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# The dehydration of phosphates monitored by DSC/TGA and in situ Raman spectroscopy

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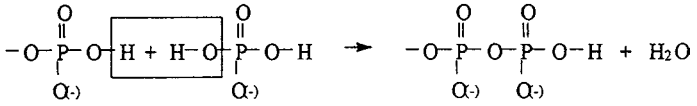
**Abstract**

Phosphates can be thermally dehydrated to polyphosphates or metaphosphates. This is an important reaction in the preparation of glasses, catalysts and flame retardants. In this study, we have monitored the dehydration process of potassium and sodium dihydrogen phosphates, using in situ Raman spectroscopy, thermal analysis, X-ray powder diffraction and infrared spectroscopy. We obtained a good correlation between the thermal data and the structural phase transitions observed during the reactions, using Raman and infrared spectroscopy. Deuteration of the samples assisted us in assigning some of the vibrational bands. 

*Keywords:* Phosphates; Raman; TGA; DSC

## 1. Introduction

Phosphates and polyphosphates are important ingredients in flame retardants and catalysts. A polyphosphate is generally classified as an inorganic polymer and also regarded as a condensed phosphate. The preparation of a condensed phosphate can be considered as a polymerization reaction where P–O–P linkages are formed upon the release of water molecules (Eq. (1))



(1)

Cations balance the negatively charged $PO_4$ units in the equation.

Flame retardants can be protected from oxidation by coating the char with phosphates and polyphosphates during manufacturing [1]. Miller also discussed a paper on the intumescents that focussed on the processability of polyphosphate in polypropylene [2] and the importance of this reaction in the preparation of glasses and catalysts is well known. An understanding of this reaction (1) is of the utmost importance in both these applications and this, together with the availability of phosphates in South Africa, instigated our interest in this study.

Raman and infrared spectroscopy are excellent methods for studying $PO_4$ units in different environ-

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ments as the number and positions of P–O bands in the spectra depend on the crystal structure and resultant bond strength. Factor group analysis is necessary to understand the spectra completely and various Raman and crystallographic studies of monobasic potassium and sodium phosphates have been published [3–8]. For the purpose of this study, we were interested in two regions of the spectra: 3000–3600 $cm^{-1}$, where the vibrations of water molecules occur, and 600–1400 $cm^{-1}$ where the skeletal P–O stretch vibrations occur.

We used Raman spectroscopy to follow the reactions in situ and to distinguish between the phases present at different temperatures. As for our studies on the dehydration of phosphates, we used X-ray powder diffraction, thermal analysis and FTIR spectroscopy in addition to Raman spectroscopy to effectively monitor structural changes during the dehydration of monobasic potassium and sodium phosphates. Deuteration of the samples assisted further in assigning some of the bands.

## 2. Experimental

The condensed phosphates were prepared by heating alkalimetal dihydrogen phosphate. Sodium phosphate glasses were made by heating $NaH_2PO_4$ above the melting temperature of 630°C. The melt was quenched in air at room temperature and dissolved in water.

Raman spectra of the glasses and crystalline forms at room and elevated temperatures were recorded in situ in glass tubes, using a high temperature cell obtained from DILOR®. The spectra were recorded on a Dilor® XY Raman spectrometer, excited with the 514.5 nm line of a Coherent Innova®90 $Ar^+$-laser, with a resolution of at least 2 $cm^{-1}$.

Mid-infrared transmission spectra were recorded with a BRUKER® 113v FTIR instrument. The samples were pressed between two KBr pellets to avoid water loss, which could occur if the usual method of mixing the sample with KBr was followed. The sample chamber was evacuated ($P = 170$ mbar) during the recordings.

Thermogravimetric data were collected by a Stanton-Redcroft® STA 780 Simultaneous Thermal Analyser. Samples (±100 mg) were put in a platinum crucible and heated at a scan rate of 5°C $min^{-1}$, while an air-flow, with a flow rate of 20 $cm^3$ $min^{-1}$, was used to remove gaseous decomposition products. Differential scanning calorimetry (DSC) was performed on a Du Pont® 910 Calorimeter, controlled by a 1090 Thermal Analyser System.

Powder X-ray diffraction data were recorded on a Siemens® D501 automated diffractometer equipped with a secondary graphite monochromator. The applied potential was 40 kV and the corresponding current 40 mA. The primary X-ray beam was Cu Kα radiation. A pattern was recorded from 3 to 70° ($2\theta$) in steps of 0.05°. The measuring time per step was 1 s and the scanning speed 3° ($2\theta$) per minute.

## 3. Results and discussion

### 3.1. Condensation of monobasic potassium phosphate

In Fig. 1, the thermogravimetric and differential scanning calorimetry (TGA/DSC) curves of monobasic potassium phosphate ($KH_2PO_4$) are presented. The peaks in the DSC curve before 200°C have previously been identified as a phase transition connected to the onset of disordered hindered rotation of the $H_2PO_4$ groups around all three axes [9]. No mass loss could be observed below 200°C and the total mass loss between 200 and 350°C corresponds to the loss of one water molecule for every $KPO_3$ unit. Peaks in the DSC curve after 200°C are probably due to phase transitions connected with the breaking up of the hydrogen network. Powder X-ray diffraction analysis identified the end product as potassium polyphosphate. The DSC peak at 810°C represents the transition to the melt, with no accompanying mass loss as confirmed by the TGA curve.

