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$K_7B_2P_5O_{19}$: A Novel Alkali Metal Borophosphate with Zero Dimensional $[B_2P_5O_{19}]^{7-}$ Anionic Units†

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Equipment

Powder XRD data were collected on a Bruker D2 PHASER diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 5-70° with a step size of 0.02° and a fixed counting time of 1 s/step. Vibrational spectra were obtained at room temperature via a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in a range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} (5 mg of the sample, 500 mg of KBr). The UV-Vis-NIR optical diffuse reflectance spectrum was measured at room temperature with a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range 190 − 2600 nm. The reflectance spectrum was converted to absorbance with the Kubelka–Munk function.[S1]Thermal analysis was carried out on NETZSCH STA 449C instrument at a temperature range of 50 - 900 °C with a heating rate of 10 °C /min in an atmosphere of flowing N_2.

Computational Details

First-principles density functional theory (DFT) electronic structure calculations for the two compounds were performed with the total-energy code CASTEP.[S2] The exchange-correlation effects were treated with the general gradient approximation (GGA) using Perdew-Burke-Emzerhoff (PBE) functional.[S3] The interactions between the ionic cores and the electrons were described by the Norm-conserving pseudopotentials.[S4] The Monkhorst–Pack scheme *k*-points grid sampling was set at 3×3×2 in the primitive cell of the Brillouin zone (BZ) for the total energy calculations. The plane-wave cutoff energy was set to 750.0 eV, which was proven to be an optimal level of the total energy convergence. The following orbital electrons were treated as valence electrons: K, $3s^23p^64s^1$, B, $2s^22p^1$, P, $3s^23p^3$, and O, $2s^22p^4$. The other parameters used in the calculations were set by the default values of the CASTEP code.

S1(a) J. Tauc, *Mater. Res. Bull.*, 1970, **5**, 721; (b) P. Kubelka and F. Z. Munk, *Tech. Phys.*, 1931, **12**, 593.

S2 (a)M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, *J. Phys.: Condens. Matter* 2002, **14**, 2717. (b)V. Milman, B. Winkler, J. A.White, C. J. Pickard, M. C. Payne, E. V. Akhmatskaya, R. H. Nobes, *Int. J. Quantum Chem.* 2000, **77**, 895.

S3 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865.

S4 J. S. Lin, A. Qteish, M. C. Payne, V. Heine, *Phys. Rev. B* 1993, **47**, 4174.

Table S1. Atomic Coordinates, Equivalent Isotropic Displacement Parameters (Å^2) and Bond Valence Sums for $K_7B_2P_5O_{19}$.

