The Canadian Mineralogist
Vol. 54, pp. 1021-1032 (2016)
DOI: 10.3749/canmin.1500100

ARROJADITE-(BaNa), $BaNa_3(Na,Ca)Fe^{2+}_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$, A NEW PHOSPHATE MINERAL FROM THE LUNA ALBITE PEGMATITE, DORIO COMMUNE, LECCO PROVINCE, ITALY

PIETRO VIGNOLA

CNR, Istituto per la dinamica dei processi ambientali, via Botticelli 23, 20133 Milano, Italia
Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, via Botticelli 23, 20133 Milano, Italia

FRÉDÉRIC HATERT, MAXIME BAIJOT, AND FABRICE DAL BO

Laboratoire de Minéralogie, Département de Géologie, Universitè de Liège, Bâtiment B18, Sart Tilman, B-4000 Liège, Belgique

SERGIO ANDÒ

Dipartimento di Scienze Geologiche e Ambientali, Università Milano-Bicocca, Piazzale della Scienza 4-U4 – 20126 Milano, Italia

DANILO BERSANI

Dipartimento di Fisica e Scienze della Terra, Università di Parma, Viale G.P. Usberti 7/a, 43124 Parma, Italia

ALESSANDRO PAVESE AND ANDREA RISPLENDENTE

Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, via Botticelli 23, 20133 Milano, Italia

FRANCESCO VANINI

via Gradisca 18, 21100 Varese, Italia

ABSTRACT

Arrojadite-(BaNa), $BaNa_3(Na,Ca)Fe^{2+}_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$, is the Na-, Ba-rich member of the arrojadite group. This primary phosphate was found at the Luna albite pegmatite, Dorio, Lecco province, Italy where it occurs associated with fluorapatite in the blocky-albite unit of the pegmatite. This new phosphate forms greenish or yellowish translucent masses, or rough crystals up to 4–5 cm in diameter hosted by albite. Arrojadite-(BaNa) is anisotropic with α 1.656(2), β 1.660(2), and γ 1.664(2), and is non-fluorescent under both short-wave (254 nm) and long-wave (366 nm) ultraviolet light. The mineral is brittle with an irregular fracture and a good cleavage parallel to {110}; its Mohs hardness is 4–5. Its measured specific gravity is 3.54(2). The empirical formula, calculated on the basis of 12 (P + Si + As) atoms per formula unit is $(Ba_{0.62}K_{0.27}Pb_{0.13}Sr_{0.07})_{\Sigma 1.09}Na_3(Na_{1.19}Ca_{0.85})_{\Sigma 2.04}(Fe^{2+}_{9.82}Mg_{1.92}Mn^{2+}_{1.64})_{\Sigma 13.38}Al_{1.01}(PO_4)_{11}(HPO_4)(OH_{1.75}F_{0.25})_{\Sigma 2}$, with the water content calculated considering 2 ($OH^- + F$) per formula unit. Arrojadite-(BaNa) is monoclinic with space group *C*2/c; its unit-cell parameters are *a* 16.4984(6) Å, *b* 10.0228(3) Å, *c* 24.648(1) Å, β 105.850(4)°, and *V* 3920.8(2) Å^3, for $Z = 4$. The eight strongest lines in the X-ray powder diffraction pattern are [*d* in Å (*I*/I_0) *hkl*]: 3.137 (100) 5 1 0, 2.818 (61) 3 1 6, 3.303 (46) $\bar{1}$ 3 2, 2.667 (35) 2 0 8, 2.878 (32) 3 3 1, 3.488 (28) 1 1 6, 4.621 (22) $\bar{3}$ 1 3, and 2.936 (22) 3 3 0. The mineral, which has been approved by the CNMNC under number IMA 2014-071, is named arrojadite-(BaNa) since it corresponds to the Ba-Na-rich member of the arrojadite mineral group, in which Ba is the principal element at the X5 (= A1) site and $^{M}Fe^{*} \leq 0.5$ *apfu*. Sodium is the unique element at the cation X1 (= Ca) site.

Keywords: arrojadite-(BaNa), new phosphate mineral species, arrojadite group, Luna albite pegmatite, Piona pegmatite swarm, Lecco province, central Southern Alps, Italy.

§ *Corresponding author e-mail address*: pietro.vignola@idpa.cnr.it

Introduction

Minerals belonging to the arrojadite group are omnipresent phosphates occurring in metamorphic, igneous, and sedimentary environments (Robertson 1982). Members of the arrojadite–dickinsonite series form primary phosphate minerals in granite pegmatites, where they occur as masses up to 15 cm in diameter, exhibiting good cleavage and ranging in color from pale yellow to dark bottle green or brownish (Simmons *et al*. 2003). Arrojadite–dickinsonite is typical of Lithium-Cesium-Tantalum (LCT) pegmatites belonging to the beryl-columbite-phosphate subtype in the classification of Černý & Ercit (2005). Recently, the crystal-chemistry of this group of phosphates has been reinvestigated by Cámara *et al*. (2006) and Chopin *et al*. (2006), who established a new classification scheme for the group, based on the general formula $A_2B_2CaNa_{2-x}M_{13}Al(PO_4)_{11}(PO_3OH_{1-x})W_2$. In this formula, A corresponds to large divalent cations (Ba, Sr, Pb) and vacancies (A1), or monovalent cations (K, Na) (A2); B corresponds to small divalent cations (Fe, Mn, Mg) and vacancies or monovalent Na cations; M sites contain small divalent cations which define the root names arrojadite (Fe) or dickinsonite (Mn); and the W site may be occupied by OH or F (arrojadite or fluorarrojadite).

During the last five years, one of the authors (FV) has found, in the mine dumps of the Luna dike mining locality, several masses or roughly crystallized individuals of a mineral corresponding to a member of the arrojadite group. These masses, up to 5 cm in diameter, are hosted by albite and associated fluorapatite. The crystallochemical investigations indicated that the mineral was a new phosphate, which was named arrojadite-(BaNa). It corresponds to the Ba-Na-rich member of the arrojadite mineral group, in which Ba is the principal element at the A1 site, with $Fe^{2+} \leq 0.5$ *apfu* at the M site, and with Na as a unique element at the Ca cation site. The name is in accordance with the nomenclature of the arrojadite group established by Chopin *et al*. (2006), and the new species was accepted by the CNMNC-IMA under number IMA 2014-071 (Vignola *et al*. 2015). All analyses were performed using a single specimen which was broken into several fragments. The co-type samples used for the characterization of the new species arrojadite-(BaNa) are stored in the Mineralogical Collection of the Museo Civico di Storia Naturale, Milano, Italy (number 38718: samples used for density measurement, Raman spectroscopy, electron-microprobe analyses, X-ray powder diffraction), as well as in the collections of the Laboratory of Mineralogy, University of Liège (number 20391: grains used for the crystal structure determination and for the optical measurements). Other fragments from the co-type (numbered from 1 to 8) are stored by one of the authors (PV) and in the mineralogical collections of the Department of Min-

FIG. 1. Rough crystal of arrojadite-(BaNa) from the Luna pegmatite. The crystal is 4 cm in diameter.

