Chapter 4

Growth of Bi$_2$S$_3$ Crystals by Gel Method
Chapter 4: Growth of Bi$_2$S$_3$ Crystals by Gel Growth

4.1 Introduction:

The gel growth technique due to its simplicity and effectiveness has gain considerable importance in growing crystals of certain compounds. Gel-growth is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. In gel method, the growth of single crystals is a self purifying process; free from thermal strains which is common in crystal grown from the melt. Crystals are the base for the different applications in the field of science and technology. The advances in these fields depend upon the availability of good quality crystals. Hence, large amount of efforts are made on the development of crystal growth methods and one of them method is Gel growth. The present chapter is a brief review about the growth of bulk Bismuth Sulphide (Bi$_2$S$_3$) crystals that can be grown by gel technique. Gel growth technique is quite simple and well suited for the crystal growth of compounds, which are sparingly soluble in water and decompose before melting. Without any need of sophisticated instruments and high temperature furnaces, gel technique can be set up in a laboratory with simple glass-wares. Good quality crystals can be grown by carefully selecting the specific gravity of gel, pH and concentration of the reactants, at room temperature. Gel growth technique is popular amongst researchers even today.

For the production of homogeneous, highly stoichiometric and high quality ultrafine structures, Gel method is used due to its low temperature, highly controllable and cost effective properties. For shape-dependent applications and comparative accessibility, Gel route is adoptable way to choose desired shape of the metal Sulphides(MS). An MS-based structure has wide ranges of applications such as magnetic applications, energy generation, conversion, storage devices, electronic device applications, sensors and actuators materials. In this chapter, we have discussed about the comprehensive ideas of gel technique to synthesis metal sulphide Bi$_2$S$_3$ bulk crystals.
4.1.1 Historical Perspective

Advances in solid state science depends critically on the availability of defect free single crystal specimens, has long been appreciated. For the development of crystal growth methods an enormous amount of labor and care has been lavished. All the methods in terms of crystal size, purity and perfection, used for the growth of single crystals from melt, vapour, and solution have their own inherent advantages and disadvantages those were briefly discussed in Chapter-2.

Crystal growing is still an extremely difficult task requiring great expertise and skill, instead of the technological advancement in condensed matter physics. Defects and lattice strains are frequently incorporated in the growing matrix. In these context, for getting good quality single crystals the gel technique is found to be promising one. By using this method, the crystals which cannot be satisfactorily grown from melt and vapor are grown successfully. A complete survey made by Henisch in this field gave a fantastic idea to the crystal growers to grow crystals using gel technique. The art and science of growing crystals in gel is historically an old phenomenon. Precisely in 1896, the German colloid chemist and photographer, Robert Eduard Liesegang first made the discovery of the periodic precipitation phenomenon in gels.

The growth of single crystals in gels received the attention after him who observed rings consisting of tiny crystals and each ring separated by a clear spacing when two components are counter diffused through gels, it is certain that it has given birth to a novel idea of crystal growing. One of the examples of pattern formation is the Liesegang rings in precipitation reactions, in chemical reaction–diffusion systems. Such patterns arise from the interplay between the reaction kinetics and the diffusion of chemical species. The structures are formed by the non uniform spatial distribution of crystals in a precipitation reaction in a gel, which are often rings in circular geometries, and bands in linear geometries. Both the rings and bands of Liesegang patterns are not spatially uniform; instead their width and spacing vary regularly according to the distance from the origin of the imposed concentration gradient.

