Electronic Supplementary Information

Two Alkali Calcium Borates Exhibiting Second Harmonic Generation and Deep-UV Cutoff Edges

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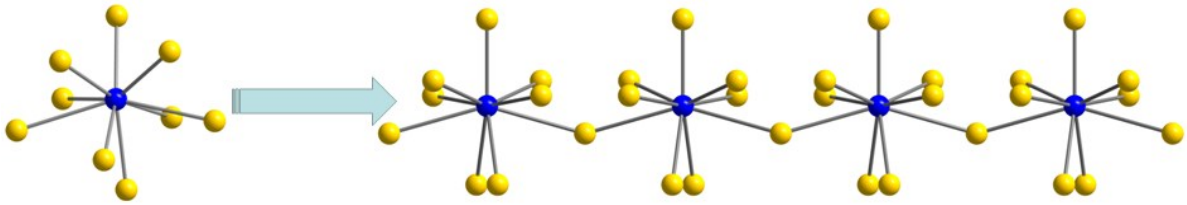

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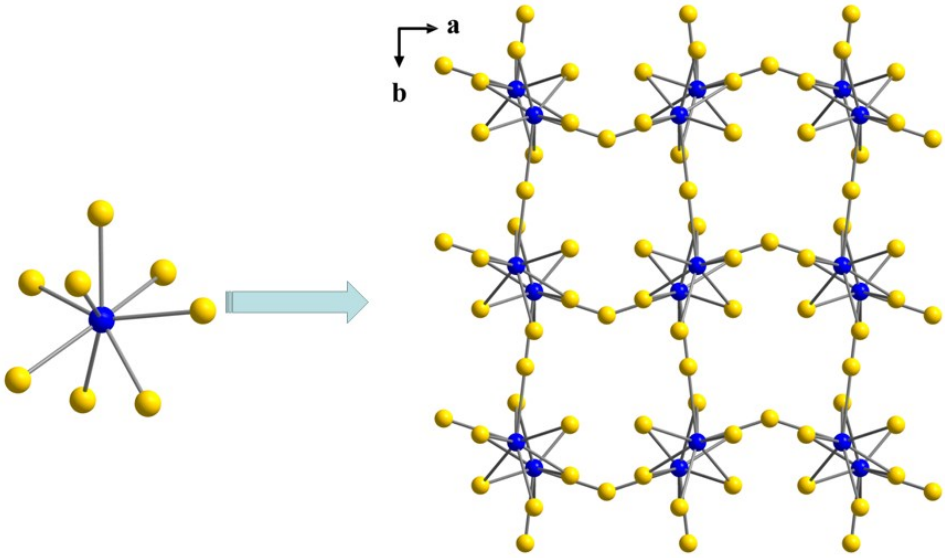

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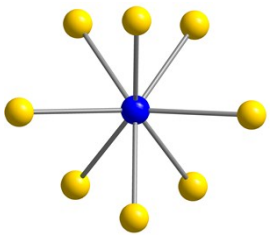

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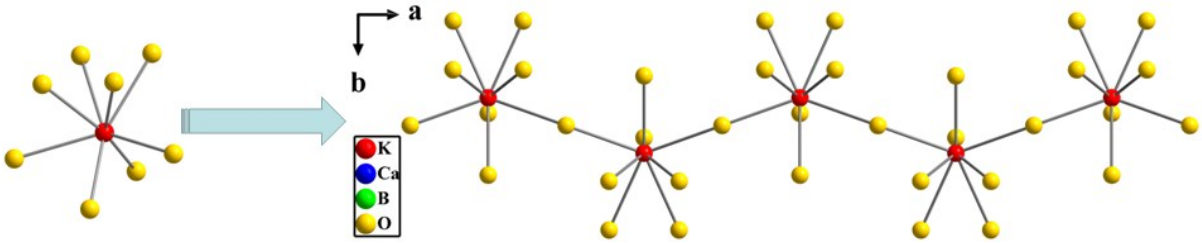


(d)

Figure S2. The $^{\infty}_{1}[KO_7]$ chains extend along the *a*-axis.

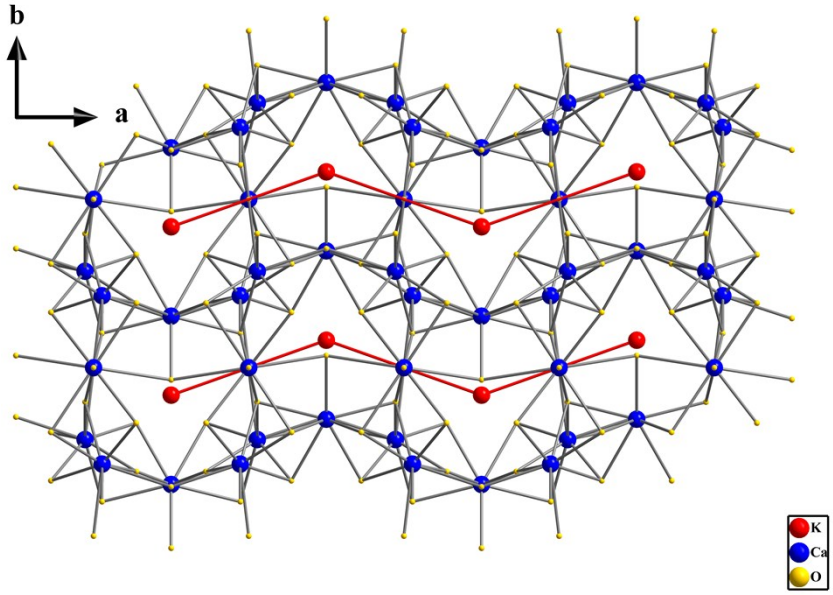


Figure S3. The (a) $^{\infty}_{1}[KO_7]$ chain and (b) $^{\infty}_{1}[MO_7]$ (M = K/Rb) chain.

