

THE EFFECT OF pH GROWTH OF
AMMONIUM DIHYDROGEN PHOSPHATE CRYSTALS

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Ammonium dihydrogen phosphate crystals grown in solutions at different pH have different physical properties. This fact suggests that the pH effects the chemical composition of the crystals obtained. In order to explain the observed effect, it is postulated that H_3O^+ ions are incorporated into the crystal as an impurity. This conclusion is supported by the assumptions previously published in papers on the mechanism of a pH modification effect on ADP crystal growth.

1. Introduction

Ammonium dihydrogen phosphate (ADP) crystals grown from aqueous solution at different values of pH have been studied in several papers /1-3/. ADP crystallises in the tetragonal system (space group D_{2d}^{12}). The crystal habit comprises prismatic (100) and pyramidal (101) faces.

Pure supersaturated aqueous solutions of ADP have pH=3,5:3,8 /1,3/. Crystals grown from this solution are elongated in the [001] direction /1,3/. By increasing the pH of the growth solution to about 6,0 by the addition of NH_4OH , the growth rates of the {100} faces of ADP crystals are significantly increased so that the crystals with greater cross section normal to [001] are obtained /1,3/.

The effect of modification of a pH of the solution on ADP crystal growth has been previously explained in different ways:

1. Assuming /3/ that at pH = 3,8 there exist in the solution H_3O^+ ions that are hydrated as $H_3O^+ \cdot 3H_2O$ and absorbed in different manners on different crystal faces. In other words, the crystal growth rate in various directions is determined by the adsorption phenomenon.

The increase of the pH causes the increase of OH^- ions concentration which decreases the H_3O^+ ions equilibrium concentration, modifies the adsorption process and allows the crystal faces to grow faster.

2. Assuming /1/ that the increase of the pH effects the processes in the solution itself, ADP crystal growth rates in various directions are explained by the difference of heats of hydration of NH_4^+ and H_2PO_4^- ions.

By increasing the pH, i.e. OH^- ions concentration, H^+ ions concentration in the solution is decreased, and that contributes to the dissociation of H_2PO_4^- ions concentration, and effects ADP crystal growth rate in various directions. According to the authors /1/ the fact that ADP crystal solubility increases with the increase of pH is an argument contributing to this explanation.

3. Assuming that /1/ decrease of the pH causes formation of the complex



in the solution which effects the relation of the effective concentrations of NH_4^+ and H_2PO_4^- ions as well as the crystal growth rate. As a contribution to this explanation it is mentioned that by a decrease of the pH the increase of ADP solubility is obtained.

The aim of this paper was to show that in ADP crystal growth pH, plays a role in processes not only occurring in the solution and on the crystal surface, but also causes changes in the chemical composition of the crystal.

2. Experimental

Pure supersaturated solutions of ADP obtained by dissolving $\text{NH}_4\text{H}_2\text{PO}_4$ in deionized water have pH = 3,60. The pH of ADP solutions increases with the addition of NH_4OH , and decreases with the addition of H_3PO_4 . The experiments were done using ADP solutions with pH=2,00; 3,60; 4,00; 4,50; and 5,25. The values for pH of the solution were determined by means of K-200 and G 200B electrodes. During the crystal growth the pH of the solution remained constant.

ADP crystal samples were obtained by means of the Holden type crystallizer (4 l. in volume) in which ADP solution of an appropriate

pH at the starting temperature of 35°C was poured. Crystal seeds of pure ADP (5x4x4 mm³) were added to the solution, and the solution temperature lowered at a constant rate by means of a clock mechanism that turned the rotating magnet of the contact thermometer in the temperature interval of 25-40°C was determined for every value of pH by a gravimetric method. The temperature decrease of the solution was so adjusted that its relative supersaturation was $\sigma = 0,005$ for all samples. Mixing of the solution was performed by means of the seed holder which rotated in alternate directions in the solution. The mean linear velocity of the crystal through the solution was 4 cm/s. Crystal growth experiments lasted as long as 30 days.

