

MAGNESIUM PHOSPHATE

Part VII. Study of X-ray Powder Diffraction, Infrared Absorption and Differential Thermal Analyses of the Compounds $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{H}_2\text{PO}_4)_2$ and $\text{Mg}(\text{PO}_3)_2$

SIDDIQUE AHMED*

Departments of Silicate Research and Inorganic Chemistry, Chalmers University of Technology, Gothenburg, Sweden

(Received May 1, 1971; revised August 4, 1971)

Abstract. The compound $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ has been prepared from phosphoric acid and magnesium carbonate. The substance is finely crystalline to X-rays; its X-ray powder diffraction data have been indexed. IR spectrum of the compound has been recorded and studied in detail. Differential thermal analysis has shown that the compound loses its water of crystallization in several steps producing the compounds $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{H}_2\text{PO}_4)_2$ and $\text{Mg}(\text{PO}_3)_2$. All of these three compounds are crystalline to X-rays; their X-ray powder diffraction data have been indexed. Their IR spectra have been recorded and discussed. The anhydrous compound $\text{Mg}(\text{PO}_3)_2$ forms glass when its melt is cooled rapidly to room temperature. The IR spectrum of the glass has been recorded. The recrystallization temperature of this glass has been determined by differential thermal analysis and it is found to be 834°C .

Anhydrous magnesium metaphosphate, $\text{Mg}(\text{PO}_3)_2$, was used as a source of P_2O_5 during the investigation of the systems $\text{MgO}-\text{P}_2\text{O}_5$ and $\text{MgO}-\text{P}_2\text{O}_5-\text{Cr}_2\text{O}_3$. Generally this substance is prepared by heating calculated proportions of magnesium oxide and diammonium hydrogen phosphate, $(\text{NH}_4)_2\text{HPO}_4$. But during the present work it was found necessary to prepare it by a wet process. And the substance was obtained as the end product of dehydration of the compound $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. This hydrated substance was mentioned in the literature¹ but the details of its preparation are not available. Stoklasa² prepared the compounds $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{H}_2\text{PO}_4)_2$ by digesting magnesium oxide with phosphoric acid on a water-bath. Belopolskii and his co-workers³ identified these two substances during the investigation of the system $\text{MgO}-\text{H}_2\text{O}-\text{P}_2\text{O}_5$. In the course of the present work the compounds have been detected by the differential thermal analysis of the compound $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Experimental

Magnesium carbonate (MgCO_3) was dissolved in phosphoric acid (H_3PO_4) with the intention of preparation of a sample rich in P_2O_5 . A clear solution was obtained. On standing for a few days at room temperature an opaque crystalline substance was formed. There were no well-shaped crystals, only hard lumps. This substance was found to be readily soluble in cold water to give a clear solution. On standing at room temperature for 3-4 days, again hard lumps were formed. The lumps were powdered finely and dried (P_2O_5) for 24 hr. This dry powder was used for chemical, X-ray and differential thermal analyses, to record IR spectrum and to determine density.

For chemical analysis a weighed amount of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in minimum amount of water. A few drops of HNO_3 (concd) was added

and the solution was heated to almost dryness. Thus PO_3^- ion, if any formed in the solution, was converted to PO_4^{3-} ion. The substance was again dissolved in water. Phosphate ion was separated from magnesium ion by allowing the solution to pass through a cation exchange column. Phosphate was estimated as ammonium phosphomolybdate and magnesium as ammonium magnesium phosphate hexahydrate. X-ray analysis was made with the help of a Philips X-ray diffractometer using copper target and nickel filter. The scanning speed was $0.5^\circ/\text{min}$. The IR spectrum was recorded by KBr tablet method on a Beckman spectrophotometer model IR9. Differential thermal analysis was made with the help of the instrument developed in the department of Silicate Research, Chalmers University of Technology, Gothenburg, raising the temperature 10°C per minute. Calcined kaolin was used as reference material. Density of the substance was estimated by the method described by Zintl⁴ and Hagg.⁵ $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{H}_2\text{PO}_4)_2$, both nonhygroscopic, were obtained by heating $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 153°C and 250°C separately for 30 min. They are insoluble in water but soluble in mineral acids. The anhydrous substance $\text{Mg}(\text{PO}_3)_2$ was also obtained by heating $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 400°C for 30 min. It is nonhygroscopic, insoluble in water but soluble in hot HCl. Chemical, X-ray, IR, differential thermal analyses and the determination of densities were made as in the case of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. For chemical analyses the latter three compounds were dissolved in minimum amount of hydrochloric acid instead of water.

