Electronic Supplementary Information

Variable Dimensionality of Anion Framework in Four New Borophosphates and Fluoroborophosphates with Short Cutoff Edge

Ruonan Zhang,†[a,b] Siru Guo,†[a,b] Xuping Wang,*[a,c] Rong Yang,[a,b] Zhen Chen,[a,b] Wenyao Zhang,[a,b]

Fangfang Zhang,[a] Zhiyong Guo,[d] Shujuan Han,*[a] Zhihua Yang[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.

[b]Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

[c]Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China.

[d]Xuchang Quality and Technical Supervision, Inspection and Testing Center, National Quality Supervision and Inspection Center for Ceramic Products of China, West Section of Longxing Road, Dongcheng District, Xuchang 461000, China.

*Corresponding author, E-mail: hansj@ms.xjb.ac.cn

Table S1. Crystal data and structure refinement for four new compounds.

Empirical formula	$Cs_3B_3P_4O_{16}$	$Li(NH_4)_2B_3P_4O_{16}$	$K_4B_2P_2O_9F_2$	$Rb_3B_2PO_5F_4$
Formula weight	811.04	455.33	421.96	465
Temperature	302.0 K	300.0 K	302.0	298.0 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions (Å)	a=13.0515(8) b=15.3256(10) c=7.9289(5) β = 96.283(2)°	a=7.3237(4) b=25.6466(14) c=7.6796(4) β = 119.951(4)°	a=13.1574(7) b=12.3117(6) c=7.0252(4) β = 90.351(2)°	a=7.3447(6) b=10.3803(8) c=12.3628(9) β = 94.699(3)°
Volume ($Å^3$)	1574.43(17)	1249.81(12)	1137.99(10)	939.37(13)
Z, Calculated density ($g·cm^{-3}$)	4, 3.417	4, 2.420	4, 2.463	4, 3.288
Absorption coefficient	7.398 mm^{-1}	0.713 mm^{-1}	1.908 mm^{-1}	15.794 mm^{-1}
F(000)	1472	912	824	848
Theta range for data collection (°)	2.057 to 25.023	3.163 to 27.489	1.548 to 27.101	2.566 to 27.531
Limiting indices	−16 ≤ h ≤ 16, −19 ≤ k ≤ 17, −10 ≤ l ≤ 10	−9 ≤ h ≤ 9, −33 ≤ k ≤ 33, −9 ≤ l ≤ 9	−16 ≤ h ≤ 16, −15 ≤ k ≤ 15, −9 ≤ l ≤ 9	−9 ≤ h ≤ 9, −13 ≤ k ≤ 13, −16 ≤ l ≤ 16
Reflections collected/unique	2780 / 2780 [R(int)=0.0381]	12631 / 2865 [R(int)=0.0754]	18995 / 2501 [R(int)=0.0762]	25049 / 2168 [R(int)=0.1172]
Completeness to theta	99.6%	99.7%	100.0%	100.0%
Max. and min. transmission	0.5580 and 0.4200	0.7455 and 0.6537	0.7407 and 0.6540	0.4891 and 0.3118
Data/restraints/parameters	2780 / 0 / 231	2865 / 38 / 259	2501 / 0 / 173	2168 / 0 / 137
Goodness-of-fit on F^2	1.104	1.034	1.048	1.039
Final R indices [I>2sigma(I)][a]	R_1 = 0.0420, wR_2 = 0.0867	R_1 = 0.0384, wR_2 = 0.0868	R_1 = 0.0542, wR_2 = 0.1588	R_1 = 0.0331, wR_2 = 0.0703
R indices (all data [a]	R_1 = 0.0493, wR_2 = 0.0867	R_1 = 0.0592, wR_2 = 0.0946	R_1 = 0.0704, wR_2 = 0.1724	R_1 = 0.0451, wR_2 = 0.0760
Extinction coefficient	0.00046(10)	N/A	N/A	0.0036(5)
Largest diff. peak and hole ($e·Å^{-3}$)	1.443 and -0.992	0.376 and -0.610	1.522 and -0.717	0.712 and -0.698

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

Table S2**.** Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for four title compounds. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
		$Cs_3B_3P_4O_{16}$			
Cs(1)	7592(1)	2348(1)	8690(1)	21(1)	1.05
Cs(2)	5593(1)	8340(1)	3868(1)	33(1)	1.07
Cs(3)	9223(1)	8221(1)	4252(1)	34(1)	0.75
B(1)	7648(7)	4958(6)	7834(11)	14(2)	3.21
B(2)	8682(7)	5051(7)	3614(11)	15(2)	3.19
B(3)	5867(7)	5253(6)	3384(11)	12(2)	3.12
P(1)	7060(2)	4629(1)	11050(3)	12(1)	5.15
P(2)	9395(1)	4255(1)	6811(3)	12(1)	5.26
P(3)	7392(2)	6220(1)	5214(3)	13(1)	5.25
P(4)	3982(1)	5930(1)	3946(3)	11(1)	5.14
O(1)	6667(4)	3747(4)	10601(8)	22(1)	2.02
O(2)	7377(4)	5170(4)	9546(7)	15(1)	2.13
O(3)	7090(4)	4236(4)	7053(7)	18(1)	2.17
O(4)	9438(5)	3314(4)	7128(8)	33(2)	1.88
O(5)	8738(5)	4740(4)	8021(8)	28(2)	2.10
O(6)	8979(5)	4427(4)	4967(8)	26(1)	2.15
O(7)	7995(4)	4551(4)	2391(7)	18(1)	2.17
O(8)	9562(4)	5291(5)	2755(8)	27(2)	2.07
O(9)	8222(4)	5844(4)	4197(8)	24(1)	2.06
O(10)	7475(6)	5790(4)	6963(8)	33(2)	2.29
O(11)	6309(4)	6000(4)	4351(9)	29(2)	2.02
O(12)	6252(4)	5235(4)	1724(7)	18(1)	2.13
O(13)	6090(4)	4420(4)	4245(7)	22(1)	2.12
O(14)	4745(4)	5369(4)	3071(7)	16(1)	2.06
O(15)	4177(4)	6875(4)	4014(8)	22(1)	1.99
O(16)	7516(5)	7168(4)	5424(8)	25(1)	1.82
		$Li(NH_4)_2B_3P_4O_{16}$			
Li(1)	6844(8)	-3835(2)	5334(8)	18(1)	1.08
N(1)	-4472(5)	-4991(1)	3106(4)	22(1)	–
N(2)	-5276(5)	-2592(1)	2583(4)	28(1)	–
B(1)	-196(5)	-3010(1)	11945(5)	9(1)	3.12
B(2)	-598(5)	-4396(1)	1413(5)	10(1)	3.1
B(3)	2464(5)	-3660(1)	8126(5)	9(1)	3.12
P(1)	-672(1)	-5463(1)	1445(1)	8(1)	5.02
P(2)	-493(1)	-2978(1)	8120(1)	8(1)	5.17
P(3)	6599(1)	-3679(1)	11135(1)	9(1)	5.03
P(4)	2144(1)	-3790(1)	4460(1)	8(1)	5.05
O(1)	-1582(3)	-4908(1)	1280(3)	11(1)	1.96
O(2)	-1979(3)	-3192(1)	12130(3)	10(1)	1.95

