6.1 Introduction

The problem of nucleation is of great importance in practical operation, since the crystal which grows in any particular gel system competes with other crystals for solute. This competition limits their size and perfection and it is obviously desirable to suppress nucleation until, ideally only one crystal grows in a predetermined location. The available techniques have not yet reached this level of perfection.

The suppression of nucleation is the principal function of the gel, but it is apparent that the degree of suppression ordinarily obtained is insufficient for many of the crystals one wishes to
grow. Though ionic diffusion is slowed by the soft three dimensional gel framework, this suppression reaction rate is still larger than the one required for liquid nucleation. Hence nucleation control in a gel medium remains one of the serious problems for a crystal grower. It may be envisaged that the potential nuclei are physically enclosed in gel cells of varying size and varying degree of communication with neighbouring cell. Gel cell size is influenced by gel density, gel age, pH of gel, temperature etc. Hence, nucleation control can be achieved to some extent by the varying these parameters. Other conventional methods such as neutral gel technique, seeding, addition of impurities have also been employed by some crystal growers.

Recently, the growth of single crystals in silica gel media under the influence of an externally applied electric field has drawn the attention of many crystal growers and is under modification in several laboratories. Magnetic and electric fields have been used in liquid-solid growth and the theory of accelerated diffusion under constant electric field has been developed by Mysels, Lamm and Simnad and Ling Yang. Influence of different gel parameters, temperature
concentration programme, replenishment programme etc. on nucleation and growth/crystals are discussed in this chapter. A study of nucleation and growth of SnI₄ and SnI₂ crystals under an externally uniform electric field is also reported in this chapter.

6.2 Experimental

The gels were prepared by mixing pure sodium meta silicate solution of known density with required amount of 1.0 N or 1.5 N SnCl₂ solution as described in section 5.2 (chapter 5). As per convention, density of sodium meta silicate is treated as gel density. The pH of the resulting solution is kept at 3. The gel solutions thus prepared were transferred to 2.3 cm diameter and 30 cm long glass test tubes and allowed to set at room temperature. To study effect of temperature on growth, tubes containing gels were kept in a constant temperature water bath having accuracy ±1°C. After the gels were set, the feed solution, 1.0 N KI was placed above the set gel for crystallization.

6.3 Observations and Discussion

Different gel parameters such as gel density, gel aging, temperature etc. which influence the pore
size of the gel were manipulated to secure optimum conditions for the growth of better crystals.

6.3.1 Effect of gel density

The gels of different densities were obtained by mixing sodium meta silicate solution of specific gravities from 1.03 to 1.06 with 1.0 N and 1.5 N, SnCl₂ solutions, keeping the pH constant at 3. It is observed that the transparency of the gel increases as the gel density decreases. Figure 6.1 shows crystals growing in gels of three different densities. Figure 6.2 is a plot of nucleation density versus gel density. The greater gel density implies smaller pore size and poor communication among the pores and thus decreases the nucleation density. Gel density 1.03 g cm⁻³ gives good transparent crystals but size is too small while 1.05 to 1.06 give translucent crystals. It may be noted that gel density 1.04 g cm⁻³, is the optimum value for the growth of well defined single crystals of SnI₄.

6.3.2 Effect of gel aging

To investigate the effect of gel aging, the acidified gels were allowed to age for different periods before adding the feed solution. Crystals growing
in gels allowed to age for different periods are shown in fig. 6.3. Figure 6.4 is a plot of age of gels versus the nucleation density. It is evident that a longer setting time result in greater amount of water evaporating out of the gel. The effect of water evaporation should be considered in two parts, namely before and after the formation of gel framework. Before the gel is set, evaporation of water will cause an increase in gel density, which in turn will decrease the diffusivity of ions in gel. After the gel is set, evaporation of water causes not only the lack of ionic carriers in the channel of gel framework but also discontinuities in the channels due to the shrinkage of the gel. Both these effects would adversely affect the diffusion of ions.

6.3.3 Effect of temperature

The temperature has considerable influence on reaction and diffusion. Influence of temperature on chloride nucleation and growth of cuprous chloride has been studied by Armington and O’Connor. It is easy to investigate that there should be an optimum temperature for nucleation. As the temperature increases, the free energy of formation of critical nucleus increases but
the degree of supersaturation diminishes\textsuperscript{16}. Single tube experiments were carried out in a constant temperature range 25 to 40\degree C. Variation in temperature showed that at constant cation (Sn\textsuperscript{+++}) and anion (I\textsuperscript{−}) concentration, more crystals grow at lower temperature than at higher temperature. Figure 6.5 shows variation of nucleation density with temperature. The decrease in nucleation density at higher temperature is due to the fact that an increase in temperature causes an increase in the aqueous solubility of stannic iodide. Thus the size of grown crystals at higher temperatures is smaller than that at low temperatures. When growth experiments were carried out at 40\degree C the crystals did not nucleate. By decreasing the temperature at a constant rate nucleation of SnI\textsubscript{4} was observed at 37\degree C and further decrease in temperature increased the size of crystals, which must be due to gradual increase in supersaturation by lowering temperature.

