Electronic Supplementary Information

Ions-induced structural and optical performances evolution in LBO-like crystals: Experimental and theoretical investigation

Yun Yang,[a] Shilie Pan*,[a]

[a]*CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China*

*To whom correspondence should be addressed

E-mail: slpan@ms.xjb.ac.cn (Shilie Pan)

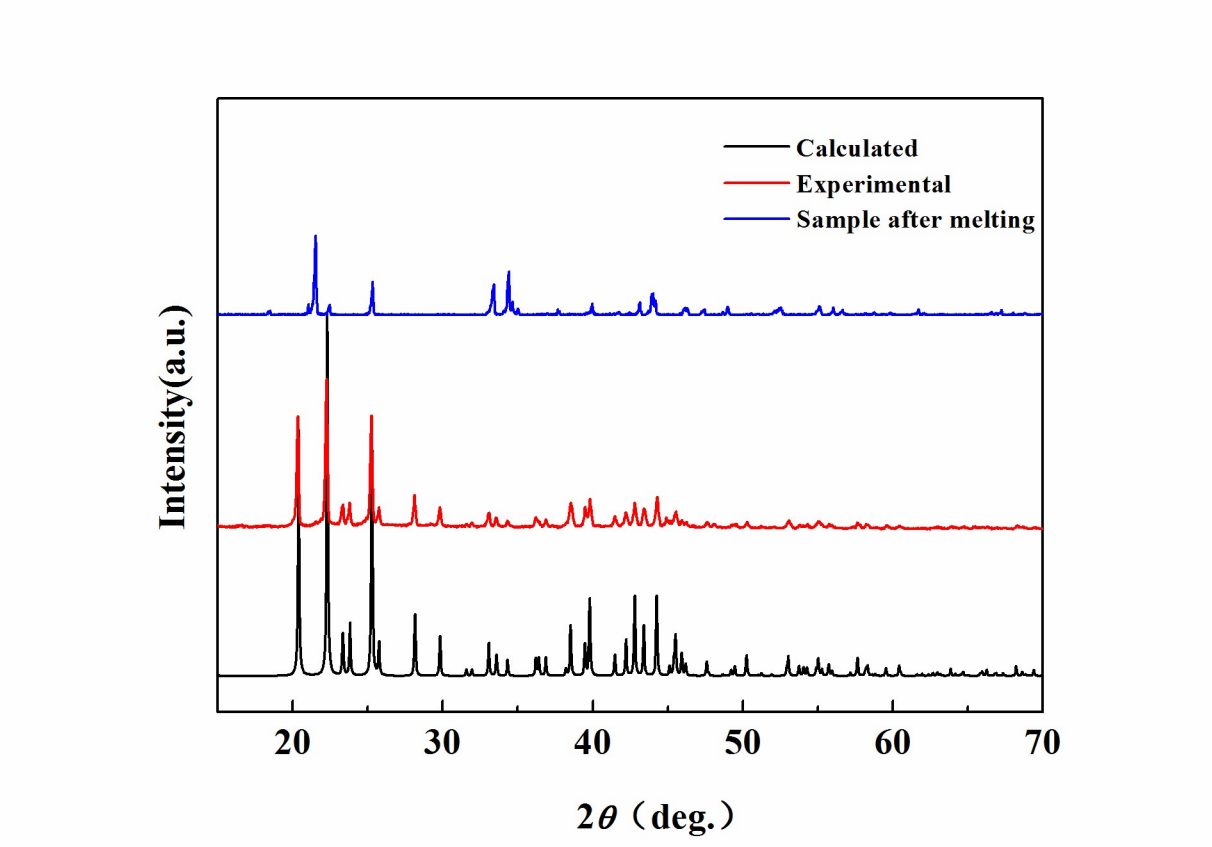
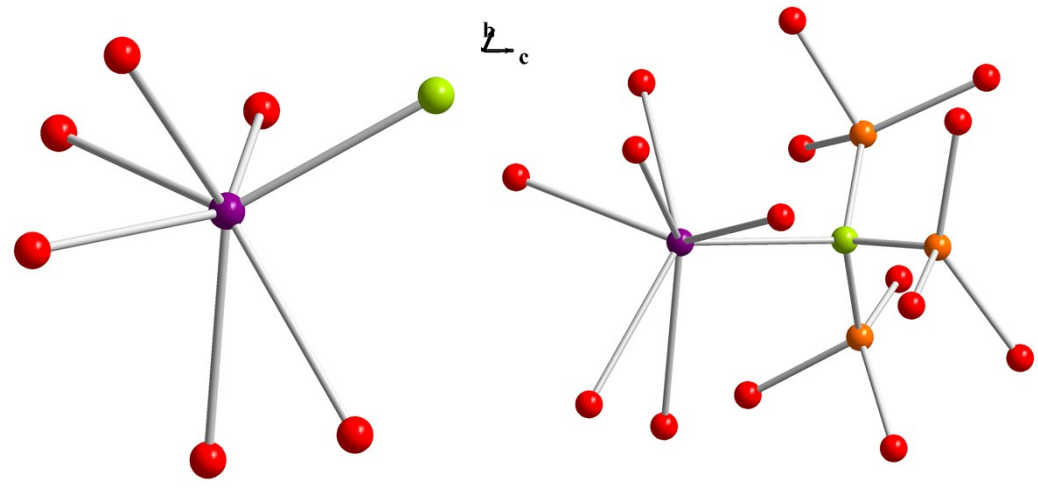
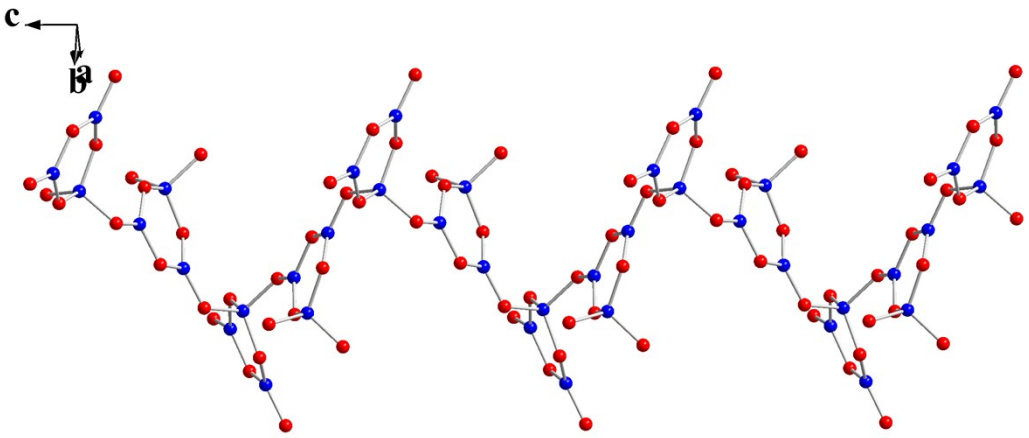


