Chapter 4

GROWTH STUDIES

Abstract

Chemistry associated with growth of rare earth mixed oxalate crystals and the optimum conditions for growing good quality crystals are presented in this chapter. Detailed investigations on the effect of various growth parameters like pH of the gel, age of the gel, density of the gel, concentrations of the reactants and the acidity of the feed solution, which governs the morphology, number, size and the quality of the crystals are also presented in this chapter.
4.1 INTRODUCTION

The oxalate crystals have low aqueous solubility and high thermal decomposing behaviour. Rare earth oxalates are usually co-precipitated in hydrated form. Hence crystals of such compounds cannot be grown either by slow evaporation or flux method\(^1\). Gel method is found to be the best suitable technique for the growth of oxalate crystals\(^2\). A large variety of oxalate crystals have been grown by this method\(^3\)-\(^4\). Many researchers have grown single crystals of mono rare earth oxalates, doped rare earth oxalates and mixed rare earth oxalates by gel method\(^5\)-\(^7\).

This chapter reports the growth of Yttrium Oxalate (YOx), Yttrium Barium Oxalate (YBaOx), Yttrium Copper Oxalate (YCuOx), Yttrium Barium Copper Oxalate (YBaCuOx), Praseodymium Barium Copper Oxalate (PrBaCuOx), Neodymium Barium Copper Oxalate (NdBaCuOx), Gadolinium Barium Copper Oxalate (GdBaCuOx) and Dysprosium Barium Copper Oxalate (DyBaCuOx) in hydro silica gel by chemical reaction method. Detailed investigations had been made on the effect of various growth parameters like pH of the gel, ageing of the gel, density of the gel, concentration of the reactants and the acidity of the feed solution, which governs the morphology, size and quality of the crystals.
4.2 CHEMISTRY ASSOCIATED WITH GROWTH OF RARE EARTH OXALATE CRYSTALS

Halide of rare earth, barium chloride and cuprous nitrate when treated with oxalic acid in gel properly, to form corresponding rare earth barium copper oxalate and is represented by

\[ 2RCl_3 + BaCl_2 + Cu(NO_3)_2 + 5H_2C_2O_4 \rightarrow R_2BaCu(C_2O_4)_{5n}H_2O + 8HCl + 2HNO_3 \]

where ‘R’ stands for the rare earth to be incorporated in the crystal.

4.3 HYDRO SILICA GEL AS GROWTH MEDIUM

The gel was found to be one of the best media to grow a number of organic and inorganic crystals including rare earth oxalates\(^2\). The three dimensional network of gel medium provides a controlled diffusion environment to the ions which is necessary for the crystallization \(^8\). It was prepared from commercially available Sodium meta silicate. The assay of the Sodium meta silicate salt helps to start nucleation in the gel.

4.4 PREPARATION OF HYDRO SILICA GEL

A known mass of finely powdered Sodium meta silicate (SMS) was dissolved in a known volume of double distilled water. The solution was kept undisturbed for two days in a dark room for the sedimentation of the insoluble particles or impurities. The pure solution collected from the top of the solution was centrifuged and filtered by using double filter paper to get
impurity free SMS solution. The solution thus obtained was treated as ‘stock solution’. The density of this filtrate was adjusted to the desired value. The density of this clear solution was measured accurately, as it is critical for the gelation and quality of the gel, which controls the quality of the crystals. By plotting a graph between the specific gravity versus the percentage of water in the stock solution (Fig.4.1), the quantity of water required to be added, to fix the density of the gel for any desired value was found out. The stock solution of required volume was taken and mixed with the double distilled water. The volume of water to be added was found out from the graph and the solution of desired density was prepared.

![Graph showing specific gravity vs. percentage of water](image)

**Fig.4.1** Specific gravity of SMS vs. practical volume of water
In order to get proper gel, the pH of the Sodium meta silicate solution must be lowered. This can be achieved by adding a proper acid to the SMS solution. Since the aim of the experiment was to grow rare earth oxalate crystals, Oxalic acid was selected as the acidifying agent. It was added to adjust the pH value and act as an inner reactant needed for the crystallization of the compounds.

In single tube experiment it was necessary to incorporate any one of the reactants into the gel prior to gelation. Since rare earth ions are found reacting with Sodium meta silicate, it is not possible to incorporate them in the gel. Hence oxalic acid was used to acidify the medium and also as a source of anions. 1M Oxalic acid solutions were prepared from its analar grade salt.

Sodium meta silicate of the desired density was added drop by drop to oxalic acid (1M) taken in a beaker and stirred gently to ensure homogeneity. The pH of the resulting mixture was continuously monitored to get the required pH.

