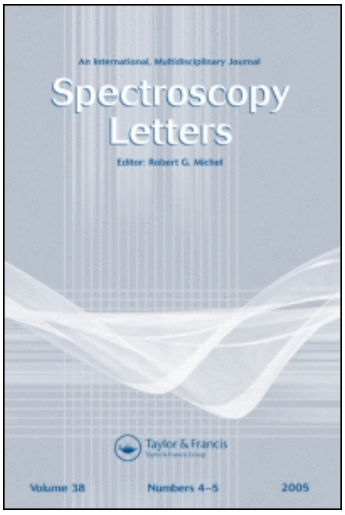

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Thermal Dehydration and Vibrational Studies of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$

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Abstract: The thermal dehydration of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$ was studied in the range 25–500°C by thermogravimetric analysis (TGA and DSC) and X-ray diffraction. We found, based on the TGA and DSC scans, the dehydration of this salt takes place in three stages with a loss of the six water molecules. The infrared and Raman spectra of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$ have been recorded and interpreted using a factor group analysis. The internal modes are assigned in terms of POP and PO_2 structural units using experimental and theoretical IR and Raman frequencies.

Keywords: Cyclotriphosphate, DSC, infrared (IR), Raman spectroscopies, TGA, thermal behavior

INTRODUCTION

Detailed structural analysis of a number of cyclotriphosphates has been carried out for the generalization of their structural features and related

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properties.[1–3] A few reports are available on the interpretation of Raman spectra of cyclotriphosphates.[4–7]

$ZnK_4(P_3O_9)_2 \cdot 4H_2O$ crystallizes in the monoclinic system (C2/m) (C_{2h}^3) with two formula units per unit cell[8] and the ring P_3O_9 having a C_s symmetry. The two water molecules are not well localized, but a subsequent study on its isotype $ZnRb_4(P_3O_9)_2 \cdot 6H_2O$[9] reveals their existence.

The objective of the current study is to understand the nature of the vibrations of the cyclotriphosphates ions in $ZnK_4(P_3O_9)_2 \cdot 6H_2O$ and calculate the theoretical frequencies.

MATERIALS AND METHODS

$ZnK_4(P_3O_9)_2 \cdot 6H_2O$ was prepared by a new elaboration process. Polycrystalline sample was prepared by adding slowly a dilute cyclotriphosphoric acid to an aqueous suspension of basic zinc carbonate (3Zn(OH)2 · 2ZnCO3) and potassium carbonate (K_2CO_3) with a stoichiometric ratio $K/Zn = 4$, according to the following chemical reaction:

$$2H_3P_3O_9 + 1/5[3Zn(OH)_2 \cdot 2ZnCO_3] + 2K_2CO_3 \longrightarrow ZnK_4(P_3O_9)_2 \cdot 6H_2O + 12/5CO_2$$

The so-obtained solution was then slowly evaporated at room temperature until the precipitation of a polycrystalline sample of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$. This polycrystalline sample is stable in air for many months under normal conditions of temperature and hygrometry. The cyclotriphosphoric acid used in this reaction was prepared from an aqueous solution of $Na_3P_3O_9$ passed through an ion-exchange resin, Amberlite IR 120.[10]

The purity of the initial compound and the heated product at 500°C is controlled by X-ray diffraction. The thermal analysis curves were recorded on SeteramTGA 92 and DCS 92 type devices (France) equipped with an Epson calculator, at atmospheric pressure, at a heating rate of 10°C/mn in nitrogen atmosphere. A multicanal XY-Dilor was used for recording the Raman spectra of the samples. The 457.9-nm line was used for excitation, and the spectra were recorded with a resolution about 1 cm^{-1}. The infrared spectra have been registered with an ATI Mattson Genesis spectrometer (USA) and KBr disk method (4000–450 cm^{-1}).

RESULTS AND DISCUSSION

Thermal Behavior

The thermographic analysis (Fig. 1a) showed that the dehydratation of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$ takes place in three mass losses. The first one is between

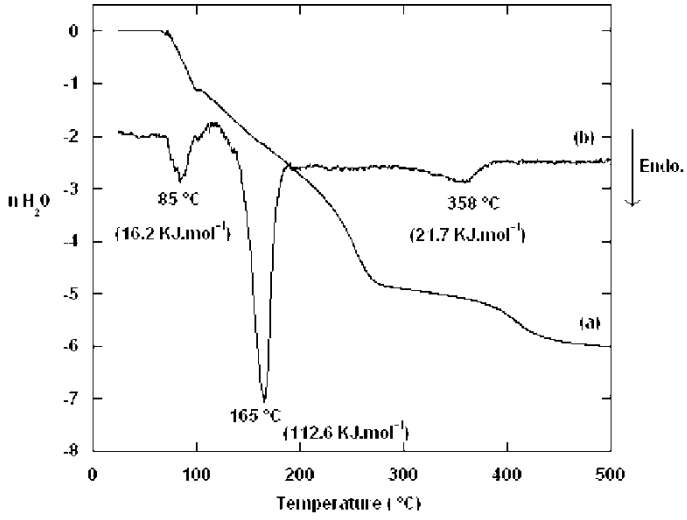

Figure 1. TGA (a) and DSC (b) curves of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$ at rising temperature ($10°C \cdot min^{-1}$).

