CHAPTER 6

Growth and study of gel grown crystals of Bismuth Tri-Sulphide $\text{Bi}_2\text{S}_3$

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CHAPTER 6

Growth and study of gel grown crystals of Bismuth Tri-

Sulphide Bi$_2$S$_3$

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CHAPTER 6
Growth and study of gel grown crystals of Bismuth Tri-Sulphide $\text{Bi}_2\text{S}_3$

6.1 Introduction:


A variety of crystals required for the purpose of research and application can be grown in silica gels. The gel medium prevents turbulence and being chemically inert, it provides a three-dimensional crucible which permits the reagents to diffuse at a desirable controlled rate. Its softness and uniform nature of constraining forces that it exerts upon the growing crystals encourages orderly growth (Patel and Venkateswara Rao 1978; Shitole and Saraf 2001).

The growth of crystals in gel at an ambient temperature, which are sparingly soluble in water, is a fascinating alternative to the techniques involving high temperature and expensive equipments (Sangawal and Patel 1974). During the last few years, successful application of gel growth technique has been demonstrated by the preparation of crystals of alkaline earth metal iodate (Joshi and Trivedi 1983). The gel growth technique appeared quite attractive for growing crystals of such compounds on account of its unique advantages in terms of crystals produced and the simplicity of process (Armington and O’Connor 1968; Blank and Brenner 1969; Blank et al 1969, Randive et al 1969; Blank 1973).
Crystals of iodate exhibit nonlinear optical properties (Kurtz and Perry 1968; Morosin et al 1973) and piezoelectric properties (Bach and Kuppers 1978). Nonlinear optical phenomenon have found a wide variety of applications in many areas of modern science, technology and engineering. The nonlinear devices find large applications in optical communication, image processing, and wave-guide coupling.

In recent years, few attempts have been made to study growth and characterization of Sulphide crystals in general and Bismuth Tri-Sulphide crystals in particular. However, there are no reports in the literature on the growth of these crystals by gel method. Hence, the growth of Bismuth Tri-Sulphide crystals by gel technique by single diffusion method is undertaken.

The present chapter reviews several aspects regarding the growth procedure of Bismuth Tri-Sulphide crystals, optimum growth conditions and the kinetics i.e. influence of different growth parameters to obtain optimization conditions for the growth of these crystals. This chapter also predicts the results obtained from the different techniques used for the characterization of gel grown crystals of Bismuth Tri-Sulphide.

6.2 Crystal growth:

The growth of Bismuth Tri-Sulphide crystals in gel media is based on the diffusion method. In the present work Single diffusion method is used for the growth of Bismuth Tri-Sulphide crystals in gel media.

6.2.1 Apparatus used:-

- Borosil glass test tubes
- Magnetic stirrer
- Digital pocket-sized pH meter (HANNA instrument)
- Burettes and pipettes
- Beakers
• Specific gravity bottle

6.2.2 Chemicals used:

• Commercial grade sodium Meta silicate \(\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}\)
• Acetic acid, AR grade, Loba chemicals (CH\(_3\)COOH)
• Bismuth chloride, AR grade, Loba chemicals (BiCl\(_3\))
• \(\text{H}_2\text{S}\) gas water solution.

6.2.3 Experimental procedure:

The chemical reaction method is used to grow the Bismuth Tri-Sulphide crystals. This method involves growing of crystals by allowing the reaction of solution of soluble salt Bismuth chloride and \(\text{H}_2\text{S}\) gas water solution by diffusion through a gel with subsequent nucleation and the crystal growth, which continues due to the gradual precipitation of insoluble product.

In the present work, single diffusion method was used. In actual procedure, 5cc, 2N acetic acid was taken in a small beaker, to which sodium Meta silicate solution of density 1.04 gm/cc was added drop by drop with constant stirring by using magnetic stirrer, till pH of the solution reaches a value of 4.40. A digital pocket sized pH meter of HANNA instruments is used for this purpose. Continuous stirring process avoids excessive ion concentration which otherwise causes premature local gelling and makes the final medium inhomogeneous and turbid. To this mixture, 5cc of Bismuth Chloride (one of the reactants) was added with constant stirring. The pH of the mixture was maintained at 4.4. Numbers of experiments were carried out in order to secure appropriate range of pH values which in turn gives a good gel allowing to growing good quality crystals.

The chemical reactions inside the gel can be expressed as

\[
2\text{XCl}_3 + 3\text{Y}_2\text{S} \rightarrow \text{X}_2\text{S}_3 + 6\text{YCl}
\]

Where \(\text{X}=\text{Bi}\) and \(\text{Y}=\text{H}\)
6.3 Results and discussions:

Crystals in Circular rings of little mm size were obtained. Study of kinetics of growth parameters reveals some interesting information. These types of Circular rings of crystals were reported by Liesegang and have been explained previously (Bolotov 1968). The result of this is a rounded crystal, but at first the basal planes (the plane of the sheet of the paper) are bent at random. These serves as the base for two-dimensional nuclei, which grow and fill up the recesses on the outer surface, thus giving crystal a circular shape.

Higher density gel sets more rapidly. It decreases nucleation density. Increased density reduces diffusivity of ions which in turn reduces growth rate (Andreazza et al. 1988). Lower density gel takes long time to set and can be easily fractured. Increase in aging of gel reduces number of nucleation centers and growth rate. The reason may be the formation of additional cross-linkages between siloxane chains with increasing gel age, resulting in a gradually reducing cell size (Halberstadt 1969). This, in turn, reduces nucleation centers, since many nuclei find themselves in cells of very small size, where further growth is not possible. Insufficient gel aging leads to the formation of fragile gel and often breaks at the time of addition of supernatant. The effect of pH on growth rate was studied by changing pH without a change of gel composition and concentration of reactants. With pH values less than 4, gel takes longer time to set and is unstable. There is no considerable effect on the quality of crystal. Higher pH value gel sets early, becomes turbid, and the size of crystal becomes smaller. As the pH increases, the gel structure changes from distinctly box-like network to a structure of loosely bound platelets, which appear to lack cross-linkages and the cellular nature becomes less distinct. Less concentration of reactants does not yield any crystals at all. High concentration yields crystals of smaller size with increased nucleation centers. Reported concentration of reactants when used yields smaller
spherulites near the gel interface with more number of nuclei. This may be due to high diffusion gradient near the gel interface. As the distance from the gel interface increases, number of nuclei reduces and size of spherulite increases due to smaller concentration gradient. Slow diffusion should lead to better nuclei, which because of their higher energy content should be less likely to reach their critical size. So the pH value 4.40 is well for growth of good quality crystals. The optimum growth conditions for various parameters were found and are reported in Table 6.1. 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.

Table 6.1: Optimum conditions for growth of Bismuth Tri-Sulphide crystals

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Bismuth Tri-Sulphide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of sodium meta silicate solution</td>
<td>1.04 g/cm³</td>
</tr>
<tr>
<td>Amount of 2N acetic acid</td>
<td>5ml</td>
</tr>
<tr>
<td>pH of the gel</td>
<td>4.40</td>
</tr>
<tr>
<td>Temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Concentration of BiCl₃</td>
<td>0.5 M</td>
</tr>
<tr>
<td>Concentration of H₂S gas water solution</td>
<td>-------</td>
</tr>
<tr>
<td>Gel setting time</td>
<td>13 days</td>
</tr>
<tr>
<td>Gel aging time</td>
<td>72 hours</td>
</tr>
<tr>
<td>Period of growth</td>
<td>31 days</td>
</tr>
</tbody>
</table>

6.4 Observations:-

On the quality of the crystals, various concentrations of reactants have different effects. Figure 6.1 shows Bismuth Tri-Sulphide crystals incorporated in the gel. Spherulites of Bismuth Tri-Sulphide crystals grown for these different concentrations of BiCl₃ ranging from 0.1 M to 1 M are shown in the figures 6.1. It is observed that as the concentration of Bismuth Tri-Sulphide increased from 0.1M to 1M, the size and the quality of the spherulites also goes on increasing. The crystals so formed are spherical in shape, opaque and
well isolated. Figure 6.2 shows few spherical Bismuth Tri-Sulphide crystals on a graph paper with their scaling.

Fig. 6.1 Crystals of Bismuth -Trisulphide inside the Test-tube.

Fig 6.2 Few Crystals of Bismuth-Trisulphide on graph paper.
6.5 Effect of various parameters on crystal growth:

Study of kinetics of growth parameters reveals some interesting information. Effect of concentration of reactants, gel density, pH of the gel, gel aging and concentration programming etc. was studied and is presented in this section with respect to the results obtained.

