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Introduction. Potassium titanyl phosphate, KTiOPO4 (KTP), has excited interest for some time as a nonlinear optical material for various applications in optical physics (Zumsteg, Bierlein & Gier, 1976). Many of the physical properties of KTP and its analogue crystals have been documented including the observation of twinning (Bierlein & Ahmed, 1987; Loiacono & Stolzenberger, 1988). Domains have been observed indirectly using various techniques including electrooptic, second-harmonic generation and pyroelectric measurements, although a structural explanation of how they arise has not yet been put forward.

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The gyration tensor for point group mm2 is

\[
\begin{bmatrix}
0 & g_{12} & 0 \\
g_{12} & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

When this tensor is diagonalized, the eigenvectors which correspond to the eigenvalues ±g₁₂ are at ±45° from the [100] and [010] directions in the (001) plane. As the a lattice parameter (12.818 Å) of KTP is almost twice the b lattice parameter (6.399 Å), the maxima in the gyration are along directions only 0.04° from the crystallographic directions (120). The variation of the gyration as a function of direction in the (001) plane is shown schematically.

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Potassium titanyl phosphate, KTiOPO4. I. Experimental investigation of optical gyration, absolute optical chirality and twinning


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Abstract. The optical gyrations of a domain-free section and of a twinned section of the nonlinear optical crystal KTiOPO4 have been measured using a high-accuracy universal polarimeter. An optical gyration at 6328 Å equivalent to an optical rotation of +22° mm⁻¹ together with a significant circular dichroic contribution was found in the domain-free (210) section whereas equivalent rotations varying between +14 and -20° mm⁻¹ were found in different regions of the twinned section. The absolute indices of the faces of the samples and the existence of twinning in the second section have been established using X-ray anomalous scattering. The regions of opposite optical chirality in the twinned sample have been shown to correlate with those of opposite structural chirality. The results are used to show that the twinning operation in this KTiOPO4 crystal must be one of the twofold rotations 2[010] or 2[100].

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in Fig. 1. Note that the point-group symmetry implies that the 
rotation, and therefore the equivalent optical rotation 
rotates through 90° about the [001]
changes sign for propagation vectors in different quadrants of the (001) plane.

Experimental. A crystal of KTP which was flux grown by 
the method of Jacco, Loiacono, Jaso, Mizell & Greenberg (1984) was aligned along one of the directions (120). A 
section was cut from the crystal normal to this direction. The crystal was then rotated through 90° about the [001] 
direction and therefore the equivalent optical rotation in Fig. 1. Note that the point-group symmetry implies that 
rotations of opposite signs and equal magnitudes.

HAUP measurements and X-ray experiments on sample (1). Sample (1) (thickness ~30 μm) was investigated using the 
HAUP apparatus across a range of wavelengths in the visible region. An optical gyration equivalent to an optical 
rotation of +22(2)° mm⁻¹ (at 6328 Å) was measured for 
this sample. A small piece of KTP (~0.5 mm² in area) was cut 
from sample (1) for use in an X-ray anomalous-scattering 
experiment. The crystal was mounted on a goniometer 
head on a Stoe Stadi-4 four-circle diffractometer. In order 
to correlate the positive observed gyration with the crystal 
structure, it was necessary to establish in which quadrant 
of the (001) plane the light was propagating in the HAUP 
apparatus across a range of wavelengths in the 
visible region. An optical gyration equivalent to an optical 
rotation of +22(2)° mm⁻¹ (at 6328 Å) was measured for 
this sample.