Atom	*Wyck.*	S.O.F.	x/*a*	y/*b*	z/*c*	U_{eq}[a]	∑V
K(1)	2i	1	0.9718(1)	0.6345(1)	-0.1195(1)	0.0034(1)	1.02
K(2)	2i	1	0.9344(1)	0.8618(1)	0.3826(1)	0.0036(1)	0.99
K(3)	2i	1	0.7142(1)	0.0364(1)	0.2065(1)	0.0024(1)	1.23
K(4)	1a	1	1	1	0	0.0033(1)	0.80
K(5)	2i	1	0.4632(1)	0.2425(1)	0.0975(1)	0.0028(1)	1.14
K(6)	2i	1	0.4452(1)	0.6165(1)	0.2029(1)	0.0031(1)	1.21
K(7)	2i	1	0.7508(1)	0.2684(1)	0.5023(1)	0.0038(1)	0.86
K(8)	2i	0.495	0.5623(2)	0.5100(2)	0.4791(2)	0.0035(1)	1.00
B(1)	2i	1	0.7068(4)	0.0161(4)	0.7153(3)	0.0018(1)	3.05
B(2)	2i	1	0.9228(4)	0.2817(4)	0.7967(3)	0.0019(1)	3.08
P(1)	2i	1	0.7729(1)	0.6590(1)	0.1032(1)	0.0020(1)	5.13
P(2)	2i	1	0.3075(1)	0.8505(1)	0.0956(1)	0.0018(1)	4.80
P(3)	2i	1	0.8401(1)	0.4915(1)	0.2851(1)	0.0024(1)	4.95
P(4)	2i	1	0.6550(1)	0.8837(1)	0.4981(1)	0.0020(1)	4.81
P(5)	2i	1	0.2017(1)	0.1997(1)	0.2922(1)	0.0019(1)	4.97
O(1)	2i	1	0.1794(3)	0.7019(2)	0.1354(2)	0.0021(1)	2.00
O(2)	2i	1	0.2265(3)	0.9051(3)	0.0039(2)	0.0026(1)	1.98
O(3)	2i	1	0.3895(2)	0.9677(2)	0.2128(2)	0.0018(1)	2.03
O(4)	2i	1	0.4274(3)	0.8179(3)	0.0660(2)	0.0027(1)	2.08
O(5)	2i	1	0.5165(3)	0.7476(3)	0.4256(2)	0.0033(1)	2.15
O(6)	2i	1	0.7342(4)	0.7668(3)	0.1523(3)	0.0046(1)	1.96
O(7)	2i	1	0.9518(3)	0.7289(3)	0.1172(3)	0.0040(1)	2.10
O(8)	2i	1	0.6942(4)	0.5966(5)	-0.0202(3)	0.0072(1)	1.96
O(9)	2i	1	0.7315(3)	0.5249(4)	0.1813(3)	0.0065(1)	2.17
O(10)	2i	1	0.2467(3)	0.0947(3)	0.2320(2)	0.0028(1)	2.10
O(11)	2i	1	0.2239(3)	0.1664(3)	0.4278(2)	0.0027(1)	2.20
O(12)	2i	1	0.3117(4)	0.3595(3)	0.2892(3)	0.0052(1)	2.17
O(13)	2i	1	0.0330(3)	0.1475(4)	0.2469(3)	0.0043(1)	1.95
O(14)	2i	1	0.7577(3)	0.0054(3)	0.4361(2)	0.0029(1)	1.95
O(15)	2i	1	0.8391(3)	0.1561(3)	0.7066(2)	0.0027(1)	2.07
O(16)	2i	1	0.6040(3)	0.9427(2)	0.5956(2)	0.0021(1)	1.99
O(17)	2i	1	0.8439(5)	0.5595(4)	0.3983(3)	0.0072(1)	1.81
O(18)	2i	1	0.0044(3)	0.5746(3)	0.2540(2)	0.0026(1)	2.09
O(19)	2i	1	0.7768(3)	0.3271(3)	0.2675(2)	0.0032(1)	1.99

Table S2. Selected Bond Distances (Å) and Angles (deg) for $K_7B_2P_5O_{19}$.

K(1)-O(13)#1	2.712(3)	K(7)-O(14)	2.811(3)
K(1)-O(18)#1	2.754(3)	K(7)-O(15)	2.834(3)
K(1)-O(2)#2	2.793(3)	K(7)-O(19)	2.858(3)
K(1)-O(7)	2.989(3)	K(7)-O(5)#10	2.888(3)
K(1)-O(1)#3	2.993(2)	K(7)-O(17)	3.014(4)
K(1)-O(8)	3.073(4)	K(7)-O(16)#10	3.073(2)
K(1)-O(1)#2	3.121(3)	K(7)-O(18)#13	3.154(3)
K(1)-O(12)#1	3.143(3)	K(7)-O(16)	3.234(2)
K(1)-O(19)#1	3.204(3)		
		K(8)-O(5)#12	2.689(3)
K(2)-O(15)#5	2.750(3)	K(8)-O(5)	2.733(3)
K(2)-O(17)#6	2.785(3)	K(8)-O(12)#11	2.740(4)
K(2)-O(6)	2.842(3)	K(8)-O(12)#5	2.754(4)
K(2)-O(11)#5	2.913(3)	K(8)-O(17)#6	2.960(4)
K(2)-O(14)	2.920(3)	K(8)-O(11)#5	2.965(3)
K(2)-O(11)	2.997(3)		
K(2)-O(14)#5	3.011(3)	B(1)-O(15)	1.428(4)
K(2)-O(13)	3.164(3)	B(1)-O(3)#10	1.459(4)
		B(1)-O(16)	1.491(4)
K(3)-O(2)#7	2.658(2)	B(1)-O(10)#5	1.511(4)
K(3)-O(14)	2.683(3)		
K(3)-O(13)	2.747(3)	B(2)-O(15)	1.420(5)
K(3)-O(19)	2.764(3)	B(2)-O(1)#10	1.477(4)
K(3)-O(4)	2.777(3)	B(2)-O(18)#13	1.485(4)
K(3)-O(6)	2.916(3)	B(2)-O(7)#5	1.490(5)
K(3)-O(3)	2.986(2)		
		P(1)-O(8)	1.462(3)
K(4)-O(2)#7	2.847(2)	P(1)-O(6)	1.469(3)
K(4)-O(2)#2	2.847(2)	P(1)-O(7)	1.543(3)
K(4)-O(7)#1	2.979(2)	P(1)-O(9)	1.590(3)
K(4)-O(7)	2.979(2)		
K(4)-O(10)	3.051(3)	P(2)-O(4)	1.484(2)
K(4)-O(10)#1	3.051(3)	P(2)-O(2)	1.490(3)
K(4)-O(13)	3.113(3)	P(2)-O(3)	1.590(2)
K(4)-O(13)#1	3.113(3)	P(2)-O(1)	1.597(2)
K(5)-O(4)#7	2.582(3)	P(3)-O(17)	1.468(3)
K(5)-O(10)#8	2.781(3)	P(3)-O(19)	1.472(2)
K(5)-O(9)#9	2.803(3)	P(3)-O(18)	1.567(2)
K(5)-O(8)#7	2.816(4)	P(3)-O(9)#9	1.615(3)
K(5)-O(3)	2.960(2)		
K(5)-O(19)	3.058(3)	P(4)-O(5)	1.483(3)

