

Supporting Information

Crystallographic investigations into the polar polymorphism of BaTeW₂O₉: Phase transformation, controlled crystallization, and linear and nonlinear optical properties

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1. **Figure S1.** Calculated and experimental powder X-ray diffraction patterns for polycrystalline β -BTW.
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10. References.

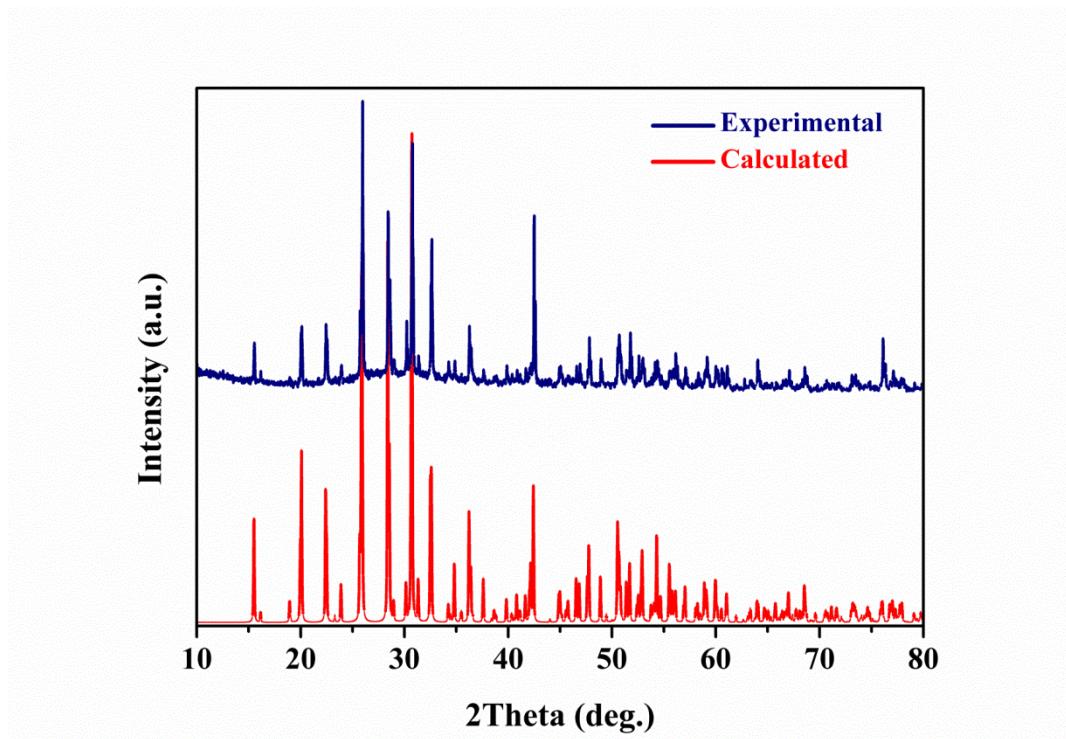


Figure S1. Calculated and experimental powder X-ray diffraction patterns for polycrystalline $\beta\text{-BTW}$.

Table S1. The product of powder $\alpha\text{-BTW}$ after annealing at various temperatures and times.

Temperature/Time	5 h	10 h	20 h	30 h	50 h	100 h
530 °C	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$
550 °C	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$
580 °C	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$
600 °C	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$
650 °C	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$	$\alpha\text{-BTW}$

