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Comparative study of semicoductors bismuth iodate, bismuth triiodide and bismuth trisulphide crystals

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ABSTRACT

In the present investigation, crystals of Bismuth Iodate[$Bi(IO_3)_3$], Bismuth Iodide[BiI_3] and Bismuth- Tri Sulphide [Bi_2S_3] were grown by a simple gel technique using single diffusion method. The optimum growth conditions were established by varying various parameters such as pH of gel solution, gel concentration, gel setting time, concentration of reactant etc. Gel was prepared by mixing sodium meta silicate ($Na_2SiO_35H_2O$), glacial acetic acid (CH_3COOH) and supernant bismuth chloride ($BiCl_3$) at pH value 4.4 and transferred in glass tube of diameter 2.5 cm and 25 cm in length. The mouth of test tube was covered by cotton plug and kept it for the setting. After setting the gel, it was left for aging. After 13 days duration the second supernant $K(IO_3)$, KI_3 and H_2S water gas solution was poured over the set gel by using pipette then it was kept undisturbed. After 72 hours of pouring the second supernatant, the small nucleation growth was observed at below the interface of gel. The good quality crystals of [$Bi(IO_3)_3$], [BiI_3] and [Bi_2S_3] were grown. These grown crystals were characterized by EDAX, SEM, and Magnetic Succebtibility.

Keywords: Gel Grown [$Bi(IO_3)_3$], BiI_3 and Bi_2S_3 Crystals, EDAX, SEM, and Magnetic Succebtibility.

INTRODUCTION

Large no of National and International laboratories are busy to grow various types of crystals. Their indusial efforts are to grow Iodate of various compounds similarly various Iodides, Sulphide and Oxalates as well as tartarates at same time some of scientist trying to make study of Iodate of various compounds for example Amit Patil [1-2],Garud [3-6] and Sharda Shitole [7-12] have tried for the comparative study of Iodates, and Bhavsar,Blank and Patel [13-17] had studied Iodide and Sulphide. Also the study of Iodates, Iodide and Sulphide by Nakamoto, Ranadive and Selvarajan [18-23]. In the present work, sincere efforts have been made to concentrate on single antiferromagnetic Bismuth and hence three important compounds of it i.e. crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide have been successfully grown.

However, there are very few reports in the literature on the growth of these crystals by gel method. These three types of crystals were grown by single diffusion gel method in which respective crystals were synthesized by control precipitation. These crystals have been characterized by different techniques. Paper deals with comparative study of all these crystals regarding their growth and characterization. All the results obtained regarding growth and characterization are tried to put at a glance of three types of crystals in the present work. .

MATERIALS AND METHODS

Growth

Crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide were grown by gel method by using single diffusion techniques. Table 1 gives details about method and chemicals used, different habits of crystals obtained, their transparency, etc.

Monoclinic Bismuth Iodate crystals were obtained. Most of the Bismuth Iodate crystals were transparent, shining, well isolated and very few of them were opaque. Single diffusion method is found more suitable for growth of these crystals.

Table 1: Crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide

Type	Method	Chemicals used	Crystal habits	Quality
Bismuth Iodate [$Bi(IO_3)_3$]	Gel method by using single diffusion techniques	$Na_2SiO_3 5H_2O$, CH_3COOH, $BiCl_3$ and KIO_3	Monoclinic	Transparent, few opaque
Bismuth Iodide [BiI_3]	Gel method by using single diffusion techniques	$Na_2SiO_3 5H_2O$, CH_3COOH, $BiCl_3$ and KI	Hexagonal	Transparent, few opaque, at center
Bismuth Tri-Sulphide [Bi_2S_3]	Gel method by using single diffusion techniques	$Na_2SiO_3 5H_2O$, CH_3COOH, $BiCl_3$ and H_2S gas in water solution	Orthorhombic OR Rhombus	Opaque Transparent, Both type

Some of grown Bismuth Iodide crystals found to be hexagonal shaped micro crystals. These crystals were found to be grown near the gel interface. Most of them were opaque and very few of them were transparent crystals. Single diffusion technique proved to be suitable for growth. The structure of Bismuth Tri-Sulphide crystals found to be Orthorhombic or Rhombus. It was found that as the concentration of the reactant $BiCl_3$ in the gel is increased, the size of the spherulites is also increased. Single diffusion method is found more suitable for growth of these crystals.

RESULT AND DISCUSSION

These crystals possess better habits and better transparency among the grown crystals. Better transparency of Bismuth Tri-Sulphide may be due to presence of more Bismuth. Optimum growth conditions for gel grown crystals established by varying various parameters such as gel density, pH of gel, gel setting time, gel aging time, etc. are reported in Table 2.