4.2 Principle of gel growth
Under controlled growth, Gel technique is a simple and elegant method of growing single crystals at room temperature. In the steady-state, Gel is defined as a substantially dilute cross-linked system which exhibits no flow. A gel is a solid, jelly-like material that can have properties ranging from soft and weak to hard and tough. The principles of crystal growth technique are very simple. Solution of two suitable compounds which gave rise to the required insoluble crystalline substance by mere chemical reaction between them is allowed to diffuse into the gel medium and chemically react as follows:

\[
AX + BY \rightarrow AB + XY
\]

Where AX and BY are the solutions of the two compounds in which reactions produce increase to the insoluble or sparingly soluble substance AB and also the waste product XY being highly soluble in water. By the establishment of a three dimensional system of cross linkage between the molecules of one component, Gels are formed from suspensions or solutions. The second component permeates this system as a continuous phase. A gel can thus be regarded as a loosely interlinked polymer. Gels are mostly liquid, by weight yet they behave like solids due to a three-dimensional cross-linked network within the liquid. It is the crosslinks within the fluid that give a gel its structure (hardness) and contribute to stickiness (tack).

In this way gels are a dispersion of molecules of a liquid within a solid in which the solid is the continuous phase and the liquid is the discontinuous phase. The gel is a very intelligent substance sensitive to the minute changes in the ambience. This method can also utilize for growing crystals from the solutions of substances having very high solubility. If brief study of literature done then any problematic growth of substances by the conventional methods, can be successfully achieved by gel technique.

### 4.3 Various types of gel
A gel is a two component system, highly viscous, semi-solid in nature and having fine pores through which diffusion takes place and gel can be classified as follows:

1. **Physical Gel**: Gel which is obtained by physical process like cooling is called physical gel.  
   e.g. (a) Gelatin, (b) agar

   [a] **Gelatin Gel**: Gelatin has properties such as translucent, colorless, brittle, nearly tasteless solid substance. Substances which contains gelatin are called gelatinous. Gelatin is a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from the skin, bones, and connective tissues of animals. It is an irreversibly hydrolyzed form of collagen which is closely related to proteins. Gelatin gels are connected by much weaker forces. Without mechanical agitation, it can be reliquified by heating.

   [b] **Agar Agar Gel**: Agar or agar-agar is a jelly-like substance, obtained from red algae. It is a complex mixture of polysaccharides composed of two major fractions - agarose, a neutral polymer, and agarpectin, a charged, sulfated polymer. Agar-agar may come in several forms: powdered, flakes, bars and threads. It is insoluble in cold water, but it dissolves readily in boiling water. The gelling portion of agar-agar has a double helical structure.
2. Chemical Gel: Gels which are created by chemical reactions such as hydrolysis or polymerizations are called chemical gels. e.g. (a) Silica gel

[a] Silica gel: Silica gel, a highly porous, noncrystalline form of silica made synthetically from sodium silicate. Silica gels has high specific surface area (around 800 m²/g) allows it to absorb water readily, making it useful as a desiccant (drying agent). It is a solid. The crystals grow generally better in silica gel than in gelatin or agar gel. Silica gels with a molecular silica-to-water ratio of 1:30 or 1:40 can easily be cut with a knife. It is used to remove moisture from gases and liquids, to thicken liquids, to impart a dull surface to paints and synthetic films, and for other purposes.

4.3.1 Reason for Choosing Sodium Meta Silicate (SMS)

By the choice of the reagents, the growth habit and degree of perfection are influenced. The Precise comparisons are difficult, but change in the acid radical, changes the pH in which the crystals grow as well as change the rate of diffusion and hence growth. In particular, to grow good quality single crystals, silica gel is the best and most versatile growth media. The gel matrix has fine pores of different sizes and a varying degree of surface roughness and the pores are ultra microscopical. The X-ray investigations of silica gel show some close resemblance with silica glass but have some in homogenities.

4.3.2 Preparation of the hydro-silica gel

Hydro – silica gel is the most favorite gel for the crystal growth experiments. By changing the level of the hydrogen ion concentration of the solution and dissolving Sodium Meta Silicate powder in water the gel can be prepared. The pH factor is the important parameter, which determines the rate of polymerization and the speed of gel setting. For growing the crystals of a good number of materials, the pH between the ranges 6-8 are found suitable. The pH level of the system is maintained by an acid component added to the solution. One of the important factors which affect the hardness of the gel medium is the density of the sodium meta silicate solution. It is found that the densities ranging in between 1.03 to 1.06 g/cm³ yields better experimental results in many systems.

