PART -II

Growth morphology and characterisation

Crystal growth in gel

Growth of single crystals
of
Ammonium Hydrogen
d - tartarate (d-AHT)

Characterisation of gel
grown crystal of d-AHT

CHAPTER 3

Crystal Growth in Gel

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CRYSTAL GROWTH IN GEL

3.1 Introduction

The art and science of growing crystals in gel, largely dormant during the period 1930-60 and now in the midst of a general renaissance, enjoyed a long period of vogue beginning close to the end of the previous century and lasting well into the 1920's. During most of this time, the centre of interest was held by the phenomena of Leisegang's rings. Leisegang a German colloid chemist and photographer observed the periodic precipitation of slightly soluble salts (1,2,3).

The Leisegang ring phenomena attracted many investigators. Among the early researchers were Ostwald (4) Raleigh (5) Holmes (6,7,8) Fells and Firth (9) and Fisher and Simons (10,11). There is an intensive early literature on the general subject of the role of the gels (12,13,14).

The research work of Hefsechak (15) Morse and Pierace (16), Marriage (17), Holmes (8) and Davies (18) have helped a great deal in understanding the intricacies of the phenomena in gels.

The gel technique was revived by Henisch (19) who reported growth of several crystals which had defied attempts of growth by conventional techniques. His work attracted the attention of many crystal growers towards crystal growth in gels, as it offered a simple and relatively inexpensive means of accomplishing the growth of strain free crystals of high perfection at ambient conditions. Most of the basic techniques of crystal growth and their modifications are described by Pamplin (20) and Gilman (21).

Direct application of gels in crystal growth is evident by works of Marriage (17) who reported growth of lead iodide crystals in fruit jellies and jams. Copper and Gold crystals were grown by Holmes (8) by diffusing a reducing agent into gels charged with the respective salts. According to Fischer and Simons (10,11) gels form excellent media for the growth of crystals of almost any substance, preferably insoluble substance under absolutely controlled conditions. The pioneering work of Holmes (6,7,8) Fells and Firth (9), Fisher and Simons (10,11), Morse and Donnay (22) etc. established application of gels in crystal growth. Stong (23) suggested the possibility of crystal growth in a gel medium. It was soon followed by a report of Vand et al (24) describing results of a study into the full potential of crystal growth in gels. Henisch et al (25) published a very useful paper describing all the details of gel method.

Crystal growth in viscous media is manifested in a number of cases, whether natural (26) or artificial. For example, occasional growth of ice crystals in ice-cream, the growth of tartrate crystals in cheese, the growth of sulphur in rubber (27), the crystallization of zinc salts in dry batteries, formation of sugar crystals in Fruit jellies (28), the formation of magnesium ammonium phosphate crystals during putrefaction of meat (29) and the growth of uric acid crystals in joints and stones in human organs.

There is a realization of tremendously increasing application of gel growth to a variety of crystals by material scientists. One of the recent developments of this subject is, the growing realization of its scope and application in the field of medical services to investigate the crystallization of uric acid and formation of stones in human organs leading to various diseases (30,31).

Gel method offers means to understand several phenomena of crystal growth. In this way, the study of nucleation and growth of crystals in gels has tremendous research applications. This technique has helped in the study of electron spin resonance measurements of Mn^{2+} in Calcium tartrate. Gel grown PBI_2 has been intensively studied partly with a view to clarify its complicated band and defect level structures (32) and partly to understand polytypism (33)(34). Such investigations had greatly suffered because of the lack of suitable specimens and major discrepancies had slipped into the literature, before the advent of gel method. Gel method provided crystals appropriate for such studies. It gives new possibilities for investigating dependence of polytypism on parameters of crystal growth (34). Certain unusual crystals grown by gel technique have been used for the determination of lattice constants (35). Metallic lead dendrites have been grown in gels with ease and used for metallurgical studies, particularly concerning relationship between growth hillocks, etch pits and structural defects (36).

