Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

$Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$: Unprecedented combination of the largest two highly polymerized isolated B-O clusters with novel isolated B_9O_{18} FBB

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Table S1 Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for $Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.[a,b]

Atom	x	y	z	U(eq)	BVS
Li(1)	2983(8)	3669(9)	5951(2)	19(1)	1.06
Na(1)	6000(2)	6512(2)	6879(1)	17(1)	1.05
Na(2A)/Li(2A)	3333	6667	5130(1)	14(1)	1.16
Sr(1)	6667	3333	6294(1)	11(1)	1.77
Sr(2)	0	0	5954(1)	11(1)	2.07
B(1)	8488(5)	6823(5)	4999(2)	9(1)	3.05
B(2)	6079(5)	5927(4)	5651(2)	7(1)	3.01
B(3)	2382(4)	2386(5)	6994(2)	8(1)	2.99
B(4)	4833(6)	2657(6)	7500	7(1)	3.05
O(1)	10062(3)	7857(3)	5278(1)	9(1)	2.05
O(2)	7289(3)	5681(3)	5408(1)	10(1)	2.05
O(3)	5810(3)	7169(3)	5443(1)	11(1)	2.12
O(4)	5238(3)	5010(3)	6082(1)	9(1)	2.04
O(5)	1639(3)	2426(3)	6531(1)	10(1)	2.10
O(6)	1754(4)	2547(5)	7500	11(1)	2.05
O(7)	3793(3)	2242(3)	6998(1)	10(1)	1.99
O(8)	5583(4)	1621(4)	7500	13(1)	1.95
Cl(1)	3333	6667	7500	28(1)	0.65

[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.

Table S2 Selected bond lengths [Å] and angles [deg.] for $Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$.

Li(1)-O(4)	1.855(7)	Sr(1)-O(7)#1	2.897(2)
Li(1)-O(5)	1.857(7)	Sr(1)-O(7)#2	2.897(2)
Li(1)-O(1)#2	2.019(7)	Sr(2)-O(1)#1	2.607(2)
Li(1)-O(3)#10	2.186(7)	Sr(2)-O(1)#3	2.607(2)
Na(1)-O(4)	2.285(3)	Sr(2)-O(1)#4	2.607(2)
Na(1)-O(5)#10	2.344(3)	Sr(2)-O(5)	2.439(2)
Na(1)-O(6)#10	2.648(3)	Sr(2)-O(5)#5	2.439(2)
Na(1)-O(7)#2	2.450(3)	Sr(2)-O(5)#6	2.439(2)
Na(1)-O(8)#2	2.480(3)	B(1)-O(1)	1.457(4)
Na(1)-Cl(1)	2.9698(15)	B(1)-O(1)#11	1.466(4)
Na(2A)-O(2)#11	2.357(3)	B(1)-O(2)	1.475(4)
Na(2A)-O(2)#12	2.357(3)	B(1)-O(3)#14	1.482(4)
Na(2A)-O(2)#13	2.357(3)	B(2)-O(2)	1.388(4)
Na(2A)-O(3)	2.243(3)	B(2)-O(3)	1.394(4)
Na(2A)-O(3)#3	2.243(3)	B(2)-O(4)	1.330(4)
Na(2A)-O(3)#10	2.243(3)	B(3)-O(5)	1.333(4)
Sr(1)-O(2)	2.914(2)	B(3)-O(6)	1.401(4)
Sr(1)-O(2)#1	2.914(2)	B(3)-O(7)	1.384(4)
Sr(1)-O(2)#2	2.914(2)	B(4)-O(7)	1.485(4)
Sr(1)-O(4)#1	2.558(2)	B(4)-O(7)#8	1.485(4)
Sr(1)-O(4)#2	2.558(2)	B(4)-O(8)	1.446(6)
Sr(1)-O(4)	2.558(2)	B(4)-O(8)#2	1.450(6)
Sr(1)-O(7)	2.897(2)		
O(1)#1-Li(1)-O(3)#3	67.3(2)	O(7)#1-Sr(1)-O(2)#1	120.15(7)
O(4)-Li(1)-O(1)#1	121.3(4)	O(7)-Sr(1)-O(2)	120.15(7)
O(4)-Li(1)-O(3)#3	128.5(4)	O(7)-Sr(1)-O(2)#1	86.42(7)
O(4)-Li(1)-O(5)	118.1(3)	O(7)-Sr(1)-O(2)#2	150.58(7)
O(5)-Li(1)-O(1)#1	106.4(3)	O(7)#2-Sr(1)-O(2)#1	150.58(7)
O(5)-Li(1)-O(3)#3	104.0(3)	O(7)#1-Sr(1)-O(2)#2	86.42(7)
O(4)-Na(1)-O(5)#10	100.71(10)	O(7)#1-Sr(1)-O(7)#2	88.68(7)
O(4)-Na(1)-O(6)#10	156.73(10)	O(7)-Sr(1)-O(7)#2	88.68(7)
O(4)-Na(1)-O(7)#2	92.98(10)	O(7)#1-Sr(1)-O(7)	88.68(7)
O(4)-Na(1)-O(8)#2	99.11(9)	O(1)#3-Sr(2)-O(1)#1	84.50(8)