4.3.3 Structure of silica -hydro gel
When sodium meta-silicate dissolves into aqueous solution, mono-silicic acid is produced with the liberation of NaOH in accordance with the reaction,

\[ \text{Na}_2\text{SiO}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 + 2\text{NaOH}. \]

With the liberation of water, Mono-silicic acid can polymerize which occur repeatedly. A three dimensional network of Si-O links is established as silica hydro gel.

**4.3.4 Effect of pH value:**

With the pH and the temperature, the gelation period varies from a few minutes to hours. The subsequent changes cannot be monitored or controlled; only the initial pH level can be adjusted. The initial values of pH between the ranges 6-8 are suitable in most cases. In less acidic solutions, the pH variation is very high and during the polymerization of the gel it increases steadily. The commonly employed acids for polymerization are Nitric acid, Hydrochloric acid, Oxalic acid, Acetic acid Tartaric acid, etc.

**4.3.5 Points to remember while preparing gel**

1. Small air bubbles during gelation may get crippled in, which grow and become lenticular in shape which diminishes the efficiency of the system. Hence, the acid must be poured very slowly and the mixture is agitated well to eliminate the air bubbles.
2. For proper setting, it is necessary kept the crystallization vessel undisturbed and in controlled thermal conditions.
3. Crystals in denser gels are poorer and more contaminated with silica. So, the lowest gel concentration is preferred though it takes a long time to set silica gel.
4. The practical limit for the Concentrations of specific gravity appears between 1.02 and 1.06.

**4.4 Gelling Mechanism and Structure of gel:**
Structures of many of the gels are complicated and many of them are still not understood well. Depending upon the nature of the material and its temperature, the gelling process itself takes an amount of time which varies from minutes to days. By the developing of a three dimensional system of cross-linkages between the molecules of one component, gels are formed from substance or solution. This system is permitted by the second component as a continuous phase. During gelling, a gel can depend on the experimental conditions. The mechanism has not yet been fully understood, by which the silica gel is formed. When it polymerizes with liberation of water, it is assumed that mono-silicic acid is produced. The formation should be called as hydrogel, when the dispersion medium is water. It has been seen experimentally that in the cases of electrolytes and dilute gels the reactants diffuse as rapidly through gels as through water.

In order to have a clear idea regarding the function of silica gel, the Sodium Meta Silicate solution is considered. During a prolonged period after mixing (incubation time), the liquid hydro gel remains outwardly unchanged. This is followed by a rapid increase in viscosity and then in quasi solidification. The mechanical properties of fully developed gels can vary widely depending on the density and conditions during gelling. This can be pictured in accordance with the dynamic equilibrium as

\[
\text{Na}_2\text{SiO}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 + 2\text{NaOH}.
\]

This is a reversible process and the unwanted reaction product NaOH remains in the solution. The monosilicic acid liberates the hydroxyl ions and polymerises.

\[
\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \\
\mid \quad \mid \quad \mid \quad \mid \\
\text{HO} - \text{Si} - \text{OH} - \text{HO} - \text{Si} - \text{OH} \rightarrow \text{OH} - \text{Si} - \text{O} - \text{Si} - \text{OH} + \text{H}_2\text{O} \\
\mid \quad \mid \quad \mid \quad \mid \\
\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH}
\]
With the liberation of water, Mono-silicic acid can polymerize which occur repeatedly. A three dimensional network of Si-O links is established as silica hydro gel.

As polymerization proceeds water accumulates continuously on top of the gel structure, a phenomenon known as syneresis takes place. Until the entire molecule becomes three-dimensional network of Si O links, this process continues. The process is irreversible once they cross a certain limit, as the oxygen – silica bond is extremely strong. As much of the water is believed to have its origin in the above condensation process, and some may arise from purely mechanical factors connected with a small amount of gel shrinkage. As soon as the silicic acid monomer is formed, the polymerization begins.

