Supporting Information

Effect of the $[Ba_2BO_3F]_\infty$ Layer on Band Gap: Synthesis, Characterization and Theoretical Study of $BaZn_2B_2O_6 \cdot nBa_2BO_3F$ (n = 0, 1, 2)

Hongping Wu,[†] Xin Su,[†,‡] Shujuan Han,[†] Zhihua Yang,[†] Shilie Pan[†,*]

[†]*Xinjiang Technical Institute of Physics & Chemistry, Key Laboratory of Functional Materials and Devices under Special Environments, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China*
[‡]*University of Chinese Academy of Sciences, Beijing 100049, China*

*To whom correspondence should be addressed. Phone: (+86)991-3674558.
Fax: (+86)991-3838957. E-mail: slpan@ms.xjb.ac.cn (S. Pan).

Table S1a. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $Ba_3Zn_2B_3O_9F$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Ba(1)	2924(1)	2500	11342(1)	14(1)	1.98
Ba(2)	-399(1)	3790(1)	8433(1)	23(1)	1.84
Zn(1)	5744(1)	4139(1)	10945(1)	21(1)	2.18
B(1)	1764(14)	2500	5718(14)	20(2)	2.78
B(2)	7420(10)	5396(5)	9023(11)	24(2)	3.04
F(1)	-110(8)	2500	10697(9)	56(2)	1.06
O(1)	3513(6)	4010(3)	10261(7)	28(1)	2.03
O(2)	6856(6)	4658(3)	8887(7)	31(1)	2.02
O(3)	2342(10)	2500	7484(9)	41(2)	1.68
O(4)	6059(7)	4459(5)	13479(7)	52(2)	2.05
O(5A)	1960(30)	3218(6)	4695(15)	26(5)	1.91
O(5B)	1000(40)	3044(12)	4820(20)	47(7)	2.15

Table S1b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound $Ba_5Zn_2B_4O_{12}F_2$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Ba(1)	1675(1)	943(1)	9011(1)	11(1)	1.85
Ba(2)	743(1)	3880(1)	1639(1)	11(1)	2.06
Ba(3)	0	692(1)	-2500	10(1)	2.07
Zn(1)	1912(1)	3464(1)	5163(1)	11(1)	2.11
B(1)	764(3)	1900(9)	5299(8)	13(1)	2.96
B(2)	2248(3)	3457(8)	2236(8)	12(1)	2.96
F(1)	771(1)	3143(4)	-1486(4)	16(1)	1.17
O(1)	-250(2)	2530(5)	409(5)	19(1)	1.76
O(2)	2178(2)	5928(5)	5569(5)	13(1)	2.05
O(3)	1812(2)	2737(5)	2724(5)	14(1)	1.88
O(4)	2249(2)	1441(5)	6634(5)	13(1)	2.08
O(5)	862(2)	148(5)	5907(5)	17(1)	1.85
O(6)	1179(2)	3142(5)	5326(5)	18(1)	2.06

Table S2a. Selected bond distances (Å) and angles (deg) for $Ba_3Zn_2B_3O_9F$.

Ba(1)-F(1)	2.597(7)	B(1)-O(3)	1.335(12)
Ba(1)-F(1)#1	2.662(7)	B(1)-Ba(1)#13	3.232(11)
Ba(1)-O(1)#2	2.745(5)	B(1)-Ba(2)#5	3.312(9)
Ba(1)-O(1)	2.745(5)	B(1)-Ba(2)#6	3.312(9)
Ba(1)-O(3)	2.760(7)	B(1)-Ba(2)#2	3.446(9)
Ba(1)-O(5A)#3	2.784(11)	B(2)-O(2)	1.356(10)
Ba(1)-O(5A)#4	2.784(12)	B(2)-O(4)#14	1.360(10)
Ba(1)-O(5B)#5	2.87(4)	B(2)-O(1)#15	1.382(10)
Ba(1)-O(5B)#6	2.87(4)	F(1)-Ba(1)-F(1)#1	138.55(15)
Ba(1)-O(5B)#3	3.08(3)	F(1)-Ba(1)-O(1)#2	97.44(12)
Ba(1)-O(5B)#4	3.08(3)	F(1)#1-Ba(1)-O(1)#2	96.00(11)
Ba(2)-F(1)	2.739(4)	F(1)-Ba(1)-O(1)	97.44(12)
Ba(2)-O(4)#7	2.748(6)	F(1)#1-Ba(1)-O(1)	96.00(11)
Ba(2)-O(5A)#8	2.77(3)	O(1)#2-Ba(1)-O(1)	141.4(2)
Ba(2)-O(2)#9	2.768(5)	F(1)-Ba(1)-O(3)	69.7(2)
Ba(2)-O(1)#8	2.783(5)	F(1)#1-Ba(1)-O(3)	151.8(2)
Ba(2)-O(2)#8	2.914(5)	O(1)#2-Ba(1)-O(3)	76.08(11)
Ba(2)-O(3)#8	2.990(6)	O(1)-Ba(1)-O(3)	76.08(11)
Ba(2)-O(4)#10	3.054(8)	F(1)-Ba(1)-O(5A)#3	82.0(6)
Ba(2)-O(5B)	3.08(2)	F(1)#1-Ba(1)-O(5A)#3	61.2(5)
Ba(2)-O(3)	3.268(7)	O(1)#2-Ba(1)-O(5A)#3	134.9(2)
Zn(1)-O(4)	1.886(5)	O(1)-Ba(1)-O(5A)#3	82.5(3)
Zn(1)-O(5A)#5	1.935(14)	O(3)-Ba(1)-O(5A)#3	141.5(4)
Zn(1)-O(2)	1.941(5)	F(1)-Ba(1)-O(5A)#4	82.0(6)
Zn(1)-O(1)	1.952(5)	F(1)#1-Ba(1)-O(5A)#4	61.2(5)
Zn(1)-O(5B)#5	1.964(19)	O(1)#2-Ba(1)-O(5A)#4	82.5(3)
B(1)-O(5B)#2	1.301(13)	F(1)-Ba(2)-O(1)#8	133.04(14)
B(1)-O(5B)	1.301(13)	O(4)#7-Ba(2)-O(1)#8	146.10(17)
O(1)-Ba(1)-O(5A)#4	134.9(2)	O(5A)#8-Ba(2)-O(1)#8	103.2(4)
O(3)-Ba(1)-O(5A)#4	141.5(4)	O(2)#9-Ba(2)-O(1)#8	76.12(15)
O(5A)#3-Ba(1)-O(5A)#4	52.6(5)	F(1)-Ba(2)-O(2)#8	132.92(17)
F(1)-Ba(1)-O(5B)#5	146.9(4)	O(4)#7-Ba(2)-O(2)#8	86.49(15)
F(1)#1-Ba(1)-O(5B)#5	70.3(5)	O(5A)#8-Ba(2)-O(2)#8	166.6(3)
O(1)#2-Ba(1)-O(5B)#5	93.7(3)	O(2)#9-Ba(2)-O(2)#8	109.58(17)
O(1)-Ba(1)-O(5B)#5	56.7(3)	O(1)#8-Ba(2)-O(2)#8	67.78(14)
O(3)-Ba(1)-O(5B)#5	83.1(5)	F(1)-Ba(2)-O(3)#8	65.39(17)
O(5A)#3-Ba(1)-O(5B)#5	111.1(10)	O(4)#7-Ba(2)-O(3)#8	139.85(17)
O(5A)#4-Ba(1)-O(5B)#5	130.4(9)	O(5A)#8-Ba(2)-O(3)#8	47.8(3)
F(1)-Ba(1)-O(5B)#6	146.9(4)	O(2)#9-Ba(2)-O(3)#8	83.75(18)
F(1)#1-Ba(1)-O(5B)#6	70.3(5)	O(1)#8-Ba(2)-O(3)#8	71.88(15)
O(1)#2-Ba(1)-O(5B)#6	56.7(3)	O(2)#8-Ba(2)-O(3)#8	132.24(16)
O(1)-Ba(1)-O(5B)#6	93.7(3)	O(3)-Ba(1)-O(5B)#6	83.1(5)
O(5A)#3-Ba(1)-O(5B)#6	130.4(9)	F(1)-Ba(2)-O(4)#10	143.59(14)

