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Correlation of KH_2PO_4 hillock chirality with absolute structure

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Abstract

An understanding of potassium dihydrogen phosphate, KH_2PO_4 crystal growth at the atomic scale first requires a correlation of the absolute structure and morphology with the chirality of its growth hillocks. This correlation is established here in four ways: by X-ray diffraction, by dyeing the growing surfaces with chiral molecules, as well as by determination of the signs of optical rotation, and the piezoelectric effect. We show that the (1 0 0) face, according to the X-ray coordinates given herein, is that face whose step edges run along the diagonal from lower right to upper left.

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1. Introduction

Potassium dihydrogen phosphate, KH_2PO_4 (KDP) is arguably the most well studied crystal grown from solution and has served as a model system for studies of crystal growth mechanisms [1]. The tetragonal crystals (space group $I\bar{4}2d$, point group $\bar{4}2m$) express two forms, {1 0 0} and {1 0 1}, that grow by spiral dislocations leading to chiral hillocks on enantiomorphous faces. Penetrating insights into the role of nanoscopic and mesoscopic secondary surface structures notwithstanding [2,3], an appreciation of KDP growth at the levels of ions [4,5] requires detailed models of step structure whose representation in turn requires correlation of the chirality of the hillocks with the absolute configuration of the crystallographic surfaces. To the best of our knowledge, this correlation has not been established. In the absence of this knowledge, the development of an ion-by-ion KDP crystal growth mechanism is not possible because mirror image hillocks on any one face will have different structures and energies. Thus, establishing which handed face is associated with which handed hillock is of paramount importance [6]. One need only point to the thalidomide tragedy [7] to appreciate the fact that

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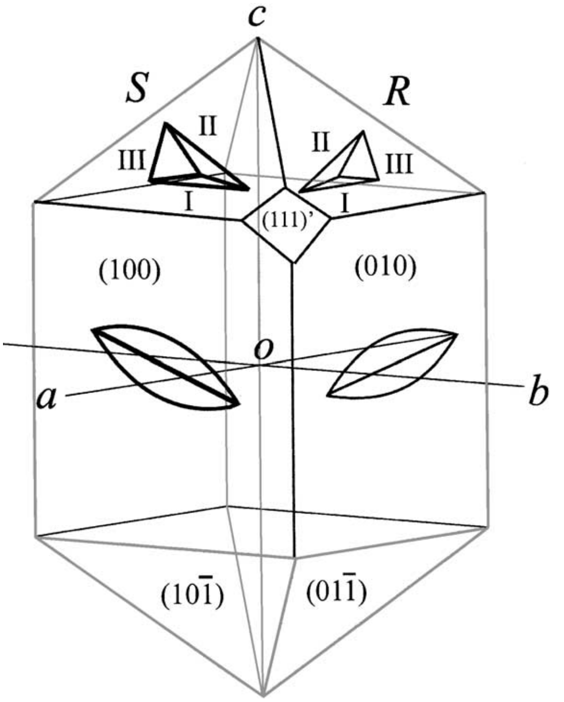

Fig. 1. Schematic representation of KH_2PO_4 morphology and hillocks. I, II, and III refer to slopes of pyramid hillocks of decreasing inclination. R and S specify the absolute configurations of these structures according to the conventions defined in the text. Dark diagonal lines define the hillock slopes schematically while the gray lines mark the crystal edges and crystallographic axes.

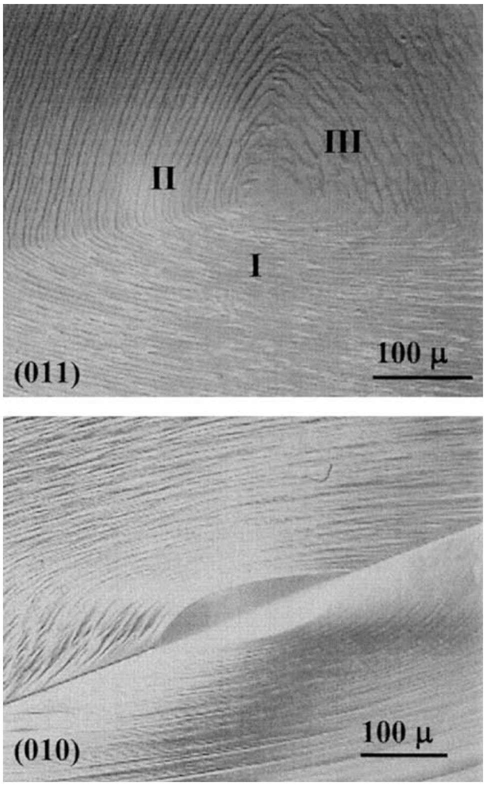

Fig. 2. Typical differential interference micrographs of (top) pyramid (0 1 1) and (bottom) prism (0 1 0) hillocks.

