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## A Comparative Structural Study of a Flux-Grown Crystal of $K_{0.86}Rb_{0.14}TiOPO_4$ and an Ion-Exchanged Crystal of $K_{0.84}Rb_{0.16}TiOPO_4$

BY P. A. THOMAS

*Department of Physics, University of Warwick, Coventry CV4 7AL, England*

R. DUHLEV

*Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, England*

AND S. J. TEAT

*Department of Physics, University of Warwick, Coventry CV4 7AL, England*

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### Abstract

The crystal structures of a flux-grown crystal,  $K_{0.86}Rb_{0.14}TiOPO_4$ , and an Rb/Ba ion-exchanged  $KTiOPO_4$  crystal,  $K_{0.84}Rb_{0.16}TiOPO_4$ , are refined

and compared. Both crystals are isostructural with potassium titanyl phosphate,  $KTiOPO_4$ . In both crystals, Rb substitutes for K only on the K(2) site with the crystallographically distinct K(1) site being solely occupied by K. However, in the ion-exchanged

crystal, a residual electron density ( $2.6 \text{ e } \text{Å}^{-3}$ ) is found on a site that is normally a void in the  $\text{KTiOPO}_4$  structure and that has been suggested as an essential site in the process of domain inversion by ion exchange in  $\text{KTiOPO}_4$ . This residual density was refined as part-occupancy of the site by either Rb or Ba, and this gave occupancies of 0.038 (3) or 0.027 (2), respectively. The results of these structural analyses are discussed in the context of structural models for domain inversion by ion exchange. Crystal data for potassium rubidium titanyl phosphates at room temperature: (1)  $\text{K}_{0.86}\text{Rb}_{0.14}\text{TiOPO}_4$ ,  $M_r = 204.44$ , orthorhombic,  $\text{Pna}2_1$ ,  $a = 12.8500$  (8),  $b = 6.4136$  (3),  $c = 10.5912$  (7) Å,  $Z = 8$ ,  $R = 0.021$  for 2584 reflections with  $I > 3\sigma(I)$ . (2)  $\text{K}_{0.84}\text{Rb}_{0.16}\text{TiOPO}_4$ ,  $M_r = 205.34$ , orthorhombic,  $\text{Pna}2_1$ ,  $a = 12.858$  (3),  $b = 6.4125$  (7),  $c = 10.592$  (1) Å,  $Z = 8$ ,  $R = 0.032$  for 1576 unique reflections with  $I > 1.2\sigma(I)$ .

## 1. Introduction

Optical waveguides can be fabricated in the non-linear optical crystal  $\text{KTiOPO}_4$  (KTP) by ion exchange of potassium by rubidium (Bierlein, Ferretti, Brixner & Hsu, 1987) or other more polarizable ions. It has also been observed that the addition of barium to the ion-exchange melt can lead to the formation of a structure that is inverted with respect to that of the original  $\text{KTiOPO}_4$  substrate (van der Poel, Bierlein, Brown & Colak, 1990). This means that the sense of the polar  $c$ -axis in the ion-exchanged regions is reversed. Thus, by performing ion exchange through a suitably patterned mask it is possible to form a periodically inverted structure. So-called periodically poled waveguides are of great use in optical devices where they can circumvent the problem of birefringent phase-matching and allow the efficient *quasi*-phase-matched frequency doubling of any wavelength of choice within the transparency range of the crystal, an idea first suggested by Armstrong, Bloembergen, Ducuing & Pershan (1962).

The structural mechanism by which domain inversion occurs in KTP is not currently understood, although prototype devices based on this technique are already available. A model has been proposed for domain inversion of ion exchange (Thomas & Glazer, 1991) based on studies of the crystal structures of the KTP family and naturally occurring domains in KTP itself (Thomas, Tebbutt & Glazer, 1991). In order to check the validity of this model, a series of experimental investigations on  $\text{K}_x\text{Rb}_{1-x}\text{TiOPO}_4$  crystals produced by both ion exchange and conventional flux growth has been undertaken.

