

Joachim C. M. Gustafsson,^{a*}
Stefan T. Norberg^b and Göran
Svensson^a^aInorganic Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden, and ^bCeramics Research Laboratory, Nagoya Institute of Technology, 507-0071 Gifu, Japan

Correspondence e-mail: jogu@chalmers.se

Key indicators

Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{P}-\text{O}) = 0.005$ Å
Disorder in main residue
 R factor = 0.033
 wR factor = 0.079
Data-to-parameter ratio = 20.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The langbeinite type $\text{Rb}_2\text{TiY}(\text{PO}_4)_3$

Dirubidium titanium yttrium triphosphate belongs to the langbeinite structure type with a framework of MO_6 octahedra ($M = \text{Ti}, \text{Y}$) sharing corners with PO_4 tetrahedra and *vice versa*, creating cages in which the Rb^+ cations are located. The compound exhibits mixed Ti/Y populations in the two crystallographically independent octahedral sites of symmetry 3. More than two-thirds of the yttrium is found in one site and the remaining amount in the other; this is caused by the difference in coordination for the two sites.

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Comment

The title compound belongs to a large group of synthetic $A_xM_z(\text{XO}_4)_3$ compounds, the parent structure of which is the mineral langbeinite, $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ (Zemann & Zemann, 1957). Langbeinites containing titanium and phosphate have been synthesized in the past, *e.g.* $\text{KTi}_2(\text{PO}_4)_3$, $\text{K}_2\text{Ti}_2(\text{PO}_4)_3$, $\text{K}_{1+x}\text{Ti}_{2-y}\text{Al}_y(\text{PO}_4)_3$, $\text{K}_2\text{MTi}(\text{PO}_4)_3$ ($M = \text{Er}, \text{Yb}$ or Y), $\text{Rb}_2\text{ErTi}(\text{PO}_4)_3$ and $\text{Rb}_2\text{YbTi}(\text{PO}_4)_3$ (Masse *et al.*, 1972; Leclaire *et al.*, 1989; Slobodyanik *et al.*, 1991; Norberg, 2002; Carvajal *et al.*, 2003; Gustafsson *et al.*, 2005). Some of these compounds contain mixed-valence cations that prefer an octahedral coordination, such as $\text{Ti}^{3+}/\text{Ti}^{4+}$ in $\text{K}_2\text{Ti}_2(\text{PO}_4)_3$. The

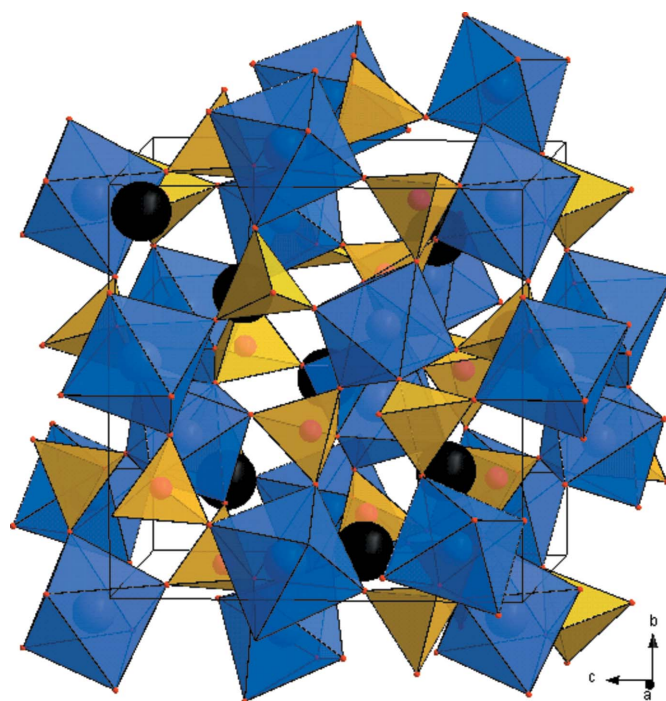


Figure 1
The framework of $\text{Rb}_2\text{TiY}(\text{PO}_4)_3$, viewed in a polyhedral representation. PO_4 groups are yellow and Ti/YO_6 groups are blue. The Rb^+ cations are depicted in black.

small number of phosphate langbeinites is due to the fact that most $A_xM_z(XO_4)_3$ compounds tend to crystallize in the closely related NASICON structure type, e.g. $Na_3Zr_2(PO_4)(SiO_4)_2$ (Sljukic *et al.*, 1967; von Alpen *et al.*, 1979). There are also examples where the same compound crystallizes in both the langbeinite and the NASICON structure types (Masse *et al.*, 1972; Perret, 1988).

