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Growth and structural analysis of Doped Bismuth tri sulphide crystals: Gel method

K.B.Patil*[1], B.K. Sonawane[2], S. K. Bachhav [3]

*Corresponding Author

[1]*Department of Physics, Arts, Science and Commerce College, Varangaon, Jalgaon (MS)*

[2]*Departments of Electronics, Shri.S.S.Patil Arts, Shri.Bhausaheb T.T.Salunkhe Commerce and Shri.G.R.Pandit Science College, Jalgaon (MS)*

[3]*Departments of Physics, Arts, Science and Commerce College, Varangaon, Jalgaon (MS)*

Abstract:

The single crystals of Chromium doped Bismuth tri sulphide crystals were grown by Single diffusion technique, in silica gel at room temperature. Chromium doped Bismuth tri sulphide crystals have been prepared by single gel method. Surface morphology of materials was studied by scanning electron microscopy [SEM) and dispersive analysis of X-ray [EDAX). SEM shows grown crystals are nanowires in shape, flat and the plates with the sharp edges were observed. And nanoscale rod like structure of the grown crystals and not affected significantly by the doping. The incorporation of Chromium in the Bismuth tri sulphide crystals well confirmed by EDAX.

Fourier transforms infrared spectroscopy (FTIR), the confirmation of the crystal formation was done by carrying out XRD study. FTIR study gives the information of functional groups in a crystal.

Keywords: Doped Bismuth tri sulphide crystals, XRD, SEM, EDAX, FTIR,

1. INTRODUCTION

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

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 Na_2S 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 0.5M 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^{0}C. 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 Na_2S 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) Sodium sulphide ((A. R. grade)) Na_2S
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.

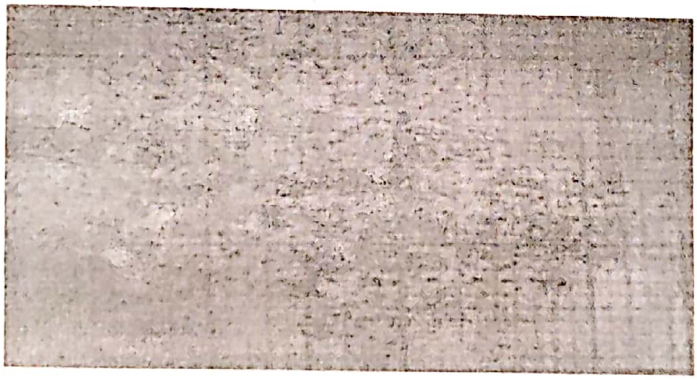

Fig.1: Mn-doped Bi_2S_3 grown crystals

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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

XRD data of Mn-doped Bi_2S_3

3.1 X-Ray Diffraction Study

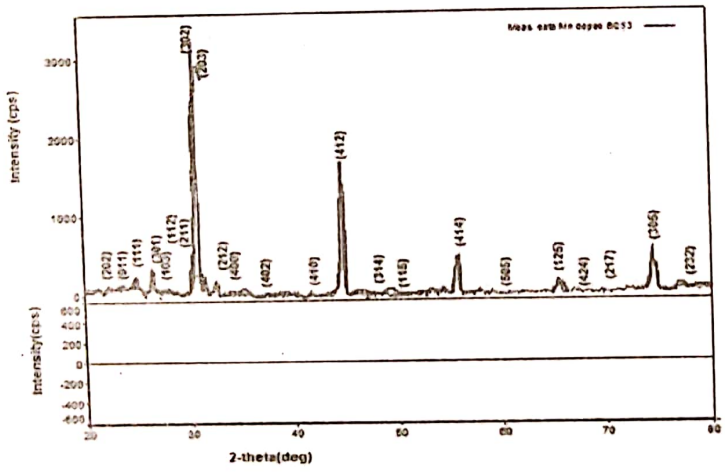

Fig.2: XRD spectra of Mn-doped Bi_2S_3 grown crystal powder

The sample was Scan between 20 ° to 80 °.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.

