# Nizamoffite, $\mathrm{Mn}^{2+} \mathrm{Zn}_{2}\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}$, the Mn analogue of hopeite from the Palermo No. 1 pegmatite, North Groton, New Hampshire 

Anthony R. KAmpF ${ }^{1, *}$, Alexander U. Falster ${ }^{2}$, William B. Simmons ${ }^{2}$ and Robert W. Whitmore ${ }^{3}$

${ }^{1}$ Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, U.S.A.
${ }^{2}$ Department of Earth and Environmental Science, University of New Orleans 2000 Lakeshore Drive, New Orleans, Louisiana 70148, U.S.A. ${ }^{3} 934$ S. Stark Highway, Weare, New Hampshire 03281, U.S.A.


#### Abstract

Nizamoffite, ideally $\mathrm{Mn}^{2+} \mathrm{Zn}_{2}\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}$, 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 $31 / 2$, 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 $2.961 \mathrm{~g} / \mathrm{cm}^{3}$, respectively. It is optically biaxial $(-), \alpha=1.580(1), \beta=1.590(1), \gamma=$ $1.591(1)$ (white light), $2 V_{\text {meas }}=28(1)^{\circ}$, and $2 V_{\text {calc }}=35^{\circ}$. 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 $\mathrm{H}_{2} \mathrm{O}$ calculated on structural grounds, provided: $\mathrm{CaO} 0.20, \mathrm{MgO} 0.61$, $\mathrm{MnO} 15.80, \mathrm{ZnO} 33.34, \mathrm{Fe}_{2} \mathrm{O}_{3} 2.81, \mathrm{Al}_{2} \mathrm{O}_{3} 0.10, \mathrm{P}_{2} \mathrm{O}_{5} 32.05, \mathrm{H}_{2} \mathrm{O} 15.95$, total $100.23 \mathrm{wt} \%$. The empirical formula (based on 12 O atoms) is: $\left(\mathrm{Mn}_{0.99}^{2+} \mathrm{Ca}_{0.02}\right)_{\Sigma 1.01}\left(\mathrm{Zn}_{1.82} \mathrm{Fe}_{0.12}^{3+} \mathrm{Mg}_{0.07}\right)_{\Sigma 2.01}\left(\mathrm{P}_{1.00} \mathrm{O}_{4}\right)_{2}\left(\mathrm{H}_{1.96} \mathrm{O}\right)_{4}$. The mineral dissolves readily in cold, dilute HCl . Nizamoffite is orthorhombic, Pnma, with the unit-cell parameters: $a=10.6530(4), b=18.4781(13), c=5.05845(15) \AA, V=995.74(8) \AA^{3}$, and $Z=4$. The eight strongest lines in the X-ray powder diffraction pattern are $\left[d_{\text {obs }}\right.$ in $\left.\AA(I)(h k l)\right]: 9.27(71)(020) ; 4.62(37)(040,220)$; 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 $\left(R_{1}=1.7 \%\right.$ for $1014 F_{\mathrm{o}}>$ $4 \sigma F$ ) contains corner-sharing zigzag chains of $\mathrm{ZnO}_{4}$ tetrahedra along [001]. The chains are connected by corner sharing with $\mathrm{PO}_{4}$ tetrahedra to form sheets parallel to $\{010\}$. Three of the four $\mathrm{PO}_{4}$ vertices link to $\mathrm{ZnO}_{4}$ 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. ( $43^{\circ} 45.038^{\prime} \mathrm{N} 71^{\circ} 53.378^{\prime}$ 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-

[^0]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 phosphatecarbonate 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.

