

The Crystal Structure of NaMnPO₄

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Received May 6, 1985; in revised form July 24, 1985

NaMnPO₄ crystallizes in the space group *Pmnb* with $a = 6.9041(1)$, $b = 9.0882(1)$, and $c = 5.1134(1)$ Å. For $Z = 4$ the calculated density is 3.580 g/cm³ ($V = 320.84$ Å³). Refinement ($R = 0.044$, $R_w = 0.045$) was carried out on hydrothermally grown crystals. NaMnPO₄ is isostructural to Na(Fe,Zn)PO₄ and the mineral maricite. © 1986 Academic Press, Inc.

Introduction

The mineral maricite [Na_{1.00}(Fe_{0.90}Mn_{0.06}Mg_{0.03}Ca_{0.01})PO₄] and the synthetic compound Na(Fe,Zn)PO₄ crystallize in the same olivine-related structure. Both have been investigated using single-crystal X-ray diffraction (1, 2). We have grown single crystals of NaMnPO₄ which is isostructural to these compounds. The mineral natrophilite (3) [Na(Mn_{0.93}Fe_{0.07})PO₄], a polymorph of NaMnPO₄, is isostructural to triphylite (4). Paques-Ledent (5) has synthesized NaMnPO₄ as a brown powder ($a = 5.30$, $b = 8.90$, $c = 6.78$ Å) for which she proposes the Na₂SO₄-III structure on the basis of spectroscopic data.

Experimental

Crystals of NaMnPO₄ were grown hydrothermally from a mixture of 90 mg Mn₃(PO₄)₂ · 7H₂O and 40 mg Na₂HPO₄ · 7H₂O with 0.3 ml 0.1 M H₃PO₄ sealed in a 5-cm gold tube held at 55 kpsi and 420°C for 6

days. The crystals were transparent with a pale pink tint. A crystal ground to an approximately spherical shape (diameter 0.013 cm) was selected for data collection. Systematic extinctions in precession photographs indicated space groups *Pmnb* or *P2₁nb*.

Lattice parameters were determined in a least-squares refinement using 21 reflections within the angular range $37^\circ < 2\theta < 56^\circ$, each automatically centered on a Picker FACS-I four-circle diffractometer using MoK α radiation ($\lambda = 0.70930$ Å). At 25°C the lattice parameters were found to be $a = 6.9041(1)$, $b = 9.0882(1)$, and $c = 5.1134(1)$ Å, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated volume is 320.84(1) Å³, giving a calculated density, with $Z = 4$, of 3.580 g cm⁻³.

Diffraction intensities were measured using Zr-filtered MoK α radiation at a take-off angle of 0.5° with the diffractometer operating in the ω -scan mode. Ten-second background counts were taken at both ends of a 1.4° scan (1° min⁻¹) corrected for dispersion. Of the 590 independent data investi-

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TABLE I
FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL PARAMETERS FOR NaMnPO_4^a

Atom	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{eq}^b
Mn	0	0	0	1.08(4)	1.03(4)	1.03(4)	-0.36(4)	0.38(5)	-0.45(4)	0.92(2)
P	$\frac{1}{2}$	8228(2)	5298(4)	0.85(7)	0.48(6)	0.41(6)	0	0	0.02(6)	0.55(3)
Na	$\frac{1}{2}$	8515(3)	5257(7)	1.30(12)	1.20(11)	1.09(13)	0	0	0.17(11)	1.19(7)
O(1)	$\frac{1}{2}$	8787(7)	2436(11)	1.35(22)	0.76(18)	0.76(18)	0	0	0.23(15)	0.89(11)
O(2)	4313(6)	8776(4)	6697(7)	1.02(14)	1.23(13)	0.88(13)	-0.26(14)	-0.17(12)	-0.29(11)	0.96(3)
O(3)	$\frac{1}{2}$	6509(5)	5414(10)	0.93(20)	0.54(17)	1.07(20)	0	0	0.07(16)	0.81(11)

^a Numbers in parentheses are estimated standard deviations in the last significant figures. The B 's are defined by the general temperature factor $\exp[-\frac{1}{2}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

^b Isotropic thermal parameter calculated from the anisotropic B 's.

gated in the angular range $2\theta < 60^\circ$, 354 were considered observable according to the criterion $|F_o| > 3.0\sigma_F$, where σ_F is defined as $0.2|F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$; the total scan count is C , k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored; the maximum variation in intensity observed was never greater than $\pm 5\%$ over the data collection period.

Intensity data were corrected for Lorentz and polarization effects, and spherical absorption corrections ($\mu = 47.8 \text{ cm}^{-1}$, $\text{MoK}\alpha$) were made. The maximum relative absorption correction was less than 1% of $|F_o|$.

