JAHNSITE-(MnMnFe), $Mn^{2+}Mn^{2+}Fe^{2+}{}_2Fe^{3+}{}_2(PO_4)_4(OH)_2\cdot8H_2O$, A NEW PHOSPHATE MINERAL FROM THE MALPENSATA PEGMATITE, OLGIASCA, COLICO MUNICIPALITY, LECCO PROVINCE, ITALY

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ABSTRACT

Jahnsite-(MnMnFe), $Mn^{2+}Mn^{2+}Fe^{2+}{}_2Fe^{3+}{}_2(PO_4)_4(OH)_2\cdot8H_2O$ (IMA 2018-096), is a new phosphate belonging to the jahnsite subgroup of the jahnsite group of minerals. It was found in the dumps of the Malpensata pegmatite mine close to the village of Olgiasca, Colico municipality, Lecco province, Italy by one of the authors (F.V.). The mineral occurs on the surfaces of a hydrothermal cavity as prisms elongated along **a**, weakly flattened on {010}, and twinned by reflection on {001}, up to 130 μm in size. The new species occurs in close association with rockbridgeite as a late stage product of alteration of primary phosphate minerals including graftonite-(Mn). Its color is dark brown and it is partially transparent with a vitreous luster. The streak is pale greenish brown. Jahnsite-(MnMnFe) is brittle with a good cleavage on {001}. Its Mohs hardness is 4 and the calculated density is 2.654 g/cm³. The mineral is optically biaxial (–) with $\alpha = 1.673$, $\beta = 1.685$, $\gamma = 1.689$, and $2V$ (calc.) = 60 °, and it is non-fluorescent under 254 nm (short wave) and 366 nm (long wave). The empirical formula is: $(Mn_{0.40}Ca_{0.25}Na_{0.05})_{\Sigma0.70}$ $Mn(Fe^{2+}{}_{1.39}Mn_{0.43}Mg_{0.14}Zn_{0.03})_{\Sigma2.00}(Fe^{3+}{}_{1.99}Al_{0.01})_{\Sigma2}(PO_4)_4(OH)_{1.35}\cdot8H_2O$. Jahnsite-(MnMnFe) is monoclinic, with space group $P2/a$ and unit-cell parameters $a = 15.1559(6)$ Å, $b = 7.1478(2)$ Å, $c = 10.0209(4)$ Å, and $\beta = 112.059(4)°$ with $V = 1006.11(6)$ Å³ for $Z = 2$. The eight strongest measured lines in the XRPD pattern are [d in Å, (I/I_0), (hkl)]: 2.590 (**100**) ($\overline{4}21$), 9.221 (**89**) (001), 2.840 (**82**) (320), 4.932 (**78**) ($\overline{2}11$), 4.651 (**78**) (002), 3.971 (**71**) (211), 3.504 (**64**) ($\overline{4}00$), and 3.295 (**46**) ($\overline{2}03$). Its crystal structure was refined and conforms with the general structure described for jahnsite-group minerals.

Keywords: jahnsite-(MnMnFe), jahnsite-group, jahnsite-subgroup, new mineral species, pegmatitic phosphate, Malpensata, Lecco, Italy.

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Introduction

According to the new nomenclature of the jahnsite group of minerals, represented by the general formula $XM1M2_2M3_2(PO_4)_4(OH)_2\cdot 8H_2O$, the group can be divided into the jahnsite subgroup ($M3 = Fe^{3+}$) and the whiteite subgroup ($M3 = Al$) (Kampf *et al*. 2018a). The jahnsite subgroup now consists of 11 different mineral species and this number is growing continuously thanks to the extremely flexible crystal-chemical features of these phosphates. The mineral species belonging to the jahnsite subgroup, as explained in Kampf *et al*. (2018a), show the general formula $XM1M2Fe^{3+}(PO_4)_4(OH)_2\cdot 8H_2O$, in agreement with the formula of Moore & Ito (1978). The X site is generally occupied by the largest cations whereas the $M1$ and $M2$ sites are occupied by small cations like Fe^{2+}, Fe^{3+}, Mn^{2+}, and Mg^{2+}. The crystal structure of "jahnsite" was first described by Moore & Araki (1974) in the monoclinic space group $P2/a$ and with isotropic thermal parameters. Subsequently, Kampf *et al*. (2008) described the structure of the new species jahnsite-(NaFeMg) from the Tip Top Mine (South Dakota, U.S.A.) in the same space group, locating the protons and giving anisotropic thermal parameters. Jahnsite-group minerals are commonly found as accessory minerals in granitic pegmatites, where they form by hydrothermal alteration of earlier-formed phosphate minerals, both primary and secondary, under relatively oxidizing conditions (Simmons *et al*. 2003, Vignola *et al*. 2011a, Vignola 2018).