O(5)#10-Na(1)-O(6)#10	56.02(8)	O(1)#3-Sr(2)-O(1)#4	84.50(8)
O(5)#10-Na(1)-O(7)#2	92.75(10)	O(1)#4-Sr(2)-O(1)#1	84.50(8)
O(5)#10-Na(1)-O(8)#2	144.64(12)	O(5)-Sr(2)-O(1)#1	75.88(8)
O(7)#2-Na(1)-O(6)#10	88.74(11)	O(5)-Sr(2)-O(1)#3	120.27(8)
O(7)#2-Na(1)-O(8)#2	57.17(10)	O(5)#6-Sr(2)-O(1)#3	75.88(7)
O(8)#2-Na(1)-O(6)#10	101.27(9)	O(5)#5-Sr(2)-O(1)#1	120.27(8)
O(4)-Na(1)-Cl(1)	116.74(8)	O(5)#5-Sr(2)-O(1)#3	145.90(8)
O(5)#10-Na(1)-Cl(1)	102.76(8)	O(5)#6-Sr(2)-O(1)#1	145.90(8)
O(6)#10-Na(1)-Cl(1)	72.95(8)	O(5)-Sr(2)-O(1)#4	145.90(8)
O(7)#2-Na(1)-Cl(1)	142.51(8)	O(5)#5-Sr(2)-O(1)#4	75.88(7)
O(8)#2-Na(1)-Cl(1)	93.93(8)	O(5)#6-Sr(2)-O(1)#4	120.27(8)
O(2)#12-Na(2A)-O(2)#13	92.16(12)	O(5)#5-Sr(2)-O(5)#6	90.18(8)
O(2)#12-Na(2A)-O(2)#11	92.16(12)	O(5)-Sr(2)-O(5)#6	90.18(8)
O(2)#11-Na(2A)-O(2)#13	92.16(12)	O(5)-Sr(2)-O(5)#5	90.18(8)
O(3)-Na(2A)-O(2)#13	97.58(9)	O(1)-B(1)-O(1)#11	112.8(3)
O(3)#3-Na(2A)-O(2)#12	97.58(9)	O(1)#11-B(1)-O(2)	111.2(3)
O(3)#10-Na(2A)-O(2)#11	97.58(9)	O(1)-B(1)-O(2)	108.0(3)
O(3)#10-Na(2A)-O(2)#13	153.17(11)	O(1)-B(1)-O(3)#14	111.9(3)
O(3)-Na(2A)-O(2)#12	153.17(11)	O(1)#11-B(1)-O(3)#14	104.7(3)
O(3)#10-Na(2A)-O(2)#12	62.65(8)	O(2)-B(1)-O(3)#14	108.0(3)
O(3)#3-Na(2A)-O(2)#11	153.17(11)	O(2)-B(2)-O(3)	118.5(3)
O(3)-Na(2A)-O(2)#11	62.65(8)	O(4)-B(2)-O(2)	119.7(3)
O(3)#3-Na(2A)-O(2)#13	62.65(8)	O(4)-B(2)-O(3)	121.7(3)
O(3)#3-Na(2A)-O(3)	109.11(10)	O(5)-B(3)-O(6)	119.3(3)
O(3)#10-Na(2A)-O(3)	109.11(10)	O(5)-B(3)-O(7)	122.6(3)
O(3)#10-Na(2A)-O(3)#3	109.11(10)	O(7)-B(3)-O(6)	118.1(3)
O(2)#2-Sr(1)-O(2)	71.26(7)	O(7)#8-B(4)-O(7)	110.7(4)
O(2)#2-Sr(1)-O(2)#1	71.26(7)	O(8)-B(4)-O(7)	107.2(3)
O(2)-Sr(1)-O(2)#1	71.26(7)	O(8)#2-B(4)-O(7)	109.2(3)
O(7)#2-Sr(1)-O(2)#2	120.15(7)	O(8)-B(4)-O(7)#8	107.2(3)
O(7)#1-Sr(1)-O(2)	150.58(7)	O(8)#2-B(4)-O(7)#8	109.2(3)
O(7)#2-Sr(1)-O(2)	86.42(7)	O(8)-B(4)-O(8)#2	113.3(4)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x-y,z #2 -x+y+1,-x+1,z #3 -x+y,-x+1,z
#4 x-1,y-1,z #5 -x+y,-x,z #6 -y,x-y,z #7 -y+1,x-y+1,-z+3/2
#8 x,y,-z+3/2 #9 -x+y,-x+1,-z+3/2 #10 -y+1,x-y+1,z
#11 y,-x+y+1,-z+1 #12 x-y,x,-z+1 #13 -x+1,-y+1,-z+1
#14 x-y+1,x,-z+1

