

FERROBOBFERGUSONITE, $\square\text{Na}_2\text{Fe}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$, A NEW MINERAL OF THE BOBFERGUSONITE GROUP FROM THE VICTORY MINE, CUSTER COUNTY, SOUTH DAKOTA, USA

HEXIONG YANG[§], TOMMY YONG, AND ROBERT T. DOWNS

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

ABSTRACT

A new mineral species, ferrobobfergusonite, ideally $\square\text{Na}_2\text{Fe}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$, has been found in the Victory Mine, Custer County, South Dakota, USA. It is massive and associated with ferrowyllieite, schorl, fillowite, arrojadite, quartz, and muscovite. Broken pieces of ferrobobfergusonite are blocky or tabular with single crystals up to $0.9 \times 0.7 \times 0.4$ mm. No twinning or parting is observed macroscopically. The mineral is deep green-brown and transparent with a pale green-yellow streak and vitreous luster. It is brittle and has a Mohs hardness of ~ 5 , with perfect cleavage on {010}. The measured and calculated densities are 3.68(1) and 3.69 g/cm³, respectively. Optically, ferrobobfergusonite is biaxial (+), with $\alpha = 1.698$ (2), $\beta = 1.705$ (2), $\gamma = 1.727$ (2) (white light), $2V$ (meas.) = 65(2)°, $2V$ (calc.) = 60°, with orientation of the optic axes $\alpha \wedge X = 16^\circ$, $\beta = Y$, with $X =$ yellowish brown, $Y =$ brown, and $Z =$ deep brown. The dispersion is very strong with $r > v$. The calculated compatibility index based on the empirical formula is 0.017 (superior). An electron microprobe analysis yielded an empirical formula (based on 24 O *apfu*) of $(\text{Na}_{1.72}\square_{1.28})_{\Sigma 3.00}(\text{Fe}^{2+}_{3.50}\text{Mn}_{0.89}\text{Mg}_{0.44}\text{Ca}_{0.13})_{\Sigma 4.96}(\text{Fe}^{3+}_{0.77}\text{Al}_{0.23})_{\Sigma 1.00}\text{Al}(\text{PO}_4)_6$.

Ferrobobfergusonite is isostructural with bobfergusonite, a member of the alluaudite supergroup. It is monoclinic, with space group $P2_1/n$ and unit-cell parameters $a = 12.7156(3)$, $b = 12.3808(3)$, $c = 10.9347(3)$ Å, $\beta = 97.3320(10)^\circ$, and $V = 1707.37(7)$ Å³. The crystal structure of ferrobobfergusonite contains six octahedral M ($= \text{Fe}^{2+}$, Mg, Mn²⁺, Al, Fe³⁺) sites and five X ($= \text{Na}$, Mn²⁺, Ca) sites with coordination numbers between 6 and 8. The six MO_6 octahedra share edges to form two types of kinked chains extending along [101], with one consisting of $M1$ – $M4$ – $M5$ linkages and the other of $M2$ – $M3$ – $M6$ linkages. These chains are joined by PO_4 tetrahedra to form sheets parallel to (010), which are linked together through corner-sharing between PO_4 tetrahedra and MO_6 octahedra in the adjacent sheets, leaving open channels parallel to \mathbf{a} , where the large X cations are situated. The M cations are strongly ordered over the six sites, with $M1$, $M2$, $M3$, and $M4$ being dominantly occupied by Fe²⁺, and $M5$ and $M6$ by Fe³⁺ and Al, respectively. Among the five X sites, the $X1$ site is filled with Mn²⁺ and Ca, whereas the $X2$ – $X5$ sites are partially occupied by Na.

Keywords: ferrobobfergusonite, wyllieite, alluaudite, crystal structure, X-ray diffraction, Raman spectra.

INTRODUCTION

A new mineral species, ferrobobfergusonite, ideally $\square\text{Na}_2\text{Fe}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$, was found on a specimen from the Victory Mine, Custer County, South Dakota, USA. The specimen is from the Rock Currier research collection, donated to the University of Arizona in 2012. It is named for the dominant presence of Fe²⁺ in its structure over Mn²⁺, with respect to bobfergusonite, ideally $\square\text{Na}_2\text{Mn}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification

(CNMNC) of the International Mineralogical Association (IMA 2017-006). The cotype samples have been deposited at the University of Arizona Mineral Museum (Catalogue # 21437) and the RRUFF Project (deposition # R140993) (<http://rruff.info>).

Ferrobobfergusonite, isotypic with bobfergusonite, is closely related to minerals of the wyllieite and alluaudite groups. Nevertheless, the minerals in the bobfergusonite group differ from those in the wyllieite and alluaudite groups in both chemical composition and structure. Moore & Molin-Case (1974) showed that the $P2_1/n$ wyllieite structure is a subgroup of the

[§] Corresponding author e-mail address: hyang@arizona.edu



FIG. 1. The specimen on which ferrobobfergusonite was found.

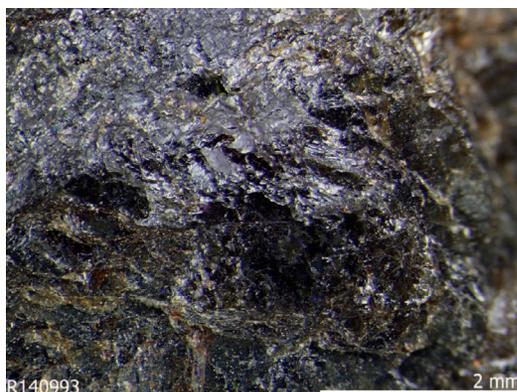


FIG. 2. A microscopic view of massive deep green-brown ferrobobfergusonite crystals.

$C2/c$ alluaudite structure, as a consequence of cation ordering. Moore & Ito (1979) introduced a nomenclature for the minerals of the alluaudite and wyllieite groups. Ercit *et al.* (1986) reported the crystal structure of bobfergusonite with space group $P2_1/n$ and demonstrated that it is also based on the alluaudite topology, like wyllieite, but has a more ordered cation distribution than that in wyllieite, resulting in a doubling of its unit-cell c dimension. Recently, a new nomenclature of the alluaudite supergroup indicated that the group consists of 16 phosphate and 19 arsenate minerals (Hatert 2019). This paper describes the physical and chemical properties of ferrobobfergusonite and its crystal structure deter-

mined from single-crystal X-ray diffraction data, illustrating its structural relationships to bobfergusonite in particular and alluaudite-type minerals in general.