Table 2: Optimum growth condition for gel grown Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide crystals

Parameters	Bismuth Iodate	Bismuth Iodide	Bismuth Tri-Suphide
Density of sodium meta silicate solution	1.04gm/cm^3	1.04gm/cm^3	1.04gm/cm^3
Amount of acetic acid	2N, 5 cc	2N, 5 cc	2 N, 5 c c
pH of mixture	4.4	4.4	4.4
Temperature	Room temperature	Room temperature	Room temperature
Gel setting time	13 days	13 days	13 days
Gel aging time	72 hours	72 hours	72 hours
Period of growth	36 days	33 days	31 days

For all these three crystals, suitable value of density of sodium Meta silicate solution is found to be 1.04 gm/cc, pH value for Bismuth Iodate, Bismuth Iodide and Bismuth Tri-Sulphide is found to be 4.4. For pH 4.4, gel took 13 days to set and this gel was allowed to age for 72 hours, Crystals were removed from test tubes after 36, 33 and 31days respectively. Further growth was not noticed. Sometimes crystal became opaque or translucent due to inclusion of silica in them. Reason may be the unnecessary exposure to silica gel. Various concentrations of reactants were tried. Experiments by interchanging the positions of reactants were also carried out. Once the optimum values of concentration of reactants were obtained, experiments of concentration programming were also carried out. All these parameters have more or less effect on growth and habit of these crystals.

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

Energy Dispersive Analysis by X rays (EDAX) is used for the quantitative analysis. In the present work elemental analysis of gel grown Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide crystals, was carried out at NCL National Chemical Laboratory Pune. fig 1 shows EDAX spectrum of Bismuth Iodate. Table 3. 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 $Bi(IO_3)_3$ in given crystals measured EDAX are close to with the estimated values calculated from molecular formula.

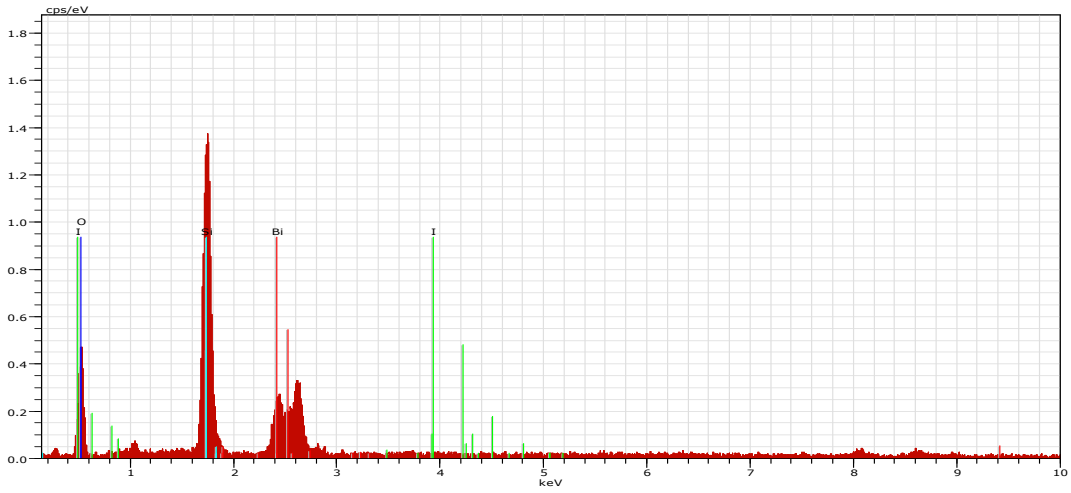

Fig 1 Energy Dispersive Spectrum of $Bi(IO_3)_3$

Table 3 for calculation of elemental analysis of gel grown Bismuth Iodate

Element	Content measured by EDAX		Content as calculated from molecular formula $Bi(IO_3)_3$	
	Wt %	At %	Wt %	At %
Bismuth	26.96	15.63	28.48	15.68
Iodine	49.54	59.45	51.88	60.46
Oxygen	22.42	24.58	19.64	23.86
	98.92		100.00	

Fig 2 shows EDAX spectrum of Bismuth Iodide. Table 4 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 BiI_3 in given crystals measured EDAX are close to with the estimated values calculated from molecular formula

