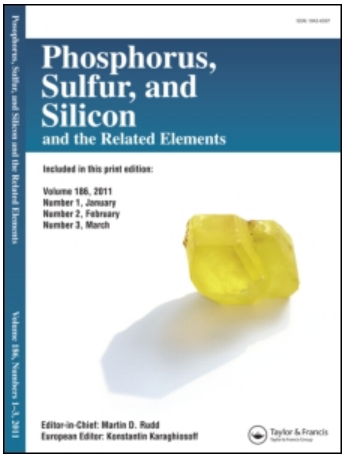

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THERMAL TRANSFORMATIONS AND INFRARED STUDIES OF $Mn_2P_2O_7$ · $2H_2O$

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Online publication date: 16 August 2010

To cite this Article Brouzi, K. , Ennaciri, A. and Harcharras, M.(2004) 'THERMAL TRANSFORMATIONS AND INFRARED STUDIES OF $Mn_2P_2O_7$ · $2H_2O$', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 7, 1329 — 1339
To link to this Article: DOI: 10.1080/10426500490468137
URL: http://dx.doi.org/10.1080/10426500490468137

Phosphorus, Sulfur, and Silicon, 179:1329–1339, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490468137

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THERMAL TRANSFORMATIONS AND INFRARED STUDIES OF $Mn_2P_2O_7 \cdot 2H_2O$

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(Received June 24, 2003; in final form October 28, 2003)

The thermal dehydration of $Mn_2P_2O_7 \cdot 2H_2O$ was studied, in the range 25–600°C by thermogravimetric analysis (TG-DTG and DSC), x-ray diffraction, and infrared spectroscopy. According to the (TG-DTG and 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, $Mn_2P_2O_7 \cdot 2H_2O$ decomposes to an amorphous product which crystallizes at 544°C to give anhydrous diphosphate $MN_2P_2O_7$. The free enthalpy of the dehydration of $Mn_2P_2O_7 \cdot 2H_2O$ and of the formation of $Mn_2P_2O_7$ have been calculated from thermogravimetric data. The infrared spectroscopic study of $Mn_2P_2O_7 \cdot 2H_2O$ 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 for the initial product and a linear POP bridge is observed in the diphosphate $Mn_2P_2O_7$. The infrared spectrum of $Mn_2P_2O_7 \cdot 2H_2O$ has been interpreted using factor group analysis.

Keywords: Dehydration; diphosphates; infrared spectra; manganese; thermal analyses (TG-DTG and DSC); x-ray diffraction

Many structural and studies of the vibational spectra of anhydrous diphosphates of general formula $M_2P_2O_7$ (where M is a bivalent metal) have been reported in the literature.[1–18] On the contrary, few investigations have also included structural, vibrational, and thermal studies of the hydrated forms $M_2P_2O_7 \cdot nH_2O$. For such compounds, the only known structures correspond to the Mg ($n = 1, 2, 3, 5, 6$),[19–21] Mn($n = 2$),[22] Co ($n = 2, 6$),[23,32] Fe($n = 2$),[24] and Ca ($n = 2, 4$)[25–26] species. Investigations of the thermal behaviour of these diphosphates have been carried out only for $Ni_2P_2O_7 \cdot nH_2O$ ($n = 6, 8$), $Zn_2P_2O_7 \cdot 5H_2O$, $Cu_2P_2O_7 \cdot 5, 3H_2O$[27–29] and $Mg_2P_2O_7 \cdot 6H_2O$,[30] while

