Solvothermal synthesis of Bi_2S_3nanoparticles and nanorods towards solar cell application

J.Arumugam[1], A.Dhayal Raj[1*], A.Albert Irudayaraj[1], M.Thambidurai[2]

1. PG & Research Department of Physics, Sacred Heart College, Tirupattur, Vellore, Tamil Nadu -635601.
2. LUMINOUS! Centre of Excellence for Semiconductor Lighting and Displays, School of Electrical & Electronic Engineering, The Photonics Institute (TPI), Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore.

E-mail addresses:
dhayalraj03@gmail.com (A.Dhayal Raj)

Abstract

One-dimensional nanostructures have gained more attraction in recent years because of their high aspect ratio. Uniform Bi_2S_3 nanorods have been grown using N,N-dimethylformamide (DMF) and ethylene glycol (EG) as solvents by solvothermal method, inorder to study the effect of solvent on the properties of the prepared Bi_2S_3. Also the reaction temperature has been changed to examine its role in tuning the property of the Bi_2S_3 nanorods. The x-ray diffraction (XRD) results show that the Bi_2S_3 nanorods are of orthorhombic phase. The high resolution scanning electron microscope (HRSEM) and high resolution transmission electron microscope (HRTEM) studies reveal the appearance of rod-like structures with the typical length in the range of 1µm and average diameter is around 150nm. The solvent effects and reaction temperatures are discussed in detailed. The band gap of the prepared samples have been estimated using tauc plot and this suggests that the prepared Bi_2S_3 nanostructures may find potential applications in the fabrication of solar cells.

Keywords: Solar cells; Bi_2S_3 nanoparticles and nanorods; XRD; FTIR;

1. Introduction

One-dimensional semiconducting nanomaterials are being projected as the new-age material for application in device fabrication due to their various advantages over the other forms of the material in the nanorange[1-2]. Nanocrystalline materials are receiving extensive attention due to their unusual properties include the thermal, mechanical, electron transport, phonon transport, optical and non-linear optical properties, which make nano-sized compounds suitable for applications such as electronic and optoelectronic devices, solar cell and automotive applications. Due to its quantum size effects its nanocrytalline materials have been found to alter the performance of photochemical cells significantly. Especially, control over both nanocrystalline morphology and the crystal size is a new challenge to synthetic chemist and materials scientists [3]. Binary metal chalcogenides $A_2^{V}B_3^{VI}$ (A= As, Sb, Bi; B= S, Se, Te) have been drawn extensive attention[4]. Among them, Bi_2S_3 is an excellent semiconductor with band gap (1.3eV) suitable for application in photovoltaic conversion, IR spectroscopy, decorative coating, etc. Especially, bismuth sulfide with orthorhombic system is a candidate for photodiode arrays and photovoltaic converters due to its low band gap which has been widely used in thermoelectric cooling technology[5-10].

Herein, orthorhombic structured bismuth sulfide nanoparticles and nanorods have been prepared by a solvothermal approach using different solvent and different reaction temperatures. The effect of solvent and the reaction temperature on the properties of the Bi_2S_3 nanostructures have been investigated and reported.

2. Experimental

In typical experiments, bismuth nitrate (1mM), thiourea (1mM), citric acid (1mM), cetyltrimethylammonium (0.7mM) were mixed in 40ml DMF. The mixture was stirred until all the chemicals were dissolved and the solution was sonicated for 15 minutes. The mixture was

transferred into stainless steel autoclave. The autoclave was tightly packed and maintained at 180°C for 24hours. After cooling down to room temperature, the mixture was centrifuged and the solid product was collected. The solid product was then washed with acetone and water for several times followed by centrifugation to collect the solid product. Finally, the solid product was dried in hot air oven at 70°C for 8hours to obtain Bi_2S_3 nanostructures. DMF was replaced with EG and the same procedure was followed to obtain Bi_2S_3samples. The final products were subjected to further characterization, thus the effect of solvent can be investigated.