3.2 TECHNIQUE OF GEL GROWTH

Gel technique of crystal growth is defined as the one in which two solutions of soluble salts are brought together by diffusion through gel with subsequent nucleation and crystal growth taking place by precipitation of an insoluble phase within the gel. The function of gel is mainly to limit the number of critical size nuclei that are formed and decrease the growth rate i) by controlling diffusion of the reacting ions and ii) by governing the speed of reaction at the crystals growing surface.

It distinguishes itself from other solution growth techniques by making use of the role played by gel in establishing a single pattern of concentration gradients by suppressing convection currents. The gel assumes a role of a three dimensional crucible which supports the crystal and at the same time, allows it to grow further without exerting forces of large magnitude upon it.

A gel is defined as a two component system of semi-solid nature, rich in liquid (37). Gels are made of variety of materials. Silica gel is prepared from sodium metasilicate solution, agar gel is a carbohydrate polymer derived from sea- weed, gelatin gel is a substance closely related to proteins, soft soaps are potassium salts of high fatty acids, gels are prepared from a variety of oleates and stearates, polyvinyl alcohol and various hydroxides in water. Different gel materials are classified in accordance with semi- quantitative criterion for resistance to shear.

Gel is regarded as a loosely interlinked polymer. It is known as a "hydrogel" if the dispersion medium is water. The process of gelling can be brought about in the following ways:

i) by cooling of a solution;

ii) by chemical reaction;

iii) by addition of a precipitating agent or incompatible solids.

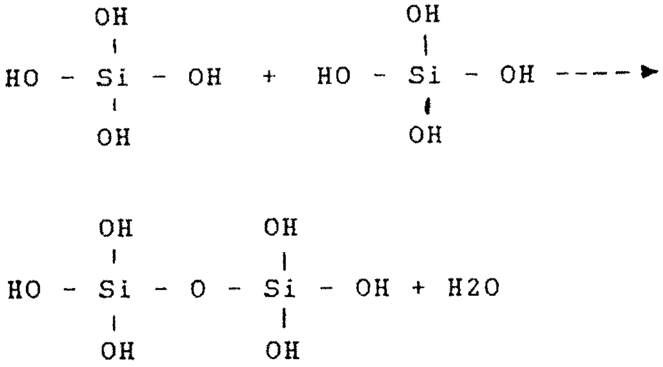
Bartell (38) has described a variety of practical gel preparation recipes e.g. for oil, nitrocellulose, anilinenitrate and pectin gels. The process of gelling takes sometime which varies widely (from a few minutes to several days) depending upon the temperature, nature and history of the material. For silica gel, this has been documented by Treadwell and Willand (39). The mechanical properties of gelatin gels have been intensively investigated more systematically (40- 44).

For reagents to diffuse through the gel medium, the most important parameter is the size of the diffusing particles relative to the pore size in the gel. The next is the amount of interaction between solute and internal gel surfaces. Stonham & Kragh (45) investigated diffusion through gelatin gels. Determination of reagent concentration in gels is quite often needed in the course of experiments on crystal growth, but the absorptive properties of gels makes this a difficult problem. One finds a variety of substances which absorb in silica hydrogels easily (46).

Silica hydrogels have been found to be the ideal gel for experiments on crystal growth. A study of its gelling mechanism and structure is considered to be important. When sodium metasilicate goes into solution, monosilicic acid is formed, in accordance with the dynamic equilibrium.

$Na_2SiO_3 + 3\ H_2O \longrightarrow H_4SiO_4 + 2\ NaOH$

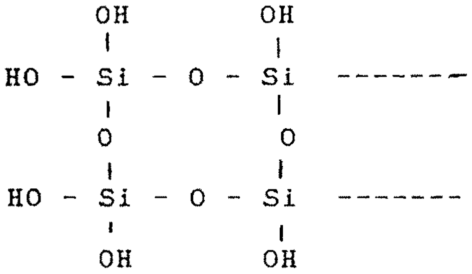
and it is generally accepted that monosilicic acid can polymerise with the liberation of water.