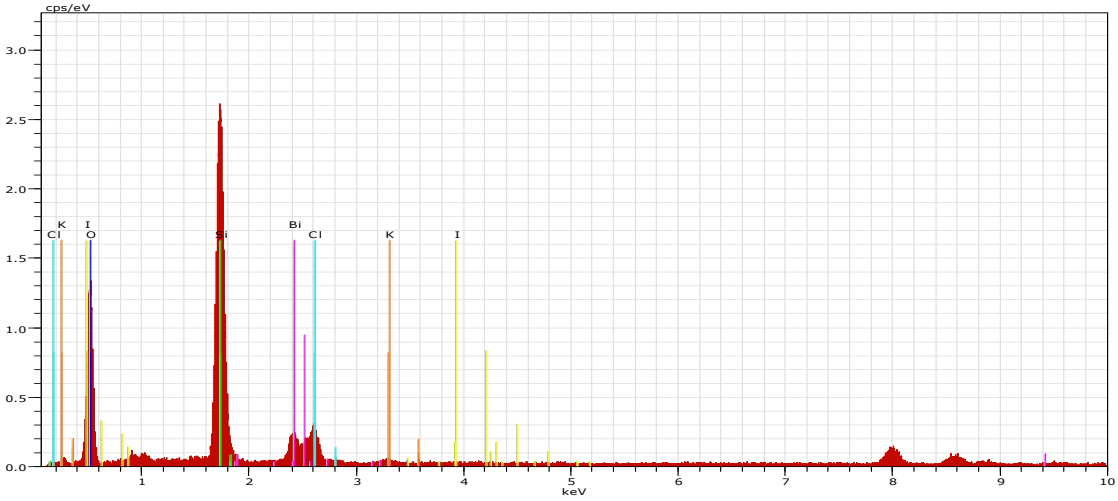

Fig 2 Energy Dispersive Spectrum of BiI_3

Table 4 Calculation of elemental analysis of gel grown Bismuth Iodide

Element	Content measured by EDAX		Content as calculated from molecular formula BiI_3	
	Wt %	At %	Wt %	At %
Bismuth	34.66 %	40.88	35.43 %	39.87
Iodide	63.83 %	57.98	64.55 %	58.92

Fig 3 shows EDAX spectrum of Bismuth Tri Sulphide Table 5 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_2S_3 in grown crystals measured EDAX are close to with the estimated values calculated from molecular formula

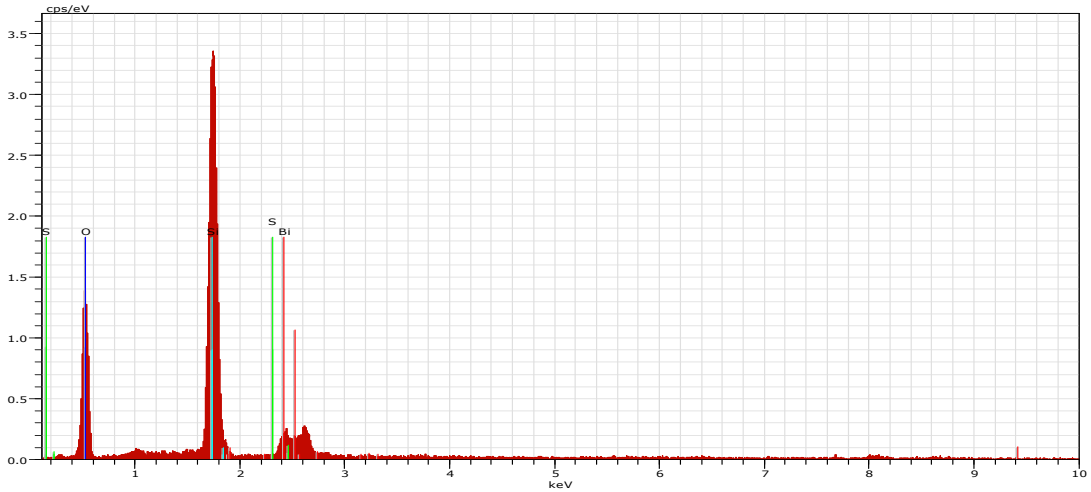

Fig 3 Energy Dispersive Spectrum of Bi_2S_3

Table 5 Calculation of elemental analysis of gel grown Bismuth Tri Sulphide

Element	Content measured by EDAX		Content as calculated from molecular formula Bi2S3	
	Wt %	At %	Wt %	At %
Bismuth	79.87 %	73.88	81.28 %	74.76
Sulphur	17.56 %	24.57	18.70 %	25.23

5.2 SEM: - Scanning Electron Microscopy of Bismuth Iodate Bi $(IO_3)_3$

In present work Scanning Electron Microscopy of powdered sample of gel grown Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide crystals, was carried at NCL (National Chemical Laboratory) Pune and the successive photograph were taken at the magnification of 1.00, 5.00, 10.00 KX all the photographs were taken at common width 9 mm and EHT magnification 20 KV. And represented as Fig 4 to 6.

Fig 4.I ,4.II and 4.III shows SEM images of the powdered sample of Bismuth Iodate. If Fig 4.I is considered the whole surface is uniformly illuminated. i.e. no difference of intensities means the surface is optically uniform. Fig 4. I also shows mainly two types of geometrical figures it shows some pentagons of difference size with different orientations. It also shows large no of grains of different size. Fig 4.II & Fig 4.III shows parts of phase on higher magnification, if the regions on individual pentagons in Fig are 4.I minutely observed. It also shows the well defined boundaries with no attachment of micro crystals, as the surface is optically uniform & with no attachment of micro crystals these facts manifest, the growth conditions of crystals of Bismuth Iodate are somewhat controlled. If figs 4.II & 4.III are considered the region marked by [a] from fig is 4.II magnified as region [b] in fig 4.III which supports the controlled growth conditions.