3. Results

ADP crystals obtained at various values of pH show characteristic changes of the habit previously reported in /1,3/. The following investigations have been made in order to determine whether or not growth at different pH's results in crystals of different composition:

a. Measurement of dielectric permittivity ϵ and hence the Curie temperature. Plates normal to $[001]$ were cut from the crystals obtained. The electrodes were made by paste coating. The measurements were made by use of the measuring bridge RFT (DDR), Model 1511 at 800 Hz. Temperature regulation was done by means of the control system of the thermostat Prufherate-Werk (DDR), Model TT.

The results of measurement at pH = 2,0 and pH = 5,25 are given in fig. 1. The ordinates show ϵ in the relative scale reduced to the value of $\epsilon = 1$ at 173 K.

b. Determination of the magnetic susceptibility at ambient temperature was performed by application of the Faraday method. The electromagnet ALPHA (Systron-Donner, USA), Model M 6000 was used. Force measurement was performed by use of the Sartorius electronic balance (DBR), Model 4102.

The dependence of diamagnetic susceptibility on pH of the solution was determined. The results of the measurements are shown in fig. 2.

c. Investigation by the nuclear magnetic resonance method (NMR) using a High Resolution Nuclear Resonance Spectrometer, Bruker (DDR), Model SXP-100 (at 90 MHz). The measurements were made on

monocrystal samples at ambient temperature.

In fig. 3 are shown NMR spectra for two crystal samples obtained at pH = 2,0 and 5,25 with the magnetic field direction parallel to $[001]$.

4. Discussion

Investigation of the experimental results shown in figs. 1-3 shows that there exist clearly defined differences in physical properties of ADP crystal samples obtained at different pH:

- they have different Curie temperatures similar to ADP crystals doped with different concentrations of Tl^+ ions /4/;

- † they have different diamagnetic susceptibilities; similar to the susceptibility modification shown by the solid solution Inp-GaP /5/;

- they show different NMR spectra; the appearance of a number of peaks in NMR spectra indicates the presence of protons at different sites i.e. different hydrogen bonds in the crystal structure /6/.

The observed changes of physical properties of samples investigated suggest that the pH effects the chemical composition of ADP crystals. The analysis of papers on crystal growth problem shows that the influence of pH is best explained by the different role of H_3O^+ ions:

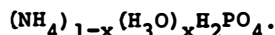
- in paper /3/ it is supposed that the adsorption processes related to the existence of this ion have the determining role;

- in paper /1/ it is supposed that the change of H_3O^+ ion concentration (i.e. H^+ ions) or the formation of hydronium complex is the most important; i.e. formulae (1) can be rewritten in the form $NH_4H_2PO_4 \cdot H_3OH_2PO_4$. It is quite possible that H_3O^+ ion can be incorporated into ADP crystal as an impurity: by changing the pH the concentration of H_3O^+ ions is changed as well as the probability of this ion incorporating as an impurity. Such assumptions can be explained by the fact that several acids form crystal monohydrates which are in fact hydronium compounds /7/. Specially interesting is the example of perchloric acid which is in fact hydronium compound H_3OC10_4 and is isomorphous with NH_4C10_4 /8/.

5. Conclusion

Investigation of physical properties of ADP crystals obtained at different values of pH in the interval of 2,0-5,25 suggests that the chemical composition of the crystal is a function of pH. The investigations done so far have shown that it is possible for H_3O^+ ions

to be incorporated into the crystal as an impurity. At present it is not possible to determine if the isomorphous replacement of NH_4^+ ions with H_3O^+ ions or some other mechanism of incorporation occurs. In case of the isomorphous replacement it would follow that ADP crystals obtained at different pH have the formulae



