Supporting Information

$NaBa_4(GaB_4O_9)_2X_3$ (X=Cl, Br) with NLO-active GaO_4 tetrahedral unit: experimental and ab initio studies

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Table S1a. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for $NaBa_4(GaB_4O_9)_2Cl_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Ba(1)	2286(1)	4850(1)	1681(2)	17(1)
Ga(1)	1998(1)	8002(1)	1742(2)	8(1)
Na(1)	5000	5000	5080(20)	95(4)
B(1)	2655(7)	5389(7)	7092(13)	17(2)
B(2)	2628(7)	7372(7)	8000(20)	6(2)
B(3)	3147(7)	6853(7)	4707(15)	12(2)
Cl(1)	0	5000	4375(13)	83(2)
Cl(2)	5000	5000	1035(8)	34(1)
O(1)	3008(4)	6992(4)	2667(9)	11(1)
O(2)	2947(4)	5656(4)	5223(8)	14(1)
O(3)	1928(4)	8072(4)	9085(9)	11(1)
O(5)	2404(4)	6198(4)	8434(7)	20(1)
O(6)	2407(5)	9331(4)	2767(8)	23(1)
O(7)	2436(5)	7564(5)	5907(12)	9(2)

Table S1b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $NaBa_4(GaB_4O_9)_2Br_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Ba(1)	4832(1)	2319(1)	5128(2)	16(1)
Ga(1)	2992(1)	2992(1)	10197(4)	9(1)
Na(1)	5000	5000	8650(30)	66(5)
B(1)	5364(10)	2669(10)	10530(20)	16(3)
B(2)	2319(11)	2319(11)	6500(30)	12(4)
B(3)	1844(12)	1844(12)	13160(30)	16(4)
Br(1)	5000	5000	4270(7)	39(1)
Br(2)	5000	0	2819(10)	89(1)
O(1)	2530(6)	2530(6)	14333(18)	6(2)
O(2)	6173(7)	2422(7)	1867(13)	19(2)
O(3)	5647(6)	2953(6)	8653(13)	12(2)
O(4)	1977(6)	1977(6)	11113(18)	13(2)
O(5)	3042(6)	3042(6)	7552(16)	8(2)
O(6)	4325(7)	2604(7)	11175(14)	19(2)

Table S2a. Selected bond distances (Å) and angles (deg) for $NaBa_4(GaB_4O_9)_2Cl_3$.