$$HO - \underset{OH}{\overset{OH}{Si}} - OH \;+\; HO - \underset{OH}{\overset{OH}{Si}} - OH \longrightarrow$$

$$HO - \underset{OH}{\overset{OH}{Si}} - O - \underset{OH}{\overset{OH}{Si}} - OH + H2O$$

This can happen repeatedly until a three dimensional network of SiO links is established, as in Silica -



$$\begin{array}{ccccccc} & & OH & & OH & & \\ & & | & & | & & \\ HO & - & Si & - \; O \; - & Si & & ------- \\ & & | & & | & & \\ & & O & & O & & \\ & & | & & | & & \\ HO & - & Si & - \; O \; - & Si & & ------- \\ & & | & & | & & \\ & & OH & & OH & & \end{array}$$

As polymerisation continues water accumulates on top of the gel surface. This phenomenon known as syneresis has possibly its origin in the above condensation process and may also arise from purely mechanical factors connected with a small amount of gel shrinkage.

There seems to be distribution of pore sizes within each gel and one gel is distinguished from another by the nature of this distribution. Hydrogels are characterised by two types of pores viz. "primary" pores of nearly molecular dimensions and coarser "secondary" pores which behave more or less like normal capillaries (47).

The time required for gelation is very sensitive to pH. Calcium tartarate crystals do not nucleate at pH values below 3. It is established that two types of ions are produced during gelation: $H_3SiO_4^-$ and $H_2SiO_4^{2+}$ in relative amounts which depend on the hydrogen ion concentration and hence the pH. High pH values favour the formation of $H_2SiO_4^{2+}$ ions which are more reactive, but the higher charge results in greater degree of mutual repulsion. Moderately low pH values favour the formation of $H_3SiO_4^-$ ions which is held responsible for the initial formation of long-chain polymerization products (48). Cross linkages formed between these chains in due course contribute to the sharp increase of viscosity which indicates the onset of gelation. Very long chains have lower mobility and thus cross-link more slowly than short chains. At very low pH values, the chain formation is slowed on account of diminished tendency towards polymerisation. The time taken for gelation is strongly dependent on temperature (37),but a high degree of temperature stability does not seem to be required.

3.3 GROWTH MECHANISMS AND CHARACTERISTICS

Convection currents are suppressed above a certain magnitude. With an ordinary microscope it is possible to verify that particles have streaming and Brownian motion in the ungelled solution, but are at rest after gelling. With a laser ultramicroscope this motion can be shown for smaller particles e.g. down to about $60A^{o}$ and even below depending on the wavelength and intensity of the laser light. In the absence of convection, diffusion is the only mechanism responsible for the supply of solute to the growing crystal. Frank (49) has developed equations giving a description of diffusion controlled growth rates for several different idealized geometries. Henish et al (50) applied Frank's model in the study of crystal growth in gels.

In systems which depend on the diffusion of one reagent through a gel charged with another, the average crystal growth rate is greatest near the top of the diffusion column where the concentration gradients are also small (19). It is quite relevant here to make a mention of "crust formation" at the gel reactant interface as a result of almost instantaneous reaction between the two reactants in the case of crystal growth of Lanthanum and Gadolinium tartrate (51).

Once new solute has been brought to the surface by diffusion, growth takes place either by screw dislocations or by 2-dimensional surface nucleation. Surface diffusion which is dependent on temperature (52) is the mechanism through which solute molecules reach the active growth centres.

Gel helps in suppressing nucleation which in turn, reduces the competitive nature of growth. The utlimate success of the gel method for growing crystals lies in the nucleation control. The growth mechanism operative after nucleation do not seem to be different from those in stagnant solutions, though there may be complications in cases where gel serves both as a reaction medium and as a diffusion medium.

In all simple gel growth systems (i.e. those without constant concentration reservoirs), the crystals reach a stable and utlimate size. The ultimate crystal size is determined by either of the following mechanisms which are simultaneously at work.

1. There is a progressive exhaustion of the reagents. Reagent exhaustion often reduces the speed of growth to levels which amount to practically zero growth.

