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In vitro studies on crystallization of SeMHP and strategies for nucleation reduction

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Abstract. **Naturally many types of crystals grow in our human body. Especially different crystals or minerals are deposited in human urinary tracts. These crystals are named as octacalcium phosphate (OCP), calcium hydrogen phosphate (CHP), hydroxyapatite (HAP), magnesium hydrogen phosphate (MHP) etc. The SeMg-HPO_4 crystals are also known as Selenio–Newberryite crystals. The main reasons for the formation of crystals are due to the increased concentration of magnesium and phosphate ions in the human urine. In the present study, SeMHP crystals are grown in silica gel medium at various concentrations and different pH values in sun light medium and laser exposed medium. It has been observed that the nucleation rate was partially and completely reduced in sunlight and laser exposed medium, respectively. During the growth period, Liesegang rings were observed. Characteristic studies of SeMHP crystals such as FTIR, AAS, SEM, XRD, TGA/DTA and etching were done. The results are compared with the reported values and discussed in detail.**

Keywords. **Inorganic compounds; crystal growth; sol–gel chemistry; thermogravimetric analysis; crystal structure.**

1. Introduction

In the modern world, the growth of high quality single crystal plays an important role in pharmaceutical, organic and chemical industries etc. Artificial crystal growth is important to identify the properties of the material and provides information about the structure, composition and physico-chemical properties of the grown crystals.

Lots of minerals are present in all living mammal's body at different degrees of concentration. When the body fluid gets supersaturated, crystallization (Dieppe and Calver 1986) takes place automatically which have beneficial as well as pathological effect in the human body. The beneficial role of crystallization is bone and teeth formation, which contains micro crystals of hydroxyapatite, and helps in our sense of balance and dynamic nature i.e. depends on small calcite crystal present in the inner ear. Kidney stone (KS) or renal stone (RS), is one of the pathological effects of crystallization and is a huge painful urological disease (Arthure and Obst 1953; Sutor 1989; Hess and Kok 1996). The urinary tract or system consists of kidneys, ureters, bladder and urethra. Kidney removes extra water and waste from the blood in the form of urine. Kidney helps to maintain the normal mineral contents of the blood. Naturally, urine has some chemicals known as inhibitor that restrict the crystal formation. Increase in mineral value decreases the level of inhibitors thereby leading to stone formation (Henisch 1988). If the size of crystal is too small, it will travel through the urinary tract and excreted in urine without pain or notice. If the stone size is large, it produces a lot of pain and side effects. Kidney stones are made of varying chemical compositions. Generally it contains magnesium and calcium in combination with either oxalate or phosphate. The kidney stone occurs most frequently in men compared to women and it occurs in the age group of 20 to 50 years (Alexander and Honson 1949; Eitel 1954; Gilman 1958; Yean *et al* 1961; Henisch *et al* 1965; Corns 1983). Selenium magnesium hydrogen phosphate crystal belongs to one of the kidney stone compositions. These crystals are grown artificially by single diffusion method.

2. Experimental

Selenium magnesium hydrogen phosphate crystals are grown by single diffusion method. The silica gel, also known as water glass, was used in the present work as an intermediate growth medium. SMS (AR-sodium meta silicate powder) was added to the double distilled water in the ratio of 1 : 1, mixed and stirred well and kept undisturbed for a few days to allow sedimentation. Then the clear top solution was filtered and stored in a light protected glass container. This is known as a stock solution.

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Table 1. Growth parameters of SeMHP crystals.

SMS gel density (g/cc)	OPA concentration (N)	Gel + H_3PO_4 pH value	Gel setting time (h)	Supernatant concentration ZnSe + $MgCl_2$ (M)	Nucleation observed (h)	Growth period (days)	Types of crystal observed/harvested crystal size
1·04	0·5	6·5	24	1 : 1	16	70	Many poly crystals
		6·9	1	-do-	20		
		7·2	34	-do-	100		
	1	6·5	14	-do-	10	80	Dendrite crystals
		7·0	1	-do-	06		
		7·5	28	-do-	64		
1·05	0·5	6·4	34	-do-	10	60	Liesegang rings are observed
		6·9	16	-do-	12		
		7·3	48	-do-	38		
	1	6·5	16	-do-	24	65	Single crystals
		6·8	1	-do-	10		
		7·3	24	-do-	64		

Figure 1. Growth of SeMHP crystal within laboratory environment (SDP).