O(3)	1581(3)	-3375(1)	12796(3)	10(1)	1.97
O(4)	-2323(3)	-4030(1)	265(3)	11(1)	1.98
O(5)	4624(3)	-3452(1)	9275(3)	12(1)	1.95
O(6)	569(3)	-4249(1)	3519(3)	12(1)	1.99
O(7)	1660(3)	-3533(1)	6011(3)	11(1)	1.98
O(8)	2434(3)	-4220(1)	8458(3)	10(1)	1.95
O(9)	1480(3)	-5540(1)	3155(3)	14(1)	1.70
O(10)	1189(3)	-3407(1)	8844(3)	13(1)	2.05
O(11)	864(3)	-4423(1)	624(3)	12(1)	1.95
O(12)	-1003(3)	-2911(1)	9810(3)	15(1)	2.05
O(13)	656(3)	-2524(1)	13065(3)	13(1)	1.97
O(14)	6106(3)	-3938(1)	12562(3)	15(1)	1.76
O(15)	-2449(3)	-3090(1)	6210(3)	17(1)	1.68
O(16)	4331(3)	-3977(1)	5337(3)	16(1)	1.80

$K_4B_2P_2O_9F_2$

K(1)	3365(1)	3577(1)	1172(2)	30(1)	1.08
K(2)	1675(1)	8742(1)	6589(2)	28(1)	1.06
K(3)	580(1)	3538(1)	13689(2)	27(1)	0.86
K(4)	4406(1)	6342(1)	13793(2)	24(1)	0.86
B(1)	2957(5)	4298(5)	6216(10)	24(1)	3.08
B(2)	2009(5)	5897(5)	6409(10)	26(1)	3.07
P(1)	1262(1)	4175(1)	8348(2)	25(1)	5.01
P(2)	3755(1)	5900(1)	8408(2)	24(1)	5.02
O(1)	345(4)	3613(4)	7547(8)	47(1)	1.95
O(2)	2245(4)	3670(3)	7392(7)	37(1)	2.01
O(3)	1395(4)	4131(4)	10445(7)	38(1)	2.08
O(4)	1263(3)	5402(4)	7692(7)	40(1)	2.10
O(5)	2438(3)	5116(3)	5144(5)	29(1)	1.91
O(6)	3779(3)	4750(4)	7386(7)	39(1)	2.12
O(7)	2789(3)	6479(4)	7508(8)	40(1)	2.00
O(8)	4671(4)	6526(4)	7826(8)	44(1)	1.97
O(9)	3612(4)	5745(4)	10483(7)	41(1)	2.07
F(1)	3428(3)	3532(3)	4989(5)	37(1)	1.04
F(2)	1473(3)	6708(3)	5351(5)	34(1)	1.09

$Rb_3B_2PO_5F_4$

Rb(1)	2640(1)	5241(1)	3518(1)	26(1)	1.21
Rb(2)	-3956(1)	6630(1)	9119(1)	28(1)	1.13
Rb(3)	9137(1)	2908(1)	9268(1)	28(1)	1.00
B(1)	3689(7)	3793(5)	8160(4)	18(1)	3.10
B(2)	2491(7)	4769(5)	6373(4)	20(1)	3.04
P(1)	1265(2)	5754(1)	8214(1)	22(1)	5.09
O(1)	1148(4)	5455(3)	6962(3)	24(1)	2.25
O(2)	-589(5)	5592(3)	8596(3)	26(1)	2.02
O(3)	2151(5)	7019(3)	8445(3)	35(1)	1.91

O(4)	2545(5)	4652(4)	8728(3)	33(1)	2.17
O(5)	3763(5)	4051(3)	7052(3)	28(1)	2.17
F(1)	3426(4)	5687(3)	5765(2)	31(1)	1.03
F(2)	1518(5)	3977(3)	5588(3)	36(1)	1.01
F(3)	3075(5)	2514(3)	8343(3)	48(1)	0.97
F(4)	5474(4)	3856(3)	8695(3)	37(1)	1.08

Table S3. Selected bond distances (Å) and angles (deg) for $Cs_3B_3P_4O_{16}$.

