Supporting Information

The New type of Complex Alkali and Alkaline Earth Metal Borates with Isolated $(B_{12}O_{24})^{12-}$ Anionic Group

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Table S1(a). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Li_3KB_4O_8$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
K(1)	0	0	0	17(1)	0.957
K(2)	3333	6667	-59(1)	21(1)	1.054
Li(1)	3333	6667	1667	18(1)	1.084
Li(2)	3333	6667	-1643(2)	18(1)	0.817
Li(3)	7369(3)	501(3)	-508(1)	16(1)	0.917
B(1)	5035(2)	4920(2)	-1658(1)	9(1)	3.035
B(2)	6623(2)	7365(2)	-872(1)	10(1)	3.007
O(1)	5141(1)	6154(1)	-1164(1)	12(1)	2.014
O(2)	1859(1)	2358(1)	1148(1)	11(1)	2.032
O(3)	3313(1)	8811(1)	1320(1)	9(1)	1.974
O(4)	6613(1)	8234(1)	-335(1)	11(1)	2.153

Table S1(b). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $LiNa_2Sr_8B_{12}O_{24}F_6Cl$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Sr(1)	6968(1)	7428(1)	1256(1)	10(1)	1.985
Sr(2)	6667	3333	1073(1)	9(1)	2.204
Na(1)	3333	6667	388(2)	24(1)	0.952
Li(1)	0	0	0	26(6)	1.022
B(1)	3965(6)	3774(6)	639(2)	9(1)	2.995
B(2)	6933(6)	8525(6)	15(2)	7(1)	3.033
F(1)	9655(3)	8069(3)	1476(1)	13(1)	1.065
Cl(1)	3333	6667	1667	21(1)	0.671
O(1)	7906(4)	7926(4)	270(1)	9(1)	2.079
O(2)	6003(4)	8716(4)	468(1)	9(1)	2.090
O(3)	4917(4)	4629(4)	1053(1)	10(1)	2.038
O(4)	8421(4)	5761(4)	377(1)	11(1)	1.961

Table S2(a). Selected bond lengths (Å) and angles (deg) for $Li_3KB_4O_8$.

K(1)-O(4)	2.7817(10)	O(4)-K(1)-O(4)#4	65.446(15)
K(1)-O(4)#1	2.7817(10)	O(4)#1-K(1)-O(4)#4	114.554(15)
K(1)-O(4)#2	2.7817(10)	O(4)#2-K(1)-O(4)#4	65.446(15)
K(1)-O(4)#3	2.7817(10)	O(4)#3-K(1)-O(4)#4	114.554(15)
K(1)-O(4)#4	2.7817(10)	O(4)-K(1)-O(4)#5	114.554(14)
K(1)-O(4)#5	2.7817(10)	O(4)#1-K(1)-O(4)#5	65.446(15)
K(1)-O(2)#1	3.0080(11)	O(4)#2-K(1)-O(4)#5	114.554(15)
K(2)-O(4)#6	2.6729(10)	O(4)#3-K(1)-O(4)#5	65.446(15)
K(2)-O(4)#7	2.6729(10)	O(4)#4-K(1)-O(4)#5	180
K(2)-O(4)	2.6729(10)	O(4)-K(1)-O(2)#1	48.12(3)
K(2)-O(1)#7	2.9183(11)	O(4)#1-K(1)-O(2)#1	131.88(3)
K(2)-O(1)#6	2.9183(11)	O(4)#2-K(1)-O(2)#1	115.07(3)
K(2)-O(1)	2.9183(11)	O(4)#3-K(1)-O(2)#1	64.93(3)
Li(1)-O(3)#10	2.0990(10)	O(4)#4-K(1)-O(2)#1	106.95(3)
Li(1)-O(3)	2.0990(10)	O(4)#5-K(1)-O(2)#1	73.05(3)
Li(1)-O(3)#6	2.0990(10)	O(4)#6-K(2)-O(4)#7	115.982(15)
Li(1)-O(3)#7	2.0990(10)	O(4)#6-K(2)-O(4)	115.982(15)
Li(1)-O(3)#11	2.0990(10)	O(4)#7-K(2)-O(4)	115.982(15)
Li(1)-O(3)#12	2.0990(10)	O(4)#6-K(2)-O(1)#7	74.18(3)
Li(2)-O(1)#6	2.162(2)	O(4)#7-K(2)-O(1)#7	49.75(3)
Li(2)-O(1)#7	2.162(2)	O(4)-K(2)-O(1)#7	117.66(4)
Li(2)-O(1)	2.162(2)	O(4)#6-K(2)-O(1)#6	49.75(3)
Li(2)-O(2)#18	2.251(2)	O(4)#7-K(2)-O(1)#6	117.66(4)
Li(2)-O(2)#19	2.251(2)	O(4)-K(2)-O(1)#6	74.18(3)
Li(2)-O(2)#20	2.251(2)	O(1)#7-K(2)-O(1)#6	70.49(4)
Li(3)-O(4)	1.872(3)	O(4)#6-K(2)-O(1)	117.66(4)
Li(3)-O(4)#4	1.907(3)	O(4)#7-K(2)-O(1)	74.18(3)
Li(3)-O(3)#8	1.938(3)	O(4)-K(2)-O(1)	49.75(3)
Li(3)-O(2)#3	2.135(3)	O(1)#7-K(2)-O(1)	70.49(4)
B(1)-O(1)	1.4622(16)	O(1)#6-K(2)-O(1)	70.49(4)
B(1)-O(3)#3	1.4652(16)	O(4)#6-K(2)-O(3)	69.79(3)
B(1)-O(3)#22	1.4812(16)	O(4)#7-K(2)-O(3)	130.85(3)
B(1)-O(2)#20	1.4846(17)	O(4)-K(2)-O(3)	100.58(3)
B(2)-O(4)	1.3297(18)	O(1)#7-K(2)-O(3)	136.01(3)
B(2)-O(1)	1.3845(17)	O(1)#6-K(2)-O(3)	102.64(3)
B(2)-O(2)#1	1.3999(17)	O(1)-K(2)-O(3)	150.26(2)

