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Revision 2

Zhanghuifenite, $\text{Na}_3\text{Mn}^{2+}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$, a new mineral isostructural with bobfergusonite, from the Santa Ana mine, San Luis province, Argentina

Hexiong Yang^{*1}, Anaïs Kobsch², Xiangping Gu³, Robert T. Downs¹, Xiande Xie⁴

¹Department of Geosciences, University of Arizona, 1040 E. 4th Street, Tucson, AZ 85721-0077, USA

²Univ Lyon, ENSL, Univ Lyon 1, CNRS, LGL-TPE, F-69007 Lyon, France

³School of Geosciences and Info-Physics, Central South University, Changsha, Hunan 410083, China

⁴Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, CAS, and Guangdong Key Laboratory of Mineral Physics and Materials, Guangzhou 510640, China

*Corresponding author: hyang@arizona.edu

Abstract

A new mineral species, zhanghuifenite, ideally $\text{Na}_3\text{Mn}^{2+}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$, has been found in the Santa Ana mine, San Luis province, Argentina. It occurs in irregular veinlets or patches, 5 mm thick, in a nodule of beusite interlaminated with lithiophilite. Broken pieces of zhanghuifenite are blocky or tabular. Single crystals are up to 0.8 x 0.5 x 0.5 mm. No twinning or parting is observed macroscopically. The mineral is deep green, transparent with pale green streak and vitreous luster. It is brittle and has a Mohs hardness of ~5 with good cleavage on {010}. The measured and calculated densities are 3.63(2) and 3.62 g/cm³, respectively. Optically, zhanghuifenite is biaxial (+), with $\alpha = 1.675(2)$, $\beta = 1.680(2)$, $\gamma = 1.690(2)$ (white light), $2V(\text{meas.}) = 74(2)^\circ$, and $2V(\text{calc.}) = 71^\circ$. The calculated compatibility index based on the empirical formula is 0.020 (excellent). An electron microprobe analysis yields an empirical formula (based on 24 O apfu)

$$(\text{Na}_{2.80}\text{Ca}_{0.11})_{\Sigma 2.91}(\text{Mn}^{2+}_{3.09}\text{Fe}^{2+}_{0.47}\text{Mg}_{0.36})_{\Sigma 3.92}(\text{Mg}_{1.31}\text{Fe}^{2+}_{0.69})_{\Sigma 2.00}(\text{Al}_{0.81}\text{Fe}^{3+}_{0.19})(\text{PO}_4)_6.$$

Zhanghuifenite is insoluble in water or hydrochloric acid.

32 Zhanghuifenite is isostructural with bobfergusonite, a member of the alluaudite
33 super-group. It is monoclinic, with space group $P2_1/n$, $Z=4$, and unit-cell parameters $a =$
34 $12.8926(3)$, $b = 12.4658(3)$, $c = 10.9178(2)$ Å, $\beta = 97.9200(10)^\circ$, and $V = 1737.93(7)$ Å³.
35 The crystal structure of zhanghuifenite contains six octahedral M (= Mn, Fe, Mg, Al)
36 sites and five X (= Na, Mn, Ca) sites with coordination numbers between 6 and 8. The six
37 M octahedra share edges to form two types of kinked chains extending along $[101]$, with
38 one consisting of $M1-M4-M5$ and the other $M2-M3-M6$. These chains are joined by PO_4
39 tetrahedra to form sheets parallel to (010) , which are linked together through corner-
40 sharing between PO_4 tetrahedra and MO_6 octahedra in the adjacent sheets, leaving open
41 channels parallel to a , where the large X cations are situated. Zhanghuifenite differs from
42 bobfergusonite in two major aspects. One is that the $M4$ and $M5$ sites in the former are
43 mainly occupied by Mg, but by Fe^{2+} and Fe^{3+} , respectively, in the latter. The other is that
44 the $X2-X5$ sites in zhanghuifenite are all nearly or fully filled with Na, resulting in 3 Na
45 apfu in the ideal formula, but $X4$ and $X5$ are merely half-occupied in bobfergusonite,
46 giving rise to 2 Na apfu.

47

48 **Key words:** zhanghuifenite, wylлиеite, alluaudite, crystal structure, X-ray diffraction,
49 Raman spectra

50

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Introduction

52 A new mineral species, zhanghuifenite, ideally $Na_3Mn^{2+}_4Mg_2Al(PO_4)_6$, has been
53 found in the Santa Ana mine, San Luis province, Argentina. It is named in honor of the
54 late Chinese mineralogist, Prof. Huifen Zhang (1934-2012). Prof. Zhang received her
55 undergraduate and graduate educations in China and the former USSR, respectively. She
56 became a professor at the Institute of Geochemistry (in both Guiyang and Guangzhou),
57 the Chinese Academy of Sciences, where she was the director of the division for mineral
58 physics and materials research from 1980 to 1994. Prof. Zhang established the first

59 Raman spectroscopy laboratory for mineralogical research in China and served as a
60 member of the IMA Commission on Mineral Physics from 1990 to 1994. Her major
61 research interests were particularly focused on synthetic quartz, rutile, pyrophyllite, and
62 turquoise. The new mineral and its name have been approved by the Commission on New
63 Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical
64 Association (IMA 2016-074). The cotype samples have been deposited at the University
65 of Arizona Mineral Museum (Catalogue # 21321) and the RRUFF Project (deposition #
66 R160030) (<http://rruff.info>).

67 Zhanghuifenite, isotypic with bobfergusonite, is closely related to minerals of the
68 wyllieite and alluaudite groups. However, it differs from all known members of these
69 groups in both chemical composition and structure. Moore and Molin-Case (1974)
70 showed that the crystal structure of wyllieite is a superstructure derivative of the
71 alluaudite structure. Moore and Ito (1979) introduced a nomenclature for the minerals of
72 the alluaudite and wyllieite groups. Recently, a new nomenclature of the alluaudite
73 supergroup, which contains totally 16 phosphate and 19 arsenate minerals by 2019, has
74 been presented by Hatert (2019). Khorari et al. (1997) examined the compositional
75 relations between the alluaudite and garnet structures and revealed that the alluaudite
76 structure, like the garnet structure, is extremely chemically compliant. This paper
77 describes the physical and chemical properties of zhanghuifenite and its crystal structure
78 determined from single-crystal X-ray diffraction data, illustrating its structural
79 relationships to bobfergusonite in particular and alluaudite-type minerals in general.

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82 **Sample Description and Experimental Methods**

83 *Occurrence, physical and chemical properties, and Raman spectra*

84 Zhanghuifenite was found on a specimen collected from the the Santa Ana mine
85 (32°53'32" S, 65°55'43" W), San Luis province, Argentina (Fig. 1). It is massive in a

86 matrix consisting of beusite and lithiophilite (Fig. 2). Detailed geological and
87 mineralogical studies of the Santa Ana pegmatite have been presented by Galliski et al.
88 (2009) and Roda-Robles et al. (2012). The association zhanghuifenite – beusite –
89 lithiophilite occurs in a granitic pegmatite. According to Galliski et al. (2009), the
90 original primary phosphates of the nodule are believed to have crystallized with a
91 chemical composition of a Li-bearing beusite enriched in Mg, derived possibly by
92 contamination by the host rock after the crystallization of the border and wall zones of
93 the pegmatite. The exsolution of this precursor led to the formation of a lamellar
94 intergrowth of beusite and lithiophilite enriched in Mg. Subsequent crystallization of
95 zhanghuifenite is attributed to veining, produced possibly by a late-stage, fluid-rich
96 peraluminous melt.

97 Zhanghuifenite crystals occur in irregular veinlets or patches, 5 mm thick, in a
98 nodule of beusite interlaminated with lithiophilite (Figs. 1 and 2). Broken pieces of
99 zhanghuifenite are blocky or tabular. Single crystals are found up to 0.8 x 0.5 x 0.5 mm.
100 No twinning or parting is observed macroscopically. The mineral is deep jade-green,
101 transparent with pale green streak and vitreous luster. It is brittle and has a Mohs
102 hardness of ~5; cleavage is good on {010}. The measured and calculated densities are
103 3.63(2) and 3.62 g/cm³, respectively. Optically, zhanghuifenite is biaxial (+), with $\alpha =$
104 1.675 (2), $\beta = 1.680$ (2), $\gamma = 1.690$ (2) (white light), $2V$ (meas.) = 74(2)°, $2V$ (calc.) = 71°,
105 and the orientation $\alpha \wedge X = 8^\circ$, $\beta = Y$, with $X =$ deep blue green, $Y =$ pale green, $Z =$
106 yellowish green, and $X > Y > Z$. The pleochroism is deep green and the dispersion is very
107 strong with $r \gg v$. The calculated compatibility index based on the empirical formula is
108 0.020 (excellent) (Mandarino 1981). Zhanghuifenite is insoluble in water or hydrochloric
109 acid.