The new phosphate mineral described in this article, jahnsite-(MnMnFe), and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2018-096). The type sample used for the complete characterization of the new species is deposited in the Mineralogical Collection of the Laboratoire de Minéralogie, University of Liège, Belgium (number 21168).

Occurrence, General Appearance, and Physical Properties

Jahnsite-(MnMnFe) was found by one of the authors (F.V.) in the dumps of the Malpensata pegmatite mine, near the village of Olgiasca, Colico municipality, Lecco province, Italy (46°07′20″N, 9°19′33″E) in 2010. This albite pegmatite shows an interesting primary and secondary phosphate association and is the type locality for karenwebberite (Vignola *et al*. 2013). The primary phosphate association is dominated by minerals belonging to the graftonite group in close association with sarcopside and triphylite (Vignola 2018). Arrojadite-(KNa),
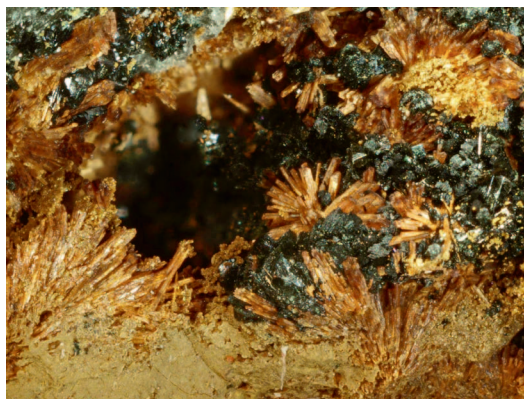

Fig 1. Prismatic crystals of jahnsite-(MnMnFe) associated with rockbridgeite (field of view is 3.6 mm).

arrojadite-(BaNa) (Vignola unpublished data, Vignola *et al*. 2016), wyllieite, ferrowyllieite, and karenwebberite (Vignola *et al*. 2010, Vignola *et al*. 2011b, Hatert *et al*. 2016) are rare primary phosphates occurring in the association. Alteration of primary phosphates in the Malpensata dike is quite pervasive and results in the formation of about 15 secondary phosphates. Among these are jahnsite-(CaMnFe) and jahnsite-(CaMnMn), which occur as prismatic crystals growing on the surfaces of hydrothermal cavities (Vignola *et al*. 2011b).

