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Thermal behavior of semiconductor bismuth iodide [BiI_3] crystals grown by silica gel

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ABSTRACT

The Bismuth Iodide [BiI_3] crystals have been grown in Sodium Meta silicate 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 Hexagonal, having lattice parameters a = 9.766 A° , b = 9.360 A° , and c = 17.875 A° . Thermal study reveals that Bismuth Iodide crystal is Un-hydrous. TGA, DTA, DTG and DSC analysis shows a remarkable thermal stability.

Keywords: Bismuth Iodide [BiI_3] Crystals, XRD, Thermal Properties [TGA, DTA, DTG and DSC]

INTRODUCTION

Very few literatures are available on the study of Bismuth Iodide [BiI_3] crystals. Most of the Iodates and Iodides exhibit prominent non-linear optics (NLO) behavior. Iodides have important electrooptical properties [1, 2] because of the un-bond electron pair of Iodine atoms in (I_3)-anions [3]. A lot of related compounds containing (I_3^-) anions have been synthesized since 70 s [4–7]. Hence, it has been decided to Grow and study the Bismuth Iodide crystals in view of crystallographic, optical, and thermal properties. Most of the iodide 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]. The growth of single crystals in gel is a self-purifying process, free from thermal strains, which is common in crystals grown from melt [9-10]. In this investigation, Bismuth Iodide [BiI_3] crystals were grown by single diffusion gel technique using the AR grade Acetic Acid and Potassium Iodide. 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 [BiI_3] crystals.

MATERIALS AND METHODS

To grow the Bismuth Iodide [BiI_3] crystals, the required silica gel medium was prepared by adding the Sodium Metasilicate (Na_2SiO_3 $5H_2O$) 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(CH_3COOH) 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 in-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 0.1 M, Potassium Iodide (KI) 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. Spherical shaped on higher magnification, 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 Potassium Iodide in gel medium resulted in the growth of Circular shaped Bismuth Iodide [BiI_3] crystals. The reaction that takes place in the gel

$$\mathbf{BiCl_3 + 3KI \rightarrow BiI_3 + 3KCl}$$

RESULTS AND DISCUSSION

It was observed that nucleation takes place after 7 to 8 days on the surface of the gel and rarely inside the gel. Number of nuclei produced is inversely proportional to the distance from the gel interface.

The number of nuclei decreases as we go away from the gel interface. Formation of nuclei depends upon number of parameters such as pH, density of gel, aging period and concentration of reactants. The optimum growth conditions for the growth of Bismuth Iodide crystals are represented in table. Different parameters such as gel density, gel setting time, gel aging time, concentrations of reactants, pH of gel etc have the considerable effect on the growth rate. Crystals having different morphologies were obtained.

Table 1: Optimum conditions for growth of BiI_3 crystals

Conditions	Bismuth Iodide
Density of sodium meta silicate solution	1.04 g/cm^3
Amount of 2N acetic acid	5ml
pH of the gel	4.40
Temperature	Room temperature
Concentration of KI	0.5 M
Concentration of $BiCl_3$	O.5 M
Gel setting time	13 days
Gel aging time	72 hours
Period of growth	*38 days*

In the steady state of concentration gradient, growth rate also becomes steady which favors growth of well developed crystals. Large numbers of micro crystals were obtained near the gel interface. The crystal size was smaller obtained from gel. It was observed that the number of crystals growing diminished with the increase in the distance from the gel interface. It may be due to the reduced rate of diffusion of supernatant. Second reason may be attributed to the gel aging, since the crystals in this region nucleate in a comparatively older gel. The number of nucleation centers and growth rate decreases with increase in aging of gel. Insufficient gel aging often causes the fracturing of gel at the time of incorporating the supernatant. High concentration of reactants results in to formation of a thick layer created by large number of micro crystals attached themselves at the interface. This may be happened due to high diffusion gradient near the gel interface.

