Medium dependant green synthesis of Bismuth Selenide (Bi_2Se_3) using Bismuth Chloride and L-Ascorbic acid

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Abstract:

In the present study, a greener synthetic method has been developed using economically cheap desktop chemicals such as ascorbic acid (vitamin C),$BiCl_3$, EDTA(Ethylene diamine tetra acetic disodium salt) and SeO_2 (Selenium dioxide). Bi_2Se_3 nanoparticles are prepared by using three different bases. XRD (X-ray Diffraction) characterization revealed that the product consisted of rhombohedralphase of Bi_2Se_3. Further the products were also characterised by using UV-VIS(Ultra violet visible spectra), IR(Infrared spectra),SEM (Scanning electron microscopy) and
TEM (Transmission electron microscopy).

Keywords: Green synthesis; Nano Bismuth Selenide (Bi_2Se_3); Bismuth Chloride;
L-Ascorbic acid; UV-VIS spectra, morphology studies; SEM and TEM

Introduction : Among the bismuth chalcogenides ,bismuth selenide a member of a family V-VI is gaining momentum due to its wide range of applications as thermoelectric devices[1-5],optical devices[6-10] topological insulators[11-13], semiconductors[14-16].Bismuth based semiconductors have become a promising group of advanced photocatalytic materials[17-18]. In recent years synthesis of BismuthSelenide (Bi_2Se_3) at nanoscale has received quite some attention during the past decades owing to low toxicity ,environmentally friendly element, easily available andeconomical.Bi2Se3 compounds have been prepared into thin films or nano structuressuch as nano films[19-22], nanoparticles[23-25],heterostructured nanowires[26-28],nanobelts[29-30] and nanotubes[31-32].

In the current synthesis Hydrothermal method was replaced by simple reflux and compound obtained shows XRD which is in good agreement with the reported one. In the present work we have choosen ascorbic acid as a reducing agent as itmakes the process economical, nontoxic and environment friendly. Pure ascorbic acid is a white, crystalline solid with a molecular formula $C_6H_8O_6$. Ascorbic acid is nothing but Vitamin-C which is well

soluble in water. It is readily available in citrus fruits and some vegetables and can also be extracted from the fruits. Bismuth selenide production using chemical reduction process is hazardous and makes the process toxic in some cases. We have used ascorbic acid in our chemical reduction process to prepare Bi_2Se_3 in green environment.

2. Experimental Details:

2.1 Materials:

All the reagents including Bismuth chloride ($BiCl_3$), Selenium di oxide (SeO_2), Ethylene diammine tetra acetate (EDTA), L-Ascorbic acid, Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH), Ammoina solution (NH_3) are analytical pure grade purchased from Aldrich chemicals.

2.2 Synthesis of Bismuth nanoparticles:

In this study, Bismuth selenide nanoparticles were synthesized under an aqueous condition. In a typical synthesis process 1.7294g of SeO_2 ,2.1g of $BiCl_3$,0.7 g of EDTA salt were mixed with 135 ml distilled water in a 250 ml R.B flask .After thorough mixing 1.166 g of NaOH , 1.166 g ascorbic acid were added to the contents of R.B flask .The contents of the flask were heated in an oil bath to a temperature of 150 ºC with constant stirring for 48 hrs with a speed of 100 rpm . After the reaction completed , the resulting black precipitates were filtered and washed with distilled water and absolute ethanol for several times to remove impurities thus nanometer sized Bismuth nanoparticles were obtained and subjected to various characterization.

