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Thermal behavior of semiconductor bismuth tri-sulphide [Bi_2S_3] crystals grown by silica gel

T. K. Patil

Smt. G. G. Khadse Science, Arts and Comm. College, Muktainagar, India

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ABSTRACT

The Bismuth Tri-Sulphide [Bi_2S_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 A°, b = 11.256 A°, and c = 3.968 A° . 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 [Bi_2S_3] Crystals, XRD, Thermal Properties [TGA, DTA, DTG and DSC]

INTRODUCTION

Very few literatures are available on the study of [Bi_2S_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 (S_3)-anions [3]. A lot of related compounds containing (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, [Bi_2S_3], crystals were grown by single diffusion gel technique using the AR grade Acetic Acid (CH_3COOH) Titrate with Sodium-Matasilicate (Na_2SiO_3 $5H_2O$) with adding $BiCl_3$ as first supernant and H_2S gas water solution as second supernant with at P^H 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 [Bi_2S_3], crystals.

MATERIALS AND METHODS

To grow the Bismuth Tri-Sulphide [Bi_2S_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 ($BiCl_3$) 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 to72 Hours for gel ageing and then the outer reagent, the aqueous solution of H_2S 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_2S Gas Water solution in gel medium resulted in the growth of Circular shaped Bismuth Tri-Sulphide [Bi_2S_3], crystals. The reaction that takes place in the gel medium is given below

$$\mathbf{2BiCl_3 + 3H_2S \rightarrow BI_2S_3 + 6YCl}$$

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

Conditions	Bismuth Tri-Sulphide
Density of sodium meta silicate solution	1.04 g/cm^3
Amount of 2N acetic acid	5 ml
pH of the gel	4.40
Temperature	Room temperature
Concentration of $BiCl_3$	0.5 M
Concentration of H_2S gas water solution.	----
Gel setting time	13 days
Gel aging time	72 hours
Period of growth	31 days

Fig. 1 Crystals of Bismuth -Trisulphide inside the Test-tube

Fig 2 Few Crystals of Bismuth-Trisulphide on graph paper

X-ray diffractometry (XRD):-Bismuth Tri-Sulphide [Bi_2S_3] was recorded at NCL PUNE with the help of "miniflex goniometer (1.5405 A˚) 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.

