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Growth and morphology of mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals

Prakasha Shenoy, Kasturi V. Bangera*, G.K. Shivakumar

Department of Physics, National Institute of Technology, Surathkal, Srinivasnagar–575 025, Mangalore, Karnataka, India

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ABSTRACT

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 grown by slow evaporation from the supersaturated solution at an ambient temperature $26 \pm 1\,^{\circ}C$ for ammonium concentration x in the range $0.0 \leq x \leq 1.0$. The morphology changes from tetragonal prism to needles when the concentration of either of the components approaches that of the other. Induction periods were measured for various compositions of mixed crystals of ADP and KDP by the direct vision method. Crystal compositions were determined by flame atomic absorption spectroscopy and also by chemical analysis. Results of the X-ray analysis of the grown crystals are also reported. Maximum size of the grown mixed crystal was around $16 \times 10 \times 4\,mm^3$.

1. Introduction

Nowadays much interest has been focused on phosphates, arsenates, sulphates and selenates. Among these solids, compounds of MH_2XO_4 (M = K, Rb, Cs, NH_4; X = P or As) of the KDP family have received greater attention from researchers, due to their structural and physical properties [1,2]. It is known that many crystals with hydrogen bonds undergo high temperature phase transitions, in addition to the low temperature ferroelectric or anti ferroelectric phase transitions [3–7].

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 [8,9]. 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 as monochromators for X-ray fluorescence analysis [10–12].

Ammonium dihydrogen orthophosphate, $NH_4H_2PO_4$ (abbreviated as ADP), belongs to scalenohedral class of tetragonal crystal system. It has the tetra molecular unit cell having the dimensions [13] given as $a = b = 7.510$ Å and $c = 7.564$ Å. ADP is soluble in water and its solubility at 30 °C is 46.4 parts by weight per 100 parts by weight of water [14]. Potassium dihydrogen phosphate, KH_2PO_4 (abbreviated as KDP), belongs to scalenohedral (12-sided polyhedron) class of tetragonal system with the tetra molecular unit cell having the dimensions [13] given as $a = b = 7.448$ Å and $c = 6.977$ Å. KDP is soluble in water and its solubility at 30 °C is 28.0 parts by weight per 100 parts by weight of water [14].

Nucleation process is the first and most important phenomenon in liquid–solid phase transition. Nagalingam et al. [15,16] have reported nucleation studies in supersaturated aqueous ADP solutions with and without some added impurities (doping concentration, 100 ppm only). In the case of ADP, it was found [17–19], that the nucleation parameters like interfacial tension of the solid relative to its solution, energy of formation of a critical nucleus and radius of the nucleus increased with increase in impurity concentration. Pramila Rachelin and Mahadevan [17] attempted to explain this result qualitatively by considering the density values of ADP and impurities. Nucleation studies on aqueous KDP solutions with and without some added impurities (impurity concentration in the range 100–500 ppm) have already been reported [20–22].

The ferroelectric and anti ferroelectric properties are among the most spectacular manifestations of co-operative phenomena in condensed materials. ADP and KDP are well-known antiferroelectric and ferroelectric crystals, respectively, belonging to the KDP family. Ferroelectric phase transition in KDP occurs at −150 °C and anti ferroelectric phase transition in ADP occurs at −125 °C [23]. The study of the mixed crystals of KDP and ADP has attracted considerable attention in recent years due to their potential applications in the area of quantum electronics and optoelectronics. Because of ferroelectric and antiferroelectric properties of these crystals and potential applications, the studies on growth, structural, chemical, optical and electrical properties are important. 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

* Corresponding author.
E-mail address: crystalnitk@gmail.com (K.V. Bangera).