2.3 Characterization

The phase and purity of Bismuth selenide nanostrcutures were determined by X-ray powder diffraction (XRD) using a Rikagu diffractometer (Tokyo, Japan, Cu Kα radiation, λ= 0.1546 nm) radiation in a 2θ range of 10-70º at room temperature running at 40 kV and 40mA. XRD peaks were indexed with the powder X software and the material is confirmed by comparing the XRD results with the standard JCPDS card number. The morphology of the products was examined by transmission electron microscopy (FEI-Model Tecnai G2S Twin -200 kV) and selected area electron diffraction (SAED) the samples were dispersed in ethanol by ultrasonic treatment and dropped on formvar coated-copper grids. All UV-Vis DRS characterization were recorded under ambient conditions using a Shimadzu 2100 UV-Vis spectrophotometer in the range of 200-800 nm with a scan rate of 60 nm/min (Braeside, Australia with quartz cuvette cells with a 1-cm path length. $BaSO_4$ was used as the reference. The morphology of the products was examined by scanning electron microscopy (SEM, Quanta 200), Elemental analysis was performed by using an EDAX Bruker Nano GmbH, X Flash Detector (Model5010).

3 Results and Discussion

3.1 XRD :

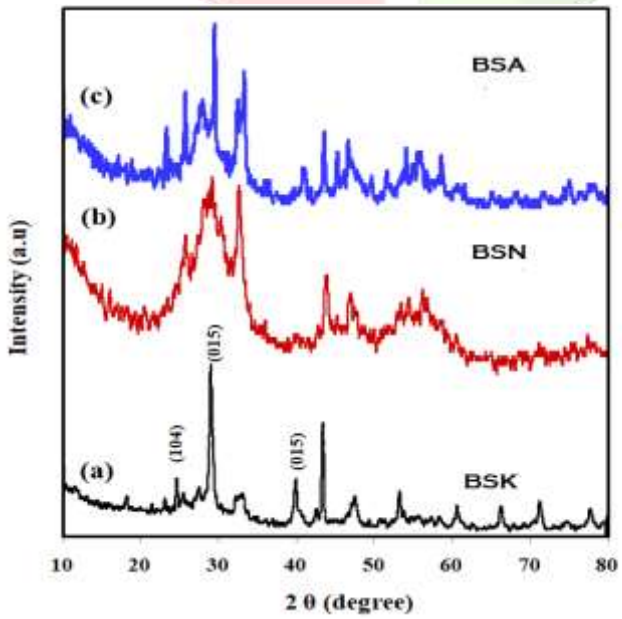
Figure 1 shows the XRD patterns of the Bi_2Se_3 nanostructure prepared in three different bases (namely KOH, NaOH and NH_4OH) at 150 °C for 48 h. In this pattern, all of the diffraction peaks can be steadily indexed to a rhombohedral geometry phase of Bi_2Se_3 (JCPDS: 33-0214) preferential growth orientation along (015) direction. XRD results reveal that the bismuth selenide nanostructures prepared with KOH exhibit high tendency of acquiring crystalline nature. No peaks for Bi_2O_3 or bismuth selenium oxide (Bi_2O_5Se) that could possibly form during the synthesis process, indicating the high purity of the Bi_2Se_3 samples. This procedure enables us to synthesize Bi_2Se_3 nanostructure successfully in thermal method. The crystallite size was determined from the (015) peak using the scherrer's formula and these values presented in the Table 1.

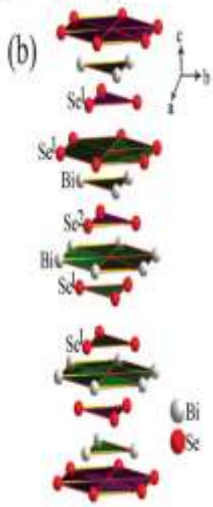
$D=0.94\lambda/ \beta Cos\ \theta$

where D is the grain size of the crystallite, λ is the wavelength of the X-rays used, β the full width at half maximum of the peak in radian, θ the Bragg angle of the X-ray diffraction peak .

Table 1: Crystallite size of Bismuth Selenide powder prepared by using various bases.