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 $\mathrm{Fe}^{2+}$ and $\mathrm{Fe}^{3+}$ stability, as indicated by the presence of minerals containing $\mathrm{Fe}^{2+}$, minerals containing $\mathrm{Fe}^{3+}$, and minerals containing both $\mathrm{Fe}^{2+}$ and $\mathrm{Fe}^{3+}$. 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 $31 / 2$, 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 $2.961 \mathrm{~g} / \mathrm{cm}^{3}$. 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 $2 V$, measured directly by conoscopic observation, is $28(1)^{\circ}$. The calculated $2 V$ is $35^{\circ}$. 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 $\mathrm{kV}, 10 \mathrm{nA}$, and $2-3 \mu \mathrm{~m}$ 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 $\mathrm{H}_{2} \mathrm{O}$ 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 $\left(\mathrm{Mn}_{0.99}^{2+}\right.$ $\left.\mathrm{Ca}_{0.02}\right)_{11.01}\left(\mathrm{Zn}_{1.82} \mathrm{Fe}_{0.12}^{3+} \mathrm{Mg}_{0.07}\right)_{\Sigma 2.01}\left(\mathrm{P}_{1.00} \mathrm{O}_{4}\right)_{2}\left(\mathrm{H}_{1.96} \mathrm{O}\right)_{4}$. The simplified formula is $\mathrm{MnZn}_{2}\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}$, which requires $\mathrm{MnO} 15.84, \mathrm{ZnO}$ $36.35, \mathrm{P}_{2} \mathrm{O}_{5} 31.71, \mathrm{H}_{2} \mathrm{O} 16.10$, total $100.00 \mathrm{wt} \%$.

The Gladstone-Dale compatibility index $1-\left(K_{\mathrm{P}} / K_{\mathrm{C}}\right)$ 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 $\mathrm{Mo} K \alpha$ 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), $c=5.047(2) \AA$, and $V=991.4(7) \AA^{3}$.

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

TABLE 1. Analytical results for nizamoffite (average of 10 analyses)

| Constituent | $w t \%$ | Range | S.D. | Standard |
| :--- | ---: | :---: | :---: | :---: |
| CaO | 0.20 | $0.18-0.23$ | 0.02 | Fluorapatite $(K \alpha)$ |
| 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 $(K \alpha)$ |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 0.10 | $0.07-0.12$ | 0.02 | Amblygonite $(K \alpha)$ |
| $\mathrm{Fe}_{2} \mathrm{O}_{3}$ | 2.18 | $1.90-2.33$ | 0.15 | Triphylite $(K \alpha)$ |
| $\mathrm{P}_{2} \mathrm{O}_{5}$ | 32.05 | $31.88-32.30$ | 0.13 | Triphylite $(K \alpha)$ |
| $\mathrm{H}_{2} \mathrm{O}^{*}$ | 15.95 |  |  |  |
| Total |  |  |  | 100.23 |
| Calculated from the structure. |  |  |  |  |