The crystallization vessels used were glass test tubes of length 15cm and internal diameter 1.5 / 2 cm. These tubes were rinsed several times in distilled water and dried in the oven in order to get perfectly clean tubes free from any acidic or alkaline impurities. The gel solution adjusted to a
desired pH was taken in these tubes and kept undisturbed for proper setting of the gel. The openings of the test tubes were tightly covered to prevent contamination of gel surface by atmospheric impurities. Gel provides a medium for crystallization at ambient temperature.

The value of pH had an important role in the gelation period. Depending on the pH value of the gel, polymerization time varied from few minutes to many hours (Fig. 4.2). When the pH of the resulting medium was just above the neutral value, i.e., the gel was slightly basic, quick setting of the gel was observed. As the gelation time is very short, the solution should be poured into the test tubes very quickly. But this may result in trapping of air bubbles in the setting gel. Hence extreme care was taken while preparing gels of pH values in the range 6 to 7\textsuperscript{11}. It was observed that the gelation period is high for both higher and lower pH values. The pH values are very critical in the growth of crystals. The dependence of the pH on the various aspects of crystal growth was investigated in this study.
PREPARATION OF SUPERNATANT SOLUTION

Analar grades Yttrium Chloride, Praseodymium Chloride, Neodymium Chloride, Gadolinium Chloride and Dysprosium Chloride (99.9% pure, supplied by Indian Rare Earths Ltd., Udyogamandal, Cochin) were used for the preparation of the feed solution. 1M aqueous solution of each of these rare earth salts were prepared. In order to grow crystals containing Rare Earth, Barium and Copper, ie R BaCuOx (where R=Y, Pr, Nd, Gd, & Dy) with a specific stoichiometry, the corresponding Rare Earth solution, Barium chloride and Cuprous nitrate were mixed in the proper ratio by volume and this will serve as the supernatant feed solution. For growing YOx, YBaOx and YCuOx crystals, Yttrium Chloride solution, Yttrium Chloride solution mixed with Barium chloride solution in the proper ratio by volume and Yttrium Chloride
solution mixed with Cuprous Nitrate solution in the proper ratio by volume were used as the supernatant solutions respectively.

The feed solution was then gently poured over the gel as the outer reactant without damaging the gel. The crystallizer tubes were then covered with stoppers and left undisturbed for crystallization. The growth rate and morphology of crystals grown were found to depend on factors like pH of the medium, density of the gel, ageing of the gel, acidity of the supernatant solution, concentration of the reactants etc. These are discussed in detail in the following section.

4.6 GROWTH OF RARE EARTH OXALATE CRYSTALS

The growth details of YOx, YBaOx, YCuOx, and Rare Earth mixed Barium Copper Oxalate crystals (RBaCuOx, where R=Y, Pr, Nd, Gd, Dy), are described in the following section.

4.6.1 Growth of Yttrium Oxalate crystals

To grow Yttrium Oxalate crystals the outer reactant Yttrium Chloride of desired concentration was poured over the required aged gel. After pouring the feed solution a thin white precipitate layer of small thickness was found to form at the gel solution interface. Thickness of the precipitate was
increased with the concentration of the upper reactants because of the greater concentration of the ions at the gel solution interface.

The precipitated form was actually spurious nucleation. Slow diffusion and a specific concentration are essential for perfect crystal growth. When all the required conditions were satisfied, nucleation started. The concentration programming of the reactants showed remarkable changes in growth rate and quality of the crystals. It was found that the thickness of the precipitation zone near the gel solution interface was considerably reduced when the concentration of the Yttrium Chloride solution was reduced. Almost similar results had been observed by the reduction of Oxalic acid concentration in the gel. This might be due to the fast diffusivity of the ions at first and then its propensity to reduce the negative potential 2.

The precipitation zone is found to be predominant at the time of pouring of feed solution. As the time advanced the thickness of the precipitation front reduced. White tiny crystals were appeared at the lower part of it after about 25 –30 hours of continuous diffusion. The proposed chemical reaction in this case is

\[ 2\text{YCl}_3 + 3 \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O} + 6\text{HCl} \]
During the initial trials of experiments, the gel cracked when top reactant Yttrium Chloride solution was poured over the set gel. The experiment was repeated by changing the concentration of the feed solution in steps and was not successful.