2. The second stabilizing factor arises from pH and related considerations. In cases of the salts of weak acids, viz. Calcium-tartrate, there is a major change towards lower pH values during crystal growth, since the reaction yields rapidly diffusing hydrogen ions. In the increasingly acid environment, the crystal is increasingly soluble and a steady state may eventually be reached in which growth and solution are in balance, in spite of the reagents being available.

The problem of growing larger crystals is connected with the problems of limiting nucleation, of ensuring a continued reagent supply and of removing the waste products. Continued reagent supply can be achieved by using reservoirs and continuous flow systems. The removal of waste products is easily achieved for the decomplexing procedure (19), in which one end of the diffusion column is in permanent contact with distilled water. Crystals grown in primary gel media are often associated with cusp-like cavities. Cusp like cavities are the regions in which the gel has been split and separated from the growing faces (19). The cusp formation is due to the pressure of the advancing growth surface leading to gel displacements. These cusps get filled with solution. As a result, the crystal is almost entirely surrounded not by gel, but by solution (19,26). It supports the view that the crystals do nucleate in the gel, but they grow increasingly from solution. The diffusion process supplies solute to the cusps and thus controls the growth rate. It only applies to primary growth in which development of crystal and cusps go hand-in-hand. Re-implantation followed by immediate growth disturbs these relationships. This is because it involves crystals of substantial size being confronted by initially cusp-less gel media. In these cases, the growth is considered to be by diffusion until after sufficient growth cusps are produced. The initial period after reimplantation is therefore similar to the initial period of primary growth.

The subsequent growth of crystals differs from ordinary solution growth. The gel surrounding the crystal allows diffusion which tends to replenish matter taken from the cusp volume by the growing crystal. It also protects the growth region from secondary (foreign) nuclei.

The nucleation suppressing characters of the gel distinguishes it from other solution growth methods and it may be achieved by the following:

1. Adjustment of the pore size distribution and the degree of communication among pores. Greater gel density (which

intuitively implies small pore size) diminishes nucleation but tends to increase the contamination of the crystal by silica and thereby to spoil their perfection and shape (19,53,54).

2. By the deliberate addition of foreign elements, but it is open to the same objections as in 1) above.
3. Concentration programming (53):

In this method, the concentration of the diffusing reagent is initially kept below the level at which nucleation is known to occur. It is then increased in a series of small steps till a few nuclei begin to form. Such nuclei act as sinks and lead to the establishment of radial diffusion patterns which actually reduce the reactant concentrations in some of the neighbouring locations. In this way, the formation of additional nuclei would be prevented. The method of concentration programming has been successfully applied to the nucleation control in several systems, and has resulted into growth of crystals of better (larger) size and perfection than those produced without programming.

In the case of a single tube growth system the number of growing crystals decreases and also their perfection increases as the distance from the gel rectant interface increases. It happens as a result of the difference in the diffusion gradients in different regions. Factors arising from gel ageing can also contribute to this cause. Faust (55) has reported that the growth rates are drastically reduced with increasing time after gelling. This effect of ageing could be due to progressive formation of cross-linkages between siloxene chains, which gradually reduces the cell size. Consequently it lowers nucleation probability since many potential nuclei, whether homogeneous or heterogeneous, should find themselves in cells of too small a size to support visible growth.

Nucleation of crystals is also affected by light (25,28). Calcium tartrate crystals are observed to have grown more prolifically under or after irradiation of the gel system than in darkness. Illumination is reported to have an adverse effect on the quality of copper chloride crystal grown from gel (56).

3.4 BASIC TECHNIQUES OF GEL GROWTH

There are four basic methods of growing crystals in gels; each one of them has special advantages:

a) Reaction method;
b) Complex - decomplex method;
c) Chemical reduction method;
d) Solubility reduction method.

