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K-Nenadkevichite, a New Representative of the Nenadkevichite–Labuntsovite Series

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Abstract – The structure of a new representative of the nenadkevichite–labuntsovite family was determined. Crystals of K-nenadkevichite are monoclinic, with the parameters $a = 14.692(4)$, $b = 14.164(4)$, $c = 7.859(3)$ Å, $\beta = 117.87(2)°$, $V = 1445.75$ Å^3, sp. gr. Cm, $Z = 4$, and $\rho_{calc} = 2.67$ g/cm^3. The structure was solved by direct methods from X-ray data for a microtwin crystal collected on an Enraf–Nonius diffractometer (MoK_α radiation, 1443 reflections with $|F| \geq 3\sigma_F$, R_{hkl} are 6.9 and 5.5% for isotropic and anisotropic refinement, respectively). It was found that Nb and Ti are distributed statistically over two symmetrically nonequivalent octahedral positions, while K, Na, and H_2O are statistically distributed over the positions inside the framework.

The nenadkevichite–labuntsovite family of rare niobium-titanosilicates includes orthorhombic as well as monoclinic representatives with lattice parameters, which are a multiple of ~7 Å, and monoclinic angles ranging from 117° to 118°.

The crystals found in hydrothermally modified pyrochlore carbonatites from Vuoriyarvi (the Kola Peninsula) made a powder X-ray pattern very similar to that of nenadkevichite. Results of the electron-probe analysis averaged over five measurements enabled us to write their chemical formula in the following generalized form: $(Na_{1.8}K_{2.8})(Ca, Sr, Ba)_{0.4}(Nb_{1.98}Ti_{1.62})\ Si_{8.0}O_{25.8}(OH)_{2.2} \cdot 4.43H_2O$. Hence, the discovered mineral could not be classified either as nenadkevichite [1], because of an excess of K over Na, or as labuntsovite [2], in view of the predominance of Nb over Ti.

The detailed crystal-chemical investigation of labuntsovite and nenadkevichite [3] on the basis of their cationic composition and symmetry enabled us to divide the minerals of this series into three groups: (1) monoclinic labuntsovites with a predominance of K over Na and Ti over Nb, (2) monoclinic Ti-nenadkevichites with predominance of Na over K and Ti over Nb, and (3) orthorhombic nenadkevichites containing predominantly Na and Nb. The characteristic feature of the crystal structure, exhibited by representatives of all these groups, is the existence of columns formed from Ti(Nb) octahedra, which are connected by shared *trans*-corners and are joined by fourfold silicon–oxygen rings. The structure of minerals of the first group is distinguished by the presence of additional Ti octahedra that join the octahedral columns to form layers. The remarkable lability of the structure of minerals of this family and the apparently unusual composition of the new representative was the impetus to determine its structure.

The following parameters of the orthorhombic F unit cell were derived and refined using 25 reflections where $15° < \theta < 20°$ on an Enraf–Nonius CAD-4F diffractometer (MoK_α radiation, graphite monochromator): $a = 14.692(4)$, $b = 14.164(4)$, $c = 27.79(4)$ Å, and $V = 5783$ Å^3.

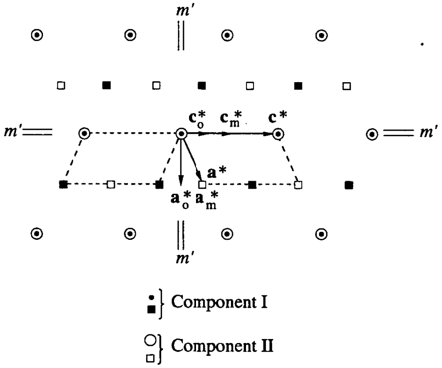

Fig. 1. The diffraction pattern and choice of the unit cell in the reciprocal space of the structure of K-nenadkevichite: the initial orthorhombic unit cell with $\mathbf{a}_o^*$ and $\mathbf{c}_o^*$ vectors, monoclinic (labuntsovite) unit cell with $\mathbf{a}_m^*$ and $\mathbf{c}_m^*$ vectors, and the monoclinic (nenadkevichite) unit cell with $\mathbf{a}^*$ and $\mathbf{c}^*$ vectors. The points of the reciprocal lattice where $k = 2n$ are shown by open and black circles; the points of the reciprocal lattice where $k \neq 2n$ are shown by squares. The twinning planes are labeled by m.

