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Synthesis and Characterisation of Anhydrous Magnesium Phosphate $Mg_3(PO_4)_2$

A. BAYKAL, M. KIZILYALLI*
Departmen of Chemistry,
Middle East Technical University, Ankara-TURKEY
R. KNIEP,
T. H. Darmstad, Chemistry Department, Eduard Zintl Institute, Darmstad-GERMANY

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The synthesis and characterization of anhydorus $Mg_3(PO_4)_2$ was investigated. $Mg_3(PO_4)_2$ is reported to have similar structural arrangements with $Co_3(PO_4)_2$ and γ-$Zn_3(PO_4)_2$ compounds. The sample was prepared by a new technique which is the reaction of $MgCl_2.6H_2O$ and $Na_3PO_4.12H_2O$ solutions at pH=5.1, which was adjusted by adding concentrated H_3PO_4 to the reaction mixture and heating the precipitated product at 600° C untill constant weight. The purity of the product was checked by X-ray powder diffraction, IR, density measurement, SEM and DTA analysis. The monoclinic unit cell dimensions of product are a=7.605 (2), b=8.233 (3), c=5.080 (1)A° and β= 94.19° (3), which was in good agreement with the reported data for $Mg_3(PO_4)_2$. In the IR spectra, peaks due to PO_4 anion of T_d symmetry split because of the monoclinic crystal structure with the space group of $P2_1/m$. The SEM micrographs showed a spongy appearance with cavities. DTA analysis proved that anhydrous $Mg_3(PO_4)_2$ is stable up to melting point which is 1184° C.

Key Words: Magneisum Phosphate, X-Ry Data of Magnesium Phosphate, SEM of Magnesium Phosphate, Microporous Materials

Introduction

Our former works[1] on the synthesis and crystal structure studies of borophosphates of magnesium in our laboratory stimulated the preparation of Mg_3BPO_7 through different solid state reactions to confirm its existence and structure. We tried a reaction represented by the following equation:

$$Mg_3(PO_4)_2(s) + Mg_3B_2O_6(s) \underset{Heat}{\rightarrow} 2Mg_3BPO_7(s)$$

The results of the solid-state reactions and the structure of Mg_3BPO_7 will be published soon. Since the commercial $Mg_3(PO_4)_2$ contains crystal and water, and due to disturbances in the solid state reactions of phospates due to hydrogen bonding, we tried to prepare $Mg_3(PO_4)_2$ in the laboratory by a simple

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* Author to whom correspondence should be addressed.

method, which has not been reported before, and which gives a pure product. Anhydrous $Mg_3(PO_4)_2$ was not available on the market.

On the other hand, in recent years several researchers reported the synthesis of microporous phosphate materials; thus our interst to investigate the prepared $Mg_3(PO_4)_2$ by SEM to examine its morphology.

In the literature, the synthesis of $Mg_3(PO_4)_2$ was reported first by Bronnicov et al.[2] They obtained it together with CaO and $CaSO_4$ during fusion and sintering of apatite concentrate with K_2SO_4, $MgSO_4$, and K_2SO_4, $MgSO_4$ double salt.

Higashi et al.[3] patented the preparation of zn, Ca, Mg, Ba, Fe and Al orthophosphates by treating the metal compounds with H_3PO_4, below 30°C at pH 1.5-2.5 and then above 60°C at pH 2.5 - 3.5. Hydrated orthophosphates were heated at 650°C for 30 minutes and anhydrous salts were obtained. They were particularly interested in zinc orthophosphate tetrahydrate which was useful in the manufacture of dental impression pastes.

Nord et al.[4] obtained $Mg_3(PO_4)_2$ as single crystals by sealing equivalent mixtures of magnesium diphosphate and magnesium oxide in thin-walled platinum tubes which were heated to 1100°C over a period of 10 hrs. Heating was continued for about 2 weeks. The d-values and intensities were obtained from a powder pattern.

In 1972 a more closely packed modification of $Mg_3(PO_4)_2$ is isostrucural with monoclinic[6] was prepared from $MgLiPO_4$ and $MgSO_4$ by Berthet et al.[5] sarcopside and $Ni_3(PO_4)_2^7$.

The high pressure form of $Mg_3(PO_4)_2$, prepared by Annerstein and Nord [8], has also sarcopside structure. The cell parameters are a = 10.25 (2), b= 4.72(1), c=5.92 (1)Å, β=90.9 (1)°, Z=2 and the space group is $P2_1/a$.

