Chapter III

Crystal Growth Technique

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3.1 Introduction

*Free energy barrier is a major burden.*

*Transformation cannot happen without aid.*

*The question is what can we do to make it happen.*

*The answer is something has to nucleate.*

*In the beginning there was incubation.*

*The question is "When will we get to steady state?"*

*Patience will lead to further fluctuation.*

*Then nuclei will show and grow at a steady rate.*

*Rolling down the gradient slope.*

*Gathering buddies along the way.*

*Which one of them will have hope?*

*The truth is only the big ones will stay.*

*Such is the story of nucleation and growth.*

*Nature has chosen this approach.*


A crystal is a solid material whose constituent atoms, molecules, or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions. A systematic and scientific study of crystals including process of crystallization, internal structure, external morphology, properties and classification of crystals is known as “Crystallography”. The study of the formation of crystals is covered under the subhead “Crystal Growth”. The process of crystal formation is known as crystallization.

The growth of crystals occurs either in nature or artificially in a laboratory. The Mother Nature grows a variety of crystals in the crust of Earth,
which are mainly the natural mineral crystals including diamond, precious stones and rocks. Mostly these crystals were grown from the molten state by freezing. It is also possible to form crystals directly from a gas without passing through the liquid state; example is, the hoarfrost, i.e., ice crystals which are grown from water vapour in the air. Also, a few mineral substances which are found mainly around volcanoes, where sulphur and ammonium chloride crystals are formed from the gases emitted during eruption. There are other examples of crystals grown in nature, which are famous Amarnath Shivalinga of ice in Himalayan cave, large crystals grown around Dead Sea in Israel and gigantic mineral crystals in Naica caves, Chihuahua state of Mexico.

Today, the growth of crystals does not remain the phenomena only occurring in nature, but it has become a well advanced as well as widely used laboratory technique. It is interesting to note that the crystal growth can be regarded as an ancient subject, owing to the fact that the crystallization of salt and sugar was known to the ancient Indian and Chinese civilizations. The subject of crystal growth was treated as a part of crystallography and never had an independent identity until the last century. It is important to note that both structural crystallography and the science of crystal growth emerged from curiosity about the large variety in crystal forms existing in nature. The fundamental aspects of crystal growth had been derived from early crystallization experiments in the 18th and the 19th century [1,2]. Theoretical understanding started with the development of thermodynamics in the late 19th century and with the development of nucleation and crystal growth theories and later on the increasing understanding of the role of transport phenomena in the 20th century. There always has been a requirement of good quality crystals for various
applications. The demand of the modern day science and technology has tempted scientists to synthesize and grow several new varieties of crystals. The requirement for better, cheaper, and larger single crystals has driven extensive research and development in crystal growth. This has brought the field of crystal growth into the lime light. As a result the congeries of crystals is ever expanding day by day.

Crystals are the back bone of today’s technological development. Crystals are the unacknowledged pillars of modern technology. The world crystal production was estimated to be more than 20,000 ton per year in the year 1999 [3]. Out of that the largest share of about 60% was from semiconductor materials, for instance, silicon, gallium arsenide, indium phosphate, gallium phosphate, cadmium telluride and its alloys. As can be seen in Figure 3.1, optical crystals, scintillator crystals, and acousto-optic crystals had about equal shares of 10%, whereas laser and nonlinear-optic crystals and crystals for jewelry and watch industry had shares of a few % only.

![Figure 3.1 Estimated shares of world crystal production in 1999](image)

However, over the last decade the demands on synthetic biomaterials have increased significantly with the progress in fields of medicine, material science and engineering, biochemistry, pharmaceutics and nanotechnology.
Furthermore, crystal growth is divided into five major areas by H. J. Scheel, namely, [4]:

1. Fundamental theoretical and experimental crystal growth studies.
2. Laboratory crystal growth for preparing research samples.
3. Industrial fabrication of single crystals, their characterization and machining.
4. Fabrication of metallic / dendritic crystals (e.g. turbine blades).
5. Mass crystallization (salt, sugar, chemicals).

### 3.2 Crystal Growth Techniques

Crystal growth techniques range from a simple inexpensive process to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. The process of crystal growth is a controlled change of state, or phase change, to the solid state. This transition may occur from the solid, liquid or vapour state. Hence, depending on the phase transitions involved in the process, the crystal growth methods can generally be classified into three basic categories [5]:

**Solid Growth** : $S \rightarrow S$ processes involving solid to solid phase transitions.

**Melt Growth** : $L \rightarrow S$ processes involving liquid to solid phase transitions.

**Vapour Growth** : $V \rightarrow S$ processes involving vapour to solid phase transitions.

#### 3.2.1 Solid Growth Techniques

The $S \rightarrow S$ processes are not commonly used except for certain metals where strain annealing is effective and certain cases where a crystal structure alters between the melting point and room temperature. These processes include annealing or sintering, strain annealing, deformation growth and polymorphic phase transitions. Single crystals are developed by the preferential growth of a polycrystalline mass, which can be achieved by straining the material and subsequent annealing.
Large crystals of several materials, especially, metals have been grown by this method [6].

3.2.2 Liquid Growth Techniques: The L → S processes are many and important also. The growth of crystals from the liquid phase is treated as two categories – (i) Melt Growth and (ii) Solution Growth due to the independent behaviour of melt and solution techniques.

Melt growth is the process of crystallization by fusion (melting) and re-solidification of the pure material. It is the fastest of all crystal growth methods and is widely used for the preparation of large single crystals. Melt growth methods are limited to the materials which melt congruently and having an experimentally viable vapour pressure at its melting point. The material to be grown into crystal form is melted and after that it may progressively cooled to yield the crystalline matter. The normal freezing or directional freezing is a very important process for the crystals which melt congruently without decomposing. When an ingot is gradually frozen from one end to the other, it is said to be frozen normally or directionally. This process comprises of many techniques, which are used world wide for industrial crystallizations, including growth of metals, semiconductor crystals for electronic and computer chip making industries and laser host crystals. Sometimes, the liquid phase contains deliberately added foreign materials as in solution growth or flux growth or liquid phase epitaxy. Bridgman technique and Czochralski technique are the well known melt growth techniques.

The solution growth is also very popular for the growth of numerous crystals for industry. The growth of crystals by precipitation from aqueous solution is the most simple and the oldest technique. In this process, a
saturated solution of the material to be grown into crystal is taken and in an appropriate solvent the crystallization takes place as this solution becomes critically supersaturated. The supersaturation can be achieved either by lowering the temperature of the solution or by slow evaporation. The advantage of the method is that the crystals can be grown from a solution at temperatures well below its melting point, perhaps even at room temperature and, therefore, it turns out to be more applicable in many cases. Solution growth can be broadly classified into high temperature solution growth, hydrothermal method, low temperature solution growth and gel growth.

