

Refinement of the layered titanosilicate AM-1 from single-crystal X-ray diffraction data

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(i-O) = 0.002$ Å; R factor = 0.024; wR factor = 0.061; data-to-parameter ratio = 13.1.

The structure of the layered noncentrosymmetric titanosilicate AM-1 (also known as JDF-L1, disodium titanium tetrasilicate dihydrate), $\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22}\cdot 4\text{H}_2\text{O}$, grown as small single crystals without the use of organics, has been refined from single-crystal X-ray diffraction data. The H atom has been located for the first time, and the hydrogen-bonding scheme is also characterized by IR and Raman spectroscopy. All atoms are in general positions except for the Na, the Ti, one Ti-bound O, one Si-bound O and the water O atoms (site symmetries 2, 4, 4, 2 and 2, respectively).

Related literature

For general background, see: Anderson *et al.* (1995); Roberts *et al.* (1996); Du *et al.* (1996); Ferdov *et al.* (2002); Kostov-Kytin *et al.* (2004).

Experimental

Crystal data

$\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22}\cdot 4\text{H}_2\text{O}$
 $M_r = 418.27$
Tetragonal, $P4_212$
 $a = 7.374$ (1) Å
 $c = 10.709$ (2) Å
 $V = 582.31$ (16) Å³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 1.29$ mm⁻¹
 $T = 293$ (2) K
 $0.07 \times 0.07 \times 0.01$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (SCALEPACK; Otwinowski *et al.*, 2003)
 $T_{\min} = 0.915$, $T_{\max} = 0.987$

1399 measured reflections
706 independent reflections
631 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.061$
 $S = 1.16$
706 reflections
54 parameters
All H-atom parameters refined

$\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³
Absolute structure: Flack (1983),
247 Friedel pairs
Flack parameter: -0.01 (6)

Table 1

Selected bond lengths (Å).

Si—O2	1.588 (2)	Ti—O2 ⁱⁱ	1.9505 (18)
Si—O4	1.5958 (8)	Na—O ⁱⁱⁱ	2.378 (3)
Si—O1	1.6202 (18)	Na—O2 ^{iv}	2.405 (2)
Si—O1 ⁱ	1.6223 (18)	Na—O1	2.519 (2)
Ti—O3	1.689 (4)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
OW—H \cdots O3	0.76 (3)	2.24 (3)	2.9029 (16)	145 (3)

Data collection: COLLECT (Nonius, 2003); cell refinement: SCALEPACK (Otwinowski *et al.*, 2003); data reduction: SCALEPACK and DENZO (Otwinowski *et al.*, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2055).

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supplementary materials

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Refinement of the layered titanosilicate AM-1 from single-crystal X-ray diffraction data

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Comment

The first synthesis of the layered, non-centrosymmetric titanosilicate AM-1 (chemical formula $\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22}\cdot 4\text{H}_2\text{O}$) was reported by Anderson *et al.* (1995). However, later independent work of Roberts *et al.* (1996) and Du *et al.* (1996) reported the same compound with the name JDF-L1 and described a new synthesis approach, as well as a crystal-structure determination. The layered character of AM-1 allows pillaring and intercalation with different organic molecules that can provide certain catalytic properties.

The crystal structure of AM-1 was originally determined by *ab initio* methods from synchrotron powder X-ray data (Roberts *et al.*, 1995), but the position of the H atom could not be located. Here we report for the first time the successful hydrothermal growth and structure refinement of AM-1 single crystals. The refined single-crystal unit-cell parameters are in good agreement with those reported by Roberts *et al.* (1996) and Ferdov *et al.* (2002).

