Thermal behavior of semiconductor bismuth tri-sulphide \([\text{Bi}_2\text{S}_3]\) crystals grown by silica gel

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ABSTRACT

The Bismuth Tri-Sulphide \([\text{Bi}_2\text{S}_3]\) crystals have been grown in Sodium-Metasilicate gel using the single diffusion method at room temperature. The grown crystals were characterized by thermo analytical techniques (TGA, DTA, DTG and DSC), X-ray powder diffraction (XRD). By powder X-ray diffraction analysis the crystal structure is confirmed to be Orthorhombic or Rhombus, having lattice parameters \(a = 11.136 \, \text{Å}, b = 11.256 \, \text{Å}, \) and \(c = 3.988 \, \text{Å}\). Thermal study reveals that Bismuth Tri-Sulphide crystal is Di-hydrous. TGA, DTA, DTG and DSC analysis shows a remarkable thermal stability.

Keywords: Bismuth Tri-Sulphide \([\text{Bi}_2\text{S}_3]\) Crystals, XRD, Thermal Properties [TGA, DTA, DTG and DSC]

INTRODUCTION

Very few literatures are available on the study of \([\text{Bi}_2\text{S}_3]\), crystals. Most of the Sulphides exhibit prominent non-linear optics (NLO) behavior. Sulphides have important electrooptical properties [1, 2] because of the un-bond electron pair of Sulpher atoms in \((\text{S}_3)^-\)anions [3]. A lot of related compounds containing \((\text{S}_3)^-\) anions have been synthesized since 70 s [4–7]. Hence, it has been decided to Grow and study the Bismuth Tri-Sulphide crystals in view of crystallographic, optical, and thermal properties. Most of the Sulphide compounds are insoluble in water and decompose before melting. Hence, crystals of such type of compounds cannot be grown by either slow evaporation or melt techniques. In this situation, gel method is the appropriate one for their growth. The gel growth technique has gained considerable importance due to its simplicity and effectiveness in growing single crystals of certain compounds. Gel growth is an alternative technique to solution-growth with controlled diffusion and the growth process is free from convection [8-10]. The growth of crystals in gel is a self-purifying process, free from thermal strains, which is common in crystals grown from gel [11]. In this investigation, \([\text{Bi}_2\text{S}_3]\), crystals were grown by single diffusion gel technique using the AR grade Acetic Acid (\(\text{CH}_3\text{COOH}\)) Titrate with Sodium-Metasilicate (\(\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}\)) with adding \(\text{BiCl}_3\) as first supernant and \(\text{H}_2\text{S}\) gas water solution as second supernant with at \(\text{pH} \, 4.4\).

The grown crystals have been subjected to different characterizations. To the best of the knowledge, there is no literature is available on the study and thermal analysis of gel-grown \([\text{Bi}_2\text{S}_3]\), crystals.

MATERIALS AND METHODS

To grow the Bismuth Tri-Sulphide \([\text{Bi}_2\text{S}_3]\) crystals, the required Silica gel medium was prepared by adding the Sodium-Metasilicate solution of specific gravity 1.04 g/cc drop by drop with constant stirring by using magnetic stirrer into the 5 ML (2 N) Acetic Acid till the pH value 4.4 was set for the mixture. To the above Sodium Meta Silicate solution of pH 4.4, 15 ML aqueous solution of 0.1 M Bismuth Chloride (\(\text{BiCl}_3\)) was added as inner reagent.
with constant stirring. This mixture was then transferred to the test tube of length 15 and 2.5 cm diameter. To keep the solution free from dust and impurities, care was taken to cover the test tube with cotton. The gel was usually set within 13 days. It was left for 66 to 72 Hours for gel ageing and then the outer reagent, the aqueous solution of H$_2$S Gas Water solution was added on to the top of the gel. The outer reagent was added down the sides of the test tube using a pipette and not directly on to the gel medium. Owing to the diffusion of the outer reagent into the gel medium and its reaction with the inner reagent, crystals started growing. Nucleation was observed within 48 Hours of addition of the outer reagent. Circular shaped, opaque and brittle crystals were observed. The experiment was carried out at an ambient temperature of about 28 $^0$C. The reaction between Bismuth Chloride and H$_2$S Gas Water solution in gel medium resulted in the growth of Circular shaped Bismuth Tri-Sulphide [Bi$_2$S$_3$] crystals. The reaction that takes place in the gel medium is given below

$$2\text{BiCl}_3 + 3\text{H}_2\text{S} \rightarrow \text{Bi}_2\text{S}_3 + 6\text{YCl}$$