The intensity data set, which was obtained on the same diffractometer in the hemisphere of reciprocal space with $\sin\theta/\lambda \leq 0.6$, consisted of 2696 reflections with $|F| \geq 3\sigma(F)$; after averaging the equivalent (within the Laue symmetry mmm) reflections ($R_{av} = 0.023$), the data set contained 823 reflections. All calculations were carried out using the AREN program package [4] on a PC-AT computer.

The structure was solved by direct methods, assuming the centrosymmetric space group $Fmmm$. The structure exhibits pronounced translational pseudosymmetry along three axes. This pseudosymmetry manifests itself in the fact that the average values of normalized structure factors E with even h, k, l indices significantly exceed those E with odd indices, while the structure factors E_{hkl}, involved in triplet phase relationships, have only even indices. The model of the structure was obtained using the special procedure [5] suggested for determination of pseudosymmetric structures by direct methods within the scope of the AREN program system (the transfer to the reduced unit cell with parameters $a/2$, $b/2$, and $c/2$, followed by the editing of obtained E syntheses). All atoms comprising the mixed framework of the structure and two positions of alkaline cations in channels were revealed by successive approximations [6]. The minimal R factor obtained in acentric space group $Fmm2$ was 24%; however, we failed to refine the deduced model (the R factor remained higher than 20%, and the crystal-chemical characteristics were unreasonable).

Further investigations demonstrated that the sample studied was a crystal twin. Analysis of systematically absent reflections revealed extinctions that were not typical for an orthorhombic system: the data set contained only reflections with Miller indices that satisfied the conditions $h + l = 4n$ and $k = 2n$ ("twinning" extinctions). The schematic sketch of this diffraction pattern (Fig. 1) shows that it can be represented as an overlap of two monoclinic diffraction patterns; in this case, the monoclinic b-axis coincides with the b-axis of the orthorhombic twin lattice, and the unit cell for a single crystal twin components is C-centered.

Basis vectors of the monoclinic unit cell for twin components can be obtained from the basis vectors of the orthorhombic F-centered unit cell of the twin lattice with 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 parameters of the corresponding unit cell are $a = 14.692(4)$, $b = 14.164(4)$, $c = 7.859(3)$ Å, $\beta = 117.87(2)°$, and $V = 1445.75$ Å^3. The relationship between the unit cells is displayed in Fig. 2. Thus, according to the Friedel classification [7], here we observe the twinning by reticular pseudomerohedry with the twin index $n = 2$. If such twinning takes place, the points of the reciprocal lattice of a single

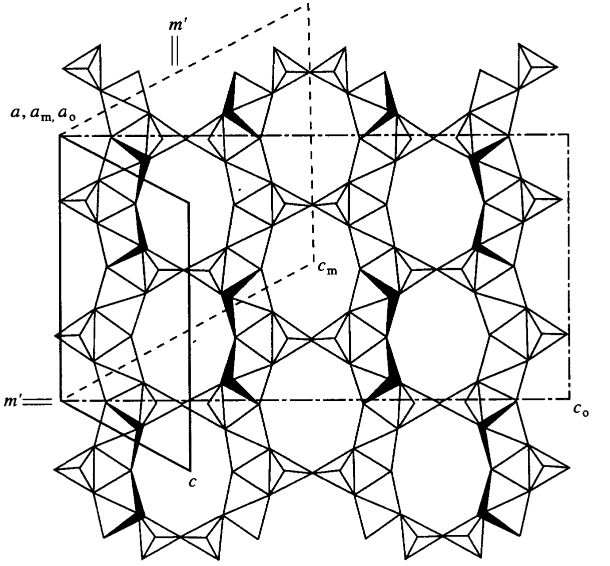

Fig. 2. The mixed framework of octahedra and tetrahedra in the K-nenadkevichite structure. Unit cells in the real space are indicated in the same way as in Fig. 1.

