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COMPARATIVE STUDY OF CHROMIUM AND IRON DOPED BISMUTH TRI SULPHIDECRYSTALS BY 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
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

Abstract:
Growth of Chromium doped Bismuth tri Sulphide single crystals from silica gel by the process of diffusion and a comparative study with Iron doped Bismuth tri Sulphide are discussed.
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 metasilicate ($Na_2SiO_35H_2O$), Acetic acid (CH_3COOH) and supernant Bismuth chloride ($BiCl_3$) with dopant at pH value 4.4 and transferred in glass tube.
The grown crystals were characterized by XRD, EDAX and SEM. the confirmation of the crystal formation was done by carrying out XRD study. The UV-VIS analysis gives band gap energy of gel-grown crystals.
Key words: Cr doped Bi_2S_3 and Fe doped Bi_2S_3; XRD, EDAX, SEM, UV-Vis spectroscopy

1 INTRODUCTION

Bismuth tri Sulphide is a very important material. Bi_2S_3 exhibits pronounced positive photoconductivity upon visible light exposure, and are a good candidate for optical switches.[1] 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) [2-3]. 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 Cr-doped Bi2S3 crystals, Fe-doped

Bi2S3 and their characterization by EDAX, powder XRD, FT-IR spectroscopy, and UV-Visible Spectrophotometer. The effects of dopant on various purposes of crystals are of great interest from solid-state science as well as technological point of view. However, there are very few reports in the literature on the growth of these crystals by gel method. Dishovsky and Boncheva-M Ladenova [4], Dennis, and Henisch [5] have extensively studied the effect of doping on gel-grown crystals.

2. MATERIALS AND METHODS

Crystals of Chromium doped Bismuth tri Sulphide and Iron Bismuth Tri-sulphide were grown by gel method by using single diffusion techniques. Table 1 gives details about method and chemicals used, different habits of crystals obtained, their transparency, etc.
. Single diffusion method is found more suitable for growth of these crystals.

Table1: Cr- doped Bismuth tri Sulphide and

Crystals type	Method	Chemical used	Crystal habit
Cr-doped Bi2S3	Gel method by using single diffusion techniques	**Na 2SiO35H2O, CH3COOH, CrCl3, BiCl3 and H2S gas in water solution**	Orthorhombic
Fe-doped Bi2S3	Gel method by using single diffusion techniques	**Na 2 SiO35H2O, CH3COOH, FeCl3 , BiCl3 and H2S gas in water solution**	Orthorhombic

The structure of Bismuth Tri-Sulphide crystals found to be Orthorhombic or Rhombus. It was found that as the concentration of the reactant BiCl3 in the gel is increased, the size of the Spherulites is also increased. Single diffusion method is found more suitable for growth of these crystals

3. RESULT AND DISCUSSION

These crystals possess better habits and better transparency among the grown crystals. Better

transparency of Bismuth Tri-Sulphide may be due to presence of more Bismuth. Optimum growth conditions for gel grown crystals established by varying various parameters such as gel density, pH of gel, gel setting time, gel aging time, etc. are reported in Table 2.

Iron doped Bismuth tri Sulphide crystals

grown Cr-doped Bismuth Tri-sulphide crystals

Fe dopedBi$_2$S$_3$

Table 2: Optimum growth condition for gel gro

Parameters	Cr- doped Bismuth Tri-sulphide	Fe-doped Bismuth Tri-sulphide
Density of sodium meta silicate solution	1.04 gm/cc	1.04 gm/cc
Amount of acetic acid(2N)	6CC	6CC
pH of mixture	4.42	4.4
Temperature	Room Temp (25^{0}c)	Room Temp (28^{0}c)
Gel setting time	3days	5days
Gel aging time	2 days	2 days
Period of growth	6weeks	4 weeks