6.3.4 **Replenishment programme**

In fact two mechanism are simultaneously at work, the progressive exhaustion of reagents and diminishing diffusion gradient due to diffusion of reaction waste. The size of the grown crystals can be considerably increased as well as nucleation centres can be
controlled by continued supply of reagent and removing the waste product. In simplest way this can be achieved is by periodically replacing the feed solution of same concentration and incorporating the gel with higher concentration of SnCl₂ i.e. 1.5 N. Over the set gel, 30 ml of 1.0 N KI solution was placed and after a fixed period, 4 days this solution was completely replaced by the fresh 1.0 N KI solution. This process was continued for a month. Figures 6.6(a) and 6.6(b) show crystals growing in gels without and with the renewal programme. It is considered that after adding feed solution, a diffusion gradient of solute at the growing crystals will be set up. The replaced solution will be able to maintain a dynamic equilibrium and a flux of solute owing to diffusion at the growing crystals. Thus there will be a constant uniform diffusion gradient throughout the crystal growth. Hence the probability of formation of a new nuclei is considerably reduced and the size of growing crystals becomes greater. Crystals grown by this method are transparent and larger than those grown otherwise. This method has the following advantages:

(i) The concentration of feed solution will remain almost constant throughout the growth. This
maintains a uniform diffusion gradient at the growing crystals, enabling them to grow larger in size.

(ii) Growth will continue till the incorporated reagent is exhausted.

(iii) Some reaction waste product will come out while replacing the feed solution.

6.3.5 Concentration programming

In this procedure, 30 ml of 0.2 N KI solution was placed over the set gel. The strength of this feed solution was increased at the rate of 0.2 N day$^{-1}$ by removing 20 ml of the above feed solution and replacing it by an equal amount of more concentrated feed solution. Initially, with lower concentration, SnI$_2$ needles emerged and at higher concentrations (about 0.8 N) nucleation of SnI$_4$ crystal began. The nutrient concentrations were systematically increased from 1 N to 1.25 N and then to 1.5 N KI solutions, over a period of 3 weeks, one week for each solution. This resulted in a few nucleation centres which acted as sinks and resulted in the establishment of a radial diffusion pattern that substantially reduced the reagent concentrations in the neighbouring locations and hence
the formation of additional nuclei was inhibited. On increasing the concentration, the existing crystals grew faster and non-competitively, so that their quality was corresponding good. Starting and stepping with very low concentration of feed solution (KI) leads to utilization of the incorporated solution (SnCl$_2$) for the formation of SnI$_2$ crystals only. Figures 6.7(a) and 6.7(b) show crystals growing without and with concentration programming.

Figures 6.8 and 6.9 show respectively some typical crystals grown by the replenishment and concentration programming.

6.3.6 **Growth by electrolysis**

Another method for growth employing an electrolytic technique was used$^7$. The crystallization apparatus used in the present study is an electrolyte cell of length 20 cm and diameter 2.5 cm as shown in fig. 6.10. Procedure for preparation of gels are same as described earlier. However, data relating to electrolytic growth is as under:

Specific gravity of sodium metasilicate solution = 1.04
Concentration of SnCl$_2$ solution = 1.5 N
pH of gel mixture = 3
Mean experimental temperature = 27°C.
The gels were transferred to the electrolyte cell and were allowed to set. Over the set gel 1.0 N KI solution was poured. Care was taken to ensure that no air bubbles existed between the electrodes and solution. A suitable d.c. voltage was applied between two carbon electrodes acting as anode and cathode. The current in the circuit was measured by means of a sensitive milliammeter (mA). Higher current i.e. above 0.9 mA dissociates, KI immediately while voltage above 0.5 V give tin metal crystals around the electrodes.

After 4 to 5 hours, a large number of nucleation centres of SnI$_2$ begins to appear just at the periphery of the gel solution interface after forming a small yellow precipitate column. After 2-3 days, the nucleation of SnI$_4$ crystals started. SnI$_4$ crystals are reddish in colour and have octahedral habit while SnI$_2$ crystals are yellow in colour and are in the form of needles. As the time elapsed, the length of SnI$_2$ needles increases and nucleation of SnI$_4$ crystals also increased. After 10-12 days, growth ceases, by this time the crystallization was almost completed.

