

Single Crystal X-Ray Structural Investigation of Alluaudite Related Monophosphate $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$

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Abstract

The compound $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$ has been successfully isolated with the alluaudite structural type. Accurate single crystal x-ray diffraction has allowed solving the structure with reliability factors of R_1 and R_w equal to 0.0322 and 0.0790 respectively. It was found that the symmetry is monoclinic with a space group of $C2/c$ and lattice parameters: $a = 12.180(2) \text{ \AA}$, $b = 12.660(2) \text{ \AA}$, $c = 6.500(2) \text{ \AA}$, $\beta = 114.528(3)^\circ$, unit cell volume = $911.8(3) \text{ \AA}^3$, $Z = 8$ and $d_{\text{cal}} = 3.618 \text{ g.cm}^{-3}$. Three-dimensional network is formed by the $[\text{MnO}_6]$ octahedra linked in pairs to form Mn-based octahedral dimers: $([\text{Mn}_2\text{O}_{10}])$. Each dimer shares six vertices with six tetrahedra $[\text{P}(2)\text{O}_4]$ to form sheets within the plane (100). The latter are connected by tetrahedra $[\text{P}(1)\text{O}_4]$ delimiting cages and tunnels which house either Fe^{3+} or Na^+ cations. Each $[\text{FeO}_6]$ octahedron is linked to two $[\text{Mn}_2\text{O}_{10}]$ dimers belonging to two adjacent sheets to form mixed Fe-Mn chains of the type: $-\text{Fe}^{3+} - \text{Mn}^{2+} - \text{Mn}^{2+} - \text{Fe}^{3+} - \text{Mn}^{2+} - \text{Mn}^{2+} - \text{Fe}^{3+} - \dots$, running along the direction [101].

Introduction

As reported by Fischer fillowite related alluaudite is a naturally occurring mineral which has been investigated later by Moore(1-2). The fillowite group concerns more specifically five minerals with sodium based mixed cation (Mg, Ca, Mn, Fe) phosphates [3]: i) pure fillowite $\text{Na}_2\text{CaMn}_7(\text{PO}_4)_6$; ii) chladniite $\text{Na}_2\text{CaMg}_7(\text{PO}_4)_6$; iii) galileiite $\text{Na}_2\text{Fe}^{2+}_8(\text{PO}_4)_6$; iv) johnsomervilleite $\text{Na}_2\text{CaFe}^{2+}_7(\text{PO}_4)_6$; v) stornesite-(Y) $(\text{Y,Ca})_2\text{Na}_6(\text{Ca,Na})_8(\text{Mg,Fe})_{43}(\text{PO}_4)_{36}$. These compounds were found to crystallize with a trigonal space group $R\bar{3}$, and large lattice parameters [4, 5]. As reported by Araki and Moore for $\text{Na}_2\text{Ca}(\text{Mn,Fe})^{2+}_7(\text{PO}_4)_6$ [4] the latter are equal to $a = 15.282(2) \text{ \AA}$, and $c = 43.507(3) \text{ \AA}$, with $Z = 18$.

In recent years, this family of minerals has been subject to various crystal-chemical analysis and new compounds have been synthesized. For example Hatert et al. [6-8] have refined the structures from powder x-ray diffraction data of various phases by Reitveld method. It is also worth to mention the structural refinements reported by Daidouch et al. [9, 10] using also powder diffraction patterns: XRD for the compounds $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$ and $\text{NaAgFeMn}_2(\text{PO}_4)_3$ and neutron for $\text{Ag}_2\text{FeMn}_2(\text{PO}_4)_3$, by Daidouh et al. These Authors have found a rather high reliability factors of order of 9, 11 respectively for the pure silver and sodium phase and even a higher value of 15.4 for $\text{NaAgFeMn}_2(\text{PO}_4)_3$.

The title compound and related solid solutions have been more recently investigated for Li-Na batteries applications and some structural refinements were made by the same Authors, using powder Rietveld method [11, 12]. The reliability

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factors are of the same order as reported by Daidouch et al. [9, 10]. To the best of our knowledge no single crystal structural resolution of the sodium iron manganese alluaudite phosphates has been yet performed. The purpose of the present work is to give reliable and accurate structural data from x-ray structural determination on single crystal of $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$.

