Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

$Ba_7(BO_3)_3GeO_4X$ (X=Cl, Br): the borogermanate halides with rigid GeO_4 Tetrahedra and flexible XBa_6 octahedra

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Table S1. The substitution of Ge for Si in borate.

Compouds	Space group	Structural features of Si−O and B−O groups	R=O/M (M=Si or Ge)	References
KSi_2BO_6	*I*-43*d*	0D	3	1
KGe_2BO_6	$P2_12_12_1$	3D	3	2
$Cs_2SiB_4O_9$	*I*-4	3D	9	3
$Cs_2GeB_4O_9$	*I*-4	3D	9	4
$LiSiBO_4$	*I*-4	3D	4	5
$LiGeBO_4$	*I*-4	3D	4	5
$SrSi_2B_2O_8$	*Pnma*	3D	4	6
$SrGe_2B_2O_8$	*Pnma*	3D	4	7
$Ba_3Si_2B_6O_{16}$	*P*-1	2D	8	8
$Ba_3Ge_2B_6O_{16}$	*P*-1	2D	8	9
$LaSiBO_5$	$P\,3_1$	1D	5	10
$LaGeBO_5$	$P\,3_1$	1D	5	11

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Table S2a. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for$Ba_7(BO_3)_3GeO_4Cl$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U (eq)
Ba(1)	1318(1)	6206(1)	0	12(1)
Ba(2)	836(1)	8671(1)	5000	10(1)
Ba(3)	2253(1)	5299(1)	5000	10(1)
Ba(4)	0	0	1875(1)	10(1)
Ba(5)	1840(1)	1978(1)	2322(1)	15(1)
Ba(6)	0	5000	2646(1)	15(1)
Ge(1)	826(1)	2912(2)	5000	9(1)
B(1)	1601(5)	7260(13)	2759(10)	9(2)
B(2)	485(8)	2860(20)	0	15(3)
Cl(1)	2232(2)	9488(5)	0	25(1)
O(1)	1640(4)	2132(11)	5000	10(2)
O(2)	159(4)	7679(11)	0	14(2)
O(3)	1868(3)	5644(8)	2401(6)	17(2)
O(4)	3021(3)	3317(8)	6457(6)	17(2)
O(5)	804(3)	3102(8)	1065(6)	16(2)
O(6)	815(5)	5243(12)	5000	19(2)
O(7)	451(3)	1946(9)	3743(7)	19(2)
O(8)	995(3)	7836(9)	2405(7)	19(2)

Table S2b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $Ba_7(BO_3)_3GeO_4Br$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U (eq)
Ba(1)	2257(1)	9672(1)	5000	10(1)
Ba(2)	1282(1)	8817(1)	0	13(1)
Ba(3)	833(1)	6332(1)	5000	10(1)
Ba(4)	0	5000	1886(1)	10(1)
Ba(5)	0	0	2683(1)	14(1)
Ba(6)	1839(1)	2931(1)	2356(1)	14(1)
Ge(1)	832(1)	2087(1)	5000	7(1)
B(1)	1599(4)	7741(10)	2780(7)	10(2)
B(2)	483(5)	2209(14)	0	9(2)
Br(1)	2215(1)	5471(2)	0	22(1)
O(1)	154(3)	7241(9)	0	13(1)
O(2)	3042(2)	1661(6)	6446(4)	15(1)
O(3)	1863(3)	9330(7)	2414(4)	18(1)
O(4)	804(2)	1890(6)	1077(4)	14(1)
O(5)	981(3)	7210(7)	2437(4)	22(1)
O(6)	455(2)	3069(6)	3738(4)	17(1)
O(7)	1646(3)	2820(9)	5000	17(2)
O(8)	809(4)	9765(9)	5000	18(2)

Table S3a. Selected bond distances (Å) and angles (deg) for $Ba_7(BO_3)_3GeO_4Cl$

Ba(1)-O(2)	2.601(9)	O(2)-Ba(1)-O(5)#1	90.3(2)
Ba(1)-O(5)#1	2.793(7)	O(2)-Ba(1)-O(5)	90.3(2)
Ba(1)-O(5)	2.793(7)	O(5)#1-Ba(1)-O(5)	50.2(3)
Ba(1)-O(3)	2.925(7)	O(2)-Ba(1)-O(3)	114.02(13)
Ba(1)-O(3)#1	2.925(7)	O(5)#1-Ba(1)-O(3)	114.41(19)
Ba(1)-O(8)	3.008(7)	O(5)-Ba(1)-O(3)	68.83(19)
Ba(1)-O(8)#1	3.008(7)	O(2)-Ba(1)-O(3)#1	114.02(13)
Ba(1)-Cl(1)	3.063(4)	O(5)#1-Ba(1)-O(3)#1	68.83(19)
Ba(1)-Cl(1)#2	3.214(4)	O(5)-Ba(1)-O(3)#1	114.41(19)
Ba(2)-O(6)#3	2.542(9)	O(3)-Ba(1)-O(3)#1	131.8(3)
Ba(2)-O(4)#4	2.847(7)	O(2)-Ba(1)-O(8)	68.44(14)
Ba(2)-O(4)#5	2.847(7)	O(5)#1-Ba(1)-O(8)	128.77(19)
Ba(2)-O(7)#6	2.909(7)	O(5)-Ba(1)-O(8)	82.64(19)
Ba(2)-O(7)	2.909(7)	O(3)-Ba(1)-O(8)	47.88(19)
Ba(2)-O(8)	2.970(8)	O(3)#1-Ba(1)-O(8)	162.31(18)
Ba(2)-O(8)#6	2.970(8)	O(2)-Ba(1)-O(8)#1	68.44(14)
Ba(2)-O(7)#7	3.003(7)	O(5)#1-Ba(1)-O(8)#1	82.64(19)
Ba(2)-O(7)#8	3.003(7)	O(5)-Ba(1)-O(8)#1	128.77(19)
Ba(2)-O(1)	3.044(8)	O(3)-Ba(1)-O(8)#1	162.31(18)
Ba(3)-O(1)#9	2.632(9)	O(3)#1-Ba(1)-O(8)#1	47.88(19)
Ba(3)-O(1)#3	2.660(8)	O(8)-Ba(1)-O(8)#1	125.6(3)
Ba(3)-O(4)#6	2.689(7)	O(2)-Ba(1)-Cl(1)	102.5(2)
Ba(3)-O(4)	2.689(7)	O(5)#1-Ba(1)-Cl(1)	151.96(14)
Ba(3)-O(4)#4	2.819(7)	O(5)-Ba(1)-Cl(1)	151.96(14)
Ba(3)-O(4)#5	2.819(7)	O(3)-Ba(1)-Cl(1)	83.16(13)
Ba(3)-O(6)#3	2.926(10)	O(3)#1-Ba(1)-Cl(1)	83.16(13)
Ba(3)-O(3)	3.006(7)	O(8)-Ba(1)-Cl(1)	79.27(13)
Ba(3)-O(3)#6	3.006(7)	O(8)#1-Ba(1)-Cl(1)	79.27(13)
Ba(4)-O(8)	2.650(7)	O(2)-Ba(1)-Cl(1)#2	178.5(2)
Ba(4)-O(8)#7	2.650(7)	O(5)#1-Ba(1)-Cl(1)#2	90.99(15)
Ba(4)-O(7)	2.690(7)	O(5)-Ba(1)-Cl(1)#2	90.99(15)
Ba(4)-O(7)#7	2.690(7)	O(3)-Ba(1)-Cl(1)#2	65.93(13)
Ba(4)-O(2)	2.724(6)	O(3)#1-Ba(1)-Cl(1)#2	65.93(13)
Ba(4)-O(2)#10	2.724(6)	O(8)-Ba(1)-Cl(1)#2	111.11(13)
Ba(4)-O(5)#11	2.963(7)	O(8)#1-Ba(1)-Cl(1)#2	111.11(13)
Ba(4)-O(5)#12	2.963(7)	Cl(1)-Ba(1)-Cl(1)#2	75.97(7)
Ba(5)-O(5)	2.664(7)	O(6)#3-Ba(2)-O(4)#4	85.5(2)
Ba(5)-O(3)	2.721(7)	O(6)#3-Ba(2)-O(4)#5	85.5(2)
Ba(5)-O(3)#14	2.810(7)	O(4)#4-Ba(2)-O(4)#5	69.4(3)
Ba(5)-O(4)#6	2.934(7)	O(6)#3-Ba(2)-O(7)#6	146.11(18)
Ba(5)-O(1)#3	3.008(3)	O(4)#4-Ba(2)-O(7)#6	91.36(19)
Ba(5)-O(4)#9	3.049(7)	O(4)#5-Ba(2)-O(7)#6	124.80(19)

