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Vibrational Spectra of Dizincate Sodium Triphosphte Nonahydrate $Zn_2NaP_3O_{10}.9H_2O$

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- ✓ Infrared spectrum;
- ✓ Raman spectrum;
- ✓ POP bridging

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Abstract

The compound with $Zn_2NaP_3O_{10}.9H_2O$ formula that has been found to be of triclinic symmetry was resynthesized by wet methods and investigated by vibrational spectroscopy. So, the measured infrared and Raman spectra of this compound has been interpreted at room temperature using factor group analysis and previous works. The non-coincidences observed between most infrared and Raman bands are consistent with a centrosymmetric structure of $Zn_2NaP_3O_{10}.9H_2O$ triphosphate. The vibrational spectra point to a bent POP bridging angle in this material.

1. Introduction

The present study aims to follow the works that we have already realized on the determination of crystal structures of condensed phosphate including the $(P_nO_{3n+1})^{(n+2)-}$ anions such as $(NH_4)_2Zn(H_2P_2O_7)_2.2H_2O$ and $K_2M(H_2P_2O_7)_2.2H_2O$ (M = Zn, Cu) by using as well as the X-ray diffraction on single crystals and the IR and Raman spectroscopy [1-3]. So, the compound that we will study here is the phosphate material $Zn_2NaP_3O_{10}.9H_2O$ including the $(P_3O_{10})^{5-}$ anions. The previous study of this compound was limited to the determination of the atomic arrangement by using X-ray diffraction on the single crystal [4]. This study showed that the compound crystallized in the triclinic system with the space group $P\bar{1}$ (Z =2), ie with the factor group C_i. To complete this structural study, it seems us interesting in the present manuscript to develop the analysis of the normal vibration modes in the factor group of this compound and the assignment of bands in the IR and Raman spectra. It is worthy to note that the spectroscopic works that have been realized for this material type are very few and need to be investigated. This allows us to verify the relationship between the structural study made elswhere on $Zn_2NaP_3O_{10}.9H_2O$ and the vibrational study that we develop in the present manuscript.

2. Experimental details

2.1. Synthesis

The $Zn_2NaP_3O_{10}.9H_2O$ compound was prepared by the following method: the aqueous solution of zinc chloride $ZnCl_2{\cdot}4H_2O$ (0.1 M) was added dropwise to the sodium triphosphate $Na_5P_3O_{10}$ (0.1 M). The mixture solution was stirred and allowed to stand at room temperature. After 2 weeks, colorless crystals were collected.

2.2. Infrared measurements

The infrared measurements were performed by a FT-IR-40A Biorad spectrometer with resolution of 2 cm^{-1} in the spectral range 400–4000 cm^{-1}, adopting the KBr pellet technique (1 mg sample per 400 mg KBr).

2.3. Raman measurements

Micro-Raman measurements were performed in back-scattering geometry at room temperature using a Dilor XY triple spectrometer with a liquid nitrogen cooled CCD detector (Charged Coupled Device) and an adapted Olympus microscope. The spectra were excited with an Ar^+ laser (514.5 nm, 300 mW) and focused onto a spot of 2 nm in diameter. The scattered light was not analyzed in polarization; spectral resolution was 0.5 cm^{-1}; lines of neon lamp were used for frequency scale calibration.

3. Results and Discussion

3.1. Structural characteristics of $Zn_2NaP_3O_{10}.9H_2O$

The structural determination showed that the title compound crystallized in the triclinic space group $P\bar{1}$ (Z=2) (C^1_i). The projection of the $Zn_2NaP_3O_{10}.9H_2O$ structure on the (ac) plane (**fig.1)** shows the presence of a three-dimensional atomic structure [4]. The cohesion of structure has been found to be ensured by Zn(1), Zn(2), Zn(3) and Na cations. The latter atoms have two types of environment:

- An octahedral coordination for zinc and sodium atoms [Zn(1), Zn(2) and Na],
- An tetrahedral coordination for the zinc atom Zn(3)

The atomic arrangement shows the presence of four water molecules that are not linked to the [O(W6), O(W7), O(W8), O(W9)] cations. In this structure, there exist the interconnected channels that are delimited by the oxygens of $P_3O_{10}^{5-}$ anions and containing the water molecules.

