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Thermal Behavior 0f Semicoductor Bismuth Iodate [$Bi(IO_3)_3$] Crystals Grown by Silica Gel

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1. Abstract
The Bismuth Iodate [$Bi(IO_3)_3$] 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 Monoclinic, having lattice parameters a = 6.09 A° , b = 16.68 A° , and c = 5.58 A° . Thermal study reveals that Bismuth Iodate crystal is Octa-hydrous. TGA, DTA, DTG and DSC analysis shows a remarkable thermal stability.

2. Keywords- Bismuth Iodate [$Bi(IO_3)_3$] Crystals, XRD, Thermal properties [TGA ,DTA,DTG and DSC]

3. Introduction

Very few literatures are available on the study of Bismuth Iodate [$Bi(IO_3)_3$], crystals. Most of the Iodates exhibit prominent non-linear optics (NLO) behavior. Iodates have important electrooptical properties [1, 2] because of the un-bond electron pair of Iodine atoms in (IO_3)-anions [3]. A lot of related compounds containing $(IO_3)_3$ anions have been synthesized since 70 s [4–7]. Hence, it has been decided to Grow and study the Bismuth Iodate crystals in view of crystallographic, optical, and thermal properties. Most of the Iodate 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]. In this investigation, Bismuth Iodate [$Bi(IO_3)_3$], crystals were grown by single diffusion gel technique using the AR grade Acetic Acid and Potassium Iodate. 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 Bismuth Iodate [$Bi(IO_3)_3$], crystals.

4. Experimental

To grow the Bismuth Iodate [$Bi(IO_3)_3$], 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 (BiCl3) 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 0.1 M, Potassium Iodate $K(IO_3)$ 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 Potassium Iodate in gel medium resulted in the growth of Circular shaped Bismuth Iodate [$Bi(IO_3)_3$], crystals. The reaction that takes place in the gel medium is given below

$$\mathbf{BiCl_3 + 3K(IO_3) \rightarrow Bi(IO_3)_3 + 3KCl}$$

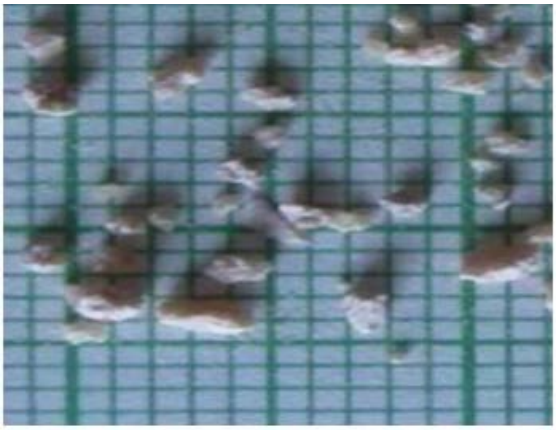

Fig: 1 Crystals of Bismuth Iodate inside the test tube Fig: 2 Few crystals of bismuth Iodate

5. Results and discussion

The optimum growth conditions for the growth of Bismuth Iodate crystals are represented 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. In the present investigation, the growth of Bismuth Iodate occurs in three different forms viz. whisker dendritic and spherical. The whisker and dendritic growth occurs near the gel interface. It does mean that opaque whiskers and dendrites are found to grow in the region of high concentration gradient respectively when the growth rate is very high. Just below the gel interface the concentration gradient is very high and hence the growth rate is also very high causing the whiskers of Bismuth Iodate to grow in this region. Away from the gel interface, the concentration gradient goes on decreasing and hence the growth rate is also goes on decreasing. Hence below the whisker growth or the dendrite growth there is a growth of the Bismuth Iodate. Near the bottom of the test tube far away from the gel interface, the rate of diffusion of the feed on solution reduces and becomes steady causing growth of well developed spherical crystals. Rate of arrival of the solute at the crystal surface influences perfection of the crystal. Hence, growth of more perfect crystals occurs due to slow and steady diffusion of feed solution. No gel inclusion is observed in these crystals. Figures 1 and 2 show photographs of Bismuth Iodate crystals, inside and outside the gel medium, respectively. These crystals are sufficient for different characterizations.

