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

Preproof article

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ABSTRACT

Melcherite, ideally $Ba_2Na_2Mg[Nb_6O_{19}].6H_2O$, 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, 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 -1 0] displacement so as to produce a *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. Mg^{2+} cations 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. Both the description and the name were approved by the CNMNC-IMA (Nomenclature Proposal 2015-018). Melcherite is the second natural hexaniobate. The first one is peterandresenite and the third is hansesmarkite.

KEYWORDS: Melcherite, new mineral, hexaniobate, crystal structure, chemical composition, Jacupiranga mine, Cajati, Brazil.

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Introduction

Melcherite is the second natural hexaniobate. The first one is peterandresenite (Friis *et al*., 2014) and the third is hansesmarkite (Friis *et al*., 2016). 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). 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 hexametalates 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 CNMNC-IMA (Nomenclature Proposal 2015-018). 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 (http://rruff.info/R130752).

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 please 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 genetically related. Pauloabibite is trigonal $NaNbO_3$, isostructural with ilmenite (Menezes Filho *et al.,* 2015). The synthetic analog of pauloabibite was reported by

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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, $(\square,Ba,K)_{12}(\square,Mg)_3Zr_4(BaNb_{12}O_{42}).12H_2O$, cubic (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 favored 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 be originally formed, under acid conditions, and posteriorly, under basic conditions, menezesite and pauloabibite 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.

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Mineral chemistry

Melcherite crystals were embedded in epoxy resin and polished. In the backscattered 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 (WDS mode, 15 kV, 10 nA, 20 μm beam diameter). H_2O was inferred from the crystal structure determination of melcherite. 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 backscattered 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 4 point analyses). 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 8 point analyses). 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 gray observed in backscattered electron images distributed in different crystals. These analyses were ordered in ascending Ba apfu numbers, numbered from 1 to 25, and served as the basis for the construction of the graph of Figure 3.

Chemical composition varies from $Ba_2Na_2Mg[Nb_6O_{19}].6H_2O$ to $(BaK)(NaCa)Mg[Nb_6O_{19}].6H_2O$. 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 progressively replaced by K^+, and to maintain charge balance, the atom Na^+ is progressively replaced 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 $(BaK)(NaCa)Mg[Nb_6O_{19}].6H_2O$. We could imagine a solid solution series from $Ba_2Na_2Mg[Nb_6O_{19}].6H_2O$ to $K_2Ca_2Mg[Nb_6O_{19}].6H_2O$, 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 $BaCa_2Mg[Nb_6O_{19}].6H_2O$ (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

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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 , Z = 3.

A single-crystal X-ray study was carried-out using a Bruker APEX II CCD diffractometer with graphite-monochromated Mo*K*α (λ = 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, $c : a$ = 2.5965, V = 1645.64(19) Å^3, Z = 3. The X-ray absorption correction was applied to intensity data using the program SADABS from Bruker.

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 EMP analysis. A final difference Fourier synthesis 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 R1 of 0.017 and the crystal chemical formula obtained is $(Ba_{1.06}K_{0.94})(Na_{1.09}Ca_{0.91})Nb_6Mg[O_{18.98}(OH)_{0.02}]_{\Sigma 19.00}$, 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.$6H_2O$. Details of the data collection and structure refinement are given in Tables 3 and 4. Selected

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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 -1 0] displacement so as to produce a *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, 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. The Na/Ca is coordinated by six oxygen atoms in a distorted octahedron and the OAV and OQE values are 354.100 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 indice values of OAV, 12.285, and OQE, 1.003 (Table 6).

The mineral is structurally similar to the synthetic compounds $Cs_6Na_2(Nb_6O_{19}).18H_2O$ and $Rb_6(H_2Nb_6O_{19}).19H_2O$, studied by Nyman *et al.* (2006) (Table 7). They have the same space group of melcherite, *R*-3. The unit cell dimensions and arrangement of 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.

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

283 TABLE 2**.** X-ray powder diffraction data for melcherite.

284 TABLE 3**.** Structure refinement results for melcherite.

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

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

287 TABLE 6. Selected interatomic bond lengths (Å) and octahedral distortion indices for

288 melcherite ($Ba_2Na_2MgNb_6O_{19}$•$6H_2O$), peterandresenite ($Mn_4Nb_6O_{19}$•$14H_2O$) and

289 hansesmarkite ($Ca_2Mn_2Nb_6O_{19}$•$20H_2O$).