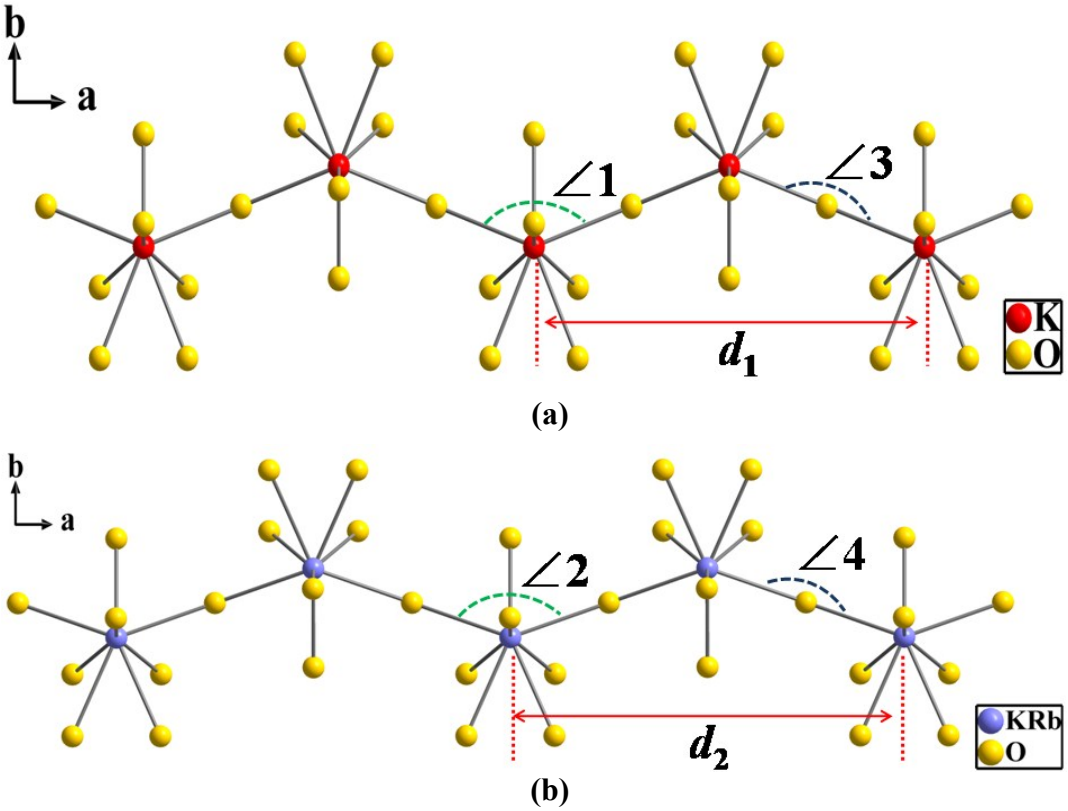
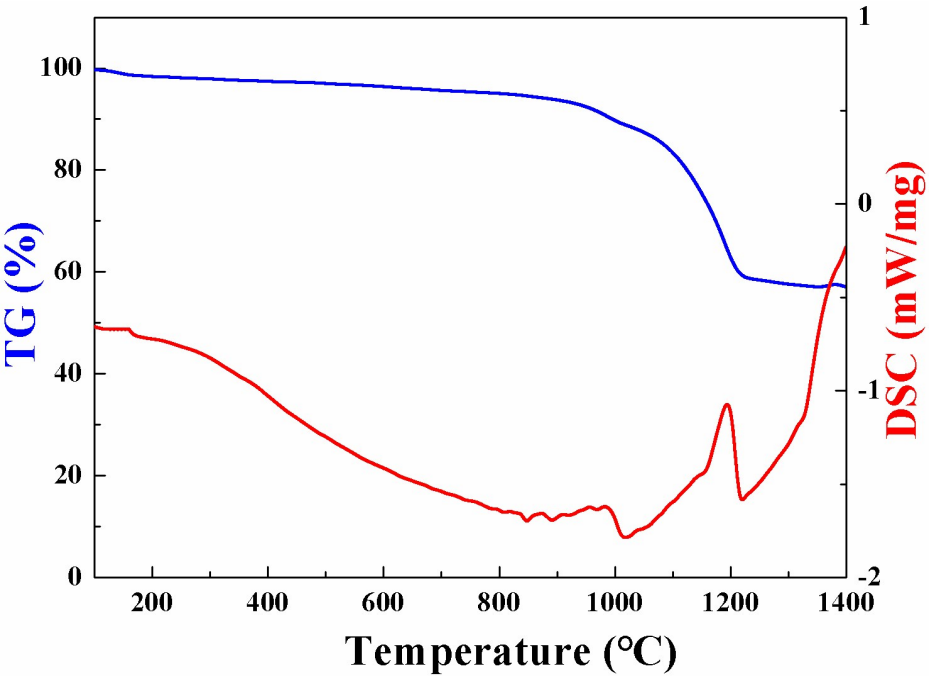
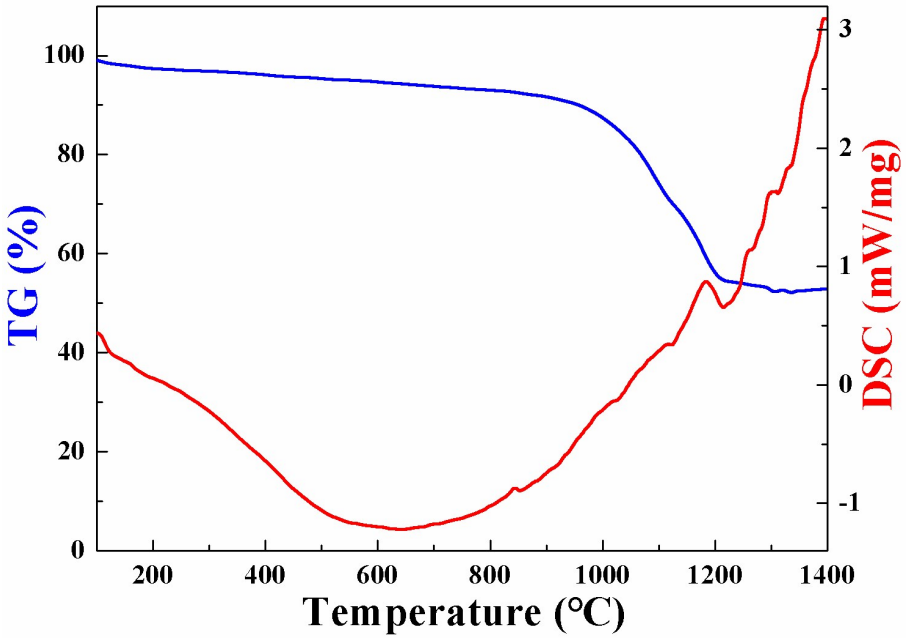


Figure S4. The TG and DSC curves of (a) $KCa_4B_3O_9$ and (b) $K_{0.59}Rb_{0.41}Ca_4B_3O_9$.

