

THERMAL ANALYSIS OF DIHYDRATED SODIUM ORTHOPHOSPHATE CRYSTALS IN THE TEMPERATURE RANGE 25–600 °C

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ABSTRACT

Single crystals of dihydrated sodium orthophosphate $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (SDP) were grown from supersaturated aqueous solution by slow evaporation. The crystal structure of these crystals was investigated by X-ray diffraction. Simultaneous TG, DTG and DTA analyses for SDP were conducted over the temperature range 25–600 °C. These thermal analyses showed that the dihydrated sodium orthophosphate crystal loses its water of crystallisation and becomes anhydrous at 150 °C. The sodium orthophosphate transforms to sodium pyrophosphate as an intermediate product at around 250 °C. The sodium pyrophosphate converts to sodium metaphosphate as the end product at around 350 °C. The values of the activation energy for the thermal processes associated with the peaks at 56, 90, 130, 215 and 345 °C are estimated as 104.35, 92.01, 73.43, 137.82 and 175.69 kJ mol^{-1} by the Kissinger method, and 109.83, 98.49, 80.21, 146.06 and 185.98 kJ mol^{-1} by the Ozawa method. X-ray diffraction and IR absorption spectra confirmed the thermal behaviour of dihydrated sodium orthophosphate.

INTRODUCTION

Potassium dihydrogen phosphate (KDP) belongs to a group of materials that are hydrogen-bonded ferroelectrics. The hydrogen atoms play the main role in the ferroelectric properties which appear at the ferroelectric phase transition [1–3]. This KDP-type class of crystals also includes crystals in which either the potassium atom is replaced by NH_4 , Rb or Cs atoms, or the phosphate group, PO_4 , is replaced by an arsenate group, AsO_4 . Ferroelectric crystals have been classified into two groups: the order–disorder group and the displacive group. In the first group the phase transition is associated with the ordering of ions; the second group is associated with the displacement of a whole sublattice of ions of one type relative to another sublattice. KDP-type materials belong to the order–disorder class of ferroelectrics

which includes crystals with hydrogen bonds in which the motion of the protons is related to the ferroelectric properties of the materials [4]. In our earlier papers, the thermal analysis and d.c. electrical conductivity of KDP and ADP were reported [5–7]. Considerable information is available in the literature for KDP and ADP, but, as far as we know, little work on sodium dihydrogen phosphate (SDP) has been presented. This could be due to its hygroscopic properties and difficulties of single-crystal preparation. The electron paramagnetic resonance and electro-optic properties of orthorhombic SDP have been studied [8,9]. In addition, laser Raman spectroscopy between 700 and 1350 cm^{-1} of powdered crystals and pure aqueous solutions of ADP, KDP and SDP at 30 °C has been used to identify the crystal structure of these materials [10].

In the present work, pure single crystals of SDP were carefully grown, and their thermal analyses, X-ray diffraction and IR absorption spectra were investigated to explain the ambiguity of this material.

EXPERIMENTAL PROCEDURE

Single crystals of SDP were grown by slow evaporation from supersaturated aqueous solution. The crystal structure of SDP was identified by means of a Shimadzu(XD-3) X-ray diffractometer. The sample was used in the form of a fine homogeneous powder. A monochromatic Cu K_{α} X-ray beam of wavelength 0.1542 nm was used. Some samples of SDP crystals were heated at different temperatures between 25 and 500 °C for 2 h and quenched in air to preserve their thermal transformations; their X-ray diffraction patterns were then recorded at room temperature.

The thermal behaviour of SDP was studied at 5, 10 and 15 °C min^{-1} using a Setaram GDTD 16 thermoanalyser which records TG, DTG and DTA simultaneously. In the thermoanalyser, the oven temperature was controlled by means of a PRT 3000 temperature programmer in order to obtain a constant rate of heating. The temperature of the sample and reference was measured using a platinum/rhodium–platinum 10% (Pt/Rh–10% Pt) thermocouple. A sample size of about 30 mg was contained in an alumina crucible while a calcinated alumina crucible was used as reference. A recording system with a B70 balance, C3ATD amplifier, DT25 derivator and a four-pen recorder was used. The thermal behaviour of SDP was also studied using differential scanning calorimetry, DSC, at 2, 5 and 10 °C min^{-1} and also using a Shimadzu DT-30 differential thermal analyser at 5, 10, 15, 20 and 30 °C min^{-1} .