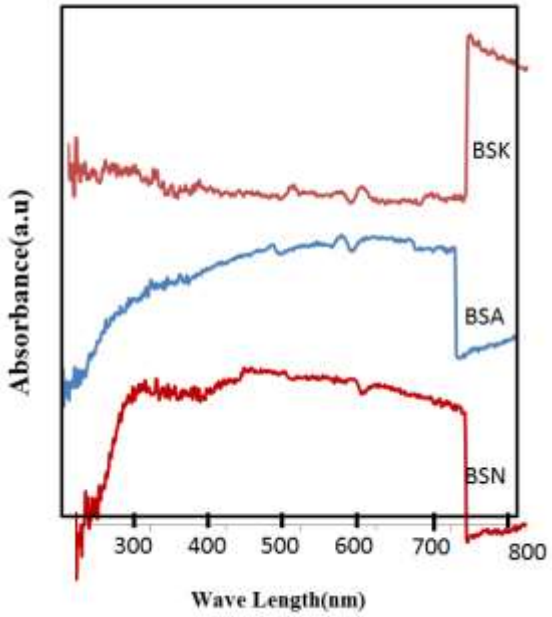
Material	FWHM (015) peak	Crystallite size(nm)
BSK (KOH)	0.2755	29.53
BSN (NaOH)	0.3542	27.57
BSA (NH_3)	0.2362	36.19





3.2 UV-DRS :

Figure 2 shows the UV-DRS of Bi_2Se_3 nanostructures synthesized with base KOH ,NH_3 and NaOH. UV-Vis spectrum of the prepared compounds were recorded in the range of 250-750 nm. No characteristic absorption peak is observed in UV-Visible range due to the extremely narrow band gap and in the case of BSK nano compound it shows relatively high transmittance than the other two compounds in the graph . The theoretical band gap energy for bulk Bi_2Se_3 is f 0.35 eV [optical] hence the absorption band does not fall in the range of 250-750 nm.



SEM Analysis:

Surface property of the prepared bismuth selenide powder was studied by recording SEM micrographs(Fig.no 3) .Morphology of SEM reveals the form of Bi nanoparticles to nanorods obtained in the range of 10-200nm. With the introduction of different bases the compound resulted in the formation of Bi_2Se_3 material at nanoscale with different kinds of morphologies. Thus the surface nature of material is influenced by the base employed during the reaction process.