Jahnsite-(MnMnFe) was found in one cm diameter hydrothermal cavity, hosted in the albite matrix. The crystals are prismatic, up to 0.2 mm in length, and grow on the surface of the cavity in close association with rockbridgeite and mitridatite (Fig. 1); they are elongated along **a** (from the orientation inferred from the crystal used for the single-crystal data collection), slightly flattened on (010) (Fig. 1), and are twinned by reflection on {001}, as described by Kampf *et al*. (2008) (Fig. 2). The crystals are translucent, dark orange-brown, with a vitreous luster, and the streak is pale greenish-brown. The hardness could not be measured due to the small size of the crystals, but the Mohs hardness is inferred to be 4 by analogy with the other species belonging to the jahnsite subgroup. Jahnsite-(MnMnFe) is brittle with an irregular fracture and a perfect {001} cleavage (Fig. 2). The density based on the empirical formula weight and single crystal unit-cell parameters is 2.654 g/cm³. The mineral is optically biaxial negative with measured indices of refraction α 1.673(3), β 1.685(1), γ 1.689(1) (sodium light). The 2V could not be measured. The calculated 2V is 60° with a moderate dispersion r < v. The optical orientation is: X along [010], Y approximately along [001], and Z along [100]. Pleochroism is:
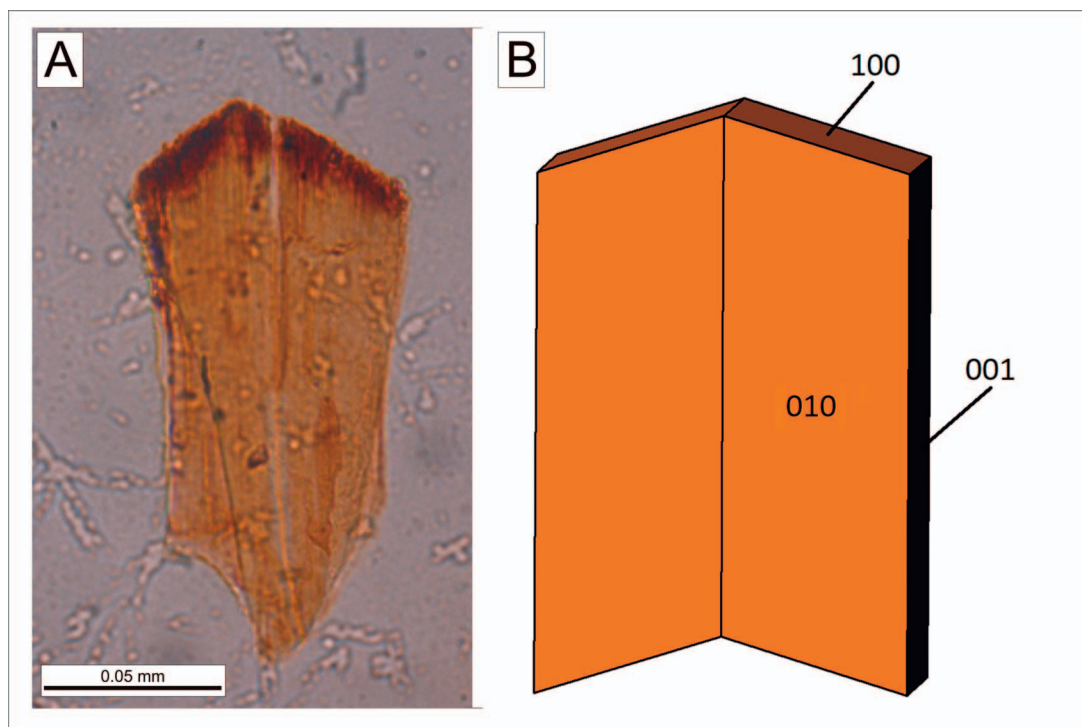
FIG. 2. (A) The crystal of jahnsite-(MnMnFe) used for the optical determinations. Note the trace of the perfect {001} cleavage. (B) Crystal drawing of a jahnsite-(MnMnFe) crystal twinned by reflection on {001}.

α = dark brown, β = brownish orange, γ = yellow, with $X = \mathbf{b}$. The Gladstone-Dale compatibility index, calculated from the chemical composition, calculated density, and measured refractive indices, is 0.002, superior according to Mandarino (1981).

CHEMICAL COMPOSITION

The chemical composition was obtained from a polished and carbon coated section of jahnsite-MnMnFe using a JEOL JXA-8200 electron microprobe working in wavelength-dispersion mode at the Department of Earth Sciences, University of Milan. The system was operated using an accelerating voltage of 15 kV, a beam current of 5 nA, a spot size of 5 μm, and a counting time of 30 s on the peaks and 10 s on the backgrounds. The following minerals were used as standards: graftonite KF16 (Fransolet 1975) for (P $K\alpha$, Fe $K\alpha$, Mn $K\alpha$, and Ca $K\alpha$), anorthite An 137 for (Al $K\alpha$), olivine – USNM 2566 for (Mg $K\alpha$), rhodonite for (Zn $K\alpha$), omphacite USNM 110607 for (Na $K\alpha$), orthoclase PSU OR 1A for (K $K\alpha$), and hornblende – Hbl 123 (F $K\alpha$). K and F were below detection limit for all analyzed points. The raw data were corrected for matrix effects using the $\Phi(\rho Z)$ method from the JEOL series of programs. The electron microprobe analysis (six points) of jahnsite-(MnMnFe) is reported in Table 1. The empirical formula calculated on the basis of four P atoms per formula unit is $(Mn_{0.40}Ca_{0.25}Na_{0.05})_{\Sigma0.70}Mn(Fe^{2+}_{1.39}$

TABLE 1. ELECTRON-MICROPROBE COMPOSITION OF JAHNSITE-(MnMnFe)

	wt.%	Range	SD
P_2O_5	33.68	33.23–34.15	0.41
Al_2O_3	0.04	0.00–0.07	0.02
Fe_2O_3*	18.88	28.30–29.13(FeO$_{tot}$)	0.31
FeO	11.88		
MnO	15.40	14.63–16.25	0.52
CaO	1.69	1.24–2.37	0.40
MgO	0.68	0.50–0.94	0.16
ZnO	0.33	0.11–0.48	0.13
Na_2O	0.17	0.09–0.27	0.07
H_2O**	18.54		
Total	101.30		

* Calculated to have 2 (Fe^{3+} + Al) *apfu* at the M^{3+} structural site; ** Calculated to have 8 H_2O molecules *pfu*, and OH *apfu* to balance the charges.