Table S3 Basic information of anhydrous borates containing two kinds of isolated B−O clusters.

No.	Chemical Formula [a]	Space Group	B-O Clusters (I-B-O + II-B-O + III-B-O)	N_B [b]	Cation /Boron Ratio	Reference
1	$Ho_{31}O_{27}(BO_3)_3(BO_4)_6$	$R\bar{3}$	$[BO_3]+[BO_4]$	2	3.40	[1]
2	$Ni_7U(BO_3)_2(BO_4)_2O_2$	*Pnnm*	$[BO_3]+[BO_4]$	2	2.00	[2]
3	$Al_8(BO_3)_4(B_2O_5)F_8$	$P4_2/nmc$	$[BO_3]+[B_2O_5]$	3	1.50	[3]
4	$Ba_3Zn(BO_3)(B_2O_5)F$	$P2_1/c$	$[BO_3]+[B_2O_5]$	3	1.33	[4]
5	$Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$	$C2/c$	$[BO_3]+[B_2O_5]$	3	1.50	[4]
6	$Ba_2Sc_2(BO_3)_2(B_2O_5)$	$P2_1/c$	$[BO_3]+[B_2O_5]$	3	1.00	[5]
7	$Ba_5(BO_3)_2(B_2O_5)$	$C2/c$	$[BO_3]+[B_2O_5]$	3	1.20	[6]
8	$Cu_{15}(BO_3)_6(B_2O_5)_2O_2$	$P\bar{1}$	$[BO_3]+[B_2O_5]$	3	1.50	[7]
9	$Cu_9Ti_2(BO_3)_2(B_2O_5)_2O_6$	$P\bar{1}$	$[BO_3]+[B_2O_5]$	3	1.83	[8]
10	$K_4Sr_4(UO_2)_{13}(BO_3)_2(B_2O_5)_2O_{12}$	$P\bar{1}$	$[BO_3]+[B_2O_5]$	3	1.33	[9]
11	$LiNa_5Be_{12}(BO_3)_6(B_2O_5)_3$	*Pc*	$[BO_3]+[B_2O_5]$	3	1.50	[10]
12	$Na_2Be_4(BO_3)_2(B_2O_5)$	*P*1	$[BO_3]+[B_2O_5]$	3	1.50	[10]
13	$Pb_8(BO_3)_2(B_2O_5)O_3$	*Ama*2	$[BO_3]+[B_2O_5]$	3	2.00	[11]
14	$Pb_3Ba_7(BO_3)_5(B_2O_5)F$	$Pmn2_1$	$[BO_3]+[B_2O_5]$	3	1.43	[12]
15	$Sr_2Sc_2(BO_3)_2(B_2O_5)$	$P\bar{1}$	$[BO_3]+[B_2O_5]$	3	1.00	[5]
16	$Sr_2LiBe(BO_3)(B_2O_5)$	$P2_1/c$	$[BO_3]+[B_2O_5]$	3	1.33	[13]
17	$Ca_{10}Ge_{16}(BO_4)_2(B_2O_7)_2O_{29}$	*Pba*2	$[BO_4]+[B_2O_7]$	3	4.33	[14]
18	$CsZn_2B_3O_7/Cs_3Zn_6(BO_3)_3(B_3O_6)_2$	$Cmc2_1$	$[BO_3]+[B_3O_6]$	4	1.00	[15]
19	$Cs_3Zn_6(BO_3)_3(B_3O_6)_2$	$Cmc2_1$	$[BO_3]+[B_3O_6]$	4	1.00	[16]

