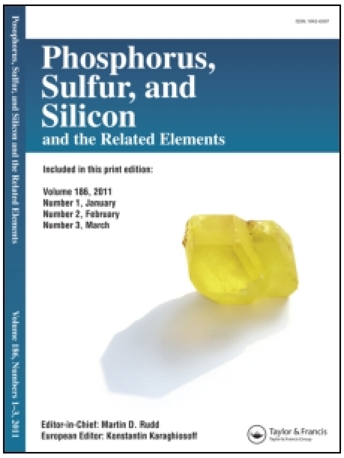

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Thermal Dehydration and Infrared Studies of Mg 2 P 2 O 7 · 6H 2 O Diphosphate

M. Harcharras[a]; A. Ennaciri[a]; N. Khay[a]; K. Brouzi[a]
[a] University Ibn Tofail, Kenitra, Morocco

To cite this Article Harcharras, M. , Ennaciri, A. , Khay, N. and Brouzi, K.(2003) 'Thermal Dehydration and Infrared Studies of Mg 2 P 2 O 7 · 6H 2 O Diphosphate', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 6, 1247 — 1254

To link to this Article: DOI: 10.1080/10426500307908

URL: http://dx.doi.org/10.1080/10426500307908

Phosphorus, Sulfur, and Silicon, 178:1247–1254, 2003
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print
DOI: 10.1080/10426500390200521

THERMAL DEHYDRATION AND INFRARED STUDIES OF $Mg_2P_2O_7 \cdot 6H_2O$ DIPHOSPHATE

M. Harcharras, A. Ennaciri, N. Khay, and K. Brouzi
University Ibn Tofail, Kenitra, Morocco

(Received October 17, 2002; accepted November 19, 2002)

The thermal dehydration of $Mg_2P_2O_7 \cdot 6H_2O$ were studied, in the range 25–800°C, by thermogravimetric analysis (TG-DSC), x-ray diffraction, and infrared spectroscopy. According to the TG-DSC curves, the dehydration of this salt takes place in two stages. The results of thermal analysis, x-ray patterns, and infrared spectra of this compound heated at different temperatures showed that, after dehydration, $Mg_2P_2O_7 \cdot 6H_2O$ decomposes into dihydrate $Mg_2P_2O_7 \cdot 2H_2O$ diphosphate then to an amorphous $Mg_2P_2O_7$ product which crystallises at 665°C to give anhydrous diphosphate $\alpha Mg_2P_2O_7$. The ΔH enthalpy of the dehydration of $Mg_2P_2O_7 \cdot 6H_2O$ and of the formation of $\alpha Mg_2P_2O_7$ have been calculated from thermogravimetric data. The infrared spectroscopic study of $Mg_2P_2O_7 \cdot 6H_2O$ and of its heated products, reveals the existence of the characteristic bands of the P_2O_7 group (ν^{as} POP and ν^{s} POP) and showed that the POP angle is bent in these salts. In these compounds, the POP angle values are estimated using the Lazarev's relationship.

Keywords: Diphosphates; thermal dehydration; thermal analyses (TG-DSC); x-ray diffraction; infrared spectra

Several structural studies of anhydrous diphosphates $M_2P_2O_7$ (where M is a divalent metal) are reported in the literature.[1–12] However very few investigations also have included structural and thermal study of hydrates $M_2P_2O_7 \cdot nH_2O$. For the latter, the only known structure corresponds to the Mg (n = 2; 3.5; 1 and 6),[13–15] Mn (n = 2),[16] Co (n = 2),[17] Fe (n = 2),[18] and Ca (n = 2 and 4)[19,20] salts. Investigations on the thermal study of these types of diphosphates have been made only for $Ni_2P_2O_7 \cdot nH_2O$ (n = 6 and 8), $Zn_2P_2O_7 \cdot 5H_2O$ and $Cu_2P_2O_7 \cdot 5.3H_2O$.[21–23]

The authors are thankful to Professsor A. Rulmont of the University of Liege, Belgium for obtaining x-ray powder data and TG-DSC curves.