$Mn_{0.43}Mg_{0.14}Zn_{0.03})_{\Sigma 2.00}(Fe^{3+}_{1.99}Al_{0.01})_{\Sigma 2}(PO_4)_4$ $(OH)_{1.35}\cdot 8H_2O$, with H_2O calculated to give eight water molecules per formula unit; charges were balanced by adjusting the OH^- content. The cations were distributed at the X, $M1$, $M2$, and $M3$ sites as suggested by Kampf *et al.* (2018a). The $M3$ site is populated by trivalent cations (Fe^{3+} and Al) up to 2 Fe^{3+} + Al *apfu*, and $M1$ is completely occupied by Mn^{2+}. The $M2$ site is occupied by the small cations Mg and Zn, the remnant fraction of Fe^{2+}, and up to 1 *apfu* by Mn^{2+}. The further fraction of Mn^{2+} (0.40 *apfu*) is accommodated at the X site together with the large cations Ca and Na. The ideal formula is $Mn^{2+}Mn^{2+}Fe^{2+}_2Fe^{3+}_2(PO_4)_4(OH)_2\cdot 8H_2O$, which requires P_2O_5 31.85, Fe_2O_3 17.92, FeO 16.12, MnO 15.92, H_2O 18.19, total 100.00 wt.%.

X-Ray Diffraction Data and Crystal Structure Refinement

The X-ray powder diffraction pattern of jahnsite-(MnMnFe) was collected using an Agilent Xcalibur 4-circle diffractometer, with an EOS CCD detector and Mo$K\alpha$ radiation (λ 0.71073 Å), and using Debye-Sherrer geometry, in the Geology Department of the University of Liege, Belgium. Operating conditions were 50 kV, 30 mA, and a sample to detector distance of 40 mm. The very low amount of sample was mounted on a 50 µm-diameter glass fiber. Refinement of unit-cell parameters was performed using the program CelRef 3 (Laugier & Bochu 1999), starting with the unit-cell parameters reported for jahnsite-(CaMnMg) (jahnsite *auctorum*) by Moore & Araki (1974). The powder pattern reflections were found to be consistent with the space group $P2/a$. The refined unit-cell parameters are a = 14.941(52), b = 7.143(3), c = 9.925(38) Å, β = 110.2(4)° with Z = 2. The complete list of indexed reflections is reported in Table 2.

Single-crystal X-ray diffraction data were obtained from a twinned crystal of jahnsite-(MnMnFe) using a Rigaku-Oxford Diffraction Supernova goniometer (in the Department of Geosciences at the University of Padova) equipped with an X-ray micro-source and a Pilatus 200K Dectris detector. Details about the data collection are reported in Table 3. The micro-X-ray source produces Mo$K\alpha$ radiation and was operated at 50 kV and 0.8 mA, with a sample to detector distance of 68 mm. The X-ray beam spot size was 0.120 mm. To maximize the reciprocal space coverage, a combination of omega and phi scans was used, with a step size of 1° and an exposure time of 30 s/frame. A total of 127,750 reflections in the range 2.18 < θ < 56.65° was collected, of which 3550 were unique, giving a metrically monoclinic unit-cell with a =

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR JAHNSITE-(MnMnFe)

