

## THERMAL BEHAVIOUR OF AMMONIUM DIHYDROGEN PHOSPHATE CRYSTALS IN THE TEMPERATURE RANGE 25–600 °C

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### ABSTRACT

A slow evaporation technique was used to grow single crystals of ammonium dihydrogen phosphate (ADP) from supersaturated aqueous solutions. An identification of crystal structure for as-grown ADP crystals was achieved. Simultaneous TG, DTG and DTA showed that the ADP crystals decompose at 210 °C to orthophosphoric acid with evolution of ammonia. The orthophosphoric acid converts to pyrophosphoric acid and then to metaphosphoric acid. A pronounced resolution of the overlap between phase transition, melting and decomposition of ADP crystals was obtained at relatively high heating rates. Differential scanning calorimetry (DSC) confirmed the phase transition in ADP crystals at 175 °C. Kissinger and Ozawa methods were applied to calculate the activation energies for the thermal processes occurring at 210 °C, which are 90.37 kJ mol<sup>-1</sup> and 99.12 kJ mol<sup>-1</sup> respectively. The phase transitions and thermal decompositions of ADP crystals have been confirmed by X-ray diffraction and infrared absorption spectra.

### INTRODUCTION

The ammonium dihydrogen phosphate crystal (ADP) belongs to a tetragonal structure in the paraelectric phase, where its space group is  $I\bar{4}2d$ . The crystal has two sublattices which transform to each other through the glide plane (110). There are two chemically equivalent NH<sub>4</sub><sup>+</sup> sites in the primitive unit cell which have  $\bar{4}$  symmetry [1–5]. Although ADP is isomorphous with the tetragonal potassium dihydrogen phosphate (KDP) in the paraelectric phase, it has some properties which are qualitatively different from those of KDP in the ferroelectric phase. Below the Curie temperature,  $T_c = 148$  K, for ADP, the crystal belongs to an orthorhombic crystal structure with space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> in the anti-ferroelectric phase [6–10].

Nuclear magnetic resonance studies [11–12] on the ADP crystal showed a double peaked proton resonance which changed to a single peak as the temperature of the sample was raised from 25 to 144 °C. These changes have been attributed to the decomposition of ADP. Viswanath and Miller [13] reported a high temperature phase transition at 160 °C via differential

scanning calorimetry (DSC) and thermogravimetry (TG) studies. On the other hand, the dielectric constant measurements [14] on ADP crystals showed a high temperature phase transition at 133°C. The previous study for a high temperature phase transition of ADP indicates a discrepancy in phase transition temperature. This discrepancy could be because of the variation in crystal size, degree of crystallinity, purity and number of defects in single crystals, or possibly the fact that the high temperature phase transition occurs very close to the decomposition of ADP, so that they overlap to a certain extent and are difficult to separate. Therefore more accurate techniques for crystal growth and measurements are needed to overcome the overlap between the phase transition and decomposition.

In the present work, thermal analyses of ADP crystals over the 25–600°C range have been carried out by simultaneous TG, DTG and DTA, as well as differential scanning calorimetry (DSC) studies. X-ray diffraction and IR absorption spectra are also obtained for as-grown crystals as well as heat-treated ADP samples at various temperatures to elucidate each thermal process observed at high temperature.

## EXPERIMENTAL TECHNIQUES

Single crystals of ADP were grown from supersaturated aqueous solutions using the well-known slow evaporation technique. The starting ADP powder used for growth was of analytical reagent grade, and was supplied by Osaka Hayashi Pure Chemical Industries Ltd., Japan.

A Shimadzu XD-3 X-ray diffractometer was used to identify the ADP crystal structure using a monochromatic Cu  $K\alpha$  X-ray beam of wavelength 0.1542 nm. The sample was investigated in the form of a fine homogeneous powder. The ADP samples were heated at various temperatures for 2 h in the temperature range 25–500°C, then quenched in ice, and X-ray diffraction of the heat-treated ADP samples was carried out at room temperature.

