Mineralogical Magazine, February 2018, Vol. 82(1), pp. 111–120

Melcherite, trigonal $Ba_2Na_2Mg[Nb_6O_{19}]\cdot 6H_2O$, the second natural hexaniobate, from Cajati, São Paulo, Brazil: Description and crystal structure

Marcelo B. Andrade[1,*], Daniel Atencio[2], Luiz A. D. Menezes Filho[3,†] and John Spratt[4]

[1] Department of Physics and Interdisciplinary Science, São Carlos Institute of Physics, University of São Paulo, Caixa Postal 369, 13560-970 São Carlos, SP, Brazil
[2] Departamento de Mineralogia e Geotectônica, Instituto de Geociências, Universidade de São Paulo, Rua do Lago 562, 05508-080 São Paulo, SP, Brazil
[3] Instituto de Geociências, Universidade Federal de Minas Gerais, Avenida Antonio Carlos 6627, 31270-901, MG, Brazil.
[4] Core Research Laboratories, Natural History Museum, Cromwell Road, London SW7 5BD, United Kingdom

[*Received 13 June 2016; Accepted 18 April 2017; Associate Editor: Ian Graham*]

ABSTRACT

Melcherite (IMA2015-018), ideally $Ba_2Na_2Mg[Nb_6O_{19}]\cdot 6H_2O$, occurs as a vug mineral in the carbonatite of the Jacupiranga mine, Cajati county, São Paulo state, Brazil, associated with dolomite, calcite, magnetite, pyrrhotite, tochilinite, 'pyrochlore' and fluorapatite. This is also the type locality for zirkelite, quintinite, menezesite and pauloabibite. The mineral forms irregular, tabular crystals up to 200 µm in maximum dimension. Melcherite is transparent and displays a vitreous lustre; it is beige with a white streak. It is non-fluorescent. The mineral displays perfect cleavage on {001}. Chemical composition varies from $Ba_2Na_2Mg[Nb_6O_{19}].6H_2O$ to $(BaK)(NaCa)Mg[Nb_6O_{19}].6H_2O$. Empirical formulae for the first and the second compositions are: $(Ba_{1.75}K_{0.19})_{\Sigma 1.94}(Na_{1.80}Ca_{0.19})_{\Sigma 1.99}(Mg_{0.96}Mn_{0.02}Al_{0.02})_{\Sigma 1.00}Nb_{6.02}O_{19.00}\cdot 6H_2O$ and $(Ba_{0.99}K_{1.00})_{\Sigma 1.99}(Na_{1.02}Ca_{0.96})_{\Sigma 1.98}(Mg_{0.95}Mn_{0.05})_{\Sigma 1.00}Nb_{6.02}O_{19.00}\cdot 6H_2O$, respectively. Data for a single crystal with the second composition are: trigonal, $R\bar{3}$, $a = 9.0117(6)$ Å, $c = 23.3986(16)$ Å, $V = 1645.64(19)$ Å^3 and $Z = 3$. Calculated density for this formula is 3.733 g/cm^3, and the calculated mean refractive index is 1.924. Melcherite is a hexaniobate that has structural layers parallel to the *xy* plane that stack along the *c* axis with simultaneous 1/3 $[1\bar{1}0]$ displacement so as to produce an *R* lattice. The melcherite structure is built by layers of $[(Ba,K)(O,H_2O)_9]$ polyhedra and the $[Nb_6O_{19}]^{8-}$ super-octahedron (Lindqvist anion) interconnected by $[(Na,Ca)O_6]$ polyhedra. Cations of Mg^{2+} are bonded to six water molecules each and are not associated with Lindqvist oxygen ions. The mineral is named in honour of Geraldo Conrado Melcher (1924–2011), a pioneer in Jacupiranga carbonatite studies.

Keywords: melcherite, new mineral, hexaniobate, crystal structure, chemical composition, Jacupiranga mine, Cajati, Brazil.

Introduction

Melcherite is the second natural hexaniobate. The first described was peterandresenite (Friis *et al.*, 2014) and hansesmarkite was recently discovered (Friis *et al.*, 2017). Polyoxometalates of niobium are dominated by the Linqdvist hexaniobate ion, $(Nb_6O_{19})^{8-}$, and its synthesis and stability requires alkaline conditions. The crystal structure of these compounds was first described by Lindqvist (1953). Hexaniobates are negatively charged clusters of six mutually edge-sharing NbO_6 octahedra forming a super-octahedron (Nyman, 2011).

*E-mail: mabadean@terra.com.br
†Deceased July 2014
https://doi.org/10.1180/minmag.2017.081.026

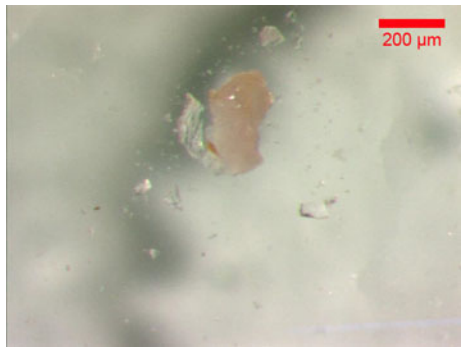

FIG. 1. Melcherite from the Cajati mine, São Paulo, Brazil.

Possible polyoxoniobate applications include their use as reagents in the break-down of nerve agents and in the development of filter media protection against chemical warfare agents (Kinnan *et al.*, 2014). Polyoxometalates have also been investigated in coordination chemistry, leading to the development of hybrid organometallic hexametalate complexes (Abramov *et al.*, 2016), and the synthesis of new polyoxoniobates coordinated to copper complexes (Wang *et al.*, 2008).

The mineral is named in honour of Geraldo Conrado Melcher (1924–2011). He was professor at the Department of Mining Engineering at the Polytechnic School, University of São Paulo and was also a pioneer in Jacupiranga carbonatite studies (Melcher, 1966).

