

CHEMISTRY

New Zinc-Rich Representative of the Labuntsovite Group: Crystal Structure and Microtwinning

K. A. Rozenberg*, R. K. Rastsvetaeva^{1**}, I. V. Pekov*, and N. V. Chukanov^{***}

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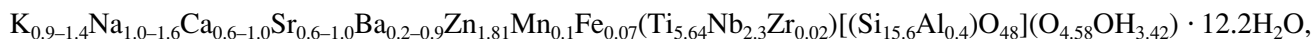
Taking into account that many alkali-metal titano- and niobosilicates possess zeolite-like structures and properties, these compounds can be considered as candidates for practical use in chromatography, catalysis, water treatment, etc. In spite of advances having been made in the synthesis of microporous titano- and niobosilicates [1–3], synthetic representatives are much smaller in number than natural compounds of this class. In this connection, knowledge of the crystal structures of new alkali Ti,Nb-silicate minerals is of practical interest. We studied a new mineral with a high zinc content and established its crystal-chemical characteristics, which supplement the data on the Fe- and Mn-containing specimens investigated earlier.

The labuntsovite group includes more than 20 minerals (among which 14 minerals were recognized by the Commission on New Minerals and Mineral Names of the International Mineralogical Association), which differ in composition, IR spectral characteristics, and structural parameters. The new representative of this

group was found in hydrothermally altered pegmatites at the Lepkhe-Nelm mountain of the Lovozero alkaline massif (the Kola Peninsula) in association with natrolite, neptunite, minerals of the apatite group, and tsepinite-Na. The latter mineral, which is another representative of the labuntsovite group, typically forms a fine intergrowth with the new mineral along phase boundaries. The new zinc-rich analogue of labuntsovite occurs as long-prismatic (up to needle-like) crystals elongated along the *b* axis up to 7 mm in length and 0.3–0.4 mm in thickness. The crystals are colorless or pale brown and are, generally, transparent.

The new mineral has a unique IR spectrum, although there are some features in common with the spectra of other representatives of the labuntsovite group with space group *Cm*.

The chemical composition of the sample was established by electron microprobe analysis based on six points (the water content was not determined). The empirical formula (with respect to 16 silicon atoms),



reflects the chemical inhomogeneity of the sample.

The parameters of the orthorhombic unit cell determined in the X-ray diffraction study are four times as large as those of the orthorhombic representatives of the labuntsovite group ($c = 27.73 \text{ \AA}$), which is indicative of the vuoriyarvite-type twinning [4]. To convert the experimental orthorhombic unit cell to the true monoclinic unit cell, we used the matrices $[-1 \ 0 \ 0/0 \ -1 \ 0/0.25 \ 0 \ 0.25]$ and $[1 \ 0 \ 0/0 \ 1 \ 0/-0.25 \ 0 \ 0.25]$. The refined weight coefficients of the twin components are 0.59 and 0.41.

¹e-mail: rast@ns.crys.ras.ru

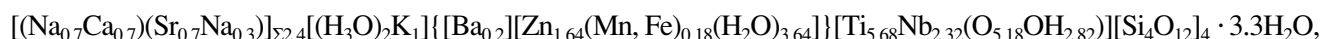
* Moscow State University, Vorob'evy gory,
Moscow, 119992 Russia

** Shubnikov Institute of Crystallography, Russian Academy
of Sciences, Leninskii pr. 59, Moscow, 117333 Russia

*** Institute of Problems of Chemical Physics,
Russian Academy of Sciences, Chernogolovka,
Moscow oblast, 142432 Russia

Initially, the structure was solved within the centrosymmetrical space group *C2/m* typical of labuntsovites starting from the atomic coordinates of an earlier-studied mineral [5]. However, the data of chemical analysis are in rather poor agreement with the model established by X-ray diffraction analysis. Because of this, we solved the structure within the lower-symmetry space group *Cm* using the atomic coordinates of calcium-rich labuntsovite [6] as the starting model. This allowed us to reveal additional partially occupied positions and refine them with the use of mixed atomic scattering curves.

The principal characteristics of the crystal and the details of the X-ray diffraction study are given in Table 1. The atomic coordinates are listed in Table 2. The compositions of the atomic positions and the interatomic distances are given in Table 3. The crystal-chemical formula of the mineral ($Z = 1$) can be written as



where the compositions of the key *A*, *B*, *C*, and *D*(H₂O)₂ positions in the structure are enclosed in the first four pairs of square brackets, respectively (Fig. 1).