Simultaneous TG, DTG and DTA measurements were conducted on ADP crystals at heating rates of 5, 10 and 15°C min<sup>-1</sup> using a Setaram GDTD 16 thermoanalyser. A sample of size  $\approx$  38 mg was contained in the alumina crucible. Calcined  $\alpha$ -alumina was used as reference material. In this thermoanalyser the experimental zone of the furnace was evacuated and a low flow of argon gas, at a rate of 10 ml min<sup>-1</sup>, was maintained during the test. A PRT3000 regulator programmer in connection with a platinum/rhodium–platinum 10% (Pt/Rh–Pt 10%) thermocouple was used to control and measure the temperature. The recording system consisted of a B70 balance, a C3ATD amplifier, a DT 25 derivator and a four pen recorder. Thermal analyses of ADP crystals at different heating rates were also conducted using a Shimadzu DT-30 thermoanalyser and DSC.

For IR absorption spectra measurements, a few milligrammes of the ADP sample were thoroughly mixed and ground with a large quantity of KBr. A transparent disc of KBr was formed by pressing the mixtures at 5 tons. The IR absorption spectra for as-grown and heat-treated ADP samples at various temperatures between 25 and 500 °C were recorded using a Perkin–Elmer 598 double beam spectrophotometer in the spectral range of 200–4000  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

Single crystals of ADP were grown by the slow evaporation technique [15,16]. Crystal samples of reasonable dimensions were selected for various measurements and stored in a desiccator ready for use when needed. The X-ray diffraction pattern for the as-grown ADP sample, illustrated in Fig. 1, showed sharp lines indicating a high degree of crystallinity. The interplanar distance,  $d$ , for each line was calculated using the well-known Bragg law. The estimated data were then compared with index cards of the American Society for Testing and Materials (ASTM). At room temperature, the ADP crystal was found to have a tetragonal crystal structure. The lattice constants of these crystals were calculated using the equation for tetragonal structure [17]

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

The lattice constants  $a = b = 0.7485$  nm and  $c = 0.7561$  nm have been estimated. The volume of the unit cell,  $V_c$ , was calculated as  $0.4236 \text{ nm}^3$

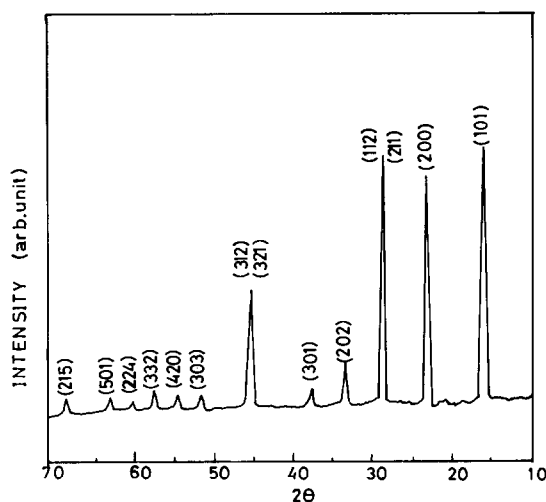


Fig. 1. X-ray diffraction pattern for an as-grown ADP crystal.

using the expression  $V_c = a^2c$ . The volume of one molecule,  $V_m$ , was estimated as  $0.1063 \text{ nm}^3$  using the formula

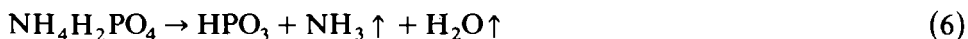
$$V_m = \frac{M}{\rho N} \quad (2)$$

where  $M$  is the molecular weight of the material,  $\rho$  is its density and  $N$  is the Avogadro number. It was found that the unit cell comprises four ADP molecules as given by  $V_c/V_m$ . These estimated values of the lattice constants, the volume of the unit cell and the number of molecules per unit cell are in good agreement with the data previously reported by other investigators [4,18]. It is evident from these X-ray analyses that the techniques used for crystal growth of ADP from aqueous solution are fairly reliable and satisfactory.

