

Growth of Iron doped Bi_2S_3 crystal by gel Methodology and its analysis

K.B.Patil^{#1}, B.K.Sonawane²

^{1#} Department of Physics, Arts, Science and Commerce College, Varangaon, Jalgaon (MS)

^{2*} Department of Electronics, Shri.S.S.Patil Arts, Shri.Bhauasaheb T.T.Salunkhe Commerce and

Shri.G.R.Pandit Science College, Jalgaon

¹kbpatil1531969@gmail.com

² bksonawane@rediffmail.com

Abstract— In the present work Fe doped Bismuth tri sulphide crystals were grown in silica gel medium at room temperature by single diffusion method. The effects of parameters such as gel aging, gel pH, the density of gel on growth of crystals were studied. Grown crystals were characterized by XRD analysis the grain sizes of grown crystals were 37.66 nm. EDAX studies of powder sample confirmed presence of Fe, Bi and S. The UV-VIS analysis gives band gap energy 1.78 eV of gel grown crystals. Band gap energy of Bismuth tri-sulphide increases due to doping of Fe in Bi_2S_3 .

Keywords— Fe doped Bi_2S_3 Crystal, XRD, EDAX, UV-Vis spectroscopy, SEM.

I. INTRODUCTION

Crystal growth in gel is simple technique for growing single crystals. Several investigators used gel method for growing different crystals [1-3] Bismuth sulphide is V-VI group compound semiconductors and has application in a fields, such as thermoelectric, electronic and optoelectronic devices [4-5]. Bismuth sulphide semiconductor with band gap energy ranges 1.3 to 1.7 eV. [6-7]. Optical and structural properties of Bi_2S_3 with various dopants are studied. Fe was reported [8-10] all these researchers have used different synthesis methods. There are no reports in the literature on the synthesise of Iron doped Bi_2S_3 crystals by gel method. In this paper we report a method of growing Fe-doped Bismuth Tri-Sulphide crystals in silica gel medium by single diffusion technique. The samples have been characterized

II. MATERIALS AND METHODS

In order to grow Iron doped Bismuth Tri-Sulphide crystals, the required Silica gel medium. Gel was prepared by adding sodium metasilicate solution of specific gravity 1.04gcm^{-3} with 5ml

Acetic acid (2N) and 5ml H₂S water solution which acted as an inner reactant. The solution was continuously stirred to avoid local ion concentration. 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 3 days. It was left for 66 to 71 Hours for gel ageing. The outer reactants solution of 0.5 M BiCl₃ and 0.2 M FeCl₃ were added on the top of the gel. The outer reactants were added slowly along the sides of test tube using a pipette and not directly on to the gel medium. Due to the diffusion of the outer reagent into the gel medium it reacts with the inner reagents, crystals started growing. Nucleation was observed within 48 hours of addition of the outer reagent. Circular shaped, opaque and brittle crystals were observed. Experiment carried out at an ambient temperature of about 28 °C. The optimum conditions for grown Fe doped Bi₂S₃ crystals were found and given in Table I The reaction between Bismuth Chloride, dopant and H₂S Gas Water in gel medium resulted in the growth Fe doped Bi₂S₃ crystals. Following reaction that takes place in the gel medium.



Chemicals used

- 1) Sodium metasilicate powder (A.R. grade) Na₂SiO₃, 9H₂O (M.W.284.20)
- 2) Acetic acid (A.R. grade) CH₃COOH
- 3) H₂S Solution
- 4) Bismuth chloride (A. R. grade) BiCl₃ (M.W. 315.33)
- 5) Double distilled water
- 6) Ferric chloride (A.R.grade) FeCl₃ (M.W.162.21)

Figure 1 shows the Fe-doped Bi₂S₃ crystals inside the test tube.



