Supporting Information

$K_3B_4PO_{10}$ and $K_2MB_4PO_{10}$ (M = Rb/Cs): Rare Mixed-Coordinated Borophosphates with Large Birefringence

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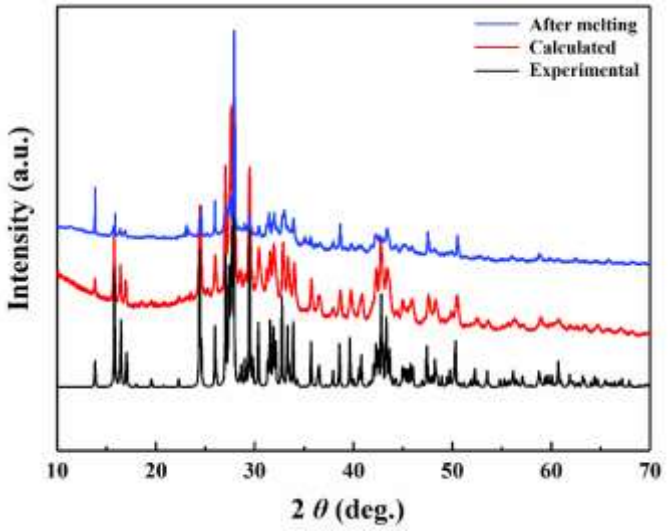

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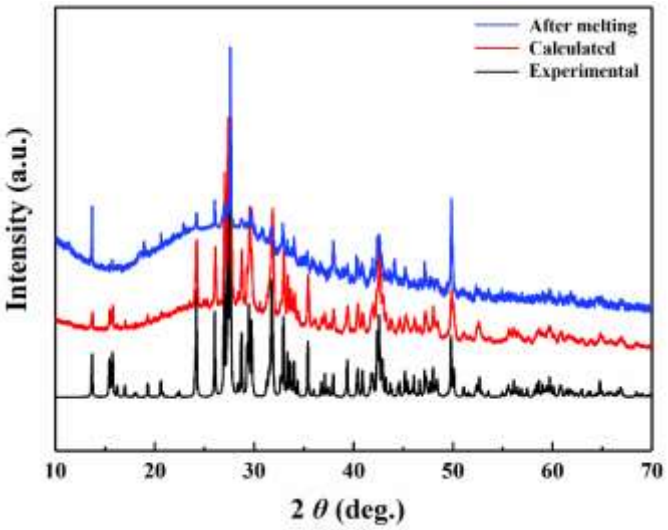

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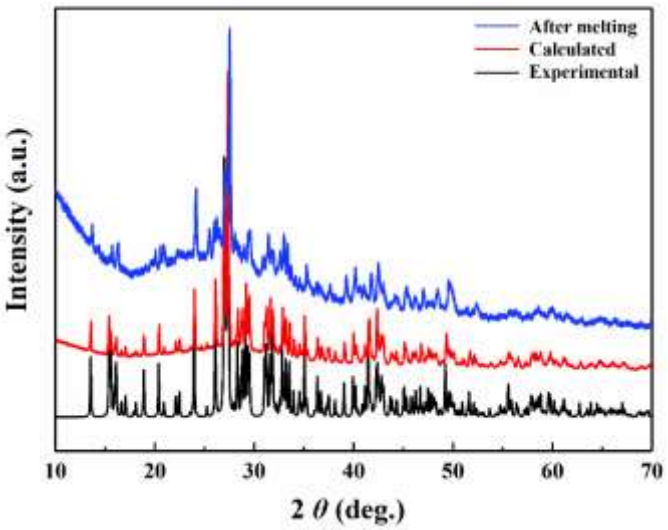


(c)

Figure S1. X-ray powder diffraction patterns of $K_3B_4PO_{10}$ (a), $K_2RbB_4PO_{10}$ (b) and $K_2CsB_4PO_{10}$ (c)

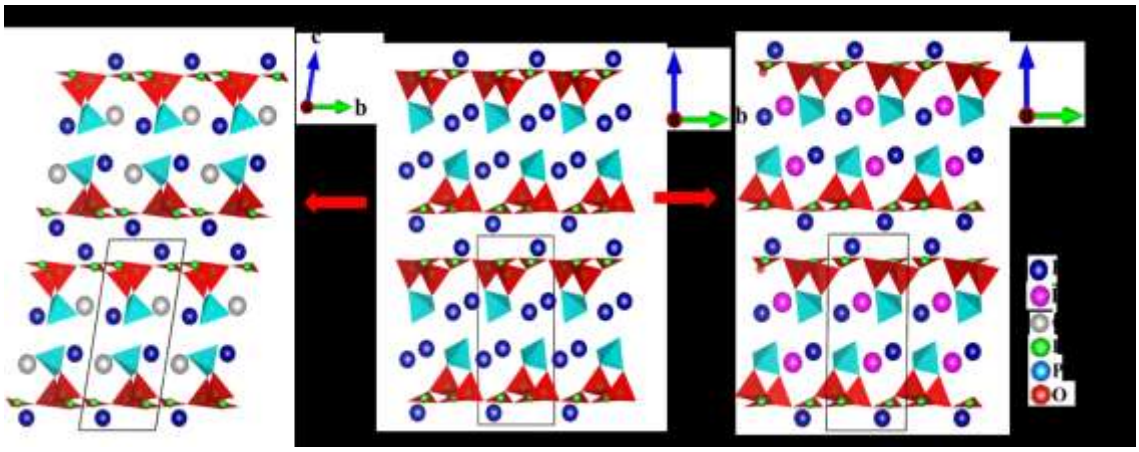


Figure S2. Crystal structures of $K_2RbB_4PO_{10}$ and $K_2CsB_4PO_{10}$.