O(4)-K(1)-O(4)#1	180.00(4)	O(3)#10-Li(1)-O(3)	180
O(4)-K(1)-O(4)#2	114.554(15)	O(3)#10-Li(1)-O(3)#6	70.05(2)
O(4)#1-K(1)-O(4)#2	65.446(15)	O(3)-Li(1)-O(3)#6	109.95(2)
O(4)-K(1)-O(4)#3	65.446(15)	O(3)#10-Li(1)-O(3)#7	70.05(2)
O(4)#1-K(1)-O(4)#3	114.554(15)	O(1)#6-Li(2)-O(2)#20	158.77(4)
O(4)#2-K(1)-O(4)#3	180	O(1)#7-Li(2)-O(2)#20	96.95(4)
O(3)-Li(1)-O(3)#7	109.95(2)	O(1)-Li(2)-O(2)#20	64.46(4)
O(3)#6-Li(1)-O(3)#7	109.95(2)	O(2)#18-Li(2)-O(2)#20	99.36(13)
O(3)#10-Li(1)-O(3)#11	109.95(2)	O(2)#19-Li(2)-O(2)#20	99.36(13)
O(3)-Li(1)-O(3)#11	70.05(2)	O(4)-Li(3)-O(4)#4	105.47(12)
O(3)#6-Li(1)-O(3)#11	180	O(4)-Li(3)-O(3)#8	120.95(13)
O(3)#7-Li(1)-O(3)#11	70.05(2)	O(4)#4-Li(3)-O(3)#8	131.18(14)
O(3)#10-Li(1)-O(3)#12	109.95(2)	O(4)-Li(3)-O(2)#3	118.76(13)
O(3)-Li(1)-O(3)#12	70.05(2)	O(4)#4-Li(3)-O(2)#3	100.64(12)
O(3)#6-Li(1)-O(3)#12	70.05(2)	O(3)#8-Li(3)-O(2)#3	70.95(9)
O(3)#7-Li(1)-O(3)#12	180	O(1)-B(1)-O(3)#3	109.96(10)
O(3)#11-Li(1)-O(3)#12	109.95(2)	O(1)-B(1)-O(3)#22	112.29(10)
O(1)#6-Li(2)-O(1)#7	102.32(13)	O(3)#3-B(1)-O(3)#22	109.71(12)
O(1)#6-Li(2)-O(1)	102.32(13)	O(1)-B(1)-O(2)#20	106.09(10)
O(1)#7-Li(2)-O(1)	102.32(13)	O(3)#3-B(1)-O(2)#20	112.71(10)
O(1)#6-Li(2)-O(2)#18	96.95(4)	O(3)#22-B(1)-O(2)#20	106.02(10)
O(1)#7-Li(2)-O(2)#18	64.46(4)	O(4)-B(2)-O(1)	120.98(12)
O(1)-Li(2)-O(2)#18	158.77(4)	O(4)-B(2)-O(2)#1	120.44(12)
O(1)#6-Li(2)-O(2)#19	64.46(4)	O(1)-B(2)-O(2)#1	118.57(12)
O(1)#7-Li(2)-O(2)#19	158.77(4)	O(2)#18-Li(2)-O(2)#19	99.36(13)
O(1)-Li(2)-O(2)#19	96.95(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z #2 -x+y+1,-x+2,z

