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Growth and study of gel grown crystals of Bismuth-Trisulphide(Bi_2S_3)

Tukaram Kautik Patil* and Kishor Bansilal Saraf **

**Smt. G. G. Khadse Science, Arts and Com. College, Muktainagar(India)*
***Department of Physics, Pratap College, Amalner(India)*

ABSTRACT

Crystals of Bismuth-Trisulphide were grown by a simple gel technique using single diffusion method. The optimum growth condition were established by varying various parameters such as PH of gel solution gel concentration and gel setting time, concentration of reactants etc. crystals having different morphologies and habits, the crystal structure of Bi_2S_3 is Rhombus These crystals are transparent some were opaque and some translucent. The crystals were characterized using XRD, FTIR and chemical analysis.

Keywords: - Gel Technique Bismuth-Trisulphide crystals, XRD, FTIR, Chemical Analysis, gravimetric analysis, volumetric or titrimetric analysis and sp. Gravity.

INTRODUCTION

A large no of crystals required for the purpose of research and application can be grown by gel technique. The gel medium prevents turbulence and it provides a three dimensional crucible which permits the reagents to diffuse at a desirable controlled rate its softness and uniform nature constraining forces that exert on growing crystals (1,2) In initial stage of crystal growth Liessegang and Holms had observed beautiful Liessegang rings (3,4,5). The growth of crystals in gel media at an ambient temp which are insoluble or slightly soluble in water is fascinating alternative to the technique at high temp studied (6) gel technique have been illustrated by preparation of crystals of alkaline metal sulphide (7)& Brenner(8)crystals of sulphide exhibit nonlinear optical properties (9,10) and piezoelectric properties (11) Such Optical properties are found to be variety of application in large area of modern science, engendering and technology. In present work crystal of Bismuth-Trisulphide Bi_2S_3 was grown by gel technique using single diffusion method and optimum growth were established and reported.

MATERIALS AND METHODS

Test tube of diameter 2.5cm and 25cm in length were used as crystallizing vessels.gel was prepared by glacial acetic acid and Sodium metasilicate ($Na_2SiO_35H_2O$) having different pH

values .The chemical used for growth of crystals of Bismuth-Trisulphide were Ch_3CooH, $Na_2Sio_35H_2o$, $Bicl_3$ or $Bi(No_3)_3$, $_{H2S\ gas\ solution}$ all chemicals are of AR grade. The crystals were grown by usual single diffusion technique using following chemical reaction.

$2XCl_3 + 3Y_2S \rightarrow X_2S_3 + 6YCl$

Or

$2X\ (NO_3)_3 + 3Y_2S \rightarrow X_2S_3 + 6Y\ (NO_{3)}$

Where X=Bi and Y=K or Na.

RESULTS AND DISCUSSION

The various optimum conditions for growing crystals were established and are given in table (2) optimum conditions for growth of Bismuth-Trisulphide crystals.

Table (1) Effect of concentration of reactant on habit & size of Bismuth-Trisulphide crystals

Sr. No.	Concentration of reactant in gel	Concentration of reactant above gel	Remark
1	$Bicl_3$ 0.5m 5ml	H_2S gas water solution,15ml	Large no of micro crystals were produced. They were attached to themselves and form a thick larger of crystals at the interface crystals were transparent shining tinny (smaller) in size there were no diffusion of crystals below interface.
2	$Bicl_3$ 1.0m, 5ml	H_2S gas water solution, 15ml	Large no of microcrystal's 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	$Bicl_3$ 1.5m, 5ml	H_2S gas water solution, 15ml	Large no of micro crystals produced but they are negligible and the size of crystals are smaller than previous cases.

Table (2) Optimum conditions for growth of Bi2S3 crystals

Sr. No	Conditions	Bismuth-Trisulphide
1	Density of sodium metasilicate solution	1:04 gm/cm^3
2	Amount of 2N Acetic Acid	5ml
3	pH of gel	4.40
4	Temperature	Room temperature
5	Concentration of $BiCl_3$	0.5m, 1m
6	Concentration of H2S gas water solution	---------
7	Gel Setting time	13 days
8	Gel aging time	72hrs.
9	Period of growth crystal	31 days

Fig. (1) shows transparent crystals of Bismuth-Trisulphide attached to themselves and forming a thick layer at the interface of test tube. Fig (2) shows different habits with their scaling on a graph paper Grown Bismuth-Trisulphide crystals were characterized by XRD FTIR and the percentage in component of Bismuth and Sulphar is calculated and examined.