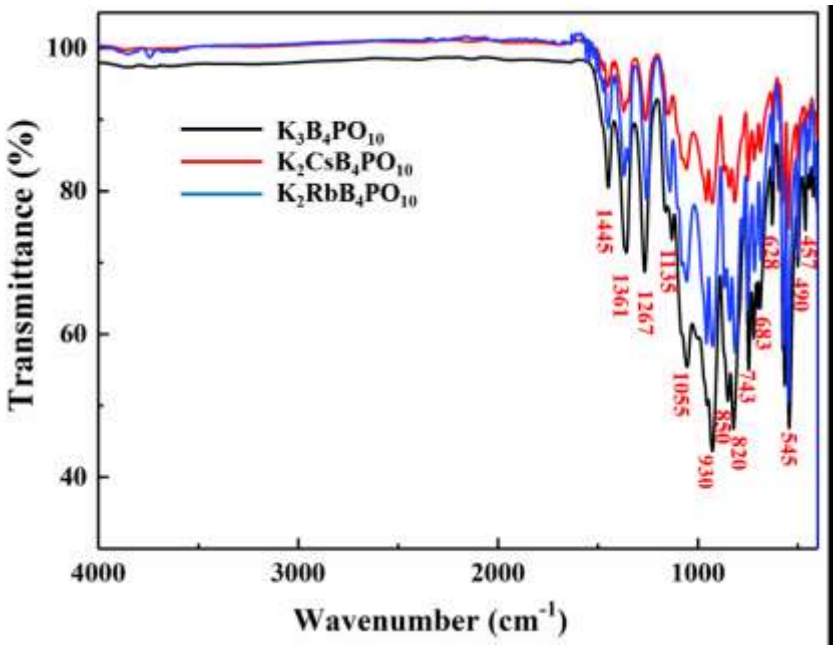
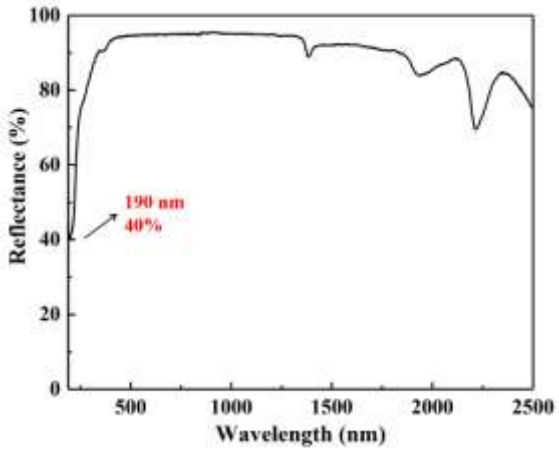
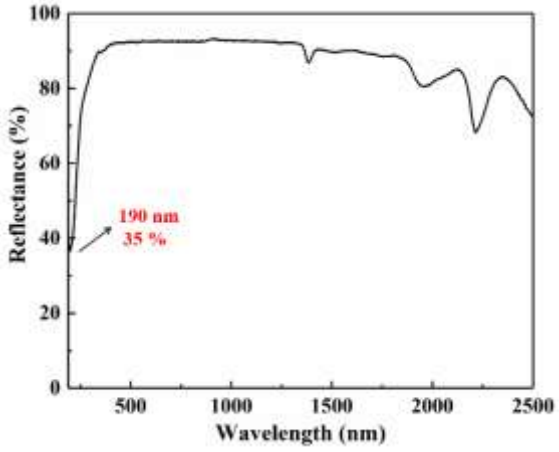


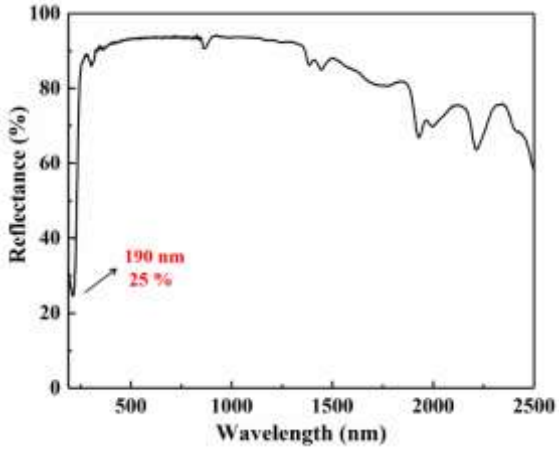
Figure S3. IR spectra of $K_3B_4PO_{10}$, $K_2RbB_4PO_{10}$ and $K_2CsB_4PO_{10}$.



(a)



(b)



(c)

Figure S4. UV−vis−NIR diffuse reflectance spectra of $K_3B_4PO_{10}$ (a), $K_2RbB_4PO_{10}$ (b) and $K_2CsB_4PO_{10}$ (c).

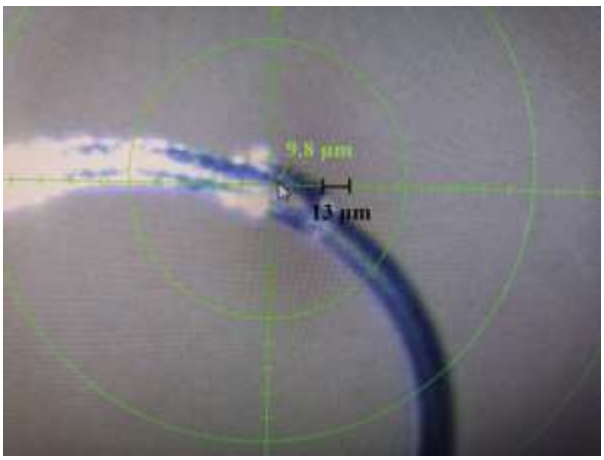
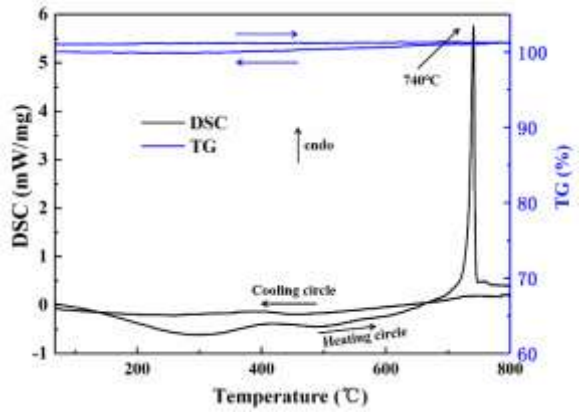
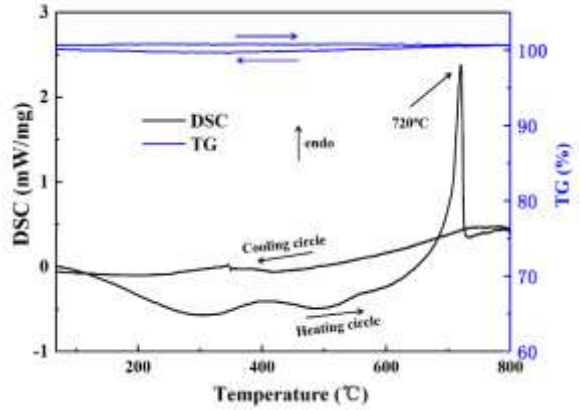


Figure S5. Photograph of crystal size.



