Electronic Supplementary Information

Cadmium Phosphates with Two Types of Fundamental Building Units and Wide Ultraviolet Transparency Window

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CONTENTS

Synthesis and general characterization

Synthesis of $KCd_6P_7O_{24}$ and $KCd_3P_3O_{11}$: All reagents for synthesis were commercially available and used as received. The raw materials used are as follows: KH_2PO_4 (Aladdin Chemistry Co., Ltd, 99.5%), CdO (Rhawn 99%), MoO_3 (Beijing hawk Chemistry Co., Ltd, 99.95%), $NH_4H_2PO_4$ (Aladdin Chemistry Co., Ltd, 99.5%), and K_2CO_3 (Aladdin Chemistry Co., Ltd, 99.5%). Single crystals of $KCd_6P_7O_{24}$ and $KCd_3P_3O_{11}$ were grown by a spontaneous crystallization approach. A mixture of KH_2PO_4 (0.01 mol, 1.36 g), MoO_3 (5 mmol, 0.721 g), and CdO (5 mmol, 0.640 g) was packed into an alumina crucible. Then, the crucible was slowly heated to 600 °C and held for 24 h to homogenize the solution. After that, the temperature was cooled down to 450 °C at a rate of 2 °C·h^{-1} and cooled rapidly to 30 °C at a rate of 30 °C·h^{-1}. Colorless block crystals for both compounds were found in the crucible for further structural determination. The resulting yields are about 25% and 33% for $KCd_6P_7O_{24}$ and $KCd_3P_3O_{11}$, respectively.

Polycrystalline samples of $KCd_6P_7O_{24}$ and $KCd_3P_3O_{11}$ were synthesized by the traditional solid-state reaction route. Mixtures of $NH_4H_2PO_4$, K_2CO_3, and CdO with stoichiometric ratios were ground thoroughly and put into corundum crucibles. Then, the mixtures were put inside a muffle furnace and preheated at 300 °C for 24 h to release CO_2 and NH_3. After that, the temperature was gradually raised to 700 °C for $KCd_6P_7O_{24}$ (650 °C for $KCd_3P_3O_{11}$) and held at this temperature for 48 h with several intermediate grindings. Pure polycrystalline samples of $KCd_6P_7O_{24}$ and $KCd_3P_3O_{11}$ were successfully obtained. The phases were checked by the powder X-ray diffraction (XRD) measurement.

General characterization: The single-crystal XRD data were collected on a Bruker D8 VENTURE diffractometer equipped with a PHOTON II detector and Mo IμS 3.0 microfocus X-ray sources (λ = 0.71073 Å). The collected data were processed using the Olex2 software.[1] Atomic positions and isotropic thermal parameters are refined using the least squares method according to $F_o^2 \geq 2\sigma(F_o^2)$. The structures were checked by the program PLATON,[2] and no higher symmetries were found. The crystal data and structural information are summarized in Table S1. The atomic coordinates and the equivalent isotropic displacement parameters are available in Table S2. The selected bond lengths and angles are listed in Table S3.

Powder XRD data were measured on a Dandong Haoyuan DX-27mini X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å). The powder XRD pattern was scanned over the 2θ angles range of 10-70 °, at a scanning step width of 0.02 ° and a fixed counting time of 2 s. Scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) spectroscopy was performed on a Hitachi TM4000 Plus microscope applied at an operating voltage of 15 kV. The IR spectra of samples were measured at room temperature by a Shimadzu IR Affinity-1 spectrometer. The powder samples were evenly mixed with the dried KBr. The UV spectra were collected on a METASH UV-8000 UV visible spectrophotometer in the wavelength range of 200-1100 nm. The reflectance was converted into absorption using the Tauc plot method: $(\alpha h\nu)^{1/n} = B(h\nu\text{-}Eg)^3$ (α: absorption coefficient; *h*: Planck constant; *v*:

frequency). The thermal gravimetric (TG) analysis and differential scanning calorimetry (DSC) were studied with a NETZSCH5 instrument under air. The sample was placed in an alumina crucible and heated from 30 to 1000 °C with a heating rate of 10 °C·min^{-1}.

Computational methods: The first-principles calculations on electronic structure, band structure, and optical properties of the title compounds were carried out by using the CASTEP software package.[4] The generalized gradient approximation (GGA)[5] was adopted, and Perdew-Burke-Ernzerhof (PBE)[6] functional with norm-conserving pseudopotentials was chosen to calculate the exchange-correlation potential. The energy cutoff for the plane wave was chosen as 850 eV. The following orbital electrons are considered as valence electrons: K-4s^1, Cd-5s^{2}4p^{6}4d^{10}**,** P-3s^{2}3p^3, and O-2s^{2}2p^4.

Table S1. Crystal data and structure refinements for $KCd_6P_7O_{24}$ and $KCd_3P_3O_{11}$.

Empirical formula	$KCd_6P_7O_{24}$	$KCd_3P_3O_{11}$
Formula weight	1314.29	645.21
Temperature/K	273.15	273.15
Crystal system, space group	Monoclinic	Orthorhombic
Unit cell dimensions/Å	$P2_1/m$	$Pbcm$
	a = 5.4887(4)	a = 8.2828(3)
	b = 27.154(2)	b = 9.1660(3)
	c = 6.7732(5)	c = 12.4341(5)
β (deg)	107.148(3)	
Volume/Å^3	964.61(12)	944.00(6)
Z	2	4
Absorption coefficient (mm^{-1})	74.19	77.02
Calculated density (g/cm^3)	4.525	4.540
F (000)	1208	1184
Theta range for data collection (deg.)	3.00 to 27.51	2.459 to 27.491
Limiting indices	$-7 \le h \le 7$, $-35 \le k \le 35$, $-8 \le l \le 8$	$-10 \le h \le 10$, $-11 \le k \le 11$, $-16 \le l \le 16$
Data/restraints/ parameters	2257/0/178	1128/0/90
GOF on F^2	1.268	1.127
Final R indexes [$I \ge 2\sigma(I)$] [a]	R_1 = 0.0330, wR_2 = 0.0677	R_1 = 0.0166, wR_2 = 0.0390
Final R indexes [all data][a]	R_1 = 0.0367, wR_2 = 0.0691	R_1 = 0.0192, wR_2 = 0.0404
Largest diff. peak and hole (e Å^{-3})	1.31 to -1.22	0.43 to -0.65