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

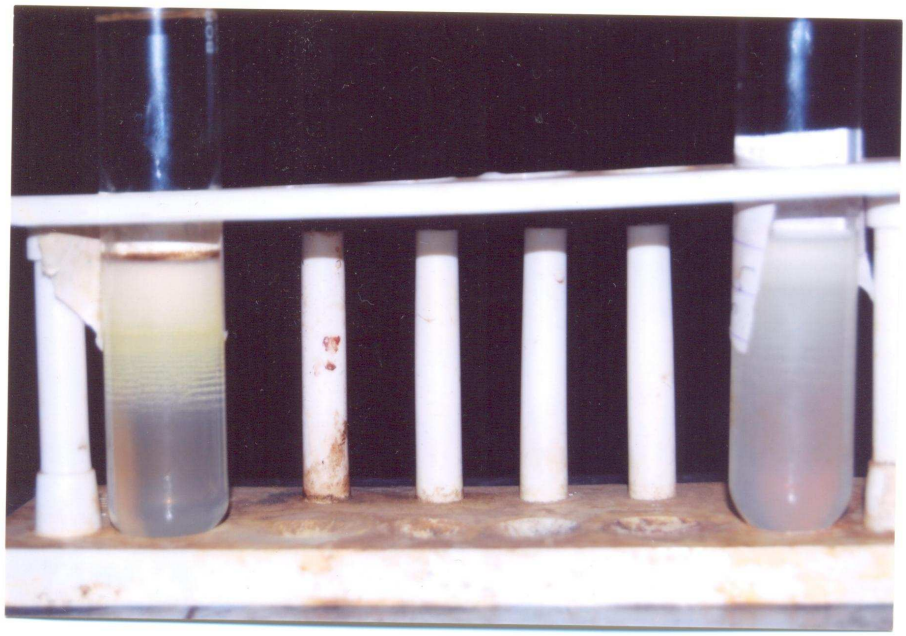


Fig. 2 Few Crystals of Bismuth-Trisulphide

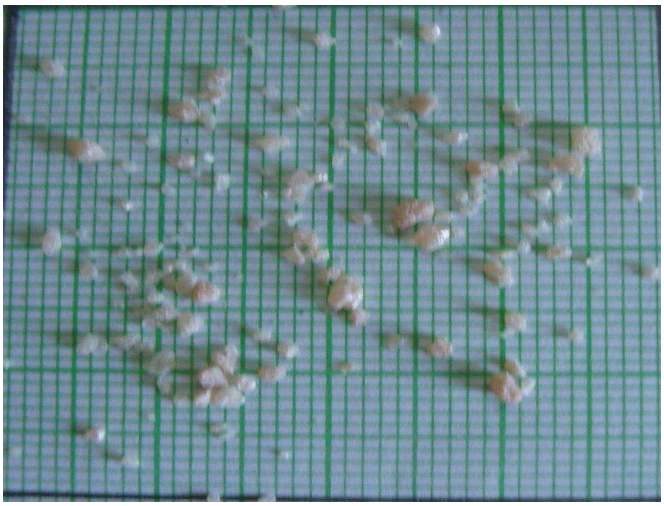
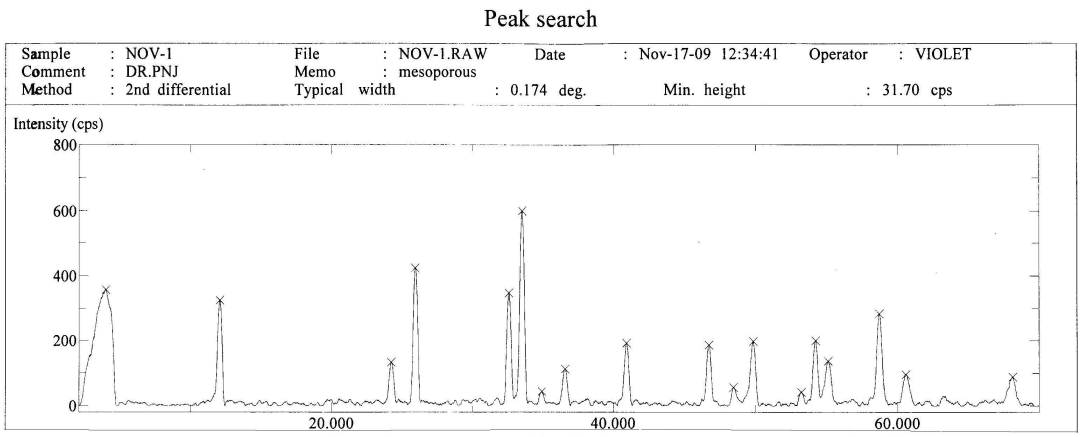