The structure of the mineral under study is characterized by a mixed framework typical of labuntsovites. This framework consists of columns of the vertex-sharing TiO₆ octahedra linked through four-membered rings of the SiO₄ tetrahedra. The channels, which are parallel to the coordinate axes, are occupied by K, Sr, Na, Ca, Ba, Zn, Mn, and Fe atoms and water molecules (Figs. 1, 2). The Na and Ca atoms together occupy one of the *A* positions related by an axis 2 (in Table 2, this position is denoted as Na). In the new mineral, the typical eight-vertex Na polyhedron [5] is reduced to a seven-vertex polyhedron due to the absence of one water molecule. The position of the latter (with a shift of approximately 0.3 Å) is occupied by Sr and, to a smaller degree, by Na. The Sr–Na distance is 1.70 Å, and, hence, both positions under consideration are alternately occupied. The coordination environment about the Sr atom is also a seven-vertex polyhedron.

The crystal structures of typical labuntsovites contain two independent positions of water molecules, one

of which (denoted as H₂O(1) in the study [5]) is bound to the cationic *A* and *B* positions, whereas the H₂O(2) position is coordinated only to the *A* position. Both positions occupied by water molecules can be displaced toward the *A* position. In the structure of tsepinite-Na [9], both water positions are shifted and occupied by oxonium ions (as well as the *A* position by itself). In kuzmenkoite [10], the H₂O(1) position persists, whereas the H₂O(2) position is replaced by oxonium. On the contrary, the H₂O(2) position in the new mineral persists, whereas the H₂O(1) position is displaced and is occupied by Sr (Table 2).

Apparently, the new mineral contains oxonium ions, which occupy the *B* position together with K. The partial replacement of K by H₃O⁺ was also observed in some other members of the labuntsovite group. Direct evidence of incorporation of oxonium ions into the labuntsovite structure is presently lacking. However, the presence of H₃O⁺ ions in labuntsovites is highly probable from the crystal-chemical considerations (taking into account that H₃O⁺ and K⁺ are similar both in ionic radius and charge) and agrees well with the chemical compositions of many samples (the deficiency of extraframework cations, which is often accompanied by an increased “water” content). Like in other minerals, the oxonium group in the new mineral is characterized by high mobility, which is manifested in the high thermal parameters of its O atom (Table 2).

In the structure of the new zinc-rich analogue of labuntsovite, the Ba atoms are selectively incorporated into one of the vertices of the Zn octahedron, which is occupied predominantly by the H₂O(4) molecule. This is one of the reasons for the lowering of the symmetry. Another characteristic feature of the mineral is almost complete occupancy of the *D* position by medium-sized cations with Zn predominating.

Hence, the new mineral is similar to kuzmenkoite-Mn [10] in its symmetry, unit cell parameters, and occupancy of the *D* position. The difference is that the *A* position in the new mineral is characterized by a high total occupancy with Na atoms predominating, and the *B* position contains predominantly cationic vacancies (in the kuzmenkoite-Mn structure, the *A* cations are absent, the *B* position contains predominantly potassium atoms, and the *D* position is occupied by manganese atoms).

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Table 1. Crystallographic data and details of the X-ray diffraction study

Characteristic	Data and conditions
Parameters of orthorhombic unit cell, Å	<i>a</i> = 14.491(6), <i>b</i> = 13.911(6), <i>c</i> = 27.73(4)
Parameters of monoclinic unit cell, Å deg	<i>a</i> = 14.491(6), <i>b</i> = 13.911(6), <i>c</i> = 7.822(4) β = 117.59(1)
Unit-cell volume, Å ³	<i>V</i> = 1397.5
Space group; <i>Z</i>	<i>Cm</i> ; 1
Radiation; λ, Å	CuK _α ; 1.5418
Density (calc), g/cm ³	2.9
Crystal dimensions, mm	0.15 × 0.1 × 0.25
Diffractionmeter	SYNTEX P2 ₁
Ranges of the indices of measured reflections	–16 < <i>h</i> < 16; 0 < <i>k</i> < 16; 0 < <i>l</i> < 32;
sinθ/λ	< 0.58
Total number of reflections	1761
Number of independent reflections	1523
<i>F</i> > 4σ(<i>F</i>)	
<i>R</i> factor upon anisotropic refinement	0.058
Program used for refinement	AREN [7]
Program used for absorption correction	DIFABS [8]