Keizo et al.[9] prepared $Mg_3(PO_4)_2.5H_2O$ from the homogeneous; precipitation reaction of NaH_2PO_4.-$2H_2O$ and $MgCl_2.6H_2O$ using the hydrolysis of urea for pH control. Heating the sample at 220°C two moles of its crystal water were lost. At 500°C the compound was reported to be amorphous with the loss of 3 moles of H_2O and at 670°C crystalline $Mg_3(PO_4)_2$ was obtained.

$Mg_3(PO_4)_2$ as given by Nord et al.[4] has a monoclic structure with the space group $P2_1/n$ (No.14). The X-ray powder diffraction data of $Mg_3(PO_4)_2$, which was reporded in J.C.P.D.S. (Card no. 33-876), obtained from a mineral from Spring Water pallasite meteorite[10]. It was heated at 800°C for 18 hrs before it was subjected to X-ray analysis. On the other hand, the powder data obtained by Nord et al.[4] using Guinier Hagg camera and CuKα radiation agreed to some extent with the J.C.P.D.S. data with the same space group. The following cell dimensions were obtained by Nord et al.: a=7.5957$\mp$8, b=8.2305$\mp$5,0.775Å$\mp$ 5 and β = 94.05°$\mp$1.

We tried to prepare polycrystalline $Mg_3(PO_4)_2$ by a new simple technique and the purity of the compound was checked by X-ray powder diffractionand IR spectroscoply. In this technique, anhydrous $Mg_3(PO_4)_2$ was prepared by heating the precipitate obtained by the reaction of $MgCl_2.6H_2O$ an $Na_3PO_4.12\ H_2O$ water solution in the presence of dilute H_3PO_4 at pH=5.1.

Experimental

Materials and Instrumentation

The following reagent grade chemicals were used as received; $MgCl_2.6H_2O$, $Na_3PO_4\ 12H_2O$ and concentrated H_3PO_4 (14M) Picnometric density measurements were done using n-decane as solvent. X-Ray powder diffraction analysis were carried out on a Philips Powder Diffractometer (PW 1050/25, 30-40kV, 15-

20 mA)with position sensitive detector, silicon monochromator and CoKα radiation and checked by huber Guinier difractometer (Type 642) with Cu Kα radiation. The refinement of the unit cell parameters was done by Huber diffractometer software programs. IR spectrum of the product was recorded by Nicolet 50 DX FTIR Spectrometer using KBr pellets. The morphology of the product was examined using Jeol JSM 6400 Scanning Electron Microscope. DTA measurements were performed between the temperature ranges of 25 to 1200 °C by using General V4. I.C. Dupont 2000 Differential Thermal Analyzer at a heating rate of 10°C/min under Ar flow.

Procedure

$Mg_3(PO_4)_2$ was synthesized by the homogeneous precipitation reaction from a mixture of $Na_3PO_4.12\,H_2O$ (0.2 M) and $MgCl_2.\ 6\ H_2O$ (0.3 M) solutions at room temperature according to the following reaction:

$$3MgCl_2(aq) + 2Na_3PO_4(aq) \quad \xrightarrow[pH=5.1]{H_3PO_4} \quad Mg_3(PO_4)_2(s) + 6NaCl(aq)$$

Equivalent amounts of the two solutions were mixed and concentrated H_3PO_4 (14M) was added dropwise to the solution till pH=5.1. Several experiments showed that pH=5.1 was found to be optimum for the production of pure compound. Formation of hydrogen phosphates was possible at lower pH and excess H_3PO_4 may cause the formation of hydroxy apatite[11]. Product of the above reaction was filtered with Whatman 41 filter paper and washed with distilled water, dried in air, then heated at 600 °C for about 20 hr until it reaches to a constant weight. Finally, sample was subjected to X-ray powder diffaraction, IR, density, DTA and SEM analysis.

Results and Discussion

The X-ray powder diffraction pattern of the product dried in air showed that it is completely amorphous. After several heat treatments, it was found that heating at 600°C for 20 hr in a porcelain crucible the sample reached to a constant weight and all its water content was removed. Calculations showed that the non-heat treated product contained 4.5 moles of water.

In the X-ray powder diffraction pattern of the heated product only $Mg_3(PO_4)_2$ (J.C.P.D.S. Card No 33 - 876) was observed.

Nord et al.[4] stated that $Mg_3(PO_4)_2$ has a structure built from somewhat distorted MgO_6 octahedra and MgO_5 polyhedra and nearly regular PO_4 tetrahedra. The groups are linked together by sharing corners and edges to give a three dimensional framework[12].