The results of the in situ Raman analysis of this transition are shown in Fig. 2. The room temperature spectrum of potassium dihydrogen phosphate (Fig. 2A) displays only one band at 914 $cm^{-1}$, which is the total symmetric breathing vibration ($A_1$) of $P(OH)_4$. This is in accordance with the tetragonal ($T_d$) structure of $KH_2PO_4$crystals, where each $PO_4$ tetrahedron is hydrogen bonded to four others [10]. Protons are equally shared between oxygen atoms of two different phosphate units, making all the oxygen

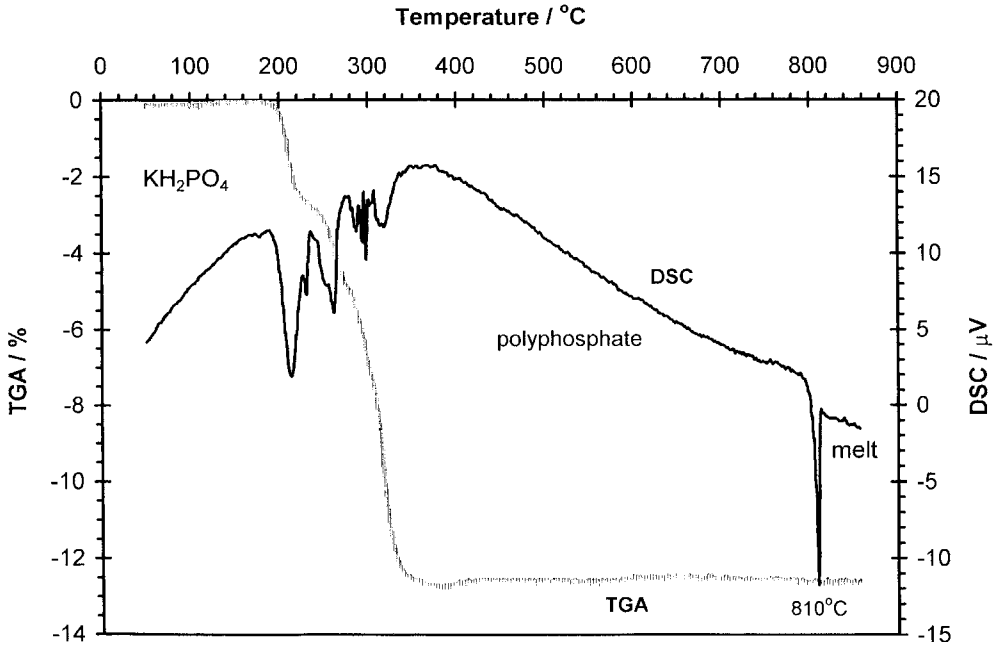



Fig. 1. TGA/DSC curves of potassium dihydrogen phosphate.

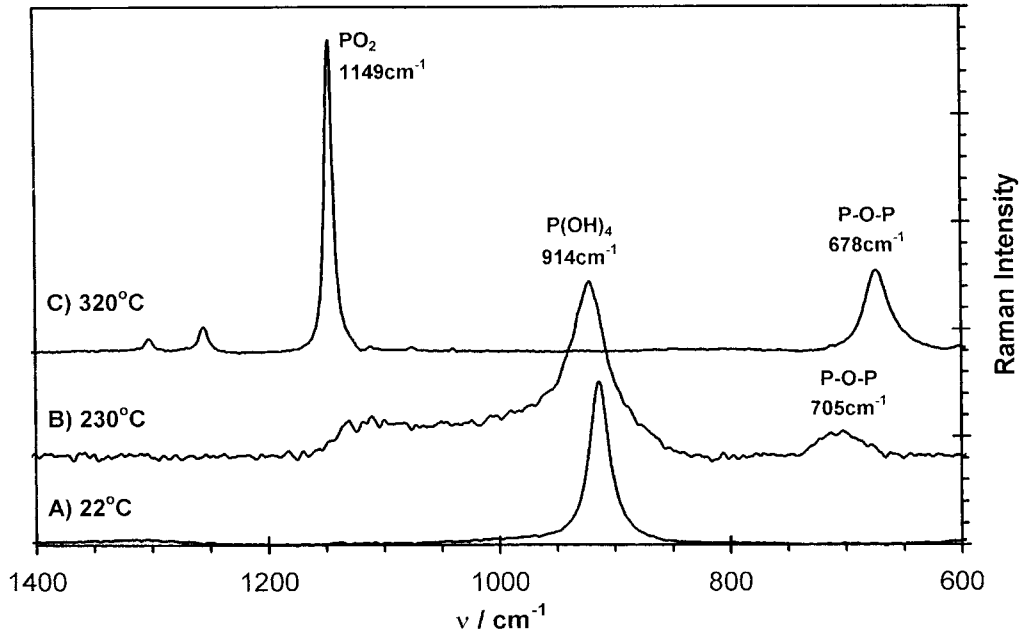
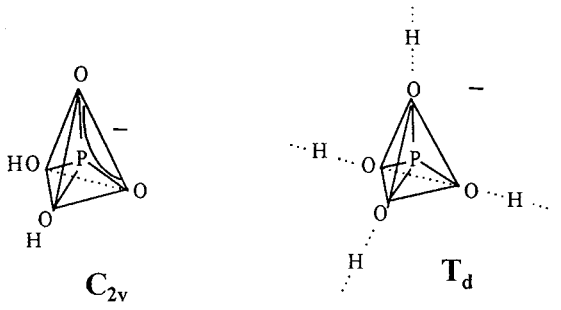



