3. GROWTH OF SAMPLE CRYSTALS

In this chapter we present some details about the various crystal growth methods like melt growth, vapour growth and solution growth along with a brief description about the gel method. The crystal growth methods adopted and results obtained in the present study are also explained.

Even though more than one technique can be employed for growing single crystals of the given material on the basis of thermodynamics, the selection of the technique may be made on the basis of growth kinetics and requirements such as shape, size, transparency and purity.

3.1 Growth from Melt

Crystal growth from melt is probably the most widely practiced commercial process for growing single crystals. All the methods of growth from melt rely on cooling the liquid below its freezing point. If care is exercised, single crystal can be made to grow which will otherwise end up with polycrystalline mass. The technique by which this is done can be split into three: Czochralski technique, Bridgman technique and Verneuil technique. In the Czochralski method [1] the melt is contained in a crucible but the crystals are grown at the free top surface of the melt so that there is no contact between the crystal and crucible (Fig. 3.1). In this method, as the crystal grows, it is slowly pulled upwards so that the solid-liquid interface is just above the level of the liquid surface. The melt temperature and pulling rate depend upon the rate at which the heat is removed and they can be changed independently. By the rotation of the crucible and the crystal, asymmetries in the temperature gradient of the melt are reduced and a better mixing of the melt is achieved. Crystals such as sapphire and silicon have been grown by this method [2,3].
Figure 3.1: Schematic diagram of Czochralski apparatus used for crystal growth by the melt technique.
In the Bridgman technique [4] the melt is contained in a sealed crucible and is progressively frozen from one end which can be achieved by:

1. moving the crucible down the temperature gradient
2. moving the furnace over the crucible or
3. by keeping both the furnace and the crucible stationary and cooling the furnace so that the freezing isotherm moves steadily through the originally molten charge (Fig. 3.2)

The latent heat of solidification, which is evolved as the crystal grows, is removed by the conduction through the crystal and the crucible. In this method, at least some part of the solid-liquid interface is in contact with crucible. The advantage of this technique is that the shape of the crystal can be controlled by the crucible while the disadvantage lies in the fact that the crystal gets strained and the melt-crystal-crucible contact can result in the nucleation differently aligned crystals. Crystals such as calcium fluoride [5,6] have been grown by this method.

Liquid Encapsulated Vertical Bridgman Method (LEVBM) is a modified form of Bridgman method. It is extensively used to grow single crystals of volatile compounds such as superconducting chevrel phase compounds [7-11] and semiconducting gallium arsenide and gallium phosphide.

In the Verneuill method [12], a fine dry powder of the material (particle size 2-100 μm) to be grown is fed through a wire mesh. The powder melts as it falls through the oxygen-hydrogen flame (Fig. 3.3). A film of liquid is formed on top of the seed crystal. This freezes progressively as the crystals are slowly lowered. To maintain symmetry the seed is rotated. The art of the method is to balance the rate of powder feed and rate of lowering to maintain a constant growth rate and diameter. The method is used extensively for the growth of ruby, sapphire and Mg-Al spinel crystals [13,14].
Figure 3.2: Schematic diagram of Bridgman apparatus used for crystal growth by the melt technique.
Figure 3.3: Schematic diagram of Verneuil apparatus used for the growth of crystals from melt.
3.2 Growth from Vapour

Single crystals can be grown from the vapour phase by sublimation, chemical vapour transport (CVT) and chemical vapour deposition (CVD). Crystal growth from vapour [1] is often suitable for materials that decompose before melting at atmospheric pressure.

For the growth of large single crystals, in evacuated and sealed silica ampoules from the vapour phase, the following points are considered as important.

1. Use of undercritical supercooling to allow only selective nucleation on a small number of active sites on the walls. Tapered ampoule tip is used to localize nucleation and to promote the formation of one large single crystal at the tip of the ampoule.