O(5A)#4-Ba(1)-O(5B)#6	111.1(10)	O(4)#7-Ba(2)-O(4)#10	70.3(2)
O(5B)#5-Ba(1)-O(5B)#6	38.0(5)	O(5A)#8-Ba(2)-O(4)#10	101.4(2)
F(1)-Ba(1)-O(5B)#3	67.7(5)	O(2)#9-Ba(2)-O(4)#10	47.02(15)
F(1)#1-Ba(1)-O(5B)#3	72.9(4)	O(1)#8-Ba(2)-O(4)#10	79.45(13)
O(1)#2-Ba(1)-O(5B)#3	127.0(5)	O(2)#8-Ba(2)-O(4)#10	67.84(14)
O(1)-Ba(1)-O(5B)#3	91.7(5)	O(3)#8-Ba(2)-O(4)#10	127.91(16)
O(3)-Ba(1)-O(5B)#3	133.5(4)	F(1)-Ba(2)-O(5B)	96.4(4)
O(5A)#3-Ba(1)-O(5B)#3	16.0(3)	O(4)#7-Ba(2)-O(5B)	131.0(6)
O(5A)#4-Ba(1)-O(5B)#3	46.1(7)	O(5A)#8-Ba(2)-O(5B)	123.6(8)
O(5B)#5-Ba(1)-O(5B)#3	127.1(11)	O(2)#9-Ba(2)-O(5B)	129.6(4)
O(5B)#6-Ba(1)-O(5B)#3	143.1(8)	O(1)#8-Ba(2)-O(5B)	53.9(3)
F(1)-Ba(1)-O(5B)#4	67.7(5)	O(2)#8-Ba(2)-O(5B)	60.0(7)
F(1)#1-Ba(1)-O(5B)#4	72.9(4)	O(3)#8-Ba(2)-O(5B)	75.9(7)
O(1)#2-Ba(1)-O(5B)#4	91.7(5)	O(4)#10-Ba(2)-O(5B)	119.1(4)
O(1)-Ba(1)-O(5B)#4	127.0(5)	F(1)-Ba(2)-O(3)	60.57(17)
O(3)-Ba(1)-O(5B)#4	133.5(4)	O(4)#7-Ba(2)-O(3)	97.4(2)
O(5A)#3-Ba(1)-O(5B)#4	46.1(7)	O(5A)#8-Ba(2)-O(3)	115.2(3)
O(5A)#4-Ba(1)-O(5B)#4	16.0(3)	O(2)#9-Ba(2)-O(3)	167.95(16)
O(5B)#5-Ba(1)-O(5B)#4	143.1(8)	O(1)#8-Ba(2)-O(3)	97.67(16)
O(5B)#6-Ba(1)-O(5B)#4	127.1(11)	O(2)#8-Ba(2)-O(3)	76.73(15)
O(5B)#3-Ba(1)-O(5B)#4	35.3(10)	O(3)#8-Ba(2)-O(3)	84.50(5)
F(1)-Ba(2)-O(4)#7	80.64(18)	O(4)#10-Ba(2)-O(3)	142.84(15)
F(1)-Ba(2)-O(5A)#8	60.5(3)	O(5B)-Ba(2)-O(3)	44.0(3)
O(4)#7-Ba(2)-O(5A)#8	97.5(3)	O(4)-Zn(1)-O(5A)#5	112.5(5)
F(1)-Ba(2)-O(2)#9	116.19(17)	O(4)-Zn(1)-O(2)	120.3(3)
O(4)#7-Ba(2)-O(2)#9	93.31(19)	O(5A)#5-Zn(1)-O(2)	86.8(6)
O(5A)#8-Ba(2)-O(2)#9	57.6(3)	O(4)-Zn(1)-O(1)	113.7(2)
O(5A)#5-Zn(1)-O(1)	111.1(8)	O(3)-B(1)-O(5A)#2	115.1(9)
O(2)-Zn(1)-O(1)	109.4(2)	O(5B)#2-B(1)-O(5A)	115.4(13)
O(4)-Zn(1)-O(5B)#5	121.5(6)	O(5B)-B(1)-O(5A)	36.6(9)
O(5A)#5-Zn(1)-O(5B)#5	25.8(5)	O(3)-B(1)-O(5A)	115.1(9)
O(2)-Zn(1)-O(5B)#5	100.5(6)	O(5A)#2-B(1)-O(5A)	118.1(11)
O(1)-Zn(1)-O(5B)#5	85.9(11)	O(2)-B(2)-O(4)#14	118.7(8)
O(5B)#2-B(1)-O(5B)	92(2)	O(2)-B(2)-O(1)#15	121.0(7)
O(5B)#2-B(1)-O(3)	129.4(8)	O(4)#14-B(2)-O(1)#15	120.2(8)
O(5B)-B(1)-O(3)	129.4(8)	O(5B)-B(1)-O(5A)#2	115.4(13)
O(5B)#2-B(1)-O(5A)#2	36.6(9)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,y,-z+5/2 #2 x,-y+1/2,z #3 x,y,z+1