(a)



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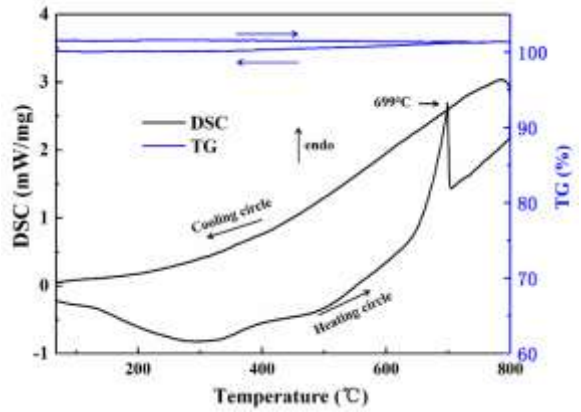

(c)

Figure S6. DSC-TG curves of $K_3B_4PO_{10}$ (a), $K_2RbB_4PO_{10}$ (b) and $K_2CsB_4PO_{10}$ (c)

Table S1. A summary of mixed-coordinated *borophosphates*.

Borophosphates	B:P	BO_3:BO_4	Synthesis	$Q^{n/CN}$	D
$M_2[BP_3O_{12}]$(M = Cr, V, Fe)	1:3	3:0	Solid-state	$B^{3/3}$, $P^{1/4}$	0
$Co_5[BPO_6][PO4]_2$	1:3	1:0	Low-temperature flux	$B^{1/3}$, $P^{1/4}$	0
$CsSc[B_2P_3O_{11}(OH)_3]$	2:3	1:1	Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{1/4}$, $P^{2/4}$	0
$[C_6H_{14}N_2]_2[VOB_3P_4O_{15}(OH)_5]\cdot 4H_2O$	3:4	1:2	Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{1/4}$,	0
$Na_2M[B_3P_2O_{11}(OH)]\cdot 0.67H_2O$ (M = Cu, Mg, Mn-Zn)	3:2	1:2	Low-temperature flux/Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{2/4}$	1
$Na_5(H_3O)M_3[B_3P_2O_{11}(OH)]_3\cdot 2H_2O$ M = (Mg, Mn-Zn)	3:2	1:2	Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{2/4}$	1
$Na_5(NH_4)Mn_3[B_9P_6O_{33}(OH)_3]\cdot(H_2O)_{1.5}$	3:2	1:2	Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{2/4}$	1
$Na_8[Cr_4B_{12}P_8O_{44}(OH)_4][P_2O_7]\cdot n(H_20)$	3:2	1:2	Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{2/4}$	3
$Na_2[VB_3P_2O_{12}(OH)]\cdot 2.92(H_2O)$	3:2	1:2	Low-temperature flux	$B^{2/3}$, $B^{4/4}$, $P^{2/4}$	3
$Na_5KCu_3[B_9P_2O_{33}(OH)_3]\cdot(H_2O)$	3:2	1:2	Low-temperature flux	$B^{2/3}$, $B^{2/4}$, $B^{4/4}$, $P^{1/4}$	1
$LiNa_2B_5P_2O_{14}$	5:2	2:3	Solid-state	$B^{3/3}$, $B^{3/4}$, $P^{3/4}$	2
$Li_2B_3PO_8$	3:1	2:1	Solid-state	$B^{3/3}$, $B^{4/4}$, $P^{2/4}$	2
$Li_3[B_3PO_6(OH)_3]$	3:1	2:1	Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{2/4}$	1
$(NH_4)_2[B_3PO_7(OH)_2]$	3:1	2:1	Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{2/4}$	1
$(NH_4)[B_3PO_6(OH)_3]\cdot 0.5H_2O$	3:1	2:1	Solvothermal	$B^{2/3}$, $B^{4/4}$, $P^{2/4}$	1
$K_3[B_5PO_{10}(OH)_3]$	5:1	2:3	Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{2/4}$	1
$Na_3[B_6PO_{13}]$	6:1	4:2	Low-temperature flux	$B^{3/3}$, $B^{4/4}$, $P^{2/4}$	1
$K[B_6PO_{10}(OH)_4]$	6:1	4:2	Hydrothermal	$B^{2/3}$, $B^{4/4}$, $P^{4/4}$	1
$K_3B_4PO_{10}$ (in this paper) $K_2MB_4PO_{10}$ (M = Rb/Cs)	4:1	2:2	Solid-state	$B^{3/3}$, $B^{4/4}$, $P^{2/4}$	2

$Q^{n/CN}$: the parameter connectedness; CN: the coordination number; n: the number of shared oxygen atoms.

Table S2. Crystal data and structure refinement for $K_3B_4PO_{10}$, $K_2RbB_4PO_{10}$, and $K_2CsB_4PO_{10}$.

Empirical formula	**$K_3B_4PO_{10}$**	**$K_2RbB_4PO_{10}$**	**$K_2CsB_4PO_{10}$**
Formula weight	351.51	397.88	445.32
Temperature	299(2) K	273(2) K	301(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a =6.546(4) Å	a = 6.5577(17) Å	a = 6.6235(9) Å
	b = 6.567(4) Å	b = 6.5931(17) Å	b = 6.6243(10) Å
	c = 12.930(9) Å	c = 13.098 (3) Å	c = 13.273(2) Å
	α= 86.04(2) °	α= 84.626(9) °	α= 79.738(4) °
	β = 81.40(2) °	β = 80.514(9) °	β = 86.558(4) °
	γ= 60.420(15) °	γ= 60.457(8) °	γ= 60.095(4) °
Volume	477.9(6) Å^3	485.9(2) Å^3	496.47(13) Å^3
Z	2	2	2
Density (g/cm^3)	2.443	2.719	2.979
Absorption coefficient (mm^{-1})	1.637	6.158	4.770
F(000)	344	380	416
Theta range for data collection	3.19 to 27.69°	3.15 to 27.53°	3.12 to 27.55°
Limiting indices	-8≤ h ≤8, -8≤ k ≤8, -16 ≤ l ≤16	-8≤ h ≤8, -8≤ k ≤8, -16 ≤ l ≤16	-8≤ h ≤8, -8≤ k ≤8, -17 ≤ l ≤17
Reflections collected / unique	6430 / 2210 [R(int) = 0.0415]	8699 / 2234 [R(int) = 0.0380]	11152 / 2295 [R(int) = 0.0405]
Completeness to theta	98.50%	99.6%	99.8%
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	2210 / 0 / 163	2234 / 0 / 163	2295 / 0 / 163
Goodness-of-fit on F^2	0.962	1.098	0.939
Final R indices [F_o^2>2σ(F_o^2)][a]	R_1 =0.0384 wR_2 = 0.1226	R_1 = 0.0437 wR_2 = 0.1399	R_1 = 0.0293 wR_2 = 0.1050
R indices (all data)[a]	R_1 = 0.0482 wR_2 =0.1350	R_1 = 0.0576 wR_2 = 0.1529	R_1 = 0.0338 wR_2 = 0.1134
Largest diff. peak and hole	0.703 and -0.778 e·Å^{-3}	0.745 and -1.199 e·Å^{-3}	1.847 and -0.915 e·Å^{-3}