Fig.3 X-Ray diffractogram of Bismuth-trisulphide



X-ray diffractometry (XRD) :- X-ray diffractogram of gel grown crystals of Bismuth-Trisulphide 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.

Table 3.Calculated unit cell parameters

Sr. No.	Lattice parameters	Bismuth-Trisulphide $Bi2S_3$
1	System	Rhombus or orthorhombic
2	A	1.1136 nm
3	B	1.1256 nm
4	C	0.3968 nm
5	α	93.640 A˚
6	β	93.640 A˚
7	γ	93.640 A˚
8	V	3.060 eV

Table (4) calculated and observed values of d and h, k, l.

Peak No	Intensity	2 Theta in degree 2˚		FWHM	Indices h k l	d spacing value(A˚)	
		Observed	calculated			Observed	Calculated
1	357	3.940	3.848	0.188	3 0 2	22.4066	22.4078
2	326	12.060	12.266	0.447	2 3 0	7.3323	7.3318
3	134	24.200	24.040	0.447	1 1 1	3.6746	3.6756
4	424	25.900	25.910	0.424	3 1 0	3.4371	3.4300
5	348	32.600	32.594	0.424	3 0 1	2.7444	2.7404
6	600	33.540	33.499	0.424	3 1 1	2.6696	2.6490
7	44	34.940	34.798	0.235	2 4 0	2.5658	2.5600
8	113	36.560	36.528	0.400	2 3 1	2.4557	2.4560
9	192	40.940	40.985	0.376	1 4 1	2.2025	2.2045
10	187	46.720	46.732	0.424	4 3 1	1.9423	1.9450
11	56	48.440	48.508	0.376	0 6 0	1.8776	1.8740
12	198	49.820	49.818	0.471	6 1 0	1.8287	1.8340
13	42	53.240	53.276	0.29	0 6 1	1.7190	1.7130
14	200	54.240	54.301	0.447	1 6 1	1.6897	1.6820
15	138	55.120	55.098	0.471	6 1 1	1.6648	1.6650
16	285	58.700	58.697	0.471	2 4 2	1.5715	1.5720
17	96	60.560	60.564	0.212	7 2 0	1.5276	1.5230
18	88	68.160	68.158	0.353	1 1 6	1.3746	1.3700

Copper target and nickel filter were used from the powder diffraction data of Bismuth-Trisulphide shows Eighteen different peaks, corresponding d values and 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 are very well match with calculated values from computer program and also match with JCPDS card No - 06 - 0333 of Bi_2S_3 observed peaks in diffractogram shows Bismuth-Trisulphide crystals passes Rhombus or Orthorhombic structure. as shown in table(4) In Rhombus crystal structure the length of unit cells are different .but the three axis are perpendicular to each other i.e. $a \neq b \neq c$ & $\alpha = \gamma = \beta = 90$ degree as shown in table (3).

1) In rhombus or orthorhombic crystal structure The no. of different lattice is four and lattice symbol denoted by P, C, I and F cells..