#4 x,-y+1/2,z+1 #5 x+1/2,y,-z+3/2

#6 x+1/2,-y+1/2,-z+3/2 #7 x-1/2,y,-z+5/2

#8 x-1/2,y,-z+3/2 #9 x-1,y,z #10 -x+1/2,-y+1,z-1/2

#11 x+1,y,z #12 -x+1/2,-y+1,z+1/2 #13 x,y,z-1 #14 -x+3/2,-y+1,z-1/2 #15 -x+1,-y+1,-z+2 #16 -x+3/2,-y+1,z+1/2

Table S2b. Selected bond distances (Å) and angles (deg) for $Ba_5Zn_2B_4O_{12}F_2$.

Ba(1)-O(4)	2.730(4)	O(2)#1-Ba(1)-O(4)#3	94.54(11)
Ba(1)-O(2)#1	2.743(4)	F(1)#2-Ba(1)-O(4)#3	135.80(10)
Ba(1)-F(1)#2	2.763(4)	O(4)-Ba(1)-O(5)	80.08(13)
Ba(1)-O(4)#3	2.816(4)	O(2)#1-Ba(1)-O(5)	135.41(10)
Ba(1)-O(5)	2.848(4)	F(1)#2-Ba(1)-O(5)	66.21(10)
Ba(1)-O(2)#4	2.885(4)	O(4)#3-Ba(1)-O(5)	130.05(11)
Ba(1)-O(3)#3	2.918(4)	O(4)-Ba(1)-O(2)#4	49.60(11)
Ba(1)-O(5)#3	3.003(4)	O(2)#1-Ba(1)-O(2)#4	66.76(13)
Ba(1)-O(3)#2	3.178(4)	F(1)#2-Ba(1)-O(2)#4	144.79(10)
Ba(1)-O(6)	3.296(4)	O(4)#3-Ba(1)-O(2)#4	65.97(11)
Ba(2)-F(1)	2.578(4)	O(5)-Ba(1)-O(2)#4	126.34(11)
Ba(2)-F(1)#1	2.620(3)	O(4)-Ba(1)-O(3)#3	74.66(11)
Ba(2)-O(1)	2.670(4)	O(2)#1-Ba(1)-O(3)#3	146.21(11)
Ba(2)-O(6)#6	2.768(4)	F(1)#2-Ba(1)-O(3)#3	130.92(10)
Ba(2)-O(3)	2.783(4)	O(4)#3-Ba(1)-O(3)#3	67.16(11)
Ba(2)-O(6)	2.914(4)	O(5)-Ba(1)-O(3)#3	68.70(10)
Ba(2)-O(5)#7	3.014(4)	O(2)#4-Ba(1)-O(3)#3	79.67(10)
Ba(2)-O(1)#8	3.126(4)	O(4)-Ba(1)-O(5)#3	165.68(10)
Ba(2)-O(1)#9	3.159(4)	O(2)#1-Ba(1)-O(5)#3	107.27(11)
Ba(3)-F(1)#10	2.628(3)	F(1)#2-Ba(1)-O(5)#3	63.28(11)
Ba(3)-F(1)	2.628(3)	O(4)#3-Ba(1)-O(5)#3	76.08(12)
Ba(3)-O(1)#7	2.847(4)	O(5)-Ba(1)-O(5)#3	86.46(12)
Ba(3)-O(1)#11	2.847(4)	O(2)#4-Ba(1)-O(5)#3	140.48(10)
Ba(3)-O(5)#8	2.869(4)	O(3)#3-Ba(1)-O(5)#3	95.95(11)
Ba(3)-O(5)#12	2.869(4)	O(4)-Ba(1)-O(3)#2	130.76(11)
Ba(3)-O(1)	2.902(4)	O(2)#1-Ba(1)-O(3)#2	46.74(10)
Ba(3)-O(1)#10	2.902(4)	F(1)#2-Ba(1)-O(3)#2	77.08(9)
Ba(3)-O(5)#11	3.083(4)	O(4)#3-Ba(1)-O(3)#2	69.46(11)
Ba(3)-O(5)#7	3.083(4)	O(5)-Ba(1)-O(3)#2	140.47(11)
Zn(1)-O(2)	1.911(4)	O(2)#4-Ba(1)-O(3)#2	92.20(10)
Zn(1)-O(4)	1.937(4)	O(3)#3-Ba(1)-O(3)#2	135.36(10)
Zn(1)-O(6)	1.942(4)	O(5)#3-Ba(1)-O(3)#2	63.45(10)
Zn(1)-O(3)	1.972(4)	O(4)-Ba(1)-O(6)	57.64(11)
B(1)-O(5)	1.361(7)	O(2)#1-Ba(1)-O(6)	91.68(11)
B(1)-O(1)#8	1.372(7)	F(1)#2-Ba(1)-O(6)	58.76(9)
B(1)-O(6)	1.395(7)	O(4)#3-Ba(1)-O(6)	164.88(10)
B(2)-O(4)#5	1.369(7)	O(5)-Ba(1)-O(6)	45.45(10)
B(2)-O(2)#6	1.373(7)	O(2)#4-Ba(1)-O(6)	104.25(10)
B(2)-O(3)	1.386(8)	O(3)#3-Ba(1)-O(6)	100.47(11)
O(4)-Ba(1)-O(2)#1	85.95(12)	O(5)#3-Ba(1)-O(6)	115.11(11)
O(4)-Ba(1)-F(1)#2	114.63(10)	O(3)#2-Ba(1)-O(6)	123.96(11)
O(2)#1-Ba(1)-F(1)#2	82.22(11)	B(2)#2-Ba(1)-O(6)	115.67(14)
O(4)-Ba(1)-O(4)#3	109.04(13)	B(2)#5-Ba(1)-O(6)	79.47(13)