Fig. S1 Powder X−ray diffraction patterns of $Li_3KB_9O_{15}F$.

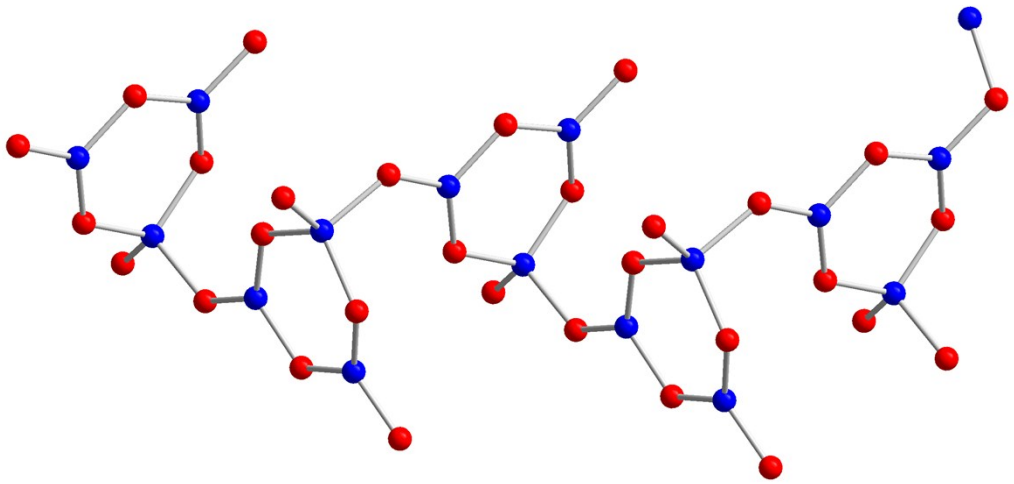


(a) **(b)**

Fig. S2 (a) KO_6F polyhedron. (b) $Li_3KO_{15}F$ cluster is formed by three LiO_3F and one KO_6F through sharing F ions.



(a)



(b)

Fig. S3 The 1D B-O chain in (a) $CsLiB_6O_{10}$ and (b) CsB_3O_5.

