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Electronic Supplementary Information

$Ba_{n+2}Zn_n(BO_3)_n(B_2O_5)F_n$(n = 1,2): New Members of the Zincoborate Fluoride Series with Two Kinds of Isolated B-O Units

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Table S1. Atomic coordinates equivalent isotropic displacement parameters and bond valence Sum (BVS) for $Ba_3Zn(BO_3)(B_2O_5)F$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	U_{eq}(Å^2)	BVS
Ba(1)	0.4278(1)	0.8607(1)	0.1530(1)	0.016(1)	2.084
Ba(2)	0.7178(1)	0.8688(1)	0.2030(1)	0.015(1)	2.109
Ba(3)	0.1328(1)	0.8331(1)	0.0756(1)	0.016(1)	1.879
Zn(1)	0.8965(1)	0.8950(1)	0.5396(1)	0.015(1)	2.108
B(1)	0.5816(6)	0.8866(11)	0.4573(9)	0.016(2)	2.909
B(2)	0.9610(6)	0.9012(10)	0.2500(9)	0.014(2)	2.889
B(3)	0.7120(6)	1.0764(11)	0.5934(9)	0.017(2)	3.023
O(1)	0.9448(3)	0.6471(6)	0.5918(5)	0.017(1)	-1.938
O(2)	0.5763(3)	0.9799(7)	0.3209(5)	0.021(1)	-2.185
O(3)	0.9499(3)	1.1014(7)	0.6743(5)	0.019(1)	-1.955
O(4)	0.8928(3)	0.9556(7)	0.3209(5)	0.018(1)	-2.069
O(5)	0.3716(3)	1.0131(7)	0.4065(5)	0.020(1)	-2.157
O(6)	0.5509(4)	0.7902(7)	-0.0212(6)	0.025(1)	-1.935
O(7)	0.7718(4)	0.9675(8)	0.5342(6)	0.027(1)	-1.959
O(8)	0.7262(4)	1.2487(7)	0.1533(6)	0.030(1)	-1.799
F(1)	0.2634(3)	1.0698(6)	0.0956(4)	0.024(1)	-1.297

Table S2. Atomic coordinates equivalent isotropic displacement parameters and bond valence Sum (BVS) for $Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	U_{eq}(Å^2)	BVS
Ba(1)	0.3410(1)	0.2214(1)	0.0735(1)	0.010(1)	2.017
Ba(2)	0.4535(1)	0.2459(1)	0.3848(1)	0.011(1)	2.070
Zn(1)	0.1994(1)	0.1857(1)	0.2200(1)	0.010(1)	2.003
B(1)	0.2086(2)	0.7000(8)	0.1009(3)	0.010(1)	2.917
B(2)	0.0627(2)	0.2445(8)	0.2728(4)	0.011(1)	2.906
O(1)	0.3358(1)	0.3033(6)	0.4676(2)	0.015(1)	-1.843
O(2)	0.4333(1)	-0.0001(5)	0.1983(2)	0.016(1)	-1.951
O(3)	0.1145(1)	0.0717(5)	0.2605(2)	0.014(1)	-1.963
O(4)	0.2549(1)	0.3628(5)	0.3292(2)	0.012(1)	-1.980
O(5)	0.5000	0.6182(8)	0.2500	0.013(1)	-2.191
O(6)	0.2182(1)	0.4252(5)	0.1073(2)	0.013(1)	-2.069
F(1)	0.4506(1)	0.2526(4)	-0.0285(2)	0.018(1)	-1.010

Table S3. Selected bond lengths (Å) for $Ba_3Zn(BO_3)(B_2O_5)F$.