Fig (5.1) to (5.6) shows SEM images of the powdered sample of Bismuth Iodide. Fig (5.1) shows the part of the crystal of Bismuth Iodide. It is observed that the face is in general dark, but which is covered with bright figures of different geometrical shapes randomly. Some of the bright figures have regular geometrical shape. Some of them are triangular in shape while others are pentagonal in shape and some remaining is seen to be circular in shape. They do not have equal size and shape and randomly oriented throughout the surface. The magnified version of portion (I) is shown in figure (5.2), i.e. figure (5.2) shows that the various figures of portion (I) from figure (5.1) is made up of grains having various size. Magnified version of portion (II) from figure (5.2) is shown in figure (5.3), which manifest the large grain size of portion (II) from figure (5.2). The enlarge size of portion (III) from figure (5.3) is shown in figure (5.4), which conformed spherical shape of the various grains of almost same size. Figure (5.5) shows enlarge size of grains of portion (IV), which conformed the shape of the grains are spherules.

Fig 4.I

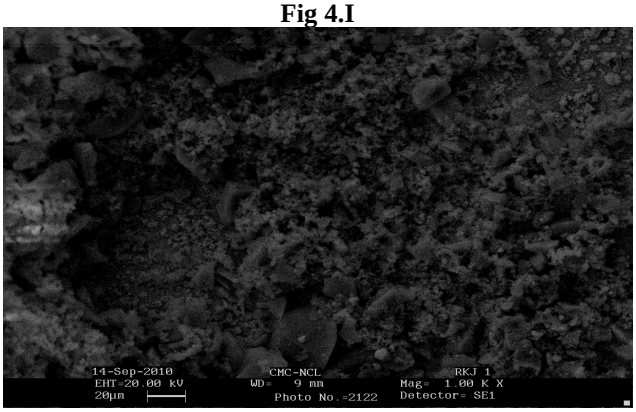

Fig 4. II region (a)

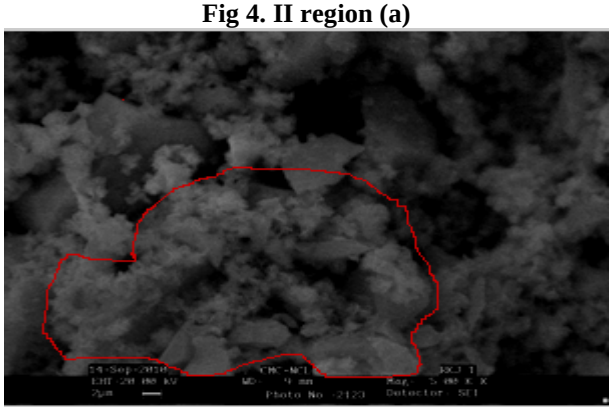

Fig 4. III region (b)

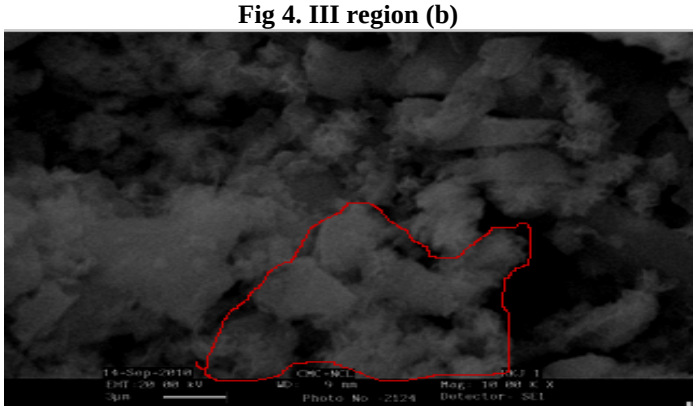

Fig 4.I ,4.II and 4.III shows SEM images of the powdered sample of Bismuth Iodate