The IR absorption spectra of SDP were recorded using a Perkin–Elmer 598 double-beam spectrophotometer in the spectral region 200–4000 cm^{-1} . Samples were prepared using the KBr disc technique.

RESULTS AND DISCUSSION

Single crystals of SDP were grown by double recrystallisation from supersaturated aqueous solutions using the slow evaporation technique [11–14]. The X – ray diffraction pattern for an as-grown sample is shown in Fig. 1. The estimated interplanar distance d for each (hkl) plane was compared with the ASTM index data. The SDP crystal was found to have an orthorhombic crystal structure. The lattice constants a , b and c of SDP were calculated using the equation for this type of structure [15]:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

The estimated lattice constants are 0.7225 nm, 1.1462 nm and 0.6612 nm for a , b and c respectively. The volume of the unit cell, V_c and the volume of one molecule, V_m , were estimated as 0.5476 nm³ and 0.1355 nm³ respectively, from which the number of molecules per unit cell, n , was found to be four using the expression $n = V_c/V_m$. The high degree of crystallinity of the prepared crystals shows that the slow evaporation technique for crystal growth from aqueous solution is fairly reliable and satisfactory.

Simultaneous TD, DTG and DTA curves for the SDP sample at heating rates of 5, 10 and 15 °C min⁻¹ in the temperature range 25–600 °C are shown in Figs. 2(a), 2(b) and 2(c). At a heating rate of 5 °C min⁻¹, the DTA curve shows endothermic peaks centred at 72, 123, 225, 325 and 342 °C. All peaks are coincident with those appearing on the DTG curve. The positions of these peaks shift towards higher temperatures with increasing heating rates. The DTA and DTG curves return to their baselines at 400 °C. Beyond this temperature the TG curve shows a constant weight, indicating the complete decomposition of the sample. The weight loss (TG) over the

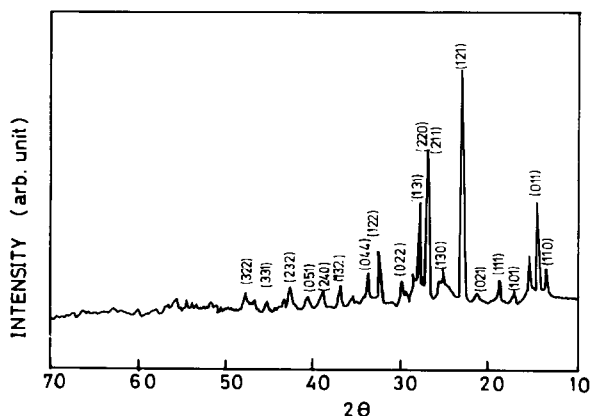


Fig. 1. X-ray diffraction pattern for as-grown SDP crystals at room temperature.