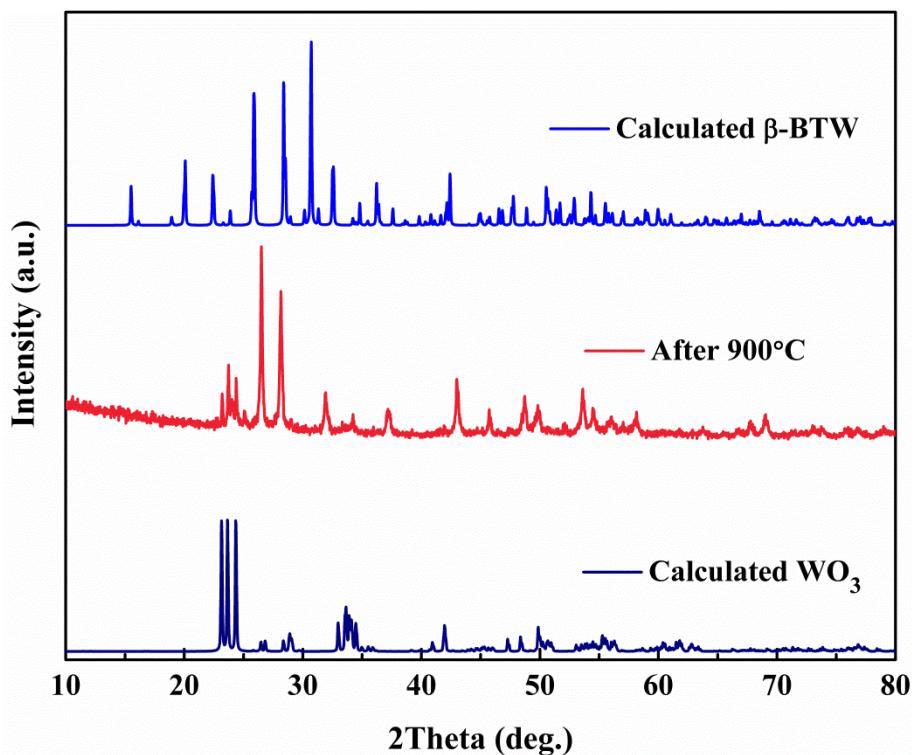


Figure S2. The experimental patterns of powder XRD of the residue in the platinum pan after melt at 900 °C.

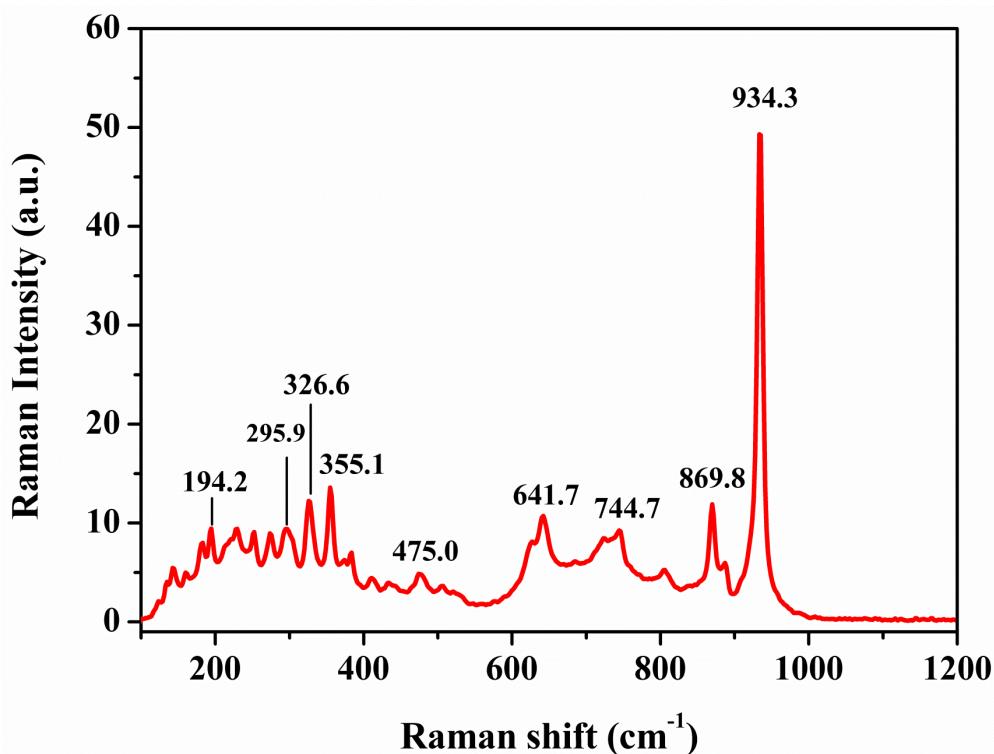


Figure S3. Room temperature spontaneous Raman spectra of β -BTW. The Raman shift with the highest intensity is at 934.3 cm⁻¹.

