Supporting Information

$NaCa_5BO_3(SiO_4)_2$ with Interesting Isolated $[BO_3]$ and $[SiO_4]$ Units in Alkali and Alkaline-earth Metal Borosilicates

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Table S1. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3) and bond valence sums (BVS) for $NaCa_5BO_3(SiO_4)_2$.

Atom	**x/a**	**y/b**	**z/c**	**U(eq)**	**BVS**
Ca(1)	8260(1)	5053(3)	6371(2)	11(1)	1.946
Ca(2)	4690(1)	-499(2)	7484(2)	12(1)	1.992
Ca(3)	9184(1)	8402(2)	8649(2)	12(1)	1.842
Ca(4)	8376(1)	-14(3)	5579(2)	11(1)	2.124
Ca(5)	3810(1)	2247(3)	4549(2)	12(1)	1.763
Na(1)	7131(3)	1672(5)	7982(4)	21(1)	0.830
B(1)	7137(7)	7163(13)	3245(9)	8(2)	2.889
Si(1)	9386(2)	2772(3)	8690(2)	10(1)	3.923
Si(2)	6128(2)	2489(3)	5281(2)	10(1)	3.977
O(1)	7702(4)	6934(9)	4472(5)	12(1)	2.023
O(2)	6168(4)	7398(9)	3123(6)	16(1)	1.928
O(3)	7578(4)	6944(9)	2166(6)	13(1)	1.993
O(4)	9043(4)	5049(8)	8672(6)	12(1)	1.999
O(5)	10509(4)	2559(8)	8573(6)	14(1)	1.943
O(6)	8695(4)	1717(9)	7489(6)	14(1)	2.004
O(7)	9217(4)	1680(9)	10041(6)	16(1)	1.792
O(8)	5609(5)	1096(10)	6215(6)	22(2)	1.873
O(9)	6891(5)	1173(10)	4686(6)	22(2)	1.859
O(10)	6618(4)	4279(9)	6199(6)	14(1)	1.895
O(11)	5330(4)	3237(9)	4065(6)	15(1)	1.978

Table S2. Bond lengths [Å] and angles [deg.] for $NaCa_5BO_3(SiO_4)_2$.

Ca(1)-O(10)	2.356(6)	Ca(4)-O(7)#1	2.675(8)
Ca(1)-O(1)	2.385(7)	Ca(5)-O(11)	2.395(6)
Ca(1)-O(7)#1	2.422(6)	Ca(5)-O(3)#12	2.423(6)
Ca(1)-O(5)#2	2.435(7)	Ca(5)-O(2)#4	2.453(7)
Ca(1)-O(4)	2.471(6)	Ca(5)-O(10)#4	2.537(9)
Ca(1)-O(3)#3	2.473(8)	Ca(5)-O(1)#4	2.595(6)
Ca(1)-O(6)	2.585(9)	Ca(5)-O(8)#7	2.600(9)
Ca(2)-O(8)	2.297(6)	Ca(5)-O(9)#7	2.713(9)
Ca(2)-O(11)#6	2.329(7)	Ca(5)-O(2)#12	2.814(7)
Ca(2)-O(2)#6	2.450(7)	Ca(5)-O(8)	2.926(7)
Ca(2)-O(2)#4	2.466(8)	Na(1)-O(6)	2.361(7)
Ca(2)-O(11)#7	2.475(8)	Na(1)-O(9)#6	2.389(8)
Ca(2)-O(10)#8	2.505(6)	Na(1)-O(10)	2.591(8)
Ca(2)-O(8)#8	2.767(9)	Na(1)-O(8)	2.607(8)
Ca(2)-O(9)#7	2.928(7)	Na(1)-O(3)#6	2.724(10)
Ca(3)-O(4)	2.298(9)	Na(1)-O(1)#6	2.950(9)
Ca(3)-O(1)#3	2.417(6)	Na(1)-O(11)#6	2.971(7)
Ca(3)-O(7)#9	2.427(6)	Si(1)-O(6)	1.620(7)
Ca(3)-O(5)#2	2.517(6)	Si(1)-O(5)	1.621(7)
Ca(3)-O(3)#3	2.525(6)	Si(1)-O(4)	1.628(7)
Ca(3)-O(6)#5	2.604(9)	Si(1)-O(7)	1.658(7)
Ca(3)-O(7)#5	2.669(8)	Si(2)-O(9)	1.613(7)
Ca(3)-O(5)#9	2.945(6)	Si(2)-O(11)	1.627(6)
Ca(4)-O(9)	2.289(7)	Si(2)-O(8)	1.632(7)
Ca(4)-O(6)	2.302(7)	Si(2)-O(10)	1.633(7)
Ca(4)-O(5)#10	2.350(7)	B(1)-O(1)	1.397(11)
Ca(4)-O(4)#1	2.362(6)	B(1)-O(2)	1.362(11)
Ca(4)-O(1)#11	2.491(8)	B(1)-O(3)	1.399(11)
Ca(4)-O(3)#6	2.541(6)	O(5)#10-Ca(4)-O(3)#6	74.5(2)
O(10)-Ca(1)-O(1)	83.3(2)	O(4)#1-Ca(4)-O(3)#6	147.4(2)
O(10)-Ca(1)-O(7)#1	119.5(2)	O(1)#11-Ca(4)-O(3)#6	72.2(2)
O(1)-Ca(1)-O(7)#1	85.2(2)	O(9)-Ca(4)-O(7)#1	91.3(3)
O(10)-Ca(1)-O(5)#2	148.2(2)	O(6)-Ca(4)-O(7)#1	73.9(2)
O(1)-Ca(1)-O(5)#2	76.7(2)	O(5)#10-Ca(4)-O(7)#1	112.7(2)
O(7)#1-Ca(1)-O(5)#2	83.4(2)	O(4)#1-Ca(4)-O(7)#1	64.5(2)
O(10)-Ca(1)-O(4)	109.7(2)	O(1)#11-Ca(4)-O(7)#1	139.5(2)
O(1)-Ca(1)-O(4)	147.3(2)	O(3)#6-Ca(4)-O(7)#1	147.8(2)
O(7)#1-Ca(1)-O(4)	111.4(2)	O(11)-Ca(5)-O(3)#12	120.4(2)
O(5)#2-Ca(1)-O(4)	77.5(2)	O(11)-Ca(5)-O(2)#4	109.4(2)
O(10)-Ca(1)-O(3)#3	76.9(2)	O(3)#12-Ca(5)-O(2)#4	127.8(2)
O(1)-Ca(1)-O(3)#3	75.2(2)	O(11)-Ca(5)-O(10)#4	81.0(2)
O(7)#1-Ca(1)-O(3)#3	153.1(2)	O(3)#12-Ca(5)-O(10)#4	74.5(2)

