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STRUCTURES OF INORGANIC COMPOUNDS

Refined Crystal Structure of Kuzmenkoite

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Abstract—The structure of the mineral kuzmenkoite found in the Lovozero massif (the Kola Peninsula) was reinvestigated by the X-ray diffraction analysis. This mineral belongs to the labuntsovite family and differs from other members of this family by the absence of Na atoms, a high Mn content, and the new type of filling framework channels because of the replacement of Na atoms by H_2O molecules and H_3O groups. It was found that the disorder of atoms in the channels leads to lowering of the symmetry to *Cm*. *© 2000 MAIK "Nauka/Interperiodica".*

Kuzmenkoite is a mineral of the labuntsovite family. Recently, representatives of this family have attracted the attention of researchers because of their ion-exchange properties. The mineral was found in the near-contact zone of the Lovozero alkaline massif and was structurally studied by Golovina *et al.* [1] in the centrosymmetric sp. gr. *C*2/*m* typical of labuntsovites. However, the cited work did not give a detailed picture of the cation distribution in the structure channels. Using the analogy with other minerals of this family, e.g., vuoriyarvite [2, 3] and the oxonium mineral [4] from the Khibiny massif, one can associate a high degree of decationization of the sample with probable lowering of the symmetry. Our reinvestigation of the mineral in the sp. gr. *Cm* showed a number of additional statistically occupied and split positions. We also refined the occupancies of a number of positions using the mixed atomic scattering curves.

The principal characteristics of the crystal and the details of the X-ray diffraction study are indicated in Table 1. The coordinates of the basis atoms are listed in Table 2. The compositions of the positions and selected interatomic distances are given in Table 3.

The structure of kuzmenkoite (figure) is characterized by a mixed framework consisting of "deformable" chains of Ti(Nb)-octahedra linked via four-membered rings of Si-tetrahedra characteristic of labuntsovites and nenadkevichites. The channels along the coordinate axes are filled with small and large cations and water molecules. The structure of kuzmenkoite is characterized by a high Mn-content and an almost complete absence of Na atoms (which are replaced by oxonium ions and water molecules). The crystallochemical formula of the mineral provides a rather low value or the *R*-factor (3.4%) and is in good agreement with the data of the local X-ray spectral analysis ($Z = 1$): $\{K_{3.2}(H_3O)_{1.5}Na_{0.35}Ba_{0.1}[Mn_{1.12}Nb_{0.28}] \cdot 8.5H_2O\}$ $\{[(Ti_{3.2}Fe^{3+}_{0.8})(Ti_{3.6}Nb_{0.4})](OH_{7.6}O_{0.4})(Si_4O_{12})_4\}$.

Because of the mineral decationization, about half of the cations (out of 10–12 cations, usually present in labuntsovites and nenadkevichites) are retained in the structure channels (the first braces). At the same time, two peaks were localized in the vicinity of the Na posi-

Table 1. Structural data and details of X-ray diffraction experiment

Unit-cell parameters, Å, deg	$a = 14.369(3)$
	$b = 13.906(3)$
	$c = 7.812(1)$
	$\beta = 117.09(2)$
Unit-cell volume, Å^3	1389.7
Sp. gr., *Z*	*Cm*, 4
Radiation; λ, Å	MoK_α, 0.70926
Calculated density, g/cm^3	2.6
Crystal dimensions, mm	$0.2 \times 0.15 \times 0.05$
Diffractometer	KM-4
$\sin\theta/\lambda$	<0.98
Ranges of index variations for measured reflections	$-26 < h < 25$, $0 < k < 21$, $0 < l < 8$
Total number of reflections	3269
Number of independent reflections	1167 $\lvert F\rvert > 4\sigma(F)$
R-factor upon anisotropic refinement	0.034
Extinction parameter	0.0000156
Program used in calculation	AREN [5]

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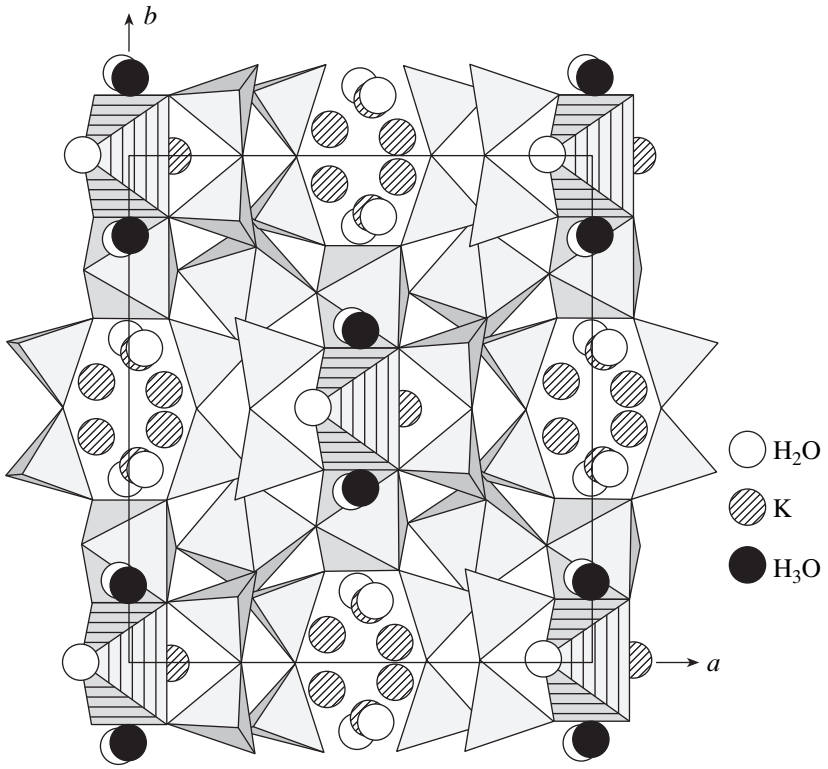
Table 2. Coordinates, equivalent thermal parameters (B_{eq}), multiplicities (Q), and occupancies (q) of the atomic positions in the kuzmenkoite structure