The crystal structures of the samples were confirmed by x-ray diffraction (XRD) method (Rigaku Miniflex II). FEI Quanta FEG 200-High Resolution Scanning Electron Microscope was employed for obtaining the micrographs. JEOL JEM-2000 High Resolution Transmission Electron Microscopy was employed for obtaining the micrographs. Fourier-transform infrared spectroscopy spectra for the Bi_2S_3 nanostructures have been obtained from PerkinElmer Spectrum Version.

3. Results and discussion

Figure 1 shows the XRD pattern of the Bi_2S_3 nanoparticles and nanorods. All the peaks can be indexed as the orthorhombic structure of Bi_2S_3. The XRD pattern in figure 1 (a and b) correspond to Bi_2S_3 prepared in the presence of EG different reaction temperatures 160°C and 180°C respectively. The lattice constants area=11.11Å, b= 11.25 Å and c=3.97 Å. (JCPDF# 75-1306). The broadening of the peaks clearly indicates that the size of the product is in nanoscale. The average crystallite sizes are 27nm and 33nm for samples prepared at 160°C and 180°C with EG. The X-ray diffraction peaks in figure1 (c and d) correspond to the Bi_2S_3 sample prepared with DMF at 160°C and 180°C respectively. All the diffraction peaks can be indexed to a pure orthorhombic phase of bismuth sulfide with cell constants a=11.14Å, b= 11.30Å and c=3.95Å

(JCPDF # 17-0320) [11-13]. The crystallite sizes are calculated using scherrers formula and found to be 32nm and 42nm for the sample prepared at 160°C and 180°C with DMF.

The morphology of the prepared Bi_2S_3 nanostructures studied by HRSEM and HRTEM displayed in Figure 2. The HRSEM and HRTEM images and selected area electron diffraction patterns (SAED) of Bi_2S_3 synthesized by a simple solvothermal approach with different solvents and different temperatures. The Bi_2S_3 samples prepared with EG at 160°C shows the formation of nanoparticles of diameter around 16nm (figure 2a). The corresponding HRTEM image in figure 2b clearly depicts the size of the nanoparticles. When the reaction temperature is increased to 180°C the particles get agglomerated as seen in the HRSEM image (figure 2c) and the corresponding HRTEM image is shown in figure 2d. It is clearly revealed that the average size is around 18nm. SAED pattern (inset of figure 2d) shows crystalline nature of the sample and this agrees well with X-ray diffraction results. Form these results it can be concluded that as the reaction temperature is increases, the particles size also increases. The HRSEM image in figure 2c corresponds to the Bi_2S_3 prepared with DMF at 160°C. The formation of nanorods with some agglomerations is clearly witnessed. HRTEM analysis shows one dimensional nanorods with breadth around 200nm and length around 750nm is seen. When the reaction temperature was prolonged to 180°C, uniform nanorods were obtained as shown in figure 2g. The formation of nanorods has been further confirmed with HRTEM in figure 2h. The Bi_2S_3 nanorods formed in the presence of DMF has breadth around 127nm and length around 450nm. The SAED pattern given as an insert in figure 2h reveals the high crystalline nature of the nanorods.

The composition and quality of the product were analyzed by fourier-transform infrared (FTIR) spectroscopy. Figure 3 shows the FTIR spectra of the samples. The FTIR results in figure 3a belongs to the sample obtained by ethylene glycol at 160°C and 180°C respectively. The broad

band at 3300-3500cm^{-1}may be attributed to the stretching vibration of H_2O, while the band centered at 1634cm^{-1} corresponds to the bending vibrations of CO_2. The strong peaks at 1378cm^{-1} may be due to C–S and C–N stretching vibration [14]. The absorption bands at 2853cm^{-1} and 2925cm^{-1} belong to asymmetric and symmetric stretching vibrations of methylene groups, respectively [15]. The appearance of methylene groups may be indicative of the existence of residual FTIR absorbed on the product surface. FTIR peaks of the as-prepared Bi_2S_3nanorods prepared with DMF at 160°C and 180°C shown in figure 3a. No peaks of other impurity are detected in the IR spectrum. The broad absorption peak form 3000 to 4000 cm^{-1} corresponding to the –OH group of H_2O, while the peak centered around 1634cm^{-1} belongs to the C=O stretching mode. The week peaks located at 1111cm^{-1}correspond to the C-O bond and two weak peaks ranging from 2925cm^{-1} and 2853cm^{-1}can be assigned to the bond of the $–CH_3$ and $–CH_2$ groups [16]. The carboxylate stretching vibrations are illustrated by the corresponding bands at 1378cm^{-1} and are partially overlapped by the NH_2 bending vibration and the C-S stretching frequency [17]. The broad one around 619cm^{-1} and 506 cm^{-1} originates from the Bi vibration [18]. The EDAX (Figure 3b) results show that Bi and S are present in the sample.

