Supporting Information

Effect of Cation Substitution on Structural Transition: Synthesis, Characterization and Theoretical Studies of $NaCa_4B_3O_9$, $NaCaBO_3$, $NaSrBO_3$ and $Li_4CaB_2O_6$

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Fig. S1. X-ray powder diffraction pattern of compounds about experimental and calculated XRD patterns and sample after melting XRD patterns: (a) $NaCa_4B_3O_9$ (b) $NaCaBO_3$ (c) $NaSrBO_3$ and (d) $Li_4CaB_2O_6$.

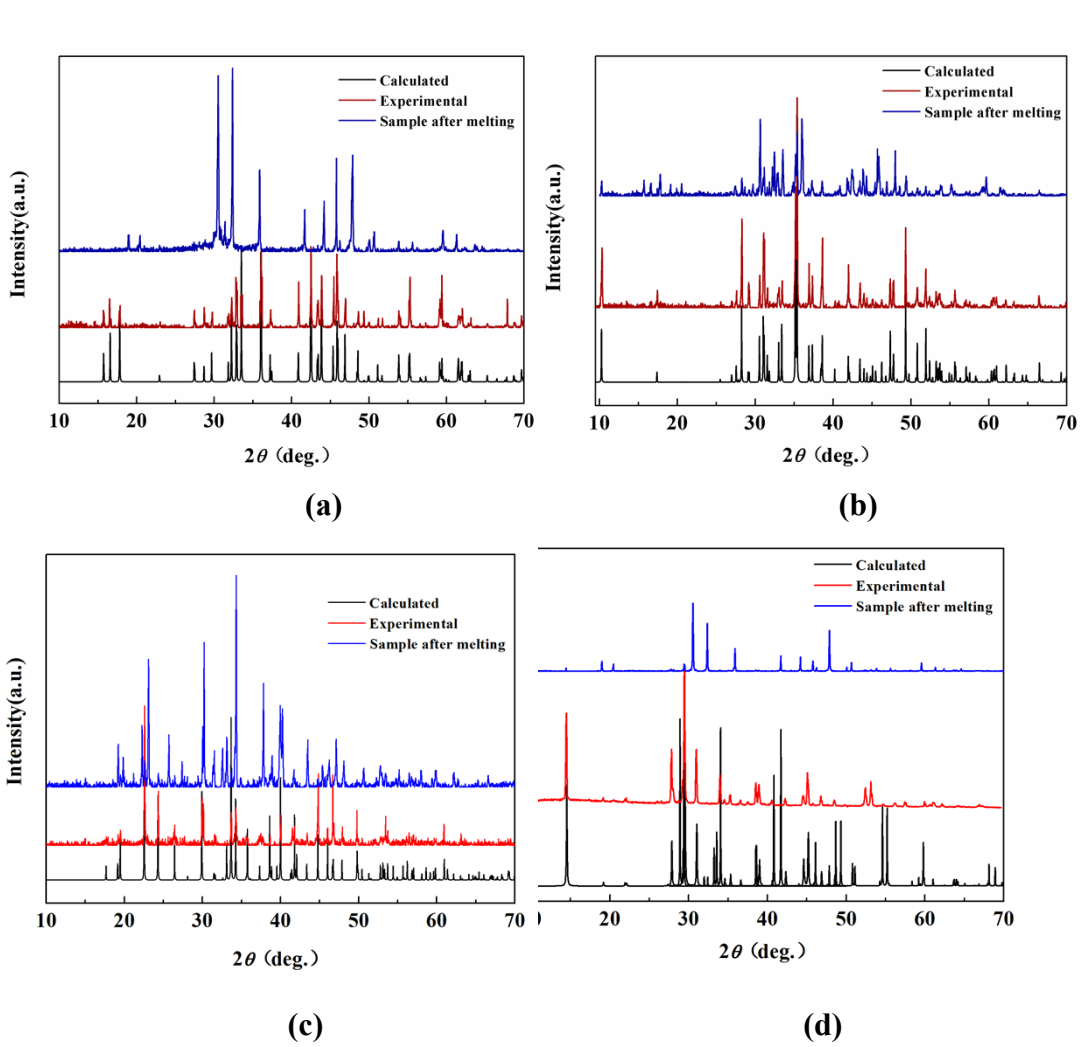


Fig. S2. The crystal structure of $NaCa_4B_3O_9$. (a) The cation-coordinated environments. (b) The Na-O polyhedra are interconnected via sharing the O atoms into a 1D chain along the *c* axis. (c) 1D Na-O polyhedra chains are bridged by the B(2) atoms forming a 3D framework. (d) The $Ca(1)O_8$, $Ca(2)O_9$ and $Ca(3)O_8$ polyhedra are interconnected by shared oxygen atoms forming the 3D framework.

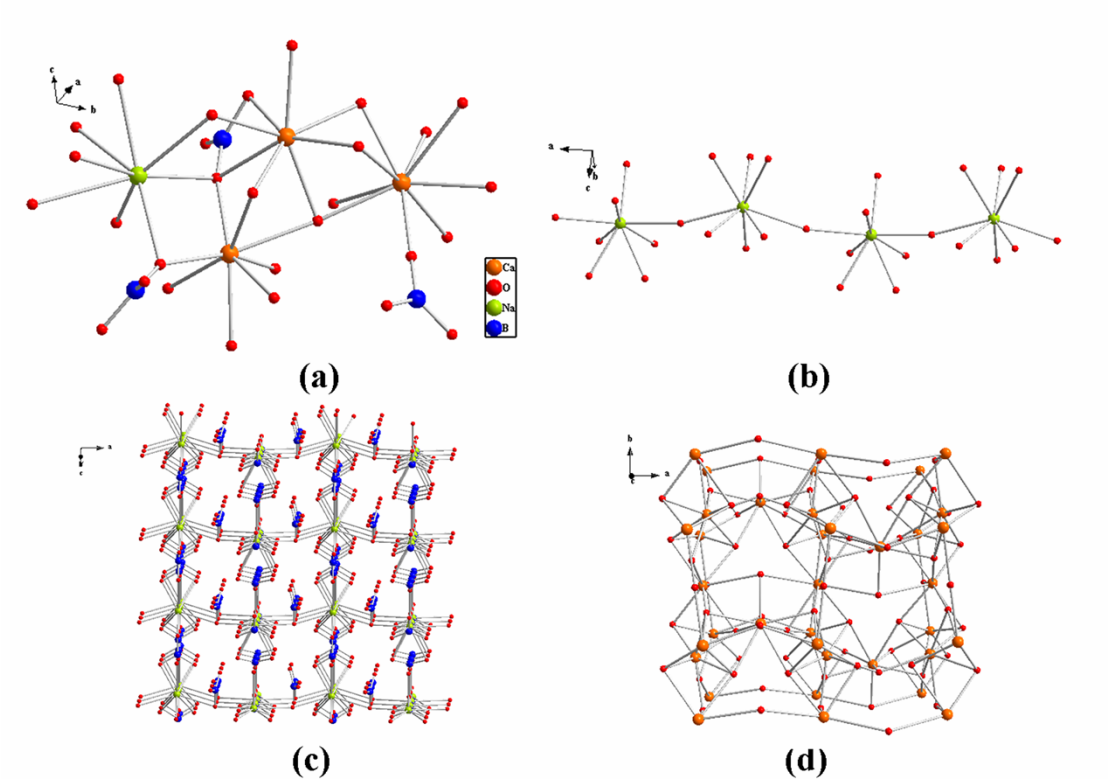


Fig. S3. The crystal structure of $NaCaBO_3$ (a) The cation-coordinated environments. (b) The CaO_6 polyhedra are interconnected via sharing edges into a 1D chain along the *c* axis (c) Ca^{2+} cations and Na^+ cations share the same sites and Ca/NaO_7 polyhedra are interconnected via sharing O atoms and edges into a 3D framework along the *c* axis. (d) The Na-O polyhedra are interconnected via sharing the O atoms into 1D channel along *a* axis.