#3 x-y+1,x,-z #4 y,-x+y+1,-z #5 -y+2,x-y+1,z

#6 -y+1,x-y+1,z #7 -x+y,-x+1,z #8 -x+1,-y+2,-z

#9 y-1,-x+y,-z #10 -x+2/3,-y+4/3,-z+1/3

#11 y-1/3,-x+y+1/3,-z+1/3 #12 x-y+2/3,x+1/3,-z+1/3

#13 -y+2/3,x-y+1/3,z+1/3 #14 -x+y+2/3,-x+4/3,z+1/3

#15 x-y,x,-z #16 -x+1,-y+1,-z #17 x-1/3,y+1/3,z+1/3

#18 -y+4/3,x-y+2/3,z-1/3 #19 x-2/3,y-1/3,z-1/3

#20 -x+y+1/3,-x+5/3,z-1/3 #21 -x+4/3,-y+5/3,-z-1/3

#22 x+1/3,y-1/3,z-1/3 #23 -y+5/3,x-y+4/3,z+1/3

#24 x+2/3,y+1/3,z+1/3

Table S2(b). Selected bond lengths (Å) and angles (deg) for $LiNa_2Sr_8B_{12}O_{24}F_6Cl$.

Sr(1)-F(1)	2.413(3)	F(1)#1-Sr(1)-O(1)	92.44(9)
Sr(1)-O(3)	2.478(3)	F(1)-Sr(1)-F(1)#2	68.20(10)
Sr(1)-F(1)#1	2.502(3)	O(3)-Sr(1)-F(1)#2	63.49(10)
Sr(1)-O(1)	2.521(4)	F(1)#1-Sr(1)-F(1)#2	124.69(4)
Sr(1)-F(1)#2	2.571(3)	O(1)-Sr(1)-F(1)#2	123.05(10)
Sr(1)-O(3)#3	2.616(4)	F(1)-Sr(1)-O(3)#3	83.08(9)
Sr(1)-O(2)	2.692(3)	O(3)-Sr(1)-O(3)#3	113.48(11)
Sr(1)-Cl(1)	3.3642(14)	F(1)#1-Sr(1)-O(3)#3	62.51(9)
Sr(2)-O(3)#6	2.562(3)	O(1)-Sr(1)-O(3)#3	154.45(10)
Sr(2)-O(3)#7	2.562(3)	F(1)#2-Sr(1)-O(3)#3	73.19(10)
Sr(2)-O(3)	2.562(3)	F(1)-Sr(1)-O(2)	128.11(9)
Sr(2)-F(1)#8	2.572(3)	O(3)-Sr(1)-O(2)	95.22(10)
Sr(2)-F(1)#5	2.572(3)	F(1)#1-Sr(1)-O(2)	75.97(9)
Sr(2)-F(1)#2	2.572(3)	O(1)-Sr(1)-O(2)	53.92(10)
Sr(2)-O(4)#6	2.697(3)	F(1)#2-Sr(1)-O(2)	158.71(9)
Sr(2)-O(4)#7	2.697(3)	O(3)#3-Sr(1)-O(2)	118.69(10)
Sr(2)-O(4)	2.697(3)	F(1)-Sr(1)-Cl(1)	149.87(7)
Na(1)-O(2)#4	2.350(3)	O(3)-Sr(1)-Cl(1)	68.99(7)
Na(1)-O(2)	2.350(3)	F(1)#1-Sr(1)-Cl(1)	96.73(6)
Na(1)-O(2)#10	2.350(3)	O(1)-Sr(1)-Cl(1)	124.12(7)
Na(1)-O(4)#11	2.806(4)	F(1)#2-Sr(1)-Cl(1)	95.38(6)
Na(1)-O(4)#9	2.806(4)	O(3)#3-Sr(1)-Cl(1)	67.69(7)
Na(1)-O(4)#12	2.806(4)	O(2)-Sr(1)-Cl(1)	75.29(7)
Na(1)-Cl(1)	3.106(5)	O(3)#6-Sr(2)-O(3)#7	119.963(5)
Li(1)-O(1)#13	2.121(3)	O(3)#6-Sr(2)-O(3)	119.963(5)
Li(1)-O(1)#14	2.121(3)	O(3)#7-Sr(2)-O(3)	119.963(5)
Li(1)-O(1)#1	2.121(3)	O(3)#6-Sr(2)-F(1)#8	62.35(9)
Li(1)-O(1)	2.121(3)	O(3)#7-Sr(2)-F(1)#8	81.12(9)
Li(1)-O(1)#12	2.121(3)	O(3)-Sr(2)-F(1)#8	131.39(10)
Li(1)-O(1)#15	2.121(3)	O(3)#6-Sr(2)-F(1)#5	131.39(10)
B(1)-O(3)	1.335(6)	O(3)#7-Sr(2)-F(1)#5	62.35(9)
B(1)-O(4)#7	1.387(6)	O(3)-Sr(2)-F(1)#5	81.12(9)
B(1)-O(2)#10	1.396(6)	F(1)#8-Sr(2)-F(1)#5	71.10(10)
B(2)-O(1)#12	1.452(6)	O(3)#6-Sr(2)-F(1)#2	81.12(9)
B(2)-O(1)	1.467(6)	O(3)#7-Sr(2)-F(1)#2	131.39(10)
B(2)-O(4)#12	1.486(6)	O(3)-Sr(2)-F(1)#2	62.35(9)

