Supporting Information

Structure of High-Pressure Phase IV of KH₂PO₄ (KDP)

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Experimental Section

Diamond-anvil cell (DAC) X-ray experiment

Potassium dihydrogen phosphate, KH_2PO_4 , KDP, purchased from POCh (Polskie Odczynniki Chemiczne), purity 99.5%, was used as delivered. Single crystals of KDP were grown *in situ* in a modified Merrill-Bassett DAC.¹ The gasket was made of 0.3 mm thick tungsten or INCONEL foil with the spark-eroded hole in diameter 0.4 mm. Pressure was calibrated with a Photon Control spectrometer by using the ruby-fluorescence method,² with a precision of 0.03 GPa.

The mixture of distilled water and methanol in different ratios were used as the solvent and pressure transmitting medium. Firstly, small KDP crystals were selected and loaded in the DAC chamber, and topped up with the water-methanol (12:1 *vol.*) mixture. Pressure was increased to 1.10 GPa, and the DAC was heated by a hot-air gun to 418 K when all crystals except one seed dissolved. Then temperature was slowly decreased to room temperature, to allow the single crystal of KDP to grow. Finally, it filled the *ca*. 60% of the chamber and the pressure stabilized at 0.96 GPa/296 K (Fig. S1). Diffraction data were collected for this single crystal. Other single crystal data with the same phase II were collected at 0.21, 1.46, 1.68, 1.76, 1.91 and 2.28 GPa/296 K, respectively.

Then KDP sample was loaded again by using the water-methanol (9:1 *vol.*) mixture as solvent. First pressure was increased to 2.61 GPa, then the DAC was heated to 435 K, and then pressure was increased again by tightened the DAC screws. When several crystals appeared in the chamber, temperature was quickly increased to 450 K, and finally two crystals were left in the chamber. The temperature was cooling slowly to let the crystals grow. During this process, one crystal on the left side of the chamber was dissolved (most likely phase II), and one plate-like single crystal finally filled about one-third of the chamber at 1.62 GPa /296 K (Fig. S2). The diffraction measurement was carried out for this single crystal.

After recording the diffraction data, pressure was increased to 2.17 GPa and temperature to 587 K, and a twin of triangular crystal seeds was left in the chamber; then temperature was cooling down slowly to allow the twinned crystal grow. The final pressure stabilized at 1.11 GPa/296 K (Fig. S3).



Fig. S1 *In situ* isochoric crystallization of KDP (phase II) dissolved in water-methanol mixture (12:1 *vol.*): (a-b) one seed at 418 K; (c) at 398 K; (d-e) at 360 K and (f) at 0.96 GPa/296 K. Two ruby chips for pressure calibration lie at the top left and bottom right sides of the chamber.



Fig. S2 *In situ* isochoric crystallization of KDP (phase IV) dissolved in water-methanol mixture (9:1, *vol.*): (a) one seed at 450 K; (b) at 443 K; (c) at 413 K; (d-e) at 373 K and (f) at 1.62 GPa/296 K. Two ruby chips for pressure calibration lie at bottom right side of the chamber.



Fig. S3 *In situ* isochoric crystallization of KDP (phase I) dissolved in water-methanol mixture (9:1 *vol.*): (a) a seed at 587 K; (b) at 528 K; (c-e) at 473 K; (f) at 453 K; (g) at 443 K; (h) at 393 K and (i) at 1.11 GPa/296 K. Two ruby chips for pressure calibration lie at the bottom and top sides of the chamber.

High pressure structure determination

Single-crystal diffraction data were collected on diffractometers KUMA KM4-CCD and Oxford Diffraction Xcalibur EOS, with graphite-monochromated MoK_{α} radiation. The centering of the DAC was performed by the gasket-shadowing method.³ CrysAlis software⁴ was used for the data collections and the preliminary reduction of the data. After correcting the intensities for the effects of DAC absorption, sample shadowing by the gasket and the sample absorption,⁵ the diamond reflections were eliminated. The structures were solved by direct methods and refined by full-matrix least squares for heavy atoms by program SHELXL-97.⁶ The anisotropic values of few potassium, phosphorus and oxygen atoms were restrained to approximate isotropic shape by using command ISOR 0.01 of SHELXL-97 in phases IV (at 1.62 GPa) and I (at 1.11 GPa).

For phase II ($I\overline{4}2d$), the ambient-pressure structure was applied as the starting model for full-matrix least-squares and the hydrogen atoms were added with the aid of AFIX 83 command with the SOF value equals to 0.5.

For phase I ($P2_1/c$), the structure was refined of the model at ambient conditions.⁷ Protons H2 and H3 were added by the AFIX 83 command, and restrained to their parent sites at O3 and O4 atoms, respectively. The coordinates of H1 were calculated from the positions of O1 and O2ⁱ (symmetry code *i*: *x*, *y*–1, *z*).

