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## LETTER TO THE EDITOR

# The crystal structure of potassium titanyl phosphate (KTP) in its high-pressure phase

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**Abstract.** The structure of the high-pressure phase of KTP has been determined at 6.2 GPa using Patterson projections, Fourier difference maps and least-squares refinement. Although the phase transition is strongly first-order and involves a 4.2% reduction of the unit-cell volume, the  $Pna2_1$  space-group symmetry of the low-pressure phase is retained. The main structural changes involve tilting of the  $PO_4$  tetrahedra relative to the  $TiO_6$  octahedra, while both units remain relatively unchanged in size and shape. In particular, the  $TiO_6$  octahedra remain highly distorted and retain their anomalously short Ti-O bonds. The potassium atoms are observed to undergo relatively large movements of about 0.5 Å along the polar  $c$ -axis.

Potassium titanyl phosphate (KTP) and its family of structural analogues form a unique class of non-linear optical materials. KTP is an extremely efficient second-harmonic generator (SHG) of Nd-YAG laser light [1] and is a particularly important material for many opto-electronic applications. The structure of KTP assumes the acentric  $Pna2_1$  space group at atmospheric pressure ( $a = 12.819(3)$  Å,  $b = 6.399(1)$  Å,  $c = 10.584(2)$  Å,  $V = 868.1(4)$  Å<sup>3</sup> [2]) and is characterized by chains of  $TiO_6$  octahedra linked by  $PO_4$  tetrahedra. The  $TiO_6$  octahedra are highly distorted and contain anomalously short Ti-O bonds. It is these anomalously short bonds that have been associated with the non-linear optical properties of the crystal [3]. The KTP structure exhibits a strong pseudosymmetry derived from the centric  $Pnan$  space group and it has been reported that the isomorphous thallium analogue  $TlTiOPO_4$  (TTP) undergoes a second-order transition into this  $Pnan$  symmetry at 923 K [4]. Recently, it has been demonstrated by Kourouklis *et al* [5] that KTP exhibits a structural phase transition at a pressure of 5.5 GPa. Their high-pressure Raman study shows that there is an increase in the number of detectable modes at 5.5 GPa, which was taken to indicate a lowering of the crystal symmetry into an antiferroelectric phase. In contrast, Serhane *et al* [6] have located a phase transition in TTP at 6 GPa where the number of Raman modes *decreases* by about a factor of two. They postulate that TTP adopts a centrosymmetric phase which is paraelectric and closely related to the high-temperature phase. It is of considerable interest to determine what relationship these high-pressure phases have to the high-temperature phase, and whether the high-pressure phases of KTP and TTP have different structures. We have recently carried out a detailed investigation of the changes that occur as the high-pressure transition

in KTP is approached [7]. We now report the successful determination of the structure of the high-pressure phase.

A single crystal of flux grown KTP was cut to the dimensions of  $50 \times 100 \times 100 \mu\text{m}^3$  and mounted in a Diacell diamond-anvil pressure cell so that the *b*- and *c*-axes were parallel to the diamond-anvil faces. From the previous study of the low-pressure phase [7], this orientation of the sample was found to give the lowest correlations and ESDs for the positional parameters during structural refinement of the restricted data. A tungsten gasket was used to enclose the sample and the ethanol-methanol pressure-transmitting fluid. The pressure cell was then taken to a pressure of  $6.2 \pm 0.1$  GPa (measured using the ruby fluorescence method [8]) to place the sample crystal into the high-pressure phase. The cell was mounted on an Enraf-Nonius CAD4 diffractometer and oriented using the same indexing scheme as that used for the low-pressure phase [7], and a search was made along the [100], [110] and [111] directions for new reflections. No new reflections were found in the survey; the unit cell appears to remain primitive, with axes parallel to those of the low-pressure phase. (A series of precession photographs also showed no new reflections strong enough to be detected on film.) The unit-cell dimensions were then determined accurately by the four-equivalent-settings procedure of King and Finger [9] and found to be  $a = 12.477(9) \text{ \AA}$ ,  $b = 6.322(3) \text{ \AA}$  and  $c = 10.058(4) \text{ \AA}$ , giving a unit-cell volume  $V = 793(1) \text{ \AA}^3$ . Comparing these values with an extrapolation to 6.2 GPa from our previous unit-cell measurements [7] indicates that there is a 4.2% volume reduction at the phase transition. The transition is, therefore, strongly first-order.