Ba(5)-O(7)#3	3.240(7)	O(6)#3-Ba(2)-O(7)	146.11(18)
Ba(5)-Cl(1)#3	3.274(3)	O(4)#4-Ba(2)-O(7)	124.80(19)
Ba(6)-O(7)#3	2.731(7)	O(4)#5-Ba(2)-O(7)	91.36(19)
Ba(6)-O(7)#7	2.731(7)	O(7)#6-Ba(2)-O(7)	57.4(3)
Ba(6)-O(5)#11	2.784(7)	O(6)#3-Ba(2)-O(8)	78.06(13)
Ba(6)-O(5)	2.784(7)	O(4)#4-Ba(2)-O(8)	116.42(19)
Ba(6)-O(8)	2.931(7)	O(4)#5-Ba(2)-O(8)	48.59(19)
Ba(6)-O(8)#11	2.931(7)	O(7)#6-Ba(2)-O(8)	132.10(19)
Ba(6)-O(6)#3	3.105(6)	O(7)-Ba(2)-O(8)	74.73(19)
Ba(6)-O(6)#8	3.105(6)	O(6)#3-Ba(2)-O(8)#6	78.06(13)
Ge(1)-O(6)	1.729(9)	O(4)#4-Ba(2)-O(8)#6	48.59(19)
Ge(1)-O(7)	1.747(7)	O(4)#5-Ba(2)-O(8)#6	116.42(19)
Ge(1)-O(7)#6	1.747(7)	O(7)#6-Ba(2)-O(8)#6	74.73(19)
Ge(1)-O(1)	1.755(9)	O(7)-Ba(2)-O(8)#6	132.10(19)
B(1)-O(8)	1.364(12)	O(8)-Ba(2)-O(8)#6	152.8(3)
B(1)-O(3)	1.374(12)	O(6)#3-Ba(2)-O(7)#7	80.4(2)
B(1)-O(4)#5	1.402(12)	O(4)#4-Ba(2)-O(7)#7	164.40(18)
B(2)-O(5)	1.363(10)	O(4)#5-Ba(2)-O(7)#7	115.7(2)
B(2)-O(5)#1	1.363(10)	O(7)#6-Ba(2)-O(7)#7	96.66(18)
B(2)-O(2)#13	1.369(18)	O(7)-Ba(2)-O(7)#7	70.6(2)
Cl(1)-Ba(1)#16	3.214(4)	O(8)-Ba(2)-O(7)#7	67.09(19)
Cl(1)-Ba(5)#12	3.274(3)	O(8)#6-Ba(2)-O(7)#7	121.04(19)
Cl(1)-Ba(5)#17	3.274(3)	O(6)#3-Ba(2)-O(7)#8	80.4(2)
O(1)-Ba(3)#5	2.632(8)	O(4)#4-Ba(2)-O(7)#8	115.7(2)
O(1)-Ba(3)#12	2.660(8)	O(4)#5-Ba(2)-O(7)#8	164.40(18)
O(1)-Ba(5)#15	3.008(3)	O(7)#6-Ba(2)-O(7)#8	70.6(2)
O(1)-Ba(5)#12	3.008(3)	O(7)-Ba(2)-O(7)#8	96.66(18)
O(2)-B(2)#13	1.369(18)	O(8)-Ba(2)-O(7)#8	121.04(19)
O(2)-Ba(4)#10	2.724(6)	O(8)#6-Ba(2)-O(7)#8	67.09(19)
O(3)-Ba(5)#4	2.810(7)	O(7)#7-Ba(2)-O(7)#8	55.5(3)
O(4)-B(1)#9	1.402(12)	O(6)#3-Ba(2)-O(1)	148.4(3)
O(4)-Ba(3)#9	2.819(7)	O(4)#4-Ba(2)-O(1)	68.81(18)
O(4)-Ba(2)#9	2.847(7)	O(4)#5-Ba(2)-O(1)	68.81(18)
O(4)-Ba(5)#6	2.934(7)	O(7)#6-Ba(2)-O(1)	56.03(19)
O(4)-Ba(5)#5	3.049(7)	O(7)-Ba(2)-O(1)	56.03(19)
O(5)-Ba(4)#3	2.963(7)	O(8)-Ba(2)-O(1)	96.74(13)
O(6)-Ba(2)#12	2.542(9)	O(8)#6-Ba(2)-O(1)	96.74(13)
O(6)-Ba(3)#12	2.926(10)	O(7)#7-Ba(2)-O(1)	126.68(18)
O(6)-Ba(6)#12	3.105(6)	O(7)#8-Ba(2)-O(1)	126.68(18)
O(6)-Ba(6)#8	3.105(6)	O(1)#9-Ba(3)-O(1)#3	149.1(2)
O(7)-Ba(6)#12	2.731(7)	O(1)#9-Ba(3)-O(4)#6	77.5(2)
O(7)-Ba(2)#8	3.003(7)	O(1)#3-Ba(3)-O(4)#6	77.9(2)
O(7)-Ba(5)#12	3.240(7)	O(1)#9-Ba(3)-O(4)	77.5(2)
O(3)#14-Ba(5)-O(1)#3	96.3(2)	O(1)#3-Ba(3)-O(4)	77.9(2)