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)2 / \Sigma w\, F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K_3B_4PO_{10}$ U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
K1	8580(1)	9243(2)	6540(1)	45(1)	0.76
K2	4756(1)	3246(1)	4029(1)	27(1)	1.16
K3	11015(1)	2051(1)	632(1)	20(1)	1.26
P1	8046(1)	7275(1)	3721(1)	18(1)	4.83
B1	5592(5)	2939(5)	1388(2)	14(1)	3.07
B2	4674(5)	6949(5)	1448(3)	18(1)	3.08
B3	7288(5)	8671(5)	1698(2)	14(1)	3.05
B4	11434(5)	5963(5)	2032(3)	16(1)	3.06
O1	9521(3)	6576(3)	1455(1)	15(1)	2.01
O2	7387(3)	730(3)	1238(2)	18(1)	2.11
O3	3328(3)	3529(3)	1789(2)	17(1)	2.06
O4	6242(3)	4644(3)	1157(2)	26(1)	2.14
O5	5353(3)	8587(3)	1293(2)	23(1)	2.11
O6	2413(3)	7587(3)	1863(2)	24(1)	2.04
O7	6658(4)	9070(4)	2874(2)	28(1)	2.00
O8	10690(3)	5965(4)	3189(2)	33(1)	2.06
O9	7893(4)	8648(4)	4638(2)	31(1)	1.88
O10	7150(5)	5563(5)	3961(2)	42(1)	1.87

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K_2RbB_4PO_{10}$ U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
Rb1	8678(1)	9293(1)	6536(1)	37(1)	0.86
K1	10980(2)	2022(2)	630(1)	18(1)	1.25
K2	4674(2)	3259(2)	4022(1)	25(1)	1.11
B1	7231(9)	8646(9)	1676(4)	16(1)	3.05
B2	5541(9)	2909(9)	1369(4)	16(1)	3.05
B3	4617(9)	6902(9)	1460(4)	17(1)	3.06
B4	11382(9)	5898(8)	1998(4)	16(1)	3.06
P1	8010(2)	7256(2)	3681(1)	18(1)	4.79
O1	9457(6)	6558(5)	1433(2)	16(1)	1.99
O2	7298(5)	721(5)	1182(3)	19(1)	2.10
O3	3260(5)	3494(6)	1741(3)	18(1)	2.07
O4	6220(6)	4623(6)	1179(3)	27(1)	2.11
O5	2334(6)	7536(6)	1822(3)	22(1)	2.08
O6	5268(6)	8577(6)	1338(3)	22(1)	2.11
O7	6674(6)	9103(6)	2837(3)	26(1)	2.00
O8	10638(6)	5848(6)	3145(3)	27(1)	2.07
O9	7923(7)	8621(6)	4567(3)	28(1)	1.85
O10	6988(8)	5660(7)	3970(3)	35(1)	1.89

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K_2CsB_4PO_{10}$ U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
Cs1	9406(1)	1841(1)	3468(1)	25(1)	1.03
K1	3283(1)	12137(1)	5981(1)	15(1)	0.97
K2	1991(1)	-2853(2)	9363(1)	19(1)	1.22
P1	7207(2)	4834(2)	6375(1)	15(1)	4.78
B1	6841(7)	-1363(8)	8568(3)	14(1)	3.08
B2	2865(7)	1723(8)	8662(3)	13(1)	3.07
B3	8594(7)	4282(7)	8350(3)	12(1)	3.03
B4	5867(8)	2854(8)	8072(4)	13(1)	3.02
O1	6506(4)	4166(5)	8599(2)	13(1)	1.99
O2	3459(5)	3395(5)	8324(2)	16(1)	2.07
O3	669(4)	2164(5)	8872(2)	15(1)	2.07
O4	5799(5)	3635(6)	6913(2)	22(1)	2.04
O5	7494(5)	294(5)	8281(2)	18(1)	1.92
O6	8495(5)	-3642(5)	8639(2)	20(1)	2.08
O7	4531(5)	-653(6)	8785(3)	25(1)	2.12
O8	5640(6)	7461(6)	6066(3)	28(1)	1.85
O9	8528(6)	3589(6)	5511(2)	24(1)	1.71
O10	9071(5)	4315(6)	7215(2)	21(1)	1.98

Table S6. Selected distances (Å) and angles (deg) for $K_3B_4PO_{10}$.

