Supplementary Materials: Single crystal growth of Sillén–Aurivillius perovskite oxyhalides Bi4NbO8X (X = Cl, Br)

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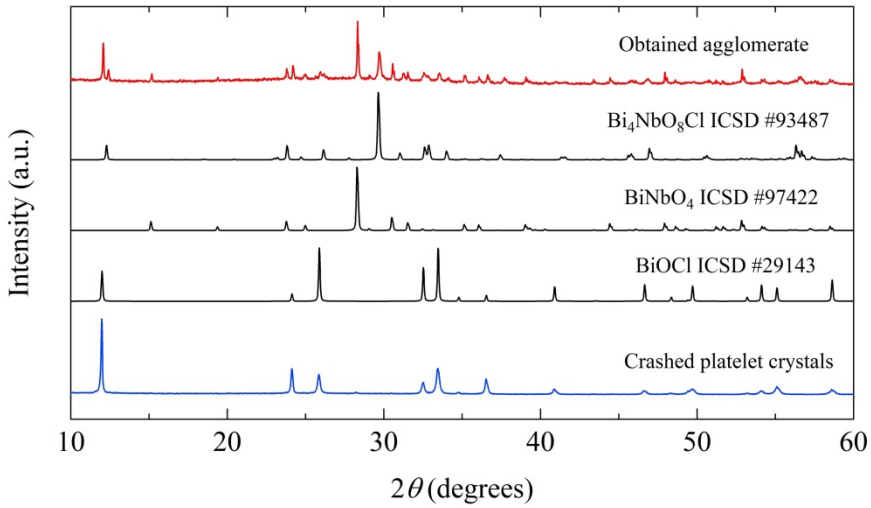

Figure S1. Powder XRD of obtained product when using reported condition (red line) and peak data of Bi_4NbO_8Cl, BiOCl, $BiNbO_4$ from ICSD database.

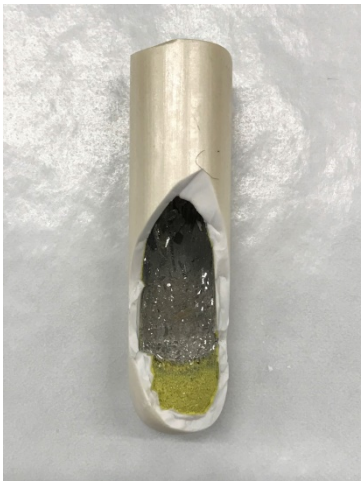

Figure S2. A picture of obtained product. The grey agglomerate is $BiNbO_4$ attached with transparent platelet single crystal of BiOCl on it. The yellow crystalline mass is Bi_4NbO_8Cl.

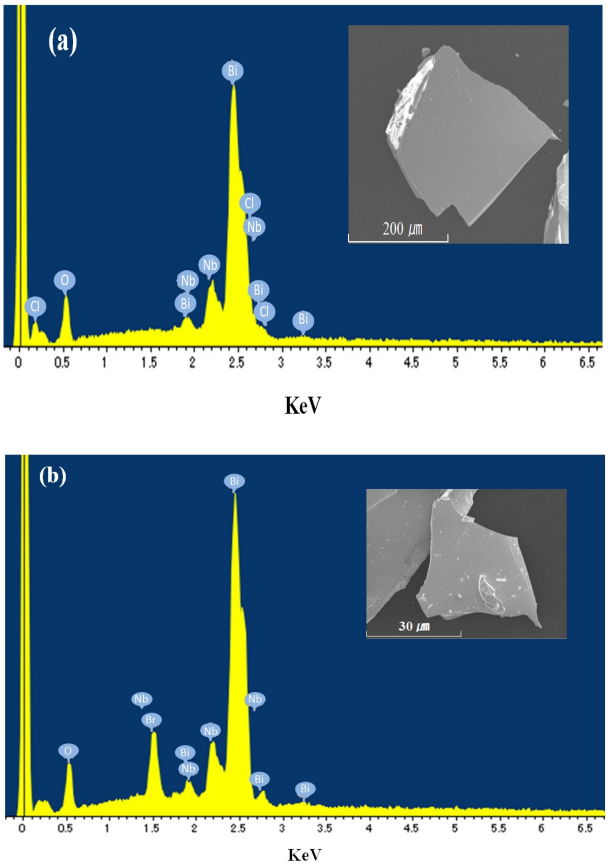

Figure S3. EDX spectrum of (a) Bi_4NbO_8Cl and (b) Bi_4NbO_8Br crystal. The inset shows the crystal in backscattered electron (BSE) mode, highlighting elemental contrast.

