

The crystal structure of a new natural sodium titanosilicate

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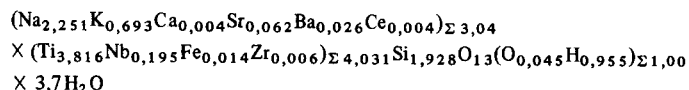
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(Presented by Academician V. A. Zharikov, March 25, 1988)

(Submitted March 26, 1988)

Dokl. Akad. Nauk SSSR 307, 114-117 (July 1989)

A new natural sodium titanosilicate with the empirical chemical formula



was found by Yu. P. Men'shikov in a study of the of the Khibinskii alkaline massif.

The parameters of the tetragonal unit cell were determined by the Laue and oscillation methods, and refined on a Syntex P1 automatic diffractometer: $a = 7.819(2)$, $c = 12.099(4)$ Å, $V = 735.4(4)$ Å³. The experimental material for the structure determination consisted of the intensities of 334 independent nonzero ($I \geq 1.96 \sigma I$) reflections (max $\sin \theta / \lambda = 0.992$ Å⁻¹), recorded using MoK α radiation and a crystal with linear dimensions $0.063 \times 0.035 \times 0.030$ mm by the ($2\theta: \theta$) method at a varying scanning rate of 2-24° per min on the same automatic diffractometer. The change from intensities to $|F_{hkl}|$ without allowance for absorption ($\mu_{\text{rmax}} = 0.17$) was carried out using the INEXTL specialized computing system. The systematic absences of the reflections indicated two space groups, $P4_2/mcm$ and $P4_2$ cm.

The structure of the mineral was determined by the direct method for the first space group, of higher symmetry, using the system of programs AREN.¹ The fragment of the structure obtained was studied by an automatic procedure for refining the phases of the structure factors,² which made

it possible to obtain the positions of all the basis atoms after five iterations. The refinement of the structure and all the calculations were carried out using the same system of programs.

The IR spectroscopic data showed that the structure of the mineral contains H₂O molecules and OH groups. A calculation of the local balance of valence forces at the anions, carried out by the published method,³ showed that fourfold positions are occupied by the O₁ of H₂O molecules and the O₂ of hydroxide groups (in the ratio O:OH = 1:1). The remaining H₂O molecules and the K atoms were located from a series of difference electron density syntheses, calculated with a correction for the termination of the Fourier series, in six positions with low populations: O₅-O₈ and K₁₋₂, respectively. The O₈ position, situated at distances of 2.56-2.82 Å from the basis atoms O₁ and O₄, may be occupied not only by H₂O but also by Na atoms (0.55 H₂O + 0.22 Na), in agreement with the chemical analysis data.

The refinement of the structural model obtained for the mineral with allowance for the filling of the positions O₅₋₈ and K₁₋₂ ($\text{K}_{1,38}\text{Na}_{0,22} \cdot 3.41 \text{H}_2\text{O}$) lowered R_{hkl} to 6.4% in the isotropic approximation and to 4.0% in the anisotropic approximation. The coordinates, the isotropic temperature factors of the basis atoms, and the interatomic distances in the structure of the mineral are given in Tables I and II.

The titanium atoms (Ti_{0,95}Nb_{0,05}) are situated in regular oxygen octahedra, one vertex (O₂) of

TABLE I. Coordinates and Isotropic Temperature Factors (Å²) in the Structure of the New Natural Sodium Titanosilicate