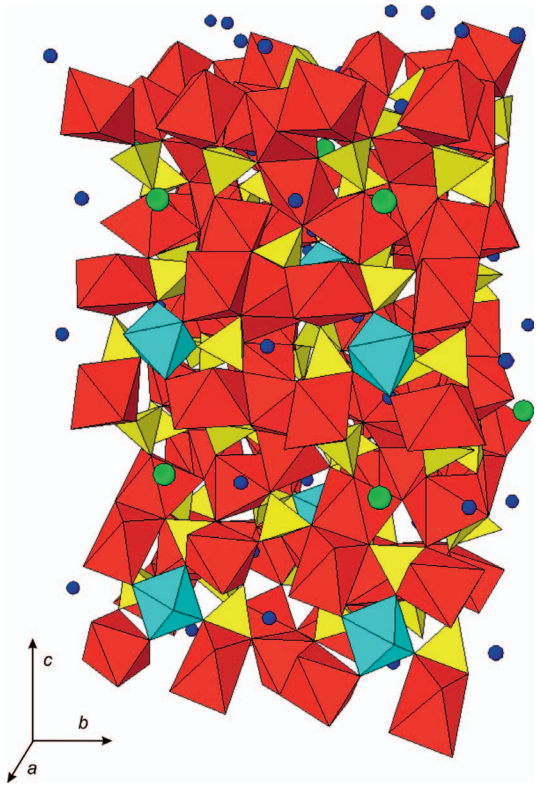

FIG. 2. The crystal structure of arrojadite-(BaNa). FeO_6 octahedra are red, AlO_6 octahedra are blue, PO_4 tetrahedra are yellow. Blue circles represent Na atoms, and green circles represent Ba atoms.

TABLE 1. DETERMINATION OF THE DENSITY OF ARROJADITE-(BaNa)

Sample	Weight in air (g)	Weight in water (g)	delta	T (°C)	Correction factor for temperature	Density (g/cm^3)
First experiment						
Arj-ba1	0.0730	0.0525	0.0205	20.00	0.9982	3.555(1)
Arj-ba2	0.0592	0.0426	0.0166	20.00	0.9982	3.560(1)
Second experiment (dried for 4 hours in oven at 50 °C)						
Arj-ba1	0.0731	0.0524	0.0207	20.40	0.99815	3.525(1)
Arj-ba2	0.0593	0.0424	0.0169	20.40	0.99815	3.502(1)
AVERAGE						3.54(2)

eral Sciences of the National Museum of Natural History (Smithsonian Institution, Washington DC) and of the Department of Geology and Petrography of the Moravian Museum (Brno, Czech Republic).

Occurrence, General Appearance, and Physical Properties

Arrojadite-(BaNa) was found by one of the authors (FV) in the mine dumps of the Luna albite pegmatite, Dorio commune, Lecco province, Italy (46°, 06′, 36″ N; 9°, 19′, 59″ E). The Luna pegmatite was mined for ceramic albite from 1960 to 1970 and consists of three different albite pegmatite dikes belonging to the Late Triassic Piona pegmatite swarm (Vignola *et al*. 2011). Arrojadite-(BaNa) occurs as a primary phosphate mineral in the blocky-plagioclase zone as rounded masses or roughly crystallized individuals up to 4–5 cm in diameter that are hosted by albite (Fig. 1). It is frequently associated with fluorapatite. The color is pale greyish-green, translucent or pale yellowish brown when altered, and the luster is greasy. The mineral is brittle with an irregular fracture and a Mohs hardness of 4–5 was determined by comparison with the other members of the arrojadite group. A good cleavage was observed on {110}.

A specific gravity of 3.54(2) was measured by means of hydrostatic weighting using a Mettler Toledo balance (model JB1603-C/FACT accurate to four decimal places) and two rounded masses of the mineral taken from the holotype. The balance was stabilized for 12 hrs before the measurement and

TABLE 2. AVERAGE ELECTRON MICROPROBE ANALYSIS OF ARROJADITE-(BaNa)

	average of 20 analyses				stoichiometry based on 12 P *apfu*	
	wt.%	e.s.d.	min	max		
P_2O_5	39.73	*0.45*	38.88	40.67	P	12.000
Al_2O_3	2.40	*0.06*	2.33	2.52	Al	1.010
FeO	32.91	*0.28*	32.34	33.35	Fe2	9.820
MnO	5.41	*0.12*	5.23	5.65	Mn2	1.636
MgO	3.60	*0.11*	3.26	3.76	Mg	1.916
PbO	1.35	*0.12*	1.15	1.50	Pb	0.130
BaO	4.43	*0.25*	3.73	4.90	Ba	0.620
SrO	0.35	*0.08*	0.21	0.53	Sr	0.072
CaO	2.22	*0.18*	1.84	2.40	Ca	0.849
Na_2O	6.06	*0.13*	5.82	6.32	Na	4.190
K_2O	0.59	*0.04*	0.52	0.65	K	0.268
H_2O^{+} (*)	0.42				H^{+}	1.000
H_2O^{-} (**)	0.70				OH^{-}	1.753
F	0.22	*0.05*	0.15	0.30	F	0.247
sum	100.39				O	50.157
F Cl eq	–0.09					
TOTAL	100.30				sum cations	20.510
					sum charges	–0.181

Notes: Si, As, Zn, S, and Cl were below detection limit; (*) calculated for 1 H *apfu* in stoichiometry; (**) calculated for 2 (OH, F, Cl) *apfu* in stoichiometry.

