ISSN 1063-7745, Crystallography Reports, 2017, Vol. 62, No. 1, pp. 60–65. © Pleiades Publishing, Inc., 2017.
Original Russian Text © R.K. Rastsvetaeva, K.A. Rozenberg, N.V. Chukanov, S.M. Aksenov, 2017, published in Kristallografiya, 2017, Vol. 62, No. 1, pp. 54–59.

STRUCTURE OF INORGANIC COMPOUNDS

Dedicated to the memory of V.V. Ilyukhin (1934–1982)

Crystal Structure of Ilyukhinite, a New Mineral of the Eudialyte Group

R. K. Rastsvetaeva[a],*, **K. A. Rozenberg**[a], **N. V. Chukanov**[b], **and S. M. Aksenov**[a]

[a] *Shubnikov Institute of Crystallography, Crystallography and Photonics Federal Scientific Research Center, Russian Academy of Sciences, Moscow, 119333 Russia*

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

**e-mail: rast@crys.ras.ru*

Received June 23, 2016

Abstract—The crystal structure of ilyukhinite, a new mineral of the eudialyte group, is studied by X-ray diffraction. The mineral found in pegmatite bodies of the Kukisvumchorr Mountain (Khibiny alkaline complex) is characterized by low sodium content, high degree of hydration, and predominance of manganese over iron. The trigonal cell has the following parameters: $a = 14.1695(6)$ and $c = 31.026(1)$ Å; space group $R3m$. The structure is refined to final $R = 0.046$ in the anisotropic approximation of atomic displacements using $1527 F > 3\sigma F$. The idealized formula of ilyukhinite ($Z = 3$) is written as $(H_3O,Na)_{14}Ca_6Mn_2Zr_3Si_{26}O_{72}(OH)_2 \cdot 3H_2O$. The new mineral differs from other representatives of the eudialyte group by the predominance of both oxonium in the N positions of extra-framework cations and manganese in the $M2$ position centering the tetragonal pyramid.

DOI: 10.1134/S1063774517010199

INTRODUCTION

Minerals of the eudialyte group are characterized by a wide crystal-chemical variety. At the present time, this group includes more than 20 mineral species [1]. These minerals are widespread in nature as accessory typomorphic (and sometimes rock-forming) minerals in some types of agpaite rocks. They are characterized by complex mechanisms of cation ordering and isomorphic substitutions of cations, anions, and polyatomic groups. Distinguishing of new mineral varieties in the eudialyte group is of importance because, in particular, these minerals are indicators of formation conditions and changes in physicochemical properties of mineral-forming medium. Wide crystal-chemical variety of the eudialyte-group minerals owes to a large degree of postcrystallization processes (leaching, ion exchange, and hydration) unaffecting the heteropolyhedral framework of eudialyte.

The eudialyte specimen studied in this work was found as aggregations of brownish orange transparent grains to 1mm in cross section in a pegmatite body of the Kukisvumchorr Mountain (Khibiny alkaline complex) in association with albite, microcline, aegirine, murmanite, fluorite, sphalerite, and molybdenite. It attracted attention by an unusual chemical composition, namely, low sodium content and high degree of hydration, as well as by abnormally low density and refractive index. Further studies showed that it is a new Mn-dominant oxonium member of the eudialyte group.

The mineral and its name ilyukhinite have been approved by the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association (CNMNC IMA) October 20, 2015, IMA no. 2015-065, and a standard sample of the mineral has been deposited in the geological collection of the Natural History Museum, Oslo under no. GM 43578. The mineral was named after an outstanding Soviet crystallographer, Doctor of Physics and Mathematics Vladimir Valentinovich Ilyukhin (1934–1982) (Fig. 1), author of more than 450 scientific publications including fundamental works on methodology of crystal structure determination and crystal chemistry of hydrosilicates and minerals with heteropolyhedral structures. Vladimir Valentinovich Ilyukhin began his scientific studies in 1956 as a postgraduate under supervision of academician N.V. Belov and worked at the Shubnikov Institute of Crystallography of the Academy of Sciences of the USSR till 1980. Talented scientist, V.V. Ilyukhin had an exhaustible energy; his name is also associated with the development of speleology and speleotourism in the USSR. He was 48 when his vivid life tragically ceased during a

