

## Rankamaite from the Urubu pegmatite, Itinga, Minas Gerais, Brazil: Crystal chemistry and Rietveld refinement

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### ABSTRACT

A new occurrence of rankamaite is here described at the Urubu pegmatite, Itinga municipality, Minas Gerais, Brazil. The mineral forms cream-white botryoidal aggregates of acicular to fibrous crystals, intimately associated with simpsonite, thoreaulite, cassiterite, quartz, elbaite, albite, and muscovite. The average of six chemical analyses obtained by electron microprobe is (range in parentheses, wt%): Na<sub>2</sub>O 2.08 (1.95–2.13), K<sub>2</sub>O 2.61 (2.52–2.74), Al<sub>2</sub>O<sub>3</sub> 1.96 (1.89–2.00), Fe<sub>2</sub>O<sub>3</sub> 0.01 (0.00–0.03), TiO<sub>2</sub> 0.02 (0.00–0.06), Ta<sub>2</sub>O<sub>5</sub> 81.04 (79.12–85.18), Nb<sub>2</sub>O<sub>5</sub> 9.49 (8.58–9.86), total 97.21 (95.95–101.50). The chemical formula derived from this analysis is (Na<sub>1.55</sub>K<sub>1.28</sub>)<sub>Σ2.83</sub>(Ta<sub>8.45</sub>Nb<sub>1.64</sub>Al<sub>0.89</sub>Fe<sub>0.01</sub>Ti<sub>0.01</sub>)<sub>Σ11.00</sub>[O<sub>25.02</sub>(OH)<sub>5.98</sub>]<sub>Σ31.00</sub>. Rankamaite is an orthorhombic “tungsten bronze” (OTB), crystallizing in the space group *Cmmm*. Its unit-cell parameters refined from X-ray diffraction powder data are: *a* = 17.224(3), *b* = 17.687(3), *c* = 3.9361(7) Å, *V* = 1199.1(3) Å<sup>3</sup>, *Z* = 2. Rietveld refinement of the powder data was undertaken using the structure of LaTa<sub>5</sub>O<sub>14</sub> as a starting model for the rankamaite structure. The structural formula obtained with the Rietveld analyses is: (Na<sub>2.21</sub>K<sub>1.26</sub>)<sub>Σ3.37</sub>(Ta<sub>9.12</sub>Nb<sub>1.30</sub>Al<sub>0.59</sub>)<sub>Σ11.00</sub>[O<sub>26.29</sub>(OH)<sub>4.71</sub>]<sub>Σ31.00</sub>. The tantalum atoms are coordinated by six and seven oxygen atoms in the form of distorted TaO<sub>6</sub> octahedra and TaO<sub>7</sub> pentagonal bipyramids, respectively. Every pentagonal bipyramid shares edges with four octahedra, thus forming Ta<sub>5</sub>O<sub>14</sub> units. The potassium atom is in an 11-fold coordination, whereas one sodium atom is in a 10-fold and the other is in a 12-fold coordination. Raman and infrared spectroscopy were used to investigate the room-temperature spectra of rankamaite.

**Keywords:** Rankamaite, tungsten bronze, tantalate, Urubu pegmatite, Itinga, Minas Gerais, Brazil, Rietveld refinement

### INTRODUCTION

Rankamaite and its potassium analog sosedkoite are natural orthorhombic “tungsten bronzes” (OTB). “Tungsten bronze” is a nebulous expression used to describe alkali metal tungstates, vanadates, molybdates, titanates, tantalates, and niobates. The term was originally coined to describe Na<sub>x</sub>WO<sub>3</sub> compounds, whose crystals look much like the copper-tin alloy known as bronze. “Tungsten bronzes” have long been the subject of investigations for their interesting structural, electronic, and electro-optical properties. Due to these interesting properties and structural phase transitions, much attention has been paid to the dielectric ceramics with a “tungsten-bronze” structure (Zheng and Zhou 2006). The structural flexibility of these synthetic compounds allows their properties to be tailored to a specific application (for example, formation of superstructures). Several synthetic compounds with “tungsten bronze” structure have been described.

Rankamaite has only been described from five occurrences: (1) the Mumba cassiterite gravels, Masisi Mountains, Kivu province, Democratic Republic of Congo (von Knorring et al.

