

Crystallochemical Properties of $\text{NH}_4(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4\cdot\text{H}_2\text{O}$

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The industrial and agricultural uses of orthorhombic metal ammonium phosphates of formula $\text{NH}_4\text{MPO}_4\cdot\text{H}_2\text{O}$ [M = Fe(II), Mn(II), Mg, Co(II), or Cu(II)] justify their detailed study. In this work, the X-ray diffraction patterns and the stability of $\text{NH}_4(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4\cdot\text{H}_2\text{O}$ to oxidation were investigated. In the study of six members of this series ($x = 0, 0.2, 0.4, 0.6, 0.8,$ and 1.0) stability to heating and oxidation increased with increasing Mn content. The unit-cell parameters a , b , and c of 52 products with different values of x and degrees of oxidation could be predicted by x and the Fe(II)/(Fe + Mn) ratio. Accordingly, there was good agreement between measured crystallographic d -spacings and spacings calculated from predicted a , b , and c values. For the Fe end member, the calculated crystalline parameters were $a = 5.6659$, $b = 8.7885$, and $c = 4.8325$.

INTRODUCTION

The synthesis of $\text{NH}_4\text{MPO}_4\cdot\text{H}_2\text{O}$ [M being Mg, Mn(II), Fe(II), Co(II), or Cu(II)] has been known for more than 100 years (Debray, 1861), and the possibility exist to prepare these compounds by a simple continuous process (McCullough et al., 1964). Metal ammonium phosphates have been used as pigments for protective paint finishes on metal and as fire retardants in paints and plastics (Erskine et al., 1944; Vol'fkovich and Remen, 1956). As fertilizers, they can be a source of macro- and micronutrients (P, N, Mg, Fe, Zn, Mn, Cu, and Co) (Bridger et al., 1962). Recently, Campillo et al. (1992) have shown the value of $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$ as a fertilizer to correct iron deficiency (iron chlorosis) in plants grown in calcareous soils. The relatively low solubility of this product makes it a promising slow-release fertilizer.

Many of the chemical and physical properties as well as the synthesis procedures of $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$ have been studied by the authors cited above. Infrared spectra were studied by Corbridge and Lowe (1954). However, minimal X-ray diffraction data exist for this compound. Erskine et al. (1944) reported a diffraction pattern obtained with a Debye-Scherrer camera. Bridger et al. (1962) also reported X-ray diffraction data but, according to the authors, some of the values were difficult to interpret. Tranqui et al. (1968) refined the crystalline structure (orthorhombic system and $Pmn2_1$ space group) and gave values for unit-cell dimensions. The JCPDS Powder Diffraction File does not include, however, the pattern of this product, whereas the patterns for other isomorphous monohydrate ammonium phosphates are given (Mg: 15-762, 20-663, 36-1491; Ca: 20-202; Co: 21-793; Cd: 33-48; Mn: 3-0027, 35-574). This absence can lead to erroneous identification of natural and synthetic phases having the $\text{NH}_4\text{MPO}_4\cdot\text{H}_2\text{O}$ structure when the computerized JCPDS file is used. For example, niahite, $\text{NH}_4(\text{Mn}^{2+}, \text{Mg}, \text{Ca})\text{PO}_4\cdot\text{H}_2\text{O}$, a mineral recognized only a few years ago (Bridge and Robinson, 1983), shows a diffraction pattern (JCPDS, 35-574) very similar to that of $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$. Furthermore, that mineral occurs associated with other natural iron phosphates, such as strengite, $\text{FePO}_4\cdot 2\text{H}_2\text{O}$, and vivianite, $\text{Fe}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$, which can be synthesized in conditions relatively similar to those required for $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$.

The first objective of this study was to characterize the X-ray diffraction patterns of the isomorphous series $\text{NH}_4(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4\cdot\text{H}_2\text{O}$ because a correct identification of these products may be needed in the future (e.g., to identify some Fe-Mn fertilizers or natural minerals). The second objective was to evaluate the effect of Mn on the stability of Fe(II) to oxidation, as a recent work has suggested that the effectiveness of iron phosphates as Fe fertilizers depends on their Fe(II) content (Eynard et al., 1992).