20	$K_3Be_6(BO_3)_3(B_3O_6)_2$	$P2_1$	$[BO_3]+[B_3O_6]$	4	1.00	[17]
21	$La_4(BO_3)(B_3O_8)F_2$	$P2_1/c$	$[BO_3]+[B_3O_8]$	4	1.00	[18]
22	$Ca_3Be_6(BO_3)_2(B_3O_{10})F$	$P6_3/m$	$[BO_3]+[B_3O_{10}]$	4	2.20	[19]
23	α-$Pb_2Ba_4Zn_4(B_2O_5)(B_6O_{13})_2$	$P1$	$[B_2O_5]+[B_6O_{13}]$	8	0.71	[20]
24	β-$Pb_2Ba_4Zn_4(B_2O_5)(B_6O_{13})_2$	Cc	$[B_2O_5]+[B_6O_{13}]$	8	0.71	[20]
25	γ-$Pb_2Ba_4Zn_4(B_2O_5)(B_6O_{13})_2$	$P3_2$	$[B_2O_5]+[B_6O_{13}]$	8	0.71	[20]
26	$Ba_2KZn_3(B_3O_6)(B_6O_{13})$	$P\bar{1}$	$[B_2O_5]+[B_6O_{13}]$	9	0.67	[21]
27	$Ba_4K_2Zn_5(B_3O_6)_3(B_9O_{19})$	$P2_1/n$	$[B_3O_6]+[B_9O_{19}]$	12	0.61	[22]
28	$Cs_{18}Mg_6(B_5O_{10})_3(B_7O_{14})_2F$	$C2/c$	$[B_5O_{10}]+[B_7O_{14}]$	12	0.83	[23]
29	$Rb_{18}Mg_6(B_5O_{10})_3(B_7O_{14})_2F$	$C2/c$	$[B_5O_{10}]+[B_7O_{14}]$	12	0.83	[23]
30	$Ca_3Na_4LiBe_4B_{10}O_{24}F$ /$Ca_6Na_8Li_2Be_8(BO_3)_8(B_{12}O_{24})F_2$	$R\bar{3}$	$[BO_3] + [B_{12}O_{24}]$	13	1.20	[24]
31	$Cd_3Na_4LiBe_4B_{10}O_{24}F$ /$Cd_6Na_8Li_2Be_8(BO_3)_8(B_{12}O_{24})F_2$	$R\bar{3}$	$[BO_3] + [B_{12}O_{24}]$	13	1.20	[25]
32	$Sr_3Na_4LiBe_4B_{10}O_{24}F$ /$Sr_6Na_8Li_2Be_8(BO_3)_8(B_{12}O_{24})F_2$	$R\bar{3}$	$[BO_3] + [B_{12}O_{24}]$	13	1.20	[25]
33	$Ba_6Al_4(BO_3)_2(B_6O_{13})(B_6O_{14})$	$P\bar{1}$	$[BO_3]+[B_6O_{13}]$ +$[B_6O_{14}]$	13	0.71	[26]
34	$Ba_4Na_2Zn_4(B_3O_6)_2(B_{12}O_{24})$	$P\bar{1}$	$[B_3O_6]+[B_{12}O_{24}]$	15	0.67	[27]
35	$Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$	$P6_3/m$	$[B_9O_{18}]+[B_{12}O_{24}]$	21	0.86	This work

[a] The compounds on either side of the " / " sign are the same one in the chemical formula column.