K(5)-O(2)	3.102(3)	P(4)-O(14)	1.491(3)
K(5)-O(6)#7	3.152(3)	P(4)-O(16)	1.556(2)
K(5)-O(12)#8	3.424(4)	P(4)-O(11)#5	1.632(3)
K(6)-O(12)#11	2.634(3)	P(5)-O(12)	1.469(3)
K(6)-O(8)#3	2.637(3)	P(5)-O(13)	1.473(3)
K(6)-O(4)	2.678(3)	P(5)-O(10)	1.550(2)
K(6)-O(5)	2.700(3)	P(5)-O(11)	1.623(3)
K(6)-O(6)	2.736(3)		
K(6)-O(1)	3.134(2)	O(17)-P(3)-O(19)	117.66(18)
		O(17)-P(3)-O(18)	111.44(19)
O(15)-B(1)-O(3)#10	113.5(3)	O(19)-P(3)-O(18)	110.06(15)
O(15)-B(1)-O(16)	109.7(3)	O(17)-P(3)-O(9)#9	108.6(2)
O(3)#10-B(1)-O(16)	107.6(3)	O(19)-P(3)-O(9)#9	105.60(18)
O(15)-B(1)-O(10)#5	112.8(3)	O(18)-P(3)-O(9)#9	102.16(14)
O(3)#10-B(1)-O(10)#5	106.2(3)		
O(16)-B(1)-O(10)#5	106.7(3)	O(5)-P(4)-O(14)	118.10(16)
		O(5)-P(4)-O(16)	109.46(15)
O(15)-B(2)-O(1)#10	112.9(3)	O(14)-P(4)-O(16)	113.41(14)
O(15)-B(2)-O(18)#13	110.9(3)	O(5)-P(4)-O(11)#5	108.61(15)
O(1)#10-B(2)-O(18)#13	104.9(3)	O(14)-P(4)-O(11)#5	102.36(15)
O(15)-B(2)-O(7)#5	111.9(3)	O(16)-P(4)-O(11)#5	103.53(13)
O(1)#10-B(2)-O(7)#5	107.0(3)		
O(18)#13-B(2)-O(7)#5	108.9(3)	O(12)-P(5)-O(13)	116.85(19)
		O(12)-P(5)-O(10)	111.50(18)
O(8)-P(1)-O(6)	115.2(2)	O(13)-P(5)-O(10)	109.75(16)
O(8)-P(1)-O(7)	108.5(2)	O(12)-P(5)-O(11)	108.45(16)
O(6)-P(1)-O(7)	111.38(18)	O(13)-P(5)-O(11)	106.55(16)
O(8)-P(1)-O(9)	109.3(2)	O(10)-P(5)-O(11)	102.65(13)
O(6)-P(1)-O(9)	108.5(2)		
O(7)-P(1)-O(9)	103.42(15)		
O(4)-P(2)-O(2)	117.85(15)		
O(4)-P(2)-O(3)	107.29(14)		
O(2)-P(2)-O(3)	110.09(13)		
O(4)-P(2)-O(1)	107.93(13)		
O(2)-P(2)-O(1)	109.36(13)		
O(3)-P(2)-O(1)	103.33(12)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+2,-z; #2 x+1,y,z; #3 -x+1,-y+1,-z; #4 x,y-1,z-1; #5 -x+2,-y+2,-z+1; #6 x,y-1,z;
#7 -x+1,-y+2,-z; #8 x-1,y,z; #9 x,y+1,z; #10 -x+1,-y+2,-z+1; #11 x-1,y-1,z; #12 -x+1,-y+1,-z+1;
#13 -x+2,-y+3,-z+1; #14 x,y+1,z+1; #15 x+1,y+1,z