TABLE 3. THE X-RAY POWDER DIFFRACTION DATA OF ARROJADITE-(BaNa) (EIGHT STRONGEST LINES ARE IN BOLD)

I/I_0	d_{obs}	d_{calc}	h k l	I/I_0	d_{obs}	d_{calc}	h k l
5	8.498	8.530	1 1 0	13	2.344	2.343	6 2 2
5	7.666	7.672	1 1 1	5	2.297	2.298	$\overline{4}$ 4 1
5	7.455	7.496	$\overline{1}$ 1 2	7	2.275	2.275	0 4 6
11	5.941	5.959	0 0 4	5	2.264	2.264	2 0 10
9	5.577	5.609	$\overline{2}$ 0 4	1	2.237	2.238	3 1 9
9	5.282	5.296	$\overline{1}$ 1 4	4	2.183	2.183	$\overline{6}$ 2 9
10	5.068	5.089	0 2 0	6	2.153	2.153	$\overline{8}$ 0 0
10	4.823	4.847	$\overline{3}$ 1 2	4	2.143	2.144	$\overline{1}$ 3 10
7	4.742	4.746	3 1 0	5	2.125	2.126	6 0 6
16	4.678	4.693	0 2 2	8	2.121	2.118	$\overline{2}$ 4 8
22	**4.621**	**4.626**	**$\overline{3}$ 1 3**	3	2.097	2.097	5 3 5
12	4.264	4.273	2 0 4	9	2.090	2.090	$\overline{8}$ 2 3
4	4.104	4.096	3 1 2	13	2.084	2.084	$\overline{7}$ 3 5
9	3.904	3.909	0 2 4	3	2.041	2.041	$\overline{6}$ 4 3
10	3.548	3.534	0 2 5	5	2.037	2.037	$\overline{5}$ 3 10
28	**3.488**	**3.474**	**1 1 6**	2	2.025	2.025	7 3 1
16	3.400	3.397	$\overline{4}$ 0 6	2	2.014	2.013	$\overline{6}$ 4 5
8	3.327	3.320	2 2 4	3	1.985	1.985	$\overline{9}$ 1 2
46	**3.303**	**3.306**	**$\overline{1}$ 3 2**	12	1.956	1.956	$\overline{9}$ 1 7
14	3.226	3.222	$\overline{5}$ 1 3	7	1.944	1.944	5 3 7
100	**3.137**	**3.130**	**5 1 0**	3	1.932	1.933	6 2 7
5	3.072	3.072	1 3 3	3	1.928	1.928	1 1 13
5	3.026	3.024	$\overline{4}$ 2 5	4	1.904	1.905	9 1 1
5	2.973	2.973	$\overline{2}$ 2 7	3	1.890	1.890	7 3 4
21	2.954	2.952	$\overline{3}$ 1 8	2	1.886	1.887	$\overline{7}$ 3 10
22	**2.936**	**2.943**	**3 3 0**	2	1.879	1.878	$\overline{3}$ 5 8
15	2.910	2.912	1 3 4	4	1.873	1.873	5 3 8
12	2.890	2.891	$\overline{4}$ 0 8	5	1.870	1.870	$\overline{10}$ 0 4
32	**2.878**	**2.877**	**3 3 1**	6	1.864	1.864	5 5 2
20	2.861	2.868	$\overline{6}$ 0 2	8	1.829	1.828	$\overline{6}$ 4 10
61	**2.818**	**2.815**	**3 1 6**	3	1.816	1.817	$\overline{8}$ 4 5
6	2.780	2.783	3 3 2	3	1.800	1.800	$\overline{10}$ 2 3
3	2.733	2.732	$\overline{3}$ 3 5	4	1.794	1.795	9 3 0
11	2.714	2.719	$\overline{4}$ 2 7	5	1.791	1.792	$\overline{2}$ 2 15
14	2.677	2.672	0 2 8	3	1.768	1.767	$\overline{10}$ 2 8
35	**2.667**	**2.668**	**2 0 8**	3	1.734	1.735	$\overline{6}$ 0 16
12	2.633	2.628	0 4 1	3	1.723	1.723	8 0 8
5	2.553	2.549	$\overline{6}$ 2 3	2	1.716	1.716	4 6 4
8	2.542	2.541	1 1 9	3	1.704	1.704	7 3 8
3	2.412	2.412	2 2 8	5	1.692	1.692	4 6 5
5	2.398	2.400	3 1 8	4	1.686	1.687	$\overline{1}$ 7 3
6	2.359	2.359	7 1 0	4	1.645	1.645	$\overline{10}$ 4 8

distilled H_2O was used as the medium. The weight in air was recorded after 60 s and the weight in water was after 120 s (after complete stabilization). Before performing the experiment on the arrojadite samples, the system was tested using two quartz grains with a comparable weight to that of the two specimens of arrojadite. The obtained data are summarized in Table 1. The calculated density is 3.76 g/cm^3.

Arrojadite-(BaNa) is biaxial (+) with intermediate dispersion. The birefringence is low with first order white or yellow interference colors. The measured refractive indices (wavelength = 589 nm, sodium) are α 1.656(2), β 1.660(2), and γ 1.664(2). The measured $2V = 40(1)°$ and the calculated angle is 45°. The optical axial plane is perpendicular to {110} (cleavage); the measured Z^c = 17–18°. The compatibility index, 1 –

TABLE 4. DETAILS PERTAINING TO THE DATA COLLECTION AND THE STRUCTURE REFINEMENT OF ARROJADITE-(BaNa)

Crystal shape	Irregular prism
Crystal size (mm^3)	0.17 × 0.15 × 0.07
Crystal color	Transparent yellow
T (K)	298
Unit-cell constants	$a = 16.4984(6)$ Å $b = 10.0228(3)$ Å $c = 24.648(1)$ Å $\beta = 105.850(4)°$ $V = 3920.8(2)$ $Å^3$
Chemical formula	$BaNa_3(NaCa)Fe_{13}Al(PO_4)_{11}(PO_3OH)OH_2$
Space Group	$C2/c$
Z	4
Radiation (Å)	0.7107
Diffractometer	Xcalibur – EOS CCD
Data-collection method	ω/φ scan
Step size	0.5°
Max. θ (°)	57.44
Number of frames	414 $-20 < h < 20$ $-12 < k < 13$ $-30 < l < 33$
No. measured reflections	16452
No. unique reflections	4608
No. refined parameters	392
Refinement on	F^2
R_1 (F) with $F_o > 4\sigma(F_o)$	0.0581
R_1 (F) for all the unique reflections	0.0688
GooF	1.031
Weighting scheme: a, b	0.01, 0
Residuals (e^-/ $Å^3$)	–3.393/+4.654

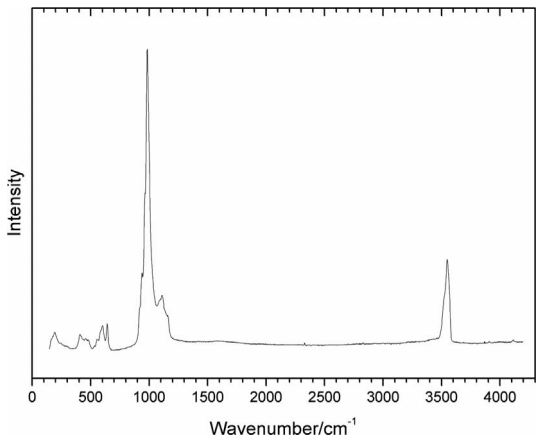

FIG. 3. The Raman spectrum of arrojadite-(BaNa) from the Luna albite pegmatite.