Table 1. Observed and calculated Friedel differences for KTP samples used in the HAUP and X-ray anomalous-
scattering experiments

<table>
<thead>
<tr>
<th></th>
<th>Untwinned Sample (1)</th>
<th>Upper region of Sample (2)</th>
<th>Lower region of Sample (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h k l</td>
<td>I(h k l)(o)</td>
<td>I(h k l)(o)</td>
<td>I(h k l)(o)</td>
</tr>
<tr>
<td></td>
<td>ΔIₜₜₜₜ</td>
<td>ΔIₜₜₜₜ</td>
<td>ΔIₜₜₜₜ</td>
</tr>
<tr>
<td>2 0 4</td>
<td>3281(18)</td>
<td>2745(16)</td>
<td>+17.8%</td>
</tr>
<tr>
<td></td>
<td>3459(18)</td>
<td>2887(16)</td>
<td>+18.0%</td>
</tr>
<tr>
<td>6 0 1</td>
<td>2109(13)</td>
<td>2297(14)</td>
<td>8.5%</td>
</tr>
<tr>
<td></td>
<td>1347(10)</td>
<td>1456(11)</td>
<td>-7.8%</td>
</tr>
<tr>
<td>1 1 4</td>
<td>6251(28)</td>
<td>5732(26)</td>
<td>8.7%</td>
</tr>
<tr>
<td></td>
<td>6246(28)</td>
<td>5691(26)</td>
<td>+9.3%</td>
</tr>
<tr>
<td>1 0 4</td>
<td>6507(29)</td>
<td>5822(27)</td>
<td>+11.0%</td>
</tr>
<tr>
<td></td>
<td>6141(28)</td>
<td>5557(26)</td>
<td>+10.8%</td>
</tr>
<tr>
<td>0 2 4</td>
<td>1301(49)</td>
<td>12557(43)</td>
<td>+3.6%</td>
</tr>
<tr>
<td></td>
<td>11813(406)</td>
<td>115158(396)</td>
<td>+2.5%</td>
</tr>
<tr>
<td>1 1 5</td>
<td>1339(25)</td>
<td>13114(50)</td>
<td>+2.1%</td>
</tr>
<tr>
<td></td>
<td>12963(50)</td>
<td>12711(49)</td>
<td>+2.0%</td>
</tr>
<tr>
<td>3 3 3</td>
<td>12393(48)</td>
<td>12469(49)</td>
<td>-0.6%</td>
</tr>
<tr>
<td></td>
<td>5675(26)</td>
<td>5594(27)</td>
<td>-5.5%</td>
</tr>
<tr>
<td>3 2 3</td>
<td>9655(39)</td>
<td>9921(40)</td>
<td>-2.7%</td>
</tr>
<tr>
<td></td>
<td>7123(61)</td>
<td>7400(32)</td>
<td>-3.9%</td>
</tr>
<tr>
<td>1 3 4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>975(9)</td>
<td>1086(10)</td>
<td>-10.8%</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>927(8)</td>
<td>1072(9)</td>
<td>-14.5%</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>819(8)</td>
<td>946(9)</td>
<td>-14.4%</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>949(9)</td>
<td>1067(9)</td>
<td>-11.7%</td>
</tr>
</tbody>
</table>

and indexing procedures were initially used to orient the 
KTP unit cell with respect to the diffractometer axes. After 
centering of reflections and refinement, a satisfactory unit 
cell [a = 12.85(2), b = 6.420(3), c = 10.613(9) Å, α = β = γ = 90°] to within ±0.03° was obtained. The polished 
faced crystal was then indexed as (2.28, -1.08, -0.04) 
so that the normal to the face was identified as [120] (to 
within a total angular misfitting of 1.8°).

Having established the indices of the crystal face corre-
sponding to the choice of the unit-cell axes on the diffrac-
tometer, it was necessary to find the orientation of the 
crystal structure with respect to this axial set. As the point 
group is mm2, there are only two choices to consider, i.e. 
the coordinate sets (x, y, z) and (x, y, -z) [identical with 
the coordinate set (x, -y, z)]. The distinction between 
these two coordinate sets can only be made using X-ray 
anomalous scattering.

