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Nucleation studies and crystal growth of $(NH_4)H_2PO_4$ doped with thiourea in supersaturated aqueous solutions

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Abstract

The metastable zone width studies were carried out for various temperatures for supersaturated aqueous solutions of ammonium dihydrogen orthophosphate added with 1 mol% of thiourea. The metastable zone width is increased with the addition of thiourea. The induction period was studied and various critical nucleation parameters were calculated based on the classical theory for homogeneous crystal nucleation. The induction period is increased with the increase of thiourea addition. The critical nucleation parameters vary with increase in doping concentration. The results are reported and discussed. The crystals were grown for various doping concentrations of thiourea and the morphological changes are discussed. © 2002 Published by Elsevier Science B.V.

Keywords: Solution growth; Metastable zone width; Induction period; Nucleation parameters; ADP; Thiourea

1. Introduction

The isomorphous salt ammonium dihydrogen orthophosphate (ADP) and potassium dihydrogen orthophosphate (KDP) are two of the oldest crystals grown in large size for applications [1–3]. ADP crystal is of more interest because of its piezo-electric property [4]. This crystal has got non-linear optical and electro-optical properties and also it is widely used in X-ray monochromators [3]. ADP belongs to scalenohedral class of tetragonal crystal system. It has the tetramolecular unit cell, having the unit cell parameters, $a = b = 7.510$ Å and $c = 7.564$ Å [5]. ADP crystal has been grown from solution by low temperature solution growth.

Metastable zone width is an essential parameter for the growth of good crystals from solution, since it is the direct measure of the stability of the solution in its supersaturated region [6]. The control of crystallization habit is clearly linked to the additives added to the system and the internal parameters like pH.

In the present work, metastable zone width of the aqueous solution of ADP saturated at different temperatures was determined by nucleation method with and without small quantity (1 mol%) of the well-known organic non-linear optical material thiourea. Thiourea belongs to the orthorhombic crystal system.

An attempt has been made in the present study to determine the nucleation parameters of pure ADP crystals and also to investigate the effect of organic substance thiourea as added additive (additive concentration is 1–5 mol%) on the nucleation of these crystals. Induction period was measured for various supersaturated solutions by direct vision method. Various critical nucleation parameters have been calculated and the effect of supersaturation and concentration on doping on them is also reported and discussed. The optical transmission and microhardness studies are carried out.

2. Nucleation parameters

Nucleation process is the initial and most important phenomenon in liquid–solid phase transition. Based on the classical theory for homogeneous crystal nucleation, certain critical nucleation parameters like interfacial tension (σ) of the solid relative to its solution, free energy of formation (ΔG) of the critical nucleus and radius of the nucleus (r) in equilibrium with its solution can be calculated using the induction period which can be measured.

The free energy change associated with the process of homogenous nucleation may be considered as follows.

The overall excess free energy (ΔG) between an embryo and solute in the solution is equal to the sum of the surface excess free energy (ΔG_s) and the volume excess free energy

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Nomenclature

A	factor depends on the surface energy
D	average diagonal length of the indentation
k	Boltzmann constant
K	constant
N	Avogadro's number
P	applied load
R	universal gas constant
S	supersaturation
T	absolute temperature
U_1	energy of activation for the molar transition from phase I (solution) to phase II (crystal)
v	volume per molecule in solid phase
V	Vicker's microhardness number

Greek letters

μ_d	chemical potential of nucleus of dimension d
μ_∞	chemical potential of nucleus of infinite size
σ_1	surface free energy

(ΔG_v) [7] given by

$$\Delta G = \Delta G_s + \Delta G_v$$

where ΔG_v is given by

$$\Delta G_v = \left(\frac{kT}{v}\right) \ln(S) \tag{1}$$

According to Gibbs formation in terms of surface thermodynamics, the end and lateral surface of a cylinder will have different surface energies. We also assume here that there are two kinds of surfaces, viz., curved and flat and they will have different surface energies for flat and curved. Also, in order to reduce complexity, we assume same surface energy for all the surfaces in the tetragonal and orthorhombic cases.

