STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 73 (2017)

Supporting information for article:

A new high-pressure polymorph of phosphoric acid

Craig L. Bull, Nicholas P. Funnell, Colin R. Pulham, William G. Marshall and David R. Allan

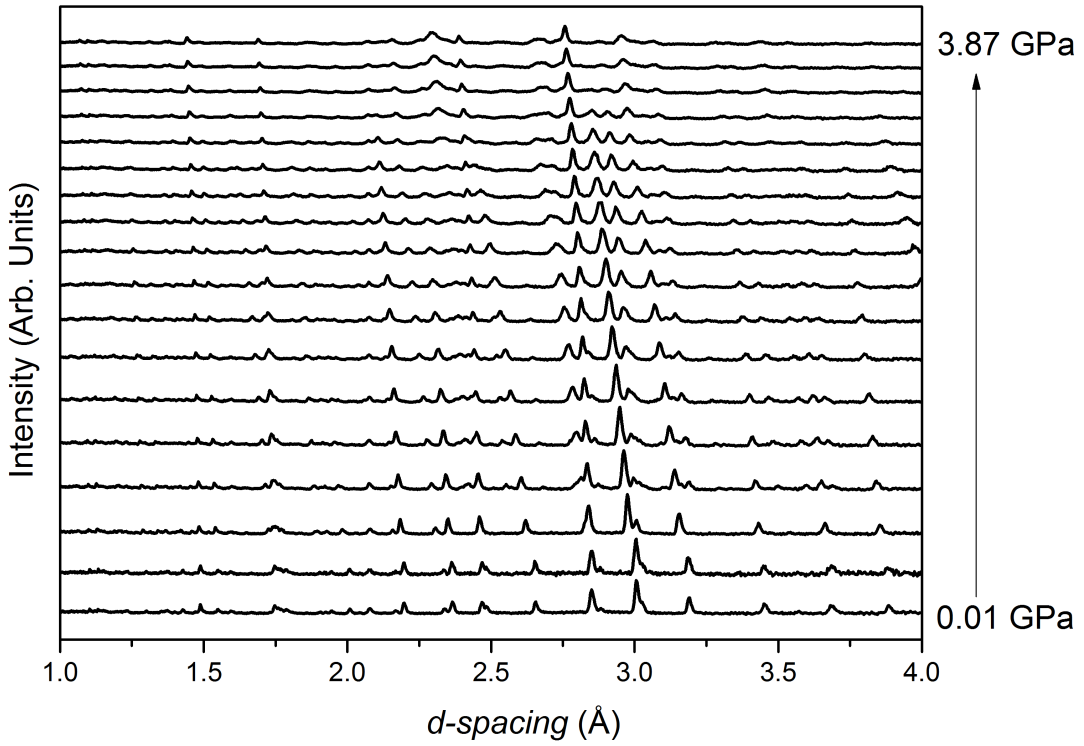

Figure S1: Variation in the neutron-diffraction pattern of phosphoric acid upon increasing pressure from 0.01 to 3.87 GPa.

