C H A P T E R - 1

A BRIEF SURVEY ON GROWTH OF SINGLE CRYSTAL IN GELS

1.1 INTRODUCTION :-

Crystals have fascinated men and women for many hundreds of years. The significance of that beauty for a technological society and for the development of scientific knowledge has been realised about a few decades ago. The basis of the beauty is now known to be such things as symmetry, structural simplicity, and purity. At one time natural specimens were the only source of large well formed crystals. Most of them were gems or museum pieces and so they were not readily available for scientific or technological purposes. Therefore methods for producing large crystals artificially by providing conditions similar to natural growth conditions in the laboratory were developed. And this provided a source of specimens for intensive scientific study which caused major developments to occur in inorganic chemistry, metallurgy, ceramics, geology and geophysics as well as the fast expansion of solid state physics especially when transistor and it's sister devices were invented.

The systematic production of artificial crystals i.e. crystal growth techniques are classified into four main groups with respect to the nature of the phase transition used.

They are as follows :

1) Solution growth

2) Melt growth

3) Vapour growth

4) Solid state growth.

Each of these methods have been subdivided into a number of growth methods to grow a variety of single crystals.

While crystal growth from aqueous, organic and salt solutions has been carried out for a quite number of years, it is only recently that a systematic work on crystal growth in gels has been undertaken. In recent years considerable attention has been drawn towards such work and the number of research centres engaged in such investigations has greatly increased. Modern technology badly needs perfect single crystals having various valuable properties such as semiconductors, piezoelectrics, dielectrics and so on. Single crystals are expected to be not only highly pure but also of high perfection of crystalline structure i.e. with least number of defects, deformation of growth forms, dislocations etc.

In the first place such criteria are satisfied with single crystals grown under the most favourable conditions. In this respect high melting and water insoluble substances are the most difficult to grow because at the melting temperature they react with silica or other container materials and are insoluble in water. The same is true, for substances that decompose on melting, especially those including volatile components. When gels are used the requirements for the crystallization process are less rigid and growth from gels at room temperatures leads to more perfect single crystals.

The use of gels to grow crystal has received sporadic attention since 1896 when R.E. Liesegang[1] first observed the periodic precipitation of slightly soluble salts in gelatin. These "Liesegang Rings" inspired many other chemists and also meneralogists to study other reactions in various colloids. Among the early workers were Hatschek[2], Holmes[3-5], Fells and Firth[6], Fisher and simons[7, 8], Horse and Donnay[9] etc.

Interest was revived for the method by stong[10] and soon after him Vand, Henisch and McCauley[11] published a note describing the full potential of growing single crystals in gels. Later Henisch et al[12] published detailed procedures of growing single crystals in gels. A variety of single crystal suitable for solid state experimentation can be grown in silica hydrogel[13-17] small cystals, including calcium tartrate[18], strontium tartrate[18], strontium tartrate,[18] calcium tungstate,[18] Lithium flouride,[18] Cuprous chloride[19,20], lead sulphide[21], maganese sulphide,[22] and lead hydroxy-iodide silver halides, II-VI semiconducting compounds[25], phosphates[26,27], molybdates[28,29], have been prepared by gel method. It is also advantageous in that gel method could be used to grow various sorts of crystals - ionic, organic, even metallic and semiconducting crystals - at ambient temperatures[30] the apparatus and methods are very simple.

The gel method can be fully explored because it has the following several important advantages over other crystals growth methods.

1. It is well known that crystals grown at room temperature should have lower concentrations of equilibrium defects than those grown at elevated temperatures. Crystals grown at ambient temperatures are free from strain often present in crystals grown by melt or from the vapour.

2. Crystals can be observed practically in all stages of growth.

3. All cystals are delicately held in the position of their formation in the gel, limiting their damage due to impact either on the bottom or sides of the container.

4. All nuclei are spatially seperate, minimizing precipitate-precipitate interaction.

5. The procedure can be conviniently used for mass production of crystals.

6. Crystals with different morphologies and sizes can be obtained by changing growth conditions.

7. The method is extremely simple and very economical since elaborate apparatus is not needed.

8. It is especially useful for crystals which by virtue of their low dissociation temperatures or low solubilities or both cannot be grown from low or high temperature techniques i.e. from the melt, the vapour or directly from solution.

1.2 CRYSTALS GROWTH:

The enormous flow of information related to crystal growth in gels has been divided in the following four basic parts, each one of them having special advantages.

1) Crystal growth by reaction.
2) Crystallization by complex dilution method.
3) Growth of crystals by chemical reduction.
4) Crystals growth by reduction of solubility.