O(4)#6-Ba(5)-O(1)#3	68.9(2)	O(4)#6-Ba(3)-O(4)	74.1(3)
O(5)-Ba(5)-O(4)#9	125.85(19)	O(1)#9-Ba(3)-O(4)#4	76.1(2)
O(3)-Ba(5)-O(4)#9	150.9(2)	O(1)#3-Ba(3)-O(4)#4	127.46(19)
O(3)#14-Ba(5)-O(4)#9	65.55(18)	O(4)#6-Ba(3)-O(4)#4	153.58(15)
O(4)#6-Ba(5)-O(4)#9	91.11(17)	O(4)-Ba(3)-O(4)#4	101.7(2)
O(1)#3-Ba(5)-O(4)#9	66.8(2)	O(1)#9-Ba(3)-O(4)#5	76.1(2)
O(5)-Ba(5)-O(7)#3	64.4(2)	O(1)#3-Ba(3)-O(4)#5	127.46(19)
O(3)-Ba(5)-O(7)#3	90.58(18)	O(4)#6-Ba(3)-O(4)#5	101.7(2)
O(3)#14-Ba(5)-O(7)#3	143.02(19)	O(4)-Ba(3)-O(4)#5	153.58(15)
O(4)#6-Ba(5)-O(7)#3	119.47(19)	O(4)#4-Ba(3)-O(4)#5	70.2(3)
O(1)#3-Ba(5)-O(7)#3	53.1(2)	O(1)#9-Ba(3)-O(6)#3	149.7(3)
O(4)#9-Ba(5)-O(7)#3	81.78(17)	O(1)#3-Ba(3)-O(6)#3	61.2(3)
O(5)-Ba(5)-Cl(1)#3	87.42(16)	O(4)#6-Ba(3)-O(6)#3	125.01(19)
O(3)-Ba(5)-Cl(1)#3	125.71(16)	O(4)-Ba(3)-O(6)#3	125.01(19)
O(3)#14-Ba(5)-Cl(1)#3	66.31(16)	O(4)#4-Ba(3)-O(6)#3	79.23(19)
O(4)#6-Ba(5)-Cl(1)#3	110.88(15)	O(4)#5-Ba(3)-O(6)#3	79.23(19)
O(1)#3-Ba(5)-Cl(1)#3	146.68(17)	O(1)#9-Ba(3)-O(3)	100.31(13)
O(4)#9-Ba(5)-Cl(1)#3	80.02(15)	O(1)#3-Ba(3)-O(3)	87.31(13)
O(7)#3-Ba(5)-Cl(1)#3	126.40(14)	O(4)#6-Ba(3)-O(3)	67.6(2)
O(7)#3-Ba(6)-O(7)#7	126.9(3)	O(4)-Ba(3)-O(3)	141.04(19)
O(7)#3-Ba(6)-O(5)#11	154.00(19)	O(4)#4-Ba(3)-O(3)	115.70(19)
O(7)#7-Ba(6)-O(5)#11	70.5(2)	O(4)#5-Ba(3)-O(3)	47.77(18)
O(7)#3-Ba(6)-O(5)	70.5(2)	O(6)#3-Ba(3)-O(3)	74.98(12)
O(7)#7-Ba(6)-O(5)	154.00(19)	O(1)#9-Ba(3)-O(3)#6	100.31(13)
O(5)#11-Ba(6)-O(5)	101.7(3)	O(1)#3-Ba(3)-O(3)#6	87.31(13)
O(7)#3-Ba(6)-O(8)	113.8(2)	O(4)#6-Ba(3)-O(3)#6	141.04(19)
O(7)#7-Ba(6)-O(8)	71.2(2)	O(4)-Ba(3)-O(3)#6	67.6(2)
O(5)#11-Ba(6)-O(8)	89.2(2)	O(4)#4-Ba(3)-O(3)#6	47.77(19)
O(5)-Ba(6)-O(8)	84.21(19)	O(4)#5-Ba(3)-O(3)#6	115.70(19)
O(7)#3-Ba(6)-O(8)#11	71.2(2)	O(6)#3-Ba(3)-O(3)#6	74.98(12)
O(7)#7-Ba(6)-O(8)#11	113.8(2)	O(3)-Ba(3)-O(3)#6	148.2(2)
O(5)#11-Ba(6)-O(8)#11	84.21(19)	O(8)-Ba(4)-O(8)#7	154.3(3)
O(5)-Ba(6)-O(8)#11	89.2(2)	O(8)-Ba(4)-O(7)	83.8(2)
O(8)-Ba(6)-O(8)#11	169.5(3)	O(8)#7-Ba(4)-O(7)	76.3(2)
O(7)#3-Ba(6)-O(6)#3	59.5(2)	O(8)-Ba(4)-O(7)#7	76.3(2)
O(7)#7-Ba(6)-O(6)#3	75.8(2)	O(8)#7-Ba(4)-O(7)#7	83.8(2)
O(5)#11-Ba(6)-O(6)#3	144.8(2)	O(7)-Ba(4)-O(7)#7	78.9(3)
O(5)-Ba(6)-O(6)#3	104.4(2)	O(8)-Ba(4)-O(2)	72.4(2)
O(8)-Ba(6)-O(6)#3	70.5(2)	O(8)#7-Ba(4)-O(2)	130.1(2)
O(8)#11-Ba(6)-O(6)#3	119.2(2)	O(7)-Ba(4)-O(2)	152.9(2)
O(7)#3-Ba(6)-O(6)#8	75.8(2)	O(7)#7-Ba(4)-O(2)	107.0(2)
O(7)#7-Ba(6)-O(6)#8	59.5(2)	O(8)-Ba(4)-O(2)#10	130.1(2)
O(5)#11-Ba(6)-O(6)#8	104.4(2)	O(8)#7-Ba(4)-O(2)#10	72.4(2)
O(5)-Ba(6)-O(6)#8	144.8(2)	O(7)-Ba(4)-O(2)#10	107.0(2)