MATERIALS AND METHODS

Six $\text{NH}_4(\text{Fe}, \text{Mn})\text{PO}_4\cdot\text{H}_2\text{O}$ compounds having a Mn/(Fe + Mn) mole fraction (x) of 0, 0.2, 0.4, 0.6, 0.8, and 1 (hereafter referred to as M0, M2, M4, M6, M8, and M10, respectively) were prepared by slow addition of solid $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and/or MnSO_4 to 0.2 M $(\text{NH}_4)_2\text{HPO}_4$, which was continuously stirred, at 373 K. The amount of Fe and Mn added was dependent on the Mn/(Fe + Mn) ratio; for example, to obtain sample M0, 25 g of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ was used. The resulting suspensions were kept in an oven at 373 K for 3 days (this procedure increased the particle size and homogeneity of the precipitate). The solid products were washed with deionized water and dried at 303 K in a circulating air oven.

The oxidation treatment was carried out by placing the dried samples in an air oven at 373 K for different times (0, 10, 20, 30, 60, 150, 300, 4320, and 10 080 min).

Total Fe and Mn were determined by atomic absorption spectrophotometry after the samples were dissolved in 6 M HCl. To determine Fe(II), 100 mg of sample was dissolved in 1 mL of H_2SO_4 and 5 mL of 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$ was added to oxidize the Fe. Excess $\text{K}_2\text{Cr}_2\text{O}_7$ was backtitrated with 0.1 N FeSO_4 , using orthophenanthroline as an indicator.

Instrumentation. Thermograms (ATG) were obtained with a SETARAM TG-DTA92 apparatus. The XRD powder data were obtained with a Siemens D5000 diffractometer, $\lambda(\text{Co K}\alpha) = 1.79026$ radiation, and a graphite monochromator. The powder was mixed with Si as an internal standard. Step-scan recordings at $0.05^\circ 2\theta$ step sizes and 10-s counting times were obtained. To prevent preferred orientation of the crystallites, the sample was thoroughly mixed with ground ($< 5 \mu\text{m}$) glass wool and the mixture was introduced to the holder by pouring through a lateral slit. From the recorded d -spacings, unit-cell parameters were refined by a least-squares procedure.

RESULTS AND DISCUSSION

Suspensions of the compounds showed the opalescent appearance typical of suspensions of particles having flakelike morphology (observed with an optical microscope). All samples were of similar particle size (width,

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Table 1. Dependence of the Unit-Cell Parameters of $\text{NH}_4(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4\cdot\text{H}_2\text{O}$ on Mn Substitution and Heating Time^a

heating time, min	M0 ($x = 0$)			M2 ($x = 0.2$)			M4 ($x = 0.4$)			M6 ($x = 0.6$)			M8 ($x = 0.8$)		
	$a, \text{Å}$	$b, \text{Å}$	$c, \text{Å}$	$a, \text{Å}$	$b, \text{Å}$	$c, \text{Å}$	$a, \text{Å}$	$b, \text{Å}$	$c, \text{Å}$	$a, \text{Å}$	$b, \text{Å}$	$c, \text{Å}$	$a, \text{Å}$	$b, \text{Å}$	$c, \text{Å}$
0	5.6641	8.8057	4.8264	5.6787	8.8203	4.8450	5.6880	8.8231	4.8606	5.7016	8.8148	4.8746	5.7163	8.8163	4.8902
10	5.6586	8.8148	4.8253	5.6764	8.8295	4.8435	5.6800	8.8263	4.8539	5.6974	8.8218	4.8745	5.7158	8.8181	4.8893
20	5.6641	8.8289	4.8273	5.6713	8.8293	4.8401	5.6829	8.8262	4.8548	5.6997	8.8215	4.8747	5.7159	8.8182	4.8920
30	5.6635	8.8318	4.8260	5.6641	8.8434	4.8447	5.6875	8.8362	4.8575	5.7063	8.8279	4.8759	5.7137	8.8161	4.8904
60	5.6497	8.8866	4.8160	5.6764	8.8851	4.8420	5.6797	8.8521	4.8536	5.6969	8.8250	4.8676	5.7149	8.8193	4.8917
150	5.6415	8.9404	4.8054	5.6579	8.9292	4.8223	5.6697	8.8981	4.8429	5.6968	8.8492	4.8700	5.7139	8.8236	4.8932
300	5.6368	8.9545	4.7985	5.6532	8.9652	4.8152	5.6706	8.9526	4.8344	5.6871	8.9137	4.8606	5.7155	8.8405	4.8918
1200	5.6265	8.9769	4.7941	5.6559	8.9758	4.8133	5.6673	8.9718	4.8278	5.6831	8.9445	4.8516	5.7134	8.8881	4.8750
3000	5.6403	9.0129	4.8093	5.6806	8.9975	4.8256	5.6704	8.9810	4.8263	5.6908	8.9586	4.8493	5.7182	8.9232	4.8836
4320				5.6366	8.9793	4.8026	5.6595	8.9868	4.8250	5.6899	8.9673	4.8450	5.7023	8.9155	4.8709
10080							5.6524	8.9803	4.8264	5.6715	8.9713	4.8340	5.6910	8.9225	4.8772

