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Supporting information for article:

When the difference between incommensurate and commensurate structures becomes elusive: the case of Bi_4BO_7X (X = Cl, Br) oxyhalides

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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_7Cl.

Atom	SOF	Wyckoff site	*x*	*y*	*z*	U_{eq}	*BVS*
Bi	1	4*g*	0.5	0.15371(3)	0.5	0.02037(19)	2.643(1)–3.453(1)
Cl	0.5	2*a*	0	0	0	0.044(2)	0.556(1)–0.664(1)
B	0.5	2*a*	0	0	0	0.044(2)	2.873(1)–3.487 (1)
				0.2475(7)		0.019(2)	2.135(1)–2.315(1)
O1	1	8*l*	0		0.5		
O2	0.5	8*l*	0	–0.078(4)	0	0.019(5)	1.701(1)–2.292(1)
O3	0.25	8*m*	–0.184(8)	–0.090(3)	0	0.037995	1.806(1)–1.982(1)
O4	0.5	8*n*	–0.363	0	0	0.130968	1.374(1)–1.496(1)

Table S2 Anisotropic parameters of atomic displacements in the structure of Bi_4BO_7Cl.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	0.0254(4)	0.0179(3)	0.0178(3)	0	0	0
Cl	0.063(5)	0.028(4)	0.041(4)	0	0	0
B	0.063(5)	0.028(4)	0.041(4)	0	0	0
O1	0.018(4)	0.025(5)	0.014(3)	0	0	0
O2	0.019(8)	0.011(9)	0.026(8)	0	0	0
O3	0.037995	0.037995	0.037995	0	0	0
O4	0.130968	0.130968	0.130968	0	0	0

Table S3 Selected distances (Å) in the crystal structure of Bi_4BO_7Cl.

	Ave.	Min.	Max.
Bi–O1 × 2	2.326(10)	2.209(17)	2.371(17)
Bi–O1 × 2	2.335(14)	2.105(18)	2.609(18)
Bi–O3 × 4	3.394(19)	3.33(2)	3.48(2)
Bi–O4 × 4	2.7959(9)	2.7525(14)	2.8608(14)
Bi–O2 × 4	2.851(10)	2.48(2)	3.34(2)
Bi–Cl × 4	3.461(4)	3.408(6)	3.495(6)
B–O2 × 2	1.306(19)	1.24(2)	1.37(2)
B–O3 × 4	1.40 (3)	1.40 (3)	1.40 (3)
B–O4 × 4	1.4258(12)	1.4258(12)	1.4258(12)

Table S4 Atomic coordinates, displacement parameters (Å^2), site-occupancy factors (SOFs) and bond valence sums (BVS, v.u.) in the structure of Bi_4BO_7Br.

Atom	SOF	Wyckoff site	*x*	*y*	*z*	$U_{eq/iso}$	*BVS*
Bi	1	4*g*	0.5	0.15510(3)	0.5	0.02038(19)	2.74(13)–3.26(13)
Br	0.5	2*a*	0	0	0	0.0221 (7)	0.60(13)–0.76(13)
B	0.5	2*a*	0	0	0.1192	0.0221 (7)	2.40(13)–3.36(13)
O1	1	8*l*	0	0.2440 (11)	0.5	0.014(3)	2.15(13)–2.29(13)
O2	0.25	8*l*	0	0.1042(2)	0.0631(9)	0.057(8)*	1.57(13)–1.90(13)
O3	0.25	8*m*	0.2516(14)	–0.0609(3)	0	0.057(8)*	1.94(13)–2.21(13)
O4	0.5	4*e*	0	0	0.4268(8)	0.1158(8)	1.80(13)–2.14(13)

*Isotropic ADP

Table S5 Anisotropic parameters of atomic displacements in the structure of Bi_4BO_7Br.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	0.0291(4)	0.0172(2)	0.0148(3)	0	0	0
Br	0.0125(12)	0.0214(10)	0.0323(15)	0	0	0
B	0.0125(12)	0.0214(10)	0.0323(15)	0	0	0
O1	0.012(5)	0.019(4)	0.013(5)	0	0	0

Table S6 Selected distances (Å) in the crystal structure of Bi_4BO_7Br.