Because of the suspected relationship to Na(Fe,Zn)PO_4 , the formula NaMnPO_4 ($Z = 4$) and space group $Pnma$ were used as input to the direct methods crystallographic program MULTAN (6). Isotropic refinement of the positions produced by MULTAN showed that the compounds are isostructural. The space group was transformed to $Pmnb$ conforming to the Donnay convention. A full-matrix anisotropic least-squares refinement (7) in $Pmnb$ using transformed positions from $Pnma$, a $1/\sigma^2$ weighting scheme, zero-valent scattering factors (8) for Na, Mn, P, and O, and corrections for secondary extinction and anomalous dispersion yielded a residual R

TABLE II
 NaMnPO_4 : BOND DISTANCES, POLYHEDRAL EDGE LENGTHS, AND BOND ANGLES FOR THE CATION POLYHEDRA

	Distance (Å)	Angle (°)	Edge (Å)
Mn octahedron			
Mn-O(2)	2× 2.077(4)		
Mn-O(3)	2× 2.215(3)		
Mn-O(1)	2× 2.397(4)		
O(2)-Mn-O(3)		2× 85.7(2)	2.919(5)
O(2)-Mn-O(1)		2× 94.3(2)	3.149(6)
O(2)-Mn-O(1)		2× 89.3(2)	3.153(6)
O(2)-Mn-O(1)		2× 90.7(2)	3.191(6)
O(3)-Mn-O(1)		2× 76.9(2)	2.872(8)
O(3)-Mn-O(1)		2× 103.1(2)	3.613(2)
Na octahedron			
Na-O(2)	2× 2.332(4)		
Na-O(1)	2.370(7)		
Na-O(3)	2.476(6)		
Na-O(3)	2.638(6)		
Na-O(1)	2.721(7)		
O(2)-Na-O(1)		2× 86.61(1)	3.226(6)
O(2)-Na-O(3)		2× 108.5(1)	3.902(6)
O(2)-Na-O(3)		2× 71.6(1)	2.919(5)
O(2)-Na-O(1)		2× 76.8(1)	3.153(6)
O(1)-Na-O(3)		117.5(2)	4.144(8)
O(1)-Na-O(3)		61.5(2)	2.570(8)
O(3)-Na-O(1)		116.2(2)	4.414(8)
O(3)-Na-O(1)		64.8(2)	2.872(8)
P tetrahedron			
P-O(2)	2× 1.525(4)		
P-O(1)	1.549(6)		
P-O(3)	1.564(5)		
O(2)-P-O(2)		110.3(3)	2.504(8)
O(2)-P-O(1)		2× 109.6(2)	2.513(6)
O(2)-P-O(3)		2× 108.0(2)	2.499(6)
O(1)-P-O(3)		111.3(3)	2.570(8)

TABLE III
NaMnPO₄: OXYGEN ATOM ENVIRONMENTS

	Distance (Å)	Angle (°)	Edge (Å)
O(1) polyhedron			
O(1)–P	1.549(6)		
O(1)–Na	2.370(7)		
O(1)–Mn	2× 2.397(4)		
O(1)–Na'	2.721(7)		
P–O(1)–Na		98.9(3)	3.026(4)
P–O(1)–Mn	2×	129.9(1)	3.593(2)
P–O(1)–Na'		83.4(3)	2.973(4)
Na–O(1)–Mn	2×	99.3(3)	3.633(3)
Mn–O(1)–Mn		92.1(2)	3.4520(1)
Mn–O(1)–Na'	2×	79.1(2)	3.269(3)
O(2) polyhedron			
O(2)–P	1.564(6)		
O(2)–Mn	2.077(4)		
O(2)–Na	2.332(4)		
P–O(2)–Mn		138.0(2)	3.369(2)
P–O(2)–Na		126.4(2)	3.4619(3)
Mn–O(2)–Na		95.5(2)	3.269(3)
O(3) polyhedron			
O(3)–P	1.549(6)		
O(3)–Mn	2× 2.215(3)		
O(3)–Na	2.476(6)		
O(3)–Na'	2.638(6)		
P–O(3)–Mn	2×	127.0(1)	3.407(2)
P–O(3)–Na'		92.7(3)	2.990(4)
P–O(3)–Na		88.3(2)	3.026(4)
Mn–O(3)–Mn		102.4(2)	3.4520(1)
Mn–O(3)–Na'		95.2(2)	3.468(3)
Mn–O(3)–Na	2×	84.2(2)	3.269(3)

= 0.044 and a weighted $R_2 = 0.045$ (data: parameter ratio of 8.6 for 41 independently varied parameters).¹ The maximum extinction correction (9) was 14% of $|F_o|$ for the 031 reflection.

Results and Discussion

Table I presents the final positional pa-

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rameters and anisotropic temperature factors for NaMnPO₄. The manganese and sodium ions are six-coordinated. Bond distances and polyhedral dimensions are given in Table II which includes the relevant parameters for the phosphate tetrahedra. Table III details the oxygen environments.

The structure of NaMnPO₄ consists of chains of edge-sharing Mn-containing octahedra parallel to the *a*-direction. Each pair of adjacent Mn octahedra shares one face each with a single Na-containing octahedron. Neighboring Mn-containing chains are linked by corner-sharing phosphate tetrahedra and by corner sharing between the Mn octahedra of one chain and the Na octahedra of adjacent chains. A portion of the Na–Mn octahedral chain is shown in Fig. 1.