Experimental

The title compound has been isolated from the melt of a stoichiometric mixture of the starting materials Bi_2O_3 , MnCO_3 , Fe_2O_3 and $\text{NH}_4\text{H}_2\text{PO}_4$, taken in the following molar ratio: 1:2:1:8. The melt was slowly cooled down to room temperature. Pure purple single crystals have been collected from the water washed solid preparation. As the melt is achieved within a porcelain crucible, the latter has served as reservoir of sodium which has not been added within the starting compounds mixture. X-ray crystallography has shown that the XRD patterns of ground crystals can be totally indexed iso-typically with the alluaudite structural type. After evidence of alluaudite-like single crystals in the cooled melt, we have considered worth to resolve the crystal structure in order to get more information about the atomic arrangement within the lattice and check more particularly the originality of the chemical bonds in this newly synthesized material.

Therefore, a high quality single crystal of $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$ with a needle like and dimension

of $(0.02 \times 0.02 \times 0.07) \text{ mm}^3$ was selected under optical microscope before to be mounted on a goniometric head using a glass fiber to fix the crystal. The diffraction intensities were collected at 293K using a Nonius four-circle diffractometer equipped with a Kappa CCD and a molybdenum anode giving x-ray wavelenth $\lambda(\text{K}_{\alpha}(\text{Mo})) = 0.71073 \text{ \AA}$.

X-Ray crystallography and structural analysis

Structure Refinement

Before any further analysis, the diffraction patterns have been corrected for: i) Lorentz factor; ii) polarization; iii) absorption effect [13]. The structure of $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$ was determined by the direct method using the program SIR 97 [14] and refined by the method of least squares using the program SHELX-97 [15]. The refinement of this structure was made from 1053 independent reflections ($I > 2 \sigma(I)$) over 4250 recorded reflections. The reliability factors obtained after refinement of all parameters as well as isotropic (& anisotropic) temperature factors were found to be equal to $R = 3 \%$ and $R_w = 8\%$. Table 1 summarizes the crystallography data and the conditions of diffraction intensities recording. The atomic coordinates and the corresponding isotropic temperature factors are given in Table 2 while Table 3 recapitulates the main interatomic distances and bond angles of $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$ structure.

Table 1
Crystallography data and conditions of XRD diffraction intensities recording on single crystal of $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$.

Chemical Formula:	$\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$	Absorption coefficient :	4.993 mm^{-1}
Molar Mass:	$496,62 \text{ g.mol}^{-1}$	F(000) :	956
Temperature:	293(2) K	$\theta_{\text{min.}} - \theta_{\text{max.}}$:	$5.03 - 27.51(^{\circ})$
Mo anode with $\lambda(\text{K}_{\alpha}(\text{Mo}))$:	0.71073 \AA	Measured space:	<ul style="list-style-type: none"> • $-15 < h < 15$, • $-16 < k < 16$, • $-8 < l < 8, \text{\AA}$
Crystal size:	$0.02 \times 0.02 \times 0.07 \text{ mm}^3$	Number of collected intensities:	4250
Crystalline system :	Monoclinic	Number of collected intensities:	1053
Space Group:	$C2/c$	Final reliability factors [for $I > 2\sigma(I)$]:	<ul style="list-style-type: none"> • $R1 = 0.03$, • $Rw = 0.08$
Lattice Parameters:	<ul style="list-style-type: none"> • $a = 12.180(2) \text{ \AA}$, • $b = 12.660(2) \text{ \AA}$ • $c = 6.500(2) \text{ \AA}$ • $\beta = 114.528(3) (^{\circ})$ • Volume: $911.8(3) \text{ \AA}^3$ • $Z (d_{\text{cal}})$: $8 (3.618 \text{ g.cm}^{-1})$ 		

Table 2
Atomic coordinates and corresponding isotropic temperature factors of Na₂FeMn₂(PO₄)₃

Atome	x	y	z	U(eq)
Fe(1)	5000	2303(1)	2500	11(1)
Mn(1)	2746(1)	3451(1)	3569(1)	15(1)
Na(1)	0	188(3)	2500	46(1)
Na(2)	5000	0	5000	24(1)
P(1)	5000	2195(1)	7500	15(1)
P(2)	2386(1)	1054(1)	1314(2)	17(1)
O(1)	4509(3)	2904(2)	5385(5)	21(1)
O(2)	5944(3)	1453(3)	7281(6)	29(1)
O(3)	2293(3)	1740(2)	3210(5)	21(1)
O(4)	3709(3)	903(3)	1794(6)	28(1)
O(5)	1742(3)	3(3)	1169(5)	28(1)
O(6)	1705(3)	1628(2)	-972(5)	24(1)

Table 3
Main inter-atomic distances (Å) and bond angles (°) of Na₂FeMn₂(PO₄)₃ structure

