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Supporting information for article:

The first bismuth borate oxyiodide, Bi4BO7I: commensurate or incommensurate?

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Table S1 Atomic coordinates, displacement parameters (Å^2), site–occupancy factors (SOFs) and bond valence sums (BVS, v.u.) in the structure of Bi_4BO_7I.

Atom	SOF	Wyckoff site	*x*	*y*	*z*	$U_{eq/iso}$	*BVS*
Bi	1	4*g*	0.5	0.15756(5)	0.5	0.0296(2)	2.54(8)–3.15 (8)
I	0.5	2*a*	0	0	0	0.0206(7)	0.88(8)–1.26(8)
B	0.5	2*a*	0	0	0	0.0206(7)	2.35 (8)–2.41(8)
O1	1	8*l*	0	0.2489(7)	0.5	0.017(3)	2.01(8)–2.21(8)
O2	0.125	8*l*	0	–0.093(2)	–0.102(9)	0.023(11)	1.67(8)–1.86(8)
O3	0.125	8*m*	0.120(10)	0	0.682(7)	0.076(16)	1.54(8)–1.64(8)
O4	0.125	8*n*	0.259(11)	–0.060(4)	0	0.10(2)	1.78(8)–2.00(8)

*isotropical ADP

Table S2 Anisotropic parameters of atomic displacements in the structure of Bi_4BO_7I.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	0.0327(4)	0.0239(4)	0.0324(5)	0	0	0
I	0.0180(12)	0.0220(14)	0.0216(11)	0	0	0
B	0.0180(12)	0.0220(14)	0.0216(11)	0	0	0
O1	0.016(4)	0.021(5)	0.015(5)	0	0	0

Table S3 Parameters of the crenel functions in the structure of Bi_4BO_7I.

Atom	x_4^0	Δ
I	0	0.5
B	0.5	0.5
O2	0.476(2)	0.5
O3	0.5488	0.25
O4	0.5	0.5

Table S4 Amplitudes of the displacive modulation waves and atomic positional parameters of Bi_4BO_7I.

Atom	Harmonic	*x*	*y*	*z*
Bi	sin,1	0	0	0.0511(3)
	cos,1	0	0.00708(9)	0
	sin,2	0	0	0.0032(5)
	cos,2	0	0.00010(11)	0
I	ort,1	0	0	0.0118(5)
	ort,2	0	0	0

O1	sin,1	0	0	-0.010(3)
	cos,1	0	-0.0007(12)	0
	sin,2	0	0	-0.006(3)
	cos,2	0	-0.0023(15)	0

Table S5 Amplitudes of the modulation of the atomic displacement parameters of the atoms in Bi_4BO_7I.

Atom	Harmonic	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	sin,1	0	0	0	0	0	–0.0068(5)
	cos,1	–0.0147(6)	–0.0074(5)	–0.0204(7)	0	0	0
	sin,2	0	0	0	0	0	–0.0077(6)
	cos,2	–0.0029(7)	–0.0040(8)	0.0143(8)	0	0	0
	sin,3	0	0	0	0	0	0
	cos,3	0	0	–0.0109(18)	0	0	0
I	ort,1	0	0	0	0	0	0
	ort,2	0.0225(17)	0.0284(18)	0.0138(14)	0	0	0
B	sin,1	0	0	0	0	0	0
	cos,1	0.0225(17)	0.0284(18)	0.0138(14)	0	0	0
O1	sin,1	0	0	0	0	0	–0.001(7)
	cos,1	0.011(9)	–0.013(9)	–0.013(7)	0	0	0

Table S6 Selected distances (Å) in the crystal structure of Bi_4BO_7I.

	Ave.	Min.	Max.
Bi–O1 × 2	2.34(2)	2.26(3)	2.37(3)
Bi–O1 × 2	2.35(2)	2.13(2)	2.57(2)
Bi–O4 × 4	2.47(3)	2.40(3)	2.63(3)
Bi–O3 × 4	2.63(3)	2.61(3)	2.68(3)
Bi–O2 × 4	2.61(3)	2.56(3)	2.73(3)
Bi–I × 4	3.591(13)	3.503(14)	3.644(14)
B–O2 × 4	1.32(3)	1.32(3)	1.32(3)
B–O3 × 4	1.35(3)	1.35(3)	1.35(3)
B–O4 × 4	1.31(5)	1.31(5)	1.31(5)

Table S7 Selected angles (°) in the crystal structure of Bi_4BO_7I.

	Ave.	Min.	Max.

