

Crystal Structure of a New Natural (Na,Mn,Ti)-Phyllosilicate

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Abstract—The crystal structure of a new natural (Na,Mn,Ti)-phyllosilicate, $(\text{Na}_{0.80}\text{K}_{0.45})\text{Na}_5\text{Mn}^{2+}(\text{Ti}_{0.75}\text{Nb}_{0.25})[\text{Si}_{10}\text{O}_{24}(\text{OH})](\text{O},\text{OH})(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, is determined (Syntex P1 automated diffractometer, 1881 reflections, a heavy-atom method, anisotropic approximation, and $R = 6.6\%$). The unit-cell parameters are: $a = 13.033(6)$, $b = 18.717(9)$, $c = 12.264(6)$ Å; $\beta = 99.62(4)^\circ$; sp. gr. $I2/m$, and $Z = 4$, $d_{\text{exp}} = 2.42$, and $d_{\text{calc}} = 2.43$ g/cm³. The structure of the mineral contains silicon–oxygen layers parallel to (100), in which five-, six-, and eight-membered rings of Si-tetrahedra can be recognized. The layers are bound along [001] by the bands consisting of Na,Mn,Ti-octahedra to form a framework. The way of linking of the tetrahedral and octahedral building blocks into a new mineral structure allows one to assign it to the band-layered silicates.

A new natural alkali titanosilicate of Na and Mn was discovered by A.P. Khomyakov in pegmatoid-hydrothermal formations of the ultra-agpaitic type (the town of Aluaiv of the Lovozero alkaline massif).¹ The mineral was found in the form of grains of irregular shape, 1–2 mm in size, in the axial zone of an ussingite veinlet, together with makatite and serandite. The mineral is bright yellow and in some places pinkish in color; it has a glassy to oily look, a steplike fracture, a weakly defined (100) cleavage plane, its hardness is 3–4, and its measured density is 2.42 g/cm³. The results of X-ray microprobe analysis (H_2O was taken by weight-loss upon annealing) conform to the empirical formula $(\text{Na}_{5.84}\text{K}_{0.42})\Sigma_{6.26}(\text{Mn}_{0.94}\text{Fe}_{0.04}\text{Ca}_{0.02}) \cdot (\text{Ti}_{0.75}\text{Nb}_{0.25})\text{Si}_{10}\text{O}_{24.5}(\text{OH})_{3.5} \cdot 4 \cdot 5\text{H}_2\text{O}$.

An idealized composition is $\text{Na}_6\text{Mn}(\text{Ti},\text{Nb})\text{Si}_{10}(\text{O},\text{OH})_{28} \cdot 4\text{H}_2\text{O}$ or $\text{Na}_6\text{MnTiSi}_{10}\text{O}_{24}(\text{OH})_4 \cdot 4\text{H}_2\text{O}$. The Na, Ti, and Nb contents vary markedly from grain to grain, with the Na and Nb contents directly proportional and the Ti and Nb contents inversely proportional. As compared with the ideal formula $\text{Na}_6\text{MnTiSi}_{10}\text{O}_{24}(\text{OH})_4 \cdot 4\text{H}_2\text{O}$, the real composition exhibits essential (~25%) Ti substitution by Nb as well as an excessive number of alkali cations entering the mineral (~0.25 atoms per formula unit) according to the probable scheme: $\text{TiO}_2 = \text{NaNb}(\text{OH})_6 \cdot 1 - 2\text{H}_2\text{O}$. This can be accounted for by high supersaturation of the flux by alkaline, volatile and rare elements characteristic of residual differentiates of ultra-alkaline magmas [1].

A single crystal $0.075 \times 0.150 \times 0.225$ mm in size was taken for the X-ray structure study. The dimensions

and symmetry of a monoclinic (Laue class $2/m$) unit cell [$a = 13.033(6)$, $b = 18.717(9)$, $c = 12.264(6)$ Å; $\beta = 99.62(4)^\circ$; and $V = 2950(2)$ Å³], determined by A. Roberts using Laue and oscillation methods, were refined on an automated P1 Syntex diffractometer (MoK_α -radiation, flat graphite monochromator). The experimental data set—the intensities of 1977 non-equivalent nonzero reflections [$I \geq 1.96\sigma(I)$ —was obtained by the $2\theta : \theta$ method with a variable scan speed of 4–24 deg/min on the same diffractometer ($\sin\theta/\lambda \leq 1.064$ Å^{–1}). The transformation of intensities into $|F_{hkl}|$ without allowing for absorption ($\mu_{\text{r}}^{\text{max}} = 0.14$) and all subsequent calculations were performed with a special computing system E-XTL Syntex. An analysis of the systematic absences among hkl reflections with $h + k + l = 2n$ indicated three possible space groups: $I2/m$, $I2$, and Im . The structure was solved by the heavy-atom method. The three-dimensional Patterson function allowed us to localize the Mn and Ti atoms. The remaining Si, Na, and O atoms were located from successive electron density syntheses.

