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MAGNETIC AND ELECTRIC PROPERTIES OF SEMICONDUTER BISMUTH TRI SULPHIDE (BI_2S_3) GROWN BY GEL METHOD

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In the present investigation, crystals of 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 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 Orthorhombic or Rhombus Bi_2S_3 crystals were grown in* 31 *days. These grown crystals were characterized by Magnetic Susceptibility, Electrical Conductivity, EDAX and SEM.*

Keywords: *GEL GROWN BI_2S_3 CRYSTALS, MAGNETIC SUSCEPTIBILITY, ELECTRICAL CONDUCTIVITY, EDAX AND SEM.*

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1. INTRODUCTION

Now a day, various crystals have been used in electronic industry for controlling the frequency of radio waves, optical property in polarizing microscopes, in microwave communication, in digital telephonic instrumentation, in wireless and optical communication, in electronic and photonic devices [1-7]. A systematic study of crystallization in gel begins with Leisgang's famous discovery of periodic crystallization in gels. This method has gained considerable attention because of its simplicity and effectiveness in growing single crystal of certain compounds. This method is an alternative technique to solution growth with controlled diffusion. This growth process is free from convection. This is purifying process, free from thermal strain [8, 9]. Crystal habit of various crystals, grown under different conditions and also by different methods were described by H. E. Buckley [10], P. Hartman [11], K. Kern [12], A. A. Chernor [13], W. K. Burton [14] and J. W. Mullin [15]. The various process parameters such as degree of saturation, type of solvent [16], pH of the gel media [17, 18], presence of impurities [19] and the change in growth temperature also presumably affect significantly the morphology of the crystal [20]. In the present study, crystals of Bi_2S_3 were grown by a simple gel technique using single diffusion method. The optimum growth conditions for crystals were obtained. These conditions were established & reported.

2. MATERIALS AND METHODS

Test tubes are used as crystallizing vessels. Sodium met silicate ($Na_2SiO_35H_2O$) gel was used as a growth media. Gel was prepared by glacial acetic acid and sodium metal silicate, having different pH values .The chemical used for growth of single crystals of Bismuth Tri-Sulphide were CH_3COOH, $Na_2Sio_35H_2o$, $Bicl_3$ or $Bi(No_3)_3$ and H_2S water gas solution all chemicals are of AR grade .Different molar masses were tried to determined the optimum growth conditions one of the reactant having different concentration were incorporated into gel. This solution was then transferred into borosil glass tube of diameter 2.5 cm and 25 cm in length (height). The mouth of the tube was covered by cotton plug. After setting of the gel it was left for aging for different periods of time other reactant having different concentrations was then added as supernant over the set gel. Experiments were carried out by changing different concentration of the reactants. The Chemical reaction inside the gel can be expressed as,

$$XCl_3 + 3Y_2S \rightarrow X_2S_3 + 6YCl$$

Or

$$2X(NO_3)_3 + 3Y_2S \rightarrow X_2S_3 + 6Y(NO)_3$$

Where X = Bi and Y = K or Na

3. RESULT AND DISCUSSION

The optimum conditions for growth of bismuth Tri Sulphide crystals' are as shown in Table 1 and effect of concentration of reactant on habit and size of Bismuth Tri Sulphide crystals are given in Table 2.

Table 1 *– Optimum conditions for growth of bismuth Tri Sulphide crystals*

Sr. No	**Conditions**	**Bismuth Iodate**
1	Density of sodium metasilicate solution	1:04 gm/cm^3
2	Amount of 2N Acetic Acid	5 ml
3	pH of gel	4.40
4	Temperature	Room temperature
5	Concentration of $BiCl_3$	0.5 m, 1 m
6	Concentration of H_2S water gas solution	0.5 m
7	Gel Setting time	13 days
8	Gel aging time	72 hrs.
9	Period of growth crystal	31 days

Table 2 – *Effect of concentration of reactant on habit and size of Bismuth Tri Sulphide crystals*