when two different chiral moieties interact—whether they be drug molecule and receptor, or chiral face and screw dislocation—two symmetry inequivalent combinations are possible that can have drastically different manifestations. Here, we link the hillock chiralities with the absolute hand of the *a* and *b* crystallographic axes by X-ray diffraction, by the adsorption of chiral luminophores, as well as by determination of the signs of optical rotation, and the piezoelectric effect.

Dislocation hillocks on the dipyramidal faces of KDP have the shapes of trihedral pyramids. The boundaries joining adjacent vicinal slopes do not correspond to crystallographic directions and the angles between them, while variable depending on growth conditions, are approximately 167°, 115°, and 78° [8]. If we label the vicinal slopes of the pyramidal hillocks from the steepest to the shallowest as I, II, and III as is common in the literature [9], then, by borrowing the method of assigning absolute configuration to asymmetric tetrahedra from organic chemistry, we can assign the configuration of the hillocks as R or S according to whether the cycle I → II → III runs clockwise, or counterclockwise, respectively (Fig. 1).

The hillocks on the prismatic faces are elliptical in shape [10]. Their configuration is defined with respect to the pyramidal faces with *h* like indices as indicated in Fig. 1. R pyramid hillocks are associated with prism hillocks in the same crystal quadrant whose step edges run from lower left to upper right. This drawing may contradict others that have appeared in the literature in which internal consistency between the chirality of the hillocks on the pyramid and prism faces was not emphasized. Fig. 2 shows typical differential interference contrast images of prism and pyramid hillocks.

2. Crystal growth and hillock morphology

KDP crystals measuring approximately 5 cm^3 were grown unidirectionally from seeds on alternately rotating platforms [11] in 3 L beakers submerged within variable temperature water baths. Crystals were grown by temperature reduction of a saturated aqueous solution from 40°C to 35°C at a rate of 0.5°C/day. The crystals were removed from the solutions and their surfaces were quickly blotted with tissue paper. The vicinal slopes of the hillocks were visible to the naked eye in reflected room light. Their chirality could be determined by inspection. These observations were confirmed by an examination of the crystals in reflected light using a Leica DMLM microscope equipped with a differential interference contrast prism.

3. Optical rotation

Given the ambiguity in assigning absolute configuration with automated indexing routines implemented in proprietary, commercial X-ray diffractometer software packages, we checked our assignment first by measuring the optical rotation; KDP crystals are achiral but nevertheless are optically active along the [1 0 0] and [0 1 0] diad axes. A {1 0 0} crystal plate was cut with a wet wire saw, and polished on glass with sapphire powder and fine emerald paper to a thickness of 0.64 mm. In order to measure circular birefringence in directions that are also linearly birefringent, we employed the tilter-method of Kaminsky and Glazer [12], a modification of high-accuracy universal polarimetry (HAUP) [13]. The crystal plate was tilted such that the wave vector was progressively inclined from one principal crystal axis to each of the other two. The optical rotation derived from these measurements was 6.5(5)°/mm at the 670 nm wavelength of a laser diode; the gyration surface is shown in Fig. 3. This is only about half of the value given by Kobayashi et al. [14] but, in excellent agreement with Arzt who had determined that the (1 0 0) face is levorotatory [15]. Accordingly, our dextrorotatory sample was taken from a (0 1 0) slice, a judgement confirmed by the adjacent {0 1 1} faces that were decorated by hillocks with R configurations.

