Thermochimica Acta, 167 (1990) 225–233
Elsevier Science Publishers B.V., Amsterdam

HIGH-TEMPERATURE PHASE TRANSITION IN POTASSIUM DIHYDROGEN PHOSPHATE CRYSTALS

A. ABDEL-KADER, A.A. AMMAR and S.I. SALEH

Physics Department, Faculty of Science, Menoufia University, Menoufia (Egypt)

(Received 21 December 1989; in revised form 19 February 1990)

ABSTRACT

Single crystals of potassium dihydrogen phosphate (KDP) were grown by slow evaporation from supersaturated aqueous solution. The crystal structure of KDP was identified by X-ray diffraction analysis. Simultaneous TG, DTG and DTA thermal analysis of KDP crystals over the temperature range 25–600 °C showed that the potassium orthophosphate decomposed to potassium pyrophosphate and then to metaphosphate as end product. DTA studies at the higher heating rates of 50 and 100 °C min^{-1} showed a clear resolution of the first peak into two peaks; the first was attributed to a phase transition at 200 °C and the second was due to the decomposition of the sample. It is interesting to note that the high-temperature phase transition for KDP was also obtained at 175 °C by DSC studies at 2 °C min^{-1}. The activation energies for the thermal processes of KDP occurring at 230, 265 and 310 °C were calculated as 155.56, 286.56 and 81.46 kJ mol^{-1} by the Kissinger method, and 164.01, 294.97 and 91.34 kJ mol^{-1} by the Ozawa method. X-ray diffraction and infrared absorption spectra confirmed the high-temperature phase transition obtained by DTA and DSC as well as the thermal decomposition of the KDP samples.

INTRODUCTION

Potassium dihydrogen phosphate crystals (KDP) have a tetragonal crystal structure at room temperature with space group $I\bar{4}2d$ in paraelectric phase [1–4]. Below the Curie temperature $T_C = 123$ K, KDP crystals transform to an orthorhombic crystal structure with space group *Fdd*2 in ferroelectric phase [5–7]. There are numerous publications concerning the low-temperature phase transition which is well established; several models have been proposed to explain its mechanisms. The model of Imry et al. [8] is widely accepted; thus shows that these hydrogen-bonded crystals exhibit both a low-temperature ferroelectric transition and a high-temperature one. The latter phase transition has been subjected to further investigations related to its detection using dielectric measurements, infrared reflection studies and differential thermal analysis [9–12]. Partial vapour pressure studies [13] have suggested that KDP starts to decompose above 180 °C. Duval [14] has shown that the thermal decomposition of KDP begins at around 220 °C

0040-6031/90/$03.50

(TG). Blinc et al. [11] reported a high-temperature phase transition for KDP crystals before the onset of its thermal decomposition. They showed that the transition was connected with a breaking down of the hydrogen bond network rather than with the onset of disordered hindered rotation of the H_2PO_4 groups around three axes. They also showed that X-ray diffraction patterns for KDP started to disappear at 200 °C, which indicated the occurrence of a complete breakdown of the crystal structure. Grinberg et al. [10] showed that KDP has a distinct phase transition at 175 °C which is dependent on the PO_4 group. Rapopert [12] determined the phase diagram for KDP by DTA measurements made under pressures from 0 to 40 kbar, by heating the KDP crystals in a sealed capsule at zero pressure; this showed two phase transitions at around 190–197 °C and 233 °C.

Although the high-temperature phase transition has been subjected to extensive study, it is still uncertain and ambiguous. In our previous work [15,16] on thermal behaviour, in addition to some temperature-dependent properties of KDP, differential thermal analysis showed two endothermic peaks at 240 and 275 °C with decomposition starting at 205 °C. The peak due to phase transition cannot be recognized; this may be due to overlap between the phase transition and the decomposition of KDP crystal.

The present work reports on further investigations on KDP, such as simultaneous TG, DTG and DTA. DSC as well as DTA at different heating rates has also been performed in order to resolve the overlapping between the phase transition and the decomposition of KDP crystals. X-ray diffraction and infrared absorption spectra were also carried out for KDP heat-treated at selected temperatures in order to confirm the phase transition and the thermal decomposition of the crystals.

EQUIPMENT AND EXPERIMENTAL TECHNIQUES

Single crystals of KDP were grown by slow evaporation from supersaturated aqueous solution. KDP powder of purest grade was supplied by Osaka Hayashi Pure Chemical Industries Ltd, Japan.