2) Grain size determination of Bismuth-Trisulphide from XRD spectra. As seen from the XRD pattern each peak has got a finite width the grain size is determined by measuring the width of the line with highest intensity peak. The grain size can be calculated using formula .is 0.3415nm

FTIR of Bismuth-Trisulphide Bi_2S_3 1M, 0.5 M FTIR spectra of Bismuth-Trisulphide (Bi_2S_3) crystals spectrum of sample was recorded using SIMADZU Spectrometer at department of chemistry, university of Poona

Table (5) FTIR spectra analysis of Bismuth-Trisulphide(Bi_2S_3) crystals

Sr. No.	IR Peaks (Spectrum) cm^-	Intensity	Assignment
1	3662.94to3603.15	Broad band, strong	O-H stretching
2	3603.15 to 3064.99	Strong and broad	O-H stretching
3	2860	Normal and weak	C-H stretching with high energy
4	1712.85	strong, sharp	C=O stretching
5	966.37and960.58	Strong, sharp	O-H out of plane stretching (olefinic)
6	806.27and800.49	Strong, sharp	C-H bond out of plane stretching
7	752.26to704.04	Weak and broad	C-O or C-C stretching out of plane vibration
8	462.93 to 428.21	strong and sharp	Bimuth metal to sulpher

Fjg (4) FTIR spectra of Bismuth-Trisulphide (Bi_2S_3) crystals (1M)

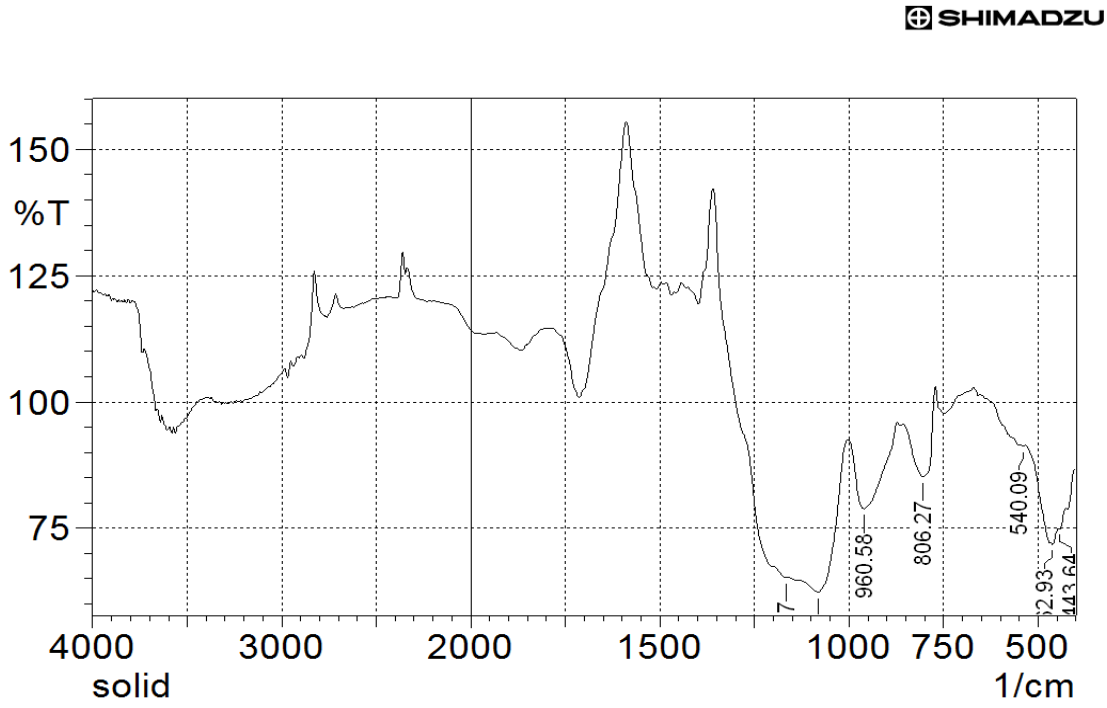
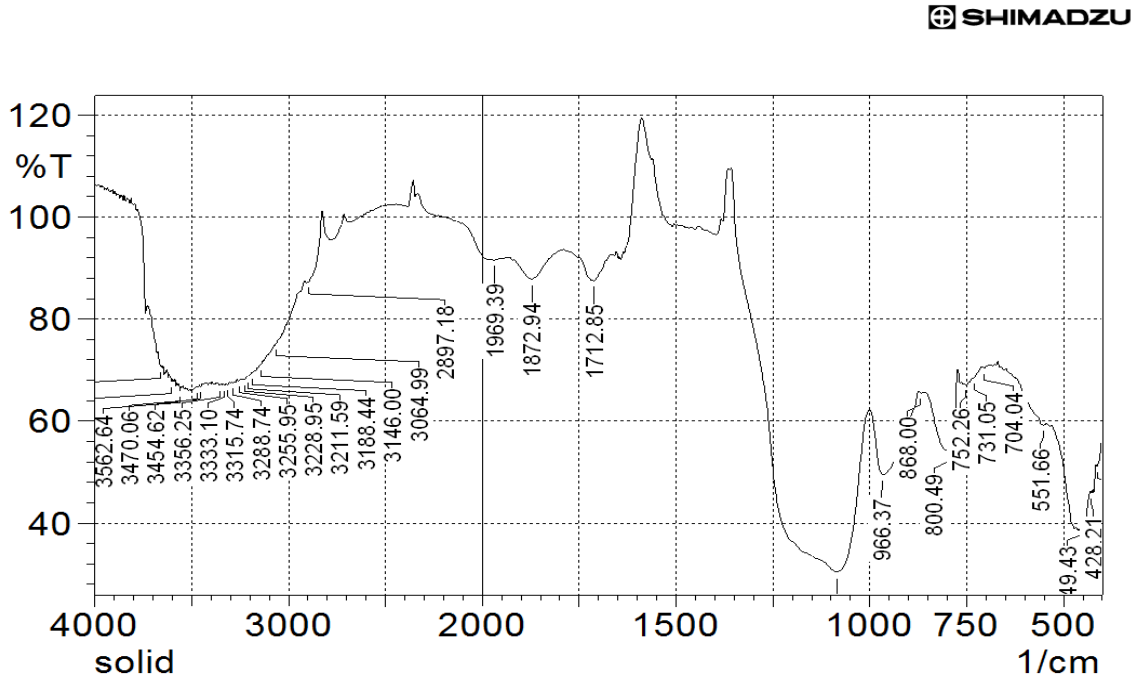