They are now discussed in brief:

a) Reaction method:

It has an advantage of growing single crystals whch are mostly insoluble (or slightly soluble) in water and which decompose before reaching their melting point. In this method two soluble reactants are allowed to diffuse through a gel where they react and form an insoluble or relatively less soluble crystalline product (56). The chemical reaction is expressed as follows:

$$AX + BY \longrightarrow AY + BX$$

where A and B are cations and X and Y are anions. The requirements to grow single crystals by this method are as follows:

i) The gel must remain stable in the presence of the reacting solutions and must not react with these solutions or with the product formed.

ii) Some solubility of product crystal is required in order to grow crystals of any size (25).

iii) The reactants employed must be soluble in solvent (usually water) and product crystal must be relatively less soluble.

Reaction method is a very common method to grow single crystals in gels. Many workers have followed this method to grow single crystals such as phosphates of Zirconium, Titanium, Tin (57) and Calcium (58), Hydrogen phosphates of Potassium (59), Calcium, Lead (60) and Ammonium (61) molybdates of Nickel (62), Calcium and Strontium (63), Lead (36) and Barium (64), perchlorates of Potassium, Rubidium and Cesium (65), oxalates of Zinc, Copper and Manganese (66) and Cadmium (67,68) halides of metals such chlorides of Lead (69) and Copper (70), bromide of Lead (71) iodides of Lead (72), Nickel, Cobalt, Manganese, Potassium and

Rubidium (70), sulphates of Barium, Strontium (73) and Calcium (74) and triglycine and diglycine (75), carbonates of Lead (76) and Calcium (77) and tartarates of Potassium (78), Lead (79) Strontium (80), Cadmium (81), Calcium (82), Didymium (83) and Lanthanum (84).

A gel is prepared by mixing a definite quantity and pH of aqueous solution (acidic in nature) with a definite quantity and specific gravity of aqueous solution of sodium metasilicate and allowing the resulting mixture of certain pH to form a gel in a test tube or a beaker. The feed solution (the other aqueous solution) is gently poured on the set gel. Alternatively the U-tube is employed for neutral gelation and then the two reacting solutions are poured in two vertical limbs. For greater degree of lateral diffusion of ions to growth sites the modified apparatus was devised (73,85). The arrangement has been successfully employed to grow single crystals of mixed configuration,

$Sr_xCa_{1-x}C_4H_4O_6.4H_2O$ (86).

The present work reports a successful use of this technique to grow single crystals of ammonium-hydrogen-d- tartarate. The details are given in the concerned chapter.

b) <u>Complex - decomplex method:</u>

This method was reported by O'Conner et al (87). It consists of first forming a chemical complex of the material of the eventual crystal to be grown with an aqueous solution of some suitable substance, called complexing agent, in which former is homogeneously miscible and then providing externally a suitable conditon to decomplex or dissociate the complex formed. A standard procedure adopted for decomplexing is to steadily increase the dilution while the complex solution is diffusing through the gels. In the case of growth of $CuCl_2$, the large solubility of CuCl in HCl solution and its marked decrease with increasing dilution immediately favours the growth by complex-decomplex method. The method has been successfully used to grow good ionic conductors of α-AgI (88), β-HgS (89)γ-HgS (90).

c) Chemical Reduction Method:

This method is suitable for growing only metal crystals. Hatschek and Simon (91) grew gold crystals by adding 8% oxalic acid solution over gel which contained gold chloride solution. Single crystals of gold with triangular shape (92), of lead crystals with hexagonal habits (93), of copper (94) and cupric oxide (95) were grown by this method.

d) Solubility Reduction Method:

This method is particularly useful for growing single crystals of highly water soluble substances. Gocker and Soest (61) first reported the growth of dihydrogenphosphate single crystals by this method. The substance to be grown is dissolved in water and incorporated with the gel forming solution. After the setting of gel, a solution which reduces the solubility of the substance is added over the gel to induce crystallization. Sodium chloride crystals have been grown by adding concentrated hydrochloric acid over the gel containing a saturated solution of sodium chloride (96). The formation of crystal is due to the reduction of solubility of sodium chloride in the liquid phase by concentrated HCl. Potassium dihydrogen phosphate crystals were grown by reducing solubility using ethyl alcohol (97,98).

