Final Progress Report of UGC Major Research Project for the period01/04/2013 to 31/03/2017

Title of the research project:

Synthesis and characterization of V_2 -VI₃ compound in single crystal/nanomaterial/thin film forms

Reference: UGC Major research project vide. Sanctioned letter F. No. 42-826/2013 (SR) Dated: 22nd March, 2013

Principal Investigator: Prof. M. P. Deshpande Department of Physics Sardar Patel University VallabhVidyanagar, Anand Gujarat-388120

P. G.Department of Physics Sardar Patel University Vallabh Vidyanagar- 388120

STATEMENT OF EXPENDITURE IN RESPECT OF MAJOR RESEARCH PROJECT

1. Name of Principal Investigator : **Prof. M. P. Deshpande**

2. Department of Principal Investigator: Department of Physics,

University

: Sardar Patel University,

VallabhVidyanagar- 388 120,

Gujarat, INDIA

- 3. UGC approval Letter No. and Date: F.No.42-826/2013 (SR) dated 22nd March, 2013
- 4. Title of the Research project: "Synthesis and characterization of V_2 -VI₃ compound in single crystal/nanomaterial/thin film forms"
- 5. Effective date of starting the project $: 1^{st}$ April 2013
- 6. **a.** Period of Expenditure : **From 01/04/2013 to 31/03/2014** (1stYear)

:

01/04/2014 to 31/03/2015 (2ndYear)

01/04/2015 to 31/03/2016 (3rdYear)

01/04/2016 to 31/03/2017(extended Year)

			Expenditure Incurred (Rs.)				
Sr. No.	Item	Amount Approve d (Rs.)	01/04/2013 to 31/03/2014 (1 st Year)	01/04/2014 to 31/03/2015 (2 nd Year)	01/04/2015 to 31/03/2016 (3 rd Year)	01/04/2016 to 31/03/2017 (ext. Year)	Total
i	Equipments (SILAR control system, Bridgman mechanical set up)	4,00,000	3,58,620	-	-		3,58,620
ii	Contingency	50,000	5,155	6,025	14,995	7,895	34,070

b. Details of Expenditure

iii	Field Work/Travel (Give details in theproforma at Annexure- IV).	15,000	1,280	7,440	2,188	-	10,908
iv	Chemicals & Glassware	60,000	16,725	12,973	-	-	29,698
v	Overhead	63,800	63,800	-	-	-	63,800
J	Fotal (Rs.)	5,88,800	4,45,580	26,438	17,183	7,895	4,97,096

c. Staff : Miss. Kamakshi R.Patel (Project Fellow)

Date of Appointment : 1st July 2013

S. No.	ltems	From	Amount Approved (Rs.)	Expenditure incurred (Rs.)
1	Project Fellow @Rs. 14,000/-p.m.	1 st July 2013 to 31 st March 2014		1,12,000/-
2	Project Fellow @Rs. 14,000/-p.m.	1 st April 2014 to 31 st March 2015		1,68,000/-
3	Project Fellow @Rs. 14,000/-p.m. Project Fellow @Rs. 16,000/-p.m.	1 st April 2015 To June 2015 1 st July 2015 To 31 st March 2016	5,28,000/-	2,00,000/-
4	Project Fellow @Rs. 16,000/-p.m.	1 st April 2016 To June 2016		48,000/-
	Total(Rs.)			5,28,000/-

1. It is certified that the appointment(s) have been made in accordance with the terms and conditions laid down by the Commission.

2. If as a result of check or audit objection some irregularity is noticed at later date, action will be taken to refund, adjust or regularize the objected amounts.

3. Payment @ revised rates shall be made with arrears on the availability of additional funds.

4. It is certified that the grant of Rs. 7,90,300.00 (Rupees Seven lakhs ninety thousand three hundred only) (1st installment) + Rs. 2,18,000.00 (Two lakhs eighteen thousand only) (2nd installment) = 10,08,300.00 (Ten lakhs eight thousand three hundred only) has been received from the University Grants Commission under the scheme of support for Major Research Project single characterization of V2-VI3 compound in and entitled "Synthesis crystal/nanomaterial/thin film forms" vide UGC letter No. F. No. 42-826/2013 (SR) dated 22nd March, 2013. Out of this Rs.5, 57,580 (Rupees Five lakhs fifty seven thousand five hundred eighty only) (1st Year) +Rs.1, 94,438 (Rupees one lakhs ninety four thousand four hundred thirty eight only) (2nd Year) + Rs.2, 17,183 (Rupees two lakhs seventeen thousand one hundred eighty three only) (3rd Year) + Rs. 55,895 (Rupees fifty five thousand eight hundred ninety five only) (extended Year 01/04/2016 to 31/03/2017) = total Rs.10,25,096 (Rupees ten lakhs twenty five thousand ninety six only) has been utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

SIGNATURE OF PRINCIPAL INVESTIGATOR

(Prof. M. P. Deshpande)

Prof. M. P. Deshpande Principal Investigator UGC/MPD/2013-16 Sanction F. No. 42-826/2013(SR) Dated 22 March 2013 REGISTRAR Registral Sardar Patel University Vallabh Vidyanagar

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V.V.

NAGAR

Annexure – IV

P.G. Department of Physics Sardar Patel University Vallabh Vidyanagar- 388120

STATEMENT OF EXPENDITURE INCURRED ON FIELD WORK

Name of the Principal Investigator: Prof. M. P. Deshpande

Sr. No.	Name of visitor	Name of the Place visited	Date of the visit	Mode of Journey	Expenditure Incurred (Rs.)
1	Prof. K. C. Poria	Surat to V.V. Nagar	29/06/2013	Train	1280.00
2.	Kamakshi R. Patel	V.V.Nagar to Indore	02/11/2014 To 08/11/2014	Bus and train	1949.00
3.	Prof. M. P. Deshpande	V.V.Nagar to Delhi	11/01/2015 To 13/01/2015	Train	5491.00
4.	Kamakshi R. Patel	V.V.Nagar to Indore	08/06/2015 To 13/06/2015	Bus and train	2188.00
	10,908.00/-				

Certified that the above expenditure is in accordance with the UGC norms for Major Research Projects.

SIGNATURE OF PRINCIPAL INVESTIGATOR

(Prof. M. P. Deshpande)

Prof. M. P. Deshpande Principal Investigator UGC/MPD/2013-16 Sanction F No. 42-826/2013(SR) Dated ∠2 March 2013

REGISTRAR Sardar Patel University Vallabh Vidyanagar EL

V.V.

NAGAR

P.G. Department of Physics Sardar Patel University

Vallabh Vidyanagar- 388120

Report of the work done on the Major Research Project

- 1. Project report No. : Final
- 2. UGC Reference No. :F.42-826/2013 (SR)
- 3. Period of report from : 01/04/2013to31/03/2014 (1stYear)
- 01/04/2014 to 31/03/2015 (2nd Year)
- 01/04/1015 to 31/03/1016 (3rdYear)

01/04/1016 to 31/03/1017 (extendedYear)

- 4. Title of research project : "Synthesis and characterization of V₂-VI₃compound in single crystal/nanomaterials/thin film forms"
- 5. (a) Name of the Principal Investigator: Prof. M. P. Deshpande(b) Deptt. : Department of Physics
- (c) University/College-where work has progressed: Sardar Patel University,

VallabhVidyanagar-388120,

Gujarat, INDIA

- 6. Effective date of starting of the project : 01/04/2013
- 7. Grant approved and expenditure incurred during the period of the report:
- a. Total amount approved: Rs. 11, 16,800.00

b. Total expenditure: Rs.10, 25, 096/-

 $(Rs.5, 57,580/- (1^{st}Year) + Rs.1, 94,438/- (2^{nd}Year) + Rs.2, 17,183/-(3^{rd}Year) + Rs.55,895/- (extended Year01/04/2016 to 31/03/2017) = Rs.10, 25, 096/-)$

- c. Report of the work done: See Enclosure I
- i. Brief objective of the project
- a. Synthesis and characterization of V₂-VI₃compound in single crystal/nanomaterials/thin film forms
- b. Characterization of synthesized compound
- c. Study onstructural, opticaland thermal properties.
- **ii.** Work done so far and results achieved and publications, if any, resultingfrom the work (Give details of the papers and names of the journals inwhich it has been published or accepted for publication.....
 - (1) Sb_2S_3 microspheres prepared by solvothermal method
 - M. P. Deshpande, Pallavi Sakariya, Sandip V. Bhatt, Kamakshi R. Patel, Nikita H. Patel and S. H. Chaki.

Advanced Science Letters, 20, (2014), 1102-1106.

(2) Characterization of Bi₂S₃ nanorods prepared at room temperature
 M. P. Deshpande, Pallavi N. Sakariya, Sandip V. Bhatt, Nitya Garg, Kamakshi Patel,
 S. H. Chaki

Materials Science in Semiconductor Processing, 21, (2014), 180-185.

- iii. Has the progress been according to original plan of work and towards achieving the objective? If not, state reasons: YES
- iv. Please indicate the difficulties, if any, experienced in implementing the project: N.A.
- v. If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet: N.A.
- vi. If the project has been completed, please enclose a summary of the findings of the study. One bound copy of the final report of work done may also be sent to University Grants Commission: See Enclosure I
- vii. Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained (b) Ph. D. awarded (c) Publication of results (d) other impact, if any paper communicated

(a) Manpower trained : Research Fellow Kamakshi R. Patel has been trained in the above field and can now work independently.