Fig. 2. In situ Raman spectra of potassium dihydrogen phosphate at 22°C (A); 230°C (B); and 320°(C).

ligands identical and increasing the symmetry of the phosphate species in the crystal. The increase in symmetry from $C_{2v}$ (in solution) to $T_d$ caused by hydrogen bonding in the solid can be seen in the structure below.




However, the monobasic phosphate species occupies a $S_4$ site in the crystal, which means that the symmetry of the tetrahedral phosphate ion should be lower. This was observed in the Raman spectrum of the crystal below 700 $cm^{-1}$ [4], but we observed no sign of a split of the band at 914 $cm^{-1}$ due to a reduction in the symmetry. The difference between $S_4$ and $T_d$ symmetry is only due to a slight difference in spatial orientation and since the vibrational modes behave essentially as individual molecular vibrations, it is concluded that the splitting effect on the phosphate band is negligible small.

Spectra recorded at temperatures above 230°C reflect the water loss seen in the TGA curve and gradual changes are observed in the spectrum as seen in Fig. 2B. As water is extracted from the crystal structure, the $A_1$ stretch vibration of the $P(OH)_4$ species of $KH_2PO_4$ at 914 $cm^{-1}$ is replaced by the $A_1$ stretch vibration of the $PO_2$ species in the polyphosphate at 1149 $cm^{-1}$, accompanied by the appearance of a broad band at 705 $cm^{-1}$, which is assigned to P–O–P backbone vibrations [11,12]. The $A_1$ band of the monophosphate has completely disappeared at 320°C (Fig. 2C) and the shift to higher wave numbers of the P–O band is an indication of the increase in the bond strength in the polymeric species between the terminal oxygen atoms and phosphorous atoms as compared to $P(OH)_4$. In contrast, the P–O–P band originating at 705 $cm^{-1}$ at 230°C shifts to 670 $cm^{-1}$ at 360°C, which is an indication of a decrease in bond strength caused by the polymerization reaction where linkages between monophosphates through oxygen are formed. At 360°C, no significant changes in the spectrum could be observed, except a minor shift of the P–O–P band. Polymerization is complete and only condensation between polymers could occur at higher temperatures.

According to the Raman spectra, condensation takes place without the formation of stable and detectable intermediates. The Raman spectra are consistent with the TGA/DSC curves.

The condensation of $KH_2PO_4$ to the polymer is relatively simple compared to the condensation reaction of $NaH_2PO_4{\cdot}2H_2O$, where the reaction mechanism is influenced by the formation of a hydrate at room temperature as discussed below.

### *3.2. Thermogravimetric analysis of the dehydration of monobasic sodium phosphate*

TGA/DSC curves of the dehydration of sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$) (Fig. 3) shows that the dehydration occurs in three steps. According to mass loss calculations, the first section represents the loss of two crystal water molecules during the temperature increase to 122°C. It should be noted that on the TGA curve the mass loss has already started at the onset of the recording. The difficulty in preparing separate phases of the hydrates necessitated the in situ measurements of this study. In the second part, one constitutional water molecule per two phosphate units is lost at 210°C. Finally, one constitutional water molecule per two phosphate units is released in the temperature range 210–343°C.

Close scrutiny of the first part of the curve, i.e. the process of loosing crystal water, revealed that the loss seems to proceed in at least two steps, indicating the presence of at least two different sites for water molecules. The structural changes that occur in the temperature range (40–180°C) during the process were studied by means of infrared and in situ Raman spectroscopy.

#### *3.2.1. The release of crystal water from $NaH_2PO_4{\cdot}2H_2O$ (40–150°C)*

Infrared spectroscopy is very sensitive to the presence of water in any sample and water bands corresponding to the symmetric and anti-symmetric OH stretching vibrations occur in the region 3000–3700 $cm^{-1}$, as well as OH-bending vibrations in the region 1600–1670 $cm^{-1}$. In Fig. 4, the infrared spectra