The gel technique is a very appropriate and convenient one for doping studies. Dopant is either added to the gel or supernatant reagent in solution form. A variety of dopants like nickel, chromium, iron, cobalt are reported to have been incorporated in Calcium tartarates (19). Armington et al (56) reported studies on doping Neodymium in calcium tartrate crystals. Dishovsky et al (99) and Franke et al (100) performed experiments on doping of silver-selinate and Manganese carbonate crystals.

Mixed crystals have been successfully grown by the gel technique. Patel and Arora (86) reported growth of mixed crystals of strontium calcium tartrate of different compositions. Wikkorowska et al (101) have grown $Ca_xSi_{1-x}C_4H_4O_6 . 4H_2O$ mixed crystals in silica gels.

Silica gel has been the most frequently used medium for the growth of crystals by this technique. However many other gels have been tried very successfully in several cases. As early as in 1891, Marriage (17) used fruit jellies and jams for the growth of lead iodide. Besides silica gels, agar gels, gelatin and other organic gels can be used for crystal growth. Studies on the effects of gelatin gels on the nucleation and growth of silver iodide crystals in photographic emulsions have been reported (102,103). In 1970's organic gels were known to be potentially useful, as growth media. Growth of KDP (104), alkaline earth orthophosphates (105), calcium carbonate (106) and Lead monohydrogen orthophosphate (107) crystals were accomplished in gelatin gels. Calcium carbonate crystals were grown in polyethylene oxide gels (106), acrylic acid gels, styrene- maleic anydride gels styrene-maleic anhydride gels (108) and polyacrylamide gels (109) have been used for the growth of crystals of sodium, zeolite, selenium, and HgS respectively. Blank et al (110) reported a detailed study on organic gels and aimed at a conclusion that polyacrylamide and polyethylene oxide gels are very promising as crystal growth media. A comparative study of gypsum crystals grown in silica and agar gels in the presence of additiv es was carried out by Van Rosmalen and his co-workers (111). Kanniah et al (112) and Ambrose et al (113) have respectively reported studies on periodic crystallization of AgI_2 in agar gels.

Gel growth has attracted the attention of scientists for crystal growth in space. The scope of gel growth under microgravity conditions in space ships have been discussed by Bhat (114).

The number of papers published under crystal growth in gel in the recent years, is so large that it is impossible to do justice to each one of them in such a short review.

To mention a few, are the works of Del et al (115) in growing piezoelectric crystals of $PbTiO_3$ and ferroelectric calcium tartrate by Gou (116). Studies on the electrical conductivity and dielectric properties of gel grown ferroelectric lead nitrate phosphate & rubidium hydrogen phosphate by Desai et al (117,118) and influence of gel-pH on the growth of ammonium dehydrogen orthophosphate crystals by Sengupta et al (119) are to be noted. Work was also conducted in mediums other than silica, like agar-agar gel grown Lead oxide (120) crystals and growth of 3-methyl-4-nitropyridine-1-oxide organic crystals in tetramethoxysilane gel (121).

The application of gel growth in the field of medical science has taken a new dimension by the work of Narayana et al (122) growing steroids (testoterone) in silica gel. More advancement and progress are thus anticipated which might do justice to mankind in the area of curing diseases and ailments.

The above cited literature sufficiently indicates that the gel technique has established its application and utility in solving research problems of great curiosity and importance, in the areas of chemical physics, material science and solid state physics in general. There is a tremendous scope for further development which will depend on the extent to which its mechanism can be thoroughly understood and controlled. The following are some of the future scope of work:

1) The gel method has bright future in tackling the problems related to nucleation. It offers a means for better understanding of homogeneous nucleation, as it permits investigations in the absence of unwanted foreign nuclei.

2) The chemical role played by the internal gel surface and the extent to which these are governed by the gel structure, are the basic factors which need to be thoroughly investigated. Different gel media support nucleation and growth to different degrees. This needs to be studied in detail.

3) The basic problems are connected with the conditions which govern whether the gel structure will be displaced intact by the growing crystal (e.g. calcium tartarate (19)) or incorporated into the new solid by crystal growth in the gel interstices (e.g in Calcite (19) Henisch.