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

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $KCd_6P_7O_{24}$ and $KCd_3P_3O_{11}$. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}	BVS*
			$KCd_6P_7O_{24}$		
K1	-0.2872(5)	0.750000	0.6375(4)	0.0305(6)	1.12
Cd1	0.78510(9)	0.59894(2)	0.92042(8)	0.01331(12)	2.19
Cd2	0.10837(9)	0.68303(2)	0.29369(8)	0.01347(12)	2.20
Cd3	0.81775(9)	0.45666(2)	0.31354(8)	0.01439(12)	2.10
P1	0.5288(5)	0.750000	1.1047(4)	0.0111(4)	4.82
P2	0.2444(3)	0.66975(6)	0.8217(3)	0.0106(3)	4.85
P3	0.6724(3)	0.60852(6)	0.3919(3)	0.0114(3)	4.85
P4	0.2912(3)	0.52498(6)	0.2086(3)	0.0105(3)	4.87
O1	0.8089(13)	0.750000	1.2250(10)	0.0134(13)	2.00
O2	0.3465(13)	0.750000	1.2328(11)	0.0133(13)	1.93
O3	0.4847(9)	0.70402(18)	0.9569(8)	0.0169(10)	2.06
O4	0.0564(9)	0.66773(18)	0.9487(8)	0.0168(10)	1.97
O5	0.1368(10)	0.69681(19)	0.6209(8)	0.0197(11)	1.91
O6	0.3760(9)	0.62188(17)	0.8076(8)	0.0149(10)	1.99
O7	0.8492(9)	0.59547(18)	0.6057(7)	0.0156(10)	1.78
O8	0.4817(11)	0.6469(2)	0.3987(9)	0.0276(13)	2.05
O9	0.8263(9)	0.62111(19)	0.2435(8)	0.0172(10)	2.12
O10	0.5385(10)	0.5574(2)	0.3063(9)	0.0257(12)	1.99
O11	0.1376(9)	0.52085(18)	0.3616(7)	0.0162(10)	1.92
O12	0.1375(9)	0.54878(18)	0.0103(7)	0.0139(9)	1.93
O13	0.4089(9)	0.47602(17)	0.1753(8)	0.0156(10)	2.06
			$KCd_3P_3O_{11}$		
K1	0.11670(13)	0.25	0.5	0.0207(2)	1.04
Cd1	-0.05849(3)	0.39577(3)	0.25	0.01060(8)	2.15
Cd2	0.43307(2)	0.60001(2)	0.60885(2)	0.01233(8)	2.04
P1	0.69126(12)	0.81684(11)	0.75	0.0093(2)	4.78
P2	0.22339(9)	0.59178(7)	0.36821(6)	0.00811(15)	4.79
O1	0.0661(2)	0.5136(2)	0.38282(17)	0.0131(4)	1.98
O2	0.2072(2)	0.7573(2)	0.37359(16)	0.0115(4)	1.96
O3	0.2956(3)	0.5524(3)	0.25	0.0102(6)	1.88
O4	0.3537(2)	0.5363(2)	0.44448(16)	0.0123(4)	2.12
O5	0.6056(3)	0.7698(2)	0.64741(19)	0.0209(5)	1.85
O6	0.8681(4)	0.7766(3)	0.75	0.0207(7)	1.84
O7	0.6852(3)	0.9916(3)	0.75	0.0120(6)	2.10

*Bond valence sum (BVS)[7] were calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond " I " and B = 0.37.

Table S3. Bond lengths [Å] and angles [deg] for $KCd_6P_7O_{24}$ and $KCd_3P_3O_{11}$.

$KCd_6P_7O_{24}$			
K1–O5	2.769(6)	P4–O11	1.520(5)
K1–O5$^{\#1}$	2.769(6)	P4–O13	1.524(5)
K1–O2$^{\#2}$	2.882(8)	P4–O10	1.590(5)
K1–O1$^{\#2}$	2.992(7)	Cd1–O9$^{\#5}$	2.216(5)
K1–O3$^{\#3}$	3.066(5)	Cd1–O6	2.237(5)
K1–O3$^{\#4}$	3.066(5)	Cd1–O7	2.263(5)
K1–O4	3.263(6)	Cd1–O12$^{\#6}$	2.296(5)
K1–O4$^{\#1}$	3.263(6)	Cd1–O13$^{\#7}$	2.300(5)
K1–O8$^{\#4}$	3.295(6)	Cd1–O4$^{\#8}$	2.361(5)
K1–O8$^{\#3}$	3.295(6)	Cd1–Cd3$^{\#9}$	3.4028(7)
P1–O2	1.505(7)	Cd1–Cd2$^{\#6}$	3.4797(7)
P1–O1	1.513(7)	Cd2–O8	2.193(5)
P1–O3	1.574(5)	Cd2–O5	2.208(5)
P1–O3$^{\#1}$	1.574(5)	Cd2–O9$^{\#4}$	2.243(5)
P2–O6	1.504(5)	Cd2–O4$^{\#10}$	2.307(5)
P2–O5	1.505(5)	Cd2–O2$^{\#10}$	2.346(4)
P2–O4	1.527(5)	Cd2–O1$^{\#2}$	2.403(4)
P2–O3	1.653(5)	Cd3–O13	2.225(5)
P3–O8	1.487(5)	Cd3–O11$^{\#7}$	2.226(5)
P3–O7	1.528(5)	Cd3–O7$^{\#9}$	2.248(5)
P3–O9	1.530(5)	Cd3–O12$^{\#11}$	2.283(5)
P3–O10	1.596(5)	Cd3–O6$^{\#7}$	2.416(5)
P4–O12	1.505(5)	Cd3–O11$^{\#8}$	2.427(5)
K1–O5	2.769(6)	P4–O11	1.520(5)
K1–O5$^{\#1}$	2.769(6)	P4–O13	1.524(5)
K1–O2$^{\#2}$	2.882(8)	P4–O10	1.590(5)
K1–O1$^{\#2}$	2.992(7)	Cd1–O9$^{\#5}$	2.216(5)
K1–O3$^{\#3}$	3.066(5)	Cd1–O6	2.237(5)
K1–O3$^{\#4}$	3.066(5)	Cd1–O7	2.263(5)
K1–O4	3.263(6)	Cd1–O12$^{\#6}$	2.296(5)
K1–O4$^{\#1}$	3.263(6)	Cd1–O13$^{\#7}$	2.300(5)
K1–O8$^{\#4}$	3.295(6)	Cd1–O4$^{\#8}$	2.361(5)
K1–O8$^{\#3}$	3.295(6)	Cd1–Cd3$^{\#9}$	3.4028(7)
P1–O2	1.505(7)	Cd1–Cd2$^{\#6}$	3.4797(7)
P1–O1	1.513(7)	Cd2–O8	2.193(5)
P1–O3	1.574(5)	Cd2–O5	2.208(5)
P1–O3$^{\#1}$	1.574(5)	Cd2–O9$^{\#4}$	2.243(5)
P2–O6	1.504(5)	Cd2–O4$^{\#10}$	2.307(5)

