1.1   Introduction

The existence of large and apparently perfect crystals of many materials in nature has attracted the attention of many scientists in the field of crystal growth and crystallography and inspired them to grow such crystals in the laboratory. Hence, crystal growth studies have become a subject of considerable interest to those whose work is concerned with crystals. Various applications that single crystals find in modern devices like transistors, rectifiers, polarizers, lasers, modulators, computer memory, strain gauges, etc. have created new demands for large single crystals and crystalline thin films of various materials. This has accelerated the progress in the art and science of crystal growth during recent years.

Crystal growth methods can be broadly categorized by the types of phases undergoing transformation during growth as follows :

$$Solid \longrightarrow Solid$$

$$Vapour \longrightarrow Solid$$

$$Liquid\ (melts\ or\ solutions) \longrightarrow Solids$$

The choice depends on the properties of the materials
involved. 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 by
single crystals grown under the most favourable con-
ditions. Several precise techniques, depending on the
properties of materials to be grown in crystalline
form are invented till date. For the materials of high
melting points and insoluble in aqueous solutions, can-
be grown from the melt at elevated temperatures. For
the materials which decomposes before melting at atmo-
spheric pressure and for which a suitable solvent is
not available, crystal growth is convenient from its
vapour phase. For highly water soluble compounds,
crystal growth from aqueous solution is well known.
Crystals of sufficiently large size can be grown by
this method at room temperature but control of nucleation
is a problem. Such crystals can be grown by employing
gel method. When gels are used for crystallization
process, nucleation control becomes easier and growth
occurs at room temperature, leading to fairly perfect
and transparent crystals. Since the present work deals

with growth and characterization of some ferroelectric
single crystals by gel technique, it would be appro-
priate to concentrate on various aspects of crystal
growth in gel media.

1.2   Historical

Growth of single crystals in gels has
received considerable importance since Liesegang[1]
first observed the periodic precipitation of sparingly
soluble salts in gelation. This observation inspired
many chemists and mineralogist to study such reactions
in various colloid. Among the early workers were
Hatschek[2], Holmes[3-5], Bradford[6], Fells and Firth[7],
Morse and Donnay[8], etc. Fisher and Simons[9,10]first
claimed that gels could form excellent media for
crystal growth. Interest in gel growth was reviewed/by Stong[11]
and soon after him Vand et al[12] published a
note describing high potential of growing single
crystals in gels. Later a comprehensive survey of the
gel method by Henisch and co-workers[13-15] gave
momentum to crystal growers all over the world.

1.3   Gels : Nature, Preparation and Properties

The gels used for crystal growth are

hydrogels. They are two-phase media : a liquid phase soaking a microporous solid phase. The solid phase does not form a rigid skeletion. It is the mode of polymeric chains,either entangled in the case of physical gels or cross linked in the case of chemical gels. For physical gels, the gelling process is achieved through a variation of physical parameters. For chemical gels, the gelling process results from a polymerization reaction. The various types of physical and chemical gels are as follows :

1. Sodium metasilicate (also known as silica hydrogel, water glass, or silicate glass).

2. Agar gel (a carbohydrate polymer derived from seaweeds).

3. Gelatin gel (which resembles protein structure)

4. Glay gel

5. Soap fluid

6. Polyacrylamide gel

7. Metal hydroxides

8. Dense solution

9.   Polyvinyl alcohol

10.   Oleates

11.   Steartes

12.   Aluminates, etc.

Above substances are known as gels and subjected to a number of treatments like warming, cooling, chemical reaction, addition of external reagent for gelation[16-21]. It may be mentioned that silica hydrogel has been most commonly used due to its far better stability than all organic gels[22,23], though in certain specific cases gelatin gel[24,25], agar gel[26] and polyacrylamide gel[27,28] have been preferred in some other cases[29] both inorganic and organic gels have been found equally good for crystal growth in the laboratory.
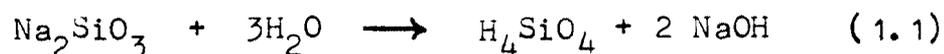
In order to obtain a gel medium of desired pH, the requisite amount of a suitable acid is normally added to the constantly agitated aqueous solution of sodium metasilicate $Na_2SiO_3.9 H_2O$. The acidity of the resulting solution determines the course and rate of polymerization[30]. The gelling process itself takes an amount of time which can vary