**Growth of crystals in gels**

By providing a framework of nucleation sites (Henisch et al) the gel medium prevents turbulence and helps the formation of good crystals. One of the most significant advantage to be observed is that the convection is absent in gel growth experiments. The high degree of perfection and the lesser number of defects have been observed in gel growth experiments. By using the gel techniques there are multiple latest materials have been crystallized.

4.5 **Importance of gel technique**

It is found that in an ideal crystal a uniform spatial arrangements of other atoms are there surrounding every single atoms. If the arrangement of atom is not perfect, various kinds of imperfections determine the physical properties like electrical, optical and mechanical properties of crystals. Hence, crystal growth involves not only preparation of large single crystals but also control of the defect formation. The following points describe all the significance of the gel method.

1. It forms three dimensional structure entrapping water.
2. The gelation structure provides an ideal medium for the diffusion of reacting ions separated until reaction is desired.
3. It is chemically inert and therefore, it does not involve the chemical reactions between the reactants during crystallization.
4. It permits the reactant to diffuse through the gel within a controllable slow rate.
5. This method has the ability to control the rate of reaction required for crystallization of a particular material.
6. It retards convection during growth. Hence formation of defects is highly minimized.
7. Concentration of the reactants can be easily varied.
8. Nucleation can be controlled by varying the density of gel and the growth at each stage can be observed in a transparent medium.
9. It holds the crystals in fixed positions without overlapping irrespective of internal disturbances.
10. The growth crystals can be harvested easily without damaging the crystal faces. Crystals grown by this technique are found to be less defective than the crystals grown by other methods.

**Advantages of gel method:**

1. At ambient temperatures crystal growth takes place and hence crystal defects are reduced.
2. In all stages of their growth the crystals can be observed practically.
3. This method enables the control of the rate of reaction required for crystallization for a particular material.
4. The gel medium prevents convection currents and turbulence.
5. The number of nucleation sites and the size and morphology of the crystals can be controlled by changing the growth conditions.
6. All crystals are held in the position of their formation and this limits the effects due to impact on the sides of the container.
7. Since all nuclei are spatially separated, the interaction between them is considerably diminished.
8. The growth procedure is simple and economical.

A few disadvantages of this method are the limitation of the crystal size and the time delay in growing the samples.

**4.6 Classification of Gel Growth Methods**
The gel technique can be categorized into four groups, depending on the attitude of chemical reactions and physical changes involved.

![Gel Growth Methods Diagram]

### 4.6.1 Growth by chemical reaction

This chemical reaction method is famous to grow more crystals. It is specifically suitable for growing crystals which are insoluble or partially soluble and those having thermal unsteadiness. In this method, two aqueous solutions of soluble reactants are allowed to react inside the gel medium by the processes of diffusion through gel where they react and form an insoluble or sparingly soluble crystalline product (Crystal). The basic requirements for chemical reaction are

1. Reactants should be soluble in the solvent and product crystal must be relatively less soluble.
2. The gel must not react with other solution and remain stable in presence of the reacting solution.

Two various methods are employed in the present experiments.

1. Single diffusion method
2. Double diffusion method

#### 1. Single diffusion method

In single diffusion method, one of the regents, which are highly soluble in water and chemically inactive with the gel either AX or BY, is impregnated in the acidified gel medium (known as inner reactant). The other regents solution (known as outer reactant), is then diffused over the set gel after the gelation. Through gel medium, this solution on diffusion reacts with the inner reactant and yields the crystals. At the same time, some other compounds are being formed such as XY during the chemical reactions are highly soluble in water and dissolve in water present in the hydrogel medium (Figure 4.1(a))
2. Double diffusion method

When both the reactants are found chemically reactive with the hydrogel or found insoluble in water, double diffusion principle is used. The two components can meet each other at the common region of the gel medium, due to the diffusion, normally the bent portion of the U tube (Figure 4.1(b)). Then without vigorous chemical effect they react chemically, allowing the formation of crystals in gel. A number of modifications are incorporated depending upon the requirements of the materials, with the usual procedures for the purpose of growing large crystals in gel.
4.6.2 Chemical reduction method

By conventional method, this method is suitable for growing metal crystals from gel media. Crystals of Nickel, Cobalt, Selenium, Lead and cooper have been obtained by using this method. The gel is prepared by adding the complex solution of the metal to the gelling solution. After gelation, reducing agent such as hydrophosphoric acid is added from the top as the outer reactant over the set gel. Due to slow reduction reaction it may leads to the formation of the metallic crystals in it.