Address correspondence to M. Harcharras, Laboratory of Spectroscopy, Department of Chemistry, Faculty of Science, University lbn Tofail, BP 133, 14000 Kenitra, Morocco. E-mail: mharch2002@yahoo.co.uk

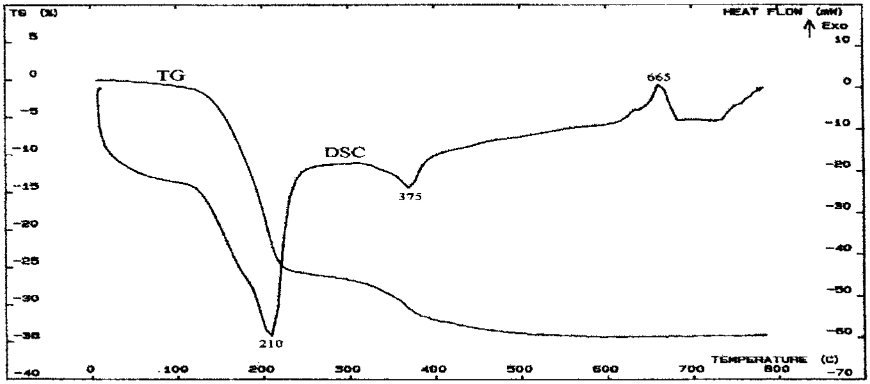

FIGURE 1 TG and DSC curves of $Mg_2P_2O_7 \cdot 6H_2O$.

RESULTS AND DISCUSSION

Analysis of the TG-DSC Curves

According to the thermal analysis data, the dehydration of $Mg_2P_2O_7 \cdot 6H_2O$ occurs over a wide temperature range (25–800°C). As follows from the TG-DSC curves (Figure 1), the dehydration of this salt takes place in two stages corresponding to the existence of more than one type of water molecules; the first strong endothermic peak with a maximum rate at 210°C is accompanied by a loss of four water molecules. The second endothermic peak, with maximum rate at 375°C corresponds to the removal of the last two water molecules. The exothermic peak, with a maximum rate observed at 665°C is accompanied by the transformation to the other phase. The calculated enthalpy of the dehydration and of the phase transition of $Mg_2P_2O_7 \cdot 6H_2O$ are summarised in Table I.

TABLE I Enthalpy (ΔH) of Dehydration and Phase Transition of $Mg_2P_2O_7 \cdot 6H_2O$

Peaks	Ti (°C)	Tf (°C)	Ts (°C)	ΔH (mJ/mg)
1 endo.	112	258	210	581.839
2 endo.	317	406	375	91.798
3 exo.	603	688	665	−94.207

endo.: endothermic, exo.: exothermic, Ti: initial temperature, Tf: final temperature, Ts: temperature with maximum rate.

X-Ray Diffraction

The $Mg_2P_2O_7 \cdot 6H_2O$ diphosphate crystallizes in the monoclinic system, with space group $P2_1/c$ and four molecules per unit cell with the following parameters: $a = 7.189$, $b = 18.309$, $c = 7.665$ Å, $\beta = 92.360°$. The $P_2O_7^{4-}$ anion has a bent POP angle (125.6°).[15]

According to the x-ray diffraction data of this compound, the removal of the first four water molecules after heating the initial product at 210°C, leads to the formation of the dihydrate $Mg_2P_2O_7 \cdot 2H_2O$ diphosphate.[13] The loss of water molecules decreases the number of interferences on the x-ray diffraction pattern of $Mg_2P_2O_7 \cdot 6H_2O$, with a change in the position of the principal atomic planes. The removal of the other two water molecules also is characterized on the diffraction patterns by a decrease in the intensity of a number of reflections and eventually by the disappearance of all of them. The sample thus obtained at 375°C is amorphous to the x-ray analysis. At 665°C, we obtained anhydrous diphosphate $\alpha Mg_2P_2O_7$.[1] The x-ray patterns of the $Mg_2P_2O_7 \cdot 6H_2O$ and of its heated products are listed in Table II.

Infrared Spectra

In the infrared spectrum of $Mg_2P_2O_7 \cdot 6H_2O$ shown in Figure 2 (25°C), the bands observed in the range 3800–2700 cm^{-1} and 1700–1600 cm^{-1} can be attributed to OH and H_2O vibrations.[24] The bands between 1250 and 400 cm^{-1} are attributed to the $P_2O_7^{4-}$ modes and to the libration and rocking modes of H_2O. The bands of H_2O bending modes detected at 1668 and 1651 cm^{-1} confirmed the existence of more than one type of water molecules in the crystal of $Mg_2P_2O_7 \cdot 6H_2O$.[25] In the region 1250–400 cm^{-1}, the bands observed at 1179, 1148, 1110, and 1034 cm^{-1} are ascribed to antisymmetric ν^{as} PO_3 and symmetric $\nu^{s}PO_3$ stretching mode of the PO_3 groups. Bands detected at 924 cm^{-1} and 760 cm^{-1} were assigned respectively to the antisymmetric (ν^{as} POP) and symmetric (ν^{s} POP) stretching modes of the POP group. The broad band observed at 856 cm^{-1} is due to the H_2O libration mode.[24] The rocking mode of H_2O (ρH_2O) appear at 635 cm^{-1}.[25] The deformation modes of the PO_3 groups (δPO_3) are detected in the range 600–400 cm^{-1}.[26]