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(b) Ph. D. awarded : No (on the verge of completion)
(c) Publication of results : See the papers attached (Published)
(d) Other impact : N/A

SIGNATURE OF THE PRINCIPAL INVESTIGATOR

etpo

(Prof. M. P. Deshpande)

Prof. M. P. Deshpande Principal Investigator UGC/MPD/2013-16 Summer No. 42-826/2013(SR) Dated 22 March 2013



RREGISTERAR Sardar Patel University Vallabh Vidyanagar



Enclosure - I

The literature survey of the project work on V_2 -VI₃ semiconducting materials in different forms have been collected as per the proposal submitted from internet as well as from library. Necessary chemicals and glassware has been purchased during this year of the project. The equipment sanctioned in the mentioned project, SILAR controller and Bridgman mechanical set up are purchased from Holmarc Opto-Mechatronics (P) Ltd. Instruments, Kochi, Kerala and Vi Micro Systems Pvt .Ltd. Perungudi, Chennai respectively which are shown in **figure 1**. Efforts are underway to prepare thin films by SILAR technique.We have started to calibrate high temperature dual zone furnace with the facility available in the department for the growth of single crystals by Bridgman in the required temperaturerange by applying the range of trials.



Bridgman mechanical set up

SILAR control unit

Figure 1 Photograph of equipments purchased

The equipments are installed and working satisfactorily. The project fellow has been trained accordingly to the requirement of project.

In continuation with the above work, in next duration we have synthesized single crystal of Sb_2S_3 by chemical vapor transport technique, microsphere of Sb_2S_3 by solvothermal method, Sb_2S_3 thin film by SILAR coating unit and Bi_2S_3 nanorods prepared at room temperature and studied their various properties by different characterization techniques.

The complete description of this work is described below.

Single crystals of Sb₂S₃

(A) Growth method

Single crystals of Sb₂S₃ were prepared from high purity (99.999%)antimony (Sb) and sulfur (S) powder.First of all, the powder were weighed and loaded into thick walledquartz ampoule.The ampoule was then evacuated (10^{-5} torr) and sealed and thenplaced in the horizontal single zone furnace to prepare charge at500°C for 3 days.The prepared charge was taken in another quartz ampoule withNH₄Cl used as a transporting agent and then again sealed at 10^{-5} torr and placed in the dual zone furnace at temperature 500°C to450°C of the source zone and growth zone respectively.After 6 days, the furnace was cooled to room temperature and thenampoule was taken out from the furnace and broken which which resulted in the growth of single crystals of Sb₂S₃ in the form of needle shape shown in **Figure2**.The length of the single crystals shown in **Figure 2**varied from 0.1cm to 1.2 cm.



Figure 2 Single crystals of Sb₂S₃

(B) Characterization

1. Energy Dispersive Analysis of X rays (EDAX)



Figure 3 EDAX spectra of Sb₂S₃ single crystal

The composition of the grown crystals determined from the EDAX spectra shown in **figure 3** are shown in the below **table 1**.

Table 1 wt % of the elements

Composition	Element	Wt% (obtained)	Wt% (calculated)
Sh ₂ S ₂	Sb	72.20	71.68
00203	S	27.80	28.32

2. X-ray diffraction

X-ray diffraction pattern of Sb₂S₃ powder (polycrystalline) made from single crystals is shown in **figure 4**.All the diffraction peaksshown in **figure 4**were indexed with the help of powder-X software topure orthorhombic phase of Sb₂S₃ with calculated lattice parameters: a = 11.239A°, b = 11.313 A° and c = 3.841 A°.



Figure 4 X- ray diffractogram of Sb₂S₃compound

The results are in good agreement with standard data card (JCPDS 42-1393)[1] and previously reported data for $Sb_2S_3[2,3]$ We have used Scherrer's formula[4] to calculate the crystallite size for various reflections and it indicates that these sizes vary between 23A°to 65A°. The sharp diffraction peaks are an indication of good crystallinity of Sb_2S_3 sample.

3. Scanning Electron Microscopy (SEM)

The surface morphology of grown single crystals of Sb_2S_3 different magnification of 100X, 50X and 500X using SEM are shown in below **figures 5** (**a**,**b**),(**c**,**d**),(**e**,**f**) respectively. It is seen that crystals surfaces are possessing cracks and visible inclusions.



Figure 5 SEM photographs of Sb₂S₃

4. Raman spectroscopy

Figure 6shows the Raman spectrum of Sb_2S_3 single crystal atroom temperature using Ar laser source.



Figure 6 Raman spectra of Sb₂S₃ single crystal

This exhibits seven resonantpeaks at about 115, 147, 190, 252, 282, 300 and 373 cm⁻¹ in the range of 100 - 400 cm⁻¹. The presence of sharp peaks at 190 and 252 cm⁻¹ suggests the formation of well crystalline product[5]. The low intensitypeaks at 282, 300 and 373cm⁻¹ can be assigned to the unit Sb_2S_3 pyramidof the material having C_{3v} symmetric mode [6]. All these results are in goodagreement with the reported Raman spectrum[7]. At room temperature Sb₂S₃ crystallizes in orthorhombic form withfour molecules and 20 atoms per unit cell, stibnite has 60 normal Г modes, which according to the group theory decompose in $as10A_g + 5B_{1g} + 10B_{2g} + 5B_{3g} + 5A_u + 10B_{1u} + 5B_{2u} + 10B_{2u}$. The acoustic modeshave character $B_{1u}+B_{2u}+B_{3u}$. The A_u modes are silent whereas all theother modes are active. The optical modes are distributed over a narrow0-350 cm⁻¹ frequency range. The infrared reflectivity spectrum shows amultitude of peaks which are poorly differentiated and highlyoverlapping. The Raman spectrum is better differentiated with five mainpeaks. The main infrared mode lies around 246 cm^{-1} and represents as upper position of at least one B_{3u} and one B_{1u} modes [8].

5. TGA analysis

Figure 7shows the TGA curve of Sb_2S_3 crystal under nitrogen (N₂)atmosphere. It is observed from thermogram that Sb_2S_3 decomposesslowly from 27°C to 472°C having small weight loss of nearly 2%.



Figure 7 TGA spectra of Sb₂S₃ crystal powder under N₂ atmosphere

The continuous decomposition occurs after 472° C to 575° C, which showsweight loss of nearly 5%. From the TGA curve, we have calculated the activation energy in the weight loss region (which is nearly 5%) by using three models viz Broido relation (BR), Piloyan-Novikova (PN) relation and Coats Redfern (CR). Values of calculated activation energy for three different models are given in the **table2**. Since the electrical resistance of Sb₂S₃ material is very high in

theorder of MegaOhm, therefore, measurement of electrical resistivity,thermoelectric power and Hall Effect of Sb_2S_3 could not be measured. We determined only thermal conductivity of Sb_2S_3 crystal pellet at 100°C and it comes out to be 0.422 Wcm⁻¹deg⁻¹. Thus we were not able tocalculate the figure of merit of Sb_2S_3 single crystal, so as to prove itsutility for thermoelectric material.

Table 2 activation energy for the Sb_2S_3 single crystal

Name of model	Broido relation	Piloyan-Novikova relation	Coats-Redfern relation
Activation energy	0.97eV	0.38eV	0.38eV

Microspheres of Sb₂S₃

(A) Synthesis of Sb₂S₃ microsphere using solvothermal Method

All of the chemical reagents used in this experiment were of analytical grade and were used without further purification. In a typical procedure, 0.23 g antimony chloride (SbCl₃) and 0.45 g tartaric acid were dissolved in 16 mL N, N-dimethylformamide (DMF). In this solution about 0.244 g sulfur powder was added with stirring. This mixed solution was transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 120° C for 4 h and then cooled to room temperature naturally. The precipitates were collected and washed with distilled water for several times. Then, the precipitates were dried in air. Finally, the resultant burgundy colored powder sample which is shown in **figure 8**were obtained and characterized by various techniques.



Figure 8 Microspheres of Sb₂S₃

(B) Characterization

1. Energy Dispersive Analysis of X-rays (EDAX)



Figure 9 Spectra of Sb₂S₃ microspheres

The elemental compositions of Sb_2S_3 microspheres synthesized are shown in **table 3**below indicates no impurity content in it as it seen from **figure 9**.

Table 3 wt% of elements

Composition	Wt% of present	element in Sb ₂ S ₃
Sb ₂ S ₃	Sb	S
SD ₂ S ₃	71.08	28.92

2. X-ray diffraction (XRD)



Figure 10 X-ray diffractogram of Sb_2S_3 microspheres

XRD pattern of Sb₂S₃ microspheres is shown in **figure 10**in the 2 θ range of 0-90°. All the diffraction peaks were indexed with the help ofpowder-X software to a pure orthorhombic phase of Sb₂S₃ withcalculated lattice parameters a=11.24 A°, b= 11.31 A° and c= 3.84 A°, which matches well with the values reported in JCPDS 42-1393.

3. X-ray photoelectron spectroscopy (XPS)

The chemical state, purity and composition of the as-obtained product were further checked by XPS analysis. **Figure 11(a)** shows thescanned XPS spectra of the product. The peaks arising from Sb_2S_3 (Sb4d, 3d, 3p and S 2s, 2p) are clearly seen, and a small contaminant C1speak is also evident. The high-resolution XPS spectra of Sb 3d, 4d and S2p were obtained using C1s as the reference at 287.5eV. In order toanalyze the composition of the as-obtained product in detail, curve fitting S 2p and Sb 3d, 4d were performed.



Figure 11 XPS spectra of Sb₂S₃ microspheres

Figure 11 (b) shows the high-resolution spectra of the S 2p with thepeak at 161.19 eV whereas the high resolution spectra of the Sb 3d is shown in **Figure 11 (c)** which shows the presence of two peaks for $Sb3d_{5/2}$ and $Sb3d_{3/2}$ at 530.29 eV and 539.69 eV, respectively. **Figure 11 (d)** represents the high-resolution spectra of the Sb 4d with the peak at33.52 eV. The peak position for both Sb and S agree well with those reported in the literature[**9**]. The average weight percentage ratio obtained from quantification of Sb3d and S2p peaks is 73:27, which is close to anticipated value and are supporting the EDAX results also.

4. Scanning Electron Microscopy (SEM)

The surface morphology of the Sb₂S₃ microspheres is studied bySEM. The three SEM images of the sample were obtained at differentplaces with same magnification. **Figure 12**shows that the product contains sphere like structure and the diameter of these spheres varies from 1 to 5 μ m.



