Bobshannonite, Na2KBa(Mn,Na)8(Nb,Ti)4(Si2O7)4O4(OH)4(O,F)2, a newTS-block mineral from Mont Saint-Hilaire,Québec,Canada: Description and crystal structure

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Abstract

Bobshannonite, $Na_2KBa(Mn,Na)_8(Nb,Ti)_4(Si_2O_7)_4O_4(OH)_4(O,F)_2$, is a new TS-block mineral from Mont Saint-Hilaire, Québec, Canada. It occurs as blocky crystals 0.5–1 mm across, perched on sérandite and albite. Other associated minerals are epididymite, catapleiite, aegirine, kupletskite, rhodochrosite and rhabdophane-(Ce). Bobshannonite occurs as vitreous to frosty, transparent to translucent very pale brown to orange brown crystals, has a very pale brown streak, hackly fracture and does not fluoresce under cathode or ultraviolet light. Cleavage is {001} very good, no parting was observed, and Mohs hardness is ~4, and it is brittle, $D_{calc.}$ = 3.790 g/cm^3. Crystals are extensively twinned and do not extinguish in cross-polarized light. Bobshannonite is triclinic, $C\bar{1}$, a = 10.839(6), b = 13.912(8), c = 20.98(1) Å, α = 89.99(1), β = 95.05(2), γ = 89.998(9)°, V = 3152(5) Å^3. The six strongest reflections in the X-ray powder diffraction data [d (Å), I, (h k l)] are: 2.873, 100, ($\bar{2}$ $\bar{4}$ 1, $\bar{2}$ 4 1, 0 4 4, 0 $\bar{4}$ 4, 2 4 1, 2 $\bar{4}$ 1); 3.477, 60, (0 0 6); 3.193, 59, (2 2 4, 2 $\bar{2}$ 4); 2.648, 40, ($\bar{4}$ 0 2, 2 4 3, 2 $\bar{4}$ 3); 2.608, 35, (0 0 8, 2 2 6, 2 $\bar{2}$ 6); 1.776, 30, (2 4 9). Chemical analysis by electron microprobe gave Ta_2O_5 0.52, Nb_2O_5 19.69, TiO_2 5.50, SiO_2 26.31, Al_2O_3 0.06, BaO 7.92, ZnO 1.02, FeO 0.89, MnO 26.34, MgO 0.06, Rb_2O 0.42, K_2O 2.38, Na_2O 4.05, F 0.70, $H_2O_{calc.}$ 1.96, O=F –0.29, total 97.53 wt.%, where the H_2O content was calculated from the crystal-structure analysis. The empirical formula on the basis of 38 anions is $Na_{1.89}(K_{0.94}Rb_{0.04})_{\Sigma 0.98}Ba_{0.96}(Mn_{6.84}Na_{0.53}Zn_{0.24}Fe^{2+}_{0.23}Mg_{0.02}Al_{0.02})_{\Sigma 7.88}$ $(Nb_{2.74}Ti_{1.26}Ta_{0.04})_{\Sigma 4.04}(Si_{8.07}O_{28})O_{9.32}H_{4.01}F_{0.68}$, Z = 4. The crystal structure was refined to R_1 = 2.55% on the basis of 7277 unique reflections [$F > 4\sigma(F)$] and can be described as a combination of a TS (Titanium Silicate) block and an **I** (intermediate) block. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral). The topology of the TS block is as in Group II of the Ti disilicates: Ti + Nb = 2 a.p.f.u. per $(Si_2O_7)_2$ [as defined by Sokolova (2006)]. In the O sheet, ten $^{[6]}M^O$ sites are occupied mainly by Mn, less Na and minor Zn, Fe^{2+}, Mg and Al, with $\langle M^O–\varphi\rangle$ = 2.223 Å. In the H sheet, four $^{[6]}M^H$ sites are occupied by Nb and Ti (Nb > Ti), with $\langle M^H–\varphi\rangle$ = 1.975 Å, and eight $^{[4]}Si$ sites are occupied by Si, with <Si–O> = 1.625 Å. The M^H

50 octahedra and Si_2O_7 groups constitute the H sheet. The TS blocks link via common vertices of
51 M^H octahedra. In the **I** block, Ba and K are ordered at the $A^P(1)$ and $A^P(2)$ sites with Ba:K = 1:1
52 and the two B^P sites are occupied by Na. The ideal composition of the **I** block is Na_2KBa a.p.f.u.
53 Bobshannonite, perraultite, surkhobite and jinshajiangite are topologically identical Group-II TS-
54 block minerals. Bobshannonite is the Nb-analogue of perraultite. The mineral is named
55 *bobshannonite* after Dr. Robert (Bob) D. Shannon (b. 1935), in recognition of his major
56 contributions to the field of crystal chemistry in particular and mineralogy in general through his
57 development of accurate and comprehensive ionic radii and his work on dielectric properties of
58 minerals.
59
60 **Keywords:** bobshannonite, new mineral species, TS block, electron microprobe, crystal
61 structure, IR and Raman spectroscopy, Mont Saint-Hilaire, Québec, Canada.
62

Introduction

Bobshannonite, $Na_2KBa(Mn,Na)_8(Nb,Ti)_4(Si_2O_7)_4O_4(OH)_4(O,F)_2$, is a new TS-block mineral of Group II, Ti + Nb = 2 a.p.f.u. per $(Si_2O_7)_2$ (Sokolova, 2006).

The TS (Titanium Silicate) block is the main structural unit in thirty-nine minerals (including bobshannonite): 34 minerals are listed in Sokolova and Cámara (2013), and information on four minerals, kolskyite, emmerichite, saamite and betalomonosovite, can be found in Cámara *et al*. (2013), Aksenov *et al*. (2014), Cámara *et al*. (2014) and Sokolova *et al*. (2014), respectively. The TS block consists of a central trioctahedral (O) sheet and two adjacent heteropolyhedral (H) sheets of [5-7]-coordinated polyhedra and Si_2O_7 groups. The TS block is characterized by a planar cell based on minimal lengths of translational vectors, $t_1 \sim 5.5$ and $t_2 \sim 7$ Å, and $\mathbf{t_1} \wedge \mathbf{t_2} \approx 90°$. The general formula of the TS block is $A^P{}_2B^P{}_2M^H{}_2M^O{}_4(Si_2O_7)_2X_{4+n}$, where $M^H{}_2$ and $M^O{}_4$ = cations of the H and O sheets; M^H = Ti, Nb, Zr, Mn, Ca + REE, Ca; M^O = Ti, Zr, Nb, Fe^{2+}, Fe^{3+}, Mg, Mn, Ca, Na; A^P and B^P = cations at the peripheral (*P*) sites = Na, Ca + REE, Ca, Ba, Sr, K; X = anions, O, OH, F, and H_2O groups; $X_{4+n} = X^O{}_4 + X^P{}_n$, n = 0, 1, 1.5, 2, 4 (Sokolova and Cámara, 2013). Sokolova (2006) developed general structural principles for the TS-block minerals. There are three topologically distinct TS blocks based on three types of linkage of H and O sheets. In the crystal structures of TS-block minerals, TS blocks either link directly or alternate with intermediate (**I**) blocks. The **I** block consists of alkali and alkaline-earth cations, oxyanions (PO_4), (SO_4) and (CO_3), and H_2O groups. Sokolova (2006) divided TS-block structures into four Groups, based on the topology and stereochemistry of the TS block. Each group of structures has a different linkage, content and stereochemistry of Ti (+ Nb + Zr + Fe^{3+} + Mg + Mn) (atoms per formula unit) per $(Si_2O_7)_2$ (Fig. 1). In Group I, Ti (+ Nb + Zr) = 1 a.p.f.u. (Fig. 1*a*); in Group II, Ti (+ Nb) = 2 a.p.f.u. (Fig. 1*b*); in Group III, Ti (+ Nb + Mg + Fe^{3+}) = 3 a.p.f.u. (Fig. 1*c*); in Group IV, Ti (+ Mg + Mn) = 4 a.p.f.u. (Fig. 1*d*). In a TS-block structure, four types of self-linkage between adjacent TS blocks occur. Sokolova and Cámara (2013) introduced the concept of *basic* and *derivative structures* for TS-block minerals. A *basic*

89 *structure* has the following four characteristics: (1) There is only one type of TS block; (2) The
90 two H sheets of the TS block are identical; (3) There is only one type of **I** block or it is absent;
91 (4) There is only one type of self-linkage of TS blocks. *Basic structures* obey the general
92 structural principles of Sokolova (2006). A *derivative structure* has one or more of the three
93 following characteristics: (1) There is more than one type of TS block; (2) There is more than
94 one type of **I** block; (3) There is more than one type of self-linkage of TS blocks. A *derivative*
95 *structure* is related to two or more *basic structures* of the same Group: it can be derived by
96 adding these structures via sharing the central O sheet of the TS blocks of adjacent structural
97 fragments which represent *basic structures*. There are thirty-four basic TS-block structures and
98 five derivative TS-block structures.
99 In the crystal structure of bobshannonite, the TS block has the stereochemistry and
100 topology of Group II where Ti + Nb = 2 a.p.f.u. In Group II, the TS block exhibits linkage 2 where
101 the Si_2O_7 groups of two H sheets link to M^O octahedra adjacent along $\mathbf{t}_2$ in the O sheet (Fig. 1*b*)**.**
102 The crystal structure of bobshannonite is of the same topology as those of Group-II TS-block
103 minerals perraultite, surkhobite and jinshajiangite and is related to cámaraite, a Group-II mineral
104 (Table 1). Bobshannonite is the Nb-analogue of perraultite.
105 Bobshannonite was found in the fall of 1996 in a blast pile by L. Horváth and E.
106 Pfenninger-Horváth in the Poudrette quarry, Mont Saint-Hilaire, Québec, Canada. The mineral
107 is named after Dr. Robert (Bob) D. Shannon (b. August 28,1935) from Boulder, Colorado,
108 U.S.A., in recognition of his major contributions to the field of crystal chemistry in particular and
109 mineralogy in general through his development of accurate and comprehensive ionic radii and
110 his work on dielectric properties of minerals. A comprehensive list of the radii of ions in a series
111 of different materials (Shannon, 1976) is the highest formally-cited database of all time (Van
112 Noorden *et al.*, 2014). The Shannon (1976) paper is listed under #22 in the top 100 papers of all
113 times (Van Noorden *et al.*, 2014). The new mineral and mineral name have been approved by
114 the Commission on New Minerals, Nomenclature and Classification, International Mineralogical

Association (IMA 2014-52). The holotype specimen has been deposited at the Canadian Museum of Nature, Ottawa, Canada, registration number CMNMC 86886. The current paper reports the description and crystal structure of bobshannonite.

Occurrence

The mineral occurs in the pegmatite-rich western part in the Poudrette quarry, Mont Saint-Hilaire, La Vallée-du-Richelieu RCM, Monterégie, Québec, Canada (45°33′46″N 73°08′30″W). The type specimen was not found *in situ*, hence not much is known about the size, shape or complete mineral assemblage of the source pegmatite which was completely destroyed by blasting, but the observed mineralogy is typical for Mont Saint-Hilaire sérandite and epididymite-rich pegmatites. Associated minerals are sérandite, albite, epididymite (rich), catapleiite, aegirine (2 generations), kupletskite, rhodochrosite (two generations), rhabdophane-(Ce) and a black undetermined botryoidal mineral, possibly a Mn oxide. Bobshannonite is of hydrothermal origin and exceedingly rare.

Physical properties

Bobshannonite occurs as vitreous to frosty, transparent to translucent (thin crystals), orange-brown (large fragments) blocky crystals some 0.5–1.0 mm across, perched on sérandite and albite (Fig. 2). The type specimen is 2.5 x 2.3 x 2 cm and consists of ~90% sérandite with the associated minerals making up the balance. Bobshannonite occurs as euhedral crystals and platy cleavage fragments, and the main forms are {001}, {110}, {$1\bar{1}0$} and {010}. Small fragments are very pale brown. Bobshannonite has a very pale brown streak, hackly fracture and does not fluoresce under cathode or ultraviolet light. Cleavage is {001} very good, no parting was observed, Mohs hardness is ~4, and it is brittle, $D_{calc.}$ = 3.790 g/cm^3 (using the empirical formula and the single-crystal unit cell). Macroscopically, individual crystals do not show twinning. However diffraction data shows the presence of twinning and refinement gives