O(5)#2-Ca(1)-O(3)#3	74.3(2)	O(2)#4-Ca(5)-O(10)#4	100.2(2)
O(4)-Ca(1)-O(3)#3	78.7(2)	O(11)-Ca(5)-O(1)#4	149.2(2)
O(10)-Ca(1)-O(6)	89.4(2)	O(3)#12-Ca(5)-O(1)#4	72.4(2)
O(1)-Ca(1)-O(6)	150.5(2)	O(2)#4-Ca(5)-O(1)#4	56.43(19)
O(7)#1-Ca(1)-O(6)	73.7(2)	O(10)#4-Ca(5)-O(1)#4	75.7(2)
O(5)#2-Ca(1)-O(6)	119.8(2)	O(11)-Ca(5)-O(8)#7	80.6(2)
O(4)-Ca(1)-O(6)	61.8(2)	O(3)#12-Ca(5)-O(8)#7	87.4(2)
O(3)#3-Ca(1)-O(6)	130.8(2)	O(2)#4-Ca(5)-O(8)#7	116.5(2)
O(8)-Ca(2)-O(11)#6	84.9(2)	O(10)#4-Ca(5)-O(8)#7	142.7(2)
O(8)-Ca(2)-O(2)#6	82.2(3)	O(1)#4-Ca(5)-O(8)#7	129.8(2)
O(11)#6-Ca(2)-O(2)#6	87.2(3)	O(11)-Ca(5)-O(9)#7	134.0(2)
O(8)-Ca(2)-O(2)#4	75.4(2)	O(3)#12-Ca(5)-O(9)#7	81.7(2)
O(11)#6-Ca(2)-O(2)#4	74.1(3)	O(2)#4-Ca(5)-O(9)#7	74.3(2)
O(2)#6-Ca(2)-O(2)#4	151.8(2)	O(10)#4-Ca(5)-O(9)#7	144.7(2)
O(8)-Ca(2)-O(11)#7	85.3(3)	O(1)#4-Ca(5)-O(9)#7	72.4(2)
O(11)#6-Ca(2)-O(11)#7	157.92(12)	O(8)#7-Ca(5)-O(9)#7	59.2(2)
O(2)#6-Ca(2)-O(11)#7	71.9(2)	O(11)-Ca(5)-O(2)#12	66.86(19)
O(2)#4-Ca(2)-O(11)#7	122.1(2)	O(3)#12-Ca(5)-O(2)#12	54.17(19)
O(8)-Ca(2)-O(10)#8	154.2(3)	O(2)#4-Ca(5)-O(2)#12	172.12(9)
O(11)#6-Ca(2)-O(10)#8	83.0(2)	O(10)#4-Ca(5)-O(2)#12	72.63(19)
O(2)#6-Ca(2)-O(10)#8	119.7(2)	O(1)#4-Ca(5)-O(2)#12	123.01(19)
O(2)#4-Ca(2)-O(10)#8	79.4(2)	O(8)#7-Ca(5)-O(2)#12	70.4(2)
O(11)#7-Ca(2)-O(10)#8	113.3(2)	O(9)#7-Ca(5)-O(2)#12	113.4(2)
O(8)-Ca(2)-O(8)#8	146.9(2)	O(11)-Ca(5)-O(8)	58.97(19)
O(11)#6-Ca(2)-O(8)#8	106.2(3)	O(3)#12-Ca(5)-O(8)	157.4(2)
O(2)#6-Ca(2)-O(8)#8	67.6(2)	O(2)#4-Ca(5)-O(8)	64.92(19)
O(2)#4-Ca(2)-O(8)#8	137.4(2)	O(10)#4-Ca(5)-O(8)	124.7(2)
O(11)#7-Ca(2)-O(8)#8	72.9(2)	O(1)#4-Ca(5)-O(8)	120.74(19)
O(10)#8-Ca(2)-O(8)#8	58.9(2)	O(8)#7-Ca(5)-O(8)	70.1(2)
O(8)-Ca(2)-O(9)#7	93.2(2)	O(9)#7-Ca(5)-O(8)	85.2(2)
O(11)#6-Ca(2)-O(9)#7	143.5(2)	O(2)#12-Ca(5)-O(8)	116.25(18)
O(2)#6-Ca(2)-O(9)#7	128.7(2)	B(1)#4-Ca(5)-O(8)	92.1(2)
O(2)#4-Ca(2)-O(9)#7	70.3(2)	O(4)#1-Ca(4)-O(1)#11	76.9(2)
O(11)#7-Ca(2)-O(9)#7	56.8(2)	O(9)-Ca(4)-O(3)#6	88.3(2)
O(10)#8-Ca(2)-O(9)#7	83.4(2)	O(6)-Ca(4)-O(3)#6	74.7(2)
O(8)#8-Ca(2)-O(9)#7	95.1(2)	O(6)-Na(1)-O(9)#6	114.9(3)
O(4)-Ca(3)-O(1)#3	79.6(2)	O(6)-Na(1)-O(10)	89.1(2)
O(4)-Ca(3)-O(7)#9	92.6(2)	O(9)#6-Na(1)-O(10)	93.4(3)
O(1)#3-Ca(3)-O(7)#9	125.1(2)	O(6)-Na(1)-O(8)	122.1(3)
O(4)-Ca(3)-O(5)#2	79.2(2)	O(9)#6-Na(1)-O(8)	114.6(3)
O(1)#3-Ca(3)-O(5)#2	128.0(2)	O(10)-Na(1)-O(8)	60.0(2)
O(7)#9-Ca(3)-O(5)#2	102.8(2)	O(6)-Na(1)-O(3)#6	70.3(2)
O(4)-Ca(3)-O(3)#3	81.0(2)	O(9)#6-Na(1)-O(3)#6	150.1(3)

