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CRYSTALLIZATION AND THERMAL CHARACTERIZATION OF CALCIUM HYDROGEN PHOSPHATE DIHYDRATE CRYSTALS

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Calcium hydrogen phosphate dihydrate (CHPD) is found quite frequently in urinary calculi (stones). The CHPD crystals were grown by the single diffusion gel growth technique in sodium metasilicate gel. The crystals were found to be having platelet and broad needle type morphologies. The crystals were analyzed by FTIR spectroscopy. The thermal properties were studied by employing the thermogravimetric analysis (TG). Various kinetic and thermodynamic parameters for dehydration were estimated from the TG curve. The selected platelet was studied by scanning electron microscope (SEM) for the growth morphologies indicating that the crystals grew in the form of leaflets having prominent (010) faces. This was in agreement with earlier reported studies.

Keywords: *calcium hydrogen phosphate dihydrate crystals, FTIR, kinetic parameters, morphology, SEM, TG, thermodynamic parameters*

Introduction

Calcium stones are most commonly occur form of nephrolithiasis, that is, kidney stones. Calcium oxalate stones are more common than calcium phosphate, but mixed calcium oxalate-phosphate is the most common variety. Struvite stones, usually seen in the setting of urinary tract infections, are the most common type of renal stone. Calcium phosphate is present in urinary calculi as either apatite [$Ca_{10}(PO_4)_6(OH)_2$] or brushite [$CaHPO_4{\cdot}2H_2O$] [1]. It is interesting to grow these crystals and characterize them by various techniques. This has attracted several researchers [2, 3] to grow brushite, that is, calcium hydrogen phosphate dihydrate (CHPD) crystals by the gel growth technique. SEM, FTIR and thermal analysis are very useful techniques to materials characterization. Therefore, many authors have used SEM, FTIR and thermal analysis to characterize various materials including materials containing calcium and phosphate [4–39]. The aim of this study is to investigate the growth morphology of selected crystal by SEM and also study the crystals by Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TG).

Experimental

Preparation of CHPD crystals

The CHPD crystals have been grown by the single diffusion gel growth technique in the present investigation. Glass test tubes of 25 mm diameter and 140 mm length were used as a crystallization apparatus. The AR grade chemicals were used to grow the crystals. 2.5 M orthophosphoric acid solution was mixed with sodium metasilicate solution of 1.06 specific gravity so that the pH of the mixture could be set to 6.0. The mixture was transferred into different test tubes. After setting gels, the supernatant solution of 1 M calcium chloride was poured without disturbing the set gels. The nucleation started immediately. The first Liesegang ring was observed within 12 min of pouring the supernatant solution. The number of Liesegang rings increased with time and total eighteen Liesegang rings were observed after five days. However, at the same time the first few Liesegang rings started diffusion. The distance between two consecutive Liesegang rings was found to be increasing towards bottom of test tubes. The elongated platelet shape crystals as well as broad needle type crystals were grown within the Liesegang rings. Also several platelets originating from a single point as in star or floral formations were also observed.

Measurements

The FTIR spectrum of CHPD crystals was recorded on a NICOLET MAGNA IR 500 series II FTIR spectrometer having DTGS-KBr detector and KBr beam splitter. The spectrum of powdered sample in KBr medium was recorded in the range from 400 to 4000 cm^{-1}.

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The thermogravimetric analysis (TG) was performed on powder samples on a STA-409C set up. The TG curve was obtained by heating a sample from room temperature to 900°C, in an atmosphere of nitrogen, with heating rate of 15°C min^{-1} using Al_2O_3 as standard reference.

The SEM was taken at magnification values from 37X to 5.03 kX with maximum value of EHT 13.00 kV using LEICA S 440 Model 7060.

Results and discussion

The gel technique is found to be promising method to grow CHPD crystals. This technique provides much simplified method to understand the growth of urinary crystal in-vitro. The formation of Liesegang rings was observed in the present study. Recently, a detail study has been reported on the effect of various parameters such as, the gel pH, the concentration of reactants, the height of the column of supernatant solutions on the formation of Liesegang rings [3]. The gel and its structure have been found to be playing an important role.

The FTIR spectrum of CHPD crystals is shown in Fig. 1. Several researchers [2, 40] reported the IR spectroscopic study of CHPD crystals. The absorptions at 3545, 3490, 3284 and 3168 cm^{-1} are due to intermolecular and weakly H bonded OH because of water of crystallization. The weak absorptions at 2375 and 1722 cm^{-1} are due to HPO_4^{2-} [41]. The H–O–H bending gives rise to absorption at 1651 cm^{-1}. The absorptions at 1217 and 1137 cm^{-1} are due to P=O associated stretching vibrations. Whereas, the absorption at 1061 cm^{-1} is due to P=O stretching vibrations. The P–O–P asymmetric stretching vibrations give rise to absorptions at 987, 874 and 794 cm^{-1}. The absorption at 665 cm^{-1} is due to (H–O–) P=O. However, the strong absorptions at 577 and 525 cm^{-1} are again due to acid phosphates.

