Rb₃Ti₂(TiO)(PO₄)₃P₂O₇: a New Non-Centrosymmetric Titanyl Phosphate

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Abstract

Rubidium titanium titanyl monophosphate diphosphate has been synthesized for the first time. The structure consists of corner-shared TiO_6 and PO_4 groups with Rb atoms occupying nine-, ten- and eleven-coordinate sites. The TiO_6 octahedra are highly distorted and two of them are linked through a shared O atom. Two of the PO_4 groups share an O atom, thus forming a diphosphate group P_2O_7, two of the O atoms of which are terminal (*i.e.* not bonded to a Ti atom). Taking these structural features into account, the chemical formula can be written as $Rb_3Ti_2(TiO)(PO_4)_3P_2O_7$.

Comment

Potassium titanyl phosphate ($KTiOPO_4$) has been of interest in the past decade because of its unique combination of non-linear optical and electro-optical properties (Stucky, Phillips & Gier, 1989). These properties depend on the lack of an inversion centre in the structure and strong deformation of the TiO_6 octahedra, shown by the presence of a very short Ti—O bond. The title compound is a result of our attempt to produce new non-centrosymmetric titanyl phosphates with strongly distorted TiO_6 octahedra.

$Rb_3Ti_3P_5O_{20}$ was one of two crystal phases obtained at high temperature from Rb_2CO_3, TiO_2 and $NH_4H_2PO_4$ in the molar ratio 2.25:1:3.3. They were mixed in a platinum crucible and heated to 1373 K, kept at that temperature for 10 h, then cooled slowly (5° h⁻¹) to 923 K and removed from the furnace. The resulting crystals were recovered from the solidified flux by dissolving it in boiling water. The powder pattern showed that the crystals were a mixture of $RbTi_2(PO_4)_3$ and a phase that was not in the powder pattern database (ICDD). During the course of X-ray analysis, this phase was identified as $Rb_3Ti_3P_5O_{20}$, a new compound which has not been reported before.

The bond lengths and angles (Table 2) are within the expected range. The structure consists of a three-dimensional framework of corner-shared TiO_6 octahedra and PO_4 tetrahedra with Rb atoms located on the cage sites within the framework (Fig. 1). The six O atoms around any of the three crystallographically distinct Ti atoms form a distorted octahedron. The distortion is larger for the environments of Ti(1) and Ti(3), which form a titanyl bridge *via* O(13), and this results in the formation of one very short [1.780 (6) and 1.831 (6) Å, respectively] and one very long [2.036 (6) and 2.015 (5) Å, respectively] Ti—O bond, causing a maximum difference between the Ti—O bond lengths in Ti(1)O₆ and Ti(3)O₆ of 0.26 and 0.18 Å, respectively. In terms of bond strengths (Brown & Altermatt, 1985), this means that the short bond is twice as strong as the long one [1.10 *versus* 0.55 v.u. in Ti(1)O₆]. There are five crystallographically distinct P atoms, two of which [P(1) and P(5)] are linked *via* O(14). The formation of the diphosphate group is achieved at the expense of a strong distortion (in both angles and bond lengths) of the P(1)O₄ and P(5)O₄ tetrahedra [very long P—O bonds to the bridging atom O(14)], and one of the four bonding O atoms becoming terminal. The P(1)—O(14)—P(5) bridge forms an angle of 135.7 (3)° and the P—O bond lengths are 1.471(9)–1.496(9)Å (terminal), 1.501(6)–1.554(9)Å (O also bonded to Ti) and 1.600(5)–1.613(5)Å (bridging). Considering the diphosphate and titanyl bridging in the structure, the chemical formula can be written as $Rb_3Ti_2(TiO)(PO_4)_3P_2O_7$. The three crystallographically distinct Rb atoms are bonded to nine, ten
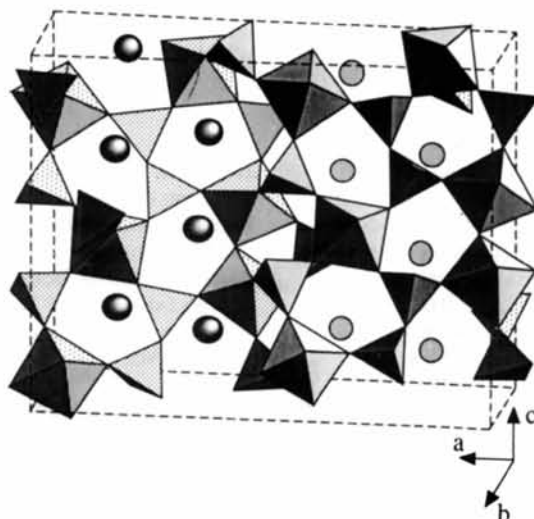

