Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 891–905

THERMO-RAMAN STUDIES ON DEHYDRATION OF $Na_4P_2O_7 \cdot 10H_2O$ AND PHASE TRANSFORMATIONS OF $Na_4P_2O_7$

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(Received August 20, 2000; in revised form March 6, 2001)

Abstract

In this work, dehydration of sodium diphosphate decahydrate $Na_4P_2O_7 \cdot 10H_2O$ and phase transformations of $Na_4P_2O_7$ in open air have been studied in detail by thermo-Raman spectroscopy. The spectra were measured continuously in a temperature range from room temperature up to 600°C for the bands of $P_2O_7^{4-}$ and H_2O. The spectral variation showed one step of dehydration and four-phase transformations. The thermo-Raman intensity (TRI) and differential thermo-Raman intensity (DTRI) curves calculated from the characteristic bands of H_2O also showed one step of dehydration with the loss of all hydrated water in the temperature interval from 45 to 69°C. Thermogravimetric measurements supported this result. The thermo-Raman investigation indicated the transformation of $Na_4P_2O_7$ from low temperature phase to high temperature phase proceed through pre-transitional region from 75 to 410°C before the major orientational disorder at 418°C and minor structural modifications at 511, 540 and 560°C. The results from differential scanning calorimetry and differential thermal analysis on $Na_4P_2O_7$ showed endotherms at 407, 517, 523, 548, 557°C and 426, 528, 534, 555, 565°C, respectively.

Keywords: dehydration, $Na_4P_2O_7 \cdot 10H_2O$, phase transformations, thermo-Raman spectroscopy

Introduction

Thermal methods like thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are used to study the thermal properties of solids in a dynamic thermal process [1]. The changes in mass measured *vs*. time or temperature in TG give some information regarding the composition changes and chemical reactions involved. The differences in temperature and enthalpy changes measured in DTA and DSC, respectively, reveal the composition changes and phase transformations too. But no direct information about the composition and phase of the sample can be obtained in a dynamic thermal process from these thermal analysis methods.

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1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
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Raman spectroscopy has the advantage in identification of compositions and phases of a solid from vibrational bands [2]. Hence, Raman spectra measured during a dynamic thermal process have been developed for thermal analysis as thermo-Raman spectroscopy (TRS). It can provide the information *in situ* on the composition changes and phase transformations in solid by the characteristic vibrational bands [3–12]. Furthermore, the intensity of the main band, which can indicate the amount of each species, can be plotted *vs*. temperature. It is thermo-Raman intensity (TRI) curve and is comparable to TG curve. Its derivative gives differential thermo-Raman intensity (DTRI) curve which clearly reveals the variation in the amount of each species and is also comparable to DTG, DTA and DSC curves. $CaC_2O_4{\cdot}H_2O$ has been used first to demonstrate the capability of this thermo-Raman spectroscopy [3]. The studies on dehydration of $CuSO_4{\cdot}5H_2O$ [4], $CaSO_4{\cdot}2H_2O$ and $CaSO_4{\cdot}0.5H_2O$ [5] were followed. Sol-gels of TiO_2 have also been studied for sintering processes by this method [6, 7]. The phase transformations in KNO_3 [8, 9] and Na_2SO_4 [10], dehydration and phase transformations of hydrated MoO_3 [11] and thermal decomposition of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ [12] have been studied by this thermo-Raman spectroscopy, too.

It was known that sodium diphosphate existed as decahydrate $Na_4P_2O_7{\cdot}10H_2O$ and anhydrous $Na_4P_2O_7$. Sodium diphosphate $Na_4P_2O_7$ exhibits rich variety of phase transformations from room temperature up to 600°C. For $Na_4P_2O_7$, five phases as phase V, IV, III, II and I have been reported [13] and the transformation temperatures were as follows:

$$Na_4P_2O_7(V)\xrightarrow{400^\circ C}(IV)\xrightarrow{510^\circ C}(III)\xrightarrow{520^\circ C}(II)\xrightarrow{545^\circ C}(I)$$

Recent thermal, microscopic and X-ray diffraction studies [14, 15] on $Na_4P_2O_7$ indicated that it undergoes following phase transformations before melting at 995°C as:

$$Na_4P_2O_7(\varepsilon)\xrightarrow{390^\circ C}(\delta)\xrightarrow{504^\circ C}(\gamma)\xrightarrow{512^\circ C}(\beta)\xrightarrow{550^\circ C}(\alpha)$$

Apparently, these two sets were the same. Recently, Villain *et al.* [16] studied polycrystalline $Na_4P_2O_7$ by complex impedance spectroscopy measurements at variable temperatures supplemented by thermal analysis. Their results were almost the same at 395, 505, 515 and 550°C as reported by others [13–15]. In addition, one more phase transformation at around 563°C was predicted by Villain *et al.* [16].