O(1)#3-Ca(3)-O(3)#3	58.0(2)	O(10)-Na(1)-O(3)#6	116.5(3)
O(7)#9-Ca(3)-O(3)#3	172.3(2)	O(8)-Na(1)-O(3)#6	81.2(2)
O(5)#2-Ca(3)-O(3)#3	72.0(2)	O(6)-Na(1)-O(1)#6	87.1(2)
O(4)-Ca(3)-O(6)#5	148.6(2)	O(9)#6-Na(1)-O(1)#6	100.3(3)
O(1)#3-Ca(3)-O(6)#5	94.3(2)	O(10)-Na(1)-O(1)#6	166.1(2)
O(7)#9-Ca(3)-O(6)#5	115.3(2)	O(8)-Na(1)-O(1)#6	111.4(2)
O(5)#2-Ca(3)-O(6)#5	80.8(2)	O(3)#6-Na(1)-O(1)#6	49.8(2)
O(3)#3-Ca(3)-O(6)#5	70.0(2)	O(6)-Na(1)-O(11)#6	170.1(3)
O(4)-Ca(3)-O(7)#5	145.3(2)	O(9)#6-Na(1)-O(11)#6	56.8(2)
O(1)#3-Ca(3)-O(7)#5	79.3(2)	O(10)-Na(1)-O(11)#6	96.5(2)
O(7)#9-Ca(3)-O(7)#5	77.6(2)	O(8)-Na(1)-O(11)#6	67.7(2)
O(5)#2-Ca(3)-O(7)#5	135.3(2)	O(3)#6-Na(1)-O(11)#6	113.8(2)
O(3)#3-Ca(3)-O(7)#5	110.0(2)	O(1)#6-Na(1)-O(11)#6	89.2(2)
O(6)#5-Ca(3)-O(7)#5	60.3(2)	O(6)-Si(1)-O(5)	111.3(3)
O(4)-Ca(3)-O(5)#9	76.4(2)	O(6)-Si(1)-O(4)	106.2(3)
O(1)#3-Ca(3)-O(5)#9	66.92(18)	O(5)-Si(1)-O(4)	112.3(3)
O(7)#9-Ca(3)-O(5)#9	58.44(19)	O(6)-Si(1)-O(7)	107.9(4)
O(5)#2-Ca(3)-O(5)#9	148.05(17)	O(5)-Si(1)-O(7)	108.5(3)
O(3)#3-Ca(3)-O(5)#9	123.18(19)	O(4)-Si(1)-O(7)	110.5(3)
O(6)#5-Ca(3)-O(5)#9	129.55(19)	O(9)-Si(2)-O(11)	106.8(4)
O(7)#5-Ca(3)-O(5)#9	70.1(2)	O(9)-Si(2)-O(8)	108.2(4)
O(9)-Ca(4)-O(5)#10	155.4(3)	O(11)-Si(2)-O(8)	109.4(4)
O(6)-Ca(4)-O(5)#10	91.0(3)	O(9)-Si(2)-O(10)	113.8(4)
O(9)-Ca(4)-O(4)#1	97.7(2)	O(11)-Si(2)-O(10)	112.9(4)
O(6)-Ca(4)-O(4)#1	134.3(2)	O(8)-Si(2)-O(10)	105.7(4)
O(5)#10-Ca(4)-O(4)#1	88.3(2)	O(2)-B(1)-O(1)	120.0(8)
O(9)-Ca(4)-O(1)#11	81.9(3)	O(2)-B(1)-O(3)	121.5(8)
O(6)-Ca(4)-O(1)#11	146.6(2)	O(1)-B(1)-O(3)	118.2(8)
O(5)#10-Ca(4)-O(1)#11	76.2(3)		