67°C and 103°C, which is accompanied by a loss of one water molecule. The second stage between 105°C and 323°C corresponds with loss of four water molecules. The last water molecule is removed between 323°C and 472°C. The final product at 500°C was identified by XRD (Fig. 2) as a mixture of $ZnK_2(PO_3)_4$ and KPO_3 · This agrees with $Zn(PO_3)_2$–KPO_3 binary diagram.[11]

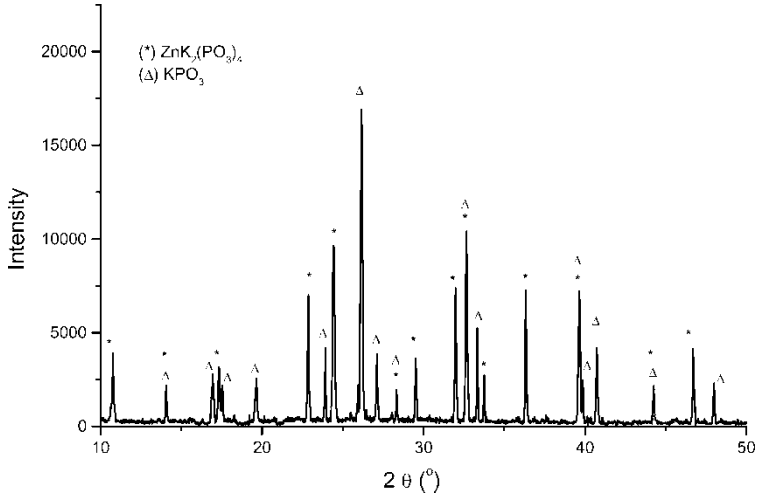

Figure 2. X-ray diffraction pattern of the heated product of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$ at 500°C.

Table 1. Summary of the factor group analysis of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$

	4 $P_3O_9^{3-}$ (C_s sites)								
Factor group species (C_{2h})	Internal modes	External modes	2Zn (C_i)	4K (1) (C_s)	4($O_{(w2)}$) (C_s)	4K (2) (C_2)	8($O_{(w1)}$) (C_1)	Optical modes	Acoustic modes
A_g	34	4T, 2R	—	4T	4T	2T	6T	56	—
B_g	26	2T, 4R	—	2T	2T	4T	6T	46	—
A_u	26	2T, 4R	3T	2T	2T	2T	6T	47	1
B_u	34	4T, 2R	3T	4T	4T	4T	6T	61	2
	120	12T, 12R	6T	12T	12T	12T	24T	210	3

The differential scaning calorimetry (Fig. 1b) reveals three endothermic peaks at 85°C, 165°C, and 358°C. All peaks are attributed to loss of water molecules.

Vibrational Studies

The factor group analysis is carried out to get the irreducible representations. The results are summarized in Table 1. The factor group analysis predicts the following selection rules: $\Gamma_{210} = 56A_g + 46A_u + 47A_g + 61A_u$ (excluding acoustic modes). Spectral predictions for the internal modes of $P_3O_9^{3-}$ ions in $ZnK_4(P_3O_9)_2 \cdot 6;H_2O$ under C_s symmetry are given in Table 2.

Several authors have studied the infrared spectra of P_3O_9 rings[1,4,5] but only few attempted to interpret them in the far infrared frequencies.[4] All the previous studies are based on three kinds of approximation:

- The separation of internal and external modes;
- The possiblity to separate stretching and bending modes;
- The increase of energy levels in the region of the stretching modes is as follows: ν_s POP $<$ ν_{as} POP $<$ ν_s PO_2 $<$ ν_{as} PO_2 ·

We proposed to calculate the theoretical frequencies of the ring P_3O_9 with C_s symmetry.[6,7] These theoretical frequencies (Table 3) were compared with experimental spectra (Figs. 3 and 4). By using a theoretical isotopic substitution, we determinated for each frequency the percentage of involvement of each of the two internal (POP) and external (PO_2) groupings.

For ring C_s symmetry, the 30 internal modes are separated in 12 stretching modes, $\Gamma_{stretch} = 7A' + 5A''$, and in 18 bending modes, $\Gamma_{bend} = 10A' + 8A''$. Stretching and bending vibrations are not all separated (Table 3).