In phase IV ($P2_1/c$), the protons were located in this way: H7 and H12 were added with the AFIX 83 command with half occupation, the coordinates of remaining hydrogen atoms (H1, H4, H2, H11, H3, H8, H5, H6, H9 and H10) were located between H-bonded O1…O4, O2…O11, O3…O8, O5…O6 and O9…O10 atoms at 1.0 Å from the O sites, all the SOF values of the protons were set as 0.5, which averages the charges to the mono-anion for each of symmetry-independent $[H_2PO_4]^-$ groups in this structure.

Crystallographic data, refinements factors, bond lengths and angles are summarized in Tables S3, S4 and S5 for phase I at 1.11 GPa/296 K and IV at 1.62 GPa/296 K, and in Tables S6 and S7 for phase II at 0.21, 0.96, 1.46, 1.68, 1.76, 1.91, 2.28 GPa/296 K, respectively.

Further data, in the format of a crystallographic information file (CIF) can be obtained free of charge from the Fachinformationszentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany (Fax:+49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers: CSD-424765 (at 0.21 GPa), CSD-424766 (at 0.96 GPa), CSD-424767 (at 1.11 GPa), CSD-424768 (at 1.46 GPa), CSD-424769 (at 1.62 GPa), CSD-424770 (at 1.68 GPa), CSD-424771 (at 1.76 GPa), CSD-424772 (at 1.91 GPa), and CSD-424773 (at 2.28 GPa), all at 296 K.

Table S1 Torsion angles $P-O\cdots O-P$ describing the arrangement of H-bonded PO_4 groups in KDP polymorphs. The torsion angles symmetry-independent H-bonds have been listed, and hence the negative values also exist where appropriate.

Phase	Pressure	P−O···O−P angles(°)
Ι	0.1 MPa	95.0, 180, 180
II	0.1 MPa	77.4
II'	0.1 MPa	$-164.8, \pm 180, 63.3, 73.3$
III	0.1 MPa	77.3
IV^a	1.62 GPa	-170.7, -96.0, -92.9, 95.7, 164.9, 180, 180
VIII	0.1 MPa	-108.7, -178.6, -83.2, 178.9, 105.9, 176.5, 85.5, 177.8
А	0.1 MPa	-66.2, -165.7
С	0.1 MPa	-165.3, -158.5, -66.7, -73.3, 60.0, 66.5, 165.9, 175.2, 174.0, 177.8

^a This work.

Table S2 The K-coordination numbers of KDP phases

Phase	Space group	K-coordination/PO ₄ group
Ι	$P2_{1}/c$	8/6
II	$I\overline{4}2d$	8/6
II'	$P\overline{1}$	8/6
III	Fdd2	8/6
IV ^a	$P2_{1}/c$	8/6 and 8/7
VIII	Cc	8/6 and 8/7
А	P2/c	8 /6
В	$P2_{1}/c$	8/6 and 10/6
С	<i>P</i> 2 ₁	8/6

^a This work.

Pressure	0.1 MPa ^o	1.11 GPa	1.62 GPa
Phase	Ι	Ι	IV
Temperature	296 K	296 K	296 K
Crystal size(mm)	0.31/0.31/0.25	0.35/0.18/0.15	0.42/0.20/0.19
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_{1}/c$	$P2_{1}/c$
a/Å	6.1413(3)	6.148(5)	14.384(3)
b/Å	4.4990(2)	4.484(11)	4.449(5)
$c/\text{\AA}$	14.2725(6)	13.909(11)	18.305(6)
β/deg	91.552(2)	91.53(7)	108.11(2)
$V/Å^3$	394.20(3)	383.3(11)	1113.3(13)
Ζ	4	4	12
$\rho_{\rm cal} ({\rm g}/{\rm cm}^3)$	2.293	2.358	2.436
θ range(°)	2.86-25.31	4.48-28.55	4.33-26.51
$\mu(\mathrm{mm}^{-1})$	-	1.661	1.715
F(000)	272	272	816
	$-6 \le h \le 6$	$-7 \le h \le 7$	$-17 \le h \le 17$
Limiting indices	$-5 \leq k \leq 5$	$-1 \le k \le 1$	$-1 \le k \le 1$
-	−17 ≤ <i>l</i> ≤ 16	$-17 \le l \le 17$	$-20 \le l \le 20$
$R_{ m int}$	0.052	0.2501	0.1223
Data/constrains/parameters	603/0/55	172/36/56	440/96/163
$R_l/wR_2 (I>4\sigma_l)^a$	0.0431/0.0977	0.1368/0.2738	0.0741/0.1865
R_1/wR_2 indices(all data)	0.0581/0.1228	0.1589/0.2888	0.0814/0.2004
Goodness-of-fit on F_0^2	1.131	1.388	1.164
Largest neak/hole (e·Å ⁻³)	0 421/-0 370	0.26/-0.26	0.52/-0.52

Table S3 Crystal data of phases I and IV of KDP at 0.1 MPa, 1.11 GPa and 1.62 GPa. The high R_{int} values of the measurement at 1.11 GPa are due to the crystal twinning (see Figure S3) and to the inclusion of reflections close to the edge of the DAC window.