6.5.1 Effect of gel density:

The gels of different densities were obtained by mixing sodium Meta silicate solutions of specific gravity 1.03 to 1.06 with 2N acetic acid, keeping pH value constant. It was observed that as the gel density increases, transparency of the gel decreases. Gels with higher densities taken less gel setting time compared to the gels with lower densities. It may be noted that Well-defined and transparent single crystals were obtained with sodium Meta silicate density 1.04 gm/cc. On the other hand, gels with densities below 1.04 gm/cc taken longer time to set and still gels were not stable. Density of 1.03 gm/cc was the lower practical limit.

It is observed that the nucleation density decreases with increase in gel density. Table 6.2 shows the effect of density on number of nuclei formed. It has been graphically shown in Fig. 6.3. A greater gel density implies smaller pore size and poor communication among the pores and thus decreasing the nucleation density. Bechhold et al showed that diffusion coefficient becomes distinctly smaller as gel densities increase. There is no evidence that the diffusion constant of small atoms and ions is greatly influenced by the silica gel density as long as the density is low. Thus, the diffusion constants are not greatly influenced by the presence of dilute gel. In the present work, gel density of the value 1.04 gm/cc is the optimum condition for the growth of good quality crystals.
Table 6.2: Effect of gel density on nucleation density \([\text{pH} = 4.4, \text{feed solution H}_2\text{S water gas solution}]\)

<table>
<thead>
<tr>
<th>Test tube No.</th>
<th>Acetic acid IN (cc)</th>
<th>BiCl\textsubscript{3} incorporated in gel l.OM (cc)</th>
<th>Density of gel (gm/cc)</th>
<th>Number of nuclei formed</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>5</td>
<td>1.02</td>
<td>58</td>
<td>High nucleation density, very small sphere shaped crystals</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>5</td>
<td>1.03</td>
<td>52</td>
<td>Small sphere shaped crystals in ring form</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>5</td>
<td>1.04</td>
<td>44</td>
<td>Small gray coloured spheres near gel interface, in ring form</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>5</td>
<td>1.05</td>
<td>30</td>
<td>Small gray coloured in ring form</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
<td>1.06</td>
<td>24</td>
<td>Small gray coloured in ring form</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>5</td>
<td>1.07</td>
<td>18</td>
<td>Small gray coloured in ring form</td>
</tr>
</tbody>
</table>

Figure 6.3 Plot of gel density against nucleation density
6.5.2 Effect of pH of gel:

By changing the pH of gel without changing gel composition and concentration of reactants, the effect of pH on growth rate was studied.

Table 6.3: Effect of pH on gel [Aging period = 72 hrs, feed solution H₂S water gas solution]

<table>
<thead>
<tr>
<th>Test tube No.</th>
<th>Acetic acid 2N (cc)</th>
<th>BiCl₃ incorporated in gel 1.0M (cc)</th>
<th>Sodium metasilicate 1.04 (gm/cc)</th>
<th>pH of Mixture</th>
<th>Gel Setting Time (hours)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>5</td>
<td>17.5</td>
<td>2.0</td>
<td>-</td>
<td>Gel is not set</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>5</td>
<td>17.8</td>
<td>2.5</td>
<td>-</td>
<td>Gel is not set</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>5</td>
<td>18.2</td>
<td>3.0</td>
<td>-</td>
<td>Gel set in 18 days but still unstable</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>5</td>
<td>18.7</td>
<td>3.5</td>
<td>360</td>
<td>Cream coloured spherulites</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
<td>19.0</td>
<td>4.2</td>
<td>336</td>
<td>Spherulites less in number</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>5</td>
<td>19.5</td>
<td>4.4</td>
<td>312</td>
<td>Small spheres less in number</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>5</td>
<td>20.1</td>
<td>4.5</td>
<td>264</td>
<td>Small spheres</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>5</td>
<td>21.6</td>
<td>5.0</td>
<td>180</td>
<td>Small spheres</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>5</td>
<td>21.1</td>
<td>5.5</td>
<td>120</td>
<td>Very small crystals</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>5</td>
<td>21.6</td>
<td>6.0</td>
<td>96</td>
<td>Very small spherical crystals</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>5</td>
<td>22.5</td>
<td>6.5</td>
<td>48</td>
<td>small spheres with very low nucleation density</td>
</tr>
</tbody>
</table>

The pH value of gel was varied from 2 to 6. It was observed that gel of pH less than 4.0 took longer time to set and was unstable. There was no considerable effect of change in pH on the quality of crystals. Higher pH value gel sets early, becomes turbid, and the size of crystal becomes smaller. As pH increases, the gel structure changes from distinctly boxlike network to a structure.
of loosely bound platelets, which appears to lack cross-linkages and the cellular nature becomes less distinct. Number of nuclei also decreases and the crystals are not well defined, due to improper formation of cells at high pH values. Table 6.3 shows the effect of different pH values on the quality of crystals. Fig. 6.4 illustrates the graph of setting time versus pH of mixture. In the present work, pH value of 4.4 is the optimum condition for the growth of good quality crystals.

![Graph of pH against gel setting time](image)

**Figure 6.4 Plot of pH against gel setting time**

**6.5.3 Effect of gel aging:**

Gel aging plays an effective role on the growth of crystals as reported by Henisch et al. To investigate the effect of aging on gels, gels of same pH and density were allowed to age for various periods before adding the feed solution. It was found that the nucleation density decreases as the aging increases. Aging of gel reduces number of nucleation centers and growth rate. The reason may be the formation additional cross-linkages between siloxane chains with increasing gel age, resulting in a gradually diminishing cell size. This in turn reduces nucleation centers, since many nuclei find themselves in cells of very small size, where further growth is not possible. Insufficient gel aging leads to the formation of fragile gel and it often breaks at the time of addition of supernatant. The effect of gel aging
time on the number and the quality of crystals is as shown in the table 6.4. Figure 6.5 shows the graph of aging time in hours against the number of crystals.

**Table 6.4: Effect of gel aging time (pH = 4.4, feed solution H₂S water gas solution)**

<table>
<thead>
<tr>
<th>Test Tube No.</th>
<th>Acetic acid (cc)</th>
<th>BiCl₃ incorporated in gel 1.OM (cc)</th>
<th>Sodium meta silicate 1.04</th>
<th>Aging time (hours)</th>
<th>Number Of crystals</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>5</td>
<td>18</td>
<td>36</td>
<td>100</td>
<td>High nucleation density, very small crystals</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>5</td>
<td>18</td>
<td>48</td>
<td>92</td>
<td>Still High nucleation centre’s with same size as above</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>5</td>
<td>18</td>
<td>72</td>
<td>80</td>
<td>High nucleation, density, medium size as above</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>5</td>
<td>18</td>
<td>96</td>
<td>60</td>
<td>Small crystals near gel interface, tinny at the middle of the gel column.</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
<td>18</td>
<td>120</td>
<td>42</td>
<td>Nucleation density reduces, small and spherical</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>5</td>
<td>18</td>
<td>144</td>
<td>35</td>
<td>Less in number, smaller in size</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>5</td>
<td>18</td>
<td>168</td>
<td>24</td>
<td>Less in number, smaller in size</td>
</tr>
</tbody>
</table>

**Figure 6.5 Plot of gel aging time against nucleation density**

In the present work, aging of 72 hours was found suitable because it makes the gel neither dry or brittle nor fragile. The aim of reduction in nucleation centers can
also be achieved. Hence aging period of 72 hours is the optimum condition for the growth of good quality crystals.

**6.5.4 Effect of concentration of reactants:-**

The effects of concentration of feed solutions can be investigated by preparing the gel of the same pH and density. Feed solution of BiCl₃ of different concentrations and H₂S gas water solution as a supernant are used. [H₂S gas passed for fix time 6 to 8 hours ] Table 6.5 summarizes the effects of concentration of reactants on habit, quality, and size of single crystals.

**Table 6.5: Effect concentration of reactants on habit, quality and size of Bi₂S₃ 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>BiCl₃ 0.1 M; 5 ml</td>
<td>H₂S gas water solution</td>
<td>Smaller spherulites, less in number</td>
<td>Gray coloured, opaque</td>
</tr>
<tr>
<td>BiCl₃ 0.2 M; 5 ml</td>
<td>H₂S gas water solution</td>
<td>Smaller spherulites</td>
<td>Gray coloured, opaque</td>
</tr>
<tr>
<td>BiCl₃ 0.3 M; 5 ml</td>
<td>H₂S gas water solution</td>
<td>Spherulites of smaller size more in number</td>
<td>Gray coloured, opaque</td>
</tr>
<tr>
<td>BiCl₃ 0.5 M; 5 ml</td>
<td>H₂S gas water solution</td>
<td>Spheres more in number</td>
<td>Gray coloured, opaque</td>
</tr>
<tr>
<td>BiCl₃ 0.6 M; 5 ml</td>
<td>H₂S gas water solution</td>
<td>Spheres of medium size more in number</td>
<td>Whitish, Opaque</td>
</tr>
<tr>
<td>BiCl₃ 1.0 M; 5 ml</td>
<td>H₂S gas water solution</td>
<td>Larger spherulites, well isolated</td>
<td>Opaque, Gray coloured</td>
</tr>
</tbody>
</table>

Experiments were carried out by changing the solution of BiCl₃ of different molarities ranging from 0.1M to 1.0M was incorporated in gel and preparation i.e. pass H₂S gas in double distilled water for 7,8,10,11 and 12 hours was put over the set gels. It had been observed that the use of H₂S gas water solution and BiCl₃ yields better quality crystals, in terms of size and shape. Therefore, after getting
the optimized conditions, all experiments were carried out by incorporating 5 cc, 0.5 M BiCl₃ solution in gel and H₂S gas water solution as Supernatant.