Fig. 1 shows the optimized crystals of Bismuth Iodide grown near the gel interface inside the test tube. The shape of these crystals appeared to be Spherical on higher magnification. Figure 2 shows few crystals of Bismuth Iodide having different habits on a graph paper with their scaling. Crystals so formed were Spherical in shape, transparent and well isolated

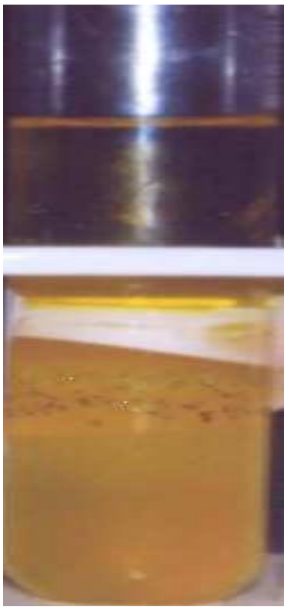

Fig 1Crystals of Bismuth Iodide inside the test tube crystals

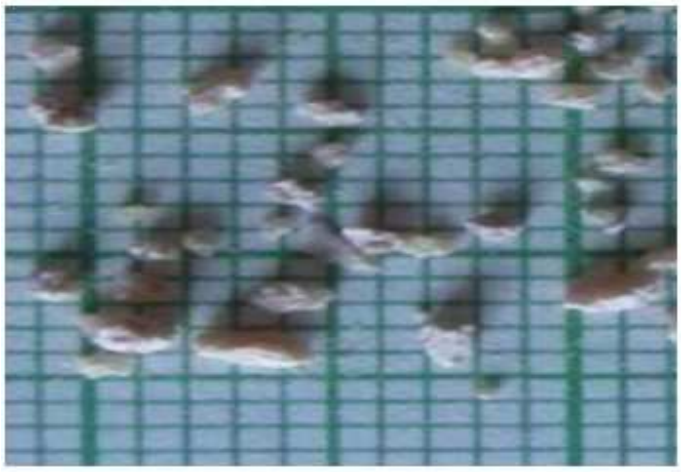

Fig 2. Few crystals of bismuth Iodide on graph paper

X-ray diffractometry (XRD)

Bismuth Iodate [BiI_3] crystals were powdered and X-ray diffractogram of gel grown crystals of Bismuth Iodide BiI_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 nicked filter were used from the powder diffracts on data of Bismuth Iodide shows Seven 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. The observed values nearly match with calculated values from computer program and also nearly match with JCPDS card No - 72 - 2373 of BiI_3 [11]. An observed peak in diffractogram shows Bismuth Iodide crystals passes Hexagonal structure. In Hexagonal crystal structure Three axis of unit cell are equal in one plane at 120^0 with each other the fourth axis is perpendicular to this plane i.e. $\mathbf{a = b \neq c}$ **&** $\boldsymbol{\alpha = \beta = 90^0}$ and $\boldsymbol{\gamma = 120^0}$ Bismuth Iodide [BiI_3] crystals fulfil the condition of Hexagonal structure, having lattice parameters **a** = 9.766 A˚, **b** =9.360 A˚ and **c** =17.875 A˚ While $\boldsymbol{\alpha}$ =90. 48˚ $\boldsymbol{\beta}$ = 90. 36˚, and $\boldsymbol{\gamma}$ =119.68˚. 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** = = 3.3997 A˚= 0.3399 nm.