Both the description and name were approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA2015-018). Type material is deposited in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080 – São Paulo, SP, Brazil. Specimen number: DR982. Part of the cotype sample has been deposited at the University of Arizona Mineral Museum, RRUFF Project (deposition no. R130752).

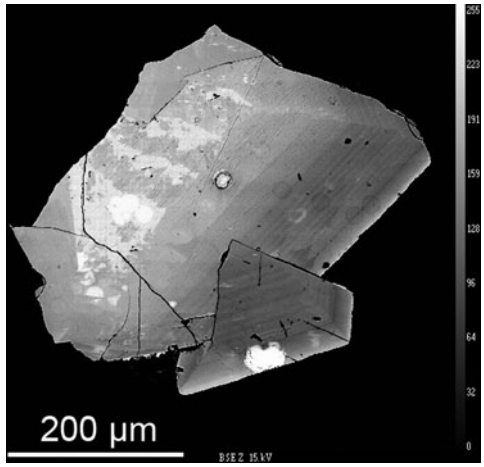

FIG. 2. Back-scattered electron image of melcherite.

Occurrence

The mineral occurs in the carbonatite of the Jacupiranga mine (24°43′47″S, 48°06′37″W), Cajati County, São Paulo, Brazil (Menezes Filho and Martins, 1984). For general information about this carbonatite see Menezes Filho *et al.* (2015). This is also the type locality for zirkelite (Hussak and Prior, 1895), quintinite (Chao and Gault, 1997), menezesite (Atencio *et al.*, 2008) and pauloabibite (Menezes Filho *et al.*, 2015). Although the joint occurrence of menezesite, pauloabibite and melcherite has not been observed, these minerals may be related genetically. Pauloabibite is trigonal $NaNbO_3$, isostructural with ilmenite (Menezes Filho *et al.*, 2015). The synthetic analogue of pauloabibite was reported by Kinomura *et al.* (1984) and Kumata *et al.* (1990) from a two-step synthesis method, involving the preparation of $Na_8Nb_6O_{19}\cdot 13H_2O$ (a hexaniobate) followed by hydrothermal reaction with NaOH in a silver-lined vessel at 250°C. Menezesite is a heteropolyoxoniobate, cubic $(\square,Ba,K)_{12}(\square,Mg)_3Zr_4(BaNb_{12}O_{42})\cdot 12H_2O$ (Atencio *et al.*, 2008). According to Nyman *et al.* (2002), the heteropolyanions of W, Mo and V are formed simply by acidification of solutions of their oxoanions. Under similar conditions, these oxoanion precursors are not available for Nb, and Nb-oxo chemistry is dominated by formation of the Lindquist ion $[Nb_6O_{19}]^{8-}$ (present in melcherite). However, heteropolyniobate (present in menezesite) formation is favoured in hydrothermal reactions of aqueous, alkaline precursor mixtures. A competing phase to the formation of polyoxoniobates in hydrothermal aqueous reactions involving Nb and an alkali hydroxide is $NaNbO_3$, avoided by using short reaction times (i.e. 24 hours or less) (Nyman *et al.,* 2002). So melcherite could have originally formed under acid conditions, and afterwards, under basic conditions, menezesite and pauloabibite could have formed.

Quintinite, menezesite, pauloabibite and melcherite occur in the so-called ‘intermediate

zone', characterized by a high dolomite and slightly anomalous 'pyrochlore' content. Associated minerals are dolomite, calcite, magnetite, pyrrhotite, tochilinite, 'pyrochlore', pyrite and fluorapatite. Melcherite formed as a carbonatite vug mineral.

Habit and physical properties

Melcherite forms irregular, tabular crystals up to 200 µm in maximum dimension (Fig. 1). The mineral is transparent and displays a vitreous lustre; it is beige and the streak is white. It is non-fluorescent under both short (254 nm) and long wavelength (366 nm) ultraviolet radiation. The mineral displays perfect cleavage on {001}. Fracture was not determined. Twinning and parting were not observed. The Mohs hardness and density were not measured due to the paucity of material but the calculated density is 3.733 g/cm^3 [based on the empirical formula $(Ba_{0.99}K_{1.00})_{\Sigma 1.99}(Na_{1.02}Ca_{0.96})_{\Sigma 1.98}(Mg_{0.95}Mn_{0.05})_{\Sigma 1.00}Nb_{6.02}O_{19.00}\cdot 6H_2O$]. Refractive indices were not measured due to paucity of material. The mean refractive index is estimated as 1.924 using the Gladstone-Dale relationship (Mandarino, 1981).

Mineral chemistry

Melcherite crystals were embedded in epoxy resin and polished. In the back-scattered electron images, we can see that the crystals are zoned (Fig. 2). The chemical analyses (Table 1) were done by means of a Cameca SX100 electron microprobe (wavelength dispersive spectroscopy mode, 15 kV, 10 nA and 20 µm beam diameter). H_2O was inferred from the crystal structure determination. H_2O was initially assumed by difference prior to the matrix correction (PAP) and then calculated by stoichiometry post matrix correction due to software limitations. Analyses from the brighter areas of the melcherite crystal, (Fig. 2 back-scattered electron image) have the following composition: $(Ba_{1.75}K_{0.19})_{\Sigma 1.94}(Na_{1.80}Ca_{0.19})_{\Sigma 1.99}(Mg_{0.96}Mn_{0.02}Al_{0.02})_{\Sigma 1.00}Nb_{6.02}O_{19.00}\cdot 6H_2O$ (mean of four analytical points). Those from the darker areas correspond to $(Ba_{0.99}K_{1.00})_{\Sigma 1.99}(Na_{1.02}Ca_{0.96})_{\Sigma 1.98}(Mg_{0.95}Mn_{0.05})_{\Sigma 1.00}Nb_{6.02}O_{19.00}\cdot 6H_2O$ (mean of eight analytical points). The enrichment in Ba is coupled to the enrichment in Na and depletion of K and Ca. The analyses were obtained in points of several shades of grey observed in back-scattered electron

TABLE 1. Chemical composition of melcherite from the Cajati mine (in wt.%).

