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

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Bobshannonite, $\text{Na}_2\text{KBa}(\text{Mn},\text{Na})_8(\text{Nb},\text{Ti})_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH})_4(\text{O},\text{F})_2$, a new TS-block mineral from
Mont Saint-Hilaire, Québec, Canada: Description and crystal structure

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24 **Abstract**

25 Bobshannonite, $\text{Na}_2\text{KBa}(\text{Mn,Na})_8(\text{Nb,Ti})_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH})_4(\text{O,F})_2$, is a new TS-block mineral from
26 Mont Saint-Hilaire, Québec, Canada. It occurs as blocky crystals 0.5–1 mm across, perched on
27 sérandite and albite. Other associated minerals are epididymite, catapleiite, aegirine,
28 kupletskite, rhodochrosite and rhabdophane-(Ce). Bobshannonite occurs as vitreous to frosty,
29 transparent to translucent very pale brown to orange brown crystals, has a very pale brown
30 streak, hackly fracture and does not fluoresce under cathode or ultraviolet light. Cleavage is
31 $\{001\}$ very good, no parting was observed, and Mohs hardness is ~4, and it is brittle, $D_{\text{calc.}} =$
32 3.790 g/cm^3 . Crystals are extensively twinned and do not extinguish in cross-polarized light.
33 Bobshannonite is triclinic, $C\bar{1}$, $a = 10.839(6)$, $b = 13.912(8)$, $c = 20.98(1) \text{ \AA}$, $\alpha = 89.99(1)$, $\beta =$
34 $95.05(2)$, $\gamma = 89.998(9)^\circ$, $V = 3152(5) \text{ \AA}^3$. The six strongest reflections in the X-ray powder
35 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,
36 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, ($0 0 8$, $2 2 6$,
37 $2 \bar{2} 6$); 1.776, 30, ($2 4 9$). Chemical analysis by electron microprobe gave Ta_2O_5 0.52, Nb_2O_5
38 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
39 0.06, Rb_2O 0.42, K_2O 2.38, Na_2O 4.05, F 0.70, $\text{H}_2\text{O}_{\text{calc.}}$ 1.96, $\text{O}=\text{F} -0.29$, total 97.53 wt.%, where
40 the H_2O content was calculated from the crystal-structure analysis. The empirical formula on the
41 basis of 38 anions is $\text{Na}_{1.89}(\text{K}_{0.94}\text{Rb}_{0.04})_{\Sigma 0.98}\text{Ba}_{0.96}(\text{Mn}_{6.84}\text{Na}_{0.53}\text{Zn}_{0.24}\text{Fe}^{2+}_{0.23}\text{Mg}_{0.02}\text{Al}_{0.02})_{\Sigma 7.88}$
42 $(\text{Nb}_{2.74}\text{Ti}_{1.26}\text{Ta}_{0.04})_{\Sigma 4.04}(\text{Si}_{8.07}\text{O}_{28})\text{O}_{9.32}\text{H}_{4.01}\text{F}_{0.68}$, $Z = 4$. The crystal structure was refined to $R_1 =$
43 2.55% on the basis of 7277 unique reflections [$F > 4\sigma(F)$] and can be described as a
44 combination of a TS (Titanium Silicate) block and an I (intermediate) block. The TS block
45 consists of HOH sheets (H-heteropolyhedral, O-octahedral). The topology of the TS block is as
46 in Group II of the Ti disilicates: $\text{Ti} + \text{Nb} = 2$ a.p.f.u. per $(\text{Si}_2\text{O}_7)_2$ [as defined by Sokolova (2006)].
47 In the O sheet, ten $^{[6]}\text{M}^{\text{O}}$ sites are occupied mainly by Mn, less Na and minor Zn, Fe^{2+} , Mg and
48 Al, with $\langle \text{M}^{\text{O}}-\varphi \rangle = 2.223 \text{ \AA}$. In the H sheet, four $^{[6]}\text{M}^{\text{H}}$ sites are occupied by Nb and Ti ($\text{Nb} > \text{Ti}$),
49 with $\langle \text{M}^{\text{H}}-\varphi \rangle = 1.975 \text{ \AA}$, and eight $^{[4]}\text{Si}$ sites are occupied by Si, with $\langle \text{Si}-\text{O} \rangle = 1.625 \text{ \AA}$. 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 $A^{\text{P}}(1)$ and $A^{\text{P}}(2)$ 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

63 Introduction

64 Bobshannonite, $\text{Na}_2\text{KBa}(\text{Mn,Na})_8(\text{Nb,Ti})_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH})_4(\text{O,F})_2$, is a new TS-block mineral of
65 Group II, $\text{Ti} + \text{Nb} = 2$ a.p.f.u. per $(\text{Si}_2\text{O}_7)_2$ (Sokolova, 2006).

66 The TS (Titanium Silicate) block is the main structural unit in thirty-nine minerals
67 (including bobshannonite): 34 minerals are listed in Sokolova and Cámara (2013), and
68 information on four minerals, kolskyite, emmerichite, saamite and betalomonosovite, can be
69 found in Cámara *et al.* (2013), Aksenov *et al.* (2014), Cámara *et al.* (2014) and Sokolova *et al.*
70 (2014), respectively. The TS block consists of a central trioctahedral (O) sheet and two adjacent
71 heteropolyhedral (H) sheets of [5-7]-coordinated polyhedra and Si_2O_7 groups. The TS block is
72 characterized by a planar cell based on minimal lengths of translational vectors, $t_1 \sim 5.5$ and $t_2 \sim$
73 7 \AA , and $t_1 \wedge t_2 \approx 90^\circ$. The general formula of the TS block is $A^P_2B^P_2M^H_2M^O_4(\text{Si}_2\text{O}_7)_2X_{4+n}$, where
74 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,
75 Nb, Fe^{2+} , Fe^{3+} , Mg, Mn, Ca, Na; A^P and B^P = cations at the peripheral (P) sites = Na, Ca + REE,
76 Ca, Ba, Sr, K; X = anions, O, OH, F, and H_2O groups; $X_{4+n} = X^O_4 + X^P_n$, $n = 0, 1, 1.5, 2, 4$
77 (Sokolova and Cámara, 2013). Sokolova (2006) developed general structural principles for the
78 TS-block minerals. There are three topologically distinct TS blocks based on three types of
79 linkage of H and O sheets. In the crystal structures of TS-block minerals, TS blocks either link
80 directly or alternate with intermediate (I) blocks. The I block consists of alkali and alkaline-earth
81 cations, oxyanions (PO_4), (SO_4) and (CO_3), and H_2O groups. Sokolova (2006) divided TS-block
82 structures into four Groups, based on the topology and stereochemistry of the TS block. Each
83 group of structures has a different linkage, content and stereochemistry of $\text{Ti} (+ \text{Nb} + \text{Zr} + \text{Fe}^{3+} +$
84 $\text{Mg} + \text{Mn})$ (atoms per formula unit) per $(\text{Si}_2\text{O}_7)_2$ (Fig. 1). In Group I, $\text{Ti} (+ \text{Nb} + \text{Zr}) = 1$ a.p.f.u.
85 (Fig. 1a); in Group II, $\text{Ti} (+ \text{Nb}) = 2$ a.p.f.u. (Fig. 1b); in Group III, $\text{Ti} (+ \text{Nb} + \text{Mg} + \text{Fe}^{3+}) = 3$
86 a.p.f.u. (Fig. 1c); in Group IV, $\text{Ti} (+ \text{Mg} + \text{Mn}) = 4$ a.p.f.u. (Fig. 1d). In a TS-block structure, four
87 types of self-linkage between adjacent TS blocks occur. Sokolova and Cámara (2013)
88 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 t_2 in the O sheet (Fig. 1b).
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 cámaraité, 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

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

118

119 **Occurrence**

120 The mineral occurs in the pegmatite-rich western part in the Poudrette quarry, Mont Saint-
121 Hilaire, La Vallée-du-Richelieu RCM, Monterégie, Québec, Canada (45°33'46"N 73°08'30"W).