I/I_0	d_{obs} (Å)	d_{calc} (Å)	$h\ k\ l$
89.3	**9.221**	**9.315**	**0 0 1**
13	6.199	6.364	1 1 0
42.8	5.749	5.687	1 1 $\bar{1}$
78	**4.932**	**4.945**	**$\bar{2}$ 1 1**
78	**4.651**	**4.657**	**0 0 2**
70.5	**3.971**	**4.014**	**2 1 1**
63.5	**3.504**	**3.505**	**$\bar{4}$ 0 0**
45.8	**3.295**	**3.291**	**$\bar{2}$ 0 3**
81.6	**2.84**	**2.838**	**3 2 0**
100	**2.59**	**2.581**	**$\bar{4}$ 2 1**
40.3	2.358	2.355	$\bar{3}$ 2 3
35.8	1.974	1.97	4 3 0
42.7	1.936	1.936	2 1 4
47.2	1.882	1.879	$\bar{4}$ 1 5
31	1.781	1.784	$\bar{8}$ 1 1
27.3	1.739	1.735	2 3 3
25.7	1.667	1.668	3 4 0
25.5	1.576	1.576	6 3 1
38.4	1.51	1.51	1 4 3
32.2	1.428	1.427	9 1 1
25.9	1.354	1.354	$\overline{10}$ 2 1
24.8	1.296	1.297	$\bar{8}$ 0 7
23.7	1.247	1.246	$\overline{10}$ 3 1
23	1.173	1.173	$\bar{2}$ 6 1
21.6	1.133	1.134	0 5 5
20.1	1.105	1.106	$\bar{5}$ 6 1
17.8	1.069	1.069	4 6 2
16.3	1.027	1.027	$\bar{7}$ 6 3
16.6	1.001	1.001	6 6 2

Bold numbers indicate the most intense reflections

15.1559(6), b = 7.1478(2), c = 10.0209(4) Å, β = 112.059(4)°, and V = 1006.11(6) Å³ (Table 3).

Space group tests using CrysAlis (Agilent 2012) led to the $P2/a$ space group. The crystal structure of jahnsite-(MnMnFe) was solved using the SUPER-FLIP program (based on the charge flipping algorithm, Palatinus & Chapuis 2007), implemented in JANA2006 (Petricek *et al.* 2014), on the basis of the intensity data collected in the Department of Geosciences at the University of Padova. The atomic positions (Table 4) were found to be in good agreement with those described by Kampf *et al.* (2008) for jahnsite-(NaFeMg). We finalized the refinement using anisotropic thermal parameters for cations (Mn, Mg, Fe, P) and oxygen atoms. Only cation occupancies of Mn, Fe were refined and those of P and O were fixed to 1. When convergence was achieved, no peak higher than +4.19 and valley lower than –2.43 e⁻/Å³ were present in the final

TABLE 3. DETAILS OF DATA COLLECTION AND STRUCTURE REFINEMENT FOR JAHNSITE-(MnMnFe)

Crystal shape	Elongated prism
Crystal size (μm)	150 × 80 × 70
Crystal color	Dark brown transparent
T (K)	298
Unit-cell constants	$a = 15.1559(6)$ Å
	$b = 7.1478(2)$ Å
	$c = 10.0209(4)$ Å
	$\beta = 112.059(4)°$
	$V = 1006.10(6)$ Å^3
Ideal chemical formula	$MnMnFe_2Fe^{3+}_2(PO_4)_4(OH)_2 \cdot 8H_2O$
Space Group	$P2/a$
Z	2
Radiation type	X-ray Mo$K\alpha$
Wavelength (Å)	0.7107
Max. (°)	32.21 (original 56.65)
h_{min}, h_{max}	−35, +35
k_{min}, k_{max}	−16, +16
l_{min}, l_{max}	−23, +23
No. measured reflections	127,750
No. unique reflections	3550
No. unique refl. with $F_o > 4(F_o)$	2779
No. refined parameters	180
Refinement on	F^2
R indices [$F_o > 4(F_o)$]	8.20/7.05
R indices (all data)	8.38/8.33
GooF	3.24
Residuals (e$^-$/Å^3)	4.07/−2.35

$R_{int} = \sum|F^2_{obs} - F^2_{obs}(mean)|/\sum(F^2_{obs})$; $R_1 = \sum(|F_{obs} - F_{calc}|)/\sum|F_{obs}|$; $wR_2 = (\sum(w(F^2_{obs} - F^2_{calc})2)/\sum(w(F^2_{obs})^2)^{0.5}$, $w = 1/(\sigma^2(F^2_{obs}))$.

difference-Fourier map. These high residuals are due to the low quality of the crystals of this new mineral; moreover, the refinement was carried out using data from a twinned crystal evidencing two more or less equal (0.55 and 0.45) domains. After considering the two twin components, the R value dropped, at the end of the anisotropic refinement, from *ca.* 10% to 7.05% (Table 3). Due to the low quality, the observed data were cut at 32.21 ° (sinΘ/λ = 0.75). Anisotropic thermal parameters and selected bond distances for jahnsite-(MnMnFe) are reported in Tables 5 and 6.