6.5.5 Concentration programming:-

Once the optimum growth conditions for concentration of reactants are established, single diffusion experiments of concentration programming were carried out in order to observe the nucleation control phenomenon. Good H₂S gas water solution [passed H₂S gas for 6 to 8 hours] was prepared. After setting and sufficient aging of gel, 20 ml of H₂S gas water solution was slowly poured over the acidified gel. This feed solution was replaced by another equal volume feed solution in next 48 hours. The strength of feed solution was increased in quantity 20 to 25 ml. It was found that the nuclei previously formed, began to grow to their optimum size.

6.6 Characterization of gel grown crystals of mercuric iodate

6.6.1 Introduction:-

There are no perfect crystals in reality and all crystals grown by any technique contain some defects, impurities and in homogeneities. Most of the physical properties are sensitive to the deviation from ideality. Hence, characterization of the grown crystals is essential. The need for high quality crystals is increasing and only systematic characterization makes it possible for the crystal grower to optimize the growth parameters in order to obtain better crystals. The assessment of the physical and chemical perfection of materials is generally known as characterization.

Experimental techniques used to characterize Bismuth Tri-Sulphide crystals are already discussed in the chapter 3 in detail. This chapter deals with the results, which are obtained from the different techniques used for the characterization of gel grown single crystals of Bismuth Tri-Sulphide. The results of these observations have been described and discussed below.
6.6.2 X-ray diffractometry (XRD):

Every crystalline substance has a unique X-ray powder diffraction pattern from which a characteristic set of interplaner spacings (d) and relative intensities can be derived. Materials are identified from these values in conjunction with the JCPDS powder diffraction file. X-ray is today a widely used tool to determine crystal structures.

X-ray diffractogram of gel grown crystals of Bismuth trisulphide Bi$_2$S$_3$ was recorded at NCL PUNE with the help of “miniflex goniometer (1.5405 Å)" X-Ray diffractogram in the range of 0° to 70° was obtained and the scanning speed was kept 2° per minute also chart kept 2 cm per minute. Copper target and nickel filter were used from the powder diffraction data of Bismuth trisulphide shows Eighteen different peaks and corresponding d values & [h,k,l] values was computed by using computer program POWD [an interactive powder diffraction data interpretation and indexing program] The recorded X-Ray diffractogram is as shown in fig 6.6.

![Fig 6.6 X- Ray diffractogram of Bismuth-Trisulphide](image)
The Powder diffraction data for gel grown crystals is as shown in table –6.6. The observed values are very well match with calculated values from computer program and also match with JCPDS card No - 06 - 0333 of Bi$_2$S$_3$ observed peaks in diffractogram shows Bismuth-trisulphide crystals passes Rhombus or Orthorhombic structure is as shown in table 6.7

**Table 6.6 Powder diffraction data for gel grown crystals**

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>2 Theta</th>
<th>FWHM</th>
<th>d-value</th>
<th>Intensity</th>
<th>I/lo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.940</td>
<td>0.188</td>
<td>22.4066</td>
<td>357</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>12.060</td>
<td>0.447</td>
<td>7.3323</td>
<td>326</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>24.200</td>
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<tr>
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<td>0.400</td>
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<td>19</td>
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<tr>
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<td>1.9423</td>
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<td>32</td>
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<td>48</td>
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<tr>
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<td>0.353</td>
<td>1.3746</td>
<td>88</td>
<td>15</td>
</tr>
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</table>
Table 6.7 Calculated and observed values of d and h, k, l.

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<thead>
<tr>
<th>Peak No</th>
<th>Intensity</th>
<th>2 Theta in degree 2°</th>
<th>FWHM</th>
<th>Indices h k l</th>
<th>d spacing value(A˚)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Observed</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>3.940</td>
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<td>25.910</td>
<td>0.424</td>
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<tr>
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<td>48.440</td>
<td>48.508</td>
<td>0.376</td>
<td>0 6 0</td>
</tr>
<tr>
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<td>49.818</td>
<td>0.471</td>
<td>6 1 0</td>
</tr>
<tr>
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<td>42</td>
<td>53.240</td>
<td>53.276</td>
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<td>1 6 1</td>
</tr>
<tr>
<td>15</td>
<td>138</td>
<td>55.120</td>
<td>55.098</td>
<td>0.471</td>
<td>6 1 1</td>
</tr>
<tr>
<td>16</td>
<td>285</td>
<td>58.700</td>
<td>58.697</td>
<td>0.471</td>
<td>2 4 2</td>
</tr>
<tr>
<td>17</td>
<td>96</td>
<td>60.560</td>
<td>60.564</td>
<td>0.212</td>
<td>7 2 0</td>
</tr>
<tr>
<td>18</td>
<td>88</td>
<td>68.160</td>
<td>68.158</td>
<td>0.353</td>
<td>1 1 6</td>
</tr>
</tbody>
</table>

In Rhombus crystal structure the length of unit cells are different but the three axis are perpendicular to each other i.e. a ≠ b ≠ c & α = γ = β=90° as shown in table 6.8

Table 6.8 Calculated unit cell parameters

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Lattice parameters</th>
<th>Bismuth trisulphide Bi₂S₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>System</td>
<td>Rhombus or orthorhombic</td>
</tr>
<tr>
<td>2</td>
<td>a</td>
<td>11.136 A˚</td>
</tr>
<tr>
<td>3</td>
<td>b</td>
<td>11.256 A˚</td>
</tr>
<tr>
<td>4</td>
<td>c</td>
<td>3.968 A˚</td>
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<tr>
<td>5</td>
<td>α</td>
<td>90.18°</td>
</tr>
<tr>
<td>6</td>
<td>β</td>
<td>90.42°</td>
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<tr>
<td>7</td>
<td>γ</td>
<td>90.36°</td>
</tr>
<tr>
<td>8</td>
<td>v</td>
<td>496.84 ( A˚)³</td>
</tr>
</tbody>
</table>
Result and discussion
1) In rhombus or orthorhombic crystal structure the no. of different lattice is four and lattice symbol denoted by P, C, I and F cells.

2) Grain size determination of Bismuth trisulphide from XRD spectra. As seen from the XRD pattern each peak has got a finite width the grain size is determined by measuring the width of the line with highest intensity peak. The grain size is 0.3415nm. The grain size can be calculated by using formula.

Grain size $D = \frac{0.9 \lambda}{\beta \cos \theta}$

Where $\lambda$= wavelength = 1.54056 A˚

$\beta$ = Is full width of half maxima (FWHM) in radian=0.424radian

$D$ = grain size of crystal

$\theta$ = 16.77 degree Highest peak intensity at 600

D=0.9 x 1.54056 / 0.424 x Cos [16.77]

= 1.38645 / 0.424 x 0.9574 = 1.38645 / 0.4059

= 3.3457 A˚ = 0.3415 nm

6.6.3 Fourier Transform Infrared Spectroscopy (FTIR)

An FTIR spectrum of Bismuth Trisulphide (Bi$_2$S$_3$ of 1M and 0.5 M) crystals was recorded using SIMADZU Spectrometer at department of chemistry, university of Poona.

The FTIR Spectrum for a particular chemical compound is unique characteristics alone. Reflecting as it does the geometry. Band strength and atomic masses of the substance. Therefore an important use of FTIR is the Identification of unknown functional group present in the chemical compounds. The FTIR Spectra of Bismuth trisulphide (Bi$_2$S$_3$) is as shown in fig 6.7 the spectrum is scanned in region 4000 to 500 cm$^{-1}$ using SHIMADZU spectrometer at department of chemistry in University of Pune. The result of FTIR spectra of Bismuth trisulphide crystals with observed band and their assignment are shown in table (6.9)
Fig 6.7  FTIR Spectra of Bismuth Trisulphide (0.5M).