The infrared spectra (at 210 and 665°C) respectively of $Mg_2P_2O_7 \cdot nH_2O$ ($n = 2, 0$), resulting from the calcination of the initial product $Mg_2P_2O_7 \cdot 6H_2O$, are illustrated in Figure 2. The infrared spectroscopic study of $Mg_2P_2O_7 \cdot 6H_2O$ and of its heated products, reveals the existence of the characteristic bands of the P_2O_7 group (ν^{as} POP and ν^{s} POP) and showed, by the existence of the ν^{s} POP mode,[26] that the POP angle is bent in all these salts. After heating the

TABLE II X-Ray Patterns of $Mg_2P_2O_7 \cdot 6H_2O$ and Its Heated Products

$Mg_2P_2O_7 \cdot 6H_2O$ (25°C)		$Mg_2P_2O_7 \cdot 2H_2O$ (210°C)		Amorphous (260–600°C)	$\alpha Mg_2P_2O_7$ (665°C)	
dhkl	Intensity	dhkl	Intensity		dhkl	Intensity
9.15	17	7.06	80	Amorphous phase	6.44	4
7.98	2	6.5	40		5.12	8
7.07	16	5.08	100		4.37	6
6.68	23	3.95	36		4.19	2
5.66	85	3.71	8		4.15	40
5.14	60	3.66	2		3.88	2
4.95	36	3.56	4		3.84	2
4.77	3	3.48	10		3.72	2
4.65	12	3.44	4		3.5	6
4.63	22	3.24	8		3.21	10
4.48	22	3.14	5		3.08	75
4.03	5	2.88	8		3.02	100
3.93	3	2.86	3		3.01	85
3.83	3	2.66	4		2.98	2
3.6	14	2.62	26		2.94	5
3.53	38	2.56	5		2.83	2
3.43	8	2.55	18		2.68	2
3.37	3	2.4	6		2.63	2
3.32	3	2.38	4		2.62	1
3.3	35	2.36	6		2.54	18
3.26	17	2.32	5		2.53	2
3.25	14	2.29	2		2.52	1
3.21	27	2.24	2		2.43	15
3.15	35	2.22	10		2.3	1
3.1	27					
3.05	18					
3.02	5					
2.98	6					
2.93	100					
2.91	14					
2.83	3					
2.8	4					
2.68	11					
2.62	16					
2.61	11					
2.56	27					
2.55	9					
2.52	14					
2.47	9					
2.46	10					
2.45	10					
2.41	23					

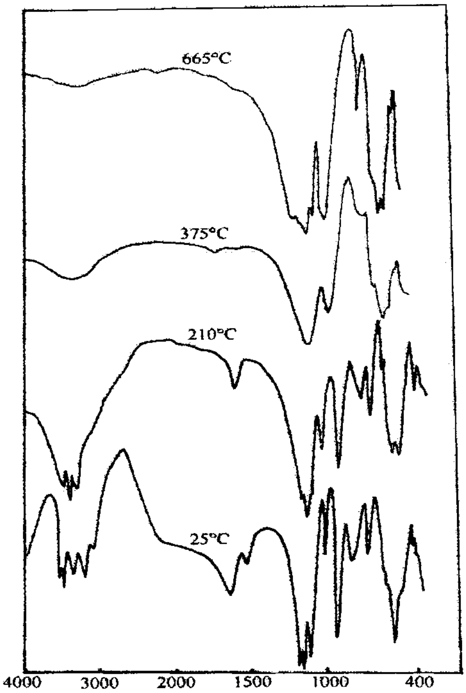

FIGURE 2 IR spectra of $Mg_2P_2O_7 \cdot 6H_2O$ (25°C) and of its thermal treatment products at 210, 375, and 665°C.

initial diphosphate $Mg_2P_2O_7 \cdot 6H_2O$ at 210°C, the infrared spectrum of the resulting salt does not present a great change compared to the initial compound. Broadened bands appearing on the infrared spectrum after heating the initial salt at 375°C confirms the formation of an amorphous phase. After calcination at 665°C, the heated compound shows a infrared spectrum similar to that of $\alpha Mg_2P_2O_7$, as previously published.[27,28]

On the whole, the results of the x-ray diffraction and infrared spectroscopic studies confirm the thermal transformation of $Mg_2P_2O_7 \cdot 6H_2O$. The corresponding band assignments of $Mg_2P_2O_7 \cdot nH_2O$ (n = 6, 2, 0) are given in Table III.

