Zhanghuifenite, $Na_3Mn_4^{2+}Mg_2Al(PO_4)_6$, a new mineral isostructural with bobfergusonite, from the Santa Ana mine, San Luis province, Argentina

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Abstract

A new mineral species, zhanghuifenite, ideally $Na_3Mn_4^{2+}Mg_2Al(PO_4)_6$, 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 $0.8 \times 0.5 \times 0.5$ 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/cm^3, respectively. Optically, zhanghuifenite is biaxial (+), with $\alpha = 1.675(2)$, $\beta = 1.680(2)$, $\gamma = 1.690(2)$ (white light), $2V$ (meas) $= 74(2)°$, and $2V$ (calc) $= 71°$. 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) $(Na_{2.80}Ca_{0.11})_{\Sigma2.91}(Mn_{3.09}^{2+}Fe_{0.47}^{2+}Mg_{0.36})_{\Sigma3.92}(Mg_{1.31}Fe_{0.69}^{2+})_{\Sigma2.00}$ $(Al_{0.81}Fe_{0.19}^{3+})(PO_4)_6$. Zhanghuifenite is insoluble in water or hydrochloric acid.

Zhanghuifenite is isostructural with bobfergusonite, a member of the alluaudite supergroup. It is monoclinic, with space group $P2_1/n$, $Z = 4$, and unit-cell parameters $a = 12.8926(3)$, $b = 12.4658(3)$, $c = 10.9178(2)$ Å, $\beta = 97.9200(10)°$, and $V = 1737.93(7)$ $Å^3$. The crystal structure of zhanghuifenite contains six octahedral M (= Mn, Fe, Mg, Al) sites and five X (= Na, Mn, Ca) sites with coordination numbers between 6 and 8. The six M octahedra share edges to form two types of kinked chains extending along [101], with one consisting of $M1$-$M4$-$M5$ and the other $M2$-$M3$-$M6$. 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 a, where the large X cations are situated. Zhanghuifenite differs from bobfergusonite in two major aspects. One is that the $M4$ and $M5$ sites in the former are mainly occupied by Mg, but by Fe^{2+} and Fe^{3+}, respectively, in the latter. The other is that the $X2$-$X5$ sites in zhanghuifenite are all nearly or fully filled with Na, resulting in 3 Na apfu in the ideal formula, but $X4$ and $X5$ are merely half-occupied in bobfergusonite, giving rise to 2 Na apfu.

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

Introduction

A new mineral species, zhanghuifenite, ideally $Na_3Mn_4^{2+}$ $Mg_2Al(PO_4)_6$, has been found in the Santa Ana mine, San Luis province, Argentina. It is named in honor of the late Chinese mineralogist, Prof. Huifen Zhang (1934–2012). Zhang received her undergraduate and graduate educations in China and the former USSR, respectively. She became a professor at the Institute of Geochemistry (in both Guiyang and Guangzhou), the Chinese Academy of Sciences, where she was the director of the division for mineral physics and materials research from 1980 to 1994. Prof. Zhang established the first Raman spectroscopy laboratory for mineralogical research in China and served as a member of the IMA Commission on Mineral Physics from 1990 to 1994. Her major research interests were particularly focused on synthetic quartz, rutile, pyrophyllite, and turquoise. 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 2016-074). The co-type samples have been deposited at the University of Arizona Mineral Museum (catalog no. 21321) and the RRUFF Project (deposition no. R160030) (http://rruff.info).

Zhanghuifenite, isotypic with bobfergusonite, is closely related to minerals of the wyllieite and alluaudite groups. However, it differs from all known members of these groups in both chemical composition and structure. Moore and Molin-Case (1974) showed that the crystal structure of wyllieite is a superstructure derivative of the alluaudite structure. Moore and Ito (1979) introduced a nomenclature for the minerals of the alluaudite and wyllieite groups. Recently, a new nomenclature of the alluaudite supergroup, which

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Figure 1. The rock specimen on which the new mineral zhanghuifenite was found. (Color online.)

contains a total of 16 phosphate and 19 arsenate minerals by 2019, has been presented by Hatert (2019). Khorari et al. (1997) examined the compositional relations between the alluaudite and garnet structures and revealed that the alluaudite structure, like the garnet structure, is extremely chemically compliant. This paper describes the physical and chemical properties of zhanghuifenite and its crystal structure determined 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