P2–O5	1.505(5)	Cd2–O2$^{\#10}$	2.346(4)
P2–O3	1.653(5)	Cd3–O13	2.225(5)
P3–O8	1.487(5)	Cd3–O11$^{\#7}$	2.226(5)
P3–O7	1.528(5)	Cd3–O7$^{\#9}$	2.248(5)
P3–O9	1.530(5)	Cd3–O12$^{\#11}$	2.283(5)
P3–O10	1.596(5)	Cd3–O6$^{\#7}$	2.416(5)
P4–O12	1.505(5)	Cd3–O11$^{\#8}$	2.427(5)
O9–Cd1–O6	93.53(18)	O7–Cd3–O12	83.28(17)
O9–Cd1–O7	160.53(19)	O13–Cd3–O6	77.13(16)
O6–Cd1–O7	96.26(18)	O11–Cd3–O6	119.14(18)
O9–Cd1–O12	93.82(18)	O7–Cd3–O6	76.80(17)
O6–Cd1–O12	159.74(17)	O12–Cd3–O6	77.16(17)
O7–Cd1–O12	82.66(17)	O13–Cd3–O11	119.14(17)
O9–Cd1–O13	115.01(18)	O11–Cd3–O11	78.81(18)
O6–Cd1–O13	79.36(17)	O7–Cd3–O11	85.14(18)
O7–Cd1–O13	83.41(18)	O12–Cd3–O11	84.08(17)
O12–Cd1–O13	80.42(17)	O6–Cd3–O11	155.23(16)
O9–Cd1–O4	80.02(17)	O2–P1–O1	115.6(4)
O6–Cd1–O4	110.68(17)	O2–P1–O3	111.3(3)
O7–Cd1–O4	80.79(18)	O1–P1–O3	106.5(3)
O12–Cd1–O4	89.19(18)	O2–P1–O3	111.3(3)
O13–Cd1–O4	162.07(17)	O1–P1–O3	106.5(3)
O8–Cd2–O5	88.1(2)	O3–P1–O3	105.0(4)
O8–Cd2–O9	104.5(2)	O6–P2–O5	115.6(3)
O5–Cd2–O9	96.91(19)	O6–P2–O4	114.9(3)
O8–Cd2–O4	94.16(19)	O5–P2–O4	112.1(3)
O5–Cd2–O4	177.01(19)	O6–P2–O3	101.6(3)
O9–Cd2–O4	80.67(17)	O5–P2–O3	105.2(3)
O8–Cd2–O2	83.6(2)	O4–P2–O3	105.6(3)
O5–Cd2–O2	99.6(2)	O8–P3–O7	112.9(3)
O9–Cd2–O2	161.8(2)	O8–P3–O9	113.2(3)
O4–Cd2–O2	82.6(2)	O7–P3–O9	110.8(3)
O8–Cd2–O1	157.2(2)	O8–P3–O10	111.5(3)
O5–Cd2–O1	84.7(2)	O7–P3–O10	103.8(3)
O9–Cd2–O1	97.80(18)	O9–P3–O10	103.9(3)
O4–Cd2–O1	93.9(2)	O12–P4–O11	111.2(3)
O2–Cd2–O1	76.37(19)	O12–P4–O13	113.1(3)
O13–Cd3–O11	98.88(18)	O11–P4–O13	112.4(3)
O13–Cd3–O7	153.90(18)	O12–P4–O10	108.6(3)
O11–Cd3–O7	95.03(18)	O11–P4–O10	109.5(3)

