GROWTH AND CHARACTERIZATION OF BISMUTH TRISULPHIDE (Bi_2S_3) CRYSTALS: BULK TO NANO CRYSTALS

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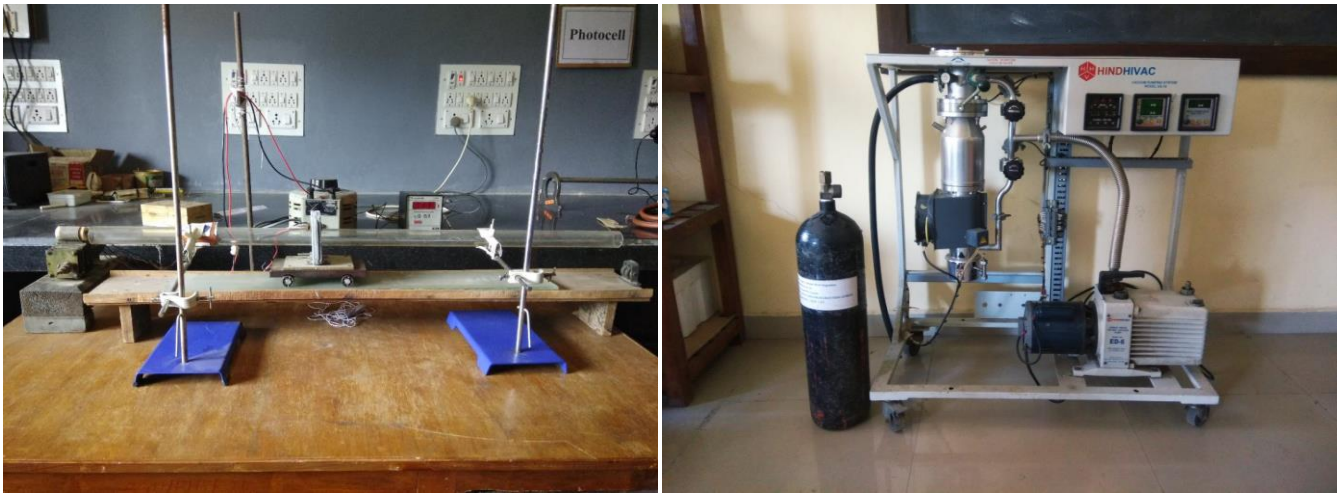
1.1 Abstract:
Binary Compound Bismuth Sulphide (Bi_2S_3)are narrow band gap semiconductor with layered structure and are interesting and important because of major contribution in solar cells, photo detectors, Opto-electronic light amplifiers, Lasers, photo electronic cells. Thin films are grown by chemical bath deposition, chemical vapor Deposition technology. Many researchers grow nano crystals of Bi_2S_3in different shapes and sizes. Flower like pattern with well aligned nanorods are useful in Hydrogen storage, High energy battery, and catalytic field. In present communication single crystals of Bi_2S_3 using gel technique is reported. Dependence of crystal count on gel density, Gel pH, reactant concentration and temperature are studied and optimum condition for these crystals are worked out. Single Crystal are also grown by Zone Refining method and the formation of Bi_2S_3seeds in the solution through a homogeneous nucleation process, solvo thermal reaction method gives different shape and sizes of nano crystals of Bi_2S_3. The growth mechanics involves a special solid-solution. The grown crystals are characterized by X-ray Diffraction (XRD), Tunneling Electron Microscopy (TEM) and selective area electron diffraction (SAED).
Key Words: *Bulk and Nano Crystals, Zone Refining, Gel Method, XRD*

1.2 Introduction:
Single crystals are important for high efficiency photovoltaic cells and detector for alternative energy and for fabrication of bright long lifetime Light Emitting Diode (LED)s, Integrated Circuits and optoelectronic devices. Crystals of high power lasers and radiation resistant frequency multiplying crystals of oxide compounds are useful. Oxide superconductors have great and wide potential applications in Morden science. The ever increasing demand for single crystals arising from electronic industries, optoelectronic industries and other modern technologies like information technology, nanotechnology etc. and it depicts the task of science and technology of crystal growth. A decrease of crystal defects and in homogeneities is demanded simultaneously with the development of greater crystal dimensions. On the other hand, researchers are still far from a complete understanding of Bi_2S_3 properties. The colloidal synthesis of bismuthinite bulk and nanostructures, although cheap and environmentally friendly, does not allow a perfect control on stoichiometry and surface passivation. Attempts are made to grow and synthesize Bi_2S_3 crystals and nanoparticles using different methods.