O(8)-Ba(6)-O(6)#8	119.2(2)	O(7)#7-Ba(4)-O(2)#10	152.9(2)
O(8)#11-Ba(6)-O(6)#8	70.5(2)	O(2)-Ba(4)-O(2)#10	80.0(3)
O(6)#3-Ba(6)-O(6)#8	65.0(3)	O(8)-Ba(4)-O(5)#11	91.1(2)
O(6)-Ge(1)-O(7)	113.9(3)	O(8)#7-Ba(4)-O(5)#11	96.7(2)
O(6)-Ge(1)-O(7)#6	113.9(3)	O(7)-Ba(4)-O(5)#11	147.1(2)
O(7)-Ge(1)-O(7)#6	106.3(5)	O(7)#7-Ba(4)-O(5)#11	68.3(2)
O(6)-Ge(1)-O(1)	110.0(4)	O(2)-Ba(4)-O(5)#11	48.8(2)
O(7)-Ge(1)-O(1)	106.1(3)	O(2)#10-Ba(4)-O(5)#11	101.1(2)
O(7)#6-Ge(1)-O(1)	106.1(3)	O(8)-Ba(4)-O(5)#12	96.7(2)
O(8)-B(1)-O(3)	123.2(9)	O(8)#7-Ba(4)-O(5)#12	91.1(2)
O(8)-B(1)-O(4)#5	120.0(8)	O(7)-Ba(4)-O(5)#12	68.3(2)
O(3)-B(1)-O(4)#5	116.8(8)	O(7)#7-Ba(4)-O(5)#12	147.1(2)
O(5)-B(2)-O(5)#1	120.7(13)	O(2)-Ba(4)-O(5)#12	101.1(2)
O(5)-B(2)-O(2)#13	119.6(7)	O(2)#10-Ba(4)-O(5)#12	48.8(2)
O(5)#1-B(2)-O(2)#13	119.6(7)	O(5)#11-Ba(4)-O(5)#12	144.6(3)
O(3)-Ba(5)-O(4)#6	68.26(19)	O(5)-Ba(5)-O(3)	73.8(2)
O(3)#14-Ba(5)-O(4)#6	48.56(19)	O(5)-Ba(5)-O(3)#14	150.1(2)
O(5)-Ba(5)-O(1)#3	113.6(2)	O(3)-Ba(5)-O(3)#14	109.32(15)
O(3)-Ba(5)-O(1)#3	86.2(2)	O(5)-Ba(5)-O(4)#6	141.78(19)

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

Table S3b. Selected bond distances (Å) and angles (deg) for $Ba_7(BO_3)_3GeO_4Br$.

Ba(1)-O(7)#1	2.630(7)	O(2)#1-Ba(3)-O(6)#9	164.79(14)
Ba(1)-O(7)	2.662(7)	O(6)#6-Ba(3)-O(6)#9	96.93(13)
Ba(1)-O(2)	2.718(5)	O(6)#7-Ba(3)-O(6)#9	70.65(17)
Ba(1)-O(2)#2	2.718(5)	O(5)#2-Ba(3)-O(6)#9	66.57(14)
Ba(1)-O(2)#1	2.837(5)	O(5)-Ba(3)-O(6)#9	120.66(14)
Ba(1)-O(2)#3	2.837(5)	O(6)#8-Ba(3)-O(6)#9	55.82(19)
Ba(1)-O(8)	2.951(7)	O(8)-Ba(3)-O(7)#6	148.8(2)
Ba(1)-O(3)	3.010(5)	O(2)#3-Ba(3)-O(7)#6	68.85(14)
Ba(1)-O(3)#2	3.010(5)	O(2)#1-Ba(3)-O(7)#6	68.85(14)
Ba(2)-O(1)	2.583(7)	O(6)#6-Ba(3)-O(7)#6	55.56(14)
Ba(2)-O(4)	2.770(5)	O(6)#7-Ba(3)-O(7)#6	55.56(14)
Ba(2)-O(4)#4	2.770(5)	O(5)#2-Ba(3)-O(7)#6	97.66(11)
Ba(2)-O(3)	2.971(5)	O(5)-Ba(3)-O(7)#6	97.66(11)
Ba(2)-O(3)#4	2.971(5)	O(6)#8-Ba(3)-O(7)#6	126.21(14)
Ba(2)-O(5)#4	3.039(5)	O(6)#9-Ba(3)-O(7)#6	126.21(14)
Ba(2)-O(5)	3.039(5)	O(5)-Ba(4)-O(5)#10	153.3(2)
Ba(2)-Br(1)	3.1424(15)	O(5)-Ba(4)-O(6)#8	75.41(15)
Ba(2)-Br(1)#5	3.3052(17)	O(5)#10-Ba(4)-O(6)#8	84.05(15)
Ba(3)-O(8)	2.567(7)	O(5)-Ba(4)-O(6)#6	84.05(15)
Ba(3)-O(2)#3	2.815(5)	O(5)#10-Ba(4)-O(6)#6	75.41(15)
Ba(3)-O(2)#1	2.815(5)	O(6)#8-Ba(4)-O(6)#6	79.3(2)
Ba(3)-O(6)#6	2.922(5)	O(5)-Ba(4)-O(1)#11	130.51(18)
Ba(3)-O(6)#7	2.922(5)	O(5)#10-Ba(4)-O(1)#11	73.12(17)
Ba(3)-O(5)#2	2.954(5)	O(6)#8-Ba(4)-O(1)#11	152.94(18)
Ba(3)-O(5)	2.954(5)	O(6)#6-Ba(4)-O(1)#11	107.83(16)
Ba(3)-O(6)#8	3.014(5)	O(5)-Ba(4)-O(1)	73.12(17)
Ba(3)-O(6)#9	3.014(5)	O(5)#10-Ba(4)-O(1)	130.51(18)
Ba(3)-O(7)#6	3.106(7)	O(6)#8-Ba(4)-O(1)	107.83(16)
Ba(4)-O(5)	2.667(5)	O(6)#6-Ba(4)-O(1)	152.94(18)
Ba(4)-O(5)#10	2.667(5)	O(1)#11-Ba(4)-O(1)	78.0(2)
Ba(4)-O(6)#8	2.688(5)	O(5)-Ba(4)-O(4)#8	89.92(15)
Ba(4)-O(6)#6	2.688(5)	O(5)#10-Ba(4)-O(4)#8	98.12(15)
Ba(4)-O(1)#11	2.711(4)	O(6)#8-Ba(4)-O(4)#8	68.00(14)
Ba(4)-O(1)	2.711(4)	O(6)#6-Ba(4)-O(4)#8	147.25(14)
Ba(4)-O(4)#8	2.985(5)	O(1)#11-Ba(4)-O(4)#8	100.52(16)
Ba(4)-O(4)#6	2.985(5)	O(1)-Ba(4)-O(4)#8	49.18(17)
B(1)-O(2)#1	1.391(9)	O(5)-Ba(4)-O(4)#6	98.12(15)
B(2)-O(1)#12	1.362(12)	O(5)#10-Ba(4)-O(4)#6	89.92(15)
B(2)-O(4)	1.390(7)	O(6)#8-Ba(4)-O(4)#6	147.25(14)
B(2)-O(4)#4	1.390(7)	O(6)#6-Ba(4)-O(4)#6	68.00(14)
O(1)-B(2)#12	1.362(12)	O(1)#11-Ba(4)-O(4)#6	49.18(17)
O(1)-Ba(4)#11	2.711(4)	O(1)-Ba(4)-O(4)#6	100.52(16)

