

## Crystal Structures of $\text{RbTiOAsO}_4$ , $\text{KTiO}(\text{P}_{0.58}, \text{As}_{0.42})\text{O}_4$ , $\text{RbTiOPO}_4$ and $(\text{Rb}_{0.465}, \text{K}_{0.535})\text{TiOPO}_4$ , and Analysis of Pseudosymmetry in Crystals of the $\text{KTiOPO}_4$ Family

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### Abstract

The crystal structures of  $\text{RbTiOAsO}_4$ ,  $\text{KTiO}(\text{P}_{0.58}, \text{As}_{0.42})\text{O}_4$ ,  $\text{RbTiOPO}_4$  and  $(\text{Rb}_{0.465}, \text{K}_{0.535})\text{TiOPO}_4$ , all of which are orthorhombic (space group  $Pna2_1$ ) and isostructural with  $\text{KTiOPO}_4$ , have been determined from single-crystal X-ray diffraction data and refined to  $R$  factors between 0.027 and 0.040. The results are used for an analysis of structural trends in crystals of the  $\text{KTiOPO}_4$  family by comparison of the room-temperature structures with that proposed for the high-temperature prototypic phase (space group  $Pnan$ ).

### Introduction

$\text{KTiOPO}_4$  (KTP) is a well-known nonlinear optical material which is extensively used for frequency doubling of Nd:YAG lasers. Since the crystal structure of KTP was first reported by Tordjman, Masse & Guitel (1974), many isostructural analogues have been synthesized [an extensive list is found in the review paper by Stucky, Phillips & Gier (1989)] and, therefore, this family of compounds now forms a particularly advantageous series for the investigation of the relationship between crystal structure and optical properties.

As a continuation of our investigation of crystals of the KTP series, the crystal structures of four compositional analogues  $\text{RbTiOAsO}_4$  (RTA),  $\text{KTiO}(\text{P}_{0.58}, \text{As}_{0.42})\text{O}_4$  (KTAP),  $\text{RbTiOPO}_4$  [RTP, first identified by Masse & Grenier (1971)] and  $(\text{Rb}_{0.465}, \text{K}_{0.535})\text{TiOPO}_4$  (RKTP) are reported here. KTAP and RKTP are of particular interest because they represent the first reported single-crystal investigations of mixed analogues *i.e.* crystals in which there are shared (As,P) and (K,Rb) sites. An earlier

study of the weakly nonlinear optical and pseudo-centrosymmetric crystal  $\text{KSnOPO}_4$  (Thomas, Glazer & Watts, 1990, hereafter TGW) indicated that the structures of KTP-type crystals show pseudosymmetry which is consistent with the derivation of the room-temperature structure from a high-temperature prototype structure of symmetry  $Pnan$ . The program *MISSYM* (Le Page, 1988) was used to analyse the degree of pseudosymmetry in  $\text{KSnOPO}_4$  and KTP. This approach is extended here to all of the analogues of KTP for which suitable structural data are available (11 compounds in all). This method of quantifying the distortion of the whole structure from the centrosymmetric prototype (the natural zero for the nonlinear optical properties) is discussed in relation to the physical properties exhibited by these compounds.

### Experimental

#### *Preparation of samples*

Crystals of RTA, KTAP, RTP and RKTP were grown by spontaneous nucleation from the flux by the method normally used for the growth of KTP (Jacco, Loiacono, Jago, Mizell & Greenberg, 1984) with suitable modifications to the starting composition. Each of the phases was identified using X-ray powder diffraction and all of the compounds were found to be isomorphous with KTP. A small piece was cut from each of the crystals for single-crystal X-ray structure determination. For the most highly absorbing crystal RTA, a fragment was ground in order to obtain a more regularly shaped crystal. The quality of each of the small crystals obtained was checked prior to automatic data collection by polarized light microscopy and X-ray photographs.