Table S2. Observed Raman wavenumbers (cm^{-1}) and vibrational assignments for β -BTW.¹⁻³

Raman spectra	Assignments
100-400 (w)	W, Te, Ba translation and libration
475.0 (vw)	WO_6 and TeO_4 bending
641.7 (w)	TeO_4 asymmetric stretching
744.7 (w)	TeO_4 asymmetric stretching
869.8 (m)	WO_6 symmetric stretching
934.3 (vs)	WO_6 symmetric stretching

In the table, vs: very strong; m: medium; w: weak; vw: very weak

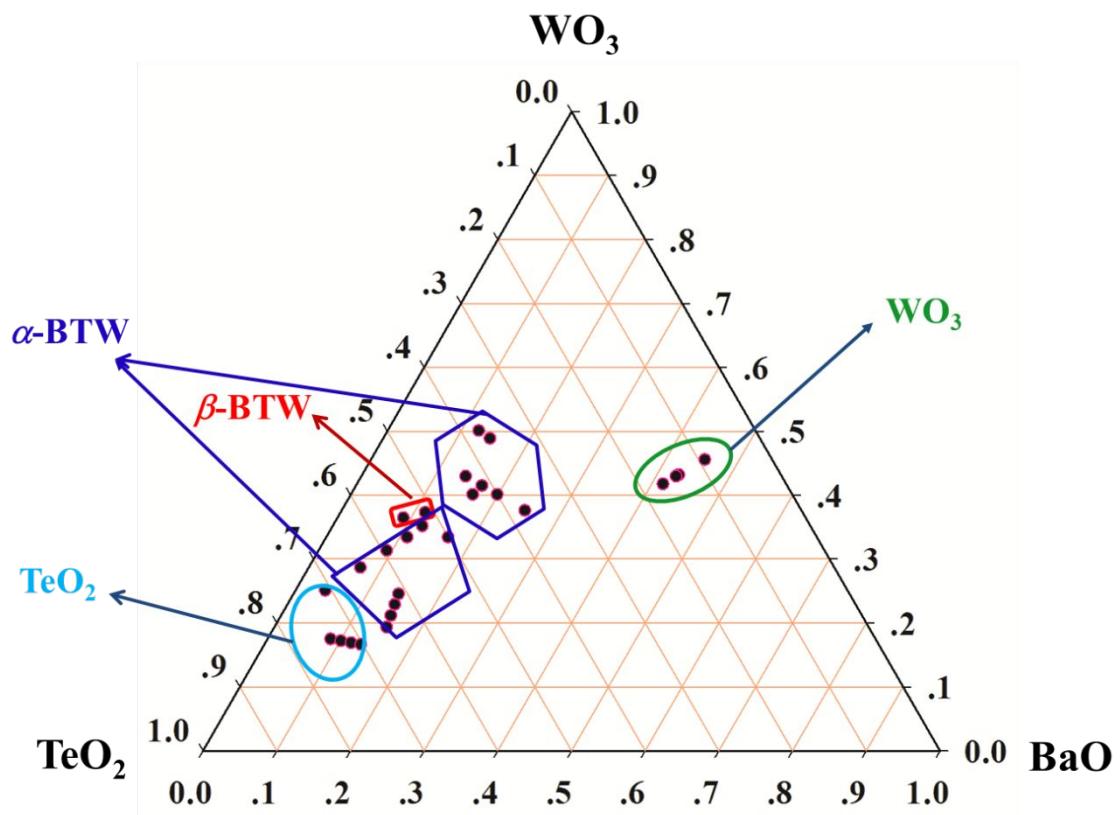


Figure S4. The crystallization region of crystallized product in the quasi-ternary WO_3 - TeO_2 - BaO system. (the red rectangle presents crystallized β -BTW crystals; the blue frame means crystallized α -BTW crystals).

