# 2

# CRYSTAL GROWTH BY GEL TECHNIQUE

## 2.1 Introduction

Advances in modern solid state technology depend on the availability of good quality defect free crystalline materials. A good number of crystals have been grown by different gel techniques. All the methods used to grow the crystals have their own potentiality and constraints. In spite of the technological advancement in condensed matter physics, crystal growing is still an extremely difficult task requiring great expertise and skill. In this context the gel method has emerged as a convenient growth technique to grow several crystals having advanced technological application in the fields of optics, acousto-optics, optoelectronics and electronics.

All the techniques used for the growth of single crystals from melt, vapour and solution have their own inherent constraints. In the case of high temperature growth, the crystals have lattice disruption by pronounced thermal vibration during growth. The chances of lattice contamination by impurities are increased due to the increase in solubility of one of the components taking part in the growth at high temperature.

Defects and lattice strains are frequently incorporated into the growing matrix. In this context, the gel technique is found to be promising one, for getting good quality single crystals.

It was in 1896, the German chemist, Robert Edward Liesegang[1,2,3] first observed the periodic precipitation phenomenon. He first observed it, when a few drops of silver nitrate solution was introduced in gelatine gel impregnated with potassium dichromate. Periodic precipitation of infinite rings were observed. The mechanism of the phenomenon was well described by the German chemist Ostwald[4] at the end of nineteenth century. These discoveries[5,6] led to many investigators[7,8,9,10,11,12] concentrating their studies on colloids to observe this particular phenomenon. Loyd[13] has given a comprehensive review on the early developments of the ring phenomenon.

The utilisation of gel as a medium of crystal growth was put forward by Fisher and Siemen[14,15,16] in 1926. However it did not evoke much interest of crystal growers and remained as an unused work till 1962. The fast developments in the semiconducting materials during the second half of this century prompted the search for new intelligent materials. The increased interest in crystal growth led scientists to turn to the less noticed gel technique who realised its capability and advantage in generating perfect defect free crystals. The reports describing the growth of crystals appeared frequently in popular journals during this period[17,18,19,20,21]. The method became very popular due to the pioneering work of Henish H.K.[22] who gave an authentic and narrative record of this method. Following him, number of investigators have used this elegant and relatively easy method for growing perfect or defectless crystals. Nowadays this method has been employed to grow not only the inorganic crystals but also to grow biological crystals in vitro because of its resemblance with biological environment[2].

## 2.2 Advantages of gel technique

There are several well-known and well-established methods for crystal growth, but of all techniques of crystallisation at ambient condition, the gel technique hold the greatest promise. This is due to several advantageous characteristics of the technique:

The crystals can be observed practically in all stages of growth due to the action of gel as a transparent crucible.

The gel medium prevents the convection currents and turbulence considerably and thus the crystals formed are defect free or perfect in nature.

The gel medium remaining chemically inert and harmless, the gel framework acts like a three dimensional crucible in which the crystal nuclei are delicately held in the position of their formation and growth, thereby preventing damage due to the impact with either the bottom or the walls of the container. It forms three-dimensional structure by entrapping water.

Thermodynamic considerations reveal that, as the growth is happening at ambient temperature, the grown crystals would have less defects and are nearly perfect in nature.

The gel being soft and porous, yields mechanically to the growing crystals.

Since the gel reduces, in effect, the speed of chemical reagents, crystals could be made to grow to much larger sizes than if, they were formed by a similar reaction in water or in molten stage by decomposition process[23]

The gellation structure provides an ideal medium for the diffusion of reacting ions and can be used to keep the reacting ions separated until reaction is desired. Concentration of the reactants can be easily varied.

The nuclei are distributed individually in the medium and thereby the effects of precipitate interaction are drastically diminished.

The crystal grower can control diffusion rates and nucleation probability and thus design his own crystallisation equipment for different size and morphology of different crystals. The technique is highly economical when compared with other methods. The grown crystals can be harvested easily without damaging the crystal faces. It yields good quality crystals with less expensive equipment. The technique is widely used by several investigators to grow crystals having a variety of properties.