The title compound contains $[\text{Ti}_2\text{Si}_8\text{O}_{22}]^{4-}$ layers composed of five-member rings built up of four SiO_4 tetrahedra and one TiO_5 square pyramid (Figs. 1 and 2). The interconnection between two of these rings form small cage-type units. The negative charge of the titanosilicate layers is counter-balanced by Na^+ cations residing in the interlayer space. A layer of water molecules is sandwiched between two layers of Na^+ ions. The hydrogen atom H bonded to the OW atom could be located for the first time and was refined isotropically. It is involved in a weak hydrogen bond to O3 ($\text{OW}\cdots\text{O3} = 2.9029$ (16) Å), the oxygen ligand strongly bonded to the Ti atom. The hydrogen bonding scheme thus reinforces the structure across the titanosilicate layers (Fig. 2).

Single-crystal Raman and powder and single-crystal IR spectra are presented in Figs. 3 and 4, respectively. The powder IR spectrum is similar to that reported by Du *et al.* (1996). The Raman spectrum shows a small broad peak at *ca* 3350 cm^{-1} , and a smaller satellite peak at *ca* 3200 cm^{-1} (O—H stretching vibrations). A minute broad band at roughly 1617 cm^{-1} may be attributed to the water bending vibration. The IR spectra in the high-frequency region are similar to the Raman spectrum. The powder IR spectrum shows a very broad, large hump centered at *ca* 3380 cm^{-1} , with a shoulder at *ca* 3200 cm^{-1} . The three small peaks between 3000 and 2800 cm^{-1} are caused by organic impurities in the KBr pellet. The water bending vibration causes the relatively sharp band at 1620 cm^{-1} . The single-crystal IR spectrum contains a broad peak centered at *ca* 3360 cm^{-1} but with two shoulders at *ca* 3480 and 3200 cm^{-1} . Clearly, this reflects a range of O··O donor-acceptor distances. A positional disorder of the water molecule seems unlikely, since the well refined H atom is characterized by a quite small isotropic displacement parameter. In both Raman and IR spectra, the region below 1200 cm^{-1} shows more or less sharp bands due to vibrations involving the TiO_5 , SiO_4 and $\text{Na}-(\text{O},\text{H}_2\text{O})$ units.

Experimental

The hydrothermal syntheses of AM-1 were carried out from gels of the following molar composition: 5–6 Na₂O, 1–1.3 TiO₂, 10 SiO₂, 675 H₂O. In a typical synthesis, 2.96 g of SiO₂ (Merck) was added to a solution of 2.2 g NaOH (Merck) in 40 ml distilled water. Then the solution was brought to the boiling point. Subsequently, 0.66 ml TiCl₄ (Merck) hydrolyzed in 20 ml distilled water was added to the above solution. After cooling to room temperature the mixture was homogenized for 40 min by a mechanical mixer at 200 rpm. The gel was then transferred into 250 ml teflon-lined autoclaves. The crystallization was performed under static conditions at 473 K for 24 h. After fast cooling with flowing H₂O the samples were filtered and washed with distilled water and dried at 323 K overnight.

Refinement

The structure model of Roberts *et al.* (1996) was originally used as a starting model, but the coordinates had to be standardized in order to achieve a connected set of atoms. A Flack parameter of $-0.01(6)$ shows that the crystal was not racemically twinned. The H atom was refined freely.

Figures



Fig. 1. Connectivity in AM-1, shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $y + 1/2, 1/2 - x, z$; (ii) $1/2 - y, x + 1/2, z$; (iii) $y - 1/2, 1/2 - x$; (iv) $-x, 1 - y, z$.]

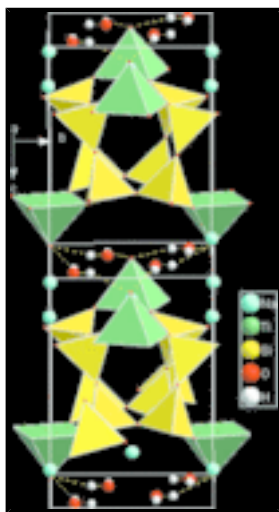


Fig. 2. Polyhedral representation of AM-1 along [010]. The interconnection between four SiO₄ tetrahedra and one TiO₅ square pyramid results in five-member rings which are the main building units of the [Ti₂Si₈O₂₂]⁴⁻ layers. The interlayer space is filled with Na⁺ cations and H₂O molecules.