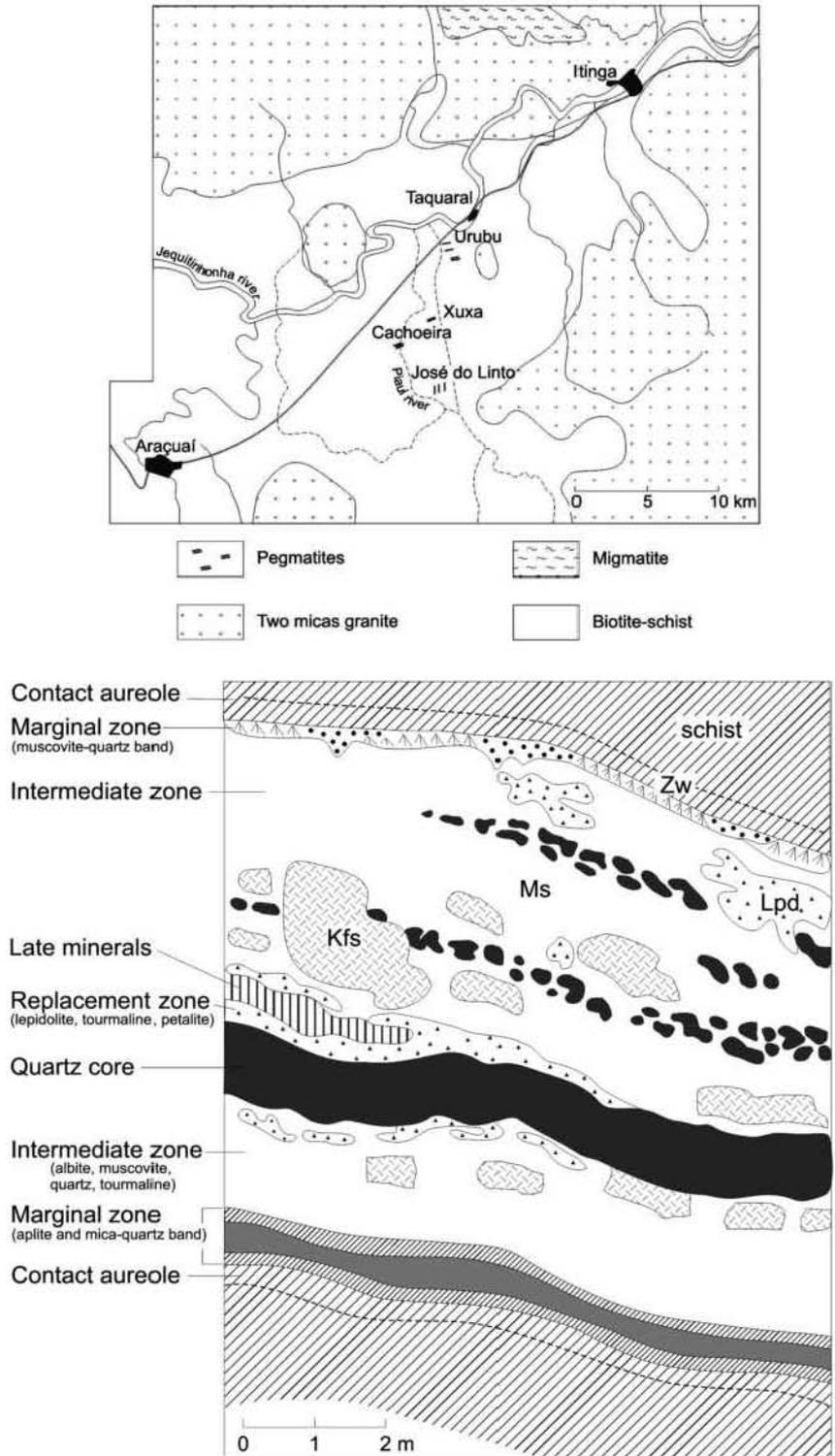
1969; von Knorring and Fadipe 1981; Voloshin et al. 1982; Kristiansen 2001); (2) the Ognévka tantalum deposit, Kalba Mountains, Eastern Kazakhstan (Voloshin et al. 1983; Voloshin and Pakhomovsky 1988); (3) Siberia, Russia (Nekrasov et al. 1984); (4) Tanco, Manitoba, Canada (Černý et al. 1996, 1998); and (5) the Manono pegmatite, Katanga province, Democratic Republic of Congo (Voloshin and Pakhomovsky 1988; Uher et al. 2008). According to von Knorring et al. (1969), A. Safiannikoff was aware of the existence of this mineral in alluvial deposits, probably derived from spodumene-bearing pegmatites between Goma and Masisi to the northwest of Lake Kivu, long before its discovery. The potassium analog of rankamaite, sosedkoite, was described by Voloshin et al. (1982) in a granite pegmatite from Mt. Vasin-Myl'k, Voron'i Tundry massif, Kola Peninsula, Russia. According to Černý et al. (1985), occurrences of both rankamaite and sosedkoite are restricted to highly fractionated, simpsonite-bearing granitic pegmatites. Rankamaite is found as a felty replacement of simpsonite and of cassiterite generated by oxidation of thoreaulite. Sosedkoite is known as a late post-simpsonite mineral developed along fractures and intergranular contacts in microlite-group minerals and stibiotantalite. Here we describe a new occurrence of rankamaite in Brazil.