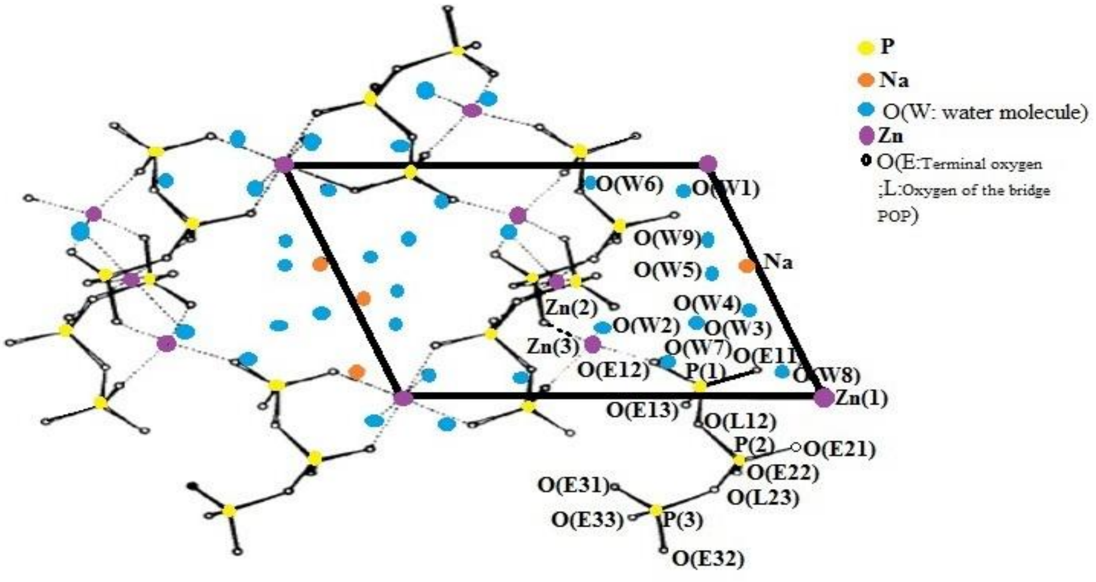

Figure 1: The projection of the structure $Zn_2NaP_3O_{10}.9H_2O$ on the ac plane [4]

In this structure, the cations have been found to have different symmetries of site; the Zn(1) and Zn(2) cations were placed on special positions, exactly on centers of symmetry (0,0,0) and (½, ½, ½) , ie have the site of symmetry C_i, while the Zn(3) and Na were observed on general positions, ie have the site of symmetry C_1. Similarly the atoms of phosphorus and oxygen are on general positions (C_1), the water molecules and $P_3O_{10}^{5-}$ ions have the C_1 site symmetry. To illustrate clearly the positional and sites symmetry of the different atoms and molecules in $Zn_2NaP_3O_{10}.9H_2O$ structure, we give the Symmetry and Wyckoff position of these elements in the **Table 1.**

3.2. Enumeration of atoms movements using theory of groups: group factor analysis

To better interpretate the vibrational spectra of the title compound, it is important to indicate the number of normal vibration modes that we have performed using the theory of groups. The method of Bhagavatam [5] provides a rigorous analysis of the different atoms movements, considering the invariant atoms under the effect of group symmetry operations. The character of the reducible representation is given by the famous formula:

$$\boldsymbol{\chi_R = u_R (\pm 1 + 2\cos\theta_R)}$$

(U_R is the number of atoms which is invariant under the action of a symmetry operation R, θ being the angle of rotation)

Table1. Wyckoff position of atoms and their site symmetries in $Zn_2NaP_3O_{10}.9H_2O$

Atoms	Wyckoff position	Site group Symmetry
Na	2i	C_1
Zn(1)	1a	C_i
Zn(2)	1h	C_i
Zn(3)	2i	C_1
P(1)	2i	C_1
P(2)	2i	C_1
P(3)	2i	C_1
10O(P)	2i	C_1
9O(water)	2i	C_1
18H(water)	2i	C_1

