Ab initio structure determination of layered sodium titanium silicate containing edge-sharing titanate chains (AM-4) $Na_3(Na,H)Ti_2O_2[Si_2O_6]{\cdot}2.2H_2O$

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The synthesis of a novel layered sodium titanosilicate, $Na_3(Na,H)Ti_2O_2[Si_2O_6]_2.H_2O$ (AM-4), and the solution of its crystal structure by *ab initio* methods are reported.

Mixed framework minerals and synthetic compounds with structures built from common polyhedral units (octahedra and tetrahedra sharing all oxygens with at least two other neighbouring polyhedra) are of great interest, particularly with respect to host–guest chemistry, structural diversity, ion-exchange and adsorption properties, and shape selective catalysis. The large class of titanium silicates encompasses more than 70 minerals, mainly with mixed cation frameworks. During the last decade ynthetic inorganic and materials chemists have attempted to prepare titanium silicates by using high-temperature solid state ceramic and hydrothermal methods. Recently, we have reported the synthesis of analogues of minerals nenadkevichite,[1] umbite, narsarsukite[2] and penkvilksite.[3,4] We have also solved the structures of the important microporous material ETS-10,[5] as well as rhombohedrally distorted $Na_4[Ti_4O_4(SiO_4)_3]_6{\cdot}H_2O$.[6] Here, we wish to report the synthesis and structure determination of a novel titanium silicate layered compound, monoclinic $Na_3(Na,H)Ti_2O_2[Si_2O_6]_2{\cdot}2H_2O$.

In a typical AM-4 synthesis, an alkaline solution was prepared by mixing 27.04 g sodium silicate solution (27% m/m SiO_2, 8% m/m Na_2O, Merck), 14.76 g NaOH (EKA Nobel) and 38.46 g H_2O. To this 40.30 g of $TiCl_3$ (15% m/m solution of $TiCl_3$ in 10% m/m HCl, Merck) were added and stirred thoroughly. The gel, with a composition 5.6 Na_2O : 3.1 SiO_2 : 1 TiO_2 : 123 H_2O, was autoclaved at 230 °C under autogeneous pressure for 4 d. The Teflon-lined autoclaves were then quenched in cold water. The crystals, obtained in 80% yield, were filtered off, washed at room temp. with distilled water and dried overnight at 100 °C.

Thermogravimetry (TGA-50 Shimadzu analyzer) gives a total mass loss between 20 and 500 °C of *ca.* 7.4%. The crystal morphology and elemental analysis of crystals were studied on a JEOL JSM-6400 (SEM) and JEOL 2000FX (TEM). The sample studied has an Na : Ti : Si composition ratio of *ca.* 2 : 1 : 2. Diffraction data were collected with a Siemens D500 powder diffractometer using Co-Kα X-radiation (1.799 Å). Intensity data for *h*, *k*, *l* were collected by the step counting method (step 0.01° and time 30 s) in the range 2θ 5–100°. X-Ray diffraction pattern autoindexing was performed with the PROSZKI package[7] from the well resolved first 40 lines with an absolute error of 0.02 (2θ) on peak positions. A monoclinic cell swas indicated by the DICVOL[8] and POWDER[9] indexing programs with high figures of merit. Since different programs employing various indexing strategies yielded the same results, the unit cell parameters obtained were taken as correct and were refined with a non-peak weighting scheme by APPELMAN[10] which yielded a = 5.19(3), b = 8.59(5), c = 29.35(5) Å and β = 89.40(2)°. The space group $A2/a$ (no. 15) was unambiguously determined from systematic absences: $k + l = 2n$ (hkl) and $h + l = 2n$ ($h0l$). Peak intensities were altered by changing the method of sample preparation indicating the occurrence of preferred orientation effects. Scanning electron microscopic observations of crystal morphology showed that the crystalline material consists of 10–15 μm platelet single crystals likely to produce orientation effects. In order to reduce preferred orientation effects the side-loading technique was used. The program EXTRA[11] was used to extract structure factor amplitudes of 439 reflections occurring in the 2θ interval measured by the LeBail method.[12] At this stage, the following refined unit cell parameters were obtained: a = 5.187, b = 8.582, c = 29.239 Å and β = 89.49°.