122 The type specimen was not found *in situ*, hence not much is known about the size, shape or
123 complete mineral assemblage of the source pegmatite which was completely destroyed by
124 blasting, but the observed mineralogy is typical for Mont Saint-Hilaire sérandite and epididymite-
125 rich pegmatites. Associated minerals are sérandite, albite, epididymite (rich), catapleiite,
126 aegirine (2 generations), kupletskite, rhodochrosite (two generations), rhabdophane-(Ce) and a
127 black undetermined botryoidal mineral, possibly a Mn oxide. Bobshannonite is of hydrothermal
128 origin and exceedingly rare.

129

130 **Physical properties**

131 Bobshannonite occurs as vitreous to frosty, transparent to translucent (thin crystals), orange-
132 brown (large fragments) blocky crystals some 0.5–1.0 mm across, perched on sérandite and
133 albite (Fig. 2). The type specimen is 2.5 x 2.3 x 2 cm and consists of ~90% sérandite with the
134 associated minerals making up the balance. Bobshannonite occurs as euhedral crystals and
135 platy cleavage fragments, and the main forms are {001}, {110}, $\{1\bar{1}0\}$ and {010}. Small
136 fragments are very pale brown. Bobshannonite has a very pale brown streak, hackly fracture
137 and does not fluoresce under cathode or ultraviolet light. Cleavage is {001} very good, no
138 parting was observed, Mohs hardness is ~4, and it is brittle, $D_{\text{calc.}} = 3.790 \text{ g/cm}^3$ (using the
139 empirical formula and the single-crystal unit cell). Macroscopically, individual crystals do not
140 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 $2V$ 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 $4000\text{--}650\text{ cm}^{-1}$ 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 $100\text{--}1200\text{ cm}^{-1}$ and $3000\text{--}4000\text{ cm}^{-1}$ 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 $\sim 1\text{ }\mu\text{m}$, 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. 3a and 3b, respectively. Both spectra show a strong peak at $\sim 3610\text{ cm}^{-1}$ and a weak
161 peak/shoulder at $\sim 3655\text{ cm}^{-1}$ 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 ($100\text{--}1200\text{ cm}^{-1}$). In the $1200\text{--}650\text{ cm}^{-1}$ 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 $\sim 400\text{ cm}^{-1}$ ($341, 310, 240, 207$ 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); $\text{Mn}(\text{Ta}_{1.7}\text{Nb}_{0.3})\text{O}_6$
174 (Ta); $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (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 $\text{OH} = 4$ 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 $\text{Na}_{1.89}(\text{K}_{0.94}\text{Rb}_{0.04})_{\Sigma 0.98}\text{Ba}_{0.96}(\text{Mn}_{6.84}\text{Na}_{0.53}\text{Zn}_{0.24}\text{Fe}^{2+}_{0.23}$
182 $\text{Mg}_{0.02}\text{Al}_{0.02})_{\Sigma 7.88}(\text{Nb}_{2.74}\text{Ti}_{1.26}\text{Ta}_{0.04})_{\Sigma 4.04}(\text{Si}_{8.07}\text{O}_{28})\text{O}_{9.32}\text{H}_{4.01}\text{F}_{0.68}$, $Z = 4$; the simplified formula is
183 $\text{Na}_2\text{KBa}(\text{Mn,Na})_8(\text{Nb,Ti})_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH})_4(\text{O,F})_2$.

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, $\text{Ti:Nb} \approx 1:1$, $\text{Ba:K} \approx 1:1$ and $\text{Na} = 2$ 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: $\text{Nb}_2\text{O}_5 = 1.24$, minor; $\text{K}_2\text{O} = 1.67$, $\text{Na}_2\text{O} = 2.76$ and $\text{CaO} = 1.48$ wt.%. Hence in the
191 formula unit of perraultite (2), $\text{Ti} \geq \text{Nb}$, $\text{Ba} > \text{K}$ and $\text{Na} + \text{Ca} = 2$ a.p.f.u., where $\text{Na} > \text{Ca}$.

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 CuK 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, $\alpha = 90.00(3)$, β
198 $= 95.01(3)$, $\gamma = 90.00(3)^\circ$, $V = 3139(1)$ Å³ 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 $60^\circ 2\theta$ using 5 s per 0.3° frame. Unit-cell dimensions were
207 determined by least-squares refinement of 9550 reflections with $I > 10\sigma I$, 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 $C2/m$ and $C2$.
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^{II} sites. The $C2$ 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: $a = 8.818(2)$, $b = 8.818(2)$, $c = 20.982(4)$

219 Å, $\alpha = 93.09(3)$, $\beta = 93.11(3)$, $\gamma = 104.16(3)^\circ$, $V = 1576(3) \text{ \AA}^3$, $P\bar{1}$, $Z = 2$. The $P\bar{1}$ unit cell can be
220 derived from the $C\bar{1}$ unit cell via the transformation matrix $[\frac{1}{2}-\frac{1}{2}0 \frac{1}{2}\frac{1}{2}0 001]$. We chose the
221 unconventional space group $C\bar{1}$ for better comparison with the structures of perraultite,
222 surkhobite, jinshajiangite and cámaraitite (Table 1). Scattering curves for neutral atoms were
223 taken from the International Tables for Crystallography (Wilson, 1992). In the crystal structure of
224 bobshannonite, we identify 3 groups of cation sites: M^O sites of the O sheet, M^H and Si sites of
225 the H sheet, and peripheral A^P and B^P sites which occur in the I block; site labeling is in accord
226 with Sokolova (2006). We observed disorder at the $A^P(2)$ site which is split into three $A^P(21,22$
227 and 23) subsites, partly occupied by K and minor Rb and separated by short distances: $A^P(21)$ –
228 $A^P(22) = 1.064$, $A^P(21)$ – $A^P(23) = 0.532$, and $A^P(22)$ – $A^P(23) = 0.544 \text{ \AA}$. Site-scattering values
229 were refined for the $M^O(1-10)$ sites with the scattering curve of Mn, $M^H(1-4)$ sites (scattering
230 curves of Nb + Ti), $A^P(1)$ site (scattering curve of Ba), $A^P(21-23)$ subsites (scattering curve of K)
231 and $B^P(1,2)$ sites (scattering curve of Na). The site-scattering values for the $A^P(21-23)$ subsites
232 were refined and then fixed. At the last stages of the refinement, four peaks were found in the
233 difference-Fourier map which were included in the refinement as the H(1-4) atoms. The D
234 (donor)–H distances were softly constrained to 0.98 \AA . Final atom coordinates and anisotropic-
235 displacement parameters are listed in Table 5, selected interatomic distances and framework
236 angles are given in Table 6, refined site-scattering and assigned site-populations for selected
237 cation sites are given in Table 7, bond-valence values in Table 8 and details of hydrogen
238 bonding in Table 9. Observed and calculated structure-factors and a CIF file have been
239 deposited with the Principal Editor of *Mineralogical Magazine* and are available from
240 www.minersoc.org/pages/e_journals/dep_mat.html.