In this paper, the results of the structural studies on a flux-grown  $\text{K}_{0.86}\text{Rb}_{0.14}\text{TiOPO}_4$  crystal and  $\text{K}_{0.84}\text{Rb}_{0.16}\text{TiOPO}_4$  produced by ion exchange in a barium-containing melt are reported. These results are combined with information obtained by other methods and discussed in the context of the device applications of these crystals.

## 2. Experimental

### 2.1. Flux-grown crystal

$\text{K}_2\text{CO}_3$ ,  $\text{Rb}_2\text{CO}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{TiO}_2$  in the molar ratio 3:1:5.808:1.425 were mixed in a platinum crucible and heated to 1213 K. According to the solubility curve for  $\text{KTiOPO}_4$  in a  $\text{K}_6\text{P}_4\text{O}_{13}$  flux (Jacco, Loiacono, Jaso, Mizell & Greenberg, 1984), this starting composition was expected to produce  $\text{K}_x\text{Rb}_{1-x}\text{TiOPO}_4$  crystals with  $x \text{ ca } 0.25$  at around 1173 K. The mixture was soaked at 1273 K for 5 h and then cooled at  $5^\circ \text{ h}^{-1}$  until 923 K when the furnace was switched off and natural cooling allowed. Colourless transparent crystals were recovered by dissolution of the flux in boiling water. Many were found to show the typical KTP-like morphology and X-ray powder diffraction confirmed that the phase was isomorphous with KTP. A single crystal of suitable size and quality was selected for the structure determination.

### 2.2. Ion-exchanged crystal

A flux-grown KTP crystal was crushed to produce fragments of average dimensions  $\text{ca } 0.1 \times 0.1 \times 0.1$  mm suitable for X-ray structure determination. These were added to a mixture of 20 mol %  $\text{Ba}(\text{NO}_3)_2$  and 80 mol %  $\text{RbNO}_3$ , which had previously been fused. This was then heated to a temperature of 653 K and maintained for approximately 48 h. This composition and temperature were chosen because previous experiments had shown that ion-exchange to depths  $> 100 \mu\text{m}$  in a few hours would be obtained under these conditions. Therefore, it was expected that the fragments would exchange completely during the course of the treatment. Although domain inversion can be obtained in melts with as little as 2 mol % Ba present, a much higher concentration was chosen for two reasons: (1) because a higher Ba concentration speeds up the exchange and increases the exchange depth; (2) because it was hoped that a concentration of Ba large enough to detect in the structural analysis would be incorporated in the crystal.

After cooling and dissolving the melt, the fragments were recovered by filtration. Examination under the polarizing microscope proved many of them still extinguished sharply and had the appear-

ance of good single crystals suitable for X-ray analysis. However, these same crystals were frequently found to give split spots on transmission Laue photographs. Eventually, a fragment suitable for structure determination was found and used for the analysis.

As an independent test of the composition, an (001) KTP plate was immersed in the same ion-exchange melt for 14 h, after which energy-dispersive X-ray analysis was undertaken. This revealed that the incorporation of Rb in the crystal was highly inhomogeneous, although the average composition of an exchanged layer of approximately 100  $\mu\text{m}$  in depth was K<sub>0.85</sub>Rb<sub>0.15</sub>TiOPO<sub>4</sub>.

### 2.3. Data collection and refinement

The details of data collection and refinement are given in Table 1.\* In both refinements, the scattering factors for neutral atoms and the anomalous scattering factors appropriate to Mo  $K\alpha$  radiation were taken from *International Tables for Crystallography* (1974, Vol. IV). The floating origin in space group  $Pna2_1$  was handled *via* the constraint  $\sum \Delta z = 0$  within full-matrix least squares refinement in *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). The occupancies on the  $M(1)$  and  $M(2)$  sites were initially constrained to unity. Refinements were undertaken assuming the presence of K only on the  $M(1)$  and  $M(2)$  sites, after which difference Fourier maps were generated. These revealed that excess density was present on the  $M(2)$  site. By considering the lengths of the  $a$  and  $b$  lattice parameters compared with those of the  $\text{KTiOPO}_4$  and  $\text{RbTiOPO}_4$  end members, the Rb concentration in both crystals was estimated to be approximately 20%. Therefore, the  $M(2)$  site was refined as a shared site with initial values of the occupancies being 0.2 for Rb and 0.8 for K. The positional and thermal parameters for the atoms on the shared site were made equivalent in the refinement.

