I}$	$u_{Eq.}$
	*P*4*mm*	*Pm*$\bar{3}$*m*												
Ba	1(*a*)	1(*b*)	0	0	0.01(1)	0.0065	0	0	0	0	0	0.026	0.03	0.07
Ti	1(*b*)	1(*a*)	½	½	0.527(2)	0.5235	½	½	½	0	0	0.095	0.10	0.07
O1	1(*b*)		½	½	-0.023(8)	-0.0265	½	½	0	0	0	-0.107	-0.11	0.09
		3(*c*)												
O2	2(*c*)		½	0	0.5	0.4965	½	0	½	0	0	-0.014	-0.01	0.09

Table S22. Atomic coordinates of ambient $BaTiO_3$ in phase II (Buttner & Maslen, 1992). See also introductory material to phase I → phase II transition.

a = 3.9998(8); c = 4.0180(8) Å. $z^* = = z$ - 0.0032.

	Wyckoff *P*4*mm*	position $Pm\bar{3}m$	x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}	Δy_{II-I}	Δz_{II-I}	$\Delta\xi_{II-I}$	$u_{Eq.}$
Ba	1(*a*)	1(*b*)	0	0	0	-0.0032	0	0	0	0	0	-0.0129	0.03	0.07
Ti	1(*b*)	1(*a*)	½	½	0.482(1)	0.4788	½	½	½	0	0	-0.0853	0.10	0.07
O1	1(*b*)		½	½	0.016(5)	0.0128	½	½	0	0	0	0.0515	-0.11	0.09
		3(*c*)												
O2	2(*c*)		½	0	0.515(3)	0.5118	½	0	½	0	0	0.0475	-0.01	0.09

Table S23. Atomic coordinates of ambient $BaTiO_3$ in phase II ((Jiang *et al*. 1988). See also introductory material to phase I → phase II transition.

a = 4.0065, c = 4.017 Å . $z^* = z$ +0.0088.

	Wyckoff *P*4*mm*	position $Pm\bar{3}m$	x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}[†]	Δy_{II-I}	Δz_{II-I}	$\Delta\xi_{II-I}$
Ba	1(*a*)	1(*b*)	0	0	0	0.009	0	0	0	0	0	0.036	0.04
Ti	1(*b*)	1(*a*)	½	½	0.515(5)	0.524	½	½	½	0	0	0.096	0.10
O1[†]	1(*b*)		½	½	-0.031(3)	-0.022	½	½	0	0	0	-0.088	0.09
		3(*d*)											
O2	2(*c*)		½	0	0.481(3)	0.490	½	0	½	0	0	-0.040	0.04

[†] O1 stated as in 4(*d*) at 0.521(6), 0.521(6), -0.031(3).

Table S24. Atomic coordinates of ambient $BaTiO_3$ in phase II (Harada *et al.*, 1970). See also introductory material to phase I → phase II transition.

a = 3.9945, c = 4.0335 Å. $z^* = z + 0.0064$.

	Wyckoff position		x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I} †	Δy_{II-I}	Δz_{II-I}	$\Delta\zeta_{II-I}$	$u_{Eq.}$
	*P*4*mm*	$Pm\bar{3}m$												
Ba	1(*a*)	1(*b*)	0	0	0	0.0064	0	0	0	0	0	0.026	0.03	0.06
Ti	1(*b*)	1(*a*)	½	½	0.5135(4)	0.5199	½	½	½	0	0	0.080	0.08	0.06
O1	1(*b*)		½	½	-0.024(1)	-0.0176	½	½	0	0	0	-0.071	0.07	0.06
		3(*d*)												
O2	2(*c*)		½	0	0.4850(9)	0.4914	½	0	½	0	0	-0.035	0.04	0.06

Additional studies of $BaTiO_3$ in *Amm*2 (phase III) to *P*4*mm* (phase II)

Table S25. Atomic coordinates of $BaTiO_3$ in phase III. (Shirane *et al.*, 1957). See also introductory material to phase II → phase III transition in Table S6.

a = 3.99, b = 5.669, c = 5.682 Å. $z^* = z$ - 0.0019.

