



Science Arena Publications
Specialty Journal of Chemistry
ISSN:2521-3164

Available online at www.sciarena.com
2019, Vol, 4 (2): 10-17

Interpretation of the IR Spectrum of Manganese Cyclotetraphosphate $Mn_2P_4O_{12}$ and Vibrational Analysis of the Cycle $P_4O_{12}^{4-}$

Soufiane Zerraf*, Malika Tridane, Said Belaouad

Laboratory of Physical Chemistry of Materials LCPM, Ben M'sik Faculty of Sciences, Hassan II University of Casablanca, Morocco.

*Corresponding Author

Abstract: *The X-ray diffraction structural study showed that the cyclotetraphosphate of manganese, $Mn_2P_4O_{12}$ crystallizes in the monoclinic system, $Z = 4$, with space group $C_{2/c}$ (C_6^{2h}), with the following lattice parameters: $a = 11.883$ (1) Å - $b = 8.588$ (2) Å $c = 10.137$ (1) Å, $\beta = 119.21$ (2) °. The crystal lattice contains 4 cycles $P_4O_{12}^{4-}$ with symmetry C_i . All the atoms occupy the sites "8f" of symmetry C_i except manganese Mn atoms, which are non equivalent, half occupy the 4 sites "e" of symmetry C_i and the other half occupy the 4 sites "d" of symmetry C_2 .*

Keywords: *X-ray Diffraction, Cyclotetraphosphate, Condensed Phosphates, Infrared Vibration Spectrometry*

INTRODUCTION

G. Foumakoye and al. (1990) have studied a large number of cyclotetraphosphates of structures determined by X-ray diffraction by IR spectroscopy and Raman scattering and have adopted the same approach as that adopted by K. Sbai (1984) for a cycle of order 3. They confirmed and extended the findings of A. N. Lazarev (1974) and showed that it is possible to characterize the $P_4O_{12}^{4-}$ cyclic anion, particularly by its IR spectrum, and to some extent to forecast the symmetry of Cycle P_4O_{12} , as well as a P_3O_9 cycle, by exploiting the number, profile and position of the sPOP).¹ Observed IR bands in the POP valence symmetric vibration domain the diagram of figure 1 gives the bands observed in the IR spectra of cyclotetraphosphates as a function of the symmetry of the cycle of each class of isomorphous compounds.

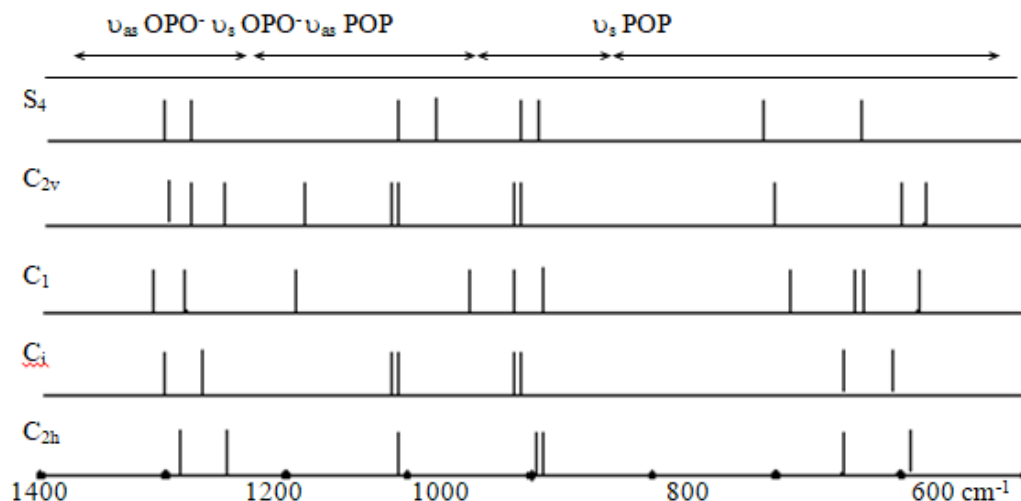


Figure 1: Diagram of the bands in the IR spectra of cyclotetraphosphates according to the symmetry of the cycle.

