# Nizamoffite, Mn<sup>2+</sup>Zn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>, the Mn analogue of hopeite from the Palermo No. 1 pegmatite, North Groton, New Hampshire

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## ABSTRACT

Nizamoffite, ideally Mn<sup>2+</sup>Zn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>, is a new mineral from the Palermo No.1 pegmatite in North Groton, Grafton County, New Hampshire, U.S.A. It formed as the result of secondary alteration of primary triphylite and associated sphalerite. The crystals occur as colorless prisms up to 1 mm in length and 0.5 mm in diameter. The prisms are elongated and lightly striated parallel to [001] and exhibit the forms  $\{100\}$ ,  $\{010\}$ ,  $\{230\}$ ,  $\{011\}$ ,  $\{031\}$ , and  $\{111\}$ . The mineral is transparent and has a white streak, vitreous luster, Mohs hardness of about 3<sup>1</sup>/<sub>2</sub>, brittle tenacity, irregular fracture, and three cleavages: perfect on {010}, good on {100}, and fair on {001}. The measured and calculated densities are 3.00(1) and 2.961 g/cm<sup>3</sup>, respectively. It is optically biaxial (-),  $\alpha = 1.580(1)$ ,  $\beta = 1.590(1)$ ,  $\gamma =$ 1.591(1) (white light),  $2V_{\text{meas}} = 28(1)^\circ$ , and  $2V_{\text{calc}} = 35^\circ$ . Nizamoffite exhibits strong dispersion, r < v. The optical orientation is  $X = \mathbf{a}$ ,  $Y = \mathbf{c}$ ,  $Z = \mathbf{b}$ , and the mineral is nonpleochroic. Electron-microprobe analyses (average of 10), with H<sub>2</sub>O calculated on structural grounds, provided: CaO 0.20, MgO 0.61, MnO 15.80, ZnO 33.34, Fe<sub>2</sub>O<sub>3</sub> 2.81, Al<sub>2</sub>O<sub>3</sub> 0.10, P<sub>2</sub>O<sub>5</sub> 32.05, H<sub>2</sub>O 15.95, total 100.23 wt%. The empirical formula (based on 12 O atoms) is:  $(Mn_{0.99}^{2+9}Ca_{0.02})_{\Sigma 1.01}(Zn_{1.82}Fe_{0.12}^{3+1}Mg_{0.07})_{\Sigma 2.01}(P_{1.00}O_4)_2(H_{1.96}O)_4$ . The mineral dissolves readily in cold, dilute HCl. Nizamoffite is orthorhombic, Pnma, with the unit-cell parameters:  $a = 10.6530(4), b = 18.4781(13), c = 5.05845(15) \text{ Å}, V = 995.74(8) \text{ Å}^3, and Z = 4$ . The eight strongest lines in the X-ray powder diffraction pattern are  $[d_{obs} \text{ in } Å(I)(hkl)]$ : 9.27(71)(020); 4.62(37)(040,220); 4.43(24)(111); 3.424(52)(240,221); 2.873(100)(241); 2.644(36)(400,331); 2.540(33)(420,161,002); and 1.953(36)(281). Nizamoffite is isostructural with hopeite. The structure ( $R_1 = 1.7\%$  for 1014  $F_0$  >  $4\sigma F$ ) contains corner-sharing zigzag chains of ZnO<sub>4</sub> tetrahedra along [001]. The chains are connected by corner sharing with PO<sub>4</sub> tetrahedra to form sheets parallel to  $\{010\}$ . Three of the four PO<sub>4</sub> vertices link to  $ZnO_4$  tetrahedra in the sheet, while the fourth links to an octahedron between the sheets. Each octahedron links to one tetrahedron from each of two adjacent sheets, thereby linking the sheets in the [010] direction. The octahedron contains Zn in hopeite and Mn in nizamoffite.

**Keywords:** Nizamoffite, new mineral, crystal structure, hopeite, secondary phosphate, Palermo No. 1 pegmatite, New Hampshire, U.S.A.