[Fe(1) - O₆]		[Mn(1)O₆]	
Fe(1)-O(4)	2.286(3)	Mn(1)-O(2)#4	2.002(4)
Fe(1)-O(4)#1	2.286(3)	Mn(1)-O(5)#5	2.040(3)
Fe(1)-O(1)#1	2.320(3)	Mn(1)-O(6)#3	2.060(3)
Fe(1)-O(1)	2.320(3)	Mn(1)-O(1)	2.093(3)
Fe(1)-O(6)#2	2.329(3)	Mn(1)-O(3)#6	2.128(3)
Fe(1)-O(6)#3	2.329(3)	Mn(1)-O(3)	2.222(3)
<Fe(1) - O₆> = 2.312		<Mn(1) - O₆> = 2.091	
[P(1)O₄]		[P(2)O₄]	
P(1)-O(2)#12	1.536(3)	P(2)-O(4)	1.521(3)
P(1)-O(2)	1.536(3)	P(2)-O(5)	1.535(3)
P(1)-O(1)#12	1.540(3)	P(2)-O(6)	1.549(3)
P(1)-O(1)	1.540(3)	P(2)-O(3)	1.549(3)
<P(1) - O₄> = 1.538		<P(2) - O₄> = 1.538	
O(2)#12-P(1)-O(2)	104.7(3)	O(4)-P(2)-O(5)	111.9(2)
O(2)#12-P(1)-O(1)#12	107.56(17)	O(4)-P(2)-O(6)	110.78(19)
O(2)-P(1)-O(1)#12	114.25(17)	O(5)-P(2)-O(6)	107.09(18)
O(2)#12-P(1)-O(1)	114.25(17)	O(4)-P(2)-O(3)	109.14(19)
O(2)-P(1)-O(1)	107.56(17)	O(5)-P(2)-O(3)	109.51(18)
O(1)#12-P(1)-O(1)	108.7(2)	O(6)-P(2)-O(3)	108.29(17)

Symmetry code:

#1 -x+1,y,-z+1/2

#2 x+1/2,-y+1/2,z+1/2

#3 -x+1/2,-y+1/2,-z

#4 x-1/2,-y+1/2,z-1/2

#5 -x+1/2,y+1/2,-z+1/2

#6 -x+1/2,-y+1/2,-z+1

#7 x,-y,z+1/2

#8 -x,-y,-z

#9 -x,y,-z+1/2

#10 -x,-y,-z+1

#11 -x+1,-y,-z+1

#12 -x+1,y,-z+3/2

#13 -x+1/2,y-1/2,-z+1/2

Structure Description and Chemical Bond

Projections of the structure of $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$ along various directions are given in Figs.1-3. Sodium ions occupy large sites X (1) and X (2) while the sites M (1) and M(2) are fully occupied by transition element cations Fe^{3+} and Mn^{2+} respectively. As evidenced from these different views, the lattice of $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$ can be seen as made of sheets (Fig. 2) with the composition $[\text{Mn}_2\text{O}_{10} - \text{P}(2)\text{O}_4]$ linked by $[\text{FeO}_6]$ octahedra and $[\text{P}(1)\text{O}_4]$ tetrahedra in order to build a 3-D network $[\text{Mn}_2\text{O}_{10}]$ octahedral dimmers (Fig. 3). Each dimer is sharing six vertices with six neighbour $[\text{P}(2)\text{O}_4]$ tetrahedra (Fig. 2) to form foils like planes parallel to (100). As shown in Figs. 1 & 3, the connexions by tetrahedra $[\text{P}(1)\text{O}_4]$ allows to delimit cages and tunnels housing Fe^{3+} and Na^+ respectively.

One of the main features of the title structure is also the existence of the cation chains $\cdots\text{Mn}^{2+} - \text{Mn}^{2+} - \text{Fe}^{3+} - \text{Mn}^{2+} - \text{Mn}^{2+} - \text{Fe}^{3+}\cdots$, running along the direction [101]. Such arrangement of corrugated chains results from the fact that each $[\text{FeO}_6]$ octahedron is linked to $[\text{Mn}_2\text{O}_{10}]$ octahedral dimmers belonging to two adjacent sheets.

The P – O bond lengths in the tetrahedra $[\text{P}(1)\text{O}_4]$ take two values 1.536 and 1.540 Å while in $[\text{P}(2)\text{O}_4]$ they spread between 1.521 and 1.549 Å. These values are consistent with those generally given in the literature [6 - 10]. Although, the main P – O distance is the same in the two tetrahedra, it is worth to mention that P – O distance is more distorted within $[\text{P}(2)\text{O}_4]$ than in $[\text{P}(1)\text{O}_4]$, which shows that the mechanical tensions are more stronger within the layers parallel to (100), than between these sheets.