290 TABLE 7. Comparative data for melcherite and synthetic compounds (all trigonal, *R*-3).

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

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

FIG. 2. Backscattered electron image of melcherite.

FIG. 3. Chemical variability in melcherite.

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.

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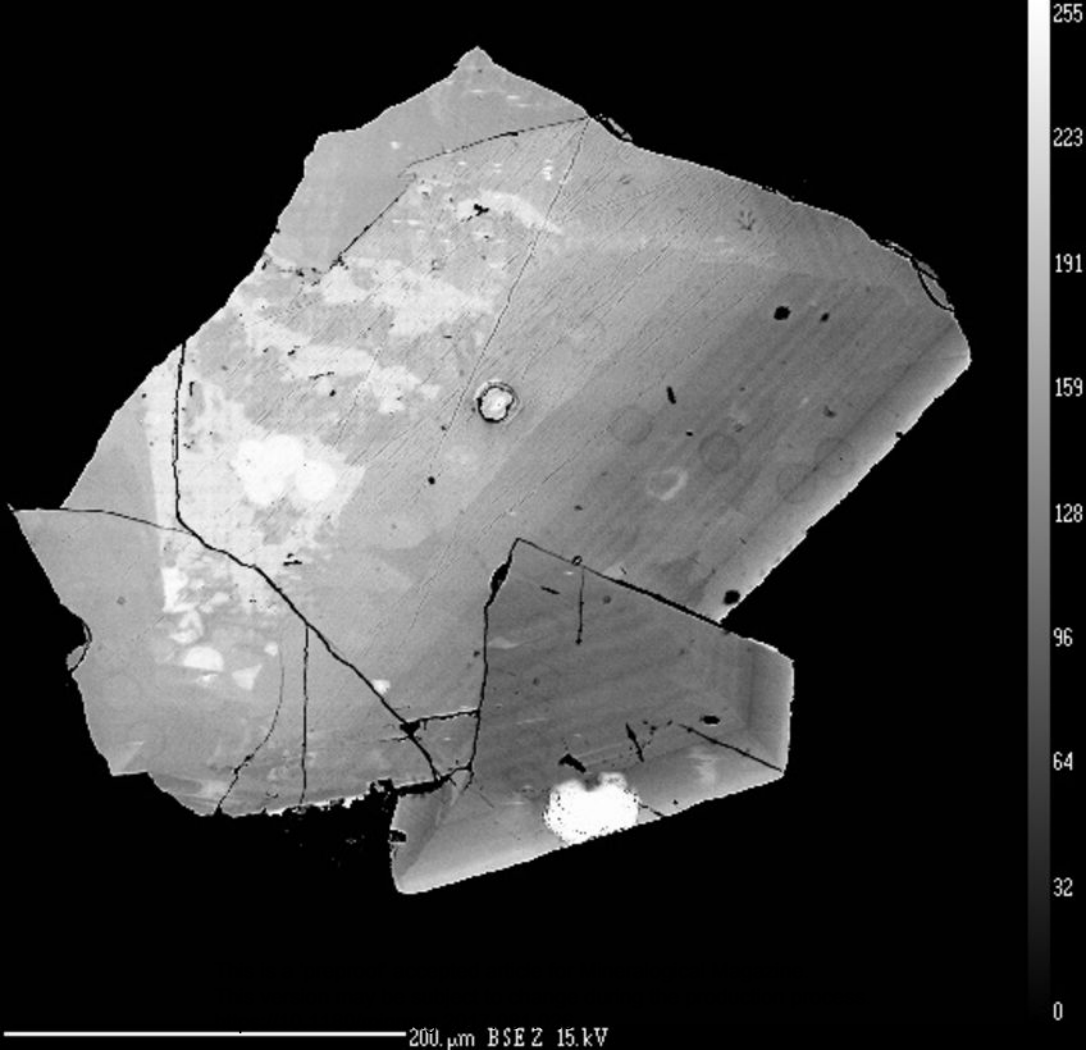
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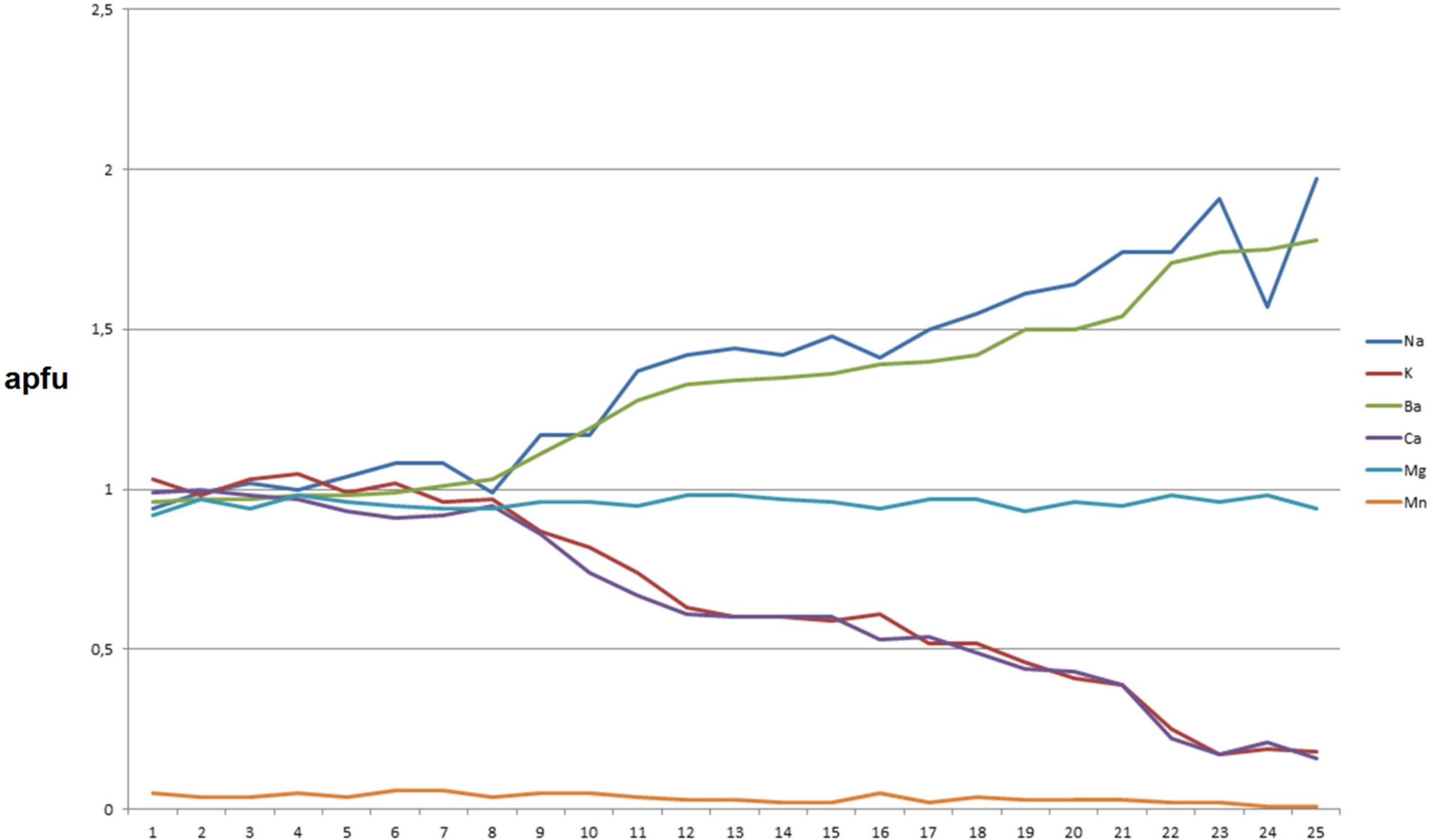