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**OCCURRENCE**

The Urubu pegmatite is located in a quarry near the junction of the Piauí (a north-south tributary) and the Jequitinhonha Rivers, in Itinga county, Minas Gerais, Brazil (Fig. 1). With a general strike of east-northeast and a gentle north-northwest dip,

the Urubu pegmatite is granitic, heterogeneous, and albitized. It is divided into two lenses in its eastern part by a mica schist intercalation. Its thickness seems to be about 10–15 m. The wallrock comprises a dark-gray biotite schist with quartz beds. The contact between the two rocks is always sharp, undulating, and dips more



**FIGURE 1.** Schematic geological map and cross-section of the Urubu pegmatite (Quéméneur and Lagache 1999); abbreviations: Ms = muscovite, Zw = zinnwaldite, Lpd = lepidolite, Kfs = potassium feldspar.

at the south than at the north contact, where offsets are frequent. Where the contact zone is visible, it is marked by an increased modal content of small black tourmaline needles, which locally transform the schist into tourmalinite (south of the quarry entry). Main minerals in the pegmatite are represented by quartz, potassium feldspar, albite, muscovite, lepidolite, zinnwaldite, elbaite, amblygonite, petalite, spodumene, beryl, pollucite, cassiterite, columbite-group minerals, thoreaulite, monazite, and xenotime (Cassedanne and Cassedanne 1981; Quéméneur and Lagache 1999). In addition, microlite-group minerals (currently under study) and simpsonite have been identified. Rankamaite forms cream-white botryoidal aggregates of acicular to fibrous crystals, intimately associated with simpsonite, thoreaulite, cassiterite, quartz, elbaite, albite, and muscovite (Figs. 2 and 3).

### CHEMICAL DATA

Rankamaite from the Urubu mine was embedded in epoxy resin and polished. Six point analyses were obtained at Instituto de Geociências of the Universidade de São Paulo by means of a JEOL JXA-8600 electron microprobe (wavelength-dispersive mode, 15 kV, 20 nA, and 10  $\mu\text{m}$  beam diameter) and a NORAN system for automation and data reduction. The analytical results and atomic proportions [calculated on the basis of 11 (Ta + Nb + Al + Fe + Sb + Si + Sn + Ti + Bi)] for the Urubu material are compared with the published data for rankamaite and sosedkoite in Table 1. No elements with  $Z > 8$ , other than those reported in Table 1, were detected by energy-dispersive X-ray spectrometry. The small amount of  $\text{SiO}_2$  detected in some samples was attributed to muscovite by von Knorring et al. (1969) and to orthoclase by Nekrasov et al. (1984), which may not be correct. Here, we present the formulas before and after the deduction of these potential impurities. If we consider the rankamaite analysis of Nekrasov et al. (1984) without the deduction, their mineral actually corresponds to sosedkoite. The mineral of Černý et al. (1996, 1998) is practically at the middle point of the rankamaite-sosedkoite series. The empirical formula derived from the analyses of rankamaite from the Urubu mine is  $(\text{Na}_{1.55}\text{K}_{1.28})_{\Sigma 2.83}(\text{Ta}_{8.45}\text{Nb}_{1.64}\text{Al}_{0.89}\text{Fe}_{0.01}^{3+}\text{Ti}_{0.01})_{\Sigma 11.00}[\text{O}_{25.02}(\text{OH})_{5.98}]_{\Sigma 31.00}$ .