The published structural coordinates for KTP (Thomas, 
Glazer & Watts, 1990) were used to calculate a list of 
structure factors appropriate to measurement with Mo Kα 
radiation. From this, a set of enantiomer-sensitive Friedel 
pairs of reflections, which showed calculated intensity dif-
fferences arising from anomalous scattering in the range of 
3-20%, was chosen for measurement. Each reflection and 
its equivalents and their Friedel partners were measured so 
that there were eight measurements for a general reflection 
(hkl). Although large differences between equivalent 
reflections appeared because of the effects of absorption 
in the highly anisotropic crystal plate, the Friedel pairs 
were measured at geometrically equivalent positions to
minimize these errors. A good correspondence between the observed and calculated intensity differences was obtained (Table 1) indicating that the normal to the face had been correctly identified as [120] with respect to the established crystal structure of KTP.

Results of the experiment on sample (1). The gyration in this section was positive which corresponded to a positive equivalent optical rotation, \( \rho \). Using the known birefringence of KTP (Fan, Huang, Hu, Eckardt, Fan, Byer & Feigelson, 1987), the value of \( \rho \) was calculated at each wavelength. A smooth dispersion curve was obtained (Fig. 2) which, when fitted with a Drude-type expression, showed a significant circular dichroism peak centred on approximately 300 nm. The exact form of the peak is difficult to detect because the transmitted intensities become very small below 350 nm (the fundamental absorption edge of KTP is at \( \sim 330 \) nm).

As the anomalous-scattering experiment showed that the face normal was [120] with respect to our choice of structural coordinates, the combined optical and X-ray experiments have demonstrated that a positive gyration is associated with this direction.

HAUP measurements and X-ray experiments on sample (2). Sample (2) (again of thickness \( \sim 30 \) \( \mu \)m) was investigated as before using HAUP with the result that the gyration in this section was initially found to be positive [and equivalent to an optical rotation of \( +14(1) ^\circ \text{ mm}^{-1} \)] in conflict with the requirements of crystal symmetry. We could only explain the positive result in sample (2) on the assumption that the crystal was twinned (see below) in a way which caused the reversal in sign of the gyration from one domain to the other in the crystal. This was investigated with HAUP measurements as a function of position across sample (2). Positive, zero and negative gyrations [corresponding to optical rotations of \( +14(1), \sim 0 \) and \( -22(2) ^\circ \text{ mm}^{-1} \)] were observed in the upper, central and lower regions of the sample, respectively.

For the X-ray experiment, sample (2) was mounted on the diffractometer and the upper region (gyration positive) was centred in the beam (collimator diameter 0.8 mm). The indices of the polished face in the upper region were found to be (1.92, -1.24, 0.10) indicating that the face normal was close to [120]. Friedel differences were measured for a similar set of reflections as those for sample (1) (Table 1). The crystal was then displaced vertically so that the lower portion (gyration negative) was centred in the beam. The indices of the polished face were (-1.97, 1.23, 0.12), i.e. the face normal was near [120]. The orientation matrix for the lower region was transformed into that for the upper part by applying the transformation \( a_{\text{new}} = -a_{\text{old}}, b_{\text{new}} = -b_{\text{old}}, c_{\text{new}} = c_{\text{old}} \). This ensured that the Friedel pairs were collected with the unit cell in equivalent orientations in both parts of the experiment.

The Friedel pairs of the reflections were then measured as before (Table 1). As a final check, the reflections 204, 204 and their Friedel partners were measured as a more detailed function of position in the plate (Table 2).

Interpretation of experimental results for sample (2). Note that the observed Friedel differences changed sign between the upper and lower regions of sample (2). The Friedel difference for the 204 reflections is positive in the upper region, close to zero in the middle and negative in the lower region. This can be interpreted as a scan from a domain of one structural polarity through the domain wall region (Friedel difference approximately zero) into the domain of the opposite polarity. The change in sign of the Friedel differences correlates with the observed change in sign of the optical rotation in sample (2) and is explained by twinning as set out below.

1. For point group \( mm2 \) the Friedel differences are determined by \( \pm l \) reflection indices.
2. Comparison of the observed and calculated Friedel differences thus allows us to determine the structural polarity, i.e. whether \( +c \) or \( -c \) points upward on the diffractometer with respect to our choice of structural coordinates which were taken from Thomas et al. (1990).
3. The X-ray measurements therefore indicate that for the top region of sample (2) \( +c \) points upward, whereas in the lower region \( +c \) is downward.
4. The HAUP measurements show that the gyration is positive in the upper region of sample (2) and negative in the lower region.