widely from minutes to many days, depending on the
nature of the material, its temperature and history.
The mechanical properties of a fully developed gels
can vary widely, depending on the density and on the
precise conditions during gelling[10].
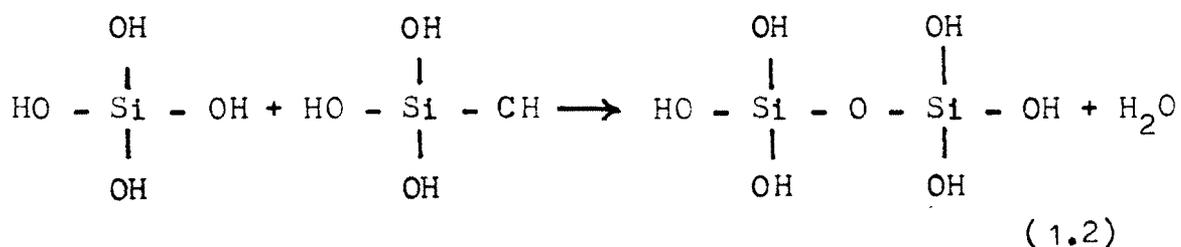
1.4   Gelling Mechanism and Structure of Silica

        Hydrogel

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

$$Na_2SiO_3 + 3H_2O \longrightarrow H_4SiO_4 + 2 NaOH \qquad (1.1)$$

produces a dimer :

$$
\begin{array}{ccccc}
OH & & OH & & OH \qquad OH \\
| & & | & & | \qquad\quad | \\
HO - Si - OH & + & HO - Si - CH & \longrightarrow & HO - Si - O - Si - OH + H_2O \\
| & & | & & | \qquad\quad | \\
OH & & OH & & OH \qquad OH
\end{array}
$$

$$(1.2)$$
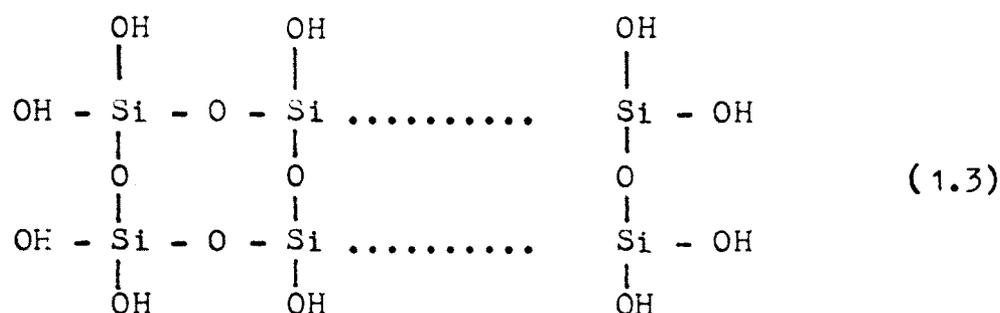
and then a trimer and then a polymer until a three
dimensional network of Si-O (Siloxane) link is

is established.

```
        OH          OH                 OH
        |           |                  |
OH  -  Si  -  O  -  Si  ..........     Si  -  OH
        |           |                  |
        O           O                  O                    (1.3)
        |           |                  |
OH  -  Si  -  O  -  Si  ..........     Si  -  OH
        |           |                  |
        OH          OH                 OH
```

As the polymerization continues, water accumulate
on the top of the gel surface, a phenomenon known as
"syneresis", oozes away gradually to result into a
set gel. The acid added to sodium-metasilicate serves
to naturalise the NaOH of the reaction (1.1). A weak
acid such as CH_3COOH (acetic acid) is generally
preferred unless otherwise unsuitable as gelling agent,
first because of the pH of the gel set with it changes
only slightly with time[31] and secondly the mineral
acids tend more or less, 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 with the process of poly-
merization. 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 mechanisms. 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 used, strength and purity of sodium metasilicate, and 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[32,33]. One gel is distinguished from other by nature of pores distribution. Biltz[34] 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[35] showed that the gel consists of sheets 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 0.05 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 net work 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 which
in turn leads to a lowering of nucleation probability.