The derived model was refined within the centrosymmetric sp. gr. $I2/m$ by the full-matrix least-squares procedure until $R_{hkl} = 8.4\%$ in the isotropic and $R_{hkl} = 6.6\%$ in the anisotropic approximation ($R_w = 7.1\%$, $s = 1.49$). The mineral composition determined by the structure analysis looks like: $(\text{Na}_{0.80}\text{K}_{0.45})\text{Na}_5\text{Mn}^{2+}(\text{Ti}_{0.75}\text{Nb}_{0.25})[\text{Si}_{10}\text{O}_{24}(\text{OH})](\text{O},\text{OH})(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ($Z = 4$; $d_x = 2.43$ g/cm³). Attempts to refine the same model within the acentric space groups resulted in a significant increase in the reliability factors and unacceptable values of the Si–O interatomic distances. The coordinates of the basis atoms and corresponding interatomic distances are listed in

¹ The papers necessary to approve this silicate as a new mineral have been submitted to the Commission for New Minerals and Mineral Names of the International Mineralogical Association.

Table 1. Coordinates of the basis atoms and thermal parameters in the structure of (Na,Mn,Ti)-phyllosilicate

Atom	Position multiplicity	x/a	y/b	z/c	$B_{eq}, \text{\AA}^2$
Mn	4	0.5	0.5859(1)	0	1.02(5)
(Ti, Nb)	4	0	0.0842(1)	0	2.21(6)
Si(1)	8	0.2299(2)	0.0818(1)	0.1436(2)	0.72(5)
Si(2)	8	0.6973(2)	0.4179(1)	0.2005(2)	0.52(5)
Si(3)	8	0.7188(2)	0.6853(1)	0.0202(2)	0.62(5)
Si(4)	8	0.1745(3)	0.3084(2)	0.1869(2)	1.73(8)
Si(5)	8	0.7929(2)	0.1602(1)	0.0741(2)	0.66(5)
Na(1)	4	0	0.2581(4)	0	2.8(2)
Na(2)	4	0.0309(3)	0.1695(2)	0.2567(3)	1.6(1)
Na(3)	4	0.9745(5)	0	0.7478(5)	1.4(1)
Na(4)	4	0.5	0.2283(4)	0	4.0(3)
(Na, K) 5	4	0.6929(8)	0	0.5554(8)	6.3(2)
(Na, K) 6	4	0.6253(8)	0	0.0634(7)	4.3(3)
O(1)**	4	0.9292(9)	0	0.0631(9)	1.9(3)
O(2)	4	0.2744(8)	0	0.1452(9)	1.4(3)
O(3)*	4	0.913(1)	0	0.542(1)	3.3(4)
O(4)	8	0.1086(5)	0.0866(3)	0.1441(6)	1.3(2)
O(5)	8	0.5733(5)	0.4106(3)	0.1640(5)	0.9(2)
O(6)	8	0.3975(6)	0.3306(4)	0.0367(6)	1.8(2)
O(7)	8	0.9163(5)	0.1641(4)	0.0723(6)	1.4(2)
O(8)	8	0.2663(5)	0.1199(4)	0.0379(6)	1.4(2)
O _w (9)	8	0.554(1)	0.2049(8)	0.188(1)	7.4(4)
O(10)	8	0.7626(5)	0.1135(4)	0.1761(5)	1.2(2)
O(11)	8	0.1953(6)	0.3165(4)	0.0612(6)	1.6(2)
O(12)	4	0.2403(7)	0	0.7035(8)	0.8(2)
O(13)*	4	0	0.400(1)	0	10.0(5)
O(14)	8	0.2974(7)	0.1150(4)	0.2530(6)	2.2(2)
O(15)	8	0.7593(5)	0.3746(4)	0.1159(5)	1.0(2)
O(16)	8	0.7319(6)	0.2354(4)	0.0794(6)	1.6(2)
O(17)	4	0.75	0.25	0.75	8.5(6)
O(18)**	8	0.0565(9)	0.2943(6)	0.1823(9)	6.7(3)
O _w (19)	4	0.5	0.1028(7)	0	9.9(5)
O _w (20)	4	0.582(1)	0	0.688(1)	5.9(5)

Note: (Ti, Nb) = (Ti_{0.75}Nb_{0.25}), (Na, K)(5) = (Na_{0.25}K_{0.25}), (Na, K)(6) = (Na_{0.55}K_{0.20}).