The 43 atoms of the triphosphate crystal lattice $Zn_2NaP_3O_{10}.9H_2O$ give rise to 255 movements. The using of Bhagavatam method tacking to account the site symmetry of the different atoms of the title compound **(Table 1)** and the values given in **Table 2** allows us to determine the irreducible representation of the normal vibration modes in two symmetries A_g and A_u as it is given in the following formula:

$$\mathbf{\Gamma_{vib}^{(Zn_2NaP_3O_{10}.9H_2O)} = 126A_g\,(Ra) + 132A_u\,(IR)}$$

The representation contains 3 acoustic vibrational modes and 255 optical modes given as the following:

$$\mathbf{\Gamma_{optic}^{(Zn_2NaP_3O_{10}.9H_2O)} = 126A_g\,(Ra) + 129A_u\,(IR)}$$

$$\mathbf{\Gamma_{acoustic}^{(Zn_2NaP_3O_{10}.9H_2O)} = 3A_u(IR)}$$

Table 2. Factor group analysis C_i for the $Zn_2NaP_3O_{10}.9H_2O$ crystals

Ci	E	i		
A_g	1	1	R_x, R_y, R_z	x^2, y^2, z^2, xy, xz, yz
A_u	1	-1	x, y, z	
Zn(1)	1	1		
Zn(2)	1	1		
Zn(3)	2	0		
Na	2	0		
P1	2	0		
P2	2	0		
P3	2	0		
O(E11)	2	0		
O(E12)	2	0		
O(E13)	2	0		
O(L12)	2	0		
O(E21)	2	0		
O(E22)	2	0		
O(L23)	2	0		
O(E31)	2	0		
O(E32)	2	0		
O(E33)	2	0		
O(W1)	2	0		
O(W2)	2	0		
O(W3)	2	0		
O(W4)	2	0		
O(W5)	2	0		
O(W6)	2	0		
O(W7)	2	0		
O(W8)	2	0		
O(W9)	2	0		
18H(W)	36	0		
U_R	86	2		
$2\cos\theta\pm1$	3	-3		
Γ_{total}	258	-6		

Since the factor group C_i is centrosymmetric, the selection rule indicates that the infrared active modes are not Raman actives and inversely. Therefore, the A_g species are Raman actives, while the A_u species are infrared actives. According to the selection rule, we have 126 bands that will be actives in the Raman spectrum and 129 bands in the infrared spectrum.

3. 3. Analysis of internal and external vibrations: Correlation scheme

The crystal structure of the triphosphate $Zn_2NaP_3O_{10}.9H_2O$ characterized by existence of $P_3O_{10}^{5-}$ isolated groups, H_2O molecules, AO_6 groups [A= Na, Zn(1), Zn(2)] and $Zn(3)O_4$ which are characterized by the relatively low wavenumbers corresponding to the A-O and Zn(3)-O vibrations [the A-O and Zn(3)-O bonds are very weak]. So, the normal modes vibrations of the title compound are corresponding to the following movement's types:

i) The internal vibrations of P_3O_{10} groups and H_2O molecules
ii) The external vibrations of P_3O_{10} groups, H_2O molecules, Na and Zn atoms.

i.1) The internal vibrations of $Zn_2NaP_3O_{10}.9H_2O$

a) $P_3O_{10}^{5-}$ in the free state

The free ion $P_3O_{10}^{5-}$ considered in the cis configuration possesses the C_{2v} molecular symmetry group; the total number of internal vibrations of this ion is equal to: (33 × 13) - 6 = 33. These vibrations are given by the following irreducible representation:

$$\boldsymbol{\Gamma_{vib}\ P_3O_{10}^{5-} = 11A_1\ (IR, Ra) + 6A_2\ (Ra) + 9B_1\ (IR, Ra) + 7B_2\ (IR, Ra)}$$

The selection rules show except for the A_2 modes that are Raman active and not Infrared active; all the remaining modes are active in Raman and infrared spectra.

b) $P_3O_{10}^{5-}$ in C_1 symmetry site of the $Zn_2NaP_3O_{10}.9H_2O$ crystal

The local symmetry of $P_3O_{10}^{5-}$ groups in $Zn_2NaP_3O_{10}.9H_2O$ is found to be C_1. In the **Table 3,** we give the enumeration of the $P_3O_{10}^{5-}$ vibrations, in the site group and factor group that we have established by means of correlations from the vibrations of the anion in its molecular group of C_{2v} symmetry.

