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Growth of $CaHPO_4$ Crystals in Silica Gel Media and Its Characterization Studies, Nucleation Reduction Process

P. SUNDARAMOORTHI* and S. KALAINATHAN†
Department of Physics, Mahendra Engineering College, Mallasamudram(W) Namakkal-637 503, India
Fax: (91)(4288)238999 Tel: (91)(4288)238888, 238777
E-mail: sundara78@rediffmail.com

The calcium hydrogen phosphate crystals were grown in sodium meta silicate gel media. The growth processes were done by single diffusion method for different physical and chemical parameters. In the present investigation, calcium hydrogen phosphate crystals optimum growth parameters were identified. The sunlight exposure medium of growth gave better nucleation reduction. The grown crystals were analyzed by XRD, FTIR, TGA, SEM, AAS and etching.

Key Words: Calcium hydrogen phosphate, Biological crystals, XRD, FTIR, AAS, TGA/DTA, Etching.

INTRODUCTION

Human body contains a lot of organic and inorganic minerals in the form of fluids, with a different specific concentration. Our physiological organs balance human body mineral values. One of the organs namely kidney, which removes extra water, wastes and minerals from the human body in the form of urine. The human body fluids contain calcium, magnesium, strontium, sodium, phosphates, *etc*[1]. When the body fluid gets super saturated, automatic nucleation or crystal deposition starts. Calcium hydrogen phosphate (CHP) is one of the urinary substances available in the form of insoluble nature[2,3]. The crystal deposition starts any where with in the urinary tract and this is one of the diseases named as urinary calculi. The ($CaHPO_4 \cdot xH_2O$) apatite and brushite crystals were grown in silica gel media at human physiological environment. In the present investigation CHP crystals were grown in a single diffusion method at different environments. (i) growth of CHP crystals at room temperature [with in laboratory (29 ºC)], (ii) CHP crystal growth in sunlight exposure medium [out side the laboratory (42 ºC)].

The main objectives of the present investigations are to identify the optimum growth condition of CHP crystals and observation of nucleation

†Department of Physics, School of Science and Humanities, VIT University, Vellore-632 014, India.

rate. The characterization part of the research such as X-ray diffraction (XRD), scanning electron microscopy (SEM), thermo gravimetric analysis (TGA), fourier transform infrared spectrum (FTIR), etching and atomic absorption spectrum (AAS) analysis data confirms the CHP grown crystals.

EXPERIMENTAL

AR grade sodium meta silicate pure powder (Na_2SiO_3) was used to prepare the silica gel as per the literature[4]. Distilled water, neutral pH was used for all the dissolution and washing purposes.

RESULTS AND DISCUSSION

The initial pH of hydro gel is being around 13.8. The gel density used in this work was 1.04 gm/cm^3, 1.03 gm/cm^3 and the remaining densities do not give better results. The hydro gel or stock solution was mixed with orthophosphoric acid at a different concentration. After the gel set the supernatant or top solution ($CaCl_2$) reactant was added at required concentration gently. Table-1 gives the growth parameter of CHP crystals.

TABLE-1
GROWTH PARAMETERS OF CHP CRYSTALS

Gel density (g/cm^3)	Phosphoric acid concentration	Gel + H_3PO_4 pH value	Gel setting time (h)	Supernantant concentration $CaCl_2$ (M)	Nucleation observed (h)	Growth period (d)	Types of crystal observed / Harvested crystal size
1.03	0.5 N	6.5	24.00	1,1.5,2	10	60	Needle like crystals
		6.7	6.00	-do-	16		
		6.9	0.16	-do-	24		
		7.2	24.00	-do-	96		
	1 N	6.5	24.00	-do-	8	70	Dendrite crystals
		6.8	2.00	-do-	24		
		7.0	1.00	-do-	36		Platelet crystals
		8.2	48.00	-do-	48		
1.04	0.5 N	6.4	24.00	-do-	10	60	Leaf like crystals
		6.7	5.00	-do-	12		
		6.9	0.16	-do-	24		
		7.3	48.00	-do-	48		
	1 N	6.5	24.00	-do-	3	75	Single crystals
		6.8	1.00	-do-	10		
		7.0	12.00	-do-	24		
		7.3	48.00	-do-	72		

