Supporting Information

Effect of Halogen (Cl, Br) on the Symmetry of Flexible Perovskite-related Framework

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Table S1 Atomic coordinates, equivalent isotropic displacement parameters ($Å^2$) and bond valence analyses for $Na_3B_6O_{10}Cl$, $RbNa_2B_6O_{10}Cl$, $RbNa_2B_6O_{10}Br$.

$Na_3B_6O_{10}Cl$						
Atom	Wyck	x	y	z	U(eq) [a]	BVS [b,c]
Na(1)	4a	0.4478(2)	0.2095(1)	0.2429(1)	0.028(1)	1.023
Na(2)	4a	0.9748(2)	0.2590(1)	0.2543(1)	0.030(1)	0.913
Na(3)	4a	0.1312(2)	0.0032(2)	0.4427(1)	0.044(1)	0.819
B(1)	4a	0.2514(4)	0.4990(3)	0.2436(2)	0.012(1)	3.036
B(2)	4a	0.0227(5)	0.7333(3)	0.5195(3)	0.012(1)	3.072
B(3)	4a	0.7522(4)	0.1307(3)	0.5902(3)	0.011(1)	3.074
B(4)	4a	0.1141(4)	0.5023(4)	0.5660(2)	0.012(1)	3.047
B(5)	4a	0.0169(5)	0.2692(3)	0.5237(3)	0.012(1)	3.071
B(6)	4a	0.7600(4)	0.8702(3)	0.5884(3)	0.010(1)	3.065
O(1)	4a	0.1856(2)	0.5001(2)	0.4553(1)	0.009(1)	2.057
O(2)	4a	0.1282(3)	0.2612(2)	0.4395(2)	0.015(1)	2.031
O(3)	4a	0.1360(3)	0.7385(2)	0.4348(2)	0.014(1)	2.027
O(4)	4a	0.2480(3)	0.3782(2)	0.2958(2)	0.013(1)	2.197
O(5)	4a	0.2721(3)	0.6175(2)	0.2974(2)	0.013(1)	2.191
O(6)	4a	0.9973(3)	0.3847(2)	0.5809(2)	0.017(1)	1.976
O(7)	4a	0.2354(2)	0.5017(2)	0.1384(2)	0.019(1)	1.828
O(8)	4a	0.0076(3)	0.6233(2)	0.5811(2)	0.019(1)	1.945
O(9)	4a	0.9307(3)	0.1540(2)	0.5504(2)	0.016(1)	2.010
O(10)	4a	0.9362(3)	0.8501(2)	0.5424(2)	0.015(1)	2.081
Cl(1)	4a	0.1810(1)	0.0163(1)	0.2200(1)	0.030(1)	0.644
$RbNa_2B_6O_{10}Cl$						
Rb(1)	4a	0.4800(1)	0.7522(1)	0.2620(1)	0.038(1)	1.081
Na(1)	4a	0.2708(2)	0.5033(2)	0.0354(2)	0.042(1)	0.769
Na(2)	4a	0.4606(2)	0.7203(1)	0.7576(1)	0.035(1)	0.995
B(1)	4a	0.5484(4)	0.7383(4)	0.5221(2)	0.012(1)	3.085
B(2)	4a	0.4585(4)	0.7655(3)	0.9871(2)	0.012(1)	3.085
B(3)	4a	0.1996(3)	0.0047(4)	0.2270(2)	0.013(1)	3.096

B(4)	4a	0.2085(4)	0.8672(3)	0.0609(2)	0.010(1)	3.084
B(5)	4a	0.1170(3)	0.0007(3)	0.4218(2)	0.010(1)	3.068
B(6)	4a	0.7916(4)	0.6355(3)	0.4402(3)	0.010(1)	3.082
O(1)	4a	0.2812(2)	0.0010(2)	0.0201(1)	0.008(1)	2.024
O(2)	4a	0.2210(2)	0.0044(3)	0.3322(2)	0.023(1)	1.963
O(3)	4a	0.6872(2)	0.7508(2)	0.4664(1)	0.015(1)	2.100
O(4)	4a	0.3221(2)	0.7555(2)	0.0459(2)	0.015(1)	2.111
O(5)	4a	0.5140(3)	0.6229(2)	0.5798(2)	0.016(1)	2.0161
O(6)	4a	0.4494(3)	0.8493(2)	0.5150(2)	0.016(1)	1.999
O(7)	4a	0.1864(2)	0.8824(2)	0.1746(2)	0.014(1)	2.206
O(8)	4a	0.5581(2)	0.6556(2)	0.9920(2)	0.015(1)	1.978
O(9)	4a	0.2040(3)	0.1276(2)	0.1744(2)	0.014(1)	2.213
O(10)	4a	0.4890(3)	0.8784(2)	0.9252(2)	0.020(1)	1.983
Cl(1)	4a	0.7415(1)	0.9872(1)	0.1958(1)	0.044(1)	0.771
$RbNa_2B_6O_{10}Br$						
Rb(1)	4b	0.5000	0	0	0.043(1)	1.081
Na(1)	4c	0.2048(3)	0.2500	0.2675(5)	0.035(1)	0.829
Na(2)	4a	0.5000	0	0.5000	0.034(1)	0.877
B(1)	4c	0.3288(7)	0.7500	0.3884(1)	0.011(2)	3.037
B(2)	8d	0.2669(5)	0.9875(7)	0.4620(7)	0.014(1)	3.069
B(3)	8d	0.1901(4)	0.8855(6)	0.2162(7)	0.009(1)	3.061
B(4)	4c	0.5242(6)	0.7500	0.3015(1)	0.011(2)	3.167
O(1)	8d	0.2076(3)	0.9981(4)	0.3264(4)	0.014(1)	2.120
O(2)	8d	0.1735(3)	0.1273(4)	0.9934(5)	0.017(1)	1.991
O(3)	4c	0.2297(4)	0.7500	0.2890(6)	0.009(1)	1.995
O(4)	4c	0.4190(4)	0.7500	0.2861(7)	0.021(1)	1.949
O(5)	8d	0.0758(3)	0.8728(4)	0.1977(5)	0.013(1)	2.231
O(6)	8d	0.2575(3)	0.0950(4)	0.5649(4)	0.016(1)	1.966
Br(1)	4c	0.4469(1)	0.2500	0.2622(1)	0.035(1)	0.860

[a] U(eq) is defined as the one-third of the trace of the orthogonalized U_{ij} tensor;

[b] Bond valences calculated with the program Bond Valence Calculator Version 2.00, C. Hormillosa,

S. Healy, T. Stephen, McMaster University, 1993;

[c] Valence sums calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond "i" and B = 0.37.