Bi^{i}–I–Bi^{ix}	52.95(4)	52.59(4)	53.09(4)
Bi^{i}–I–Bi^{iii}	66.90(5)	65.81(4)	68.82(5)
Bi^{i}–I–Bi^{ii}	70.50(6)	68.43(6)	71.82(6)
Bi^{i}–I–Bi^{v}	74.08(5)	71.52(6)	77.20(6)
Bi^{i}–I–Bi	105.90(5)	105.61(5)	106.16(5)
Bi^{i}–I–Bi^{vii}	109.51(7)	107.12(6)	114.65(10)
Bi^{i}–I–Bi^{vi}	113.05(4)	111.20(4)	114.19(4)
Bi^{i}–I–Bi^{iv}	127.02(5)	124.50(6)	129.77(6)
Bi^{iv}–I–Bi^{ix}	177.64(6)	176.53(8)	180
O2–B–$O2^{x}$	36(2)	36(2)	36(2)
$O3^{iii}$–B–$O3^{v}$	41(2)	41(2)	41(2)
O2–B–O4	54(2)	54(2)	54(2)
O2–B–$O3^{iii}$	73.2(14)	73.2(14)	73.2(14)
$O3^{iii}$–B–O4	74.0(13)	74.0(13)	74.0(13)
O4–B–$O4^{xi}$	77(3)	77(3)	77(3)
O4–B–$O4^{x}$	103(3)	103(3)	103(3)
$O3^{iii}$–B–$O4^{vi}$	106.0(13)	106.0(13)	106.0(13)
Bi^{ii}–O1–Bi^{xiv}	106.4(4)	99.5(6)	112.2(4)
O2–B–$O3^{xii}$	106.8(14)	106.8(14)	106.8(14)
Bi^{ix}–O1–Bi^{xiv}	115.1(8)	108.0(15)	120.2(15)
O2–B–$O4^{vi}$	126(2)	126(2)	126(2)
O2–B–$O2^{vi}$	144(2)	144(2)	144(2)
O2–B–$O2^{xi}$	180	180	180

Symmetry codes: (i) *x*–1,*y*,*z*–1; (ii) *x*–1,*y*,*z*; (iii) *x*,*y*,*z*–1; (iv) *x*–1/2,*y*–1/2,*z*–1/2; (v) –*x*,–*y*,*z*–1; (vi) –*x*,–*y*,*z*; (vii) –*x*+1,–*y*,*z*–1; (viii) –*x*+1,–*y*,*z*; (ix) –*x*+1/2,–*y*+1/2,*z*–1/2; (x) –*x*,*y*,–*z*; (xi) *x*,–*y*,–*z*; (xii) –*x*,*y*,–*z*+1; (xiii) *x*,–*y*,–*z*+1; (xiv) –*x*+1/2,–*y*+1/2,*z*+1/2

Figure S1 Intensity profiles for the powder X-ray Rietveld refinement of Bi_4BO_7I with (*a*–*c*) the $a \times b \times 4c$ fourfold model and (*d*–*f*) incommensurately modulated $a \times b \times c$ model with $\mathbf{q}$ = (0,0,0.2405 (2)). The difference profile is plotted at the bottom. Vertical bars indicate the positions of the Bragg and satellite reflections.