A detailed examination of the IR spectra of a series of cyclotetraphosphates of different symmetries: S_4 , C_{2v} , C_1 , C_{2h} and C_i allowed G. Foumakoye and al. (1990) to reveal a general pattern characterized

From 1330 to 1180 cm^{-1} : antisymmetric vibration of ν_{as} OPO $^-$

From 1180 to 1080 cm^{-1} : symmetrical vibration of ν_s OPO $^-$

From 1060 to 960 cm^{-1} : antisymmetric vibration of ν_{as} POP

From 850 to 660 cm^{-1} : symmetrical vibration of ν_s POP

<660 cm^{-1} : deformation of the cycle + translations and rotations.

Results and Discussion

The experimental IR spectra were in accordance with the theoretical predictions of Table 1. As a result, the authors revealed the spectral characteristics of each type of symmetry:

- The presence of two bands, in the area of ν_s POP vibrations, of medium intensity, one towards 800 cm^{-1} accompanied by another (possibly split) around 700 cm^{-1} , characterizes a cyclotetraphosphate with anion of symmetry S_4 . When these two bands are observed, a third band is observed of very low intensity situated between 690-660 cm^{-1} , there is a cyclotrophosphate anion of C_{2v} symmetry (theoretically, we can also expect the splitting of the Band at 700 cm^{-1});
For symmetries C_i (or C_{2h}), we see the disappearance of the band located around 800 cm^{-1} , observed in the case of the symmetry S_4 and C_{2v} , and the splitting of that around 700 cm^{-1} ;
- in the case of symmetry C_1 , the known cases show that it is translated into IR by the presence of a band towards 800 cm^{-1} , accompanied by a doublet between 730-770 cm^{-1} and a very Low band to 670 cm^{-1} .

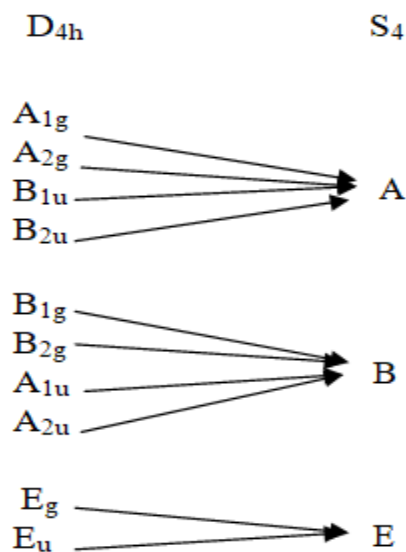
1. Theoretical analysis of a $P_4O_{12}^{4-}$ cycle of molecular symmetry D_{4h}

We have found all the results given by G. Foumakoye and al. (1990) for the various symmetries encountered in the $P_4O_{12}^{4-}$ anion. But K. Sbai (1984) detected an error on the way in which modes are transformed during the transition from the symmetry D_{4h} to the symmetry S_4 . Indeed, during the transition from symmetry D_{4h} to symmetry S_4 the modes are transformed in the following way:

Table 1: Description of normal valence vibration modes of the P_4O_{12} cycle for the known symmetries.