O(2)-B(1)#15	1.391(9)	O(4)#8-Ba(4)-O(4)#6	144.72(18)
O(2)-Ba(3)#15	2.815(5)	O(6)-Ba(5)-O(6)#8	129.1(2)
O(2)-Ba(1)#15	2.837(5)	O(6)-Ba(5)-O(4)#8	153.18(14)
O(2)-Ba(6)#2	2.950(5)	O(6)#8-Ba(5)-O(4)#8	69.92(14)
O(6)-Ba(3)#9	3.014(5)	O(6)-Ba(5)-O(4)	69.92(14)
O(7)-Ba(1)#15	2.630(7)	O(6)#8-Ba(5)-O(4)	153.18(14)
O(7)-Ba(6)#2	2.9813(15)	O(4)#8-Ba(5)-O(4)	100.6(2)
O(7)-Ba(3)#13	3.106(7)	O(6)-Ba(5)-O(5)	114.15(15)
O(8)-Ba(5)#9	3.074(4)	O(6)#8-Ba(5)-O(5)	70.88(15)
O(7)#1-Ba(1)-O(7)	149.6(2)	O(4)#8-Ba(5)-O(5)	88.85(14)
O(7)#1-Ba(1)-O(2)	77.72(16)	O(4)-Ba(5)-O(5)	84.21(14)
O(7)-Ba(1)-O(2)	77.96(16)	O(6)-Ba(5)-O(5)#8	70.88(15)
O(7)#1-Ba(1)-O(2)#2	77.72(16)	O(6)#8-Ba(5)-O(5)#8	114.15(15)
O(7)-Ba(1)-O(2)#2	77.96(16)	O(4)#8-Ba(5)-O(5)#8	84.21(14)
O(2)-Ba(1)-O(2)#2	72.9(2)	O(4)-Ba(5)-O(5)#8	88.85(14)
O(7)#1-Ba(1)-O(2)#1	76.38(16)	O(5)-Ba(5)-O(5)#8	169.1(2)
O(7)-Ba(1)-O(2)#1	126.97(15)	O(6)-Ba(5)-O(8)	60.30(17)
O(2)-Ba(1)-O(2)#1	154.04(11)	O(6)#8-Ba(5)-O(8)	76.79(17)
O(2)#2-Ba(1)-O(2)#1	102.83(16)	O(4)#8-Ba(5)-O(8)	145.24(16)
O(7)#1-Ba(1)-O(2)#3	76.38(16)	O(4)-Ba(5)-O(8)	104.73(16)
O(7)-Ba(1)-O(2)#3	126.97(15)	O(5)-Ba(5)-O(8)	70.68(16)
O(2)-Ba(1)-O(2)#3	102.83(16)	O(5)#8-Ba(5)-O(8)	119.36(16)
O(2)#2-Ba(1)-O(2)#3	154.04(11)	O(6)-Ba(5)-O(8)#9	76.79(17)
O(2)#1-Ba(1)-O(2)#3	69.42(19)	O(6)#8-Ba(5)-O(8)#9	60.30(17)
O(7)#1-Ba(1)-O(8)	149.6(2)	O(4)#8-Ba(5)-O(8)#9	104.73(16)
O(7)-Ba(1)-O(8)	60.8(2)	O(4)-Ba(5)-O(8)#9	145.24(16)
O(2)-Ba(1)-O(8)	125.19(14)	O(5)-Ba(5)-O(8)#9	119.36(16)
O(2)#2-Ba(1)-O(8)	125.19(14)	O(5)#8-Ba(5)-O(8)#9	70.68(16)
O(2)#1-Ba(1)-O(8)	78.71(15)	O(8)-Ba(5)-O(8)#9	65.3(2)
O(2)#3-Ba(1)-O(8)	78.71(15)	O(4)-Ba(6)-O(3)	74.66(15)
O(7)#1-Ba(1)-O(3)	100.46(10)	O(4)-Ba(6)-O(3)#14	148.82(14)
O(7)-Ba(1)-O(3)	87.18(11)	O(3)-Ba(6)-O(3)#14	110.50(12)
O(2)-Ba(1)-O(3)	140.73(14)	O(4)-Ba(6)-O(2)#2	143.85(14)
O(2)#2-Ba(1)-O(3)	68.44(14)	O(3)-Ba(6)-O(2)#2	69.66(14)
O(2)#1-Ba(1)-O(3)	47.83(14)	O(3)#14-Ba(6)-O(2)#2	48.36(14)
O(2)#3-Ba(1)-O(3)	114.97(14)	O(4)-Ba(6)-O(7)	114.78(17)
O(8)-Ba(1)-O(3)	74.69(10)	O(3)-Ba(6)-O(7)	87.19(17)
O(7)#1-Ba(1)-O(3)#2	100.46(10)	O(3)#14-Ba(6)-O(7)	96.34(17)
O(7)-Ba(1)-O(3)#2	87.18(11)	O(2)#2-Ba(6)-O(7)	69.57(17)
O(2)-Ba(1)-O(3)#2	68.44(14)	O(4)-Ba(6)-O(2)#15	123.75(14)
O(2)#2-Ba(1)-O(3)#2	140.73(14)	O(3)-Ba(6)-O(2)#15	152.46(14)
O(2)#1-Ba(1)-O(3)#2	114.97(14)	O(3)#14-Ba(6)-O(2)#15	65.62(14)
O(2)#3-Ba(1)-O(3)#2	47.83(14)	O(2)#2-Ba(6)-O(2)#15	91.65(12)
O(8)-Ba(1)-O(3)#2	74.69(10)	O(7)-Ba(6)-O(2)#15	66.91(16)

