Chapter 4

The Growth Process

4.1 Introduction

Growing crystals in gels is probably the most versatile among the various techniques of crystal growth from solutions at ambient temperature. In the growth process, one is mostly concerned with the chemistry and physics of heat and mass transfer in fluid-solid transitions and in a wide sense, with the technology of controlling phase transitions that lead to solids. Successful application of gel method has been reported [1] regarding crystal growth of materials whose solubilities range from $10^{-5}$ to $10^{-7}$ weight percent. Due to the low aqueous solubility and thermal instability of oxalate compounds, the gel method stands out as the most appropriate technique for the growth of oxalate crystals. A large variety of oxalate crystals have been grown by this method [2 –6]. As earlier reports show, mixed rare earth oxalate crystals also have been grown by gel method since one rare earth can readily be substituted for another in the lattice of almost any rare earth crystal with very little strain [7-9].

The growth of single crystals of Gadolinium Samarium Oxalate (GSO), Gadolinium Cerium Oxalate (GCO) and Gadolinium Neodymium Oxalate (GNO) in hydrosilica gel by single diffusion method employing chemical reaction is described in this chapter. The influence of various parameters on the growth of these crystals has been studied in detail.
4.2 The medium of crystal growth

Controlled diffusion of chemical reagents through hydrosilica gel (the growth medium) is made use of for the growth of mixed oxalate crystals. The gel medium provides a three dimensional structure in which crystal nuclei are directly held in position for their formation and development without generating convection currents and turbulence by maintaining chemical inertness. This relative freedom from constraints may be an important factor in the achievement of high structural perfection. Further, the three dimensional network of the gel provides a controlled diffusion environment to the ions which is necessary for crystallization [10].

In the present work, hydrosilica gel was chosen as the medium for the growth of GSO, GCO and GNO crystals.

4.3 Chemistry associated with growth

The trivalent rare earth ions easily combine with oxalate ligand to form oxalate complexes having the general formula \( R_2 (C_2O_4)_3 \cdot nH_2O \) where \( R \) represents the rare earth element. The chemical reaction is

\[ 2 R^{3+} + 3 (C_2O_4)^{2-} \rightarrow R_2 (C_2O_4)_3 \]

Halide or nitrate salts of rare earths when admixed with oxalic acid react to form the corresponding oxalates. Mixed double rare earth oxalates can be prepared by using two rare earth salt solutions having the rare earth ions in the required ratio. The proposed reaction is

\[ A^{3+} + B^{3+} + 3 (C_2O_4)^{2-} \rightarrow AB (C_2O_4)_3 \]

where \( A \) and \( B \) represent the rare earth ions.

4.4 Preparation of hydrosilica gel

To prepare hydrosilica gel, sodium metasilicate (AR grade supplied by CDH) was used. Finely powdered sodium metasilicate (SMS) was dissolved in double distilled water and the solution was kept undisturbed for two days for sedimentation of the insoluble particles. Decanted clear
solution was filtered and stored as stock solution. The density of the solution was accurately determined by specific gravity bottle method. The density of the SMS solution has considerable influence on the gelation process and the quality of the gel and hence the quality of the grown crystals [11]. By plotting a graph between the density of SMS solution and the partial volume of water in the solution [Figure 4.1], the quantity of water to be added to the stock solution to prepare the gel of any desired density can be found out. Thus SMS solutions having different values of density can be prepared.

![Figure 4.1](image)

**Figure 4.1** Density of SMS solution Vs partial volume of water

The pH of the SMS solution requires to be lowered for proper gelation. This can be done by mixing an acid with the solution. For the growth of oxalate crystals, oxalic acid is used as the acidifying agent. One of the reactants should be incorporated into the gel prior to gelation, in single tube experiments [10]. Since rare earth ions are found to be reacting with SMS, the incorporation of other component (oxalic acid), in the gel is inevitable. Oxalic acid was used to acidify the medium and also serves as a source of anions.
Oxalic acid of 1 M concentration was prepared from its AR grade salt. SMS solution of the desired density was added dropwise to oxalic acid. To ensure the homogeneity of the medium, the mixture was stirred well [12,13] and the pH of the mixture was measured immediately. After preparing the solution mixture with desired pH and density, it was transferred into borosil glass tubes of length 15 cm and internal diameter 1.5 cm and kept undisturbed for gelation. The tubes should be clean, dry and free from any acidic or alkaline impurities. The mouths of the test tubes were covered tightly to prevent contamination of the gel surface by the atmospheric impurities.

The time required for gelation varied from few minutes to several days depending on pH [Figure 4.2]. The gel sets very quickly, when the pH of the solution is slightly above the neutral pH. The gelation period is found to be high, for higher and lower pH values.