Table 1. Atomic coordinates, isotropic thermal parameters, and occupancies for atoms in the structure of K-nenadkevichite

Atom	B_j, Å^2	x/a	y/b	z/c	Multiplicity (occupancy of the position)
Si1	1.4(1)	0.2170(5)	0.8920(3)	0.7800(9)	4
Si2	1.7(1)	0.6918(7)	0.8916(5)	0.736(1)	4
Si3	0.9(1)	0.8055(5)	0.8901(3)	0.186(1)	4
Si4	0.9(1)	0.3287(5)	0.8914(4)	0.230(1)	4
*M*1	0.48(4)	0	0.7691(1)	0.5000(1)	4
*M*2	0.48(4)	0.7434(3)	0.7480(1)	0.4644(6)	4
K1	3.7(1)	0.5001(9)	0.8194(4)	0.983(2)	4(0.76)
K2	5.6(3)	0.432(2)	0	0.705(3)	2(0.53)
K3	3.1(5)	0.910(2)	0	0.649(4)	2(0.44)
K4	3.3(3)	0.081(2)	0	0.288(3)	2(0.49)
Na1	5.0(5)	0.009(2)	0	0.468(3)	2(0.58)
Na2	6.7(6)	0.796(6)	0	0.53(1)	2(0.39)
Na3	7(1)	0.006(9)	0	0.11(2)	2(0.25)
O1	3.9(1)	0.911(2)	0.766(1)	0.586(3)	4
O2	1.7(3)	0.925(1)	0.873(1)	0.308(2)	4
O3	1.2(3)	0.268(1)	0.867(1)	0.341(2)	4
O4	3.0(4)	0.274(2)	0.823(1)	0.702(3)	4
O5	1.1(3)	0.429(1)	0.826(1)	0.285(2)	4
O6	2.8(5)	0.375(2)	0	0.280(4)	2
O7	2.0(4)	0.251(1)	0.879(1)	0.003(2)	4
O8	2.3(5)	0.227(2)	0	0.730(4)	2
O9	0.5(2)	0.104(1)	0.768(1)	0.372(2)	4
O10	2.2(4)	0.092(1)	0.870(1)	0.665(2)	4
O11	1.7(3)	0.747(1)	0.865(1)	0.601(2)	4
O12	0.7(2)	0.732(1)	0.824(1)	0.245(2)	4
O13	2.3(4)	0.591(1)	0.826(1)	0.672(2)	4
O14	1.3(4)	0.656(2)	0	0.711(3)	2
O15	2.6(4)	0.771(1)	0.872(1)	0.956(2)	4
O16	1.7(5)	0.777(1)	0	0.204(4)	2
$(H_2O)1$	2.6(6)	0.030(2)	0.879(2)	0.981(4)	4(0.56)
$(H_2O)2$	4(1)	0.564(4)	0	0.21(1)	2(0.61)
$(H_2O)3$	3(2)	0.299(6)	0	0.51(1)	2(0.32)
$(H_2O)4$	7(1)	0.036(5)	0.827(5)	0.03(1)	4(0.37)
$(H_2O)5$	4(2)	0.514(7)	0	0.89(1)	2(0.36)

crystal component can be divided into two equal portions; points of the first portion are common for both components (points with $k = 2n$), and points of the second portion (with $k = 2n + 1$) are individual. In the X-ray experiment, intensities of overlapping reflections from both components are measured in the points of the first portion, while reflections from individual twin components are only measured in the points of the second portion. The ratio of the second type of intensities, related by the twin symmetry elements, is determined by the ratio of volumes of twin components (1 : 1 in our case). Refined mass coefficients of twin components are 0.52 and 0.48. The symmetry elements of twinning are the planes (0 0 1) and (–4 0 1) of the monoclinic lattice or the planes (1 0 0) and (0 0 1) of the twin orthorhombic lattice.

The monoclinic lattice symmetry corresponds to three space groups: *C*2/*m*, *C*2, and *Cm*. The independent structure determination by the Patterson method in the space group *C*2/*m* confirmed the structure motif identified earlier. The refinement of the structure was carried out using matrices of twinning mentioned above. The averaged experimental data set (within the Laue diffraction symmetry 2/*m*) contained 1443 reflections with $|F| \geq 3\sigma(F)$; $R_{av} = 0.03$.

The minimal *R* value (8%) was obtained in the acentric group *Cm*. The peaks, identified as K and Na atoms and O atoms of H_2O molecules, were localized from the series of the difference electron density maps calculated with the data set, corresponding to one twin component. As these atoms, occupying the positions within the framework, were characterized by high thermal parameters, so their refinement was carried out with regard to the partial occupancies of positions: the occupancy parameters were refined with fixed thermal parameters, then the thermal parameters were refined. Small amounts of impurities of cations Ba, Sr, and Ca, which were determined by the chemical analysis, were ignored in the distribution of K and Na. The composition of octahedral positions was refined using combined atomic scattering curves because, when Nb and Ti atoms were located at positions *M*1 and *M*2, respectively, the first position was characterized by the thermal parameter of 1.2 Å, while the second position had an abnormally low value (0).

