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Reevaluation of Raman Spectra for KH_2PO_4 High-Temperature Phases

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The common tetragonal form of KH_2PO_4 undergoes two high-temperature transformations that have been studied extensively by vibrational spectroscopy. But, because these changes are strikingly heterogeneous, the previously reported spectra, averages over polycrystalline and single crystal domains, have remained ill-defined. We recently identified the crystalline domains by polarization microscopy, physically isolated them, and determined their structures by X-ray diffraction (Subramony, J. A.; Lovell, S.; Kahr, B. *Chem. Mater.* **1998**, *10*, 2053−2057). Here, using micro-Raman spectroscopy, we have deconvoluted the signals of the polycrystalline and crystalline domains, showing that the inescapable pyro- and metaphosphate dehydration products are localized in the polycrystalline material. Those debating whether the transformations are genuine structural phase transformations or are merely dehydration reactions can all be vindicated in certain parts of any one sample.

Introduction

The importance of KH_2PO_4 (KDP) crystals[1] for the development of the sciences of ferroelectricity and nonlinear optics is hard to overestimate.[2] For this reason, the mysterious, ill-defined high-temperature behavior of KDP has been a source of constant scrutiny. Of the many methods of analysis applied to the high-temperature KDP phases, none has been more widely used than vibrational spectroscopy, especially Raman scattering, the focus of 10 prior studies.[3,4] The authors of these studies have proposed two phase transitions at ∼195 and ∼220 °C,[5] while revisionists have reinterpreted changes in physical properties as due solely to decomposition/dehydration reactions.[6] Most recently, we analyzed single crystals by hot-stage polarization microscopy.[7] This work enabled the isolation and single-crystal structure determination of three new KDP phases, including the two high-temperature phases that form near the above-specified temperatures. Equipped for the first time with detailed structures of the high-temperature polymorphs we are now in a position to build upon the pioneering Raman studies, while discriminating and resolving inconsistencies among them. In other words, we can use structural information to reevaluate the vibrational spectra rather than use spectra to derive structures.

Prior to our work, interpretations of the high-temperature behavior of KDP have been diverse, and the many vibrational studies have added to this multiplicity of opinion. Grunberg and co-workers in 1972 failed to find a correspondence between the vibrational spectra of KDP at high-temperature with those of KD_2PO_4 (KDDP) which undergoes a well-defined tetragonal to monoclinic transition at 130 °C, thereby ruling out a strict isomorphism between the high-temperature forms of the isotopomers.[3a] She and Pan interpreted changes in the polarized Raman spectra at high temperature as resulting from an unspecified alteration of the hydrogen bond network,[3b] but Dalterio and Owens ascribed some of the changes to decomposition,[3c] as did Abdel-Kader and co-workers.[3d] Serra et al. assumed that their heat-treated powders were monoclinic in accordance with a fragmentary X-ray study;[8] more importantly, they demonstrated that the first high-temperature phase, II′ (Figure 1), whatever it is, is metastable at room temperature in the absence of moisture and mechanical vibration.[3e] Choi showed that the second high-temper-

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(5) These temperatures vary from crystal to crystal and are highly dependent on heating rates.

(6) Lee, K.-S.; *J. Phys. Chem. Solids* **1996**, *57*, 333−342. Park, J.-H.; Lee, K.-S.; Kim, J.-N. *J. Korean Phys. Soc.* **1998**, *32*, S1149−S1151. Ortiz, E.; Vargas, R. A.; Mellander, B. E.; Lunden, A. *Pol. J. Chem.* **1997**, *71*, 1797−1802. Ortiz, E.; Vargas, A.; Mellander, B.-E. *J. Phys. Chem. Solids*, **1998**, *59*, 305−310.

(7) Subramony, J. A.; Lovell, S.; Kahr, B. *Chem. Mater.* **1998**, *10*, 2053−2057.

(8) 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. See: Itoh, K.; Matsubayashi, T.; Nakamura, E.; Motegi, H. *J. Phys. Soc. Jpn.* **1975**, *39*, 843−844.

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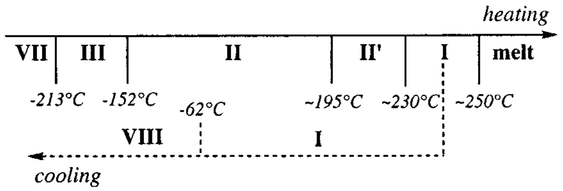

Figure 1. Thermal transformations of room-temperature KDP phase II. I is formed after substantial decomposition while heating, and VIII is formed exclusively from I (denoted by dotted lines in the figure) on cooling. Therefore, I and VIII may not belong to the KDP single-component phase diagram.

