Electronic Supplementary Information

The Structural Diversity of Halogen-centered Secondary Building Units: Two New Mixed-metal Borate Halides with Deep-Ultraviolet Cut-Off Edges

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Table S1. Atomic coordinates equivalent isotropic displacement parameters and bond valence Sum (BVS) for compound **I**.

Atoms	*x*	*y*	z	S.O.F	U_{eq}(Å^2)	BVS
Ba(1)	1.0000	0.2777(1)	0.2500	1	0.021(1)	2.067
Ba(2)	1.0948(1)	-0.0108(1)	0.1714(1)	1	0.017(1)	2.187
Ba(3)	0.8779(1)	0.5006(1)	-0.0010(1)	1	0.028(1)	2.027
Ba(4)	1.0000	-0.3067(1)	0.2500	1	0.028(1)	2.338
Ba(5)	0.7308(1)	0.2202(2)	0.2351(1)	0.5	0.025(1)	-
Na(1)	0.7308(1)	0.2202(2)	0.2351(1)	0.5	0.025(1)	-
Mg(1)	1.1169(3)	0.4863(4)	0.2332(4)	1	0.014(1)	2.045
B(1)	0.9726(12)	0.6849(14)	-0.0584(13)	1	0.014(4)	3.109
B(2)	1.0693(14)	-0.1636(15)	-0.0132(15)	1	0.020(4)	3.039
B(3)	1.2520(12)	0.6072(14)	0.4296(12)	1	0.013(4)	2.925
B(4)	1.1476(13)	-0.1518(14)	0.3881(14)	1	0.016(4)	2.982
B(5)	1.2521(14)	0.3682(14)	0.4138(15)	1	0.016(4)	3.036
B(6)	1.0825(13)	-0.1689(15)	0.5067(14)	1	0.018(4)	3.061
B(7)	0.8482(14)	0.1227(15)	0.1074(17)	1	0.023(4)	3.002
O(1)	0.9958(8)	-0.1184(8)	-0.0034(9)	1	0.016(2)	2.182
O(2)	0.7337(8)	0.6198(10)	-0.0272(8)	1	0.022(3)	2.149
O(3)	0.6615(7)	0.3532(9)	0.0822(9)	1	0.021(3)	2.181
O(4)	0.7380(8)	0.3787(9)	-0.0121(9)	1	0.022(3)	2.032
O(5)	0.8285(7)	0.1181(9)	0.4153(8)	1	0.017(2)	2.130
O(6)	0.11367(8)	-0.1681(8)	0.2970(8)	1	0.019(2)	2.113
O(7)	0.9298(7)	0.1206(9)	0.1029(8)	1	0.019(3)	2.031
O(8)	0.9436(8)	0.2703(9)	0.0311(10)	1	0.024(3)	1.977
O(9)	1.0412(8)	0.4052(9)	0.0989(9)	1	0024(3)	2.139
O(10)	1.0744(8)	-0.1683(9)	0.4072(8)	1	0021(3)	1.987
O(11)	1.1648(7)	0.5850(9)	0.3496(8)	1	0.016(2)	1.990
O(12)	1.1730(7)	0.3686(9)	0.3291(11)	1	0.030(3)	2.065
O(13)	0.8542(9)	0.1363(10)	0.1965(10)	1	0.027(3)	2.111
O(14)	0.9056(8)	0.7293(9)	-0.0468(9)	1	0.024(3)	1.933
F(1)	1.0000	0.4798(10)	0.2500	1	0.022(3)	0.962
F(2)	1.0503(7)	0.6000(8)	0.1327(7)	1	0.027(2)	0.907
F(3)	1.2190(7)	0.5045(11)	0.2065(8)	1	0.044(3)	1.036

Table S2. Atomic coordinates equivalent isotropic displacement parameters and bond valence Sum (BVS) for compound **II**.

Atoms	*x*	*y*	*z*	U_{eq}(Å^2)	BVS
Ba(1)	0.0021(1)	0.4674(1)	0.8031(1)	0.012(1)	2.053
Ba(2)	0.1674(1)	0.2098(1)	1.0312(1)	0.011(1)	2.322
Na(1)	-0.5000	0.5000	1.0000	0.017(1)	1.034
B(1)	0.4992(7)	0.5089(4)	0.7424(4)	0.011(1)	3.094
B(2)	-0.0396(7)	0.2183(4)	1.3000(4)	0.009(1)	3.007
B(3)	0.6897(7)	0.2730(4)	0.9726(4)	0.010(1)	3.058
B(4)	0.3038(7)	0.3096(4)	1.2864(4)	0.011(1)	3.006
B(5)	0.1414(7)	0.2009(4)	0.6950(4)	0.009(1)	3.005
O(1)	0.4336(4)	0.2603(2)	1.1979(2)	0.008(1)	2.088
O(2)	-0.0934(4)	0.6957(2)	0.7482(2)	0.010(1)	2.089
O(3)	0.3571(4)	0.5682(2)	0.8007(2)	0.014(1)	2.154
O(4)	0.0065(5)	0.1084(2)	1.2354(3)	0.019(1)	1.977
O(5)	0.5052(4)	0.3017(2)	0.9280(2)	0.010(1)	2.122
O(6)	0.2528(4)	0.2510(2)	0.7929(2)	0.012(1)	1.980
O(7)	-0.2589(4)	0.2708(2)	1.0871(2)	0.013(1)	1.954
O(8)	-0.1583(4)	0.2559(3)	0.8976(2)	0.012(1)	2.235
O(9)	-0.3512(4)	0.5670(2)	0.6909(3)	0.017(1)	1.971
F(1)	-0.1833(3)	0.5584(2)	0.9777(2)	0.017(1)	0.999
Br(1)	0.0000	0.5000	0.5000	0.024(1)	0.800

Table S3. Selected bond lengths (Å) for compound **I**.