Although the polymorphic structures and phase transformations were studied by many techniques, the nature and sequence of transformations have not completely known, yet. Hence, in this work, dehydration of sodium diphosphate decahydrate $Na_4P_2O_7{\cdot}10H_2O$ and phase transformations of $Na_4P_2O_7$ were studied by thermo-Raman spectroscopy. Furthermore, the Raman spectra of these phases were recorded.

Experimental

Raman spectra were measured by the excitation of a laser light (30 mW) at a wavelength of 514.5 nm from an argon ion laser (Coherent, Innova 100–15). The scattered light was collected at right angles, dispersed by a spectrometer (Spex, 0.5 m) and detected by a CCD camera (Princeton Instrument, 1024×1024 pixels). The sample was packed in a sample holder and kept in a home-made oven. The Raman spectra were recorded in open air. The temperature was monitored by a thermocouple and controlled by a programmable controller. The positions of the spectral bands were calibrated using an argon spectral tube and the resolution was about 2 cm^{-1}.

Analytical grade $Na_4P_2O_7\cdot10H_2O$ from Showa Chemicals was used without further purification. For dehydration, the thermal process was set from 25 to 110°C at a heating rate of 1°C min^{-1}. The exposure time for the CCD camera was 60 s in a way that one spectrum covered 1°C. Anhydrous $Na_4P_2O_7$ was prepared from $Na_4P_2O_7\cdot10H_2O$ by heating up to 150°C for one h and was used for the phase transformation studies. Both hydrated ($Na_4P_2O_7\cdot10H_2O$) as well as anhydrated ($Na_4P_2O_7$) sample showed the same phase transformation temperatures, but better Raman spectra could be obtained from the anhydrated one. For the phase transformation studies, the temperature range was set from 25 to 600°C at a heating rate of 2°C min^{-1}. The exposure time was 30 s in a way one spectrum covered 1°C.

TG curves were obtained from crystalline samples of $Na_4P_2O_7\cdot10H_2O$ by a thermogravimetric analyzer (Perkin Elmer, TG 6) from 25 to 110°C with a heating rate of 1°C min^{-1} in a flow of air with a flow rate of 20 mL min^{-1}. DTA (Seiko ISSC, TG/DTA-300) and DSC (Seiko ISSC 5040) curves of $Na_4P_2O_7\cdot10H_2O$ were measured from 25 to 600°C with an increasing rate of 5°C min^{-1} in a flow of air with a flow rate of 100 mL min^{-1}.

Results and discussion

The crystal structure investigations on $Na_4P_2O_7\cdot10H_2O$ indicated that it crystallizes in the monoclinic system I2/c with four formula units in a unit cell [17]. Diphosphate ion $P_2O_7^{4-}$ consists of two PO_3 tetrahedra with a central P–O–P bridge bond [18]. The internal modes of $P_2O_7^{4-}$ are in the range from 300 to 1500 cm^{-1}. The stretching modes of PO_3 usually occur in the range from 1250 to 975 cm^{-1} and the bridge stretching modes of P–O–P are in the range from 975 to 675 cm^{-1} [19]. Other bands can be grouped into two regions from 450 to 620 cm^{-1} and around 340 cm^{-1}. They are the deformation modes of PO_3 and P–O–P. The symmetric stretching mode of PO_3 at around 1025 cm^{-1} is the most intense [20]. The stretching modes of H_2O are in the range from 2700 to 3800 cm^{-1}. In this work, Raman spectra of $P_2O_7^{4-}$ and H_2O were measured in two separate runs.

Dehydration

The spectral variation observed during dehydration $Na_4P_2O_7\cdot10H_2O$ from 2500 to 4000 cm^{-1} for stretching vibrations of H_2O in a temperature range from 42 to 72°C is shown in Fig. 1. There were two strong and broad bands at around 3415 and 3285 cm^{-1} and a shoulder at 3066 cm^{-1} as the spectrum at 42°C showed. During dehydration, the intensity of the bands decreased from 45 to 69°C. Around 69°C, both bands and shoulder disappeared leaving only a weak and broad background as the