4.6.3 Complex-Decomplexion method

A material with solubility in the presence of another soluble material increases in a nonlinear way with the concentration of the soluble material suitable for this method. The concentration of the combined solution is reduced during diffusion and therefore the material reappears as crystals. Some of the cuprous halides and silver iodide are crystals grown by decomplexing.
4.6.4 Solubility reduction method

Materials which are highly soluble in water are the most suitable for this method. By reducing the water content using water absorbing agent like alcohol, in this method the super saturation is provided. Using this method some important water soluble crystals such as KDP, ADP, etc., have been grown.

4.7 Growth Mechanism in Gel

Crystallization in gel happens out of the diffusion of the ions through it and their inclusion at their growing phase. It is depends on the various parameters like pH value, density, temperature, age and quality of the medium, purity of the interacting components, etc. The process of analyzing the mechanism, the gel could be considered as a diffusion medium and the whole process of crystallization will be a diffusion controlled phenomenon. It can be very well compared to the general solution growth. The super saturation near the growing phase of the crystal in gel is usually high enough for this as the gel favors homogeneous nucleation. One of the principal functions of the gel is the establishment of a stable pattern of concentration gradients.

Convection is completely absent in the gel and by diffusion the solute is supplied to the growing crystal. When a solute is thus supplied, the growth takes place either by screw dislocation or by two-dimensional surface nucleation mechanism. The average crystal growth is the largest near the top of the gel column, where the concentration gradient is higher than that near the bottom. The super saturation of the gel medium self-adjusts to the needs of the growth process. This leads to the formation of crystals with a high degree of perfection. Thus, where the concentration gradients are high and the smallest near the bottom where the concentration gradients are the least the distribution of growth rates from the top to the bottom of the gel column is the greatest.

4.8 Nucleation Concept of Gel Media:

Since the crystals which grow in any particular gel system, compete with one another for solute, the problem of nucleation is of crucial importance in practical operations. This competition limits their size and perfection. In a predetermined and convenient place, it is obviously desirable to suppress nucleation until only one crystal grows. Crystal growth in gels is evidently a variant of growth in solution, with additional complications arising from the presence of the gel. It is clear that the nucleation probability is reduced by gel. Gel methods are
distinguishes from ordinary diffusion method by the nucleation suppressing character. It has been known that the formation of crystals is sensitively dependent on the presence of impurities. By soluble and insoluble additives, crystallization could be increased.

Two basic nucleation mechanisms such as homogeneous nucleation and heterogeneous nucleation have been recognized. Homogeneous nucleation does not require the presence of foreign substances, while Heterogeneous Nucleation, demands a pre-existing foreign crystalline substrate. From the vapour, melt or from solute a new material can be deposited on that substrate. It is highly difficult to free system entirely from foreign particle contamination and to guarantee that all the observed nucleation is ever homogeneous. It can be easy to show that homogeneous nucleation sometimes prevails in gels. On a pre-existing substrate, the deposition of solute is energetically cheaper. It, hence, occurs at lower super saturations and so one can expect that the homogeneous nucleation is delayed until the available heterogeneous nuclei are used up.

It is forecast that, a number of atoms, ions or molecules can come together and form a rudimentary crystal as a result of statistical accident. Simple energetic considerations show that this crystal is likely to dissolve again unless it reaches a certain minimum critical size. Beyond that size, the energy relations favour continued growth. It is a common observation that, large crystals can grow at the expense of small ones. Based on the simplest models, calculations lead to critical radii of 10 Å and too much small can be seen even by the electron microscope. The identification of the nucleation mechanism is not an easy matter. Homogeneous and heterogeneous both the processes are supposed to depend on solute concentration, pH, impurities and molecular size.