Table 1. Space, Site, and Factor Groups for KDP Phases

phase	space group	phosphate site symmetry	factor group
III	$Fdd2$	C_2	C_2
II	$I\bar{4}2d$	S_4	D_{2d}
II′	$P\bar{1}$	C_1	C_i
I	$P2_1/c$	C_1	C_{2h}
VIII	Cc	C_1	C_s

ature phase (I) was also metastable.[4] To understand the structure of these phases, he compared the spectrum of a powdered KDP pellet at high temperature with that of several other monoclinic dihydrogen phosphates with varying structures, leading to the prediction of monoclinic symmetry for both high-temperature phases II′ and I.[4] In summary, simple conclusions were not forthcoming from vibrational studies regarding the origin of the transitions and the symmetries of the high-temperature phases.

On the basis of our X-ray study,[7] we can quickly summarize the high-temperature behavior of KDP (Figure 1). The room-temperature tetragonal structure (II) becomes triclinic (II′) at ~195 °C, monoclinic primitive (I) at ~230 °C. On cooling to −62 °C, I becomes monoclinic *C*-centered (VIII). X-ray analysis revealed that II′ is a “jumbled” version of II, whereas I and VIII are layered phases, differing only in small rotations of the $H_2PO_4^-$ ions, and isomorphous with a pair of TlH_2PO_4 phases.[14] From this structural information we have identified and summarized (Table 1) the relevant symmetries required for the factor group analysis of the various KDP phases.

Nevertheless, this summary of phase changes is incomplete because thermogravimetric analysis and differential thermal analysis show unequivocally that dehydration begins at ~175 °C.[9] This fact can only be reconciled with the structural transformations by the observation that only parts of the original sample appear optically as single crystals; the remainder is polycrystalline. As we recently described,[7] a heated KDP crystal first becomes polycrystalline at ~195 °C and shatters. The new single-crystal phase (II′) then forms as islands. Further heating produces single-crystalline phase I which also coexists with polycrystalline material. To develop a clear understanding of the transformations, it is therefore important to distinguish the Raman spectra of the polycrystalline materials from that of the single crystals. For this reason, only single-crystal specimens of II are appropriate for high-temperature studies in which the heterogeneities can be distinguished microscopically. Here we report the Raman scattering of single crystals of KDP heated from room temperature to 250 °C and then cooled to −70 °C. The various polycrystalline and single-crystal regions were identified and their spectra obtained using a Raman microscope.

Experimental Section

The following reagents and chemicals were purchased from commercial vendors and were used without further purification: KDP (99.9%, Mallinckrodt), Tl_2CO_3 (99.99% Aldrich), *o*-phosphoric acid (85%, Fisher Scientific). Single crystals of KDP were grown by evaporating water from aqueous solutions at room temperature. KDP crystals were also grown from seeds on an alternately rotating platform immersed in a saturated solution while gradually lowering the temperature from 55 °C to 40 °C.[2c] Thallium dihydrogen phosphate (TlDP) was crystallized by treating aqueous solutions of Tl_2CO_3 and *o*-phosphoric acid in the molar ratio 1:2.1.[10] Piles of lamellae were obtained by slow evaporation of the solution. Pellets (5 mm diameter, 1 mm thick) were prepared from KDP that was finely powdered with a mortar and pestle, placed in an oven at 105 °C for 24 h, and pressed at 200 MPa. An Instec HS400 stage was used to heat the samples. Single crystals of KDP were placed on their prism faces on a piece of brass within the heating stage to avoid background scattering from silica.

A MMR vacuum-assisted Joule-Thompson refrigerator with quartz windows and nitrogen inlet/outlet was used for cooling. The sample was mounted on a pad connected to the cold stage of the refrigerator using thermal conducting epoxy. The entire system was evacuated to 10^{-5} mmHg. Temperature was regulated with a MMR model K-77 manual temperature indicator/controller equipped with a silicon diode thermometer and a resistive heater.