## INTRODUCTION

The new mineral described herein was discovered at the Palermo No.1 pegmatite (Segeler et al. 1981; Whitmore and Lawrence 2004) in North Groton, Grafton County, New Hampshire, U.S.A. (43° 45.038'N 71° 53.378'W), by James Nizamoff and one of the authors (R.W.W.) in 2003. The Palermo No. 1 pegmatite is the type locality for 11 new phosphate species, not including the new mineral described herein: whitlockite (Frondel 1941); wolfeite and xanthoxenite (Frondel 1949); palermoite (Frondel and Ito 1965); bjarebyite (Moore et al. 1973); whitmoreite (Moore et al. 1974); foggite, goedkenite, and samuelsonite (Moore et al. 1975); schoonerite (Moore and Kampf 1977); and falsterite (Kampf et al. 2012). The paper describing the last of these includes a synopsis of the mineralogy and geology of the deposit.

The new species is named nizamoffite in honor of James W. Nizamoff (b. 1971) in recognition of his research on peg-

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matite mineralogy in general, and especially on the phosphate mineralogy of the Palermo pegmatites at North Groton, New Hampshire. J.W. Nizamoff is one of the discoverers of the new mineral and provided the specimens used for its characterization. He is a co-author of the descriptions of the new minerals falsterite, galliskiite, and zigrasite. He has agreed to the naming of the mineral in his honor. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2012-076). Two co-type specimens are deposited in the Natural History Museum of Los Angeles County under catalog numbers 64009 and 64010.

#### **OCCURRENCE AND PARAGENESIS**

Nizamoffite was found in a Zn- and Pb-rich phosphate– carbonate assemblage (Nizamoff et al. 2007) along the margin of a 1.5 m triphylite crystal in the core-margin of the Palermo No. 1 pegmatite. The triphylite crystal is rimmed on one side by a 10 to 30 cm thick rind of siderite, fluorapatite, and quartz.

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This carbonate-rich zone also contains minor amounts of sulfide minerals including pyrite, sphalerite, galena, and chalcopyrite. A significant portion of the sulfides have been altered by aqueous solutions, resulting in the formation of numerous secondary Zn- and Pb-bearing phosphate and carbonate species. Nizamoffite is a relatively late-formed phase occurring as well-formed crystals in vugs in direct association with childrenite-eosphorite, crandallite-goyazite, fairfieldite-messelite, falsterite, fluorapatite, frondelite-rockbridgeite, mitridatite, phosphophyllite, pyrite, quartz, siderite, schoonerite, sphalerite, and vivianite. Other secondary species observed in the assemblage include cerussite, keckite, parascholzite, pyromorphite, and smithsonite.

The redox conditions for this assemblage span the boundary between  $Fe^{2+}$  and  $Fe^{3+}$  stability, as indicated by the presence of minerals containing  $Fe^{2+}$ , minerals containing  $Fe^{3+}$ , and minerals containing both  $Fe^{2+}$  and  $Fe^{3+}$ . We have assumed all Fe in nizamoffite to be 3+ because that is most consistent with its presence in the tetrahedral Zn site in the structure. Furthermore, the structural site occupancy calculations using the program OccQP (see below), indicate that all Fe in nizamoffite is 3+.

## **PHYSICAL AND OPTICAL PROPERTIES**

Nizamoffite crystals occur as colorless prisms up to 1 mm in length and 0.5 mm in diameter. The mineral is orthorhombic holosymmetric (point group *mmm*). Prisms are elongated and lightly striated parallel to [001] and exhibit the forms {100}, {010}, {230}, {011}, {031}, and {111} (Fig. 1). Nizamoffite is colorless and has a white streak. Crystals are transparent and have vitreous luster. Nizamoffite does not fluoresce in long- or short-wave ultraviolet light. The Mohs hardness is about  $3\frac{1}{2}$ , the tenacity is brittle, the fracture is irregular, and there are three cleavages: perfect on {010}, good on {100}, and fair on {001}. The density measured by sink-float in an aqueous solution of lithium metatungstate is 3.00(1). The calculated density based on



**FIGURE 1.** Crystal drawing of nizamoffite; clinographic projection in standard orientation.

the empirical formula and single-crystal unit cell is 2.961 g/cm<sup>3</sup>. Nizamoffite dissolves readily in cold, dilute HCl.

