

Polymorphism of Potassium Dihydrogen Phosphate

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Potassium dihydrogen phosphate (KH_2PO_4 , KDP), exemplar of solution grown crystals,¹ stands out in the variety of its valued physical properties. It is the prototypical ferroelectric² and principal material for controlling laser radiation,³ critical to the success of the National Ignition Facility.⁴

Since the room-temperature paraelectric phase (tetragonal, $\bar{4}2d$)⁵ and the low-temperature ferroelectric phase (orthorhombic, $Fdd2$),⁶ traditionally labeled II and III,⁷ respectively, have each inspired industries, much effort has been focused upon characterizing new phases. During the past 30 years, researchers have returned time and again to the changes in the tetragonal form of KDP upon heating because no single study paints a clear picture of what is happening. While reexamining the progression of the high-temperature transformations, we noticed the growth of new phases as single-crystal islands within polycrystalline fragments that remained metastable at room temperature. From these phases, we obtained by X-ray diffraction three new crystal structures of KDP that we show herein. This rich polymorphism dispels the notion⁸ that low symmetry structures previously detected in KDP at elevated temperatures result exclusively from dehydration products.

On the basis of the temperature dependence of dielectric constant and infrared spectra, Grinberg et al. found a KDP phase (II') at 180 °C;⁹ Rapoport found another (I) at 233 °C by differential thermal analysis.⁷ Subsequently, a great range of techniques has been employed in an unsuccessful effort to define II' and I, including the following: calorimetry, vibrational spectroscopy, X-ray diffraction, neutron scattering, light scattering, nuclear magnetic resonance, as well as measurements of thermal expansion, conductivity, and dielectric constant.⁸ These studies report varying transition temperatures and are invariably tempered with

the observation that the crystals crack and become opaque on heating; it is well-known that dehydration begins at ~ 180 °C.¹⁰

Itoh and co-workers proposed a monoclinic structure (space group $P2_1$ or $P2_1/m$) for II' based on a single, partially indexed Weissenberg photograph and only after invoking a twinning model.¹¹ Their data suggested that II' is isomorphous with the monoclinic phase of KD_2PO_4 , and this supposition has been adopted by others¹² despite the fact that Grünberg had earlier shown that the IR spectra of II' and the monoclinic phase of KD_2PO_4 were not comparable.¹³ On the basis of Raman spectra, Choi¹⁴ assumed a monoclinic structure for I as well as II'. Lee⁸ and Ortiz et al.¹⁵ concluded that the tendency of researchers to report monoclinic high temperature phases is merely due to formation of monoclinic decomposition products.

In trying to determine to what extent included dyes affect the bulk properties of crystalline KDP,^{16,17} we were prompted to reexamine the high-temperature behavior of pure KDP because we could not find adequate descriptions nor photographs of the thermal changes. Brown et al. provided the best description of the heating, yet omitted cooling.¹⁸ Baranov et al. studied KDP crystals by hot stage polarization microscopy, but could not identify the high-temperature symmetry because their samples cracked and became opaque.¹⁹

We grew crystals of KDP (Mallinckrodt, 99.9%) at room temperature by evaporation of distilled, deionized water solutions. Single crystals ($\sim 5 \times 5 \times 3 \text{ mm}^3$) were placed on their prism faces in an Instec HS400 heating stage with a platinum resistance temperature detector. The stage was mounted on an Olympus BH2 polarizing microscope equipped with a camera and oriented between crossed polarizers so that the crystals were in the extinction position (Figure 1a). The crystals were heated at a rate of 1 °C s^{-1} from room temperature to 195 °C and held at this temperature for 10 min. Usually, after approximately 2 min, one or two islands began to appear that were detected as depolarized light (Figure 1b). These islands grew with fronts parallel to c propagating in the a or b directions, with serrated

