

Sodium Titanium Silicate, Na₂TiSiO₅

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Abstract. Na₂TiSiO₅, *P4/nmm*; $a = 6.480$ (1), $c = 5.107$ (1) Å; $Z = 2$; $D_c = 3.13$ g cm⁻³; $V = 214.4$ Å³. $R = 0.027$. The structure contains layers of SiO₄ tetrahedra and TiO₅ square pyramids joined by sharing corners and separated by layers of Na⁺ ions. There is one short Ti–O distance: 1.695 (5) Å.

Introduction. Crystals of Na₂TiSiO₅ suitable for structure determination were prepared hydrothermally at 350°C and 2 kbar by reaction of SiO₂, TiO₂ and NaOH in aqueous solution sealed in a gold tube. Nikitin, Ilyukhin, Kel'nikov & Belov (1964) obtained the same compound during investigation of the Na₂O–ZnO–TiO₂–SiO₂–H₂O system and reported a crystal structure with symmetry *P4/nmm*. Na₂TiGeO₅ is reported to be isostructural (Verkhovskii, Kuz'min, Ilyukhin & Belov, 1970). As reported and illustrated, the structure is subject to ambiguities [thus, in Wyckoff's (1968) interpretation there is an improbably short Ti–O distance of 0.97 Å] because there is a misprint in the coordinates for one O atom in the original paper. The final R for the refinement was reported as 0.12. As there are several features of interest in the structure, it was redetermined.

The cell dimensions were refined by least squares from 20 lines of a powder pattern obtained in a Guinier–Hägg focusing camera with Cu $K\alpha_1$, and KCl ($a = 6.2929$ Å) as an internal standard.

Data were collected from a crystal in the form of a small square plate with a CAD-4 four-circle diffractometer and Mo $K\alpha_1$ radiation ($\lambda = 0.70930$ Å). Intensities over one octant of reciprocal space out to $\theta = 27^\circ$ were recorded at a take-off angle of 6° by the ω – 2θ scan technique and with $\Delta\omega = 2.5^\circ + 1.0^\circ \times \tan \theta$. Intensities $I < 3\sigma(I)$ were rejected as unobserved. The data were corrected for polarization but not for absorption ($\mu = 24.7$ cm⁻¹).

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Table 1. Fractional atomic coordinates

	<i>x</i>	<i>y</i>	<i>z</i>
Ti	$\frac{1}{2}$	0	0.9343 (2)
Na	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
Si	0	0	0
O(1)	0	0.2071 (4)	0.1831 (4)
O(2)	$\frac{1}{2}$	0	–0.7338 (9)

Table 2. Interatomic distances (Å) and angles (°) in Na₂TiSiO₅

TiO ₅ square pyramid			
Ti–O(2)	1.695 (5)	O(1)–Ti–O(1)	84.8 (1)
–O(1)	1.990 (2) (4×)	O(1)–Ti–O(1)	144.9 (1)
		O(1)–Ti–O(2)	107.5 (1)
SiO ₄ tetrahedron			
Si–O(1)	1.636 (2) (4×)	O(1)–Si–O(1)	109.1 (1)
		O(1)–Si–O(1)	110.3 (1)
NaO ₆ octahedron			
Na–O(1)	2.307 (1) (4×)	O(1)–Na–O(1)	108.8 (1)
–O(2)	2.583 (2) (2×)	O(1)–Na–O(2)	92.3 (1)
O(1)–Na–O(1)	180	O(1)–Na–O(2)	87.7 (1)
O(1)–Na O(1)	71.2 (1)	O(2)–Na–O(2)	180
Metal–metal distances			
Si–Ti	3.257 (1) (4×)	Ti–Na	3.189 (1) (4×)
Si–Na	3.431 (1) (8×)	Na–Na	3.240 (1) (4×)

The space group *P4/nmm* was confirmed by precession photographs, so intensities for hkl and khl were averaged. A Patterson synthesis led to coordinates similar to those reported by the Russian group with the exception of the O atom in 2(*c*) (for which $z = -0.734$ rather than 0.742). Refinement with isotropic temperature factors converged to $R_w = 0.055$. A subsequent refinement with anisotropic temperature factors for all atoms [the symmetry restriction for position 4(*e*) given by Peterse & Palm (1966) is wrong and should be $\beta_{13} = -\beta_{23}$] and scattering factors from *International Tables for X-ray Crystallography* (1974) proceeded satisfactorily to $R = 0.027$, $R_w = 0.037$, $S = 1.1$; the weights were calculated from $w^{-1} = \sigma^2(|F_o|) +$