	Wyckoff *Amm*2 4×5.67×5.67†	position *P*4*mm* 4×5.63×5.63†	x_{III}	y_{III}	z_{III}	z'_{III}	x_{II}	y_{II}	z_{II}	Δx_{III-II}†	Δy_{III-II}	Δz_{III-II}	$\Delta\xi_{III-II}$	$u_{Eq.}$
Ba	2(*a*)	1(*a*),1(*b*)	0	0	0.	-0.0019	0	0	0	0	0	-0.011	0.01	0.04
Ti	2(*b*)	2(*c*)	½	0	0.51	0.5081	½	0	0.5297	0	0	-0.123	0.12	0.06
O1	2(*a*)	2(*c*)	½	0	0.49	0.4881	0	0	0.4649	0	0	0.132	0.13	0.07
O2	4(*e*)	4(*f*)	¼	0.253	0.237	0.2351	½	0.255	0.2347	0	-0.01	0.002	0.00	0.06

† Tetragonal unit cell rotated 45ºabout 4-fold axis to match larger orthorhombic cell, doubling the multiplicity of each atom.

Additional studies of $BaTiO_3$ in *R*3*m* (phase IV) to *Amm*2 (phase III)

Table S26. Atomic coordinates of $BaTiO_3$ in phase IV at 77 K. (Hewat, 1974). See also introductory material to phase III → phase IV transition in Table S11.

a = 4.001, (b = 5.658, c = 5.658 Å), α = 89.868º. $z^* = z - 0.000$ (Note $4.001\sqrt{2} = 5.658$.) Values of z_{II} in *Amm*2 are the average of all five determinations in Kwei *et al.*'s Table III.

	Wyckoff position *R*3*m* 4×5.66×5.66†	*Amm*2 4×5.66×5.66†	x_{II}†	y_{II}	z_{II}	z'_{II}	x_I††	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\zeta_{II-I}$	$u_{Eq.}$
Ba	2×1(*a*)	2(*a*)	0	0	0	-0.001	0	0	0.0000	0	0	-0.001	0.00	n/a
Ti	2×1(*a*)	2(*b*)	0.487(3)	-0.009(3)	0.491(3)	0.490	½	0	0.5137	-0.052	0.052	-0.134	0.15	n/a
O1	3(*b*)	2(*a*)	0.018(2)	0.013(2)	0.513(2)	0.512	0	0	0.4891	0.072	0.074	0.130	0.17	n/a
O2	3(*b*)	4(*e*)	0.518(2)	0.263(2)	0.263(2)	0.262	½	0.2559	0.2594	0.028	0.006	0.003	0.03	n/a

Table S27. Atomic coordinates of $BaTiO_3$ in phase IV (Schildkamp *et al.*, 1981) at both 132 and 196 K. See also introductory material to phase III → phase IV transition in Table S11.

a = 4.004(3), b = 5.663(3), c = 5.663(3) Å; $z^* = z + 0.0011$. Values of z_{II} in *Amm*2 are the average of all five determinations in Kwei *et al.*'s Table III.

	Wyckoff position *R*3*m* cell *ca.* 4×5.66×5.66†	*Amm*2 4×5.66×5.66†	x_{II}†	y_{II}	z_{II}	z'_{II}	x_I††	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\zeta_{II-I}$	$u_{Eq.}$
Ba	2×1(*a*)	2(*a*)	0	0	0	0.0011	0	0	0.0000	0	0	0.006	0.05	neg.
Ti	2×1(*a*)	2(*b*)	0.4889(3)	-0.0079(3)	0.4921(3)	0.4932	½	0	0.5137	-0.044	0	-0.116	0.21	0.04
O1	3(*b*)	2(*a*)	0.0180(2)	0.0078(6)	0.5078(2)	0.5089	0	0	0.4891	0.044	0.029	0.112	0.12	0.05
O2	3(*b*)	4(*e*)	0.5180(6)	0.2578(6)	0.2578(2)	0.2589	½	0.2559	0.2594	0.044	0.029	-0.003	0.15	0.05