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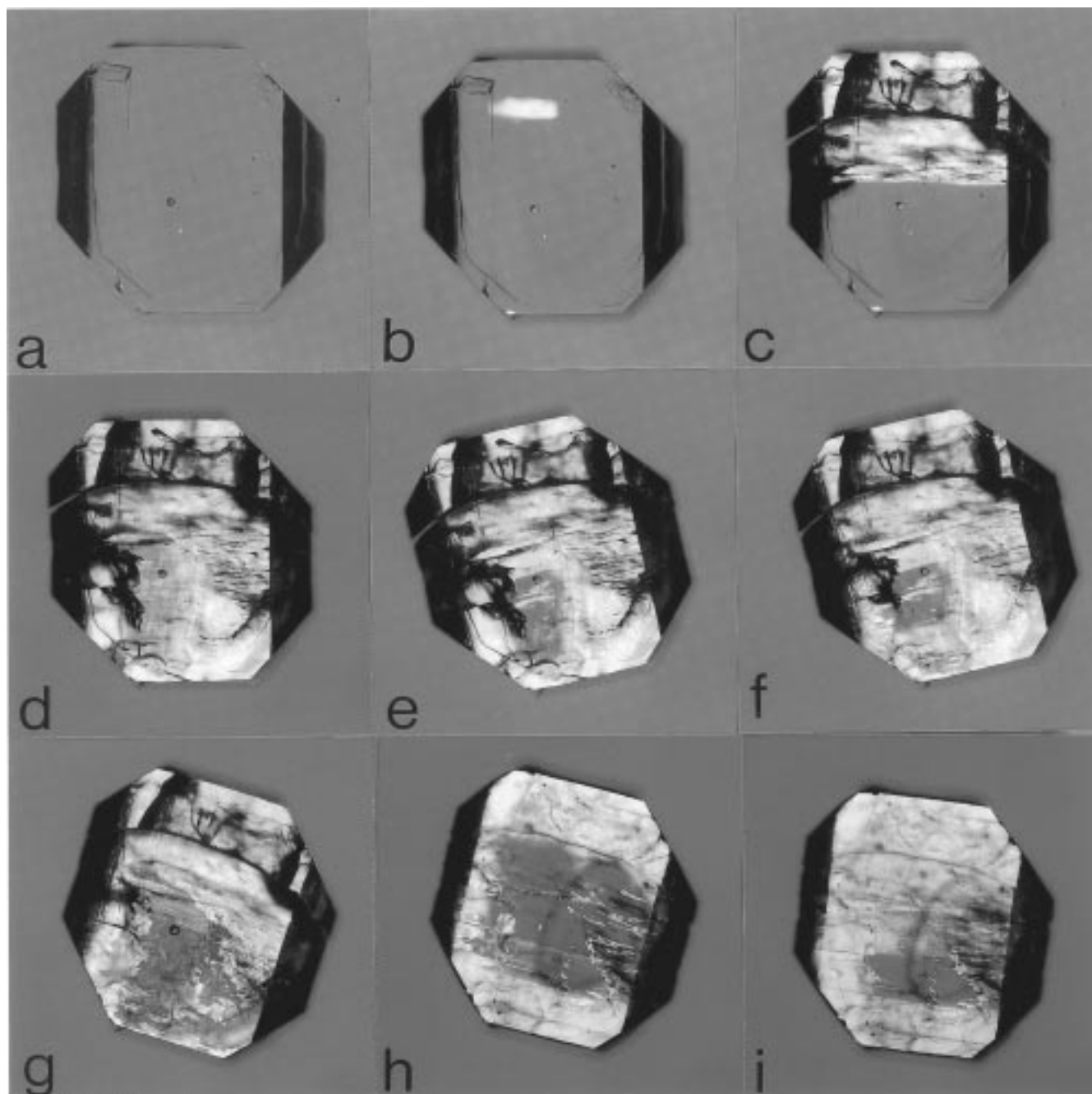


Figure 1. Changes in a crystal of KDP ($5 \times 5 \times 3 \text{ mm}^3$) on heating while being viewed through crossed polarizers and a first-order red quartz retarder: (a) 22 °C, Single crystal of KDP in the extinction position, c horizontal; (b) 195 °C, appearance of polycrystalline islands indicated as depolarized light; (c) propagation of islands; (d) formation of II', as evidenced by the appearance of new crystalline regions (red); (e) extinction position for II'; (f) 210 °C, disappearance of II' at the expense of polycrystals; (g) 230 °C, release of water; (h) formation of I evidenced by the appearance of new crystalline regions; (i) 22 °C, retreat of phase I on cooling.

edges (0° and $\sim 45^\circ$ from c , though not captured in Figure 1) moving along c at twice the rate (Figure 1c). The majority of the mass was transformed in this way, and the now opaque sample was cracked into discrete pieces. Usually, after approximately 5 min, the mass began to recrystallize (Figure 1d). In some samples this process was concomitant with the first optical changes. The new crystalline phase had its vibration directions, the planes in the crystal where the electric field of the light is constrained to vibrate, rotated by 22° – 35° (range for 20 crystals) with respect to the principal directions of the tetragonal KDP crystal envelope (Figure 1e). Sometimes, the transformation began at 180 °C, and

at other times we had to heat the crystal to 210 °C in order to encourage the change in a reasonable period of time. Other samples failed to recrystallize at higher temperatures. The progression of changes was quite different from crystal to crystal grown in the same batch.

