Thermo-Raman Studies on $NaH_2PO_4 \cdot 2H_2O$ for Dehydration, Condensation, and Phase Transformation

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Thermo-Raman spectroscopy was applied to study the thermal properties of $NaH_2PO_4 \cdot 2H_2O$ from room temperature up to 600 °C. Raman spectra recorded at every degree of the temperature interval by monitoring the internal modes gave the microscopic picture of dehydration of $NaH_2PO_4 \cdot 2H_2O$, the condensation of NaH_2PO_4, and the phase transformation of $NaPO_3$. The spectral variation observed could distinguish two steps of dehydration, resulting in the formation of $NaH_2PO_4 \cdot H_2O$ and NaH_2PO_4 as compositional species from $NaH_2PO_4 \cdot 2H_2O$. The thermo-Raman intensity (TRI) and differential thermo-Raman intensity (DTRI) thermograms also showed two steps of dehydration in the temperature range from 42 to 52 °C and from 60 to 72 °C with a maximum rate at 48 and 68 °C, respectively. Furthermore, condensation resulted in sodium dihydrogen diphosphate ($Na_2H_2P_2O_7$) and sodium metaphosphate ($NaPO_3$) in two steps at 212−224 and 260−360 °C, respectively. Clear evidence in the spectral variation representing two phase transformations of $NaPO_3$ at the temperature of 345 and 515 °C with three different polymorphs (phase III, phase II, and phase I of $NaPO_3$ in increasing order of temperature) was also observed. The thermal methods thermogravimetry, differential thermogravimetry , differential thermal analysis, and differential scanning calorimetry also supported the results but could not give a clear idea due to the lack of direct structural information.

Introduction

The thermal property of sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) is very interesting for its variety and attracted many researchers in the recent past.[1−3] It experiences dehydration to sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$) and anhydrous sodium dihydrogen phosphate (NaH_2PO_4), and it experiences condensation to sodium dihydrogen diphosphate ($Na_2H_2P_2O_7$) and then to sodium metaphosphate ($NaPO_3$). Finally, $NaPO_3$ shows two phase transformations before it melts.

Thermogravimetry (TG), differential thermogravimetry (DTG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) are always used to study the thermal properties of a solid sample in a dynamic thermal process.[4] Yet no direct information about the compositions and phases involved can be obtained. Thermo-Raman spectroscopy, which is the successive collection of Raman spectra in a dynamic thermal process, provides direct qualitative information. The composition changes and phase transformations are monitored on a time scale of seconds or on a temperature scale of one degree. The intensity and its derivative of the characteristic band plotted as a function of temperature are the thermo-Raman intensity (TRI) and differential thermo-Raman intensity (DTRI) thermograms, respectively. They give detailed quantitative information about the composition changes and phase transformations[5−11] and are comparable to the thermograms of TG, DTG, DTA, and DSC.

In this work, the thermal variations of $NaH_2PO_4 \cdot 2H_2O$ just before it melted were studied by thermo-Raman spectroscopy in a dynamic thermal process in the temperature range from 25 to 600 °C. Spectral variation observed in the H_2O and PO_4^{3-} regions showed two steps of dehydration, resulting in the formation of $NaH_2PO_4 \cdot H_2O$ and NaH_2PO_4 from $NaH_2PO_4 \cdot 2H_2O$. The thermo-Raman intensity (TRI) thermogram for the H_2O band revealed two steps of dehydration with a proportionate loss of water in each step. The differential thermo-Raman intensity (DTRI) thermogram also showed two dips at 48 and 68 °C for the maximum rate of dehydration. The TG, DTG, and DTA thermograms showed a consistent result. The formation of $Na_2H_2P_2O_7$ at 220 °C in the first condensation process from NaH_2PO_4 and in the second condensation process resulting in $NaPO_3$ at about 260−360 °C were observed. Further, with a rise in temperature, two phase transformations of $NaPO_3$ from phase III to phase II and from phase II to phase I were detected at 345 and 515 °C, respectively. The DTA and DSC thermograms confirmed the phase transformations but were not informative due to a lack of direct structural information. By the way, the characteristic Raman spectra of all of the species presented in the dynamic thermal process were recorded.

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(1) Quimby, O. T. *Chem. Rev.* **1947**, *40*, 141−180.
(2) Rudy, H.; Schloesser, H.; Watzel, R. *Angew. Chem.* **1940**, *53*, 525−531.
(3) Thilo, E. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1061−1071.
(4) Wendlandt, W. W. *Thermal Analysis*, 3rd ed.; Wiley: New York, 1986.
(5) Chang, H.; Huang, P. J. *J. Raman Spectrosc.* **1998**, *29*, 97−102.
(6) Chang, H.; Huang, P. J. *Anal. Chem.* **1997**, *69*, 1485−1491.
(7) Murugan, R.; Huang, P. J.; Ghule, A.; Chang, H. *Thermochim. Acta* **2000**, *346*, 83−90.
(8) Murugan, R.; Ghule, A.; Chang, H. *J. Phys.: Condens. Matter* **2000**, *12*, 677−700.
(9) Ghule, A.; Murugan, R.; Chang, H. *Thermochim. Acta* **2001**, *371*, 127−135.
(10) Murugan, R.; Ghule, A.; Chang, H. *J. Appl. Phys.* **1999**, *86*, 6779−6788.
(11) Murugan, R.; Ghule, A.; Bhongale, C.; Chang, H. *J. Mater. Chem.* **2000**, *10*, 2157−2162.