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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)	Morphology
1:0	1.0	20	Transparent, elongated, tetragonal prism
9:1	0.96	45	Transparent, elongated, tetragonal prism
8:1	0.92	43	Transparent, elongated, tetragonal prism
7:1	0.90	42	Transparent, elongated, tetragonal prism
6:1	0.89	42	Transparent, elongated, tetragonal prism
5:1	0.85	40	Transparent, elongated, tetragonal prism
4:1	0.80	38	Opaque, tetragonal prism
3:1	0.74	35	Multiple twinning
2:1	0.60	30	Dendrites
1:1	0.33	27	Spherulitic
1:2	0.15	20	Dendrites
1:3	0.10	15	Opaque, tetragonal prism
1:4	0.09	13	Transparent, elongated, tetragonal prism
1:5	0.06	10	Transparent, elongated, tetragonal prism
1:6	0.02	08	Transparent, elongated, tetragonal prism
1:7	<0.02	06	Transparent, elongated, tetragonal prism
1:8	<0.02	06	Transparent, elongated, tetragonal prism
0:1	0.00	05	Transparent, elongated, tetragonal prism

crystals from all compositions [24,25]. 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 [26,27]. Mixed crystals of ADP and KDP have been grown on pure ADP and KDP seeds by slow cooling method by determining the mutual solubility in water [28]. Mixed crystals of ADP and KDP have been grown with 19 different compositions by restricted evaporation of solvent at 308 K [29]. Nevertheless, up to now, good single crystals of $K_{1-x}(NH_4)_xH_2PO_4$ with perfect quality are still difficult to prepare, especially, for the crystals with intermediate concentration. In the present study we have succeeded to grow bigger size of mixed crystals of ADP-KDP with wide variations of '*x*' by isothermal evaporation of mixed supersaturated solution at room temperature.

2. Experimental details

2.1. Crystal growth

ADP and KDP powders of analytical reagent grade 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. It was found that the molar concentration of ADP in the saturated solution is approximately two times that of KDP, which influences the solution stability and consequently the crystal growth [27]. 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. The filtered saturated solutions of KDP and ADP were mixed together at different selected volume ratio of ADP:KDP as 9:1 to 1:9 and allowed for slow evaporation at the lab temperature of 27 °C. Super saturation was attained by ambient evaporation.

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.

2.2. Determination of crystal composition

Transparent crystals were obtained from KDP and ADP rich solutions whereas 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).

2.3. 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 Kα radiation.

3. Results and discussion

Several nucleation runs were carried out under controlled and unstirred conditions and reproducible results on induction period with accuracy of ±2.5% were obtained. Transparent crystals were obtained from KDP and ADP rich solutions whereas needle type crystals were harvested from the middle regions as shown in Table 1. In the mixed crystals of $K_{1-x}(NH_4)_xH_2PO_4$, the ammonium content *x* of the mixed crystals could be controlled by varying the ratio of the volumes of the precursor solutions.

Appearance of the smallest crystallite was considered as the time of nucleation. It may be mentioned that the formation of a stable nuclei is not observable even by microscopy as they consist of only a few molecules. However once the stable cluster is formed, the growth into a crystallite of observable size is quite fast. Hence it is assumed that the error, common to all observations, is small compared to the induction periods which extend to several days. 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. This is in agreement with the fact that the solubility of ADP in water is much higher than that of KDP at an ambient temperature. The degree of super saturation required for nucleation was achieved in lesser time for KDP than ADP during the isothermal evaporation of the solvent. Further, addition of KDP to ADP or vice versa results in an increase in the induction period. Xiue [27] have reported the growth of KDP, ADP and KADP crystals and have observed the