Table 2. Friedel differences for 204 reflections as a function of position in sample (2)

<table>
<thead>
<tr>
<th>h k l</th>
<th>Region of crystal</th>
<th>( l(l h l)_{(c)} )</th>
<th>( l(l H l)_{(c)} )</th>
<th>( \Delta l_{\text{obs}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 0 4</td>
<td>bottom</td>
<td>4670(23)</td>
<td>5345(25)</td>
<td>-13.5%</td>
</tr>
<tr>
<td>2 0 4</td>
<td>bottom</td>
<td>5119(25)</td>
<td>6166(28)</td>
<td>-21.4%</td>
</tr>
<tr>
<td>2 0 4</td>
<td>lower</td>
<td>4964(24)</td>
<td>5710(26)</td>
<td>-13.9%</td>
</tr>
<tr>
<td>2 0 4</td>
<td>lower</td>
<td>4505(22)</td>
<td>5314(24)</td>
<td>-16.5%</td>
</tr>
<tr>
<td>2 0 4</td>
<td>middle</td>
<td>5252(25)</td>
<td>5373(25)</td>
<td>-2.3%</td>
</tr>
<tr>
<td>2 0 4</td>
<td>middle</td>
<td>4815(23)</td>
<td>5056(24)</td>
<td>-4.9%</td>
</tr>
<tr>
<td>2 0 4</td>
<td>middle</td>
<td>5670(26)</td>
<td>5530(26)</td>
<td>+2.5%</td>
</tr>
<tr>
<td>2 0 4</td>
<td>middle</td>
<td>5123(24)</td>
<td>5074(24)</td>
<td>+1.0%</td>
</tr>
<tr>
<td>2 0 4</td>
<td>upper</td>
<td>6258(28)</td>
<td>5105(25)</td>
<td>+20.3%</td>
</tr>
<tr>
<td>2 0 4</td>
<td>upper</td>
<td>5336(25)</td>
<td>4677(23)</td>
<td>+13.2%</td>
</tr>
</tbody>
</table>
(5) From the HAUP measurement on the single-domain sample (1), we know that the gyration is positive in quadrants 1 and 3 and negative in quadrants 2 and 4.

(6) The space group describing the high-temperature phase of KTP is $Pnan$ (Thomas et al., 1990; Harrison, Gier, Stucky & Schultz, 1990). Space group $Pnan$ is generated from $Pna2_1$ by any of the symmetry operations $2[010]$ at $(0, y, 1/4), 2[100]$ at $(x, 0, 0)$ or an $n$-glide plane perpendicular to $[001]$ at $z = 0$. Therefore at the ferroic structural phase transition $mmmFmm2$ between the high- and room-temperature phases, it is possible for KTP to twin via any of the point operations $2[010], 2[100]$ or $m[001]$.

(7) Now consider the effect of these operations on a crystal described by point group $mm2$.

(a) The $m[001]$ operation can reverse the sense of $c$ but cannot transform quadrant 1 (or 3) into quadrant 2 (or 4). Therefore, $m[001]$ cannot change the sign of the gyration and must be discounted as the twinning operation for our crystal.

(b) Both of the operations $2[010]$ and $2[100]$ reverse the sense of $c$ and transform quadrant 1 (or 3) into quadrant 2 (or 4). Therefore, either of the twofold operations can change the sign of the gyration and could be the twinning operation in our crystal.

Discussion. The choice of any of the above twin operations is consistent with the observation of Bierlein & Ahmed (1987) that both the electrooptic coefficient $(r_{223})$ and the pyroelectric coefficient undergo a change in sign from one domain to the next in a twinned hydrothermally grown crystal. If we assume that the twinning mechanisms are the same in our flux-grown and their hydrothermally grown material, our experiment has eliminated the twinning operation $m[001]$ from consideration because it cannot account for the simultaneous reversal in sign of a third-rank polar electrooptic $(r_{223})$ and a second-rank axial gyration $(g_{12})$ tensor coefficient.