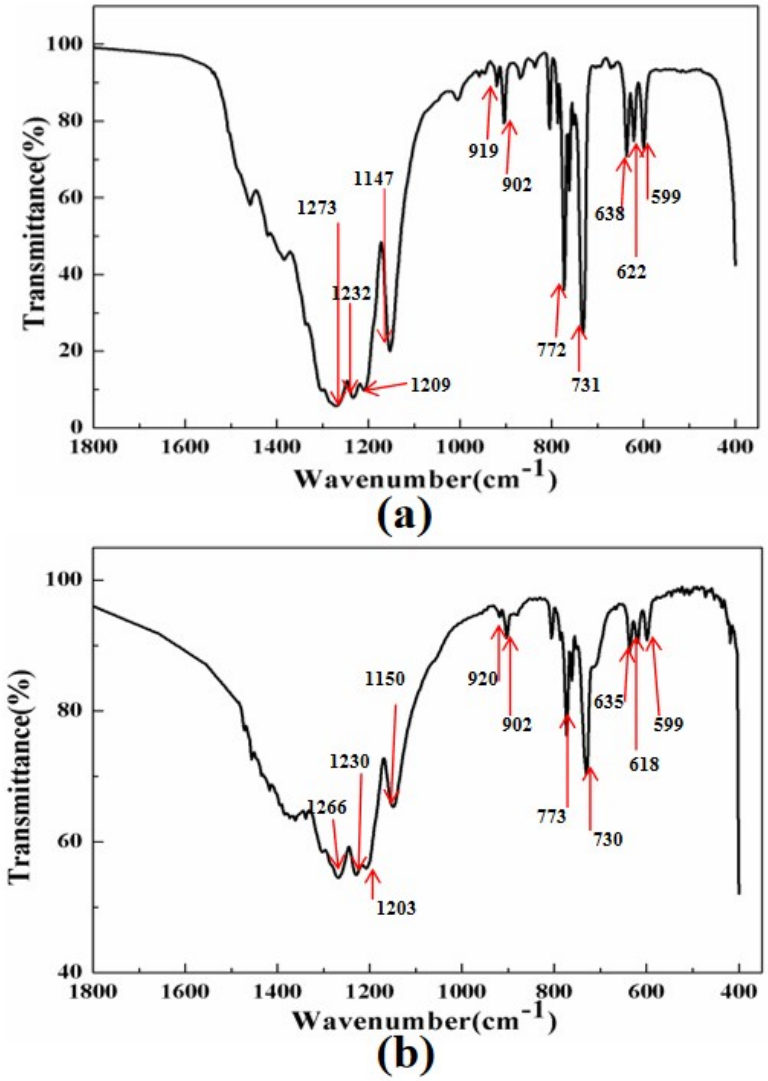


(a)



(b)

Figure S5. IR spectra of (a) $KCa_4B_3O_9$ and (b) $K_{0.59}Rb_{0.41}Ca_4B_3O_9$.