Ba(1)-O(2)	2.603(5)	Ba(3)-O(3)$^{\#4}$	2.750(5)
Ba(1)-O(6)	2.659(5)	Ba(3)-O(1)$^{\#6}$	2.787(5)
Ba(1)-O(2)$^{\#1}$	2.680(5)	Ba(3)-O(3)$^{\#1}$	2.835(5)
Ba(1)-O(5)	2.734(5)	Ba(3)-O(4)$^{\#1}$	2.845(5)
Ba(1)-O(6)$^{\#2}$	2.748(5)	Ba(3)-O(1)$^{\#7}$	2.885(5)
Ba(1)-F(1)	2.861(5)	Ba(3)-O(8)$^{\#1}$	2.964(6)
Ba(1)-O(8)$^{\#1}$	3.219(6)	Ba(3)-O(7)$^{\#1}$	3.174(6)
Ba(1)-O(6)$^{\#3}$	3.299(5)	Ba(3)-O(8)$^{\#2}$	3.232(6)
Ba(1)-O(8)$^{\#2}$	3.323(6)	Zn(1)-O(1)	1.909(5)
Ba(2)-O(2)	2.659(5)	Zn(1)-O(3)	1.951(5)
Ba(2)-O(8)	2.704(5)	Zn(1)-O(7)	1.953(5)
Ba(2)-F(1)$^{\#2}$	2.716(4)	Zn(1)-O(4)	1.954(5)
Ba(2)-F(1)$^{\#1}$	2.722(4)	B(1)-O(6)$^{\#3}$	1.348(9)
Ba(2)-O(4)	2.743(5)	B(1)-O(2)	1.352(9)
Ba(2)-O(5)$^{\#1}$	2.918(5)	B(1)-O(5)$^{\#4}$	1.457(9)
Ba(2)-O(7)	2.956(5)	B(2)-O(4)	1.352(10)
Ba(2)-O(6)	2.972(6)	B(2)-O(3)$^{\#10}$	1.397(9)
Ba(2)-O(7)$^{\#4}$	2.973(6)	B(2)-O(1)$^{\#5}$	1.406(9)
Ba(3)-F(1)	2.566(4)	B(3)-O(8)$^{\#12}$	1.336(9)

Symmetry transformations used to generate equivalent atom	
#1	-x+1,y-1/2,-z+1/2
#2	-x+1,-y+2,-z
#3	x,-y+3/2,z+1/2
#4	-x+1,-y+2,-z+1

Table S4. Selected bond lengths (Å) for $Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$.

Ba(1)-F(1)	2.659(3)	Ba(2)-O(5)	2.760(3)
Ba(1)-O(2)	2.674(3)	Ba(2)-O(3)$^{\#3}$	2.817(3)
Ba(1)-O(6)$^{\#1}$	2.705(3)	Ba(2)-O(2)$^{\#6}$	2.873(3)
Ba(1)-O(1)$^{\#2}$	2.749(3)	Zn(1)-O(3)	1.920(3)
Ba(1)-O(6)	2.757(3)	Zn(1)-O(6)	1.949(3)
Ba(1)-O(3)$^{\#3}$	2.901(3)	Zn(1)-O(4)$^{\#5}$	1.986(3)
Ba(1)-O(1)$^{\#4}$	2.965(3)	Zn(1)-O(4)	1.989(3)
Ba(1)-O(4)$^{\#5}$	2.979(3)	B(1)-O(1)$^{\#3}$	1.346(5)
Ba(2)-F(1)$^{\#6}$	2.650(3)	B(1)-O(6)	1.390(5)
Ba(2)-O(1)	2.693(3)	B(1)-O(4)$^{\#3}$	1.411(5)
Ba(2)-F(1)$^{\#7}$	2.739(3)	B(2)-O(2)$^{\#3}$	1.332(5)
Ba(2)-O(2)	2.744(3)	B(2)-O(3)	1.379(5)
Ba(2)-F(1)$^{\#8}$	2.753(3)	B(2)-O(5)$^{\#9}$	1.445(5)

Symmetry transformations used to generate equivalent atom	
#1	-x+1/2,-y+1/2,-z
#2	x,-y+1,z-1/2
#3	-x+1/2,y+1/2,-z+1/2
#4	x,-y,z-1/2
#5	-x+1/2,y+1/2,-z+1/2
#6	-x+1,y,-z+1/2
#7	x,-y,z+1/2
#8	x,-y+1,z+1/2

Table S5. The basic information of the existing fluorine-containing zincoborates

Empirical Formula	**V** ($Å^3$)	**n**	**M/B**	**Number density ($\times 10^{-3}$)**
$Ba_3Zn(BO_3)(B_2O_5)F$	917.4	$n(BO_3)= 6$ $n(B_2O_5)= 4$	1.33	$d(BO_3)= 6.54$ $d(B_2O_5)= 4.36$
$Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$	1330.7	$n(BO_3)= 6$ $n(B_2O_5)= 4$	1.5	$d(BO_3)= 4.51$ $d(B_2O_5)= 3.01$
$Ba_3Zn_2(BO_3)_3F$	738.19	$n(BO_3)= 12$	1.67	$d(BO_3)= 16.25$
$Ba_5Zn_2(BO_3)_4F_2$	1090.68	$n(BO_3)= 16$	1.75	$d(BO_3)= 14.67$
$BaZnBO_3F$	95.11	$n(BO_3) = 1$	2	$d(BO_3)= 10.51$