Symmetry transformations used to generate equivalent atoms:

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

Table S3. Anhydrous and disorder-free alkali and/or alkaline-earth metal cations-containing borosilicates.

	Compounds	**Space Group**	**B-O Group**	**Si-O Group**	**B-Si-O Group**
1	$NaCa_5BO_3(SiO_4)_2$	$P2_1/c$	isolated $[BO_3]$	isolated $[SiO_4]$	no connection
2	$LiBSiO_4$	$I\bar{4}$	isolated $[BO_4]$	isolated $[SiO_4]$	3D framework
3	$NaBSiO_4$	$P6_3$	isolated $[BO_4]$	isolated $[SiO_4]$	3D framework
4	$NaBSiO_4$	$P12_1/n$	isolated $[BO_4]$	isolated $[SiO_4]$	3D framework
5	$Ca_2B_2SiO_7$	$P\bar{4}2_1m$	isolated $[B_2O_7]$	isolated $[SiO_4]$	2D layer
6	$Cs_2B_4SiO_9$	$I112$	isolated $[B_4O_9]$	isolated $[SiO_4]$	3D framework
7	$Cs_2B_4SiO_9$	$I\bar{4}$	isolated $[B_4O_{10}]$	isolated $[SiO_4]$	3D framework
8	CsB_3SiO_7	$Pna2_1$	isolated $[B_3O_6]$	isolated $[SiO_4]$	3D framework
9	$SrB_2Si_2O_8$	$Pnma$	isolated $[B_2O_7]$	isolated $[Si_2O_7]$	3D framework
10	$Ba(B_2Si_2O_8)$	$Pnma$	isolated $[B_2O_7]$	isolated $[Si_2O_7]$	3D framework
11	$CaB_2Si_2O_8$	$Pnam$	isolated $[B_2O_7]$	isolated $[Si_2O_7]$	3D framework
12	$CsBSi_2O_6$	$I4_1/acd$	isolated $[BO_4]$	isolated $[Si_4O_{12}]$	3D framework
13	$Ba_2Ca(BSi_2O_7)_2$	$I\bar{4}2m$	isolated $[B_4O_{12}]$	isolated $[Si_4O_{12}]$	3D framework
14	$Li_4B_4Si_8O_{24}$	$P2_1$	isolated $[BO_4]$	$[Si_2O_6]$ chains	3D framework
15	$KBSi_2O_6$	$P2_12_12_1$	isolated $[BO_4]$	$[Si_4O_{12}]$ chains	3D framework
16	$NaBSi_3O_8$	$P\bar{1}$	isolated $[BO_4]$	$[Si_6O_{16}]$ chains	3D framework
17	$KNa_2B_3Si_{12}O_{30}$	$P6/mcc$	isolated $[BO_4]$	isolated $[Si_{12}O_{30}]$	3D framework