The crystal structure of KDP was identified by means of a Shimadzu XD-3 X-ray diffractometer. The sample was a fine homogeneous powder. A monochromatic Cu *Kα* X-ray beam of wavelength 0.15420 nm was obtained by using a Cu target and Ni filter. Some samples of KDP 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 KDP was studied by means of a Setaram GDTD 16 thermoanalyser which records TG, DTG and DTA simultaneously. The oven temperature was controlled by means of a PRT 300 temperature regulator programmer to obtain a constant rate of heating. The temperature of the sample and reference was measured using a platinum/rhodium–platinum 10% (Pt/Rh–Pt10%) thermocouple. The sample was contained in an alumina crucible while a calcinated alumina crucible was used as reference. A recording system consisting of a B70 balance, a C3ATD amplifier, a DT 25 derivator and a four-pen recorder was used. The thermal analysis of KDP was also studied using differential scanning calorimetry (DSC) as well as a Shimadzu DT-30 differential thermal analyser at different heating rates.

The infrared absorption spectra of KDP were measured using a Perkin–Elmer 598 double-beam spectrophotometer in the spectral region of 200–4000 cm^{-1} for the heat-treated KDP crystals. Samples were prepared by employing the KBr disc technique.

RESULTS AND DISCUSSION

Single crystals of KDP were grown by double recrystallization from supersaturated aqueous solution using the evaporation technique [17,18]. The KDP crystal was found to have a tetragonal crystal structure with space group $I\bar{4}2d$. The lattice constants, a and b, were calculated as 0.7387 and 0.6985 nm.

Figure 1 shows simultaneous TG, DTG and DTA curves recorded for KDP samples at the heating rate of 10 °C min^{-1} in the temperature range 25–600 °C. The DTA curve shows endothermic peaks centred at 195, 235, 275, 300 and 335 °C. All peaks are coincident with those appearing on the DTG curve except the peak at 235 °C which is absent. Above 350 °C, the DTA and DTG curves return to their baselines and a constant weight was obtained, indicating a complete decomposition of KDP samples. The peak at 195 °C is associated with a weight loss of 6.5%; therefore potassium

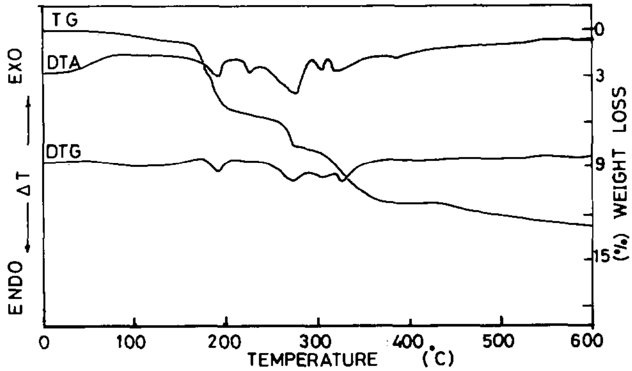

Fig. 1. Simultaneous TG, DTG, and DTA for KDP at a heating rate of 10 °C min^{-1}.

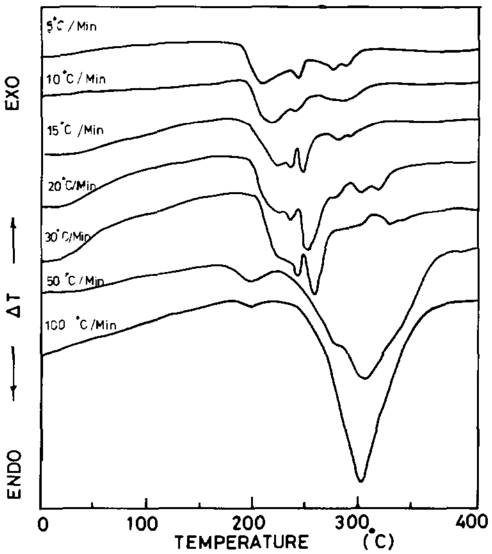

Fig. 2. DTA curves for KDP at various heating rates.