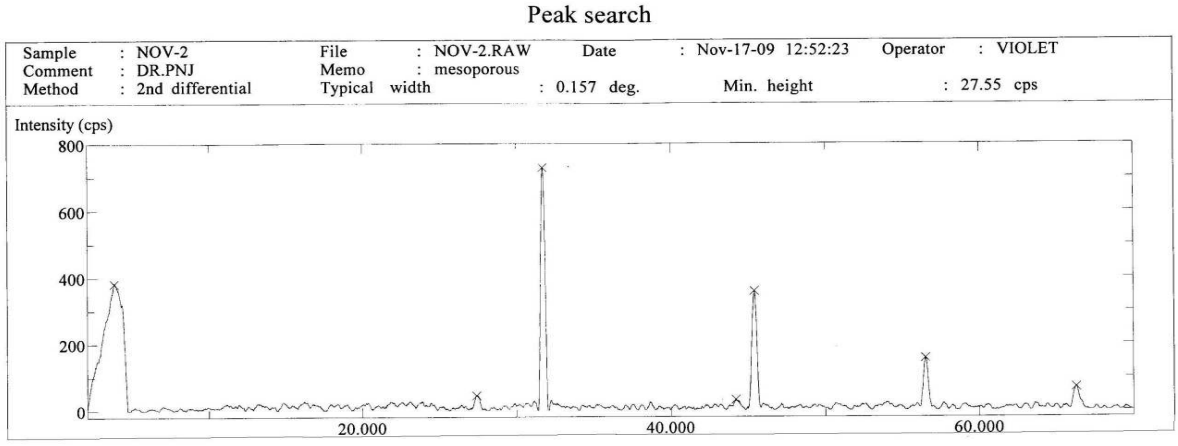

Fig 3.X-Ray diffractogram of BiI_3

Thermal Analysis or Thermal studies

The thermal decomposition behavior of the grown crystals was studied by thermogravimetry (TGA) and differential thermal analysis (DTA). Diamond TGA/DTA thermal analyzer was used for obtaining the TGA and DTA curves at NCL Pune. Recrystallization alumina sample holders were used and the heating rate was 30^0 C/min. the weight of sample was 08.993 mg for TGA/DTA/DTG studies and 05.600 mg for DSC. Figure 4 shows the TGA/DTA/DTG curve of Bismuth Iodide crystal. TGA curves shows that, Bismuth Iodide crystal is thermally stable up to 39.246 ^{0}C temperature [12-16].

Thermal Gravimetric Analysis (TGA)

It was confirmed that the thermal decomposition of Bismuth Iodide passes through an intermediate $5BiI_3 + 6O_2$ which is unstable and finally decomposes to Bi_2O_3. As reported by Bachir Bentria and Djamal Bendetral [17], journal of chemical crystallography, vol 33 no 11 November 2003

According to following reactions

$5\ Bi\ I_3+6O_2 \xrightarrow[\text{Step I heating}]{39.246 \text{ to } 104.246} [4I_2\uparrow]$

$Bi_5+3.5I_2+6O_2 \xrightarrow[\text{Step II heating}]{104.246 \text{ to } 369.246} [\ I_2O_5\uparrow\ ]$

$Bi_5+2.5I_2+3.5O_2 \xrightarrow[\text{Step III heating}]{369.246 \text{ to } 934.246} [\ 2\ I_2\uparrow\ ]$