Table 6.9 FTIR spectra analysis of Bismuth Trisulphide (Bi$_2$S$_3$) crystals

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>IR Peaks (Spectrum) cm$^{-1}$</th>
<th>Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3662.94 to 3603.15</td>
<td>Broad, strong</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>2</td>
<td>3603.15 to 3064.99</td>
<td>Strong and broad</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>3</td>
<td>2860</td>
<td>Normal and weak</td>
<td>C-H stretching with high energy</td>
</tr>
<tr>
<td>4</td>
<td>1712.85</td>
<td>Strong, sharp</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>5</td>
<td>966.37 and 960.58</td>
<td>Strong, sharp</td>
<td>O-H out of plane stretching (olefinic)</td>
</tr>
<tr>
<td>6</td>
<td>806.27 and 800.49</td>
<td>Strong, sharp</td>
<td>C-H bond out of plane stretching</td>
</tr>
<tr>
<td>7</td>
<td>752.26 to 704.04</td>
<td>Weak and broad</td>
<td>C-O or C-C stretching out of plane vibration</td>
</tr>
<tr>
<td>8</td>
<td>462.93 to 428.21</td>
<td>Strong and sharp</td>
<td>Bismuth metal to Sulpher</td>
</tr>
</tbody>
</table>

A few of the prominent vibration modes are empirically assigned here. The bands around 3662.94 to 3603.15 cm$^{-1}$ attributed to asymmetric and
symmetric O-H stretching of water. The O-H stretching freq appeared between 3603.15 to 3064.99 cm\(^{-1}\) is probably due to stretching vibration of Hydroxyl group-H bonded may be due to Si-OH or O-H stretching of acetic acid. The weak band appearing at 2860 cm\(^{-1}\) can be attributed to C-H stretching of Alkyl group. It may be due to the present of impurity of Bismuth acetate.

The strong & sharp band appearing at 1712.85 cm\(^{-1}\) can be attributed stretching vibration of Acetyl carbonyl group \(\text{CH}_3-\text{C}^=\text{O}\) with C=O stretching. The frequency Band appearing at 966.37 to 960.58 cm\(^{-1}\) can be attributed to bending freq. of O-H group out of plane. (Olefinic) The freq band appearing at 806.27 to 800.49 cm\(^{-1}\) can be attributed to bending freq. of C-H group out of plane.

The freq. band appearing at 752.26 to 704.04 cm\(^{-1}\) can be attributed to stretching freq of C-O or C-C stretching out of plane. The freq band appearing at 462.93 to 428.21 can be attributed to metal Bismuth to Sulpher bond in same plane. The Crystal structure of Bismuth Trisulphide is as shown below.

![Fig 6.8 Crystal structure of Bismuth trisulphide](image)

### 6.6.4 Thermal Analysis or Thermal studies

The Thermograms were obtained with the help of Diamond TGA/DTA thermal analyzer available at National Chemical Laboratory (NCL), Pune 7. Recrystallization alumina sample holders were used and the heating rate was 30\(^0\) C/min. the weight of sample was 08.785 mg for TGA/DTA/DTG studies and
03.600 mg for DSC.

6.6.4.1 Thermal Gravimetric Analysis (TGA)

It was confirmed that the thermal decomposition of Bismuth Tri-Sulphide passes through an intermediate $2[\text{Bi}_2\text{S}_3\cdot\text{H}_2\text{O}]$ which is unstable and immediately decomposes to $\text{Bi}_2\text{O}_3$. It has a one stage course until $\text{Bi}_2\text{O}_3$ is obtained an intermediate $2[\text{Bi}_2\text{S}_3\cdot\text{H}_2\text{O}]$ is obtained in this process analogously as in the thermal decomposition of the alkaline earth Sulphides. However unlike $2[\text{Bi}_2\text{S}_3\cdot\text{H}_2\text{O}]$ immediately after it is obtained begins to decomposition to $\text{Bi}_2\text{O}_3$. Di-Hydrus Bismuth Tri-Sulphide decomposes at high temperature.

According to following reactions

\[
2 \,[\text{Bi}_2\text{S}_3\cdot\text{H}_2\text{O}] + 9\text{O}_2 \xrightarrow{37.271\text{ to } 102.271} [2\text{H}_2\text{O} \uparrow 2\text{SO}_2 \uparrow] \\
\text{Step I heating} \\
+ \xrightarrow{102.271\text{ to } 947.271} [4\text{SO}_2 \uparrow] \\
\text{Step II heating} \\
[2\text{Bi}_2\text{O}_3 \downarrow] \\
\text{Stable Residue + } \rightarrow [2\text{Bi}_2\text{O}_3 \downarrow] \text{ Stable}
\]

Fig 6.9 TGA curve of Bismuth Tri-Sulphide
Table 6.10 TGA data of Bismuth Tri-Sulphide

<table>
<thead>
<tr>
<th>Stages</th>
<th>Temperature (°C)</th>
<th>Observed weight loss %</th>
<th>Calculated weight loss %</th>
<th>Probable loss of molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>37.271 to 102.271</td>
<td>13.543 %</td>
<td>12.130 %</td>
<td>2 H₂O↑, 2SO₂↑</td>
</tr>
<tr>
<td>II</td>
<td>102.271 to 947.271</td>
<td>14.984 %</td>
<td>18.934 %</td>
<td>4SO₂↑</td>
</tr>
<tr>
<td></td>
<td>Total weight loss</td>
<td>28.527 %</td>
<td>31.064 %</td>
<td></td>
</tr>
<tr>
<td>Residue</td>
<td>Stable [2Bi₂O₃↓]</td>
<td>71.472 %</td>
<td>68.930 %</td>
<td>2 Bi₂O₃ ↓</td>
</tr>
</tbody>
</table>

**Observed Weight Loss:-**

1. 37.271 to 102.271

   99.748 – 86.205 = 13.543 %

2. 102.271 to 947.271

   86.205 – 71.221 = 14.984 %

**Calculated Weight Loss**

\[
2 \left[ \text{Bi}_2\text{S}_3\cdot\text{H}_2\text{O} \right] + 9\text{O}_2 \rightarrow \left[ 2 \text{H}_2\text{O}↑ + 2\text{SO}_2↑ \right]
\]

\[
2 \times 514 + 18 \times 2 + 18 \times 16 = 18 \times 2 + 2 \times 32 + 4 \times 16
\]

\[
= 1028 + 36 + 288 = 1352
\]

\[
= 164 \times 100/1352 = 12.130 \%
\]

\[
\rightarrow \left[ 4\text{SO}_2↑ \right]
\]

\[
= 4 \times 32 + 16 \times 8
\]

\[
= 128 + 128 = 256
\]

\[
= 256 \times 100/1352 = 18.934\%
\]

**Residue**

\[
2\text{Bi}_2\text{O}_3
\]

\[
= 4 \times 209 + 6 \times 16
\]
\[
\begin{align*}
&= 836 + 96 = 932 \\
&= 932 \times \frac{100}{1352} \\
&= 68.930
\end{align*}
\]

The TGA curve for Bismuth Tri-Sulphide gel grown crystals is as shown in fig 6.9. The TGA data collected from this curve and the theoretical values as calculated from molecular formula using the reaction are listed in table 6.10.

TGA data and curve of Bismuth Tri-Sulphide showed clearly two stages of decomposition. TGA curve did not show an appreciable weight changes in the temperature 0\(^\circ\)C to 37.271\(^\circ\)C indicating that the crystals of Bismuth Tri-Sulphide are thermally stable in this range. The crystals becomes thermally unstable from 37.271\(^\circ\)C.

1. The first stage of decomposition occurs in the temperature range 37.271 to 102.271 \(^\circ\)C in which observe weight loss of 13.543 % agree with calculated weight loss 12.130 %. This weight loss is attributed to loss of \([2 \text{H}_2\text{O} \uparrow + 2\text{SO}_2 \uparrow]\) and decomposition is in continuous manner.

2. The second stage of decomposition occurs in the temperature range 102.271 to 947.271\(^\circ\)C in which observed weight loss of 14.984 % nearly agree with calculated weight loss 18.934 %. Here observed weight loss appear to be less as compared with calculated can be attributed to incomplete decomposition of Bi\(_2\)S\(_3\). The further weight loss expected may be seen at still higher temperature up to which we could not proceed our experiment. This weight loss is attributed to loss of \([4\text{SO}_2 \uparrow]\) and decomposition is in continuous manner.