F(1)-Ba(2)-F(1)#1	136.33(8)	O(1)#7-Ba(3)-O(5)#8	93.93(11)
F(1)-Ba(2)-O(1)	80.70(11)	O(1)#11-Ba(3)-O(5)#8	72.88(11)
F(1)#1-Ba(2)-O(1)	112.98(12)	F(1)#10-Ba(3)-O(5)#12	124.53(11)
F(1)-Ba(2)-O(6)#6	70.99(11)	F(1)-Ba(3)-O(5)#12	67.62(11)
F(1)#1-Ba(2)-O(6)#6	67.82(12)	O(1)#7-Ba(3)-O(5)#12	72.88(11)
O(1)-Ba(2)-O(6)#6	126.31(12)	O(1)#11-Ba(3)-O(5)#12	93.93(11)
F(1)-Ba(2)-O(3)	87.66(11)	O(5)#8-Ba(3)-O(5)#12	164.20(15)
F(1)#1-Ba(2)-O(3)	101.18(11)	F(1)#10-Ba(3)-O(1)	67.99(10)
O(1)-Ba(2)-O(3)	140.91(12)	F(1)-Ba(3)-O(1)	75.66(11)
O(6)#6-Ba(2)-O(3)	83.31(12)	O(1)#7-Ba(3)-O(1)	141.80(13)
F(1)-Ba(2)-O(6)	147.36(11)	O(1)#11-Ba(3)-O(1)	88.24(12)
F(1)#1-Ba(2)-O(6)	68.10(11)	O(5)#8-Ba(3)-O(1)	48.86(11)
O(1)-Ba(2)-O(6)	112.18(11)	O(5)#12-Ba(3)-O(1)	141.65(11)
O(6)#6-Ba(2)-O(6)	116.29(12)	F(1)#10-Ba(3)-O(1)#10	75.66(11)
O(3)-Ba(2)-O(6)	63.14(11)	F(1)-Ba(3)-O(1)#10	67.99(10)
F(1)-Ba(2)-O(5)#7	65.12(10)	O(1)#7-Ba(3)-O(1)#10	88.24(12)
F(1)#1-Ba(2)-O(5)#7	157.30(10)	O(1)#11-Ba(3)-O(1)#10	141.80(13)
O(1)-Ba(2)-O(5)#7	73.10(12)	O(5)#8-Ba(3)-O(1)#10	141.65(11)
O(6)#6-Ba(2)-O(5)#7	127.65(12)	O(5)#12-Ba(3)-O(1)#10	48.86(11)
O(3)-Ba(2)-O(5)#7	68.16(11)	O(1)-Ba(3)-O(1)#10	125.26(16)
O(6)-Ba(2)-O(5)#7	89.26(10)	F(1)#10-Ba(3)-O(5)#11	63.54(10)
F(1)-Ba(2)-O(1)#8	142.29(10)	F(1)-Ba(3)-O(5)#11	135.51(10)
F(1)#1-Ba(2)-O(1)#8	77.26(11)	O(1)#7-Ba(3)-O(5)#11	47.26(10)
O(1)-Ba(2)-O(1)#8	67.68(14)	O(1)#11-Ba(3)-O(5)#11	110.72(11)
O(6)#6-Ba(2)-O(1)#8	145.08(11)	O(5)#8-Ba(3)-O(5)#11	84.60(11)
O(3)-Ba(2)-O(1)#8	103.84(11)	O(5)#12-Ba(3)-O(5)#11	92.27(12)
O(6)-Ba(2)-O(1)#8	45.62(11)	O(1)-Ba(3)-O(5)#11	122.63(11)
O(5)#7-Ba(2)-O(1)#8	85.75(11)	O(1)#10-Ba(3)-O(5)#11	69.06(12)
F(1)-Ba(2)-O(1)#9	77.24(11)	F(1)#10-Ba(3)-O(5)#7	135.51(10)
F(1)#1-Ba(2)-O(1)#9	64.09(11)	F(1)-Ba(3)-O(5)#7	63.54(10)
O(1)-Ba(2)-O(1)#9	84.15(12)	O(1)#7-Ba(3)-O(5)#7	110.72(11)
O(6)#6-Ba(2)-O(1)#9	46.13(11)	O(1)#11-Ba(3)-O(5)#7	47.26(10)
O(3)-Ba(2)-O(1)#9	129.45(11)	O(5)#8-Ba(3)-O(5)#7	92.27(12)
O(6)-Ba(2)-O(1)#9	132.08(10)	O(5)#12-Ba(3)-O(5)#7	84.60(11)
O(5)#7-Ba(2)-O(1)#9	138.32(10)	O(1)-Ba(3)-O(5)#7	69.06(12)
O(1)#8-Ba(2)-O(1)#9	117.53(12)	O(1)#10-Ba(3)-O(5)#7	122.63(11)
F(1)#10-Ba(3)-F(1)	94.80(15)	O(5)#11-Ba(3)-O(5)#7	157.18(14)
F(1)#10-Ba(3)-O(1)#7	109.94(11)	O(2)-Zn(1)-O(4)	121.61(16)
F(1)-Ba(3)-O(1)#7	140.41(11)	O(2)-Zn(1)-O(6)	114.30(17)
F(1)#10-Ba(3)-O(1)#11	140.41(11)	O(4)-Zn(1)-O(6)	98.89(17)
F(1)-Ba(3)-O(1)#11	109.94(11)	O(2)-Zn(1)-O(3)	111.37(16)
O(1)#7-Ba(3)-O(1)#11	69.60(16)	O(4)-Zn(1)-O(3)	108.53(16)
F(1)#10-Ba(3)-O(5)#8	67.62(11)	O(6)-Zn(1)-O(3)	99.35(16)
F(1)-Ba(3)-O(5)#8	124.53(11)	O(5)-B(1)-O(1)#8	121.8(5)

O(5)-B(1)-O(6)	122.0(5)	O(4)#5-B(2)-O(3)	121.9(5)
O(1)#8-B(1)-O(6)	116.3(5)	O(2)#6-B(2)-O(3)	119.4(5)
O(4)#5-B(2)-O(2)#6	118.7(5)		

Symmetry transformations used to generate equivalent atoms:

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

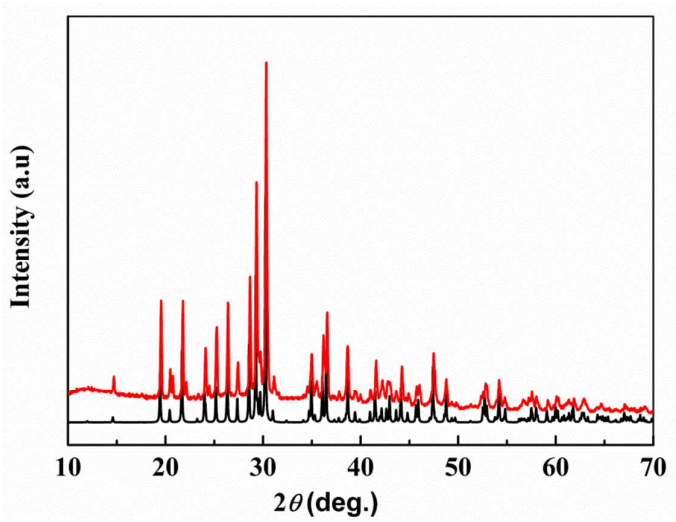


Figure S1a. Experimental and calculated XRD patterns of $BaZn_2B_2O_6$. The red curve is experimental pattern; the black one is calculated one.