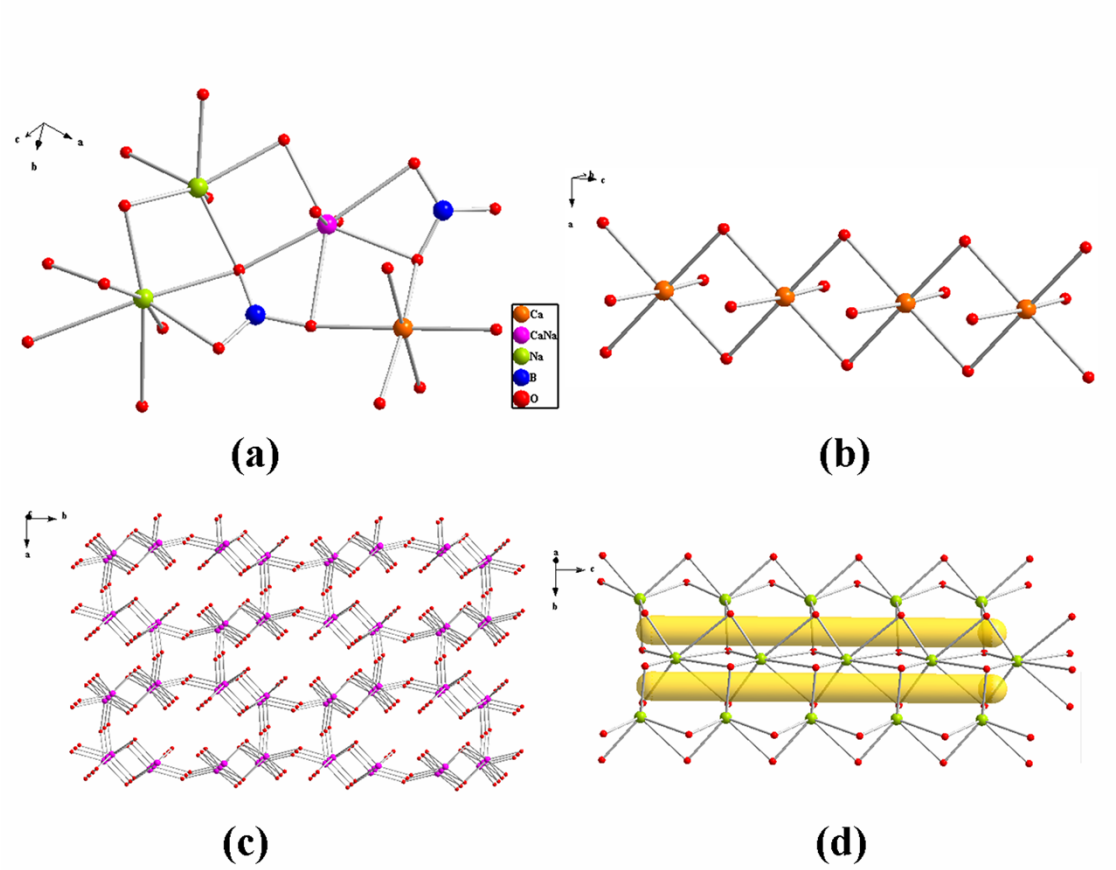


Fig. S4. The crystal structure of $NaSrBO_3$ (a) The cation-coordinated environments. (b) Isolated BO_3 structural building unit along the *c* axis (c) Na^{2+} cations and BO_3 are interconnected via sharing O atoms and edges into a 3D framework along the *c* axis. (d) The Sr-O polyhedra are interconnected via sharing the O atoms into a 3D framework along the *c* axis.

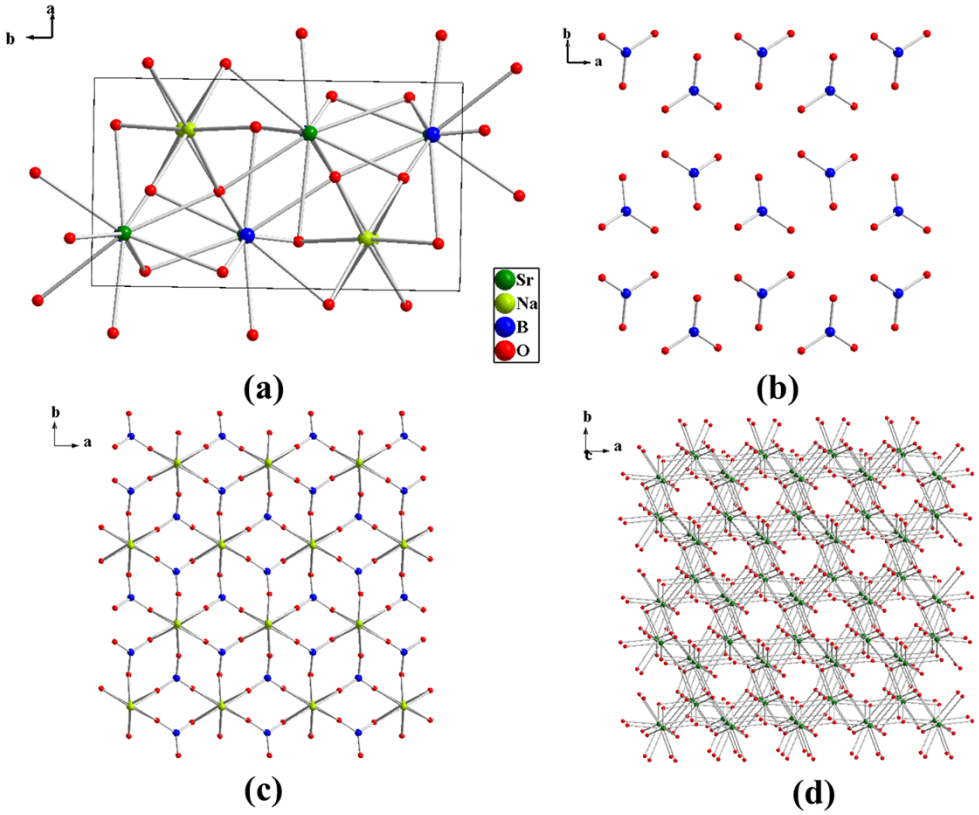


Fig. S5. The crystal structure of $Li_4CaB_2O_6$ (a) The cation-coordinated environments. (b) Isolated BO_3 structural building unit along the *c* axis (c) Li^+ cations and BO_3 are interconnected via sharing O atoms and edges into a 3D framework along the *c* axis. (d) Ca^{2+} cations and BO_3 are interconnected via sharing O atoms and edges into a 3D framework along the *c* axis.

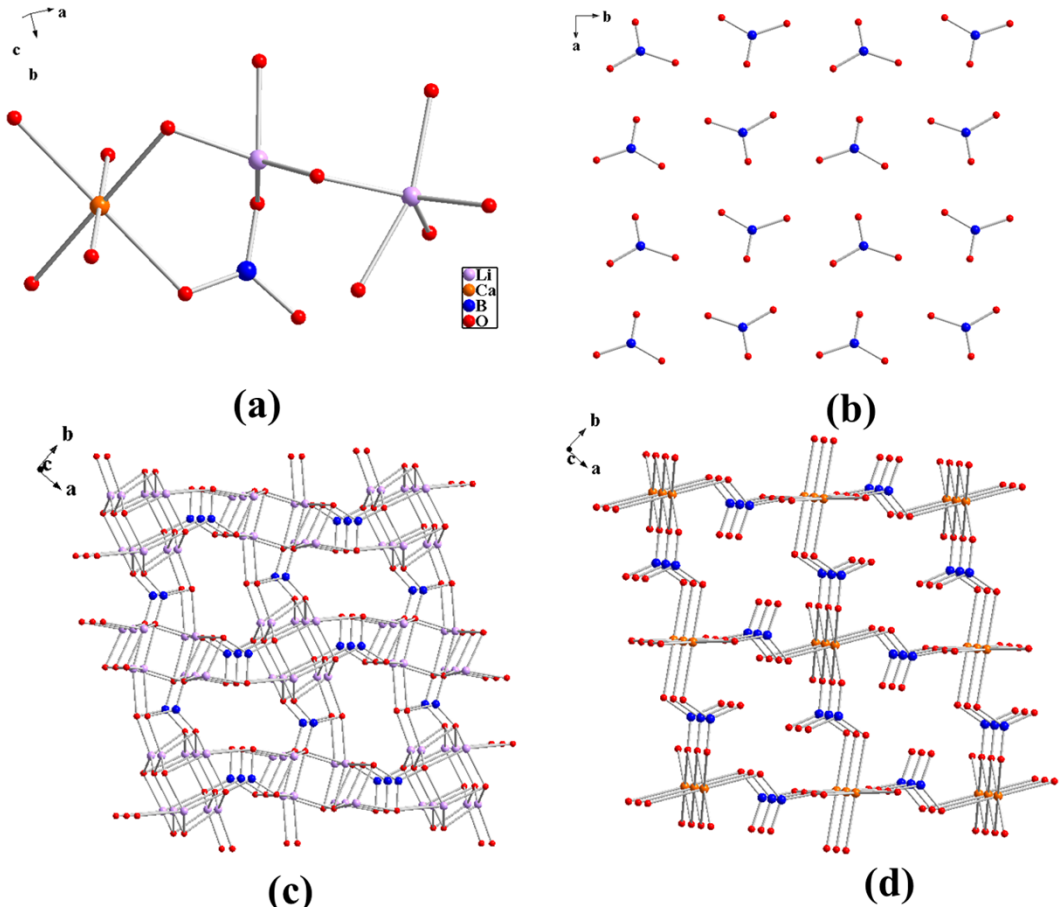
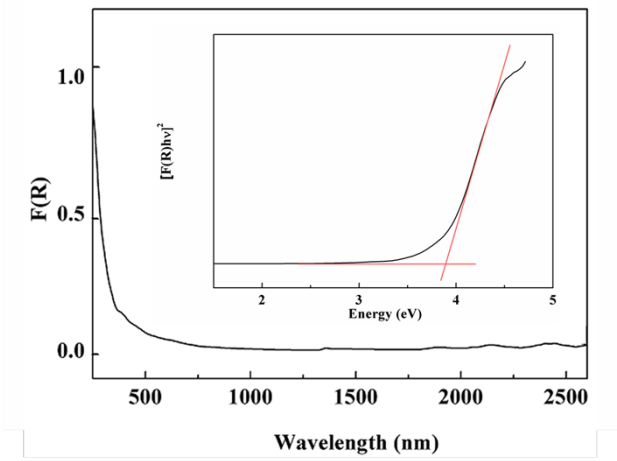
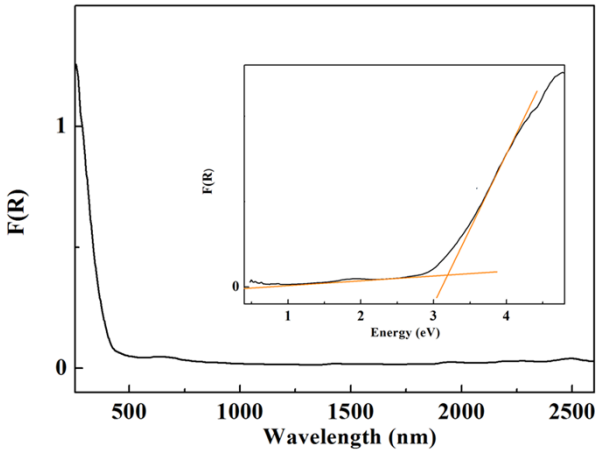