Table 1. *Details of data collection and refinement*

	RbTiOAsO <sub>4</sub> (RTA)	KTiO(P <sub>0.58</sub> ,As <sub>0.42</sub> )O <sub>4</sub> (KTAP)	RbTiOPO <sub>4</sub> (RTP)	(K <sub>0.535</sub> ,Rb <sub>0.465</sub> )TiOPO <sub>4</sub> (RKTP)
Crystal colour, shape and size	Yellow disc, max. and min. dimensions 0.133 and 0.076 mm	Light brown fragment, max. dimension 0.16 mm	Colourless transparent plate-like fragment, 0.22 × 0.14 × 0.07 mm	Pale straw-coloured cuboid, 0.15 × 0.23 × 0.09 mm
Linear absorption coefficient (cm <sup>-1</sup> )	197.5	60.7	137.53	79.31
Diffractometer	Stoe Stadi-4	Stoe Stadi-4	Stoe Stadi-4	Stoe Stadi-4
Radiation	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
Scan	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
Lattice parameters (Å)	$a = 13.264$ (2), $b = 6.682$ (2), $c = 10.7697$ (9)	$a = 12.962$ (2), $b = 6.479$ (2), $c = 10.691$ (3)	$a = 12.974$ (2), $b = 6.494$ (3), $c = 10.564$ (6)	$a = 12.908$ (6), $b = 6.436$ (3), $c = 10.597$ (5)
Ranges of $h, k, l$	-21 to 21, 0 to 11, 0 to 17	2 unique sets 3 < 2 $\theta$ < 70, maximum $h = 20, k = 10, l = 17$	2 unique sets 3 < 2 $\theta$ < 70, maximum $h = 21, k = 10, l = 17$	-21 to 21, -10 to 10, -17 to 17
Intensity control	Every hour	Every hour	Every hour	Every hour
Orientation control	Every 4 h or $\Delta(I) > 10\%$ or offcentre by > 0.13	Every 2 h or $\Delta(I) > 10\%$ or offcentre by > 0.25	Every hour or $\Delta(I) > 10\%$ or offcentre by > 0.25	Every 3 h or $\Delta(I) > 10\%$ or offcentre by > 0.11
No. of reflections measured	9313	7857	8766	9101
No. of reflections used for refinement	2948, $I > 2\sigma(I)$	3540, $I > 3\sigma(I)$	2365, $I > 3.5\sigma(I)$	3110, $I > 3\sigma(I)$
$R_{int}$	0.042	0.039	0.037	0.030
Absorption correction	Empirical $\psi$ scans	Empirical $\psi$ scans	Empirical $\psi$ scans	Empirical $\psi$ scans
Min. and max. transmission	0.1941, 0.2882	0.1627, 0.3206	0.0562, 0.1359	0.2160, 0.3231
Data reduction	Stoe REDU4 and CRYSTALS*	Stoe REDU4 and CRYSTALS*	Stoe REDU4 and CRYSTALS*	Stoe REDU4 and CRYSTALS*
Model structure	KTiOAsO <sub>4</sub>	KTiOPO <sub>4</sub>	KTiOPO <sub>4</sub>	KTiOPO <sub>4</sub>
Refinement method†	FMLS (CRYSTALS)*	FMLS (CRYSTALS)*	FMLS (CRYSTALS)*	FMLS (CRYSTALS)*
Weighting scheme	1 $\sigma^2$	1 $\sigma^2$	1 $\sigma^2$	1 $\sigma^2$
No. of parameters	147	149	147	149
$R$ ( $wR$ )	0.040 (0.028)	0.028 (0.031)	0.027 (0.024)	0.026 (0.028)
Extinction parameter‡	33.9 (6)	124 (2)	85 (1)	97 (1)
Rogers polarity parameter or Flack parameter	0.44 (1)	0.99 (4)	1.09 (3)	0.53 (2)
$\Delta\rho_{min}, \Delta\rho_{max}$ (e Å <sup>-3</sup> )	0.9, 1.6	1.2, 1.5	-1.9, 1.7	1.14, 1.04

\* Watkin, Carruthers &amp; Betteridge (1985).

† Full-matrix least-squares (FMLS) refinements were on structure factors ( $F$ 's) except that for KTAP which was on  $F^2$ 's.

‡ Larsen extinction parameter (Larsen, 1970).

### Data collections and refinements

The details of the data collections and refinements are summarized in Table 1.\*

(a) *RTA*. Many of the higher-angle data measured were weak and were rejected by the  $I > 3\sigma(I)$  criterion initially applied to the reflections. However, it was found that some of the oxygen anisotropic temperature factors were non-positive definite upon refinement. In order to increase the number of high-angle data, the acceptance criterion was opened to  $I > 2\sigma(I)$ . This allowed physically reasonable anisotropic refinement of all temperature factors to  $R = 0.040$  ( $wR = 0.028$ ). The Flack parameter (Flack, 1983) refined to 0.44 (1) indicating that the crystal was close to a 50:50 mixture of domains of opposite structural polarity. The isotropic extinction parameter refined to a lower value [33.9 (6)] than we have usually found for KTP-type crystals possibly reflecting the obviously poorer quality of the crystals grown.

(b) *KTAP*. Following the scale-factor refinement, the occupancies of the shared (P,As) sites were refined together with the (P,As)(1) and (P,As)(2)

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55039 (122 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0083]

structural coordinates which were treated as equivalent parameters. The occupancies of As(1) and As(2) were allowed to ride upon those of P(1) and P(2) subject to the constraint that the total occupancy on each of the shared sites should be 1. The occupancies quickly converged to values of 0.592 (9) for P(1) [0.408 (9) for As(1)] and 0.57 (1) for P(2) [0.43 (1) for As(2)] showing that As was distributed almost equally on the P(1) and P(2) sites. Isotropic refinement to  $R = 0.046$  ( $wR = 0.051$ ) was followed by anisotropic refinement (with the thermal parameters of site-sharing atoms equivalenced) to  $R = 0.028$  ( $wR = 0.031$ ). The Rogers polarity parameter (Rogers, 1981) refined to 0.99 (4) indicating that the crystal was of single structural polarity.

(c) *RTP*. Refinement of these data from the KTP starting model was straightforward. Isotropic refinement to  $R = 0.054$  ( $wR = 0.045$ ) was followed by anisotropic refinement to  $R = 0.027$  ( $wR = 0.024$ ). The crystal was again of a single structural polarity [polarity parameter 1.09 (3)].

