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Electronic Supplementary Information

$Ba_3Ca_4(BO_3)_3(SiO_4)Cl$: a new non-centrosymmetric complex alkaline-earth metal borosilicate chloride with deep-ultraviolet cut-off edge

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Table S1. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ba_3Ca_4(BO_3)_3(SiO_4)Cl$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	$U_{(eq)}$	BVS
Ba(1)	1476(1)	2953(1)	3479(1)	12(1)	2.1
Ca(1)	4765(1)	5235(1)	-54(3)	12(1)	1.9
Ca(2)	3333	6667	6247(6)	16(1)	1.7
Si(1)	3333	6667	2094(10)	28(1)	4.0
B(1)	8063(5)	6125(10)	2927(15)	11(2)	3.1
Cl(1)	0	0	1203(8)	19(1)	1.0
O(1)	3333	6667	-280(20)	26(3)	1.8
O(2)	6825(5)	5842(5)	1971(8)	21(1)	2.0
O(3)	4146(3)	8291(6)	3018(8)	17(2)	2.0
O(4)	8355(5)	6711(10)	4699(13)	41(2)	1.9

Table S2. Selected bond lengths (Å) and angles (°) for $Ba_3Ca_4(BO_3)_3(SiO_4)Cl$.

Ba(1)-O(4)#1	2.602(9)	Ca(1)-O(4)#10	2.944(6)
Ba(1)-O(2)#2	2.890(5)	Ca(2)-O(1)#11	2.376(15)
Ba(1)-O(2)#3	2.890(5)	Ca(2)-O(2)#12	2.666(5)
Ba(1)-O(2)#4	2.961(5)	Ca(2)-O(2)#13	2.666(5)
Ba(1)-O(2)#5	2.961(5)	Ca(2)-O(2)#14	2.666(5)
Ba(1)-O(3)#6	3.0236(12)	Ca(2)-O(2)#2	2.666(5)
Ba(1)-O(3)#4	3.0236(12)	Ca(2)-O(2)#15	2.666(5)
Ba(1)-O(4)#4	3.040(6)	Ca(2)-O(2)#3	2.666(5)
Ba(1)-O(4)#7	3.040(6)	Ca(2)-O(3)#6	2.677(6)
Ba(1)-Cl(1)#1	3.324(3)	Ca(2)-O(3)	2.677(6)
Ba(1)-Cl(1)	3.162(3)	Ca(2)-O(3)#4	2.677(6)
Ca(1)-O(3)#4	2.396(6)	Si(1)-O(1)	1.619(15)
Ca(1)-O(2)	2.412(5)	Si(1)-O(3)	1.641(6)
Ca(1)-O(2)#5	2.412(5)	Si(1)-O(3)#6	1.641(6)
Ca(1)-O(3)#8	2.422(6)	Si(1)-O(3)#4	1.641(6)
Ca(1)-O(2)#1	2.535(5)	B(1)-O(4)	1.328(14)
Ca(1)-O(2)#9	2.535(5)	B(1)-O(2)	1.374(7)
Ca(1)-O(1)	2.6734(19)	B(1)-O(2)#16	1.374(7)
Ca(1)-O(4)#1	2.944(6)		
O(4)#1-Ba(1)-O(2)#2	140.61(19)	O(2)#5-Ca(1)-O(4)#10	142.5(2)
O(4)#1-Ba(1)-O(2)#3	140.61(19)	O(3)#8-Ca(1)-O(4)#10	106.31(16)
O(2)#2-Ba(1)-O(2)#3	48.19(18)	O(2)#1-Ca(1)-O(4)#10	114.1(2)
O(4)#1-Ba(1)-O(2)#4	69.27(10)	O(2)#9-Ca(1)-O(4)#10	50.1(2)
O(2)#2-Ba(1)-O(2)#4	83.02(11)	O(1)-Ca(1)-O(4)#10	68.01(15)
O(2)#3-Ba(1)-O(2)#4	129.93(14)	O(4)#1-Ca(1)-O(4)#10	135.8(3)
O(4)#1-Ba(1)-O(2)#5	69.27(10)	O(1)#11-Ca(2)-O(2)#12	79.31(14)
O(2)#2-Ba(1)-O(2)#5	129.93(14)	O(1)#11-Ca(2)-O(2)#13	79.31(14)
O(2)#3-Ba(1)-O(2)#5	83.02(11)	O(2)#12-Ca(2)-O(2)#13	52.53(18)
O(2)#4-Ba(1)-O(2)#5	138.4(2)	O(1)#11-Ca(2)-O(2)#14	79.31(14)
O(4)#1-Ba(1)-O(3)#6	77.8(2)	O(2)#12-Ca(2)-O(2)#14	65.18(19)
O(2)#2-Ba(1)-O(3)#6	63.94(14)	O(2)#13-Ca(2)-O(2)#14	116.64(8)
O(2)#3-Ba(1)-O(3)#6	85.12(14)	O(1)#11-Ca(2)-O(2)#2	79.31(14)
O(2)#4-Ba(1)-O(3)#6	59.70(13)	O(2)#12-Ca(2)-O(2)#2	116.64(8)
O(2)#5-Ba(1)-O(3)#6	107.87(14)	O(2)#13-Ca(2)-O(2)#2	65.18(19)
O(4)#1-Ba(1)-O(3)#4	77.8(2)	O(2)#14-Ca(2)-O(2)#2	157.7(3)
O(2)#2-Ba(1)-O(3)#4	85.12(14)	O(1)#11-Ca(2)-O(2)#15	79.31(14)
O(2)#3-Ba(1)-O(3)#4	63.94(14)	O(2)#12-Ca(2)-O(2)#15	116.64(8)
O(2)#4-Ba(1)-O(3)#4	107.87(14)	O(2)#13-Ca(2)-O(2)#15	157.7(3)
O(2)#5-Ba(1)-O(3)#4	59.70(13)	O(2)#14-Ca(2)-O(2)#15	52.53(18)
O(3)#6-Ba(1)-O(3)#4	51.4(2)	O(2)#2-Ca(2)-O(2)#15	116.64(8)

