

A new mineral species rossovskyite, $(\text{Fe}^{3+}, \text{Ta})(\text{Nb}, \text{Ti})\text{O}_4$: crystal chemistry and physical properties

Sergey I. Konvalenko¹ · Sergey A. Ananyev² · Nikita V. Chukanov³ ·
Ramiza K. Rastsvetaeva⁴ · Sergey M. Aksenov^{4,5} · Anna A. Baeva¹ ·
Ramil R. Gainov^{6,7,8} · Farit G. Vagizov⁶ · Oleg N. Lopatin⁶ · Tatiana S. Nebera¹

Received: 19 March 2015 / Accepted: 7 July 2015 / Published online: 26 July 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract A new mineral rossovskyite named after L.N. Rossovsky was discovered in granite pegmatites of the Bulgut occurrence, Altai Mts., Western Mongolia. Associated minerals are microcline, muscovite, quartz, albite, garnet of the almandine–spessartine series, beryl, apatite, triplite, zircon, pyrite, yttröbetafite-(Y) and schorl. Rossovskyite forms flattened anhedral grains up to $6 \times 6 \times 2$ cm. The color of the mineral is black, and the streak is black as well. The luster is semi-metallic, dull. Mohs hardness is 6. No cleavage or parting is observed. Rossovskyite is brittle, with uneven fracture. The density measured by the hydrostatic weighing method is 6.06 g/cm^2 , and the density calculated from the empirical formula is 6.302 g/cm^3 . Rossovskyite is biaxial, and the color in reflection is gray to dark gray.

The IR spectrum contains strong band at 567 cm^{-1} (with shoulders at 500 and 600 cm^{-1}) corresponding to cation–oxygen stretching vibrations and weak bands at 1093 and 1185 cm^{-1} assigned as overtones. The reflection spectrum in visible range is obtained. According to the Mössbauer spectrum, the ratio $\text{Fe}^{2+}:\text{Fe}^{3+}$ is 35.6:64.4. The chemical composition is as follows (electron microprobe, Fe apportioned between FeO and Fe_2O_3 based on Mössbauer data, wt%): MnO 1.68, FeO 5.92, Fe_2O_3 14.66, TiO_2 7.69, Nb_2O_5 26.59, Ta_2O_5 37.51, WO_3 5.61, total 99.66. The empirical formula calculated on four O atoms is: $\text{Mn}_{0.06}^{2+}\text{Fe}_{0.21}^{2+}\text{Fe}_{0.47}^{3+}\text{Ti}_{0.25}\text{Nb}_{0.51}\text{Ta}_{0.43}\text{W}_{0.06}\text{O}_4$. The crystal structure was determined using single-crystal X-ray diffraction data. The new mineral is monoclinic, space group $P2/c$, $a = 4.668(1)$, $b = 5.659(1)$, $c = 5.061(1) \text{ \AA}$, $\beta = 90.21(1)^\circ$; $V = 133.70(4) \text{ \AA}^3$, $Z = 2$. Topologically, the structure of rossovskyite is analogous to that of wolframite-group minerals. The crystal-chemical formula of rossovskyite is $[(\text{Fe}^{3+}, \text{Fe}^{2+}, \text{Mn})_{0.57}\text{Ta}_{0.32}\text{Nb}_{0.11}][\text{Nb}_{0.40}\text{Ti}_{0.25}\text{Fe}_{0.18}\text{Ta}_{0.11}\text{W}_{0.06}]\text{O}_4$. The strongest lines of the powder X-ray diffraction pattern [d , Å (I , %) (hkl)] are as follows: 3.604 (49) (110), 2.938 (100) ($-1-11$), 2.534 (23) (002), 2.476 (29) (021), 2.337 (27) (200), 1.718 (26) (-202), 1.698 (31) ($-2-21$), 1.440 (21) (-311). The type specimen of rossovskyite is deposited in the Mineralogical Museum of the Tomsk State University, Tomsk, 634050 Russia, with the inventory number 20927.

✉ Ramil R. Gainov
g_ramil@mail.ru; ramil.gainov@helmholtz-berlin.de

¹ Tomsk State University, 36 Lenina Prospekt, Tomsk, Russia 634050

² Siberian Federal University, 79 Svobodny, Krasnoyarsk, Russia 660041

³ Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, Russia 142432

⁴ Institute of Crystallography, Russian Academy of Sciences, Leninskii Prospekt 59, Moscow, Russia 119333

⁵ Department of Crystallography, St Petersburg State University, University Embankment 7/9, St Petersburg, Russia 199034

⁶ Kazan Federal University, Kremlyovskaya Street 18, Kazan, Russia 420008

⁷ Johannes Gutenberg Universität Mainz, Staudingerweg 9, 55099 Mainz, Germany

⁸ Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, 14109 Berlin, Germany

Keywords New mineral · Rossovskyite · Structure · Granite-pegmatite · Mongolia

Introduction

A new mineral rossovskyite $(\text{Fe}^{3+}, \text{Ta})(\text{Nb}, \text{Ti})\text{O}_4$ was discovered in granitic pegmatites of the Bulgut pegmatite

occurrence, Altai Mountains, Mongolia (46°36′57.3″N 91°23′40.5″E). This occurrence belongs to a large Hercynian-age pegmatite belt stretching for a distance of almost 600 km along the Mongolian Altai Ridge, Western Mongolia (Gavrilova and Leont'ev 1976). The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA No. 2014-056).

