# CHAPTER 1

**GEL - A MEDIUM FOR CRYSTAL GROWTH**

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1.1 Introduction

Existence of large and apparently perfect crystals of many minerals in nature has attracted attention of many scientists in the field of crystallography and inspired them to grow such crystals in the laboratory. Materials required in modern devices should not only be of high purity but should also have high degree of perfection in crystalline structure with minimum defects. Such criteria can be fulfilled only by single crystals grown under the most favourable conditions. Consequently, enormous amount of labour and care has been lavished on the development of growth techniques. Several precise
techniques, depending on the properties of the material to be grown in crystalline form have been invented till date.

The growth of single crystals in gels has received considerable importance since Liesegang\textsuperscript{1}) first observed the periodic precipitation of slightly soluble salts in gelation. These "Liesegang's rings" inspired many other chemists and also mineralogists to study other reactions in various colloids. Among early workers were Hatschek\textsuperscript{2}), Holmes\textsuperscript{3-4}), Fells and Firth\textsuperscript{5}), Fisher and Simons\textsuperscript{6,7}), Morse and Donnay\textsuperscript{8}) etc. Interest was revived for the method by Stong\textsuperscript{9}) and soon after him Vand et. al.\textsuperscript{10}) published a note describing the full potential of growing single crystals in gels. Later a comprehensive survey of the technique by Henisch et. al.\textsuperscript{11}) gave momentum to crystal growers all over the world. Since the present work deals with growth of single crystals of tin-iodides by gel technique, it would be appropriate to concentrate on various aspect of crystal growth in gel media.

\section{Gels : Nature, Preparation and Properties}

A highly viscous two component system of semi-solid nature, rich in liquid and having fine pores
in it, may be referred to as 'gel'. Silica gel (synonymically called silica hydrogel, water glass or silicate glass, usually prepared from sodium meta silicate solution) agar gel (a carbohydrate polymer derived from sea weeds), gelatin gel (which resembles protein structure), clay gel, soap fluid, polyacrylamide, dense solution metal hydroxides, polyvinyl alcohol, oleates, stearates, aluminates etc., are some substances to be categorized as gels. And, a sol subjected to a number of treatments such as warming, cooling, chemical reaction, addition of external reagents, can be developed for gelation.

It may be mentioned that silica hydrogel has been most commonly used, due to its far better stability than all organic gels; though in certain specific cases gelatin gel, agar gel, and polyacrylamide have been preferred, while in some other cases both inorganic and organic gels have been found equally good for crystal growth in laboratory.

In order to obtain gel medium of desired pH, requisite amount of a suitable acid is normally added to the constantly agitated aqueous solution of Na₂SiO₃·9H₂O. The acidity of the resulting solution determines the course and rate of polymerization. The time of gelation
varies widely from a few minutes to several days depending on the nature of materials used, their history, temperature and source. Also the mechanical properties of a fully set gel are at variance with gelling condition.

1.3 Gelling Mechanism and Structure of Silica Hydrogels

When the solution of sodium meta silicate is mixed with any mineral or organic acid, the monosilicic acid that is formed in reaction:

$$\text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 + 2\text{NaOH} \quad (1.1)$$

produces a dimer:

$$\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH}$$

$$\text{HO} - \text{Si} - \text{OH} + \text{HO} - \text{Si} - \text{OH} \rightarrow \text{HO} - \text{Si} - \text{O} - \text{Si} - \text{OH} + \text{H}_2\text{O} \quad (1.2)$$

and then a trimer and then a polymer until a three dimensional network of \(\text{Si} - \text{O}\) (Siloxane) link is established.
As the polymerization continues, water accumulates on the top of gel surface, a phenomenon known as Syneresis, oozes away gradually to result into a set gel. The acid added to sodium-meta-silicate serves to neutralise the NaOH of the relation (1.1). A weak acid such as CH$_3$COOH is generally preferred unless otherwise unsuitable as gelling agent, first because the pH of the gel set with it changes only slightly with time$^{26}$), and secondly the mineral acids tend, more or less, the spoil the growing crystal. It is noteworthy that in less acidic gel solutions the reaction between the acid and sodium metasilicate occurs with liberation of hydroxyl ions and thus pH of the solution rapidly increases during the process of polymerization. In highly acidic media, in contrast, there would be no change in pH except due to very little difference in the dissociation
of acids of different complexities, as well as the requirements of reaction mechanism. Obviously then the pH must be a significant factor to decide the gel structure which in turn, would play a vital role in crystal growth. Doubtlessly, many other variables, characteristics of gels, e.g., nature and molarity of acid, strength and purity of sodium meta silicate, environmental temperature are no less influential to govern crystal growth in gels.