(d) *RKTP*. At the beginning of the refinement, Rb and K were assumed to share equally both the K(1) and K(2) sites of the initial model (the KTP structure). Refinement of the positional parameters and occupancies of the K(1) and K(2) sites (treated in the same way as the shared sites in KTAP above) gave rapid convergence to the site occupancies 0.872 (4) for K(1) [0.128 (4) for Rb(1)] and 0.199 (4) for K(2)

Table 2. Atomic coordinates and thermal parameters

	x	y	z	$U_{eq}(\text{Å}^2)$
<b>KTiO(P<sub>0.58</sub>As<sub>0.42</sub>)O<sub>4</sub></b>				
Ti(1)	0.37381 (4)	0.5019 (1)	0.00036 (7)	0.0069 (1)
Ti(2)	0.24698 (5)	0.26967 (8)	0.74914 (7)	0.0070 (1)
(As,P)(1)	0.49832 (4)	0.33205 (7)	0.74080 (7)	0.0063 (1)
(As,P)(2)	0.18015 (4)	0.50396 (9)	0.48799 (7)	0.0083 (1)
K(1)	0.37724 (7)	0.7800 (1)	0.6868 (1)	0.0224 (3)
K(2)	0.10667 (7)	0.6991 (1)	0.9321 (1)	0.0230 (3)
O(1)	0.4872 (2)	0.4898 (5)	0.8525 (2)	0.0125 (8)
O(2)	0.5085 (2)	0.4647 (5)	0.6130 (3)	0.0124 (8)
O(3)	0.3975 (2)	0.1912 (4)	0.7200 (2)	0.0120 (8)
O(4)	0.5956 (2)	0.1852 (4)	0.7598 (2)	0.0133 (8)
O(7)(1)	0.2232 (2)	0.9621 (4)	0.3578 (2)	0.0095 (7)
O(7)(2)	0.2209 (2)	0.0468 (5)	0.6096 (2)	0.0096 (7)
O(5)	0.1103 (2)	0.3081 (4)	0.4569 (2)	0.0111 (7)
O(6)	0.1094 (2)	0.6972 (4)	0.5136 (2)	0.0128 (7)
O(7)	0.2562 (2)	0.5406 (5)	0.3698 (2)	0.0127 (8)
O(8)	0.2556 (2)	0.4615 (5)	0.6036 (2)	0.0135 (8)
<b>(Rb<sub>0.465</sub>K<sub>0.535</sub>)TiOPO<sub>4</sub></b>				
Ti(1)	0.37312 (4)	0.49367 (9)	0.00154 (7)	0.0051 (1)
Ti(2)	0.24924 (5)	0.26404 (9)	0.74734 (7)	0.0049 (1)
P(1)	0.49988 (7)	0.3344 (1)	0.7410 (1)	0.0053 (2)
P(2)	0.18169 (6)	0.4965 (1)	0.4882 (9)	0.0059 (2)
(K,Rb)(1)	0.37876 (6)	0.7770 (1)	0.68696 (8)	0.0194 (2)
(K,Rb)(2)	0.10318 (3)	0.68387 (7)	0.92873 (6)	0.0173 (1)
O(1)	0.4857 (2)	0.4786 (4)	0.8538 (2)	0.0092 (7)
O(2)	0.5118 (2)	0.4685 (4)	0.6195 (2)	0.0083 (8)
O(3)	0.4033 (2)	0.1965 (4)	0.7202 (2)	0.0072 (7)
O(4)	0.5965 (2)	0.1964 (4)	0.7578 (2)	0.0094 (7)
O(7)(1)	0.2215 (2)	0.9582 (4)	0.3563 (2)	0.0079 (7)
O(7)(2)	0.2242 (2)	0.0352 (4)	0.6092 (2)	0.0068 (7)
O(5)	0.1144 (2)	0.3042 (4)	0.4599 (2)	0.0086 (8)
O(6)	0.1125 (2)	0.6844 (4)	0.5144 (2)	0.0094 (7)
O(7)	0.2506 (2)	0.5365 (4)	0.3709 (2)	0.0090 (7)
O(8)	0.2548 (2)	0.4551 (4)	0.5992 (2)	0.0092 (7)
<b>RbTiOPO<sub>4</sub></b>				
Ti(1)	0.37284 (6)	0.4998 (1)	0.00081 (9)	0.0066 (3)
Ti(2)	0.24836 (7)	0.2678 (1)	0.74858 (9)	0.0067 (3)
P(1)	0.4997 (1)	0.3332 (2)	0.7422 (1)	0.0070 (4)
P(2)	0.18035 (9)	0.5014 (2)	0.4884 (1)	0.0079 (4)
Rb(1)	0.38504 (4)	0.78347 (8)	0.67465 (7)	0.0205 (2)
Rb(2)	0.10537 (4)	0.69184 (9)	0.92598 (8)	0.0176 (2)
O(1)	0.4862 (3)	0.4786 (7)	0.8535 (4)	0.008 (1)
O(2)	0.5141 (3)	0.4604 (7)	0.6199 (3)	0.009 (1)
O(3)	0.4024 (2)	0.2026 (5)	0.7207 (3)	0.009 (1)
O(4)	0.5949 (3)	0.1943 (6)	0.7616 (4)	0.011 (1)
O(7)(1)	0.2218 (3)	0.9607 (6)	0.3564 (4)	0.008 (1)
O(7)(2)	0.2226 (3)	0.0437 (7)	0.6097 (3)	0.009 (1)
O(5)	0.1141 (3)	0.3109 (6)	0.4583 (3)	0.009 (1)
O(6)	0.1128 (3)	0.6894 (6)	0.5174 (4)	0.012 (1)
O(7)	0.2505 (3)	0.5423 (6)	0.3729 (3)	0.009 (1)
O(8)	0.2522 (3)	0.4576 (6)	0.6010 (4)	0.011 (1)
<b>RbTiOAsO<sub>4</sub></b>				
Ti(1)	0.37382 (8)	0.5046 (2)	0.0015 (1)	
Ti(2)	0.2488 (1)	0.2693 (3)	0.7514 (1)	
As(1)	0.49960 (6)	0.32823 (9)	0.7444 (1)	
As(2)	0.17996 (5)	0.5049 (1)	0.4903 (1)	
Rb(1)	0.38303 (6)	0.7825 (1)	0.6729 (7)	
Rb(2)	0.10900 (5)	0.6938 (1)	0.9261 (1)	
O(1)	0.4875 (4)	0.4889 (9)	0.8614 (4)	
O(2)	0.9892 (4)	0.962 (1)	0.1107 (4)	
O(3)	0.3940 (4)	0.1878 (7)	0.7228 (4)	
O(4)	0.9000 (3)	0.6775 (7)	0.2469 (4)	
O(7)(1)	0.2169 (4)	0.0544 (5)	0.6103 (4)	
O(7)(2)	0.7188 (4)	0.5489 (9)	0.3620 (4)	
O(5)	0.1093 (4)	0.3032 (8)	0.4527 (4)	
O(6)	0.6073 (4)	0.7961 (8)	0.5222 (4)	
O(7)	0.2576 (4)	0.5445 (9)	0.3675 (4)	
O(8)	0.7576 (4)	0.0408 (9)	0.6098 (4)	