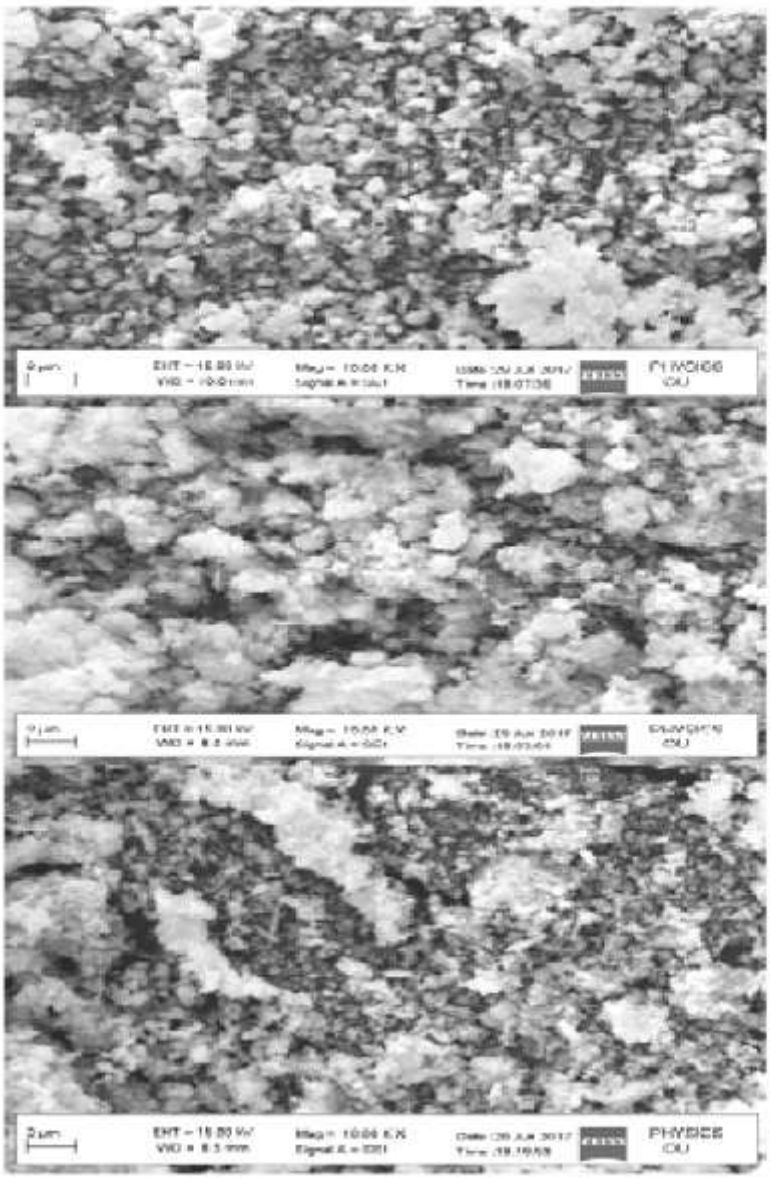
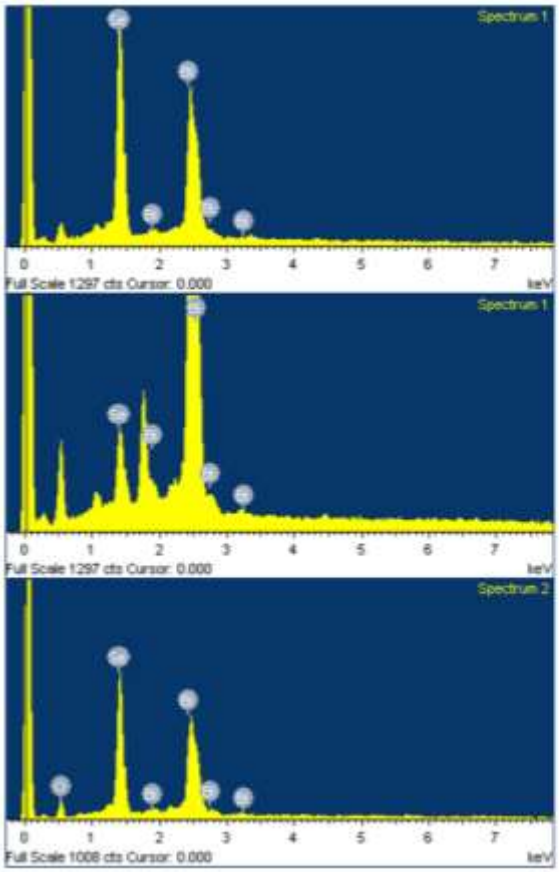


Fig 3 SEM images of Bi2Se3 nanoflowers to nanopowders

Elemental analysis by EDAX :

The quantitative elemental analysis of Bi_2Se_3 was carried out at room temperature of the composition of Bi_2Se_3 from EDAX. Table No. Presents the elemental theoretically expected stoichiometric composition of Bi_2Se_3 (in terms of atomic %) is Bi= 65, Se= 26. The compound is nonstiochiometric in nature.



Element	Weight%	Atomic%
Se L	38.22	62.08
Bi M	61.78	37.92
Totals	100.00	

Element	Weight%	Atomic%
Se L	7.91	18.51
Bi M	92.09	81.49
Totals	100.00	

Element	Weight%	Atomic%
O K	10.84	49.49
Se L	33.65	31.11
Bi M	55.51	19.40
Totals	100.00	