Table S3. Structure Table for the Known Borophosphates Containing P-O-P Connection.

compound	space group	FBU	anionic partial structures	ref
$Cs_2Cr_3(BP_4O_{14})(P_4O_{13})$	$P2_1/c$	$[B(P_2O_7)_2]^{5-}$	$[B(P_2O_7)_2]_n^{5n-}$ chains (1D)	5
$CsFeBP_3O_{11}$	*Pnma*	$[B(PO_4)(P_2O_7)]^{4-}$	$[BP_3O_{11}]_n^{4n-}$ framework (3D)	5
$Li_2Cs_2B_2P_4O_{15}$	*P*	$[B_4P_8O_{30}]^{8-}$	$[B_2P_4O_{15}]_n^{4n-}$ layer (2D)	6
$Li_3K_2BP_4O_{14}$	*Cmca*	$[B(P_2O_7)_2]^{5-}$	$[B(P_2O_7)_2]_n^{5n-}$ layer (2D)	6
$Li_3Rb_2BP_4O_{14}$	*Cmca*	$[B(P_2O_7)_2]^{5-}$	$[B(P_2O_7)_2]_n^{5n-}$ layer (2D)	6

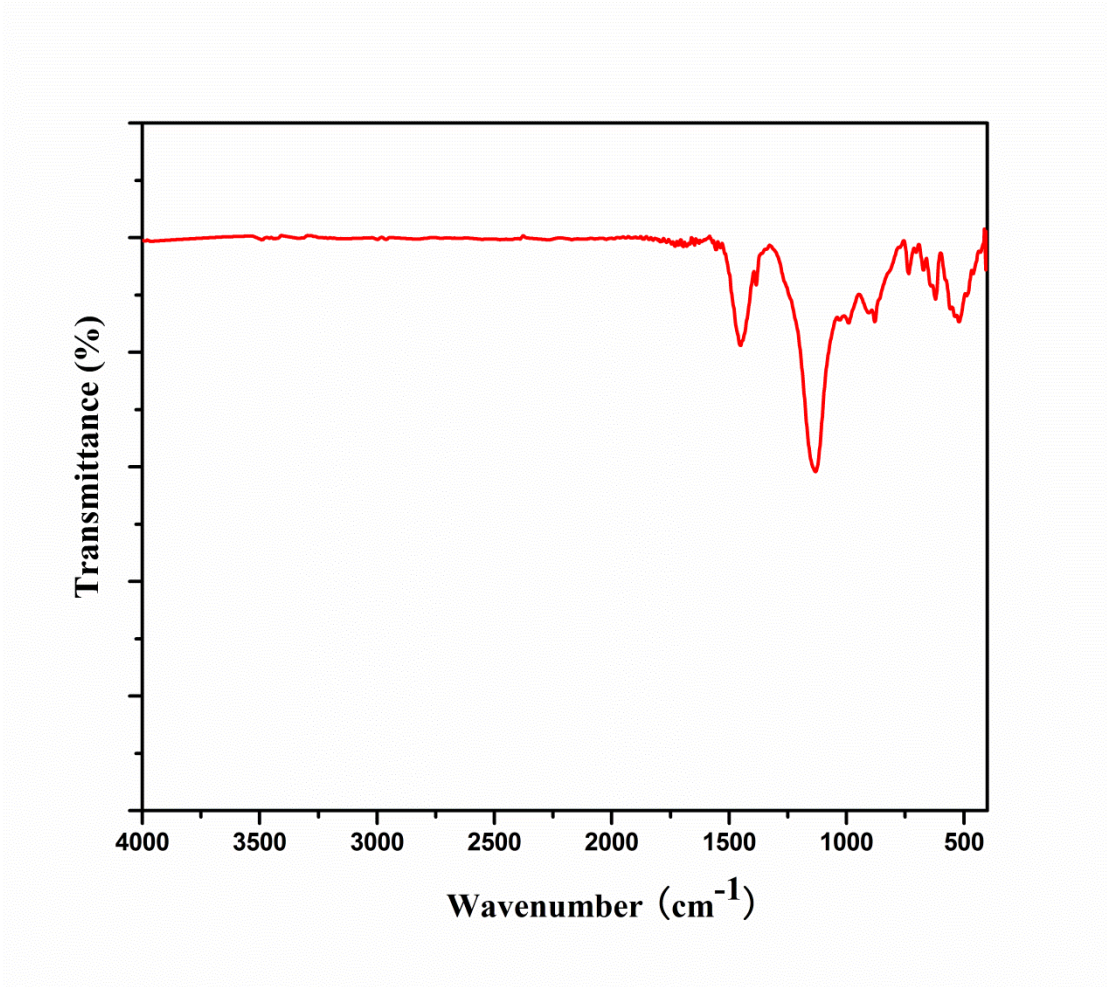

Figure S1. IR spectroscopy of $K_7B_2P_5O_{19}$.

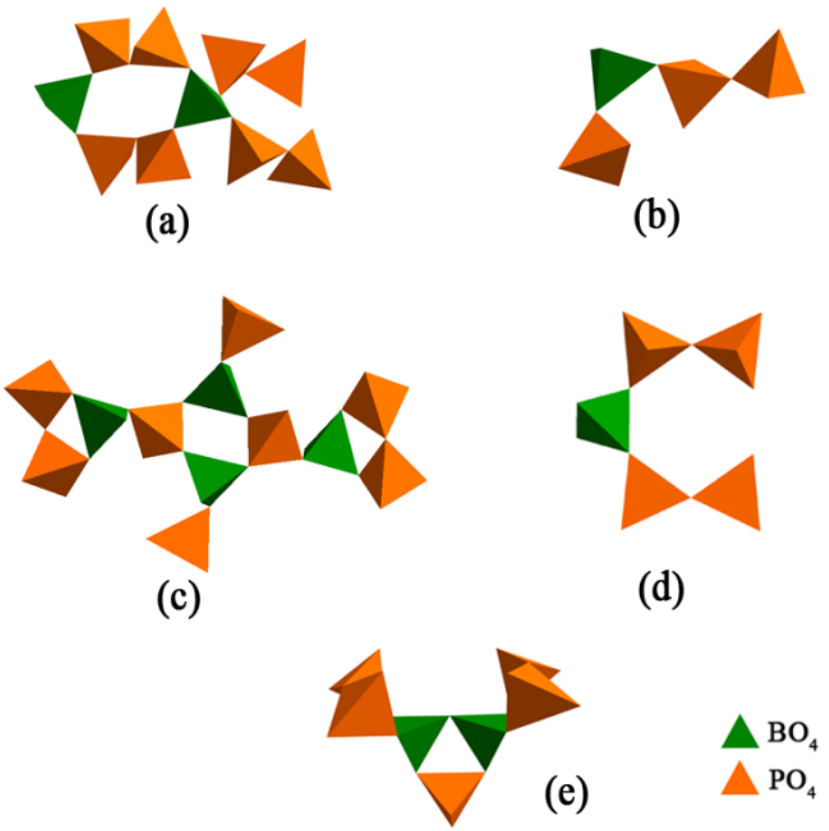

Figure S2. View of four different kinds of FBUs with P-O-P connections: (a) $[B(P_2O_7)_2]^{5-}$ unit with B:P=1:4; (b) $[B(PO_4)(P_2O_7)]^{4-}$ unit with B:P =1:3; (c) $[B_4P_8O_{30}]^{8-}$ unit with B:P = 1:2 (d) another kind of $[B(P_2O_7)_2]^{5-}$ unit with B:P=1:4 and (e) $[B_2P_5O_{19}]^{7-}$ unit with B:P =2:5.