However the quality of the crystals grown in gel is good but the size is invariably small compared to other methods.

## 2.3 The structure and properties of gel

The gel is defined as a highly viscous two component semisolid system rich in liquid and having fine pores. These fine pores may allow the free passage of electrolytes and sustain nucleation. The gel medium works as a 'Smart' material ie, sensitive to the minutest changes in the ambience. Gels are broadly divided into two: organic and inorganic. If water is in the place of liquid it is called hydro gel.

The various types of gels used in crystal growth experiments are hydrosilica gel (sodium meta silicate), agar-agar gel, carbohydrate polymer gelatin gel (resembling protein structure), clay gel, soap fluid, poly-acrylamide, hydroxide in water, oleates, stereates etc. The silica gel made out of sodium meta silicate (SMS) is often used because of its easy availability and better performance in growing many crystal compounds[24,25]. In some particular cases organic gels are preferred[26,27] and the selection of the gel depends entirely on the nature of the electrolytes involved[28].

## 2.4 Preparation of hydrosilica gel

The water glass (sodium meta silicate) powder of AR grade is dissolved in doubly distilled water and by changing the hydrogen ion concentration (pH) of the solution, the desired gel can be prepared. The pH factor is the important parameter, which determines the rate of polymerisation and the speed of gel setting[29]. For maintaining

the acidity or the hydrogen ion concentration, an acid in requisite concentration is added to the system. During gellation the pH of the mixture varies and the gellation period varies from few minutes to hours or days. One can adjust only the initial pH of the mixture, the subsequent changes are not easily monitored and controlled. For growing the crystals of a good number of materials, the pH between 6-8 are found suitable; however the minute changes in the ambience affect the habit of the crystals. Acids commonly used to acidify the gel are nitric acid, hydrochloric acid, tartaric acid, acetic acid, oxalic acid, selenous acid etc. It is observed that the fresh gels between a pH range of 6-8 are highly transparent in nature[30,31]. Ageing hardens the gel and decreases its transparency and easiness of diffusion.

The efficiency of the system mainly depends on the physical quality of the medium. If small bubbles may crippled into the medium during the gellation it will grow in size and become lenticular in size. This will diminish the efficiency of the system[32]; therefore great care has to be taken to prevent the entry of the air bubbles. After adjusting the pH of the mixture it is taken in the crystallisation vessels for polymerisation. Test tubes, U- tubes etc. are commonly used as crystallizers, the size and shape of which depend on the requirements of the crystalline materials[26,33]. The vessels are used as crystallizers and are kept under controlled thermal condition for proper setting. This actually enhances the efficiency of the system.

One of the most important factors affecting the hardness of the gel medium is the density of the sodium meta silicate solution. In almost all the cases, it is observed that the dense gels produce poor quality crystals. On the other hand gels of insufficient density take a long time for formation and it is mechanically unstable. It is found that a minimum density is desired for getting good quality gels for growth purpose. It is observed that the range of densities in between 1.03 to 1.06 gm/cc yields better experimental results in many systems. The optimum density allows the growth of reasonably bigger crystals by this technique.

## 2.5 The gelling mechanism

Structures of many of the gels are complicated and most of them are still not understood fully well. However, the structure and properties of the hydro silica gel has been described in great detail[31,34,35]. It is worth noting that the hydrosilica gel is the polymerised form of silicic acid. When sodium meta silicate is dissolved in water, mono-silicic acid is produced due to the reaction

$$Na_2SiO_3 + 3H_2O \leftrightarrow H_4SiO_4 + 2NaOH$$

This is a reversible process and the by-product, which is the strong alkali NaOH remains in the solution. This is the reason for the alkaline habit of the solution. The mono-silicic acid liberates the hydroxyl ions and polymerises as shown below:

$$
\begin{array}{ccccccc}
& OH & & OH & & OH & OH \\
& | & & | & & | & | \\
OH-Si-OH & + & OH-Si-OH & \rightarrow & OH-Si-O-Si-OH & + & H_2O \\
& | & & | & & | & | \\
& OH & & OH & & OH & OH
\end{array}
$$