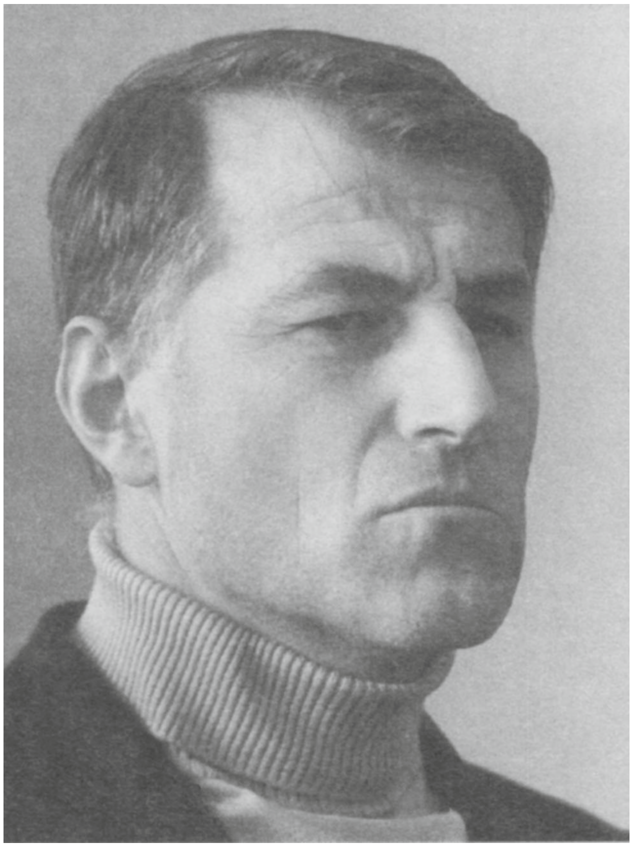

Fig. 1. Vladimir Valentinovich Ilyukhin (1934–1982).

rescue mission in Abkhazia. Since that time a cave system in the Gagra Range bears the name of V.V. Ilyukhin, and now his name was given to the mineral.

EXPERIMENTAL

The chemical composition of ilyukhinite was determined on a Tescan VEGA-II XMU INCA Energy 450 electron microscope. The content of H_2O was determined by gas-chromatographic analysis of the products of calcination at 1400°C on a Vario Micro cube elemental analyzer. The empirical formula of ilyukhinite calculated for 25.41 Si atoms is written as $H_{36.04}(Na_{3.82}K_{0.20})(Ca_{5.65}Ce_{0.22}La_{0.14}Nd_{0.07})(Mn_{1.285}Fe_{0.48})(Zr_{2.645}Ti_{0.34})Nb_{0.31}Si_{25.41}S_{0.42}Cl_{0.23}O_{86.82}$ [2].

X-Ray diffraction study. The diffraction data for the mineral were obtained at room temperature on a Bruker Smart Apex II diffractometer equipped with an area detector from an isometric single crystal. Based on close chemical compositions of the mineral studied and aqualite [3], the coordinates of the framework atoms of the latter mineral were used as a starting set for the refinement. The remaining positions were found in a series of difference electron density syntheses. The coordinates, composition, site occupancies, and isotropic—anisotropic thermal displacement parameters of atoms were refined by the least-squares procedure to $R = 0.046$ using $1527 F > 3\sigma F$ with the AREN program package [4]. Mixed atomic scattering curves were used for the refinement of cations at positions with isovalent or heterovalent substitutions. Crystal data and details of the experiment are given in Table 1. The coordinates of positions, atomic displacement parameters, site multiplicities, and site occupancies are listed in Tables 2 and 3. Characteristics of coordination polyhedra are given in Table 4.