Optically, nizamoffite is biaxial negative, with  $\alpha = 1.580(1)$ ,  $\beta = 1.590(1)$ ,  $\gamma = 1.591(1)$ , measured in white light. The 2V, measured directly by conoscopic observation, is 28(1)°. The calculated 2V is 35°. Nizamoffite exhibits strong dispersion, r < v. The optical orientation is  $X = \mathbf{a}$ ,  $Y = \mathbf{c}$ ,  $Z = \mathbf{b}$ , and there is no pleochroism.

#### CHEMICAL COMPOSITION

Ten chemical analyses were carried out using an ARL-SEMQ electron microprobe in the Department of Earth and Environmental Science, University of New Orleans (WDS mode, 15 kV, 10 nA, and 2–3  $\mu$ m beam diameter). No other elements were detected by EDS. Other likely elements were sought by EMPA, but none were found to be above the limit of detection. Insufficient material is available for direct water determination. The H<sub>2</sub>O content is calculated by stoichiometry based upon the structure determination. Analytical data and standards are given in Table 1.

The empirical formula (based on 12 O atoms) is  $(Mn_{0.99}^{2+})$ Ca<sub>0.02</sub>)<sub>21.01</sub>(Zn<sub>1.82</sub>Fe<sub>0.12</sub><sup>3+</sup>Mg<sub>0.07</sub>)<sub>22.01</sub>(P<sub>1.00</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>1.96</sub>O)<sub>4</sub>. The simplified formula is MnZn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>, which requires MnO 15.84, ZnO 36.35, P<sub>2</sub>O<sub>5</sub> 31.71, H<sub>2</sub>O 16.10, total 100.00 wt%.

The Gladstone-Dale compatibility index  $1 - (K_{\rm F}/K_{\rm C})$  as defined by Mandarino (1981) provides a measure of the consistency among the average index of refraction, calculated density, and chemical composition. For nizamoffite, the compatibility index is 0.033 based on the empirical formula, within the range of excellent compatibility.

## X-RAY CRYSTALLOGRAPHY AND STRUCTURE REFINEMENT

Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized MoK $\alpha$  radiation. For the powder-diffraction study, a Gandolfi-like motion on the  $\varphi$  and  $\omega$  axes was used to randomize the sample and observed *d*-spacings and intensities were derived by profile fitting using JADE 2010 software. The powder data are presented in Table 2. The orthorhombic (*Pnma*) unit-cell parameters refined from the powder data using whole pattern fitting are: a = 10.647(4), b =18.451(8), c = 5.047(2) Å, and V = 991.4(7) Å<sup>3</sup>.

The Rigaku CrystalClear software package was used for processing the structure data, including the application of an empirical multi-scan absorption correction using ABSCOR (Higashi 2001). The structure was solved by direct methods using SIR2004 (Burla et al. 2005), after which the coordinates

<b>TABLE 1.</b> Analytical results for nizamoffite (average of 10 analyses)	s)
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Constituent	wt%	Range	S.D.	Standard
CaO	0.20	0.18-0.23	0.02	Fluorapatite ( <i>K</i> α)
MgO	0.61	0.45-0.71	0.08	Triphylite ( $K\alpha$ )
MnO	15.80	15.55-15.91	0.10	Lithiophilite ( $K\alpha$ )
ZnO	33.34	33.01-33.66	0.22	ZnO (Kα)
Al <sub>2</sub> O <sub>3</sub>	0.10	0.07-0.12	0.02	Amblygonite ( $K\alpha$ )
Fe <sub>2</sub> O <sub>3</sub>	2.18	1.90-2.33	0.15	Triphylite (Kα)
$P_2O_5$	32.05	31.88-32.30	0.13	Triphylite ( <i>K</i> α)
H <sub>2</sub> O*	15.95			
Total	100.23			

\* Calculated from the structure.