Incontrovertible proof is not available, but the following observations support the hypothesis that homogeneous nucleation can occur. Nucleation control is thus one of the serious problems facing gel growth. Even although the diffusion rate can be controlled to a great extent, this will not be enough for controlling the population of nucleation centers in gel. The restricted knowledge of the actual structure of the gel prevents one from taking any effective measures for nucleation control. Hence, only external means are alone acquire for minimizing the spurious nucleation in gels.

Some of the major techniques adopted are, (1) Optimizing of the gel density (2) Gel ageing (3) Use of neutral gel (4) Stabilizing the thermal conditions.
Programming the concentration of nutrients (6) Use of additives (7) Field utilization. Gel densities which are ranging from 1.03 to 1.06 g/cm³ are results in give good outcomes. Due to the ageing of the gel, the pore size of the gel network will become small. Hence, aged gel show less nucleation centers. Neutral gel zones are also leads to minimize the nucleation centers. The concentration has been regularly increased for enhancing the growth, once a steady growth is established on these nucleation centers. Another method of nucleation control is use of additives which will increase the activation energy required for the formation of the critical nucleus. This results in reduces the number of nucleation centers in the medium.

4.9 Effect of Various Parameters:

1. Effect of pH on gel setting time

The gelling process takes an amount of time, depending on the nature of the material, its temperature and history, which can vary widely, from minutes to many days. To study the effect of pH on gel setting time, Sodium Meta Silicate solution of relative density 1.04 are mixed with a particular mole of ortho phosphoric acid in various ratios, so that the resulting pH of the mixed solutions are maintained between 4.0 to 9.0. The solutions are allowed to set undisturbed. The gel setting time is noted in each case moderately. Very high and low pH values evidently results into high surface charges which inhibit gelation.

2. Effect of gel density

By keeping the constant value of pH, the gels of different density are obtained by mixing SMS solutions of relative density 1.03 – 1.06 g/cm³ with ortho-phosphoric acid. With decrease in gel density, the transparency of the gel increases. As a general rule, poor crystals are produce due to dense gel. On the other hand, gels of insufficient density are mechanically unstable and take a long time to form. The lower practical limit of relative density is, 1.02.

3. Effect of gel aging
Aging of gel plays vital role in the growth of crystals, before adding the feed solution. To investigate the impact of aging of gels, gels of same pH and density are allowed to age for various periods. It was observed that as aging increases, the number of crystals decreases along with reduction in the crystal size. With the decrease in pore size, aging also decreases the diffusion and nucleation density. The greater the amount of water evaporates out of the gel when gel is set for longer period of time at the room temperature. The evaporation of water causes an increase in gel density, before the gel is set which results in decreases the diffusivity of ions in the gel thereby decreasing the number of nucleation sites. After the gel is set, evaporation of water causes the lack of ionic carriers in the channel of gel framework.

**Quality of the Crystals:**

The gel method provides in most cases better quality single crystals. The only limitation in gel method is its inability to produce large sized crystals. In case of purity of the crystals, the gel is very efficient in producing pure samples. For the deliberate addition of impurities into the body of the crystal, the gel method also provides an effective mechanism. The morphology of the crystals in which they are growing depends on the physio-chemical environment.

**Scope of the Thesis:** In view of the importance of Bismuth Sulphide in Nano and bulk region the attempt are made to derive the gel growth conditions for these crystals. Crystallization processes and growth conditions of these important research problems have been chosen for the present investigation.

Bi$_2$S$_3$ crystals were grown in silica gel by varying the growth parameters such as pH of gel, concentration of supernatant and reactant etc. The Optimum condition to grow doped Bi$_2$S$_3$ crystals has been obtained. If the crystals were grown at constant temperature, it is established that the transparency and size of the grown Crystals are increased. Crystals having different morphologies and habits, the crystal structure of Bi$_2$S$_3$ is Rhombus.