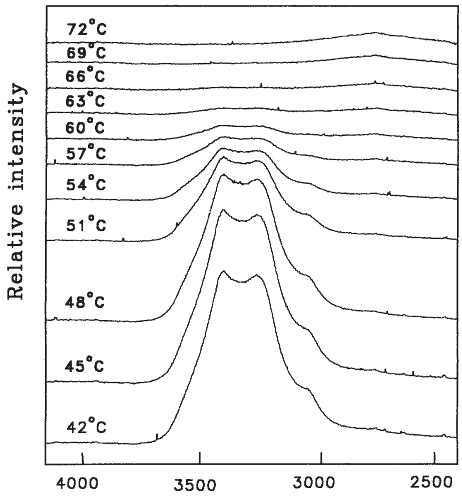

Fig. 1 The variation of the thermo-Raman spectra of $Na_4P_2O_7 \cdot 10H_2O$ in the region from 2400 to 4150 cm^{-1} for H_2O bands from 42 to 72°C during dehydration

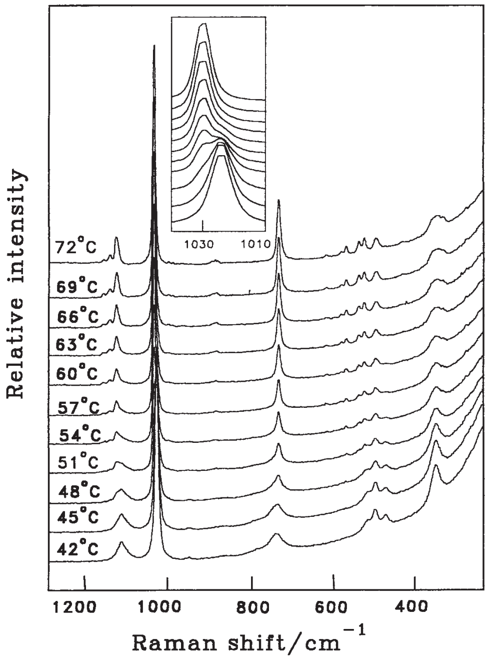

Fig. 2 The variation of the thermo-Raman spectra of $Na_4P_2O_7 \cdot 10H_2O$ in $P_2O_7^{4-}$ region from 42 to 72°C during dehydration

spectrum at 72°C showed. Apparently, dehydration was started at 45°C and completed at around 69°C.

The spectral variation observed in $P_2O_7^{4-}$ region also indicated one step dehydration as shown in Fig. 2. The band at 1104 cm^{-1} disappeared and a sharp band at 1116 cm^{-1} along with two weak bands at 1130 and 1145 cm^{-1} rose during dehydration. The strongest band at 1021 cm^{-1} was gradually disappeared and a new band at 1027 cm^{-1} appeared instead. The detail was shown in inset. A very weak and broad band at 881 cm^{-1} appeared and clearly observed at 72°C and onwards. The broad band at 737 shifted to lower wavenumber 732 cm^{-1} and became sharp. Three new bands at 616, 580 and 567 cm^{-1} appeared during dehydration. Also the band initially at 513 cm^{-1} gave rise to a doublet at 536 and 523 cm^{-1}. The band at 495 shifted to 493 cm^{-1} and the band at 471 cm^{-1} disappeared. The band at 345 shifted to 338 having a shoulder at 327 cm^{-1} and became broad. These variations were corresponding to the change of the environments of $P_2O_7^{4-}$ from hydrated to anhydrous form.

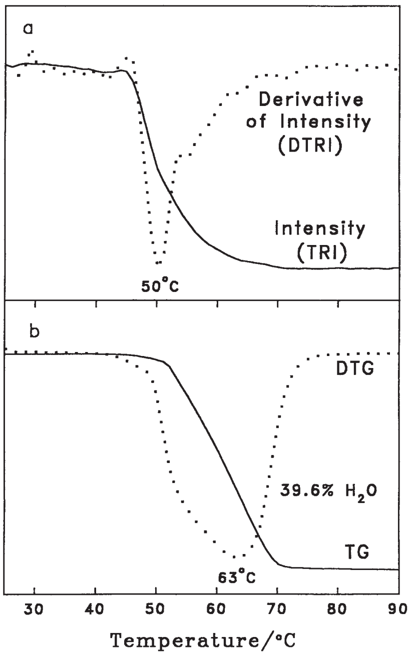

Fig. 3 The thermo-Raman intensity (TRI) and differential thermo-Raman intensity (DTRI) curves of the H_2O bands (a) and TG and DTG curves of $Na_4P_2O_7 \cdot 10H_2O$ for dehydration (b)

The intensity of the Raman band can show the amount of that species. The plot of band intensity (area) *vs*. the temperature indicates the amount of each species in the thermal process and is thermo-Raman intensity or TRI curve. The intensity calculated from 2870 to 3740 cm^{-1} region of H_2O is shown in Fig. 3a. It started to decrease from 45 and vanished around 69°C. It indicated that dehydration was one step directly from $Na_4P_2O_7\cdot10H_2O$ to $Na_4P_2O_7$ and all the hydrated water was lost. The nature of the intensity curve indicated the rate of dehydration was not constant. The derivative of the band intensity can give a better view of the dehydration process and is also plotted in Fig. 3a. It is the differential thermo-Raman intensity or DTRI curve. It showed the rate of dehydration. Dehydration started around 45 and ended around 69 with a dip at 50°C. Apparently, dehydration was faster at first due to dehydration of the surface layer and slowed down afterwards due to dehydration of the bulk sample. At surface, it was in equilibrium between anhydrated and hydrated species.