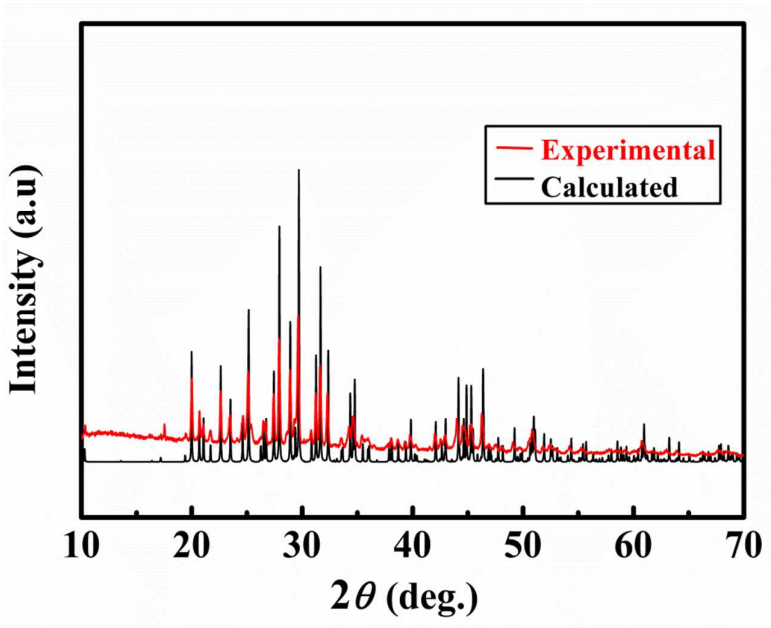


Figure S1b. Experimental and calculated XRD patterns of $Ba_3Zn_2B_3O_9F$. The red curve is experimental pattern; the black one is calculated one.

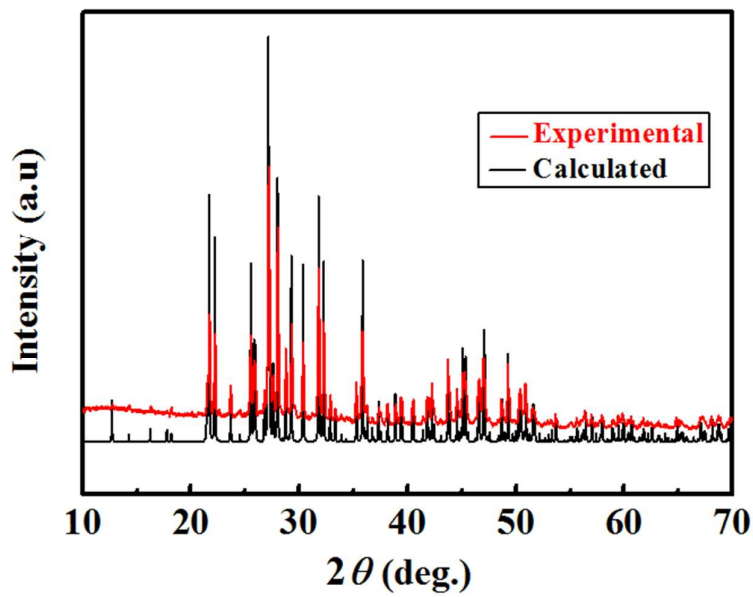


Figure S1c. Experimental and calculated XRD patterns of $Ba_5Zn_2B_4O_{12}F_2$. The red curve is experimental pattern; the black one is calculated one.

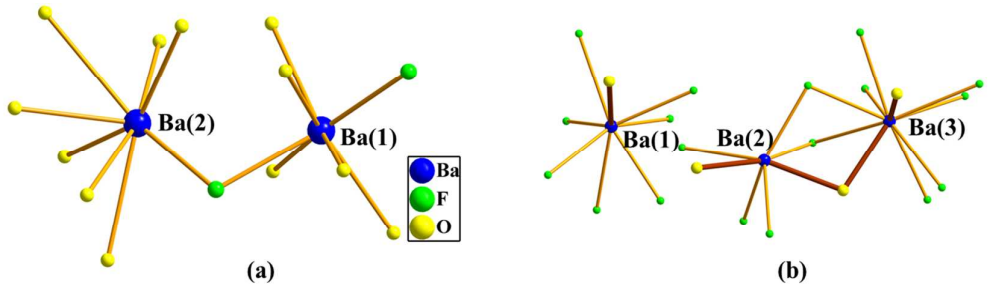


Figure S2. The coordination environments of Ba atoms for $Ba_3Zn_2B_3O_9F$ (a) and $Ba_5Zn_2B_4O_{12}F_2$ (b).

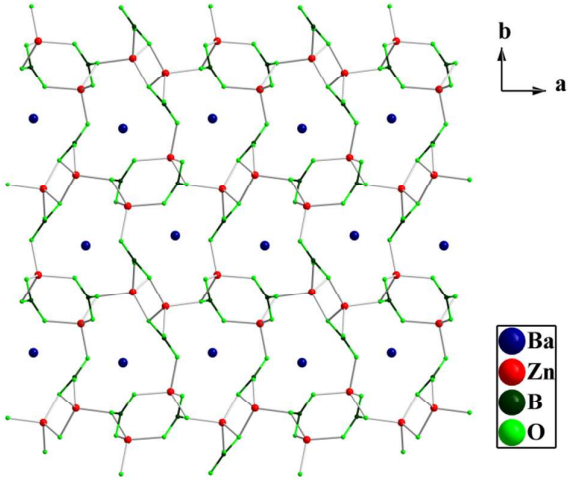


Figure S3. The structure of $BaZn_2B_2O_6$ (all the Ba-O bonds are omitted).