Table 2. Atomic coordinates, multiplicities, occupancies, and equivalent thermal parameters of the atoms

Position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>Q</i>	<i>q</i>	<i>B</i> _{eq} , Å ²
Ti(1)	−0.0002(1)	0.2316(1)	0.5002(1)	4	1	1.82(5)
Ti(2)	0.2514(3)	0.2498(1)	0.4956(7)	4	1	1.92(6)
Si(1)	0.2114(2)	0.1082(2)	0.8006(4)	4	1	1.6(1)
Si(2)	0.7965(2)	0.1104(2)	0.1970(4)	4	1	1.2(1)
Si(3)	0.3201(2)	0.1099(2)	0.2438(5)	4	1	1.7(1)
Si(4)	0.6888(2)	0.1111(2)	0.7510(4)	4	1	1.1(1)
Zn	0.0012(3)	0	0.4978(7)	2	0.91(1)	1.97(8)
Na	0.923(1)	0.2367(8)	0.011(3)	4	0.35(1)	3.0(2)
Sr	0.5067(8)	0.1799(6)	0.003(2)	4	0.25(1)	3.65(9)
K	0.5757(7)	0	0.278(1)	2	1	5.8(1)
H ₃ O	0.429(5)	0	0.737(9)	2	0.47(4)	10.2(7)
O(1)	0.2418(7)	0.1290(8)	0.022(1)	4	1	3.1(5)
O(2)	0.7750(6)	0.1289(5)	0.979(1)	4	1	1.6(3)
O(3)	0.2730(6)	0.1789(6)	0.734(1)	4	1	1.9(3)
O(4)	0.7303(6)	0.1839(6)	0.265(1)	4	1	1.9(3)
O(5)	0.1020(7)	0.2317(5)	0.385(1)	4	1	1.2(3)
O(6)	0.905(1)	0.2293(7)	0.602(2)	4	1	3.1(4)
O(7)	0.2478(8)	0	0.788(2)	2	1	2.4(5)
O(8)	0.7579(9)	0	0.207(2)	2	1	1.8(5)
O(9)	0.4201(5)	0.1763(5)	0.305(1)	4	1	1.5(3)
O(10)	0.5873(8)	0.1844(7)	0.696(2)	4	1	3.2(3)
O(11)	0.2685(7)	0.1264(6)	0.382(1)	4	1	2.1(3)
O(12)	0.7450(6)	0.1303(6)	0.619(1)	4	1	1.8(3)
O(13)	0.366(1)	0	0.274(2)	2	1	3.0(5)
O(14)	0.6485(9)	0	0.733(1)	2	1	1.4(5)
O(15)	0.859(6)	0.1204(5)	0.668(1)	4	1	1.4(3)
O(16)	0.9194(7)	0.1144(6)	0.335(1)	4	1	2.5(3)
H ₂ O(2)	0.015(2)	0.135(2)	0.002(2)	4	0.83(4)	7.3(5)
H ₂ O(3)	0.103(2)	0	0.349(4)	2	0.93(8)	7.0(8)
H ₂ O(4)	0.9077(6)	0	0.655(1)	2	1	4.3(3)

Note: Ti(1) = Ti(2) = Ti_{0.7}Nb_{0.3}; Zn = Zn_{0.9}(Fe,Mn)_{0.1}; Sr = Sr_{0.7}Na_{0.3}; Na = Na_{0.5}Ca_{0.5}; H₂O(4) = (H₂O)_{0.9}Ba_{0.1}; K = K_{0.5}(H₃O)_{0.5}.

