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Thermochimica Acta 371 (2001) 127–135

thermochimica acta

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Thermo-Raman studies on dehydration of $Na_3PO_4 \cdot 12H_2O$

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Received 3 July 2000; received in revised form 12 September 2000; accepted 14 September 2000

Abstract

In this work, dehydration of $Na_3PO_4 \cdot 12H_2O$ has been studied dynamically in detail by thermo-Raman spectroscopy. The dehydration was observed in the temperature range from 30 to 200°C. Spectral variation could distinguish six characteristic spectra of different hydrated species. The thermo-Raman intensity for the stretching bands of H_2O showed four distinct steps of dehydration with $Na_3PO_4 \cdot 12H_2O$, $Na_3PO_4 \cdot 8H_2O$, $Na_3PO_4 \cdot 7H_2O$, $Na_3PO_4 \cdot 6H_2O$ and $Na_3PO_4 \cdot 0.5H_2O$ as the compositional species. The differential thermo-Raman intensity thermogram indicated the possibility of the existence of a new hydrated intermediate species $Na_3PO_4 \cdot 4H_2O$ during the dehydration. The first four steps of dehydration occurred below 84°C and the last step of loosing 0.5 H_2O could not be detected. The results of TG measurement showed only two stages of dehydration.

Keywords: $Na_3PO_4 \cdot 12H_2O$; Dehydration; Thermal analysis; Thermo-Raman spectroscopy

1. Introduction

Trisodium orthophosphate dodecahydrate $Na_3PO_4 \cdot 12H_2O$ is a commercially important compound because of its wide applications in industries and domestic uses. Few detailed studies on its thermal properties have been carried out. Thermal analysis instruments, such as thermogravimetric analyzers (TGA), differential thermal analyzers (DTA) and differential scanning calorimeters (DSC) are used in analyzing the thermal properties of solids [1]. The mass changes measured as a function of temperature in a TG give information regarding changes in composition. The temperature differences and enthalpy changes measured by DTA and DSC, respectively, reveal compositional changes and phase transformations, but no direct identification of the phases and their compositions can be obtained during the thermal process. Raman spectroscopy is used to study the composition at a particular temperature and also phase transformation in a small temperature range. Thermo-Raman spectroscopy (TRS) involves measuring the Raman spectra dynamically as a function of temperature and the technique has been applied successfully in in situ investigations of dehydration, solid state phase transformations and composition changes [2–6].

An investigation of the system Na_2O–P_2O_5 and the formation of various hydrated forms of Na_3PO_4 at different temperatures was reported in the solubility studies by Wendrow and Kobe [7]. The phase diagram resulting from that work gave various hydrated forms of trisodium phosphate, hemihydrate, hexahydrate, octahydrate and dodecahydrate. The solubility studies of Na_3PO_4 by Menzel and von Sahr [8] suggested the presence of $Na_3PO_4 \cdot 12H_2O$, $Na_3PO_4 \cdot 8H_2O$ (or $7H_2O$

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0040-6031/01/$ – see front matter
PII: S0040-6031(00)00719-X

in doubt), $Na_3PO_4{\cdot}6H_2O$, $Na_3PO_4{\cdot}0.5H_2O$ (or H_2O) and Na_3PO_4. Four steps of hydration were clearly evident from the breaks in the ''solubility'' curve and the fifth was observed at 43°C. The hydrated form of hexahydrate or octahydrate was uncertain and the argument for the presence of hemihydrate or monohydrate was not clearly stated [9]. Menzel and von Sahr [8] also indicated that the hexahydrate and hemihydrate were chemical compounds. The existence of $Na_3PO_4{\cdot}7H_2O$ is in doubt, although suggested by Ingerson and Morey [10]. Dehydration studies of $Na_3PO_4{\cdot}12H_2O$ were reported by Steinbrecher and Hazer [11] and Duval [12,13] using TGA. Their TG thermograms showed only two stages indicating two hydrates, $Na_3PO_4{\cdot}12H_2O$ and $Na_3PO_4{\cdot}0.5H_2O$ (formed at 100°C) and an anhydrated Na_3PO_4 (formed at 165°C).