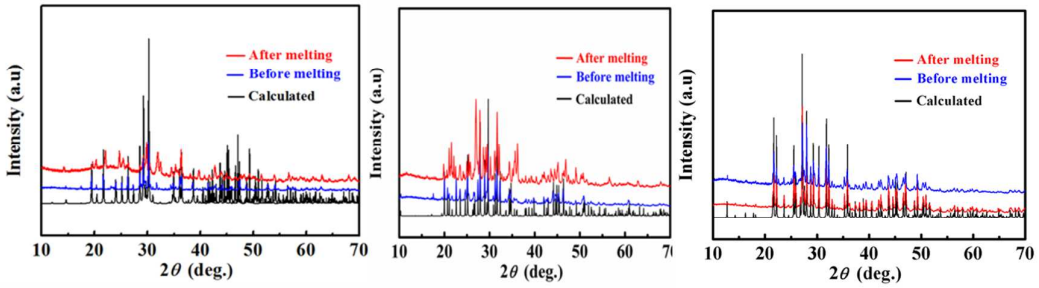
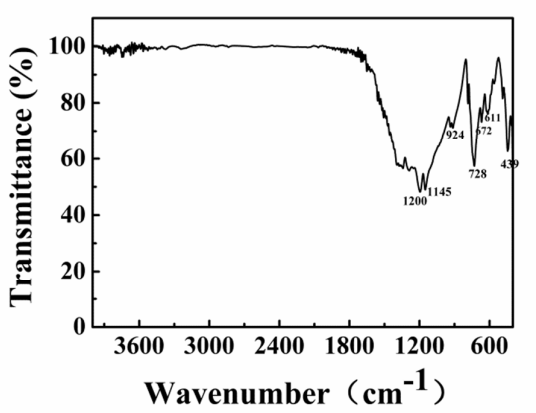
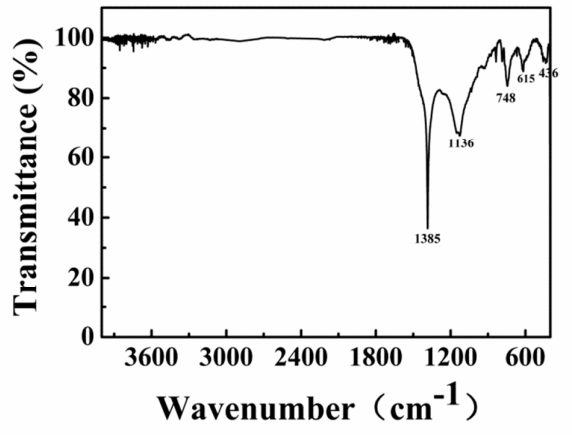


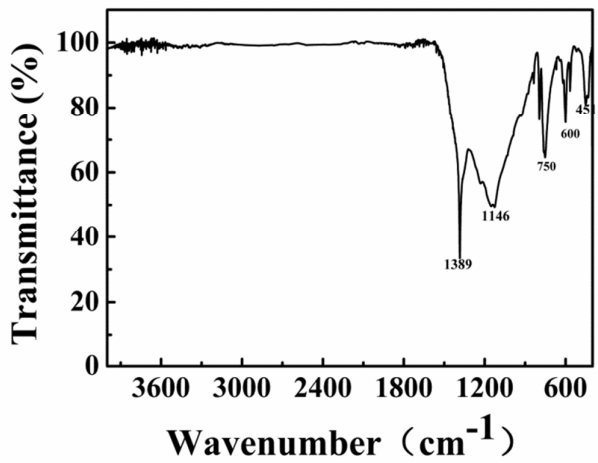
Figure S4. The XRD patterns of $BaZn_2B_2O_6$ (a), $Ba_3Zn_2B_3O_9F$ (b) and $Ba_5Zn_2B_4O_{12}F_2$ (c).



(a)

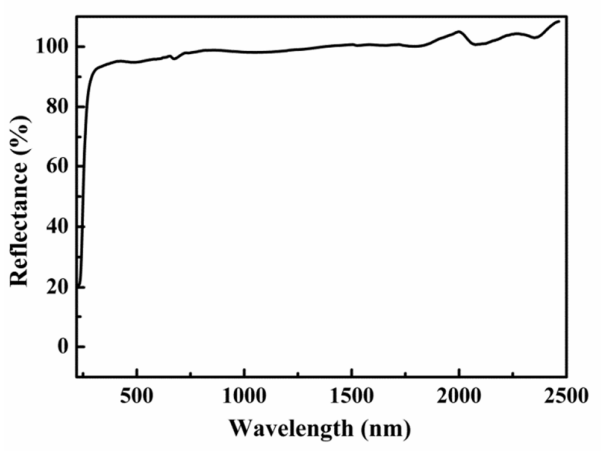


(b)

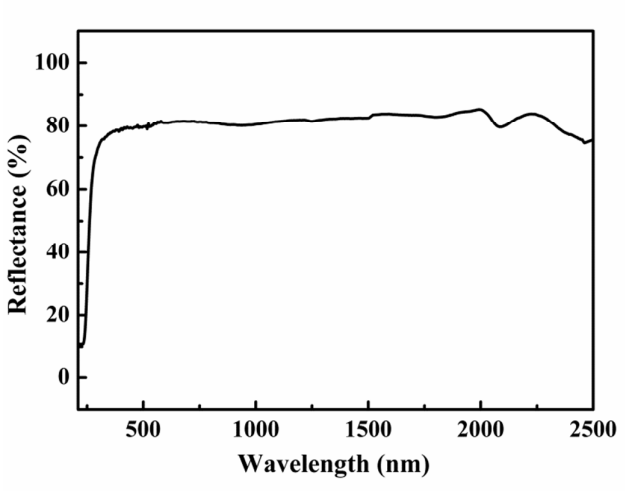


(c)

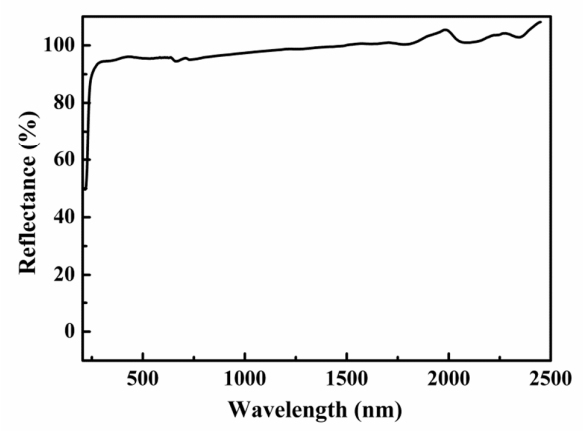
Figure S5. IR spectra for $BaZn_2B_2O_6$ (a), $Ba_3Zn_2B_3O_9F$ (b) and $Ba_5Zn_2B_4O_{12}F_2$ (c).