Description des vibrations	Groupe de maille		Groupes de sites					
	D_{4h}		S_4	C_{2v}	C_{2h}		C_i	C_1C_1
				σ_v	C'_2	C''_2		
$\nu_{as} OPO^-$	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra
A_{2u}	a -	A - a	A_1 a a	B_u B_u a -	A_{1u} a -	A_{1u} a -	A' A a a	A'' A a a
B_{1u}	- -	B a a	A_2 - a	A_u B_u a -	A_{1u} a -	A_{1u} a -	A' A a a	A'' A a a
E_g	- a	E a a	$\begin{Bmatrix} B_1 \\ B_2 \end{Bmatrix}$ a a	$\begin{Bmatrix} A_g \\ B_g \end{Bmatrix}$ $\begin{Bmatrix} A_g \\ B_g \end{Bmatrix}$ - a	$\begin{Bmatrix} A_g \\ A_g \end{Bmatrix}$ - a	$\begin{Bmatrix} A_g \\ A_g \end{Bmatrix}$ - a	$\begin{Bmatrix} A' \\ A'' \end{Bmatrix}$ $\begin{Bmatrix} A \\ A \end{Bmatrix}$ a a	$\begin{Bmatrix} A' \\ A'' \end{Bmatrix}$ $\begin{Bmatrix} A \\ A \end{Bmatrix}$ a a
$\nu_s OPO^-$	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra
A_{1g}	- a	A - a	A_1 a a	A_g B_g - a	A_g - a	A_g - a	A' A a a	A'' A a a
B_{2g}	- a	B a a	A_2 - a	B_g A_g - a	A_g - a	A_g - a	A' A a a	A'' A a a
E_u	a -	E a a	$\begin{Bmatrix} B_1 \\ B_2 \end{Bmatrix}$ a a	$\begin{Bmatrix} A_u \\ B_u \end{Bmatrix}$ $\begin{Bmatrix} A_u \\ B_u \end{Bmatrix}$ a -	$\begin{Bmatrix} A_u \\ A_u \end{Bmatrix}$ a -	$\begin{Bmatrix} A_u \\ A_u \end{Bmatrix}$ a -	$\begin{Bmatrix} A' \\ A'' \end{Bmatrix}$ $\begin{Bmatrix} A \\ A \end{Bmatrix}$ a a	$\begin{Bmatrix} A' \\ A'' \end{Bmatrix}$ $\begin{Bmatrix} A \\ A \end{Bmatrix}$ a a
$\nu_{as} POP$	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra
A_{2g}	- -	A - a	A_2 - a	B_g B_g - a	A_g - a	A_g - a	A'' A a a	A'' A a a
B_{2g}	- a	B a a	A_2 - a	B_g A_g - a	A_g - a	A_g - a	A'' A a a	A'' A a a
E_u	a -	E a a	$\begin{Bmatrix} B_1 \\ B_2 \end{Bmatrix}$ a a	$\begin{Bmatrix} A_u \\ B_u \end{Bmatrix}$ $\begin{Bmatrix} A_u \\ B_u \end{Bmatrix}$ a -	$\begin{Bmatrix} A_u \\ A_u \end{Bmatrix}$ a -	$\begin{Bmatrix} A_u \\ A_u \end{Bmatrix}$ a -	$\begin{Bmatrix} A' \\ A'' \end{Bmatrix}$ $\begin{Bmatrix} A \\ A \end{Bmatrix}$ a a	$\begin{Bmatrix} A' \\ A'' \end{Bmatrix}$ $\begin{Bmatrix} A \\ A \end{Bmatrix}$ a a
$\nu_s POP$	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra	IR Ra
A_{1g}	- a	A - a	A_1 a a	A_g A_g - a	A_g - a	A_g - a	A' A a a	A' A a a
B_{1g}	- a	B a a	A_1 a a	A_g B_g - a	A_g - a	A_g - a	A' A a a	A' A a a
E_u	a -	E a a	$\begin{Bmatrix} B_1 \\ B_2 \end{Bmatrix}$ a a	$\begin{Bmatrix} A_u \\ B_u \end{Bmatrix}$ $\begin{Bmatrix} A_u \\ B_u \end{Bmatrix}$ a -	$\begin{Bmatrix} A_u \\ A_u \end{Bmatrix}$ a -	$\begin{Bmatrix} A_u \\ A_u \end{Bmatrix}$ a -	$\begin{Bmatrix} A' \\ A'' \end{Bmatrix}$ $\begin{Bmatrix} A \\ A \end{Bmatrix}$ a a	$\begin{Bmatrix} A' \\ A'' \end{Bmatrix}$ $\begin{Bmatrix} A \\ A \end{Bmatrix}$ a a

a = actif, - = inactif, $\begin{Bmatrix} \\ \end{Bmatrix}$ = doublet.



While for G. Foumakoye and al. (1990), the mode A_{2u} of the symmetry D_{4h} is transformed into A of the symmetry S₄, which is incorrect.