Table S6. The basic information of the existing anhydrous-zincoborates

No.	Chemical formula	A/B	B-O cluster
1	$Zn_5Mn(BO_3)_2O_4$	3	isolated BO_3
2	$KZn_2(BO_3)Cl_2$	3	isolated BO_3
3	$BaZn(BO_3)F$	2	isolated BO_3
4	$CdZn_2KB_2O_6F$	2	isolated BO_3
5	α-$LiZnBO_3$	2	isoalted BO_3
6	β-$LiZnBO_3$	2	isolated BO_3
7	$Ba_5Zn_2B_4O_{12}F_2$	1.75	isolated BO_3
8	$CsZn_4(BO_3)_3$	1.67	isolated BO_3
9	$KZn_4B_3O_9$	1.67	isolated BO_3
10	$KZn_4(BO_3)_3$	1.67	isolated BO_3
11	$Ba_3Zn_2B_3O_9F$	1.67	isolated BO_3
12	α-$Zn_3(BO_3)_2$	1.5	isolated BO_3
13	β-$Zn_3(BO_3)_2$	1.5	isolated BO_3
14	$BaZn_2(BO_3)_2$	1.5	isolated BO_3
15	$PbZn_2(BO_3)_2$	1.5	isolated BO_3
16	$Cd_3Zn_3(BO_3)_4$	1.5	isolated BO_3
17	$Bi_2(ZnB_2O_7)$	1.5	isolated B_2O_5 and B_2O_7
18	$Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$	1.5	isolated BO_3 and B_2O_5
19	$Ba_3Zn(BO_3)(B_2O_5)F$	1.33	isolated BO_3 and B_2O_5
20	$CsZn_2B_3O_7$	1	isolated B_3O_6 and BO_3
21	$Cs_3Zn_6(B_9O_{21})$	1	isolated B_3O_6 and BO_3
22	$Zn_8Se_2(BO_2)_{12}$	0.83	3D network
23	$K_2Na(ZnB_5O_{10})$	0.8	isolated B_5O_{10}
24	$K_3ZnB_5O_{10}$	0.8	isolated B_5O_{10}
25	α-$Na_3Zn(B_5O_{10})$	0.8	isolated B_5O_{10}
26	β-$Na_3Zn(B_5O_{10})$	0.8	isolated B_5O_{10}
27	$Rb_3Zn(B_5O_{10})$	0.8	isolated B_5O_{10}
28	$ZnV_{12}B_{18}O_{63}$	0.72	isolated $B_{18}O_{42}$
29	α-$Pb_2Ba_4Zn_4B_{14}O_{31}$	0.71	isolated B_2O_5 and B_6O_{13}
30	β-$Pb_2Ba_4Zn_4B_{14}O_{31}$	0.71	isolated B_2O_5 and B_6O_{13}
31	γ-$Pb_2Ba_4Zn_4B_{14}O_{31}$	0.71	isolated B_2O_5 and B_6O_{13}
32	$Zn_4(B_6O_{12})O$	0.67	3D network
33	$KBa_2Zn_3B_9O_{19}$	0.67	isolated B_3O_6 and B_6O_{13}
34	$KZnB_3O_6$	0.67	isolated B_6O_{12}
35	$Ba_4K_2Zn_5(B_3O_6)_3(B_9O_{19})$	0.61	isolated B_3O_6 and B_9O_{19}
36	$Pb_4Zn_2B_{10}O_{21}$	0.6	$B_5O_8O_{5/2}$ layer
37	$Ba_4Na_2Zn_4(B_3O_6)_2(B_{12}O_{24})$	0.55	isolated B_3O_6 and $B_{12}O_{24}$
38	$NdZn(B_5O_{10})$	0.5	isolated B_5O_{10}
39	$Ba_2Zn(B_3O_6)_2$	0.5	isolated B_3O_6

40	$Na_2Zn(B_6O_{11})$	0.5	$B_3O_4O_{3/2}$ layer
41	$Zn_3(B_7O_{13})Br$	0.43	3D network
42	$Zn_3(B_7O_{13})Cl$	0.43	3D network
43	$CeZn(B_5O_{10})$	0.4	isolated B_5O_{11}
44	$EuZn(BO_2)_5$	0.4	B_5O_{10} layer
45	$LaZn(B_5O_{10})$	0.4	B_5O_{10} layer
46	$TbZn(B_5O_{10})$	0.4	isolated B_5O_{10}
47	α-$Zn(B_4O_7)$	0.25	3D network
48	β-$Zn(B_4O_7)$	0.25	3D network

Table S7. The calculated bond lengths (Å) in comparison with experimental data, Mulliken bond overlap populations (BOP) for $Ba_3Zn(BO_3)(B_2O_5)F$.