**RESULTS AND DISCUSSION**

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. The optimum growth conditions for various parameters were found and are reported in Table 1.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Bismuth Tri-Sulphide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of sodium metasilicate solution</td>
<td>1.04 g/cm$^3$</td>
</tr>
<tr>
<td>Amount of 2N acetic acid</td>
<td>5 ml</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 BiCl$_3$</td>
<td>0.5 M</td>
</tr>
<tr>
<td>Concentration of H$_2$S 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>

Table 1 Optimum condition for growth of Bismuth Tri-Sulphide crystals

![Fig. 1 Crystals of Bismuth -Trisulphide inside the Test-tube](image1)

![Fig 2 Few Crystals of Bismuth-Trisulphide on graph paper](image2)
X-ray diffractometry (XRD):- Bismuth Tri-Sulphide \([\text{Bi}_2\text{S}_3]\) 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 3.

From the Powder diffraction data for gel grown crystals The observed values nearly match with calculated values from computer program [12] An observed peak in diffractogram shows Bismuth Tri-Sulphide crystals passes Orthorhombic or Rhombus structure. In Orthorhombic crystal structure the length of unit cells are different .but the three axis are perpendicular to each other i.e. \(a \neq b \neq c \& \alpha = \gamma = \beta =90^0\). Bismuth Tri-Sulphide \([\text{Bi}_2\text{S}_3]\) crystals fulfill the condition of Orthorhombic structure, having lattice parameters \(a =11.136 \text{ Å}, b = 11.256 \text{ Å}, \text{and } c = 3.968 \text{ Å}\) ‘While \(\alpha =90.18^\circ, \beta = 90.42^\circ \text{ and } \gamma =90.36^\circ \). The grain size of the particles of powder sample were calculated using Scherrer equation \(D = \frac{0.9k}{b \cos \theta}\), where \(b\) represents the full width at half maximum (FWHM) of XRD lines and \(k = 1.54051 \text{ Å}\). The average grain size of the particles is \(D = 3.3457 \text{ Å} = 0.3415 \text{ nm}\).

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 300 °C/min. the weight of sample was 08.785 mg for TGA/DTA/DTG studies and 03.600 mg for DSC.

Thermal Gravimetric Analysis (TGA)
It was confirmed that the thermal decomposition of Bismuth Tri-Sulphide passes through an intermediate \(2[\text{Bi}_2\text{S}_3\text{H}_2\text{O}]\) 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 \(2[\text{Bi}_2\text{S}_3\text{H}_2\text{O}]\) is obtained in this process analogously as in the thermal decomposition of the alkaline earth Sulphides. However unlike \(2[\text{Bi}_2\text{S}_3\text{H}_2\text{O}]\) immediately after it is obtained begins to decomposition to \(\text{Bi}_2\text{O}_3\text{Di-Hydrus Bismuth Tri-Sulphide decomposes at high temperature.}

According to following reactions

\[2[\text{Bi}_2\text{S}_3\text{H}_2\text{O}]\rightarrow 37.271 \text{ to } 102.271 \rightarrow \left[2\text{H}_2\text{O} \uparrow + 2\text{SO}_2 \uparrow \right] \]

\[\text{Step I heating} \]

\[+ 102.271 \text{ to } 947.271 \rightarrow [4\text{SO}_2 \uparrow] \]

\[\text{Step II heating} \]

\[2\text{Bi}_2\text{O}_3 \downarrow \] Stable Residue + \[\text{[2Bi}_2\text{O}_3 \downarrow] \text{ Stable} \]

The TGA curve for Bismuth Tri-Sulphide gel grown crystals is as shown in fig 4. The TGA data collected from this curve and the theoretical values as calculated from molecular formula using the reaction are listed in table 2.
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°C to 37.271°C indicating that the crystals of Bismuth Tri-Sulphide are thermally stable in this range. The crystals become thermally unstable from 37.271°C.