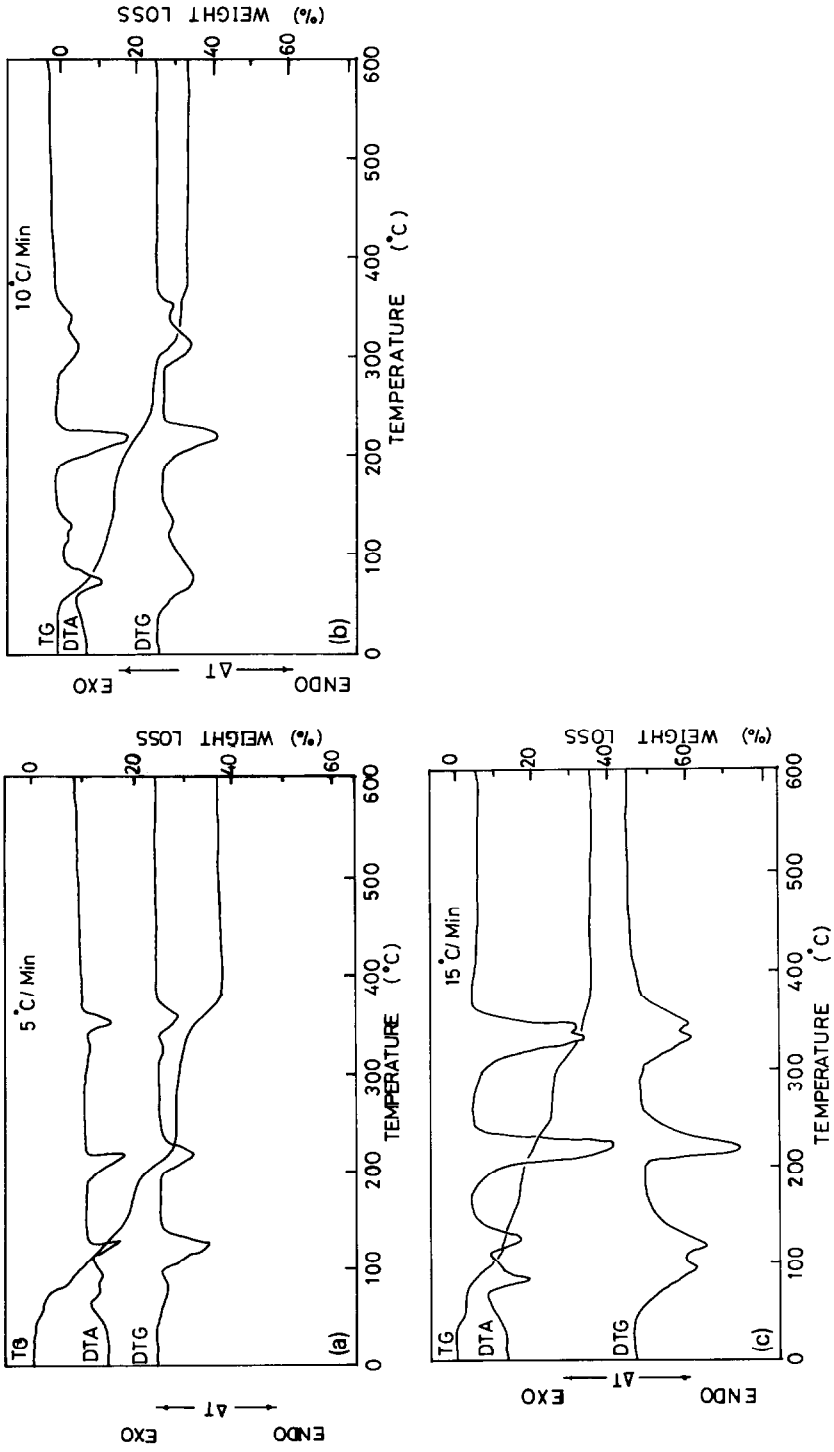
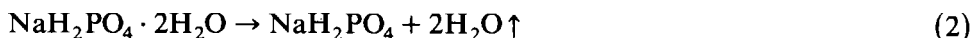


Fig. 2. Simultaneous TG, DTG and DTA curves for SDP crystals at (a) 5 °C min⁻¹, (b) 10 °C min⁻¹ and (c) 15 °C min⁻¹.

temperature range 50–150°C is due to the formation of anhydrous sodium dihydrogen phosphate according to the reaction



i.e. the crystal loses its water of crystallisation and becomes anhydrous. The endothermic peak at 225°C is associated with a weight loss of about 27.95%; the anhydrous sodium orthophosphate has transformed to sodium pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, as intermediate product according to the reaction



The peak at 342°C is accompanied by a weight loss of about 34.63% which can be attributed to the formation of sodium metaphosphate as end product in accordance with the reaction



The sum of the above reactions is



In order to calculate the activation energy for the thermal processes of the SDP samples, differential thermal analysis (DTA) was performed at heating rates of 5, 10, 15, 20 and 30°C min⁻¹; the results are shown in Fig. 3.