Table S2

Selected bond distances (in Å) and angles (in deg.) for $Na_3B_6O_{10}Cl$.[a]

Na(1)-O(5)#1	2.333(3)	B(1)-O(5)	1.373(4)
Na(1)-O(4)	2.341(3)	B(1)-O(4)	1.374(4)
Na(1)-O(6)#2	2.470(3)	B(2)-O(8)	1.352(4)
Na(1)-O(8)#3	2.676(3)	B(2)-O(10)	1.359(4)
Na(1)-O(9)#2	2.976(4)	B(2)-O(3)	1.375(4)
Na(1)-O(10)#3	2.772(4)	B(3)-O(9)	1.441(4)
Na(1)-Cl(1)	2.777(3)	B(3)-O(4)#12	1.463(4)
Na(2)-O(5)#4	2.405(3)	B(3)-O(2)#12	1.466(4)
Na(2)-O(4)	2.411(3)	B(3)-O(1)#12	1.508(4)
Na(2)-O(3)#4	2.565(4)	B(4)-O(8)	1.453(4)
Na(2)-O(2)	2.632(4)	B(4)-O(7)#10	1.454(4)
Na(2)-Cl(1)#5	2.826(3)	B(4)-O(6)	1.470(4)
Na(2)-Cl(1)	2.892(3)	B(4)-O(1)	1.513(4)
Na(3)-O(10)#8	2.460(3)	B(5)-O(9)	1.356(4)
Na(3)-O(9)	2.524(3)	B(5)-O(2)	1.362(4)
Na(3)-O(2)	2.564(4)	B(5)-O(6)	1.368(4)
Na(3)-O(7)#4	2.917(4)	B(6)-O(10)	1.451(4)
Na(3)-O(6)#2	2.957(4)	B(6)-O(3)#13	1.451(4)
Na(3)-O(3)#8	2.633(4)	B(6)-O(5)#13	1.470(4)
Na(3)-Cl(1)	2.878(4)	B(6)-O(1)#13	1.510(4)
B(1)-O(7)	1.353(4)	O(5)#1-Na(1)-O(4)	155.73(10)
O(5)#1-Na(1)-O(6)#2	85.44(10)	O(4)-Na(1)-Cl(1)	94.16(11)
O(4)-Na(1)-O(6)#2	95.83(10)	O(6)#2-Na(1)-Cl(1)	86.62(8)
O(5)#1-Na(1)-O(8)#3	87.78(9)	O(8)#3-Na(1)-Cl(1)	115.85(8)
O(4)-Na(1)-O(8)#3	81.84(10)	O(10)#3-Na(1)-Cl(1)	88.67(7)
O(6)#2-Na(1)-O(8)#3	157.48(10)	O(5)#1-Na(1)-O(9)#2	114.41(9)
O(5)#1-Na(1)-O(10)#3	55.50(7)	O(4)-Na(1)-O(9)#2	52.35(8)
O(4)-Na(1)-O(10)#3	128.21(9)	O(6)#2-Na(1)-O(9)#2	50.72(9)
O(6)#2-Na(1)-O(10)#3	135.94(9)	O(8)#3-Na(1)-O(9)#2	114.25(11)
O(8)#3-Na(1)-O(10)#3	51.47(9)	O(10)#3-Na(1)-O(9)#2	159.05(9)
O(5)#1-Na(1)-Cl(1)	110.10(10)	Cl(1)-Na(1)-O(9)#2	112.25(7)

O(5)#4-Na(2)-O(4)	172.33(10)	O(2)-Na(3)-O(6)#2	68.26(8)
O(5)#4-Na(2)-O(3)#4	56.55(8)	O(3)#8-Na(3)-O(6)#2	111.11(9)
O(4)-Na(2)-O(3)#4	121.18(10)	Cl(1)-Na(3)-O(6)#2	76.33(5)
O(5)#4-Na(2)-O(2)	125.71(10)	O(7)#4-Na(3)-O(6)#2	145.69(9)
O(4)-Na(2)-O(2)	55.38(8)	O(7)-B(1)-O(5)	119.5(3)
O(3)#4-Na(2)-O(2)	172.01(10)	O(7)-B(1)-O(4)	120.0(3)
O(5)#4-Na(2)-Cl(1)#5	104.36(10)	O(5)-B(1)-O(4)	120.5(3)
O(4)-Na(2)-Cl(1)#5	82.81(9)	O(8)-B(2)-O(10)	121.6(3)
O(3)#4-Na(2)-Cl(1)#5	92.86(7)	O(8)-B(2)-O(3)	122.8(3)
O(2)-Na(2)-Cl(1)#5	93.73(7)	O(10)-B(2)-O(3)	115.4(3)
O(5)#4-Na(2)-Cl(1)	82.84(10)	O(9)-B(3)-O(4)#12	112.5(3)
O(4)-Na(2)-Cl(1)	89.82(10)	O(9)-B(3)-O(2)#12	111.7(3)
O(3)#4-Na(2)-Cl(1)	87.76(7)	O(4)#12-B(3)-O(2)#12	106.8(3)
O(2)-Na(2)-Cl(1)	85.07(7)	O(9)-B(3)-O(1)#12	107.8(3)
Cl(1)#5-Na(2)-Cl(1)	171.75(6)	O(4)#12-B(3)-O(1)#12	109.0(2)
O(5)#4-Na(2)-B(6)#6	28.47(8)	O(2)#12-B(3)-O(1)#12	109.0(2)
O(10)#8-Na(3)-O(9)	74.67(10)	O(9)-B(3)-Na(1)#12	73.91(17)
O(10)#8-Na(3)-O(2)	128.45(10)	O(8)-B(4)-O(7)#10	110.9(2)
O(9)-Na(3)-O(2)	53.83(8)	O(8)-B(4)-O(6)	108.6(2)
O(10)#8-Na(3)-O(3)#8	53.83(8)	O(7)#10-B(4)-O(6)	110.5(2)
O(9)-Na(3)-O(3)#8	128.49(9)	O(8)-B(4)-O(1)	109.2(2)
O(2)-Na(3)-O(3)#8	176.86(8)	O(7)#10-B(4)-O(1)	109.0(2)
O(10)#8-Na(3)-Cl(1)	128.17(8)	O(6)-B(4)-O(1)	108.5(2)
O(9)-Na(3)-Cl(1)	126.19(9)	O(9)-B(5)-O(2)	115.9(3)
O(2)-Na(3)-Cl(1)	86.57(6)	O(9)-B(5)-O(6)	121.5(3)
O(3)#8-Na(3)-Cl(1)	90.29(6)	O(2)-B(5)-O(6)	122.5(3)
O(10)#8-Na(3)-O(7)#4	68.32(10)	O(10)-B(6)-O(3)#13	112.9(3)
O(9)-Na(3)-O(7)#4	69.24(10)	O(10)-B(6)-O(5)#13	111.1(3)
O(2)-Na(3)-O(7)#4	89.50(8)	O(3)#13-B(6)-O(5)#13	107.7(3)
O(3)#8-Na(3)-O(7)#4	89.64(8)	O(10)-B(6)-O(1)#13	107.3(2)
Cl(1)-Na(3)-O(7)#4	76.57(7)	O(3)#13-B(6)-O(1)#13	109.1(3)
O(10)#8-Na(3)-O(6)#2	145.99(9)	O(5)#13-B(6)-O(1)#13	108.7(2)
O(9)-Na(3)-O(6)#2	112.07(10)		