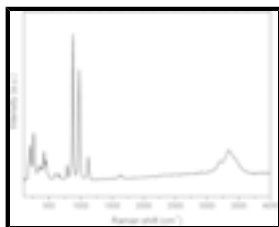


Fig. 3. Single-crystal laser-Raman spectrum of AM-1.

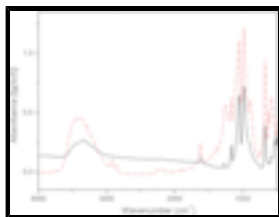


Fig. 4. Powder (red dashed line) and single-crystal IR spectra of AM-1.

disodium titanium tetrasilicate dihydrate

Crystal data

$\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22}\cdot 4\text{H}_2\text{O}$

$M_r = 418.27$

Tetragonal, $P42_12$

Hall symbol: P 4ab 2ab

$a = 7.374 (1) \text{ \AA}$

$b = 7.374 (1) \text{ \AA}$

$c = 10.709 (2) \text{ \AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 582.31 (16) \text{ \AA}^3$

$Z = 2$

$F_{000} = 416$

$D_x = 2.386 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 901 reflections

$\theta = 2.0\text{--}30.0^\circ$

$\mu = 1.29 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Plate, colorless

$0.07 \times 0.07 \times 0.01 \text{ mm}$

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2) \text{ K}$

φ and ω scans

Absorption correction: multi-scan
(SCALEPACK; Otwinowski *et al.*, 2003)

$T_{\min} = 0.915$, $T_{\max} = 0.987$

1399 measured reflections

706 independent reflections

631 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 27.8^\circ$

$\theta_{\min} = 3.4^\circ$

$h = -9 \rightarrow 9$

$k = -6 \rightarrow 6$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.061$

$S = 1.16$

All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.065P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.35 \text{ e \AA}^{-3}$

supplementary materials

706 reflections	Extinction correction: SHELXL97 (Sheldrick, 1997), $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
54 parameters	Extinction coefficient: 0.006 (2)
Primary atom site location: isomorphous structure methods	Absolute structure: Flack (1983)
Secondary atom site location: difference Fourier map	Flack parameter: -0.01 (6)
Hydrogen site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Na	0.0000	0.0000	0.16928 (14)	0.0252 (4)
Ti	0.0000	0.5000	0.22310 (9)	0.0119 (2)
Si	0.31962 (8)	0.23967 (8)	0.35624 (7)	0.01197 (19)
O1	0.2502 (2)	0.0354 (2)	0.32757 (18)	0.0179 (4)
O2	0.2289 (2)	0.3811 (2)	0.2635 (2)	0.0218 (5)
O3	0.0000	0.5000	0.0654 (4)	0.0215 (8)
O4	0.2846 (3)	0.2846 (3)	0.5000	0.0351 (8)
OW	0.1476 (3)	0.1476 (3)	0.0000	0.0343 (8)
H	0.148 (5)	0.251 (4)	0.001 (4)	0.036 (11)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na	0.0263 (8)	0.0259 (8)	0.0235 (8)	0.0076 (8)	0.000	0.000
Ti	0.0097 (3)	0.0097 (3)	0.0163 (5)	0.000	0.000	0.000
Si	0.0095 (3)	0.0092 (3)	0.0173 (4)	0.0006 (3)	0.0009 (3)	-0.0011 (3)
O1	0.0192 (9)	0.0095 (8)	0.0250 (11)	-0.0004 (8)	-0.0037 (8)	0.0006 (7)
O2	0.0124 (9)	0.0144 (9)	0.0386 (13)	0.0008 (7)	-0.0049 (9)	0.0068 (9)
O3	0.0239 (12)	0.0239 (12)	0.0167 (19)	0.000	0.000	0.000
O4	0.0402 (12)	0.0402 (12)	0.0247 (17)	-0.0094 (14)	0.0137 (11)	-0.0137 (11)
OW	0.0325 (12)	0.0325 (12)	0.0379 (19)	-0.0094 (16)	0.0092 (13)	-0.0092 (13)