The gel densities of 1·04 and 1·05 g/cc were used. Simple test tubes of 25 mm diameter and 150 mm length were used. The concentrations of orthophosphoric acid used in the experiments were 0·5 N and 1 N and the concentration of supernatant solution (ZnSe + $MgCl_2$) varied from 0·5 M to 2 M (Alexander 1949; Eitel 1954). One of the reactants, orthophosphoric acid, was mixed within the gel solution. The gel solution was taken as one third of its volume of the test tubes and after the gel set, the supernatant solution was added slowly along the sides of the test tubes. ZnSe + $MgCl_2$ diffused through the gel medium, which contained orthophosphoric acid. The chemical reaction took place which led to the growth of $SeMgHPO_4$ crystal (Sundaramoorthi *et al* 2007a, b).

Figure 2. Growth of SeMHP crystal SDP within the sunlight exposed medium.

The chemical reaction was

$$Se^{2+} + Mg^{2+} + HPO_4^{2-} + 2H_2O \rightarrow SeMgHPO_4{\cdot}2H_2O + \text{byproducts.}$$

3. Results and discussion

The $SeMgHPO_4$ crystals are grown in three different growth faces by applying various growth parameters. Figures 1–3 represent three different growth columns, respectively. Table 1 gives the growth parameters of $SeMgHPO_4$ crystals and the bold letters show the optimum growth para-

meters. Among them, the laser exposed (semiconductor diode laser source, wavelength of laser is 7300 Å, 20 mW laser power passed continuously with using SMPS power supply) growth medium shows better nucleation reduction and no crystals were formed, because of the inability to attain supersaturation as shown in figure 4. In sun light exposed medium partial nucleation was observed, since exposure of sunlight to the growth medium was (During sunlight exposure, the kinetic energy of growth solution increases since it was unable to attain continuous supersaturation) only in day time i.e. 8 h per day and the growth column is as shown in figure 3, growth period was seven months.

3.1 *FTIR spectral analysis of SeMHP crystal*

SeMHP–FTIR spectrum was recorded by using SHIMADZU FTIR-435 instrument. The FTIR spectrometer has KBr pellets sample holder and KBr detector. The KBr pellet samples were used and the absorption frequencies range from 600–4000 cm^{-1}. The FTIR spectrum is as shown in figure 6. The spectrum was interpreted with the earlier reported values (Yean *et al* 1961; Corns 1983). The absorption bonds, absorption frequencies and % of transmittance were compared with the reported values. The values are tabulated in table 2.

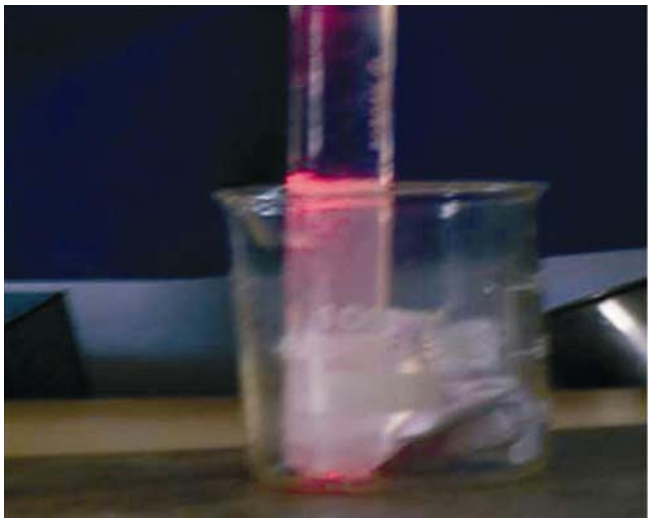

Figure 3. Growth of SeMHP crystal within laser exposed medium in SDP.