1.3 Experimental:
1.3.1 Zone Levelling Method:
5N pure Bismuth material was obtained from Nuclear Fuel complex, Hyderabad. High purity (99.999%) bismuth was square rod type. Small slices of this material are uniformly mixed with Sulphur powder. This mixed powder was weighted proportional ratio and leaded into thoroughly cleaned thick walled Pyrex tube. 10cm length and 1 cm in diameter. The ampoule was then evacuated to 10^{-5}Torr and sealed and then placed in horizontal quarts tube 1 m long and 1-inch diameter. The boat (Pyrex tube) is set in quartz container tube. A movable trolley furnace having a temperature gradient of 52°C/cm travelled with speed of 1cm/6Hrs, 1.5 cm/6Hs and 0.5 cm/6Hrs. unidirectional passes are given. (Fig.1).

Fig.1 zone leveling method



After several passes good quality single crystals were obtained. The crystals were cleaved at liquid nitrogen temperatures in conventional manner. After 10 passes with different speed of motors, the Furness was cooled at room temperature and then boat was taken out from the container and broken at liquid nitrogen temperature which reacted in the growth of single crystals of Bi_2S_3 in shape of needles. The shape and length of these crystals are shows in (Fig. 2).

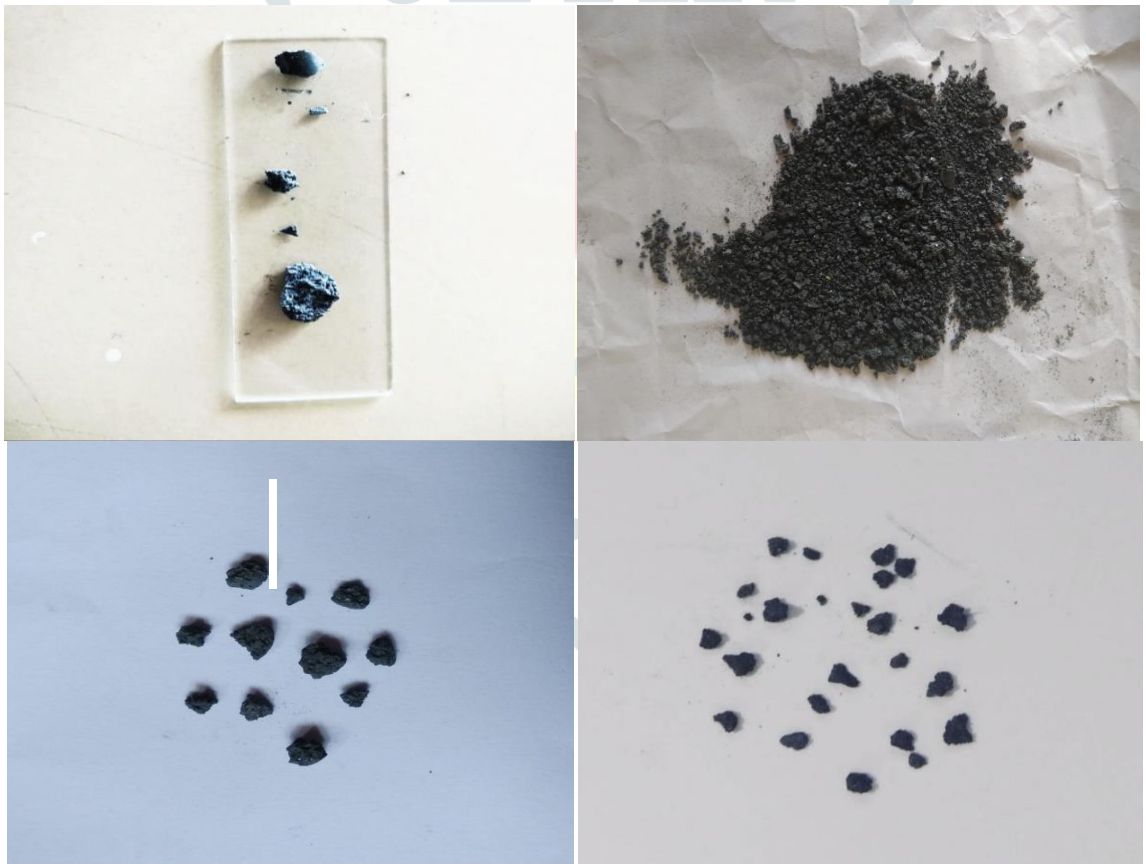


Fig. 2 grown crystals using zone levelling method

1.3.2 Gel Method:

Crystals of Bismuth Trisulfide (Bi_2S_3) were grown by Gel method by using single diffusion technique. The gel medium prevents turbulence and it provides a three-dimensional crucible which permits the reagents to diffuse at a desirable controlled rate. Test tube of diameter 2.5cm and 15cm length were used as crystallizing vessels. The required silica gel medium was prepared by adding the sodium-meta silicate ($NO_2SiO_3.5H_2O$) of specific gravity 1.04 gm/cm^3 drop by drop with constant stirring by using stirrer into the 5ml (2N) glacial Acetic Acid till pH of the solution reaches a value of 4.40. This mixture was then transferred to the test tube. After that H_2S gas was passed through the gel solution for different time intervals (say 5, 10, 15 min etc...). Then after 6 to 7 days when gel was set, outer reagent Bi_2O_3 dissolved in HCL was poured over the set gel. Grown crystals in Circular rings of small (mm) size were obtained after 31 days.All chemicals used for growth are of AR grade. The crystals were grown using following chemical reaction. The grown crystals are shown in Fig.3.