The experimental details and growth parameters are summarized in Table 6.1.
Table 6.1  Growth parameters for growing Sn, SnI₂ and SnI₄ single crystals

<table>
<thead>
<tr>
<th>pH of the gel</th>
<th>Age of gel in hrs.</th>
<th>Conc. of feed solution</th>
<th>Current in mA</th>
<th>Size of SnI₂ crystals in mm</th>
<th>Period of crystallization in days</th>
<th>Size of SnI₄ crystals in mm</th>
<th>Period of crystallization in days</th>
<th>Size of Sn crystals in mm</th>
<th>Period of crystallization in days</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>24</td>
<td>1.0 N</td>
<td>0.05</td>
<td>3</td>
<td>6</td>
<td>1.5</td>
<td>11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>1.0 N</td>
<td>0.1</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>1.0 N</td>
<td>0.3</td>
<td>9</td>
<td>3</td>
<td>3</td>
<td>7</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>1.0 N</td>
<td>0.5</td>
<td>11</td>
<td>2</td>
<td>4.5</td>
<td>5</td>
<td>8</td>
<td>2</td>
</tr>
</tbody>
</table>
Under electric field $\text{Sn}^{++}/\text{Sn}^{++++}$ and $I^-$ ions move in opposite direction. $\text{Sn}^{++}/\text{Sn}^{++++}$ ions are repelled from the anode and attracted by cathode where a supersaturated meta stable state is formed. The ionic velocity is therefore accelerated to value adequate for the formation of metallic white Sn (tin) single crystals.

A chemical inhomogeneity is also produced in the medium which changes the structure and nature of the growth system. In other words, an anisotropic effect in diffusion is produced under electric field\textsuperscript{17).} The theory of diffusion of Simnad and Ling Yang\textsuperscript{12)}, Lamm\textsuperscript{11)}, Mysels\textsuperscript{10,18)} and Kauman and Bach\textsuperscript{19)} anticipates an accelerated diffusion region:

$$D_e = D_0 + U^2 E/2k \quad \ldots \quad (6.1)$$

where $U$ is the product of ionic mobility and charge, $E$ the intensity of the field and $k$ a rate constant. $\text{Sn}^{++}/\text{Sn}^{++++}$ and $I^-$ ions drift in opposite directions under the action of electric field and a supersaturated meta stable region is formed just below the gel-solution interface, which ultimately leads to crystallization of SnI\textsubscript{2} needle crystals. Meanwhile $\text{Sn}^{++++}$ ions reaching to cathode, created a moderately supersaturated region just
ahead of the crystallization front which later yielded the octahedral crystals of SnI$_4$. Application of electric field promoted linear growth of SnI$_2$ needle crystals and is conjectured as being due to the accelerated diffusion.

It has been found that an electric field affects the growth of crystals in silica gel media in the following ways:

(i) Single crystals of tin, SnI$_2$ and SnI$_4$ are synthesized together in the same experimental set up.

(ii) The crystals require a shorter time to attain maximum size.

(iii) A suitable and definite control over growth rate and nucleation centre formation is exercised.

(iv) Crystal quality was unaffected by the electric field.

6.4 Conclusions

1. Nucleation control can be achieved by changing a variety of gel parameters such as gel aging, gel density, concentration programme
and replenishment programme.

2. Highly transparent and small single crystals of SnI₄ can be obtained (at pH 3) with low gel density (below 1.04).

3. By replenishment and concentration programmes the size of the crystals can be increased.

4. Above the temperature of 37°C, the growth of SnI₄ crystals ceases completely.

5. Although the period of crystallization was considerably reduced by applying an externally uniform electric field the quality of the crystals is unaffected. By this method, single crystals of Sn (tin), SnI₂ and SnI₄ have been synthesized together in the same experimental set up.
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Captions of the figures

Fig. 6.1 Crystals growing at three different densities of gel solution (a) 1.03 g cm$^{-3}$, (b) 1.05 g cm$^{-3}$, (c) 1.06 g cm$^{-3}$.

Fig. 6.2 Nucleation density $N$ vs gel density for two different SnCl$_2$ solutions.

Fig. 6.3 Crystals growing at three different gel ages: (a) 24 h, (b) 48 h, (c) 96 h.

Fig. 6.4 Nucleation density $N$ vs gel aging (h) for two different concentrations of SnCl$_2$ solution.

Fig. 6.5 Nucleation density $N$ vs temperature (°C) for two different concentrations of SnCl$_2$ solution.

Fig. 6.6 Crystals growing (a) without and (b) with replenishment programme.

Fig. 6.7 Crystals growing (a) without and (b) with concentration programming.

Fig. 6.8 Some of the typical crystals of SnI$_4$ grown using the replenishment programme (mm scale).

Fig. 6.9 Some of the typical crystals of SnI$_4$ grown using the concentration programming. (mm scale).

Fig. 6.10 Schematic diagram of the electrolytic cell.