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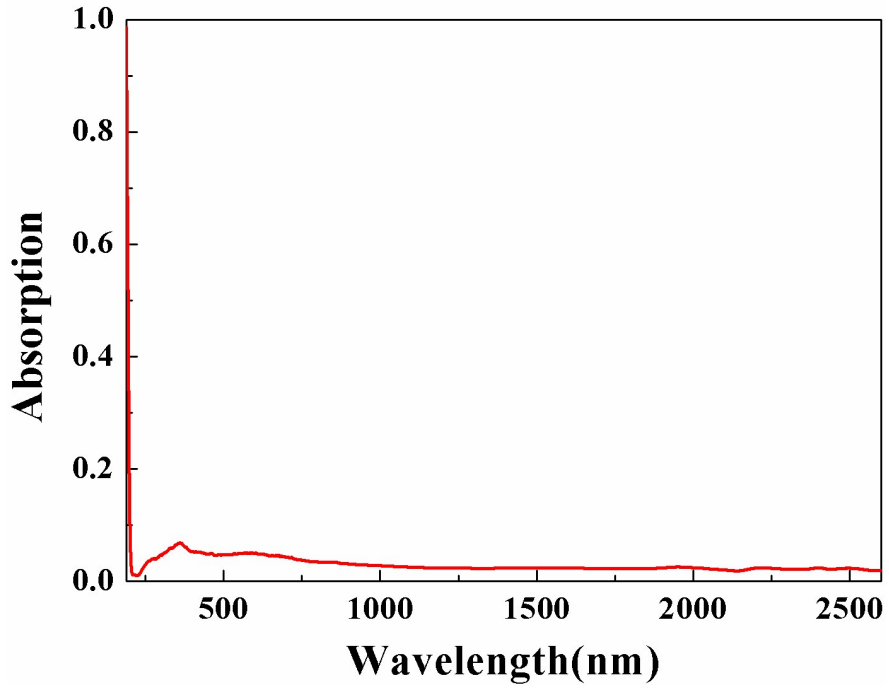
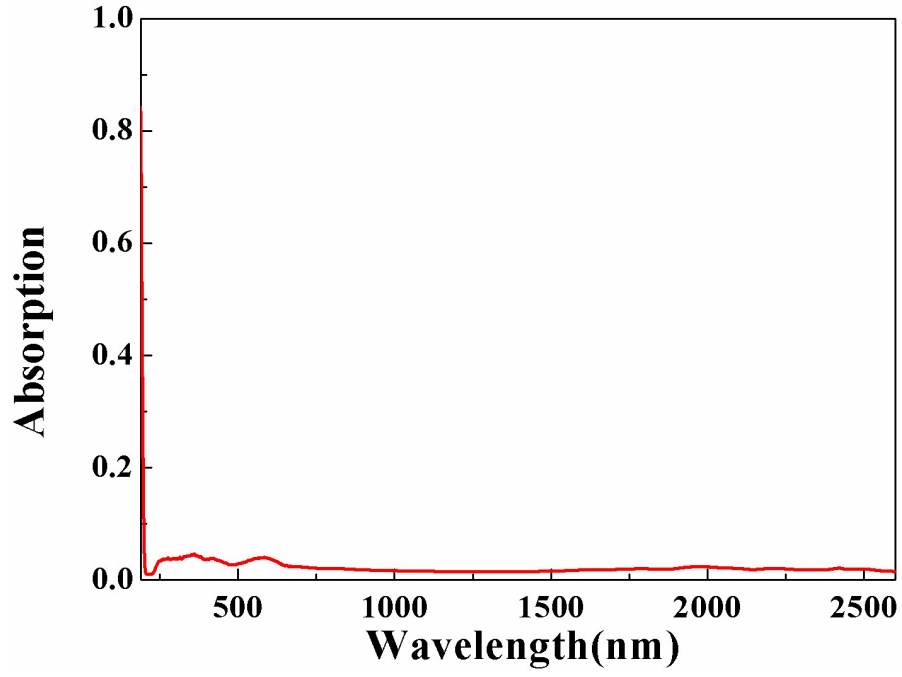
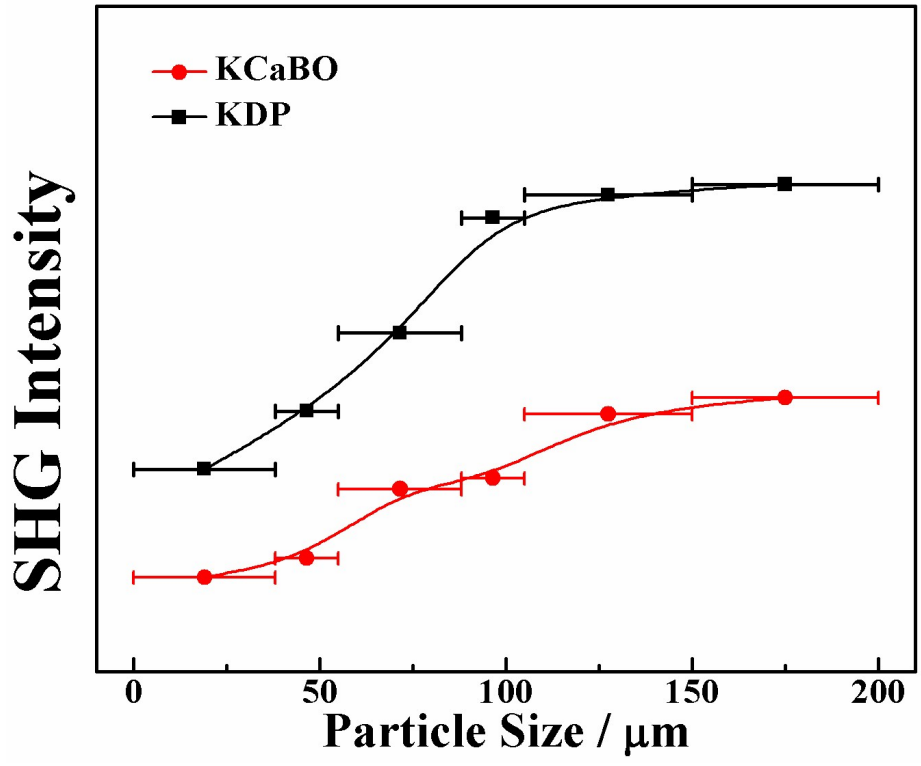


(a)

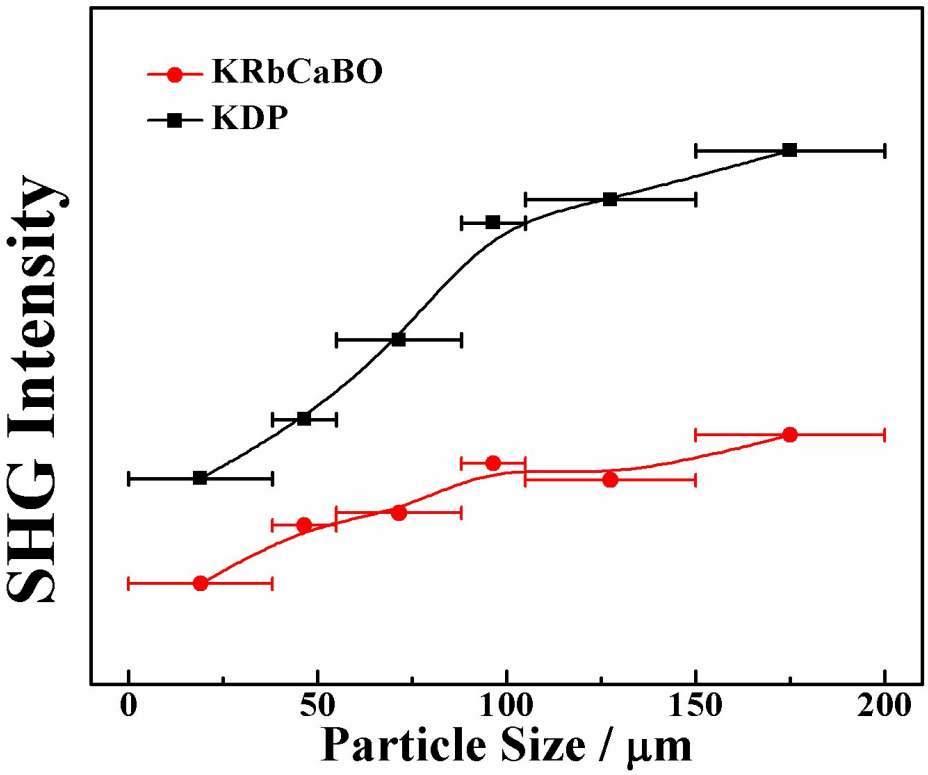


(b)

Figure S7. Particle sizes versus SHG intensities of (a) $KCa_4B_3O_9$ and KDP, (b) $K_{0.59}Rb_{0.41}Ca_4B_3O_9$ and KDP.

