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Flexible Coordination of Pb Atoms and Variable Zinc-Borate Framework to Construct Three $Pb_5Zn_4B_6O_{18}$ Polymorphs

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for α-$Pb_5Zn_4B_6O_{18}$

Atom	x	y	z	U(eq)[a]
Pb(1)	550(1)	-253(1)	7526(1)	12(1)
Pb(2)	2417(1)	-247(1)	6604(1)	16(1)
Pb(3)	1411(1)	191(1)	4954(1)	11(1)
Pb(4)	3684(1)	5178(1)	5070(1)	11(1)
Pb(5)	2440(1)	4800(1)	6717(1)	14(1)
Pb(6)	1418(1)	5024(1)	5069(1)	11(1)
Pb(7)	3668(1)	142(1)	5041(1)	11(1)
Pb(8)	2478(1)	4912(1)	8315(1)	13(1)
Pb(9)	2633(1)	-117(1)	8316(1)	14(1)
Pb(10)	5024(1)	9556(1)	2515(1)	22(1)
Zn(1)	4054(1)	2706(1)	3921(1)	9(1)
Zn(2)	1059(1)	-2446(1)	8781(1)	8(1)
Zn(3)	5904(1)	7572(1)	3579(1)	11(1)
Zn(4)	4077(1)	7722(1)	3957(1)	9(1)
Zn(5)	1066(1)	2488(1)	8712(1)	8(1)
Zn(6)	4112(1)	7630(1)	1477(1)	11(1)
Zn(7)	930(1)	2495(1)	6274(1)	8(1)
Zn(8)	879(1)	-2466(1)	6221(1)	8(1)
B(1)	-124(9)	1(13)	6189(6)	8(3)
B(2)	5080(9)	10203(13)	1109(6)	8(3)
B(3)	2587(10)	2316(14)	9523(7)	9(3)
B(4)	1644(11)	2419(15)	7522(7)	17(4)
B(5)	4948(10)	10186(14)	3878(7)	12(3)
B(6)	2426(9)	7629(13)	792(6)	7(3)
B(7)	7563(10)	7636(14)	4240(7)	9(3)
B(8)	3557(10)	7105(14)	2674(7)	12(3)
B(9)	18(10)	-4980(14)	6198(7)	14(4)
B(10)	6405(9)	7182(14)	2345(7)	9(3)
B(11)	2597(10)	-2651(13)	9529(7)	8(3)
B(12)	1602(10)	7378(14)	7518(7)	13(4)
O(1)	2524(5)	-926(8)	4646(3)	9(2)
O(2)	2525(5)	1104(8)	5513(4)	13(2)
O(3)	2577(5)	4066(8)	4680(4)	11(2)
O(4)	2480(5)	6109(8)	5538(4)	14(2)

O(5)	3225(5)	4052(8)	7568(4)	15(2)
O(6)	3367(5)	7162(8)	4570(4)	11(2)
O(7)	5043(5)	6607(8)	3950(4)	13(2)
O(8)	-114(5)	-1413(8)	6129(4)	13(2)
O(9)	1423(5)	-1922(8)	7001(4)	12(2)
O(10)	1684(5)	3037(8)	5699(4)	12(2)
O(11)	1731(5)	-1846(8)	5737(4)	14(2)
O(12)	1696(5)	970(8)	7546(4)	13(2)
O(13)	706(5)	-4377(8)	6073(4)	14(2)
O(14)	1863(6)	2956(8)	9357(4)	14(2)
O(15)	647(5)	670(8)	8565(4)	16(2)
O(16)	4284(6)	4616(8)	4136(4)	17(2)
O(17)	3076(6)	7078(8)	1141(4)	19(2)
O(18)	1396(5)	-1897(8)	8007(4)	15(2)
O(19)	1903(6)	6092(8)	7535(4)	18(2)
O(20)	616(6)	604(8)	6373(4)	20(2)
O(21)	1584(5)	3136(8)	8016(4)	16(2)
O(22)	3189(5)	-906(8)	7483(4)	18(2)
O(23)	4070(6)	7802(8)	2333(4)	15(2)
O(24)	5866(6)	7671(8)	2722(4)	22(2)
O(25)	1621(6)	3016(8)	6982(4)	18(2)
O(26)	4568(6)	9487(9)	1440(4)	23(2)
O(27)	1928(5)	-1900(8)	9330(4)	15(2)
O(28)	3318(5)	2049(8)	4486(4)	12(2)
O(29)	6945(6)	6994(8)	3899(4)	20(2)
O(30)	5023(6)	1621(8)	3862(4)	17(2)
O(31)	837(5)	-4349(8)	8900(4)	15(2)
O(32)	4325(6)	9622(9)	4115(4)	20(2)
O(33)	3451(6)	2913(9)	3163(4)	21(2)
O(34)	-47(5)	3599(8)	6163(4)	15(2)
O(35)	3418(6)	7503(9)	3240(4)	22(2)
O(36)	5543(6)	9489(9)	3610(4)	27(2)

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

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for β-$Pb_5Zn_4B_6O_{18}$

Atom	x	y	z	U(eq)[a]
Pb(1)	-4879(1)	7282(1)	5029(1)	14(1)
Pb(2)	5273(2)	4876(2)	1669(1)	48(1)
Pb(3A)	5487(4)	849(2)	41(2)	22(1)
Pb(3B)	5000	0	0	22(1)
Zn(1)	247(4)	8041(3)	2698(2)	12(1)
Zn(2)	71(4)	1851(3)	2271(2)	15(1)
B(1)	-4810(40)	9990(30)	2680(20)	15(4)
B(2)	10360(50)	3080(30)	-180(20)	21(5)
B(3)	260(40)	5040(30)	3796(18)	10(4)
O(1)	-1230(30)	6512(16)	3760(12)	12(3)
O(2)	2970(30)	5102(15)	4088(13)	15(3)
O(3)	-1030(30)	3551(18)	3416(14)	22(3)
O(4)	-2120(30)	9910(17)	2533(17)	26(4)
O(5)	8930(30)	2580(20)	772(15)	32(4)
O(6)	-6110(30)	11270(20)	2222(18)	33(4)
O(7)	-6140(30)	8701(19)	3170(16)	24(3)
O(8)	6970(30)	6640(20)	92(17)	36(4)
O(9)	870(40)	6740(30)	1201(16)	48(6)