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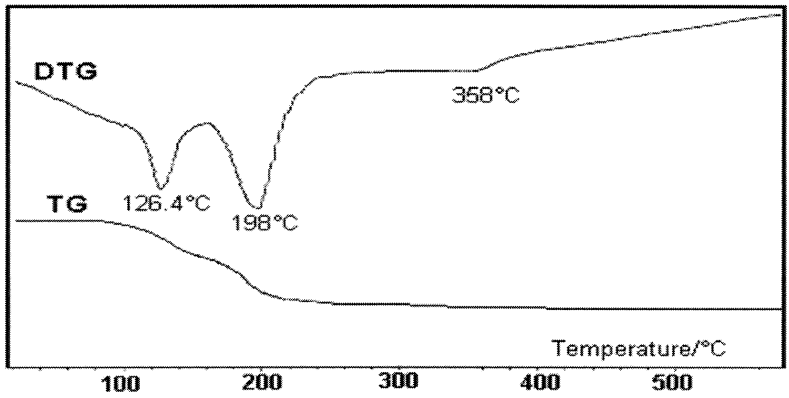

FIGURE 1 DTG-TG curve of $Mn_2P_2O_7 \cdot 2H_2O$.

for $Ca_2P_2O_7 \cdot 2H_2O$ only the vibrational study has been performed.[31] In this article, we report thermal and infrared spectroscopic studies on $Mn_2P_2O_7 \cdot 2H_2O$.

RESULTS AND DISCUSSION

Thermal Study of $Mn_2P_2O_7 \cdot 2H_2O$ by TG-DTG and DSC Curves

From room temperature up to 600°C, Figures 1 and 2 show the TG-DTG and DSC thermograms of $Mn_2P_2O_7 \cdot 2H_2O$ respectively. In the TG curve, the weight loss can be divided into two stages.

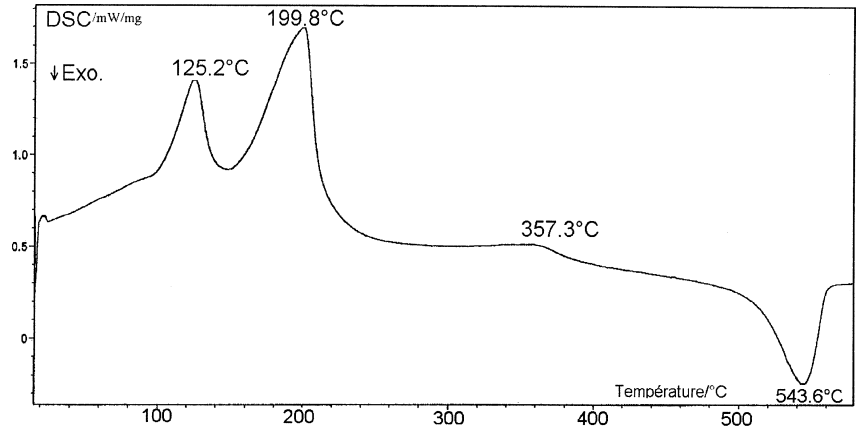

FIGURE 2 DSC curve of $Mn_2P_2O_7 \cdot 2H_2O$.

TABLE I Enthalpy (ΔH) of Dehydration and Phase Transition of $Mn_2P_2O_7 \cdot 2H_2O$

Peaks	T^i (°C)	T^f (°C)	T^m (°C)	ΔH (J/g)
1 endo.	80	138	125.2	62.86
2 endo.	185	240	199.8	232.6
3 exo.	485	570	543.6	−99.97

endo.: endothermic, exo.: exothermic, T^i: initial temperature, T^f: final temperature, T^m: temperature at a maximum rate.

In the range 85–260°C, the two observed endotherms in the DSC curve at 125.2 and 199.8°C are considered to result from the removal of water molecules from the structure of $Mn_2P_2O_7 \cdot 2H_2O$. The endothermic peak at a maximum rate at 357.3°C corresponds to the formation of amorphous phase; according to the scheme:

$$Mn_2P_2O_7 \cdot 2H_2O \rightarrow Mn_2P_2O_7 \text{ (amorphous)} + 2H_2O\cdot$$

In the range 400–600°C, the DSC curve exhibits an exothermic peak, at 543.6°C which is accompanied by the transformation of the title compound to another phase.

The calculated enthalpy, ΔH of these two stages of the dehydration and for the phase transition of the title salt are summarized in Table I.