$[Bi_5\ O_7\ I] \longrightarrow [\ BiOI + 2\ Bi_2\ O_3\downarrow\ ]$

Stable Stable Residue +

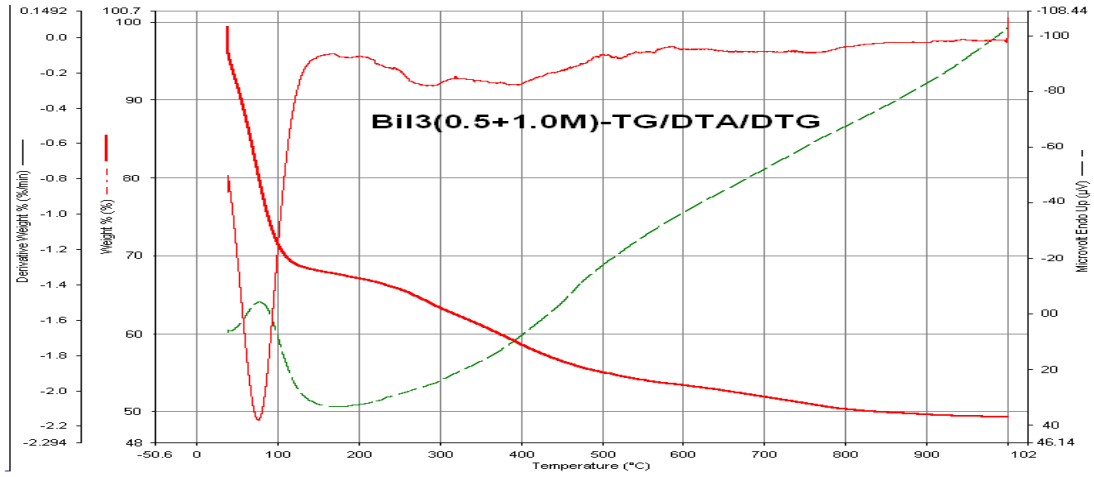

Fig 4 TGA curve of Bismuth Iodide gel grown crystals.

Table 2 TGA data of Bismuth Iodide

Stages	temperature (^{o} C)	Observed weight loss %	Calculated weight loss %	Probable loss of molecule
I	39.246 to 104.246	29.253 %	32.336 %	$4I_2\uparrow$
II	104.246 to 369.246	10.363 %	10.630 %	$I_2O_5\uparrow$
III	369.246 to 934.246	10.366 %	16.168 %	$2\ I_2\uparrow$
	Total weight loss %	49.982 %	59.134 %	
	Residue Stable $Bi_5\ O_7\ I$ $[BiOI + 2\ Bi_2\ O_3]$	 50.018 % [100.000 %]	 40.865 % [99.997 %]	$Bi_5\ O_7\ I$ $BiOI + 2\ Bi_2O_3\downarrow$

The TGA curve for Bismuth Iodide 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 Iodide showed clearly three stages of decomposition. TGA curve did not show an appreciable weight changes in the temperature 0 ^{0} C to 39.246 ^{0} C indicating that the crystals of Bismuth Iodide are thermally stable in this range. The crystals becomes thermally unstable from 39.246 0C.

1. The first stage of decomposition occurs in the temperature range 39.246 to 104.246 ^{0}C in which observe weight loss of 29.253 %agree with calculated weight loss 32.336 %. This weight loss is attributed to loss of [$4I_2\uparrow$] and decomposition is in continuous manner.

2. The second stage of decomposition occurs in the temperature range 104.246 to 369.246 ^{0}C in which observe weight loss of 10.363 % agree with calculated weight loss 10.630 %. This weight loss is attributed to loss of [$I_2O_5\uparrow$] and decomposition is in continuous manner.

3. The third stage of decomposition occurs in the temperature range 369.246 to 934.246 ^{0}C in which observe weight loss of 10.366 % agree with calculated weight loss 16.168 %. This weight loss is attributed to loss of [$2I_2\uparrow$].

The observed trend above 500 ^{0}C suggests that the product formed is continuously getting decomposed. We may attribute this process to the conversion of $Bi5\ O_7I$ into Bi_2O_3 (stable Bismuth Oxide) and BiOI may be unstable component. It is suggested further that BiOI is decomposing $Bi_5O_7I \longrightarrow BiOI + 2\ Bi_2O_3$, while, BiOI must be partially getting influenced by thermal energy and hence showing a continuous loss in weight from TGA curve. It is expected that BiOI will finally get converted to a stable variety of Bi_2O_3 and a subsequent loss of Iodine molecule. This is possible only after 1600-1800 ^{0}C of a temperature at which we could not extend our experiment TGA-DTA studies. The final Bi_2O_3 phase is tetragonal as reported in literature of Bachir. Thus, the Hexagonal BiI_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 Hexagonal structure to a tetragonal Bi_2O_3 analogue is being characterized above three endothermic stages. The observed residue weight is 50.018 %. This is agreement with calculated residual weight 40.865%.The difference in weightloss i.e. observed in residue may be attributed to impurities in gel and possibility of combination of atmospheric moisture with Bismuth forms a compound which could not be decomposes up to 1000^0 C so observed residues more than expected one. This confirms presents of Bismuth in grown crystals. [18-19]