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

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for γ-$Pb_5Zn_4B_6O_{18}$

Atom	x	y	z	U(eq)[a]
Pb(1)	564(2)	7319(1)	5987(1)	23(1)
Pb(2)	0	10000	5000	40(1)
Pb(3)	9667(2)	5389(1)	3512(1)	22(1)
Zn(1)	5053(5)	9235(2)	3041(2)	16(1)
Zn(2)	5291(5)	7176(2)	3690(3)	18(1)
B(1)	10370(50)	8251(16)	3600(20)	11(5)
B(2)	5310(50)	5909(15)	5600(20)	11(5)
B(3)	4650(60)	6135(18)	1530(20)	18(6)
O(1)	4120(30)	9460(11)	1463(15)	22(4)
O(2)	2410(60)	8667(16)	5900(20)	68(8)
O(3)	9000(40)	9020(11)	3274(16)	26(4)
O(4)	5770(70)	6510(20)	2430(30)	108(13)
O(5)	3050(30)	8196(10)	3359(15)	20(4)
O(6)	4090(40)	10329(11)	3768(17)	29(5)
O(7)	9030(30)	7583(10)	4139(12)	11(3)
O(8)	3910(40)	6572(12)	4992(19)	37(5)
O(9)	7910(30)	5683(10)	5270(13)	15(3)

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

Table S4. Selected bond distances (Å) and angles (deg) for α-$Pb_5Zn_4B_6O_{18}$

Pb(1)-O(12)	2.222(8)	O(14)#3-Pb(3)-O(11)	150.9(3)
Pb(1)-O(18)	2.342(8)	O(31)#4-Pb(3)-O(11)	114.8(2)
Pb(1)-O(9)	2.527(8)	O(3)-Pb(4)-O(6)	93.3(3)
Pb(1)-O(15)	2.544(9)	O(3)-Pb(4)-O(4)	72.8(3)
Pb(2)-O(17)#2	2.374(9)	O(6)-Pb(4)-O(4)	75.6(3)
Pb(2)-O(22)	2.394(9)	O(3)-Pb(4)-O(16)	84.6(3)
Pb(2)-O(9)	2.519(8)	O(6)-Pb(4)-O(16)	80.8(3)
Pb(2)-O(11)	2.711(8)	O(4)-Pb(4)-O(16)	146.0(3)
Pb(2)-Zn(8)	3.3881(16)	O(25)-Pb(5)-O(5)	81.0(3)
Pb(3)-O(1)	2.276(8)	O(25)-Pb(5)-O(19)	86.4(3)
Pb(3)-O(2)	2.332(8)	O(5)-Pb(5)-O(19)	74.4(3)
Pb(3)-O(14)#3	2.412(8)	O(25)-Pb(5)-O(29)#5	83.6(3)
Pb(3)-O(31)#4	2.665(8)	O(5)-Pb(5)-O(29)#5	92.1(3)
Pb(3)-O(11)	2.703(8)	O(19)-Pb(5)-O(29)#5	164.3(3)
Pb(4)-O(3)	2.244(8)	O(4)-Pb(6)-O(3)	75.5(3)
Pb(4)-O(6)	2.287(8)	O(4)-Pb(6)-O(10)	89.2(3)
Pb(4)-O(4)	2.482(9)	O(3)-Pb(6)-O(10)	78.2(3)
Pb(4)-O(16)	2.485(9)	O(4)-Pb(6)-O(27)#3	73.6(3)
Pb(5)-O(25)	2.302(9)	O(3)-Pb(6)-O(27)#3	74.4(3)
Pb(5)-O(5)	2.379(8)	O(10)-Pb(6)-O(27)#3	150.5(3)
Pb(5)-O(19)	2.473(9)	O(4)-Pb(6)-O(13)#6	81.7(3)
Pb(5)-O(29)#5	2.503(9)	O(3)-Pb(6)-O(13)#6	144.5(3)
Pb(6)-O(4)	2.245(8)	O(10)-Pb(6)-O(13)#6	74.6(3)
Pb(6)-O(3)	2.347(8)	O(27)#3-Pb(6)-O(13)#6	124.4(2)
Pb(6)-O(10)	2.437(8)	O(1)-Pb(7)-O(28)	88.9(3)
Pb(6)-O(27)#3	2.667(8)	O(1)-Pb(7)-O(2)	73.4(3)
Pb(6)-O(13)#6	2.721(9)	O(28)-Pb(7)-O(2)	76.4(3)
Pb(7)-O(1)	2.275(8)	O(1)-Pb(7)-O(32)#1	87.7(3)
Pb(7)-O(28)	2.300(8)	O(28)-Pb(7)-O(32)#1	78.3(3)
Pb(7)-O(2)	2.417(9)	O(2)-Pb(7)-O(32)#1	148.5(3)
Pb(7)-O(32)#1	2.502(9)	O(19)-Pb(8)-O(5)	79.1(3)
Pb(8)-O(19)	2.277(9)	O(19)-Pb(8)-O(21)	85.7(3)
Pb(8)-O(5)	2.332(9)	O(5)-Pb(8)-O(21)	82.4(3)
Pb(8)-O(21)	2.337(8)	O(22)-Pb(9)-O(12)	79.1(3)
Pb(9)-O(22)	2.309(9)	O(22)-Pb(9)-O(33)#2	85.7(3)
Pb(9)-O(12)	2.495(8)	O(12)-Pb(9)-O(33)#2	81.4(3)