TABLE 2. Powder X-ray data for nizamoffite

$I_{obs}$	$d_{\rm obs}$		d <sub>calc</sub>	$I_{calc}$	hkl	I <sub>obs</sub>	$d_{\rm obs}$		$d_{\rm calc}$	$I_{calc}$	hkl
71	9.27(8)		9.2389	89	020	4	1.794(19)		1.7915	2	291
8	5.35(14)		5.3265	10	200			(	1.7449	2	480
12	5.14(10)		5.1181	17	210	7	1.741(12)	Ł	1.7436	4	620
21	4.88(5)		4.8788	19	011			ι	1.7340	2	551
27	162(2)	S	4.6195	38	040	12	1 704(0)	s	1.7055	2	082
57	4.02(3)	ι	4.6145	4	220	12	1.704(9)	ι	1.7045	6	442
24	4.43(4)		4.4358	21	111			(	1.6841	6	182
			4.0958	4	121	11	1.677(11)	Ł	1.6769	3	391
19	4.05(4)		4.0289	19	230			ι	1.6654	2	103
14	3.91(4)	~	3.9090	15	031			1	1.6502	3	2.10.1
7	3 67(6)	ł	3.6698	3	131	13	1 647(7)	J	1.6495	3	481
,	5107 (0)	C	3.6679	4	201	15	1.047(7)	1	1.6484	3	621
52	3 4 2 4 (1 3)	Ş	3.4898	23	240			Ļ	1.6390	2	123
52	5.424(15)	ι	3.4091	40	221	8	1 611(9)	Ş	1.6263	3	033
5	3.15(5)		3.1514	6	231	0	1.011(2)	ι	1.6047	5	522
5	3 01(5)	ł	3.0363	3	250	18	1.576(5)	_	1.5749	12	641
5	5.01(5)	ι	2.9840	6	051	17	1 538(6)	Ş	1.5398	8	0.12.0
100	2.873(8)		2.8725	100	241	.,	1.550(0)	ι	1.5382	9	660
			2.6661	4	260	23	1.517(5)		1.5182	15	243
26	2 644(0)	ł	2.6633	19	400	7	1.490(12)		1.4920	4	0.10.2
50	2.044(9)	L	2.6284	22	331			ſ	1.4716	3	661
		ſ	2.5590	14	420	8	1.465(11)	Ł	1.4649	2	163
33	2.540(8)	4	2.5538	5	161			Ļ	1.4541	4	4.10.1
		L	2.5292	17	002			ſ	1.4465	2	343
17	2.440(11)		2.4394	12	022	13	1.444(7)	ſ	1.4403	2	562
10	2.357(16)		2.3585	9	261			Ļ	1.4363	5	482
		_	2.3097	5	080			ſ	1.4250	4	263
		ſ	2.2857	5	171	14	1.423(6)	ſ	1.4204	2	413
22	2.286(8)	1	2.2851	4	132			ι	1.4198	2	2.12.1
		Ļ	2.2835	6	421	4	1.382(13)	_	1.3862	3	642
		ſ	2.2184	2	042	10	1.361(6)	Ł	1.3653	5	363
8	2.215(19)	1	2.2179	4	222			ι	1.3561	4	681
_		L	2.2010	2	431	5	1.332(13)		1.3330	3	4.12.0
9	2.170(17)	~	2.1718	7	142			ſ	1.3194	4	283
12	2.116(11)	ł	2.1191	3	280	8	1.316(11)	ſ	1.3152	2	0.12.2
		ç	2.1137	8	361			L	1.3142	2	662
18	2.013(7)	ł	2.0145	9	460	4	1.301(16)		1.3017	2	4.10.2
~	4.052(5)	C	2.0107	8	322	7	1.277(6)	~	1.2754	4	821
36	1.953(5)	~	1.9545	30	281	10	1.241(4)	ł	1.2443	4	124
22	1.834(6)	ł	1.8349	5	262			L	1.2419	4	2.14.1
		ι	1.8340	14	402						