The positional, thermal, and occupancy parameters corresponding to the final *R* factors 6.9 and 5.5% for isotropic and anisotropic refinement, respectively (no absorption correction was applied, for the absorption coefficient μ is 22.16 cm^{-1}), are listed in Table 1; the interatomic distances are given in Table 2.

The columns of (Nb, Ti) octahedra, linked by four-membered $[Si_4O_{12}]$ rings to form a mixed framework, may be considered the main structural units of the new mineral and of other representatives of the labuntsovite–nenadkevichite series. The central cations in (Nb, Ti) octahedra are obviously displaced from the plane of the square base towards one of the bridging vertices (*M*1–O1 1.73, *M*2–O9 1.84 Å), with a simultaneous increase of the distance to the second vertex (*M*1–O9 2.18, *M*2–O1 2.20 Å). The similar displacement of Nb and Ti, resulting in the pseudotetragonal-pyramidal coordination, was observed in nenadkevichite [1], Na-niobate, fersmite, murmanite, lomonosovite, and other minerals [8]. Undulating octahedral columns are typical for a wide range of compounds [9]. The translational periodicity along the column axis (*a*) depends on the degree of its deformation and varies in

Table 2. Interatomic distances (Å) in the K-nenadkevichite structure

Si-tetrahedra							
Si1–O4	1.58(2)	Si2–O15	1.59(1)	Si3–O2	1.57(1)	Si4–O3	1.55(2)
O7	1.59(1)	O14	1.60(1)	O16	1.63(1)	O7	1.61(1)
O8	1.60(1)	O13	1.61(1)	O12	1.64(1)	O5	1.61(1)
O10	1.65(1)	O11	1.64(2)	O15	1.65(1)	O6	1.65(1)
⟨Si–O⟩	1.61	⟨Si–O⟩	1.61	⟨Si–O⟩	1.62	⟨Si–O⟩	1.61
M-octahedra				Na-polyhedra			
*M*1–O1	1.73(3)	*M*2–O9	1.84(1)	Na1–O2	2.21(1) × 2	Na2–O11	2.20(5) × 2
O13	1.92(1)	O11	1.96(1)	O10	2.35(1) × 2	O16	2.43(9)
O10	1.97(1)	O12	1.97(1)	O8	2.88(3)	O14	3.0(1)
O5	2.02(1)	O4	1.97(2)	O16	3.05(3)	$(H_2O)2$	3.13(7)
O2	2.03(1)	O3	2.01(1)	⟨Na–O⟩	2.51	O12	3.17(4) × 2
O9	2.18	O1	2.20(2)	Na1–K4	2.12(4)	⟨Na–O⟩	2.76
⟨*M*–O⟩	1.98	⟨*M*–O⟩	1.99	K3	2.45(4)	Na2–K3	1.49(7)
						Na3–$(H_2O)1$	2.1(1) × 2
						$(H_2O)4$	2.62(9) × 2
						O2	2.9(1) × 2
						⟨Na–O⟩	2.54
						Na3–K4	1.31(9)

K-polyhedra					
K1–$(H_2O)5$	2.68(3)	K2–O6	3.04(3)	K3–$(H_2O)1$	2.92(3) × 2
$(H_2O)1$	2.85(3)	O8	3.10(4)	O11	2.95(2) × 2
O9	2.97(1)	O14	3.27(4)	O16	3.09(3)
O4	3.00(2)	O3	3.32(2) × 2	O10	3.19(3) × 2
O5	3.01(2)	O4	3.40(2) × 2	O2	3.30(3) × 2
O1	3.01(2)	O13	3.49(2) × 2	O1	3.34(1) × 2
$(H_2O)2$	3.01(3)	$(H_2O)2$	3.52(6)	⟨K–O⟩	3.13
O12	3.05(1)	⟨K–O⟩	3.35	K3–Na2	1.49(7)
O13	3.28(2)	K2–$(H_2O)5$	1.39(7)	Na1	2.45(4)
⟨K–O⟩	2.98	$(H_2O)3$	1.82(7)		
K1–$(H_2O)4$	2.13(7)				
K4–$(H_2O)1$	2.75(3) × 2				
$(H_2O)3$	2.85(7)				
O2	2.97(2) × 2				
$(H_2O)4$	3.06(7) × 2				
O8	3.11(3)				
O3	3.18(3) × 2				
O9	3.33(1) × 2				
O10	3.43(2) × 2				
⟨K–O⟩	3.10				
K4–Na3	1.31(9)				
Na1	2.12(4)				