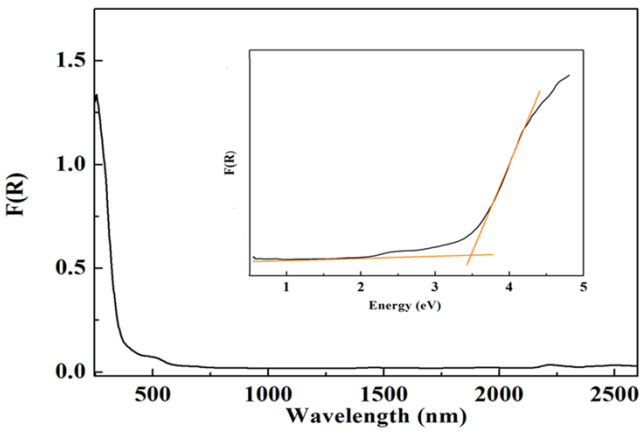
Fig. S6. The diffuse reflectance spectra for (a) $NaCaBO_3$ (b) $NaSrBO_3$ (c) $Li_4CaB_2O_6$.



(a)

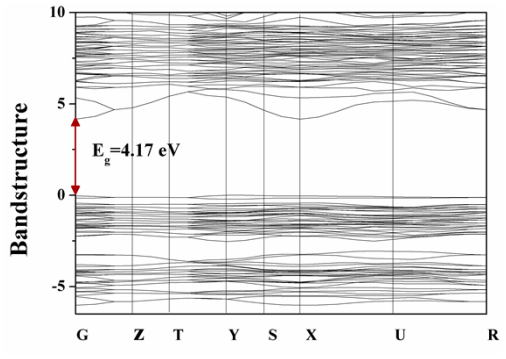


(b)

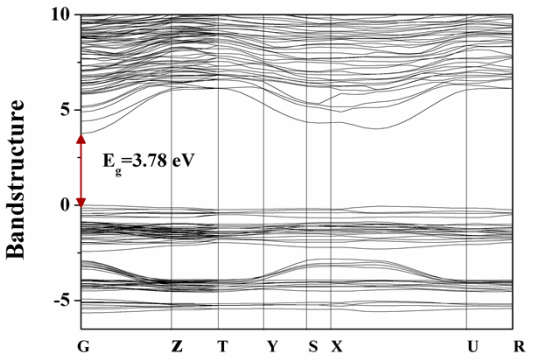


(c)

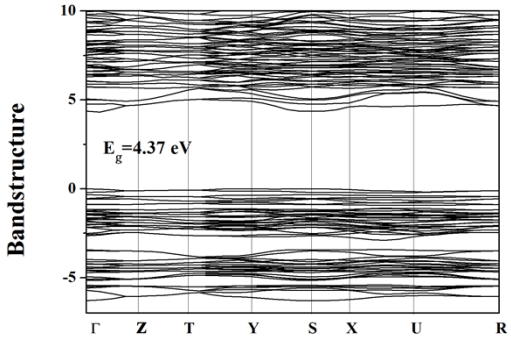
Fig. S7. The calculated band structures of (a) $NaCa_4B_3O_9$ (b) $NaCaBO_3$ (c) $KCa_4B_3O_9$ and (d) $KSr_4B_3O_9$.



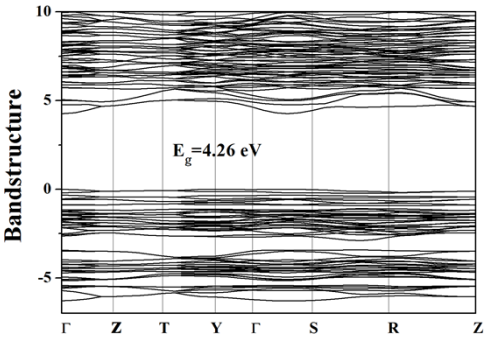
(a)



(b)

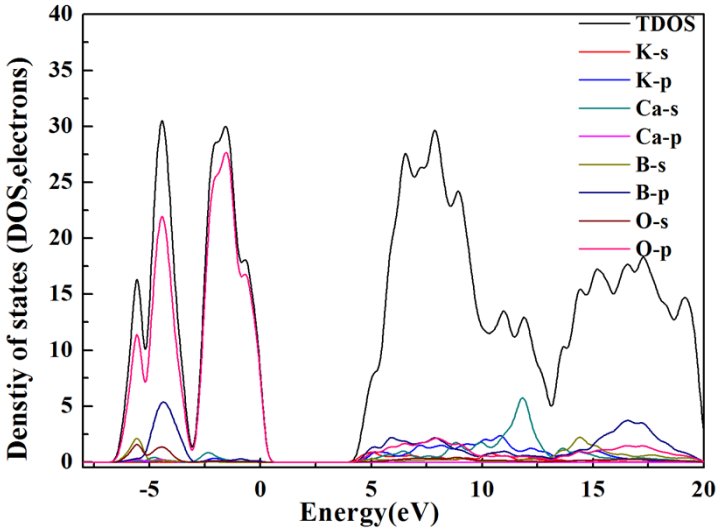


(c)

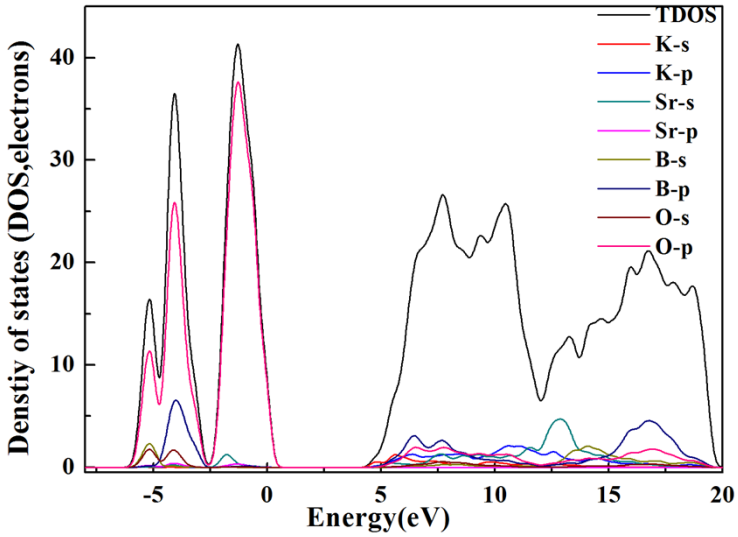


(d)

Fig. S8. The total and partial densities of states of (a) $KCa_4B_3O_9$ and (b) $KSr_4B_3O_9$.



(a)



(b)

Fig. S9. SHG intensities of $NaCa_4B_3O_9$ with commercial KDP as a reference: Oscilloscope traces for the powder of KDP and $NaCa_4B_3O_9$.