110 The chemical composition was determined using a Cameca SX-100 electron
111 microprobe (WDS mode, 15 kV, 20 nA, and a beam diameter of 5 μ m). The standards
112 used are listed in Table 1, along with the determined compositions (12 analysis points all

113 from one crystal). The resultant chemical formula, calculated on the basis of 24 O atoms
114 *pfu* (from the structure determination), is
115 $(\text{Na}_{2.80}\text{Ca}_{0.11})_{\Sigma 2.91}(\text{Mn}^{2+}_{3.09}\text{Fe}^{2+}_{0.47}\text{Mg}_{0.36})_{\Sigma 3.92}(\text{Mg}_{1.31}\text{Fe}^{2+}_{0.69})_{\Sigma 2.00}(\text{Al}_{0.81}\text{Fe}^{3+}_{0.19})(\text{PO}_4)_6$,
116 which can be simplified to $\text{Na}_3\text{Mn}^{2+}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$.

117 The Raman spectrum of zhanghuifenite was collected on a randomly oriented
118 crystal with a Thermo Almega microRaman system, using a solid-state laser with a
119 frequency of 532 nm at the full power of 150 mW and a thermoelectric cooled CCD
120 detector. The laser is partially polarized with 4 cm^{-1} resolution and a spot size of 1 μm .

121

122 *X-ray crystallography*

123 Both the powder and single-crystal X-ray diffraction data for zhanghuifenite were
124 collected on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-
125 monochromatized MoK_α radiation. Listed in **Table 2** are the measured powder X-ray
126 diffraction data, along with those calculated from the determined structure using the
127 program XPOW (Downs et al. 1993). The unit-cell parameters obtained from the powder
128 X-ray diffraction data are: $a = 12.888(5)$, $b = 12.466(3)$, $c = 10.910(4)$ Å, $\beta = 97.86(3)^\circ$,
129 and $V = 1736.4(8)$ Å³.

130 A nearly equidimensional crystal (0.08 x 0.08 x 0.07 mm) of zhanghuifenite was
131 picked for the structure determination from the large crystal used for the electron
132 microprobe analysis. The X-ray diffraction intensity data were collected with frame
133 widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed on the
134 basis of a monoclinic unit-cell (**Table 3**). The intensity data were corrected for X-ray
135 absorption using the Bruker program SADABS. The systematic absences of reflections
136 suggest the unique space group $P2_1/n$. The crystal structure was solved and refined using
137 SHELX2018 (Sheldrick 2015a, 2015b). To facilitate the direct comparison with
138 bobfergusonite, the site nomenclature used by Ercit et al. (1986) and Tait (2004) was

139 adopted for the zhanghuifenite structure, which has 5 *X*, 6 *M*, 4 *P*, and 24 *O* sites for an
140 asymmetric unit, where *X* = Na, Ca, and Mn, and *M* = Mn, Fe, Mg, and Al.

141 A preliminary structure refinement indicated that *M1*, *M2*, and *X1* are fully
142 occupied by Mn, and *X2* and *X5* by Na. These sites, therefore, were all fixed in the
143 subsequent refinements. The refinements revealed that Mg is dominant in the *M4* and *M5*
144 sites, and Al in *M6*. The small amount of Ca was found to be in *X3* and some vacancy in
145 *X4*. For simplicity, in the subsequent refinements, all *M* and *X* sites, except for *X3*, were
146 assumed to be completely filled, which requires a re-normalization of the empirical
147 formula to

148 $(\text{Na}_{2.80}\text{Ca}_{0.11})_{\Sigma 2.91}(\text{Mn}^{2+}_{3.15}\text{Fe}^{2+}_{0.48}\text{Mg}_{0.37})_{\Sigma 4.00}(\text{Mg}_{1.31}\text{Fe}^{2+}_{0.69})_{\Sigma 2.00}(\text{Al}_{0.81}\text{Fe}^{3+}_{0.19})_{\Sigma 1.00}(\text{PO}_4)_6$.

149 Based on this chemical formula, the final refined site occupancies are given in **Table 4**,
150 together with those determined by Tait et al. (2004) for bobfergusonite from the Nancy
151 pegmatite, San Luis Range, Argentina. Final coordinates and displacement parameters of
152 atoms in zhanghuifenite are listed in **Tables 5 and 6**, respectively, and selected bond-
153 distances in **Table 7**.

154 It should be pointed out that the *M3* site in zhanghuifenite appears to have more
155 Fe^{2+} than any other elements. However, we do not specify it in the ideal chemical
156 formula to keep consistency with bobfergusonite, which shows a variation from the
157 Mn^{2+} - to Fe^{2+} -rich in its *M3* site, but all Fe^{2+} was treated as Mn^{2+} in its ideal formula
158 (Ercit et al. 1986; Tait et al. 2004). Another reason for doing so is because X-ray
159 structure analysis is insufficient in distinguishing Fe from Mn due to their similar X-ray
160 scattering powers.

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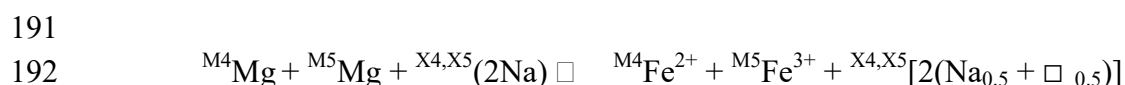
162 **Crystal structure description and discussion**

163 Zhanghuifenite is isostructural with bobfergusonite, $\text{Na}_2\text{Mn}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$ (Ercit
164 *et al.*, 1986; Tait *et al.*, 2004), a member of the alluaudite super-group. All these minerals
165 have the same structure topology. They differ from one another mainly in chemical

166 compositions and M-cation ordering patterns (see Hatert 2019 for a thorough review).
167 The crystal structure of zhanghuifenite contains six octahedral *M* sites and five *X* sites
168 that have coordination numbers 6, 8, 8, 7, and 7 for *X*1, *X*2, *X*3, *X*4, and *X*5, respectively.
169 The six *M* octahedra share edges to form two types of kinked chains extending along
170 [101], with one consisting of *M*1-*M*4-*M*5 (the A chain) and the other *M*2-*M*3-*M*6 (the B
171 chain). These octahedral chains are joined by PO₄ tetrahedra to form sheets parallel to
172 (010) (Figure 3), which are linked together through corner-sharing between PO₄
173 tetrahedra and MO₆ octahedra in the adjacent sheets, leaving open channels parallel to *a*,
174 where the large *X* cations are situated (Figure 4).

175 There is strong cation order over the six *M* sites in zhanghuifenite (Table 4),
176 which is the cause for the differences among the alluaudite-, wyllieite-, and
177 bobfergusonite-structure types (Ercit et al. 1986, Tait et al. 2004). Among five *X* sites, the
178 *X*1 site is filled with Mn²⁺, whereas *X*2–*X*5 sites are predominately or fully occupied by
179 Na. The average bond lengths for *M*3, *M*4, and *M*5 are noticeably shorter than those for
180 *M*1, *M*2 and *X*1, consistent with the results that the former three sites are primarily
181 occupied by Mg and Fe²⁺. The site preference of Mg is *M*5 > *M*4 > *M*3, which is
182 opposite to that of Fe²⁺, in agreement with the decrease in the average bond length from
183 *M*3 to *M*5.

