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Barium Magnesium Hydrogen Phosphate Single Crystal Growth in Silica Gel Medium: Characterization Studies and Laser Irradiated Nucleation Reduction Process Strategy

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In the chemical reaction method, barium magnesium hydrogen phosphate (BMHP) crystals are grown in silica gel medium using different gel densities and various concentrations of orthoposphoric acid and supernatant solutions. The gel pH gives an important role in the formation of different H_3PO_4 species in the phosphoric system, the pH range in which HPO_4^{2-} ions dominates were considered, which in turn is necessary for the growth of BMHP crystals .The characteristics of well grown crystals are carried out by FTIR, TGA/DTA, SEM, XRD and etching.

Key Words: Renal stones, Barium magnesium hydrogen phosphate, Laser light, Calculi, Surface morphology, Growth, Parameters and Trace elements.

INTRODUCTION

Barium hydrogen phosphate (BHP) and strontium hydrogen phosphate (SHP) are grown in silica gel medium at room temperature[1,2]. The next approach is to grow mixed crystal in silica gel medium, which contains one major mineral (phosphate), one minor mineral (barium) and one inhibitor (magnesium). In this attempt, barium magnesium hydrogen phosphate (BMHP) is a mixed crystal and typically representative of the family of the biological crystal, which specifically formed in the human urinary tracts and called as renal stone. In BMHP crystal, barium is a toxic element, which may be absorbed in three ways. One is *via* air-by breathing. The average consumption rate is 1 μg/d. The second is *via* liquid-by liquid /water in take. The average consumption rate was 1-20 μg/L. The third one is *via* solid-by food intake. The average consumption of barium present is 600-900 μg/d. For a normal man, the barium consumption bar limit is 1240

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μg/d, which is the tolerance level. Various authors have done a series of experiments with silica gel at different pH values ranging from 5.5 to 11. One can obtained the periodic precipitation, Liesegang rings[3-5] of biological crystals named as hydroxyapatite (HAP), brushite, struvite, BMHP, *etc*.

EXPERIMENTAL

The dissociation of phosphoric acid system can be represented by three-dissociation equilibrium and the presence of various ions at various pH values are reported[6]. Because of these results, the gel pH in the range from 6 to 10 has been used (Milwaukee QS-MN pH-600, packet digital pHmeter are used for measurements) in which the HPO_4^{2-} ions dominates or alone exist. This decreases the possibility of barium magnesium phosphate (BMP) crystals occurring during the BMHP growth. The crystallization apparatus employed are glass test tube of 25 mm diameter and 150 mm long for single diffusion method (SDM) and thick walled 30 mm diameter and 180 mm long glass U tubes for double diffusion method (DDM). The chemicals used are Excelar-Qualigens (E-Q) AR grade $BaCl_2$ and $Mg(NO_3)_2{\cdot}2H_2O$ and E-Q, AR grade orthophosphoric acid (sp.gr. 1.75). The SMS gel or water glass are prepared as per the literature[7] .One of the reactants orthophosphoric acid was mixed with silica gel at desired gel density and elevated temperatures. After the gel set, the supernatant mixture (barium chloride + magnesium nitrate) at a required mole solutions is slowly added along the walls of the growth columns (test tubes, U-tubes) over the set gels and tightly closed to prevent evaporation. Then the growth systems were allowed to react within the gel medium and the following chemical reaction take place.

$$BaCl_2 + Mg(NO_3)_2{\cdot}2H_2O + H_3PO_4 + \text{Set gel} \rightarrow BaMgHPO_4 + \text{by products}$$

The following observations have been made in the present work.

1. The reaction starts immediately after the addition of supernatant solutions. But the nucleation are observed only after 10 h and the growth process took a period of 2-3 months for completion.

2. Fiber, dendrites crystals are observed along with Lies gang rings in the first half of the gel column from the top of the test tube.

3. Some well-developed single crystals are observed in the double diffusion growth columns (U-tubes) after 1 month. The growth processes were allowed for 6 months but the crystals size are not found to be increased.

