

CHEMISTRY

Crystal Structure of the New Mineral Tsepinite-K

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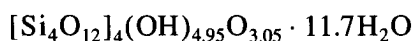
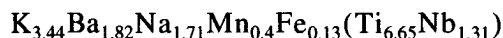
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Minerals of the labuntsovite group have attracted considerable attention in recent years. Although these minerals have long been thought to be rare, they were already discovered in 14 alkaline massifs, and about 20 mineral species are presently known. This diversity of species is associated with wide cation isomorphism and its related structural variations. Since minerals of the labuntsovite group are structurally similar to zeolites, they are also of practical interest as potent new microporous materials.

In this study, we established the crystal structure of tsepinite-K, which is a new mineral discovered at the Karnasurt Mountain of the Lovozero alkaline massif (the Kola Peninsula). The mineral was found in the aegirine zone of high-alkaline pegmatites and forms pseudomorphs after murmanite.

The chemical composition of the new mineral was studied by electron probe analysis and corresponds to the following empirical formula (with respect to $\text{Si}_{16}\text{O}_{48}(\text{OH},\text{O})_8$):



(the water content was estimated from the deficiency sum obtained in the analysis).

The principal characteristics of the crystal and details of X-ray data collection are given in Table 1.

Initially, the structure was studied within the centrosymmetric space group $C2/m$ typical of labuntsovites. The coordinates of cation-deficient labuntsovite [2] were used as the starting model. However, the resulting model was in rather poor agreement with the data of chemical analysis, and the R factor was higher than 6% (the empirical absorption correction was

applied taking into account the habitus of the single crystal). In the subsequent structure solution within the lower-symmetry space group Cm , the splitting of the B and B' positions was revealed from a difference electron density synthesis, and these positions were refined taking into account the mixed atomic scattering curves and partial occupancies. In particular, we found additional positions occupied by the $\text{H}_3\text{O}(1)$ and $\text{H}_3\text{O}(2)$ oxonium groups, which compensate for the deficiency of the K cations according to the scheme $4\text{K} = 2.58\text{K} + 1.34\text{H}_3\text{O} + 0.08\Box$.

The final atomic coordinates are given in Table 2. The compositions of the positions and the interatomic distances are listed in Table 3. The crystal-chemical

Table 1. Crystal-structural data and details of X-ray data collection

Characteristic	Parameter
Monoclinic unit-cell parameters, Å	$a = 14.326(3)$ $b = 13.802(2)$ $c = 7.783(1)$ $\beta = 116.949(3)$ $V = 1371.8$
Monoclinic unit-cell volume, Å ³	
Space group Z	$Cm; 1$
Radiation; λ , Å	$\text{MoK}\alpha; 0.71073$
Density (calc), g/cm ³	2.9
Crystal dimensions, mm	$0.15 \times 0.10 \times 0.10$
Diffractionmeter	Bruker AXS SMART CCD
Ranges of the indices of measured reflections	$-22 < h < 15; -21 < k < 18;$ $-12 < l < 12$
$\sin\theta/\lambda$	0.79
Total number of independent reflections	2814
Number of independent reflections in refinement	$1112 F > 3\sigma(F)$
R factor upon anisotropic refinement	0.033
Program used for refinement	AREN [1]

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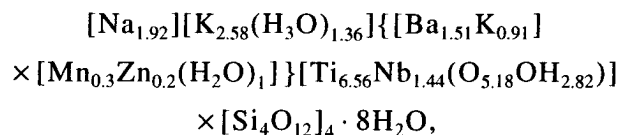
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Table 2. Atomic coordinates, multiplicities, occupancies of positions, and equivalent atomic displacement parameters

