Synthesis and Characterization of Nickel and Cobalt doped Bismuth Sulphide

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Abstract **– Elegant Bi_2S_3 were prepared via simple precipitation method by different capping agent and doping. The synthesized powders were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), Dynamic Light Scattering (DLS) and Ultraviolet and visible spectroscopy (UV-Vis). The formation mechanism of the Bi_2S_3 nanostructures with different morphologies was discussed.**

Index Terms **- nanostructures, semiconductors, chemical synthesis, Bismuth Sulphide, SEM, XRD**

I. INTRODUCTION

Nano-sized materials exhibit novel physical, chemical and biological properties compared with their bulk counterparts due to high specific surface area, small particle size, reduced number of free electrons and possible quantum confinement effect.

Semiconductor nano-particles are of particular interest for both, fundamental research (e.g. for quantum size phenomena) and technology. Due to their low production costs, simple handling and novel size dependent properties, unlike their bulk counterparts, they have become potential candidates for technological applications like Photo catalytic applications, Opto-electronic devices, Solar Cells, Single Electron Tunneling devices, and computing devices.

In the past few years $A^{V}{}_2B^{VI}{}_3$ (where A= As, Sb, Bi and B =S, Se, Te), have received ever increasing attention as valuable semiconductors. As a representative of good semiconductor, Bismuth Sulphide (Bi_2S_3) has been attracting a considerable interest owing to its potential application in thermoelectric, electronic and optoelectronic devices and IR spectroscopy, etc.

In addition, it has an energy band gap of 1.3 to 1.7 eV, which is suitable for making photodiode arrays and photovoltaics. A band gap can be tuned depending on the size of the subcomponents.

A. Synthesis using precipitation method

Samples were prepared by precipitation method. Total seven samples were made. Those are listed as below.

1) Bi_2S_3 by CTAB as capping agent
2) Bi_2S_3 by UREA as capping agent
3) Bi_2S_3 by TEA as capping agent
4) Bi_2S_3 by CTAB as capping agent with doping of Co^{+2}
5) Bi_2S_3 by CTAB as capping agent with doping of Ni^{+2}
6) Bi_2S_3 by UREA as capping agent with doping of Ni^{+2}
7) Bi_2S_3 by TEA as capping agent with doping of Ni^{+2}

Bi_2S_3 with Cetyl TriMethyl Ammonium Bromide (CTAB) as Capping Agent

1) 2 mmol Bismuth Chloride (Bi_2Cl_3) was dissolved in to distilled water at room temperature and then hydrochloric acid (HCl, 6M) was added drop wise until a clean solution was formed.Another solution was formed with 2 mmol CTAB dissolved in water. These two solutions were mixed and stirred vigorously for 30 minutes to gives white precipitates of $BiCl_4^-CTA^+$.. 1.588 gm of the obtained $BiCl_4^-CTA^+$ precipitates was dissolved in 200ml conductivity water.
2) 25ml from this dissolved mixture was taken and 150 ml Methanol was added in it.
3) 1.3 gm Na_2S was dissolved in 25ml conductivity water. This solution was added drop wise into the above mixture containing Methanol to obtain brown black precipitates of Bi_2S_3.
4) The concentration of Na_2S was reduced four times and the same procedure as above was repeated.

For doping Ni^{+2} and Co^{+2}

1) 0.794 gm $BiCl_4^-CTA^+$ obtained from step 1 was taken and dissolved in 75 ml conductivity water.
2) Similar to step 3, 0.325 gm Na_2S was added in 25 ml conductivity water.
3) 0.0209 $CoCl_2$ was added in the solution obtained in step 4.and Na_2S solution was added drop wise under constant stirring.
4) The above three steps were repeated for doping of Ni^{+2} by using Nickel Acetate.

Bi_2S_3 with UREA As Capping Agent:-

1) 0.73 g Bi $(NO_3)_3$ was dissolved in 50ml conductivity water.
2) To this mixture was added the solution obtained by mixing 0.6 gm of urea ($(NH_2)_2CO$) in 25ml conductivity water.
3) 1.53 gm Na_2S was dissolved in 25 ml conductivity water.
4) After the starting materials dissolved completely, the Na_2S solution was added drop wise into the Bismuth Nitrate

solution under vigorous stirring. This whole mixture is developed in a round bottom flask. This will give brownish black precipitates of Bi_2S_3.