[0.801 (4) for Rb(2)]. Therefore, a marked preference for occupation of the K(2) site was shown by Rb. Isotropic refinement of all atoms led to  $R = 0.048$  ( $wR = 0.048$ ) and anisotropic refinement to  $R = 0.026$  ( $wR = 0.028$ ). The Rogers polarity parameter refined to 0.53 (2) showing that the crystal was a mixture of domains of opposite structural polarity.

Table 3. Bond lengths (Å) in KTP, RKTP, RTP, KTAP, KTA and RTA

	KTP	RKTP	RTP	KTAP	KTA	RTA
<b>Ti(1)—O6 octahedron</b>						
Ti(1)—O(1)	2.150 (3)	2.138 (2)	2.146 (4)	2.160 (2)	2.138 (15)	2.135 (5)
Ti(1)—O(2)	1.958 (3)	1.956 (3)	1.950 (4)	1.955 (3)	1.947 (16)	1.949 (5)
Ti(1)—O(7)(1)	1.981 (3)	1.978 (2)	1.973 (4)	1.993 (2)	1.957 (16)	1.973 (5)
Ti(1)—O(7)(2)	1.716 (3)	1.717 (2)	1.714 (4)	1.719 (2)	1.735 (16)	1.717 (5)
Ti(1)—O(5)	2.043 (3)	2.052 (3)	2.076 (4)	2.048 (3)	2.002 (18)	2.075 (5)
Ti(1)—O(6)	1.987 (3)	2.003 (3)	2.032 (4)	1.991 (3)	2.004 (19)	2.037 (5)
<b>Ti(2)—O6 octahedron</b>						
Ti(2)—O(3)	2.044 (3)	2.056 (3)	2.063 (3)	2.040 (3)	2.024 (14)	2.026 (5)
Ti(2)—O(4)	1.981 (3)	1.989 (3)	2.011 (4)	1.987 (2)	1.989 (14)	2.011 (4)
Ti(2)—O(7)(1)	1.733 (3)	1.742 (2)	1.737 (4)	1.747 (3)	1.770 (19)	1.755 (5)
Ti(2)—O(7)(2)	2.092 (3)	2.102 (2)	2.094 (4)	2.103 (3)	2.097 (19)	2.133 (4)
Ti(2)—O(7)	1.964 (3)	1.963 (3)	1.967 (4)	1.967 (3)	1.941 (19)	1.962 (6)
Ti(2)—O(8)	1.990 (3)	1.994 (2)	1.989 (4)	1.994 (3)	1.983 (18)	1.993 (5)
<b>As,P(1)—O4 tetrahedron</b>						
P(1)—O(1)	1.518 (2)	1.523 (2)	1.518 (4)	1.579 (3)	1.630 (19)	1.663 (5)
P(1)—O(2)	1.548 (2)	1.559 (2)	1.544 (4)	1.620 (3)	1.720 (18)	1.699 (5)
P(1)—O(3)	1.544 (3)	1.547 (3)	1.538 (3)	1.609 (3)	1.714 (14)	1.701 (5)
P(1)—O(4)	1.541 (3)	1.542 (3)	1.543 (4)	1.593 (3)	1.656 (14)	1.684 (6)
<b>As,P(2)—O4 tetrahedron</b>						
P(2)—O(5)	1.535 (3)	1.541 (3)	1.538 (4)	1.594 (3)	1.694 (16)	1.691 (5)
P(2)—O(6)	1.528 (3)	1.528 (3)	1.533 (4)	1.575 (3)	1.635 (18)	1.678 (5)
P(2)—O(7)	1.548 (3)	1.551 (2)	1.545 (4)	1.620 (2)	1.704 (16)	1.698 (5)
P(2)—O(8)	1.537 (2)	1.531 (3)	1.538 (4)	1.600 (2)	1.679 (18)	1.676 (5)
<b>M(1)—O cage</b>						
M(1)—O(1)	2.894 (3)	2.952 (3)	3.036 (4)	2.951 (3)	2.981*	3.145 (5)
M(1)—O(2)	2.738 (3)	2.720 (3)	2.747 (4)	2.773 (3)	2.771*	2.808 (6)
M(1)—O(3)	2.712 (3)	2.740 (3)	2.774 (3)	2.701 (3)	2.653*	2.765 (5)
M(1)—O(7)(1)	2.996 (3)	3.017 (3)	3.162 (4)	3.046 (3)	3.098*	3.297 (5)
M(1)—O(7)(2)	2.723 (3)	2.724 (3)	2.786 (4)	2.788 (3)	2.872*	2.935 (5)
M(1)—O(5)	2.871 (3)	2.899 (3)	3.002 (4)	2.898 (2)	2.895*	3.017 (4)
M(1)—O(6)			3.395 (4)			3.390 (5)
M(1)—O(7)	3.057 (4)	3.062 (3)	3.210 (4)	3.109 (3)	3.154*	3.307 (5)
M(1)—O(8)	2.755 (3)	2.778 (3)	2.838 (4)	2.745 (3)	2.717*	2.811 (6)
<b>M(2)—O cage</b>						
M(2)—O(1)	2.677 (3)	2.765 (3)	2.749 (4)	2.681 (3)	2.691*	2.753 (6)
M(2)—O(2)	2.982 (3)	3.105 (3)	3.105 (4)	2.988 (3)	3.009*	3.109 (5)
M(2)—O(3)	3.045 (3)	3.091 (3)	3.117 (4)	3.079 (2)	3.128*	3.196 (4)
M(2)—O(4)	3.117 (4)	3.045 (3)	3.052 (4)	3.100 (3)	3.067*	3.030 (5)
M(2)—O(7)(1)	2.765 (3)	2.796 (3)	2.797 (4)	2.802 (3)	2.861*	2.885 (5)
M(2)—O(7)(2)	3.056 (2)	3.088 (3)	3.110 (4)	3.093 (3)	3.150*	3.183 (5)
M(2)—O(5)	2.806 (3)	2.829 (3)	2.870 (4)	2.826 (3)	2.848*	2.910 (5)
M(2)—O(7)	2.917 (3)	3.014 (3)	2.998 (4)	2.915 (3)	2.908*	3.002 (6)
M(2)—O(8)	3.047 (3)	3.109 (3)	3.132 (4)	3.072 (3)	3.117*	3.192 (5)