Table 3. Correlation scheme for internal modes of $P_3O_{10}^{5-}$ ions in $Zn_2NaP_3O_{10}.9H_2O$

Molecular group	Site group	Factor group
C_{2v}	C_1	C_i
$11A_1$(IR Ra) →		↗ 33 A_g(Ra)
$6A_2$(Ra) →		
$9B_1$(IR,Ra) →	33A(Ra,IR)	
$7B_2$(IR,Ra) →		↘ 33A_u(IR)

Activities	C_{2v}	C_1	C_i
Raman	33	33	33
Infrared	27	33	33
Coincidence	27	33	0

It can be seen from **Table 3** that the 33 internal modes of the molecular point group C_{2v} correlate with the 66 internal modes of the factor group C_i, and consist of the following species:

$$\boldsymbol{\Gamma_{vib}\ P_3O_{10}^{5-}(Cristal) = 33A_g\ (Ra) + 33A_u\ (IR)}$$

i.2) Internal vibrations of H_2O molecule in $Zn_2NaP_3O_{10}.9H_2O$

Table 4 illustrates the correlation scheme for the vibrational modes of H_2O molecule between molecular group C_{2v}, site group C_1 and factor group $C_{i.}$. Considering 9 H_2O molecules in the compound formula and Z = 2 (unit cell), it can be seen that the 27 internal modes of water molecule in the molecular group C_{2v} correlate with the 54 internal modes in the factor group C_i as the following : $\Gamma_{vib}\ (H_2O) = 27A_g(Ra) + 27A_u\ (IR)$

We note that the crystallographic data carried on the compound $Zn_2NaP_3O_{10}.9H_2O$ [4] showed that they are 9 types of water molecules.

Table 4. Correlation scheme for internal modes of H_2O molecule in $Zn_2NaP_3O_{10}.9H_2O$

Molecular group group	Site group	Factor
C_{2V}	C_1	Ci

$$\begin{tikzcd}
2A_1(IR\ ,Ra) \arrow[dr] & & 3A_g(Ra) \\
& 3A(IR\ ,Ra) \arrow[ur] \arrow[dr] & \\
B_2(IR\ ,Ra) \arrow[ur] & & 3A_u(IR)
\end{tikzcd}$$

Activities	C_{2v}	C_1	C_i
Raman	3	3	
		3	
Infrared	3	3	
		3	
Coincidence	3	3	
0			

ii.1) The external vibrations of $Zn_2NaP_3O_{10}.9H_2O$

The external vibrations of $Zn_2NaP_3O_{10}.9H_2O$ correspond to librational motions of $P_3O_{10}^{5-}$ ions and H_2O molecules and to translational motions of Na^+, Zn^{2+} cations, $P_3O_{10}^{5-}$ ions and H_2O molecules. For the lattice modes involving $P_3O_{10}^{5-}$ and H_2O, the correlation scheme (Table 5) predicted 6 translational and 6 librational modes (for $P_3O_{10}^{5-}$) and 54 translational and 54 librational modes (for H_2O). For the Na^+ and Zn^{2+} cations, a similar procedure was followed, and 18 translational modes were determined

No rotational modes are possible with a monatomic ion. The external modes for $Zn_2NaP_3O_{10}.9H_2O$ compound are distributed (excluding acoustic modes) as follows:

$$\boldsymbol{\Gamma_{Vib}\ \text{(external modes)}= 60A_g(Ra) + 75A_u(IR)}$$

3. 4. Interpretation of IR and Raman spectra of $Zn_2NaP_3O_{10}.9H_2O$

The IR and Raman spectra of $Zn_2NaP_3O_{10}.9H_2O$ triphosphate are shown in **Figs 2 and 3**, respectively. The band assignments are listed in **Table 6**.