4. The gel density above 1.07 g/cm^3 and with pH above 9 yielded no crystals, but mean time reaction takes place.

5. Some of the test tubes of gel density 1.03 g/cm^3 with pH around 7 and below 7 are allowed for the reactions to take place. After a period of 6 months, a less number of nucleation is observed near the bottom of the test tubes. Some of them grew in a needle and well transparent platelet crystals.

6. From the investigation, the optimum growth parameters of BMHP crystals are identified and reported in Tables 1 and 2.

TABLE-1
SINGLE DIFFUSION GROWTH PROCESS (REACTION TEST TUBES)
BMHP CRYSTAL GROWTH PARAMETERS

Gel density (g/cc^3)	Phosphoric acid concentration	Gel + H_3PO_4 pH value	Gel setting time	Supernatant concentration $BaCl_2$ + Mg $(NO_3)_2.2H_2O$ (M)	Nucleation observed (h)	Growth period days	Types of crystal observed & harvested crystal size
1.04†	0.5 N	6.5	24 h	1:2	10	60	Dendrite crystal
		6.7	6 h	1:2	16		
		6.9	0.17 h	1:2	24		
		7.2	**14 h**	**1:2**	**96**		
	1.0 N†	6.5	24 h	1:2	8	70†	Leaf like crystal
		6.8	**2 h**	**1:2**	**24**		
		7.0	1 h	1:2	36		
		8.2	48 h	1:2	48		
1.05‡	0.5 N	6.4	24 h	1:2	10	90	Single crystals
		6.7	5 h	1:2	12		
		6.9	**0.17 h**	**1:2**	**10**		
		7.3	48 h	1:2	48		
	1.0 N‡	6.5	24 h	1:2	13	75‡	(2.5 mm × 3 mm × 3 mm)
		6.8	**1 h**	**1:2**	**10**		
		7.0	12 h	1:2	24		
		7.3	48 h	1:2	72		

†Best crystal growth. ‡Optimum growth conditions.

7. An extension of the reaction period even up to 10 months did not improve the size of these crystals.

8. The growth columns (single diffusion, double diffusion) of BMHP crystals.

9. Some of the harvested BMHP crystals.

10. The maximum dimension of the crystals obtained is 3 mm × 5 mm × 6 mm.

Crystal analysis

FTIR spectral analysis: FTIR Spectrometer having KBr pellets sample holder and KBr detector are used for the analysis. The KBr pellet samples are used and the absorption frequencies range from 4000-600 cm^{-1}. Present results match with Socrater *et al.*[8]. The absorption bonds, absorption frequencies and percentage of transmittance are compared with the reported values. The values are presented in Table-3.

TABLE-2
DOUBLE-DIFFUSION GROWTH PROCESS (U-TUBES)
BMHP CRYSTAL GROWTH PARAMETERS

Gel density (g/cc^3)	Phosphoric acid concentration	Gel + H_3PO_4 pH value	Gel setting time	Supernatant concentration $BaCl_2 + Mg(NO_3)_2{\cdot}2H_2O$ (M)	Nucleation observed (h)	Growth period (days)	Types of crystal observed & harvested crystal size
1.03	0.5 N	6.0	40 h	1:2	25	96	Dendrite crystal
		6.5	**16 h**	**1:2**	**26**		
		6.9	0.25 h	1:2	28		
		7.0	24 h	1:2	104		
	1.0 N	6.1	36 h	1:2	19	90	Leaf like crystal
		6.7	**4 h**	**1:2**	**42**		
		7.2	5 h	1:2	66		
		8.0	48 h	1:2	88		
1.04†	1.0 N	6.0	44 h	1:2	30	80	Single, poly crystals
		6.6	**15 h**	**1:2**	**42**		
		7.0	0.33 h	1:2	44		
		7.4	68 h	1:2	78		
	2.0†	6.1	68 h	1:2	10	95†	(3 mm × 3.5 mm × 3 mm)
		6.9	**3 h**	**1:2**	**19**		
		7.0	2 h	1:2	22		
		7.3	18 h	1:2	92		

†Optimum growth conditions.