O13–Cd3–O12	89.54(17)	O13–P4–O10	101.4(3)
		$KCd_3P_3O_{11}$	
K1–O1$^{\#9}$	3.019(2)	K1–O6$^{\#7}$	3.1206(3)
K1–O1	2.852(2)	P1–O5$^{\#11}$	1.522(2)
K1–O1$^{\#2}$	3.019(2)	P1–O5	1.522(2)
K1–O2$^{\#2}$	3.110(2)	P1–O6	1.511(3)
K1–O2$^{\#9}$	3.110(2)	P1–O7	1.603(3)
K1–O4	3.349(2)	P2–O1	1.498(2)
K1–O4$^{\#8}$	3.349(2)	P2–O2	1.525(2)
K1–O5$^{\#10}$	2.947(3)	P2–O3	1.6273(14)
K1–O5$^{\#4}$	2.947(3)	P2–O4	1.524(2)
Cd1–O1$^{\#1}$	2.227(2)	Cd2–O2$^{\#6}$	2.293(2)
Cd1–O1	2.227(2)	Cd2–O4$^{\#4}$	2.263(2)
Cd1–O2$^{\#2}$	2.343(2)	Cd2–O4	2.225(2)
Cd1–O2$^{\#3}$	2.343(2)	Cd2–O5	2.167(2)
Cd1–O6$^{\#4}$	2.232(3)	Cd2–O7$^{\#7}$	2.2421(17)
Cd1–O7$^{\#5}$	2.360(3)		
O1–Cd1–O1	95.74(10)	O1–K1–O6	64.10(7)
O1–Cd1–O2	91.14(7)	O1–K1–O6	116.66(7)
O1–Cd1–O2	91.14(7)	O1–K1–O6	123.86(7)
O1–Cd1–O2	173.11(7)	O1–K1–O6	58.89(7)
O1–Cd1–O2	173.11(7)	O1–K1–O6	116.66(7)
O1–Cd1–O6	90.91(8)	O2–K1–O2	60.77(8)
O1–Cd1–O6	90.91(8)	O2–K1–O4	112.62(5)
O1–Cd1–O7	101.82(7)	O2–K1–O4	128.81(5)
O1–Cd1–O7	101.82(7)	O2–K1–O4	112.62(5)
O2–Cd1–O2	81.97(10)	O2–K1–O4	128.81(5)
O2–Cd1–O7	76.35(7)	O2–K1–O6	122.44(7)
O2–Cd1–O7	76.35(7)	O2–K1–O6	122.44(7)
O6–Cd1–O2	89.32(8)	O2–K1–O6	62.16(7)
O6–Cd1–O2	89.32(8)	O2–K1–O6	62.16(7)
O6–Cd1–O7	160.87(11)	O4–K1–O4	108.23(7)
O4–Cd2–O2	89.78(7)	O5–K1–O1	137.40(6)
O4–Cd2–O2	168.42(7)	O5–K1–O1	92.70(6)
O4–Cd2–O4	79.43(8)	O5–K1–O1	92.70(6)
O4–Cd2–O7	118.27(8)	O5–K1–O1	137.40(6)
O5–Cd2–O2	96.15(8)	O5–K1–O2	170.53(6)
O5–Cd2–O4	125.93(8)	O5–K1–O2	111.13(6)
O5–Cd2–O4	86.95(8)	O5–K1–O2	170.53(6)
O5–Cd2–O7	115.67(9)	O5–K1–O2	111.13(6)

O7–Cd2–O2	79.73(9)	O5–K1–O4	67.81(6)
O7–Cd2–O4	109.02(9)	O5–K1–O4	57.49(6)
O1–K1–O1	64.20(7)	O5–K1–O4	67.81(6)
O1–K1–O1	106.73(6)	O5–K1–O4	57.49(6)
O1–K1–O1	64.20(7)	O5–K1–O5	77.37(9)
O1–K1–O1	163.11(9)	O5–K1–O6	49.02(7)
O1–K1–O1	106.73(6)	O5–K1–O6	49.02(7)
O1–K1–O1	119.78(8)	O5–K1–O6	126.36(8)
O1–K1–O2	98.61(6)	O5–K1–O6	126.36(8)
O1–K1–O2	78.21(6)	O6–K1–O4	80.34(7)
O1–K1–O2	66.23(6)	O6–K1–O4	96.92(7)
O1–K1–O2	66.23(6)	O6–K1–O4	80.34(7)
O1–K1–O2	78.21(6)	O6–K1–O4	96.92(7)
O1–K1–O2	48.61(5)	O6–K1–O6	175.38(12)
O1–K1–O2	48.61(5)	O5–P1–O5	113.88(19)
O1–K1–O2	98.61(6)	O5–P1–O7	105.57(11)
O1–K1–O4	80.27(5)	O5–P1–O7	105.57(11)
O1–K1–O4	80.27(5)	O6–P1–K1	61.49(2)
O1–K1–O4	139.20(5)	O6–P1–K1	61.49(2)
O1–K1–O4	148.77(6)	O6–P1–O5	112.52(11)
O1–K1–O4	46.93(5)	O1–P2–O2	113.24(12)
O1–K1–O4	148.77(6)	O1–P2–O3	108.84(13)
O1–K1–O5	112.35(6)	O1–P2–O4	112.38(12)
O1–K1–O5	112.34(6)	O2–P2–K1	60.39(8)
O1–K1–O5	81.32(6)	O2–P2–K1	144.54(9)
O1–K1–O5	81.32(6)	O2–P2–O3	107.01(13)
O1–K1–O6	123.86(7)	O4–P2–O2	111.54(12)

Symmetry transformations used to generate equivalent atoms:

(1) $KCd_6P_7O_{24}$: #1: +X, 1.5-Y, +Z; #2: -1+X, +Y, -1+Z; #3: -1+X, 1.5-Y, +Z; #4: -1+X, +Y, +Z; #5: +X, +Y, 1+Z; #6: 1+X, +Y, 1+Z; #7: 1-X, 1-Y, 1-Z; #8: 1+X, +Y, +Z; #9: 2-X, 1-Y, 1-Z; #10: +X, +Y, -1+Z; #11: 1-X, 1-Y, -Z; #12: 1+X, 1.5-Y, 1+Z; #13: +X, 1.5-Y, 1+Z;

(2) $KCd_3P_3O_{11}$: #1: +X, +Y, 0.5-Z; #2: -X, -0.5+Y, +Z; #3: -X, -0.5+Y, 0.5-Z; #4: 1-X, 1-Y, 1-Z; #5: -1+X, 1.5-Y, -0.5+Z; #6: +X, 1.5-Y, 1-Z; #7: 1-X, -0.5+Y, 1.5-Z; #8: +X, 0.5-Y, 1-Z; #9: -X, 1-Y, 1-Z; #10: 1-X, -0.5+Y, +Z; #11: 1-X, 1-Y, 0.5+Z; #12: +X, +Y, 1.5-Z; #13: -X, 0.5+Y, 0.5-Z; #14: 1-X, 0.5+Y, 1.5-Z; #15: 1+X, 1.5-Y, 0.5+Z; #16: 1-X, 0.5+Y, +Z;

Table S4. Metal phosphates with multiple P-O FBUs.