The remaining product finally turns into residue Bi\(_2\)O\(_3\) (Bismuth Oxide) is conformed at 947.271\(^\circ\)C the observed residue weight is 71.472 %. This is nearly agreement with calculated residual weight 68.930%. This confirms presents of Bismuth in grown crystals.
6.6.4.2 Differential Thermal Analysis (DTA)

The DTA curve for Bismuth Tri-Sulphide gel grown crystal is as shown in the fig 6.10 and DTA data collected from this curve is tabulated in table 6.11

![DTA curve of Bismuth Tri-Sulphide](image)

**Fig 6.10 DTA curve of Bismuth Tri-Sulphide**

**Table 6.11 DTA data of Bismuth Tri-Sulphide**

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Peak recorded</th>
<th>Nature</th>
<th>Peak height µV</th>
<th>On set c</th>
<th>Area (m J)</th>
<th>∆H (J/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>82.28 0 c</td>
<td>Endothermic</td>
<td>16.625</td>
<td>37.57 0 c</td>
<td>328.65</td>
<td>56.954</td>
</tr>
<tr>
<td>2</td>
<td>302.57 0 c</td>
<td>Endothermic</td>
<td>0.547</td>
<td>197.66 0 c</td>
<td>206.40</td>
<td>24.117</td>
</tr>
</tbody>
</table>

In DTA curve we can observe two endothermic peaks at 82.28 0 c and 302.57 0 c. However exothermic peak was not noticed in the DTA graph.

1. The endothermic peak at 82.28 0 c is due to the decomposition of Bismuth Tri-Sulphide losing [2H₂O↑+2SO₂↑] molecules means in the first stage of decomposition peak at 82.28 0 c is attributed to the loss of 2 water and 2SO₂ molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of 2 water and 2SO₂ molecules in TGA curve.
2. The second endothermic peak at 302.57 °C is due to the decomposition of compound and this peak in the second stage of decomposition is attributed to the loss of 4SO₂ molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of 4SO₂ molecules in the DTA curve.

Above 947.271 °C the reaction proceeds once finally residue Bi₂O₃ remains up to end of the analysis.

6.6.4.3 Differential Thermal Gravimetric (DTG) The DTG curve for Bismuth Tri-Sulphide gel grown crystal is as shown in the fig 6.11 and DTG data collected from this curve is tabulated in table 6.12

Table 6.12 DTG data of Bismuth Tri-Sulphide

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Peak</th>
<th>On set</th>
<th>Inflection point</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>73.33</td>
<td>46.66</td>
<td>63.73</td>
</tr>
<tr>
<td>2</td>
<td>183.33</td>
<td>102.271</td>
<td>121.33</td>
</tr>
</tbody>
</table>

Fig 6.11 DTG curve of Bismuth Tri-Sulphide
1. The exothermic peak at 73.33 °C is due to the decomposition of Bismuth Tri-Sulphide losing 2 water and 2SO₂ molecules in the first stage of decomposition. This exothermic peak observed in the DTG curve indicates that the reaction starts at 46.66 °C and the inflection occurs at 63.73 °C. The peak observed in DTG curve corresponds to the weight loss of 2 water and 2SO₂ molecules in TGA curve.

2. The endothermic peak at 183.33 °C is due to the decomposition of compound and this peak in second stage of decomposition is attributed to the loss of 4SO₂ molecules. This endothermic peak observed in the DTG curve indicates that the reaction starts at 102.271 °C and the inflection occurs at 121.33 °C. The peak observation in DTG curve corresponds to the weight loss of 4SO₂ molecules in TGA curve.

Above 947.271 °C the reaction proceeds once finally stable residue Bi₂O₃ remains up to end of the analysis.

6.6.4.4 Differential Scanning Calorimetry (DSC)

The DSC curve for Bismuth Tri-Sulphide gel grown crystal is as shown in the fig 6.12 and DSC data collected from this curve is tabulated in table 6.13.

![Fig 6.12 DSC curve of Bismuth Tri-Sulphide](image)
Table 6.13 DSC data of Bismuth Tri-Sulphide

<table>
<thead>
<tr>
<th>Sample [Bi₂S₃]</th>
<th>Weight of sample</th>
<th>Change in Enthalpy (ΔH)</th>
<th>Transition temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth Tri-Sulphide</td>
<td>3.600 mg</td>
<td>0.0775 KJ/mole</td>
<td>66.86 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0149 KJ/mole</td>
<td>237.73 °C</td>
</tr>
</tbody>
</table>

There are two stages of DSC curves under study as follows

**Stage I**
1. The initiation temperature is 34.22 °C and equilibrium temperature is 118.33 °C at 34.22 °C (initiation temperature) initiation of phase change starts and is completed at peak endo-down temperature of 66.86 °C transition temperature [peak height is 1.2673 mW]. The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 118.33 °C.

2. Area under the curve is 279.126 mJ.

3. Heat of transition ΔH i.e. enthalpy change of transition is 77.5350 J/g which is 0.0775 KJ/mole since molecular weight is 1.000 g/mole

   \[ \Delta H_{\text{tran}} = \Delta H_{\text{F}} \text{ of phase transformation} = 0.0775 \text{ KJ/mole} \]

   where ΔHF is enthalpy change of new phase formation or it is called heat of phase formation.

**Stage II**
1. The initiation temperature is 177.00 °C and equilibrium temperature is 343.89 °C at 177.00 °C (initiation temperature) peak height is 0.0887 mW initiation of phase change starts and is completed at peak endo-down temperature of 273.73 °C (transition temperature). The temperature at which the sample and the reference come to the thermal equilibrium by thermal
diffusion appears to be at 343.89 °C

2). Area under the curve is 53.717 mJ.

3). Heat of transition $\Delta H$ i.e. enthalpy change of transition is 14.9213 J/g which is 0.0149 KJ/mole since molecular weight is 1.000 g/mole

$\Delta H_{\text{tran}} = \Delta H_{\text{i.e.}}$ i.e. heat of phase transformation is also 0.0149 KJ/mole where $\Delta H_{\text{F}}$ is enthalpy change of new phase formation or it is called heat of phase formation.

**6.6.5 Chemical Analysis**

**6.6.5.1 Gravimetric Chemical Analyses of $\text{Bi}_2\text{S}_3$ Bismuth Trisulphide**

**Estimate of Bismuth (Bi) From $\text{Bi}_2\text{S}_3$**

Bismuth is estimated gravimetrically using dil HCl by Homogenous precipitation. Accurately weighed 0.1gm of sample in powder form was dissolved in small quantity of double distilled water. Few drops of HCl (Hydrochloric Acid) were added to dissolve the powder completely. A volume of solution was accurately made equal to 100 ml by adding double distill water to it. Sodium Acetate and 2N Acitic acid ($\text{CH}_3\text{COOH}$) were added to this solution so as to make the pH between 4.40 to 4.60.

This solution was then heated for 40-45 minutes in water bath. The solution was filtered through Dr. Watts filter paper and washed several times with warm distilled water. There was remaining residue of $\text{BiCl}_3$ on the filter paper. The residue was cooled and dried in oven. Weight of $\text{BiCl}_3$ residue obtained was 0.1187gm.

- Weight of sample = 0.1 gm
- Weight of filter paper + precipitate = 1.1587 gm
- Weight of filter paper = 1.04 gm
- Weight of the residue = 0.1187 gm

1. **Theoretical percentage of Bismuth (Bi)** Theoretically $\text{Bi}_2\text{S}_3$ having molecular
weight = 514.20 gm/mole. The amount of Bismuth is 208.98 gm/mole for Bi₂, 208.98 X 2 = 417.96 %

% of Bismuth = 417.96x100/514.20
= 41796/514.20 = 81.28 %

Thus theoretically in 100 gm of Bi₂S₃ there is 81.28% of Bismuth.

2. Practicial Percentage of Bismuth (Bi):- Practically in BiCl₃ having molecular weight 315.17gm/mole. The amount of Bismuth in BiCl₃ is 208.98 gm/mole.

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

Therefore In 0.1187 gm of BiCl₃ residue.

Amount of Bismuth (Bi) = 208.98 X 0.1187/315.17
= 24.8227/315.17
=0.07876 gm

Thus amount of Bismuth in Bismuth Chloride is practically 0.07876 gm. Since in 0.1 gm of sample powder there is 0.07876 gm of Bismuth

% of Bi =0.07876x100/0.1
=7.876/0.1 =78.76%

Thus practically in 0.1 gm of Bi₂S₃ sample there is 78.76 % Bismuth.