This process continues until the entire molecule becomes part of the three dimensional network. The oxygen silicon linkage is extremely strong and which is irreversible. A section of the cross-linked polymer is shown below.

$$
\begin{array}{cccccccccccc}
OH & & OH & & OH & & OH & & OH & & OH \\
| & & | & & | & & | & & | & & | \\
OH-Si-O-Si-O-Si-O-Si-O-Si-O-Si & -------- \\
| & & | & & | & & | & & | & & | \\
O & & O & & O & & O & & O & & O \\
| & & | & & | & & | & & | & & | \\
OH-Si-O-Si-O-Si-O-Si-O-Si-O-Si & -------- \\
| & & | & & | & & | & & | & & | \\
OH & & OH & & OH & & OH & & OH & & OH
\end{array}
$$

The by-product resulting from the reaction is water and it accumulate on the top of the gel because it is lighter than the gel. This phenomenon is called syneresis[32]. The period of gellation is controlled by the pH value of the solution[36], though it is very difficult to control the total period of gellation precisely.

In the above structure it can be observed that $H_3SiO_4^-$ and $H_2SiO_4^-$ are also formed during the process of gellation [32]. The relative abundance of these products depends on the pH value. When the pH is high $H_2SiO_4^{2-}$ ions are abundant and it is more active. The $H_3SiO_4^-$ is favoured by low pH and they are believed to be responsible for triggering the plolymerisation[36]. In due course, cross linkages are formed between the chains; and these contribute to the sharp increase of viscosity that is clearly visible in gellation. The first result of such a linking process would be the production of sol particles, and the extent to which such particles then continue to associate to form macroscopic gel depend on their surface charge. Very high as well as very low pH values evidently lead to high surface charges (-ve and +ve ) which inhibit gellation. Plank and Darke[32,36] reported that the pH of the gelling solution cannot remain steady due to the progressive and stabilising hydroxyl substitutes for oxygen in the polymerised structure, which indicates that the initial measurement of pH is not likely to be very important. Greenberg and Sinclair[37] also reported that the gelling rate is rather sensitively temperature dependent. Though a linear relationship has been found, the actual reason for it remains ambiguous[38]. The low mobility of the chain molecules will increase the time for cross linkage. The formation of this can be encouraged by substitution of Al for Si particles and because of the difference in valency cross-links form easily. The gelling time is reduced and the resulting gels have a higher density and smaller pore size than those without Al.[36]

The important feature of gel is its abundance of pores. The matrices contain fine pores having different dimensions. The pore is usually of the order of a micrometer in size. The pores may behave as capillary for the transport of ions. X-ray studies on silica gel show that it has close resemblance with silica glass but with some inhomogeneities. The full structure and behaviour of the gel is still remaining to be unravelled[39].

## 2.6 Crystallisation process in gel medium

The experimental technique to grow crystals by gel diffusion technique is categorised according to the formation process of crystals,

1. Growth by chemical reaction
2. By chemical reduction
3. Complex decomplexion method
4. Solubility reduction method

### 2.6.1 The chemical reaction method

This is one of the widely used methods to grow a large number of crystals. The basis of the reaction method is the chemical reaction of the components used for the growth purpose. It has specially suited for growing crystals which are insoluble or partially soluble and those having thermal instabilities[1].

There are two types of growth which can take place in the chemical reaction: one in which the growth takes place by the reaction of one component with the other and in the other with the reaction of one component impregnated in the gel medium. In this method the crystals grow inside the gel. The process is a highly controlled one because the reactants combine due to the diffusion of ions through fine pores. The reaction can be represented as

$$AX + BY \rightarrow AY + BX$$

The diffusion of the ions in the gel can take place in different ways as depicted in the figures 2.1.(a-c).