[a] Symmetry transformations used to generate equivalent atoms:

(#1) -x+1, y-1/2, -z+1/2, (#2) x+1/2, -y+1/2, -z+1, (#3) -x+1/2, -y+1, z-1/2, (#4) -x, y-1/2, -z+1/2, (#5) -x, y+1/2, -z+1/2, (#6) -x-1/2, -y+1, z-1/2, (#7) x-1, y, z, (#8) x, y-1, z, (#9) -x+1, y+1/2, -z+1/2, (#10) -x+1/2, -y+1, z+1/2, (#11) x, y+1, z, (#12) x-1/2, -y+1/2, -z+1, (#13) x-1/2, -y+3/2, -z+1, (#14) -x-1/2, -y+1, z+1/2, (#15) x+1/2, -y+3/2, -z+1.

Table S3

Selected bond lengths (in Å) and angles (in deg.) for $RbNa_2B_6O_{10}Cl$.[a]

Rb(1)-O(7)	2.966(2)	B(1)-O(6)	1.354(4)
Rb(1)-O(9)#1	3.004(2)	B(1)-O(3)	1.362(3)
Rb(1)-O(4)	3.0540(19)	B(1)-O(5)	1.366(4)
Rb(1)-O(6)	3.370(2)	B(2)-O(8)	1.348(4)
Rb(1)-O(2)	3.374(2)	B(2)-O(4)	1.364(4)
Rb(1)-O(3)	3.1252(19)	B(2)-O(10)	1.370(4)
Rb(1)-O(8)	3.627(2)	B(3)-O(2)	1.354(4)
Rb(1)-Cl(1)#1	3.1996(11)	B(3)-O(7)	1.361(4)
Rb(1)-Cl(1)	3.2560(11)	B(3)-O(9)	1.364(4)
Na(1)-O(3)#1	2.462(3)	B(4)-O(8)#4	1.439(4)
Na(1)-O(4)	2.476(3)	B(4)-O(4)	1.447(4)
Na(1)-O(10)#4	2.657(3)	B(4)-O(7)	1.469(4)
Na(1)-O(5)#5	2.725(3)	B(4)-O(1)	1.518(4)
Na(1)-O(6)#1	2.837(3)	B(5)-O(2)	1.434(3)
Na(1)-O(8)	2.862(3)	B(5)-O(10)#10	1.464(4)
Na(1)-Cl(1)#4	2.960(2)	B(5)-O(5)#11	1.470(3)
Na(2)-O(9)#7	2.273(2)	B(5)-O(1)#10	1.513(3)
Na(2)-O(7)#2	2.294(2)	B(6)-O(6)#12	1.440(4)
Na(2)-O(5)#8	2.496(2)	B(6)-O(3)	1.451(4)
Na(2)-O(10)	2.637(2)	B(6)-O(9)#1	1.464(4)
Na(2)-Cl(1)#4	2.7729(19)	B(6)-O(1)#1	1.521(4)
O(7)-Rb(1)-O(9)#1	173.12(6)	O(7)-Rb(1)-Cl(1)	99.10(4)
O(7)-Rb(1)-O(4)	45.70(5)	O(9)#1-Rb(1)-Cl(1)	76.34(4)
O(9)#1-Rb(1)-O(4)	128.66(6)	O(4)-Rb(1)-Cl(1)	92.65(4)
O(7)-Rb(1)-O(3)	140.36(5)	O(3)-Rb(1)-Cl(1)	81.40(4)
O(9)#1-Rb(1)-O(3)	44.76(5)	Cl(1)#1-Rb(1)-Cl(1)	170.50(3)
O(4)-Rb(1)-O(3)	171.99(5)	O(7)-Rb(1)-O(6)	100.36(5)
O(7)-Rb(1)-Cl(1)#1	85.81(4)	O(9)#1-Rb(1)-O(6)	85.36(5)
O(9)#1-Rb(1)-Cl(1)#1	97.99(4)	O(4)-Rb(1)-O(6)	145.98(5)
O(4)-Rb(1)-Cl(1)#1	84.95(4)	O(3)-Rb(1)-O(6)	40.92(5)
O(3)-Rb(1)-Cl(1)#1	100.05(4)	Cl(1)#1-Rb(1)-O(6)	91.01(4)

Cl(1)-Rb(1)-O(6)	96.05(4)	O(6)#1-Na(1)-Cl(1)#4	81.84(7)
O(7)-Rb(1)-O(2)	42.88(5)	O(8)-Na(1)-Cl(1)#4	81.96(7)
O(9)#1-Rb(1)-O(2)	141.00(5)	O(9)#7-Na(2)-O(7)#2	161.70(11)
O(4)-Rb(1)-O(2)	87.54(5)	O(9)#7-Na(2)-O(5)#8	85.76(8)
O(3)-Rb(1)-O(2)	97.73(5)	O(7)#2-Na(2)-O(5)#8	91.93(8)
Cl(1)#1-Rb(1)-O(2)	99.44(4)	O(9)#7-Na(2)-O(10)	93.35(8)
Cl(1)-Rb(1)-O(2)	89.62(5)	O(7)#2-Na(2)-O(10)	82.61(8)
O(6)-Rb(1)-O(2)	59.79(5)	O(5)#8-Na(2)-O(10)	159.83(10)
O(7)-Rb(1)-O(8)	84.24(5)	O(9)#7-Na(2)-Cl(1)#4	99.83(8)
O(9)#1-Rb(1)-O(8)	89.80(5)	O(7)#2-Na(2)-Cl(1)#4	98.40(7)
O(4)-Rb(1)-O(8)	38.98(5)	O(5)#8-Na(2)-Cl(1)#4	92.29(7)
O(3)-Rb(1)-O(8)	133.78(5)	O(10)-Na(2)-Cl(1)#4	107.68(7)
Cl(1)#1-Rb(1)-O(8)	93.29(4)	O(6)-B(1)-O(3)	114.3(3)
Cl(1)-Rb(1)-O(8)	79.21(4)	O(6)-B(1)-O(5)	123.6(3)
O(6)-Rb(1)-O(8)	173.93(6)	O(3)-B(1)-O(5)	122.1(3)
O(2)-Rb(1)-O(8)	123.52(5)	O(8)-B(2)-O(4)	115.5(3)
O(3)#1-Na(1)-O(4)	161.70(9)	O(8)-B(2)-O(10)	122.6(3)
O(3)#1-Na(1)-O(10)#4	123.54(9)	O(4)-B(2)-O(10)	121.8(3)
O(4)-Na(1)-O(10)#4	73.71(7)	O(2)-B(3)-O(7)	119.7(3)
O(3)#1-Na(1)-O(5)#5	71.52(7)	O(2)-B(3)-O(9)	119.1(3)
O(4)-Na(1)-O(5)#5	125.36(9)	O(7)-B(3)-O(9)	121.0(3)
O(10)#4-Na(1)-O(5)#5	52.02(6)	O(8)#4-B(4)-O(4)	113.1(2)
O(3)#1-Na(1)-O(6)#1	50.40(7)	O(8)#4-B(4)-O(7)	111.6(2)
O(4)-Na(1)-O(6)#1	112.70(8)	O(4)-B(4)-O(7)	106.7(2)
O(10)#4-Na(1)-O(6)#1	173.19(9)	O(8)#4-B(4)-O(1)	108.4(2)
O(5)#5-Na(1)-O(6)#1	121.81(9)	O(4)-B(4)-O(1)	109.1(2)
O(3)#1-Na(1)-O(8)	112.83(8)	O(7)-B(4)-O(1)	107.7(2)
O(4)-Na(1)-O(8)	50.27(6)	O(2)-B(5)-O(10)#10	111.6(2)
O(10)#4-Na(1)-O(8)	123.63(9)	O(2)-B(5)-O(5)#11	111.2(2)
O(5)#5-Na(1)-O(8)	175.63(9)	O(10)#10-B(5)-O(5)#11	107.2(2)
O(6)#1-Na(1)-O(8)	62.56(6)	O(2)-B(5)-O(1)#10	108.8(2)
O(3)#1-Na(1)-Cl(1)#4	91.91(8)	O(10)#10-B(5)-O(1)#10	108.8(2)
O(4)-Na(1)-Cl(1)#4	92.17(8)	O(5)#11-B(5)-O(1)#10	109.2(2)
O(10)#4-Na(1)-Cl(1)#4	95.89(7)	O(6)#12-B(6)-O(3)	112.2(2)
O(5)#5-Na(1)-Cl(1)#4	98.58(7)	O(6)#12-B(6)-O(9)#1	112.3(2)