K(1)-O(9)	2.654(3)	K(3)-O(4)	2.719(3)
K(1)-O(6)#9	2.807(3)	K(3)-O(3)#1	2.793(2)
K(1)-O(7)#9	3.025(3)	K(3)-O(1)#2	2.803(3)
K(1)-O(10)#8	3.037(3)	K(3)-O(5)#3	2.837(2)
K(1)-O(8)#8	3.213(4)	K(3)-O(1)	2.859(3)
K(1)-O(3)#5	3.231(3)	K(3)-O(2)#4	2.871(3)
K(1)-O(5)#9	3.359(3)	B(1)-O(2)	1.345(3)
K(1)-O(9)#10	3.373(3)	B(1)-O(3)	1.359(3)
K(2)-O(10)	2.659(3)	B(1)-O(4)	1.382(4)
K(2)-O(10)#5	2.696(3)	B(2)-O(4)	1.384(4)
K(2)-O(8)#6	2.713(3)	B(2)-O(5)	1.346(4)
K(2)-O(7)#7	2.818(3)	B(2)-O(6)	1.355(4)
K(2)-O(9)#7	2.826(3)	B(3)-O(1)	1.437(3)
K(2)-O(9)#5	2.909(3)	B(3)#7-O(2)	1.466(4)
K(2)-O(3)	3.141(3)	B(3)-O(5)	1.467(3)
P(1)-O(9)	1.500(2)	B(3)-O(7)	1.521(4)
P(1)-O(10)	1.501(3)	B(4)-O(1)	1.424(4)
P(1)-O(8)	1.570(2)	B(4)#6-O(3)	1.479(3)
P(1)-O(7)	1.574(2)	B(4)#6-O(6)	1.482(4)
K(3)-O(2)	2.896(2)	B(4)-O(8)	1.502(4)
K(3)-O(6)#3	3.017(3)	O(9)-K(1)-O(6)#9	147.02(8)
O(9)-K(1)-O(7)#9	85.28(8)	O(9)#7-K(2)-O(3)	113.66(7)
O(6)#9-K(1)-O(7)#9	80.80(7)	O(9)#5-K(2)-O(3)	105.27(7)
O(9)-K(1)-O(10)#8	80.72(8)	O(9)-P(1)-O(10)	115.67(15)
O(6)#9-K(1)-O(10)#8	129.79(8)	O(9)-P(1)-O(8)	108.50(13)
O(7)#9-K(1)-O(10)#8	133.01(8)	O(10)-P(1)-O(8)	109.78(15)
O(9)-K(1)-O(8)#8	81.23(7)	O(9)-P(1)-O(7)	107.85(14)
O(6)#9-K(1)-O(8)#8	127.11(8)	O(10)-P(1)-O(7)	109.92(15)
O(7)#9-K(1)-O(8)#8	86.39(6)	O(8)-P(1)-O(7)	104.52(12)
O(10)#8-K(1)-O(8)#8	47.30(7)	O(4)-K(3)-O(3)#1	110.11(8)
O(9)-K(1)-O(3)#5	109.29(8)	O(5)#3-K(3)-O(1)	111.91(7)
O(6)#9-K(1)-O(3)#5	88.46(8)	O(4)-K(3)-O(2)#4	116.28(7)
O(7)#9-K(1)-O(3)#5	58.37(6)	O(3)#1-K(3)-O(2)#4	131.68(6)
O(10)#8-K(1)-O(3)#5	84.60(8)	O(1)#2-K(3)-O(2)#4	49.85(7)
O(8)#8-K(1)-O(3)#5	42.92(6)	O(5)#3-K(3)-O(2)#4	85.06(7)
O(9)-K(1)-O(5)#9	129.50(8)	O(1)-K(3)-O(2)#4	144.90(6)
O(6)#9-K(1)-O(5)#9	43.29(6)	O(4)-K(3)-O(2)	48.10(7)
O(7)#9-K(1)-O(5)#9	44.29(6)	O(3)#1-K(3)-O(2)	132.30(7)
O(10)#8-K(1)-O(5)#9	131.68(7)	O(1)#2-K(3)-O(2)	103.11(6)
O(8)#8-K(1)-O(5)#9	95.31(6)	O(5)#3-K(3)-O(2)	109.91(8)
O(3)#5-K(1)-O(5)#9	52.42(6)	O(1)-K(3)-O(2)	110.36(7)
O(9)-K(1)-O(9)#10	86.98(8)	O(2)#4-K(3)-O(2)	90.51(6)

O(6)#9-K(1)-O(9)#10	83.91(7)	O(4)-K(3)-O(6)#3	104.71(7)
O(7)#9-K(1)-O(9)#10	138.31(7)	O(3)#1-K(3)-O(6)#3	93.15(7)
O(10)#8-K(1)-O(9)#10	85.57(8)	O(1)#2-K(3)-O(6)#3	136.67(6)
O(8)#8-K(1)-O(9)#10	132.58(6)	O(5)#3-K(3)-O(6)#3	46.81(6)
O(3)#5-K(1)-O(9)#10	159.29(6)	O(1)-K(3)-O(6)#3	126.49(7)
O(5)#9-K(1)-O(9)#10	126.26(6)	O(2)#4-K(3)-O(6)#3	87.82(8)
O(4)-K(3)-O(1)#2	89.51(7)	O(2)-K(3)-O(6)#3	63.15(6)
O(3)#1-K(3)-O(1)#2	120.42(7)	O(4)-K(3)-O(5)#2	136.90(7)
O(4)-K(3)-O(5)#3	145.90(7)	O(3)#1-K(3)-O(5)#2	89.65(8)
O(3)#1-K(3)-O(5)#3	62.31(7)	O(1)#2-K(3)-O(5)#2	48.19(6)
O(1)#2-K(3)-O(5)#3	123.68(7)	O(5)#3-K(3)-O(5)#2	77.18(8)
O(4)-K(3)-O(1)	66.49(6)	O(1)-K(3)-O(5)#2	105.39(6)
O(3)#1-K(3)-O(1)	49.86(6)	O(2)#4-K(3)-O(5)#2	46.65(6)
O(1)#2-K(3)-O(1)	96.79(7)	O(2)-K(3)-O(5)#2	136.71(7)
O(10)-K(2)-O(10)#5	93.48(8)	O(6)#3-K(3)-O(5)#2	112.24(6)
O(10)-K(2)-O(8)#6	108.76(10)	O(2)-B(1)-O(3)	124.7(3)
O(10)#5-K(2)-O(8)#6	96.30(9)	O(2)-B(1)-O(4)	114.5(2)
O(10)-K(2)-O(7)#7	120.30(9)	O(3)-B(1)-O(4)	120.7(2)
O(10)#5-K(2)-O(7)#7	133.42(8)	O(5)-B(2)-O(6)	119.4(2)
O(8)#6-K(2)-O(7)#7	101.10(8)	O(5)-B(2)-O(4)	120.6(3)
O(10)-K(2)-O(9)#7	105.29(10)	O(6)-B(2)-O(4)	120.0(3)
O(10)#5-K(2)-O(9)#7	90.58(8)	O(1)-B(3)-O(2)#11	111.0(2)
O(8)#6-K(2)-O(9)#7	144.71(8)	O(1)-B(3)-O(5)	112.2(2)
O(7)#7-K(2)-O(9)#7	52.24(7)	O(2)#11-B(3)-O(5)	107.1(2)
O(10)-K(2)-O(9)#5	145.97(8)	O(1)-B(3)-O(7)	110.6(2)
O(10)#5-K(2)-O(9)#5	53.72(7)	O(2)#11-B(3)-O(7)	107.3(2)
O(8)#6-K(2)-O(9)#5	86.15(9)	O(5)-B(3)-O(7)	108.6(2)
O(7)#7-K(2)-O(9)#5	84.62(8)	O(1)-B(4)-O(3)#1	110.4(2)
O(9)#7-K(2)-O(9)#5	70.30(9)	O(1)-B(4)-O(6)#1	113.2(2)
O(10)-K(2)-O(3)	107.10(7)	O(3)#1-B(4)-O(6)#1	110.4(2)
O(10)#5-K(2)-O(3)	141.61(8)	O(1)-B(4)-O(8)	111.6(2)
O(8)#6-K(2)-O(3)	46.79(6)	O(3)#1-B(4)-O(8)	104.5(2)
O(7)#7-K(2)-O(3)	61.42(6)	O(6)#1-B(4)-O(8)	106.3(2)

Symmetry transformations used to generate equivalent atoms:

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

#4 -x+3, -y, -z #5 -x+2, -y+1, -z #6 -x+2, -y+1, -z+1

#7 x+1, y, z #8 x, y+1, z

#9 -x+1, -y, -z+1 #10 -x+1, -y+1, -z+1 #11 -x+1, -y+2, -z+1

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

Table S7. Selected distances (Å) and angles (deg) for $K_2RbB_4PO_{10}$.