241

242 *Site-population assignment*

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

245 sites based on our knowledge from previous work on Ti-disilicate minerals: Nb-dominant M^H
246 sites are always fully occupied. Table 2 shows that the four M^H sites are occupied by 2.73 Nb,
247 1.27 Ti and 0.04 Ta, total 4.04 a.p.f.u. and the aggregate refined scattering at these sites
248 (139.52 e.p.f.u., Table 7) is in close accord with this composition. Hence in accord with
249 individual site-scattering values, we assign Nb + Ti to these four sites (Table 7) and the
250 simplified composition of the four Nb-dominant M^H sites is $(\text{Nb,Ti})_4$ a.p.f.u.

251 In the structures of Group-II TS-block minerals perraultite, jinshajiangite and surkhobite
252 (Table 1), the peripheral A^P and B^P sites in the I (intermediate) block are occupied mainly by Ba
253 > K and Na > Ca, respectively (Sokolova and Cámara, 2013). Bobshannonite does not contain
254 Ca (Table 2); in accord with the refined site-scattering values for the $B^P(1,2)$ sites, we assign
255 0.95 Na + 0.05 \square to the $B^P(1)$ site and 0.94 Na + 0.06 \square to the $B^P(2)$ site (Table 7). There are
256 two A^P sites in the crystal structure of bobshannonite. The refined site-scattering value at the
257 [10]-coordinated $A^P(1)$ site is 53.1 e.p.f.u. (Table 7) and mean bond-length $\langle A^P(1)\text{-O} \rangle = 2.924$ Å
258 (Table 6) is consistent with ionic radius of Ba ($^{[10]}r = 1.52$ Å, Shannon, 1976). Therefore we
259 assign all available Ba (Table 2) to the $A^P(1)$ site: 0.95 Ba + 0.05 \square (Table 7). The $A^P(2)$ site is
260 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
261 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
262 $A^P(2)$ site [calculated scattering of 19.34 e.p.f.u., Table 7]. Mean bond-length for three subsites
263 varies from 3.058 to 3.211 Å (Table 6), consistent with the ionic radii of K ($^{[9]}r = 1.55$ and $^{[10]}r =$
264 1.59 Å, Shannon, 1976) and Rb ($^{[9]}r = 1.63$ and $^{[10]}r = 1.66$ Å, Shannon, 1976).

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

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

273

274 **Description of the structure**

275 *Topology of the structure*

276 Bobshannonite is a TS-block mineral of Group II, Nb + Ti = 2 a.p.f.u. per $(\text{Si}_2\text{O}_7)_2$ (Sokolova,
277 2006). The overall topology of the crystal structure of bobshannonite (sp. gr. $C\bar{1}$) (Fig. 5a) is in
278 accord with the perraultite structure-type (sp. gr. $C2$) (Yamnova *et al.*, 1998). In the structure of
279 bobshannonite, the $M^O(1-10)$ octahedra form a close-packed O sheet (Fig. 5b). In the H sheet,
280 SiO_4 tetrahedra link *via* common vertices to form Si_2O_7 groups that are oriented along **b** ($b = 2t_2$)
281 (Figs. 5a,b,c). The Si_2O_7 groups and M^H octahedra share common vertices to form the two
282 identical H sheets. An O sheet and two adjacent H sheets link through common vertices of SiO_4
283 tetrahedra and M^H and M^O octahedra to form a TS (Titanium Silicate) block parallel to (001) (Fig.
284 5a). Figure 5a shows that in the TS block, Si_2O_7 groups link to two M^O octahedra of the O sheet
285 adjacent along **b**, as in Group II of Sokolova (2006). In bobshannonite, TS blocks are connected
286 through common vertices of M^H octahedra (which are O and F atoms, $O > F$), plus cations of the
287 **I** block: Ba and K at the A^P sites and Na at the B^P sites (Fig. 5a). In the cation layer of the **I**
288 block, Ba and K are ordered at the A^P sites (Fig. 5c).

289

290 *Cation sites*

291 As stated above, the cation sites are divided into 3 groups: M^O sites of the O sheet, M^H and *Si*
292 sites of the H sheet, and peripheral A^P and B^P sites which occur in the **I** block. Also in accord
293 with Sokolova (2006), we label the X anions: $2X^O_M$ = common vertices of $3M^O$ and M^H polyhedra;
294 $2X^O_A$ = common vertices of $3M^O$ and A^P polyhedra (where $A^P-X^O_A < 3 \text{ \AA}$); $2X^P_M$ = apical anions of
295 M^H cations at the periphery of the TS block.

296

297 *O sheet*

298 There are ten [6]-coordinated M^O sites in the O sheet (Tables 6, 7) that contain 6.85 Mn
299 + 0.52 Na + 0.25 Zn + 0.23 Fe²⁺ + 0.03 Mg + 0.02 Al = 3.90 a.p.f.u. (Table 2). The
300 $M^O(1,2,4,5,8,9)$ atoms are coordinated by four O atoms and two monovalent anions, X^O_A
301 (see discussion below) with $\langle M^O-\varphi \rangle = 2.190-2.251$ Å (where φ = unspecified anion),
302 respectively. The $M^O(3,6,7,10)$ atoms are coordinated by five O atoms and a monovalent
303 X^O_A anion, with $\langle M^O-\varphi \rangle = 2.212-2.233$ Å. We group the divalent cations (6.85 Mn + 0.25
304 Zn + 0.23 Fe²⁺ + 0.03 Mg = 7.36 M^{2+} = 7.36Mn*) and write the composition of the O
305 sheet as follows 7.36 Mn* + 0.52 Na + 0.02 Al + 0.10 □ p.f.u., ideally (Mn₈Na) a.p.f.u. In
306 perraultite, eight [6]-coordinated M^O sites give Mn₅Fe²⁺₃ (Yamnova *et al.*, 1998), ideally
307 Mn₈ a.p.f.u.

308

309 *H sheet*

310 There are four [6]-coordinated Nb-dominant M^H sites in the H sheet (Tables 6, 7) each of
311 which is coordinated by five O atoms and one X^P_M anion, (O,F), with $\langle M^H-\varphi \rangle = 1.975$ Å.
312 Note the short distances from each M^H cation to each X^O_M anion: $M^H(1)-X^O_M(1) = 1.875$
313 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
314 6). There are eight tetrahedrally coordinated Si sites occupied solely by Si, with $\langle Si-O \rangle$
315 = 1.625 Å (Table 4). The cations of the two H sheets give (Nb,Ti)₄ a.p.f.u., *cf.* Ti₄ a.p.f.u.
316 in perraultite.