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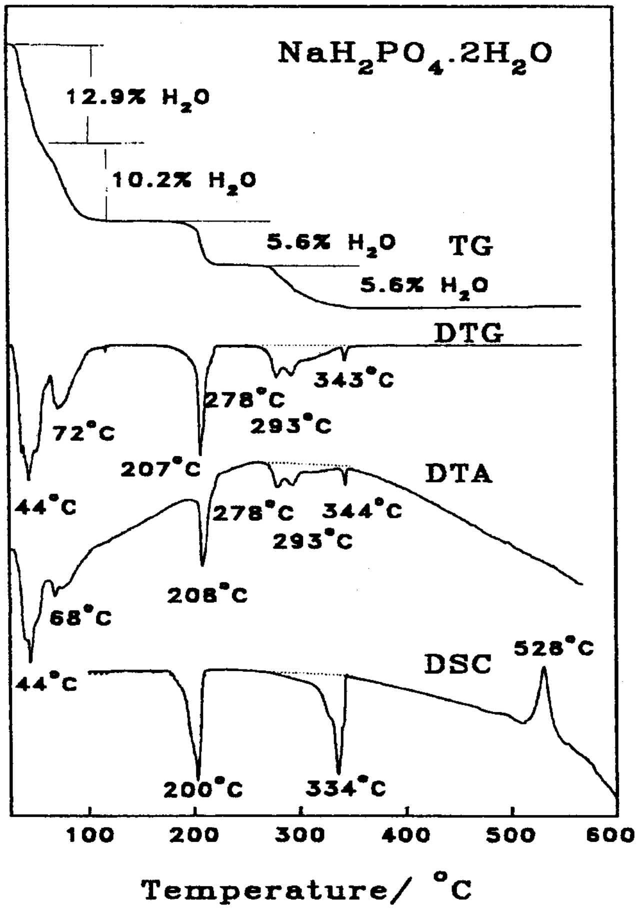

Figure 1. TG, DTG, DTA, and DSC thermograms started with $NaH_2PO_4 \cdot 2H_2O$.

Experimental Section

The crystalline sample $NaH_2PO_4 \cdot 2H_2O$ was obtained from Riedal-de-Haen. The rhombohedral crystals of size about 2 and 3 mm^3 were used for the experiments slightly crushed to powders.

The Raman spectra were excited by a laser beam at a wavelength of 514.5 nm (30 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, was dispersed by a single spectrometer (Spex, 0.5 m) with a resolution of 5 cm^{-1}, and was detected by a CCD camera (Princeton Instruments, 1024 × 1024 pixels). A Notch filter was set in front of the spectrometer to remove the Rayleigh-scattered light. The sample was in a sample holder mounted on the thermocouple in a homemade oven in a stagnant air atmosphere. The thermal process was set from 25 to 600 °C at a rate of 2 °C min^{-1} and was controlled by a temperature controller. The exposure time for CCD was 30 s which is equivalent to one spectrum for every degree.

A thermogravimetric analyzer, a differential thermal analyzer (SEIKO ISSC 5000, TGA/DTA-300), and a differential scanning calorimeter (SEIKO ISSC 5000, DSC-200) were used to record the thermograms in the temperature range from 25 to 600 °C with a heating rate of 2 °C min^{-1} in a flow of air at 100 mL min^{-1}.

Results and Discussion

Thermograms. The TG, DTG, DTA, and DSC thermograms of $NaH_2PO_4 \cdot 2H_2O$ in the temperature range from 25 to 600 °C are shown in Figure 1. The TG thermogram showed a loss of 23.2 wt % in the entire dehydration process, contributing to the loss of two water molecules against the calculated weight loss of 23.1%. The first dehydration extended in the temperature range from 42 to 52 °C and showed a loss of 12.9 wt % equivalent to 1.1 molecules of water. The second dehydration occurred in the temperature range from 60 to 72 °C, indicating a loss of 10.2 wt % equivalent to 0.9 molecule of water. The entire dehydration process for $NaH_2PO_4 \cdot 2H_2O$ extended up to 74 °C. After 90 °C, there was no considerable weight loss until 200 °C. After 200 °C, loss in weight was observed again which corresponded to the condensation. This extended into the temperature range from 190 to 210 °C and was the first condensation process resulting in $Na_2H_2P_2O_7$ formation. The calculated weight loss (5.6%) matched the observed weight loss (5.6%) for 0.5 molecule of water, confirming the formation of $Na_2H_2P_2O_7$. The second condensation was observed in the temperature range from 260 to 360 °C. This suggested the formation of $NaPO_3$ in which the weight loss was 5.6% compared with the calculated weight loss of 5.6% for 0.5 molecule of water. This condensation occurred in a considerably large temperature range and indicated that it would be complicated. Beyond 360 °C, there was no appreciable weight loss which indicated the completion of the composition changes.

The DTG thermogram, which is the derivative of the TG thermogram, is also shown in Figure 1. It showed a weight loss at 44 and 72 °C as a result of the first and the second dehydration, respectively. The dip at 207 °C was observed due to the first condensation process. Two dips at 278 and 293 °C followed and are assigned to the second condensation. It continued to the small dip at 343 °C (the dashed line is the baseline). This indicates that the condensation was complicated by three stages. The corresponding weight loss at 343 °C was infinitesimal (from the TG thermogram). No further information could be extracted at a higher temperature.