Sr. No.	Concent-ration of reactant in gel	Concent-ration of reactant above gel	Remark
1	$BiCl_3$ 0.5 m 5 ml	H_2S water gas solution 15 ml	Large no of micro crystals were produced. They were attached to themselves and form a thick layer of crystals at the interface crystals were transparent shining tinny (Smaller) in size there were no diffusion of crystals below interface
2	$BiCl_3$ 1.0 m, 5 ml	H_2S water gas solution 15 ml	Large no of microcrystals were produced The shape of crystals appeared spherical and like a stones with high magnification color is reddish, white the crystals were opaque form a circular ring in test tube and day by day their smaller size remain constant.
3	$BiCl_3$ 1.5 m, 5 ml	H_2S water gas solution 15 ml	Large no of micro crystals produced but they are negligible and the size of crystals are more smaller than previous cases.

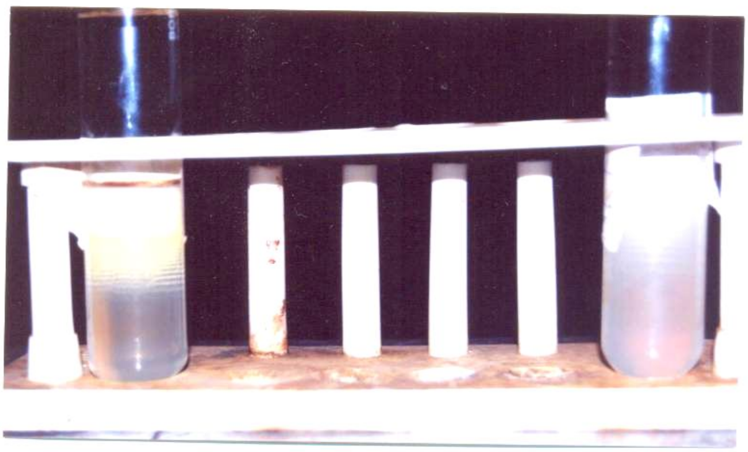


Fig. 1 – *Crystals of Bismuth Tri Sulphide inside the test tube*

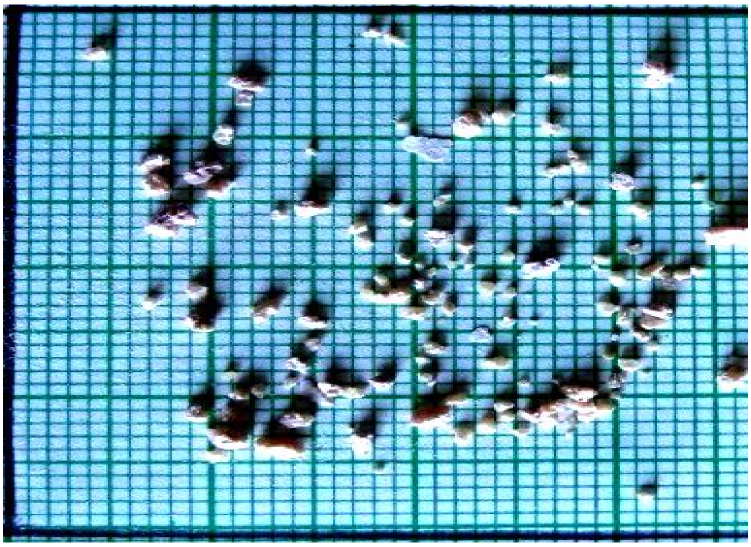


***Fig. 2** – Few crystals of Bismuth Tri Sulphide*

Fig. 1. Shows transparent crystals of Bismuth Tri Sulphide attached to themselves and forming a thick layer at the interface Fig. 2. Shows different habits with their scaling on a graph paper .Grown Bismuth Tri Sulphide crystals were characterized by Magnetic Susceptibility, Electrical Conductivity, and EDAX and SEM.