Full anisotropic refinement with both data sets was undertaken and after convergence was reached, difference Fourier maps were generated, which for the flux-grown crystal gave  $\Delta\rho_{\text{max}} = 1.24 \text{ e } \text{\AA}^{-3}$ , a typical residual density for refinements of these structures. However, after repeated refinements with different weighting schemes and  $I:\sigma(I)$  acceptance ratios,  $\Delta\rho_{\text{max}}$  for the ion-exchanged crystal took values between 2.6 and  $3.5 \text{ e } \text{\AA}^{-3}$ , a larger residual density than that typically observed. This peak in the electron density was of a good shape and signifi-

Table 1. *Details of data collection and refinement*

Compound	K <sub>0.86</sub> Rb <sub>0.14</sub> TiOPO <sub>5</sub> (flux grown)	K <sub>0.84</sub> Rb <sub>0.16</sub> TiOPO <sub>4</sub> (ion exchanged)
Temperature (K)		293 K
Diffractometer		Stoe Stadi-4
Radiation		Mo $K\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )
Crystal system		Orthorhombic
Space group		$Pna2_1$
Range of data collection		2 unique sets, $3 < 2\theta < 70^\circ$ maximum $h = 18, k = 9, l = 14$
Scan type		$\omega$ - $2\theta$
Step width ( $^\circ$ )		$\Delta\omega = 0.03$
Minimum & maximum time per step (s)		0.5 & 2
Intensity control		3 reflections, 50 m
Data reduction		Stoe <i>REDU4</i> and <i>CRYSTALS</i> *
Initial model		KTiOPO <sub>4</sub>
Refinement method		<i>FMLS</i> on <i>F(CRYSTALS)</i>
$M_r$	204.44	205.34
Crystal colour	Colourless crystal	Colourless fragment.
Crystal size (mm)	$0.19 \times 0.20 \times 0.23$	$0.16 \times 0.12 \times 0.06$
$D_x$ ( $\text{Mg m}^{-3}$ )	3.11	3.12
$\mu$ ( $\text{mm}^{-1}$ )	4.74	5.06
Cell parameters ( $\text{\AA}$ )	$a = 12.8500$ (8) $b = 6.4136$ (3) $c = 10.5912$ (7)	$a = 12.858$ (3) $b = 6.4125$ (7) $c = 10.592$ (1)
Cell volume ( $\text{\AA}^3$ )	$V = 872.9$ (2)	$V = 873.3$ (4)
$Z$	8	8
Lattice parameters determination	142 reflections ( $30 < 2\theta < 48^\circ$ )	28 reflections ( $25 < 2\theta < 30^\circ$ )
Number of reflections measured	8910	6842
Number of reflections used for the refinement	2584 unique, $I > 3.0\sigma(I)$	1576 unique, $I > 1.2\sigma(I)$
Number of parameters refined	148	153
$R_{\text{int}}$	0.024	0.044
Absorption correction	Empirical ( $\varphi$ -scans of 20 reflections)	Empirical ( $\varphi$ -scans of 7 reflections)
Minimum, maximum transmission	0.3521, 0.4780	0.5186, 0.6581
Weighting scheme	$w^{-1} = \sigma(F)^2$ $+ 0.00129F^2$	'robust-resistant' (Tukey, 1974), 4 parameters
Number of reflections used	2594 unique, $I > 3.0\sigma(I)$	1576 unique, $I > 1.2\sigma(I)$
Final r.m.s. shift/e.s.d.	0.00009	0.00018
Maximum shift/e.s.d.	0.001	0.002
$R(wR)$	0.021 (0.028)	0.032 (0.025)
Extinction parameter†	101 (4)	19 (1)
Flack enantiopole parameter‡	0.84 (1)	0.04 (3)
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ ( $\text{e } \text{\AA}^{-3}$ )	-0.38, +1.24	-1.12, +0.90

\* Watkin, Carruthers & Betteridge (1985).