Although studies on dehydration of $Na_3PO_4{\cdot}12H_2O$ were extensive, a satisfactory and detailed dehydration mechanism is still lacking. Hence, in this work, TRS was used to study dehydration of $Na_3PO_4{\cdot}12H_2O$. The thermo-Raman investigation identified the following hydrates: $Na_3PO_4{\cdot}12H_2O$, $Na_3PO_4{\cdot}8H_2O$, $Na_3PO_4{\cdot}7H_2O$, $Na_3PO_4{\cdot}6H_2O$, $Na_3PO_4{\cdot}0.5H_2O$ and Na_3PO_4. The thermo-Raman intensity (TRI) for the stretching bands of H_2O and differential thermo-Raman intensity (DTRI) showed four distinct steps of dehydration but the last step was not resolved. DTRI indicated the possibility of the existence of a new hydrated intermediate species $Na_3PO_4{\cdot}4H_2O$.

The crystal structure of $Na_3PO_4{\cdot}12H_2O$ is hexagonal with space group $P\bar{3}c1$ [14,15]. $Na_3PO_4{\cdot}8H_2O$ is triclinic with space group $P\bar{1}$ [16] and $Na_3PO_4{\cdot}0.5H_2O$ is monoclinic with space group C2/c [17]. The crystal structures of the other hydrated forms are not known yet.

2. Experimental

The crystalline sample $Na_3PO_4{\cdot}12H_2O$ was prepared by recrystallizing the commercially available sample from Riedel–deHaen. The transparent needle-like crystals formed were kept in moist atmosphere to avoid the loss of hydrated water. The crystalline sample was used as such with slight crushing to powders.

The Raman spectra was excited by a laser light at a wavelength of 514.5 nm (50 mW) from an argon ion laser (Coherent, Innova 100-15). A filter was used to remove the plasma lines. The scattered light was collected at right angles, dispersed by a single spectrometer (Spex, 0.5 m) with a resolution of 10 cm^{-1} and detected by a CCD camera (Princeton Instruments, 1024 × 1024 pixels). The sample in a sample holder was mounted on the thermocouple in a homemade oven in stagnant air atmosphere. The temperature controller was used to control the temperature. Thermo-Raman spectra were collected in a thermal process set from 25 to 200°C at a rate of 2°C min^{-1}. The temperature covered by each spectrum was 1°C.

Free PO_4^{3-} ion is tetrahedral with point group T_d symmetry. Its four internal modes are at 938 cm^{-1} (ν_1), 411 cm^{-1} (ν_2), 1002 cm^{-1} (ν_3) and 546 cm^{-1} (ν_4) [18]. In crystals, the structure may undergo some distortion hence the symmetry of PO_4^{3-} may be lowered and bands may shift and split. The bands in the range from 400 to 1200 cm^{-1} may give some information about PO_4^{3-} during dehydration and phase transformation. The Raman bands observed in the spectral range from 2800 to 3650 cm^{-1} are the stretching bands of H_2O. Its intensity indicates the amount of H_2O. In this work, Raman spectra were recorded from 30 to 200°C in the range from 2200 to 4000 cm^{-1} for H_2O and from 200 to 1400 cm^{-1} for PO_4^{3-} separately.

Thermogravimetric analyzer (SEIKO ISSC 5000, TGA) was used to record the thermograms in the temperature range from 30 to 200°C with a heating rate of 2°C min^{-1} in a flow of air with flow rate of 100 ml min^{-1}.

3. Results and discussion

3.1. Dehydration

The present thermo-Raman investigations revealed five distinct spectral variations in the temperature range from 30 to 200°C. It indicated that the dehydration was stepwise with the existence of five hydrated forms of Na_3PO_4.

3.1.1. First step of dehydration

The variation in Raman spectra for H_2O in the temperature range from 33 to 40°C shown in Fig. 1(a) represented first step of dehydration. Raman