Simultaneous TG, DTG and DTA curves for ADP at heating rates of 5, 10 and  $15^\circ\text{C min}^{-1}$  in the temperature range  $25\text{--}600^\circ\text{C}$  are presented in Fig. 2a, b and c. In general, two endothermic peaks at  $210$  and  $350^\circ\text{C}$  were revealed by DTA. The TG curve showed a continuous weight loss up to  $600^\circ\text{C}$ , while DTA and DTG curves returned to their baselines above  $450^\circ\text{C}$ . At  $5^\circ\text{C min}^{-1}$ , details of the second endothermic peaks were observed. Also the peaks shifted towards the high temperature direction with increasing heating rate. As the ADP crystal melts at  $190^\circ\text{C}$  [19], the first peak at  $210^\circ\text{C}$  (temperature depending on the heating rate) could be ascribed to the melting process of ADP samples. However, this peak is found to be associated with a weight loss, in contrast generally with the melting processes, indicating that the peak at  $210^\circ\text{C}$  corresponds not only to the melting process but also to the decomposition of ADP. Also, the width of this peak is greater than the normal width due to melting processes. Therefore, the peak at  $210^\circ\text{C}$  could be attributed to melting and decomposition of ADP sample. The ADP sample decomposed to orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , with evolution of ammonia. In other words the melting and decomposition processes are very close to each other. According to the percentage weight loss in the TG curve, the second structured endothermic peak could be attributed to the formation of pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ . The pyrophosphoric acid in turn was transformed into metaphosphoric acid,  $\text{HPO}_3$ . Therefore, the thermal decomposition of ADP crystals proceeds according to the following reactions



or the sum of the reactions is



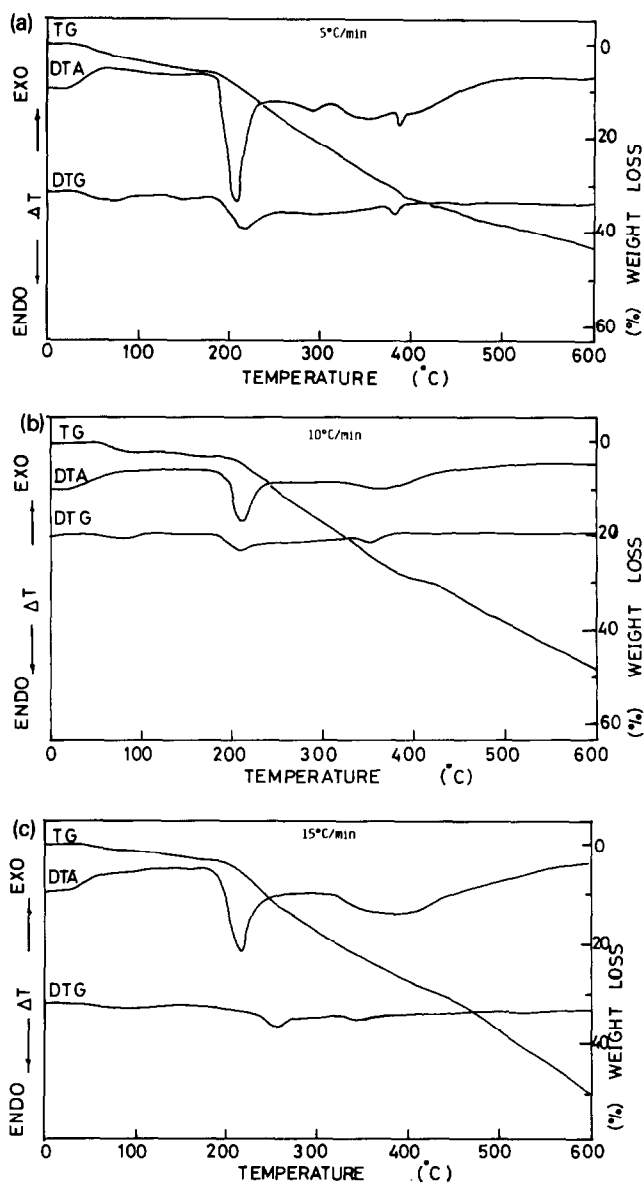


Fig. 2. Simultaneous TG, DTG and DTA for ADP at heating rates of (a) 5; (b) 10 and (c)  $15^{\circ}\text{C min}^{-1}$ , respectively.

The TG curve of ADP showed a continuous weight loss up to the available maximum temperature of  $600^{\circ}\text{C}$ , with two different rates of weight loss and without any constant segment. Therefore the above reactions take place continuously in a very complex manner and cannot be separated as individual reactions.

