

## Growth and Characterization Studies of $\text{SeMnHPO}_4$ Single Crystal in Agar-Agar Medium at Ambient Temperature

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**Abstract.**  $\text{SeMnHPO}_4$  (selenium manganese hydrogen phosphate) crystals are grown in agar-agar medium at various concentrations of ortho-phosphoric acid and supernatant solutions in single diffusion process. The pH plays an important role in the formation of  $\text{SeMnHP}$  crystals. The characterizations of grown crystals are studied by FTIR, SEM, XRD and etching. The results are discussed and compared with the reported literature.

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### 1 Introduction

SeHP (selenium hydrogen phosphate) and BaHP (barium hydrogen phosphate) are grown in silica gel medium at room temperature [1-2]. In the present investigations, single crystals along with the trace elements or mixed crystals are grown in agar-agar medium at different growth parameters, which contain one major element (Phosphate), and two minor or trace elements (Selenium, Manganese).  $\text{SeMnHP}$  is a single crystal which typically represents the biological crystals formed in the human urinary tracts called renal stones. A normal human body weighing 70 kg contains about 12–25 mg Mn. It is distributed throughout the body tissues such as body fluids, bones, kidney, liver, pancreas and pituitary contain more Manganese in comparison with other tissues will cause side effects. Manganese is present naturally in many foods such as spices, sea foods, cereals, grains and green leafy vegetables. There are some evidences that Manganese is essential for the growth of animals, especially for the normal skeletal growth. Manganese has a vital role in the functioning of central nervous system. It is also essential for the normal reproductive functions. If the mineral level of

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the body fluid increases, automatic mineral deposition starts which leads to the development of renal stones along with other minerals.

Selenium is a mineral and an important nutrient to fight diseases like cancer and heart disease. Selenium is synergistic with vitamin E, meaning that the two work stronger together. Both are potent antioxidants that help to prevent or slow down aging and hardening of the tissues through oxidations. This trace mineral is essential to human body functions and can be found in every body cell, but especially in the kidneys, liver, spleen, pancreas, and testes. In males, approximately half of the body's Selenium concentrates in the testicles and parts of the seminal ducts around the prostate gland. Selenium serves as an antioxidant with glutathione peroxides to prevent damages by free radicals. It is involved in the metabolism of prostaglandins which are used by the body in various ways in different times and ages. The amount of Selenium provided by plant sources depends a great deal on the soil quality in which the plants are grown. Poor Selenium soil will yield plants that may not provide the correct levels of Selenium. Those who follow a vegetarian diet, particularly a vegan diet, must be extremely vigilant in making sure they consume enough Selenium in their daily diets. Some natural sources of Selenium are Brazil nuts, garlic, fish, red meat, and grains. Lobster, tuna, shrimp, oysters, fish, herring, liver, egg, ham, beef, bacon, chicken, lamb, veal, Brazil nuts, oats, brown rice, garlic, broccoli, wheat germ, whole grains, mushrooms, red grapes, and sesame seeds. Authors have done a series of experiments with agar-agar gel crystal growth medium at different pH values ranging from 5.5 to 11. One can obtain the periodic precipitation, Liesegang rings [3-4] of biological crystals named as HAP, Brushite, Struvite, BaMgHP, SrMgHP, *etc.*

## **2 Materials and Methods**

The dissociation of ortho-phosphoric acid system, equilibrium is used in the presence of various ions and pH values reported in [5]. Based on these results, the gel pH in the range from 4e to 10 has been used (Milwaukee QS-MN pH-600, packet digital pH-meter used for measurements) in which the  $\text{HPO}_4^{2-}$  ion dominates or alone exists. This decreases the possibility of the occurrence of SeMnP crystals during SeMnHP growth. The crystallization apparatus employed are glass test tubes of 22 mm diameter and 160 mm long for single diffusion process (SDP). The chemicals used are Excelar-Qualigens (E-Q) AR grade  $\text{MnCl}_2$ ,  $\text{SeCl}_2$  and E-Q, AR grade ortho-phosphoric acid (Sp.gr.1.88). The agar-agar is prepared and set as per the literature [6]. After the gel set, the supernatant mixture (selenium chloride, manganese chloride) at a required mole solution is slowly added along the walls of the growth columns (test tubes) over the set gel and tightly closed to prevent evaporation and avoid inclusions. Then the growth systems are allowed to react within the gel medium and the following chemical reaction takes place