SAMPLE DESCRIPTION AND EXPERIMENTAL METHODS

Occurrence, physical and chemical properties, and Raman spectra

Ferrobobfergusonite was found on a specimen collected from the Victory Mine ($43^{\circ}46'57''$ N, $103^{\circ}34'09''$ W), Custer County, South Dakota, USA (Fig. 1). It is massive and associated with ferrowyl-

TABLE 1. COMPARISON OF CHEMICAL COMPOSITIONS FOR BOBFERGUSONITE, ZHANGHUIFENITE, AND FERROBOBFERGUSONITE

Mineral Mine Location	Bobfergusonite Cross Lake Manitoba, Canada	Bobfergusonite Nancy Mine Argentina	Zhanghuifenite Santa Ana Mine Argentina	Ferrobobfergusonite Victory Mine South Dakota, USA	Standards
P ₂ O ₅ (wt.%)	45.30	43.64	45.21(29)	45.26(37)	Apatite
Al ₂ O ₃	7.50	4.88	4.36(5)	6.59(17)	Anorthite
Fe ₂ O ₃	6.70	9.16	1.58*	6.50*	Forsterite
MgO	0.30	2.28	7.14(8)	1.84(5)	Rhodochrosite
MnO	31.50	23.48	23.15(13)	6.64(11)	Fayalite
FeO	0.30	7.73	8.84(8)	26.45(21)	
ZnO	0.50		0.66(2)	0.77(16)	Anorthite
CaO	1.20	0.65	9.19(3)	5.61(23)	Albite
Na ₂ O	6.70	6.41			
K ₂ O	0.02				
H ₂ O	0.30				
Total	100.30	98.23	100.13	99.66	
	Ercit <i>et al.</i> (1986)	Tait <i>et al.</i> (2004)	Yang <i>et al.</i> (2021)	This study	

* Obtained by adjusting the Fe²⁺/Fe³⁺ ratio for electroneutrality.

TABLE 2. POWDER X-RAY DIFFRACTION DATA FOR FERROBOBFERGUSONITE

%	d_{meas}	d_{calc}	h	k	l
26	6.182	6.193	0	2	0
18	5.400	5.421	0	0	2
34	4.180	4.139	2	1	2
35	4.085	4.079	0	2	2
21	3.452	3.469	0	1	3
7	3.349	3.358	2	3	1
2	3.181	3.207	2	1	3
24	3.019	3.036	4	1	1
12	2.890	2.886	4	0	2
34	2.845	2.848	4	1	1
28	2.790	2.807	4	2	0
10	2.683	2.689	0	4	2
16	2.621	2.616	4	2	2
11	2.584	2.585	4	0	2
37	2.489	2.495	4	3	1
4	2.381	2.385	4	2	2
4	2.303	2.305	2	5	0
9	2.208	2.207	2	3	4
11	2.159	2.162	4	3	3
13	2.134	2.136	0	1	5
26	2.070	2.070	6	1	0
14	2.041	2.043	0	5	3
4	1.987	1.984	4	4	2
6	1.966	1.968	4	3	3
12	1.922	1.920	0	3	5
4	1.888	1.891	4	5	1
6	1.847	1.849	4	2	4
5	1.799	1.797	2	5	4
4	1.780	1.779	2	1	6
4	1.745	1.744	6	4	1
12	1.727	1.727	4	3	5
4	1.702	1.703	2	7	0
5	1.641	1.642	4	4	4
6	1.605	1.604	4	2	6
24	1.562	1.566	8	0	2
10	1.515	1.514	4	7	1
8	1.489	1.488	4	0	6
10	1.464	1.465	2	7	4
14	1.451	1.451	4	7	3
8	1.406	1.403	8	4	0
4	1.340	1.338	6	7	2

lieite, schorl, fillowite, arrojadite, quartz, and muscovite (Fig. 2). A detailed geological and mineralogical study of the Victory pegmatite was presented by Pray *et al.* (1953) and Moore & Ito (1973). According to Moore & Ito (1973), the Victory Mine pegmatite is chemically unique due to an unusual abundance of Na-rich primary phosphates rarely encountered elsewhere. The pegmatite has a wall zone ranging from 3 to 18 cm in thickness consisting of albite-quartz-muscovite

which grades into a coarse quartz-perthite-albite core. The interesting mineral assemblage appears to be confined, as nodules, to the region between the wall zone and the core (Pray *et al.* 1953), which is typical of Na-metasomatic products of primary phosphate phases in granitic pegmatites (Moore 1971).

Broken pieces of ferrobobfergusonite are blocky or tabular (due to good cleavage). Single crystals within the massive aggregates are found in sizes up to $0.9 \times 0.7 \times 0.4$ mm. No twinning or parting is observed macroscopically. The mineral is deep green-brown and transparent with a pale green-yellow streak and vitreous luster. It is brittle and has a Mohs hardness of ~ 5 , with perfect cleavage on $\{010\}$. The measured and calculated densities are 3.68 (1) and 3.69 g/cm³, respectively. Optically, ferrobobfergusonite is biaxial (+), with $\alpha = 1.698$ (2), $\beta = 1.705$ (2), $\gamma = 1.727$ (2) (white light), $2V$ (meas.) = 65(2)°, $2V$ (calc.) = 60°, and orientation $\alpha \wedge X = 16^\circ$, $\beta = Y$, with $X =$ yellowish brown, $Y =$ brown, and $Z =$ deep brown. The dispersion is very strong with $r > v$. The calculated compatibility index based on the empirical formula is 0.017 (superior) (Mandarino 1981). Ferrobobfergusonite is insoluble in water or hydrochloric acid.

The chemical composition was determined using a Cameca SX-100 electron microprobe (WDS mode, 15 kV, 20 nA, and a beam diameter of 5 μm). The standards used for the probe analysis are given in Table 1, along with the determined compositions (15 analysis points). The resultant chemical formula, calculated on the basis of 24 O atoms *pfu* (from the structure determination) is $(\text{Na}_{1.72}\square_{1.28})_{\Sigma 3.00}(\text{Fe}^{2+}_{3.50}\text{Mn}_{0.89}\text{Mg}_{0.44}\text{Ca}_{0.13})_{\Sigma 4.96}(\text{Fe}^{3+}_{0.77}\text{Al}_{0.23})_{\Sigma 1.00}\text{Al}(\text{PO}_4)_6$, which can be simplified to $\square\text{Na}_2\text{Fe}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$, where \square indicates the vacant site (see below for discussion).