	Ave.	Min.	Max.
Bi–O1 × 2	2.306(10)	2.187(14)	2.365(14)
Bi–O1 × 2	2.376(15)	2.064(17)	2.655(17)
Bi–O3 × 4	2.4470(14)	2.3578(18)	2.6377(18)
Bi–O2 × 4	2.6393(16)	2.5704(19)	2.7945(19)
Bi–Br × 4	3.4542(3)	3.4178(18)	3.5557(18)
B–O2 × 2	1.3987	1.3987	1.3987
B–O3 × 2	1.3596(6)	1.3596(6)	1.3596(6)
B–O4 × 4	1.2055	1.2055	1.2055

Table S7 Assignment of the vibrational bands observed in the infrared and Raman spectra for Bi_4BO_7Br.

Raman band, cm^{-1}	IR, cm^{-1}	Assignment
88		Bi–O lattice vibrations
115		
		stretching frequencies of the BiO units with Bi–O bonds <2.4 Å
157		
226		
296		
450–608		stretching frequencies of the BiO units with Bi–O bonds >2.4 Å
	705	Bending vibrations of BO_3 groups
		Stretching vibrations of BO_3 groups
915		
1155		
	1210	
	1314	
	1415	Asymmetric stretching vibration of the Bi–Cl band
	1525	

Table S8 Optimized lattice parameters (Å) for Bi_4BO_7Br.

	Optimized	Initial model
a (Å)	4.157	3.935
b (Å)	13.451	13.250
c (Å)	16.194	15.673

Table S9 The decomposition products of Bi_4BO_7Br compound, as obtained from the Materials Project database.

Compound	ICSD #	MP ID #[a]	Space group
$Bi_4Br_2O_5$	412591	mp-23544	$P2_1$
$Bi_4B_2O_9$	250426	mp-23356	$P2_1/c$

[a]The unique ID # from the Materials Project database.