Zhanghuifenite was found on a specimen collected from the Santa Ana mine (32°53′32″S, 65°55′43″W), San Luis province, Argentina (Fig. 1). It is massive in a matrix consisting of beusite and lithiophilite (Fig. 2). Detailed geological and mineralogical studies of the Santa Ana pegmatite have been presented by Galliski et al. (2009) and Roda-Robles et al. (2012). The association zhanghuifenite–beusite–lithiophilite occurs in a granitic pegmatite. According to Galliski et al. (2009), the original primary phosphates of the nodule are believed to have crystallized with a
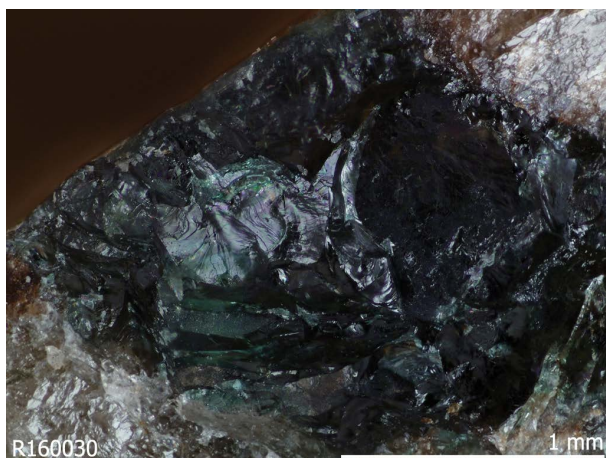
Figure 2. A microscopic view of massive dark-green zhanghuifenite crystals. (Color online.)

chemical composition of a Li-bearing beusite enriched in Mg, derived possibly by contamination by the host rock after the crystallization of the border and wall zones of the pegmatite. The exsolution of this precursor led to the formation of a lamellar intergrowth of beusite and lithiophilite enriched in Mg. Subsequent crystallization of zhanghuifenite is attributed to veining, produced possibly by a late-stage, fluid-rich peraluminous melt.

Zhanghuifenite crystals occur in irregular veinlets or patches, 5 mm thick, in a nodule of beusite interlaminated with lithiophilite (Figs. 1 and 2). Broken pieces of zhanghuifenite are blocky or tabular. Single crystals are found up to $0.8 \times 0.5 \times 0.5$ mm.

No twinning or parting is observed macroscopically. The mineral is deep jade-green, transparent with pale green streak and vitreous luster. It is brittle and has a Mohs hardness of ~5; cleavage is good 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), $2V$ (measured) = 74(2)°, $2V$ (calculated) = 71°, and the orientation $\alpha \wedge X = 8°$, $\beta = Y$, with $X =$ deep blue green, $Y =$ pale green, $Z =$ yellowish-green, and $X > Y > Z$. The pleochroism is deep green and the dispersion is very strong with r >> v. The calculated compatibility index based on the empirical formula is 0.020 (excellent) (Mandarino 1981). Zhanghuifenite 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 are listed in Table 1, along with the determined compositions (12 analysis points all from one crystal). The resultant chemical formula, calculated on the basis of 24 O atoms pfu (from the structure determination), is $(Na_{2.80}Ca_{0.11})_{\Sigma2.91}$ $(Mn^{2+}_{3.09}Fe^{2+}_{0.47}Mg_{0.36})_{\Sigma3.92}(Mg_{1.31}Fe^{2+}_{0.69})_{\Sigma2.00}(Al_{0.81}Fe^{3+}_{0.19})(PO_4)_6$, which can be simplified to $Na_3Mn^{2+}_4Mg_2Al(PO_4)_6$. CIF[1] is available.

The Raman spectrum of zhanghuifenite was collected on 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 zhanghuifenite were collected on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized MoKα 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: $a = 12.888(5)$, $b = 12.466(3)$, $c = 10.910(4)$ Å, $\beta = 97.86(3)°$, and $V = 1736.4(8)$ Å³.

