Study on Mn doped Bi_2S_3 Crystals grown by gel technique and its analysis

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Abstract: In the present work Manganese doped Bismuth tri sulphide crystals were grown in silica gel medium at room temperature by the single diffusion technique. 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 the presence of Mn, Bi and S. The UV-VIS analysis gives band gap energy E= 1.77 eV of gel grown crystals. Band gap energy of Bismuth tri-sulphide increases due to doping of Fe in Bi_2S_3. SEM images show crystal morphology. FTIR study gives the information of functional groups in a crystal. Size, band gap energy and morphology can be changed by doping.

Keywords: Mn doped Bi_2S_3, Crystal, XRD, EDAX, UV-Vis spectroscopy, SEM, FTIR.

1. INTRODUCTION

Gel method is very simple and useful method to grow the crystals which are insoluble or slightly soluble. There are various parameters by which this method can be controlled [1-3]

Bismuth tri sulphide has been attracting a considerable interest owing to its potential application in thermoelectric, electronic and optoelectronic devices and IR spectroscopy. In addition, it has an energy band gap of 1.3 to 1.7 eV, which is suitable for making photodiode arrays and photovoltaic. A band gap can be tuned depending on the size of the subcomponents [4]Bi_2S_3 exhibits pronounced positive photoconductivity upon visible light exposure, and are a good candidate for optical switches.[5] Bi_2S_3 is a layered semiconductor that crystallizes in the orthorhombic system and is structural to antimony sulphide (Sb_2S_3) and selenide (Sb_2Se_3) [6-7].

Doping a suitable metal ion, such as Mn, Fe Cr and Cu into a semiconductor host material it change the band gap. In the present Paper, the authors report the growth of Mn-doped Bi2S3 crystals and their characterization by EDAX, powder XRD, FT-IR spectroscopy, EDAX and UV-Visible Spectrophotometer.

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2. Experimental

To grow bismuth Tri-Sulphide crystals, the desired silica gel medium was ready by adding Sodium-Met silicate solution of specific gravity 1.04 g/cc drop by drop with constant stirring by using magnetic stirrer into the 5 ml (2N) acetic acid until the pH value 4.4 was set for the mixture. To the above sodium Meta silicate solution of ph 4.4, 15 ml the aqueous solution of H_2S Gas Water solution was added as inner reactant with constant stirring. This mixture was then transferred to the test tube. To keep the solution free from dust and impurities, care was taken to cover the test tube with cotton. The gel was typically set within 13 days. It was left for 48 to72 Hours for gel ageing and then the outer reactant, aqueous solution of 0.5 M bismuth Chloride ($BiCl_3$) and 0.05M $MnCl_2$ added as supernant over the set gel.

The outer reagent was added down the sides of the test tube using a pipette and ultimately on to the gel medium. The diffusion of the outer reactant into the gel medium. Its reaction with inner reactant, Nucleation was observed within 48 Hours of addition of the outer reactant. The experiment was carried out at an ambient temperature of about 28^0C. The various optimum conditions for the growing Mn-doped Bi_2S_3crystals were found and are given in Table 1. The reaction between bismuth Chloride, dopent and H_2S Gas Water solution in gel medium resulted within the growth of Mn-doped bismuth Tri-Sulphide crystals. Shown in Fig. 1

2.1 Chemicals used:-

1) Sodium metasilicate powder (A.R. grade) $Na_2SiO_3, 9H_2O$ (M.W.284.20)
2) Acetic acid (A.R. grade) CH_3COOH
3) H_2S Solution
4) Bismuth chloride (A. R. grade) $BiCl_3$ (M.W. 315.33)
5) Double distilled water
6) Manganese chloride (A.R.grade) $MnCl_2$

The crystals were grown using following chemical reaction.

$2XCl_3 + 3Y_2S \rightarrow X_2S_3 + 6Y\,(Cl)$ Where X=Bi and Y= H or Na.