Ba(1)-O(2)	2.730(5)	O(1)-Ba(1)-O(7)#3	154.87(16)
Ba(1)-O(5)#1	2.757(5)	O(2)-Ba(1)-O(3)#3	70.33(16)
Ba(1)-O(6)#2	2.772(6)	O(5)#1-Ba(1)-O(3)#3	152.50(14)
Ba(1)-O(1)	2.818(3)	O(6)#2-Ba(1)-O(3)#3	109.76(15)
Ba(1)-O(7)#3	2.837(5)	O(1)-Ba(1)-O(3)#3	116.76(19)
Ba(1)-O(3)#3	2.869(4)	O(7)#3-Ba(1)-O(3)#3	48.40(19)
Ba(1)-Cl(1)#4	3.189(4)	O(2)-Ba(1)-Cl(1)#4	132.21(16)
Ba(1)-O(5)#3	3.258(5)	O(5)#1-Ba(1)-Cl(1)#4	67.28(15)
Ba(1)-Cl(2)	3.3192(9)	O(6)#2-Ba(1)-Cl(1)#4	69.68(17)
Ba(1)-Cl(1)	3.328(5)	O(1)-Ba(1)-Cl(1)#4	109.55(12)
Ga(1)-O(3)#1	1.820(6)	O(7)#3-Ba(1)-Cl(1)#4	93.80(12)
Ga(1)-O(6)	1.823(5)	O(3)#3-Ba(1)-Cl(1)#4	127.84(13)
Ga(1)-O(6)#5	1.823(5)	O(2)-Ba(1)-O(5)#3	95.27(14)
Ga(1)-O(1)	1.840(6)	O(5)#1-Ba(1)-O(5)#3	144.33(18)
Na(1)-O(2)#6	2.611(5)	O(6)#2-Ba(1)-O(5)#3	102.68(14)
Na(1)-O(2)#7	2.611(5)	O(1)-Ba(1)-O(5)#3	143.90(16)
Na(1)-O(2)	2.611(5)	O(7)#3-Ba(1)-O(5)#3	45.54(19)
Na(1)-O(2)#5	2.611(5)	O(3)#3-Ba(1)-O(5)#3	45.22(15)
Na(1)-Cl(2)	2.764(17)	Cl(1)#4-Ba(1)-O(5)#3	83.03(11)
Cl(1)-Ba(1)#9	3.189(4)	O(2)-Ba(1)-Cl(2)	78.95(14)
Cl(1)-Ba(1)#10	3.189(4)	O(5)#1-Ba(1)-Cl(2)	79.00(14)
Cl(1)-Ba(1)#11	3.328(5)	O(6)#2-Ba(1)-Cl(2)	75.60(15)
Cl(2)-Ba(1)#6	3.3192(9)	O(1)-Ba(1)-Cl(2)	71.01(12)
Cl(2)-Ba(1)#5	3.3192(9)	O(7)#3-Ba(1)-Cl(2)	84.93(13)
Cl(2)-Ba(1)#7	3.3192(9)	O(3)#3-Ba(1)-Cl(2)	77.82(12)
B(1)-O(6)#12	1.363(10)	Cl(1)#4-Ba(1)-Cl(2)	142.16(16)
B(1)-O(2)	1.364(10)	O(5)#3-Ba(1)-Cl(2)	119.66(10)
B(1)-O(5)	1.375(9)	O(2)-Ba(1)-Cl(1)	74.55(16)
B(2)-O(3)	1.409(15)	O(5)#1-Ba(1)-Cl(1)	117.11(14)
B(2)-O(7)	1.466(14)	O(6)#2-Ba(1)-Cl(1)	131.11(16)
B(2)-O(5)	1.477(8)	O(1)-Ba(1)-Cl(1)	94.31(12)
B(2)-O(5)#5	1.477(8)	O(7)#3-Ba(1)-Cl(1)	104.76(16)
B(3)-O(1)	1.414(12)	O(3)#3-Ba(1)-Cl(1)	90.01(12)
B(3)-O(7)	1.466(12)	Cl(1)#4-Ba(1)-Cl(1)	63.184(16)
B(3)-O(2)#5	1.511(9)	O(5)#3-Ba(1)-Cl(1)	60.41(9)
B(3)-O(2)	1.511(9)	Cl(2)-Ba(1)-Cl(1)	153.28(15)
O(1)-Ba(1)#5	2.818(3)	O(3)#1-Ga(1)-O(6)	110.8(2)
O(3)-Ga(1)#13	1.820(6)	O(3)#1-Ga(1)-O(6)#5	110.8(2)
O(3)-Ba(1)#10	2.869(4)	O(6)-Ga(1)-O(6)#5	109.3(4)
O(3)-Ba(1)#14	2.869(4)	O(3)#1-Ga(1)-O(1)	113.9(3)
O(5)-Ba(1)#13	2.757(5)	O(6)-Ga(1)-O(1)	105.9(2)

O(5)-Ba(1)#10	3.258(5)	O(6)#5-Ga(1)-O(1)	105.9(2)
O(6)-B(1)#15	1.363(10)	O(2)#6-Na(1)-O(2)#7	54.5(2)
O(6)-Ba(1)#14	2.772(6)	O(2)#6-Na(1)-O(2)	125.3(2)
O(7)-Ba(1)#10	2.837(5)	O(2)#7-Na(1)-O(2)	175.7(8)
O(7)-Ba(1)#14	2.837(5)	O(2)#6-Na(1)-O(2)#5	175.7(8)
O(2)-Ba(1)-O(5)#1	119.11(15)	O(2)#7-Na(1)-O(2)#5	125.3(2)
O(2)-Ba(1)-O(6)#2	153.78(16)	O(2)-Na(1)-O(2)#5	54.5(2)
O(5)#1-Ba(1)-O(6)#2	49.52(15)	O(2)#6-Na(1)-Cl(2)	92.1(4)
O(2)-Ba(1)-O(1)	50.81(17)	O(2)#7-Na(1)-Cl(2)	92.1(4)
O(5)#1-Ba(1)-O(1)	68.39(16)	O(2)-Na(1)-Cl(2)	92.1(4)
O(6)#2-Ba(1)-O(1)	113.41(17)	O(2)#5-Na(1)-Cl(2)	92.1(4)
O(2)-Ba(1)-O(7)#3	118.64(18)	O(6)#12-B(1)-O(2)	123.6(7)
O(5)#1-Ba(1)-O(7)#3	114.9(2)	O(6)#12-B(1)-O(5)	115.5(7)
O(6)#2-Ba(1)-O(7)#3	65.39(19)	O(2)-B(1)-O(5)	120.9(7)
O(1)-B(3)-O(7)	114.4(9)	O(3)-B(2)-O(7)	108.9(8)
O(1)-B(3)-O(2)#5	109.0(5)	O(3)-B(2)-O(5)	111.3(7)
O(7)-B(3)-O(2)#5	109.7(5)	O(7)-B(2)-O(5)	108.6(7)
O(1)-B(3)-O(2)	109.0(5)	O(3)-B(2)-O(5)#5	111.3(7)
O(7)-B(3)-O(2)	109.7(5)	O(7)-B(2)-O(5)#5	108.6(7)
O(2)#5-B(3)-O(2)	104.6(8)	O(5)-B(2)-O(5)#5	108.1(9)