Table S4 The bond population analysis of $NaCa_5BO_3(SiO_4)_2$.

compound	bond	Bond length/Å	population
$NaCa_5BO_3(SiO_4)_2$	B-O	1.37-1.40	0.79-0.84
	Si-O	1.64-1.66	0.60-0.56
	Ca-O	2.28-2.37	0.18-0.13
	Na-O	2.3714	<0.17

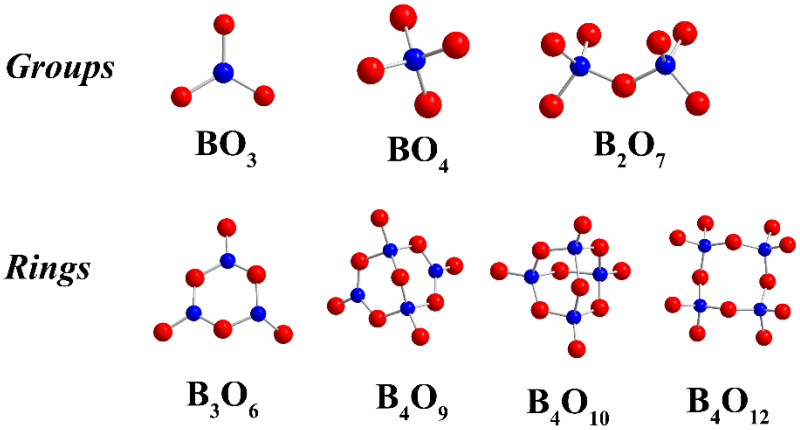

Fig. S1 Isolated B−O structures including groups and rings.

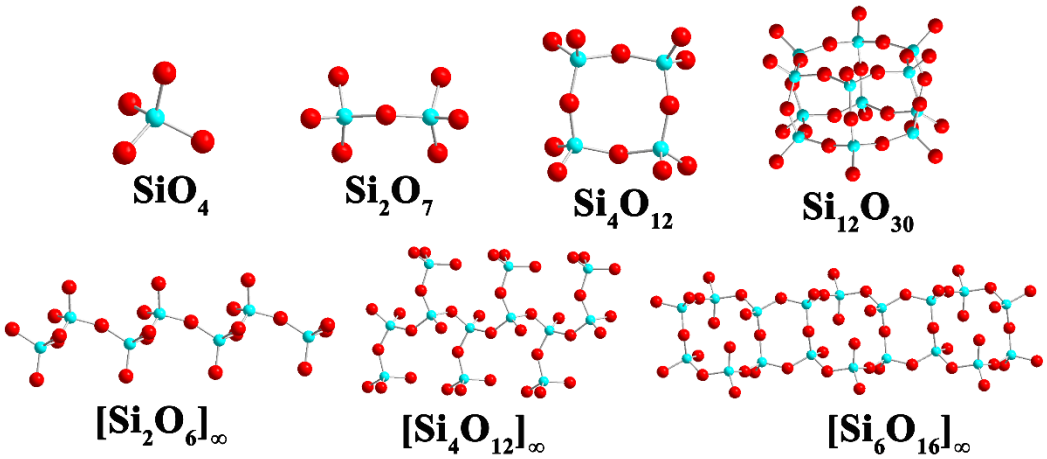

Fig. S2 The Si-O structures in the 17 compounds.