B(2)-O(2)	1.490(6)	F(1)#8-Sr(2)-F(1)#2	71.10(10)
F(1)-Sr(1)-O(3)	119.75(10)	F(1)#5-Sr(2)-F(1)#2	71.10(10)
F(1)-Sr(1)-F(1)#1	74.92(12)	O(3)#6-Sr(2)-O(4)#6	81.01(10)
O(3)-Sr(1)-F(1)#1	164.97(10)	O(3)#7-Sr(2)-O(4)#6	52.93(9)
F(1)-Sr(1)-O(1)	85.57(10)	O(3)-Sr(2)-O(4)#6	136.28(10)
O(3)-Sr(1)-O(1)	92.02(11)	F(1)#8-Sr(2)-O(4)#6	92.03(10)
F(1)#5-Sr(2)-O(4)#6	114.91(9)	O(4)#9-Na(1)-O(4)#12	80.84(14)
F(1)#2-Sr(2)-O(4)#6	159.70(9)	O(2)#4-Na(1)-Cl(1)	85.27(12)
O(3)#6-Sr(2)-O(4)#7	136.28(10)	O(2)-Na(1)-Cl(1)	85.27(12)
O(3)#7-Sr(2)-O(4)#7	81.01(10)	O(2)#10-Na(1)-Cl(1)	85.27(12)
O(3)-Sr(2)-O(4)#7	52.93(10)	O(4)#11-Na(1)-Cl(1)	131.52(9)
F(1)#8-Sr(2)-O(4)#7	159.70(9)	O(4)#9-Na(1)-Cl(1)	131.52(9)
F(1)#5-Sr(2)-O(4)#7	92.03(10)	O(4)#12-Na(1)-Cl(1)	131.52(9)
F(1)#2-Sr(2)-O(4)#7	114.91(9)	O(1)#13-Li(1)-O(1)#14	110.89(8)
O(4)#6-Sr(2)-O(4)#7	84.83(11)	O(1)#13-Li(1)-O(1)#1	180.00(17)
O(3)#6-Sr(2)-O(4)	52.93(9)	O(1)#14-Li(1)-O(1)#1	69.11(8)
O(3)#7-Sr(2)-O(4)	136.28(10)	O(1)#14-Li(1)-O(1)	180
O(3)-Sr(2)-O(4)	81.01(10)	O(1)#1-Li(1)-O(1)	110.89(8)
F(1)#8-Sr(2)-O(4)	114.91(9)	O(1)#13-Li(1)-O(1)#12	110.89(8)
F(1)#5-Sr(2)-O(4)	159.70(9)	O(1)#14-Li(1)-O(1)#12	110.89(8)
F(1)#2-Sr(2)-O(4)	92.03(10)	O(1)#1-Li(1)-O(1)#12	69.11(8)
O(4)#6-Sr(2)-O(4)	84.83(11)	O(1)-Li(1)-O(1)#12	69.11(8)
O(4)#7-Sr(2)-O(4)	84.83(11)	O(1)#13-Li(1)-O(1)#15	69.11(8)
O(2)#4-Na(1)-O(2)	119.33(4)	O(1)#14-Li(1)-O(1)#15	69.11(8)
O(2)#4-Na(1)-O(2)#10	119.33(4)	O(1)#1-Li(1)-O(1)#15	110.89(8)
O(2)-Na(1)-O(2)#10	119.33(4)	O(1)-Li(1)-O(1)#15	110.89(8)
O(2)#4-Na(1)-O(4)#11	54.48(11)	O(1)#12-Li(1)-O(1)#15	180.00(16)
O(2)-Na(1)-O(4)#11	91.95(12)	O(3)-B(1)-O(4)#7	119.1(4)
O(2)#10-Na(1)-O(4)#11	135.31(16)	O(3)-B(1)-O(2)#10	120.8(4)
O(2)#4-Na(1)-O(4)#9	91.95(12)	O(4)#7-B(1)-O(2)#10	120.1(4)
O(2)-Na(1)-O(4)#9	135.31(16)	O(1)#12-B(2)-O(1)	111.1(4)
O(2)#10-Na(1)-O(4)#9	54.48(11)	O(1)#12-B(2)-O(4)#12	109.4(4)
O(4)#11-Na(1)-O(4)#9	80.84(14)	O(1)-B(2)-O(4)#12	111.0(4)
O(2)#4-Na(1)-O(4)#12	135.31(16)	O(1)#12-B(2)-O(2)	111.6(4)
O(2)-Na(1)-O(4)#12	54.48(11)	O(1)-B(2)-O(2)	106.5(4)
O(2)#10-Na(1)-O(4)#12	91.95(12)	O(4)#12-B(2)-O(2)	107.1(4)
O(4)#11-Na(1)-O(4)#12	80.84(14)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+1,-x+2,z #2 -x+5/3,-y+4/3,-z+1/3