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

Table S2b. Selected bond distances (Å) and angles (deg) for $NaBa_4(GaB_4O_9)_2Br_3$.

Ba(1)-O(3)	2.750(11)	O(6)#1-Ba(1)-O(4)#2	113.3(3)
Ba(1)-O(2)	2.800(11)	O(3)-Ba(1)-O(1)#1	120.0(3)
Ba(1)-O(6)#1	2.824(12)	O(2)-Ba(1)-O(1)#1	115.0(3)
Ba(1)-O(4)#2	2.870(7)	O(6)#1-Ba(1)-O(1)#1	65.8(3)
Ba(1)-O(1)#1	2.906(8)	O(4)#2-Ba(1)-O(1)#1	157.0(2)
Ba(1)-O(5)	2.913(8)	O(3)-Ba(1)-O(5)	71.4(3)
Ba(1)-Br(2)	3.284(5)	O(2)-Ba(1)-O(5)	153.9(2)
Ba(1)-Br(1)	3.369(5)	O(6)#1-Ba(1)-O(5)	110.5(3)
Ba(1)-Br(2)#3	3.420(6)	O(4)#2-Ba(1)-O(5)	118.1(3)
Ga(1)-O(5)	1.830(12)	O(1)#1-Ba(1)-O(5)	48.7(3)
Ga(1)-O(6)	1.842(9)	O(3)-Ba(1)-Br(2)	130.97(19)
Ga(1)-O(6)#4	1.842(9)	O(2)-Ba(1)-Br(2)	67.1(2)
Ga(1)-O(4)	1.883(11)	O(6)#1-Ba(1)-Br(2)	69.7(2)
Na(1)-O(3)#6	2.650(8)	O(4)#2-Ba(1)-Br(2)	108.7(2)
Na(1)-O(3)#4	2.650(8)	O(1)#1-Ba(1)-Br(2)	92.76(18)
Na(1)-O(3)	2.650(8)	O(5)-Ba(1)-Br(2)	126.5(2)
Na(1)-O(3)#7	2.650(8)	O(3)-Ba(1)-Br(1)	81.57(19)
Na(1)-Br(1)	3.03(2)	O(2)-Ba(1)-Br(1)	77.14(18)
B(1)-O(6)	1.361(16)	O(6)#1-Ba(1)-Br(1)	73.81(18)
B(1)-O(3)	1.387(18)	O(4)#2-Ba(1)-Br(1)	71.76(19)
B(1)-O(2)#8	1.396(16)	O(1)#1-Ba(1)-Br(1)	86.51(17)
B(2)-O(5)	1.46(2)	O(5)-Ba(1)-Br(1)	81.20(19)
B(2)-O(2)#5	1.473(14)	Br(2)-Ba(1)-Br(1)	140.10(17)
B(2)-O(2)#3	1.473(14)	O(3)-Ba(1)-Br(2)#3	74.6(2)
B(2)-O(1)#1	1.54(3)	O(2)-Ba(1)-Br(2)#3	116.1(2)
B(3)-O(4)	1.43(2)	O(6)#1-Ba(1)-Br(2)#3	130.06(19)
B(3)-O(1)	1.45(2)	O(4)#2-Ba(1)-Br(2)#3	93.9(2)
B(3)-O(3)#5	1.537(14)	O(1)#1-Ba(1)-Br(2)#3	103.7(2)
B(3)-O(3)#3	1.537(14)	O(5)-Ba(1)-Br(2)#3	89.4(2)
Br(1)-Ba(1)#7	3.369(5)	Br(2)-Ba(1)-Br(2)#3	62.01(15)
Br(1)-Ba(1)#6	3.369(5)	Br(1)-Ba(1)-Br(2)#3	156.10(14)
Br(1)-Ba(1)#4	3.369(5)	O(5)-Ga(1)-O(6)	110.2(4)
Br(2)-Ba(1)#9	3.284(5)	O(5)-Ga(1)-O(6)#4	110.2(4)
Br(2)-Ba(1)#10	3.420(6)	O(6)-Ga(1)-O(6)#4	109.3(6)
Br(2)-Ba(1)#2	3.420(6)	O(5)-Ga(1)-O(4)	112.3(5)
O(1)-B(2)#8	1.54(3)	O(6)-Ga(1)-O(4)	107.3(3)
O(1)-Ba(1)#11	2.906(8)	O(6)#4-Ga(1)-O(4)	107.3(3)
O(1)-Ba(1)#8	2.906(8)	O(3)#6-Na(1)-O(3)#4	54.9(3)
O(2)-B(1)#1	1.396(16)	O(3)#6-Na(1)-O(3)	180.0(11)
O(2)-B(2)#2	1.473(14)	O(3)#4-Na(1)-O(3)	125.1(3)
O(3)-B(3)#2	1.537(14)	O(3)#6-Na(1)-O(3)#7	125.1(3)