[a] $R_1 = \sum ||F_o| - |F_c|| \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$; $wR_2 = \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2 F_o^2 + (AP)^2 + BP]$, and $P = (Fo^2 + 2Fc^2)/3$

[b] J. A. Subramony, S. Lovell and B. Kahr, Chem. Mater., 1998, 10, 2053.

Table S4 Bond lengths (Å) and angles ([°]) in the structure of phase I of KDP at 0.1 MPa and 1.11 GPa/296 K and phase IV at 1.62 GPa/296 K.

]	Phase I		Phase IV at 1.62 GPa					
Pressure	0.1 Mpa	1.11 GPa	P(1)-O(1)	1.46(2)	K(1)-O(2)	2.784(13)		
P(1)-O(1)	1.543(3)	1.11 GPa	P(1)-O(2)	1.524(11)	K(1)-O(5)	2.784(12)		
P(1)-O(2)	1.509(3)	1.76(4)	P(1)-O(3)	1.542(12)	$K(1) - O(11)^{x}$	2.720(16)		
P(1)-O(3)	1.532(3)	1.50(5)	P(1)-O(4)	1.51(2)	$K(1) - O(4)^{xi}$	2.950(16)		
P(1)-O(4)	1.534(3)	1.56(2)	P(2)-O(5)	1.45(2)	$K(1) - O(10)^{xii}$	2.889(15)		
O(2)-P(1)-O(3)	109.3(2)	1.63(4)	P(2)-O(6)	1.49(2)	K(1) - P(2)	3.348(4)		
O(2)-P(1)-O(4)	112.11(19)	113(2)	P(2)-O(7)	1.511(9)	K(1) - P(3)	3.396(5)		
O(3)-P(1)-O(4)	110.06(19)	120.6(13)	P(2)-O(8)	1.498(11)	$K(1) - P(3)^{x}$	3.655(7)		
O(2)-P(1)-O(1)	109.32(17)	114.4(11)	P(3)-O(9)	1.49(2)	K(1)-P(1)	3.760(7)		
O(3)-P(1)-O(1)	108.7(3)	110.6(17)	P(3)-O(10)	1.495(19)	$K(2) - O(12)^{xiii}$	2.721(16)		
O(4)-P(1)-O(1)	107.27(18)	107.1(14)	P(3)-O(11)	1.522(13)	$K(2)$ - $O(8)^{xiv}$	2.780(15)		
$K(1) - O(4)^{i}$	2.797	88(2)	P(3)-O(12)	1.516(10)	$K(2) - O(11)^{x}$	2.896(11)		
$K(1) - O(3)^{ii}$	2.696	2.55(2)	O(4) - P(1) - O(2)	107.9(7)	$K(2) - O(3)^{xi}$	2.897(15)		
K(1)-O(2)	2.858	2.68(3)	O(4) - P(1) - O(3)	109.7(11)	$K(2) - O(12)^{xiv}$	2.937(17)		
$K(1) - O(1)^{iii}$	2.972	2.72(3)	O(2) - P(1) - O(3)	110.3(5)	$K(2) - O(5)^{xiii}$	2.994(14)		
$K(1) - O(2)^{iv}$	2.849	2.897(17)	O(4) - P(1) - O(1)	107.9(9)	K(2)-O(2)	3.035(15)		
K(1)-O(1)	2.904	2.88(3)	O(2)-P(1)-O(1)	111.8(12)	$K(2) - O(9)^{xiv}$	2.856(11)		
$K(1) - O(4)^{v}$	3.145	2.99(2)	O(3) - P(1) - O(1)	109.2(8)	$K(2)-P(3)^{xiv}$	3.499(7)		
$K(1) - O(3)^{iii}$	3.321	3.02(2)	O(6)-P(2)-O(5)	106.8(10)	$K(2) - P(1)^{xi}$	3.650(7)		
K(1) - P(1)	3.478	3.31(4)	O(6) - P(2) - O(7)	104.6(7)	$K(2)-P(2)^{xiv}$	3.758(7)		
$K(1) - P(1)^{i}$	3.728	3.419(9)	O(5)-P(2)-O(7)	118.7(12)	$K(2)-K(2)^{xi}$	4.449(5)		
$K(1) - P(1)^{iii}$	3.743	3.778(17)	O(6)-P(2)-O(8)	109.7(12)	$K(3) - O(3)^{xi}$	2.670(17)		
$K(1)\cdots K(1)^{vi}$ (×2)	4.499	3.837(18)	O(5)-P(2)-O(8)	108.5(8)	$K(3) = O(7)^{xv}$	2.740(15)		
$K(1)\cdots K(1)^{vii}$	4.769	4.484(22)	O(7)-P(2)-O(8)	108.2(6)	K(3)-O(1)	2.846(15)		
$K(1)\cdots K(1)^{viii}$	4.847	4.623(7)	O(9)-P(3)-O(10)	105.6(9)	$K(3) = O(1)^{xvi}$	2.756(13)		
$K(1)\cdots K(1)^{ix}(\times 2)$	4.979	4.697(7)	O(9)-P(3)-O(11)	109.0(13)	$K(3) - O(4)^{xvi}$	2.858(14)		
			O(10)-P(3)-O(11)	111.1(7)	$K(3) - O(6)^{xvi}$	2.850(13)		
			O(9) - P(3) - O(12)	105.2(7)	$K(3) - O(7)^{xvi}$	2.935(17)		
			O(10)-P(3)-O(12)	114.4(10)	$K(3) = O(8)^{\overline{xiv}}$	3.031(13)		
			O(11)-P(3)-O(12)	111.1(5)	K(3)-P(1)	3.766(8)		
			K(1)-O(9)	2.819(15)	$K(3)-P(1)^{xvi}$	3.407(4)		
			K(1)-O(10)	2.720(13)	$K(3) - P(2)^{xvi}$	3.516(8)		
			K(1)-O(6)	2.719(14)	$K(3) - P(1)^{xi}$	3.746(7)		