Bond type	Exp.	Cal.	BOP
Ba(1)-O(2)	2.603(5)	2.659(8)	-0.25
Ba(1)-O(6)	2.659(5)	2.659(5)	-0.25
Ba(1)-O(2)$^{\#1}$	2.680(5)	2.679(9)	-0.25
Ba(1)-O(5)	2.734(5)	2.737(1)	-0.15
Ba(1)-O(6)$^{\#2}$	2.748(5)	2.748(5)	-0.15
Ba(1)-F(1)	2.861(5)	2.861(5)	-0.17
Ba(1)-O(8)$^{\#1}$	3.219(6)	3.221(3)	-0.13
Ba(1)-O(6)$^{\#3}$	3.299(5)	3.299(5)	-0.13
Ba(1)-O(8)$^{\#2}$	3.323(6)	3.325(1)	-0.13
Ba(2)-O(2)	2.659(5)	2.657(8)	-0.25
Ba(2)-O(8)	2.704(5)	2.706(2)	-0.15
Ba(2)-F(1)$^{\#2}$	2.716(4)	2.716(4)	-0.32
Ba(2)-F(1)$^{\#1}$	2.722(4)	2.722(4)	-0.25
Ba(2)-O(4)	2.743(5)	2.742(9)	-0.15
Ba(2)-O(5)$^{\#1}$	2.918(5)	2.919(6)	-0.14
Ba(2)-O(7)	2.956(5)	2.959(4)	-0.14
Ba(2)-O(6)	2.972(6)	2.972(6)	-0.14
Ba(2)-O(7)$^{\#4}$	2.973(6)	2.974(1)	-0.14
Ba(3)-F(1)	2.566(4)	2.566(4)	-0.68
Ba(3)-O(3)$^{\#4}$	2.750(5)	2.750(5)	-0.15
Ba(3)-O(1)$^{\#6}$	2.787(5)	2.779(9)	-0.15
Ba(3)-O(3)$^{\#1}$	2.835(5)	2.835(5)	-0.14
Ba(3)-O(4)$^{\#1}$	2.845(5)	2.839(6)	-0.14
Ba(3)-O(1)$^{\#7}$	2.885(5)	2.890(9)	-0.14
Ba(3)-O(8)$^{\#1}$	2.964(6)	2.964(6)	-0.14
Ba(3)-O(7)$^{\#1}$	3.174(6)	3.179(3)	-0.13
Ba(3)-O(8)$^{\#2}$	3.232(6)	3.232(6)	-0.13
Zn(1)-O(1)	1.909(5)	1.909(5)	0.23
Zn(1)-O(3)	1.951(5)	1.951(5)	0.23
Zn(1)-O(7)	1.953(5)	1.953(5)	0.25
Zn(1)-O(4)	1.954(5)	1.954(5)	0.25

B(1)-O(6)$^{\#3}$	1.348(9)	1.348(9)	0.92
B(1)-O(2)	1.352(9)	1.353(7)	0.92
B(1)-O(5)$^{\#4}$	1.457(9)	1.459(2)	0.74
B(2)-O(4)	1.352(10)	1.350(9)	0.86
B(2)-O(3)$^{\#10}$	1.397(9)	1.397(9)	0.86
B(2)-O(1)$^{\#5}$	1.406(9)	1.410(7)	0.79
B(3)-O(8)$^{\#12}$	1.336(9)	1.336(9)	0.92

Table S8. The calculated bond lengths (Å) in comparison with experimental data, Mulliken bond overlap populations (BOP) for $Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$.