This work showed that the current hypotheses for ordering the frequencies values of stretching vibrations have some flaws. For example, the ν_{as} POP_2 (A′) was observed at 1155 cm^{-1} in the IR spectrum (calculated: 1188 cm^{-1}), whereas the ν_s PO_2 (A′) was observed at 1155 cm^{-1} in the IR spectrum (calculated: 1155 cm^{-1}), in clear contradiction to the third approximation while the ν_{as} POP $<$ ν_s PO_2 ·

Table 2. Correlation schemes for the internal modes of $P_3O_9^{3-}$ in $ZnK_4(P_3O_9)_2 \cdot 6H_2O$

Site symmetry (C_s)	Factor group symmetry (C_{2h})
17 A′	34 A_g
	34 B_u
13 A″	26 B_g
	26 A_u

Table 3. Assignment and percentage (in brackets) of involvement of each of the two internal (POP) and external (PO_2) groupings for C_s symmetry in $ZnK_4(P_3O_9)_2 \cdot 6H_2O$

υ_{obs} (cm^{-1})					υ_{cal} (cm^{-1})				
IR	Raman	υ_{cal} (cm^{-1})	(%) of involvement	Mode	IR	Raman	υ_{cal} (cm^{-1})	(%) of involvement	Mode
1290	1295	1299	$\upsilon_{as}(PO_2)[98]$	A′			427	$\delta(POP)[24]\ \delta(PO_2)[76]$	A″
1255	1262	1280	$\upsilon_{as}(PO_2)[100]$	A′			420	$\delta(POP)[44]\ \delta(PO_2)[56]$	A′
	1248	1280	$\upsilon_{as}(PO_2)[100]$	A″		413	415	$\gamma_W(PO_2)[77]$	A″
		1200	$\upsilon_{as}(POP)[98]\ \upsilon_s(PO_2)[2]$	A″		408			
1194	1208	1188	$\upsilon_{as}(POP)[96]\ \upsilon_s(PO_2)[4]$	A′		344			
1155	1167	1155	$\upsilon_s(PO_2)[98]$	A′		321			
	1093	1099	$\upsilon_{as}(POP)[18]\ \upsilon_s(PO_2)[82]$	A″		306	305	$\delta(POP)[11]\ \delta(PO_2)[89]$	A′
1095	1081	1095	$\upsilon_{as}(POP)[21]\ \upsilon_s(PO_2)[79]$	A′		293	303	$\gamma(POP)[16]\ \gamma_T(PO_2)[84]$	A″
1008	1048	1032	$\upsilon_{as}(POP)[94]$	A″			297	$\delta(POP)[30]\ \gamma_W(PO_2)[70]$	A′
	1005						287	$\gamma(POP)[14]\ \gamma_T(PO_2)[86]$	A′
827							268	$\delta(POP)[33]\ \gamma_W(PO_2)[67]$	A″
740	777	794	$\upsilon_s(POP)[77]\ \delta(PO_2)[23]$	A″		258	255	$\delta(POP)[24]\ \gamma_W(PO_2)[76]$	A″
		792	$\upsilon_s(POP)[76]\ \delta(PO_2)[24]$	A′			252	$\delta(POP)[20]\ \gamma_W(PO_2)[80]$	A′
640	644	698	$\upsilon_s(POP)[64]\ \delta(PO_2)[36]$	A′		219	214	$\gamma_T(PO_2)[99]$	A″
560	553	563	$\delta(POP)[71]\ \delta(PO_2)[29]$	A′		143			
531	497	513	$\gamma(POP)[63]\ \gamma_R(PO_2)[37]$	A′		116	104	$\gamma(POP)[22]\ \gamma_R(PO_2)[78]$	A′
464		447	$\gamma(POP)[62]\ \gamma_T(PO_2)[38]$	A″		108	89	$\gamma(POP)\ [31]\ \gamma_R(PO_2)[69]$	A″
		447	$\gamma(POP)[49]\ \gamma_T(PO_2)[51]$	A′			59	$\gamma(POP)\ [31]\ \gamma_R(PO_2)[69]$	A′

ν_s, symmetric stretching; ν_{as}, asymmetric stretching; δ, deformation (bending); γ_R, rocking; γ_T, twisting; γ_W, wagging; γ, out of plane P_3Oi_3; Oi, internal oxygen atom; Oe, external oxygen atom.