The general framework of jahnsite-(MnMnFe) conforms to that proposed by Moore & Araki (1974) and Kampf *et al.* (2008, 2018a). The jahnsite-(MnMnFe) structure is characterized by a chain of $M3^{3+}$ octahedra linked on opposite corners *via* OH anions (Fig 3). As described in Kampf *et al.* (2008), the chains are linked together through perpendicular dense slabs with composition $[XM1M3_2(OH)_2(PO_4)_4]^{4-}$ parallel to {001}. In our case, $X = Mn^{2+}$, $M1 = Mn^{2+}$, $M2 = Fe^{2+}$, and $M3 = Fe^{3+}$ (Fig. 2).

DISCUSSION

The mineral is named jahnsite-(MnMnFe) since it corresponds to the MnMnFe member of the jahnsite subgroup, jahnsite group, in which Mn is the principal element at the X site and is the unique element at the $M1^{2+}$ site. Ferrous iron predominates at the $M2^{2+}$ site, and Fe^{3+} represent the main element at the $M3^{3+}$ site. The Dana classification is 42.11.02, hydrated phosphates containing hydroxyl or halogen. The Strunz classification is 8.DH.15, phosphates with additional anions (OH$^-$) and H_2O, with large- and medium-sized cations. The crystal structure of jahnsite-(MnMnFe) conforms very well with previous structure refinements of jahnsite-(NaMnMg) (Kampf *et al.* 2018b and references therein). The only relevant difference between the structures of jahnsite-(NaMnMg) described by Kampf *et al.* (2018b) and jahnsite-(MnMnFe) described in this work consists of a stronger deformation of the X site polyhedron in terms of bond lengths in the latter species (metal–oxygen bond distances which vary from 2.2 to 3.1 Å). This deformation is attributed to the contemporaneous

TABLE 4. REFINED POSITIONAL AND THERMAL DISPLACEMENT PARAMETERS (Å^2)
FOR JAHNSITE-(MnMnFe) AT 298 K

Atom	Occ	x	y	z	U_{iso}/U_{eq}
Mn(X)	0.883(12)	0.25	0.9693(3)	0	0.0227(6)
Mn(M1)	1.012(11)	0.25	0.4703(3)	0	0.0188(5)
Fe1(M2)	1.011(7)	0.5	0	0.5	0.0194(5)
Fe2(M2)	0.923(6)	0.25	0.50604(16)	0.5	0.0154(5)
Fe3(M3)	1.017(10)	0	0	0	0.0128(5)
Fe4(M3)	1.075(12)	0	0.5	0	0.0111(5)
P1	1	0.18420(11)	0.25664(18)	0.19095(17)	0.0147(5)
P2	1	0.08558(11)	0.75058(18)	0.80245(18)	0.0156(5)
O1	1	0.2691(4)	0.2106(8)	0.1488(5)	0.039(2)
O2	1	0.2180(5)	0.3006(7)	0.3486(5)	0.0295(18)
O3	1	0.1157(4)	0.0915(6)	0.1552(6)	0.041(2)
O4	1	0.1392(3)	0.4291(5)	0.0941(5)	0.0182(13)
O5	1	0.1907(3)	0.6923(6)	0.8541(5)	0.0257(16)
O6	1	0.0495(4)	0.7906(7)	0.6427(6)	0.0275(17)
O7	1	0.0856(4)	0.9269(6)	0.8915(5)	0.0260(18)
O8	1	0.0247(3)	0.5955(6)	0.8291(5)	0.0236(16)
Oh	1	0.0253(3)	0.7506(5)	0.0976(4)	0.0169(12)
Ow1	1	0.2272(5)	0.7270(7)	0.3448(7)	0.035(2)
Ow2	1	0.4514(5)	0.2153(7)	0.3397(6)	0.036(2)
Ow3	1	0.6332(4)	0.9888(7)	0.4728(9)	0.034(3)
Ow4	1	0.3978(4)	0.5129(7)	0.5226(9)	0.028(2)