DTA for the ADP crystal at heating rates of 5, 10, 15, 20, 30, 50 and  $100^{\circ}\text{C min}^{-1}$  are shown in Fig. 3. It can be easily seen that the first peak,

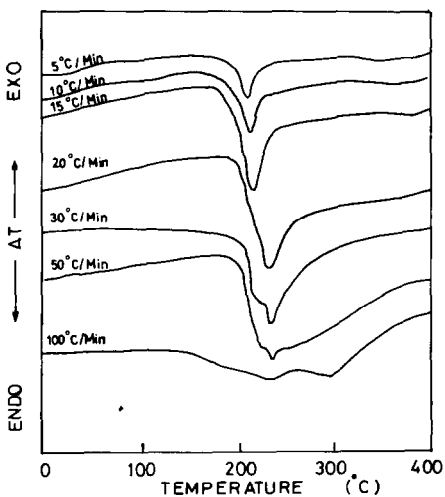


Fig. 3. DTA curves for ADP at various heating rates.

around 210 °C, shifted to higher temperature with increase of the heating rate. At higher heating rates, particularly at 30, 50 and 100 °C min<sup>-1</sup>, a pronounced resolving of this peak into three peaks around 175, 235 and 295 °C is observed with the onset of the first peak at 150 °C. On the basis of the TG curve, these resolved peaks could be attributed to phase transition, melting and decomposition of ADP samples respectively.

The activation energy for the thermal process at 210 °C was calculated using the Kissinger and Ozawa equations [20,21]. These two equations are respectively

$$\ln(T_p^2/\phi) = E/RT_p + \text{constant} \quad (7)$$

$$\ln \phi = E/RT_p + \text{constant} \quad (8)$$

where  $\phi$  is the heating rate,  $T_p$  is the peak temperature and  $R$  is the universal gas constant. The variation of  $\ln \phi$ , as well as  $\ln(T_p^2/\phi)$ , versus  $1/T_p$  for the ADP endothermic peak at 210 °C is shown in Fig. 4. The value of activation energy was fitted by the least squares method and estimated as 90.37 kJ mol<sup>-1</sup> and 99.12 kJ mol<sup>-1</sup> by the Kissinger and Ozawa methods respectively.

It is desirable to obtain other independent technical evidence to reinforce the obtained phase transition. Therefore DSC in the temperature range of 25–350 °C was carried out on ADP samples at 2, 5 and 10 °C min<sup>-1</sup>, as shown in Fig. 5. The DSC curve revealed two endothermic peaks at 175 and 210 °C as well as a structured exothermic peak consisting of three weak peaks at 262, 265 and 267 °C. The endothermic peak at 175 °C is consistent with the first peak obtained by DTA at a heating rate of 100 °C min<sup>-1</sup>. As the weight loss at 175 °C is negligible, therefore, this peak was attributed to

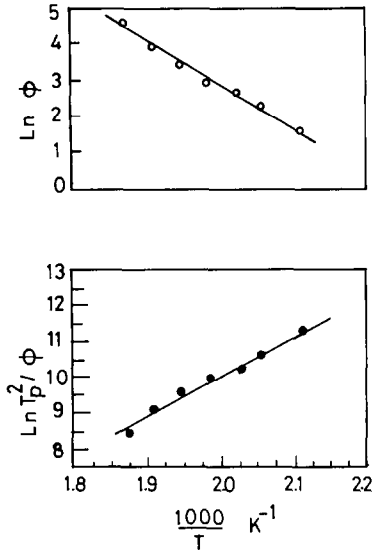


Fig. 4. The variation of  $\ln \phi$  and  $\ln(T_p^2/\phi)$  versus  $1/T_p$  for the ADP peak at  $210^\circ\text{C}$ .

a phase transition. As the peaks at  $210^\circ\text{C}$  and  $265^\circ\text{C}$  are associated with a weight loss, they were attributed to the two respective decompositions of the ADP samples. As the exothermic peak at  $265^\circ\text{C}$  is compatible with the second endothermic peak observed by DTA, it could be attributed to the formation of pyrophosphoric acid. The exothermic nature of this peak is a result of the oxidation process when DSC on the ADP sample is carried out under a static atmosphere.