component	P-O form
$Cs_2PbBi_2(PO_4)_2(P_2O_7)$[8]	PO_4, P_2O_7
$Rb_2PbBi_2(PO_4)_2(P_2O_7)$[8]	PO_4, P_2O_7
$K_2PbBi_2(PO_4)_2(P_2O_7)$[9]	PO_4, P_2O_7
$Rb_2CdBi_2(PO_4)_2(P_2O_7)$[9]	PO_4, P_2O_7
$Rb_6Bi_4(PO_4)_2(P_2O_7)_3$[10]	PO_4, P_2O_7
$Cs_6Bi_4(PO_4)_2(P_2O_7)_3$[11]	PO_4, P_2O_7
$RbCs_5Bi_4(PO_4)_2(P_2O_7)_3$[11]	PO_4, P_2O_7
$KCs_5Bi_4(PO_4)_2(P_2O_7)_3$[11]	PO_4, P_2O_7
$Pb_2Cd_3(PO_4)_2(P_2O_7)$[12]	PO_4, P_2O_7
$Th_4(PO_4)_4(P_2O_7)$[13]	PO_4, P_2O_7
$Na_4Ni_5(PO_4)_2(P_2O_7)_2$[14]	PO_4, P_2O_7
$Na_4Co_3(PO_4)_2(P_2O_7)$[15]	PO_4, P_2O_7
$Na_4Mg_3(PO_4)_2(P_2O_7)$[16]	PO_4, P_2O_7
$Na_4Mn_3(PO_4)_2(P_2O_7)$[17]	PO_4, P_2O_7
$Na_4Fe_3(PO_4)_2(P_2O_7)$[18]	PO_4, P_2O_7
$Ni_4TI_2(PO_4)_2(P_2O_7)$[19]	PO_4, P_2O_7
$Li_9Al_3(PO_4)_2(P_2O_7)_3$[20]	PO_4, P_2O_7
$LiMg_3(PO_4)(P_2O_7)$[21]	PO_4, P_2O_7
$KNi_3(PO_4)(P_2O_7)$[22]	PO_4, P_2O_7
$Eu_2Si(PO_4)(P_2O_7)$[23]	PO_4, P_2O_7
$MnSr_2(PO_4)(P_2O_7)$[24]	PO_4, P_2O_7
$VCa_2(PO_4)(P_2O_7)$[25]	PO_4, P_2O_7
$AgCr_2(PO_4)(P_2O_7)$[26]	PO_4, P_2O_7
$Na_7V_2Al_2(PO_4)(P_2O_7)_4$[27]	PO_4, P_2O_7
$Li_{1.52}Na_{4.48}Cd_8(PO_4)_2(P_2O_7)_4$[28]	PO_4, P_2O_7
$KCd_3P_3O_{11}$	PO_4, P_2O_7
$Cs_3Sr_2P_7O_{21}$[29]	$(PO_3)_\infty$, P_4O_{12}
$Th_2(PO_4)(P_3O_{10})$[30]	PO_4, P_3O_{10}
$U_2(PO_4)(P_3O_{10})$[31]	PO_4, P_3O_{10}
$KMg_6(P_2O_7)_2(P_3O_{10})$[32]	P_2O_7, P_3O_{10}
$NaMn_6(P_2O_7)_2(P_3O_{10})$[33]	P_2O_7, P_3O_{10}
$AgMn_6(P_2O_7)_2(P_3O_{10})$[34]	P_2O_7, P_3O_{10}
$KMn_6(P_2O_7)_2(P_3O_{10})$[34]	P_2O_7, P_3O_{10}
$Na_7Y_2(P_2O_7)_2(P_3O_{10})$[35]	P_2O_7, P_3O_{10}
$KCd_6P_7O_{24}$	P_2O_7, P_3O_{10}
$Pb_{12}[Li_2(P_2O_7)_2(P_4O_{13})_2](P_4O_{13})$[36]	P_2O_7, P_4O_{13}

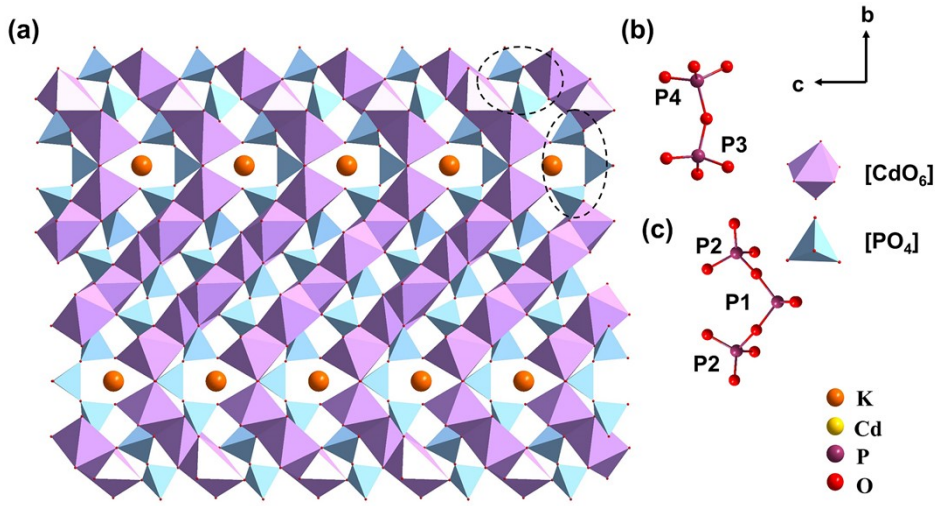

Fig. S1. (a) The polyhedral structure of $KCd_6P_7O_{24}$. (b) $[P_2O_7]$ dimer; (c) $[P_3O_{10}]$ trimer.