Symmetry codes: (i) -x+2, y+1/2, -z+3/2; (ii) -x+1, y-1/2, -z+3/2; (iii) -x+1, y+1/2, -z+3/2; (iv) -x+2, y-1/2, -z+3/2; (v) x, -y+1/2, z-1/2; (vi) x, y-1, z; (vii) 2-x, 1-y, 1-z; (viii) 1-x, 1-y, 1-z; (ix) 2-x, -0.5+y, 1.5-z; (x) -x,y-1/2,-z+1/2; (xi) x, y-1,z; (xii) -x, y+1/2, -z+1/2; (xiii) x, -y-1/2, -z-1/2; (xiv) x, -y+1/2, -z+1/2; and (xvii) -x+1, y-1/2, -z+1/2.

Pressure	0.1 MPa	1.11 GPa	Pressure	1.62 GPa		
O1-H1···O2 ⁱ			$O4^{iv}$ – $H4^{iv}$ ···O1		$O9^{ix}$ – $H9^{ix}$ ··O10	
D–H	1.1751	1.0	D–H	1.0 D–H		1.0
H···A	_	1.317	H···A	H…A 1.61 H…A		1.56
D····A	2.490(5)	2.36(6)	D···A	2.610(27)	D···A	2.582(33)
D−H···A	-	179.2	D−H···A	179.4	D–H···A	179.3
O3–H2…O3 ⁱⁱ			O8 ^v –H8 ^v ····O3		O11 ^x -H11 ^x ···O2	
D–H	1.1991	0.82	D–H	1.0	D–H	1.0
H…A	-	1.61	H···A	1.47	H···A	1.45
D···A	2.395(5)	2.42 (4)	D···A	2.451(25)	D···A	2.448(23)
D–H···A	_	127.8	D–H···A	179.4	D–H…A	179.2
O4−H3···O4 ⁱⁱⁱ			O7 ^{vi} –H7 ^{vi} ···O7		Donohue an	gles
D–H	1.2454	0.82	D–H	0.82	P1–O1····O4 ^{iv}	118.2(7)
H···A	—	2.27	H···A	1.59	0104 ^{iv} –P1 ^{iv}	117.0(7)
D····A	2.491(4)	3.05(7)	D····A	2.393(15)	P1-O3···O8 v	114.3(13)
D–H···A	—	152.4	D–H···A	166.5	O3…O8 ^v –P2 ^v	118.6(14)
Dono	hue angles		012 ^{vii} –H12 ^{vii} …012		P2–O7…O7 ^{vi}	118.4(8)
P1-O1···O2 ⁱ	121.38	123.4(10)	D–H	0.82	O7···O7 ^{vi} –P2 ^{vi}	118.4(8)
$O1 \cdots O2^{i} - P2^{i}$	120.75	113.2(16)	H···A	1.67	P3–O12…O12 ^{vii}	113.4(6)
P1-O3····O3 ⁱⁱ	120.10	117.7(22)	D····A	2.488(17)	O12···O12 ^{vii} –P3 ^{vii}	113.4(6)
O3···O3 ⁱ –P1 ⁱⁱ	120.10	117.7(22)	D–H···A	174.2	P2–O5···O6 ^{viii}	116.1(8)
P1-O4···O4 ⁱⁱⁱ	118.97	95.9(28)	O6 ^{viii} –H6 ^{viii} ···O5		O5···O6 ^{viii} −P2 ^{viii}	120.2(7)
$O4\cdots O4^{iii} - P1^{iii}$	118.97	95.9(28)	D–H	1.0	P3–O9…O10 ^{viii}	120.3(7)
			H····A	1.60	O9···O10 ^{viii} –P3 ^{viii}	117.6(7)
			D····A	2.628(41)	P102····011 ^{ix}	119.8(12)
			D–H···A	174.2	$O2 \cdots O11^{x} - P3^{ix}$	117.8(14)