2. Use of cylindrical-conical ampoule geometry with large tube diameter to stimulate convective transport.

The simple experimental arrangement is a closed horizontal tube with feed material and transporter. The tube is introduced into a double zone furnace maintaining the two ends of the tube (Fig. 3.4) at two different temperatures $T_1$ and $T_2$ (appropriate for crystal growth). The transport of the material takes place via vapour phase and deposited in the growth zone. For endothermic reactions, the transport proceeds from the hot end to the cold end and for exothermic reactions the transport proceeds from the cold end to the hot end.

The rate of transport should not exceed the rate of growth. The crystallization chamber should be large enough in order to prevent intergrowth between adjacent seeds. The temperature distribution in the growth zone should be adjusted to avoid partial re-evaporation of the already grown crystals. Cadmium sulphide and cerium telluride crystals have been grown by this method [15,16].
Figure 3.4: Schematic diagram of double zone furnace used for the growth of crystals from vapour.
3.3 Growth from Solution

Crystallization from solution [17,18] has been used extensively as a method for obtaining single crystals of a variety of inorganic and organic materials. Aqueous and organic solutions and melts of inorganic compounds have been used as solvents. Crystals will grow from solution if the solution is supersaturated.

The growth of crystals from solution is possible in two different ways:
(i) low temperature solution growth; and
(ii) high temperature solution growth.

In the low temperature solution growth the methods used to produce the required supersaturation are:

(a) the slow cooling of the solution;
(b) the slow evaporation of the solvent; and
(c) the establishment of a temperature gradient between a relatively hot zone containing undissolved solid and a cooler zone in which the crystal grows (Fig. 3.5).

Potassium Dihydrogen Phosphate (KDP), Ammonium Dihydrogen Phosphate (ADP) and Tri Glycine Sulphate (TGS) have been grown by this method [19-21].

The high temperature solution growth [22] or flux growth is used for crystallisation of complex multicomponent systems. By this method Yttrium Aluminium Garnet (YAG) crystals and superconducting crystals like Bismuth-Strontium-Calcium-Copper-Oxide (BSCCO) have been grown [23-25]. In this method, the crucible with the charge is heated to high temperature at which the total charge dissolves in the solvent. The necessary supersaturation can be obtained by reducing the
1 – Thermostat for dissolution at a temperature $T_1$
2 – Nutrient
3 – Connecting tubes
4 – Thermostat for growth at a temperature $T_2$, $T_2<T_1$
5 – Vane type agitator
6 – growing crystal

Figure 3.5: Schematic diagram of solution growth apparatus
temperature or by evaporating the solvent. Growth of single crystals at elevated temperatures poses the following problems:

1. Lattice disruptions by pronounced thermal vibrations,
2. Changes of lattice contamination by impurities at high solubilities,
3. Introduction of lattice strains during the cooling process,
4. Decomposition before melting,
5. Exertion of high vapour pressure, and

An alternative technique at room temperature is demanded in order to overcome the above said restrictions. A very efficient room temperature growth technique with controlled nucleation is the gel technique. Since the work presented in the thesis is the growth of pure and doped calcium tartrate crystals in silica gel, much attention has been devoted towards this growth technique.

3.4 Growth in Gels

Amongst the wide variety of techniques prevalent today for the growth of single crystals, the gel technique gained considerable importance due to its simplicity and feasibility. Gel growth is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection.

For materials which are insoluble in water or sparingly soluble in water and for materials which decompose before melting, gel growth is found to be a versatile technique and for the same reasons in the present work attempt was made to grow pure and doped crystals of calcium tartrate by the gel growth technique. It has the added advantage that the crystals can be grown at room temperature and therefore the grown crystals will be free from the defects arising from the growth at elevated temperatures.
An extensive survey of the gel technique has been published by Henisch [26]. The origin of the gel growth of crystals dates back to the year 1889, when periodic precipitation of silver chromate in the form of concentric rings was discovered by Liesegang, a photographer cum colloid chemist. Since then, except during the dormant period from 1930-60, active and continuous works are being carried out on the gel growth of crystals. For all practical purposes, the growth of crystals in gel medium is not totally different from that in solution.