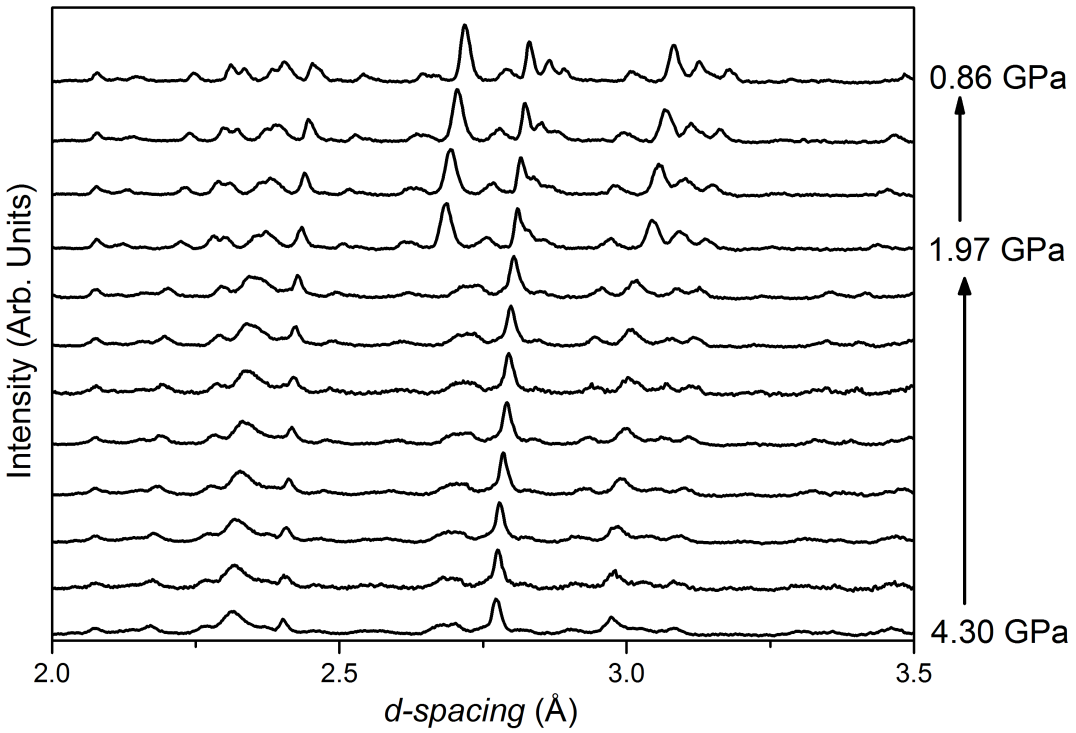

Figure S2: Variation in the neutron-diffraction pattern of phosphoric acid on downloading from 4.30 GPa to 0.86 GPa. Upon downloading, a clear change in the diffraction pattern is observed at $\sim$1.97 GPa. Clear changes are observed at $\sim$ 2.96 Å and 2.87 Å and the resulting pattern can only be indexed as orthorhombic phase II.