Table S5 Hydrogen bonds in phase I (at 0.1 MPa and 1.11 GPa) and IV (at 1.62 GPa).

-y,1-z;(viii) x, 1+y,z; and (ix) -x, 0.5+y, 0.5-z.

Table S6 Crystal data of phase II of KDP at different pressures at 296 K. The	high $R_{\rm int}$ values of the measurements
at 0.21, 1.76 and 2.28 GPa due to the inclusion of reflections close to the edge	of the DAC window.

Pressure	0.21 GPa	0.96 GPa	1.46 GPa	1.68 GPa	1.76 GPa	1.91 GPa	2.28 GPa
Crystal size(mm)	0.35/0.24/0.20	0.37/0.25/0.24	0.37/0.25/0.22	0.35/0.23/0.20	0.32/0.15/0.14	0.26/0.17/0.14	0.35/0.22/0.18
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	<i>I</i> 42d	<i>I</i> 42d	<i>I</i> 42d	<i>I</i> 42d	<i>I</i> 42d	<i>I</i> 42d	<i>I</i> 42d
a/Å	7.455(8)	7.390(4)	7.366(4)	7.345(5)	7.340(7)	7.330(4)	7.305(6)
b/Å	7.455(8)	7.390(4)	7.366(4)	7.345(5)	7.340(7)	7.330(4)	7.305(6)
$c/\text{\AA}$	6.947(2)	6.9266(19)	6.8894(18)	6.8756(16)	6.865(3)	6.8542(13)	6.8316(18)
$V/Å^3$	386.1(6)	378.3(3)	373.8(3)	371.0(3)	369.9(5)	368.3(3)	364.5(4)
Ζ	4	4	4	4	4	4	4
$\rho_{\rm cal} (\rm g \ cm^{-3})$	2.341	2.389	2.418	2.437	2.444	2.454	2.480
θ range(°)	4.01-27.57	4.03-25.85	4.05-27.82	4.06-27.88	4.06-27.55	4.07-27.98	4.09-27.61
$\mu(\text{mm}^{-1})$	1.649	1.682	1.703	1.716	1.721	1.728	1.746
F(000)	272	272	272	272	272	272	272
	$-1 \le h \le 1$	$-1 \le h \le 1$	$-9 \le h \le 9$	$-1 \le h \le 1$	$-9 \le h \le 9$	$-1 \le h \le 1$	$-9 \le h \le 9$
Limiting indices	$-9 \le k \le 9$	$-9 \le k \le 9$	$-1 \le k \le 1$	$-9 \le k \le 9$	$-1 \le k \le 1$	$-9 \le k \le 9$	$-1 \le k \le 1$
	$-9 \le l \le 9$	$-8 \le l \le 8$	$-8 \le l \le 9$	$-9 \le l \le 9$	$-8 \le l \le 9$	$-9 \le l \le 9$	$-8 \le l \le 8$
$R_{ m int}$	0.2656	0.1385	0.1512	0.1192	0.2944	0.0805	0.2294
Absolute structure parameter	-0.3(4)	-0.4(3)	-0.3(3)	0.0(4)	-0.1(3)	0.1(4)	0.1(3)
Data/constrains/parameters	56/0/15	50/0/15	48/0/15	52/0/16	44/0/15	57/0/15	47/0/15
$Data(I>4\sigma_I)$	39	50	48	51	43	57	46
R_{I}/wR_{2} (I>4 σ_{I}) ^a	0.0418/0.0716	0.0380/0.0849	0.0423/0.0984	0.0367/0.0819	0.0358/0.0456	0.0361/0.0725	0.0378/0.0815
R_1/wR_2 indices (all data)	0.0535/0.0727	0.0380/0.0849	0.0423/0.0984	0.0375/0.0832	0.0364/0.0459	0.0361/0.0725	0.0381/0.0814
Goodness-of-fit on F_0^2	1.023	1.277	1.135	1.155	1.087	1.326	1.193
Extinction coefficient	-	-	-	0.03(3)	-	-	-
Largest peak/hole (e·Å ⁻³)	0.27/-0.22	0.29/-0.19	0.22/-0.20	0.25/-0.16	0.15/-0.17	0.12/-0.12	0.10/-0.09
$[a] R_I = \sum F_o - F_c / \sum$	$ F_o $ for $F_o^2 > 2\sigma (F_o^2)$	$WR_2 = \sum [w(F_o^2 - F_o^2)]$	$(\overline{F_{c}^{2}})]/\sum[w(\overline{F_{o}^{2}})^{2}]^{1/2}, w$	where $w = 1/[\sigma^2 F_o^2 +$	$(AP)^2 + BP$], and P	$=(Fo^2+2Fc^2)/3$	