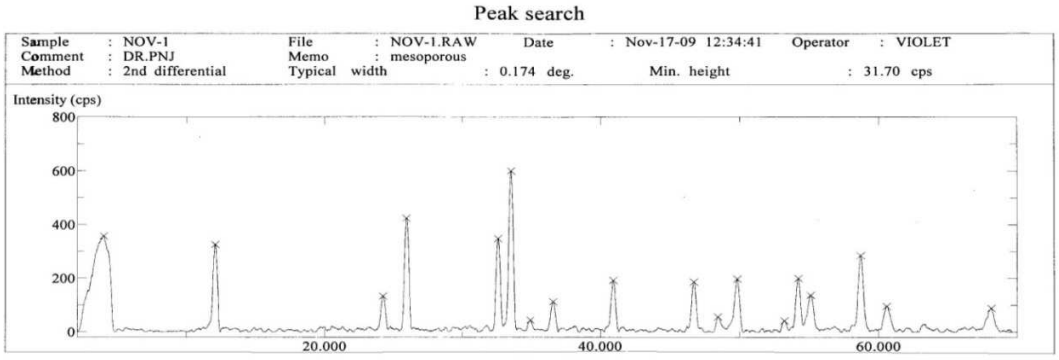

Fig 3. X- Ray diffractogram of Bismuth-Trisulphide

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 [$Bi_2S_3$] crystals fulfil the condition of Orthorhombic structure, having lattice parameters a =11.136 A˚, b = 11.256 A˚ , and c = 3.968 A˚ ,While α =90.18 ˚, β = 90.42 ˚and γ =90.36 ˚. The grain size of the particles of powder sample were calculated using Scherrer equation D = 0.9k/bcosh, where b represents the full width at half maximum (FWHM) of XRD lines and k = 1.54051 A ° . The average grain size of the particles is D = 3.3457 A˚ = 0.3415 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 30^0 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[Bi_2S_3.H_2O] which is unstable and immediately decomposes to Bi_2O_3. It has a one stage course until Bi_2O_3 is obtained an intermediate 2[Bi_2S_3.H_2O] is obtained in this process analogously as in the thermal decomposition of the alkaline earth Sulphides. However unlike 2[Bi_2S_3.H_2O] immediately after it is obtained begins to decomposition to Bi_2O_3 Di-Hydrus Bismuth Tri-Sulphide decomposes at high temperature.

According to following reactions

$$2[Bi_2S_3.H_2O] + 9O_2 \xrightarrow[\text{Step I heating}]{37.271 \text{ to } 102.271} [2H_2O\uparrow + 2SO_2\uparrow]$$

$$+ \xrightarrow[\text{Step II heating}]{102.271 \text{ to } 947.271} [4SO_2\uparrow]$$

$$[2Bi_2O_3\downarrow]$$

$$\text{Stable Residue} + \longrightarrow [2Bi_2O_3\downarrow] \text{ Stable}$$

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 0^0 C to 37.271^0 C indicating that the crystals of Bismuth Tri-Sulphide are thermally stable in this range. The crystals become thermally unstable from 37.271^0 C.

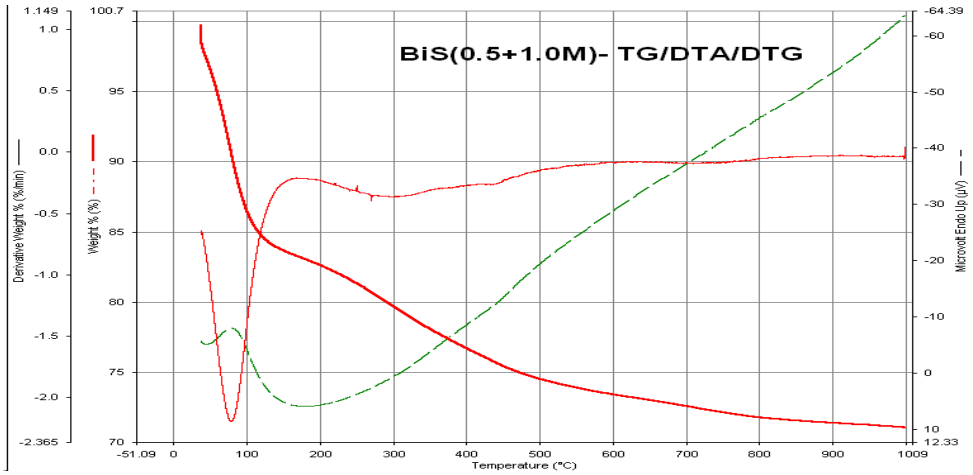

Fig 4 TGA curve of Bismuth Tri-Sulphide

Table 2 TGA data of Bismuth Tri-Sulphide

Stages	temperature (° C)	Observed weight loss %	Calculated weight loss %	Probable loss of molecule
I	37.271 to 102.271	13.543 %	12.130 %	$2H_2O\uparrow + 2SO_2\uparrow$
II	102.271 to 947.271	14.984 %	18.934 %	$4SO_2\uparrow$
	Total weight loss	28.527 %	31.064 %	
	Residue Stable $[2Bi_2O_3\downarrow]$	71.472 %	68.930 %	$2Bi_2O_3\downarrow$

1. The first stage of decomposition occurs in the temperature range 37.271 to 102.271 ^{0}C in which observe weight loss of 13.543 % agree with calculated weight loss 12.130 %. This weight loss is attributed to loss of [$2H_2O\uparrow + 2SO_2\uparrow$] and decomposition is in continuous manner.

2. The second stage of decomposition occurs in the temperature range 102.271 to 947.271^0C 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_2S_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 [$4SO_2\uparrow$] and decomposition is in continuous manner.