Cs(1)-O(3)	3.210(6)	B(1)-O(10)	1.456(11)
Cs(1)-O(1)	2.957(6)	B(2)-O(9)	1.452(11)
Cs(1)-O(1)#2	3.102(6)	B(2)-O(6)	1.458(11)
Cs(1)-O(7)#3	3.150(6)	B(2)-O(8)	1.445(10)
Cs(1)-O(13)#3	3.401(6)	B(2)-O(7)	1.464(11)
Cs(1)-O(15)#1	3.175(6)	B(3)-O(13)	1.462(11)
Cs(1)-O(15)#4	3.203(6)	B(3)-O(11)	1.461(11)
Cs(1)-O(6)#3	3.362(6)	B(3)-O(14)	1.469(10)
Cs(1)-O(4)	3.192(7)	B(3)-O(12)	1.460(10)
Cs(2)-O(14)#6	3.475(6)	P(1)-O(2)	1.546(5)
Cs(2)-O(2)#5	3.263(6)	P(1)-O(12)#11	1.544(6)
Cs(2)-O(12)#7	3.195(6)	P(1)-O(1)	1.476(6)
Cs(2)-O(1)#8	3.088(6)	P(1)-O(7)#11	1.533(6)
Cs(2)-O(13)#6	3.532(6)	P(2)-O(8)#10	1.534(6)
Cs(2)-O(15)	2.919(6)	P(2)-O(5)	1.546(7)
Cs(2)-O(16)	3.220(6)	P(2)-O(6)	1.526(6)
Cs(2)-O(10)#5	3.303(7)	P(2)-O(4)	1.465(7)
Cs(3)-O(2)#5	3.472(5)	P(3)-O(11)	1.539(6)
Cs(3)-O(5)#5	3.313(7)	P(3)-O(9)	1.532(6)
Cs(3)-O(16)	2.981(6)	P(3)-O(16)	1.469(6)
Cs(3)-O(10)#5	3.144(7)	P(3)-O(10)	1.529(6)
Cs(3)-O(4)#9	3.196(7)	P(4)-O(14)	1.537(6)
Cs(3)-O(4)#10	3.194(7)	P(4)-O(3)#4	1.552(6)
B(1)-O(2)	1.476(10)	P(4)-O(13)#4	1.544(6)
B(1)-O(3)	1.428(11)	P(4)-O(15)	1.469(6)
B(1)-O(5)	1.453(11)		
O(3)-Cs(1)-O(13)#3	132.53(14)	O(5)-B(1)-O(2)	106.7(7)
O(3)-Cs(1)-O(6)#3	158.53(15)	O(5)-B(1)-O(10)	110.4(7)
O(1)-Cs(1)-O(3)	58.46(16)	O(10)-B(1)-O(2)	101.7(7)
O(1)#2-Cs(1)-O(3)	97.12(15)	O(8)-B(2)-O(7)	106.4(7)
O(1)-Cs(1)-O(1)#2	130.6(2)	O(8)-B(2)-O(9)	108.4(7)
O(1)-Cs(1)-O(7)#3	158.30(15)	O(8)-B(2)-O(6)	110.7(7)
O(1)#2-Cs(1)-O(7)#3	46.11(14)	O(9)-B(2)-O(7)	113.8(7)
O(1)#2-Cs(1)-O(13)#3	59.44(15)	O(9)-B(2)-O(6)	113.6(7)
O(1)-Cs(1)-O(13)#3	103.78(15)	O(6)-B(2)-O(7)	103.7(7)
O(1)-Cs(1)-O(15)#1	60.60(15)	O(12)-B(3)-O(14)	106.6(6)
O(1)-Cs(1)-O(15)#4	76.64(16)	O(12)-B(3)-O(13)	109.5(7)
O(1)#2-Cs(1)-O(15)#4	58.87(15)	O(12)-B(3)-O(11)	109.5(7)
O(1)#2-Cs(1)-O(15)#1	94.87(16)	O(13)-B(3)-O(14)	109.2(7)
O(1)-Cs(1)-O(6)#3	131.97(16)	O(11)-B(3)-O(14)	108.8(7)
O(1)#2-Cs(1)-O(6)#3	87.15(15)	O(11)-B(3)-O(13)	113.0(7)
O(1)#2-Cs(1)-O(4)	100.92(17)	O(1)-P(1)-O(2)	114.9(3)

O(1)-Cs(1)-O(4)	103.32(17)	O(1)-P(1)-O(12)#11	113.6(3)
O(7)#3-Cs(1)-O(3)	137.29(15)	O(1)-P(1)-O(7)#11	109.0(3)
O(7)#3-Cs(1)-O(13)#3	54.93(14)	O(7)#11-P(1)-O(2)	108.5(3)
O(7)#3-Cs(1)-O(15)#1	97.71(15)	O(7)#11-P(1)-O(12)#11	109.2(3)
O(7)#3-Cs(1)-O(15)#4	104.99(14)	O(6)-P(2)-O(8)#10	110.5(4)
O(7)#3-Cs(1)-O(6)#3	41.17(14)	O(6)-P(2)-O(5)	110.4(4)
O(7)#3-Cs(1)-O(4)	98.12(16)	O(4)-P(2)-O(8)#10	113.1(4)
O(15)#4-Cs(1)-O(3)	45.08(14)	O(4)-P(2)-O(5)	112.4(4)
O(15)#1-Cs(1)-O(3)	107.99(14)	O(4)-P(2)-O(6)	109.7(4)
O(15)#4-Cs(1)-O(13)#3	90.00(15)	O(8)#10-P(2)-O(5)	100.5(4)
O(15)#1-Cs(1)-O(13)#3	43.84(14)	O(9)-P(3)-O(11)	110.6(4)
O(15)#1-Cs(1)-O(15)#4	87.31(15)	O(16)-P(3)-O(11)	110.6(4)
O(15)#4-Cs(1)-O(6)#3	145.83(15)	O(16)-P(3)-O(9)	110.9(4)
O(15)#1-Cs(1)-O(6)#3	92.51(15)	O(16)-P(3)-O(10)	109.1(4)
O(15)#1-Cs(1)-O(4)	162.81(17)	O(10)-P(3)-O(11)	106.2(4)
O(6)#3-Cs(1)-O(13)#3	67.37(15)	O(10)-P(3)-O(9)	109.3(4)
O(4)-Cs(1)-O(3)	63.54(15)	O(12)#11-P(1)-O(2)	101.3(3)
O(4)-Cs(1)-O(13)#3	152.87(16)	O(14)-P(4)-O(3)#4	105.6(3)
O(4)-Cs(1)-O(15)#4	95.00(16)	O(14)-P(4)-O(13)#4	109.4(3)
O(4)-Cs(1)-O(6)#3	95.01(16)	O(13)#4-P(4)-O(3)#4	105.9(3)
O(3)-B(1)-O(2)	114.0(7)	O(15)-P(4)-O(14)	116.7(3)
O(3)-B(1)-O(5)	108.3(7)	O(15)-P(4)-O(3)#4	108.9(3)
O(3)-B(1)-O(10)	115.3(7)	O(15)-P(4)-O(13)#4	109.7(4)

Symmetry transformations used to generate equivalent atoms:

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

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

#9 -x+2,y+1/2,-z+3/2 #10 -x+2,-y+1,-z+1 #11 x,y,z+1 #12 -x+2,y-1/2,-z+3/2

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

Table S4. Selected bond lengths (Å) and angles (deg.) for $Li(NH_4)_2B_3P_4O_{16}$.