The Raman spectrum of ferrobobfergusonite was collected from a randomly oriented crystal with a Thermo Almega microRaman system using a solid-state laser with a frequency of 532 nm at the full power of 150 mW and a thermoelectric cooled CCD detector. The laser is partially polarized with 4 cm⁻¹ resolution and a spot size of 1 μm .

X-ray crystallography

Both the powder and single-crystal X-ray diffraction data for ferrobobfergusonite were collected using a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized MoK α radiation. Listed in Table 2 are the measured powder X-ray diffraction data, along with those calculated from the determined structure using the program XPOW (Downs *et al.* 1993). The unit-cell parameters obtained from the powder X-ray diffraction data are $a =$

TABLE 3. COMPARISON OF CRYSTALLOGRAPHIC DATA FOR FERROBOBFERGUSONITE, BOBFERGUSONITE, AND ZHANGHUIFENITE

	Ferrobobfergusonite	Bobfergusonite	Zhanghuifenite
Ideal chemical formula	$\square\text{Na}_2\text{Fe}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$	$\square\text{Na}_2\text{Mn}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$	$\text{Na}_3\text{Mn}^{2+}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$
Crystal symmetry	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	12.7156(3)	12.796(3)	12.8926(3)
b (Å)	12.3808(3)	12.465(2)	12.4658(3)
c (Å)	10.9347(3)	11.001(2)	10.9178(2)
β (°)	97.3320(10)	97.39(3)	97.9200(10)
V (Å ³)	1707.37(7)	1740.1(5)	1737.93(7)
Z	4	4	4
ρ_{calc} (g/cm ³)	3.689	3.66	3.619
2θ range for data collection	≤ 65.18	≤ 60.10	≤ 65.18
No. of reflections collected	25,246	13,000	25,050
No. of independent reflections	6204	5035	6296
No. of reflections with $I > 2\sigma(I)$	3836	2959	4692
No. of parameters refined	374		373
R(int)	0.030	0.026	0.024
Final R_1 , wR_2 factors [$I > 2\sigma(I)$]	0.031, 0.072	0.027, 0.064	0.024, 0.063
Goodness-of-fit	1.016		1.021
Crystal locality	Victory Mine, S.D.	Nancy mine, Argentina	Santa Ana mine, Argentina
Reference	This study	Tait <i>et al.</i> (2004)	Yang <i>et al.</i> (2021)

12.695(7), $b = 12.386(7)$, $c = 10.929(7)$ Å, $\beta = 97.25(5)^\circ$, and $V = 1705(1)$ Å³.

Single-crystal X-ray diffraction data for ferrobobfergusonite were collected from a nearly equidimensional crystal (0.08 × 0.07 × 0.06 mm) with frame widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed on the basis of a monoclinic unit-cell (Table 3). The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The systematic absences of

reflections suggested the unique space group $P2_1/n$. The crystal structure was solved and refined using SHELX2018 (Sheldrick 2015a, 2015b). To facilitate direct comparison with bobfergusonite, the site nomenclature used by Ercit *et al.* (1986) and Tait *et al.* (2004) was adopted for the ferrobobfergusonite structure, which has 5 X , 6 M , 4 P , and 24 O sites for an asymmetric unit, where $X = \text{Na}$, Ca , and Mn and $M = \text{Fe}$, Mg , Mn , and Al .

TABLE 4. COMPARISON OF CATION SITE OCCUPATIONS BETWEEN BOBFERGUSONITE AND FERROBOBFERGUSONITE

Site	Site sym.	B.L.	Bobfergusonite (Tait <i>et al.</i> 2004)	B.L.	Ferrobobfergusonite (This study)
M1	1	2.216	1.00Mn	2.195	1.00Fe ²⁺
M2	1	2.237	0.89Mn + 0.11Ca	2.215	0.86Fe ²⁺ + 0.14Ca
M3	1	2.116	0.38Fe ²⁺ + 0.32Mn + 0.24Fe ³⁺ + 0.06Mg	2.098	0.91Fe ²⁺ + 0.09Mg
M4	1	2.092	0.53Fe ²⁺ + 0.25Fe ³⁺ + 0.22Mg	2.079	0.65Fe ²⁺ + 0.14Fe ³⁺ + 0.21Mg
M5	1	2.059	0.28Fe ²⁺ + 0.42Fe ³⁺ + 0.30Mg	2.020	0.63Fe ³⁺ + 0.23Al + 0.14Mg
M6	1	1.918	0.94Al + 0.06Fe ³⁺	1.911	1.00Al
X1	1	2.238	1.00Mn	2.208	0.90Mn ²⁺ + 0.10Fe ²⁺
X2	-1	2.55	0.46Na + 0.04□	2.538	0.42Na + 0.08□
X3	-1	2.572	0.44Na + 0.06□	2.555	0.40Na + 0.10□
X4	1	2.654	0.57Na + 0.43□	2.630	0.48Na + 0.52□
X5	1	2.635	0.53Na + 0.47□	2.650	0.42Na + 0.58□