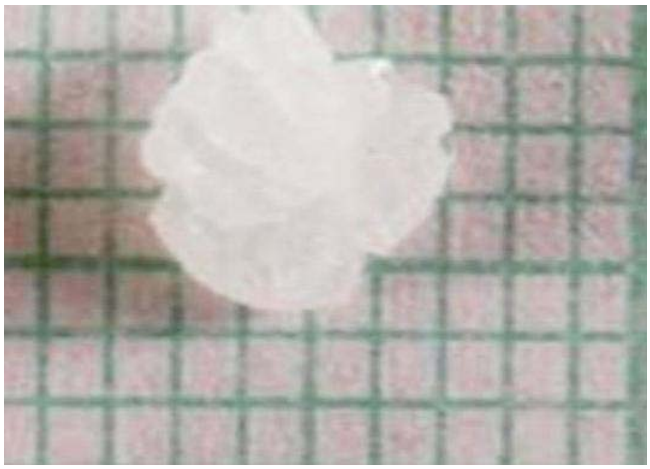

Figure 4. Harvested SeMHP crystal in SDP.

3.2 *Thermogravimetric (TGA and DTA) analysis of SeMHP crystal*

The TGA and DTA of SeMHP crystals were carried out by STA 11500-PLTS instruments. The MHP crystal of 5·487 mg sample was taken to the TGA process. The TGA was started from room temperature to 900°C by heating at a constant rate. Figure 7 shows the TGA and DTA graph of SeMHP crystals (Sundaramoorthi *et al* 2007a, b). The % of weights present in the SeMHP sample at a particular temperature was tabulated in table 3.

3.3 *Etching study of SeMHP crystal*

A well-grown SeMHP crystal was immersed in HCl solution at a desired concentration. The dissolution of SeMHP crystal depends upon the etchant concentration, temperature, crystal morphology, etching time etc. The etch pits were photographed. Figure 8 shows the etch pits of SeMHP crystal (Gilman *et al* 1956, 1958; New Kirk 1962). The etch pit patterns are observed in spirals, dendrites, vallies and strights.

3.4 *Scanning electron microscopic studies of SeMHP crystal*

A well-grown SeMHP single crystal was selected for the investigation of surface morphology of the grown crystal

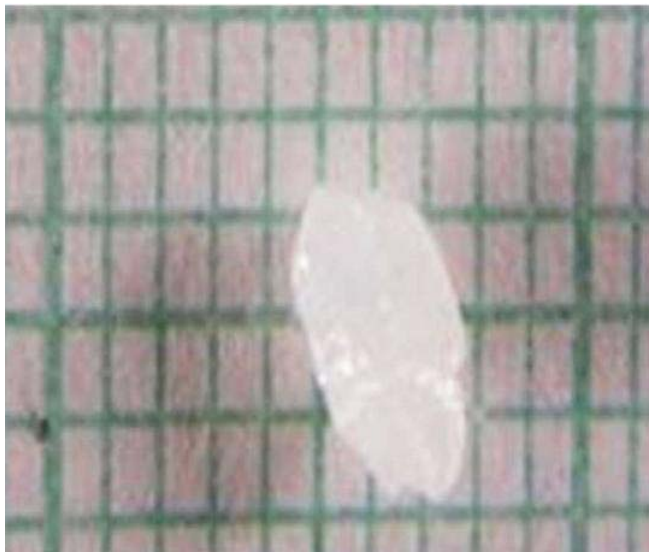

Figure 5. Harvested SeMHP crystal in SDP.

Table 2. Comparative table of FTIR–SeMHP crystal.

Sl. no.	Bonds/vibrations	Reported values (cm^{-1})	Observed values (cm^{-1})	% of Transmittance
01	Symmetric and asymmetric stretching O–H bond	3284	3267·2	6
02	H–O–H bond	1651	1608·5	16
03	Alkyle symmetric stretching	2852·3	2852·2	13·6
04	P–O–P asymmetric stretching bond	874	898·8	13
05	PO_4 bond	1000 to 1100	1020·3	3·8
			1064·6	4·8
06	Weak absorption of HPO_4^{2-}	2375	2345·3	17
07	Alkyle asymmetric stretching	1465·3	1508·2	15
08	Se, Mg–H in plane stretching	1240·1	1240·1	10
09	P=O stretching	1137	1168·8	5·6
10	Acid phosphate strong absorption	525	507·2	7

Table 3. Thermal decomposition of SeMHP crystal.