Fig 1 Fe doped Bi₂S₃

TABLE I
Conditions for the growth of Iron - doped Bi₂S₃ crystals

Condition	doped Bi ₂ S ₃
H ₂ S GAS water solution	---
Conc. of Bismuth chloride	0.5 M
Conc. of FeCl ₃	0.2M
Conc. of Acetic acid	2N
Gel setting period	3 days
Gel aging period	2 days
Period of growth	32 days
Temperature	Room temperature (about 28 °C)
Gel pH	4.4
Gel density	1.04 gm/cm ³

III. RESULTS AND DISCUSSION

X-Ray Diffraction Study

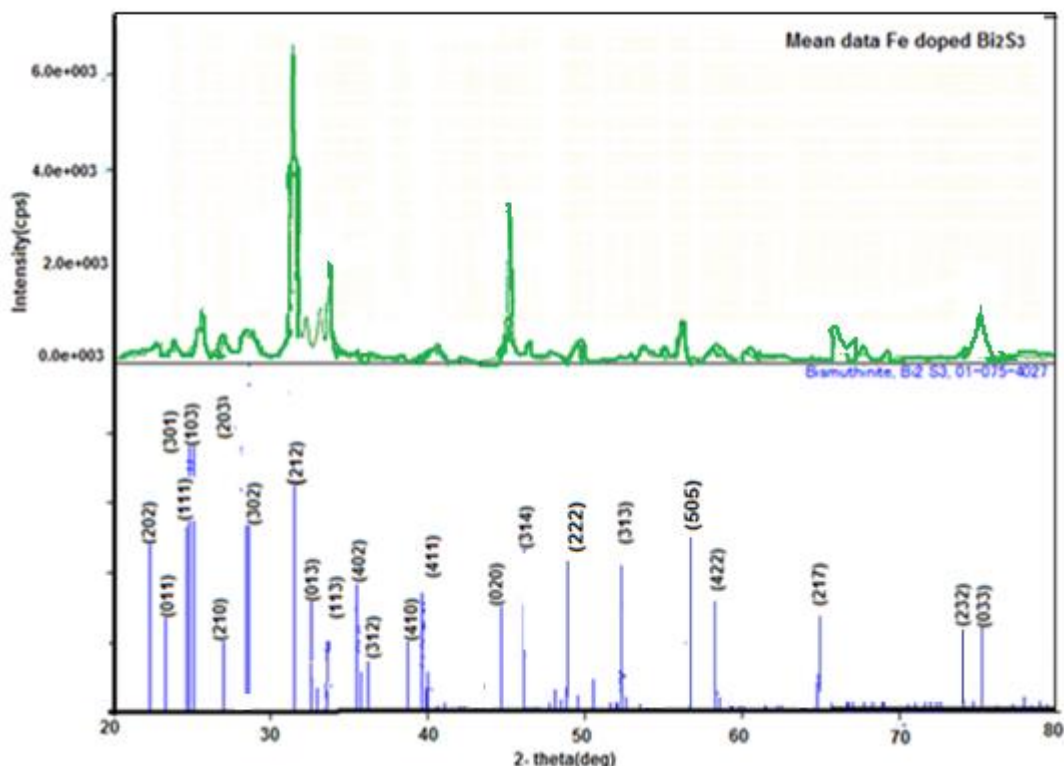


Fig.2 XRD spectra of Fe-doped Bi₂S₃ grown crystal powder
Sample of grown crystals used for X-ray diffraction analysis. The sample was Scanned between twenty 20⁰ to 80⁰. XRD data of Iron - doped Bi₂S₃ given Table II. In fig 2. It is found

that no peak from impurities observed in the spectrum of the Fe-doped Bi_2S_3 sample, proving that none other different crystalline phases was formed. Grain sizes were calculated from the broadening of XRD peaks using the Scherer's formula

$D = K\lambda/\beta\cos\theta$ Where K is constant = 0.9, λ is wavelength of $\text{CuK}\alpha$ radiation ($\lambda = 1.5409 \text{ \AA}$), β is the full width at half maxima of diffraction peaks. In the present work, the grain size of Iron-doped Bismuth tri sulphide estimated from X-ray line broadening of the maximum intensity peak. The crystal grains mainly oriented along the (212) plane.