Table 1: Optimum conditions for growth of $Bi(IO_3)_3$ crystals

Conditions	**Bismuth Iodate**
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 KIO_3	0.5 M

Concentration of $BiCl_3$	l.OM
Gel setting time	13 days
Gel aging time	72 hours
Period of growth	*36 days*

5.1 X-ray diffraction

Bismuth Iodate [$Bi(IO_3)_3$] crystals were powdered and X-ray powder diffraction (XRD) data were collected at room temperature on a Rigaku, Miniflex model. All diffraction patterns were obtained using CuKa radiation (k = 1.54051 A °), at 30 kV and 15 mA. The observed values nearly match with calculated values from computer program and also nearly match with JCPDS card No - 75 - 1467 of $Bi(IO_3)_3$ [10] . An observed peak in diffractogram shows Bismuth Iodate crystals passes Monoclinic structure. In monoclinic crystal structure the length of unit cell are different. Two axis are right at angles to each other and third axis is obliquely inclined i.e. $\mathbf{a \neq b \neq c}$ & $\boldsymbol{\alpha = \beta = 90^0 \neq \gamma}$.

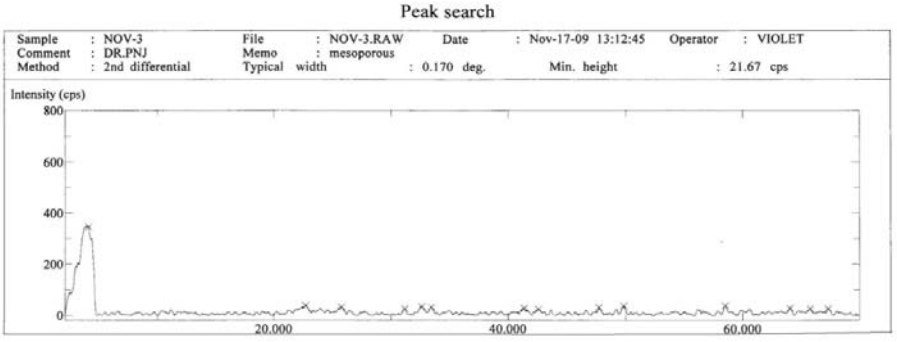

Fig 3 X-ray diffractogram of Bismuth Iodate

Bismuth Iodate [$Bi(IO_3)_3$] crystals fulfil the condition of Monoclinic structure, having lattice parameters a = 6.09 A° , b = 16.68 A° , and c = 5.58 A° ,While α =90.36 ˚ , β = 90.48 ˚ and γ =119.63 ˚ . 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 = = 7.3825 A˚ (0.7382 nm).

5.2 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 Iodate crystal. TGA curves shows that, Bismuth Iodate crystal is thermally stable up to 44.020 ^{0}C temperature [11-15].

5.2.1 Thermal Gravimetric Analysis (T G A)

It was confirmed that the thermal decomposition of Bismuth Iodate passes through an intermediate 5[Bi $(IO_3)_3$ 2H2O] which is unstable and finally decomposes to Bi_2O_3. As reported by Bachir Bentria and Djamal Bendetral [16], journal of chemical crystallography, vol 33 no 11 November 2003.

Decade – Hydrus Bismuth Iodate decomposes at high temperature,According to following reaction

$$5\,[Bi\,(IO_3)_3\,2H_2O] \xrightarrow[\text{Step I heating}]{44.020 \text{ to } 129.020} [10\,H_2O \uparrow + I_2 \uparrow]$$

$$+ \xrightarrow[\text{Step II heating}]{129.020 \text{ to } 259.020} [1.5\,I_2 \uparrow + 8O_2 \uparrow]$$

$$+ \xrightarrow[\text{Step III heating}]{259.020 \text{ to } 904.020} [4.5\, I_2\uparrow + 11O_2\uparrow]$$

$[\, Bi_5O_7I\downarrow\,]$

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

The TGA curve for Bismuth Iodate 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 Iodate showed clearly three stages of decomposition. TGA curve did not show an appreciable weight changes in the temperature 0 ^{0} C to 44 ^{0} C indicating that the crystals of Bismuth Iodate are thermally stable in this range. The crystals becomes thermally unstable from 44.020 ^{0}C.