Estimation of Sulphur:-

Accurately weighed 0.1 gm of sample in powder form was dissolved in small quantity of double distilled water. Few drops of Nitric Acid were added while heating to dissolve the powder completely. Few ml of dilute silver Nitrate (AgNO₃) was then added. The mixture was heated in water bath until the precipitate was obtained. It was allowed to stand for some time. Precipitate was then filtered through Dr. Watt’s filter paper and washed several times with warm distilled water. The residue obtained in this procedure was weighed after heating it in oven along with the fitter paper.
• Weight of sample = 0.1 gm
• Weight of filter paper with precipitate = 1.1703 gm
• Weight of filter paper = 1.04 gm
• Weight of residue = 0.1303 gm

**Theoretical percentage of Sulpher (S)**

Theoretically in $\text{Bi}_2\text{S}_3$ having molecular weight 514.20 gm/mole the amount of Sulpher (S) is 32.06 gm/mole for $\text{S}_3$ 32.06x3 = 96.18 gm/mole

Percentage of Sulpher (S) = $\frac{96.18 \times 100}{514.20} = \frac{9618}{514.20} = 18.70\%$

Thus theoretically in 100 gm of $\text{Bi}_2\text{S}_3$ there is 18.70% Sulpher (S)

**Practical percentage of Sulpher (S)**

Practically in $\text{Ag}_2\text{S}$ having molecular weight 247.86 gm/mole.
For $3\text{Ag}_2\text{S} = 247.86 \times 3 = 743.58$ gm/mole and amount of Sulpher is 32.06 gm/mole. For $\text{S}_3 = 32.06 \times 3 = 96.18$ gm/mole.

$\text{Bi}_2\text{S}_3 + 6\text{AgNO}_3 \rightarrow 2\text{Bi(NO}_3)_3 + 3\text{Ag}_2\text{S}$

% of Sulpher (S) = $\frac{96.18 \times 0.1303}{743.58} = \frac{12.5367}{743.58} = 0.01686$ gm

Thus amount of Sulpher in $3\text{Ag}_2\text{S}$ is practically = 0.01686 gm since in 0.1gm of sample powder of there is 0.01686 gm of Sulpher (S).

Percentage of Sulpher (S) = $\frac{0.01686 \times 100}{0.1} = \frac{1.686}{0.1} = 16.86\%$

Thus practically in 0.1 gm of $\text{Bi}_2\text{S}_3$ sample there is 16.86 % of Sulpher (S)

Thus result of chemical analysis is as shown in the table 6.14 from table we observed that the experimental values of Bismuth (Bi) and Sulpher (S) are in good agreement with the theoretical ones. (Values)
Table 6.14 Result of chemical Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Theoretical values (%)</th>
<th>Practical values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth</td>
<td>81.28</td>
<td>78.76</td>
</tr>
<tr>
<td>Sulpher</td>
<td>18.70</td>
<td>16.86</td>
</tr>
<tr>
<td></td>
<td>99.98</td>
<td>95.62</td>
</tr>
</tbody>
</table>

6.6.5.2 Volumetric / Titrimetric Analysis of Bi$_2$S$_3$ Bismuth trisulphide

**Estimation / Determination of Bismuth from Bi$_2$S$_3$ :-**

Bismuth trisulphide Bi$_2$S$_3$ solution was quantitatively (volumetrically) estimated with standard EDTA solution. Take 0.5 gm Bismuth trisulphide crystals dissolved in small quantity of double distilled water. Add few drops of concentrated HCl to dissolved sample powder completely. The volume of solution becomes 250 ml by adding double distilled water. Then 10 ml solution pipetted in titration flask. Add Hexamine buffer till the PH is 4.40. Add 2 or 3 drops of Xylenol orange as an indicator the solution become red then titrate it with standard EDTA solution until the color changes from red to yellow.

Reading of titration = 7.65 ml

Practically 1 mole EDTA = 1 mole of Bi$^{+++}$

In 1000 ml, 1 mole EDTA Solution contain = 208.98 gm of Bismuth hence 0.01 mole EDTA solution, Contain

% of Bismuth = 208.98x0.01x7.65/1000
               = 2.0898x7.65/1000
               = 15.9869/1000
               = 0.01598

As 10 ml diluted solution = 0.01598 gm of Bismuth.

250 ml diluted solution contain
0.5 gm of Bismuth trisulphide = 0.3996
For 100 gm of Bismuth trisulphide
\[
\text{= 0.3996x100/0.5} \\
\text{=39.96/0.5} \\
\text{= 79.93%}
\]
Thus practically in Bi$_2$S$_3$ there is 79.93% of Bismuth.

Theoretically in Bismuth trisulphide the Bismuth = 81.28%
i. e. Bi$_2$S$_3$ have mole wt = 514.20 gm/mole amount of Bismuth = 208.98 gm/mole
\[
\text{hence for Bi$_2$ = 208.98x2 = 417.96 gm} \\
\text{\% of Bismuth =417.96x100/514.20} \\
\text{= 41796/514.20} \\
\text{= 81.20 %}
\]
Thus theoretically in Bi2S3 there is 81.20% of Bismuth.

**Estimation / Determination of Sulpher from Bi$_2$S$_3$ :-**

Bismuth trisulphide Bi$_2$S$_3$ solution was quantitatively i.e. Volumetrically / Titrmetrically Estimated with standard 0.05M Iodine solution.

Take 0.5 gm Bismuth trisulphide crystals dissolved in small quantity of double distilled water. Add few drops concentrated HCl to dissolve the sample powder completely. The volume of solution becomes 250 ml by Adding double distilled water. Then 10ml solution pipetted in titration flask Add hexamine buffer till the pH is 4.40 Add 2 or 3 drops of starch as an indicator. The solution becomes Blue. Then titrate it with 0.05M standard iodine solution until the color changes from Blue colorless.

\[
\text{Reading of titration = 3.80 ml}
\]
Theoretically in Bismuth trisulphide having Mole wt = 524.20 gm

Amount of Sulpher = 32.06

For S\textsubscript{3} = 32.06x3 = 96.18

For Sulpher = 96.18x100/514.20 = 18.70 %

Theoretically in 100 gm of Bi\textsubscript{2}S\textsubscript{3} there is 18.70 % of Sulpher.

Practically 1 mole of Iodine = 1 mole of Sulpher \text{S}^-$

In 1000 ml contain, 1 ml of Iodine 96.18 gm Sulpher

Hence 0.01 Iodine Contain = 96.18x0.01x3.80/1000

= 3.6548/1000 = 0.003652

As 10 ml diluted solution = 0.003652 gm of Sulpher.

Hence 250 ml diluted solution contain = 0.003652x250/10

= 0.9131/10

= 0.09131

0.5 gm of Bismuth Tri-Sulphide = 0.0931.

Hence 100 gm of Bismuth trisulphide = 0.09131x100/0.5

= 9.13/0.5

= 18.26%

Practically 0.5 gm of Bi\textsubscript{2}S\textsubscript{3} sample there is 18.26% of Sulpher. From table we observed that Experimental values by volumetric analysis match with theoretical values.

**Table 6.15 Result of volumetric analysis for Bi\textsubscript{2}S\textsubscript{3}**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Element</th>
<th>Theoretical value (%)</th>
<th>Practical Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bismuth</td>
<td>81.28</td>
<td>79.93</td>
</tr>
<tr>
<td>2</td>
<td>Sulpher</td>
<td>18.70</td>
<td>18.26</td>
</tr>
</tbody>
</table>

99.98  97.19
6.6.5.3 Specific gravity of Bismuth Trisulphide Bi$_2$S$_3$

Specific gravity -- specific gravity may be defined as the ratio of mass of substance to the mass of an equal volume of other substance taken as standard. Example for Bi$_2$S$_3$ water may be standard.

Take 0.257 gm of Bismuth Trisulphide Bi$_2$S$_3$ powder dissolve it with small quantity of double distilled water. Add few drops of HCl to dissolve powder completely. A volume of solution is accurately made 50 ml. this is solution of 0.01 m.

\[
\text{As \[ \frac{M \times Q}{1000} \] where \ M= \text{molecular weight}}
\]

\[
\text{C = concentration}
\]

\[
\text{Q= quantity}
\]

\[
= 514.20 \times 0.01 \times 50/1000
\]

\[
= 0.257 \text{ gm}
\]

Take 25 ml solution of Bi$_2$S$_3$ to determine specific gravity

[25 ml sp. Gravity Bottle is used]

* Weight of empty sp gravity bottle \( w_1 = 13.80 \text{ gm} \)

* Weight of sp gravity bottle + water \( w_2 = 44.40 \text{ gm} \)

* Weight of bottle + liquid [solution of Bi$_2$S$_3$] \( w_3 = 230.29 \text{ gm} \)

* Weight of liquid solution of Bi(lo$_3$)$_3$

\[
W_4 = w_3 - w_1 \quad W_4 = 216.49 \text{ gm}
\]

* Weight of water \( w_5 = w_2 - w_1 \quad w_5 = 30.60 \text{ gm} \)

* Density of water \( w_6 = 0.9979 \text{ gm/m} \)

Sp gravity of Liquid Bi$_2$S$_3$

\[
\frac{w_4}{w_5} = \frac{\text{Weight of liquid}}{\text{Weight of water}} \times \text{density of water}
\]

\[
W_4/W_5 = 216.49 \times 0.9979/30.60
\]
\[
\text{Sp gravity of Bi}_2\text{S}_3 \text{ Practically is } 7.07 \text{ gm/cm}^3 \text{ is well match with Theoretical value 7.39 gm/cm}^3
\]

**6.6.6 EDAX: - Energy Dispersive Analysis by X rays (EDAX).**

Elemental Dispersive Analysis by X rays (EDAX) is used for the quantitative analysis. In the present work elemental analysis of gel grown Bismuth Tri Sulphide, crystals was carried out at the NCL National Chemical Laboratory Pune fig 6.13 shows EDAX spectrum of Bismuth Tri Sulphide Table 6.16 shows the values of elemental content of the crystals as measured by the EDAX technique and the theoretical calculations from molecular formula. From the table it is clear that values of (wt %) and (At %) of Bi\(_2\)S\(_3\) in grown crystals measured EDAX are close to with the estimated values calculated from molecular formula.