3.2.3 Vapour Growth Techniques: The $V \rightarrow S$ processes include sublimation, which is strictly speaking a kind of $S \rightarrow V \rightarrow S$ process, and the vapour phase reactions which are used in the epitaxial growth of semiconductors. Sometimes deliberately added gases are helpful as transporting agents for the growing materials. Vapour growth techniques can be adopted for the growth of materials which lack a suitable solvent and sublime before melting at normal pressure. Vapour growth methods have been employed to produce bulk crystals and to prepare thin layers on crystals with a high degree of purity.

The development and refinement of methods of crystal growth to achieve useful products have relied heavily on empirical engineering and on trial and error methods. Crystal growth still remains, by and large, as an art along with a science [7]. A phalanx of crystal growers has developed various crystal growth techniques after their pain-staking efforts of years together.
Table 3.1 shows the classification scheme for various growth techniques as summarized by Laudise, which is very important for the neophytes [8,9].

**Table 3.1 : Crystal Growth Techniques**

<table>
<thead>
<tr>
<th>Crystal Growth Techniques</th>
<th>Mono-component</th>
<th>Poly-component</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Solid $\rightarrow$ Solid (Solid Growth)</td>
<td>Solid $\rightarrow$ Solid (Solid Growth)</td>
</tr>
<tr>
<td>1. Strain annealing</td>
<td></td>
<td>1. Precipitation from solid solution</td>
</tr>
<tr>
<td>2. Devitrification</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Polymorphic-phase change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Liquid $\rightarrow$ Solid (Melt Growth)</td>
<td>Liquid $\rightarrow$ Solid (Solution Growth)</td>
</tr>
<tr>
<td>1. Conservative</td>
<td></td>
<td>1. Growth from Solution (evaporation, slow cooling and temperature differential)</td>
</tr>
<tr>
<td>(a) Directional solidification</td>
<td></td>
<td>(a) Aqueous solvents</td>
</tr>
<tr>
<td>(Bridgman-Stockbarger)</td>
<td></td>
<td>(b) Organic solvents</td>
</tr>
<tr>
<td>(b) Cooled seed (Kyropoulos)</td>
<td></td>
<td>(c) Molten-salt solvents</td>
</tr>
<tr>
<td>(c) Pulling (Czochralski)</td>
<td></td>
<td>(d) Solvents under hydrothermal</td>
</tr>
<tr>
<td>2. Non Conservative</td>
<td></td>
<td>(e) Other organic solvents</td>
</tr>
<tr>
<td>(a) Zone Melting</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(horizontal, vertical, float zone, growth on a pedestal)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Verneuil (Flame fusion, plasma, arc image)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Gas $\rightarrow$ Solid (Vapor Growth)</td>
<td>Gas $\rightarrow$ Solid (Vapor Growth)</td>
</tr>
<tr>
<td>1. Sublimation-condensation</td>
<td></td>
<td>1. Growth by reversible reaction (temperature change, concentration change)</td>
</tr>
<tr>
<td>2. Sputtering</td>
<td></td>
<td>(a) Van Arkel (hot wire processes)</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>2. Growth by irreversible reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) Epitaxial processes</td>
</tr>
</tbody>
</table>

The designing and development of various crystal growth techniques of the present day is a result of continuous and fruitful modifications occurring since last several decades and still today the modification process is continuing.
Table 3.2 shows the multi-disciplinary nature and complexity of crystal growth processes as explained by Scheel [4].

**Table 3.2: Multi-Disciplinary Nature and Complexity of Crystal Growth**

<table>
<thead>
<tr>
<th>Multi-Disciplinary Nature of Crystal Growth</th>
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</thead>
<tbody>
<tr>
<td>• Theoretical Physics (especially thermodynamics, non-equilibrium thermodynamics, statistical mechanics)</td>
</tr>
<tr>
<td>• Solid-State Physics</td>
</tr>
<tr>
<td>• Crystallography and Crystal Chemistry</td>
</tr>
<tr>
<td>• Materials Science &amp; Engineering</td>
</tr>
<tr>
<td>• Chemistry (all fields) including Chemical Engineering</td>
</tr>
<tr>
<td>• Mechanical &amp; Electrical Engineering (especially hydrodynamics, machine design, process control)</td>
</tr>
<tr>
<td>• Mineralogy</td>
</tr>
<tr>
<td>• Metallurgy</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complexity of Crystal Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Phase Transformation from Fluid (melt, solution, vapour) to Crystal</td>
</tr>
<tr>
<td>• Scaling Problem: Control of surface on nm scale in growth system of ~m size, hampers numerical simulation</td>
</tr>
<tr>
<td>• Complex Structure &amp; Phenomena in Melts and Solutions</td>
</tr>
<tr>
<td>• Multi-Parameter Processes: Optimize and compromise</td>
</tr>
</tbody>
</table>

Schieber [10] has well explained the required three aspects of crystal growth (i) Theory of nucleation and growth (ii) Experimental crystal growth and (iii) Characterization of crystals. A poem of L. I. Preston describes the competitive nucleation in crystal, which is explained by many authors, in detail [5,11-13]. This has been correctly quoted in a different manner by Gilman [7] in his book “The Arts and Science of Growing Crystals” as, “The Systematic production of artificial crystals might be viewed as a new agriculture that has begun flourish. It differs from true agriculture in that its products are mostly
inorganic at present, but it has many features common with normal agriculture and promises to have a somewhat comparable effect on society. The new agriculture consists of growing solid crystals from a nutrient phase (gas, liquid or solid). To start the growth process, the nutrient is often seeded with small crystal to be grown, and some workers speak of repeating the harvest after a certain length of time.”

Over the years, many successful attempts have been made to describe the art and science of crystal growth, and many review articles, monographs, symposium volumes, and handbooks have been published to present comprehensive reviews of the advances made in this field.

There are many well written books available on subjects like fundamentals of crystal growth [14]; different crystal growth techniques, their theories, characterization and applications [15-21] and understanding the growth mechanism [22]. Even books are available with wonderful photographs of crystals [23]. Whereas, the authors Stangl and Stang [24] have considered the growth of a variety of beautiful crystals as the growth of flowers in a garden, thereby, they have agreed to the concept of Gilman [7].

Various crystal growth techniques have been discussed in detail by several authors [25,26]. The different techniques of each category are found in reviews and books by Faktor and Garrett [27] on vapour growth, Brice [28] on melt growth, Henisch [29] on gel growth, Buckley [30] on solution growth and Elwell and Scheel [1] on high temperature solution growth. A review on the advances in crystal growth techniques are discussed by Mirkin and Moreno [31]. Recently, a “Handbook of Crystal Growth” is published [32], which describes the fundamentals of crystal growth and defect formation; bulk
growth from the melt, solution, and vapor; epitaxial growth; crystallization from gels; modeling of growth processes and defects; and techniques of defect characterization.