(K_p/K_c), is –0.013, which is in the superior category (Mandarino 1981). Arrojadite-(BaNa) is non-fluorescent under both short-wave (254 nm) and long-wave ultraviolet light (366 nm).

CHEMICAL COMPOSITION

Quantitative chemical analyses were performed on a polished section of arrojadite-(BaNa), using a JEOL JXA-8200 electron microprobe working in wavelength-dispersion mode, at the laboratory of the Department of Earth Sciences, University of Milan. The system was operated using an accelerating voltage of 15 kV, a beam current of 5 nA, a spot size of 5 μm, and a counting time of 30 s on the peaks and 10 s on the background. The following natural minerals were used as standards: graftonite KF16 (Fransolet 1975) for P, Fe, Mn, and Ca; anorthite-An137 for Al and Si; olivine-USNM2566 for Mg; galena for Pb; barite for Ba; celestine for Sr; omphacite-USNM110607 for Na; orthoclase-PSU OR1A for K; hornblende-Hbl123 for F; realgar for As and S; rhodonite for Zn; and scapolite

TABLE 5. REFINED POSITIONAL AND ANISOTROPIC (EXCEPT Na AT X4) DISPLACEMENT PARAMETERS (Å2) OF ARROJADITE-(BaNa)

Site	atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
X1	Na	0.2332(2)	0.2781(3)	0.48556(14)	0.021(2)	0.022(2)	0.032(2)	–0.0150(13)	0.0218(16)	–0.0184(14)	0.0219(11)
X2	Na	0.1352(4)	–0.0167(4)	0.11998(17)	0.086(4)	0.0159(18)	0.022(2)	–0.0094(19)	–0.020(2)	0.0025(15)	0.0481(14)
X3	Na	0.5	0	0.5	0.037(3)	0.013(2)	0.024(3)	0.0043(18)	–0.006(2)	0.0013(18)	0.0274(12)
X4	Na	0	–0.628(2)	0.25							0.051(8)
X5	Ba	0	–0.00168(8)	0.25	0.0197(4)	0.0335(5)	0.0501(6)	0	0.0174(4)	0	0.0329(2)
Al	Al	0	0	0.5	0.0077(13)	0.0070(13)	0.0081(14)	0.0001(9)	0.0026(11)	0.0000(10)	0.0075(6)
M1	Ca	0.22108(13)	–0.3939(2)	0.47407(10)	0.0249(11)	0.0374(13)	0.0469(14)	0.0140(8)	0.0201(9)	0.0237(10)	0.0344(8)
M2	Fe	0.21148(7)	–0.51064(10)	0.26772(5)	0.0160(6)	0.0128(5)	0.0138(5)	–0.0004(4)	0.0028(4)	0.0003(4)	0.0145(3)
M3	Fe	0.39391(9)	–0.01540(13)	0.35984(6)	0.0277(7)	0.0254(7)	0.0285(7)	–0.0001(5)	0.0066(6)	–0.0005(5)	0.0274(3)
M4	Fe	0.02189(7)	0.24995(11)	0.40296(5)	0.0179(6)	0.0155(6)	0.0200(6)	0.0019(4)	0.0065(4)	0.0016(4)	0.0176(3)
M5	Fe	0.03372(7)	–0.24503(10)	0.39977(4)	0.0106(5)	0.0132(5)	0.0123(5)	0.0005(4)	0.0029(4)	0.0005(4)	0.0121(2)
M6	Fe	0.20415(7)	–0.20051(11)	0.35194(4)	0.0145(5)	0.0161(5)	0.0119(5)	0.0012(4)	0.0030(4)	–0.0007(4)	0.0143(2)
M7	Fe	0.21882(7)	0.20516(12)	0.34291(5)	0.0154(5)	0.0233(6)	0.0144(6)	–0.0052(4)	0.0040(4)	0.0011(4)	0.0177(3)
P1	P	0.11525(19)	–0.5107(2)	0.36780(15)	0.0150(13)	0.0124(12)	0.0218(17)	–0.0016(9)	0.0124(13)	–0.0024(10)	0.0149(6)
P1X	P	0.0793(5)	–0.4975(6)	0.3342(3)	0.007(3)	0.007(3)	0.004(3)	0.000(2)	0.003(3)	0.000(2)	0.0058(12)
P2	P	0.12956(11)	0.03269(18)	0.42316(8)	0.0079(8)	0.0094(8)	0.0131(9)	0.0010(6)	0.0045(6)	0.0015(7)	0.0098(3)
P3	P	0.37355(11)	–0.25214(17)	0.46097(7)	0.0080(8)	0.0090(8)	0.0100(8)	0.0008(6)	0.0033(6)	0.0010(6)	0.0088(3)
P4	P	0.39786(11)	0.23255(17)	0.45188(7)	0.0101(8)	0.0077(8)	0.0101(8)	–0.0004(6)	0.0025(6)	–0.0013(6)	0.0094(3)
P5	P	0.12974(11)	–0.22550(18)	0.21279(7)	0.0113(8)	0.0089(8)	0.0086(8)	0.0002(6)	0.0012(6)	0.0000(6)	0.0099(3)
P6	P	0.14283(12)	0.19998(18)	0.20541(8)	0.0133(8)	0.0082(8)	0.0115(9)	0.0001(6)	–0.0001(7)	0.0001(6)	0.0117(4)
O1	O	0.0258(3)	0.4371(5)	0.3680(2)	0.017(3)	0.012(2)	0.020(3)	–0.0005(19)	0.012(2)	0.002(2)	0.0151(10)
O2	O	0.1129(3)	–0.3605(5)	0.3630(2)	0.016(3)	0.010(2)	0.019(3)	–0.0024(19)	0.007(2)	–0.002(2)	0.0150(10)
O3	O	0.1464(4)	–0.5800(6)	0.3237(3)	0.041(4)	0.017(3)	0.046(4)	–0.008(3)	0.035(3)	–0.012(3)	0.0301(15)
O4	O	0.1817(5)	0.4563(9)	0.4232(4)	0.033(4)	0.044(5)	0.067(6)	0.003(4)	0.001(4)	0.011(4)	0.051(2)
O5	O	0.0510(3)	0.0567(5)	0.4451(2)	0.009(2)	0.012(2)	0.012(2)	0.0016(18)	0.0062(18)	0.0000(18)	0.0101(9)
O6	O	0.1186(3)	–0.0962(5)	0.3894(2)	0.015(3)	0.012(2)	0.026(3)	–0.0010(19)	0.013(2)	–0.004(2)	0.0163(11)
O7	O	0.1285(3)	0.1572(5)	0.3855(2)	0.014(3)	0.015(3)	0.023(3)	0.0026(19)	0.012(2)	0.007(2)	0.0159(11)
O8	O	0.2115(3)	0.0348(6)	0.4707(3)	0.009(3)	0.033(3)	0.020(3)	–0.001(2)	0.000(2)	0.004(2)	0.0217(12)
O9	O	0.4165(3)	–0.1667(5)	0.4251(2)	0.014(2)	0.013(2)	0.016(3)	0.0012(19)	0.008(2)	0.0028(19)	0.0133(10)
O10	O	0.4046(3)	–0.3961(5)	0.4634(2)	0.012(2)	0.008(2)	0.012(2)	0.0001(18)	0.0014(19)	–0.0010(18)	0.0110(10)
O11	O	0.3914(3)	–0.1893(5)	0.5206(2)	0.015(2)	0.017(3)	0.011(2)	0.005(2)	0.0008(19)	–0.002(2)	0.0147(10)
O12	O	0.2771(3)	–0.2527(5)	0.4362(2)	0.007(2)	0.014(2)	0.023(3)	0.0012(18)	0.003(2)	0.006(2)	0.0148(10)
O13	O	0.4537(3)	0.3574(5)	0.4517(2)	0.012(2)	0.012(2)	0.012(2)	–0.0008(18)	0.0052(19)	–0.0011(19)	0.0116(10)
O14	O	0.4353(3)	0.1277(5)	0.4200(2)	0.013(2)	0.007(2)	0.017(3)	0.0008(18)	0.0054(19)	–0.0051(19)	0.0121(10)
O15	O	0.4037(3)	0.1856(5)	0.5117(2)	0.022(3)	0.014(3)	0.010(2)	–0.003(2)	0.005(2)	0.0007(19)	0.0155(10)
O16	O	0.3059(3)	0.2648(5)	0.4222(2)	0.009(2)	0.019(3)	0.020(3)	–0.0011(19)	–0.001(2)	–0.001(2)	0.0170(11)
O17	O	0.0486(3)	–0.1749(5)	0.1717(2)	0.012(2)	0.013(2)	0.016(3)	0.0021(19)	–0.0006(19)	0.000(2)	0.0145(10)