3.1 Magnetic Susceptibility

Experiment for Bismuth Tri Sulphide

***Table 3** – Magnetic Susceptibility of Bi_2S_3*

Sr.No	Current in A	Magnetic Field (H) Guass	Weight of sample in gm	Difference in wt m	$\chi_m \times 10^{-6}$ cm^3 mole^{-1}
1	0	0	4.615	----	0
2	0.2	172	4.617	- 0.002	- 0.05385
3	0.4	366	4.617	- 0.002	- 0.01189
4	0.6	524	4.617	- 0.002	- 0.005802
5	0.8	703	4.616	- 0.001	- 0.001611
6	1.0	868	4.616	- 0.001	- 0.001057
7	1.2	1044	4.614	+ 0.001	+ 0.0007309
8	1.4	1187	4.614	+ 0.001	0.0005654
9	1.6	1354	4.614	+ 0.001	0.0004345
10	1.8	1543	4.613	+ 0.002	0.0006692
11	2.0	1720	4.613	+ 0.002	0.0003885

Observations:

a) Weight of empty holder + Holder Assembly (test tube) without magnetic field = 4.595 gm

b) Weight of empty holder + Holder Assembly (test tube) + sample powder without magnetic field = 4.615 gm
c) Weight of sample powder $M = b - a = 4.615 - 4.595 = 0.020$ gm

- m = Change in weight (m) of sample powder with magnetic field = 0.002 gm
- L = Height of sample powder in test tube = 1.1 cm
- ρ = Density of specimen = 7.39 g/cm^3
- H = Applied magnetic field = 366 gauss (for 0.4 A current)
- M = Weight of specimen examine = 0.020 gm
- g = Acceleration due to gravity = 980 cm/sec^2

Formula: The magnetic succeptibility (χ) of Bismuth Tri Sulphide (Bi_2S_3) powder is given by relation. $\chi = 2mgL\rho / MH^2 = 2 \times 980 \times 1.1 \times 7.39 \times (-0.002) / 0.020 \times (366)^2$ $\chi = -0.01189$

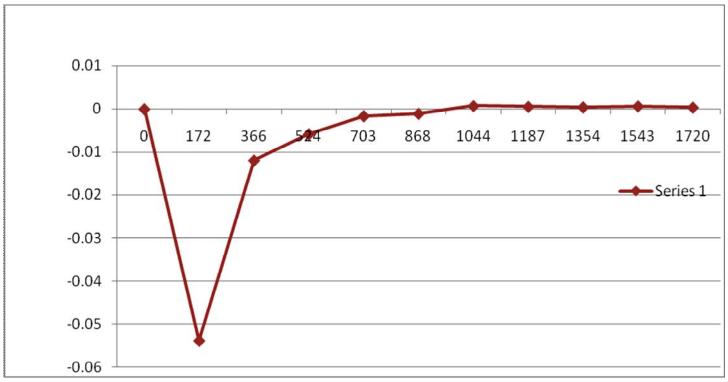


Fig. 3 *– Graph of Magnetic Field (H) Guass V/s* $\chi_m \times 10^{-6}$ *cm*^{3} *mole*$^{-1}$

3.2 Electrical Conductivity Of Bismuth Tri Sulphide Bi_2S_3

OBSERVATIONS: 1) Height / thickness of pallet = 0.536 cm
OBSERVATIONS: 2) Diameter of the pallet = 0.942 cm
OBSERVATIONS: 3) Radius of pallet = r = 0.471 cm = $d/2$
OBSERVATIONS: 4) Voltage = 0.50 mv (constant)
$K = l/RA$ $K = l/R\pi r^2$ (since A = πr^2) l = 0.536 cm = 5.36×10^{-4} m
r = 0.471 cm = 4.71×10^{-4} m)
$K = 5.36 \times 10^{-4} / R \times 3.142 \times (4.71 \times 10^{-4})^2$
$K = 5.36 \times 10^{-4} / R \times 3.142 \times (4.71)^2 \times 10^{-8}$
$K = 5.36 / R \times 3.142 \times (4.71)^2 \times 10^{-4}$
$K = 5.36 \times 10^4 / R \times 3.142 \times 22.18$, $K = 5.36 \times 10^4 / R \times 69.702$
$K = 0.07690 \times 10^4 / R$, $K = 7.6901 \times 10^2 / R$, K = 769.01 / R