Table S1. Refined structural parameters for Bi_4NbO_8Cl at 293 K in the space group $P2_1cn$. Lattice parameters: a = 5.4835(3) Å, b = 5.4850(3) Å, c = 28.682(2) Å.

Atom	x	y	z	U_{iso} (× 100, Å²)
Nb(1)	−0.0056(16)	0.2509(8)	0.2498(2)	0.83(5)
Bi(1)	0	0.7901(5)	0.15930(8)	U_{eq} = 1.50(5)[a]
Bi(2)	0.0021(6)	0.2447(4)	0.42887(9)	0.83(4)
Bi(3)	−0.0405(6)	0.7509(4)	0.34088(10)	U_{eq} = 1.56(6)[a]
Bi(4)	−0.0156(6)	0.2646(4)	0.07119(9)	U_{eq} = 1.35(6)[a]
Cl(1)	0.508(4)	0.2492(12)	0.0002(3)	2.51(19)
O(1)	0.750(10)	0.485(11)	0.3903(17)	1.06(16)[b]
O(2)	0.262(5)	0.512(11)	0.3931(17)	1.06(16)
O(3)	0.754(5)	0.003(12)	0.3898(17)	1.06(16)
O(4)	0.235(5)	0.004(12)	0.3906(18)	1.06(16)
O(5)	0.566(5)	0.659(12)	0.316(2)	1.06(16)
O(6)	0.403(6)	0.839(12)	0.185(2)	1.06(16)
O(7)	0.274(5)	−0.034(13)	0.261(2)	1.06(16)
O(8)	0.772(5)	0.004(12)	0.264(2)	1.06(16)

[a]Anisotropic displacement parameters were refined for Bi(1), Bi(2), and Bi(4).
[b]A common isotropic atomic displacement parameter was refined for oxygen atoms.

Table S2. Selected bond lengths (Å) and angles (°) for Bi_4NbO_8Cl (I: this work; II: Lightfoot [19]).

	I	II
Nb(1)-O(5)	1.87(3)	2.05(2)
Nb(1)-O(6)	2.06(3)	1.96(3)
Nb(1)-O(7)	2.11(3)	2.01(2)
	1.86(3)	1.97(2)
Nb(1)-O(8)	2.24(3)	2.02(2)
	1.78(3)	1.94(2)
Bi(1)-O(1)	2.21(3)	2.37(2)
Bi(1)-O(2)	2.33(3)	2.27(2)
Bi(1)-O(3)	2.69(3)	2.71(2)
Bi(1)-O(4)	2.56(3)	2.58(2)
Bi(1)-O(5)	2.24(3)	2.21(1)
Bi(1)-O(6)	2.36(4)	2.38(3)
Bi(1)-O(7)	3.07(3)	3.02(2)
Bi(1)-O(8)	2.76(3)	3.22(3)
Bi(2)-Cl(1)	3.35(1)	3.25(2)
	3.31(3)	3.40(2)
	3.37(3)	3.45(2)
	3.41(1)	3.32(2)
Bi(2)-O(1)	2.17(3)	2.21(2)
Bi(2)-O(2)	2.2(3)	2.18(2)
Bi(2)-O(3)	2.25(3)	2.29(2)
Bi(2)-O(4)	2.22(3)	2.27(2)
Bi(3)-O(1)	2.54(3)	2.52(2)
Bi(3)-O(2)	2.82(3)	2.56(2)
Bi(3)-O(3)	2.18(3)	2.31(2)
Bi(3)-O(4)	2.35(3)	2.32(2)
Bi(3)-O(5)	2.43(3)	2.36(2)
Bi(3)-O(6)	2.37(3)	3.04(3)
	3.31(3)	2.67(3)

Bi(3)-O(7)	3.03(3)	2.94(2)
Bi(3)-O(8)	3.14(2)	2.86(3)
Bi(4)-Cl(1)	3.37(3)	3.38(2)
	3.29(1)	3.37(2)
	3.48(3)	3.32(2)
	3.39(1)	3.39(1)
Bi(4)-O(1)	2.38(3)	2.17(2)
Bi(4)-O(2)	2.09(3)	2.24(2)
Bi(4)-O(3)	2.23(3)	2.17(2)
Bi(4)-O(4)	2.31(3)	2.24(2)
O(5)-Nb(1)-O(6)	161(1)	172(1)
O(5)-Nb(1)-O(7)	83(1)	82(1)
	95(1)	100(1)
O(5)-Nb(1)-O(8)	79(1)	82(1)
	94(1)	96(1)
O(6)-Nb(1)-O(7)	86(1)	94(1)
	97(1)	87(1)
O(6)-Nb(1)-O(8)	84(1)	89(1)
	97(1)	91(1)
O(7)-Nb(1)-O(7)	174(1)	165(1)
O(7)-Nb(1)-O(8)	71(1)	89(1)
	83(1)	72(1)
	103(1)	106(1)
	103(1)	93(1)
O(8)-Nb(1)-O(8)	153(1)	161(1)
Nb(1)-O(7)-Nb(1)	156(1)	152(3)
Nb(1)-O(8)-Nb(1)	156(1)	156(4)

Table S3. Calculated bond valence sum values of I (this work), II (Lightfoot[19]) and III (Ackerman[9]). Valence parameter of R_o and B are from Brown and Altermatt (1985), Acta Cryst. B41, 244-247.