Geometric parameters (\AA , $^\circ$)

Si—O2	1.588 (2)	Ti—O2	1.9505 (18)
Si—O4	1.5958 (8)	Na—OW ^v	2.378 (3)

Si—O1	1.6202 (18)	Na—OW	2.378 (3)
Si—O1 ⁱ	1.6223 (18)	Na—O2 ⁱⁱⁱ	2.405 (2)
Ti—O3	1.689 (4)	Na—O2 ^{vi}	2.405 (2)
Ti—O2 ⁱⁱ	1.9505 (18)	Na—O1	2.519 (2)
Ti—O2 ⁱⁱⁱ	1.9505 (18)	Na—O1 ^v	2.519 (2)
Ti—O2 ^{iv}	1.9505 (18)	OW—H	0.76 (3)
OW ^v —Na—OW	80.69 (13)	O2 ⁱⁱ —Ti—O2 ^{iv}	87.18 (3)
OW ^v —Na—O2 ⁱⁱⁱ	122.24 (5)	O2 ⁱⁱⁱ —Ti—O2 ^{iv}	87.18 (3)
OW—Na—O2 ⁱⁱⁱ	96.09 (6)	O3—Ti—O2	102.81 (7)
OW ^v —Na—O2 ^{vi}	96.09 (6)	O2 ⁱⁱ —Ti—O2	87.18 (3)
OW—Na—O2 ^{vi}	122.24 (5)	O2 ⁱⁱⁱ —Ti—O2	87.18 (3)
O2 ⁱⁱⁱ —Na—O2 ^{vi}	130.39 (12)	O2 ^{iv} —Ti—O2	154.38 (15)
OW ^v —Na—O1	153.59 (4)	O2—Si—O4	113.50 (9)
OW—Na—O1	97.48 (7)	O2—Si—O1	111.04 (10)
O2 ⁱⁱⁱ —Na—O1	84.17 (7)	O4—Si—O1	108.96 (12)
O2 ^{vi} —Na—O1	62.41 (6)	O2—Si—O1 ⁱ	105.33 (11)
OW ^v —Na—O1 ^v	97.48 (7)	O4—Si—O1 ⁱ	109.36 (11)
OW—Na—O1 ^v	153.59 (4)	O1—Si—O1 ⁱ	108.47 (13)
O2 ⁱⁱⁱ —Na—O1 ^v	62.41 (6)	Si—O1—Si ^{vi}	149.48 (13)
O2 ^{vi} —Na—O1 ^v	84.17 (7)	Si—O2—Ti	142.96 (13)
O1—Na—O1 ^v	95.41 (10)	Si ^{vii} —O4—Si	176.3 (2)
O3—Ti—O2 ⁱⁱ	102.81 (7)	Na ^{viii} —OW—Na	99.31 (13)
O3—Ti—O2 ⁱⁱⁱ	102.81 (7)	Na ^{viii} —OW—H	118 (3)
O2 ⁱⁱ —Ti—O2 ⁱⁱⁱ	154.38 (15)	Na—OW—H	116 (3)
O3—Ti—O2 ^{iv}	102.81 (7)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
OW—H \cdots O3	0.76 (3)	2.24 (3)	2.9029 (16)	145 (3)