The remaining product finally turns into residue Bi_2O_3 (Bismuth Oxide) is conformed at 947.271^OC 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

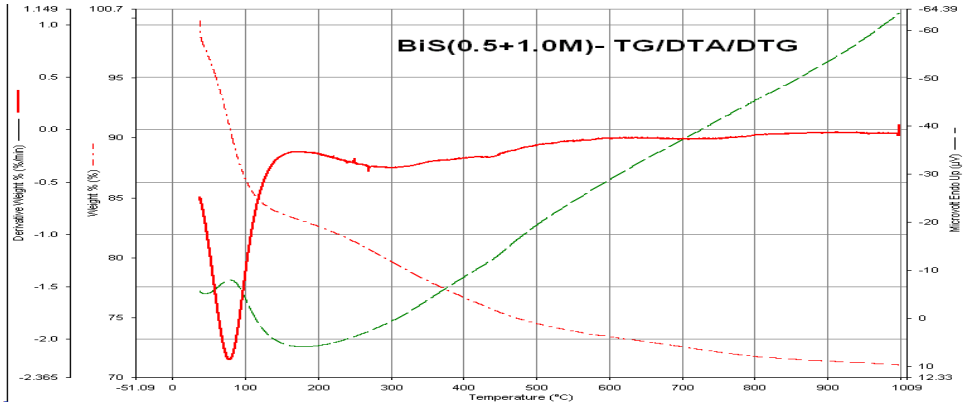

Fig 5 DTA curve of Bismuth Tri-Sulphide

Table 3 DTA data of Bismuth Tri-Sulphide

Sr. No	Peak recorded	Nature	Peak height µV	On set	Area (m J)	ΔH (J/gm)
1	82.28 ^{0}c	Endothermic	16.625	37.57 ^{0}c	328.65	56.954
2	302.57 ^{0}c	Endothermic	0.547	197.66 ^{0}c	206.40	24.117

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 [$2H_2O\uparrow + 2SO_2\uparrow$] molecules means in the first stage of decomposition peak at 82.28 ^{0}c is attributed to the loss of 2 water and $2SO_2$ molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of 2 water and $2SO_2$ molecules in TGA curve.

2. The second endothermic peak at 302.57 ^{0}c is due to the decomposition of compound and this peak in the second stage of decomposition is attributed to the loss of $4SO_2$ molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of $4SO_2$ molecules in the DTA curve.

Above 947.271 ^{0}c the reaction proceeds once finally residue Bi_2O_3 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

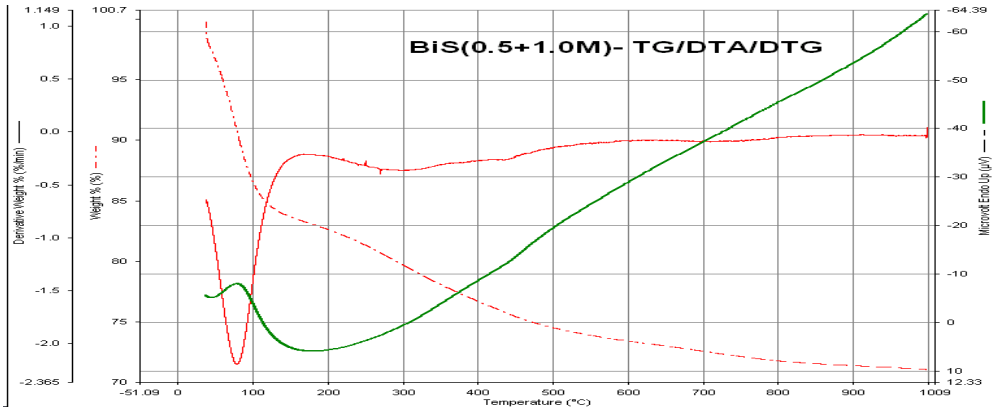

Fig 6. DTG curve of Bismuth Tri-Sulphide

Table 4 DTG data of Bismuth Tri-Sulphide

Sr. No	Peak	On set	Inflection point
1	73.33 ^{0}c	46.66 ^{0}c	63.73 ^{0}c
2	183.33 ^{0}c	102.271 ^{0}c	121.33 ^{0}c