Table 3. Crystal metrics of minerals of the nenadkevichite–labuntsovite family*

Mineral	Unit-cell parameters (Å, deg)				Sp. gr.
	a	*b*	*c*	β	
Nenadkevichite (Canada)	7.41	14.20	7.15	–	*Pbam***
Nenadkevichite (Lovozero)	14.71	27.93	14.27	–	*C*222
Nenadkevichite (Canada)	14.67	28.23	14.21	–	*C*222
K-nenadkevichite (Vuoriyarvi)	14.69	14.16	7.86	117.87°	*Cm***
Niobolabuntsovite (SSSR)	14.57	28.32	14.37	–	*F*
Labuntsovite (the Khibini mountains)	14.29	13.78	7.82	117°15′	*C*
Labuntsovite (Wyoming)	14.27	13.75	15.57	117°15′	*C*2/*m*
Labuntsovite (the Khibini mountains)	14.18	13.70	15.48	117°	*I*2/*m***
K-labuntsovite (the Khibini mountains)	7.78	14.34	14.05	117°	*C*2/*m*

Notes: * All of the data is taken from the handbooks on mineralogy (with the exception of K-nenadkevichite).
** Minerals studied by X-ray analysis.

the minerals under consideration from 7.1 to 7.8 Å (Table 3). For the structure in question, this value is 7.35 Å, and doubling of the period arises from the nonequivalence of octahedra (the difference in composition and sizes), as well as from their slight rotation (Fig. 3). The second period, which is perpendicular to the column axis and, for monoclinic representatives, coincides with the unique axis, ranges from 13.7 to 14.3 Å (in our case, 14.16 Å). This period is double the distance between columns, as every second column is rotated relative to the first one (Fig. 4). In our opinion, and according to Organova *et al.* [3], the twofold increase of this period (27.93 - 28.32 Å) for orthorhombic representatives may be the result of twinning, as it takes place in the sample under investigation (with regard to the interchanging of *b*- and *c*-axes). The *c*-period corresponds to the distance between columns and varies over a wide range (from 7.0 to 7.86 Å); the latter fact apparently depends on the degree of distortion of the four-membered rings comprised of Si-tetrahedra (Fig. 5). The doubling of this period in some structures (labuntsovite) may be the result of the rotation of octahedral columns relative to each other. It should be mentioned that in the structure under investigation, the doubling of the *c*-period gives rise to the *C*-centered unit cell, correlated with the *I* cell of labuntsovite [2] (in the β setting), but the *C* unit cell is a twin pseudocell, related to the orthorhombic twin cell by the transformation matrix 1 0 0 / 0 1 0 / –0.5 0 0.5 (the latter cell is shown by a dashed line in Fig. 2).

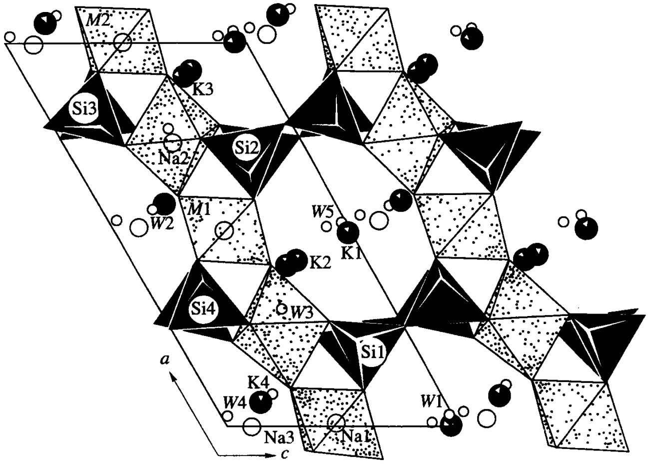

Fig. 3. Projection of the K-nenadkevichite structure to the (010) plane. Si rings are black; *M* polyhedra are dashed. K and Na atoms and H_2O molecules are indicated by circles.