The predecessors of the present author [33-38] have discussed various growth techniques in detail; therefore, it is avoided in the present thesis. Among various techniques of growing crystals, gel growth technique occupies a prominent place owing to its versatility and simplicity. The present author has employed the gel growth technique to grow struvite and related crystals; therefore, this technique is discussed in somewhat more elaborately, hereby.

### 3.3 Gel Growth Technique

The roots of gel growth technique are associated with the earlier observations of the remarkable series of layers due to the phenomenon of periodic precipitation in gel systems in 1896 made by German chemist Raphael Eduard Liesegang [39-41]. A systematic study of crystallization in gels began with Liesegang’s famous discovery of the periodic precipitation in gels [39]. His studies described the conditions of nucleation and growth for chromates, halides, phosphates, tartrates with metallic ions such as: Ag⁺, Cu²⁺, Ca²⁺, Ba²⁺, Pb₂⁺, in gelatin, in agar, potassium silicate and macromolecular gels [29]. In its early days the gel was not used as a medium of crystal growth, but only used to study the phenomenon of periodic precipitation in gel. (The phenomenon is known as Liesegang ring and will be discussed later on in section 3.11 of this chapter.) The phenomenon was first explained and named as *Liesegang rings* by Wilhelm Ostwald [42] in 1897. Later on this phenomenon received the attention of Lord Rayleigh [43] because of his curious nature and thereby achieved wide acceptance and
reputation. This has inspired workers like Morce and Pierce [44], Holmes [45], Hatschek [46], Fells and Firth [47], etc. A comprehensive review on the earlier developments of this field has been described by Lloyd [48].

The potential application of gel as a medium for crystal growth was introduced by Fisher and Simons [49-51] in the 1920’s. However it did not evoke much interest of crystal growers and remained as an unused work till early 1960’s. The rapid developments in semiconducting and laser active materials prompted the search for new materials. This has increased the interests in crystal growth and researchers even turned to the less noticed gel technique. The science of growing crystals in gels has developed since 1920’s but after 1970, the gel growth technique became very popular due to the pioneering work of famous experimentalist Henisch [29], who narrated not only the authentic survey of the work carried out in the field, but also explained the various aspects of the gel growth in his famous book on “Crystal Growth in Gels”. Since then, it has attracted wide interest for growing a variety of 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.

The gel growth technique is a one kind of modified alternative version of solution growth technique. In which the growth occurs due to reaction between two suitable reactants (solutions) in a gel medium or achieving super-saturation by diffusion in gel medium. It is the simplest technique under ambient conditions. This technique is well suited for the crystal growth of compounds, which are sparingly soluble and decompose at fairly low temperatures. Crystals with dimensions of several mm can be grown in a
period of 3 to 4 weeks. Crystal growth by the gel technique has attracted the attention of numerous researchers, as this technique is comparatively simple and can be set up in a laboratory with simple glass-wares and without any need of sophisticated instruments and high temperature furnaces.

The gel growth technique is elaborately described by Henisch [29], Henisch and Hanoka [52], P.S. Raghavan and P. Ramasamy [15] as well as Patel and Venkateswara Rao [53]. An attempt has been made by the present author to review the gel growth technique briefly.

### 3.4 Types of Gels

Out of four states of matter - solid, liquid, gas and plasma, the three states of matter-solid, liquid and gas are more familiar. Even there are many exotic materials, which are yet not fully understood. Material scientists are trying to understand their structures and properties to derive their useful applications. One of the exotic states of matter is gels. They are neither solids nor liquids. In early stage, gel has been defined as a two component system of a semi solid nature rich in liquid [54]. A gel may also be defined as a semi-solid formulation having an external solvent phase, apolar (organo-gels) or polar (hydro-gel), immobilized within the spaces available of a three dimensional networked structure [55]. Recently, according to IUPAC 2007 recommendations gel is defined as non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid [56]. A characteristic property of gel is that they contain a conspicuously high percentage of solvent and little solid matter. The gel forming substances and solvents stabilize each other in the gel structure. Most gels are mechanically and optically isotropic, except when under strain.
As shown in Table 3.3, gels can be classified according to constituent (matrix) phase, solvent phase and cross-linkages.

**Table 3.3: Classification of Gels**

<table>
<thead>
<tr>
<th>Classification of Gel</th>
<th>Surfactant Bilayers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constituent Or Matrix Phase</strong></td>
<td></td>
</tr>
<tr>
<td>Polymers</td>
<td>Natural gel</td>
</tr>
<tr>
<td></td>
<td>Synthetic gel</td>
</tr>
<tr>
<td></td>
<td>Hybrid gel</td>
</tr>
<tr>
<td><strong>Solvent Phase</strong></td>
<td></td>
</tr>
<tr>
<td>Solid-Liquid</td>
<td>Hydro-gel (Water Solvent)</td>
</tr>
<tr>
<td></td>
<td>Organo-gel (Organic Solvent)</td>
</tr>
<tr>
<td></td>
<td>Lio-gel (Oily Solvent)</td>
</tr>
<tr>
<td></td>
<td>Alco-gel (Alcohol Solvent)</td>
</tr>
<tr>
<td>Solid-Gas</td>
<td>Xero-gel (air)</td>
</tr>
<tr>
<td></td>
<td>Aero-gel (air)</td>
</tr>
<tr>
<td>Solid-Solid</td>
<td>Polymer-gel (polymer)</td>
</tr>
<tr>
<td><strong>Cross-linkage</strong></td>
<td></td>
</tr>
<tr>
<td>Physical Gel (Noncovalently Crosslinked Polymer Networks)</td>
<td>Coulombic Interaction</td>
</tr>
<tr>
<td></td>
<td>Hydrogen Bonding</td>
</tr>
<tr>
<td></td>
<td>Coordinate Bonding</td>
</tr>
<tr>
<td></td>
<td>Hydrophobic Bonding</td>
</tr>
<tr>
<td>Chemical Gel (Covalently Crosslinked Polymer Networks)</td>
<td>Covalent crosslinking</td>
</tr>
</tbody>
</table>

The materials which can be categorized as gels are silica gel, agar (a carbohydrate polymer derived from seaweed), gelatin (a substance closely related to proteins), soft soaps (potassium salts of higher fatty acids), a variety of oleates and stearates, polyvinyl alcohol, various hydroxides in water, and even water-insoluble tetraethoxysilane in the presence of electrolytes and co-solvents (e.g. methanol) and surface active agents [29, 57]. It is also noted that two-component systems, usually known as sols are the materials which are closest to gels in structure, but they resemble liquids more than solids.
The process, through which a network is formed from solution by a progressive change of liquid precursor into a sol, to a gel, is known as sol-gel process. The coagels are hybrid media which consist of small jelly-like particles separated by relative large tracts of liquid phase.