3.4.1 The gel

Gel is a loosely linked polymer of a two component system formed by the establishment of a three dimensional system of cross linkages between molecules of one of the components. The system as a whole is permeated in the other component as a continuous phase giving a semi-solid; generally rich in liquid.

Silica gel, silica alumina gel, gelatin gel, ferric hydroxide gel, cellulose nitrate gel [27], agar gel, tetramethoxysilane (TMS), methyl cellulose gel and styrene maleic anhydride gel [28] are the different varieties of gels available. Special gels like pectin have also been prepared [29]. Of all these different gels, silica gel seems to be the best and the most versatile growth medium; as was observed by Hatschek [30] and Henisch [26] in their systematic study of gel growth of crystals.

3.4.2. Structure of silica gel

On dissolution in water, sodium metasilicate produces monosilicic acid and sodium hydroxide in accordance with the dynamic equilibrium

$$\text{Na}_2\text{SiO}_3 + 3 \text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 + 2 \text{NaOH} \quad (3.1)$$

The monosilicic acid polymerises with the liberation of water.
The above change occurs continuously until a three-dimensional network of Si-O links is established. It is known that two types of ions, viz. $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ are produced whose relative amounts depend on the hydrogen ion concentration. High pH value favours the formation of $H_2SiO_4^{2-}$. This is more reactive and the higher charges amount to greater degree of mutual repulsion. Low pH value favours the formation of $H_3SiO_4^-$ which is responsible for the initiation of long chain polymerization [31,32]. The cross-linkages formed in due course contribute to the sharp increase in viscosity, which signals the onset of gelation. As the polymerization process proceeds, water accumulates on the top of gel surface - a phenomenon known as syneresis. Much of the water is believed to have its origin in the above condensation process and a part may arise from purely mechanical factors connected with a small amount of gel shrinkage.

The structure has considerable influence on the quality and size of the crystals grown. The ultimate structure of the gel is too small to be resolved by an ordinary microscope. From an examination of a gel, using a scanning electron microscope, Halberstadt et al [33] have shown that the gel consists of sheet-like structures, of varying degrees of surface roughness and porosity forming inter-connected cells. The diameters of pores of cell walls in high and low density gels are, respectively, in the ranges 10 to 50 Å and 100 to 400 Å. Blitz [34] concluded that the hydrogels are characterized by two types of pores: "primary" pores of nearly molecular dimensions and much coarser "secondary" pores which look like normal capillaries.
3.4.3 Principle of gel method

Solution of two soluble compounds, which give rise to the required insoluble crystalline substance by mere chemical reactions between them, is allowed to diffuse into the gel medium. Crystallization takes place according to the chemical reaction

\[
AX + BY \rightarrow AB + XY \quad (3.2)
\]

where AX and BY are the solutions of the compounds which on reaction give rise to the insoluble or sparingly soluble substance AB and also the unwanted product XY which is highly soluble in water.

3.4.4 Importance of gel method

The following points emphasize the importance of the gel method:

1. The gel acts as an ideal medium for the diffusion of the reacting ions/solvents.
2. It forms a three dimensional crucible yielding to the growth of crystals without exerting much force upon them.
3. Crystals can be grown at ambient temperature using simple crystallizing systems.
4. The gel remains chemically inert and therefore does not involve in the chemical reaction between the reactants during crystallization.
5. This method has the ability to control the rate of reaction required for crystallization of particular material.
6. It holds the crystals in fixed positions without overlapping; irrespective of internal disturbances.
7. Nucleation can be controlled effectively by changing the density of the gel
8. The growth at every stage can be observed clearly in a transparent medium.
9. It is practically free from convection during growth.
10. The grown crystals can be easily harvested without damaging the crystal's faces.
11. Gel grown crystals are found to be comparatively less defective than the crystals grown by other methods.