After cooling back to room temperature, about 80% of the new crystalline phase gradually became polycrystalline once again. From the remaining intact, crystalline material, we excised fragments with a razor blade. These were mounted on a Nonius KappaCCD diffractometer at room temperature and indexed as triclinic (Table 1). This phase, II', is highly sensitive to moisture and mechanical vibrations, as previously reported.¹³

Table 1. Summary of KH_2PO_4 (fw = 136.09 g mol⁻¹) Crystal Structure Determinations^a

	II'	I	VIII		II'	I	VIII
$F(000)$	272	272	1088	ρ_{calc} , g cm ⁻³	2.289	2.293	2.329
space group	$P1$	$P2_1/c$	Cc	$\mu(\text{Mo K}\alpha)$, mm ⁻¹	1.612	1.615	1.640
crystal system	triclinic	monoclinic	monoclinic	$T_{\text{min}}/T_{\text{max}}$	0.620/0.663	0.611/0.725	0.621/0.648
Z	4	4	16	$2\theta_{\text{max}}$, deg	56	51	56
a , Å	7.4382(3)	6.1413(3)	12.2677(6)	total reflections	5916	8968	12251
b , Å	7.3926(4)	4.4990(2)	8.9662(2)	unique reflections	1357	603	2563
c , Å	7.1996(4)	14.2725(6)	14.1207(7)	parameters	109	55	217
α , deg	88.489(3)	90	90	final $R(F^2, I > 4\sigma(I))$	0.0321	0.0431	0.0526
β , deg	86.920(3)	91.552(2)	91.722(2)	final $R_w(F^2, \text{all data})$	0.0959	0.1228	0.1674
γ , deg	87.783(3)	90	90	GOF (F^2 , all data)	1.109	1.131	1.116
V , Å ³	394.90(3)	394.20(3)	1552.5(1)	$e_{\text{max}}, e_{\text{min}}$ (e Å ⁻³)	0.344, -0.427	0.421, -0.370	0.745, -0.882
temp, °C	23	23	-112				

^a Data were collected with a Nonius KappaCCD diffractometer. Data reduction and cell refinements were performed using DENZO and HKL SCALEPACK.²⁰ Structures were solved by direct methods using SIR-92²¹ and refined with SHELXL-97.²² Data were corrected for absorption anisotropy using SORTAV.²³ Heavy atoms were refined anisotropically. Hydrogen atoms were identified in difference maps and refined with a riding model except for one hydrogen with a required half occupancy that was placed on an inversion center in II', and four hydrogen atoms in VIII that were placed between the four shortest remaining O...O distances and attached to that oxygen of the pair with the longer P-O bond. The U_{iso} values for hydrogens were fixed such that they were 1.1 U_{eq} of their parent atom.