This work illustrates the possibility of obtaining information about the POP angle from the infrared spectra results. From available spectroscopic data for the bridge stretching frequencies, it is possible to estimate the POP angle values in these salts using the magnitude of an empirical factor Δ[29] defined as:

$$100\,\Delta = (\nu^{as}\,\mathrm{POP} - \nu^{s}\,\mathrm{POP})/(\nu^{as}\,\mathrm{POP} + \nu^{s}\,\mathrm{POP}) \qquad (1)$$

TABLE III Infrared Spectra Data (cm^{-1}) and Band Assignments of $Mg_2P_2O_7 \cdot nH_2O$ (n = 6, 2, 0)

$Mg_2P_2O_7 \cdot 6H_2O$ IR (25°C)	$Mg_2P_2O_7 \cdot 2H_2O$ IR (210°C)	$\alpha Mg_2P_2O_7$ IR (665°C)	αMg_2P_2O IR [27, 28]	Assignment
3563 m				
3496 s				$\nu OH + \nu H_2O$
3465 b	3478 m			
3364 m	3341 s			
3222 m	3203 s			
3109 m				
1668 m	1525 b			δH_2O
1651 b				
		1209 bs	1211	
1179 s	1184 s	1187 bs	1193	ν^{as} PO_3 + ν^{s} PO_3
1148 vs	1163 vs	1128 bs	1138	
1110 s	1102 b	1102 vs	1118	
1034 m	1056 m		1105	
		1052 s	1081	
924 s	926 s	980 s	982	ν^{as} POP
856 bm	808 b			H_2O Libration
760 m	761 m	755 b	761	ν^{s} POP
		745 m	740	
635 w	647 w	636 b	638	ρH_2O
586 w	622 w	585 vs	587	δPO_3
574 w	598 bs	558 s	558	
568 w	587 sb	505 w	509	
561 s	584 s	450 s	457	
498 w	557 b		437	
485 w	546 s			
467 w	487 b			
452 w	471 w			
	463 m			

TABLE IV Values of the POP Angle in $Mg_2P_2O_7 \cdot nH_2O$ (n = 6, 2, 0)

	$Mg_2P_2O_7 \cdot 6H_2O$	$Mg_2P_2O_7 \cdot 2H_2O$	$\alpha Mg_2P_2O_7$
ν^{as} POP (cm^{-1})	924	926	980
ν^{s} POP (cm^{-1})	760	761	745
100 Δ	9.74	9.78	13.62
POP(°)exp.	125.6[15]	125.7[13]	144[1]
POP(°)*	125.2*	125.3*	143*

*this work, exp.: experimental.

and the plot given by A. Rulmont et al.[30] The numerical values are presented in Table IV.

The parameter (100 Δ) observed for these three salts corresponds respectively to a calculated POP angle values, which differs only slightly from the experimental values.[1,13,15]

CONCLUSION

The $Mg_2P_2O_7 \cdot 6H_2O$ was synthesized by an ion-exchange resin method and characterized by thermal analysis, x-ray powder diffraction, and infrared spectroscopy. Infrared spectrum of this salt was interpreted. The dehydration and phase transition of $Mg_2P_2O_7 \cdot 6H_2O$ can be described by the scheme

$$\begin{aligned} Mg_2P_2O_7 \cdot 6H_2O(25\text{–}260^\circ C) &\rightarrow Mg_2P_2O_7 \cdot 2H_2O(260\text{–}600^\circ C) \\ &\rightarrow \text{amorphous}Mg_2P_2O_7(600\text{–}800^\circ C) \\ &\rightarrow \alpha Mg_2P_2O_7 \qquad (2) \end{aligned}$$

EXPERIMENTAL

Synthesis

The starting materials were "analytically pure." An aqueous solution of $Na_4P_2O_7$ (0.1 M) passed through an ion-exchange resin "Amberlite IR 120," the diphosphoric acid $H_4P_2O_7$ thus obtained is immediately neutralised by a solution of Mg carbonate (0.1 M). After filtration, the limpid solution was kept for three days, the solid phase that formed was filtered by squeezing under a press and finally dried in air to give the title salt.

