

$K_2TiSi_3O_9 \cdot H_2O$

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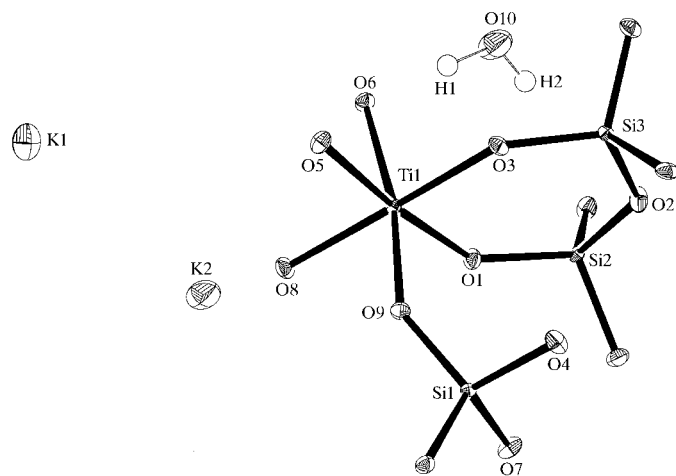
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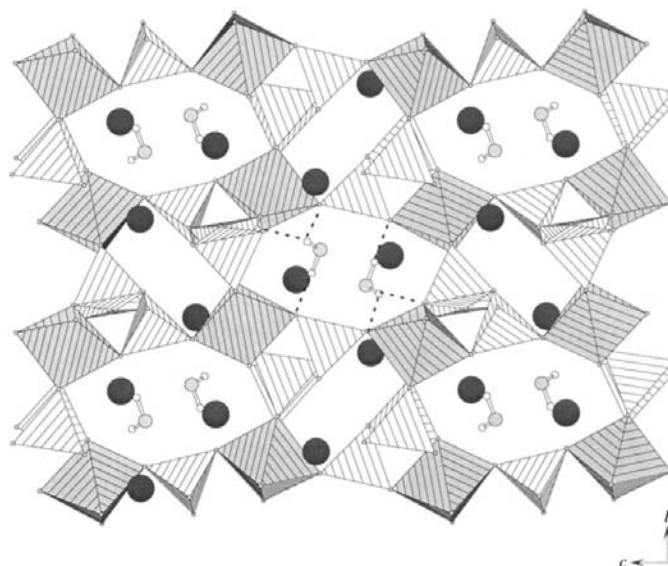
Single crystals of dipotassium titanium trisilicate hydrate were synthesized and the crystal structure was refined using data from single-crystal X-ray diffraction. The structure is a three-dimensional mixed framework and contains channels formed by six- and eight-membered rings. K^+ ions and water molecules are located in the channels.

Comment

The synthesis and structure refinement of the title compound were undertaken as part of an ongoing project aimed at preparing Ti–Si mixed framework compounds. There has recently been much interest in synthesizing open-framework titanium silicates because of their zeolite-like properties and potential applications as molecular sieves, ion-exchange materials and catalysts. Despite extensive worldwide synthetic efforts, only some titanium silicates analogous to minerals and a few titanium silicates with new structures have been reported, for example, $Na_2TiSi_5O_{13} \cdot xH_2O$ (Kuznicki, 1989; Anderson *et al.*, 1995; Wang & Jacobson, 1999), $Na_4Ti_2Si_8O_{22} \cdot 4H_2O$ (Roberts, *et al.* 1996), $Na_3(Na,H)Ti_2O_2[Si_2O_6]_2 \cdot 2H_2O$ (Dadachov *et al.* 1997) and $Na_4[Ti_4O_4(SiO_4)_3] \cdot 6H_2O$ (Dadachov & Harrison, 1997). We have also synthesized a new


Figure 1

A plot (*DIAMOND*; Bergerhoff, 1996) of the asymmetric unit with the atoms labelled and displacement ellipsoids at the 50% probability level.


Figure 2

Polyhedral representation of the structure of $K_2TiSi_3O_9 \cdot H_2O$ viewed along the a axis. The dark polyhedra are TiO_6 and the light polyhedra are SiO_4 . K^+ ions are represented by filled large circles, and the O and H atoms in the water molecules by filled and open small circles, respectively. Hydrogen bonds between the water molecules and framework O atoms are shown.

titanium silicate, $K_2TiSi_3O_9 \cdot H_2O$, and the crystal structure was determined using X-ray powder data (Dadachov & Le Bail, 1997). All non-H atoms were found and their positions were refined isotropically. The structure appeared to be isostructural with the alkaline Zr–silicate umbite $K_2ZrSi_3O_9 \cdot H_2O$ (Ilyukhin *et al.*, 1981) and $K_2(Zr_{0.86}Ti_{0.14})Si_3O_9 \cdot H_2O$ minerals (Ilyushin, 1993). Recently, we prepared crystals of $K_2TiSi_3O_9 \cdot H_2O$ in sizes suitable for single-crystal structure determination. We report here the accurate crystal structure of $K_2TiSi_3O_9 \cdot H_2O$.