![Figure 4.2 Period of gelation Vs pH of the medium](image)

4.5 Preparation of supernatant solution

Analar grade nitrates of gadolinium, samarium, cerium and neodymium supplied by CDH were used for the preparation of feed
solution or supernatant solution. Aqueous solutions of the corresponding nitrates (1 M) were used as the source of rare earth ions. To grow mixed crystals containing two rare earth ions with a specific stoichiometry, the corresponding rare earth solutions were mixed in proper ratio by volume and this mixture was poured over the set gel column. The feed solution is acidified with nitric acid and the acidity of the feed solution is found to have a direct control over the growth process. The feed solution should be carefully poured over the gel column without disturbing the gel surface. The incorporation of a particular rare earth into the body of the crystal depends on the availability of that ion. Hence by adjusting the proportion of rare earth salt solutions in the feed solution, crystals having the required stoichiometry can be prepared.

4.6 Growth of Gadolinium Samarium Oxalate (GSO) crystals

Single diffusion method employing chemical reaction is used for the growth of GSO Crystals. Hydrosilica gel in which oxalic acid is incorporated, is prepared as described in the previous sections. A mixture of equal volumes of 0.5M solutions of gadolinium nitrate and samarium nitrate is used as the feed solution. It was found that irrespective of the concentration or ratio of the feed solution the gel cracked on adding the feed solution over the set gel. Even after effecting a change in the density and pH of the gel, the same observations were repeated. In certain cases the gel system withstood up to two or three days and in such cases a precipitate column extending to the bottom of the gel could be seen in the growth system.

On repeating the experiment with the feed solution acidified with dilute nitric acid, it was observed that the density of the precipitate column lowered with increase in the acidity of feed solution. When concentrated nitric acid was used to acidify the feed solution, no precipitate was formed and tiny crystals were observed after two days. It can be concluded that the rare earth ions diffused into the gel in a controlled fashion and their
reaction with the oxalate ions resulted in the growth of GSO crystals. With proper acidification of the feed solution, any precipitate formed gets dissolved in the acid medium and creates nucleation centres leading to crystal growth. The possible chemical reaction is

$$\text{Gd (NO}_3\text{)}_3 + \text{Sm (NO}_3\text{)}_3 + 3 \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{GdSm (C}_2\text{O}_4\text{)}_3 \cdot n\text{H}_2\text{O} + 6\text{HNO}_3$$

The morphology, size and the number of crystals were found to vary with gel density, pH of gel, concentration of the reactants and acidity of the feed solution. Pale yellowish transparent GSO crystals were formed in a period of 25 days. The optimum condition for growing good quality crystals of maximum size is found to be at pH 6 of hydrosilica gel having density 1.03 g / cc impregnated before setting with 1M oxalic acid, and the concentration of the feed solution at 0.5 M. The average size of the crystals is found to be $3.5 \times 2 \times 1 \text{ mm}^3$.

Figure 4.3. Growth system of GSO Crystals
4.7 Growth of Gadolinium Cerium Oxalate (GCO) crystals

Hydrosilica gel was prepared from SMS solution with the incorporation of required amount of oxalic acid as described in the previous section. A mixture of 0.5M solutions of gadolinium nitrate and cerium nitrate in 1:1 ratio, acidified with concentrated nitric acid was poured gently over the set gel. The slowly diffusing rare earth ions react with oxalate ions to form single crystals of gadolinium cerium oxalate. The possible chemical reaction is

\[
\text{Gd (NO}_3\text{)}_3 + \text{Ce (NO}_3\text{)}_3 + 3\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Gd Ce (C}_2\text{O}_4\text{)}_3 \cdot \text{nH}_2\text{O} + 6\text{HNO}_3
\]

The growth kinetics change depending on the growth parameters such as pH of the medium, gel density, acidity of the feed solution and the concentration of the reactants. The nature of the crystals was found to vary from tiny crystals to well faceted, colourless, transparent crystals of average size 3 x 2 x 1 mm\(^3\), on optimization of the growth parameters.

**Figure 4.4** Growth System of GCO Crystals
4.8 Growth of Gadolinium Neodymium Oxalate (GNO) Crystals.

The method of growth of GNO crystals is the same as in the two earlier cases. SMS solution charged with oxalate ions is taken in test tubes to establish gelation. Over the set gel column a mixture consisting of equal volumes of 0.5M gadolinium nitrate solution and 0.5M neodymium nitrate solution acidified with concentrated nitric acid is added slowly. The controlled diffusion of the rare earth ions through the gel and their reaction with oxalate ions lead to the formation of gadolinium neodymium oxalate crystals. The chemical reaction may be represented as

\[
\text{Gd (NO}_3\text{)}_3 + \text{Nd (NO}_3\text{)}_3 + 3\text{H}_2\text{C}_2\text{O}_4 \\
\rightarrow \text{Gd Nd (C}_2\text{O}_4\text{)}_3, \text{nH}_2\text{O} + 6\text{HNO}_3
\]