Ba(1)-F(1)	2.762(14)	Ba(4)-F(1)#9	2.919(14)
Ba(1)-O(12)	2.770(11)	Ba(5)-O(13)	2.663(12)
Ba(1)-O(12)#1	2.770(11)	Ba(5)-O(6)#10	2.679(11)
Ba(1)-O(13)#1	2.868(13)	Ba(5)-O(3)	2.690(12)
Ba(1)-O(13)	2.868(13)	Ba(5)-O(5)	2.728(12)
Ba(1)-O(7)#1	2.872(12)	Ba(5)-F(3)#11	2.971(15)
Ba(1)-O(7)	2.872(12)	Ba(5)-O(12)#1	3.038(13)
Ba(1)-O(8)	2.945(13)	Ba(5)-F(2)#11	3.046(11)
Ba(1)-O(8)#1	2.945(13)	Ba(5)-	3.098(11)
Ba(2)-O(13)#1	2.648(13)	Ba(5)-O(14)#3	3.144(12)
Ba(2)-F(3)#4	2.666(10)	Mg(1)-F(3)	1.953(11)
Ba(2)-O(6)	2.712(11)	Mg(1)-O(11)	2.028(12)
Ba(2)-O(1)	2.714(12)	Mg(1)-O(12)	2.040(13)
Ba(2)-O(1)#5	2.810(12)	Mg(1)-F(2)	2.054(11)
Ba(2)-O(3)#6	2.838(12)	Mg(1)-O(9)	2.074(13)
Ba(2)-O(5)#1	2.862(11)	Mg(1)-F(1)	2.087(5)
Ba(2)-O(7)	2.978(11)	B(1)-O(9)#2	1.34(2)
Ba(2)-O(10)#1	3.238(12)	B(1)-O(14)	1.36(2)
Ba(3)-O(9)	2.664(12)	B(1)-O(8)#2	1.37(2)
Ba(3)-F(3)#2	2.665(10)	B(2)-O(1)	1.44(2)
Ba(3)-O(2)	2.750(12)	B(2)-O(8)#5	1.48(2)
Ba(3)-O(9)#2	2.780(12)	B(2)-O(3)#6	1.48(2)
Ba(3)-O(4)	2.793(11)	B(2)-O(7)#5	1.49(2)
Ba(3)-F(2)	2.853(10)	B(3)-O(11)	1.357(19)
Ba(3)-O(11)#1	2.962(11)	B(3)-O(2)#1	1.383(19)
Ba(3)-F(2)#2	3.124(10)	B(3)-O(5)#13	1.403(18)
Ba(3)-F(1)	3.2657(16)	B(4)-O(6)	1.31(2)
Ba(3)-O(8)	3.284(12)	B(4)-O(10)	1.41(2)
Ba(3)-O(14)	3.286(12)	B(4)-O(2)#15	1.41(2)
Ba(4)-F(2)#8	2.650(10)	B(5)-O(12)	1.28(2)
Ba(4)-F(2)#9	2.650(10)	B(5)-O(4)#1	1.42(2)
Ba(4)-O(6)	2.752(11)	B(5)-O(3)#1	1.42(2)
Ba(4)-O(6)#1	2.752(11)	B(6)-O(10)	1.44(2)

Ba(4)-O(11)#9	2.772(10)	B(6)-O(1)#1	1.45(2)
Ba(4)-O(11)#8	2.772(10)	B(6)-O(14)#8	1.49(2)
Ba(4)-O(10)#1	2.780(12)	B(6)-O(5)#16	1.50(2)
Ba(4)-O(10)	2.780(12)	B(7)-O(13)	1.32(2)

Symmetry transformations used to generate equivalent atom

#1	-x+2,y,-z+1/2	#11	x-1/2,y-1/2,z
#2	-x+2,-y+1,-z	#12	x,y+1,z
#3	x,-y+1,z+1/2	#13	x+1/2,y+1/2,z
#4	-x+5/2,y-1/2,-z+1/2	#14	-x+5/2,y+1/2,-z+1/2
#5	-x+2,-y,-z	#15	x+1/2,-y+1/2,z+1/2
#6	x+1/2,y-1/2,z	#16	-x+2,-y,-z+1
#7	x,-y,z-1/2	#17	x,-y,z+1/2
#8	-x+2,y-1,-z+1/2	#18	-x+3/2,-y+1/2,-z
#9	x,y-1,z	#19	x-1/2,-y+1/2,z-1/2
#10	x-1/2,y+1/2,z	#20	-x+2,y+1,-z+1/2
#21	x,-y+1,z-1/2		

Table S4. Selected bond lengths (Å) for compound **II**.