The basic relationship of equilibrium between solid and its solution which connects the solubility: expressed as the chemical potential to the particle size is the Thomson equation

$$\mu_d - \mu_\infty = \frac{2\sigma_1 v}{d} \tag{2}$$

When the crystal attains a size of dimension d, surface free energy will be in equilibrium with the solution and under these conditions, the chemical potentials of the two co-existing phases are equal. The free energy of formation of the nucleus of the new phase in equilibrium with its solution may be expressed as

$$\Delta G = \frac{A}{\mu_d - \mu_\infty} \tag{3}$$

The change in chemical potential is given by [8]

$$\mu_d - \mu_\infty = kT \ln(S) \tag{4}$$

The frequency of formation of critical nuclei from their respective supersaturated solutions have been given as [9]

$$J = K \exp\left(\frac{-U_1}{kT}\right) \exp\left(\frac{\Delta G}{kT}\right) \tag{5}$$

After we prepared supersaturated solutions, there is often a period where no phase change can be observed, the induction period: then minute nuclei appear and grow into visible crystals. For a given volume of solution, based on the probabilistic approach [7], the frequency of formation of nuclei is inversely proportional to the induction period (τ):

$$\ln(\tau) = \ln(K^{-1}) + \frac{U_1}{kT} + \frac{\Delta G}{kT} \tag{6}$$

For an isotherm, the term U_1/kT is a constant and the equation can be written as

$$\ln(\tau) = B + \frac{\Delta G}{kT} \tag{7}$$

Applying Eqs. (1)–(7), we get

$$\ln(\tau) = B + \frac{A}{k^3 T^3 \ln^2(S)} = B + \frac{AN^3}{R^3 T^3 \ln^2(S)}$$

The above equation suggests a straight line for $\ln(\tau)$ against $1/\ln^2(S)$ with the slope given by

$$m = \frac{AN^3}{R^3 T^3}$$

Consider the nucleus to be cylindrical in shape. The overall excess free energy of a cylindrical nucleus of radius r_c and height h can be written as

$$\Delta G = 2\pi r_c^2 \sigma_D + 2\pi r_c h\sigma + \pi_c^2 h \Delta G$$

Therefore, for the critical nucleus

$$r_c = \frac{2\sigma_v N}{RT \ln(S)}$$

$$h = \frac{4\sigma_0 v N}{RT \ln(S)}$$

$$\sigma = \frac{RT}{\sqrt{\pi}} \left[\frac{m}{4v^2 N^3}\right]^{1/3}$$

The number of molecules in critical nucleus is

$$n_c = \frac{\pi r_c^2 h}{v}$$

Using the experimentally observed m and v values various nucleation parameters can be calculated.

3. Experimental

The solubility diagrams of ADP solution at different temperatures were obtained by using the relation by Mullin and Amaravivadhana [10] and also it was experimentally verified by thermogravimetric analysis:

$$c = (16.73 \pm 0.35) + [(0.484 \pm 0.012)t \pm 0.18]$$

3.1. Metastable zone width studies

Four hundred milliliters of ADP solution saturated at 30 °C was prepared in accordance with the solubility diagram. Then the solution was taken in two beakers each containing 200 ml. In one beaker, 1 mol% of thiourea was added. The solutions were filtered using a borosil filter paper. These beakers were loaded in a constant temperature bath with cryostat facility. The bath is capable of controlling the temperature with an accuracy of ±0.01 °C. The solutions were stirred continuously for 6 h for stabilization. Then, the temperature of the bath was reduced at the rate of 4 °C h^{-1}, while stirring the solution continuously. The temperature at which the first speck of the particle has been observed corresponds to the width of metastable zone. The experiment was repeated for solutions saturated at temperatures 30, 35, 40, 45 and 50 °C. The metastable zone width for different saturation temperatures for pure and thiourea added solutions are shown in Fig. 1. It is seen from the figure that the zone width decreases as the temperature increases in the case of both pure and thiourea added solutions. Also, it was observed during the experiment that the number of tiny crystals formed by spontaneous nucleation was appreciably reduced in the case of thiourea added solution compared to the pure one. There was no remarkable change in pH with the addition of thiourea (1–5 mol%).