In the case of hydrosilica gel this process is relatively easy and is accomplished by the mixing of aqueous solution of the compound, say 'AX', into the sodium meta silicate solution. The second component (feed solution) may be gently poured over the properly set and aged gel. The method shown in fig. 2.1 illustrates that AX is in

the form of a solid, the gel surrounding it. The AX component slowly goes into the gel and BY component is poured over the set gel. Controlled diffusion will take place in the gel media and the crystals are formed in the gel itself. To achieve a better control of diffusion, double gel techniques have to be used of which one is neutral gel technique[40,41]. Since the neutral gel medium is the region where the chemical reaction takes place, the crystals show high degree of perfection.
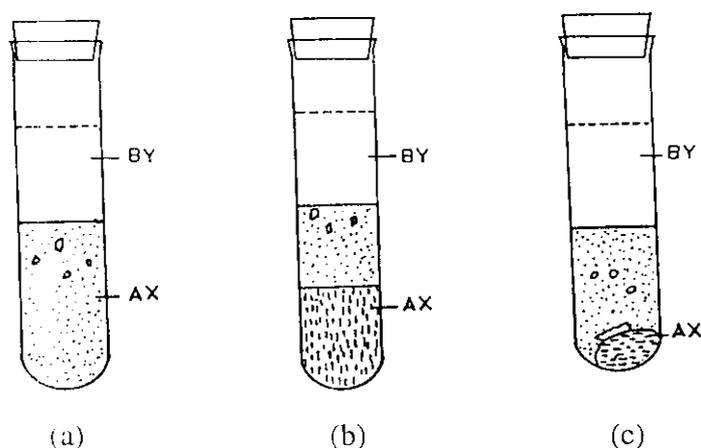


(a)      (b)      (c)

Fig. 2.1. Crystallisation in single tubes by chemical reaction method
(a) Gel uniformly changed with AX (b) Gel containing the salt in the solid form (c) Neutral gel technique

Similar to neutral gel technique, the U-tube method[42] is useful which avoids the reaction of one of the component with the gel. In this case both interacting compounds are allowed to diffuse into the gel, which is previously set by a neutral acid component. All of the above techniques have their own natural merits and demerits[43].

The nature of diffusion has a great influence on the shape of the crystals, nucleation density, precipitation region and the space of growth. The perfection of the crystals depends on several factors.

1. The type and strength of the reacting components
2. The property and concentration of the by-products
3. The speed with which equilibrium is established

On the basis of these factors and to achieve good results several different models have been proposed[44]. The chemical reaction technique is widely used to grow both metallic and non-metallic inorganic and organic crystals. Rare earth molybdate and sulphates[45], $A_2MCl_4$ and $A_2MCl$ (A= Rb, Cs, K; M= Pt, Pd) [46,47], ammonium nickel sulphates, potassium nickel sulphates, ammonium alum, potash alum etc.[48] have also been grown by this method. The author has also used this technique to grow mixed and single hydrogen selenite crystals of rare earths (Nd, Pr, Sm etc)
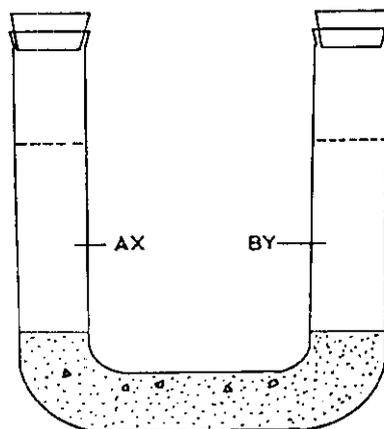