The heating and cooling stages were mounted on an Olympus BX 60 polarizing microscope equipped with a Raman probe. Spectra were collected with a Kaiser Optical Systems Hololab Series 5000 Raman microscope consisting of a Holoprobe transmission holographic spectrograph interfaced to the infinity-corrected, fiber-coupled microscope. The Raman spectra were measured using a thermoelectrically cooled charge-coupled device (CCD). A beam splitter in the collimated space between the fiber-optic probe head and the microscope provided a real-time visual channel for the simultaneous full-color display of the sample image and the laser spot on the sample. The microscope used in this study was configured with a single mode (8 μm i.d.) excitation fiber and a multimode (100 μm i.d.) collection fiber. These fiber diameters, along with the 10×, 0.25 numerical aperture (NA) microscope objective lens gave a confocal 5.5-μm-diameter spot at the sample. The optical power at the sample was ~50 mW. The Holoprobe was configured with a 785-nm stabilized external cavity diode laser and a split configuration Holoplex transmission grating for simultaneous collection of the high (1600 cm^{-1}) and low (200 cm^{-1}) frequency Raman spectra. Data were acquired using a 50-μm slit width and a detector temperature of −40 °C. The spectra were the average of five accumulations of 5-s exposures. The difference spectra were obtained after normalizing a peak that minimized the overall negative intensity in the difference spectrum.

Results and Discussion

The Raman spectrum of a single crystal of KDP at room temperature (Figure 2) resembles the spectrum published by Agrawal and Perry.[11] The Raman-active modes of the paraelectric phase ($I\bar{4}2d$) belong to the A_1, B_1, B_2, and E representations of the factor group D_{2d}

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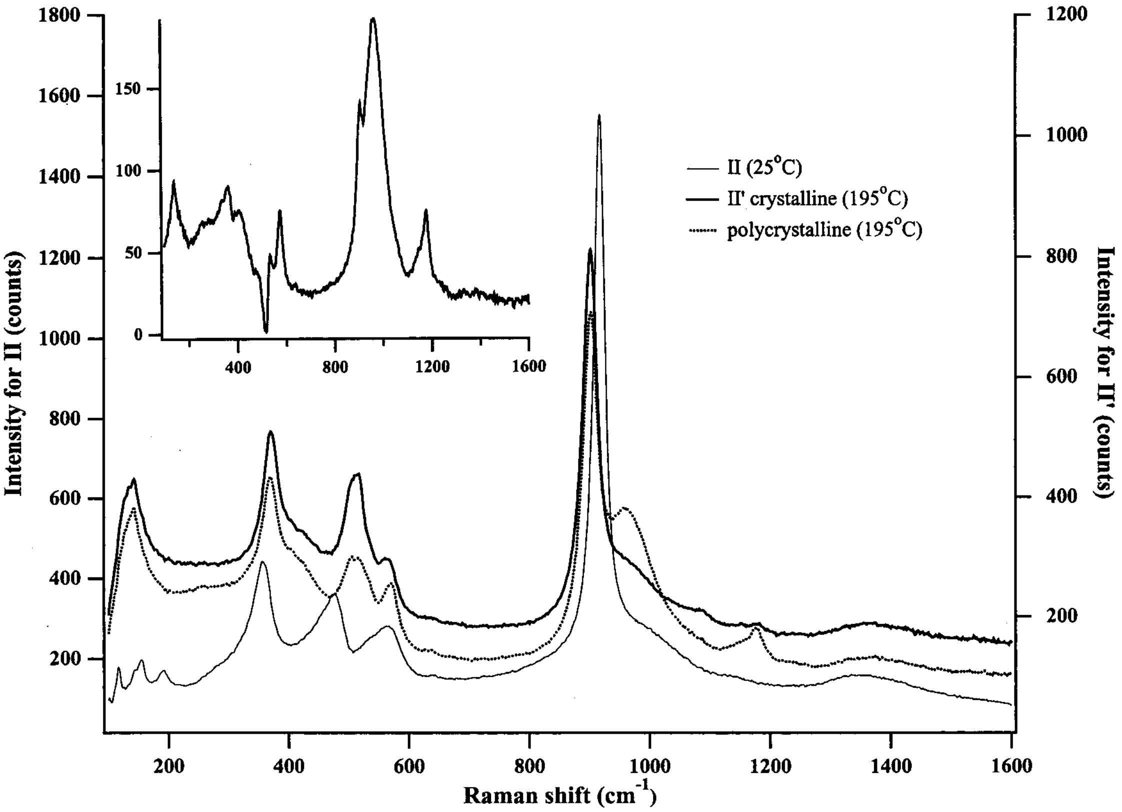

Figure 2. Raman spectra of KDP at room-temperature (II), and the polycrystalline and single-crystal (II′) regions at 195 °C. Inset shows the difference spectrum for the polycrystalline and single crystal material. Right-hand scale applies to all 195 °C spectra.

Table 2. Observed Raman Active Mode Frequencies (cm^{-1}) for KDP Polymorphs

II (25 °C)		II′ (195 °C)	II′ (25 °C)	I (230 °C)	I (25 °C)
114	E[a]			124	
155	B_1	142	140	142	
190	E		185		
360	A_1	369	359	367	365
476	B_1	511	471		
565	E	563		553	549
911	A_1	897	914	924	927

[a] Assigned modes refer to phase II only.