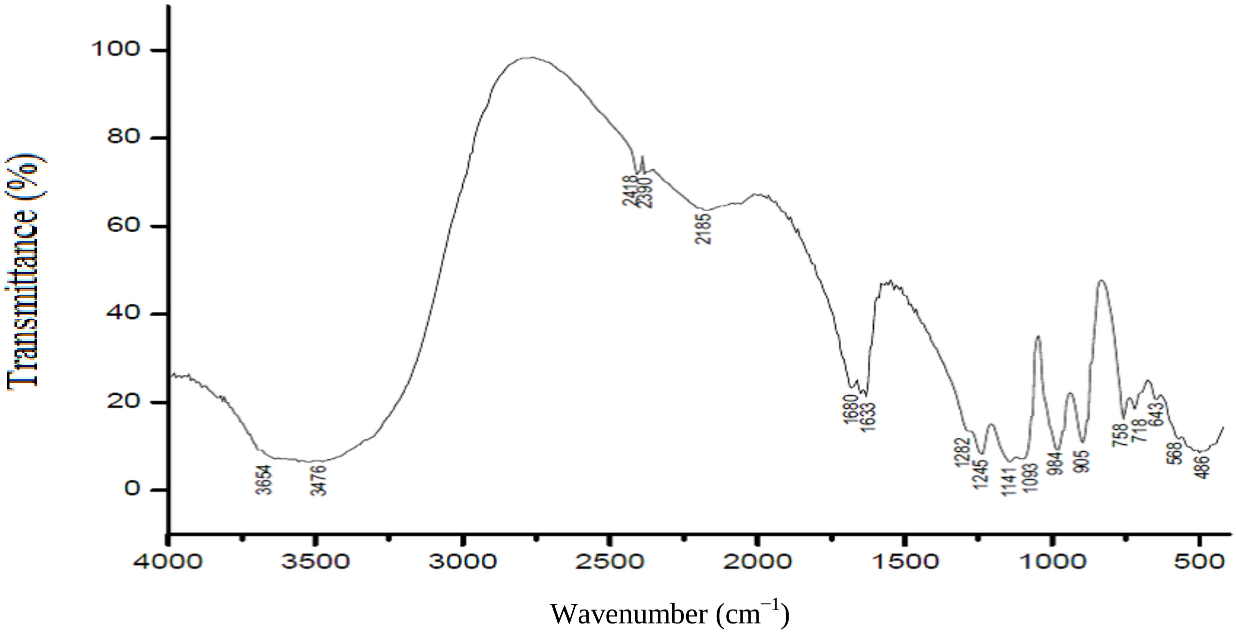

Fig. 2. IR spectrum of $Zn_2NaP_3O_{10}.9H_2O$

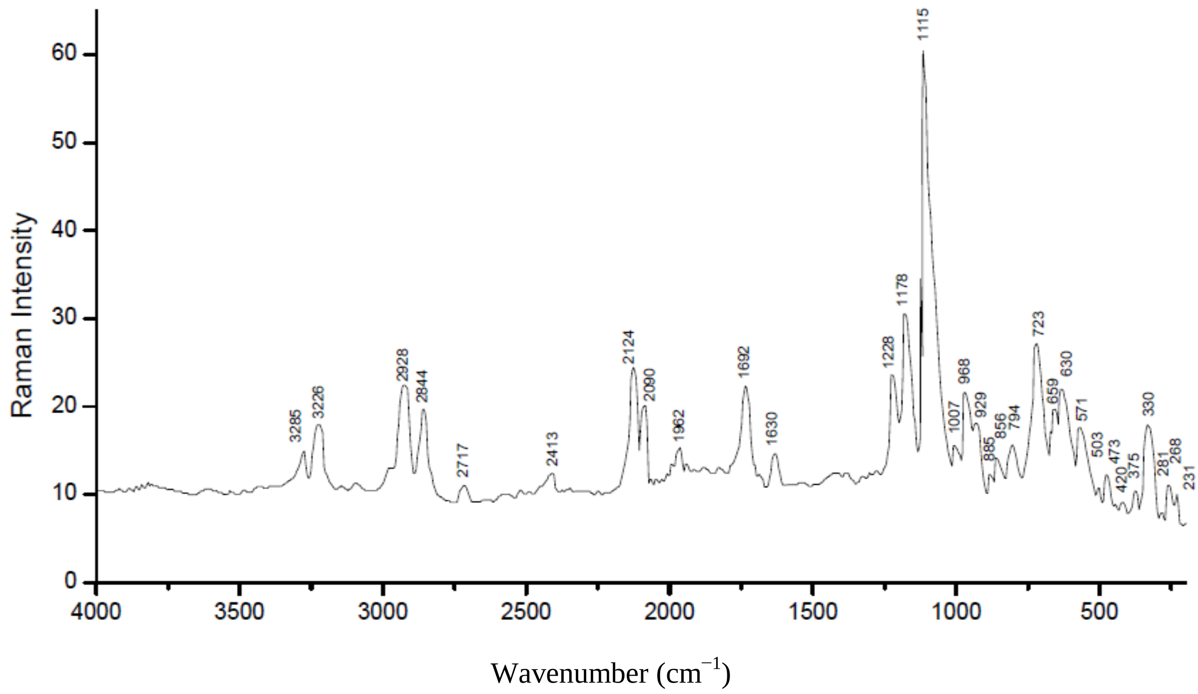

Fig. 3. Raman spectrum of $Zn_2NaP_3O_{10}.9H_2O$

The $P_3O_{10}^{5-}$ group is formed by two P_2O_7 groups **(fig. 4)**, characterized by the P-O-P angles and three types of distances P-O. For this reason, three types of bonds can be distinguished in the $P_3O_{10}^{5-}$ groups:

-The P-O bonds in P(3)-O(L23)-P(2), P(1)-O(L12)-P(2) and in O(L23)-P(2)-O(L12),

-The P-O bonds in PO_2 (corresponding to the central phosphorus P(2)-O(E22) and P(2)-O(E21)),