[b] N_B displays the total number of B atoms in two isolated B-O clusters.

Table S4 Basic information of anhydrous borates with petal-like $B_{12}O_{24}$ clusters.

No.	Chemical Formula [a]	Space Group	B-O Clusters	Unit Cell Dimensions		Reference
1	$Li_3NaBaB_6O_{12}$ /$Li_6Na_2Ba_2(B_{12}O_{24})$	$R\bar{3}$	$[B_{12}O_{24}]$	a = 9.462(9) (Å) b = 9.462(9) (Å) c = 18.71(3) (Å)	α = 90 ° β = 90 ° γ = 120 °	[28]
2	$Li_3KB_4O_8$ / $Li_9K_3(B_{12}O_{24})$	$R\bar{3}$	$[B_{12}O_{24}]$	a = 9.2106(12) (Å) b = 9.2106(12) (Å) c = 19.705(5) (Å)	α = 90 ° β = 90 ° γ = 120 °	[29]
3	$LiNa_2Sr_8(B_{12}O_{24})F_6Cl$	$R\bar{3}$	$[B_{12}O_{24}]$	a = 9.677(4) (Å) b = 9.677(4) (Å) c = 24.30(2) (Å)	α = 90 ° β = 90 ° γ = 120 °	[29]
4	$Li_7Na_2KRb_2(B_{12}O_{24})$	$R\bar{3}$	$[B_{12}O_{24}]$	a = 9.548(6) (Å) b = 9.548(6) (Å) c = 19.55(2) (Å)	α = 90 ° β = 90 ° γ = 120 °	[30]
5	$Li_{7.35}Na_{2.36}K_{1.50}Cs_{0.78}(B_{12}O_{24})$	$R\bar{3}$	$[B_{12}O_{24}]$	a = 9.479(7) (Å) b = 9.479(7) (Å) c = 19.493(14) (Å)	α = 90 ° β = 90 ° γ = 120 °	[30]
6	$Li_{6.97}Na_{2.63}K_{1.24}Cs_{1.15}(B_{12}O_{24})$	$R\bar{3}$	$[B_{12}O_{24}]$	a = 9.5297(12) (Å) b = 9.5297(12) (Å) c = 19.534(5) (Å)	α = 90 ° β = 90 ° γ = 120 °	[30]
7	$Li_{7.27}Na_{2.67}Rb_{2.06}(B_{12}O_{24})$	$R\bar{3}$	$[B_{12}O_{24}]$	a = 9.4530(9) (Å) b = 9.4530(9) (Å) c = 19.413(3) (Å)	α = 90 ° β = 90 ° γ = 120 °	[30]
8	$Ca_3LiNa_4Be_4B_{10}O_{24}F$ /$Ca_6Li_2Na_8Be_8(BO_3)_8(B_{12}O_{24})F_2$	$R\bar{3}$	$[BO_3]$+ $[B_{12}O_{24}]$	a = 9.2851(11) (Å) b = 9.2851(11) (Å) c = 38.042(8) (Å)	α = 90 ° β = 90 ° γ = 120 °	[24]
9	$Cd_3LiNa_4Be_4B_{10}O_{24}F$ /$Cd_6Li_2Na_8Be_8(BO_3)_8(B_{12}O_{24})F_2$	$R\bar{3}$	$[BO_3]$+ $[B_{12}O_{24}]$	a = 9.3019(8) (Å) b = 9.3019(8) (Å) c = 37.782(7) (Å)	α = 90 ° β = 90 ° γ = 120 °	[25]

10	$Sr_3LiNa_4Be_4B_{10}O_{24}F$ /$Sr_6Li_2Na_8Be_8(BO_3)_8(B_{12}O_{24})F_2$	$R\bar{3}$	$[BO_3]$+ $[B_{12}O_{24}]$	a = 9.4645(1) (Å) b = 9.4645(1) (Å) c = 38.842(8) (Å)	α = 90 ° β = 90 ° γ = 120 °	[25]
11	$Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$	$P6_3/m$	$[B_9O_{18}]$+ $[B_{12}O_{24}]$	a = 9.3046(2) (Å) b = 9.3046(2) (Å) c = 24.3239(7) (Å)	α = 90 ° β = 90 ° γ = 120 °	This work

[a] The compounds on either side of the " / " sign are the same one in the chemical formula column.