2. Interpretation of the IR spectrum of manganese cyclotetraphosphate Mn₂P₄O₁₂ Vibrational analysis of the cycle P₄O₁₂⁴⁻ isolated with local symmetry C_i

According to E. Steger and A. Simon (1957), the highest symmetry which the anion P₄O₁₂⁴⁻ can possess is D_{4h}. For this idealized symmetry the reduced representation is: $\Gamma = 4A_{1g} + 2A_{2g} + 3B_{1g} + 4B_{2g} + 4E_g + A_{1u} + 3A_{2u} + 3B_{1u} + 2B_{2u} + 6E_u$. The separation of normal modes of vibration into stretching and bending modes, $\Gamma = \Gamma_{\text{stretching}} + \Gamma_{\text{bending}}$, of the cycle P₄O₁₂⁴⁻ was also given by the authors G. Foumakoye and al. (1990):

$$\Gamma_{\text{stretching}} = 2A_{1g} + A_{2g} + B_{1g} + 2B_{2g} + E_g + A_{2u} + B_{1u} + 3E_u.$$

$$\Gamma_{\text{bending}} = 2A_{1g} + A_{2g} + 2B_{1g} + 2B_{2g} + 3E_g + A_{1u} + 2A_{2u} + 2B_{1u} + 2B_{2u} + 3E_u.$$

In the case of the "isolated" cycle P₄O₁₂⁴⁻ with symmetry C_i, The group theory predicts 42 normal modes : $\Gamma_{\text{int}} = 21 A_u + 21 A_g$. The mode A_u is active only in IR and the mode A_g is active only in Raman. The separation of normal modes of vibration of the isolated cycle with symmetry C_i is given in Table 2.

It is clear from this analysis that the site symmetry of the P₄O₁₂⁴⁻ cycle is C_i. The group theory predicts two IR observed frequencies (2A_u) and two Raman frequencies (2A_g) in each of the four domains of stretching vibrations. The site group C_i is centrosymmetric, no IR / Raman coincidence is possible Table 3.

Table 2: Separation of the normal modes of vibration, IR and Raman activities of the cycle P₄O₁₂⁴⁻ isolated with symmetry C_i (Steger and al., 1957)

	IR	Raman
Internal vibration modes of cycle with symmetry C _i	21 A _u	21 A _g
Stretching modes	8 A _u	8 A _g
Bending modes	13 A _u	13 A _g

The experimental IR spectrum of Mn₂P₄O₁₂ prepared by dry method and that obtained during the dehydration of Mn(NH₄)₄(P₃O₉)₂.6H₂O between 320 and 970°C are the same. It shows, three very distinct spectral regions, in the domain of stretching vibrations of the cycle (1400-650 cm⁻¹) by S. zerraf and al. (2017): From 1330 to 1180 cm⁻¹: in this vibrations domain $\nu_{\text{as}} \text{OPO}^-$, 3 frequencies are observed (1315, 1301 and 1275 cm⁻¹),

From 1180 to 970 cm⁻¹: in these two vibrations domains $\nu_{\text{s}} \text{OPO}^-$ and $\nu_{\text{as}} \text{POP}$, 4 frequencies are observed (1116, 1101 cm⁻¹) and (1048, 1017 cm⁻¹),

From 850 to 700 cm⁻¹: vibrations domain of $\nu_{\text{s}} \text{POP}$, three frequencies are observed at 733 cm⁻¹, 712 cm⁻¹ and 669 cm⁻¹.

The position and the profile of the bands situated at 733 and 712 cm⁻¹ for the stretching vibrations $\nu_{\text{s}} \text{POP}$ suggest that the ring P₄O₁₂⁴⁻ has the symmetry C_i or C_{2h}. In fact, all the other known symmetries S₄, C_{2v} and C₁, present in the domain of the stretching vibrations $\nu_{\text{s}} \text{POP}$, in addition to the two bands at 733 and 712 cm⁻¹, a band around 800 cm⁻¹ (Foumakoye et al., 1990). But for both the symmetries C_i and C_{2h} of an isolated P₄O₁₂⁴⁻ ring, two frequencies are predicted in each of the four domains of the stretching vibrations ($\nu_{\text{as}} \text{OPO}^-$, $\nu_{\text{s}} \text{OPO}^-$, $\nu_{\text{as}} \text{POP}$, $\nu_{\text{s}} \text{POP}$) of the ring P₄O₁₂⁴⁻ (Table 3). The IR spectrum of Mn₂P₄O₁₂ shows three frequencies in the domain of the stretching vibrations $\nu_{\text{as}} \text{OPO}^-$: 1330-1180 cm⁻¹. These frequencies are observed at 1315, 1301 and 1275 cm⁻¹. The site symmetry C_i doesn't allow the explanation of the three frequencies observed in the domain of the stretching vibrations $\nu_{\text{as}} \text{OPO}^-$. Therefore, we make the analysis of the vibrations of the