The DTA thermogram recorded in the same temperature range is also shown in Figure 1 (the dashed line is the baseline). This thermogram is similar to the DTG thermogram. The DTA thermogram showed two endotherms at 44 and 68 °C which corresponded to the first and second dehydration. At 208 °C, the endotherm observed was attributed to the first condensation process. That the second condensation process was prolonged showed two endotherms at 278 and 293 °C, representing the formation of $NaPO_3$. An endotherm at 344 °C was also observed, but TG and DTG thermograms indicated minute weight loss at this temperature. However, the transformation from phase III to phase II of $NaPO_3$ was also observed at this temperature (see TRS). The endotherm for the transformation to phase I of $NaPO_3$ could not be detected. Partridge et al.[12] reported the observation of two phases of $NaPO_3$ by differential thermal analysis with transformation at 500 °C and assigned them as B and A. This might be the transformation of phase II to phase I.

The DSC thermogram recorded in the temperature range from 100 to 600 °C is also shown in Figure 1 (dashed line is the baseline). The endotherm at 200 °C represented the condensation for the formation of $Na_2H_2P_2O_7$. The second endotherm started around 260 °C and decreased slowly, and finally an endotherm at 334 °C with two shoulders at 325 and 340 °C was observed just as the TG, DTG, and DTA thermograms showed. This also showed that the second condensation to phase III of $NaPO_3$ continued to the phase transformation of phase III to phase II of $NaPO_3$ around 340 °C. Besides this, an exotherm at 528 °C was also observed which corresponded to the transformation from phase II to phase I of $NaPO_3$.

Thermo-Raman Spectroscopy. During the heating process, three different species, PO_4^{3-}, $P_2O_7^{2-}$, and PO_3^{-}, appeared successively. These had different characteristic bands and could

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[12] Partridge, E. P.; Hicks, V.; Smith, G. W. *J. Am. Chem. Soc.* **1941**, *63*, 454–466.

be used for the identification of the composition and the phase of the sample. Their Raman spectra are well-known, and a simple description is given as following: The phosphate ion (PO_4^{3-}) is tetrahedral with a point group T_d symmetry. Its four internal modes are at 938 (ν_1), 411 (ν_2), 1002 (ν_3), and 546 (ν_4).[13] In crystal, the structure may undergo some distortion; hence, the symmetry may be lowered, and bands may shift and split. The broad band from 3100 to 3700 cm^{-1} is from the stretching modes of H_2O. The diphosphate ion ($P_2O_7^{2-}$) with C_{2v} symmetry, composed of two PO_3 groups and of a nonlinear P−O−P bridge, shows two strong bands at 1018 and 738 cm^{-1}. The band at 1018 cm^{-1} is assigned to the symmetric stretching mode of PO_3. The other distinct band at 738 cm^{-1} is characterized as the symmetric P−O−P stretching mode.[14] On the other hand, the metaphosphate ion (PO_3^-) linked like a polymer, which may have a straight chain or a cyclic ring with P−O−P and O−P−O structure, showed strong bands at 1161, 672, 638, 537, and 374 cm^{-1}. The characteristic frequencies of ν_s(P−O−P) at 672 cm^{-1} and of ν_s(O−P−O) at 1161 cm^{-1} for the internal vibration of PO_3^- are distinct.[15]

Dehydration. Sodium dihydrogen phosphate is mainly found in the hydrated form as $NaH_2PO_4{\cdot}2H_2O$ at room temperature. However, $NaH_2PO_4{\cdot}4H_2O$ was reported to be present at −20 °C.[16] The solubility studies suggest the existence of two hydrated forms, $NaH_2PO_4{\cdot}2H_2O$ and $NaH_2PO_4{\cdot}H_2O$, and an anhydrous form, NaH_2PO_4, above room temperature.[17]

$NaH_2PO_4{\cdot}2H_2O$ is orthorhombic at room temperature with a space group of $P2_1P2_1P2_1(D_24)$ and $Z = 4$. The crystal structure of $NaH_2PO_4{\cdot}2H_2O$ was well-resolved by X-ray diffraction and by neutron scattering by Bartl et al.[18] The four oxygen atoms are not equivalent, but the structural stability is achieved due to the strong hydrogen bonding. The two acidic hydrogens of the $H_2PO_4^-$ group form strong hydrogen bonds with the oxygen of the adjacent $H_2PO_4^-$, and the water molecules are weakly bounded in the structure.[16,19] This should be the reason for the complicated spectrum of $NaH_2PO_4{\cdot}2H_2O$ at room temperature and for the first dehydration to occur at such a low temperature.

$NaH_2PO_4{\cdot}H_2O$ with an orthorhombic form crystallizes in space group $Pna2_1$ with $Z = 4$. $NaH_2PO_4{\cdot}H_2O$ shows two forms as pseudo-orthorhombic and monoclinic.[16,20] $NaH_2PO_4{\cdot}H_2O$ has pairs of centrosymmetrical chains linked by sharing edges of polyhedra. Straight single chains with polyhedra sharing two edges in the pseudo-orthorhombic form and bent single chains with polyhedra sharing two vertexes in the monoclinic form were found.[16] However, its spectrum was simple.

Anhydrous NaH_2PO_4 was obtained by heating $NaH_2PO_4{\cdot}2H_2O$ at about 90 °C.[19] This work showed that all of the water was lost below 72 °C at a much lower temperature. The weakly bounded water molecules were released easily in the thermal process, and the anhydrous form was obtained. The structure of anhydrous NaH_2PO_4 was reported as monoclinic $P2_{1/c}$ with $Z = 8$.[21] This might be the reason for the complicated spectrum.

