

STRUCTURES OF INORGANIC COMPOUNDS

Acentric Niobium-Rich Analogue of Labuntsovite-Fe: Crystal Structure and Microtwinning

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Abstract—A new mineral of the labuntsovite group from Vuoriyarvi (North Karelia) was studied by the method of X-ray diffraction analysis. The unit-cell parameters are $a = 14.450(6)$ Å, $b = 13.910(6)$ Å, $c = 7.836(4)$ Å, $\beta = 117.42(1)^\circ$, $V = 1398.1$ Å³, sp. gr. *Cm*. The symmetry, unit-cell parameters, splitting of the *A* position, and ordered distribution of the cations over the *B* and *C* positions of the new mineral makes it similar to the zinc-rich analogue of labuntsovite. Unlike the zinc-rich analogue, the *D* position in the new representative of the labuntsovite group is dominated by Fe atoms when the position occupancy is lower. In addition, the new representative is characterized by high occupancies of the *A* and *B* positions and the ordered distribution of the Ti and Nb atoms over two octahedral positions. In both minerals, the *A* position is split into two positions, with one of the positions in both minerals being occupied by Na and the other position being occupied by K in the new mineral and Sr in the Zn-analogue. © 2002 MAIK "Nauka/Interperiodica".

In recent years, the minerals of the labuntsovite group have attracted interest because of their ion-exchange properties. We performed X-ray diffraction analysis on a single crystal of a new representative of this group discovered in hydrothermal paragenesis from the Vuoriyarvi carbonatite massif (North Karelia). The mineral was found in a test core of a prospecting borehole in the form of 3 mm-long brown prismatic crystals.

The chemical composition of the mineral was determined by local X-ray spectral analysis (averaging over six points). The empirical formula (with respect to 16 Si atoms), $K_{4.3-4.8}Na_{2.4-2.7}Ba_{0.7-0.9}Fe_{0.6-0.8}Mg_{0.4-0.7}Mn_{0.1-0.2} \cdot (Ti_{4.6-4.8}Nb_{3.2-3.5})[Si_4O_{12}]_4 \cdot nH_2O$, reflects the phase inhomogeneity.

The observed doubled unit-cell parameter c is indicative of lemmleinite-type twinning. To convert the experimental unit cell to a true monoclinic unit cell, we used the matrix $[1 \ 0 \ 0 / 0 \ 1 \ 0 / 0 \ 0 \ 0.5] + [1 \ 0 \ 0 / 0 \ 1 \ 0 / -0.5 \ 0 \ -0.5]$ used elsewhere [1]. The refined weight coefficients of the twin components are 0.53 and 0.47.

Assuming the structural similarity of the new mineral and the zinc-rich analogue of labuntsovite, we used the atomic coordinate of the latter [2] as the starting

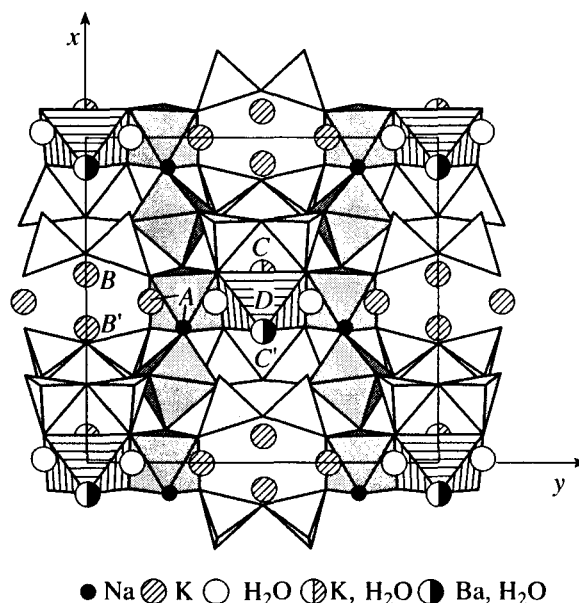


Fig. 1. Crystal structure of the mineral projected onto the (001) plane. Fe-octahedra are hatched. Circles of different types represent large cations and water molecules. The key positions are indicated by letters A, B, C, and D.

Table 1. Main characteristics of the mineral and details of the X-ray diffraction experiment

Characteristic	Data and conditions	Characteristic	Data and conditions
Parameters of the double unit cell, Å, deg	$a = 14.450(6)$ $b = 13.910(6)$ $c = 15.672(4)$ $\beta = 117.420(5)$	Crystal dimensions, mm	$0.15 \times 0.2 \times 0.35$
Parameters of monoclinic unit cell, Å, deg	$a = 14.450(6)$ $b = 13.910(6)$ $c = 7.836(4)$ $\beta = 117.420(5)$	Diffraction meter	SYNTEX P2 ₁
Unit-cell volume, Å ³	$V = 1398.1$	Ranges of the indices of measured reflections	$-16 < h < 14$ $-14 < k < 15$ $0 < l < 18$
Sp. gr.; Z	$Cm; 1$	Maximum $\sin \theta / \lambda$	0.58
Radiation, Å; λ	$\text{CuK}\alpha; 1.5418$	Total number of reflections	1738
Density (calc.), g/cm ³	2.76	Number of independent reflections	$1523 F > 4\sigma(F)$
		R factor upon anisotropic refinement	0.066
		Program used for refinement	AREN [3]
		Program used for introduction of absorption correction	DIFABS [4]