Figure 12 SEM images of Sb₂S₃ microspheres

5. Transmission electron microscopy (TEM)

Further, we studied the detailed structure and morphology of thesample by TEM analysis and is presented in below **figure 13**. The TEM image in (**a**) shows individual sphere of Sb_2S_3 with a diameter range from100nm to 300nm and selected area electron diffraction pattern (SAED) of these spheres is given in (**b**) which shows diffraction spots indicating single crystalline nature of these Sb_2S_3 microspheres. Fewdiffraction spots are indexed based on orthorhombic structure of Sb_2S_3 which is shown in (**b**) and the zone axis determined as [001]suggests the preferred orientation.



Figure 13 TEM image and SEAD pattern of Sb₂S₃ microspheres

6. Raman Spectroscopy

Raman spectrum was obtained at room temperature with Ar+ laser source as excitation source which is displayed in **Figure 14**.



Figure 14Raman spectrum of the Sb₂S₃ microsphere

The appearance of the peaks at 151, 188, 252, 305, 372 and 450 cm⁻¹ is in good agreement with the reported Raman spectra. The presence of sharp peaks at 151cm⁻¹, 188cm⁻¹and 252cm⁻¹ suggests the formation of well crystalline products. The low intensity peak at 305 cm⁻¹ and 372 cm⁻¹ can be assigned to the unit SbS₃ pyramid of the material having C3v symmetric mode. The presence of a relatively broad peak at 450 cm⁻¹ may be due to the symmetric stretching of the Sb-S-Sb bond of Sb₂S₃, which can be accounted on the basis of existing literature[**10**].

7. TGA



Figure 15TGA plot of Sb₂S₃ microspheres in air atmosphere

A TGA spectrum in air of the prepared Sb_2S_3 microspheres is shown in **Figure 15**which reflects weight loss between 178-292°C. The weight loss may be due to formation of oxide of antimony

and sulfur evaporation in this temperature range. We have used the theoreticalmodels viz. Broido (BR)[11], Coats Redfern (CR)[12] and Piloyan-Novikova (PN)[13] relations for calculating the activation energy in the weight loss region of TGA curve. The calculated values of activation energy from these relations are shown in below **table4**.

Table 4 activation energy from TGA

Name of	Broido relation	Coats-Redfern	Piloyan-Novikova
Model		relation	relation
Activation energy	0.79eV	0.64eV	0.16eV

8. UV-Vis Spectroscopy



Figure $16(ahv)^2$ versus hv curve for the Sb₂S₃ microspheres

Figure 16 shows $(\alpha hv)^2 - hv$ graph, from which we determined the value of bandgap which comes out to be 1.62eV which is near to optimum value for photovoltaic conversion, suggesting that these microspheres may be suitable for applications in solar energy and optoelectronic devices[14].

9. Photoluminescence spectroscopy (PL)



Figure 17Photoluminescence spectra of the Sb₂S₃ microspheres

The PL spectra of the Sb_2S_3 microspheres were recorded at different excitation wavelength 350nm, 400nm and 430nm, as shown in**figure 17**. From the observed emission peak values for different excitation wavelength, it is clear that Sb_2S_3 microspheres are showing luminescent behavior in different regions of the spectrum and this property can also be utilized for optical applications.

Synthesis of Sb₂S₃ thin film by SILAR coating unit

(A) Thin film deposition on glass substrate

We made $0.1 \text{ M Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$ solution in 100 ml of ethylene glycol and 0.05 M SbCl_3 in 100 ml of ethylene glycol in beaker 1 and beaker 3 respectively. Then taken two other beakers with 100 ml of distilled water and named them as beaker 2 and beaker 4. Now we set the program in

the SILAR unit as (a) dipping time: 10 s for beaker 1 and 3 and 5 s for beaker 2 and 4. (b) Drying time: 10s for all the 4 beakers. This program is set for 35 cycles and we have thin film of Sb_2S_3 deposited on glass substrate as shown in **figure 18**.



Figure 18Sb₂S₃thin film on glass substrate

(B) Charecterization

1. Energy Dispersive Analysis of X-rays (EDAX)

The EDAX spectra of deposited Sb_2S_3 thin films on glass substrates using SILAR method with different cycles and concentrations {cycles: 25 cycle, 30 cycle, 33cycle, 50 cycle; concentration: 0.05:0.1 M, 0.1:0.2M} are shown in **figure 19** [a, b, c, d]respectively indicating the presence of elements of S and Sb and the atomic percentage of Sb and S are shown in **table 5** (a,b,c,d) respectively.



Figure 19EDAX spectra of Sb_2S_3 thin films

Table 5(a)

Element	Weight % (calculated)	Weight % (observed)	Atomic % (calculated)	Atomic % (observed)
Sb	71.68	94.26	59.02	81.21
S	28.29	5.74	41.97	18.79

Table 5(b)

Elements	Weight % (calculated)	Weight % (observed)	Atomic % (calculated)	Atomic % (observed)
Sb	71.68	94.46	59.02	81.77
S	28.29	5.54	41.97	18.23

Tab	le	5	(c)
1 a0	ιυ	\mathcal{I}	(\mathbf{U})

Elements	Weight % (calculated)	Weight % (observed)	Atomic % (calculated)	Atomic % (observed)
Sb	71.68	88.46	59.02	66.88
S	28.29	11.54	41.97	30.12

Elements	Weight % (calculated)	Weight % (observed)	Atomic % (calculated)	Atomic % (observed)
Sb	71.68	95.59	59.02	85.11
S	28.29	4.41	41.97	14.89

Table 5(d)

2. X-ray diffraction

Figure 20 shows X-ray diffractograms of Sb_2S_3 thin films with different concentrations and depositing cycles. From these diffractograms we calculated lattice parameters and crystallite size whose values are narrated below for each film with different concentrations and depositing cycles.



Figure 20 X-ray diffractogram of Sb₂S₃ thin films

The lattice parameter $a = 11.23 \text{ A}^\circ$, $b = 11.07 \text{ A}^\circ$, $c = 3.81 \text{ A}^\circ$ and crystallite size D = 13.8 nm. (Cycles: 25, SbCl₃:0.05M, Na₂O₂S₃ 5H₂O:0.1M)

The lattice parameter $a = 11.11 \text{ A}^\circ$, $b = 11.31 \text{ A}^\circ$, $c = 3.85 \text{ A}^\circ$ and crystallite size D = 15.06 nm. (Cycles: 30, SbCl₃:0.05M, Na₂S₂O₃ 5H₂O:0.1M)

The lattice parameter $a = 10.78 \text{ A}^\circ$, $b = 11.64 \text{ A}^\circ$, $c = 3.85 \text{ A}^\circ$ and crystallite size D = 11.06 nm. (Cycles: 33, SbCl₃:0.05M, Na₂S₂O3 5H₂O:0.1M)

The lattice parameter $a = 11.74 \text{ A}^\circ$, $b = 11.28 \text{ A}^\circ$, $c = 3.66 \text{ A}^\circ$ and crystallite size D = 9.19 nm. (Cycles: 50, SbCl₃:0.1M, Na₂O₂O₃ 5H₂O:0.2M). Calculated lattice parameters are in agreement with the reported values (JCPDS -42 - 1933) $a = 11.23 \text{ A}^\circ$, $b = 11.32 \text{ A}^\circ$, $c = 3.841 \text{ A}^\circ$ [15].

3. Photoluminescence spectroscopy

Room temperature PL spectra of Sb_2S_3 thin films, for different cycles and concentrations are shown in **figure 21**.



Figure 21 PL spectra of Sb₂S₃ thin films at room temperature

The emission peaks presents broad bandsover 430-480nm range with strong violet emission peaks centered at same wavelengths of 460nm [2.70eV] for all thin films[16].

4. Scanning electron microscopy



Figure 22 Scanning Electron Microscopy images

Figure 22 shows SEM images of non-stoichiometric Sb_2S_3 thin films for different cycles and concentrations. We could observe some aggregation in these synthesized films as seen from the SEM images.

5. Raman spectroscopy

Raman spectra of Sb_2S_3 thin films for different cycles and concentrations are shown in **figure 23**. Raman shifts in **figure 23(a)** are observed at 125, 300, 498 and 580cm⁻¹, for **figure 23(b)** at 300, 450 and 500 cm⁻¹, for **figure 23(c)** at 300 and 720 cm⁻¹, and **figure 23(d)** at 130, 150, 250, 300, 450, 500 and 600 cm⁻¹. These values of Raman shift are in agreement with the Raman spectrum reported by Lopez et al. [7].



Figure 23 Raman spectra of Sb₂S₃ thin films

Bi₂S₃nanorods prepared at room temperature

(A) Synthesis method for Bi₂S₃ nanorods

All chemicals were analytical grade and used without any further purification. In typical synthesis, 1ml hydrochloric acid (36Wt%) and 0.243g of bismuth nitrate (Bi(NO₃)₃·5H₂O) were added into 10 ml of distilled water. after stirring for 2 minute, 0.0564g thioacetamide (TAA) was introduced and stirring was continued (the final concentration of Bi (NO₃)₃ and TAA was 0.05 mol L⁻¹). This resulted solution was kept at room temperature for 24 h under static condition. The solution turned transparent to brown then to black gradually and precipitates at last were settled

down. The resulting product was filtered, collected and washed with distilled for several times and dried in air and shown in **figure 24**.



Figure 24 Bi₂S₃ nanorods

(A) Charectsrization

1. Energy dispersive analysis of X-ray (EDAX)

Figure 25 shows the EDAX spectra for the Bi_2S_3 nanostructure. The wt% and at% are stated in table 6 given below.