The thermal analyses were performed using TGA. The existence of three stages can be observed in figure 3c. The first region around 25-170°C correspond to the loss of physisorbed water. While, the second region around 170-350°C correspond to the loss of surface hydroxyl group. Weight loss beyond 307°C may be attributed to the vaporization of excess of elemental S form the preferentially during the growth process of the Bi_2S_3 nanorods [19].

The optical properties of the Bi_2S_3 nanoparticles and nanorods were measured using UV-Vis spectroscopy. The optical bandgap (Eg) of the semiconductor materials could be calculated from the equation of $(\alpha h\upsilon)^2 = A(h\upsilon\text{-}Eg)$, Where, α, υ, Eg and A were the absorption coefficient,

frequency, band gap and a constant respectively. Form the plot (Figure 3d) of $(\alpha h\upsilon)^2$ vs $h\upsilon$, the band gap values obtained for the sample prepared with EG at 160°C and 180°C are 1.93eV and 1.89eV respectively. Similarly the bandgap of the samples prepared with DMF were found to decrease from 1.83eV to 1.80 eV when the reaction temperature is increased form 160°C to 180°C. The absorption for the four Bi_2S_3 samples showed a blue shift compared with the typical direct band gap of 1.3eV of the bulk crystal, which could be associated with the morphology, size and structure. Chen et.al. [20] and Tahir et.al. [21] have reported similar shifting of band gap to higher values.

4. Conclusion

The Bi_2S_3 nanoparticles and nanorods have been synthesized by a simple solvothermal approach with different solvent and different reaction temperature for 24hours. In this work, the solvent and temperature played a crucial role in the shape controlled synthesis of the Bi_2S_3 nanostructures. The nanorods present a high crystalline nature with orthorhombic structure. The breadth of the nanorods is around 127nm and length 450nm. The FTIR studies show that the occurrence of chemical interaction between bismuth and sulfide. The synthesized Bi_2S_3 nanoparticles and nanorods suggest that these samples will be a promising material for solar cell application.

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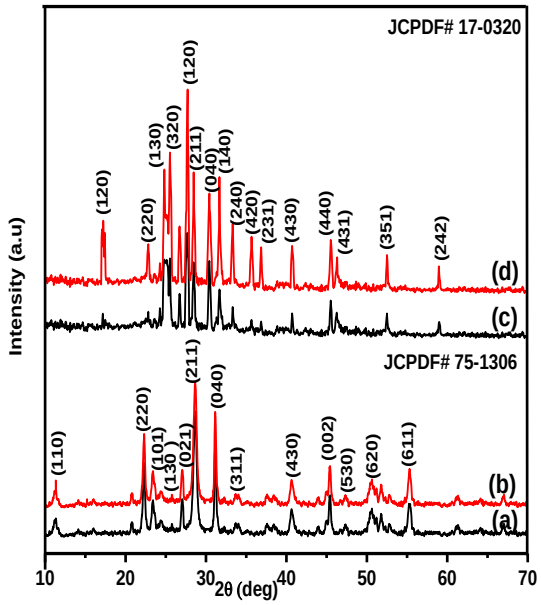

Figure 1. XRD Patterns of Bi_2S_3 prepared at (a) 160°C, (b) 180°C with EG, and (c) 160°C, (b) 180°C with DMF.