For all these three crystals, suitable value of density of sodium Meta silicate solution is found to be 1.04 gm/cc, pH value for Cr doped Bi_2S_3 is found to be 4.42 and Fe-doped Bi_2S_3 is found to be 4.4. Gel took 3 days to set and this gel was allowed to age for 2 days, Crystals were removed from test tubes after 40 and 32day respectively. Further growth was not noticed. Sometimes crystal became opaque or translucent due to inclusion of silica in them. Reason may be the unnecessary exposure to silica gel. Various concentrations of reactants were tried. Experiments by interchanging the positions of reactants were also carried out. Once the optimum values of concentration of reactants were obtained, experiments of concentration programming were also carried out. All these parameters have more or less effect on growth and habit of these crystals.

EDAX:-Energy Dispersive Analysis by X-rays (EDAX).

Energy Dispersive Analysis by X rays (EDAX) is used for the quantitative analysis. In the present, work elemental analysis of gel grown Cr-doped Bismuth tri Sulphide and
Fe-doped Bismuth Tri-sulphide crystals, was carried out at SAIF LAB, University Institute of Chemical Technology Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon.. Fig 1 shows EDAX spectrum of Cr-doped Bismuth tri Sulphide. Table. 3. 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 Cr-doped Bi2S3 in given crystals measured EDAX are close to with the estimated values calculated from molecular formula

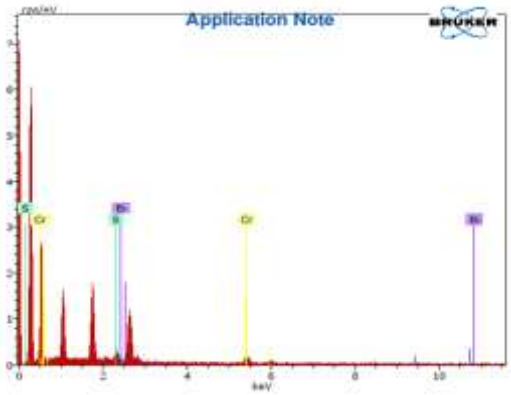

Fig 1 Energy Dispersive Spectrum Cr doped Bismuth tri sulphide

Table 3. Values of elementals content of Cr doped Bismuth tri sulphide crystals.

Experimental Values						
Elements	AN	Series	unn. C [wt. %]	norm.C [Wt. %]	Atomic% C	Error(1 Sigma) [Wt %]
S	16	K-Series	1.14	28.32	42.30	0.10
Cr	24	K-Series	2.41	59.64	54.94	0.17
Bi	83	L-Series	0.49	12.04	2.76	0.22
		Total	4.04	100.00	100.00	

Fig 2 shows EDAX spectrum of Fe-doped Bismuth tri Sulphide. Table 4. 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 Fe-doped Bi2S3 in given crystals measured EDAX are close to with the estimated values calculated from molecular formula. The peaks show the presence of Iron, Sulpher and Bismuth in the doped crystals this is a clear indication of presence of the Iron doping in the crystals table 4 shows the elemental and atomic percentage of the elements Fe, S and Bi in the doped crystals. From the table, it was found that the Mass % and atomic % of Bismuth tri sulphide crystals.

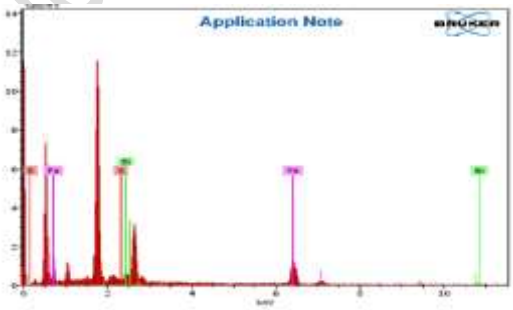

Fig 2 Energy Dispersive Spectrum Fe doped Bismuth tri sulphide

Table 4. Values of elementals content of Fe doped Bismuth tri sulphide crystals.

