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Characteristics Studies of Strontium Hydrogen Phosphate Crystals

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Strontium hydrogen phosphate [SHP] crystals are found rarely in urinary tract. The crystals were grown artificially by single and double diffusion gel growth technique. The grown crystals were found to be having good single, polycrystalline, dendrite and platelets types of morphologies. The crystal cell parameters were determined by powdered XRD method. The thermal properties were studied by thermogravimetric analysis. The surface morphology and crystal defects of well-grown crystals were analyzed by SEM and Etching studies. The SHP crystal growth processes were observed in focusing laser light and sunlight to the growth column. From the results SHP crystal nucleation rates were reduced.

Key Words: Strontium hydrogen phosphate, Laser light, Calculi, Surface morphology, Growth parameters, Trace elements.

INTRODUCTION

Calcium stones are most frequently occurs in nephrolithiasis that is kidney stones or renal caluli. COM or COD are most usual occurrence than calcium phosphate but mixtures of calcium and phosphate is the natural common variety. Usually urinary tract infections cause struvite stones, which is also common types of renal stone. Calcium phosphate is present in urinary calculi as HAP or CHP[1]. It is interesting to grow these crystals artificially and characterize them by lot of different techniques. In past several researches[2,3] grow biological crystals. In present work, strontium hydrogen phosphate (SHP) crystals have been grown by the gel growth technique. The main objectives of this study, the SHP crystal growth morphologies and identify the optimum growth conditions. With the optimum growth conditions and different environments, many attempts were made to reduce the nucleation rate or growth rate of SHP crystals. The SHP

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crystals were grown in three environments first was with in laboratory room temperature (29°C); second was in sunlight-exposed medium at (40°C) outside the laboratory. The third one was in front of laser-exposed medium. [Diode laser source-the wavelength 7300Å]. From the three environments, keen growth observations were made. The growth rate, nucleation rate were maximum reduced by the laser-exposed medium. The harvested crystals were selected for characterization process such as XRD, SEM, etching and TGA/DTA and the results reported.

EXPERIMENTAL

The SHP crystals have been grown by the single and double diffusion SMS gel technique. The SMS gel preparation and its detailed studies are reported. Glass tubes [Reaction test tubes] which is thin walled 25 mm diameter and 150 mm length was used in single diffusion process. Similarly in double diffusion process - U tubes (thick walled 30 mm diameter and 160 mm height) were used as crystallization apparatus. The AR grade chemicals were used to grow the crystals. One of the reactants orthophosporic acid solutions was mixed with the stock solution of desired specific gravity. So that the pH of the mixture could be set at a required value. The mixture was transferred into the different growth columns [test tubes, U tubes]. After gel set, the supernatant solution strontium chloride at a required molarity are prepared and pour to the growth column without disturbing the set gel. After pouring the top solution with in the gel column, chemical reaction starts immediately, Lies gang rings were formed and the nucleation starts. The first Lies gang rings were observed within 10 h of pouring the top solution in all the growth columns. The number of rings increased with time but the rings width and rings gap varies in different growth tubes. The distance between two consecutive Lies gang rings was found to increase towards the bottom of the test tubes. The growth parameters of SHP crystals, optimum growth condition and growth morphologies were reported in Tables 1 and 2.

The chemical reaction is:

$$H_3PO_4 + H_3SiO_4 + SrCl_2 \rightarrow SrHPO_4.{}_xH_2O + \text{Waste}$$

Ions involved in the chemical reactions

$$Sr^{2+} + HPO_4^{3-} \rightarrow SrHPO_4.{}_xH_2O \text{ (Solid form-crystal)}$$

The gel technique is found to be promising method to grow SHP crystals. This technique provides much simple method to understand the growth of urinary calculi crystal *in vitro*[4]. The formation of Lies gang rings was observed in the present study. The optimum growth parameters of SHP crystals in single diffusion method were mention in the Table-1 in bold letters. Double diffusion method, the optimum growth parameters were mentioned in Table-2 in bold letters.