Bi_2S_3 with TEA as Capping Agent

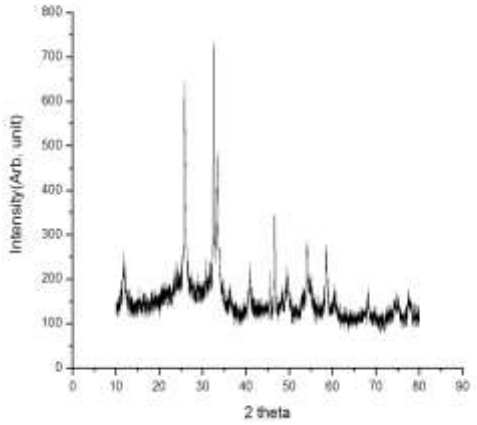
1) Repetition of the step 2 by using 0.7 ml TEA instead of UREA
2) Repetition of the same procedure to obtain nano Bi_2S_3.

For doping of Ni^{+2}

1) Add 0.0212 gm nickel acetate to the solution obtained from step1 and repeat the procedure.
2) Add 0.0212 gm nickel acetate to the solution obtained from step5 and repeat the procedure.

B. ***analysis***

XRD



Graph 1- X-ray diffraction pattern of Bi_2S_3

Experimental data
Table 1

d A^0	I/I_0	2θ
2.7525	100	32.49
3.4424	88	25.85
2.6826	66	33.36
2.2048	32	40.88
1.9928	29	45.46
1.9443	47	46.66
1.8392	31	49.5
1.6932	39	54.1
1.6658	38	55.06
1.5734	39	58.6

Graph-1 shows the XRD pattern of Bi_2S_3. It has several peaks at different 2θ values as mentioned in table 1. Corresponding to the 2θ values, d values have been calculated using the formula

$n\lambda = 2d.\sin\theta_n$. They have been matched with standard 2θ values obtained from JCPDS card (17-0320). Some of the 2θ values and d values for data available in JCPDS card and that obtained for the synthesized sample are in good agreement.

Calculation of crystallite size

k=0.94(constant)

λ=1.54 A˙

2θ	θ	cos θ	FWHM (B)	L=k λ/B cos θ (nm)
32.4898	16.2449	0.9601	0.2099	64.5
25.85	12.925	0.9746	0.4432	23.38

Table-2

The peaks show some broadening .The FWHM values for peaks at 2θ values 32.48 and 25.85 have been found to around 0.21 and 0.44 respectively. The crystallite size calculated by Scherrer formula L=k λ/B cos θ using these values of FWHM are given in table 2.

Scanning Electron Microscope (SEM)

