

Surkhobite: revalidation and redefinition with the new formula, (Ba, K)₂CaNa(Mn, Fe²⁺, Fe³⁺)₈Ti₄(Si₂O₇)₄O₄(F, OH, O)₆

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Abstract: Surkhobite, a new mineral related to the members of the jinshajiangite-perraultite series, was approved in 2002 (IMA No. 2002-037) and later discredited (IMA decision 06-E). It is redefined here with a new formula and revalidated with the original name (IMA 07-A). It occurs as platy crystals up to 1 mm and grains up to $2 \times 1 \times 0.4$ cm in the association with aegirine, microcline, albite, quartz, amphibole, annite, bafertisite, astrophyllite, zircon, fluorite, polyolithionite, stillwellite, sordianite, tadjikite in alkaline pegmatite at the massif Dara-i-Pioz, Tajikistan. Surkhobite is translucent, brownish-red, lustre vitreous, streak white, cleavage perfect on {001}; hardness is anisotropic: the minimum value $H_1 = 250$ kg/mm², the maximum value $H_2 = 482$ kg/mm²; Mohs' hardness is $4\frac{1}{2}$. Biaxial, negative, $\beta = 1.858(10)$, $\gamma = 1.888(10)$; $2V = 65(5)^\circ$; $\alpha = 1.790$ (calculated from $2V$). Optical orientation: $X = b, Z \wedge a = 34^\circ$. Dispersion is strong, $r < v$. Pleochroism: Y (orange) $> Z$ (bright-yellow) $\geq X$ (yellow). Microtwinning on (001) is observed. $D_{\text{calc}} = 3.98$ g/cm³; $D_{\text{meas}} = 3.84(10)$ g/cm³. IR and Mössbauer spectra are given. Chemical composition is (electron microprobe combined with Mössbauer data, wt.%): Na₂O 2.27, K₂O 1.87, CaO 2.53, SrO 0.26, BaO 11.16, MgO 0.13, MnO 16.32, FeO 13.92, Fe₂O₃ 2.11, Al₂O₃ 0.02, SiO₂ 27.17, TiO₂ 16.14, Nb₂O₅ 2.14, ZrO₂ 0.34, F 2.94, H₂O (by Penfield method) 1.17, -O=F₂ -1.24, total 99.25. The empirical formula is $(Z = 2)$: Na_{2.60}K_{1.41}Ca_{1.60}Sr_{0.09}Ba_{2.58}(Mn_{8.17}Fe_{6.88}²⁺Fe_{0.94}³⁺Mg_{0.115}Al_{0.01})_{Σ16.115}(Ti_{7.17}Nb_{0.57}Zr_{0.10})_{Σ7.84}Si_{16.06}Hf_{4.61}F_{5.49}O_{70.51}. The simplified formula, taking into account the crystal structure, is $(Z = 2)$: KBa₃Ca₂Na₂(Mn, Fe²⁺, Fe³⁺)₁₆Ti₈(Si₂O₇)₈O₈(OH)₄(F, OH)₈. The crystal structure was refined on a single crystal to $R = 0.043$ with 3686 independent reflections ($F > 2\sigma$). Surkhobite is monoclinic, $C2$, $a = 10.723(1)$, $b = 13.826(2)$, $c = 20.791(4)$ Å, $\beta = 95.00(1)^\circ$. Surkhobite is the Mn-dominant analogue of jinshajiangite and differs from perraultite in that Ca is ordered onto and is dominant in the site A(6). The strongest lines of the powder diffraction pattern [d , Å (I , %) (hkl)] are: 10.39 (20) (002), 3.454 (100) (006), 3.186 (15) (321), 2.862 (15) (225), 2.592 (70) (008), 2.074 (40) (048).

Key-words: surkhobite, new mineral, revalidation, IR spectrum, heterophyllosilicate, bafertisite polysomatic series, crystal structure, perraultite, jinshajiangite, Dara-i-Pioz, Tajikistan.

Introduction

Surkhobite was approved in 2002 as a new mineral (IMA No. 2002-037) with the formula (Ca, Na)(Ba, K)(Fe²⁺, Mn)₄Ti₂(Si₄O₁₄)O₂(F, OH, O)₃ based on the results of wet chemical analysis (Eskova *et al.*, 2003). Surkhobite was considered as a Ca-dominant mineral related to the members of the jinshajiangite-perraultite series. However, later a proposal to discredit surkhobite was submitted to the IMA CNMMN. This proposal was based only on electron-microprobe analysis carried out for the holotype specimen of surkhobite, which demonstrated predominance of Na

over Ca. According to the results of voting on the latter proposal, surkhobite was discredited with the conclusion: "Name and species surkhobite are discredited because the species corresponds to jinshajiangite and this species has priority" (decision 06 – E of the IMA CNMMN).