1. The exothermic peak at 73.33 ^{0}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 ^{0}c and the inflection occurs at 63.73 ^{0}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 ^{0}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 ^{0}c and the inflection occurs at 121.33 ^{0}c. The peak observation in DTG curve corresponds to the weight loss of $4SO_2$ molecules in TGA curve.

Above 947.271 ^{0}c the reaction proceeds once finally stable residue Bi_2O_3 remains up to end of the analysis.

Differential Scanning Calorimetery (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.

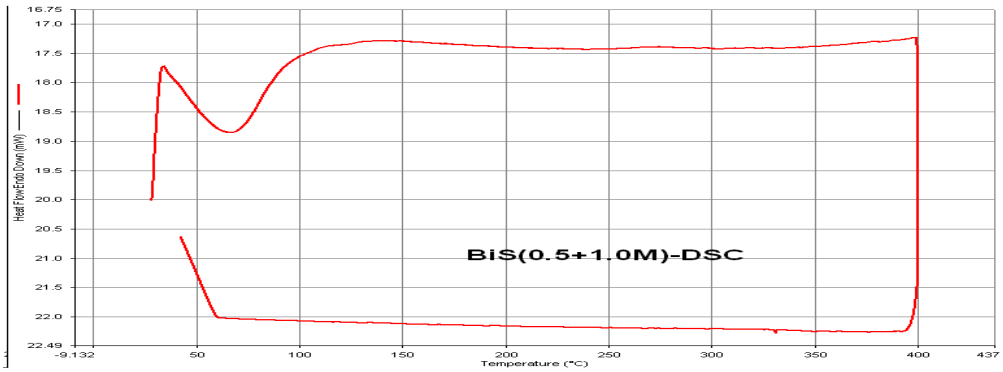

Fig 7 DSC curve of Bismuth Tri-Sulphide

Stage I

1. The initiation temperature is 34.22 ^{0}c and equilibrium temperature is 118.33 ^{0}c at 34.22 ^{0}c (initiation temperature) initiation of phase change starts and is completed at peak endo-down temperature of 66.86 ^{0}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 ^{0}c.

2. Area under the curve is 279.126 mJ.

Table 5 DSC data of Bismuth Tri-Sulphide

Sample	Weight of sample	Change in Enthalpy (ΔH)	Transition temperature
Bismuth Tri-Sulphide [Bi_2S_3]	3.600 mg	0.0775 KJ/mole	66.86 ^{0}c
		0.0149 KJ/mole	237.73 ^{0}c

There are two stages of DSC curves under study as follows

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

ΔH tran = ΔHF of phase transformation is also 0.0775 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 ^{0}c and equilibrium temperature is 343.89 ^{0}c at 177.00 ^{0} 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 ^{0}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 ^{0}c

2. Area under the curve is 53.717 mJ.

3. Heat of transition ΔH 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

ΔH tran = ΔHF i.e. heat of phase transformation is also 0.0149 KJ/mole where ΔHF 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 ^{0}C to 37.271^{0}C. The crystal becomes thermally unstable from 37.271^{0}C and above this temperature; it decomposes with the evolution of Oxygen and Sulpher. The final Bi_2O_3 phase is tetragonal Thus, the Orthorhombic Bismuth Tri-Sulphide [Bi_2S_3] synthesized and characterized by X-ray in present study will yield a tetragonal Bi_2O_3 phase at very high temperature as seen in TGA-DTA studies. The conversion of Orthorhombic structure to a tetragonal Bi_2O_3 analogue is being characterized above three endothermic stages. The remaining product finally turns into residue Bi_2O_3 (Bismuth Oxide) is conformed at 947.271^{O}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 Sulpher in grown crystals

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