

Growth and thermal studies on pure ADP, KDP and mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals

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The investigations on the formation of mixed crystals of ammonium dihydrogen orthophosphate (ADP) and potassium dihydrogen orthophosphate (KDP) i.e. potassium ammonium dihydrogen phosphate, $K_{1-x}(NH_4)_xH_2PO_4$ have been presented in this paper. Pure and mixed crystals of ADP and KDP have been grown by slow evaporation technique from the supersaturated solution at an ambient temperature 26 ± 1 °C for ammonium concentration x in the range $0.0 \leq x \leq 1.0$ in the case of mixed crystals. Crystal compositions were determined by flame atomic absorption spectroscopy and chemical analysis. The results of the X-ray analysis of the grown crystals are also reported. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to study the kinetic process of dehydration and the high temperature phase behaviour. DTA showed the distinct thermal events attributed to dehydration of ADP, KDP and $K_{1-x}(NH_4)_xH_2PO_4$. The results of thermal analysis and chemical analysis are consistent with each other.

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1 Introduction

Ammonium dihydrogen phosphate, $NH_4H_2PO_4$ (abbreviated as ADP) and potassium dihydrogen phosphate, KH_2PO_4 (abbreviated as KDP) are well-known antiferroelectric and ferroelectric crystals, respectively, belonging to the KDP family. Ferroelectric phase transition in KDP occurs at -150 °C and antiferroelectric phase transition in ADP occurs at -125 °C [1]. KDP crystal exhibits excellent electro-optical and non-linear optical properties and is commonly used in frequency conversion applications such as second, third and fourth harmonic generation and in electro-optical modulation [2,3]. Studies on ADP crystals still attract interest in view of their dielectric, anti ferroelectric and optical properties and their varied uses as electro-optical modulator, harmonic generators, and parametric generator and as monochromators for X-ray fluorescence analysis [4-6]. Because of ferroelectric and antiferroelectric properties of these crystals and potential applications, the studies on growth, structural, chemical, optical, electrical properties are highly required. The ferroelectric and antiferroelectric properties are among the most spectacular manifestations of co-operative phenomena in condensed materials.

On the other hand, the KDP-type compounds, for different heating cycles, show a high temperature phase transitions (HTPT) at a characteristic temperature T_p . There are, however, large discrepancies in the literature concerning the nature of this transition, as well as regarding the number of additional transitions at higher temperatures. For example, a structural phase transition from tetragonal to monoclinic symmetry has been proposed for KDP at 180 °C [7,8]. Other researchers have proposed that when the KDP-type compounds are heated above room temperature, loss of water will take place, as in the following chemical reaction [10];



where n is the number of molecules participating in the thermal decomposition, s and v (enclosed in parentheses) denote solid or vapour state, respectively. This means that a polymerization of the phosphate salt takes place forming KPO_3 repeating units. It was further presumed that the polymerization sets in at particular

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sites on the surface. According to Lee [9], as a consequence of reaction, the term HTPT at T_p should be replaced by the term *onset of partial polymerization at reaction sites on the surface*.

Boukhiris et al. [10], have shown through X-ray diffraction studies on $K_{1-x}(NH_4)_xH_2PO_4$ ($0.0 < x < 1.0$) that the thermal vibration of the phosphate group as well as the cell parameters vary considerably with composition x . These observations below room temperature may be due to a static disorder because of the large difference between cell parameters of KDP and ADP, or due to fluctuations of their concentration throughout the system of mixed crystals. At a higher temperature, it is then expected to show a higher degree of disorder and other phase transitions related to it.

In the present study, we have succeeded to grow crystals of ADP, KDP and mixed crystals of ADP-KDP by isothermal evaporation of pure and mixed supersaturated solution at room temperature. These crystals are characterised by X-ray diffraction. We have used thermo gravimetric analysis (TGA), differential thermal analysis (DTA) to study the dehydration and thermal behaviour in pure and mixed ADP-KDP crystals.

2 Experimental

Crystal growth ADP and KDP powders of analytical reagent grade (G. R. Merck) and distilled water are used in the present experiments. The solution stability is an important physical parameter for the single crystal growth, which is usually evaluated by the measurement of the induction period. The solubility of KDP and ADP was experimentally measured by the traditional weight method. ADP is soluble in water and its solubility at 27 °C is 44.0 parts by weight of water. KDP is soluble in water and its solubility at 27 °C is 24.0 parts by weight of water. It was found that the molar concentration of ADP in the saturated solution is approximately two times that of KDP [11]. The saturated KDP and ADP solutions were prepared by dissolving the required amount of ADP and KDP at temperature of 35 °C and allowing them to stabilize at the room temperature of 27 °C for 24 h. The filtered saturated solutions of KDP and ADP were mixed together at different selected volume ratio and allowed for slow evaporation at the lab temperature of 27 °C. Super saturation was attained by ambient evaporation. The humidity during the growth process was constant at less than 20%.