Table II
XRD data of Iron - doped Bi_2S_3

No.	2θ	$d \text{ \AA}^0$	Height(cps)	FWHM(deg)	Indices h k l
1	25.67	3.468	655	0.39	2 0 2
2	27.107	3.2869	581	0.20	0 1 1
3	28.34	3.146	263	0.31	1 0 3
4	31.449	2.8423	6485	0.229	2 1 2
5	32.217	2.7763	547	0.22	0 1 3
6	33.14	2.701	804	0.21	1 1 3
7	36.277	2.4743	294	0.14	4 0 2
8	40.63	2.219	201	0.23	4 1 1
9	45.1349	2.00717	4346	0.171	0 2 0
10	46.35	1.9572	395	0.21	3 1 4
11	49.42	1.843	191	0.37	2 2 2
12	54.76	1.6749	170	0.23	3 1 3
13	56.234	1.6345	1609	0.171	5 0 5
14	58.34	1.5805	222	0.36	4 2 2
15	66.01	1.4142	503	0.186	2 1 7
16	75.022	1.26503	1097	0.224	0 3 3

D is grain size (i.e. the diameter of the crystal particle in the material) the calculated average particle size is 37.66nm.

EDAX analysis

The compositional analysis of Iron-doped Bi_2S_3 crystal is carried out using EDAX analysis. In fig.3. The EDAX confirms the presence of Bismuth (Bi), Sulphur(S) and Iron (Fe) with their atomic percentage It was observed that atomic % of Bi, S and Fe are in good agreement with stoichiometrically expected atomic % 8.18, 3.73 and 88.08 respectively. Value of elemental content of Iron doped Bi_2S_3 crystal and EDAX data for the confirmation of Fe, Bi and sulphur in the grown crystal is shown in Table III