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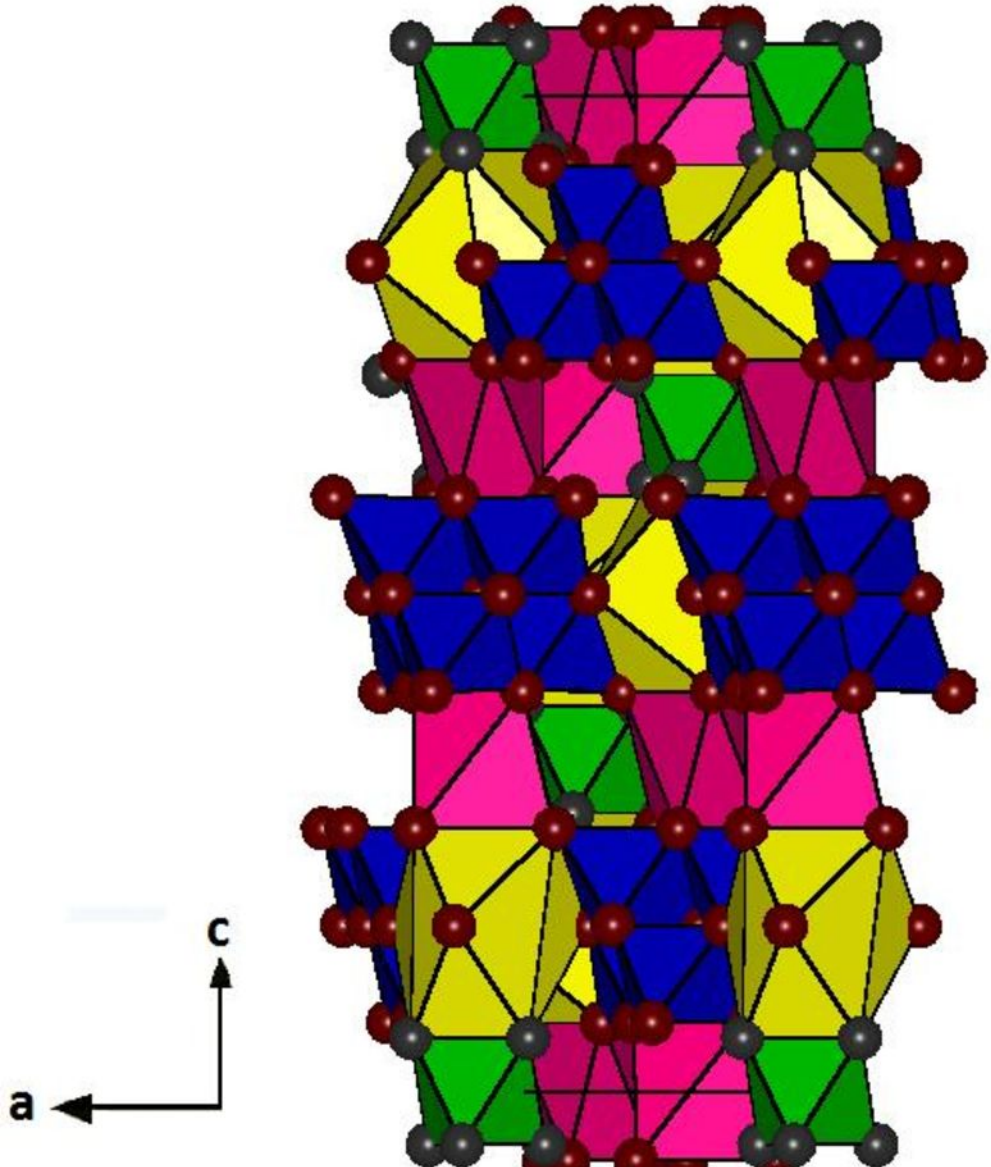