The experimental setup used for the determination of induction period consisted of a 35 W mercury vapour lamp source to illuminate the growth system comprising of clear solution in clear glass beakers. The nuclei were observed with a low magnification (10×) travelling microscope. Experiments were carried out in a dust free atmosphere to avoid the effects of heterogeneous nucleation by dust particles. Since the growth of the crystal is very rapid as compared to the time required for the formation of a critical cluster, time taken for the formation of an observable nucleus is taken as the induction time.

Determination of crystal composition Transparent crystals were obtained from KDP and ADP rich solutions where as needle type crystals were harvested for intermediate compositions. In the mixed crystals of $K_{1-x}(NH_4)_xH_2PO_4$, the composition of potassium has been estimated using flame atomic absorption spectrophotometer (Chemito AA 203). The composition of nitrogen has been determined using elemental analyzer (EURO EA).

XRD analysis The crystals obtained were then ground mechanically to a fine powder and used for X-ray analysis. The change in the lattice parameters with composition was studied by the X-ray powder diffractometry method using Rigaku MiniFlex (30 kV, 15 mA) X-ray diffractometer with nickel filtered Cu K α radiation.

Thermal analysis The course of thermal dehydration and phase transition was investigated using TG/DTA 6300 system (model EXSTAR-6000) SII Nano Tech. Inc. Japan at the heating rate of 10 K/min. An inert nitrogen atmosphere with a flow rate of 80 ml/min was used to remove gaseous decomposition products.

3 Results and discussion

Several runs were carried out under controlled and unstirred conditions and reproducible results on induction period with accuracy of $\pm 2.5\%$ were obtained. The induction period for the crystals grown at different concentrations of ADP and KDP is listed in table 1. It has been observed that the induction time for the growth of pure ADP is large in comparison with that for the growth of pure KDP single crystals. Further, addition of KDP to ADP or vice versa results in an increase in the induction period.

Although the system ADP-KDP forms a continuous series of solid solutions over the whole range of compositions, it is not possible to grow bulk single crystals from all compositions [12,13]. The development of

internal stress due to the strong chemical bonding interaction between K^+ and $H_2PO_4^-$ ions and the competitive growth of NH_4^+ and K^+ ions affects the quality and morphology of the crystal [11,14]. It has been observed that it is difficult to grow good quality single crystals in the intermediate range of concentration, i.e., ($0.09 \leq x \leq 0.85$). The grown crystals of ADP, KDP and $K_{1-x}(NH_4)_xH_2PO_4$ are shown in figure 1. Transparent crystals were obtained from ADP and KDP rich solutions, where as needle type crystals have been harvested from the intermediate range of concentration, i.e., ($0.09 \leq x \leq 0.85$) due to spherulitic growth. Similar results have been proposed by Sen Gupta et al. [15] on the growth of mixed KADP crystals. They have reported that the crystals of pure ADP and KDP could be grown relatively easily and growth was dendritic in the intermediate range of concentration, i.e. $0.25 \leq x \leq 0.75$.

Table 1 Growth characteristics of mixed ADP-KDP crystals, i.e., $K_{1-x}(NH_4)_xH_2PO_4$.

Mixed ratio in terms of volume ADP:KDP	Ammonium content (in fraction x)	Induction period (in days)
1:0	1.0	20
9:1	0.96	46
8:1	0.92	45
7:1	0.90	44
6:1	0.89	44
5:1	0.85	40
1:4	0.09	13
1:5	0.06	10
1:6	0.02	08
1:7	<0.02	06
0:1	0.00	05

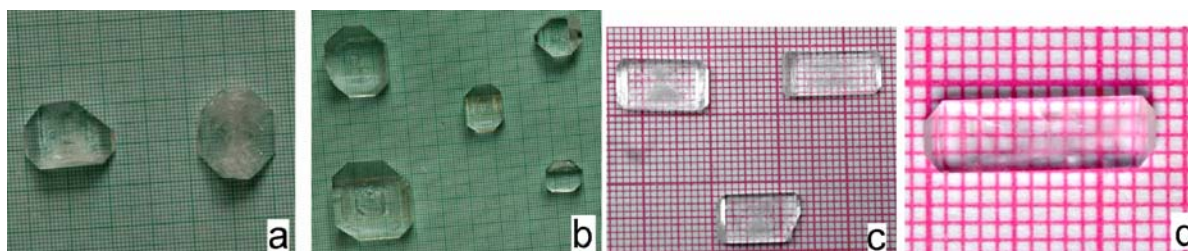
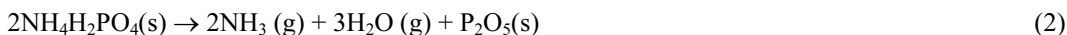