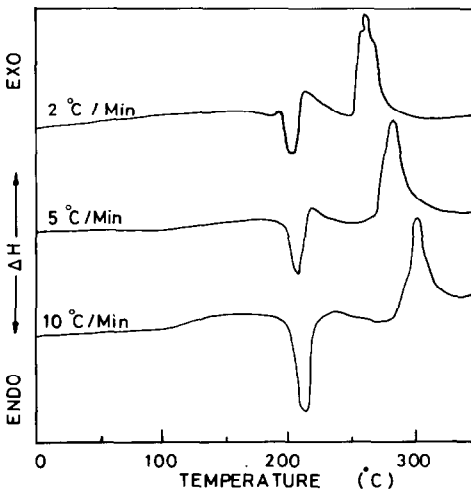


Fig. 5. DSC curves for ADP at 2, 5 and  $10^\circ\text{C min}^{-1}$ .

X-ray diffraction and infrared absorption spectra were also used to confirm the phase transition and different thermal processes in ADP. The ADP crystals were heated for 2 h at 130, 135, 150, 175, 200, 225, 250, 300, 350, 400 and 500 °C and quenched in ice to maintain their thermal behaviour, and then X-ray diffraction for as-grown and heat-treated ADP samples was carried out; results are shown in Fig. 6a, b and c. For as-grown ADP samples, sharp peaks corresponding to the Miller indices (101), (112), (200), (312) and (202) planes were revealed, with the (101) plane representing the maximum intensity. X-ray diffraction pattern for heat-treated ADP at 135 °C showed that the intensities of peaks corresponding to the (202), (332) and (212) planes are increased, indicating an improvement in the degree of crystallinity. Furthermore, the (112) plane showed the maximum intensity, instead of the (101) plane for as-grown ADP crystals. The intensities of the (101), (200) and (202) planes for heat-treated ADP samples at 175 °C showed significant anomalous changes, with the (202) plane having the maximum intensity, in contrast to the (101) and (112) planes for as-grown and heat-treated ADP samples at 135 °C respectively. These anomalous changes for heat-treated ADP at 175 °C confirmed the attribution of the peak at 175 °C in DTA at 100 °C min<sup>-1</sup>, as well as in DSC at 2 °C min<sup>-1</sup>, to phase transition. When the ADP crystal is heat-treated to 200 °C, the degree of crystallinity breaks down. This breakdown agrees well with melting and decomposition of the sample. X-ray diffraction for heat-treated ADP samples at 250 °C again showed recrystallization of the sample; some peaks started to disappear and new peaks were generated at  $2\theta \approx 16^\circ$  and  $41.5^\circ$ , indicating a build-up of new crystal structure form. It is interesting to note that the X-ray diffraction pattern for heat-treated ADP at 250 °C is comparable with the ASTM card of H<sub>3</sub>PO<sub>4</sub>, confirming conclusively the formation of this acid at this thermal stage.

X-ray diffraction patterns for heat-treated ADP samples at 350, 400 and 500 °C showed a complete breakdown, i.e. transition to an amorphous state. This breakdown confirmed the thermal decomposition of crystalline orthophosphoric acid, H<sub>3</sub>PO<sub>4</sub>, to pyrophosphoric acid, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, and then to metaphosphoric acid, HPO<sub>3</sub>; the two latter acids are amorphous.

Figure 7a, b and c shows the infrared absorption spectra for as-grown and heated ADP samples at 25, 75, 100, 125, 130, 135, 150, 175, 200, 250, 300, 400 and 500 °C. The absorption bands at 3200, 2000, 1620, 1400, 1290, 1100, 910, 530 and 420 cm<sup>-1</sup> are evident in the IR absorption spectra for as-grown samples. On the basis of the previously reported data [22,23], the characterization and assignments of bands are summarized in Table 1. All bands showed lower absorbance for the ADP sample heat-treated at 150 °C. The absorption spectrum for ADP samples heat-treated at 175 °C showed a pronounced change; the bands at 3200 and 2400 cm<sup>-1</sup> were much broadened, while the bands at 1400, 1290, 1100 and 900 cm<sup>-1</sup> were increased in intensity. These changes are consistent with that obtained by thermal