Later this method was tried again with acidified solution. Yttrium Chloride solution was acidified with Nitric acid in various proportions before pouring over the gel. The observations revealed that the acidification of the feed solution plays an important role in defining the nature of precipitation. As the quantity of HNO₃ in the feed solution was increased the precipitation front got thinner. When concentrated HNO₃ was used to acidify the feed solution, there was no formation of precipitation, crystallization started. On addition of HNO₃, it dissolved the precipitate and the nucleation of the crystals started. Hence the acidification of the feed solution was found to be an extremely necessary step in the growth of this group of crystals. As a typical example for all the rare earth oxalate crystals grown, photographs related to YOₓ are presented in this section (Fig.4.3 to Fig.4.6).
**Fig. 4.3** Yttrium Oxalate tetragonal crystals heaped on a glass plate in red background (left). Crystallization of the Yttrium Oxalate crystals in the dissolution area – magnified (right).

**Fig. 4.4** A well faceted Yttrium Oxalate crystal (x20)
Fig. 4.5 An enlarged Yttrium Oxalate crystal with its growth layers (x50).

Fig. 4.6 Microscopic view of Yttrium Oxalate crystals (*20 magnification) Single, multi nucleated, branched, additional growth can be observed.
4.6.2 Growth of Yttrium Barium Oxalate Crystals

The growth of Yttrium Barium Oxalate crystals was accomplished by the controlled diffusion of Yttrium and Barium ions through silica gel impregnated with Oxalic acid. As described in the previous section, the hydro silica gel was prepared from Sodium meta silicate. A mixture of solutions of Yttrium Chloride, Barium Chloride and HNO₃ in the proper ratio was poured gently over the set gel. Yttrium and Barium cations of the outer reactants slowly diffused into the gel column containing oxalate cations and they slowly combined to form crystals of Yttrium Barium Oxalate. The proposed chemical reaction in this case is

\[ 2\text{YCl}_3 + \text{BaCl}_2 + 4\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Y}_2\text{Ba} (\text{C}_2\text{O}_4)_4 \cdot \text{nH}_2\text{O} + 8\text{HCl} \]

4.6.3 Growth of Yttrium Copper Oxalate Crystals

The growth of Yttrium Copper Oxalate crystals was accomplished by the controlled diffusion of Yttrium and Copper ions through silica gel impregnated with Oxalic acid. As described in the previous sections, the hydro silica gel was prepared from Sodium meta silicate. A mixture of solutions of Yttrium Chloride, Cuprous Nitrate and Nitric acid in the proper ratio was poured gently over the set gel. Yttrium and Copper cations of the outer reactants slowly diffused into the gel containing oxalate cations and they
slowly combined to form crystals of Yttrium Copper Oxalate. The proposed chemical reaction in this case is

\[ 2YCl_3 + Cu(NO_3)_2 + 4H_2C_2O_4 \rightarrow Y_2Cu(C_2O_4)_4 \cdot nH_2O + 6HCl + 2HNO_3 \]

4.6.4 Growth of Rare Earth mixed Barium Copper Oxalate Crystals

The growth of Rare earth mixed Barium Copper Oxalate Crystals (RBaCuOx) was accomplished by the controlled diffusion of Rare Earth, Barium and Copper ions through silica gel impregnated with Oxalic acid. As described in the previous sections, the hydro silica gel was prepared from Sodium meta silicate. A mixture of solutions of Rare Earth Chloride, Barium chloride, Cuprous Nitrate and Nitric acid in the proper ratio was poured gently over the set gel. Rare Earth, Barium and Copper cations of the outer electrolyte slowly diffused into the gel medium containing oxalate cations and they slowly combined to form crystals of Rare Earth mixed Barium Copper Oxalate. The proposed chemical reaction in this case is

\[ 2RCl_3 + BaCl_2 + Cu(NO_3)_2 + 5H_2C_2O_4 \rightarrow R_2BaCu(C_2O_4)_5 \cdot nH_2O + 8HCl + 2HNO_3 \]

Where ‘R’ stands for rare earth (R=Y, Pr, Nd, Gd & Dy).

4.7 GROWTH KINETICS

The environment of crystallization influenced highly the nucleation process and subsequent growth mechanism. To optimize the growth condition for attaining well faceted good quality crystals, the effect of various growth
parameters such as density of SMS solution, pH of the gel, concentration of reactants, ageing of the gel were explored. Gel method is noted for its remarkable characteristic of nucleation control by controlling diffusion of ions. The studies on the nucleation control are very important as the size and quality of the crystals depend on the nucleation rate. Hence the present investigation was conducted with a view to control the number of crystals and to optimize the condition to grow perfect crystals. The various gel parameters were monitored to optimize the environment for the growth of large sized good quality crystals. It was found that the best results were achieved for a gel of density 1.03gm/cc, pH of 6, inner reactant of 1M concentration and outer reactant (0.5M rare earth solution mixed with 0.3M Barium Chloride solution and 0.3M Cuprous Nitrate solution) acidified by concentrated HNO₃ having 50% by volume of feed solution.