Fig. 1. TiO_6 octahedra, PO_4 tetrahedra and Rb atoms (spheres) in the structure of $Rb_3Ti_2(TiO)(PO_4)_3P_2O_7$. The darker shading represents those polyhedra and spheres that are centred around $y = 0.14$–0.37, while the lighter shading is for $y = 0.63$–0.86.

and eleven O atoms, respectively, with Rb—O bond lengths between 2.763 (6) and 3.457 (8) Å. Bond–valence analysis shows consistency between bond–valence balance and the oxidation state of each atom, apart from the higher bond-strength sum around the Ti and a few O atoms.

The lack of a centre of symmetry as well as the strongly distorted TiO_6 octahedra, though to a lesser extent than in $KTiOPO_4$ (Thomas, Glazer & Watts, 1990), suggested that this compound may show significant second-harmonic generation (SHG) response. Our measurements based on the Kurtz test on a powder sample (Kurtz & Perry, 1968), however, showed an SHG signal which was lower than that of KDP (KH_2PO_4).

Experimental

Crystal data

$Rb_3Ti_2(TiO)(PO_4)_3P_2O_7$	Mo $K\alpha$ radiation
$M_r = 874.90$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 36
$Pca2_1$	reflections
$a = 18.281$ (2) Å	$\theta = 17$–$22°$
$b = 6.2932$ (7) Å	$\mu = 11.03$ mm^{-1}
$c = 14.773$ (2) Å	Room temperature
$V = 1699.6$ (6) Å^3	$0.34 \times 0.27 \times 0.23$ mm
$Z = 4$	Colourless
$D_x = 3.42$ Mg m^{-3}	

Data collection

Stoe Stadi-4 diffractometer	2519 observed reflections
2θ–ω scans	$[I > 2\sigma(I)]$
Absorption correction:	$R_{int} = 0.0331$
empirical (ψ scan of 16	$\theta_{max} = 30°$
reflections)	$h = -25 \rightarrow 25$
$T_{min} = 0.0624$, $T_{max} =$	$k = -8 \rightarrow 8$
0.1626	$l = -20 \rightarrow 20$
11 014 measured reflections	3 standard reflections
4114 independent reflections	frequency: 50 min
	intensity variation: 8%