† Larson (1970).

‡ Flack (1983).

cantly higher than any other residual density [the next peak in the map was  $1.2 \text{ e } \text{\AA}^{-3}$  at  $0.67 \text{ \AA}$  from O(4)]. In particular, the location of this peak was of significance because it lay close to the coordinates of the  $h(1)$  'hole site' in the structure, as identified in the domain-inversion model of Thomas & Glazer (1991).

Since the possible occupancy of the  $h(1)$  site is an important element of the domain-inversion theory, atomic occupancy at the coordinates of the peak was included explicitly in the calculated model. In separate refinements, this site was assumed to be occu-

\* Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: HA0130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{\text{eq}}$	Site occupancy
(1) Flux-grown $\text{K}_{0.86}\text{Rb}_{0.14}\text{TiOPO}_4$					
K(1)	0.37846 (5)	0.77913 (9)	0.68696 (7)	0.0179 (3)	
(K,Rb)(2)	0.10408 (3)	0.69029 (8)	0.93056 (6)	0.0193 (2)	{ K 0.714 (3) Rb 0.286 (3)
Ti(1)	0.37304 (3)	0.49738 (7)	0.00006 (6)	0.0062 (1)	
Ti(2)	0.24767 (4)	0.26711 (6)	0.74747 (5)	0.0064 (1)	
P(1)	0.49886 (5)	0.33558 (9)	0.73995 (7)	0.0064 (2)	
P(2)	0.18111 (4)	0.50000 (11)	0.48726 (7)	0.0067 (2)	
O(1)	0.4860 (2)	0.4837 (3)	0.8508 (2)	0.0106 (8)	
O(2)	0.5111 (2)	0.4666 (4)	0.6180 (2)	0.0105 (8)	
O(3)	0.4019 (1)	0.1977 (3)	0.7194 (2)	0.0101 (8)	
O(4)	0.5946 (1)	0.1939 (3)	0.7582 (2)	0.0093 (7)	
O(5)	0.1136 (1)	0.3076 (4)	0.4584 (2)	0.0100 (8)	
O(6)	0.1115 (2)	0.6878 (3)	0.5136 (2)	0.0114 (8)	
O(7)	0.2522 (2)	0.5387 (3)	0.3712 (2)	0.0100 (8)	
O(8)	0.2536 (2)	0.4587 (3)	0.6000 (2)	0.0107 (7)	
O(9)	0.2234 (2)	0.9629 (3)	0.3554 (2)	0.0087 (7)	
O(10)	0.2236 (2)	0.0391 (4)	0.6094 (2)	0.0101 (8)	
(2) ion-exchanged $\text{K}_{0.84}\text{Rb}_{0.16}\text{TiOPO}_4$					
K(1)	0.3790 (1)	0.7796 (2)	0.6871 (2)	0.0210 (7)	
(K,Rb)(2)	0.1035 (1)	0.6877 (2)	0.9312 (1)	0.0217 (6)	{ K 0.962 (3) K 0.718 (7) Rb 0.282 (7)
Rb(3)	0.099 (2)	0.344 (3)	0.041 (1)	0.010 (5)	Rb 0.038 (3)
Ti(1)	0.37280 (7)	0.4978 (2)	-0.0003 (2)	0.0056 (4)	
Ti(2)	0.2480 (1)	0.2671 (2)	0.7467 (2)	0.0063 (3)	
P(1)	0.4992 (2)	0.3363 (2)	0.7390 (2)	0.0065 (6)	
P(2)	0.1814 (1)	0.4992 (3)	0.4869 (2)	0.0068 (5)	
O(1)	0.4871 (4)	0.4838 (9)	0.8512 (4)	0.011 (2)	
O(2)	0.5114 (4)	0.4670 (9)	0.6176 (3)	0.014 (2)	
O(3)	0.4016 (4)	0.1985 (7)	0.7193 (4)	0.010 (2)	
O(4)	0.5953 (3)	0.1951 (7)	0.7582 (5)	0.009 (2)	
O(5)	0.1124 (4)	0.3089 (8)	0.4583 (4)	0.010 (2)	
O(6)	0.1122 (4)	0.6887 (7)	0.5122 (5)	0.012 (2)	
O(7)	0.2529 (5)	0.5395 (8)	0.3710 (4)	0.011 (2)	
O(8)	0.2539 (4)	0.4616 (8)	0.5993 (4)	0.010 (2)	
O(9)	0.2242 (4)	0.9625 (7)	0.3567 (4)	0.009 (2)	
O(10)	0.2244 (4)	0.0391 (9)	0.6082 (4)	0.011 (2)	

