

The Crystal Structure of the Nonlinear Optical Material Thallium Titanyl Phosphate, TlTiOPO_4 , above the Ferroelectric to Paraelectric Phase Transition

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The high-temperature crystal structure of thallium titanyl phosphate, TlTiOPO_4 , (TITP) is described and compared with its room-temperature KTiOPO_4 isomorph.

Potassium titanyl phosphate, KTiOPO_4 (KTP), is the premier material for second harmonic generation (SHG) of 1.06 μ Nd-YAG laser light,¹ and other electro-optic applications.² Extensive reviews of KTP solid-state chemistry are available.³ KTP⁴ and all its known isomorphs³ crystallize in the acentric,

orthorhombic space group $Pna2_1$ at room temperature. The characteristic features of this structure are the infinite zigzag TiO_6 chains in the $[011]$ and $[0\bar{1}1]$ directions, and the long-short alternation of Ti-O bond lengths within these chains. In 1980, Yanovskii and Voronkova⁵ discovered a

high-temperature ferroelectric to paraelectric phase transition in several KTP-type materials, including KTP itself (T_c 934 °C), RbTiOPO_4 (RbTP: T_c 789 °C), and TlTiOPO_4 (TlTP: T_c 583 °C). The transition was assumed to be displacive and strongly second-order, possibly involving a space-group transition from room-temperature $Pna2_1$ to high-temperature $Pnam$. However, no further studies have been made since on the crystal structure of the high-temperature phase. In this communication we report the high-temperature paraelectric structure of TlTP for the first time (space group: $Pnan$), which shows a quite different titanium–oxygen chain geometry and thallium co-ordination to that found in the KTP-like room-temperature phase.

Single crystals of TlTP were synthesised by slow-cooling a melt of Ti_2CO_3 , TiO_2 , and H_3PO_4 , resulting in slightly translucent crystals with dimensions of up to 3 mm. Normal safety precautions were taken during the preparation steps due to the high toxicity of thallium. X-Ray powder patterns of some of the ground crystals indicated a pure, highly crystalline KTP-type phase, and a single crystal X-ray study at room temperature⁶ indicated that the Ti–O chain geometry in TlTP was very similar to that in KTP.†

The crystal structure of TlTP is shown in Figure 1. The centric, high-temperature crystal structure contains ten atoms in the asymmetric unit (two titanium, two phosphorus, five oxygen, and one thallium site). The Ti and P atoms are in four-fold special positions and the O's and Tl are in eight-fold general positions. The most striking features of the high-temperature structure are the quite different geometries of the two TiO_6 octahedra and the univalent thallium cation to those found in the room-temperature structure. The differences in chain configuration are mainly due to the fact that the Ti–O–Ti 'chain' oxygens, denoted O(9) and O(10) in the low-temperature structure,⁶ become equivalent in the 650 °C phase, as O(15). Ti(11) [equivalent to Ti(1) in the low temperature phase] is thus surrounded by three crystallographically distinct oxygens and the two *cis* chain O(15)s have the same bond length [1.823(9) Å]. Ti(12) [equivalent to Ti(2)] is also bound to three distinct oxygens, and the two *trans* O(15)s in the octahedral chain are both at 1.899(7) Å. The chain configuration of TlTP is illustrated in Figure 2. Both phosphate groups retain their typical tetrahedral geometries as found at room temperature. The single, distinct thallium is bound to five nearest-neighbour oxygen atoms (distance

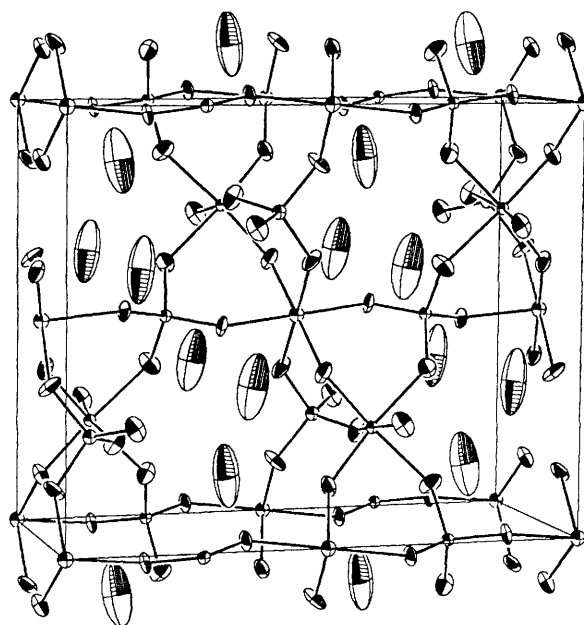


Figure 1. The crystal structure of TlTiOPO_4 viewed along the b unit-cell direction, showing the three-dimensional network of octahedral titanium–oxygen and tetrahedral phosphorus–oxygen polyhedra. The thallium ions show gross thermal anisotropy in the c -direction.