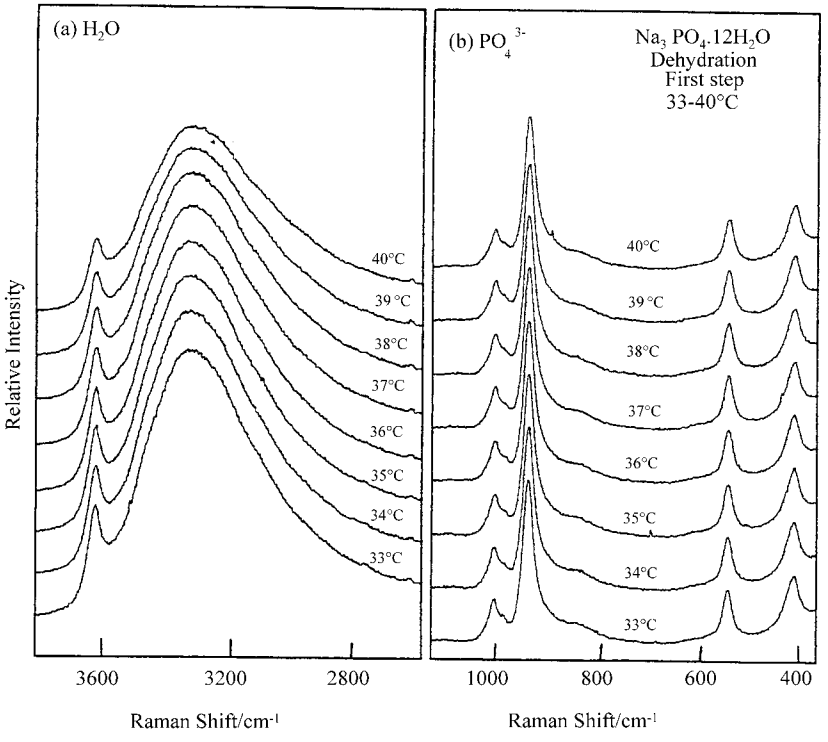

Fig. 1. Thermo-Raman spectra of $Na_3PO_4 \cdot 12H_2O$ in the temperature from 33 to 40°C for first step of dehydration (a) from 2600 to 3800 cm^{-1} in water vibration region and (b) from 375 to 1100 cm^{-1} in phosphate region.

spectra for H_2O below 33°C showed a strong and broad band at 3327 cm^{-1} and a sharp band at 3622 cm^{-1} for $Na_3PO_4 \cdot 12H_2O$. The intensity of the broad band at 3327 cm^{-1} started to decrease around 34°C and showed considerable decrease and broadening until 40°C. In addition to this a slight shift in the position from 3327 to 3321 cm^{-1} was also observed. This revealed the first dehydration step that occurred in a small temperature range from 33 to 40°C.

The corresponding spectral variation in the PO_4^{3-} region in this temperature range is shown in Fig. 1(b). No apparent change was observed except for a decrease in intensity of the Raman bands. This implied that the environment of PO_4^{3-} did not change much during the first step of dehydration.

3.1.2. Second step of dehydration

The variation in the spectra in the H_2O vibration region during second step of dehydration from 42 to 50°C is shown in Fig. 2(a). The spectral variation was distinct as a band at 3546 cm^{-1} appeared around 42°C and its intensity increased gradually up to 50°C. The band at 3622 cm^{-1} showed some decrease in intensity. In addition to broadening, drop in intensity was also noted for the band at 3321 cm^{-1}. These were the spectral variations observed in H_2O vibration region during the second step of dehydration extended from 42 to 50°C.

Spectral variation in the PO_4^{3-} region corresponding to the second dehydration step is shown in Fig. 2(b). Development of two shoulders at 961 and 897 cm^{-1} to the band at 937 cm^{-1} was observed. These overlapped bands were resolved and are shown in inset. This indicated that there might be three different symmetry sites for PO_4^{3-}. The ratio (area) of the three bands was about 0.4:1:1 indicating the relative amounts of each species. The band at 897 cm^{-1} was much broader. The band at 1002 cm^{-1} (ν_3 mode) became four weak bands at 1076, 1049, 1029 and 1003 cm^{-1} during this trans-