Spectrum: 10571 Date: 6/7/2019 4:21:36 PM HV: 20.0kV Puls th.:3.73kcps

Experimental Values						
Elements	AN	Series	unn. C [wt. %]	norm.C [Wt. %]	Atomic% C	Error (1 Sigma) [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	

Scanning electron microscopy (SEM)

In present work Scanning electron Microscopy of powdered sample of gel grown Fe-doped Bismuth tri sulphide was carried out at Chemical Technology of KBC NMU Jalgaon and successive photograph were taken at the magnification of 5.00, 40.0, 50.0 um all the photograph were taken at common width 9.2mm and EHT magnification 1.0KV. The figure. 3 (a, to b) illustrate SEM photographs of Fe -doped Bismuth tri sulphide crystals.

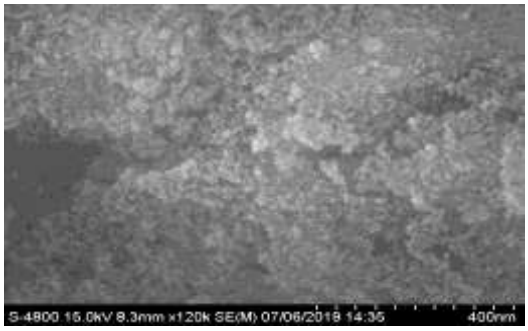

Fig .3 a)

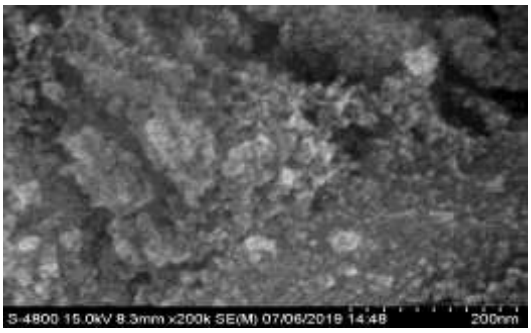

Fig .3 b)

The Scanning Electron Microscope (SEM) was used to characterize the size, shape and morphologies of formed Nanoparticles. The SEM images of Fe- doped Bi2S3 particles shows that the as synthesized samples contain mainly the grains of Fe-doped Bi2S3 Nanoparticles with regular shape. It was also observed that the microscopic images resemble like spherical doped Bi2S3 Nanoparticles.

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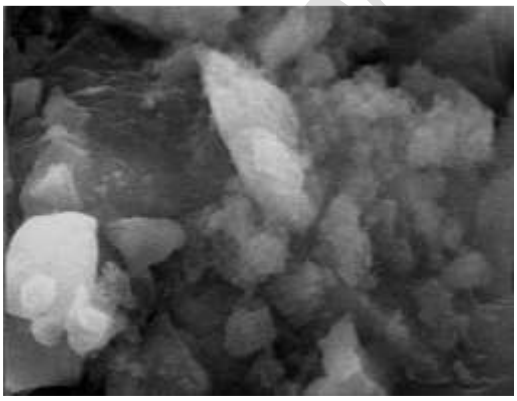


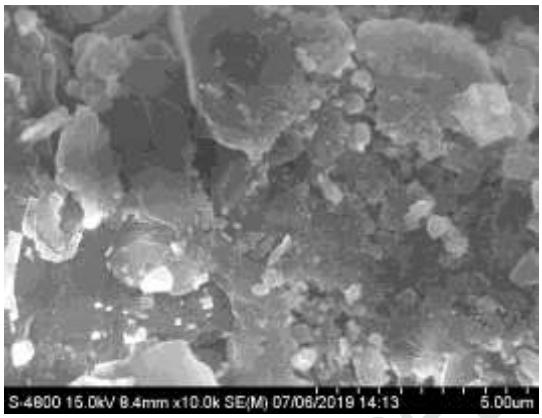


Fig 4 a)