Figure 25EDAX spectra of the as obtained Bi_2S_3 nanostructure

Table 6wt% and at% of the Bi_2S_3 nanostructure

composition	Elements	Wt %	At %
Bi ₂ S ₃	Bi	84.45	45.46
	S	15.55	54.54

 $\begin{array}{c|cccc} We & can & conclude & fromEDAX & spectra & that no other impurities are incorporated in the sample and excess of Bi is observed in & comparison to Swhich is nearly consistent with the desirable stoichiometry of Bi _2S_3. \end{array}$



2. X-ray diffraction (XRD)

Figure 26 XRD spectra of Bi₂S₃nanorods

Figure 26 shows the powder X-ray diffraction of Bi_2S_3 sample. X-ray powder diffraction (XRD) analysis confirms that the as-synthesized product belongs to the orthorhombic system and

diffraction peaks are indexed with the help of powder X-software. The calculated lattice constants are a = 11.15Å, b = 11.30Å and c = 3.98Å (spacegroup pbnm), which are consistent with the JCPDS no.43-1471[**17**].

3. X-ray photoelectron spectroscopy (XPS)

XPS spectra shown in **figure 27(a)**. The binding energies obtained in the XPS analysis were corrected for specimen charging by referring the C_{1s} line to 284.60 eV. All other peaks can be assigned to O, Bi and S elements.



Figure 27(a) XPS spectra of prepared Bi₂S₃ sample (b, c) high resolution spectra of Bi and S regions of the prepared Bi₂S₃ sample

shownin figure 27(b) whereas The peak at 225.29 eV corresponds to S_{2s} as thetwostrongpeaksat159.3and164.5eV figure 27(c) areassignedtoBi_{4f7/2} in andBi_{4f5/2} spin-orbitdoubletsplittingof5.2eV, respectively, with a typicalBi_{4f} which is consistent with the reported values [18].

4. Transmission electron microscopy (TEM)

The morphology, size of as-obtained product and selected areadiffraction (SAED) pattern of Bi_2S_3 nanostructure were observed bytransmission electron microscope (TEM) (Philips Tecnai 20, 200KV). The shape of the nanorods can be seen in **figure 28**.



Figure 28 TEM images of Bi₂S₃ nanostructure

5. Raman spectroscopy



Figure 29 Raman spectroscopy of Bi₂S₃ nanorods

Raman spectrum of Bi_2S_3 nanorods shown in **figure 29** indicate two peaks at 238 cm⁻¹ corresponding to Ag phonon mode and 972 cm⁻¹ may be related to surface phonon modes

because of the high surface-to-volume ratio, which is in good agreement with values for commercial Bi_2S_3 as well as the nanoparticles[19].

6. UV-vis spectroscopy

UV-vis absorption spectrum in figure 30 shows a broad absorption peak at 262nm correspondingtothebandgapof2.74eVwhichshowsthesizeeffectandblueshiftinwavelengthincomparisontobulkmaterial[20]whichguitesimilartothatsynthesizedbyaphotochemical synthesis method.



Figure 30UV-Vis spectra of Bi₂S₃ nanorods

7. Thermal gravimetric analysis (TGA)

Figure 31 shows the TGA plot of Bi_2S_3 as-synthesized nanorods. It shows that the weight of the material continuously decreases with temperature. We have used the Broido relation for analysis of TGA spectra for calculating the activation energy in the entire weight loss region. The activation energy comes out to be 0.38eV.



Figure 31 TGA plot for the Bi₂S₃nanorods

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Annexure – VII

P. G. Department of Physics Sardar Patel University Vallabh Vidyanagar- 388120

MAJOR RESEARCH PROJECT COPY OF THE SPECIMEN OF HOUSE RENT FOR PROJECT FELLOW

Certified that Ms. Kamakshi R. Patel is paying House Rent of Rs.1400/- and is eligible to draw House Rent Allowances @10% <u>1400</u> *24 + 1600*12 = Rs. <u>52,800/-</u> as per University Rules.

SIGNATURE OF THE PRINCIPAL INVESTIGATOR Prof. M. P. Deshpande

Prof. M. P. Deshpande Principal Investigator UGC/MPD/2013-16 Sanction F. No. 42-826/2013(SR) Dated 22 March 2013

gistrar Sardar FGISTRAEniversity Vallabh Vidyanagar,



STATEMENT OF THE HOUSE RENT IN RESPECT OF MAJOR RESEARCH PROJECT F. NO. 42-826\2013(SR) Dated on 1-4-2013:

Name: Kamakshi R. Patel

Department: Department of Physics

Sr No.	Month	How much to be reimburse
1.	July 2013	1400/-
2.	August 2013	1400/-
3.	September 2013	1400/-
4.	October 2013	1400/-
5.	November 2013	1400/-
6.	December 2013	1400/-
7.	January 2014	1400/-
8.	February 2014	1400/-
9.	March 2014	1400/-
10.	April 2014	1400/-
11.	May 2014	1400/-
12.	June 2014	1400/-
13.	July 2014	1400/-
14.	August 2014	1400/-
15.	September 2014	1400/-
16.	October 2014	1400/-
17.	November 2014	1400/-
18.	December 2014	1400/-
19.	January 2015	1400/-
20.	February 2015	1400/-
21.	March 2015	1400/-
22.	April 2015	1400/-
23.	May 2015	1400/-
24.	June 2015	1400/-
25.	July 2015	1600/-
26.	August 2015	1600/-
27.	September 2015	1600/-
28.	October 2015	1600/-
29.	November 2015	1600/-
30.	December2015	1600/-
31.	January 2016	1600/-
32.	February 2016	1600/-
33.	March 2016	1600/-
34.	April 2016	1600/-
35.	May 2016	1600/-
36.	June 2016	1600/-
		<u> TOTAL - Rs. 52,800/-</u>

P. G. Department of Physics Sardar Patel University Vallabh Vidyanagar- 388120

PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

1. Title of the Project: Synthesis and characterization of V_2 -VI₃ compound in single crystal/nanomaterial/thin film forms

2. NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR: Prof. M. P. Deshpande Department of Physics, Sardar Patel University

Anand, Gujarat

3. NAME AND ADDRESS OF THE INSTITUTION: Department of Physics, Sardar Patel University, Vallabh Vidyanagar, Anand, Gujarat

4. UGC APPROVAL LETTER NO. AND DATE: F.No. 42-826/2013 (SR) dated 22nd March 2013.

5. DATE OF IMPLEMENTATION: 1st April 2013

6. TENURE OF THE PROJECT: 4 years

7. TOTAL GRANT ALLOCATED: Rs. 11, 16,800

8. TOTAL GRANT RECEIVED: Rs. 10, 08,300

9. FINAL EXPENDITURE: **Rs. 10, 25,096**

10. TITLE OF THE PROJECT: Synthesis and characterization of V₂-VI₃ compound in single crystal/nanomaterial/thin film forms

11. OBJECTIVES OF THE PROJECT:

a. Synthesis and characterization of $V_2\mbox{-}VI_3\mbox{compound}$ in single crystal/ nanomaterials/ thin film forms.

b. Characterization of synthesized material structurally, optically, and thermally by various techniques.

12. WHETHER OBJECTIVES WERE ACHIEVED: **Yes** (GIVE DETAILS)

We undertook the preparation of **single crystal of Sb**₂**S**₃ by chemical vapor transport technique, **microsphere of Sb**₂**S**₃ by solvothermal method, **Sb**₂**S**₃ **thin film** by SILAR coating unit and **Bi**₂**S**₃ **nanorods** prepared at room temperature and studied their various properties by different charactrization techniques successfully.

The equipment sanctioned in the mentioned project, SILAR controller and Bridgman mechanical set up are purchased from Holmarc Opto-Mechatronics (P) Ltd. Instruments, Kochi, Kerala and

Vi Micro Systems Pvt .Ltd. Perungudi, Chennai respectively are installed and working satisfactorily. The project fellow has been trained accordingly to the requirement of project.

13. ACHIEVEMENTS FROM THE PROJECT:

Single crystals of Sb_2S_3 , Microspheres of Sb_2S_3 , Sb_2S_3 thin film by SILAR coating unitand Bi_2S_3 nanorods were successfully prepared and characteristed by different techniques available in the department and other nearby institutes. Single crystals of Sb_2S_3 grown by vapour phase technique has not been seen reported so far in the literature.

Single crystals of Sb₂S₃ were prepared in the dual zone furnace at temperature 500°C to450°C of the source zone and growth zone respectively. The grown single crystals of Sb₂S₃were in the form ofneedle shape. The composition of the grown crystals were determined from EDAX spectra. X-ray diffraction pattern of Sb₂S₃ powder (polycrystalline) were indexed with the help of powder-X software topure orthorhombic phase of Sb₂S₃ with calculated lattice parameters: $a = 11.239A^\circ$, $b = 11.313 A^\circ$ and $c = 3.841 A^\circ$. The surface morphology of grown single crystals of Sb₂S₃at different magnification of 100X, 50X and 500X using SEM showed that crystals surfaces are possessing cracks and visible inclusions. The Raman spectrum of Sb₂S₃ single crystal atroom temperature using Ar laser source exhibits seven resonantpeaks at about 115, 147, 190, 252, 282, 300 and 373 cm⁻¹ in the rangeof 100 - 400 cm⁻¹. The presence of sharp peaks at 190 and 252cm⁻¹suggests the formation of well crystalline product. The TGA curve of Sb₂S₃ crystal under nitrogen (N₂)atmosphere showed that Sb₂S₃ decomposesslowly from 27°C to 472°C having small weight loss of nearly 2%.