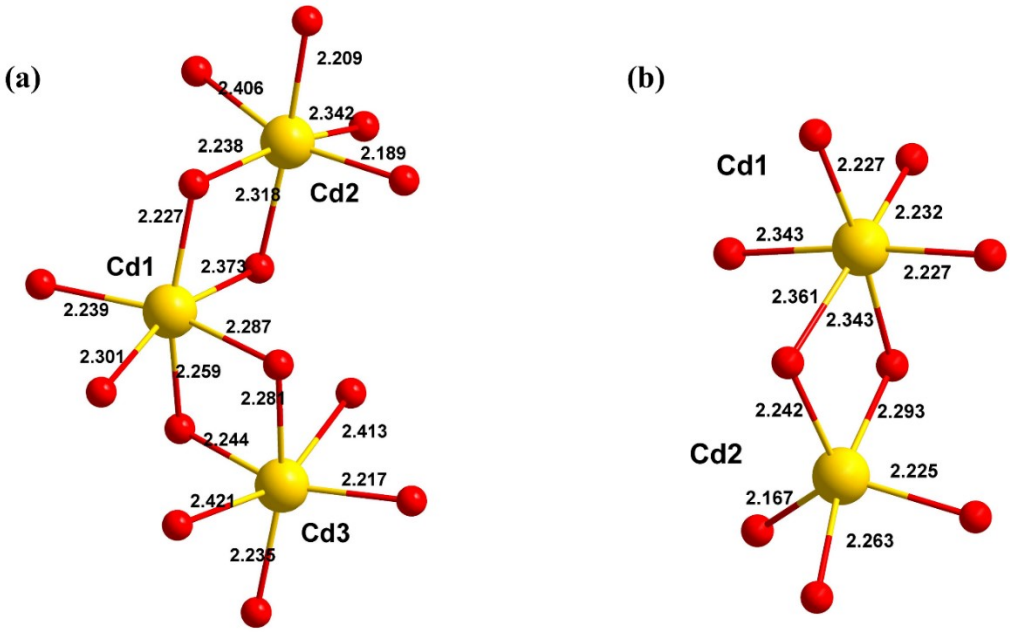

Fig. S2. Ball-and-stick representation of the coordination environment of Cd atoms in (a) $KCd_6P_7O_{24}$ and (b) $KCd_3P_3O_{11}$.

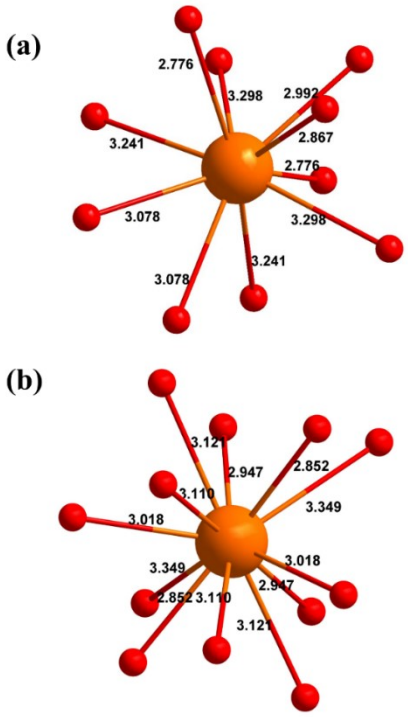

Fig. S3. Ball-and-stick representation of the coordination environment of K atoms in (a) $KCd_6P_7O_{24}$ and (b) $KCd_3P_3O_{11}$.

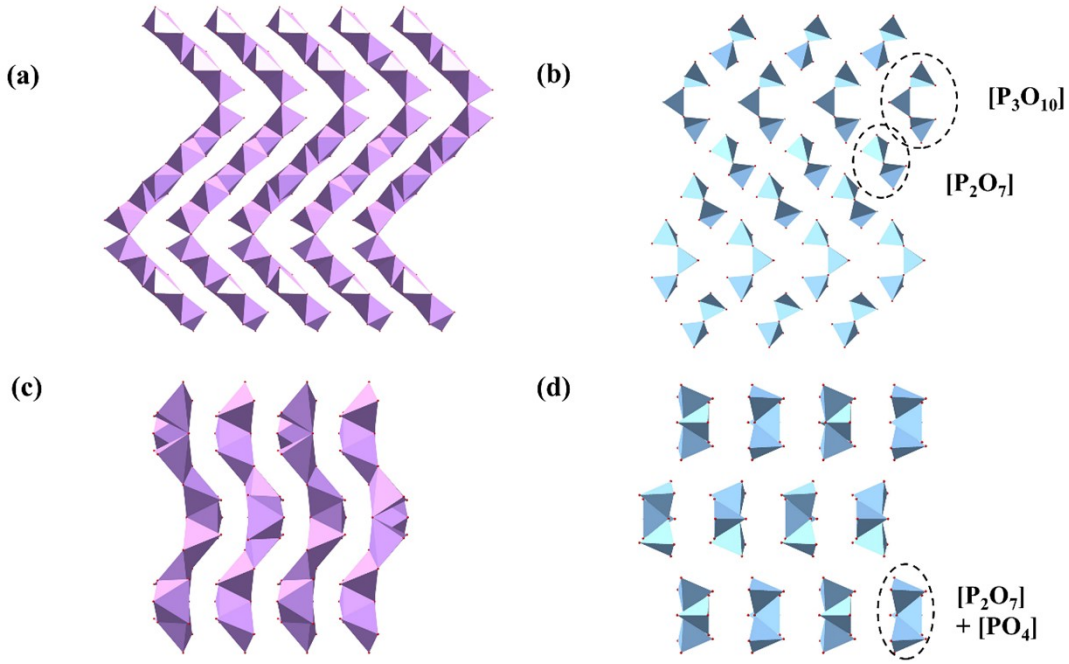

Fig. S4. Polyhedral view of the (a) Cd-O and (b) P-O connections in $KCd_6P_7O_{24}$. Polyhedral view of the (c) Cd-O and (d) P-O connections in $KCd_3P_3O_{11}$.

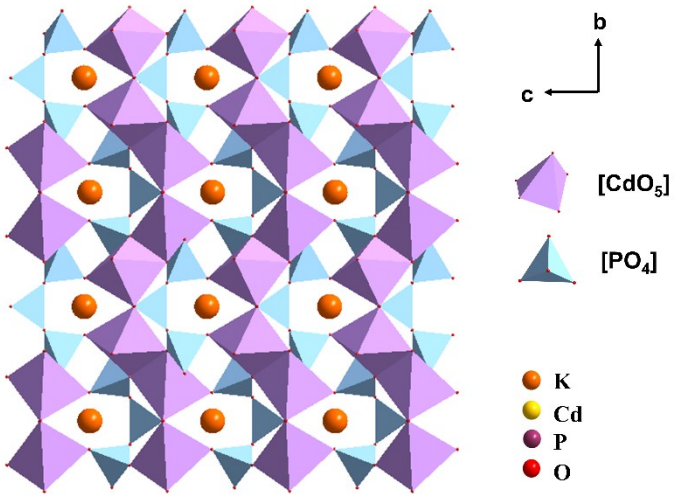

Fig. S5. The crystal structure of $KCd_2P_3O_{10}$.