| $I_{\text {obs }}$ | $d_{\text {obs }}$ | $d_{\text {calc }}$ | $I_{\text {calc }}$ | hkl | $I_{\text {obs }}$ | $d_{\text {obs }}$ | $d_{\text {calc }}$ | $I_{\text {calc }}$ | $h k l$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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) | 1.7436 | 4 | 620 |
| 21 | 4.88(5) | 4.8788 | 19 | 011 |  |  | 1.7340 | 2 | 551 |
| 37 |  | $\left\{\begin{array}{l} 4.6195 \\ 4.6145 \end{array}\right.$ | 38 | 040 | 12 | 1.704(9) | 1.7055 | 2 | 082 |
| 37 | 4.62(3) |  | 4 | 220 |  |  | 1.7045 | 6 | 442 |
| 24 | 4.43(4) | 4.4358 | 21 | 111 | 11 | $1.677(11)\{$ | 1.6841 | 6 | 182 |
|  |  | 4.0958 | 4 | 121 |  |  | 1.6769 | 3 | 391 |
| 19 | 4.05(4) | 4.0289 | 19 | 230 |  |  | 1.6654 | 2 | 103 |
| 14 | 3.91(4) | 3.9090 | 15 | 031 | 13 | 1.647(7) | 1.6502 | 3 | $2 \cdot 10 \cdot 1$ |
| 7 | 3.67(6) | $\left\{\begin{array}{l}3.6698\end{array}\right.$ | 3 | 131 |  |  | 1.6495 | 3 | 481 |
|  |  | 3.6679 | 4 | 201 |  |  | 1.6484 | 3 | 621 |
| 52 | 3.424(13) | $\{3.4898$ | 23 | 240 | 8 | 1.611(9) | 1.6390 | 2 | 123 |
|  |  | $\{3.4091$ | 40 | 221 |  |  | 1.6263 | 3 | 033 |
| 5 | 3.15(5) | 3.1514 | 6 | 231 |  |  | 1.6047 | 5 | 522 |
| 5 | 3.01(5) | $\{3.0363$ | 3 | 250 | 18 | 1.576(5) | 1.5749 | 12 | 641 |
|  |  | \{ 2.9840 | 6 | 051 | 17 |  | 1.5398 | 8 | $0 \cdot 12 \cdot 0$ |
| 100 | 2.873(8) | 2.8725 | 100 | 241 | 17 | 1.538(6) | 1.5382 | 9 | 660 |
|  |  | 2.6661 | 4 | 260 | 23 | 1.517(5) | 1.5182 | 15 | 243 |
| 36 | 2.644(9) | $\{2.6633$ | 19 | 400 | 7 | 1.490(12) | 1.4920 | 4 | $0 \cdot 10 \cdot 2$ |
|  |  | \{ 2.6284 | 22 | 331 |  |  | 1.4716 | 3 | 661 |
| 33 | 2.540(8) | ¢ 2.5590 | 14 | 420 | 8 | 1.465(11) | 1.4649 | 2 | 163 |
|  |  | 2.5538 | 5 | 161 |  |  | 1.4541 | 4 | 4-10-1 |
|  |  | ( 2.5292 | 17 | 002 |  |  | 1.4465 | 2 | 343 |
| 17 | 2.440(11) | 2.4394 | 12 | 022 | 13 | 1.444(7) | 1.4403 | 2 | 562 |
| 10 | 2.357(16) | 2.3585 | 9 | 261 |  |  | 1.4363 | 5 | 482 |
|  |  | 2.3097 | 5 | 080 |  |  | 1.4250 | 4 | 263 |
| 22 | 2.286(8) | ¢ 2.2857 | 5 | 171 | 14 | 1.423(6) | 1.4204 | 2 | 413 |
|  |  | 2.2851 | 4 | 132 |  |  | 1.4198 | 2 | $2 \cdot 12 \cdot 1$ |
|  |  | ( 2.2835 | 6 | 421 | 4 | 1.382(13) | 1.3862 | 3 | 642 |
| 8 | 2.215(19) | [ 2.2184 | 2 | 042 | 10 | 1361 (6) | 1.3653 | 5 | 363 |
|  |  | 2.2179 | 4 | 222 |  | . 361 (6) | 1.3561 | 4 | 681 |
|  |  | ( 2.2010 | 2 | 431 | 5 | 1.332(13) | 1.3330 | 3 | $4 \cdot 12 \cdot 0$ |
| 9 | $2.170(17)$ | 2.1718 | 7 | 142 |  |  | 1.3194 | 4 | 283 |
| 12 | $2.116(11)$ | $\left\{\begin{array}{l}2.1191\end{array}\right.$ | 3 | 280 | 8 | 1.316(11) | 1.3152 | 2 | $0 \cdot 12 \cdot 2$ |
|  |  | $\{2.1137$ | 8 | 361 |  |  | 1.3142 | 2 | 662 |
| 18 | 2.013(7) | 2.0145 | 9 | 460 | 4 | 1.301(16) | 1.3017 | 2 | $4 \cdot 10 \cdot 2$ |
|  |  | $\{2.0107$ | 8 | 322 | 7 | 1.277(6) | 1.2754 | 4 | 821 |
| 36 | 1.953(5) | 1.9545 | 30 | 281 | 10 | 1.241(4) | $1.2443$ | 4 | 124 |
|  | 1834(6) | 1.8349 | 5 | 262 |  |  | 1.2419 | 4 | $2 \cdot 14 \cdot 1$ |
| 22 | 1.834 (6) | $\{1.8340$ | 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 $(\mathrm{Mn})$ and large tetrahedral $(\mathrm{Zn})$ 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 $\mathrm{Mn}^{2+} \mathrm{Zn}_{2}\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}$.