Thermal Study of $Mn_2P_2O_7 \cdot 2H_2O$ by X-Ray Diffraction and Infrared Spectroscopy

X-Ray Diffraction

According to the x-ray diffraction data of $Mn_2P_2O_7 \cdot 2H_2O$, this salt is stable in the range 25–80°C. In the range 80–360°C, the removal of all the water molecules destroyed the crystalline network yielding an intermediate amorphous phase indicated by a decrease in the intensity of a number of reflections and by the disappearance of the most of them.

In the range, 400–600°C the sample thus obtained is identified by x-ray patterns as anhydrous diphosphate $Mn_2P_2O_7$;[10,12] in relation with the DSC curve, the exothermic peak observed at 543.6°C, can be attributed to the crystallisation of the anhydrous diphosphate $Mn_2P_2O_7$. X-ray patterns of $Mn_2P_2O_7 \cdot 2H_2O$ and of its heated products are listed in Table II.

Infrared Spectroscopy

The infrared spectra of the products formed upon heating of $Mn_2P_2O_7 \cdot 2H_2O$ at different temperatures are illustrated in Figure 3.

TABLE II X-Ray Patterns of $Mn_2P_2O_7 \cdot 2H_2O$ and of the Products, Obtained During the Process of Heating

$Mn_2P_2O_7 \cdot 2H_2O$ 25–80°C			$Mn_2P_2O_7$ 400–600°C	
d_{hkl}	I/Io	Amorphous 260–380°C	d_{hkl}	I/Io
7.182	80		5.168	10
6.681	76		4.433	8
5.871	10		3.110	58
5.193	100		3.085	100
4.787	7		2.944	65
4.690	5		2.618	20
4.460	30		2.587	44
4.170	15		2.376	4
4.034	30		2.347	5
3.924	35	Amorphous phase	2.210	7
3.834	18		2.182	12
3.771	10		2.171	22
3.645	55		2.146	8
3.582	18		2.094	23
3.495	12		2.078	29
3.336	13		2.071	28
3.298	15		2.053	15
3.235	23			
3.217	29			
3.139	18			
2.992	15			
2.958	51			
2.935	23			
2.869	73			
2.846	34			
2.811	60			
2.678	85			
2.668	59			
2.661	79			
2.612	42			
2.596	47			
2.577	44			
2.564	40			
2.525	85			
2.501	7			
2.462	40			
2.414	30			

d_{hkl}: x-ray data.

According to the infrared spectra of $Mn_2P_2O_7 \cdot 2H_2O$ and of its heated products, this salt is stable in the range 25–80°C.

With the help of the TG-DTG and DSC study of $Mn_2P_2O_7 \cdot 2H_2O$, we can suggest that infrared spectra in the range 85–380°C indicate