A nearly equidimensional crystal ($0.08 \times 0.08 \times 0.07$ mm) of zhanghuifenite was picked for the structure determination from the large crystal used for the electron microprobe analysis. The X-ray diffraction intensity data were collected 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 suggest the unique space group $P2_1/n$. The crystal structure was solved and refined using SHELX2018 (Sheldrick 2015a, 2015b). To facilitate the direct comparison with bobfergusonite, the site nomenclature used by Ercit et al. (1986) and Tait et al. (2004) was adopted for the zhanghuifenite structure, which has 5 X, 6 M, 4 P, and 24 O sites for an asymmetric unit, where $X =$ Na, Ca, and Mn, and $M =$ Mn, Fe, Mg, and Al.

A preliminary structure refinement indicated that $M1$, $M2$, and $X1$ are fully occupied by Mn, and $X2$ and $X5$ by Na. These sites, therefore, were all fixed in the subsequent refinements. The refinements revealed that Mg is dominant in the $M4$ and $M5$ sites, and Al in $M6$. The small amount of Ca was found to be in $X3$ and some vacancy in $X4$. For simplicity, in the subsequent refinements, all M and X sites, except for $X3$, were assumed to be completely filled, which requires a re-normalization of the empirical formula to $(Na_{2.80}Ca_{0.11})_{\Sigma2.91}(Mn^{2+}_{3.15}Fe^{2+}_{0.48}Mg_{0.37})_{\Sigma4.00}$ $(Mg_{1.31}Fe^{2+}_{0.69})_{\Sigma2.00}(Al_{0.81}Fe^{3+}_{0.19})_{\Sigma1.00} (PO_4)_6$. Based on this chemical formula, 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 parameters of atoms in zhanghuifenite are listed in Tables 5 and 6, respectively, and selected bond distances in Table 7.

It should be pointed out that the M3 site in zhanghuifenite appears to have more Fe²⁺ than any other elements. However, we do not specify it in the ideal chemical formula to keep consistency with bobfergusonite, which shows a variation from the Mn²⁺- to Fe²⁺-rich in its M3 site, but all Fe²⁺ was treated as Mn²⁺ in its ideal formula (Ercit et al. 1986; Tait et al. 2004). Another reason for doing so is because X-ray structure analysis is insufficient in distinguishing Fe from Mn due to their similar X-ray scattering powers.

TABLE 1. Chemical compositions for qingheiite and zhanghuifenite

	Qingheiite Santa Ana Argentina	Qingheiite Santa Ana Argentina	Qingheiite Qinghe China	Zhanghuifenite Santa Ana Argentina	Standards
P_2O_5	45.11	45.67	45.63	45.21(29)	Apatite
Al_2O_3	5.07	4.70	4.53	4.36(5)	Anorthite
Fe_2O_3	4.09	5.96	2.24	1.58[a]	
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_2O	9.24	9.26	8.73	9.19(30)	Albite
K_2O	0.02		0.04	b.d.	
Total	100.99	100.63	99.64	100.13	
	Galliski et al. (2009)	Frost et al. (2013)	Ma et al. (1983)	This study	

Note: b.d. = below detection.
[a] Obtained by adjusting the Fe^{2+}/Fe^{3+} ratio for electroneutrality.

TABLE 2. Powder X-ray diffraction data of zhanghuifenite

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	$\bar{2}$ 1 1
2	4.767	4.795	2 1 1
2	4.436	4.460	2 2 0
2	4.160	4.178	$\bar{2}$ 1 2
3	4.073	4.083	0 2 2
13	3.445	3.461	0 1 3
12	3.078	3.083	$\bar{4}$ 1 1
8	3.026	3.032	$\bar{2}$ 3 2
9	2.928	2.929	4 0 2
25	2.877	2.874	4 1 1
10	2.750	2.752	$\bar{2}$ 4 1
100	2.697	2.700	0 4 2
11	2.647	2.651	$\bar{4}$ 2 2
8	2.585	2.597	4 0 2
34	2.527	2.526	$\bar{4}$ 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	$\bar{2}$ 3 4
10	2.187	2.186	$\bar{4}$ 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	$\bar{2}$ 5 4
4	1.781	1.781	$\bar{2}$ 1 6
14	1.742	1.740	$\bar{4}$ 3 5
4	1.718	1.715	2 7 0
8	1.645	1.644	4 4 4
9	1.594	1.591	$\bar{8}$ 0 2
13	1.561	1.560	0 4 6
8	1.526	1.525	4 7 1
4	1.507	1.506	$\bar{2}$ 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	$\bar{6}$ 7 2
4	1.351	1.351	0 0 8
4	1.326	1.326	$\bar{8}$ 4 4
4	1.296	1.297	6 7 2
6	1.284	1.285	$\bar{8}$ 0 6