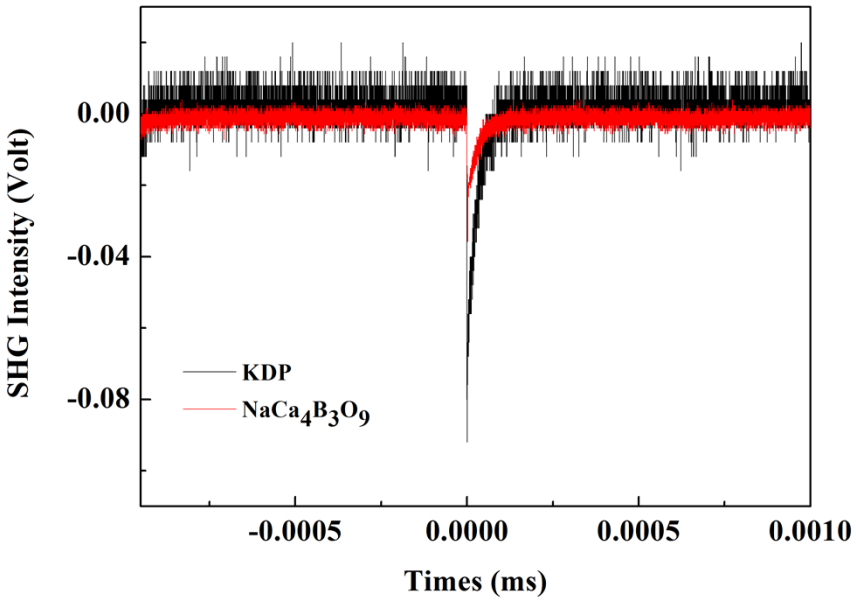
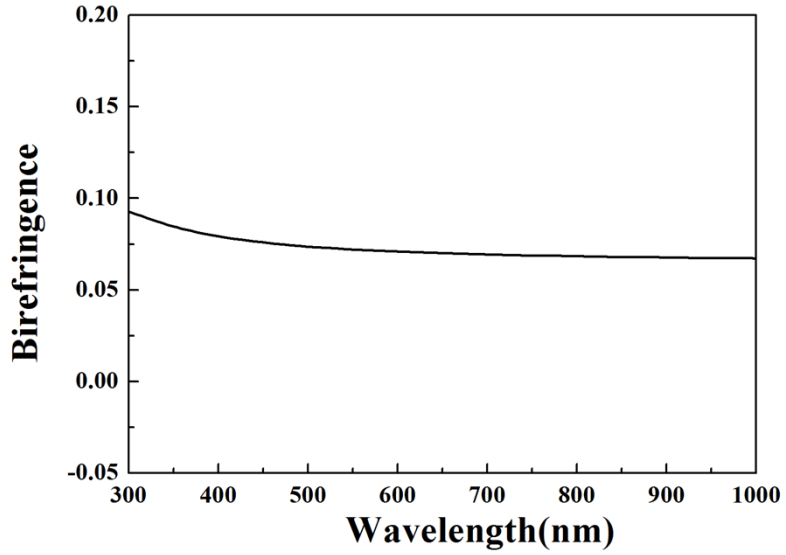
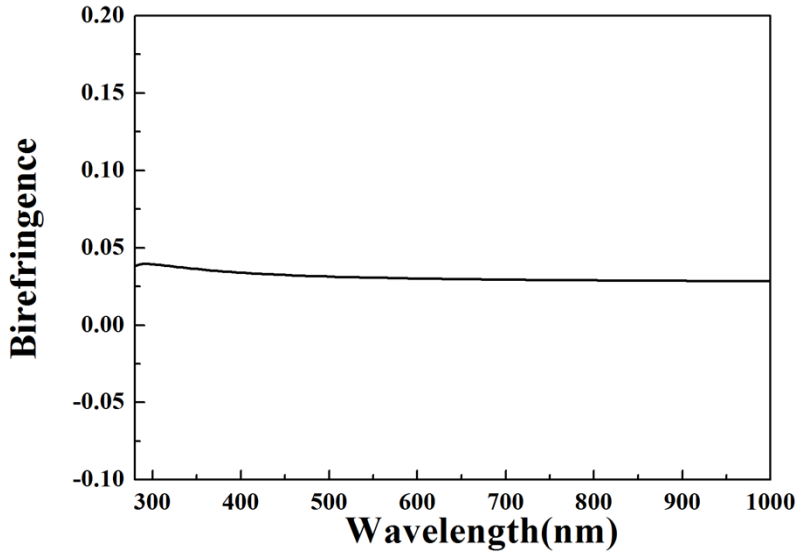


Fig. S10. The wavelength dependence of refractive indices where the direction of the electric field parallels to *a*-axis (n_x) or *c*-axis (n_z) of (a) $KCa_4B_3O_9$ and (b) $KSr_4B_3O_9$.



(a)



(b)

Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $NaCa_4B_3O_9$, $NaCaBO_3$, $NaSrBO_3$ and $Li_4CaB_2O_6$.

			$NaCa_4BO_9$		
Atom	Wyckoff position	x	y	z	U_{eq}
Ca(1)	8c	9724(1)	7141(1)	11087(1)	8(1)
Ca(2)	4a	0	0	9669(1)	12(1)
Ca(3)	4b	7500	6498(1)	7422(1)	8(1)
Na(1)	4b	7500	4249(2)	385(3)	33(1)
B(1)	4b	7500	6715(4)	3161(7)	9(1)
B(2)	4b	7500	3779(4)	4541(8)	12(1)
B(3)	4a	0	0	3924(7)	9(1)
O(1)	4b	7500	6419(2)	1127(5)	12(1)
O(2)	8c	8611(2)	6906(2)	4217(3)	12(1)
O(3)	8c	8611(2)	8385(2)	8622(3)	12(1)
O(4)	4a	0	0	6021(6)	16(1)
O(5)	8c	9714(2)	1021(2)	2877(3)	10(1)
O(6)	4b	7500	4555(3)	6124(5)	23(1)
			$NaCaBO_3$		
Atom	Wyckoff position	x	y	z	U_{eq}
Ca(1)	2a	7500	7500	4664(2)	12(1)
Ca(2)	8g	5337(1)	5985(1)	7620(1)	11(1)
Na(1)	8g	5337(1)	5985(1)	7620(1)	11(1)
Na(2)	2b	2500	7500	6213(5)	19(1)
Na(3)	4e	2500	5829(1)	2076(3)	16(1)
B(1)	4e	7500	5399(2)	3206(7)	9(1)
B(2)	4f	4737(3)	7500	1585(8)	11(1)
O(1)	8g	3680(1)	4973(1)	7643(3)	15(1)
O(2)	8g	4166(1)	6750(1)	2513(4)	19(1)
O(3)	4f	5914(2)	7500	-387(5)	14(1)
O(4)	4e	7500	6121(1)	5274(5)	13(1)
			$NaSrBO_3$		
Atom	Wyckoff position	x	y	z	U_{eq}
Sr(1)	4e	7466(1)	862(1)	2178(1)	9(1)
Na(1)	4e	7554(4)	-2582(2)	321(3)	13(1)
B(1)	4e	7493(11)	4204(6)	2403(9)	9(1)
O(1)	4e	7738(7)	-605(4)	-1890(6)	11(1)

O(2)	4e	9259(7)	3553(4)	1350(6)	10(1)
O(3)	4e	4615(7)	-1571(4)	2166(6)	12(1)
		$Li_4CaB_2O_6$			
Atom	Wyckoff position	x	y	z	U_{eq}
Li(1)	4g	3023(5)	-128(5)	5000	14(1)
Li(2)	4g	5487(5)	1690(6)	0	16(1)
Ca(1)	2a	0	0	10000	9(1)
B(1)	4g	2909(3)	2290(3)	10000	9(1)
O(1)	4g	1424(2)	2525(2)	10000	11(1)
O(2)	4g	3508(2)	733(2)	10000	12(1)
O(3)	4g	1190(2)	-1343(2)	5000	10(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Selected bond distances (Å) and angles (deg) for $NaCa_4B_3O_9$, $NaCaBO_3$, $NaSrBO_3$ and $Li_4CaB_2O_6$.