| Atom | Multiplicity of the position | Filling factor | x/a | y/b | z/c | B _{iso} |
|------------------------------------|------------------------------|----------------|------------|------------|------------|------------------|
| Ti | 8 | 8 | 0,1387 (1) | 0,1387 (1) | 0,6535 (1) | 0,62 (2) |
| Si | 4 | 4 | 0 | 0,5 | 0,25 | 1,04 (5) |
| Na | 4 | 4 | 0 | 0,5 | 0 | 3,3 (1) |
| O ₁ (H ₂ O) | 4 | 4 | 0,269 (1) | 0,269 (1) | 0 | 3,4 (2) |
| O ₂ | 4 | 4 | 0,1426 (8) | 0,1426 (8) | 0,5 | 1,0 (1) |
| O ₃ | 8 | 8 | 0,1142 (5) | 0,1142 (5) | 0,1723 (4) | 1,2 (1) |
| O ₄ | 16 | 16 | 0,1195 (5) | 0,3828 (5) | 0,6700 (2) | 1,3 (1) |
| O ₅ (H ₂ O) | 2 | 1,67 | 0,5 | 0,5 | 0,25 | 4,7 (5) |
| O ₆ (H ₂ O) | 4 | 0,40 | 0,5 | 0,5 | 0,31 (2) | 6,6 (3,0) |
| O ₇ (H ₂ O) | 8 | 0,79 | 0,478 (4) | 0,478 (4) | 0,421 (5) | 6,4 (3,0) |
| O ₈ (H ₂ O)* | 8 | 0,77 | 0,42 (1) | 0,42 (1) | 0,161 (8) | 4,4 (3,0) |
| K ₁ | 4 | 0,77 | 0,398 (3) | 0,398 (3) | 0,5 | 5,1 (6) |
| K ₂ | 8 | 0,61 | 0,463 (5) | 0,463 (5) | 0,372 (3) | 6,7 (3,0) |

* (H₂O)_{0,55} Na_{0,22}.

TABLE II. Interatomic Distances (Å) in the Structure of the New Natural Sodium Titanosilicate

| Ti-octahedron | | Na-octahedron | |
|---------------------|-----------|-----------------------|-----------|
| Ti-O ₂ | 1,858 (1) | Na-O ₁ (2) | 2,772 (8) |
| O ₃ (2) | 2,000 (4) | O ₄ (4) | 2,438 (3) |
| O ₁ | 2,125 (5) | Average | 3,549 |
| O ₄ (2) | 1,925 (4) | (O-O) _{av} | 3,528 |
| Average | 1,972 | Si-tetrahedron | |
| (O-O) _{av} | 2,771 | Si-O ₄ (4) | 1,628 (3) |
| | | (O-O) _{av} | 2,658 |

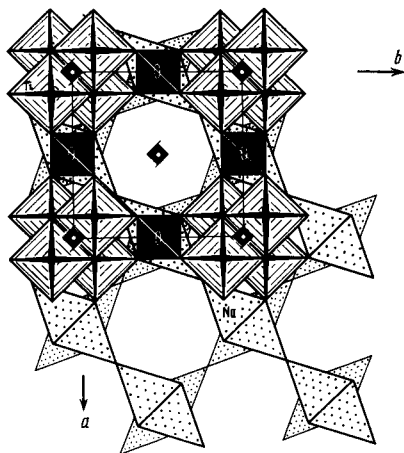


FIG. 1. The xy projection of the structure of the new natural sodium titanosilicate.

which is occupied randomly by (OH) groups and O atoms. $(\text{Ti}-\text{O})_{\text{av}} = 1.972 \text{ \AA}$, and the lengths of the O-O edges vary from 2.912 Å to 2.526 Å. Four Ti-octahedra, joined by shared shortened edges (2.593-2.526 Å) form clusters with the composition $[\text{Ti}_4\text{O}_{12}(\text{O}, \text{OH})_4]$, which in turn are joined through shared vertices O₂ to form columns $[\text{Ti}_4\text{O}_{12}(\text{O}, \text{OH})_2]_{\infty}$ along the 4₂ axes that pass through the origin of coordinates of the unit cell (Figs 1 and 2a). The translationally identical columns are joined by $[\text{SiO}_4]$ ortho-tetrahedra (Si-O = 1.628 Å and O-O = 2.617-2.691 Å) to form a mixed Ti-Si framework. Chains of distorted Na-octahedra can be distinguished along the $[110]$ and $[\bar{1}\bar{1}0]$ diagonals of the cell of the mineral. Four O atoms (O₄) of the Na-octahedron are separated from the central cation by 2.438 Å, and two vertices, occupied by H₂O molecules (O₁) through which the Na octahedra are connected in chains, are separated by 2.772 Å. Analysis of the interatomic distances from O₁ to the nearest anions indicates that hydrogen bonds may be formed in the direction of two O₃ atoms of neighboring clusters of a Ti column (O₁-O₃ = 2.697 Å). The Na octahedra and Si tetrahedra, which are joined through shared edges shortened to 2.617 Å, alternate along the 2_z axis (Fig. 2b).

