Crystal structure of the alkali titanosilicate labuntsovite

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The crystal structure of labuntsovite $(K, Ba, Na, Ca)_8(Ti, Nb)_9(O, OH)_{10}[Si_4O_{12}]_4 \cdot nH_2O$ (Fedorov group I2/m, a = 14.18, b = 15.48, c = 13.70 Å, γ = 117°, Z = 2) is determined. The structure is solved by minimizing the three-dimensional Patterson function, with successive approximations to the electron density distribution, the parameters then being refined by the method of least squares. The two halves of the unit cell of this crystal (along the b axis) are very similar to each other, the difference being of the nature of a partial lack of order.

Labuntsovite was first discovered by A. N. Labuntsov in the Khibinsk and Lovozersk alkali massifs (Kol'sk peninsula) in 1926 and described under the name of titanoelipidite.[1] In 1955 Semenov and Burova[2] showed that titanoelpidite was a new mineral with a chemical formula of $(K, Na, Ba, Ca, Mn)(Ti, Nb)[Si_2(O, OH)_7] \cdot 0.6H_2O$, and called it labuntsovite. Later Semenov[3] described several varieties of labuntsovite with considerably differing chemical compositions; he suggested that these varieties formed an isomorphic series together with another titanium–niobium silicate, nenadkevichite, although nenadkevichite and labuntsovite had different unit cells. The two extreme representatives of the proposed series (on the labuntsovite side) are characterized by the following compositions: brown labuntsovite $(K_{0.43}Na_{0.29}Ba_{0.16}Ca_{0.06}Mn_{0.09})(Ti_{0.89} \cdot Nb_{0.03}Fe_{0.05}Mg_{0.03})[Si_{1.83}Al_{0.07}O_{5.79}(OH)_{1.21}] \cdot 0.6H_2O$, and light-brown labuntsovite $(K_{0.16}Na_{0.22}Ba_{0.11}Ca_{0.18})(Ti_{0.77} \cdot Nb_{0.19}Fe_{0.07})[Si_{1.54}Al_{0.07}O_{4.48}(OH)_{2.52}] \cdot 0.38H_2O$.

Our own labuntsovite samples were obtained from E. I. Semenov, and we assumed that they belonged to the brown variety. Oscillation and rotation x-ray diffraction photographs gave the parameters of the monoclinic cell of labuntsovite as: a = 14.18, b = 7.74, c = 13.70 Å, γ = 117°. For a density of 2.96-2.90 g/cm³ the cell contains about eight formula units of labuntsovite. The systematic extinctions of the reflections indicated a centered B face of the cell, so that the labuntsovite crystals belonged to one of the three Fedorov groups B2/m, B2, or Bm.

Semenov received a private communication from C. Milton, who was studying American labuntsovite samples; the unit cell parameters in this case were a = 14.27, b = 15.57, c = 13.75 Å, γ = 116°55' with a fixed Fedorov group of I2/m. These parameters are quoted in the Mineralogical Tables of H. Strunz,[4] with a mention of ref. 2, although the parameters of the labuntsovite cell were not given in the latter paper. Attempts at detecting any intermediate layer lines on the x-ray rotation and Weissenberg photographs which would represent a doubling of the 7.74 Å spacing failed, although in the last stage of the structural analysis these layers did appear in oscillation x-ray photographs taken with a long exposure; they consisted not of spots but of weak, diffuse strokes, thus indicating a partial loss of order by the crystal structure.

The x-ray diffraction pattern of the labuntsovite was recorded photographically in a Weissenberg goniometer (Mo radiation, layer lines $h0l-h6l$, $hk0-hk2$, and $0kl$). The intensities of 1450 independent, nonzero reflections were measured with the aid of a photometric density scale.

In the P(xyz) Patterson function there were no sharply expressed "bundles" of peaks corresponding to 2/m symmetry; together with the weak piezoeffect, this led us to exclude the B2/m group from the class of possible Fedorov groups in the initial stages. However, a statistical analysis of the $h0l$ and $hk0$ reflections indicated that the corresponding projections of the crystal structure had centrosymmetrical properties, and in the course of the structural determination we finally chose the B2/m group, with a center of symmetry.