Compared to maricite and Na(Fe,Zn)PO₄, all corresponding lattice parameters in NaMnPO₄ are increased (Table IV) because of the larger size of Mn²⁺ ($r = 0.83$ Å) compared to Fe²⁺ ($r = 0.78$ Å) (10). The average divalent metal–oxygen distance is 2.23 Å in NaMnPO₄ compared to 2.19 Å in Na(Fe, Zn)PO₄. In the Mn octahedron, only the Mn–O(3) distance is the same as the corresponding distance in Na(Fe,Zn)PO₄; the Mn–O(2) distance increases by 4.4% with a large component in the *c*-direction. The Mn–O(1) distance is increased by 3.7%.

The Na-containing octahedron, elongated in the *c*- and *b*-directions, is highly

TABLE IV
LATTICE PARAMETERS (Å) OF ISOSTRUCTURAL COMPOUNDS

	Parameter (transformed to <i>Pmnb</i>)			% Increase in parameter over Na(Fe,Zn)PO ₄		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
Na(Fe,Zn)PO ₄	6.854	8.972	5.031	—	—	—
Maricite	6.861	8.987	5.045	0.10	0.17	0.28
NaMn(PO) ₄	6.9041	9.0882	5.1134	0.73	1.30	1.64

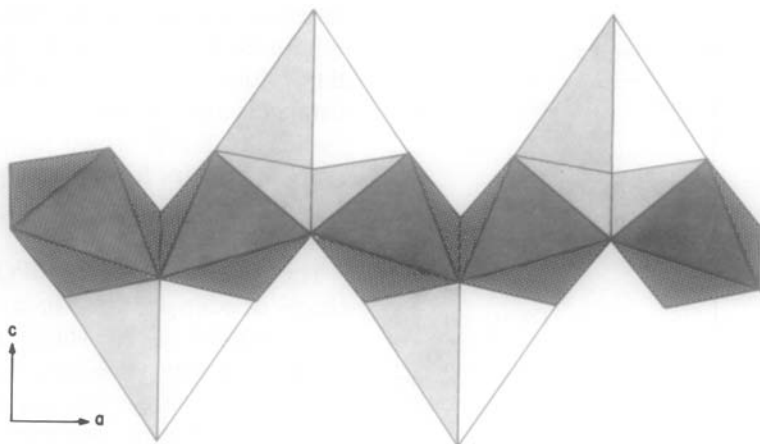


FIG. 1. The chain of Na and Mn octahedra projected on (010). The edge-sharing Mn octahedra are shaded dark grey.

distorted (Fig. 2) with the sodium ion 0.94 Å above the averaged central "plane" of the octahedron. The longest Na–O distance, 2.721 Å, is to O(1') at the rear of the figure.

In natrophilite $[\text{Na}(\text{Mn}_{0.93}\text{Fe}_{0.07})\text{PO}_4]$ the metal octahedra share only edges, not faces. Relative to the synthetic NaMnPO_4 reported here, the Na and Mn ions have "exchanged places"; that is, Na ions occupy the edge-sharing chains of octahedra parallel to the *a*-direction, and Mn ions oc-

cupy the "branch" octahedra, which now share edges with the Mn chains (3). Therefore, these compounds are not isostructural. Natrophilite is isostructural to triphylite (4), LiFePO_4 , but unusual in that the Na^+ ion is larger than Mn^{2+} . In triphylite and all other isostructural $M^+M^{2+}\text{PO}_4$ compounds, M^+ is smaller than M^{2+} (3). In natrophilite, the cation of higher charge, Mn^{2+} , occupies the branch octahedra, the site with fewer shared edges (3). In synthetic NaMnPO_4 the chain (Mn^{2+}) octahedra have two shared faces, while the branch (Na^+) octahedra have not only two shared faces but also one edge which is shared with a phosphate tetrahedron. This cation arrangement should minimize cation–cation repulsion, according to Pauling's rules.

On the basis of the anomalous cation distribution, Moore (3) has postulated that the mineral natrophilite is a product of metasomatic exchange. It would be expected, however, that a mineral isostructural to synthetic NaMnPO_4 should exist.

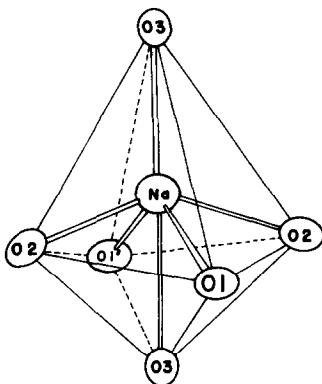


FIG. 2. The Na octahedron projected on (010) and then rotated 20° about the *c*-axis for clarity. O(1), Na, and O(3) lie in a mirror plane.

Acknowledgment

Computations were carried out at the University of Connecticut Computer Center.

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