-The P-O bonds of the PO_3 terminal groups.

Therefore, the allocation of the bands observed in infrared and Raman spectra of this compound will be made based on two essential points:

1) The characteristic vibrations of (PO_3 and PO_2) groups, POP bridge and POP chains,
2) The spectroscopic previous work realized on the triphosphate containing $P_3O_{10}^{5-}$ groups [6-8].

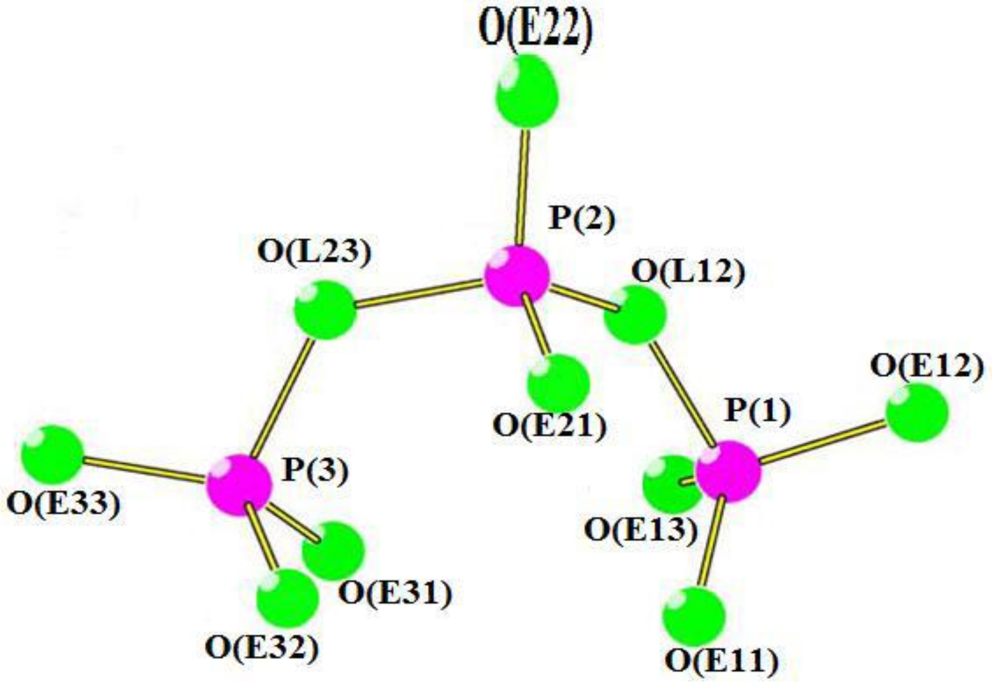

Fig.4. $P_3O_{10}^{5-}$ groups, combination of two P_2O_7 groups [8].

Table 5. Correlation scheme for external modes of $P_3O_{10}^{5-}$ ions, Na^+ and Zn^{2+}cations and H_2O molecule in $Zn_2NaP_3O_{10}.9H_2O$.