TABLE 5. CONTINUED.

Site	atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
O18	O	0.1316(3)	–0.1751(5)	0.2714(2)	0.021(3)	0.015(3)	0.010(2)	0.003(2)	0.003(2)	–0.0013(19)	0.0153(10)
O19	O	0.1357(4)	–0.3796(5)	0.2108(2)	0.028(3)	0.008(2)	0.017(3)	0.002(2)	–0.004(2)	0.000(2)	0.0194(12)
O20	O	0.2053(3)	–0.1663(5)	0.1945(2)	0.012(2)	0.017(3)	0.017(3)	–0.002(2)	0.005(2)	0.001(2)	0.0152(10)
O21	O	0.0583(3)	0.1541(5)	0.1657(2)	0.017(3)	0.012(2)	0.016(3)	–0.003(2)	0.000(2)	0.002(2)	0.0159(11)
O22	O	–0.1503(4)	0.1438(6)	0.2360(2)	0.031(3)	0.019(3)	0.015(3)	0.009(2)	–0.001(2)	–0.005(2)	0.0229(12)
O23	O	0.1475(3)	0.3537(5)	0.2059(2)	0.021(3)	0.010(2)	0.012(3)	0.000(2)	–0.002(2)	–0.0002(19)	0.0156(11)
O24	O	0.2170(3)	0.1443(6)	0.1842(2)	0.014(3)	0.018(3)	0.021(3)	0.002(2)	0.003(2)	–0.002(2)	0.0182(11)
O25	O	0.2703(3)	–0.0024(5)	0.3630(2)	0.008(2)	0.015(3)	0.018(3)	–0.0012(17)	0.004(2)	–0.0014(19)	0.0137(10)

Notes: The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

for Cl. The raw data were corrected for matrix effects using the φρZ method from the JEOL series of programs.

The averaged analytical results are reported in Table 2. The water content was calculated considering $2(OH^- + F)$ per formula unit. The empirical formula was calculated on the basis of 12 (P + Si + As) atoms per formula unit, which assumes that Si and As can substitute for P at the tetrahedral sites (essentially 12 P *apfu* because As and Si were below detection limit in all analyzed points). The calculated formula is: $(Ba_{0.62}K_{0.27}Pb_{0.13}Sr_{0.07})_{\Sigma 1.09}Na_3(Na_{1.19}Ca_{0.85})_{\Sigma 2.04}(Fe^{2+}_{9.82}Mg_{1.92}Mn^{2+}_{1.64})_{\Sigma 13.38}Al_{1.01}(PO_4)_{11}(PO_3OH)(OH_{1.75}F_{0.25})_{\Sigma 2}$. The simplified formula is $BaNa_3(NaCa)Fe^{2+}_{13}Al(PO_4)_{11}(PO_3OH)OH_2$, which theoretically requires: BaO 7.07, Na_2O 5.72, CaO 1.29, FeO 43.06, Al_2O_3 2.35, P_2O_5 39.72, and H_2O 1.25 wt.% for a total of 100.00 wt.%.