O(4)#1-Ba(1)-O(4)#4	108.71(17)	O(1)#11-Ca(2)-O(2)#3	79.31(14)
O(2)#2-Ba(1)-O(4)#4	64.71(17)	O(2)#12-Ca(2)-O(2)#3	157.7(3)
O(2)#3-Ba(1)-O(4)#4	106.64(18)	O(2)#13-Ca(2)-O(2)#3	116.64(8)
O(2)#4-Ba(1)-O(4)#4	46.10(19)	O(2)#14-Ca(2)-O(2)#3	116.64(8)
O(2)#5-Ba(1)-O(4)#4	160.14(17)	O(2)#2-Ca(2)-O(2)#3	52.53(18)
O(3)#6-Ba(1)-O(4)#4	90.48(18)	O(2)#15-Ca(2)-O(2)#3	65.18(19)
O(3)#4-Ba(1)-O(4)#4	140.07(18)	O(1)#11-Ca(2)-O(3)#6	145.53(13)
O(4)#1-Ba(1)-O(4)#7	108.71(17)	O(2)#12-Ca(2)-O(3)#6	96.98(12)
O(2)#2-Ba(1)-O(4)#7	106.64(18)	O(2)#13-Ca(2)-O(3)#6	71.80(15)
O(2)#3-Ba(1)-O(4)#7	64.71(17)	O(2)#14-Ca(2)-O(3)#6	130.50(19)
O(2)#4-Ba(1)-O(4)#7	160.14(17)	O(2)#2-Ca(2)-O(3)#6	71.80(15)
O(2)#5-Ba(1)-O(4)#7	46.10(19)	O(2)#15-Ca(2)-O(3)#6	130.50(18)
O(3)#6-Ba(1)-O(4)#7	140.07(18)	O(2)#3-Ca(2)-O(3)#6	96.98(12)
O(3)#4-Ba(1)-O(4)#7	90.48(18)	O(1)#11-Ca(2)-O(3)	145.53(13)
O(4)#4-Ba(1)-O(4)#7	121.8(3)	O(2)#12-Ca(2)-O(3)	71.80(15)
O(4)#1-Ba(1)-Cl(1)	67.5(2)	O(2)#13-Ca(2)-O(3)	96.98(12)
O(2)#2-Ba(1)-Cl(1)	138.15(12)	O(2)#14-Ca(2)-O(3)	71.80(15)
O(2)#3-Ba(1)-Cl(1)	138.15(12)	O(2)#2-Ca(2)-O(3)	130.50(19)
O(2)#4-Ba(1)-Cl(1)	83.67(10)	O(2)#15-Ca(2)-O(3)	96.98(12)
O(2)#5-Ba(1)-Cl(1)	83.67(9)	O(2)#3-Ca(2)-O(3)	130.50(18)
O(3)#6-Ba(1)-Cl(1)	136.72(13)	O(3)#6-Ca(2)-O(3)	58.7(2)
O(3)#4-Ba(1)-Cl(1)	136.72(13)	O(1)#11-Ca(2)-O(3)#4	145.53(13)
O(4)#4-Ba(1)-Cl(1)	77.62(15)	O(2)#12-Ca(2)-O(3)#4	130.50(19)
O(4)#7-Ba(1)-Cl(1)	77.62(14)	O(2)#13-Ca(2)-O(3)#4	130.50(19)
O(3)#4-Ca(1)-O(2)	76.59(17)	O(2)#14-Ca(2)-O(3)#4	96.98(12)
O(3)#4-Ca(1)-O(2)#5	76.59(17)	O(2)#2-Ca(2)-O(3)#4	96.98(12)
O(2)-Ca(1)-O(2)#5	73.1(2)	O(2)#15-Ca(2)-O(3)#4	71.80(15)
O(3)#4-Ca(1)-O(3)#8	151.75(19)	O(2)#3-Ca(2)-O(3)#4	71.80(15)
O(2)-Ca(1)-O(3)#8	80.80(16)	O(3)#6-Ca(2)-O(3)#4	58.7(2)
O(2)#5-Ca(1)-O(3)#8	80.80(16)	O(3)-Ca(2)-O(3)#4	58.7(2)
O(3)#4-Ca(1)-O(2)#1	127.74(15)	O(1)-Si(1)-O(3)	112.6(3)
O(2)-Ca(1)-O(2)#1	154.64(15)	O(1)-Si(1)-O(3)#6	112.6(3)
O(2)#5-Ca(1)-O(2)#1	103.24(17)	O(3)-Si(1)-O(3)#6	106.1(3)
O(3)#8-Ca(1)-O(2)#1	73.85(15)	O(1)-Si(1)-O(3)#4	112.6(3)
O(3)#4-Ca(1)-O(2)#9	127.74(14)	O(3)-Si(1)-O(3)#4	106.1(3)
O(2)-Ca(1)-O(2)#9	103.24(17)	O(3)#6-Si(1)-O(3)#4	106.1(3)
O(2)#5-Ca(1)-O(2)#9	154.64(15)	O(2)#9-Ca(1)-O(1)	76.5(3)
O(3)#8-Ca(1)-O(2)#9	73.85(15)	O(3)#4-Ca(1)-O(4)#1	82.60(17)
O(2)#1-Ca(1)-O(2)#9	69.0(2)	O(2)-Ca(1)-O(4)#1	142.5(2)
O(3)#4-Ca(1)-O(1)	64.4(3)	O(2)#5-Ca(1)-O(4)#1	71.96(19)
O(2)-Ca(1)-O(1)	126.4(2)	O(3)#8-Ca(1)-O(4)#1	106.31(16)
O(2)#5-Ca(1)-O(1)	126.4(2)	O(2)#1-Ca(1)-O(4)#1	50.1(2)
O(3)#8-Ca(1)-O(1)	143.8(3)	O(2)#9-Ca(1)-O(4)#1	114.1(2)
O(2)#1-Ca(1)-O(1)	76.5(3)	O(1)-Ca(1)-O(4)#1	68.01(15)