(a)



(b)



(c)

Figure S6. UV-vis-NIR spectra for $BaZn_2B_2O_6$ (a), $Ba_3Zn_2B_3O_9F$ (b) and $Ba_5Zn_2B_4O_{12}F_2$ (c).

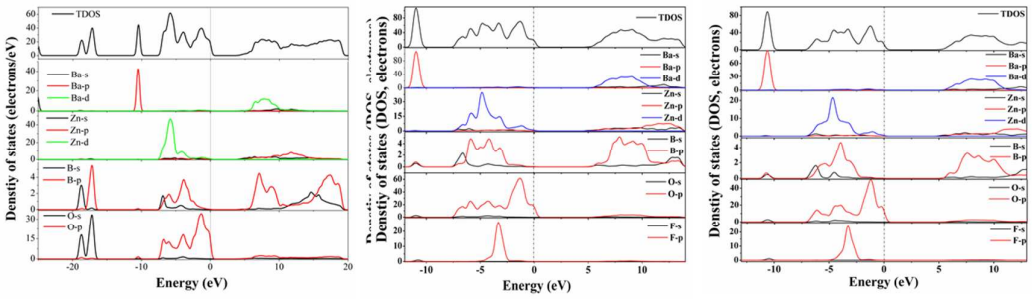
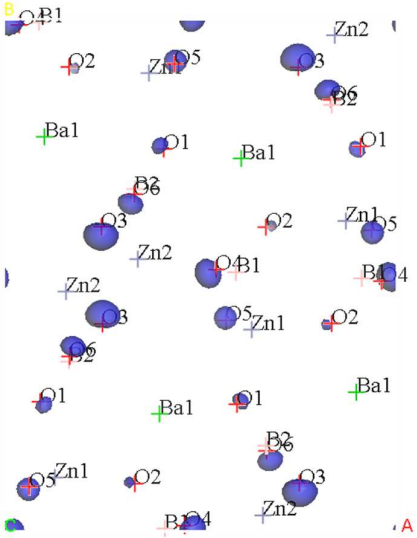
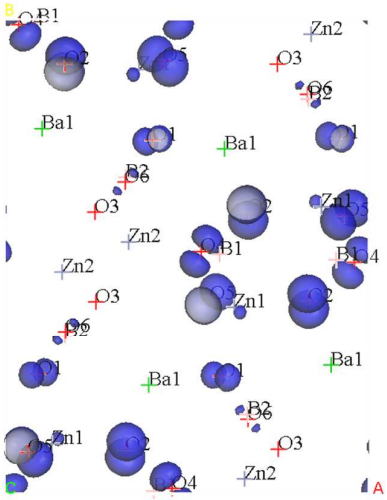


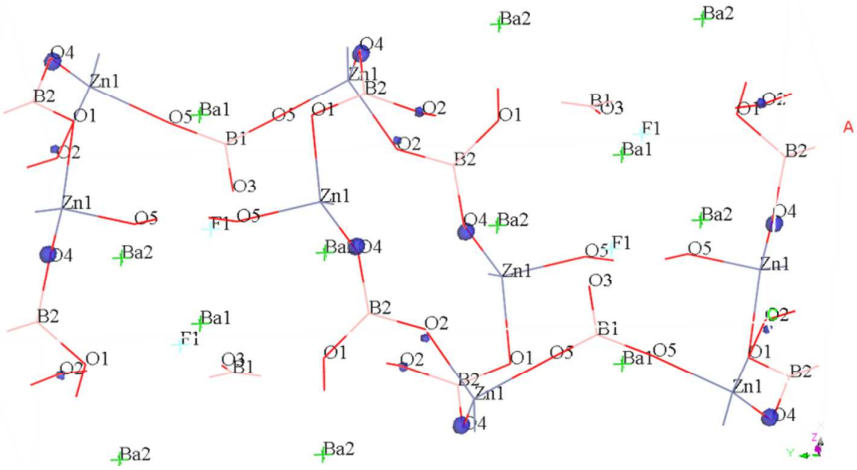
Figure S7. Total Density of states and the corresponding partial density of orbitals of $BaZn_2B_2O_6$ (a), $Ba_3Zn_2B_3O_9F$ (b) and $Ba_5Zn_2B_4O_{12}F_2$ (c).


Zn2
O2
Zn1
O5
O3
O6
B2
Ba1
O1
Ba1
O1
B2
O6
O3
O2
Zn1
O5
Zn2
O4
B1
B1
O4
Zn2
O3
O5
Zn1
O2
O6
B2
O1
Ba1
O1
Ba1
B2
O6
O5
Zn1
O2
O3
Zn2
B2
O4
A

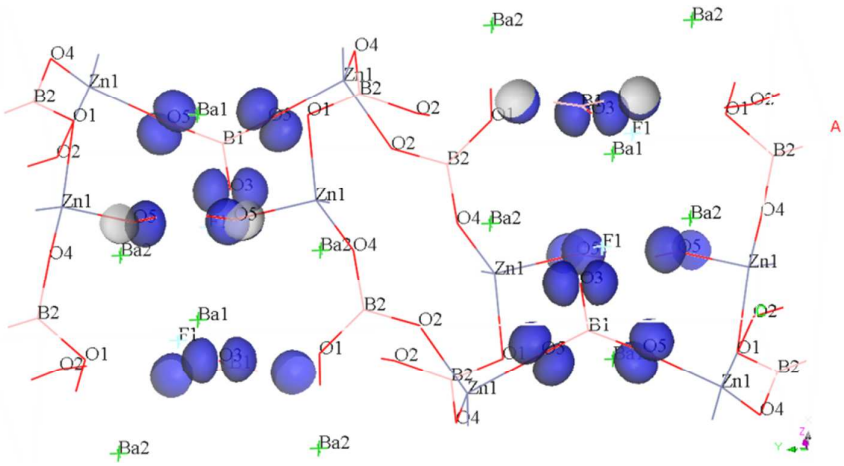
(a)


B1
Zn2
O2
O5
O3
O6
B2
Ba1
O1
Ba1
O1
B2
O6
O3
Zn1
O5
O2
Zn2
O4
B1
B1
O4
Zn2
O3
O5
Zn1
O2
O6
B2
O1
Ba1
O1
Ba1
B2
O6
Zn1
O2
O3
O4
Zn2
A

