

BRIEF COMMUNICATION

Ambient Pressure and Temperature Synthesis of New Layered Magnesium Phosphate: $\text{MgHPO}_4 \cdot 0.78\text{H}_2\text{O}$ A. Bensalem¹ and G. Iyer*Long Island University, Chemistry Department, Brooklyn Campus, 1 University Plaza, Brooklyn, New York 11201*

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We report the synthesis and characterization of a new hydrated magnesium acid phosphate, isostructural with $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$, which has a layered structure. The sample was prepared under ambient pressure and temperature by the reaction of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and phosphoric acid at pH 6.0. The orthorhombic unit cell dimensions of the prepared product were found to be $a = 9.295 \text{ \AA}$, $b = 8.038 \text{ \AA}$, and $c = 10.482 \text{ \AA}$. © 1995 Academic Press, Inc.

INTRODUCTION

Acid phosphates, specifically those of tetravalent elements, are layered materials and represent a vast class of intercalating compounds with useful chemical and thermal properties. One representative of this class of materials, corresponding to the formula $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ($\alpha\text{-ZrP}$) (1, 2), shows promise for applications in the field of ion exchange and catalysis (3-5). However, very little is known about layered magnesium acid phosphates. The best known compound is $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, with a structure that consists of alternating P and Mg strata parallel to the (100) plane. Unfortunately the water molecules between the layers cannot be removed without the collapse of the whole structure. Recently Chen and co-workers (6) prepared hydrothermally a new layered magnesium phosphate $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$, which undergoes reversible hydration at temperatures up to 200°C.

We report here the preparation of a new layered magnesium phosphate isostructural with $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$ using a simple ambient pressure and temperature route.

EXPERIMENTAL

The compound was prepared by the reaction of magnesium chloride hexahydrate with phosphoric acid. The re-

action was performed at room temperature by mixing these compounds, at the desired ratio, in distilled water. Then, with rapid stirring, the formation of a gelatinous white precipitate was initiated by raising the pH to 6.0 by the addition of ammonium hydroxide. The precipitate was recovered by filtration, washed with hot water, and immediately dried in air for 3 hr at 100°C. The dry white powder was analyzed by X-ray powder diffraction using a Phillips XRD 3100 diffractometer ($\text{CuK}\alpha$ radiation).

Thermogravimetric and the differential thermal analysis were performed using a TG7-DT7 Perkin-Elmer analyzer under flowing nitrogen at a heating rate of 10°C/min. Infrared studies were performed by using a NICOLET (IMPACT 400) spectrometer with an instrument resolution of 4.00 cm^{-1} . The FTIR spectra were taken on KBr pellets. The spectra were composites of 64 individual scans and were all taken under dry nitrogen atmosphere at room temperature.

RESULTS AND DISCUSSION

A fine white powder was obtained after drying the gelatinous precipitate. The sample analyzed by X-ray powder diffraction (XRD) appears to be isostructural with $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$ (Fig. 1). However, after indexing the X-ray powder pattern in an orthorhombic cell, the least-squares refinement of the indexed pattern gave a cell with dimensions $a = (9.295 \pm 0.014) \text{ \AA}$; $b = (8.038 \pm 0.009) \text{ \AA}$; $c = (10.482 \pm 0.008) \text{ \AA}$. These cell dimensions appear to be slightly different from those of $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$, especially the c axis (Table 1). From Fig. 2, we note that when the sample is heated at 100°C for 1 hr, it has an XRD pattern similar to the as-prepared sample with a small shift of the first diffraction peak toward a high angle from 8.43° to 8.50°. However, when the sample is heated at 200°C for 1 hr, we observe a larger shift (8.43° to 10.35°)

¹ To whom correspondence should be addressed.

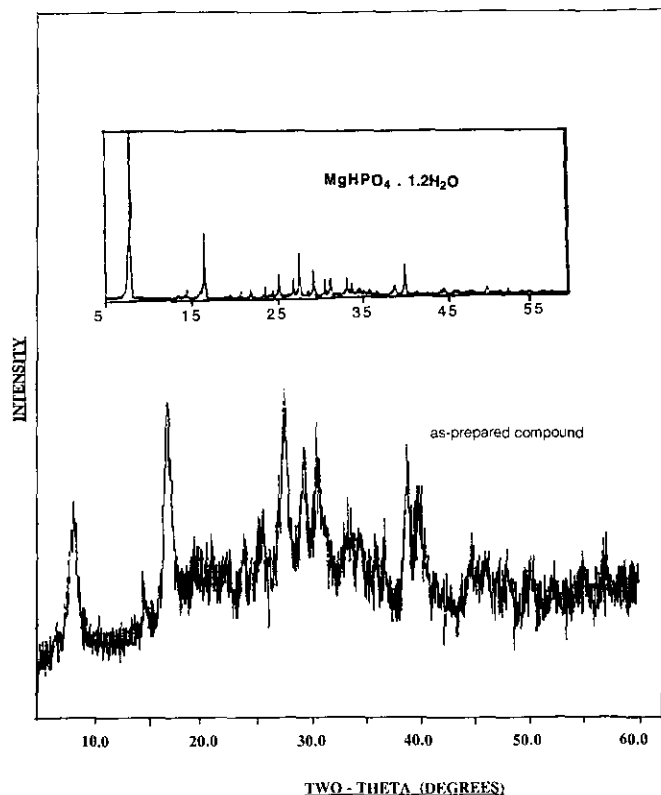


FIG. 1. X-ray powder diffraction patterns of the as-prepared sample and of $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$.