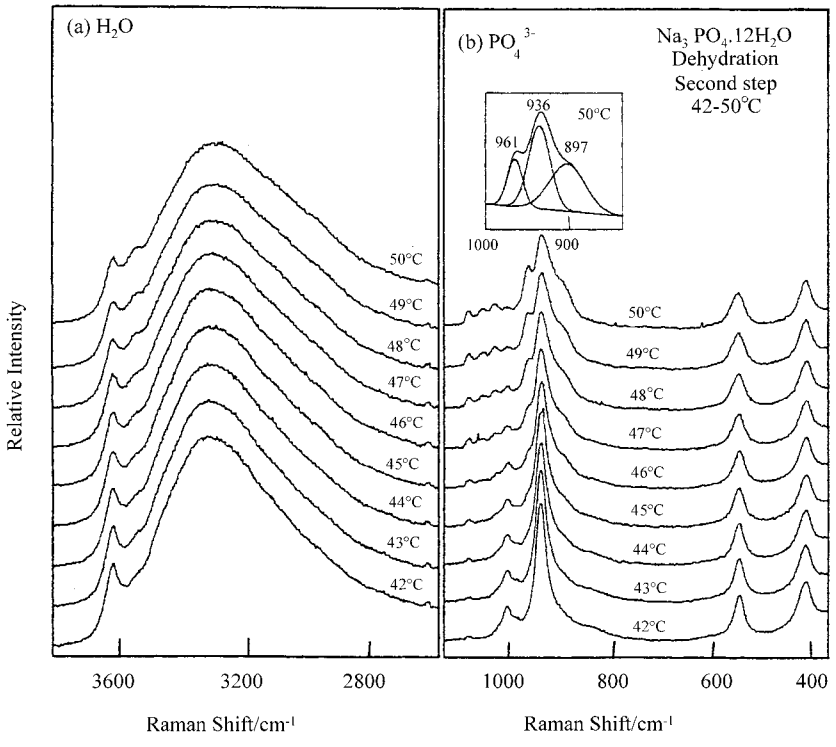

Fig. 2. Thermo-Raman spectra of $Na_3PO_4{\cdot}12H_2O$ in the temperature from 42 to 50°C for second step of dehydration (a) from 2600 to 3800 cm^{-1} in water vibration region and (b) from 375 to 1100 cm^{-1} in phosphate region. The inset is the deconvoluted spectra in the range 800–1000 cm^{-1} at 50°C.

formation. This also signified the distortion in the sites of PO_4^{3-}. The sharp bands at 546 and 410 cm^{-1} also showed some broadening.

3.1.3. Third step of dehydration

The third dehydration step from 50 to 59°C showed further decrease in intensity of the stretching bands of H_2O as shown in Fig. 3(a). Thermo-Raman spectra in this temperature range showed shift of the band from 3321 to 3292 cm^{-1}. This band became broad with the appearance of a hump at around 2967 cm^{-1} due to the background. The band at 3622 cm^{-1} disappeared at around 59°C.

The effect of this third stage of dehydration process in the PO_4^{3-} region was clearly visible as shown in Fig. 3(b). The three overlapping bands at 961, 928 and 897 cm^{-1} at 59°C were resolved and found that the ratio (area) was about 0.5:1:0.6 as shown in the inset. The shoulder at 961 cm^{-1} developed as a strong and sharp band. The shift in band position from 937 to 928 cm^{-1} was detected. The shoulder at 897 cm^{-1} was much weaker as temperature rose from 50 to 59°C. Shift was also observed in the band from 546 to 553 cm^{-1}. The three bands at 1076, 1049 and 1029 cm^{-1} became distinct with the disappearance of the fourth band at 1003 cm^{-1} at around 54°C.

3.1.4. Fourth step of dehydration

The fourth step of dehydration from 60 to 84°C showed a decrease in intensity and broadening of the stretching bands of H_2O as shown in Fig. 4(a). The weak band at 3546 cm^{-1} and strong broad band at 3292 cm^{-1} gradually disappeared at around 84°C but the hump at around 2967 cm^{-1} due to the background still persisted.

The spectral variation observed in the PO_4^{3-} region during the fourth stage of dehydration process is as shown in Fig. 4(b). The three bands at 1076, 1049 and 1029 cm^{-1} changed into a strong band at 1074 cm^{-1} and a weak broad band at 1021 cm^{-1} as the tempera-