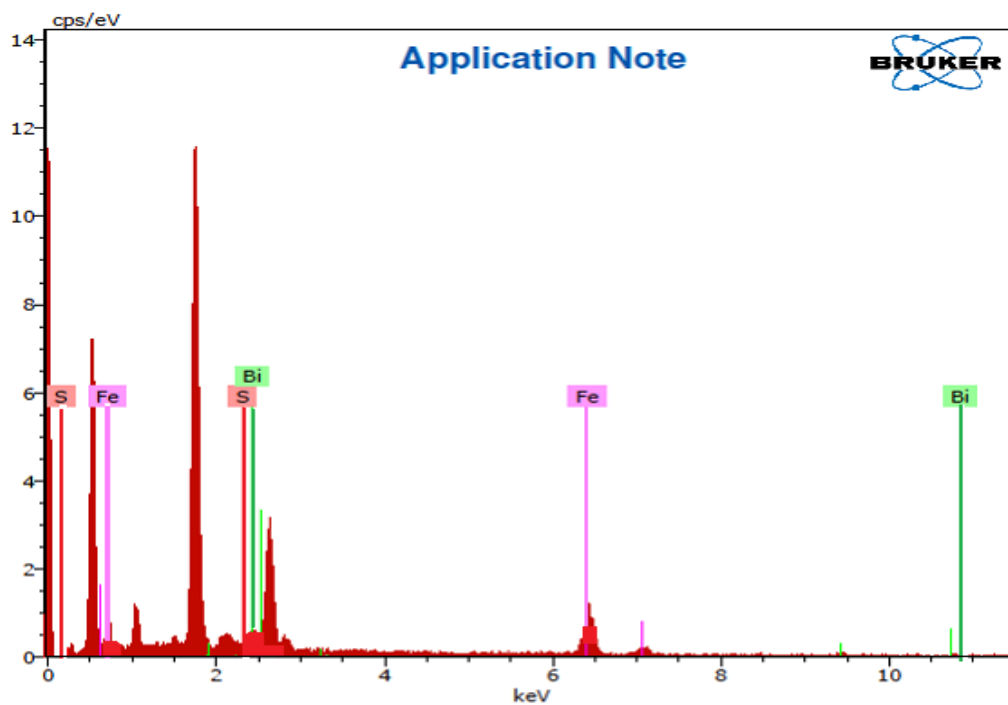


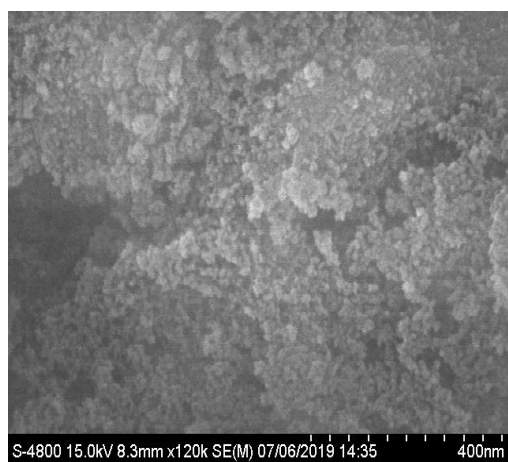
Fig.3 EDAX data of Iron - doped Bi_2S_3

Table III

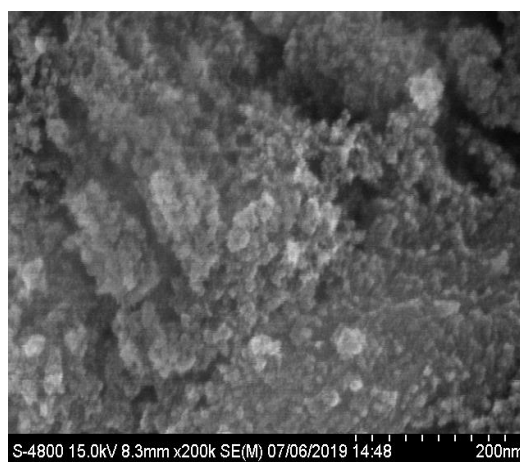
EDAX data for the confirmation of Fe, Bi and sulphur in the grown crystal

El	AN	Series	nn.C wt.%]	norm. C [wt.%]	Atom. [at.%]	C Error (1Sigma) [wt.%]
S	16	K-Series	0.49	1.77	3.73	0.07
Fe	26	K-Series	20.08	72.89	88.08	0.71
Bi	83	L-Series	6.98	25.34	8.18	0.79
		Total	27.55	100.00	100.00	

SEM analysis



a)



b)