(Tables 1 and 2). The prominent bands between 300 and 1200 cm^{-1} are due to internal vibrations of the PO$_4$ group, the bands below 200 cm^{-1} are lattice modes. Upon heating the crystal, spectral frequency and intensity changes were observed (Figure 2) that are distinct in the polycrystalline and single-crystal regions (Figure 3). Upon focusing on the polycrystalline region formed at 195 °C, we saw that the room temperature B_1 internal mode of the phosphate at 476 cm^{-1} is shifted to higher energy, 511 cm^{-1} (Figure 2). The A_1 mode at 911 cm^{-1} is however shifted to lower energy, 897 cm^{-1} with a pronounced shoulder around 960 cm^{-1} a signature of pyrophosphate ($^{2-}O_3P{-}O{-}PO_3{}^{2-}$).[12] Choi assigned this peak to the new KDP phase II′.[4c] We also saw the presence of a meta-phosphate peak at 1160 cm^{-1}.

From the crystalline region, identified as triclinic ($P\bar{1}$, II′) by X-ray diffraction,[7] a subset of the transitions in the polycrystalline spectrum was observed (Figure 2).

Figure 3. Photograph of KDP crystal (8 (H) × 5 (W) × 3 (D) mm^3) at 195 °C viewed between crossed polarizers. Hemispherical, extinguished (black) region at left is II′. Extinguished band in right half of crystal is untransformed II. Bright regions are polycrystalline.

There are no longer peaks corresponding to pyrophosphate and metaphosphate. The inset in Figure 2 shows the difference spectrum between the polycrystalline and single crystal domains, that emphasize the dehydration products.

On continued heating of the crystal to 230 °C, we noticed further changes in the vibrational spectrum

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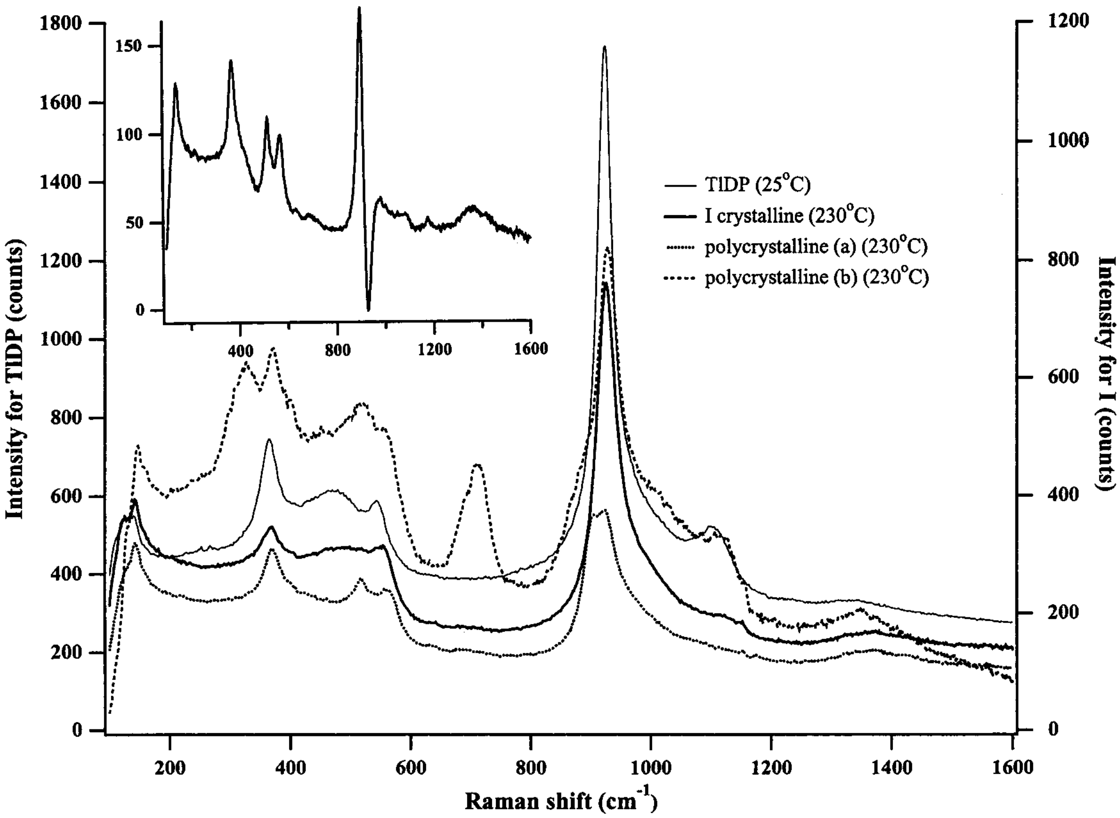

Figure 4. Raman spectra of TlDP at room temperature, and single-crystal (I) region at 230 °C, as well as two spectra from polycrystalline regions (a and b). Inset shows the difference between the spectra of the polycrystalline (a) and crystalline material. Right-hand scale applies to all 230 °C spectra.