O(4)-Ba(1)#3	2.870(7)	O(3)#4-Na(1)-O(3)#7	180.0(11)
O(4)-Ba(1)#5	2.870(7)	O(3)-Na(1)-O(3)#7	54.9(3)
O(5)-Ba(1)#4	2.913(8)	O(3)#6-Na(1)-Br(1)	90.0(5)
O(6)-Ba(1)#8	2.824(12)	O(3)#4-Na(1)-Br(1)	90.0(5)
O(3)-Ba(1)-O(2)	118.9(3)	O(3)-Na(1)-Br(1)	90.0(5)
O(3)-Ba(1)-O(6)#1	154.5(2)	O(3)#7-Na(1)-Br(1)	90.0(5)
O(2)-Ba(1)-O(6)#1	49.2(3)	O(6)-B(1)-O(3)	124.0(11)
O(3)-Ba(1)-O(4)#2	50.6(3)	O(6)-B(1)-O(2)#8	116.4(12)
O(2)-Ba(1)-O(4)#2	68.4(3)	O(3)-B(1)-O(2)#8	119.6(11)
O(4)-B(3)-O(1)	114.8(15)	O(5)-B(2)-O(2)#5	111.6(10)
O(4)-B(3)-O(3)#5	108.0(10)	O(5)-B(2)-O(2)#3	111.6(10)
O(1)-B(3)-O(3)#5	110.1(10)	O(2)#5-B(2)-O(2)#3	112.8(15)
O(4)-B(3)-O(3)#3	108.0(10)	O(5)-B(2)-O(1)#1	106.2(13)
O(1)-B(3)-O(3)#3	110.1(10)	O(2)#5-B(2)-O(1)#1	107.1(11)
O(3)#5-B(3)-O(3)#3	105.3(13)	O(2)#3-B(2)-O(1)#1	107.1(11)

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

Table S3. Assignments of the infrared absorption peaks for $NaBa_4(GaB_4O_9)_2Cl_3$ and $NaBa_4(GaB_4O_9)_2Br_3$.

Mode description	$NaBa_4(GaB_4O_9)_2Cl_3$ (cm^{-1})	$NaBa_4(GaB_5O_9)_2Br_3$ (cm^{-1})
Asymmetric stretching of B_3–O	1371, 1313	1380, 1313
Asymmetric stretching of B_4–O	1146, 1038	1130, 1033
Symmetric stretching of B_3–O	973	975
Symmetric stretching of B_4–O	847	874
out-of-plane bending of B_3–O	702	705
Bending of B_4–O and B_3–O	596	601
stretching-bending vibrations of GaO_4 units	516, 470	517, 472