O(3)-Ba(1)-O(3)#2	147.5(2)	O(4)-Ba(6)-O(6)	64.70(14)
O(1)-Ba(2)-O(4)	93.75(17)	O(3)-Ba(6)-O(6)	92.11(14)
O(1)-Ba(2)-O(4)#4	93.75(17)	O(3)#14-Ba(6)-O(6)	142.41(13)
O(4)-Ba(2)-O(4)#4	51.5(2)	O(2)#2-Ba(6)-O(6)	121.42(13)
O(1)-Ba(2)-O(3)	114.46(10)	O(7)-Ba(6)-O(6)	53.84(16)
O(4)-Ba(2)-O(3)	68.84(14)	O(2)#15-Ba(6)-O(6)	80.36(13)
O(4)#4-Ba(2)-O(3)	115.31(14)	O(4)-Ba(6)-Br(1)#13	85.66(11)
O(1)-Ba(2)-O(3)#4	114.46(10)	O(3)-Ba(6)-Br(1)#13	125.72(11)
O(4)-Ba(2)-O(3)#4	115.31(14)	O(3)#14-Ba(6)-Br(1)#13	66.12(10)
O(4)#4-Ba(2)-O(3)#4	68.84(14)	O(2)#2-Ba(6)-Br(1)#13	110.54(10)
O(3)-Ba(2)-O(3)#4	130.4(2)	O(7)-Ba(6)-Br(1)#13	145.92(13)
O(1)-Ba(2)-O(5)#4	68.93(11)	O(2)#15-Ba(6)-Br(1)#13	79.09(9)
O(4)-Ba(2)-O(5)#4	130.26(14)	O(6)-Ba(6)-Br(1)#13	124.16(9)
O(4)#4-Ba(2)-O(5)#4	82.41(14)	O(4)-Ba(6)-Br(1)#5	83.52(11)
O(3)-Ba(2)-O(5)#4	160.90(14)	O(3)-Ba(6)-Br(1)#5	61.10(11)
O(3)#4-Ba(2)-O(5)#4	46.99(14)	O(3)#14-Ba(6)-Br(1)#5	73.61(10)
O(1)-Ba(2)-O(5)	68.93(11)	O(2)#2-Ba(6)-Br(1)#5	74.52(10)
O(4)-Ba(2)-O(5)	82.41(14)	O(7)-Ba(6)-Br(1)#5	138.64(14)
O(4)#4-Ba(2)-O(5)	130.26(14)	O(2)#15-Ba(6)-Br(1)#5	134.77(9)
O(3)-Ba(2)-O(5)	46.99(14)	O(6)-Ba(6)-Br(1)#5	143.55(9)
O(3)#4-Ba(2)-O(5)	160.90(14)	Br(1)#13-Ba(6)-Br(1)#5	66.84(3)
O(5)#4-Ba(2)-O(5)	127.3(2)	O(8)-Ge(1)-O(7)	109.8(3)
O(1)-Ba(2)-Br(1)	100.09(15)	O(8)-Ge(1)-O(6)#2	113.8(2)
O(4)-Ba(2)-Br(1)	150.81(10)	O(7)-Ge(1)-O(6)#2	106.4(2)
O(4)#4-Ba(2)-Br(1)	150.81(10)	O(8)-Ge(1)-O(6)	113.8(2)
O(3)-Ba(2)-Br(1)	82.03(10)	O(7)-Ge(1)-O(6)	106.4(2)
O(3)#4-Ba(2)-Br(1)	82.03(10)	O(6)#2-Ge(1)-O(6)	106.1(3)
O(5)#4-Ba(2)-Br(1)	78.88(10)	O(3)-B(1)-O(5)	121.9(6)
O(5)-Ba(2)-Br(1)	78.88(10)	O(3)-B(1)-O(2)#1	118.9(7)
O(1)-Ba(2)-Br(1)#5	174.83(15)	O(5)-B(1)-O(2)#1	119.2(6)
O(4)-Ba(2)-Br(1)#5	90.90(10)	O(1)#12-B(2)-O(4)	120.0(4)
O(4)#4-Ba(2)-Br(1)#5	90.90(10)	O(1)#12-B(2)-O(4)#4	120.0(4)
O(3)-Ba(2)-Br(1)#5	65.27(10)	O(4)-B(2)-O(4)#4	119.9(9)
O(3)#4-Ba(2)-Br(1)#5	65.27(10)	O(6)#6-Ba(3)-O(5)#2	132.91(14)
O(5)#4-Ba(2)-Br(1)#5	109.55(10)	O(6)#7-Ba(3)-O(5)#2	75.20(14)
O(5)-Ba(2)-Br(1)#5	109.55(10)	O(8)-Ba(3)-O(5)	77.27(10)
Br(1)-Ba(2)-Br(1)#5	74.74(3)	O(2)#3-Ba(3)-O(5)	116.97(15)
O(8)-Ba(3)-O(2)#3	85.89(16)	O(2)#1-Ba(3)-O(5)	48.76(15)
O(8)-Ba(3)-O(2)#1	85.89(16)	O(6)#6-Ba(3)-O(5)	75.20(14)
O(2)#3-Ba(3)-O(2)#1	70.0(2)	O(6)#7-Ba(3)-O(5)	132.91(14)
O(8)-Ba(3)-O(6)#6	146.09(13)	O(5)#2-Ba(3)-O(5)	151.7(2)
O(2)#3-Ba(3)-O(6)#6	124.37(14)	O(8)-Ba(3)-O(6)#8	80.48(17)
O(2)#1-Ba(3)-O(6)#6	90.60(14)	O(2)#3-Ba(3)-O(6)#8	164.79(14)
O(8)-Ba(3)-O(6)#7	146.09(13)	O(2)#1-Ba(3)-O(6)#8	115.33(14)