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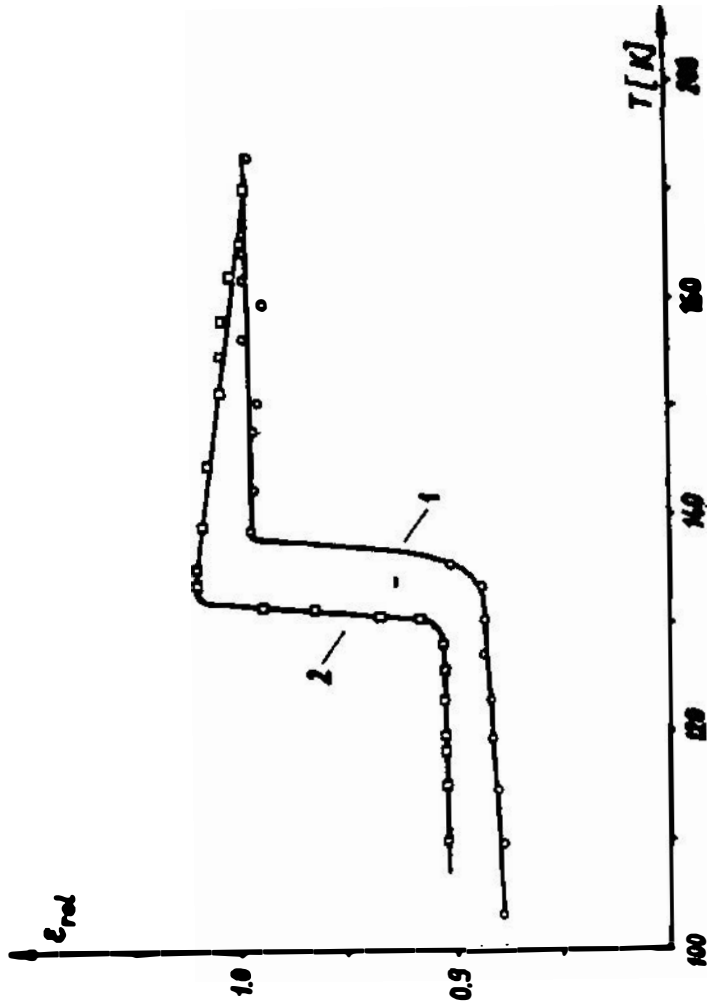


Fig. 1. The relative dielectric permittivity of ADP crystals ϵ_{rel} for the sample cuts normal to the $[001]$ direction (1 : pH = 5,25; 2 : pH = 2,0) Experimental data are reduced by putting $\epsilon_r = 1$ for $T = 173K$.