Li(1)-O(9)#2	1.998(5)	P(1)-O(1)	1.5509(19)
Li(1)-O(14)#3	1.934(5)	P(1)-O(8)#4	1.558(2)
Li(1)-O(15)#1	2.008(5)	P(1)-O(9)	1.4760(19)
Li(1)-O(16)	1.876(6)	P(1)-O(11)#5	1.5519(19)
B(1)-O(2)	1.458(4)	P(2)-O(10)	1.5335(19)
B(1)-O(3)	1.463(3)	P(2)-O(12)	1.529(2)
B(1)-O(12)	1.462(3)	P(2)-O(13)#6	1.550(2)
B(1)-O(13)	1.468(3)	P(2)-O(15)	1.480(2)
B(2)-O(1)	1.474(4)	P(3)-O(2)#1	1.5617(19)
B(2)-O(4)	1.463(4)	P(3)-O(4)#7	1.550(2)
B(2)-O(6)	1.454(3)	P(3)-O(5)	1.5521(19)
B(2)-O(11)	1.472(4)	P(3)-O(14)	1.472(2)
B(3)-O(5)	1.474(4)	P(4)-O(3)#3	1.5541(18)
B(3)-O(7)	1.461(3)	P(4)-O(6)	1.5525(19)
B(3)-O(8)	1.462(3)	P(4)-O(7)	1.549(2)
B(3)-O(10)	1.453(4)	P(4)-O(16)	1.474(2)
O(14)#3-Li(1)-O(9)#2	106.5(3)	O(1)-P(1)-O(8)#4	98.67(10)
O(14)#3-Li(1)-O(15)#1	112.4(3)	O(1)-P(1)-O(11)#5	105.91(11)
O(16)-Li(1)-O(9)#2	99.4(3)	O(9)-P(1)-O(8)#4	115.39(11)
O(16)-Li(1)-O(14)#3	103.9(2)	O(9)-P(1)-O(11)#5	113.32(12)
O(16)-Li(1)-O(15)#1	105.8(3)	O(11)#5-P(1)-O(8)#4	107.23(11)
O(2)-B(1)-O(3)	113.2(2)	O(10)-P(2)-O(13)#6	104.88(11)
O(2)-B(1)-O(12)	106.6(2)	O(12)-P(2)-O(10)	105.47(11)
O(2)-B(1)-O(13)	110.6(2)	O(12)-P(2)-O(13)#6	107.13(11)
O(3)-B(1)-O(13)	104.9(2)	O(15)-P(2)-O(10)	115.23(11)
O(12)-B(1)-O(3)	112.6(2)	O(15)-P(2)-O(12)	109.70(12)
O(12)-B(1)-O(13)	108.9(2)	O(15)-P(2)-O(13)#6	113.80(11)
O(4)-B(2)-O(1)	106.6(2)	O(4)#7-P(3)-O(2)#1	108.49(11)
O(4)-B(2)-O(11)	111.7(2)	O(4)#7-P(3)-O(5)	105.17(11)
O(6)-B(2)-O(1)	107.5(2)	O(5)-P(3)-O(2)#1	103.72(10)
O(6)-B(2)-O(4)	110.8(2)	O(14)-P(3)-O(2)#1	110.30(11)
O(6)-B(2)-O(11)	108.9(2)	O(14)-P(3)-O(4)#7	115.29(11)
O(11)-B(2)-O(1)	111.2(2)	O(14)-P(3)-O(5)	113.10(11)
O(7)-B(3)-O(5)	107.6(2)	O(6)-P(4)-O(3)#3	107.92(10)
O(7)-B(3)-O(8)	112.3(2)	O(7)-P(4)-O(3)#3	105.81(10)
O(8)-B(3)-O(5)	110.9(2)	O(7)-P(4)-O(6)	106.11(11)
O(10)-B(3)-O(5)	108.2(2)	O(16)-P(4)-O(3)#3	112.42(11)
O(10)-B(3)-O(7)	110.2(2)	O(16)-P(4)-O(6)	110.53(12)

O(10)-B(3)-O(8)	107.7(2)	O(16)-P(4)-O(7)	113.66(11)

Symmetry transformations used to generate equivalent atoms:

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

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

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

Table S5. Selected bond lengths (Å) and angles (deg.) for $K_4B_2P_2O_9F_2$.