Data on the Bulgut occurrence are published in numerous papers (Khasin and Chernyavskiy 1963; Konovalenko 1999; Konovalenko et al. 2000; Baeva et al. 2012). Pegmatites of this area are genetically related to the large (30 × 12 km) Indertinskiy massif of leucocratic aluminiferous granites having the age of 218 ± 10 Ma (Gavrilova and Leontev 1976; Borisenko et al. 1988). The massif was formed as a result of two stages of intrusion. At the main first stage, coarse-grained porphyreous biotite granites were formed. Aplites and pegmatites are related to fine- and medium-grained binary and muscovite granites of the second (subordinate) stage. Some pegmatites occur in biotite granites of the first stage, but most part of the pegmatite-forming fluid was displaced into host rocks (biotite and binary mica schists with sillimanite, garnet and staurolite).

Rossovskyite was discovered in a lens-shaped zoned pegmatite body (20 × 60 m) occurring at the contact of porphyreous biotite granite with crystalline schist. The outer aplite zone has the thickness from 20 to 200 cm. It consists of fine-grained quartz–feldspar–muscovite aggregate with subordinate garnet (spessartine–almandine) and schorl. Next zones (from aplite to quartz core) are that of medium-grained graphic pegmatite and blocky microcline. The pegmatoid zone is up to 3–5 m thick and contains beryl, schorl and garnet, as well as laths of biotite (at the lying side) and large greenish gray plates of muscovite (up to 15–30 cm, at the hanging wall). The core consists of smoky to pink quartz. Large (up to 6 × 6 × 2 cm) grains of rosovskyite are present in associations occurring along the contact between quartz core and microcline zone and

including large (up to 70 cm) crystals of muscovite, blocks of triplite (up to 30 cm), albite, apatite, pyrite, schorl and tantaloniobates. Smaller (1–1.5 cm) single-crystal grains of rosovskyite (Fig. 1) occur in adjacent parts of the microcline zone.

Rossovskyite was formed as one of the latest minerals at the autometasomatic albitization stage. Apatite, yttrobetafite-(Y) and later generations of muscovite and schorl crystallized after rosovskyite. Yttrobetafite-(Y) forms veinlets in rosovskyite grains.

Rossovskyite is named in memory of the late scientist Lev Nikolaevich Rossovsky (1933–2009), a specialist in the geology, geochemistry and mineralogy of granite pegmatites. In particular, L.N. Rossovsky investigated numerous pegmatite localities in Central Asia and Russia.

The type specimen of rosovskyite is deposited in the collections of the Mineralogical Museum of the Tomsk State University, Tomsk, 634050 Russia, with the inventory number 20927.

Physical properties

General appearance and mechanical properties

Rossovskyite forms flattened anhedral grains up to 6 × 6 × 2 cm (Fig. 1). The color is black, and the streak is black as well. The luster is semi-metallic, dull. Mohs hardness is 6. No cleavage or parting is observed. Rossovskyite is brittle, with uneven fracture. The density measured by the hydrostatic weighing method is 6.06 g/cm³, and the density calculated from the empirical formula is 6.302 g/cm³.

Reflectance spectroscopy in the visible range

Rossovskyite is optically biaxial. Its color in reflected light is gray. The mineral shows distinct bireflectance and pleochroism (gray on R_{\min} to light gray on R_{\max}). The reflectance spectra of rosovskyite are given in Fig. 2. The reflectance values (R_{\max}/R_{\min}) measured in air are given in Table 1.

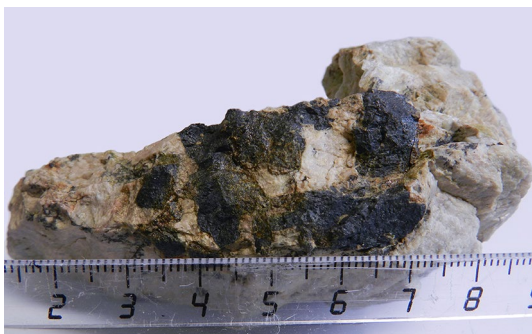


Fig. 1 Grains of rosovskyite (black) in feldspar–muscovite aggregate

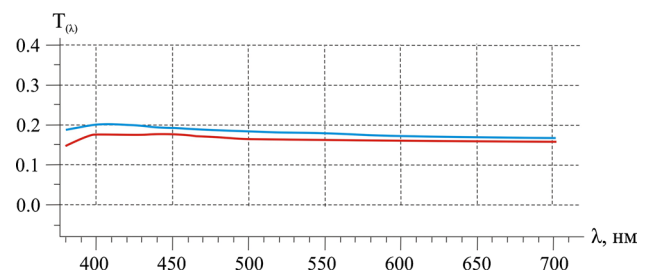


Fig. 2 Reflectance spectra of rosovskyite (blue line for R_{\max} , red line for R_{\min})

Table 1 Reflectance values (R_{\max}/R_{\min}) for rossovskyite in air

Wavelength (nm)	R_{\max}	R_{\min}
400	20.27	17.66
420	20.03	17.86
440	19.52	17.62
460	19.04	17.29
470 (COM)	18.87	17.07
480	18.7	16.84
500	18.41	16.6
520	18.15	16.38
540	17.93	16.24
546 (COM)	17.85	16.22
560	17.69	16.17
580	17.51	16.1
589 (COM)	17.44	16.05
600	17.36	15.98
620	17.23	15.88
640	17.06	15.91
650 (COM)	17.01	15.88
660	16.96	15.85
680	16.88	15.82
700	16.85	15.8