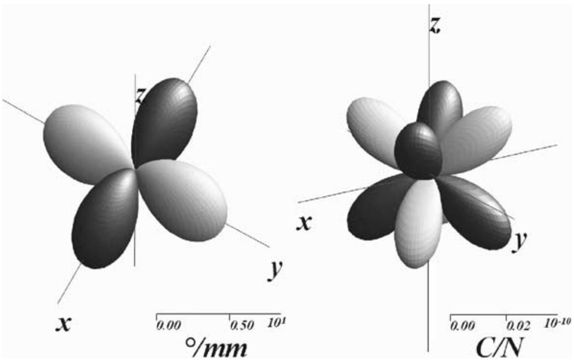

Fig. 3. Representation surfaces for the gyration (optical rotation) and piezoelectric tensors of KDP.

4. X-ray diffraction

The structure of the KDP crystal used in the optical experiments was solved and refined with a Nonius KappaCCD diffractometer and its attendant software [16,17]. The Flack-enantiopole parameter was 0.0(2). Selected Bijvoet pairs are shown in Table 1, where $\Delta = 2(I^+ - I^-)/(I^+ - I^-)$. I^+ and I^- are diffraction intensities of reflections of the type $h\,k\,l$ and $h\,k\,\bar{l}$ respectively. These values are compared with those calculated on the basis of the structure with the configuration as given by the set of coordinates in Table 2 [18]. We repeated the Bijvoet analysis many times. In this way, it was determined that (1 0 1) and (0 1 1) surfaces are decorated with S and R hillocks, respectively.

5. Piezoelectricity

Measurements of optical rotation along birefringent directions in crystals are non-trivial [19]. As these measurements are routinely carried out in only a few laboratories worldwide, it would be of value to correlate the absolute

Table 1
Selected Bijvoet pairs

$h\,k\,l$	I^+	I^-	Δ_{measured}	$\Delta_{\text{calculated}}$
4 1 3	3013(65)	3430(74)	-13.0 ± 2.2	-14.71
4 1 5	1096(38)	836(21)	27.4 ± 3.2	27.14
5 2 1	7109(152)	6327(123)	11.7 ± 2.1	12.78
5 2 3	4784(136)	3929(92)	19.4 ± 2.7	15.31
5 4 1	962(28)	1238(37)	-25.1 ± 3.0	-27.39

Table 2
Fractional atom coordinates

Atom	x/a	y/b	z/c	U_{iso}
P	0	0	0	0.017(1)
K	0	0	$\frac{1}{2}$	0.023(1)
O	0.1482(4)	0.0821(4)	0.1256(4)	0.022(1)
H	0	$\frac{1}{4}$	$\frac{1}{8}$	0.13(5)

configuration of the faces with physical properties that are more easily accessed. We chose to correlate the sign of the piezoelectric moduli with the handedness of the hillocks [20]. For the description of tensorial properties, we introduce a Cartesian reference system with axes e_i parallel to the crystallographic axes as defined in Fig. 1. It is well established that KDP has two independent piezoelectric components $d_{123} = 0.65(2)$ and $d_{312} = -10.5(2)$ pC/N [21]. A representation surface of the piezoelectric tensor is shown in Fig. 3. In order to connect the sign of the piezoelectric effect with the hillock pattern on the {1 0 1} faces, we measured the longitudinal piezoelectric effect along the space diagonal $e' = (e_1 + e_2 + e_3)$ of the Cartesian reference system by employing a commercial charge amplifier. For this purpose, we prepared a rectangular parallelepiped of a KDP crystal (~12 × 12 × 12 mm) clearly decorated with hillocks. One pair of plane-parallel faces was oriented perpendicular to e'. The upper face designated $(1\,1\,1)'$ emerges near the lower right hand corner of the (1 0 1)-S face (Fig. 1). The opposite surface was designated $(\bar{1}\,\bar{1}\,\bar{1})'$. Upon applying a positive, quasi-static uniaxial stress (pulling) perpendicular to $(1\,1\,1)'$, we observed the generation of a negative electric charge on the $(1\,1\,1)'$ face. At 293 K, the corresponding longitudinal piezoelectric effect $d'_{111} = (4d_{123} + 2d_{312})\sqrt{3/9}$ exceeds the piezoelectric effect (d_{111}) of α-quartz by about a factor of 1.5 and is therefore easily measured. The value obtained was −4.9 pC/N. This compares favorably to that given by Wirth [22] but is larger than the older value in Landölt-Bornstein [21]. The determination of the sign of the longitudinal piezoelectric effect in KDP can now be used as a reliable method for assigning the handedness of the crystallographic axes of KDP crystals which do not exhibit an easily recognizable hillock pattern.