Rb(1)-O(9)	2.818(4)	K(2)-O(9)#4	2.910(4)
Rb(1)-O(5)#1	2.905(4)	K(2)-O(3)	3.239(4)
Rb(1)-O(7)#1	3.108(4)	P(1)-O(10)	1.496(4)
Rb(1)-O(10)#2	3.132(5)	P(1)-O(9)	1.510(4)
Rb(1)-O(8)#2	3.188(4)	P(1)-O(8)	1.572(4)
Rb(1)-O(9)#3	3.246(4)	P(1)-O(7)	1.577(4)
Rb(1)-O(3)#4	3.266(3)	B(4)-O(1)	1.427(6)
Rb(1)-O(6)#1	3.346(4)	B(1)-O(1)	1.440(6)
K(1)-O(4)	2.723(3)	B(2)-O(2)	1.343(6)
K(1)-O(3)#5	2.777(4)	B(1)#10-O(2)	1.475(6)
K(1)-O(1)#6	2.789(3)	B(2)-O(3)	1.360(6)
K(1)-O(2)#7	2.843(4)	B(4)#9-O(3)	1.476(6)
K(1)-O(6)#8	2.845(3)	B(3)-O(4)	1.384(6)
K(1)-O(1)	2.889(3)	B(2)-O(4)	1.395(6)
K(1)-O(2)	2.905(3)	B(3)-O(5)	1.351(6)
K(1)-O(5)#8	2.996(4)	B(4)#9-O(5)	1.477(6)
K(2)-O(10)	2.670(4)	B(3)-O(6)	1.355(6)
K(2)-O(10)#4	2.694(4)	B(1)-O(6)	1.450(6)
K(2)-O(8)#9	2.724(4)	B(1)-O(7)	1.528(6)
K(2)-O(9)#10	2.840(4)	B(4)-O(8)	1.504(6)
K(2)-O(7)#10	2.866(4)	O(9)-Rb(1)-O(5)#1	148.71(11)
O(9)-Rb(1)-O(7)#1	84.80(11)	O(1)#6-K(1)-O(5)#8	135.90(10)
O(5)#1-Rb(1)-O(7)#1	81.19(10)	O(2)#7-K(1)-O(5)#8	86.36(10)
O(9)-Rb(1)-O(10)#2	79.66(11)	O(6)#8-K(1)-O(5)#8	46.75(9)
O(5)#1-Rb(1)-O(10)#2	129.96(10)	O(1)-K(1)-O(5)#8	127.58(10)
O(7)#1-Rb(1)-O(10)#2	131.01(10)	O(2)-K(1)-O(5)#8	63.93(9)
O(9)-Rb(1)-O(8)#2	80.36(10)	O(4)-K(1)-O(6)#6	137.49(11)
O(5)#1-Rb(1)-O(8)#2	125.66(10)	O(3)#5-K(1)-O(6)#6	89.36(10)
O(7)#1-Rb(1)-O(8)#2	84.89(10)	O(1)#6-K(1)-O(6)#6	47.28(9)
O(10)#2-Rb(1)-O(8)#2	46.90(10)	O(2)#7-K(1)-O(6)#6	45.70(9)
O(9)-Rb(1)-O(9)#3	89.47(11)	O(6)#8-K(1)-O(6)#6	78.36(11)
O(5)#1-Rb(1)-O(9)#3	83.41(10)	O(1)-K(1)-O(6)#6	105.46(9)
O(7)#1-Rb(1)-O(9)#3	139.50(10)	O(2)-K(1)-O(6)#6	135.38(10)
O(10)#2-Rb(1)-O(9)#3	86.76(10)	O(5)#8-K(1)-O(6)#6	111.83(9)
O(8)#2-Rb(1)-O(9)#3	133.54(9)	B(1)#6-K(1)-O(6)#6	26.94(11)
O(9)-Rb(1)-O(3)#4	108.66(10)	O(10)-K(2)-O(10)#4	89.74(12)
O(5)#1-Rb(1)-O(3)#4	86.85(10)	O(10)-K(2)-O(8)#9	109.79(13)
O(7)#1-Rb(1)-O(3)#4	57.25(9)	O(10)#4-K(2)-O(8)#9	100.73(13)
O(10)#2-Rb(1)-O(3)#4	84.48(9)	O(10)-K(2)-O(9)#10	105.30(13)
O(8)#2-Rb(1)-O(3)#4	43.02(9)	O(10)#4-K(2)-O(9)#10	91.08(12)
O(9)#3-Rb(1)-O(3)#4	158.00(9)	O(8)#9-K(2)-O(9)#10	142.86(13)
O(9)-Rb(1)-O(6)#1	128.60(10)	O(10)-K(2)-O(7)#10	120.47(13)
O(5)#1-Rb(1)-O(6)#1	42.88(9)	O(10)#4-K(2)-O(7)#10	135.04(12)