184 Zhanghuifenite differs from bobfergusonite in two major aspects. One is that the
185 *M*4 and *M*5 sites in the former are mainly occupied by Mg, but by Fe²⁺ and Fe³⁺,
186 respectively, in the latter. The other is that the *X*2-*X*5 sites in zhanghuifenite are all nearly
187 or fully filled with Na, resulting in 3 Na apfu in the ideal formula, but *X*4 and *X*5 are
188 merely half-occupied in bobfergusonite, giving rise to 2 Na apfu. Therefore, based on the
189 ideal chemical formulas, zhanghuifenite may be obtained from bobfergusonite through
190 the following coupled substitution:



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194

Zhanghuifenite

Bobfergusonite

195 The Raman spectrum of zhanghuifenite between 100 and 4000 cm^{-1} was collected
196 (<https://rruff.info/R160030>), but only the range from 100 to 1300 cm^{-1} is displayed in
197 **Figure 5**, because the spectrum above 1400 cm^{-1} is flat and featureless. Based on the
198 previous Raman spectroscopic study on qingheite (Frost et al. 2013), which is also a
199 member of the wyllieite group (see below for more discussion), we made the following
200 tentative assignments of the major Raman bands for zhanghuifenite. The bands between
201 930 and 1160 cm^{-1} are ascribable to the P-O stretching vibrations within the PO_4 group,
202 whereas those from 400 to 660 cm^{-1} are attributed to the O-P-O bending vibrations. The
203 bands below 400 cm^{-1} are mainly associated with the rotational and translational modes
204 of PO_4 tetrahedra, as well as the M-O (M = Mn, Fe, Mg, Al) interactions and lattice
205 vibrational modes. For comparison, the Raman spectrum of bobfergusonite from the
206 RRUFF Project (<http://rruff.info/R160069>) was also included in **Figure 5**. The
207 resemblance between the two spectra are apparent. The difference in peak intensities
208 between the two spectra principally results from the different crystal orientations when
209 the data were collected.

210

Implications

211 Qingheite, ideally $\text{Na}_2\text{Mn}^{2+}\text{MgAl}(\text{PO}_4)_3$ (Ma et al. 1983), has a similar
212 composition to zhanghuifenite (**Table 1**). Chemically, zhanghuifenite can be obtained
213 from qingheite (with the doubled cell content, as its unit-cell volume is only half that of
214 zhanghuifenite) by the coupled substitution of 2Mn^{2+} for (Na + Al). Structurally,
215 qingheite contains only one type of edge-sharing octahedral chains, made of M1 (=Mn),
216 M2a (=Mg), and M2b (=Al) (**Figure 6**) (Ma et al. 1983), rather than two types, as in
217 zhanghuifenite (**Figure 3**). In other words, due to the above chemical substitution, the two
218 adjacent, symmetrically-equivalent octahedral chains in qingheite become nonequivalent

219 in zhanghuifenite. Specifically, we have the following structural relationship between the
220 two minerals:

221	<u>Qingheiite</u>		<u>Zhanghuifenite</u>	
222	One chain		A chain	B chain
223	2M1 (= Mn)	→	M1 (= Mn) + M2 (= Mn)	
224	2M2a (= Mg)	→	M4 (= Mg) + M3 (= Mn)	
225	2M2b (= Al)	→	M5 (= Mg) + M6 (= Al)	

226 By the same token, we can find the chemical and structural relationships between
227 rosemaryite and bobfergusonite, and between ferrosemaryite and ferrobobfergusonite,
228 as shown in **Table 8**. These relationships established between the known minerals in the
229 wyllieite and bobfergusonite groups lead us to postulate the existence of three more
230 possible new minerals in the bobfergusonite group, labelled as postulated new minerals 1,
231 2, and 3 in **Table 8**. Among them, postulated new mineral 1, $\text{Na}_3\text{Fe}^{2+}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$, can
232 be derived from ferroqingheiite through the coupled substitution of 2Fe^{2+} for $(\text{Na}^+ + \text{Al}^{3+})$
233 and may be regarded as “ferrozhanghuifenite”. Similarly, postulated new minerals 2 and
234 3 are related to wyllieite and ferrowyllieite, respectively, through the coupled
235 substitutions of 2Mn^{2+} for $(\text{Na}^+ + \text{Al}^{3+})$ and 2Fe^{2+} for $(\text{Na}^+ + \text{Al}^{3+})$.

236 The zhanghuifenite sample we examined was originally donated to the RRUFF
237 Project as “qingheiite”, which has been studied previously by Galliski et al. (2009) using
238 powder X-ray diffraction and electron microprobe analysis and by Frost et al. (2013)
239 using electron microprobe analysis, along with Raman and IR spectroscopy. **Table 1**
240 shows the similarity in the chemical compositions between zhanghuifenite and qingheiite
241 from the same locality, as well as that from the type locality, Qinghe, China. However,
242 without single-crystal X-ray structure analysis, it is unclear whether “qingheiite”
243 examined by Galliski *et al.* (2009) and Frost *et al.* (2013) is actually zhanghuifenite. This
244 argument then begs question whether or not qingheiite can be distinguished from
245 zhanghuifenite via careful inspection of powder X-ray diffraction data. Figure 7 displays
246 the powder X-ray diffraction patterns of qingheiite and zhanghuifenite calculated from
247 the structure data from Ma et al. (1983) and this study, respectively. Evidently, the major

248 features of two profiles are considerably similar, except for some relatively weak peaks.
249 Therefore, cautions must be exercised when powder X-ray diffraction data are used to
250 identify these two minerals.

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307 **List of Figure Captions**

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309 Fig. 1. The rock specimen on which the new mineral zhanghuifenite was found.

310

311 Fig. 2. A microscopic view of massive dark-green zhanghuifenite crystals.

312

313 Fig. 3. Crystal structure of zhanghuifenite, showing a sheet made of two types of edge-
314 sharing MO_6 octahedral chains ($\text{M} = \text{Mn, Fe, Mg, Al}$) connected by PO_4 tetrahedra. The
315 yellow, green, and red octahedra represent MnO_6 , MgO_6 , and AlO_6 , respectively.

316

317 Fig. 4. Sheets made of MO_6 octahedra and PO_4 tetrahedra parallel to (010) are linked together
318 through corner-sharing between PO_4 tetrahedra and MO_6 octahedra in the adjacent sheets, leaving
319 open channels parallel to a , where the large X cations (spheres) are situated ($\text{X} = \text{Na, Ca, Mn}$).
320 The yellow, green, and red octahedra represent MnO_6 , MgO_6 , and AlO_6 , respectively.

321

322 Figure 5. Raman spectrum of zhanghuifenite, along with that of bobfergusonite for
323 comparison.

324

325 Figure 6. Crystal structure of qingheite, showing a sheet made of edge-sharing MO_6
326 octahedral chains ($\text{M} = \text{Mn, Mg, Al}$) connected by PO_4 tetrahedra. The structure data
327 were taken from Ma et al. (1983).

328

329 Figure 7. Powder X-ray diffraction patterns for zhanghuifenite (bottom) and qingheite
330 (top) calculated with Cu radiation from the structure data from this study and Ma et al.
331 (1983), respectively.

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344 Table 4. Refined site occupancies for zhanghuifenite.

345

346 Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters
347 (\AA^2) for zhanghuifenite.

348

349 Table 6. Atomic displacement parameters (\AA^2) for zhanghuifenite.

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351 Table 7. Selected bond distances (\AA) for zhanghuifenite.

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Table 1. Chemical compositions for qingheite and zhanghuifenite.

	Qingheite Santa Ana Argentina	Qingheite Santa Ana Argentina	Qingheite Qinghe China	Zhanghuifenite Santa Ana Argentina	
					standards
P ₂ O ₅	45.11	45.67	45.63	45.21(29)	Apatite
Al ₂ O ₃	5.07	4.70	4.53	4.36(5)	Anorthite
Fe ₂ O ₃	4.09	5.96	2.24	1.58*	
MgO	6.21	7.42	9.75	7.14(8)	Forsterite
MnO	24.21	21.76	23.60	23.15(13)	Rhodochrosite
FeO	6.38	4.95	3.94	8.84(8)	Fayalite
ZnO	0.12	0.16	0.23	b.d.	
CaO	0.50	0.71	0.93	0.66(2)	Anorthite
Na ₂ O	9.24	9.26	8.73	9.19(30)	Albite
K ₂ O	0.02		0.04	b.d.	
Total	100.99 (1)	100.63 (2)	99.64 (3)	100.13 This study	

References: (1) Galliski et al. (2009); (2) Frost et al. (2013); (3) Ma et al. (1983).