O(3)-B(6)-O(9)#1	106.6(2)	O(3)-B(6)-O(1)#1	109.9(2)
O(6)#12-B(6)-O(1)#1	108.6(2)	O(9)#1-B(6)-O(1)#1	107.3(2)

[a] Symmetry transformations used to generate equivalent atoms:

(#1) -x+1, y-1/2, -z+1/2, (#2) x+1/2, -y+3/2, -z, (#3) -x+1, y+1/2, -z+1/2, (#4) x-1/2, -y+3/2, -z, (#5) -x+1/2, -y+1, z-1/2, (#6) -x+1/2, -y+1, z+1/2, (#7) -x+1/2, -y+2, z-1/2, (#8) x, y, z-1, (#9) x, y, z+1, (#10) -x+1/2, -y+2, z+1/2, (#1) 1 x-1/2, -y+3/2, -z+1, (#12) x+1/2, -y+3/2, -z+1.

Table S4

Selected bond distances (in Å) and angles (in deg.) for $RbNa_2B_6O_{10}Br$ [a].

Rb(1)-O(5)#1	2.977(4)	Na(2)-O(2)#6	2.531(4)
Rb(1)-O(5)#2	2.977(4)	Na(2)-O(2)#2	2.531(4)
Rb(1)-O(1)#1	3.025(4)	Na(2)-Br(1)	3.1960(15)
Rb(1)-O(1)#2	3.025(4)	Na(2)-Br(1)#8	3.1960(15)
Rb(1)-Br(1)	3.3275(16)	B(1)-O(4)	1.436(10)
Rb(1)-Br(1)#3	3.3275(16)	B(1)-O(2)#6	1.472(7)
Rb(1)-O(6)#1	3.456(4)	B(1)-O(2)#10	1.472(7)
Rb(1)-O(6)#2	3.456(4)	B(1)-O(3)	1.515(10)
Na(1)-O(1)#4	2.471(4)	B(2)-O(6)	1.352(8)
Na(1)-O(1)	2.471(4)	B(2)-O(2)#6	1.366(7)
Na(1)-O(2)	2.615(6)	B(2)-O(1)	1.371(7)
Na(1)-O(2)#4	2.615(6)	B(3)-O(1)	1.441(7)
Na(1)-O(6)#4	2.983(6)	B(3)-O(6)#1	1.447(7)
Na(1)-O(6)	2.983(6)	B(3)-O(5)	1.472(7)
Na(1)-Br(1)	3.091(4)	B(3)-O(3)	1.525(6)
Na(1)-Br(1)#5	3.303(5)	B(4)-O(4)	1.349(10)
Na(2)-O(5)#6	2.277(4)	B(4)-O(5)#2	1.353(5)
Na(2)-O(5)#2	2.277(4)	B(4)-O(5)#11	1.353(5)
O(5)#1-Rb(1)-O(5)#2	180.00(13)	O(1)#2-Rb(1)-Br(1)#3	97.77(8)
O(5)#1-Rb(1)-O(1)#1	45.75(10)	Br(1)-Rb(1)-Br(1)#3	180
O(5)#2-Rb(1)-O(1)#1	134.25(10)	O(5)#1-Rb(1)-O(6)#1	86.17(10)
O(5)#1-Rb(1)-O(1)#2	134.25(10)	O(5)#2-Rb(1)-O(6)#1	93.83(10)
O(5)#2-Rb(1)-O(1)#2	45.75(10)	O(1)#1-Rb(1)-O(6)#1	40.86(9)
O(1)#1-Rb(1)-O(1)#2	180	O(1)#2-Rb(1)-O(6)#1	139.14(9)
O(5)#1-Rb(1)-Br(1)	101.55(8)	Br(1)-Rb(1)-O(6)#1	83.83(7)
O(5)#2-Rb(1)-Br(1)	78.45(8)	Br(1)#3-Rb(1)-O(6)#1	96.17(7)
O(1)#1-Rb(1)-Br(1)	97.77(8)	B(2)#1-Rb(1)-O(6)#1	22.65(13)
O(1)#2-Rb(1)-Br(1)	82.23(8)	B(2)#2-Rb(1)-O(6)#1	157.35(13)
O(5)#1-Rb(1)-Br(1)#3	78.45(8)	O(5)#1-Rb(1)-O(6)#2	93.83(10)
O(5)#2-Rb(1)-Br(1)#3	101.55(8)	O(5)#2-Rb(1)-O(6)#2	86.17(10)
O(1)#1-Rb(1)-Br(1)#3	82.23(8)	O(1)#1-Rb(1)-O(6)#2	139.14(9)