The langbeinite framework in the title compound consists of MO_6 octahedra sharing corners with PO_4 tetrahedra, making the MO_6 octahedra isolated (Fig. 1). Several alternative descriptions of the langbeinite structure have been proposed. (i) The structure is commonly described using $[M_2X_3O_{18}]$ units composed of two MO_6 octahedra linked together by three XO_4 tetrahedra. (ii) Norberg (2002) suggested a description based on much larger $M_5X_6O_{39}$ units as building blocks. These larger units allow for a greatly enhanced view of the cages and tunnels in langbeinite and NASICON, respectively. (iii) O'Keeffe & Andersson (1977) described the langbeinite structure in terms of packed $\langle 111 \rangle$ rods.

In the langbeinite framework, large cages are formed in which the two alkali cations are located. The $Rb1^+$ and $Rb2^+$ cations are best described as twelve- and nine-coordinate, respectively. Gustafsson *et al.* (2005) discussed the cages in terms of MO_6 -octahedra arranged around the cations with the possibility for a smaller cation to reside in the cage in $Rb_2YbTi(PO_4)_3$. A similar arrangement is found in the title compound.

Selected bond distances are given in Table 1 and compared with those of the analogous structures of $Rb_2YbTi(PO_4)_3$, $K_2TiY(PO_4)_3$ and $K_2TiYb(PO_4)_3$. The two crystallographically independent MO_6 ($M = Ti, Y$) octahedra are nearly regular, with the metal atoms slightly off-centre. All distances, except for the P–O distances (Table 2) are enlarged compared to $Rb_2YbTi(PO_4)_3$. As expected, some tendencies of disorder can be seen in the slightly enlarged displacement parameters for the O atoms, with the resulting ellipsoids mostly oriented with the principal axis perpendicular to the P–O bond (Fig. 2). This disorder is expected because of the statistical distribution of Ti and Y in the two octahedral sites.

The distribution of Ti and Y is not equal in the two octahedral sites as more than two-thirds of the yttrium is found in the $M1O_6$ octahedra and the residual yttrium is found in the $M2O_6$ octahedra. The $M1O_6$ octahedra define the shared triangular face between the $Rb2-(MO_6)_6$ octahedra and the $Rb1-(PO_4)_4$ tetrahedra. The $M1O_6$ octahedra are thus more influenced by the Rb cations than the $M2O_6$ octahedra, which might have an impact on the distribution of Y and Ti between the two MO_6 octahedra.

Experimental

The crystal used for the determination originated from a high-temperature flux crystal growth experiment with a 1.3:2:0.25 molar mixture of TiO_2 , $RbCO_3$, NH_4HPO_4 and Y_2O_3 for a total of 10 g in the batch. The chemicals were carefully mixed in a 35 ml platinum crucible and slowly heated to 1273 K for about 3 d. The melt was then

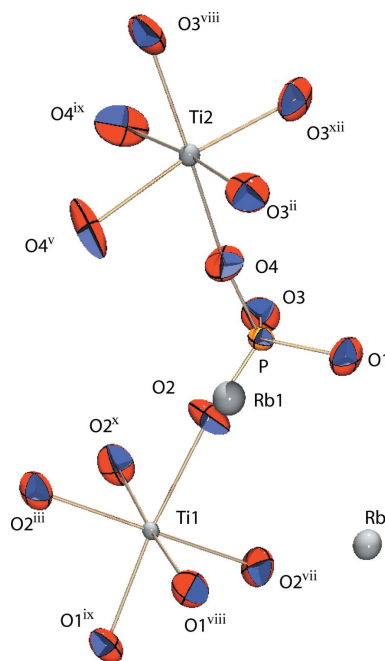


Figure 2

Part of the structure of $Rb_2TiY(PO_4)_3$, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (ii) $\frac{1}{2} - x, 2 - y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, 2 - z$; (v) $y - 1, z, 1 + x$; (vii) $y - \frac{1}{2}, \frac{3}{2} - z, 1 - x$; (viii) $-y, z + \frac{1}{2}, \frac{3}{2} - x$; (ix) $1 + z, 1 + x, y$; (x) $1 - z, \frac{1}{2} + x, \frac{3}{2} - y$; (xii) $z - \frac{1}{2}, \frac{3}{2} - x, 2 - y$.]

kept at this temperature for 2 d and thereafter slowly cooled to 1023 K at a rate of 1.5 K h^{-1} . The crystals were recovered by dissolving the flux in water. Well shaped tetrahedral crystals appeared, along with crystals of $RbTiOPO_4$ (Thomas *et al.*, 1992). The tetrahedrally shaped crystals were found to belong to the langbeinite-type structure. Energy dispersive X-ray analysis (Electro-scan S4-8DV equipped with a Link eX1 EDX system) was used in order to verify the atomic content of the crystal used for the structural work.