*Note*: Only calculated lines with intensities greater than 2 are shown unless they correspond to observed lines.

were transformed to conform with those reported for hopeite in most earlier reports (Hill and Jones 1976; Haussühl et al. 1991). SHELXL-97 software (Sheldrick 2008) was used with neutral atom scattering factors for the refinement of the structure. The occupancies of the octahedral (Mn) and large tetrahedral (Zn) sites were calculated using the program OccQP (Wright et al. 2001), which uses quadratic equations in a constrained leastsquares formulation to optimize occupancy assignments based upon site scattering, chemical composition, charge balance, bond valence, and cation-anion bond lengths. The optimization indicates deficiencies at both cation sites and somewhat different distributions of cations compared with what we deem most likely and have provided in the empirical formula; however, both are consistent with the ideal formula  $Mn^{2+}Zn_2(PO_4)_2(H_2O)_4$ .

The positions of H atoms in the three H<sub>2</sub>O groups, OW1, OW2, and OW3, were located in the difference-Fourier maps and were refined using soft O–H distance constraints of 0.82(5) Å and no H–H distance constraints. The isotropic displacement parameters for the H sites were fixed at 0.05 Å<sup>2</sup> and, because more than one configuration was indicated for two of the H<sub>2</sub>O groups (OW2 and OW3), the occupancies of the H sites were refined. One H site (H1) on a general position is associated with the OW1 site on a mirror plane. This site refined to nearly full occupancy. The OW2 site, also on the mirror plane, has two H sites associated with it. One (H2a) is on the mirror plane and refined to nearly full occupancy, while the second (H2b) is on a general position and refined to close to half occupancy. These H sites, therefore, define two different configurations for the OW2 H<sub>2</sub>O group. The third H<sub>2</sub>O group (OW3) is on a general position has four H sites (H3a, H3b, H3c, and H3d) also on general positions associated with it. The H3a site refined to nearly full occupancy, while the H3b, H3c, and H3d site occupancies refined roughly to  $\frac{1}{2}$ ,  $\frac{1}{4}$ , and  $\frac{1}{4}$ , respectively. The OW3 H<sub>2</sub>O group, therefore, has three different configurations. In the final refinement, the occupancies of the H sites were fixed at full,  $\frac{1}{2}$ , and  $\frac{1}{4}$  occupancies, in accord with their refined occupancies.

The details of the data collection and the final structure refinement are provided in Table 3. The final fractional coordinates and atom displacement parameters are provided in Table 4. Selected interatomic distances are listed in Table 5 and bond valences in Table 6. (CIF and structure factors table are on deposit<sup>1</sup>.)

## **DESCRIPTION OF THE STRUCTURE**

Nizamoffite is isostructural with hopeite (Whitaker 1975; Hill and Jones 1976; Haussühl et al. 1991). The structure contains corner-sharing zigzag chains of  $ZnO_4$  tetrahedra along [001]. The chains are connected by corner sharing with  $PO_4$ tetrahedra to form sheets parallel to {010} (Fig. 2). Three of the four  $PO_4$  vertices link to  $ZnO_4$  tetrahedra in the sheet, while

<sup>1</sup> Deposit item AM-13-1004, CIFs. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