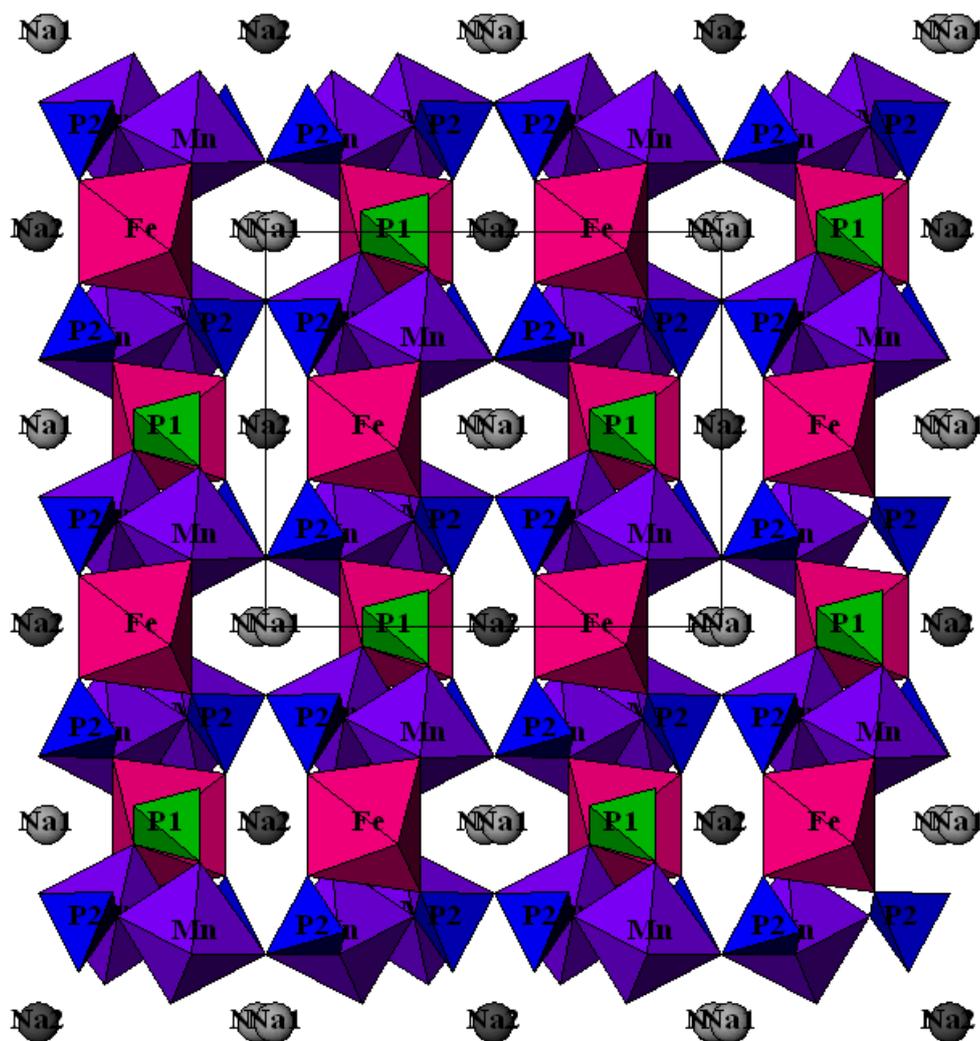


Fig. 1. Projection of $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$ structure along the direction [001].