	TGA		
Points	Temperature (°C)	% of SeMHP crystal present	DTA (°C)
1	30	100	128·47
2	131·60	101·240	182·53
3	199·76	74·948	249·77
4	452·24	67·941	669·10
5	–	–	691·28

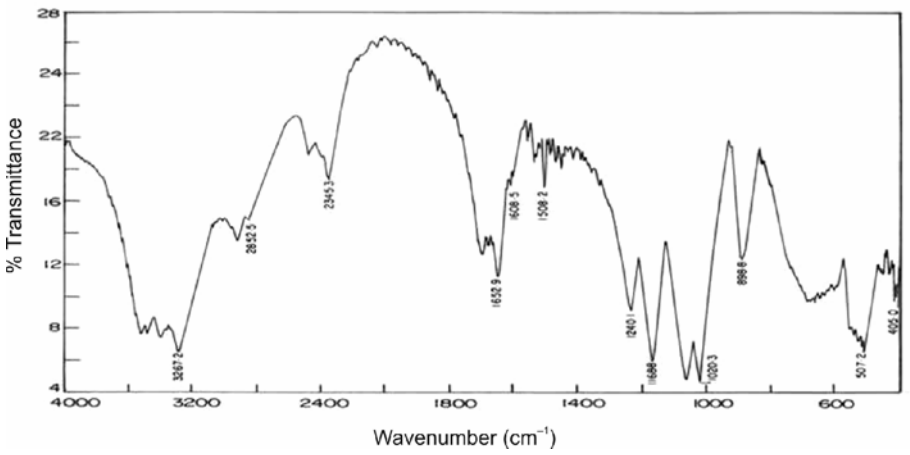

Figure 6. FTIR spectrum of SeMHP crystal.

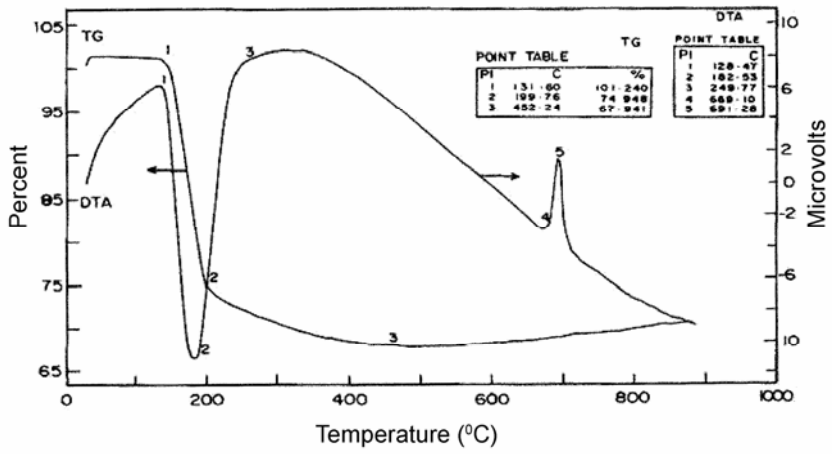

Figure 7. Thermogravimetric (TGA and DTA) analysis of SeMHP crystal.

by using SEM. The SEM photograph was obtained in the version S-300-I instrument. The sample named as VCA-600 was kept in lobe middle; the data size was 640 × 480 μm. The minor and major magnifications of SEM were about 250 times. SEM acceleration voltage was 25000 V and the sample was kept in a highly vacuum state. 18200 micrometer work distance was maintained and monochromatic colour mode was employed. Figure 9 shows the SEM pattern and surface morphologies of SeMHP crystal (Gates 1975; Taukamot 1983; Bethage *et al* 1987; Albon *et al* 1996; Sundaramoorthi 2007a, b).

Figure 8. Shows the etch pit pattern of SeMHP crystal [at 1N normality] of HCl solution as etchant, the etching time was 5 min in room temperature.

Figure 9. SEM photograph of SeMHP crystal.

4. Conclusions

The SeMHP crystals were grown at room temperature and exposed to sunlight and laser medium. It was found that SeMHP crystal nucleation rate was reduced fully in laser exposed medium than the sunlight-exposed medium, which is due to variation of supersaturation (low power laser light may apply through endoscope cable via the exposed urinary tract to avoid renal stones). FTIR spectrum recorded the functional frequencies of SeMHP crystal constituents. These results were recorded and compared with the reported values. Chemical etching was done at room temperature, which revealed the grown crystal defects. SEM analysis was also done to analyse the surface morphology of SeMHP crystal. The decomposition temperature and percentage of weight loss of the grown crystal was recorded by TGA and DTA spectrum.

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