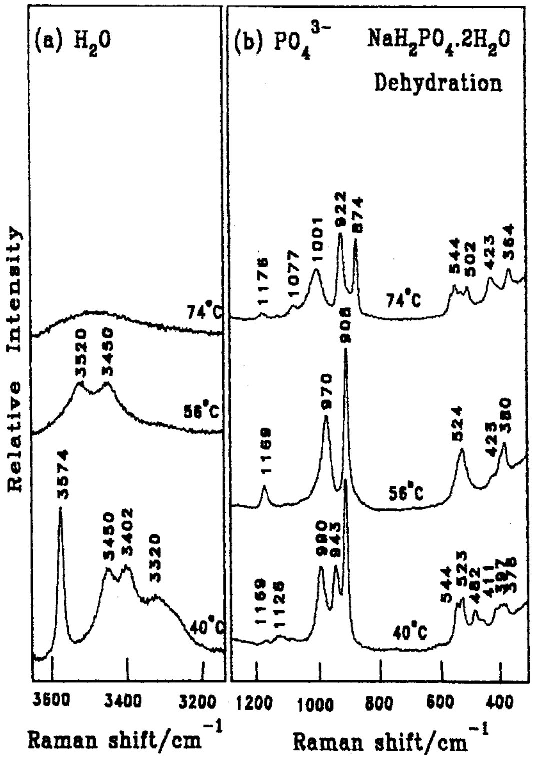

Figure 2. Thermo-Raman spectra of $NaH_2PO_4{\cdot}2H_2O$ at temperature 40 ($NaH_2PO_4{\cdot}2H_2O$), 56 ($NaH_2PO_4{\cdot}H_2O$), and 74 °C (NaH_2PO_4) for the first and second dehydration in (a) the H_2O region from 3150 to 3650 cm^{-1} and in (b) the PO_4^{3-} region from 300 to 1300 cm^{-1}.

Characteristic Spectra for Dehydration. The first 96 Raman spectra from 25 to 120 °C in both the H_2O and PO_4^{3-} regions showed considerable variations for the two dehydration steps. The characteristic spectra of each intermediate species encountered during dehydration in both of the regions from 3100 to 3700 cm^{-1} and from 300 to 1300 cm^{-1} are shown in Figure 2a and b, respectively, for $NaH_2PO_4{\cdot}2H_2O$ at 40 °C, $NaH_2PO_4{\cdot}H_2O$ at 56 °C, and NaH_2PO_4 at 74 °C. The band positions and assignments are listed in Table 1.

First Dehydration. The room-temperature spectrum (same as that at 40 °C) in the H_2O region showed a strong band at 3574 cm^{-1}. Three strong, broad bands at 3450, 3402, and 3320 cm^{-1} were observed as the stretching bands of H_2O. The Raman spectra of solid $NaH_2PO_4{\cdot}2H_2O$ in H_2O region at room temperature and well below room temperature were reported by Toupry et al.[19] A strong band at 3575 cm^{-1} was also observed in this work and was assigned to the OH antisymmetric vibration (ν_3 mode) of one of the H_2O molecules, of which the OH was almost free of hydrogen bonding, followed Toupry et al.[19]

The spectral variations in the H_2O region for the first dehydration in the temperature range from 40 to 56 °C were observed. With the rise in temperature, the intensity of the strong band at 3574 cm^{-1} started to decrease at about 42 °C and disappeared around 52 °C. The intensity of the band at 3450 cm^{-1} was also decreasing. The bands at 3402 and 3320 cm^{-1} disappeared around 52 °C. A new band at 3520 cm^{-1} appeared around 48 °C and showed an increase in intensity with an increase in temperature. Only two bands at 3520 and 3450 cm^{-1} were distinct after 52 °C.

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(13) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1978.

(14) Philip, D.; George, B. L.; Aruldhas, G. *J. Raman Spectrosc.* **1990**, *21*, 523−524.

(15) Attfield, J. P. In *Phosphates: Solid State Chemistry, Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley & Sons: New York, 1994; Vol. 6.

(16) Catti, M.; Ferraris, G. *Acta Crystallogr., Sect. B* **1976**, *32*, 359−363.

(17) Toy, A. D. F. In *Phosphorus, Comprehensive Inorganic Chemistry*, 1st ed.; Trotman-Dickenson, A. F., Ed.; Pergamon: Oxford, 1973.

(18) Bartl, H.; Catti, M.; Ferraris, G. *Acta Crystallogr., Sect. B* **1976**, *32*, 987−994.

(19) Toupry-Krauzman, N.; Poulet, H.; Postollec, M. Le. *J. Raman Spectrosc.* **1979**, *8*, 115−121.

(20) Ferraris, G.; Jones, D. W.; Sowden, J. M. *Atti. Accad. Sci. Torino* **1974**, *108*, 507−527.

(21) Catti, M.; Ferraris, G. *Acta Crystallogr., Sect. B* **1974**, *30*, 1−6.

Table 1. Raman Bands for $NaH_2PO_4{\cdot}2H_2O$, $NaH_2PO_4{\cdot}H_2O$, NaH_2PO_4, and $Na_2H_2P_2O_7$[a]

$NaH_2PO_4{\cdot}2H_2O$ 40 °C	$NaH_2PO_4{\cdot}H_2O$ 56 °C	NaH_2PO_4 74 °C	assign-ments[b]	$Na_2H_2P_2O_7$ 226 °C	assign-ments[c]
3574s			OH^-		
	3520m				
3450s	3450m		H_2O		
3402s					
3320m					
1169w	1169m	1176w			
1126w					
		1077w			
				1018s	PO_3
990s	970s	1001s	ν_3 PO_4^{3-}		
943s					
910s	908s	922s	ν_1 PO_4^{3-}		
		874s			
				738s	P−O−P
		559w			
544w		544w		548w	
523w	524s	528w	ν_4 PO_4^{3-}		
		502w			
482w			ν_2 PO_4^{3-}	468w	
411w	423w	423m		405w	
397w					
378w	380m				
		364m			

[a] s-strong, m-medium, and w-weak. [b] Reference 13. [c] Reference 14.