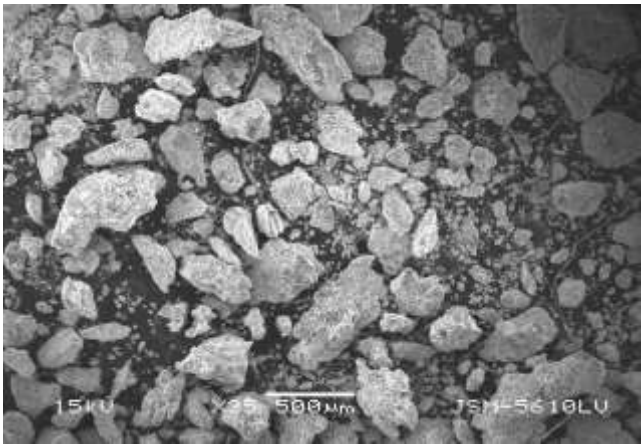


Figure 2 SEM image of Bi_2S_3 with capping agent CTAB

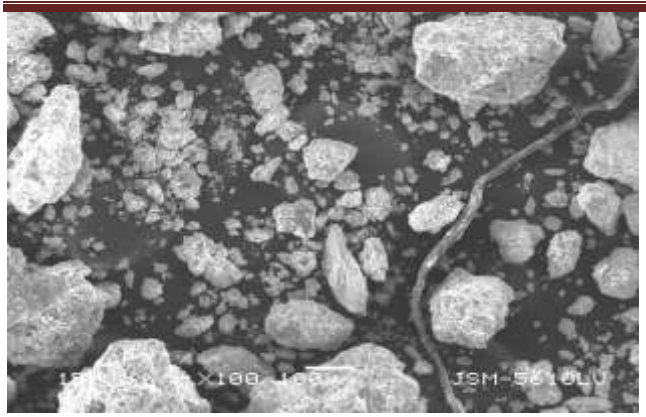


Figure 3 SEM image of Bi_2S_3 with capping agent CTAB

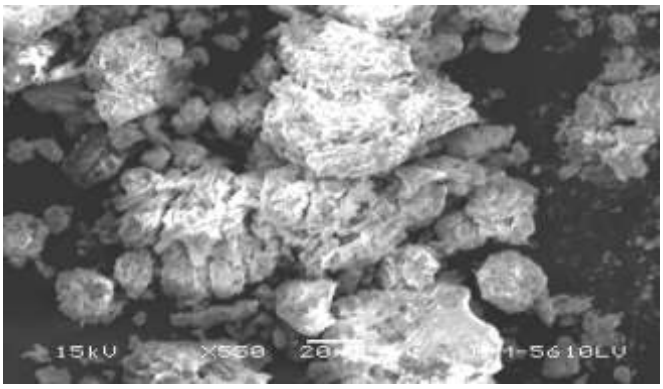


Figure 4 SEM image of Bi_2S_3 with capping agent CTAB

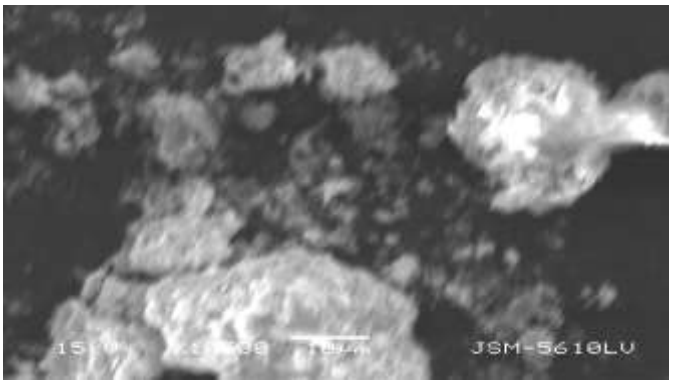


Figure 5 SEM images of Bi_2S_3 with CTAB as capping agent

The samples were subjected to Scanning Electron Microscopy on a machine of JOEL make (M/s. Japan Electronics) model JSM-5610 LV. The scans were taken for different resolutions and scales as shown in the above images (figure 2 to 5 SEM images of Bi_2S_3 with CTAB as capping agent). Here the accelerating potential is 15 KV. It shows wide variation in diameter. The hazy images are due to accumulation of surface charges.

The images are of a single specimen PNS – 1. As the original sample was very small in quantity, it was prepared again. The repeated sample was given for SEM analysis.

The image in Figure 2 for a scale of 500 µm distinctly 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.

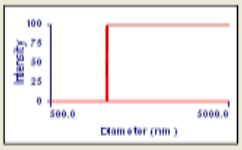
The second image in Figure 3 at the scale of 100 µm reinforces the above contention. The wide variation in size is more evident in this image.

Figure 4 focuses on the closer features of the individual chunks, which shows cracks, voids and certain degree of porosity.

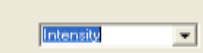
A further close investigation in the image of Figure 5 indicates the agglomeration of smaller features.

Dynamic Light Scattering Result

Sample ID	PNS-1 r (Combined)
Operator ID	Namrata
Elapsed Time	00:02:00
Mean Diam.	1039.3 nm
Rel. Var.	0.000
Skew	0.049

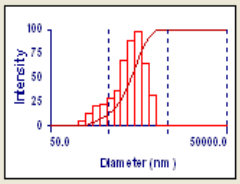


d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
963.7	0	0	1033.1	71	35	1107.4	0	100
969.8	0	0	1039.6	100	68	1114.5	0	100
975.9	0	0	1046.2	65	90	1121.5	0	100
982.1	0	0	1052.8	30	100	1128.6	0	100
988.4	0	0	1059.5	0	100	1135.8	0	100
994.6	0	0	1066.2	0	100	1143.0	0	100
1000.9	0	0	1073.0	0	100	1150.2	0	100
1007.3	0	0	1079.8	0	100	1157.5	0	100
1013.7	0	0	1086.6	0	100	1164.9	0	100
1020.1	0	0	1093.5	0	100	1172.3	0	100
1026.6	36	12	1100.5	0	100	1179.7	0	100