Position	x/a	y/b	z/c	Q	q	$U_{eq} \times 100, \text{\AA}^2$
Ti(1)*	0	0.2268(1)	0.5000	4	1	1.85(5)
Ti(2)*	0.2501(4)	0.2484(3)	0.496(1)	4	1	1.76(2)
Si(1)	0.2087(2)	0.1112(1)	0.7992(3)	4	1	1.1(2)
Si(2)	0.7928(1)	0.1090(1)	0.1929(3)	4	1	0.5(2)
Si(3)	0.3197(2)	0.1114(1)	0.2442(3)	4	1	0.9(4)
Si(4)	0.6802(2)	0.1105(1)	0.7454(3)	4	1	0.7(2)
<i>D</i> *	-0.001(2)	0	0.504(3)	2	0.25(1)	0.7(2)
<i>C</i> *	0.9162(1)	0	0.6548(2)	2	0.89(1)	2.5(2)
<i>C</i> '*	0.0896(2)	0	0.3391(3)	2	0.82(1)	2.24(5)
<i>A</i>	0.915(1)	0.235(1)	0.004(2)	4	0.48(5)	2.9(7)
<i>B</i> (a)	0.4222(4)	0	0.6961(5)	2	0.64(2)	4.1(2)
<i>B</i> (b)	0.436(1)	0.027(2)	0.750(1)	4	0.16(4)	3.7(2)
<i>B</i> '(a)	0.5817(5)	0	0.297(1)	2	0.65(2)	4.4(2)
<i>B</i> '(b)	0.574(1)	0.049(1)	0.277(3)	4	0.18(4)	5.3(2)
O(1)	0.2332(5)	0.1254(4)	0.027(1)	4	1	1.1(9)
O(2)	0.7656(5)	0.1291(5)	0.975(1)	4	1	1.5(7)
O(3)	0.2747(5)	0.1850(4)	0.738(1)	4	1	1.0(7)
O(4)	0.7307(5)	0.1798(5)	0.267(1)	4	1	1.3(9)
O(5)	0.1044(5)	0.2273(5)	0.394(1)	4	1	1.4(7)
O(6)	0.9043(5)	0.2231(4)	0.608(1)	4	1	1.3(9)
O(7)	0.249(1)	0	0.774(1)	2	1	1.3(9)
O(8)	0.755(1)	0	0.206(1)	2	1	1.4(9)
O(9)	0.425(1)	0.1837(5)	0.300(1)	4	1	1.8(9)
O(10)	0.5844(5)	0.1772(4)	0.691(1)	4	1	1.4(9)
O(11)	0.2676(4)	0.1248(3)	0.392(1)	4	1	0.1(1)
O(12)	0.740(1)	0.126(1)	0.623(1)	4	1	3.5(9)
O(13)	0.366(1)	0	0.272(1)	2	1	2.0(9)
O(14)	0.636(1)	0	0.728(2)	2	1	1.3(9)
O(15)	0.0841(4)	0.1188(4)	0.676(1)	4	1	0.7(1)
O(16)	0.9192(5)	0.1155(5)	0.332(1)	4	1	1.9(9)
H ₂ O(1)	-0.004(2)	0.338(1)	-0.0287(2)	4	1	8.7(5)
H ₂ O(2)	0.015(3)	0.116(1)	0.010(4)	4	1	6.9(6)

Note: Hereinafter, the positions related by a pseudocenter of symmetry are primed. The split positions are denoted by a and b. The positions characterized by mixed compositions are marked with asterisks.

formula of the mineral ($Z = 1$) can be written as



where the compositions of the key *A*, *B*, *C*, and *D* positions in the structure are enclosed in the first four pairs of brackets, respectively.

The structure of tsepinite-K is characterized by a mixed framework typical of labuntsovites. This frame-

work consists of columns of the vertex-sharing (Ti,Nb)O₆ octahedra linked through the four-membered rings of the SiO₄ tetrahedra. The channels parallel to the coordinate axes are occupied by the K, Na, and Ba atoms, oxonium ions, and water molecules. The oxonium ions, which are highly likely to be present in the structure of the new mineral, occupy the split *B* positions together with potassium atoms (Fig. 1) and are characterized by a high thermal parameter.