The corresponding changes observed in the PO_4^{3-} region in the first dehydration were distinct in the temperature range from 40 to 56 °C. During dehydration, the weak band at 1126 cm^{-1} disappeared, and the intensity of the other weak band at 1169 cm^{-1} gradually increased with the temperature. The strong bands at 990 and 943 cm^{-1} showed a gradual decrease in intensity and disappeared around 50 °C. A new band at 970 cm^{-1} showed up around 46 °C and replaced these bands at 990 and 943 cm^{-1}. Two bands were observed at 544 and 523 cm^{-1} which merged to form a broad band at 524 cm^{-1}. A band at 482 cm^{-1} with a broad shoulder was also observed but disappeared gradually around 48 °C. The bands at 411, 397, and 378 cm^{-1} combined to form a distinct band at 380 cm^{-1} and a weak shoulder at 423 cm^{-1} around 48 °C. The spectral changes were distinctly evident in the temperature range from 42 to 52 °C as seen from the characteristic spectra at 40 and 56 °C shown in Figure 2. The first dehydration was the transformation of $NaH_2PO_4{\cdot}2H_2O$ to $NaH_2PO_4{\cdot}H_2O$.

Second Dehydration. Spectral variations in the H_2O region during the second dehydration in the temperature range from 56 to 74 °C were observed as shown in Figure 2a. At around 60 °C, the broad bands at 3520 and 3450 cm^{-1} started disappearing and became almost flat around 72 °C which should be the background. This indicated that the remaining water was lost in the second dehydration in the temperature range from 60 to 72 °C, and NaH_2PO_4 was formed.

The spectral variations in this second dehydration in the PO_4^{3-} region were distinct. The spectra observed at 56 and 74 °C are shown in Figure 2b. The band at 1169 cm^{-1} showed a gradual decrease in intensity and shifted to 1176 cm^{-1} with the rise in temperature up to 72 °C. The strong broad band at 970 cm^{-1} showed a steady decrease in intensity from 60 °C and vanished at 72 °C. Instead, two bands at 1077 and 1001 cm^{-1} were observed and showed an increase in intensity with a rise in temperature to 72 °C. The strong sharp band at 908 cm^{-1} showed a gradual decrease from 60 °C until it disappeared at 72 °C and was replaced by two bands at 922 and 874 cm^{-1} which started appearing around 60 °C. The band at 524 cm^{-1} dispersed into four bands at 559, 544, 528, and 502 cm^{-1} as the temperature rose to 72 °C. Similarly, the weak bands at 423 cm^{-1} showed an increase in intensity with a rise in temperature. The band at 380 cm^{-1} disappeared around 68 °C and was replaced by a band at 364 cm^{-1}. This second dehydration was observed in the temperature range from 60 to 72 °C.

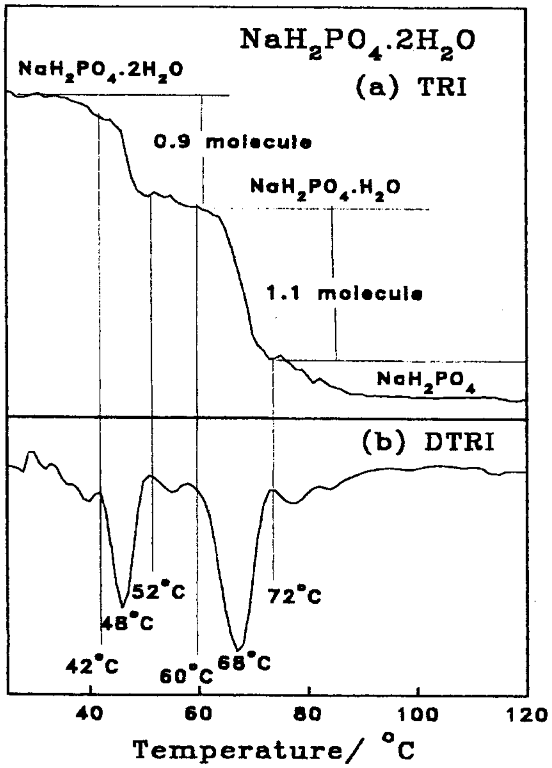

Figure 3. (a) Thermo-Raman intensity (TRI) thermogram and (b) differential thermo-Raman intensity (DTRI) thermogram for the stretching bands of H_2O during dehydration of $NaH_2PO_4{\cdot}2H_2O$ in the temperature range from 25 to 120 °C.

During dehydration, the PO_4^{3-} group was intact; however, the symmetric site varied while H_2O was removed from the crystal lattice. Thus, the spectra had four groups of bands as shown in Figure 2b. The modifications in spectra in terms of the shift and the split in the bands were due to the presence of H_2O. This was also observed in the earlier work in $CaC_2O_4{\cdot}H_2O$,[6] $CuSO_4{\cdot}5H_2O$,[22] and $CaSO_4{\cdot}2H_2O$.[23]

Intensity Variation. The intensity (area) of the water bands in the range from 3300 to 3700 cm^{-1} and in the temperature range from 25 to 120 °C is shown in Figure 3a. It is the thermo-Raman intensity (TRI) thermogram. The entire intensity was assigned to be equivalent to two molecules of water. The steep slope in the TRI thermogram indicated the loss of a water molecule, and the stagnant stage implied that an intermediate was formed. The TRI thermogram showed two steep slopes and one stagnant stage which corresponded to the two steps of dehydration. A steep slope for the first dehydration was observed in the temperature range from 42 to 52 °C. It revealed a loss of 45% of intensity which is equivalent to 0.9 molecule of water. This resulted in the formation of $NaH_2PO_4{\cdot}H_2O$ from $NaH_2PO_4{\cdot}2H_2O$. The second steep decrease was in the temperature range from 60 to 72 °C. It showed a loss of 55% of intensity which is equivalent to 1.1 molecules of water, resulting in the formation of anhydrous NaH_2PO_4. After 74 °C, there was a slow,

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(22) Chang, H.; Huang, P. J. *J. Chin. Chem. Soc.* **1998**, *45*, 59−66.
(23) Chang, H.; Huang, P. J.; Hou, S. C. *Mater. Chem. Phys.* **1999**, *58*, 12−19.