 TABLE 3.
 Data collection and structure refinement details for nizamoffite

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	Μο <i>Κ</i> α (λ = 0.71075 Å)
Temperature	298(2) K
Structural formula*	$(Mn_{0.819}^{2+}Fe_{0.080}^{3+}Mg_{0.063}AI_{0.008}Ca_{0.004})_{\Sigma 0.974}$
	$(Zn_{1.796}Mn_{0.154}Fe_{0.033}^{3+})_{\Sigma_{1.983}}(PO_4)_2(H_2O)_4$
Space group	Pnma
Unit-cell dimensions	<i>a</i> = 10.6530(4) Å
	b = 18.4781(13) Å
	c = 5.05845(15) Å
V	995.74(8) Å <sup>3</sup>
Ζ	4
Density (for above formula)	2.940 g/cm <sup>3</sup>
Absorption coefficient	6.058 mm <sup>-1</sup>
F(000)	863.8
Crystal size	110×45×25 μm
θrange	3.83 to 27.47°
Index ranges	$-13 \le h \le 13, -23 \le k \le 23, -4 \le l \le 6$
Reflections collected/unique	$5260/1160 [R_{int} = 0.023]$
Reflections with $F_{o} > 4\sigma F$	1014
Completeness to $\theta = 27.47^{\circ}$	98.8%
Max. and min. transmission	0.863 and 0.556
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Parameters refined	102
GoF	1.072
Final R indices $[F_{\circ} > 4\sigma(F)]$	$R_1 = 0.017$ , w $R_2 = 0.037$
R indices (all data)	$R_1 = 0.022, wR_2 = 0.038$
Largest diff. peak/hole	+0.32/−0.35 e Å-3

Notes:  $R_{int} = \Sigma |F_0^2 - F_0^2(mean)|/\Sigma [F_0^2]$ . GoF =  $S = \{\Sigma [w(F_0^2 - F_0^2)^2]/(n-p)\}^{1/2}$ .  $R_1 = \Sigma ||F_0| - |F_0|/\Sigma |F_0|$ .  $wR_2 = \{\Sigma [w(F_0^2 - F_0^2)^2]/\Sigma [w(F_0^2)^2]\}^{1/2}$ .  $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$  where *a* is 0.0177, *b* is 0.4086, and *P* is  $[2F_0^2 + Max(F_0^2,0)]/3$ .

\* Site occupancies calculated using the program OccQP (Wright et al. 2001).

TABLE 4. Fractional coordinates and atom displacement parameters (Å<sup>2</sup>) for nizamoffite

			1	1	. ,					
	x/a	y/b	z/c	$U_{eq}$	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Mn*	0.25984(3)	1/4	0.06749(8)	0.01561(10)	0.01387(19)	0.0193(2)	0.0136(2)	0.000	-0.00115(16)	0.000
Zn*	0.143185(19)	0.499051(11)	0.20876(4)	0.01274(7)	0.01190(11)	0.01533(11)	0.01099(11)	-0.00080(8)	0.00021(8)	-0.00030(8)
Р	0.39727(4)	0.40719(2)	0.22699(9)	0.01341(11)	0.0161(2)	0.0118(2)	0.0123(2)	0.00082(17)	-0.00014(17)	0.00119(17)
OW1	0.10778(19)	3/4	0.2453(4)	0.0234(4)	0.0234(10)	0.0272(11)	0.0198(10)	0.000	-0.0023(9)	0.000
H1	0.110(2)	0.7142(14)	0.159(5)	0.050						
OW2	0.1076(2)	1/4	0.3479(5)	0.0322(5)	0.0193(10)	0.0509(15)	0.0264(12)	0.000	0.0016(10)	0.000
H2a	0.037(3)	1/4	0.301(8)	0.050						
H2b*	0.116(4)	0.221(2)	0.471(9)	0.050						
OW3	0.34053(15)	0.66755(9)	0.3260(3)	0.0304(4)	0.0298(9)	0.0265(8)	0.0347(9)	0.0030(7)	0.0027(7)	0.0080(6)
H3a	0.392(2)	0.6355(15)	0.390(6)	0.050						
H3b*	0.282(5)	0.636(3)	0.280(11)	0.050						
H3c*	0.377(9)	0.706(4)	0.38(2)	0.050						
H3d*	0.349(10)	0.670(7)	0.158(10)	0.050						
04	0.35988(13)	0.32957(7)	0.2834(3)	0.0228(3)	0.0322(8)	0.0169(7)	0.0193(7)	0.0023(5)	-0.0081(6)	-0.0059(6)
05	0.10004(15)	0.57806(7)	0.4318(3)	0.0302(3)	0.0555(9)	0.0201(7)	0.0149(7)	-0.0037(5)	-0.0065(7)	0.0120(6)
06	0.02485(12)	0.42282(7)	0.1428(3)	0.0220(3)	0.0147(6)	0.0181(6)	0.0334(8)	-0.0052(6)	0.0028(6)	-0.0020(5)
07	0.30179(11)	0.46036(7)	0.3610(2)	0.0181(3)	0.0151(6)	0.0234(7)	0.0158(6)	-0.0036(5)	-0.0028(5)	0.0048(5)
* Assigned	site occupanci	es: Mn: Mn <sub>0.819</sub> Fe	e <sub>0.080</sub> Mg <sub>0.063</sub> Al <sub>0.008</sub>	Ca <sub>0.004</sub> ; Zn: Zn <sub>0.898</sub>	Mn <sub>0.077</sub> Fe <sub>0.017</sub> ; H2	b: 0.5; H3b: 0.5;	H3c: 0.25; H3d:	0.25. All other	sites assigned f	ull occupancy.