Infrared absorption spectroscopy

In order to obtain infrared (IR) absorption spectrum, rossovskyite powder was mixed with anhydrous KBr, pelletized and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) with the resolution of 4 cm^{-1} ; 16 scans were obtained. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

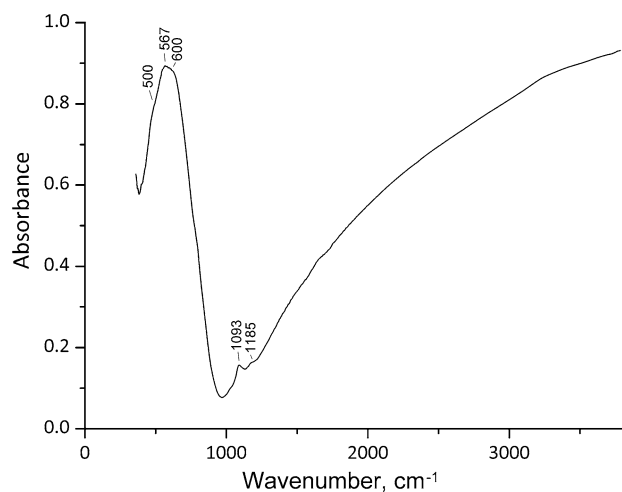
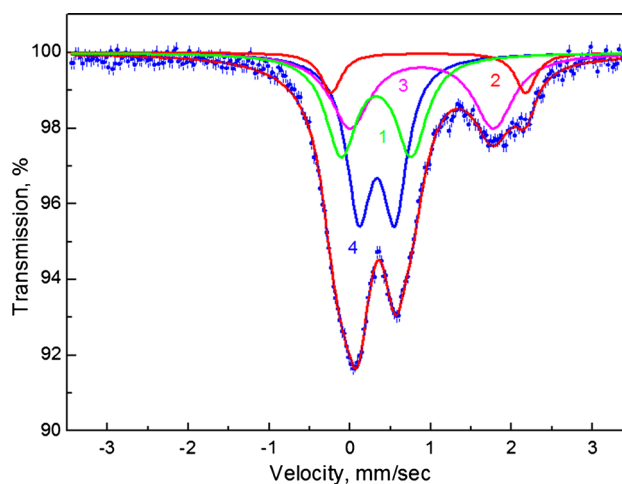
The IR spectrum of rossovskyite (Fig. 3) contains a strong band at 567 cm^{-1} (with shoulders at 500 and 600 cm^{-1}) corresponding to cation–oxygen stretching vibrations and weak bands at 1093 and 1185 cm^{-1} assigned as overtones. Characteristic bands of O–H and O–C bonds are absent in the spectrum.

Mössbauer spectroscopy

Gamma-resonance studies have been carried out by means of a commercial Mössbauer spectrometer (Wissel) in order to clarify the valence state of iron in rossovskyite. The spectrometer is equipped with a standard source of radioactive isotope, ^{57}Co , in a rhodium matrix (Ritverc). The absorption-mode measurements have been taken at room temperature. In order to get optimal conditions for Mössbauer measurements, the sample powder has been crushed in an agate mortar, distributed homogeneously within the punchholder and packed in the form of a tablet with the density of 32 mg/cm^2 . The mathematical analysis of the experimental

Mössbauer spectrum has been carried out by the method of least squares under the assumption of Lorentz-shaped spectral lines. Isomer shifts are given relative to metallic iron.

The mathematical analysis performed by commercial Mössbauer software—SpectRelax version 2.1 (S.Petersburg) shows that the experimental spectrum of rossovskyite (Fig. 4) can be described as a superposition of

**Fig. 3** Powder IR absorption spectrum of rossovskyite**Fig. 4** Mössbauer spectrum of rossovskyite**Table 2** Parameters of the Mössbauer spectrum of rossovskyite

	Doublet	IS (mm/s)	QS (mm/s)	Γ (mm/s)	S (%)	Fe/Site
1		0.32	0.87	0.46	28.85	Fe^{3+} at $M1$
2		0.97	2.40	0.30	7.79	Fe^{2+} at $M1$
3		0.88	1.77	0.59	27.81	Fe^{2+} or mixed-valence Fe at $M2$
4		0.33	0.44	0.37	35.55	Fe^{3+} at $M1$

Table 3 Chemical composition of rossovskyite based on five electron microprobe analyses

Constituent	Content (wt%)	Range	Standard deviation	Probe standard
MnO	1.68	1.03–2.21	0.49	Mn
FeO ^a	5.92	19.34–23.20 ^b	1.45 ^b	Fe
Fe ₂ O ₃ ^a	14.66			
TiO ₂	7.69	6.47–8.75	0.81	TiO ₂
Nb ₂ O ₅	26.59	25.64–28.39	0.94	Nb
Ta ₂ O ₅	37.51	35.19–39.15	1.38	Ta
WO ₃	5.61		0.24	W
Total	99.66			

^a The total iron content analyzed using a microprobe and initially calculated as Fe₂O₃ was 21.24 wt%; it was apportioned between FeO and Fe₂O₃ based on the Mössbauer data