317

318 *Peripheral (P) sites*

319 Four peripheral sites, 2 A^P and 2 B^P , are shifted from the TS block and occur as
320 interstitial sites in the I block. The ^[10] $A^P(1)$ site is occupied by Ba at 95% and is
321 coordinated by ten O atoms, with $\langle A^P(1)-O \rangle = 2.924$ Å (Tables 6,7). Ideal composition
322 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

323 $^{[10]}A^P(23)$ subsites which are 0.532–1.064 Å apart (Table 6) and are partly occupied by K
324 + Rb, giving in total 0.93 K + 0.07 Rb, ideally K a.p.f.u. (Table 7). The total content of two
325 A^P sites sums to ideally KBa a.p.f.u., with $Z = 4$. In perraultite (sp. gr. C2), two A^P sites
326 (out of three) have partial occupancy; the total content of the $^{[10]}A^P(1)$, $^{[9]}A^P(2)$ and $^{[9]}A^P(3)$
327 sites is $Ba_{1.26}K_{0.60}\square_{0.14}$, ideally Ba_2 a.p.f.u., with $Z = 4$.

328 The [10]-coordinated $B^P(1,2)$ sites are occupied by Na at 95 and 94%,
329 respectively, with a mean distance of 2.658 Å (Table 7). The ideal composition of the two
330 $B^P(1,2)$ sites is Na_2 a.p.f.u. In perraultite, the three [10]-coordinated B^P sites are
331 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
332 $Na_{1.50}Ca_{0.50}$ a.p.f.u., ideally Na_2 p.f.u., $Z = 4$. We write the cation part of the structural
333 formula of bobshannonite as the sum of (a) interstitial B^P_2 and A^P_2 cations (Na_2KBa), (b)
334 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
335 $Na_2KBa(Mn,Na)_8(Nb,Ti)_4$.

336

337 *Anion considerations*

338 There are twenty-eight anions, O(1–28) (Table 5), that coordinate the Si cations and they are O
339 atoms: bond-valence sums on these anions vary from 1.92 to 2.05 vu (valence units) (Table 8).
340 Four anions, $X^O_M(1–4)$, are ligands of three M^O cations and an M^H cation (Table 6) and they are
341 O atoms, with bond-valence sums from 1.76 to 1.78 vu (Table 8). The anions at the $X^O_A(1–4)$
342 sites are O atoms of OH groups (Tables 5, 7), with bond-valence sums of 1.14–1.15 vu (Table
343 8). Each OH group is bonded to three M^O cations of the O sheet (Fig. 5b). The H(1–4) atoms
344 are involved in a weak hydrogen bonding with O atoms that belong to the H sheets (Table 9).
345 There are two $X^P_M(1,2)$ anions which are bridging anions for two M^H cations ($M^H \approx Nb_{0.67}Ti_{0.33}$)
346 (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
347 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
348 sums of 1.65 vu at each X^P_M anion (Table 8). The composition of an X^P_M anion correlates with

349 the composition of M^H cations: where M^H sites are locally occupied by Nb, the bridging anion is
350 an O atom; where M^H sites are locally occupied by Ti, the bridging anion is an F atom. A similar
351 phenomenon was noted for astrophyllite-group minerals (*cf.* niobophyllite, Cámara *et al.*, 2010).
352 We can write the anion part of the formula as the sum of (1) the H sheet: O_{28} belonging to four
353 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
354 bridging anions of the M^H polyhedra at the periphery of the TS block: two X^P_M sites, giving
355 $(O,F)_2$, ideally $(Si_2O_7)_4O_4(OH)_4(O,F)_2$.

356 In accord with the doubled perraultite-type general formula, $B^P_2A^P_2M^{O6}_8M^H_4(Si_2O_7)_4$
357 $X^O_8(X^P_M)_2$ (Sokolova, 2006), we write the structural formula of bobshannonite as Na_2KBa
358 $(Mn,Na)_8(Nb,Ti)_4(Si_2O_7)_4O_4(OH)_4(O,F)_2$, $Z = 4$, in agreement with the empirical formula given
359 above. The ideal structural formula of perraultite is $Na_2Ba_2Mn_8Ti_4(Si_2O_7)_4O_4(OH)_4F_2$, $Z = 4$
360 (Sokolova, 2006).

361

362 **Related minerals of Group II**

363 Ideal structural formulae for Group-II minerals bobshannonite, perraultite and jinshajiangite (the
364 perraultite structure type) and cámaraitite (related to the perraultite structure type) are presented
365 in Table 10 (except for surkhobite as its ideal formula is similar to that of perraultite).

366 Bobshannonite, perraultite and jinshajiangite have basic structures in accord with Sokolova and
367 Cámara (2013), i.e., they have one type of TS block, one type of I block and adjacent TS blocks
368 link to each other in the same way. In bobshannonite, perraultite and jinshajiangite, the O sheet
369 has ideal compositions $(Mn,Na)_8$, Mn_8 and Fe^{2+}_8 , respectively (Table 10). In bobshannonite, TS
370 blocks are connected through O and F atoms at common vertices of Nb-dominant M^H
371 octahedra, whereas in jinshajiangite and perraultite, TS blocks are connected through F atoms
372 at common vertices of Ti-dominant M^H octahedra. In jinshajiangite and perraultite, Ba ($Ba > K$)
373 and Na ($Na > Ca$) are the dominant constituents at the A^P and B^P sites in the I block,
374 respectively. Bobshannonite does not have any Ca; $Ba:K \sim 1:1$, and Ba and K are ordered.

375 Bobshannonite is related to cámaraité, ideally $\text{NaBa}_3\text{Fe}^{2+}_8\text{Ti}_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH})_4\text{F}_3$. The structure of
376 cámaraité has one type of TS block, two types of I block, and TS blocks link to each other in two
377 different ways. Cámaraité has a derivative structure, i.e., its structure can be built of structural
378 fragments of minerals of the same group, jinshajiangite and bafertisite. The *jinshajiangite* part of
379 the cámaraité structure is topologically identical to the bobshannonite structure. The general
380 and ideal structural formulae of cámaraité are written as sums of the corresponding formulae of
381 bafertisite and jinshajiangite (Table 10).

382 Bobshannonite is a Nb-analogue of perraultite. To go from perraultite to bobshannonite,
383 Nb substitutes for Ti in the H sheets, and to compensate for the increase in positive charge, Na
384 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
385 sheets.

386

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456

457 **Figure captions**

458

459 Fig. 1. Four groups of structures corresponding to different types of TS block: (a) Group I,
460 linkage 1 of H and O sheets; (b) Group II, linkage 2; (c) Group III, linkage 1; (d) Group IV,
461 linkage 3. *Linkage 1* occurs where two H sheets connect to the O sheet so that two Si_2O_7
462 groups on opposite sides of the O sheet link to *trans* edges of the same octahedron of the O
463 sheet. *Linkage 2* occurs where two Si_2O_7 groups link to two octahedra of the O sheet
464 adjacent along \mathbf{t}_2 . *Linkage 3* occurs where two Si_2O_7 groups link to two octahedra adjacent
465 approximately along \mathbf{t}_1 . Only the Si_2O_7 groups of the H sheets are shown; dashed black lines
466 represent positions of Si_2O_7 groups on the lower surface; M^{H} polyhedra are omitted for clarity.
467 Si, Na, Ti and Mn polyhedra are orange, blue, pale yellow and magenta, respectively. F
468 atoms are shown as yellow spheres, OH groups are shown as turquoise spheres in
469 yoshimuraite and red spheres in epistolite. A typical mineral is indicated for each group.