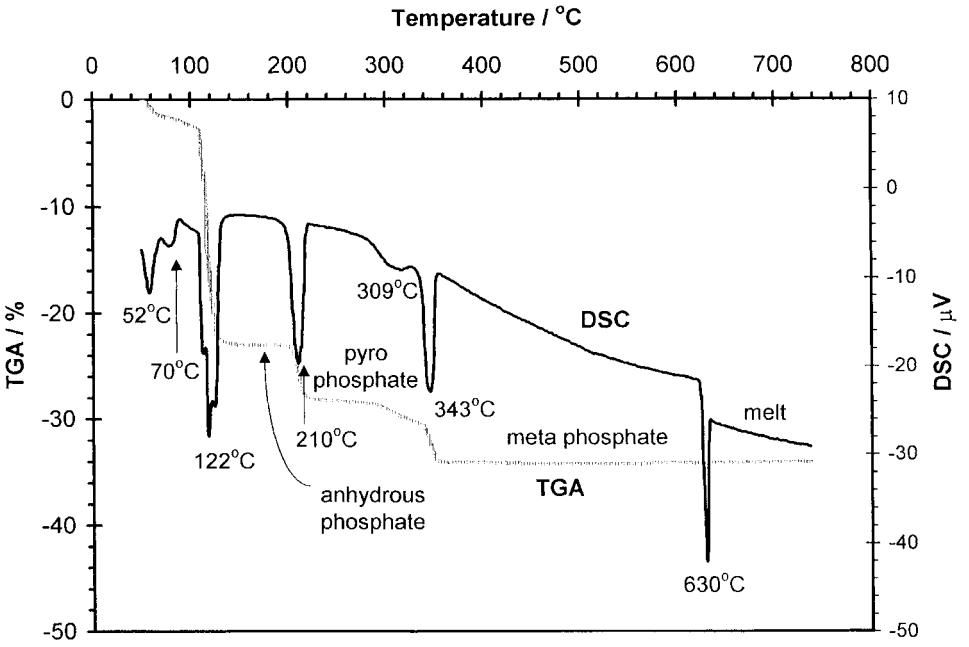



Fig. 3. TGA/DSC curves of sodium dihydrogen phosphate.

of $NaH_2PO_4{\cdot}2H_2O$ (A); are compared to that of $NaH_2PO_4{\cdot}H_2O$ (sodium dihydrogen phosphate monohydrate) (B); and $NaH_2PO_4$ (sodium dihydrogen phosphate) (C). In the spectrum of $NaH_2PO_4{\cdot}2H_2O$ (Fig. 4A) an asymmetric band at 1650 $cm^{-1}$ represents the bending vibrations of crystal water and around 3450 $cm^{-1}$ a broad band represents the stretching vibrations as mentioned above. At 3570 $cm^{-1}$ a narrow band is also present, which is absent in the spectrum of $NaH_2PO_4{\cdot}H_2O$. We conclude that this peak is associated with loosely bonded crystal water, which is lost before 60°C (Fig. 4A) upon transition to the mono hydrate. This is in agreement with Bartl et al. [5] who detected the existence of a water molecule at the boundaries of very weak hydrogen bonds. The 1650 $cm^{-1}$ band becomes more symmetrical in appearance when the weakly bonded crystal water is removed and disappears after removing all the crystal water at 122°C. In fact, even the hydroxy groups originating from the phosphates cannot be detected in the spectrum, although they are still present. It is, therefore, suggested that the large band at 3450 $cm^{-1}$ in Fig. 3 represents only the strongly bonded crystal water.

The infrared results were confirmed with Raman spectroscopy and in Fig. 5, the two different positions of water molecules are clearly visible, with the sharp peak at 3577 $cm^{-1}$ representing the water molecule loosely bonded to the phosphate species and the peaks between 3200 and 3600 $cm^{-1}$ representing the other crystal water. As in the infrared spectra, the peak at 3572 $cm^{-1}$ disappears at 60°C.

The loss of the crystal water is not only observed in the regions where water bands occur, but also indirectly through the changes in the positions of the P–O bands caused by the change in crystal structure as water molecules are removed from the crystal lattice. It was found that P–O bands in the infrared spectrum overlap heavily, however, in Raman spectroscopy the various bands representing different crystallographic phases are well defined, which made it an ideal technique for in situ analysis of the structural changes during the dehydration process.

The Raman spectra recorded in situ at various temperatures during the dehydration process are presented in Fig. 6. The spectrum of $NaH_2PO_4{\cdot}2H_2O$ (Fig. 6A) at room temperature displays three strong bands at 910, 945 and 992 $cm^{-1}$. In comparison with the one band in this region in the spectrum of $KH_2PO_4$ ($S_4$ symmetry), it is an indication of lower symmetry for the $PO_4$ tetrahedra, which is in accordance with Bartl et al. who reported a