Microspheres of Sb₂S₃were prepared using solvothermal method. The elemental compositions of Sb₂S₃ microspheres synthesized indicated no impurity content in it. XRD pattern of Sb₂S₃ microspheres were indexed with the help ofpowder-X software to a pure orthorhombic phase of Sb₂S₃ withcalculated lattice parameters a=11.24 A°, b= 11.31 A° and c= 3.84 A°, which matches well with the values reported in JCPDS 42-1393. The chemical state, purity and composition of the as-obtainedproduct were further checked by XPS analysis. The peaks arising from Sb₂S₃ (Sb4d, 3d, 3p and S 2s, 2p) were clearly seen, and a small contaminant C1speak is also evident. The high-resolution XPS spectra of Sb 3d, 4d and S2p were obtained using C1s as the reference

at 287.5eV.The surface morphology of the Sb₂S₃ microspheres is studied bySEM showing spheres from 1 to 5 μ m and TEM analysis showed range from100nm to 300nm. The selected area electron diffraction pattern (SAED) of these spheres indicated single crystalline nature of these Sb₂S₃ microspheres. Raman spectrum was obtained at room temperature with Ar+ laser source as excitation source .The appearance of the peaks at 151, 188, 252, 305, 372 and 450 cm⁻¹ is in good agreement with the reported Raman spectra. TGA spectrum in air of the prepared Sb₂S₃ microspheres reflects weight loss between 178-292°C.The value of bandgap which comes out to be 1.62eVwhich is near to optimum value for photovoltaic conversion, suggesting that these microspheres may be suitable for applications in solar energy and optoelectronic devices.From the observed emission peak values for different regions of the spectrum and this property can also be utilized for optical applications.

Sb₂**S**₃ **thin film** were synthesized by **by SILAR coating unit** purchased in this project. The EDAX spectra of deposited Sb₂S₃ thin films on glass substrates using SILAR method with different cycles and concentrations {cycles: 25 cycle, 30 cycle, 33cycle, 50 cycle; concentration: 0.05:0.1 M, 0.1:0.2M} indicated the presence of elements of S and Sb. X-ray diffractograms of Sb₂S₃ thin films with different concentrations and depositing cycles were recorded and we calculated lattice parameters which were in agreement with the reported values (JCPDS – 42 – 1933) a = 11.23A°, b = 11.32 A°, c = 3.841 A°.Room temperature PL spectra of Sb₂S₃ thin films, for different cycles and concentrations showed the emission peaks presents broad bandsover 430-480nm range with strong violet emission peaks centered at same wavelengths of 460nm [2.70eV] for all thin films. We could observe some aggregation in these synthesized films as seen from the SEM images.Raman spectra of Sb₂S₃ thin films for different cycles and concentrations showed Raman shiftswhich were in agreement with the Raman spectrum reported.

 Bi_2S_3 nanorods were prepared at room temperature by chemical route. We can conclude from EDAX spectra that no other impurities are incorporated in the sample and excess of Bi is observed in comparison to S which is nearly consistent with the desirable stoichiometry of Bi_2S_3 .

The powder X-ray diffraction of Bi_2S_3 sample. X-ray powder diffraction (XRD) analysis confirms that the as-synthesized product belongs to the orthorhombic system and diffraction

peaks are indexed with the help of powder X-software. The calculated lattice constants are a= 11.15Å, b=11.30Å and c = 3.98Å(spacegroup pbnm), which are consistent with the JCPDSno.43-1471. The binding energies obtained in the XPS analysis were corrected for specimen charging by referring the C_{1s} line to 284.60 eV. All other peaks can be assigned to O, Bi and S elements. The peak at 225.29 eV corresponds to S_{2s} whereas the two strong peaks at 159.3 and 164.5 eV in are assigned to Bi_{4f7/2} and Bi_{4f5/2} respectively, with a typical Bi_{4f} spin-orbit doublet splitting of 5.2eV, which is consistent with the reported values. The morphology, size of asobtained product and selected areadiffraction (SAED) pattern of Bi2S3 nanostructure were observed bytransmission electron microscope (TEM) (Philips Tecnai 20, 200KV).Raman spectrum of Bi₂S₃ nanorods indicated two peaks at 238cm⁻¹ corresponding to Ag phonon mode and 972 cm⁻¹ may be related to surface phonon modes because of the high surface-to-volume ratio, which is in good agreement with values for commercial Bi₂S₃ as well as the nanoparticles.UV-vis absorption spectrum showed a broad absorption peak at 262nm corresponding to the bandgap of 2.74eVwhich shows the size effect and blue shift in wavelength in comparison to bulk material .The TGA plot of Bi₂S₃ as-synthesized nanorods. It shows that the weight of the material continuously decreases with temperature.

For industrial applications, the most important question is the product's price in relation to its properties. In most cases, single crystals/thin films/nanomaterials of different materials and products utilizing this form are significantly more expensive than conventional products. In the case of single crystals/thin films/nanomaterialsthe increase in price is sometimes more pronounced than improvement in properties, and therefore economically interesting applications of them are often found only in areas where specific properties are demanded that are beyond the reach of conventional materials. Hence, as long as the use of single crystals/thin films/nanomaterials with new properties provide the solution to a problem which cannot be solved with conventional materials, the price becomes much less important. Finally, only those materials which exhibit new properties leading to novel applications, beyond the reach of conventional materials, promise interesting results.

Therefore, properties studied of V_2 -VI₃ compound in the present study in different forms like single crystal/ thin films/nanoparticles can help to provide their use in near future as photovoltaic and thermoelectric devices. The man power trained as JRF in this project is also a direct contribution to the society.

16. WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT: On the verge of completion.

17. NO. OF PUBLICATIONS OUT OF THE PROJECT: 2 (Papers attached) (PLEASE ATTACH)

(PRINCIPAL INVESTIGATOR)

Prof. M. P. Deshpande Principal Investigator UGC/MPD/2013-16 Sanction F No. 42-826/2013(SR) Dated 22 March 2013

RHRAY

(REGISTRAR PRINCHAL) Sardas antel University Vallabh Vidyanagar



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DEPARTMENT OF PHYSICS

SARDAR PATEL UNIVERSITY, VALLABH VIDYANAGAR-388 120, Gujarat (India)

No. PG/PHY/

Date: - -201 Annexure VI Annexure IX

UGC FILE NO. F. 42-826/2013(SR) (HRP) YEAR OF COMMENCEMENT: 01/04/2013

TITLE OF THE PROJECT: "Synthesis and characterization of V_2 - VI_3 compound in single crystal/ nanomaterial/thin film forms".

1.	Name of the Principal Investigator:	Prof. M. P. Deshpande				
2.	Name of the University/College	Department of Physics, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat				
3.	Name of the Research Personal appointed	Kamakshi .R. Patel				
4	Academic qualification	S.No.	Qualifications	Year	Marks	%age
		1.	M.Sc.	2011	1584/2600	61
		2.	M.Phil	2012	686/1000	69
		3.	Ph.D.	-	-	-
5.	Date of joining	01/07/2013				
6.	Date of Birth of Research Personnel	26/09/1986				
7.	Amount of HRA, if drawn	nil				
8.	Number of Candidate applied for the post	Total: 6, out of them 4 candidates appeared for the interview.				

CERTIFICATE

This is to certify that all the rules and regulations of UGC Major Research Project outlined in the guidelines have been followed. Any lapse on the part of the University will be liable to terminate of said UGC project.

ery Principal Investigator

Head of the Deptt. if.

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Registrar/Principal ardar Patel University Vallabh Vidyanagar



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Advanced Science Letters Vol. 20, 1102–1106, 2014

Sb₂S₃ Microspheres Prepared by Solvothermal Method

M. P. Deshpande¹, Pallavi Sakariya^{1.2.*}, Sandip V. Bhatt¹, Kamakshi R. Patel¹, Nikita H. Patel¹, and S. H. Chaki¹

¹Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388120, Gujarat, India ²Babaria Institute of Technology, NH-8, Varnama, Vadodara 391240, Gujarat, India

We report here synthesis of Sb₂S₃ microsphere via solvothermal method using SbCl₃ (Antimony chloride) and sulfur powder as a starting materials and *N*,*N*-dimethylformamide (DMF) as solvent. Energy dispersive analysis of X-rays (EDAX) and X-ray diffraction (XRD) studies indicated that the prepared microspheres are nearly stoichiometry in composition and corresponds to pure orthorhombic phase of Sb₂S₃. The purity and composition of obtained product was further confirmed by X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies show the sphere like structure of Sb₂S₃ particles with diameter ranging between 100 nm to 300 nm. Optical absorption experiment has shown that Sb₂S₃ microspheres could be used in solar energy and optoelectronic application. We further studied thermal properties of Sb₂S₃ microspheres are stable upto 200 °C. Photoluminesence studies are done on this sample which shows its luminesence behaviour. Raman spectra at room temperature has been used to study various phonon modes in Sb₂S₃ microspheres.

Keywords:

1. INTRODUCTION

V–VI group binary chalcogenides $(A_2^V B_3^{VI}; A = As, Sb, Bi; B = S, Se, Te)$ have attracted much attention due to their good photovoltaic properties and high thermoelectric power, which allow potential applications in optical, electronic and thermoelectric cooling devices.¹ Binary chalcogenides compound have received attention recently because of their potential for optical storage.²

Antimony sulfide (Sb_2S_3) (stibnite) is a direct band gap and highly anisotropic V–VI group binary chalcogenide semiconductor with a layered structure parallel to growth direction and crystallizes in an orthorhombic phase well known for its high photosensitivity and high thermoelectric properties.³ Antimony sulfide (Sb_2S_3) has been extensively studied due to its device applications in photoconducting targets of television cameras, electronic devices, optoelectronics devices and infrared spectroscopy.^{4,5}

One important function of Sb_2S_3 is that it can be used as the starting material for synthesizing other related compounds.^{6.7} It has also been used in thermoelectric cooling technologies and optoelectronics in the IR region.^{5.8}

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The literature survey shows that several morphologies of antimony trisulfide (stibnite) have been fabricated including nanoparticles,⁹ nanorods,¹⁰⁻¹² nanowhiskers,¹³ microtubular,^{14, 15} and microspheres¹⁶ by various methods. But a very few workers have prepared the microspheres via solvothermal method. Here in we prepared Sb₂S₃ microspheres using SbCl₃ (Antimony chloride) and sulfur powder as a starting material. The structural, optical and thermal properties of the prepared Sb₂S₃ microspheres were studied and the results obtained are discussed in detail in this paper.