Pb(9)-O(33)#2	2.566(9)	O(22)-Pb(9)-O(35)#2	55.7(3)
Pb(9)-O(35)#2	2.666(9)	O(12)-Pb(9)-O(35)#2	126.8(3)
Pb(9)-O(18)	2.722(9)	O(33)#2-Pb(9)-O(35)#2	117.4(3)
Pb(10)-O(24)	2.323(9)	O(22)-Pb(9)-O(18)	84.4(3)
Pb(10)-O(23)	2.332(9)	O(12)-Pb(9)-O(18)	71.0(3)
Pb(10)-O(26)	2.531(9)	O(33)#2-Pb(9)-O(18)	152.0(3)
Pb(10)-O(36)	2.601(10)	O(35)#2-Pb(9)-O(18)	77.4(3)
Pb(10)-Zn(6)	3.3073(16)	O(24)-Pb(10)-O(23)	80.8(3)
Pb(10)-Zn(3)	3.3603(16)	O(24)-Pb(10)-O(26)	108.0(3)
Zn(1)-O(30)	1.919(9)	O(23)-Pb(10)-O(26)	70.0(3)
Zn(1)-O(28)	1.942(9)	O(24)-Pb(10)-O(36)	68.5(3)
Zn(1)-O(33)	1.951(9)	O(23)-Pb(10)-O(36)	108.9(3)
Zn(1)-O(16)	1.952(8)	O(26)-Pb(10)-O(36)	176.5(3)
Zn(2)-O(31)	1.910(8)	O(30)-Zn(1)-O(28)	114.9(4)
Zn(2)-O(27)	1.911(9)	O(30)-Zn(1)-O(33)	111.3(4)
Zn(2)-O(34)#7	1.957(9)	O(28)-Zn(1)-O(33)	109.4(4)
Zn(2)-O(18)	1.974(9)	O(30)-Zn(1)-O(16)	113.3(4)
Zn(3)-O(29)	1.895(10)	O(28)-Zn(1)-O(16)	105.2(4)
Zn(3)-O(7)	1.940(9)	O(33)-Zn(1)-O(16)	101.8(4)
Zn(3)-O(36)	1.959(9)	O(31)-Zn(2)-O(27)	108.4(4)
Zn(3)-O(24)	1.969(10)	O(31)-Zn(2)-O(34)#7	108.9(4)
Zn(4)-O(35)	1.916(10)	O(27)-Zn(2)-O(34)#7	114.1(4)
Zn(4)-O(7)	1.920(9)	O(31)-Zn(2)-O(18)	117.3(4)
Zn(4)-O(32)	1.922(9)	O(27)-Zn(2)-O(18)	106.1(4)
Zn(4)-O(6)	1.965(9)	O(34)#7-Zn(2)-O(18)	102.2(4)
Zn(5)-O(15)	1.919(8)	O(29)-Zn(3)-O(7)	110.4(4)
Zn(5)-O(8)#8	1.947(9)	O(29)-Zn(3)-O(36)	122.3(4)
Zn(5)-O(14)	1.960(9)	O(7)-Zn(3)-O(36)	102.4(4)
Zn(5)-O(21)	1.966(9)	O(29)-Zn(3)-O(24)	111.6(4)
Zn(6)-O(17)	1.892(10)	O(7)-Zn(3)-O(24)	119.4(4)
Zn(6)-O(30)#9	1.933(9)	O(36)-Zn(3)-O(24)	90.1(4)
Zn(6)-O(26)	1.960(9)	O(35)-Zn(4)-O(7)	110.2(4)
Zn(6)-O(23)	1.982(9)	O(35)-Zn(4)-O(32)	111.6(4)
Zn(7)-O(20)	1.927(8)	O(7)-Zn(4)-O(32)	112.4(4)
Zn(7)-O(34)	1.929(9)	O(35)-Zn(4)-O(6)	105.1(4)
Zn(7)-O(10)	1.945(9)	O(7)-Zn(4)-O(6)	112.2(3)
Zn(7)-O(25)	1.982(9)	O(32)-Zn(4)-O(6)	105.0(4)
Zn(8)-O(13)	1.908(8)	O(15)-Zn(5)-O(8)#8	104.9(4)