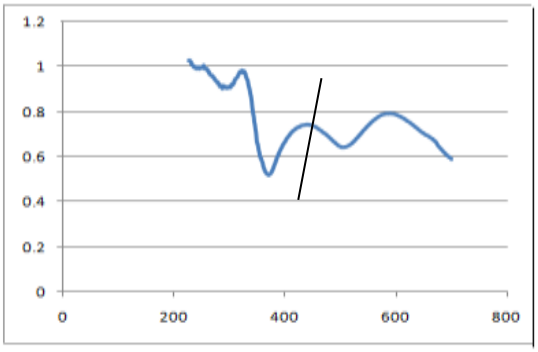
Fig. 4b)

The Scanning Electron Microscope (SEM) was used to characterize the size, shape and morphologies of formed Nanoparticles. The SEM images of Cr- doped Bi2S3 particles shows that the as synthesized samples contain mainly the grains of Cr-doped Bi2S3 Nanoparticles with regular shape. It was also observed that the microscopic images resemble like spherical doped Bi2S3 Nanoparticles. 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 shows the random nature of particles, many of whom are identical. It shows the size distribution in the synthesized sample. The size variation is seen to be very wide.

UV-VI Study

The high values of absorption coefficient validate their use in photovoltaic applications. Optical conductivity and thermal conductivity also show good values. The recorded absorption spectrum is shown in fig.5 In which lower cut-off wavelength is greater than 386 nm. The optical absorption spectrum of grown crystal shows a good absorbance in the entire visible region. This is useful for optoelectronic applications.

Absorption %



Wavelength in nm

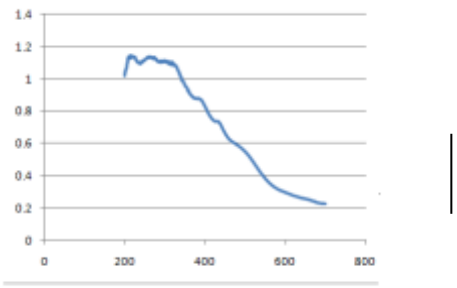
Fig.5. Graph of Absorption verses wavelength Cr-Bi_2S_3 crystals

The resulting graph obtained on Cr-Bi_2S_3 is shown in Fig.5 the spectral data recorded showed the strong cut off at 386 nm; where the absorbance value is minimum. The data is corroborated in the % Reflectance mode.

E = h x $\frac{c}{\lambda}$ =6.626 x 10^{-34}x **3**.0 x 10^8/386nm = 3.21eV

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.

.Absorption %



Wavelength in nm

Fig.6. Graph of Absorption verses wavelength Fe-Bi_2S_3 crystals

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 shows a good absorbance in the entire visible region. This is useful for optoelectronic applications. The resulting spectrum obtained on Fe-dopedBi2S3 is shown in Figure the spectral data recorded showed the strong cut off at 600 nm; where the absorbance value is minimum.

Band Gap Energy (E) = h*C/λ

E = h x $\frac{c}{\lambda}$ =6.626 x 10^{-34}x **3**.0 x 10^8/600 nm

E= 2.07 eV Where 1eV = 1.6 X 10^{-19}Joules (conversion factor)

CONCLUSION

1. Gel growth technique is suitable for growing crystals of Cr-doped Bismuth tri Sulphide and Fe-doped Bismuth tri Sulphide
2. Different habits of Cr-doped Bismuth tri Sulphide and Fe-doped Bismuth tri Sulphide crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants etc.
3. From EDAX Observed values of all the grown samples, are well match with values calculated from molecular formula.
4. From SEM the grain size of Cr-doped Bismuth tri Sulphide and Fe-doped Bismuth tri Sulphide are spherical & pentagonal. While from SEM the grain size of Bismuth Iodide crystals are spherical,
5. Energy band gap of Cr-doped Bismuth tri Sulphide crystal is 3.21 eV and Energy band gap of Fe-doped Bismuth tri Sulphide crystal is 2.07 eV

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