Results and Discussion

The results of chemical analyses of the above substances have been shown in Table 1. The experimental results are in good agreement with those calculated on the basis of the chemical formulae $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{H}_2\text{PO}_4)_2$ and $\text{Mg}(\text{PO}_3)_2$ showing that the compounds are pure.

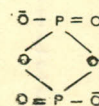
*Now at PCSIR Laboratories, Dacca 5.

X-ray powder diffraction data for the two compounds $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ have been shown in Table 2. No X-ray powder diffraction data for these compounds are available in the literature. The X-ray powder diffraction data for $\text{Mg}(\text{H}_2\text{PO}_4)_2$, along with those published previously, have been shown in Table 3. When the data recorded during the present work are compared with the published one, it is found that they are not in agreement. This disagreement may be due to the fact that the substance used previously was not pure and the present improved instrumentation also helps to record X-ray diffraction data more accurately. The X-ray powder diffraction data for $\text{Mg}(\text{PO}_3)_2$ have been given in Table 4. The right hand side of the table contains the previously published data and they are not much different from those recorded during the present work.

The IR spectrum (Fig. 1a) of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ shows that there is a deep valley in the region 3600–2600 cm^{-1} . In this valley there is one absorption band at 3375 cm^{-1} which seems to be due to O—H stretching. There are a few more absorption bands in this valley and it means that there are some hydrogen bonding in the hydrated crystals of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. There is a weak absorption and at 3015 cm^{-1} and it seems that this band is due to P—OH stretching. The absorption band at 2360 cm^{-1} is very weak and it is due to P—H linkage. The absorption band due to O—H bending is at 1640 cm^{-1} . From 1400 cm^{-1} to 850 cm^{-1} there is again a deep valley which contains several well-defined absorption bands. These absorption bands are mainly due to PO_4^{3-} ion. The IR absorption spectrum (Fig. 1b) of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is similar to that of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ except the

fact that the absorption bands due to P—OH and P—H in the second spectrum are sharper.

In the spectrum (Fig. 2a) of the compound $\text{Mg}(\text{H}_2\text{PO}_4)_2$, the absorption bands, in the region 1400–850 cm^{-1} and in the region 800–400 cm^{-1} , have become sharper and well-defined. This is due to the fact that with the loss of water molecules the complexity of the bondings are reduced. The IR absorption spectrum of the substance $\text{Mg}(\text{PO}_3)_2$ has been shown in Fig. 2b. It is a characteristic spectrum of a cyclic metaphosphate. In the region 1400–1250 cm^{-1} there is one valley and this valley contains three absorption bands; the absorption band at 1300 cm^{-1} is well-defined and the other two are ill-defined but they are strong. In this region the absorption bands arise due to P=O bonding. The absorption band in the region 1200–900 cm^{-1} is broad but very strong and is due to P—O ionic stretching. Now the more important characteristic of a cyclic metaphosphate is the appearance of two very sharp and very strong absorption bands in the region 800–700 cm^{-1} . They are due to P—O—P bonding in the ring system of the metaphosphate ion. So the metaphosphate ion PO_3^- seems to have one of the resonance structures of the type:



Differential thermal analysis shows that $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ loses all of its water in three steps (Fig. 3).