We have re-investigated the specimen of surkhobite (the original holotype material prepared by the late V.D. Dusmatov), from which earlier a single crystal was selected by us for structural analysis (we have then deposited this crystal as holotype material in the Fersman Mineralogical Museum, RAS, Moscow, and it was used for electron-microprobe analysis by the authors of the

proposal to discredit surkhobite). In addition to our previous data, this re-investigation included Mössbauer spectroscopy, electron-microprobe analysis and refinement of the structure taking into account refined chemical data.

As a result, we have found that in the empirical formula of surkhobite Mn prevails over Fe^{2+} (unlike jinshajiangite, which is a Fe^{2+} -dominant mineral). Thus, the conclusion that "...surkhobite... corresponds to jinshajiangite..." turned out to be incorrect.

On the other hand, surkhobite is not identical with perraultite, another Mn-dominant mineral of this group, because surkhobite contains a Ca-dominant site (80 % Ca with minor Na and Sr), whereas perraultite does not have Ca-dominant sites. Refined chemical composition corresponds to lower *R* factor (0.043 instead of 0.047 obtained earlier, Rozenberg *et al.*, 2003) and better agreement between calculated and measured values of density.

Correspondingly a nomenclature voting proposal 07 – A, "Revalidation and redefinition of surkhobite", has been approved by the IMA CNMNC with the following conclusion: "The mineral surkhobite and its name are revalidated. Surkhobite is redefined as $(\text{Ba}, \text{K})_2\text{CaNa}(\text{Mn}, \text{Fe}^{2+}, \text{Fe}^{3+})_8\text{Ti}_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{F}, \text{OH}, \text{O})_6$, differing from jinshajiangite because Mn prevails over Fe^{2+} , and differing from perraultite because Ca dominates in the A(6) site".

This paper presents the results of the reinvestigation of surkhobite.

Occurrence, appearance and properties

Surkhobite (named for discovery locality in the basin of the Surkhob river) was found by V.D. Dusmatov in 1976 in an alkaline pegmatite at the massif Darai-Pioz, Tajikistan, in association with aegirine, microcline, albite, quartz, amphibole, annite, bafertisite, astrophyllite, zircon, fluorite, polyolithionite, stillwellite, sogdianite, tadjikite. Surkhobite replaces astrophyllite and bafertisite in zoned syenite pegmatite. It occurs as coarse platy crystals up to 1 mm and grains up to $2 \times 1 \times 0.4$ cm, the pinacoid {001} is the main form. Well-formed crystals are not observed. Twinning on {001} is typical.

Surkhobite is translucent, brownish-red, lustre is vitreous, streak is white, cleavage is perfect on {001}. Hardness measured by micro-indentation method using the PMT device (load on the indenter 20–30 g) is strongly anisotropic. For the cleavage plane {001}, the mean value of hardness is 482, the range 432–543 kg/mm²; for the plane perpendicular to {001} the mean hardness value is 250, the range 212–292 kg/mm². The latter range corresponds to Mohs' hardness of 4^{1/2}.

The mineral is optically biaxial, negative, $\beta = 1.858(10)$, $\gamma = 1.888(10)$; $2V = 65(5)^\circ$; $\alpha = 1.790$ (calculated from $2V$). Optical orientation: $X = b, Z \wedge a = 34^\circ$. Dispersion is strong, $r < v$. Pleochroism: Y (orange) $> Z$ (bright-yellow) $\geq X$ (yellow). Microtwinning on {001} is observed.

Density measured by volumetric method is $D_{\text{meas}} = 3.84(10)$ g/cm³; calculated density is $D_{\text{calc}} = 3.98$ g/cm³.

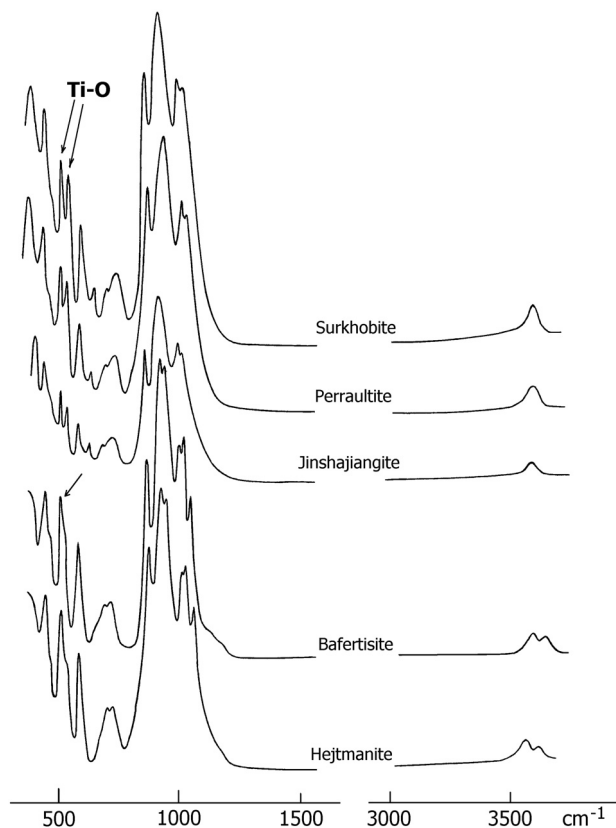


Fig. 1. IR spectra of surkhobite and related minerals.