Intensity data were collected with the  $\omega$ -scan method at the position of least attenuation of the pressure cell, according to the fixed- $\phi$  technique [10]. All accessible reflections in the hemisphere  $\pm h, k, \pm l$  up to a maximum  $\sin \theta / \lambda$  of  $0.59 \text{ \AA}^{-1}$ , totalling 1056, were measured with graphite-monochromated  $\text{MoK}_\alpha$  radiation. The systematic absences were consistent with either the  $Pna2_1$  or  $Pnam$  space groups. Although observation of the  $h0l$  layer of reflections was restricted by the pressure cell, a sufficient number of systematic absences could be recorded to establish that the *a*-glide was present. After applying a correction for the absorption of the sample the data were used to generate Patterson projections. Comparing the 6.2 GPa Patterson projections with those for the low-pressure data sets, the major structural changes were identified and an initial structural model developed in the  $Pna2_1$  symmetry. (A satisfactory model could not be found in the  $Pnam$  space group since the atoms would have to undergo unrealistically large movements to conform to the mirror plane. These movements would require severe disruption of the  $\text{TiO}_6\text{-PO}_4$  framework and the breaking of several bonds.) The model was then successfully refined using the Prometheus suite of crystallographic programs [11]. Fourier difference maps were generated at each stage of the refinement to check the quality of the fit. The atomic coordinates refined freely to a structure in which the  $\text{TiO}_6$  octahedra and  $\text{PO}_4$  tetrahedra have internal bond lengths and bond angles very similar to the low-pressure structure. Also, the fit to the data compared well with the fits obtained in refinements of equivalent data sets from the low-pressure phase.

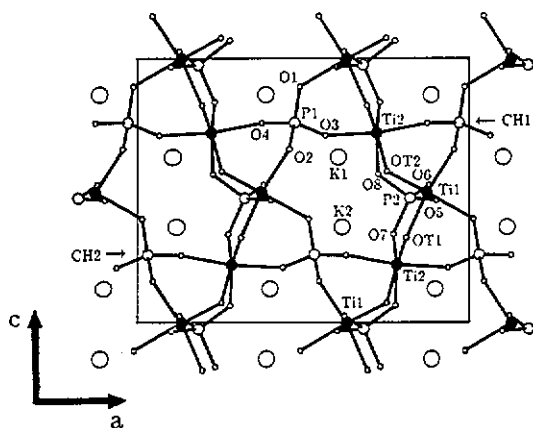
If the true symmetry of KTP were lower than  $Pna2_1$  as proposed by Kourouklis *et al* [5] from their high-pressure Raman study, the structure would have to be only slightly distorted from the one refined in the  $Pna2_1$  space group, so the apparently absent reflections are in fact present but too weak to be observed. The only space groups allowing such a small distortion of the structure, and not introducing further reflection conditions, are monoclinic  $Pn$ ,  $Pa$  and  $P2_1$ . Using the coordinates refined

with the  $Pna2_1$  space group as starting values, refinements were performed in each of these space groups. However, the refinements did not give a significantly better fit to the data and the atomic positions differed by less than 0.1 Å from their  $Pna2_1$  positions. It appears, then, that the  $Pna2_1$  space group is retained after the phase transition, unless there is twinning not resolvable in this experiment.

The  $Pna2_1$  refinement was completed by removing the systematically absent reflections from the data and averaging over symmetry-equivalent reflections, after their intensities had been corrected for extinction. The oxygen atoms were all refined with isotropic temperature factors while the potassium, titanium and phosphorus atoms were refined with anisotropic temperature factors (the anisotropic thermal parameters for the atomic motion directed along  $a$ , the direction of lowest resolution in the data, were constrained to their ambient values). Similar constraints were applied to the low-pressure refinements [7] and were shown not to bias the refinement of the positional parameters significantly. The final cycle of refinement resulted in a weighted  $R$ -factor,  $R_w$ , of 3.6% for 533 independent reflections and 88 refinable parameters. Table 1 presents the refined atomic coordinates and the structure is shown in figure 1.