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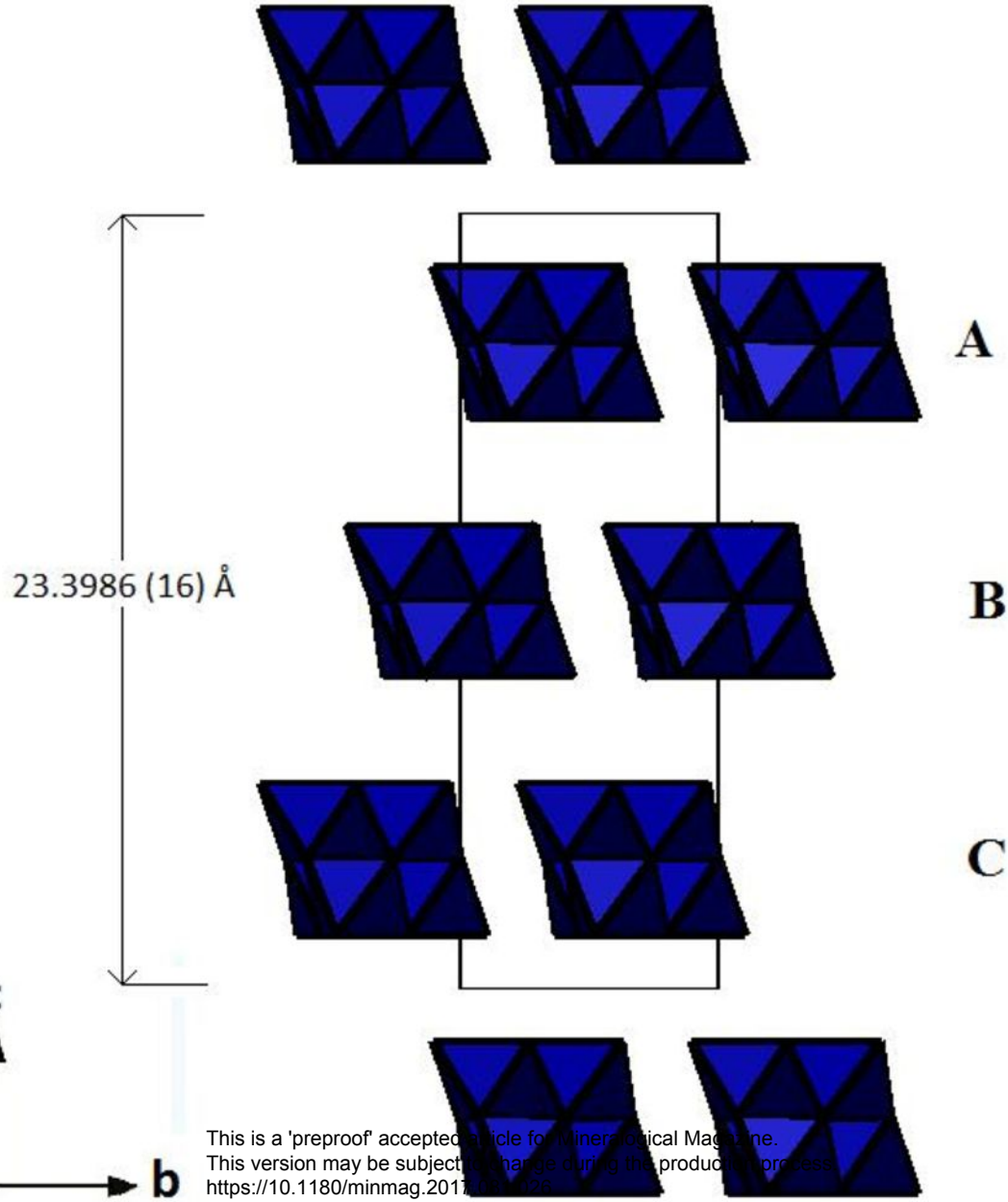

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TABLE 1. Chemical composition of melcherite from the Cajati mine (in wt%).

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 jadeite
Na_2O	4.30	3.76-4.68	0.42	2.60	2.41-2.76	0.13	barite
BaO	20.66	20.29-20.92	0.27	12.44	12.13-12.91	0.29	wollastonite
CaO	0.83	0.70-0.97	0.14	4.41	4.20-4.60	0.16	forsterite
MgO	3.00	2.90-3.06	0.08	3.15	3.07-3.23	0.06	pyrophanite
MnO	0.09	0.06-0.13	0.03	0.28	0.22-0.38	0.06	corundum
Al_2O_3	0.08	0.07-0.10	0.02	0.02	b.d.-0.08	0.03	
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**			

Note: b.d.l. = below detection limits.

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)

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TABLE 2**.** X-ray powder diffraction data for melcherite.