Crystal data

$Rb_2TiY(PO_4)_3$
 $M_r = 592.66$
 Cubic, $P2_13$
 $a = 10.2674(4) \text{ \AA}$
 $V = 1082.38(7) \text{ \AA}^3$
 $Z = 4$

$D_x = 3.637 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 15.51 \text{ mm}^{-1}$
 $T = 296(2) \text{ K}$
 Tetrahedron, colourless
 $0.25 \times 0.25 \times 0.25 \text{ mm}$

Data collection

Enraf–Nonius CAD-4
 diffractometer
 ω - 2θ scans
 Absorption correction: analytical
 (Alcock, 1970)
 $T_{\min} = 0.837, T_{\max} = 0.867$
 4075 measured reflections

1254 independent reflections
 1091 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$
 $\theta_{\text{max}} = 31.9^\circ$
 2 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.079$
 $S = 1.06$
 1254 reflections
 60 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 1.5P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.61 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.83 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 539 Friedel pairs
 Flack parameter: $-0.012(14)$

Table 1

Selected bond lengths (Å).

P—O1	1.508 (4)	P—O4	1.535 (5)
P—O2	1.520 (4)	P—O3	1.535 (5)

Table 2Bond distances of Rb₂TiY(PO₄)₃ compared to Rb₂TiYb(PO₄)₃ (Gustafsson *et al.*, 2005) K₂TiY(PO₄)₃ and K₂TiYb(PO₄)₃ (Norberg, 2002) (Å) (*M* = Y, Yb).

	Rb ₂ TiY(PO ₄) ₃	Rb ₂ TiYb(PO ₄) ₃	K ₂ TiY(PO ₄) ₃	K ₂ TiYb(PO ₄) ₃
Rb1/K1—O1	2.978 (5)	2.966 (5)	2.886 (17)	2.882 (8)
Rb1/K1—O2	3.359 (5)	3.306 (6)	-	-
Rb1/K1—O2 ⁱⁱ	3.135 (5)	3.153 (6)	3.146 (19)	3.112 (9)
Rb1/K1—O4 ⁱ	3.084 (5)	3.064 (5)	3.054 (19)	3.023 (9)
Rb2/K2—O2	3.240 (5)	3.222 (5)	3.246 (17)	3.240 (9)
Rb2/K2—O3 ⁱⁱⁱ	3.004 (5)	2.990 (5)	2.921 (14)	2.902 (7)
Rb2/K2—O4	3.326 (7)	3.305 (6)	3.15 (2)	3.199 (9)
M1/Ti1—O1 ^{iv}	2.149 (4)	2.115 (5)	2.100 (15)	2.087 (7)
M1/Ti1—O2	2.163 (5)	2.128 (5)	2.097 (16)	2.085 (8)
M2/Ti2—O3	2.046 (5)	2.019 (6)	2.047 (14)	2.014 (7)
M2/Ti2—O4 ^v	2.036 (4)	2.041 (5)	2.066 (18)	2.030 (8)

Symmetry codes: (i) 1/2+x, 3/2-y, 2-z; (ii) y-1/2, 3/2-z, 1-x; (iii) 1/2-x, 2-y, 1/2+z; (iv) x-1/2, 3/2-y, 2-z; (v) 1/2-x, 2-y, z-1/2.

Since the structure was confirmed to belong to the langbeinite family, coordinates were taken from Gustafsson *et al.* (2005). During refinement, the mixed Ti/Y populations were indicated by *M*—O bonds longer than the usual Ti—O bond distance of 2.01 Å for octahedrally coordinated Ti (Shannon, 1976). This difference was more pronounced for the *M1* site. The Ti/Y mixing was also supported by the observation of excess electron density at both sites, when 100% Ti occupancies were used. The displacement parameters of the Y and Ti atoms at the *M* sites were equated to ensure a stable refinement. During refinement, the overall ratio of Y/Ti was close to 1:1 and was therefore restrained to that in the later stages. The rubidium cation occupancies were initially set to refine freely but remained near full occupancy and were finally fixed at unity.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97*

(Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *DIAMOND* (Brandenburg, 2004) and *POV-RAY* (Persistence of Vision Raytracer Pty. Ltd., 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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