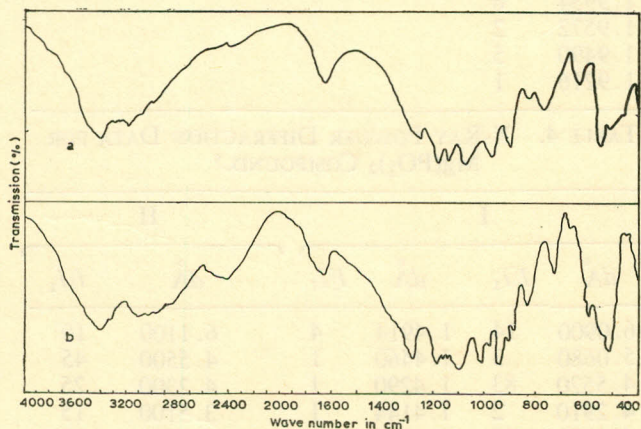


Fig. 1. Infrared spectra of the compound $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

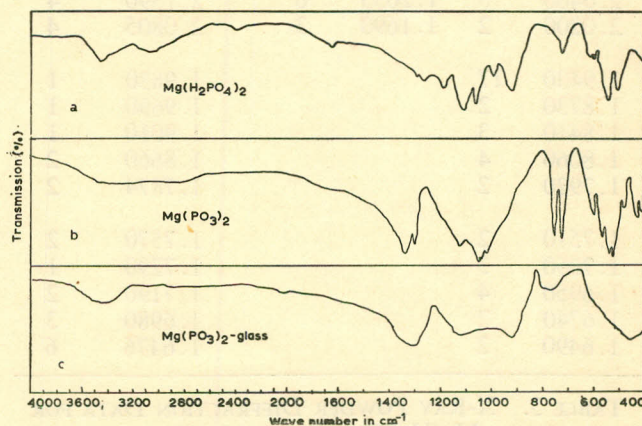


Fig. 2. Infrared spectra of (a) $\text{Mg}(\text{H}_2\text{PO}_4)_2$, (b) $\text{Mg}(\text{PO}_3)_2$ and (c) $\text{Mg}(\text{PO}_3)_2$ -glass.

TABLE 1. CHEMICAL ANALYSES.

Compound	Found (%)			Calculated (%)		
	MgO	P ₂ O ₅	H ₂ O	MgO	P ₂ O ₅	H ₂ O
$\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	13.91	48.68	37.30	13.89	48.86	37.25
$\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	15.90	55.78	28.40	15.85	55.82	28.33
$\text{Mg}(\text{H}_2\text{PO}_4)_2$	20.01	71.05	9.11	20.13	70.87	9.00
$\text{Mg}(\text{PO}_3)_2$	21.97	77.92		22.17	77.83	

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR MAGNESIUM PHOSPHATES.

Mg(H ₂ PO ₄) ₂ ·4H ₂ O				Mg(H ₂ PO ₄) ₂ ·2H ₂ O	
dÅ	I/I _T	dÅ	I/I _T	dÅ	I/I _T
5.8100	28	1.6284	2	7.5000	100
4.9300	18	1.6080	2	4.9200	2
4.6460	3	1.5850	2	4.3400	2
4.4740	46	1.5752	2	3.8900	27
4.0700	32	1.5594	1	3.7850	84
3.7700	4	1.5280	2	3.6250	18
3.6050	11	1.5130	1	3.5280	54
3.3950	100	1.4980	1	3.3820	70
3.3150	11	1.4774	1	3.2730	4
3.1480	43	1.4590	5	3.1310	8
2.9940	40	1.4290	2	3.0280	6
2.9055	4	1.4136	1	2.9550	26
2.7425	2	1.4010	1	2.7975	5
2.5425	7	1.3876	2	2.7550	2
2.5600	4	1.3732	2	2.6365	4
2.4685	2	1.3628	8	2.6185	6
2.3380	22	1.3235	1	2.5740	2
2.2750	2	1.2885	2	2.6000	39
2.2430	53	1.2745	2	2.4300	1
2.2170	2	1.2685	2	2.3035	4
2.1260	5	1.2480	2	2.2655	1
2.1175	4	1.2397	3	2.2170	4
2.0670	2	1.2196	1	2.1885	4
2.0400	5	1.2055	6	2.1390	4
2.0200	2	1.1690	3	2.0805	4
1.9430	17			1.9830	1
1.8730	2			1.9690	1
1.8410	3			1.9010	1
1.8060	4			1.8660	2
1.7920	2			1.7874	2
1.7510	2			1.7570	2
1.7350	3			1.7290	1
1.6950	4			1.7190	2
1.6740	2			1.6980	3
1.6490	2			1.6476	6