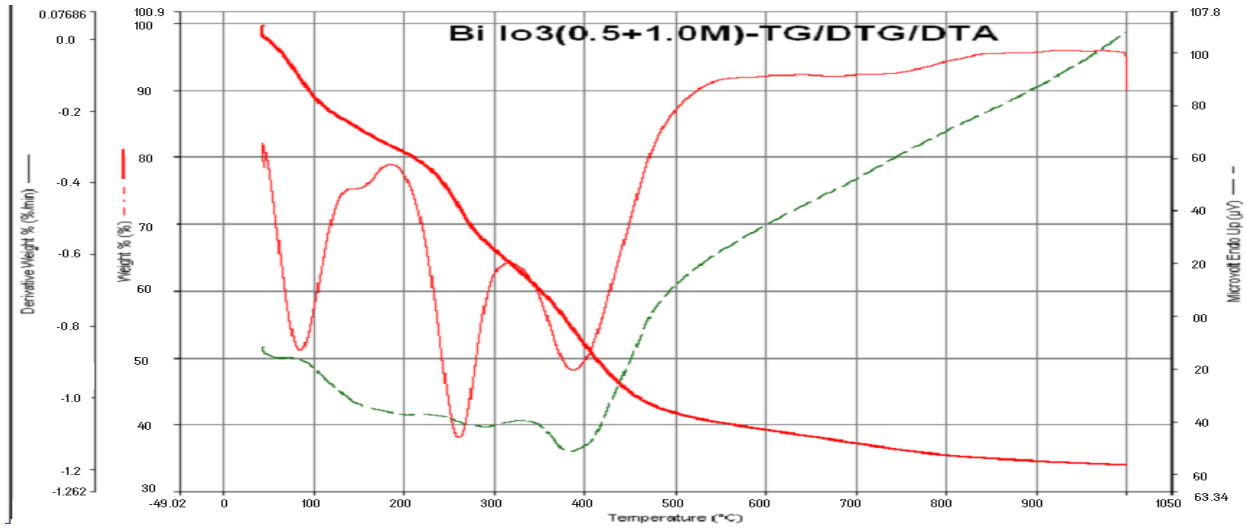

Fig 4 The TGA curve for Bismuth Iodate gel grown crystal

Table 2. TGA data of Bismuth Iodate

Stages	**temperature (^{o} C)**	**Observed weight loss %**	**Calculated weight loss %**	**Probable loss of molecule**
I	44.020 to 129.020	12.908 %	11.272 %	$10\, H_2O\uparrow + I_2\uparrow$
II	129.020 to 259.020	15.470 %	16.545 %	$1.5\, I_2\uparrow + 8O_2\uparrow$
III	259.020 to 904.020	36.219 %	38.831 %	$4.5\, I_2\uparrow + 11O_2\uparrow$
	Total weight loss %	64.597 %	66.648 %	
	Residue Stable Bi_5O_7I $[BiOI + 2\, Bi_2O_3]$	35.403 % [100.000 %]	33.349 % [99.997 %]	Bi_5O_7I $BiOI + 2\, Bi_2O_3\downarrow$

1. The first stage of decomposition occurs in the temperature range 44.020 to 129.020 ^{0}C in which observe weight loss of 12.908 % agree with calculated weight loss 11.272 %. This weight loss is attributed to loss of [10 H_2O I_2] and decomposition is in continuous manner.

2. The second stage of decomposition occurs in the temperature range 129.020 to

259.020 ^{0} C in which observe weight loss of 15.470 % agree with calculated weight loss 16.545 %. This weight loss is attributed to loss of [1.5 I_2 $8O_2$] and decomposition is in continuous manner.

3. The third stage of decomposition occurs in the temperature range 259.020 to 904.020 ^{0} C in which observe weight loss of 36.219 % agree with calculated weight loss 38.831 %. This weight loss is attributed to loss of [4.5 I_2 $11O_2$].