TABLE 3. Comparison of mineralogical data for zhanghuifenite, bobfergusonite, and qingheiite

	Zhanghuifenite	Bobfergusonite	Qingheiite
Ideal chemical formula	$Na_3Mn_2^{2+}$ $Mg_2Al(PO_4)_6$	$Na_2Mn_5^{2+}Fe^{3+}$ $Al(PO_4)_6$	Na_2Mn^{2+} $MgAl(PO_4)_3$
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 $I > 2σ(I)$	4692	2959	2294
No. of parameters refined	373		
R_{int}	0.024	0.026	
Final R_1, wR_2 factors [$I > 2σ(I)$]	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 symmetry	Average bond length	Bobfergusonite (Tait et al. 2004)	Average bond length	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

CRYSTAL STRUCTURE DESCRIPTION AND DISCUSSION

Zhanghuifenite is isostructural with bobfergusonite, $Na_2Mn_5^{2+}Fe^{3+}Al(PO_4)_6$ (Ercit et al. 1986; Tait et al. 2004), a member of the alluaudite supergroup. All these minerals have the same structure topology. They differ from one another mainly in chemical compositions and M-cation ordering patterns (see Hatert 2019 for a thorough review). The crystal structure of zhanghuifenite contains six octahedral M sites and five X sites that have coordination numbers 6, 8, 8, 7, and 7 for $X1$, $X2$, $X3$, $X4$, and $X5$, respectively. The six M octahedra share edges to form two types of kinked chains extending along [101], with one consisting of $M1$-$M4$-$M5$ (the A chain) and the other $M2$-$M3$-$M6$ (the B chain). These octahedral chains are joined by PO_4 tetrahedra to form sheets parallel to (010) (Fig. 3), which 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 are situated (Fig. 4).

There is strong cation order over the six M sites in zhanghuifenite (Table 4), which is the cause for the differences among the alluaudite-, wyllieite-, and bobfergusonite-structure types (Ercit et al. 1986; Tait et al. 2004). Among five X sites, the $X1$ site is

filled with Mn^{2+}, whereas $X2$–$X5$ sites are predominately or fully occupied by Na. The average bond lengths for $M3$, $M4$, and $M5$ are noticeably shorter than those for $M1$, $M2$, and $X1$, consistent with the results that the former three sites are primarily occupied by Mg and Fe^{2+}. The site preference of Mg is $M5 > M4 > M3$, which is opposite to that of Fe^{2+}, in agreement with the decrease in the average bond length from $M3$ to $M5$.

Zhanghuifenite differs from bobfergusonite in two major aspects. One is that the $M4$ and $M5$ sites in the former are mainly occupied by Mg, but by Fe^{2+} and Fe^{3+}, respectively, in the latter.
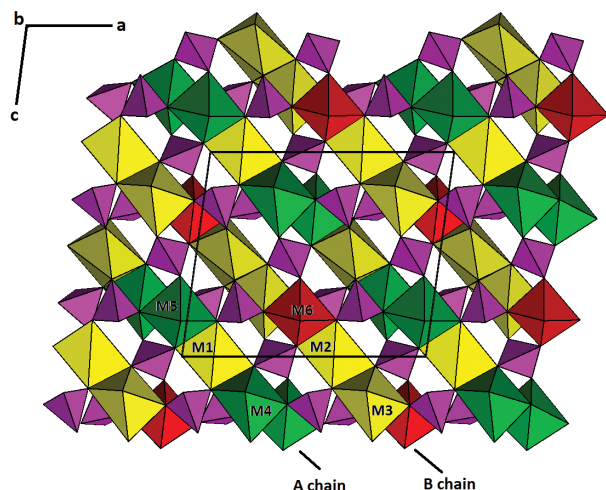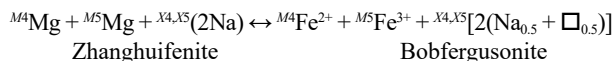