Table 1. Crystal data, details of data collection, and results of structure refinement for ilyukhinite

Idealized formula	$(H_3O,Na)_{14}Ca_6Mn_2Zr_3Si_{26}O_{72}(OH)_2 \cdot 3H_2O$
a, c, Å	14.1695(6); 31.026(1)
V, Å^3	5394.7(7)
Crystal system, space group, Z	Trigonal, $R3m$, 3
Crystal dimensions, mm	0.15 × 0.20 × 0.20
Diffractometer	Bruker Smart Apex II, CCD detector
Radiation; λ, Å	MoK_α; 0.71073
Scan mode	ω
Limiting indices	$-20 < h < 20$, $-20 < k < 20$, $-44 < l < 44$
$\sin\theta/\lambda$	<0.715
Number of reflections: measured/unique with $F > 3\sigma F$; R_{int}, %	24533/1527; 3.1
Refinement method	Least squares on F
R, %	4.6
Programs	AREN

Table 2. Coordinates of the framework atoms, site multiplicities (Q), and equivalent atomic displacement parameters (B_{eq}) in the structure of ilyukhinite

Position	x/a	y/b	z/c	Q	q	B_{eq}, Å^2
Z	0.3328(1)	0.1664(1)	0.1668(1)	9	1	1.59(3)
$M1$	0.0008(2)	0.2626(1)	0.0006(1)	18	1	1.57(3)
Si1	0.5263(2)	0.2631(1)	0.2530(1)	9	1	1.21(9)
Si2	–0.0093(1)	0.6036(1)	0.0992(1)	18	1	1.67(7)
Si3	0.2056(1)	0.4113(1)	0.0781(1)	9	1	1.61(9)
Si4	0.0811(2)	0.5405(1)	0.2581(1)	9	1	1.56(9)
Si5	0.0551(1)	0.3253(1)	0.2351(1)	18	1	1.61(6)
Si6	0.1421(2)	0.0710(1)	0.0817(1)	9	1	1.34(9)
O1	0.4668(8)	0.2334(6)	0.2085(3)	9	1	2.7(3)
O2	0.2498(5)	0.0228(4)	0.2041(2)	18	1	2.7(2)
O3	0.4099(5)	0.3104(6)	0.1330(2)	18	1	2.7(2)
O4	0.6034(3)	0.3966(3)	0.2519(3)	9	1	2.1(3)
O5	0.444(1)	0.2215(7)	0.2919(2)	9	1	2.8(3)
O6	0.4016(7)	0.0502(7)	0.0519(2)	18	1	4.2(2)
O7	0.0962(4)	0.3734(5)	0.1052(2)	18	1	2.4(2)
O8	0.0238(7)	0.5119(5)	0.1111(4)	9	1	2.8(3)
O9	0.2720(3)	0.5439(4)	0.0760(3)	9	1	3.1(3)
O10	0.1814(5)	0.3628(7)	0.0290(3)	9	1	3.2(4)
O11	0.0265(7)	0.5133(5)	0.3037(2)	9	1	2.0(3)
O12	0.1805(3)	0.3619(5)	0.2223(2)	9	1	1.7(3)
O13	0.0387(5)	0.2975(5)	0.2879(2)	18	1	2.2(2)
O14	0.3902(4)	0.4306(5)	0.2266(1)	18	1	2.0(2)
O15	0.3950(4)	0.6050(4)	0.2576(5)	9	1	3.9(3)
O16	0.0604(3)	0.1208(4)	0.0801(3)	9	1	2.3(3)
O17	0.2048(7)	0.1024(5)	0.1285(3)	9	1	2.6(3)
O18	0.2163(8)	0.1081(5)	0.0398(3)	9	1	2.8(3)

STRUCTURE DESCRIPTION, RESULTS, AND DISCUSSION

In the mineral studied, the heteropolyhedral framework is analogous to those in the structures of other representatives of the eudialyte group. It is formed by [Si_3O_9] and [Si_9O_{27}] silicon—oxygen rings and six-membered rings of edge-sharing CaO_6 octahedra, which are linked by discrete ZrO_6 octahedra. Voids of the framework accommodate alkali and alkaline-earth cations, admixtures of transition metal cations, large additional anions, anionic groups, and water molecules.