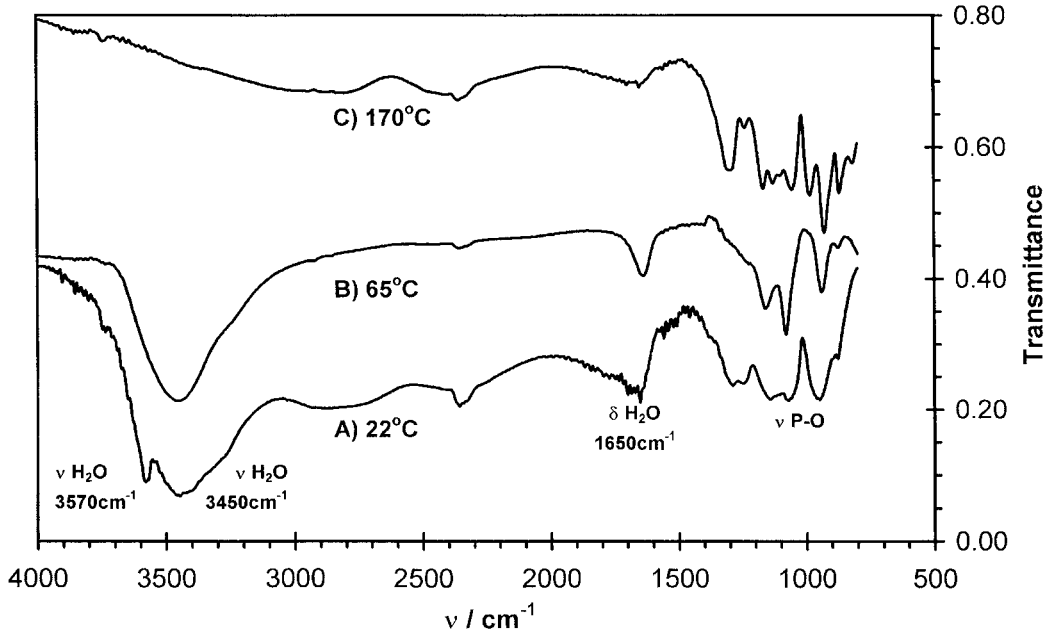



Fig. 4. Infrared spectra of sodium dihydrogen phosphate at 22°C (A); 65°C (B); and 170°(C).

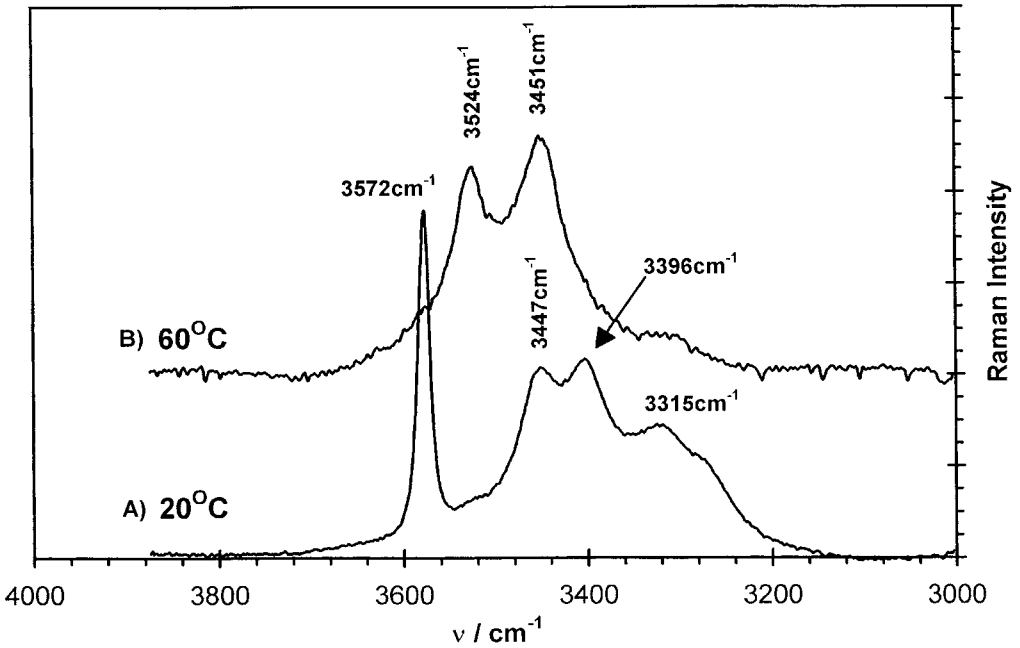



Fig. 5. In situ Raman spectra of sodium dihydrogen phosphate at 20°C (A); and 60°C (B) in the region of the water stretch vibrations.