2. EXPERIMENTAL PROCEDURE

All of the chemical reagents used in this experiment were of analytical grade and were used without further purification. In a typical procedure, 0.23 g antimony chloride (SbCl₃) and 0.45 g tartaric acid were dissolved in 16 mL N,N-dimethylformamide (DMF). In this solution about 0.244 g sulfur powder was added with stirring. This mixed solution was transfered into a teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 120 °C for 4 h and then cooled to room temperature naturally. The precipitates were collected and washed with distilled water for several times. Then, the precipitates were dried in

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^{*}Author to whom correspondence should be addressed.



air. Finally, the resultant burgundy colored powder sample were obtained and characterized by various techniques.

3. CHARACTERIZATION TECHNIQUES

The as prepared sample was characterized by X-ray powder diffraction (XRD) on a X-ray diffractrometer (Philips Xpert MPD) with Cu-K α radiation ($\lambda = 1.54$ Å) to study structural properties and the chemical composition of the prepared sample was analyzed by energy dispersive analysis of X-ray (EDAX) (Philips EM 400 electron microscope). XPS measurements were performed for confirmation of EDAX results on a ESCA lab X-ray photoelectron spectrometer with an excitation source of AlK α = 1486.6 eV. The surface morphology was studied by using scanning electron microscopy (SEM) (Model-XL 30 ESEM) and transmission electron microscope (TEM) (Philips Tecnai 20, 200 KV). The Raman scattering experiments were carried out at room temperature under the backscattering geometry using Jobin-Yvon Horiba labram, HR800 single monochromatic coupled with "peltier cooled" charged coupled device (CCD) and 488 nm line of an Argon (Ar+) laser was used for excitation. Absorption spectra in UV-VIS range for prepared sample was carried at room temperature using UV-VIS-NIR spectrometer (Perkin Elmer). A Photoluminessence (PL) spectrum was obtained by Fluoromax-Compact spectrometer with Xe lamp at room temperature. We also studied thermogravimetric analysis (TGA) on the sample in the range between room temperature to 500 °C in air atmosphere.

4. RESULTS AND DISCUSSION

Figure 1 shows the EDAX spectra of prepared Sb_2S_3 microspheres suggesting that the sample contain only antimony and sulfur elements. Table I provides the elemental composition in terms of weight percentage of elements obtained from EDAX result reveal the desirable stoichiometry of Sb_2S_3 .

Table I.	Elemental	composition	of Sb ₂ S	microspheres
----------	-----------	-------------	----------------------	--------------

Composition	Wt% of present	element in Sb ₂ S ₃
ShaSa	Sb	S
2-0	71.08	28.92



Fig. 2. The powder XRD pattern of the prepared Sb₂S₃ microspheres.

XRD pattern of Sb₂S₃ microspheres is shown in Figure 2 in the 2θ range of 0–90°. All the obtained diffraction peaks were indexed with the help of powder-X software to a pure orthorhombic phase of Sb₂S₃ with calculated lattice parameters a = 11.24 Å, b = 11.31 Å and c = 3.84 Å, which matches well with the values reported in JCPDS 42-1393.

The chemical state, purity and composition of the as-obtained product was further checked by XPS analysis. Figure 3(a) shows the scanned XPS spectra of the product. The peaks arising from Sb₂S₃ (Sb 4d, 3d, 3p and S 2s, 2p) are clearly seen, and a small contaminant C1s peak is also evident. The high-resolution XPS spectra of Sb 3d, 4d and S 2p were obtained using C1s as the reference at 287.5 eV. In order to analyze the composition of the as-obtained product in detail, curve fitting of S 2p and Sb 3d, 4d were performed. Figure 3(b) shows the high-resolution spectra of the S 2p with the peak at 161.19 eV whereas the high resolution spectra of the Sb 3d is shown in Figure 3(c) which shows the presence of two peaks for Sb 3d5/2 and Sb 3d3/2 at 530.29 eV and 539.69 eV, respectively. Figure 3(d) represents the highresolution spectra of the Sb 4d with the peak at 33.52 eV. The peak position for both Sb and S agree well with those reported in the literature.¹⁷ The average weight percentage ratio obtained from quantification of Sb3d and S2p peaks is 73:27, which is close to anticipated value.

The surface morphology of the Sb₂S₃ microspheres was determined by SEM. The three SEM images of the sample were obtained at different places with same magnification. Figure 4 shows that the product contains a large quantity of sphere like structure without any visible by products, suggesting that the product is of good quality. The diameter of these spheres varies from 1 to 5 μ m.

The detailed structure and morphology of the sample were studied by TEM analysis and is presented in Figure 5. The TEM image in Figure 5(a) shows individual sphere of Sb_2S_3 with a diameter range from 100 nm to 300 nm and selected area electron diffraction pattern (SAED) of these spheres is given in Figure 5(b) which shows diffraction spots indicating single crystalline nature of these Sb_2S_3 microspheres. This diffraction spots are indexed based on orthorhombic structure of Sb_2S_3 , which is shown in Figure 5(b) and we also determined the zone axis as [001] suggesting the preferred orientation.



Fig. 3. (a) XPS pattern of survey scan of the as obtained product Sb_2S_3 microspheres (b) high resolution S 2p region (c) high resolution Sb 3d region (d) high resolution Sb 4d region.

Boosting Energy (PT)

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Fig. 4. SEM images of Sb₂S₃ microspheres.

Raman spectra was obtained at room temperature with Ar⁺ laser source as excitation source which is displayed in Figure 6. The appearance of the peaks at 151, 188, 252, 305, 372 and 450 cm⁻¹ is in good agreement with the reported Raman spectrum.¹⁸ The presence of sharp peaks at 151 cm⁻¹, 188 cm⁻¹ and 252 cm⁻¹ suggests the formation of well crystalline products.¹⁹ The low intensity peak at 305 cm⁻¹ and 372 cm⁻¹ can be assigned to the unit SbS₃ pyramid of the material having C_{3v} symmetric mode.²⁰ The presence of a relatively broad peak at 450 cm⁻¹ may be due to the symmetric stretching of the Sb-S-S-Sb bond of Sb₂S₃, which can be accounted on the basis of existing literature.²¹

A TGA spectrum in air of the prepared Sb_2S_3 microspheres is shown in Figure 7 which reflects weight loss between 178–292 °C. The weight loss may be due to formation of oxide of antimony and sulfur evaporation in this temperature range. We have used the theoretical model viz. Broido (BR) relation,²² for calculating the activation energy in the weight loss region of

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Fig. 5. (a) TEM images of ${\rm Sb}_2{\rm S}_3$ microspheres (b) SAED pattern of the ${\rm Sb}_2{\rm S}_3$ microspheres.

TGA curve. The corresponding plot of BR model is shown in Figure 8. The calculated value of activation energy from broido relations is shown in Table II.

Since Sb_2S_3 is important from the optoelectronic application point of view and hence its band gap determination is carried out using UV-Vis absorption spectra. The direct band gap energy (E_g) for the sample is determined by fitting the absorption data to the direct transition equation $(\alpha h\nu)^2 = A(h\nu-\text{E}_g)$, where α is the optical absorption coefficient, $h\nu$ is the corresponding photon energy, E_g is the direct band gap energy of the semiconductor and A is a constant.²³ The plot $(\alpha h\nu)^2$ versus $h\nu$ is shown in Figure 9. The band gap is given by extrapolating the linear part



Fig. 6. Raman spectrum of the Sb₂S₃ microsphere.

Fig. 8. Plot of BR model of TGA in the weight loss region.

of the curve $(\alpha h\nu)^2$ with respect to $h\nu$ on the x-axis and is found to be 1.62 eV which is comparable with the reported values. This value of the band gap energy for Sb₂S₃ microsphere is near the optimum value for photovoltaic conversion, suggesting that Sb₂S₃ microspheres may be suitable for applications in solar energy and optoelectronics.^{24, 25} It is also noted that these microspheres do not show quantum confinement effect, a fact also established by these workers. This may be attributed to the lower Bohr's radius of this material.

Luminescence spectra is important for evaluating the optical nature of the materials. The PL spectra of the Sb_2S_3 microspheres were recorded at different excitation wavelength 350, 400 and 430 nm, as shown in Figure 10. The observed emission peak values for different excitation wavelength are given in Table III.

Table II. Calculated values of activation energy (eV) obtained from BR relation, PN relation and CR relation.

Name of model	Broido relation
Activation energy	0.79 eV



Fig. 9. $(\alpha h v)^2$ versus h v curve for the Sb₂S₃ microspheres.



Fig. 10. Photoluminescence spectra of the Sb₂S₃ microspheres.

Table III. emission peak values at three-excitation wavelength.

Excitation wavelength (nm)	Peak 1	Peak 2	Peak 3	Peak 4
350	384 V (3.23)	476 B (2.61)	574 Y (2.16)	667 R (1.86)
400	439 V (2.83)	545 G (2.27)	656 R (1.89)	762 R (1.63)
430	472 B (2.63)	586 Y (2.12)	646 R (1.92)	705 R (1.76)

From results shown in Table III and Figure 10. It is clear that Sb_2S_3 microspheres are showing luminescent behavior in different regions of the spectrum and probably this property can be utilized for its further applications.

5. CONCLUSION

 $\rm Sb_2S_3$ microspheres were successfully synthesized by solvothermal method using SbCl_3 and sulfur as raw materials. $\rm Sb_2S_3$

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microspheres of desired stoichiometry are obtained as shown in EDAX results. XRD shows that Sb_2S_3 microspheres belong to pure orthorhombic phase (JCPDS 42-1393). The phase purity of the microspheres was also confirmed by XPS. SEM and TEM images show that Sb_2S_3 particles are spherical in shape having diameter in micrometer range and spot diffraction pattern of Sb_2S_3 microsphere indicating single crystalline nature of microspheres. The band gap of the microspheres can be used for application in solar energy and optoelectronic applications. Room temperature PL studies with different excitation wavelength suggests that Sb_2S_3 microspheres are showing luminescence behavior in different parts of the spectrum.