K(1)-O(2)#2	3.031(5)	K(4)-O(5)#8	3.148(5)
K(1)-O(2)#1	3.251(4)	K(4)-O(6)#8	3.304(5)
K(1)-O(3)#2	2.726(5)	K(4)-O(6)#10	2.867(4)
K(1)-O(6)#2	3.078(5)	K(4)-O(7)#8	3.382(5)
K(1)-O(8)#3	2.676(5)	K(4)-O(8)#8	2.861(6)
K(1)-O(9)#2	2.733(5)	K(4)-O(8)#4	2.734(5)
K(1)-F(1)	2.683(4)	K(4)-O(9)	2.647(5)
K(1)-F(1)#1	2.727(4)	K(4)-F(1)#10	2.975(4)
K(2)-O(1)#6	2.735(5)	B(1)-O(2)	1.472(8)
K(2)-O(3)#5	2.764(5)	B(1)-O(5)	1.428(8)
K(2)-O(4)#5	2.980(5)	B(1)-O(6)	1.464(8)
K(2)-O(5)#4	3.032(4)	B(1)-F(1)	1.422(7)
K(2)-O(7)#5	3.239(6)	B(2)-O(4)	1.469(8)
K(2)-O(7)	3.212(5)	B(2)-O(5)	1.428(8)
K(2)-O(9)#5	2.743(5)	B(2)-O(7)	1.466(8)
K(2)-F(2)	2.664(4)	B(2)-F(2)	1.428(7)
K(2)-F(2)#4	2.715(4)	P(1)-O(1)	1.498(5)
K(3)-O(1)#9	2.783(6)	P(1)-O(2)	1.588(5)
K(3)-O(1)#8	2.731(6)	P(1)-O(3)	1.483(5)
K(3)-O(2)#8	3.395(5)	P(1)-O(4)	1.579(4)
K(3)-O(3)	2.628(5)	P(2)-O(6)	1.588(4)
K(3)-O(4)#7	2.915(5)	P(2)-O(7)	1.586(5)
K(3)-O(5)#8	3.282(5)	P(2)-O(8)	1.490(5)
K(3)-F(2)#7	2.804(4)	P(2)-O(9)	1.484(5)
O(2)#2-K(1)-O(2)#1	92.55(13)	F(1)#1-K(1)-O(9)#2	150.71(14)
O(2)#2-K(1)-O(6)#2	46.59(12)	F(1)-K(1)-F(1)#1	106.51(10)
O(3)#2-K(1)-O(2)#2	50.93(13)	O(5)-B(1)-O(2)	111.3(5)
O(3)#2-K(1)-O(2)#1	80.22(14)	O(5)-B(1)-O(6)	112.1(5)
O(3)#2-K(1)-O(6)#2	83.90(13)	O(6)-B(1)-O(2)	110.8(5)
O(3)#2-K(1)-O(9)#2	80.59(15)	F(1)-B(1)-O(2)	105.8(4)
O(3)#2-K(1)-F(1)#1	102.22(14)	F(1)-B(1)-O(5)	110.9(5)
O(6)#2-K(1)-O(2)#1	135.22(13)	F(1)-B(1)-O(6)	105.6(5)
O(8)#3-K(1)-O(2)#2	134.07(15)	O(5)-B(2)-O(4)	111.7(5)
O(8)#3-K(1)-O(2)#1	109.18(14)	O(5)-B(2)-O(7)	112.2(5)
O(8)#3-K(1)-O(3)#2	167.55(16)	O(5)-B(2)-F(2)	110.0(5)
O(8)#3-K(1)-O(6)#2	94.25(14)	O(7)-B(2)-O(4)	110.3(5)
O(8)#3-K(1)-O(9)#2	88.70(15)	F(2)-B(2)-O(4)	106.2(5)
O(8)#3-K(1)-F(1)#1	90.23(15)	F(2)-B(2)-O(7)	105.9(5)
O(8)#3-K(1)-F(1)	73.28(15)	O(1)-P(1)-O(2)	108.4(3)
O(9)#2-K(1)-O(2)#2	82.28(14)	O(1)-P(1)-O(4)	109.6(3)
O(9)#2-K(1)-O(2)#1	158.78(14)	O(3)-P(1)-O(1)	116.5(3)
O(9)#2-K(1)-O(6)#2	50.72(13)	O(3)-P(1)-O(2)	108.3(3)

F(1)-K(1)-O(2)#2	152.65(14)	O(3)-P(1)-O(4)	109.0(3)
F(1)-K(1)-O(2)#1	74.36(13)	O(4)-P(1)-O(2)	104.4(2)
F(1)#1-K(1)-O(2)#2	77.56(12)	O(7)-P(2)-O(6)	103.8(2)
F(1)#1-K(1)-O(2)#1	44.37(11)	O(8)-P(2)-O(6)	108.6(3)
F(1)-K(1)-O(3)#2	102.46(15)	O(8)-P(2)-O(7)	107.9(3)
F(1)-K(1)-O(6)#2	150.31(13)	O(9)-P(2)-O(6)	109.4(3)
F(1)#1-K(1)-O(6)#2	100.23(11)	O(9)-P(2)-O(7)	110.1(3)
F(1)-K(1)-O(9)#2	101.18(14)	O(9)-P(2)-O(8)	116.3(3)

Symmetry transformations used to generate equivalent atoms:

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

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

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

Table S6. Selected bond lengths (Å) and angles (deg.) for $Rb_3B_2PO_5F_4$.