FIGURE 3. Crystal structure of zhanghuifenite, showing a sheet made of two types of edge-sharing MO_6 octahedral chains (M = Mn, Fe, Mg, Al) connected by PO_4 tetrahedra. The yellow, green, and red octahedra represent MnO_6, MgO_6, and AlO_6, respectively. (Color online.)
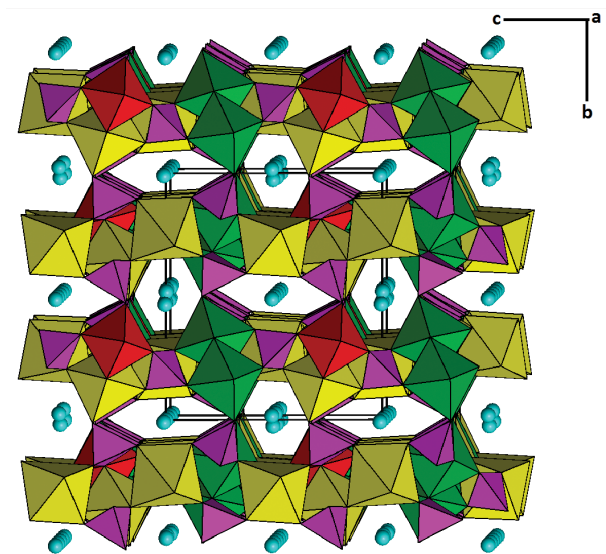
FIGURE 4. Sheets made of MO_6 octahedra and PO_4 tetrahedra parallel to (010) are linked together through corner-sharing between PO_4 tetrahedra and MO_6 octahedra in the adjacent sheets, leaving open channels parallel to a, where the large X cations (spheres) are situated (X = Na, Ca, Mn). The yellow, green, and red octahedra represent MnO_6, MgO_6, and AlO_6, respectively. (Color online.)

The other is that the $X2$–$X5$ sites in zhanghuifenite are all nearly or fully filled with Na, resulting in 3 Na apfu in the ideal formula, but $X4$ and $X5$ are merely half-occupied in bobfergusonite, giving rise to 2 Na apfu. Therefore, based on the ideal chemical formulas, zhanghuifenite may be obtained from bobfergusonite through the following coupled substitution:

$$^{M4}Mg + {}^{M5}Mg + {}^{X4,X5}(2Na) \leftrightarrow {}^{M4}Fe^{2+} + {}^{M5}Fe^{3+} + {}^{X4,X5}[2(Na_{0.5} + \square_{0.5})]$$
$$\text{Zhanghuifenite} \qquad\qquad \text{Bobfergusonite}$$

The Raman spectrum of zhanghuifenite between 100 and 4000 cm^{-1} was collected (https://rruff.info/R160030), but only the range from 100 to 1300 cm^{-1} is displayed in Figure 5, because the spectrum above 1400 cm^{-1} is flat and featureless. Based on the previous Raman spectroscopic study on qingheiite (Frost et al. 2013), which is also a member of the wyllieite group (see below for more discussion), we made the following tentative assignments of the major Raman bands for zhanghuifenite. The bands between 930 and 1160 cm^{-1} are ascribable to the P-O stretching vibrations within the PO_4 group, whereas those from 400 to 660 cm^{-1} are attributed to the O-P-O bending vibrations. The bands below 400 cm^{-1} are mainly associated with the rotational and translational modes of PO_4 tetrahedra, as well as the M-O (M = Mn, Fe, Mg, Al) interactions and lattice vibrational

TABLE 5. Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for zhanghuifenite

Atom	x	y	z	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	0	0	0.0213(2)
X3	0.5	0	0	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(8)	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 (Å^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)	0.0036 (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 (12)	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)

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		

TABLE 7.—CONTINUED

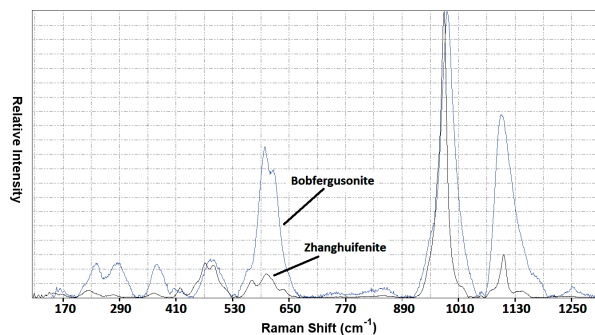| Distance (Å)		Distance (Å)	
X2-O7	2.3692(10) ×2	X3-O8	2.3228(11) ×2
X2-O14	2.4126(11) ×2	X3-O13	2.3821(11) ×2
X2-O16	2.6764(11) ×2	X3-O15	2.7287(11) ×2
X2-O5	2.7452(12) ×2	X3-O6	2.7932(12) ×2
<X2-O>	2.551	<X3-O>	2.557
X4-O21	2.3776(13)	X5-O22	2.4121(13)
X4-O23	2.4050(13)	X5-O24	2.4317(13)
X4-O22	2.4983(14)	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