Bond type	Exp.	Cal.	BOP
Ba(1)-F(1)	2.659(3)	2.659(3)	-0.49
Ba(1)-O(2)	2.674(3)	2.675(7)	-0.41
Ba(1)-O(6)$^{\#1}$	2.705(3)	2.705(3)	-0.27
Ba(1)-O(1)$^{\#2}$	2.749(3)	2.750(4)	-0.27
Ba(1)-O(6)	2.757(3)	2.757(3)	-0.27
Ba(1)-O(3)$^{\#3}$	2.901(3)	2.898(9)	-0.21
Ba(1)-O(1)$^{\#4}$	2.965(3)	2.964(5)	-0.21
Ba(1)-O(4)$^{\#5}$	2.979(3)	2.980(2)	-0.21
Ba(2)-F(1)$^{\#6}$	2.650(3)	2.650(3)	-0.49
Ba(2)-O(1)	2.693(3)	2.695(0)	-0.41
Ba(2)-F(1)$^{\#7}$	2.739(3)	2.739(3)	-0.54
Ba(2)-O(2)	2.744(3)	2.742(9)	-0.27
Ba(2)-F(1)$^{\#8}$	2.753(3)	2.753(3)	-0.54
Ba(2)-O(5)	2.760(3)	2.759(6)	-0.27
Ba(2)-O(3)$^{\#3}$	2.817(3)	2.812(9)	-0.21
Ba(2)-O(2)$^{\#6}$	2.873(3)	2.875(1)	-0.21
Zn(1)-O(3)	1.920(3)	1.920(3)	0.27
Zn(1)-O(6)	1.949(3)	1.949(3)	0.27
Zn(1)-O(4)$^{\#5}$	1.986(3)	1.986(3)	0.14
Zn(1)-O(4)	1.989(3)	1.989(3)	0.14
B(1)-O(1)$^{\#3}$	1.346(5)	1.345(6)	0.90
B(1)-O(6)	1.390(5)	1.389(3)	0.90
B(1)-O(4)$^{\#3}$	1.411(5)	1.409(9)	0.77
B(2)-O(2)$^{\#3}$	1.332(5)	1.334(3)	0.92
B(2)-O(3)	1.379(5)	1.380(1)	0.92
B(2)-O(5)$^{\#9}$	1.445(5)	1.446(3)	0.77

Fig. S1. Coordination of the Ba atoms in $Ba_3Zn(BO_3)(B_2O_5)F$ (a, b and c) and $Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$ (d and e).

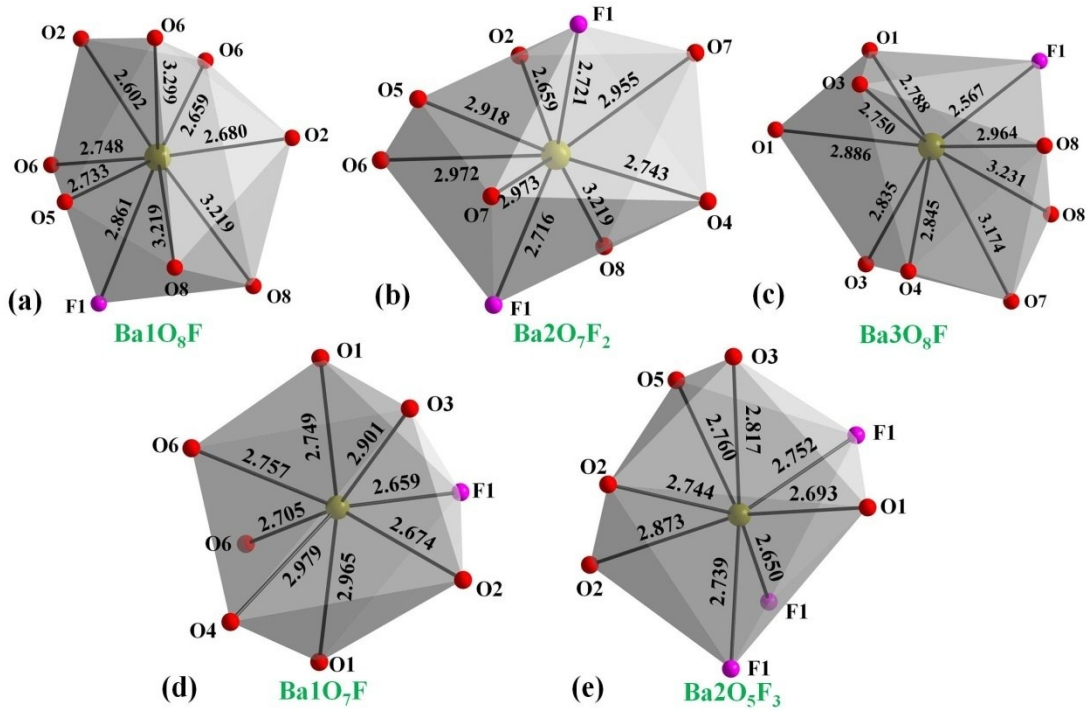

Fig. S2. The B-O groups in $Ba_3Zn(BO_3)(B_2O_5)F$ (a) and $Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$ (b).