O(2)#3-Ba(3)-O(6)#7	90.60(14)	O(6)#6-Ba(3)-O(6)#8	70.65(17)
O(2)#1-Ba(3)-O(6)#7	124.37(14)	O(6)#7-Ba(3)-O(6)#8	96.93(13)
O(6)#6-Ba(3)-O(6)#7	57.74(19)	O(5)#2-Ba(3)-O(6)#8	120.66(14)
O(8)-Ba(3)-O(5)#2	77.27(10)	O(5)-Ba(3)-O(6)#8	66.57(14)
O(2)#3-Ba(3)-O(5)#2	48.76(15)	O(8)-Ba(3)-O(6)#9	80.48(17)
O(2)#1-Ba(3)-O(5)#2	116.97(15)	O(2)#3-Ba(3)-O(6)#9	115.33(14)

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

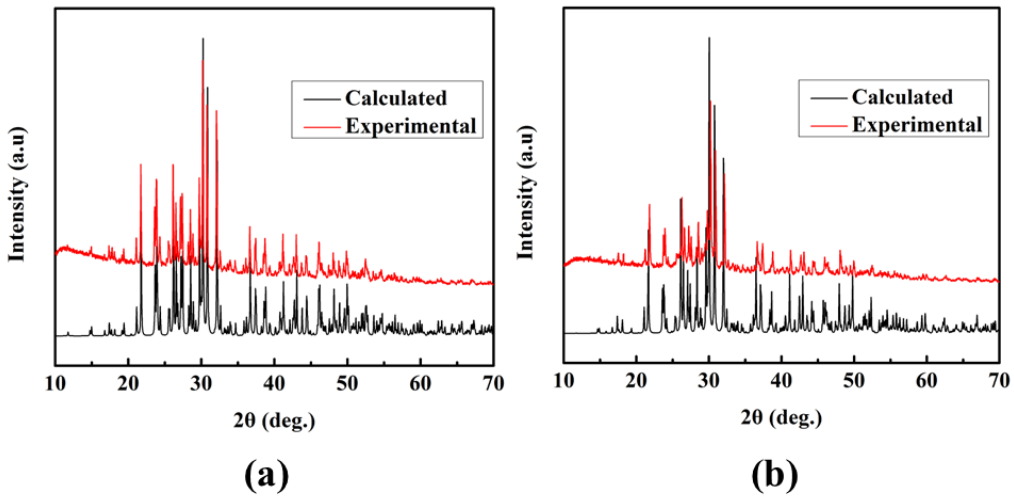


Figure S1. Experimental and calculated XRD patterns of $Ba_7(BO_3)_3GeO_4Cl$ (a) and $Ba_7(BO_3)_3GeO_4Br$ (b)

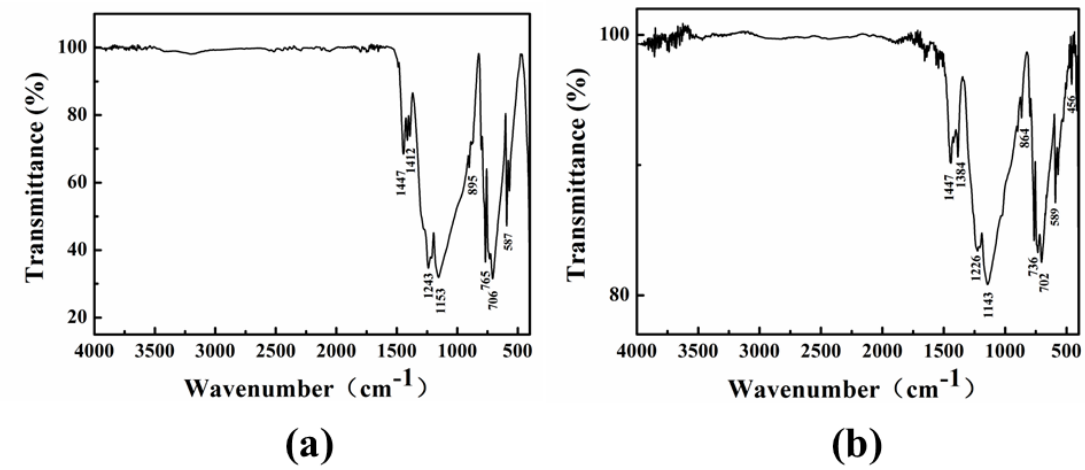


Figure S2. IR spectra of $Ba_7(BO_3)_3GeO_4Cl$ (a) and $Ba_7(BO_3)_3GeO_4Br$ (b)

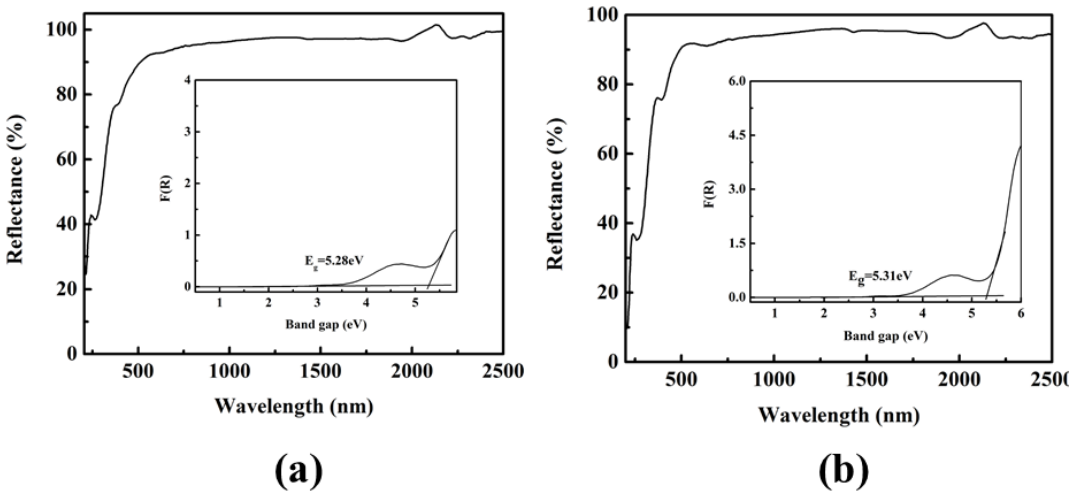


Figure S3. UV−vis−NIR diffuse reflectance spectra of $Ba_7(BO_3)_3GeO_4Cl$ (a) and $Ba_7(BO_3)_3GeO_4Br$ (b)