TG curve and its derivative DTG curve are shown in Fig. 3b. The TG curve was similar to TRI one. It also showed one step of dehydration from 45 to 70°C with a loss in mass of 39.6% corresponding to ten water molecules. The calculated mass loss was 40.36%. The mass loss was also gradual. The DTG curve also showed a variation from 45 to 70, but with a dip at 63°C. A steep part of the DTG curve from 50 to 53°C showed that dehydration was fast because it was from the surface layer. It slowed down after 53°C because hydrated water in the bulk had to diffuse out. The difference in dehydration process observed by TRI, DTRI and TG, DTG had been discussed elsewhere [21].

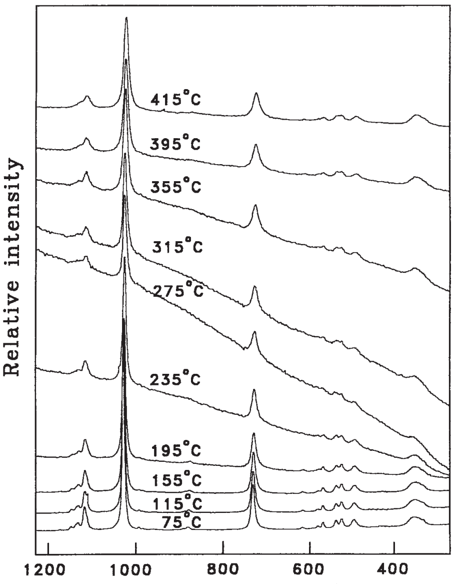

Fig. 4 The variation of the thermo-Raman spectra of $Na_4P_2O_7$ in $P_2O_7^{4-}$ region from 75 to 415°C

Phase transformations

According to Leung and Calvo, $Na_4P_2O_7$ crystallizes at ambient temperature in orthorhombic space group $P2_12_12_1$ [22]. Some studies also reported that $Na_4P_2O_7$ at room temperature belongs to hexagonal structure [23]. Although the exact crystal structure of other phases was not well known, the available crystallographic studies indicated that they were more similar to each other and belong to the ordered version of hexagonal phase [23]. Phase transformation temperatures reported in recent literature [16] for five crystalline polymorphs of $Na_4P_2O_7$ were at 390, 504, 512 and 550°C with an additional one at 563°C. We also observed four transformations based on the variations in the thermo-Raman spectra.

From 75°C onwards, the spectrum was gradually and continuously changing with the temperature up to 415°C before the first phase transformation. These spectral changes are shown in Fig. 4. During this course of change, three bands at 1145, 1130 and 1116 cm^{-1} became overlapped and appeared as a broad band centred at 1111 with a shoulder at 1128 cm^{-1}. The strongest band at 1027 shifted to 1023 cm^{-1} with a decrease in the intensity. The band at 881 shifted to 875 cm^{-1} and became broad and weak and the one at 732 broadened with the shift to 725 cm^{-1}. The band at 616 shifted to 614 cm^{-1}. The bands around 580, 567, 536, 523 and 493 cm^{-1} broadened and over-

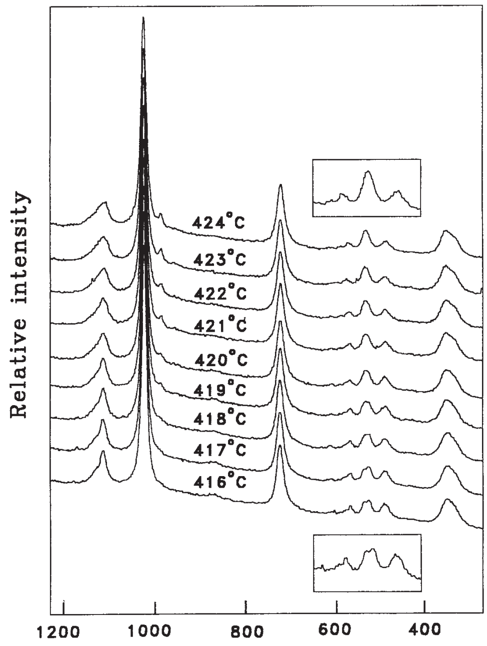

Fig. 5 The variation of the thermo-Raman spectra of $Na_4P_2O_7$ in $P_2O_7^{4-}$ region from 416 to 424°C for phase transformation from phase ε to phase δ

lapped and appeared as one overlapped doublet at 535, 524 cm^{-1} and three singlets at 579, 566 and 489 cm^{-1}.