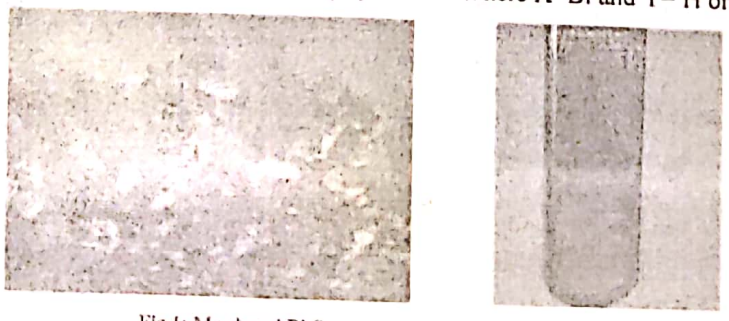

Fig.1: Mn-doped Bi_2S_3 grown crystals

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2.2 Optimum Conditions for Gel Method:-

Condition	doped Bi_2S_3
Conc. of Na_2S	0.5 M
Conc. of Bismuth chloride	0.5 M
Conc. of MnCl2	0.05M
Conc. of Acetic acid	2N
Gel setting period	3 days
Gel aging period	2 days
Period of growth	32 days
Temperature	28°C Room temperature
Gel pH	4.41
Gel density	1.04 gm/cm^3

Table 1: Optimum condition for the growth of Mn-doped Bi_2S_3 crystals

3. Results and Discussion

3.1 X-Ray Diffraction Study

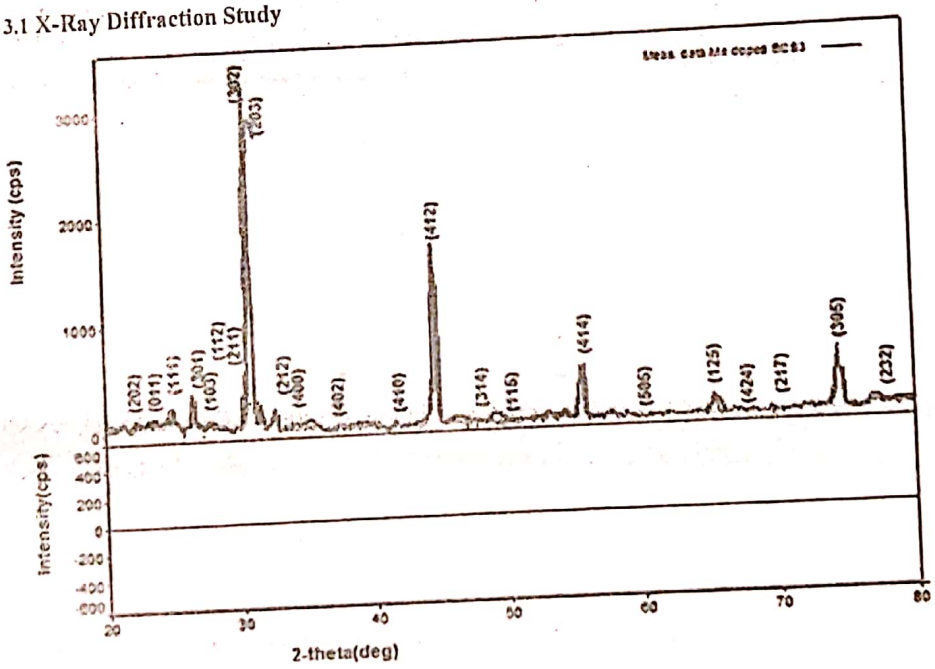

Fig.2: XRD spectra of Mn-doped Bi_2S_3 grown crystal powder

The powder sample of gel grown crystal was used to x-ray diffraction analysis. XRD data of Mn-doped Bi_2S_3 grown crystal powder is given in Table 2. The sample was Scan between 20 ^{0} to

80^0.Figure.2 shows XRD spectrum of Mn-doped Bi_2S_3 sample. It found that no peak from impurities can be observed in XRD spectrum of Mn-doped Bi_2S_3 sample, proving that none of the other different crystalline phases was formed. Crystal sizes calculated from broadening of XRD peaks using the Scherer's formula

$D = K\lambda/\beta\cos\theta$ Where K is constant equal to 0.9, λ is wavelength of CuKα radiation (λ= 1.5409 Å), β is the full width at half maxima (FWHM) of XRD peaks. In the present work, the crystallite size of the Mn-doped Bi_2S_3 estimated from X-ray line broadening of the maximum intensity peak. The crystalline grains mainly oriented along the (302) plane.