FIGURE 2. Rankamaite (cream-white) with cassiterite (black) from the Urubu mine.

### RAMAN AND FTIR SPECTROSCOPY

Raman spectra of selected crystal fragments were acquired with a confocal microscope Alpha 300 (WITec, Ulm, Germany), equipped with a  $\times 100$  Nikon objective ( $\text{NA} = 0.9$ ). A polarized beam generated by a Nd:YAG laser ( $\lambda = 532 \text{ nm}$ ) was focused on the sample and the Raman signal was detected by a back-illuminated spectroscopic CCD behind a 600  $\text{g/mm}$  grating. The Fourier transform infrared (FTIR) spectra were recorded using attenuated total reflectance (ATR) between 600 and 4000  $\text{cm}^{-1}$  using a VERTEX 70 instrument (Bruker, Ettlingen, Germany) with 64 scans at a spectral resolution of 4  $\text{cm}^{-1}$ . Samples were deposited on the ATR crystal without further preparation. All Raman and FTIR analyses were performed at room temperature.

The Raman and FTIR spectra of rankamaite are shown in Figure 4. In the region 200–350  $\text{cm}^{-1}$ , three Raman modes are clearly identified at 239, 275, and 328  $\text{cm}^{-1}$ . They can be assigned to  $\text{TaO}_6$  octahedra (Ikeya and Senna 1978; Dobal et al. 2000; Hornebecq et al. 2003; Teixeira et al. 2007; Amira et al. 2010). The most intense peak at 633  $\text{cm}^{-1}$  can be assigned to

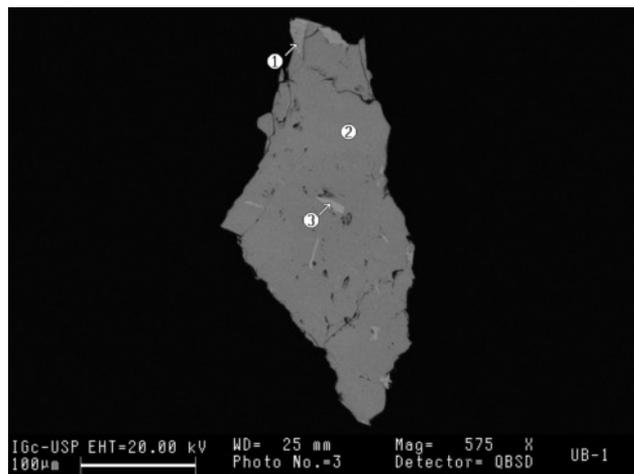


FIGURE 3. Back-scattered electron image of rankamaite (1 and 3) with thoreaulite (2) from the Urubu mine.

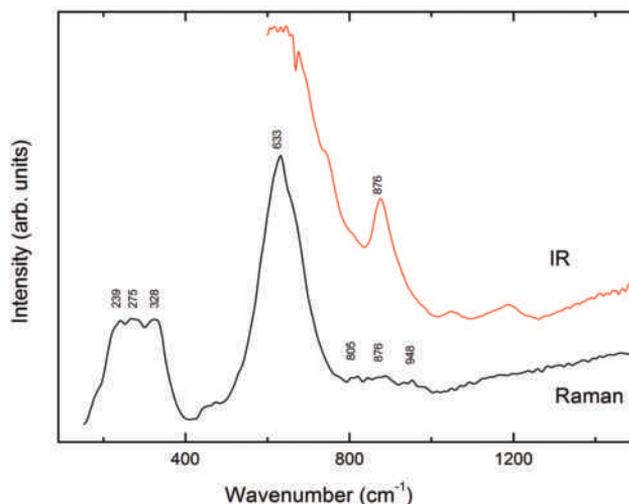


FIGURE 4. FTIR and Raman spectra of rankamaite from the Urubu mine.