Villain *et al*. [16] could distinguish two temperature ranges in conductivity measurement below 221°C with low activation energy (4.4 kJ mol^{-1}) and between 221 and 395°C with high activation energy (83.3 kJ mol^{-1}) before $Na_4P_2O_7$ underwent the first phase transformation at around 400°C. The observation of gradual modifications in the vibrational bands in the $P_2O_7^{4-}$ region before the first phase transformation was an indication of a pre-transition region in advance of the structural transition at 420°C. In the pre-transitional region, however, there has been some rearrangement of atoms i.e., an onset of rotation of $P_2O_7^{4-}$, the skeleton structure was nearly the same at 75°C.

First phase transformation

The spectral variation observed during the first phase transformation, is shown in Fig. 5 in the temperature range from 416 to 424°C. During this phase transformation, the most distinct variation was appearance of a small hump at 987 cm^{-1} close to the band at 1024 cm^{-1}. It started to appear at 418°C and could be clearly observed at 423°C. In addition, some minor spectral variations were also observed. The band at 1111 with a shoulder at 1128 cm^{-1} apparently became single broad band. The bands at 875 and 614 cm^{-1} disappeared. The band at 579 shifted to 588 cm^{-1} and the one at 566 shifted to 571 cm^{-1}. The overlapped bands at 535 and 524 cm^{-1} became weak and appeared as a singlet at 531 cm^{-1} (see the insets). The band at 489 shifted to 484 cm^{-1}. Also the band at 342 shifted to 347 cm^{-1} with the development of a shoulder at 327 cm^{-1}. The temperature range covered this transformation was approximately from 418 to 423°C and the transformation temperature was around 420°C.

Based on the conductivity results, Villain *et al*. [16] concluded that a phase transformation observed between 395 and 400°C might be order–disorder transformation. The observation of the broadening of the strong band at 1024 and 1111 cm^{-1} in the thermo-Raman spectra in the temperature range from 418 to 423°C confirmed the order–disorder transformation.

Second phase transformation

The spectral variation in the temperature range from 508 to 515°C showed the second phase transformation shown in Fig. 6. The hump at 987 cm^{-1} became weak and observed as a shoulder to the main band, at around 513°C. The bands at 1110, 1024, 588, 484 and 347 cm^{-1} shifted to 1108, 1022, 590, 481 and 342 cm^{-1}, respectively. The temperature range covered by this transformation was from 509 to 513°C and the transformation temperature was 511°C.

Although, Villain *et al*. [16] reported moderate order–disorder phase transformation at 505 and another phase transformation at 515°C based on the jump in the conductivity, this thermo-Raman investigation could show minor spectral variation only at around 511°C.

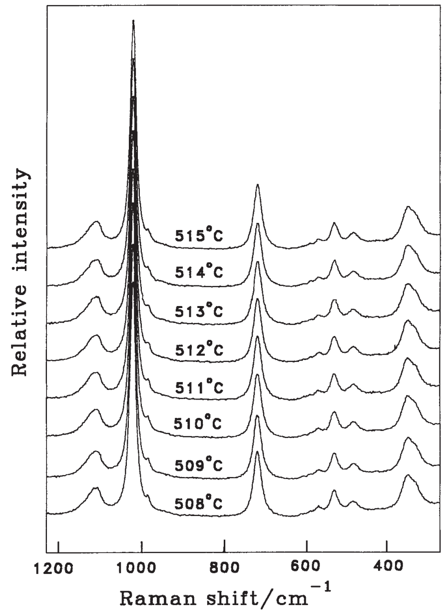

Fig. 6 The variation of the thermo-Raman spectra of $Na_4P_2O_7$ in $P_2O_7^{4-}$ region from 508 to 515°C for phase transformation from phase γ to phase β

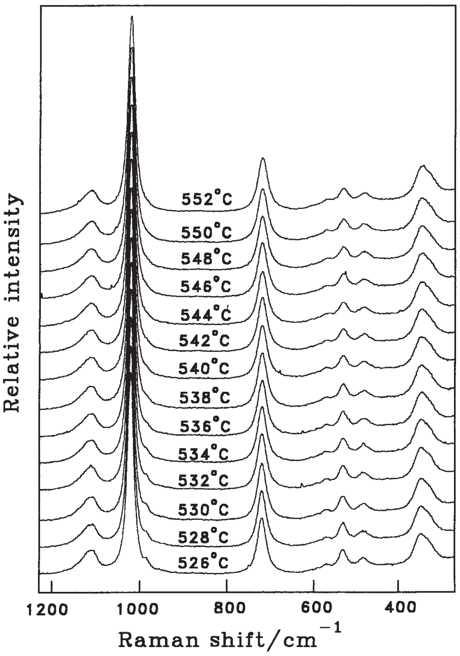

Fig. 7 The variation of the thermo-Raman spectra of $Na_4P_2O_7$ in $P_2O_7^{4-}$ region from 526 to 550°C for phase transformation from phase β to phase α