Constituent	1	Range	Standard deviation	2	Range	Standard deviation	Probe standard
K_2O	0.70	0.61–0.89	0.13	3.88	3.71–4.07	0.14	orthoclase
Na_2O	4.30	3.76–4.68	0.42	2.60	2.41–2.76	0.13	jadeite
BaO	20.66	20.29–20.92	0.27	12.44	12.13–12.91	0.29	barite
CaO	0.83	0.70–0.97	0.14	4.41	4.20–4.60	0.16	wollastonite
MgO	3.00	2.90–3.06	0.08	3.15	3.07–3.23	0.06	forsterite
MnO	0.09	0.06–0.13	0.03	0.28	0.22–0.38	0.06	pyrophanite
Al_2O_3	0.08	0.07–0.10	0.02	0.02	b.d.l.–0.08	0.03	corundum
Nb_2O_5	61.74	61.21–62.21	0.43	65.79	65.22–66.27	0.37	Nb
SiO_2	0.02	b.d.l.–0.06	0.03	0.00	b.d.l.–b.d.l.	0.00	wollastonite
H_2O	8.35			8.90			
Total	99.77			101.47			

1. $(Ba_{1.75}K_{0.19})_{\Sigma 1.94}(Na_{1.80}Ca_{0.19})_{\Sigma 1.99}(Mg_{0.96}Mn_{0.02}Al_{0.02})_{\Sigma 1.00}Nb_{6.02}O_{19.00}\cdot 6H_2O$ ($n = 4$)
2. $(Ba_{0.99}K_{1.00})_{\Sigma 1.99}(Na_{1.02}Ca_{0.96})_{\Sigma 1.98}(Mg_{0.95}Mn_{0.05})_{\Sigma 1.00}Nb_{6.02}O_{19.00}\cdot 6H_2O$ ($n = 8$)
b.d.l. = below detection limits.

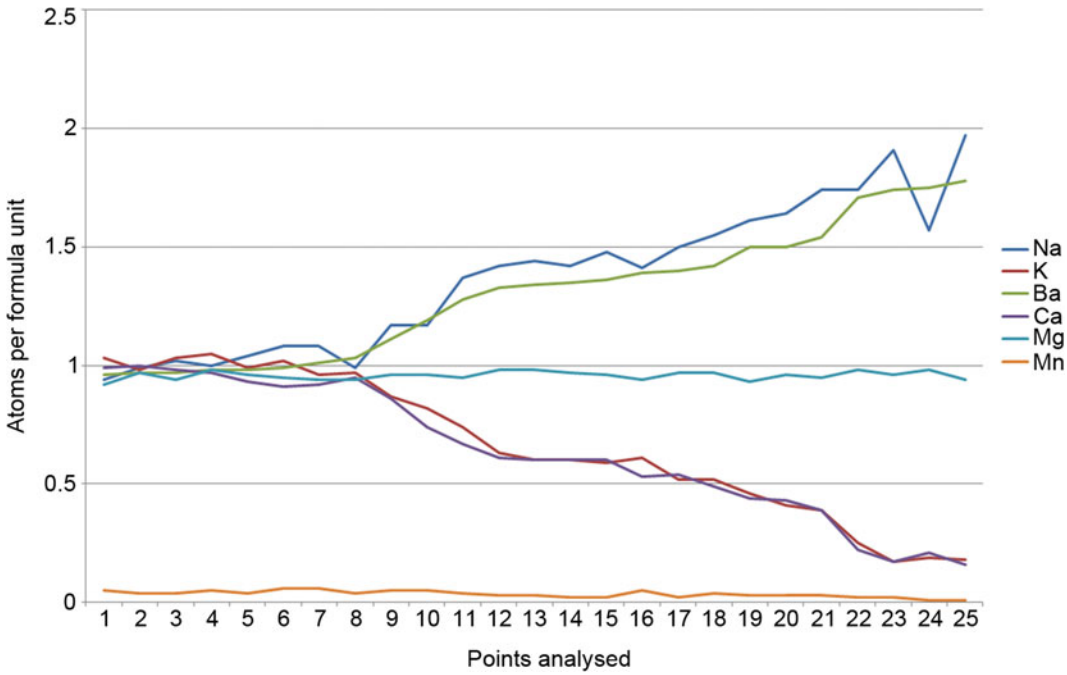

FIG. 3. Chemical variability in melcherite.

images distributed in different crystals. These analyses were ordered by ascending Ba atoms per formula unit, numbered from 1 to 25, and served as the basis for the construction of the graph in Fig. 3.

Chemical composition varies from $Ba_2Na_2Mg[Nb_6O_{19}]\cdot 6H_2O$ to $(BaK)(NaCa)Mg[Nb_6O_{19}]\cdot 6H_2O$. Coupled heterovalent substitutions at two sites are verified. As discussed by Hatert and Burke (2008), where a heterovalent substitution occurs at a given crystallographic site, the charge balance can also be maintained by coupling this substitution to another heterovalent substitution at a different site. At the *Ba* site, the atom Ba^{2+} is replaced progressively by K^+, and to maintain charge balance, the atom Na^+ is replaced progressively by Ca^{2+} at the *Na* site. The substitution mechanism is $Ba^{2+} + K^+ \leftrightarrow Na^+ + Ca^{2+}$. The boundary site occupancies between the two members of the series is $(BaK)(NaCa)Mg[Nb_6O_{19}]\cdot 6H_2O$. We could imagine a solid-solution series from $Ba_2Na_2Mg[Nb_6O_{19}]\cdot 6H_2O$ to $K_2Ca_2Mg[Nb_6O_{19}]\cdot 6H_2O$, with two mineral species, but the composition varies only from the first end-member to the intermediate member. As no analyses correspond to predominant K and Ca, only one mineral species is defined.