In the absence of heavy atoms, the crystal structure was solved by direct methods using the program SIRPOW optimised for powder data.[13] Structure factors of 254 (excluding the first and several other high-angle overlappings) reflections were used. The solution of the crystal structure was performed in absence of reliable data on the chemical composition of the compound, its density and unit cell contents. This resulted in the

Table 1 Atomic coordinates and isotropic thermal parameters for $Na_3(Na,H)Ti_2O_2[Si_2O_6]_2{\cdot}2H_2O$

Atom	Site	*x*	*y*	*z*	*B*/Å²
Ti	8f	0.580(3)	0.4127(5)	0.1686(4)	0.5
Na(1)	8f	0.113(5)	0.193(2)	0.1649(9)	1.6
Na(2)	4e	3/4	0.357(5)	0	2.5
Na(3)	4e	1/4	0.037(6)	0	1.6
Si(1)	8f	0.241(1)	0.414(1)	0.2705(6)	0.6
Si(2)	8f	0.597(5)	0.108(1)	0.0928(7)	0.7
O(1)	8f	0.538(7)	−0.031(8)	0.2085(8)	0.8
O(2)	8f	0.723(9)	0.260(2)	0.2108(10)	0.8
O(3)	8f	0.516(5)	0.254(3)	0.1257(10)	0.8
O(4)	8f	0.547(6)	0.117(4)	0.0392(7)	0.8
O(5)	8f	0.922(4)	0.393(2)	0.1523(8)	0.8
O(6)	8f	0.878(6)	0.029(5)	0.1055(7)	0.8
O(7)	8f	0.280(6)	0.460(4)	0.2172(5)	0.8
Ow	8f	0.052(5)	0.407(2)	0.05223(11)	2.5

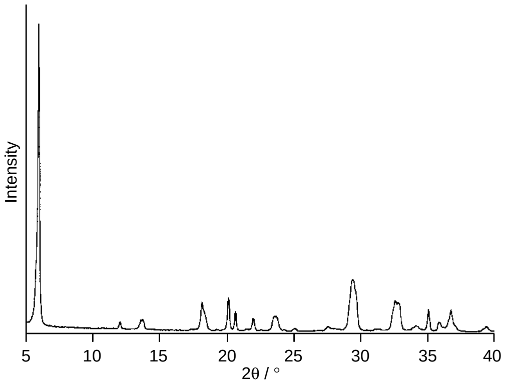

Fig. 1 X-Ray diffraction pattern of AM-4 recorded with Cu-Kα radiation (this was not the data used for structure refinement which was recorded with Co-Kα radiation)

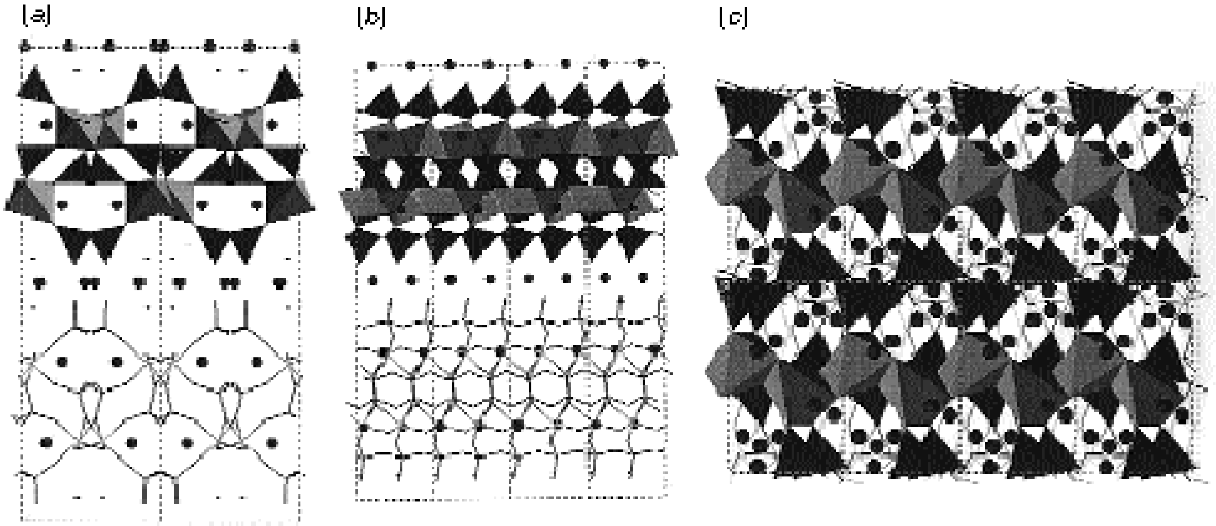

Fig. 2 Structure of AM-4: (*a*) viewed down [100] showing the small cages containing sodium cations within the titanosilicate layers and further sodium cations between the layers; (*b*) viewed down [010]; (*c*) viewed down [001] showing chains of edge-sharing TiO_6 octahedra connected by chains of corner-sharing SiO_4 tetrahedra