^b For total iron calculated as Fe₂O₃

Table 4 Powder X-ray diffraction data for rossovskyite

<i>I</i> _{meas}	<i>d</i> _{meas} (Å)	<i>I</i> _{calc}	<i>d</i> _{calc} (Å) ^a	<i>hkl</i>
3	4.666	4	4.668	100 ^b
49	3.604	65	3.601	110
100	2.938	100	2.938	−1−11
16	2.837	15	2.829	020
23	2.534	27	2.531	002
29	2.476	33	2.470	021
27	2.337	12	2.334	200
7	2.226	8	2.228	−102
10	2.186	3	2.185	−1−21
		14	2.181	121
14	2.074	11	2.073	−112
		10	2.068	112
2	1.888	11	1.886	022
7	1.805	10	1.801	220
19	1.753	30	1.749	130
26	1.718	19	1.719	−202
		19	1.713	202
31	1.698	27	1.698	−2−21
11	1.528	14	1.529	−113
		15	1.526	113
11	1.451	21	1.449	023
21	1.440	12	1.440	−311
		14	1.440	−132
4	1.355	10	1.362	041

^a Calculated for unit cell parameters obtained from single-crystal data

^b Reflection which corresponds to monoclinic distortion confirmed by powder and single-crystal X-ray data

Table 5 Crystal data, data collection and refinement of rossovskyite

<i>Crystal data</i>	
Formula	(Fe ³⁺ ,Ta)(Nb,Ti)O ₄
Formula weight (g)	254.1
Temperature (K)	293
Cell setting	Monoclinic
Space group	<i>P</i> 2/ <i>c</i>
<i>Lattice parameters</i>	
<i>a</i> (Å)	4.668(1)
<i>b</i> (Å)	5.659(1)
<i>c</i> (Å)	5.061(1)
β (°)	90.21(1)
<i>V</i> (Å ³)	133.70(3)
<i>Z</i>	2
Calculated density <i>D</i> _x (g cm ^{−3})	6.309
Crystal size (mm)	0.2 × 0.2 × 0.25
Crystal form	Anhedral grain
<i>Data collection</i>	
Diffractometer	Xcalibur Oxford Diffraction (CCD detector)
Radiation; λ	MoK α ; 0.71073
Absorption coefficient, μ (mm ^{−1})	26.952
<i>F</i> (000)	227
Data range θ (°); <i>h</i> , <i>k</i> , <i>l</i>	4.35–55.89; −10 < <i>h</i> < 10, −13 < <i>k</i> < 13, −6 < <i>l</i> < 10
No. of measured reflections	7188
Total reflections (<i>N</i> _{tot})/unique (<i>N</i> _{ref})	1532/1367
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)
Matrix of twinning	[−1 0 0/0 −1 0/0 0 1]
Twin component ratio	0.861(4)/0.139(4)
<i>Refinement</i>	
Refinement on	Full-matrix least squares on <i>F</i>
<i>R</i> ₁ , <i>wR</i> ₂ (all reflection)	3.98/4.44
<i>R</i> , <i>wR</i> [<i>F</i> > 4 σ (<i>F</i>)]	5.80/6.14
<i>R</i> _{int} (%)	4.38
No. of refinement parameters (<i>N</i> _{par})	30
<i>N</i> _{ref} / <i>N</i> _{par}	45.9
Weight scheme	1/($\sigma^2 F + 0.001444F^2$)
Max./min. residual <i>e</i> density (<i>e</i> Å ^{−3})	−4.45/3.60
GooF (Goodness of fit)	1.06

$$R_1 = \sum ||F_{\text{obs}}| - |F_{\text{calc}}|| / \sum |F_{\text{obs}}|; wR_2$$

$$= \left\{ \sum [w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2] / \sum [w(F_{\text{obs}}^2)^2] \right\}^{1/2}$$

GOF = $\left\{ \sum [w(F_{\text{obs}}^2 - F_{\text{calc}}^2)] / (n - p) \right\}^{1/2}$ where *n* is the number of reflections and *p* is the number of refined parameters

Table 6 Fractional atomic coordinates, site symmetry, refined number of electrons (e_{ref}) and equivalent atomic displacement parameters (U_{eq}) for rossovskyite

Site	<i>x</i>	<i>y</i>	<i>z</i>	Site symmetry	e_{ref}	U_{eq} (Å ²)
<i>M1</i>	0	0.3313(1)	0.25	2 <i>e</i>	42.7	0.0097(1)
<i>M2</i>	0.5	0.8274(3)	0.25	2 <i>f</i>	39.1	0.0071(5)
O	0.2718(3)	0.1153(3)	0.4210(4)	4 <i>g</i>		0.0081(3)
O	0.7700(3)	0.6164(3)	0.0841(4)	4 <i>g</i>		0.0081(3)

M1 and *M2* sites have mixed occupancies (see footnote to Table 3). Consequently, U_{eq} may reflect not only amplitudes of thermal vibrations of atoms, but also unresolved site splitting (exact coordinates of Fe³⁺ and Ta present in *M1* should be slightly different because of the different nature of these cations, including configuration of electron shells)

Table 7 Anisotropic displacement parameters (Å²) for rossovskyite

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
<i>M1</i>	0.0094(1)	0.0095(1)	0.0101(2)	0	−0.0005(1)	0
<i>M2</i>	0.0074(1)	0.0068(1)	0.0071(1)	0	0.0007(1)	0
O1	0.0076(4)	0.0085(5)	0.0081(6)	0.0002(3)	0.0010(4)	−0.0015(4)
O2	0.0069(4)	0.0091(5)	0.0082(7)	0.0010(3)	0.0000(4)	−0.0004(4)

four symmetric doublets (Chi-squared = 0.94). The Mössbauer parameters of these doublets (isomer shift *IS*, quadrupole splitting *QS*, line width *Γ* and areas under resonance lines *S*) are listed in Table 2.