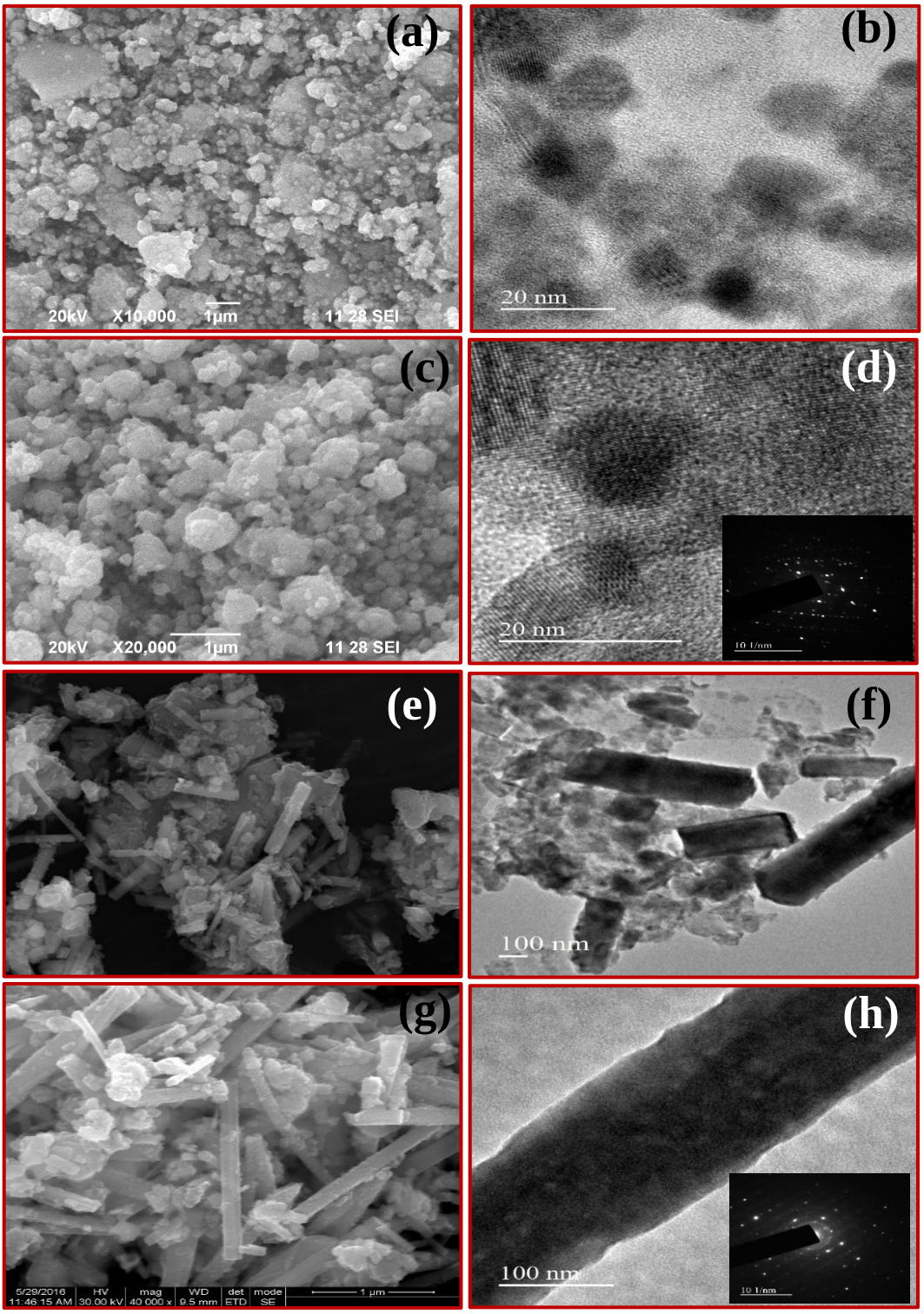

Figure 2. SEM and TEM image of Bi_2S_3 prepared at (a and b) 160°C with EG, (c and d) 180°C with EG (e and f) 160°C with DMF and (g and h) 180°C with DMF.