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Characterization of Bi₂S₃ nanorods prepared at room temperature



M.P. Deshpande ^a, Pallavi N. Sakariya ^{a,b,*}, Sandip V. Bhatt ^a, Nitya Garg ^a, Kamakshi Patel ^a, S.H. Chaki ^a

^a Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388120, Gujarat, India
^b Babaria Institute of Technology, NH-8, Varnama, Vadodara 391240, Gujarat, India

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ABSTRACT

 Bi_2S_3 is a direct band gap semiconductor with a band gap of 1.3 eV. It belongs to the family of metal chalcogenides of type $A_2^V B_3^{VI}$ (A=As, Sb, and Bi; B=S, Se, and Te), whose importance in photovoltaic and thermoelectric applications is well recognized. Although nanostructures of Bi_2S_3 have been obtained using a number of techniques, reports on assemblies of Bi_2S_3 are sparse. In the present work, we prepared single crystalline bismuth sulfide (Bi_2S_3) nanorods at room temperature by reacting $Bi(NO_3)_3$, thioacetamide (TAA), hydrochloric acid and distilled water.

Energy dispersive analysis of X-rays (EDAX) obtained from Bi_2S_3 nanorods indicated no incorporation of other foreign impurities in it. X-ray diffraction confirmed the single phase of Bi_2S_3 and different diffracting planes were indexed based on the orthorhombic structure and lattice parameters were determined. X-ray photoelectron spectroscopy (XPS) was used to evaluate its composition and purity. The synthesized nanorods with different images observed under transmission electron microscopy (TEM) are shown in the paper and the selected area electron diffraction (SAED) pattern obtained from these nanorods shows their single crystalline behavior. Raman measurement performed at room temperature using Ar⁺ laser (488 nm) confirms the presence of 238 cm⁻¹ and 972 cm⁻¹ phonon modes. The optical absorption spectra obtained by UV-vis spectrometer show blue shift in comparison to bulk Bi_2S_3 while its thermal stability was studied by thermogravimetric analysis.

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1. Introduction

Recently, semiconducting chalcogenides have received considerable attention due to their wide applications in television cameras with photoconducting targets, thermoelectric devices, infrared spectroscopy, and fabrication of optical and electronics devices [1–6]. Bismuth sulfide (Bi_2S_3) has a highly anisotropic one-dimensional orthorhombic structure adopting space group of *pbnm* [7]. The unique structure consists of Bi_2S_3 infinite chains directed along the crystallographic *c*-axis. This causes the material to grow with a long needle-like morphology. The Bi^{3+} atoms are in a highly distorted octahedral geometry and the three short covalent Bi–S bonds make the Bi_2S_3 chains [8]. Bi_2S_3 is a semiconductor with a lamellar structure whose direct band gap E_g is 1.3 eV and can be used as photovoltaic and thermoelectric materials, and imaging agents in X-ray computed tomography [9–11]. Thermoelectric materials can directly and reversibly convert waste

^{*} Corresponding author at: Babaria Institute of Technology, NH-8, Varnama, Vadodara 391240, Gujarat, India. Tel.:+91 9427514315.

E-mail addresses: vishwadeshpande@yhaoo.co.in (M.P. Deshpande), pallavisakria11@gmail.com (P.N. Sakariya), sandip.bhatt08@yahoo.com (S.V. Bhatt), physicsk@yahoo.co.in (K. Patel),

sunilchaki@yahoo.co.in (S.H. Chaki).

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heat into electrical energy, and will play a significant role in the future of energy management [12].

One-dimensional (1D) nanostructure chalcogenides are materials with unique physical properties such as electrical, catalytic and magnetic compared to their bulk counterparts. They have potential applications in fabricating optoelectronic and thermoelectric nanoscale devices [1,2].

Many techniques such as hydrothermal or solvothermal decomposition [13–18], solventless thermolysis [19], microwave irradiation [20], sonochemical method [21] and self-sacrificing template route [22] have been applied to prepare one dimensional Bi_2S_3 nanostructures, such as nanowires, nanotubes, nanoflowers and nanorods [6,14]. In spite of these exciting developments, the exploration of novel, simple and low-cost methods to synthesize 1D nanostructure is still a challenging research area.

Here, in this paper we report a simple solution based synthesis to prepare 1D Bi₂S₃ nanorods, using bismuth nitrate and thioacetamide as Bi and S source respectively.

2. Experimental details

2.1. Experimental procedure

All chemicals were of analytical grade and were used without any further purification. In typical synthesis, 1 ml

 Table 1

 Chemical composition of Bi₂S₃ sample.

Composition	Element	wt%	at%
Bi ₂ S ₃	Bi	84.45	45.46
	S	15.55	54.54

hydrochloric acid (36 wt%) and 0.243 g of bismuth nitrate $(Bi(NO_3)_3 \cdot 5H_2O)$ were added into 10 ml of distilled water. After stirring for 2 min, 0.0564 g thioacetamide (TAA) was introduced and stirring was continued (the final concentration of $Bi(NO_3)_3$ and TAA was 0.05 mol L⁻¹). This resultant solution was kept at room temperature for 24 h under static condition. The solution turned transparent to brown then to black gradually and the precipitates at last settled down. The resulting product was filtered, collected and washed with distilled water for several times and dried in air.

2.2. Characterization techniques:

The as prepared sample was characterized by X-ray diffraction (XRD) on a X-ray diffractrometer (Philips Xpert MPD) with Cu-K α radiation ($\lambda = 1.54$ Å). XPS measurements were performed on an ESCA lab X-ray photoelectron spectrometer with an excitation source of $AIK\alpha =$ 1486.6 eV. The composition was analyzed by the energy dispersive analysis of X-ray (EDAX) (Philips EM 400 electron microscope). The morphology, size of as-obtained product and selected area diffraction (SAED) pattern were observed by the transmission electron microscope (TEM) (Philips Tecnai 20, 200KV). The Raman scattering experiments were carried out at room temperature under the backscattering geometry using Jobin-Yvon Horiba labram, HR800 single monochromatic coupled with "peltier cooled" charged coupled device (CCD) and 488 nm line of an Argon (Ar⁺) laser was used for excitation. Absorption spectra in UV-vis range for Bi₂S₃ nanorods were taken at room temperature using a UV-vis-NIR spectrometer (Perkin Elmer). We also studied thermogravimetric analysis (TGA) on the sample in the range between room temperature and 750 °C in N₂ atmosphere to know the thermal stability of the material.

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Fig. 1. EDAX spectra of the as obtained Bi₂S₃ nanostructure.





Fig. 3. (a) XPS pattern of prepared Bi₂S₃ sample and (b,c) high resolution spectra of Bi and S regions of the prepared Bi₂S₃ sample.





Fig. 4. (a-d) TEM images of Bi₂S₃ nanostructure.



Fig. 5. SAED pattern of Bi₂S₃ nanorods shown in TEM images.

3. Results and discussion

3.1. Elemental and structural analysis

From EDAX it is confirmed that no other impurities are incorporated in the sample and excess of Bi is observed in comparison to S which is nearly consistent with the desirable stoichiometry of Bi_2S_3 . The values of wt% and at% of both the elements present in the sample is shown in Table 1. The stoichiometry of Bi and S of Bi_2S_3 determined in our case is nearly 2:3 (Fig. 1).

Fig. 2 shows the powder X-ray diffraction of Bi_2S_3 sample. X-ray powder diffraction (XRD) analysis confirms that the as-synthesized product belongs to the orthorhombic system and diffraction peaks are indexed with the help of powder X-software. The calculated lattice constants are a=11.15 Å,



Fig. 6. Raman spectra of Bi₂S₃ nanorods.

b=11.30 Å and c=3.98 Å (space group *pbnm*), which are consistent with the reported values [23] (JCPDS no. 43-1471). As observed in our case the obtained sample is quite pure and no XRD peaks attributed to Bi₂O₃ are observed, which is also reported in [14] though the method of preparation of Bi₂S₃ nanorods is different. The diffraction peaks seen in Fig. 2 are sharp which is a clear cut indication of good crystallinity of these nanorods.

Fig. 3(a) shows the XPS spectra of Bi_2S_3 sample prepared at room temperature. The binding energies obtained in the XPS analysis were corrected for specimen charging by referring the C_{1s} line to 284.60 eV. All other peaks can be assigned to O, Bi and S elements. The oxygen peak (532.0 eV) may be attributed to O_2 or H_2O absorbed by the sample from the atmosphere. No other impurities were observed in the XPS spectrum of Bi_2S_3 nanorods as shown in Fig. 3(a), which is consistent with EDAX and XRD results.

The peak at 225.29 eV corresponds to S_{2s} as shown in Fig. 3(b) whereas the two strong peaks at 159.3 and 164.5 eV in Fig. 3(c) are assigned to $Bi_{4f7/2}$ and $Bi_{4f5/2}$ respectively, with a typical Bi_{4f} spin-orbit doublet splitting of 5.2 eV, which is consistent with the reported values [24]. The average weight percentage ratio of Bi and S on the basis of quantification of Bi_{4f} and S_{2s} peaks is 79:21, indicating the formation of Bi_2S_3 product with an excess of Bi, which is in agreement with the values obtained from EDAX results.

Bi₂S₃ nanostructure was further characterized with the help of transmission electron microscopy (TEM). The images shown in Fig. 4(a-d) are clearly pointing out that these nanostructures are nanorod bundles obtained in a simple reaction at room temperature and ambient atmosphere without using any templates and surfactant. The length and diameter of nanorods ranges between 100-340 nm and 40-50 nm respectively. The SAED pattern obtained from these Bi₂S₃ nanorods is shown in Fig. 5 which indicates the single crystalline nature of these nanorods. We indexed each of these spots and calculated the lattice parameter which comes out to be a = 11.142 Å, b = 11.244 Å, c = 3.975 Å which matches with those obtained from the XRD results. The zone axis determined comes out to be [002] thereby suggesting the directional preferred growth of Bi₂S₃ nanorods in this direction.