TABLE 5. Selected bond distances (Å) in nizamoffite

Mn-O4 (×2)	2.1191(13)	Zn-O5	1.9016(13)	P-04	1.5155(14)		
Mn-OW2	2.1543(23)	Zn-O6	1.9196(13)	P-05	1.5179(15)		
Mn-OW1	2.1552(20)	Zn-O7	1.9896(12)	P-06	1.5376(13)		
Mn-OW3(×2)	2.2263(16)	Zn-O7	2.0004(13)	P-07	1.5681(13)		
<mn-o></mn-o>	2.1762	<zn-o></zn-o>	1.9528	<p-o></p-o>	1.5348		
		ŀ	lydrogen bonds (D =	donor, A = accepte	or)		
D-H	d(D-H)	d(H…A)	<dha< td=""><td>d(D···A)</td><td>Α</td><td><hdh< td=""><td>H-D-H</td></hdh<></td></dha<>	d(D···A)	Α	<hdh< td=""><td>H-D-H</td></hdh<>	H-D-H
OW1-H1 (×2)	0.79(2)	2.09(3)	146(3)	2.782(2)	O4	113	H1-OW1-H1
OW2-H2a	0.79(3)	2.43(3)	142.5(6)	3.093(2)	O4		
OW2-H2b (×2)	0.83(4)	2.10(4)	166(5)	2.911(3)	OW3	109	H2a-OW2-H2b
OW3-H3a	0.87(3)	1.89(3)	159(3)	2.723(2)	06		
OW3-H3b	0.89(4)	2.34(5)	143(5)	3.096(2)	O5	95	H3a-OW3-H3b
OW3-H3c	0.85(5)	2.38(8)	136(9)	3.047(3)	OW3	100	H3a-OW3-H3c
OW3-H3d	0.85(5)	2.21(9)	140(11)	2.911(3)	OW2	110	H3a-OW3-H3d

#### TABLE 6. Bond-valence analysis for nizamoffite

	OW1	OW2	OW3	04	05	06	07	Σ
Mn	0.32	0.32	$0.26 \times 2 \rightarrow$	$0.35 \times 2 \rightarrow$				1.86
Zn					0.58	0.55	0.45, 0.44	2.02
Р				1.32	1.31	1.24	1.14	5.01
H1	0.82 ×2↓			0.18				1.00
H2a		0.91		0.09				1.00
H2b		0.86	0.14					1.00
H3a			0.80			0.20		1.00
H3b			0.45		0.05			0.50
H3c			0.23, 0.02					0.25
H3d		0.03	0.22					0.25
Σ	1.96	2.12	2.12	1.94	1.94	1.99	2.03	

Notes: Values are expressed in valence units. Bond strengths are taken from Brown and Altermatt (1985) and are adjusted for site occupancies; hydrogen bond strengths are based on O-O bond lengths and are also from Brown and Altermatt (1985).