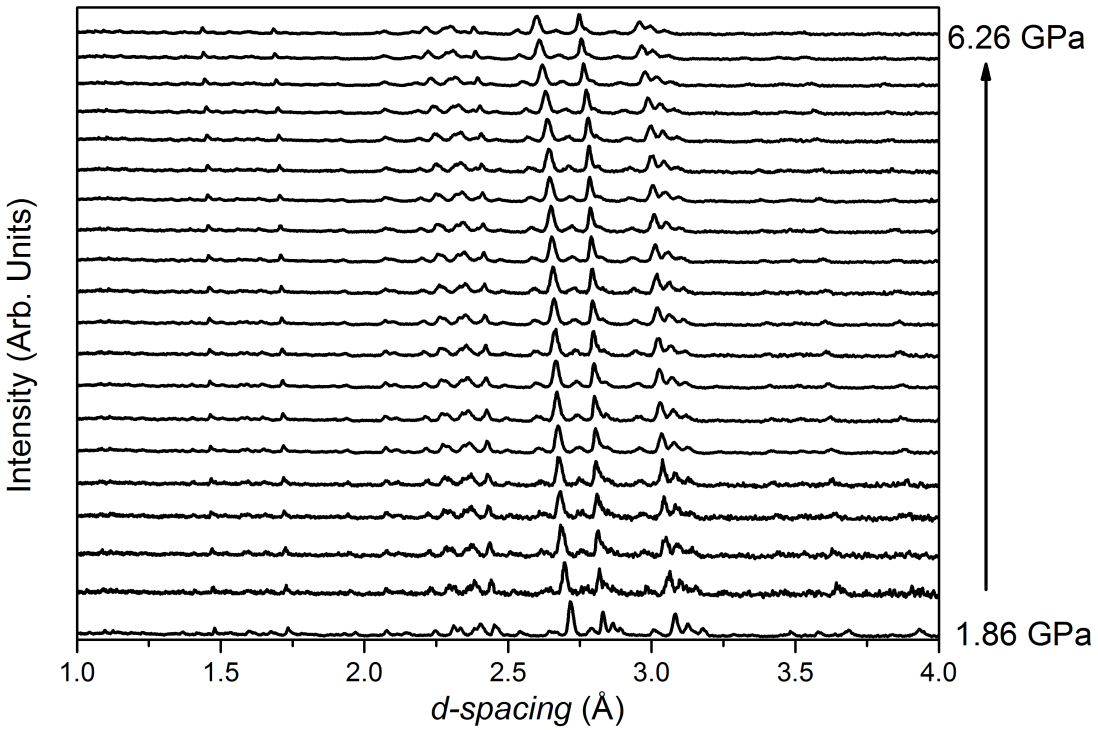

Figure S3: Variation in the neutron-diffraction pattern of phosphoric acid phase II upon increasing pressure from 1.86 to 6.26 GPa.

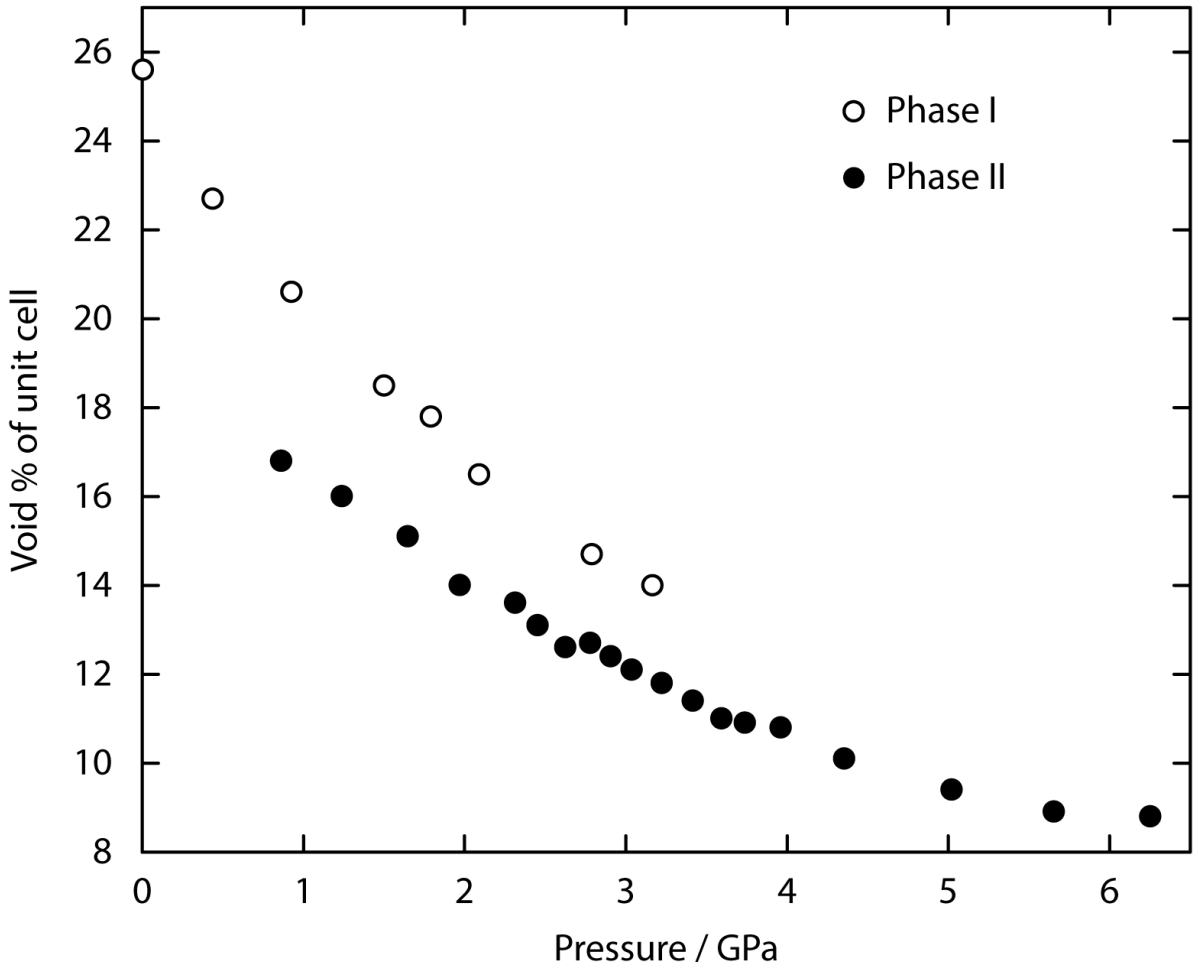

Figure S4: Percentage of unit cell volume occupied by interstitial void, as a function of pressure. Void compression trends for phases I and II are shown with open and closed symbols, respectively.