The growth of nanorods with a preferential direction of the *c*-axis can be ascribed to its particular structure. Bi_2S_3 has a lamellar structure with linked Bi_2S_3 units forming infinite chains parallel to the *c*-axis [25] and the stronger covalent bond between the planes perpendicular to the *c*-axis facilitates higher growth rate along the *c*-axis. The much weaker van der Waals bonding between the planes perpendicular to the *a*-axis limits the growth of the rod in the horizontal direction and facilitates their cleavage to form one-dimensional nanostructures [26].

3.2. Optical characterization

Raman spectra obtained at room temperature using the Raman spectrometer with Ar^+ laser (488 nm) to excite the sample is shown in Fig. 6. Bi₂S₃ is having space group *pbnm* because it belongs to orthorhombic structure having 20 atoms per primitive cell as confirmed from X-ray diffractogram. For a 20-atom Bi₂S₃ primitive cell, there are 60 zone-center phonon modes that can be classified according to the D_{2h} point-group symmetry: $10A_g + 10B_{1g} + 5B_{2g} + 5B_{3g} + 5A_u + 5B_{1u} + 10B_{2u} + 10B_{3u}$. Of these, only A_g , B_{1g} , B_{2g} , and B_{3g} modes are Ramanactive [27].

Raman spectrum of Bi_2S_3 nanorods shown in Fig. 6 shows two peaks at 238 cm⁻¹corresponding to A_g phonon mode and 972 cm⁻¹may be related to surface phonon modes because of the high surface-to-volume ratio [28], which is in good agreement with values for commercial Bi_2S_3 as well as the nanoparticles reported by Rabin et al. [29].



Fig. 9. Plot of BR model in a weight loss region.

UV–vis absorption spectrum in Fig. 7 shows a broad absorption peak at 262 nm corresponding to the band gap of 2.74 eV which shows the size effect and blue shift in wavelength in comparison to bulk material [30] which is quite similar to that synthesized by a photochemical synthesis method [31].

3.3. Thermal analysis using thermogravimetric analysis (TGA)

Thermal properties of Bi_2S_3 nanorods were studied using TGA. The materials were subjected to controlled temperature within the range of 0–750 °C and the mass of the sample under consideration was measured as a function of temperature in N₂ atmosphere.

Fig. 8 shows the TGA plot of Bi₂S₃ as-synthesized nanorods. It shows that the weight of the material continuously decreases with temperature. We have used the Broido relation (BR) [32] for analysis of TGA spectra for calculating the activation energy in the entire weight loss region. The activation energy calculated from Fig. 9 comes out to be 0.38 eV.

4. Conclusion

Bi₂S₃ nanorods were prepared successfully at room temperature by a simple chemical reaction method. The lattice parameters determined from TEM and XRD are having close resemblance with each other whereas compositional verification of Bi₂S₃ sample by EDAX and XPS are also closely matching. The optical absorption spectra show an absorption edge at 262 nm thereby showing blue shift in comparison to bulk form of the material. Raman spectra peaks obtained at 238 cm⁻¹ and 972 cm⁻¹ are matching with reported values corresponding to A_g and surface phonon modes. TGA plot shows the continuous weight loss of Bi₂S₃ from room temperature to 750 °C.

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EXECUTIVE SUMMARY OF THE REPORT

PROJECT ENTITLED "Synthesis and characterization of V2-VI3 compound in single crystal/nanomaterial/thin film forms" NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR: Prof. M. P. Deshpande **Department of Physics, Sardar Patel University** Anand, Gujarat NAME AND ADDRESS OF THE INSTITUTION: Department of Physics, Sardar Patel University, Vallabh Vidyanagar, Anand, Gujarat. UGC APPROVAL LETTER NO. AND DATE: F.No. 42-826/2013 (SR) dated 22nd March 2013. DATE OF IMPLEMENTATION: 1st April 2013 From 01/04/2013 to 31/03/2014 (1st Year) Period of Expenditure : 01/04/2014 to 31/03/2015 (2ndYear) 01/04/2015 to 31/03/2016 (3rdYear) 01/04/2016 to 31/03/2017(extended Year)

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 FINAL EXPENDITURE:

 Rs. 10, 25,096

Single crystals of Sb₂S₃ were prepared in the dual zone furnace at temperature 500°C to450°C of the source zone and growth zone respectively. The grown single crystals of Sb₂S₃were in the form of needle shape. The composition of the grown crystals were determined from EDAX spectra. X-ray diffraction pattern of Sb₂S₃ powder (polycrystalline) were indexed with the help of powder-X software to pure orthorhombic phase of Sb₂S₃ with calculated lattice parameters: a = 11.239A°, b = 11.313 A° and c = 3.841 A°. The surface morphology of grown single crystals of Sb₂S₃at different magnification of 100X, 50X and 500X using SEM showed that crystals surfaces are possessing cracks and visible inclusions. The Raman spectrum of Sb₂S₃ single crystal atroom temperature using Ar laser source exhibits seven resonantpeaks at about 115, 147, 190, 252, 282, 300 and 373 cm⁻¹ in the rangeof 100 - 400 cm⁻¹. The presence of sharp peaks at 190 and 252cm⁻¹suggests the formation of well crystalline product. The TGA curve of Sb₂S₃ crystal under nitrogen (N₂)atmosphere showed that Sb₂S₃ decomposes slowly from 27°C to 472°C having small weight loss of nearly 2%.

Microspheres of Sb_2S_3 were prepared using solvothermal method. The elemental compositions of Sb₂S₃ microspheres synthesized indicated no impurity content in it. XRD pattern of Sb₂S₃ microspheres were indexed with the help ofpowder-X software to a pure orthorhombic phase of Sb_2S_3 with calculated lattice parameters a=11.24 A°, b= 11.31 A° and c= 3.84 A°, which matches well with the values reported in JCPDS 42-1393. The chemical state, purity and composition of the as-obtained product were further checked by XPS analysis. The peaks arising from Sb_2S_3 (Sb4d, 3d, 3p and S 2s, 2p) were clearly seen, and a small contaminant C1speak is also evident. The high-resolution XPS spectra of Sb 3d, 4d and S2p were obtained using C1s as the reference at 287.5eV.The surface morphology of the Sb₂S₃ microspheres is studied bySEM showing spheres from 1 to 5μ m and TEM analysis showed range from 100nm to 300nm. The selected area electron diffraction pattern (SAED) of these spheres indicated single crystalline nature of these Sb₂S₃ microspheres. Raman spectrum was obtained at room temperature with Ar+ laser source as excitation source . The appearance of the peaks at 151, 188, 252, 305, 372 and 450 $\rm cm^{-1}$ is in good agreement with the reported Raman spectra. TGA spectrum in air of the prepared Sb₂S₃ microspheres reflects weight loss between 178-292°C. The value of bandgap which comes out to be 1.62eVwhich is near to optimum value for photovoltaic conversion, suggesting that these microspheres may be suitable for applications in solar energy and optoelectronic devices. From the observed emission peak values for different excitation wavelength, it is clear that Sb₂S₃ microspheres are showing luminescent behavior in different regions of the spectrum and this property can also be utilized for optical applications.

Sb₂**S**₃ **thin film** were synthesized by **by SILAR coating unit** purchased in this project. The EDAX spectra of deposited Sb₂S₃ thin films on glass substrates using SILAR method with different cycles and concentrations {cycles: 25 cycle, 30 cycle, 33cycle, 50 cycle; concentration: 0.05:0.1 M, 0.1:0.2M} indicated the presence of elements of S and Sb. X-ray diffractograms of Sb₂S₃ thin films with different concentrations and depositing cycles were recorded and we calculated lattice parameters which were in agreement with the reported values (JCPDS – 42 – 1933) a = 11.23A°, b = 11.32 A°, c = 3.841 A°.Room temperature PL spectra of Sb₂S₃ thin films, for different cycles and concentrations showed the emission peaks presents broad bandsover 430-480nm range with strong violet emission peaks centered at same wavelengths of 460nm [2.70eV] for all thin films.

We could observe some aggregation in these synthesized films as seen from the SEM images.Raman spectra of Sb_2S_3 thin films for different cycles and concentrations showed Raman shiftswhich were in agreement with the Raman spectrum reported.

 Bi_2S_3 nanorods were prepared at room temperature by chemical route. We can conclude from EDAX spectra that no other impurities are incorporated in the sample and excess of Bi is observed in comparison to S which is nearly consistent with the desirable stoichiometry of Bi_2S_3 .

The powder X-ray diffraction of Bi₂S₃ sample. X-ray powder diffraction(XRD)analysis confirms that the as-synthesized product belongs to the orthorhombic system and diffraction peaks are indexed with the help of powder X-software. The calculated lattice constants are a = 11.15Å, b=11.30Å and c = 3.98Å(spacegroup pbnm), which are consistent with the JCPDS no.43-1471. The binding energies obtained in the XPS analysis were corrected for specimen charging by referring the C_{1s} line to 284.60 eV. All other peaks can be assigned to O, Bi and S elements. The peak at 225.29 eV corresponds to S_{2s} whereas the two strong peaks at 159.3 and 164.5 eV in are assigned to Bi_{4f7/2} and Bi_{4f5/2} respectively, with a typical Bi_{4f} spin-orbit doublet splitting of 5.2eV, which is consistent with the reported values. The morphology, size of as-obtained product and selected area diffraction (SAED) pattern of Bi₂S₃ nanostructure were observed by transmission electron microscope (TEM) (Philips Tecnai 20, 200KV).Raman spectrum of Bi₂S₃ nanorods indicated two peaks at 238cm⁻¹ corresponding to Ag phonon mode and 972 cm⁻¹ may be related to surface phonon modes because of the high surface-to-volume ratio, which is in good agreement with values for commercial Bi₂S₃ as well as the nanoparticles.UV-vis absorption spectrum showed a broad absorption peak at 262nm corresponding to the bandgap of 2.74eVwhich shows the size effect and blue shift in wavelength in comparison to bulk material .The TGA plot of Bi₂S₃ as-synthesized nanorods. It shows that the weight of the material continuously decreases with temperature.

Publications Produced out of work : 2 (already enclosed in the final report submitted).