Fig 5. FTIR spectra of Bi_2S_3 (0.5M)



The FTIR Spectrum for a particular chemical compound is unique characteristics alone, reflecting as it does the geometry band strength and atomic masses of the substance. Therefore an important use of FTIR is the Identification of unknown functional group present in the chemical compounds. The FTIR Spectra of Bismuth-Trisulphide (Bi_2S_3) is as shown in fig. 4 & 5. The spectrum is scanned in region 4000 to 500 cm^{-1} using SHIMADZU spectrometer at dept. of chemistry in University of Pune. The result of FTIR spectra of Bismuth-Trisulphide crystals with observed band and their assignment are shown in table (5)

A few of the prominent vibration modes are empirically assigned here the bands around 3662.94to3603.15cm^{-1}attributed to asymmetric and symmetric O-H stretching of water. The O-H stretching freq appeared between3603.15to 3064.99 cm^{-1} is probably due to stretching vibration of Hydroxyl group-H bonded may be duo to Si-OH or O-H stretching of acetic acid.

The weak band appearing at 2860 cm^{-1} can be attributed to C-H stretching of Alkyl group. It may be due to the present of impurity of Bismuth acetate Acid. The strong &sharp band appearing at 1712.85 cm^{-1} can be attributed stretching vibration of Acetyl carbonyl group (CH_3-c =^{o}) with C=O stretching. The Band appearing at 966.37to960.58 cm^{-1} can be attributed to bending freq. of O-H group out of plane (olefinic). The freq. band appearing at 806.27&800.49 cm^{-1} can be attributed to bending freq. of C-H group out of plane.