An interesting feature of the structure of the mineral is the presence of zeolitic channels with a cross section of ~5 Å, which extend along the 4₂ axis at the center of the cell. The H₂O molecules of the Na polyhedra, which are related by the 4₂ axis, form the framework of the channel, occupying a tetrahedral arrangement in it. In the channel itself, K atoms and H₂O molecules are situated on the 4₂ axis and in a general position. The proximity

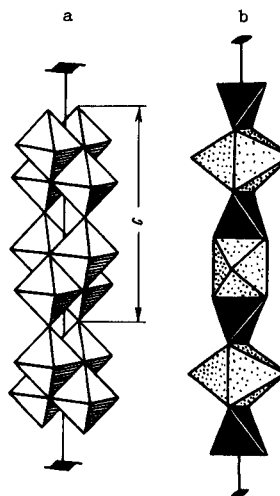
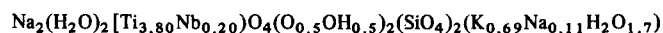


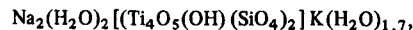
FIG. 2. Fragments of the structure of the new natural sodium titanosilicate. a) A new type of column of Ti octahedra $[\text{Ti}_4\text{O}_{12}(\text{O}, \text{OH})_2]_{\infty}$; b) alternating Si tetrahedra and Na octahedra along a 2_z axis.

of these positions (0.5-1.7 Å) indicates that they are occupied randomly.

From the x-ray structural and chemical analysis data the crystal-chemical formula of the mineral being studied can thus be written in the form



(space group $P4_2/mcm$, $Z = 2$, $d_{\text{calc}} = 2.80 \text{ g/cm}^3$, $d_{\text{expt}} = 2.78 \text{ g/cm}^3$); the idealized formula is



where the square brackets distinguish the framework part of the structure.

Since the titanosilicate is optically biaxial (angle $2V \sim 10-11^\circ$), its structure was also refined in the orthorhombic space group $Pcc2$. With comparable R-factors, this lowering of the symmetry led to a decrease in the number of independent reflections corresponding to each parameter being refined, and to unsatisfactory values of the thermal corrections of some of the O atoms of the framework (negative or almost zero values). It can be assumed, however, that the symmetry decreases to an orthorhombic symmetry in specimens with a higher concentration of "heavy" impurity Nb atoms with an ordered distribution in two octahedral Ti positions. In this specific case, the anomalous biaxial character is apparently related to a local lowering of the symmetry with filling of the channel by K atoms and H₂O molecules. A similar phenomenon is observed in the structure of eudialite,⁴ in which the filling of the "zeolite" cavity by various cations is not consistent with the threefold axis (space group $R3m$), and is also apparently responsible for the anomalous biaxial character of the mineral with the small angle $2V = 16^\circ$.

The structure of the mineral being studied has features similar to those of various natural and synthetic compounds. Similar clusters of four octahedra have been found in the crystal structures of Na $[\text{Ge}_4\text{O}_4(\text{GeO}_4)(\text{GeO}_3)]$ ($a = 14.99$, $c = 7.381 \text{ \AA}$, space group $J4_1/a$, $Z = 4$),⁵ pharmacosiderite $[\text{Fe}_4(\text{OH})_4(\text{AsO}_4)_3] \cdot 5\text{H}_2\text{O}$ ($a = 7.9816 \text{ \AA}$, space group $P43m$, $Z = 1$),⁶ and the Ge-zeolite $[\text{Ge}_4\text{O}_4(\text{GeO}_4)] \cdot \text{KH}_3(\text{H}_2\text{O})_3$ ($a = 7.707 \text{ \AA}$, space group

space group $P\bar{4}3m$, $Z = 1$).⁷ In sodium germano-germanate, isolated $[\text{Ge}_4\text{O}_{16}]$ clusters are joined through Ge-ortho-tetrahedra to form columns $[001]-[\text{Ge}_5\text{O}_{16}]_\infty = [\text{Ge}_4\text{O}_{12}(\text{GeO}_4)]_\infty$, which in turn are joined by parallel meta-chains $[\text{Ge}_4\text{O}_{12}]_\infty$ to form a three-dimensional framework. In the titanosilicate being considered, mixed columns $[\text{Ti}_4\text{O}_8(\text{O}, \text{OH})_4(\text{SiO}_4)]_\infty$, with the same configuration as in sodium germano-germanate, are detected along the two directions $[100]$ and $[010]$ (Fig. 1).