![EDAX spectrum of Bi\(_2\)S\(_3\)](image)

**Fig 6.13 Energy Dispersive Spectrum of Bi\(_2\)S\(_3\)**
Table 6.16 Calculation of elemental analysis of gel grown Bismuth Tri Sulphide

<table>
<thead>
<tr>
<th>Element</th>
<th>Content measured by EDAX</th>
<th>Content as calculated from molecular formula Bi$_2$S$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt %</td>
<td>At %</td>
</tr>
<tr>
<td>Bismuth</td>
<td>79.87 %</td>
<td>73.88</td>
</tr>
<tr>
<td>Sulphur</td>
<td>17.56 %</td>
<td>24.57</td>
</tr>
</tbody>
</table>

97.4 3 99.98

6.6.7 SEM: - Scanning Electron Microscopy of Bi$_2$S$_3$

In present work Scanning Electron Microscopy of powdered sample of gel grown Bismuth Tri Sulphide crystals was carried at NCL (National Chemical Laboratory) Pune and the successive photographs were taken at the magnification of 0.5, 1.50, 2.00, 5.00 & 10.00 KX all the photographs were taken at common width 9 mm and EHT magnification 20 KV. And represented as Fig (6.14.1) to (6.14.6) shows SEM images of the powdered sample of Bismuth Tri Sulphide. Fig (6.14.1) shows the part of crystals of Bismuth Tri Sulphide. It is observed that the face is neither dull nor very bright but it has some bright region at the left half of the fig. whole the surface is covered with figs of different shapes & size. Some of the figs are approximately seen to be triangular & pentagonal.

The edges triangle & pentagonal are clearly seen in some cases but in some cases they are not so cleared. In general the shape is clearly seen, these figs are randomly oriented on the whole surface In fig 6.14.1 a small region labeled as small (a), at 0.5 KX is shown as (A) in fig 6.14.2. At 1.50 KX the magnification all three fig in A region are pentagonal on minute observation fig (X) in region (A) is perfectly pentagonal with well defined boundaries while the remaining two figs does not have well defined start boundaries.
Fig (6.14.1) to (6.14.6) shows SEM images of the powdered sample of Bismuth Tri Sulphide.

In fig 6.14.3 shows different region with higher magnification the edges of figs have in general marked boundaries because of higher magnification attachment of micro crystals are individual grains is clearly seen. The region
marked by (B) in fig 6.14.3 shows attachment of many micro crystals. If we compare region (B), (C) & (D) on fig 6.14.3 region B has more attachment of micro crystals than region (C), also by comparing region (C) & (D) region (C) has maximum micro crystals than (D) means we compare the attachment of micro crystals in region (B), (C) & (D) simultaneously we may conclude that it is due to different growth conditions on the same face. The growth rate in the region (B) is higher as compare to region (C) & the growth rate is controlled in the region (D).

This supports the fact that the growth conditions are varying on different parts of same face of the crystals. The same thing of growth conditions are observed in region (E) of fig 6.14.4. In region (E) one defined hexagon marked by (F) is seen to be in regular shape of hexagon having marked boundary and size of equal length i.e. from fig 6.14.4 shows controlled growth condition as attachment of micro crystals in different part of fig is less. Whereas attachment of micro crystals is more in different part of fig 6.14.5 i.e. Region shown in fig 6.14.4 have controlled condition as compare to fig 6.14.5. If fig 6.14.6 is observed it indicates well defined some pentagon with no attachment of micro crystals i.e. it confirms the controlled growth conditions.

6.6.8 MAGNETIC SUCCEPCTIBILITY: -

In present work Magnetic Susceptibility of powdered sample of gel grown Bismuth Tri-Sulphide crystals was carried out at Department of Physical Science, N.M.U. Jalgaon.

Observations:-

A. Weight of empty holder + Holder Assembly (test tube) without magnetic field = 4.595 gm

B. Weight of empty holder + Holder Assembly (test tube) + sample powder without magnetic field = 4.615 gm
### Observation Table: - 6.17 MAGNETIC SUCCEPTIBILITY of Bi₂S₃

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Current in A</th>
<th>Magnetic Field (H) Gauss</th>
<th>Weight of sample in gm</th>
<th>Difference in wt m</th>
<th>$\chi m \times 10^{-6}$ cm³ mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>4.615</td>
<td>----</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>172</td>
<td>4.617</td>
<td>- 0.002</td>
<td>- 0.05385</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>366</td>
<td>4.617</td>
<td>- 0.002</td>
<td>- 0.01189</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>524</td>
<td>4.617</td>
<td>- 0.002</td>
<td>- 0.005802</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>703</td>
<td>4.616</td>
<td>- 0.001</td>
<td>- 0.001611</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>868</td>
<td>4.616</td>
<td>- 0.001</td>
<td>- 0.001057</td>
</tr>
<tr>
<td>7</td>
<td>1.2</td>
<td>1044</td>
<td>4.614</td>
<td>+ 0.001</td>
<td>+ 0.0007309</td>
</tr>
<tr>
<td>8</td>
<td>1.4</td>
<td>1187</td>
<td>4.614</td>
<td>+ 0.001</td>
<td>0.0005654</td>
</tr>
<tr>
<td>9</td>
<td>1.6</td>
<td>1354</td>
<td>4.614</td>
<td>+ 0.001</td>
<td>0.0004345</td>
</tr>
<tr>
<td>10</td>
<td>1.8</td>
<td>1543</td>
<td>4.613</td>
<td>+ 0.002</td>
<td>0.0006692</td>
</tr>
<tr>
<td>11</td>
<td>2.0</td>
<td>1720</td>
<td>4.613</td>
<td>+ 0.002</td>
<td>0.0003885</td>
</tr>
</tbody>
</table>

C. Weight of sample powder $M = b - a = 4.615 - 4.595 = 0.020$ gm
- $m =$ Change in weight (m) of sample powder with magnetic field
  - $m = 0.002$ gm
- $L =$ Height of sample powder in test tube = 1.1 cm
- $\rho =$ Density of specimen = 7.39 g/cm³
- $H =$ Applied magnetic field = 366 gauss (for 0.4 A current)
- $M =$ Weight of specimen examine = 0.020 gm
- $g =$ Acceleration due to gravity = 980 cm/sec²

**Formula:** - The magnetic susceptibility ($\chi$) of Bismuth Tri Sulphide (Bi₂S₃) powder is given by relation. \[ \chi = 2mg\rho/MH^2 \]

\[ = 2 \times (-0.002) \times 980 \times 1.1 \times 7.39 / 0.020 \times (366)^2 \]
\[ \chi = -0.01189 = -118 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1} \]

Fig 6.15. Graph of Magnetic Field (H) Gauss V/s \( \chi_m \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1} \)

6.6.9 ELECTRICAL CONDUCTIVITY of BISMUTH TRI SULPHIDE Bi2S3

In present work Electrical Conductivity of powdered sample of gel grown Bismuth Tri-Sulphide crystals was carried at Department of Chemical Science, N.M.U. Jalgaon.