orthophosphate decomposed to potassium pyrophosphate by losing half a mole of water according to the following reaction

$$2KH_2PO_4 \rightarrow K_2H_2P_2O_7 + H_2O \quad (1)$$

However the peak at 235 °C appears only in the DTA curve and is not accompanied by any weight loss; therefore this peak can be assigned to a phase transition in the sample. Potassium pyrophosphate $K_2H_2P_2O_7$, transformed to potassium metaphosphate by losing another half mole of water in the temperature range 275–335 °C according to the reaction

$$K_2H_2P_2O_7 \rightarrow 2KPO_3 + H_2O \quad (2)$$

The sum of the thermal decompositions is thus given by

$$KH_2PO_4 \rightarrow KPO_3 + H_2O \quad (3)$$

i.e. the loss of one mole of water (13.2%) leads to the formation of potassium metaphosphate as end product through the pyrophosphate intermediate product. More information about the thermal decomposition of KDP was obtained by conducting DTA analyses at heating rates of 5, 10, 15, 20, 30, 50 and 100 °C min^{-1}, as shown in Fig. 2. The endothermic peaks shift towards higher temperature by increasing the heating rates from 5 to 30 °C min^{-1}.

At the higher heating rates of 50 and 100 °C min^{-1}, the first endothermic peak is resolved into two peaks, one at 200 and the other at 300 °C, i.e. the two resolved peaks are shifted in opposite directions. It is probable that the resolved peak at 200 °C can be attributed to a phase transition while the other peak at 300 °C is due to the decomposition of the sample. This phase

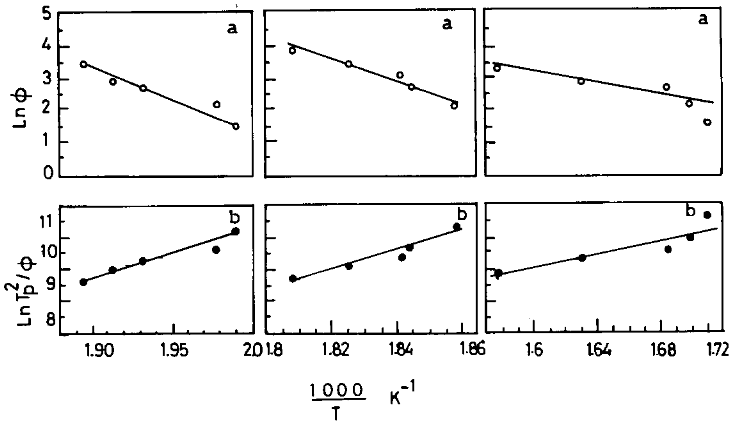

Fig. 3. The variation of ln ϕ, $\ln(T_p^2/\phi)$ versus $1/T_p$ for KDP peaks (DTA) at 230, 265 and 310 °C.

transition is compatible with other studies such as thermogravimetry (TG) [14] and differential thermal analysis (DTA) [12] as well as the infrared spectra and dielectric constant [10]. It is interesting to note that high resolution of some overlapping thermal process can be obtained by DTA at higher heating rates.

The activation energies for the thermal processes of KDP were calculated from the dependence of peak position on the heating rate using the Kissinger and Ozawa methods [19,20] which are

$$\ln\left(T_p^2/\phi\right) = E/RT_p + \text{constant} \tag{4}$$

$$\ln \phi = E/RT_p + \text{constant} \tag{5}$$

where ϕ is the heating rate, T_p is the peak temperature and R is the universal gas constant. Figure 3 shows ln ϕ and $\ln(T_p^2/\phi)$ versus $1/T_p$ for peaks at 230, 265 and 310 °C. The data were fitted by the least-squares method. The estimated values of the activation energy for the thermal processes associated with these peaks are respectively 155.56, 286.56 and 81.46 kJ mol^{-1} by the Kissinger method, and 164.01, 294.97 and 91.34 kJ mol^{-1} by the Ozawa method. The activation energies obtained by the two methods are very close to each other, therefore the two methods are applicable to these thermal processes.

Due to its high sensitivity, differential scanning calorimetry (DSC) has been found to be an important tool for the study of phase transition and decomposition occurring during the thermal treatment of samples. Therefore DSC was performed for KDP at 2 and 10 °C min^{-1}, see Fig. 4. At 2 °C min^{-1} there is a weak endothermic peak at 175 °C as well as three sharp endothermic peaks at 188, 230 and 268 °C. These peaks are shifted to higher temperatures by increasing the heating rate from 2 to 10 °C min^{-1}. On the