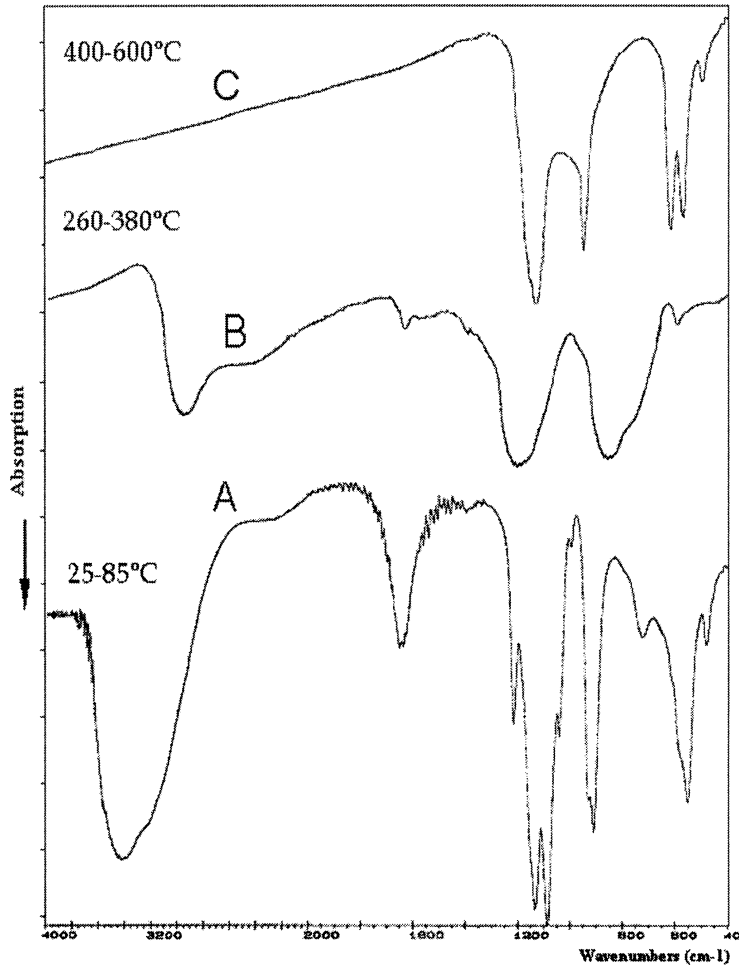

FIGURE 3 Infrared spectra of $Mn_2P_2O_7 \cdot 2H_2O$ (A) and of the products obtained during the heating process: amorphous phase (B) and $Mn_2P_2O_7$ (C).

a great change, compared to the initial one: Differences are characterized by decreases of the number of the water bands (νH_2O and δH_2O) and some bands location, they correspond to the removal of all water molecules, broadened bands appear in the infrared spectra after heating the initial product between 260–380°C indicating the formation of an amorphous phase of $Mn_2P_2O_7$. The heated product between 400–600°C shows an infrared spectrum similar to that of $Mn_2P_2O_7$, as previously published.[18]

Factor Group Analysis and Interpretation of the Infrared Spectrum of $Mn_2P_2O_7 \cdot 2H_2O$

Factor Group Analysis

$Mn_2P_2O_7 \cdot 2H_2O$ crystallizs in the monoclinic system, with space group $P2_1/n$ (C_{2h}^5) and four molecules per unit cell with the following parameters: $a = 6.461(2)$, $b = 14.325(4)$, $c = 7.570(3)$ Å and $\beta = 95.20(4)^\circ$.[22] The P_2O_7 group exibits a bent POP angle [127.5(2)°] and an eclipsed configuration, therefore the free ion group must be C_{2v}. In this structure, the salt contains two types of Mn^{2+} lying on the general position. The two water molecules and the $P_2O_7^{4-}$ ions have also C_1 as site group. The factor group analysis is carried out on the basis of the above data following the method of Fateley et al.[33] to get the irreducible representations. The results are given in Table III.

The irreducible representation of the title compound in the C_{2h} factor group (excluding acoustic modes) is:

$$\Gamma_{201} = 51A_g + 51B_g + 50A_u + 49B_u$$

The A_g and B_g species are Raman active, while A_u and B_u are infrared active. The modes belonging to the A_g species are usually more intense in the Raman spectrum than the B_g species. According to the selection rules, 102 bands (belonging to the A_g and B_g species) are active in the Raman spectrum whereas 99 bands (belonging to the A_u and B_u species) are active in the infrared spectrum.

The internal modes of the $[P_2O_7]^{4-}$ anions and H_2O of $Mn_2P_2O_7 \cdot 2H_2O$ are shown by the correlation scheme reported in, Tables IV and V respectively.

The factor group analysis predicts the distribution of irreducible representation of the internal modes of $[P_2O_7]^{4-}$ anions and H_2O in the

TABLE III Summary of the Factor Group Analysis of $Mn_2P_2O_7 \cdot 2H_2O$

Factor group species C_{2h}^5	$P_2O_7^{4-}$ modes-C_1-sites		H_2O modes-C_1-sites		Mn^{2+} C_1-sites	Optical modes	Accoustic modes
	Int.	Ext.	Int.	Ext.			
A_g	21	3T, 3L	3×2	(3T, 3L) × 2	6T	51	—
B_g	21	3T, 3L	3×2	(3T, 3L) × 2	6T	51	—
A_u	21	3T, 3L	3×2	(3T, 3L) × 2	6T	50	1
B_u	21	3T, 3L	3×2	(3T, 3L) × 2	6T	49	2
Active modes	84	12T, 12L	24	24T, 24L	24T	201	3

T: translation, L: libration, int: internal, ext.: external.