TABLE 5. REFINED ANISOTROPIC THERMAL DISPLACEMENT PARAMETERS (Å^2)
FOR JAHNSITE-(MnMnFe) AT 298 K

| Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(X)	0.0155(8)	0.0184(8)	0.0284(10)	0	0.0017(7)	0
Mn(M1)	0.0222(8)	0.0176(7)	0.0203(8)	0	0.0123(6)	0
Fe1(M2)	0.0150(6)	0.0180(7)	0.0225(8)	0.0004(4)	0.0039(5)	−0.0075(4)
Fe2(M2)	0.0147(6)	0.0153(7)	0.0185(7)	0	0.0087(5)	0
Fe3(M3)	0.0092(6)	0.0088(7)	0.0208(8)	0.0002(3)	0.0063(5)	0.0012(4)
Fe4(M3)	0.0072(6)	0.0085(6)	0.0194(8)	0.0008(3)	0.0072(5)	0.0014(3)
P1	0.0125(6)	0.0148(7)	0.0165(8)	0.0012(5)	0.0052(5)	−0.0011(5)
P2	0.0154(7)	0.0152(7)	0.0189(9)	0.0037(5)	0.0095(6)	0.0043(5)
O1	0.031(3)	0.061(4)	0.028(3)	0.026(3)	0.016(2)	0.012(2)
O2	0.046(3)	0.027(2)	0.017(2)	−0.001(2)	0.013(2)	−0.004(2)
O3	0.034(3)	0.014(2)	0.048(3)	−0.006(2)	−0.014(3)	0.007(2)
O4	0.0154(19)	0.0155(18)	0.025(2)	−0.0019(15)	0.0087(17)	0.0034(15)
O5	0.019(2)	0.033(2)	0.026(2)	0.0080(19)	0.0101(19)	0.0036(19)
O6	0.030(3)	0.027(2)	0.021(2)	0.001(2)	0.004(2)	0.008(2)
O7	0.036(3)	0.0134(18)	0.040(3)	−0.0019(18)	0.027(2)	−0.0027(18)
O8	0.037(3)	0.0142(18)	0.027(2)	−0.0018(17)	0.020(2)	−0.0001(16)
Oh	0.020(2)	0.0078(12)	0.0224(17)	0.0016(12)	0.0075(19)	0.0004(16)
Ow1	0.041(3)	0.028(3)	0.039(3)	0.013(2)	0.019(3)	0.006(2)
Ow2	0.043(3)	0.023(2)	0.029(3)	−0.004(2)	−0.001(3)	−0.003(2)
Ow3	0.020(2)	0.037(3)	0.052(5)	−0.0042(19)	0.020(3)	−0.010(2)
Ow4	0.0100(19)	0.033(3)	0.043(4)	−0.0028(18)	0.011(2)	0.006(2)
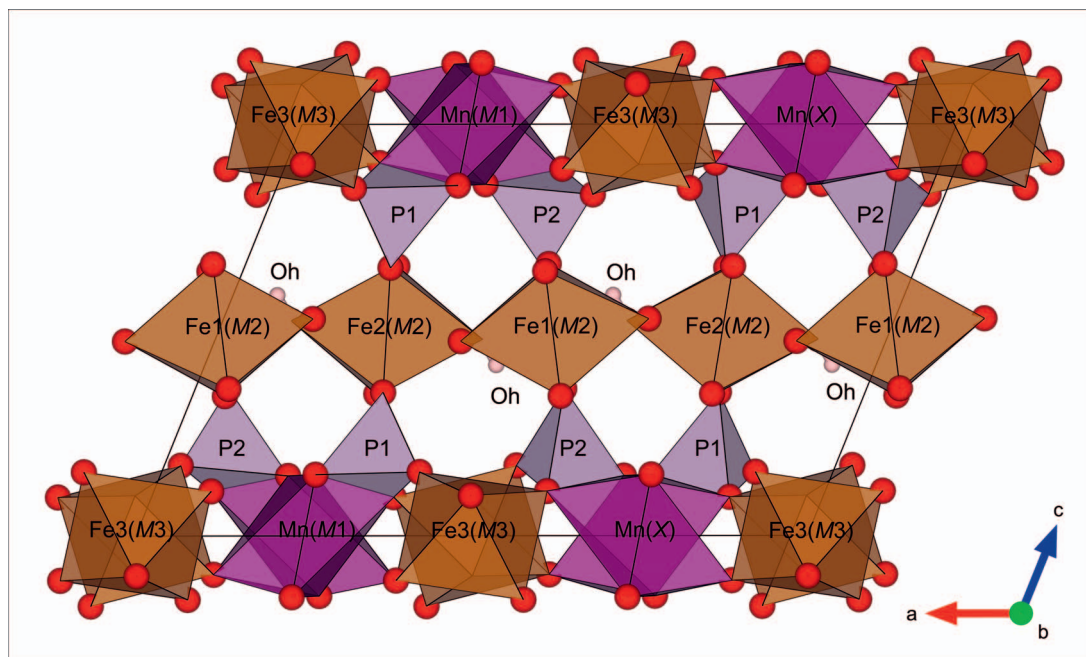
FIG. 3. Crystal structure of jahnsite-(MnMnFe) viewed along **b** (drawn using VESTA, Momma & Mizumi 2011).