Fig. 1 Crystal (each small division corresponds to 1 mm.) (a) Pure ADP (b) Pure KDP (c) $K_{0.98}(NH_4)_{0.02}H_2PO_4$ (d) $K_{0.11}(NH_4)_{0.89}H_2PO_4$. (Online color at www.crt-journal.org)

X-ray diffraction studies ADP belongs to scalenohedral class of tetragonal crystal system. It has the tetra molecular unit cell having the dimensions [16] given as $a = b = 7.510 \text{ \AA}$ and $c = 7.564 \text{ \AA}$. KDP belongs to scalenohedral (12-sided polyhedron) class of tetragonal system with the tetra molecular unit cell having the dimensions [16] given as $a = b = 7.448 \text{ \AA}$ and $c = 6.977 \text{ \AA}$. The lattice parameters of ADP reported by K. Srinivasan et al. [17] are $a = 7.5006 \text{ \AA}$ and $c = 7.5490 \text{ \AA}$ and those of KDP are $a = 7.4529 \text{ \AA}$ and $c = 6.9751 \text{ \AA}$. The standard diffraction data of JCPDS for ADP are $a = 7.5021 \text{ \AA}$ and $c = 7.5541 \text{ \AA}$ [18] and those of KDP are $a = 7.4532 \text{ \AA}$ and $c = 6.9742 \text{ \AA}$ [19]. The experimental data of powder diffraction is tabulated in table 2. This is in agreement with the above reported data, but at variance with the report of Miyazaki et al. [20]. It is observed that both the parameters 'a' and 'c' decrease with the addition of potassium in ADP crystals. It may be mentioned that the crystal structure for the mixed crystals remained tetragonal and the variation in the lattice parameter 'a' is only marginal compared to the variation in the lattice parameter 'c' and does not show a linear variation with the change in composition.

TGA-DTA studies The TGA/DTA curves for pure ammonium dihydrogen phosphate, ($NH_4H_2PO_4$) are presented in figure 2a. The DTA curve shows an endothermic peak at $205 \text{ }^\circ\text{C}$ for the pure ADP. This endothermic peak corresponds to the decomposition temperature of the crystal. The detailed data for all the crystals are shown in the table 3. $NH_4H_2PO_4$ is reported to melt at $190 \text{ }^\circ\text{C}$ and form an acidic phosphate liquid [21]. However, during the present investigation, the TGA curve exhibited negligible weight loss in the region $25 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ as shown in the figure 2a. The strong endothermic peak in DTA at $200 \text{ }^\circ\text{C}$ with the associated shoulders indicates decomposition in accordance with the following equation [22].



Equation (2) indicated a total weight loss of 38.3% and it explained well the weight loss observed in the pure ADP sample until the 580 °C – 590 °C TGA shoulder. These losses are due to dissociation of the substance, evaporation of ammonia and water respectively. Above 690 °C, P_2O_5 already formed starts evaporating, bringing the total weight loss in pure ADP to around 98%.