\* Standard deviations not supplied in the reference (El Brahimi & Durand, 1986).

## Discussion

The structural coordinates are given in Table 2. The bond lengths in the TiO<sub>6</sub> octahedra, the (P,As)O<sub>4</sub> tetrahedra and the (K,Rb)O<sub>8</sub> and (K,Rb)O<sub>9</sub> cages in the structure reported here are given in Table 3 together with those for the published structures of KTP (TGW) and KTiOAsO<sub>4</sub> (El Brahimi & Durand, 1986). The character of the Ti(1) octahedron changes very little across the range of compounds considered, apart from that in KTiOAsO<sub>4</sub> (KTA), for which the distortion [measured simply by the difference in the 'long' and 'short' Ti(1)—O(1) and Ti(1)—O(2) bonds] is significantly reduced. The Ti(1)O<sub>6</sub> group in KTAP resembles that in KTP more closely than that in KTA which appears to show anomalous features in comparison also with the rubidium analogue RTA. This anomaly is also found to a lesser extent

for the Ti(2)O<sub>6</sub> group in KTA and is the subject of further investigation.

The PO<sub>4</sub> tetrahedra change very little upon substitution of Rb for K showing only a slight lengthening of the P—O distances. The AsO<sub>4</sub> tetrahedra in KTA and RTA are considerably more distorted than their PO<sub>4</sub> counterparts and the mixed tetrahedra in KTAP are intermediate in character between these two extremes. The sites occupied by K or Rb are larger in the more open arsenate frameworks and show a smooth variation in overall size over this range of compounds.

The structure refinement of RKTP shows that Rb has a clear preference for the K(2) site. This is consistent with the results of previous structural refinements of the mixed compounds (K<sub>0.5</sub>,Na<sub>0.5</sub>)TiOPO<sub>4</sub> (KNTP; Crennel, Owen, Grey, Cheetham, Kaduk & Jarman, 1991) and (Rb<sub>0.5</sub>,Na<sub>0.5</sub>)TiOPO<sub>4</sub> (RNTP; Crennell, Owen, Cheetham, Kaduk & Jarman, 1991) from powder diffraction data. Crennell, Owen, Grey *et al.* (1991) and Crennell, Owen, Cheetham *et al.* (1991) found that there was complete preference for the K(2) site by the larger ion in each of these structures to within their errors on the site occupancies. In our refinement of RKTP, we have found to within our smaller errors that the separation of Rb and K onto the two available sites is not complete, although Rb has a strong preference for the larger K(2) site. In RTP, both the Rb(1) and Rb(2) sites tend towards nine-coordination and Rb therefore prefers the K(2) site in RKTP with only a small percentage occupying the eight-coordinated K(1) site. The degree of site sharing which is tolerated in this structure reflects the closer similarity of K to Rb than that of either K to Na or Rb to Na.