The IR spectrum of surkhobite is similar to the spectra of jinshajiangite and perraultite, but differs from the IR spectra of the related minerals bafertisite and hejtmanite (Fig. 1). The presence in the IR spectra of distinct bands in the range 530–535 cm⁻¹, the absence of the band ~ 1056 cm⁻¹ and the absence of splitting for the band of O–H-stretching vibrations (~ 3590 cm⁻¹) are diagnostic features of the minerals belonging to the jinshajiangite series (including jinshajiangite, perraultite and surkhobite). Wavenumbers of the bands for surkhobite are (cm⁻¹, s – strong band): 3590, 1033s, 1013s, 937s, 871s, 733, 690, 633, 583, 532, 504, 435s, 381s. Surkhobite, jinshajiangite and perraultite show distinct splitting of the band of Ti–(O,F)-stretching vibrations, probably due to the formation of the links Ti–OH–Ti and Ti–F–Ti (see below). This splitting does not occur for bafertisite or hejtmanite.

The Mössbauer spectrum (Fig. 2) has been obtained for a powdered sample (*ca.* 45 mg) at the temperature of 293 K, using a modified WISSEL spectrometer, simultaneously recording in 512 channels with the time of signal accumulation of 162.3 h. The spectrum can be resolved into three doublets, two of which correspond to Fe^{2+} , octahedrally coordinated by oxygen, and the third one corresponds to octahedrally coordinated Fe^{3+} (Table 1). The estimated ratio $\text{Fe}^{2+}:\text{Fe}^{3+}$ is 88:12. Any attempts to approximate the spectrum with higher or lower Fe^{3+} content result in an unacceptable increase of root-mean square deviation from experimental curve.

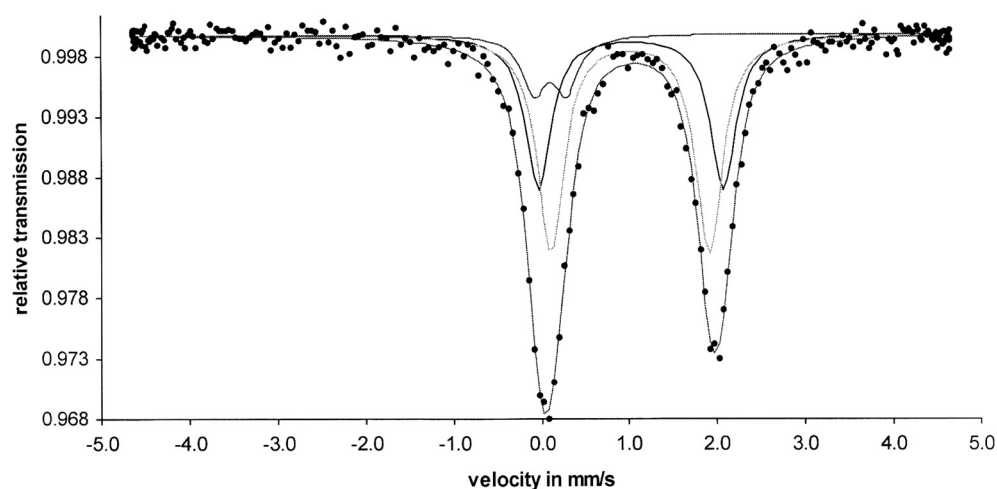


Fig. 2. Mössbauer spectrum of surkhobite.

Table 1. Mössbauer data for surkhobite.

Doublet	Line width, mm/s	Isomer shift, mm/s	Quadrupole splitting, mm/s	Relative integral intensity S, %	Accuracy for the relative integral intensity, %	Comment
Fe ²⁺ (1)	0.36	1.02	2.10	36	18	For the sum S[Fe ²⁺ (1)]+ S[Fe ²⁺ (2)] accuracy is 0.9%
Fe ²⁺ (2)	0.37	1.01	1.80	52	18	
Fe ³⁺	0.33	0.11	0.37	12	0.9	

Table 2. Chemical composition (wt.%) of surkhobite and related minerals of the bafertisite mero-plesiotype series.