* Oxygen atoms of the H₂O molecules.

** Oxygen atoms partly substituted by OH-groups.

Tables 1 and 2, respectively. Substitution of a part of the Ti atoms by Nb in the (Ti,Nb) position was established by refining the occupancy factor at fixed $B_{iso} = 0.5\text{--}0.7 \text{ \AA}^2$ followed by fitting mixed atomic scattering factors. The lowest value of the R -factor corresponds to the distribution of the Ti and Nb atoms in the ratio 0.75Ti to 0.25Nb. The suggestion that the Na and K atoms statistically enter two (Na,K)-positions was based on: (a) the chemical analysis data of the mineral; (b) a comparison of the experimental cation–oxygen

and cation–cation distances in the mineral structure with the theoretical distances characteristic of the K and Na polyhedra; and (c) refined values of the thermal parameters for the positions under consideration. A valence balance for the anions, as well as an analysis of lengths and directions of possible hydrogen bonds, allowed us to reveal the O atoms, OH groups, and H₂O molecules in the anionic part of the structure. Their presence was also corroborated by IR spectra, obtained by N.V. Chukanov. A strong absorption band in the

Table 2. Interatomic distances (Å) in the structure of (Na,Mn,Ti)-phyllosilicate

Mn-octahedron		(Ti, Nb)-octahedron		Na(1)-seven-vertex polyhedron	
Mn—O(3)	2.082(8) × 2	(Ti, Nb)—O(1)	2.043(7) × 2	Na(1)—O(7)	2.323(9) × 2
O(5)	2.079(6) × 2	O(4)	2.072(7) × 2	O(11)	2.756(8) × 2
O(6)	2.153(8) × 2	O(7)	2.130(7) × 2	O(13)	2.66(2)
				O(18)	2.33(1) × 2
	<2.105>		<2.082>		<2.497>
Na(2)-octahedron		Na(3)-octahedron		Na(4)-seven-vertex polyhedron	
Na(2)—O(4)	2.410(8)	Na(3)—O(1)	2.45(1)	Na(4)—O(6)	2.419(9) × 2
O(5)	2.339(8)	O(3)	2.52(1)	O(9)	2.34(1) × 2
O(6)	2.549(8)	O(4)	2.457(8) × 2	O(16)	3.020(8) × 2
O(7)	2.496(8)	O(5)	2.441(8) × 2	O(19)	2.35(2)
O(9)	2.74(2)				
O(18)	2.55(1)				
	<2.523>		<2.460>		<2.609>
(Na, K)(5)-eight-vertex polyhedron		(Na, K)(6)-eight-vertex polyhedron		Si(1)-tetrahedron	
(Na, K)(5)—O(3)	2.90(2)	(Na, K)(6)—O(2)	3.06(1)	Si(1)—O(2)	1.636(4)
O(20)	2.35(2)	O(8)	3.03(1) × 2	O(4)	1.584(8)
O(14)	3.17(1) × 2	O(10)	2.97(1) × 2	O(8)	1.620(7)
O(15)	3.28(1) × 2	O(12)	3.09(1)	O(14)	1.602(8)
O(13)	3.12(2) × 2	O(19)	2.56(2) × 2		
	<3.178>		<2.907>		<1.610>
Si(2)-tetrahedron		Si(3)-tetrahedron		Si(4)-tetrahedron	
Si(2)—O(5)	1.609(7)	Si(3)—O(6)	1.587(8)	Si(4)—O(11)	1.617(8)
O(10)	1.626(7)	O(11)	1.620(8)	O(14)	1.626(8)
O(12)	1.633(4)	O(15)	1.645(7)	O(17)	1.583(3)
O(15)	1.634(7)	O(16)	1.648(7)	O(18)	1.55(1)
	<1.626>		<1.625>		<1.595>
Si(5)-tetrahedron		Si—O—Si angles, deg			
Si(5)—O(7)	1.614(8)	Si(1)—O(2)—Si(1)	138.6(6)		
O(8)	1.642(7)	Si(5)—O(8)—Si(1)	135.5(5)		
O(10)	1.628(7)	Si(5)—O(10)—Si(2)	145.9(5)		
O(16)	1.623(7)	Si(4)—O(11)—Si(3)	145.9(5)		
	<1.627>	Si(2)—O(12)—Si(2)	140.3(5)		
		Si(1)—O(14)—Si(1)	140.6(5)		
		Si(3)—O(15)—Si(2)	131.1(4)		
		Si(3)—O(16)—Si(5)	141.2(5)		
		Si(4)—O(17)—Si(4)	179.9(2)		
			<144.3>		