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR Mg(H₂PO₄)₂ COMPOUND.⁴

I		II	
dÅ	I/I _T	dÅ	I/I _T
7.4350	6	1.9084	1
7.1650	35	1.8770	1
6.3500	4	1.8610	2
4.8200	3	1.8380	1
4.6220	3	1.8190	1
4.3420	50	1.7940	1
		4.9500	16
		4.4700	60
		4.0800	50
		3.7500	12
		3.6000	20
		3.3700	80

(Continued)

Table 3 continued

I				II	
dÅ	I/I _T	dÅ	I/I _T	dÅ	I/I _T
4.2000	50	1.7780	1	3.1400	100
3.8600	21	1.7664	1	2.9800	60
3.7250	39	1.7449	8	2.6400	28
3.5300	21	1.7350	3	2.5500	24
3.4350	25	1.7246	1	2.3300	70
3.2100	100	1.6910	1	2.2400	16
3.1800	13	1.6530	1	2.1600	4
3.1310	6	1.6394	3	2.0300	4
3.0680	31	1.6314	3	1.9400	24
2.9850	2	1.6120	11	1.8400	4
2.9260	1	1.5726	2	1.7400	12
2.8490	18	1.5420	1	1.6400	1
2.7760	56	1.5220	2	1.5600	12
2.7185	9	1.4970	2	1.4300	12
2.5640	6	1.4580	1	1.3600	4
2.4650	4	1.4350	1	1.3200	8
2.4050	1	1.4250	1	1.2700	4
2.3675	6	1.4040	1	1.2000	8
2.3100	5	1.3886	2	1.1600	8
2.2065	3	1.3706	1	1.1300	4
2.1710	2	1.3407	2		
2.1225	2	1.3163	1		
2.1025	8	1.2592	1		
2.0850	2	1.2350	1		
2.0300	1				
1.9934	6				
1.9572	2				
1.9490	5				
1.9216	1				

TABLE 4. X-RAY POWDER DIFFRACTION DATA FOR Mg(PO₃)₂ COMPOUND.⁵

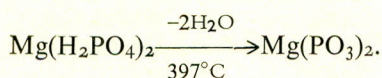
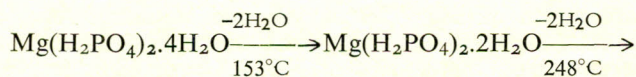
I				II	
dÅ	I/I _T	dÅ	I/I _T	dÅ	I/I _T
6.0900	14	1.4914	4	6.1100	10
5.0680	3	1.4460	1	4.5500	45
4.5520	83	1.4290	1	4.2300	25
4.2910	2	1.4144	1	3.5100	15
4.2100	48	1.4060	1	3.3600	25
3.7080	1	1.3776	5	3.2100	45
3.4930	26	1.3474	3	3.1600	35
3.3570	38	1.3219	1	2.9900	100
3.1980	24	1.3108	1	2.8600	20
3.1380	47	1.2908	1	2.7200	5
2.9830	100	1.2870	2	2.5600	20
2.8490	24	1.2665	1	2.3700	15
2.7140	4	1.2487	1	2.2700	5
2.5605	26	1.2445	1	2.2400	5
2.3600	16	1.2275	1	2.1800	10

(Continued)