	External modes			Factor group C_i	External modes	
	L	T			L	T
			Site group C_1			
$P_3O_{10}^{5-}$	3	0	A (IR, Ra)	→ A_g (Ra)	3	3
	0	3		→ A_u (IR)	3	3
			Site group C_1	Factor group C_i		
H_2O	3	0	A (Ra, IR)	→ A_g (Ra)	3	3
	0	3		→ A_u (IR)	3	3
Na^+		3	A (IR, Ra)	→ A_g (Ra)		3
				→ A_u (IR)		3
			Site group C_i			
Zn^{2+} (1)		0	A_g(Ra) →	A_g (Ra)		0
		3	A_u (IR) →	A_u (IR)		3
			Site group C_i			
Zn^{2+}(2)		0	A_g(Ra) →	A_g (Ra)		0
		3	A_u(IR) →	A_u (IR)		3
			Site group C_1			
Zn^{2+}(3)		3	A (IR, Ra)	→ A_g (Ra)		3
				→ A_u (IR)		3

L = Libration; T= Translation; IR: infrared; Ra: Raman

We can attribute the observed frequencies on the infrared and Raman spectra of the $Zn_2NaP_3O_{10}.9H_2O$ compound as the following:

a) Vibration of H_2O molecule:

The broad and medium bands localized respectively in the infrared and Raman spectra in the 3700-1900 cm^{-1} range, are assigned to the stretching vibrations modes of water molecules ν(H_2O), O-H bond (ν(OH)) links with H_2O[9], and those which are localized between 1700 and 1600 cm^{-1} in both spectra are due to deformation modes of water molecules δ(H_2O) [10]. The splitting of the stretching and bending vibrations of water molecules in the range 3700–1600 cm^{-1} is due to the presence of different hydrogen bonds, and to the correlation field effect [11]. The doublet located at 1680 and 1633 cm^{-1} in infrared spectrum and at 1692 and 1630cm^{-1} in Raman spectrum are due to deformation of water molecules (δH_2O).

The existence of these two pairs (i.e deformations modes of H_2O molecule) is probably due to the difference of the environments occupied by water molecules between them; and this is in good agreement with the results of structural $Zn_2NaP_3O_{10}.9H_2O$ which shows that a number of water molecules are not part of any cationic environment (O(W6), O(W7), O(W8), O(W9)). The bands observed at 659 and 630 cm^{-1} in Raman spectrum and at 643 cm^{-1} in infrared spectrum are due to rocking modes of H_2O molecules (ρH_2O) [12 ,13]. Point out that the bands located at 2418 and 2390 cm^{-1} in infrared spectrum can be assigned to the vibrational modes of CO_2 gas coming from the atmosphere [14].

Table 6. Infrared and Raman bands assignments for $Zn_2NaP_3O_{10}.9H_2O$.

Infrared (cm^{-1})	**Raman (cm^{-1})**	**Assignments**
3645 b 3476 b 2418 w 2390 w } νCO_2 2185 b	3285 m 3226 s 2928 s 2844 s 2717 m 2413 m 2124 s 2090 m 1962 m	νH_2O + νOH
1680 s 1633 s	1692 s 1630 m	δH_2O
1282 s 1245 s 1141 vs 1093 vs 984 s	1228 m 1178 s 1150 s 1115 vs 1007 w	$\nu_{as}PO_2$ + $\nu_{as}PO_3$ + ν_sPO_2 + ν_sPO_3
905 s 758 m 718 m	968 m 929 w 885 w 856 w 794 m 723 s	$\nu_{as}POP$ + ν_sPOP
643 w	659 m 630 m	ρH_2O
568 w 486 b	571 m 503 sh 473 m 420 sh	$\delta(PO_2) + \delta(PO_3) + \rho(PO_2) + \rho(PO_3)$ + vibration of POP and OPO chains
	375 m 330 s 281 sh 268 m 231 w	δPOP + Torsional modes + External modes

m: medium; w = weak; s = strong; vs = very strong; sh = shoulder; b = broad;
ν = stretching; δ = bending; ρ = rocking; as = antisymmetric; s =symmetric

b) Vibration of $P_3O_{10}^{5-}$ groups:

In the region between 1290 and 700 cm^{-1} we observe a set of bands on the infrared and Raman spectra which is due to different vibration of the $P_3O_{10}^{5-}$ groups and which can be classified into two areas. Taking into account the allocations made in the case of other compounds containing the P_2O_7 groups possessing a bridging POP stretching vibrations that occur at frequencies below those of PO_2 and PO_3 groups [15, 16].