Figure 5. Raman spectrum of zhanghuifenite, along with that of bobfergusonite for comparison. (Color online.)
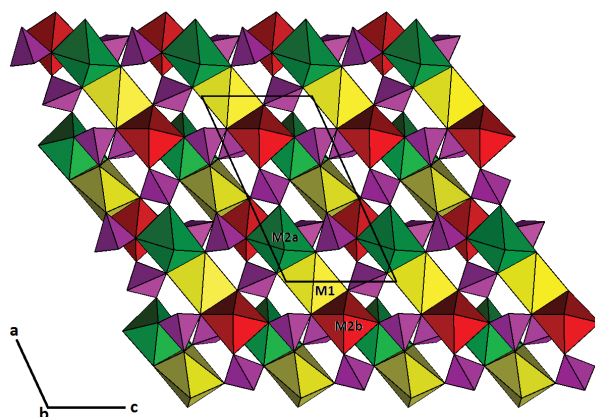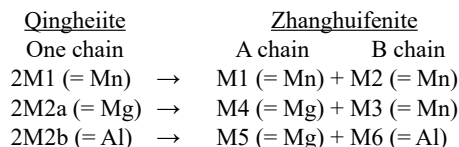

Figure 6. Crystal structure of qingheiite, showing a sheet made of edge-sharing MO_6 octahedral chains (M = Mn, Mg, Al) connected by PO_4 tetrahedra. The structure data were taken from Ma et al. (1983). (Color online.)

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 principally results from the different crystal orientations when the data were collected.

IMPLICATIONS

Qingheiite, ideally $Na_2Mn^{2+}MgAl(PO_4)_3$ (Ma et al. 1983), has a similar composition to zhanghuifenite (Table 1). Chemically, zhanghuifenite can be obtained from qingheiite (with the doubled cell content, as its unit-cell volume is only half that of zhanghuifenite) by the coupled substitution of $2Mn^{2+}$ for (Na+Al). Structurally, qingheiite contains only one type of edge-sharing octahedral chains, made of M1 (= Mn), M2a (= Mg), and M2b (= Al) (Fig. 6) (Ma et al. 1983), rather than two types, as in zhanghuifenite (Fig. 3). In other words, due to the above chemical substitution, the two adjacent, symmetrically equivalent octahedral chains in qingheiite become nonequivalent in zhanghuifenite. Specifically, we have the following structural relationship between the two minerals:

Qingheiite		Zhanghuifenite	
One chain		A chain	B chain
2M1 (= Mn)	→	M1 (= Mn) + M2 (= Mn)	
2M2a (= Mg)	→	M4 (= Mg) + M3 (= Mn)	
2M2b (= Al)	→	M5 (= Mg) + M6 (= Al)	

By the same token, we can find the chemical and structural relationships between rosemaryite and bobfergusonite, and between ferrorosemaryite and ferrobobfergusonite, as shown in Table 8. These relationships established between the known minerals in the wyllieite and bobfergusonite groups lead us to postulate the existence of three more possible new minerals in the bobfergusonite group, labeled as postulated new minerals 1, 2, and 3 in Table 8. Among them, postulated new mineral 1, $Na_3Fe_4^{2+}Mg_2Al(PO_4)_6$, can be derived from ferroqingheiite through the coupled substitution of $2Fe^{2+}$ for $(Na^+ + Al^{3+})$ and may be regarded as "ferrozhanghuifenite." Similarly, postulated new minerals 2 and 3 are related to wyllieite and ferrowyllieite, respectively, through the coupled substitutions of $2Mn^{2+}$ for $(Na^+ + Al^{3+})$ and $2Fe^{2+}$ for $(Na^+ + Al^{3+})$.