Note: (a) *Obtained by adjusting the Fe²⁺/Fe³⁺ ratio for electroneutrality.

(b) b.d. = below detection.

Table 2. Powder X-ray diffraction data of zhanghuifenite

<i>I</i>	d_{meas}	d_{calc}	h k l
7	8.130	8.166	0 1 1
21	6.201	6.233	0 2 0
3	5.258	5.302	-2 1 1
2	4.767	4.795	2 1 1
2	4.436	4.460	2 2 0
2	4.160	4.178	-2 1 2
3	4.073	4.083	0 2 2
13	3.445	3.461	0 1 3
12	3.078	3.083	-4 1 1
8	3.026	3.032	-2 3 2
9	2.928	2.929	-4 0 2
25	2.877	2.874	4 1 1
10	2.750	2.752	-2 4 1
100	2.697	2.700	0 4 2
11	2.647	2.651	-4 2 2
8	2.585	2.597	4 0 2
34	2.527	2.526	-4 3 1
5	2.476	2.479	0 2 4
6	2.394	2.397	4 2 2
2	2.319	2.322	2 5 0
4	2.214	2.216	-2 3 4
10	2.187	2.186	-4 3 3
7	2.130	2.130	0 1 5
14	2.096	2.098	6 1 0
12	2.047	2.050	0 5 3
9	1.970	1.973	4 3 3
6	1.936	1.939	0 6 2
4	1.847	1.849	4 2 4
4	1.806	1.806	-2 5 4
4	1.781	1.781	-2 1 6
14	1.742	1.740	-4 3 5
4	1.718	1.715	2 7 0
8	1.645	1.644	4 4 4
9	1.594	1.591	-8 0 2
13	1.561	1.560	0 4 6
8	1.526	1.525	4 7 1
4	1.507	1.506	-2 8 1
4	1.485	1.484	4 0 6
5	1.444	1.444	4 2 6
6	1.421	1.421	8 4 0
6	1.353	1.353	-6 7 2
4	1.351	1.351	0 0 8
4	1.326	1.326	-8 4 4
4	1.296	1.297	6 7 2
6	1.284	1.285	-8 0 6

Table 3. Comparison of mineralogical data for zhanghuifenite, bobfergusonite, and qingheite

	Zhanghuifenite	Bobfergusonite	Qingheite
Ideal chemical formula	$\text{Na}_3\text{Mn}^{2+}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$	$\text{Na}_2\text{Mn}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$	$\text{Na}_2\text{Mn}^{2+}\text{MgAl}(\text{PO}_4)_3$
Crystal symmetry	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	12.8926(3)	12.796(3)	11.856(3)
b (Å)	12.4658(3)	12.465(2)	12.411(3)
c (Å)	10.9178(2)	11.001(2)	6.421(1)
β (°)	97.9200(10)	97.39(3)	114.45(2)
V (Å ³)	1737.93(7)	1740.1(5)	860.10(3)
Z	4	4	2
ρ_{cal} (g/cm ³)	3.619	3.66	3.610
2θ range for data collection	≤ 65.18	≤ 60.10	≤ 65.00
No. of reflections collected	25050	13000	3650
No. of independent reflections	6296	5035	3650
No. of reflections with $I > 2\sigma(I)$	4692	2959	2294
No. of parameters refined	373		
R(int)	0.024	0.026	
Final R_1 , wR_2 factors [$I > 2\sigma(I)$]	0.024, 0.063	0.027, 0.064	0.055
Goodness-of-fit	1.013		
Crystal locality	Santa Ana mine, Argentina	Nancy mine, Argentina	Qinghe County China
Reference	This study	Tait et al. (2004)	Ma et al. (1983)

Table 4. Comparison of cation site occupations between bobfergusonite and zhanghuifenite

Site	Site sym.	B.L.	Bobfergusonite (Tait et al. 2004)	B.L.	Zhanghuifenite (This study)
M1	1	2.216	1.00Mn	2.220	1.00Mn
M2	1	2.237	0.89Mn + 0.11Ca	2.238	1.00Mn
M3	1	2.116	0.38Fe ²⁺ + 0.32Mn + 0.24Fe ³⁺ + 0.06Mg	2.119	0.48Fe ²⁺ + 0.37Mg + 0.15Mn
M4	1	2.092	0.53Fe ²⁺ + 0.25Fe ³⁺ + 0.22Mg	2.101	0.59Mg + 0.41Fe ²⁺
M5	1	2.059	0.28Fe ²⁺ + 0.42Fe ³⁺ + 0.30Mg	2.085	0.72Mg + 0.28Fe ²⁺
M6	1	1.918	0.94Al + 0.06Fe ³⁺	1.929	0.81Al + 0.19Fe ³⁺
X1	1	2.238	1.00Mn	2.241	1.00Mn
X2	-1	2.550	0.46Na + 0.04□	2.551	0.50Na
X3	-1	2.572	0.44Na + 0.06□	2.556	0.39Na + 0.11Ca
X4	1	2.654	0.57Na + 0.43□	2.583	0.91Na + 0.09□
X5	1	2.635	0.53Na + 0.47□	2.602	1.00Na

Note: Site sym. = site symmetry; B.L. = average bond length.

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for zhanghuifenite

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
M1	0.13336 (2)	0.23653 (2)	-0.00041 (2)	0.00864 (6)
M2	0.63016 (2)	0.23518 (2)	0.00231 (2)	0.00942 (6)
M3	0.29464 (2)	0.15001 (2)	0.72568 (2)	0.00734 (7)
M4	0.79683 (3)	0.15053 (3)	0.72831 (3)	0.00739 (9)
M5	0.46278 (3)	0.16528 (3)	0.28289 (3)	0.00778 (10)
M6	0.96056 (3)	0.16562 (3)	0.28271 (3)	0.00726 (8)
X1	0.24830 (2)	0.00080 (2)	-0.00328 (2)	0.01338 (6)
X2	0.000000	0.000000	0.000000	0.0213 (2)
X3	0.500000	0.000000	0.000000	0.0341 (3)
X4	0.37437 (6)	0.47638 (7)	0.00306 (6)	0.01888 (18)
X5	0.87300 (6)	0.47641 (7)	0.99624 (6)	0.02217 (18)
P1	0.38323 (3)	0.21446 (3)	0.00473 (3)	0.00599 (8)
P2	0.88287 (3)	0.21180 (3)	0.00956 (3)	0.00590 (8)
P3	0.20082 (3)	0.11369 (3)	0.26227 (3)	0.00568 (7)
P4	0.70651 (3)	0.11351 (3)	0.26664 (3)	0.00571 (7)
P5	0.05988 (3)	0.09512 (3)	0.73520 (3)	0.00627 (8)
P6	0.55877 (3)	0.10366 (3)	0.73671 (3)	0.00598 (8)
O1	0.29734 (8)	0.21350 (8)	0.54658 (9)	0.0085 (2)
O2	0.79922 (9)	0.21210 (9)	0.54558 (9)	0.0090 (2)
O3	0.46703 (9)	0.22123 (8)	0.45809 (9)	0.0087 (2)
O4	0.96478 (8)	0.21474 (8)	0.44879 (9)	0.0084 (2)
O5	0.33012 (9)	0.37333 (8)	0.41922 (10)	0.0107 (2)
O6	0.82885 (9)	0.36998 (8)	0.41434 (10)	0.0108 (2)
O7	0.44045 (9)	0.35694 (8)	0.61502 (10)	0.0104 (2)