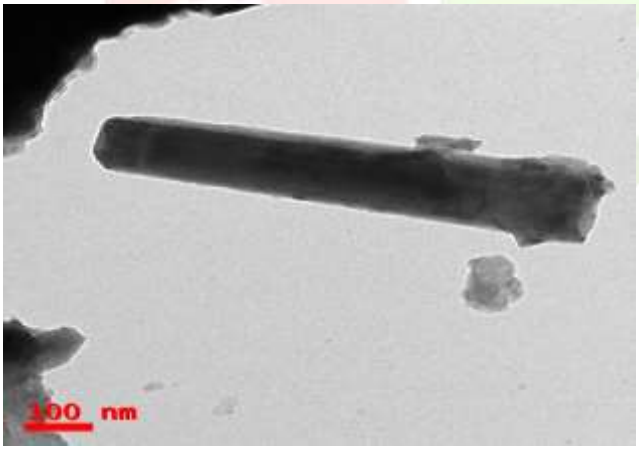


Fig. TEM images of Bi_2Se_3 rods with KOH

The TEM images showed that the material has a rod like morphology .

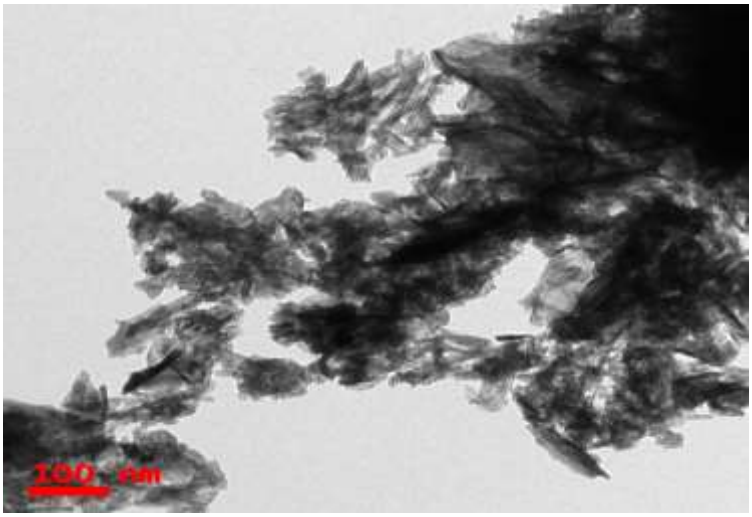


Fig.TEM images of Bi_2Se_3 nanotubes with NaOH base

The TEM showed that the material comprised of approximately tube like structures .

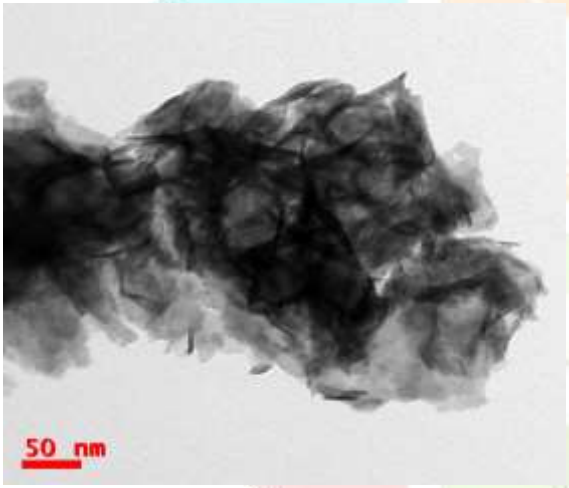


Fig.TEM images of Bi_2Se_3 nanowafers with NH_3 base

Here in this TEM image showed approximately hexagonal lamellar plates . Based on TEM images it should be pointed out that the morphology of the material is highly influenced by variation of base used during the experiment. During the preparation of the compound by regular laboratory process i.e, solvothermal method we used three different kinds of bases such as KOH, NaOH and NH_3 the images obtained here clearly demonstrates that they have influence on the morphology of the resulting compound.

4.Conclusions:

The EDAX of the compound indicated that Bi compounds were non-stoichiometric and the XRD of the bismuth selenide confirmed the formation of Bi_2Se_3 phase. Optical studies shows that the transmittance is observed for BSK where as low transmittance exhibited by other two compounds. SEM and TEM results reveals that the morphology of Bi_2Se_3 nanocompounds was greatly influenced by the kind of base used.

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