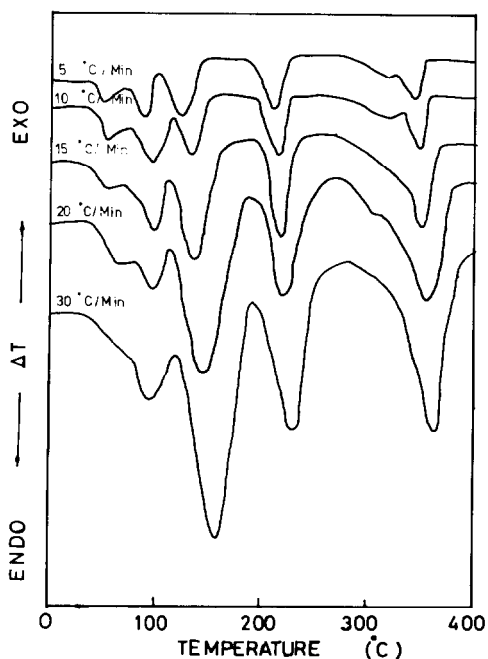


Fig. 3. DTA curves for SDP crystals at different heating rates.

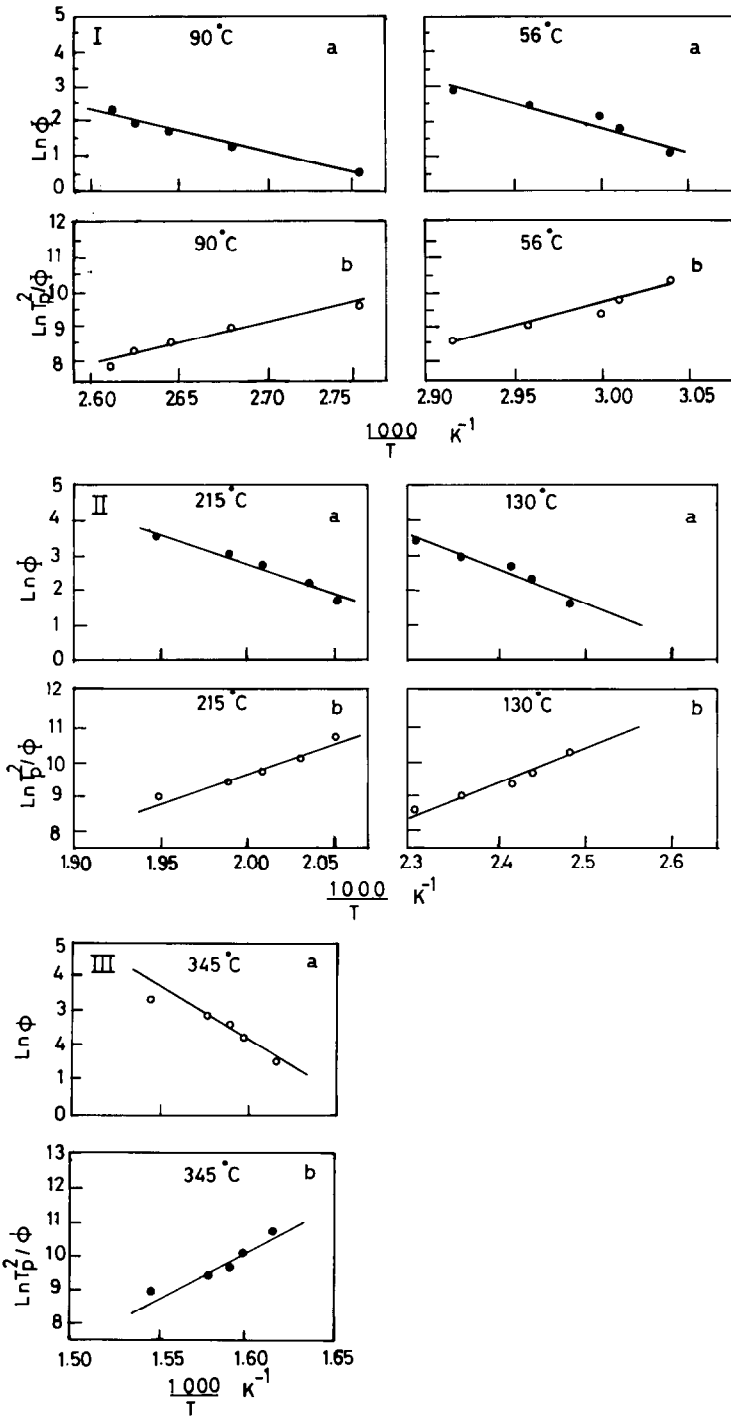


Fig. 4. $\ln \phi$ (a) and $\ln T_p^2/\phi$ (b) vs. $1/T_p$ for SDP endothermic peaks at 56, 90, 130, 215 and 345°C.

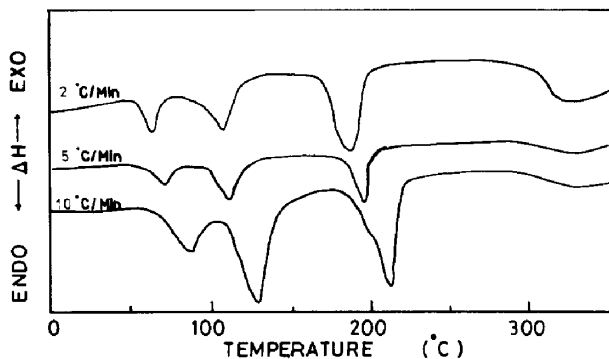


Fig. 5. DSC curves for SDP crystals at 2, 5 and 10 °C min⁻¹.

Endothermic peaks at 56, 90, 130, 215, 320 and 345 °C are observed. The positions of these peaks shifted to higher temperatures with increasing heating rates. The activation energy for each thermal process was calculated using the Kissinger and Ozawa equations [16,17] which are

$$\ln(T_p^2/\phi) = E/RT_p + \text{constant} \quad (6)$$

$$\ln \phi = E/RT_p + \text{constant} \quad (7)$$

where ϕ is the heating rate, T_p is the peak temperature and R is the universal gas constant. Figure 4 shows $\ln \phi$ and $\ln(T_p^2/\phi)$ vs. $1/T_p$ for SDP endothermic peaks at 56, 90, 130, 215 and 345 °C. The data were fitted by the least-squares method. The estimated values of the activation energy for SDP thermal processes associated with these peaks are respectively 104.35, 92.01, 73.43, 137.82 and 175.69 kJ mol⁻¹ by the Kissinger method and 109.83, 98.49, 80.21, 146.06 and 185.98 kJ mol⁻¹ by the Ozawa method. Further confirmation of the thermal analysis of SDP was obtained by differential scanning calorimetry DSC at 2, 5 and 10 °C min⁻¹. Figure 5 shows endothermic peaks at 75, 125, 215 and 330 °C; the slight difference in peak temperatures obtained by DSC and DTA are acceptable due to the difference in the two techniques; the peak temperatures obtained by DSC are more reliable because of its higher sensitivity.

The thermal transformation of sodium orthophosphate to pyrophosphate and then to metaphosphate was also confirmed by X-ray diffractometry and IR absorption spectroscopy. Figure 6(a) shows the X-ray diffraction pattern for as-grown SDP samples as well as for samples heat-treated at 100 and 125 °C. The latter two patterns have significant differences from that of the as-grown sample and agree with the ASTM card for the monohydrate (NaH₂PO₄ · H₂O), confirming the loss of one molecule of water of crystallisation. The X-ray diffraction pattern of SDP samples heat-treated at 150 °C (Fig. 6(b)) is identical with the ASTM card for NaH₂PO₄, i.e. the sample has lost two molecules of water of crystallisation and has become anhydrous;