O(3)#4-Ca(1)-O(4)#10	82.60(17)	O(2)-Ca(1)-O(4)#10	71.96(19)
O(4)-B(1)-O(2)	120.8(4)	O(2)-B(1)-O(2)#16	118.3(9)
O(4)-B(1)-O(2)#16	120.8(4)		

Symmetry transformations used to generate equivalent atoms:

#1 – x+1, – y + 1, z – 1/2 #2 x – y, – y + 1, z +1/2 #3 – x + 1, – y + 1, z + 1/2
#4 – x + y, – x + 1, z #5 – y + 1, – x + 1, z #6 – y + 1, x – y + 1, z
#7 – y + 1, x – y, z #8 x – y + 1, x, z – 1/2 #9 y, x, z – 1/2
#10 y, – x + y + 1, z – 1/2 #11 x, y, z + 1 #12 – x + 1, – x + y + 1, z + 1/2
#13 x – y, x, z + 1/2 #14 y, – x + y + 1, z + 1/2 #15 y, x, z + 1/2
#16 – x + y + 1, y, z #17 x – y + 1, x, z + 1/2 #18 – x + y + 1, – x + 1, z
#19 – x + y, – x, z #20 – y, x – y, z #21 – x, – y, z – 1/2
#22 x – y, x, z – 1/2 #23 y, – x + y, z – 1/2 #24 x, y, z – 1