		$NaCa_4B_3O_9$	
Ca(1)-O(1)	2.5113(11)	B(1)-O(1)	1.360(6)
Ca(1)-O(2)#1	2.4060(19)	B(1)-O(2)	1.387(3)
Ca(1)-O(4)#2	2.4298(7)	B(1)-O(2)#12	1.387(3)
Ca(1)-O(3)	2.435(2)	B(2)-O(6)	1.349(6)
Ca(1)-O(3)#5	2.4940(19)	B(2)-O(3)#11	1.400(3)
Ca(1)-O(5)#3	2.433(2)	B(2)-O(3)#3	1.400(3)
Ca(1)-O(5)#4	2.448(2)	B(3)-O(4)	1.360(6)
Ca(1)-O(2)	2.367(2)	B(3)-O(5)#16	1.370(3)
Ca(2)-O(4)	2.365(4)	B(3)-O(5)#10	1.370(3)
Ca(2)-O(5)	2.396(2)	Na(1)-O(1)	2.491(4)
Ca(2)-O(5)#4	2.396(2)	Na(1)-O(6)	2.784(4)
Ca(2)-O(3)	2.4445(18)	Na(1)-O(3)#2	2.600(3)
Ca(2)-O(3)#4	2.4445(18)	Na(1)-O(3)#14	2.600(3)
Ca(2)-O(2)#7	2.6261(19)	Na(1)-O(4)#2	2.8323(11)
Ca(2)-O(2)#1	2.6261(19)	Na(1)-O(4)#15	2.8323(11)
Ca(2)-O(6)#5	2.8772(15)	Na(1)-O(2)#11	2.992(3)
Ca(2)-O(6)#6	2.8772(15)	Na(1)-O(2)#3	2.992(3)
Ca(3)-O(6)	2.345(3)	Ca(3)-O(5)#11	2.4443(17)
Ca(3)-O(1)	2.404(3)	Ca(3)-O(5)#3	2.4443(17)
Ca(3)-O(2)#9	2.437(2)	Ca(3)-O(3)	2.5552(19)
Ca(3)-O(2)#10	2.437(2)	Ca(3)-O(3)#12	2.5552(19)
O(2)-Ca(1)-O(2)#1	148.58(7)	O(1)-Na(1)-O(3)#2	102.22(10)
O(2)#1-Ca(1)-O(4)#2	110.13(7)	O(1)-Na(1)-O(3)#14	102.22(10)
O(2)-Ca(1)-O(5)#3	132.33(7)	O(3)#2-Na(1)-O(3)#14	54.32(9)
O(2)-Ca(1)-O(4)#2	88.00(9)	O(1)-Na(1)-O(6)	94.03(11)
O(2)#1-Ca(1)-O(5)#3	78.66(7)	O(3)#2-Na(1)-O(6)	147.91(8)
O(4)#2-Ca(1)-O(5)#3	58.08(10)	O(3)#14-Na(1)-O(6)	147.91(8)
O(2)-Ca(1)-O(3)	112.45(6)	O(1)-Na(1)-O(4)#2	71.27(4)
O(2)#1-Ca(1)-O(3)	76.92(6)	O(3)#2-Na(1)-O(4)#2	64.13(7)
O(4)#2-Ca(1)-O(3)	128.24(9)	O(3)#14-Na(1)-O(4)#2	115.14(10)
O(5)#3-Ca(1)-O(3)	74.63(7)	O(6)-Na(1)-O(4)#2	96.17(8)
O(2)-Ca(1)-O(5)#4	79.11(7)	O(1)-Na(1)-O(4)#15	71.27(4)
O(2)#1-Ca(1)-O(5)#4	71.34(7)	O(3)#2-Na(1)-O(4)#15	115.14(10)
O(4)#2-Ca(1)-O(5)#4	144.84(9)	O(3)#14-Na(1)-O(4)#15	64.13(7)
O(5)#3-Ca(1)-O(5)#4	147.64(7)	O(6)-Na(1)-O(4)#15	96.17(8)
O(3)-Ca(1)-O(5)#4	86.82(7)	O(4)#2-Na(1)-O(4)#15	141.20(10)
O(2)-Ca(1)-O(3)#5	76.51(6)	O(1)-Na(1)-O(2)#11	156.14(4)
O(2)#1-Ca(1)-O(3)#5	84.84(7)	O(3)#2-Na(1)-O(2)#11	93.16(8)
O(4)#2-Ca(1)-O(3)#5	71.89(8)	O(3)#14-Na(1)-O(2)#11	72.10(7)
O(5)#3-Ca(1)-O(3)#5	116.32(7)	O(6)-Na(1)-O(2)#11	81.83(9)
O(3)-Ca(1)-O(3)#5	156.56(2)	O(4)#2-Na(1)-O(2)#11	132.43(7)
O(5)#4-Ca(1)-O(3)#5	73.33(6)	O(4)#15-Na(1)-O(2)#11	85.75(5)
O(2)-Ca(1)-O(1)	58.65(8)	O(1)-Na(1)-O(2)#3	156.14(4)

O(2)#1-Ca(1)-O(1)	148.15(9)	O(3)#2-Na(1)-O(2)#3	72.10(7)
O(4)#2-Ca(1)-O(1)	78.11(6)	O(3)#14-Na(1)-O(2)#3	93.16(8)
O(5)#3-Ca(1)-O(1)	80.65(8)	O(6)-Na(1)-O(2)#3	81.83(9)
O(3)-Ca(1)-O(1)	74.41(8)	O(4)#2-Na(1)-O(2)#3	85.75(5)
O(5)#4-Ca(1)-O(1)	120.05(8)	O(4)#15-Na(1)-O(2)#3	132.43(7)
O(3)#5-Ca(1)-O(1)	126.26(8)	O(2)#11-Na(1)-O(2)#3	46.77(8)
O(4)-Ca(2)-O(5)	150.22(5)	O(6)-B(2)-O(3)#11	121.97(18)
O(4)-Ca(2)-O(5)#4	150.22(5)	O(6)-B(2)-O(3)#3	121.97(18)
O(5)-Ca(2)-O(5)#4	59.56(10)	O(3)#11-B(2)-O(3)#3	115.9(4)
O(4)-Ca(2)-O(3)	73.87(5)	O(1)-B(1)-O(2)	121.08(18)
O(5)-Ca(2)-O(3)	121.40(7)	O(1)-B(1)-O(2)#12	121.08(18)
O(5)#4-Ca(2)-O(3)	87.77(7)	O(2)-B(1)-O(2)#12	117.7(4)
O(4)-Ca(2)-O(3)#4	73.87(5)	O(4)-B(3)-O(5)#16	119.7(2)
O(5)-Ca(2)-O(3)#4	87.77(7)	O(4)-B(3)-O(5)#10	119.7(2)
O(5)#4-Ca(2)-O(3)#4	121.40(7)	O(5)#16-B(3)-O(5)#10	120.6(4)
O(5)-Ca(2)-O(2)#7	68.44(6)	O(1)-Ca(3)-O(2)#9	149.21(5)
O(5)#4-Ca(2)-O(2)#7	124.15(7)	O(6)-Ca(3)-O(2)#10	82.53(9)
O(3)-Ca(2)-O(2)#7	103.55(6)	O(1)-Ca(3)-O(2)#10	149.21(5)
O(3)#4-Ca(2)-O(2)#7	72.76(6)	O(2)#9-Ca(3)-O(2)#10	58.33(8)
O(4)-Ca(2)-O(2)#1	83.59(5)	O(6)-Ca(3)-O(5)#11	80.69(5)
O(5)-Ca(2)-O(2)#1	124.15(7)	O(1)-Ca(3)-O(5)#11	82.60(6)
O(5)#4-Ca(2)-O(2)#1	68.44(6)	O(2)#9-Ca(3)-O(5)#11	70.89(7)
O(3)-Ca(2)-O(2)#1	72.76(6)	O(2)#10-Ca(3)-O(5)#11	128.03(7)
O(3)#4-Ca(2)-O(2)#1	103.55(6)	O(6)-Ca(3)-O(5)#3	80.69(5)
O(2)#7-Ca(2)-O(2)#1	167.18(10)	O(1)-Ca(3)-O(5)#3	82.60(6)
O(4)-Ca(2)-O(6)#5	109.15(7)	O(2)#9-Ca(3)-O(5)#3	128.03(7)
O(5)-Ca(2)-O(6)#5	75.52(8)	O(2)#10-Ca(3)-O(5)#3	70.89(7)
O(5)#4-Ca(2)-O(6)#5	71.38(7)	O(5)#11-Ca(3)-O(5)#3	150.96(10)
O(3)-Ca(2)-O(6)#5	141.68(7)	O(6)-Ca(3)-O(3)	152.31(4)
O(3)#4-Ca(2)-O(6)#5	52.96(7)	O(1)-Ca(3)-O(3)	74.13(8)
O(2)#7-Ca(2)-O(6)#5	114.77(7)	O(2)#9-Ca(3)-O(3)	109.22(7)
O(2)#1-Ca(2)-O(6)#5	69.77(7)	O(2)#10-Ca(3)-O(3)	82.91(7)
B(3)#8-Ca(2)-O(6)#5	70.85(7)	O(5)#11-Ca(3)-O(3)	126.56(7)
O(4)-Ca(2)-O(6)#6	109.15(7)	O(5)#3-Ca(3)-O(3)	72.32(6)
O(5)-Ca(2)-O(6)#6	71.38(7)	O(6)-Ca(3)-O(3)#12	152.31(4)
O(5)#4-Ca(2)-O(6)#6	75.52(8)	O(1)-Ca(3)-O(3)#12	74.13(8)
O(3)-Ca(2)-O(6)#6	52.96(7)	O(2)#9-Ca(3)-O(3)#12	82.91(7)
O(3)#4-Ca(2)-O(6)#6	141.68(7)	O(2)#10-Ca(3)-O(3)#12	109.22(7)
O(2)#7-Ca(2)-O(6)#6	69.77(7)	O(5)#11-Ca(3)-O(3)#12	72.32(6)
O(2)#1-Ca(2)-O(6)#6	114.77(7)	O(5)#3-Ca(3)-O(3)#12	126.56(7)
O(6)#5-Ca(2)-O(6)#6	141.71(14)	O(3)-Ca(3)-O(3)#12	55.36(8)

Note. Symmetry transformations used to generate equivalent atoms:

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

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

$NaCaBO_3$

Ca(1)-O(4)	2.2266(17)	Ca(2)-O(1)	2.3443(13)
Ca(1)-O(4)#1	2.2266(17)	Ca(2)-O(4)	2.3618(9)
Ca(1)-O(3)#2	2.3654(18)	Ca(2)-O(2)	2.4189(14)
Ca(1)-O(3)#3	2.3654(18)	Ca(2)-O(1)#7	2.4708(14)
Ca(1)-O(3)	2.3915(18)	Ca(2)-O(2)#4	2.4723(15)
Ca(1)-O(3)#1	2.3915(18)	Ca(2)-O(1)#8	2.5973(13)
Na(2)-O(2)#9	2.4502(16)	Ca(2)-O(3)#3	2.6010(9)
Na(2)-O(2)	2.4502(16)	B(1)-O(4)	1.368(3)
Na(2)-O(2)#10	2.4502(16)	B(1)-O(1)#8	1.3750(18)
Na(2)-O(2)#11	2.4502(16)	B(1)-O(1)#14	1.3750(18)
Na(3)-O(2)	2.2570(15)	B(2)-O(2)	1.3785(19)
Na(3)-O(2)#9	2.2570(15)	B(2)-O(2)#10	1.3785(19)
Na(3)-O(1)#9	2.3945(15)	B(2)-O(3)#3	1.382(3)
Na(3)-O(1)	2.3945(15)	O(4)-Ca(1)-O(3)	94.04(4)
Na(3)-O(1)#3	2.6673(16)	O(4)#1-Ca(1)-O(3)	94.04(4)
Na(3)-O(1)#13	2.6673(16)	O(3)#2-Ca(1)-O(3)	179.42(6)
O(4)-Ca(1)-O(4)#1	169.02(10)	O(3)#3-Ca(1)-O(3)	94.37(6)
O(4)-Ca(1)-O(3)#2	86.00(4)	O(4)-Ca(1)-O(3)#1	94.04(4)
O(4)#1-Ca(1)-O(3)#2	86.00(4)	O(4)#1-Ca(1)-O(3)#1	94.04(4)
O(4)-Ca(1)-O(3)#3	86.00(4)	O(3)#2-Ca(1)-O(3)#1	94.37(6)
O(4)#1-Ca(1)-O(3)#3	86.00(4)	O(3)#3-Ca(1)-O(3)#1	179.42(6)
O(3)#2-Ca(1)-O(3)#3	86.21(9)	O(3)-Ca(1)-O(3)#1	85.05(8)
O(1)-Ca(2)-O(4)	137.55(5)	O(1)-Ca(2)-O(2)	89.73(5)
O(4)-Ca(2)-O(2)	131.13(5)	O(1)-Ca(2)-O(1)#7	81.81(5)
O(4)-Ca(2)-O(1)#7	84.92(5)	O(2)-Ca(2)-O(1)#7	92.56(5)
O(1)-Ca(2)-O(2)#4	90.00(5)	O(4)-Ca(2)-O(2)#4	98.87(5)
O(2)-Ca(2)-O(2)#4	91.02(5)	O(1)#7-Ca(2)-O(2)#4	171.04(5)
O(1)-Ca(2)-O(1)#8	82.47(5)	O(4)-Ca(2)-O(1)#8	56.63(5)
O(2)-Ca(2)-O(1)#8	172.17(5)	O(1)#7-Ca(2)-O(1)#8	86.99(5)
O(2)#4-Ca(2)-O(1)#8	88.35(5)	O(1)-Ca(2)-O(3)#3	144.28(5)
O(4)-Ca(2)-O(3)#3	78.14(6)	O(2)-Ca(2)-O(3)#3	56.40(5)
O(1)#7-Ca(2)-O(3)#3	108.25(5)	O(2)#4-Ca(2)-O(3)#3	80.55(5)
O(1)#8-Ca(2)-O(3)#3	131.06(5)	O(2)#9-Na(2)-O(2)	87.69(8)
O(2)#9-Na(2)-O(2)#10	116.40(9)	O(2)-Na(2)-O(2)#10	59.01(7)
O(2)#9-Na(2)-O(2)#11	59.01(7)	O(2)-Na(2)-O(2)#11	116.40(9)
O(2)#10-Na(2)-O(2)#11	87.69(8)	O(2)-Na(3)-O(2)#9	97.53(8)
O(2)-Na(3)-O(1)#9	142.96(6)	O(2)#9-Na(3)-O(1)#9	92.46(5)
O(2)-Na(3)-O(1)	92.46(5)	O(2)#9-Na(3)-O(1)	142.96(6)
O(1)#9-Na(3)-O(1)	60.29(7)	O(2)-Na(3)-O(1)#3	87.14(5)
O(2)#9-Na(3)-O(1)#3	128.92(6)	O(1)#9-Na(3)-O(1)#3	113.59(7)
O(1)-Na(3)-O(1)#3	86.98(5)	O(2)-Na(3)-O(1)#13	128.92(6)
O(2)#9-Na(3)-O(1)#13	87.14(5)	O(1)#9-Na(3)-O(1)#13	86.98(5)
O(1)-Na(3)-O(1)#13	113.59(7)	O(1)#3-Na(3)-O(1)#13	53.59(6)
O(4)-B(1)-O(1)#8	118.87(11)	O(4)-B(1)-O(1)#14	118.87(11)

O(1)#8-B(1)-O(1)#14	122.0(2)	O(2)-B(2)-O(2)#10	122.2(2)
O(2)-B(2)-O(3)#3	118.92(12)	O(2)#10-B(2)-O(3)#3	118.92(12)

Note. Symmetry transformations used to generate equivalent atoms:

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

$NaSrBO_3$			
Sr(1)-O(2)#1	2.596(4)	Na(1)-O(1)	2.286(4)
Sr(1)-O(1)#2	2.603(4)	Na(1)-O(3)	2.289(4)
Sr(1)-O(3)#3	2.685(4)	Na(1)-O(2)#2	2.315(4)
Sr(1)-O(3)	2.718(4)	Na(1)-O(3)#8	2.374(4)
Sr(1)-O(3)#4	2.745(4)	Na(1)-O(1)#9	2.374(4)
Sr(1)-O(2)	2.750(4)	Na(1)-O(2)#5	2.608(4)
Sr(1)-O(1)#4	2.754(4)	B(1)-O(1)#1	1.366(7)
Sr(1)-O(2)#5	2.800(4)	B(1)-O(2)	1.371(7)
Sr(1)-O(1)	2.848(4)	B(1)-O(3)#3	1.396(7)
O(2)#1-Sr(1)-O(1)#2	84.05(12)	O(1)#2-Sr(1)-O(2)	72.09(11)
O(2)#1-Sr(1)-O(3)#3	75.95(12)	O(3)#3-Sr(1)-O(2)	52.43(12)
O(1)#2-Sr(1)-O(3)#3	121.87(11)	O(3)-Sr(1)-O(2)	164.74(11)
O(2)#1-Sr(1)-O(3)	106.27(11)	O(3)#4-Sr(1)-O(2)	72.50(11)
O(1)#2-Sr(1)-O(3)	118.59(12)	O(2)#1-Sr(1)-O(1)#4	105.30(11)
O(3)#3-Sr(1)-O(3)	119.33(5)	O(1)#2-Sr(1)-O(1)#4	167.40(16)
O(2)#1-Sr(1)-O(3)#4	153.99(12)	O(3)#3-Sr(1)-O(1)#4	69.40(11)
O(1)#2-Sr(1)-O(3)#4	100.59(12)	O(3)-Sr(1)-O(1)#4	51.17(11)
O(3)#3-Sr(1)-O(3)#4	80.01(9)	O(3)#4-Sr(1)-O(1)#4	74.79(11)
O(3)-Sr(1)-O(3)#4	94.03(11)	O(2)-Sr(1)-O(1)#4	116.50(11)
O(2)#1-Sr(1)-O(2)	84.93(9)	O(2)#1-Sr(1)-O(2)#5	75.70(13)
O(3)#3-Sr(1)-O(2)#5	151.56(11)	O(3)-Sr(1)-O(2)#5	71.42(12)
O(3)#4-Sr(1)-O(2)#5	127.32(11)	O(1)#2-Sr(1)-O(2)#5	52.46(11)
O(2)-Sr(1)-O(2)#5	122.32(6)	O(3)-Sr(1)-O(1)	73.73(11)
O(1)#4-Sr(1)-O(2)#5	120.92(11)	O(3)#4-Sr(1)-O(1)	49.94(11)
O(2)#1-Sr(1)-O(1)	151.49(11)	O(2)-Sr(1)-O(1)	101.48(11)
O(1)#2-Sr(1)-O(1)	71.93(12)	O(1)#4-Sr(1)-O(1)	96.66(10)
O(3)#3-Sr(1)-O(1)	129.82(11)	O(2)#5-Sr(1)-O(1)	77.51(11)
O(1)-Na(1)-O(3)	93.84(15)	O(1)-Na(1)-O(2)#2	86.52(15)
O(3)-Na(1)-O(2)#2	176.14(16)	O(1)-Na(1)-O(3)#8	83.35(15)
O(3)-Na(1)-O(3)#8	97.03(18)	O(1)-Na(1)-O(1)#9	170.43(18)
O(2)#2-Na(1)-O(3)#8	86.83(15)	O(3)-Na(1)-O(1)#9	83.22(14)
O(2)#2-Na(1)-O(1)#9	95.81(15)	O(3)#8-Na(1)-O(1)#9	106.02(15)
O(1)-Na(1)-O(2)#5	92.27(15)	O(3)-Na(1)-O(2)#5	81.99(15)