The TG curve is shown in Fig. 2 and it can be noticed that hydrated calcium phosphate becomes anhydrous at 294°C and it turns into calcium pyrophosphate ($Ca_2P_2O_7$) at 554°C. The melting point of $Ca_2P_2O_7$ is 1230°C. Therefore, it is expected to remain stable up to the end of the analysis (900°C).

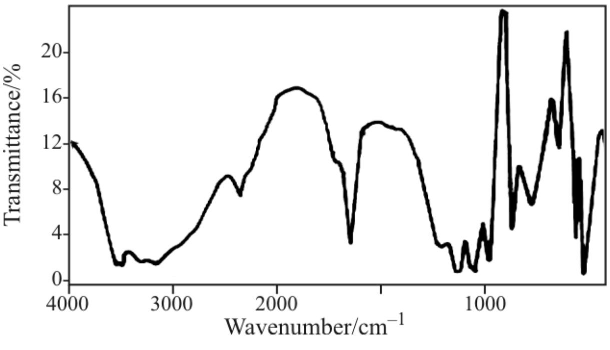

Fig. 1 FTIR spectrum of CHPD crystals

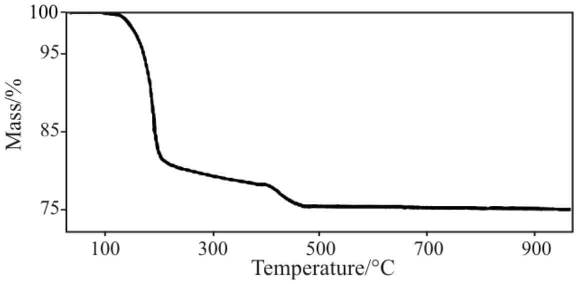

Fig. 2 TG curve of CHPD crystals

Table 1 Thermal decomposition of CHPD crystal

Temperature	Decomposition of CHPD crystal	Mass/%	
		observed	theoretical
room temperature	$2CaHPO_4{\cdot}2H_2O$	100	100
294°C	$2CaHPO_4$	79.08	79.4
554°C	$Ca_2P_2O_7$	73.83	75.72

Table 1 gives the comparison of experimentally obtained and theoretically calculated mass loss values at different temperature.

The use of TG curve to evaluate kinetic parameters of solid-state reactions involving mass loss has been explored widely [42–44]. The shape of the curve is determined by the kinetic parameters of pyrolysis such as the order of reaction, the activation energy and the frequency factor. Coats and Redfern relation [45] was applied to evaluate the kinetic parameters of dehydration from the TG curve (Fig. 2).

The Coats and Redfern relation is as follows:

$$-\log 10[\{1-(1-a)1-n\}/\{T^2(1-n)\}]= \\ =\{\log 10[AR/aE][1-2RT/E]\}-\{E/2.3RT\} \qquad (1)$$

(For n=1) where a is the fraction of original substance decomposed at time t, that is, $(W_0-W)/(W_0-W_f)$; W_0 is the initial mass; W is the mass at time t; W_f is the final mass; n is the order of reaction; A is the frequency factor; E is the activation energy; R is the gas constant and a is the heating rate in °C min^{-1}. To determine the value of activation energy and order of reaction, a plot of $-\log 10[\{1-(1-a)1-n\}/\{T^2(1-n)\}]$ *vs.* $1/T$ is drawn for different values of n and the best linear plot gives the correct value of n. This equation is valid for all values except n=1. For n=1, Eq. (1) cannot be used, therefore, it is modified as follows [45].

$$-\log 10[-\log(1-a)/T^2]= \\ =\log 10[AR/aE][1-2RT/E]-\{E/2.3RT\} \qquad (2)$$

(For n=1). In the present case the best linear fit was obtained for n=1. Therefore, the plot of X= $-$log10[$-$log(1$-a$)/T^2] and Y=(1/T)·10^{-3} was drawn, which is shown in Fig. 3. The values of activation energy and frequency factor were found to be 135.16 kJ mol^{-1} and 2.99·10^{28}, respectively, for dehydration of CHPD crystals.

Using the value of frequency factor, the values of entropy and other thermodynamic parameters were calculated. The thermodynamic parameters such as the standard entropy (ΔS^0), the standard enthalpy (ΔH^0), the standard Gibbs free energy (ΔG^0) and the standard change in internal energy (ΔU^0) were calculated using well-known formulae [44, 46] for the dehydration stage of TG curve. The values of different thermodynamic parameters for dehydration of CHPD crystals are listed in Table 2.