The results obtained by minimizing the Patterson function with respect to two interatomic vectors were used as a basis for a series of approximations of the three-dimensional electron-density distribution, first in the Bm and B2 Fedorov groups, then in the B2/m. As a result of several approximations, Ti octahedra and four-fold silicon–oxygen rings were clearly revealed in the structure (Figs. 1 and 2). The K(Ba) and Na(Ca) atoms were located less reliably, a number of difficulties arising in connection with the disposition of the K_1 atoms. Among the electron-density peaks identified with the O atoms forming the environment of the Ti_1 atom, two were sharply distinguished by their height. The distances from these peaks to the closest O atoms corresponded to the generally accepted distances between K and O atoms. Attempts at eliminating the Ti_1 atom from the calculations (this atom being superfluous with respect to the formula) and putting K atoms instead of the O atoms at the vertices of the Ti_1 octahedron made the R factor less favorable. However, on simultaneously specifying a Ti_1 atom and K atoms in place of the O atoms, the R factor fell by 5%. Furthermore, a strong peak at a distance of about 2.1 Å from the origin corresponded to the Ti_1-K_1 interatomic vector in the Patterson function, creating perplexity. One way out

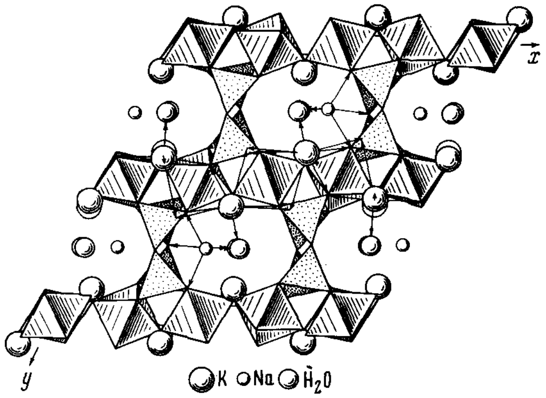

Fig. 1. Projection of the structure of labuntsovite on the xy plane.

TABLE 1. Coordinates of the Atoms (in the Half Cell) and Individual Temperature Parameters

Atom	x/a	y/b'	z/c	Multiplicity of atom	B
Ti_1	0	0	0	1.50	0.935
Ti_2	0	0	0.2291	3.80	1.065
Ti_3	0.2500	0	0.2500	3.92	1.025
Si_1	0.1806	0.2506	0.3889	8	0.889
Si_2	0.2077	0.3028	0.1105	8	0.787
K_1(+OH)	0,0892	0,8464	0	4.21	1,712
K_2	0.0807	0.8025	0.5000	2.61	2.328
Na	0.0889	0.4907	0,2355	2.74	2.084
O_1	0,0979	0,8379	0,2262	8	1.584
O_2	0.0815	0.1’18	0,1188	8	0.874
O_3	0.0819	0.1957	0.3212	8	1.179
O_4	0,2365	0.1127	0.3739	8	1.804
O_5	0.2331	0,5246	0,1287	8	1.516
O_6	0.2271	0,7630	0.3182	8	0.997
O_7	0.2456	0.2836	0	4	1.100
O_8	0.1373	0.2287	0.5000	4	1,149
$(H_2O)_1$	0.0182	0,5092	0,1161	3.34	2.448
$(H_2O)_2$	0.0231	0,5061	0,3444	3.51	2.572

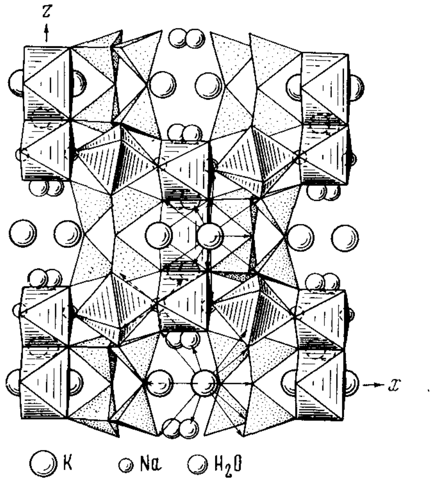

Fig. 2. Projection of the labuntsovite structure in the direction of the y axis.

of this apparently unacceptable situation (the Ti and K atoms with a mutual distance of 2.09 Å, not separated in any way) was that of doubling the b period, i.e., passing to the Milton cell. In half of the positions initially fixed as Ti_1 these atoms may then not be present at all, while the pair of O ligands is replaced by K cations in 11-pointed polyhedra, connected by a two-fold axis, with one common face.

Suitable positions for the Na atoms were found not far from the two-fold axis passing through the middle of the A face of the cell; the two O atoms separating the pair of Na atoms could then only lie on the two-fold axis, whereupon the Na−O distances would be shorter than normal. The transition to the double cell eliminated this two-fold axis, reduced the number of positions for the Na atoms by a factor of 2, and provided more suitable positions for the O atoms.