4) Other basic problems are those connected with the diffusion under static and dynamic conditions and their control over ultimate crystal size, the impurity uptake, crystal perfection, morphology and its relationship to growth speed, re-implantation and its dependence on the micro morphology of seed-surface, over doping and the production of metastable crystals, development of improved growth systems, the growth of otherwise interactable crystals, crystal growth in non-aqueous gels, etc.

The above mentioned problems are some amongst several others which warrant detailed investigation.

There is wide scope in further research

1) on improvements in the existing crystal growth procedures of gel method;

2) in resolving several unsolved problems connected with certain complex phenomena in the gel system;

3) in the applicaton of the technique to grow new materials and such others that could not be grown so far by this technique.

3.5 ADVANTAGES & LIMITATIONS OF GEL METHOD

Some of the advantages of the gel method over other crystal growth techniques are as follows:

i) Gel growth is a low temperature solution growth. It finds application in the growth of crystals with fewer defects.

ii) Crystals can be observed in practically all stages of growth. This is very helpful in the studies on growth kinetcs and in making some "in-situ" observations.

iii) All early formed crystal nuclei are delicately held in their position of formation, thus limiting effects due to impact on the bottom of a container.

iv) All nuclei are spatially separated, minimizing any effect due to precipitate- precipitate interaction.

v) The procedure lends itself to mass production and is very economical since elaborate apparatus is not required.

vi) Uniform concentration gradients can be maintained for a relatively longer time.

vii) Continuous supply of reagents can be provided by adding feed solution periodically.

viii) By-product or reaction waste product concentration can be reduced by replacing the solution over the gel surface.

ix) Crystals with different morphologies and sizes can be obtained by changing growth conditions.

The major advantages of gel method get clouded by its limitations. Elimination of these limitations by improving this technique of growth should be one of the major future research efforts. Some of the limitations and modifications are cited below:

(i) The gel technique is based on interaction between two nutrient solutions (19) except in the decomplexing procedures or in the growth of metal crystals by reduction method.

In order to achieve growth of high quality crystals, the reaction rate between the nutrients has to be quite slow. It means that one has to use nutrients of exceedingly small concentrations. Smaller concentration of the reactants may lead to depletion of nutrients prematurely and hence to the reduced size of the crystals. Therefore, the technique has to be developed or supplemented so that the rate of reaction can be kept at the level conducive to the growth of perfect crystals even with high nutrient concentration.

ii) A by-product is invariably produced when reaction between two reactants in a gel takes place. This by-product is likely to affect the quality of the grown crystal. So a modification to dispose off the by-product would increase the potentialities of gel method as a versatile growth method.

iii) The reaction leading to formation of crystal forming solute results into changes in the pH of the growth medium. As the reaction progresses, the pH slowly changes and so the growing crystals are subjected to a continuously changing environment. It may harm the quality of the crystal and the production of ill-deformed habits. If some ways and means were devised so as to allow maintenance of a constant pH of the gel medium, it could increase its efficiency considerably.

iv) The gel medium is porous and offers se internal surface to the diffusing nutrients. The internal surface must be capable of adsorption of nutrients (19). Consequently the total and free solute contents of a gel may not be the same. Basically it is only the free nutrient which is capable of interaction and generation of the material for crystal growth. If the possibility of using the property of adsorption of the gel in releasing the nutrients at the proper time could be realised, there would be steady rate of reaction and thus help in achieving high perfection of crystals.

Kurien et al (123-125) modified and improved the gel method for the growth of $PbCl_2$, $PbBr_2$ and PbI_2 crystals by introducing certain modifications such as the application of electric field to the growing crystal in a gel medium.

The gel method has enough scope for being utilized in the growth of many important materials which either have defied attempts of growth by other methods or which could not be grown of the desired perfection by other methods. Keeping the above objectives in view, attempts were made by the author to study the application of gel method for the crystallization, and subsequent studies of growth morphology and other properties of d-AHT.

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