1.5   Crystal Growth Methods

The enormous   flow of information
regarding crystal growth in gels, the gel technique
can be categorized into the following four basic
parts, each of them having special advantages :

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

1.5.1   Reaction Method

Most of the work on crystal growth in gel has been done by this method. This method is suitable for growing single crystals which are slightly soluble in water and which decompose before melting. 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[36]. The chemical reaction taking place can be expressed as :

$$Ax + By \longrightarrow Ay + Bx \qquad (1.4)$$

where A and B are cations and x and y are anions. The requirements to grow single crystals by this method are :

1.   The employed reactants 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 reactants and must not react with either of the reactants or with the product crystal.

3.   In order go grow crystals of any size some solubility of product crystal is essential[15].

In simplest way one reactant is to be incorporated in an acidify gel mixture of proper pH before occurrance of gelation in a test tube (Figure 1.1) or a beaker and pour the other reactant on the set gel (Figure 1.2). Alternatively, the U-tube (Figure 1.3) is employed for neutral gelation and then two reacting solutions are poured in two vertical limbs of U-tube. For greater degree of lateral diffusion of ions to growth sites the modified apparatus were devised in this laboratory[37,38]. The arrangement has successfully been employed to grow single crystals of $Sr_xCa_{1-x}C_4H_4O_6 \cdot 4H_2O$, and this happens to be the first time in the literature[39] for the growth of series of mixed configuration in the gel media.

1.5.2   Complex Decomplex Method

Crystal growth by this method was first reported by O'Connor et al[40]. 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 substances 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. This method has been successively

employed to grow good ionic conductors to β -AgI[41],

α- HgS   and β HgS[42].

1.5.3   Chemical Reduction Method

This method is suitable fir growing

only metal crystals. Hatschek and Simons[43]   grew

gold crystals by adding 8 % oxalic acid solution over

a set gel which contained gold chloride solution.

Recently, Kratochvil et al[44] grew gold crystals of

triangular and hexagonal habits. Lead[45], copper[46]

and cupric oxide[47] crystals have also been grown

by this method.

1.5.4 Solubility Reduction Method

This method is particularly, suitable
for growing single crystals of highly water soluble
substances. Glocker and Soest[48] first reported the
growth of Ammonium Dihydrogen Phosphate (ADP) single
crystals by this method. The substance to be grown is
dissolved in water and incorporated with the gel forming
solution. After setting the gel, a solution which
reduces the solubility of the substance is added over
the set gel to induce crystallization. Potassium
chloride and NaCl crystals have been grown by adding
concentrated hydrochloric acid over the gel containing
a saturated solution of potassium chloride and sodium
chloride[49]. The crystallization occurs due to the
reduction of the solubility of potassium chloride and
sodium chloride in the liquid phase by concentrated
hydrochloric acid. Potassium dihydrogen phosphate
crystals were grown by reducing solubility using
ethyl alcohol[50].

1.6 Studies on Gel Grown Crystals

The gel method is capable of yielding
crystals of high optical perfections of various

materials[51-75] which have various applications. Gel grown PbI_2 crystals have been studied to understand their band structure and polytypism. 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 was found to be 8.4×10^{-4} ohm cm at 25° C while it is 8.2×10^{-2} ohm cm for untreated gelina and 7.0×10^{-3} ohm cm for synthetic lead sulphide. A single filament of gel grown silver acetate revealed stresses of 1.25×10^{-6} psi in bending without fracture of permanent deformation[76]. Dendrities of metallic lead have been used for metallurgical studies carried out by Bedarida[77]. Optical absorption spectra of gel grown lead oxy-iodide was studied at 430μ. Its dielectric constant at 10 KHz is about 10.5 and magnetic susceptibility is $- 0.256 \times 10^{-6}$ C.G.S. units. The quality of gel grown KDP was judged according to dielectric properties measured in the vicinity of ferroelectric phase transition. Nassau et al[78] and Abraham et al[79] have studied structural, optical and magnetic properties of copper iodates grown in gel. Garcia-Ruiz and Martinvivalod[80] have

grown potassium sulphate single crystals upto
30 x 3 x 3 mm^3 in size in silica gel. Lefaucheux
et al[81] have reported the nucleation and growth of
KDP and ADP crystals for visulization by interfero-
metric holography. Garcia-Ruiz[82] described the
growthof of KDP doped with Ni by gel method.