Table S5 The assignments of the IR absorption peaks for $Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$

Mode description	IR (cm^{-1})
Asymmetric stretching vibration of [BO_3] groups	1443, 1281, 1234
Asymmetric stretching vibration of [BO_4] groups	1149, 1092, 1018
Symmetric stretching vibration of [BO_3] groups	952
Symmetric stretching vibration of [BO_4] groups	879
Out-of-plane bending of [BO_3] groups	732, 644
In-plane bending of [BO_3] groups	590, 517
Bending of [BO_4] groups	400–500

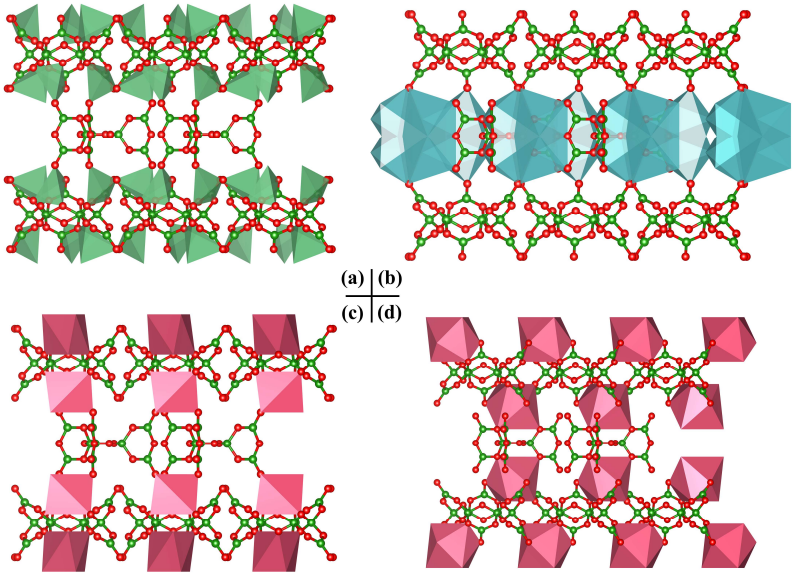

Fig. S1 Coordination polyhedra and arrangement mode of the (a) Li(1), (b) Na(1), (c) Sr(2), and (d) Sr(1) atoms in the title compound.

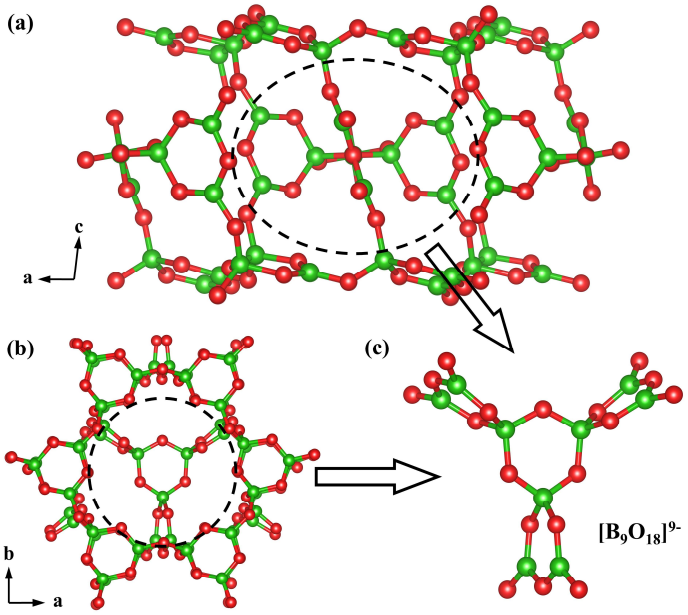

Fig. S2 The $[B_9O_{18}]^{9-}$ group in $Na_{11}B_{21}O_{36}X_2$ (X = Cl, Br) acting as a connecting unit.