The positions of H atoms in the three $\mathrm{H}_{2} \mathrm{O}$ groups, OW1, OW2, and OW3, were located in the difference-Fourier maps and were refined using soft $\mathrm{O}-\mathrm{H}$ distance constraints of 0.82(5) $\AA$ and no $\mathrm{H}-\mathrm{H}$ distance constraints. The isotropic displacement parameters for the H sites were fixed at $0.05 \AA^{2}$ and, because more than one configuration was indicated for two of the $\mathrm{H}_{2} \mathrm{O}$ groups (OW2 and OW3), the occupancies of the H sites were refined. One H site $(\mathrm{H} 1)$ on a general position is associated with the OW1 site on a mirror plane. This site refined to nearly full oc-
cupancy. 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 $\mathrm{H}_{2} \mathrm{O}$ group. The third $\mathrm{H}_{2} \mathrm{O}$ 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 $\mathrm{H} 3 \mathrm{~b}, \mathrm{H} 3 \mathrm{c}$, and H 3 d site occupancies refined roughly to $1 / 2,1 / 4$, and $1 / 4$, respectively. The OW3 $\mathrm{H}_{2} \mathrm{O}$ group, therefore, has three different configurations. In the final refinement, the occupancies of the H sites were fixed at full, $1 / 2$, and $1 / 4$ 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 ${ }^{1}$.)

## 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 $\mathrm{ZnO}_{4}$ tetrahedra along [001]. The chains are connected by corner sharing with $\mathrm{PO}_{4}$ tetrahedra to form sheets parallel to $\{010\}$ (Fig. 2). Three of the four $\mathrm{PO}_{4}$ vertices link to $\mathrm{ZnO}_{4}$ tetrahedra in the sheet, while

[^1]Table 3. Data collection and structure refinement details for nizamoffite

| Diffractometer | Rigaku R-Axis Rapid II |
| :---: | :---: |
| X-ray radiation/power | MoK $\alpha(\lambda=0.71075 \AA$ ) |
| Temperature | 298(2) K |
| Structural formula* | $\left(\mathrm{Mn}_{0.819}^{2+} \mathrm{Fe}_{0.080}^{3+} \mathrm{Mg}_{0.063} \mathrm{Al}_{0.008} \mathrm{Ca}_{0.004}\right)_{\Sigma 0.974}$ $\left(\mathrm{Zn}_{1.796} \mathrm{Mn}_{0.154} \mathrm{Fe}_{0.033}^{3+}\right)_{\Sigma 1.983}\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}$ |
| Space group | Pnma |
| Unit-cell dimensions | $\begin{gathered} a=10.6530(4) \AA \\ b=18.4781(13) \AA \\ c=5.05845(15) \AA \end{gathered}$ |
| V | 995.74(8) $\AA^{3}$ |
| $Z$ | 4 |
| Density (for above formula) | $2.940 \mathrm{~g} / \mathrm{cm}^{3}$ |
| Absorption coefficient | $6.058 \mathrm{~mm}^{-1}$ |
| F(000) | 863.8 |
| Crystal size | $110 \times 45 \times 25 \mu \mathrm{~m}$ |
| $\theta$ range | 3.83 to $27.47^{\circ}$ |
| Index ranges | $-13 \leq h \leq 13,-23 \leq k \leq 23,-4 \leq I \leq 6$ |
| Reflections collected/unique | $5260 / 1160\left[R_{\text {int }}=0.023\right]$ |
| Reflections with $F_{0}>4 \sigma F$ | 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 $F^{2}$ |
| Parameters refined | 102 |
| GoF | 1.072 |
| Final $R$ indices [ $F_{0}>4 \sigma(F)$ ] | $R_{1}=0.017, \mathrm{w}_{2}=0.037$ |
| $R$ indices (all data) | $R_{1}=0.022, \mathrm{w} R_{2}=0.038$ |
| Largest diff. peak/hole | +0.32/-0.35 e $\AA^{-3}$ |