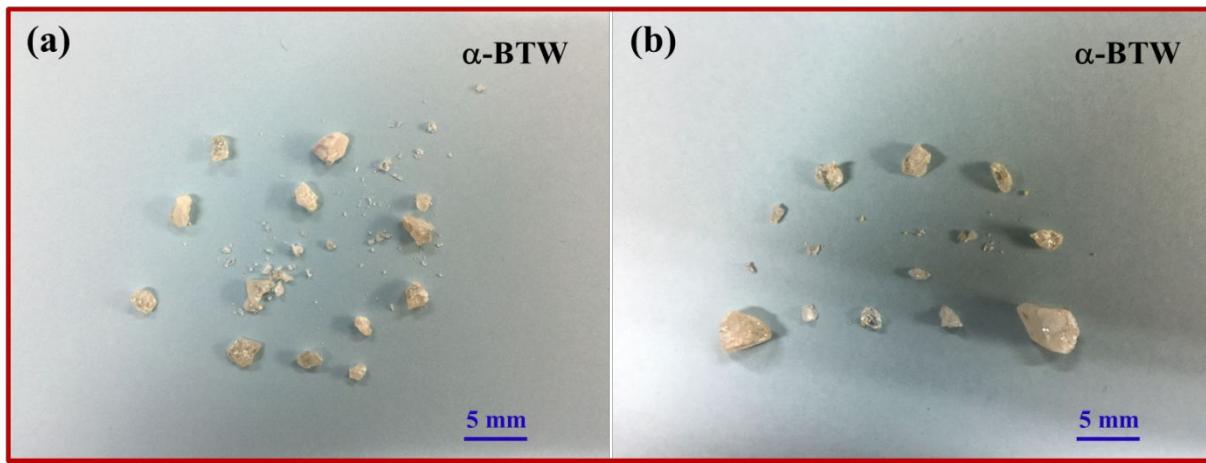


Figure S5. Photographs of the as-grown α -BTW crystals through spontaneous crystallization.

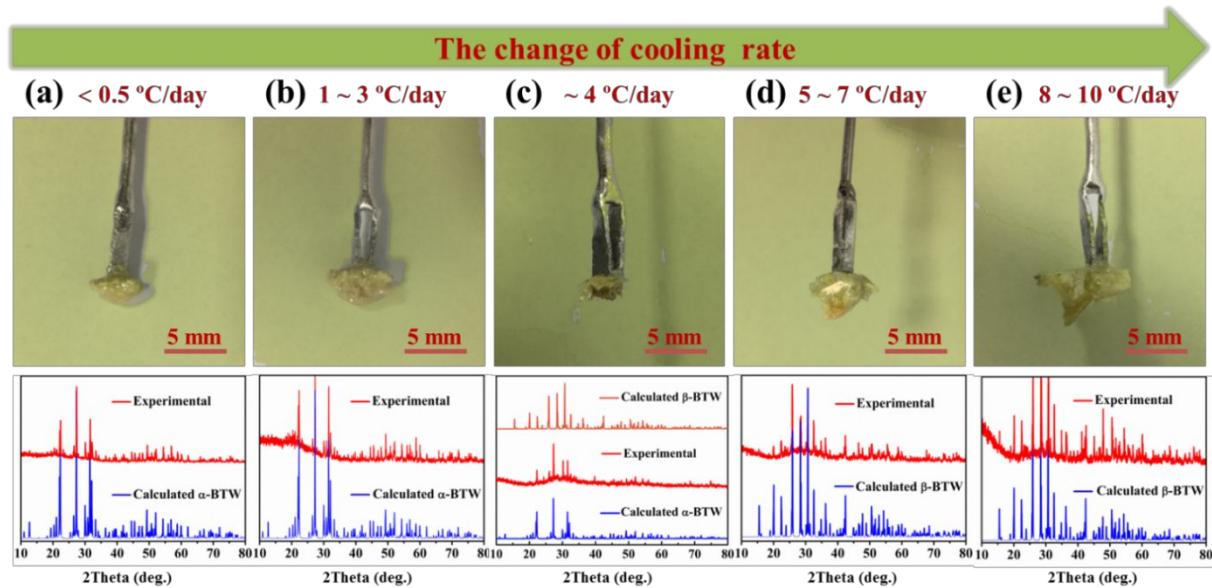


Figure S6. (a)-(e) The crystals obtained through spontaneous crystallization with different cooling rate, and the corresponding XRD patterns (below).

Table S3. Bond Distances (\AA) and Angles (deg.) for β -BaTeMo₂O₉ crystal.