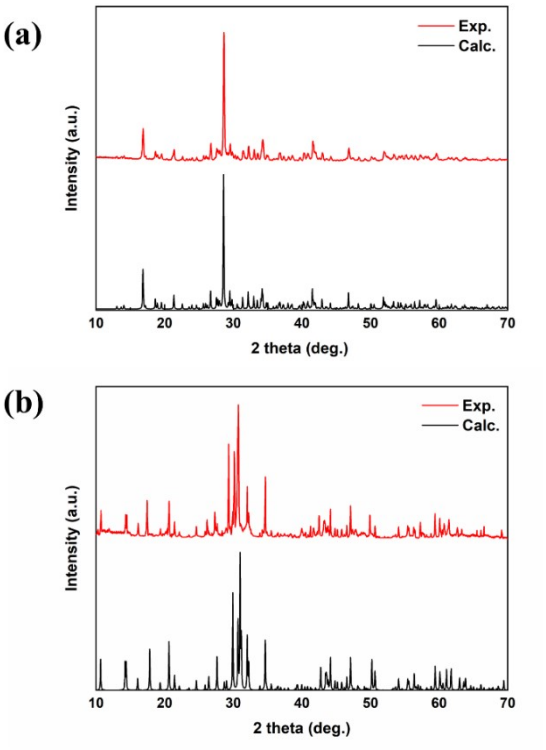

Fig. S6. Experimental and calculated PXRD patterns of (a) $KCd_6P_7O_{24}$ and (b) $KCd_3P_3O_{11}$.

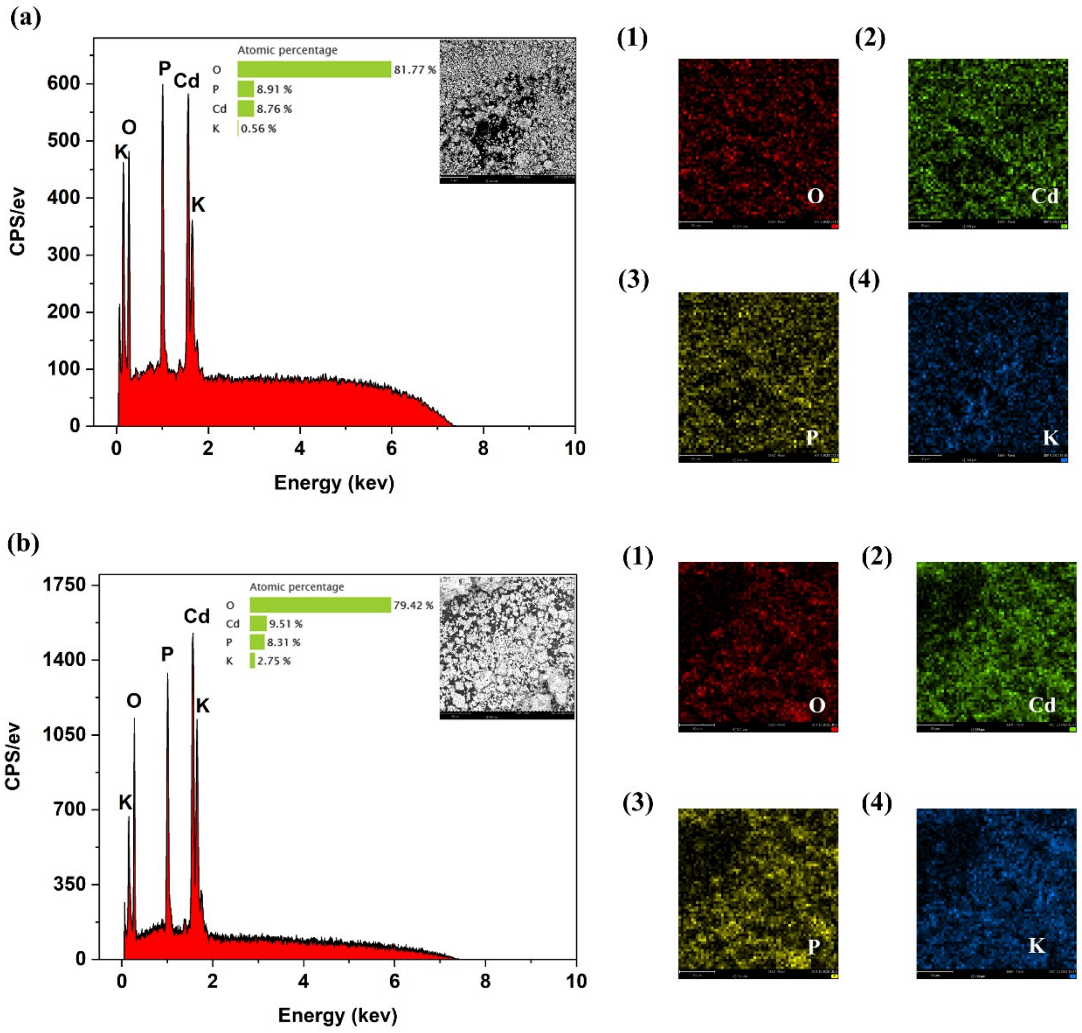

Fig. S7. EDS and element mapping of (a) $KCd_6P_7O_{24}$ and (b) $KCd_3P_3O_{11}$. (1) O ; (2) Cd ; (3) P ; (4) K.

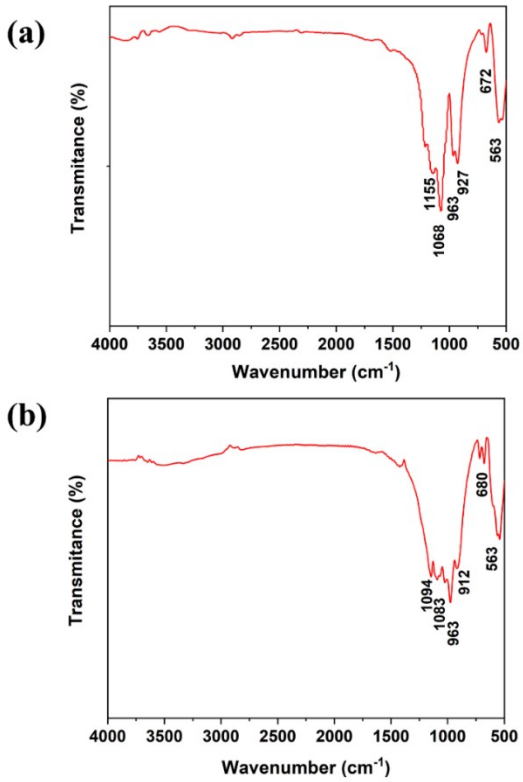

Fig. S8. IR spectra of (a) $KCd_6P_7O_{24}$ and (b) $KCd_3P_3O_{11}$.