The main specific features of the composition and structure of ilyukhinite are reflected in its crystal-chemical formula (Z = 3) (Fig. 2) which agrees well with the results of chemical analyses: $^{N1-5}[(H_3O)_{9.33}Na_{3.96}K_{0.20}Ce_{0.10}]^{M1}[Ca_{5.70}Ce_{0.30}]$ $^{Z}[Zr_{2.60}Ti_{0.40}]^{M2}[Mn_{1.29}Fe^{3+}_{0.45}]^{M3}[Si_{0.74}S_{0.26}]^{M4}[Si_{0.67}Nb_{0.33}]$ $[Si_3O_9]_2[Si_9O_{27}]_2(O,OH)_2(H_2O)_{2.46}Cl_{0.25}(SO_4)_{0.2}$, where the compositions of the key positions of the structure are enclosed in brackets. The valence of iron was not determined; it was set equal to 3+ based on the pattern found in the work on eudialyte specimens containing iron of different valence annealed at 700 and 800°C [5]: comparison of the data of X-ray diffraction and Mössbauer spectroscopy [6, 7] showed that Fe^{2+} ions are located at the position of a planar square, whereas Fe^{3+} ions are located at the positions of a square pyramid based on this square.

Ilyukhinite is characterized by zirconium deficiency at the Z position (Zr–O = 1.97–2.11 Å) of the framework, which is compensated for by titanium atoms. Isomorphism of Zr and Ti was found in many representatives of the eudialyte group, in particular, in the titanium analog of eudialyte alluaivite $Na_{38}(Ca,Mn)_{12}(Ti,Nb)_6Si_{52}O_{148}Cl_2 \cdot 4H_2O$ [8, 9].

One of the key positions $M2$ is located in the square pyramid with distances $M2$–O = 2.11–2.51 Å; it is occupied by 55% mainly by manganese atoms and an

Table 3. Coordinates of the extra-framework atoms, site multiplicities (Q), and equivalent atomic displacement parameters (B_{eq}) in the structure of ilyukhinite

Position	x/a	y/b	z/c	Q	q	B_{eq/iso^*}, Å^2
*M*2	0.4857(1)	0.5142(1)	0.0027(1)	9	0.58(2)	2.72(8)
*M*3a	0.3333	0.6667	0.2455(3)	3	0.69(2)	3.1(1)
*M*3b	0.3333	0.6667	0.274(1)	3	0.31(2)	4.0(4)
*M*4a	0.3333	0.6667	0.0609(3)	3	0.40(1)	1.2(3)
*M*4b	0.3333	0.6667	0.0957(6)	3	0.27(2)	2.4(4)
*M*4c	0.3333	0.6667	0.0348(2)	3	0.33(2)	2.92(1)
*N*1	0.1138(3)	0.2275(4)	0.1523(2)	9	1	1.13(2)
*N*2a	0.5596(2)	0.4405(2)	0.1810(2)	9	0.80(2)	1.18(2)
*N*2b	0.5843(7)	0.4258(7)	0.1697(6)	9	0.20(3)	2.1(2)
*N*3	0.2380(2)	0.4759(3)	−0.0497(1)	9	0.80(3)	1.25(2)
*N*4a	0.4612(6)	0.2307(4)	0.0483(2)	9	0.52(2)	1.54(2)
*N*4b	0.526(3)	0.263(2)	0.0546(9)	9	0.27(2)	1.2(9)
*N*4c	0.502(5)	0.251(3)	0.033(2)	9	0.21(2)	2.1(8)
*N*5	0.211(4)	0.606(3)	0.146(2)	9	0.73(4)	5.0(2)*
*X*1a	0.6667	0.3333	0.1351(5)	3	0.53(2)	3.7(3)
*X*1b	0.6667	0.3333	0.114(1)	3	0.47(5)	3.1(9)
*X*2a	0	0	0.186(3)	3	0.40(5)	5.0(5)*
*X*2b	0	0	0.251(4)	3	0.45(5)	4.9(5)*
*X*2c	0	0	0.241(3)	3	0.15(4)	3.0(9)*
S	0	0	0.298(2)	3	0.20(2)	5.7(2)
O*s*	0.133(2)	0.067(2)	0.295(2)	3	0.20(3)	2.5(6)
(O,OH)	0.3333	0.6667	0.052(2)	3	0.40(3)	5.7(4)
OH1	0.3333	0.6667	0.152(2)	3	0.27(2)	4.5(9)
OH2	0.3333	0.6667	0.330(3)	3	0.31(3)	5.6(7)*
OH3	0.3333	0.6667	0.192(3)	3	0.69(2)	4.8(9)
(OH,H2O)	0.201(2)	0.601(1)	0.0011(8)	9	0.55(4)	4.0(5)