Rb(1)-O(1)#2	2.888(3)	Rb(3)-O(2)#9	3.174(4)
Rb(1)-O(2)#2	3.034(4)	Rb(3)-O(2)#10	2.919(3)
Rb(1)-O(3)#3	2.868(4)	Rb(3)-O(3)#9	3.055(4)
Rb(1)-O(5)#1	2.885(4)	Rb(3)-O(4)#10	3.203(4)
Rb(1)-F(1)	2.829(3)	Rb(3)-F(1)#8	2.975(3)
Rb(1)-F(1)#1	3.105(3)	Rb(3)-F(2)#11	3.014(3)
Rb(1)-F(2)	3.048(3)	Rb(3)-F(3)#10	3.222(4)
Rb(1)-F(3)#4	2.888(3)	Rb(3)-F(4)	2.898(3)
Rb(1)-F(4)#1	3.302(3)	B(1)-O(4)	1.446(6)
Rb(2)-O(2)	2.821(3)	B(1)-O(5)	1.400(6)
Rb(2)-O(3)#7	2.939(4)	B(1)-F(3)	1.426(6)
Rb(2)-O(4)#5	3.079(3)	B(1)-F(4)	1.421(6)
Rb(2)-O(4)#7	3.295(4)	B(2)-O(1)	1.458(6)
Rb(2)-O(5)#6	2.909(4)	B(2)-O(5)	1.417(6)
Rb(2)-F(2)#6	3.027(3)	B(2)-F(1)	1.423(6)
Rb(2)-F(3)#5	3.274(4)	B(2)-F(2)	1.419(6)
Rb(2)-F(3)#6	3.294(4)	P(1)-O(1)	1.574(3)
Rb(2)-F(4)#7	2.951(3)	P(1)-O(2)	1.487(4)
Rb(2)-F(4)#5	3.048(3)	P(1)-O(3)	1.482(4)
Rb(3)-O(1)#8	2.964(3)	P(1)-O(4)	1.581(4)
O(1)#2-Rb(1)-O(2)#2	49.45(9)	F(1)-Rb(1)-F(4)#1	134.55(8)
O(1)#2-Rb(1)-F(1)#1	147.07(9)	F(1)#1-Rb(1)-F(4)#1	83.15(7)
O(1)#2-Rb(1)-F(2)	75.10(9)	F(2)-Rb(1)-F(1)#1	86.34(8)
O(1)#2-Rb(1)-F(4)#1	111.30(8)	F(2)-Rb(1)-F(4)#1	168.02(8)
O(2)#2-Rb(1)-F(1)#1	122.85(9)	F(3)#4-Rb(1)-O(1)#2	81.25(10)
O(2)#2-Rb(1)-F(2)	116.83(9)	F(3)#4-Rb(1)-O(2)#2	72.76(10)
O(2)#2-Rb(1)-F(4)#1	65.13(8)	F(3)#4-Rb(1)-F(1)#1	66.94(9)
O(3)#3-Rb(1)-O(1)#2	97.21(10)	F(3)#4-Rb(1)-F(2)	71.09(10)
O(3)#3-Rb(1)-O(2)#2	101.74(11)	F(3)#4-Rb(1)-F(4)#1	99.36(10)
O(3)#3-Rb(1)-O(5)#1	81.61(10)	O(5)-B(1)-O(4)	115.4(4)
O(3)#3-Rb(1)-F(1)#1	115.31(10)	O(5)-B(1)-F(3)	111.8(4)
O(3)#3-Rb(1)-F(2)	114.29(10)	O(5)-B(1)-F(4)	109.8(4)
O(3)#3-Rb(1)-F(3)#4	173.92(12)	F(3)-B(1)-O(4)	107.0(4)
O(3)#3-Rb(1)-F(4)#1	75.66(10)	F(4)-B(1)-O(4)	107.2(4)
O(5)#1-Rb(1)-O(1)#2	154.10(10)	F(4)-B(1)-F(3)	105.1(4)
O(5)#1-Rb(1)-O(2)#2	105.21(10)	O(5)-B(2)-O(1)	113.6(4)
O(5)#1-Rb(1)-F(1)#1	45.52(8)	O(5)-B(2)-F(1)	110.0(4)
O(5)#1-Rb(1)-F(2)	129.10(9)	O(5)-B(2)-F(2)	111.8(4)
O(5)#1-Rb(1)-F(3)#4	97.19(11)	F(1)-B(2)-O(1)	108.2(4)
O(5)#1-Rb(1)-F(4)#1	43.16(8)	F(2)-B(2)-O(1)	107.5(4)
F(1)-Rb(1)-O(1)#2	110.98(9)	F(2)-B(2)-F(1)	105.3(4)
F(1)-Rb(1)-O(2)#2	160.00(9)	O(1)-P(1)-O(4)	103.57(19)

F(1)-Rb(1)-O(3)#3	83.30(10)	O(2)-P(1)-O(1)	108.2(2)
F(1)-Rb(1)-O(5)#1	94.64(9)	O(2)-P(1)-O(4)	108.6(2)
F(1)-Rb(1)-F(1)#1	70.14(10)	O(3)-P(1)-O(1)	110.6(2)
F(1)-Rb(1)-F(2)	45.05(8)	O(3)-P(1)-O(2)	116.0(2)
F(1)-Rb(1)-F(3)#4	102.75(10)	O(3)-P(1)-O(4)	109.0(2)

Symmetry transformations used to generate equivalent atoms:

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

Table S7. Assignment of the absorption peaks observed in the IR spectrum of $Rb_3B_2PO_5F_4$:

Mode description	Absorption peaks (cm^{-1}) for $Rb_3B_2PO_5F_4$
$v_s(PO_4)$, $v_{as}(BO_2F_2)$, v_{as}(ring)	1200, 1150, 1038, 949
v_s (BO_2F_2), $\delta(PO_4)$	918, 791, 698, 606, 567
$\delta(BO_2F_2)$	528, 486

Table S8. Assignment of the absorption peaks observed in the IR spectrum of $Cs_3B_3P_4O_{16}$:

Mode description	Absorption peaks (cm^{-1}) for $Cs_3B_3P_4O_{16}$
$v_s(PO_4)$	1250, 1227
$v_{as}(BO_4)$, v_{as}(ring)	1157, 1088, 991
δ(B-O-P)	868, 791
$v_s(BO_4)$, $\delta(PO_4)$	891, 679, 640
δ(O-P-O)	548
$\delta(BO_4)$	490, 432

Table S9. Assignment of the absorption peaks observed in the IR spectrum of $Li(NH_4)_2B_3P_4O_{16}$:

Mode description	Absorption peaks (cm^{-1}) for $Li(NH_4)_2B_3P_4O_{16}$
$v_s(PO_4)$	1265, 1238
$v_{as}(BO_4)$, v_{as}(ring)	1103, 1034, 991, 933
δ(B-O-P)	845, 690
$v_s(BO_4)$, $\delta(PO_4)$	910, 605
δ(O-P-O)	563
$\delta(BO_4)$	486, 443

Table S10. Assignment of the absorption peaks observed in the IR spectrum of $K_4B_2P_2O_9F_2$:

Mode description	Absorption peaks (cm^{-1}) for $K_4B_2P_2O_9F_2$
$v_s(PO_4)$	1226, 1203
$v_{as}(BO_3F)$, v_{as}(ring)	1103, 1062, 990
δ(B-O-P)	845, 714
v_s (BO_3F), δ(PO_4)	953, 781, 645
δ(O-P-O)	563, 536
δ(BO_3F)	491, 459

Fig. S1. The PXRD patterns of (a) $Cs_3B_3P_4O_{16}$, (b) $Li(NH_4)_2B_3P_4O_{16}$, (c) $K_4B_2P_2O_9F_2$ and (d) $Rb_3B_2PO_5F_4$, respectively.