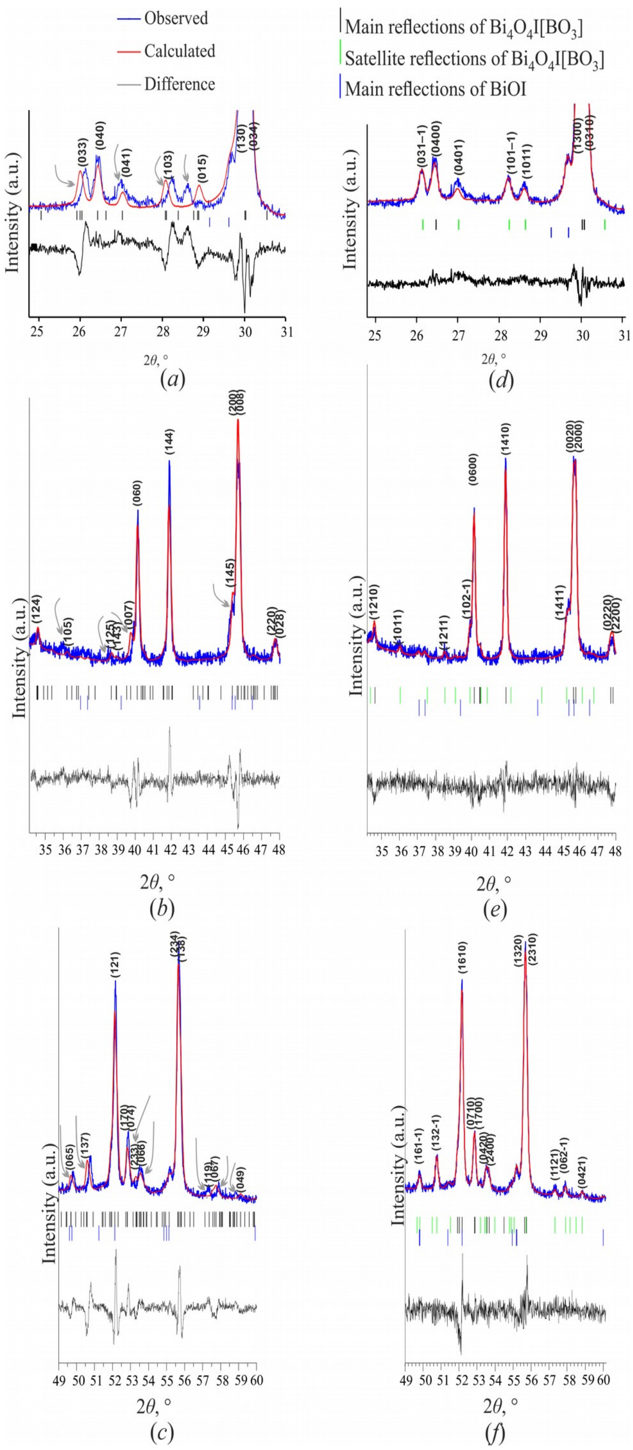

Figure S2 High-temperature X-ray powder diffraction measurements of Bi_4BO_7I. BiOI peak is marked by arrow. The dashed line indicates the melting of BiOI.

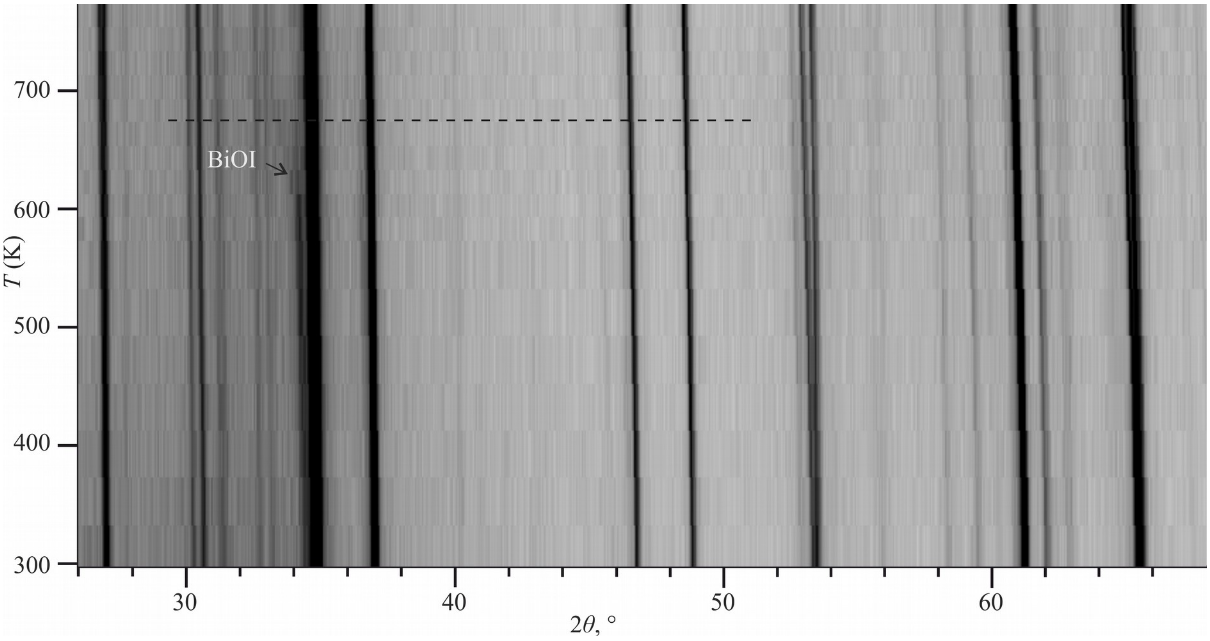

Figure S3 Temperature dependences of the unit-cell parameters and volume for Bi_4BO_7I. Uncertainties are smaller than used symbols.