Third phase transformation

The Raman spectra measured from 526 to 552°C are shown in Fig. 7. The major variation observed during this phase transformation was the disappearance of the hump at 987 cm^{-1} and the band at 590 cm^{-1}. The band at 481 shifted to 479 cm^{-1}. The bands at 720 and 342 cm^{-1} broadened slightly. The temperature range covered by this transformation was from 532 to 548°C and the transformation temperature was 540°C.

The broadening of the bands at 720, 573, 533 and 480 cm^{-1} observed from 550 to 570°C, as shown in Fig. 8, indicated that there might be a phase transformation in this temperature range. It was difficult to assign the transformation temperature from the Raman spectral variation, as there were only broadening of the bands and no distinct variation in spectra was observed. However, the phase transformation, if there was one, it should be in the temperature range from 550 to 570°C and the transformation temperature would be at around 560°C.

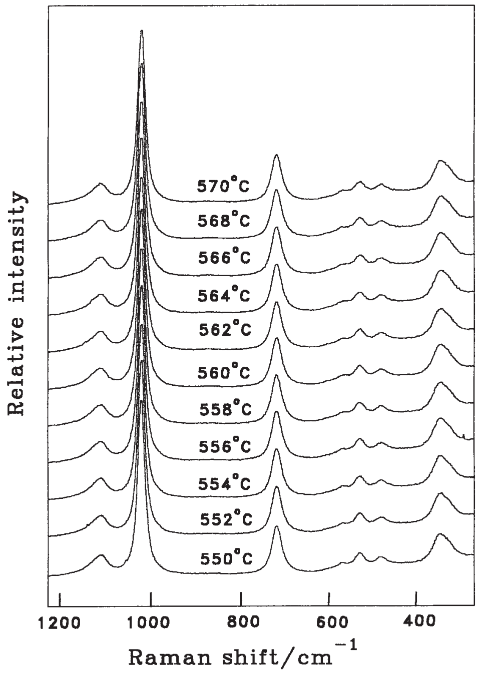

Fig. 8 The variation of the thermo-Raman spectra of $Na_4P_2O_7$ in $P_2O_7^{4-}$ region from 550 to 570°C. Probably, the phase transformation was from phase α to the one at higher temperature

DTA/DSC

DTA curve of $Na_4P_2O_7\cdot10H_2O$ showed five endothermic peaks at 426, 528, 534, 555 and 565°C, which comprised five phase transformations of $Na_4P_2O_7$ from 120 to 600°C after dehydration. This is shown in Fig. 9a. The DTA curve showed a continuous variation after dehydration up to around 400°C. This implied that there might be some continuous minor modification in the structure of the compound in that temperature range. Compared with the thermo-Raman spectra, there was certainly a gradual and continuous change in spectra after dehydration up to about 400°C. However, no distinct phase transformation could be detected in this range.

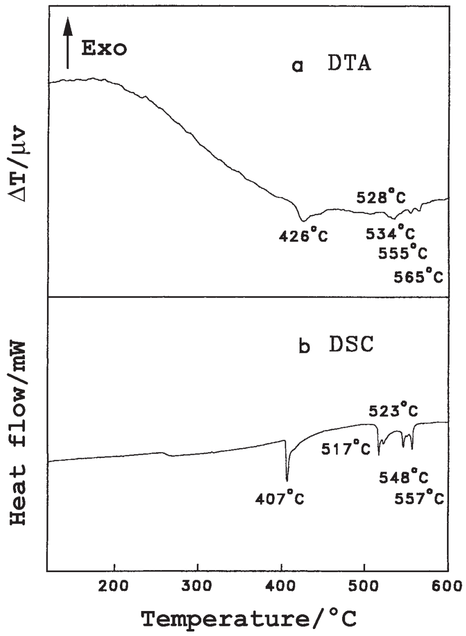

Fig. 9 DTA (a) and DSC curves (b) of $Na_4P_2O_7 \cdot 10H_2O$ from 120 to 600°C after dehydration

The DSC curve showed five endothermic peaks at 407, 517, 523, 548 and 557°C too as shown in Fig. 9b. Enthalpy variation calculated for the endotherms in DSC at these temperatures were 9.4, 1.33, 0.54, 0.98 and 1.44 mJ mg^{-1}, respectively. Since the enthalpy variation for the first phase transformation at 407°C was higher than those of remaining phase transformations, the spectral variation in thermo-Raman during the first transformation was appreciable and other transformations were difficult to specify. The results from DSC were about 10 to 20°C lower than those from DTA.