Similar structural arrangements occur among $Mg_3(PO_4)_2$, $Co_3(PO_4)_2^{13(JCPDSNo:13-503)}$ and γ-$Zn_3(PO_4)_2$ [14] and the lattice parameters of $Mg_3(PO_4)_2$ and $Co_3(PO_4)_2$ are similar to each other. But β-$Zn_3(PO_4)_2$ has a completely different crystal structure[15]. γ-$Zn_3(PO_4)_2$ crystallizes in the monoclinic crystal system with the space group $P2_1/c$ and a=5.074, b=8.469, c=8.766Å and β=120°. In $Mg_3(PO_4)_2$ the magnesium atoms are 5 and 6 coordinated but in γ-$Zn_3(PO_4)_2$, the zinc atoms are 4 and 6 coordinated.

The discovery of microporous phosphates stimulated the synthesis of other novel metal hosphates and mixed phosphates[16] with open framework structures. Whang et al.[17] prepared $Zn_3CO_4(PO_4)_4(H_2O)_5.2H_2O$ compound which contains unusually large ellipsoidal cavities and channels.

In this work X-ray powder pattern of $Mg_3(PO_4)_2$ was indexed in the monoclinic crystal system with the unit cell parameters of a=7.605 (2) b=8.233 (3) c=5.080 (1)Å and β=94.19°(3), the possible space group is with $P2_1/m$ and Z=2. Density of $Mg_3(PO_4)_2$ was found to be 2.74 g/cm^3 with the picnometer method.

Comparison of unit cell parameters of $Mg_3(PO_4)_2$ is given in Table 1 and the refined X-ray diffraction data is reported in Table 2.

Table 1. Comparison of the Unit Cell Parameters of $Mg_3(PO_4)_2$ prepared in this work with the literature data.

	Nord A.G. et al(4)	Nat. Bur Stand (10)	This work
a (Å)	7.5957	7.5995	7.5998
b (Å)	8.2305	8.2355	8.2296
c (Å)	5.0775	5.0762	5.0788
β (deg)	94.05	94.06	94.28

Examination of the d-spacings showed that there are some differences in intensities compared with the powder data of $Mg_3(PO_4)_2$ prepared by single crystal method[4]. The d values 4.35, 4.32, 2.99, and 2.124 Å were reported as weak whereas in our pattern I/I_o's are 40, 27, 25 and 22, respectively. There are more than extra 30 lines (denoted by asterisk) present in our pattern. This is probably due to using Co Kα radiation which is more eficient to investigate the splitting of the peaks in the monoclinic system. On the other hand $Mg_3(PO_4)_4$ mineral data (J.C.D.P.S. Card No.33-876) are in good agreement with our data.

IR studies

Fig.1 shows the IR data of $Mg_3(PO_4)_2$. The stretching and bending modes of a free PO_4^{3-} anion with T_d symmetry has four internal modes of vibration[18,19]. ν_1=938 cm^{-1} (R), ν_2=420 cm^{-1}, ν_3=1017 cm^{-1} (R, IR) and ν_4=567 cm^{-1} (R, IR). But due to the lowering of the site symmery of the anion to C_1, additional bands appear and ν_1 becomes IR active. Usually due to symmetric and antisymmetric stretching modes 5 bands are observed in the ν_3 region and due to O-P-O deformation modes, 4 within the ν_4 region and 2 bands within the ν_2 region are observed.