In the first method, the crystals were grown at room temperature (29 ºC). In the second method, CHP crystals were grown to exposing the gel medium into the sunlight (42 ºC). $NaBrO_3$, silver halide, silver bromide crystals were grown in solution and gel methods at exposure of light in to the growth medium. It was that the light might affect the crystal growth (reduction of nuclei)[5]. In the second method, the nucleation rate was reduced[6-8]. The growth column and grown crystals were shown in the Figs. 1-3. The shapes of the grown crystals were needle, platelet, dendrite and few single crystals are also observed. The maximum size of the harvested crystal was 2.0 mm × 3.0 mm × 1.0 mm.

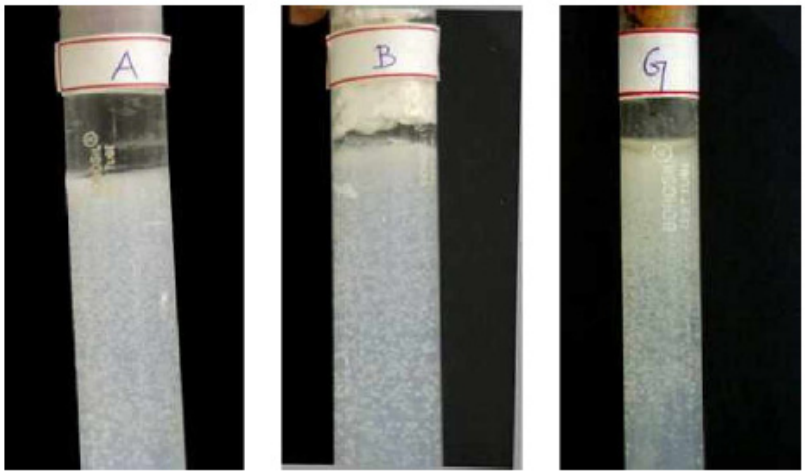

Fig. 1. Growth of crystals inside the laboratory (at 29 ºC)

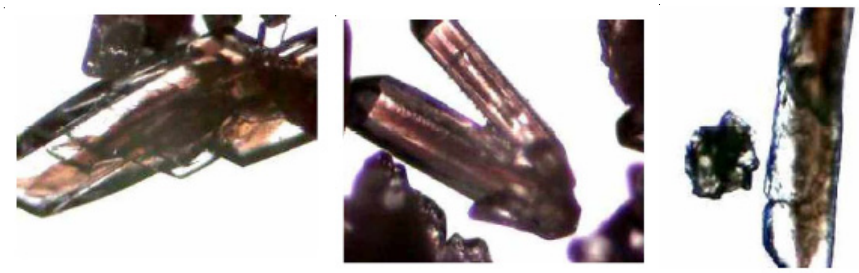

Fig. 2. Harvested crystals

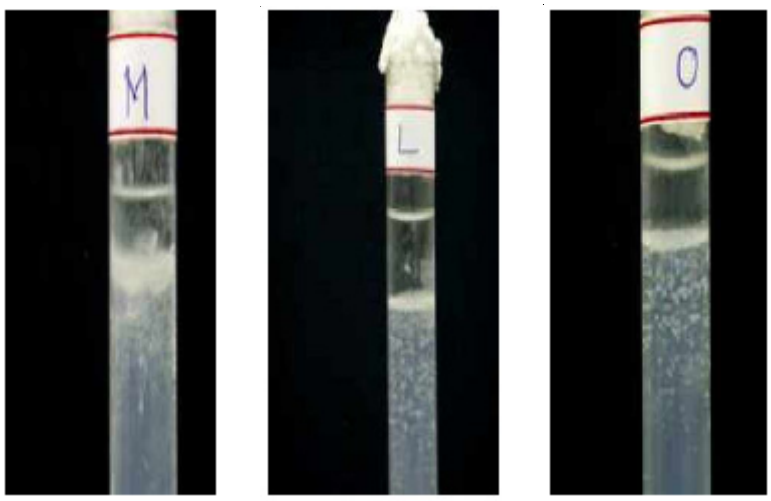

Fig. 3. Growth of crystals out side the laboratory (sunlight exposure medium - exposure time 8 h/d - the growth period was three month (at 42 ºC)

Crystal analysis

FTIR Spectral analysis of CHP crystals: FTIR Spectrometer having KBr pellets sample holder, KBr detector. The KBr pellet samples were used and the absorption frequencies range from 4000 to 600 cm^{-1}. The current results is matching with the work of Socrater *et al.*[9]. The absorption bonds, absorption frequencies and percentage of transmittance were compared with the reported values (Table-2).