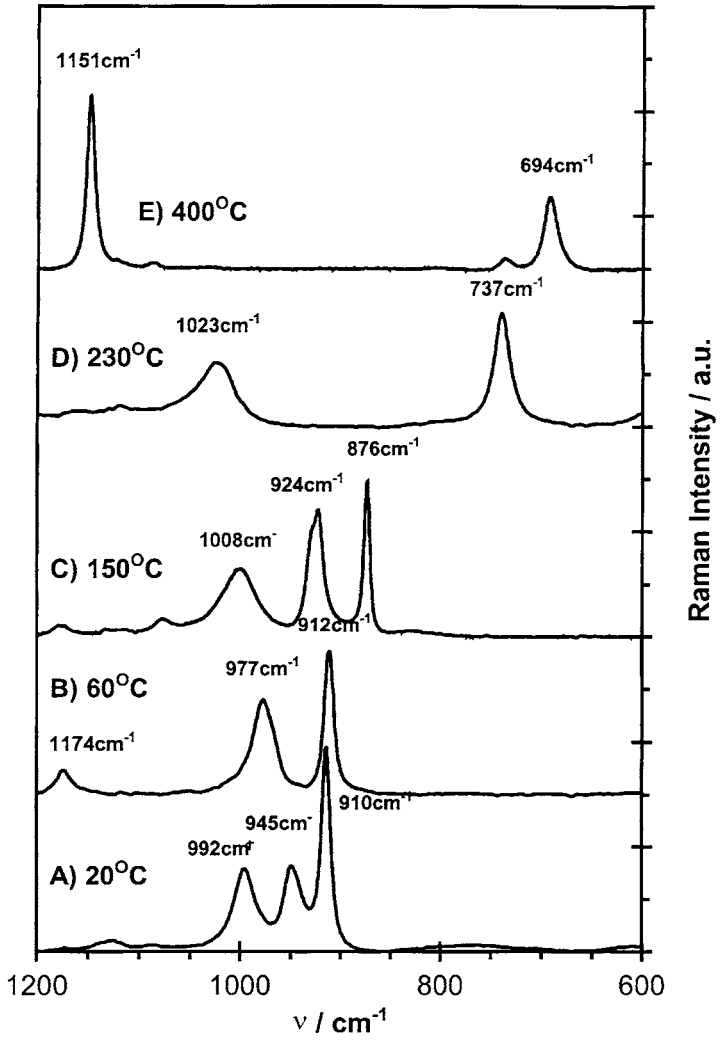



Fig. 6. In situ Raman spectra of sodium dihydrogen phosphate at 20°C (A); 60°C (B); 150°C (C); 230°C (D); and 400°C (E) in the region of the P–O stretch vibrations.

large distortion of the phosphate tetrahedron in $NaH_2PO_4{\cdot}2H_2O$ [5]. A shift of 39 $cm^{-1}$ to lower wavenumbers of the band at 910 $cm^{-1}$ in the deuterated species ($NaD_2PO_4{\cdot}2D_2O$) indicates that a $P(OH)_2$ vibration is involved. The P–O bands at 945 and 992 $cm^{-1}$ do not shift to lower wavenumbers upon deuteration and are, therefore, assigned to be $PO_2$ vibrations [13].

Removal of the loosely bonded crystal water at 60°C results in the disappearance of one of the P–O peaks (Fig. 6B), which means that the $PO_4$ units are now at a higher symmetry. Thus, although this water molecule is not strongly bonded to the phosphate species it has quite an influence on the crystal symmetry. Previously it has been reported that the two structures are quite similar [6].

The spectrum of the anhydrous phosphate in Fig. 6C shows a new band at 876 $cm^{-1}$. To determine whether the bands of the anhydrous species at 876 and 924 $cm^{-1}$ are in fact $P(OH)_2$ vibrations, it was compared with the spectrum of a deuterated phosphate. The $P(OH)_2$ vibrations of the deuterated phosphate shifted to lower wavenumbers, while the $PO_2$ vibration moved towards

higher wavenumbers. This result confirms that the bands 876 and 924 $cm^{-1}$ are $P(OH)_2$ vibrations.

The unit cell of the anhydrous phosphate contains two different types of phosphates [7]. The bands at 874 and 924 $cm^{-1}$ could reflect the two types of phosphates, but the assignments of bands might not be so straightforward. Choi et al. [8] studied the Raman spectrum of the anhydrous phosphate in detail using factor group analysis and reported 96 Raman active normal modes.

Changes in the Raman and IR spectra correspond to the peak positions in the DSC curve and the mass loss in the TGA curve, implying that thermogravimetric analysis and spectroscopy are consistent with each other (Fig. 7).

*3.2.2. Condensation of monobasic sodium phosphate*

Above 200°C, $NaH_2PO_4$ starts to condense forming disodium pyrophosphate ($Na_2H_2P_2O_7$) as can be seen in the Raman spectrum at this temperature (Fig. 6D). The band at 737 $cm^{-1}$ represents the linkage between the two phosphate units (P–O–P) as shown in Eq. (1), while the band at 1023 $cm^{-1}$ corresponds to the $PO_2$ vibration. The Raman spectra of $Na_2D_2P_2O_7$ and $Na_2H_2P_2O_7$ are compared in Fig. 8 and a definite shift of the P–O–P band at 737 $cm^{-1}$ towards lower wavenumbers is observed. This proves an effect of the hydrogen atoms on the P–O–P backbone vibration. The 737 $cm^{-1}$ band could be assigned to a P–OH vibration to explain the shift, but Raman spectra of tetra-sodium pyrophosphate ($Na_4P_2O_7$) and cyclic sodium metaphosphates ($Na_3PO_3$) showed a similar band (not shown) and ruled out this option. The literature assigned this band to a P–O–P vibration [11,12]. The authors believe that the P–O–P and P–OH vibrations cannot be regarded separately and both vibrations must be combined to one symmetric vibration in the Raman spectrum. Therefore, the 737 $cm^{-1}$ band is a symmetric H–O–P–O–P–O–H vibration, including the hydrogen atoms in the P–O–P backbone vibration. This conclusion is confirmed by the absence of a separate P–OH band between 800 and 950 $cm^{-1}$. The $PO_2$ band shifts towards higher wave numbers as expected.