range of 3600 cm⁻¹ corresponds to the main part (predominant by its amount) of the OH groups not involved with hydrogen bonding. The bands at 3390 and 3250 cm⁻¹ correspond to the OH groups that are connected by stronger bonds. The bands of smaller intensity in the ranges of 3400 and 1658 cm⁻¹ indicate the

presence in the structure of water molecules in a moderate amount (up to 3–4 H₂O molecules). The existence of a medium-intensity band (838 cm⁻¹) can most likely be accounted for by the (Si—OH) deformation vibrations (correct interpretation of this band becomes possible after warming the sample). Too high *B*_{eq} values for

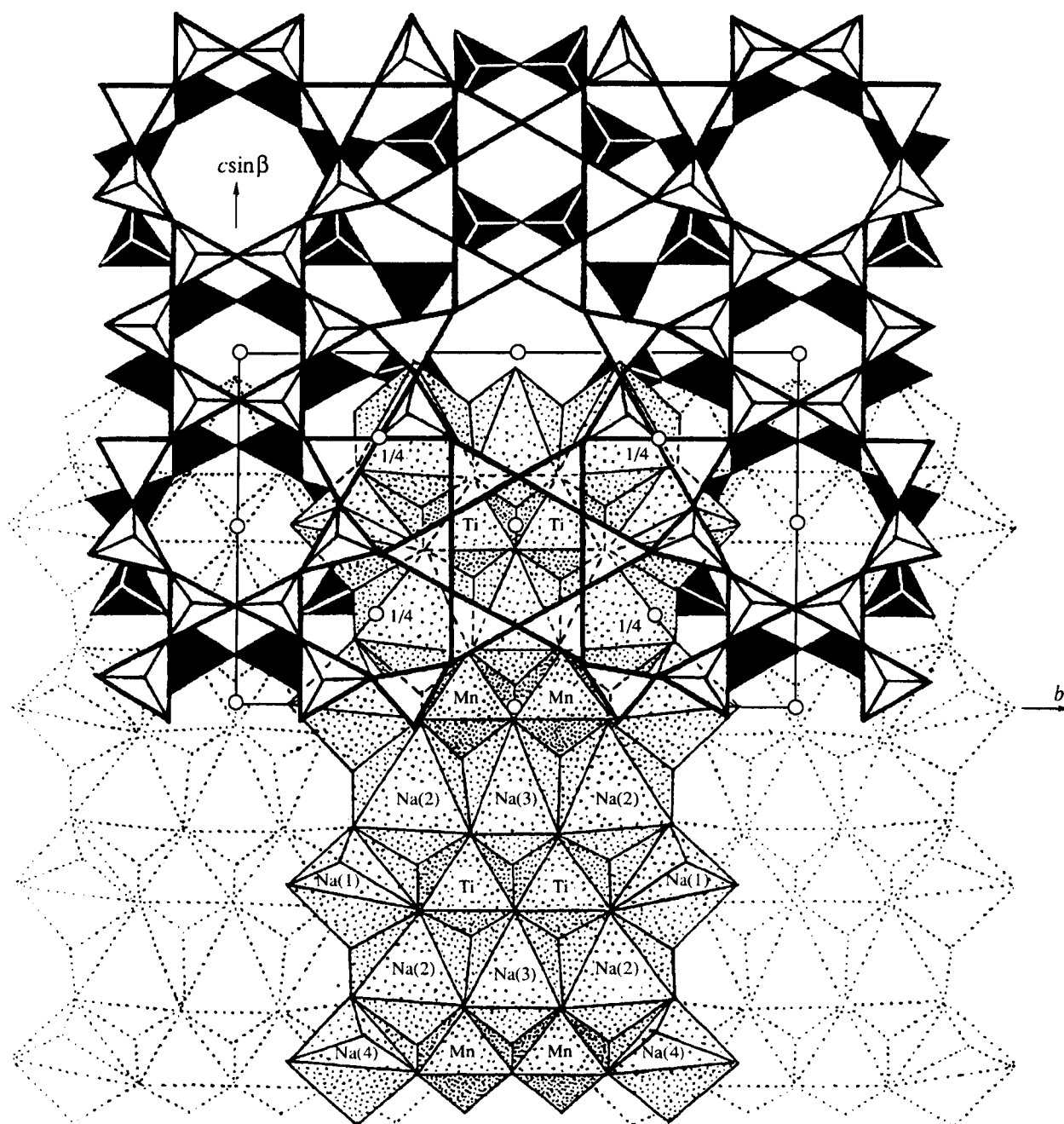


Fig. 1. The projection of the (Na,Mn,Ti)-phyllosilicate structure onto the yz plane.

some of the oxygen atoms located in the voids can be related to the strong anisotropy of thermal vibrations in the directions perpendicular to those of the chemical bonds. This fact did not allow us to locate the positions of the hydrogen atoms, and it accounts for the rather high value of the final reliability factor. To solve these problems, one should perform a low-temperature study of the mineral.

In the crystal structure of the silicate studied, the Mn and (Ti,Nb) atoms form octahedra with the Mn–O distances equal to 2.079–2.153 Å (the average is 2.105 Å) and the (Ti,Nb)–O distances equal to 2.043–2.130 Å

(the average is 2.082 Å). The Na atoms occupy octahedra with distances Na(2)–O equal to 2.339–2.735 Å (the average is 2.523 Å) and Na(3)–O, 2.441–2.517 Å (2.460 Å); and seven-vertex polyhedra with distances Na(1)–O, 2.323–2.765 Å (2.497 Å) and Na(4)–O, 2.335–3.020 Å (2.609 Å). Two (Na,K) positions have eight oxygen atoms as the nearest neighbors with distances (Na,K)(5)–O, 2.354–3.278 (3.178 Å) and (Na,K)(6)–O, 2.559–3.061 Å (2.907 Å). The Na–O_w distances fall in the category of shortened distances, which can be accounted for by intercationic interaction of the Na–O–Si type. In the tetrahedral environment of