TABLE-2
COMPARATIVE TABLE OF FTIR-CHP CRYSTAL[10,11]

Bonds/vibrations	Reported value (cm^{-1})	Observed values (cm^{-1})	Transmittance (%)
Calcium with hydrogen bond	3477	3492.8	9
H-O-H symmetric stretching bond	1620	1649.0	13
O-H out of plane bond	662, 781	663.5, 792.7	17, 14
P-O-P asymmetric stretching bond	987, 874, 794	985.6, 873.7, 792.7	7, 13, 14
PO_4 bond	1000-1100	1134, 1060.8	5, 6
(H-O-) P=O band (strong absorption) acid phosphates	665, 577, 525	663.5, 576.7, 526.5	17, 9, 7
Weak absorption	2375	2345.3	22
HPO_4^{2-}	1722	1649	13
C-C bond	885	873.7	12

Atomic absorption spectroscopy (AAS): AAS spectrum was recorded by calcium flame technique. The spectrum was recorded concentration *vs.* absorption. AAS spectrum is shown in the Fig. 4. New rationalize cure fit was used. The characterization concentration used here 7.245 mg/L. The characterization concentration and residuals are tabulated in the Table-3. Here three standard concentrations were used and the corresponding observations were tabulated. Two samples were prepared and results obtained. The following procedure was used to calculate the percentage of composition present in the CHP crystal.

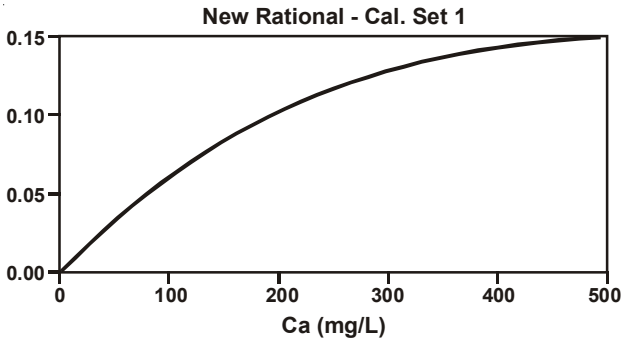

Fig. 4. AAS graph of CHP crystal

TABLE-3
CONCENTRATION AND RESIDUALS OF CHP CRYSTALS

Calculated concentration (mg/L)	Residuals
0.703	-0.703
97.414	2.588
207.150	-7.150
489.464	10.536

155 mg dissolved in 25 mL of solvent.

1254.54 mg/L, corresponding absorption value 0.0750

$$\frac{1254.5425}{155} \text{ mg} \times 100\ \% = 20.23\ \%$$ of composition present.

% of Ca = 20.23 % present in the grown CHP crystal. Phosphate lamp is not available in the AAS analysis.

Thermo gravimetric (TGA and DTA) analysis of CHP cystals: The TGA and DTA of CHP crystals were carried out by STA 11500-PLTS instrument. The CHP crystal of 2.439 mg sample was taken to the TGA process. The TGA was started from room temperature to 1000 ºC by heating at a constant rate. The % of weights present in the CHP sample at a particular temperature was tabulated in the Table-4[10].

TABLE-4
THERMAL DECOMPOSITION DATA OF CHP CRYSTALS

TGA		DTA (ºC)
Temperature (ºC)	% of CHP crystal present	
35.00	100.00	–
95.96	99.71	93.01
126.32	95.63	122.41
181.86	86.86	146.42
205.23	81.02	185.33
425.87	77.68	200.53
491.69	74.45	257.11
–	–	453.03

The TGA of CHP crystals were anhydrous up to 491.69 ºC. Here after the remaining sample is stable up to the end of the analysis.