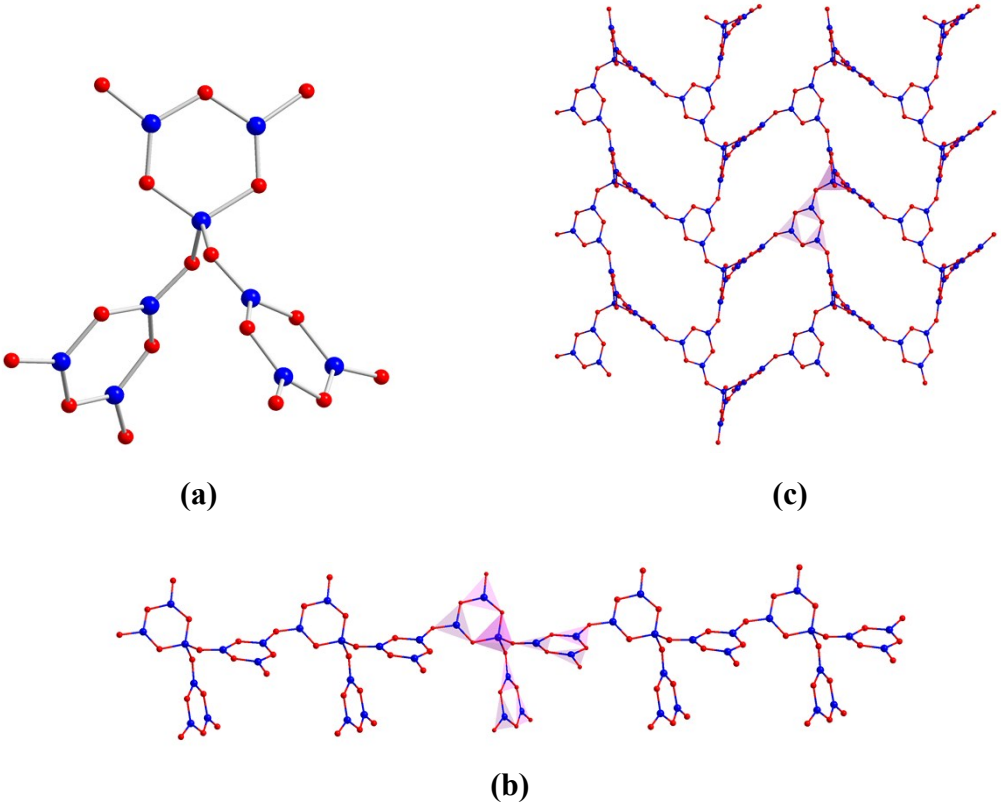


Fig. S4 Crystal structure of CsB_9O_{14}. (a) FBB B_9O_{17} (b) B_9O_{16} chain viewed along the *a* axis; (c) The 3D open-framework with 30-MR channels.

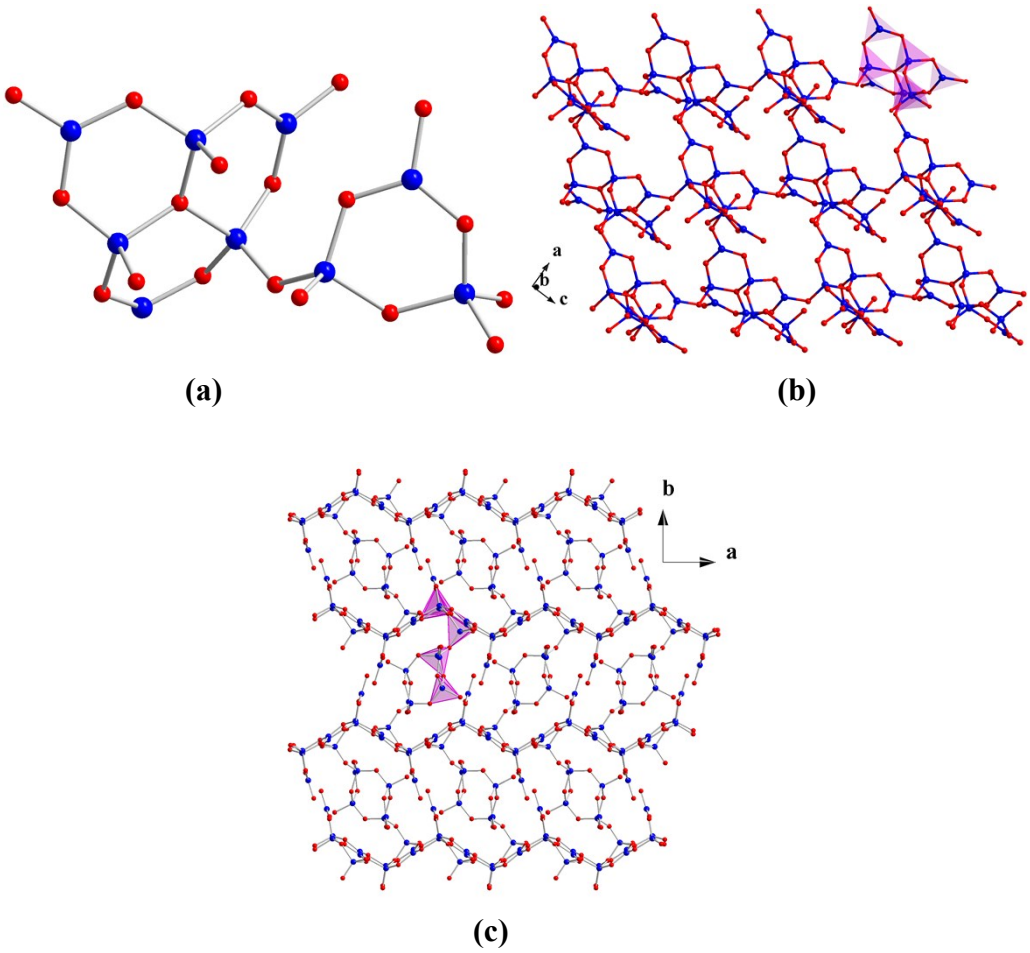


Fig. S5 Crystal structure of $AmB_9O_{13}(OH)_4(H_2O)$. (a) FBB, B_9O_{20}; (b) The 2D layered structure with18-MR channels in the *ac* plane; (c) The 3D open-framework.