Notes: $R_{\text {int }}=\Sigma \mid F_{o}^{2}-F_{o}^{2}($ mean $)\left|/ \Sigma\left[F_{0}^{2}\right] . G o F=S=\left\{\Sigma\left[w\left(F_{o}^{2}-F_{c}^{2}\right)^{2}\right] /(n-p)\right\}^{1 / 2} \cdot R_{1}=\Sigma\right|\left|F_{o}\right|-$ $\left|F_{\mathrm{c}}\right||\Sigma| F_{\mathrm{o}} \mid \cdot w R_{2}=\left\{\Sigma\left[w\left(F_{\mathrm{o}}^{2}-F_{\mathrm{c}}^{2}\right)^{2}\right] / \Sigma\left[w\left(F_{\mathrm{o}}^{2}\right)^{2}\right]\right\}^{1 / 2} . w=1 /\left[\sigma^{2}\left(F_{\mathrm{o}}^{2}\right)+(a P)^{2}+b P\right]$ where $a$ is $0.0177, b$ is 0.4086 , and $P$ is $\left[2 F_{c}^{2}+\operatorname{Max}\left(F_{0}^{2}, 0\right)\right] / 3$.
${ }^{*}$ Site occupancies calculated using the program OccQP (Wright et al. 2001). nizamoffit

X-ray radiation/power
Temperature
Structural formula*
Space group
Unit-cell dimensions
$Z$
Density (for above formula)
F(000)
Crystal size
$\theta$ range
Index ranges
s collected/unique
Reflections with ${ }_{\circ}>46$ F
Max. and min. transmission
Refinement method
Parameters refined
Final $R$ indices $\left[F_{\circ}>4 \sigma(F)\right]$
$R$ indices (all data)
Largest diff. peak/hole

Rigaku R-Axis Rapid II
298(2) K
$\left(\mathrm{Mn}_{0.819}^{2+} \mathrm{Fe}_{0.080}^{3+} \mathrm{Mg}_{0.063} \mathrm{Al}_{0.008} \mathrm{Ca}_{0.004}\right)_{\Sigma 0.974}$ $\left(\mathrm{Zn}_{1.796} \mathrm{Mn}_{0.154} \mathrm{Fe}_{0.033}^{3+}\right)_{\Sigma 1.983}\left(\mathrm{PO}_{4}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}$ Pnma
$a=10.6530(4) \AA$
$b=18.4781(13) \AA$
$=5.05845(15) \AA$
4
$2.940 \mathrm{~g} / \mathrm{cm}^{3}$
$.058 \mathrm{~mm}^{-1}$
$110 \times 45 \times 25 \mu \mathrm{~m}$
3.83 to $27.47^{\circ}$
$-13 \leq h \leq 13,-23 \leq k \leq 23,-4 \leq I \leq 6$
1014
8.8\%
0.863 and 0.556

Full-matrix least-squares on $F^{2}$

## 102

$R_{1}=0.017, w R_{2}=0.037$
$R_{1}=0.022, w R_{2}=0.038$
$+0.32 /-0.35 \mathrm{e}^{-3} \AA^{-3}$