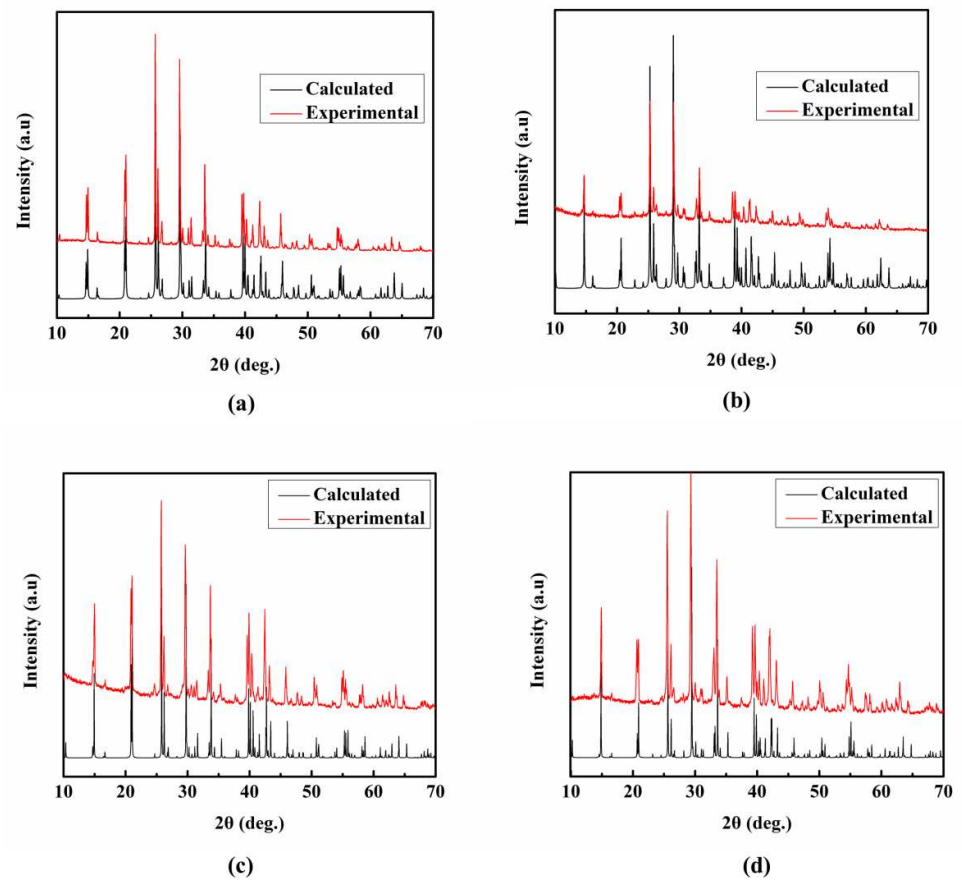


Figure S1. Experimental and calculated XRD patterns of $NaBa_4(GaB_4O_9)_2Cl_3$ (a), $NaBa_4(GaB_4O_9)_2Br_3$ (b), $NaBa_4(AlB_4O_9)_2Cl_3$ (c) and $NaBa_4(AlB_4O_9)_2Br_3$ (d)