Differential Thermal Analysis (DTA)

The DTA curve for Bismuth Iodide gel grown crystal is as shown in the fig 5. and DTA data collected from this curve is tabulated in table3.

In DTA curve we can observe three endothermic peaks at 73.33 ^{0}c, 286.66 ^{0}c and 754.18 ^{0}c. However exothermic peak was not noticed in the DTA graph.

1. The endothermic peak at 73.33 ^{0}c is due to the decomposition of Bismuth Iodide losing [$4I_2$] molecules means in the first stage of decomposition peak at 73.33 ^{0}c is attributed to the loss of 8Iodine molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of eight Iodine molecules in TGA curve.

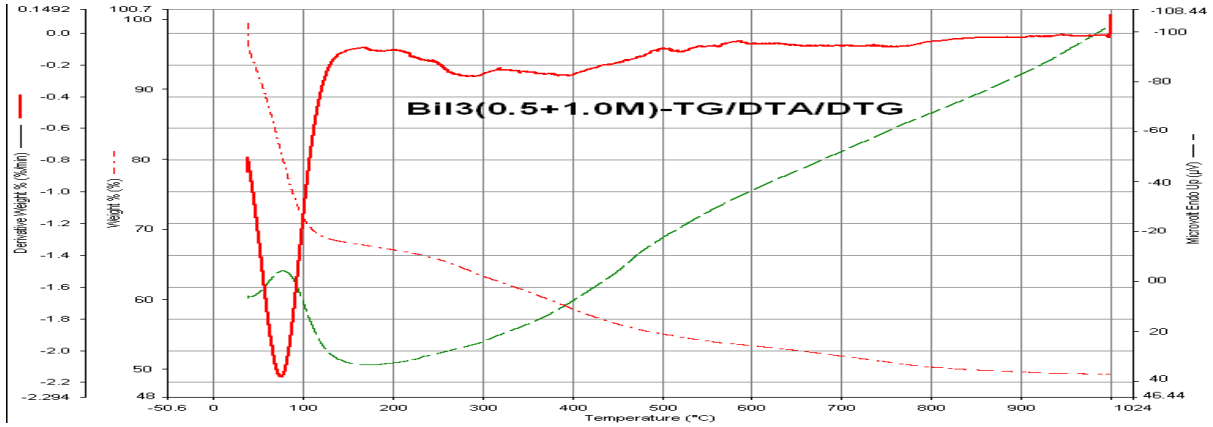

Fig 5. DTA curve of Bismuth Iodide gel grown crystal

Table 3. DTA data of Bismuth Iodide

Sr. No	Peak recorded	Nature	Peak height	On set	Area [m J]	ΔH [J/gm]
1	73.33 ^{0}c	Endothermic	37.89	40.16 ^{0}c	2346.18	4.898
2	286.66 ^{0}c	Endothermic	- 83.57	206.16 ^{0}c	-1353.59	-2.996
3	754.18 ^{0}c	Endothermic	- 94.44	612.20 ^{0}c	-968.76	-3.047

2. The second endothermic peak at 286.66 ^{0}c is due to the decomposition of compound and this peak in the second stage of decomposition is attributed to the loss of 2 Iodine and 5 oxygen molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of 2 Iodine and 5 oxygen molecules in the TGA curve.