TABLE-3
FTIR SPECTRAL ANALYSIS OF BMHP CRYSTAL[9-12]

Composition/bond	Absorption frequency reported value (cm^{-1})	Absorption frequency observed value (cm^{-1})	Transmittance (%)
Barium, magnesium & hydrogen O-H symmetric, asymmetric (in plane)	3207-3477	3278	3245
O-H out-of-plane	745	695	32
PO_4 group	1000-1100	1022-1068	2843
Magnesium/apatite group	600-1010 (high frequency)	506-1022	28
C-C bond (undesired)	885	899	46

Thermal analysis: TGA and DTA of BMHP crystals are carried out by STA 11500-PLTS instruments. The BMHP crystal of 2.439 mg sample are taken to the TGA process. The TGA was started from room temperature to 1000 ºC by heating at a constant rate.

The TGA of BMHP crystals are anhydrous up to 850 ºC. Here after the remaining sample is stable up to the end of the analysis.

The expected chemical reactions:

$BaMgHPO_4 \cdot xH_2O \rightarrow BaMgHPO_4 + xH_2O$ (vapour)

$2BaMgPO_4 \rightarrow 2Ba + 2H.PO_4$ (vapour)

Barium is stable compound with respect to the temperature up to 1230 ºC (melting point). The BMHP crystals are decomposed 67.9 percentage and remaining 32.1 % of the sample is stable (Table-4).

TABLE-4
THERMAL ANALYSIS OF BMHP CRYSTALS

Points	TGA		DTA (ºC)
	Temperature (ºC)	BMHP 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

Etching: Well-grown BMHP crystals are immersed in HCl solution at a desired concentration. The dissolution of BMHP crystal depends upon the etchant concentration, temperature, crystal morphology, etching time *etc.*[13-16]. The etch pits are shown in Fig. 1. The etch pits observed in the photo are helical pits, spiral pits and step pits.

Fig. 1. Chemical etching of BMHP crystal at room temperature (28 ºC), HCl as an etchant, etching time was 5 min, etchants normality was 2 N

Scanning electron microscopy study: Well-grown BMHP single crystals are selected for the investigation of surface morphology by using SEM. The SEM photographs are made in the version S-300-I instrument. The sample named VCA-600 kept in lobe middle; the data size was 640 × 480. The minor and major magnification of SEM were about 250 times. SEM acceleration voltages are 25000 volts and the sample is kept in a high vacuum. 18200 μm working distance and monochromatic color mode are employed. 200 μm focusing of BMHP crystal SEM is shown in the Fig. 2 in the surface analysis of SEM-BMHP crystal, smooth, fine grain boundaries and few valley regions are observed[17-20].

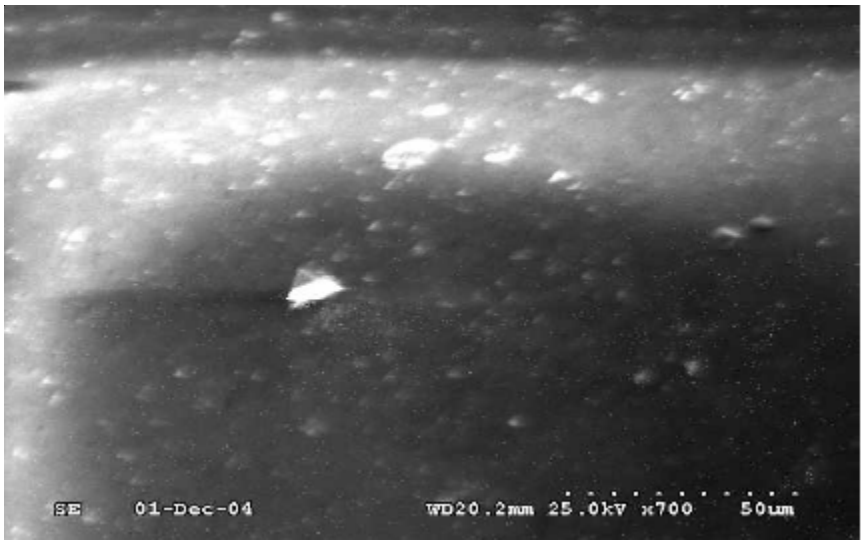

Fig. 2. SEM picture of BMHP crystals

X-ray diffraction of BMHP crystal: The XRD results revealed the crystalline property of crystal. The XRD pattern and diffraction indices of the BMHP crystals are recorded. Using the programme (Proszki) the lattice parameters of the BMHP crystal are calculated.