pied by Rb or Ba or K. In each case, the occupancy, coordinates and anisotropic temperature factors of the atom on this site were allowed to refine together with all the other parameters. The occupancies on the  $M(1)$  and  $M(2)$  sites were allowed to deviate from unity to preserve the charge balance. Anisotropic refinements were possible for partial occupancy of the site by Rb or Ba with occupancies of 0.038 (3) and 0.027 (2), respectively. However, since the convergence of the anisotropic temperature factors was poor in both cases, only the isotropic temperature factor for the atom on this site is taken to be of physical significance (Table 2). Note that anisotropic refinement for partial occupancy of the site by K was not possible.

### 3. Discussion

Both crystals are isostructural with  $\text{KTiOPO}_4$  (Tordjman, Masse & Guitel, 1974). The KTP struc-

ture consists of a three-dimensional network of corner-shared  $\text{TiO}_6$  octahedra and  $\text{PO}_4$  tetrahedra with the K atoms occupying the large cavities enclosed by the oxygen framework. The unit cell contains two asymmetric units and consequently there are two crystallographically distinct sites for each of K, Ti and P, and ten for O. In these mixed crystals, the Rb atoms are located only on the larger  $M(2)$  sites in the framework. As in other KTP analogues, the  $\text{TiO}_6$  octahedra are strongly distorted, with one short Ti—O bond per octahedron [Ti(1)—O(10) and Ti(2)—O(9); Table 3] and O—Ti—O angles within the range  $82$ – $100^\circ$  and  $166$ – $176^\circ$ . The angular distortion of the environment around Ti(2) is slightly higher than that around Ti(1). The structure of the ion-exchanged crystal is represented in Fig. 1.

It has previously been reported that Rb preferentially occupies the  $M(2)$  site in  $\text{K}_{0.5}\text{Rb}_{0.5}\text{TiOPO}_4$  (Crennell, Cheetham, Kaduk & Jarman, 1991) and  $\text{K}_{0.535}\text{Rb}_{0.465}\text{TiOPO}_4$  (Thomas, Mayo & Watts, 1992). This study confirms the presence of Rb for the large  $M(2)$  site and shows that when the overall concentration of Rb is low, it does not substitute on the  $M(1)$  site at all. The site-preference is apparently independent of the method by which Rb is incorporated into the crystals. A similar phenomenon is also observed for Na incorporation in  $\text{K}_{0.42}\text{Na}_{0.58}\text{TiOPO}_4$  powder produced by ion exchange (Crennell, Morris, Cheetham & Jarman, 1992) and  $\text{K}_{0.5}\text{Na}_{0.5}\text{TiOPO}_4$  powder made by solid-state synthesis (Crennell, Owen, Grey, Cheetham, Kaduk & Jarman, 1991).