Zn(8)-O(8)	1.921(8)	O(15)-Zn(5)-O(14)	124.0(4)
Zn(8)-O(11)	1.941(9)	O(8)#8-Zn(5)-O(14)	103.3(4)
Zn(8)-O(9)	2.015(9)	O(15)-Zn(5)-O(21)	108.8(4)
B(1)-O(31)#8	1.331(16)	O(8)#8-Zn(5)-O(21)	112.0(3)
B(1)-O(8)	1.382(15)	O(14)-Zn(5)-O(21)	103.8(4)
B(1)-O(20)	1.386(17)	O(17)-Zn(6)-O(30)#9	110.7(4)
B(2)-O(16)#9	1.346(17)	O(17)-Zn(6)-O(26)	125.3(4)
B(2)-O(26)	1.362(17)	O(30)#9-Zn(6)-O(26)	99.1(4)
B(2)-O(7)#9	1.386(15)	O(17)-Zn(6)-O(23)	109.7(4)
B(3)-O(28)#2	1.355(17)	O(30)#9-Zn(6)-O(23)	121.3(4)
B(3)-O(14)	1.370(17)	O(26)-Zn(6)-O(23)	90.3(4)
B(3)-O(3)#2	1.393(15)	O(20)-Zn(7)-O(34)	108.8(4)
B(4)-O(21)	1.340(18)	O(20)-Zn(7)-O(10)	121.8(4)
B(4)-O(25)	1.369(18)	O(34)-Zn(7)-O(10)	108.6(4)
B(4)-O(12)	1.413(16)	O(20)-Zn(7)-O(25)	106.8(4)
B(5)-O(32)	1.310(17)	O(34)-Zn(7)-O(25)	112.8(4)
B(5)-O(36)	1.370(18)	O(10)-Zn(7)-O(25)	97.8(4)
B(5)-O(30)#6	1.402(15)	O(13)-Zn(8)-O(8)	112.7(4)
B(6)-O(4)#10	1.366(15)	O(13)-Zn(8)-O(11)	107.7(4)
B(6)-O(11)#3	1.369(16)	O(8)-Zn(8)-O(11)	114.0(4)
B(6)-O(17)	1.394(17)	O(13)-Zn(8)-O(9)	117.8(3)
B(7)-O(2)#5	1.363(15)	O(8)-Zn(8)-O(9)	106.1(3)
B(7)-O(29)	1.385(17)	O(11)-Zn(8)-O(9)	97.9(4)
B(7)-O(10)#5	1.394(17)	O(31)#8-B(1)-O(8)	118.3(12)
B(8)-O(23)	1.367(17)	O(31)#8-B(1)-O(20)	125.7(11)
B(8)-O(22)#3	1.371(16)	O(8)-B(1)-O(20)	115.8(12)
B(8)-O(35)	1.393(17)	O(16)#9-B(2)-O(26)	122.8(11)
B(9)-O(13)	1.320(17)	O(16)#9-B(2)-O(7)#9	119.3(12)
B(9)-O(34)#1	1.389(15)	O(26)-B(2)-O(7)#9	117.9(12)
B(9)-O(15)#7	1.402(18)	O(28)#2-B(3)-O(14)	121.8(11)
B(10)-O(5)#5	1.353(16)	O(28)#2-B(3)-O(3)#2	118.9(12)
B(10)-O(24)	1.365(18)	O(14)-B(3)-O(3)#2	119.0(12)
B(10)-O(33)#9	1.401(17)	O(21)-B(4)-O(25)	123.2(12)
B(11)-O(6)#2	1.345(17)	O(21)-B(4)-O(12)	119.7(13)
B(11)-O(27)	1.369(17)	O(25)-B(4)-O(12)	117.0(13)
B(11)-O(1)#11	1.417(15)	O(32)-B(5)-O(36)	125.4(12)
B(12)-O(19)	1.345(16)	O(32)-B(5)-O(30)#6	120.0(13)
B(12)-O(9)#6	1.383(17)	O(36)-B(5)-O(30)#6	114.5(12)

B(12)-O(18)#6	1.388(17)	O(4)#10-B(6)-O(11)#3	122.6(12)
O(12)-Pb(1)-O(18)	83.4(3)	O(4)#10-B(6)-O(17)	121.5(12)
O(12)-Pb(1)-O(9)	81.2(3)	O(11)#3-B(6)-O(17)	115.9(11)
O(18)-Pb(1)-O(9)	56.6(3)	O(2)#5-B(7)-O(29)	123.2(12)
O(12)-Pb(1)-O(15)	78.2(3)	O(2)#5-B(7)-O(10)#5	119.9(12)
O(18)-Pb(1)-O(15)	78.6(3)	O(29)-B(7)-O(10)#5	116.8(11)
O(9)-Pb(1)-O(15)	132.4(3)	O(23)-B(8)-O(22)#3	120.9(13)
O(17)#2-Pb(2)-O(22)	87.0(3)	O(23)-B(8)-O(35)	123.0(12)
O(17)#2-Pb(2)-O(9)	90.1(3)	O(22)#3-B(8)-O(35)	116.0(12)
O(22)-Pb(2)-O(9)	80.7(3)	O(13)-B(9)-O(34)#1	119.5(13)
O(17)#2-Pb(2)-O(11)	54.3(3)	O(13)-B(9)-O(15)#7	125.6(12)
O(22)-Pb(2)-O(11)	129.3(3)	O(34)#1-B(9)-O(15)#7	114.4(12)
O(9)-Pb(2)-O(11)	69.5(3)	O(5)#5-B(10)-O(24)	121.2(12)
O(1)-Pb(3)-O(2)	75.0(3)	O(5)#5-B(10)-O(33)#9	118.2(12)
O(1)-Pb(3)-O(14)#3	84.1(3)	O(24)-B(10)-O(33)#9	120.4(12)
O(2)-Pb(3)-O(14)#3	76.6(3)	O(6)#2-B(11)-O(27)	124.0(11)
O(1)-Pb(3)-O(31)#4	79.1(3)	O(6)#2-B(11)-O(1)#11	115.1(11)
O(2)-Pb(3)-O(31)#4	146.2(3)	O(27)-B(11)-O(1)#11	120.5(12)
O(14)#3-Pb(3)-O(31)#4	79.4(3)	O(19)-B(12)-O(9)#6	122.6(13)
O(1)-Pb(3)-O(11)	74.6(3)	O(19)-B(12)-O(18)#6	123.9(13)
O(2)-Pb(3)-O(11)	78.8(3)	O(9)#6-B(12)-O(18)#6	113.4(11)

Symmetry transformations used to generate equivalent atoms:

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

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

#6 x,y+1,z #7 -x,y-1/2,-z+3/2 #8 -x,y+1/2,-z+3/2

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

#11 x,-y-1/2,z+1/2 #12 x,-y+3/2,z+1/2

#13 -x+1,y-1/2,-z+1/2

Table S5. Selected bond distances (Å) and angles (deg) for β-$Pb_5Zn_4B_6O_{18}$

Pb(1)-O(2)#1	2.254(13)	O(2)#1-Pb(1)-O(7)	82.6(5)
Pb(1)-O(1)	2.368(12)	O(1)-Pb(1)-O(7)	77.9(5)
Pb(1)-O(2)#2	2.432(13)	O(2)#2-Pb(1)-O(7)	148.7(5)
Pb(1)-O(7)	2.567(16)	O(8)-Pb(2)-O(8)#4	80.8(6)
Pb(2)-O(8)	2.521(19)	O(8)-Pb(2)-O(9)	76.7(6)
Pb(2)-O(8)#4	2.530(18)	O(8)#4-Pb(2)-O(9)	75.0(6)
Pb(2)-O(9)	2.723(16)	O(8)-Pb(2)-O(5)	85.3(6)
Pb(2)-O(5)	2.736(18)	O(8)#4-Pb(2)-O(5)	73.2(6)
Pb(3A)-O(5)	2.308(17)	O(9)-Pb(2)-O(5)	145.6(5)
Pb(3A)-O(8)#4	2.38(2)	O(5)-Pb(3A)-O(8)#4	84.3(6)
Pb(3A)-O(6)#6	2.62(2)	O(5)-Pb(3A)-O(6)#6	80.8(6)
Pb(3B)-O(6)#6	2.73(2)	O(8)#4-Pb(3A)-O(6)#6	81.6(6)
Pb(3B)-O(6)#7	2.73(2)	O(6)#6-Pb(3B)-O(6)#7	180.000(1)
Zn(1)-O(7)#8	1.918(15)	O(7)#8-Zn(1)-O(4)	112.7(6)
Zn(1)-O(4)	1.930(14)	O(7)#8-Zn(1)-O(1)	110.2(6)
Zn(1)-O(1)	1.934(13)	O(4)-Zn(1)-O(1)	112.1(6)
Zn(1)-O(9)	1.968(19)	O(7)#8-Zn(1)-O(9)	102.6(8)
Zn(2)-O(3)	1.908(16)	O(4)-Zn(1)-O(9)	112.4(8)
Zn(2)-O(5)#1	1.938(18)	O(1)-Zn(1)-O(9)	106.4(9)
Zn(2)-O(4)#10	1.939(14)	O(3)-Zn(2)-O(5)#1	105.9(7)
Zn(2)-O(6)#6	1.940(15)	O(3)-Zn(2)-O(4)#10	106.5(7)
Zn(2)-Zn(1)#10	3.153(3)	O(5)#1-Zn(2)-O(4)#10	106.2(7)
B(1)-O(4)	1.34(2)	O(3)-Zn(2)-O(6)#6	117.3(8)
B(1)-O(6)	1.36(3)	O(5)#1-Zn(2)-O(6)#6	110.2(8)
B(1)-O(7)	1.38(3)	O(4)#10-Zn(2)-O(6)#6	110.0(6)
B(2)-O(9)#4	1.33(3)	O(4)-B(1)-O(6)	116.8(19)
B(2)-O(8)#11	1.34(3)	O(4)-B(1)-O(7)	119.1(18)
B(2)-O(5)	1.38(3)	O(6)-B(1)-O(7)	123.7(17)
B(3)-O(2)	1.37(2)	O(9)#4-B(2)-O(8)#11	119(2)
B(3)-O(3)	1.39(2)	O(9)#4-B(2)-O(5)	121(2)
B(3)-O(1)	1.41(2)	O(8)#11-B(2)-O(5)	120(2)
O(2)#1-Pb(1)-O(1)	84.2(5)	O(2)-B(3)-O(3)	121.9(17)
O(2)#1-Pb(1)-O(2)#2	76.5(6)	O(2)-B(3)-O(1)	120.0(16)
O(1)-Pb(1)-O(2)#2	77.1(5)	O(3)-B(3)-O(1)	117.8(16)

Symmetry transformations used to generate equivalent atoms:

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

#4 -x+1,-y+1,-z #5 -x+1,-y,-z #6 x+1,y-1,z

#7 -x,-y+1,-z #8 x+1,y,z #9 x,y+1,z

#10 x,y-1,z #11 -x+2,-y+1,-z #12 x-1,y+1,z

Table S6. Selected bond distances (Å) and angles (deg) for γ-$Pb_5Zn_4B_6O_{18}$

Pb(1)-O(2)	2.26(2)	O(6)-Pb(2)-O(2)#2	86.8(7)
Pb(1)-O(7)#1	2.328(14)	O(2)-Pb(2)-O(2)#2	180.000(10)
Pb(1)-O(8)	2.34(2)	O(6)#2-Pb(2)-O(3)#1	102.8(6)
Pb(2)-O(6)#2	2.552(19)	O(6)-Pb(2)-O(3)#1	77.2(6)
Pb(2)-O(6)	2.552(19)	O(2)-Pb(2)-O(3)#1	86.1(7)
Pb(2)-O(2)	2.56(3)	O(2)#2-Pb(2)-O(3)#1	93.9(7)
Pb(2)-O(2)#2	2.56(3)	O(6)#2-Pb(2)-O(3)#3	77.2(6)
Pb(2)-O(3)#1	2.580(18)	O(6)-Pb(2)-O(3)#3	102.8(6)
Pb(2)-O(3)#3	2.580(18)	O(2)-Pb(2)-O(3)#3	93.9(7)
Pb(3)-O(1)#4	2.313(16)	O(2)#2-Pb(2)-O(3)#3	86.1(7)
Pb(3)-O(9)	2.337(16)	O(3)#1-Pb(2)-O(3)#3	179.999(7)
Pb(3)-O(9)#5	2.457(15)	O(1)#4-Pb(3)-O(9)	78.1(6)
Zn(1)-O(5)	1.910(16)	O(1)#4-Pb(3)-O(9)#5	86.0(6)
Zn(1)-O(3)	1.929(18)	O(9)-Pb(3)-O(9)#5	77.2(6)
Zn(1)-O(1)	1.946(19)	O(5)-Zn(1)-O(3)	109.0(7)
Zn(1)-O(6)	1.957(17)	O(5)-Zn(1)-O(1)	104.2(7)
Zn(2)-O(4)	1.84(3)	O(3)-Zn(1)-O(1)	110.7(8)
Zn(2)-O(5)	1.932(16)	O(5)-Zn(1)-O(6)	120.1(8)
Zn(2)-O(8)	1.95(2)	O(3)-Zn(1)-O(6)	109.4(7)
Zn(2)-O(7)	1.953(14)	O(1)-Zn(1)-O(6)	103.1(8)
B(1)-O(5)#7	1.34(3)	O(4)-Zn(2)-O(5)	112.0(13)
B(1)-O(7)	1.38(3)	O(4)-Zn(2)-O(8)	116.2(14)
B(1)-O(3)	1.40(3)	O(5)-Zn(2)-O(8)	110.1(8)
B(2)-O(1)#8	1.33(3)	O(4)-Zn(2)-O(7)	104.8(11)
B(2)-O(9)	1.36(3)	O(5)-Zn(2)-O(7)	107.0(6)
B(2)-O(8)	1.40(3)	O(8)-Zn(2)-O(7)	106.0(7)
B(3)-O(4)	1.31(4)	O(5)#7-B(1)-O(7)	122(2)
B(3)-O(2)#9	1.32(3)	O(5)#7-B(1)-O(3)	116(2)
B(3)-O(6)#4	1.43(3)	O(7)-B(1)-O(3)	122(2)
O(2)-Pb(1)-O(7)#1	84.6(8)	O(1)#8-B(2)-O(9)	123(2)
O(2)-Pb(1)-O(8)	98.6(9)	O(1)#8-B(2)-O(8)	120(2)
O(7)#1-Pb(1)-O(8)	78.6(6)	O(9)-B(2)-O(8)	118(2)
O(6)#2-Pb(2)-O(6)	179.999(4)	O(4)-B(3)-O(2)#9	131(3)
O(6)#2-Pb(2)-O(2)	86.8(7)	O(4)-B(3)-O(6)#4	115(3)
O(6)-Pb(2)-O(2)	93.2(7)	O(2)#9-B(3)-O(6)#4	113(2)
O(6)#2-Pb(2)-	93.2(7)		

Symmetry transformations used to generate equivalent atoms:

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

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

#6 -x+1,y+1/2,-z+1/2 #7 x+1,y,z #8 x,-y+3/2,z+1/2

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

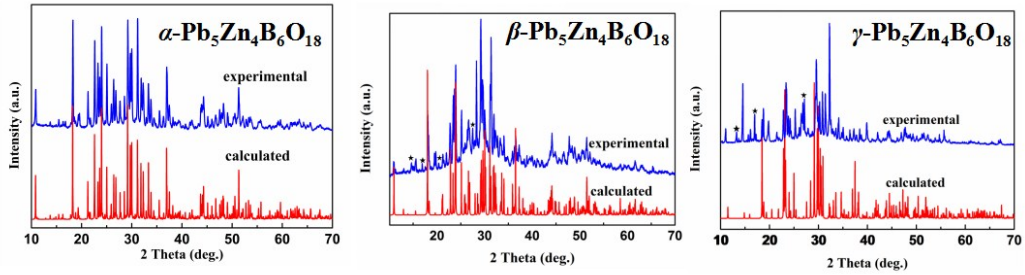

Figure S1. XRD patterns of $Pb_5Zn_4B_6O_{18}$ polymorphs. (Denotation ⋆ represents the $PbZn_2B_2O_6$ phase.)

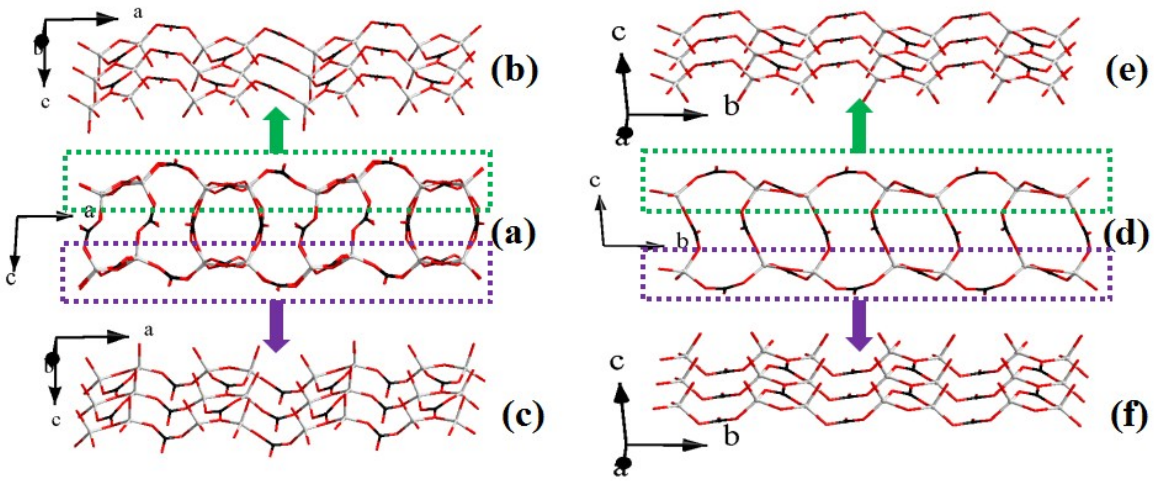

Figure S2. The $Zn_2BO_8{\cdot}2BO_3$ double layer in α- and β-$Pb_5Zn_4B_6O_{18}$, (a)&(d); The $Zn_2BO_8{\cdot}BO_3$ monolayer in α- and β-$Pb_5Zn_4B_6O_{18}$, (b),(c)&(e),(f).