In ordinary diffusion cases of rare earth oxalate crystals, different types of crystals such as multiple growth, clustered, dendritic and platelike can be observed. In this experiment, since suitable quantity of concentrated acid was added, mostly well faceted and platelike crystals were observed in the dissoluted area. Grown crystals were of average size 3mm×2mm×1mm. An average time of 25 to 30 days were needed for the completion of crystallization. Growth system of rare earth oxalate crystals is shown in Fig.4.7 and Fig.4.8.
Fig. 4.7 Growth system of Yttrium mixed Oxalate crystals

Fig. 4.8 Growth system of NdBaCuOx, PrBaCuOx, GdBaCuOx crystals
4.7.1 Influence of gel density and ageing

The gel density played an important role on the crystal size, number of crystals and quality of crystals. The gel having a density range from 1.02 to 1.08 gm/cc had been utilized to study the growth of all the crystals described in the work. This had been done keeping all other parameters constant such as temperature, pH, concentration of the reactants, etc. It was observed that the gels with higher densities set faster than that with lower densities. The transparency of the gel medium was found to decrease with the increase of gel density. The mechanical strength of lower density gel was found to be poor.

Good quality transparent crystals were obtained in the medium of gel of density 1.03 g/cc. For lower density gels, crystals became very small and appeared in clusters and for gels of higher density crystals became translucent. The decrease in the transparency of the crystals may be due to the contamination of the surface of the growing crystals by gel impurities.

It was observed that there was a sharp decrease in the number of crystals as the density of the gel increases as shown in Fig. 4.9 (a) as in the case of Yttrium series (YOx, YBaOx, YCuOx, YBaCuOx) and in Fig. 4.9(b) as in the case of R BaCuOx, where R= Pr, Nd, Gd & Dy. The lowering of the number of crystals may be due to the reduction in the pore size at higher
densities of the gel. This may retard the diffusion of the outer nutrients and the mobility of the crystallites as pointed out by Henisch\textsuperscript{2}. 

The effect of ageing of the gel on the growth kinetics of rare earth oxalate crystals was studied using identical gel system of different ageing. Gel system was prepared with density 1.03 gm/cc and pH of 6 using 1M Oxalic acid as inner reactant for different ageing. In the case of Yttrium Oxalate Crystals, the outer electrolyte was 1M solution of Yttrium Chloride acidified with HNO\textsubscript{3}. It was observed that with the ageing of the gel, the advancement of crystallization zone is reduced considerably. The observation is in good agreement with that of Henisch et al.\textsuperscript{12}. On increase
of ageing the pore size of the gel reduces, the rate of diffusion of rare earth ions decreases and the density of nucleation lowers. Fig. 4.10 (a) shows the variation of number of crystals with the ageing of gel as in the case of Yttrium series (YOx, YBaOx, YCuOx, YBaCuOx) and in Fig. 4.10 (b) as in the case of R BaCuOx, where R= Pr, Nd, Gd & Dy

![Graph](image1)

**Fig. 4.10 (a)** Number of crystals vs. Ageing of gel of Yttrium series

**Fig. 4.10 (b)** Number of crystals vs. Ageing of gel of R BaCuOx

Desai et al.\textsuperscript{13} have given a possible explanation to the effect of gel ageing on the growth process. Ageing of the gel affects the physical property of the gel; it hardens the gel medium. This is because of the dehydration of the gel. This plays an important role in nucleation control. With ageing, water molecules will evaporate from the free surface of the gel. The effect of
this evaporation is two fold. Evaporation before gelation will increase gel density. This in turn reduces the rate of diffusion of cations into the gel and decreases the nucleation density. Evaporation of water molecules after gelation causes a lack of ionic carriers in the channel of the gel framework and discontinuities in the channels due to shrinking of the gel fabric. This ageing of the gel decreases diffusion of ions and nucleation.

### 4.7.2 Effect of the pH value

The pH value of the medium was found to have a characteristic role in the growth process, morphology and quality of rare earth oxalate crystals grown. Depth of the precipitation from the interface, size of crystals, number of crystals, etc. is influenced by the pH value. When the pH value is lowered the density of nuclei is reduced. These experiments were conducted at various pH values maintaining constant temperature, density and concentration of the electrolytes. With increase of pH of the gel, number of crystals reduced, which was similar in all rare earth oxalate crystals grown. Variation of number of crystals with pH of the gel is shown in the Fig. 4.11 in the case of Rare Earth mixed Barium Copper Oxalate crystals (RBaCuOx, where R=Y, Pr, Nd, Gd, Dy). The effect of the pH of the gel on the growth kinetics and the quality of the rare earth oxalate crystals were studied by varying the pH of the gel medium from 3 to 8 by
adjusting the amount of Oxalic acid incorporated in the gel, keeping the other parameters constant. The thickness of precipitation region, number of crystals, size of the crystals and transparency of the crystals were affected by the pH value. The variation of the pH affects the transparency of the gel as well as its density.