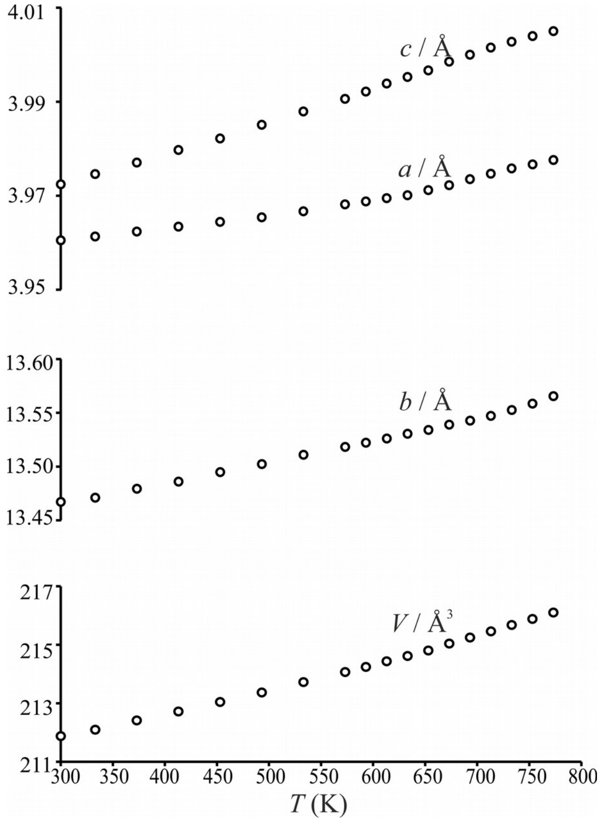

Figure S4 Temperature dependence of the **q** vector of Bi_4BO_7I.

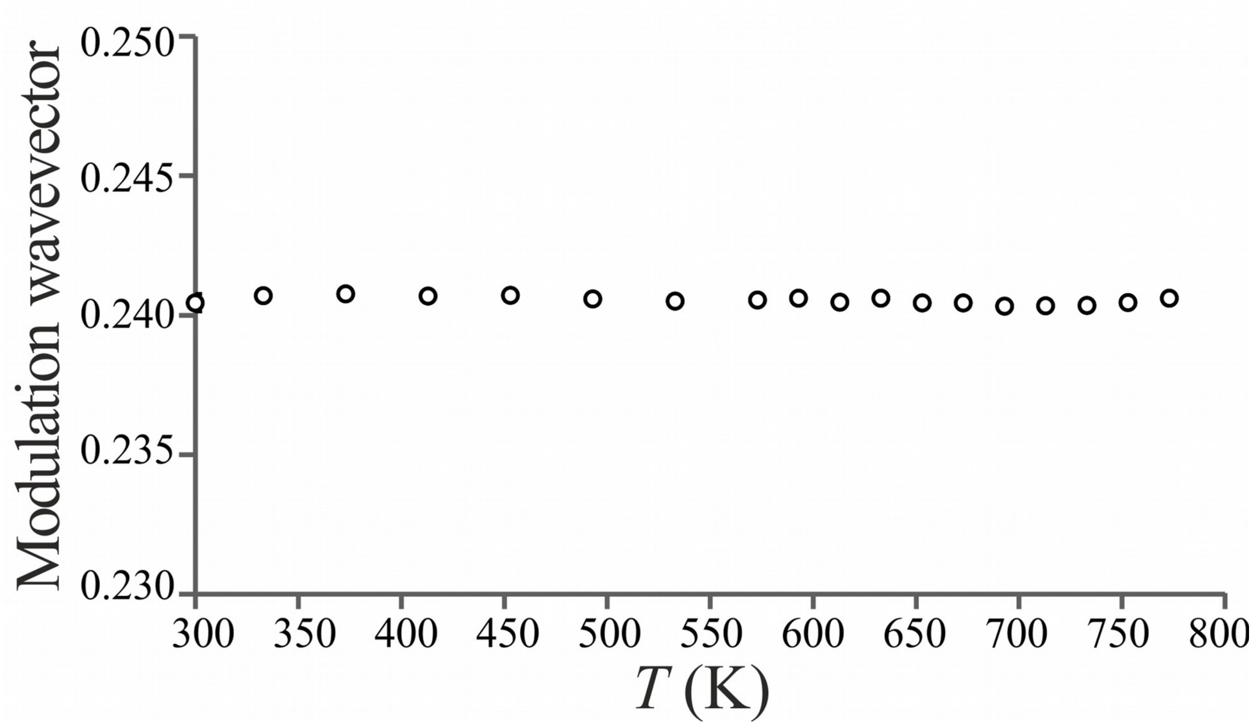

Figure S5 DSC and TG data for Bi_4BO_7I.