141 the ratio of twin components as 50:50 (see below). Because of extensive twinning,
142 bobshannonite does not extinguish properly under cross-polarized light. Thus we were unable to
143 optically orient a crystal on a spindle stage for measurement of 2*V* and refractive indices.
144 Cleavage fragments are colourless to very pale brown. There is no pleochroism in the plane of
145 the cleavage {001} but the colour changes from colourless to brown on rotation out of the plane
146 of cleavage.
147
148 **FTIR and Raman spectroscopy**
149 The FTIR spectrum of bobshannonite was collected on a crystal fragment using a Bruker
150 Hyperion 2000 IR microscope equipped with a liquid-nitrogen-cooled MCT detector. Spectra
151 over the range 4000–650 cm^{-1} were obtained by averaging 100 scans with a resolution of 4
152 cm^{-1}. Base-line correction was done using the OPUS spectroscopic software (Bruker Optic
153 GmbH). Raman spectra in the regions 100–1200 cm^{-1} and 3000–4000 cm^{-1} were collected in
154 back-scattered mode with a HORIBA Jobin Yvon-LabRAM ARAMIS integrated confocal micro-
155 Raman system equipped with a 460 mm focal length spectrograph and a multichannel air-
156 cooled (–70°C) CCD detector. A magnification of 100x was used with an estimated spot size of
157 ~1 μm, a 1800 gr/mm grating, and a 532 nm excitation laser. The wavenumber was calibrated
158 using the 520.7 cm^{-1} line of Si metal.
159 The FTIR and Raman spectra of bobshannonite in the OH-stretching region are shown
160 in Figs. 3*a* and 3*b*, respectively. Both spectra show a strong peak at ~3610 cm^{-1} and a weak
161 peak/shoulder at ~3655 cm^{-1} that are assigned to OH-stretching vibrations of the OH groups in
162 the structure of bobshannonite. Figure 4 shows the Raman spectrum of bobshannonite in the
163 fingerprint region (100–1200 cm^{-1}). In the 1200–650 cm^{-1} region, a strong peak at 901 cm^{-1} and
164 medium to low intensity peaks at 1038, 970, 716 and 680 cm^{-1} may be assigned to Si–O
165 stretching vibrations of the Si_2O_7 groups. Peaks at 608, 580, 510 and 410 cm^{-1} are assigned to
166 bending vibrations of Si_2O_7 groups and those below ~400 cm^{-1} (341, 310, 240, 207 and 143

167 cm^{-1}) are mainly due to lattice modes. The FTIR spectrum in the fingerprint region is not shown
168 because of band saturation.
169
170 **Chemical composition**
171 Crystals were analyzed with a Cameca SX-100 electron microprobe operating in wavelength-
172 dispersive mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a
173 beam diameter of 10 μm. The following standards were used: diopside (Si); $Mn(Ta_{1.7}Nb_{0.3})O_6$
174 (Ta); $Ba_2NaNb_5O_{15}$ (Nb,Ba); titanite (Ti); andalusite (Al); fayalite (Fe); spessartine (Mn);
175 forsterite (Mg); gahnite (Zn); Rb-leucite (Rb); albite (Na); orthoclase (K); fluor-riebeckite (F). The
176 elements Ca, Sr, Zr, Sn, Cs, Cr, Pb and V were sought but not detected. The data were reduced
177 and corrected by the *PAP* method of Pouchou and Pichoir (1985). The H_2O (confirmed by IR
178 spectroscopy, see above) was calculated by stoichiometry from the results of the crystal-
179 structure analysis on the basis that OH = 4 a.p.f.u. Table 2 gives the chemical composition for
180 bobshannonite (mean of nine determinations) and perraultite. The empirical formula of
181 bobshannonite on the basis of 38 anions is $Na_{1.89}(K_{0.94}Rb_{0.04})_{\Sigma 0.98}Ba_{0.96}(Mn_{6.84}Na_{0.53}Zn_{0.24}Fe^{2+}_{0.23}$
182 $Mg_{0.02}Al_{0.02})_{\Sigma 7.88}(Nb_{2.74}Ti_{1.26}Ta_{0.04})_{\Sigma 4.04}(Si_{8.07}O_{28})O_{9.32}H_{4.01}F_{0.68}$, Z = 4; the simplified formula is
183 $Na_2KBa(Mn,Na)_8(Nb,Ti)_4(Si_2O_7)_4O_4(OH)_4(O,F)_2$.
184 Bobshannonite and perraultite described by Chao (1991) [(1), Table 2] are from the
185 same locality: Poudrette quarry, Mont Saint-Hilaire, Québec, Canada. These two minerals are
186 characterized by lack of CaO and high contents of Nb_2O_5, K_2O and Na_2O: 19.69, 2.38 and 4.05
187 wt.%, respectively (bobshannonite) and 13.35, 2.68 and 3.52 wt.%, respectively (perraultite).
188 Hence in their formula units, Ti:Nb ≈ 1:1, Ba:K ≈ 1:1 and Na = 2 a.p.f.u. (Table 2). Whereas for
189 perraultite from the region by the Azov Sea [(2), Table 2], contents of Nb_2O_5, K_2O and Na_2O are
190 lower: Nb_2O_5 = 1.24, minor; K_2O = 1.67, Na_2O = 2.76 and CaO = 1.48 wt.%. Hence in the
191 formula unit of perraultite (2), Ti ≥ Nb, Ba > K and Na + Ca = 2 a.p.f.u., where Na > Ca.
192

193 **X-ray powder diffraction**

194 X-ray powder-diffraction data were collected with a Bruker D8 rotating-anode Discover
195 SuperSpeed micro-powder diffractometer with a multi-wire 2D detector using a Gandolfi
196 attachment. Data (for Cu*K*α) are given in Table 3. Unit cell parameters (space group $C\bar{1}$) refined
197 from powder data are as follows: *a* = 10.826(5), *b* = 13.896(6), *c* = 20.946(7) Å, α = 90.00(3), β
198 = 95.01(3), γ = 90.00(3)°, *V* = 3139(1) Å^3 and are close to the values determined by single-
199 crystal X-ray diffraction.
200
201 **Crystal structure**
202 *Data collection and structure refinement*
203 Single-crystal X-ray data for bobshannonite were collected using a Bruker APEX II ULTRA
204 three-circle diffractometer with a rotating-anode generator (Mo-*K*α), multilayer optics and an
205 APEX II 4K CCD detector. The intensities of 18496 reflections with –15 < *h* < 15, –19 < *k* < 19, –
206 29 < *l* < 29 were measured to 60° 2θ using 5 s per 0.3° frame. Unit-cell dimensions were
207 determined by least-squares refinement of 9550 reflections with *I* > 10σ*I*, and are given in Table
208 4, together with other miscellaneous information on data collection and structure refinement. An
209 absorption correction was done using the SADABS program (Sheldrick, 2008). All calculations
210 were done with the Bruker SHELXTL version 5.1 system of programs (Sheldrick, 2008). The
211 crystal-structure refinement of bobshannonite was done on a twinned crystal with two
212 components related by the twin matrix [100 0$\bar{1}$0 001]; lattice parameters being close to those of
213 perraultite, we tried to solve the structure in monoclinic symmetry in space groups *C*2/*m* and *C*2.
214 Both models produced high R_1 values (11.3% and 7.4%, respectively), and residual peaks
215 indicate the presence of twinning or disorder at the M^H sites. The *C*2 model yielded also non-
216 positive-definite adp's, even considering the mirror as a twin operation. The crystal structure
217 was therefore solved in space group $C\bar{1}$ and refined to R_1 = 2.55%, with a twin ratio of
218 0.5018(5):0.4982(5). The (Niggli) reduced unit cell is: *a* = 8.818(2), *b* = 8.818(2), *c* = 20.982(4)

Å, α = 93.09(3), β = 93.11(3), γ = 104.16(3)°, V = 1576(3) Å^3, $P\bar{1}$, Z = 2. The $P\bar{1}$ unit cell can be derived from the $C\bar{1}$ unit cell via the transformation matrix [½-½0 ½½0 001]. We chose the unconventional space group $C\bar{1}$ for better comparison with the structures of perraultite, surkhobite, jinshajiangite and cámaraite (Table 1). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson, 1992). In the crystal structure of bobshannonite, we identify 3 groups of cation sites: M^O sites of the O sheet, M^H and *Si* sites of the H sheet, and peripheral A^P and B^P sites which occur in the **I** block; site labeling is in accord with Sokolova (2006). We observed disorder at the A^P(2) site which is split into three A^P(21,22 and 23) subsites, partly occupied by K and minor Rb and separated by short distances: A^P(21)–A^P(22) = 1.064, A^P(21)–A^P(23) = 0.532, and A^P(22)–A^P(23) = 0.544 Å. Site-scattering values were refined for the M^O(1–10) sites with the scattering curve of Mn, M^H(1–4) sites (scattering curves of Nb + Ti), A^P(1) site (scattering curve of Ba), A^P(21–23) subsites (scattering curve of K) and B^P(1,2) sites (scattering curve of Na). The site-scattering values for the A^P(21–23) subsites were refined and then fixed. At the last stages of the refinement, four peaks were found in the difference-Fourier map which were included in the refinement as the H(1–4) atoms. The D (donor)–H distances were softly constrained to 0.98 Å. Final atom coordinates and anisotropic-displacement parameters are listed in Table 5, selected interatomic distances and framework angles are given in Table 6, refined site-scattering and assigned site-populations for selected cation sites are given in Table 7, bond-valence values in Table 8 and details of hydrogen bonding in Table 9. Observed and calculated structure-factors and a CIF file have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat.html.

Site-population assignment

Here we consider the cation sites of 3 groups: M^O sites of the O sheet, M^H and *Si* sites of the H sheet, and peripheral A^P and B^P sites. Consider first the M^H sites. We assign cations to these

sites based on our knowledge from previous work on Ti-disilicate minerals: Nb-dominant M^{H} sites are always fully occupied. Table 2 shows that the four M^{H} sites are occupied by 2.73 Nb, 1.27 Ti and 0.04 Ta, total 4.04 a.p.f.u. and the aggregate refined scattering at these sites (139.52 e.p.f.u., Table 7) is in close accord with this composition. Hence in accord with individual site-scattering values, we assign Nb + Ti to these four sites (Table 7) and the simplified composition of the four Nb-dominant M^{H} sites is $(Nb,Ti)_4$ a.p.f.u.

In the structures of Group-II TS-block minerals perraultite, jinshajiangite and surkhobite (Table 1), the peripheral A^P and B^P sites in the **I** (intermediate) block are occupied mainly by Ba > K and Na > Ca, respectively (Sokolova and Cámara, 2013). Bobshannonite does not contain Ca (Table 2); in accord with the refined site-scattering values for the B^P(1,2) sites, we assign 0.95 Na + 0.05 □ to the B^P(1) site and 0.94 Na + 0.06 □ to the B^P(2) site (Table 7). There are two A^P sites in the crystal structure of bobshannonite. The refined site-scattering value at the [10]-coordinated A^P(1) site is 53.1 e.p.f.u. (Table 7) and mean bond-length <A^P(1)–O> = 2.924 Å (Table 6) is consistent with ionic radius of Ba ($^{[10]}$r = 1.52 Å, Shannon, 1976). Therefore we assign all available Ba (Table 2) to the A^P(1) site: 0.95 Ba + 0.05 □ (Table 7). The A^P(2) site is split into three $^{[9]}A^P$(21), $^{[9]}A^P$(22) and $^{[10]}A^P$(23) subsites which are 0.532–1.064 Å apart (Table 6). Total scattering at the A^P(2) site is 19.93 e.p.f.u., and we assign 0.93 K + 0.07 Rb to the A^P(2) site [calculated scattering of 19.34 e.p.f.u., Table 7). Mean bond-length for three subsites varies from 3.058 to 3.211 Å (Table 6), consistent with the ionic radii of K ($^{[9]}$r = 1.55 and $^{[10]}$r = 1.59 Å, Shannon, 1976) and Rb ($^{[9]}$r = 1.63 and $^{[10]}$r = 1.66 Å, Shannon, 1976).

For the ten M^{O} sites, the following cations are available (Table 2): 6.85 Mn, 0.52 Na, 0.25 Zn, 0.23 Fe^{3+}, 0.03 Mg, 0.02 Al (total scattering 191.07 e.p.f.u.), and the aggregate refined scattering at these sites is 193.67 e.p.f.u. (Table 7) is in close accord with this composition. The refined site-scattering values at the ten M^{O} sites vary from 23.34 to 25.62 el per atom, hence order of Na (the second most abundant cation after Mn) does not occur in the O sheet. The mean bond-lengths around these sites are very close and values of aggregate cation radii

derived from observed mean bond-lengths are ≥ 0.83 Å ($^{[6]}$r for Mn) indicating disorder of cations over the ten Mn-dominant M^O sites.

Description of the structure

Topology of the structure

Bobshannonite is a TS-block mineral of Group II, Nb + Ti = 2 a.p.f.u. per $(Si_2O_7)_2$ (Sokolova, 2006). The overall topology of the crystal structure of bobshannonite (sp. gr. $C\bar{1}$) (Fig. 5*a*) is in accord with the perraultite structure-type (sp. gr. *C*2) (Yamnova *et al*., 1998). In the structure of bobshannonite, the M^O(1–10) octahedra form a close-packed O sheet (Fig. 5*b*). In the H sheet, SiO_4 tetrahedra link *via* common vertices to form Si_2O_7 groups that are oriented along **b** ($b = 2t_2$) (Figs. 5*a,b,c*). The Si_2O_7 groups and M^H octahedra share common vertices to form the two identical H sheets. An O sheet and two adjacent H sheets link through common vertices of SiO_4 tetrahedra and M^H and M^O octahedra to form a TS (Titanium Silicate) block parallel to (001) (Fig. 5*a*). Figure 5*a* shows that in the TS block, Si_2O_7 groups link to two M^O octahedra of the O sheet adjacent along **b,** as in Group II of Sokolova (2006). In bobshannonite, TS blocks are connected through common vertices of M^H octahedra (which are O and F atoms, O > F), plus cations of the **I** block: Ba and K at the A^P sites and Na at the B^P sites (Fig. 5*a*). In the cation layer of the **I** block, Ba and K are ordered at the A^P sites (Fig. 5*c*).

Cation sites

As stated above, the cation sites are divided into 3 groups: M^O sites of the O sheet, M^H and *Si* sites of the H sheet, and peripheral A^P and B^P sites which occur in the **I** block. Also in accord with Sokolova (2006), we label the X anions: $2X^O_M$ = common vertices of $3M^O$ and M^H polyhedra; $2X^O_A$ = common vertices of $3M^O$ and A^P polyhedra (where A^P–X^O_A < 3 Å); $2X^P_M$ = apical anions of M^H cations at the periphery of the TS block.