1.7   Nucleation and Growth Mechanism

To surpress nucleation, whether it
is homogeneous or hetrogeneous and to stabilize the
concentration gradients in the neighbourhood of
growing crystals by supression of convention currents
are the two principle functions of gel. In most of
the cases homogeneous nucleation is observed.It
involves the concept of critical nucleus. As a result
of statistical coincidence, 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. Hetrogeneous 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
substract other. In all gel growth systems, crystals
become increasingly scare and more perfect with
increasing distance from gel interface as the slow
diffusion leads to more perfect crystals.

As far as the mechanism by which
crystals grow in gels, there have been evidences to
two dimensional   pilling and spreading of growth
layers, predominantly taking place[83] 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
remain stable over long period by slow evaporation or
cooling   the crystals never grow larger, because
the supply of solute to the crystal surface is still
extremely feeble. The fact that the large crystals
are obtained in gels proves that the supersaturation
near the surface of these crystals must be much
higher in gel than in solution. This supression prevents
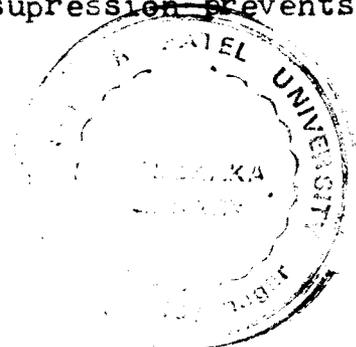
the development of heterogeneous nuclei, so only
homogeneous nucleation is left which is known to
occur at high supersaturation only. What is fact,
goes in the medium is the diffusion of dissolved
matter as a consequence of the casual character
of thermalm motion of molecules. The molecules pass
through an energy barrier, ΔG, the free energy of
activation for the molecular transport process. A
molecule or an ion changes its place with a frequency:

$$\tau^{-1} = \frac{kT}{h} \exp(-\Delta G/kT) \qquad (1.5)$$

But according to Einstein[84] the root mean square
displacement λ in time τ is :

$$\lambda = (2D\tau)^{1/2} \qquad (1.6)$$

where D is the diffusion constant. Putting $\lambda = d$,
the ionic diameter, the frequency of nucleation is :

$$f = \tau^{-1} = \frac{2D}{d^2} = \frac{kT}{h} \exp(-\Delta G/kT) \qquad (1.7)$$

The energy ΔG is, of course, equivalent to
E_c the energy available for the creation of crystal

nucleation and is given by :

$$E_c = \frac{16}{3} \frac{\sigma^3}{\rho^2} \frac{\pi}{L^2}$$

(1.8)

where σ is the surface energy per unit area,

ρ is the droplet density, and

L is the heat of desolvation.

According to Fick's law :

$$J = - D \, grad \ C$$

(1.9)

$$\frac{dc}{dt} = D \nabla^2 C$$

(1.10)

where J is the quality of matter transporting
in the direction of the concentration gradient per
unit area perpendicular to ∇C.

Assuming that the precipitates are
not too close to one another, as is true in gel
growth, the concentration in space around the crystal
or radius R is a function of the distance from
the centre, and the boundaring conditions

$$C(x, o) = C_\infty$$
$$C(R, t) = S$$
$$C(\infty, t) = C$$

$$(1.11)$$

The solution of equations (1.9) and (1.10) gives the radius R as a function of speed V of the advancing growth fronts in gel :

$$R = \left[DV (C_\infty - S)t \right]^{1/2} \qquad (1.12)$$

Since, each particle is to be treated independently to the others, the factor $V(C_\infty - S)$ is small and hence equation (1.12) reduces to :

$$R = (Dt)^{1/2} \qquad (1.13)$$

The equation (1.13) is typical of one dimensional diffusion process and has been experimentally verified by Liaw and Faust[85].

1.8   Advantages of the Gel Technique

The various techniques for the growth

of single crystals from melt, varpour or solution, which require variation in temperature, 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 lattice's higher solubility at   higer temperature.

3.   Point defects and lattice strains are frequently introduced into the growing matrix during the range of cooling cycle.

        Among the all methods for crystallization at room temperatures the gel method has following special   advantages :

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

2.   The gel medium prevents convention currents and turbulence.

3.   The gel does not prevent sufficient supply of reactants.

4.   Crystals are not altered by temperature or pressure. Therefore, the products of this technique are of high perfection i.e. show a small dislocation density.