Investigation

All x-ray diffractograms were recorded on a D-5000 Siemens diffractometer calibrated with external silicon standard using the Cu Kα line (λ kα = 1.5411 Å). Infrared spectra were recorded on a Perkin Elmer 16 PC FTIR 132 spectrophotometer, using the KBr disc method. Thermogravimetric investigations were performed at atmospheric pressure with a 40 mg sample in platinum crucibles in the range 25–800°C using the SETERAM TG-DSC 111 equipped with Epson calculator. The sample was heated in argon with a 5°C/mn heating rate.

REFERENCES

[1] C. Calvo, *Acta Cryst*., **23**, 289 (1967).

[2] D. W. J. Cruickshank, H. Lynton, and G. A. Barclay, *Acta Cryst*., **15**, 491 (1962).

[3] A. E. El Belghitti, A. Boukhari, and E. M. Holt, *Acta Cryst*., **C50**, 482 (1994).

[4] L. O. Hagman, I. Jansson, and C. Magneli, *Acta Chem. Scand*., **22**, 1419 (1968).

[5] J. T. Hoggins, J. S. Swinnea, and H. Steinfink, *J. Solid State Chem*., **47**, 278 (1983).

[6] D. Kobashi, S. Kohara, J. Yamakawa, and A. Kawahara, *Acta Cryst*., **C53**, 1523 (1997).

[7] N. Krishnamachari and C. Calvo, *Acta Cryst.*, **B28**, 2883 (1972).

[8] K. Lukaszewicz, *Bull. Acad. Pol. Sci. Ser. Sci. Chem*., **15**, 47 (1967).

[9] B. E. Robertson and C. Calvo, *J. Solid State Chem.*, **1**, 120 (1970).

[10] V. K. Tondon and C. Calvo, *Indian J. Pure Ap. Phy.*, **19**, 756 (1981).

[11] M. Weil and R. Glaum, *Acta Cryst.*, **C53**, 1000 (1997).

[12] T. Stefanidis and A. G. Nord, *Acta Cryst.*, **C40**, 1995 (1984).

[13] J. Oka and A. Kawahara, *Acta Cryst.*, **B38**, 3 (1982).

[14] K. O. Kongshaug, H. Fjellvag, and K. P. Lillerud, *Solid State Sci.*, **2**, 205 (2000).

[15] M. Souhassou, C. Lecomte, and R. H. Blessing, *Acta Cryst.*, **B48**, 370 (1992).

[16] S. Schneider and R. L. Collin, *Inorg. Chem.*, **12**, 2136 (1973).

[17] H. Effenberger and F. Pertlik, *Monat. Für Chem.*, **124**, 381 (1993).

[18] H. G. Giesber III, M. B. Korzenski, W. T. Pennington, and J.W. Kolis, *Acta Cryst.*, **C56**, 399 (2000).

[19] N. S. Mandel, *Acta Cryst.*, **B31**, 1730 (1975).

[20] T. Balic-Zunic, M. R. Christoffersen, and J. Christoferssen, *Acta Cryst.*, **B56**, 953 (2000).

[21] A. V. Lavrov and T. A. Bykanova, *Neorg. Mater.*, **15**(9), 1653 (1979).

[22] B. M. Nirsha, T. V. Khomutova, A. A. Fakeev, et al., *Russian J. Inorg. Chemi*., **25**(2), 213 (1980).

[23] V. A. Kopilevich, L. N. Shchegrov, and T. K. Panchuk, *Russ. J. Inorg. Chem.*, **38**(5), 734 (1993).

[24] B. C. Cornilsen, *J. Mol. Struc.*, **117**, 1 (1984).

[25] I. Hubert, G. Aruldhas, and G. Keresztury, *J. of Raman Spectro*., **22**, 537 (1991).

[26] M. Harcharras, A. Ennaciri, A. Rulmont, and B. Gilbert, *Spectrochim. Acta Part A*, **53**, 345 (1997).

[27] B. C. Cornilsen and R. A. Condrate, *J. Inorg. Chem.*, **41**, 602 (1979).

[28] B. C. Cornilsen and R. A. Condrate, *J. Mol. Struc.*, **73** , 231 (1981).

[29] A. N. Lazarev, *Vibrational Spectra and Structure of Silicates*, English translation (Consultants Bureau, New York, 1972).

[30] A. Rulmont, R. Cahay, M. Liegeois-Duychaerts, and P. Tarte, *Eur. J. Solid State Inorg. Chem.*, **28**, 207 (1991).