3.2 XRD data of Mn-doped Bi_2S_3

No.	20	d A^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	3 0 1
4	31.449	2.8423	6485	0.229	3 0 2
5	33.14	2.701	804	0.21	2 1 2
6	36.277	2.4743	294	0.14	4 0 2
7	40.63	2.219	201	0.23	4 1 0
8	45.1349	2.00717	4346	0.171	4 1 2
9	46.35	1.9572	395	0.21	3 1 4
10	56.234	1.6345	1609	0.171	4 1 4
11	60.21	1.5357	66	0.42	5 0 5
12	74.537	1.2721	523	0.21	3 0 5

Table 2: XRD data of Mn -doped Bi_2S_3 grown crystal powder

The crystalline size calculated using Scherer's formula

$$D = \frac{0.9\times1.54056\,A^\circ}{0.229\times cos(15.7)^\circ} = 37.66\text{nm}$$

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

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3.3 EDAX

The compositional analysis of Mn- doped Bi_2S_3crystal is carried out at SAIF LAB, University Institute of Chemical Technology Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon. In fig.3 by using EDAX data in Table 3 shows values of elemental content of the crystal. The EDAX confirm the presence of Bismuth (Bi), Sulphur(S) and Manganese (Mn) with their atomic percentage It was observed that atomic % of Bi, S and Mn are in good agreement with stoichiometrically expected atomic % 2..51, 51.05 and 46.44 respectively. .

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El	AN	Series	unn. C [wt. %]	norm. C [wt. %]	Atom. C [at. %]	Error (1 Sigma) [wt. %]
S	16	K-series	3.40	34.73	51.05	0.21
Mn	25	K-series	5.31	54.14	46.44	0.30
Bi	83	L-series	1.09	11.13	2.51	0.36
		Total:	9.80	100.00	100.00	

Table 3 EDAX data for the confirmation of Mn, Bi and sulphur in the grown crystal