The formula $BaCa_2Mg[Nb_6O_{19}]\cdot 6H_2O$ (Andrade *et al.*, 2015) is incorrect because Na was not identified. The change in formula was previously approved executively by CNMNC IMA Newsletter No. 29 (Hålenius *et al.*, 2016): "Soon after the approval of the new mineral melcherite (IMA No. 2015-018; see CNMNC Newsletter 25), the authors of the proposal have communicated results of subsequent analytical work on this mineral, which verifies essential contents of sodium. The new data were examined carefully by the CNMNC officers and were found reliable. The revised simplified formula, $Ba_2Na_2Mg[Nb_6O_{19}]\cdot 6H_2O$, has been approved executively." A fragment of the darker part was extracted from the polished section for crystal structure determination.

Crystal structure determination

Powder X-ray diffraction data (XRD) were obtained using a Siemens D5000 diffractometer equipped with a Göbel mirror and a position-sensitive detector using Cu*K*α radiation and 40 kV and 40 mA at the Instituto de Geociências of the Universidade de São Paulo (Table 2). Unit-cell parameters refined from the powder data are as follows: trigonal, space group: $R\bar{3}$, $a = 9.022(2)$ Å, $c = 23.410(6)$ Å, $V = 1650.2(8)$ Å^3 and $Z = 3$.

TABLE 2. Powder X-ray diffraction data for melcherite.

d_{obs}.(Å)	I_{obs}.	d_{calc}.(Å)	I_{calc}.	h	k	l
11.337	6	11.705	0	0	0	2
7.805	**100**	7.803	46	0	0	3
7.410	**14**	7.411	100	1	0	1
6.505	7	6.499	34	0	1	2
5.906	6	5.852	0	0	0	4
		4.684	4	1	0	4
4.508	**10**	4.511	1	1	1	0
4.018	8	4.016	9	0	1	5
3.904	**22**	3.905	13	2	$\bar{1}$	3
		3.905	3	1	1	3
		3.902	16	0	0	6
3.852	**21**	3.853	33	0	2	1
3.250	**33**	3.249	37	0	2	4
3.074	9	3.075	9	1	0	7
		3.000	14	2	0	5
2.952	**13**	2.951	10	1	1	6
		2.951	1	2	$\bar{1}$	6
		2.930	4	2	1	1
		2.930	2	3	$\bar{1}$	1
2.861	8	2.863	35	$\bar{1}$	3	2
		2.863	4	1	2	2
2.740	8	2.740	13	0	1	8
2.637	8	2.637	27	2	1	4
		2.637	5	3	$\bar{1}$	4
		2.604	3	3	0	0
		2.601	1	0	0	9
		2.541	1	0	2	7
		2.498	4	$\bar{1}$	3	5
		2.471	4	3	0	3
		2.471	2	0	3	3
		2.342	4	2	0	8
		2.253	1	2	$\bar{1}$	9
2.243	6	2.243	7	1	0	10
		2.214	19	2	1	7
		2.167	3	2	2	3
2.165	**30**	2.166	32	3	0	6
		2.166	1	0	3	6
2.160	**12**	2.158	1	1	3	1
		2.158	1	$\bar{1}$	4	1
		2.131	1	4	$\bar{1}$	2
2.078	4	2.079	1	1	2	8
2.053	5	2.053	0	1	0	11
		2.053	0	0	1	11
2.034	4	2.032	2	$\bar{1}$	4	4
		2.008	3	0	2	10
		1.967	5	3	1	5
		1.953	5	2	2	6
		1.869	1	2	0	11
		1.840	2	3	0	9
		1.840	1	0	3	9
1.836	4	1.835	1	3	$\bar{1}$	10
		1.819	3	1	3	7
		1.791	2	2	$\bar{1}$	12

(continued)

TABLE 2. (*contd.*)

d_{obs}.(Å)	I_{obs}.	d_{calc}.(Å)	I_{calc}.	h	k	l
		1.787	5	5	$\bar{2}$	1
		1.772	4	2	3	2
		1.742	6	3	1	8
		1.742	3	4	$\bar{1}$	8
		1.727	8	$\bar{1}$	3	11
1.703	5	1.705	11	1	4	0
		1.674	1	2	3	5
		1.666	4	4	1	3
		1.666	1	5	$\bar{1}$	3
		1.666	1	1	4	3
		1.666	1	$\bar{1}$	5	3
1.629	4	1.635	1	0	2	13
		1.590	2	1	3	10
		1.590	2	$\bar{1}$	4	10
		1.580	4	5	$\bar{2}$	7
		1.580	1	3	2	7
1.562	5	1.562	3	$\bar{1}$	5	6
		1.562	1	1	4	6
		1.562	1	5	$\bar{1}$	6
		1.561	8	0	3	12
		1.561	2	3	0	12
		1.561	1	0	0	15
		1.549	1	5	0	2

The strongest reflections are given in bold.

TABLE 3. Structure refinement results for melcherite.

Ideal chemical formula	$Ba_2Na_2Mg[Nb_6O_{19}].6H_2O$
Crystal size (mm)	0.07 × 0.05 × 0.05
Space group	$R\bar{3}$
a (Å)	9.0117(6)
c (Å)	23.3986(16)
V (Å^3)	1645.64(19)
Z	3
ρ_{cal} (g/cm^3)	3.748
λ (Å)	0.71073
μ (mm^{-1})	5.46
2θ max. for data collection(°)	≤66.38
No. of reflections collected	5316
No. of independent reflections	1403
No. of reflections with $I > 2\sigma(I)$	1319
No. of parameters refined	65
R_{int}	0.022
Final R factors [$I > 2\sigma(I)$]	$R_1 = 0.017$, $wR_2 = 0.042$
Final R factors (all data)	$R_1 = 0.019$, $wR_2 = 0.041$
Goodness-of-fit	1.13
Largest diff. peak and hole	1.30 and –1.59 e Å^{-3}

Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0146P)^2 + 5.6144P]$, where $P = [\max(0,F_o)^2 + (2F_c)^2]/3$.