**Table 1.** Atomic coordinates of  $\text{KTiOPO}_4$  at 6.2 GPa. The estimated standard deviations (ESDs) are given in parentheses. Note that the Prometheus refinement program requires that one atom is fixed along the polar axis. The Ti1  $z$  coordinate was chosen to be fixed to the same value used in the low-pressure study, and so no ESD is quoted for it.

	$x$	$y$	$z$		$x$	$y$	$z$
K1	0.3953(7)	0.7780(4)	0.6314(4)	O3	0.4373(21)	0.1848(11)	0.7130(9)
K2	0.1146(6)	0.7001(4)	0.8667(4)	O4	0.6246(19)	0.1795(12)	0.7590(9)
R1	0.3718(4)	0.4894(3)	-0.0004	OT1	0.1913(16)	0.9728(9)	0.3269(6)
T2	0.2800(5)	0.2572(3)	0.7240(3)	OT2	0.2510(17)	0.0398(9)	0.5783(7)
P1	0.5296(8)	0.3218(4)	0.7623(4)	O5	0.0998(15)	0.2982(11)	0.4702(7)
P2	0.1798(6)	0.4810(4)	0.4784(3)	O6	0.1218(15)	0.6777(12)	0.5285(8)
O1	0.5134(15)	0.4177(11)	0.8973(7)	O7	0.2300(16)	0.5126(9)	0.3390(7)
O2	0.5452(15)	0.5043(10)	0.6625(7)	O8	0.2754(15)	0.4380(9)	0.5672(6)



**Figure 1.** The high-pressure structure of  $\text{KTiOPO}_4$  viewed along the  $b$ -axis. The shaded circles represent the titanium atoms and the  $\text{TiO}_6$ - $\text{PO}_4$  chains labelled CH1 and CH2 exhibit parallel/antiparallel translations along the  $a$ -axis, in the directions indicated by the arrows. This figure can be compared with figure 1 of Allan *et al* [7] to reveal the deformation of the potassium cage site environments and the pronounced movements of the potassium atoms along the  $c$ -axis.

The main structural changes involve the *n*-glide-related Ti(2)O<sub>6</sub>-P(1)O<sub>4</sub> chains (labelled CH1 and CH2 in figure 1), which exhibit parallel/antiparallel translations along the *a*-axis. The cross-linking Ti(1)O<sub>6</sub>-P(2)O<sub>4</sub> chains (which are directed along the *b*-axis) are rotated by the relative shifts of the Ti(2)O<sub>6</sub>-P(1)O<sub>4</sub> chains. Within the chains there is pronounced tilting of the TiO<sub>6</sub> octahedra with respect to the PO<sub>4</sub> tetrahedra, with a considerably larger change in their relative orientation than is observed between ambient pressure and the phase transition [7]. The overall shape and distortions of the TiO<sub>6</sub> octahedra are almost unchanged by the phase transition and the distribution of the long, intermediate and short bonds is the same as in the low-pressure phase. In particular the anomalously short Ti-OT bonds are retained. However, some of the bond angles *within* the TiO<sub>6</sub> octahedra differ significantly from their values below the phase transition. This is in marked contrast with the bond-angles of the PO<sub>4</sub> tetrahedra which show almost no change. The potassium atoms undergo substantial movements along the polar *c*-axis, of the order of 0.5 Å with respect to the TiO<sub>6</sub>-PO<sub>4</sub> framework. These movements are accompanied by large distortions of the coordination (or cage site) environments of the K atoms, which reduce in volume by about 10%.

Our conclusion that there is no symmetry change through the 5.5 GPa transition disagrees with interpretation that Kourouklis *et al* make of their high-pressure Raman data [5]. The apparent contradiction may be explained if the intensities of weak and previously unobserved Raman modes are augmented after the phase transition. This would give rise to an apparent increase of the number of modes without changing the crystal symmetry.

To summarize, we have solved the high-pressure structure of KTiOPO<sub>4</sub> and have demonstrated that the phase transition is first-order in character. Our results show that the *Pna*2<sub>1</sub> space group is retained and that there are substantial deformations of the TiO<sub>6</sub>-PO<sub>4</sub> framework. The potassium atoms also exhibit relatively large movements along the polar *c*-axis. We are planning to investigate what effect the phase transition has on the SHG properties of the crystal and these results, along with a more detailed account of the structural changes, will be presented at a later date.

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