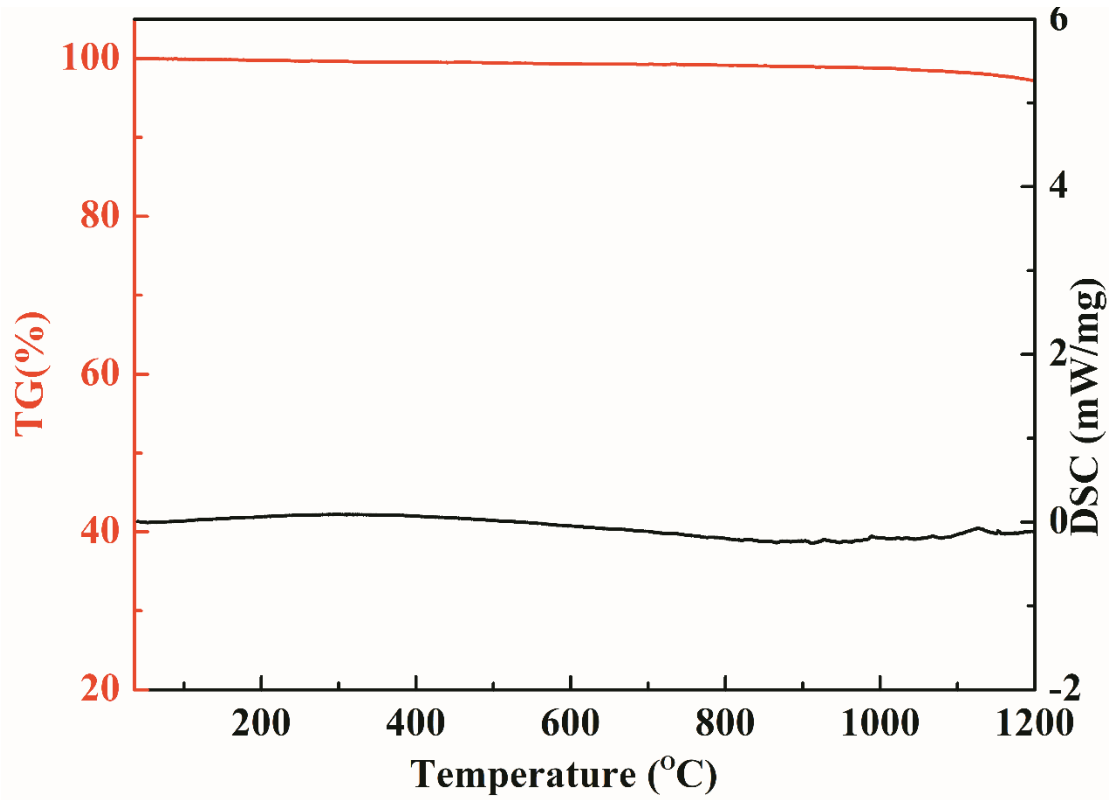

Fig. S3 The TG-DSC curves of $NaCa_5BO_3(SiO_4)_2$

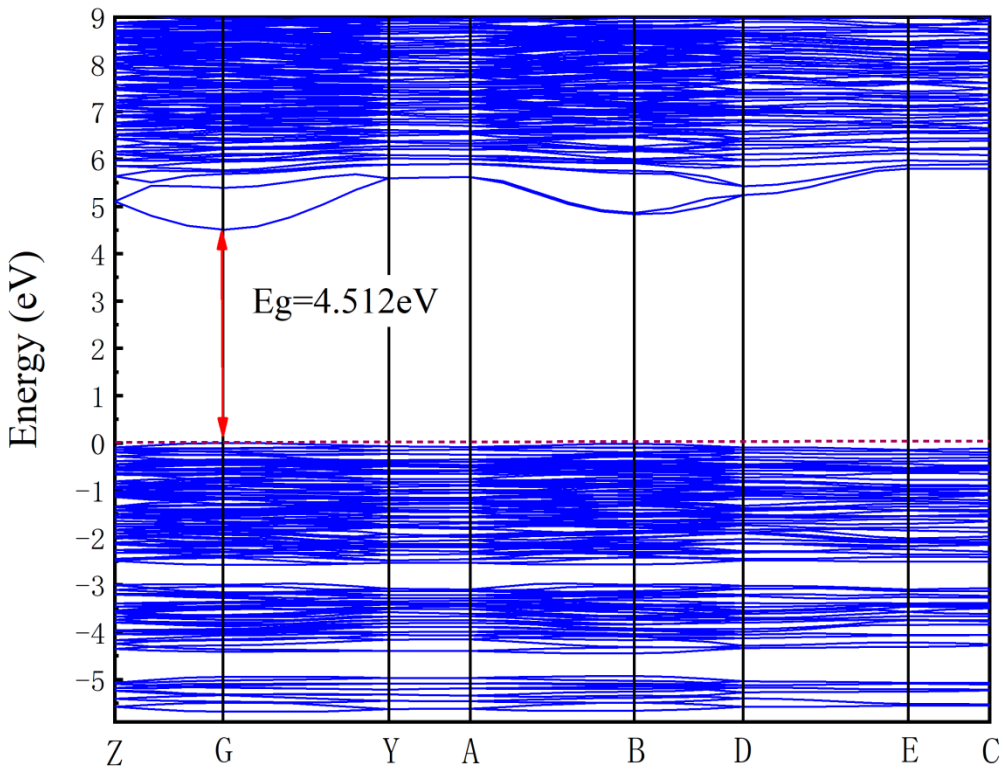

Fig. S4 Calculated band structure of $NaCa_5BO_3(SiO_4)_2$.