Table S7 Bond lengths (Å) and angles () in the structure of phase II of KDP at various pressures at 296 K.

Pressure	0.1MPa ^a	0.21 GPa	0.96 GPa	1.46 GPa	1.68 GPa	1.76 GPa	1.91 GPa	2.28 GPa
K(1)-O(1) ⁱ	2.834	2.816(6)	2.785(3)	2.764(3)	2.758(3)	2.768(4)	2.750(4)	2.739(4)
K(1)-O(1)	2.899	2.893(4)	2.876(3)	2.859(3)	2.858(3)	2.856(3)	2.850(4)	2.829(3)
K(1)–P(1)	3.4897	3.4736(10)	3.4633(9)	3.4447(9)	3.4378(8)	3.4327(17)	3.4271(6)	3.4158(9)
$K(1)-K(1)^{ii}$	4.1178	4.112(4)	4.0808(17)	4.0656(17)	4.055(2)	4.051(3)	4.046(2)	4.032(3)
P(1)-O(1)	1.5390	1.548(4)	1.5413(18)	1.544(3)	1.536(3)	1.522(3)	1.536(3)	1.537(3)
O(1)–O(1) ⁱⁱⁱ in PO ₄ group	2.5260	2.517(7)	2.510(3)	2.515(5)	2.500(5)	2.477(5)	2.497(6)	2.507(4)
$\mathbf{O}\cdots\mathbf{O}^{\mathrm{iv}}$	2.5068	2.496(9)	2.491(7)	2.490(9)	2.486(8)	2.485 (7)	2.476(9)	2.462(9)
$O(1) - P(1) - O(1)^{v}$	109.05	108.74(14)	109.03(8)	109.04(11)	108.91(11)	108.88(12)	108.82(14)	109.25(12)

Reference (a) Endo, S.; Chino, T.; Tsuboi, S.; Koto, K., Nature 1989, 340, 452-455.

Symmetry codes: (i) -x+1/2, y; (ii) -z+3/4; -x-1/2, y, -z+3/4; (iii) y, -x, -z; (iv) x, 0.5-y, 0.25-z; (v) -x, -y, z and (vi) x, 0.5-y, 0.25-z; (vii) -0.25+x, 0.75-y, 0.25+z; (viii) 0.25-x, 0.25+y, 0.25+z.

Phase I $(P2_1/c)$		Pha	Phase II $(I\overline{4}2d)$		Phase II' (<i>p</i> 1) (0.1 MPa)			Phase IV $(P2_1/c)$ (1.62 GPa)		
0.1 MF	Pa		P1-O1O1-P1	P1-O1.	··O1-P1	180)	P1-O3···O8-P2	164.25(7)	
P1-O3···O3-P1	180	0.1MPa	77.37	P1-O3·	··O6–P2	73.	29	Р1-07…07-Р2	180.00	
P1-O4O4-P1	180	0.21GPa	76.55(35)	P1-04.	··O8–P2	-16	54.82	P1-O2···O11-P3	-170.67(6)	
P1-O1O2-P1	95.0	0.96GPa	77.13(19)	P1-04.	··O7–P2	63.	29	P3-O12O12-P3	180.00	
1.11 GI	Pa	1.46GPa	77.14(24)	P2-05.	··O5–P2	-18	30	P1-O1O4-P1	96.73(11)	
P1-O3O3-P1	180.00	1.68GPa	76.27(24)	Phase I	II (Fdd2) ((0.1 N	/IPa)	P2-O5O6-P2	95.08(10)	
P1-O4O4-P1	180.00	1.76GPa	76.47(22)	P1-01.	··O2-P1	77	7.25	P3-O9O10-P3	92.65(9)	
P1-O1O2-P1	101.69(17)	1.91GPa	76.53(28)							
		2.28GPa	77.89(25)							
Phase VIII (Cc) (0.1 MF		Pa)	Phase C (MPa)			Phase A (P2/c) (0.1	MPa)		
P1-O1O14-P4		-83.22	P1-O11O21-P2		-66.74	4	P1-0	O11…O22−P2	-165.67	
P1-O2O7-P2		178.89	P1-O12···O43-P4		-73.31 P1-0		P1-0	O12…O22−P2	-66.2	
P1-O3O12-P4		-108.68	P1-O13O44-P4		-165.3	31				
P1-O4O10-P3		-178.58	P1-O14O22-P2		-158.5	54				
P2-O5O12-P3		105.96	P2-O24O42-P4		-177.7	9				
P2-O6O16-P4		-176.52	P3-O31O43-P4		174.0	5				
P2-O8O9-P3		85.49	P3-O32O44-P	4	165.8	5				
P3-O11O13-P4		177.75	P3-O33O21-P	2	66.53	3				
			P3-O34O22-P	2	60.01					
			P4-O41O23-P	2	175.24	4				