O8	0.94683 (9)	0.35205 (9)	0.60475 (10)	0.0129 (2)
O9	0.11134 (9)	0.17025 (8)	0.32053 (10)	0.0090 (2)
O10	0.62394 (9)	0.17601 (8)	0.32651 (10)	0.0096 (2)
O11	0.13315 (9)	0.15228 (8)	0.65540 (10)	0.0099 (2)
O12	0.63697 (9)	0.15791 (8)	0.66122 (10)	0.0096 (2)
O13	0.10922 (9)	0.41087 (9)	0.37312 (10)	0.0113 (2)
O14	0.61340 (9)	0.41556 (9)	0.37032 (10)	0.0111 (2)
O15	0.17183 (9)	0.40227 (8)	0.62606 (9)	0.0092 (2)
O16	0.66804 (9)	0.40155 (8)	0.62128 (9)	0.0090 (2)
O17	0.29877 (9)	0.18411 (8)	0.28114 (10)	0.0098 (2)
O18	0.80842 (9)	0.18054 (8)	0.27989 (9)	0.0084 (2)
O19	0.46154 (8)	0.17672 (8)	0.73709 (10)	0.0092 (2)
O20	0.95876 (9)	0.15851 (9)	0.73257 (10)	0.0108 (2)
O21	0.27930 (9)	0.50663 (8)	0.17162 (10)	0.0107 (2)
O22	0.77583 (9)	0.50661 (8)	0.16673 (10)	0.0109 (2)
O23	0.46459 (9)	0.48282 (8)	0.82452 (10)	0.0106 (2)
O24	0.97481 (9)	0.49708 (8)	0.82607 (10)	0.0117 (2)

Table 6. Atomic displacement parameters (\AA^2) for zhanghuifenite.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
M1	0.00841 (12)	0.00908 (11)	0.00806 (11)	0.00035 (8)	-0.00019 (8)	0.00130 (7)
M2	0.00930 (12)	0.00917 (11)	0.00909 (11)	0.00113 (8)	-0.00121 (9)	-0.00035 (8)
M3	0.00777 (14)	0.00716 (13)	0.00673 (12)	-0.00072 (10)	-0.00028 (9)	0.00015 (9)
M4	0.00740 (17)	0.00726 (16)	0.00722 (15)	-0.00011 (11)	-0.00007 (11)	-0.00015 (11)
M5	0.0080 (2)	0.00916 (18)	0.00602 (17)	0.00049 (13)	0.00036 (13)	-0.00061 (12)
M6	0.00732 (18)	0.00784 (16)	0.00658 (16)	0.00030 (13)	0.00077 (13)	-0.00028 (12)
X1	0.01921 (14)	0.00735 (11)	0.01599 (12)	-0.00092 (9)	0.01102 (10)	-0.00106 (9)
X2	0.0258 (6)	0.0117 (4)	0.0307 (6)	0.0009 (4)	0.0190 (5)	-0.0010 (4)
X3	0.0468 (7)	0.0158 (4)	0.0469 (6)	0.0020 (4)	0.0325 (5)	0.0015 (4)
X4	0.0198 (5)	0.0251 (4)	0.0130 (4)	0.0002 (3)	0.0070 (3)	0.0000 (3)
X5	0.0214 (4)	0.0303 (4)	0.0158 (4)	-0.0007 (3)	0.0062 (3)	0.0012 (3)
P1	0.00620 (17)	0.00646 (16)	0.00545 (16)	0.00019 (12)	0.00132 (13)	0.00000 (11)
P2	0.00603 (17)	0.00597 (16)	0.00594 (16)	-0.00015 (12)	0.00170 (13)	0.00008 (11)
P3	0.00624 (18)	0.00544 (16)	0.00555 (16)	0.00036 (13)	0.00150 (12)	-0.00002 (12)
P4	0.00623 (17)	0.00532 (15)	0.00575 (15)	0.00020 (13)	0.00139 (12)	-0.00035 (12)
P5	0.00580 (18)	0.00713 (16)	0.00590 (16)	-0.00068 (13)	0.00082 (12)	0.00023 (12)
P6	0.00602 (18)	0.00639 (16)	0.00558 (16)	-0.00032 (13)	0.00096 (12)	0.00022 (12)
O1	0.0066 (5)	0.0111 (5)	0.0082 (5)	-0.0037 (4)	0.0021 (4)	0.0008 (4)
O2	0.0067 (5)	0.0126 (5)	0.0079 (5)	-0.0026 (4)	0.0013 (4)	0.0012 (4)
O3	0.0073 (5)	0.0105 (5)	0.0086 (5)	0.0024 (4)	0.0018 (4)	-0.0005 (4)
O4	0.0069 (5)	0.0108 (5)	0.0077 (4)	0.0022 (4)	0.0014 (4)	0.0002 (4)
O5	0.0143 (6)	0.0090 (5)	0.0088 (5)	0.0041 (4)	0.0022 (4)	0.0023 (4)
O6	0.0141 (6)	0.0089 (5)	0.0093 (5)	0.0051 (4)	0.0015 (4)	0.0004 (4)
O7	0.0138 (6)	0.0088 (5)	0.0087 (5)	-0.0035 (4)	0.0018 (4)	-0.0014 (4)
O8	0.0180 (6)	0.0119 (5)	0.0084 (5)	-0.0065 (4)	-0.0002 (4)	-0.0004 (4)

O9	0.0086 (5)	0.0090 (5)	0.0100 (5)	0.0015 (4)	0.0035 (4)	-0.0007 (4)
O10	0.0093 (5)	0.0100 (5)	0.0097 (5)	0.0021 (4)	0.0023 (4)	-0.0019 (4)
O11	0.0083 (5)	0.0100 (5)	0.0121 (5)	-0.0003 (4)	0.0042 (4)	0.0034 (4)
O12	0.0081 (5)	0.0101 (5)	0.0114 (5)	-0.0001 (4)	0.0035 (4)	0.0022 (4)
O13	0.0139 (6)	0.0112 (5)	0.0080 (5)	-0.0003 (4)	-0.0011 (4)	-0.0012 (4)
O14	0.0131 (6)	0.0111 (5)	0.0079 (5)	0.0009 (4)	-0.0025 (4)	-0.0001 (4)
O15	0.0107 (5)	0.0097 (5)	0.0070 (5)	-0.0008 (4)	0.0011 (4)	0.0017 (4)
O16	0.0112 (5)	0.0092 (5)	0.0067 (5)	-0.0005 (4)	0.0013 (4)	0.0009 (4)
O17	0.0092 (5)	0.0098 (5)	0.0101 (5)	-0.0018 (4)	0.0009 (4)	0.0000 (4)
O18	0.0074 (5)	0.0088 (5)	0.0090 (5)	-0.0013 (4)	0.0012 (4)	-0.0009 (4)
O19	0.0065 (5)	0.0104 (5)	0.0109 (5)	0.0011 (4)	0.0017 (4)	0.0004 (4)
O20	0.0073 (5)	0.0133 (5)	0.0122 (5)	0.0018 (4)	0.0024 (4)	0.0009 (4)
O21	0.0132 (6)	0.0072 (5)	0.0116 (5)	-0.0017 (4)	0.0014 (4)	-0.0026 (4)
O22	0.0124 (6)	0.0077 (5)	0.0126 (5)	-0.0012 (4)	0.0021 (4)	-0.0022 (4)
O23	0.0125 (5)	0.0093 (5)	0.0100 (5)	0.0023 (4)	0.0012 (4)	0.0013 (4)
O24	0.0139 (6)	0.0086 (5)	0.0126 (5)	0.0031 (4)	0.0015 (4)	0.0018 (4)

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Table 7. Selected bond distances (Å) for zhanghuifenite.

Distance (Å)		Distance (Å)	
M1—O10	2.1706(11)	M2—O11	2.1783(11)
M1—O16	2.1826(11)	M2—O15	2.2022(11)
M1—O3	2.1939(11)	M2—O4	2.2212(11)
M1—O12	2.1966(11)	M2—O1	2.2364(11)
M1—O2	2.2224(11)	M2—O9	2.2923(11)
M1—O14	2.3564(11)	M2—O13	2.2961(11)
<M1—O>	2.220	<M2—O>	2.238
M3—O22	2.0595(11)	M4—O21	2.0576(11)
M3—O6	2.0613(11)	M4—O20	2.0842(11)
M3—O1	2.1142(11)	M4—O5	2.0906(11)
M3—O11	2.1176(11)	M4—O12	2.0920(11)
M3—O19	2.1640(11)	M4—O17	2.1398(11)
M3—O18	2.1944(11)	M4—O2	2.1418(11)
<M3—O>	2.119	<M4—O>	2.101
M5—O8	1.9395(11)	M6—O7	1.8350(11)
M5—O3	2.0296(11)	M6—O23	1.9048(11)
M5—O10	2.0710(12)	M6—O4	1.9075(11)
M5—O24	2.0790(11)	M6—O9	1.9318(12)
M5—O17	2.1249(12)	M6—O18	1.9663(11)
M5—O20	2.2632(12)	M6—O19	2.0279(11)
<M5—O>	2.085	<M6—O>	1.929
X1—O5	2.1553(11)		
X1—O6	2.1770(11)		
X1—O15	2.1786(10)		
X1—O16	2.1884(10)		
X1—O14	2.3141(11)		
X1—O13	2.4354(11)		
<X1—O>	2.241		
X2—O7	2.3692(10) ×2	X3—O8	2.3228(11) ×2
X2—O14	2.4126(11) ×2	X3—O13	2.3821(11) ×2
X2—O16	2.6764(11) ×2	X3—O15	2.7287(11) ×2
X2—O5	2.7452(12) ×2	X3—O6	2.7932(12) ×2
<X2—O>	2.551	<X3—O>	2.557
X4—O21	2.3776(13)	X5—O22	2.4121(13)
X4—O23	2.4050(13)	X5—O24	2.4317(13)
X4—O22	2.4983(14)	X5—O21	2.5035(14)
X4—O2	2.6074(14)	X5—O24	2.5834(14)
X4—O23	2.6526(14)	X5—O1	2.6469(14)