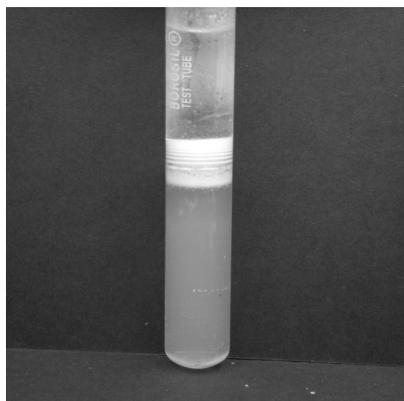


Figure 1. Growth of SeMnHP crystals within laboratory environment.

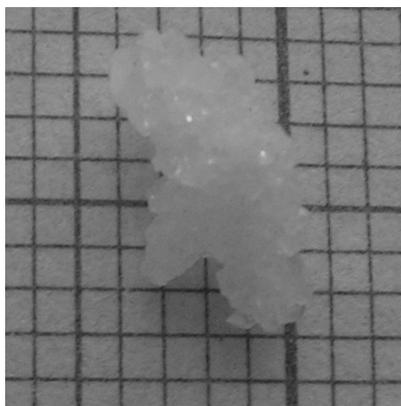
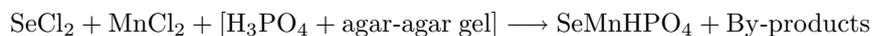


Figure 2. Harvested SeMnHP transparent crystal.



Ionic reaction is follows:



The growth columns of SeMnHP crystals and harvested SeMnHP crystal are shown in Figure 1 and Figure 2, respectively. The maximum dimension of the crystals obtained is  $3 \times 2.5 \times 2$  mm.

### 3 Characterization Studies of SeMnHP Crystals

#### 3.1 FTIR Spectral Analysis of SeMnHP Crystal

FTIR spectrometer having KBr pellets sample holder and KBr detector was used for the analysis. The KBr pellet samples were used and the absorption frequencies range from  $600$  to  $4000 \text{ cm}^{-1}$  [7-10]. The absorption bonds, absorption

Table 1. FTIR spectral analysis of SeMnHP crystal

Sample No	Composition/Bond	Absorption frequency	
		reported value, $\text{cm}^{-1}$	observed value, $\text{cm}^{-1}$
1	Selenium, Manganese and Hydrogen O-H symmetric, asymmetric (in plane)	3307 to 3471	3559, 3497, 3310
2	O-H out of plane	745	782
3	$\text{PO}_4$ group	1000 to 1110	1131, 1050
4	Selenium, Manganese with apatite group	600–1040 (high frequency)	587, 1086

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Figure 3. Etch photo of SeMnHP crystal at room temperature, HCl as an etchant, etching time – 10 minutes, etchants normality – 1.5N.

frequencies and percentage of transmittance were compared with the reported values. The values are tabulated in Table 1 which confirms the presence of SeMnHP crystal constituents.

### 3.2 Etching Study of SeMnHP Crystal

A well-grown SeMnHP crystal is immersed in HCl solution at a desired concentration. The dissolution of SeMnHP crystal depends on the etchant concentration, temperature, crystal morphology, etching time, *etc.* [1,11-12]. The etch pits are shown in Figure 3. The etch pits observed in the photo are cone pits, leaf pits and step pits.