Area 1: stretching vibration of PO_2 and PO_3 groups

These $\nu_{as}PO_2$, $\nu_{as}PO_3$, ν_sPO2 and ν_sPO_3 vibrations are located in the 1290-975 cm^{-1} spectral range [17]. In this field of vibrations we find five bands on the infrared spectrum located at 1282, 1245, 1141, 1093 and 984 cm^{-1} and five other located at 1226, 1178, 1150.1115 and 1007 cm^{-1} in the Raman spectrum.

Area 2: stretching vibration of POP groups

These modes appear usually between 970-700 cm^{-1} spectral range [10, 11]. On the infrared spectrum, three infrared bands are observed: one is intense due to the antisymmetric stretching vibration mode of POP bridging (ν_{as}POP) at 905 cm^{-1}, the two others with medium intensities are assigned to the symmetric stretching vibration modes of the POP bridging (ν_sPOP) located at 758 and 718 cm^{-1}. In Raman spectrum, these same vibrations are observed respectively for ν_{as} POP at 968, 929, 885 and 856 cm^{-1} and for ν_s POP at 794 and 723 cm^{-1}.

One of the interesting aspects of this study is the possibility of obtaining direct information about the configuration of POP bridging from spectroscopic data. The νsPOP vibrations are not observed in the infrared spectrum when the bridge is linear [18]. The appearance of ν_sPOP at 758 cm^{-1} and 718 cm^{-1} in infrared spectrum indicates a bent configuration in $Zn_2NaP_3O_{10}.9H_2O$. This is in good agreement with the structural data (P(1)-O(L12)-P(2) = 130.0 (3)° and P(2)-O(L23)-P(3)=128.9 (3)°) [4].

The vibrations observed in the spectral range between 600-400 cm^{-1} in the infrared and Raman spectra are due to the deformation and rocking modes of PO_2 and PO_3 groups ($\delta(PO_2)$, $\delta(PO_3)$, $\rho(PO_2)$, $\rho(PO_3)$) and to the vibration of POP and OPO chains. Four Raman peaks are located at 571, 503, 473 and 420 cm^{-1} and two infrared bands at 568 and 486 cm^{-1}. Finally, the peaks observed in the Raman spectrum at 375, 330, 281, 268 and 231 cm^{-1} are assigned to the deformation modes of POP groups δ(POP), the external modes and to the torsional modes [9, 11, 19].

Comments: limits of spectroscopic methods

This article illustrates some difficulties frequently encountered: some of these difficulties are due to the sample itself, others to the experimental device. First, both in Raman and in IR, the number of resolved lines is much lower than that expected by theory. Probably some of them cannot be detected by the devices because of their too low intensity; others have close frequencies and are masked in a single wide band. On the other hand, with the devices used, frequencies below 200 are difficult to access: they are, in Raman scattering, masked by Rayleigh radiation and, in IR absorption, limited by the detection of the instrument because the signal / noise ratio becomes too large for the spectrum to be significant.

Conclusion

The IR and Raman spectroscopic methods applied to the dizincate sodium triphosphate nonahydrate $Zn_2NaP_3O_{10}.9H_2O$ lead to a more precise description of the high frequency spectral domain. The set of bands located between 700 and 1300 cm^{-1} can actually be attributed to stretching modes of $P_3O_{10}^{5-}$. In the same way, the internal modes of water molecule are easily identifiable.

Also we have interpreted infrared and Raman spectra of this compound using factor group analysis. A comparison of the Raman and infrared wavenumbers of bands shows that the majority of them are not coincident; this fact confirms that $Zn_2NaP_3O_{10}.9H_2O$ possesses a centrosymmetric structure.

This spectroscopic study allows us to obtain direct information about the magnitude of the POP bridge angle in a good agreement with X-ray study of this material [4]. The appearance of the symmetric ν_sPOP and antisymmetric ν_{as}POP bridging “stretching vibrations” in the infrared and Raman spectra points to a POP bridging “bending” in $Zn_2NaP_3O_{10}.9H_2O$.

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