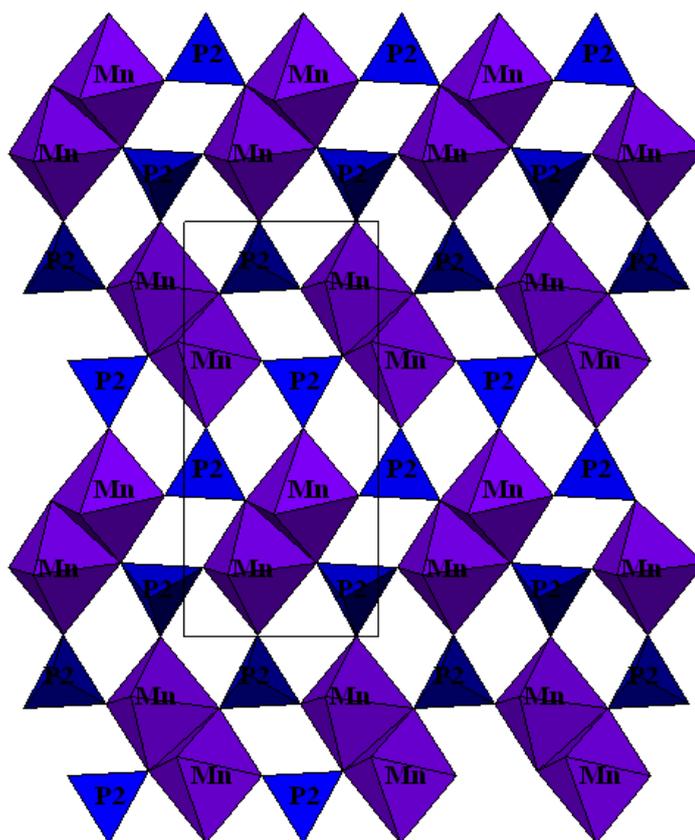


Fig. 2. Projection of the layer $[\text{Mn}_2\text{O}_{10} - \text{P}(2)\text{O}_4]$ along the plane plan (100).

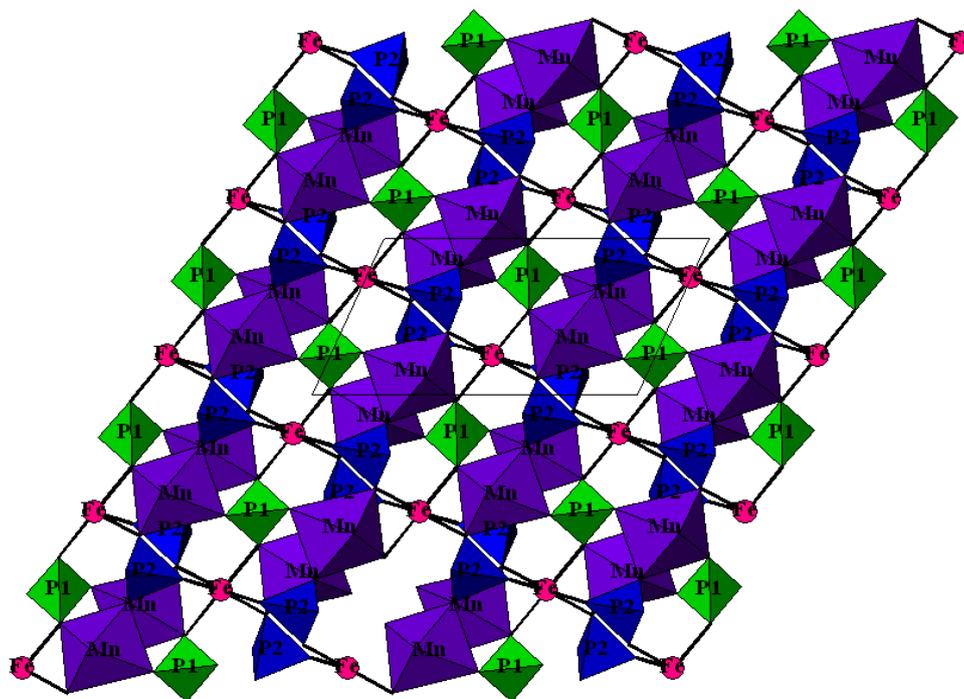


Fig. 3.- Structure of $\text{Na}_2\text{FeMn}_2(\text{PO}_4)_3$ as projected along [010] to show that the sheets of Fig.2 $[\text{Mn}_2\text{O}_{10} - \text{P}(2)\text{O}_4]$ are connected together by $[\text{FeO}_6]$ octahedra and $[\text{P}(1)\text{O}_4]$ tetrahedra. (For more clarity of the figure, Na^+ ions have not been represented).

Regarding the sites M(1) and M(2) fully occupied by Fe(III) and Mn(II) respectively, the Fe³⁺ environment is less distorted (three different Fe – O bond lengths: 2.286, 2.320 and 2.329 Å) than that of Mn²⁺, where all Mn – O bonds are different (Table 3). This is also consistent with higher tensions within the layers than between the layers as Mn – O bonds constitute the layers while Fe³⁺ ions link between the layers.

It also appears that as expected, phosphorus develops a rather strong covalent bond within the oxygen tetrahedral environment in both sites as the mean P – O distance deduced from the present structure study (Table 3) is lower than the sum of ionic radii: $\langle \text{P} - \text{O} \rangle = 1.538 \text{ \AA}$ while $[\text{r}(\text{P}^{5+}) + \text{r}(\text{O}^{2-})] = 1.57 \text{ \AA}$, according to the ionic radii values due to Shannon and Prewitt [16].

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