**4.10 Experiment method to grow the Bismuth Tri-Sulphide [Bi$_2$S$_3$] crystals**
Crystals of Bismuth-Sulphide Bi₂S₃ were grown by a simple gel technique using single diffusion method. The reactants used for the growth of Bi₂S₃ in gel are H₂S gas as the inner reactant and a solution of Bi₂O₃ (3 - 10 g of Bi₂O₃ in 100 ml of 10 N HCL) as the outer reactant. In the present work, 5 ml, 1N acetic acid was taken in a small beaker, to which sodium Meta silicate solution of density 1.04 gm/cm³ was added drop by drop with constant stirring by using magnetic stirrer, till pH of the solution reaches a value of 4.40. To the above Sodium Meta Silicate (SMS) solution of pH 4.4, H₂S gas was passed through the gel solution for different time intervals (say 5, 10, 15 min etc.) as inner reagent. For gelation this mixture was then transferred to the test tube of diameter 2.5cm and 15cm in length. To keep the solution free from dust and impurities, care was taken to cover the test tube with cotton. The period of gelation was varied from 1 to 7 days by adjusting the pH of the solution. It was left for 66 to 72 Hours for gel ageing and then the outer reactant Bi₂O₃ dissolved in 100 ml of 10 N HCL was poured over the set gel. The outer reagent was added down the sides of the test tube using a pipette and not directly on to the gel medium. This reactant on diffusion into the gel medium reacts with the inner reactant (H₂S). After a week's time nucleation sites were observed and circular shaped, opaque and brittle crystals were observed. The experiment was carried out at an ambient temperature of about 28°C. The reaction between Bismuth oxide, dopant and H₂S Gas solution in gel medium resulted in the growth of Circular shaped Bismuth Sulphide [Bi₂S₃], crystals.

**Chemicals Used:-**

1. Sodium Meta Silicate powder - Na₂SiO₃5H₂O (M.W.284.20 g/ mol) (A.R. grade)
2. Acetic acid (A.R. grade) - CH₃COOH
3. H₂S gas Solution
4. Bismuth Oxide (A. R. grade) - Bi₂O₃ (M.W. – 465.96 g/mol)
5. Hydrochloric Acid (A.R. grade) - HCL (M.W. – 36.46 g/mol)
6. Double distilled water

The crystals were grown using following chemical reaction.

\[
\text{Bi}_2\text{O}_3 + 6 \text{HCL} \rightarrow 2\text{BiCl}_3 + 3\text{H}_2\text{O}
\]

\[
2\text{BiCl}_3 + 3\text{H}_2\text{S} \rightarrow \text{Bi}_2\text{S}_3 + 6\text{HCL}
\]
The grown crystals are shown in Fig. (4.2 (a) & (b))

Figure 4.2(a) Crystal (Bi$_2$S$_3$) Grown tube
4.1 Optimum Conditions for Gel Method:-

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Conditions</th>
<th>Bismuth Sulphide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Density of Sodium Meta Silicate</td>
<td>1.04 g/cm³</td>
</tr>
</tbody>
</table>
Different parameters such as gel density, gel setting time, gel aging time, Concentrations of reactants, pH of gel etc. have the considerable effect on the growth rate.

1. Effect of gel density

It was observed that as the gel Densities increases, the transparency of the gel decreases. With higher densities gels set more rapidly than the gels with lower densities. Table 4.2 shows the effect of density on number of nuclei formed.

Table 4.2: Effect of gel density on nucleation density [pH = 4.40, feed solution H₂S gas solution]

<table>
<thead>
<tr>
<th>Test tube No.</th>
<th>Acetic acid 1 N</th>
<th>Bi₂O₃ incorporated in gel 1.0 M</th>
<th>Density of gel g/cm³</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>10</td>
<td>1.02</td>
<td>Gel was not set</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>10</td>
<td>1.03</td>
<td>Gel was not set</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>10</td>
<td>1.04</td>
<td>Small yellow colored spheres near gel interface, in ring form</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>10</td>
<td>1.05</td>
<td>Small yellow colored in ring form</td>
</tr>
</tbody>
</table>

2. Effect of pH of gel:

It was observed that the transparency of the gel decreased with increased in the pH value. At higher pH values the crystals growing were not well defined. The
reason behind it was due to contamination of the crystals with silica gel. It was observed that the number of crystals decreased with increase in pH of gel.