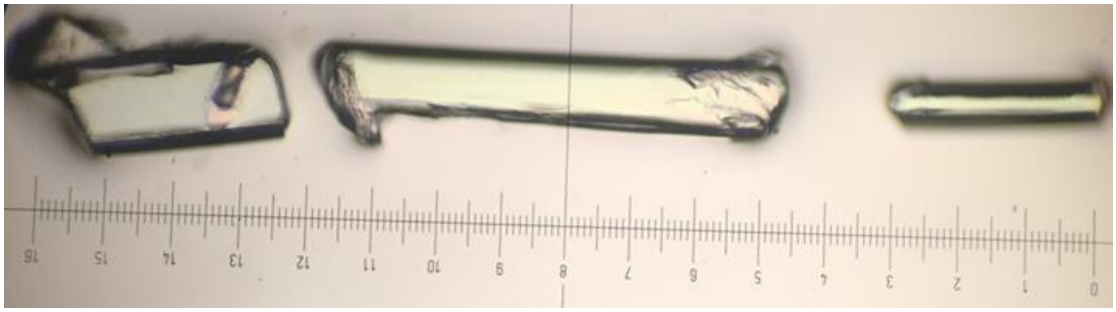

Figure S1. Strip shaped crystals of $Ba_3Ca_4(BO_3)_3(SiO_4)Cl$.

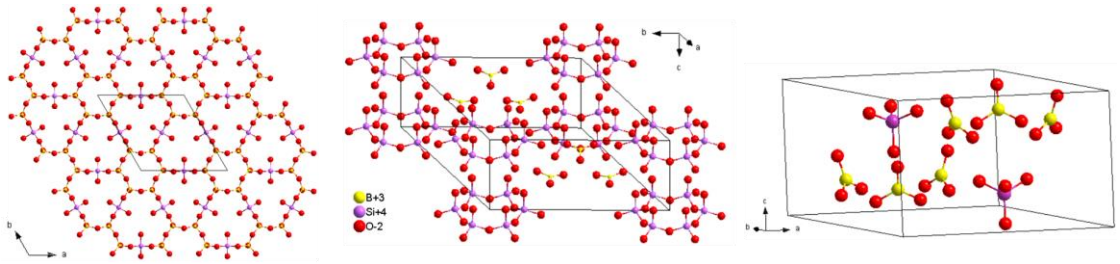

Figure S2. (a) $[Si_3B_6O_{24}]$ layer in $BaY_6B_6Si_3O_{24}F_2$; (b) Isolated $[BO_3]$ and $[Si_6O_{18}]$ in $NaAl_6B_3Fe_3Si_6O_3F$; (c) Isolated $[BO_3]$ and $[SiO_4]$ in $Ba_7(BO_3)(SiO_4)X$ (X = Cl, Br).