TABLE 4. Fractional coordinates and atom displacement parameters $\left(\AA^{2}\right)$ for nizamoffite

|  | x/a | $y / b$ | z/c | $U_{\text {eq }}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 |
| Z ${ }^{*}$ | $0.143185(19)$ | 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) |
| P | $0.39727(4)$ | 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 |  |  |  |  |  |  |
| O4 | $0.35988(13)$ | 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) |
| O6 | 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) |
| O7 | 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 occupancies: $\mathrm{Mn}: \mathrm{Mn}_{0.819} \mathrm{Fe}_{0.080} \mathrm{Mg}_{0.063} \mathrm{Al}_{0.008} \mathrm{Ca}_{0.004} ; \mathrm{Zn}^{2} \mathrm{Zn}_{0.898} \mathrm{Mn}_{0.077} \mathrm{Fe}_{0.017} ; \mathrm{H} 2 \mathrm{~b}: 0.5 ; \mathrm{H} 3 \mathrm{~b}: 0.5 ; \mathrm{H} 3 \mathrm{c}: 0.25 ; \mathrm{H} 3 \mathrm{~d}: 0.25$. All other sites assigned full occupancy.
Table 5. Selected bond distances ( $\AA$ ) in nizamoffite

| Mn-04 ( $\times 2$ ) | 2.1191(13) | Zn-O5 | 1.9016(13) | P-O4 | 1.5155(14) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Mn-OW2 | 2.1543 (23) | Zn-06 | 1.9196(13) | P-O5 | 1.5179(15) |  |  |
| Mn-OW1 | $2.1552(20)$ | Zn -07 | 1.9896(12) | P-O6 | 1.5376(13) |  |  |
| Mn-OW3( $\times 2$ ) | 2.2263(16) | Zn-07 | 2.0004(13) | P-07 | 1.5681(13) |  |  |
| <Mn-O> | 2.1762 | <Zn-O> | 1.9528 | <P-O> | 1.5348 |  |  |
| Hydrogen bonds ( $\mathrm{D}=$ donor, $\mathrm{A}=$ acceptor) |  |  |  |  |  |  |  |
| D-H | d(D-H) | d( $\mathrm{H} \cdots \mathrm{A}$ ) | <DHA | $\mathrm{d}(\mathrm{D} \cdots \mathrm{A})$ | A | <HDH | H-D-H |
| OW1-H1 ( $\times 2$ ) | 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) | 04 |  |  |
| OW2-H2b ( $\times 2$ ) | 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 | O4 | O5 | O6 | O7 | $\Sigma$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 |
| P |  |  |  | 1.32 | 1.31 | 1.24 | 1.14 | 5.01 |
| H1 | $0.82 \times 2 \downarrow$ |  |  | 0.18 |  |  |  | 1.00 |
| H2a |  | 0.91 |  | 0.09 |  |  |  | 1.00 |
| H2b |  | 0.86 | 0.14 |  |  | 0.20 |  | 1.00 |
| H3a |  |  | 0.80 |  |  | 1.00 |  |  |
| H3b |  |  | 0.45 |  | 0.05 |  |  | 0.50 |
| H3c |  |  | $0.23,0.02$ |  |  |  |  | 0.25 |
| H3d |  | 0.03 | 0.22 |  |  |  |  | 0.25 |
| $\Sigma$ | 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 $\mathrm{ZnO}_{4}$ and $\mathrm{PO}_{4}$ tetrahedra in the structure of nizamoffite viewed down $\mathbf{b}$. 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 $\mathrm{Mn}^{2+}, \mathrm{Ni}^{2+}$, 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 $\mathrm{Zn}_{3}\left(\mathrm{PO}_{4}\right)_{2} \cdot 4\left(\mathrm{H}_{2} \mathrm{O}\right)$, 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 $\left(20^{\circ} \mathrm{C}\right)$, but the structures of the two polymorphs are apparently identical except for the orientation of the H atoms of one of the $\mathrm{H}_{2} \mathrm{O}$ 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 $\mathrm{H}_{2} \mathrm{O}$ groups are essentially the same in the structures of $\alpha$-hopeite and $\beta$-hopeite, while they differ for the OW1 $\mathrm{H}_{2} \mathrm{O}$ 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 H 3 c and H 3 d 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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[^0]:    * E-mail: akampf@nhm.org

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