The grown crystals were investigated by SEM. The samples for SEM study were carefully selected. The SEM was taken at magnification values from 37X to 5.03 kX with maximum value of EHT 13.00 kV using a LEICA S 440 Model 7060. A platelet of CHPD crystal was selected for SEM study and the SEM image is shown in Fig. 4 with magnification of 1.00 kX.

This indicates that two different growths are occurring from the two different centers and the growth takes place in different leaflets. One can easily notice that small leaflets were growing on the top of large leaflets like mica sheets. Upon increasing the magnification up to 5.03 kX with EHT 13 kV, the smallest leaflet was visible. When attempt was made to increase the magnification up to 10.02 kX with EHT 15 KV, the image became blurred and no further information was obtained.

The growth morphology of CHPD crystals that appeared in the controlled system was found to be typical in form of thin platelets with prominent (010) and lateral (401) faces [47, 48]. CHPD crystallizes in monoclinic system [48]. The unit cell consists of alternating bi-layers oriented parallel to the (010) plane, one layer is consisting of calcium and hydrogen-phosphate ion while the other layer is of water molecules. The growth morphology of CHPD crystals generally reflects the crystal structure so that (010) is the prominent crystal face [49, 50]. In aqueous solutions the bi-layers of water molecules are for most of the real time exposed at the surface of (010) face, whereas the later faces have a mixed ionic character with intercalculated water molecules [49]. Because of this kind of ionic structure CHPD represents a good model crystal for studying the several aspects of interaction between additives and crystals, which has led to investigate extracts and juices of some cereals, vegetables, plants and fruits [51] as well as lemon juice [52], tartaric acid [53] and the effect of glutamate, asparate, citrate and polyasparate [54] on the growth of CHPD crystals. The leaflets are exhibiting the similar morphology as reported earlier [54], which also agrees with the earlier observations and expected to have (010) as prominent face.

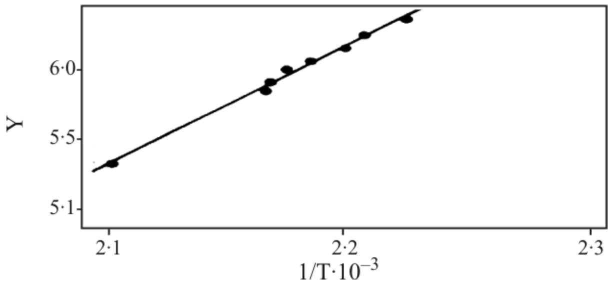

Fig. 3 Coats and Redfern curve for n=1, where X=(1/T·10^{-3}) and Y= $-$log10[$-$log10(1$-a$)/T^2]

Table 2 Thermodynamic parameters of CHPD crystal

Entropy (ΔS^0)/J K^{-1} mol^{-1}	284.60
Enthalpy (ΔH^0)/kJ mol^{-1}	143.44
Gibbs free energy (ΔG^0)/kJ mol^{-1}	11.79
Standard change in internal energy (ΔU^0)/kJ mol^{-1}	139.58

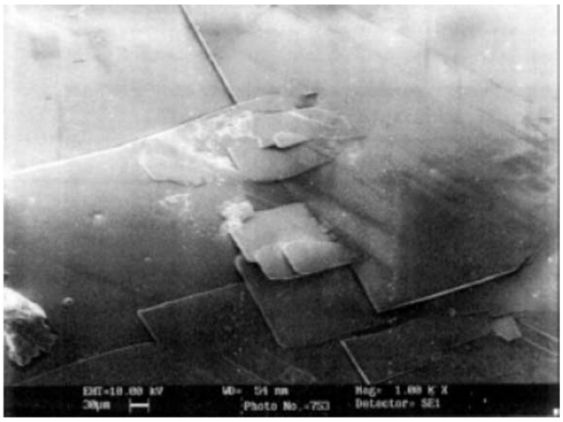

Fig. 4 SEM of the platelet of CHPD crystal exhibiting growth features at 1.00 kX magnification

Conclusions

The presence of water of crystallization, P=O bond, HPO_4^{2-} ion, P–O bond and O–H bond were confirmed by FTIR spectroscopy. The CHPD crystals were found to be thermally unstable. Upon heating, the crystals gave up water of hydration, initially, and became anhydrous, then converted into calcium pyrophosphate that remained stable up to the end of the thermal analysis experiment. The kinetic and thermodynamic parameters are obtained for dehydration of crystals estimated from the TG curve. The growth took place from different centers in form of leaflets, which were investigated by

SEM. The earlier study also reported the growth of CHPD crystals in the form of thin platelets with prominent (010) and lateral (401) faces. The present observations were in agreement with the earlier results.

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