Ba(1)-F(1)	2.616(2)	Na(1)-O(5)#1	2.423(3)
Ba(1)-O(3)	2.658(3)	Na(1)-O(3)#3	2.578(3)
Ba(1)-O(2)	2.767(3)	Na(1)-O(3)#1	2.578(3)
Ba(1)-F(1)#1	2.781(2)	B(1)-O(4)#5	1.350(6)
Ba(1)-O(8)	2.885(3)	B(1)-O(9)#6	1.360(5)
Ba(1)-O(9)	2.906(3)	B(2)-O(6)#8	1.442(5)
Ba(1)-O(1)#2	2.911(3)	B(2)-O(2)#1	1.454(5)
Ba(1)-O(6)	3.008(3)	B(2)-O(4)	1.501(5)
Ba(2)-O(1)	2.647(3)	B(2)-O(5)#8	1.510(5)
Ba(2)-F(1)#1	2.665(2)	B(3)-O(7)#6	1.350(5)
Ba(2)-O(8)	2.690(3)	B(3)-O(5)	1.370(5)
Ba(2)-O(5)	2.806(3)	B(3)-O(8)#6	1.373(5)
Ba(2)-O(2)#1	2.818(3)	B(4)-O(2)#1	1.461(5)
Ba(2)-O(6)	2.856(3)	B(4)-O(9)#1	1.473(5)
Ba(2)-O(4)	2.865(3)	B(4)-O(1)	1.476(5)
Ba(2)-O(7)	3.045(3)	B(4)-O(8)#9	1.497(5)
Ba(2)-Br(1)#4	3.3171(4)	B(5)-O(6)	1.452(5)
Na(1)-F(1)#7	2.259(2)	B(5)-O(7)#5	1.466(5)
Na(1)-F(1)	2.259(2)	B(5)-O(1)#2	1.471(5)
Na(1)-O(5)#3	2.423(3)	B(5)-O(3)#4	1.524(5)

Symmetry transformations used to generate equivalent atom

#1	-x,-y+1,-z+2	#7	-x-1,-y+1,-z+2
#2	x-1/2,-y+1/2,z-1/2	#8	x-1/2,-y+1/2,z+1/2
#3	x-1,y,z	#9	x+1/2,-y+1/2,z+1/2
#4	-x+1/2,y-1/2,-z+3/2	#10	-x+1/2,y+1/2,-z+3/2
#5	x+1/2,-y+1/2,z-1/2	#11	-x,-y+1,-z+1
#6	x+1,y,z		

Table S5. The basic information of the anhydrous halogen-containing borates.