Refinement

Refinement on F	Extinction correction:
$R = 0.0331$	Larson (1970)
$wR = 0.0344$	Extinction coefficient:
2519 reflections	219 (9)
273 parameters	Atomic scattering factors
$(\Delta/\sigma)_{max} = 0.006$	from *International Tables*
$\Delta\rho_{max} = 1.87$ e Å^{-3}	*for X-ray Crystallography*
$\Delta\rho_{min} = -0.53$ e Å^{-3}	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Rb(1)	0.34558 (5)	0.3685 (2)	0.66927 (9)	0.0178 (5)
Rb(2)	0.32487 (4)	0.34438 (11)	0.94501 (11)	0.0235 (3)
Rb(3)	0.14933 (5)	0.3655 (2)	0.72335 (9)	0.0192 (5)
Ti(1)	0.54435 (7)	0.2429 (5)	0.57026 (12)	0.0054 (7)
Ti(2)	0.35265 (5)	0.74730 (16)	0.44253 (14)	0.0057 (4)
Ti(3)	0.44904 (8)	0.7573 (5)	0.83300 (13)	0.0061 (7)
P(1)	0.27349 (12)	-0.1449 (5)	0.78672 (15)	0.0067 (10)
P(2)	0.49021 (11)	0.7445 (6)	0.59928 (14)	0.0055 (9)
P(3)	0.39710 (7)	0.2444 (2)	0.44614 (18)	0.0058 (5)
P(4)	0.49817 (10)	0.2540 (6)	0.80260 (14)	0.0061 (9)
P(5)	0.22276 (12)	-0.1450 (5)	0.59526 (16)	0.0072 (10)
O(1)	0.2723 (3)	0.0884 (15)	0.7922 (4)	0.011 (3)
O(2)	0.5393 (4)	0.5532 (15)	0.5756 (6)	0.011 (3)
O(3)	0.4181 (3)	0.7376 (17)	0.5458 (3)	0.010 (2)
O(4)	0.3482 (2)	0.0448 (6)	0.4434 (9)	0.010 (2)
O(5)	0.3452 (2)	0.4357 (6)	0.4436 (9)	0.010 (2)
O(6)	0.5540 (3)	0.7557 (5)	0.8609 (4)	0.009 (3)
O(7)	0.4406 (3)	0.2476 (5)	0.5332 (4)	0.010 (3)
O(8)	0.4506 (4)	0.0579 (14)	0.8274 (5)	0.008 (3)
O(9)	0.5163 (4)	0.2577 (18)	0.7035 (4)	0.015 (3)
O(10)	0.2221 (4)	0.0925 (14)	0.5910 (5)	0.014 (3)
O(11)	0.3454 (3)	0.7425 (16)	0.8108 (4)	0.010 (3)
O(12)	0.6481 (3)	0.2482 (18)	0.6067 (4)	0.014 (3)
O(13)	0.4290 (2)	0.7520 (7)	0.9544 (4)	0.009 (2)
O(14)	0.2653 (3)	-0.2253 (7)	0.6835 (3)	0.012 (3)
O(15)	0.2643 (3)	0.7414 (10)	0.5195 (3)	0.012 (2)
O(16)	0.2872 (3)	0.7375 (10)	0.3363 (4)	0.011 (2)
O(17)	0.4716 (4)	0.7423 (10)	0.6997 (3)	0.014 (3)
O(18)	0.5357 (4)	0.9382 (15)	0.5757 (6)	0.013 (3)
O(19)	0.4494 (4)	0.4432 (14)	0.8273 (6)	0.009 (3)
O(20)	0.4328 (3)	0.7394 (16)	0.3614 (4)	0.013 (3)

Table 2. *Bond lengths* (Å) *and angles* (°)

Ti(1)O₆ octahedron

Ti(1)—O(13)*	1.780 (6)	O(13)—Ti(1)—O(18)	94.6 (3)
Ti(1)—O(18)	1.926 (10)	O(13)—Ti(1)—O(2)	91.9 (3)
Ti(1)—O(2)	1.957 (10)	O(13)—Ti(1)—O(12)	89.9 (2)
Ti(1)—O(12)	1.971 (6)	O(13)—Ti(1)—O(7)	89.8 (2)
Ti(1)—O(7)	1.974 (6)	O(13)—Ti(1)—O(9)	176.1 (4)
Ti(1)—O(9)	2.036 (6)	O(18)—Ti(1)—O(2)	171.2 (3)
		O(18)—Ti(1)—O(12)	94.8 (4)
		O(18)—Ti(1)—O(7)	87.0 (3)
		O(18)—Ti(1)—O(9)	89.1 (4)
		O(2)—Ti(1)—O(12)	91.0 (4)
		O(2)—Ti(1)—O(7)	87.2 (3)
		O(2)—Ti(1)—O(9)	84.5 (4)
		O(12)—Ti(1)—O(7)	178.2 (4)
		O(12)—Ti(1)—O(9)	88.7 (3)
		O(7)—Ti(1)—O(9)	91.4 (3)