Characteristic spectra

Seven characteristic spectra were found during dehydration of $Na_4P_2O_7 \cdot 10H_2O$ and phase transformations of $Na_4P_2O_7$ in the dynamic thermal processes and are shown in Fig. 10. The band positions and their vibrational assignments are listed in Table 1. The assignment of Kanesaka *et al.* was followed [24]. The spectra shown in Fig. 10 were measured at (a) 42, (b) 72, (c) 412, (d) 435, (e) 518, (f) 547 and (g) 570°C, respectively. The spectrum measured at 42°C was for $Na_4P_2O_7 \cdot 10H_2O$ before dehydration and that measured at 72°C was for $Na_4P_2O_7$ just after dehydration. After dehydration, spectrum gradually changed from the spectrum shown at 72 to that at 412°C. The variation was distinct but gradual and continuous. The typical spectra measured were probably from phase ε (at 412°C), phase δ (at 435°C), phase β (at 518°C) and phase α (at 547°C). The transformations observed in this work were from phase ε to phase δ at 420°C, phase γ to phase β at 511°C, phase β to phase α at 540°C and phase α to the one at higher temperature at 560°C. Phase δ and phase γ might not be distinguished by Raman spectroscopy measured in this work. The characteristic spectrum measured at 570°C might be the possible additional phase predicted by Villain *et al.* [16].

Table 1 The band positions (in cm^{-1}) for different phases of $Na_4P_2O_7$

$Na_4P_2O_7 \cdot 10H_2O$ dehydration/°C		$Na_4P_2O_7$, phases/°C				Band assignments[a]
		ε^b	δ^b	β^b	α^b	
42	72	412	535	518	547	
	1145					
	1130	1128	1110	1109	1108	PO_3 asym. str.
1104	1116	1111				
1021	1027	1023	1024	1022	1021	PO_3 asym. Str.
			987	987		
	881	875				
737	732	725	722	720	720	P–O–P sym. Str.
	616	614				
	580	579	588	590		
	567	566	571	568	567	
513	536	535	531	529	529	PO_3 sym. bend+ P–O–P bend
	523	524				
495	493	489	484	481	479	PO_3 asym. bend
471						PO_2 rock
345	338	342	347	343	342	PO_2 twist
	327	327				

[a][24]; [b]Tentative assignment; [c]Hydrated sodium diphosphate ($Na_4P_2O_7 \cdot 10H_2O$);
[d]Dehydrated sodium diphosphate ($Na_4P_2O_7$)

The spectral variation observed in the present thermo-Raman investigation indicated the transformation of $Na_4P_2O_7$ from low temperature phase to high temperature phase proceed through pre-transitional region from 75 to 410°C before the major orientational disorder at 420°C and minor structural modifications at 511, 540 and 560°C. The transformation temperatures reported earlier and obtained in this study are listed in Table 2.

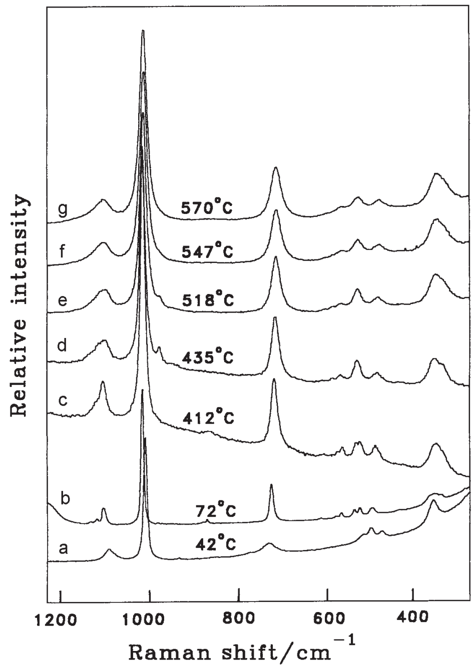

Fig. 10 Characteristic Raman spectra at a – 42°C ($Na_4P_2O_7 \cdot 10H_2O$); b – 72°C ($Na_4P_2O_7$ after dehydration); c – 412°C (phase ε); d – 435°C (phase δ); e – 518°C (phase β); f – 547°C (phase α) and g – 570°C (higher temperature phase) during a dynamical thermal process