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

TABLE 5. FRACTIONAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (\AA^2) FOR FERROBOBFERGUSONITE

Atom	x	y	z	U_{eq}
X1	0.24875 (4)	0.00126 (4)	-0.00345 (4)	0.01523 (9)
X2	0.000000	0.000000	0.000000	0.0226 (6)
X3	0.500000	0.000000	0.000000	0.0236 (6)
X4	0.3746 (2)	0.4849 (2)	0.0023 (2)	0.0288 (8)
X5	0.8720 (3)	0.4834 (3)	0.9981 (3)	0.0300 (9)
M1	0.13395 (3)	0.23974 (3)	-0.00254 (4)	0.01410 (10)
M2	0.63120 (3)	0.23856 (3)	-0.00088 (4)	0.01286 (10)
M3	0.29732 (3)	0.14659 (3)	0.72106 (3)	0.00913 (11)
M4	0.79816 (3)	0.14605 (3)	0.72413 (4)	0.00899 (12)
M5	0.46178 (4)	0.16315 (4)	0.28258 (4)	0.00835 (12)
M6	0.96052 (6)	0.16443 (6)	0.28184 (7)	0.00658 (15)
P1	0.38360 (5)	0.21556 (5)	0.00338 (6)	0.00702 (13)
P2	0.88417 (5)	0.21112 (5)	0.00827 (6)	0.00722 (13)
P3	0.20133 (5)	0.11569 (5)	0.25635 (6)	0.00718 (13)
P4	0.70635 (5)	0.11457 (5)	0.26059 (6)	0.00758 (13)
P5	0.06162 (5)	0.09505 (5)	0.73827 (6)	0.00745 (13)
P6	0.56125 (6)	0.10147 (5)	0.74018 (6)	0.00826 (13)
O1	0.29750 (15)	0.21411 (14)	0.54457 (16)	0.0118 (4)
O2	0.79781 (14)	0.21069 (14)	0.54424 (16)	0.0105 (4)
O3	0.46875 (14)	0.22231 (14)	0.45197 (16)	0.0091 (4)
O4	0.96592 (14)	0.21564 (14)	0.44507 (16)	0.0103 (4)
O5	0.33237 (15)	0.37611 (15)	0.41891 (16)	0.0128 (4)
O6	0.83020 (15)	0.37161 (15)	0.41542 (17)	0.0133 (4)
O7	0.44374 (14)	0.35386 (14)	0.61477 (16)	0.0116 (4)
O8	0.94723 (15)	0.34897 (15)	0.60681 (16)	0.0130 (4)
O9	0.11093 (14)	0.17213 (14)	0.31460 (16)	0.0102 (4)
O10	0.62009 (15)	0.17579 (14)	0.32045 (16)	0.0115 (4)
O11	0.13521 (15)	0.15272 (15)	0.65701 (18)	0.0149 (4)
O12	0.63852 (15)	0.15543 (14)	0.66077 (17)	0.0136 (4)
O13	0.11352 (15)	0.40808 (15)	0.37495 (16)	0.0144 (4)
O14	0.61424 (15)	0.41176 (15)	0.37252 (16)	0.0138 (4)
O15	0.17375 (15)	0.39902 (14)	0.62059 (16)	0.0125 (4)
O16	0.67189 (15)	0.39669 (14)	0.61593 (16)	0.0109 (4)
O17	0.30128 (14)	0.18800 (14)	0.27820 (16)	0.0106 (4)
O18	0.80843 (14)	0.18395 (14)	0.27730 (16)	0.0102 (4)
O19	0.46200 (14)	0.17423 (14)	0.73747 (16)	0.0110 (4)
O20	0.95937 (14)	0.16283 (15)	0.73461 (16)	0.0114 (4)
O21	0.27843 (16)	0.50750 (15)	0.18225 (18)	0.0172 (4)
O22	0.77621 (16)	0.50724 (15)	0.17632 (18)	0.0164 (4)
O23	0.46465 (15)	0.48191 (14)	0.81526 (16)	0.0116 (4)
O24	0.97046 (16)	0.49089 (15)	0.81410 (17)	0.0146 (4)

A preliminary structure refinement, together with the consideration of bond lengths, indicated that *X1*, *M1*, and *M6* are fully occupied by Mn, Fe, and Al, respectively, whereas *X2*, *X3*, *X4*, and *X5* are all partially occupied by Na. Magnesium appears to be disordered among the *M3*, *M4*, and *M5* sites. During the final refinements, the crystal chemistry was constrained to the electron microprobe analysis and all *M* and *X1* sites were assumed to be completely

filled. All Mn was assigned to the *X1* site, with the rest filled by Fe. The small amount of Ca was assigned to the *M2* site, as it has the longest average bond distance of all six *M* sites, consistent with the analysis of bobfergusonite by Tait *et al.* (2004). The final refined site occupancies are given in Table 4, together with those determined by Tait *et al.* (2004) for bobfergusonite from the Nancy pegmatite, San Luis Range, Argentina. Final coordinates and displacement param-