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Fig 5.1 Portion I

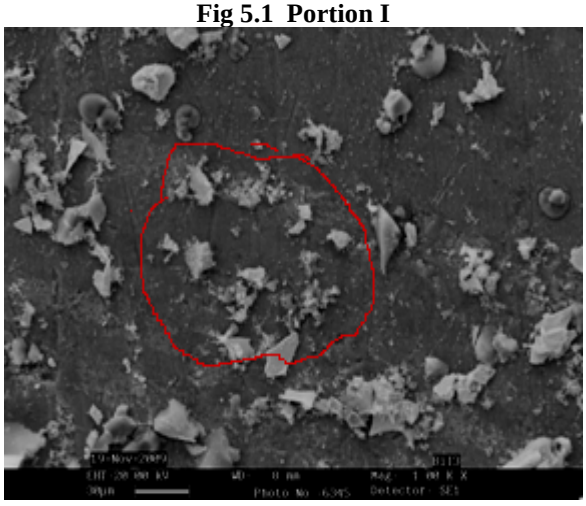

Fig 5.2 Portion II

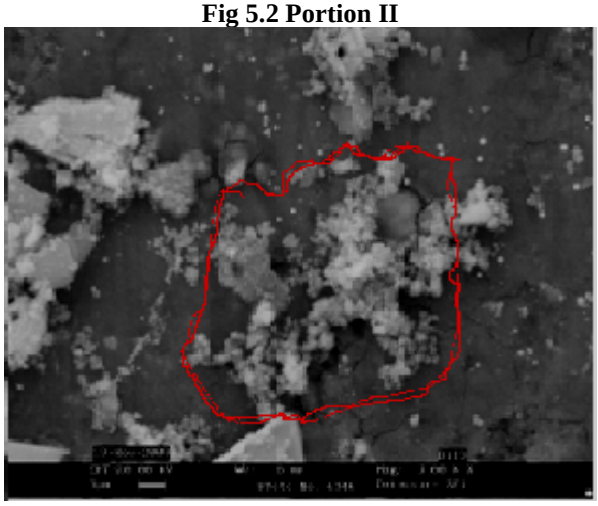

Fig 5.3 Portion III

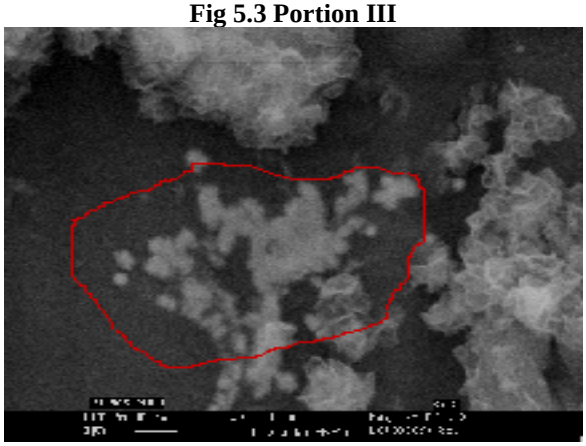

Fig 5.4 Portion IV

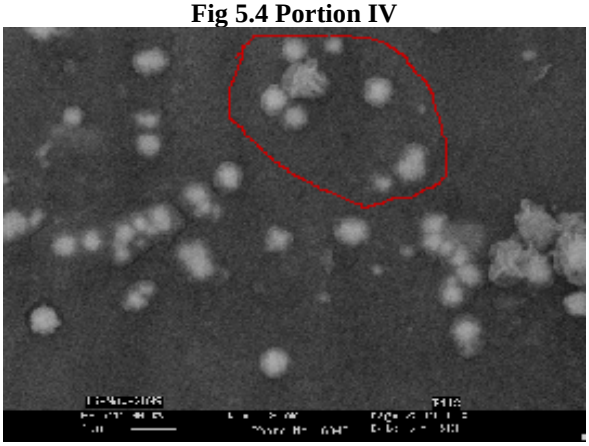

Fig 5.5

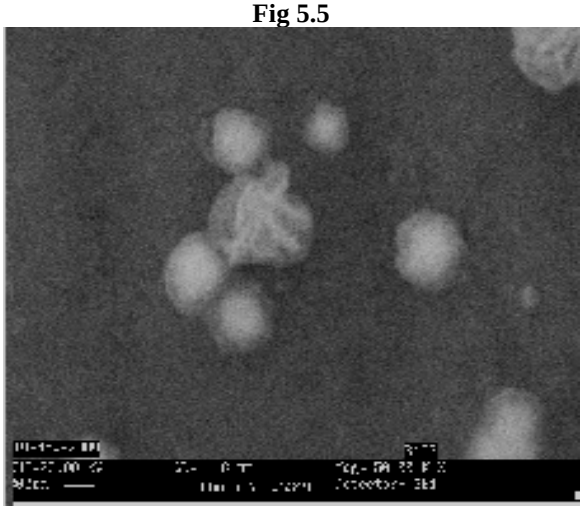

Fig 5.6

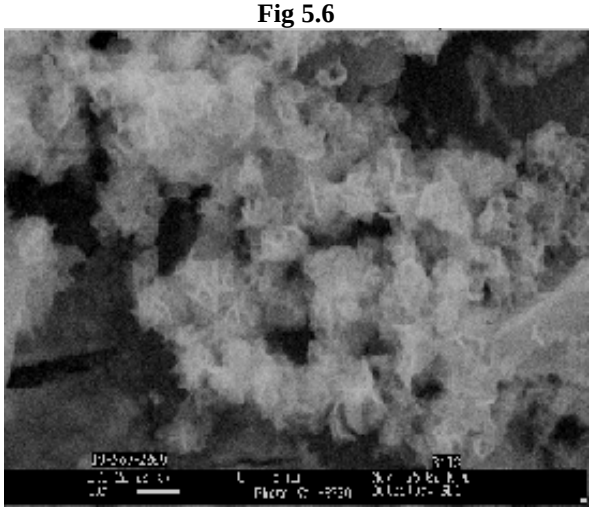

Fig. (5.1) to (5.6) Shows SEM Images of BiI3 Crystals

Fig (6.1) to (6.6) shows SEM images of the powdered sample of Bismuth Tri Sulphide. Fig (6.1) 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.