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 **$Bi5O_7I$** into **Bi_2O_3** (stable Bismuth Oxide) and BiOI may be unstable component. It is suggested further that BiOI is decomposing **Bi_5O_7I** **BiOI + $2Bi_2O_3$**, 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 Monoclinic $Bi(IO_3)_3$ 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 Monoclinic structure to a tetragonal Bi_2O_3 analogue is being characterized above three endothermic stages. The observed residue weight is 35.403 %. This is well agreement with calculated residual weight 33.349%.This confirms presents of Bismuth in grown crystals.

5.2..2 Differential Thermal Analysis (DTA) The DTA curve for Bismuth Iodate gel grown crystal is as shown in the fig 5 and DTA data collected from this curve is tabulated in table 3.

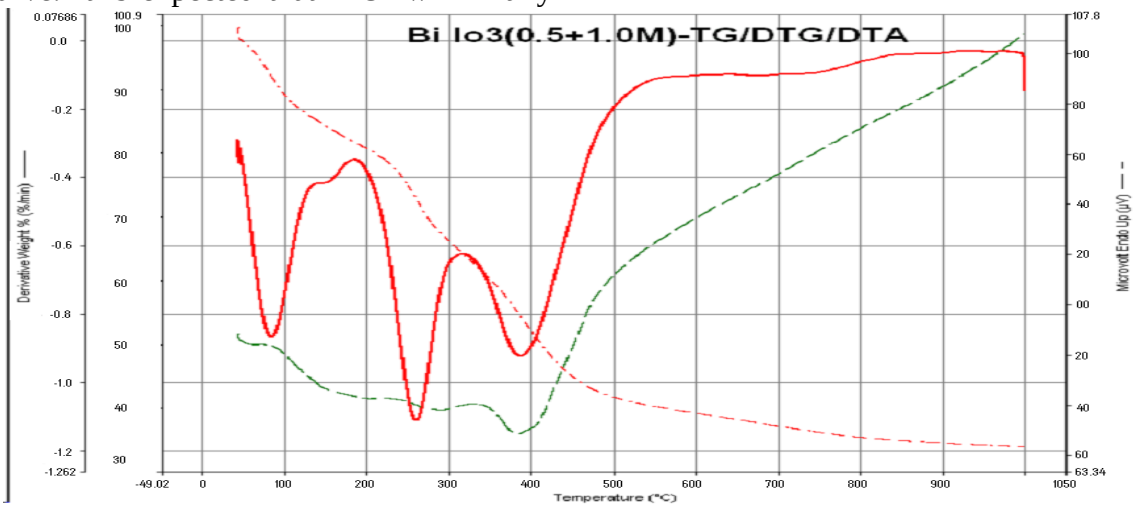

Fig 5. DTA curve for Bismuth Iodate gel grown crystal

In DTA curve we can observe three endothermic peaks at 87.50 ^{0} c, 256.25 ^{0} c and 381.26 ^{0} c. However exothermic peak was not noticed in the DTA graph.

1. The endothermic peak at 87.50 ^{0} c is due to the decomposition of Bismuth Iodate losing [10 H_2O I_2] molecules means in the first stage of decomposition peak at 87.50 ^{0} c is attributed to the loss of 10 water and 2 Iodine molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of 10 water and two Iodine molecules in TGA curve.

2. The second endothermic peak at 256.25 ^{0} c is due to the decomposition of compound and this peak in the second stage of decomposition is attributed to the loss of 03 Iodine and 16 oxygen molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of 03 Iodine and 16 oxygen molecules in the TGA curve.[17-18]

Table 3. DTA data for Bismuth Iodate gel grown crystal

Sr. No	Peak recorded	Nature	Peak height	On set	Area (m J)	ΔH (J/gm)
1	87.50 ^{0} c	endothermic	- 14.66	53.84 ^{0} c	1022.515	26.364
2	256.25 ^{0} c	endothermic	- 47.33	192.30^0 C	1591.147	42.875
3	381.26 ^{0} c	endothermic	- 23.99	330.76 ^{0} c	963.432	23.880

3. The third endothermic peak at 381.26 ^{0} c is due to the decomposition of compound and this peak in the third stage of decomposition is attributed to the loss of 09 Iodine and 22 oxygen molecules. This endothermic peak observed in the DTA curve corresponds to the weight loss of 09 Iodine and 22 oxygen molecules in the TGA curve.