TABLE IV Correlation Scheme for the Internal Modes of the $[P_2O_7]^{4-}$ Anion in $Mn_2P_2O_7 \cdot 2H_2O$

C_{2v} free ion group		C_1 site group	C_{2h} factor group
7 A_1 (ir, Ra)			21A_g (Ra)
4 A_2 (Ra)		21 A(ir, Ra)	21B_g (Ra)
6 B_1 (ir, Ra)			21A_u (ir)
4 B_2 (ir, Ra)			21B_u (ir)
Activity	Free ion	Site group	Factor group
Raman	21	21	42
Infrared	17	21	42
Coincidences	17	21	0
Total	21	21	84

Ir: infrared, Ra: Raman.

$Mn_2P_2O_7 \cdot 2H_2O$ to be as follows:

$$\Gamma^{P_2O_7}_{(internal)} = 21A_g\ (Ra) + 21B_g\ (Ra) + 21A_u\ (ir) + 21B_u\ (ir).$$

$$\Gamma^{H_2O}_{(internal)} = 6A_g\ (Ra) + 6B_g\ (Ra) + 6A_u\ (ir) + 6B_u\ (ir).$$

From the correlation between D_{3d}, C_1 and C_{2h} (Table VI) and from the spectroscopic investigation of diphosphates,[4–6] it is possible to calculate the contribution in the different frequency ranges of the $[P_2O_7]^{4-}$ anions in $Mn_2P_2O_7 \cdot 2H_2O$, using the factor group analysis.

Interpretation of the Infrared Spectrum of $Mn_2P_2O_7 \cdot 2H_2O$

The infrared spectrum of $Mn_2P_2O_7 \cdot 2H_2O$ is shown in Figure 3-A, and the corresponding band assignments are given in Table VII.

TABLE V Correlation Scheme for the Internal Modes of H_2O Molecules in $Mn_2P_2O_7 \cdot 2\ H_2O$

			C_{2h} factor group	
C_{2v} free ion group		C_1 site group	(1-site)	(2-sites)
2A_1 (ir, Ra)			3 A_g (Ra)	6A_g (Ra)
0A_2 (Ra)		3 A(ir,Ra)	3 B_g (Ra)	6B_g (Ra)
1B_1 (ir, Ra)			3 A_u (ir)	6A_u (ir)
0B_2 (ir, Ra)			3 B_u (ir)	6B_u (ir)
Activity	Free ion	Site group	Factor group	
Raman	3	3	6	12
Infrared	3	3	6	12
Coincidences	3	3	0	0
Total	3	3	12	24

TABLE VI Correlation Tables for $[P_2O_7]^{4-}$ Anions Between D_{3d}, C_1 and C_{2h}

Normal modes	D_{3d}	C_1	C_{2h}
νPO_3	$A_{1g} + A_{2u} + E_g - E_u$	6A	$6(A_g + A_u + B_g + B_u)$
νPOP	$A_{1g} + A_{2u}$	2A	$2(A_g + A_u + B_g + B_u)$
δPO_3	$A_{1g} + A_{2u} + E_g + E_u$	6A	$6(A_g + A_u + B_g + B_u)$
ρPO_3	$E_g + E_u$	4A	$4(A_g + A_u + B_g + B_u)$

Vibrations of H_2O Molecules

In the infrared spectrum of $Mn_2P_2O_7 \cdot 2H_2O$ (Figure 3-A), broad bands in the region (2800–3800 cm^{-1}) correspond to the stretching vibration of both water molecules (νH_2O).[8] The bending vibrations of H_2O (δH_2O) are seen in the range 1600–1700 cm^{-1}.[9–10] The splitting of the stretching and bending vibrations of water molecules, observed at 3400 and 3200 cm^{-1} and 1639, 1628 cm^{-1}, respectively, is probably due to different water molecules.[11] Indeed, the crystal data show two different