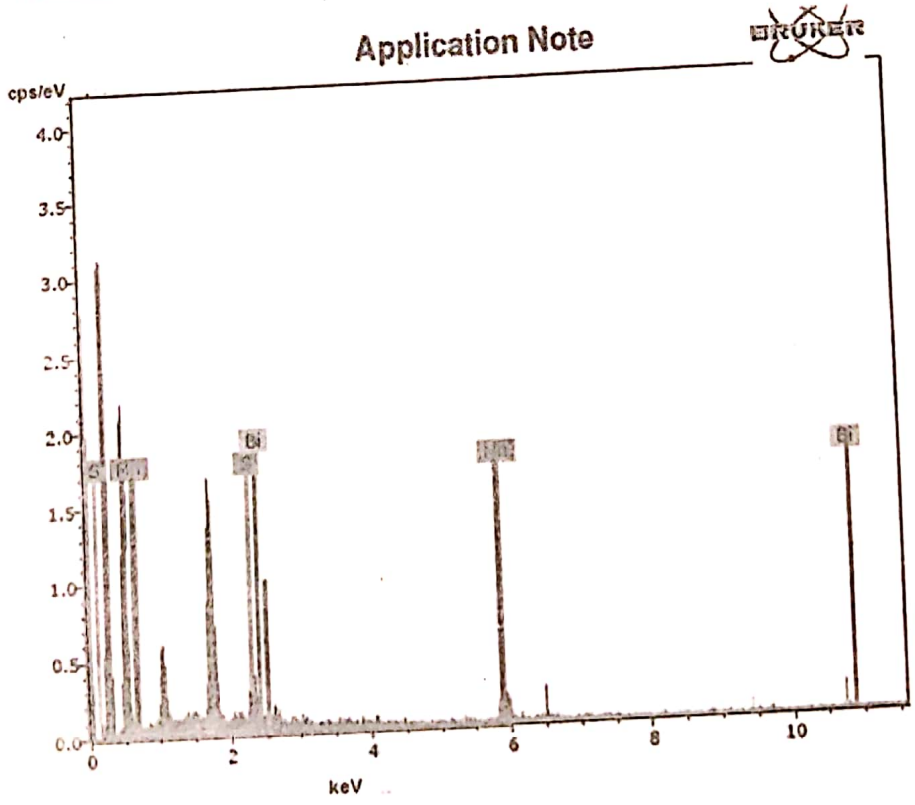

Fig.3: EDAX of Mn-doped Bi_2S_3 grown crystal powder

3.4 SEM Analysis

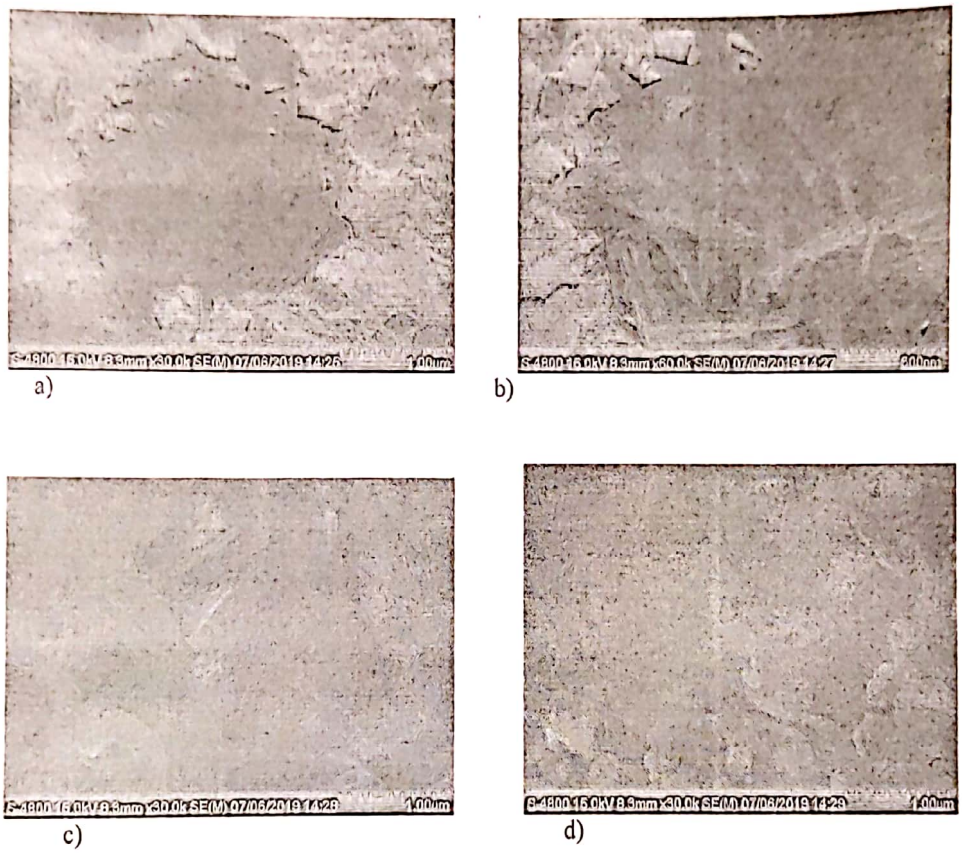

Fig.4 SEM morphology of grown Mn-doped Bi_2S_3

Fig.4 a, b The SEM images show that the nanowires, it is clearly seen that the products are composed of a large amount of nanoscale rod-shaped morphology. Thick and thin layers are seen in figures. The individual plates of samples are flat and the plates with the sharp edges were Observed. On some plates further plate like growth was observed. Shown in fig.4c Surface morphology of the Mn-doped Bi_2S_3 nanoparticles is shown in Fig. 4.d

3.5 UV-VI Study

The optical property of Mn doped Bi_2S_3crystal was studied by using UV-VIS spectrophotometer. The UV-Vis study of Mn doped Bi_2S_3 crystals were taken by SHIMADZU UV-2450. UV-Vis spectrophotometer over the wavelength range 200 – 800 nm at Nano Research

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Laboratory, Department of Physics, Pratap College, Amalner. from UV-VIS analysis data the resulting graph obtained sample crystals is given in fig 5. From the graph, it is clear that the gel grown crystal have sufficient and approximately equal transparency in the ultraviolet and visible region. The absorption coefficient is maximum at 212 nm. But the variation of absorbance (A) is studied in the wavelength range of 200-700 nm for all the samples.

The high values of absorption coefficient validate their use in photovoltaic applications. Optical conductivity and thermal conductivity also show good values. The optical absorption spectrum of grown crystal is useful for optoelectronic applications.

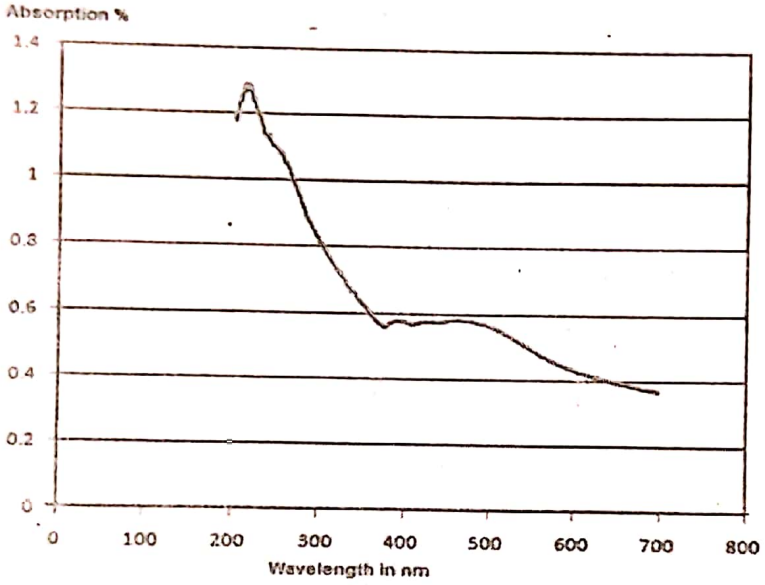

Fig.5: Graph of Absorption verses wavelength of Mn-doped-Bi_2S_3 crystals

The resulting graph obtained on Mn-doped Bi_2S_3 is shown in Fig.5 the spectral data recorded showed the strong cut off at 699 nm; where the absorbance value is minimum. The data is corroborated in the % Reflectance mode.