Table S8 Torsion angles ([°]) in the structure of P–O…O–P in different phases of KDP.

Electronic Structure Calculations

The electronic structure calculations were performed based on experimental structures of phase IV at 1.62 GPa, phase II at 0.21, 1.46 and 2.28 GPa and phase I at 0.1 MPa, by using density functional theory (DFT), as implemented in the VASP code.⁸ All the disordered H atoms were set to at the middle of the O-H…O hydrogen bonds. The energy cutoff of the plane-wave basis functions was set to be 500 eV. The interactions between electron and ion were described by projector augmented plane wave (PAW) potential.⁹ The valence electrons of the elements included H: $1s^1$; K: $3p^64s^1$; P: $3s^23p^3$ and O: $2s^2p^4$. The Perdew-Burke-Ernzerhof exchange and correlation functional was used for all the calculations.¹⁰ $3 \times 8 \times 2$, $6 \times 6 \times 8$, and $7 \times 9 \times 3$ Gamma-centered Monkhorst-Pack *k*-points grids¹¹ were used in reciprocal space integration for phase IV, II, and I, respectively. For phase IV at 1.62 GPa, the calculated band structure along high-symmetry points of the first Brillouin zone is plotted in Fig. S7, at the labeled high-symmetry k-points: Γ [0.000, 0.000, 0.000], Z [0.000, 0.000, 0.500], Y [0.000, 0.500, 0.000], A [-0.500, 0.500, 0.000], B [-0.500, 0.000, 0.000], D [-0.500, 0.000, 0.500], C [-0.500, 0.500, 0.500]. For KDP phase II, crystal data at 0.21, 1.46 and 2.28 GPa were chosen for electronic calculations. The calculated band structure along high symmetry points of the first Brillouin zone is plotted in Fig. S8, at the labeled high-symmetry k-points: Z [0.000, 0.000, 0.500], A [0.500 0.500, 0.500], M [0.500, 0.500, 0.000], G [0.000, 0.000, 0.000], R [0.000, 0.500, 0.500], X [0.000, 0.500, 0.000]. For phase I at 0.1 MPa, the calculated band structure along high-symmetry points of the first Brillouin zone is plotted in Fig. S10, where the k-points labels are : Γ [0.000, 0.000, 0.000], Z [0.000, 0.000, 0.500], Y [0.000, 0.500, 0.000], A [-0.500, 0.500, 0.000], B [0.500, 0.000, 0.000], D [-0.500, 0.000, 0.500], E [-0.500, 0.500, 0.500].

Structure Description

As shown in Table S2, the 8-fold coordinated K cation behavior is frequently found in phase I (K–O: 2.51(2) to 3.40(3) Å). In phase II the O-atoms in KO₈ from six PO₄ groups, the K–O distances up to 2.28 GPa were compressed by about 3.4% and 2.3% (see Table S7). The only exception is phase B,

where apart of 8-fold K(2)O₈: 2.747(2)–3.207(2) Å, also 10-fold coordinated K site (K(1)O₁₀: 2.755(2)–3.285(2) Å) was reported.¹² In addition, the K⁺ cations have a different number of neighboring K cations in phase IV (K1: 8; K2: 6; and K3: 8) which form rather irregular polyhedra. Only one K⁺ cation is surrounded by other four K⁺ cations and then forms zigzag chain in phase II and III. The K…K distances were compressed about 2.0% from ambient pressure to 2.28 GPa in phase II. Unlike phase II, there are six neighboring K atoms in phase I, with the distances ranging from 4.484(17) to 4.996(8) Å, which are slightly shorter than at 0.1 MPa (4.499 to 4.979 Å), but similar with phase VIII (there are four K atoms in one unit-cell).⁷