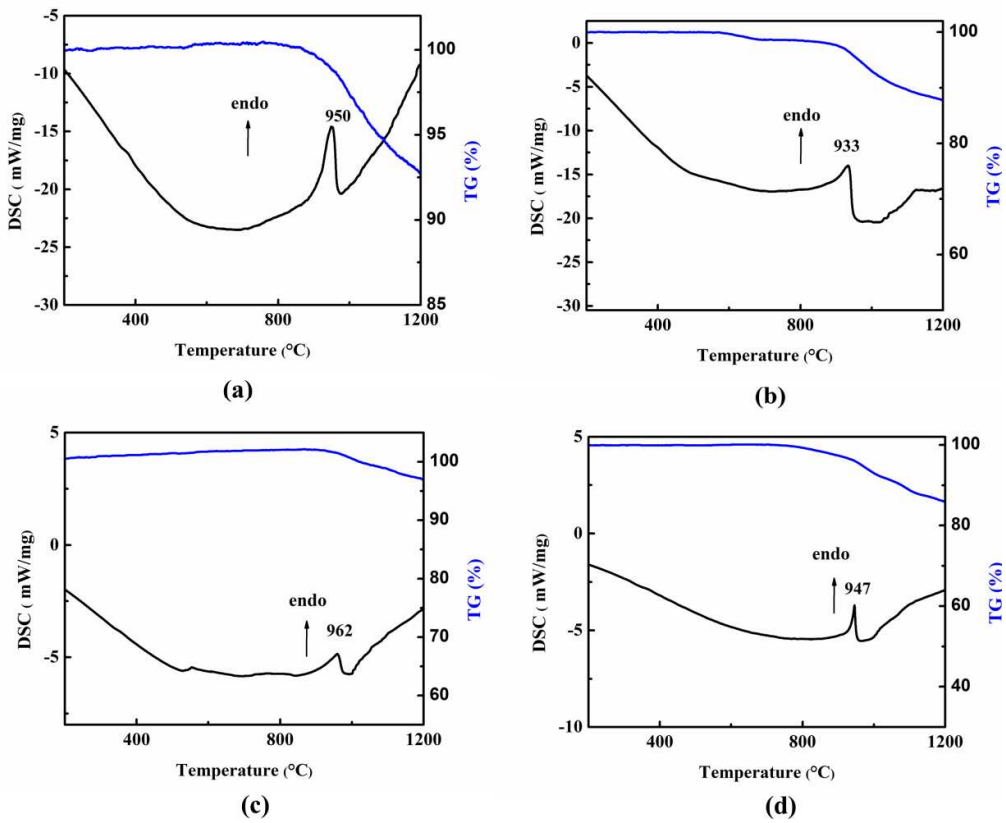


Figure S2. TG-DSC curves of $NaBa_4(GaB_4O_9)_2Cl_3$ (a), $NaBa_4(GaB_4O_9)_2Br_3$ (b), $NaBa_4(AlB_4O_9)_2Cl_3$ (c) and $NaBa_4(AlB_4O_9)_2Br_3$ (d)

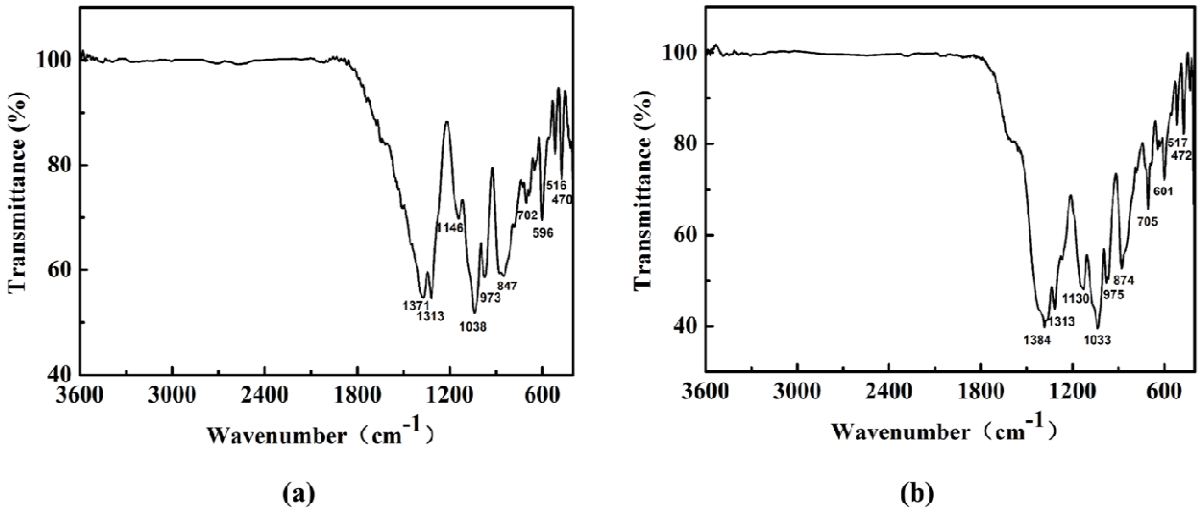


Figure S3. IR spectra of $NaBa_4(GaB_4O_9)_2Cl_3$ (a) and $NaBa_4(GaB_4O_9)_2Br_3$ (b)