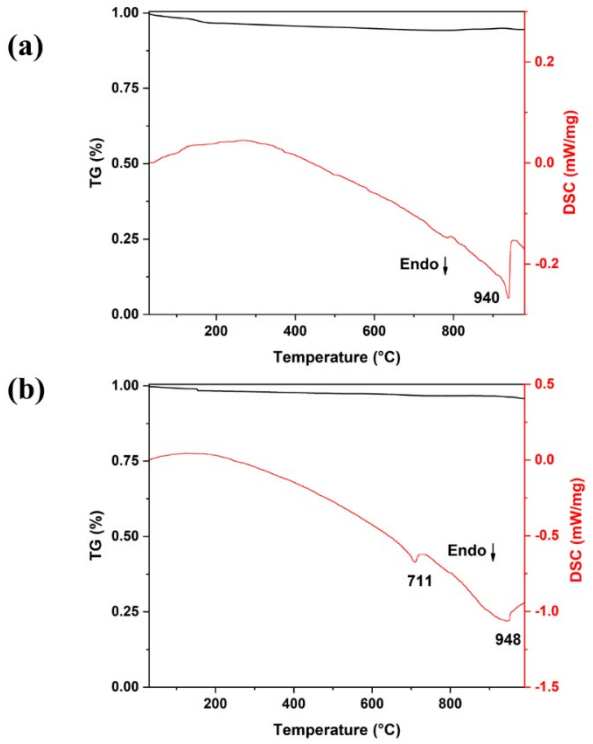

Fig. S9. TG-DSC cruves of (a) $KCd_6P_7O_{24}$ and (b) $KCd_3P_3O_{11}$.

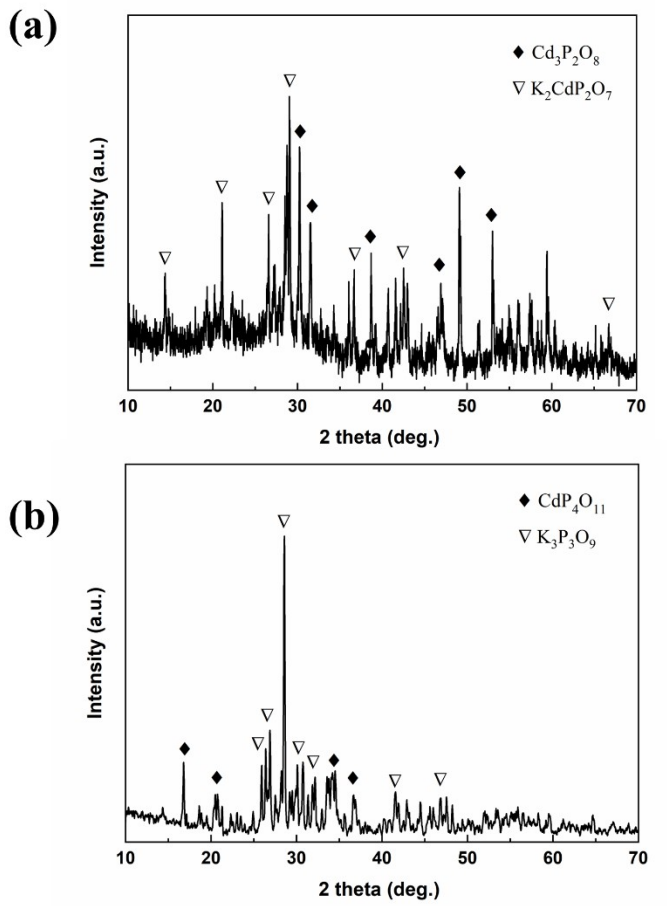

Fig. S10. The PXRD of the thermal decomposition product of (a) $KCd_6P_7O_{24}$ and (b) $KCd_3P_3O_{11}$.

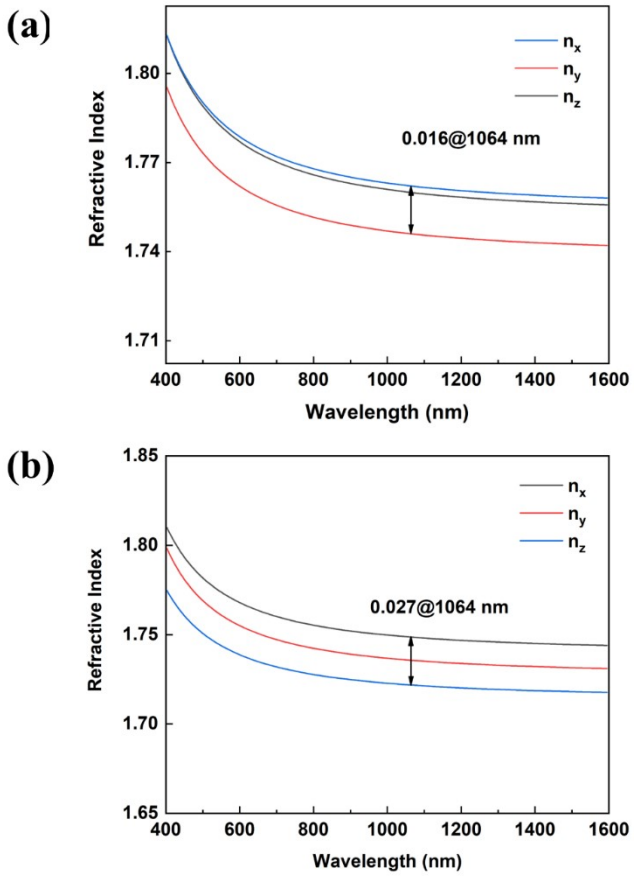

Fig. S11. Calculated refractive indices of (a) $KCd_6P_7O_{24}$ and (b) $KCd_3P_3O_{11}$.

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