(Figure 4). Focusing on a polycrystalline region (a), we saw that the original A_1 mode at 911 cm^{-1} was now red-shifted and split; however, we could no longer observe the pyrophosphate peaks, nor any other feature attributable to dehydration products. The dehydration products in the form of metaphosphate $(PO_3)_n{}^{n-}$ were localized in other regions of the polycrystalline mass (b), as evidence by a new peak at 296 cm^{-1}, a broad feature ~700 cm^{-1}, and a shoulder at 1147 cm^{-1}.[12b,13] Thus, the polycrystalline material varies in composition from place to place.

The crystalline region, identified as monoclinic ($P2_1/c$, I) by X-ray diffraction,[7] gave a spectrum with a sharp peak in the A_1 region. Since this phase is isomorphous with TlH_2PO_4 (TlDP),[14] we compared its spectrum with that of a TlDP crystal (Figure 4). The two spectra have a strong correspondence. The inset in Figure 4 shows the difference spectrum between polycrystalline region (a) and the crystalline region. It resembles the spectrum of II′, indicating the presence of the first high-temperature phase (II′) even after the second one (I) has formed.

To meaningfully compare the vibrational frequencies of the high-temperature phases with their X-ray structures determined at room temperature, we also recorded the Raman spectra for metastable II′ and I at room temperature. The various vibrational frequencies obtained for the cooled, metastable samples along with those obtained at high-temperature are given in Table 2. It is evident that the sharpest and most accurately measured peak, corresponding to the A_1 mode of the phosphate, is shifted to higher energies for both II′ (914 cm^{-1}) and I (927 cm^{-1}), on cooling. The energy of the A_1 mode is then inversely correlated with the average P−O bond lengths of the various phases (II, 1.541(5) Å; II′, 1.536(2) Å, I, 1.530(3) Å) although the differences in lengths fall within 3σ.

Recently, Falah et al. synthesized KDP hydrothermally at 180 °C, determined its structure (monoclinic, $P2_1/c$), and presumed that it was one of the high-temperature forms.[15] It consists of phosphate ions in rows such that H_3PO_4 molecules are segregated from $HPO_4{}^{2-}$ ions, and represents an improved refinement for a similar phase serendipitously precipitated by Mathew and Wong-Ng[16] which Choi assigned as II′.[4a] Our work shows that it is not either of the high-temperature phases II′ or I.[7] The aforementioned phase is nevertheless intermediate in structure between II and II′, representing the midpoint in a progressive desymmetrization (tetragonal to monoclinic to triclinic) of a structure type with collinear, or nearly collinear in the triclinic case, K and P atoms. It is curious that we have not seen this phase.

On continued heating of single KDP crystals beyond 400 °C, we observed strong peaks, indicating the presence of the metaphosphate. Even though Choi[4a] has

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reported the formation of several metaphosphate peaks in his pellet samples at temperatures above 180 °C, their intensity in the spectrum of his single-crystal sample is considerably less.[4c] When we repeated our experiments on a KDP pellet we also saw more metaphosphate peaks at 296, 679, and 1150 cm^{-1}. This is presumably because dehydration becomes facile in powder samples with larger surface areas. Upon cooling I to −62 °C, the transition temperature for the *Cc* phase (VIII), the Raman spectrum remained unchanged. This is not unexpected as the site symmetry and basic structure is not perturbed on passing through this transition. Since TlDP has a phase isomorphous with VIII at sub-zero temperatures,[17] we cooled a TlDP crystal from room temperature to −70 °C. No changes in the Raman spectrum were observed, which is in agreement with Pasquier et al.[18]

Conclusion

We have studied the high-temperature phase behavior of KDP using micro-Raman spectroscopy, while paying particular attention to the heterogeneous nature of the phase transitions. Our micro-Raman analysis of optically distinct regions that develop upon heating single crystals revealed that the spectra published previously represent averages over single crystal and polycrystalline domains, the latter of which are riddled with meta- and pyrophosphate dehydration products. In this way, we have distinguished the Raman modes of the high-temperature phases I and II′, free from decomposition products.

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