O sheet

There are ten [6]-coordinated M^{O} sites in the O sheet (Tables 6, 7) that contain 6.85 Mn + 0.52 Na + 0.25 Zn + 0.23 Fe^{2+} + 0.03 Mg + 0.02 Al = 3.90 a.p.f.u. (Table 2). The M^{O}(1,2,4,5,8,9) atoms are coordinated by four O atoms and two monovalent anions, X^{O}_{A} (see discussion below) with $<M^{O}–\varphi>$ = 2.190–2.251 Å (where φ = unspecified anion), respectively. The M^{O}(3,6,7,10) atoms are coordinated by five O atoms and a monovalent X^{O}_{A} anion, with $<M^{O}–\varphi>$ = 2.212–2.233 Å. We group the divalent cations (6.85 Mn + 0.25 Zn + 0.23 Fe^{2+} + 0.03 Mg = 7.36 M^{2+} = 7.36Mn*) and write the composition of the O sheet as follows 7.36 Mn* + 0.52 Na + 0.02 Al + 0.10 □ p.f.u., ideally (Mn_8Na) a.p.f.u. In perraultite, eight [6]-coordinated M^{O} sites give $Mn_5Fe^{2+}_3$ (Yamnova *et al*., 1998), ideally Mn_8 a.p.f.u.

H sheet

There are four [6]-coordinated Nb-dominant M^{H} sites in the H sheet (Tables 6, 7) each of which is coordinated by five O atoms and one X^{P}_{M} anion, (O,F), with $<M^{H}–\varphi>$ = 1.975 Å. Note the short distances from each M^{H} cation to each X^{O}_{M} anion: $M^{H}(1)–X^{O}_{M}(1)$ = 1.875 Å, $M^{H}(2)–X^{O}_{M}(2)$ = 1.872 Å, $M^{H}(3)–X^{O}_{M}(3)$ = 1.881 Å, and $M^{H}(4)–X^{O}_{M}(4)$ = 1.882 Å (Table 6). There are eight tetrahedrally coordinated *Si* sites occupied solely by Si, with $<Si–O>$ = 1.625 Å (Table 4). The cations of the two H sheets give $(Nb,Ti)_4$ a.p.f.u., *cf*. Ti_4 a.p.f.u. in perraultite.

Peripheral (P) sites

Four peripheral sites, 2 A^{P} and 2 B^{P}, are shifted from the TS block and occur as interstitial sites in the **I** block. The $^{[10]}A^{P}(1)$ site is occupied by Ba at 95% and is coordinated by ten O atoms, with $<A^{P}(1)–O>$ = 2.924 Å (Tables 6,7). Ideal composition of the $A^{P}(1)$ site is Ba a.p.f.u. The $A^{P}(2)$ site is split into three $^{[9]}A^{P}(21)$, $^{[9]}A^{P}(22)$ and

$^{[10]}A^{P}$(23) subsites which are 0.532–1.064 Å apart (Table 6) and are partly occupied by K + Rb, giving in total 0.93 K + 0.07 Rb, ideally K a.p.f.u. (Table 7). The total content of two A^{P} sites sums to ideally KBa a.p.f.u., with Z = 4. In perraultite (sp. gr. $C2$), two A^{P} sites (out of three) have partial occupancy; the total content of the $^{[10]}A^{P}$(1), $^{[9]}A^{P}$(2) and $^{[9]}A^{P}$(3) sites is $Ba_{1.26}K_{0.60}\square_{0.14}$, ideally Ba_2 a.p.f.u., with Z = 4.

The [10]-coordinated B^{P}(1,2) sites are occupied by Na at 95 and 94%, respectively, with a mean distance of 2.658 Å (Table 7). The ideal composition of the two B^{P}(1,2) sites is Na_2 a.p.f.u. In perraultite, the three [10]-coordinated B^{P} sites are occupied by $Na_{0.5}$, $Na_{0.25}Ca_{0.25}$ and $Na_{0.75}Ca_{0.25}$ (Yamnova *et al.*, 1998) giving in total $Na_{1.50}Ca_{0.50}$ a.p.f.u., ideally Na_2 p.f.u., Z = 4. We write the cation part of the structural formula of bobshannonite as the sum of (a) interstitial B^{P}_2 and A^{P}_2 cations (Na_2KBa), (b) M^{O}_8 cations of the O sheet $(Mn,Na)_8$, and (c) M^{H}_4 cations of the H sheets $(Nb,Ti)_4$, ideally $Na_2KBa(Mn,Na)_8(Nb,Ti)_4$.

Anion considerations

There are twenty-eight anions, O(1–28) (Table 5), that coordinate the Si cations and they are O atoms: bond-valence sums on these anions vary from 1.92 to 2.05 vu (valence units) (Table 8). Four anions, X^{O}_{M}(1–4), are ligands of three M^{O} cations and an M^{H} cation (Table 6) and they are O atoms, with bond-valence sums from 1.76 to 1.78 vu (Table 8). The anions at the X^{O}_{A}(1–4) sites are O atoms of OH groups (Tables 5, 7), with bond-valence sums of 1.14–1.15 vu (Table 8). Each OH group is bonded to three M^{O} cations of the O sheet (Fig. 5*b*). The H(1–4) atoms are involved in a weak hydrogen bonding with O atoms that belong to the H sheets (Table 9). There are two X^{P}_{M}(1,2) anions which are bridging anions for two M^{H} cations ($M^{H} \approx Nb_{0.67}Ti_{0.33}$) (Table 7). As chemical analysis gives F = 0.68 a.p.f.u. (Table 2), we assign $O_{1.32}F_{0.68}$ to the two X^{P}_{M} sites [= $O_{0.61}F_{0.39}$ per each X^{P}_{M} site]; this assignment is in accord with the bond-valence sums of 1.65 vu at each X^{P}_{M} anion (Table 8). The composition of an X^{P}_{M} anion correlates with

the composition of M^H cations: where M^H sites are locally occupied by Nb, the bridging anion is an O atom; where M^H sites are locally occupied by Ti, the bridging anion is an F atom. A similar phenomenon was noted for astrophyllite-group minerals (*cf*. niobophyllite, Cámara *et al.*, 2010). We can write the anion part of the formula as the sum of (1) the H sheet: O_{28} belonging to four Si_2O_7 groups + (2) the O sheet: four X^O_M and four X^O_A sites, giving O_4 and $(OH)_4$ + (3) the bridging anions of the M^H polyhedra at the periphery of the TS block: two X^P_M sites, giving $(O,F)_2$, ideally $(Si_2O_7)_4O_4(OH)_4(O,F)_2$.

In accord with the doubled perraultite-type general formula, $B^P_2A^P_2M^O_8{}^{[6]}M^H_4(Si_2O_7)_4X^O_8(X^P_M)_2$ (Sokolova, 2006), we write the structural formula of bobshannonite as $Na_2KBa(Mn,Na)_8(Nb,Ti)_4(Si_2O_7)_4O_4(OH)_4(O,F)_2$, $Z = 4$, in agreement with the empirical formula given above. The ideal structural formula of perraultite is $Na_2Ba_2Mn_8Ti_4(Si_2O_7)_4O_4(OH)_4F_2$, $Z = 4$ (Sokolova, 2006).

Related minerals of Group II

Ideal structural formulae for Group-II minerals bobshannonite, perraultite and jinshajiangite (the perraultite structure type) and cámaraite (related to the perraultite structure type) are presented in Table 10 (except for surkhobite as its ideal formula is similar to that of perraultite). Bobshannonite, perraultite and jinshajiangite have basic structures in accord with Sokolova and Cámara (2013), i.e., they have one type of TS block, one type of **I** block and adjacent TS blocks link to each other in the same way. In bobshannonite, perraultite and jinshajiangite, the O sheet has ideal compositions $(Mn,Na)_8$, Mn_8 and Fe^{2+}_8, respectively (Table 10). In bobshannonite, TS blocks are connected through O and F atoms at common vertices of Nb-dominant M^H octahedra, whereas in jinshajiangite and perraultite, TS blocks are connected through F atoms at common vertices of Ti-dominant M^H octahedra. In jinshajiangite and perraultite, Ba (Ba > K) and Na (Na > Ca) are the dominant constituents at the A^P and B^P sites in the **I** block, respectively. Bobshannonite does not have any Ca; Ba:K ~ 1:1, and Ba and K are ordered.

Bobshannonite is related to cámaraite, ideally $NaBa_3Fe^{2+}_8Ti_4(Si_2O_7)_4O_4(OH)_4F_3$. The structure of cámaraite has one type of TS block, two types of **I** block, and TS blocks link to each other in two different ways. Cámaraite has a derivative structure, i.e., its structure can be built of structural fragments of minerals of the same group, jinshajiangite and bafertisite. The *jinshajiangite* part of the cámaraite structure is topologically identical to the bobshannonite structure. The general and ideal structural formulae of cámaraite are written as sums of the corresponding formulae of bafertisite and jinshajiangite (Table 10).

Bobshannonite is a Nb-analogue of perraultite. To go from perraultite to bobshannonite, Nb substitutes for Ti in the H sheets, and to compensate for the increase in positive charge, Na substitutes for Mn in the O sheet, Na for Ca and K for Ba in the **I** block and O for F in the H sheets.

Acknowledgements

We thank Daniel Atencio and an anonymous reviewer for useful comments and Associate Editor Stuart Mills for handling the manuscript. We thank Mark Cooper for collecting single-crystal X-ray data for bobshannonite. This work was supported by a Canada Research Chair in Crystallography and Mineralogy and by a Discovery grant from the Natural Sciences and Engineering Research Council of Canada and by Innovation Grants from the Canada Foundation for Innovation to FCH.

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456

Figure captions

Fig. 1. Four groups of structures corresponding to different types of TS block: (*a*) Group I, linkage 1 of H and O sheets; (*b*) Group II, linkage 2; (*c*) Group III, linkage 1; (*d*) Group IV, linkage 3. *Linkage 1* occurs where two H sheets connect to the O sheet so that two Si_2O_7 groups on opposite sides of the O sheet link to *trans* edges of the same octahedron of the O sheet. *Linkage 2* occurs where two Si_2O_7 groups link to two octahedra of the O sheet adjacent along $\mathbf{t_2}$. *Linkage 3* occurs where two Si_2O_7 groups link to two octahedra adjacent approximately along $\mathbf{t_1}$. Only the Si_2O_7 groups of the H sheets are shown; dashed black lines represent positions of Si_2O_7 groups on the lower surface; M^H polyhedra are omitted for clarity. Si, Na, Ti and Mn polyhedra are orange, blue, pale yellow and magenta, respectively. F atoms are shown as yellow spheres, OH groups are shown as turquoise spheres in yoshimuraite and red spheres in epistolite. A typical mineral is indicated for each group.

Fig. 2. The crystal of bobshannonite, 0.4 x 0.4 x 0.5 mm.

Fig. 3. FTIR (*a*) and Raman (*b*) spectra of bobshannonite in the principal OH-stretching region.

Fig. 4. The Raman spectrum of bobshannonite.

Fig. 5. A general view of the crystal structure of bobshannonite which consists of TS (Titanium Silicate) and **I** (intermediate) blocks (*a*) and the details of the TS block: the close-packed O sheet of Mn-dominant octahedra (*b*) and the H sheet of Nb-dominant octahedra and Si_2O_7 groups (*c*). SiO_4 tetrahedra are orange, Nb-dominant and Mn-dominant octahedra are yellow and magenta, respectively; Ba, K and Na atoms in the **I** block are shown as raspberry, green

and blue spheres, respectively; O and H atoms of OH groups at the X^{O}_{A} sites are shown as turquoise and small white spheres.

TABLE 1. Comparison of bobshannonite, perraultite, surkhobite, jinshajiangite and cámaraite.

	Mn-dominant species				Fe^{2+}-dominant species	
Mineral *	Bobshannonite	Perraultite		Surkhobite	Jinshajiangite	Cámaraite
		[1]	[2]			
Simplified formula	$Na_2KBa(Mn,Na)_8(Nb,Ti)_4(Si_2O_7)_4O_4(OH)_4(O,F)_2$	[1] $Na_2KBaMn_8(Ti,Nb)_4(Si_2O_7)_4O_4(OH,F,H_2O)_7$ [2] $(Na,Ca)_2(Ba,K)_2(Mn,Fe)_8(Ti,Nb)_4(Si_2O_7)_4O_4(OH,F,O)_6$		$NaCa(Ba,K)_2(Mn,Fe^{2+},Fe^{3+})_8Ti_4(Si_2O_7)_4O_4(F,OH,O)_6$	$(Na,Ca)_2(Ba,K)_2Fe^{2+}{}_8Ti_4(Si_2O_7)_4O_4(OH)_4F_2$	$NaBa_3(Fe^{2+},Mn)_8Ti_4(Si_2O_7)_4O_4(OH)_4F_3$
Reference	(1)	(2)	(3,4)	(5)	(6,7)	(8,9)
Space group	$C\bar{1}$	*C*2/*m*, *Cm* or *C*2	*C*2	*C*2	*C*2/*m*	$C\bar{1}$
a (Å)	10.839(6)	10.82	10.731	10.723	10.6785	10.6965
b	13.912(8)	13.843	13.84	13.826	13.786	13.7861
c	20.98(1)	20.93	20.845	20.791	20.700	21.478
α (°)	89.99(1)	90	90	90	90	99.345
β	95.05(2)	95.09	95.06	95.00	94.937	92.315
γ	89.998(9)	90	90	90	90	89.993
Z	4	4	4	4	4	4
$D_{calc.}$ (g/cm^3)	3.790	3.808	3.67	3.98	3.767	4.018
$D_{meas.}$ (g/cm^3)	n.d.	3.71	n.d.	3.84	3.61	3.871
Strongest reflections in the X-ray powder diffraction data, *d*/n (Å) (I)	2.873(100)	3.474 (100)		3.454 (100)	3.44 (100)	2.629 (100)
	3.477(60)	10.43 (42)		2.592 (70)	3.15 (80)	2.788 (90)
	3.193(59)	2.606 (40)		2.074 (40)	2.630 (80)	1.721 (70)
	2.648(40)	3.186 (15)		10.39 (20)	2.570 (80)	3.394 (50)
	2.608(35)	2.084 (15)		3.186 (15)	10.2 (70)	3.182 (50)
	1.776(30)	2.867 (13)		2.862 (15)	1.715 (50 broad)	2.101 (50)
	1.733(28)	3.573 (11)		1.728 (15)	2.202 (40)	1.578 (50)
optical class, sign	–	biaxial (-)	biaxial (+)	biaxial (+)	biaxial (+)	biaxial (+)
α (589.3 nm)	–	1.785	1.79	$1.792_{calc.}$	1.792	> 1.80
β	–	1.81	1.810	1.801	1.801	–
γ	–	1.82	1.825	1.852	1.852	–
$2V_{meas}$ (°)	–	66(1)	80–85	72	72	93(1)

n.d. = not determined; * perraultite: [1] Mont Saint-Hilaire, Canada; [2] Azov Sea region, Russia; jinshajiangite: formula, space group, unit-cell parameters, $D_{calc.}$ (6); $D_{meas.}$ and optics (7).