1.2.1 CRYSTAL GROWTH BY REACTION:

Most of the work on crystal growth in gels has been done by reaction method. It has a special advantage of growing single crystals which are mostly insoluble or slightly soluble in water and which decompose before reaching their melting point. The requirements to grow single crystals by this method are :

i) The reactants used must be soluble in the solvent (usually water) and the product crystal must be relatively less soluble,

ii) The gel must remain stable in the presence of the reacting solutions and must not react with these solutions or with the product formed,

iii) Some solubility of the product crystal is required in order to grow crystals of any size.[31]

In this method two soluble reactants are allowed to diffuse through a gel where they react and form an insoluble or relatively less soluble crystalline product. In test tube technique one of the reactants is incorporated inside the gel and the other reactant is diffused into it. It slowly diffuses through gel and it reacts with the reactant already incorporated inside the gel and form the product of interest. The gel is used as the reaction medium in which the desired material is chemically formed.

Crystals grown by this method are $BaCO_3$, $CaCO_3$, $PbCl_2$, $CaSO_4$ etc.

1.2.2 GROWTH OF CRYSTALS BY CHEMICAL REDUCTION:

It is possible to grow metallic crystals by this method. The first report on the growth of metallic crystals by this method has been made by Hatschek and Simon[32-33] They grow gold crystals by adding 8% Oxalic acid solution over the gel containing gold chloride solution. Recently kratochvil et al[34] grew gold single crystals of triangular and hexagonal habits.

Crystals grown by this method are lead, copper and cuprous oxide.

1.2.3. CRYSTAL GROWTH BY COMPLEX DILUTION METHOD:

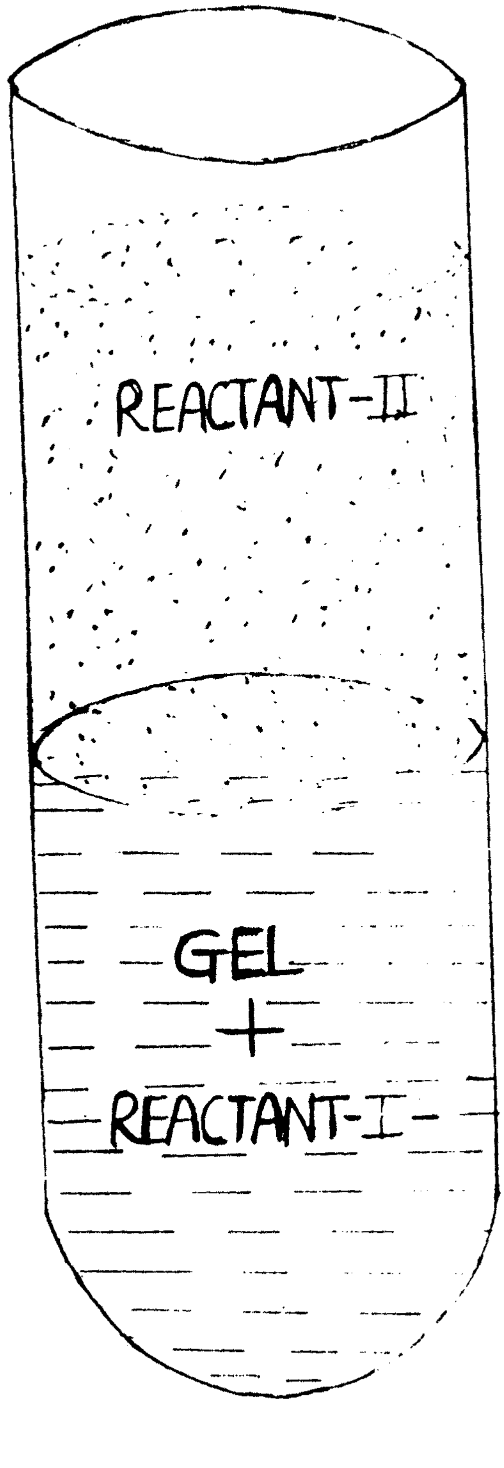
Crystal growth by complex dilution method was first reported by O'conner et al[19]. The essential feature of this method is the existence of some soluble material which itself increases the solubility of the material of interest in a non-linear fashion with concentration of the soluble material by complex formation in solution or by formation of a soluble double salt. In the crystals growth operation, the concentration of the combined solution is reduced by diffusion into the gel. Because the solubility of the material is a nonlinear function of the concentration of soluble material, it may reappear.

Using this method only mercuric sulphide, cuprous and silver halides and selenium have been grown.