#3 x-y+2/3,x+1/3,-z+1/3 #4 -y+1,x-y+1,z

#5 y-1/3,-x+y+1/3,-z+1/3 #6 -x+y+1,-x+1,z

#7 -y+1,x-y,z #8 x-y+2/3,x-2/3,-z+1/3

#9 -x+1,-y+1,-z #10 -x+y,-x+1,z #11 x-y,x,-z

#12 y,-x+y+1,-z #13 x-y+1,x,-z #14 -x+2,-y+2,-z

#15 -y+2,x-y+1,z #16 -x+2/3,-y+4/3,-z+1/3

Figure S1a. Experimental and calculated XRD patterns of compound **1**. The red curve is experimental pattern; the black one is calculated one.

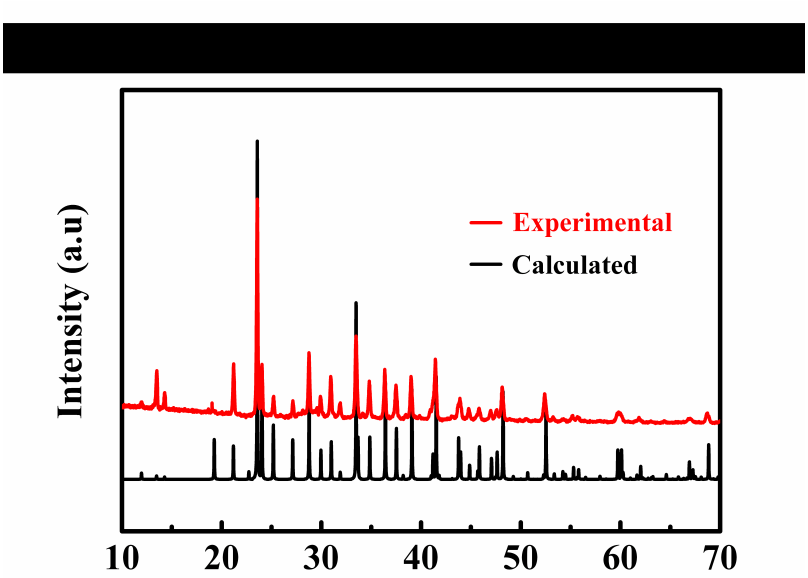


Figure S1b. Experimental and calculated XRD patterns of compound **2**. The red curve is experimental pattern; the black one is calculated one.