470

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

472

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

474

475 Fig. 4. The Raman spectrum of bobshannonite.

476

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

482 and blue spheres, respectively; O and H atoms of OH groups at the X^O_A sites are shown as
483 turquoise and small white spheres.

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

Mineral *	Mn-dominant species		Fe ²⁺ -dominant species	
	Bobshannonite	Perraultite	Surkhobite	Jinshajiangite
Simplified formula	$\text{Na}_2\text{KBa}(\text{Mn, Na})_8(\text{Nb, Ti})_4(\text{Si}_2\text{O}_7)_4(\text{O, F})_2$	$[\text{Na}_2\text{KBaMn}_8(\text{Ti, Nb})_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH, F, H}_2\text{O})_7]$ $[\text{Na, Ca}]_2(\text{Ba, K})_2(\text{Mn, Fe})_8(\text{Ti, Nb})_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH, F, O})_6$	$\text{NaCa}(\text{Ba, K})_2(\text{Mn, Fe}^{2+}, \text{Fe}^{3+})_8\text{Ti}_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{F, OH, O})_6$	$(\text{Na, Ca})_2(\text{Ba, K})_2\text{Fe}^{2+}_8\text{Ti}_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH})_4\text{F}_2$
Reference	(1)	(2)	(5)	(6,7)
Space group	$C\bar{1}$	$C2/m, Cm$ or $C2$	$C2$	$C2/m$
a (Å)	10.839(6)	10.82	10.723	10.6785
b	13.912(8)	13.843	13.826	13.786
c	20.98(1)	20.93	20.791	20.700
α (°)	89.99(1)	90	90	90
β	95.05(2)	95.09	95.00	94.937
γ	89.998(9)	90	90	90
Z	4	4	4	4
$D_{\text{calc.}}$ (g/cm ³)	3.790	3.808	3.98	3.767
$D_{\text{meas.}}$ (g/cm ³)	n.d.	3.71	3.84	3.61
Strongest reflections in the X-ray powder diffraction data, d/n (Å) (l)	2.873(100) 3.477(60) 3.193(59) 2.648(40) 2.608(35) 1.776(30) 1.733(28)	3.474 (100) 10.43 (42) 2.606 (40) 3.186 (15) 2.084 (15) 2.867 (13) 3.573 (11)	3.454 (100) 2.592 (70) 2.074 (40) 10.39 (20) 3.186 (15) 2.862 (15) 1.728 (15)	3.44 (100) 3.15 (80) 2.630 (80) 2.570 (80) 10.2 (70) 1.715 (50 broad) 2.202 (40)
optical class, sign	–	biaxial (-)	biaxial (+)	biaxial (+)
α (589.3 nm)	–	1.785	1.79	1.792 _{calc.}
β	–	1.81	1.810	1.801
γ	–	1.82	1.825	1.852
$2V_{\text{meas}}$ (°)	–	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, $D_{\text{calc.}}$ (6); $D_{\text{meas.}}$ 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.

Constituent	Chemical analysis (wt.%)			Formula unit* (a.p.f.u.)			
	Bobshannonite	Perraultite**		Bobshannonite	Perraultite		
		(1)	(2)		(1)	(2)	
Ta ₂ O ₅	0.52		0.11	Ta	0.04	0	0.01
Nb ₂ O 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	<u>1.27</u>	<u>2.08</u>	<u>3.86</u>
SiO ₂	26.31	27.32	27.72	ΣM ^H	4.04	3.87	4.04
Fe ₂ O ₃ ***	n.d.	n.d.	0.75				
Al ₂ O 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 ₂ O	0.42	n.a.	n.a.	Na	<u>0.52</u>	<u>0.02</u>	<u>0</u>
K ₂ O	2.38	2.68	1.67	ΣM ^O	7.90	8.06	7.95
Na ₂ O	4.05	3.52	2.76				
F	0.70	0.84	2.18	Ba	0.95	1.02	1.20
H ₂ O [†]	1.96	3.49	1.79	Sr	0	0	0.01
O=F	<u>-0.29</u>	<u>-0.35</u>	<u>-0.92</u>	Rb	0.08	0	0
Total	97.53	101.64	99.80	K	<u>0.93</u>	<u>1.00</u>	<u>0.61</u>
				ΣA ^P	1.96	2.02	1.81
				Ca	0	0	0.46
				Na	<u>1.89</u>	<u>2.00</u>	<u>1.54</u>
				ΣB ^P	1.89	2.00	2.00
				OH	4.01	5.62	3.44
				F	<u>0.68</u>	<u>0.78</u>	<u>1.99</u>
				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 + H₂O) 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), Fe²⁺/Fe³⁺ determined by wet chemistry;

[†] content of H₂O: (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}	$d_{meas.} (\text{Å})$	$d_{calc.} (\text{Å})$	h	k	l		I_{rel}	$d_{meas.} (\text{Å})$	$d_{calc.} (\text{Å})$	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	$\bar{2}$	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
$D_{\text{calc.}}$ (g/cm ³)	3.790
Crystal size (mm)	0.012 x 0.010 x 0.003
Radiation/monochromator	Mo-K α /graphite
$2\theta_{\text{max}}$ (°)	60.16
$R(\text{int})$ (%)	1.96
Second component (%)	49.82(5)
Reflections collected	18496
Independent reflections	9261
$F_o > 4\sigma F$	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 $R(\text{obs})$ (%)	
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 (\AA^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}^*
$X_M^O(1)$	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)
$X_M^O(2)$	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)
$X_M^O(3)$	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)
$X_M^O(4)$	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)
$X_A^O(1)$	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)
$X_A^O(2)$	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)
$X_A^O(3)$	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)
$X_A^O(4)$	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)
$X_M^P(1)$	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)
$X_M^P(2)$	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)–φ>	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)–φ>	2.224	<M ^O (3)–φ>	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)–φ>	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)–φ>	2.229		M ^O (8)–O(6)i	2.090(3)	x2	<M ^O (6)–φ>	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)–φ>	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)–φ>	2.233		<M ^O (9)–φ>	2.198		<M ^O (10)–φ>	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)–φ>	1.973		<M ^H (2)–φ>	1.976		<M ^H (3)–φ>	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)–φ>	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	<u>1.638(3)</u>	Si(5)–O(18)m	<u>1.636(3)</u>	Si(6)–O(25)j	<u>1.637(3)</u>
<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)	<u>1.643(3)</u>	Si(8)–O(25)	<u>1.634(3)</u>	Si(6)s–O(25)–Si(8)	<u>132.9(1)</u>
<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	<u>3.298(5)</u>	A ^P (22)–X ^P _M (1)	<u>3.248(5)</u>
A ^P (1)–X ^P _M (1)	<u>3.154(3)</u>	<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	<u>3.430(8)</u>	B ^P (1)–O(20)	<u>2.879(4)</u>	B ^P (2)–O(19)m	<u>2.890(3)</u>
<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+¾, -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.)	$\langle X-\varphi \rangle_{\text{obs.}}^{**}$ (Å)	Simplified composition (a.p.f.u.)
Cations					
$M^P(1)$	12.06(7)			2.195	
$M^P(2)$	25.64(9)			2.224	
$M^P(3)$	23.34(9)			2.224	
$M^P(4)$	25.62(9)			2.229	
$M^P(5)$	11.95(7)	7.36 Mn ^{***} + 0.52 Na + 0.02 Al + 0.10 □		2.240	
$M^P(6)$	23.44(9)			2.212	
$M^P(7)$	23.41(9)			2.233	
$M^P(8)$	12.08(7)			2.251	
$M^P(9)$	12.26(7)			2.198	
$M^P(10)$	23.87(9)			2.219	
$\Sigma M^P(1-10)$	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	
$\Sigma M^H(1-4)$	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	
$\Sigma A^P(2)$	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	
$\Sigma B^P(1-2)$	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 Fe²⁺ + 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} ↓					0.32				
O(2)		0.36	0.29 0.25											
O(3)				0.35		0.28 0.27								
O(4)	0.33 ^{x2} ↓					0.29	0.33							
O(5)				0.38			0.29 0.25							
O(6)						0.31	0.25	0.43 ^{x2} ↓						
O(7)			0.33						0.35 ^{x2} ↓	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 _M ^O (2)		0.29	0.35		0.15 ^{x2} ↓					0.99				
X _M ^O (3)				0.29			0.34	0.15 ^{x2} ↓				0.98		
X _M ^O (4)	0.26 ^{x2} ↓		0.15		0.37							0.98		
X _M ^O (1)		0.15							0.27 ^{x2} ↓	0.35	1.0			
[³]X _A ^O (1)		0.39	0.38						0.37 ^{x2} ↓					
[³]X _A ^O (2)		0.36			0.41 ^{x2} ↓				0.38					
[³]X _A ^O (3)	0.41 ^{x2} ↓		0.37			0.36								
[³]X _A ^O (4)				0.37		0.40		0.37 ^{x2} ↓						
X _M ^P (1)												0.68		0.67
X _M ^P (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 = Mn²⁺; 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)