TABLE 4. Final fractional coordinates and displacement parameters of atoms in melcherite.

Atom	x	y	z	Occupancy	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ba	2/3	1/3	0.172426(14)	0.5325(19)	0.01366(10)	0.01099(12)	0.01099(12)	0.01899(16)	0.000	0.000	0.00550(6)
K	2/3	1/3	0.172426(14)	0.4674(19)	0.01366(10)	0.01099(12)	0.01099(12)	0.01899(16)	0.000	0.000	0.00550(6)
Nb	0.50011(2)	0.58932(2)	0.109104(6)		0.00677(6)	0.00634(8)	0.00681(9)	0.00773(8)	−0.00028 (5)	0.00039 (5)	0.00372(6)
Ca	2/3	1/3	0.01125(4)	0.457(10)	0.0101(3)	0.0114(4)	0.0114(4)	0.0074(5)	0.000	0.000	0.0057(2)
Na	2/3	1/3	0.01125(4)	0.543(10)	0.0101(3)	0.0114(4)	0.0114(4)	0.0074(5)	0.000	0.000	0.0057(2)
Mg	2/3	1/3	1/3		0.0111(3)	0.0093(5)	0.0093(5)	0.0148(7)	0.000	0.000	0.0046(2)
O1	0.52940(18)	0.80056(17)	0.06922(6)		0.0092(2)	0.0085(6)	0.0081(6)	0.0110(6)	0.0017(4)	0.0016 (4)	0.0042(5)
O2	0.62705(19)	0.52389(19)	0.06912(6)		0.0140(3)	0.0114(6)	0.0130(7)	0.0182(7)	−0.0022(5)	0.0030 (5)	0.0066(6)
O3	0.66867(17)	0.74208(18)	0.16615(5)		0.0099(2)	0.0072(6)	0.0121(6)	0.0103(5)	−0.0021(5)	−0.0006 (4)	0.0047(5)
O4	1/3	2/3	0.1667		0.0081(6)	0.0077(9)	0.0077(9)	0.0090(13)	0.000	0.000	0.0039(4)
OW5	0.2005(2)	0.1518(2)	0.05373(8)		0.0184(3)	0.0121(7)	0.0107(7)	0.0327(9)	−0.0050(6)	−0.0064(6)	0.0060(6)
H51	0.229(4)	0.255(2)	0.0579(13)		0.030						
H52	0.286(3)	0.142(4)	0.0566(13)		0.030						

TABLE 5. Selected bond lengths and bond valences of the refined melcherite structure.

Bond	Bond length	BV (vu)*	Σ
(Ba,K)–O3	2.7189(14)	0.261(x2)	0.522
(Ba,K)–O3	2.7190(14)	0.261	0.261
(Ba,K)–OW5	2.9923(18)	0.125(x3)	0.375
(Ba,K)–O2	3.0875(15)	0.096(x3)	0.288
		Sum	1.446
Nb–O1	2.0154(13)	0.754	0.754
Nb–O1	2.0161(13)	0.753	0.753
Nb–O2	1.7906(14)	1.385	1.385
Nb–O3	1.9691(13)	0.855	0.855
Nb–O3	1.9731(13)	0.845	0.845
Nb–O4	2.3678(2)	0.291	0.291
		Sum	4.883
(Na,Ca)–O2	2.3501(15)	0.286(x3)	0.858
(Na,Ca)–O1	2.4476(15)	0.2203(x3)	0.660
		Sum	1.518
Mg–OW5	2.0602(16)	0.371	0.371
Mg–OW5	2.0603(16)	0.371(x5)	1.484
		Sum	2.226
O1–Nb	2.0154(16)	0.754	0.754
O1–Nb	2.0161(16)	0.753	0.753
O1–(Na,Ca)	2.4476(15)	0.220	0.220
		Sum	1.727
O2–Nb	1.7906(14)	1.385	1.385
O2–(Na,Ca)	2.3501(15)	0.286	0.286
O2–(Ba,K)	3.0875(15)	0.080	0.096
		Sum	1.767
O3–Nb	1.9691(13)	0.855	0.855
O3–Nb	1.9731(13)	0.845	0.845
O3–(Ba,K)	2.7189(14)	0.261	0.261
		Sum	1.961
O4–Nb	2.3678(2)	0.291(x6)	1.746
OW5–Mg	2.0603(16)	0.371	0.371
OW5–(Ba,K)	2.9923(18)	0.125	0.125
		Sum	0.496

*Bond valence in valence units.

A single-crystal X-ray study was carried-out using a Bruker APEX II CCD diffractometer with graphite-monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation and gave the following data: trigonal, space group: $R\bar{3}$, $a = 9.0117(6)$ Å, $c = 23.3986(16)$ Å, $V = 1645.64(19)$ Å^3 and $Z = 3$. The X-ray absorption correction was applied to intensity data using the program *SADABS* from Bruker.