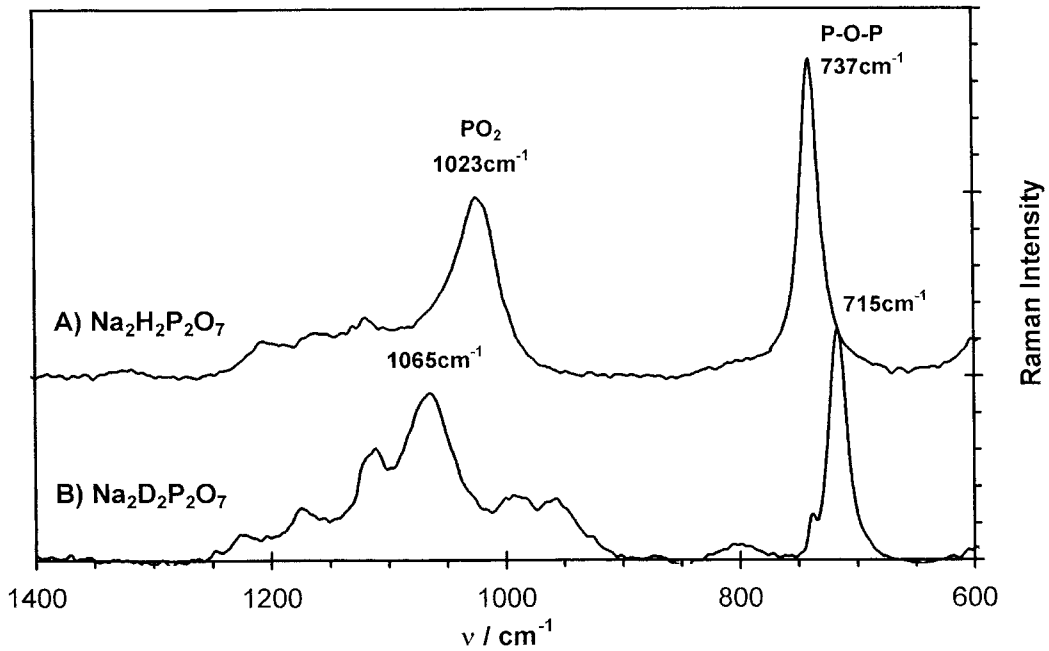



Fig. 7. In situ Raman spectra of disodium dihydrogen pyrophosphate (A); and dideuterium pyrophosphate (B) recorded at 230°C in the region of the P–O stretch vibrations.

Metaphosphate $(NaPO_3)_3$ formation starts above 300°C. The TGA/DSC curves in Fig. 3 show that this process takes place in two steps, one at 310°C and the other at 345°C. According to mass loss calculations, a combination of the two steps accounts for the loss of water in the formation of the *meta*-triphosphate. In this temperature range, the Raman spectra also change (Fig. 8A). The bands of the pyrophosphate are replaced by bands at 1151 and 694 $cm^{-1}$, which correspond to the symmetric stretch of the $PO_2$ and the –O–P–O–P–O– backbone species of cyclic meta triphosphate, respectively [11].

In contrast to the formation of potassium polyphosphate, sodium polyphosphate cannot simply be prepared by thermal dehydration of monosodium dihydrogen phosphate. Under these experimental conditions a mixture of two sodium *meta*-triphosphate phases is obtained according to a powder X-ray diffraction analysis. From 360°C, the TGA shows no further mass loss and the DSC peak at 630°C indicates the transition to the melt.

Below is a summary of the total thermogravimetric analysis of the condensation of sodium dihydrogen phosphate.

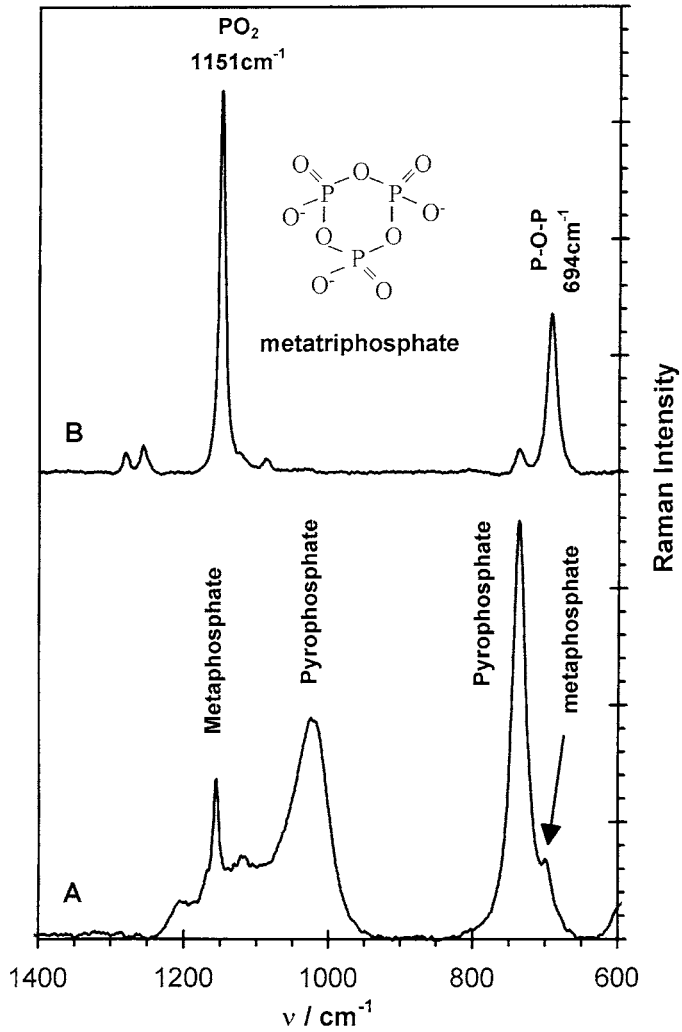
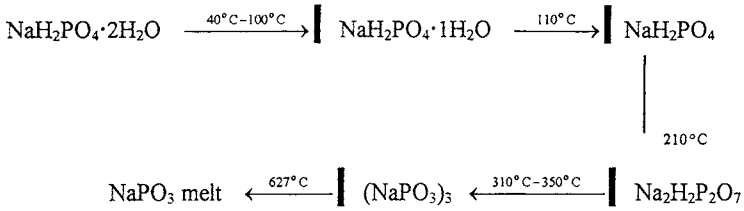