W1—Ba1 ⁱ	3.872 (4)	Te1—O5	2.19 (2)
W1—O4	2.09 (3)	Te1—O4	1.87 (3)
W1—O8 ⁱⁱ	2.15 (2)	Te1—O8	1.92 (2)
W1—O1	1.78 (2)	Te1—O9	2.03 (2)
W1—O2	1.88 (2)	Ba1—O5 ^{vii}	2.84 (2)

W1—O9 ⁱⁱ	2.17 (2)	Ba1—O5	3.24 (2)
W1—O3	1.74 (3)	Ba1—O4	2.83 (2)
W2—Ba1 ⁱⁱⁱ	3.896 (4)	Ba1—O1 ⁱⁱⁱ	2.69 (3)
W2—Ba1 ^{iv}	3.784 (4)	Ba1—O1	3.04 (2)
W2—O5	1.88 (2)	Ba1—O6	2.87 (3)
W2—O8	2.20 (2)	Ba1—O6 ^{viii}	2.95 (2)
W2—O2 ^v	1.98 (2)	Ba1—O7 ^{vii}	3.22 (3)
W2—O6	1.76 (2)	Ba1—O7 ^{viii}	3.16 (2)
W2—O9 ^{vi}	2.20 (2)	Ba1—O7 ^{ix}	2.84 (3)
W2—O7	1.72 (3)	Ba1—O3 ^x	2.79 (2)
O4—W1—Ba1 ⁱ	99.3 (6)	O1—Ba1—O5	92.4 (6)
O4—W1—O8 ⁱⁱ	77.9 (9)	O1 ⁱⁱⁱ —Ba1—O5 ^{vii}	75.1 (7)
O4—W1—O9 ⁱⁱ	81.8 (9)	O1 ⁱⁱⁱ —Ba1—O5	66.0 (6)
O8 ⁱⁱ —W1—Ba1 ⁱ	134.7 (6)	O1 ⁱⁱⁱ —Ba1—O4	119.3 (7)
O8 ⁱⁱ —W1—O9 ⁱⁱ	70.2 (8)	O1 ⁱⁱⁱ —Ba1—O1	121.4 (3)
O1—W1—Ba1 ⁱ	65.0 (8)	O1 ⁱⁱⁱ —Ba1—O6	66.6 (7)
O1—W1—O4	89.9 (10)	O1 ⁱⁱⁱ —Ba1—O6 ^{viii}	86.1 (7)
O1—W1—O8 ⁱⁱ	157.9 (9)	O1—Ba1—O7 ^{viii}	160.0 (7)
O1—W1—O2	99.9 (10)	O1 ⁱⁱⁱ —Ba1—O7 ^{vii}	59.3 (6)
O1—W1—O9 ⁱⁱ	90.1 (9)	O1—Ba1—O7 ^{vii}	62.3 (6)
O2—W1—Ba1 ⁱ	91.7 (7)	O1 ⁱⁱⁱ —Ba1—O7 ^{viii}	62.4 (7)
O2—W1—O4	167.7 (9)	O1 ⁱⁱⁱ —Ba1—O7 ^{ix}	144.3 (7)
O2—W1—O8 ⁱⁱ	90.4 (10)	O1 ⁱⁱⁱ —Ba1—O3 ^x	132.3 (7)
O2—W1—O9 ⁱⁱ	90.7 (9)	O6 ^{viii} —Ba1—W2 ^{viii}	26.9 (5)
O9 ⁱⁱ —W1—Ba1 ⁱ	155.0 (5)	O6—Ba1—W2 ^{viii}	86.0 (4)
O3—W1—Ba1 ⁱ	40.6 (8)	O6 ^{viii} —Ba1—O5	151.4 (6)
O3—W1—O4	89.4 (10)	O6—Ba1—O5	53.3 (6)
O3—W1—O8 ⁱⁱ	94.2 (10)	O6 ^{viii} —Ba1—O1	108.1 (7)
O3—W1—O1	104.1 (11)	O6—Ba1—O1	140.4 (6)
O3—W1—O2	95.3 (12)	O6—Ba1—O6 ^{viii}	111.3 (4)
O3—W1—O9 ⁱⁱ	163.4 (9)	O6—Ba1—O7 ^{vii}	108.7 (7)
Ba1 ^{iv} —W2—Ba1 ⁱⁱⁱ	91.46 (10)	O6 ^{viii} —Ba1—O7 ^{vii}	107.7 (6)
O5—W2—Ba1 ^{iv}	120.3 (6)	O6 ^{viii} —Ba1—O7 ^{viii}	51.9 (7)