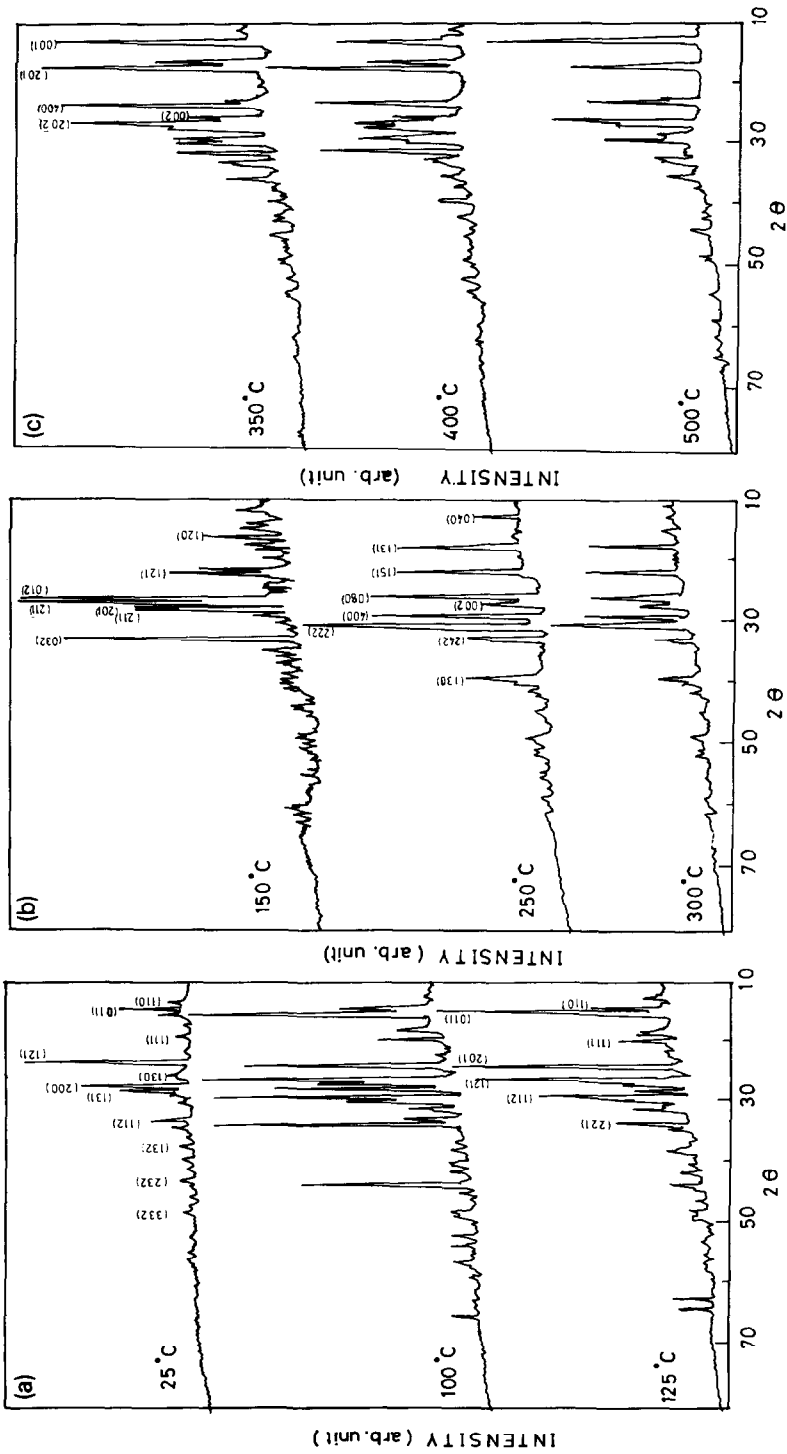


Fig. 6. (a)-(c) X-ray diffraction patterns for heat-treated SDP crystals at various temperatures.