TABLE-1
SINGLE-DIFFUSION METHOD (TEST TUBE) SHP CRYSTAL GROWTH PARAMETERS AND GROWN CRYSTALS MORPHOLOGY

Gel density gm/cc^3	Phosphoric acid concentration	Gel + H_3PO_4 pH value	Gel setting time	Supernatant concentration $SrCl_2$ (M)	Nucleation observed (h)	Growth period (d)	Types of crystal observed & harvested crystal size
1.04	**1N**	6.5	24 h	1, 1.5, 2	10	**90**	**Dendrite crystals**
		6.7	**6 h**	**1, 1.5, 2**	**20**		
		6.9	10 min	1, 1.5, 2	24		
		7.2	24 h	1, 1.5, 2	96		
	2N	6.5	24 h	1, 1.5, 2	8	**75**	**Platelet crystals**
		6.8	**2 h**	**1, 1.5, 2**	**24**		
		7.0	1 h	1, 1.5, 2	36		
		8.2	48 h	1, 1.5, 2	48		
1.05	**1N**	6.4	24 h	1, 1.5, 2	10	**80**	**Single, Poly crystals**
		6.7	5 h	1, 1.5, 2	12		
		6.9	**10 min**	**1, 1.5, 2**	**24**		
		7.3	48 h	1, 1.5, 2	48		
	2N	6.5	24 h	1, 1.5, 2	3	**90**	**2.0 × 3.0 × 1.0 mm**
		6.8	**1 h**	**1, 1.5, 2**	**10**		
		7.0	12 h	1, 1.5, 2	24		
		7.3	48 h	1, 1.5, 2	72		

TABLE-2
DOUBLE-DIFFUSION PROCESS (U-TUBES) SHP CRYSTAL GROWTH PARAMETERS AND GROWN CRYSTALS MORPHOLOGY

Gel density gm/cc^3	Phosphoric acid concentration	Gel + H_3PO_4 pH value	Gel setting time	Supernatant concentration $BaCl_2$ (M)	Nucleation observed (h)	Growth period (d)	Types of crystal observed & harvested crystal size
1.03	**1N**	6.0	40 h	1, 2	25	**96**	**Dendrite crystals**
		6.5	16 h	1, 2	26		
		6.9	**15 M**	**1, 2**	**28**		
		7.0	24 h	1, 2	104		
	2N	6.1	36h	1, 2	19	**60**	**Single, Poly crystals**
		6.7	**4 h**	**1, 2**	**42**		
		7.2	5 h	1, 2	66		
		8.0	48 h	1, 2	88		
1.04	**1N**	6.0	44 h	1, 2	30	**80**	
		6.6	**15 h**	**1, 2**	**42**		
		7.0	20 min	1, 2	44		
		7.4	68 h	1, 2	78		
	2N	6.1	68 h	1, 2	10	**75**	
		6.9	**3 h**	**1, 2**	**19**		
		7.0	2 h	1, 2	22		
		7.3	18 h	1, 2	92		

The SHP crystal growth, growth columns (optimum parameters) were focused in to the sunlight, laser light (vertically) to top to bottom. In this investigations, the laser light exposed SHP growth medium, suppressed the crystal growth compared to the crystal grown at room temperature (29ºC). In the second method, SHP crystals were grown in the exposing sunlight (40ºC) medium; the growth rate was partially reduced. Sodium bromate, silver halide and silver bromide crystals were grown in solution and gel methods at exposure of light in to the growth medium. It was noted that the light might affect the crystal growth (reduction of nuclei)[5]. In the second method, the nucleation rate was reduced[6-8]. Laser-exposure time was one month. In the sunlight exposures SHP crystal growth medium, few crystals were observed; nucleation rate was reduced but not fully. The exposure time was 2 months.

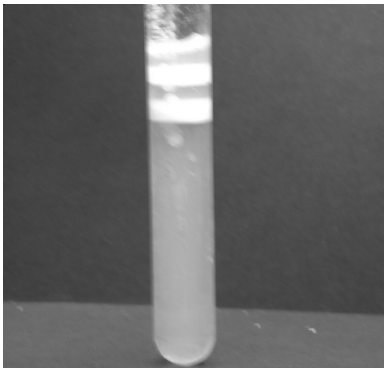

Fig. 1. SHP crystal growth in Single-Diffusion method (Test tube)