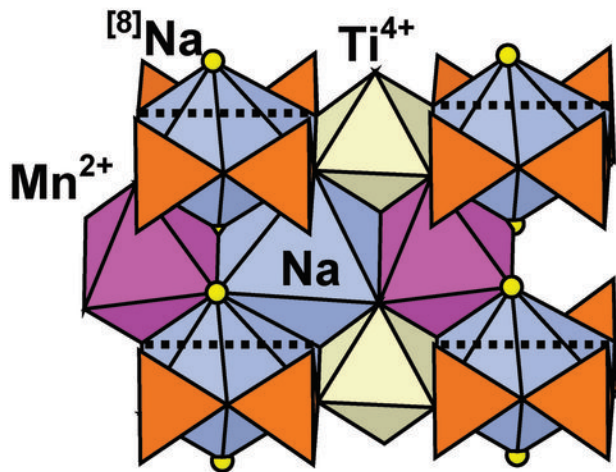
a: $-x+1/2, -y+3/2, -z+1$; b: $x-1, y, z$.

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

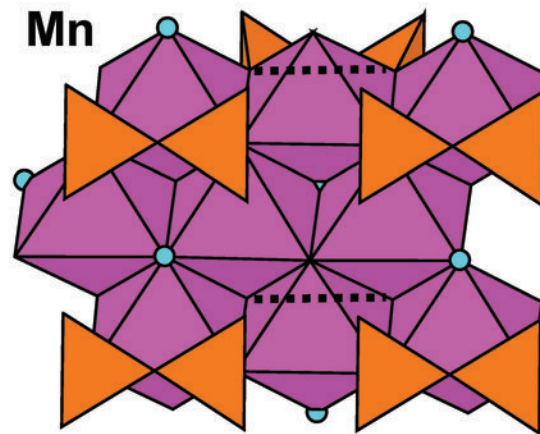
Mineral	Structure type	Structural formula, Z = 4							Ref.
		B^P_2	A^P_2	M^O_8	M^H_4	$(Si_2O_7)_4$	X^O_8	X^P_2	
Bobshannonite	B1(GII)	Na ₂	K Ba	(Mn,Na)₈	(Nb,Ti)₄	(Si₂O₇)₄	O₄(OH)₄	(O,F) ₂	(1)
Perraultite	B1(GII)	Na ₂	Ba ₂	Mn₈	Ti₄	(Si₂O₇)₄	O₄(OH)₄	F ₂	(2)
Jinshajiangite	B1(GII)	Na ₂	Ba ₂	Fe²⁺₈	Ti₄	(Si₂O₇)₅	O₄(OH)₄	F ₂	(3)
		B^P	A^P_3	M^O_8	M^H_4	$(Si_2O_7)_4$	X^O_8	X^P_3	
Cámaraite	D1(GII)	Na	Ba ₃	Fe²⁺₈	Ti₄	(Si₂O₇)₄	O₄(OH)₄	F ₃	(4)
Jinshajiangite component	B1(GII)	Na	Ba	Fe²⁺₄	Ti₂	(Si₂O₇)₂	O₂(OH)₂	F	(3)
Bafertisite component	B2(GII)		Ba ₂	Fe²⁺₄	Ti₂	(Si₂O₇)₂	O₂(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, $M^O_4M^H_2(Si_2O_7)_2X^O_4$, 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.

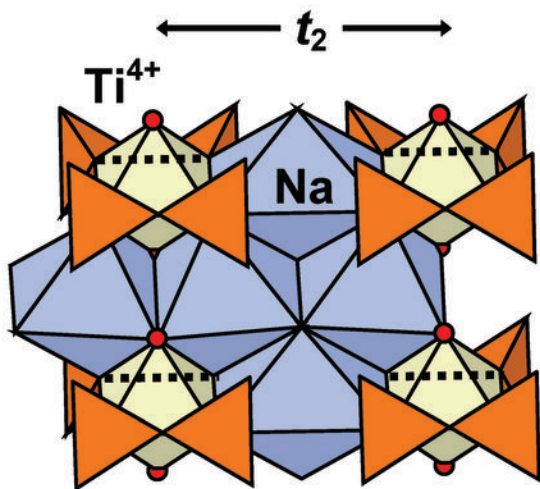
References: (1) This work; (2) Yamnova *et al.* (1998); (3) Sokolova *et al.* (2009a); (4) Cámara *et al.* (2009); (5) Guan *et al.* (1963).