	Surkhobite		Jinshajiangite		Perraultite	
	This work, EMPA*	Es'kova <i>et al.</i> (2003), Wet chemistry	Hong & Fu (1982) Holotype, EMPA	Chao (1991) Holotype, EMPA	Pekov <i>et al.</i> (1999), EMPA (+ wet chemistry for Fe)	
Na ₂ O	2.27 (2.17–2.43)	1.57	3.15	3.52		2.76
K ₂ O	1.87 (1.81–1.94)	1.30	2.31	2.68		1.67
Cs ₂ O	0.00	0.27	0.00	0.00		0.00
CaO	2.53 (2.40–2.64)	4.74	2.94	0.00		1.48
SrO	0.26 (0–0.51)	0.06	0.08	0.00		0.05
BaO	11.16 (10.86–11.58)	14.45	9.80	8.88		10.64
MgO	0.13 (0.05–0.29)	0.00	0.28	0.06		0.04
MnO	16.32 (15.93–16.76)	12.75	12.93	31.14		19.28
FeO	13.92 (15.33–16.23)**	13.00	19.07	1.12		12.06
Fe ₂ O ₃	2.11	3.47	1.64	0.00		0.75
Al ₂ O ₃	0.02 (0–0.07)	1.10	0.36	0.03		0.03
SiO ₂	27.17 (26.86–27.36)	26.68	27.10	27.32		27.72
TiO ₂	16.14 (15.98–16.59)	14.00	15.90	9.44		17.83
ZrO ₂	0.34 (0.19–0.44)	2.40	0.35	0.12		1.09
Nb ₂ O ₅	2.14 (1.86–2.40)	1.00	1.03	13.35		1.24
HfO ₂	n.d.	n.d.	0.35	n.d.		n.d.
Ta ₂ O ₅	0.00	0.09	0.07	0.00		0.11
Ce ₂ O ₃	n.d.	n.d.	0.30	n.d.		n.d.
H ₂ O	1.17	1.17	0.33	3.49		1.79
F	2.94 (2.47–3.43)	4.06	2.66	0.84		2.18
O = F ₂	–1.24	–1.71	–1.12	–0.35		–0.92
Total	99.25	100.40	99.53	101.64		99.80

Note: *Ranges are given in brackets. Probe standards are: albite for Na, microcline for K, wollastonite for Ca, SrSO₄ for Sr, BaSO₄ for Ba, MgO for Mg, Mn (metal) for Mn, Fe (metal) for Fe, Al₂O₃ for Al, Ti(metal) for Ti, ZrO₂ for Zr, LiNbO₃ for Nb, SiO₂ for Si, CaF₂ for F.

**The ranges are indicated for all Fe reduced to FeO.

Table 3. Atomic coordinates and equivalent parameters of atomic displacements.

Position	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq} \times 100, \text{\AA}^2$
Ba(1)*	0	0.0265(1)	0	0.93(2)
Ba(2)*	0.7508(1)	0.7726(1)	0.5009(1)	1.99(1)
K*	0	0.5672(1)	0	2.30(4)
Na(1)	0	0.5301(9)	0.5	2.7(1)
Na(2)	0	0.031(1)	0.5	2.4(1)
Ca*	0.2508(6)	0.7749(3)	0.0006(1)	1.61(3)
Fe(1)	0.8768(1)	0.5248(1)	0.2557(1)	1.15(3)
Fe(2)	0.1224(1)	0.6514(1)	0.2478(1)	1.16(3)
Fe(3)	0.8748(1)	0.7770(1)	0.2439(1)	1.15(4)
Mn,Fe(1)	0.8744(1)	0.0250(1)	0.2543(1)	1.17(3)
Mn,Fe(2)	0.1231(1)	0.3986(1)	0.2492(1)	1.38(3)
Mn(1)	0.8751(1)	0.2733(1)	0.2441(1)	1.11(4)
Mn(2)	0.1250(1)	0.9017(1)	0.2458(1)	1.21(3)
Mn(3)	0.1239(1)	0.1502(1)	0.2467(1)	0.99(3)
Ti(1)	0.7334(1)	0.0437(2)	0.3998(1)	1.54(4)
Ti(2)	0.7333(1)	0.5446(1)	0.3985(1)	1.39(5)
Ti(3)*	0.0166(1)	0.2554(1)	0.1008(1)	0.77(3)
Ti(4)*	0.0161(1)	0.7942(1)	0.1007(1)	1.12(2)
Si(1)	0.9796(2)	0.1655(1)	0.3810(1)	1.21(6)
Si(2)	0.9822(2)	0.6662(1)	0.3808(1)	1.30(6)
Si(3)	0.2575(2)	0.4177(1)	0.1194(1)	0.86(5)
Si(4)	0.2842(2)	0.9170(1)	0.1192(1)	0.81(5)
Si(5)	0.2836(2)	0.1344(1)	0.1201(1)	0.98(6)
Si(6)	0.2562(2)	0.6341(2)	0.1191(1)	1.20(6)
Si(7)	0.9806(2)	0.3837(1)	0.3806(1)	1.17(7)
Si(8)	0.9811(2)	0.8851(1)	0.3798(1)	1.22(7)
O(1)	0.9647(7)	0.3914(5)	0.3064(2)	1.3(1)
O(2)	0.2794(5)	0.4021(3)	0.1974(2)	0.7(2)
O(3)	0.9638(6)	0.1565(4)	0.3030(2)	0.9(1)
O(4)	0.2771(6)	0.6441(5)	0.1987(3)	1.3(2)
O(5)	0.2900(6)	0.1473(5)	0.1970(3)	1.2(2)
O(6)	0.1403(5)	0.9015(4)	0.0873(2)	0.9(2)
O(7)	0.3842(5)	0.4007(3)	0.0829(2)	0.5(2)
O(8)	0.9669(6)	0.6573(4)	0.3008(3)	1.2(1)
O(9)	0.2880(5)	0.9013(4)	0.1994(3)	1.0(2)
O(10)	0.9615(7)	0.8956(6)	0.3040(3)	1.9(2)
O(11)	0.3764(5)	0.2044(3)	0.0843(2)	0.6(2)
O(12)	0.7195(6)	0.025(2)	0.3146(3)	2.5(2)
O(13)	0.0295(5)	0.7894(4)	0.1865(2)	0.5(1)
O(14)	0.1519(5)	0.7067(4)	0.0877(2)	0.9(1)
O(15)	0.0275(7)	0.2672(5)	0.1922(4)	1.7(2)
O(16)	0.7205(6)	0.523(1)	0.3129(3)	1.4(2)
O(17)	0.3255(3)	0.0210(5)	0.1013(2)	0.4(1)
O(18)	0.8632(8)	0.6393(9)	0.4121(4)	3.0(2)
O(19)	0.6007(8)	0.9525(8)	0.4145(4)	2.6(2)
O(20)	0.1085(7)	0.6500(7)	0.4132(4)	2.4(3)
O(21)	0.8617(8)	0.912(1)	0.4136(4)	4.4(3)
O(22)	0.3815(6)	0.8458(4)	0.0877(3)	1.3(2)
O(23)	0.8724(9)	0.101(1)	0.4140(5)	3.9(4)
O(24)	0.1092(7)	0.1517(6)	0.4108(4)	1.9(2)