Gel method is therefore believed to hold substantial promise of future development on the growth of single crystals at room temperature. However, the gel technique has the following demerits: (i) it is difficult to grow large crystals by this method, (ii) the growth period is considerably longer (two or three months) and (iii) there may be gel inclusions in the grown crystals.

3.4.5 Methods of growing crystals in gels

The different methods of growing crystals in gels fall under the following classes: chemical reaction method, solubility reduction method and complex dilution method.

The chemical reaction method is suitable for crystals, which are mostly insoluble or sparingly soluble in water. In this method, two soluble reactants are allowed to diffuse through the gel where they react and form an insoluble or sparingly soluble crystalline product. The basic requirements of this method are:

(a) the gel must remain stable in the presence of reacting solutions and (b) it must not react either with the solutions or with the product crystal.

This method is suitable for crystals which are mostly insoluble or sparingly soluble in water. Sulphates [35], tungstates [36], alkali metal iodides [37], tartrates [38], rare earth double sulphates [39] and zeolites [40] have been grown by using this method.

In the chemical reduction method first proposed by Hatschek and Simons [41,42], a dilute acid is added over a gel which contains the compound corresponding to the crystal to be grown. For instance, to grow crystals of gold, oxalic acid is added over the gel containing gold chloride solution. Gold crystals of triangular and
hexagonal habits [43], crystals of selenium [44], nickel, cobalt [45], lead [46-48] and of copper oxide [49] have been grown by this method.

Solubility reduction method is particularly suitable for growing single crystals of highly water soluble substances. In this method [50] the substance to be crystallized is first dissolved in water and incorporated within the gel solution before gelation. When the gel sets in, a solution which reduces the solubility of the substance is added over the gel. This, on diffusion into the gel induces crystallization. For example KDP crystals can be grown by adding alcohol over the gel containing saturated solution of KDP [51]. Pure crystals of common salt and crystals of double chlorides have been grown by this method.

In the complex dilution method [52-56], the material to be crystallized is first complexed in some reagent which enhances its solubility. It is then allowed to diffuse into a gel, which is free from active reagents. As the complex solution diffuses through the gel, its concentration gets reduced. This results in a high supersaturation of the material to be crystallized and hence nucleation begins. By this method silver halide [57], mercuric sulphide [58], cuprous halide and selenium crystals have been successfully grown.

3.4.6 Crystallizing systems for gel growth of crystals

The different types of crystallizing systems adopted for the gel growth of crystals fall under the following classes:

a. straight tube (test tube) system,

b. double diffusion system,

c. modified U-tube system, and

d. linear column system.
The straight tube system is the simplest but versatile crystallizing system. It is easy to operate and easy to clean the system after harvesting the crystals. The inner reactant or the solute to be crystallized is incorporated in the gel and taken at the bottom of the straight tube. The outer reactant or the solvent applied to reduce the solubility is taken over the set gel (Fig. 3.6).

The double diffusion system may be a simple U-tube with a neutral gel at the bottom and the required reactants on either side (Fig. 3.7). Otherwise it may be a test tube with fritted disk at the bottom with the neutral gel over it (Fig. 3.8). The tube is kept inside a wide vessel containing one reactant or the de-complexing agent. The top of the gel may be filled with the outer reactant or complex for that purpose. The U-tube system does not offer a linear path to the diffusing material. Further, harvesting the crystal and the system after harvesting is a cumbersome task.

The modified U-tube system is basically the system used by Nickl and Henisch [59] for growing calcite crystals which was later modified by Patel and Rao [60] for growing KClO₄ crystals. It is basically a double diffusion system based on chemical reaction method. It consists of a large beaker to which two vertical side tubes are attached through ground joints. Neutral gel occupies the beaker almost completely and the space above the gel is filled with distilled water. The two side tubes are filled with the required reactants (Fig. 3.9). The distilled water prevents the gel surface from drying out. The waste product formed along with the crystallizing material diffuses into the distilled water, which could be removed and replenished.