The substitution of Rb for K in RTP leads to expansions along *a* and *b* and a contraction along *c*. However, the mixed crystal RKTP has *a* and *b* lattice parameters intermediate in value between those of KTP and RTP whereas the *c* parameter is larger than that of either end-member. The *c* parameter is also out of sequence in the series KTP, (K<sub>0.5</sub>,Na<sub>0.5</sub>)TiOPO<sub>4</sub>, NaTiOPO<sub>4</sub> and RTP, (Rb<sub>0.5</sub>,Na<sub>0.5</sub>)TiOPO<sub>4</sub>, NaTiOPO<sub>4</sub> (Table 4) which indicates that the dimension along the polar axis is particularly sensitive to the nature of the K-site cations. The anomaly in the *c* parameter may be explained by reference to the displacements made by the K-site cations at the high-temperature structural phase transition. We predicted (TGW) that the high-temperature phase of KTP and its analogues should have symmetry *Pnan* and this has been confirmed experimentally by a high-temperature study of TlTiOPO<sub>4</sub> by Harrison, Gier, Stucky & Schultz (1990). From a recent high-temperature Raman study of TlTiOPO<sub>4</sub> (Pisarev, Farhi, Moch & Voronkova, 1990), it has been demonstrated that there is a pronounced softening of

Table 4. Lattice parameters (Å) in the mixed analogues of KTP

The data for RNTP and KNTP are taken from Crennell, Owen, Grey *et al.* (1991) and Crennell, Owen, Cheetham *et al.* (1991).

	RTP	RKTP	KTP	RNTP	KNTP	NTP
<i>a</i>	12.974 (2)	12.908 (6)	12.819 (3)	12.8273 (6)	12.7613 (7)	12.611 (2)
<i>b</i>	6.494 (3)	6.436 (3)	6.399 (1)	6.3347 (3)	6.3347 (3)	6.2810 (9)
<i>c</i>	10.564 (6)	10.597 (5)	10.584 (2)	10.6052 (5)	10.6052 (5)	10.595 (2)

a mode associated mainly with the Tl motions parallel to the polar axis as the phase transition is approached. This provides further evidence of the important role played by the K-site atoms both at the structural phase transition and in the establishment of the room-temperature structure. The Raman analysis shows that the softening mode, although primarily connected with the Tl<sup>+</sup> movements, is also coupled to internal TiO<sub>6</sub> modes and therefore the interaction of the K-site ions with the structural framework is also of importance. In our model for the high-temperature phase of KTP, we used pseudosymmetry arguments to show that there should be only one independent K position in the high-temperature structure. The pseudosymmetrically related K(1) and K(2) sites of the room-temperature structure derive from the one high-temperature position *via* displacements of the K atoms primarily parallel to *c* (Thomas & Glazer, 1991). The mixed compounds RKTP, RNTP and KNTP show the same *Pnan* pseudosymmetry as the other structures of the KTP family if the chemical inequivalence of the K(1) and K(2) sites is disregarded and only the positions are considered. If the high-temperature structure of RKTP, for example, is analogous to that of KTP, this would imply that K and Rb share the one available high-temperature K site. Since K and Rb are preferentially sited on the K(1) and K(2) sites, respectively, in the room-temperature phase, this implies that they must become disordered over the K(1) and K(2) sites as the phase transition is approached.

The crystals used in these structural studies were grown at temperatures above their respective phase-transition temperatures and, therefore, the effect of cooling the crystals through the structural phase transition is of particular relevance. In the high-temperature structure of RKTP, we expect the Rb and K sites to be completely disordered. As the temperature is lowered, Rb and K must make displacements onto what become the K(1) and K(2) sites of the room-temperature framework which are known to be both chemically and symmetrically distinct. The preferential siting of Rb and K in the room-temperature structure should reflect the different couplings of the vibrations of these distinct chemical species to the vibrations of the structural framework. In the compounds KTP and RTP, the

Table 5. Deviation from *Pnan* pseudosymmetry (Å)

The deviation from *Pnan* pseudosymmetry corresponds to the detection of the additional symmetry elements (1) inversion centre at Ti(2) and (2) *n*-glide plane through Ti(1) with the program *MISSYM*. Calculated displacements are those required to bring pseudo-twofold-related K(1) and K(2) atoms into exact twofold relationship.

	Framework only	K atoms only
KSnOPO <sub>4</sub>	0.10	0.76
K(Ti <sub>0.5</sub> ,Sn <sub>0.5</sub> )OPO <sub>4</sub>	0.15	0.76
KTiOPO <sub>4</sub>	0.19	0.66
RbTiOPO <sub>4</sub>	0.19	0.72
CsTiOAsO <sub>4</sub>	0.19	0.45
KTiOPO <sub>4</sub> (90 K)	0.20	0.84
(Rb <sub>0.47</sub> ,K <sub>0.53</sub> )TiOPO <sub>4</sub>	0.21	0.64
KTiO(P <sub>0.58</sub> ,As <sub>0.42</sub> )O <sub>4</sub>	0.22	0.66
RbTiOAsO <sub>4</sub>	0.22	0.75
KTiOAsO <sub>4</sub>	0.25	0.79
(K <sub>0.4</sub> ,Na <sub>0.5</sub> )TiOPO <sub>4</sub>	0.27	0.84
(Rb <sub>0.4</sub> ,Na <sub>0.5</sub> )TiOPO <sub>4</sub>	0.27	0.97

separation onto the K(1) and K(2) sites is achieved by approximately equal displacements of a single chemical species (K or Rb). The calculated displacements (Table 5, second column) of K and Rb with respect to the pseudo *n*-glide plane in KTP and RTP, respectively, are quite different and it is interesting to note that the corresponding displacement calculated for (K,Rb) in RKTP is not simply the average of those found for K and Rb individually. Relative to the KTP and RTP end-members therefore, it is possible that the *c* axis is effectively strained in the mixed RKTP compound because of the different displacements of K and Rb associated with the structural phase transition. As the displacements of these atoms are primarily parallel to *c*, it is understandable that any anomalous effect on the lattice parameters occurs for the *c* axis in particular.