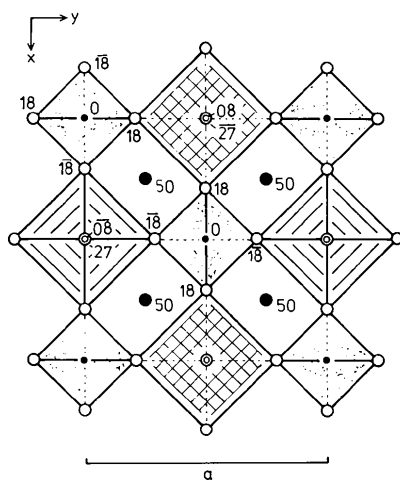


Fig. 1. The structure of $\text{Na}_2\text{TiSiO}_5$ projected along $[001]$. Large open circles O, large filled circles Na, small open circles Ti, small filled circles Si. Elevations in $c/100$. Pyramids with apices pointing down have square faces cross-hatched, others point up.

$(0.03|F_o|)^2$. The results are recorded in Table 1.* Interatomic distances and angles are presented in Table 2.

Discussion. The structure contains layers of SiO_4 tetrahedra and TiO_5 square pyramids joined by sharing corners and separated by layers of Na^+ ions (Fig. 1). The structure of this framework is formally that of bandylite, $\text{CuB}(\text{OH})_4\text{Cl}$ (Collin, 1951), and of a number of ternary oxides: NbPO_5 , VMoO_5 , MoPO_5 , VSO_5 (Wells, 1975) and $\alpha\text{-VPO}_5$ (Jordan & Calvo, 1976), although in these oxides removal of the Na^+ ions allows the layers to come together converting the square pyramids to more nearly regular octahedra.

Fivefold coordination of Ti by O with short Ti—O distances was first reported in $\text{K}_2\text{Ti}_2\text{O}_5$ (Andersson & Wadsley, 1960). The coordination polyhedron was

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33188 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

described as a distorted trigonal bipyramid with two short equatorial distances, 1.67 (± 0.02) and 1.57 (± 0.04) Å. The other possibility for fivefold coordination, the square pyramid, has been reported in $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (Moore & Louisnathan, 1967) with one short Ti—O distance, 1.66 (± 0.08) Å. Verkhovskii *et al.* (1970) found a short Ti—O distance, 1.72 Å (no error given), in $\text{Na}_2\text{TiGeO}_5$. The short distance found in this investigation, 1.695 (5) Å, should also be compared with the two short distances, 1.714 (4) and 1.738 (4) Å, reported for the two square pyramids found in KTiPO_5 (Tordjman, Masse & Guitel, 1974).

Na (Table 2) has only four nearest-neighbour O atoms at the corners of a rectangle with two other atoms further away completing an irregular octahedron.

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References

- ANDERSSON, S. & WADSLY, A. D. (1960). *Nature (London)*, **187**, 499–500.
- COLLIN, R. L. (1951). *Acta Cryst.* **4**, 204–209.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JORDAN, B. D. & CALVO, C. (1976). *Acta Cryst.* **B32**, 2899–2900.
- MOORE, P. B. & LOUISNATHAN, J. (1967). *Science*, **156**, 1361–1362.
- NIKITIN, A. V., ILYUKHIN, B. N., KEL'NIKOV, O. K. & BELOV, N. V. (1964). *Dokl. Akad. Nauk SSSR*, **157**, 1355–1356.
- PETERSE, W. J. A. M. & PALM, J. H. (1966). *Acta Cryst.* **20**, 147–150.
- TORDJMAN, I., MASSE, R. & GUITEL, J. C. (1974). *Z. Kristallogr.* **139**, 103–115.
- VERKHOVSKII, V. YA., KUZ'MIN, E. A., ILYUKHIN, V. V. & BELOV, N. V. (1970). *Dokl. Akad. Nauk SSSR*, **190**, 91–93. (English translation in *Sov. Phys. Dokl.* **15**, 7–8.)
- WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., pp. 512–514. Oxford Univ. Press.
- WYCKOFF, R. W. G. (1968). *Crystal Structures*. Vol. IV, pp. 212–213. New York: John Wiley.