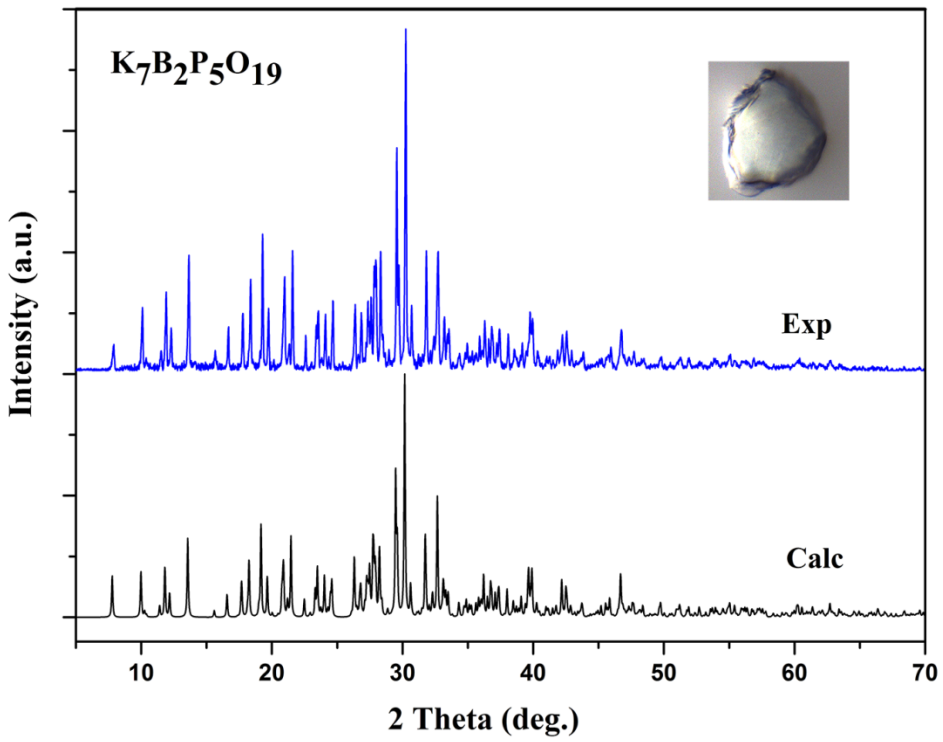

Figure S3. Powder XRD pattern of $K_7B_2P_5O_{19}$ (the inner figure shows the crystal for single crystal determination).