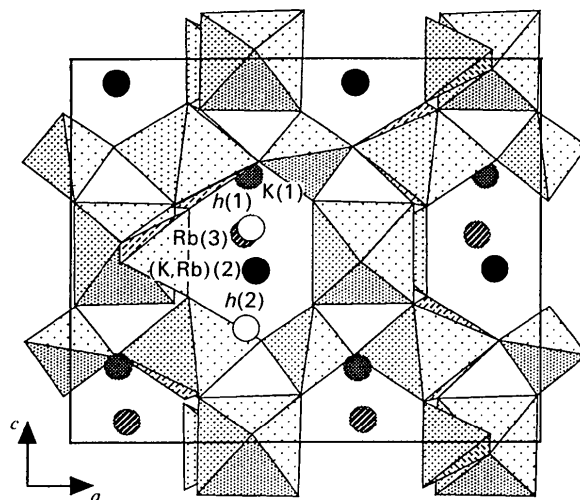


Fig. 1. A view of the structure of  $\text{K}_{0.84}\text{Rb}_{0.16}\text{TiOPO}_4$  along  $[010]$  showing the location of the hole sites,  $h(1)$  and  $h(2)$ , with respect to the K(1), (K,Rb)(2) and Rb(3) sites in a representative part of the unit cell. In Table 2, with respect to the positions listed, Rb(3) is at  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$  and (K,Rb)(2) is at  $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z$ .

Table 3. Bond lengths (Å) and selected angles (°) in K<sub>0.86</sub>Rb<sub>0.14</sub>TiOPO<sub>4</sub> (1) and K<sub>0.84</sub>Rb<sub>0.16</sub>TiOPO<sub>4</sub> (2)

The symmetry operators given refer to the O atoms, except for the two angles where they refer to Ti.

	(1)	(2)
<b>Ti(1)O<sub>6</sub> octahedron</b>		
Ti(1)—O(10 <sup>i</sup> )	1.719 (2)	1.719 (5)
Ti(1)—O(2 <sup>ii</sup> )	1.957 (2)	1.957 (5)
Ti(1)—O(9 <sup>iii</sup> )	1.983 (2)	1.974 (5)
Ti(1)—O(6 <sup>iiii</sup> )	2.001 (2)	1.996 (5)
Ti(1)—O(5 <sup>v</sup> )	2.044 (2)	2.051 (5)
Ti(1)—O(1 <sup>vi</sup> )	2.148 (2)	2.154 (5)
<b>Ti(2)O<sub>6</sub> octahedron</b>		
Ti(2)—O(9 <sup>vii</sup> )	1.738 (2)	1.748 (5)
Ti(2)—O(7 <sup>viii</sup> )	1.965 (2)	1.965 (4)
Ti(2)—O(4 <sup>ix</sup> )	1.986 (2)	1.983 (5)
Ti(2)—O(8)	1.990 (2)	2.000 (5)
Ti(2)—O(3)	2.052 (2)	2.044 (5)
Ti(2)—O(10)	2.091 (2)	2.094 (5)
Ti(1 <sup>vi</sup> )—O(9)—Ti(2 <sup>vii</sup> )	136.2 (1)	136.3 (3)
Ti(1 <sup>vi</sup> )—O(10)—Ti(2)	133.4 (1)	133.0 (3)
<b>P(1)O<sub>4</sub> tetrahedron</b>		
P(1)—O(1)	1.519 (2)	1.527 (5)
P(1)—O(4)	1.542 (2)	1.545 (5)
P(1)—O(3)	1.544 (2)	1.549 (5)
P(1)—O(2)	1.549 (2)	1.543 (4)
<b>P(2)O<sub>4</sub> tetrahedron</b>		
P(2)—O(6)	1.526 (2)	1.530 (5)
P(2)—O(8)	1.537 (2)	1.531 (5)
P(2)—O(5)	1.538 (2)	1.539 (5)
P(2)—O(7)	1.552 (2)	1.556 (5)
<b>Cage around M(1)</b>		
M(1)—O(3 <sup>xiii</sup> )	2.723 (2)	2.724 (5)
M(1)—O(10 <sup>xiiii</sup> )	2.723 (2)	2.723 (6)
M(1)—O(2)	2.731 (2)	2.731 (6)
M(1)—O(8)	2.765 (2)	2.759 (5)
M(1)—O(5 <sup>xv</sup> )	2.887 (2)	2.881 (5)
M(1)—O(1)	2.918 (2)	2.924 (5)
M(1)—O(9 <sup>xvi</sup> )	3.002 (2)	3.021 (5)
M(1)—O(7 <sup>xvii</sup> )	3.065 (2)	3.074 (5)
<b>Cage around M(2)</b>		
M(2)—O(1 <sup>xviii</sup> )	2.718 (2)	2.720 (5)
M(2)—O(9 <sup>xix</sup> )	2.770 (2)	2.761 (5)
M(2)—O(5 <sup>xx</sup> )	2.813 (2)	2.790 (5)
M(2)—O(7 <sup>xxi</sup> )	2.966 (2)	2.985 (5)
M(2)—O(2 <sup>xxii</sup> )	3.045 (2)	3.047 (5)
M(2)—O(3 <sup>xxiii</sup> )	3.060 (2)	3.053 (4)
M(2)—O(4 <sup>xxiv</sup> )	3.069 (2)	3.065 (5)
M(2)—O(10 <sup>xxv</sup> )	3.071 (2)	3.052 (5)
M(2)—O(8 <sup>xxvi</sup> )	3.087 (2)	3.101 (5)
<b>Cage around Rb(3)</b>		
Rb(3)—O(10 <sup>i</sup> )		2.69 (2)
Rb(3)—O(6 <sup>ii</sup> )		2.74 (2)
Rb(3)—O(2 <sup>iii</sup> )		2.92 (2)
Rb(3)—O(3 <sup>iiii</sup> )		2.95 (2)
Rb(3)—O(4 <sup>v</sup> )		3.01 (2)
Rb(3)—O(9 <sup>vi</sup> )		3.09 (2)
Rb(3)—O(8 <sup>vii</sup> )		3.16 (2)
Rb(3)—O(1 <sup>viii</sup> )		3.25 (2)
Rb(3)—O(7 <sup>ix</sup> )		3.27 (2)