In phase I, there are three symmetry-independent OH···O hydrogen bonds, with O···O distances 2.36(6)–3.05(7) Å at 1.11 GPa compared to 2.395(5)–2.491(4) Å at ambient pressure (Table S4).⁷ There are also three different PO₄ groups in phase I. The H-bonds are: O1–H1···O2ⁱ (symmetry code *i*: x, y=1, z), O3–H2···O3ⁱⁱ and O4–H3···O4ⁱⁱⁱ, all with proton disordered (see Table S5). The powder X-ray diffraction (PXRD) and reciprocal-lattice patterns illustrate the major difference between phase I and IV (see Figs. S11 and S12).



Fig. S4. Structural fragments with seven independent OH····O hydrogen bonds in phase IV at 1.62 GPa/296 K: (a) $O_{3}...O_{8}^{a}$; $O_{7}^{b}...O_{7}^{b}$; $O_{2}...O_{11}^{c}$; and $O_{12}^{c}...O_{12}^{d}$ (b) $O_{1}^{g}...O_{4}^{f}$, $O_{5}...O_{6}^{e}$; and (c) $O_{10}...O_{9}^{e}$. Symmetry codes: (a) *x*, 0.5-y, -0.5+z; (b) 1-x, 0.5+y, 0.5-z; (c) -x, 0.5+y, 0.5-z; (d) *x*, 0.5-y, -0.5+z; (e) *x*, -1+y, *z*; (f) *x*, 0.5-y, 0.5+z; (g) *x*, -0.5-y, 0.5+z; (h) -x, -y, 1-z; and (i) -x, -y-1, 1-z. For clarity, all H-atoms labels are omitted.



Fig. S5. The crystal structure of phase I viewed along the *b*- and *a*-direction at 1.11 GPa/296 K, the OH····O hydrogen bonds are connected with red dashed lines. Symmetry codes: (i) x, y-1, z; -x+1; (ii) -y+1, -z+2; and (iii) -x+2, -y+1, -z+2.



Fig. S6. Crystal structure of KDP at ambient conditions: (a) phase II; and (b) phase III, viewed along the *c*-direction. The OH···O hydrogen bonds are indicated with red dotted lines.



Fig. S7. (a) Band structure; and (b) total and partial DOS of phase IV at 1.62 GPa. The Fermi level E_F is marked by the dashed line at 0 eV.



Fig. S8. Band structure for phase II at (a) 0.21; (b) 1.46; and (c) 2.28 GPa/296 K. The Fermi level E_F is marked by the dashed line at 0 eV.



Fig. S9. Total and partial DOS of phase II at (a) 0.21; (b) 1.46; and (c) 2.28 GPa/296 K. The Fermi level E_F is marked by the dashed line at 0 eV.



Fig. S10. (a) Band structure; and (b) total and partial DOS of phase I at 0.1 MPa. The Fermi level E_F is marked by the dashed line at 0 eV.



Fig. S11. The comparison of simulated powder X-ray diffraction (PXRD) patterns of phase IV (red) and phase I (black).



Fig. S12. Views of recorded reciprocal lattices of phase IV in projections along a^* , b^* and c^*

References

- 1 L. Merrill and W. A. Bassett, Rev. Sci. Instrum., 1974, 45, 290.
- 2 (a) J. D. Barnett, S. Block and G. J. Piermarini, *Rev. Sci. Instrum.*, 1973, 44, 1; (b) G. J. Piermarini, S. Block, J. D. Barnett and R. A. Forman, *J. Appl. Phys.*, 1975, 46, 2774.
- 3 A. Budzianowski and A. Katrusiak, *High-Pressure Crystallography*, eds. Katrusiak, A. and McMillan, P. F., Kluwer Academic Publishers, Dordrecht, 2004, pp. 101–112.
- 4 OxfordDiffraction, in Version 1.171, Oxford Diffraction Ltd: Abingdon, Oxfordshire, UK, 2004.
- 5 (a) A. Katrusiak, A program for correcting reflections intensities for DAC absorption and gasket shadowing, Adam Mickiewicz University, Poznań, Poland, 2003. (b) A. Katrusiak, Z. Kristallogr., 2004, 219, 461.
- 6 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- 7 J. A. Subramony, S. Lovell and B. Kahr, Chem. Mater. 1998, 10, 2053.
- 8 G. Kresse, and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
- 9 P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953.
- 10 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
- 11 H. J. Monkhorst, J. D. Pack, Phys. Rev. B, 1976, 13, 5188.
- 12 C. Falah, L. Smiri-Dogguy, A. Driss and T. Jouini, J. Solid State Chem., 1998, 141, 486.