



**RESEARCH ARTICLE**

**GROWTH OF CALCIUM HYDROGEN PHOSPHATE DIHYDRATE (CHPD) CRYSTAL AND CHARACTERIZATION STUDIED BY SPECTRAL METHOD**

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**ARTICLE INFO**

**Article History:**

Received 5<sup>th</sup>, September, 2014  
Received in revised form 16<sup>th</sup>, September, 2014  
Accepted 25<sup>th</sup>, September, 2014  
Published online 1<sup>st</sup>, October, 2014

**Key words:**

Gel growth, CHPD, FT- IR, Powder XRD

**ABSTRACT**

Calcium hydrogen phosphate dihydrate [CaHPO<sub>4</sub>.2H<sub>2</sub>O] a dissolved mineral in urine. It causes stones in renal or bladder in living organisms. Calcium hydrogen phosphate dihydrate has been crystallized in silica gel by single diffusion technique. The crystals had irregular shape like square. XRD results confirmed that the product of CHPD with identical crystal structures. Thermal and spectral properties are analyzed using Fourier transform infrared spectroscopy (FTIR) powder X-ray diffraction (XRD), scanning electron microscopy (SEM) with Energy dispersive spectrum(EDS). Above studies and results are discussed.

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**INTRODUCTION**

Biom mineralization processes have attracted considerable attention due to their importance especially in life sciences with respect to pathological effects. The increasing incidence of crystal deposition diseases such as urinary stones, gallstones among people of all age groups is a major social and economic problem. The necessity to understand the situations that give rise to crystalline diseases has led to the *in vitro* investigations of the nucleation, growth and the kinetic studies of the crystalline components present in the stones [1]. Human renal calculi are due to the biological maladjustment of urine. The stone formation is attributed to the supersaturation of urine and to the retention of solid particles, which spreads by successive aggregation and crystal growth. The urinary stone induce one of the calcium content with phosphate. The CHPD crystal grown in gel method is one of the method for urinary stone formation. Calcium hydrogen phosphate dihydrate [CaHPO<sub>4</sub>. 2H<sub>2</sub>O], also known as brushite minerals is a stable form of calcium phosphate [2]. The brushite mineral is found under various pathological conditions including kidney stones, some forms of arthritis, and caries [3, 4]. It was reported that the mineral deposits in the kidney contain various form of calcium salts such as calcium oxalate and calcium phosphate [5]. The calcium phosphate minerals are thought to be the initiator of stone formation in the kidney and urinary bladder, under the favourable physiological environment. As a simple model, the single diffusion method using hydro gel (Sodium Meta silicate- SMS) provides an environment to grow the CHPD crystals successfully [8]. This study incorporates a multidisciplinary approach in characterizing the grown CHPD crystals and to help in formulating a strategy for the prevention or dissolution of these types of urinary stones. In the present work, we have investigated the crystallization of

CHPD in silica gel under laboratory conditions. Thermal, spectral properties of grown CHPD crystals are studied.

**MATERIALS AND METHODS**

Sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>.9H<sub>2</sub>O) and disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) was used for preparing the gel and glacial acetic acid was used for adjusting the pH value. All the reagents used in this experiment are of analar grade. Crystallizations were conducted in the gel densities between 1.03 and 1.06 g/cc and pH values from 4 to 6.5. Optimum values of gel density and pH values for the crystallization were found to be 1.03 g/cc and 6 respectively. Calcium chloride was placed over the set gel. Tiny crystallites appeared in the gel solution after about 24 hours. FT-IR spectrum was recorded on Shimadzu range 400-4000cm<sup>-1</sup> and KBr beam splitter. The SEM photographs are taken in the version S-300-I instrument. XRD was recorded on XPERT-PRO diffractometer system. TG/DTA was recorded on NETZSCH STA 449F3.

**RESULT AND DISCUSSION**

**Crystal growth**

CHPD crystals have been successfully grown in sodium metasilicate gel. Tiny crystals could be seen only after 24 hours from the initiation of growth. The growth of CHPD crystals is influenced by the initial Liesegang rings formation which is related to the gel formation and set. The initial gel pH range 6.0 showed better formation of Liesegang [5-7] rings which have promoted excellent crystal growth as observed in the present study Joshi et al. [3] discussed that as the number of Liesegang rings increased the initial rings tended to diffuse. The CHPD crystals grow within the Liesegang rings as shown in fig.1. The thick bands seen on the top of the test tubes were found as gel components which are not involved in the formation of Liesegang rings and were washed away during

crystal harvesting. Liesegang rings consist of insoluble precipitate of CHPD which are formed through diffusion of ions through the gel medium. In the gel medium irregular square shape crystals were observed as shown in fig.2. Generally the crystals were colourless.