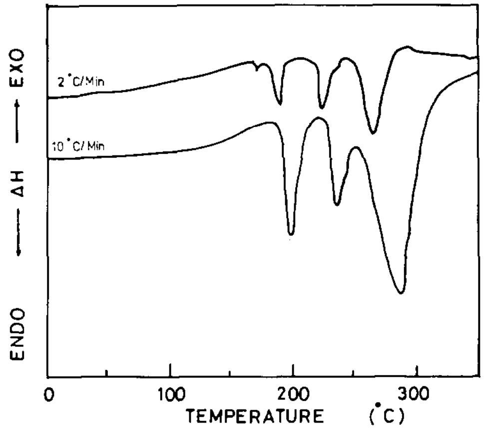

Fig. 4. DSC curves for KDP at 2 °C min^{-1} and 10 °C min^{-1}.

basis of the weight loss (TG curve), the peaks at 175 and 230 °C were assigned to the phase transition of the sample while the peaks at 188 and 268 °C were attributed to the transformation of potassium orthophosphate to potassium pyrophosphate. The difference in the peak positions in DSC and DTA are due to differences in the two techniques; the peak temperatures obtained by DSC are more favourable due to its high sensitivity and accuracy.

Figure 5a shows the X-ray diffraction patterns at room temperature for as-grown KDP samples as well as those heat-treated at 150, 175, 225 and 250 °C (Fig. 5b) 300, 350 and 500 °C (Fig. 5c). In comparison with the X-ray diffraction pattern for the as-grown sample, the intensities of all peaks of KDP samples heat-treated, at 150 and 175 °C decreased and some peaks disappeared, i.e. structural changes take place at 175 °C; this is consistent with the peak appearing at 175 °C in the DSC data, confirming the attribution of this peak to a phase transition. X-ray diffraction patterns for KDP samples heat-treated at 225 and 250 °C show a breakdown of crystallinity, which can be assigned to the transformation of potassium orthophosphate to potassium pyrophosphate and confirmed the TG and DTA results. X-ray diffraction patterns for KDP samples heated at 300 °C again show the beginning of the appearance of a new form of crystal structure. The X-ray diffraction pattern for the 350 °C sample shows a high degree of crystallinity, with a crystal form identical with the ASTM card for standard monoclinic KPO_3; this confirms the proposed thermal decomposition of the KDP samples.

The infrared absorption spectra at room temperature of KDP samples heat-treated for 2 h at temperatures between 25 and 500 °C are shown in Fig. 6a, b and c. In the infrared absorption spectra for as-grown sample, there are bands centred at 3500, 2800, 2400, 1640, 1290, 1100, 900, 530 and 420 cm^{-1}. The characterization and possible assignments of the KDP bands