The expected chemical reactions

$$CaHPO_4 \cdot xH_2O \rightarrow CaHPO_4 + xH_2O \text{ (Vapour)}$$

$$2CaHPO_4 \rightarrow Ca_2P_2O_4 + H_2O \text{ (Vapour)}$$

$Ca_2P_2O_7$ is stable compound with respect to the temperature up to 1230 ºC (melting point). The CHP crystals were decomposed and 74 % of the sample was stable.

Etching study of CHP crystals: A well-grown CHP crystal was immersed in HCl solution at a desired concentration. The dissolution of CHP crystal depends upon the etchant concentration, temperature, crystal morphology, etching time etc. The etch pits are shown in Fig. 5. The etch pits of CHP crystals were observed in steps as dots like patterns.

Fig. 5. Etch pits of CHP crystal (HCl of 1 N, 5 min etching time) at room temperature

Scanning electron microscopy study of CHP crystals: A well-grown CHP single crystal was selected for the investigation of surface morphology crystal by using SEM. The SEM photograph was got in the version S-300-I instrument. The sample named as VCA-600 kept in lobe middle; the data size was 640 × 480. The minor, major magnification of SEM about 250 times. SEM acceleration voltage was 25000 volts and kept the sample in highly vacuumed. 18200-micrometer working distance and monochromatic colour mode were employed. 200 Micrometer focusing of CHP crystal [100 plane] SEM is shown in the Fig. 6. The surface of the SEM photo shows the anisotropic nature of CHP crystal plane.

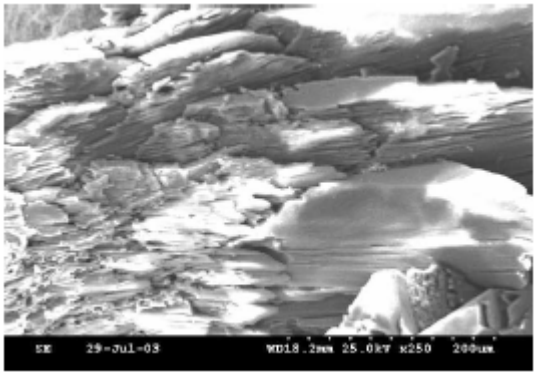

Fig. 6. SEM-Photograph of CHP crystals

X-Ray diffraction of CHP crystal: The XRPD results revealed the crystalline property of crystal. The XRPD pattern and diffraction indices of the CHP crystals are shown in the Fig. 7. Using the programme Proszki calculated the lattice parameters of the CHP crystal. The lattice parameters are a = 6.12799 Å, b = 7.96281 Å, c = 10.59583 Å, α = 102.48, β = 123.34, γ = 93.95. From this data confirmed the CHP crystal system is triclinic[13,14].

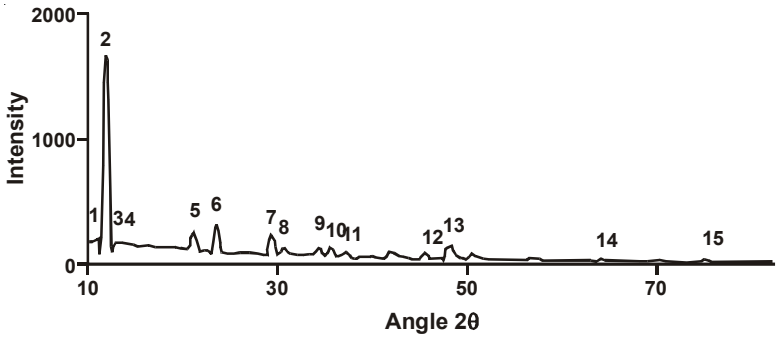

Fig. 7. XRD pattern of CHP crystal

Conclusion

The CHP crystals were grown in the room temperature and exposed to the sunlight. It is found that the nucleation rate reduced while the gel medium is exposed to the sunlight. It is due to variation of super saturation. FTIR-the group vibration frequencies were recorded and compared with the reported values. The percentage of calcium present in the CHP was calculated by AAS. Chemical etchings were done at room temperature. SEM did the surface morphology of CHP crystal. The percentages of weight loss at different temperature of CHP crystal were recorded by TGA/DTA analysis. The cell parameters of CHP crystal were calculated by XRD.

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