No.	Molecular Formula	Space Group	X-centered SBUs	Configuration Type
1	$Te_3BO_3F_{15}$	$P6_3/m$ (176)	Fte	linear configuration
2	$Al_6(BO_3)_5F_3$	$P6_3/m$ (176)	FAl_2	linear configuration
3	$Be_2(BO_3)F$	$C2/c$ (15)	FBe_2	linear configuration
4	$Be_2(BO_3)F$	$C2$ (5)	FBe_2	linear configuration
5	$Be_2(BO_3)F$	$R\bar{3}c$ (167)	FBe_2	linear configuration
6	$Cs_{18}Mg_6(B_5O_{10})_3(B_7O_{14})_2F$	$C2/c$ (15)	FMg_2	linear configuration
7	$Rb_{18}Mg_6(B_5O_{10})_3(B_7O_{14})_2F$	$C2/c$ (15)	FMg_2	linear configuration
8	$Li(B_6O_9)F$	$Pna2_1$ (33)	FLiB	linear configuration
9	$Li_2B_3O_4F_3$	$P2_12_12_1$ (19)	FLiB	linear configuration
10	$Li_2B_6O_9F_2$	Cc (9)	FLiB	linear configuration
11	$Cm_2B_{14}O_{29}Cl$	$P2_1/C$ (14)	ClCmB	linear configuration
12	$Er_2(B_2O_5)Cl_2$	$Pbam$ (55)	$ClEr_2$	linear configuration
13	$Pb_6B_3O_{10}F$	$Pbcm$ (57)	FPb_4	planar configuration
14	$Ca_3Be_6B_5O_{16}F$	$P6_3/m$ (176)	FCa_3	planar configuration
15	$Mg_5(BO_3)_3F$	$Pna2_1$ (33)	FMg_3	planar configuration
16	$Mg_5(BO_3)_3F$	$Pnma$ (62)	FMg_3	planar configuration
17	$Tb_2(BO_3)F_3$	$P2_1/C$ (14)	FTb_3	planar configuration
18	$BaZn(BO_3)F$	$P\bar{6}$ (174)	FZn_2Ba_3	spatial configuration
19	$Ca_3Na_4LiBe_4B_{10}O_{24}F$	$R\bar{3}$ (148)	FNa_3LiBe	spatial configuration
20	$Cd_3LiNa_4Be_4B_{10}O_{24}F$	$R\bar{3}$ (148)	FNa_3LiBe	spatial configuration
21	$CdZn_2KB_2O_6F$	$P\bar{3}1c$ (163)	FZn_2Cd_3	spatial configuration
22	$K_3Ba_3Li_2Al_4B_6O_{20}F$	$P\bar{6}2c$ (190)	FK_3Li_2	spatial configuration
23	$KBOF_2$	$P2_1/C$ (14)	FK_4B	spatial configuration
24	$KCaBe_2(BO_3)_2F$	$P\bar{3}1c$ (163)	FK_3Be_2	spatial configuration
25	$KSrBe_2(BO_3)_2F$	$P6_3/m$ (176)	FK_3Be_2	spatial configuration
26	$Li_3Ca_9(BO_3)_7(LiF)_2$	$P1$ (1)	FCa_3Li_2	spatial configuration
27	$Li_6RbB_2O_6F$	$Pnma$ (62)	FRb_3Li_2	spatial configuration
28	$Pb_3O(BO_3)F$	$Pbcm$ (57)	FPb_5	spatial configuration
29	$Sr_3LiNa_4Be_4B_{10}O_{24}F$	$R\bar{3}$ (148)	FNa_3LiBe	spatial configuration
30	$BaAl(BO_3)F_2$	$P\bar{6}2c$ (190)	FBa_3Al	spatial configuration
31	$Ba_3Zn_2B_3O_9F$	$Pnma$ (62)	FBa_4	spatial configuration
32	$Ba_5(B_2O_5)_2F_2$	$C2/c$ (15)	FBa_4	spatial configuration
33	$Ba_5Zn_2B_4O_{12}F_2$	$C2/c$ (15)	FBa_4	spatial configuration
34	$BaAl(BO_3)F_2$	$P6_3/m$ (176)	FBa_3Al	spatial configuration
35	$BaGa(BO_3)F_2$	$P6_3/m$ (176)	FBa_3Ga	spatial configuration
36	$Ca_5(BO_3)_3F$	Cm (8)	FCa_4	spatial configuration
37	$Cd_8B_5O_{15}F$	$Fd\bar{3}m$ (227)	FCd_3B	spatial configuration
38	$CsBe_2(BO_3)F_2$	$C2$ (5)	FCs_3Be	spatial configuration
39	$CsBe_2BO_3F_2$	$R32$ (155)	FCs_3Be	spatial configuration

40	$Dy_4B_4O_{11}F_2$	*C*2/*c* (15)	FDy_4	spatial configuration
41	$Eu_4B_4O_{11}F_2$	*C*2/*c* (15)	FEu_4	spatial configuration