Beyond 904.020 ^{0} c the reaction proceeds once finally residue Bi_5O_7 I decomposes slightly and stable residue Bi_2O_3 remains up to end of the analysis.

5.2. 3 Differential Thermal Gravimetric (DTG)

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

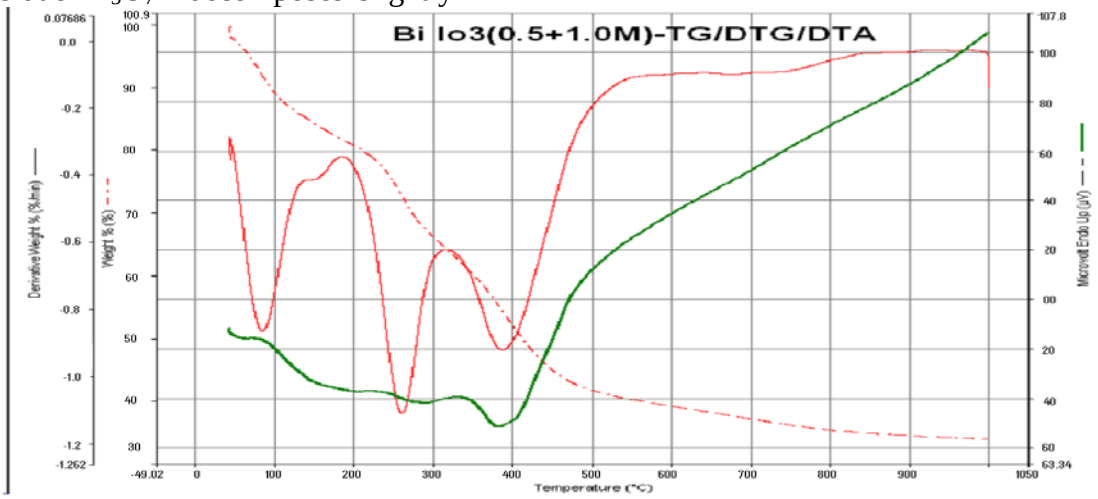

Fig 6 DTG curve for Bismuth Iodate gel grown crystals

1. The endothermic peak at 87.50 ^{0} c is due to the decomposition of Bismuth Iodate losing 10 water and Iodine molecules. In the first stage of decomposition peak at 87.50 ^{0} c is attributed to the loss of I_2 and 10 H_2O molecules. This endothermic peak observed in the DTG curve indicates that the reaction starts at 44.020 ^{0} c and the inflection occurs at 75.25 ^{0} c. the peak observation in DTG curve corresponds to the weight loss in TGA curve.

Table 4 DTG data for Bismuth Iodate gel grown crystals

Sr. No	Peak	On set	Inflection point

3.	1	87.50 ^{0}c	44.020 ^{0}c	75.25 ^{0}c
	2	256.25 ^{0}c	224.71 ^{0}c	251.25 ^{0}c
	3	381.26 ^{0}c	337.50 ^{0}c	375.50 ^{0}c

2.

The endothermic peak at 256.25 ^{0}c is due to the decomposition of compound and this peak in second stage of decomposition is attributed to the loss of 1.5 I_2 and 8O_2 molecules. This endothermic peak observed in the DTG curve indicates that the reaction starts at 224.71 ^{0} c and the inflection occurs at 251.25 ^{0} c. The peak observation in DTG curve corresponds to the weight loss in TGA curve.