Symmetry codes: (i)  $-x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, z - \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$ ; (iv)  $x, y, z - 1$ ; (v)  $-x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$ ; (vi)  $x - \frac{1}{2}, -y + \frac{1}{2}, z$ ; (vii)  $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$ ; (viii)  $x, y + 1, z$ ; (ix)  $x - \frac{1}{2}, -y + \frac{1}{2}, z$ ; (x)  $-x, -y + 1, z + \frac{1}{2}$ ; (xi)  $-x, -y + 1, z - \frac{1}{2}$ ; (xii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - 1$ .

The compositional and structural similarities prove that it is possible to produce an equilibrium structure by the ion-exchange route. These results suggest that an ion-exchange temperature of 653 K is sufficient to make the K atoms mobile, effect ion-exchange throughout the bulk of the crystal and to distribute the Rb atoms over the available sites in accordance with the usual site-preference.

### 3.1. Prototypic phase and domain inversion

The room-temperature structure of KTP is derived from the prototypic KTiOPO<sub>4</sub> phase with *Pnan* symmetry (Harrison, Gier, Stucky & Schultz, 1990; Thomas, Glazer & Watts, 1990). The sites *M*(1) and *M*(2) (at  $x, y - 1, z$ ) of the room-temperature structure are related by a pseudo-inversion centre at Ti(2), whereas in the high-temperature structure there is a crystallographic inversion centre at Ti(2). In addition to the two occupied *M*<sup>1</sup> sites of the room-temperature structure, there are two voids that closely resemble the *M*<sup>1</sup> sites. These were described as 'hole' sites [*h*(1) and *h*(2)] by Thomas & Glazer (1991) and they are pseudo-symmetrically related to the *M*(2) and *M*(1) sites, respectively, as shown in Fig. 1. *h*(1) and *h*(2) are considered to be alternative, but normally unoccupied *M*<sup>1</sup> sites in the structure. The high-temperature positions for the *M*<sup>1</sup> atoms lie halfway between the room-temperature *M*<sup>1</sup> positions and their associated hole sites, that is, halfway between *M*(1) and *h*(1) and between *M*(2) and *h*(2). On passing from the high-temperature to the room-temperature structure, the *M*<sup>1</sup> atoms move to produce two occupied sites, *M*(1) and *M*(2), and a corresponding pair of hole sites. The sense of these displacements defines the structural polarity of the crystal, the positive sense being identified with the direction of the displacement of the *M*<sup>1</sup> atoms.