TABLE 6. ATOMIC DISPLACEMENT PARAMETERS (\AA^2) OF FERROBOBFERGUSONITE

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
X1	0.0241 (2)	0.00845 (15)	0.01604 (18)	-0.00254 (14)	0.01370 (16)	-0.00222 (13)
X2	0.0261 (13)	0.0150 (10)	0.0305 (12)	0.0020 (9)	0.0180 (10)	0.0010 (8)
X3	0.0281 (14)	0.0133 (10)	0.0340 (14)	0.0020 (9)	0.0214 (11)	0.0001 (9)
X4	0.044 (2)	0.0286 (16)	0.0155 (14)	-0.0026 (13)	0.0092 (13)	0.0018 (11)
X5	0.045 (2)	0.0299 (18)	0.0166 (16)	-0.0008 (15)	0.0103 (15)	0.0001 (12)
M1	0.0113 (2)	0.0180 (2)	0.0125 (2)	0.00049 (16)	-0.00043 (16)	0.00207 (15)
M2	0.0111 (2)	0.0150 (2)	0.0117 (2)	0.00186 (16)	-0.00160 (16)	-0.00093 (15)
M3	0.0083 (2)	0.00830 (19)	0.0103 (2)	-0.00131 (14)	-0.00085 (15)	0.00126 (14)
M4	0.0086 (2)	0.0080 (2)	0.0099 (2)	-0.00024 (15)	-0.00075 (16)	0.00091 (14)
M5	0.0077 (2)	0.0103 (2)	0.0069 (2)	0.00055 (18)	0.00043 (17)	-0.00155 (16)
M6	0.0062 (4)	0.0082 (3)	0.0053 (3)	0.0004 (3)	0.0009 (3)	-0.0009 (3)
P1	0.0067 (3)	0.0079 (3)	0.0068 (3)	-0.0003 (2)	0.0019 (2)	0.0003 (2)
P2	0.0070 (3)	0.0085 (3)	0.0066 (3)	-0.0002 (2)	0.0024 (2)	-0.0001 (2)
P3	0.0070 (3)	0.0068 (3)	0.0080 (3)	0.0000 (2)	0.0021 (2)	-0.0001 (2)
P4	0.0073 (3)	0.0072 (3)	0.0088 (3)	0.0000 (2)	0.0031 (2)	-0.0003 (2)
P5	0.0066 (3)	0.0077 (3)	0.0082 (3)	-0.0001 (2)	0.0017 (2)	0.0007 (2)
P6	0.0067 (3)	0.0096 (3)	0.0087 (3)	-0.0005 (2)	0.0018 (2)	0.0000 (2)
O1	0.0101 (10)	0.0143 (9)	0.0119 (9)	-0.0043 (7)	0.0047 (7)	-0.0004 (7)
O2	0.0094 (10)	0.0122 (9)	0.0100 (9)	-0.0026 (7)	0.0022 (7)	-0.0006 (7)
O3	0.0058 (9)	0.0132 (9)	0.0086 (8)	0.0015 (7)	0.0016 (7)	-0.0001 (6)
O4	0.0097 (10)	0.0121 (9)	0.0095 (9)	0.0029 (7)	0.0027 (7)	-0.0008 (7)
O5	0.0144 (10)	0.0125 (8)	0.0114 (9)	0.0059 (8)	0.0019 (7)	0.0016 (7)
O6	0.0156 (10)	0.0120 (9)	0.0127 (9)	0.0057 (8)	0.0031 (7)	0.0013 (7)
O7	0.0146 (10)	0.0134 (9)	0.0072 (8)	-0.0045 (7)	0.0025 (7)	-0.0010 (7)
O8	0.0177 (11)	0.0127 (9)	0.0086 (8)	-0.0049 (8)	0.0021 (7)	-0.0010 (7)
O9	0.0087 (9)	0.0121 (8)	0.0103 (9)	0.0017 (7)	0.0027 (7)	-0.0009 (7)
O10	0.0114 (10)	0.0103 (8)	0.0138 (9)	0.0022 (7)	0.0060 (7)	-0.0002 (7)
O11	0.0141 (10)	0.0120 (9)	0.0209 (10)	0.0001 (8)	0.0106 (8)	0.0034 (8)
O12	0.0113 (10)	0.0121 (8)	0.0192 (10)	0.0008 (8)	0.0092 (8)	0.0031 (7)
O13	0.0144 (11)	0.0156 (9)	0.0122 (9)	0.0008 (8)	-0.0019 (8)	0.0003 (7)
O14	0.0139 (11)	0.0139 (9)	0.0125 (9)	0.0001 (8)	-0.0028 (8)	-0.0006 (7)
O15	0.0123 (10)	0.0145 (9)	0.0110 (9)	0.0014 (7)	0.0027 (7)	0.0036 (7)
O16	0.0123 (10)	0.0117 (9)	0.0086 (8)	0.0016 (7)	0.0013 (7)	0.0018 (6)
O17	0.0078 (9)	0.0138 (9)	0.0099 (8)	-0.0018 (7)	0.0002 (7)	-0.0018 (7)
O18	0.0070 (9)	0.0125 (8)	0.0113 (9)	-0.0001 (7)	0.0019 (7)	-0.0006 (7)
O19	0.0070 (9)	0.0147 (9)	0.0116 (9)	0.0009 (7)	0.0018 (7)	0.0004 (7)
O20	0.0073 (9)	0.0144 (9)	0.0127 (9)	0.0020 (7)	0.0023 (7)	0.0006 (7)
O21	0.0197 (11)	0.0107 (9)	0.0217 (10)	-0.0043 (8)	0.0047 (8)	-0.0053 (8)
O22	0.0186 (11)	0.0094 (9)	0.0222 (10)	-0.0036 (8)	0.0065 (8)	-0.0039 (8)
O23	0.0142 (10)	0.0096 (8)	0.0107 (9)	0.0017 (7)	0.0003 (7)	-0.0005 (6)
O24	0.0154 (10)	0.0126 (9)	0.0162 (9)	0.0036 (8)	0.0035 (8)	0.0018 (7)

eters of atoms in ferrobobfergusonite are listed in Tables 5 and 6, respectively, and selected bond distances in Table 7.

CRYSTAL STRUCTURE DESCRIPTION AND DISCUSSION

Ferrobobfergusonite, $\square\text{Na}_2\text{Fe}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$, is isostructural with bobfergusonite, $\square\text{Na}_2\text{Mn}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$ (Ercit *et al.* 1986, Tait *et al.* 2004), a

member of the alluaudite supergroup (Hatert 2019). Its crystal structure is topologically identical to that of wyllyite and alluaudite. Minerals in the alluaudite supergroup differ from one another mainly in chemical compositions and *M*-cation ordering patterns. Table 1 compares the chemistries of three members of the bobfergusonite group (bobfergusonite, ferrobobfergusonite, and zhanghuifenite) and Table 3 lists mineralogical data for these minerals.

TABLE 7. SELECTED BOND DISTANCES IN FERROBOBFERGUSONITE

	Distance (Å)		Distance (Å)
M1–O10	2.1873 (18)	M2–O11	2.1847 (19)
M1–O16	2.1458 (18)	M2–O15	2.1852 (19)
M1–O3	2.1480 (18)	M2–O4	2.1842 (19)
M1–O12	2.2022 (19)	M2–O1	2.1894 (19)
M1–O2	2.1697 (19)	M2–O9	2.2863 (18)
M1–O14	2.3153 (19)	M2–O13	2.2610 (19)
Ave.	2.195	Ave.	2.215
M3–O22	1.9762 (19)	M4–O21	1.9641 (19)
M3–O6	2.1250 (18)	M4–O20	2.0489 (18)
M3–O1	2.1035 (18)	M4–O5	2.1365 (18)
M3–O11	2.092 (2)	M4–O12	2.063 (2)
M3–O19	2.1067 (19)	M4–O17	2.1369 (19)
M3–O18	2.1858 (18)	M4–O2	2.1230 (18)
Ave.	2.098	Ave.	2.079
M5–O8	1.9130 (18)	M6–O7	1.8262 (18)
M5–O3	1.9833 (18)	M6–O23	1.8476 (19)
M5–O10	2.0089 (19)	M6–O4	1.8870 (19)
M5–O24	1.9387 (19)	M6–O9	1.9028 (19)
M5–O17	2.0584 (19)	M6–O18	1.943 (2)
M5–O20	2.2166 (19)	M6–O19	2.0563 (19)
Ave.	2.020	Ave.	1.911
X1–O5	2.1361 (18)		
X1–O6	2.1381 (18)		
X1–O15	2.1298 (18)		
X1–O16	2.1404 (18)		
X1–O14	2.3091 (19)		
X1–O13	2.3968 (19)		
Ave.	2.208		
X2–O7	2.3643 (17)	X3–O8	2.3475 (18) ×2
X2–O14	2.4008 (19)	X3–O13	2.3984 (19) ×2
X2–O16	2.7042 (18)	X3–O15	2.7275 (18) ×2
X2–O5	2.6832 (19)	X3–O6	2.7448 (19) ×2
Ave.	2.538	Ave.	2.555
X4–O21	2.462 (3)	X5–O22	2.444 (3)
X4–O23	2.468 (3)	X5–O24	2.503 (3)
X4–O22	2.559 (3)	X5–O21	2.569 (4)
X4–O2	2.673 (3)	X5–O24	2.698 (4)
X4–O23	2.699 (3)	X5–O1	2.695 (4)
X4–O4	2.845 (3)	X5–O3	2.901 (4)
X4–O11	2.704 (3)	X5–O12	2.741 (4)
Ave.	2.630	Ave.	2.650
P1–O8	1.5293 (19)	P2–O3	1.5440 (18)
P1–O2	1.5321 (19)	P2–O1	1.5299 (19)
P1–O6	1.5441 (19)	P2–O5	1.5462 (18)
P1–O4	1.5487 (18)	P2–O7	1.5336 (18)
Ave.	1.539	Ave.	1.538
P3–O21	1.5057 (19)	P4–O22	1.5006 (19)
P3–O17	1.5480 (19)	P4–O10	1.5457 (18)
P3–O16	1.5410 (18)	P4–O18	1.5476 (19)
P3–O9	1.5498 (18)	P4–O15	1.5434 (19)
Ave.	1.536	Ave.	1.534