O(2)#2-Na(1)-O(2)#5	94.16(17)	O(3)#8-Na(1)-O(2)#5	175.45(15)
O(1)#9-Na(1)-O(2)#5	78.32(14)	O(1)#1-B(1)-O(2)	122.1(5)
O(1)#1-B(1)-O(3)#3	117.5(5)	O(2)-B(1)-O(3)#3	120.4(5)

Note. Symmetry transformations used to generate equivalent atoms:

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

$Li_4CaB_2O_6$

Li(1)-O(2)	1.931(3)	Ca(1)-O(3)#10	2.333(2)
Li(1)-O(2)#1	1.931(3)	Ca(1)-O(3)#11	2.333(2)
Li(1)-O(3)	1.965(5)	Ca(1)-O(3)	2.333(2)
Li(1)-O(1)#2	1.969(5)	Ca(1)-O(3)#5	2.333(2)
Li(2)-O(2)#1	1.993(5)	Ca(1)-O(1)	2.435(3)
Li(2)-O(1)#6	2.050(3)	Ca(1)-O(1)#10	2.435(3)
Li(2)-O(1)#7	2.050(3)	B(1)-O(2)	1.378(3)
Li(2)-O(2)#3	2.172(5)	B(1)-O(3)#9	1.387(3)
Li(2)-O(3)#8	2.227(5)	B(1)-O(1)	1.391(4)
O(2)-Li(1)-O(2)#1	129.1(3)	O(2)-Li(1)-O(3)	112.46(14)
O(2)#1-Li(1)-O(3)	112.46(14)	O(2)-Li(1)-O(1)#2	106.73(16)
O(2)#1-Li(1)-O(1)#2	106.73(16)	O(3)-Li(1)-O(1)#2	75.05(18)
O(2)#1-Li(2)-O(1)#6	120.74(13)	O(2)#1-Li(2)-O(1)#7	120.74(13)
O(1)#6-Li(2)-O(1)#7	116.6(2)	O(2)#1-Li(2)-O(2)#3	92.5(2)
O(1)#6-Li(2)-O(2)#3	95.64(16)	O(1)#7-Li(2)-O(2)#3	95.64(16)
O(2)#1-Li(2)-O(3)#8	68.57(18)	O(1)#6-Li(2)-O(3)#8	94.25(17)
O(1)#7-Li(2)-O(3)#8	94.25(17)	O(2)#3-Li(2)-O(3)#8	161.1(2)
O(3)#10-Ca(1)-O(3)#11	96.75(11)	O(3)#10-Ca(1)-O(3)	180.0
O(3)#11-Ca(1)-O(3)	83.25(11)	O(3)#10-Ca(1)-O(3)#5	83.25(11)
O(3)#11-Ca(1)-O(3)#5	180.0	O(3)-Ca(1)-O(3)#5	96.75(11)
O(3)#10-Ca(1)-O(1)	82.25(8)	O(3)#11-Ca(1)-O(1)	82.25(8)
O(3)-Ca(1)-O(1)	97.75(8)	O(3)#5-Ca(1)-O(1)	97.75(8)
O(3)#10-Ca(1)-O(1)#10	97.75(8)	O(3)#11-Ca(1)-O(1)#10	97.75(8)
O(3)-Ca(1)-O(1)#10	82.25(8)	O(3)#5-Ca(1)-O(1)#10	82.25(8)
O(1)-Ca(1)-O(1)#10	180.0		

Note. Symmetry transformations used to generate equivalent atoms:

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

Table S3. Bond valence analysis of $NaCa_4B_3O_9$, $NaCaBO_3$, $NaSrBO_3$ and $Li_4CaB_2O_6$.[a,b]

Atoms	l	s	Atoms	l	s
$NaCa_4B_3O_9$					
Ca(1)-O(2)	2.367(2)	0.339	Ca(2)-O(4)	2.365(4)	0.341
Ca(1)-O(2)#1	2.4060(19)	0.305	Ca(2)-O(5)	2.396(2)	0.314
Ca(1)-O(4)#2	2.4298(7)	0.286	Ca(2)-O(5)#4	2.396(2)	0.314
Ca(1)-O(3)	2.435(2)	0.282	Ca(2)-O(3)	2.4445(18)	0.275
Ca(1)-O(3)#5	2.4940(19)	0.241	Ca(2)-O(3)#4	2.4445(18)	0.275
Ca(1)-O(5)#3	2.433(2)	0.284	Ca(2)-O(2)#7	2.6261(19)	0.168
Ca(1)-O(5)#4	2.448(2)	0.273	Ca(2)-O(2)#1	2.6261(19)	0.168
Ca(1)-O(1)	2.5113(11)	0.230	Ca(2)-O(6)#5	2.8772(15)	0.085
∑s		2.24	Ca(2)-O(6)#6	2.8772(15)	0.085
Ca(3)-O(6)	2.345(3)	0.360	∑s		2.025
Ca(3)-O(1)	2.404(3)	0.307	Na(1) -O(1)	2.491(4)	0.156
Ca(3)-O(2)#9	2.437(2)	0.281	Na(1)-O(6)	2.784(4)	0.071
Ca(3)-O(2)#10	2.437(2)	0.281	Na(1)-O(3)#2	2.600(3)	0.116
Ca(3)-O(5)#11	2.4443(17)	0.275	Na(1)-O(3)#14	2.600(3)	0.116
Ca(3)-O(5)#3	2.4443(17)	0.275	Na(1)-O(4)#2	2.8323(11)	0.062
Ca(3)-O(3)	2.5552(19)	0.204	Na(1)-O(4)#15	2.8323(11)	0.062
Ca(3)-O(3)#12	2.5552(19)	0.204	Na(1)-O(2)#11	2.992(3)	0.040
∑s		2.187	Na(1)-O(2)#3	2.992(3)	0.040
B(1)-O(1)	1.360(6)	1.030	∑s		0.663
B(1)-O(2)	1.387(3)	0.958	B(3) - O(4)	1.360(6)	1.030
B(1)-O(2)#12	1.387(3)	0.958	B(3)-O(5)#16	1.370(3)	1.003
∑s		2.946	B(3)-O(5)#10	1.370(3)	1.003
B(2) - O(6)	1.349(6)	1.061	∑s		3.036
B(2)-O(3)#11	1.400(3)	0.925			
B(2)-O(3)#3	1.400(3)	0.925			
∑s		2.911			
$NaCaBO_3$					
Ca(1)-O(4)	2.2266(17)	0.496	Ca(2)-O(1)	2.3443(13)	0.361
Ca(1)-O(4)#1	2.2266(17)	0.496	Ca(2)-O(4)	2.3618(9)	0.344
Ca(1)-O(3)#2	2.3654(18)	0.341	Ca(2)-O(2)	2.4189(14)	0.295
Ca(1)-O(3)#3	2.3654(18)	0.341	Ca(2)-O(1)#7	2.4708(14)	0.256
Ca(1)-O(3)	2.3915(18)	0.317	Ca(2)-O(2)#4	2.4723(15)	0.255
Ca(1)-O(3)#1	2.3915(18)	0.317	Ca(2)-O(1)#8	2.5973(13)	0.182
∑s		2.308	Ca(2)-O(3)#3	2.6010(9)	0.180
Na(2)-O(2)#9	2.4502(16)	0.174	∑s		1.873
Na(2)-O(2)	2.4502(16)	0.174	Na(3)-O(2)	2.2570(15)	0.293
Na(2)-O(2)#10	2.4502(16)	0.174	Na(3)-O(2)#9	2.2570(15)	0.293