1.2.4 CRYSTALS GROWTH BY REDUCTION OF SOLUBILITY:

This method is particularly suitable for growing single crystals of highly water soluble substances. Glocker and soest[35] first reported the growth of (ADP) ammonium di-hydrogen phosphate single crystals by this method. Firstly the saturated solution of the substance to be grown is prepared and incorporated with gel forming solution. After the setting of the gel, a solution which reduces the solubility of the substance is added over the gel to induce crystallization.

The schematic diagram of the gel growth technique is shown is fig. 1.



(Schematic Diagram Of Gel Growth)
Fig. 1

REFERENCE:

1. R.E. Liesegang
Chemishe Fernnurirking. Noch sep Von Vf Dusseldort, verlog von Ed. Liesegang. Phot. Archiv., v.21, 1986, p. 221

2. E. Hatschek
kolloid Zeitschrift, 8 (1911) 13.

3. H.N. Holmes
J. Phys. Chem. 21 (1917) 709.

4. H.N. Holmes
J. Franklin Inst. 184 (1917) 743

5. H.N. Holmes
Colloid Chemistry, V.1, J.Alexander ed. Chem. Cat. Co., New York, 1926, P-796-801

6. L.W. Fells and J.B. Firth
proc. Roy. Soc. London, 112A (1926) 468.

7. L.W. Fisher and F.L. Simons
Amer. Mineral 11 (1926) 124.

8. L.W. Fisher and F.L. Simons
Amer. Mineral 11 (1926) 200.

9. H.W. Morse and J.D.H. Donnay ,
Bulletin de la Societe 'Francaisede
Mineralogie, 54 (1931) 19.

10. C.L. Stong
Sci. Amer. 206 (1962) 155.

11. V. Vand, H.K. Henisch and J.W. Mccautey
Acta Cryst. 16 (1963) A 137.

12. H.K. Henisch, J. Dennis and J.T., Hanokal
J. Phys. Chem. Solids 26 (1965) 185.

13. Henisch H. K.
Crystal growth in gels
The Pennsylvania state University press (USA) 1970, 24.

14. Patel A.R. and Bhat H.L.
J. Crystal Growth (Netherlands), 12 (1972), 188.

15. Patel A.R. And Arora S.K.
J. Cryst. Growth (Netherlands), 18 (1973), 199.

16. Patel A.R. and Sangwalk,
J. Cryst. Growth (Netherlands) 23 (1974), 282.

17. Patel A.R. and Rao A.V.
J. Cryst. Growth (Netherlands)
37 (1977), 288 : 43 (1978) 251, 47 (1979), 213.

18. H. K. Henisch, J. Dennis and J. I. Hanoka
J. Phys. Chem. Solid S, 26 (1965) 493

19. J.J. O'Conner, M.A. Dipietro,
A.F. Armington and B. Rubin
Nature, 212 (1966) 68.

20. J.J. O'Conner and A.F. Armington.
J. Cryst. Growth. 1, (1967) 327.

21. W. Brenner, Z.Blank and Y. Okamato
Nature 212 (1966) 392.

22. A. Schwartz, A. Tauber and J.R. Shappirio
Mater. Res. Bull. 2 (1967) 375.

23. J. Dennis, H.K. Henisch and P. Cherin
J. Electro Chem. Soc. 112 (1965) 1240.

24. Suro S.K., H.K. Henisch, J.W. Faust.
J. Crystal growth 7, 277 (1970).

25. Blank, Z.
J. Crystal Growth 11, 255 (1971)

26. Blank, Z., W. Brenner, Y. Okamato
J. Crystal Growth 3/4, 372 (1968)

27. Brezina B., M. Havrankova
Mater. Res. Bull. 6, 537 (1971)

28. Cho. S.A., J.A. Gomez, R.Camisotti,
J.C. Chep
J. Mater. Sci. 12, 816 (1977).

29. Sreedharam Pillai, K., M.A. Ittyachen
J. Crystal Growth 39, 281 (1977)

30. C. Barta and J. Zemlicka
J. Cryst. Growth 10 (1971) 158.

31. A.F. Armington, J.J. O'Conner And M.A. Di Peitro
Air Force Cambridge Res. Lab. Rep. (U.S.A.) 325 (1967) 1.

32. E. Hatschek and Simon
Kolloid Zietschrift 10 (1912) 265

33. E. Hatschek and Simon
J. Soc. Chem. Ind. 31 (1921) 439

34. P. Krotochvil, B. Sprusil and M. Heyrovsky
J. Crystal Growth 3/4 (1968) 360.

35. D.A. Glocker and I.F. Soest
J. Chem. Phys.51 (1969) 3143.