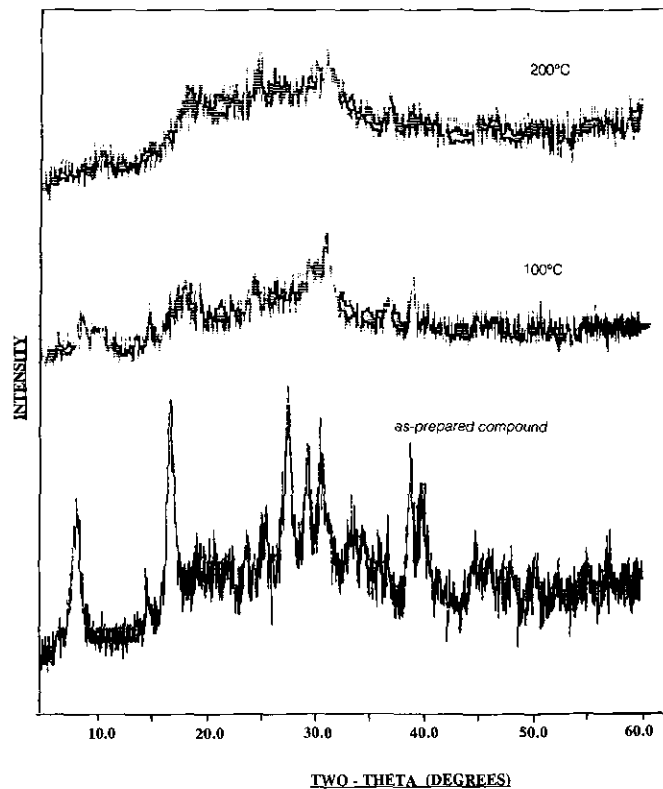


FIG. 2. X-ray powder diffraction patterns of the as-prepared sample for the sample heated at 100°C for 1 hr and for the sample heated at 200°C for 1 hr.

and completely different XRD data. At 500°C the sample is transformed to $\text{Mg}_2\text{P}_2\text{O}_7$ (7).

Figure 3 shows the IR spectra of the as-prepared sample and of $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$. The two spectra exhibit very strong similarities. From Fig. 4, we note that the IR absorption bands in the 1400–400 cm^{-1} range, which are associated with the MgHPO_4 layers (6), remain unchanged as the sample is heated from room temperature to 200°C. We also note that the observed broad band at 3250 cm^{-1} attributed to the intercalated water molecules becomes much weaker when the sample is treated at 200°C. However, it remains visible in the spectrum even at temperatures as high as 300°C. On the other hand, the absorption due to the proton-related hydroxyl, observed at 3600 cm^{-1} , undergoes noticeable changes only at temperatures above 200°C. These results, along with the XRD data, suggest an empirical formula of $\text{MgHPO}_4 \cdot n\text{H}_2\text{O}$ with n smaller than 1.2 for the as-prepared sample.

In order to analytically characterize the sample, thermogravimetric analysis (TGA) as well as differential thermal analysis (DTA) were performed. The TGA/DTA curves (Fig. 5) exhibit three endothermic heat events coin-

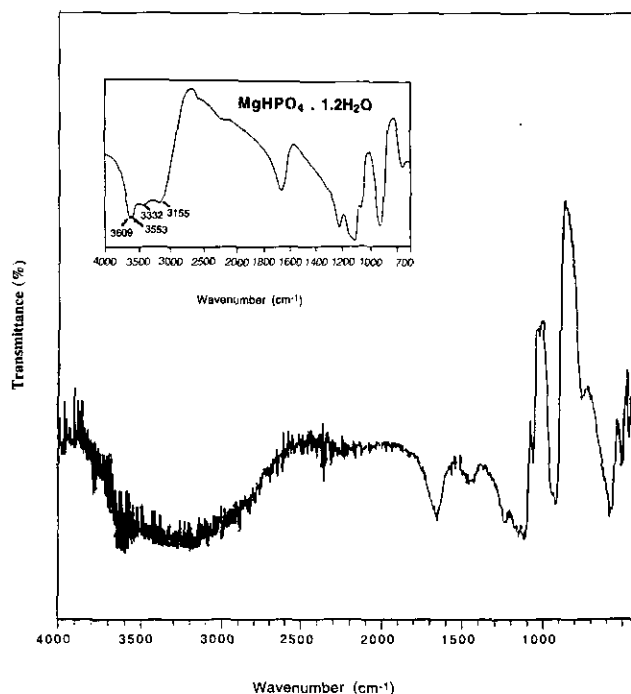


FIG. 3. FTIR spectrum of the as-prepared sample along with the spectrum of $\text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O}$.