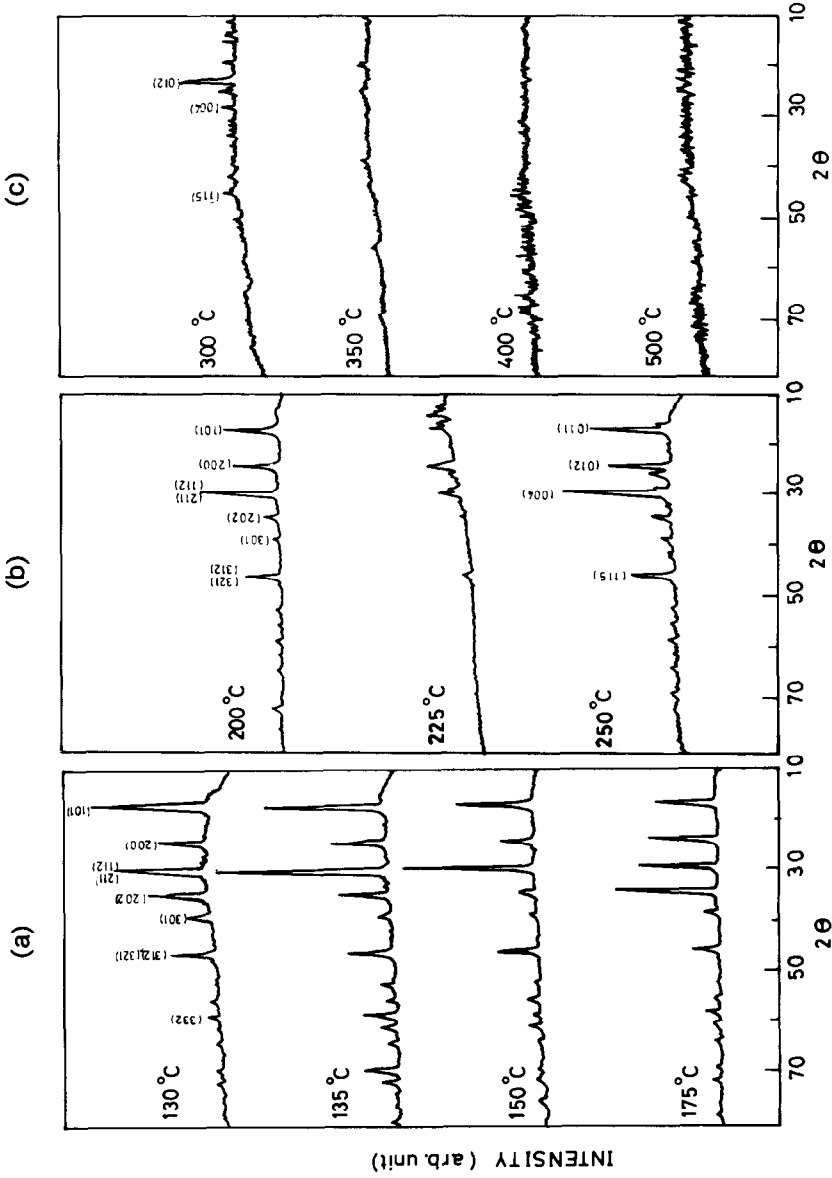


Fig. 6. X-ray diffraction patterns for heat-treated ADP samples at various temperatures.