TABLE 7. CONTINUED.

	Distance (Å)		Distance (Å)
P5–O20	1.5438 (19)	P6–O24	1.5258 (19)
P5–O11	1.5450 (19)	P6–O12	1.5439 (19)
P5–O14	1.5358 (19)	P6–O19	1.5478 (19)
P5–O23	1.5383 (18)	P6–O13	1.5418 (19)
Ave.	1.541	Ave.	1.540

In ferrobobfergusonite, six *M* sites are all octahedrally coordinated and five *X* sites have coordination numbers 6, 8, 8, 7, and 7 for *X*1, *X*2, *X*3, *X*4, and *X*5, respectively. The six *M* octahedra share edges to form two types of kinked chains extending along [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 chain). These octahedral chains are joined by PO₄ tetrahedra to form sheets parallel to (010) (Fig. 3), which are linked together through corner-sharing between PO₄ tetrahedra and MO₆ octahedra in the adjacent sheets, leaving open channels parallel to *a*, where the large *X* cations are situated (Fig. 4).

There is strong cation order over the six *M* sites in ferrobobfergusonite (Table 4), which is the reason for the differences among the alluaudite, wyllicite, and bobfergusonite structure types (Ercit *et al.* 1986, Tait *et al.* 2004, Yang *et al.* 2021). The average bond lengths for *M*3 and *M*4 are shorter than those for *M*1, *M*2, and *X*1, consistent with the former two sites containing Mg. Among the five *X* sites, the *X*1 site is filled with Mn²⁺ and Ca, whereas the *X*2–*X*5 sites are partially occupied by Na.

The Raman spectrum of ferrobobfergusonite is displayed in Figure 5. Based on a previous Raman spectroscopic study of qingheite (Frost *et al.* 2013), which is a member of the wyllicite group, we made the following tentative assignments of the major Raman bands for ferrobobfergusonite: The bands between 900 and 1100 cm⁻¹ are ascribed to P–O stretching vibrations within the PO₄ group, whereas those from 400 to 660 cm⁻¹ are due to O–P–O bending. The bands below 400 cm⁻¹ are mainly associated with the rotational and translational modes of PO₄ tetrahedra, as well as the M–O (M = Fe, Al) interactions and lattice vibrational modes. For comparison, the Raman spectrum of bobfergusonite from the RRUFF Project (<http://rruff.info/R160069>) was also included in Figure 5. The resemblance between the two spectra are apparent. The difference in peak intensities between the two spectra is ascribed to the different crystal orientations when the data were collected.

Currently, there are six minerals in the wyllicite group and three in the bobfergusonite group. Yang *et al.* (2020) noted that all members of the bobfergusonite