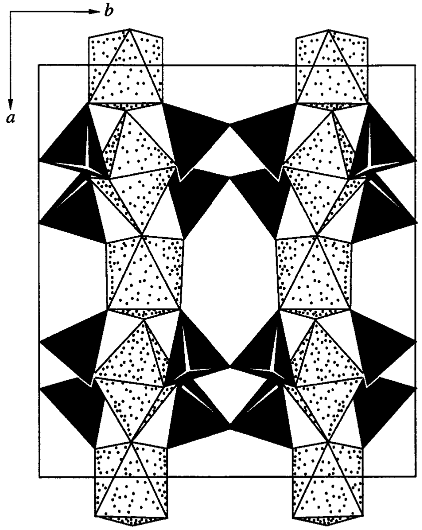

Fig. 4. Projection of the mixed framework of the K-nenadkevichite structure to the (001) plane. The rotation of octahedral columns about the *a*-axis is clearly visible.

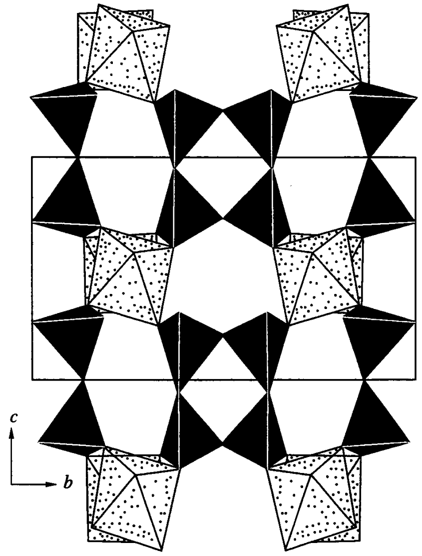

Fig. 5. Projection of the mixed framework of the K-nenadkevichite structure to the (100) plane.

The unit cell size for minerals of this family evidently depends not only on the degree of distortion of octahedral columns, but on the filling of the channels and cavities of the mixed framework as well. Because of the excess of highly charged cations *M* = Nb and Ti, some additional octahedra between columns are formed, with the result that the clusters (linear triads of octahedra sharing faces) occur in the structure, while the octahedral columns are converted into octahedral layers. The similar cationic layers, which also contain clusters, are typical for a wide variety of phosphates [10, 11]. A distinguishing feature of labuntsovite is the presence of clusters consisting of three Ti-octahedra and the associated layers, which are parallel to *ab* (the β setting). It is the absence of an additional octahedral position typical for labuntsovite that makes the structure under investigation similar to nenadkevichite.

If columns of octahedra form a mixed framework, the type of the atomic arrangement is determined basically by an *M* : *T* ratio. For *M* : *T* = 1, densely packed mixed frameworks are formed, in which the columns of octahedra are joined by orthotetrahedra as, for instance, in the phosphates tavorite, amblygonite, etc. In the case of nenadkevichite–labuntsovite, with the ratio *M* : *T* = 1 : 2, the framework becomes looser and the columns are joined by fourfold rings [Si_4O_{12}]. The planar symmetry, exhibited by these rings in K-nenadkevichite, as well as in other minerals of the nenadkevichite–labuntsovite family, makes its structure similar to kainosite and taramellite. This group of silicates consists of about 10 minerals and synthetic compounds with fourfold rings [12], the symmetry of which varies from $\bar{1}$ ($KHSiO_3$) and 2 (fosinaite) to 2*mm*, in recently determined $BaCuSi_2O_6$ [13] and 4 (baotite).

The crystal-chemical formula for the mineral is in good agreement with the chemical analysis and has the form $Na_{0.6}K_{1.5}\{(Nb_{0.6}Ti_{0.4})(Nb_{0.5}Ti_{0.5})[Si_4O_{12}](O, OH)_2\} \cdot 1.6H_2O$, $Z = 4$, and $\rho_{calc} = 2.67$ g/cm^3. It should be mentioned, however, that the determined amount of Na atoms and H_2O molecules is less than those estimated by chemical analysis. This fact can be attributed to the difficulties in localization of these atoms on electron difference maps due to the low occupancies of their positions.

The differences in composition of nenadkevichite, labuntsovite, and the mineral under investigation, which have been revealed by the X-ray structure analysis, are presented schematically (per four $[Si_4O_{12}]$ rings) in the following form:

Table 4

Mineral	Alkaline cations	*M* cations	H_2O molecules	System
Labuntsovite	$K_6Na_{2.7}$	Ti_9	$7H_2O$	Monoclinic
Nenadkevichite	Na_8	Nb_8	$8H_2O$	Orthorhombic
K-nenadkevichite	$K_6Na_{2.4}$	$Nb_{4.4}Ti_{3.6}$	$6.4H_2O$	Monoclinic

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