$$\mathbf{Bi_2O_3 + 6\ HCL \rightarrow 2Bicl_3 + 3H_2O}$$

OR

$$\mathbf{2BiCl_3 + 3H_2S \rightarrow Bi_2S_3 + 6HCl.}$$

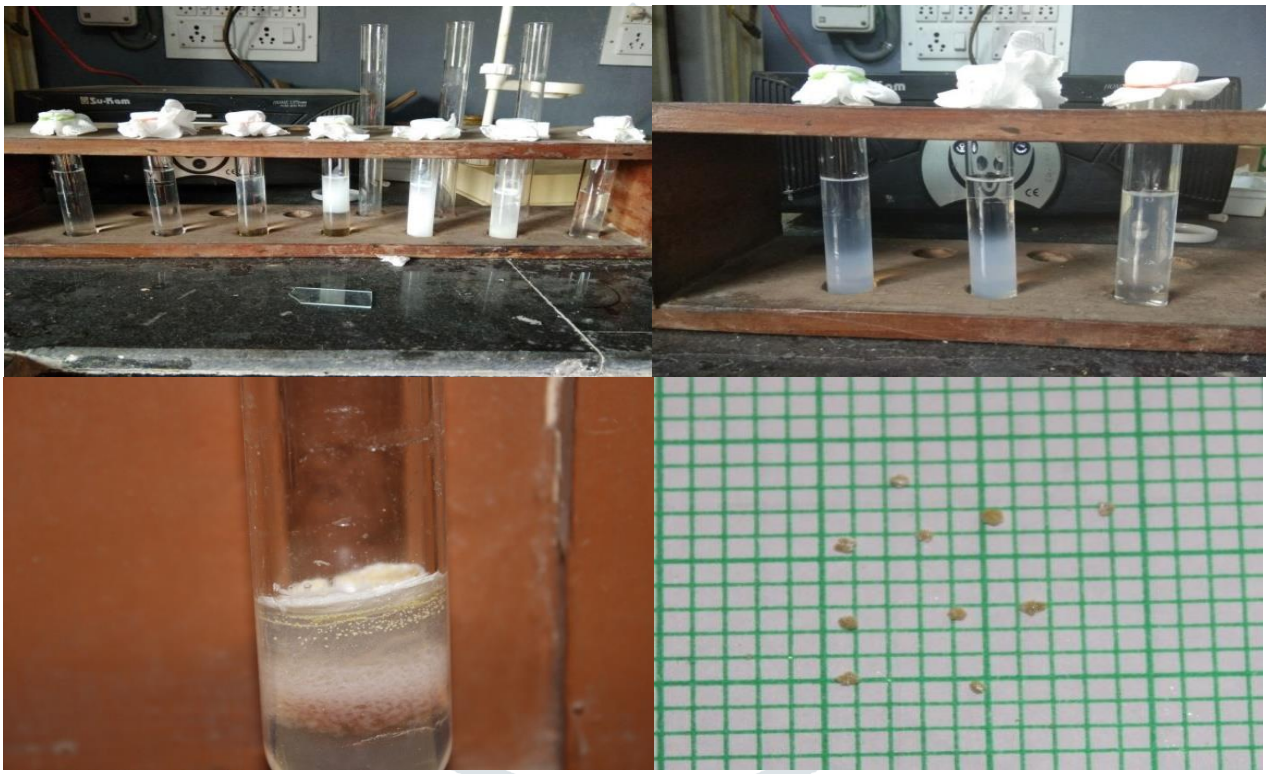


fig.3 gel method and gel grown crystals

1.3.3 Nanoparticle Synthesis Of Bi_2S_3: Hydrothermal Technique

All chemical reagents used in this work werepurchased form Merck India and used withoutfurther purification.In a typical experiment 2g of Bismuth Nitratepentahydrate $Bi(NO_3)_35H_2O$ was added into mixtureof 40 ml Triethanolamine (TEA) and 100 mldistilled water and stirred at room temperature for 1hour getting solution A.0.264g Sulphur was separately dissolved