The structure of silica gel water system has been extensively investigated in many other ways and several comprehensive reviews are available. One gel is distinguished from other by nature of pores distribution. Biltz concluded that hydrogels are characterized by two types of pores. "Primary pores" of nearly molecular dimension and much coarser "Secondary pores" which behave as more or less normal capillaries. The effective pore diameters are of the order of 50-100 Å for silica gels. From the examination of gel with scanning electron microscope, Helberstadt et.al showed that the gel consists of sheet like structure of varying degree of surface roughness and porosity, forming interconnected cells. The cell walls in dense gels have pores less than 0.1 to 0.5 μ, while 0.1 to
4.0 μ for low density gels. pH during gelling has profound influence on gel structure. As pH increases the gel structure changes from distinctly box-like network to a loosely bound platelets. Gel structure has considerable influence on controlling nucleation density which is one of the remarkable merits of gel growth. A progressive formation of cross-linkage gradually diminishes cell size to which in turn leads to a lowering of nucleation probability.

1.4 Crystal Growth Methods

The enormous flow of information related to crystal growth in gels has been divided into the following four basic parts, each one of them having special advantages which are detailed further:

1. Reaction method
2. Complex decomplex method
3. Chemical reduction method
4. Solubility reduction method

1.4.1 Reaction method

Most of the work on crystal growth in gels has been done by reaction method. It has a special advantage of growing single crystals which are mostly insoluble (or slightly soluble) in water and which
decompose before reaching their melting point. In this method two soluble reactants are allowed to diffuse through a gel where they react and form an insoluble or relatively less soluble crystalline product. The chemical reaction taking place can be expressed as:

\[ AX + BY \rightarrow AY + BX \quad (1.4) \]

where A and B are cations, and X and Y are anions.

The requirement to grow single crystals by this method are:

1. The reactants employed here must be soluble in solvent (usually water) and product crystal must be relatively less soluble,
2. The gel must remain stable in the presence of the reacting solutions and must not react with these solutions or with the product formed,
3. Some solubility of product crystal is required in order to grow crystals of any size.

In simplest way, one aqueous solution is to be incorporated in an acid silicate mixture of proper pH before occurrence of gelation in a test-tube or a beaker and pour the other aqueous solution on set gel. Alternatively, the U tube is employed for neutral
gelation and then two reacting solutions are poured in two vertical limbs. For greater degree of lateral diffusion of ions to growth sites the modified apparatus were devised in this laboratory. The arrangement has successfully been employed to grow single crystals of $\text{Sr}_x\text{Ca}_{1-x}\text{C}_4\text{H}_8\text{O}_6\cdot4\text{H}_2\text{O}$, and this happens to be the first in the literature for the growth of a series of mixed configuration in gel media.

1.4.2 Complex decomplex method

The crystal growth by complex decomplex method was first reported by O'Connor et al. This method consists of first forming a chemical complex of the material of the eventual crystal to be grown with an aqueous solution of some suitable substance, called complexing agent, in which former is homogeneously miscible, and then providing externally a conduction conductive to decomplex or dissociate the complex formed. A standard procedure adopted for decomplexion is to steadily increase the dilution while the complexed solution is diffusing through the gels. In case of growth of CuCl, the large solubility of CuCl in HCl solution and its marked decrease with increasing dilution immediately favours the growth trials by complex decomplex method. The method has been successfully
used to grow good ionic conductors of $\beta$ AgI$^{36}$ and $\alpha$ HgS and $\beta$ HgS$^{37}$.