When the dispersion medium (or the swelling agent) is water, then it is called a hydro-gel or aqua-gel having a network of polymer chains that are water-insoluble. Hydro-gels are super-absorbent natural or synthetic polymers. Hydro-gels also possess a degree of flexibility very similar to natural tissues. Moreover, hydro-gels have the ability to sense changes of pH, temperature, or the concentration. On the other hand, an organo-gel is the gel with an organic liquid is used as the dispersion medium instead of water. But in a gel if alcohol is used instead of water as the dispersion medium, it is known as alco-gel. More precisely, alco-gel is the gel in which the swelling agent consists predominantly of an alcohol or a mixture of alcohols.

Aero-gels are made from a sol-gel by carefully evacuating the solvent to leave a fragile polymer network, which is having 90-99% air by volume. Thus, the aero-gel is a gel comprised of a micro porous solid in which the dispersed phase is a gas. Microporous silica, microporous glass and zeolites (microporous aluminosilicate minerals) are common examples of aero-gels. Xero-gel is an open network formed by the removal of all swelling agents from a gel. Examples of xero-gels include silica gel and dried out, compact, macromolecular structures, such as gelatin or rubber.

Gels are materials where polymer chains form the links of a network immersed in a typically liquid environment. The polymer chains are cross-linked at the microscopic level by comparatively stronger chemical (covalent)
bonds or weaker physical bonds; the type of bond is used to label the macroscopic material as a chemical gel or a physical gel, respectively. Both physical gel and chemical gel have distinct macroscopic properties, since their microscopic behaviors of cross-links are different. Since the chemical cross-links prevent the chemical gels from dissolving in its environment solvent, chemical gels behave macroscopically like solids. Such chemical gel structures show higher resistance to slight physicochemical affects and cannot be converted into sols by warming. The gel structure cannot be disrupted except by breakdown of the polymer molecules. However, because of the weaker nature of the cross-linking bonds, physical cross-links are found in a constant cycle of creation and dissolution in physical gels. Therefore, physical gels are sometimes called thermo reversible gels, i.e., the creation and dissolution of cross-links or sol-gel transition are temperature driven and reversible. Such physical gel structures may be disrupted by slight physicochemical effects, which cause sol formation. When it is cooled down the bonds will recombine and the sol once more solidifies into a gel. Agarose (Agarose is a gelling compound extracted from certain red sea weeds of the Rhodophyceae group) is the example of the physical gel because the association of its chains is reversible upon heating.

The structure of synthetic and semi-synthetic gel is generally depending on the chemical properties of the basic substances, the relative concentration of the reagents and the solubility conditions during gel formation. The functional reactivity of monomers and their spatial orientation has pronounced effect on cross-linking. The reactions inducing cross-linkages are random processes governed by the laws of statistical probability. These
processes cause voids of dimensions and geometry, which are the characteristic of the type of gel used to form the polymer chains. These voids are known as the *pores of the gel*. Since the gel structure is not a rigid system but a mobile one, more-or-less, fixed network of polymer chains, the terms used in practice are average or effective pore size. The pore size is one of the most important parameters of the molecular phenomena (diffusion, permeability). Pore sizes may be influenced by the conditions of formation, and the solubility relationships of the initial substances and the end product.

There is a distribution of pore sizes within each gel and one gel is distinguished from another by the nature of this distribution. In course of some early experiments on gels, Biltz [58] concluded that hydro-gels are characterized by two types of pores; the *primary* pores are of nearly molecular dimensions and the other ones are much coarser *secondary* pores, which behave as normal capillaries. From the aspect of pore size, Kum and Kunin [59] distinguished two principal types of gel structures, which are micro-reticular (micro-porous) and macro-reticular structures. The more uniform repetition of the cross-links in micro-reticular gels produces smaller pores and renders the gel suitable for the separation of smaller molecules. Micro-reticular gels are obtained if the solubility of the starting substances (monomers) and the end product do not differ greatly, and if the cross-links assume the desired gel structure only gradually, for instances, by increasing the number of cross-links between the polymer chains already fixed. On the other hand, the structure of the macro-reticular gel is rather heterogeneous, the spatial distribution of the matrix being uneven. Their large pores render them suitable for the permeation and separation even of macromolecules.
Most macro- reticular gels are aero-gels; in spite of their high porosity, they are resistant to mechanical effects [60].

One of the most common gels is the silica gel; the synonyms are silica hydro-gel and water of silicate glass. This is prepared from sodium metasilicate solution. The pores are separated by a solid film of about $2 \times 10^{-5}$ cm thicknesses. The dimensions of pores depend on the concentration of gel material. The effective pore diameter of silica hydro-gel is of the order of 50 - 100 Å. In order to obtain a gel medium of desired pH, a requisite amount of aqueous sodium meta-silicate solution is normally added to the constantly agitated suitable acid of desired concentration. The acidity of the resulting solution determines the course and the rate of polymerization [53].

Agarose, agar, silica and gellan gum (Gellan gum is a high molecular weight polysaccharide gum produced by a pure culture fermentation of a carbohydrate by *Pseudomonas elodea*, purified by recovery with isopropyl alcohol, dried, and milled) have been successfully used as gel materials to obtain protein crystals. The use of an organic solvent-based gel prepared from polyethylene oxide (PEO) and a polyvinyl alcohol hydro-gel for protein crystallization was investigated by Pietras et al [61]. Chandrasekhar [62] has also discussed the crystal growth from PEO gel.

### 3.5 Gelling Mechanism

The gelation, i.e. gelling process, can be brought about in many ways, sometimes by the cooling of a sol, by chemical reaction, or by the addition of precipitation agents or incompatible solvents. Gelatin is a good example of a substance, which is readily soluble in hot water and can be gelled by cooling provided that the concentration exceeds about 10%. Formation of gel can be
obtained by the action of two reagents in concentrated solution; preparation of silica gel is an example for this. The process of gelling takes an amount of time, which can vary widely, from minutes to many days, depending on the nature of the materials, its temperature and history [29]. For silica gel, this has been described and documented by Treadwell and Wieland [63]. Silica gel structures depend significantly on the method of preparation. Mechanical properties of fully set gels can vary widely, depending on the density and on the precise conditions during gelling. For the diffusion of reagents through the gel medium, the most important operative parameter is the size of the diffusing particles relative to the pore size in the gel. Another one is the amount of interaction between the solute and internal the gel surfaces. There are varieties of substances, which absorb on silica hydro-gel with particular case [64]. Comparative merits and demerits of gels used for crystal growth are reviewed by Patel and Rao [53].

