Crystallography

Crystal structure of $Na_{11}Nb_2TiSi_4P_2O_{25}F$

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A natural phase from the Lovozersk region with the approximate formula

$$Na_{10+m}(Ti, Nb)_{4-n}P_2Si_4O_{25}F,$$
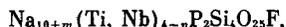
where m and n are small fractional numbers, was reported by A. P. Khomyakov[1] in 1971. Triclinic symmetry and the following lattice parameters were established by a Laue goniometric method: $a = 5.53 \pm 0.02$; $b = 7.16 \pm 0.03$; $c = 14.55 \pm 0.06$ Å; $\alpha = 94.5° \pm 0.5$; $\beta = 96° \pm 0.5$; $\gamma = 90° \pm 0.5$; $V = 571$ Å³. The unusual chemical composition and the x-ray powder photography stimulated this complete interpretation of the structure.

A three-dimensional I(hkl) set obtained in a KFOR-3 camera with Mo irradiation contained 1390 independent reflections from the 0kl-3kl layer lines recorded along the shortest period $a = 5.53$ Å. A visual evaluation of the intensities was made relative to a $2^{1/4}$ blackening scale. Only the LP factor was taken into account in the calculation of the F^2 coefficients; any allowance for absorption was ruled out by the irregular shape of the specimen. The structural calculations were made on a BÉSM-4 computer using the program in ref. 1.

The basis for the interpretation was the three-dimensional distribution of the P(uvw) function and the adhering cation fragment of the structure was found by vector-subsystem theory.[2-3] The next stages of the successive approximations of ρ(xyz) made it possible to localize all the light atoms in the cell. The refinement of this model, using the least squares method, resulted in a convincing match of the experimental data with the calculations with a final R factor of 8.8%. The final coordinates of 24 basis atoms (66 independent parameters) and the corresponding thermal constants are shown in Table 1. The last column of the tables shows the relative heights of the electron-density peaks in the ρ(xyz) distribution.

To sum up, it was established that the unit cell of this phase is characterized by the centrosymmetric distribution of the P$\bar{1}$ space group and contains one formula unit of the composition $Na_{11}Nb_2TiSi_4P_2O_{25}F$. The value of the x-ray
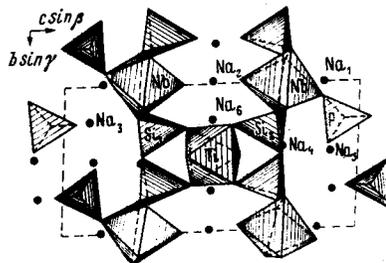
Fig. 1. A fragment of the structure in a point-polyhedra representation. The Ti, Na_2, and Na_6 atoms form the core and the Nb, Si, and Na_4 atoms are the chain mail of the trilaminate packet. Along the edges of the unit cell are sodium phosphate layers including the P, Na_1, Na_3, and Na_5.

density of 3.15 g/cm³ corresponding to this formula is in good agreement with $\rho_{ex} = 3.11$.

Most of the structural atoms are arranged in general positions and only Ti and Na_2 occupy special positions at the inversion centers. The "colored" (according to Belov) cations Nb^{5+} and Ti^{4+} are characterized by the most spread out octahedral coordination. The regularity of the octahedron, rare for Ti, and the clear anisotropy of the Nb-O bonds must be pointed out here. One of these bonds (Nb-O_6) is clearly shortened (1.76 Å) while the diametrically opposite bond Nb-O_7 is lengthened to 2.27 Å. The Si and P atoms have the usual tetrahedral environment and the Si tetrahedra are associated in [Si_2O_7] diortho-groups. The coordination of the Na^+ ions in this structure is distinguished by its great variety: The Na_5 atom is in an oxygen tetrahedron; the Na_2 and Na_6 in octahedra; the Na_1 and Na_3 in irregular six-cornered figures, and the Na_4 in an eight-cornered figure. The lengths of the cation-anion bond for all these polyhedra are shown in Table 2.

From its architectural features we can assign this structure to the Ti(Nb) silicates. The basis of its structure (Fig. 1) is the trilaminate packets parallel to (001), in which the continuous core, consisting of Ti and Na octahedra connected by an edge, is screened on two sides by an (Nb + Si) chain mail of a bafertisite type.[6] The Na_4 packing atoms are arranged in the pseudohexagonal loops

TABLE 1. Positional and Thermal Parameters of the Basis Atoms

Atom	x/a	y/b	z/c	B_j	ρ_j	Atom	x/a	y/b	z/c	B_j	ρ_j
Nb	0.699	0.008	0.716	0.55	35.7	O_2	0.050	0.195	0.252	0.37	4.9
Ti	0	0.500	0.500	0.55	16.2	O_3	0.558	0.173	0.256	0.44	5.3
Si_1	0.815	0.280	0.302	0.06	12.0	O_4	0.164	0.301	0.575	0.02	5.0
Si_2	0.200	0.294	0.685	—0.06	12.2	O_5	0.276	0.503	0.422	0.27	4.7
P	0.686	0.243	0.933	0.20	11.9	O_6	0.316	0.014	0.405	0.57	5.1
Na_1	0.199	0.007	0.866	1.16	8.0	O_7	0.743	0.070	0.872	0.31	5.2
Na_2	0	0	0.500	1.20	8.2	O_8	0.838	0.225	0.029	1.14	4.1
Na_3	0.248	0.236	0.081	1.29	7.4	O_9	0.768	0.426	0.891	0.54	4.5
Na_4	0.709	0.491	0.735	0.83	7.6	O_{10}	0.408	0.241	0.943	0.85	4.1
Na_5	0.186	0.482	0.899	0.99	7.2	O_{11}	0.471	0.210	0.719	0.55	5.2
Na_6	0.501	0.258	0.499	0.89	7.7	O_{12}	0.983	0.183	0.729	0.93	4.8
O_1	0.835	0.290	0.416	0.17	5.5	O_{13}	0.202	0.507	0.734	0.62	4.2