3.2. Induction period measurements

Experiments were performed at selected degrees of supersaturation (S), viz., 1.325, 1.350, 1.375 at the temperature of 35 °C using the conventional method [11]. Several nucleation runs were carried out under controlled and stirred conditions. Reproducible results with the accuracy of ±3% were obtained. Results are shown in Fig. 2. Various critical nucleation parameters were calculated from

$$\sigma = RT\left[\frac{3m}{16\pi V^2 N}\right]^{1/3}, \qquad \Delta G = \frac{RTm}{\ln^2(c/c_0)},$$

$$r = \frac{2\sigma V}{RT\ln(c/c_0)}$$

The values of r, σ, ΔG are plotted in Figs. 3–5.

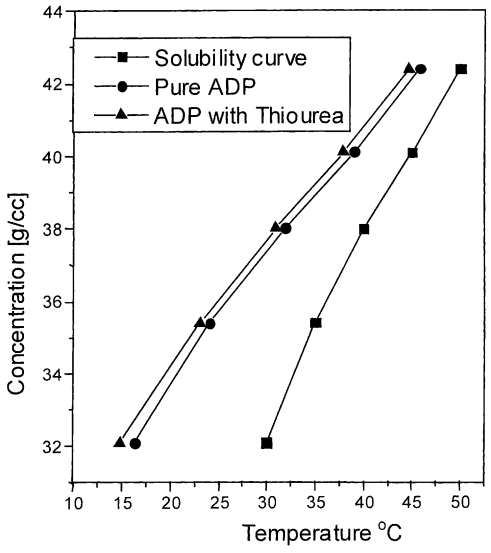

Fig. 1. Metastable zone width for different saturation temperatures for pure and thiourea added ADP.

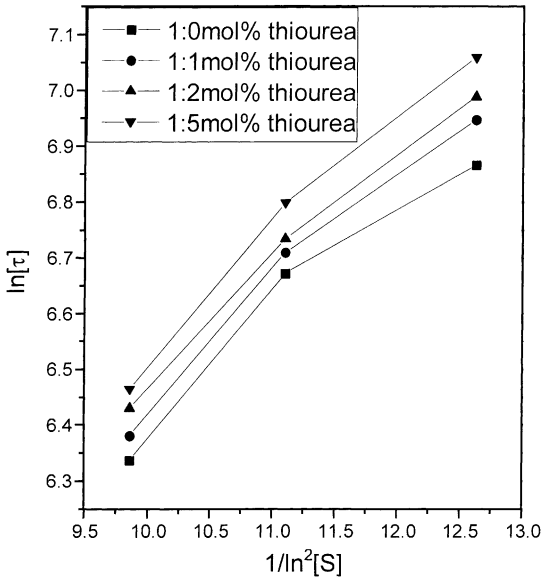

Fig. 2. Values of induction period against supersaturation.

3.3. Optical transmission studies

Optical transmission spectra were recorded for the samples obtained from the crystals of pure, 2 and 5 mol%

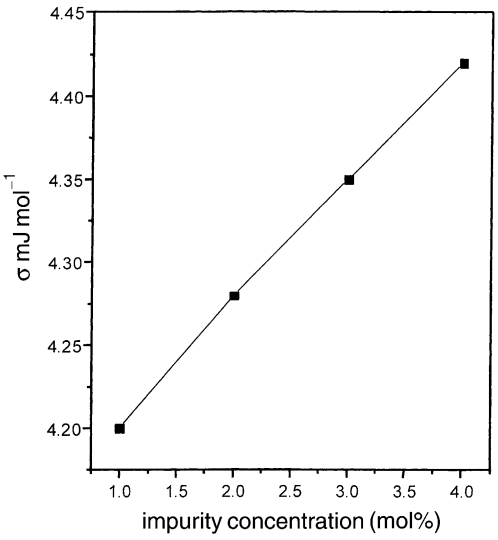

Fig. 3. Values of interfacial tension against impurity concentration.