In the experiment on the ion-exchanged fragment, residual electron density was found 1.66 Å from the K(1) site at the end of the refinement, at the position  $x = 0.401, y = 0.842, z = 0.537$ . This is close to *h*(1) at 0.397, 0.812, 0.569. From the refinements, it appears that this density corresponds to a partial occupation of the normally empty *h*(1) site by either or both of the metal cations in the ion-exchange melt. This is in agreement with the predictions of the model for domain inversion by ion exchange (Thomas & Glazer, 1991), in which occupation of the hole sites by incoming atoms from the ion-exchange melt was suggested to be the principal mechanism for driving the structure to take up the inverted configuration.

By contrast in the flux-grown crystal, no extra density appears in this position on refinement. Neither has any extra density been seen on the corresponding positions in any structural refinements

of other KTP analogues (about 20 different analogues in all including eight different members of the  $\text{Rb}_x\text{K}_{1-x}\text{TiOPO}_4$  series). Therefore, in our experience, it is a unique feature of the ion-exchanged crystal.

This experiment has shown that the  $h(1)$  site does become at least partially occupied as a result of the ion-exchange process. It is physically sensible that  $h(1)$  is occupied because this is the larger of the two sites [it is pseudo-symmetrically related to the larger  $M(2)$  site] and would be preferred to  $h(2)$  by Rb. Therefore, a plausible site-selectivity is seen here. It would have been preferable to have seen a larger occupancy on  $h(1)$ ; the indication from this experiment is that only a small percentage of the crystal has undergone the domain-inversion process. Normally, for optical device purposes, domain inversion is induced only in a shallow surface layer (ca 2–5  $\mu\text{m}$ ). The crystals are only in the melt for short times (less than 1 h). Therefore, the 'equilibrium structure' of the fragment used here, obtained after 48 h in the melt, cannot be compared directly with a device crystal. Further X-ray studies have been undertaken on a device crystal working in reflection from an ion-exchanged layer (Thomas *et al.*, 1994), but the details of the structure of the waveguiding layer have not been extracted from the data as yet.

#### 4. Concluding remarks

The results of these studies and those of Crennel *et al.* demonstrate that the structures of ion-exchanged crystals and those produced by conventional routes are almost identical. However, this does not mean that the crystals are of comparable quality. During this study, it was difficult to find an ion-exchanged crystal of suitable quality for single-crystal X-ray diffraction; many fragments were strained or cracked as a result of the processing. The diffraction peak profiles indicated multiple contributions, possibly resulting from an exaggerated mosaic structure or regions of different compositions. Although the scattering from the fragment was rather weak, both because of its small size and quality, it was still possible to collect data out to  $60^\circ$  in  $2\theta$  and to undertake full anisotropic refinement. The composition obtained from the structural refinement was in agreement with the independent findings of the energy-dispersive X-ray analysis.

These studies raise some questions about the quality of ion-exchanged crystals and their use in optical

devices. Diffraction studies of an Rb/Ba ion-exchanged waveguide of the type that would be used in a device has revealed that the Rb-substituted layer is highly strained compared with its KTP substrate. The presence of strain may be a key requirement in producing the refractive index increase required to form a waveguiding layer. Further studies of these waveguides are currently in progress.

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