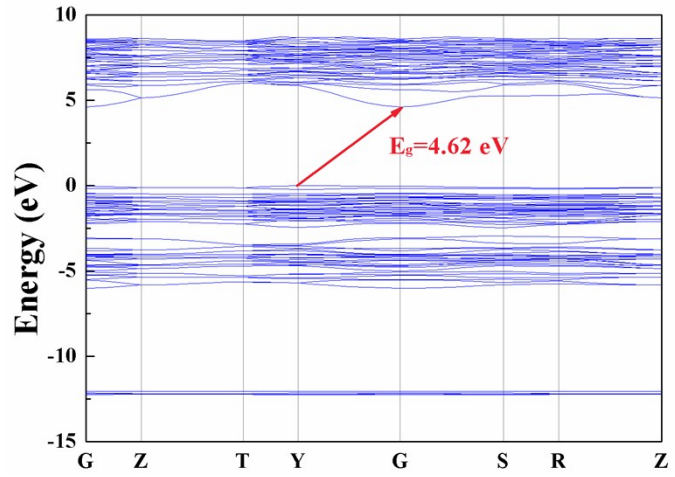


(a)

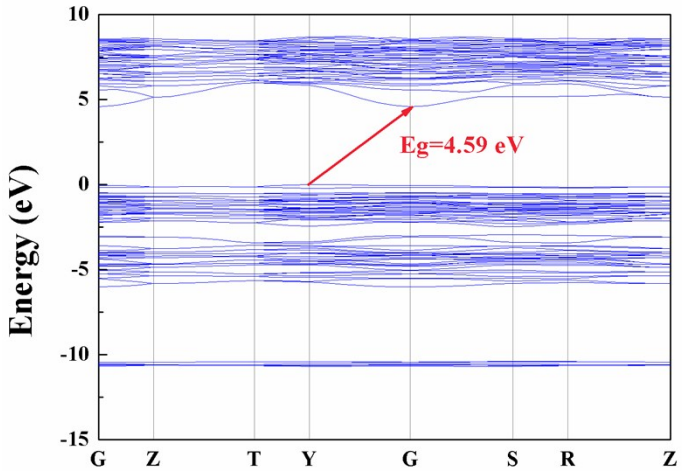


(b)

Figure S8. The calculated band structures of (a) $KCa_4B_3O_9$ and (b) $K_{0.59}Rb_{0.41}Ca_4B_3O_9$.



(a)



(b)

Figure S9. The total and partial densities of states of (a) $KCa_4B_3O_9$ and (b) $K_{0.59}Rb_{0.41}Ca_4B_3O_9$.

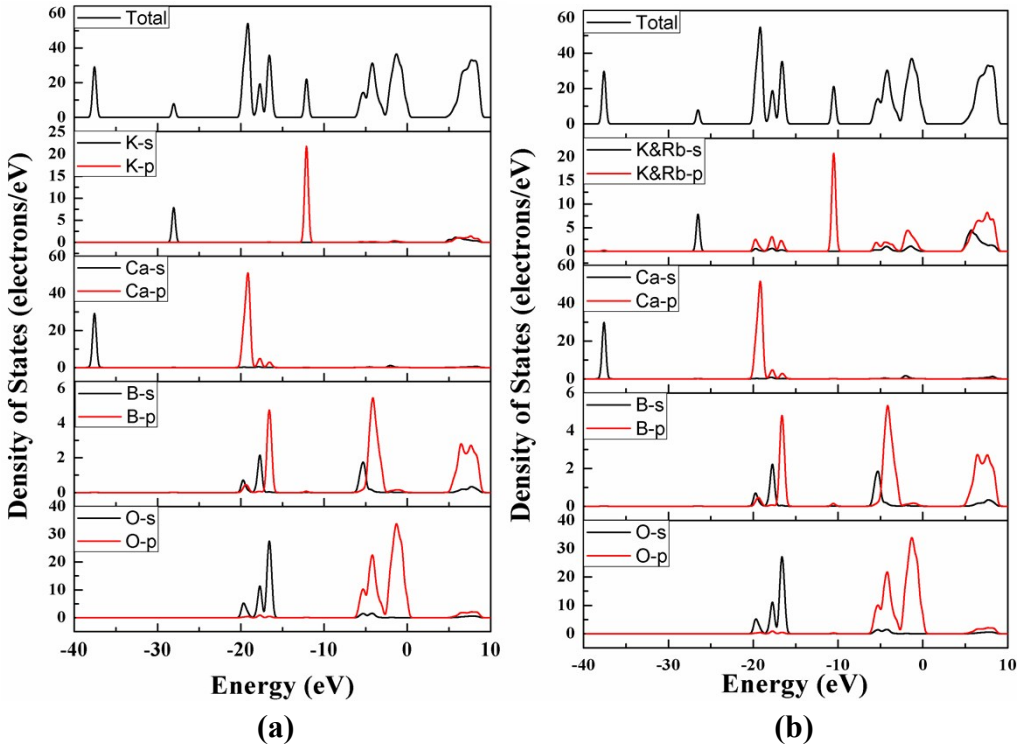
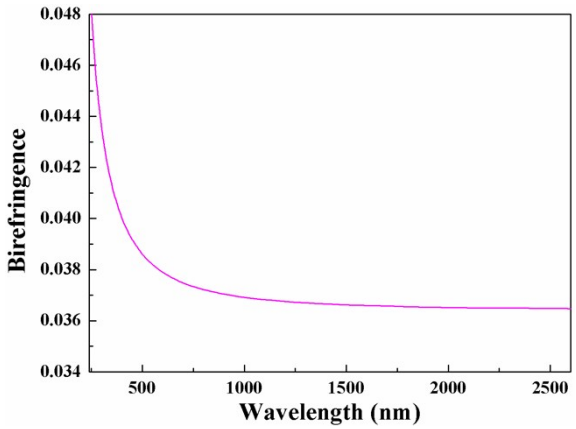
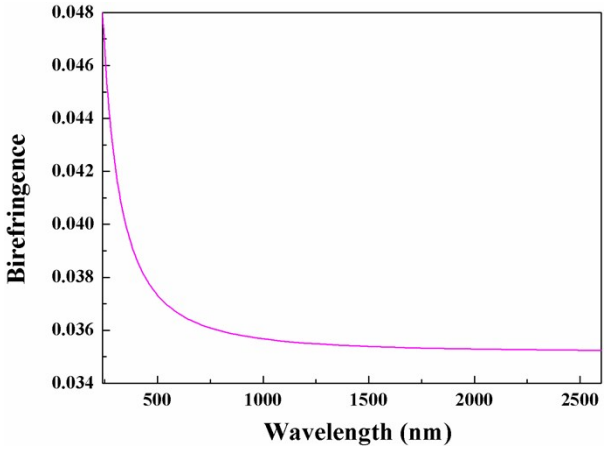