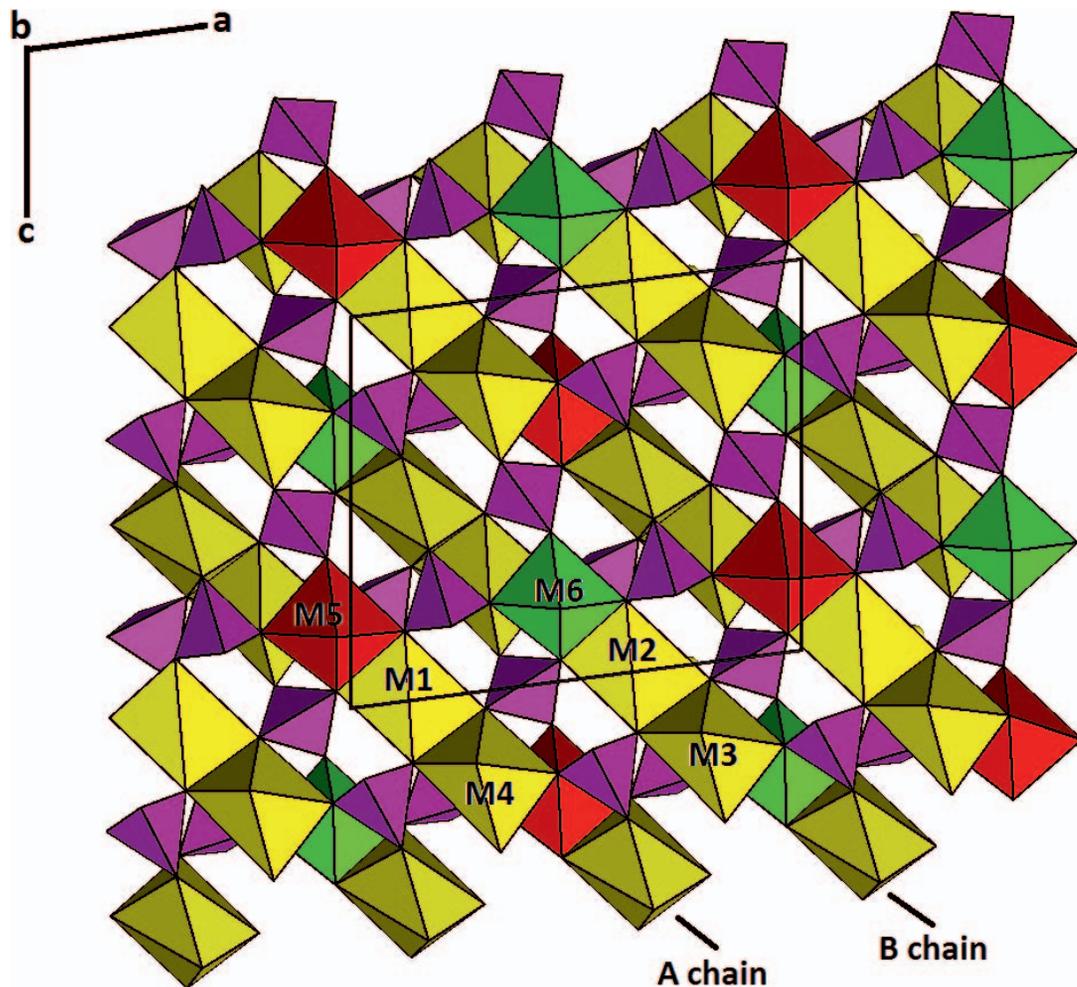


FIG. 3. Crystal structure of ferrobobfergusonite showing a sheet composed of two types of edge-sharing MO_6 octahedral chains ($M = Fe^{2+}$, Mg, Mn^{2+} , Fe^{3+} , Al) connected by PO_4 tetrahedra. The yellow, green, and red octahedra represent $Fe^{2+}O_6$, $Fe^{3+}O_6$, and AlO_6 , respectively.

group can be derived chemically from those in the wyllicite group through appropriate coupled substitutions. For example, zhanghuifenite, $Na_3Mn^{2+}_4Mg_2Al(PO_4)_6$, can be obtained from qingheite, $Na_{Na}Mn(MgAl)(PO_4)_3$, with the coupled substitution of $2Mn^{2+} \leftrightarrow (Na^+ + Al^{3+})$, and ferrobobfergusonite can be obtained from ferrosemaryite, $\square NaFe^{2+}(Fe^{3+}Al)(PO_4)_3$, with the coupled substitution of $3Fe^{2+} \leftrightarrow (Fe^{3+} + Al^{3+})$. Structurally, ferrosemaryite contains only one type of edge-sharing octahedral chain, composed of M1 ($=Fe^{2+}$), M2a ($=Al$), and M2b ($=Fe^{3+}$) octahedra (Fig. 6) (Hatert *et al.* 2005), rather than two types, as in ferrobobfergusonite (Fig. 3). In other words, due to the above coupled-chemical substitution, the two adjacent,

symmetrically equivalent octahedral chains in ferrosemaryite become nonequivalent in ferrobobfergusonite. Specifically, we have the following structural relationship between the two minerals:

Ferrosemaryite	Ferrobobfergusonite		
	One chain	A chain	B chain
2M1 ($= Fe^{2+}$)	\rightarrow	M1 ($= Fe^{2+}$) +	M2 ($= Fe^{2+}$)
2M2b ($= Fe^{3+}$)	\rightarrow	M4 ($= Fe^{2+}$) +	M3 ($= Fe^{2+}$)
2M2a ($= Al$)	\rightarrow	M5 ($= Fe^{3+}$) +	M6 ($= Al$)

Ferrobobfergusonite is the Fe^{2+} -analogue of bobfergusonite. Because of the cation radius difference

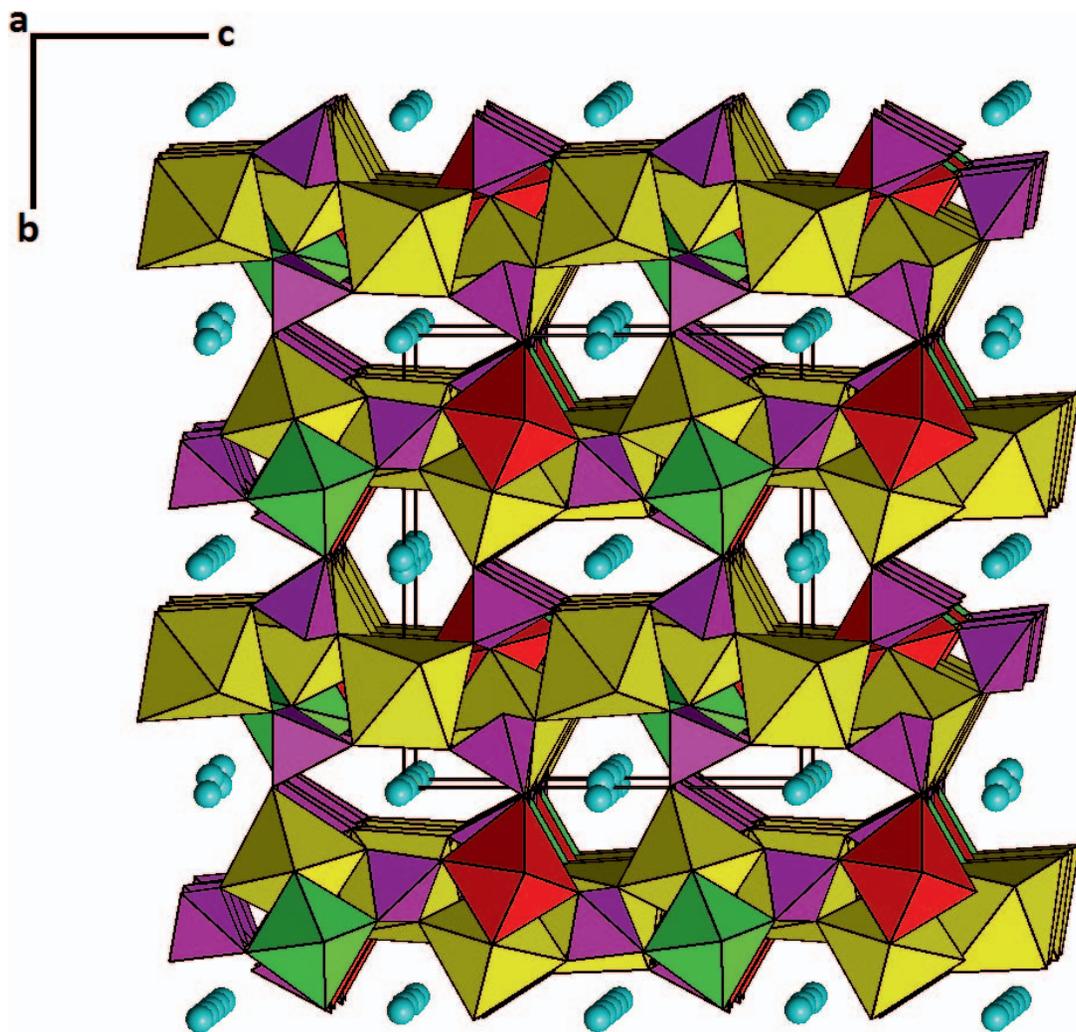


FIG. 4. Sheets composed of MO_6 octahedra and PO_4 tetrahedra parallel to (010) are linked together through corner-sharing between PO_4 tetrahedra and MO_6 octahedra in the adjacent sheets, leaving open channels parallel to a , where the large X cations (spheres) are situated ($X = Na, Ca, Mn$). The yellow, green, and red octahedra represent $Fe^{2+}O_6$, $Fe^{3+}O_6$, and AlO_6 , respectively.