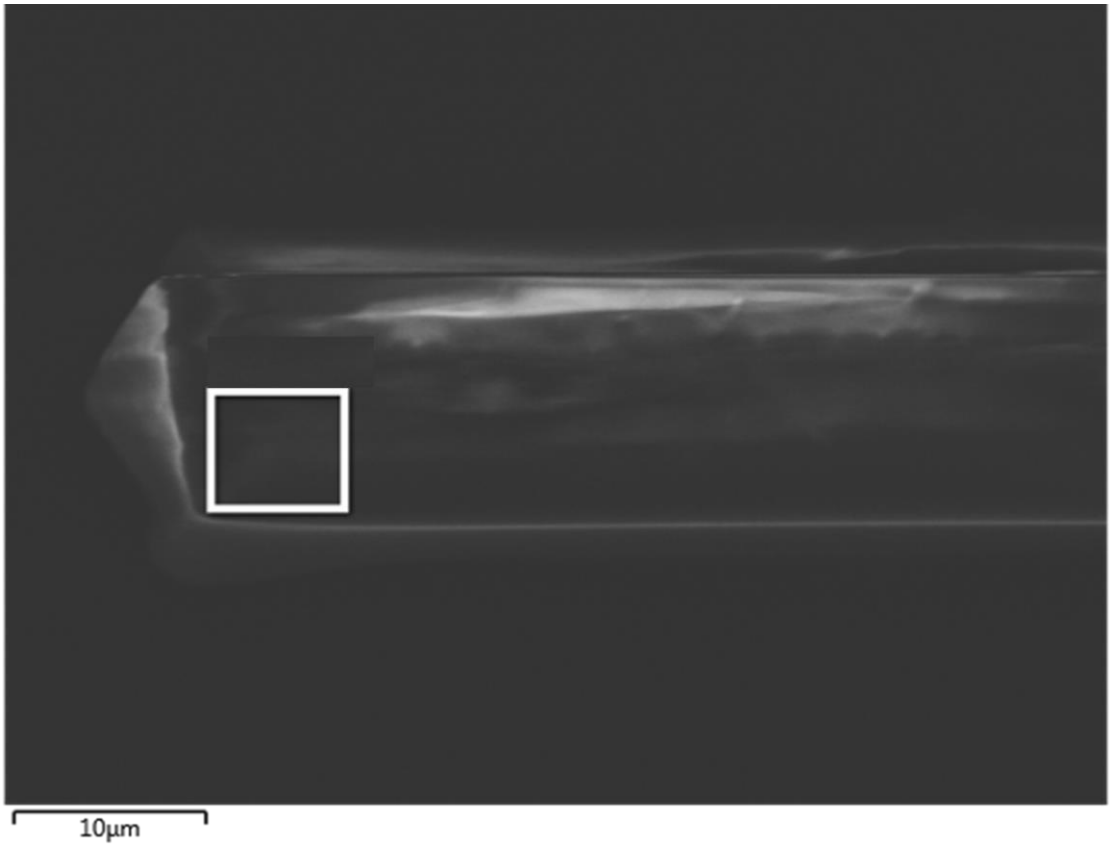

Figure S3. EDS of $Ba_3Ca_4(BO_3)_3(SiO_4)Cl$ single crystal.

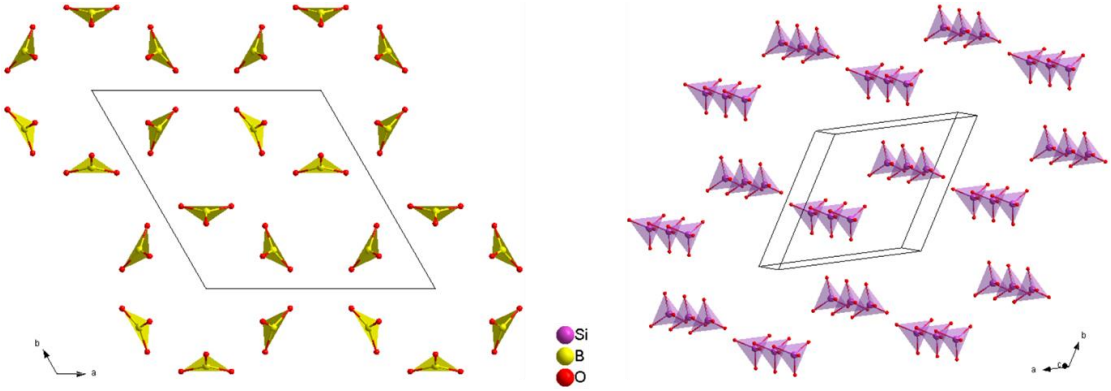

Figure S4 Arrangement of BO_3 and SiO_4 groups in $Ba_3Ca_4(BO_3)_3(SiO_4)Cl$. (a) the BO_3 groups; (b) the SiO_4 groups.

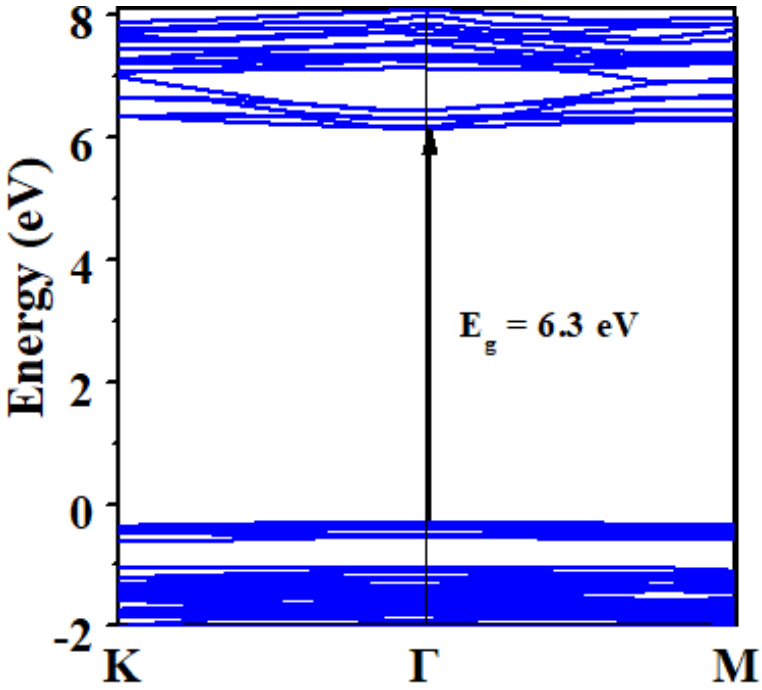

Figure S5 Calculated band structure of $Ba_3Ca_4(BO_3)_3(SiO_4)Cl$ by HSE06