Table 2. Atomic coordinates, multiplicities (Q), occupancies (q), and equivalent thermal parameters of the atoms

Position	x/a	y/b	z/c	Q	q	$B_{\text{eq}}, \text{\AA}^2$
Ti(1)	-0.0002(1)	0.2273(1)	0.5002(1)	4	1	2.82(6)
Ti(2)	0.2518(3)	0.2516(2)	0.4943(6)	4	1	2.86(5)
Si(1)	0.2104(3)	0.1097(3)	0.7970(5)	4	1	2.3(1)
Si(2)	0.7955(3)	0.1096(2)	0.1918(4)	4	1	1.7(1)
Si(3)	0.3250(3)	0.1102(4)	0.2445(6)	4	1	2.9(1)
Si(4)	0.6843(2)	0.1104(2)	0.7492(4)	4	1	1.2(1)
Fe	0.0091(9)	0	0.513(2)	2	0.55(1)	2.9(1)
Na	0.917(1)	0.232(1)	0.006(3)	4	0.60(1)	5.5(2)
K(1)	0.5807(6)	0	0.292(1)	2	0.70(1)	7.4(1)
K(2)	0.498(1)	0.178(1)	-0.002(2)	4	0.40(1)	6.5(1)
K(3)	0.421(1)	0	0.713(2)	2	0.79(3)	8.9(2)
C(1)	0.0812(7)	0	0.322(1)	2	0.90(1)	3.4(2)
C(2)	0.9075(4)	0	0.6491(7)	2	0.81(1)	4.0(1)
O(1)	0.241(1)	0.1354(9)	0.035(2)	4	1	3.7(4)
O(2)	0.7698(5)	0.1229(7)	0.981(1)	4	1	2.1(3)
O(3)	0.2763(8)	0.1771(6)	0.737(1)	4	1	2.1(3)
O(4)	0.7285(8)	0.1884(9)	0.269(1)	4	1	2.8(3)
O(5)	0.102(1)	0.224(1)	0.380(1)	4	1	2.9(3)
O(6)	0.9024(9)	0.2278(9)	0.600(2)	4	1	3.3(4)
O(7)	0.2452(9)	0	0.790(2)	2	1	2.8(5)
O(8)	0.758(1)	0	0.221(1)	2	1	3.2(4)
O(9)	0.4174(8)	0.176(1)	0.310(2)	4	1	4.3(4)
O(10)	0.5789(7)	0.1806(6)	0.694(1)	4	1	1.6(3)
O(11)	0.272(1)	0.133(1)	0.388(1)	4	1	3.8(4)
O(12)	0.7427(6)	0.1231(7)	0.622(1)	4	1	1.7(3)
O(13)	0.369(1)	0	0.275(2)	2	1	3.0(4)
O(14)	0.643(1)	0	0.723(2)	2	1	2.1(4)
O(15)	0.0881(6)	0.1267(9)	0.681(1)	4	1	2.8(4)
O(16)	0.9206(7)	0.1151(6)	0.335(1)	4	1	1.6(3)
H ₂ O(2)	0.008(3)	0.123(2)	0.015(3)	4	0.73(2)	7.5(2)

Note: Ti(1) = $\text{Ti}_{0.7}\text{Nb}_{0.3}$; Ti(2) = $\text{Ti}_{0.5}\text{Nb}_{0.5}$; Fe = $\text{Fe}_{0.6}\text{Mg}_{0.4}$; K(3) = $\text{K}_{0.5}(\text{H}_3\text{O})_{0.5}$; C(1) = $(\text{H}_2\text{O})_{0.6}\text{K}_{0.4}$; C(2) = $(\text{H}_2\text{O})_{0.7}\text{Ba}_{0.3}$.