3.6 Structure of Silica Hydro Gel

It is the general observation of the researchers that gels and, in particular, silica gels are the best, very efficient and most versatile media for growing variety of crystals [29, 52, 65-80] and hence silica hydro-gel is the most favorite gel for the crystal growth experiments. Therefore, the study of its gelling mechanism and gel structure carries considerable importance.

Silica gels are chemical gel because all inter-atomic bonds are covalent. When sodium meta-silicate goes into aqueous solution, mono-silicic acid is produced in accordance with the dynamic equilibrium,

\[
Na_2SiO_3 + 3H_2O \rightarrow H_4SiO_4 + 2NaOH
\]

This mono-silicic acid can polymerize with the liberation of water,
This can occur repeatedly and a three dimensional network of Si-O links is established as silica hydro-gel.

As the polymerization process continues, water accumulates on top of the gel surface. This phenomenon is known as Syneresis. Much of the water has its origin in the above condensation process, and some may arise from purely mechanical factors connected with a small amount of gel shrinkage. The well-known stability of the silicon-oxygen bonds is responsible for the fact that the polymerization is largely irreversible. It is interesting to note that Kononenko et al [81], studied the characteristics of light scattering in the initial stage of gel formation in silicic acid, which provides valuable information.

The time required for gelation is very sensitive to pH. As the gelation is a gradual process, there is no unique definition for gelation time. It is known that two types of ions are produced during the gelation; $\text{H}_3\text{SiO}_4^-$ and $\text{H}_2\text{SiO}_4^{-2}$, in relative amount which depends on the hydrogen ion concentration. The latter one, favored by high pH values, is in principle more reactive, but higher charge implies a greater degree of repulsions. The $\text{H}_3\text{SiO}_4^-$ is favored by moderately low pH values and found to be responsible
for initial formation for long chain polymerization products [82]. Between these chains the cross-linkages are formed in due course and these contribute to the sharp increase of viscosity that signals the onset of gelation. Because of their low mobility, very long chains will cross-link more slowly than short chains. At very low pH values, the tendency towards polymerization is diminished and chain formation is slowed. Gelation time is strongly dependent on temperature [54]. This has been described in detail by Henisch [29].

A weak acid is generally preferred to adjust the pH values, because pH of the set gel changes only slightly with time and, secondly, the mineral acids tend to spoil the growing crystals. It is noteworthy that in less acidic gel solutions the reaction between the acid and sodium meta-silicate occurs with liberation of hydroxyl ions and thus pH of the solution rapidly increases with the process of polymerization, while in highly acidic gel there is no change in pH except due to very little difference in dissociation of acids of different complexities as well as requirements of reaction mechanism. Hence pH has profound influence on the gel structure [69]. Parikh et al [83] reported the effect of gel solution pH on the gel setting time.

Even though crystals can be grown in a variety of gels, the general observation is that silica gel is the best to grow. Better crystallinity of products is the main advantage. It does not need any heating effects. There is no need of additional acid as well as alcoholic substances. Silica gels are irreversible, elastic and resist to deformation. Moreover, silica hydro-gel reduces heterogeneous and secondary nucleations [84]. Also, the gel does not react with crystals grown. It is comparatively cheap.
3.7 Classification of Gel Growth Methods

Crystal growth in gel has been mainly classified into the following five different methods.

![Gel Growth Methods Diagram]

3.7.1 Crystal Growth by Reaction

This method is the basis of all methods of gel growth and can be described as crystal growth by chemical reaction. The crystals, which are insoluble or slightly soluble in water and decompose before reaching their melting points, can be conveniently grown by this method. Two basic requirements to grow single crystals by this method are; (i) the reactants used must be soluble in the solvent and the product crystal must be relatively less soluble, and (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.

Two aqueous solutions of soluble salts are suitably chosen and allowed to diffuse through the gel, so that there can be a slow and controlled segregation of ions and molecules resulting into the precipitation of an insoluble phase as the crystal. The gel affords to limit the number of critical size nuclei and decreases the rate of crystal growth either by controlling the diffusion of reacting ions or by governing the reaction velocity on the surfaces of the growing crystals. Resulting chemical reaction can be expressed as,
\[ AX + BY \rightarrow AY + BX \]

Where, A and B are the cations, X and Y are the anions.

Figure : 3.3 Crystal Growth by Chemical Reaction

This can be achieved by the test tube technique, in which one of the reactants is incorporated in the gel and the other reactant is diffused into it, or by the U-tube technique as shown in Figure 3.3, or its modification in which the two reactants are allowed to react by diffusion into an essentially inactive gel.

There is a variety of crystallization apparatus employed to grow single crystals by this method. The disadvantages of these crystallization apparatus are the depletion of one of the reactants which is inside the gel, the incorporation of reaction waste products by the growing crystals, supporting, handling and cleaning of the apparatus and gel preparation inside the horizontal tube open at both the ends [29].

Figure : 3.4 Modified Crystal Growth by Chemical Reaction
An improved design of gel technique used by Patel and Rao [53] is depicted in Figure 3.4, which eliminates all the inconveniences of the previous gel growth techniques and it permits the growth of mixed and doped crystals by multiple diffusion. Several metallic crystals like gold, lead, copper etc. have been grown by this method.

### 3.7.2 Chemical Reduction Method

This method is suitable for growing only metal crystals from gel media. Hatschek and Simons [85] were the first to report the growth of gold crystals by adding 8% oxalic acid solution over a set gel containing gold chloride solution. By this particular method crystals of Nickel, Cobalt [86], Selenium, Lead and Copper have been obtained.

### 3.7.3 Complex Decomplexion Method

This method requires first forming a chemical complex of the material of the crystals to be grown with aqueous solutions of some suitable substance, called complexing agent, in which the former is homogeneously mixable and then providing externally a condition conducive to de-complexing or dissociation of the complex formed. A standard procedure adopted for decomplexion is to increase the dilution steadily, while complex solution is diffused through the gel. Crystal growth by this method was first attempted by O’Connor et al [87] for the growth of cupric halide crystals.

### 3.7.4 Solubility Reduction Method

This method is applicable to grow single crystals of highly water-soluble substances. The growth of ammonium dihydrogen phosphate (ADP) single crystals by this method has been first reported by Gloker and Soest [88].
In this method, the substance to be grown is dissolved in water and is incorporated with the gel forming solution. Then a solution, which reduces the solubility of the substance, is added over the set gel to induce crystallization as in Figure 3.5. For instance, potassium dihydrogen phosphate (KDP) crystals have been grown by adding ethyl alcohol over the gel containing a saturated solution of KDP [89]. Crystals are grown due to the reduction of solubility of KDP in the liquid phase by the diffusing alcohol.

3.7.5 Electrolytic Method

The electrolytic method can also be used for the growth of metallic crystals by selecting the gel medium for controlled growth. For this a very low
d.c. electric current, usually of the order of 2-10 mA, is passed through a silica gel charged with suitable acid or electrolytic solution. Details are given in Figure 3.6.