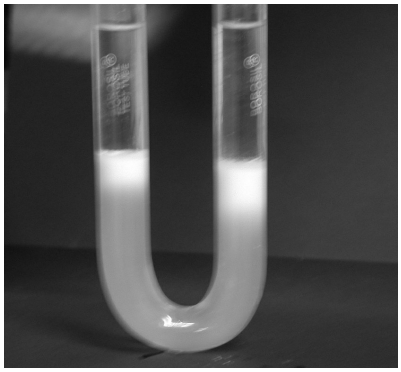

Fig. 2. SHP crystal growth in DDM-U tube

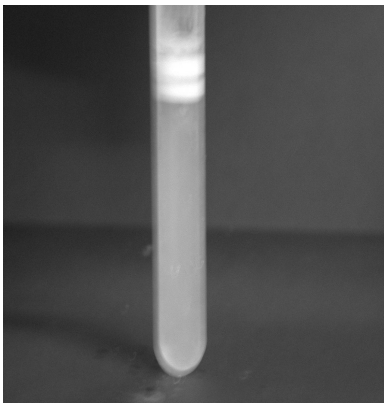

Fig. 3. SHP crystal growth in laser exposed SDM method

Fig. 4. SHP crystal growth in laser exposed (Two limbs) medium in DDM-U tube

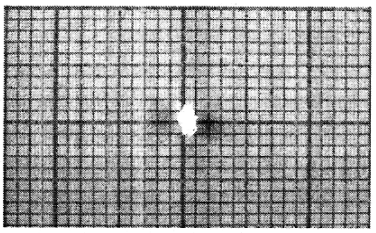

Fig. 5. Harvested SHP crystal in SDM (3 × 1.5 × 2 mm)

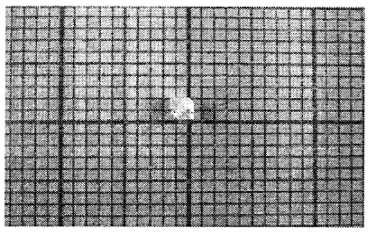

Fig. 6. Harvested SHP crystal in DDM (2.5 × 2 × 2 mm)

Crystal analysis

Thermogravimetric and differential thermal analysis (TGA and DTA) of SHP crystals: The TGA and DTA of SHP crystals were carried out by STA 11500-PLTS instruments. The SHP crystal of 2.439 mg sample was taken to the TGA process. The TGA was started from room temperature to 1000°C by heating at a constant rate. The Fig. 7. Shows the TGA and DTA graph of SHP- crystals. The % of weights present in the SHP sample at a particular temperature was tabulated in the Table-3[9].

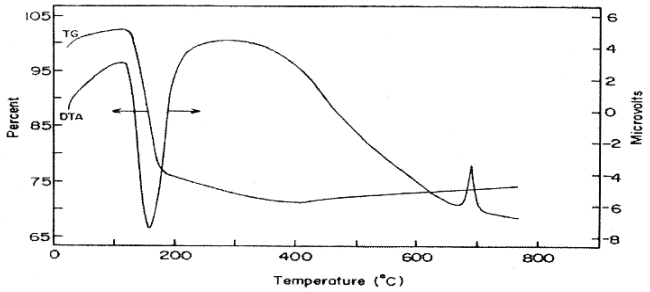

Fig. 7

TABLE-3
THERMAL ANALYSIS OF SHP CRYSTALS

Points	TGA		DTA (°C)
	Temperature (°C)	SHP crystal present (%)	
1	35.00	100.000	128.47
2	131.50	101.240	182.53
3	199.76	74.950	249.77
4	452.24	67.941	669.10
5	850.00	67.900	691.28

The TGA of SHP crystals were anhydrous up to 850°C. Here after the remaining sample is stable up to the end of the analysis.

The expected chemical reactions

$$SrHPO_4 \cdot xH_2O \rightarrow SrHPO_4 + xH_2O \text{ (Vapour)}$$

$$2SrHPO_4 \rightarrow Sr_2P_2O_4 + H_2O \text{ (Vapour)}$$

$C_2P_2O_7$ is stable compound with respect to the temperature up to 1230ºC (melting point). The SHP crystals were decomposed and 69.9 % of the sample was stable.

Etching study of SHP crystals: A well-grown SHP crystal was immersed in HCl solution at desired concentration. The dissolution of SHP crystal depends upon the etch ant concentration, temperature and crystal morphology, etching time etc. The etch pits are shown in Fig. 8.

Fig. 8. 1N, HCl-as etch ant, Etching time was 5 min at room temperature (301K)

Scanning electron microscopy study of SHP crystals: A well-grown SHP 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 *ca.* 250 times. SEM acceleration voltage was 25000 volts and kept the sample in highly vacuumed. 18200 micrometer working distance and monochromatic color mode were employed. 200 µm focusing of SHP crystal SEM is shown in the Fig. 9.