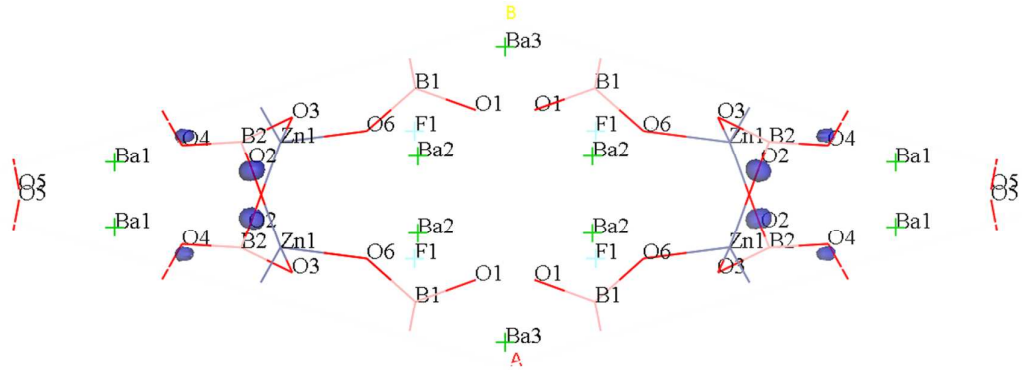
(b)


Ba2
Ba2
O4
Zn1
B2
O1
O5
Ba1
B1
O5
O1
O4
Zn1
B2
O2
O1
B1
O3
F1
Ba1
O1
O2
A
O2
B2
O3
Zn1
O5
F1
O5
Zn1
O4
Ba2
O4
Ba2
Ba2
O4
O5
F1
O5
Zn1
O3
B2
Ba1
F1
O3
B1
O1
B2
O2
O2
O1
O5
B1
Ba1
O5
O1
B2
Zn1
O4
Zn1
O4
Ba2
Ba2

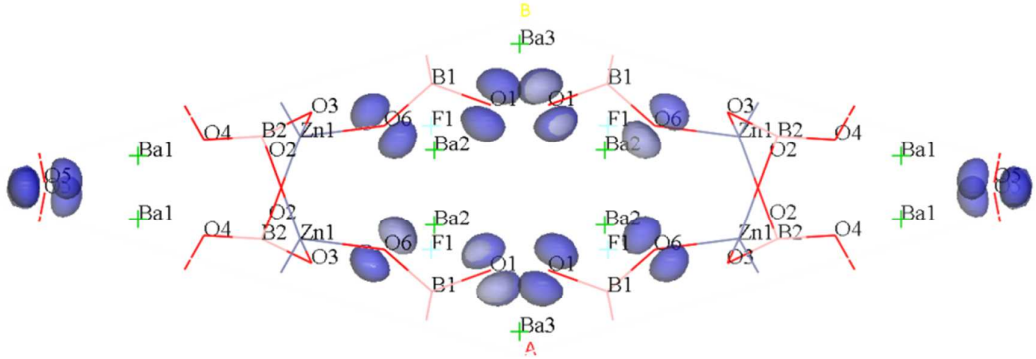
(c)



(d)



(e)



(f)

Figure S8. The highest occupied and lowest unoccupied orbitals of $BaZn_2B_2O_6$ (a, b), $Ba_3Zn_2B_3O_9F$ (c, d) and $Ba_5Zn_2B_4O_{12}F_2$ (e,f).

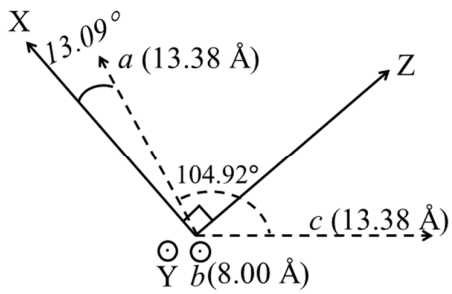
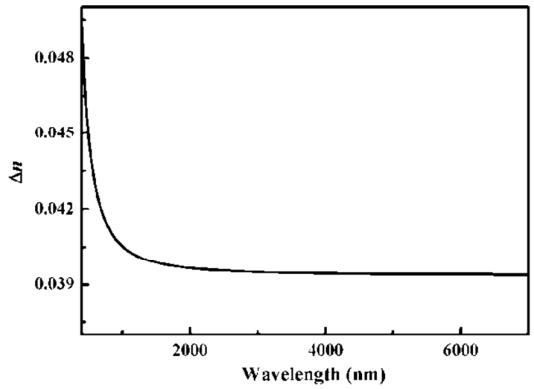
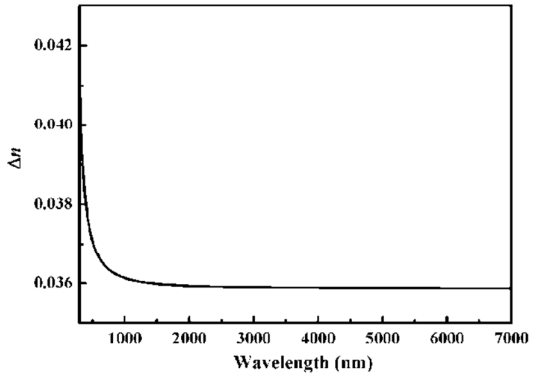


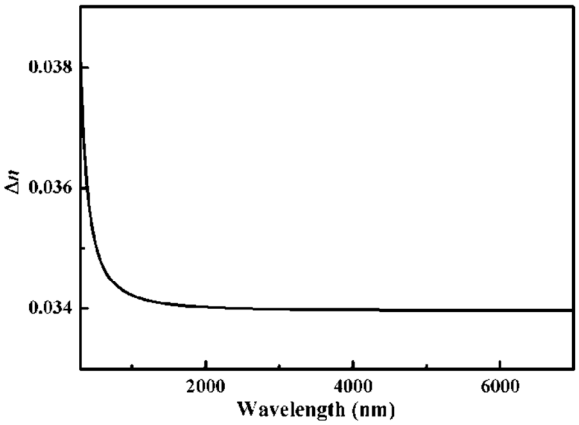
Figure S9. The included angle between the crystallographic axis *a* and the principal dielectric axis X in the *ac* plane.



(a)



(b)



(c)

Figure S10. Calculated birefringence indices of $BaZn_2B_2O_6$ (a), $Ba_3Zn_2B_3O_9F$ (b) and $Ba_5Zn_2B_4O_{12}F_2$ (c).