Table 3. Characteristics of the coordination polyhedra

Position	Composition	Coordination number	Cation–anion distances		
			Minimum	Maximum	Average
Si(1)	4Si	4	1.57(1)	1.63(1)	1.60
Si(2)	4Si	4	1.60(1)	1.65(1)	1.62
Si(3)	4Si	4	1.58(1)	1.64(1)	1.60
Si(4)	4Si	4	1.60(1)	1.67(1)	1.64
Ti(1)	2.84Ti + 1.16Nb	6	1.87(1)	2.07(1)	1.97
Ti(2)	2.84Ti + 1.16Nb	6	1.92(1)	2.00(1)	1.97
Zn	1.64Zn + 0.18(Mn, Fe)	6	2.04(1)	2.26(3)	2.14
H ₂ O(4)	1.8H ₂ O + 0.2Ba	11	2.88(1)	3.21(1)	3.05
K	1K + 1H ₃ O	9	2.93(2)	3.43(1)	3.25
H ₃ O	1H ₃ O	11	2.82(8)	3.56(6)	3.25
Na	0.70Na + 0.70Ca	7	1.97(3)	3.09(2)	2.66
Sr	0.70Sr + 0.30Na	7	2.57(2)	3.14(2)	2.97

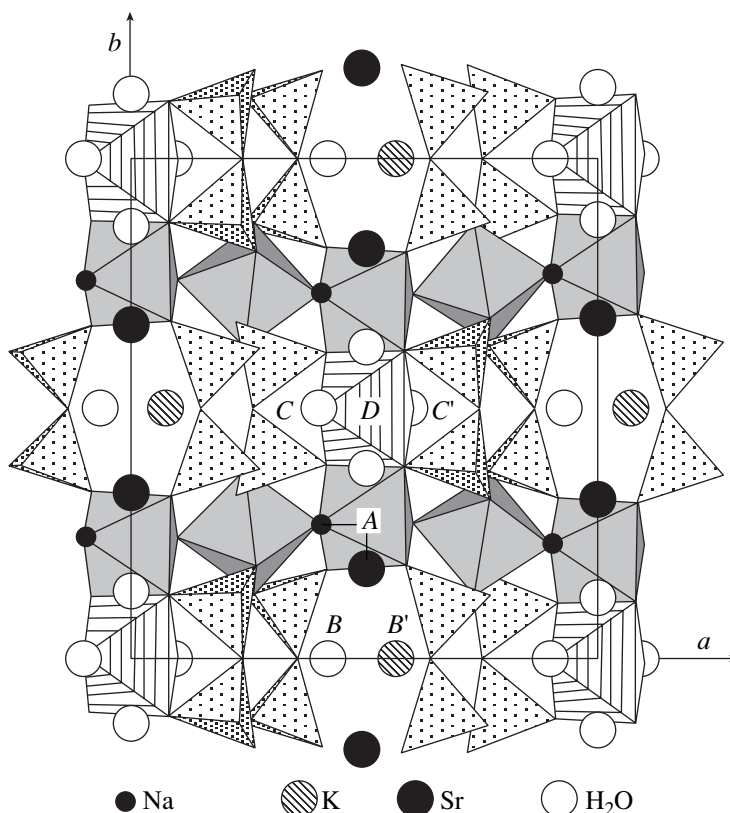


Fig. 1. Crystal structure of the mineral projected onto the (001) plane. The Zn octahedra are hatched. Circles of different types represent the large cations and the water molecules.

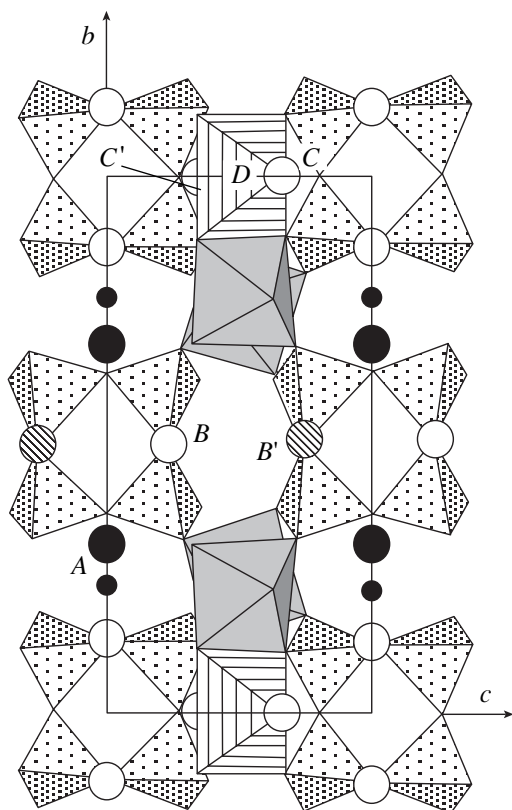


Fig. 2. Crystal structure of the mineral projected onto the (100) plane. For designations, see Fig. 1.

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