X-ray Diffraction Data and Crystal Structure Determination

The X-ray powder diffraction (XRPD) pattern of arrojadite-(BaNa) was obtained with a high-resolution PANalytical X'pert Pro X-ray powder diffractometer equipped with an X'Celerator-type detector at the Department of Earth Sciences of the University of Milan. Operating conditions were: filtered Cu*K*α radiation, 40 kV, 40 mA, 2θ-range from 5° to 105°, step size 0.017° 2θ, and a counting time of 70 s per step. Silicon NIST 640c was used as an internal standard, and the refinement of unit-cell parameters and indexing of Bragg reflections were performed using the least-squares indexing program CELREF 3, beta version (Laugier & Bochu 1999). The refined unit-cell parameters for space group *C*2/c are *a* 15.551(4) Å, *b* 10.058(2) Å, *c* 24.648(7) Å, β 106.51(2)°, and *V* 3933(2) Å^3, for $Z = 4$. The complete list of indexed reflections is reported in Table 3. The eight strongest measured lines are [*d* in Å (I/I_0) *hkl*]: 3.137 (100) 5 1 0, 2.818 (61) 3 1 6, 3.303 (46) $\bar{1}$ 3 2, 2.667 (35) 2 0 8, 2.878 (32) 3 3 1, 3.488 (28) 1 1 6, 4.621 (22) $\bar{3}$ 1 3, and 2.936 (22) 3 3 0.

The X-ray structural study was carried out with an Agilent Xcalibur four-circle diffractometer equipped with an EOS CCD detector at the Laboratoire de Minéralogie et de Cristallochimie of the University of Liège, using a fragment of arrojadite-(BaNa) measuring 0.170 × 0.150 × 0.080 mm. A total of 414 frames with a spatial resolution of 1° were collected with the φ/ω scan technique, with a counting time of 100 s per frame, in the range $5.83 < 2\theta < 57.44°$. A total of 16452 reflections were extracted from these frames, corresponding to 4608 unique reflections. The details of the single-crystal data collection and crystal

TABLE 6. BOND DISTANCE (Å) AND ANGLES (°) FOR ARROJADITE-(BaNa)

Al–O(5)	×2	1.867(5)	P(1)–O(1)	1.567(6)
Al–O(10)	×2	1.898(5)	P(1)–O(2)	1.509(6)
Al–O(13)	×2	1.884(5)	P(1)–O(3)	1.495(6)
			P(1)–O(4)	1.536(9)
M(1)–O(2)		2.849(6)		
M(1)–O(4)		1.950(10)	O(1)–P(1)–O(2)	109.2(3)
M(1)–O(8)		2.063(6)	O(1)–P(1)–O(3)	111.0(4)
M(1)–O(10)		3.109(5)	O(1)–P(1)–O(4)	104.1(5)
M(1)–O(11)		2.071(5)	O(2)–P(1)–O(3)	114.4(4)
M(1)–O(12)		2.648(6)	O(2)–P(1)–O(4)	106.3(4)
M(1)–O(12)		2.049(5)	O(3)–P(1)–O(4)	104.1(5)
M(2)–O(3)		2.086(6)	P(2)–O(5)	1.553(5)
M(2)–O(19)		2.073(5)	P(2)–O(6)	1.521(5)
M(2)–O(20)		2.119(5)	P(2)–O(7)	1.553(5)
M(2)–O(23)		2.099(5)	P(2)–O(8)	1.528(6)
M(2)–O(24)		2.108(6)		
			O(5)–P(2)–O(6)	109.6(3)
M(3)–O(25)		2.066(5)	O(5)–P(2)–O(7)	102.1(3)
M(3)–O(1)		2.183(5)	O(5)–P(2)–O(8)	112.3(3)
M(3)–O(9)		2.168(5)	O(6)–P(2)–O(7)	112.0(3)
M(3)–O(14)		2.041(5)	O(6)–P(2)–O(8)	112.3(3)
M(3)–O(19)		2.158(6)	O(7)–P(2)–O(8)	108.1(3)
M(3)–O(23)		2.053(5)		
			P(3)–O(9)	1.536(5)
X(1)–O(4)		2.358(9)	P(3)–O(10)	1.527(5)
X(1)–O(7)		2.865(7)	P(3)–O(11)	1.552(5)
X(1)–O(8)		2.477(7)	P(3)–O(12)	1.541(5)
X(1)–O(8)		2.231(7)		
X(1)–O(15)		2.306(6)	O(9)–P(3)–O(10)	110.3(3)
X(1)–O(15)		2.864(7)	O(9)–P(3)–O(11)	108.7(3)
X(1)–O(16)		2.565(7)	O(9)–P(3)–O(12)	111.3(3)
X(1)–O(16)		2.219(6)	O(10)–P(3)–O(11)	111.8(3)
			O(10)–P(3)–O(12)	108.1(3)
X(2)–O(10)		2.319(6)	O(11)-P(3)–O(12)	106.5(3)
X(2)–O(13)		2.334(6)		
X(2)–O(16)		2.714(7)	P(4)–O(13)	1.554(5)
X(2)–O(17)		2.679(8)	P(4)–O(14)	1.540(5)
X(2)–O(20)		2.407(6)	P(4)–O(15)	1.526(5)
X(2)–O(21)		2.569(8)	P(4)–O(16)	1.528(5)
X(2)–O(24)		2.401(7)		
			O(13)–P(4)–O(14)	103.1(3)
			O(13)–P(4)–O(15)	111.7(3)
M(4)–O(1)		2.072(5)	O(13)–P(4)–O(16)	109.9(3)
M(4)–O(5)		2.188(5)	O(14)–P(4)–O(15)	110.8(3)
M(4)–O(7)		2.136(5)	O(14)–P(4)–O(16)	112.6(3)
M(4)–O(9)		2.130(5)	O(15)–P(4)–O(16)	108.7(3)
M(4)–O(15)		2.222(5)		
M(4)–O(21)		2.078(5)	P(5)–O(17)	1.528(5)
			P(5)–O(18)	1.522(5)
M(5)–O(2)		2.125(5)	P(5)–O(19)	1.549(5)
M(5)–O(6)		2.108(5)	P(5)–O(20)	1.555(5)
M(5)–O(11)		2.118(5)		
M(5)–O(13)		2.314(5)	O(17)–P(5)–O(18)	107.8(3)
M(5)–O(14)		2.225(5)	O(17)–P(5)–O(19)	111.2(3)
M(5)–O(17)		2.033(5)	O(17)–P(5)–O(20)	107.9(3)

TABLE 6. CONTINUED.