O5—W2—Ba1 ⁱⁱⁱ	43.3 (7)	O6—Ba1—O7 ^{viii}	59.6 (6)
O5—W2—O8	74.6 (9)	O7 ^{viii} —Ba1—W2 ^{viii}	26.8 (5)
O5—W2—O2 ^v	156.6 (9)	O7 ^{vii} —Ba1—W2 ^{viii}	109.3 (4)
O5—W2—O9 ^{vi}	84.0 (9)	O7 ^{ix} —Ba1—W2 ^{viii}	87.3 (4)
O8—W2—Ba1 ⁱⁱⁱ	117.1 (6)	O7 ^{ix} —Ba1—O5	145.9 (6)
O8—W2—Ba1 ^{iv}	137.4 (6)	O7 ^{vii} —Ba1—O5	64.0 (6)
O2 ^v —W2—Ba1 ⁱⁱⁱ	151.0 (7)	O7 ^{viii} —Ba1—O5	106.2 (6)
O2 ^v —W2—Ba1 ^{iv}	82.5 (6)	O7 ^{ix} —Ba1—O1	60.3 (6)
O2 ^v —W2—O8	84.9 (9)	O7 ^{ix} —Ba1—O6	138.3 (7)
O2 ^v —W2—O9 ^{vi}	80.0 (9)	O7 ^{ix} —Ba1—O6 ^{viii}	62.4 (7)
O6—W2—Ba1 ^{iv}	49.3 (8)	O7 ^{ix} —Ba1—O7 ^{viii}	104.4 (6)
O6—W2—Ba1 ⁱⁱⁱ	104.3 (7)	O7 ^{viii} —Ba1—O7 ^{vii}	119.2 (8)
O6—W2—O5	98.4 (10)	O7 ^{ix} —Ba1—O7 ^{vii}	112.4 (7)
O6—W2—O8	91.3 (10)	O3 ^x —Ba1—W2 ^{viii}	104.9 (5)
O6—W2—O2 ^v	93.1 (10)	O3 ^x —Ba1—O5	89.6 (7)
O6—W2—O9 ^{vi}	165.5 (9)	O3 ^x —Ba1—O5 ^{vii}	150.2 (8)
O9 ^{vi} —W2—Ba1 ⁱⁱⁱ	87.2 (6)	O3 ^x —Ba1—O4	61.9 (7)
O9 ^{vi} —W2—Ba1 ^{iv}	140.7 (6)	O3 ^x —Ba1—O1	98.7 (6)
O9 ^{vi} —W2—O8	75.5 (9)	O3 ^x —Ba1—O6 ^{viii}	106.2 (7)
O7—W2—Ba1 ⁱⁱⁱ	54.5 (9)	O3 ^x —Ba1—O6	66.0 (7)
O7—W2—Ba1 ^{iv}	55.9 (8)	O3 ^x —Ba1—O7 ^{ix}	76.2 (8)
O7—W2—O5	97.8 (11)	O3 ^x —Ba1—O7 ^{vii}	145.0 (6)
O7—W2—O8	166.7 (9)	O3 ^x —Ba1—O7 ^{viii}	89.0 (6)
O7—W2—O2 ^v	100.0 (11)	W2—O5—Te1	105.6 (10)
O7—W2—O6	100.8 (11)	W2—O5—Ba1 ⁱⁱⁱ	109.7 (10)
O7—W2—O9 ^{vi}	93.0 (10)	W2—O5—Ba1	95.7 (8)
O4—Te1—O5	87.1 (10)	Te1—O5—Ba1 ⁱⁱⁱ	139.1 (9)
O4—Te1—O8	94.9 (10)	Te1—O5—Ba1	96.3 (9)
O4—Te1—O9	91.5 (10)	Ba1 ⁱⁱⁱ —O5—Ba1	100.0 (6)
O8—Te1—O5	74.2 (9)	W1—O4—Ba1	105.1 (9)
O8—Te1—O9	77.8 (9)	Te1—O4—W1	123.1 (11)
O9—Te1—O5	151.7 (9)	Te1—O4—Ba1	120.4 (11)
O5 ^{vii} —Ba1—W2 ^{viii}	72.6 (4)	W1 ^{vi} —O8—W2	143.7 (13)