42	$Gd_4B_4O_{11}F_2$	$P2_1/C$ (14)	FGd_4	spatial configuration
43	$KBe_2(BO_3)F_2$	*R*32 (155)	FK_3Be	spatial configuration
44	$KBe_2(BO_3)F_2$	$R\bar{3}c$ (167)	FK_3Be	spatial configuration
45	$Li_{0.8}Mg_{2.1}B_2O_5F$	$P2_1/C$ (14)	FMg_2Li_2	spatial configuration
46	$Mg_2(BO_3)F$	*Pnma* (62)	FMg_4	spatial configuration
47	$NaSr_3Be_3(BO_3)_3F_4$	*R*3*m* (160)	FSr_3Na, FBe_3Na	spatial configuration
48	$Na_3B_3O_3F_6$	*C*2/*c* (15)	FNa_3B	spatial configuration
49	$NaCaBe_2(BO_3)_2F$	*C*c (9)	FBe_2Na_2	spatial configuration
50	$Nd_4(B_4O_{11})F_2$	*C*2/*c* (15)	FNd_4	spatial configuration
51	$Nd_6Li(BO_3)_3O_4F_2$	*C*2/*c* (15)	FNd4	spatial configuration
52	$Pb_6AlB_2O_7F_7$	*Cmca* (64)	FPb_4, FPb_3Al	spatial configuration
53	$Pr_4(B_4O_{11})F_2$	*C*2/*c* (15)	FPr_4	spatial configuration
54	$Pr_4B_3O_{10}F$	$P\bar{1}$ (2)	FPr_4	spatial configuration
55	$RbBe_2(BO_3)F_2$	*C*2 (5)	FRb_3Be	spatial configuration
56	$RbBe_2(BO_3)F_2$	$R\bar{3}c$ (167)	FRb_3Be	spatial configuration
57	$TlBe_2BO_3F_2$	*R*32 (155)	FTl_3Be	spatial configuration
58	$Ba_3Sr_4(BO_3)_3F_5$	$P6_3mc$ (186)	FBa_3, FSr_4, FSr_3	spatial configuration
59	$La_4B_4O11F_2$	$P2_1/C$ (14)	FLa_4	spatial configuration
60	Pb_2BO_3F	$P6_3/m$ (176)	FPb_3, FPb_6	spatial configuration
61	$Ba_3B_6O_{11}F_2$	$P2_1$ (4)	FBa_3	spatial configuration
62	$BaCa(BO_3)F$	$P\bar{6}2m$ (189)	FCa_2Ba	spatial configuration
63	BiB_2O_4F	$P3_2$ (145)	FBi_2B	spatial configuration
64	$Ce(B_2O_4)F$	*Pbca* (61)	FCe_3	spatial configuration
65	$Eu_5(BO_3)_3F$	*Pnma* (62)	FEu_3	spatial configuration
66	LaB_2O_4F	*Pbca* (61)	FLa_3	spatial configuration
67	$Mg_3(BO_3)F_3$	$P6_3/m$ (176)	FMg_3	spatial configuration
68	$NaBe_2(BO_3)F_2$	*C*2 (5)	FNa_2, FNa_2Be	spatial configuration
69	$Sr_3B_6O_{11}F_2$	$P2_1$ (4)	FSr_3	spatial configuration
70	$Sr_5(BO_3)_3F$	*Pnma* (62)	FSr_3	spatial configuration
71	$LiBa_{12}(BO_3)_7F_4$	*I*4/*mcm* (140)	FBa_4Li_2	spatial configuration
72	$NaBa_{12}(BO_3)_7F_4$	*I*4/*mcm* (140)	FBa_5Na	spatial configuration
73	$Pb_8(B_9O_{21})F$	$R\bar{3}c$ (167)	FPb_6	spatial configuration
74	$BaMg(BO_3)F$	*C*c (9)	FMg_2Ba_2, FMg_2Ba_3	spatial configuration
75	$Ca_2(BO_3)Cl$	$P2_1/C$ (14)	$ClCa_5$	spatial configuration
76	$Dy_4O_4(BO_3)Cl$	$P2_1/C$ (14)	$ClDy_5$	spatial configuration
77	$Er_4O_4(BO_3)Cl$	$P2_1/C$ (14)	$ClEr_5$	spatial configuration
78	$Eu_4O_4(BO_3)Cl$	$P2_1/C$ (14)	$ClEu_5$	spatial configuration
79	$Gd_4O_4(BO_3)Cl$	$P2_1/C$ (14)	$ClDg_5$	spatial configuration
80	$Ho_4O_4(BO_3)Cl$	$P2_1/C$ (14)	$ClHo_5$	spatial configuration
81	$Tb_4O_4(BO_3)Cl$	$P2_1/C$ (14)	$ClDg_5$	spatial configuration
82	$Tm_4O_4(BO_3)Cl$	$P2_1/C$ (14)	$ClHo_5$	spatial configuration