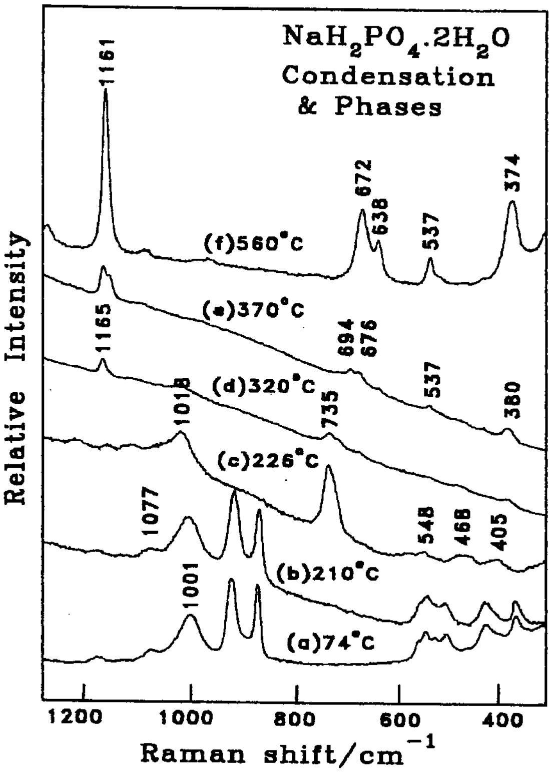

Figure 4. Typical Raman spectra at (a) 74 °C for NaH_2PO_4, (b) 210 °C for NaH_2PO_4 before condensation, (c) 226 °C for $Na_2H_2P_2O_7$, (d) 320 °C for $NaPO_3$ phase III with a small amount of $Na_2H_2P_2O_7$, (e) 370 °C for $NaPO_3$ phase II, and (f) 560 °C for $NaPO_3$ phase I.

steady decrease in intensity as the temperature reached 90 °C. This steady decrease was due to the decrease of the background.

The derivative of the thermo-Raman intensity thermogram was also plotted in the temperature range from 25 to 120 °C and is shown in Figure 3b. It is the differential thermo-Raman intensity (DTRI) thermogram. The drops indicated the temperature ranges of the dehydration, and the dips revealed the temperatures for the maximum rate of dehydration. It showed two drops; the first one was from 42 to 52 °C with a dip at 48 °C and represented the first dehydration, and the second one was from 60 to 72 °C with a dip at 68 °C and represented the second dehydration.

The TRI and DTRI thermograms obtained are comparable to the TG, DTG, and DTA thermograms, respectively, in dehydration. The TG thermogram showed two steps of dehydration similar to those observed in the TRI thermogram, indicating the loss of one H_2O molecule in each step. The endotherms at 44 and 68 °C observed in the DTA thermogram and the dips at 44 and 72 °C observed in the DTG thermogram were in close agreement with those observed in the DTRI thermogram at 48 and 68 °C. This supported the idea that the dehydration was in two steps.

Characteristic Spectra for Condensations. In the dynamic thermal process of $NaH_2PO_4 \cdot 2H_2O$ from 25 to 600 °C, four composition changes in dehydration and condensation and two phase transformations of $NaPO_3$ occurred. $NaH_2PO_4 \cdot 2H_2O$, $NaH_2PO_4 \cdot H_2O$, and NaH_2PO_4 were encountered during the dehydration and are shown in Figure 2. The typical spectra of the different species in the range from 300 to 1300 cm^{-1} are presented in Figure 4. Between 74 and 210 °C, the spectra of NaH_2PO_4 showed some broadening due to an increase in the temperature as shown in Figure 4a and b for the spectra obtained at 74 and 210 °C, respectively. NaH_2PO_4 then experienced two condensations, and $Na_2H_2P_2O_7$ and $NaPO_3$ were formed successively at phase III. In Figure 4b, c, and d, the corresponding characteristic spectra at 210, 226, and 320 °C were for NaH_2PO_4, $Na_2H_2P_2O_7$, and $NaPO_3$ in phase III, respectively, with a small amount of $Na_2H_2P_2O_7$. Three different phases of $NaPO_3$ were also observed in this study as phase III, phase II, and phase I. In Figure 4d, e, and f, their typical spectra at 320, 370, and 560 °C, respectively, are also shown for these three phases. The band positions and assignments are tabulated as in Tables 1 and 2.

Table 2. Raman Bands for Various Phases of Sodium Metaphosphates[a]

$NaPO_3$ (III) 320 °C	$NaPO_3$ (II) 370 °C	$NaPO_3$ (I) 560 °C	assignments[b]
1165m	1165s	1161s	O−P−O
	1152m		
1018w			
735m			
	716w		
	694w		
678w	676w	672m	P−O−P
	638w	638m	
	537w	537w	
380w	380w	374m	

[a] s-strong, m-medium, and w-weak. [b] Reference 15.