Finally, we have observed that thermal parameters for the atoms of the framework are very similar in all of the four crystals. However, the thermal vibrations of the Rb and K atoms show some variation. In particular, the longest axes of the thermal ellipsoids of K(2) in KTAP and Rb(2) in RTA and RTP lie almost along the [001] direction whereas those of the K(1) and Rb(1) ellipsoids are directed approximately along the  $[\bar{1}01]$  direction. However, in RKTP (Fig. 1), the direction of the maximum vibration of (Rb,K)(2) is skewed from the [001] direction by almost 40° whereas the (Rb,K)(1) ellipsoid shows the usual  $[\bar{1}01]$  orientation. The result is that the directions of the maximum vibrations of (Rb<sub>0.13</sub>,K<sub>0.87</sub>)(1) and (Rb<sub>0.80</sub>,K<sub>0.20</sub>)(2) (which should be equivalent atoms in the high-temperature structure) are almost orthogonal in the room-temperature phase of RKTP.

### Pseudosymmetry

In the above, reference has been made to the *Pnan* pseudosymmetry retained in the room-temperature phase of KTP and its analogues. In particular, the pseudosymmetry elements 2[010] passing through P(1), 2[100] passing through P(2), an *n*-glide plane

passing through Ti(1) and an inversion centre at Ti(2) can be identified. Each of these pseudosymmetry relationships is obeyed to a slightly different degree when the deviations of the atoms from exact symmetry relationships are calculated individually. However, when using *MISSYM* for the purpose of comparing structural analogues the minimum value of the structural distortion (the 'tolerance' in the terminology of the program) input by the user such that the pseudo-inversion centre at Ti(2) and the *n*-glide plane through Ti(1) are found simultaneously is interpreted as a measure of the average deviation of the atoms of the room-temperature structure from the prototypic symmetry *Pnan*. The atoms of the TiO<sub>6</sub>/PO<sub>4</sub> framework are investigated separately from the K(1) and K(2) site atoms because: (i) the major contribution to the nonlinear optical response has been believed to be the highly distorted TiO<sub>6</sub> octahedra of the framework and (ii) the largest calculated deviations occur for the K(1) and K(2) atoms which are known to be of major significance at the structural phase transition and which occupy highly asymmetrically coordinated sites within the strongly pseudosymmetric structural framework.

From Table 5, it is seen that in the sequence of compounds KSnOPO<sub>4</sub> (KSP), K(Ti<sub>0.5</sub>,Sn<sub>0.5</sub>)OPO<sub>4</sub> (KTSP) and KTP, the framework distortion increases smoothly from the quasicentrosymmetric KSP to KTP. This correlates with the increase in powder second-harmonic generation observed for solid solutions in this series as the Ti:Sn ratio is raised (Jarman & Grubb, 1988). Despite the more

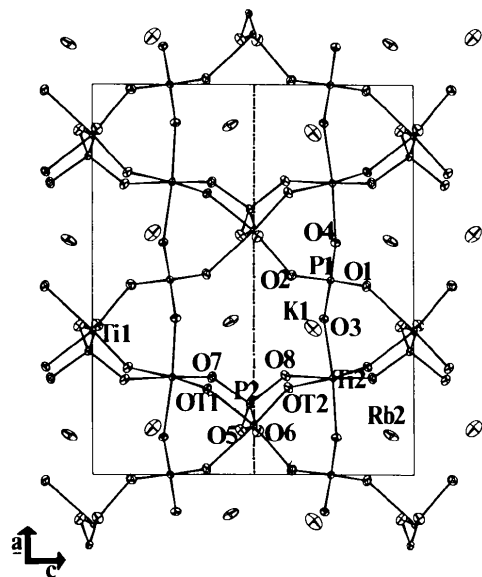


Fig. 1. A view of the crystal structure of RKTP along [010]. The atoms are represented by their thermal ellipsoids at the 80% probability level. The pseudo *n*-glide plane is indicated by the dotted line.

pseudosymmetric framework of KSP, the phase transition temperature is considerably higher (1313 to 1373 K, Yanovskii & Voronkova, 1989) than that for KTP (1207 K, Yanovskii & Voronkova, 1980). This correlates with the larger displacements of the K ions in KSP particularly if the displacements of these ions are considered to be the major feature of the structural phase transition.