It has been found that the pH of the gel medium, the concentration of the supernatant solution, the current density and the material used as electrode, have considerable influence on the habit of the crystals grown. Muzikar et al [90] have demonstrated the growth of single microcrystals of gold by electrochemical growth in a silica gel. Mohanan Pillai et al [91] grew lead dendrites, while George and Vaidyan [92] grew copper dendrites and silver dendrites and single crystals [93] using the electrolytic technique.

3.8 Growth Mechanism

As silica gels are neither liquid nor solid in nature, there are only a few methods available for quantitative investigations. From the SEM observations of dried silica gels, it has been found that the gel consists of sheet like structures of varying degrees of surface roughness and porosity, forming interconnected cells. Generally, the cell walls are curved. It has been estimated from the SEM images that the cell walls in dense gels (0.4 M Na₂SiO₃) have pores from 0.1µ to 0.5µ and 0.1µ to 4µ in low density (0.2 M Na₂SiO₃) gels. The cell walls are thicker in dense gels. During gelling the pH has a profound influence on the gel structure, changes from a distinctly box like network to a structure consisting of loosely bound platelets which appear to lack cross- linkages and the cellular nature becoming less distinct [94].

In the absence of convection, the only mechanism available for the supply of solute to the growing crystal is diffusion. One may envisage that the solute super-saturation $\phi_{\infty}$ at large distances from the crystal remains
unchanged during growth. However, at the crystal surface $\phi$ would initially have the same value but would then adjust itself in the course of growth to the lower value $\phi_0$. Hence this is determined by the dynamics of the growth processes.

For different idealized geometries, Frank [95] has developed equations, which give a description of diffusion controlled growth rates. The growth rates calculated by Frank involve the “reduced radius” ($S$) which for spherical system is defined as $r / (D t)^{1/2}$, where ' $r$ ' is the radius of the crystal, ' $D$ ' is the diffusion constant and ' $t$ ' is the time. The theory presents a simple relation,

$$\phi_\infty - \phi_0 = F(S)$$

By measuring ' $S$ ' and knowing the function ' $F$ ' the value of $\phi_0$ at any time could be determined. As long as ' $D$ ' does not alter, a constant value of ' $S$ ' implies a constant value of $\phi_0$. The constancy of ' $S$ ' can be checked by plotting $r^2$ versus $t$.

However, some limitations exist; one arising from the initial transient period during which steady–state concentration is established, and one arising from exhaustion of available solute. Both factors must be expected to give rise to nonlinearity. In general, there remains substantial uncertainty as to the effect of which the disruption of the gel structure has on the local value of ' $D$ '. This also applies to the effect of pH changes, which occurs during growth. This has been described for various crystals grown in detail by Henisch [29].

Cipanov et al [96] have developed a mathematical model of crystal growth process in gels. Calculations suggest that there is a locality in a gel that provides the best condition for nucleation and growth of crystals. They have compared the model with experimental results. Moreover, theoretical
aspects of the crystal growth in gel medium have been proposed by Desai and Hanchinal [97].

In growth systems, which depend on the diffusion of the reactant through a gel incorporating the other reagent, it has been found that the growth rate is more near the gel solution interface where the concentration gradients are high and away from the interface, the gradients are relatively low. Dislocation density is also different corresponding to the different growth rates. This further suggests that the growth rate itself determines the number of defects grown into the crystal even in the absence of foreign impurities. Occasionally, crystals grown in gels are found to have dislocation densities less than $10^3$/cm$^2$. The high degree of perfection of these crystals has been demonstrated by many authors [98,99].

In general, crystals growing in gel either displace the gel as they grow [68] or incorporate [100]. In the case of gel displacing, cusp will be formed around the growing crystals, whereas in the other case, since the crystals incorporate the gel as they grow, final crystals turn turbid instead of being transparent. The cusps like cavities are the regions in which the gel has been split and separated from the growing faces.

In the case of crystals growing in fissures in the gel, a clear boundary between opaque crystal growth in the gel and clear crystal growth in the solution can be seen [101]. In general, the progressive deterioration of crystal quality indicates an increasing incorporation of gel in the passage of time, which eventually leads to the destruction of the perfect facets observed on small crystals.
3.9 Nucleation Control

Nucleation is an important phenomenon in crystal growth and is the precursor of the overall crystallization process. Nucleation is the initiation of a phase change in a small region, such as the formation of a solid crystal from a liquid solution. Even though gel helps in suppressing nucleation, crystals growing in a gel system compete with one another for the solute atoms. This competition limits their size and perfection. It is therefore desirable to suppress nucleation so that only a few crystals are formed. Patel and Rao [53] have described some methods which control nucleation in gel to some extent, those are as follows:

3.9.1 Using Suitable Reactants

Out of various combinations of reactants, which can be used to obtain the required product crystals, only a few are found to be suitable to achieve controlled nucleation. For example, in the case of growth of potassium perchlorate crystals, various reactants were used, however, a combination of potassium chloride and perchloric acid has been found to be suitable for reducing the nucleation density. Reports of many authors confirm the importance of using suitable reactants [98, 102-105].

3.9.2 Using Gels Prepared With Various Acids

After the selection of the best combination of reactants, with particular acid set gel, it is necessary to use the same reactants with various acid set gels in order to reduce the nucleation density and grow larger crystals. Good quality neodymium carbonate crystals have been grown in hydrochloric acid set gels [106]. Moreover, for the growth of potassium perchlorate crystals, Patel and Rao [98] used four mineral acids, namely, perchloric acid,
hydrochloric acid, sulphuric acid and nitric acid; and four organic acids, namely, citric acid, tartaric acid, acetic acid and propionic acid, to set the gel and found the perchloric acid set gel gave the best results.

3.9.3 Changing the Gel Structure

It is possible to change the gel structure and reduce the nucleation density by changing the gel pH [106], gel density and gel ageing [69]. Generally, increasing gel density and gel pH decrease the nucleation density to a certain extent but the final crystals are of poor quality. On the other hand, the gel ageing reduces the nucleation density and hence the total number of crystals without affecting their quality. The decrease of nucleation centers at higher densities of gel as well as the gel aged for longer periods is due to the fact that these two parameters reduce the cell size and consequently the rate of diffusion of ions. The decrease in nucleation density at higher pH values may be due to the improper formation of gel cells [69].