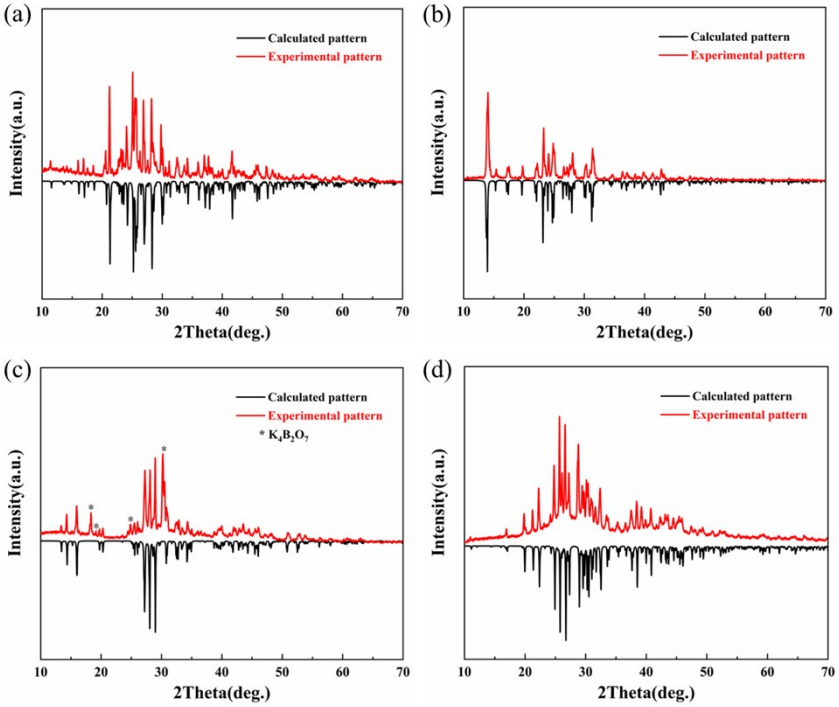

Fig. S2. The coordination of Cs(1), Cs(2) and Cs(3) in $Cs_3B_3P_4O_{16}$.

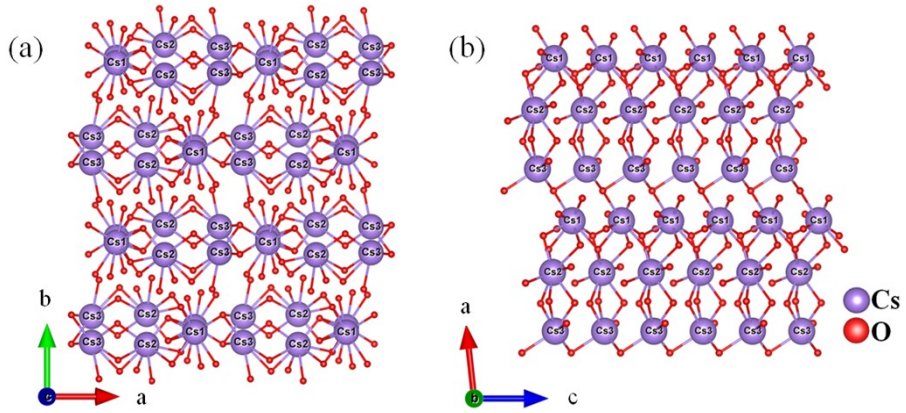

Fig. S3. The isolated [LiO_4] and [NH_4] units in $Li(NH_4)_2B_3P_4O_{16}$.

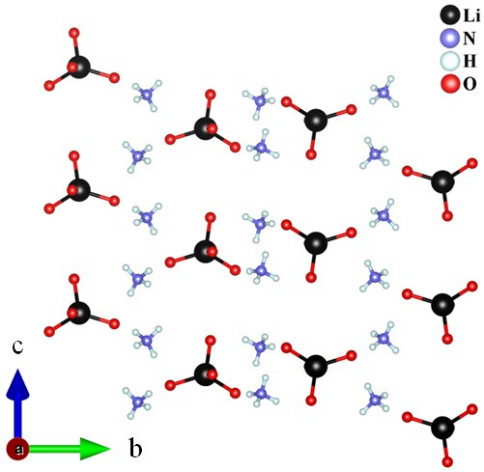

Fig. S4. The coordination of K^+ cations in $K_4B_2P_2O_9F_2$, (a) $[K(1)O_6F_2]$, (b) $[K(2)O_7F_2]$, (c) $[K(3)O_6F]$ and (d) $[K(4)O_7F]$.

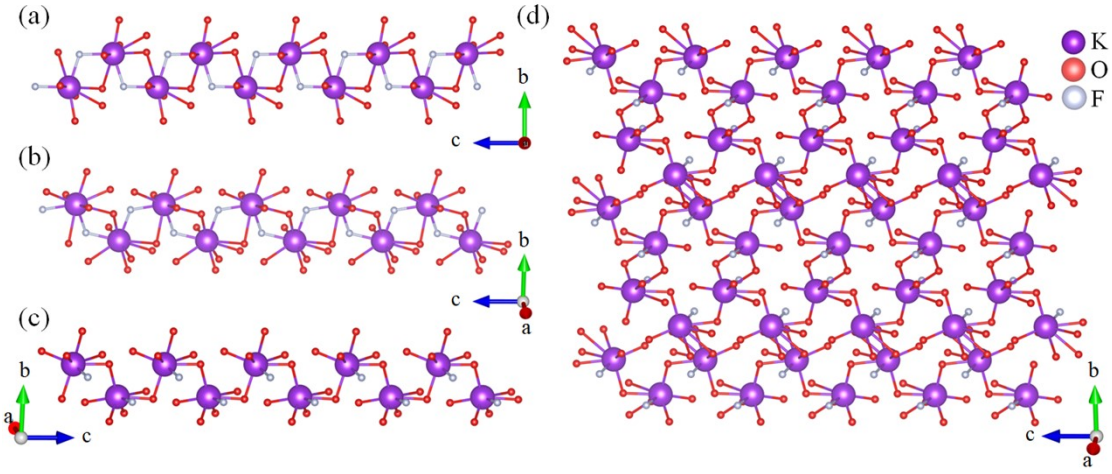

Fig. S5. The coordination of (a) Rb(1), (b) Rb(2) and (c) Rb(3) in $Rb_3B_2PO_5F_4$, respectively.