### 3.3 Scanning Electron Microscopic Studies of SeMnHP Crystal

Well-grown SeMnHP single crystal is selected for the investigation of surface morphology by using SEM. The SEM photograph is made in the version S-300-I instrument. The sample named VCA-601 is kept in lobe middle; the data size is  $640 \times 480 \mu\text{m}$ . The minor and major magnifications of SEM are about 250 times. SEM acceleration voltages are 25 kV and the sample is kept in a high vacuum and  $18200 \mu\text{m}$  working distance and monochromatic color mode are employed.  $100 \mu\text{m}$  focusing of SeMnHP crystal SEM is shown in Figure 4. In the surface analysis of SEM picture of SeMnHP crystal, smooth, fine grain boundaries and few valley regions are observed [1,11-12].

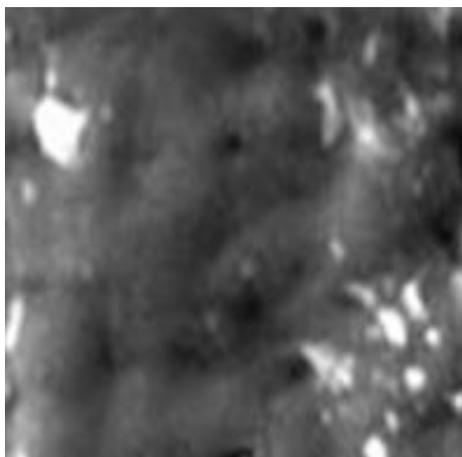


Figure 4. SEM picture of SeMnHP crystal.

### 3.4 X-ray Diffraction of SeMnHP Crystal

The single crystal XRD results revealed the crystalline property of grown crystal. The XRD pattern and diffraction indices of the SeMnHP crystals are recorded and using the programme (Proszki) the lattice parameters of the SeMnHP crystal are calculated. The lattice parameters are  $a = 11.38 \text{ \AA}$ ,  $b = 12.62 \text{ \AA}$ ,  $c = 15.68 \text{ \AA}$ ,  $\alpha = 90.46^\circ$ ,  $\beta = 90.11^\circ$  and  $\gamma = 90.32^\circ$ . The volume of the unit cell of the SeMnHP crystal is  $241.274 \text{ \AA}^3$ . From the above data it is confirmed that the grown SeMnHP crystal system is in triclinic symmetry [1].

## 4 Conclusion

The SeMnHP crystals are grown at room temperature and found optimum growth parameters. SeMnHP crystal growth columns and harvested crystal are photographed. FTIR-spectrum recorded the functional group frequencies of SeMnHP grown crystal constituents, these results are recorded, compared and confirmed the grown crystal constituents with the reported values. Chemical etching is carried at room temperature, which gives the grown crystal defects. SEM analysis is also done and it revealed the surface morphology of SeMnHP crystal. SeMnHP lattice parameters are calculated by single crystal XRD.

## References

- [1] P. Sundaramoorthi, S. Kalainathan (2007) *Asian J. Chem.* **19** 2783.
- [2] H.K. Henisch, J.M. Garcia-Ruiz (1986) *J. Crys. Growth* **75** 203.

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- [3] S. Kai, S.C. Muller (1983) *J. Chem. Phys.* **87** 806.
- [4] S.K. Arrora (1981) *Prog. Cryst. Growth Charact. Mater.* **4** 345.
- [5] J. Dennis, H.K. Henisch (1967) *J. Electrochem. Soc.* **114** 263.
- [6] H.K. Henisch (1965) *J. Electrochem. Soc.* **112** 627.
- [7] S. Joshi, J. Joshi (2003) *Cryst. Res. Technol.* **38** 817.
- [8] Yean-Chin Tsay (1961) *J. Urol.* **86** 838.
- [9] N.A. Curry, D.W. Jones (1971) *J. Chem. Soc. A* 3725.
- [10] C.M. Corns (1983) *J. Ann. Clin. Bio-Chem.* **20** 20.
- [11] K. Tasukamot (1983) *J. Cryst. Growth* **61** 199.
- [12] H.C. Gates (1975) Thirty years of progress in Surface Science, In: *Crystal Growth and Characterization*, North Holland.