References: (1) This work; (2) Chao (1991); (3) Pekov *et al.* (1999); (4) Yamnova *et al.* (1998); (5) Rastsvetaeva *et al.* (2008); (6) Sokolova *et al.* (2009a); (7) Hong and Fu (1982); (8) Sokolova *et al.* (2009b); (9) Cámara *et al.* (2009).

TABLE 2. Chemical analysis and formula unit for bobshannonite and perraultite.

Chemical analysis (wt.%)				Formula unit* (a.p.f.u.)			
Constituent	Bobshannonite	Perraultite**			Bobshannonite	Perraultite	
		(1)	(2)			(1)	(2)
Ta_2O_5	0.52		0.11	Ta	0.04	0	0.01
Nb_2O_5	19.69	13.35	1.24	Nb	2.73	1.77	0.017
ZrO_2	n.d.	0.12	1.09	Zr	0	0.02	0
TiO_2	5.50	9.44	17.83	Ti	1.27	2.08	3.86
SiO_2	26.31	27.32	27.72	ΣM^H	4.04	3.87	4.04
Fe_2O_3 ***	n.d.	n.d.	0.75				
Al_2O_3	0.06	0.03	0.03	Si	8.07	8.01	8.00
BaO	7.92	8.88	10.64	Zr	0	0	0.15
ZnO	1.02	n.d.	n.a.	Fe^{3+}	0	0	0.16
FeO	0.89	1.12	12.06	Al	0.02	0.01	0.01
MnO	26.34	31.14	19.28	Zn	0.25	0	0
MgO	0.06	0.06	0.04	Fe^{2+}	0.23	0.27	2.91
CaO	n.d.	n.d.	1.48	Mn	6.85	7.73	4.70
SrO	n.d.	n.d.	0.05	Mg	0.03	0.03	0.02
Rb_2O	0.42	n.a.	n.a.	Na	0.52	0.02	0
K_2O	2.38	2.68	1.67	ΣM^O	7.90	8.06	7.95
Na_2O	4.05	3.52	2.76				
F	0.70	0.84	2.18	Ba	0.95	1.02	1.20
H_2O †	1.96	3.49	1.79	Sr	0	0	0.01
O=F	-0.29	-0.35	-0.92	Rb	0.08	0	0
Total	97.53	101.64	99.80	K	0.93	1.00	0.61
				ΣA^P	1.96	2.02	1.81
				Ca	0	0	0.46
				Na	1.89	2.00	1.54
				ΣB^P	1.89	2.00	2.00
				OH	4.01	5.62	3.44
				F	0.68	0.78	1.99
				Σ(OH+F)	4.69	6.40	5.43
				Σcations	23.86	23.96	23.81
				Σanions	38.00	39.00	37.81

n.a. = not analyzed; n.d. = not detected;

* Formula calculated on: bobshannonite: 38 (O + F) a.p.f.u.; perraultite (1): 39 (O + F+ OH + H_2O) p.f.u.; perraultite (2): Si = 8 a.p.f.u.;

** Provenance for perraultite: (1) Mont Saint-Hilaire, Québec, Canada (Chao, 1991); (2) Eastern Azov region, Ukraine (Pekov *et al.*, 1999);

*** for perraultite (2), Fe^{2+}/Fe^{3+} determined by wet chemistry;

† content of H_2O: (a) bobshannonite: calculated from the crystal-structure refinement, supported by IR and Raman spectroscopy; (b) perraultite: (1) TGA; (2) Penfield method.

Table 3. Powder X-ray data* for bobshannonite.

	I_{rel}	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	h	k	l			I_{rel}	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	h	k	l	
	25	10.493	10.433	0	0	2			9	2.338	2.341	2	4	5	
	14	8.565	8.520	1	1	0					2.341	2	$\bar{4}$	5	
			8.520	$\bar{1}$	1	0			4	2.307	2.314	4	0	4	
Sh	8	8.126	8.085	$\bar{1}$	1	1					2.305	4	2	3	
			8.085	$\bar{1}$	$\bar{1}$	1					2.305	4	$\bar{2}$	3	
Br	6	7.740	7.704	1	1	1			10	2.230	2.235	$\bar{4}$	2	5	
			7.704	1	$\bar{1}$	1					2.235	$\bar{4}$	$\bar{2}$	5	
	25	6.612	6.592	0	2	1					2.227	$\bar{4}$	0	6	
			6.592	0	$\bar{2}$	1			19	2.199	2.199	$\bar{3}$	$\bar{5}$	1	
Br	10	5.116	5.114	2	0	1					2.199	$\bar{3}$	5	1	
Br	7	4.902	4.916	0	2	3					2.199	3	5	0	
			4.916	0	$\bar{2}$	3					2.199	$\bar{3}$	5	0	
	6	4.463	4.454	$\bar{2}$	0	3					2.197	0	6	3	
	13	4.271	4.260	2	2	0					2.197	0	$\bar{6}$	3	
			4.260	$\bar{2}$	2	0		Br	19	2.129	2.137	$\bar{2}$	4	7	
	16	4.092	4.092	2	0	3					2.137	$\bar{2}$	$\bar{4}$	7	
Br	5	3.860	3.852	2	2	2					2.130	4	4	0	
			3.852	2	$\bar{2}$	2					2.130	$\bar{4}$	4	0	
	14	3.579	3.578	0	2	5					2.116	$\bar{4}$	$\bar{4}$	2	**
			3.578	0	$\bar{2}$	5					2.116	$\bar{4}$	4	2	**
	60	3.477	3.478	0	0	6			18	2.087	2.087	0	0	10	
			3.474	0	4	0					2.080	4	2	5	
Sh	26	3.417	3.417	$\bar{2}$	2	4					2.080	4	$\bar{2}$	5	
			3.417	$\bar{2}$	$\bar{2}$	4			17	2.043	2.046	4	0	6	
	13	3.297	3.296	0	4	2					2.038	2	4	7	
			3.296	0	$\bar{4}$	2					2.038	2	$\bar{4}$	7	
	59	3.193	3.193	2	2	4			5	1.949	1.947	2	6	4	
			3.193	2	$\bar{2}$	4					1.947	2	$\bar{6}$	4	
Br	100	2.873	2.911	$\bar{2}$	$\bar{4}$	1	**		12	1.843	1.844	$\bar{2}$	6	6	
			2.911	$\bar{2}$	4	1	**				1.844	$\bar{2}$	$\bar{6}$	6	
			2.892	0	4	4					1.840	$\bar{2}$	0	11	
			2.892	0	$\bar{4}$	4			30	1.776	1.775	2	4	9	
			2.874	2	4	1					1.775	2	$\bar{4}$	9	
			2.874	2	$\bar{4}$	1		Br	28	1.733	1.739	0	8	0	**
	17	2.790	2.790	$\bar{2}$	2	6					1.728	$\bar{4}$	0	10	**
			2.790	$\bar{2}$	$\bar{2}$	6			6	1.652	1.653	$\bar{4}$	6	5	
	14	2.744	2.739	0	2	7					1.653	$\bar{4}$	$\bar{6}$	5	
			2.739	0	$\bar{2}$	7			13	1.627	1.626	$\bar{2}$	4	11	
Br	40	2.648	2.667	$\bar{4}$	0	2	**				1.626	$\bar{2}$	$\bar{4}$	11	
			2.648	2	4	3			20	1.601	1.601	$\bar{6}$	$\bar{4}$	1	
			2.648	2	$\bar{4}$	3					1.601	$\bar{6}$	4	1	
	35	2.608	2.608	0	0	8			13	1.583	1.585	4	0	10	
			2.607	2	2	6			8	1.554	1.555	0	4	12	
			2.607	2	$\bar{2}$	6					1.555	0	$\bar{4}$	12	
Wk	4	2.552	2.557	4	0	2	**				1.554	0	8	6	
Wk	6	2.488	2.489	$\bar{4}$	0	4	**				1.554	0	$\bar{8}$	6	
	16	2.447	2.448	$\bar{2}$	4	5									
			2.448	$\bar{2}$	$\bar{4}$	5									

*Br = broad reflection, Sh = shoulder, Wk = weak;
** Reflections were not used in the refinement of the unit-cell parameters.

TABLE 4. Miscellaneous refinement data for bobshannonite.

a (Å)	10.839(6)
b	13.912(8)
c	20.98(1)
α (°)	89.99(1)
β	95.05(2)
γ	89.998(9)
V (Å^3)	3152(5)
Refl. ($I_o > 10\sigma I$)	9550
Space group	$C\bar{1}$
Z	4
Absorption coefficient (mm^{-1})	6.25
F(000)	3420.6
$D_{calc.}$ (g/cm^3)	3.790
Crystal size (mm)	0.012 x 0.010 x 0.003
Radiation/monochromator	Mo-*K*α/graphite
$2\theta_{max}$ (°)	60.16
R(int) (%)	1.96
Second component (%)	49.82(5)
Reflections collected	18496
Independent reflections $F_o > 4\sigma F$	9261 7277
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
No. of refined parameters	618
Final *R*(obs) (%)	
R_1 [$F_o > 4\sigma F$]	2.55
R_1 [all data]	2.94
wR_2	7.40
Highest peak, deepest hole (e Å^{-3})	3.18 -1.32
Goodness of fit on F^2	1.072

TABLE 5. Atom coordinates and anisotropic displacement parameters (Å^2) for bobshannonite.