The new mineral possesses a number of interesting crystal-chemical traits, which impart individuality to this specimen. Thus, the centrosymmetric structures of

Table 3. Characteristics of the coordination polyhedra

Position	Composition	Coordination number	Cation–anion distances		
			minimum	maximum	average
Si(1)	4Si	4	1.60(1)	1.68(1)	1.63
Si(2)	4Si	4	1.58(1)	1.64(1)	1.61
Si(3)	4Si	4	1.59(1)	1.69(1)	1.64
Si(4)	4Si	4	1.54(1)	1.66(1)	1.59
Ti(1)	3.28Ti + 0.72Nb	6	1.89(1)	2.01(1)	1.96
Ti(2)	3.28Ti + 0.72Nb	6	1.89(1)	2.03(1)	1.97
<i>D</i>	0.30Mn + 0.20Zn	6	2.01(3)	2.20(3)	2.09
<i>C</i>	0.94Ba + 0.34K + 0.50H ₂ O	11	2.85(1)	3.20(1)	2.99
<i>C'</i>	0.57Ba + 0.57K + 0.50H ₂ O	11	2.78(2)	3.16(1)	2.99
<i>B</i> (a)	1.28K	9	2.81(1)	3.42(1)	3.15
<i>B</i> (b)	0.64H ₃ O	8	2.62(2)	3.27(2)	2.96
<i>B'</i> (a)	1.3K	9	2.86(1)	3.39(1)	3.17
<i>B'</i> (b)	0.72H ₃ O	9	2.42(2)	3.44(2)	3.04
<i>A</i>	1.92Na	7	2.17(3)	3.02(1)	2.66

minerals of the labuntsovit and lemmleinite subgroup (space group $C2/m$) [3] have two *A* positions related by a twofold axis. These positions are located at a short distance and cannot be simultaneously occupied by cat-

ions. As a result, even though the multiplicity of the independent *A* position is equal to 8, this position in centrosymmetric structures contains no more than four statistically distributed sodium atoms. In the structure

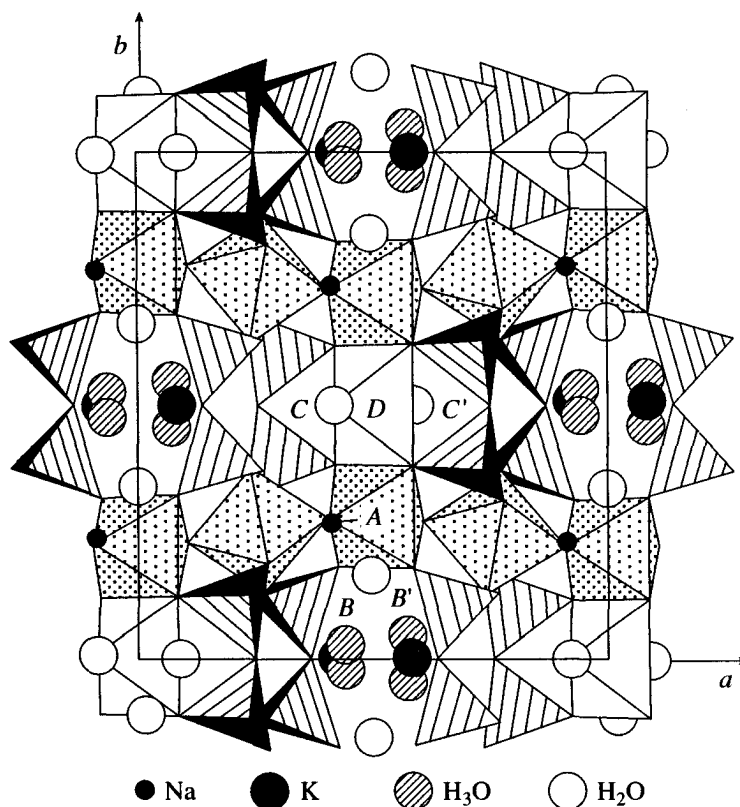


Fig. 1. Crystal structure of the mineral projected onto the (001) plane. Circles of different types represent the large cations and water molecules. The linear hatching indicates the SiO₄ tetrahedra, and the dotted hatching indicates the (Ti,Nb) octahedra.