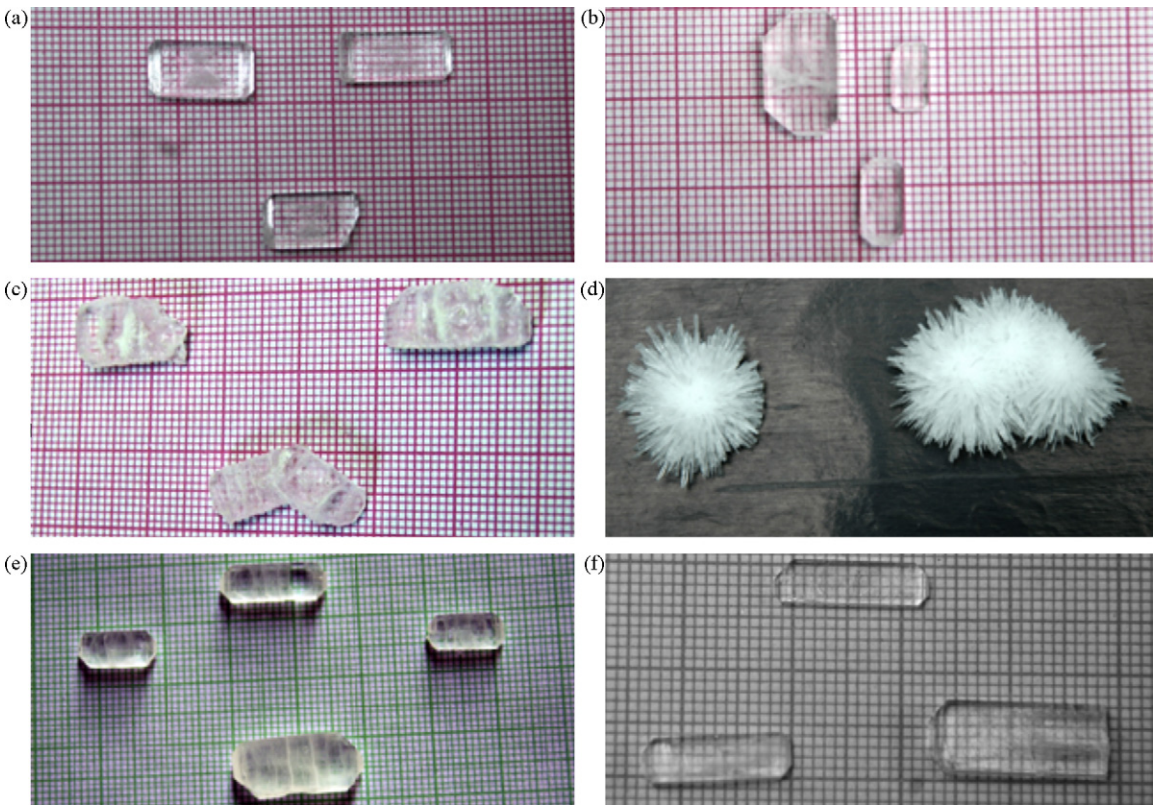

Fig. 1. Some of as-grown mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals: (each small division corresponds to 1 mm.) (a) $x = 0.96$; (b) $x = 0.89$; (c) $x = 0.80$; (d) $x = 0.33$; (e) $x = 0.09$; (f) $x = 0.02$.

induction period for the crystallization of KDP to be longer than that for ADP. It is also reported that the solubility, i.e., cluster concentration directly influences the stability of the growth solution and consequently the crystal growth rate [27]. This is contrary to our observation that the induction period for the crystallization of ADP is longer than that for KDP. The discrepancy may be traced to the fact that degree of super saturation that can be sustained in a solution prior to crystallization decides the induction period. However, once the crystallization begins, further growth rate is controlled by the solubility of the material.

The optical transparency of the crystals with composition $0 < x < 0.09$ and $0.85 < x < 1$ were comparable with that of pure ADP and KDP single crystals. 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 photograph (Fig. 1) shows some of the as-grown crystals of $K_{1-x}(NH_4)_xH_2PO_4$. The size of the biggest crystal was found to be $16 \times 10 \times 4\,mm^3$. Transparent crystals of an appropriate size, habit and fine diffraction spots 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. The crystals of different compositions $(0 \leq x \leq 1)$ were grown by suitably selecting the volume ratio of saturated solutions of ADP and KDP in the growth medium. However, the volume ratio of the two solutions did not entirely determine the combination of the grown crystals. For example, increase of ADP solution in the growth medium increased the incorporation of ammonium in the given crystal only up to an x value of 0.09 beyond which the growth was spherulitic. Similarly, increase in the KDP content gave single crystals of mixed orthophosphate down to an x value of 0.85. Similar results have been reported by Sen Guptha et al. [30] 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., $0.25 \leq x \leq 0.75$.