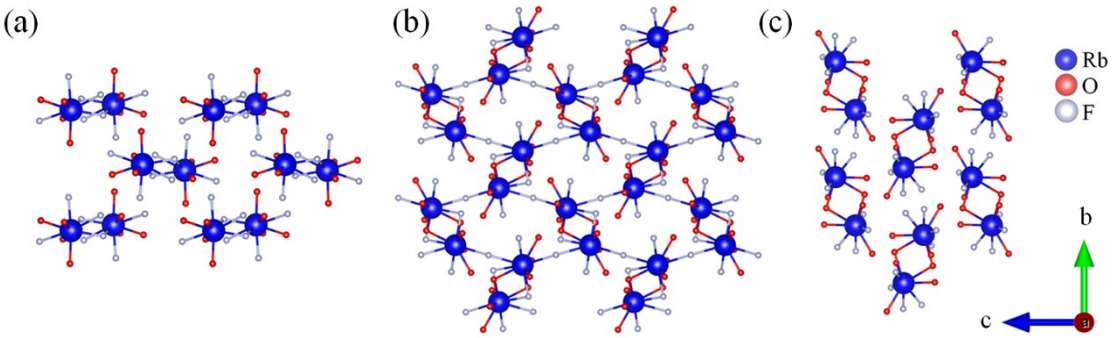

Fig. S6. The IR spectra of the title compounds.

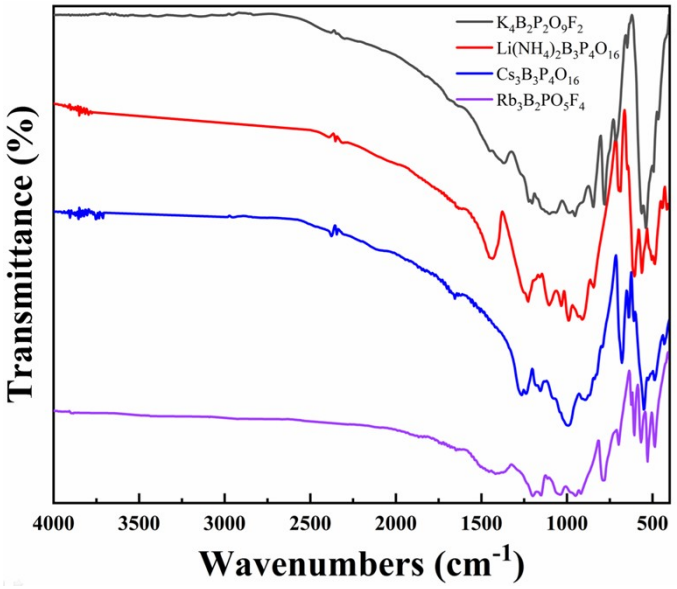

Fig. S7. UV−Vis−NIR diffuse reflectance spectra of (a) $Cs_3B_3P_4O_{16}$, (b) $Li(NH_4)_2B_3P_4O_{16}$, (c) $K_4B_2P_2O_9F_2$ and (d) $Rb_3B_2PO_5F_4$, respectively.

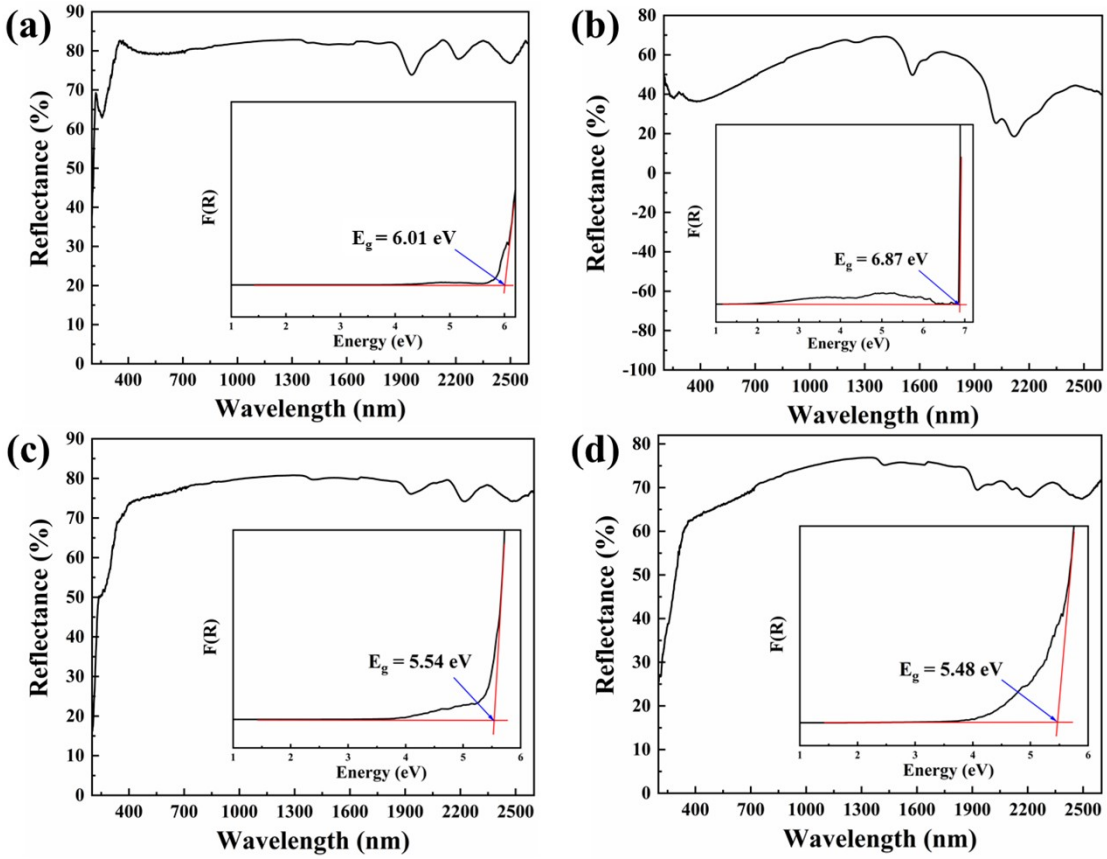

Fig. S8. Heyd−Scuseria–Ernzerhof (HSE06) hybrid functional implemented in PWmat code was performed to calculate band gap. Band structures (HSE06) of (a) $Cs_3B_3P_4O_{16}$, (b) $Li(NH_4)_2B_3P_4O_{16}$, (c) $K_4B_2P_2O_9F_2$ and (d) $Rb_3B_2PO_5F_4$, respectively.