The compounds from KTP to KTA have average framework distortions between 0.19 and 0.25 Å but the distortions when the K-site atoms are included show a much wider variation. For CsTiOAsO<sub>4</sub> (Protas, Marnier, Boulanger & Menaert, 1989), the unusually small tolerance found when the Cs atoms are included reflects their higher inertia at the structural phase transition which is known to occur at the relatively low temperature of 963 K (Mangin, Marnier, Boulanger & Menaert, 1989). In KTP at 90 K, the framework retains the room-temperature pseudosymmetry to the same degree. However, the potassium sites change considerably as the temperature is lowered and move significantly further away from their room-temperature pseudosymmetry relationship within the stable structural framework. Although there is no structural phase transition between room temperature and 90 K, the pronounced effect on the potassium sites within a framework which is essentially preserved suggests that displacements of these atoms will be of importance in driving any phase transition which may occur at lower temperature. In RKTP, the framework is slightly more distorted than that of either KTP or RTP as a result of the selective siting of the K and Rb atoms. As discussed previously, the distortion found for (Rb,K) in RKTP is not intermediate between those for Rb in RTP and K in KTP, possibly because of the different displacements made by K and Rb at the structural phase transition. However, we have observed that this transition in RKTP occurs at 1149 (5) K which is intermediate between the temperatures for the two end-members, KTP (1207 K) and RTP (1062 K) (Yanovskii & Voronkova, 1980).

According to the published structural data, KTA shows both a markedly higher framework distortion (despite the reduced distortions in the individual octahedra) and a greater K-site deviation than KTP. KTA and RTA are the only reported analogues which do not involve site-sharing atoms and which show these increases over KTP; KTA is also the only analogue so far demonstrated to have a significantly improved second-harmonic generation performance from single-crystal measurements (Bierlein, Vanherzeele & Ballman, 1989). This observation is consistent with the larger overall deviation of the KTA crystal structure from the assumed centrosymmetric prototype. The distortions are reduced when Rb is

substituted for K in the arsenate. The Rb deviations in RTA are similar to those in RTP and the structural phase transitions in these crystals occur at very similar temperatures *i.e.* 1067 and 1062 K in RTA (Mangin *et al.*, 1989) and RTP, respectively.

The KTP framework accommodates the substitution of Rb relatively easily. However, the framework distortions increase markedly for KNTP and RNTP, as do the overall distortions when the K-site atoms are included, reflecting the significantly different coordination environments of the preferentially sited Na and K or Rb cations. The greater distortion of the framework is not observed (from powder measurements) to translate into increased nonlinear optical performance because the electronic effects of substitution of the less polarizable Na ion outweigh the favourable increase in the structural distortion.

### Concluding remarks

The analysis of the physical properties of crystals in the KTP family as a function of their deviation from the prototypic symmetry is a promising approach which shows interesting trends. Future work will concentrate on high-temperature structural studies of the crystals in this series if the problems encountered so far with crystal decomposition at the temperatures required can be overcome.

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## X-ray Investigation of the Incommensurate Modulated Structure of $\text{Bi}_{2.08}\text{Sr}_{1.84}\text{CuO}_{6-\delta}$

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### Abstract

At room temperature the bismuth strontium cuprate  $\text{Bi}_{2.08}\text{Sr}_{1.84}\text{CuO}_6$  [ $a = 5.3791$  (6),  $b = 5.3811$  (9),  $c = 24.589$  (3) Å,  $\beta = 89.93$  (1)°, basic space group  $A2/a$ , superspace group  $P_{11}^{A2/a}$ ,  $M_r = 755.44$ ,  $D_x = 7.05$  g cm<sup>-3</sup>,  $V = 711.7$  Å<sup>3</sup>,  $Z = 4$ , Cu  $K\alpha$  radiation,  $\lambda = 1.541838$  Å,  $\mu = 1203$  cm<sup>-1</sup>,  $F(000) = 1278.24$ ,  $T = 294$  K] exhibits a one-dimensional incommensurate modulated structure with a modulation wavevector  $\mathbf{q}^*$  having components 0.2030 (2), 0, 0.467 (2). Both a displacive modulation wave, acting on all atoms and a density modulation wave, governing the occupancy probabilities of the Bi, Sr and apical O(2) sites are involved in the crystal. 1117 unique  $hklm$  reflections with  $I \geq 3\sigma(I)$  were used to refine the modulated structure. The final  $R$  factors (based on  $F$ ) of main reflections (292), and first- and second-order satellite reflections (563 and 262) are 0.061, 0.061 and 0.086 respectively. The modulation is anharmonic for all atoms. Evolution of the Bi, Sr and apical O(2) site occupancies throughout the crystal is correlated in a spectacular way and shows the existence of Bi and O(2) vacant sites in some unit cells; moreover, some Sr sites are occupied by Bi atoms. These features give rise to various coordinations *i.e.* square planar, pyramidal, octahedral for

copper and from six to nine for strontium. The most likely coordination for bismuth in strontium sites is ninefold coordination; owing to the displacive modulation, both dilute and Bi-condensed regions are found in the crystal. Within the condensed regions, bismuth achieves a classical fourfold coordination. To satisfy the Bi coordination in the Bi-dilute regions it is proposed that extra O atoms have to be introduced either within the Bi—O layers or between two adjacent Bi—O layers.

### Introduction

A great number of structural studies have been performed on bismuth cuprates since the discovery of superconductivity in the system Bi—Sr—Cu—O (Michel, Hervieu, Borel, Grandin, Deslandes, Provost & Raveau, 1987). In spite of this intense exploration, the structure of the 2201 oxide  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$  is still not really understood.

The oxide of nominal composition  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$  called Bi-2201 crystallizes in a pseudotetragonal subcell with basic parameters close to  $a \approx 5.4$ ,  $b \approx 5.4$  and  $c \approx 24.5$  Å. The diffraction spectrum of all the crystals studied reveals, besides main reflections, the existence of satellite reflections. The main reflections