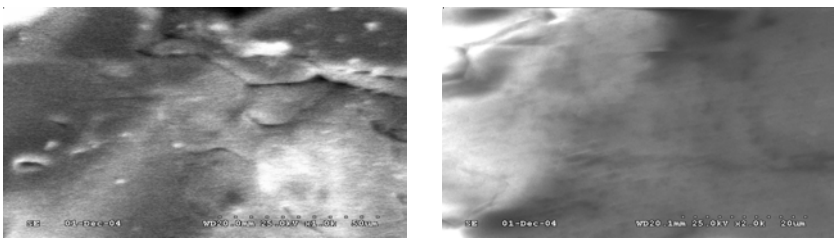

Fig. 9

X-ray diffraction of SHP crystal: The XRPD results revealed the crystalline property of crystal. The XRPD pattern and diffraction indices of the SHP crystals were recorded. Using the programme (Proszki) calculates the lattice parameters of the SHP crystal.

1H	-3.	1.	-4.	*	10.00	S	-3.38	9.10	2.70	**S	-2	0.79	2636.5
2H	-2.	1.	-5.	*	10.59	S	12.97	10.73	-1.05	**S	-1	0.75	1819.2
3H	-4.	1.	-3.	*	10.17	S	-20.14	7.80	6.67	**S	1	0.72	412.8
4H	-4.	1.	-4.	*	11.38	S	-12.58	9.53	6.56	**S	-1	0.75	1394.4
5H	-1.	0.	-6.	*	11.67	S	25.26	9.19	8.00	**S	1	0.87	4049.4
6H	0.	0.	-6.	*	11.47	S	35.97	10.46	4.08	**S	2	0.80	3206.0
7H	-2.	1.	-6.	*	12.37	S	16.63	12.09	-0.23	**S	1	0.80	11234.1
8H	-4.	2.	-4.	*	11.91	S	-9.79	13.59	-5.82	**S	1	0.83	13123.8
9H	-1.	1.	-6.	*	11.85	S	26.61	13.03	-4.21	**S	1	0.88	1140.9
10H	-4.	-2.	-2.	*	9.86	S	-43.00	-8.36	54.71	**S	1	0.75	17711.2
11H	-1.	-3.	-4.	*	9.94	S	17.37	-9.01	56.58	**S	3	0.75	28197.4
12H	-4.	-3.	-3.	*	11.67	S	-32.09	-9.59	62.50	**S	-2	0.66	1967.7
13H	-3.	-3.	-4.	*	11.49	S	-11.35	-8.21	58.57	**S	1	0.66	582.6
14H	0.	-4.	-5.	*	12.51	S	34.75	-5.87	53.85	**S	-1	0.72	2245.1
15H	-4.	-2.	-4.	*	11.90	S	-19.11	-3.32	45.32	**S	2	0.67	24786.3
16H	-2.	-2.	-4.	*	9.54	S	1.93	-5.39	46.08	**S	1	0.72	15616.1
17H	-2.	-2.	-3.	*	8.10	S	-7.34	-10.15	55.01	**S	-1	0.72	1244.5
18H	-3.	-2.	-2.	*	8.25	S	-35.75	-12.20	60.50	**S	2	0.70	1817.7
19H	-1.	4.	-3.	*	10.04	S	20.53	28.51	-55.15	**S	2	0.88	8445.4
20H	-2.	4.	-2.	*	9.76	S	-2.02	27.31	-51.90	**S	1	1.05	21079.8
21H	-3.	5.	1.	*	11.90	S	-43.69	29.79	-53.96	**S	1	1.09	8956.4
22H	-3.	5.	-1.	*	11.90	S	-20.12	29.20	-52.26	**S	1	1.14	8967.8
23H	-2.	5.	-3.	*	12.25	S	7.61	30.13	-53.93	**S	1	1.02	21325.2
24H	-2.	5.	-2.	*	11.47	S	-0.90	31.81	-59.61	**S	1	1.17	694.0
25H	-1.	4.	-1.	*	8.45	S	0.84	33.78	-73.19	**S	1	1.12	22465.5