Recent studies of $BaTiO_3$ as a function of applied pressure

P4mm (phase II) to $Pm\bar{3}m$ (phase I)

Table S28. Atomic coordinates of $BaTiO_3$ in phase II at 298 K and 0.2 GPa (Hayward *et al.*, 2005). See also introductory material to phase I → phase II transition.

a = 3.9732(2) in $Pm\bar{3}m$ and a = 3.9906(4), c = 4.0278(8) Å in *P4mm*. $z^* = z - 0.0073$.

	Wyckoff position		x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\xi_{II-I}$
	P4mm	$Pm\bar{3}m$											
Ba	1(*a*)	1(*b*)	0	0	0	-0.0073	0	0	0	0	0	-0.029	0.03
Ti	1(*b*)	1(*a*)	½	½	0.525(5)	0.5177	½	½	½	0	0	0.071	0.07
O1	1(*b*)		½	½	0.000(5)	-0.0073	½	½	0	0	0	-0.029	0.03
		3(*d*)											
O2	2(*c*)		½	0	0.504(5)	0.4967	½	0	½	0	0	-0.013	0.01

Table S29. Atomic coordinates of $BaTiO_3$ in phase II at 213 K and 3.2 GPa (Hayward *et al.*, 2005). See also introductory material to phase I → phase II transition.

a = 3.9732(2) in $Pm\bar{3}m$; a = 3.9683(3), c = 3.9922(7) Å in *P4mm*. $z^* = z - 0.0167$.

	Wyckoff position		x_{II}	y_{II}	z_{II}	z'_{II}	x_I	y_I	z_I	Δx_{II-I}†	Δy_{II-I}	Δz_{II-I}	$\Delta\xi_{II-I}$
	P4mm	$Pm\bar{3}m$											
Ba	1(*a*)	1(*b*)	0	0	0	-0.0167	0	0	0	0	0	-0.067	0.07
Ti	1(*b*)	1(*a*)	½	½	0.518(5)	0.5013	½	½	½	0	0	0.005	0.01
O1	1(*b*)		½	½	0.024(8)	0.0073	½	½	0	0	0	0.029	0.03
		3(*d*)											
O2	2(*c*)		½	0	0.525(5)	0.5083	½	0	½	0	0	0.033	0.03

Table S30. Atomic coordinates of $BaTiO_3$ in phase III at 165 K and 3.2 GPa (Hayward *et al.*, 2005). See also introductory material to phase III→ phase II transition.

a = 3.9683(3), c = 3.9922(7) Å in *P*4*mm* with a = 3.9594(6), b = 5.6266(10), c = 5.6435(10) Å in *Amm*2.
$z^* = z + 0.01125$.

	Wyckoff position		x_{III}	y_{III}	z_{III}	z'_{III}	x_{II}	y_{II}	z_{II}	Δx_{III-II}†	Δy_{III-II}	Δz_{III-II}	$\Delta\xi_{III-II}$
	*Amm*2	*P*4*mm*											
Ba	1(*a*)	1(*b*)	0	0	0	0.0113	0	0	0	0	0	0.064	0.06
Ti	1(*b*)	1(*a*)	½	0	0.515(5)	0.5263	½	0	0.518	0	0	0.047	0.05
O1	1(*b*)		½	0	0.009(7)	0.0203	½	0	0.024	0	0	-0.021	0.02
		3(*d*)											
O2	2(*c*)		¼	0.264(2)	0.498(8)	0.5093	¼	¼	0.525	0	0.084	-0.089	0.12