3. The third endothermic peak at 754.18 ^{0}c is due to the decomposition of compound and this peak in the third stage of decomposition is attributed to the loss of 4 Iodine molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of 4 Iodine molecules in the TGA curve. Beyond 904.020 ^{0}c the reaction proceeds once finally residue Bi_5O_7I decomposes slightly and stable residue Bi_2O_3 remains up to end of the analysis.

Differential Thermal Gravimetric (DTG)

The DTG curve for Bismuth Iodide gel grown crystal is as shown in the fig 6 and DTG data collected from this curve is tabulated in table 4

1The endothermic peak at 73.33 ^{0}c is due to the decomposition of Bismuth Iodide losing 8 Iodine molecules. In the first stage of decomposition peak at 73.33 ^{0}c is attributed to the loss of $4I_2$ molecules. This endothermic peak observed in the DTG curve indicates that the reaction starts at 40.16 ^{0}c and the inflection occurs at 69.22 ^{0}c. The peak observation in DTG curve corresponds to the weight loss in TGA curve.

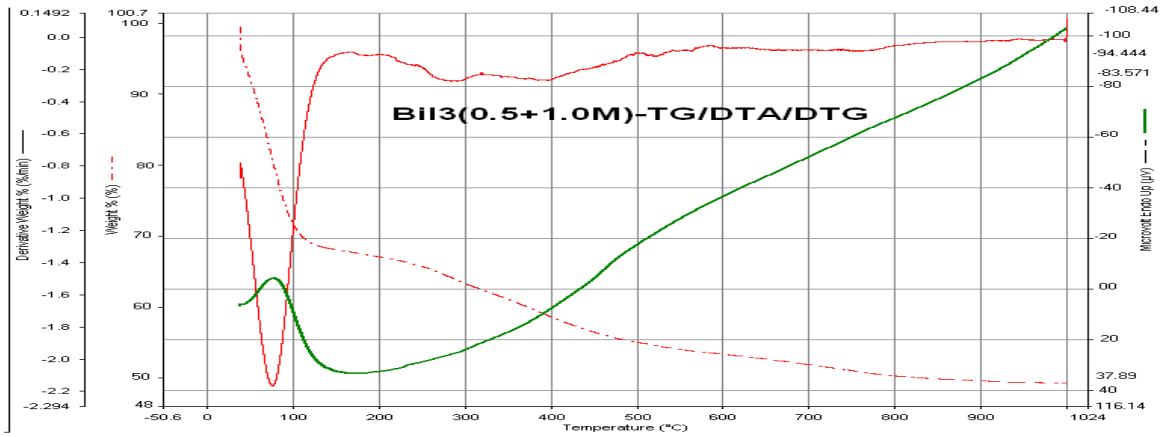

Fig 6 DTG curve of Bismuth Iodide gel grown crystal

Table 4 DTG data of Bismuth Iodide

Sr. No	Peak	On set	Inflection point
1	73.33 ^{0}c	40.16 ^{0}c	69.22 ^{0}c
2	286.66 ^{0}c	206.16 ^{0}c	246.14 ^{0}c
3	754.18 ^{0}c	612.30 ^{0}c	714.20 ^{0}c

2) The endothermic peak at 286.66 ^{0}c is due to the decomposition of compound and this peak in second stage of decomposition is attributed to the loss of 2 Iodine and 5 Oxygen molecules. This endothermic peak observed in the DTG curve indicates that the reaction starts at 206.16 ^{0}c and the inflection occurs at 246.14^{0}c. The peak observation in DTG curve corresponds to the weight loss in TGA curve.

3). The endothermic peak at 754.18 ^{0}c is due to the decomposition of compound and this peak in third stage of decomposition is attributed to the loss of 4 Iodine molecules. This endothermic peak observed in the DTG curve

indicates that the reaction starts at 612.30 ^{0}c and the inflection occurs at 714.20 ^{0}c. The peak observation in DTG curve corresponds to the weight loss in TGA curve.