			O(18)–P(5)–O(19)	O19
M(6)–O(2)		2.266(5)	O(18)–P(5)–O(20)	O20
M(6)–O(6)		2.157(5)	O(19)–P(5)–O(20)	108.0(3)
M(6)–O(12)		2.161(5)		
M(6)–O(18)		2.035(5)	P(6)–O(21)	1.538(5)
M(6)–O(24)		2.354(6)	P(6)–O(22)	1.523(6)
M(6)–O(25)		2.247(5)	P(6)–O(23)	1.542(5)
			P(6)–O(24)	1.559(6)
M(7)–O(25)		2.251(5)		
M(7)–O(7)		2.098(5)	O(21)–P(6)–O(22)	108.4(3)
M(7)–O(16)		2.169(5)	O(21)–P(6)–O(23)	109.8(3)
M(7)–O(20)		2.169(5)	O(21)–P(6)–O(24)	109.8(3)
M(7)–O(22)		2.059(6)	O(22)–P(6)–O(23)	111.7(3)
			O(22)–P(6)–O(24)	76.1(3)
X(3)–O(9)	×2	2.589(5)	O(23)–P(6)–O(24)	108.6(3)
X(3)–O(11)	×2	2.751(6)		
X(3)–O(14)	×2	2.349(5)		
X(3)–O(15)	×2	2.514(5)		
X(4)–O(1)	×2	2.898(7)		
X(4)–O(3)	×2	2.641(8)		
X(4)–O(23)	×2	2.929(6)		
X(5)–O(17)	×2	2.868(5)		
X(5)–O(18)	×2	2.718(5)		
X(5)–O(21)	×2	2.961(5)		
X(5)–O(22)	×2	2.815(6)		

structure refinement are summarized in Table 4. Unit-cell parameters refined from these reflections are in good agreement with those refined from the X-ray powder data: a 16.4984(6) Å, b 10.0228(3) Å, c 24.648(1) Å, β 105.850(4)°, and V 3920.8(2) Å^3, $Z = 4$ space group $C2/c$. Data were corrected for Lorenz, polarization, and absorption effects, the latter with an empirical method using the SCALE3 ABSPACK scaling algorithm included in the CrysAlisRED package (Oxford Diffraction 2007). The crystal structure of arrojadite-(BaNa) (Fig. 2) was refined in space group $C2/c$. Although the Cc space group displayed a worse figure of merit, we also attempted a refinement in this space group (as suggested by Cámara *et al*. 2006), but obtained a bad R_1 factor, with splitting of several sites and bad anisotropic thermal parameters. Consequently, the $C2/c$ space group and the atomic coordinates suggested by Demartin *et al*. (1996) were chosen for the crystal-structure refinement. Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from the *International Tables for X-ray Crystallography* (Wilson 1992). In the final refinement cycle, all atoms except Na occurring at the X4 site were refined anisotropically, leading to an R_1 value of 0.0581. Atomic coordinates and thermal parameters for arrojadite-(BaNa) are summarized in Table 5, and bond lengths and angles are summarized in Table 6. The crystal structure of arrojadite-(BaNa) is similar to that of arrojadite-(BaFe) (Demartin *et al*. 1996), with the X2 to X4 sites occupied by Na, the X5 site occupied by Ba, and the M2 to M7 sites occupied mainly by Fe^{2+}. The X4 site is split in arrojadite-(BaFe), while this splitting does not occur in arrojadite-(BaNa). However, as shown in Table 5, the P1 site is split in arrojadite-(BaNa), as previously observed in arrojadite-(BaFe) (Demartin *et al*. 1996). In arrojadite-(BaNa), the X1 site is occupied by Na and the M1 site by Ca (Table 5).

Spectroscopic Properties

Unpolarized micro-Raman spectra (Fig. 3) were obtained in nearly backscattered geometry, with a Jobin-Yvon Horiba "Labram" apparatus at the Department of Physics and Earth Sciences of the University of Parma. The instrument is equipped with a motorized x-y stage and an Olympus microscope with a ULWD 50× objective. The 473.1 nm line of a doubled Nd:YAG laser was used for excitation. The minimum lateral and depth resolution were set to a few micrometres. The system was calibrated using the 520.6 cm^{-1} Raman peak of silicon before each experimental session. Spectra were collected through multiple acquisitions with single counting times ranging from 20 to 180 s.

TABLE 7. RAMAN WAVENUMBERS AND VIBRATIONAL MODES IN ARROJADITE-(BaNa)

162	Lattice modes
173	
193	
220	
245	
268	
293	
409	Bending modes ν_2 of PO_4 and H_2PO_4 units
422	
433	
456	
484	
498	
530	Out-of-plane bending modes ν_4 of PO_4
557	and H_2PO_4 units
582	
602	
619	
642	
917	PO_4^{3-} ν_1 symmetric stretching modes
938	
962	
982	
998	
1020	
1055	PO_4^{3-} ν_3 antisymmetric stretching modes
1087	
1113	
1141	
1161	
1595	OH bending
3522	OH stretching
3529	
3549	
3567	

The Raman spectra of phosphate minerals are usually dominated by the strong signals of the phosphate groups. The isolated PO_4 unit is expected to show four Raman bands, ν_1 being the symmetric PO_4 stretching mode, ν_3 the asymmetric stretching mode, and ν_2 and ν_4 the bending modes (Nakamoto 1986). The attribution of the modes was made by comparison with those for arrojadite-(KFe) (Frost *et al*. 2013), and is reported in Table 7. For each phosphate mode, many bands (five to six) with different wavenumbers are observed. This indicates the presence of different non-equivalent phosphate groups in the structure, even if a strong PO_4 tetrahedron asymmetry could be the explanation for the increased multiplicity of the ν_2, ν_3, and ν_4 bands (Adler 1964). In a similar way, the presence of different OH stretching peaks in the 3500–3600 cm^{-1} region indicates the presence of non-equivalent OH groups. The Raman spectra show clear similarities with the one reported by Frost *et al.* (2013) for arrojadite-(KFe), but the differences in the band positions are large enough to allow a good discrimination of the two species.

Discussion

From the classification point of view, arrojadite-(BaNa) is a phosphate mineral belonging to the arrojadite group, arrojadite subgroup (Dana classification 41.07.02, Anhydrous phosphates containing hydroxyl or halogen – arrojadite group – arrojadite subgroup. Strunz classification 08.BF.05, Phosphates, arsenates vanadates, with additional anions, without H_2O, with medium-sized and large cations), and corresponds to the Ba- and Na-rich member of the arrojadite group. Arrojadite-(BaNa) corresponds to the Na-rich analogue of arrojadite-(BaFe) (ex sigismundite, see Demartin *et al*. 1996 and Chopin *et al*. 2006). The physical properties of the valid mineral species of the arrojadite subgroup are shown in Table 8.