O(7)#1-Rb(1)-O(6)#1	43.89(9)	O(8)#9-K(2)-O(7)#10	98.93(12)
O(10)#2-Rb(1)-O(6)#1	131.91(10)	O(9)#10-K(2)-O(7)#10	51.38(10)
O(8)#2-Rb(1)-O(6)#1	94.97(9)	O(10)-K(2)-O(9)#4	142.52(13)
O(9)#3-Rb(1)-O(6)#1	125.18(9)	O(10)#4-K(2)-O(9)#4	53.61(11)
O(3)#4-Rb(1)-O(6)#1	52.00(8)	O(8)#9-K(2)-O(9)#4	87.14(12)
O(9)-Rb(1)-O(8)#3	117.76(10)	O(9)#10-K(2)-O(9)#4	71.79(13)
O(5)#1-Rb(1)-O(8)#3	42.32(9)	O(7)#10-K(2)-O(9)#4	87.72(11)
O(7)#1-Rb(1)-O(8)#3	106.18(9)	O(10)-K(2)-O(3)	108.50(11)
O(10)#2-Rb(1)-O(8)#3	122.22(10)	O(10)#4-K(2)-O(3)	145.30(12)
O(8)#2-Rb(1)-O(8)#3	159.01(12)	O(8)#9-K(2)-O(3)	45.78(10)
O(9)#3-Rb(1)-O(8)#3	43.39(9)	O(9)#10-K(2)-O(3)	111.10(10)
O(3)#4-Rb(1)-O(8)#3	129.08(9)	O(7)#10-K(2)-O(3)	59.72(9)
O(6)#1-Rb(1)-O(8)#3	81.95(8)	O(9)#4-K(2)-O(3)	107.11(10)
B(3)#1-Rb(1)-O(8)#3	59.00(11)	O(10)-P(1)-O(9)	114.9(2)
O(4)-K(1)-O(3)#5	108.96(11)	O(10)-P(1)-O(8)	110.1(2)
O(4)-K(1)-O(1)#6	91.08(11)	O(9)-P(1)-O(8)	109.3(2)
O(3)#5-K(1)-O(1)#6	118.99(11)	O(10)-P(1)-O(7)	110.9(2)
O(4)-K(1)-O(2)#7	118.94(11)	O(9)-P(1)-O(7)	106.5(2)
O(3)#5-K(1)-O(2)#7	130.14(10)	O(8)-P(1)-O(7)	104.57(19)
O(1)#6-K(1)-O(2)#7	50.61(9)	O(1)-B(1)-O(6)	113.0(4)
O(4)-K(1)-O(6)#8	144.14(12)	O(1)-B(1)-O(2)#11	111.3(4)
O(3)#5-K(1)-O(6)#8	62.07(10)	O(6)-B(1)-O(2)#11	106.9(4)
O(1)#6-K(1)-O(6)#8	124.22(11)	O(1)-B(1)-O(7)	110.9(4)
O(2)#7-K(1)-O(6)#8	84.83(11)	O(6)-B(1)-O(7)	108.8(4)
O(4)-K(1)-O(1)	65.47(10)	O(2)#11-B(1)-O(7)	105.5(4)
O(3)#5-K(1)-O(1)	49.67(9)	O(2)-B(2)-O(3)	124.6(4)
O(1)#6-K(1)-O(1)	96.49(9)	O(2)-B(2)-O(4)	114.9(4)
O(2)#7-K(1)-O(1)	145.05(10)	O(3)-B(2)-O(4)	120.4(4)
O(6)#8-K(1)-O(1)	111.31(10)	O(5)-B(3)-O(6)	118.1(4)
O(4)-K(1)-O(2)	48.28(10)	O(5)-B(3)-O(4)	120.9(4)
O(3)#5-K(1)-O(2)	134.27(11)	O(6)-B(3)-O(4)	120.9(4)
O(1)#6-K(1)-O(2)	102.38(10)	O(1)-B(4)-O(3)#5	110.3(4)
O(2)#7-K(1)-O(2)	90.49(9)	O(1)-B(4)-O(5)#5	112.3(4)
O(6)#8-K(1)-O(2)	110.67(10)	O(3)#5-B(4)-O(5)#5	110.9(4)
O(1)-K(1)-O(2)	110.60(10)	O(1)-B(4)-O(8)	111.4(4)
O(4)-K(1)-O(5)#8	104.66(10)	O(3)#5-B(4)-O(8)	105.2(4)
O(3)#5-K(1)-O(5)#8	94.73(10)	O(5)#5-B(4)-O(8)	106.5(4)

Symmetry transformations used to generate equivalent atoms:

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

#4 -x+2, -y+1, -z+1 #5 -x+1, -y+2, -z+1 #6 -x+2, -y+2, -z+1

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

#9 -x+3, -y, -z #10 -x+2, -y+1, -z #11 x+1, y, z

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

Table S8. Selected distances (Å) and angles (deg) for $K_2CsB_4PO_{10}$.

Cs(1)-O(9)	3.047(3)	K(2)-O(5)#10	2.922(3)
Cs(1)-O(5)#1	3.051(3)	K(2)-O(3)	2.938(3)
Cs(1)-O(10)#2	3.155(3)	P(1)-O(9)	1.502(3)
Cs(1)-O(8)#3	3.175(3)	P(1)-O(8)	1.506(3)
Cs(1)-O(9)#1	3.198(3)	P(1)-O(4)	1.571(3)
Cs(1)-O(4)#3	3.239(3)	P(1)-O(10)	1.579(3)
Cs(1)-O(2)#3	3.334(3)	B(1)-O(1)	1.357(5)
Cs(1)-O(6)#1	3.343(3)	B(1)-O(1)	1.342(5)
K(1)-O(8)	2.668(4)	B(1)-O(2)	1.386(5)
K(1)-O(4)#5	2.761(3)	B(2)-O(2)	1.349(5)
K(1)-O(8)#4	2.768(4)	B(2)-O(3)	1.355(5)
K(1)-O(9)#6	2.870(3)	B(2)-O(3)	1.385(5)
K(1)-O(9)#4	2.877(3)	B(3)-O(4)	1.438(5)
K(1)-O(10)#6	2.971(3)	B(3)-O(5)	1.519(5)
K(2)-O(7)	2.727(3)	B(3)#10-O(5)	1.477(5)
K(2)-O(2)#7	2.771(3)	B(3)#7-O(6)	1.462(5)
K(2)-O(1)#8	2.771(3)	B(4)-O(6)	1.430(5)
K(2)-O(3)#9	2.807(3)	B(4)-O(7)	1.480(5)
K(2)-O(6)#10	2.866(3)	B(4)-O(7)	1.530(5)
K(2)-O(1)#7	2.887(3)	B(4)-O(10)	1.470(5)
O(9)-Cs(1)-O(5)#1	152.90(8)	O(9)#6-K(1)-O(2)#5	107.45(8)
O(9)-Cs(1)-O(10)#2	84.12(8)	O(9)#4-K(1)-O(2)#5	109.42(8)
O(5)#1-Cs(1)-O(10)#2	81.67(8)	O(10)#6-K(1)-O(2)#5	57.31(7)
O(9)-Cs(1)-O(8)#3	78.82(9)	O(7)-K(2)-O(2)#7	109.38(9)
O(5)#1-Cs(1)-O(8)#3	127.72(8)	O(7)-K(2)-O(1)#8	94.76(10)
O(10)#2-Cs(1)-O(8)#3	129.28(9)	O(2)#7-K(2)-O(1)#8	114.33(9)
O(9)-Cs(1)-O(9)#1	94.33(8)	O(7)-K(2)-O(3)#9	122.65(10)
O(5)#1-Cs(1)-O(9)#1	82.77(8)	O(2)#7-K(2)-O(3)#9	125.73(9)
O(10)#2-Cs(1)-O(9)#1	141.33(8)	O(1)#8-K(2)-O(3)#9	51.11(8)
O(8)#3-Cs(1)-O(9)#1	87.71(8)	O(7)-K(2)-O(6)#10	142.60(10)
O(9)-Cs(1)-O(4)#3	78.05(8)	O(2)#7-K(2)-O(6)#10	62.40(8)
O(5)#1-Cs(1)-O(4)#3	122.71(8)	O(1)#8-K(2)-O(6)#10	122.29(9)
O(10)#2-Cs(1)-O(4)#3	83.34(8)	O(3)#9-K(2)-O(6)#10	82.87(8)
O(8)#3-Cs(1)-O(4)#3	46.57(8)	O(7)-K(2)-O(1)#7	65.88(8)
O(9)#1-Cs(1)-O(4)#3	134.27(8)	O(2)#7-K(2)-O(1)#7	49.65(7)
O(9)-Cs(1)-O(2)#3	106.56(8)	O(1)#8-K(2)-O(1)#7	94.97(8)
O(5)#1-Cs(1)-O(2)#3	84.38(7)	O(3)#9-K(2)-O(1)#7	143.43(9)
O(10)#2-Cs(1)-O(2)#3	56.35(7)	O(6)#10-K(2)-O(1)#7	111.40(8)
O(8)#3-Cs(1)-O(2)#3	83.53(8)	O(7)-K(2)-O(5)#10	104.18(9)
O(9)#1-Cs(1)-O(2)#3	155.22(7)	O(2)#7-K(2)-O(5)#10	97.86(8)
O(4)#3-Cs(1)-O(2)#3	42.67(7)	O(1)#8-K(2)-O(5)#10	134.54(8)
O(9)-Cs(1)-O(6)#1	127.70(8)	O(3)#9-K(2)-O(5)#10	84.33(8)