Table 3. Cont.

O(25)	0.6009(7)	0.4511(7)	0.4135(4)	2.2(3)
O(26)	0.1462(5)	0.3491(3)	0.0851(2)	0.8(2)
O(27)	0.1393(5)	0.1511(3)	0.0860(3)	1.1(2)
O(28)	0.8695(8)	0.4508(7)	0.4118(4)	2.6(2)
O(29)	0.2073(4)	0.5265(7)	0.0991(2)	1.2(1)
O(30)	0.036(3)	0.278(1)	0.3922(9)	6.4(3)
O(31)	0.042(1)	0.7769(6)	0.4011(5)	2.4(2)
O(32)	0.3917(5)	0.6493(3)	0.0901(2)	0.9(2)
OH(1)	0.0350(5)	0.5284(8)	0.2092(3)	1.5(2)
OH(2)	0	0.2559(7)	0	1.1(3)
OH(3)	0	0.8053(3)	0	0.67(2)
F(1)	0.0321(6)	0.0159(3)	0.2056(3)	1.2(1)
F(2)	0.2097(7)	0.7795(5)	0.2956(3)	1.3(2)
F(3)	0.7402(4)	0.0069(7)	0.5006(2)	1.4(3)
F(4)	0.7087(7)	0.7767(5)	0.2916(3)	1.6(2)

* Positions with mixed occupancy.

Table 4. Characteristics of coordination polyhedra and selected bond distances (Å).

Position	Composition	CN	Cation-anion distances, Å		
			Min.	Max.	Mean
Ba(1)	1.5Ba + 0.5K	10	2.812(5)	3.170(1)	2.886
Ba(2)	3Ba + 1K	12	2.804(9)	3.672(1)	3.153
K	1.1K + 0.6Ba + 0.3□	9	2.950(5)	3.291(5)	3.023
Na(1)	2Na	10	2.41(1)	2.77(1)	2.61
Na(2)	2Na	10	2.36(1)	2.82(1)	2.62
Ca	3.2Ca + 0.6Na + 0.2Sr	10	2.346(6)	2.875(6)	2.624
Fe(1)	4Fe	6	2.036(8)	2.247(7)	2.173
Fe(2)	4Fe	6	2.112(8)	2.216(8)	2.178
Fe(3)	4Fe	6	2.008(5)	2.360(8)	2.162
Mn, Fe(1)	4(Mn, Fe)	6	2.050(7)	2.261(5)	2.197
Mn, Fe(2)	4(Mn, Fe)	6	2.024(6)	2.286(7)	2.193
Mn(1)	4Mn	6	2.070(6)	2.390(8)	2.202
Mn(2)	4Mn	6	2.136(7)	2.400(1)	2.210
Mn(3)	4Mn	6	2.025(7)	2.458(5)	2.205
Ti(1)	4Ti	6	1.690(7)	2.280(8)	1.977
Ti(2)	4Ti	6	1.798(7)	2.152(6)	1.967
Ti(3)	3.2Ti + 0.8(Nb, Zr)	6	1.900(9)	2.088(1)	1.971
Ti(4)	3.2Ti + 0.8(Nb, Zr)	6	1.777(5)	2.091(1)	1.972