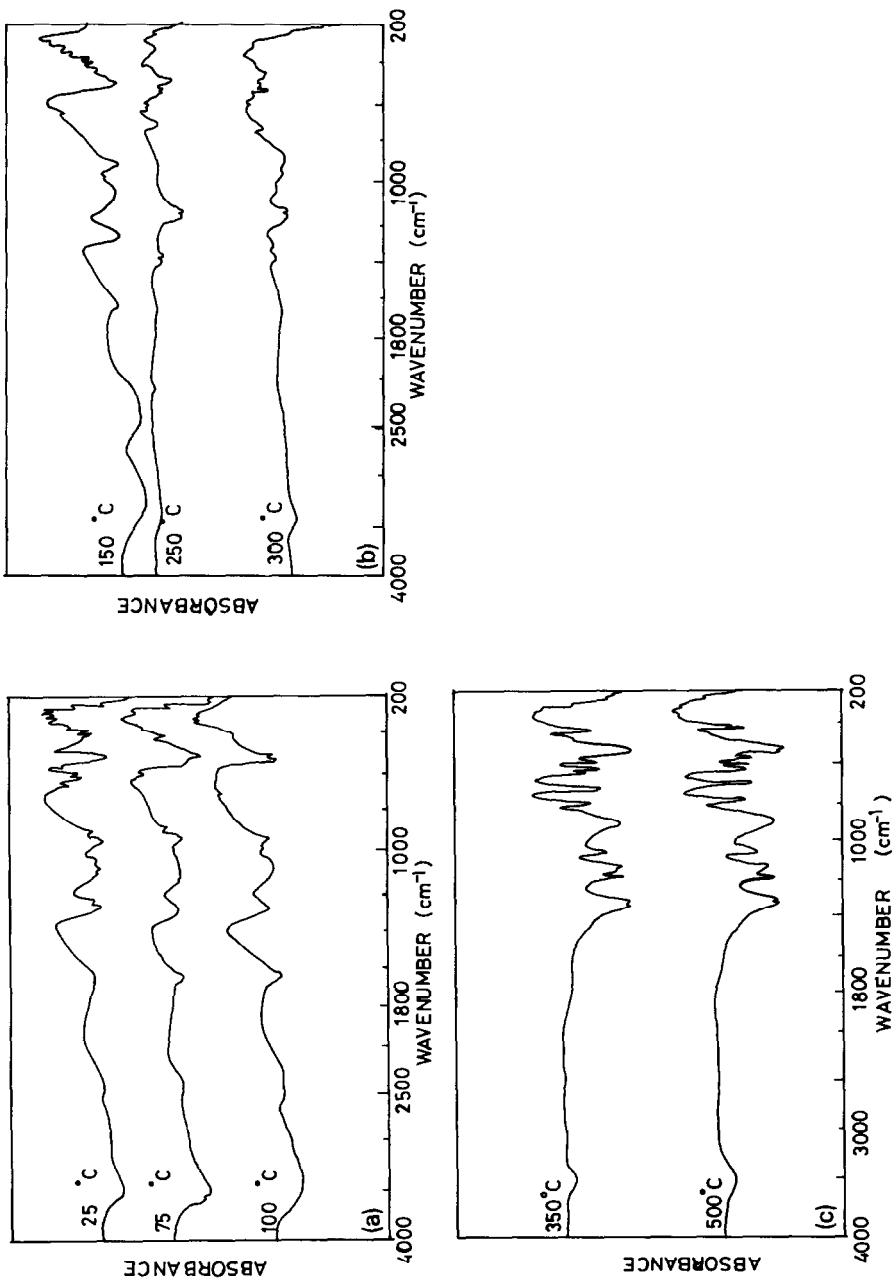


Fig. 7. (a)–(c) IR absorption spectra for as-grown and heat-treated SDP crystals at various temperatures.