On passing to the double cell, the need arose for additional information as to the intermediate (odd) layers of the reciprocal lattice. An electron density synthesis calculated from the existing even layers only gave a superposition of the two halves of the double cell, with a number of indeterminacies, arising primarily on account of the fact that one set of equivalent points in the half cell (Fedorov group B2/m) transformed into two different sets of equivalent points on doubling the cell (Fedorov group I2/m). Thus the Na atom, together with two O atoms from its environment, may be sited in two different ways on different sides of the vanishing two-fold axis. The K_2 atoms, which, in the half cell, only partly fill one set of equivalent points, occupy two sets of equivalent points in the double cell, and the question arises as to the distribution of the K_2 between these two positions. The K_1 atoms and the O atoms from the Ti_1 octahedron merge on superposition, and we can only establish their average position, whereas in actual fact their coordinates may be slightly different. These ambiguities are hard to resolve simply from crystal-chemical considerations, since the alternative positions have very little crystal-chemical differences. As already mentioned at the beginning of the article, the odd layer lines in the present case indicate a state of disorder in the structure. This state of disorder, and also the very considerable difference in the K, Ba, Na, and Ca content of different samples of labuntsovite are evidently attributable to the considerable degree of freedom which exists in the disposition of the atoms of these elements, whence also the possibility of the replacement of tetravalent Ti by pentavalent Nb.

The least-squares refinement was only carried out by reference to the even layers of the reciprocal lattice (along the b* axis), since it was assumed that the atoms might lie arbitrarily close to the two-fold axes, which are obligatory in the half cell (Fedorov group B2/m), but vanish on doubling it. Apart from the coordinates of the atoms, their individual isotropic temperature parameters and the multiplicities of the Ti, K, and Na atoms were also refined, as well as the two O atoms from the Na polyhedron, later taken as water molecules. As a result of successive approximations of the electron-density distribution, the R factor based on the three-dimensional set $|F_{hkl}|$ fell to 0.178. The least-squares refinement reduced this factor to 0.132. Table 1 gives the coordinates of the atoms in the half cell derived from this refinement, their multiplicities, and their individual isotropic temperature parameters. Although the diffuseness of the odd layer lines indicates structural disorder, to a first approximation the structure may nevertheless be regarded as or-

TABLE 2. Coordinates of the Atoms in the Double Cell

Atom	*x/a*	*y/b*	*z/c*	Multiplicity of position	Multiplicity of position (from MLS refinement)
Ti_1	0	0	0	2	3,06
Ti_2	0	0	0,2291	4	3.80
Ti_2'	0	0,5	0.2291	4	3.80
Ti_3	0,25	0	0.25	4	3.92
Ti_3'	0,25	0,5	0.25	4	3.92
Si_1	0,1806	0.1253	0.3889	8	
Si_1'	0,1806	0.6253	0,3889	8	
Si_2	0,2077	0.1514	0,1105	8	
Si_2'	0,2077	0.6514	0.1105	8	
K_1	0.0892	0.4232	0	4	6.74
K_2	0,0807	0.4013	0,5	4	2.61
K_2'	0,0807	0,9013	0.5	4	2.61
Na	0,0889	0,7453	0.2355	8	5.47
O_1	0,0979	0.4440	0.2262	8	
O_1'	0,0979	0.9440	0.2262	8	
O_2	0.0815	0,0859	0,1188	8	
O_2'	0,0815	0,5859	0,1188	8	
O_3	0.0819	0,0979	0,3212	8	
O_3'	0,0819	0.5979	0,3212	8	
O_4	0,2365	0.0564	0.3739	8	
O_4'	0.2365	0,5564	0.3739	8	
O_5	0.2331	0,2623	0.1287	8	
O_5'	0,2331	0,7623	0.1287	8	
O_6	0,2271	0,3815	0,3182	8	
O_6'	0,2271	0.8815	0.3182	8	
O_7	0.2456	0,1418	0	4	
O_7'	0.2456	0,6418	0	4	
O_8	0.1373	0,1144	0.5	4	
O_8'	0,1373	0.6144	0.5	4	
OH	0,0892	0.9232	0	4	
$(H_2O)_1$	0.0182	0,2546	0.1161	8	6.67
$(H_2O)_2$	0,0231	0,2530	0.3444	8	7.03