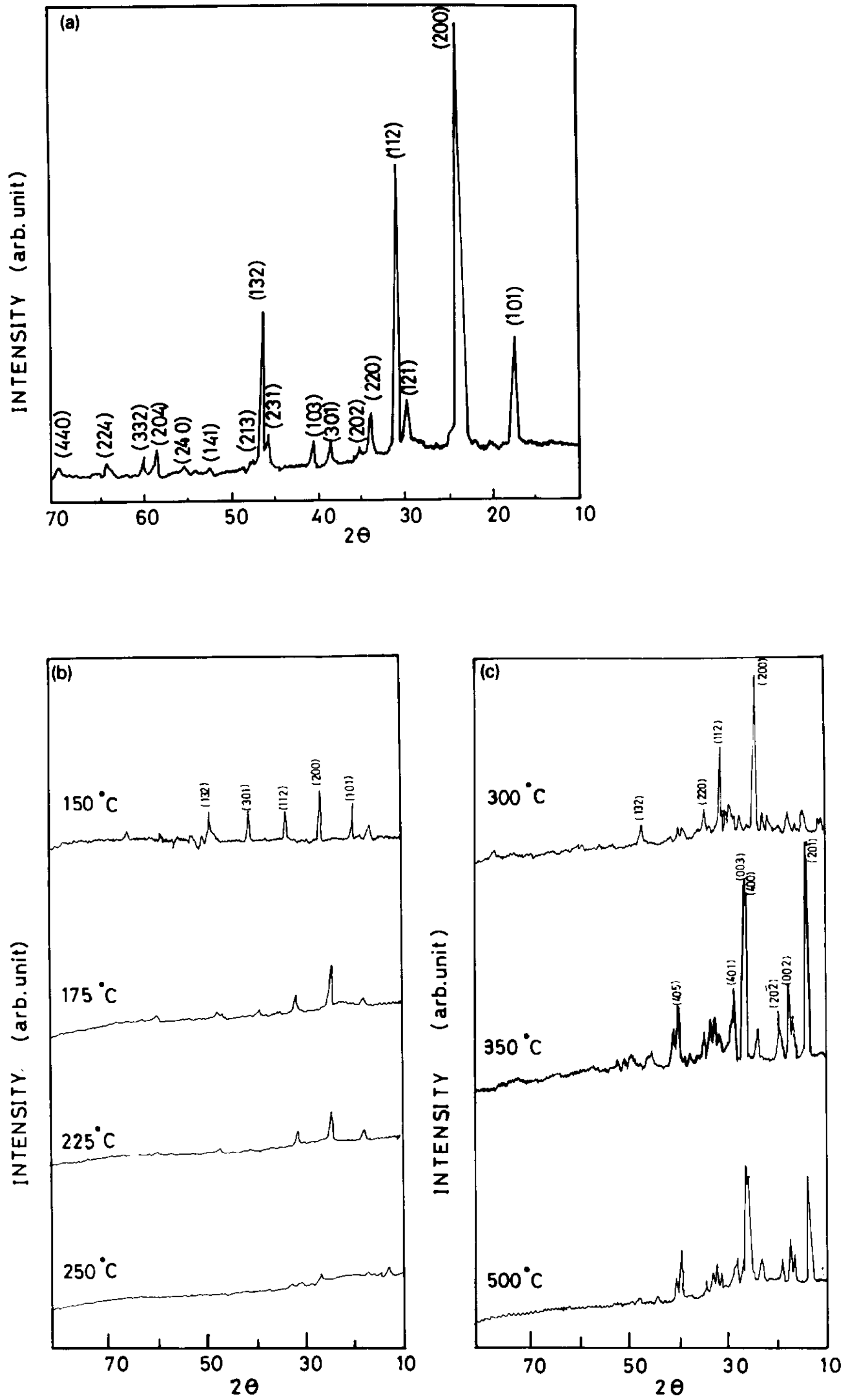

Fig. 5. X-ray diffraction patterns for as-grown (a) and KDP heat-treated at 150, 175, 225 and 250 °C (b), 300, 350 and 500 °C (c).

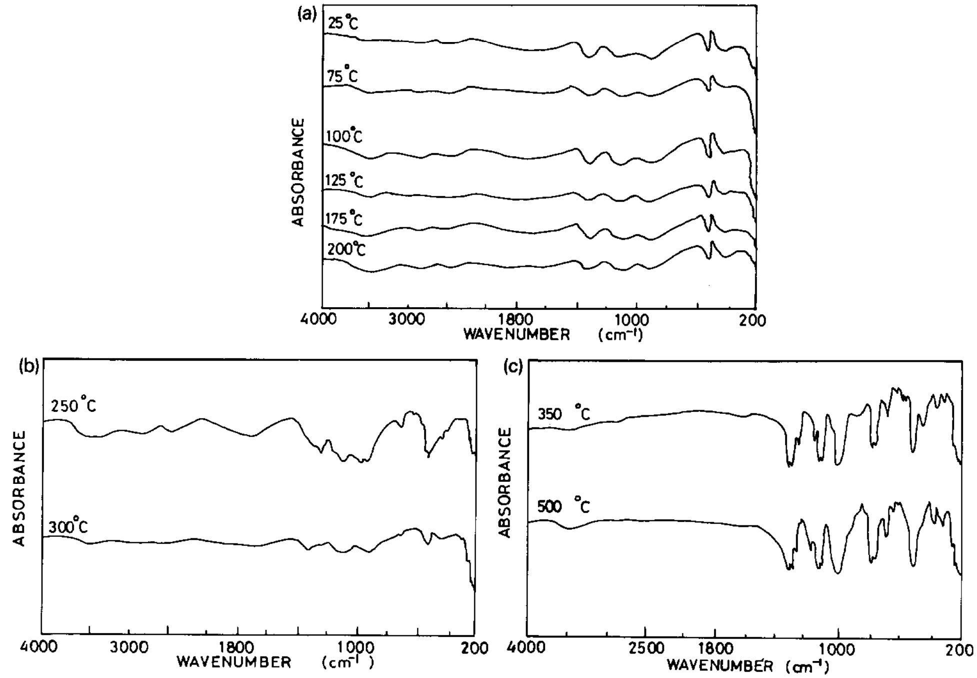

Fig. 6. a, b and c, Infrared absorption spectra for as-grown and KDP samples heat-treated at temperatures between 25 and 500 ° C.