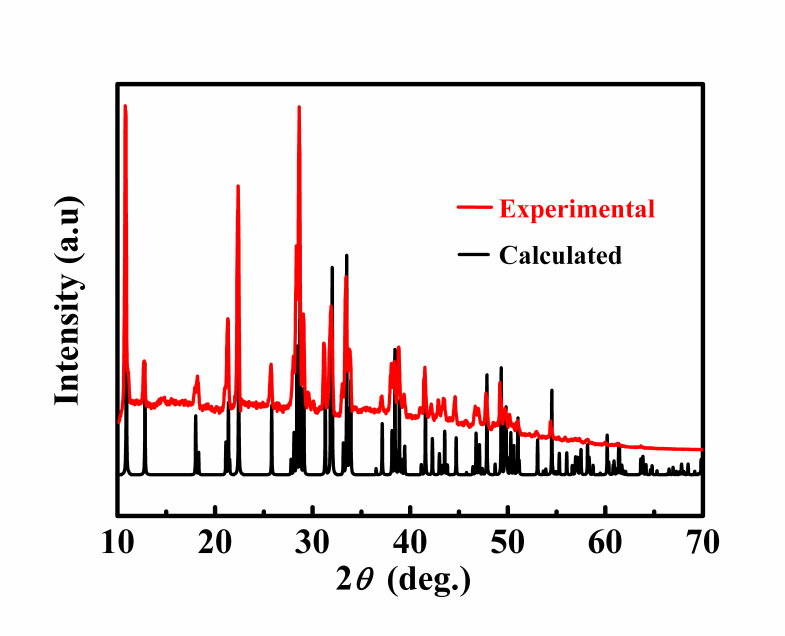


Figure S2. The coordinated environments and the connect patterns of Li atoms in the crystal structure of compound **1**.

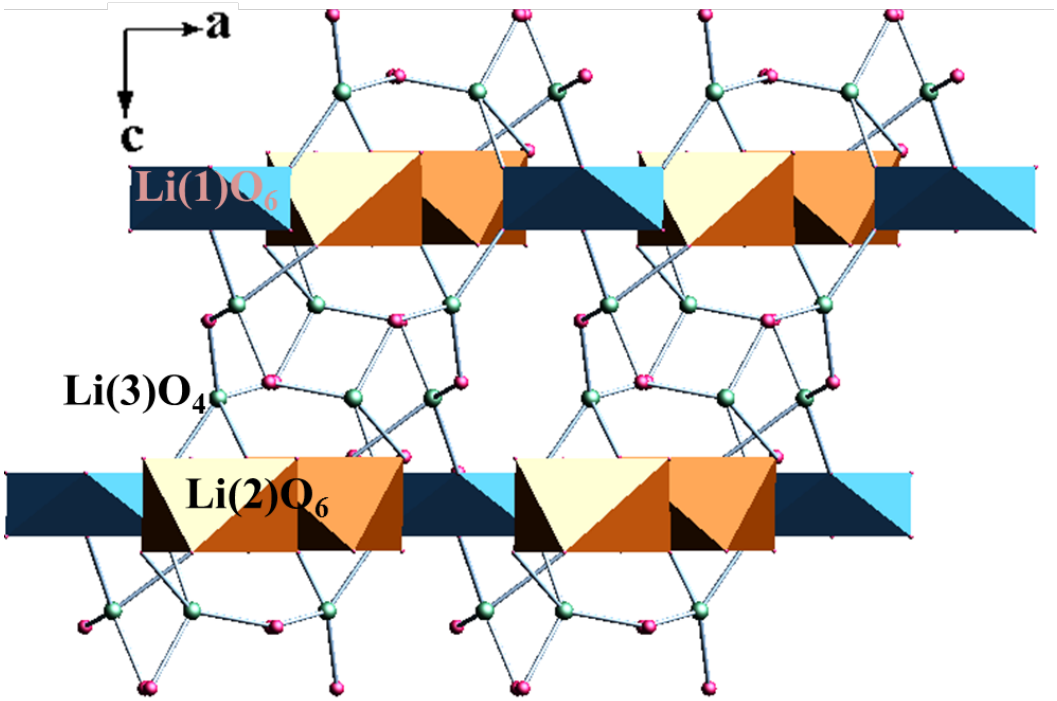


Figure S3. The coordinated environments of Li and Na atoms in the crystal structure of compound **2**.