TABLE 1

IR absorption spectra of as-grown SDP crystals at room temperature

| Absorption band (cm^{-1}) | Characterisation | Assignments [19,20] |
|--------------------------------------|------------------|--|
| 3450 | Broad band | H–OH stretching |
| 2350 | Broad band | |
| 1640 | Sharp band | HOH deformation |
| 1290 | Sharp band | P–O–H deformation |
| 1160 | Broad band | ν_{as} (PO_2) stretching (B) |
| 1100 | Broad band | |
| 1040 | Broad band | ν_{as} (PO_2) stretching (A_1) |
| 950 | Sharp band | |
| 900 | Sharp band | ν_{as} ($\text{P}(\text{OH})_2$) stretching (B) |
| 610 | Sharp band | P–O–H out-of-plane deformation |
| 530 | Broad band | $\delta(\text{P}(\text{OH})_2)$, $\delta(\text{PO}_2)$ |
| 410 | Broad band | O–P–O bending |

this is consistent with the thermal analysis. On further heating of SDP samples to 250°C , a new X-ray diffraction pattern is obtained. This pattern is identical with the ASTM card for sodium pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ confirming the proposed intermediate product of thermal decomposition. The X-ray diffraction pattern of SDP heated at 300°C is very close to that at 250°C indicating the stability of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ up to 300°C . Figure 6(c) shows a new crystal form with a high degree of crystallinity for the SDP sample heated to 350°C , which agrees with the ASTM card for sodium metaphosphate (NaPO_3). It is interesting to note that sodium metaphosphate has different forms; the most stable form is the trimetaphosphate with a ring-form anion [18]. All the other forms of sodium metaphosphate are unstable and can be transformed to trimetaphosphate. The formation of the highly stable trimetaphosphate was promoted by heating the samples beyond 350°C ; this is clear from the X-ray diffraction patterns obtained for the sample heated at 400 and 500°C .

The IR absorption spectra of SDP were recorded for as-grown samples as well as for those heat-treated at 75 and 100°C (Fig. 7(a)), 150, 250 and 300°C (Fig. 7(b)), and 350 and 500°C (Fig. 7(c)). The IR spectrum of SDP at 25°C shows bands centred at 3450, 2350, 1640, 1290, 1160, 1100, 1040, 950, 900, 610, 530 and 410 cm^{-1} . The vibration energies, characterisations and possible assignments are listed in Table 1 [19,20]. In the temperature range 100 – 150°C , a new broad band appears at 750 cm^{-1} , while the bands at 610, 530 and 410 cm^{-1} overlap forming one broad band at 520 cm^{-1} . Also the absorbance of the band at 1640 cm^{-1} increases with increasing temperature. These changes are consistent with the thermal results and X-ray diffraction data, confirming the loss of water of crystallisation. The IR absorption spectra for SDP heat-treated at 250 and 300°C show two new

bands at 320 and 710 cm^{-1} . The bands at 1290 and 1160 cm^{-1} are split into two bands and the absorbance of the band at 1640 cm^{-1} is decreased. These anomalous changes support the interpretation of the formation of sodium pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, as intermediate product. The IR absorption spectrum for the SDP sample heat-treated at 350 °C revealed new sharp bands centred at 1315, 1260, 1170, 1165 and 1000 cm^{-1} . This spectrum is consistent with that of sodium metaphosphate. At 500 °C a slight difference for bands at 870, 710, 580 and 460 cm^{-1} is observed in comparison with that at 350 °C, indicating the formation of trimetaphosphate [21].

CONCLUSION

The dihydrated sodium orthophosphate crystals lose their water of crystallisation and become anhydrous at around 150 °C. The anhydrous sodium orthophosphate transforms to sodium pyrophosphate as intermediate product at around 250 °C. This sodium pyrophosphate is converted to sodium metaphosphate as end product at 350 °C which, in turn, is transformed to the most stable trimetaphosphate form. The values of activation energy for the different thermal processes were estimated by the Kissinger and Ozawa methods. The thermal transformations of sodium orthophosphate were also confirmed by X-ray diffractometry as well as by IR absorption spectroscopy.

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