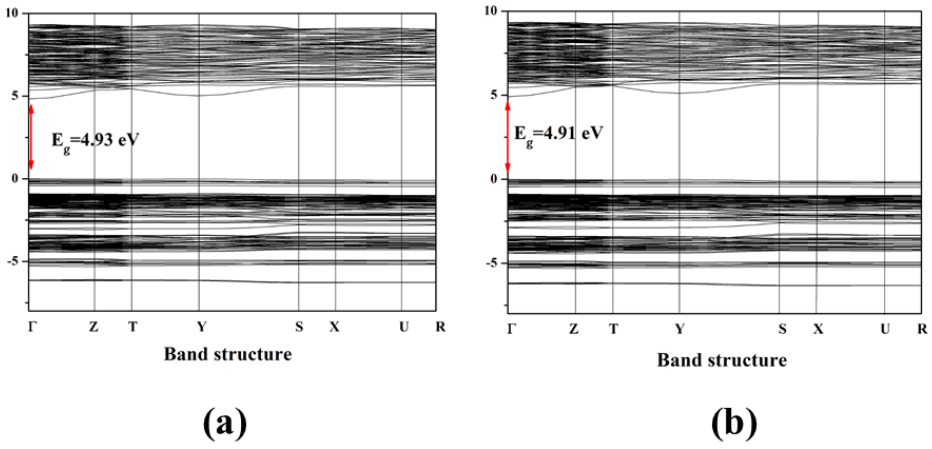
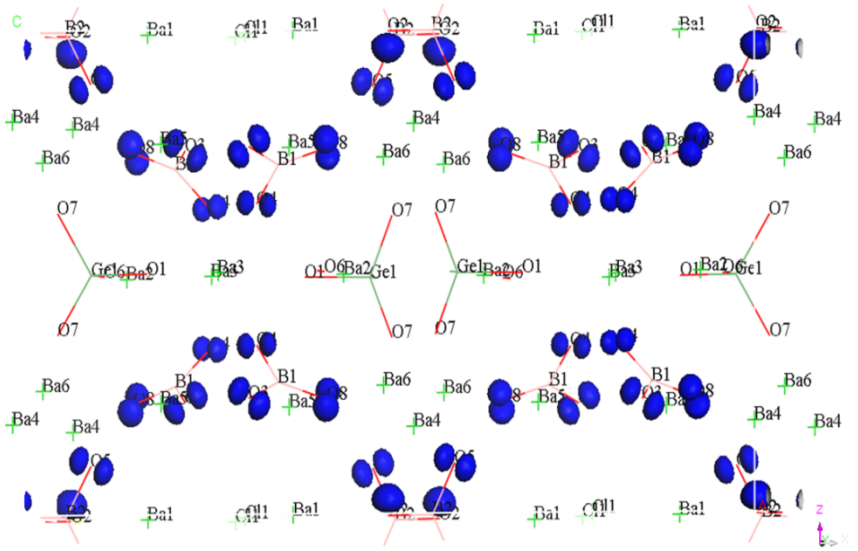
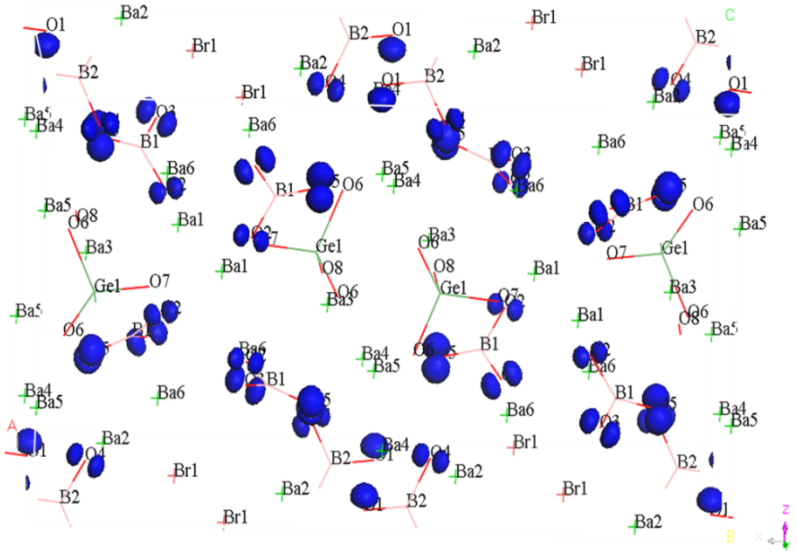


Figure S4. Band structures of $Ba_7(BO_3)_3GeO_4Cl$ (a) and $Ba_7(BO_3)_3GeO_4Br$ (b)



(a)



(b)

Figure S5. The highest occupied orbitals of $Ba_7(BO_3)_3GeO_4Cl$ (a) and $Ba_7(BO_3)_3GeO_4Br$ (b)

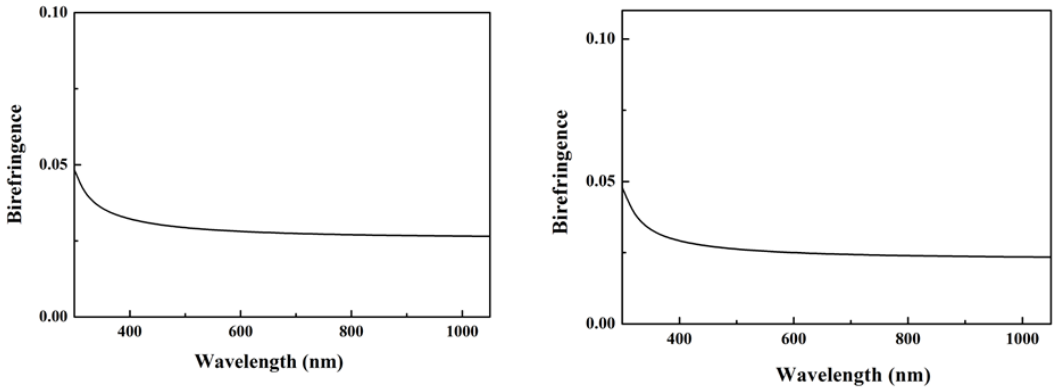


Figure S6. Calculated birefringences of $Ba_7(BO_3)_3GeO_4Cl$ (a) and $Ba_7(BO_3)_3GeO_4Br$ (b)