3.9.4 Using Intermediate Neutral Gel

In this method, first the gel is prepared in the usual way containing one of the reactants in the bottom of a test tube. A second gel called the intermediate neutral gel or the reaction gel is formed over the first gel, and the second reactant is then poured over it. The neutral gel will slow down the reaction between the reactants and hence reduce the number of nuclei. This method was used to grow single crystal like cuprous oxide - \( \{ \text{Cu}_2\text{O} \} \) [65], calcium carbonate - \( \{ \text{CaCO}_3 \} \) [66], neodymium carbonate - \( \{ \text{Nd}_2(\text{CO}_3)_3.n\text{H}_2\text{O} \} \) and calcium tungstate - \( \{ \text{CaWO}_4 \} \) crystals [106]. It has been found that the nucleation density decrease with the height of the intermediate gel [65, 69].
3.9.5 Concentration Programming

In this technique, the concentration of the diffusing reactant is initially kept below the level at which nucleation is known to occur and is then increased gradually in small steps. With very dilute reactants the amount of material diffused through the gel is small and hence smaller is the supersaturation rate. Under these circumstances, a few nuclei are formed. As the concentration is increased further the growth of the existing nuclei is preferred to the formation of additional ones. Crystals grown by this method are more perfect and larger than those grown otherwise. This method has been successfully applied for the growth of many crystals [29,69,100].

3.10 Crystal Habit

Crystals with various habits are important both commercially and also in studying their physical properties. In gel growth, crystals with various habits can be grown by changing concentration of feed solutions, crystallization temperature, adding impurities and using various types of gels. Moreover, in some cases various habits in different regions of gel are also observed.

The habit modification can be obtained by changing concentration of the feed solution. McCauley and Gehrhardt [106] observed that during the growth of neodymium carbonate, a sodium carbonate incorporated gel enhanced the formation of dendrites and spherulites, while a neodymium chloride incorporated gel favored the growth of rhombic plates. Also, Bandhopadhyay and De [102] found that as the strength of feed solution was increased from 0.2 to 0.3 M, the calcium carbonate crystals were of rhombohedral habit and for 0.4 to 0.6 M concentrations the crystals were with the edges having wavy and ripple like features. On further increasing the
strength of feed solution to 1 M or more, a large number of nucleation centers with dendritic growth were observed.

The temperature of the growth has pronounced effect on habit of crystals. For example, in the case of strontium sulphate, all crystals grown at about 35°C exhibited {011} and {102} as their habit faces, whereas the crystals grown at about 20°C developed {022} habit faces in addition to {011} and {102} faces [100]. The habit modification can be observed for various gel structures. Mc Cauley and Roy [66] investigated the growth of calcite crystals and found that the decrease in pH of the gel turned spherulites (pH 10.5) into feathery polycrystalline aggregates (pH 9 to 10.5) and, ultimately, into single crystals of rhombic habits (pH 7 to 9).

Alike to ‘solution growth’, it is possible to change the crystal habit by adding impurities in the gel growth also. Various habits of calcite were obtained by adding impurities of magnesium, strontium, nickel and barium in different proportions during the growth of these crystals [100]. A similar study was carried out by Rosmalen et al [107] on gypsum crystals.

However, the habit modification is observed by using various types of gels for crystal growth. A comparison of crystals of calcium sulphate dihydrate grown in two different gel media, i.e., sodium silicate gel and bentonite clay gel, showed that the two media clearly affect the crystal habit and surface topography [108].

Interestingly, various crystal habits have been observed at different regions of gel. For lead molybdate growth, there were different regions inside the gel, where lead molybdate crystals of different habits were grown. Near lead nitrate solute, i.e. at the gel-liquid interface, polyhedral pyramidal crystals
were formed. Altogether, octahedral bi-pyramidal crystals and platelets were observed in the central region and near the ammonium molybdate solution, respectively [109]. Nucleation of crystals in gel is also influenced by light [52,110]. Calcium tartrate crystals were observed to have grown more perfectly with irradiation of the gel than in darkness, but copper chloride crystals grown from gel had an adverse effect [111].

3.11 Liesegang Rings

Chemical reactions leading to the formation of precipitates in gels are ideal in sense that the particles of precipitates remain where they are produced and the reagent reach each other only by diffusion. This study is very important, because the chemical reactions in biological media, whether leaving or dead, and in many geological structures are of this type. The diffusion of a soluble substance from an aqueous solution into gel follows the ordinary Fick's diffusion law.

The main feature of chemical reactions is that the diffusion of one reagent into the other contained in the gel produces not only the ordinary chemical change, but also definite mechanical structure. This structure varies with conditions and can be controlled.

Hedges [112] has identified the following four types of structures produced by chemical reaction in gels.

(i) Precipitates of continuous structure, which consists of small particles uniformly distributed so that the whole mass appears homogeneous.

(ii) Discrete structures consist of particles of relatively large size, separated by considerable spaces and may contain well-formed crystals.
(iii) Cellular structures comprise of a network of honey–comb like cells of precipitates enclosing clear gel, frequently obtained with a large number of a precipitate.

(iv) Periodic structures contain definite bends or rings of precipitants separated by clear spaces, which often contain the precipitate as discrete structures [113].

The first interesting study of a periodic structure was made by Liesegang in 1896 [39,40]. He covered a glass plate with a layer of gelatin impregnated with potassium chromate and added a small drop of silver nitrate. As a result, silver chromate was precipitated in the form of a series of concentric rings; well develop with regularly varying spacing. These types of fascinating formations are called as Liesegang rings.

Several workers have observed that, in many cases, the space between the rings contains a considerable amount of precipitate. Often the rings contain a large number of small particles and the intervening spaces contain a small number of large particles. Hatschek [114] had reported very interesting case of a cadmium sulphide precipitates in silicic acid gel, where the precipitates consisted of alternate pink and yellow bands with the difference in the size of particles. Dhar and Chatterji [115] had recognized that a layer of precipitates was followed by a clear zone in some structures and by a zone of differently dispersed precipitates in others.

Generally, the distance between successive bands of Liesegang rings increases as the diffusion proceeds further. Schleussner [116] had found the spacing to confirm with the geometric series and this conclusion had been confirmed by several other investigators [117,118]. However, a different
nature was observed by Davis [119], when mercurous nitrate was allowed to
diffuse into agar gel containing sodium formate, the distance between
successive bands was found to decrease. Generally, two types of Liesegang
rings have been reported in literature [120]; they are direct type and revert
type. In the direct type, the spacing between successive rings increases with
increase in the order of the ring from the gel boundary. Gnanam et al [121]
have reported the direct type Liesegang rings of calcite. In contrast to this, the
revert type Liesegang rings exhibit the spacing between successive rings
decreasing as the order of ring increases from the gel boundary. As shown in
Figure 3.7 many parameters may affect the formation of Liesegang rings
[113].