In the structures of pharmacosiderite and the Ge-zeolite, however, similar chains are formed in three mutually perpendicular directions. These chains identical framework zeolite structures which differ only in the filling of the cation polyhedra and the large channel cavities. In pharmacosiderite, the octahedra are occupied by Fe^{3+} , the tetrahedra are occupied by As^{5+} , and the channels are occupied by H_2O molecules, and in the Ge-zeolite the cation positions are occupied by Ge^{4+} , and the channels by K^+ atoms and $(\text{H}_3\text{O})^+$ groups.

Thus all the structures which are considered contain as stable fragment a column of four octahedral clusters joined by ortho-tetrahedra $[\text{A}_4\text{O}_{12}(\text{BO}_4)]_\infty$, where $\text{A} = \text{Ge}^{4+}, \text{Fe}^{3+}, \text{Ti}^{4+}$, and $\text{B} = \text{Ge}^{4+}, \text{As}^{5+}, \text{Si}^{4+}$, corresponding to a unit cell

parameter of about 7.4-7.9 Å. It is only in the sodium titanosilicate being studied, however, that a new type of column $[\text{Ti}_4\text{O}_{12}(\text{O}, \text{OH})_2]_\infty$ consisting only of octahedra is formed.

The authors thank E. P. Zhelezin for assistance with the experiments, and A. P. Khomyakov for a discussion of the results.

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Translated by D. A. Paterson

Neutron-diffraction study of the atomic structure of $\text{Bi}_{12}(\text{V},\text{Bi})\text{O}_{20+x}$ single crystals

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(Presented by Academician B. K. Vainshtein, July 26, 1989)
(Submitted July 17, 1988)

Dokl. Akad. Nauk SSSR **307**, 606-610 (July 1989)

The unique physical properties and the expanding application in technology of crystals with the sillenite structure^{1,2} $\text{Bi}_{12}\text{MO}_{20}$ make the problem of precision structural study of these compounds a timely one. At present, the major problem reduces to establishment at the atomic level of the mechanisms for the unusually broad isomorphism with respect to the cation M in these crystals. In sillenites, the M position can be occupied statistically by cations with sharply differing ionic radii. The second problem is connected with the prevalent view in the literature that the valency of the cation or the "average" valency of an isomorphous mixture of cations in the M position in sillenites should always be equal to 4, for example, $\text{M} = \text{Si}, \text{Ge}, \text{Ti}$ (Refs. 3-5) or $\text{M} = (\text{Fe}_{1/2}^{3+} \text{Bi}_{1/2}^{5+}); (\text{Bi}_{2/3}^{5+} \text{Zn}_{1/3}^{2+})$ (Ref. 6). In a neutron-diffraction study⁷ of the compounds $\text{Bi}_{12}(\text{Ga}_{1/2}^{3+} \text{Bi}_{1/2}^{5+})\text{O}_{19.50}$, it was first proved that the M positions are occupied by trivalent cations and that there are oxygen defects in the structure.

The object of this study, with initial chemical formula $\text{Bi}_{12}(\text{V}_{0.5}\text{Bi}_{0.5})\text{O}_{20}$, attracted our attention because the linear relationship between the cubic unit cell parameter and the average ionic radius of the M cation, established in Refs. 8 and

9 for sillenites, breaks down for this compound to a great extent.

The expected value of the parameter $a_0 = 10.21$ Å differs significantly from the measured value $a = 10.247(8)$ Å. There is also a discrepancy between the pycnometric density $\rho_p = 8.89 \text{ g}\cdot\text{cm}^{-3}$ (Ref. 9) and the density $\text{Bi}_{12}(\text{V}_{0.5}\text{Bi}_{0.5})\text{O}_{20}$ $\text{g}\cdot\text{cm}^{-3}$ of the single crystals calculated from the composition $\rho_c = 9.13$.

We chose neutron diffraction as the method for structural study of V-sillenite; in this case, neutron diffraction has advantages over x-ray diffraction analysis. The weak absorption of radiation in the sample and the closeness of the scattering powers of the neutrons in the Bi and O nuclei allow us to reliably establish the structural parameters of the O atoms, while the difference in the signs of the scattering powers of the Bi and V nuclei makes it possible to determine to high accuracy the percentage content of these cations at the tetrahedral M position of the structure. The single crystals of V-sillenite were grown by the hydrothermal-synthesis method. The neutron-diffraction experiment was carried out using the VVRTs water-moderated water-cooled nuclear reactor of the