83	$Ba_2(BO_3)Br$	$P\bar{3}m1$ (164)	$BrBa_5$	spatial configuration
84	$(Ba_4Ga_2B_8O_{18}Cl_2)(NaCl)_{0.88}$	$P4_2nm$ (102)	$ClBa_4Na$	spatial configuration
85	$NaBa_4(GaB_4O_9)_2Cl_3$	$P4_2nm$ (102)	$ClBa_4Na$, $ClBa_4$	spatial configuration
86	$NaBa_4Al_2B_8O_{18}Cl_3$	$P4_2nm$ (102)	$ClBa_4Na$	spatial configuration
87	$NaBa_4(AlB_4O_9)_2Br_3$	$P4_2nm$ (102)	$BrNaBa_4$	spatial configuration
88	$NaBa_4(GaB_4O_9)_2Br_3$	$P4_2nm$ (102)	$BrBa_4Na$, $ClBa_4$	spatial configuration
89	$Ba_2AlB_4O_9Cl$	$P4_2nm$ (102)	$ClBa_4$, $ClBa_6$	spatial configuration
90	$Ba_2GaB_4O_9Cl$	$P4_2nm$ (102)	$ClBa_4$, $ClBa_6$	spatial configuration
91	$Li_5B_7O_{12.5}Cl$	$F23$ (196)	$ClLi_4$, $ClLi_6$	spatial configuration
92	$Ba_2B_5O_9Cl$	$Pnn2$ (34)	$ClBa_4$	spatial configuration
93	$Ce_3(BO_3)_2Cl_3$	$P6_3/m$ (176)	$ClCe_4$	spatial configuration
94	$Eu_2(B_5O_9)Cl$	$Pnn2$ (34)	$ClEu_4$	spatial configuration
95	$KZn_2(BO_3)Cl_2$	$R32$ (155)	ClK_3Zn	spatial configuration
96	$Pb_2(B_5O_9)Cl$	$Pnn2$ (34)	$ClPb_4$	spatial configuration
97	$Pb_6B_3O_{10}Cl$	$Pbcm$ (57)	$ClPb_4$	spatial configuration
98	$Sr_2(B_5O_9)Cl$	$Pnn2$ (34)	$ClSr_4$	spatial configuration
99	$Ca_2(B_5O_9)Br$	$Pnn2$ (34)	$BrCa_4$	spatial configuration
100	$Eu_2(B_5O_9)Br$	$Pnn2$ (34)	$BrEu_4$	spatial configuration
101	$Pb_2(B_5O_9)Br$	$Pnn2$ (34)	$BrPb_4$	spatial configuration
102	$Pb_6B_3O_{10}Br$	$Pbcm$ (57)	$BrPb_4$	spatial configuration
103	$Ce(BO_2)_2Cl$	$P\bar{1}$ (2)	$ClCe_3$	spatial configuration
104	$Fe_3(B_7O_{13})Cl$	$R3c$ (161)	$ClFe_3$	spatial configuration
105	$La(BO_2)_2Cl$	$P\bar{1}$ (2)	$ClLa_3$	spatial configuration
106	$Pr(BO_2)_2Cl$	$P\bar{1}$ (2)	$ClPr_3$	spatial configuration
107	$Zn_3(B_7O_{13})Cl$	$R3c$ (161)	$ClZn_3$	spatial configuration
108	$Co_3(B_7O_{13})Br$	$Pca2_1$ (29)	$BrCo_3$	spatial configuration
109	$Fe_3B_7O_{13}Br$	$R3c$ (161)	$BrFe_3$	spatial configuration
110	$Zn_3(B_7O_{13})Br$	$Pca2_1$ (29)	$BrZn_3$	spatial configuration
111	$Ba_2Gd(BO_3)_2Cl$	$P2_1/m$ (11)	$ClBa_6$	spatial configuration
112	$Ba_2Ho(BO_3)_2Cl$	$P2_1/m$ (11)	$ClBa_6$	spatial configuration
113	$Ba_2Lu(BO_3)_2Cl$	$P2_1/m$ (11)	$ClBa_6$	spatial configuration
114	$Ba_2Y(BO_3)_2Cl$	$P2_1/m$ (11)	$ClBa_6$	spatial configuration
115	$Ba_2Yb(BO_3)_2Cl$	$P2_1/m$ (11)	$ClBa_6$	spatial configuration
116	$Ba_5(BO_3)_3Cl$	$C222_1$ (20)	$ClBa_6$	spatial configuration
117	$Ba_7(BO_3)_3GeO_4Cl$	$Pbam$ (55)	$ClBa_6$	spatial configuration
118	$Co_3(B_7O_{13})Cl$	$R3c$ (161)	$ClCo_6$	spatial configuration
119	$Cr_3(B_7O_{13})Cl$	$F\bar{4}3c$ (219)	$ClCr_6$	spatial configuration
120	$Cr_3B_7O_{13}Cl$	$P\bar{4}2_1c$ (114)	$ClCr_6$	spatial configuration
121	$Eu_5(BO_3)_3Cl$	$C222_1$ (20)	$ClEu_6$	spatial configuration
122	$K_3(B_6O_{10})Cl$	$R3m$ (160)	ClK_6	spatial configuration
123	$Mg_3(B_7O_{13}Cl)$	$Pca2_1$ (29)	$ClMg_6$	spatial configuration
124	$Mg_3(B_7O_{13}Cl)$	$F\bar{4}3c$ (219)	$ClMg_6$	spatial configuration
125	$Mn_3(B_7O_{13})Cl$	$Pca2_1$ (29)	$ClMn_6$	spatial configuration