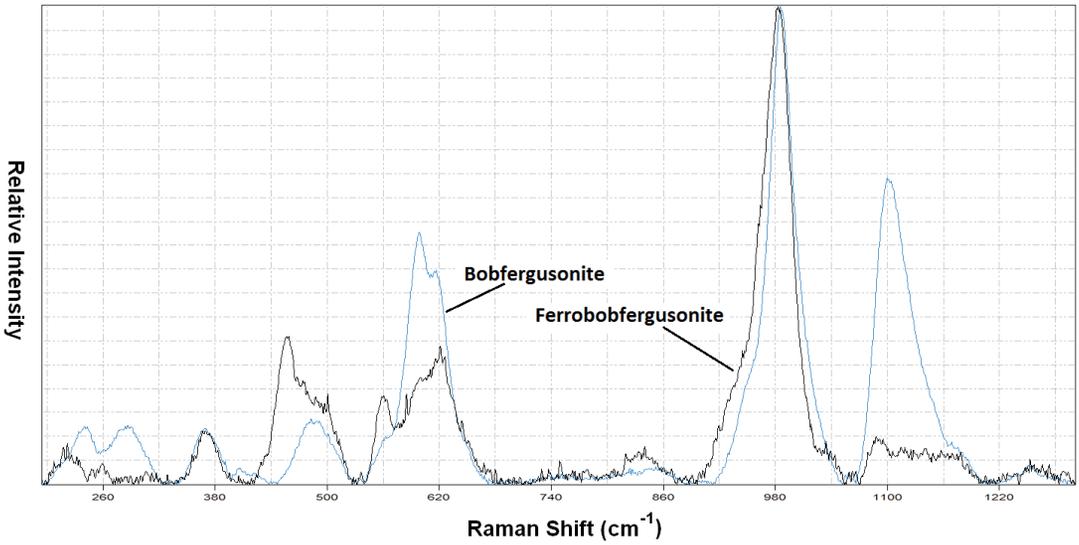


FIG. 5. Raman spectrum of ferrobobfergusonite, along with that of bobfergusonite for comparison.

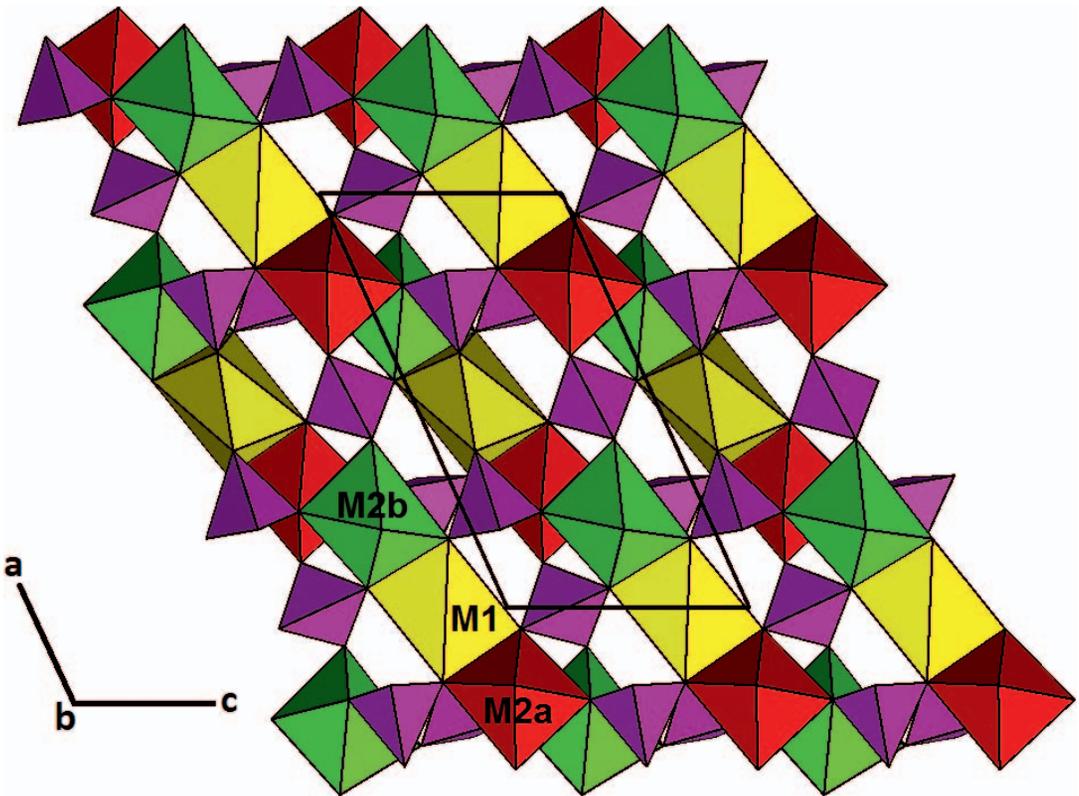


FIG. 6. Crystal structure of ferrosemaryite showing a sheet made up of edge-sharing MO_6 octahedral chains ($M = Fe^{2+}, Fe^{3+}, Al$) connected by PO_4 tetrahedra. The yellow, green, and red octahedra represent $Fe^{2+}O_6$, $Fe^{3+}O_6$, and AlO_6 , respectively. The structure data are from Hatert *et al.* (2005).

between Fe^{2+} and Mn^{2+} (0.78 versus 0.83 Å) (Shannon 1976), the unit-cell volume of ferrobobfergusonite (1707.37 Å³) is expectedly smaller than that of bobfergusonite (1746.7 in Ercit *et al.* 1986 and 1740.1 Å³ in Tait *et al.* 2004). In fact, it is this noticeable discrepancy in the unit-cell volumes that led us into the current investigation.

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