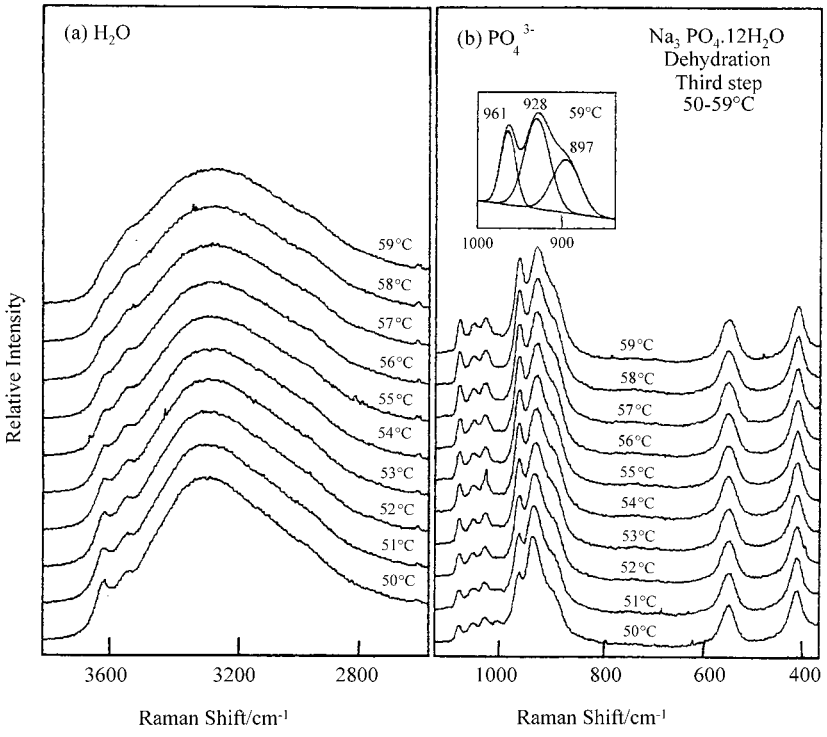

Fig. 3. Thermo-Raman spectra of $Na_3PO_4 \cdot 12H_2O$ in the temperature from 50 to 59°C for third step of dehydration (a) from 2600 to 3800 cm^{-1} in water vibration region and (b) from 375 to 1100 cm^{-1} in phosphate region. The inset is the deconvoluted spectra in the range 800–1000 cm^{-1} at 59°C.

ture rose to 84°C. The shift in band position from 928 back to 937 cm^{-1} was also observed during this stage. The other two bands at 961 and 897 cm^{-1} vanished. This indicated dramatic changes in the sites of PO_4^{3-}. Shifts in band position from 553 to 580 cm^{-1} and from 410 to 421 cm^{-1}, accompanied with band broadening were also observed during this dehydration stage.

3.1.5. Fifth step of dehydration

The fifth step of dehydration occurred at higher temperatures. The temperature range of the dehydration should be from 120 to 165°C. In the water vibration region, the broad hump at 2967 cm^{-1} (due to background) persisted even beyond 165°C. The sample is at this temperature dehydrated and the signal is thus not due to H_2O. The Raman signal of H_2O was in general weak and not distinct from the strong background hence it is not shown here.

However, for the PO_4^{3-} region (at temperatures from 120 to 165°C) spectral variations as shown in Fig. 5 were observed. The band at 937 cm^{-1} showed considerable increase in intensity. The band at 1074 cm^{-1} became distinct with rise in temperature. In addition to the broadening of the band at 580 cm^{-1}, development of a shoulder at 618 cm^{-1} was detected. This step resulted in the formation of anhydrous Na_3PO_4.

3.1.6. TG thermograms and Raman-intensity variations

The mass loss observed in the entire temperature range by TG is shown in the inset of Fig. 6(a). Two stages of dehydration were observed, the first from 25 to 100°C and the second from 140 to 190°C. The first stage showed a loss of 52.7% mass corresponding to 92.6% water loss or equivalent to 11.1 molecules of H_2O. The second stage showed 2.75% loss of water or 0.33 H_2O molecule. This result suggested the formation of $Na_3PO_4 \cdot 0.5H_2O$ from $Na_3PO_4 \cdot 12H_2O$ in the first stage in the temperature range from 33 to 100°C.