in 20 mlMonoethanalomine getting solution B.Then the solution B was added into solution A. A largenumber of brown precipitates were obtainedimmediatelyThe mixed solution was then transferred into aTeflon-lined stainless steel autoclave (100 mlcapacity), sealed and maintained at 160ºC for 20 hour.After cooling the autoclave naturally to roomtemperature, the precipitates were collected, washedwith water for several times and finally with ethanol,and dried in oven at 100ºC for 4 hours.

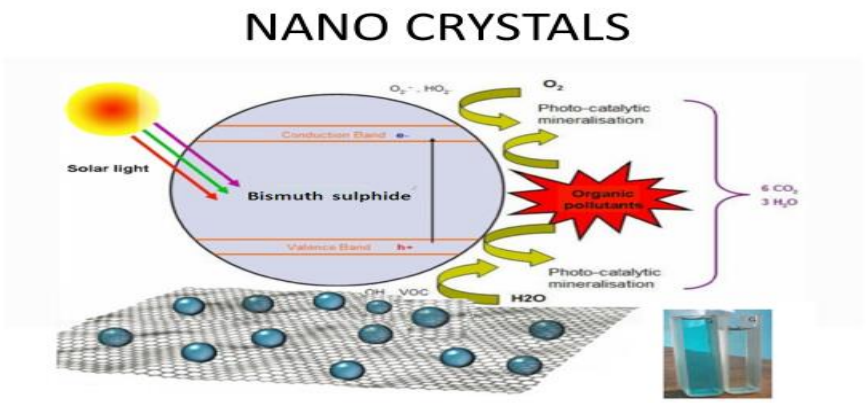


Fig.4 photocatalytic process under Bi_2S_3 nano rods and decoloration of malachite green dye