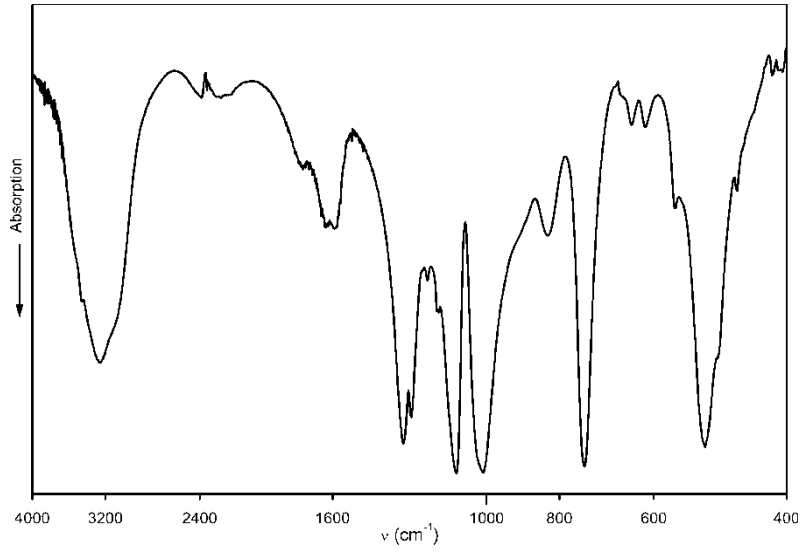

Figure 3. IR spectrum of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$.

The three high frequencies are due to the ν_{as} PO_2 vibrations, and those situated between 650 and 800 cm^{-1} are due to ν_s POP vibrations. On the other hand, the calculations show that ν_{as} POP vibrations, proceeding from E mode in ideal D_{3h} and C_3 ring symmetry, for which we have also performed

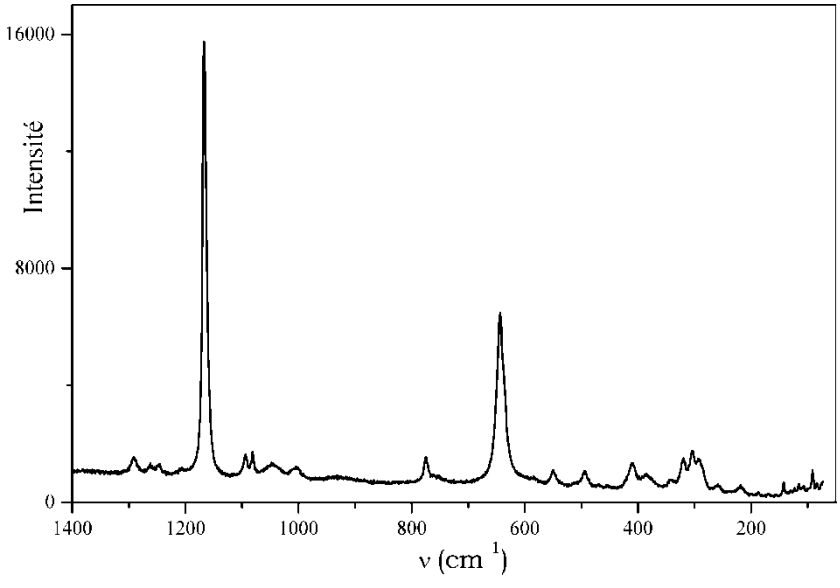

Figure 4. Raman spectrum of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$.

the calculation,[12] were observable between 1175 and 1230 cm^{-1}. The ν_{as} POP vibration frequencies at 1200 cm^{-1} (A″ mode), 1188 cm^{-1} (A′ mode), and 1032 cm^{-1} (A″ mode) were pure, whereas the frequencies situated between 670 and 800 cm^{-1} were attributable to the ν_s POP vibrations, which implicate external oxygen atoms (Table 3).

The bands at 1155 cm^{-1} in the IR spectrum and at 1167 cm^{-1} in the Raman spectrum of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$ are ν_s PO_2 (A′). These two bands are infrared inactive and Raman polarized for C_{3h} ring symmetry.[4]

The frequencies calculated at 415 and 214 cm^{-1} were respectively a pure twisting and a pure wagging external (PO_2) grouping. In the low-frequency region (<150 cm^{-1}), the frequencies calculated at 100, 89, and 59 cm^{-1} were assigned to rocking external (PO_2) grouping.

CONCLUSIONS

Thermal behavior and vibrational studies were performed. The dehydration that occurs in three stages with endothermic peaks gives a final product that is a mixture of polyphosphate. Calculation of the internal vibration frequencies of $P_3O_9^{3-}$ ring shows the existence of many mixed frequencies. The confrontation of IR and Raman spectra of $ZnK_4(P_3O_9)_2 \cdot 6H_2O$ allows us to interpret them correctly in the domain of stretching and bending vibrations of $P_3O_9^{3-}$ ring.

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