**TABLE 1.** Chemical composition (wt%) and atomic proportions for rankamaite and sosedkoite

Constituent	1	2	3	4	5	6	7	8	9	10	10 Range	10 Probe standards
Na <sub>2</sub> O	2.31	1.86	1.15	1.95	1.95	1.88	1.34	1.68	1.83	2.08	1.95–2.13	albite
K <sub>2</sub> O	1.80	2.16	2.79	3.25	2.45	2.84	1.78	1.78	2.66	2.61	2.52–2.74	orthoclase
Cs <sub>2</sub> O									0.18			
CaO		0.05	0.10				0.06	0.06	0.03			
BaO									0.11			
PbO	2.63	1.81			0.50		0.84	0.94	0.31			
MnO									0.05	0.00	0.00–0.01	olivine
UO <sub>2</sub>									0.30			
Al <sub>2</sub> O <sub>3</sub>	3.40	2.18	1.96	2.15	2.10	1.45	1.97	2.06	1.84	1.96	1.89–2.00	anorthite
Fe <sub>2</sub> O <sub>3</sub>		1.06					0.33			0.01	0.00–0.03	olivine
Li <sub>2</sub> O	0.11											
Ta <sub>2</sub> O <sub>5</sub>	69.47	73.60	91.25	72.13	73.23	88.38	89.65	89.60	85.93	81.04	79.12–85.18	Ta metal
Nb <sub>2</sub> O <sub>5</sub>	17.40	15.69	2.71	17.25	17.99	1.57	2.63	2.43	4.56	9.49	8.58–9.86	Nb metal
Sb <sub>2</sub> O <sub>5</sub>			0.47									
SiO <sub>2</sub>	0.96			3.50					0.52			
SnO <sub>2</sub>					0.45		0.28		0.90			
TiO <sub>2</sub>									0.01	0.02	0.00–0.06	rutile
Sb <sub>2</sub> O <sub>3</sub>									0.08			
Bi <sub>2</sub> O <sub>3</sub>									0.13			
H <sub>2</sub> O <sup>+</sup>	1.55									(2.34)*		
H <sub>2</sub> O <sup>-</sup>	0.35											
F									0.31			
-O=(F)									-0.13			
Total	99.98	98.41	100.43	100.23	98.67	96.12	98.88	98.41	99.62	(99.55)	95.95–101.50	
apfu	1	1a	2	3	4	4a	5	6	7	8	9	10
Na	1.65	1.55	1.30	0.85	1.44	1.24	1.36	1.52	1.01	1.29	1.37	1.55
K	0.73	0.80	1.00	1.37	1.13	1.36	1.17	1.51	0.88	0.90	1.30	1.28
Li	0.17	0.16										
Cs											0.03	
Ca			0.02	0.04					0.03	0.03	0.01	
Ba											0.02	
Pb	0.27	0.24	0.18				0.05		0.09	0.10	0.03	
Mn											0.02	
U <sup>4+</sup>											0.03	
Σ	2.82	2.75	2.50	2.26	2.57	2.60	2.58	3.03	2.01	2.32	2.81	2.83
Ta	6.96	6.55	7.22	9.58	7.50	6.45	7.13	10.00	9.49	9.62	9.00	8.45
Nb	2.91	2.73	2.56	0.47	2.98	2.57	2.92	0.29	0.46	0.43	0.80	1.64
Sb <sup>5+</sup>				0.06								
Si		0.33				1.15					0.20	
Sn							0.07		0.05		0.14	
Ti											0.01	0.01
Al	1.13	1.39	0.93	0.89	0.52	0.83	0.88	0.71	0.90	0.95	0.83	0.89
Fe <sup>3+</sup>			0.29						0.10			0.01
Sb <sup>3+</sup>											0.01	
Bi											0.01	
Σ	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00
O	24.83	23.88	24.26	24.52	25.53	23.79	24.80	25.61	24.08	24.55	24.93	25.02
OH	6.17	7.12	6.74	6.48	5.47	7.21	6.20	5.39	6.92	6.45	5.69	5.98
F											0.38	
Σ	31.00	31.00	31.00	31.00	31.00	31.00	31.00	31.00	31.00	31.00	31.00	31.00