![Graph](image)

**Fig. 4.11** Variation of pH of the gel with the number of crystals

The advancement of the crystallization zone was found to vary inversely with the pH of the gel. Number of crystals was also found to vary inversely with the pH of the gel as depicted in Fig. 4.11. As the pH increases, the gel becomes harder and that retards the free motion of the ions, which is essential for the growth of crystals. A low pH means a higher concentration of oxalate ions and that enhances the number of crystals.
Well faceted, single transparent crystals were obtained when the pH of the gel medium was lower. But due to high nucleation density, the yielded crystals were very small in size. As the pH of the gel medium increased it was found that the nucleation density decreased and crystal size increased; but transparency decreased. The crystals grown at higher pH value were observed to be opaque. The loss of transparency may be due to contamination of the crystal with particles of silica gel. As the pH increases, the three-dimensional fibrous network of the gel changes to a loosely bound plate like structure which lacks cross linkage\textsuperscript{14}. Hence one had to compromise between quality and size of crystals. It was found that well-defined high quality rare earth mixed oxalate crystals of optimum size were obtained when the pH was 6.

4.7.3 Effect of concentration of reactants

The concentrations of the electrolytes play an important role on the growth of crystals. In the case of a system where gel is of a fixed density 1.03 gm/cc, pH of 6, the nature of the growth of crystal will depend on the concentration of the electrolytes. Studies were conducted by varying the concentration of the inner reactant or by changing the concentration of the supernatant solution. It was observed that the outer reactants played a major role on the growth rate, number of crystals and morphology of the crystals.
4.7.3 (a) Effect of concentration of inner reactants

Detailed study was conducted in which the concentration of the Oxalic acid was varied in the range 0.1M to 1M, keeping all other parameters constant. At all concentrations of the oxalate ions, there was not much variation in the number of crystals. Number of crystals slightly increased with the concentration, but only negligibly. This may due to the fact that for a given pH, the availability of the oxalate ions remains almost the same, as more volume by proportion of the solution of Oxalic acid of lower concentration is needed to form the gel.

4.7.3 (b) Effect of concentration of the feed solution (Outer electrolyte)

To study the effect of concentration of the feed solution on the growth characteristics of rare earth oxalate crystals, gel system was prepared with density 1.03gm/cc and pH of 6 using Oxalic acid of 1M as the inner electrolyte. Outer electrolytes of different concentrations varying from 0.1M to 1M after acidifying were poured over the set gel gently. The quantity of Nitric acid used to acidify the feed solution was kept fixed for all concentrations of the feed solution.

It was observed that growth parameters, morphology, number and size of crystals were highly influenced by the concentration of the feed solution. The influence of the concentration of feed solution on the number
of crystals obtained is shown in Fig. 4.12. The figure indicates that number of crystals increases with the concentration of the outer electrolyte. This may be due to the increase in the availability of ions of the outer electrolyte at higher concentrations.

**Fig. 4.12** Variation of concentration of outer electrolyte with number of crystals

Good quality well faceted crystals were obtained only at a range of concentrations of 0.4M-0.6M. Below this range, the crystals formed were very small and above this range, spurious nucleation, twinning of the crystals etc were observed. The change in transparency was also observed due to the variation in feed solution concentration. The rare earth oxalate crystals (YOx, YBaOx, YCuOx, YBaCuOx, PrBaCuOx, NdBaCuOx, GdBaCuOx,
DyBaCuOx) had shown almost similar type of growth kinetics. Variation of the concentration of outer electrolyte with number of crystals of - RBaCuOx, (where R= Y, Pr, Nd, Gd and Dy) is shown in the Fig. 4.12.

4.8 CONCLUSION

The slow diffusion of the cations into the gel and their subsequent reaction with the oxalate ion will result in the formation of crystals of the expected morphology. It was found that the best results were achieved for a gel of density 1.03gm/cc, pH of 6, inner reactant of 1M concentrations and outer reactant (0.5M rare earth solution mixed with 0.3M Barium Chloride solution and 0.3M Cuprous Nitrate solution) acidified by concentrated HNO₃ having 50% by volume of feed solution. The growth parameters were found to be same for all rare earth mixed oxalate crystals grown.
4.9 REFERENCES