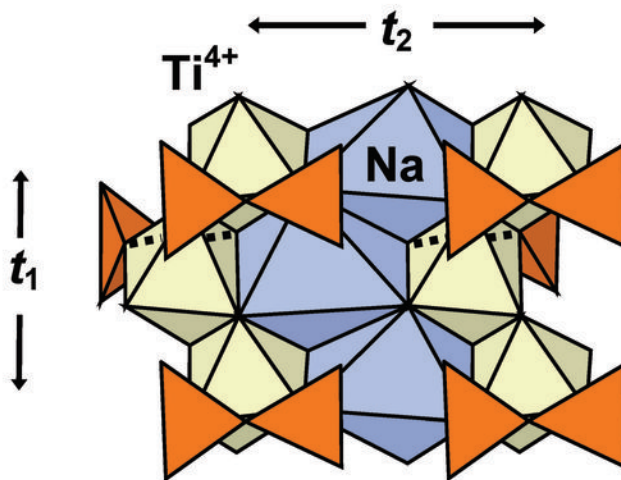
a GROUP I: Seidozerite



b GROUP II: Yoshimuraite



c GROUP III: Epistolite



d GROUP IV: Murmanite

Fig. 1

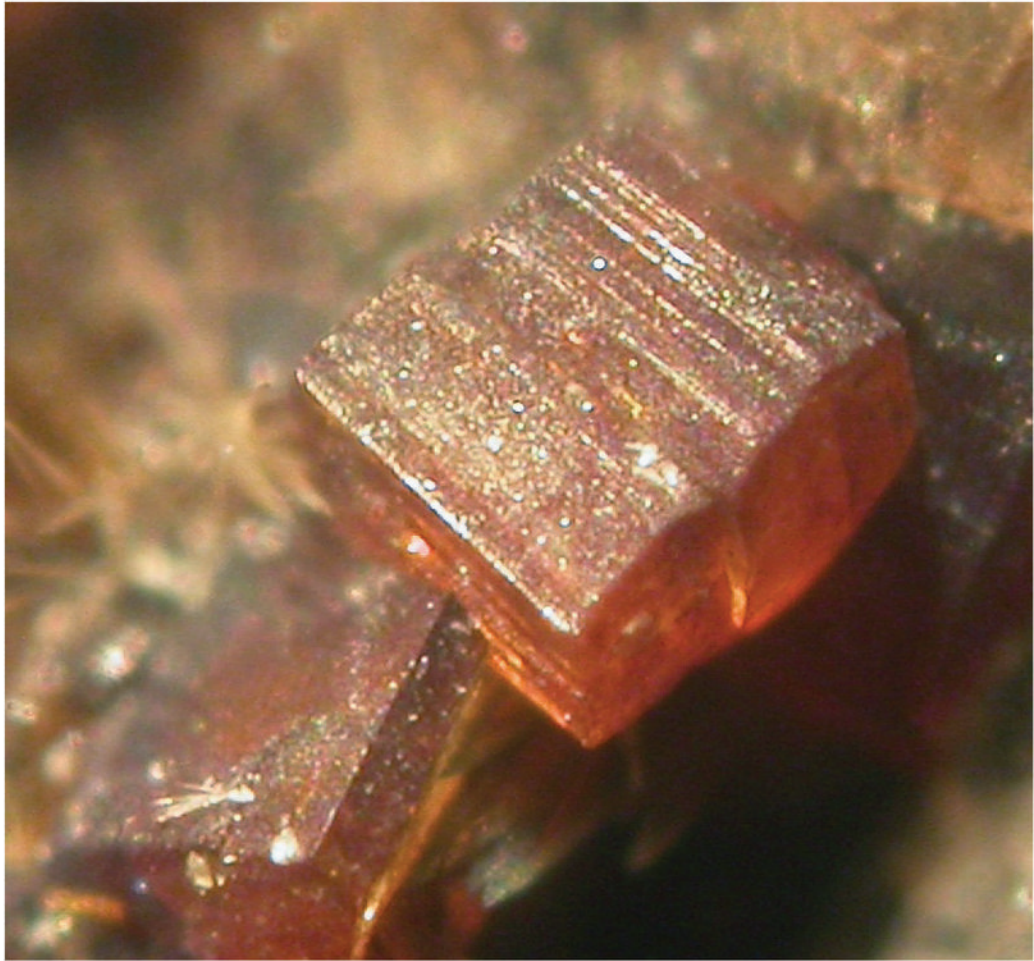


Fig. 2

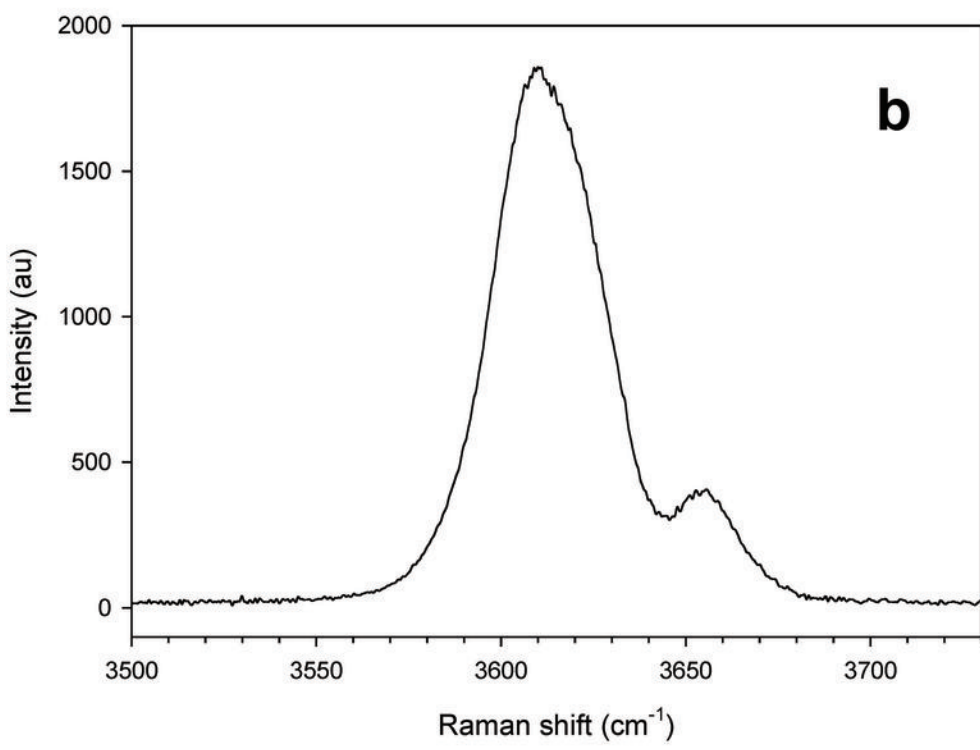
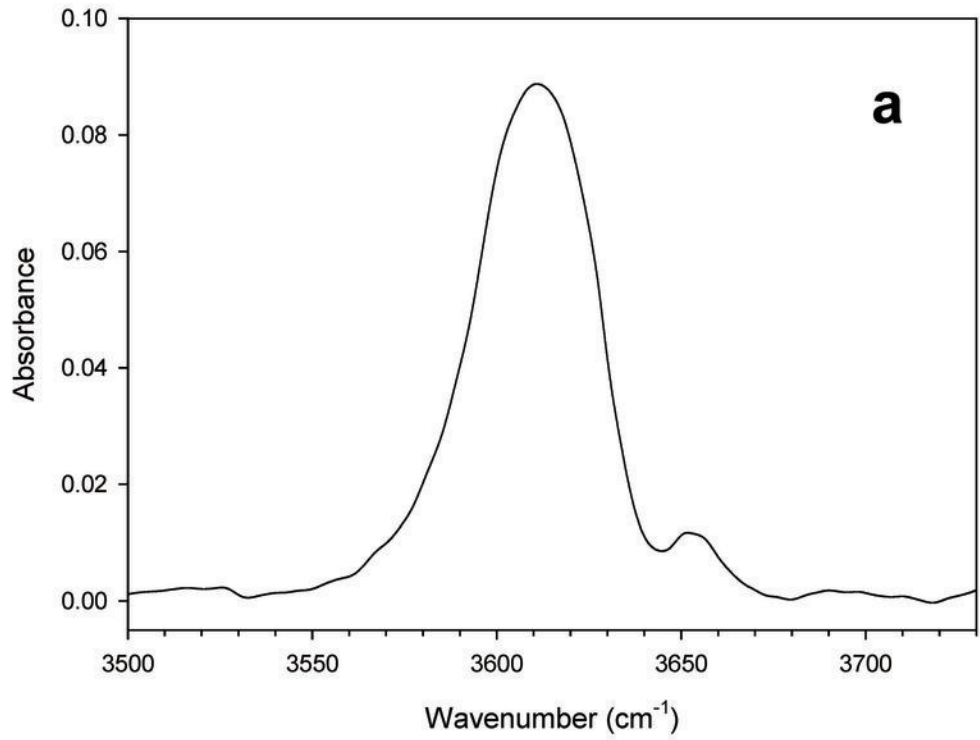