Figure S10 Calculated birefringence (Δn) of (a) $KCa_4B_3O_9$ and (b) $K_{0.59}Rb_{0.41}Ca_4B_3O_9$.



(a)



(b)

Table S1. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters ($Å^2$ × 10^3) and bond valence analyses of $KCa_4B_3O_9$ and $K_{0.59}Rb_{0.41}Ca_4B_3O_9$.[a,b] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$KCa_4B_3O_9$

Atom	x	y	z	U_{eq}	BVS
K(1)	7500	4184(3)	4177(6)	19(1)	1.12
Ca(1)	5000	5000	-495(5)	13(1)	1.942
Ca(2)	5275(2)	2136(2)	8077(4)	11(1)	2.196
Ca(3)	7500	6530(3)	6758(5)	13(1)	2.105
B(1)	5000	5000	5200(20)	4(3)	2.850
B(2)	7500	3804(16)	9730(30)	19(4)	2.997
B(3)	7500	1803(18)	6030(30)	14(4)	2.873
O(1)	7500	4640(9)	8370(17)	12(2)	1.868
O(2)	5271(6)	6020(7)	6258(12)	10(1)	2.003
O(3)	5000	5000	3090(20)	19(2)	2.157
O(4)	6379(7)	1918(8)	4936(12)	18(2)	2.139
O(5)	6373(7)	3357(7)	10546(12)	15(2)	2.059
O(6)	7500	1463(9)	8055(19)	16(2)	1.965

$K_{0.59}Rb_{0.41}Ca_4B_3O_9$

Atom	x	y	z	U_{eq}	BVS
K(1)/Rb(1)	7500	4198(1)	4232(2)	14(1)	1.265
Ca(1)	5000	5000	-514(3)	14(1)	1.907
Ca(2)	5286(1)	7136(1)	3059(2)	10(1)	2.182
Ca(3)	7500	6530(2)	6747(3)	11(1)	2.156
B(1)	5000	5000	5182(14)	7(2)	2.919
B(2)	7500	3789(9)	9735(16)	10(2)	2.896
B(3)	7500	6745(11)	986(15)	14(2)	2.968

O(1)	7500	4658(6)	8357(13)	24(2)	1.825
O(2)	5277(4)	6009(4)	6243(7)	11(1)	2.005
O(3)	5000	5000	3107(11)	14(1)	2.182
O(4)	6383(4)	6902(4)	-89(6)	12(1)	2.164
O(5)	8626(4)	3334(4)	10524(6)	13(1)	2.076
O(6)	7500	6502(5)	3033(11)	12(1)	2.047

[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 $B = 0.37$. Superscripts indicate the number of equivalent bonds for anions.

Table S2. Selected bond distances (Å) and angles (deg) for $KCa_4B_3O_9$ and $K_{0.59}Rb_{0.41}Ca_4B_3O_9$.

$KCa_4B_3O_9$			
K(1)-O(6)#1	2.718(12)	Ca(2)-O(3)#9	2.471(4)
K(1)-O(1)	2.790(12)	Ca(2)-O(5)#7	2.474(8)
K(1)-O(5)#2	2.822(9)	Ca(2)-O(6)	2.486(5)
K(1)-O(5)#3	2.822(9)	Ca(2)-O(2)#10	2.498(8)
K(1)-O(3)#4	2.903(5)	Ca(3)-O(1)	2.413(11)
K(1)-O(3)	2.903(5)	Ca(3)-O(6)#1	2.421(13)
K(1)-O(4)	2.905(10)	Ca(3)-O(4)#11	2.435(8)
K(1)-O(4)#5	2.905(10)	Ca(3)-O(4)#12	2.435(8)
Ca(1)-O(3)	2.345(14)	Ca(3)-O(2)	2.460(8)
Ca(1)-O(2)#6	2.441(9)	Ca(3)-O(2)#5	2.460(8)
Ca(1)-O(2)#2	2.441(9)	Ca(3)-O(5)#13	2.543(9)
Ca(1)-O(5)#2	2.481(8)	Ca(3)-O(5)#1	2.543(9)
Ca(1)-O(5)#6	2.481(8)	B(1)-O(3)	1.38(2)
Ca(1)-O(4)#7	2.661(9)	B(1)-O(2)	1.389(11)
Ca(1)-O(4)#1	2.661(9)	B(1)-O(2)#10	1.389(11)
Ca(1)-O(1)#6	2.788(5)	B(2)-O(1)	1.31(2)
Ca(1)-O(1)#2	2.788(5)	B(2)-O(5)#5	1.406(14)
Ca(2)-O(4)	2.377(8)	B(2)-O(5)	1.406(14)
Ca(2)-O(4)#8	2.396(9)	B(3)-O(6)	1.38(2)
Ca(2)-O(5)	2.435(8)	B(3)-O(4)	1.396(12)
Ca(2)-O(2)#9	2.443(9)	B(3)-O(4)#5	1.396(12)
O(3)-B(1)-O(2)	119.7(6)	O(5)#5-B(2)-O(5)	116.6(17)
O(3)-B(1)-O(2)#10	119.7(6)	O(6)-B(3)-O(4)	121.3(7)
O(2)-B(1)-O(2)#10	120.6(12)	O(6)-B(3)-O(4)#5	121.3(7)
O(1)-B(2)-O(5)#5	121.6(8)	O(4)-B(3)-O(4)#5	117.0(13)
O(1)-B(2)-O(5)	121.6(8)		