Band Gap Energy (E) = $E = h \times \frac{C}{\lambda}$

λ = Cut off wavelength = 699×10^{-9} meters

$E = h \times \frac{C}{\lambda}$ $= 6.626 \times 10^{-34} \times 3.0 \times 10^{8} / 699\text{nm} = 2.84/1.6\ \text{eV} = 1.77\ \text{eV}$

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3.6 Fourier transforms infrared (FT–IR) spectral analysis

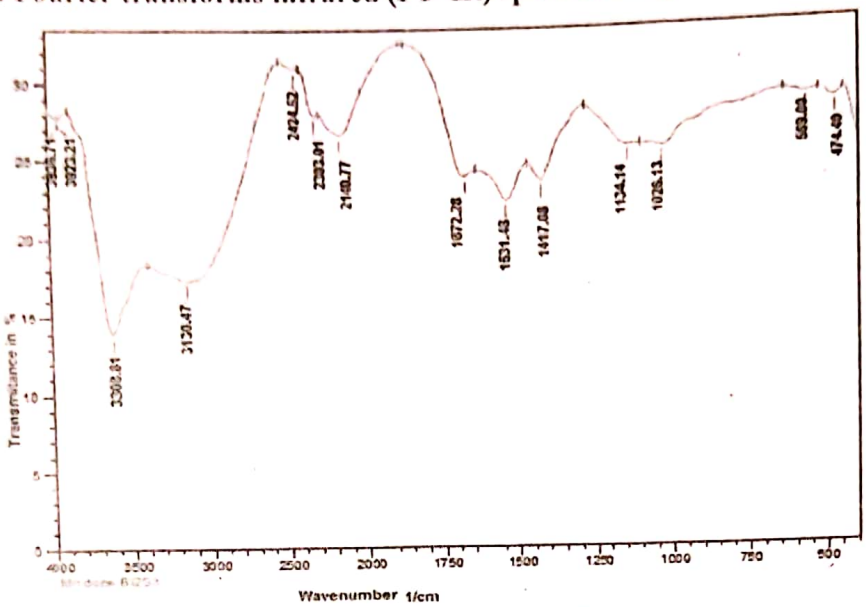

Figure 6 . FTIR spectrum of Mn doped Bi2S3 crystal

The FT-IR Spectrum was analyzed for powder crystals using Fourier Transform Infrared Spectrometer. 500cm^{-1} to 4000 cm^{-1}. The observed spectrum of grown crystal is shown in fig.6. In FT-IR the peaks at 3936.71 cm^{-1} and 3923.21 cm^{-1} are assigned to nonbonded, O-H stretch respectively. The peaks at 3308.81 cm^{-1} and 3130.47 cm^{-1} are due to O-H stretching of water. The bands at 2140.77 cm^{-1}is due assigned a C=C Stretching bond molecule. A peak at 1417.68 cm^{-1} is assigned due to C-O Strength 1134.14 and 1026.13 are due to C-O-C group. The absorptions occurring between 502.4 cm^{-1} and 427.2 cm^{-1} are due to the metal–oxygen stretching vibrations. The peaks at 474& 569 can be assigned to Bi-S bonding

4. Conclusions

i. The Mn doped Bi_2S_3 crystals can be successfully grown by silica gel method.
ii. The gel setting period is strongly dependent on the pH of a mixture of sodiummeta silicate, acidic acid and density of sodium meta silicate.
iii. X-ray diffraction pattern shows that the sample was crystalline in nature. FTIR study suggests the presence of C=C, C-O-C, nonbonded O-H, C-H bond
iv Gel grown crystal possesses uniform morphology and the size variation is seen to be very wide.
v The UV–Vis measurements indicate the band gap energy of the Mn-doped Bi_2S_3 crystals the Variation of absorbance (A) is studied in the wavelength range of 400-800 nm Band gap energy E=1.77 eV
vi The elemental composition was determined by EDAX studies, which show that the Presence of Manganese, Bismuth and sulphur.

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