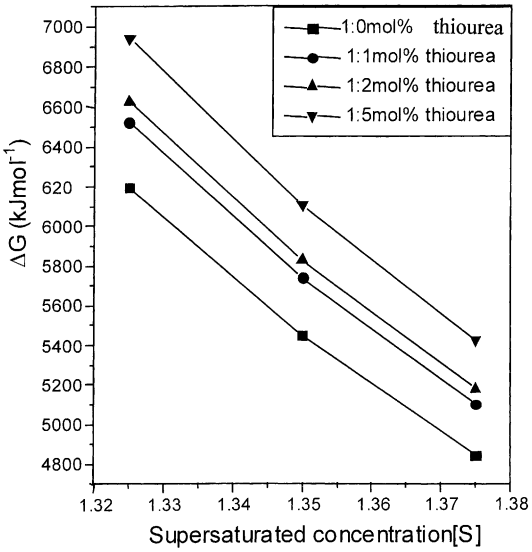

Fig. 4. Values of energy of formation against supersaturation.

thiourea added ADP crystals grown by slow evaporation method. The spectra were recorded in the wavelength region from 200 to 1700 nm using Varicon Cary 2300 spectrophotometer. C-cut crystal plates with 2 mm thickness were used for this study. The recorded spectra are shown in Fig. 8.

3.4. Microhardness studies

Microhardness tests were carried out on (1 0 0) planes of the crystals grown from pure ADP solution, and 2 and 5 mol% thiourea added ADP solution using a Leitz Wetzler hardness tester fitted with a Vicker's diamond pyramidal indenter. To evaluate the Vicker's hardness number, several indentations were made on the (1 0 0) face of the crystal. The distance between any two indentations was maintained to be greater than five times the diagonal length in order to avoid any mutual influence of the indentations. The diagonal length of the indentations was measured using a micrometer eyepiece. The Vicker's microhardness number was then calculated using the expression

$$H = 1.8544\left(\frac{P}{D^2}\right)\ (\mathrm{kg\,mm^{-2}}) \tag{8}$$

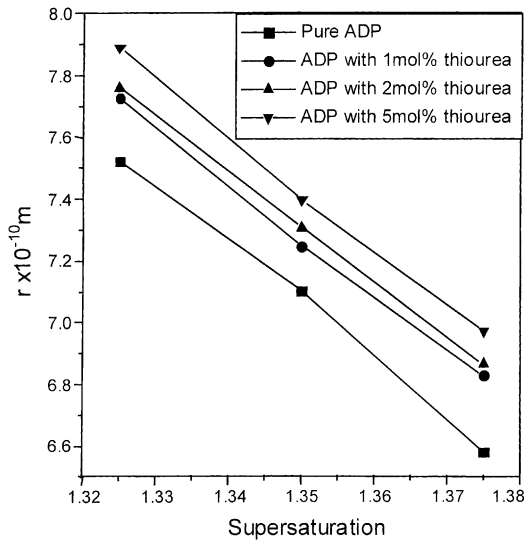

Fig. 5. Values of critical nucleus radius against supersaturation.

4. Experimental results: analysis and discussion

Results of metastable zone measurements, induction period measurements and calculated values of nucleation parameters are presented in Figs. 1–5. It can be seen in thiourea added system that the induction period increases with the increase in thiourea concentration. Plots of $\ln(\tau)$