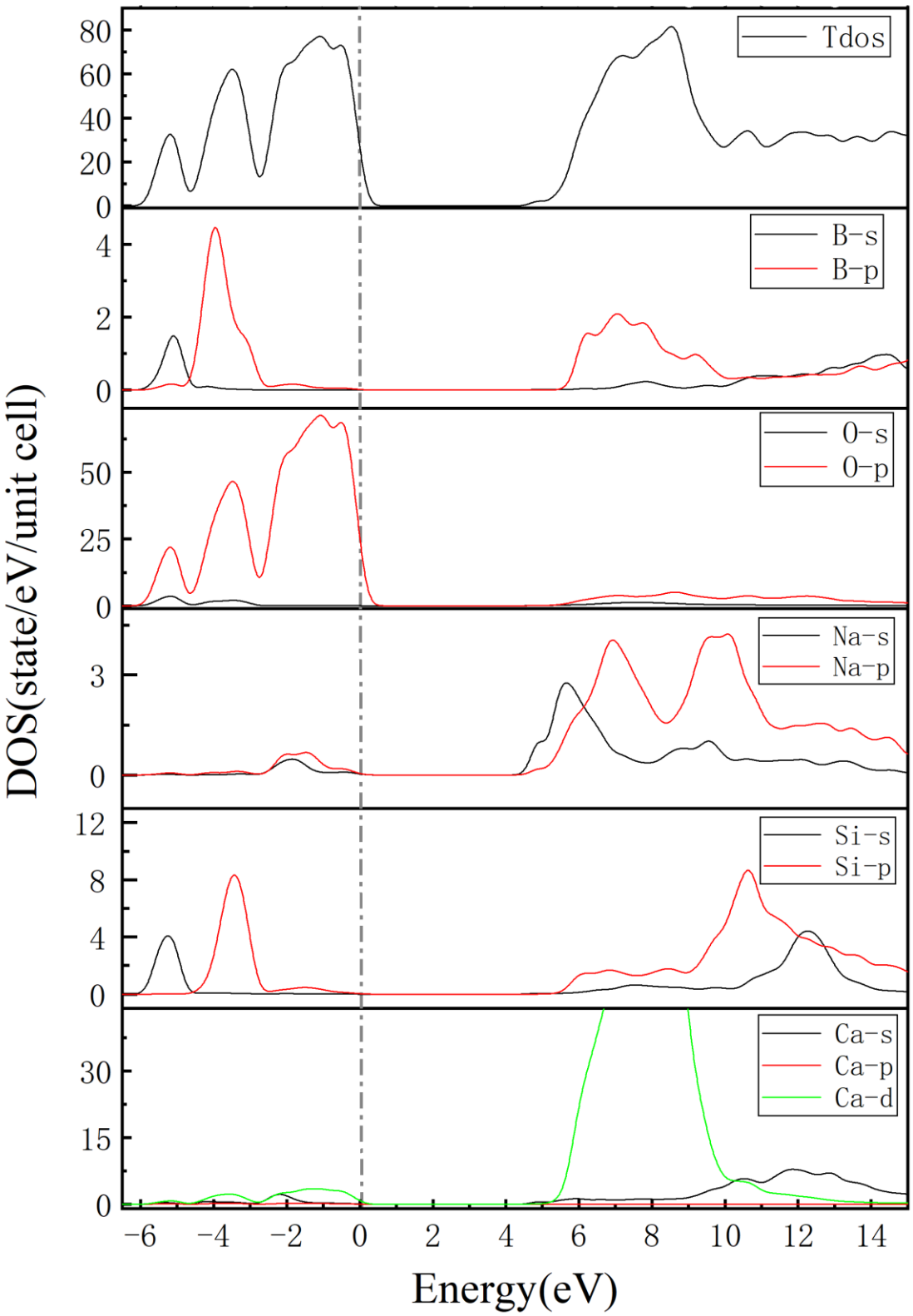

Fig. S5 TDOS and PDOS of $NaCa_5BO_3(SiO_4)_2$.