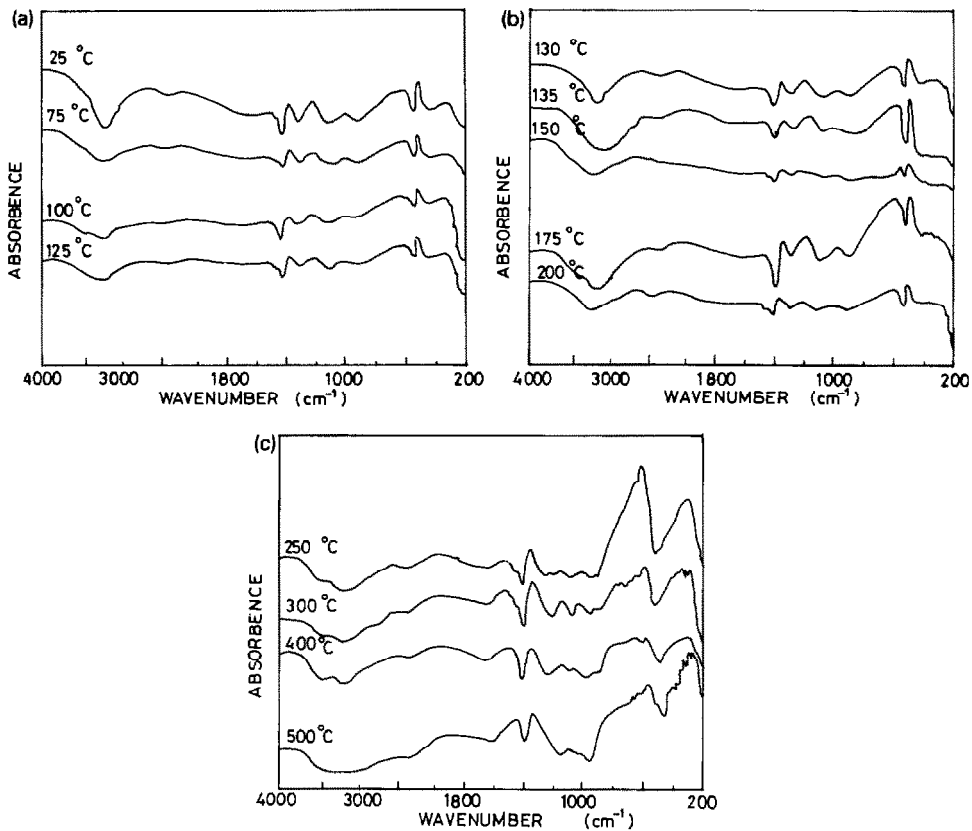


Fig. 7. IR absorption spectra for as-grown and heat-treated ADP samples at various temperatures.

TABLE 1

The IR absorption spectrum for as-grown ADP crystals at room temperature

Absorption band ( $\text{cm}^{-1}$ )	Characterization	Assignment
3200	Broad band	O-H Stretching N-H Stretching
2400	Broad band	Hydrogen band
1620	Broad band	O-H Bending
1400	Sharp band	$\text{NH}_4$ Ion
1290	Sharp band	Combination of $\nu_3(\text{PO}_4)$ with lattice
1100	Sharp band	$\nu_3(\text{PO}_4)$
910	Sharp band	$\nu_1(\text{PO}_4)$
530	Sharp band	Combination of $\nu_1(\text{PO}_4)$ with lattice
420	Broad band	$\nu_4(\text{PO}_4)$

analysis as well as X-ray diffraction, confirming the phase transition in ADP samples around 175°C. For ADP samples heat-treated at 250°C, the band at 1400 cm<sup>-1</sup> is associated with a broad band at 1425 cm<sup>-1</sup>. Also the bands at 1290, 1100 and 910 cm<sup>-1</sup> are deformed, indicating the removal of the  $\nu_3(T_2)$  and  $\nu_1(A_1)$  degeneracy. The bands at 530 cm and 420 cm<sup>-1</sup> overlap, together forming one band at 520 cm<sup>-1</sup>. Therefore these significant changes agree with the anomalous changes in X-ray diffraction for ADP samples heat-treated at 250°C. The findings are also consistent with the thermal results in the same range of temperature. On further heating of ADP samples at 300, 400 and 500°C, the absorbance of the bands at 2400 and 1620 cm<sup>-1</sup> increased with increasing temperature. The region between 1300 and 200 cm<sup>-1</sup> showed some changes for ADP samples heat-treated between 300–500°C which are consistent with the continuous TG weight losses, confirming the formation of metaphosphoric acid via pyrophosphoric acid.

## CONCLUSION

Based on the TG data, ADP crystals decompose around 210°C into orthophosphoric acid, H<sub>3</sub>PO<sub>4</sub>, with evolution of ammonia. Then the orthophosphoric acid is transformed to pyrophosphoric acid, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, which in turn is transformed to metaphosphoric acid, HPO<sub>3</sub>. The TG data show a continuous weight loss up to 600°C without any constant segment, indicating that the above reactions take place continuously in a very complex manner, and cannot be separated as individual reactions. The resolution of the phase transition from melting and decomposition processes was achieved by DTA of ADP samples at 50 and 100°C min<sup>-1</sup>; the phase transition was obtained at 175°C. This phase transition was also given by DSC at 2°C min<sup>-1</sup>. The phase transition as well as melting and decomposition of ADP samples were confirmed by the X-ray diffraction and IR absorption spectra.

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