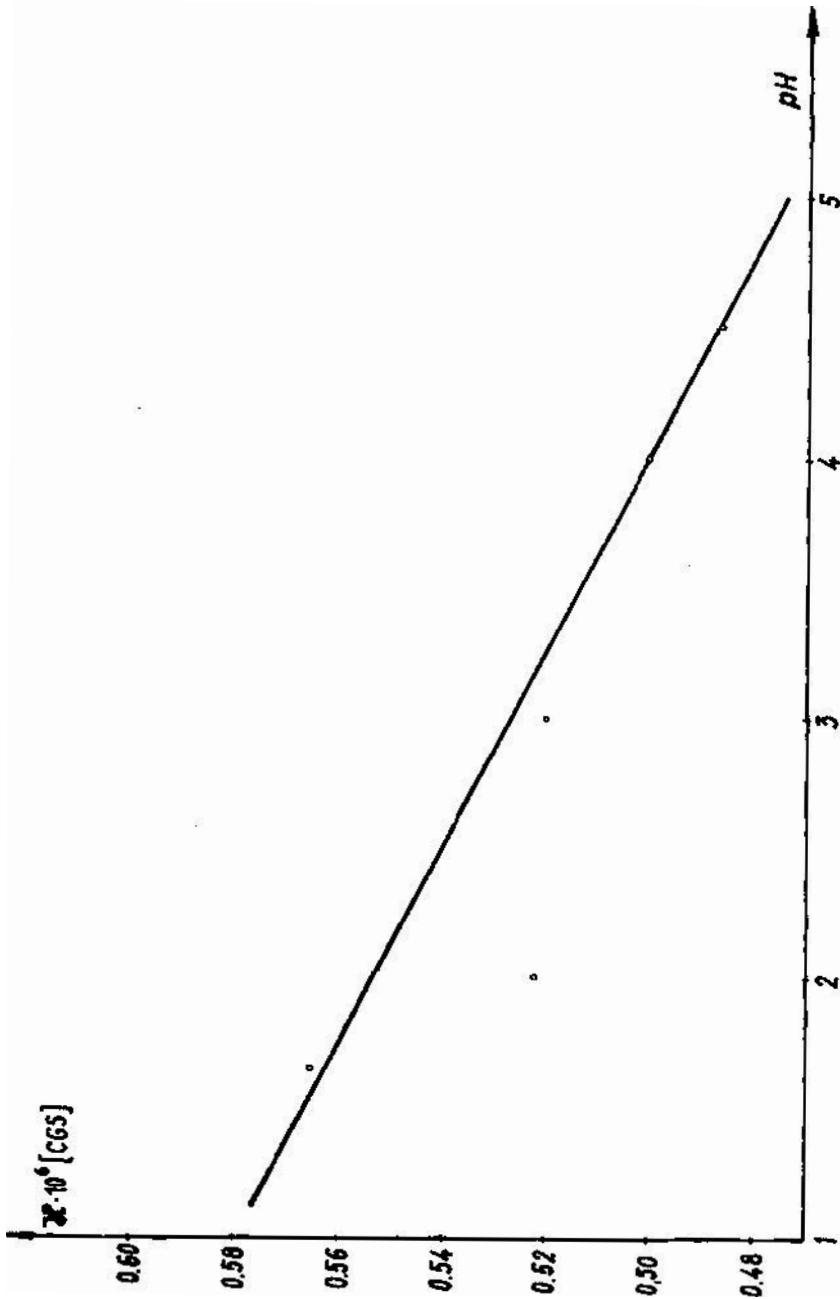


Fig. 2. Dependence of the magnetic susceptibility of ADP crystals on the pH of the solutions.

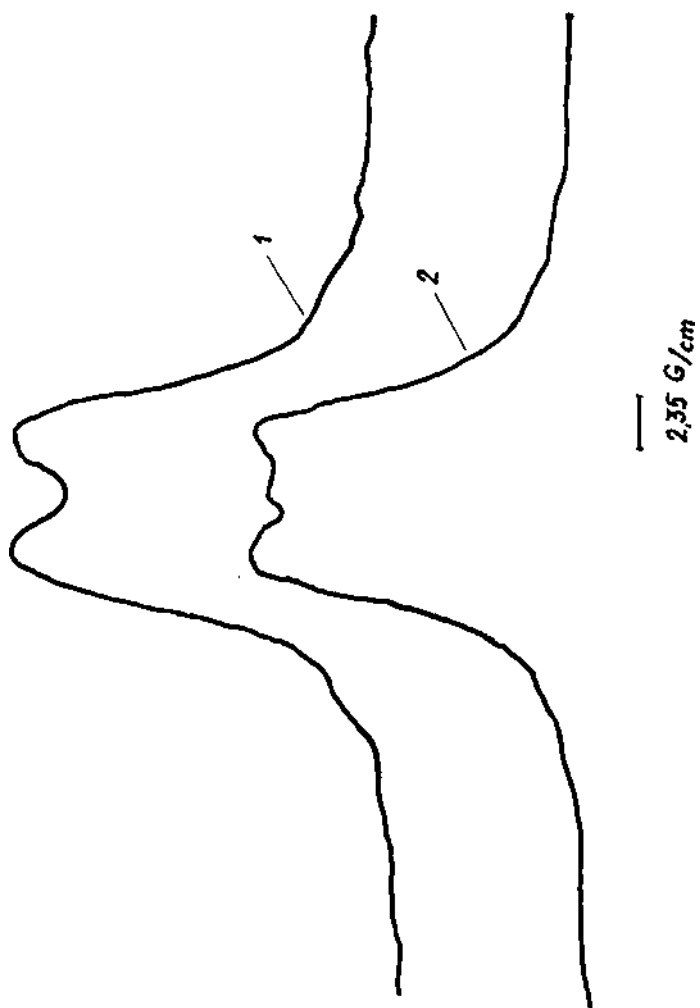


Fig. 3. The NMR spectra of ADP crystals obtained at different pH (1 : pH = 5,25; 2 :pH = 2).