Fig. 8. In situ Raman spectra showing the transition from disodium dihydrogen pyrophosphate to cyclic *meta*-triphosphate in the P–O stretch region recorded at 320°C (A). Spectrum (B) recorded at 400°C shows the reaction is complete.




The melt can be quenched in air at room temperature to form a glass essentially containing linear polyphosphates. The degree of branching depends on the $Na_2O:P_2O_5$ ratio. Even at $Na_2O:P_2O_5$ below unity, branching could still occur according to Strauss and Treitler [14]. They showed that hydrolysis of branches in a polyphosphate solution accounts for the decrease in the viscosity of the solution. All branches should have disappeared after 24 h. A titration curve of a known aliquot of polyphosphate in water with a sodium hydroxide solution has an inflection point near pH 9 representing a state in which all acidic hydrogen atoms at both ends of all the chains are replaced by sodium ions. From the amount of sodium hydroxide used, the average length of a polymer can be calculated. A typical degree of polymerization for a sodium polyphosphate polymer prepared by quenching a melt in air is 85 phosphate units per chain, which is low compared to the values in the literature (400 [15]). An important factor is the purity of the reagents as well as residual moisture. Dibasic orthophosphates terminates chain growth and polyphosphate formation is very sensitive for the amount of this phosphate species present in the sample.

## 4. Conclusion

The dehydration of potassium and sodium dihydrogen phosphate has been successfully studied, using a combination of analytical techniques. In situ Raman measurements made it possible to monitor structural changes taking place during the reaction using characteristic vibrational bands of phosphates and polyphosphates.

In the manufacturing process of glass, catalysts and flame retardant it is advantageous to modify the properties of the products by varying the chain length and degree of cross-linking in the polymer formed. Reducing the temperature at which transformation to the resultant glass takes places also reduces production cost. This can be done by the addition of additives or using mixtures of phosphates. Comparing the thermal data and Raman and infrared spectra to those of the pure reagents will be extremely useful in the understanding of the role of the additives and will make the planning of modifications to the products possible.

## References

[1] J. Green, J. Fire Sci. 14 (1996) 426.
[2] B. Miller, Plastics World (1996) 44.
[3] C.Y. She, T.W. Broberg, D.F. Edwards, Phys. Rev. B 4 (5) (1971) 1580.
[4] H. Ratajczak, J. Baran, J. Raman Spectrosc. 7 (1) (1978) 54.
[5] H. Bartl, M. Catti, G. Ferraris, Acta Cryst. B32 (1976) 987.
[6] M. Catti, G. Ferraris, Acta Cryst. B32 (1976) 359.
[7] M. Catti, G. Ferraris, Acta Cryst. B30 (1974) 1.
[8] B.K. Choi, M.N. Lee, J.J. Kim, J. Raman Spectrosc. 20 (1989) 11.
[9] R. Blinc, V. Dimic, D. Kolar, G. Lahajnar, J. Stepišnik, S. Zumer, N. Vene, D. Hadzi, J. Chem. Phys. 49 (11) (1968) 4996.
[10] D.E.C. Corbridge, Phosphorus, An Outline of Its Chemistry Biochemistry and Technology, 2nd Edition, Elsevier, Amsterdam, 1980, pp. 476–480.
[11] D.E.C. Corbridge, E.J. Lowe, J. Chem. Soc. (1954) 493.
[12] N.H. Ray, Glass Technol. 16 (5) (1975) 107.
[13] E. Von Steger, K. Herzog, Zeit. Anorg. All. Chem. 331 (1964) 169.
[14] U.P. Strauss, T.L. Treitler, J. Am. Chem. Soc. 77 (1955) 1473.
[15] E.N. Walsh, et al. (Eds.), Proceedings of the 202nd National Meeting of the American Chemical Society on Phosphorus Chemistry, 25–30 August 1991, ACS Symposium Series 486, New York, 1992, pp. 92–93.