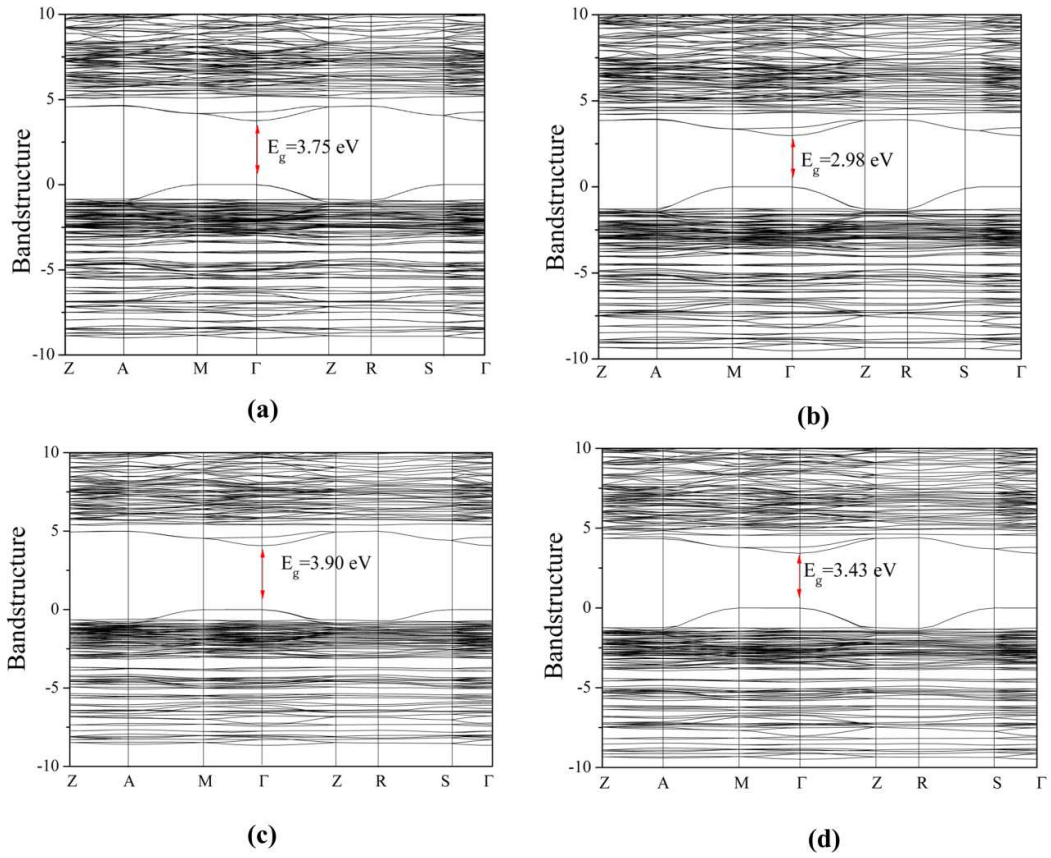
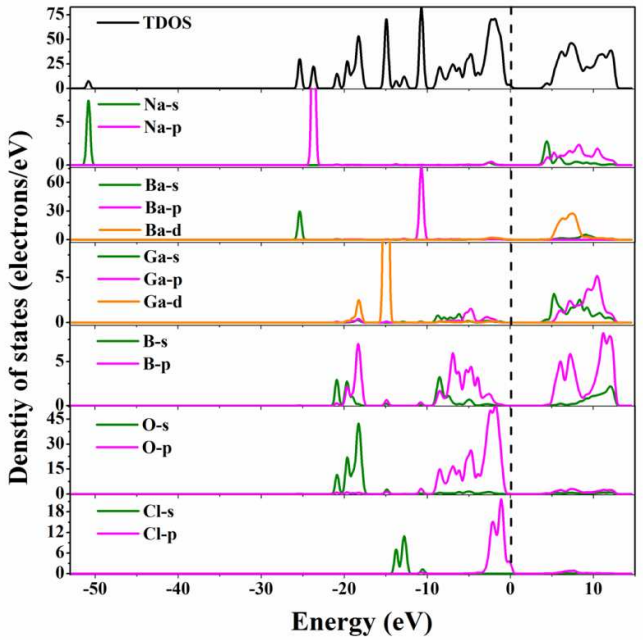
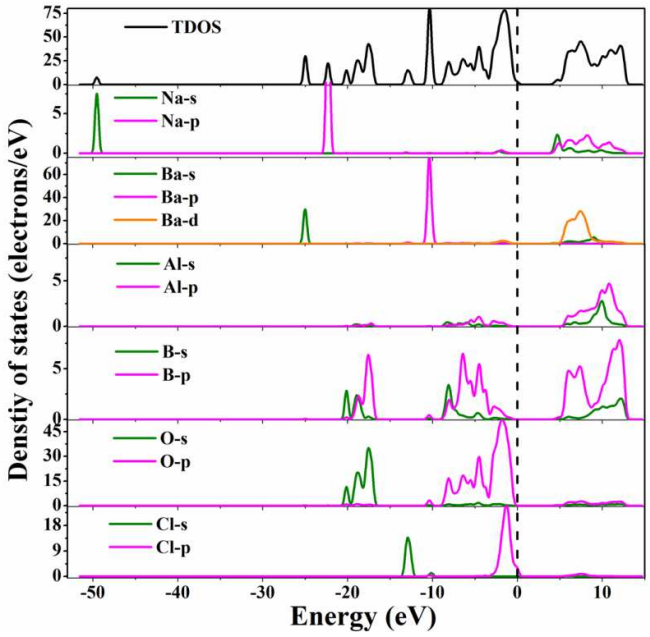