The composition of the *X*1a position ($Z = 3$) is $(H_2O)_{0.28}Cl_{0.25}$; positions *X*1b, *X*2a, *X*2b, and *X*2c include predominantly H_2O.

admixture of iron atoms. Kentbrooksite $(Na,REE)_{15}(Ca,REE)_6Mn_3Zr_3NbSi_{25}O_{73}(O,OH,H_2O)_3(F,Cl)_2$ was the first mineral of the eudialyte group, where Johnsen and coauthors found an analogous MnO_5 five-vertex polyhedron [10]. Later it was found in a number of other sodium-rich eudialytes [1]. The highest manganese content (1.56 atoms, $Z = 3$) at the *M*2 position was found in the structure of manganoeudialyte $Na_{14}Ca_6Mn_3Zr_3Si_{26}O_{72}(OH)_2(H_2O,Cl,O,OH)_6$ [11], where this position has an octahedral coordination.

The *M*3 and *M*4 positions located on axis 3 are split, as it is often the case in eudialyte-like structures, and lie at short distances from each other: *M*3a–*M*3b = 0.91, *M*4a–*M*4b = 1.08, and *M*4a–*M*4c = 0.81 Å. These positions, with the exception of *M*3a and *M*4c, are statistically populated by Si atoms; at the *M*3a subposition, Si atoms are admixed with S atoms (mixed position with the average ⟨*M*3a-O⟩ distance equal to 1.59 Å), and the *M*4c subposition is occupied by Nb in the octahedral coordination (*M*4c–O = 1.93–1.97 Å). Sulfur atoms occupying their own position at short distances from the Si (*M*4a–S = 3.07 Å) and Nb (*M*4c–S = 2.27 Å) positions are also distributed statistically. The $[SO_4]$ tetrahedron shares a vertex with the SiO_4 tetrahedron at the *M*4a subposition.

The presence of the center of symmetry in silicon-rich eudialytes (containing more than 25 atoms of silicon per asymmetric unit), is a disputable question [12, 13]. For the specimen studied with maximum high content of additional silicon (about two atoms per asymmetric unit), both the centrosymmetric and the acentric variants of the structure are possible. Acentricity of the structure of ilyukhinite is the result of distribution of Nb, S, and Si atoms over the *M*4 and *M*3 positions related by the pseudocenter, existence of the (Mn + Fe) position in five-vertex polyhedron on one side of the square, and distribution of Na and H_3O on

Table 4. Characteristics of the coordination polyhedra in the structure of ilyukhinite