Figure 4.5. Growth System of GNO crystals

The influence of various growth parameters on the growth of these crystals was studied. Pink, transparent, well faceted GNO crystals of size 3.5 x 2.5 x 1 mm\(^3\) were obtained on optimization of the parameters of growth.
4.9 The kinetics of growth

A detailed analysis of the influence of various growth parameters such as density of SMS solution, pH of the gel, concentration and acidity of the feed solution and ageing of gel was conducted for studying the kinetics of growth of crystals and the nature of crystallization. In gel growth, nucleation control can be achieved by controlling the diffusion of ions through the gel. Studies on nucleation control are very significant since the size of the crystals depends on the rate of nucleation. By changing the growth parameters, nucleation control can be effected to some extent. The influence of gel density and gel ageing on crystal growth has been reported by several researchers [14,15].

In the present work, the studies on the effect of various gel parameters helped to optimize the environment for the growth of good quality crystals with maximum size. This optimum condition is found to be at a gel pH 6, gel density 1.03 g / cc, with feed solution concentration 0.5M acidified with concentrated nitric acid (50% by volume in the feed solution).

The grown crystals (GSO, GCO and GNO) have identical chemical behaviour and showed similar type of growth kinetics. Hence the effect of various parameters of growth on crystallization process is explained choosing GSO crystals to represent the three types of grown crystals.

4.9.1 pH of the gel

The influence of pH of the gel on nucleation density and the quality of GSO crystals was studied by preparing gels with different pH values from 4 - 8. This was done by adjusting the amount of oxalic acid incorporated in the gel, keeping the other gel parameters constant.

The nucleation density was found to vary inversely with the pH of the gel. The advancement of the crystallization zone also varies inversely with pH of the gel. This may be due to the fact that as the pH increases,
the gel becomes more and more hard thereby slowing down the diffusion of the ions which is essential for growth of bigger crystals. In the present case, since oxalic acid is the acidifying agent, a low pH means a higher concentration of oxalate ions, which results in increased nucleation density. The variation of nucleation density with the pH of the gel is shown graphically.

![Graph of nucleation density vs pH of the gel](image)

**Figure 4.6** Nucleation density Vs pH of the gel

At low pH values of the gel medium, the grown crystals are transparent and well defined but very small in size due to the heavy nucleation density. As the pH of the gel increases, larger crystals can be grown due to the decrease in the nucleation density, but the transparency of the crystals decreases. This may be due to two reasons – the contamination of the crystal surface by silica gel and the lack of perfection of the crystals due to increase in the growth rate. The optimum pH was found to be 6 for growing good quality crystals.
4.9.2 Gel density

The density of SMS solution influences the mechanical properties of set gels [16]. The pore sizes of the gel vary with its density, which in turn affects the growth process. Keeping constant the parameters such as pH of the gel, concentration of the reactants, acidity of the feed solution etc., gels of varying densities in the range 1.02 –1.07 g/cc were prepared by mixing SMS solution with 1 M oxalic acid. It is observed that the period of gelation and the transparency of the gel decreases as the gel density increases. Gels of low density take a long time to set and have poor mechanical strength.

![Figure 4.7 Nucleation density Vs density of the gel](image)

The variation of nucleation density of GSO crystals with density of gel is represented graphically [Figure 4.7]. It is found that increase in gel density has adverse effect on nucleation density. Also the increase in gel density retards the advancement of crystallization zone. When the density of gel increases, the pore size of the gel gets reduced which decreases the rate of diffusion. Hence high density gels...
adversely affect the mobility of reacting ions which in turn retards the rate of reaction [11]. Good quality crystals of hexagonal morphology were obtained when gel of density 1.03 g / cc was used. With lower gel density a large number of very small crystals appeared. If the gel density is low, the mechanical strength of the gel may not be sufficient to support the growing crystals and in this case the diffusion of ions is increased resulting in the formation of imperfect crystals. An increase in gel density leads to a reduction in the size and transparency of the crystal and also a reduction in the diffusion rate. Moreover, the growth media becomes harder. This results in the exertion of more residual stress on the growing faces of the crystal which in turn produces deformation of the crystal faces.

4.9.3 Ageing of the gel

It has been reported earlier [17] that the advancement of the crystallization zone gets retarded considerably with the age of the gel. To study the impact of gel ageing on the crystal growth process, identical gel systems but with different gel age were used for the growth of GSO crystals. The pH of the gel was set at 6, the gel density at 1.03 g / cc and the concentration of inner reactant (oxalic acid) was set at 1M. An acidified mixture of equal volumes of aqueous solutions of gadolinium nitrate and samarium nitrate each of 0.5 M concentration was poured over the set gel. The advancement of crystallization zone was observed to be retarded considerably with gel ageing. The gel ageing causes saturation of the bonding of the gel network which reduces the pore size. Hence the rate of diffusion of the rare earth ions is decreased and this lowers the nucleation density.