Fig. 2.2. Crystallisation by gel method employing 'U' tube

## 2.6.2 The chemical reduction method

This is a very good technique exclusively suitable for growing metallic crystals from gel media. Crystals of copper[49], nickel[50], lead selenium, etc., have been grown by this method. For growing the copper crystals, a suitably titrated gel with $CuSO_4$ impregnated in it is taken in a test-tube. After the proper setting of the gel a reducing agent such as hydroxylamine hydrochloride or hypophosphoric acid is added from the top as an outer reactant. The chemical reduction of the $CuSO_4$ gives the desired copper crystal within the gel.[8,10]

### 2.6.3 Complex decomplexion method

This method is suitable for a material whose solubility in the presence of another soluble material increases in a nonlinear way with the concentration of the soluble material. In this at first a chemical complex of the material of the crystal is formed with an appropriate substance (solution) and it is allowed to dissociate to form the required crystal. In normal practice to achieve decomplexion the dilution is steadily increased while the complexed solution is diffusing through the gel. Armington and O'Conner[51] have pioneered in developing this technique for growing cupric halide crystals. They utilised a dumb bell shaped vessel for this purpose. Ionic conducting materials like ($\beta$AgI) crystals are grown by this technique[52,53,54]. These investigators have modified this method for growing various metallic crystals[55,56,57]. This method has provided an impetus to grow the important class of transition metal dichalcogenides by gel, because these materials when crystallised by vapour transport (CVT) methods show enormous stacking faults.[58]

### 2.6.4 Solubility reduction method

This method is applicable to water-soluble materials. When the material of the eventual crystal is dissolved in an acid and resulting solution allowed to diffuse through gel medium of that pH at which the solubility is less, then the substance should crystallise by increasing supersaturation. Glocker and Soest[59] were the first to utilise this technique to grow monobasic ammonium phosphate crystals. They diffused alcohol into a gel containing the crystal salt solution. The alcohol reduced the solubility of the compound and thereby created the nucleation leading to the formation of the crystals. Utilising this technique potassium dihydrogen phosphate (KDP) crystals of good size[60] have been grown.

## 2.7 Growth mechanism in gel

The crystallisation in gel is the result of diffusion of the ions through it and the incorporation of them at the growing phase. It has already been discussed that diffusion depends on many factors like pH, density, temperature, age, quality of the medium and the impurity of the interacting components etc.[61]. To analyse the growth

mechanism it is necessary to take gel as a diffusion medium and the complete process of crystallisation as a diffusion controlled phenomenon. The gel growth can be compared to the general solution growth as there is evidence[29,30] for two-dimensional conglomeration (piling) and spreading of growth layers taking place at one or more initiation centres. Homogeneous nucleation is favoured by gel in which supersaturation near the growing face of the crystal in gel is usually high enough for this. It is clear that in the medium the diffusion of the discharged matter is a consequence of the chaotic motion of the molecules.

A molecule or an ion changes its place with a frequency

$$\tau^{-1} = \frac{k_B T}{h} \exp\left(\frac{-\Delta G}{k_B T}\right) \qquad \textbf{2.1}$$

Where $\Delta G$ is the activation energy for the transport of the molecules. It is equated to the energy required for the formation of a nucleus. The nucleation rate can be related to the mean free path and the diffusion coefficient as

$$\lambda = (2D\tau)^{1/2}$$

$$\tau = \frac{\lambda^2}{2D} \qquad \textbf{2.2}$$

Where D is the diffusion constant. Putting $\lambda \cong d$; the ionic diameter

$$f = \tau^{-1} = \frac{2D}{d^2} = \left(\frac{k_B T}{h}\right) \exp\left(\frac{-\Delta G}{k_B T}\right) \qquad \textbf{2.3}$$

Fick's law governs the quantity of matter transported to the growth front as a function of the concentration gradient. With appropriate boundary conditions Fick's law, in the case of one-dimensional diffusion, gives the rate of growth of the crystal in gel as

$$R = D \, V(C_\alpha - C_S)^{1/2} \qquad \textbf{2.4}$$

Where 'V' is the speed at which the growths front is advancing. Since each particle is to be treated separately, the factor $V(C_\alpha - C_S)^{1/2}$ is small enough to redraft the equation as

$$R = Dt^{1/2}$$   **2.5**

These equation has been derived for a one dimensional diffusion process.