The change in the lattice parameters with composition was studied by the X-ray powder diffractometry using Rigaku Mini-Flex (30 kV, 15 mA) X-ray diffractometer with nickel filtered Cu Kα radiation (Table 2). 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*'. The change in parameter '*c*' is also small up to '*x*' value of 0.6 and increases abruptly for ammonium rich crystals (Fig. 2). Difference in incorporation of ADP and KDP into the crystal has been attributed to the difference in the effective ionic radius of NH_4^+ and K^+ ions [31]. The effective ionic radii of NH_4^+ and K^+ ions are 1.48 and 1.33 Å respectively. Since ADP and KDP have the same structure, replacement of K^+ ion by NH_4^+ should lead to an increase in the lattice parameters. Structural studies have shown O–H···O bonds in KDP lie almost in the *X*–*Y* plane [32] whereas in ADP, O–H···O bonds are inclined to the *X*–*Y* plane [33]. It has been observed that the angle between P–O and O–H···O in KDP is 113°15′ and that in ADP is 116°42′. This difference gives rise to the *c*-direction packing with a

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
0.90	7.486	7.524
0.80	7.480	7.521
0.60	7.455	7.202
0.33	7.450	7.092
0.15	7.450	7.031
0.00	7.446	6.980

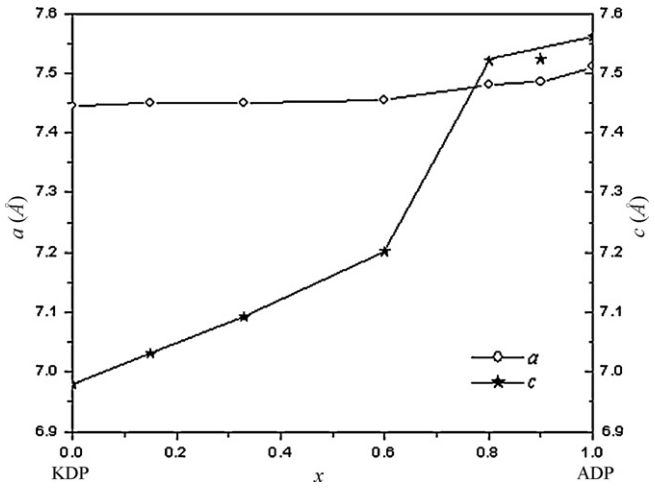

Fig. 2. Variation of lattice parameters with composition *x* for mixed crystals.

consequent elongation. Dongli and Dongfeng have reported expansion of unit cell with increasing ammonium content in the crystals [26]. There are a few reports on the chemical bond strength and natural morphology [1,2,24,25,27].

4. Conclusions

Induction period measurements were made for mixed crystals of potassium ammonium dihydrogen phosphate, $K_{1-x}(NH_4)_x H_2PO_4$ for various compositions ($0 \le x \le 1$). It is observed that the induction period is higher for mixed crystals than for the individual compounds and decreases as the concentration of KDP increases. Compositional dependence reveals that the morphology changes from tetragonal prism to spherulitic needles when the concentration of either of the components approaches that of the other. Transparent single crystals could be obtained for the mixed system $K_{1-x}(NH_4)_x H_2PO_4$ for *x* varying from 0 to 0.09 and 0.89 to 1. XRD study shows that the lattice parameter '*a*' of the mixed crystals gets modified marginally with the incorporation of small amounts of the second component, the variation being non-linear with the change in composition.

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