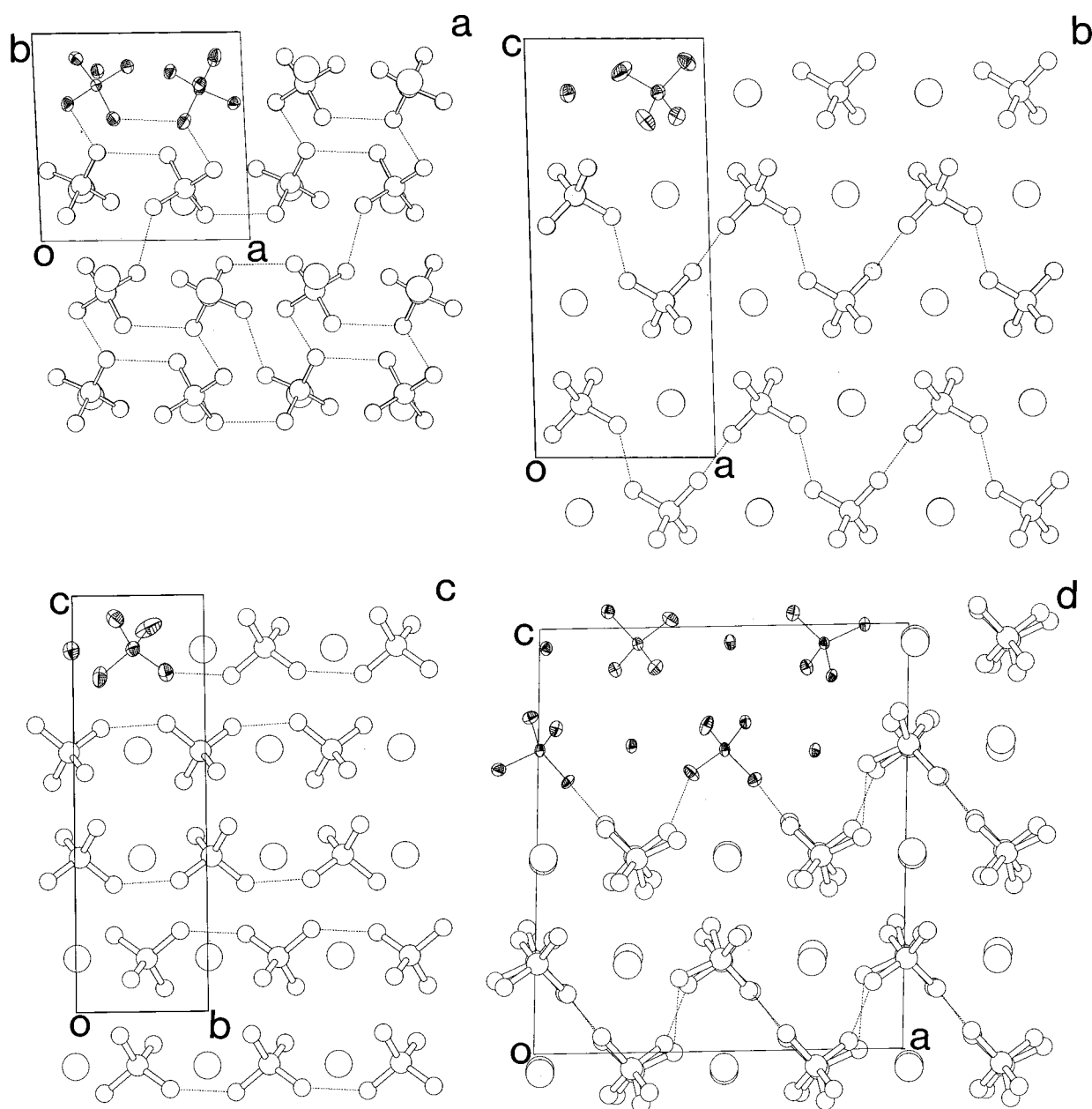


Figure 2. Crystal structures of KDP phases II', I, and VIII. In each case the atomic displacement parameters of the asymmetric unit are shown in the upper left. H-atoms have been omitted for clarity, but H-bonded oxygen atoms are joined with broken lines: (a) II' viewed along c , (b) I viewed along b , (c) I viewed along a , and (d) VIII viewed along b .

On continued heating of the crystal in Figure 1 from 195 °C to approximately 230 °C, we observed polycrystals encroaching on the triclinic single crystal phase (Figure 1f) followed by the "flowing" of a liquid, presumably water, radiating outward from discrete centers and filling the cracks of the polycrystalline mass (Figure 1g). Immediately behind these "wave fronts" the crystals once again became transparent and crystalline (Figure 1h); large cracks had healed. This process was rapid, transforming most of the material to a single-crystal phase, I. The vibration directions now varied between 24° and 40° with respect to the original tetragonal crystal, and without a clockwise or counterclockwise correlation with respect to II'. On cooling, the size of the single-crystal region diminished, but a small portion remained metastable at room temperature (Figure 1i). A piece was excised with a razor blade and indexed as monoclinic (Table 1). At -62 °C this fragment indexed as a third new crystalline structure, VIII, which is also monoclinic, though distinct from II (II' is stable at this temperature).