A number of experimental tests confirm these results[29,62,63]. The consistency of the factor $V(C_\alpha - C_S)^{1/2}$ can be verified by plotting R against 't$^{1/2}$' or $R^2$ against 't'[64]. The difference in the calculated time period during which the steady state concentration is established and depletion of the available solute destroy the linear nature of the graph. Frank[65] has developed equations for growth rates in diffusion controlled process for different structures.

Consideration of the distribution of the growth rates from top to the bottom of the gel column, in which one component diffuses through the gel charged with the other component, it is observed that the rate of growth is greatest near to the gel solution interface of the column, where the concentration gradients are high, and less near the bottom where the concentration gradient is least. The etch pits on the surface of the crystals from the top and the bottom of the column reveals the difference in growth rates[66]. It is observed that the quality of the crystals increases at slow growth rates[67,68].

The growth happens through a screw dislocation or via two-dimensional surface nucleation[69,70,71]. But the experimental results do not agree well with calculation based on the two dimensional nucleation; the disagreement is partly due to the absence of the precise measurements of various growth parameters[72].

## 2.8 Control of nucleation in gel growth

The facility to control the nucleation is one of the most important features of the gel growth. At the same time this is a sensitive and crucial aspect of the gel technique.

The diffusion rate can be controlled in this technique to a great extent, but it is not enough to control the population of nucleation centres in the gel. The lack of knowledge on actual structure of the gel prevents one from taking any effective measures for nucleation control. The commonly used methods to minimise the spurious nucleation in gels are

1. Optimisation of the gel density
2. Ageing of the gel
3. Neutral gel technique
4. Concentration of the nutrients
5. Stabilising the thermal condition
6. Use of additives
7. Field utilisation

Control on gel density is found to give good results; it is observed that for a range 1.03-1.06 gm/cc (specific gravity) gives good results[71,73]. When the age of the gel increases the size of the pores gets reduced. Therefore the aged gel allows less number of nucleation centres. Neutral gel technique is also a method to control the nucleation centres. Programming the temperature of the medium enables contraction or expansion of the dimension of the pores. Manipulation of the concentration of the reactant to control the nucleation was first proposed by Henish. The method is to keep the concentration of the outer electrolyte very low, which reduces the nucleation sites. After the establishment of nucleation centres, the concentration of the reactants is enhanced which enhances the growth[74,75]. By using additives in a controlled manner one can reduce the number of nucleation centres by increasing the activation energy for the formation of the nucleus[21,30]. The application of an electric field for controlling the growth is also used by the same investigators.

## 2.9 Habit of the gel grown crystals

This is the era of miniaturisation which requires perfect and small single crystals; the gel growth breeds small and superior quality single crystals. Face oriented perfect crystals can be obtained by this method. This technique is also highly suitable for the

inclusion of impurities to manipulate the performance of crystals[76,77]. The morphology of the crystals can be varied by the physico-chemical environment in which they are growing. Due to the miniaturisation of instruments in electronic industry and modern technology requires perfect and small single crystals. By spending tedious work, it could be possible to exploit this technique to grow various technologically important crystals.

## References

[1] Liesegang, R.E., *Phot. Archiv.*, **21** (1896) 221.

[2] Liesegang, R.E., in *'Colloid Chemistry'*, ed. Alexander,J. Che. Cat. Co. New York 1926.

[3] Liesegang, R.E., *Z.Phy. Chem.* **23** (1897) 365.

[4] Ostwald, W.Z., *Phy. Chem.* **27** (1897) 365

[5] Holmes, H.N., in *'Colloid Chemistry'* Vol.1

[6] Lord Rayleigh, *Phil. Mag.* **38** (1919) 738

[7] Holmes, H.N., *J.Phy. Chem.* **21** (1917) 709.