Fig. 1

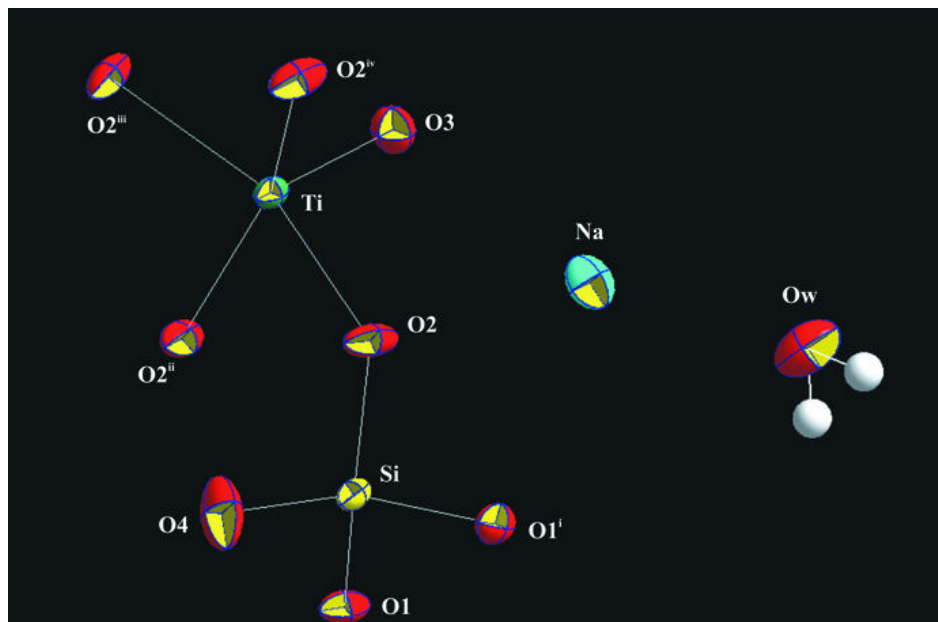


Fig. 2

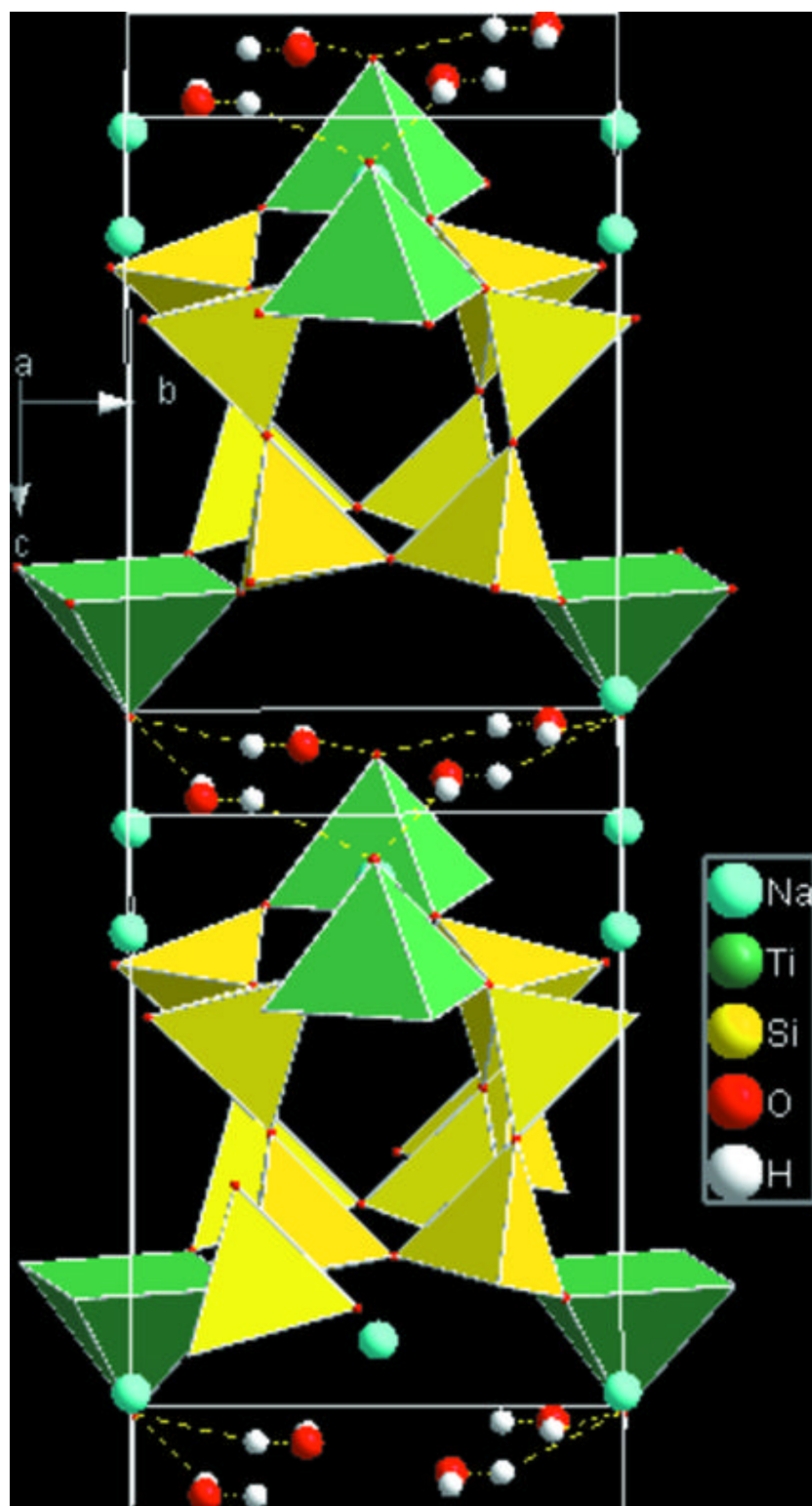