**Table 4.3: Effect of pH on gel [Aging period = 72 hrs. feed solution H₂S gas solution]**

<table>
<thead>
<tr>
<th>Test tube No.</th>
<th>Acetic acid 1N</th>
<th>Bi₂O₃ incorporated in gel 1.0 M</th>
<th>pH of Mixture</th>
<th>Gel Setting Time(hrs)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>10</td>
<td>2.0</td>
<td>----</td>
<td>Gel was not set</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>10</td>
<td>3.0</td>
<td>----</td>
<td>Gel set in 15 days but still unstable</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>10</td>
<td>4.0</td>
<td>288</td>
<td>Small spheres less in number</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>10</td>
<td>4.5</td>
<td>168</td>
<td>Very small crystals</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>10</td>
<td>5.0</td>
<td>120</td>
<td>Very small spherical crystals</td>
</tr>
</tbody>
</table>

3. Effect of gel aging time: -

Before adding the feed Solutions, gels were allowed to age for different period. It was observed that with increase in aging time of gel the number of crystals decreased. This is because the cell size gets reduced by gel aging and consequently the rate of diffusion of ions into the gel.

4. Effect of concentration of supernatant:-
Bismuth oxide is used as supernatant with different concentration from 0.2 M to 1.0 M is added over the set gel. It was observed that very few nucleations were observed at 0.2 M of concentration of supernatant with very small size of the crystals and crystals were not well defined. Table 4.4 summarizes the effects of concentration of reactants on habit and quality of crystals.

Table 4.4: Effect concentration of reactants on habit and quality of Bi$_2$S$_3$ crystals

<table>
<thead>
<tr>
<th>Concentration of reactant in gel</th>
<th>Concentration of reactant above gel</th>
<th>Habit</th>
<th>Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$O$_3$ 0.2 M; 10 ml</td>
<td>H$_2$S gas water solution</td>
<td>Smaller crystals, less in number</td>
<td>Whitish, opaque</td>
</tr>
<tr>
<td>Bi$_2$O$_3$ 0.3 M; 10 ml</td>
<td>H$_2$S gas water solution</td>
<td>Crystals of smaller size, more in number</td>
<td>Whitish, opaque</td>
</tr>
<tr>
<td>Bi$_2$O$_3$ 0.5 M; 10 ml</td>
<td>H$_2$S gas water solution</td>
<td>Spheres more in number</td>
<td>Yellow colored, opaque</td>
</tr>
<tr>
<td>Bi$_2$O$_3$ 1.0 M; 10 ml</td>
<td>H$_2$S gas water solution</td>
<td>Larger crystals, well isolated</td>
<td>Yellow colored, opaque</td>
</tr>
</tbody>
</table>

5. Effect of concentration of reactants:-

For the growth of Bi$_2$S$_3$, the reactant used in gel is H$_2$S gas as the inner reactant. Initially a gel solution (Sodium Meta Silicate) of density 1.04 g/cm$^3$ was prepared and H$_2$S gas was passed through the gel solution for different time intervals (say 5, 10, 15 minutes etc.). This gel solution after the impregnation of the inner reactant was acidified with 1N acetic acid for gelation and was taken in straight tubes. This reactant on diffusion into the gel medium reacts with the inner reactant (H$_2$S). After a week’s time nucleation sites were observed.
References

36. Au-Pang, T., 'ir,icz~lriccSinicil XII (I 963).
40. R. M. Dabhi, M. J. Joshi, Dielectric studies of gel grown zinc tartrate crystals.


51. Silva, R.S.; Silva, J.T.T.; Rocha, V.R.; Cano, N.F.; Silva, A.C.A.; Dantas, N.O. Synthesis Process Controlled Of Semimagnetic Bi2–xMnxS3