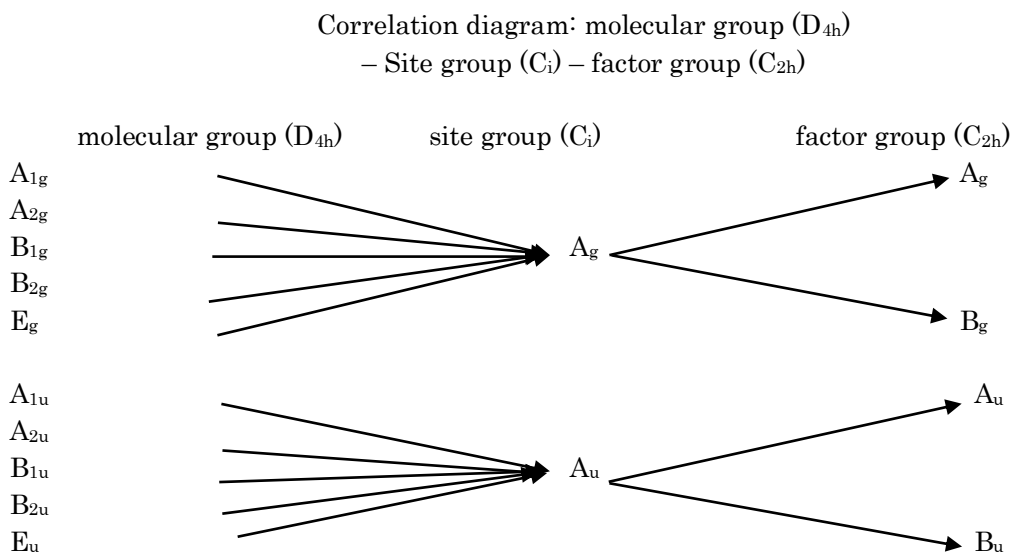
crystalline lattice in order to take into account the interaction between the four cycles of the crystalline lattice of $\text{Mn}_2\text{P}_4\text{O}_{12}$.

3. Analysis of the vibrations of the manganese cyclotetraphosphate $\text{Mn}_2\text{P}_4\text{O}_{12}$

The crystalline lattice of $\text{Mn}_2\text{P}_4\text{O}_{12}$ contains 4 cycles $\text{P}_4\text{O}_{12}^{4-}$ with symmetry C_i , $Z = 4$, while the primitive lattice contains only 2 cycles $\text{P}_4\text{O}_{12}^{4-}$. The analysis of the vibrations by the method of factor group (C_{2h}) leads to the results gathered in Table 4.

For the two cycles of the primitive lattice, the group theory leads to the existence of 42 IR active modes ($21_{A_u} + 21_{B_u}$) and the same number of modes in Raman ($21_{A_g} + 21_{B_g}$). No IR / Raman coincidence is possible for the factor group (C_{2h}) centrosymmetric.

During the passage from the isolated cycle with symmetry C_i to the primitive lattice, each band with mode A_u active in IR or mode A_g active in Raman should lead respectively to a doublet ($A_u + B_u$) or ($A_g + B_g$) according to the correlation scheme as follows :



It is useful to have a clear idea about the way the stretching vibration modes are corresponding for the idealized isolated cycle D_{4h} and the isolated cycle in the crystal with site symmetry C_i and then when the coupling is established, optionally, between the cycles in the crystal with space group $C_{2/c}$ ($C_{6_{2h}}$)(Table 3).