Table 4 Continued

I				II	
$d\overset{\circ}{A}$	I/I_I	$d\overset{\circ}{A}$	I/I_I	$d\overset{\circ}{A}$	I/I_I
2.2650	5			2.0900	20
2.2410	3			1.9400	3
2.1750	10			1.9250	5
2.1365	1			1.8870	5
2.0830	17			1.7910	5
2.0580	2			1.7520	5
1.9410	1			1.7280	5
1.9160	2			1.6890	5
1.8770	2			1.6500	5
1.8412	1			1.6260	10
1.7872	5			1.6100	10
1.7460	5			1.5350	10
1.7240	5			1.5140	10
1.6850	7			1.4970	5
1.6420	4			1.3800	10
1.6208	8				
1.6040	10				
1.5656	1				
1.5302	5				
1.5080	4				

At 153°C it loses two molecules of water and at 248°C two more molecules of water. Finally at 397°C last two molecules of water are lost giving anhydrous magnesium metaphosphate, $Mg(PO_3)_2$. The whole dehydration process may be represented as:



The densities of the substances $Mg(H_2PO_4)_2 \cdot 4H_2O$ and $Mg(H_2PO_4)_2 \cdot 2H_2O$ have been found to be 2.190 g/cm³ and 2.360 g/cm³ respectively at 23°C; while those of $Mg(H_2PO_4)_2$ and $Mg(PO_3)_2$ are 2.400 g/cm³ and 2.718 g/cm³ respectively at the same temperature.

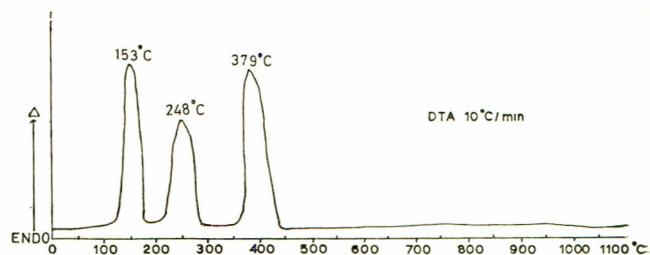


Fig. 3. Differential thermal analysis curve for the compound $Mg(H_2PO_4)_2 \cdot 4H_2O$.

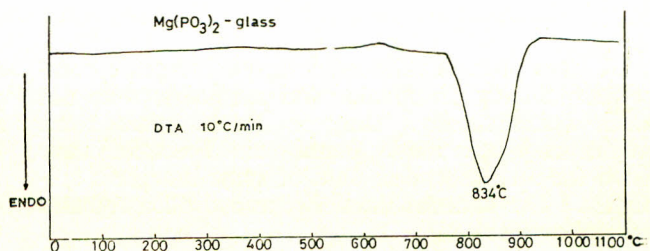


Fig. 4. Differential thermal analysis curve of $Mg(PO_3)_2$ -glass.

Anhydrous magnesium metaphosphate melts congruently at 1165°C and it forms a glass when cooled rapidly to room temperature. Differential thermal analysis (Fig. 4) shows that the glass recrystallizes at 834°C. The IR spectrum of the glass has been shown in Fig. 2c. It is the characteristic spectrum of an amorphous substance.

Acknowledgement. The author wishes to thank Dr. Folke Sandford, Associate Professor, Department of Silicate Research, for his continued interest in the progress of the work, Swedish International Development Authority (SIDA) for granting me a fellowship for higher studies in Sweden.

References

1. A.P. Blopolskii, S.Ya Shpunt and M.N. Shulgina, *J. Appl. Chem. USSR.*, **23**, 873(1950).
2. J. Stoklasa, *Z. Anorg. Allgem. Chem.*, **1**, 307 (1892), and **3**, 67 (1893).
3. Ref. 1.
4. E. Zintl, *Z. Anorg. Allg. Chem.*, **163**, 105 (1927).
5. G. Hagg, *Z. Krist.*, **74**, 95 (1930).