Notes: 1 = Rankamaite from Mumba cassiterite gravels, Democratic Republic of Congo (von Knorring et al. 1969), wet analysis; 1a = without muscovite deduction. 2 = Rankamaite from Mumba cassiterite gravels, Democratic Republic of Congo (Voloshin et al. 1982). 3 = Sosedkoite from Mt. Vasin-Myl'k, Russia (Voloshin et al. 1982). 4 = Rankamaite from Sibéria, Russia (Nekrasov et al. 1984), mean of 4 analyses; 4a = without orthoclase deduction (=sosedkoite). 5 = Rankamaite from Ognevka tantalum deposit, Eastern Kazakhstan (Voloshin and Pakhomovsky 1988). 6 = Rankamaite from Tanco, Canada (Černý et al. 1996, 1998). 7 and 8 = Rankamaite from Manomo pegmatite, Democratic Republic of Congo (Voloshin and Pakhomovsky 1988). 9 = Rankamaite from Manomo pegmatite, Democratic Republic of Congo (Uher et al. 2008). 10 = Rankamaite from the Urubu pegmatite, Brazil (this paper).

\* Calculated for charge neutrality.

stretching vibrations of TaO<sub>6</sub> octahedra (Hornebecq et al. 2003; Tomašić et al. 2004; Amira et al. 2010). It is also possible to identify a series of small peaks between 605 and 662 cm<sup>-1</sup> in the FTIR spectra. The Raman and IR bands in the region 800–1000 cm<sup>-1</sup> (Fig. 4) can be assigned to vibrations of TaO<sub>6</sub> octahedra and TaO<sub>7</sub> bipyramids (Ikeya and Senna 1978; Tomašić et al. 2004; Hornebecq et al. 2003).

### CRYSTALLOGRAPHY

Powder X-ray diffraction (XRD) data were obtained using a Siemens D5000 diffractometer equipped with a Göbel mirror

and a position-sensitive detector. The XRD data (in angstroms for CuKα) are given in Table 2. Investigation of the powder data indicated orthorhombic symmetry with the possible space groups *C222* (21), *Cmm2* (35), *Amm2* (38), or *Cmmm* (65) (*h* + *k* = even). The unit-cell parameters refined from the powder data are: *a* = 17.224(3), *b* = 17.687(3), *c* = 3.9361(7) Å, *V* = 1199.1(3) Å<sup>3</sup>, and *Z* = 2, with *a*:*b*:*c* = 0.9738:1:0.2225. As in all the other occurrences of rankamaite and sosedkoite, the crystals from the Urubu mine are extremely fine acicular to fibrous, and they are not amenable to single-crystal X-ray diffraction techniques. The crystal structure of these minerals has not been determined, but

**TABLE 2.** Powder X-ray diffraction data for rankamaite from the Urubu mine

<i>I</i> (%)	<i>d</i> <sub>meas</sub> (Å)	<i>d</i> <sub>calc</sub> (Å)	<i>h</i>	<i>k</i>	<i>l</i>
14	8.839	8.844	0	2	0
7	8.603	8.612	2	0	0
6	6.165	6.170	2	2	0
6	5.575	5.578	1	3	0
22	5.456	5.461	3	1	0
30	4.420	4.422	0	4	0
6	4.302	4.306	4	0	0
33	4.110	4.113	3	3	0
80	3.931	3.936	0	0	1
		3.934	2	4	0
19	3.868	3.871	4	2	0
3	3.592	3.596	0	2	1
47	3.463	3.465	1	5	0
47	3.378	3.381	5	1	0
30	3.189	3.193	3	1	1
10	3.083	3.085	4	4	0
79	3.010	3.012	3	5	0
100	2.972	2.974	5	3	0
30	2.946	2.948	0	6	0
18	2.868	2.871	6	0	0
12	2.841	2.844	3	3	1
38	2.787	2.789	2	6	0
8	2.757	2.760	4	2	1
8	2.728	2.730	6	2	0
9	2.599	2.601	1	5	1
12	2.562	2.565	5	1	1
3	2.431	2.432	4	6	0
13	2.390	2.392	3	5	1
21	2.371	2.373	5	3	1
4	2.317	2.319	6	0	1
10	2.274	2.276	2	6	1
4	2.151	2.153	8	0	0
7	2.140	2.141	2	8	0
12	2.090	2.092	8	2	0
2	2.052	2.055	6	4	1
20	1.966	1.968	0	0	2
6	1.934	1.936	8	4	0
6	1.901	1.903	9	1	0
29	1.858	1.859	3	9	0
4	1.819	1.820	9	3	0
8	1.768	1.769	0	10	0
8	1.750	1.752	6	8	0
27	1.737	1.739	8	6	0
9	1.721	1.722	10	0	0
8	1.709	1.711	1	5	2
18	1.680	1.681	3	9	1
9	1.639	1.641	5	3	2
3	1.612	1.613	0	10	1
16	1.589	1.590	8	6	1
5	1.576	1.578	10	0	1
5	1.541	1.542	8	8	0
4	1.512	1.513	11	3	0
4	1.505	1.506	6	10	0
5	1.486	1.487	7	3	2
3	1.473	1.474	0	12	0
5	1.456	1.457	5	11	0
5	1.435	1.436	8	8	1
6	1.432	1.433	8	2	2
5	1.366	1.367	8	10	0
4	1.350	1.352	3	9	2