The results of this theoretical analysis is that the possible interaction or vibrational couplings between the two cycles $\text{P}_4\text{O}_{12}^{4-}$ of the primitive lattice $\text{Mn}_2\text{P}_4\text{O}_{12}$ should occur on the IR spectrum and the Raman spectrum by the existence of four observed frequencies in each of the 4 domains of the stretching vibrations (ν_{as} OPO $^-$, ν_s OPO $^-$, ν_{as} POP, ν_s POP) of the $\text{P}_4\text{O}_{12}^{4-}$ ring.

Table 3: Comparison of the stretching vibration modes of the cycle P_4O_{12} «isolated" with local symmetry C_i with the two cycles of the primitive lattice interacting with each other in $Mn_2P_4O_{12}$

Vibrations description	Cycle P_4O_{12} isolated with ideal symmetry D_{4h}		Site symmetry C_i		Group factor C_{2h}	
	IR	Ra	IR	Ra	IR	Ra
$\nu_{as} OPO^-$	A_{2u}	IR -	A_u	IR -	A_u	IR -
	B_{1u}	- -	A_u	IR -	B_u	IR -
	E_g	- Ra	A_g	- Ra	A_g	- Ra
			A_g	- Ra	B_g	- Ra
$\nu_s OPO^-$	A_{1g}	- Ra	A_g	- Ra	A_g	- Ra
	B_{2g}	- Ra	A_g	- Ra	B_g	- Ra
	E_u	IR -	A_u	IR -	A_u	IR -
			A_u	IR -	B_u	IR -
$\nu_{as} POP$	A_{2g}	- -	A_g	- Ra	A_g	- Ra
	B_{2g}	- Ra	A_g	- Ra	B_g	- Ra
	E_u	IR -	A_u	IR -	A_u	IR -
			A_u	IR -	B_u	IR -
$\nu_s POP$	A_{1g}	- Ra	A_g	- Ra	A_g	- Ra
	B_{1g}	- Ra	A_g	- Ra	B_g	- Ra
	E_u	IR -	A_u	IR -	A_u	IR -
			A_u	IR -	B_u	IR -

Table 4: Separation of the normal modes of vibration, IR and Raman activities of the $P_4O_{12}^{4-}$ cycles in $Mn_2P_4O_{12}$

	IR	Raman
Active internal modes (total)	$27A_u + 27B_u$	$25 A_g + 26B_g$
Lattice vibration modes	$6 A_u + 6 B_u$	$A_g + 2 B_g$
Libration modes of the cycles	---	$3 A_g + 3 B_g$
Internal vibration modes of the cycles	$21 A_u + 21 B_u$	$21 A_g + 21 B_g$
Stretching modes	$8 A_u + 8 B_u$	$8 A_g + 8 B_g$
Bending modes	$13 A_u + 13 B_u$	$13 A_g + 13 B_g$

The experimental IR spectrum of $\text{Mn}_2\text{P}_4\text{O}_{12}$ shows two frequencies in each of the two fields of the stretching vibrations $\nu_s \text{OPO}^-$ (1116, 1101 cm^{-1}), $\nu_{as} \text{POP}$ (1048, 1017 cm^{-1}) and three frequencies in each of the two domains of the stretching vibrations $\nu_{as} \text{OPO}^-$ (1315, 1301 and 1275 cm^{-1}) and $\nu_s \text{POP}$ (733, 712 and 669 cm^{-1}). The assignment of the stretching frequencies of the $\text{P}_4\text{O}_{12}^{4-}$ cycles on the basis of factor group C_{2h} is given in Table 5. Vibrational couplings are therefore effective only for antisymmetric vibrations, $\nu_{as} \text{OPO}^-$, involving external oxygen atoms of the ring which are the most susceptible to interact with a neighbor ring through bonds between cation and external oxygen atoms of the $\text{P}_4\text{O}_{12}^{4-}$ cycle. But, for the vibrations of the groups P-Oi-P, $\nu_{as} \text{POP}$ and $\nu_s \text{POP}$, couplings are less important and can be observed as two bands instead of four theoretically expected. The results of the analysis of the IR spectrum related to the symmetry of the ring $\text{P}_4\text{O}_{12}^{4-}$ in the manganese cyclotetraphosphate, $\text{Mn}_2\text{P}_4\text{O}_{12}$, are in good agreement with the structural resolution (Hinsch and al., 1986).