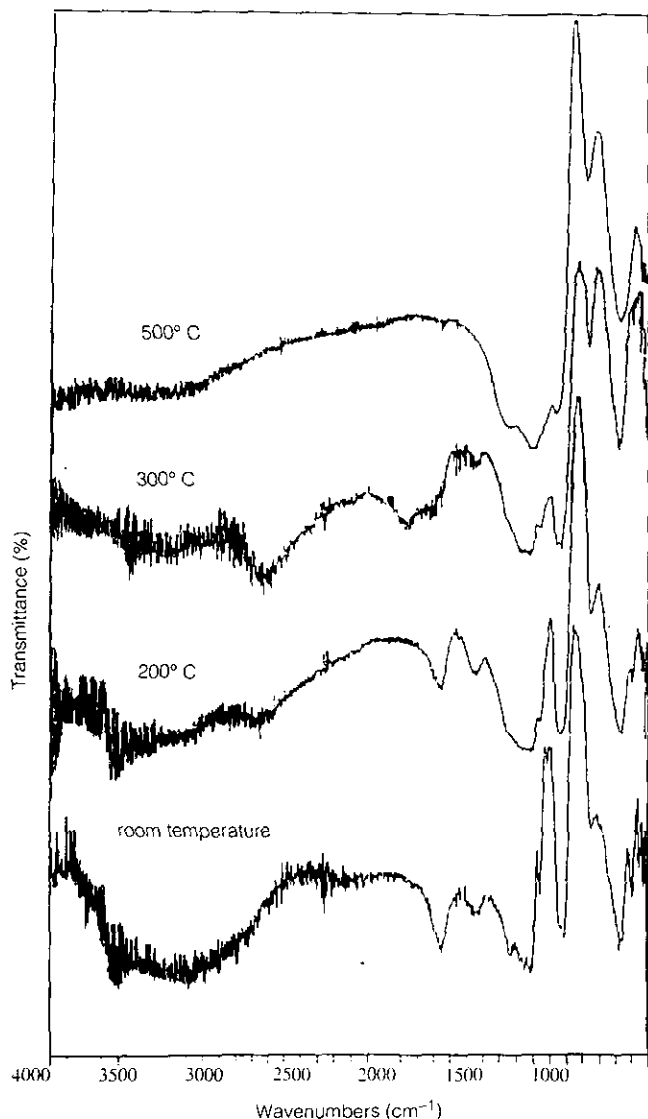


FIG. 4. FTIR spectrum of the as-prepared sample, of the sample heated at 200°C for 1 hr, of the sample heated at 300°C for 1 hr, and of the sample heated at 500°C for 1 hr.

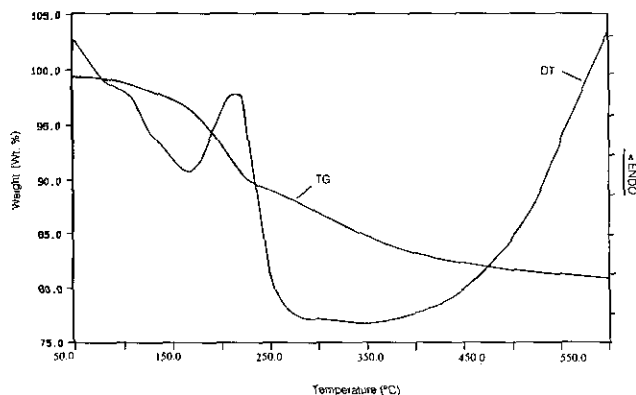


FIG. 5. TGA/DTA curves for MgHPO₄·0.78H₂O.

TABLE I
X-Ray Powder Diffraction Data for MgHPO₄·0.78H₂O

I_{obs}	d_{obs} (Å)	d_{calc} (Å)	hkl
55.95	10.474	10.482	001
26.23	6.056	6.080	110
100	5.282	5.259	111
17.19	4.633	4.647	200
23.01	4.268	4.248	201
12.80	3.961	3.969	112
19.99	3.756	3.752	021
25.41	3.485	3.494	003
88.94	3.219	3.204	013
57.17	3.031	3.040	220
60.92	2.920	2.919	221
27.07	2.673	2.629	222
18.57	2.595	2.595	031
15.87	2.496	2.491	014
17.87	2.444	2.453	320
58.40	2.312	2.321	230
52.36	2.245	2.227	313
11.11	2.148	2.136	124
20.73	1.963	1.982	115
8.10	1.852	1.859	215
16.52	1.618	1.602	216

	As-prepared sample	MgHPO ₄ ·1.2H ₂ O (6)
a (Å)	9.295 + 0.014	9.274
b (Å)	8.038 + 0.009	8.053
c (Å)	10.482 + 0.008	10.920

cluding with three weight losses. The first weight loss of about 2% is observed at 100°C, while the second, observed at 180°C, exhibits a weight loss of 8.5%. A third weight loss of about 7.5% is observed at around 300°C. By attributing the third weight loss to the removal of the proton-related hydroxyl groups, we have used the first and second weight losses to estimate the amount of water molecules intercalated in the structure. The composition of the as-prepared sample is then determined to be MgHPO₄·0.78H₂O.

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