1.4 Characterization Of Grown Crystals :

1.4.1 X- Ray Diffraction :

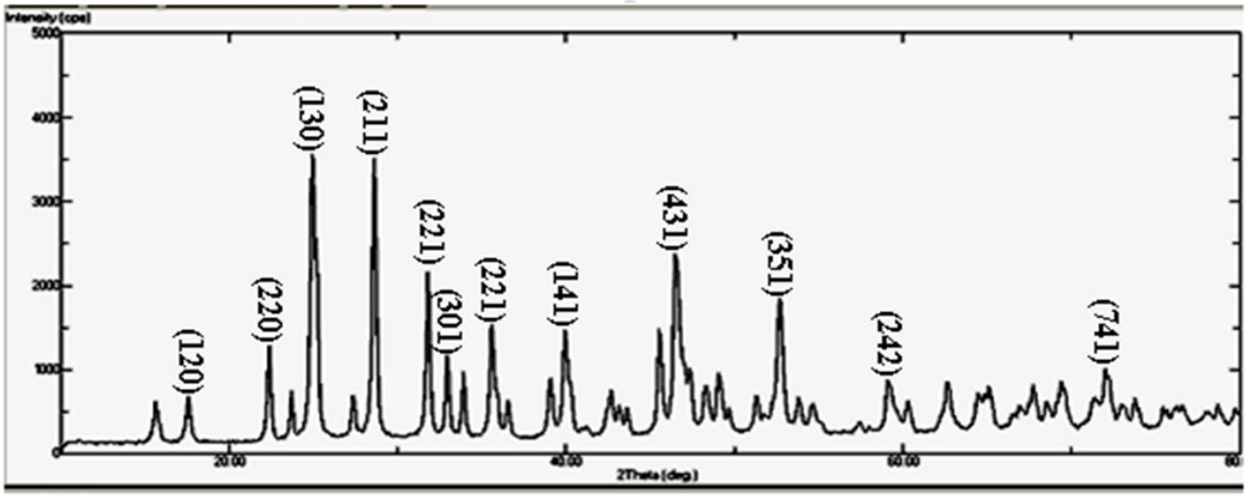


fig.4 x-ray diffraction analysis of grown bi_2s_3 crystals

XRD pattern of as –synthesized Bi_2S_3 is shown in Fig. 4. The positions and relative intensities of all the peaks are in good agreement with those of the orthorhombic crystal structure of Bi2S3 and are indexed according to JCPDS file 17-0320. The calculated lattice parameters (a= 11.75 A,b= 11.24 A, c= 3.98 A)

1.4.2 Scanning Electron Microscopy (SEM)

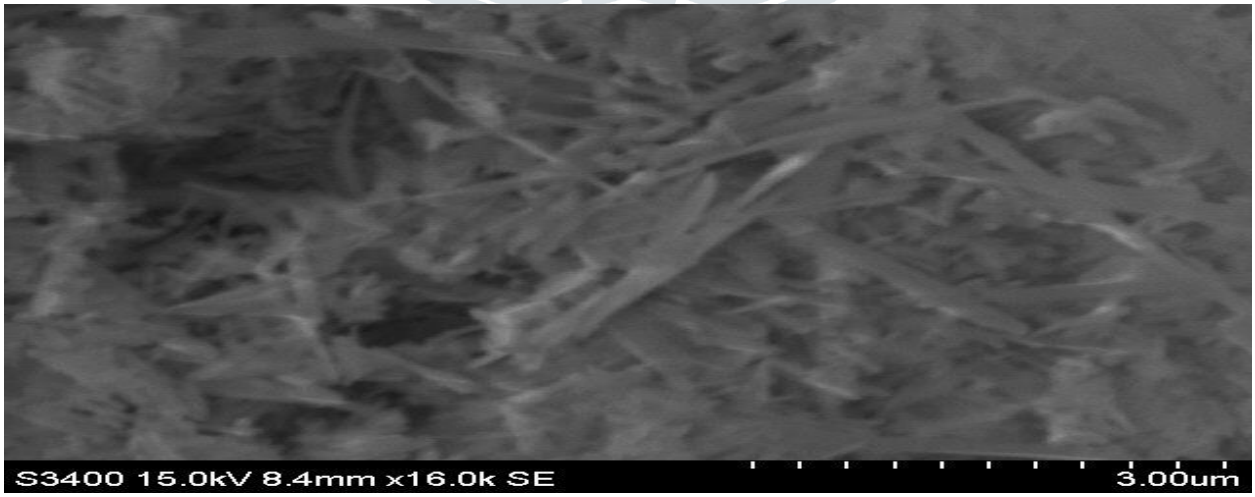


Fig. 5 scanning electron microscopy of grown bi_2s_3 crystals

Figure 5 shows the SEM photograph of as synthesized Bi_2S_3 which shows rod shaped structures. The rods are not distributed uniformly throughout the matrix.