3The endothermic peak at 381.26 ^{0}c is due to the decomposition of compound and this peak in third stage of decomposition is attributed to the loss of 4.5 I_2 and 11O_2 molecules. This endothermic peak observed in the DTG curve indicates that the reaction starts at 337.50 ^{0} c and the inflection occurs at 375.50 ^{0} c. The peak observation in DTG curve corresponds to the weight loss in TGA curve. Beyond 904.020 ^{0}c the reaction proceeds once finally residue Bi_5O_7 I decomposes slightly and stable residue Bi_2O_3 remains up to end of the analysis.

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

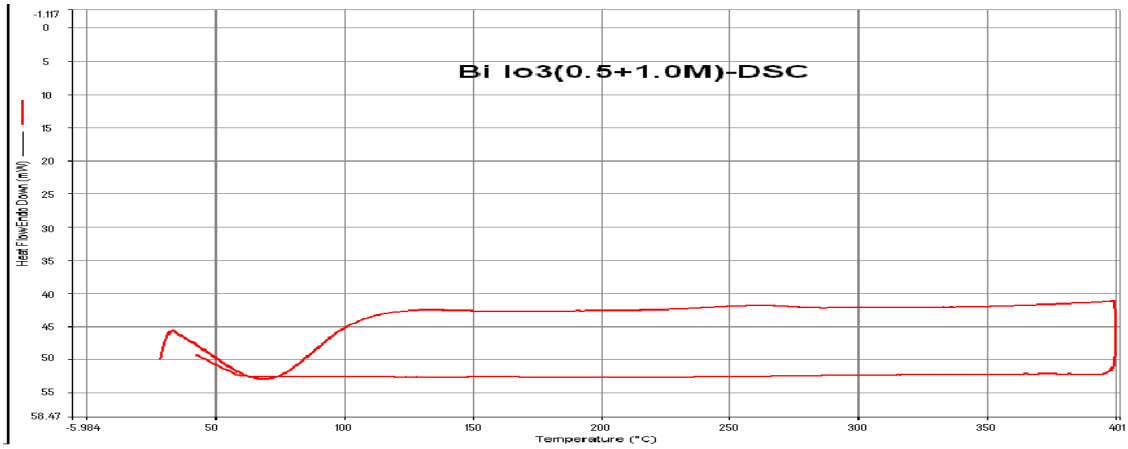

Fig 7 DSC curve for Bismuth Iodate gel grown crystals

Table 5 DSC data for Bismuth Iodate gel grown crystals

Sample	Weight of sample	Change in Enthalpy (ΔH)	Transition temperature
Bismuth Iodate $Bi(IO_3)_3$	5.600 mg	0.1163 KJ/mole	67.60 ^{0}c
		- 7852 – 0.004 KJ/mole	260.23 ^{0}c

There are two stages of DSC curves under study as follows

Stage I

1. The initiation temperature is 31.82 ^{0} c and equilibrium temperature is 110 ^{0} c at 31.82 ^{0} c (initiation temperature) initiation of phase change starts and is completed at peak endo-down temperature of 67.60 ^{0} c transition temperature [peak height is 7.1337 mw]. The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 110 ^{0}c

2. Area under the curve is 651.445 mJ.

3. Heat of transmission ΔH i.e. enthalpy change of transition is 116.3295 J/g which is 0.1163 KJ/mole since molecular weight is 1.000 g/mole

ΔH = ΔHF of phase transforma tion is also 0.1163 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 260.23 ^{0} c and equilibrium temperature is 370.55 ^{0} c at 260.23 ^{0} c (initiation temperature) peak height is 1.1875 mw initiation of phase change starts and is completed at peak endo-down temperature of 286.60 ^{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 370.55 ^{0}c

2. Area under the curve is 4.360 mJ.

3. Heat of transmission ΔH i.e. enthalpy change of transition is 0.7785 J/g which is -7.7852 – 0.004 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.

6. Conclusions

Thermal analysis reveals that Bismuth Iodate crystals grown in silica gel using the single diffusion method are structurally stable from 0 ^{0}C to 44.020 The crystals becomes thermally unstable from 44.020 ^{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 decoposes 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 Monoclinic $Bi(IO_3)_3$ 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 Monoclinic structure to a tetragonal Bi_2O_3 analogue is being characterized above three endothermic stages.

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