126	$Na_3B_4O_7Cl$	$P6_522$ (179)	$ClNa_6$	spatial configuration
127	$Na_3B_6O_{10}Cl$	$P2_12_12_1$ (19)	$ClNa_6$	spatial configuration
128	$Ni_3(B_7O_{13})Cl$	$Pca2_1$ (29)	$ClNi_6$	spatial configuration
129	$Pb_2Ba_3(BO_3)_3Cl$	$C222_1$ (20)	$ClPb_4Ba_2$	spatial configuration
130	RbNa2B6O10Cl	$P2_12_12_1$ (19)	$ClNa_4Rb_2$	spatial configuration
131	$Sr_5(BO_3)_3Cl$	$C222_1$ (20)	$ClSr_6$	spatial configuration
132	$(K_{0.80}Na_{2.20})(B_6O_{10})Br$	*Pnma* (62)	$BrNa_4K(Na)_2$	spatial configuration
133	$(K_{1.70}Na_{1.30})(B_6O_{10})$ Br	*Pnma* (62)	$BrNa_2K_2K(Na)_2$	spatial configuration
134	$(K_{2.33}Na_{0.67})(B_6O_{10})Br$	*R*3*m* (160)	$BrK(Na)_6$	spatial configuration
135	$(K_{2.87}Na_{0.126})(B_6O_{10})Br$	*R*3*m* (160)	$BrK(Na)_6$	spatial configuration
136	$Ba_3(BO_3)Br_3$	$P\bar{1}$ (2)	$BrBa_6$	spatial configuration
137	$Ba_5(BO_3)_3Br$	$C222_1$ (20)	$BrBa_6$	spatial configuration
138	$Ba_7(BO_3)_3GeO_4Br$	*Pbam* (55)	$BrBa_6$	spatial configuration
139	$Cr_3(B_7O_{13})Br$	$F\bar{4}3c$ (219)	$BrCr_6$	spatial configuration
140	$Cu_3(B_7O_{13})Br$	$F\bar{4}3c$ (219)	$BrCu_6$	spatial configuration
141	$K_3(B_6O_{10})Br$	*R*3*m* (160)	BrK_6	spatial configuration
142	$Mn_3(B_7O_{13})Br$	$Pca2_1$ (29)	$BrMn_6$	spatial configuration
143	$Mn_3(B_7O_{13})Br$	$F\bar{4}3c$ (219)	$BrMn_6$	spatial configuration
144	$Na_3B_4O_7Br$	$P6_522$ (179)	$BrNa_6$	spatial configuration
145	$Na_3B_6O_{10}Br$	*Pnma* (62)	$BrNa_6$	spatial configuration
146	$Ni_3(B_7O_{13})Br$	$Pca2_1$ (29)	$BrNi_6$	spatial configuration
147	$Pb_2Ba_3(BO_3)_3Br$	$C222_1$ (20)	$BrPb_4Ba_2$	spatial configuration
148	$RbNa_2B_6O_{10}Br$	*Pnma* (62)	$BrNa_4Rb_2$	spatial configuration
149	$Sr_5Br(BO_3)_3$	$C222_1$ (20)	BrSr6	spatial configuration
150	$Li_4(B_7O_{12})Cl$	*F*23 (196)	$ClLi_4$	spatial configuration
151	$Li_4(B_7O_{12})Cl$	$F\bar{4}3c$ (219)	$ClLi_4$	spatial configuration
152	$Pb_2(O_4Pb_8)(BO_3)_3Br_3$	*C*2/*c* (15)	$BrPb_9$	spatial configuration
153	$Pb_2(O_8Pb_{12})(BO_3)_2Br_6$	*C*2/*c* (15)	$BrPb_9$	spatial configuration
154	$Na_{11}B_{21}O_{36}Cl_2$	*C*2/*c* (15)	$ClNa_8$	spatial configuration
155	$Pb_6Ba_2(BO_3)_5Cl$	*C*2/*m* (12)	$ClPb_6Ba_2$	spatial configuration
156	$Na_{11}B_{21}O_{36}Br2$	*C*2/*c* (15)	$BrNa_8$	spatial configuration
157	$Pb_6Ba_2(BO_3)Br$	*C*2/*m* (12)	$BrPb_6Ba_2$	spatial configuration
158	$Pb_3B_6O_{11}F_2$	$P2_1$ (4)	FPb_2, FPb_3	hybrid configuration
159	$BaBOF_3$	*Pnma* (62)	FBBa, FBa_3B	hybrid configuration
160	$Gd_2(BO_3)F_3$	$P2_1/C$ (14)	FGd_3	hybrid configuration
161	$NaBa_4(B_5O_9)_2F_2Cl$	$P2_1/C$ (14)	FBa_3Na, $ClBa_4$	hybrid configuration
162	$Tm_5(BO_3)_2F_9$	*C*2/*c* (15)	FTm_3	hybrid configuration
163	$Yb_5(BO_3)_2F_9$	*C*2/*c* (15)	FYb_3	hybrid configuration
164	$Dy_5(BO_3)_2F_9$	*C*2/*c* (15)	FDy_3	hybrid configuration
165	$Er_5(BO_3)_2F_9$	*C*2/*c* (15)	FEr_3	hybrid configuration
166	$Ho_2(BO_3)F_3$	$P2_1/C$ (14)	FHo_3	hybrid configuration
167	$Ho_5(BO_3)_2F_9$	*C*2/*c* (15)	FHo_3	hybrid configuration
168	$Gd_3(BO_3)_2F_3$	*Pnma* (62)	FGd_3	hybrid configuration