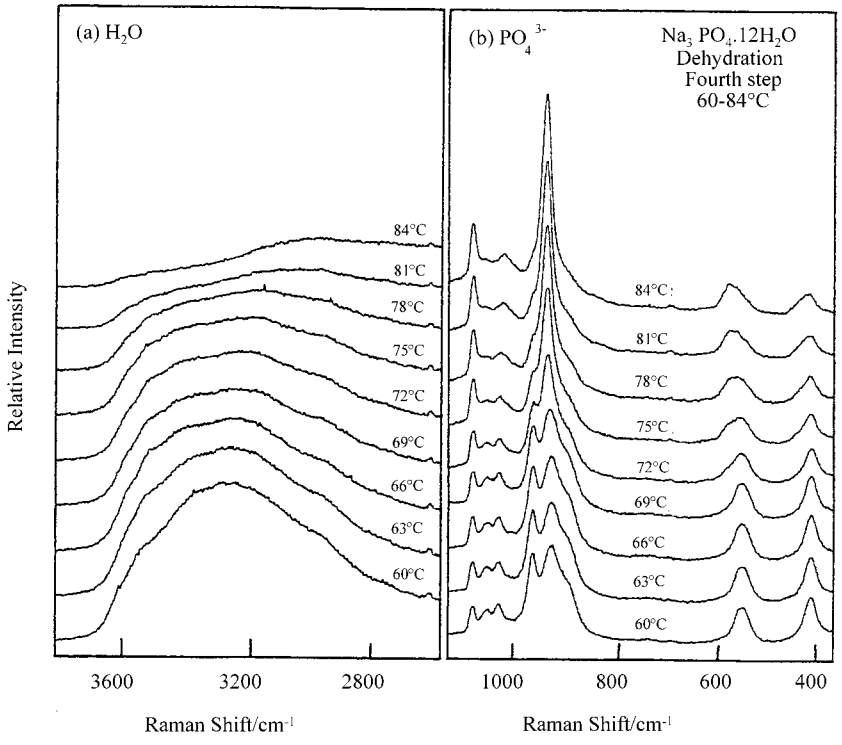

Fig. 4. Thermo-Raman spectra of $Na_3PO_4{\cdot}12H_2O$ in the temperature from 60 to 84°C for fourth step of dehydration (a) from 2600 to 3800 cm^{-1} in water vibration region and (b) from 375 to 1100 cm^{-1} in phosphate region.

The second stage of dehydration to Na_3PO_4 was in the temperature range from 120 to 165°C. TG was unable to resolve the first four steps of dehydration. Steinbrecher and Hazer [11] and Duval [12,13] showed similar TG thermograms suggesting two stages of dehydration, the first stage from 33 to 188°C and second stage from 188 to 220°C.

The intensity of the H_2O band represents the amounts or the number of H_2O molecules in the sample. The intensity variation calculated for the stretching bands of H_2O from 2625 to 3706 cm^{-1} in a temperature range from 25 to 320°C, highlighted four distinct steps of dehydration as shown in Fig. 6(a). This is the TRI thermogram. A steep decrease in intensity indicates the loss of hydrated water and a plateau implies a stable hydrated species at that temperature. This TRI thermogram is comparable to the TG results as shown in the inset. The intensity was strongest at room temperature and remained steady until 33°C. It vanished around 300°C. The total intensity should be assigned as 12 H_2O molecules. However, the intensity change in the last step of dehydration might not be reliable enough to give the amount of H_2O because its Raman signal was weak and the background was strong and not flat. In fact, the last step of dehydration should be from 120 to 165°C as the spectra in PO_4^{3-} region showed. Apparently the decrease in intensity after 200°C is due to a change in background. The loss of hydrated water from 25 to 100°C should be taken as 11.5 H_2O molecules based on the reason given above and the TG thermogram.

In this TRI thermogram, the first drop in intensity was observed from 33 to 40°C. This was the first step of dehydration and involved loss of 36.1% of 11.5 H_2O molecules or equivalent to 4.1 H_2O molecules resulting in the formation of $Na_3PO_4{\cdot}8H_2O$ from $Na_3PO_4{\cdot}12H_2O$. At 41°C, the intensity decreased gradually and became steady at 50°C. This represented as the second step of dehydration with a loss of 6.7% of 11.5 H_2O molecules or equivalent to 0.8 H_2O molecule transforming $Na_3PO_4{\cdot}8H_2O$ to

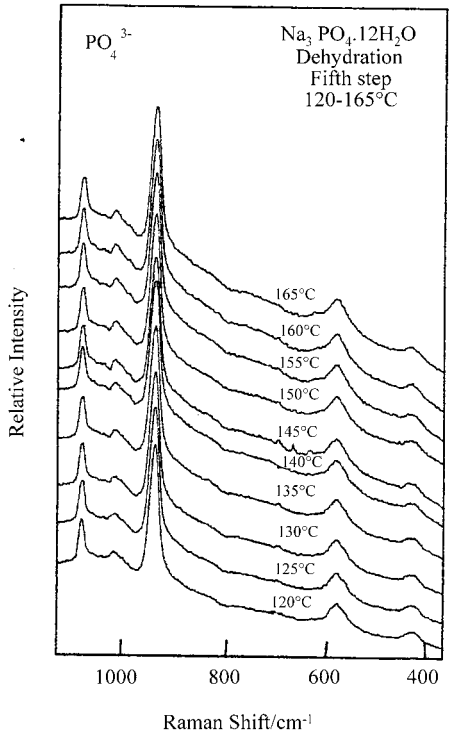

Fig. 5. Thermo-Raman spectra of $Na_3PO_4{\cdot}12H_2O$ from 375 to 1100 cm^{-1} in the phosphate region with the temperature from 120 to 165°C for fifth step of dehydration.