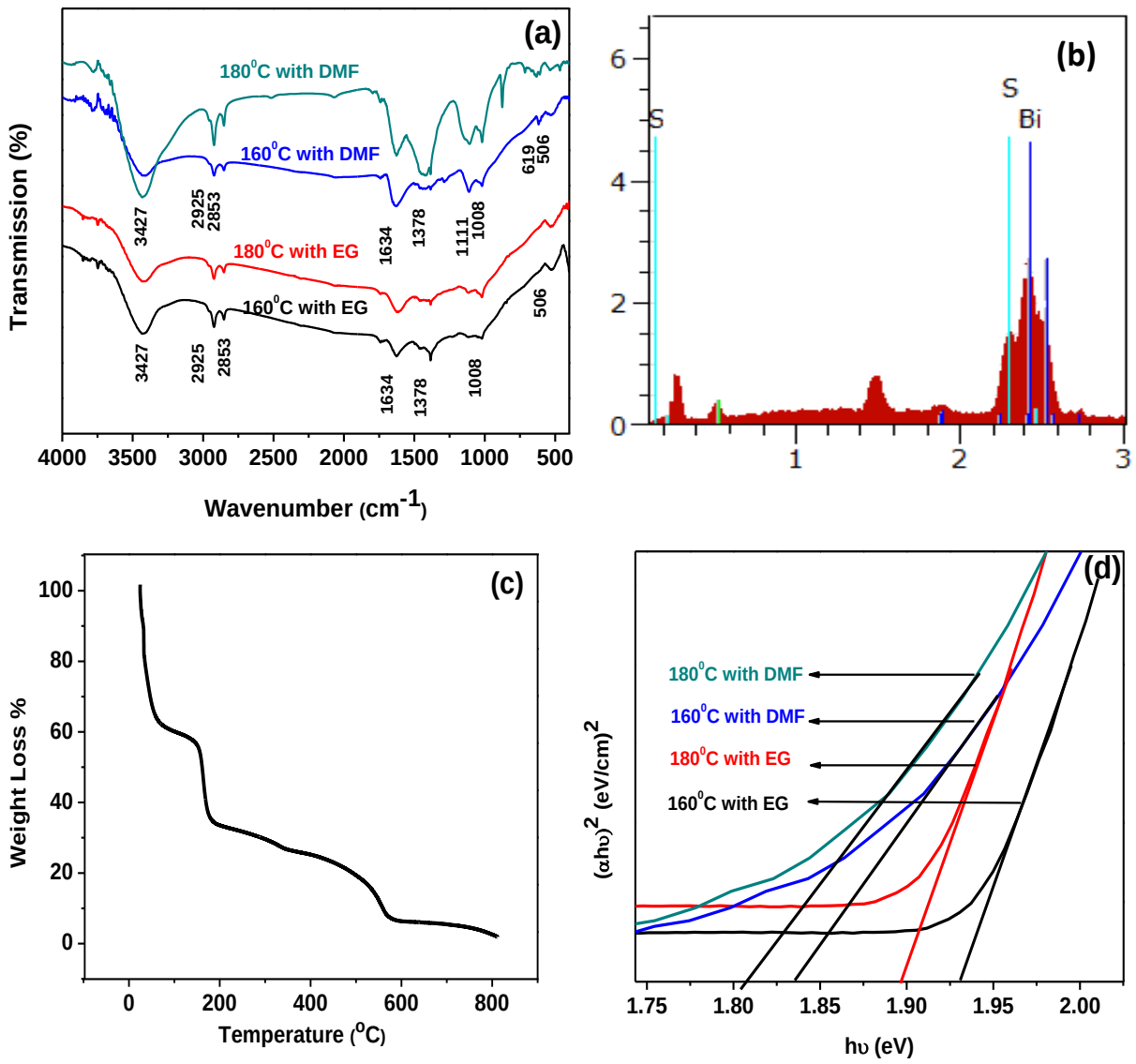

Figure 3. (a) FTIR spectra of Bi_2S_3 samples. (b) EDAX and (d) TGA spectra of Bi_2S_3 nanorod at 180°C with DMF. (d) Plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ of Bi_2S_3 samples.