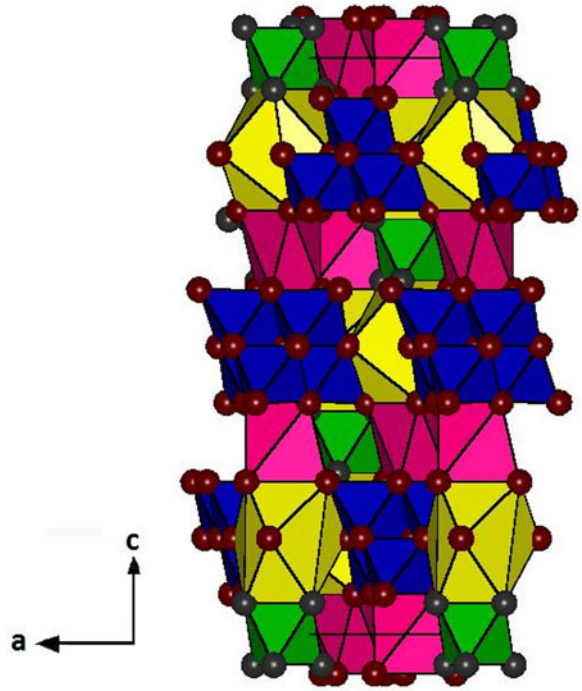

FIG. 4. Crystal structure of melcherite. (Ba,K) = yellow; (Na,Ca) = pink; Mg = green; Nb = blue; O = red and OW = grey.

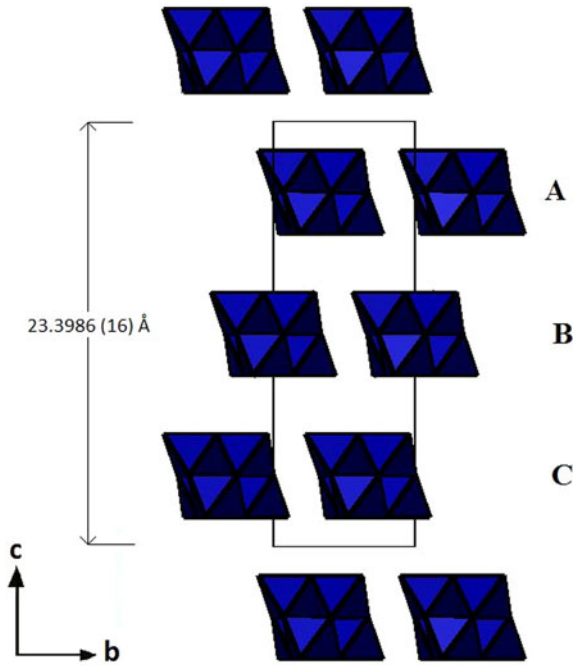

FIG. 5. Lindquist polyanions $[Nb_6O_{19}]^{8-}$ stacking sequence in the crystal structure of melcherite.

TABLE 6. Selected interatomic bond lengths (Å) and octahedral distortion indices for melcherite ($Ba_2Na_2MgNb_6O_{19}\cdot 6H_2O$), peterandresenite ($Mn_4Nb_6O_{19}\cdot 14H_2O$) and hansesmarkite ($Ca_2Mn_2Nb_6O_{19}\cdot 20H_2O$).

Melcherite (This work)		Peterandresenite (Friis *et al.*, 2014)		Hansesmarkite (Friis *et al.*, 2017)	
Nb–O1	2.0154(13)	Nb1–O1	2.3982(1)	Nb1–O1	2.3990(6)
Nb–O1	2.0161(13)	Nb1–O2	1.7685(8)	Nb1–O2	1.780(1)
Nb–O2	1.7906(14)	Nb1–O3	1.9767(8)	Nb1–O3	1.962(1)
Nb–O3	1.9691(13)	Nb1–O4	1.9799(6)	Nb1–O4	1.973(1)
⟨Nb–O⟩	1.9731(13)	Nb1–O5	2.0080(6)	Nb1–O5	2.020(1)
Nb–O4	2.3678(2)	Nb1–O6	2.0290(8)	Nb1–O6	2.034(1)
⟨Nb–O⟩	2.022	⟨Nb1–O⟩	2.027	⟨Nb1–O⟩	2.028
OV*	10.513	OV	10.506	OV	10.723
OAV	113.650	OAV	132.281	OAV	119.622
OQE	1.040	OQE	1.046	OQE	1.042
Mg–OW5	2.0602(16)	Nb2–O1	2.3679(1)	Nb2–O1	2.3576(6)
Mg–OW5	2.0603(16)	Nb2–O3	1.9716(8)	Nb2–O4	1.977(1)
⟨Mg–OW⟩	2.060	Nb2–O3	1.9716(8)	Nb2–O5	2.029(1)
OV	11.603	Nb2–O6	2.0208(8)	Nb2–O7	1.766(1)
OAV	12.285	Nb2–O6	2.0208(8)	Nb2–O8	1.982(1)
OQE	1.003	Nb2–O7	1.777(1)	Nb2–O9	2.019(1)
		⟨Nb2–O⟩	2.021	⟨Nb2–O⟩	2.021
(Na,Ca)–O2	2.3501(15)	OV	10.522	OV	10.714
(Na,Ca)–O1	2.4476(15)	OAV	110.055	OAV	108.276
OV	15.689	OQE	1.039	OQE	1.039
OAV	354.100				
OQE	1.113	Mn1–O2	2.0645	Nb3–O1	2.3764(6)
		Mn1–O2	2.0645	Nb3–O3	1.956(1)
		Mn1–O5	2.220	Nb3–O6	2.033(1)
		Mn1–O6	2.3250	Nb3–O8	1.979(1)
		Mn1–O6	2.3250	Nb3–O9	2.010(1)
		Mn1–O8	2.253(2)	Nb3–10	1.785(1)
		⟨Mn1–O⟩	2.208	⟨Nb3–O⟩	2.023
		OV	13.518	OV	10.691
		OAV	146.530	OAV	121.348
		OQE	1.044	OQE	1.044
		Mn2–O7	2.088(1)	Mn–O5	2.230(1)
		Mn2–O9	2.106(2)	Mn–O6	2.208(1)
		Mn2–O10	2.237(1)	Mn–O7	2.050(1)
		Mn2– O10	2.237(1)	Mn–O9	2.254(1)
		Mn2–O11	2.240(1)	Mn–O11	2.149(2)
		Mn2–O11	2.240(1)	Mn–O12	2.180(2)
		⟨Mn2–O⟩	2.191	⟨Mn–O⟩	2.178
		OV	13.992	OV	13.417
		OAV	4.489	OAV	104.704
		OQE	1.003	OQE	1.030

*OV = octahedral volume (Å3), OAV = octahedral angle variance (^{o2}), and OQE = octahedral quadratic elongation (Robinson *et al*. 1971).