TABLE 2. The Cation—Anion Distances (Å) in the $Na_{11}Nb_2TiSi_4P_2O_{25}F$ Structure

Nb octahedron		Ti octahedron		Si tetrahedron				P tetrahedron	
Nb—O₆*	1.76	Ti—O₅	2.00	Si₁—O₁	1.63	Si₂—O₄	1.60	P—O₇	1.53
O₁₁	1.92	O₅*	2.00	O₁₃*	1.65	O₁₃	1.63	O₁₀	1.56
O₁₂*	2.00	O₄	2.01	O₂*	1.66	O₁₂	1.66	O₈*	1.57
O₃*	2.03	O₄*	2.01	O₃	1.68	O₁₁	1.67	O₉	1.57
O₂*	2.06	O₁*	2.03						
O₇	2.27	O₁	2.03						
Average	2.01	Average	2.01	Average	1.66	Average	1.64	Average	1.55

Na₁ six-cornered figure		Na₂ octahedron		Na₃ six-cornered figure		Na₄ eight-cornered figure		Na₅ tetrahedron		Na₆ octahedron	
Na₁—O₁₀	2.21	Na₂—O₆	2.35	Na₃—O₁₀*	2.27	Na₄—O₅*	2.30	Na₅—O₁₀	2.22	Na₆—O₅ *	2.27
O₈*	2.34	O₆*	2.35	O₈*	2.32	O₉	2.34	O₈*	2.28	O₄	2.28
O₃*	2.48	O₄*	2.48	O₇*	2.35	O₁₁	2.39	O₉*	2.35	O₆	2.32
O₇	2.59	O₄*	2.48	O₉*	2.43	O₂	2.60	O₁₃	2.44	O₁	2.35
O₅*	2.61	O₁ *	2.60	O₂	2.86	O₁₂	2.69			O₅	2.43
O₁₂	2.62	O₁	2.60	O₃	2.99	O₁₃*	2.75			O₆*	2.61
						O₁₂	2.82				
						O₃ *	2.83				
Average	2.48	Average	2.48	Average	2.54	Average	2.59	Average	2.32	Average	2.38

Note: Asterisks denote atoms connected with basic symmetry operations.
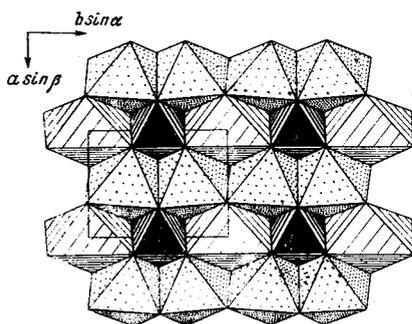
Fig. 2. Sodium titanium core of the trilaminate packet (a variant of a seidozerite wall of densely packed octahedra): The Ti is shown black; Na₂, hatched; Na₆, dotted. The contour of the cell emphasizes the centrosymmetrical position of the first and second types of polyhedra.

of this network chain mail constructed of discrete Nb octahedra and [Si₂O₇] diortho groups. Figure 2 separately illustrates the sodium—titanium core, which is one of the variants of a "seidozerite" wall,[7] in which all the Mn are replaced by Na. Finally, the Ti octahedra are mutually isolated. It is important to note that in this diorthosilicate the Nb and Ti fulfill sharply differentiated functions: one staying strictly in the armoring and the other only in the core. A similar role distribution between Ti and Nb atoms has already been noted in the related structure of another laminar diorthosilicate, epistolite.[8]

In the direction of the c axis (longest period 14.5 Å) these trilaminate packets alternate with two-tiered sodium phosphate layers, which correspond to the mineral [Na₃PO₄]₂. The different types of layers are connected together mainly by P orthotetrahedra, each of which shares one of its own apices with an Nb octahedron of the trilaminate packet. It should be noted that this particular apex of the Nb octahedron is furthest away from the central atom (2.27 Å).

Finally, let us consider for a moment the role of the univalent anions in the structure of this mineral. Although, because of their nearly equal atomic numbers, the F and

O atoms cannot be distinguished by x rays, the position of the single F in the unit can be derived unequivocally from an analysis of the local valence balance. In fact, in the anions which correspond to the O₅ position (Table 1) a significant deficit is observed in the positive valence forces, in all +1⅛. It follows that in the indicated two-fold position[2] the F⁻ can statistically replace the oxygen in a proportion close to 1 : 1. These anions form free, i.e. not associated with Si, apices of discrete Ti octahedra. Thus, the presence of a univalent anion is dictated by the specific structure of the (Na—Ti) core, in which the highly charged "colored" cations are isolated from one another. A similar pattern has previously been described in the Ba titanosilicate structure of innelite.

According to the results of this study, the phase is a new representative of the diorthosilicate family, which is headed, according to Strunz's classification,[9] by the mineral murmanite. In this case, we can isolate in the newly interpreted structure fragments of three members of the groups designated as: the epistolite armor; the innelite core;[10] and the sodium phosphate layers of lomonosovite.[11] The structural formula of this phase we have studied can be expressed in the following form:

$$Na_3Ti(O, F)_2[NaNbO(Si_2O_7)]_2 \cdot 2Na_3(PO_4).$$
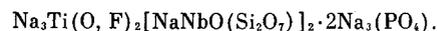
The first part of the formula symbolizes the composition of the core; the second, in square brackets, the composition of the chain mail; and the third, the contents of the interpacket space.

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