Fig. 3

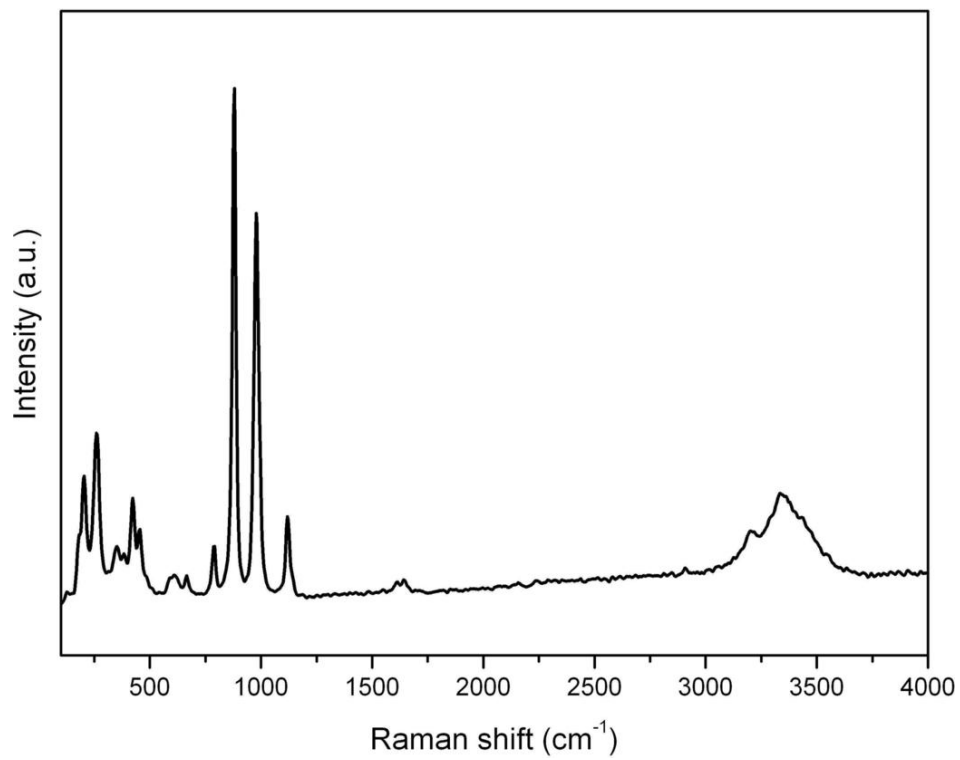


Fig. 4