![Diagram showing various parameters affecting the formation of Liesegang rings]

**Figure : 3.7 Parameters Affecting the Formation of Liesegang Rings**

Many authors have attempted to give explanations of the formation of
Liesegang rings by different models, theories and computer simulations.
Henisch and Gracia-Ruiz [122] suggested a numerical method to obtain the
formation of Liesegang rings. In other study, Henisch and Gracia-Ruiz [123]
extended the condition under which two diffusing reagents could form
precipitates either continuous or periodic in a gel media. Moreover, several
other theories and models have been suggested by different workers [124-126]. Apart from this, some computer simulation experiments also have been carried out. Bueki et al [127] studied regular Liesegang structure by means of computer simulation. Joseph and Joshi [128] reported the effect of different parameters, for instance, the gel pH, the concentration of reactants, the height of the column of supernatant solutions, on the Liesegang ring formation during the growth of brushite crystals.

3.12 Crystals Grown by Gel Method

Among the various crystallization techniques, crystallization in gels has found wide applications in the fields of biomineralization and macromolecular crystallization in addition to crystallizing materials having nonlinear optical, ferroelectric, ferromagnetic, and other properties. Furthermore, by using this method it is possible to grow single crystals with very high perfection that are difficult to grow by other techniques [78]. The use of gels as growth media has previously been reported in the literature for a wide range of compounds, including both inorganic [29,71,129,130] and organic compounds [131,132] and also proteins [132]. Numerous workers have grown various crystals by the gel growth technique. In the present author's laboratory, his predecessors [33-36,133] have made detailed survey of various crystals grown by the gel techniques, therefore, due to the page constraints, the detailed survey has been avoided here and the concentration is focused on crystal growth of some important biomaterial and particularly urinary type crystals.

Gel is an ideal medium to grow biological crystals since its structure is similar to the mucus in the living organisms. The internal surface of the organs in animals is usually covered with mucus membrane. So, the gel method has
been applied to the study the bio-mineralization, i.e., crystal formation in human body. Most of the phosphate crystals are insoluble in water and decompose before melting. Hence single crystals of such types of compounds can not be grown by either slow evaporation or melt method, but can be conveniently grown by gel method. Gel media prevent convection and crystal sedimentation, and provide an attractive growth environment for optimizing biological crystals.

Nowadays, this method has applied to the study the crystal formation of cholesterol crystals [134-137]. Moreover, the crystallization of biological macromolecules of proteins like thaumatin, pyruvate kinase, lysozyme etc and t-RNA by Cudney et al [80] using silica gel. Bierampfel et al [138] reported crystallization of some RNA binding proteins using agarose gel. Where as, Lorber et al [139] reported the crystallization of biological macromolecules like proteins and nucleic acids using both the silica and agarose gel. The gel growth technique has been used for several years not only for crystals of small molecules, but also for crystals of proteins [84], for which it is particularly useful since these crystals are often difficult to grow.

The gel method is suitable to mimic the growth of urinary crystals \textit{in vitro}. A urinary stone, however, grows in a continuous flow of urine, i.e., in a dynamic medium. The nutrients for the growth are supplied continuously. The growth of urinary stones can be simulated by a simplified gel based model, where the nutrients are supplied continuously through diffusion in a gel. Notwithstanding, the gel based model is a static model unlike the urinary system, but provides excellent opportunity to grow urinary type crystals and
monitor their growth continuously. The present author has chosen the gel growth technique for the growth of crystals.

Since, the gel method of crystallization provides an ideal and most versatile technique to study crystal deposition diseases, which could lead to better understanding of their etiology, quite significant work has been reported on different kinds of urinary crystals such as, calcium oxalate monohydrate (COM) [140-147], Brushite [73,142,148-153], uric acid crystals [154], hydroxyapatite crystals [155]. Recently, Kanchana and Sekar [156] reported the influence of sodium fluoride on synthesis of hydroxyapatite by the gel method, while Sivakumar et al [157] reported the effect of magnesium on the formation of hydroxyapatite in the silica gel medium.

Recently, a modified gel growth technique has been proposed for the micro-crystal growth and in situ observations, which has been successfully tested for calcium hydrogen phosphate dihydrate micro-crystal growth inhibition in the presence of citric acid [158]. Kanchana et al [159] reported the growth of strontium chromium magnesium hydrogen phosphate (SrCrMHP) crystal in silica gel medium in different growth environments.

However, very few attempts were made to grow struvite crystals by gel method [153,160,161]. The growth of struvite crystals by gel method is explained in chapter V.

### 3.13 Advantages and Limitations of Gel Growth Technique

The advantages of gel growth technique are as follows:

- As gel growth technique is extremely simple and inexpensive, good quality crystals can be grown even in small laboratories, which do not possess sophisticated instrument.
• By carefully selecting the gel density, pH of the reactants and concentration of the reactants, good quality single crystals with high degree of perfection can be grown at room temperatures.

• Since the crystals are grown at or near room temperature, thermal strains are absent in the gel method.

• Thermodynamic consideration reveals that as the growth proceeds at ambient temperature, the grown crystals would contain relatively less concentration of equilibrium defects.

• Crystals can be observed practically in all stages of their growth.

• The gel framework, which is chemically inert and harmless, 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, if any, due to impact with either the bottom or the walls of the container.

• The effects of precipitation are eliminated as all nuclei are spatially separated.

• Growth of crystals with different morphologies is commonly found in bio-mineralization. By changing the growth conditions, crystals with different morphologies and sizes can be obtained.

• Gel medium considerably prevents convection currents and turbulence.

• Gel is soft and it yields a suitable environment for growing crystals.

• Gel matrix suppresses nucleation, reduces the rate of growth, and generally leads to comparatively larger (than that are formed by a similar reaction in water or in molten stage by double decomposition process), higher-quality crystals of enhanced stability.

• Crystallization in gel media also prevents crystal sedimentation.
• The purity of most crystals produced by this method is quite high; crystals generally contain only a few parts per million (atomic) of impurity.

• The growth of single crystals in gel is a self-purifying process, free from thermal strains, which is common in crystals grown from melt.

• The gel method is capable of yielding crystals of high optical perfection and wide range of morphology.

• Gels also provide an efficient protection of samples during handling and transport without affecting their crystallographic analysis.

• The gelation 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.

• Crystals are suspended in the gel network so that they do not form sediments and can grow free from strain exerted by the container.

• Heterogeneous and secondary nucleations are reduced in the presence of a silica hydro-gel. Silica hydro-gel is compatible with a wide range of salts, polymers, organic solvents, and buffers used for macromolecular crystallization in a pH range from 3 to 10.

• The grown crystals can be harvested easily without damaging the crystals.

Notwithstanding, the above advantages, the gel method has following limitations also:

• Growth period is usually very long.

• Crystal size is generally small, so large crystals cannot be grown.

• When silica gel is used, gel inclusion occurs in some crystals.

• The chance of lattice contamination by impurities from the gel itself is profusely increased.
References


43. Lord Rayleigh, Phil. Mag., 38 (1919) 738.


Growth and Characterization of Struvite and Related Crystals


CHAPTER : III : Crystal Growth Technique