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}*
M^O(1)	0	½	½	0.0101(5)	0.0079(5)	0.0120(4)	-0.0010(3)	0.0019(3)	0.0006(4)	0.0099(3)
M^O(2)	0.25006(7)	0.50010(6)	0.99706(4)	0.0103(3)	0.0158(3)	0.0203(3)	-0.0081(2)	0.0080(2)	-0.0044(3)	0.01506(19)
M^O(3)	0.00056(6)	0.62412(6)	0.99471(3)	0.0084(3)	0.0097(3)	0.0105(3)	-0.0012(3)	0.00157(19)	0.0012(3)	0.0095(2)
M^O(4)	0.00007(7)	0.74953(6)	0.49732(4)	0.0101(3)	0.0161(3)	0.0228(3)	-0.0096(2)	0.0086(2)	-0.0053(3)	0.01590(19)
M^O(5)	¼	¾	0	0.0218(7)	0.0280(7)	0.0377(7)	0.0222(5)	0.0195(5)	0.0161(5)	0.0282(4)
M^O(6)	0.25142(6)	0.62283(5)	0.50642(3)	0.0074(3)	0.0078(3)	0.0093(3)	-0.0015(3)	0.00102(19)	0.0005(3)	0.0082(2)
M^O(7)	0.24922(6)	0.12620(6)	0.50514(3)	0.0090(3)	0.0092(3)	0.0115(3)	-0.0009(3)	0.0013(2)	0.0005(3)	0.0099(2)
M^O(8)	0	0	½	0.0195(6)	0.0242(6)	0.0420(7)	0.0232(5)	0.0228(5)	0.0129(5)	0.0274(4)
M^O(9)	¼	¼	0	0.0078(5)	0.0057(4)	0.0143(4)	0.0002(3)	0.0033(3)	-0.0010(4)	0.0091(3)
M^O(10)	-0.00136(6)	0.12678(6)	0.99365(3)	0.0088(3)	0.0092(3)	0.0118(3)	-0.0016(3)	0.0016(2)	-0.0003(3)	0.0099(2)
M^H(1)	0.14132(3)	0.14413(4)	0.84645(2)	0.00530(17)	0.0064(2)	0.01186(17)	0.00017(13)	0.00137(12)	0.00013(13)	0.00782(12)
M^H(2)	0.14096(3)	0.60712(4)	0.84513(2)	0.00452(17)	0.0073(2)	0.01240(17)	-0.00022(12)	0.00112(11)	0.00023(13)	0.00805(11)
M^H(3)	0.10916(3)	0.14368(4)	0.65531(2)	0.00527(17)	0.0070(2)	0.01236(17)	-0.00057(13)	0.00154(12)	-0.00006(14)	0.00817(12)
M^H(4)	0.10893(3)	0.60662(4)	0.65404(2)	0.00434(17)	0.0069(2)	0.01016(17)	-0.00030(12)	0.00076(11)	0.00007(14)	0.00713(12)
Si(1)	0.34501(11)	0.76669(9)	0.63092(5)	0.0081(5)	0.0067(5)	0.0060(4)	-0.0011(3)	0.0023(3)	-0.0017(4)	0.0069(2)
Si(2)	0.84373(11)	0.48387(8)	0.62989(5)	0.0058(4)	0.0068(5)	0.0072(4)	-0.0006(3)	-0.0003(3)	-0.0000(4)	0.0066(2)
Si(3)	0.40589(10)	0.48311(8)	0.86962(5)	0.0059(4)	0.0046(4)	0.0068(4)	0.0004(3)	-0.0003(3)	0.0009(4)	0.0058(2)
Si(4)	0.88463(10)	0.48405(8)	0.86893(5)	0.0062(4)	0.0044(5)	0.0070(4)	-0.0002(3)	0.0004(3)	-0.0000(4)	0.0059(2)
Si(5)	0.90582(11)	0.76732(8)	0.87027(5)	0.0081(5)	0.0062(4)	0.0058(4)	-0.0004(3)	-0.0000(3)	-0.0007(4)	0.0067(2)
Si(6)	0.36535(10)	0.48219(8)	0.63114(5)	0.0063(5)	0.0055(4)	0.0062(4)	0.0005(3)	0.0010(3)	0.0005(4)	0.0060(2)
Si(7)	0.38469(10)	0.76762(8)	0.86979(5)	0.0089(5)	0.0079(5)	0.0084(4)	-0.0013(4)	0.0029(3)	-0.0007(4)	0.0083(2)
Si(8)	0.86448(10)	0.76666(9)	0.63089(5)	0.0074(5)	0.0062(5)	0.0061(4)	-0.0005(3)	-0.0008(3)	0.0014(4)	0.0066(2)
A^P(1)	0.12507(3)	0.37491(4)	0.74992(1)	0.01224(8)	0.01272(8)	0.01054(7)	-0.00084(10)	0.00116(5)	-0.00049(11)	0.01183(5)
A^P(21)	0.1259(6)	0.9115(3)	0.7500(3)	0.0150(13)	0.040(2)	0.0153(13)	0.004(2)	0.0035(10)	0.000(2)	0.0231(9)
A^P(22)	0.1243(6)	0.8350(3)	0.7500(3)	0.0115(15)	0.0207(19)	0.0125(17)	0.0020(19)	-0.0034(12)	-0.000(2)	0.0152(9)
A^P(23)	0.8743(7)	0.1263(6)	0.2463(3)	0.0193(9)	0.039(2)	0.0180(14)	-0.003(3)	0.0009(9)	-0.008(3)	0.0256(9)
B^P(1)	0.3760(3)	0.6253(2)	0.75030(9)	0.0328(7)	0.0260(6)	0.0096(5)	-0.0050(7)	0.0001(4)	0.0176(9)	0.0229(4)
B^P(2)	0.8744(3)	0.6255(2)	0.75009(9)	0.0326(7)	0.0245(6)	0.0089(5)	-0.0052(7)	0.0002(4)	-0.0126(9)	0.0221(4)

TABLE 5. continued

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}*
O(1)	0.0962(3)	0.7474(3)	0.05257(14)	0.0104(13)	0.0100(13)	0.0070(11)	0.0006(10)	0.0007(9)	-0.0008(11)	0.0091(6)
O(2)	0.0952(3)	0.5074(3)	0.05471(15)	0.0153(14)	0.0177(16)	0.0084(11)	-0.0040(11)	0.0027(10)	-0.0022(13)	0.0137(6)
O(3)	0.1641(3)	0.7427(3)	0.44563(15)	0.0132(14)	0.0222(18)	0.0089(12)	-0.0044(12)	0.0045(10)	0.0027(13)	0.0145(7)
O(4)	0.8345(3)	0.4988(3)	0.55247(14)	0.0101(12)	0.0063(12)	0.0065(11)	0.0004(10)	-0.0019(9)	0.0027(11)	0.0078(5)
O(5)	0.8463(3)	0.7577(3)	0.55449(14)	0.0059(12)	0.0168(15)	0.0048(10)	-0.0001(10)	-0.0013(9)	0.0003(11)	0.0093(6)
O(6)	0.3464(3)	0.4972(3)	0.55359(14)	0.0059(12)	0.0101(13)	0.0074(11)	0.0006(10)	0.0022(9)	-0.0009(11)	0.0077(5)
O(7)	-0.0858(3)	0.7505(3)	0.94755(14)	0.0067(12)	0.0081(13)	0.0065(11)	0.0019(10)	-0.0004(9)	0.0052(11)	0.0072(5)
O(8)	0.4121(3)	0.4915(3)	0.94591(14)	0.0087(13)	0.0120(14)	0.0063(11)	0.0004(10)	0.0009(9)	0.0038(11)	0.0090(6)
O(9)	0.33585(18)	0.87588(15)	0.84886(8)	0.0100(10)	0.0087(11)	0.0133(8)	0.0021(8)	0.0003(7)	0.0026(9)	0.0107(4)
O(10)	0.2471(2)	0.69788(16)	0.66314(10)	0.0150(12)	0.0106(11)	0.0119(10)	0.0002(9)	0.0008(8)	-0.0025(9)	0.0125(5)
O(11)	0.2756(2)	0.69933(16)	0.83661(10)	0.0122(11)	0.0128(12)	0.0118(9)	-0.0008(9)	0.0009(8)	-0.0041(10)	0.0123(5)
O(12)	0.00208(19)	0.05267(16)	0.83723(10)	0.0065(10)	0.0131(11)	0.0133(10)	0.0025(9)	0.0013(7)	-0.0036(9)	0.0110(4)
O(13)	0.24776(19)	0.05245(15)	0.66414(10)	0.0075(10)	0.0093(11)	0.0138(10)	-0.0025(8)	0.0023(8)	0.0035(9)	0.0101(4)
O(14)	0.0024(2)	0.69867(16)	0.83608(10)	0.0153(12)	0.0125(12)	0.0104(10)	-0.0026(9)	-0.0004(8)	0.0030(10)	0.0128(5)
O(15)	-0.0264(2)	0.05212(16)	0.66358(10)	0.0086(10)	0.0113(11)	0.0160(10)	-0.0044(9)	0.0020(8)	-0.0043(9)	0.0119(5)
O(16)	-0.0256(2)	0.69748(16)	0.66326(10)	0.0133(11)	0.0098(11)	0.0123(10)	0.0013(8)	-0.0005(8)	0.0038(10)	0.0119(5)
O(17)	0.30150(18)	0.87549(15)	0.65001(8)	0.0103(10)	0.0099(11)	0.0151(8)	-0.0014(8)	0.0038(7)	0.0001(9)	0.0116(4)
O(18)	-0.05142(18)	0.87518(14)	0.85021(8)	0.0113(10)	0.0042(10)	0.0135(8)	0.0015(8)	0.0020(6)	0.0008(8)	0.0096(4)
O(19)	-0.01558(19)	0.49934(17)	0.66146(10)	0.0034(10)	0.0136(11)	0.0156(10)	0.0021(9)	-0.0015(8)	-0.0022(9)	0.0110(4)
O(20)	0.2653(2)	0.49947(16)	0.83815(10)	0.0106(11)	0.0082(10)	0.0154(10)	-0.0022(8)	-0.0001(8)	0.0000(9)	0.0114(4)
O(21)	0.2647(2)	0.25080(16)	0.83897(10)	0.0125(11)	0.0098(11)	0.0127(9)	0.0010(8)	-0.0031(8)	-0.0017(10)	0.0119(5)
O(22)	0.23616(19)	0.49931(17)	0.66297(10)	0.0081(10)	0.0106(11)	0.0162(10)	0.0035(9)	0.0045(8)	0.0037(9)	0.0114(4)
O(23)	0.0130(2)	0.50025(17)	0.83692(10)	0.0087(10)	0.0100(11)	0.0164(11)	-0.0011(9)	0.0026(8)	-0.0016(10)	0.0116(5)
O(24)	-0.0158(2)	0.25074(17)	0.66227(10)	0.0080(10)	0.0145(12)	0.0127(10)	-0.0033(8)	-0.0022(8)	0.0032(10)	0.0119(5)
O(25)	0.91444(18)	0.87413(15)	0.65122(8)	0.0112(10)	0.0046(11)	0.0163(8)	0.0004(8)	-0.0014(7)	-0.0009(9)	0.0109(4)
O(26)	0.2764(2)	0.05282(16)	0.83770(10)	0.0084(10)	0.0108(11)	0.0149(10)	0.0009(8)	0.0030(8)	0.0025(9)	0.0113(4)
O(27)	0.0140(2)	0.25027(17)	0.83770(10)	0.0105(11)	0.0147(12)	0.0105(10)	0.0007(8)	0.0026(8)	0.0010(10)	0.0118(5)
O(28)	0.7362(2)	0.75013(17)	0.66347(10)	0.0095(11)	0.0137(12)	0.0105(9)	-0.0018(9)	0.0036(8)	-0.0030(10)	0.0111(5)

TABLE 5. continued

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq} *
$X^{O}_{M}(1)$	0.1544(2)	0.1357(2)	0.93598(11)	0.0122(12)	0.0189(15)	0.0070(10)	-0.0014(9)	0.0037(8)	-0.0043(11)	0.0125(6)
$X^{O}_{M}(2)$	0.1529(2)	0.6123(2)	0.93463(11)	0.0120(12)	0.0098(13)	0.0102(10)	0.0009(9)	-0.0010(8)	-0.0006(10)	0.0108(6)
$X^{O}_{M}(3)$	0.0954(2)	0.1371(2)	0.56542(11)	0.0129(12)	0.0143(14)	0.0094(10)	0.0015(9)	0.0034(9)	0.0019(10)	0.0120(6)
$X^{O}_{M}(4)$	0.0972(2)	0.6147(3)	0.56415(11)	0.0117(12)	0.0273(18)	0.0116(11)	0.0006(11)	0.0000(9)	-0.0002(12)	0.0169(7)
$X^{O}_{A}(1)$	0.1636(3)	0.3750(3)	0.95578(10)	0.0151(13)	0.0056(13)	0.0024(9)	0.0024(12)	-0.0007(8)	0.0081(13)	0.0078(5)
$X^{O}_{A}(2)$	0.3341(3)	0.6264(3)	0.04255(13)	0.0085(12)	0.0176(16)	0.0222(13)	-0.0024(16)	0.0020(10)	0.0102(15)	0.0160(6)
$X^{O}_{A}(3)$	0.0849(3)	0.3778(3)	0.54474(13)	0.0160(14)	0.0166(17)	0.0190(13)	-0.0032(16)	0.0016(11)	0.0102(16)	0.0172(7)
$X^{O}_{A}(4)$	0.0861(3)	0.8740(3)	0.54288(10)	0.0192(14)	0.0081(14)	0.0010(9)	0.0024(12)	0.0003(9)	0.0077(14)	0.0095(6)
$X^{P}_{M}(1)$	0.12569(15)	0.60157(18)	0.74977(7)	0.0130(13)	0.0143(11)	0.0076(11)	0.0010(6)	-0.0013(9)	-0.0002(8)	0.0118(6)
$X^{P}_{M}(2)$	0.12494(16)	0.14852(19)	0.75064(7)	0.0126(13)	0.0182(10)	0.0021(10)	-0.0007(7)	0.0020(9)	0.0004(9)	0.0109(5)
H(1)	0.184(4)	0.348(3)	0.9152(12)							0.0093
H(2)	0.329(4)	0.651(4)	0.0862(10)							0.0192
H(3)	0.083(4)	0.394(4)	0.5901(8)							0.0206
H(4)	0.058(4)	0.902(4)	0.5824(13)							0.0114

* U_{iso} for H(1)-H(4)

TABLE 6. Selected interatomic distances (Å) and angles (°) in bobshannonite.