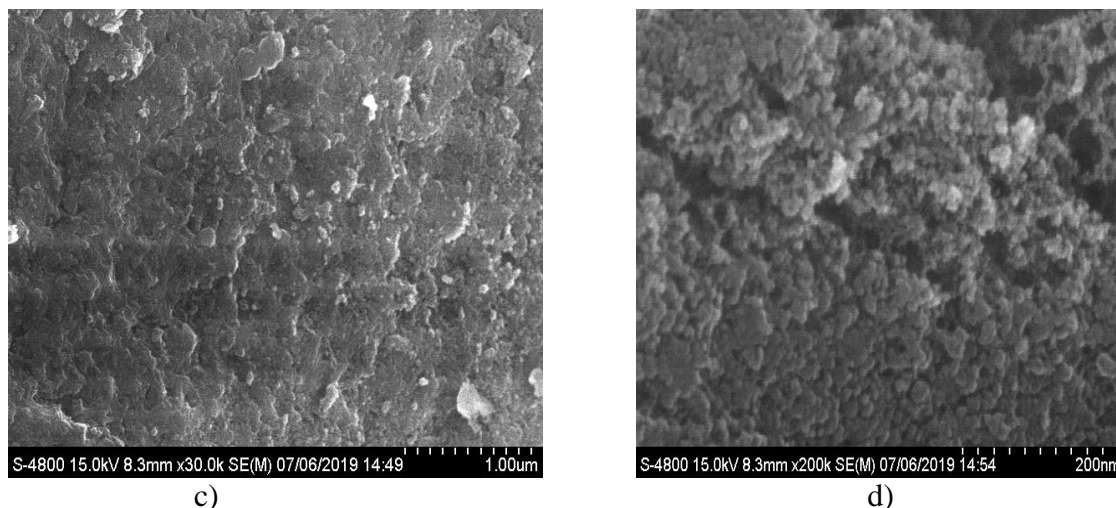


Fig 4 SEM morphology of grown Iron-doped Bi₂S₃

SEM images of the powdered sample of Fe-doped Bismuth Sulphide were taken at common width 8.5 mm and EHT magnification 15 KV. The shape of most of the grown crystals appeared spherical and in few cases, they formed small aggregates. In fig.4 (a to c) Aggregation of the nanoparticles can be detect clearly in Fig.4(d)

UV-Vis spectroscopy

The optical property of Iron doped Bi₂S₃ crystal was studied by using UV-VIS spectrophotometer. The UV-Vis study of Fe doped Bi₂S₃ crystals were taken by SHIMADZU UV-2450. UV-Vis spectrophotometer over the wavelength range 200 – 800 nm at Nano Research Laboratory, Department of Physics, Pratap College, Amalner. The graph of UV-VIS analysis is given in fig.5 from graph, it clears that grown crystals have sufficient and approximately equal transparency in the ultraviolet and visible region. The absorption coefficient is maximum at 216 nm. But the variation of absorbance (A) is studied in wavelength range of 400-800 nm for all the samples.

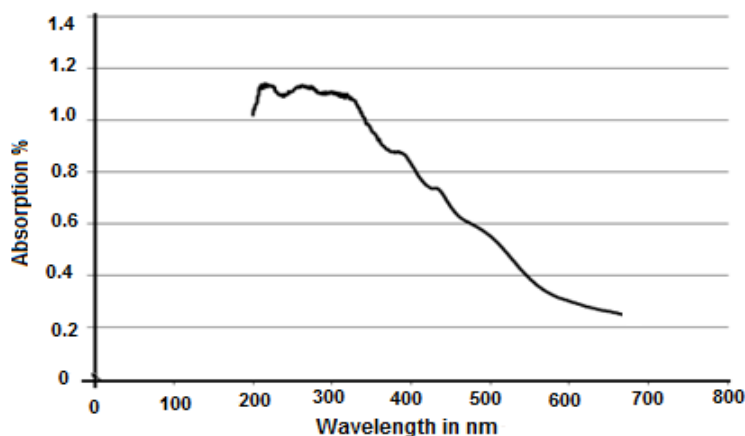


Fig.5 Graph of Absorption verses wavelength Fe-Bi₂S₃ crystals

The high values of absorption coefficient validate their use in photovoltaic applications. Optical conductivity and thermal conductivity also shows good values. The optical absorption spectrum of grown crystal shows a good absorbance in the entire visible region. This is useful for optoelectronic applications. The resulting graph obtained on Fe-doped Bi_2S_3 is shown in Fig.5 the spectral data recorded showed the strong cut off at 696 nm where the absorbance value is minimum.

$$\text{Band Gap Energy (E)} = h \times \frac{c}{\lambda} \quad h = \text{Planks constant}$$

C = Speed of light

λ = Cut off wavelength = 696 nm

E = 1.78 eV

IV. CONCLUSIONS

Iron doped Bi_2S_3 crystals can be successfully grown by silica gel method. Gel setting period is strongly dependent on pH of a mixture of sodium meta silicate, acidic acid and density of sodium meta silicate. X-ray diffraction pattern shows that the sample was crystal in nature .by using Scherer's Formula the average particle size is 37.66nm.

The shape of most of the grown crystals appeared spherical and in few cases, they formed small they formed small aggregates. Aggregates and size variation is seen.

The UV-Vis measurements indicate the band gap energy of the Fe-doped Bi_2S_3 crystals the

Variation of absorbance (A) is studied in the wavelength range of 400-800 nm Band gap energy E=1.78 eV. The elemental composition was determined by EDAX studies, which show that the Presence of Iron, Bismuth and sulphur.

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