X4—O4	2.7525(14)	X5—O3	2.8022(14)
X4—O11	2.7864(13)	X5—O12	2.8338(13)
<X4—O>	2.583	<X5—O>	2.602

P1—O8	1.5184(11)	P2—O3	1.5357(11)
P1—O2	1.5307(11)	P2—O1	1.5392(11)
P1—O6	1.5437(11)	P2—O5	1.5413(11)
P1—O4	1.5601(11)	P2—O7	1.5416(11)
<P1—O>	1.538	<P2—O>	1.539

P3—O21	1.5221(11)	P4—O22	1.5203(11)
P3—O17	1.5285(11)	P4—O10	1.5361(11)
P3—O16	1.5507(11)	P4—O18	1.5469(11)
P3—O9	1.5603(11)	P4—O15	1.5508(11)
<P3—O>	1.540	<P4—O>	1.538

P5—O20	1.5213(11)	P6—O24	1.5299(11)
P5—O11	1.5447(11)	P6—O12	1.5434(11)
P5—O14	1.5458(11)	P6—O19	1.5500(11)
P5—O23	1.5581(11)	P6—O13	1.5513(11)
<P5—O>	1.542	<P6—O>	1.544

Table 8. Comparison the minerals with wyllieite-type and bobfergusonite-type structures

Wyllieite-type, $P2_1/n$ $a \approx 11.9$, $b \approx 12.4$, $c \approx 6.4$ Å $\beta \approx 114.5^\circ$, $V \approx 850$ Å ³	Coupled substitution	Bobfergusonite-type, $P2_1/n$ $a \approx 12.8$, $b \approx 12.5$, $c \approx 11.0$ Å $\beta \approx 97.5^\circ$, $V \approx 1700$ Å ³
Rosemaryite $2 \times [\square \text{NaMn}^{2+}(\text{Fe}^{3+}\text{Al})(\text{PO}_4)_3]$	$\text{Fe}^{3+} + \text{Al}^{3+} \longrightarrow 3\text{Mn}^{2+}$	Bobfergusonite $\square \text{Na}_2\text{Mn}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$
Ferroserosemaryite $2 \times [\square \text{NaFe}^{2+}(\text{Fe}^{3+}\text{Al})(\text{PO}_4)_3]$	$\text{Fe}^{3+} + \text{Al}^{3+} \longrightarrow 3\text{Fe}^{2+}$	Ferrobobfergusonite $\square \text{Na}_2\text{Fe}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$
Qingheiite $2 \times [\text{Na}_2\text{Mn}(\text{MgAl})(\text{PO}_4)_3]$	$\text{Na}^+ + \text{Al}^{3+} \longrightarrow 2\text{Mn}^{2+}$	Zhanghuiifenite $\text{Na}_3\text{Mn}^{2+}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$
Qingheiite-(Fe ²⁺) $2 \times [\text{Na}_2\text{Fe}^{2+}\text{MgAl}(\text{PO}_4)_3]$	$\text{Na}^+ + \text{Al}^{3+} \longrightarrow 2\text{Fe}^{2+}$	Ferrozhanghuiifenite? $\text{Na}_3\text{Fe}^{2+}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$
Wyllieite $2 \times [\text{Na}_2\text{Mn}(\text{Fe}^{2+}\text{Al})(\text{PO}_4)_3]$	$\text{Na}^+ + \text{Al}^{3+} \longrightarrow 2\text{Mn}^{2+}$	Postulated new mineral 2 $\text{Na}_3\text{Mn}^{2+}_4\text{Fe}^{2+}_2\text{Al}(\text{PO}_4)_6$
Ferrowyllieite $2 \times [\text{Na}_2\text{Fe}^{2+}(\text{Fe}^{2+}\text{Al})(\text{PO}_4)_3]$	$\text{Na}^+ + \text{Al}^{3+} \longrightarrow 2\text{Fe}^{2+}$	Postulated new mineral 3 $\text{Na}_3\text{Fe}^{2+}_4\text{Fe}^{2+}_2\text{Al}(\text{PO}_4)_6$



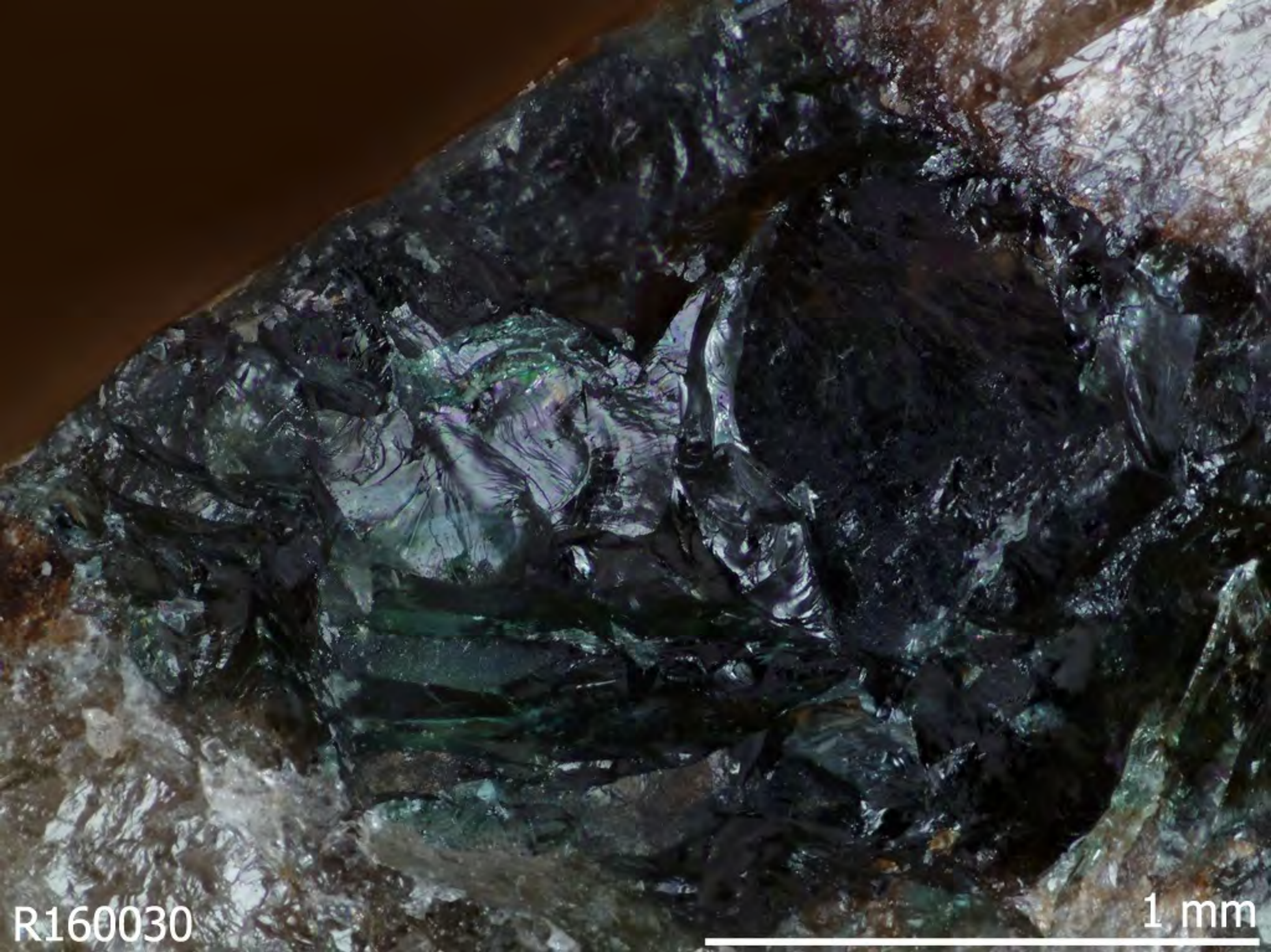
**Beusite interlaminated
with lithiophilite**