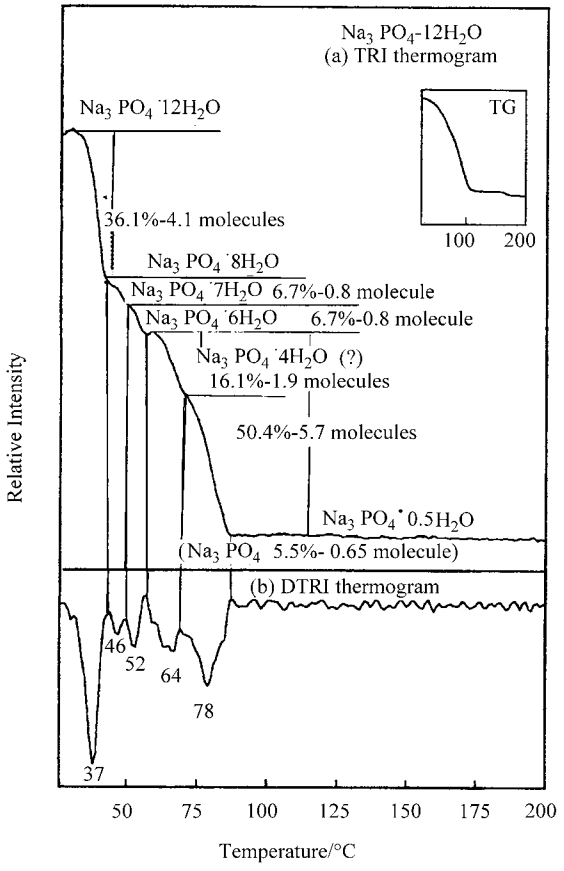

Fig. 6. (a) TRI thermogram for the stretching bands of H_2O during dehydration (inset is TG thermogram of $Na_3PO_4{\cdot}12H_2O$) and (b) DTRI thermogram for the stretching bands of H_2O during dehydration.

$Na_3PO_4{\cdot}7H_2O$. A drop in intensity from 50 to 60°C contributed to the third step of dehydration with a loss of 6.7% of 11.5 H_2O molecules. It was equivalent to 0.8 H_2O molecule with $Na_3PO_4{\cdot}7H_2O$ transforming to $Na_3PO_4{\cdot}6H_2O$. Sluggish decrease in intensity was revealed above temperature 60°C extending to 85°C. This prolonged fourth step of dehydration involved loss of 50.4% of 11.5 H_2O molecules or 5.7 H_2O molecules in which $Na_3PO_4{\cdot}6H_2O$ was transformed into $Na_3PO_4{\cdot}0.5H_2O$. The correct temperature range for the fifth dehydration step should be from 120 to 165°C as the variation of the Raman spectra in the PO_4^{3-} range and the TG curve showed. This plot of TRI against temperature (or TRI curve) revealed clearly the first four steps of the dehydration.

The derivative of the TRI curve is shown in Fig. 6(b). It is the DTRI thermogram. It showed five dips at 37, 46, 52, 64 and 78°C. The first three dips were distinct and represented the first three steps of dehydration. The two dips at 64 and 78°C both corresponds to the fourth step. Apparently, there might even be another step of dehydration in this temperature interval. A slight bend in the TRI curve was observed in this temperature interval as shown in Fig. 6(a) but no distinct spectral variation in the PO_4^{3-} part was detected. At that stage the intensity showed a loss of 16.1% of 11.5 H_2O molecules, equivalent to 2 H_2O molecules. Hence, $Na_3PO_4{\cdot}4H_2O$ might possibly be a new intermediate hydrated species. This DTRI thermogram did not show the fifth step of dehydration.