O(1)#2-Rb(1)-O(6)#2	40.86(9)	O(5)#6-Na(2)-O(5)#2	180
Br(1)-Rb(1)-O(6)#2	96.17(7)	O(5)#6-Na(2)-O(2)#6	84.45(13)
Br(1)#3-Rb(1)-O(6)#2	83.83(7)	O(5)#2-Na(2)-O(2)#6	95.55(13)
O(6)#1-Rb(1)-O(6)#2	180	O(5)#6-Na(2)-O(2)#2	95.55(13)
O(1)#4-Na(1)-O(1)	156.9(3)	O(5)#2-Na(2)-O(2)#2	84.45(13)
O(1)#4-Na(1)-O(2)	128.29(19)	O(2)#6-Na(2)-O(2)#2	180
O(1)-Na(1)-O(2)	74.71(14)	O(5)#6-Na(2)-Br(1)	87.76(11)
O(1)#4-Na(1)-O(2)#4	74.71(14)	O(5)#2-Na(2)-Br(1)	92.24(11)
O(1)-Na(1)-O(2)#4	128.29(19)	O(2)#6-Na(2)-Br(1)	99.43(9)
O(2)-Na(1)-O(2)#4	53.60(19)	O(2)#2-Na(2)-Br(1)	80.57(9)
O(1)#4-Na(1)-O(6)#4	48.73(13)	O(5)#6-Na(2)-Br(1)#8	92.24(11)
O(1)-Na(1)-O(6)#4	108.59(18)	O(5)#2-Na(2)-Br(1)#8	87.76(11)
O(2)-Na(1)-O(6)#4	174.42(18)	O(2)#6-Na(2)-Br(1)#8	80.57(9)
O(2)#4-Na(1)-O(6)#4	123.02(12)	O(2)#2-Na(2)-Br(1)#8	99.43(9)
O(1)#4-Na(1)-O(6)	108.59(18)	Br(1)-Na(2)-Br(1)#8	180
O(1)-Na(1)-O(6)	48.73(13)	O(4)-B(1)-O(2)#6	111.9(4)
O(2)-Na(1)-O(6)	123.02(12)	O(4)-B(1)-O(2)#10	111.9(4)
O(2)#4-Na(1)-O(6)	174.42(18)	O(2)#6-B(1)-O(2)#10	106.5(6)
O(6)#4-Na(1)-O(6)	59.92(18)	O(4)-B(1)-O(3)	109.9(6)
O(1)#4-Na(1)-Br(1)	89.34(13)	O(2)#6-B(1)-O(3)	108.2(4)
O(1)-Na(1)-Br(1)	89.34(13)	O(2)#10-B(1)-O(3)	108.2(4)
O(2)-Na(1)-Br(1)	98.07(14)	O(6)-B(2)-O(2)#6	122.9(5)
O(2)#4-Na(1)-Br(1)	98.07(14)	O(6)-B(2)-O(1)	115.1(5)
O(6)#4-Na(1)-Br(1)	77.67(12)	O(2)#6-B(2)-O(1)	121.8(5)
O(6)-Na(1)-Br(1)	77.67(12)	O(1)-B(3)-O(6)#1	113.2(5)
O(1)#4-Na(1)-Br(1)#5	91.69(13)	O(1)-B(3)-O(5)	106.5(4)
O(1)-Na(1)-Br(1)#5	91.69(13)	O(6)#1-B(3)-O(5)	112.1(4)
O(2)-Na(1)-Br(1)#5	77.35(13)	O(1)-B(3)-O(3)	109.5(4)
O(2)#4-Na(1)-Br(1)#5	77.35(13)	O(6)#1-B(3)-O(3)	108.0(4)
O(6)#4-Na(1)-Br(1)#5	106.75(13)	O(5)-B(3)-O(3)	107.5(4)
O(6)-Na(1)-Br(1)#5	106.75(13)	O(4)-B(4)-O(5)#2	119.1(3)
Br(1)-Na(1)-Br(1)#5	174.85(16)	O(4)-B(4)-O(5)#11	119.1(3)
B(2)#4-Na(1)-Br(1)#5	107.10(14)	O(5)#2-B(4)-O(5)#11	121.6(7)

[a] Symmetry transformations used to generate equivalent atoms:

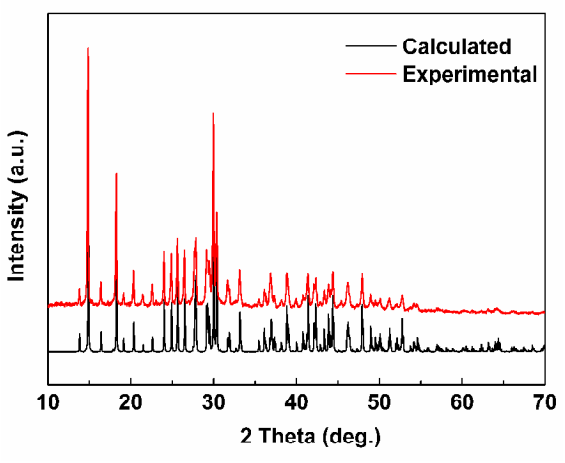
(#1) -x+1/2, -y+2, z-1/2, (#2) x+1/2, y, -z+1/2, (#3) -x+1, -y+2, -z, (#4) x, -y+5/2, z, (#5) x-1/2, y, -z+1/2, (#6) -x+1/2, -y+2, z+1/2, (#7) x-1/2, -y+5/2, -z+1/2, (#8) -x+1, -y+2, -z+1, (#9) x, y, z+1, (#10) -x+1/2, y-1/2, z+1/2, (#11) x+1/2, -y+3/2, -z+1/2, (#12) -x+1, y-1/2, -z+1, (#13) -x+1, y-1/2, -z, (#14) x, -y+3/2, z, (#15) -x+1, y+1/2, -z+1, (#16) -x+1, y+1/2, -z.

Table S5 The element analysis of $Na_3B_6O_{10}Cl$, $RbNa_2B_6O_{10}Cl$ and $RbNa_2B_6O_{10}Br$.

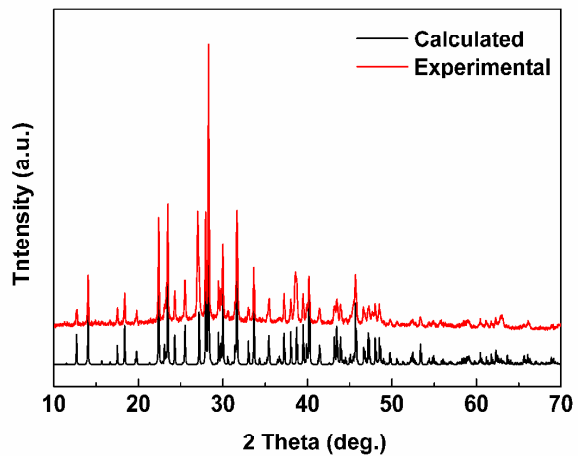
	$Na_3B_6O_{10}Cl$		$RbNa_2B_6O_{10}Cl$		$RbNa_2B_6O_{10}Br$	
Element	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
Na	20.95	21.13	11.74	11.82	10.54	10.71
B	19.70	19.65	16.56	16.62	14.87	14.93

Table S6 The assignment of infrared spectra for $Na_3B_6O_{10}Cl$ and $RbNa_2B_6O_{10}X$ (X = Cl, Br).