^a Data for $\text{NH}_4\text{MnPO}_4\cdot\text{H}_2\text{O}$ are $a = 5.7273$, $b = 8.8152$, and $c = 4.9058$.

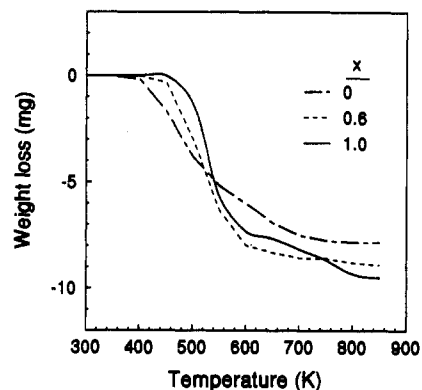


Figure 1. Thermograms of $\text{NH}_4(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4\cdot\text{H}_2\text{O}$.

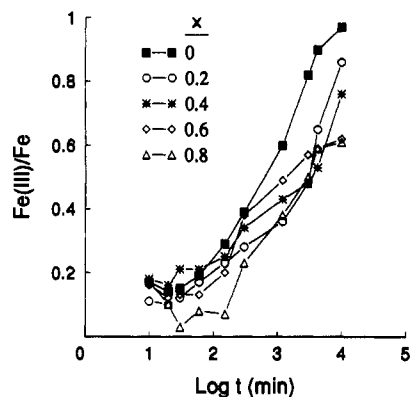


Figure 2. Effect of Mn [$x = \text{Mn}/(\text{Fe} + \text{Mn})$] on the oxidation of Fe in $\text{NH}_4(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4\cdot\text{H}_2\text{O}$ heated at different times.

7–30 μm ; length, 15–50 μm ; thickness, 0.5–2 μm). Color ranged between grayish green (Fe) and grayish pink (manganese ammonium phosphate). Chemical analysis (data not shown) confirmed the $\text{NH}_4(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4\cdot\text{H}_2\text{O}$ ($0 < x < 1$) formula. The Mn mole fraction (x) in the final product was the same as the $\text{Mn}/(\text{Fe} + \text{Mn})$ ratio used in the synthesis. An unavoidable oxidation of part of the Fe(II) occurred when the samples were dried [usually, 5–10% of the total Fe(II)]. It had been observed in previous experiments that the susceptibility to oxidation increased as particle size decreased. For this reason, a synthesis procedure to produce large crystals was used.

The presence of Mn in the structure affects the stability of the products. Thermograms for three samples with different Mn mole fractions ($x = 0, 0.6$, and 1) are shown in Figure 1. When x increases, the degradation temperature also increases; i.e., the structure becomes more stable. On heating, the product gradually releases ammonium and water and Fe(II) is oxidized. Given enough time, decomposition occurs also at temperatures below 373 K. This temperature was selected for a more detailed study

of the effect of Mn on the oxidation of Fe(II) and the crystalline stability of the isomorphous series. This latter study also shows that the presence of Mn stabilizes the structure; i.e., as Mn content increases, a longer period of heating at 373 K is needed to oxidize Fe(II) (Figure 2).

XRD analyses showed that, upon oxidation, the product is gradually transformed into an amorphous phase. This process was complete in samples with $x < 0.2$ for a heating period > 3000 min.