The hyperfine parameters (*IS*, *QS*, *Γ*) have been found within the accuracy of ±0.01 mm/s. It is important to note that the fitting of the experimental Mössbauer spectrum by three doublets only leads to an essentially higher value of goodness-of-fit parameter (Chi-squared = 1.2).

The Mössbauer studies show the presence of four kinds of iron ions in the mineral. Two doublets No.1 and No.4 (Table 2), which have isomer shifts 0.32 mm/s and 0.33 mm/s and quadrupole splittings 0.87 and 0.44 mm/s, respectively, correspond to Fe³⁺ at the octahedral sites. As regards the Fe²⁺ at the octahedral site (Stevens et al. 2005), it is known that the isomer shift for Fe²⁺ state is lying in the range of 0.83–1.33 mm/s, if this iron has the quadrupole splitting more than 1.7 mm/s. This case takes place perfectly for two other doublets No.2 and No.3 (with isomer shifts 0.97 and 0.88 mm/s and quadrupole splittings 2.40 and 1.77 mm/s, respectively), which could be attributed, as consequence, to Fe²⁺ at octahedral sites in rossovskyite. As it follows, all Fe ions have octahedral coordination geometry. The ratio Fe³⁺:Fe²⁺ calculated based on the areas under the resonance lines, with the assumption of the same Lamb–Mössbauer factors for all iron ions, is 64.4:35.6.

Chemical composition

Five chemical analyses were carried out with a VEGA II LMU electron microscope equipped with an INCA Energy

350 energy-dispersive spectrometer (EDS mode, accelerating voltage 20 kV, current strength 770 pA, beam diameter 1–2 μm). CO₂ and H₂O were not determined because of the absence of absorption bands corresponding to vibrations of C–O and O–H bonds in the IR spectrum. The analytical data are given in Table 3. The contents of other elements with atomic numbers >8 are below detection limits. The empirical formula based on four O atoms is Mn_{0.24}²⁺Fe_{0.44}³⁺Ti_{0.25}Nb_{0.51}Ta_{0.43}W_{0.06}O₄.

The simplified formula is (Fe³⁺,Ta)(Nb,Ti)O₄.

The end-member formula Fe³⁺NbO₄ requires Fe₂O₃ 37.53, Nb₂O₅ 62.47, total 100.00 wt%.

X-Ray diffraction data and crystal structure

Powder X-ray diffraction data for rossovskyite have been obtained with a diffractometer X'Pert PRO using CuKα radiation. The diffractometer represents a conventional Bragg–Brentano equipment, having the original software X'Pert, high-resolution horizontal goniometer, tube with Cu anode and maximal power 2.2 kW, sampling sensor reflection–transmission spinner PW306, detector PIXel and fixed divergence slits 1/8°, 2°. Data are given in Table 4.

The single-crystal X-ray diffraction data were collected at room temperature by means of a Xcalibur Oxford Diffraction diffractometer with graphite monochromatized MoKα radiation (λ = 0.71073 Å) and a CCD detector using the ω scanning mode. A total of 7188 reflections within the sphere limited by θ = 56.1° were obtained. The experimental details of the data collection and refinement results are listed in Table 5. A semiempirical absorption correction

based on the intensities of equivalent reflections was applied, and the data were corrected for the Lorentz, polarization and background effects. The refinement of the unit cell parameters was performed using the CrysAlis software (Oxford Diffraction 2009).

The following monoclinic (pseudo-orthorhombic) unit cell parameters have been obtained by the least squares refinement: $a = 4.668(1)$, $b = 5.659(1)$, $c = 5.061(1)$, $\beta = 90.21(1)^\circ$. Single-crystal diffraction data show a lot of additional rather strong reflections with general conditions $0kl: k = 2n + 1$, $hk0: h + k = 2n + 1$, $h0l: l = 2n + 1$, $h00: h = 2n + 1$, $0k0: k = 2n + 1$, $00l: l = 2n + 1$, that violate the extinctions for space group $Pbcn$. After Ercit et al. (1992a), space group $Pbcn$ may pass to $P2/c$ or $C2/c$, Cc and $P2$ reflecting disorder, partially ordered and fully ordered structures. Therefore, we have suggested a high-symmetric non-isomorphic monoclinic group $P2/c$, in which the single cation position degenerates into two independent sites $2e$ and $2f$, whereas O atoms are located at two common positions $4g$. After averaging equivalent reflections, the experimental data set contained 1367 reflections with $I > 2\sigma(I)$. A structure model was determined by the “charge-flipping” method using the SUPERFLIP computer software (Palatinus and Chapuis 2007). The structure refinement was carried out using the JANA2006 (Petricek et al. 2006) and AREN (Andrianov 1987) program packages. Mixed scattering curves were used for the composite cation sites. Atomic scattering factors for neutral atoms together with anomalous dispersion corrections were taken from International Tables for X-Ray Crystallography (Ibers and Hamilton 1974). Illustrations were produced with the JANA2006 program package in combination with the DIAMOND software (Brandenburg and Putz 2005). The final refinement cycles converged with $R_1 = 3.98$, $wR_2 = 6.14$, $\text{GoF} = 1.06$ for all data. The highest peak and the deepest minimum in the final residual electron density were 3.60 and $-4.45 \text{ e}\text{\AA}^{-3}$, respectively. Table 6 lists the fractional atomic coordinates, occupancy, site symmetry and equivalent atomic displacement parameters. Anisotropic atomic displacement parameters are given in Table 7.