1.4.3 Tunnelling Electron Microscopy (TEM) And Selected Area Electron Diffraction (SAED) :

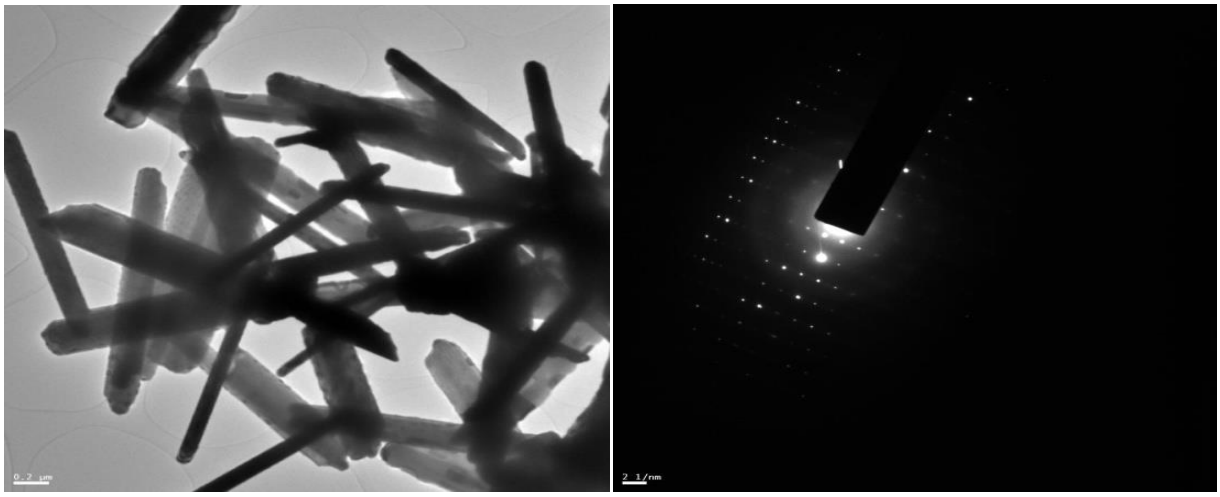


Fig.6 TEM and SAED of grown bi_2s_3 crystals

Figure 6 shows TEM image of as synthesized Bi_2S_3. It can be seen that rods are continuous across the connected part barring at some portions. The SAED pattern indicates single crystalline nature.

1.5 Results and Discussion:

The various optimum conditions for growing crystals were established and are given in Table-1 for Zone Levelling Method and Table-2 for Gel Method.

Table-1optimum conditions for zone levelling method.

Sr.No.		Condition
1	Boat: Pyrex Tube	1- Cm length and 1 Cm diameter
2	Motor speed	1.5 cm/6Hrs,1.0 cm/6 Hrs. and 0.5 cm/6Hrs.
3	Evacuation Pressure:	10-5 Torr
4	Cleaved after:	Unidirectional 10 passes.
5	Approx. Time:	60 Days.

Table-2 optimum conditions for gel method

Sr. No.		Conditions
1	Density of Sodium Metasilicate	1.04 gm/cm3
2	Amount of 2N Acetic Acid	5ml
3	pH of Gel	4.40
4	Temperature	Room Temperature
5	Concentration of Bi_2O_3	0.5 ml, 1M
6	Gel Setting Time	7-8 days
7	Gel Ageing Time	78 Hrs.
8	Period of growth of crystals	30 day

Optimum Conditions For Nanoparticles:

- We have explored the colloidal synthesis of Bi_2S_3 nano crystals, with the aim of employing them in the fabrication of solution process able and to replace toxic heavy metals AND Nano rods are used as efficient photo catalyst for the photo catalytic degradation of highly hazardous malachite green dye under visible light irradiation
- Different sizes and shapes were obtained according to the synthesis parameters and the growth process has been rationalized by comparing the predicted morphology.

1.6 Acknowledgments

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