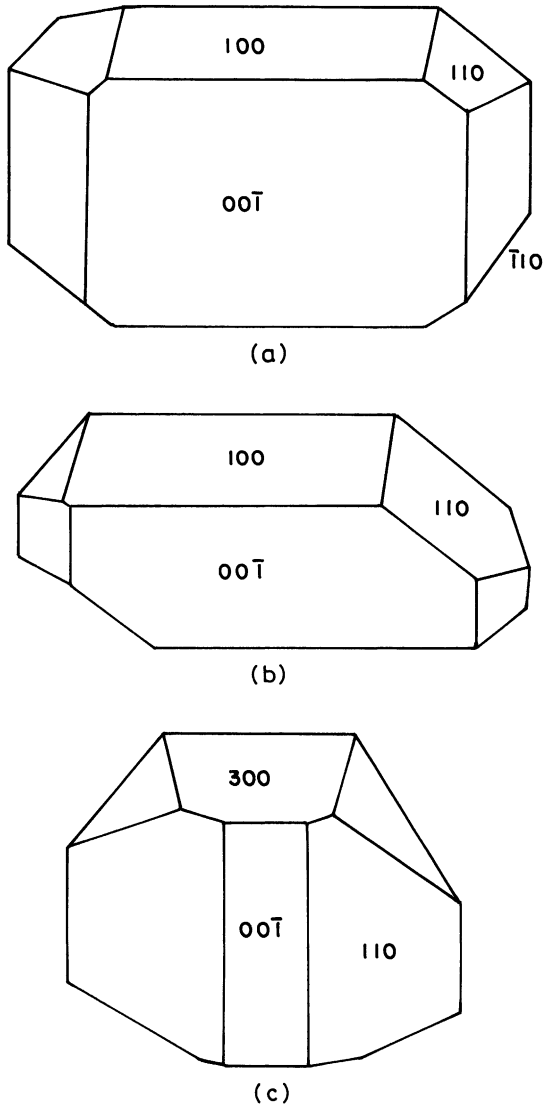

Fig. 6. Structural morphology of crystals grown by slow evaporation method: (a) pure ADP; (b) ADP with 2 mol% thiourea; (c) ADP with 5 mol% thiourea.

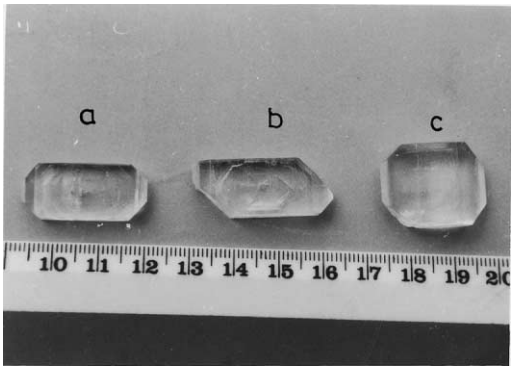

Fig. 7. Crystals grown by slow evaporation method: (a) pure ADP; (b) ADP with 2 mol% thiourea; (c) ADP with 5 mol% thiourea.

against $1/\ln^2(S)$ are nearly linear. The value of τ decreases and hence the nucleation rate increases as the supersaturated concentration of the aqueous solution is increased. This is similar to the results obtained by previous workers for their systems [12–14]. Considering the principles of homogeneous and heterogeneous nucleation theories, the free energy of formation of a nucleus under heterogeneous nucleation is less than that of homogeneous condition [9].

In order to reduce the effect of heterogeneous nucleation on the nucleation parameters, the results were obtained using the slopes determined in the linear region of the line plots of $\ln(\tau)$ against $\ln^2(S)$. It can be noticed that the induction period increases with the increase in doping concentration (Fig. 2). The thiourea arrests the behavior of impurities in the system. The presence of soluble impurities can also affect the induction period but it is impossible to predict the effect [9]. The values of r and ΔG decrease when the supersaturation is increased.

It is found that the addition of thiourea slightly enhances the metastable zone width (Fig. 1). Compared with another organic material EDTA the enhancement of metastable zone width is low [15,16]. Using EDTA, the enhancement of metastable zone for ADP is 5.2 °C, saturated at 30 °C [16] and using urea as the additive, enhancement is 3.7 °C, saturated at 30 °C [17]. It is also found from the graph that the zone width decreases with the increase in temperature. It is observed that the number of tiny crystals formed by the spontaneous nucleation was very low compared with the pure system. This is because thiourea suppresses the activities of heterogeneous nucleation.

The growth rate of a crystal mainly depends on the crystal growth parameters such as temperature, the degree of supersaturation of the solution, pH of the solution, concentration of the impurities in the solution, nature of the dopants, etc. Using thiourea as a dopant, increase in growth rate of the crystal along *a*-axis and *b*-axis has been achieved. The structural morphology of crystals grown by slow evaporation method at different mole percents of thiourea doped and pure ADP are shown in Fig. 6. In pure ADP crystal, it was observed that the growth rate along *c*-axis was higher, whereas it was much lower along *a*-axis and *b*-axis. In the case of 2 mol% thiourea doped system the growth rate along *a*-axis and *b*-axis was found to be increased. For the doping concentration of 5 mol% of thiourea, the growth rate along *a*-, *b*- and *c*-axes were nearly the same. It is clearly seen that the increase in doping concentration of thiourea increases