Since the nomenclature of the arrojadite-group minerals has been revised considering space group *Cc*, it is difficult to compare our data with the nomenclature scheme established by Cámara *et al*. (2006) and Chopin *et al*. (2006). However, the electron-microprobe analysis and crystal-structure refinement clearly show that Ba is dominant at the X5 (= A1) site, thus implying the use of "Ba" as first suffix. According to Chopin *et al*. (2006), the second suffix depends on the divalent cations at the M sites. For arrojadite-(BaNa), the $^{M}Fe^{*}$ value ($^{M}Fe^{*} = Fe^{2+} + Mn^{2+} + Mg + Zn + Li - 13$) is 0.38 (see electron-microprobe data above), thus lower than 0.5 $^{M}Fe^{*}$ per formula unit. The second prefix must consequently be "Na", in agreement with the accepted nomenclature scheme (Chopin *et al*. 2006). A careful examination of cation distributions in arrojadite-(BaNa) (Table 5) indicates, however, significant differences compared to the data previously reported in the literature (Demartin *et al*. 1996, Cámara *et al*. 2006, Chopin *et al*. 2006). Indeed, the X1 site, generally populated by Ca in arrojadite-group minerals, hosts Na in arrojadite-(BaNa), and the M1 site, dominated by Fe in arrojadite-(BaFe), is filled by Ca in arrojadite-(BaNa). Therefore, the structural formulae of arrojadite-(BaNa) and arrojadite-(BaFe) can be written as follows:

- arrojadite-(BaNa): $^{X5}Ba^{X2X3X4}Na_3(^{X1}Na^{M1}Ca)_{^{M2–M7}}Fe^{2+}_{13}{}^{Al}Al(PO_4)_{11}(PO_3OH)OH_2$
- arrojadite-(BaFe): $^{X5}Ba^{X2X3X4}Na_3(^{X1}Ca^{M1}Fe^{2+})_{^{M2–M7}}Fe^{2+}_{13}{}^{Al}Al(PO_4)_{12}OH_2$

TABLE 8. COMPARISON OF THE PHYSICAL PROPERTIES FOR MINERALS OF THE ARROJADITE SUBGROUP

Mineral	Arrojadite-(BaNa)	Arrojadite-(BaFe)	Arrojadite-(PbFe)	Arrojadite-(SrFe)	Arrojadite-(KNa)
Type locality	Luna pegmatite, Italy	Alpe Groppera, Italy	Sapucaia, Brazil	Horrsjöberg, Sweden	Big Fish River, Canada
Reference	This work	[1, 2, 3]	[2, 3]	[2, 3]	[2, 3]
Ideal formula	$BaNa_3(NaCa)Fe^{2+}_{13}Al(PO_4)_{11}(PO_3OH)OH_2$	$BaNa_3(CaFe)Fe^{2+}_{13}Al(PO_4)_{12}OH_2$	$PbFe^{2+}(Ca,Na)_2Fe^{2+}_{13}Al(PO_4)_{11}(PO_3OH)OH_2$	$SrFe^{2+}(Ca,Na)_2Fe^{2+}_{13}Al(PO_4)_{11}(PO_3OH)OH_2$	$KNa_3(Ca,Na)_2Fe^{2+}_{13}Al(PO_4)_{11}(PO_3OH)OH_2$
Space group	*C2/c*	*C2/c* or *Cc*	*Cc*	*Cc*	*Cc*
a (Å)	16.4984(6)	16.406(5)	16.4304(9)	16.3992(7)	16.5220(11)
b (Å)	10.0228(3)	9.945(3)	9.9745(5)	9.9400(4)	10.0529(7)
c (Å)	24.648(1)	24.470(5)	24.5869(13)	24.4434(11)	24.6477(16)
β (Å)	105.850(4)	105.73(2)	105.485(2)	105.489(1)	106.509(2)
Vol ($Å^3$)	3920.8(2)	3843(2)	3883.2(5)	3839.76(46)	3932.2(7)
Z	4	4	4	4	4
Strong X-ray lines	-	-	-	-	5.861(29)
	-	-	-	-	5.026(27)
	4.521 (22)	4.560 (27)	4.553(25)	-	-
	3.388 (28)	3.400 (31)	3.396(24)	3.378 (26)	-
	3.300 (16)	3.310(20)	3.305(22)	3.293(21)	-
	3.203 (46)	3.211 (47)	3.208(43)	3.192 (41)	3.186(33)
	3.037 (100)	3.032 (100)	3.019(100)	3.009 (100)	3.050 (100)
	2.854 (21)	2.841(34)	-	-	2.853(22)
	2.836 (22)	2.828(30)	2.829(35)	2.820 (23)	-
	2.810 (15)	2.824(27)	2.819(33)	–	-
	-	-	2.813(29)	-	-
	2.778 (32)	2.797 (16)	-	2.805 (2)	2.798 (25)
	-	-	-	-	2.793 (28)
	-	-	-	-	2.777 (24)
	2.761 (20)	2.758 (32)	2.750(29)	-	2.753(23)
	-	-	-	2.737 (28)	-
	2.718 (61)	2.706(39)	2.694(32)	2.685 (70)	2.691 (71)
	-	2.703(68)	2.690(55)	-	-
	2.567 (35)	2.543(38)	2.538(30)	2.529 (23)	-
Density	3.535(1)	3.54	3.65	3.57	3.44
Hardness	4–5	-	4–5	-	-
Color	Pale grayish-green, translucent	Grayish-green, translucent	Pale honey, transparent	-	Brownish transparent
Morphology	Aggregates of numerous grains	Aggregates of numerous grains	Granular masses or subhedral crystals	-	Prismatic crystals

[1] Demartin *et al.* (1996), [2] Cámara *et al.* (2006), [3] Chopin *et al.* (2006).

Acknowledgments

The authors are happy to dedicate this work to William B "Skip" Simmons and Karen Louise Webber for their research and teaching in the field of pegmatology.

The authors are particularly grateful to Sarah Hanson and an anonymous referee for their suggestions which largely improved this article and to Guest Editor Al Falster who handled the manuscript.

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Received November 4, 2015. Revised manuscript accepted January 19, 2016.