***Table 4** – Electrical Conductivity Of Bismuth Tri Sulphide Bi_2S_3*

Sr.No	Temp T, K	$1 \times 10^{-4}/T$	Current in A $I \times 10^{-4}$	Resis-tance R in Ω $R \times 10^{-4}$	Conduc-tivity in mho/cm $k \times 10^{-4}$	log K
1	423	23.64	$0.28 - 2.8 \times 10^{-4}$	01.7857	430.64	2.63411437
2	418	23.92	$0.28 - 2.8 \times 10^{-4}$	01.7857	430.64	2.63411437
3	413	24.21	$0.27 - 2.7 \times 10^{-4}$	01.8518	415.27	2.61833056
4	408	24.50	$0.26 - 2.6 \times 10^{-4}$	01.9230	399.9	2.6019514
5	403	24.81	$0.23 - 2.3 \times 10^{-4}$	02.1739	353.74	2.54868417
6	398	25.12	$0.23 - 2.3 \times 10^{-4}$	02.1739	353.74	2.54868417
7	393	25.44	$0.20 - 2.0 \times 10^{-4}$	02.5000	307.6	2.48798633
8	388	25.77	$0.19 - 1.9 \times 10^{-4}$	02.6315	292.33	2.46587339
9	383	26.10	$0.19 - 1.9 \times 10^{-4}$	02.6315	292.33	2.46587339
10	378	26.75	$0.18 - 1.8 \times 10^{-4}$	02.7777	276.85	2.44224453
11	373	26.80	$0.16 - 2.1 \times 10^{-4}$	03.1250	246.08	2.39107632
12	368	27.17	$0.16 - 1.6 \times 10^{-4}$	03.1250	246.08	2.39107632
13	363	27.54	$0.15 - 1.5 \times 10^{-4}$	03.3333	230.7	2.36304759
14	358	27.93	$0.14 - 1.4 \times 10^{-4}$	03.5714	215.32	2.33308437
15	353	28.32	$0.13 - 1.3 \times 10^{-4}$	03.8461	199.94	2.30089969
16	348	28.73	$0.12 - 1.2 \times 10^{-4}$	04.1616	184.78	2.26665496
17	343	29.15	$0.12 - 1.2 \times 10^{-4}$	04.1616	184.78	2.26665496
18	338	29.58	$0.11 - 1.1 \times 10^{-4}$	04.5454	169.18	2.22834902
19	333	30.03	$0.09 - 0.9 \times 10^{-4}$	05.5555	138.42	2.14119884
20	328	30.48	$0.09 - 0.9 \times 10^{-4}$	05.5555	138.42	2.14119884
21	323	30.95	$0.08 - 0.8 \times 10^{-4}$	06.2500	123.04	2.09004632
22	318	31.44	$0.07 - 0.7 \times 10^{-4}$	07.1428	107.66	2.03205438
23	313	31.94	$0.07 - 0.7 \times 10^{-4}$	07.1428	107.66	2.03205438
24	308	32.46	$0.06 - 0.6 \times 10^{-4}$	08.3333	92.28	1.96510759
25	305	32.78	$0.04 - 0.4 \times 10^{-4}$	12.5000	61.52	1.78901633

Calculations : 1) $I = 0.28$ m $A = 2.8 \times 10^{-4}$ A
$V = 0.5$ mV $= 5 \times 10^{-4}$ V
$R = V/I = 5 \times 10^{-4} / 2.8 \times 10^{-4} = 1.7857\ \Omega$
$K = 769.01\ /\ R = 769.01/1.7857$
$K = 4.3064 \times 100$
$K = 430.64$ mho/cm
1) $I = 0.27$ m A $= 2.7 \times 10^{-4}$ A
$V = 0.5$ mV $= 5 = 10^{-4}$ V
$R = V/I = 5 \times 10^{-4} / 2.7 \times 10^{-4} = 1.8518\ \Omega$
$K = 769.01$ / R = 769.01 / 1.8518
K = 4.1527 × 100
K = 415.27 mho/cm