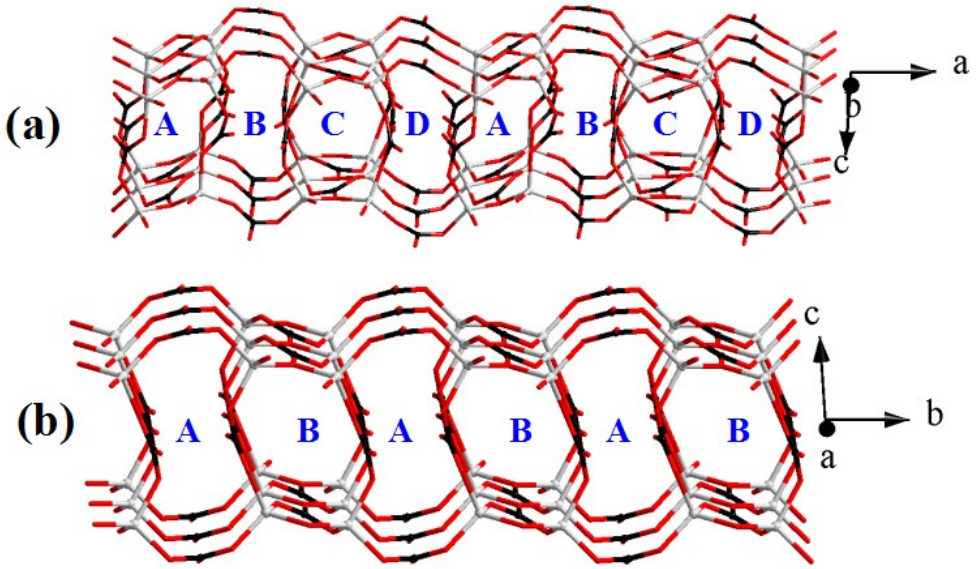

Figure S3. The tunnels in α- and β-$Pb_5Zn_4B_6O_{18}$.

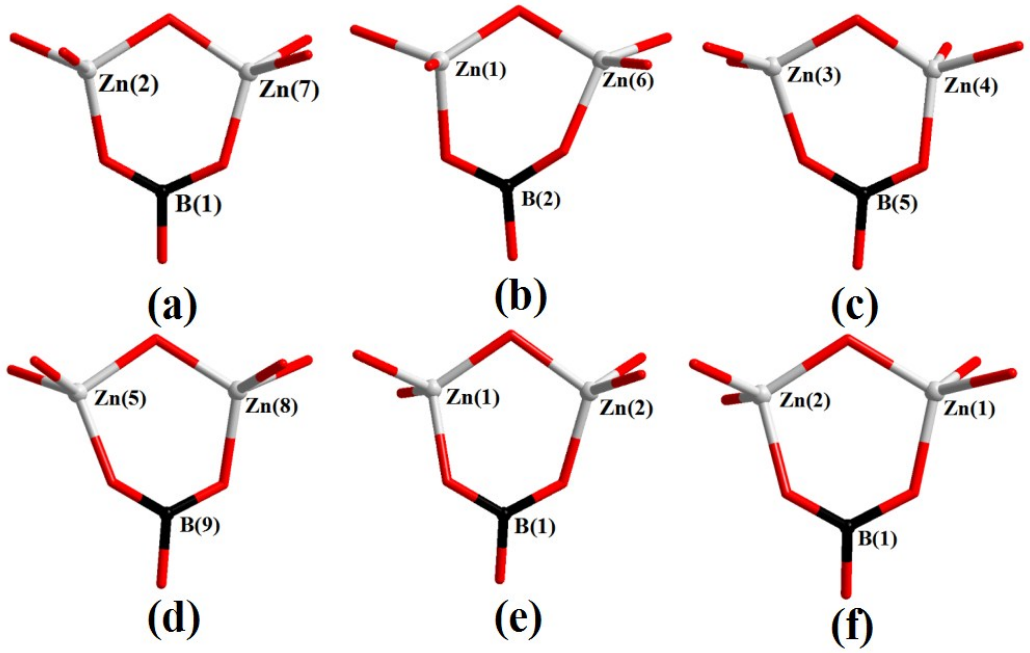

Figure S4. Zn_2BO_8 rings in α-$Pb_5Zn_4B_6O_{18}$ (a), (b), (c) and (d); β-$Pb_5Zn_4B_6O_{18}$ (e) and γ-$Pb_5Zn_4B_6O_{18}$ (f).

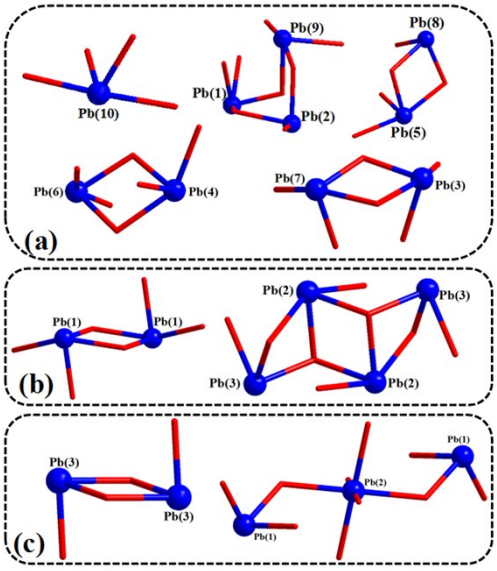

Figure S5. The environments of the Pb atoms in α-$Pb_5Zn_4B_6O_{18}$ (a), β-$Pb_5Zn_4B_6O_{18}$ (b), and γ-$Pb_5Zn_4B_6O_{18}$ (c).