Ti(2)O₆ octahedron

Ti(2)—O(4)	1.874 (4)	O(4)—Ti(2)—O(20)	93.7 (4)
Ti(2)—O(20)	1.893 (6)	O(4)—Ti(2)—O(3)	93.0 (4)
Ti(2)—O(3)	1.940 (5)	O(4)—Ti(2)—O(5)	173.5 (2)
Ti(2)—O(5)	1.966 (4)	O(4)—Ti(2)—O(16)	90.6 (4)
Ti(2)—O(16)	1.975 (5)	O(4)—Ti(2)—O(15)	88.8 (3)
Ti(2)—O(15)	1.976 (5)	O(20)—Ti(2)—O(3)	91.1 (2)
		O(20)—Ti(2)—O(5)	91.8 (4)
		O(20)—Ti(2)—O(16)	88.0 (2)
		O(20)—Ti(2)—O(15)	175.1 (3)
		O(3)—Ti(2)—O(5)	90.3 (4)
		O(3)—Ti(2)—O(16)	176.3 (4)
		O(3)—Ti(2)—O(15)	92.9 (3)
		O(5)—Ti(2)—O(16)	86.2 (4)
		O(5)—Ti(2)—O(15)	85.4 (3)
		O(16)—Ti(2)—O(15)	87.8 (3)

Ti(3)O₆ octahedron

Ti(3)—O(13)*	1.831 (6)	O(13)—Ti(3)—O(8)	93.6 (3)
Ti(3)—O(8)	1.894 (9)	O(13)—Ti(3)—O(11)	88.2 (2)
Ti(3)—O(11)	1.925 (5)	O(13)—Ti(3)—O(6)	89.4 (2)
Ti(3)—O(6)	1.962 (6)	O(13)—Ti(3)—O(19)	91.4 (3)
Ti(3)—O(19)	1.979 (9)	O(13)—Ti(3)—O(17)	176.3 (4)
Ti(3)—O(17)	2.015 (5)	O(8)—Ti(3)—O(11)	93.2 (4)
		O(8)—Ti(3)—O(6)	90.0 (3)
Ti(1)—O(13)*—Ti(3)	152.5 (3)	O(8)—Ti(3)—O(19)	175.0 (3)
		O(8)—Ti(3)—O(17)	90.1 (4)
		O(11)—Ti(3)—O(6)	176.2 (3)
		O(11)—Ti(3)—O(19)	87.0 (4)
		O(11)—Ti(3)—O(17)	91.9 (3)
		O(6)—Ti(3)—O(19)	90.0 (3)
		O(6)—Ti(3)—O(17)	90.3 (3)
		O(19)—Ti(3)—O(17)	84.9 (4)

P(1)O$_4$ tetrahedron

P(1)—O(1)†	1.471 (9)	O(1)—P(1)—O(16)	116.6 (4)
P(1)—O(16)	1.521 (5)	O(1)—P(1)—O(11)	117.5 (5)
P(1)—O(11)	1.536 (7)	O(1)—P(1)—O(14)	111.4 (3)
P(1)—O(14)‡	1.613 (5)	O(16)—P(1)—O(11)	106.7 (4)
		O(16)—P(1)—O(14)	103.6 (3)
		O(11)—P(1)—O(14)	98.8 (3)

P(2)O$_4$ tetrahedron

P(2)—O(18)	1.516 (9)	O(18)—P(2)—O(17)	110.7 (5)
P(2)—O(17)	1.522 (5)	O(18)—P(2)—O(3)	112.0 (5)
P(2)—O(3)	1.538 (6)	O(18)—P(2)—O(2)	104.9 (4)
P(2)—O(2)	1.542 (9)	O(17)—P(2)—O(3)	108.0 (3)
		O(17)—P(2)—O(2)	110.1 (5)
		O(3)—P(2)—O(2)	111.1 (5)

P(3)O$_4$ tetrahedron

P(3)—O(7)	1.513 (6)	O(7)—P(3)—O(5)	109.6 (5)
P(3)—O(5)	1.533 (4)	O(7)—P(3)—O(4)	109.7 (5)
P(3)—O(4)	1.543 (4)	O(7)—P(3)—O(6)	112.9 (2)
P(3)—O(6)	1.545 (6)	O(5)—P(3)—O(4)	106.3 (2)
		O(5)—P(3)—O(6)	109.8 (5)
		O(4)—P(3)—O(6)	108.3 (5)