Bierlein & Ahmed reported that twinning of their crystals could be eliminated by the application of a pulsed d.c. electric field to the crystal at various temperatures up to 773 K. Loiacono & Stolzenberger (1988), however, observed a domain pattern in flux-grown KTP crystals which could not be altered or eliminated by heating the crystals above the Curie temperature (1218 K for their crystals) with the application of an electric field. Since the domains in their crystals were of opposite polarity (as indicated by the reversal in sign of the pyroelectric coefficient) but could not be switched by electric field alone, they concluded that they were of similar nature to the Dauphiné twins found in quartz. Dauphiné twins are also related by a twofold rotation twin operation, $2[010]$ in quartz. Inspection of the elastic compliance $(s_{ijkl})$ tensor for point group 32 shows that the Dauphiné twin elements differ in the sign of the component $s_{1123}$. Hence, under the application of a suitable stress, $\sigma$, a free-energy difference $\Delta G = \sigma^2$ appears between the domains (Newnham, 1975). Domain switching occurs when $G$ becomes comparable with the energy required to move the domain wall. This procedure is commonly used to detwin quartz crystals and hence quartz is classified as a ferrobielastic crystal. However, when the $s_{ijkl}$ tensor for point group $mm2$ (appropriate to KTP) is considered, it is seen that all the independent components have even numbers of the suffices 1 and 3 or 2 and 3. This implies that none of the $s_{ijkl}$ changes sign under either of the twofold operations $2[100]$ or $2[010]$. Hence, a free-energy difference between the domains in KTP will not arise under the application of the stress alone. Thus, KTP is not a ferrobielastic and a detwinning method based only on the application of a stress will not be effective. In this sense, the analogy with Dauphiné twinning in quartz is misleading.

Quartz is also a ferroelastoelectric crystal because the coefficient $d_{111}$ of the piezoelectric tensor changes sign under the application of the operation $2[010]$. This implies that Dauphiné twins might also be eliminated from quartz by the application of suitable simultaneous stress and electric fields. Inspection of the piezoelectric tensor, $d_{ijk}$, for point group $mm2$ (appropriate to KTP) shows that all the independent components, $d_{111}, d_{333}, d_{322}$ and $d_{131}$, change sign under either of the twofold operations $2[100]$ or $2[010]$. Hence, if a suitable stress is applied to a twinned KTP crystal, electric polarizations of opposite sign are induced in the domains. In the most general case, the three components of the induced polarization are

$$\pm P_1 = \pm (d_{111}\sigma_{11} + d_{322}\sigma_{22} + d_{333}\sigma_{33})$$

$$\pm P_2 = \pm d_{222}\sigma_{23}$$

$$\pm P_3 = \pm d_{131}\sigma_{31}.$$ 

A free-energy difference is then generated between the domains by the simultaneous application of a suitable electric field. Including all the polarization terms above and considering the application of the general electric field $E = E_1 + E_2 + E_3$,

$$\Delta G = 2[(d_{111}\sigma_{11} + d_{322}\sigma_{22} + d_{333}\sigma_{33})F_3 + d_{222}\sigma_{23}F_2 + d_{131}\sigma_{31}F_1].$$

The form of the above expression for $\Delta G$ suggests that, in principle, KTP is also a ferroelastoelectric. Experiments need to be undertaken in order to establish which, if any, of the electric field/stress combinations is the most energetically favourable for the detwinning process in KTP.

We would like to thank Dr B. E. Watts for growing the KTP crystal, Dr A. R. Renshaw for useful discussions about the HAUP measurements, F. Wondre and A. Fitzmaurice for alignment of the crystal and G. Read for polishing the samples. We would like to acknowledge the support of the Science and Engineering Research Council and AMG also acknowledges the support of the Optoelectronics Research Centre, Southampton University, England. We would also like to thank British Telecom Research Laboratories, Martlesham Heath, Ipswich, England.
References