No	S	H	K	L	Dev-Ang	dTh	dPh	dCh	0.0093594
1	H	-2.999	1.007	-4.003	0.0757	-0.006	-0.013	0.074	0.0007065
2	H	-1.999	1.001	-5.002	0.0211	-0.002	-0.012	0.018	0.0002248
3	H	-4.000	0.993	-3.001	0.0819	0.003	-0.020	-0.079	0.0007233
4	H	-4.000	1.000	-4.001	0.0109	-0.002	-0.011	-0.003	0.0001326
5	H	-0.999	-0.003	-5.999	0.0329	0.003	-0.018	-0.028	0.0003606
6	H	0.001	-0.005	-5.990	0.0476	0.019	-0.020	-0.043	0.0010464
7	H	-2.000	0.998	-6.001	0.0226	-0.001	-0.008	-0.021	0.0002412
8	H	-4.002	2.009	-4.002	0.0764	-0.012	0.012	0.075	0.0009725
9	H	-1.000	1.001	-6.002	0.0124	-0.005	-0.005	0.011	0.0002521
10	H	-3.998	-2.004	-2.001	0.0486	0.000	-0.029	-0.044	0.0004099
11	H	-1.000	-2.992	-4.006	0.1106	0.000	0.037	0.107	0.0009394
12	H	-4.001	-2.997	-3.003	0.0351	-0.001	-0.011	0.034	0.0003537
13	H	-2.994	-2.998	-3.990	0.0425	0.020	0.001	-0.042	0.0010662
14	H	-0.003	-3.997	-5.005	0.0578	-0.002	0.063	0.033	0.0006273
15	H	-4.000	-2.000	-3.998	0.0161	0.003	0.014	-0.011	0.0002309
16	H	-2.001	-2.002	-3.996	0.0523	0.004	0.020	-0.050	0.0004614
17	H	-2.005	-2.007	-3.002	0.0712	-0.015	0.039	-0.065	0.0008623
18	H	-3.002	-2.005	-2.001	0.0525	-0.009	-0.002	-0.052	0.0005692
19	H	-1.004	3.991	-3.005	0.1136	0.007	-0.024	-0.112	0.0010373
20	H	-1.999	4.003	-2.000	0.0272	-0.005	-0.002	0.027	0.0003260
21	H	-3.003	4.999	1.003	0.0405	-0.002	0.034	-0.031	0.0004221
22	H	-3.000	5.001	-0.999	0.0141	0.000	0.016	0.007	0.0001445
23	H	-1.999	5.003	-3.001	0.0257	-0.005	-0.010	0.025	0.0003557
24	H	-1.998	5.001	-1.999	0.0216	0.000	0.003	0.022	0.0002118
25	H	-1.000	3.999	-1.000	0.0046	0.002	-0.007	-0.002	0.0000976

Reciprocal axis matrix			Direct axis matrix		
-0.076370	0.020677	0.056977	-7.659392	-5.683681	-3.047903
-0.056718	0.022057	-0.074082	2.150183	2.314292	-9.716050
-0.030411	-0.093093	-0.005037	6.504329	-8.458022	-0.559366
Niggli-values			Sigma direct axis matrix		
100.2602	104.3809	114.1573	0.002763	0.001096	0.001835
-0.1540	-0.0416	-0.0092	0.005858	0.002323	0.003891
			0.004837	0.001918	0.003212
Cell parameters			Sigma cell parameters		
10.0130	10.2167	10.6844	0.0023	0.0039	0.0033
90.0808	90.0223	90.0052	0.0285	0.0239	0.0290
-0.001411	-0.000389	-0.000090	0.000497	0.000418	0.000507
Volume=	1093.0154			0.5950	

The lattice parameters are a = 10.0130 Å, b = 10.2167 Å, c = 10.6844 Å, α = 90.0808°, β = 90°, γ = 90.0052°. From this data confirmed the SHP crystal system is triclinic[10,11].

Conclusion

The SHP crystals were grown in the room temperature, out side the laboratory-sun light exposing medium and laser exposed medium. It is found that the SHP crystal nucleation rate reduced more in the laser medium than the sunlight exposed medium. Nucleation rate is due to variation of super saturations. FTIR-spectrum gave the functional group frequencies of SHP crystals. These results were recorded and compared with the reported values. Chemical etching was done at room temperature (302 K) it finds the grown crystal defects. SEM analysis were done, it reveals the surface morphology of SHP crystal. TGA/DTA analysis results were discussed the decomposition temperature, % of weight loss of the grown crystal were recorded. SHP lattice parameters were calculated by XRD.

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