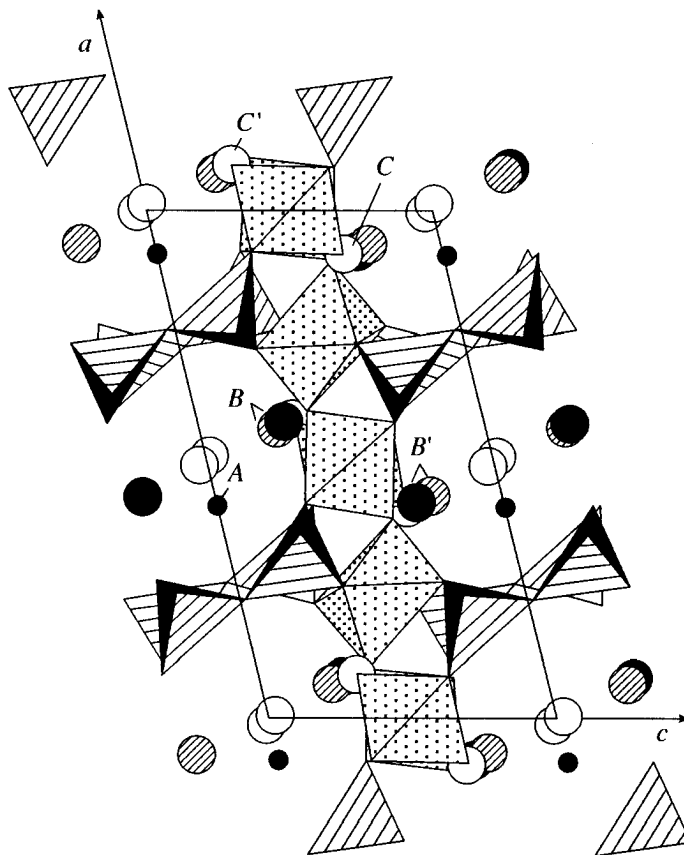


Fig. 02. Crystal structure of the mineral projected onto the (010) plane. For notations, see Fig. 1.

of tsepinite-K with its lower symmetry, both *A* positions are independent (Fig. 2), and only one position with the coordinates $x = 0.92$, $y = 0.23$, $z = 0$ is selectively occupied by sodium atoms. Hence, the new mineral is similar to minerals of the gutkovaite group [3–5]. A different situation occurs in tsepinite-Na [6], in which the *A'* position with the coordinates $x = 0.09$, $y = 0.24$, $z = 0$ is occupied. Yet another distinguishing feature of the mineral under study is the fact that the *C* position is more than half-occupied, which was observed previously only in lemmleinite-K [7] and lemmleinite-Ba [8]. However, two *C* positions related by an inversion center are equally and selectively occupied in the structures of lemmleinites (exclusively by either potassium or barium in lemmleinite-K and lemmleinite-Ba, respectively), whereas the *C* and *C'* positions in the new mineral are characterized by mixed compositions (Ba + K) and different occupancies (Table 3). In the structure of tsepinite-K, the *B* positions, which are occupied by K and H₃O, are split, as in the structures of kuzmenkoite-Mn [9] and members of the vuoriyarvite subgroup [6]. Finally, the *D* position (Fig. 1), which is occupied by the medium-sized divalent Mn, Zn, Fe, and Mg [3] cations in minerals of the labuntsovite, paralabuntsovite, kuzmenkoite, organovaitite, and gutkovaite subgroups, is only 25% occupied in the new mineral (Table 3).

Hence, the following three reasons are responsible for the disappearance of the inversion center in the structure of tsepinite-K and the lowering of its symmetry from *C2/m* to *Cm*: the vacant *A'* position and the simultaneous presence of the occupied *A* position; the difference in occupancy of the *C* and *C'* positions; and the splitting of the *B* positions. Reasoning from the presence of more than three types of nonequivalent positions occupied by extraframework cations, the fact that the *D* position is predominantly vacant, the space group *Cm*, and the metrics of the unit cell, the new mineral may be assigned to the vuoriyarvite subgroup in accordance with the nomenclature accepted for the labuntsovite group [3]. This mineral may be considered as a K-dominant analogue of tsepinite-Na, which is reflected in the name of the mineral. On the other hand, this mineral may also be considered as a Ti-dominant analogue of vuoriyarvite-K [10] in spite of the lower degree of splitting of the extraframework cationic positions and some differences in their occupancies as compared to vuoriyarvite.

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