Graph 6- Bi_2S_3 with capping agent CTAB

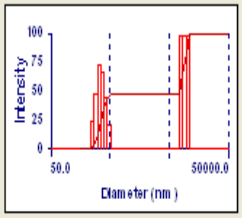
Sample ID	PNS-3 (Combined)
Operator ID	Namrata
Elapsed Time	00:02:00
Mean Diam.	1227.0 nm
Rel. Var.	0.266
Skew	0.425



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
1.0	0	0	19.8	0	0	392.0	22	12
1.3	0	0	26.0	0	0	514.2	28	18
1.7	0	0	34.1	0	0	674.5	36	26
2.3	0	0	44.7	0	0	884.8	68	40
3.0	0	0	58.6	0	0	1160.8	90	59
3.9	0	0	76.9	0	0	1522.7	100	80
5.1	0	0	100.9	0	0	1997.5	65	93
6.7	0	0	132.4	0	0	2620.4	31	100
8.8	0	0	173.6	5	1	3437.5	0	100
11.5	0	0	227.8	11	3	4509.4	0	100
15.1	0	0	298.8	21	8	5915.5	0	100

Graph 7- Bi_2S_3 with a capping agent UREA

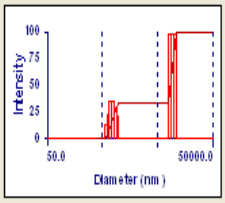
Sample ID	PNS-6 (Combined)
Operator ID	Namrata
Elapsed Time	00:02:00
Mean Diam.	4780.7 nm
Rel. Var.	0.809
Skew	-0.015



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
170.2	0	0	690.3	0	48	2799.9	0	48
193.3	0	0	784.0	0	48	3180.0	0	48
219.5	0	0	890.4	0	48	3611.8	0	48
249.3	23	4	1011.3	0	48	4102.1	0	48
283.1	47	12	1148.6	0	48	4659.0	0	48
321.6	73	25	1304.5	0	48	5291.4	0	48
365.2	66	36	1481.6	0	48	6009.8	0	48
414.8	45	44	1682.7	0	48	6825.7	0	48
471.1	21	48	1911.1	0	48	7752.3	100	65
535.1	0	48	2170.6	0	48	8804.7	100	83
607.8	0	48	2465.3	0	48	10000.0	100	100

Graph 8- Bi_2S_3 with capping agent CTAB and doping of Ni^{+2}

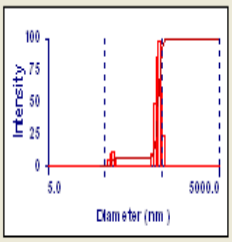
Sample ID	PNS-8 (Combined)
Operator ID	Namrata
Elapsed Time	00:02:00
Mean Diam.	6248.3 nm
Rel. Var.	0.409
Skew	-0.606



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
418.3	0	0	1245.6	0	34	3708.7	0	34
461.9	0	0	1375.5	0	34	4095.4	0	34
510.1	0	0	1518.9	0	34	4522.5	0	34
563.3	13	3	1677.3	0	34	4994.1	0	34
622.1	23	8	1852.2	0	34	5514.9	0	34
686.9	35	15	2045.3	0	34	6089.9	0	34
758.5	35	23	2258.6	0	34	6725.0	0	34
837.6	29	30	2494.1	0	34	7426.2	0	34
925.0	20	34	2754.2	0	34	8200.6	99	56
1021.4	0	34	3041.4	0	34	9055.7	100	78
1128.0	0	34	3358.5	0	34	10000.0	99	100

Graph 9- Bi_2S_3 with capping agent TEA and doping of Ni^{+2}

Sample ID	PNS-4 (Combined)
Operator ID	Namrata
Elapsed Time	00:02:00
Mean Diam.	396.1 nm
Rel. Var.	0.071
Skew	-2.217



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
43.9	0	0	115.7	0	8	304.9	0	8
48.0	0	0	126.4	0	8	333.0	9	10
52.4	0	0	138.0	0	8	363.6	49	24
57.2	4	1	150.7	0	8	397.1	87	48
62.5	9	4	164.6	0	8	433.7	100	76
68.2	10	6	179.7	0	8	473.6	61	93
74.5	5	8	196.3	0	8	517.2	23	100
81.4	0	8	214.4	0	8	564.8	0	100
88.8	0	8	234.1	0	8	616.8	0	100
97.0	0	8	255.7	0	8	673.6	0	100
106.0	0	8	279.2	0	8	735.6	0	100

Graph 10- Bi_2S_3 with capping agent CTAB and doping of Co^{+2}

In dynamic light scattering the samples were dispersed in distilled water. In the above tables, d(nm) indicates the diameter of the particles, G(d) stands for the group distribution in terms of size the particles and C(d) indicates the intensity. On the right side of the each figure the bar graph is shown.