1.4.3 Chemical reduction method

This method is suitable for growing only metal crystal. Hatschek and Simon$^{38}$ grew gold crystals by adding 8% oxalic acid solution over gel which contained gold chloride solution. Recently Kratochvil et al.$^{39}$ grew gold crystals of triangular and hexagonal habits. Lead$^{40}$, copper$^{41}$ and cupric oxide$^{41,42}$ crystals have been grown by this method.

1.4.4 Solubility reduction method

This method is particularly suitable for growing single crystals of highly water soluble substance. Glocke and Soest$^{43}$ first reported the growth of ammonium dihydrogenphosphate (ADP) single crystals by this method. The substance to be grown is dissolved in water and incorporated with the gel forming solution. After the setting of gel, a solution which reduces the solubility of the substance is added over the gel to induce crystallization. Sodium chloride crystals have been grown by adding concentrated hydrochlorid acid (above 5.0 N) over the gel containing a saturated solution of sodium chloride$^{44}$. The formation of crystals
is due to the reduction of solubility of sodium chloride in the liquid phase by concentrated HCl. KDP crystals were grown by reducing solubility using ethyl alcohol.  

1.5 Studies on Gel Grown Crystals

The gel method is capable of yielding crystals of high optical perfections of a variety of materials which have had research application on a number of occasions. Gel grown PbI$_2$ crystals have been studied to understand their band structure\(^\text{46,47}\) and polytypism\(^\text{48-50}\). These studies have been impeded because of want of suitable specimens and many contradicting results were reported. The electrical resistivity of gel grown lead sulphide crystals\(^\text{51}\) was found to be $8.4 \times 10^{-4}$ ohm cm at 25°C while it is $8.2 \times 10^{-2}$ ohm cm for untreated natural gelina and $7.0 \times 10^{-3}$ ohm cm for synthetic lead sulphide.\(^\text{52}\) A single filament of gel grown silver acetate revealed stresses of $1.25 \times 10^{-6}$ psi in bending without fracture or permanent deformation.\(^\text{53}\) Dendrites of metallic lead have been used for metallurgical studies by Bedarida\(^\text{54}\). Optical absorption spectra of gel grown lead oxyiodide were studied at 430 m. Its dielectric constant at 10 KHz is about 10.5 and magnetic susceptibility is $-0.256 \times 10^{-6}$ C.G.S. Unit. The quality of gel grown
KDP crystal\textsuperscript{45} is judged according to dielectric properties measured in the vicinity of ferroelectric phase transition. Nassau et al.\textsuperscript{56} and Abraham et al.\textsuperscript{57} studied structural, optical and magnetic properties of copper iodate grown in gel.

1.6 Nucleation and Growth Mechanism

To suppress nucleation, whether it is homogeneous or heterogeneous, and to stabilize the concentration gradients in the neighbourhood of growing crystals by suppression of convection currents are the two principal function of gel. In most of the cases homogeneous nucleation is observed. Homogeneous nucleation involves the concept of critical nucleus. As a result of statistical accident, a number of atoms or ions or molecules can come together and form a rudimentary crystal. This crystal is likely to dissolve again unless it reaches a certain critical size. Beyond this size, the energy relations favour continued growth. The heterogeneous nucleation can occur in the presence of some foreign particles. Systematic experiments with the filtering media to avoid heterogeneous nucleation could not succeed fully, because the nuclei are too small and most of the filters appear to add some particles while they subtract others. In
all gel growth systems, crystals become increasingly scarce and more perfect with increasing distance from gel interface as the slow diffusion leads to more perfect crystals.

As far the mechanism by which crystals grow in gels, there have been evidences to two-dimensional piling and spreading of growth layers, predominantly taking place from one or more initiation centres. One is, therefore, tempted to make analogical comparison with solution growth. When single crystals of slightly soluble salts are grown from highly supersaturated solution which just remains stable over long periods by slow evaporation or cooling, the crystals never grow larger, because the supply of solute to the crystal surfaces is still extremely feeble. The fact that the large crystals are obtainable in gels proves that the supersaturation near the surface of these crystals must be much higher in gel than in solution. This suppression prevents the development of heterogeneous nuclei, so only homogeneous nucleation is left which is known to occur at high supersaturation only. What in fact, goes on the medium is the diffusion of dissolved matter as a consequence of the casual character of thermal motion of molecule. The molecules pass through an energy barrier,
\[ \Delta G, \text{ the free energy of activation for the molecular transport process. A molecule or anion changes its place with a frequency} \]

\[ \tau^{-1} = \frac{kT}{h} \exp \left( \frac{-\Delta G}{kT} \right) \quad \text{.. (1.5)} \]

But according to Einstein\(^{59}\) the root mean square displacement \( \lambda \) in time \( \tau \) is

\[ \lambda = (2DT)^{1/2} \quad \text{.. (1.6)} \]

where \( D \) is the diffusion constant.