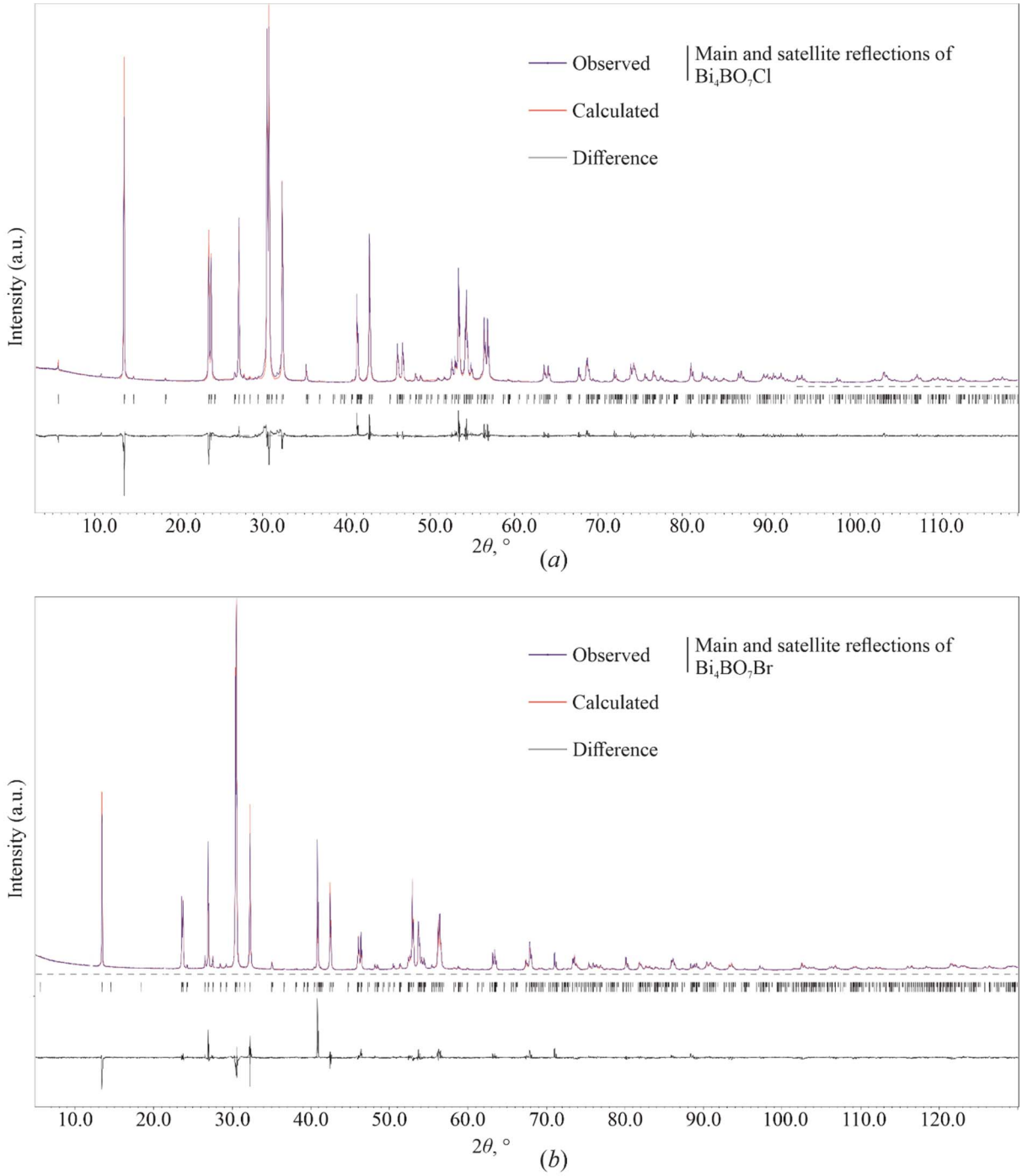

Figure S1 Intensity profiles for the powder X-ray Rietveld refinement of (a) Bi_4BO_7Cl and (b) Bi_4BO_7Br. The observed and calculated profiles are represented in blue and red lines, respectively. The difference profile is plotted at the bottom.

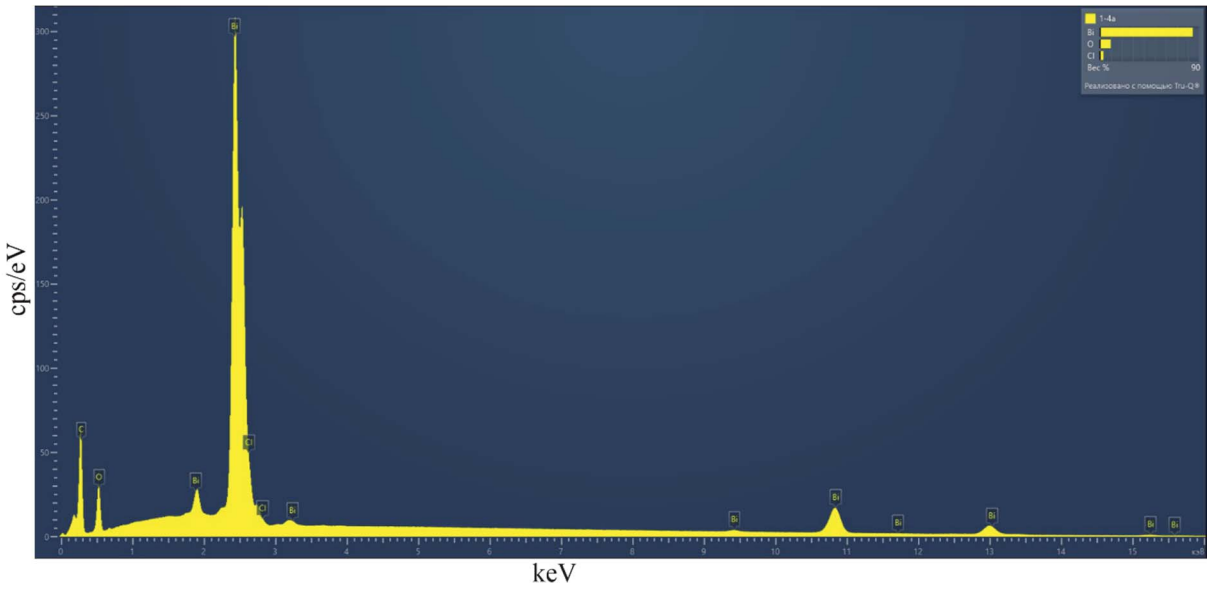

Figure S2 EDX spectrum of Bi_4BO_7Cl.