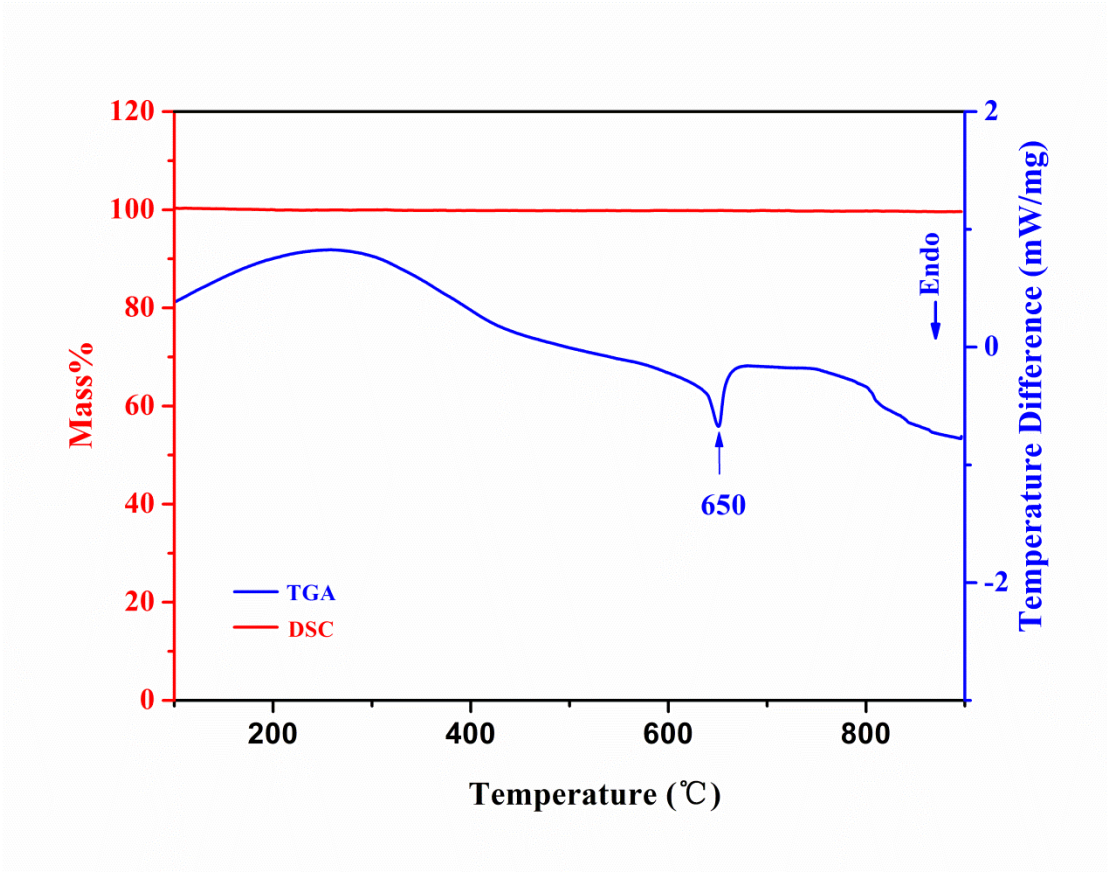

Figure S4. Thermal behaviour of $K_7B_2P_5O_{19}$ (thermal gravimetric analysis: red curve; differential scanning calorimetry: blue curve).

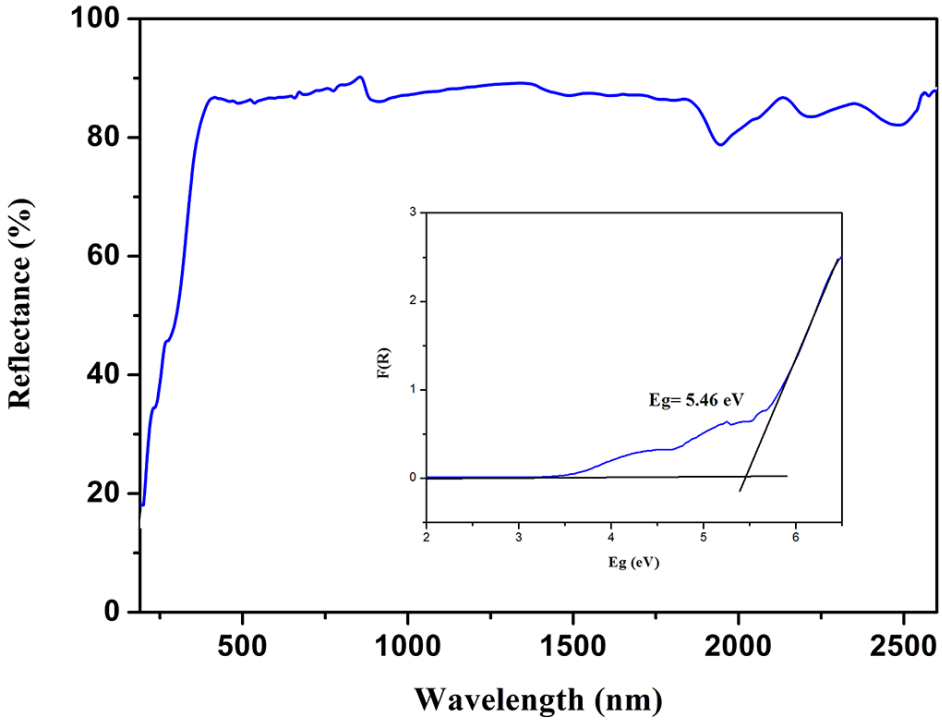

Figure S5. UV-vis–NIR diffuse reflectance spectroscopy of $K_7B_2P_5O_{19}$.