The linear column system was designed by Armington and O'Connor for the gel growth of cuprous chloride crystals by complex dilution method [26]. In this system the gel offers a linear path to the diffusing material (Fig. 3.10). The basic set up is a cylindrical tube containing the neutral gel at the middle connected to two reservoirs filled with the complex and diluting agent separately. It is easy to operate the system
Figure 3.6: Schematic diagram of straight tube system used for the growth of crystals by gel method
Figure 3.7: Schematic diagram of U-tube system used for crystal growth by the gel method
Figure 3.8: Schematic diagram of a tube with fritted disc used to grow crystals by gel method
Figure 3.9: Schematic diagram of the modified U-tube system used in gel growth
Figure 3.10: Schematic diagram of the linear column system used in gel growth
and to harvest the crystals. Requirement of large amount of materials is a drawback of this method.

3.5 Nucleation Control

As the competition for growth among the growing crystals in the gel medium limits the quality and size of the crystals grown, nucleation control is desirable to suppress nucleation until only a few crystals grow. This is achieved by employing intermediate neutral gel and by employing concentration programming.

3.5.1 Neutral gel technique

In this method, the neutral gel is prepared using a weak acid like acetic acid and introduced over the set gel incorporated with the inner reactant. The outer reactant is introduced over it (Fig. 3.11) after the setting of the neutral gel [61]. In this method, the outer reactant has to diffuse through an additional thickness in reaching the required site. The introduction of the neutral gel controls the formation of spontaneous nucleation at the gel-solution interface.

3.5.2 Concentration programming

In concentration programming the concentration of the outer reactant is initially kept below the level at which nucleation is known to occur [62]. The concentration is then increased in a series of small steps at frequent and equal intervals. Nucleation will take place at some stage and a few crystallites will be formed which will act as sinks thereafter. Subsequent increase in concentration will lead to faster growth of the crystallites and not in the formation of new crystallites. It has been experimentally found that frequent small concentration steps are more beneficial than a few large steps.
Figure 3.11: Schematic diagram of test tube system used in neutral gel technique
3.6 Growth of Pure and Impurity Added Calcium Tartrate Single Crystals

In the present study, calcium tartrate tetrahydrate single crystals (pure and Sr\(^{2+}\) added) were grown in silica gels prepared from sodium metasilicate (SMS) by chemical reaction method using straight tubes of length 200 mm and 25 mm diameter.

The materials used were sodium metasilicate, tartaric acid, calcium formate, formic acid (85%) and strontium chloride. All the chemical used were AnalaR grade.

The test tube diffusion method [26] was employed to grow calcium tartrate single crystals in a gel medium. 0.5M sodium metasilicate (Na\(_2\)SiO\(_3\).9H\(_2\)O) was titrated with 0.5M tartaric acid till the mixture attains the pH 4.2. This gelling mixture was allowed to set in glass tubes of length 200 mm and diameter 25 mm. The gel was set in about 48 hours. After a gel aging of one day, the supernatant solution was added over the set gel. The supernatant solution was a mixture of 0.5 M calcium formate and 85% formic acid so that the pH of the solution was between 1 and 1.5.

The expected chemical reaction is,

\[
\text{Ca(HCOO)\textsubscript{2}} + \text{C}_4\text{H}_6\text{O}_6 \rightarrow \text{CaC}_4\text{H}_4\text{O}_6 + 2\text{HCOOH} \quad (3.3)
\]

Strontium added calcium tartrate tetrahydrate crystals were grown in six different impurity concentrations, viz. 0.4, 0.8, 1.2, 1.6, 2.0 and 10 mole %. The impurity with the required concentration was mixed with the supernatant solution and allowed to diffuse into the gel medium containing tartaric acid.

3.7 Results and Discussion

The pH is the key factor in the gel technique. Calcium tartrate does not crystallize below pH 3 [38]. This is because calcium tartrate is highly soluble in acidic
media. Therefore in the present study we have tried to maintain the pH of the gel medium constant during reaction by using a suitable pH buffer.