[8] Homes, H.N., *J. Frank. Inst.* **184** (1917) 743.

[9] Fells, H.A. and Firth, J.B., *Proc. Roy. Soc. London* **112A** (1926) 468.

[10] Hatschek E., *Kolloid Z.* **8** (1911) 13.

[11] Hatschek, E., *Brit. Assoc. Reports*, **1919** (1919) 23.

[12] Brad ford, S.C., in *'Colloid Chem.'* ibid.

[13] Lloyd, D.J., in *'Colloid Chem'* ibid.

[14] Fisher, L W. and Simons. F.L., *Amer. Mineral.* **11** (1926) 124

[15] Fisher, L.W. and Simons F.L., *Amer. Mineral.* **11** (1926) 200

[16] Fisher, L.W., *Amer. J. Sci.* **15** (1928) 39.

[17] Vand, V, Henisch, H.K and Mc Cauley, J.W., *Acta. Cryst.* **16** (1963) 137.

[18] Stong, C.L., *Sci. Amer.* **206** (1962) 155

[19] Henisch, H.K, Dennis, J and Hanoka, J. I., *J. Phy. Chem. Solids* **26** (1965) 493.

[20] Wakim, F.G. Henisch H.K. and Atwater, H., *J.Chem. Phys.* **42** (1965) 2619.

[21] Henisch, H.K, Dennis, J. and Hanoka, H.I., *J.Electrochem. Soc.* **112** (1965) 627.

[22] Henisch, H.K., *'Crystal Growth in Gels'*, The Penysylvania State University Press 1970.

[23] Patel, A.R. and Arora, S.K., *J. Crystal. Growth.***18** (1973) 199.

[24] Chta, M, Tsutsumi and Ueno, S., *J. Crystal Growth.* **47** (1979) 135.

[25] Barta, C., Zemelicka, Z. and Rane, V., J. *Crystal Growth* **100** (1971) 158.

[26] Patel, A.R. and Rao, A.V., *Krystall. Tech.* **14** (1979) 151.

[27] Blank, E., Chianelli, R. and Pintchovsky, F., *J. Crystal Growth* **18** (1973) 185.

[28] Blank, E., Chianell, R. and Pintchovsky, F., *Nat. Conf. on Crystal Growth*, Princeton, USA 1970 (Amer. Assoc. Cr. Growth).

[29] Au-Pang, T., *Scientia Sinica* **XII** (1963) 1311.

[30] Patel, A.R. and Arora, S.K., *J.Mat. Sci.* **11** (1976) 846.

[31] Arora, S.K. and Tomy Abraham, *J. Crystal Growth* **52** (1981) 851.

[32] Plank, C.J. and Drake, L.C., *J. Colloid Sci.* **2** (1947) 399

[33] Patel, A.R. and A.V. Rao, J. Crystal Growth **49** (1980) 281.

[34] Hurd, C.B. and Letteron, H.A., *J.Phy. Chem.* **38** (1932) 663.

[35] Alexander, G.B., *J.Amer. Chem. Soc.* **75** (1953) 5655.

[36] Plank, C.J.and L.C.Drake., *J.Colloid Sci.* **2** (1947) 413

[37] Greenberg, S.A., and Sinclair, D., *J.Phy. Chem.* **59** (1955) 435.

[38] Alexander, G.B., *J.Amer. Chem. Soc.* **76** (1954) 2094

[39] Warren., *Chem. Rev.*, **26** (1940)237

[40] Roopkumar, R, Gnanam, F.D. and Raman, G., *Cryst. Res. Technol.* **25** (1990) 289.

[41] Roopkumar, R. and Gnanam, F.D., *J.Mat.Sci.* **24** (1989), 4535 (1990)

[42] Khan, A.S, Devore, T.C and Reed, W.F., *J. Crystal Growth* **35** (1976) 337.

[43] Laudise, R.A., *'The growth of single crystals'* Prentice-Hall Inc., New Jersey 1970.