are listed in Table 1. The absorbances of the bands at 3500, 530 and 420 cm^{-1} decrease for the KDP heat-treated at 175 ° C which is attributable to some changes in the degree of crystallinity, in agreement with the thermal and X-ray diffraction results. In the infrared absorption spectra for KDP samples heat-treated at 250 ° C, the bands at 1100 and 900 cm^{-1} are transformed into three bands at 1070, 960 and 915 cm^{-1}. Furthermore, a

TABLE 1

Infrared absorption spectrum of as-grown KDP crystal sample at room temperature

Absorption band cm^{-1}	Characterisation	Assignments [8]
3500	broad band	O–H stretching
2800	broad band	O–H vibration
2400	broad band	Hydrogen bond
1640	broad band	O–H bending
1290	sharp band	Combination of ν_3 of (PO_3) with lattice
1100	broad band	ν_3 of (PO_4)
900	sharp band	ν_1 of (PO_4)
530	sharp band	Combination of ν_4 of (PO_4) with lattice
420	broad band	ν_4 of (PO_4)

new sharp band appears at around 700 cm^{-1} and the bands at 530 and 420 cm^{-1} overlap to give a broad band at 510 cm^{-1}. These changes in the spectra are due to the formation of potassium pyrophosphate and are consistent with the results of the thermal studies. The infrared absorption spectrum for the KDP sample heat-treated at 350 ° C is completely different from previous spectra and has a large number of sharp bands in the range 1400–200 cm^{-1}. The spectrum is identical with the standard spectrum of KPO_3, confirming the thermal decomposition of KH_2PO_4 to KPO_3 as end product.

CONCLUSION

The KDP started to decompose into potassium pyrophosphate at around 190 ° C. The potassium pyrophosphate product undergoes a phase transition at 235 ° C and converts to potassium metaphosphate as end product. DTA analysis for KDP at the higher heating rates of 50 and 100 ° C min^{-1} revealed a pronounced resolution of the first peak into two peaks; the first was attributed to a phase transition while the second was due to the decomposition of the sample. Therefore, high resolution was obtained at higher heating rates. X-ray diffraction as well as infrared spectra confirmed the phase transition and decomposition of the KDP sample.

REFERENCES

1 B. Wyncke and F. Brehat, J. Phys. C: Solid State Phys., 19 (1986) 2649.
2 V.Yu. Davydov and E.V. Chisler, Sov. Phys: Solid State, 23 (1981) 1978.
3 G.E. Bacon and R.S. Pease, Proc. R. Soc. (London), A 220 (1953) 397; A 230 (1955) 359.
4 J. West, Z. Kristallogr., 74 (1930) 306.
5 A.R. Ubelohde and I. Woodward, Proc. R. Soc. (London), A 188 (1947) 358.
6 S. Hausshl, Z. Kristallogr., 120 (1964) 401.
7 W.R. Cook, J. Appl. Phys., 38 (1967) 1673.
8 Y. Imry, I. Pelah and E. Wiener, J. Chem. Phys., 43 (1965) 2332.
9 J. Grinberg, S. Levin, I. Pelah and Wiener, Solid State Commun., 5 (1967) 863.
10 J. Grinberg, S. Levin, I. Pelah and D. Gerlich, Phys. Status Solidi B: 49 (1972) 857.
11 R. Blinc, V. Dimic, D. Kolar, G. Lahajnar, J. Stepisink, S. Zumer, N. Vene and D. Hadzi, J. Chem. Phys., 49 (1968) 4996.
12 E. Rapopert, J. Chem. Phys., 53 (1970) 311.
13 S.J. Kiehl and G.H. Wallace, J. Am. Chem., 49 (1927) 375.
14 C. Duval, Inorganic Thermogravimetric Analysis, 2nd edn., Elsevier, New York, 1963, p. 258.
15 H.I. Farag, M.S. Elmanharawy and A. Abdel-Kader, Egypt. J. Sol., 5 (1984) 1.
16 H.I. Farag, M.S. Elmanharawy and A. Abdel-Kader, Acta Phys. Hung., 60 (1986) 19.
17 V.K. Subhadra, U. Syamaprasad and C.P.G. Vallabhan, J. Appl. Phys., 54 (1983) 2593.
18 P.F. Bordui, J.J. Zola and G.M. Loiacono, J. Cryst. Growth, 71 (1985) 269.
19 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
20 T. Ozawa, J. Therm. Anal., 2 (1970) 301.