169	$KBa_7Mg_2B_{14}O_{28}F_5$	*C*2/*c* (15)	FMg_2K_2, $FMgK_3$	hybrid configuration
170	Compound **I**	*C*2/*c* (15)	FMg_2Na_2, $FMgNa_3$	hybrid configuration
171	$Dy_2(BO_3)F_3$	$P2_1/C$ (14)	FDy_3	hybrid configuration
172	$NaBa_4(B_5O_9)_2F_2Cl$	$P2_1/C$ (14)	FBa_3Na, $ClBa_4$	hybrid configuration
173	Compound **II**	$P2_1/C$ (14)	FBa_3Na, $BrBa_4$	hybrid configuration

Table S6. The basic information of the anhydrous halogen-containing borates.

Halogen	Linear configuration	Planar configuration	Spatial configuration	Hybrid configuration	Total
F	10	5	57	14	86
Cl	2	0	51	1	54
Br	0	0	32	1	33
Total	12	5	140	16	173

Fig S1. The $[Mg_2B_{14}O_{30}F_6]^{20-}$ 10-member rings in compound **I**

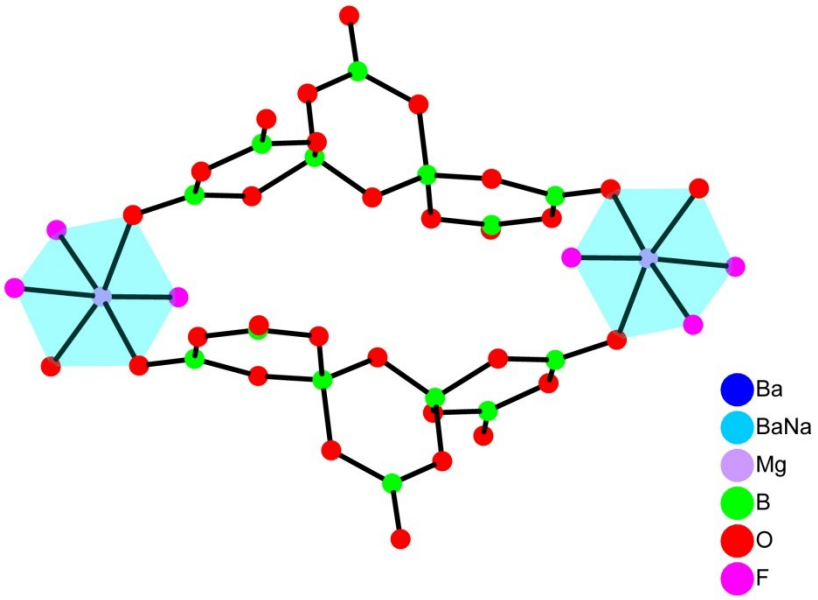

Fig. S2 Perpendicular relation between FPb_4 SUBs in $Pb_6B_3O_{10}F$

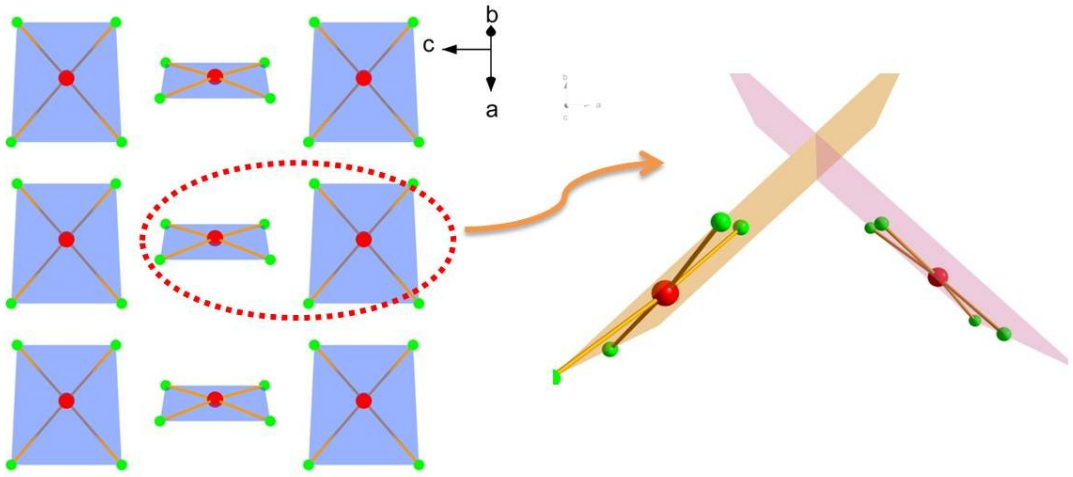

Fig. S3 Parallel relation between FCa_3 SUBs in $Ca_3Be_6B_5O_{16}F$

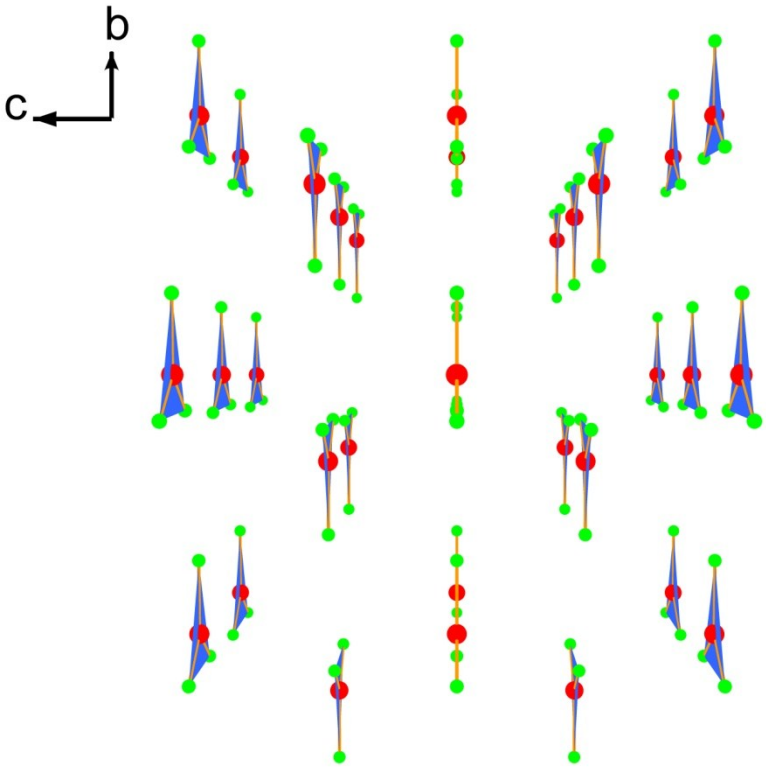

Fig. S4 The F-Be-A layer in $ABe_2(BO_3)F_2$ (A=K, Rb, Cs) viewed along ***c*** axis.