Table 3. Characteristics of the coordination polyhedra

Position	Composition	Coordination number	Cation-anion distances, Å		
			minimum	maximum	average
Si(1)	4Si	4	1.55(1)	1.74(1)	1.62
Si(2)	4Si	4	1.53(1)	1.74(1)	1.64
Si(3)	4Si	4	1.50(1)	1.65(1)	1.59
Si(4)	4Si	4	1.58(1)	1.68(1)	1.64
Ti(1)	2.8Ti + 1.2Nb	6	1.90(1)	2.08(1)	1.97
Ti(2)	2Ti + 2Nb	6	1.84(1)	2.04(1)	1.96
Fe	0.66Fe + 0.44Mg	6	2.12(1)	2.18(1)	2.16
C(1)	0.72K + 1.1H ₂ O	11	2.86(1)	3.18(1)	3.04
C(2)	0.48Ba + 1.1H ₂ O	11	2.74(2)	3.31(1)	3.06
K(1)	1.4K	9	2.86(2)	3.44(1)	3.20
K(2)	1.6K	7	2.77(2)	3.15(1)	3.00
K(3)	0.79K + 0.79H ₃ O	9	2.86(2)	3.43(1)	3.19
Na	2.4Na	8	1.97(3)	3.08(1)	2.68

model. The structure was refined using mixed atomic scattering curves. The relatively high *R* factor is associated with the poor quality of the X-diffraction data collected from the twinned crystal.

The main characteristics of the crystal and the details of the X-ray diffraction experiment are given in Table 1. The atomic coordinates are listed in Table 2. The elemental compositions of the atomic positions and the interatomic distances are indicated in Table 3.

The mixed framework, consisting of octahedral chains of Ti-octahedra along the *a*-axis and the four-membered rings of the SiO₄-tetrahedra (Fig. 1) is common to all the minerals of the labuntsovitse group. In the mineral under study, the channels parallel to the coordinate axes are occupied by Na, K, and Ba atoms, H₃O⁺ ions, and water molecules. The crystallochemical formula of the mineral (*Z* = 1) can be written as [Na_{2.4}K_{1.6}] · [K_{2.2}(H₃O)_{0.8}][K_{0.72}Ba_{0.48}][Fe_{0.66}Mg_{0.44}(H₂O)_{2.2}][Ti_{4.8}Nb_{3.2} · (OH_{5.27}O_{2.73})] [Si₄O₁₂]₄ · 2.92H₂O, where

the compositions of the key *A*, *B*, *C*, and *D*(H₂O)₂ positions in the structure channels are indicated in the first four pairs of square brackets, respectively. The cations with high values of force characteristics (Fe and Mg) occupy the sites of the *D* position where the chains approach each other at the shortest distances. In this case, their polyhedra are built up to octahedra with two additional water molecules.

In the new mineral, like its Zn-analogue [2], the *A* position is split into two positions separated by a spacing of 1.73 Å. These two positions are statistically occupied by the Na and K(2) atoms, respectively (Fig. 2). The K(2) atom is located in the position occupied by an H₂O(1) molecule in conventional labuntsovitse. This position is shifted toward Na (like the Sr position in the Zn-analogue). The somewhat shortened Na–H₂O(2) distance (1.97 Å) is explained by incomplete occupancies of both cationic and water-molecule positions.

The *B* position is occupied by K atoms and H₃O⁺ ions distributed over two subpositions, *B* = K(1) and mixed *B'* = K(3). A similar filling of the *B* position is also observed in the analogous noncentrosymmetric Zn-dominant representative of the labuntsovitse group, where one position is that of H₃O⁺ and the second position is mixed (K, H₃O⁺). The incorporation of oxonium ions into the mineral structure is confirmed by the presence of a weak band (*v*) at 1715 cm^{−1} in the IR spectrum. According to the IR spectral data [5], the frequency of the (Ti,Nb) stretching vibration is 683 cm^{−1}, which corresponds to a relatively high occupancy of the *D* position (1.2 (Fe, Mg, Mn) atoms per unit cell). The new mineral is characterized by the ordered distribution of Ti and Nb atoms over two octahedral positions (one position is occupied mainly by Ti atoms, and the second position, by equal amounts of Ti and Nb atoms) and by selective K and Ba distribution over two *C* positions.

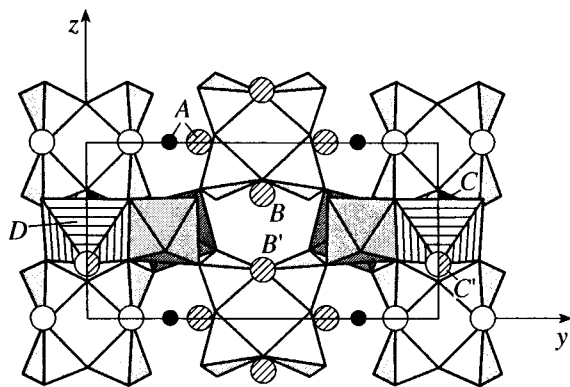


Fig. 2. Crystal structure of the mineral projected onto the (100) plane. Notation as in Fig. 1.

Thus, the symmetry, unit-cell parameters, splitting of the *A* position, and the ordered distribution of the cations over the *B* and *C* positions of the new mineral are similar to those of the zinc-rich analogue of labuntsovite. However, unlike the zinc-rich analogue, the *D* position in the new mineral is dominated by Fe atoms when its occupancy is lower. At the same time, the *A* and *B* positions in the new mineral have high occupancies, whereas Ti and Nb atoms are orderly distributed over two octahedral positions.

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