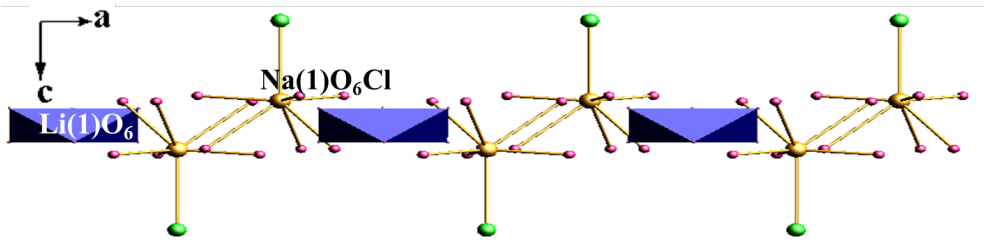


Figure S4. The arrangement of $(B_{12}O_{24})^{12-}$ groups in the crystal structure of compounds **1 (a, b)** and **2 (c, d)**.

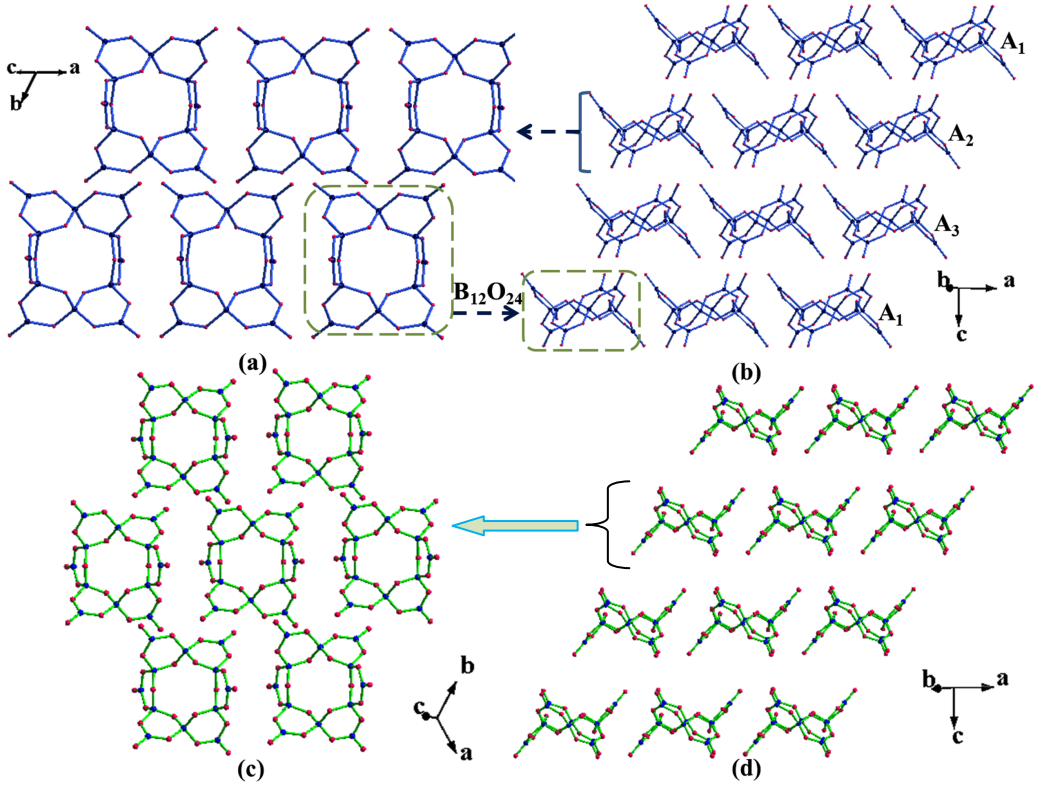


Figure S5. (a) The distribution of K atoms in the $(B_{12}O_{24})^{12-}$ groups. (b) The distribution of Sr atoms in the $(B_{12}O_{24})^{12-}$ groups.