TABLE VII Band Assignments for $Mn_2P_2O_7 \cdot 2H_2O$

$Mn_2P_2O7 \cdot 2H_2O$ infrared data	Assignments
3400 s,b	νH_2O
3200 s,sh	
1639 m	δH_2O
1628 m	
1211 m	$\nu^{as}PO_3$
1133 s	+
1089 vs	$\nu^{s}PO_3$
1048 m	
1000 w	
928 s	ν^{as} POP
911 s	
733 m	ν^{s} POP
662 w	ρH_2O
607 sh	$\delta PO_3 + \rho PO_3$
583 sh	
550 s	
489 m	
425 vw	

s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder, ν = stretching, δ = bending, ρ = rocking.

molecules of water.[1] According to the thermal analysis the departure of water molecules takes place in two stages. The rocking vibration for the water molecules ρH_2O is located at 662 cm^{-1}.[31]

The PO_3 Stretching Modes

The asymmetric (ν^{as} PO_3) and symmetric (ν^{s} PO_3) terminal stretching vibrational modes of PO_3 usually occur in the region 1250–975 cm^{-1}.[35–41] These vibrational modes belong to the following representations: $6A_g + 6A_u + 6B_g + 6B_u$. The intense band observed at 1089 cm^{-1} correspond to the asymmetric vibration mode of the PO_3 group.

The POP Bridge Stretching Vibrations

For the POP bridge vibrations, two components are observed in the infrared spectrum at ν^{as} POP: 928, 911 cm^{-1}; ν^{s} POP: 733 cm^{-1}.[35–38] These vibrational modes belong to the following representations:

$$\Gamma \nu_{as\ POP} = 2A_g + 2A$$
$$\Gamma \nu_{s\ POP} = 2A_g + A_u. \quad (1)$$

The Deformation and Rocking Vibrations of PO_3

The vibrational modes belong to the following representations: $\Gamma(\delta PO_3) = 6(A_g + A_u + B_g + B_u)$; $\Gamma(\rho PO_3) = 4(A_g + A_u + B_g + B_u)$. They correspond to the deformation and rocking modes of the PO_3 groups (δPO_3, ρPO_3) which are detected in the range, 600–400 cm^{-1}, at 583, 550 cm^{-1}, and 489 cm^{-1}.[35–37]

CONCLUSION

The thermal transformation of $Mn_2P_2O_7 \cdot 2H_2O$ diphosphate has been studied by (TG-DTG and DSC) analysis, x-ray diffraction, and infrared spectroscopy. The dehydration and phase transition of this salt can be described by the scheme:

$$Mn_2P_2O_7 \cdot 2H_2O(25{-}80^\circ C) \rightarrow \text{amorphous phase } (80{-}360^\circ C)$$
$$\rightarrow Mn_2P_2O_7\ (400{-}600^\circ C).$$

The infrared spectrum of $Mn_2P_2O_7 \cdot 2H_2O$ has been interpreted using group analysis.

EXPERIMENTAL

Synthesis

The starting materials were "analytically pure." An aqueous solution of $Na_4P_2O_7$ (0.1 M) was 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 $MnCO_3$ (0.1 M). After filtration, the pink solution was kept for 3 days, the solid phase thus formed was filtered then dried in air to give the title salt.

Investigation

All x-ray diffractograms were recorded on a D-5000 Siemens diffractometer calibrated with an external silicon standard using the Cu Kα line ($\lambda k\alpha = 1.5411$ Å). The infrared spectra were recorded on a Perkin Elmer 16 PC FTIR 132 spectrophotometer, using the KBr disc method. The thermal analysis curves were recorded on Seteram G 70 and DCS 92 type devices equipped with an Epson calculator, at atmospheric pressure, at a heating rate of 10°C/mn.

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