Fig 6.1 Region I

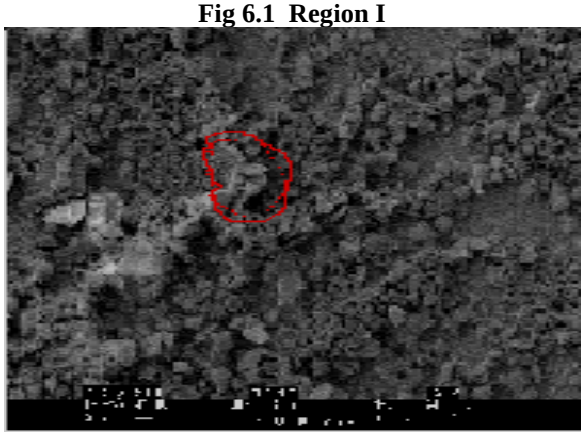

Fig 6.2 Region II

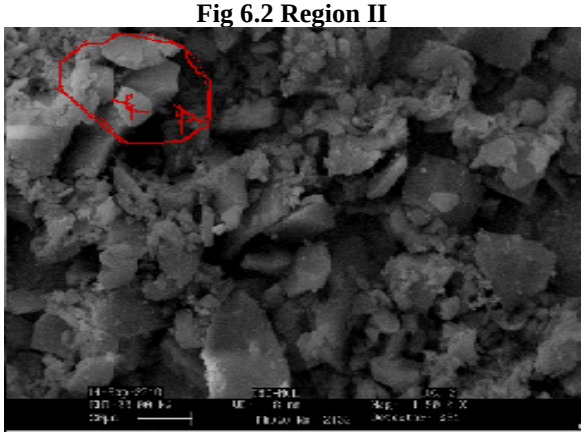

Fig 6.3 Region III

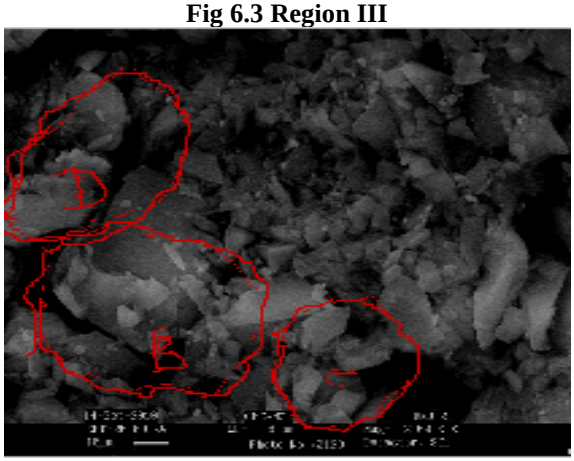

Fig 6.4 Region IV

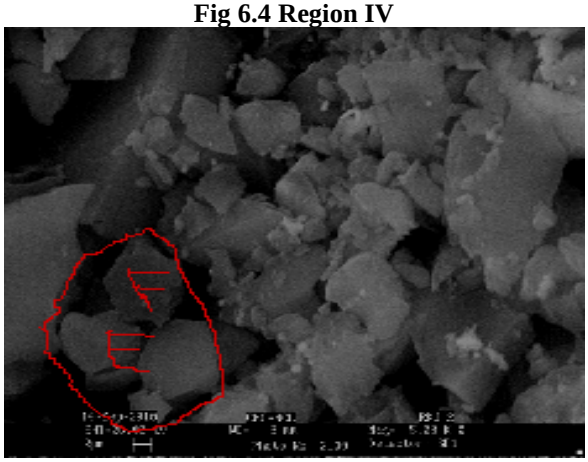

Fig 6.5

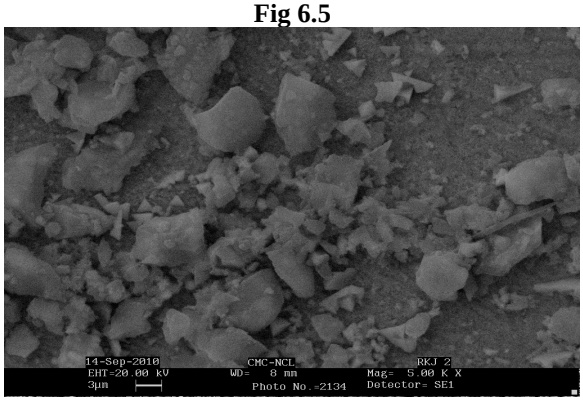

Fig 6.6

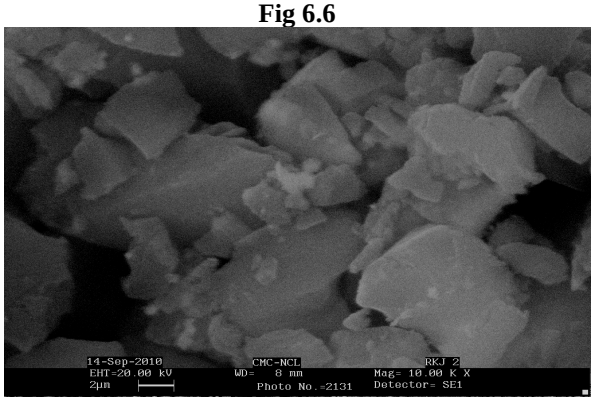

Fig (6.1) to (6.6) shows SEM Images of sample of Bismuth Tri Sulphide

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 6.1 a small region labeled as small (a), at 0.5 KX is shown as (A) in fig 6.2. 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. In fig 6.3 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 6.3 shows attachment of many micro crystals. If we compare region (B), (C) & (D) on fig 6.3 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 6.4. 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 6.4 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 6.5 i.e. Region shown in fig 6.4 have controlled condition as compare to fig 6.5. If fig 6.6 is observed it indicates well defined some pentagon with no attachment of micro crystals i.e. it confirms the controlled growth conditions.