need to vary the unit cell contents and the default settings of SIRPOW. Most atoms were located simultaneously, however, relabelling of atoms was necessary coupled with bond distance and bond angle changes. This procedure was alternated with least-squares refinement.

The coordinates of atoms obtained from direct methods were used in the Rietveld refinement of the structure by GSAS and are given in Table 1.[14] The final profile analysis refinement was carried out in the range 2θ 13–70° and involved the following parameters: structural, 42 atomic coordinates, 14 isotropic temperature factors; profile, one scale factor, three halfwidth, three cell parameters, one peak asymmetry parameter; global parameters, one zero point, six coefficients of polynomial background. Because of instability of the peak shape coefficients several soft constraints to some of the bond distances were applied. The final results of the refinement fit correspond to a satisfactory model of the crystal structure, [$R(F^2$ = 4.5%] and profile factors (R_p = 6.8%, wR_p = 9.4%) indicators: space group $A2/a$ (no. 15), a = 5.2012(8), b = 8.573(2), c = 29.300(6) Å, β = 89.26(1)°, U = 1306.4(4) Å^3, Z = 4, D_c = 2.74 g cm^{-3}, atoms in the asymmetric unit 14, relative mass of cell 2224.38. The experimental X-ray diffraction pattern for AM-4 is shown in Fig. 1.

The crystal structure of AM-4 is built from TiO_6 octahedra and SiO_4 tetrahedra which form layers perpendicular to [001]. Each layer consists of a five-tier sandwich of $Si_T : Ti_O : Si_T : Ti_O$-$Si_T$ (O = octahedral, T = tetrahedral) and this can be seen in Figs. 2(*a*) and (*b*). Between the layers are Na^+ cations and water molecules. Sodium cations also exist in small cages within the layers.

The major features of the structure are zigzag chains of edge-sharing TiO_6 octahedra running along [100] which are connected together by corner sharing pyroxene type SiO_4 tetrahedra, Fig. 2(*c*). Within the titanate chains the Ti···Ti cation repulsion is manifested in a shifting of the Ti by *ca.* 0.1 Å from the centre of the octahedron away from the shared edge. Consequently, Ti–O distances in the Ti octahedra vary widely, ranging from 1.841 Å in the oversaturated Ti–O(5) bond to 2.138 Å in the undersaturated Ti–O(7) bond. Such distortions from the average value of 1.969 Å have been observed in many so-called 'shared structures' and it produces a shortening of the shared edge O(5)···O(7) to 2.387 Å and an elongation of the opposite edge. Similar octahedral distortions take place in the structure of mineral vinogradovite.[15] The two one-dimensional and independent pyroxene-type $[Si_2O_6]$ chains are also present in the structure of vinogradovite. The Si(1)–O(non-bridging) bonds are shorter than the Si(1)–O(bridging) bonds, and the O(2)–Si(1)–O(7) angle, with its two non-bridging oxygen atoms, is much larger (122.7°) than other angles.

In conclusion, we report the successful synthesis and structural determination of a novel layered titanosilicate, AM-4, which may have applications in heterogeneous catalysis, adsorption, molecular sieving and cation exchange. Work is in progress to determine whether such layered materials can be pillared in a similar manner to smectite clays.

Footnotes and References

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† *Crystal data for AM-4*: $Na_3(Na,H)Ti_2O_2[Si_2O_6]_2\cdot 2H_2O$, space group $A2/a$, a = 5.2012(8), b = 8.573(2), c = 29.300(6) Å, β = 89.26(1)°, U = 1306.4(4) Å^3, Z = 4, D_c = 2.74 g cm^{-3}, atoms in asymmetric unit 14, rel. mass of cell 2224.38, Co-Kα radiation (1.799 Å). Intensity data for h,k,l were collected by the step counting method (step 0.01° and time 30 s) in the angular range 2θ 5–100°.

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