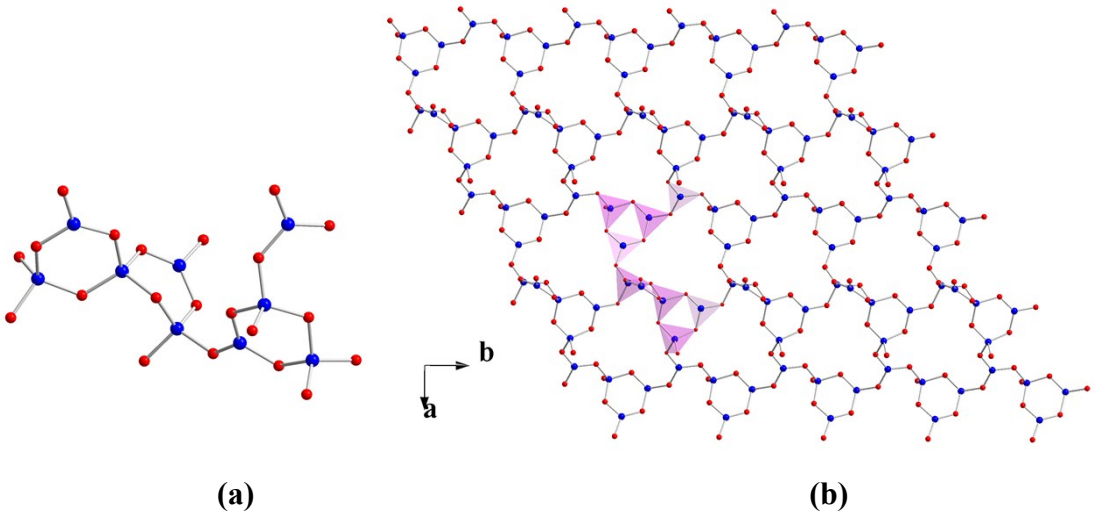


Fig. S6 Crystal structure of $NdB_{18}O_{25}(OH)_{13}Br_3$. (a) FBB B_9O_{21}; (b) The 2D layered structure viewed along the *a* axis.