The crystalline size calculated using Scherer's formula

$$D = \frac{0.9 \times 1.54056\ A^{\circ}}{0.229 \times cos(15.7)^{\circ}} = 37.66\text{nm}$$

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

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

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	

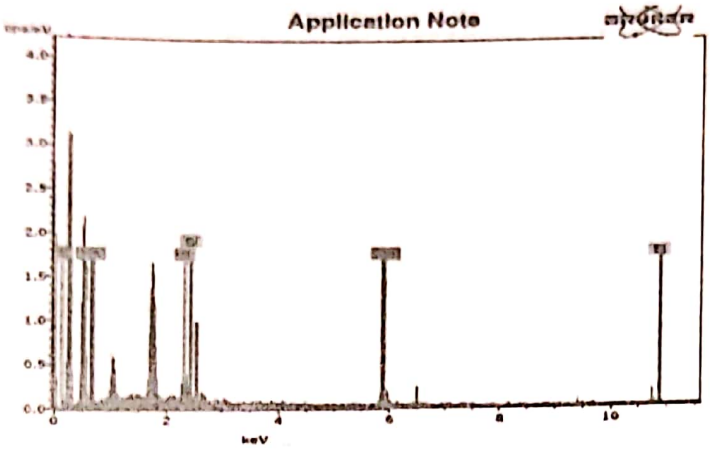

Fig.3: EDAX of Mn-doped Bi_2S_3 grown crystal powder

3.3 SEM Analysis

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.

a b

Fig.4 SEM morphology of grown Mn-doped Bi_2S_3

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3.4 Fourier transforms infrared (FT–IR) spectral analysis

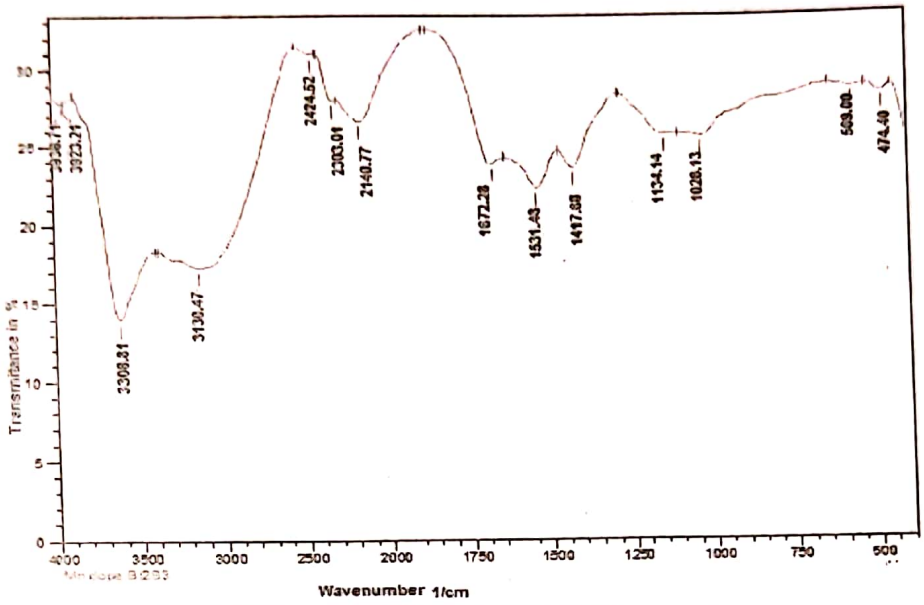

Figure5. FTIR spectrum of Mn doped Bi2S3 crystal

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.5. 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

Conclusions

The Mn doped Bi_2S_3 crystals can be successfully grown by silica gel method. The gel setting period is strongly dependent on the 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 crystalline in nature. FTIR study suggests the presence of C=C, C-O-C, nonbonded O-H, C-H bond. Gel grown crystal possesses uniform morphology and the size variation is seen to be very wide. SEM shows grown crystals are nanowires in shape, flat and the plates with the sharp edges were observed. The elemental composition was determined by EDAX studies, which show that the Presence of Manganese, Bismuth and sulphur.

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