Zhanghuifenite

R160030

4 mm

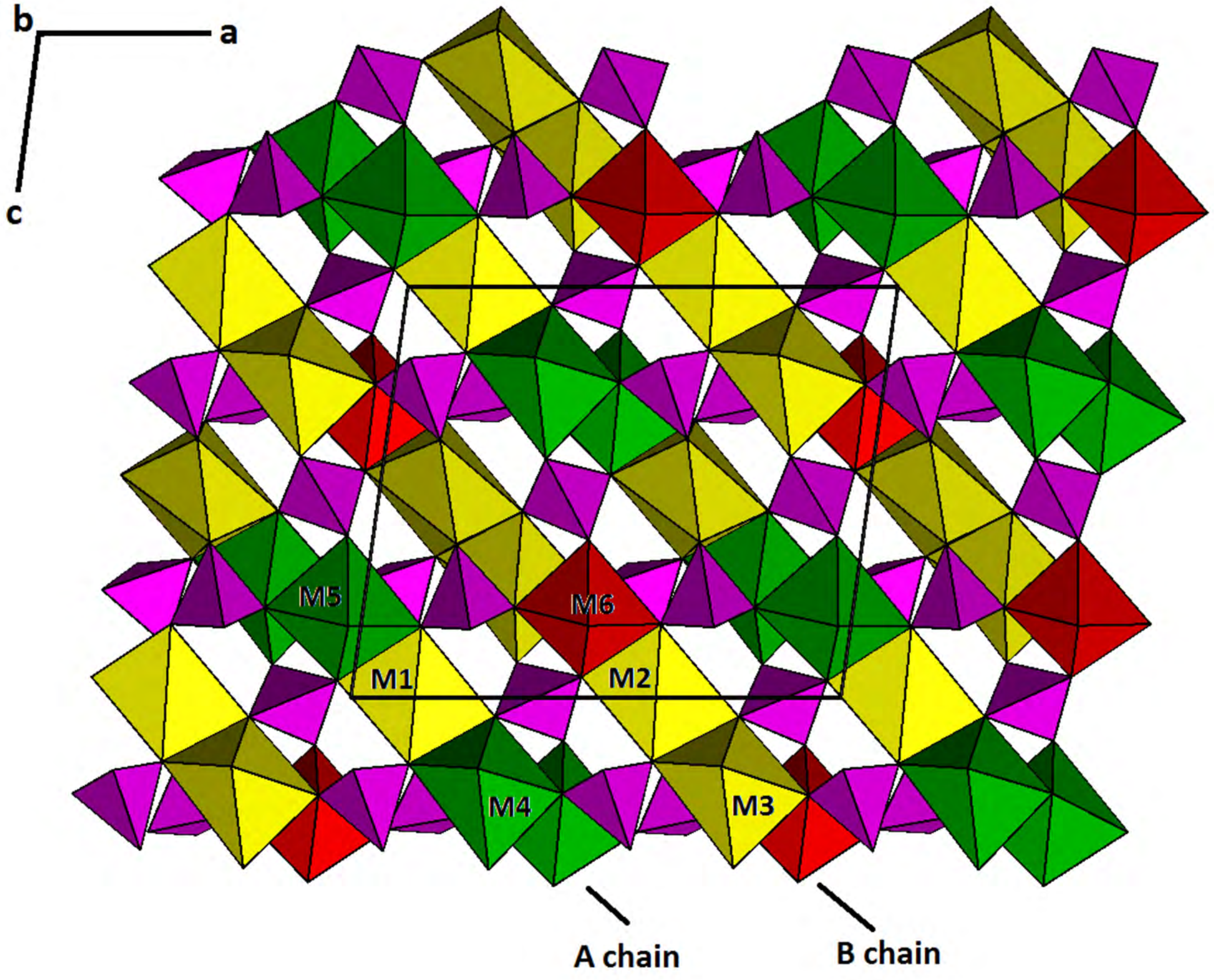
Figure 1

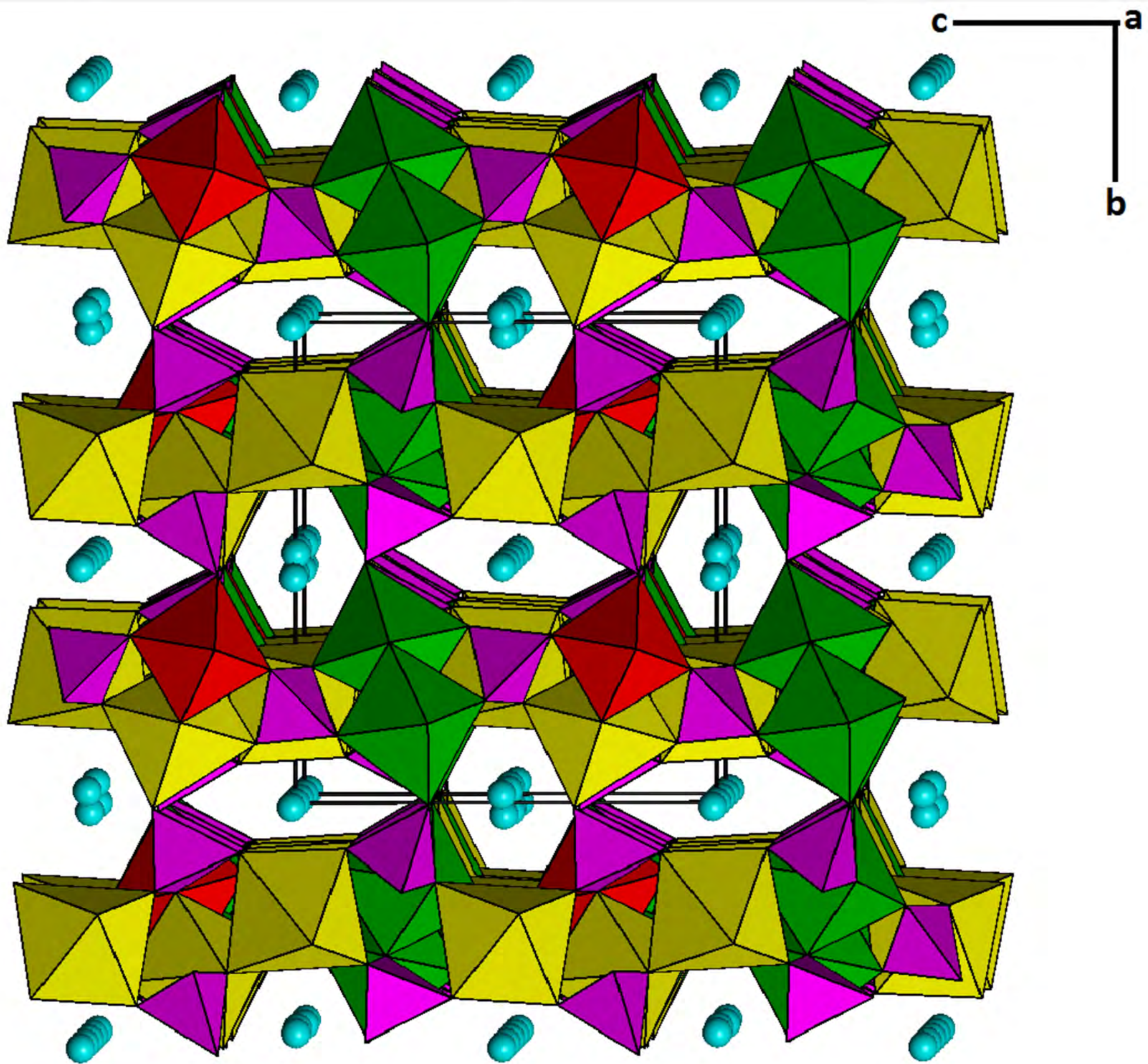


R160030