Fig.1 CHPD crystals grown in gel medium



Fig.2 Irregular square shape of CHPD crystal

**FTIR analyses**

FT-IR spectrum of CHPD crystal was shown in fig3. The respective assignments of the vibrations are given in table-2.

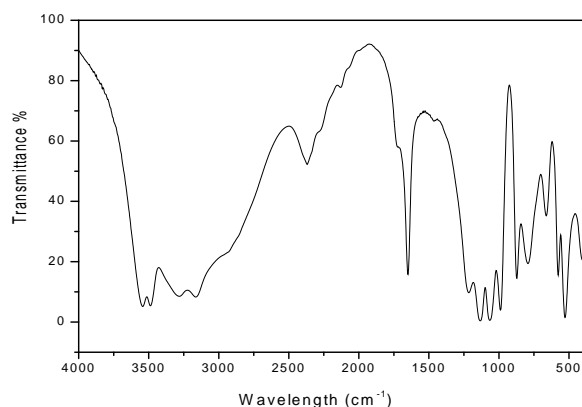


Fig.3 FT-IR spectrum of CHPD crystal

The presence of water of crystallization was referred from absorbed at 3543, 3487 and 3165cm<sup>-1</sup> which is due to inter molecular and weakly H bonded OH. The symmetric bending of H- O - H gives rise to absorption at 1649cm<sup>-1</sup>, while P=O associated stretching vibrations were observed at three different wave numbers likewise (1215, 1134, and 1065cm<sup>-1</sup>). The P-O-P asymmetric stretching vibrations were observed at 989, 872 and 793 cm<sup>-1</sup> The strong absorption at 576 and 528

are due to acid phosphates (H-O-) P=O bond vibrations. Joshi and Joshi [3] confirmed the grown CHPD crystals are due to the presence of water crystallization, P=O bond and O-H bond by FT-IR crystallization, P=O bond, HPO<sub>4</sub><sup>-2</sup> ion P-O bond and O-H bond were confirmed by FT-IR spectroscopy

**Table1** FT-IR wave numbers and vibrations assignment of CHPD crystal

| Wave numbers (cm <sup>-1</sup> ) | Bonds / Vibrations  |
|----------------------------------|---|
| 354                              | O-H stretching (weakly H bonded OH vibrations)            |
| 3488                             | O-H stretching (weakly H bonded OH vibrations)            |
| 3165                             | O-H stretching (weakly H bonded OH vibrations)            |
| 1649                             | H-O-H symmetric bending vibrations                        |
| 1215                             | PO <sub>4</sub> P=O associated stretching vibrations      |
| 1134                             | PO <sub>4</sub> bond P=O associated stretching vibrations |
| 1065                             | PO <sub>4</sub> bond P=O associated stretching vibrations |
| 989                              | P-O-P asymmetric stretching bond                          |
| 872                              | P-O-P asymmetric stretching bond                          |
| 793                              | P-O-P asymmetric stretching bond                          |
| 577                              | (H-O-) P=O bond (strong absorption) acid phosphates       |
| 529                              | (H-O-) P=O bond (strong absorption) acid phosphates       |

**SEM analysis with EDS**

Fig.4 shows SEM picture of CHPD and Fig. 5 shows EDX analysis of CHPD Crystal.

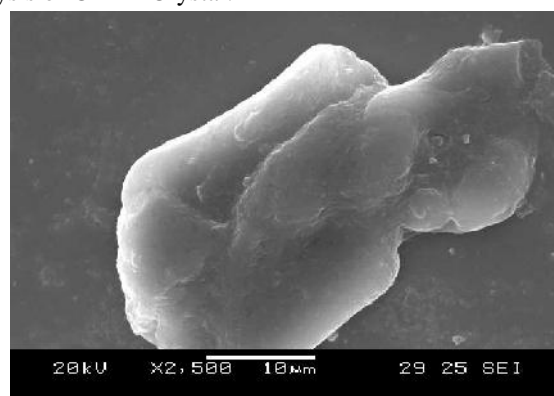


Fig 4(a)