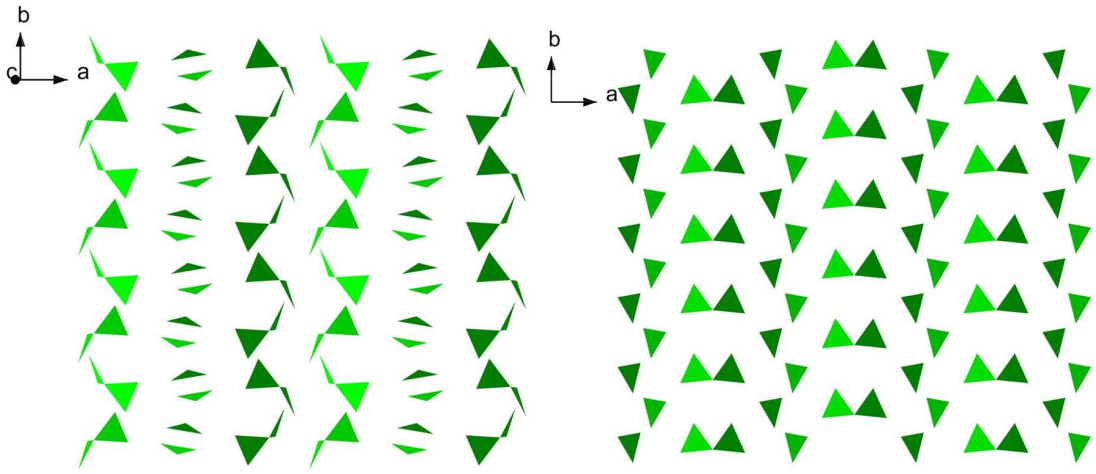

Fig. S3. The angles between two planes built up by two single $[BO_3]^{3-}$ units $Ba_3Zn(BO_3)(B_2O_5)F$ (a) and $Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$ (b).

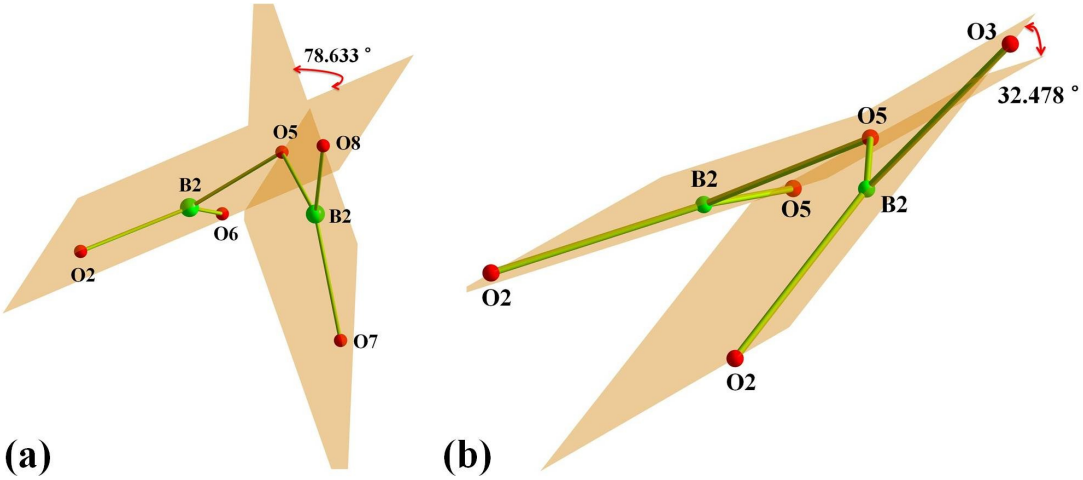

Fig. S4. Coordination of the Zn atoms in $Ba_3Zn(BO_3)(B_2O_5)F$ (a) and $Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$ (b), $Ba_3Zn_2(BO_3)_3F$ (c), $Ba_5Zn_2(BO_3)_4F_2$(d), and $BaZnBO_3F$ (e), respectively.