The lattice parameters are a = 10.0315 Å, b = 10.2169 Å, c = 10.6804 Å, α = 90.0614, β = 90.0767, γ = 90.0557. The volume of the unit cell of the BMHP crystal is 1094.6399 Å. From this data, one can confirmed the BMHP crystal system is triclinic[21,22].

Conclusion

The BMHP crystals are grown at room temperature and exposed to sunlight and laser medium. It was found that, BMHP crystal nucleation rate are reduced more in the laser medium than the sunlight-exposed

medium, which is due to variation of super saturation. FTIR-spectrum recorded the functional frequencies of BMHP crystal constituents. These results are recorded and compared with the reported values. Chemical etchings are done at room temperature (28 ºC), which revealed the grown crystal defects. SEM analyses are also done and it reveals the surface morphology of BMHP crystal. The decomposition temperature and percentage of weight loss of the grown crystal are recorded by TGA and DTA analysis. BMHP lattice parameters are calculated by XRD.

REFERENCES

1. P. Sundaramoorthi, S. Kalainathan and G. Kanchana, National Conference on Recent Trends in Material Science and Technology, Proceeding, p. 72 (2005).
2. P. Sundaramoorthi, S. Kalainathan and G. Kanchana, Tenth National Seminar on Crystal Growth, Proceeding, p. 31 (2005).
3. R.E Lesegang, *Naturewiss. Wochenschr.*, **11**, 353 (1896).
4. H.K. Hnisch and J.M. Garcia-Ruiz, *J. Crystal Growth*, **75**, 195 (1986).
5. H.K. Hnisch and J.M. Garcia-Ruiz, *J. Crystal Growth*, **75**, 203 (1986).
6. R.L. Pecsok, L.D. Shields, T. Cairns and I.G. McWillian, Modern Methods of Chemical Analysis, John Willy & Sons Inc., New York, pp. 438-442 (1976).
7. H.K. Henisch, Crystals in Gel and Liesegang Rings, Cambridge University Press, Cambridge, p. 11 (1986).
8. G. Socrater, Infrared Cha Group Friq, John Wiley, Chichester (1980).
9. E. Hatscheck, *J. Kollid*, **37**, 297 (1925).
10. Y.C. Tsay, *J. Urol.*, **86**, 838 (1961).
11. C.M. Corns, *Ann. Clin. Biochem.*, **20**, 20 (1983).
12. A. Hesse and D. Bach, in ed.: A. Rose, Stone Analysis by Infrared Spectroscopy, Urinary Stones, Clinical and Laboratory Aspects, University Park Press, Baltimore, pp. 87-105 (1982).
13. J.J. Gilman, J. Johnsion and G.W. Sears, *J. Appl. Phys.*, **29**, 749 (1958).
14. J.J. Gilman and W.G. Johnston, *J. Appl. Phys.*, **27**, 1018 (1956).
15. J.C. Fisher, Dissolutions and Mechanical Properties of Crystals, John Wiley & Sons, New York (1957).
16. J.B. New Kirk, Director Observation of Imperfection in Crystals, Inter Science Publishers, New York (1962).
17. K. Taukamot, *J. Crystal Growth*, **61**, 199 (1983).
18. H.C. Gates, Thirty Years of Progress in Surface Science, Crystal Growth and Characterization, North Holland (1975).
19. H. Bethge and J. Heydenreich, Electron Microscopy in Solid State Physics, Elsevier, Amsterdam (1987).
20. N. Albon and W.J. Dunning, Growth and Perfection of Crystals, Wiley, New York, p. 446 (1958).
21. G. Machennan and C.A. Reevers, *J. Acta Crystals*, **8**, 579 (1955).
22. N.A. Curry and D.W. Jones, *J. Chem. Soc. A*, 3725 (1971).

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