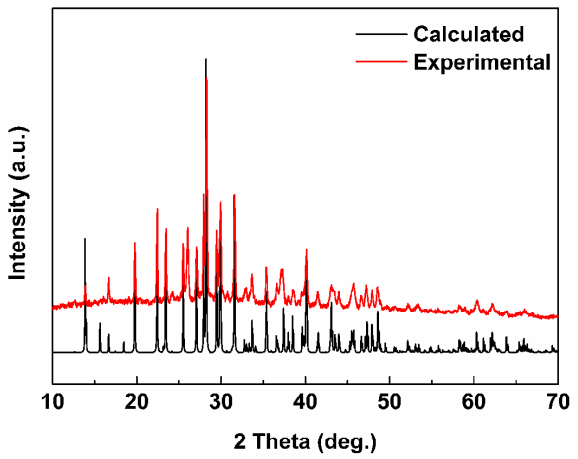
$Na_3B_6O_{10}Cl$ (cm^{-1})	$RbNa_2B_6O_{10}Cl$ (cm^{-1})	$RbNa_2B_6O_{10}Br$ (cm^{-1})	Assignment
1341, 1187	1347, 1201	1346, 1194	asymmetric stretching vibrations of BO_3
1083, 1017	1081, 1012	1075, 1024	asymmetric stretching vibrations of BO_4
961, 908	963, 945	962, 945	symmetric stretching vibrations of BO_3
860, 800	858, 826, 798	856, 829, 797	symmetric stretching vibrations of BO_4
744, 691, 628	733, 693, 641	727, 686, 641	out-of-bending of BO_3
587, 563, 519	572, 523	573, 537, 515	bending of BO_3 and BO_4



(a) $Na_3B_6O_{10}Cl$



(b) $RbNa_2B_6O_{10}Cl$



(c) $RbNa_2B_6O_{10}Br$

Figure S1. Powder XRD patterns of calculated and experimental for crystals: (a) $Na_3B_6O_{10}Cl$, (b) $RbNa_2B_6O_{10}Cl$, (c) $RbNa_2B_6O_{10}Br$.

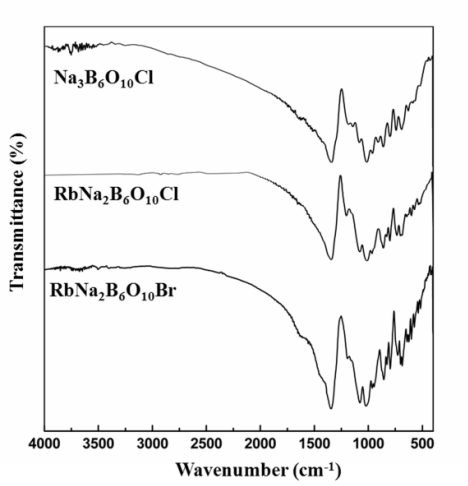


Figure S2. The infrared spectra of $Na_3B_6O_{10}Cl$, $RbNa_2B_6O_{10}Cl$ and $RbNa_2B_6O_{10}Br$.

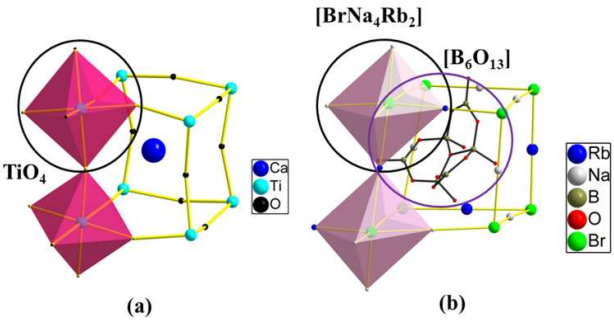


Figure S3 (a) The perovskite structure of $CaTiO_3$. (b) The perovskite-related structure of $RbNa_2B_6O_{10}Br$.

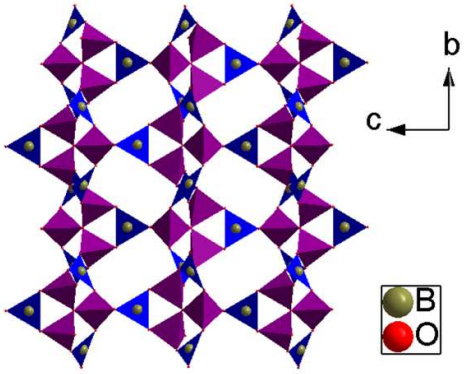


Figure S4.1 The boron-oxygen framework in the crystal structure of $RbNa_2B_6O_{10}Cl$ in *bc* plane (BO_3 triangles and BO_4 tetrahedra are shown in blue and violet, respectively).

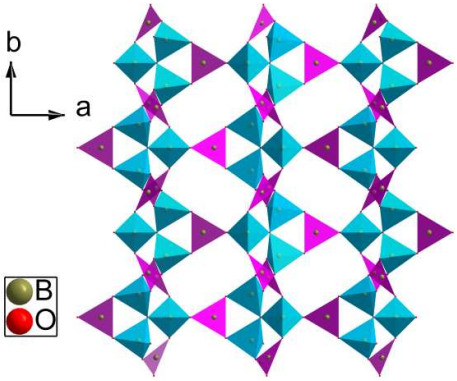
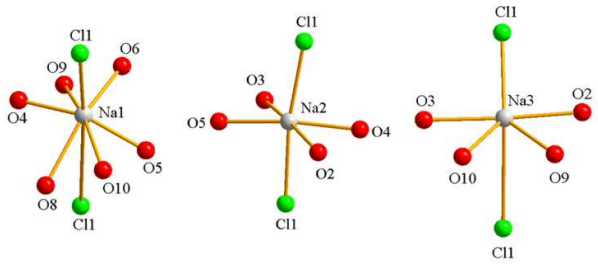
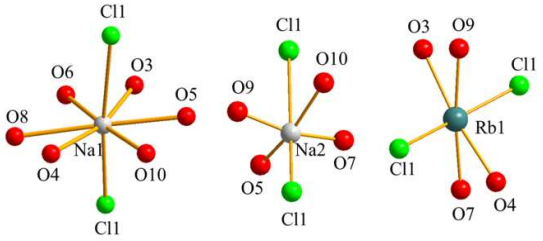


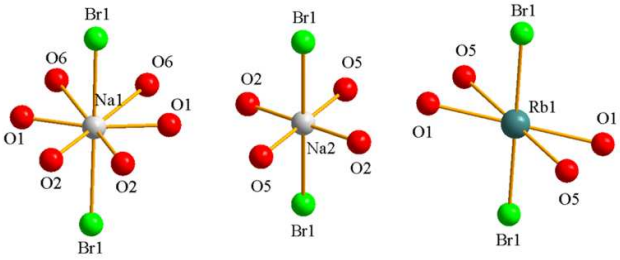
Figure S4.2 The boron-oxygen framework in the crystal structure of $RbNa_2B_6O_{10}Br$ in *ab* plane (BO_3 triangles and BO_4 tetrahedra are shown in pink and sky blue, respectively).