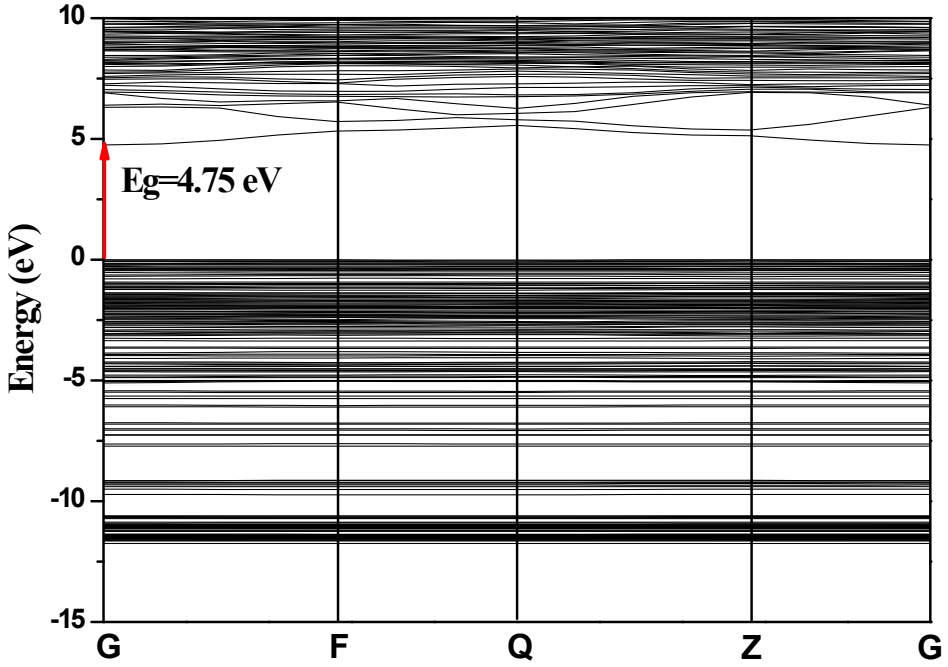

Figure S6. Band structure of $K_7B_2P_5O_{19}$.

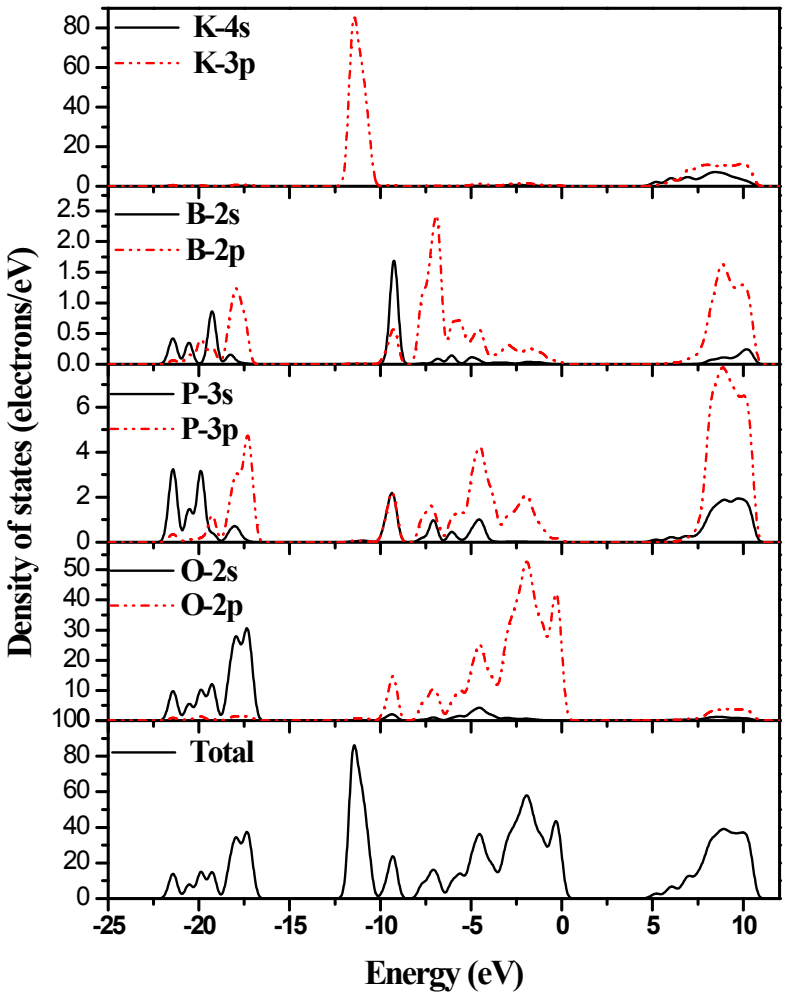

Figure S7. Density of states of $K_7B_2P_5O_{19}$.