Putting \( \lambda = d \), the ionic diameter, the frequency of nucleation is

\[ f = \frac{\tau^{-1}}{d^2} = \frac{kT}{h} \exp \left( \frac{-\Delta G}{kT} \right) \quad \text{.. (1.7)} \]

The energy \( \Delta G \) is, of course, equivalent to \( E_c \), the energy available for the creation of crystal nucleus given by

\[ E_c = \frac{16}{3} \frac{\sigma^3}{f^2} \frac{\pi}{L^2} \quad \text{.. \text{.. (1.8)}} \]

where \( \sigma \) is the surface energy per unit area, \( f \) is
the droplet density and L is the heat of desolvation. According to Fick's law:

\[ J = -D \nabla C \] \hspace{1cm} (1.9)

and

\[ \frac{dc}{dt} = D \nabla^2 C \] \hspace{1cm} (1.10)

where \( J \) is the quantity of matter transporting in the direction of the concentration gradient per unit area perpendicular to \( \nabla C \). Assuming that the precipitates are not too close to one another, as is true of gel growth, the concentration in space around the crystal of radius \( R \) is a function of the distance from the centre, and the boundary conditions become

\[ C(x,0) = C_\infty \]
\[ C(R, t) = S \]
\[ C(\infty, t) = C_\infty \]

The solution of diffusion equations (1.6) and (1.7) gives the radius \( R \) as a function of speed \( V \) of the advancing growth fronts in gel,

\[ R = \left[ DT (C_\infty - S) t \right]^{1/2} \] \hspace{1cm} (1.11)
Since each particle is to be treated independently of the others, the factor $V(C_\infty - S)$ is small, and hence equation (1.11) reduces to

$$R^2 = (Dt)^{1/2}$$  \hspace{1cm} (1.12)

The equation (1.12) is typical one dimensional diffusion process and has been experimentally verified by Liaw and Faust\textsuperscript{60}.

1.7 Advantages of Gel Technique

Of the various techniques for the growth of single crystals from melt, vapour or solution, those require elevated temperatures have the following inherent difficulties.

1. Crystalline imperfections are more apt to occur due to the lattice disruption by pronounced thermal vibrations.

2. The changes of lattice contamination by impurities are profusely increased due to latter's higher solubility at higher temperature.

3. Point defects and lattice strains are frequently introduced into the growing matrix during the range of cooling cycle.
Of all the methods for crystallization at room temperature, the gel method is believed to hold substantial promise of future development due to the following advantages, characteristics of this method.

1. The crystals can be observed practically in all stages of their growth.

2. The gel medium prevents convection currents and turbulence.

3. By remaining chemically inert and harmless the gel frame-work acts like a three dimensional crucible in which the crystal nuclei are delicately held in the position of their formation, thereby preventing damage, if any, due to impact with their bottom or the walls of container.

4. The gel is soft and yields mechanically to the growing crystals.

5. Thermodynamic considerations reveal that since the growth proceeds at near ambient temperature, the grown crystals would contain relatively lesser equilibrium concentration of defects.

6. Since the gel reduces, in effect, the speed of chemical reaction, crystals could be made to grow
much larger than those formed by a similar reaction in water or in molten stage by double decomposition process.

7. All the nuclei are spatially separated whereby the detrimental effects of precipitate-to-precipitate interaction are drastically diminished.

8. One can control diffusion rates and nucleation probability and thus design one's own crystallization equipment for obtaining different sizes and morphology of different crystals.

9. The growth procedure is highly economical, it yields a good crop of crystals with the simple and almost inexpensive equipment. The method can be exploited even in smaller laboratories which do not possess sophisticated equipments to grow perfect crystals.
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