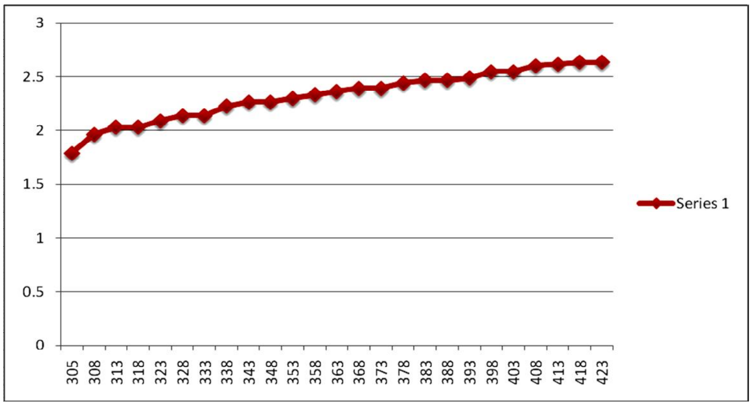


Fig. 4 *– Graph of Temp T º k V/s* log *K*

3.3 EDAX

Elemental Dispersive Analysis by X rays (E-DAX). Elemental analysis by X ray (EDAX) is used for the quantitative analysis. In the present work elemental analysis of gel grown Bismuth Tri Sulphide, crystals was carried out at the NCL National Chemical Laboratory Pune. Fig. 5 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.

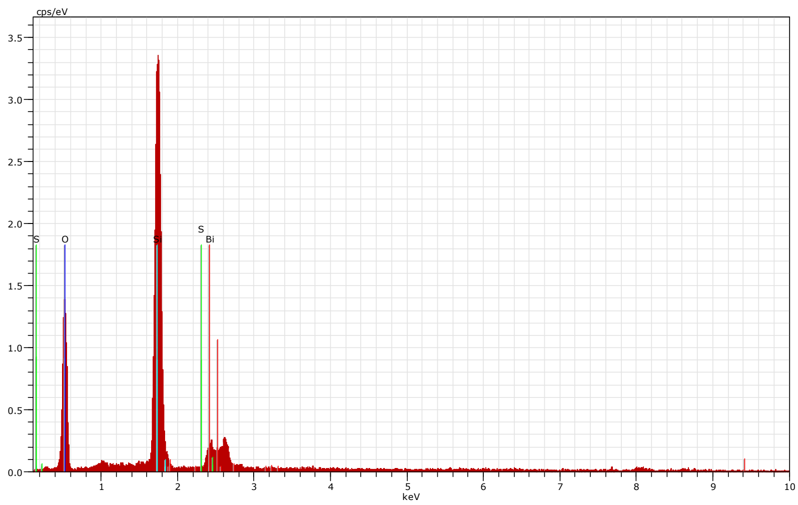


Fig. 5 *– Energy Dispersive Spectrum of* Bi_2S_3

***Table 5** – For calculation of elemental analysis of gel grown Bismuth Tri Sulphide*

Element	Content measured by EDAX		Content as calculated from molecular formula Bi_2S_3	
	Wt %	At %	Wt %	At %
Bismuth	76.07 %	67.48	81.28 %	74.76
Sulphur	15.26 %	20.57	18.70 %	21.68
Total	91.33 %	-	99.98 %	-

3.4 SEM

In present work Scanning Electron Microscopy of powdered sample of gel grown Bismuth Tri Sulphide crystals was carried at NCL (National Chemical Laboratory) Pune and the successive photographs were taken at the magnification of 0.5, 1.50, 2.00, 5.00 and 10.00 KX all the photographs were taken at common width 9 mm and EHT magnification 20 KV. And represented as 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. whole the surface is covered with figs of different shapes and size. Some of the figs are approximately seen to be triangular and pentagonal.