The *SHELXL-97* package (Sheldrick, 2008) was used for the direct methods structure solution and its subsequent refinement. The *Ba* and *Na* sites were refined assuming full but joint occupation by Ba/K and Na/Ca respectively, which yielded occupancy values close to those indicated by the empirical formula based on the electron microprobe analysis. A final difference-Fourier synthesis

TABLE 7. Comparative data for melcherite and synthetic compounds (all trigonal, $R\bar{3}$).

	Chemical formula	Unit-cell parameters (Å)	
Melcherite*	$Ba_2Na_2Mg[Nb_6O_{19}].6H_2O$	$a = 9.0117(6)$	$c = 23.3986(16)$
Synthetic†	$Cs_6Na_2(Nb_6O_{19})\cdot 18H_2O$	$a = 12.609(2)$	$c = 22.745(5)$
Synthetic†	$Rb_6(H_2Nb_6O_{19})\cdot 19H_2O$	$a = 12.271(2)$	$c = 20.686(3)$

*This work.
†Nyman *et al.* (2006).

TABLE 8. Comparison of melcherite with other naturally-occurring hexaniobates.

Name Formula	melcherite $Ba_2Na_2MgNb_6O_{19}\cdot 6H_2O$	peterandresenite[1] $Mn_4Nb_6O_{19}\cdot 14H_2O$	hansesmarkite[2] $Ca_2Mn_2Nb_6O_{19}\cdot 20H_2O$
Space group	$R\bar{3}$	$C2/m$	$P\bar{1}$
a (Å)	9.0117(6)	15.3444(3)	9.081(4)
b (Å)	9.0117(6)	9.4158(2)	9.982(8)
c (Å)	23.3986(16)	11.2858(4)	10.60(1)
α (°)	90	90	111.07(8)
ß (°)	90	118.632(1)	101.15(6)
γ (°)	120	90	99.39(5)
Z	3	2	1
V (Å^3)	1645.64(19)	1431.18(7)	851.5(13)
Strongest PXRD lines $d(I)$	7.805 (100); 3.250 (33); 2.165 (30)	2.9260 (100); 9.8977 (82); 7.1026 (63)	8.610 (100); 9.282 (36); 3.257 (30)
Optics	Uniaxial (?)	Biaxial (–)	Biaxial (+)

1: Friis *et al.* (2014); 2: Friis *et al.* (2017)

allowed the H atom positions of the water molecule to be located, which were then refined with soft restraints of 0.86 Å on the O–H distances and 1.40 Å on the H–H distance, and with U_{iso} values fixed at ~1.5 times that of the O atom. Refinement of this final model converged to an R_1 of 0.017 and the crystal chemical formula obtained is $(Ba_{1.06}K_{0.94})(Na_{1.09}Ca_{0.91})Nb_6Mg[O_{18.98}(OH)_{0.02}]_{\Sigma 19.00}\cdot 6H_2O$, where a small fraction of the oxygen atoms in the hexaniobate polyanion is assumed to be replaced by OH groups in order to balance the slight positive charge deficiency associated with the Ba/K and Na/Ca sites. Details of the data collection and structure refinement are given in Tables 3 and 4. Selected bond distances and associated bond-valence sum calculations, using the parameters of Brese and O'Keefe (1991), are given in Table 5.

Melcherite is a hexaniobate that has structural layers parallel to the *xy* plane that stack along the *c* axis with simultaneous 1/3 [1 $\bar{1}$ 0] displacement so as to produce an *R* lattice. The melcherite structure (Figs 4 and 5) is built by layers of $[(Ba,K)(O,H_2O)_9]$ polyhedra and the $[Nb_6O_{19}]^{8-}$ super-octahedron (Lindqvist anion) interconnected by $[(Na,Ca)O_6]$ polyhedra. There is a significant distortion present in the Nb–O octahedron forming the hexaniobate polyanion, as measured by the octahedral angle variance (OAV), = 113.650°^{2}, and quadratic elongation (OQE), = 1.040 indices (Robinson *et al.*, 1971). The results are comparable to the NbO_6 octahedra present in the crystal structure of peterandresenite and hansesmarkite (Table 6). Ba/K is coordinated by six oxygens and three water molecules. Na/Ca is coordinated by six oxygen atoms in a distorted octahedron and the OAV and OQE values are 354.100°^{2} and 1.113, respectively. Mg^{2+} cations are bonded to six water molecules each and are not associated with Lindqvist oxygen ions. The comparison with MnO_6 in peterandresenite and hansesmarkite shows that the octahedral coordination of the Mg cation is relatively undistorted, as indicated by the values of OAV = 12.285°^{2} and OQE = 1.003 (Table 6).

The mineral is similar structurally to the synthetic compounds $Cs_6Na_2(Nb_6O_{19})\cdot 18H_2O$

and $Rb_6(H_2Nb_6O_{19}).19H_2O$, studied by Nyman *et al.* (2006) (Table 7). They have the same space group as melcherite, $R\bar{3}$. The unit-cell dimensions and arrangement of the Lindqvist ion $[Nb_6O_{19}]^{8-}$ are very similar. The crystallographic parameters of melcherite are compared with those of the other hexaniobate minerals in Table 8.

Acknowledgements

We acknowledge the Sao Paulo Research Foundation for financial support (Grants: 2011/22407-0 and 2013/03487-8); the Principal Editor: Peter Williams, reviewers Robert T. Downs, Hexiong Yang (University of Arizona) and Peter Leverett, and the members of the Commission on New Minerals and Mineral Names of the International Mineralogical Association (CNMNC-IMA) for their helpful suggestions and comments.