Beyond 904.246 ^{0}c the reaction proceeds once finally residue Bi_5O_7I decomposes slightly and stable residue Bi_2O_3 remains up to end of the analysis.

Differential Scanning Calorimetery (DSC)

The DSC curve for Bismuth Iodate gel grown crystal is as shown in the fig 7. and DSC data collected from this curve is tabulated in table 5.

Table 5. DSC data of Bismuth Iodide

Sample	Weight of sample	Change in Enthalpy (ΔH)	Transition temperature
Bismuth Iodide BiI_3	4.600 mg	0.0496 KJ/mole	63.99 ^{0}c
		0.0338 KJ/mole	302.38 ^{0}c

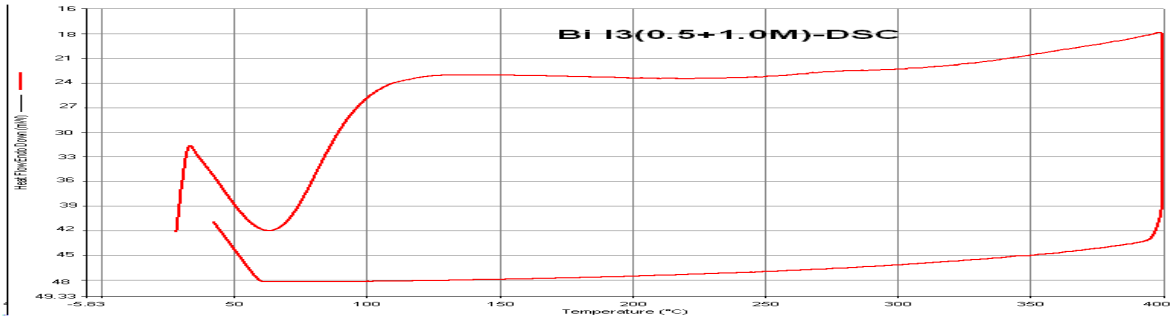

Fig 7. DSC curve of Bismuth Iodide gel grown crystal

There are two stages of DSC curves under study as follows

Stage I

1. The initiation temperature is 33.73^{0}c and equilibrium temperature is 93 ^{0} c at 33.73 ^{0} c (initiation temperature) initiation of phase change starts and is completed at peak endo-down temperature of 63.99 ^{0} c transition temperature [peak height is 15.018 mw]. The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 93 ^{0}c.

2. Area under the curve is 228.056 mJ.

3. Heat of transmission ΔH i.e. enthalpy change of transition is 49.5775 J/g which is 0.04957 KJ/mole since molecular weight is 1.000 g/mole

ΔH = ΔHF of phase transformation is also 0.04957 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 185.26 ^{0} c and equilibrium temperature is 363.14 ^{0} c at 185.26 ^{0} c (initiation temperature) initiation of phase change starts and is completed at peak endo-down temperature of 302.38 ^{0} c (transition temperature) peak height is 1.5214 mw. The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 363.14 ^{0}c

2. Area under the curve is 155.419 mJ.

3. Heat of transmission ΔH i.e. enthalpy change of transition is 33.7868 J/g which is 0.0338 KJ/mole since molecular weight is 1.000 g/mole

ΔH= ΔHF i.e. heat of phase transformation is also 7.785 - 004 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 Iodide crystals grown in silica gel using the single diffusion method are structurally stable from 0 ^{0}C to 39.246 ^{0}C The crystals becomes thermally unstable from 39.246 ^{0}C. and above this temperature; it decomposes with the evolution of Oxygen and Iodine. . It is expected that from **Bi_5O_7I** , BiOI may be decomposes at higher temperature and BiOI will finally get converted to a stable variety of Bi_2O_3 and a subsequent loss of Iodine molecule. The final Bi_2O_3 phase is tetragonal Thus, the Hexagonal BiI_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 Hexagonal structure of BiI_3 to a tetragonal Bi_2O_3 analogue is being characterized above three endothermic stages.

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