Single-crystal X-ray scattering patterns were measured for each of these new crystals, II', I, and VIII. Refined KDP structures (Table 1) in the space groups $P\bar{1}$, $P2_1/c$, and Cc , respectively, were fit to these data.²⁰⁻²³ Figure 2a shows that the crystal structure of II' resembles II in the general arrangement of K^+ and $H_2PO_4^-$ ions; it most likely results from a genuine structural phase transition. On the other hand, I (Figure 2b,c) is not simply derived from II' structurally and forms only after the appearance of water within the crystals; it may not belong to a single component phase diagram but coexists with the dehydration products¹⁸ $K_2H_2P_2O_7$ and $(KPO_3)_x$ ²⁴ in other parts of the heterogeneous sample. Unlike the three-dimensional H-bond networks in II and II', the phosphates in I are bound only in two dimensions by nearly linear chains along b and zigzagging chains along a . Phase VIII is derived from I by doubling the a and b axes (Figure 2d). This produces a centered cell from a primitive one by rotation of every other $H_2PO_4^-$ ion and quadrupling of the asymmetric unit. Phase I is isomorphous with the crystal structures of TiH_2PO_4 and TiD_2PO_4 ,^{25,26} which also have type VIII phases on cooling.²⁷

Mathew and Wong-Ng²⁸ recently reported a crystal structure of KH_2PO_4 containing $H_4PO_4^+$ ions. The crystals that they analyzed were precipitated serendipitously after many months from a KOH solution (pH 10) containing KH_2PO_4 , $K_4P_2O_7$, and $Ca(OC(O)CH_3)_2$. This structure is monoclinic and can be viewed as intermediate between the tetragonal phase II and the triclinic

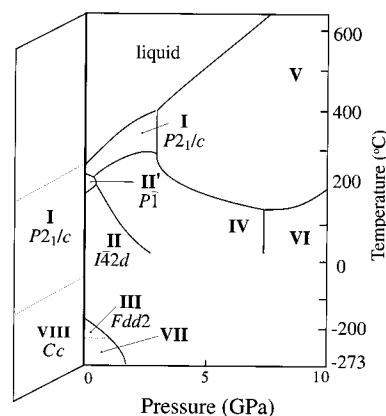


Figure 3. Phase diagram of KDP shown as a function of temperature and pressure. IV, V, and VI are high-pressure phases observed by Rapoport,⁷ Kobayashi and Endo,³¹ and Kobayashi et al.,³² respectively. VII was discovered by Melo et al.³³ Phase I does not belong to a single component phase diagram and appears only after substantial decomposition (see the text). Nevertheless, we have indicated I on the KDP temperature–pressure phase diagram to be consistent with previous representations.^{7,32} VIII, represented on the orthogonal flange, is presumably metastable with respect to II and also does not belong on the KDP phase diagram. Since VIII is obtained only from I on cooling, we have extended I with dotted lines that represent ill-defined separations between phases into the metastable plane.

phase II', but it has problematic features that encourage further analysis: phosphate ions are arranged in planes with PO_4^{3-} ions segregated from $H_4PO_4^+$ ions that have exceptionally long P–O bond lengths of 1.622(2) and 1.617(2) Å, in sharp contrast to the invariable average P–O bond lengths in accumulated PO_4^{3-} , HPO_3^{2-} , $H_2PO_4^-$, and H_3PO_4 structures (~ 1.535 Å)²⁹ and the average bond lengths in II', I, and VIII of 1.536(2), 1.530(3), and 1.538(7) Å, respectively. [Not one of the 28 measured bonds in II', I, and VIII exceeded 1.582(7) Å and the P–O and P–O(H) bond lengths follow the well-known correlation with O···O distances]. Moreover, we performed an ab initio molecular orbital calculation (RHF/6-31G*) for a $H_4PO_4^+$ ion with a $\bar{4}$ conformation. The geometry was optimized with P–O bond lengths of 1.536 Å, quite distinct from the reported value of 1.62 Å.

Having thus obtained the structural identity of the high-temperature phases, we have updated Rapoport's⁷ pseudo-phase diagram of KDP (Figure 3). There is no evidence in the literature for more than two transitions between room temperature and 240 °C, and therefore we affixed our structures to those positions in the phase diagram previously reserved for II' and I. The high-temperature phases II' and I are centrosymmetric and thereby cannot display the valuable properties associated with II and III. However, it is likely that the troublesome time dependent decay of second-order nonlinear optical properties of KDP³⁰ results from the

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local formation of II' and I, and their role in KDP degradation will be the focus of future research.

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Supporting Information Available: Tables of crystallographic data, fractional atomic coordinates, anisotropic and isotropic thermal parameters, interatomic distances and angles, X-ray crystallographic files in CIF format for II', I, and VIII (25 pages); observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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