Position	Composition, $Z = 3$	C.N.	Cation—anion distances, Å		
			Minimal	Maximum	Average
Z	2.60Zr + 0.40Ti	6	1.970(9)	2.114(7)	2.07
M1	5.70Ca + 0.30Ce	6	2.296(6)	2.410(7)	2.35
M2	1.29Mn + 0.45Fe	5	2.11(1)	2.515(5)	2.29
M3a	0.43Si + 0.26S	4	1.558(4)	1.67(5)	1.59
M3b	0.31Si	4	1.59(1)	1.72(6)	1.62
M4a	0.40Si	4	1.577(6)	1.73(2)	1.62
M4b	0.27Si	4	1.62(1)	1.73(7)	1.65
M4c	0.33Nb	6	1.93(2)	1.97(1)	1.95
S	0.20S	4	1.26(6)	1.63(2)	1.54
N1	2.40H_3O + 0.60Na	8	2.510(9)	2.765(7)	2.64
N2a	1.20H_3O + 1.20Na	9	2.45(1)	2.99(1)	2.67
N2b	0.60Na	7	2.36(1)	2.86(2)	2.60
N3	2.10H_3O + 0.20Na + 0.10Ce	8	2.527(8)	3.11(1)	2.76
N4a	1.36Na + 0.2K	7	2.25(1)	3.08(1)	2.77
N4b	0.81H_3O	5	2.49(4)	3.19(3)	2.77
N4c	0.63H_3O	5	2.32(6)	3.2(5)	2.63
N5	2.19H_3O	5	2.54(5)	3.11(3)	2.81

For Si1–6 tetrahedra of the framework, distances are omitted, since they are standard; C.N. is coordination number.

both sides of the interring void at the (N1, N3) and (N2, N4) positions, respectively.

Large Cl anions and H_2O molecules occupy the X1 and X2 positions on axis 3. These positions are also split and populated statistically predominantly with water molecules. A sulfur atom forming an additional SO_4 tetrahedron with the average distance $\langle S–O \rangle$ = 1.54 Å is also located near one of the split positions (X2b).

The main specific feature of the mineral studied is low content of Na and other cations of alkali and alkaline-earth metals occupying as a rule extra-framework N1–5 positions. In the structure of ilyukhinite, all N positions are occupied by oxygen atoms of oxonium groups completely or partially substituting for sodium.

The predominance of oxonium over sodium, manganese over iron, and silicon over axial octahedral cations is reflected in the idealized formula, which is represented as $(H_3O,Na)_{14}Ca_6Mn_2Zr_3Si_{26}O_{72}(OH)_2 \cdot 3H_2O$ ($Z = 3$).

About 17 hydrated representatives of the eudialyte group, which are usually formed during the postcrystallization hydrothermal treatment of "primary" eudialytes, have been studied [11]. The main specific feature of "hydroeudialytes" is low content of Na, Fe, and Mn and presence of large Ba, Sr, and K cations. Ion exchange can result in enriching of "hydroeudialytes" with additional anions, such as sulfate or phosphate groups [1]. Sulfate groups were found in the structures of a number of minerals of the eudialyte group on axis 3 or near X positions, or at the M3 and M4 positions centering nine-membered rings. In the

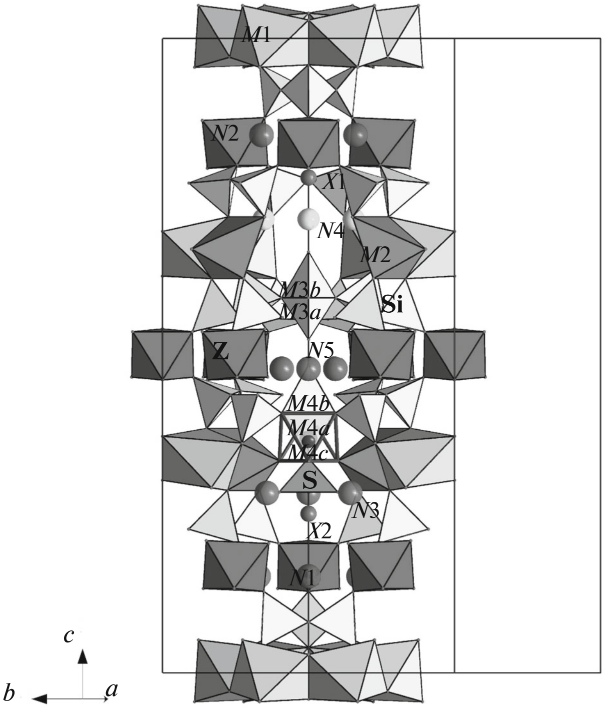

Fig. 2. Crystal structure of ilyukhinite.