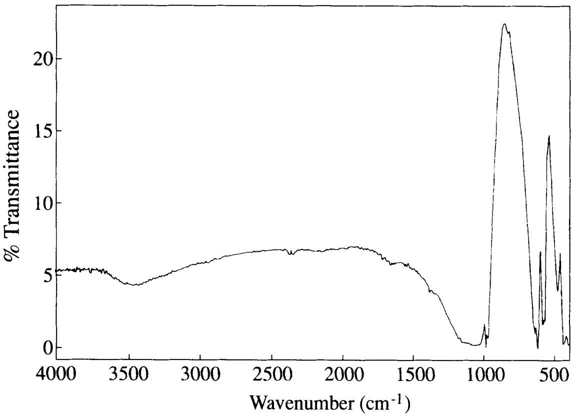

Figure 1. IR spectra of the prepared $Mg_3(PO_4)_2$

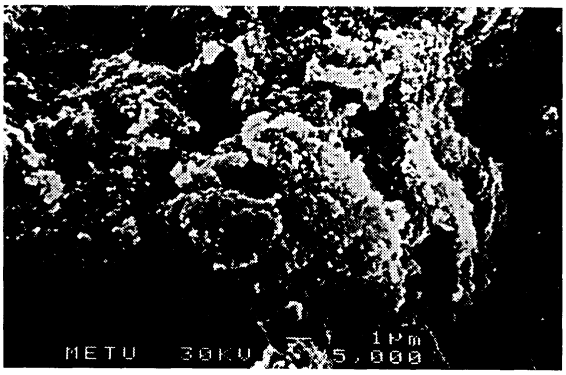

Figure 2. SEM micrograph of the prepared $Mg_3(PO_4)_2$

SEM Photographs

Fig. 2 shows the SEM micrograph of the material sintered at 600°C. It has a sponge like appearance with cavities explaining its adsorbing properties and several technological applications.

Table 2. X-ray powder diffraction data of $Mg_3(PO_4)_2$, Rad. CoKα

I/Io	d obs.	d calc.	hkl
6*	7.532	7.584	1 0 0
14	5.568	5.578	1 1 0
6*	5.079	5.066	0 0 1
40	4.349	4.363	1 0 -1
27	4.332	4.315	0 1 1
43	4.111	4.116	0 2 0
38	4.095	4.077	1 0 1
100	3.855	3.855	1 1 -1
17*	3.786	3.792	2 0 0
32	3.648	3.654	1 1 1
14	3.623	3.618	1 2 0
100	3.441	3.444	2 1 0
19	3.194	3.195	0 2 1
6*	3.151	3.148	2 0 -1
25	2.993	2.994	1 2 -1
3*	2.936	2.935	2 0 1
8	2.900	2.897	1 2 1
19	2.791	2.789	2 2 0
8*	2.761	2.764	2 1 1
19*	2.526	2.528	3 0 0
22	2.497	2.500	2 2 -1
38	2.410	2.413	0 3 1
6	2.349	2.351	1 0 2
8	2.324	2.323	1 3 -1
11	2.244	2.243	3 1 -1
3*	2.222	2.223	2 3 0
8	2.179	2.181	2 0 -2
3*	2.154	2.154	3 2 0
22	2.124	2.124	3 1 1
17*	2.110	2.109	2 1 -2
8	2.606	2.068	2 3 -1
8	2.058	2.058	0 4 0
14	2.041	2.039	2 0 2
3*	2.004	2.004	2 3 1
3*	1.978	1.979	2 1 2
6	1.928	1.928	2 2 -2
6*	1.894	1.896	4 0 0
8	1.860	1.860	3 3 0
3*	1.846	1.848	4 1 0

11	1.830	1.831	1 3 -2
8*	1.826	1.827	2 2 2
3*	1.815	1.813	3 1 -2
8	1.776	1.776	3 3 -1
8*	1.725	1.723	2 4 -1
8	1.723	1.722	4 2 0
11	1.694	1.694	3 2 -2
3*	1.689	1.689	0 0 3
1*	1.675	1.665	1 0 -3
3*	1.665	1.665	4 2 -1
3*	1.653	1.654	0 1 3
8*	1.641	1.641	1 1 -3
6*	1.624	1.624	1 0 3
3*	1.596	1.596	3 4 0
6*	1.586	1.586	2 0 -3
3*	1.508	1.509	1 2 3
3*	1.497	1.497	2 4 -2
3*	1.479	1.477	2 1 3
3*	1.468	1.465	3 0 -3
3*	1.447	1.447	2 4 2
2*	.373	1.373	2 3 -3
1*	1.371	1.372	3 2 -3
2*	1.362	1.363	4 4 -1
1*	1.358	1.358	3 0 3
1*	1.325	1.325	4 4 1

DTA Analysis:

DTA results showed that there is no structural change within the region studied and the melting of the product takes place around 1200 °C.

Conclusion

Anhydrous $Mg_3(PO_4)_2$ was synthesized by a homogeneous precipitation reaction at pH =5.1 and heating the product at 600 °C. X-ray powder diffraction, IR, density, SEM and DTA analysis showed that a pure polycrystalline product was obtained. The spongy appearance of the SEM micrograph of the product proved that $Mg_3(PO_4)_2$ is a microporous material with an open framework strucure. This may explain the adsorptive capacity and catalytic activity of $Mg_3(PO_4)_2$.

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