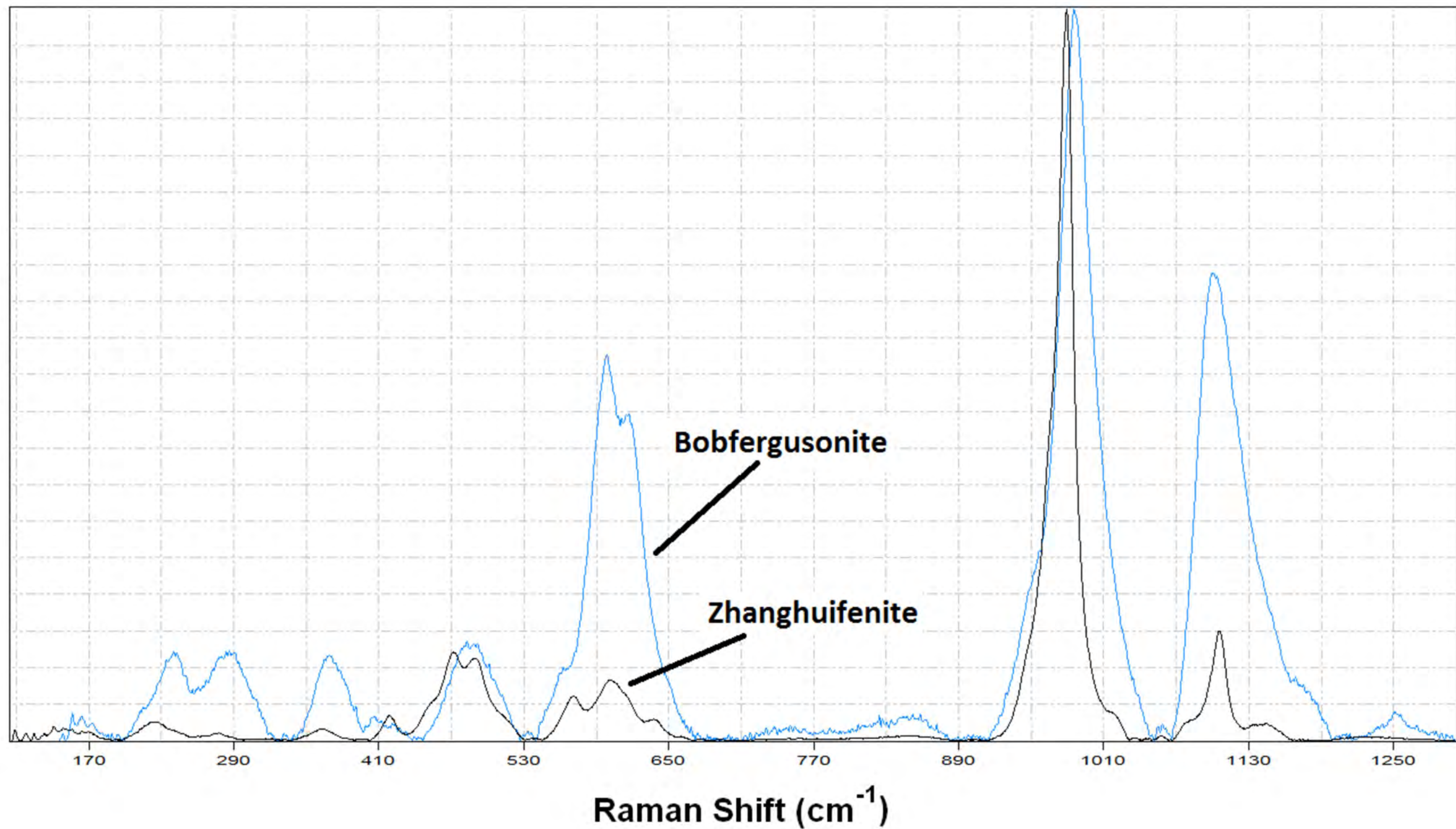
1 mm

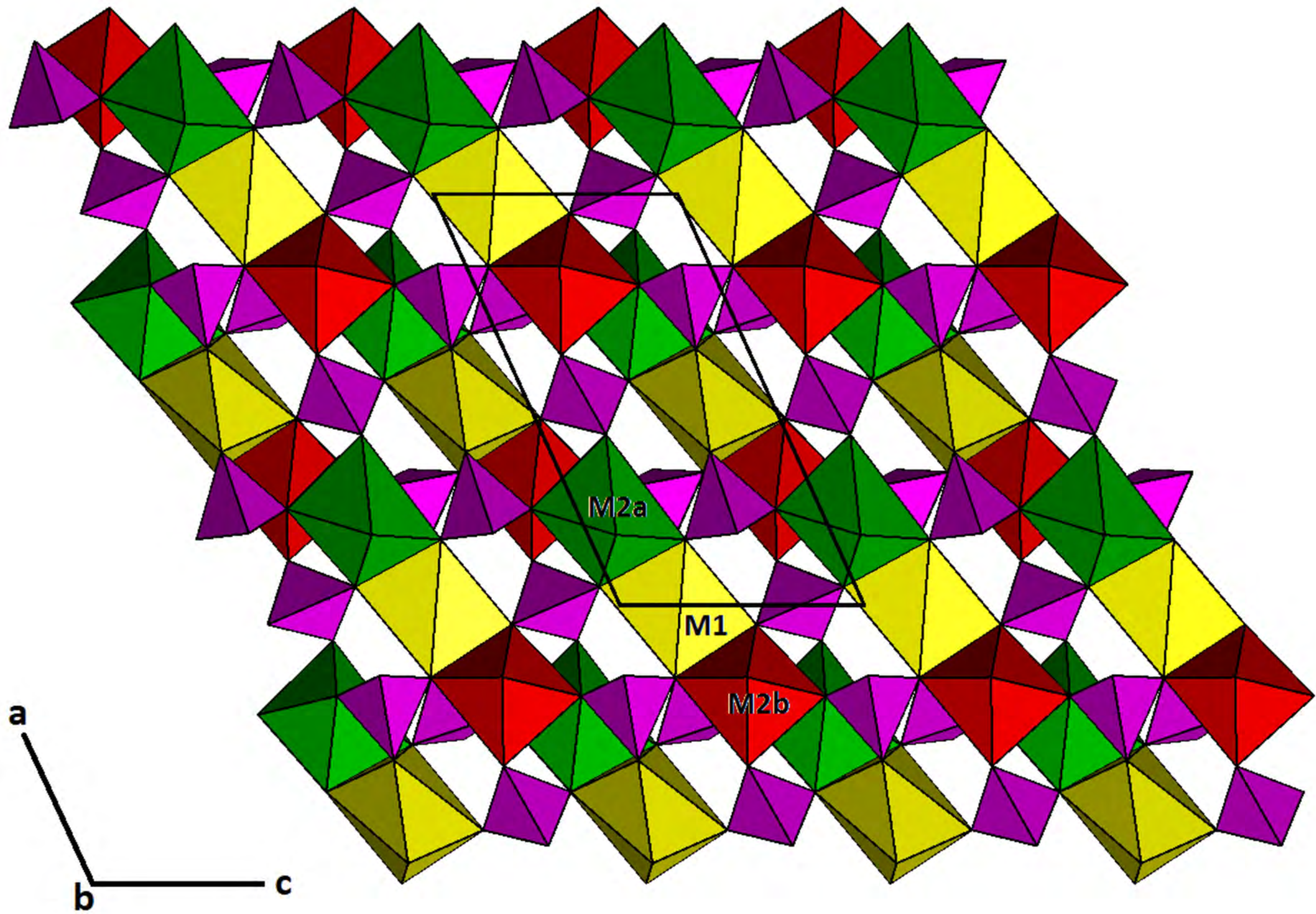
Figure 2





Relative Intensity





Relative intensity