TABLE 3. Interatomic Distances in Å

Ti octahedron	
$Ti_1 - O_2$	2,082 (×4)
$Ti_1 - OH$	2.082 (×2)
Average 2.082	
Ti_2 octahedron	
$Ti_2 - O_1$	1.940 (×2)
$Ti_2 - O_2$	1.933 (×2)
$Ti_2 - O_3$	1.899 (×2)
Average 1.944	
Ti_3 octahedron	
$Ti_3 - O_1$	1.954 (×2)
$Ti_3 - O_4$	1.953 (×2)
$Ti_3 - O_6$	1.935 (×2)
Average 1.947	
Si_1 tetrahedron	
$Si_1 - O_3$	1.570
$Si_1 - O_4$	1.599
$Si_1 - O_5$	1.615
$Si_1 - O_8$	1.621
Average 1.601	
Si_2 octahedron	
$Si_2 - O_2$	1.611
$Si_2 - O_5$	1.590
$Si_2 - O_6$	1.578
$Si_2 - O_7$	1.636
Average 1.604	
Na five-pointed polyhedron	
$Na - O_3$	2.511
$Na - O_5$	2.432
$Na - O_6$	2.401
$Na - (H_2O)_1$	2.240
$Na - (H_2O)_2$	2.340
Average 2.385	
K_1 eleven-pointed polyhedron	
$K_1 - O_1$	3.112 (×2)
$K_1 - O_2$ (1)	2.868 (×2)
$K_1 - O_2$ (2)	3.019 (×2)
$K_1 - O_4$	2.917 (×2)
$K_1 - O_7$	3.062 (×1)
$K_1 - (H_2O)_1$	2.815 (×2)
Average 2.957	
K_2 eleven-pointed polyhedron	
$K_2 - O_3$	3.360 (×2)
$K_2 - O_4$	2.957 (×2)
$K_2 - O_6$	3.340 (×2)
$K_2 - O_7$	2.829 (×1)
$K_2 - O_8$ (1)	2.990 (×1)
$K_2 - O_8$ (2)	2.994 (×1)
$K_2 - (H_2O)_2$	2.950 (×2)
Average 3.093	

dered, within the framework of the doubled unit cell and the Fedorov I2/m, and the atoms will then have the coordinates indicated in Table 2. Table 3 gives the interatomic distances.

The balance of valences led to the conclusion that the two vertices of the Ti_1 octahedron contained not O atoms but OH groups (these were linked to only a single Ti_1 cation), while two H_2O molecules took part in the environment of the Na atoms (one of these also entered into the polyhedron around the K_1 atom, the other into the environment of the K_2 atom). The replacement of some of the O_1 atoms by OH groups was also quite possible.

The refinement of the multiplicities of the Ti, K, and Na cations revealed an excess multiplicity for the Ti_1 atom (1.5, for a multiplicity of the position in the half cell equal to unity), which might have been due to the partial replacement of Ti by Nb atoms. The multiplicity of the K_1 atoms (together with the OH groups) was found to be 4.2, or 3.4 without the OH groups, for a multiplicity of the position equal to two. Here the increase in multiplicity may be explained as being due to the replacement of K by Ba atoms. The multiplicities of the K_2 and Na (Table 2) show that the corresponding positions are only partly occupied by the atoms. We see from a comparison of the multiplicities of the atoms obtained by the refinement of the structure with the number of these in the formula of brown labunstovite that niobium (which is practically absent from the formula) plays a considerable part in the crystal under consideration, while the actual amount of sodium is lower than the formula would imply.

Projections of the structure of labuntsovite are shown in Figs. 1 and 2. In the direction of the *a* edge of the cell, infinite chains of Ti_2 and Ti_3 octahedra, connected by their vertices, stretch along the whole structure. The chains are connected into strips (lying in planes parallel to the B face of the cell) by octahedra containing Ti_1 atoms. Neighboring strips are linked by four-fold silicon–oxygen rings $[Si_4O_{12}]$, the planes of these being parallel to the c axis. The K atoms lie in m symmetry planes, in eleven-pointed figures of three types. The K_1 polyhedron touches the symmetrical K_1 polyhedron and the Ti_2 octahedron along the faces, and the Ti_3 octahedra and Si_2 tetrahedra along the edges. The K_2 and K_2' atoms lie in only slightly differing eleven-pointed polyhedra (owing to the different positions of the H_2O molecules relative to the K_2 and K_2' atoms). These eleven-pointed polyhedra have no faces in common with the other polyhedra; they are connected by their edges to the Na, Ti_3, and Si_1 polyhedra. The distances from the K_2 atom to the O_3 and O_6 atoms lying in its eleven-pointed polyhedron are rather long (3.34 and 3.36 Å). Without these atoms the K_2 polyhedron transforms into a heptahedron with very long edges (most of them longer than 4 Å). In the five-pointed polygon around the Na atom, two vertices are occupied by H_2O molecules. The sixth O atom (O_2), close to the Na atom, lies at 2.884 Å from the latter, as is often the case, this being greater than the ordinary Na–O distance (2.25-2.78 Å). On the basis of the foregoing structural data, the approximate formula of labuntsovite may be written: $(K, Ba, Na, Ca)_8(Ti, Nb)_9(O, OH)_{10} \cdot [Si_4O_{12}]_4 \cdot nH_2O$, in which n ~ 7 for our own sample.

As already mentioned, the disorder of the structure, indicated by the diffuse character of the odd layer lines in the oscillation photograph taken around the b axis, may evidently be attributed to the irregular replacement of Ti_1 octahedra by pairs of K_1 polyhedra, the ambiguous disposition of the Na atoms and the water molecules entering into their environment, and the different dispositions of the K_2 atoms with respect to their two positions in the I2/m space group found in the different subcells. Refinement of these "errors" in the structure awaits further research.

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