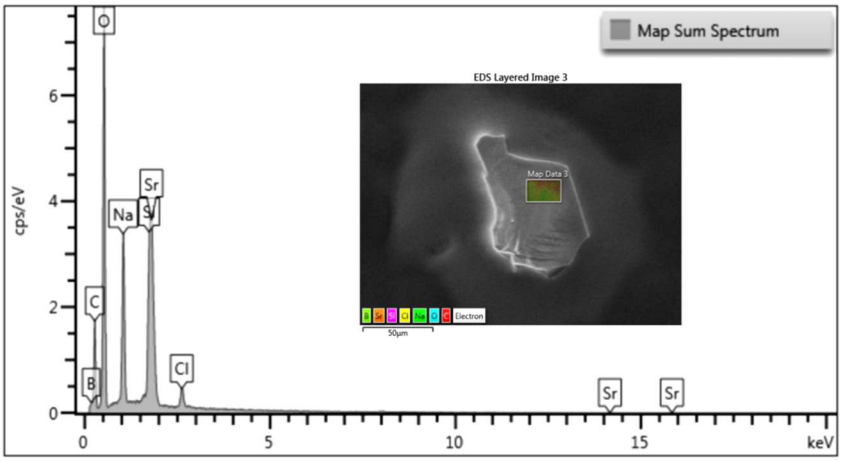

Fig. S3 Elemental analysis of $Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$. Energy dispersive X-ray spectroscope (EDS) was performed to verify the presence of the corresponding elements (except Li) in the compound.

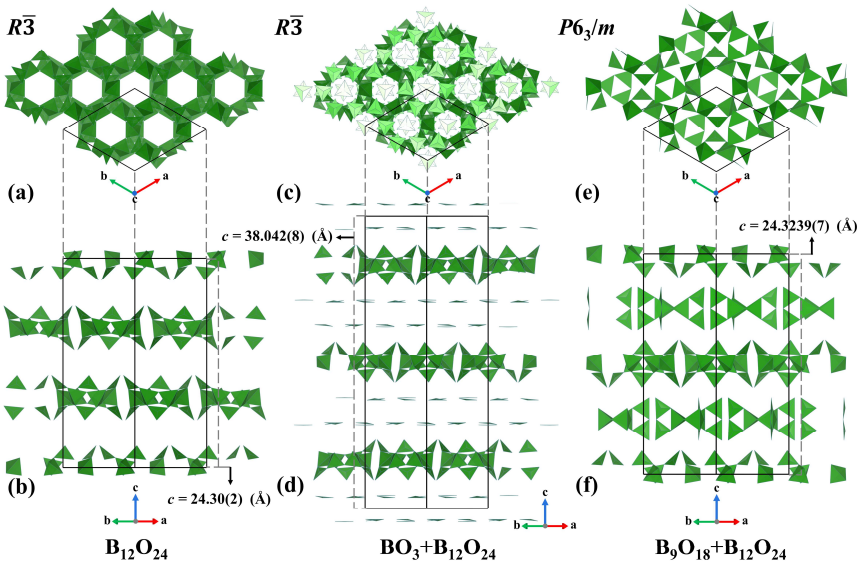

Fig. S4 The structural transformation of space group from $LiNa_2Sr_8(B_{12}O_{24})F_6Cl$ to $Ca_6Li_2Na_8Be_8(BO_3)_8(B_{12}O_{24})F_2$ to $Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$. (Considering about the great influence of the B-O clusters on the structure of the compounds, and in order to keep the picture simple and easy to understand, only the arrangement of the B-O polyhedra is shown in the picture.)