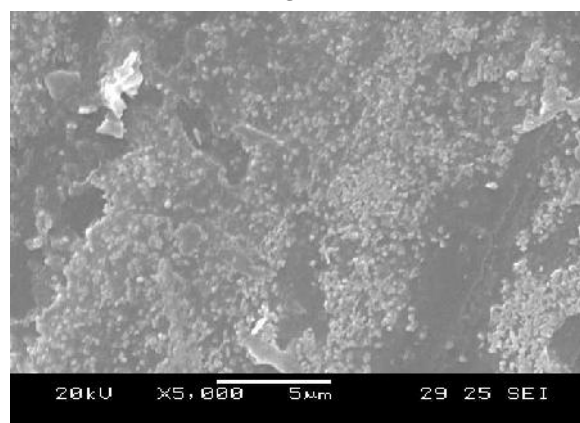


Fig. 4(b) SEM image of CHPD crystal

Regimented, long crystals different sizes can be seen in the sample. Crystals have pyramidal shaped morphology with clear and defect-free surface.

The elemental amount (Ca) and phosphorus (P) present in the crystal ratio 42:58 from the measurement of EDS. The result indicates that the crystal is composed of primarily calcium and phosphorus.

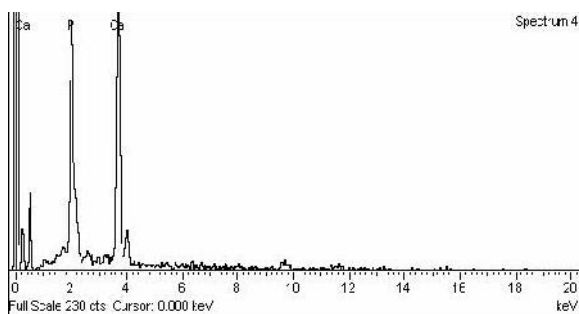


Fig. 5 Energy dispersive X-ray analysis of CHPD crystal

**Powder XRD analysis**

Fig.6 shows the powder X-ray diffraction pattern of CHPD crystallites. The results agree well with the literature values the [JCPDS no.77-0128]. The lattice parameters of CHPD a=9.973 , b=7.288 , c=6.293 and  $\beta=106.87^\circ$  from this data the CHPD Crystal system is Monoclinic.

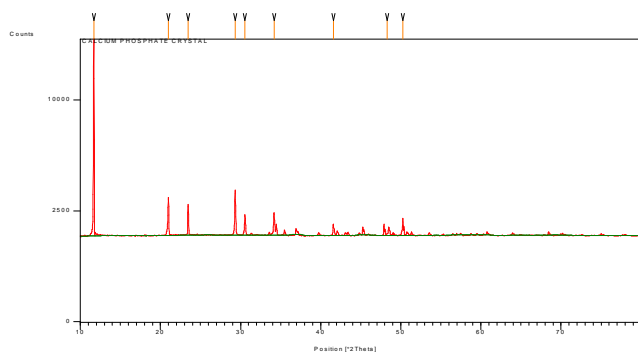


Fig.6 powder XRD analysis of CHPD crystal

**Table 2** XRD analysis of CHPD Crystal

| Pos. [°2Th.] | Height [cts] | FWHM [°2Th.] | d-spacing [Å] | Rel. Int. [%] |
|--------------|--------------|--------------|---------------|---------------|
| 11.6878      | 15101.80     | 0.0787       | 7.57161       | 100.00        |
| 20.9819      | 1626.05      | 0.0787       | 4.23402       | 10.77         |
| 23.4583      | 1284.02      | 0.0787       | 3.79236       | 8.50          |
| 29.3206      | 2008.88      | 0.1181       | 3.04611       | 13.30         |
| 30.5437      | 809.90       | 0.1378       | 2.92685       | 5.36          |
| 34.1764      | 904.04       | 0.0787       | 2.62361       | 5.99          |
| 41.6001      | 386.42       | 0.1574       | 2.17098       | 2.56          |
| 48.3224      | 123.53       | 0.9446       | 1.88351       | 0.82          |
| 50.2662      | 473.15       | 0.2880       | 1.81366       | 3.13          |

**CONCLUSION**

Calcium hydrogen phosphate [CaHPO<sub>4</sub>. 2H<sub>2</sub>O] crystals have been grown in silica gel by single diffusion technique and the morphology has irregular like square shape. FTIR spectra confirmed the P-O-P asymmetric stretching. Powder X-ray analysis confirmed the crystal nature. SEM analysis confirmed the smooth surface of the CHPD crystal. EDS analysis confirmed the presence of calcium and phosphorus.

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