Table 2 The phase transformation temperatures

Phase[a] transformations	ε to δ	δ to γ	γ to β	β to α		References
	400	510	520	545		[13][b]
	390	504	512	550		[14, 15]
	395	505	515	550	563	[16]
TRS	420	511	c	540	560	this work
DTA	426	528	534	555	565	this work
DSC	407	517	523	548	557	this work

[a] Phases ε, δ, γ, β and α were assigned by Berak and Znamierowski [14, 15];
[b] Phases IV, III, II and I were assigned by Farr [13]; [c] No apparent spectral change

Conclusions

In this work, thermo-Raman spectroscopic studies on $Na_4P_2O_7 \cdot 10H_2O$ and $Na_4P_2O_7$ were performed for dehydration and phase transformation, respectively, in a dynamic thermal process. The spectral changes observed in the H_2O and $P_2O_7^{4-}$ regions of the

$Na_4P_2O_7\cdot 10H_2O$ during dehydration indicated a single step process. Dehydration started at 45 and completed at around 69°C. The TRI curve for the intensity of the H_2O bands also clearly indicated the dehydration temperature range. The DTRI curve showed a dip at about 50 compared with a dip at 63°C in DTG curve. The difference in these two temperatures might be due to the properties measured at the surface layer and on the bulk in TRS and TG, respectively. The internal modes of $P_2O_7^{4-}$ in the range from 200 to 1265 cm^{-1} showed some significant changes corresponding to this dehydration process.

For the phase transformation, the variation in thermo-Raman spectra was not distinct and only minor changes could be observed. However, four phase transformations could be detected. The phase transformations occurred in the temperature ranges from 418 to 423, from 509 to 513, from 532 to 548 and from 550 to 570°C. The spectral variation observed in the present thermo-Raman investigation indicated the transformation of $Na_4P_2O_7$ from low temperature phase to high temperature phase proceed through continuous modification in the crystal structure from 75 to 410°C, major orientational disorder at 420 and minor structural modifications at 511, 540 and 560°C.

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This work was supported by the National Science Council of the Republic of China (NSC-89-2113-M007-013 and NSC-88-CPC-M007-002).

References

1 W. W. Wendlandt, Thermal Analysis, Wiley, New York 1986.
2 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York 1986.
3 H. Chang and P. J. Huang, Anal. Chem., 69 (1998) 59.
4 H. Chang and P. J. Huang, J. Chin. Chem. Soc., 45 (1998) 59.
5 H. Chang, P. J. Huang and S. C. Hou, Mater. Chem. Phys., 58 (1999) 12.
6 P. J. Huang, H. Chang, C. T. Yeh and C. W. Tsai, Thermochim. Acta, 297 (1997) 85.
7 H. Chang and P. J. Huang, J. Raman Spectrosc., 29 (1998) 97.
8 R. Murugan, A. Ghule and H. Chang, J. Appl. Phys., 86 (1999) 6779.
9 R. Murugan, P. J. Huang, A. Ghule and H. Chang, Thermochim. Acta, 346 (2000) 83.
10 R. Murugan, A. Ghule and H. Chang, J. Phys.: Condensed Matt., 12 (2000) 677.
11 R. Murugan, A. Ghule, C. Bhongale and H. Chang, J. Mater. Chem., 10 (2000) 2157.
12 R. Murugan and H. Chang, to be published.
13 T. D. Farr, Phosphorus, Properties of the element and some of its compounds, Chemical Engineering Report No. 8, T. V. A. Wilson Dam, Alabama, 1950, p. 39.
14 J. Berak and T. Znamierowski, Roczniki Chem. Part II, 46 (1972) 1697.
15 J. Berak and T. Znamierowski, Roczniki Chem. Part III, 46 (1972) 1921.
16 S. Villain, E. Nigrelli and G. Nihoul, Solid State Ionics, 116 (1999) 73.
17 D. W. J. Cruickshank, Acta Cryst., 17 (1964) 672.
18 D. M. MacArthur and C. A. Beevers, Acta Cryst., 10 (1957) 428.
19 B. C. Cornilsen, J. Mol. Struct., 117 (1984) 1.

20 D. Philip, B. L. George and G. Aruldhas, J. Raman Spectrosc., 21 (1990) 523.
21 H. Chang, R. Murugan and A. Ghule, to be published.
22 K. Y. Leung and C. Calvo, Can. J. Chem., 50 (1972) 2519.
23 Joint Council for Powder Diffraction Standards. Powder Diffraction File 10-0187, 1997, Inorganic Phases, International Centre for Diffraction data, 1601 Park Lane, Swarthmore, Pa 19081, USA 1992.
24 I. Kanesaka, K. Ozaki and I. Matsuura, J. Raman Spectrosc., 26 (1995) 997.