References

Abramov, P.A., Vicent, C., Kompankov, N.B., Gushchin, A. L. and Sokolov, M.N. (2016) Coordination of $\{C_5Me_5Ir\}^{2+}$ to $[M_6O_{19}]^{8-}$ (M = Nb, Ta) – Analogies and differences between Rh and Ir, Nb and Ta. *European Journal of Inorganic Chemistry*, **1**, 154–160.

Andrade, M.B., Atencio, D. and Menezes Filho, L.A.D. (2015) Melcherite, IMA 2015-018. CNMNC Newsletter No. 25, June 2015, page 547; *Mineralogical Magazine*, **79**, 541–547.

Atencio, D., Coutinho, J.M.V., Doriguetto, A.C., Mascarenhas, Y.P., Ellena, J.A. and Ferrari, V.C. (2008) Menezesite, the first natural heteropolyniobate, from Cajati, São Paulo, Brazil: Description and crystal structure. *American Mineralogist*, **93**, 81–87.

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica Section B: Structural Science*, **47**(2), 192–197.

Chao, G.Y. and Gault, R.A. (1997) Quintinite-2*H*, quintinite-3*T*, charmarite-2*H*, charmarite-3*T* and caresite-3*T*, a new group of carbonate minerals related to the hydrotalcite-manasseite group. *Canadian Mineralogist*, **35**, 1541–1549.

Friis, H., Larsen, A.O., Kampf, A.R., Evans, R.J., Selbekk, R.S., Sánchez, A.A. and Kihle, J. (2014) Peterandresenite, $Mn_4Nb_6O_{19}\cdot 14H_2O$, a new mineral containing the Lindqvist ion from a syenite pegmatite of the Larvik Plutonic Complex, southern Norway. *European Journal of Mineralogy*, **26**, 567–576.

Friis, H., Weller, M.T. and Kampf, A.R. (2017) Hansesmarkite, $Ca_2Mn_2Nb_6O_{19}\cdot 20H_2O$, a new hexaniobate from a syenite pegmatite in the Larvik Plutonic Complex, southern Norway. *Mineralogical Magazine*, **81**, 543–554.

Hålenius, U., Hatert, F., Pasero, M. and Mills, S.J. (2016) New minerals and nomenclature modifications approved in 2015 and 2016. CNMNC Newsletter 29. *Mineralogical Magazine*, **80**, 199–205,.

Hatert, F. and Burke, E.A.J. (2008) The IMA-CNMNC dominant-constituent rule revisited and extended. *Canadian Mineralogist*, **46**, 717–728.

Hussak, E. and Prior, G.T. (1895) Lewisite and zirkelite, two new Brazilian minerals. *Mineralogical Magazine*, **11**, 80–88.

Kinnan, M.K., Creasy, W.R., Fullmer, L.B., Schreuder-Gibson, H.L. and Nyman, M. (2014) Nerve agent degradation with polyoxoniobates. *European Journal of Inorganic Chemistry*, **2014**(14), 2361–2367.

Kinomura, N., Kumata, N. and Muto, F. (1984) A new allotropic form with ilmenite-type structure of $NaNbO_3$. *Materials Research Bulletin*, **19**, 299–304.

Kumata, N., Kinomura, N. and Muto, F. (1990) Crystal structure of ilmenite-type $LiNbO_3$ and $NaNbO_3$. *Journal of the Ceramic Society of Japan*, **98**, 384–388.

Lindqvist, I. (1953) The structure of the hexaniobate ion in $7Na_2O\cdot 6Nb_2O_5\cdot 32H_2O$. *Arkiv for Kemi*, **5**(3), 247–250.

Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist*, **19**, 441–450.

Melcher, G.C. (1966) The carbonatites of Jacupiranga, São Paulo, Brazil. Pp. 169–181 in: *Carbonatites* (O.F. Tuttle and J. Gittins, editors). John Wiley and Sons, New York.

Menezes Filho, L.A.D. and Martins, J.M. (1984) The Jacupiranga mine, São Paulo, Brazil. *Mineralogical Record*, **15**, 261–270.

Menezes Filho, L.A.D., Atencio, D., Andrade, M.B., Downs, R.T., Chaves, M.L.S.C., Romano, A.W., Scholz, R. and Persiano, A.I.C. (2015) Pauloabibite, trigonal $NaNbO_3$, isostructural with ilmenite, from the Jacupiranga carbonatite, Cajati, São Paulo, Brazil. *American Mineralogist*, **100**, 442–446.

Nyman, M. (2011) Polyoxoniobate chemistry in the 21st century. *Dalton Transactions*, **40**(32), 8049–8058.

Nyman, M., Bonhomme, F., Alam, T.M., Rodriguez, M. A., Cherry, B.R., Krumhansl, J.L., Nenoff, T.M., and Sattler, A.M. (2002) A general synthetic procedure for heteropolyniobates. *Science*, **297**, 996–998.

Nyman, M., Alam, T.M., Bonhomme, F., Rodriguez, M. A., Frazer, C.S. and Welk, M.E. (2006) Solid-State structures and solution behaviour of alkali salts of the $[Nb_6O_{19}]^{8-}$ Lindqvist Ion. *Journal of Cluster Science*, **17**, 197–219.

Robinson, K., Gibbs, G.V. and Ribbe, P.H. (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science*, **172**, 567–570.

Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.

Wang, J.P., Niu, H.Y. and Niu, J.Y. (2008) A novel Lindqvist type polyoxoniobate coordinated to four copper complex moieties: $\{Nb_6O_{19}[Cu(2,2'\text{-bipy})]_2[Cu(2,2'\text{-bipy})_2]_2\}\cdot 19H_2O$. *Inorganic Chemistry Communications*, **11**(1), 63–65.