Table 5: Assignments of the stretching vibrations of the $\text{P}_4\text{O}_{12}^{4-}$ cycles in $\text{Mn}_2\text{P}_4\text{O}_{12}$

Vibrations description	Cycle P_4O_{12} isolated with ideal symmetry D_{4h}		Site symmetry C_i		Group factor C_{2h}		Observed IR frequencies	Calculated frequencies S_4 [7]	
	IR	Ra	IR	Ra	IR	Ra		IR	Ra
$\nu_{as} \text{OPO}^-$	A_{2u}	IR -	→	A_u	IR -	→	A_u IR - Bu IR -	1315 1301	1275 -
	B_{1u}	- -	→	A_u	IR -	→	A_u IR - Bu IR -	1275	1261 -
	E_g	- Ra	↘	A_g	- Ra	↘	A_g - Ra A_g - Ra Bg - Ra		
$\nu_s \text{OPO}^-$	A_{1g}	- Ra	→	A_g	- Ra	→	A_g - Ra Bg - Ra		- 1128
	B_{2g}	- Ra	→	A_g	- Ra	→	A_g - Ra		- -
	Eu	IR -	↘	Au	IR -	↘	Au IR - Bu IR - Au IR - Bu IR -	1116 1101	1121 -
$\nu_{as} \text{POP}$	A_{2g}	- -	→	A_g	- Ra	→	A_g - Ra Bg - Ra		
	B_{2g}	- Ra	→	A_g	- Ra	→	A_g - Ra	1048	
	Eu	IR -	↘	Au	IR -	↘	Au IR - Bu IR - Au IR -	1017	994 -
$\nu_s \text{POP}$	Eu	IR -	↘	Au	IR -	↘	- Au IR - Bu IR - Au IR - Bu IR -	733 712	739 -
	A_{1g}	- Ra	→	A_g	- Ra	→	A_g - Ra	669	
	B_{1g}	- Ra	→	A_g	- Ra	→	Bg - Ra A_g - Ra		

Conclusion

With further increase in temperature, the latest amorphous phase is converted to a mixture of $\text{Mn}_2\text{P}_2\text{O}_7$ and $\text{Mn}_2\text{P}_4\text{O}_{12}$. Finally the mixture $\text{Mn}_2\text{P}_2\text{O}_7$ and $\text{Mn}_2\text{P}_4\text{O}_{12}$ leads by heating at higher temperature to $\text{Mn}_2\text{P}_4\text{O}_{12}$. So, the final product of the total thermal dehydration of $\text{Mn}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$ under atmospheric pressure is its corresponding anhydrous cyclotetraphosphate $\text{Mn}_2\text{P}_4\text{O}_{12}$. The vibrational spectra $\text{Mn}_2\text{P}_4\text{O}_{12}$ is examined and interpreted in the domain of the stretching vibrations of the P_4O_{12} rings.

References

1. E. Steger Et A. Simon. *Z. Anorg. Allg. Chem.*, 291, 76, (1957).
2. G. Foumakoye, R. Cahay Et P. Tarte, *Spectrochimica. Acta.*, 46A(8), 1245-1257, (1990).
3. K. El Kababi, PhD Thesis, Ben M'Sik Faculty of Sciences, Casablanca. Morocco. (2000).
4. K. Sbai, State Theses, Dijon. France. (1984).
5. Kh. Mulglaiev, A. N. Lazarev Et A. P. Mirgodsku. *Izv. Acad. Nauk. Sssr Neorg. Mater.* 10(4), 563, (1974).
6. Th. Hinsch, W. Guse and H. SAALFELD. *J. Cryst. Growth*, 79, 205, (1986).
7. Zerraf, S.; Belhabra, M.; Kheireddine, A.; Lamsatfi, R.; Tridane, M.; Moutaabbid, M.; Baptiste, B.; Moutaabbid, M and Belaouad, S.; *Phosphorus, Sulfur, and Silicon and the Related Elements.* 192(12), 1286-1293 (2017).