(a) $Na_3B_6O_{10}Cl$



(b) $RbNa_2B_6O_{10}Cl$



(c) $RbNa_2B_6O_{10}Br$

Figure S5. Coordination environment of the cation: (a) $Na_3B_6O_{10}Cl$, (b) $RbNa_2B_6O_{10}Cl$, (c) $RbNa_2B_6O_{10}Br$

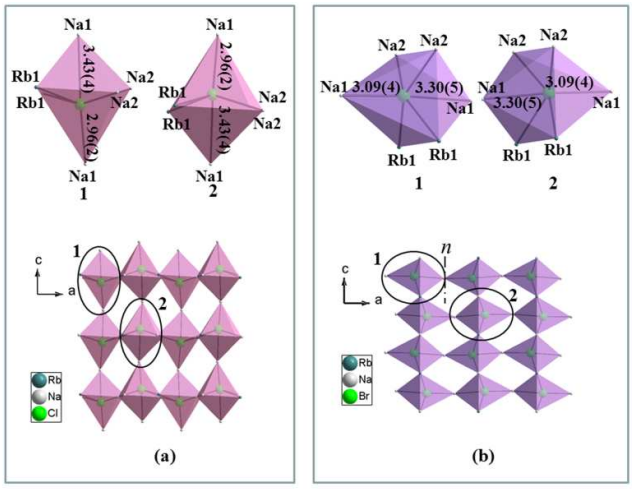


Figure S6.1. The *n*-glide plane comparison of (a) $ClNa_4Rb_2$ and (b) $BrNa_4Rb_2$ networks in $RbNa_2B_6O_{10}Cl$ and $RbNa_2B_6O_{10}Br$. (The $ClNa_4Rb_2$ octahedra are shown in rose and the $BrNa_4Rb_2$ octahedra are shown in lavender).

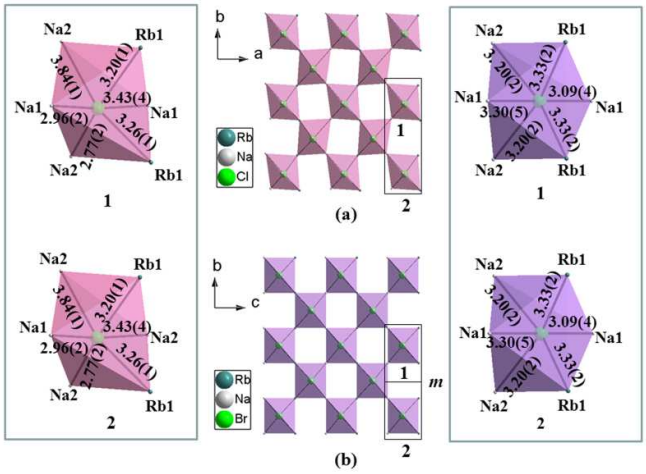


Figure S6.2. The *m*-mirror plane comparison of (a) $ClNa_4Rb_2$ and (b) $BrNa_4Rb_2$ networks in $RbNa_2B_6O_{10}Cl$ and $RbNa_2B_6O_{10}Br$. (The $ClNa_4Rb_2$ octahedra are shown in rose and the $BrNa_4Rb_2$ octahedra are shown in lavender).

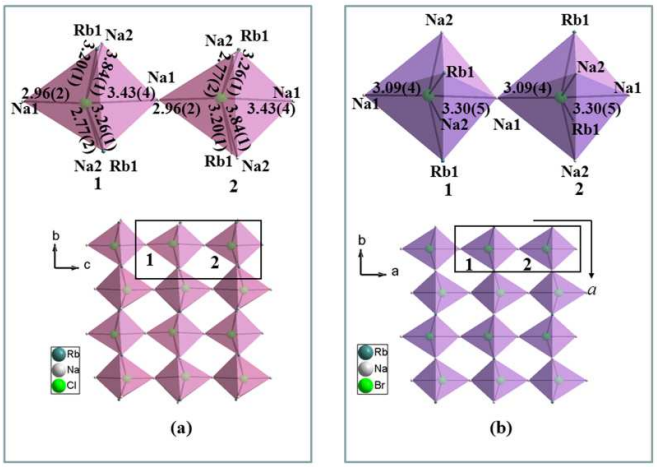


Figure S6.3. The *a*-glide plane comparison of (a) $ClNa_4Rb_2$ and (b) $BrNa_4Rb_2$ networks in $RbNa_2B_6O_{10}Cl$ and $RbNa_2B_6O_{10}Br$. (The $ClNa_4Rb_2$ octahedra are shown in rose and the $BrNa_4Rb_2$ octahedra are shown in lavender).

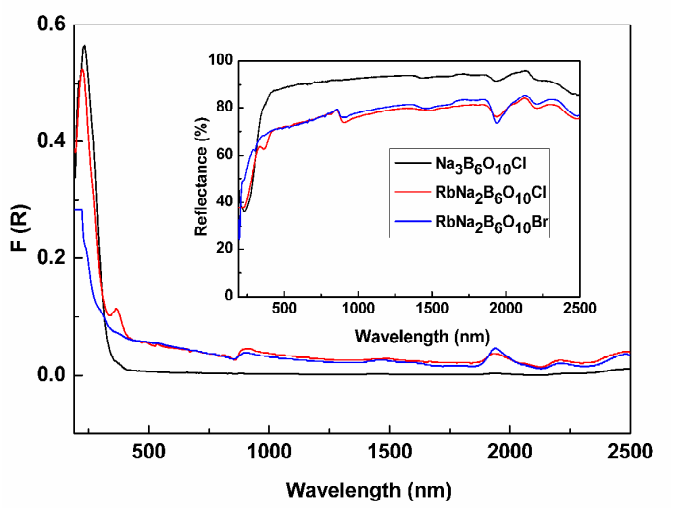
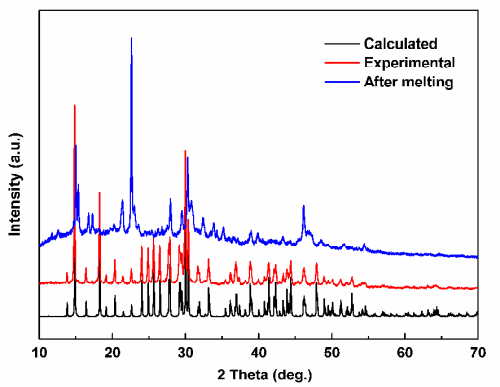
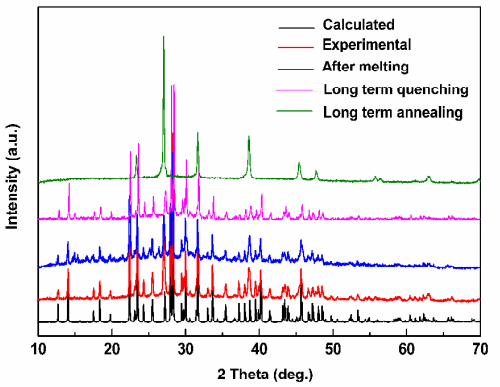