$d_{obs.}$(Å)	$d_{calc.}$(Å)	$I_{obs.}$	*h*	*k*	*l*
11.337	11.705	6	0	0	2
7.805	**7.813**	**100**	**0**	**1**	**0**
	7.803		0	0	3
7.410	**7.411**	**14**	**0**	**1**	**1**
6.505	6.499	7	0	1	2
5.906	5.853	6	0	0	4
4.508	**4.511**	**10**	**1**	**1**	**0**
4.018	4.016	8	0	1	5
3.904	**3.907**	**22**	**0**	**2**	**0**
	3.905		1	1	3
3.852	**3.853**	**21**	**0**	**2**	**1**
3.250	**3.249**	**33**	**0**	**2**	**4**
	3.249		1	1	5
3.074	**3.074**	**9**	**0**	**1**	**7**
2.952	**2.953**	**13**	**1**	**2**	**0**
	2.951		1	1	6
2.861	2.863	8	1	2	2
2.740	2.740	8	0	1	8
2.637	2.637	8	1	2	4
2.243	2.245	6	2	2	1
	2.243		0	1	10
2.165	**2.166**	**30**	**0**	**3**	**6**
	2.165		0	2	9
2.160	**2.158**	**12**	**1**	**3**	**1**
2.078	2.079	4	1	2	8
	2.078		1	1	10

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2.053	2.055	5	0	3	7
	2.053		0	1	11
2.034	2.032	4	1	3	4
	2.032		2	2	5
1.836	1.835	4	1	2	10
1.703	1.704	5	2	2	9
1.629	1.629	4	2	3	6
1.562	1.562	5	1	4	6
	1.562		0	4	9

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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 mm
Space group	*R*-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 $P = [\max(0,F_o)^2 + (2F_c)^2]/3$.

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

Atom	*x*	*y*	*z*	Occ.	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	0.6667	0.3333	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	0.6667	0.3333	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	0.6667	0.3333	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	0.6667	0.3333	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	0.6667	0.3333	0.3333		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	0.3333	0.6667	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						

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

Bond	**Bond length**	**BV(v.u)**	**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
			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
			4.883
(Na,Ca)-O2	2.3501(15)	0.286(x3)	0.858
(Na,Ca)-O1	2.4476(15)	0.2203(x3)	0.660
			1.518
Mg-OW5	2.0602(16)	0.371	0.371
Mg-OW5	2.0603(16)	0.371(x5)	1.484
			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
			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
			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
			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
			0.496

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

	melcherite		peterandresenite[1]		hansesmarkite[2]
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-O3	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)
Mean	2.022	Mean	2.027	Mean	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)
Mean	2.060	Nb2-O3	1.9716(8)	Nb2-O5	2.029(1)
		Nb2-O6	2.0208(8)	Nb2-O7	1.766(1)
OV	11.603	Nb2-O6	2.0208(8)	Nb2-O8	1.982(1)
OAV	12.285	Nb2-O7	1.777(1)	Nb2-O9	2.019(1)
OQE	1.003	Mean	2.021	Mean	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
		OQE	1.039	OQE	1.039
OV	15.689				
OAV	354.100	Mn1-O2	2.0645	Nb3-O1	2.3764(6)
OQE	1.113	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)
		Mean	2.208	Mean	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)
		Mean	2.191	Mean	2.178
		OV	13.992	OV	13.417
		OAV	4.489	OAV	104.704
		OQE	1.003	OQE	1.030

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1: Friis *et al*. (2014); 2: Friis *et al*. (2016)

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

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TABLE 7. Comparative data for melcherite and synthetic compounds (all trigonal, *R*-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†	$Cs_6Na_2(Nb_6O_{19}).18(H_2O)$	*a* = 12.609 (2)	*c* = 22.745 (5)
synthetic†	$Rb_6(H_2Nb_6O_{19}).19(H_2O)$	*a* = 12.271 (2)	*c* = 20.686 (3)

*This work.

† Nyman *et al.* (2006).

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

Name	melcherite	peterandresenite[1]	hansesmarkite[2]
Formula	Ba_2Na_2Mg $Nb_6O_{19}•6H_2O$	$Mn_4Nb_6O_{19}•14H_2O$	$Ca_2Mn_2Nb_6O_{19}•$ $20H_2O$
Space group	R-3	C2/m	P-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*. (2016)

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