It was observed that when the pH is increased beyond 5 the gel becomes rigid and therefore the crystals were so smaller and sometimes they grew from the gel solution interface into the gel medium in the form of needles. When the pH was maintained between 3.5 to 4.5, we were able to get good, transparent calcium tartrate tetrahydrate single crystals. It was observed that there was no discernible difference appeared between the crystals grown in the pH range 3.5 to 4.5. We observed that when the gel solution was in the pH range 3.5 to 4, it took about 5 to 7 days for the gel to set. When the gel solution was in the pH range between 4 and 4.5 the gel was set in about 1 to 3 days. An overnight was enough for a gel with pH 4.5 to set firm and rigid, but a gel with pH 4 took about 72 hours to set rigid so that it can hold the supernatant solution without damaging the gel.

Various concentrations of tartaric acid were used keeping the other parameters constant. The concentration of tartaric acid was varied from 0.25M to 1.25M in steps of 0.25M. 0.25M concentration of tartaric acid was not suitable for setting the gel for the required pH. Tartaric acid of concentration 1.25M was found to render the gel medium harder, thereby resisting the diffusion of the upper reactant through it. The concentration between 0.5M and 1.0 M was found to be suitable for the growth of calcium tartrate tetrahydrate crystals.

In the present study, with formic acid in the supernatant solution, crystals of reasonable size with good morphological perfection and transparency were obtained for 0.5M concentration of tartaric acid. When the concentration of the tartaric acid was increased to 1M the crystals grew densely around the gel solution interface like a band.

To study the effect of pH of the supernatant solution, we prepared a gel solution of the desired pH and allowed it to set firmly. After the gel was set, 0.5M calcium
formate solution mixed with 85% formic acid was taken as the supernatant solution. The pH of the supernatant solution was varied between 0.5 and 2.5. It was observed that, when the pH was between 1 and 1.5, we were able to suppress nucleation inside the gel and those crystals grew well inside the gel column were found to be larger in size. When the pH was reduced below 1 we found excessive nucleation and small crystals appeared throughout the gel column. When the pH was increased above 1.5, it was observed that there was no excessive nucleation, however, the crystals were smaller in size.

We also tried to grow calcium tartrate tetrahydrate crystals by varying the concentration of the calcium formate in the supernatant solution. When the concentration of the upper reactant was 0.25M, we observed tiny crystals just below the gel solution interface. As we increased the concentration to 0.5M, good quality and transparent crystals grew well below the gel solution interface. If the concentration of the upper reactant was increased further, we observed a dense growth near the gel solution interface and few opaque and poor quality crystals below it.

The optimized growth parameters used in the present study for the growth of calcium tartrate tetrahydrate single crystals are summarized as follows:

1. Crystallizer
2. Concentration of lower reactant
3. Concentration of sodium metasilicate (gel)
4. pH of the gel solution
5. Concentration of upper reactant
6. Volume of gel solution
7. Volume of supernatant solution
8. Gel setting time
9. Aging of gel
10. Growth period

<table>
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<th>Parameter</th>
<th>Value</th>
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</thead>
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<td>Crystallizer</td>
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<tr>
<td>Concentration of lower reactant</td>
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<tr>
<td>Concentration of sodium metasilicate (gel)</td>
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<td>24 hours</td>
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<td>Growth period</td>
<td>30 days</td>
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The parameters used for the growth of impurity added calcium tartrate tetrahydrate crystals were similar to the growth parameters used for the growth of pure crystals. To grow Sr\(^{2+}\) added calcium tartrate tetrahydrate crystals, strontium chloride was mixed with the supernatant solution in six different molecular ratios, viz. 0.4, 0.8, 1.2, 1.6, 2.0 and 10 mole%.