6. Luminescence labeling

We had previously shown that KDP is a remarkably general host for a wide variety of anionic organic dyes [23–25] and have recently extended our studies to biomolecules. A visible blue luminescence was localized in the pyramidal {1 0 1} growth sectors of KDP grown from a solution containing 5×10^{-4} M adenosine triphosphate (ATP)[1] (hydrolysis produced some adenosine monophosphate and adenosine diphosphate as well). This is a common pattern of anion zoning in KDP [23–25]. The crystals contained one nucleotide per 5×10^{4} KDP molecules as determined by measuring the absorbance of dissolved crystals. Comparisons of the luminescence viewed perpendicular to the prism surfaces revealed that one subset of opposing {1 0 1} sectors was brighter than the other (Fig. 4). As these sets of sectors are mirror images of one another in the space group I$\bar{4}$2d, the chiral nucleotides must have recognized these faces enantioselectively, as we have previously observed with hematein and the prismatic faces. For other examples of enantioselective crystal adsorption, see Refs. [26–30]. Upon indexing the crystal absolutely with X-rays, we determined that the ATP lights up the (0 1 0) face of KDP. The mechanism of this selective adsorption is at present not known.

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[1] Under the conditions of crystal growth ATP must undergo some hydrolysis.

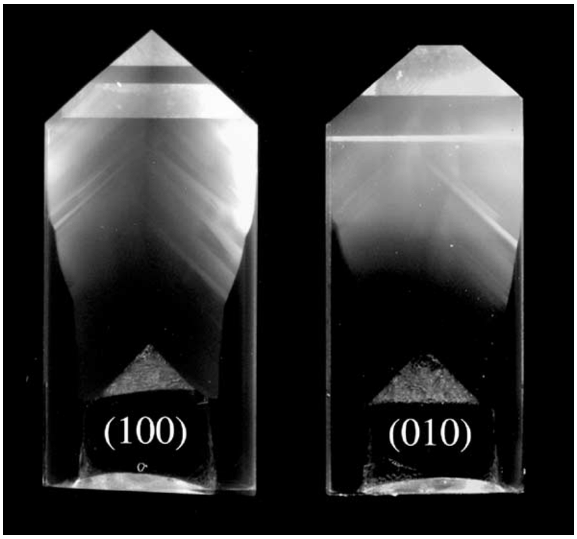

Fig. 4. KDP containing adenosine phosphates, viewed normal to the enantiomorphous (1 0 0) (left) and (0 1 0) (right) faces. Seed crystal is visible at the base.

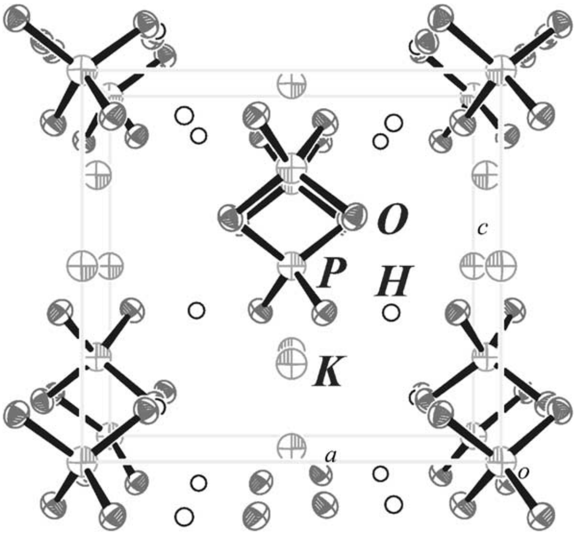

Fig. 5. Absolute configuration of the (0 1 0) face based on the coordinates in Table 2 with hillock step edges running from the lower left to the upper right.

7. Conclusion

Given the correlation of the configuration of the growth hillocks with the absolute identities of the crystallographic axes, we can conclude that the (0 1 0) face has the chiral structure as shown in Fig. 5, and a positive optical rotation (clockwise when looking toward the light source). We have further shown as to how this assignment can be made through the measurement of one other physical property, piezoelectricity, and by luminescence labeling with adenosine phosphates. The construction of atomic models of the growth steps can now proceed without the ambiguity associated with the assignment of absolute configuration.

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