The structure is built up from $[Si_3O_9]_n$ wollastonite-type chains running parallel to the a axis. These chains are connected by isolated TiO_6 octahedra forming a three-dimensional framework structure. Two types of channels are found along the a axis, *i.e.* eight-ring channels formed by alternating SiO_4 tetrahedra and TiO_6 octahedra, and six-ring channels formed by alternating SiO_4 tetrahedral pairs and TiO_6 octahedra. Two K^+ ions are located inside the eight-ring channels and the other two K^+ ions are located inside the six-ring channels. Two water molecules are also located inside the eight-ring channels, forming hydrogen bonds with the framework O atoms; O–H...O distances are 1.76 (2) (H1...O6), 1.92 (3) (H2...O8) and 2.57 (4) Å (H2...O9).

Experimental

The synthesis of the title compound was carried out by hydrothermal reaction. KOH (10.240 g) and colloidal silica Ludox (2.531 g; HS-40, Aldrich) were added to distilled water (59.974 g). KF (0.968 g) followed by $TiCl_3$ (5.760 g) solution (15wt% $TiCl_3$, 10wt% HCl, Aldrich) were added under continuous stirring. The $TiCl_3:SiO_2:KF:KOH:H_2O$ molar ratio was 1:3:3:32:600 and the pH was 1.5. Excess

Table 1
Selected geometric parameters (Å).

Ti1—O1	1.920 (2)	Si1—O4	1.649 (2)
Ti1—O9	1.953 (2)	Si2—O1	1.609 (2)
Ti1—O3	1.954 (2)	Si2—O8 ⁱⁱ	1.612 (2)
Ti1—O8	1.961 (2)	Si2—O4 ⁱⁱⁱ	1.632 (3)
Ti1—O5	1.984 (2)	Si2—O2	1.644 (3)
Ti1—O6	2.000 (2)	Si3—O5 ^{iv}	1.605 (2)
Si1—O9	1.596 (2)	Si3—O3	1.607 (2)
Si1—O6 ⁱ	1.622 (2)	Si3—O2	1.644 (3)
Si1—O7	1.644 (3)	Si3—O7 ^v	1.647 (3)

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (iv) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

KOH was added to increase the pH to 14.0. The solution was heated in a 23 ml Teflon-lined autoclave at 488 K for 100 h under autogeneous pressure. The colourless transparent crystals which formed were filtered off and washed, first with water, then with acetone, and finally dried at 328 K.

Crystal data

$\text{K}_2\text{TiSi}_3\text{O}_9 \cdot \text{H}_2\text{O}$
 $M_r = 372.39$
 Orthorhombic, $P2_12_12_1$
 $a = 7.1543$ (7) Å
 $b = 9.9408$ (11) Å
 $c = 12.9460$ (10) Å
 $V = 920.71$ (15) Å³
 $Z = 4$
 $D_x = 2.686$ Mg m⁻³

Data collection

Stoe IPDS diffractometer
 Area-detector scans
 Absorption correction: numerical
 (XRED; Stoe & Cie, 1997)
 $T_{\min} = 0.850, T_{\max} = 0.921$
 8937 measured reflections
 1302 independent reflections (plus
 913 Friedel-related reflections)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.068$
 $S = 0.993$
 2215 reflections
 151 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

Mo $K\alpha$ radiation
 Cell parameters from 1183
 reflections
 $\theta = 2.5\text{--}28.0^\circ$
 $\mu = 2.266$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.10 \times 0.06 \times 0.04$ mm

1983 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.073$
 $\theta_{\text{max}} = 28.03^\circ$
 $h = -9 \rightarrow 9$
 $k = -13 \rightarrow 13$
 $l = -15 \rightarrow 17$

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.59$ e Å⁻³
 Absolute structure: Flack (1983)
 Flack parameter = -0.01 (3)

The positions of the non-H atoms were refined anisotropically using the model obtained by X-ray powder diffraction (Dadachov & Le Bail, 1997). H-atom positions were obtained from the difference Fourier map and were refined isotropically with U_{iso} equal to $1.5U_{\text{eq}}(\text{O})$, and O—H and H \cdots H distances restrained to 0.95 (2) and 1.50 (2) Å, respectively. The Flack (1983) parameter of -0.01 (3) indicated that the crystal was not twinned.

Data collection: *EXPOSE* (Stoe & Cie, 1997); cell refinement: *CELL* (Stoe & Cie, 1997); data reduction: *INTEGRATE* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1103). Services for accessing these data are described at the back of the journal.

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