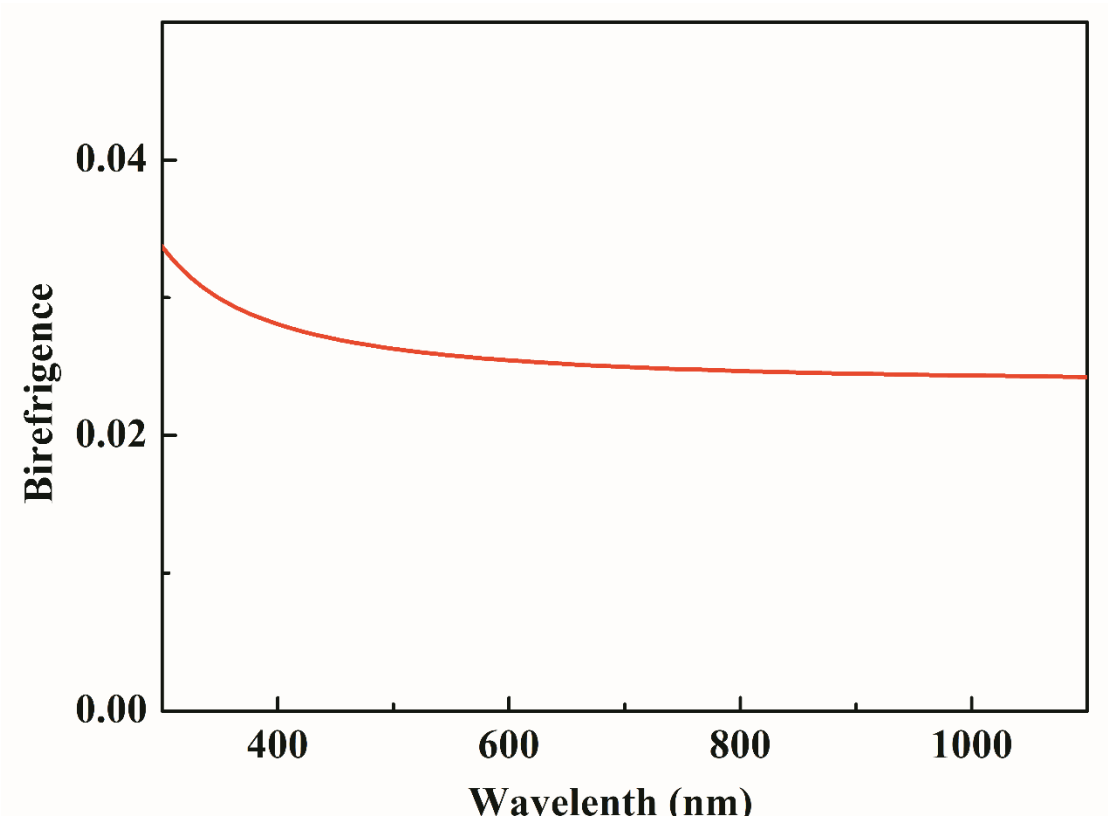

Fig. S6 The birefringence of $NaCa_5BO_3(SiO_4)_2$.

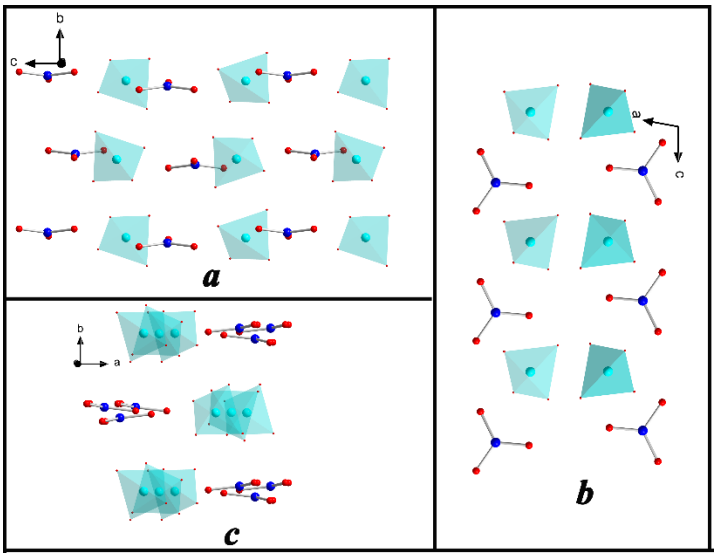

Fig. S7 a, b, and c. The relative position of anionic groups along the three different polarized directions expressed by lattice vector (**a** [0.0709928, 0, 0.005516], **b** [0, -0.1453519, 0], **c** [0.0091377, 0, 0.0962079]).