Na(2)-O(2)#11	2.4502(16)	0.174	Na(3)-O(1)#9	2.3945(15)	0.202
Na(2)-O(2)#13	3.028	0.036	Na(3)-O(1)	2.3945(15)	0.293
Na(2)-O(2) #11	3.028	0.036	Na(3)-O(1)#3	2.6673(16)	0.097
Na(2)-O(2)#16	3.028	0.036	Na(3)-O(1)#13	2.6673(16)	0.097
Na(2)-O(2)#3	3.028	0.036	∑s		1.275
∑s		0.84	B(2)-O(2)	1.3785(19)	0.980
B(1)-O(4)	1.368(3)	1.008	B(2)-O(2)#10	1.3785(19)	0.980
B(1)-O(1)#8	1.3750(18)	0.989	B(2)-O(3)#3	1.382(3)	0.971
B(1)-O(1)#14	1.3750(18)	0.989	∑s		2.931
∑s		2.986			
$NaSrBO_3$					
Sr(1)-O(2)#1	2.595(4)	0.275	Na(1)-O(1)	2.285(4)	0.272
Sr(1)-O(1)#2	2.603(4)	0.27	Na(1)-O(3)	2.288(4)	0.270
Sr(1)-O(3)#3	2.685(4)	0.216	Na(1)-O(2)#2	2.314(4)	0.251
Sr(1)-O(3)	2.718(4)	0.198	Na(1)-O(3)#8	2.372(4)	0.214
Sr(1)-O(3)#4	2.746(4)	0.183	Na(1)-O(1)#9	2.375(4)	0.213
Sr(1)-O(2)	2.750(4)	0.181	Na(1)-O(2)#5	2.609(4)	0.113
Sr(1)-O(1)#4	2.754(4)	0.179	∑s		1.333
Sr(1)-O(2)#5	2.800(4)	0.158	B(1)-O(1)#1	1.366(7)	1.014
Sr(1)-O(1)	2.848(4)	0.139	B(1)-O(2)	1.371(7)	1.001
∑s		1.799	B(1)-O(3)#3	1.398(7)	0.930
			∑s		2.945
$Li_4CaB_2O_6$					
Li(1)-O(2)	1.931(3)	0.285	Ca(1)-O(3)#10	2.333(2)	0.372
Li(1)-O(2)#1	1.931(3)	0.285	Ca(1)-O(3)#11	2.333(2)	0.372
Li(1)-O(3)	1.965(5)	0.260	Ca(1)-O(3)	2.333(2)	0.372
Li(1)-O(1)#2	1.969(5)	0.257	Ca(1)-O(3)#5	2.333(2)	0.372
∑s		1.087	Ca(1)-O(1)	2.435(3)	0.282
Li(2)-O(2)#1	1.993(5)	0.241	Ca(1)-O(1)#10	2.435(3)	0.282
Li(2)-O(1)#6	2.050(3)	0.206	∑s		2.052
Li(2)-O(1)#7	2.050(3)	0.206	B(1)-O(2)	1.378(3)	0.981
Li(2)-O(2)#3	2.172(5)	0.148	B(1)-O(3)#9	1.387(3)	0.958
Li(2)-O(3)#8	2.227(5)	0.128	B(1)-O(1)	1.391(4)	0.947
∑s		0.929	∑s		2.886

[a] Bond valences calculated with the program Bond Valence Calculator Version 2.00, Hormillosa, C., Healy, S., Stephen, T. McMaster University (1993).

[b] Valence sums calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond "i" and B = 0.37. Superscripts indicate the number of equivalent bonds for anions.

Table S4. Dipole moment of $NaCa_4B_3O_9$ and $NaCaBO_3$.

$NaCa_4B_3O_9$ dipole moment					
species	x(*a*)	y(*b*)	z(*c*)	magnitude	
				debye	$\times 10^{-4}$esu·cm/Å^3
$B(1)O_3$	0.00	-0.97	0.35		
	0.00	-0.97	0.35		
	0.00	0.97	0.35		
	0.00	0.97	0.35		
$\varepsilon(B(1)O_3)$	0.00	0.00	1.40	1.40	17.96
$B(2)O_3$	0.00	0.08	-1.44		
	0.00	0.08	-1.44		
	0.00	-0.08	-1.44		
	0.00	-0.08	-1.44		
$\varepsilon(B(2)O_3)$	0.00	0.00	-5.75	5.53	70.83
$B(3)O_3$	0.00	0.00	0.09		
	0.00	0.00	0.09		
	0.00	0.00	0.09		
	0.00	0.00	0.09		
$\varepsilon(B(3)O_3)$	0.00	0.00	0.38	0.38	4.85
$Na(1)O_8$	0.00	3.48	2.63		
	0.00	3.48	2.63		
	0.00	-3.48	2.63		
	0.00	-3.48	2.63		
$\varepsilon(Na(1)O_8)$	0.00	0.00	10.53	10.53	134.95
$Ca(1)O_8$	1.18	3.06	-0.28		
	-1.18	3.06	-0.28		
	1.18	-3.06	-0.28		
	-1.18	-3.06	-0.28		
	1.18	3.06	-0.28		
	-1.18	3.06	-0.28		
	1.18	-3.06	-0.28		
	-1.18	-3.06	-0.28		
ε(Ca(1)O8)	0.00	0.00	-2.27	2.23	28.62
$Ca(2)O_9$	0.00	0.00	5.46		
	0.00	0.00	5.46		
	0.00	0.00	5.46		
	0.00	0.00	5.46		
$\varepsilon(Ca(2)O_9)$	0.00	0.00	21.86	21.86	280.08
$Ca(3)O_8$	0.00	-5.49	-2.21		

	0.00	5.49	-2.21		
	0.00	-5.49	-2.21		
	0.00	5.49	-2.21		
ε(Ca(3)O8)	0.00	0.00	-8.85	8.85	113.35
Unit Cell	0	0	17.30		

$NaCaBO_3$ dipole moment					
species	x(*a*)	y(*b*)	z(*c*)	magnitude	
				debye	$\times 10^{-4}$esu·cm/Å^3
$B(1)O_3$	0.00	0.31	1.40		
	0.00	-0.31	1.40		
	0.00	0.31	-1.40		
	0.00	-0.31	-1.40		
ε($B(1)O_3$)	0.00	0.00	0.00	0.00	0.00
$B(2)O_3$	0.34	0.00	-0.41		0.00
	-0.34	0.00	-0.41		
	0.34	0.00	0.41		
	-0.34	0.00	0.41		
ε($B(2)O_3$)	0.00	0.00	0.00	0.00	0.00
$Na(1)O_6$	0.00	5.97	2.18		
	0.00	-5.97	2.18		
	0.00	5.97	-2.18		
	0.00	-5.97	-2.18		
ε($Na(1)O_6$)	0.00	0.00	0.00	0.00	0.00
$Na(2)O_8$	0.00	0.00	-9.76		
	0.00	0.00	9.76		
ε($Na(2)O_8$)	0.00	0.00	0.00	0.00	0.00
$Ca(1)O_6$	0.00	0.00	2.04		
	0.00	0.00	-2.04		
ε($Ca(1)O_6$)	0.00	0.00	0.00	0.00	0.00
$Ca(2)O_7$	-1.98	-0.81	-1.02		
	1.98	-0.81	-1.02		
	-1.98	0.81	-1.02		
	1.98	0.81	-1.02		
	-1.98	-0.81	1.02		
	1.98	-0.81	1.02		
	-1.98	0.81	1.02		
	1.98	0.81	1.02		
ε($Ca(2)O_7$)	0.00	0.00	0.00	0.00	0.00
Unit Cell	0.00	0.00	0.00	0.00	0.00

Table S5. State energies (eV) of the highest valence band (H-VB) and the lowest conduction band (L-CB) at same k-points of $NaCa_4B_3O_9$, $NaCaBO_3$, $KCa_4B_3O_9$ and $KSr_4B_3O_9$.

K-piont	H-VB (eV)	L-CB (eV)
	$NaCa_4B_3O_9$	
Γ(0.000, 0.000, 0.000)	0	4.17048
Z (0.000, 0.000, 0.500)	-0.11341	4.79526
T (-0.500,0.000, 0.000)	-0.12065	5.43394
Y(-0.500,0.000, 0.000)	-0.00333	5.37046
S (-0.500,0.500, 0.000)	-0.02354	4.66665
X (0.000,0.500, 0.000)	-0.06551	4.94604
U (0.000, 0.500, 0.500)	-0.10784	5.14019
R (0.500, 0.500, 0.500)	-0.11797	4.68390
	$NaCaBO_3$	
Γ(0.000, 0.000, 0.000)	0	3.78088
Z (0.000, 0.000, 0.500)	-0.14419	6.16210
T (-0.500,0.000, 0.000)	-0.22984	6.20165
Y(-0.500,0.000, 0.000)	-0.16456	4.25982
S (-0.500,0.500, 0.000)	-0.17075	4.66665
X (0.000,0.500, 0.000)	-0.17075	4.23522
U (0.000, 0.500, 0.500)	-0.11484	5.30744
R (0.500, 0.500, 0.500)	-0.15374	6.09875
	$KCa_4B_3O_9$	
Γ (0.000, 0.000, 0.000)	0	4.37001
Z (0.000, 0.000, 0.500)	-0.01650	4.71320
T (-0.500,0.000, 0.000)	-0.07455	4.87639
Y(-0.500,0.000, 0.000)	-0.03807	4.97568
Γ (0.000,0.000, 0.000)	0	4.37001
S (-0.500,0.500, 0.000)	-0.07207	4.65136
R (0.500, 0.500, 0.500)	-0.17070	4.67886
Z (0.000, 0.000, 0.500)	-0.11316	4.71200
	$KSr_4B_3O_9$	
Γ(0.000, 0.000, 0.000)	0	4.26006
Z (0.000, 0.000, 0.500)	-0.05875	4.68503
T (-0.500,0.000, 0.000)	-0.07738	4.95820
Y(-0.500,0.000, 0.000)	-0.03807	4.99692
Γ(0.000, 0.000, 0.000)	0	4.26006
S (-0.500,0.500, 0.000)	-0.04004	4.60431
R (0.500, 0.500, 0.500)	-0.17593	4.66766
Z (0.000, 0.000, 0.500)	-0.11263	4.68503