P(4)O$_4$ tetrahedron

P(4)—O(9)	1.501 (6)	O(9)—P(4)—O(19)	110.4 (5)
P(4)—O(19)	1.531 (9)	O(9)—P(4)—O(20)	111.8 (4)
P(4)—O(20)	1.533 (6)	O(9)—P(4)—O(8)	111.5 (5)
P(4)—O(8)	1.554 (9)	O(19)—P(4)—O(20)	108.9 (5)
		O(19)—P(4)—O(8)	103.6 (3)
		O(20)—P(4)—O(8)	110.4 (5)

P(5)O$_4$ tetrahedron

P(5)—O(10)†	1.496 (9)	O(10)—P(5)—O(12)	115.1 (7)
P(5)—O(12)	1.521 (7)	O(10)—P(5)—O(15)	116.1 (4)
P(5)—O(15)	1.529 (6)	O(10)—P(5)—O(14)	110.7 (4)
P(5)—O(14)‡	1.600 (5)	O(12)—P(5)—O(15)	109.1 (4)
		O(12)—P(5)—O(14)	102.2 (3)
P(1)—O(14)‡—P(5)	135.7 (3)	O(15)—P(5)—O(14)	102.0 (3)

Environment around Rb(1) with CN = 10

Rb(1)—O(7)	2.763 (6)	Rb(1)—O(11)	3.148 (9)
Rb(1)—O(1)	2.864 (8)	Rb(1)—O(9)	3.238 (8)
Rb(1)—O(14)	2.955 (5)	Rb(1)—O(3)	3.238 (8)
Rb(1)—O(19)	3.045 (8)	Rb(1)—O(17)	3.323 (9)
Rb(1)—O(10)	3.074 (8)	Rb(1)—O(5)	3.361 (13)

Environment around Rb(2) with CN = 9

Rb(2)—O(10)	2.811 (8)	Rb(2)—O(13)	3.198 (4)
Rb(2)—O(19)	2.932 (8)	Rb(2)—O(2)	3.210 (8)
Rb(2)—O(1)	2.935 (7)	Rb(2)—O(11)	3.217 (9)
Rb(2)—O(5)	3.162 (4)	Rb(2)—O(8)	3.398 (8)
Rb(2)—O(15)	3.179 (6)		

Environment around Rb(3) with CN = 11

Rb(3)—O(6)	2.784 (6)	Rb(3)—O(5)	3.285 (13)
Rb(3)—O(10)	2.923 (8)	Rb(3)—O(17)	3.337 (7)
Rb(3)—O(12)	2.981 (10)	Rb(3)—O(14)	3.387 (5)
Rb(3)—O(2)	3.013 (8)	Rb(3)—O(9)	3.409 (10)
Rb(3)—O(1)	3.021 (7)	Rb(3)—O(20)	3.457 (8)
Rb(3)—O(16)	3.101 (6)		

* Bridging atom between Ti(1)O$_6$ and Ti(3)O$_6$.
† Terminal atom from a PO$_4$ group (not connected to Ti).
‡ Bridging atom between two PO$_4$ groups.

Data collection, cell refinement and data reduction were carried out using Stoe software. Precise cell refinement was performed by double-step-scan technique. The structure was solved using CRYSTALS (Watkin, Carruthers & Betteridge, 1985). To avoid the strong correlations between nine pairs of positional (y) and displacement parameters for atoms related by pseudo-symmetry, the parameters within these pairs were refined riding on one another. The Flack enantiopole parameter (Flack, 1983) was refined to 0.94 (1). Weights $w = 1/[\sigma^2(F) + kF^2]$ were used until the last few cycles when robust-resistant weights (Tukey, 1974) were applied (parameters used 9.07, −7.01 and 7.16).

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RbTi$_2$(PO$_4$)$_3$

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Abstract

Rubidium titanium monophosphate forms trigonal crystals, isostructural with its lithium, sodium and potassium analogues. The structure consists of a three-dimensional framework of corner-shared TiO$_6$ octahedra and PO$_4$ tetrahedra with the Rb atoms alternating along the $\bar{3}$ axis with Ti$_2$P$_3$O$_{18}$ units, composed of two TiO$_6$ octahedra linked through three PO$_4$ tetrahedra.

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