Fig. 3

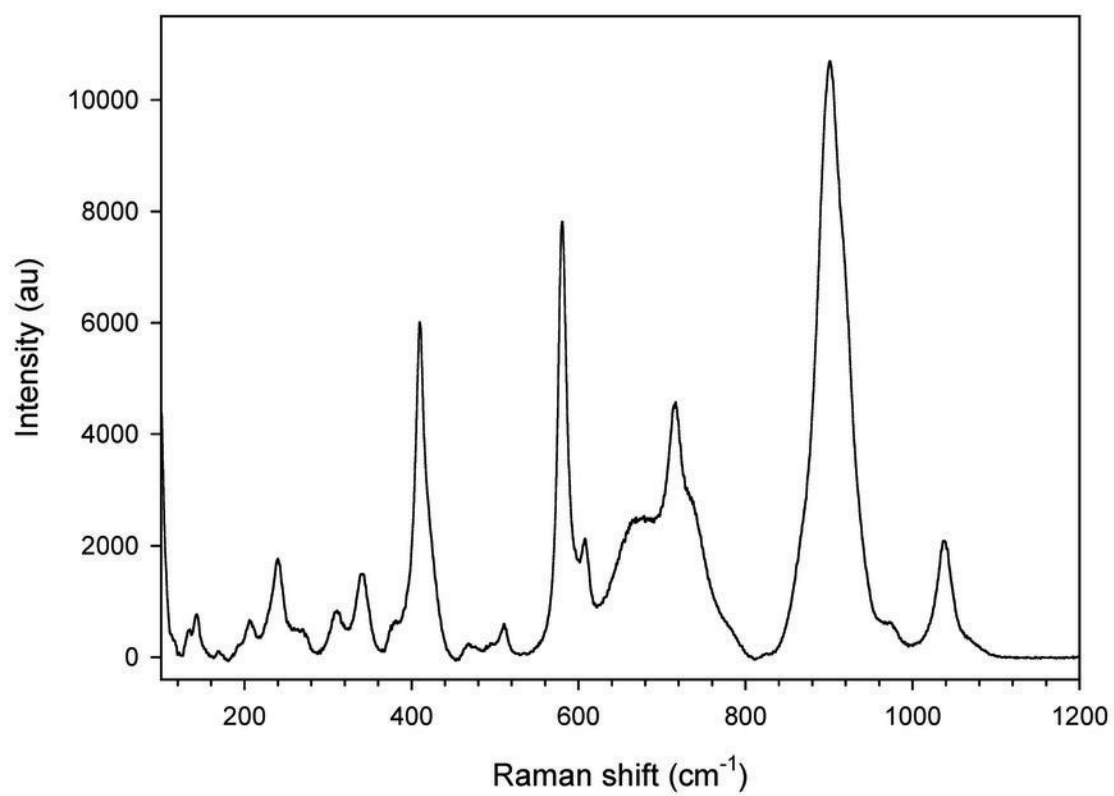


Fig. 4

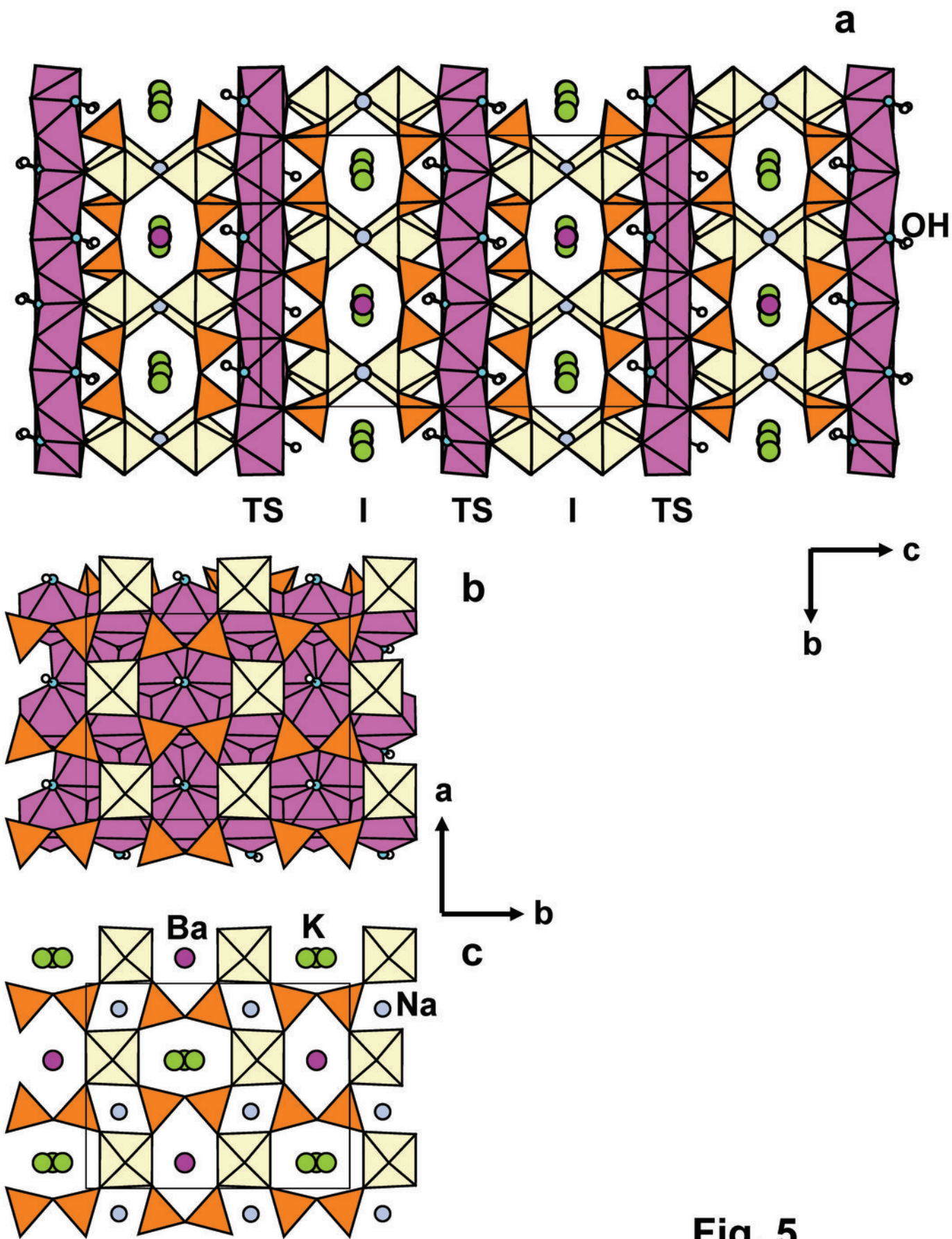


Fig. 5