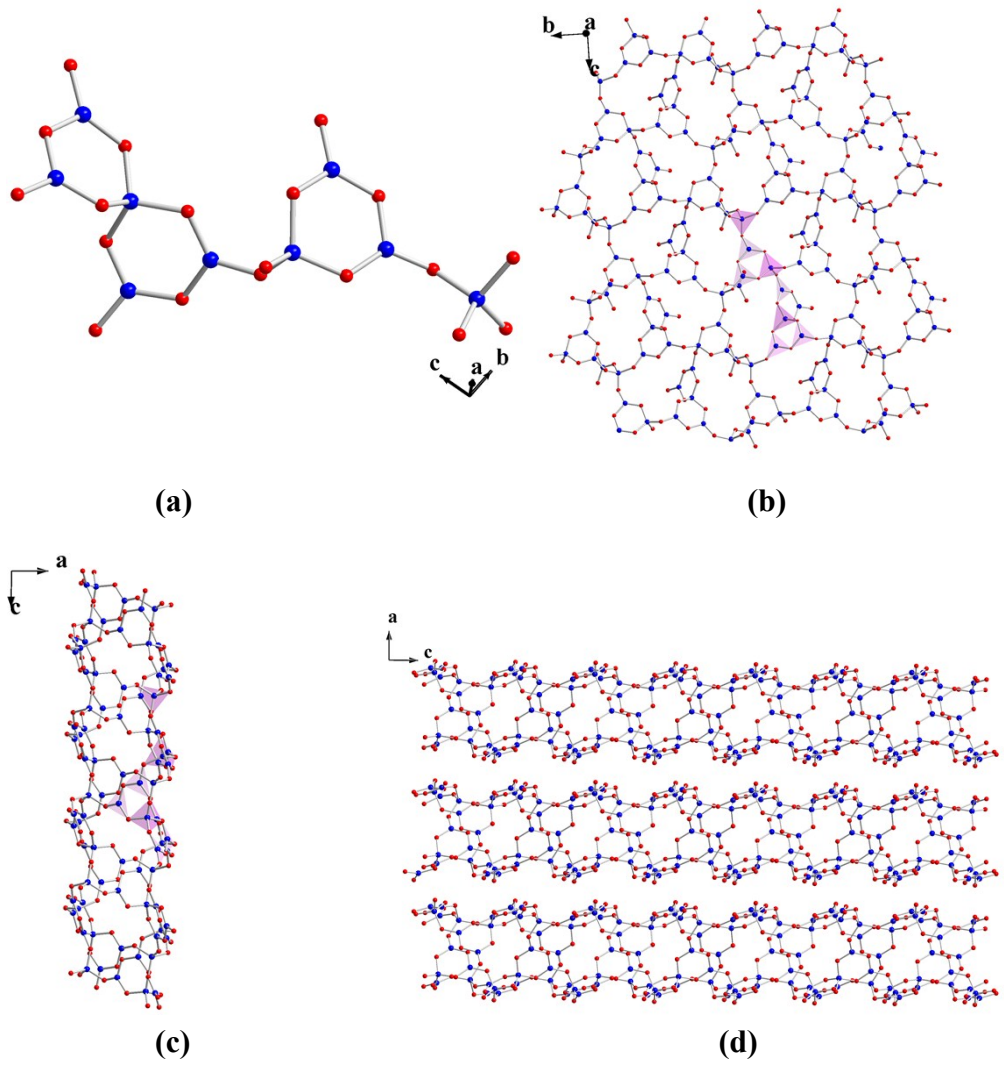


Fig. S7 Crystal structure of $Na_2B_6O_{10}$. (a) FBB B_9O_{19}; (b) The 2D layered structure viewed in the *bc* plane for single chains; (c) and (d) The double-layered structure viewed along the *b* axis.

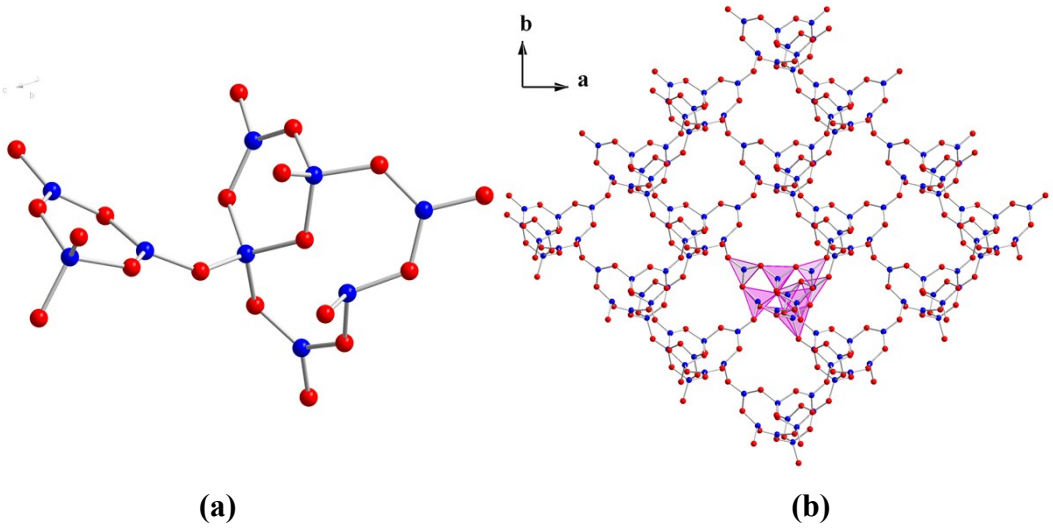


Fig. S8 Crystal structure of $Na_2B_9O_{15}(H_2O)(H_3O)$. (a) FBB B_9O_{19}; (b) The 3D open framework formed through sharing O atoms between B_3O_7 and B_6O_{13} clusters, in which big channels are observed along the *b* axis.