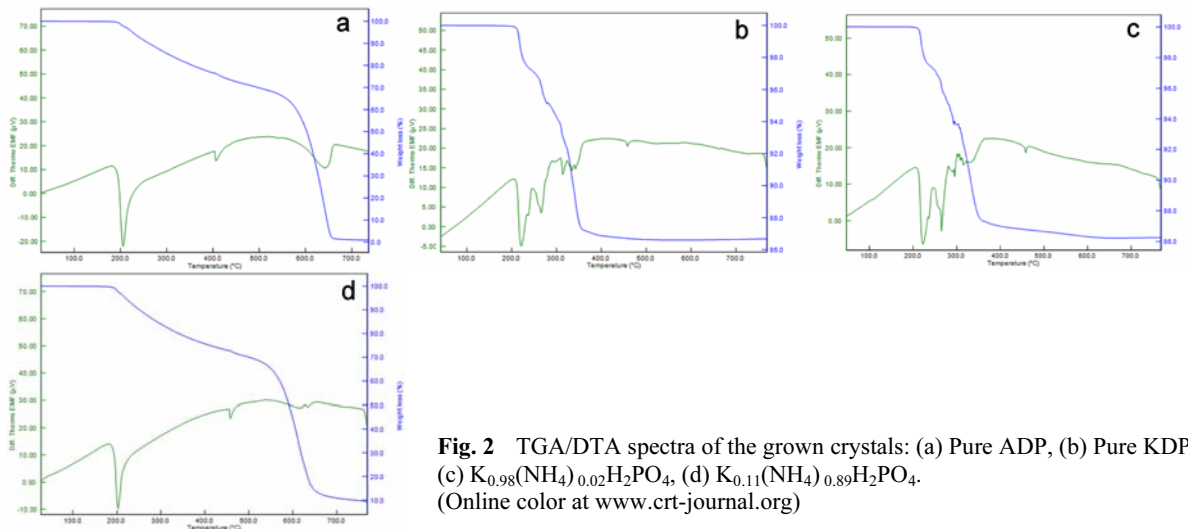


Fig. 2 TGA/DTA spectra of the grown crystals: (a) Pure ADP, (b) Pure KDP, (c) $K_{0.98}(NH_4)_{0.02}H_2PO_4$, (d) $K_{0.11}(NH_4)_{0.89}H_2PO_4$. (Online color at www.crt-journal.org)

Table 2 The observed lattice parameters of $K_{1-x}(NH_4)_xH_2PO_4$ at room temperature.

Ammonium x	a (Å)	c (Å)
1.00	7.511	7.562
0.96	7.489	7.548
0.90	7.486	7.524
0.89	7.480	7.521
0.09	7.478	7.080
0.06	7.476	7.051
0.02	7.470	7.023
0.00	7.446	6.980

Table 3 Thermal analysis data of the grown crystals.

Crystal	Endothermic peak (°C)
Pure ADP	205
Pure KDP	221 and 265
$K_{0.98}(NH_4)_{0.02}H_2PO_4$	222 and 264
$K_{0.11}(NH_4)_{0.89}H_2PO_4$	202

In figure 2b, the TGA and DTA curves of pure potassium dihydrogen phosphate, (KH_2PO_4) are presented. The peaks in the DSC curve below 200 °C have previously been identified as due to a phase transition involving the onset of disordered hindered rotation of H_2PO_4 groups around all three axes [23]. It is also observed that at higher temperatures, approximately above 200 °C, the DTA curve bends downwards indicating thermal decomposition of KDP as previously reported earlier [24]. No mass loss could be observed below 200 °C and the TG analysis shows that between 200 °C and 360 °C, there is an endothermic weight loss of 13%. This indicates the loss on dehydration of one water molecule, which is strongly bounded for every KPO_3 unit. The strong endothermic peaks in DTA at 221 °C and 265 °C with the associated shoulders indicate the removal of one water molecule for every KPO_3 unit. Powder X-ray diffraction analysis identified the end product as potassium polyphosphate.



Figures 2c and d show TG/DTA curves for the mixed crystals of $K_{1-x}(NH_4)_xH_2PO_4$ with concentration ($x=0.02, 0.89$). For $K_{0.98}(NH_4)_{0.02}H_2PO_4$, weight loss takes place in the temperature range from 220 °C to 360 °C and the

weight remains constant beyond that temperature. It loses one water molecule in the expected temperature range 220 °C to 350 °C as indicated by the sharp endothermic peaks in DTA at 222 °C and 264 °C respectively. Beyond 350 °C, it starts losing ammonia and the weight change is complete at 360 °C.

For the mixed crystal $K_{0.11}(NH_4)_{0.89}H_2PO_4$, weight loss takes place in the temperature ranging from 200 °C to 650 °C and then the weight remains practically constant. It loses one water molecule that is strongly bonded at the expected temperature range 220 °C to 350 °C and then dissociation of NH_3 takes place continuously beyond that temperature range.

From the TG curves of pure ADP and KDP, it is observed that they lose 98% and 13% of weights respectively. Theoretical calculation was also made on the basis of weight loss expected as per equations (2) and (3). For crystal $K_{0.98}(NH_4)_{0.02}H_2PO_4$, the weight loss observed from the TGA graph in the temperature range 200 °C to 400 °C is 13% where as the theoretically calculated value is 13.18%. For the crystal $K_{0.11}(NH_4)_{0.89}H_2PO_4$, the weight loss observed from the TGA graph in the temperature range 200 °C to 500 °C is 30% where as the theoretically calculated value is 29%.

4 Conclusion

Pure ADP, KDP and mixed crystals of $K_{1-x}(NH_4)_xH_2PO_4$ have been grown by slow evaporation from the supersaturated solution at an ambient temperature 27 °C. The present investigation has revealed that the induction period for the nucleation of ADP single crystals is larger than that for KDP single crystals. Further, it has been confirmed that the induction period is higher for mixed crystals than for the individual compounds and decreases as the concentration of KDP increases. XRD study shows that the incorporation of small amounts of the second component modifies the lattice parameters, the variation being non-linear with the change in composition. TGA/DTA studies indicate that total weight loss due to the escape of all gaseous species calculated from the reactions match with the observed total weight loss. It is observed that the thermal dehydration in ADP, KDP and mixed crystals is associated with decomposition and an increase in NH_4 concentration decreases the decomposition temperature.

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