Graph	Mean particle size (nm)	Size range (nm)
1	1039.3	1026.6 to 1052.8
2	1227	173.6 to 2620.4
3	4780.7	249.3 to 471.1 7752.3 to 10000
4	6248.3	622.1 to 925 8200 to 10000
5	396.1	57.2 to 74.5 333 to 517.2

Graph 6 shows the DLS of Bi_2S_3 with capping agent CTAB. Here the mean size of particles is 1039.3nm and the particle size varies from 1026.6 nm to 1052.8 nm. The graph is a straight line. It can be easily concluded that the material is mono disperse. The size distribution is in a very short range

and the average of the group distribution is around 1039.6nm.

Graph 7 shows the DLS of Bi_2S_3 with a capping agent UREA. The mean size of the particles is 1227nm and the size distribution is from 173.6 to 2620.4nm. From the graph it can be concluded that there is a wide variation in the particle size with average around 1522.7 nm.

Graph 8 shows the DLS of Bi_2S_3 with capping agent CTAB and doping of $Ni^{+2.}$ Here the size distribution of the particles is in two range as shown in the table. The first range is from 249.3 to 471.1nm and the second range from 7752.3 to 10000nm. There are no particles in between these range. Hence mean size of the particles is 4780.7 nm. The bar chart clearly indicates the dual size distribution.

Graph 9 shows the DLS of Bi_2S_3 with capping agent TEA and doping of Ni^{+2} . Here also, the size distribution of the particles is in two range as shown in the table. The first range is from 622.1 to 925 nm and the second range from 8200 to 10000nm. Hence mean size of the particles is 6248.3 nm.

Graph 10 shows the DLS of Bi_2S_3 with capping agent CTAB and doping of Co^{+2} . Here, the dual distribution is between 57.2 to 74.5 nm and 333 to 517.2 nm. The mean size of the particles is 396.1 nm.

Ultraviolet and Visible Spectroscopy (UV-Vis)