Atom	Ⅰ	Ⅱ	Ⅲ
Nb(1)	5.35	4.84	5.26
Bi(1)	3.14	2.91	3.20
Bi(2)	3.31	3.16	2.90
Bi(3)	2.79	2.73	5.23
Bi(4)	3.08	3.39	3.39
Cl(1)	0.73	0.75	0.85
O(1)	2.31	2.34	2.54
O(2)	2.43	2.38	2.79
O(3)	2.34	2.15	2.85
O(4)	2.05	2.10	2.51
O(5)	2.19	1.94	2.15
O(6)	1.63	1.69	3.27
O(7)	1.88	1.76	1.82
O(8)	2.06	1.83	1.20

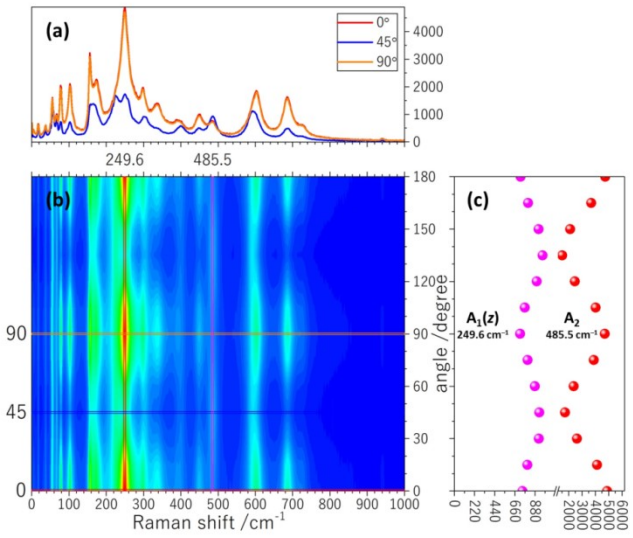

Figure S4. (a) Raman spectra obtained in cross nicol geometries in a spectral range from 0 to 1000 cm^{-1}. (b) Contour plots of angular dependences of the polarized Raman intensity. (c) Angular dependence of integrated Raman intensities of $A_1(z)$ modes (pink), and A_2 modes (red).

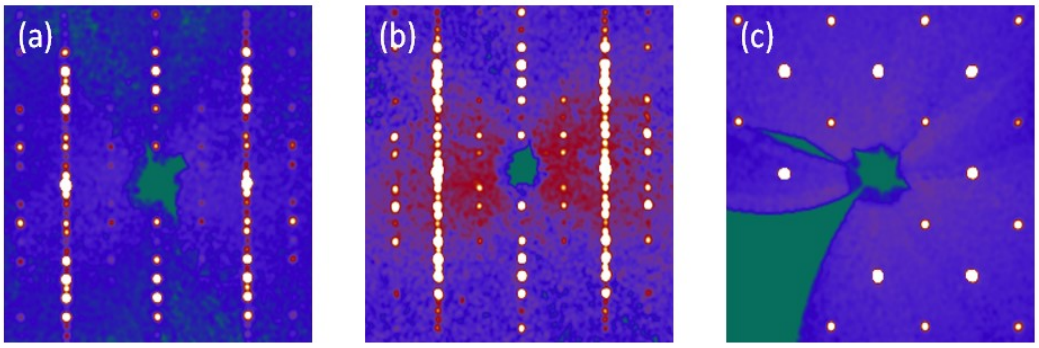

Figure S5. Reciprocal lattice plane of (a) 0*kl* (b) *h*0*l*, and (c) *hk*0 reconstructed from raw single crystal diffraction data.

Table S4. Refined structural parameters for Bi_4NbO_8Br at 293 K in the space group $P2_1cn$. Lattice parameters: a = 5.51190(10) Å, b = 5.51190(10) Å, c = 29.0984(14) Å.