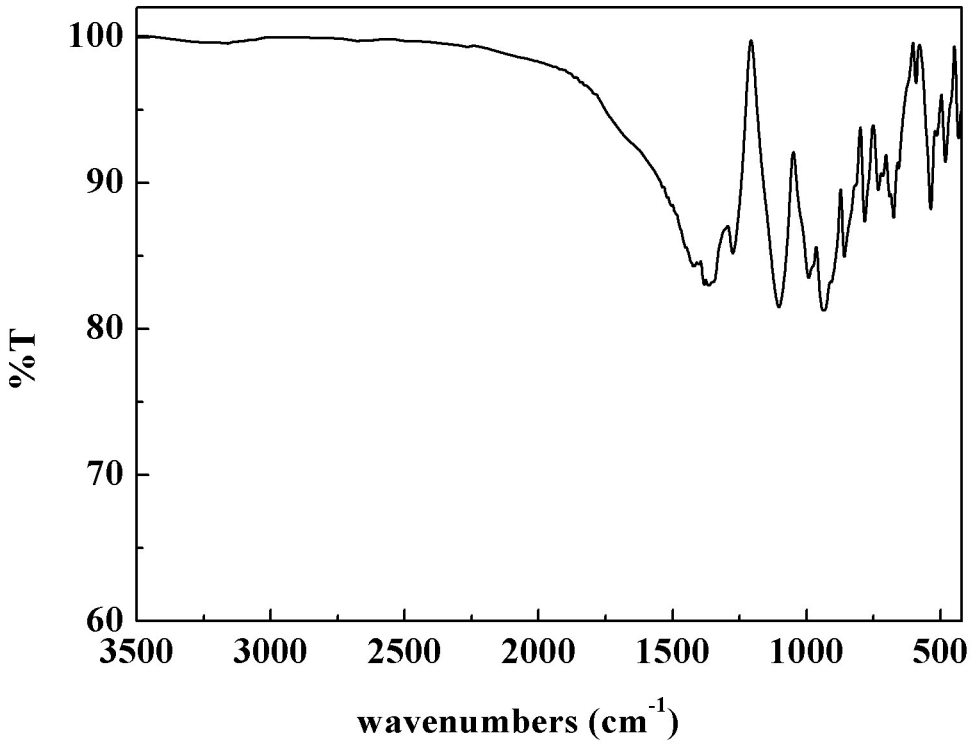


Fig. S9 Infrared spectrum of $Li_3KB_9O_{15}F$.

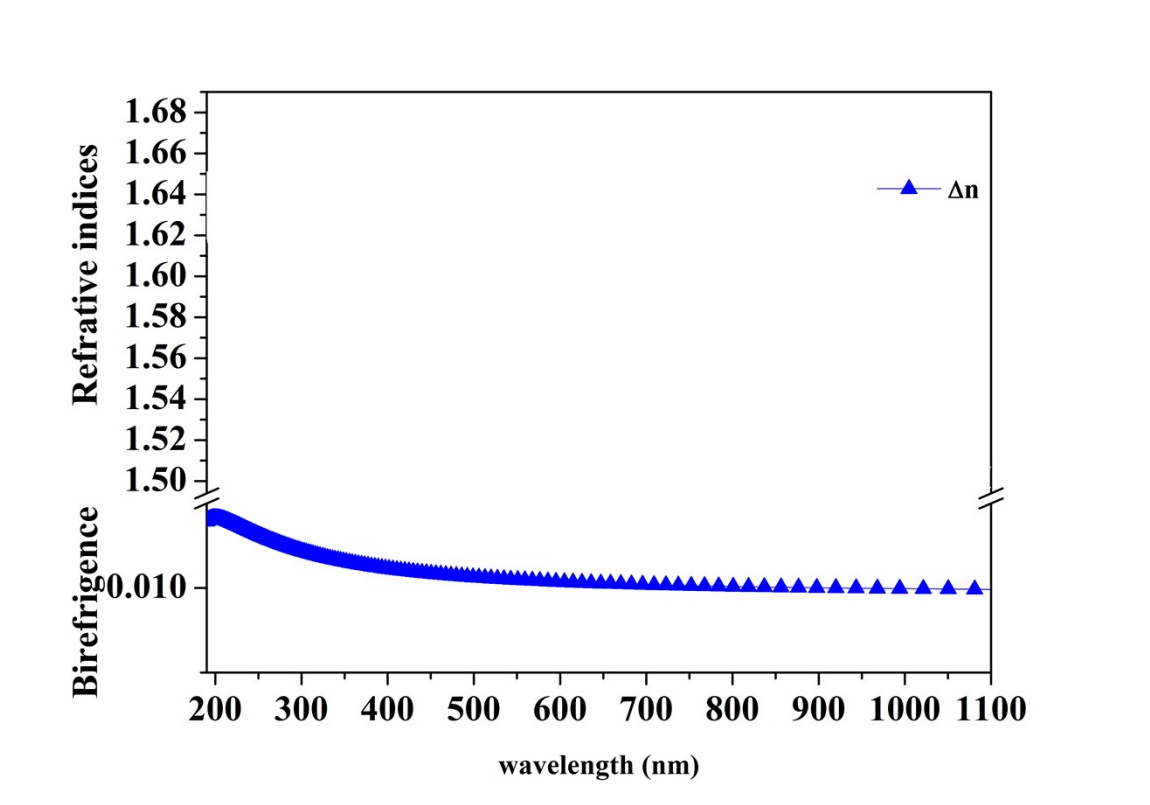


Fig. S10 The obtained birefringence of $Li_3KB_9O_{15}F$.