Chemical data

Six point analyses (Table 2) were carried out using an electron microprobe (EDS mode, accelerating voltage 15.7 kV, beam current 0.5 nA, 8 μm beam diameter) using scanning electron microscope VEGA TS 5130MM with Si(Li) detector *INCA Energy*. Probe standards used are: albite for Na, microcline for K, wollastonite for Ca, SrSO_4 for Sr, BaSO_4 for Ba, Mn for Mn, Fe for Fe, MgO for Mg, Al_2O_3 for Al, Ti for Ti, LiNbO_3 for Nb, ZrO_2 for Zr, SiO_2 for Si, CaF_2 for F.

H_2O was analysed by the Penfield method (one analysis). Wet chemical analysis (Eskova *et al.*, 2003) and IR spectrum (this work) show the absence of CO_3 groups.

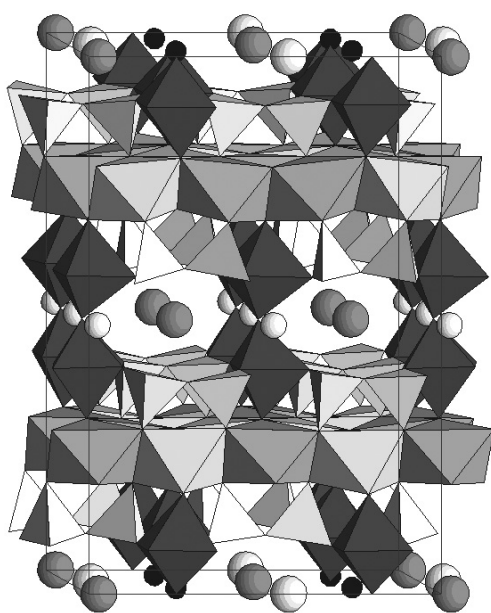


Fig. 3. Crystal structure of surkhobite. Ti-octahedra are dark, (Mn,Fe)-octahedra are light, large dark circles are Ba and light K sites; medium light circles are Na sites; small black circles are Ca sites.

Division of Fe into Fe^{2+} and Fe^{3+} was made in accordance with Mössbauer data (see above). Gladstone-Dale compatibility with optical data and density is $1 - (K_P/K_C) = 0.006$ ("Superior").

The empirical formula based on 76 anions (*i.e.* $Z = 2$) is: $\text{Na}_{2.60}\text{K}_{1.41}\text{Ca}_{1.60}\text{Sr}_{0.09}\text{Ba}_{2.58}(\text{Mn}_{8.17}\text{Fe}_{6.88}^{2+}\text{Fe}_{0.94}^{3+}\text{Mg}_{0.115}\text{Al}_{0.01})\Sigma_{16.115}(\text{Ti}_{7.17}\text{Nb}_{0.57}\text{Zr}_{0.10})\Sigma_{7.84}\text{Si}_{16.06}\text{H}_{4.61}\text{F}_{5.49}\text{O}_{70.51}$.

Thus in surkhobite Mn prevails over Fe^{2+} in atomic proportions. Moreover, in the studied sample Mn prevails over total Fe.

The simplified formula (*i.e.* $Z = 2$), taking into account crystal structure (see below) is: $\text{KBa}_3\text{Ca}_2\text{Na}_2(\text{Mn}, \text{Fe}^{2+}, \text{Fe}^{3+})_{16}\text{Ti}_8(\text{Si}_2\text{O}_7)_8\text{O}_8(\text{OH})_4(\text{F}, \text{O}, \text{OH})_8$.

Crystallography

The mineral is monoclinic, $C2$; $a = 10.723(1) \text{ \AA}$, $b = 13.826(2) \text{ \AA}$, $c = 20.791(4) \text{ \AA}$, $\beta = 95.00(1)^\circ$, $V = 3070.7(9) \text{ \AA}^3$, $Z = 4$. The acentric space group $C2$ was established earlier in the perraultite structure and is related to a shift of Ba and K atoms from the centre of symmetry along b . The real space group of jinshajiangite is unknown yet.

The crystal structure was refined in the anisotropic approximation of atomic displacements to $R = 0.043$ with 3686 independent reflections ($F > 2\sigma$), collected using a 4-circle ENRAF NONIUS diffractometer with Mo radiation. X-ray data were processed with the programme for structure determination and refinement AREN (Andrianov, 1987). At the final stage, the absorption correction was introduced and the mixed atomic-scattering curves were used. The separation of the F and OH from O anions was made on the basis of the calculated local balance of valence

Table 5. X-ray powder diffraction data of surkhobite.