**TABLE 3.** Atomic coordinates and equivalent isotropic displacement parameters for rankamaite

Atom	Wyck	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Occ	<i>B</i> <sub>iso</sub>
K1	4 <i>h</i>	0.8322(17)	0	0.5	0.63	4.5
Na2	4 <i>h</i>	0.4990(29)	0	0.5	0.43	4.5
Na3	4 <i>f</i>	0.25	0.25	0.5	0.68	4.5
Ta1	2 <i>a</i>	0	0	0	0.71	2
Nb1	2 <i>a</i>	0	0	0	0.29	2
Ta2	4 <i>i</i>	0	0.67188(32)	0	0.72	2
Nb2	4 <i>i</i>	0	0.67188(32)	0	0.28	2
Ta3	8 <i>p</i>	0.18037(27)	0.39406(18)	0	0.85	2
Al3	8 <i>p</i>	0.18037(27)	0.39406(18)	0	0.15	2
Ta4	8 <i>p</i>	0.11190(18)	0.82225(21)	0	0.89	2
Nb4	8 <i>p</i>	0.11190(18)	0.82225(21)	0	0.11	2
O1	8 <i>q</i>	0.3235	0.1061	0.5	1	1
O2	8 <i>q</i>	0.6165	0.6777	0.5	1	1
O3	8 <i>p</i>	0.1376	0.2915	0	1	1
O4	8 <i>p</i>	0.0711	0.5780	0	1	1
O5	8 <i>p</i>	0.2790	0.3377	0	1	1
O6	8 <i>p</i>	0.1103	0.9442	0	1	1
O7	4 <i>j</i>	0	0.3334	0.5	1	1
O8	4 <i>i</i>	0	0.2011	0	1	1
O9	4 <i>g</i>	0.7108	0	0	1	1
O10	2 <i>d</i>	0	0	0.5	1	1

**TABLE 4.** Selected interatomic distances (Å)

K1	O1 x2	3.26(1)	Na2	O4 x4	2.697(22)
	O2 x2	3.27(1)		O4 x4	2.705(23)
	O6 x4	2.414(11)		O7 x2	2.945(85)
	O9 x2	2.872(22)		average	2.750
	O10	2.890(20)			
average		2.850			
*Na3	O5 x4	2.555			
	O2 x2	2.632			
	O1 x2	2.843			
	O3 x4	2.857			
average		2.716			
*Ta1	O10 x2	1.96803	Ta2	O7 x2	1.97028(41)
	O6 x4	2.14104		O4 x2	2.06351(71)
	average	2.083		O8	2.24691(57)
			O3 x2	2.45685(14)	
			average	2.175	
Ta3	O4	1.94561(71)	Ta4	O5	1.89852(31)
	O9	1.94579(30)		O2 x2	1.96959(10)
	O3	1.95715(29)		O8	1.97111(32)
	O1 x2	1.96915(83)		O3	2.06085(37)
	O5	1.9704(16)		O6	2.15701(38)
average	1.960	average	2.004		

\* Fixed positions.

von Knorring et al. (1969) recognized the close similarity of the rankamaite powder XRD pattern to those of “tungsten bronze”-derived structures.

Comparison with natural and synthetic phases showed a striking similarity between the XRD patterns of rankamaite and OTB phases crystallizing in the space group *Cmmm*. Based on this fact, the structure of LaTa<sub>5</sub>O<sub>14</sub> (Schaffrath and Gruehn 1989) was chosen (because of its similarity) as a starting model for the rankamaite structure.