Figure S4. Band structures of $NaBa_4(GaB_4O_9)_2Cl_3$ (a), $NaBa_4(GaB_4O_9)_2Br_3$ (b), $NaBa_4(AlB_4O_9)_2Cl_3$ (c) and $NaBa_4(AlB_4O_9)_2Br_3$ (d)



(a)



(b)

Figure S5. DOS of (a) $NaBa_4(GaB_4O_9)_2Cl_3$ and (b) $NaBa_4(AlB_4O_9)_2Cl_3$.

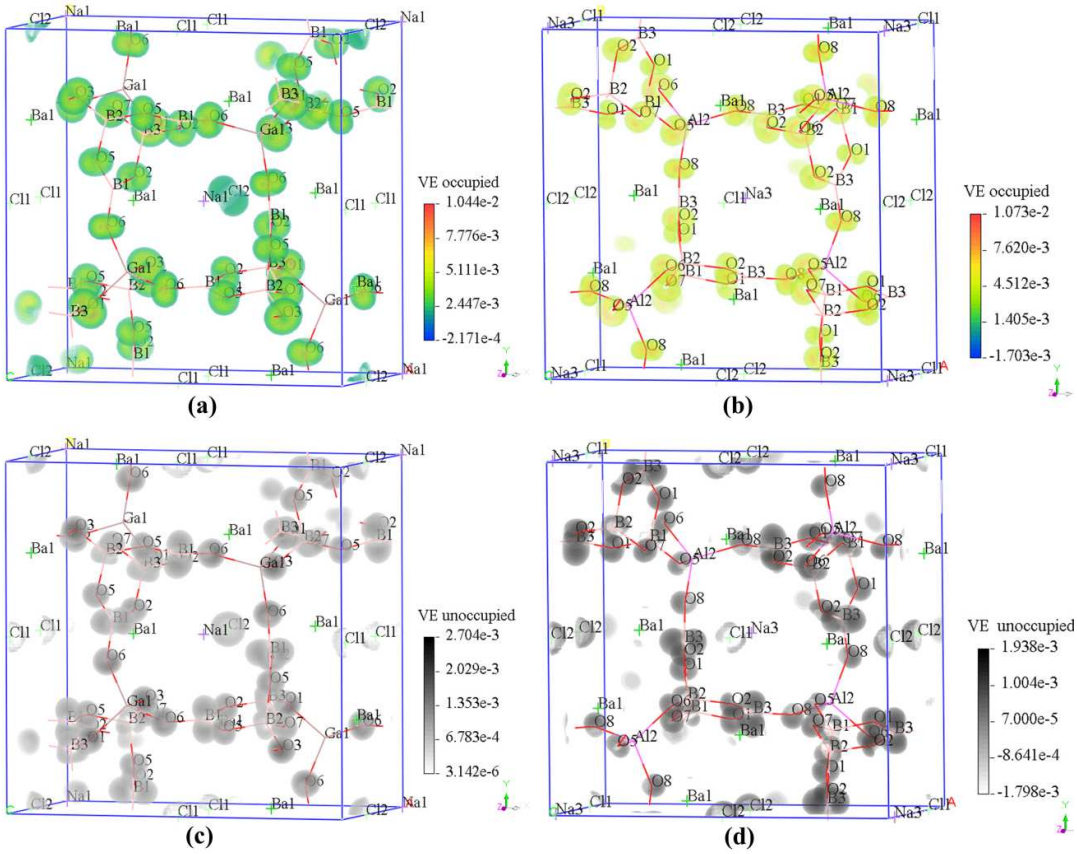


Figure S6. The occupied SHG densities of (a) $NaBa_4(GaB_4O_9)_2Cl_3$ and (b) $NaBa_4(AlB_4O_9)_2Cl_3$. The unoccupied SHG densities of (c) $NaBa_4(GaB_4O_9)_2Cl_3$ and (d) $NaBa_4(AlB_4O_9)_2Cl_3$.