I_{meas}	$d_{\text{meas}}, \text{\AA}$	$d_{\text{calc}}, \text{\AA}$	hkl
20	10.39	10.36	002
10	5.18	5.18	004
5	4.06	4.05	203
5	3.82	3.82	222
5	3.56	3.56	204, 003
100	3.454	3.454	006
5	3.390	3.394	-224
15	3.186	3.189	312
15	2.862	2.860	225
5	2.772	2.772	-226
3	2.725	2.724	-243, -136
		2.722	027
10	2.630	2.631	243, 136
70	2.592	2.590	008
5	2.468	2.468	-422
3	2.435	2.434	-245
3	2.327	2.326	245
3	2.285	2.283	423
5	2.212	2.209	-406
3	2.187	2.188	063
		2.186	-209
5	2.124	2.125	-247
3	2.104	2.104	-512, -426
40	2.074	2.074	048
5	2.030	2.033	512
		2.027	406
3	1.779	1.779	600
		1.778	0.4.10
5	1.764	1.765	-429
		1.763	249
15	1.728	1.728	602, -3.3.10,
			-371, 370
3	1.712	1.712	3.1.10, -4.0.10
10	1.589	1.589	-607
3	1.573	1.573	-376
3	1.470	1.471 1.469	-5.1.11
		1.470	286
		1.469	607
5 (broad)	1.445	1.446	4.2.11
		1.444	-647
10	1.427	1.428	3.3.12, 482
		1.427	539, -2.4.13
		1.426	-734, 557
3	1.355	1.355	-6.0.11, -649
5	1.296	1.296	-2.6.13
		1.295	0.0.16, 4.2.13

at anions. Of the four F atoms, one is located at the vertex shared by two Ti octahedra, while the shared vertices of (Ti, Zr, Nb) octahedra are filled with OH groups. The remaining F atoms are located at shared vertices of three (Fe, Mn) octahedra of the O-layer. The ordering of OH and F in surkhobite is in agreement with the IR spectrum: unlike bafertisite and hejtmannite, surkhobite shows only one band of O-H-stretching vibrations.

The distribution of Mn and Fe on the three types of sites is based on the bond length in their octahedra.

Table 6. Comparative data for surkhobite, jinshajiangite and perraultite.

Mineral	Surkhobite	Jinshajiangite*	Perraultite**
Formula	(Ba, K) ₄ Ca ₂ NaNa (Mn, Fe ²⁺ , Fe ³⁺) ₁₆ Ti ₈ (Si ₂ O ₇) ₈ O ₈ (F, OH) ₁₂	(Ba, K) (Na, Ca) (Fe ²⁺ , Mn) ₄ Ti ₂ (Si ₄ O ₁₄)O ₃ (F, O, OH) ₂	(Ba, K) ₄ Na ₄ (Mn, Fe ²⁺) ₁₆ Ti ₈ (Si ₂ O ₇) ₈ O ₈ (OH, F) ₁₂
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2	C2/m, Cm, orC2	C2
<i>Unit-cell dimensions</i>			
<i>a</i> , Å	10.723	10.732	10.820
<i>b</i> , Å	13.826	13.847	13.843
<i>c</i> , Å	20.791	20.817	20.93
β , °	95.00	95.05	95.09
<i>V</i> , Å ³	3071	3081	3122.6
<i>Z</i>	2	8	2
<i>Optical properties</i>			
α	1.790	1.792	1.785
β	1.858	1.801	1.81
γ	1.888	1.825	1.82
Optical sign,			
2 <i>V</i>	−65°	+72°	−66°
<i>D</i> _{meas} , g/cm ³	3.84	3.61	3.71
Strongest lines	10.39(20)(002),	10.2(70)(002), 3.44(100)	10.43(42)(002),
of the X-ray powder	3.454(100)(006),	(−311, 310, −202, 006),	3.573(11)(025),
diffraction pattern	3.186(15)(312),	3.15(80)(205),	3.474(100)(006),
<i>d</i> , Å(<i>I</i> , %)(<i>hkl</i>)	2.862(15)(225),	2.85(70)(241),	3.186(15)(224),
	2.590(70)(008),	2.63(70)(136,243),	2.867(13)(241),
	2.074(40)(048)	2.570(80)(−403)	2.606(40)(008),
			2.084(15)(0.0.10)
References	This work	Hong Wenxing & Pingu (1982); Ferraris <i>et al.</i> (2001)	Fu Chao (1991); Ferraris <i>et al.</i> (2001); Yamnova <i>et al.</i> (1998); Pekov <i>et al.</i> (1999)

Note: * The crystal structure of jinshajiangite has not been investigated. However, the chemical composition, X-ray powder diffraction pattern and physical properties (including IR spectrum: Fig. 1) show that the mineral is an obvious analogue of perraultite and surkhobite rather than of bafertisite and hejtmante. ** Unit-cell dimensions are given for the holotype sample (Chao, 1991).

The final atomic coordinates are given in Table 3; for site composition and cation-anion distances see Table 4. We did not give the whole set of bond distances to avoid an excessive table length. However, it is necessary to note that two Si-O distances are not satisfactory. These Si1-O20 and Si2-O24 distances are equal to 1.484(8) Å and 1.476(8) Å respectively. Such a shifting of two oxygen atoms can be explained by insufficient absorption correction for the needle-shaped Ba-bearing crystal of size 0.2 × 0.2 × 0.4 mm.