In all the cases, it was observed that small crystals appeared below the gel solution interface in about 2 days and large crystals with good morphological perfection appeared deep in the gel column within a week. The maximum size of the crystals grown was about 8 mm x 6 mm x 3 mm. Photograph of pure and impurity added calcium tartrate tetrahydrate crystals growing inside the test tube is shown in Figure 3.12 and a photograph showing the absence of growth veils in the pure crystal grown in the present study is shown in Figure 3.13.

Now we present the discussions on the crystal growth experiment. Calcium tartrate is an example for a crystal involving the salts of weak acid. In such cases, during growth, the environment of the crystal becomes acidic since the reaction yields rapidly diffusing hydrogen ions. In the increasingly acid environment calcium tartrate is increasingly soluble. Therefore the nucleus reaching critical size is reduced. As mentioned earlier, calcium tartrate does not nucleate at pH values less than 3.

Also, during the growth of calcium tartrate crystals, the original tartaric acid content of the gel is completely exhausted partly through the formation of calcium tartrate crystals and partly through the demonstrable loss of tartaric acid to the solution at the top in the gel region close to the supernatant liquid. Normally, many small crystals grow in the gel medium and only a few of them are larger in size.

In order to suppress the nucleation and to improve the size of calcium tartrate crystals it is essential to eliminate the factors said above. We have tried to eliminate the first factor by using a suitable pH buffer and the second factor by acidifying the
Figure 3.12: Photograph of the crystals growing inside the test tube in the present study

[1 - Pure, 2 - 0.4 mole{%}, 3 - 0.8 mole{%}, 4 - 1.2 mole{%}, 5 - 1.6 mole{%},
6 - 2 mole{%}, 7 - 10 mole{%}]
Figure 3.13: Photograph showing the absence of growth veils in the pure crystal grown in the present study
supernatant solution. Cipanov et al [63] have shown that the variation of the acidity of the crystallogenetic media strongly influenced the depth of the first crystal arising in the gel. They have used calcium chloride mixed with hydrochloric acid as the supernatant solution. The nucleation suppression was achieved by converting the tartrate ions ($\text{C}_4\text{H}_4\text{O}_6^{2-}$) present near the gel solution interface into its molecular form ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$) by proton introduction.

It was observed that the nucleation suppression near the gel solution interface was high when a strong acid, like HCl, was used. On the other hand when a weak acid, like formic acid, was used we observed that nucleation suppression was not to that level. The first crystal arising in the gel when HCl was used was about one inch deep into the gel, whereas it was 2 to 3 mm when formic acid was used. However, considering the size and perfection of the grown crystals we found that those crystals grown by using formate-formic acid as the supernatant solution were superior to those crystals grown with calcium chloride-HCl. Most of the crystals were larger in size and only a very few crystals very close to the gel solution interface were smaller in size.

The mean mass of the pure crystals was determined. It was found to be 92.8 mg when the pH of the supernatant solution was 1 and 81.3 mg when pH was 1.3. For the crystals grown from calcium chloride mixed with HCl, it was reported that [63] the mean mass was 39.4 and 46.5 mg for pH = 1.08 and 1.3 respectively.

Earlier workers [26,64] have reported that calcium tartrate crystals exhibit growth veils near their geometrical centre. These veils evidently formed during the initial stages of growth and may be well associated with the non-linearities near the origin. We have observed that no growth veils are present in the crystals grown by using formate-formic acid as the supernatant solution. Figure 3.14 illustrates the absence of veils in the grown crystals.
It is expected that formate/formic acid acts as a pH buffer and maintains the pH of the gel medium throughout the growth process. Hence the crystals growing deep into the gel are larger in size as the pH of the environment surrounding the growing crystal is conducive for the growth of calcium tartrate crystals. Also, according to equation (3.3), formic acid is yielded as the byproduct in the reaction. Since formic acid is a weak acid, its effect on the pH of the gel medium is less compared to HCl, yielded as the byproduct when calcium chloride is used. In addition to this, formic acid prevents algae growth which disturbs the growth of calcium tartrate crystals during long growth periods.
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