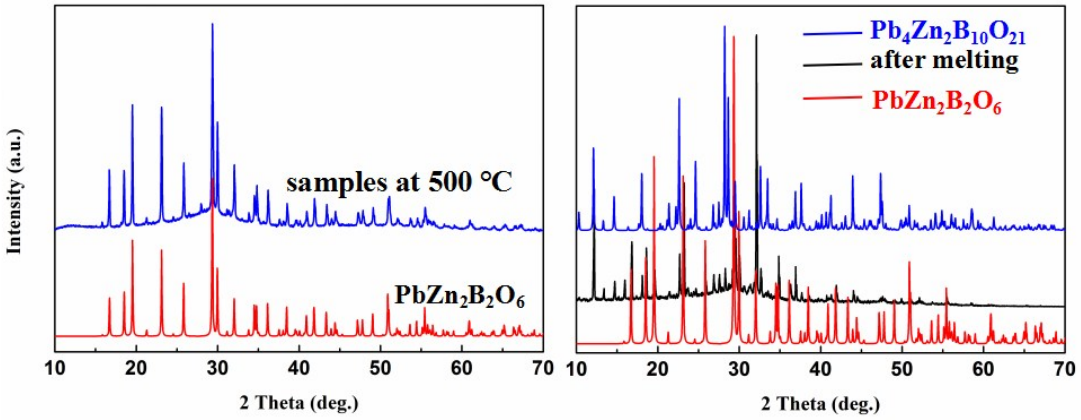

Figure S6. XRD patterns of samples at 500 ℃ and after melting. ($PbZn_2B_2O_6$, PDF-#, 19-0709; $Pb_4Zn_2B_{10}O_{21}$, PDF-#, 19-0710)

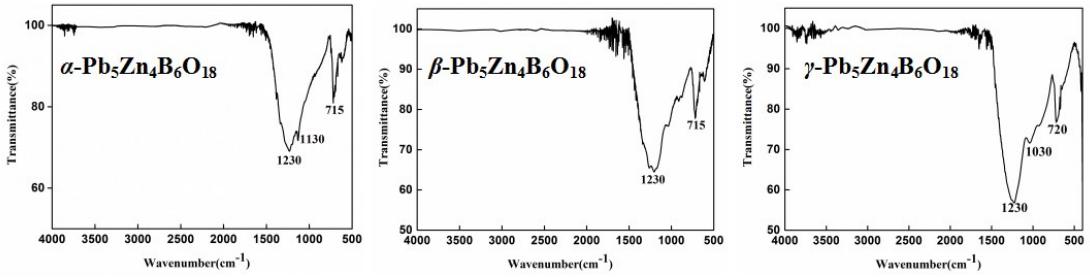

Figure S7. IR Spectroscopy of α-$Pb_5Zn_4B_6O_{18}$, β-$Pb_5Zn_4B_6O_{18}$ and γ-$Pb_5Zn_4B_6O_{18}$.

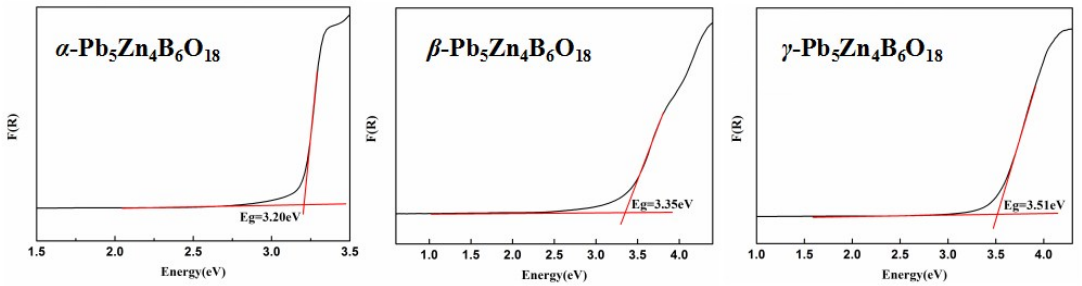

Figure S8. Absorption spectra for α-$Pb_5Zn_4B_6O_{18}$, β-$Pb_5Zn_4B_6O_{18}$ and γ-$Pb_5Zn_4B_6O_{18}$

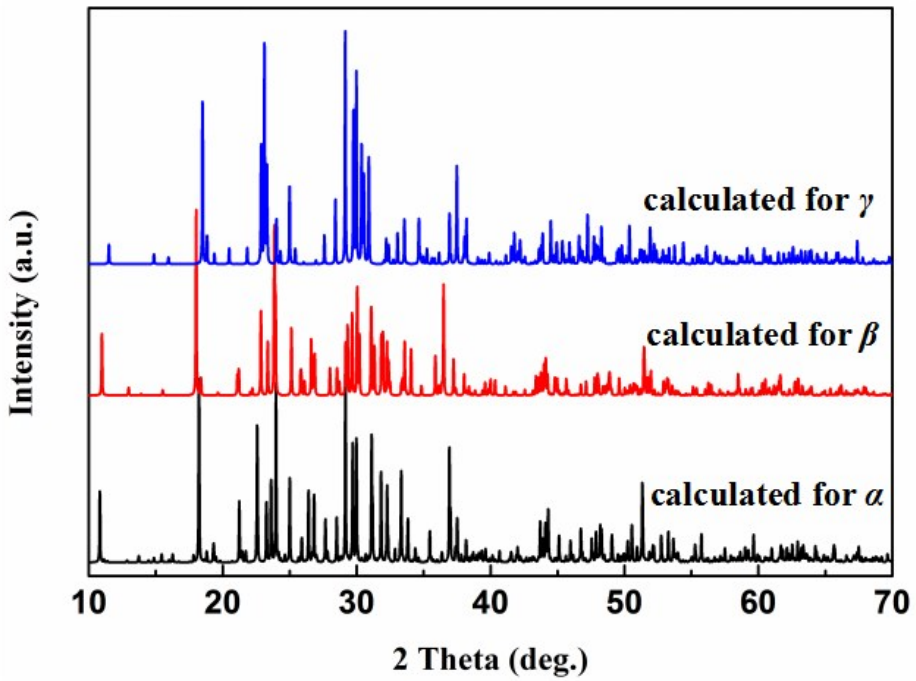

Figure S9. The calculated XRD patterns of $Pb_5Zn_4B_6O_{18}$ polymorph.