Fig 6.1 Region I

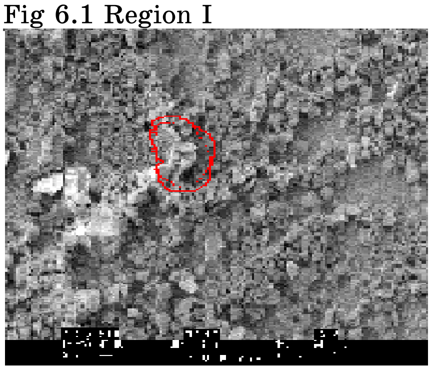


Fig 6.2 Region II

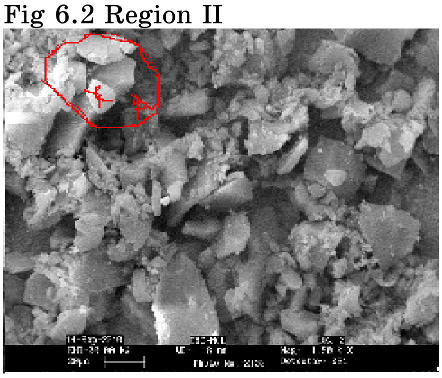


Fig 6.3 Region III

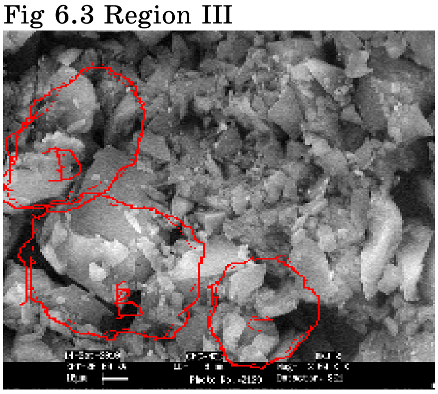


Fig 6.4 Region IV

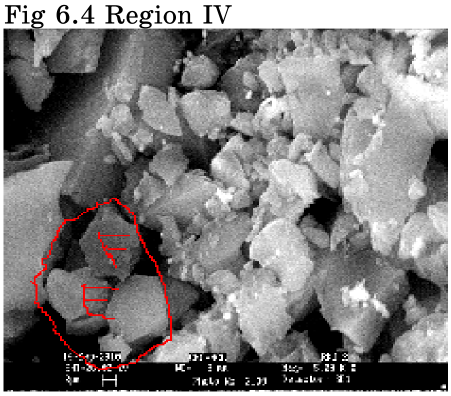


Fig 6.5

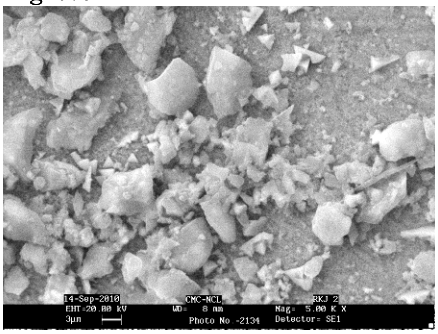
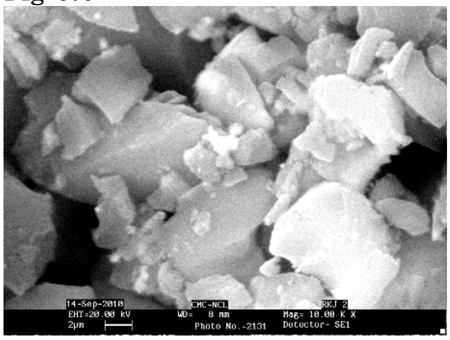


Fig 6.6



The edges triangle and 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 Figures in A region are pentagonal on minute observation Figure (X) in region (A) is perfectly pentagonal with well defined boundaries while the remaining two figs does nit 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) and (D) on Fig. 3 region B has more attachment of micro crystals than region (C), also by comparing region (C) and (D) region (C) has maximum micro crystals than (D) means we compare the attachment of micro crystals in region (B), (C) and (D) simultaneously we may conclude that it is die to different growth conditions on the same face. The growth rate in the region (B) is higher as compare to region (C) and 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 ie from Fig. 6.4 shows controlled growth condition as attachment of micro crystals in different part of fig is less. Where as 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 confrms the controlled growth conditions.