Condensation. After dehydration, no change until 210 °C was observed except the bandwidths increased as the temperature increased. Thus, the bands at 559 and 528 cm^{-1} were not distinct around 210 °C. As a result, the bands at 544 and 502 cm^{-1} appeared as a doublet.

First Condensation (Formation of $Na_2H_2P_2O_7$). $NaH_2PO_4 \cdot 2H_2O$, after dehydration to anhydrous NaH_2PO_4, condensed into $Na_2H_2P_2O_7$ around 220 °C in the first condensation process. The spectral variations in the temperature range from 210 to 226 °C were observed and are represented by the characteristic spectra at 210 and 260 °C as in Figure 4b and c, respectively. With an increase in temperature, the band at 1001 cm^{-1} shifted to 1018 cm^{-1}. The two sharp, strong bands at 922 and 874 cm^{-1} showed a gradual decrease in intensity and disappeared around 224 °C. A new band at 738 cm^{-1} was observed; it appeared at 212 °C and became stronger with an increase in temperature. The broad bands at 544, 502, 423, and 364 cm^{-1} observed at 210 °C disappeared around 220 °C and were replaced by weak bands at 548, 468, and 405 cm^{-1}. In this first condensation, the characteristic bands at 1018 and 738 cm^{-1} of $P_2O_7^{4-}$ replaced the characteristic bands at 922 and 874 cm^{-1} for PO_4^{3-}. This was the first condensation in the temperature range from 212 to 224 °C and resulted in the formation of $Na_2H_2P_2O_7$ in the expenses of NaH_2PO_4.

Second Condensation (Formation of $NaPO_3$). The spectral variations observed in the second condensation process in the temperature range from 260 to 360 °C are represented by the characteristic spectra at 226, 320, and 370 °C as shown in Figure 4c, d, and e, respectively. The spectra observed in this temperature range were weak. At 260 °C, a band at 1165 cm^{-1} was observed which showed a gradual increase in intensity as the temperature rose to 316 °C. The broad band of $Na_2H_2P_2O_7$ at 1018 cm^{-1} observed around 260 °C showed a decrease in intensity when the temperature reached 316 °C. Similarly, the band at 738 cm^{-1} showed a decrease in intensity with some broadening. Two weak bands at 678 and 380 cm^{-1} emerged around 260 °C and gradually became distinct as the temperature rose to 316 °C. The characteristic bands at 1018 and 738 cm^{-1} for $P_2O_7^{4-}$ became very weak but still persisted, indicating the presence of traces of $Na_2H_2P_2O_7$. This showed that the condensation was a prolonged process. Those bands disappeared completely around 360 °C, and the intensity of the bands at 1165 and 735 cm^{-1} representing PO_3^- increased gradually during this condensation. However, the condensation of $Na_2H_2P_2O_7$ to $NaPO_3$ was observed in the temperature range from 260 to 360 °C.

It was reported that $Na_2H_2P_2O_7$ is prepared by heating $NaH_2PO_4 \cdot 2H_2O$ at 210 °C for 12 h.[17] This temperature, 210 °C, is lower than our observation, but maintaining it for 12 h can ensure the formation of $Na_2H_2P_2O_7$. Similarly, $NaPO_3$ was formed by heating $NaH_2PO_4 \cdot H_2O$ at 275 °C for 18 h as reported by Partridge et al.[12] and is also at a lower temperature than our observation; hence, a long heating time is needed to complete the condensation. However, no study was reported to follow the condensation processes after the dehydration of $NaH_2PO_4 \cdot 2H_2O$.

Phase Transformation of Metaphosphate ($NaPO_3$). The $NaPO_3$ that formed after condensation was in phase III.[12] Two phase transformations of $NaPO_3$ were observed in the ranges from 325 to 360 °C and from 490 to 520 °C.

Phase Transformation from Phase III to Phase II of $NaPO_3$. The spectral variations in the temperature range from 320 to 370 °C for the transformation from phase III to phase II of $NaPO_3$ were observed, and the characteristic spectra at 320 and 370 °C are as shown in Figure 4d and e, respectively. The sharp band at 1165 cm^{-1} showed an increase in intensity with the development of a shoulder at 1152 cm^{-1} which appeared like a doublet as the temperature approached 360 °C. The weak, broad bands at 1018 and 738 cm^{-1} of $Na_2H_2P_2O_7$ gradually disappeared as the temperature rose to 360 °C. The shoulder at 716 cm^{-1} to the band at 738 cm^{-1} appeared as a weak band around 360 °C. The weak band at 678 cm^{-1} observed around 320 °C further developed into a doublet at 694 and 676 cm^{-1} and into a weak band at 638 cm^{-1}. A new band at 537 cm^{-1} appeared around 325 °C and showed an increase in intensity with a rise in temperature. Similarly, the band at 380 cm^{-1} also showed an increase in intensity. This indicated the transformation from phase III to phase II of $NaPO_3$ in the temperature range from 325 to 360 °C. However, traces of $Na_2H_2P_2O_7$ that were present vanished around 360 °C. Phase II might have two kinds of symmetry sites for $NaPO_3$ because the band at 1152 cm^{-1} appeared as a doublet, and many weak bands were visualized around 676 cm^{-1}.