structure of ilyukhinite, S atoms are found in both types of positions.

CONCLUSIONS

By chemical composition ilyukhinite best resembles aqualite, in which *N*1, *N*3, and *N*4 positions are also populated by oxonium cations. However, the key *M*2 position of aqualite is occupied by sodium atoms in square coordination remaining predominantly vacant. In other specimens of hydrated eudialytes, iron atoms or minor amount of manganese were found at this position in addition to sodium atoms but it remains to a large extent vacant. Ilyukhinite, a new hydrated mineral of the eudialyte group is characterized by the presence of oxonium in all of the *N*1-5 positions of extra-framework cations, minimal sodium content at these positions, and significant population of the *M*2 position with manganese. Obviously, the new mineral from the Khibiny alkaline massif is a product of hydrothermal transformation of manganoeudialyte.

ACKNOWLEDGMENTS

This study was supported by the Russian Science Foundation, project no. 16-05-00739_a.

REFERENCES

1. R. K. Rastsvetaeva, N. V. Chukanov, and S. M. Aksenov, *Minerals of the Eudialyte Group: Crystal Chemistry, Properties, and Genesis* (Nizhny Novgorod State Univ., Nizhny Novgorod, 2012) [in Russian].
2. N. V. Chukanov, R. K. Rastsvetaeva, K. A. Rozenberg, et al., Zap. Ros. Mineral. O-va **145** (2), 44 (2016).
3. R. K. Rastsvetaeva and A. P. Khomyakov, Crystallogr. Rep. **47** (2), 232 (2002).
4. V. I. Andrianov, Kristallografiya **32** (1), 228 (1987).
5. R. K. Rastsvetaeva, S. M. Aksenov, K. A. Rozenberg, and I. A. Verin, Crystallogr. Rep. **56** (2), 202 (2011).
6. E. V. Pol'shin, A. N. Platonov, B. E. Borutzky, et al., Phys. Chem. Miner. **18**, 117 (1991).
7. A. P. Khomyakov, V. V. Korovushkin, Yu. D. Perfiliev, and V. M. Cherepanov, Phys. Chem. Miner. **37**, 543 (2010).
8. R. K. Rastsvetaeva, A. P. Khomyakov, and V. I. Andrianov, Dokl. Akad. Nauk SSSR **312** (6), 1379 (1990).
9. A. P. Khomyakov, G. N. Nechelyustov, and R. K. Rastsvetaeva, Zap. Vsesoyuz. Mineral. O-va, **119** (1), 117 (1990).
10. O. Johnsen, J. D. Grice, and A. Gault, Eur. J. Mineral. **10**, 207 (1998).
11. S. F. Nomura, D. Atencio, N. V. Chukanov, et al., Zap. Ros. Mineral. O-va **139** (4), 35 (2010).
12. O. Johnsen and J. D. Grice, Can. Mineral. **37** (4), 865 (1999).
13. K. A. Rozenberg, R. K. Rastsvetaeva, and S. M. Aksenov, *Int. Mineral. Seminar "Mineral. Intervention in Micro- and Nanoworld", Syktyvkar, 2009* (Geoprint, Syktyvkar, 2009), 149.
14. K. A. Rozenberg, R. K. Rastsvetaeva, and A. P. Khomyakov, Eur. J. Mineral. **17**, 875 (2005).

Translated by I. Polyakova