Surkhobite is isostructural with perraultite (Yamnova *et al.*, 1998) and belongs to the bafertisite polysomatic series (Ferraris *et al.*, 2001). Unlike other heterophyllosilicates, H-O-H layers in the structures of surkhobite and perraultite are not isolated but connected into a framework by the Ti-OH-Ti and Ti-F-Ti links (Fig. 3). This linking is possible owing to mutual shifts of neighbouring

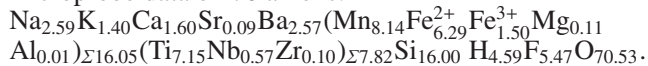
H-O-H layers (0.25 along *X* and *Y* directions compared with bafertisite and its Mn-analogue hejtmante). As a result, the interlayer space is transformed into two types of channels in perraultite and surkhobite. Wide zeolite-like channels with octagonal cross-section are stretched along the *x* axis and populated by Ba and K. Narrow channels with hexagonal cross-section are stretched along the *y* axis and populated by Na and Ca. The crystal structures of perraultite-type minerals (including surkhobite) contain two independent H-O-H layers instead of one layer, as in the case of bafertisite-type species. For this reason, perraultite-type minerals are characterized by a doubling of the *c* parameter. The unit cell of these minerals is (*Z* = 1): [A(1)₂A(2)₂A(3)₄][A(4)₂A(5)₂A(6)₄](Mn, Fe²⁺, Fe³⁺)₃₂(Ti, Nb, Zr)₁₆(Si₂O₇)₁₆O₁₆X₂₄, where A(1–3) = Ba, K; A(4–6) = Na, Ca, (Sr); X = F, OH, O.

Different extra-framework cations occupy large (Ba, K) and small (Ca and Na) cavities. Unlike perraultite, surkhobite is characterized by the presence of a distinct Ca-dominant site. Ordering of Ca and Na is confirmed by local bond-valence balance.

X-ray powder diffraction data are presented in Table 5. These were obtained using a URS-50 IM diffractometer with $\text{FeK}\alpha$ radiation. The cell parameters refined from these data are: $a = 10.719(3) \text{ \AA}$, $b = 13.838(8) \text{ \AA}$, $c = 20.805(10) \text{ \AA}$, $\beta = 95.09(8)^\circ$, $V = 3074(3) \text{ \AA}^3$.

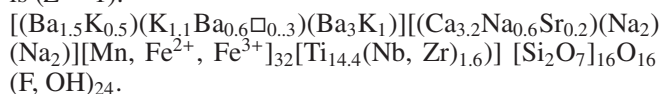
Discussion

Wet-chemical analysis of surkhobite (Eskova *et al.*, 2003; see Table 2) resulted in $\text{Fe}^{2+}:\text{Fe}^{3+} = 80.7:19.3$, in fair agreement with the Mössbauer data. It corresponds to the following empirical formula calculated from our microprobe data on 76 anions:



Thus our results show a Mn-dominant composition for surkhobite, this all the more if $\text{Fe}^{2+}:\text{Fe}^{3+}$ determination data are taken into account.

The crystal-chemical formula of surkhobite obtained as a result of single-crystal refinement of the structure is ($Z = 1$):



The crystal-chemical formula of the structurally investigated perraultite from the Azov Sea region (Yamnova *et al.*, 1998) is: $[\text{Ba}_{2.0}(\text{Ba}_{1.0}\text{K}_{0.8}\square_{0.2})(\text{Ba}_{2.0}\text{K}_{1.6}\square_{0.4})][(\text{Na}_{3.0}\text{Ca}_{1.0})(\text{Na}_{2.0})(\text{Na}_{1.0}\text{Ca}_{1.0})](\text{Mn}, \text{Fe})_{32}(\text{Ti}_{14.7}\text{Nb}_{1.3})(\text{Si}_2\text{O}_7)_{16}\text{O}_{16}(\text{OH}, \text{F})_{24}$. Therefore, Ca-dominant sites in perraultite are absent. Note that the holotype perraultite from Mont Saint-Hilaire does not contain Ca.

Thus surkhobite differs from jinshajiangite because Mn prevails over Fe^{2+} and differs from perraultite because Ca dominates in the site A(6). Surkhobite is therefore the Na-Ca ordered analogue of perraultite (see Table 6).

Type material

One part of the holotype sample of surkhobite (the structurally investigated crystal) is deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, Russia (reg. No. 2882/1).

Another part of the holotype sample used for electron-microprobe and Mössbauer spectroscopic investigations is deposited in the Mineralogical Collection of the Technische Universität Bergakademie Freiberg (Brennhaus-

gasse 14, D-09599 Freiberg, Germany), with the inventory number 81570.

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