Phase Transformation from Phase II to Phase I of $NaPO_3$. The spectral variations in the temperature range from 480 to 530 °C for the transformation from phase II to phase I of $NaPO_3$ were observed. The characteristic spectrum of phase I at 560 °C is shown in Figure 4f. At 490 °C, the band at 1165 cm^{-1} with a shoulder at 1152 cm^{-1} merged to form a sharp band at 1161 cm^{-1} as the temperature rose to 520 °C. The doublet at 694 and 676 cm^{-1} gradually developed into a singlet at 672 cm^{-1}. The weak adjacent bands at 638 and 537 cm^{-1} showed an increase in intensity and became distinct. The broad band at 380 cm^{-1} shifted to 374 cm^{-1} as the temperature rose to 520 °C. This showed the transformation from phase II to phase I of $NaPO_3$. It was observed in the temperature range from 490 to 520 °C. The singlet which developed at 1161 cm^{-1} might indicate only one symmetric site for phase I of $NaPO_3$.

The thermal properties of $NaPO_3$ formed on condensation of $Na_2H_2P_2O_7$ are interesting because $NaPO_3$ appeared in many different forms.[3] X-ray diffraction studies by Ondik reported the crystal structure of sodium trimetaphosphate ($Na_3P_3O_9$) with space group *Pmcn*. They observed that the $P_3O_9^{3-}$ anion had their configuration of a six-membered ring.[24] Pascal had indicated the presence of at least six different crystalline forms of $NaPO_3$, but very little is known about them.[25] According to the X-ray studies by Boulle,[26] only two patterns indicating two phases were observed, and the third phase was assigned from some peculiar observations in the X-ray pattern. He assigned the phases to be A′, B, and A. Thermal studies done by Partrige et al.[12] using differential thermal analysis could get only two distinct phases of $NaPO_3$. However, in the X-ray diffraction studies, they observed three X-ray patterns revealing three forms of $NaPO_3$, namely phase III, phase II, and phase I. These were in agreement with the one observed by Boulle.[27] In this work too, three different spectra were recorded for phase III, phase II, and phase I.

During condensation, the spectrum changed completely as the composition of each species, $Na_2H_2P_2O_7$, $NaPO_3$ phase III, $NaPO_3$ phase II, and $NaPO_3$ phase I in Figure 4c, d, e, and f, respectively, was different. The band intensities observed became weak due to the reorganization of the atoms and the change in the crystal structure during condensation. The spectra for the three phases of $NaPO_3$ were similar with only a little shift in the band positions because in the phase transformations only minor changes occurred in the lattice structure. This, in turn, might contribute to very little changes in the intramolecular vibrations.

Conclusion

In this work, the thermal properties of $NaH_2PO_4 \cdot 2H_2O$ were studied and were monitored by thermo-Raman spectroscopy in the temperature range from 25 to 600 °C. It experienced dehydration, condensation, and phase transformations as the temperature was increasing. Below 210 °C, the thermo-Raman spectra showed the characteristic spectrum of PO_4^{3-} with four groups of bands around 922 (ν_1), 423 (ν_2), 1001 (ν_3), and 544 (ν_4). These bands shifted and split during the removal of H_2O in dehydration. However, spectral variations were detected for two steps of dehydration, resulting in the formation of $NaH_2PO_4 \cdot H_2O$ and NaH_2PO_4 as constitutional species from $NaH_2PO_4 \cdot 2H_2O$. The TRI thermogram based on the intensity of the stretching modes of H_2O showed two steps of dehydration in the corresponding temperature ranges from 42 to 52 °C and from 60 to 72 °C, respectively. The DTRI thermogram indicated the maximum rates of dehydration were at 48 and 68 °C.

The change in thermo-Raman spectra from PO_4^{3-} to $P_2O_7^{4-}$ in the temperature range from 210 to 226 °C, characterized by the bands at 1018 and 738 cm^{-1} of $P_2O_7^{4-}$, was observed. This indicated the formation of $Na_2H_2P_2O_7$ at 220 °C in the first condensation process from NaH_2PO_4. At a higher temperature, about 260 °C, the second condensation process initiated and resulted in $NaPO_3$ formation with the appearance of the characteristic bands of PO_3^- at 1165 and 678 cm^{-1} at the cost of bands for $P_2O_7^{4-}$. The condensation overlapped with the phase transformation from phase III to phase II. Further, with a rise in temperature, another phase transformation of $NaPO_3$ from phase II to phase I was also observed at 515 °C. The spectrum revealed only minor shifts of the band positions during the phase transformation as the intramolecular vibrations changed.

The TG and DTG thermograms also showed two steps of dehydration in the temperature range which corresponded to

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(24) Ondik, H. M. *Acta Crystallogr.* **1965**, *18*, 226−232.
(25) Pascal, P. *Bull. Soc. Chim.* **1924**, *35*, 1131−1141.
(26) Boulle, A. *Compt. Rend.* **1935**, *200*, 658−660.
(27) Boulle, A. *Compt. Rend.* **1935**, *200*, 832−834.

the two steps observed in the thermo-Raman study with the weight losses of 12.9 and 10.2% in correspondence to TRI and DTRI. The DTA thermogram also showed two endotherms at 44 and 68 °C. TG and DTG thermograms detected two condensation steps in the temperature range from 190 to 210 °C and from 260 to 360 °C, respectively, with a loss of 5.6 wt % observed for each. The DTA showed endotherms corresponding to the first condensation process at 208 °C and at 278, 325, and 343 °C for the second condensation (with a possible first phase transformation of $NaPO_3$ around 344 °C) but could not detect the other. The DSC showed endotherms at 200 and 334 °C and one phase transformation of $NaPO_3$ at 528 °C, respectively. Yet the condensation and the transformation from phase III and phase II of $NaPO_3$ were not clearly resolved. Earlier, only an X-ray diffraction study could observe the three forms of $NaPO_3$ which are clearly visible in the thermo-Raman study.

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