Discussion

In rossovskyite, two kinds of zigzag-like chains are present (Figs. 5, 6, 7). Each chain is formed by equivalent M -octahedra in which each octahedron shares edges with two neighboring octahedra. Neighboring chains are linked via common vertices of octahedra in such a way that each oxygen atom is coordinated by three cations. Oxygen atoms form close-packed hexagonal layers which are perpendicular to the a axis.

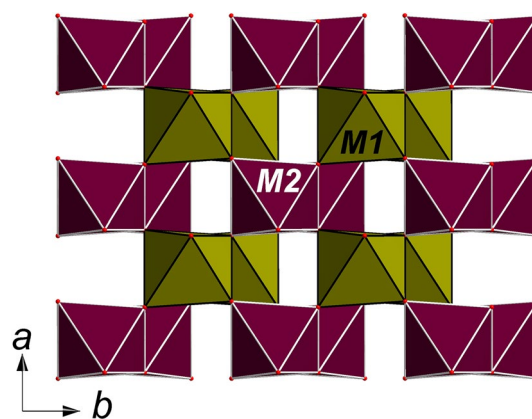


Fig. 5 The crystal structure of rossovskyite projected on the (001) plane

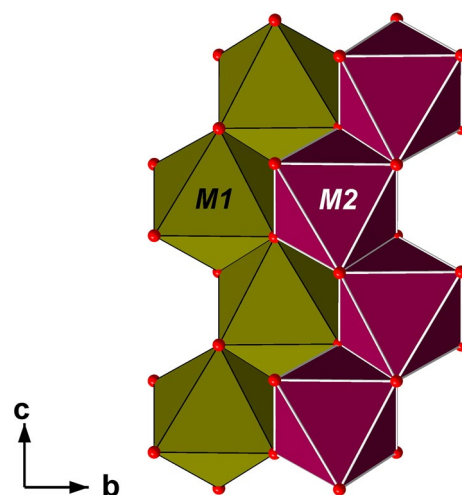


Fig. 6 Staggered chains formed by $M1$ and $M2$ octahedra in the structure of rossovskyite

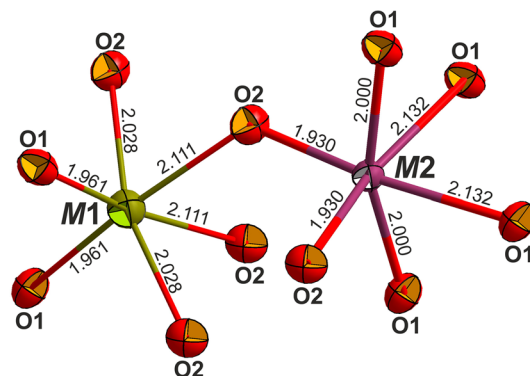


Fig. 7 Bond lengths (\AA) in the $M1$ - and $M2$ -centered octahedra of rossovskyite. Octahedral distortions $\Delta = (1/6) \sum_{i=1-6} \{ [(M-O)_i - \langle M-O \rangle] / \langle M-O \rangle \}^2 \times 10^4$ (Brown and Shannon 1973) are: $\Delta^{(M1)} = 9.107$ and $\Delta^{(M2)} = 17.173$

Table 8 Comparative data for rosovskyite and some related minerals

Mineral	Rosovskiyte	Ferberite	Ferrotitano-wodginite	Ixiolite
Formula	(Fe ³⁺ , Ta) (Nb, Ti)O ₄	Fe ²⁺ WO ₄	Fe ²⁺ TiTa ₂ O ₈	(Ta, Fe, Nb, Mn)O ₂
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic or orthorhombic
Space group	<i>P2/c</i>	<i>P2/c</i>	<i>C2/c</i>	<i>P2/c</i> or <i>Pbcn</i>
<i>a</i> (Å)	4.668	4.75	9.403	9.481 or 4.74–4.76
<i>b</i> (Å)	5.659	5.72	11.384	11.494 or 5.70–5.74
<i>c</i> (Å)	5.061	4.97	5.075	5.158 or 5.10–5.16
β (°)	90.21	90.17	90.55	90.8 or 90
<i>V</i> (Å ³)	133.7	135.03	543.24	562.04 or 138.4–140.6
<i>Z</i>	2	2	4	16 or 4
Strong lines in the powder X-ray diffraction pattern: <i>d</i> , Å (<i>I</i> , %)	3.604 (49) 2.938 (100) 2.534 (23) 2.476 (29) 2.337 (27) 1.718 (26) 1.698 (31) 1.440 (21)	4.69 (80) 3.75 (60) 3.65 (50) 2.940 (100) 2.476 (60) 2.195 (50)	3.626 (70) 2.963 (100) 2.939 (90) 2.484 (45) 1.759 (45) 1.715 (50) 1.711 (45) 1.447 (40)	3.65 (32) 2.98 (100) 2.57 (13) 2.51 (20) 1.746 (17) 1.722 (24) 1.459 (29)
Density (g cm ⁻³)	6.06 (meas.) 6.302 (calc.)	7.3–7.5 (meas.) 7.60 (calc.)	7.368 (calc.)	6.94–7.39 (meas.) 7.34 (calc.)
References	This work	Escobar et al. (1971), Palache et al. (1951)	Galliski et al. (1999)	Nickel et al. (1963), Wenger et al. (1991), Ercit et al. (1992a), Ferguson et al. (1976), Grice et al. (1976), Chukhrov and Bonshtedt-Kupletskaya (1967), Fekhtichev (1989)