4. CONCLUSIONS

From the above studies, we observe that:

I. Magnetic measurement are importance in solving problems of molecular structure and bond type of the material. Offers, a means of detecting the presence of singly occupied electronic orbit. The value of magnetic susceptibility of Bi_2S_3 closely related to theoretical ones. I.e. material Bi_2S_3 is diamagnetic upto 1 K Gauss and behaves as a paramagnetic substance above 1 K Gauss. Magnetic susceptibility is decreased as increase in temperature.

II. The electrical conductivity of semiconductor crystals closely related to theoretical values with chemical nature of compound the electrical conductivity increases as increase in temperature

III. Gel growth technique is suitable for growing crystals of Bismuth Tri Sulphide.

IV. Different habits of Bismuth Tri Sulphide crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants etc.

V. Crystals are quite transparent, and are of good quality.

VI. From EDAX the observed values well match with values calculated from molecular formula.

VII. From SEM the grain size of sample is pentagonal and traingular.

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REFERENCES

1. S.L. Garud, K.B. Saraf, *B. Mater. Sci.* **31,** 639 (2008).
2. S.L. Garud, K.B. Saraf, *B. Mater. Sc.* **32,** 187 (2009).
3. Z. Blank, *J. Cryst. Growth* **18,** 281 (1973).
4. H. Bach, H. Kuppers, *Acta Crystall. B-Stru.* **34,** 263 (1978).
5. M. Schieber, A. Gril, I. Shidlovsky, *J. Cryst. Growth* **3-4,** 467 (1968).
6. K. Sangwal, A.R. Patel, *J. Cryst. Growth* **23,** 282 (1974).
7. M.S. Joshi, S.G. Trivedi, *Indian J. Pure Ap. Phy.* **21**, 435 (1983).
8. Z. Blank, W. Brenner, Y. Okamoto, *Mater. Res. Bull.* **3,** 555 (1968).
9. S.K. Kurtz, T.T. Perry, *J Appl. Phys.* **39,** 3798 (1968).
10. B. Morosin, J.G. Bergman, G.R. Crane, *Acta Crystall. B-Stru.* **29,** 1067 (1973).
11. Z. Blank, W. Brenner, *Nature* **222,** 79 (1969).
12. A.R. Patel, A.V. Rao, *J. Cryst. Growth* **43,** 351 (1978).
13. K. Nakamoto, *Infrared spectra of inorganic and coordination compounds* (New York: John Wiley and sons Inc.: 1970).
14. S.J. Shitole, K.B. Saraf, *B. Mater. Sci.* **24,** 461 (2001).
15. D. Ranadive, Z. Blank, W. Brenner, Y. Okamoto, *Nature* **223,** 829 (1969).
16. X.S. Shajan, C. Mahadevan, *B. Mater. Sci.* **27,** 327 (2004).
17. B.S. Kumar, M.H.R. Kutty, M.R.S. Kumar, K.R. Babu, *B. Mater. Sci.* **30,** 349 (2007).
18. S.K. Arora, A.J. Kothari, R.G. Patel, K.M. Chauhan, B.N. Chudasama, *J. Phys. Conf. Ser.* **28,** 48 (2006).
19. P. Selvarajan, B.N. Das, H.B. Gon, K.V. Rao, *J. Mater. Sci. Lett.* **12,** 1210 (1993).
20. S.K. Arora, A.R. Patel, *J. Mater. Sci.* **11,** 843 (1976).