Atom	*x*	*y*	*z*	U_{iso} (× 100, Å²)
Nb(1)	0.0510(3)	0.2509(8)	0.2498(2)	0.0104(15)
Bi(1)	0	0.7901(5)	0.15930(8)	0.0202(8)
Bi(2)	0.0450(2)	0.2447(4)	0.42887(9)	0.0122(7)
Bi(3)	0.0020(2)	0.7509(4)	0.34088(10)	0.0131(7)
Bi(4)	0.0480(2)	0.2646(4)	0.07119(9)	0.0112(7)
Br(1)	0.5530(3)	0.2492(12)	0.0002(3)	0.0210(17)
O(1)	0.8000(16)	0.485(11)	0.3903(17)	0.019(5) [a]
O(2)	0.3110(15)	0.512(11)	0.3931(17)	0.019(5)
O(3)	0.8060(15)	0.003(12)	0.3898(17)	0.019(5)
O(4)	0.2880(16)	0.004(12)	0.3906(18)	0.019(5)
O(5)	0.6280(14)	0.659(12)	0.316(2)	0.019(5)
O(6)	0.6180(14)	0.839(12)	0.185(2)	0.019(5)
O(7)	0.3210(13)	-0.034(13)	0.261(2)	0.019(5)
O(8)	0.8660(13)	0.004(12)	0.264(2)	0.019(5)

[a] A common isotropic atomic displacement parameter was refined for O(1)-O(8)

Table S5. Selected bond lengths (Å) and angles (°) for Bi_4NbO_8Br.

Bond lengths	(Å)	Angles	(°)
Nb(1)-O(5)	2.01(5)	O(5)-Nb(1)-O(6)	157(3)
Nb(1)-O(6)	2.20(7)	O(5)-Nb(1)-O(7)	84(2)
Nb(1)-O(7)	2.27(7)		99(3)
	1.76(7)	O(5)-Nb(1)-O(8)	82(3)
Nb(1)-O(8)	2.27(7)		95(3)
	1.74(7)	O(6)-Nb(1)-O(7)	80(3)
Bi(1)-O(1)	2.60(7)		98(3)
Bi(1)-O(2)	2.26(6)	O(6)-Nb(1)-O(8)	82(3)
Bi(1)-O(3)	2.64(7)		97(3)
Bi(1)-O(4)	2.36(7)	O(7)-Nb(1)-O(7)	176(4)
Bi(1)-O(5)	2.49(6)	O(7)-Nb(1)-O(8)	79(3)
Bi(1)-O(6)	2.29(7)		87(3)
Bi(1)-O(7)	3.15(7)		96(3)
Bi(1)-O(8)	2.76(6)		98(4)
Bi(2)-Br(1)	3.391(8)	O(8)-Nb(1)-O(8)	166(4)
	3.412(11)	Nb(1)-O(7)-Nb(1)	161(4)
	3.479(11)	Nb(1)-O(8)-Nb(1)	153(4)
	3.512(8)		
Bi(2)-O(1)	2.19(9)		
Bi(2)-O(2)	2.27(9)		
Bi(2)-O(3)	2.19(8)		
Bi(2)-O(4)	2.32(8)		
Bi(3)-O(1)	2.42(7)		
Bi(3)-O(2)	2.73(6)		
Bi(3)-O(3)	2.23(7)		
Bi(3)-O(4)	2.40(7)		
Bi(3)-O(5)	2.21(7)		
Bi(3)-O(6)	2.25(6)		
	3.61(6)		
Bi(3)-O(7)	3.10(6)		
Bi(3)-O(8)	3.39(7)		
Bi(4)-Br(1)	3.423(8)		
	3.429(11)		
	3.463(8)		
	3.472(11)		
Bi(4)-O(1)	2.22(9)		
Bi(4)-O(2)	2.17(9)		
Bi(4)-O(3)	2.29(8)		
Bi(4)-O(4)	2.25(8)		

Table S6. Crystallographic data for Bi_4NbO_8Cl and Bi_4NbO_8Br.

Crystal data		
Empirical formula	Bi_4NbO_8Cl	Bi_4NbO_8Br
Crystal habit (color)	Platelet, yellow	Platelet, yellow
Crtsral size (μm)		
Cell ststem, space group	Orthorhombic, $P2_1cn$	Orthorhombic, $P2_1cn$
Cell dimensions (Å)		
a	5.4835(3)	5.51190(10)
b	5.4850(3)	5.51190(10)
c	28.682(2)	29.0984(14)
Volume (Å^3)	862.67(10)	884.04(5)
Z	4	4
Temperature (K)	293	293
θ_{max} (°)	26.31	26.36
Number of independent reflections	1846 [R_{int}=0.0494]	1978 [R_{int}=0.1167]
No. of parameters	68	54
R_1,wR_2	0.0374, 0.1000	0.0850, 0.2450
S	1.038	1.161