**FIGURE 2.** The sheet of corner-sharing  $ZnO_4$  and  $PO_4$  tetrahedra in the structure of nizamoffite viewed down **b**. Oxygen atoms are labeled with numbers. (Color online.)



**FIGURE 3.** The structure of nizamoffite viewed down **c**. Oxygen atoms are labeled with numbers. (Color online.)

the fourth links to an octahedron between the sheets. Each octahedron links to one tetrahedron from each of two adjacent sheets, thereby linking the sheets in the [010] direction (Fig. 3). The octahedron contains Zn in hopeite and Mn in nizamoffite. The dominance of Mn in the octahedral site in nizamoffite is confirmed by computations using the program OccQP, which optimizes site occupancies based upon site scattering, chemical composition, charge balance, bond valence, and cation-anion bond lengths.

Synthetic hopeites, including those substituted with cations such as Mn<sup>2+</sup>, Ni<sup>2+</sup>, and Mg, have been studied extensively



**FIGURE 4.** Hydrogen bonding in nizamoffite,  $\alpha$ -hopeite, and  $\beta$ -hopeite. Hydrogen bonds are shown as thin black lines. The gray spheres are the octahedrally coordinated cations and the bonds to the O atoms surrounding them are shown as sticks. Oxygen atoms in the nizamoffite structure are labeled with numbers and H atoms with letters as appropriate.

because of their technological applications, particularly with respect to corrosion resistant coatings on galvanized steel (cf. Arnaud et al. 1988; Haussühl et al. 1991; Herschke et al. 2004; Schofield et al. 2007). In nature, there are two polymorphs of Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4(H<sub>2</sub>O), hopeite (orthorhombic) and parahopeite (triclinic). In laboratory studies, two orthorhombic polymorphs with somewhat different properties have been reported and have been designated  $\alpha$ -hopeite and  $\beta$ -hopeite. As noted by Herschke et al. (2004),  $\alpha$ -hopeite is considered more stable and  $\beta$ -hopeite forms at lower temperature (20 °C), but the structures of the two polymorphs are apparently identical except for the orientation of the H atoms of one of the H<sub>2</sub>O groups. The differing properties of  $\alpha$ -hopeite and  $\beta$ -hopeite have been attributed to the resultant difference in hydrogen bonding.

The locations of the H atoms and the configuration of the hydrogen bonds in nizamoffite are shown in Figure 4, and are compared to those determined for  $\alpha$ -hopeite and  $\beta$ -hopeite by Herschke et al. (2004). [It should be noted that Herschke et al. (2004) used a different space group setting (Pbnm) and atom numbering scheme, so our foregoing comments are based upon our scheme.] Herschke et al. (2004) showed that the configurations of the H atoms of the OW2 and OW3 H<sub>2</sub>O groups are essentially the same in the structures of  $\alpha$ -hopeite and  $\beta$ -hopeite. while they differ for the OW1  $H_2O$  group. For  $\alpha$ -hopeite, the H atoms of the OW1 group correspond to a single site on a general position reflected across the mirror plane containing the OW1 site, while for  $\beta$ -hopeite, the H atoms of this group lie on the mirror plane [although Herschke et al. (2004) apparently located only one of these H atom sites]. As seen in Figure 4, the H atom positions and hydrogen bonds for nizamoffite most closely correspond with those in  $\alpha$ -hopeite. The only significant difference is the 1/4-occupied H3c and H3d sites. The H3c atoms form hydrogen bonds to adjacent OW3 atoms in the same octahedral coordination. The H3d atoms form hydrogen bonds to an OW2 atom in a different octahedral coordination.

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