5.   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 the container.

6.   The gel is soft and yields no mechanical strains to the growing crystals.

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

8.   Since the gel reduces in effect, the speed

of chemical reaction, crystals could be made to grow much larger than those grown by a similar reaction in water or in molten state by double decomposition process.

9. All the nuclei are spatially separated whereby the determinantel effects of precipitate-to-precipitate interactions are drastically diminished.

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

11. The growth procedure is highly economical, it yields a good crop of crystals with simple and almost inexpensive equipment.

12. The method can be easily exploited even in smaller laboratories which do not possess sophisticated equipment to grow perfect crystals.

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Captions of the figures

Figure 1.1   Crystal Growth in Gels
                        (Test Tube Method)

Figure 1.2   Crystal Growth in Gels
                        (Beaker Method)
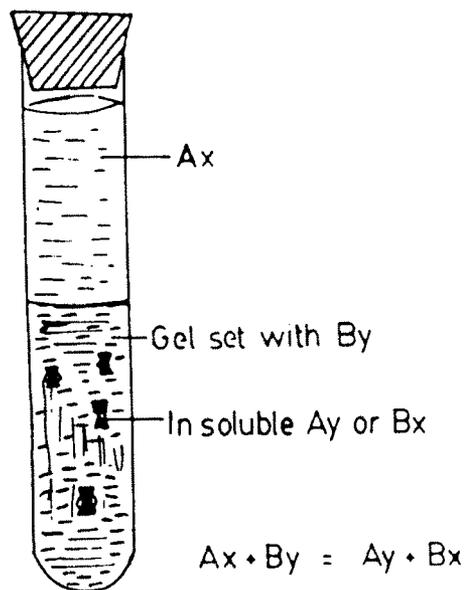
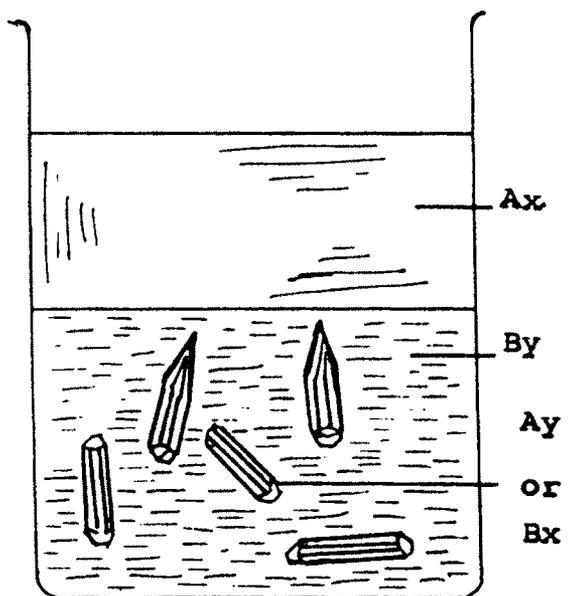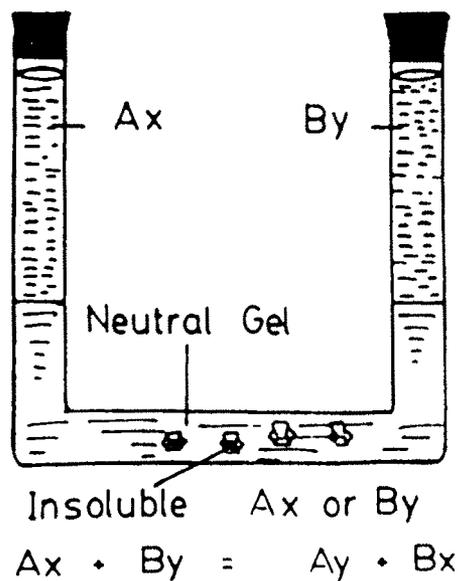Figure 1.3   Crystal Growth in Gels
                        (U-Tube Method).

Ax

Gel set with By

Insoluble Ay or Bx

$$Ax \cdot By = Ay \cdot Bx$$

Fig. 1.1

Ax

By

Ay

or

Bx

Fig. 1.2

Ax

By

Neutral Gel

Insoluble   Ax or By

$$Ax \cdot By = Ay \cdot Bx$$

Fig. 1.3