Symmetry transformations used to generate equivalent atoms:

#1x,y+1/2,z-1/2	#2x,y,z-1	#3-x+3/2,y,z-1	#4x+1/2,-y+1,z
#5-x+3/2,y,z	#6-x+1,-y+1,z-1	#7-x+1,-y+1/2,z-1/2	#8-x+1,-y+1/2,z+1/2
#9x,y-1/2,z+1/2	#10-x+1,-y+1,z	#11-x+3/2,y+1/2,z+1/2	#12x,y+1/2,z+1/2
#13-x+3/2,y+1/2,z-1/2	#14x,y,z+1	#15x+1/2,-y+1,z+1	#16x,y-1/2,z-1/2

$K_{0.59}Rb_{0.41}Ca_4B_3O_9$			
K(1)/Rb(1)-O(1)	2.743(9)	Ca(2)-O(6)	2.463(2)
K(1)/Rb(1)-O(6)	2.772(6)	Ca(2)-O(5)#8	2.477(4)
K(1)/Rb(1)-O(5)#1	2.877(4)	Ca(2)-O(3)	2.4843(18)
K(1)/Rb(1)-O(5)#2	2.877(4)	Ca(2)-O(2)#9	2.519(4)
K(1)/Rb(1)-O(3)	2.906(2)	Ca(3)-O(1)	2.402(7)
K(1)/Rb(1)-O(3)#3	2.906(2)	Ca(3)-O(4)#11	2.419(4)
K(1)/Rb(1)-O(4)#4	2.937(5)	Ca(3)-O(4)#12	2.419(4)
K(1)/Rb(1)-O(4)#5	2.937(5)	Ca(3)-O(6)	2.423(7)
Ca(1)-O(3)	2.362(8)	Ca(3)-O(2)	2.459(4)
Ca(1)-O(2)#14	2.432(5)	Ca(3)-O(2)#13	2.459(4)
Ca(1)-O(2)#2	2.432(5)	Ca(3)-O(5)#10	2.530(5)
Ca(1)-O(5)#1	2.508(4)	Ca(3)-O(5)#7	2.530(5)
Ca(1)-O(5)#8	2.508(4)	B(1)-O(3)	1.353(12)
Ca(1)-O(4)#15	2.656(5)	B(1)-O(2)	1.386(6)
Ca(1)-O(4)	2.656(5)	B(1)-O(2)#15	1.386(6)
Ca(1)-O(1)#14	2.783(3)	B(2)-O(1)	1.348(12)
Ca(1)-O(1)#2	2.783(3)	B(2)-O(5)	1.404(7)
Ca(2)-O(4)	2.376(4)	B(2)-O(5)#13	1.404(7)
Ca(2)-O(4)#6	2.415(4)	B(3)-O(6)	1.364(12)
Ca(2)-O(5)#7	2.415(4)	B(3)-O(4)	1.390(7)
Ca(2)-O(2)	2.451(5)	B(3)-O(4)#13	1.390(7)
O(3)-B(1)-O(2)	120.0(4)	O(1)-B(2)-O(5)	121.5(4)
O(3)-B(1)-O(2)#15	120.0(4)	O(1)-B(2)-O(5)#13	121.5(4)
O(2)-B(1)-O(2)#15	120.1(8)	O(5)-B(2)-O(5)#13	116.8(9)
O(6)-B(3)-O(4)	121.4(4)	O(4)-B(3)-O(4)#13	117.2(8)

O(6)-B(3)-O(4)#13	121.4(4)	

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y,z-1	#2 x,y,z-1	#3 x+1/2,-y+1,z	#4 x,y-1/2,z+1/2
#5 -x+3/2,y-1/2,z+1/2	#6 -x+1,-y+3/2,z+1/2	#7 -x+3/2,y+1/2,z-1/2	#8 x-1/2,-y+1,z-1
#9 -x+1,-y+3/2,z-1/2	#10 x,y+1/2,z-1/2	#11 -x+3/2,y,z+1	#12 x,y,z+1
#13 -x+3/2,y,z	#14 -x+1,-y+1,z-1	#15 -x+1,-y+1,z	#16 x+1/2,-y+1,z+1

Table S3. Dipole moment calculations of $K_{0.59}Rb_{0.41}Ca_4(BO_3)_3$.

$K_{0.59}Rb_{0.41}Ca_4(BO_3)_3$					
species	x(a)	y(b)	z(c)	magnitude	
				debye	$\times 10^{-4}$ esu·cm/Å^3
$B(1)O_3$	0	-0.82	-0.53	0.97	48.64
$B(2)O_3$	0	-0.20	1.08	1.10	55.20
$B(3)O_3$	0	0	0.10	0.10	5.02
ΣBO_3	0	0	2.62	2.62	131.03

Table S4. The B-O connection modes of the disorder-free compounds in the system of M-M'-B-O (M = alkali and M' = alkaline metal cations).