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2	*Q*	*q*
Si(1)	0.1830(1)	0.3892(1)	0.7538(2)	0.43(7)	4	1
Si(2)	0.8170(1)	0.6109(1)	0.2476(3)	1.16(7)	4	1
Si(3)	0.2932(1)	0.3906(1)	0.1963(2)	0.63(7)	4	1
Si(4)	0.7064(1)	0.6099(1)	0.8027(2)	0.83(7)	4	1
M(1)	0.0000(1)	0.2301(1)	0.5000(1)	1.22(2)	4	1
M(2)	0.2510(3)	0.2511(3)	0.5028(6)	1.02(2)	4	1
Mn	–0.0024(5)	0	0.5017(9)	1.25(3)	2	0.70(1)
K(1)	0.0945(7)	0	0.336(2)	3.5(1)	2	0.30(1)
K(2)	0.5725(4)	0.0393(5)	0.2865(7)	3.6(2)	4	0.41(1)
K(3)	0.4275(6)	0.0543(7)	0.731(1)	3.3(1)	4	0.30(1)
K(4)	0.518(1)	0.112(2)	0.027(6)	5.0(7)	4	0.06(1)
H_3O	0.497(2)	0.346(1)	0.011(3)	5.1(4)	4	0.65(1)
O(1)	0.0835(4)	0.3221(3)	0.6918(8)	1.5(2)	4	1
O(2)	0.2399(3)	0.3717(3)	0.6203(6)	0.9(2)	4	1
O(3)	0.7696(4)	0.6790(4)	0.7304(8)	1.5(2)	4	1
O(4)	0.4176(2)	0.3791(3)	0.3275(6)	0.5(2)	4	1
O(5)	0.3563(5)	0	0.2724(9)	0.7(3)	2	1
O(6)	0.2665(3)	0.3723(3)	0.9740(7)	1.2(2)	4	1
O(7)	0.2409(5)	0	0.786(1)	1.3(3)	2	1
O(8)	0.9193(3)	0.6794(4)	0.3107(7)	1.1(2)	4	1
O(9)	0.7617(4)	0.6288(3)	0.3832(8)	1.3(2)	4	1
O(10)	0.2264(3)	0.3192(3)	0.2621(7)	0.8(2)	4	1
O(11)	0.5816(4)	0.6204(4)	0.6710(8)	1.8(2)	4	1
O(12)	0.1411(6)	0.5	0.7335(9)	2.2(3)	2	1
O(13)	0.7324(4)	0.6303(4)	0.0244(7)	1.5(2)	4	1
O(14)	0.2578(5)	0.5	0.2123(9)	1.3(3)	2	1
OH(1)	0.0999(3)	0.2306(3)	0.6059(6)	0.9(2)	4	1
OH(2)	0.0994(3)	0.7722(4)	0.3918(7)	1.3(2)	4	1
H_2O(1)	0.896(1)	0	0.656(2)	2.7(2)	2	0.80(2)
H_2O(2)	0.491(1)	0.139(2)	–0.048(2)	9.3(3)	4	0.50(1)
H_2O(3)	0.977(1)	0.162(1)	0.980(2)	1.7(4)	4	0.35(1)
H_2O(4)	0.085(1)	0	0.333(2)	3.1(3)	2	0.70(1)
H_2O(5)	0.531(2)	0.119(2)	0.129(4)	1.6(8)	4	0.20(2)

Table 3. Characteristics of the coordination polyhedra in the kuzmenkoite structure

Position	Composition	Coordination number	Cation–anion distances		
			minimum	maximum	average
Si(1)	4 Si	4	1.587(5)	1.635(3)	1.609
Si(2)	4 Si	4	1.607(7)	1.631(4)	1.622
Si(3)	4 Si	4	1.613(3)	1.626(2)	1.619
Si(4)	4 Si	4	1.592(7)	1.629(3)	1.615
M(1)	3.6Ti + 0.4Nb	6	1.884(4)	2.018(4)	1.96
M(2)	3.2Ti + 0.8Fe	6	1.930(6)	1.988(7)	1.96
Mn	1.12Mn + 0.28Nb	6	2.14(1)	2.28(2)	2.17
K(1)	0.54K + 0.06Ba	11	2.88(1)	3.37(1)	3.13
K(2)	1.64K	9	2.46(2)	3.32(1)	2.97
K(3)	0.84K + 0.36Na	9	2.85(1)	3.33(1)	3.03
K(4)	0.24K	9	2.87(1)	3.44(1)	3.26
H_3O	1.3H_3O + 1.3H_2O	11	2.84(2)	3.57(2)	3.19



Kuzmenkoite structure projected onto the (001) plane. The Mn-octahedra are hatched with solid lines. Cations, water molecules, and H_3O groups are indicated by circles of different types.

tion on the electron-density maps. These peaks were identified with the positions partly occupied by oxygen. We assumed that one of these peaks corresponds to an H_2O molecule, whereas the second one spaced by ~0.3 Å from the first peak corresponds to the oxonium group. The presence of oxonium ions in this position has also been indicated in [4]. In the structure under consideration, the presence of these ions is explained by a low cation content.

The structure of this mineral is also highly disordered. Thus, all the positions within the channels are split spaced by shortened distances from one another, and only partly occupied. Different occupancies of the positions (related by a twofold rotation pseudoaxis) indicate a lowered symmetry.

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