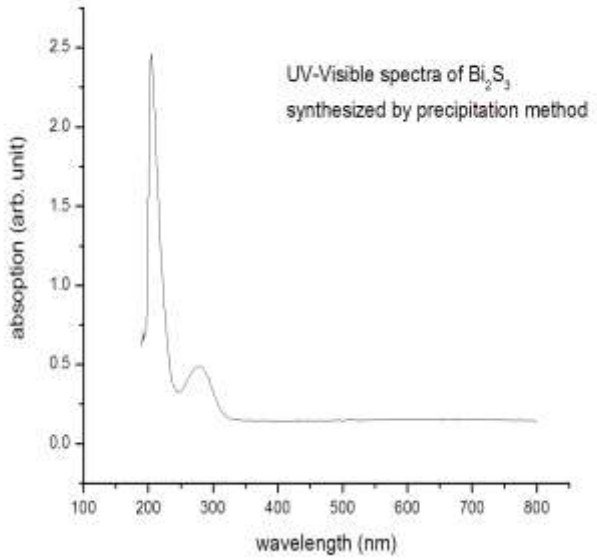


Figure 11- Bi_2S_3 with TEA as capping agent

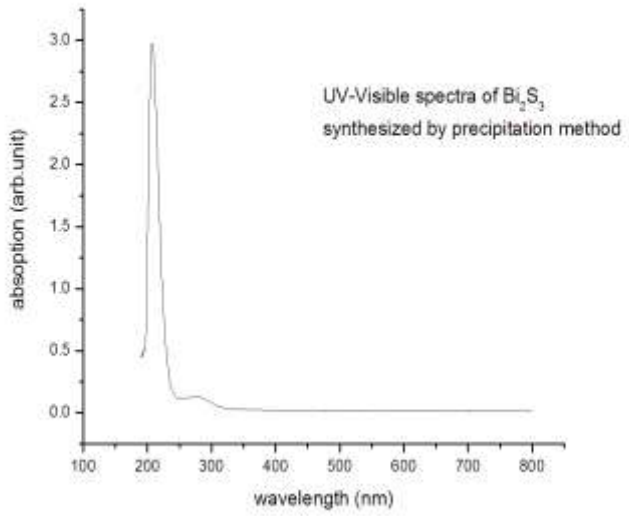


Figure 12- Bi_2S_3 with UREA as capping agent

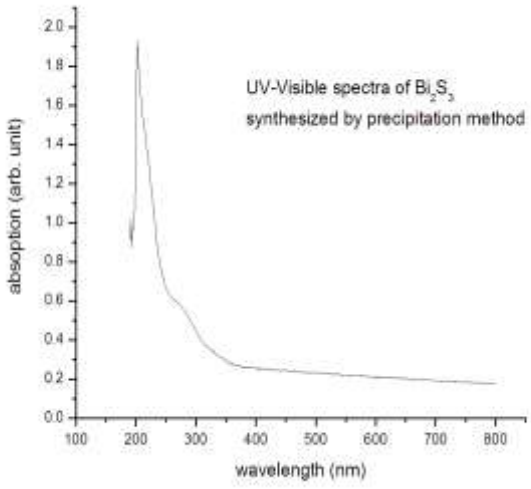


Figure 13- Bi_2S_3 with CTAB as capping agent with doping of Co^{+2}

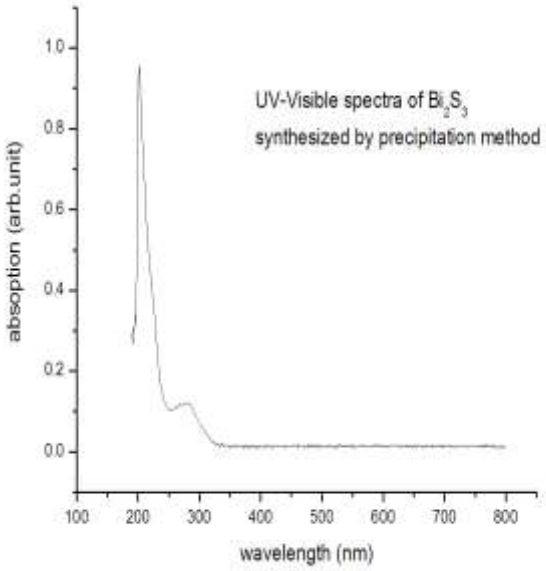


Figure 14- Bi_2S_3 with CTAB as capping agent

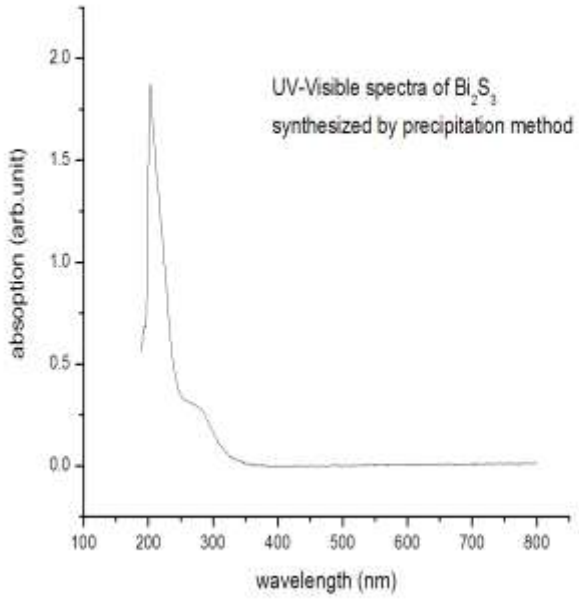


Figure 15- Bi_2S_3 with CTAB as capping agent with doping of Ni^{+2}

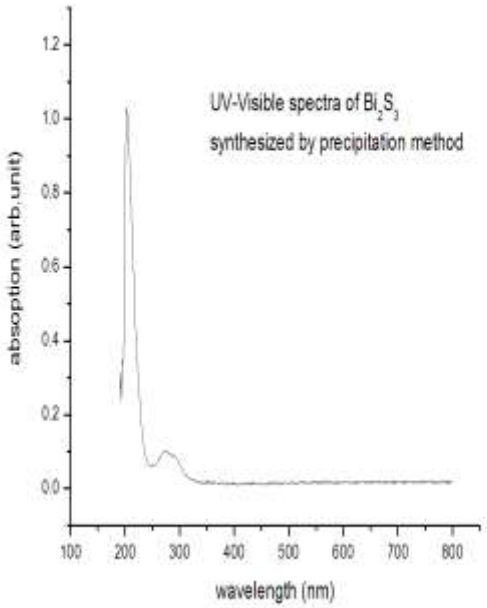


Figure 16- Bi_2S_3 with UREA as coping agent with doping of Ni^{+2}

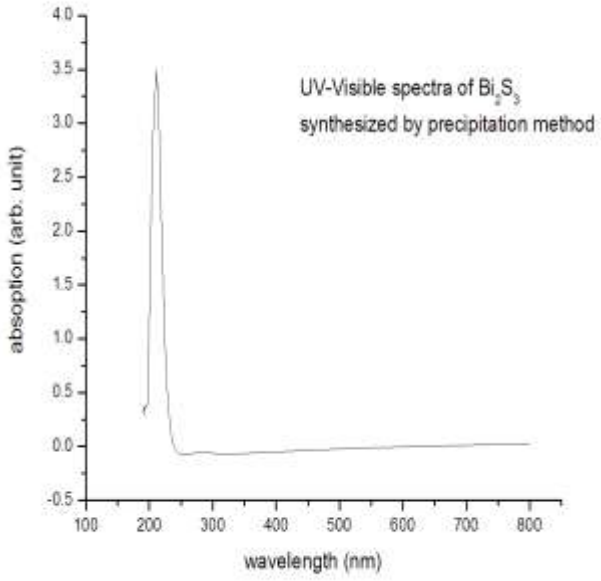
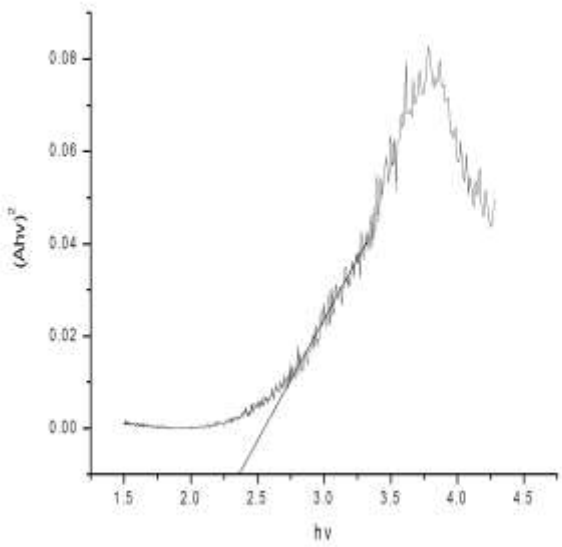


Figure 17- Bi_2S_3 with TEA as capping agent with doping of Ni^{+2}



Graph 18-band gap measurement

Figure 11 to 18 show the UV-Visible characteristics of the synthesized Bi_2S_3 samples. The samples are allowed to disperse in the methanol.

In fig.-11 the maximum peak is seen at wavelength 205 nm. At this wavelength the absorbance is at 2.459 unit. The second peak at 279 nm which shows absorbance is at 0.488 unit.

In fig.-12 the maximum peak is seen at wavelength 207 nm.At this wavelength the absorbance at 2.973 unit. The second peak at 278 nm which is seen absorbance at 0.127 unit.

In fig.-13 the maximum peak is seen at wavelength 202 nm.at this wavelength the absorbance is at 1.932 unit. The second peak at 270 nm which shows absorbance at 0.589 unit.

In fig.-14 the maximum peak is seen at wavelength 201 nm.at this wavelength the absorbance is at 0.955 unit. The second peak at 281 nm which shows absorbance at 0.12 unit.

In fig.-15 the maximum peak is seen at wavelength 203 nm.at this wavelength the absorbance is at 1.876 unit. The second peak at 281 nm which shows absorbance at 0.282 unit.

In fig.-16 the maximum peak is seen at wavelength 203 nm.at this wavelength the absorbance is at 1.876 unit. The second peak at 277 nm which shows absorbance at 0.289 unit.

In fig.-17 the maximum peak is seen at wavelength 202 nm.at this wavelength the absorbance at 3.5 unit. The second peak is at 280 nm which shows absorbance at 0.488 unit.

By graphical analysis, the band gap of the material for a typical sample has been found to be around 2.5 eV.

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