The freq. band appearing at 752.26 to704.04 cm^{-1} can be attributed to stretching freq of C-O or C-C stretching out of plane. The freq band appearing at 462.93to428.21 can be attributed to metal Bismuth to Sulpher bond in same plane. The reaction of Acetic Acid [CH_3COOH] with Sodium-metasilacate ($Na_2Sio_35H_2O$) for titration and its supernant ($BiCl_3$) will be form Bismuth Acetate react with H_2S gas water solution to form Bismuth-Trisulphide as shown below:

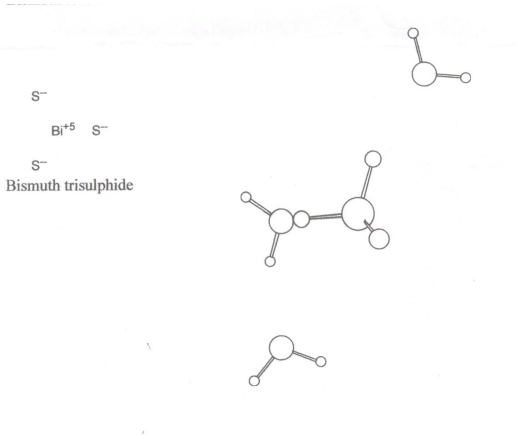


Fig. 6 Crystal structure of Bismuth-Trisulphide

Chemical Analysis:-

1) **Gravimetric Chemical Analysis of Bi_2S_3 Bismuth-Trisulphide** - *Estimation of Bismuth (Bi) From Bi_2S_3* Theoretically in 100 gm of Bismuth-Trisulphide there is 81.28% of Bismuth and practically 78.76% of Bismuth

Estimation of Sulpher (S) from Bismuth-Trisulphide

Theoretically in 100 gm of Bi_2S3_3 there is 18.70% sulpher (S) and practically 16.86% of sulpher (S)

Table 6.Result of gravimetric chemical Analysis

Element	Theoretical values (%)	Practical values (%)
Bismuth	81.28	78.76
Sulpher	18.70	16.86
	99.98	95.62

2) Volumetric / Titrimetric Analysis of Bi_2S_3 Bismuth-Trisulphide

Estimation / Determination of Bismuth from Bi_2S3 :-

Theoretically in 100gm of Bi_2S_3 there is 81.28% of Bismuth and Practically 79.93%of bismuth.

Estimation of Sulpher from Bismuth-Trisulphide Bi_2S_3 :- Theoretically in 100 gm of Bi_2S_3 there is 18.70% of sulpher and practically 18.26%of Iodine.

Table7. Result of volumetric analysis for Bi_2S_3

Sr. No.	**Element**	**Theoretical value (%)**	**Practical Value (%)**
1	Bismuth	81.28	79.93
2	Sulpher	18.70	18.26
		99.98	98.19

The results of gravimetric and volumetric chemical analysis are as shown in the table 6 &7. From tables we observed that the experimental values of Bismuth (Bi) and sulpher (S) are in good agreement with the theoretical ones. (Values)

3) Specific gravity of Bismuth-Trisulphide Bi_2S_3- Specific gravity of $Bi2S_3$ Practically is 7.06 gm/cm^3 is well match with Theoretical value 7.39 gm/cm^3

CONCLUSION

From the above studies we observe that -

- Gel growth technique is suitable for growing crystals of Bismuth-Trisulphide.
- Different habits of Bismuth-Trisulphide crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants etc.
- Well known Liesegang phenomenon is observed in the growth of Bismuth-Trisulphide crystals.
- Unit cell parameter values match very well with the reported ones and the structure of Bismuth-Trisulphide is rhombic or orthorhombic confirmed by XRD.
- Fundamental infrared frequencies observed in all sulphide compounds in general, are also found in the present FT-IR analysis, of Bismuth-Trisulphide
- Chemical compositions of the grown crystal by volumetric analysis, gravimetric analysis is well match with the theoretical calculation from molecular formula.
- Crystals are quite transparent, and are of good quality.

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