O(5)#1-Cs(1)-O(6)#1	42.04(7)	O(6)#10-K(2)-O(5)#10	47.03(8)
O(10)#2-Cs(1)-O(6)#1	43.61(7)	O(1)#7-K(2)-O(5)#10	130.47(8)
O(8)#3-Cs(1)-O(6)#1	131.11(8)	O(7)-K(2)-O(3)	47.88(8)
O(9)#1-Cs(1)-O(6)#1	123.46(7)	O(2)#7-K(2)-O(3)	137.57(9)
O(4)#3-Cs(1)-O(6)#1	94.46(7)	O(1)#8-K(2)-O(3)	104.05(8)
O(2)#3-Cs(1)-O(6)#1	51.89(7)	O(3)#9-K(2)-O(3)	92.13(8)
O(9)-Cs(1)-O(4)#1	122.95(8)	O(6)#10-K(2)-O(3)	111.29(9)
O(5)#1-Cs(1)-O(4)#1	42.09(7)	O(1)#7-K(2)-O(3)	111.70(8)
O(10)#2-Cs(1)-O(4)#1	106.76(8)	O(5)#10-K(2)-O(3)	64.26(8)
O(8)#3-Cs(1)-O(4)#1	122.64(8)	O(7)-K(2)-O(6)#11	139.35(10)
O(9)#1-Cs(1)-O(4)#1	43.41(7)	O(2)#7-K(2)-O(6)#11	85.94(8)
O(4)#3-Cs(1)-O(4)#1	156.86(9)	O(1)#8-K(2)-O(6)#11	45.51(7)
O(2)#3-Cs(1)-O(4)#1	126.39(7)	O(3)#9-K(2)-O(6)#11	44.75(7)
O(6)#1-Cs(1)-O(4)#1	80.24(7)	O(6)#10-K(2)-O(6)#11	78.01(9)
O(9)-Cs(1)-O(8)#2	74.69(8)	O(1)#7-K(2)-O(6)#11	103.48(8)
O(5)#1-Cs(1)-O(8)#2	79.19(8)	O(5)#10-K(2)-O(6)#11	110.86(8)
O(10)#2-Cs(1)-O(8)#2	43.01(7)	O(3)-K(2)-O(6)#11	135.74(8)
O(8)#3-Cs(1)-O(8)#2	153.01(11)	O(9)-P(1)-O(8)	114.35(19)
O(9)#1-Cs(1)-O(8)#2	99.26(8)	O(9)-P(1)-O(4)	109.38(18)
O(4)#3-Cs(1)-O(8)#2	121.04(8)	O(8)-P(1)-O(4)	111.00(18)
O(2)#3-Cs(1)-O(8)#2	99.02(7)	O(9)-P(1)-O(10)	106.99(18)
O(6)#1-Cs(1)-O(8)#2	65.41(7)	O(8)-P(1)-O(10)	110.08(19)
O(4)#1-Cs(1)-O(8)#2	77.38(7)	O(4)-P(1)-O(10)	104.51(16)
O(8)-K(1)-O(4)#5	111.23(11)	O(6)-B(1)-O(5)	117.7(4)
O(8)-K(1)-O(8)#4	87.33(11)	O(6)-B(1)-O(7)	122.9(4)
O(4)#5-K(1)-O(8)#4	104.97(10)	O(5)-B(1)-O(7)	119.4(4)
O(8)-K(1)-O(9)#6	105.69(10)	O(2)-B(2)-O(3)	124.8(4)
O(4)#5-K(1)-O(9)#6	139.44(10)	O(2)-B(2)-O(7)	120.5(3)
O(8)#4-K(1)-O(9)#6	92.72(10)	O(3)-B(2)-O(7)	114.7(4)
O(8)-K(1)-O(9)#4	139.69(10)	O(1)-B(3)-O(6)#5	112.1(3)
O(4)#5-K(1)-O(9)#4	89.23(10)	O(1)-B(3)-O(3)#13	111.3(3)
O(8)#4-K(1)-O(9)#4	53.18(9)	O(6)#5-B(3)-O(3)#13	107.9(3)
O(9)#6-K(1)-O(9)#4	72.51(11)	O(1)-B(3)-O(10)	111.8(3)
O(8)-K(1)-O(10)#6	119.88(10)	O(6)#5-B(3)-O(10)	108.5(3)
O(4)#5-K(1)-O(10)#6	95.67(9)	O(3)#13-B(3)-O(10)	104.9(3)
O(8)#4-K(1)-O(10)#6	136.94(9)	O(1)-B(4)-O(5)	113.3(3)
O(9)#6-K(1)-O(10)#6	50.15(8)	O(1)-B(4)-O(2)	109.5(3)
O(9)#4-K(1)-O(10)#6	90.55(9)	O(5)-B(4)-O(2)	111.0(3)
O(8)-K(1)-O(2)#5	109.33(9)	O(1)-B(4)-O(4)	110.6(3)
O(4)#5-K(1)-O(2)#5	44.43(7)	O(5)-B(4)-O(4)	106.7(3)
O(8)#4-K(1)-O(2)#5	148.40(10)	O(2)-B(4)-O(4)	105.3(3)

Symmetry transformations used to generate equivalent atoms:

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

#4 -x-1, -y+1, -z+1 #5 -x, -y+1, -z+1 #6 x+1, y, z

#7 x, y+1, z #8 -x, -y, -z+1 #9 x-1, y+1, z

#10 -x+2, -y-1, -z #11 -x+1, -y, -z #12 -x+2, -y, -z