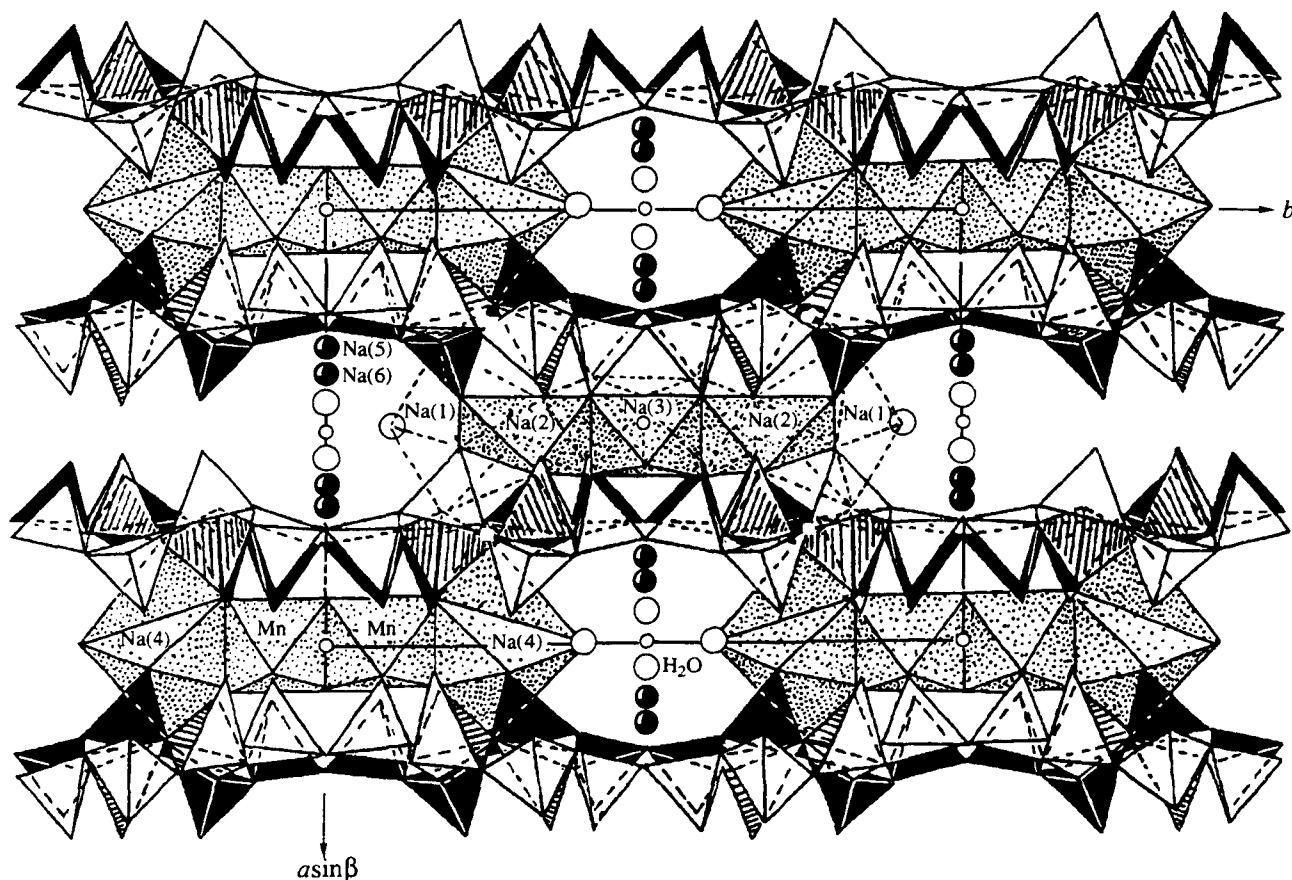


Fig. 2. The projection of the (Na,Mn,Ti)-phyllosilicate structure onto the xy plane. The end planes of octahedral (Mn,Ti,Na)-bands are arranged in a staggered mode. The (Na,K) cations and H_2O molecules are seen in the channels along the c -axis. The (Si,O) tetrahedra located at different levels along the c -axis are hatched in different ways.

each of the five Si atoms (the average Si–O distances are 1.595–1.627 Å), the distances between the central atom and the oxygen atoms of the apical vertices are also shortened (Table 2).

The structure of the mineral contains, parallel to (100) layers of the (Si,O), tetrahedra bound into a unified framework by the octahedral Na,Mn,Ti(Nb) bands, which run in the direction of the c -axis of a unit cell (Fig. 1). There are three-layered blocks (T – O – T) formed in the structure, due to different (polar) orientations of the apical vertices of the Si tetrahedra in the layer. Each of the blocks is formed by an octahedral core band (O) framed by a (Si,O) tetrahedra (T) on both sides. The projections of the ends of these packs onto the xy -plane are staggered, resembling a similar projection of the amphibole structures (Fig. 2). Tetrahedral chains $[Si_5O_{15}]^{10-}$ extended along the c -axis of the unit cell can be considered as building blocks of a silicon–oxygen layer. The condensation of these chains in the [010] direction by reflection in the m_y -mirror plane results in the formation of the $[Si_{10}O_{28}]^{16-}$ bands composed of alternating six- and eight-membered rings of the Si tetrahedra. Through the inversion cen-

ters, the (Si,O)-bands unite into a layer, with five- and six-membered rings formed between the bands. According to F. Liebau [2], the structural formula of a new layered (Si,O)-complex in the studied structure can be presented as $\{UB, 1^2_\infty\}[^5Si_{10}O_{25}]^{10-}$.

The core part of three-layered blocks is constituted by the pairs of the Ti and Mn octahedra connected through common edges. These pairs alternate at intervals of half T_z translation, and are in contact with Na seven-vertex polyhedra. They are integrated into a band by triplets of Na-octahedra, which are also connected through common edges. In this case, each pair of Ti octahedra in the block is sandwiched between overlying and underlying six-membered rings of the (Si,O)-layer, and a pair of Mn octahedra is sandwiched between similar eight-membered rings. In the channels of the structure extended along the above-described blocks are arranged large (Na,K) cations and the H_2O molecules. The way of linking tetrahedral (T) and octahedral (O) units (T – O – T) in the structure of a new silicate allows one to assign it to the band-layered silicates, such as sepiolite $Mg_8Si_{12}O_{30}(OH)_4 \cdot 10H_2O$ [3] and

palygorskite $\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ [4], whose structures are also made up of the (T–O–T) units.

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