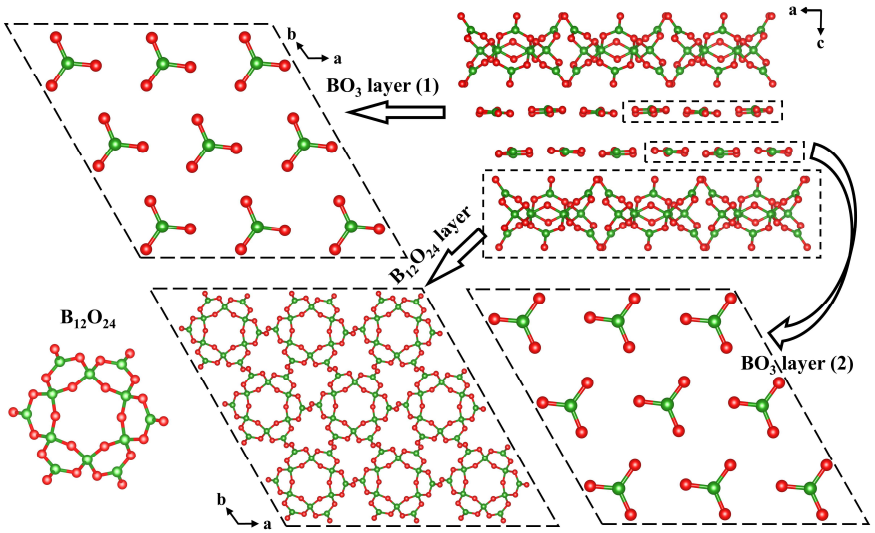

Fig. S5 The BO_3 and $B_{12}O_{24}$ groups in $M_3LiNa_4Be_4B_{10}O_{24}F$ (M = Sr, Cd, Ca) with the lamellar arrangement.

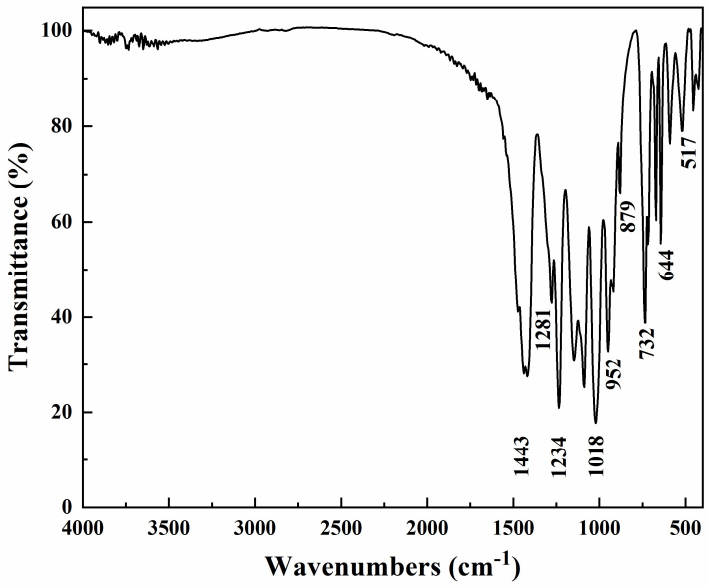

Fig. S6 The infrared spectrum of $Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$.

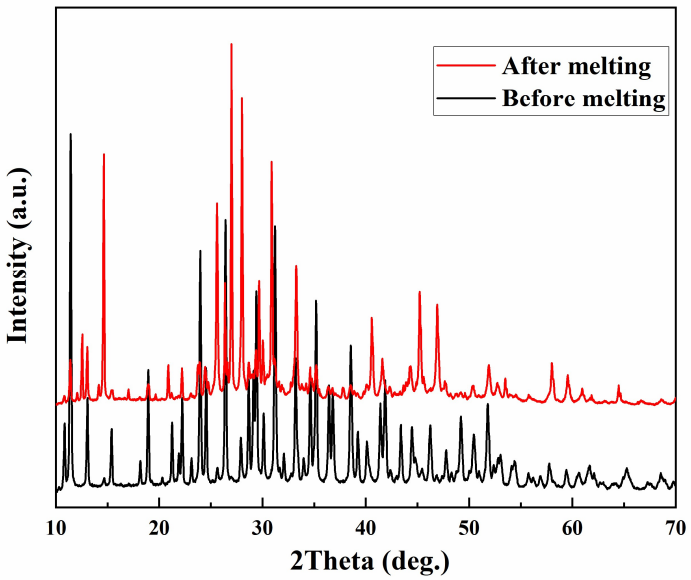

Fig. S7 The X-ray diffraction patterns of $Li_{6.58}Na_{7.43}Sr_4(B_9O_{18})(B_{12}O_{24})Cl$ before and after melting.

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