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

**Table 2 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>Total weight loss</td>
<td>29.527 %</td>
<td>31.064 %</td>
<td></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>

1. The first stage of decomposition occurs in the temperature range 37.271 to 102.271°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 H₂O ‥ 2SO₂ ‥] and decomposition is in continuous manner.

2. The second stage of decomposition occurs in the temperature range 102.271 to 947.271°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 Bi₂S₃. 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 [4SO₂ ‥] and decomposition is in continuous manner.

The remaining product finally turns into residue Bi₂O₃ (Bismuth Oxide) is conformed at 947.271°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.

Differential Thermal Analysis (DTA)
The DTA curve for Bismuth Tri-Sulphide gel grown crystal is as shown in the fig 5 and DTA data collected from this curve is tabulated in table 3.
In DTA curve we can observe two endothermic peaks at 82.28 °C and 302.57 °C. However exothermic peak was not noticed in the DTA graph.

1. The endothermic peak at 82.28 °C is due to the decomposition of Bismuth Tri-Sulphide losing \([2H_2O + 2SO_2]\) molecules means in the first stage of decomposition peak at 82.28 °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.

Differential Thermal Gravimetric (DTG) The DTG curve for Bismuth Tri-Sulphide gel grown crystal is as shown in the fig 6, and DTG data collected from this curve is tabulated in table 4.
Table 4 DTG data of Bismuth Tri-Sulphide

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

1. The exothermic peak at 73.33 °C is due to the decomposition of Bismuth Tri-Sulphide losing 2 water and 2SO$_2$ 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 2SO$_2$ 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 4SO$_2$ 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 4SO$_2$ molecules in TGA curve.

Above 947.271 °C the reaction proceeds once finally stable residue Bi$_2$O$_3$ remains up to end of the analysis.

Differential Scanning Calorimetry (DSC)
The DSC curve for Bismuth Tri-Sulphide gel grown crystal is as shown in the fig 7 and DSC data collected from this curve is tabulated in table 5.

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

Table 5 DSC data of Bismuth Tri-Sulphide

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight of sample</th>
<th>Change in Enthalpy ($\Delta$H)</th>
<th>Transition temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth Tri-Sulphide [ Bi$_2$S$_3$ ]</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

3. Heat of transition $\Delta$H 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 tran = $\Delta$HF of phase transformation is also 0.0775 KJ/mole where $\Delta$HF 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 endothermic 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.

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

CONCLUSION
Thermal analysis reveals that Bismuth Tri-Sulphide crystals grown in silica gel using the single diffusion method are structurally stable from 0 °C to 37.271 °C. The crystal becomes thermally unstable from 37.271 °C and above this temperature; it decomposes with the evolution of Oxygen and Sulpher. The final Bi$_2$O$_3$ phase is tetragonal Thus, the Orthorhombic Bismuth Tri-Sulphide [Bi$_2$S$_3$] synthesized and characterized by X-ray in present study will yield a tetragonal Bi$_2$O$_3$ phase at very high temperature as seen in TGA-DTA studies. The conversion of Orthorhombic structure to a tetragonal Bi$_2$O$_3$ analogue is being characterized above three endothermic stages. The remaining product finally turns into residue Bi$_2$O$_3$ (Bismuth Oxide) is confirmed at 947.271 °C with the observed residue weight is 71.472 %. This is nearly agreement with calculated residual weight 68.930%. This confirms presents of Bismuth and Sulphur in grown crystals.

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The authors would like to acknowledge Prof. S. P. Patil, Prashant Nikam and M. I. Talele from Bhusawal for the fruitful discussion on TGA-DTA, DTG and DSC analysis, Head, Department of Physics, Pratap College, Amalner for providing laboratory facilities. Our special thanks to authorities of NCL, Pune for help in XRD and Thermal analysis.

REFERENCES
[13] CPDSC card No. 06-0333 of Bi$_2$S$_3$.