$M^{O}(1)$–$X^{O}_{A}(3)$a	2.113(4)	x2	$M^{O}(2)$–$X^{O}_{A}(1)$	2.125(4)		$M^{O}(3)$–$X^{O}_{A}(1)$e	2.138(3)
$M^{O}(1)$–O(4)b	2.186(3)	x2	$M^{O}(2)$–O(8)	2.141(3)		$M^{O}(3)$–$X^{O}_{M}(2)$	2.170(3)
$M^{O}(1)$–$X^{O}_{M}(4)$	2.285(2)	x2	$M^{O}(2)$–O(2)c	2.156(3)		$M^{O}(3)$–O7	2.187(4)
$<M^{O}(1)–\varphi>$	2.195		$M^{O}(2)$–$X^{O}_{A}(2)$c	2.162(4)		$M^{O}(3)$–O(2)c	2.246(4)
			$M^{O}(2)$–$X^{O}_{M}(2)$	2.240(3)		$M^{O}(3)$–O(1)c	2.296(4)
			$M^{O}(2)$–$X^{O}_{M}(1)$d	2.521(3)		$M^{O}(3)$–O(2)a	2.304(4)
			$<M^{O}(2)–\varphi>$	2.224		$<M^{O}(3)–\varphi>$	2.224
$M^{O}(4)$–O(5)f	2.141(3)					$M^{O}(6)$–$X^{O}_{A}(4)$h	2.120(3)
$M^{O}(4)$–$X^{O}_{A}(3)$a	2.150(5)		$M^{O}(5)$–O(1)	2.079(3)	x2	$M^{O}(6)$–$X^{O}_{M}(4)$	2.152(3)
$M^{O}(4)$–$X^{O}_{A}(4)$	2.151(4)		$M^{O}(5)$–$X^{O}_{A}(2)$	2.108(4)	x2	$M^{O}(6)$–O(6)	2.216(4)
$M^{O}(4)$–O(3)	2.164(3)		$M^{O}(5)$–$X^{O}_{M}(2)$g	2.532(3)	x2	$M^{O}(6)$–O(4)b	2.248(3)
$M^{O}(4)$–$X^{O}_{M}(3)$a	2.248(3)		$<M^{O}(5)–\varphi>$	2.240		$M^{O}(6)$–O(3)	2.257(4)
$M^{O}(4)$–$X^{O}_{M}(4)$	2.517(4)					$M^{O}(6)$–O(3)h	2.278(4)
$<M^{O}(4)–\varphi>$	2.229		$M^{O}(8)$–O(6)i	2.090(3)	x2	$<M^{O}(6)–\varphi>$	2.212
			$M^{O}(8)$–$X^{O}_{A}(4)$a	2.146(4)	x2		
$M^{O}(7)$–$X^{O}_{A}(3)$i	2.160(3)		$M^{O}(8)$–$X^{O}_{M}(3)$	2.518(3)	x2	$M^{O}(10)$–$X^{O}_{A}(2)$k	2.134(3)
$M^{O}(7)$–$X^{O}_{M}(3)$	2.185(3)		$<M^{O}(8)–\varphi>$	2.251		$M^{O}(10)$–$X^{O}_{M}(1)$	2.165(3)
$M^{O}(7)$–O(4)j	2.196(4)					$M^{O}(10)$–O(1)a	2.210(4)
$M^{O}(7)$–O(5)b	2.240(4)		$M^{O}(9)$–$X^{O}_{A}(1)$g	2.147(4)	x2	$M^{O}(10)$–O(8)d	2.244(4)
$M^{O}(7)$–O(6)i	2.306(4)		$M^{O}(9)$–O(7)a	2.173(3)	x2	$M^{O}(10)$–O(7)e	2.264(4)
$M^{O}(7)$–O(5)j	2.310(4)		$M^{O}(9)$–$X^{O}_{M}(1)$g	2.273(3)	x2	$M^{O}(10)$–O(8)j	2.294(4)
$<M^{O}(7)–\varphi>$	2.233		$<M^{O}(9)–\varphi>$	2.198		$<M^{O}(10)–\varphi>$	2.219
$M^{H}(1)$–$X^{O}_{M}(1)$	1.875(3)		$M^{H}(2)$–$X^{O}_{M}(2)$	1.872(3)		$M^{H}(3)$–$X^{O}_{M}(3)$	1.881(3)
$M^{H}(1)$–O(26)	1.959(2)		$M^{H}(2)$–O(11)	1.963(2)		$M^{H}(3)$–O(15)	1.963(2)
$M^{H}(1)$–O(12)	1.971(2)		$M^{H}(2)$–O(14)	1.966(2)		$M^{H}(3)$–O(13)	1.963(2)
$M^{H}(1)$–$X^{P}_{M}(2)$	2.003(2)		$M^{H}(2)$–$X^{P}_{M}(1)$	1.995(2)		$M^{H}(3)$–$X^{P}_{M}(2)$	1.994(2)
$M^{H}(1)$–O(21)	2.013(2)		$M^{H}(2)$–O(20)	2.029(2)		$M^{H}(3)$–O(28)j	2.020(2)
$M^{H}(1)$–O(27)	2.018(3)		$M^{H}(2)$–O(23)	2.030(2)		$M^{H}(3)$–O(24)	2.027(2)
$<M^{H}(1)–\varphi>$	1.973		$<M^{H}(2)–\varphi>$	1.976		$<M^{H}(3)–\varphi>$	1.975
$M^{H}(4)$–$X^{O}_{M}(4)$	1.882(3)						
$M^{H}(4)$–O(16)	1.952(2)						
$M^{H}(4)$–O(10)	1.960(3)						
$M^{H}(4)$–$X^{P}_{M}(1)$	2.002(2)						
$M^{H}(4)$–O(19)	2.027(2)						
$M^{H}(4)$–O(22)	2.030(2)						
$<M^{H}(4)–\varphi>$	1.976						
Si(1)–O(3)h	1.606(4)		Si(2)–O(19)m	1.623(3)		Si(3)–O(8)	1.600(3)
Si(1)–O(24)s	1.608(3)		Si(2)–O(13)s	1.625(2)		Si(3)–O(12)s	1.616(3)
Si(1)–O(10)	1.621(3)		Si(2)–O(4)	1.632(3)		Si(3)–O(20)	1.622(3)
Si(1)–O(17)	1.645(2)		Si(2)–O(17)n	1.642(3)		Si(3)–O(18)n	1.633(2)
<Si(1)–O>	1.620		<Si(2)–O>	1.631		<Si(3)–O>	1.618

TABLE 6. continued

Si(4)–O(2)b	1.602(4)	Si(5)–O(21)s	1.627(3)	Si(6)–O(22)	1.621(2)
Si(4)–O(26)s	1.608(3)	Si(5)–O(14)m	1.629(2)	Si(6)–O(15)s	1.627(2)
Si(4)–O(23)m	1.613(3)	Si(5)–O(7)m	1.633(3)	Si(6)–O(6)	1.636(3)
Si(4)–O(9)n	1.638(3)	Si(5)–O(18)m	1.636(3)	Si(6)–O(25)j	1.637(3)
<Si(4)–O>	1.615	<Si(5)–O>	1.631	<Si(6)–O>	1.630
Si(7)–O(27)s	1.626(2)	Si(8)–O(5)	1.603(3)	Si(1)–O(17)–Si(2)o	133.6(1)
Si(7)–O(11)	1.625(3)	Si(8)–O(28)	1.619(2)	Si(3)o–O(18)–Si(5)f	133.3(1)
Si(7)–O(1)h	1.637(4)	Si(8)–O(16)m	1.632(3)	Si(4)o–O(9)–Si(7)	133.2(1)
Si(7)–O(9)	1.643(3)	Si(8)–O(25)	1.634(3)	Si(6)s–O(25)–Si(8)	132.9(1)
<Si(7)–O>	1.633	<Si(8)–O>	1.622	<Si–O–Si>	133.3
A^P(1)–O(28)j	2.853(2)	A^P(21)–O(9)	2.983(7)	A^P(22)–O(25)f	2.990(6)
A^P(1)–O(22)	2.857(3)	A^P(21)–O(17)	2.996(6)	A^P(22)–O(11)	3.004(6)
A^P(1)–O(24)	2.864(2)	A^P(21)–O(25)f	2.997(7)	A^P(22)–O(14)	3.004(6)
A^P(1)–O(23)	2.870(2)	A^P(21)–O(18)	3.014(6)	A^P(22)–O(9)	3.008(6)
A^P(1)–O(20)	2.872(2)	A^P(21)–O(13)p	3.042(6)	A^P(22)–O(18)	3.011(7)
A^P(1)–O(27)	2.870(3)	A^P(21)–O(15)p	3.051(6)	A^P(22)–O(17)	3.019(7)
A^P(1)–O(21)	2.875(3)	A^P(21)–O(26)p	3.064(6)	A^P(22)–O(16)	3.016(5)
A^P(1)–O(19)	2.875(3)	A^P(21)–O(12)p	3.073(6)	A^P(22)–O(10)	3.027(6)
A^P(1)–X^P_M(2)	3.150(3)	A^P(21)–X^P_M(2)p	3.298(5)	A^P(22)–X^P_M(1)	3.248(5)
A^P(1)–X^P_M(1)	3.154(3)	< A^P(21)–O>	3.058	< A^P(22)–φ>	3.036
< A^P(1)–φ>	2.924				
A^P(23)–O(9)b	2.894(7)	B^P(1)–O(12)s	2.404(3)	B^P(2)–O(13)s	2.395(3)
A^P(23)–O(18)b	2.911(7)	B^P(1)–O(15)s	2.410(3)	B^P(2)–O(14)m	2.404(3)
A^P(23)–O(25)q	3.000(7)	B^P(1)–O(10)	2.422(4)	B^P(2)–O(16)m	2.418(3)
A^P(23)–O(17)b	3.016(7)	B^P(1)–O(11)	2.423(3)	B^P(2)–O(26)s	2.423(3)
A^P(23)–O(11)b	3.324(8)	B^P(1)–X^P_M(2)s	2.717(4)	B^P(2)–X^P_M(2)s	2.724(4)
A^P(23)–O(14)b	3.333(7)	B^P(1)–X^P_M(1)	2.733(4)	B^P(2)–X^P_M(1)m	2.745(4)
A^P(23)–O(12)r	3.388(8)	B^P(1)–O(27)s	2.853(3)	B^P(2)–O(28)	2.841(4)
A^P(23)–O(26)r	3.388(7)	B^P(1)–O(22)	2.871(3)	B^P(2)–O(23)m	2.851(4)
A^P(23)–O(16)b	3.429(7)	B^P(1)–O(24)s	2.866(4)	B^P(2)–O(21)s	2.885(3)
A^P(23)–O(10)b	3.430(8)	B^P(1)–O(20)	2.879(4)	B^P(2)–O(19)m	2.890(3)
< A^P(23)–O>	3.211	< B^P(1)–φ>	2.658	< B^P(2)–φ>	2.658
Short distances					
A^P(21)– A^P(22)	1.064(4)				
A^P(21)– A^P(23)b	0.532(8)				
A^P(22)– A^P(23)b	0.544(8)				

φ = O, F, OH

Symmetry operators: a: -*x*, -*y*+1, -*z*+1; b: -*x*+1, -*y*+1, -*z*+1; c: *x*, *y*, *z*+1; d: -*x*+½, -*y*+½, -*z*+2; e: -*x*, -*y*+1, -*z*+2; f: *x*-1, *y*, *z*; g: *x*, *y*, *z*-1; h: -*x*+½, -*y*+$^3/_2$, -*z*+1; i: -*x*+½, -*y*+½, -*z*+1; j: *x*-½, *y*-½, *z*; k: *x*-½, *y*-½, *z*+1; m: *x*+1, *y*, *z*; n: *x*+½, *y*-½, *z*; o: *x*-½, *y*+½, *z*; p: *x*, *y*+1, *z*; q: -*x*+2, -*y*+1, -*z*+1; r: -*x*+1, -*y*, -*z*+1; s: *x*+½, *y*+½, *z*.

TABLE 7. Refined site-scattering values and assigned site-populations for bobshannonite.

Site *	Refined site-scattering (e.p.f.u.)	Assigned site-population (a.p.f.u.)	Calculated site-scattering (e.p.f.u.)	<X-φ>$_{obs.}$** (Å)	Simplified composition (a.p.f.u.)
		Cations			
M^{O}(1)	12.06(7)			2.195	
M^{O}(2)	25.64(9)			2.224	
M^{O}(3)	23.34(9)			2.224	
M^{O}(4)	25.62(9)			2.229	
M^{O}(5)	11.95(7)	7.36 Mn*** + 0.52 Na + 0.02 Al + 0.10 □		2.240	
M^{O}(6)	23.44(9)			2.212	
M^{O}(7)	23.41(9)			2.233	
M^{O}(8)	12.08(7)			2.251	
M^{O}(9)	12.26(7)			2.198	
M^{O}(10)	23.87(9)			2.219	
ΣM^{O}(1-10)	193.67	7.36 Mn*** + 0.52 Na + 0.02 Al + 0.10 □	191.07		$(Mn,Na)_8$
M^{H}(1)	35.04(9)	0.69 Nb + 0.31 Ti	35.11	1.973	
M^{H}(2)	35.22(9)	0.71 Nb + 0.29 Ti	35.49	1.976	
M^{H}(3)	34.74(9)	0.67 Nb + 0.33 Ti	34.73	1.975	
M^{H}(4)	34.52(9)	0.66 Nb + 0.34 Ti	34.54	1.976	
ΣM^{H}(1-4)	139.52	2.73 Nb + 1.27 Ti	139.87		$(Nb,Ti)_4$
$^{[10]}A^{P}$(1)	53.10(6)	0.95 Ba + 0.05 □	53.20	2.924	Ba
$^{[9]}A^{P}$(21)	7.05†			3.058	
$^{[9]}A^{P}$(22)	5.02†	0.93 K + 0.07 Rb		3.036	
$^{[10]}A^{P}$(23)	7.86†			3.211	
ΣA^{P}(2)	19.93	0.93 K + 0.07 Rb	19.34		K
$^{[10]}B^{P}$(1)	10.43(6)	0.95 Na + 0.05 □	10.45	2.658	
$^{[10]}B^{P}$(2)	10.32(6)	0.94 Na + 0.06 □	10.34	2.658	
ΣB^{P}(1-2)	20.75	1.89 Na + 0.11 □	20.79		Na_2
		Anions			
X^{O}_{M}(1-4)		4.00 O			O_4
X^{O}_{A}(1-4)		4.00 (OH)			$(OH)_4$
X^{P}_{M}(1,2)		1.32 O + 0.68 F			$(O,F)_2$

* coordination number is given only for non-[6]-coordinated sites;
** X = cation, φ = O, OH, F; 7.36 Mn*** = 6.85 Mn + 0.25 Zn + 0.23 Fe^{2+} + 0.03 Mg;
† site scattering was refined and then fixed.