In accordance with the refined site-scattering factors and chemical data, the crystal-chemical formula of rossovskyite can be written as follows ($Z = 2$): $M1[(Fe^{3+}, Fe^{2+}, Mn)_{0.57}Ta_{0.32}Nb_{0.11}]^{M2}[Nb_{0.40}Ti_{0.25}Fe_{0.18}Ta_{0.11}W_{0.06}]O_4$. Both cation sites are characterized by closed cation–anion distances (Fig. 7). However, the distortions of octahedra are considerably different. The presence of Ti and a major part of Nb at the $M2$ site is consistent with a rather strong distortion of the $M2O_6$ octahedron. Doublet No.3 in the Mössbauer spectrum (Fig. 2; Table 2) corresponding to 0.19 Fe^{2+} atoms pfu can be correlated with 0.18 Fe atoms at the $M2$ site. We point here also that the line width of doublet No. 3 ($\Gamma = 0.59$ mm/s) is larger than the line width for other doublets. This implies that, strictly speaking, it is impossible to exclude the mixed-valence state for iron, corresponding to this doublet, in the manner $Fe^{2+}-Fe^{3+}$ with the dominance of Fe^{2+} . Indeed, the mixed-valence state is sometimes observed in connection with similarly involved Mn or Ti ions, like in ilvaite (Ghazi-Bayat et al. 1992) or neptunite (Lottermoser et al. 1997), respectively. The problem of mixed-valence state in rossovskyite and other physical properties is a topic for further temperature Mössbauer and neutron measurements. The other three doublets correspond to $Fe_{0.44}^{3+}$ and $Fe_{0.05}^{2+}$, where $Fe_{0.44}^{3+}$ is distributed between $Fe_{0.20}^{3+}$ and $Fe_{0.24}^{3+}$ at the $M1$ site (the doublets No. 1 and No. 4, respectively), having different Mössbauer parameters due to influence of adjacent octahedrons from second coordination sphere. Indeed, the octahedrons $M1O_6$, containing Fe^{3+} , Fe^{2+} , Mn, Ta and Nb, are jointed by common oxygen vertexes. Different elements at the $M1$ site of adjacent octahedrons could lead to different electronic distribution for oxygen. As a result, this leads to different quadrupole splittings for Fe^{3+} at the $M1$ site. The doublets No.1 and No.4 may correspond to the pairs of edge-sharing $M1Fe^{3+}O_6$ octahedra and to the single $M1Fe^{3+}O_6$ octahedra, respectively.

In terms of topology and stoichiometry (Σ cations: $O = 1 : 2$), rossovskyite is analogous to ferberite and other wolframite-group minerals, as well as tantaloniobates of the columbite family including columbite, ixiolite and wodginite mineral groups (Escobar et al. 1971; Ercit et al. 1992a, b).

The minerals of the columbite family are distinguished by the unit cell parameters ranging from minimal values (ixiolite and rossovskyite) to doubled values along one or two directions. In case of monoclinic (pseudo-orthorhombic) cells, the angle β varies within the range of 90° – 91.21° (Ercit et al. 1992b). The unit cells of these minerals could be considered as supercells of ixiolite, and thus, the structure of ixiolite serves as a prototype of structures of minerals belonging to the columbite family. Depending on the degree of cation ordering, these minerals are

characterized by different space groups ($Pbcn$, $P2/c$, $C2/c$, Cc or $P2$).

Rosovskyite is the only monoclinic Nb-dominant mineral among the members of the columbite family. Consequently, this mineral can be considered as an indicator of mineralogenetic specialization in pegmatites of the Mongolian Altai zone. Actually, not only Nb, but also Ti, REE and U play an important role in the accessory mineralization of this zone. Ti minerals (ilmenite and ilmenorutile) belong to the earliest paragenesis. The niobates (columbite-(Fe), columbite-(Mn) and rossovskyite) and, finally, yttrobetafite-(Y), Pb-bearing betafite and Pb, U-bearing microlite crystallized thereafter.

Comparative data for rossovskyite and some related minerals are given in Table 8.

Acknowledgments This work is supported by the projects of the Russian Science Foundation, Grant No. 14-17-00048, and the Foundation of the President of the Russian Federation, Grant No. MK-4990.2014.5 (in part of structural investigations) as well as German foundation BMBF-05K12CB1. The authors are grateful to both reviewers for detailed reading and very useful corrections of the article.