OBSERVATIONS :-
1) Height / thickness of pallet = 0.536 cm
2) Diameter of the pallet = 0.942 cm
3) Radius of pallet = \( r = 0.471 \text{ cm} = \frac{d}{2} \)
4) Voltage = 0.50 mv (constant)

\[ K = \frac{I}{RA} \quad K = \frac{I}{R\pi r^2} \quad (\text{since } A = \pi r^2) \quad \text{I} = 0.536 \text{ cm} = 5.36 \times 10^{-4} \text{ m} \]
\[ r = 0.471 \text{ cm} = 4.71 \times 10^{-4} \text{ m} \]

\[ K = 5.36 \times 10^{-4} / R \times 3.142 \times (4.71 \times 10^{-4})^2 \]
\[ K = 5.36 \times 10^{-4} / R \times 3.142 \times (4.71)^2 \times 10^{-8} \]
\[ K = 5.36 / R \times 3.142 \times (4.71)^2 \times 10^{-4} \]
\[ K = 5.36 \times 10^4 / R \times 3.142 \times 22.18 \quad K = 5.36 \times 10^4 / R \times 69.702 \]
\[ K = 0.07690 \times 10^4 / R \quad K = 7.6901 \times 10^3 / R \quad K = 769.01 / R \]
\[ K = 415.27 \text{ mho/cm} \]
### Table: - 6.18 ELECTRICAL CONDUCTIVITY of BISMUTH TRI SULPHIDE Bi$_2$S$_3$

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Temp T °k</th>
<th>1x10^-4</th>
<th>Current in A I x 10^-4</th>
<th>Resistance R in Ω</th>
<th>Conductivity in mho/cm K x 10^-4</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>423</td>
<td>23.64</td>
<td>0.28 = 2.8 x 10^-4</td>
<td>0.17857</td>
<td>430.64</td>
<td>2.63411437</td>
</tr>
<tr>
<td>2</td>
<td>418</td>
<td>23.92</td>
<td>0.28 = 2.8 x 10^-4</td>
<td>0.17857</td>
<td>430.64</td>
<td>2.63411437</td>
</tr>
<tr>
<td>3</td>
<td>413</td>
<td>24.21</td>
<td>0.27 = 2.7 x 10^-4</td>
<td>0.18518</td>
<td>415.27</td>
<td>2.61833056</td>
</tr>
<tr>
<td>4</td>
<td>408</td>
<td>24.50</td>
<td>0.26 = 2.6 x 10^-4</td>
<td>0.19230</td>
<td>399.9</td>
<td>2.6019514</td>
</tr>
<tr>
<td>5</td>
<td>403</td>
<td>24.81</td>
<td>0.23 = 2.3 x 10^-4</td>
<td>0.21739</td>
<td>353.74</td>
<td>2.54868417</td>
</tr>
<tr>
<td>6</td>
<td>398</td>
<td>25.12</td>
<td>0.23 = 2.3 x 10^-4</td>
<td>0.21739</td>
<td>353.74</td>
<td>2.54868417</td>
</tr>
<tr>
<td>7</td>
<td>393</td>
<td>25.44</td>
<td>0.20 = 2.0 x 10^-4</td>
<td>0.25000</td>
<td>307.6</td>
<td>2.48798633</td>
</tr>
<tr>
<td>8</td>
<td>388</td>
<td>25.77</td>
<td>0.19 = 1.9 x 10^-4</td>
<td>0.26315</td>
<td>292.33</td>
<td>2.46587339</td>
</tr>
<tr>
<td>9</td>
<td>383</td>
<td>26.10</td>
<td>0.19 = 1.9 x 10^-4</td>
<td>0.26315</td>
<td>292.33</td>
<td>2.46587339</td>
</tr>
<tr>
<td>10</td>
<td>378</td>
<td>26.44</td>
<td>0.18 = 1.8 x 10^-4</td>
<td>0.27777</td>
<td>276.85</td>
<td>2.44224453</td>
</tr>
<tr>
<td>11</td>
<td>373</td>
<td>26.80</td>
<td>0.16 = 2.1 x 10^-4</td>
<td>0.31250</td>
<td>246.08</td>
<td>2.39107632</td>
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<td>12</td>
<td>368</td>
<td>27.17</td>
<td>0.16 = 2.1 x 10^-4</td>
<td>0.31250</td>
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<tr>
<td>13</td>
<td>363</td>
<td>27.45</td>
<td>0.15 = 1.5 x 10^-4</td>
<td>0.33333</td>
<td>230.7</td>
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<tr>
<td>14</td>
<td>358</td>
<td>27.93</td>
<td>0.14 = 1.4 x 10^-4</td>
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<td>215.32</td>
<td>2.33308437</td>
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<td>15</td>
<td>353</td>
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<td>0.13 = 1.3 x 10^-4</td>
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<td>2.30089969</td>
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<tr>
<td>16</td>
<td>348</td>
<td>28.73</td>
<td>0.12 = 1.2 x 10^-4</td>
<td>0.41616</td>
<td>184.78</td>
<td>2.26665496</td>
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<tr>
<td>17</td>
<td>343</td>
<td>29.15</td>
<td>0.12 = 1.2 x 10^-4</td>
<td>0.41616</td>
<td>184.78</td>
<td>2.26665496</td>
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<tr>
<td>18</td>
<td>338</td>
<td>29.58</td>
<td>0.11 = 1.1 x 10^-4</td>
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<td>169.18</td>
<td>2.22834902</td>
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<td>19</td>
<td>333</td>
<td>30.03</td>
<td>0.09 = 0.9 x 10^-4</td>
<td>0.55555</td>
<td>138.42</td>
<td>2.14119884</td>
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<tr>
<td>20</td>
<td>328</td>
<td>30.48</td>
<td>0.09 = 0.9 x 10^-4</td>
<td>0.55555</td>
<td>138.42</td>
<td>2.14119884</td>
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<tr>
<td>21</td>
<td>323</td>
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<td>0.08 = 0.8 x 10^-4</td>
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<td>22</td>
<td>318</td>
<td>31.44</td>
<td>0.07 = 0.7 x 10^-4</td>
<td>0.71428</td>
<td>107.66</td>
<td>2.03205438</td>
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<tr>
<td>23</td>
<td>313</td>
<td>31.94</td>
<td>0.07 = 0.7 x 10^-4</td>
<td>0.71428</td>
<td>107.66</td>
<td>2.03205438</td>
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<td>24</td>
<td>308</td>
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<td>0.04 = 0.4 x 10^-4</td>
<td>12.50000</td>
<td>61.52</td>
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</table>

**Calculations :-**

1) \[ I = 0.28 \text{ mA} = 2.8 \times 10^{-4} \text{ A} \]

\[
V = 0.5 \text{ mV} = 5 \times 10^{-4} \text{ V} \\
R = V/I = 5 \times 10^{-4} / 2.8 \times 10^{-4} = 1.7857 \Omega \\
K = 769.01 / R = 769.01 / 1.7857 \\
K = 4.3064 \times 100 \]

\[
K = 430.64 \text{ mho/cm} \\

2) \[ I = 0.27 \text{ mA} = 2.7 \times 10^{-4} \text{ A} \]

\[
V = 0.5 \text{ mV} = 5 \times 10^{-4} \text{ V} \\
R = V/I = 5 \times 10^{-4} / 2.7 \times 10^{-4} = 1.8518 \Omega \\

273
\[ K = 769.01 \div R = 769.01 \div 1.8518 \]
\[ K = 4.1527 \times 100 \quad K = 415.27 \text{ mho/cm} \]

**Fig 6.16 Graph of Temp T °k V/s Log K**

6.7 Conclusions:

1. Gel growth technique is suitable for growing crystals of Bismuth-Trisulphide.
2. Different habits of Bismuth trisulphide crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants etc.
3. Well known Liesegang phenomenon is observed in the growth of Bismuth-Trisulphide crystals.
4. Unit cell parameter values nearly match with the reported ones and the structure of Bismuth-Trisulphide is Rhombus or Orthorhombic, confirmed by XRD.
5. Fundamental infrared frequencies observed in all Sulphide compounds in general, are also found in the present FT-IR analysis, of Bismuth-Trisulphide.
6. Chemical compositions of the grown crystal by volumetric Analysis, and gravimetric Analysis well match with the theoretical calculation from molecular formula.

7. Crystals are quite transparent, and are of good quality.

8. Magnetic measurement is importance in solving problems of molecular structure and bond type of the material. Offers, a means of detecting the presence of singly occupied electronic orbit. The value of magnetic susceptibility of Bi$_2$S$_3$ closely related to theoretical ones. i.e. material Bi$_2$S$_3$ is diamagnetic up to 1K Gauss and behaves as a paramagnetic substance above 1K Gauss. Magnetic susceptibility is decreased as increase in temperature.

9. The electrical conductivity of crystals closely related to theoretical values with chemical nature of compound the electrical conductivity increases as increase in temperature. The energy gap of Bi$_2$S$_3$ is found to be 0.4640 eV which suggest that sample is semiconductor.

10. Chemical analysis confirms the presence of Bismuth and Sulpher, Chemical compositions of the grown crystal by EDAX match with the theoretical calculation from molecular formula.

11. Circular shape of Bismuth Tri-Sulphide crystals of appreciable size can be grown by single diffusion gel technique.

12. From SEM the grain size of sample is pentagonal and triangular.

13. Water of crystallization is present in grown crystals confirmed by TGA, DTA and FT-IR analysis.
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