TABLE 8. Bond-valence values* for bobshannonite.

Atom**	$M^O(1)$	$M^O(2)$	$M^O(3)$	$M^O(4)$	$M^O(5)$	$M^O(6)$	$M^O(7)$	$M^O(8)$	$M^O(9)$	$M^O(10)$	$M^H(1)$	$M^H(2)$	$M^H(3)$	$M^H(4)$
O(1)			0.25		$0.44^{x2}\downarrow$					0.32				
O(2)		0.36	0.29 0.25											
O(3)				0.35		0.28 0.27								
O(4)	$0.33^{x2}\downarrow$					0.29	0.33							
O(5)				0.38			0.29 0.25							
O(6)						0.31	0.25	$0.43^{x2}\downarrow$						
O(7)			0.33						$0.35^{x2}\downarrow$	0.28				
O(8)		0.38								0.29 0.26				
O(9)														
O(10)														0.80
O(11)												0.80		
O(12)											0.78			
O(13)													0.80	
O(14)												0.78		
O(15)													0.80	
O(16)														0.81
O(17)														
O(18)														
O(19)														0.67
O(20)												0.67		
O(21)											0.70			
O(22)														0.67
O(23)												0.67		
O(24)													0.67	
O(25)														
O(26)											0.80			
O(27)											0.69			
O(28)													0.69	
$X^O_M(2)$		0.29	0.35		$0.15^{x2}\downarrow$						0.99			
$X^O_M(3)$				0.29			0.34	$0.15^{x2}\downarrow$				0.98		
$X^O_M(4)$	$0.26^{x2}\downarrow$		0.15		0.37							0.98		
$X^O_M(1)$		0.15							$0.27^{x2}\downarrow$	0.35	1.0			
$^{[3]}X^O_A(1)$		0.39	0.38						$0.37^{x2}\downarrow$					
$^{[3]}X^O_A(2)$		0.36			$0.41^{x2}\downarrow$				0.38					
$^{[3]}X^O_A(3)$	$0.41^{x2}\downarrow$		0.37			0.36								
$^{[3]}X^O_A(4)$				0.37		0.40		$0.37^{x2}\downarrow$						
$X^P_M(1)$												0.68		0.67
$X^P_M(2)$											0.67		0.68	
Total	2.00	1.93	1.85	1.91	2.00	1.92	1.82	1.90	1.98	1.88	4.64	4.59	4.62	4.60
Aggr. Charge											4.70	4.71	4.67	4.66

* Bond-valence parameters (vu) are from Brown (1981); bond-valence contributions calculated for $M^O = Mn^{2+}$; bond-valence contributions from $M^H(1)$-$M^H(4)$ cations calculated for $M^H = Nb_{0.67}Ti_{0.33}$; coordination numbers are shown for non-4-coordinated anions.

TABLE 8. continued.

	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Si(6)	Si(7)	Si(8)	$A^P(1)$	$A^P(21)$	$A^P(22)$	$A^P(23)$	$B^P(1)$	$B^P(2)$	Σ
O(1)							0.96								1.97
O(2)				1.05											1.95
O(3)	1.04														1.94
O(4)		0.97													1.92
O(5)								1.05							1.97
O(6)						0.96									1.95
O(7)					0.97										1.93
O(8)			1.06												1.99
O(9)				0.96			0.96			0.03	0.02	0.03			2.00
O(10)	1.00										0.02	0.01	0.17		2.00
O(11)							0.99				0.02	0.01	0.17		1.99
O(12)			1.02							0.02		0.01	0.17		2.00
O(13)		0.99								0.03				0.18	2.00
O(14)					0.98						0.02	0.01		0.18	1.97
O(15)						0.99				0.03			0.17		1.99
O(16)								0.97			0.02	0.01		0.17	1.98
O(17)	0.94	0.95								0.03	0.02	0.02			1.96
O(18)			0.97		0.96					0.03	0.02	0.03			2.01
O(19)		1.00							0.20					0.08	1.95
O(20)			1.00						0.20				0.09		1.96
O(21)					0.99				0.20					0.08	1.97
O(22)						1.0			0.21				0.09		1.97
O(23)				1.02					0.20					0.08	1.97
O(24)	1.04								0.20				0.09		2.00
O(25)						0.96		0.97		0.03	0.02	0.02			2.00
O(26)				1.04						0.02		0.01		0.17	2.04
O(27)							0.99		0.20				0.09		1.97
O(28)								1.01	0.21					0.08	1.99
$X^O_M(1)$															1.77
$X^O_M(2)$															1.78
$X^O_M(3)$															1.76
$X^O_M(4)$															1.76
$^{[3]}X^O_A(1)$															1.14
$^{[3]}X^O_A(2)$															1.15
$^{[3]}X^O_A(3)$															1.14
$^{[3]}X^O_A(4)$															1.14
$X^P_M(1)$									0.10		0.01		0.10	0.09	1.65
$X^P_M(2)$									0.10	0.01			0.10	0.09	1.65
Total	4.02	3.91	4.05	4.07	3.90	3.91	3.90	4.00	1.82	0.23	0.17	0.16	1.24	1.20	
Aggr. Charge	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	1.90	←	0.98	→	0.95	0.94	

TABLE 9. Hydrogen bonding in bobshannonite.

D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	∠ DHA (°)
X^{O}_{A}(1)OH–H(1)…O(21)	0.98(1)	2.32(2)	3.266(3)	163(4)
X^{O}_{A}(2)OH–H(2)…O(9)a	0.98(1)	2.37(4)	3.054(4)	126(4)
X^{O}_{A}(3)OH–H(3)…O(19)	0.98(1)	2.41(3)	3.242(4)	143(4)
X^{O}_{A}(3)OH–H(3)…O(22)	0.98(1)	2.61(4)	3.315(4)	129(4)
X^{O}_{A}(4)OH–H(4)…O(25)b	0.99(1)	2.25(3)	3.062(3)	139(4)

a: $-x+½, -y+{}^{3}/_{2}, -z+1$; b: $x-1, y, z$.

TABLE 10. Structural formulae of selected Group-II TS-block minerals*.

Mineral	Structure type	Structural formula, Z = 4							Ref.
		B^{P}_{2}	A^{P}_{2}	$\mathbf{M^{O}_{8}}$	$\mathbf{M^{H}_{4}}$	$\mathbf{(Si_2O_7)_4}$	$\mathbf{X^{O}_{8}}$	X^{P}_{2}	
Bobshannonite	B1(GII)	Na_2	K Ba	$\mathbf{(Mn,Na)_8}$	$\mathbf{(Nb,Ti)_4}$	$\mathbf{(Si_2O_7)_4}$	$\mathbf{O_4(OH)_4}$	$(O,F)_2$	(1)
Perraultite	B1(GII)	Na_2	Ba_2	$\mathbf{Mn_8}$	$\mathbf{Ti_4}$	$\mathbf{(Si_2O_7)_4}$	$\mathbf{O_4(OH)_4}$	F_2	(2)
Jinshajiangite	B1(GII)	Na_2	Ba_2	$\mathbf{Fe^{2+}_8}$	$\mathbf{Ti_4}$	$\mathbf{(Si_2O_7)_5}$	$\mathbf{O_4(OH)_4}$	F_2	(3)
		B^{P}	A^{P}_{3}	$\mathbf{M^{O}_{8}}$	$\mathbf{M^{H}_{4}}$	$\mathbf{(Si_2O_7)_4}$	$\mathbf{X^{O}_{8}}$	X^{P}_{3}	
Cámaraite	D1(GII)	Na	Ba_3	$\mathbf{Fe^{2+}_8}$	$\mathbf{Ti_4}$	$\mathbf{(Si_2O_7)_4}$	$\mathbf{O_4(OH)_4}$	F_3	(4)
Jinshaijiangite component	B1(GII)	Na	Ba	$\mathbf{Fe^{2+}_4}$	$\mathbf{Ti_2}$	$\mathbf{(Si_2O_7)_2}$	$\mathbf{O_2(OH)_2}$	F	(3)
Bafertisite component	B2(GII)		Ba_2	$\mathbf{Fe^{2+}_4}$	$\mathbf{Ti_2}$	$\mathbf{(Si_2O_7)_2}$	$\mathbf{O_2(OH)_2}$	F_2	(5)

*Formulae are given only for minerals with accurately refined structures. Structure types for basic (B) and derivative (D) structures of Group II (GII) and general formulae are from Sokolova and Cámara (2013). The invariant core of the TS block, $\mathbf{M^{O}_4M^{H}_2(Si_2O_7)_2X^{O}_4}$, is shown in bold: M^{H} = cations of the H sheet, M^{O} = cations of the O sheet, X^{O}_4 = anions of the O sheet not shared with Si; A^{P} and B^{P} = cations at the peripheral (*P*) sites (Sokolova, 2006). The formula of cámaraite is the sum of the formulae of jinshajiangite and bafertisite.

References: (1) This work; (2) Yamnova *et al*. (1998); (3) Sokolova *et al*. (2009a); (4) Cámara *et al*. (2009); (5) Guan *et al*. (1963).

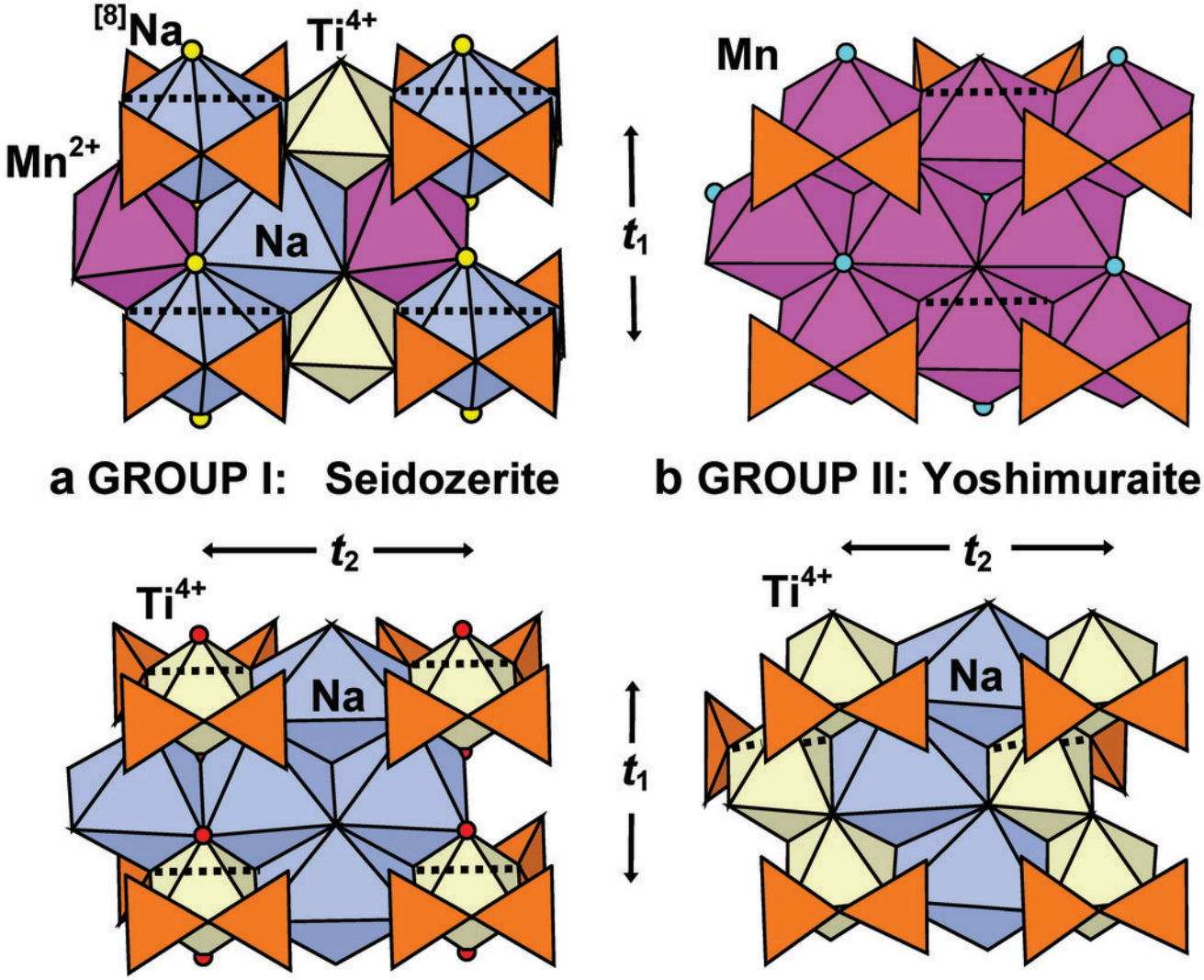
[8]Na
Ti4+
Mn2+
Na
t1
Mn
a GROUP I: Seidozerite
b GROUP II: Yoshimuraite
t2
Ti4+
Na
t1
t2
Ti4+
Na
c GROUP III: Epistolite
d GROUP IV: Murmanite