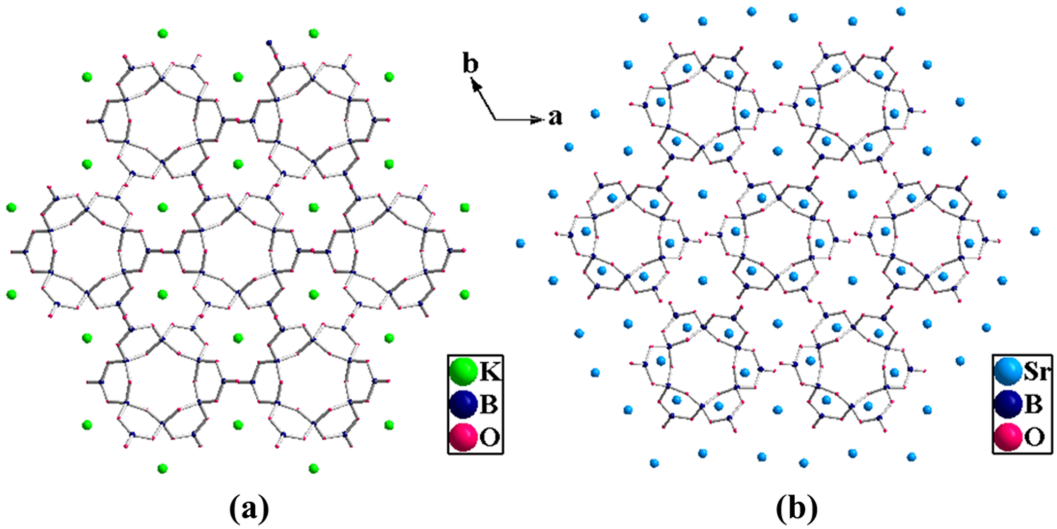
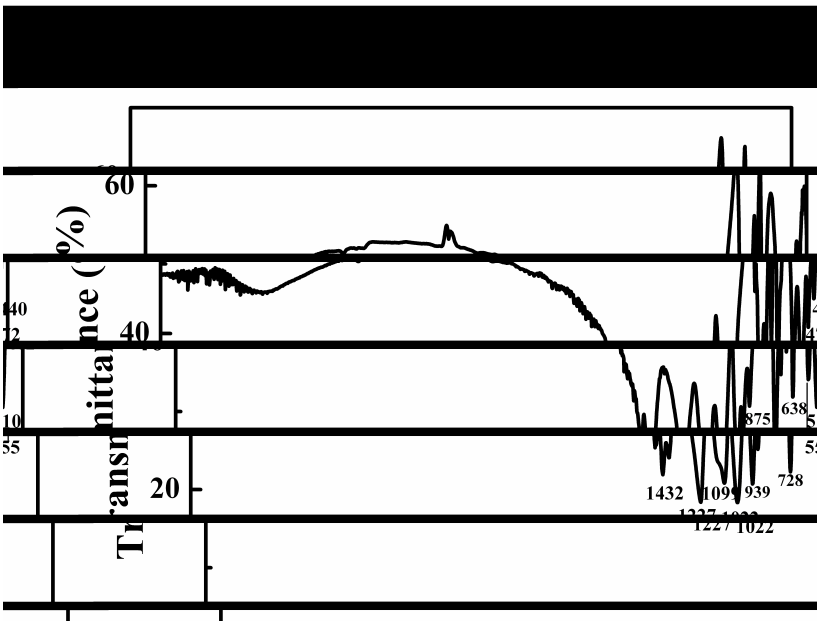
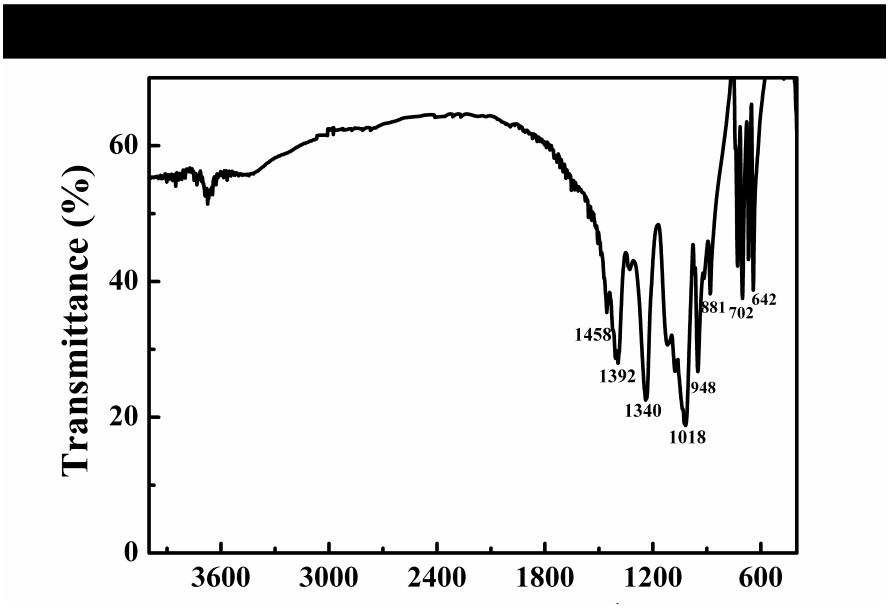


Figure S6. IR spectra for compounds **1 (a)** and **2 (b)**.



(a)



(b)

Figure S7. The TG-DSC curves for compound **2**.