The zhanghuifenite sample we examined was originally donated to the RRUFF Project as "qingheiite," which has been

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 $\beta \approx 114.5°, V \approx 850$ Å^3	Coupled substitution	Bobfergusonite-type, $P2_1/n$ $a \approx 12.8, b \approx 12.5, c \approx 11.0$ Å $\beta \approx 97.5°, V \approx 1700$ Å^3
Rosemaryite $2 \times [\square NaMn^{2+}(Fe^{3+}Al)(PO_4)_3]$	$Fe^{3+} + Al^{3+} \rightarrow 3Mn^{2+}$	Bobfergusonite $\square Na_2Mn_5^{2+}Fe^{3+}Al(PO_4)_6$
Ferrorosemaryite $2 \times [\square NaFe^{2+}(Fe^{3+}Al)(PO_4)_3]$	$Fe^{3+} + Al^{3+} \rightarrow 3Fe^{2+}$	Ferrobobfergusonite $\square Na_2Fe_5^{2+}Fe^{3+}Al(PO_4)_6$
Qingheiite $2 \times [Na_2Mn(MgAl)(PO_4)_3]$	$Na^+ + Al^{3+} \rightarrow 2Mn^{2+}$	Zhanghuifenite $Na_3Mn_4^{2+}Mg_2Al(PO_4)_6$
Qingheiite-(Fe^{2+}) $2 \times [Na_2Fe^{2+}MgAl(PO_4)_3]$	$Na^+ + Al^{3+} \rightarrow 2Fe^{2+}$	Ferrozhanghuifenite? $Na_3Fe_4^{2+}Mg_2Al(PO_4)_6$
Wyllieite $2 \times [Na_2Mn(Fe^{2+}Al)(PO_4)_3]$	$Na^+ + Al^{3+} \rightarrow 2Mn^{2+}$	Postulated new mineral 2 $Na_3Mn_4^{2+}Fe_2^{2+}Al(PO_4)_6$
Ferrowyllieite $2 \times [Na_2Fe^{2+}(Fe^{2+}Al)(PO_4)_3]$	$Na^+ + Al^{3+} \rightarrow 2Fe^{2+}$	Postulated new mineral 3 $Na_3Fe_4^{2+}Fe_2^{2+}Al(PO_4)_6$
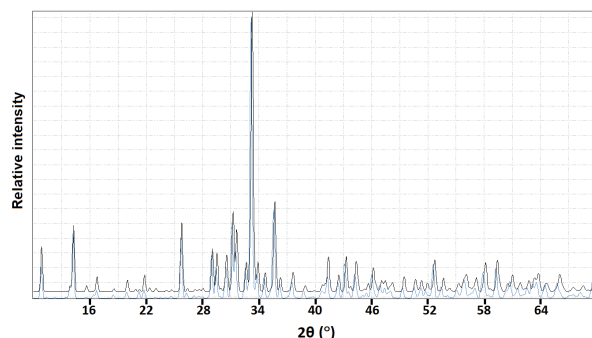
Figure 7. Powder X-ray diffraction patterns for zhanghuifenite (bottom) and qingheiite (top) calculated with Cu$K\alpha$ radiation from the structure data from this study and Ma et al. (1983), respectively. (Color online.)

studied previously by Galliski et al. (2009) using powder X-ray diffraction and electron microprobe analysis and by Frost et al. (2013) using electron microprobe analysis, along with Raman and IR spectroscopy. Table 1 shows the similarity in the chemical compositions between zhanghuifenite and qingheiite from the same locality, as well as that from the type locality, Qinghe, China. However, without single-crystal X-ray structure analysis, it is unclear whether "qingheiite" examined by Galliski et al. (2009) and Frost et al. (2013) is actually zhanghuifenite. This argument then begs the question of whether or not qingheiite can be distinguished from zhanghuifenite via careful inspection of powder X-ray diffraction data. Figure 7 displays the powder X-ray diffraction patterns of qingheiite and zhanghuifenite calculated from the structure data from Ma et al. (1983) and this study, respectively. Evidently, the major features of two profiles are considerably similar, except for some relatively weak peaks. Therefore, caution must be exercised when powder X-ray diffraction data are used to identify these two minerals.

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Endnote:

[1]Deposit item AM-21-67598, CIF. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2021/Jun2021_data/Jun2021_data.html). The CIF has been peer reviewed by our Technical Editors.