The presence of Mn affects the unit-cell parameters (Table 1) and, consequently, the position of the diffraction lines. For the nonheated samples the a and c parameters changed linearly with Mn content (following thus Vegard's law, which states that the lattice constants of the solid solution series vary linearly from one pure end member to the other)

$$a = 5.6646 + 0.0628x \quad n = 6 \quad r^2 = 0.997 \quad (1)$$

$$c = 4.8280 + 0.0784x \quad n = 6 \quad r^2 = 0.998 \quad (2)$$

where n is the number of samples and r is the correlation coefficient.

The b parameter was not correlated to x and differed little from sample to sample.

Heating (and consequent oxidation) changed the unit-cell parameters (Table 1). The b parameter was correlated (for each heating series with $x = \text{constant}$) with the ratio $\text{Fe(II)}/(\text{Fe} + \text{Mn})$ (henceforth called y), according to

$$\text{M0} \quad b = 9.0915 - 0.288y \quad n = 9 \quad r^2 = 0.83 \quad (3)$$

$$\text{M2} \quad b = 9.1494 - 0.412y \quad n = 10 \quad r^2 = 0.75 \quad (4)$$

$$\text{M4} \quad b = 9.1210 - 0.548y \quad n = 11 \quad r^2 = 0.78 \quad (5)$$

$$\text{M6} \quad b = 9.0970 - 0.786y \quad n = 11 \quad r^2 = 0.99 \quad (6)$$

$$\text{M8} \quad b = 9.0081 - 1.038y \quad n = 11 \quad r^2 = 0.95 \quad (7)$$

For all the samples of Table 1, multiple regression analysis gave the following equations relating unit-cell parameters to x and y :

$$a = 5.6058 + 0.1186x + 0.0602y \quad n = 52 \quad r^2 = 0.89 \quad (8)$$

$$b = 9.1898 - 0.3331x - 0.4013y \quad n = 52 \quad r^2 = 0.70 \quad (9)$$

$$c = 4.7621 + 0.1378x + 0.0704y \quad n = 52 \quad r^2 = 0.91 \quad (10)$$

The a , b , and c parameters for the pure $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$ were estimated using eqs 8–10 for $x = 0$ and $y = 1$, resulting in 5.6659 for a , 8.7885 for b , and 4.8325 for c . The

Table 2. X-ray Powder Data for $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$

d calcd ^a	d calcd ^b	d obsd ^b	I/I_0 ^b	hkl
8.7885	8.8250	8.8101	100.0	010
4.7620	4.7646	4.7675	13.9	110
4.3942	4.4125	4.4087	2.9	020
4.2345	4.2343	4.2341	16.8	011
3.6768	3.6725	3.6758	2.4	101
3.3919	3.3906	3.3908	9.9	111
3.2511	3.2565	3.2567	3.6	021
2.9295	2.9417	2.9379	6.4	030
2.8199	2.8227	2.8234	55.0	121
2.5051	2.5118	2.5105	5.3	031
2.4162	2.4130	2.4138	4.9	002
2.3546	2.3530	2.3544	5.2	211
2.2912	2.2959	2.2957	7.4	131
2.1358	2.1362	2.1375	6.5	221
2.1173	2.1171	2.1170	3.3	022
2.0485	2.0556	2.0548	1.5	140
1.8886	1.8868	1.8903	2.8	300
1.8640	1.8656	1.8655	1.9	032
1.8384	1.8362	1.8369	1.4	202
1.7994	1.7977	1.7984	5.2	212
1.7577	1.7650	1.7631	1.7	050
1.7362	1.7400	1.7401	2.7	240
1.7248	1.7235	1.7232	2.4	311
1.6788	1.6850	1.6841	2.7	150
1.6331	1.6326	1.6333	5.8	321
1.6256	1.6283	1.6274	1.0	042
1.5081	1.5086	1.5087	3.3	331
1.4936	1.4976	1.4972	2.8	250
1.4322	1.4339	1.4324	2.1	340

^a Data for "pure" $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$. ^b Data for the MO-O sample.

d -spacings of the diffraction lines calculated from the former values are shown in Table 2. The values corresponding to sample MO-O, which is partially oxidized ($y = 0.91$), were also calculated and compared to the observed spacings (Table 2). The agreement between the two sets of values is good.

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