[44] Patel, A.R. and Venkateshwara Rao, A., *Bull. Mat. Sci.* **4** (1982) 527.

[45] Pradyumnan, P.P., Cyria Joseph and Ittyachan, M.A., *Ind. J. of Pur. & App. Phy.* **36** (1998) 319.

[46] J.Marchee, W.G. andVan Rosmalen, G.M., *J. Crystal Growth* **23** (1977) 358.

[47] Brower, G. and Van Rosmalen, G.M., *J.Crystal Growth* **23** (1974) 228.

[48] Joshi, M.S., Mohan Rao, P. and Antony, A.V., *Bull Mat. Sci.* **2** (1980) 127.

[49] Hatschek, E. and Simons, F.L. *J. Soc. Chem.* Ind. **31** (1912) 439.

[50] Arora, S.K., and Sangwal, K., *J.Phy.* **53 a** (1979) 612

[51] Conner, J.J.O, Dipctro, M.A., Armington, A.F and Rubin, B., *Nature* **212** (1968) 68.

[52] Helbertstadt, E.S., *Nature* **216** (1967) 574

[53] Casalavsky, J.L. and Suri, S.K., *J. Crystal Growth* **6** (1970) 213.

[54] Suri, S A.K, Henisch, H.K and Faust, J.W., *Jr., J. Crystal Growth* **7** (1970) 277.

[55] Conner, J.J.O and Armington, A.F., *J. Crystal Growth* **1** (1967) 327.

[56] Armington, A.F. and Conner, J.J.O., *Mat. Res. Bull* **2** (1967) 907.

[57] Murphy, J.S, Keres, H.A and Bohandy, J. *Nature* **218** (1968) 165

[58] K.Nagi Reddi, *'Studies in Crystal Growth and Perfection in Tungsten di sulphide single crystals'*, Ph.D. Thesis, Sardar Patel University, 1980.

[59] Glocker, D.A and Soe St, I.F., *J. Chem. Phys.* **51** (1969) 3143.

[60] Brezina, B and Havrankova, *Mat. Res. Bull.* **87** (1971) 537

[61] Blank, Z., *J. Crystal Growth* **18** (1973) 281.

[62] Liaw, H.M. and Fau St. *Jr.* , J.W., *J. Crystal Growth* **8** (1971) 8

[63] Patel, S.M and George V., *J.Electr. Mate.* **6** (1977) 499.

[64] Crank, J.,*'Mathematics of Diffusion'*, Oxford University Press 1956.

[65] F.C.Frank, *Proc. Roy. Sco.* **201A** (1950) 586.

[66] Jagodzinski, H., *'Crystallography and Crystal Perfection'*, (ed). G.N. Ramachandran, Academic Press, New York (1963).

[67] .Kirov, G.K, *Kristall und Technik.* **3** (1968) 573.

[68] .Kirov, G.K., *J. Crystal Growth.* **15** (1972) 102

[69] Pillai, K.M.and Ittyachen, M.A., *Pramana.* **10** (1978) 613,

[70] Pillai, K.M. and Ittyachen, M.A., *Current Science.* **48** (1979) 202.

[71] Pillai, K.M, Ittyachen, M.A. and Vaidyan, V.K., *Nat. Acad. Sci. Lett.* **3** (1980) 37.

[72] Vasudevan, S., Nagalingham, S., Dhanasekharan, R and Ramaswamy, P., *Cryst. Res. and Techno.* **16** (1981) 293.

[73] Patel, A.R. and Bhat, H.L., *J. Crystal Growth.* **12** (1972) 288

[74] Patel, A.R. and Rao, A.V., *J. Crystal Growth.* **43** (1978) 351

[75] Patel, A.R. and Arora, S.K., *J. Crystal Growth.* **18** (1973)

[76] Nickl, J. and Henisch, H.K., *J.Electro Chem. Soc.* **116** (1969) 1258.

[77] Shiojiri, M., et al. *J. CrystalGrowth.* **543** (1978) 61.