In the initial structural model, Na was substituted for La and all other atoms remained the same as for LaTa<sub>5</sub>O<sub>14</sub>. In the initial Rietveld analyses [using TOPAS v3.0 (Bruker 2004)], the positions of Ta and Na atoms were allowed to refine, whereas all O atoms were fixed and anisotropic peak broadening was fitted using fourth-order spherical harmonics (Järvinen 1993). In the next steps, the Ta and their associated O atoms were refined separately and carefully checked to ensure that all bond lengths remained sensible. After all atoms had been refined, the occupancies for the Ta atoms were refined with Nb placed at each position. Inspection of the bond lengths indicated that Ta3 was a likely site for Al substitution. All other Ta sites were refined only with Nb, although it is likely that Al also substitutes for Ta in these other sites. The occupancies of the three Na sites were then refined; the occupancy of Na1 indicated that K was a better fit. The thermal parameters (*B*<sub>iso</sub>) for K, Na, and Ta sites were then refined with the parameter constrained to be equal for K1,

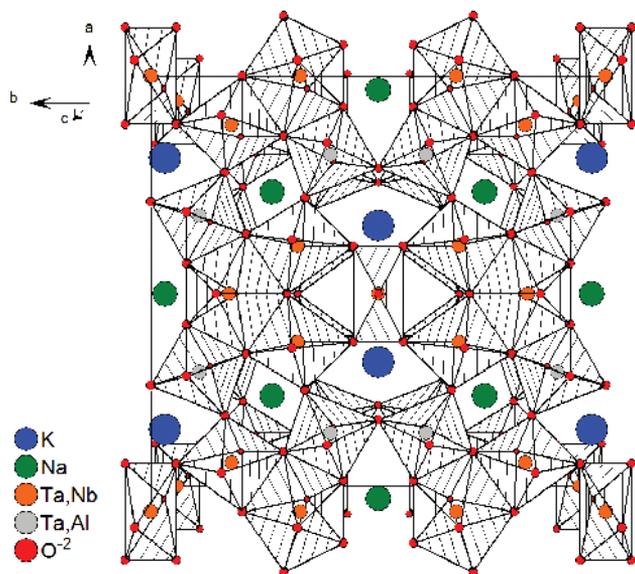


FIGURE 5. The crystal structure of rankamaite.

Na<sub>2</sub>, Na<sub>3</sub>, and Ta<sub>1–4</sub>. The  $B_{iso}$  value for all O atoms was not refined and left equal to 1. In the last stage of refinement ( $R_p = 3.63$ ,  $R_{wp} = 4.21\%$ ,  $GooF = 3.84$ ,  $d = 0.3$  over  $5–70\ 2\theta$ ), the O atom positions, occupancies and  $B_{iso}$  values were fixed, while the atomic positions for K, Na, and Ta atoms were allowed to refine. The structural formula derived from the Rietveld analyses is:  $(Na_{2.21}K_{1.26})_{\Sigma 3.37}(Ta_{9.12}Nb_{1.30}Al_{0.59})_{\Sigma 11.00}[O_{26.29}(OH)_{4.71}]_{\Sigma 31.00}$ , which is reasonably close to the chemical formula, but because three different elements cannot be simultaneously refined in the same site (leading to an underestimated Al content), the refined formula is only a close approximation. The final atomic coordinates and bond lengths are presented in Tables 3 and 4, respectively.

The Ta atoms are coordinated by six and seven atoms of oxygen in the form of distorted TaO<sub>6</sub> octahedra and TaO<sub>7</sub> pentagonal bipyramids, respectively. Every tetragonal bipyramid is linked by edges to four octahedra (Ta<sub>3</sub> and Ta<sub>4</sub>), thus forming Ta<sub>5</sub>O<sub>14</sub> units. The coordination number of K1, which is equivalent to La1 in the LaTa<sub>5</sub>O<sub>14</sub> structure, should be 9 according to Schaffrath and Gruehn (1989). However, in rankamaite, we consider the coordination to be 11, because the 11 K–O bonds are all within the range 2.4–3.3 Å. The coordination numbers of Na<sub>2</sub> and Na<sub>3</sub>, which are equivalent to La<sub>2</sub> and La<sub>3</sub> in the LaTa<sub>5</sub>O<sub>14</sub> structure, are 10 and 12, respectively (Fig. 5).

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