The effect of gel ageing on the growth process was explained by Desai et al. [18]. The dehydration of the gel during the ageing affects the rate of nucleation. Water molecules evaporate from the gel when the free surface of the gel is in contact with air. The effect of this water evaporation
can be observed before and after the formation of gel framework. Before the gel is set, evaporation of water causes an increase in gel density which in turn decreases the rate of diffusion of cations into the gel thereby decreasing the number of nucleation centres. After the gelation, any evaporation of water molecules causes not only a lack of ionic carriers in the channel of the gel framework, but also causes discontinuities in the channels due to shrinking of the gel. The diffusion of ions and the nucleation density are adversely affected by both these effects.

4.9.4 Acidity in the feed solution

The nucleation, growth and morphology of the crystals are influenced by the acidity of the feed solution [19]. To investigate this, studies were conducted on gel having density 1.03 g/cc, pH 6, strength of oxalic acid 1 M with the feed solution at a concentration 0.5 M. The feed solution was mixed with different volume proportions of concentrated nitric acid. When the acid concentration is low (below 20% by volume), heavy nucleation resulted especially at the gel-solution interface. Thin, needle-like and spherullitic crystals are observed. As the acid concentration is increased (30% by volume) the nucleation density decreased and crystallization occurred in a region below the gel solution interface. The spherullitic nature of the crystals disappeared and transparent crystals of cubic, rod-like and hexagonal morphology appeared. As the acidity of the feed solution was further increased, the crystals were reduced in number but the size of the crystals increased. The distance of the crystallization zone from the gel-solution interface increased with increase in acid concentration of feed solution. It was also observed that increase in acidity of feed solution led to an improvement in the transparency of the crystals.

The variation of nucleation density with acid concentration in the feed solution is shown graphically in Figure 4.8.
Increasing the acidity helps to dissolve the micro crystals thus reducing the nucleation centres. This increases the availability of rare earth ions at the growth centres. Hence nucleation rate is reduced and bigger and good quality crystals are developed. Growth system of GSO crystals with different acid concentration in the feed solution is shown in Figure 4.9.
Occasionally it is observed that a few crystals grow at the gel interface. This may be due to the counter diffusion of oxalate ions upwards through the gel and reaction with rare earth ions in the supernatant solution. The number and size of these crystals are found to increase with increase in acidity of the feed solution. Similar results are obtained for the other two growth systems.

**4.9.5 Concentration of the reactants**

To study the influence of concentration of the feed solution on the growth of GSO crystals, gel systems of pH 6, density 1.03 g / cc were prepared using 1 M oxalic acid to adjust the pH. Feed solutions of different concentrations (0.2 M, 0.4 M, 0.6 M, 0.8 M, 1 M and 1.5 M) were added over the set gel. The acidity of the feed solution was kept at the same value.

It was observed that the nucleation density increases with concentration of the feed solution. The rate of advancement of the crystallization zone also enhances with the increase in the feed solution concentration. These effects may be due to the increased availability of the rare earth ions. At lower concentrations the crystals formed are less in number and not well defined. At higher concentrations, though the size of the crystals increases, crystals are found to lose their regular morphology.

**4.9.6 Concentration programming**

Big crystals of good quality can be grown by the process known as concentration programming. To investigate the effect of concentration programming in the case of GSO crystals, the gel with pH 6 and density 1.03 g / cc was set using 1 M oxalic acid to adjust the pH. The acidified feed solution of 0.5 M was poured carefully over the set gel. The feed solution was replaced daily with fresh feed solution of slightly higher
concentration. Big crystals of regular morphology were grown by this method.

When the reactant is of very low concentration, only a small amount of rare earth ions could diffuse into the gel and hence only a few crystal nuclei are formed. As the concentration of the reactants increases, the already formed nuclei act as sinks. This leads to the establishment of a radial diffusion pattern which reduces the reagent concentration in the neighbouring regions. Hence formation of additional nuclei is inhibited which results in the formation of large crystals of good quality.

4.10 Conclusion

Single crystals of GSO, GCO and GNO were grown by single diffusion method. The quality and morphology of the crystals grown depend critically on various growth parameters. It is generally found that in all the three growth systems, the crystals grow slowly due to the controlled nature of diffusion. Crystals with well defined hexagonal morphology are obtained under higher acidity condition of the feed solution. In all cases it is observed that an increase in concentration of the reactants leads to an increase in the number of crystals but the size of the crystals is reduced. The effect of age of the gel, acidity of the feed solution and the concentration of the reactants on the crystal size and morphology were studied. Optimum condition for the growth of good quality crystals is found to be at pH 6 of hydrosilica gel with density 1.03 g / cc acidified before setting with I M oxalic acid.
References