presence at the X site of the small Mn^{2+} ion and the large Ca ion as described for jahnsite-(MnMnMg) (Vignola *et al.* 2019). As a consequence the refined occupancy of the X site is strongly affected by this deformation (refined 22.1 e$^-$ *versus* 15.55 e$^-$ obtained from the empirical formula). The $M1$ site is fully occupied by Mn, as confirmed by structure refinement occupancy (refined 25.3 e$^-$ *versus* 25.0 e$^-$). The $M2$ (average) site is mainly occupied by Fe, Mn, and Mg, as confirmed by structure refinement occupancy (average refined 25.15 e$^-$ *versus* 24.73 e$^-$). The $M3$

(average) site is almost fully occupied by Fe, as confirmed by structure refinement occupancy (average refined 27.15 e$^-$ *versus* 25.93 e$^-$). The bond-valence of ions for jahnsite-(MnMnFe), calculated as in Brown (1996), confirms the charge balance for $M1$, $M2$, and $M3$ sites, whereas the X site appears to be "under-bonded" due to the two long bond-distance values (Tables 6 and 7). Due to the lack of hydrogen atoms in the refinement, the Oh and Ow atoms show a deficit in the electrostatic values.

TABLE 6. SELECTED BOND DISTANCES (Å) FOR JAHNSITE-(MnMnFe) AT 298 K

Mn1(X)–O3	3.115(5)	×2	Mn2($M1$)–O5	2.116(4)	×2	P1–O2	1.502(5)
Mn1(X)–O1	2.228(5)	×2	Mn2($M1$)–O1	2.330(5)	×2	P1–O3	1.523(5)
Mn1(X)–O7	2.332(5)	×2	Mn2($M1$)–O4	2.233(5)	×2	P1–O1	1.531(6)
Mn1(X)–O5	2.427(4)	×2	<**Mn2–O**>	**2.226**		P1–O4	1.556(4)
<**Mn1–O**>	**2.525**					<**P1–O**>	**1.528**
Fe1($M2$)–O6	2.014(5)	×2	Fe2($M2$)–O2	2.029(5)	×2	P2–O6	1.511(5)
Fe1($M2$)–Ow3	2.144(7)	×2	Fe2($M2$)–Ow1	2.148(6)	×2	P2–O8	1.531(5)
Fe1($M2$)–Ow2	2.148(5)	×2	Fe2($M2$)–Ow4	2.166(5)	×2	P2–O5	1.535(5)
<**Fe1–O**>	**2.102**		<**Fe2–O**>	**2.114**		P2–O7	1.545(5)
						<**P2–O**>	**1.531**
Fe3($M3$)–O3	1.967(4)	×2	Fe4($M3$)–O4	2.027(4)	×2		
Fe3($M3$)–OH	1.999(3)	×2	Fe4($M3$)–OH	2.007(3)	×2		
Fe3($M3$)–O7	2.048(6)	×2	Fe4($M3$)–O8	2.006(5)	×2		
<**Fe3–O**>	**2.005**		<**Fe4–O**>	**2.013**			

TABLE 7. BOND VALENCE FOR JAHNSITE-(MnMnFe)

	Mn1(×2)*	Mn2(×2)	Fe1(×2)	Fe2(×2)	Fe3(×2)	Fe4(×2)	P1	P2	Sum
O1	0.306	0.232						1.262	1.800
O2				0.426			1.365		1.791
O3	0.028				0.57		1.289		1.887
O4		0.382				0.485	1.179		2.046
O5	0.179	0.414						1.248	1.841
O6			0.443					1.332	1.775
O7	0.231				0.458			1.215	1.904
O8						0.513		1.262	1.775
Oh**					0.523	0.512			1.035
Ow1**				0.309					0.309
Ow2**			0.309						0.309
Ow3**			0.312						0.312
Ow4**				0.294					0.294
Sum	1.488	2.056	2.128	2.058	3.102	3.02	5.095	5.057	

* The deficit in the charge is due to the strong distortion of the *X* site polyhedron; ** The deficit in the charge is due to the lack of hydrogen atoms in the refinement.

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