3.1.7. Characteristic spectra

Among the 200 Raman spectra, six typical spectra for the PO_4^{3-} region were found for the entire dehy-

Table 1
Raman bands for various hydrated forms of Na_3PO_4

Na_3PO_4. $12H_2O$ 25°C	Na_3PO_4. $8H_2O$ 41°C	Na_3PO_4. $7H_2O$ 49°C	Na_3PO_4. $6H_2O$ 56°C	Na_3PO_4. $0.5H_2O$ 84°C	Na_3PO_4 165°C	Assignments[a]
3622	3622	3622				
	3546	3546	3546			H_2O
3328	3321	3292	3292			
		2967*	2967*	2967*		
		1076	1076	1076	1076	
		1049	1049			$\nu_3(PO_4^{3-})$
		1029	1028	1021	1015	
1002	1002	1003				
		961	962			
938	938	938	928	937	937	$\nu_1(PO_4^{3-})$
		897	897		618	
546	546	546	553	580	580	$\nu_4(PO_4^{3-})$
411	411	410	410	421	432	$\nu_2(PO_4^{3-})$

[a] Ref. (18).
* Background.

dration process and these are shown in Fig. 7. These spectra were measured at (a) 36, (b) 41, (c) 49, (d) 56, (e) 84 and (f) 165°C corresponding to (a) $Na_3PO_4 \cdot 12H_2O$, (b) $Na_3PO_4 \cdot 8H_2O$, (c) $Na_3PO_4 \cdot 7H_2O$, (d) $Na_3PO_4 \cdot 6H_2O$, (e) $Na_3PO_4 \cdot 0.5H_2O$ and (f) Na_3PO_4, respectively. Probably, there might be another hydrate $Na_3PO_4 \cdot 4H_2O$ in the temperature range from 56 to 68°C, which might have similar spectrum to $Na_3PO_4 \cdot 6H_2O$. The band positions and their assignments are listed in Table 1.

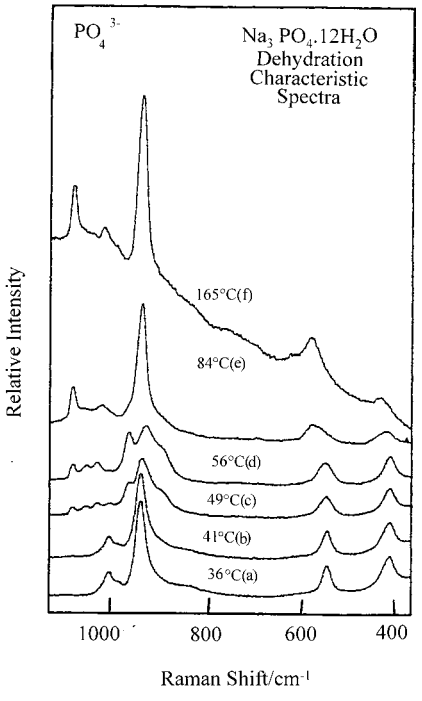

Fig. 7. Typical Raman spectra of: (a) $Na_3PO_4 \cdot 12H_2O$ at 36°C; (b) $Na_3PO_4 \cdot 8H_2O$ at 41°C; (c) $Na_3PO_4 \cdot 7H_2O$ at 49°C; (d) $Na_3PO_4 \cdot 6H_2O$ at 56°C; (e) $Na_3PO_4 \cdot 0.5H_2O$ at 84°C; (f) Na_3PO_4 at 165°C.

4. Conclusion

In this work, TRS was used to study dehydration of $Na_3PO_4 \cdot 12H_2O$ dynamically. The spectral variations observed in the H_2O and PO_4^{3-} regions in the thermal process showed distinct spectra corresponding to five hydrated forms. The intensity of the stretching bands of H_2O showed losses of 36.1, 6.7, 6.7 and 50.4% of 11.5 H_2O molecules corresponding approximately to loss of 4, 1, 1 and 5.5 molecules of water in each step, respectively. Unfortunately, the amount of water lost in the last step could not be detected. The present thermo-Raman investigations revealed the existence of the following hydrated forms of Na_3PO_4: $Na_3PO_4 \cdot 12H_2O$, $Na_3PO_4 \cdot 8H_2O$, $Na_3PO_4 \cdot 7H_2O$, $Na_3PO_4 \cdot 6H_2O$ and $Na_3PO_4 \cdot 0.5H_2O$. DTRI curve showed distinctly the four steps involved in dehydration with exception of the fifth step of dehydration as a result of a weak signal and a strong background in the stretching bands in the H_2O region. The possible existence of a new intermediate hydrated species,

$Na_3PO_4 \cdot 4H_2O$ in the temperature interval from 56 to 68°C was also indicated by DTRI thermogram. The TG thermograms showed only two steps of dehydration.

Acknowledgements

This work was supported by the National Science Council of Republic of China (NSC-89-2113-M007-013).

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