Table S1. Atomic coordinates, equivalent isotropic displacement parameters ($Å^2$) and bond valence sum (BVS) for $Li_3KB_9O_{15}F$. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Li(1)	-1541(4)	-1193(5)	-555(3)	21(1)
K(1)	0	0	1524(1)	24(1)
B(1)	2063(3)	2969(3)	1887(2)	16(1)
B(2)	2691(3)	2023(3)	2993(2)	14(1)
B(3)	980(3)	3550(3)	733(2)	13(1)
O(1)	1744(2)	2064(2)	2527(1)	22(1)
O(2)	1083(2)	2731(2)	1370(1)	18(1)
O(3)	3295(2)	3956(2)	1812(1)	15(1)
O(4)	628(2)	4446(2)	1135(1)	16(1)
O(5)	2298(2)	1155(2)	3624(1)	14(1)
F(1)	0	0	-130(2)	18(1)

Table S2. Selected bond distances (Å) and angles (deg) for $Li_3KB_9O_{15}F$.

K(1)-F(1)	2.646(3)	B(1)-O(3)	1.358(3)
K(1)-O(1)	2.808(2)	B(1)-O(1)	1.399(3)
K(1)-O(1)#1	2.808(2)	B(1)-O(2)	1.344(3)
K(1)-O(1)#2	2.808(2)	B(2)-O(1)	1.378(3)
K(1)-O(2)#1	2.862(2)	B(2)-O(4)#3	1.372(3)
K(1)-O(2)#2	2.862(2)	B(2)-O(5)	1.353(3)
K(1)-O(2)	2.862(2)	B(3)-O(2)	1.462(3)
Li(1) -F(1)	1.808(5)	B(3)-O(3)#6	1.481(3)
Li(1)-O(4)#6	1.962(5)	B(3)-O(4)	1.481(3)
Li(1)-O(3)#9	1.982(5)	B(3)-O(5)#5	1.464(3)
Li(1)-O(5)#10	2.074(5)	O(1)#1-K(1)-O(1)#2	90.54(6)
F(1)-K(1)-O(1)	124.88(4)	F(1)-K(1)-O(2)#1	85.07(4)
F(1)-K(1)-O(1)#1	124.88(4)	O(1)-K(1)-O(2)#1	94.04(5)
O(1)-K(1)-O(1)#1	90.54(6)	O(1)#1-K(1)-O(2)#1	48.01(5)
F(1)-K(1)-O(1)#2	124.88(4)	O(1)#2-K(1)-O(2)#1	138.26(6)
O(1)-K(1)-O(1)#2	90.54(6)	F(1)-K(1)-O(2)#2	85.07(4)
O(1)-K(1)-O(2)#2	138.26(6)	O(1)#1-K(1)-O(2)#2	94.04(5)
O(1)#2-K(1)-O(2)#2	48.01(5)	O(2)#1-K(1)-O(2)#2	119.269(13)
F(1)-K(1)-O(2)	85.07(4)	O(1)-K(1)-O(2)	48.01(5)
O(1)#1-K(1)-O(2)	138.26(6)	O(1)#2-K(1)-O(2)	94.04(5)
O(2)#1-K(1)-O(2)	119.269(13)	O(2)#2-K(1)-O(2)	119.269(13)
O(2)-B(1)-O(3)	125.7(3)	O(2)-B(1)-O(1)	114.5(2)
O(3)-B(1)-O(1)	119.8(2)	O(2)-B(3)-O(5)#5	113.5(2)
O(2)-B(3)-O(4)	109.5(2)	O(5)#5-B(3)-O(4)	105.7(2)

O(2)-B(3)-O(3)#6	106.4(2)	O(5)#5-B(3)-O(3)#6	110.9(2)
O(4)-B(3)-O(3)#6	111.0(2)	O(5)-B(2)-O(4)#3	123.7(2)
O(5)-B(2)-O(1)	117.0(2)	O(4)#3-B(2)-O(1)	119.4(2)
F(1)-Li(1)-O(4)#6	108.4(2)	F(1)-Li(1)-O(3)#9	118.2(3)
O(4)#6-Li(1)-O(3)#9	94.5(2)	F(1)-Li(1)-O(5)#10	106.1(2)
O(4)#6-Li(1)-O(5)#10	136.1(3)	O(3)#9-Li(1)-O(5)#10	92.4(2)

Note. Symmetry transformations used to generate equivalent atoms:

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

Table S3. Bond valence analysis of $Li_3KB_9FO_{15}$.[a,b]

Atoms	l	s	Atoms	l	s
K(1)-F(1)	2.646(3)	0.2486	B(1)-O(3)	1.358(3)	1.0393
K(1)-O(1)	2.808(2)	0.1381	B(1)-O(1)	1.399(3)	1.0688
K(1)-O(1)#1	2.808(2)	0.1381	B(1)-O(2)	1.344(3)	0.9303
K(1)-O(1)#2	2.808(2)	0.1381	∑s		3.0384
K(1)-O(2)#1	2.862(2)	0.1596	B(2)-O(1)	1.378(3)	0.9810
K(1)-O(2)#2	2.862(2)	0.1596	B(2)-O(4)#3	1.372(3)	0.9960
K(1)-O(2)	2.862(2)	0.1596	B(2)-O(5)	1.353(3)	1.0499
∑s		1.1416	∑s		3.0269
Li(1) -F(1)	1.808(5)	0.3969	B(3)-O(2)	1.462(3)	0.7819
Li(1)-O(4)#6	1.962(5)	0.2613	B(3)-O(3)#6	1.481(3)	0.7435
Li(1)-O(3)#9	1.982(5)	0.2469	B(3)-O(4)	1.481(3)	0.7445
Li(1)-O(5)#10	2.074(5)	0.1937	B(3)-O(5)#5	1.464(3)	0.7768
∑s		1.0993	∑s		3.0467

[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 S4. Cation-O bond distances (Å) for several compounds.