Table S1: Crystallographic data for the high-pressure neutron powder studies of phosphoric acid (additional information in supplementary CIFs). Representative fits for the monoclinic and orthorhombic phases can be seen in Figure 2 of the main text. The individual diffraction patterns can be seen in Figures 1–3 above. [a]For the neutron powder data the number of parameters relate only to the phosphoric acid phase and background, and not contaminant phases (from the anvils and pressure marker). [b]The number of reflections is across the *d*-spacing range 0.5–4.2 Å and include reflections from the anvils and pressure marker. [c] For these data, collection times were significantly shorter than those for the other data points due to experimental time constraints and, as a result, the lattice parameters have been extracted by the LeBail method and not a full Rietveld refinement.

P(GPa)	Space group	a(Å)	b(Å)	c(Å)	β(°)	V(Å^3)	Density (g cm^{-3})	Z'	Variables[a]	Reflections collected[b]	R_{wp}	χ^2
0.01	$P2_1/c$	5.7493(5)	4.8392(3)	11.6170(8)	95.150(7)	321.90(3)	2.145	1	36	1768	5.10	1.602
0.44	$P2_1/c$	5.6927(4)	4.8161(3)	11.4468(7)	94.704(6)	312.78(2)	2.084	1	36	1768	4.58	1.323
0.65[c]	$P2_1/c$	5.6605(19)	4.8043(19)	11.3767(19)	94.469(19)	308.444(19)	2.175	1	17	1768	4.84	0.418
0.93	$P2_1/c$	5.6334(4)	4.7900(3)	11.3055(8)	94.255(7)	304.23(3)	2.205	1	36	1768	5.66	1.769
1.20[c]	$P2_1/c$	5.6015(3)	4.7771(3)	11.2434(7)	94.040(5)	300.12(2)	2.236	1	17	1768	4.31	0.9539
1.50	$P2_1/c$	5.5686(4)	4.7647(4)	11.1762(9)	93.810(7)	295.88(3)	2.268	1	36	1768	5.71	1.681
1.79	$P2_1/c$	5.5356(5)	4.7522(4)	11.1169(9)	93.561(8)	291.88(3)	2.299	1	36	1768	5.79	1.639
2.09	$P2_1/c$	5.5049(5)	4.7401(4)	11.0668(10)	93.355(9)	288.28(3)	2.327	1	36	1768	6.39	1.825
2.45[c]	$P2_1/c$	5.4684(4)	4.7298(5)	11.0084(10)	93.075(8)	284.32(3)	2.36	1	17	1768	4.75	1.118
2.79	$P2_1/c$	5.4357(6)	4.7148(5)	10.9698(12)	92.874(11)	280.79(4)	2.389	1	36	1768	6.31	1.81
3.17	$P2_1/c$	5.4030(7)	4.7036(6)	10.9238(14)	92.633(12)	277.32(4)	2.419	1	36	1768	6.31	1.857
3.55[c]	$P2_1/c$	5.3716(5)	4.6970(7)	10.8794(12)	92.410(10)	274.25(3)	2.446	1	17	1768	4.48	1.042
3.87[c]	$P2_1/c$	5.3438(7)	4.6935(9)	10.8526(15)	92.260(13)	271.98(4)	2.467	1	17	1768	4.39	1.934
4.30[c]	$P2_1/c$	5.3264(9)	4.6818(1)	10.8294(22)	92.349(19)	269.82(6)	2.373	1	17	1768	4.97	2.459
1.97	$P2_12_12_1$	4.6206(5)	8.4810(9)	14.3880(14)	90.000	563.83(6)	2.38	2	67	1810	3.92	1.452
1.65	$P2_12_12_1$	4.6332(6)	8.5169(10)	14.4323(15)	90.000	569.51(7)	2.356	2	67	1810	4.47	1.717
1.24	$P2_12_12_1$	4.6494(5)	8.5580(9)	14.5078(14)	90.000	577.26(6)	2.325	2	67	1810	4.54	1.798
0.86	$P2_12_12_1$	4.6648(4)	8.6057(7)	14.5932(11)	90.000	585.83(5)	2.291	2	67	1810	4.28	1.74
1.86[c]	$P2_12_12_1$	4.6228(14)	8.4994(20)	14.3904(32)	90.000	565.41(12)	2.373	2	16	1810	11.8	0.741
2.05[c]	$P2_12_12_1$	4.6185(13)	8.4788(20)	14.3570(30)	90.000	562.21(12)	2.387	2	16	1810	11.06	0.696