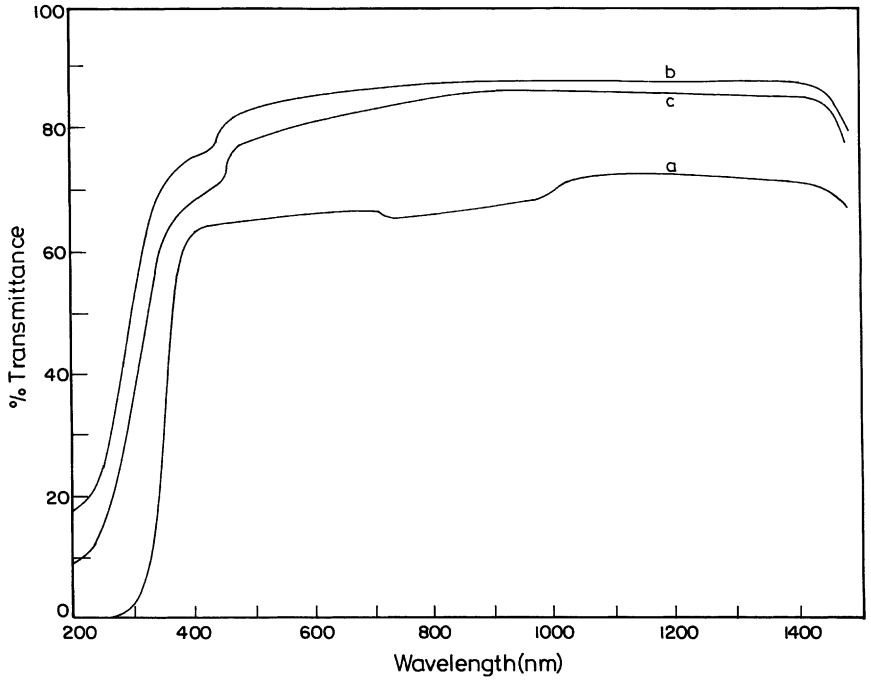

Fig. 8. UV–VIS spectra for: (a) pure ADP; (b) ADP with 2 mol% thiourea; (c) ADP with 5 mol% thiourea.

Table 1
Vicker's microhardness number for pure and thiourea added crystals

System	Vicker's hardness number
Pure ADP	77.17
ADP with thiourea (5 mol%)	75.13
ADP with thiourea (2 mol%)	75.16

the growth rate along *a*- and *b*-axes. This addition of 5 mol% thiourea yields good quality crystal and the grown crystal is shown in Fig. 7.

The reported value of the optical transparency for ADP is from 184 to 1500 nm [18]. The UV–VIS spectra recorded for pure and thiourea doped ADP crystals (unpolished and without any antireflection coating) is shown in Fig. 8. It can be seen that the optical transmission efficiency is very good. It is also clear from Fig. 8 that the percentage of transmission efficiency enhanced from 60 to 80% on 2 mol% thiourea addition, which reduced marginally on further addition of thiourea to 5 mol%.

The hardness value was found to decrease with the applied load for the thiourea added systems. This may be the result of loosely packed lattice with reduced bond energy due to the introduction of thiourea into the crystal. We do not have explicit experimental evidence such as X-ray measurements to explain this fact. Vicker's hardness number measured for pure ADP and thiourea added systems are shown in Table 1.

5. Conclusion

The fundamental growth parameters have been estimated for pure and thiourea added ADP crystal for growth by low temperature solution. The experimental results show that the metastable zone width, induction period increases with increase of thiourea doping concentration. From the grown crystals, it is observed that thiourea increases the [0 0 1] direction and suppresses the [1 0 0] direction growth. The critical nucleation parameters are also calculated. The UV–VIS spectra analysis revealed that the transmission efficiency improves considerably for lower concentration of thiourea. The microhardness measurement studies illustrate a decrease in hardness with the addition of thiourea.

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