References

- Andrianov VI (1987) Development of the system of crystallographic programs RENTGEN for the computers NORD, CM-4 and EC. *Kristallografiya* (now Crystallography reports) 32:228–231 (in Russian)
- Baeva AA, Konovalenko SI, Bukharova OV (2012) Mineralogy of the rare-earth pegmatites of Indertinskii formation (Mongolian Altai). In: Konovalenko SI (ed) *Mineralogy, geochemistry and mineral resources of Asia*, vol 2. CNTI, Tomsk, pp 34–42 (in Russian)
- Borisenko AS, Skuridin VA, Lebedev VI et al (1988) Metallogeny of the ore region of southeastern Gorny Altai and northwestern Mongolia. In: Smirnov VI (ed) *Regularities of the distribution of mineral resources*, vol XV. Nauka, Moscow, pp 131–139 (in Russian)
- Brandenburg K, Putz H (2005) DIAMOND Version 3. Crystal Impact GbR, Postfach 1251, D-53002 Bonn, Germany
- Brown ID, Shannon RD (1973) Empirical bond strength–bond lengths curves for oxides. *Acta Crystallogr A* 29:266–282
- Chukhrov FV, Bonshtedt-Kupletskaia EM (eds) (1967) *Minerals* (v II, issue 3). Nauka, Moscow, p 676 (in Russian)
- Diffraction Oxford (2009) CrysAlisPro. Oxford Diffraction Ltd, Abingdon
- Ercit TS, Hawthorne FC, Černý P (1992a) The wodginite group. I. Structural crystallography. *Can Miner* 30:597–611
- Ercit TS, Černý P, Hawthorne FC, McCammon CA (1992b) The wodginite group. II. Crystal chemistry. *Can Miner* 30:613–631
- Escobar C, Cid-Dresden H, Kittl P, Dumler I (1971) The relation between “light wolframite” and common wolframite. *Am Miner* 56:489–498
- Feklichev VG (1989) *Diagnostic constants of minerals*. Nedra, Moscow, p 480 (in Russian)
- Galliski MA, Černý P, Márquez-Zavalía MF, Chapman R (1999) Ferrotitanowodginite, $Fe^{2+}TiTa_2O_8$, a new mineral of the wodginite

- group from the San Elías pegmatite, San Luis, Argentina. *Am Miner* 84:773–777
- Gavrilova SP, Leontev AN (1976) Structural position and zonality of the pegmatite region of Mongolian Altai. In: Kuzmenko MV (ed) *Pegmatite rare-earth deposits*, vol 5. IMGRE, Moscow, pp 20–42 **(in Russian)**
- Ghazi-Bayat B, Behruzi M, Litterst FJ, Lottermoser W, Amthauer G (1992) Crystallographic phase transition and valence fluctuation in synthetic Mn-bearing ilvaite $\text{CaFe}_{2-x}\text{Mn}_x^{2+}\text{Fe}^{3+}[\text{Si}_2\text{O}_7/\text{O}/(\text{OH})]$. *Phys Chem Miner* 18:491–496
- Grice JD, Ferguson RB, Hawthorne FC (1976) The crystal structures of tantalite, ixiolite and wodginitite from Bernic lake, Manitoba I. Tantalite and ixiolite. *Can Miner* 14:540–549
- Ibers JA, Hamilton WC (eds) (1974) *International Tables for X-ray Crystallography*, v IV. The Kynoch Press, Birmingham
- Khasin RA, Chernyavskiy VI (1963) Pegmatites of middle course of Bulgan-gol river in Western Mongolia. In: Marinov NA (ed) *Abstracts for geology of Mongolian People's Republic*. Gostoptechizdat, Moscow, pp 191–218 **(in Russian)**
- Konovalenko SI (1999) Mineral composition and several geochemical peculiarities of facial granite pegmatites for middle course of Bulgan-gol river in Western Mongolia. In: Ревушкин АС (ed) *Natural conditions, history and culture of Western Mongolia and adjacent regions*. Tomsk State University, Tomsk, pp 55–57 **(in Russian)**
- Konovalenko SI, Sazontova NA, Bukharova OV (2000) Structural distribution, mineral composition and peculiarities of formation of variable-depth pegmatites of Mongolian Altai. In: Babanskiy MD (ed) *Ore deposits. Mineralogy. Geochemistry*. Tomsk State University, Tomsk, pp 71–80 **(in Russian)**
- Lottermoser W, Forcher K, Amthauer G, Kunz M, Armbruster T (1997) Site occupation and electric field gradient in acentric nepuntite—measurements and evaluations concerning powder- and single crystal—Mössbauer spectroscopy and x-ray diffractometry. *Phys Chem Miner* 24:2–6
- Nickel EH, Rowland JF, McAdam RC (1963) Ixiolite—a columbite substructure. *Am Miner* 48:961–979
- Palache C, Berman H, Frondel C (1951) *Dana's system of mineralogy* (7th edition), vol II. Wiley, New York, pp 1064–1072
- Palatinus L, Chapis G (2007) SUPERFLIP—a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J Appl Crystallogr* 40:786–790
- Petriček V, Dušek M, Palatinus L (2006) Jana2006. Structure determination software programs. Institute of physics, Praha
- Smith DGW, Nickel EH (2007) A system for codification for unnamed minerals: report of the subcommittee for unnamed minerals of the IMA commission on new minerals, nomenclature and classification. *Can Miner* 45:983–1055
- Stevens JG, Khassanov AM, Miller JW, Pollak H, Li Z (2005) *Mössbauer mineral handbook*. Mossbauer effect data center. University of North Carolina, Asheville, p 626