Table S2: Crystallographic data, continued.

P(GPa)	Space group	a(Å)	b(Å)	c(Å)	β(°)	V(Å^3)	Density (g cm^{-3})	Z'	Variables[a]	Reflections collected[b]	R_{wp}	χ^2
2.20	$P2_12_12_1$	4.6060(10)	8.4714(18)	14.3519(29)	90.000	560.00(12)	2.396	2	67	1810	9.45	1.09
2.32	$P2_12_12_1$	4.6022(5)	8.4597(9)	14.3291(14)	90.000	557.88(6)	2.405	2	67	1810	4.05	1.434
2.45	$P2_12_12_1$	4.5980(6)	8.4429(10)	14.3036(16)	90.000	555.27(7)	2.417	2	67	1810	4.70	1.048
2.63	$P2_12_12_1$	4.5932(5)	8.4323(8)	14.2795(13)	90.000	553.06(6)	2.426	2	67	1810	4.00	1.503
2.78	$P2_12_12_1$	4.5868(7)	8.4232(13)	14.2653(19)	90.000	551.15(8)	2.435	2	67	1810	5.46	0.9163
2.91	$P2_12_12_1$	4.5831(5)	8.4110(9)	14.2424(14)	90.000	549.02(6)	2.444	2	67	1810	3.99	1.435
3.04	$P2_12_12_1$	4.5791(8)	8.4031(14)	14.2214(21)	90.000	547.22(9)	2.452	2	67	1810	5.78	1.008
3.23[c]	$P2_12_12_1$	4.5778(8)	8.3853(14)	14.1949(16)	90.000	544.90(7)	2.462	2	16	1810	4.71	1.468
3.42	$P2_12_12_1$	4.5689(7)	8.3733(12)	14.1755(18)	90.000	542.32(8)	2.474	2	67	1810	5.03	1.149
3.60	$P2_12_12_1$	4.5639(6)	8.3606(10)	14.1535(15)	90.000	540.05(7)	2.485	2	67	1810	4.01	1.451
3.74	$P2_12_12_1$	4.5599(9)	8.3496(15)	14.1332(23)	90.000	538.10(0)	2.494	2	67	1810	5.97	1.029
3.96	$P2_12_12_1$	4.5549(7)	8.3362(12)	14.1067(18)	90.000	535.64(8)	2.505	2	67	1810	4.76	1.309
4.36	$P2_12_12_1$	4.5456(7)	8.3104(13)	14.0631(19)	90.000	531.25(8)	2.526	2	67	1810	4.62	1.37
5.02	$P2_12_12_1$	4.5337(7)	8.2726(12)	13.9867(18)	90.000	524.58(8)	2.558	2	67	1810	3.91	1.622
5.66	$P2_12_12_1$	4.5214(6)	8.2332(11)	13.9189(16)	90.000	518.14(7)	2.59	2	67	1810	4.07	1.193
6.26	$P2_12_12_1$	4.5121(7)	8.2009(12)	13.8569(17)	90.000	512.75(7)	2.617	2	67	1810	4.04	1.114
0.04	$P2_1/c$	5.7464(18)	4.8382(17)	11.6026(15)	95.108(19)	321.30(32)	2.088	1	17	1768	10.06	0.753