5.3 MAGNETIC SUCCEPTIBILITY: -

In present work Magnetic Susceptibility of powdered sample of gel grown Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide crystals, was carried out at Department of Physical Science, N.M.U. Jalgaon the graphical representation of Magnetic Field (H) Gauss V/s χ_m x 10^{-6} cm^3 $mole^{-1}$ of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide crystals, is as shown in fig 7 ,8 and 9 respectively.

From graphical representation of Magnetic Field (H) Gauss V/s χ_m x 10^{-6} cm^3 $mole^{-1}$ of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide crystals, it is clear that Grown samples in initial steps behaves as diamagnetic substance in low magnetic field and behaves as paramagnetic substance at high magnetic field.

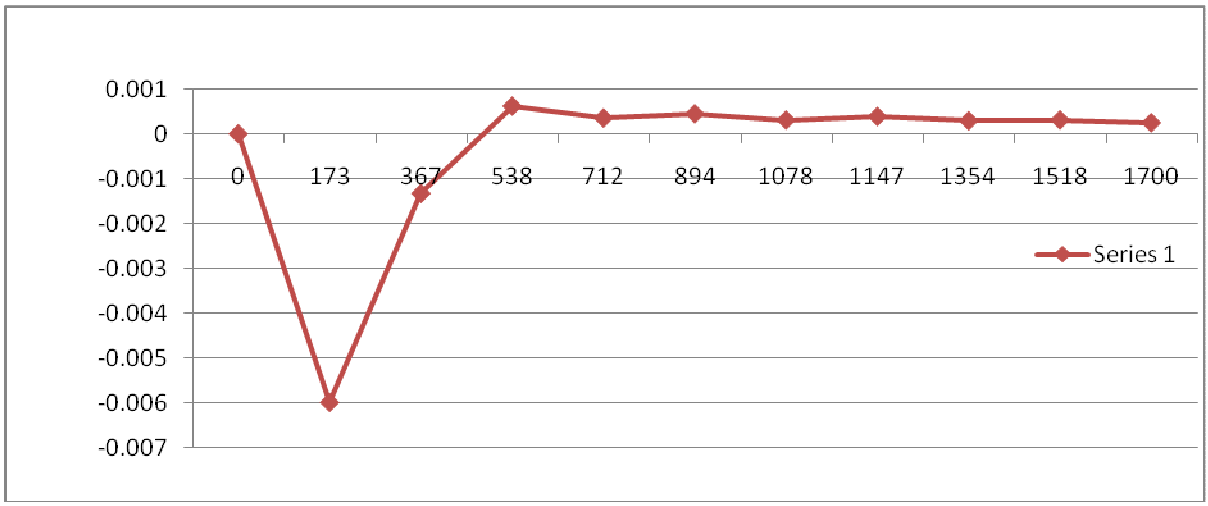

Fig 7 Graph of Magnetic Field (H) Gauss V/s χ_m x 10^{-6} cm^3 $mole^{-1}$ of $Bi(IO_3)_3$