Fig. 1

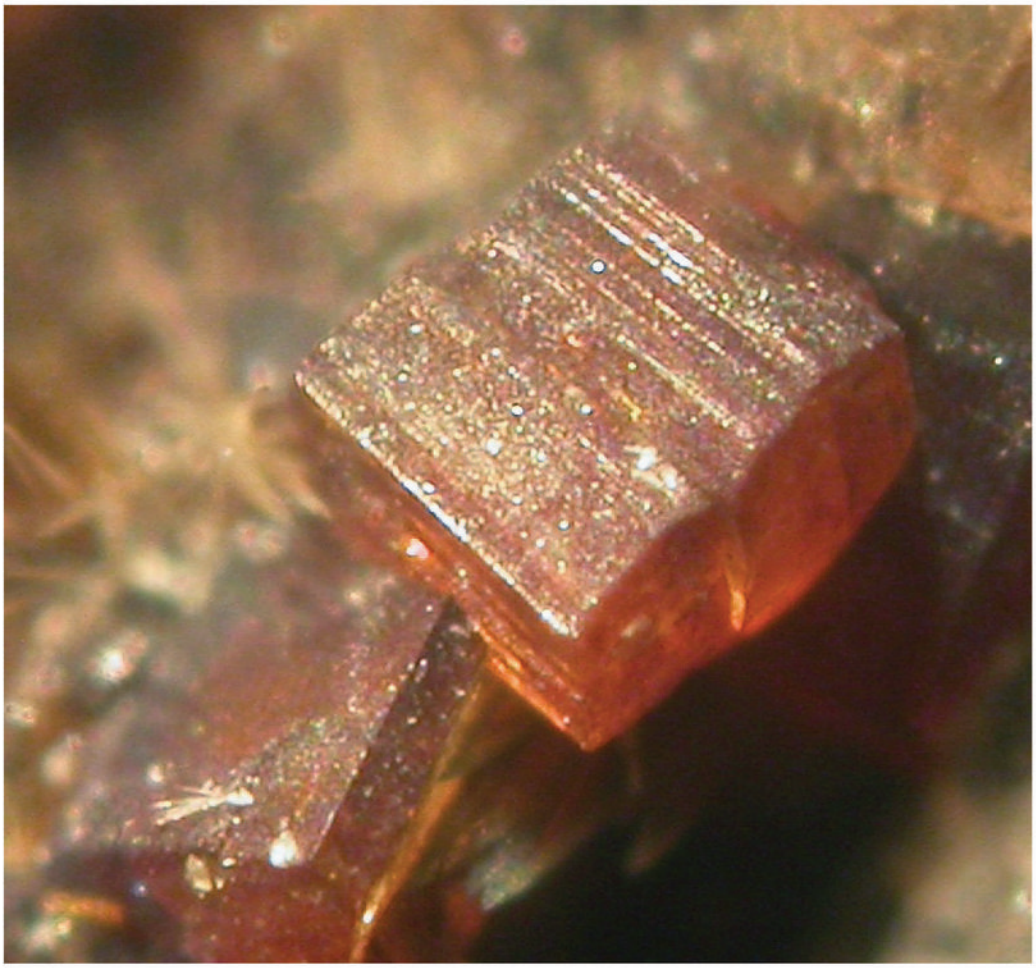

Fig. 2

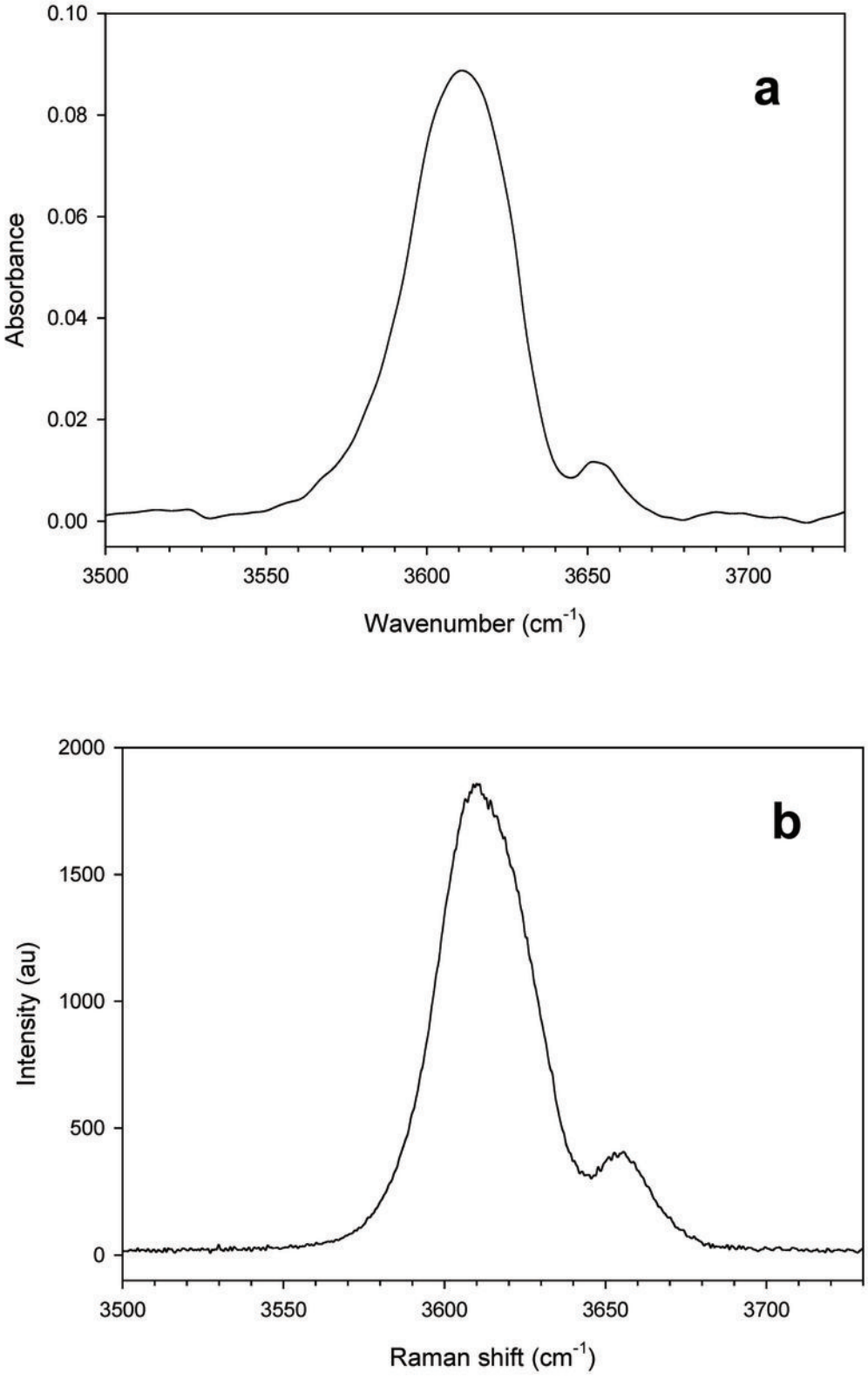
a
Absorbance
0.10
0.08
0.06
0.04
0.02
0.00
3500
3550
3600
3650
3700
Wavenumber (cm-1)
b
Intensity (au)
2000
1500
1000
500
0
3500
3550
3600
3650
3700
Raman shift (cm-1)

Fig. 3

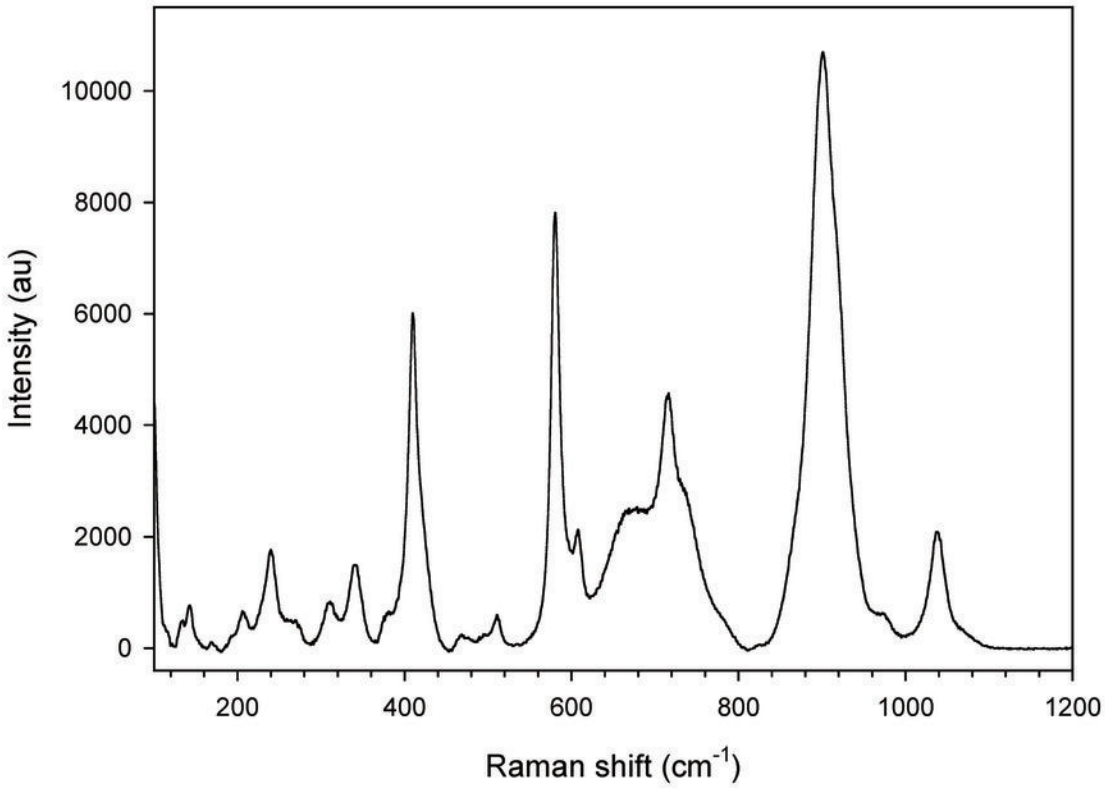
Intensity (au)
10000
8000
6000
4000
2000
0
200
400
600
800
1000
1200
Raman shift (cm-1)

Fig. 4

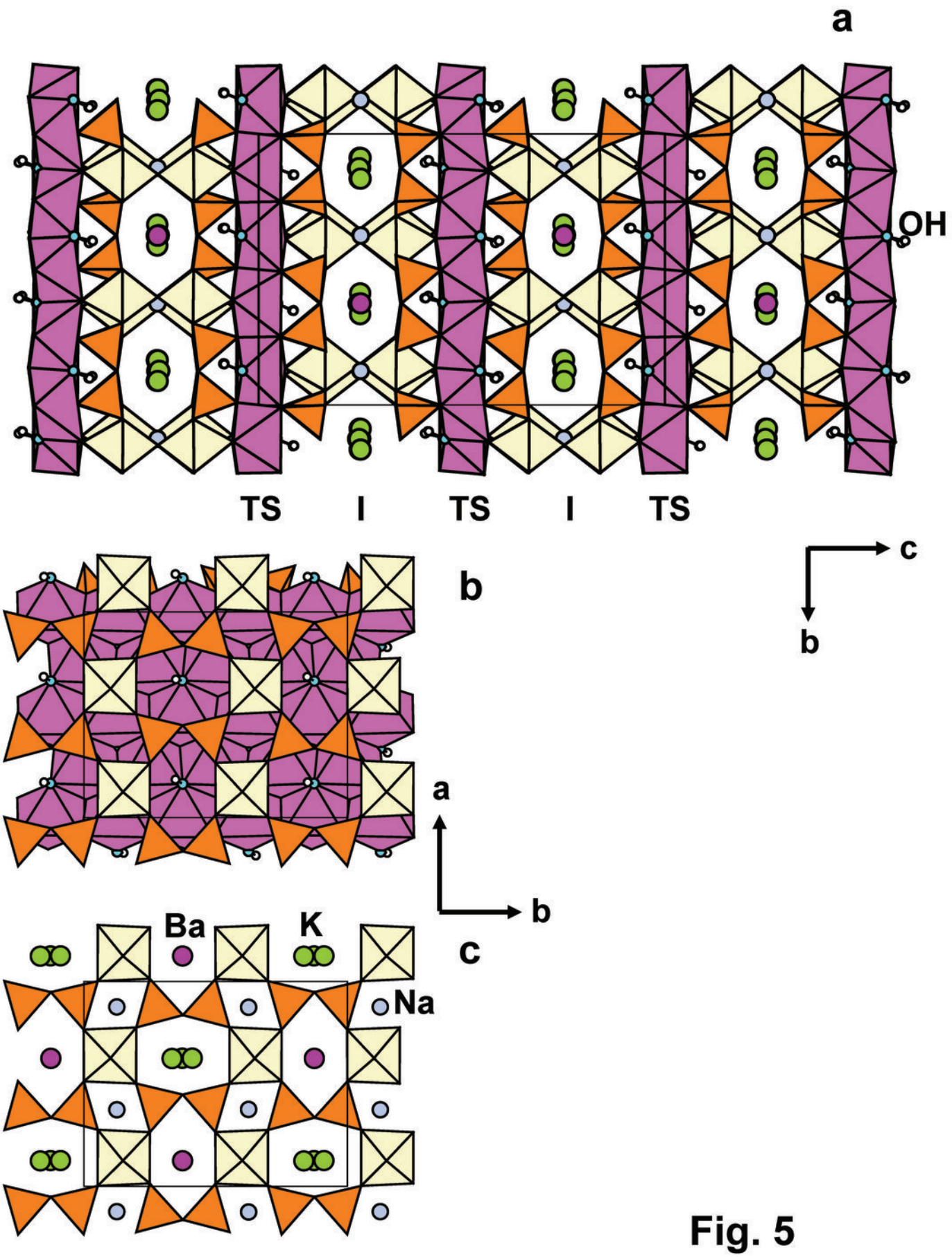

Fig. 5