ICSD number	compounds	*P*/*Q*	Space group	B-O units	B-O framework
433331	$K_2BaB_{16}O_{26}$	0.25	$C222_1$	BO_3, BO_4	$[B_{16}O_{26}]$ network
426537	$LiBa(B_9O_{15})$	0.33	*R*3*cH*	BO_3, BO_4	$[B_9O_{15}]$ network
93015	$LiSr(B_9O_{15})$	0.33	*R*3*cH*	BO_3, BO_4	$[B_9O_{15}]$ network
93014	$NaBa(B_9O_{15})$	0.33	*R*3*cH*	BO_3, BO_4	$[B_9O_{15}]$ network
426110	$LiBa(B_9O_{15})$	0.33	*R*-3*cH*	BO_3, BO_4	$[B_9O_{15}]$ network
CCDC 1848456	$RbBaB_7O_{12}$	0.43	$P2_1/c$	BO_3, BO_4	$[B_7O_{12}]$ network
241859	$KBaB_5O_9$	0.6	$P2_1/c$	BO_3, BO_4	$[B_5O_9]$ layer
79716	$KSr(B_5O_9)$	0.6	$P2_1/c$	BO_3, BO_4	$[B_5O_9]$ layer
424353	$NaBa(B_5O_9)$	0.6	$P2_1/c$	BO_3, BO_4	$[B_5O_9]$ layer
245570	$NaSrB_5O_9$	0.6	$P2_1/c$	BO_3, BO_4	$[B_5O_9]$ layer
424308	$Li_2Sr_4(B_{12}O_{23})$	0.83	$P2_1/c$	BO_3, BO_4	isolated $[B_2O_5]^{4-}$, $[B_{10}O_{18}]$ network
61165	$Na_3Ca(B_5O_{10})$	1	*P*-1	BO_3, BO_4	isolated $[B_5O_{10}]^{5-}$
417958	$Na_3Ca(B_5O_{10})$	1	*P*-1	BO_3, BO_4	isolated $[B_5O_{10}]^{5-}$

260005	$Na_3Sr(B_5O_{10})$	1	*P*-1	BO_3, BO_4	isolated $[B_5O_{10}]^{5-}$
71875	$LiBa_2(B_5O_{10})$	1	$P12_1/m1$	BO_3, BO_4	$[B_5O_{10}]$ chain
417919	$CsBa(B_3O_6)$	1	*P*321	BO_3	isolated $[B_3O_6]^{3-}$ ring
417959	$Na_3Mg(B_5O_{10})$	1	*Pbca*	BO_3, BO_4	isolated $[B_5O_{10}]^{5-}$
248201	NaBe(B3O6)	1	$Pna2_1$	BO_3	$[BO_2]$ chain
248202	$KBe_2B_3O_7$	1.67	*C*2/*c*	BO_3	isolated $[B_3O_7]^{5-}$
248204	$K_3Be_6(B_3O_7)_3$	1.67	$P2_1$	BO_3	isolated $[BO_3]^{3-}$, isolated $[B_2O_5]^{4-}$
248203	$KBe_2B_3O_7$	1.67	$Pmn2_1$	BO_3	isolated $[BO_3]^{3-}$, $[BO_2]$ chain
248205	$RbBe_2B_3O_7$	1.67	$Pmn2_1$	BO_3	isolated $[BO_3]^{3-}$, $[BO_2]$ chain
249341	$Na_2(BeB_2O_5)$	2	*C*2/*c*	BO_3	isolated $[B_2O_5]^{4-}$
237764	$Na_2Be_4B_4O_{11}$	2.5	*P*1	BO_3	Isolated $[BO_3]^{3-}$, isolated $[B_2O_5]^{4-}$
171422	$KCa_4(BO_3)_3$	3	*Ama*2	BO_3	isolated $[BO_3]^{3-}$
171423	$KSr_4(BO_3)_3$	3	*Ama*2	BO3	isolated $[BO_3]^{3-}$
171421	$NaCa_4(BO_3)_3$	3	*Ama*2	BO_3	isolated $[BO_3]^{3-}$
Not included	$RbSr_4(BO_3)_3$	3	*Ama*2	BO_3	isolated $[BO_3]^{3-}$
249567	$NaMg(BO_3)$	3	*C*2/*c*	BO_3	isolated $[BO_3]^{3-}$
80110	$NaBa(BO_3)$	3	*C*2/*m*	BO_3	isolated $[BO_3]^{3-}$
170861	$LiSr_4(BO_3)_3$	3	*Ia*-3*d*	BO_3	isolated $[BO_3]^{3-}$
250195	$NaBa_4(BO_3)_3$	3	*Ia*-3*d*	BO_3	isolated $[BO_3]^{3-}$
170862	$NaSr_4(BO_3)_3$	3	*Ia*-3*d*	BO_3	isolated $[BO_3]^{3-}$
427287	LiBe (BO_3)	3	*P*-1	BO_3	isolated $[BO_3]^{3-}$

250598	$Cs_4Mg_4(BO_3)_4$	3	$P2_1/c$	BO_3	isolated $[BO_3]^{3-}$
73218	$LiBa(BO_3)$	3	$P2_1/c$	BO_3	isolated $[BO_3]^{3-}$
172420	$NaSrBO_3$	3	$P2_1/c$	BO_3	isolated $[BO_3]^{3-}$
92842	$LiSr(BO_3)$	3	$P2_1/c$	BO_3	isolated $[BO_3]^{3-}$
253696	$CsCaBO_3$	3	$P2_13$	BO_3	isolated $[BO_3]^{3-}$
174336	$KMg(BO_3)$	3	$P2_13$	BO_3	isolated $[BO_3]^{3-}$
253695	$RbCaBO_3$	3	$P2_13$	BO_3	isolated $[BO_3]^{3-}$
236575	$RbMg(BO_3)$	3	$P2_13$	BO_3	isolated $[BO_3]^{3-}$
99386	$LiCa(BO_3)$	3	*Pbca*	BO_3	isolated $[BO_3]^{3-}$
190738	$CsBe_4(BO_3)_3$	3	*Pnma*	BO_3	isolated $[BO_3]^{3-}$
171666	$RbBe_4(BO_3)_3$	3	*Pnma*	BO_3	isolated $[BO_3]^{3-}$
99503	$Li_4Ca(BO_3)_2$	3	*Pnnm*	BO_3	isolated $[BO_3]^{3-}$

Table S5. Assignment of absorption peaks in the infrared spectra of the title compounds.

mode description (cm^{-1})	$KCa_4B_3O_9$	$K_{0.59}Rb_{0.41}Ca_4B_3O_9$
asymmetric stretching of B_3-O	1273, 1232, 1209, 1147	1266, 1230, 1203, 1150
symmetric stretching of B_3-O	919, 902	920, 902
out-of-plane bending of B_3-O	772, 731	773, 730
in-plane bending of B_3-O	638, 622, 599	635, 618, 599