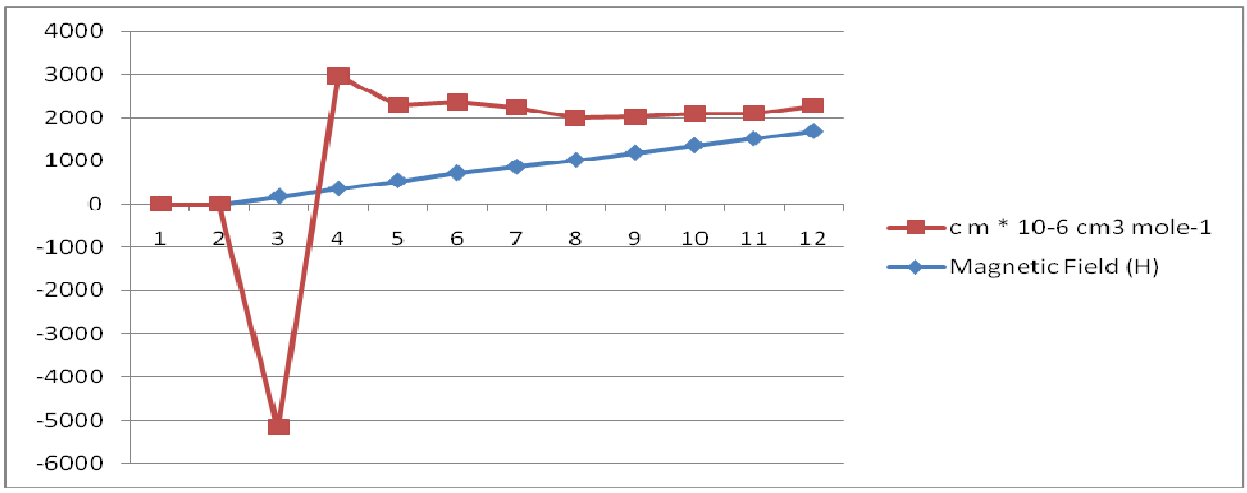

Fig 8 Graph of Magnetic Field (H) Gauss V/s χ_m x 10^{-6} cm^3 $mole^{-1}$ of BiI_3

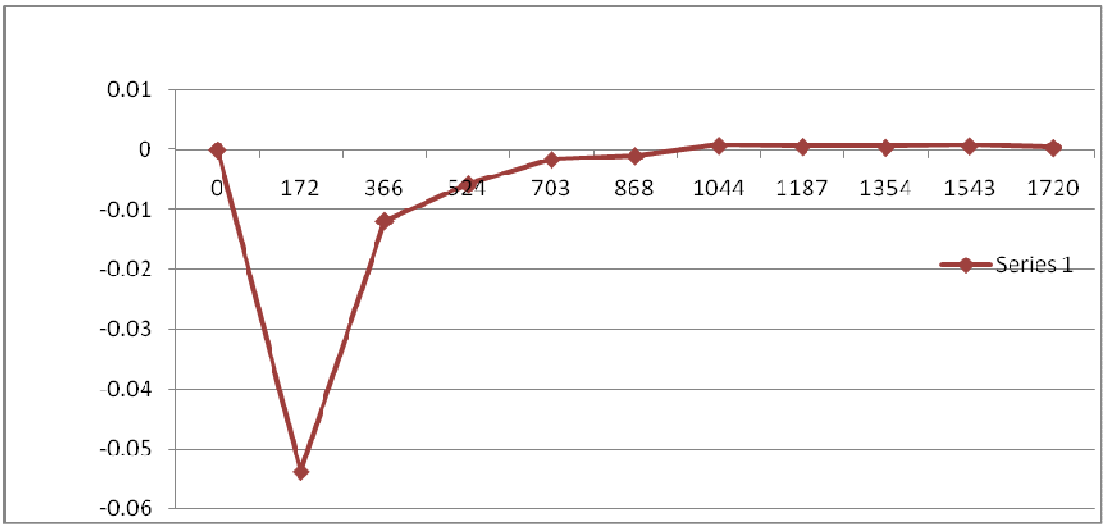

Fig 9 Graph of Magnetic Field (H) Gauss V/s χ_m x 10^{-6} cm^3 $mole^{-1}$ of Bi_2S_3

CONCLUSION

1. Crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tr-Sulphide are quite transparent, shining and are of good quality.
2. Gel growth technique is suitable for growing crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-Sulphide.
3. Different habits of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-Sulphide crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants etc.
4. Well known Liesegang phenomenon is observed in the growth of Bismuth Iodate and Bismuth Tri-Sulphide crystals.
5. From EDAX Observed values of all the grown samples, are well match with values calculated from molecular formula.
6. From SEM the grain size of Bismuth Iodate and Bismuth Tri-Sulphide crystals are spherical & pentagonal. While from SEM the grain size of Bismuth Iodide crystals are spherical,
7. The value of magnetic susceptibility of Bismuth Iodate, Bismuth Iodide and Bismuth Tr-Sulphide are closely related to theoretical ones. i.e. Material Bismuth Iodate, Bismuth Iodide and Bismuth Tri-Sulphide are diamagnetic up to 1000 Gauss and behaves as a paramagnetic substance above 1000 Gauss. Magnetic susceptibility is decreased as increase in temperature.
8. Most suitable value of gel density is found to be 1.04 gm/cc. Aging helps in controlling nucleation rate and the pH value of 4.4 is found to be suitable for growing these crystals.

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