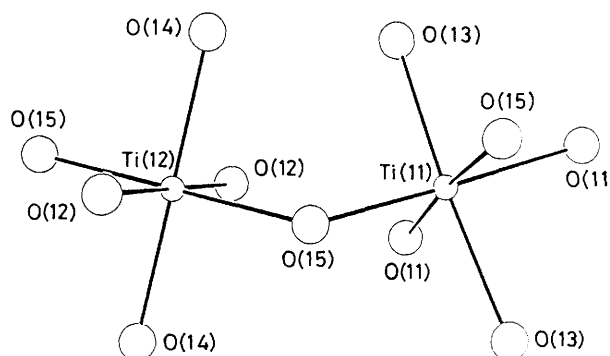


Figure 2. Close-up view of the titanium–oxygen chain geometry. Bond distances (Å): Ti(11)–O(11) 2.055(10), Ti(11)–O(13) 2.065(7), Ti(11)–O(15) 1.823(9), Ti(12)–O(12) 2.047(5), Ti(12)–O(14) 1.971(7), Ti(12)–O(15) 1.899(7).

2.67–3.00 Å) and four next nearest oxygens, the closest being 3.42 Å from Tl. By comparison, at room temperature, the two crystallographically distinct thalliums are each nine-fold oxygen co-ordinated [Tl(1), distance 2.74–3.35 Å; Tl(2), distance 2.70–3.22 Å].⁶ Both these co-ordinations may be described as 6 + 3, with six oxygens within 3.12 Å in each case. At 650 °C, the thallium thermal ellipse is grossly asymmetric in the crystallographic z -direction, which may well be indicative of disorder, but attempts to model more than one site were inconclusive.

In conclusion, we have solved the paraelectric crystal structure of TlTiOPO_4 and demonstrated the second-order nature of the phase transition. Our initial results suggest that Tl has moved substantially in the new unit cell, and this motion may be the 'driving force' for the phase transition. We are currently investigating the structure of TlTP at intermediate temperatures to fully characterize this phase transition behavi-

† Crystal data for TlTP: high-temperature single crystal time-of-flight neutron diffraction data were collected on the diffractometer SCD⁷ at the Intense Pulsed Neutron Source, IPNS, at Argonne National Laboratory as outlined previously.⁸ At 650 °C, the unit cell obtained was orthorhombic with $a = 13.033(4)$, $b = 6.539(2)$ and $c = 10.522(4)$ Å, and nineteen histograms of intensity data were collected. F^2 values were extracted in the standard manner and systematic absences uniquely indicated the centric space group $Pnan$ (No. 52). The high temperature structure was solved by transforming the $Pna2_1$ room temperature co-ordinates by $(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$, and performing a distance-least-squares (DLS)-type optimization⁹ for the titanium–oxygen and phosphorus–oxygen polyhedra in $Pnan$. Atomic connectivity was maintained and a chemically reasonable solution was achieved in the DLS-refinement. This model was refined using the Argonne variable wavelength least-squares refinement program (ANVLS) on a VAX780 computer as described previously.⁸ The final cycle of anisotropic refinement resulted in residuals of $R = 0.12$, $R_w = 0.18$ for 843 observed reflections [$I > 5\sigma(I)$]; full details will be published later. Crystal data: $M = 363.3$, $D_c = 5.4 \text{ g cm}^{-3}$, $Z = 8$, $V = 896.7 \text{ Å}^3$. Thallium and the oxygen atoms were modelled anisotropically: due to lack of data, the titanium and phosphorus atoms were refined as isotropic. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Institut für Anorganische Chemie, Bonn. See Notice to Authors, Issue No. 1.

our. Owing to the similarities in physical behaviour of KTP and TITP as a function of temperature, it is likely that a similar crystallographic transition occurs in the parent phase also.

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