O5—Ba1—W2 ^{viii}	126.6 (4)	Tel—O8—W1 ^{vi}	106.7 (9)
O5 ^{vii} —Ba1—O5	116.2 (5)	Tel—O8—W2	103.7 (10)
O5 ^{vii} —Ba1—O1	67.3 (6)	W1—O1—Ba1	106.6 (10)
O5 ^{vii} —Ba1—O6 ^{viii}	58.1 (6)	W1—O1—Ba1 ^{vii}	134.4 (12)
O5 ^{vii} —Ba1—O6	141.1 (6)	Ba1 ^{vii} —O1—Ba1	108.7 (7)
O5 ^{vii} —Ba1—O7 ^{ix}	74.1 (7)	W1—O2—W2 ^{xi}	131.4 (12)
O5 ^{vii} —Ba1—O7 ^{viii}	97.1 (6)	W2—O6—Ba1 ^{iv}	103.8 (11)
O5 ^{vii} —Ba1—O7 ^{vii}	52.8 (7)	W2—O6—Ba1	112.7 (10)
O4—Ba1—W2 ^{viii}	166.6 (5)	Ba1—O6—Ba1 ^{iv}	114.2 (7)
O4—Ba1—O5 ^{vii}	120.0 (7)	W1 ^{vi} —O9—W2 ⁱⁱ	131.1 (10)
O4—Ba1—O5	54.6 (7)	Tel—O9—W1 ^{vi}	102.1 (9)
O4—Ba1—O1	55.6 (7)	Tel—O9—W2 ⁱⁱ	126.6 (11)
O4—Ba1—O6	85.9 (6)	W2—O7—Ba1 ^{xii}	132.9 (12)
O4—Ba1—O6 ^{viii}	154.0 (8)	W2—O7—Ba1 ⁱⁱⁱ	99.8 (11)
O4—Ba1—O7 ^{ix}	91.7 (7)	W2—O7—Ba1 ^{iv}	97.3 (10)
O4—Ba1—O7 ^{viii}	142.6 (7)	Ba1 ^{xii} —O7—Ba1 ^{iv}	108.9 (8)
O4—Ba1—O7 ^{vii}	83.5 (6)	Ba1 ^{xii} —O7—Ba1 ⁱⁱⁱ	100.4 (8)
O1—Ba1—W2 ^{viii}	133.6 (5)	Ba1 ^{iv} —O7—Ba1 ⁱⁱⁱ	119.2 (8)
O1 ⁱⁱⁱ —Ba1—W2 ^{viii}	66.6 (4)	W1—O3—Ba1 ⁱ	115.6 (11)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, y+1/2, -z+1$; (iii) $-x+1, y-1/2, -z+2$; (iv) $-x+2, y-1/2, -z+2$; (v) $x+1, y-1, z$; (vi) $-x+1, y-1/2, -z+1$; (vii) $-x+1, y+1/2, -z+2$; (viii) $-x+2, y+1/2, -z+2$; (ix) $x, y+1, z$; (x) $x+1, y, z$; (xi) $x-1, y+1, z$; (xii) $x, y-1, z$.

References

1. L. S. Cavalcante, J. C. Sczancoski, L. F. Lima, J. Espinosa, P. S. Pizani, J. A. Varela and E. Longo, *Cryst. Growth Des.* 2009, **9**, 1002–1012.
2. M. Maczka, A. Majchrowski and I. V. Kityk, *Vib. Spectrosc.* 2013, **64**, 158–163.
3. Z. H. Zhang, X. T. Tao, J. J. Zhang, Y. X. Sun, C. Q. Zhang and B. Li, *CrystEngComm* 2013, **15**, 10197–10204.