Compounds	M-O	M′-O
LiB_3O_5	Li-O:1.986-2.003	
$LiCsB_6O_{10}$	Li-O: 1.926	Cs-O:3.145-3.552
CsB_3O_5		Cs-O:3.030-3.342
$LiK_3B_9O_{15}F$	Li-O:1.986-2.003; Li-F: 1.808	K–O :2.808; K-F: 2.646
$BaLiB_9O_{15}$,	Li-O:1.91-2.76	Ba-O:2.91-3.55
$BaNaB_9O_{15}$	Na-O:2.29-2.48	Ba-O:2.96-3.56
$SrLiB_9O_{15}$	Li-O:1.99-2.48	Sr-O:2.84-3.35

Table S5. Nine-polymeric fundamental building blocks (FBBs).

Formula	Space group	FBB	
CsB_9O_{14}	$P222_1$	B_9O_{17}	9:[(3:2Δ+T)+2(3:3Δ)]
α-$Na_3B_9O_{15}$	$P2_1/c$	B_9O_{18}	9:[(5:4Δ+ T)+(4:2Δ+2T)]
β-$Na_3B_9O_{15}$	$P2_1/c$	B_9O_{19}	9:[(5:4Δ+T)+(3:2Δ+T)+(1:T)]
$Na_2B_6O_{10}$	$P2_1/c$	B_9O_{19}	9:[(5:4Δ+T)+(3:2Δ+T)+(1:T)]
$(Na_{0.8}K_{0.2})K_2(B_3O_5)_3$	$P2_1/c$	B_9O_{19}	9:[3(3:2Δ+T)]
$Na(Na_{0.17}K_{0.83})_2(B_3O_5)_3$	$P2_1/c$	B_9O_{19}	9:[3(3:2Δ+T)]
$NaK_2(B_3O_5)_3$	$P2_1/c$	B_9O_{19}	9:[3(3:2Δ+T)]
KB_3O_5	$P2_1/c$	B_9O_{19}	9:[3(3:2Δ+T)]
$LiBaB_9O_{15}$	$R3c$	B_9O_{19}	9:[3(3:2Δ+T)]
$NaBaB_9O_{15}$	$R3c$	B_9O_{19}	9:[3(3:2Δ+T)]
$LiSrB_9O_{15}$	$R3c$	B_9O_{19}	9:[3(3:2Δ+T)]
$Na_2Cs_2SrB_{18}O_{30}$	$P2_1/c$	B_9O_{19}	9:[3(3:2Δ+T)]
$Na_2Cs_2BaB_{18}O_{30}$	$P2_1/c$	B_9O_{19}	9:[3(3:2Δ+T)]
$Na_2B_9O_{15}(H_2O)(H_3O)$	$P2_1$	B_9O_{19}	9:[(6:3Δ+3T)+(3:2Δ+1T)]
$AmB_9O_{13}(OH)_4(H_2O)$	$P2_1/c$	B_9O_{20}	9:[(6:3Δ+3T)+(3:Δ+2T)]
$SmB_9O_{13}(OH)_4(H_2O)$	$P2_1/c$	B_9O_{20}	9:[(6:3Δ+3T)+(3:Δ+2T)]
$NdB_{18}O_{25}(OH)_{13}Br_3$	$P2/c$	B_9O_{21}	9:[(5:2Δ+3T)+(3:Δ+2T)+Δ]

Table S6. The volume (Å^3) of a single cell and the number and density (per unit volume) of FBB in a unit cell of several compounds

Compounds	V	N(B_3O_7)	ρ(B_3O_7)	N(BO_3)	ρ(BO_3)	N(BO_4)	ρ(BO_4)
LiB_3O_5	320.42	4	0.0124	8	0.0249	4	0.0124
$SrLiB_9O_{15}$	1712.38	18	0.0105	36	0.0210	18	0.0105
$BaLiB_9O_{15}$	1777.79	18	0.0101	36	0.0202	18	0.0101
$BaNaB_9O_{15}$	1853.54	18	0.0097	36	0.0194	18	0.0097
$Li_3KB_9O_{15}F$	1986.44	18	0.0090	36	0.0181	18	0.0090
CsB_3O_5	485.47	4	0.0082	8	0.0164	4	0.0082
$LiCsB_6O_{10}$	984.4	8	0.0081	16	0.0162	8	0.0081