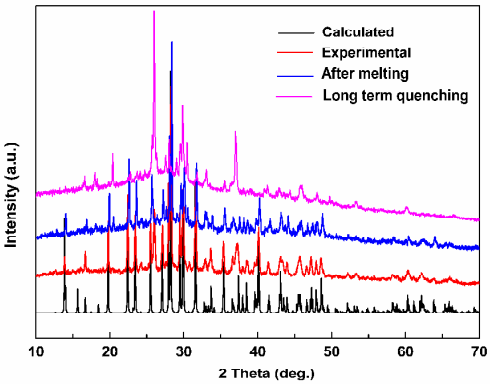
Figure S7. The UV–Vis–NIR diffuse-reflectance spectra of $Na_3B_6O_{10}Cl$, $RbNa_2B_6O_{10}Cl$ and $RbNa_2B_6O_{10}Br$.



(a) $Na_3B_6O_{10}Cl$

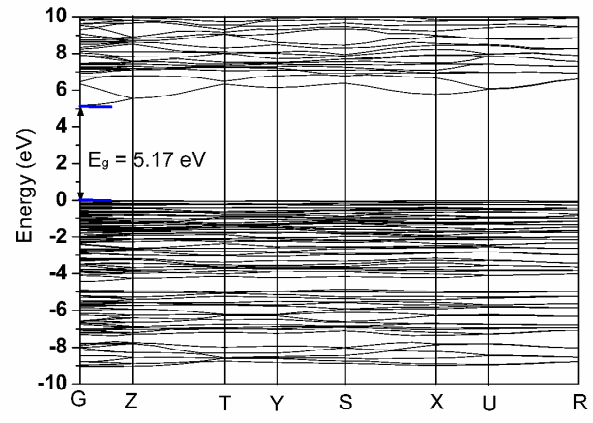


(b) $RbNa_2B_6O_{10}Cl$

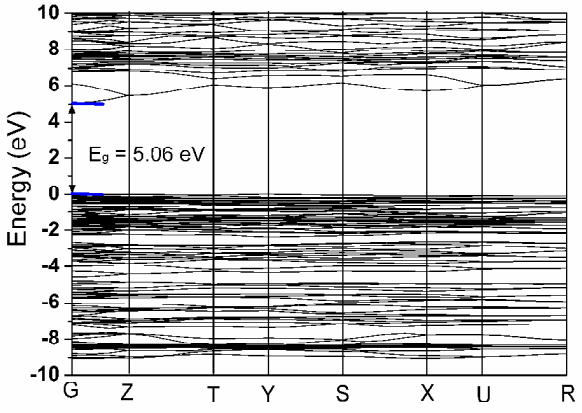


(c) $RbNa_2B_6O_{10}Br$

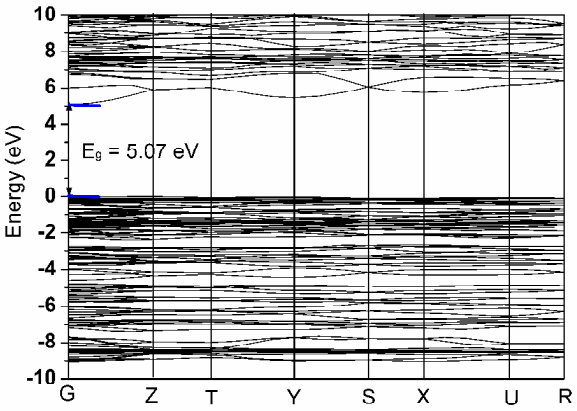
Figure S8. The powder XRD patterns of (a) $Na_3B_6O_{10}Cl$, (b) $RbNa_2B_6O_{10}Cl$, (c) $RbNa_2B_6O_{10}Br$ compounds before and after melting, long term quenching and annealing.



(a) $Na_3B_6O_{10}Cl$

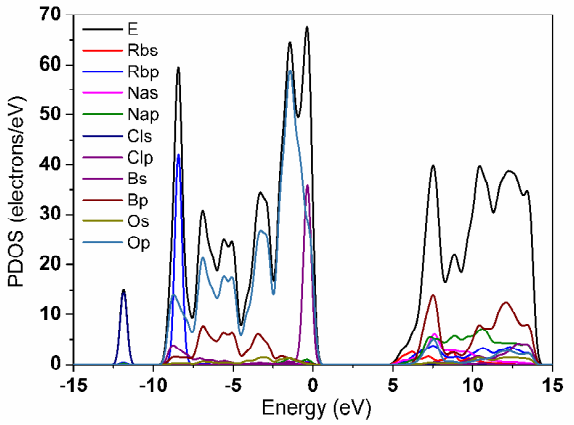


(b) $RbNa_2B_6O_{10}Cl$

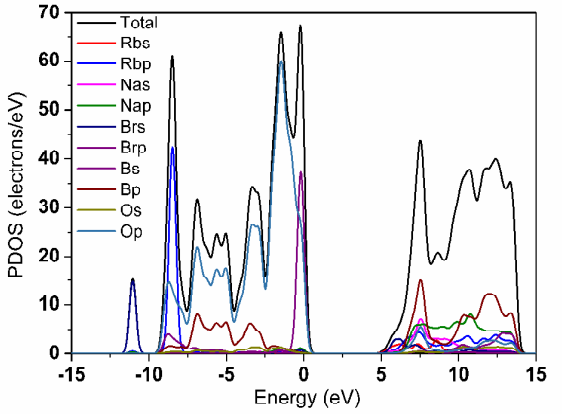


(c) $RbNa_2B_6O_{10}Br$

Figure S9. Calculated band structures of (a) $Na_3B_6O_{10}Cl$, (b) $RbNa_2B_6O_{10}Cl$, (c) $RbNa_2B_6O_{10}Br$.



(a) $RbNa_2B_6O_{10}Cl$



(c) $RbNa_2B_6O_{10}Br$

Figure S10. The full density of states (DOS) and partial density of states (PDOS): (a) $RbNa_2B_6O_{10}Cl$, (b) $RbNa_2B_6O_{10}Br$.