Structural and Electrical Studies of Bi_2Se_3 Nanomaterials by Solvothermal Method for Thermoelectric Applications

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Abstract

The Bi_2Se_3 nanoparticles were synthesized by the solvothermal method. The structural and morphological characterization has been done using XRD, HRSEM and Raman while electrical studies at room temperature were analyzed using impedance spectroscopy and cyclic voltmetry. The phase formation was confirmed through XRD measurement and average grain size was found to be 25 nm for as-prepared sample and 37 nm for 650 °C for 12 hours annealed sample. Raman spectrum appears in the higher frequency range, this is due to stronger bonding forces, i.e the peak at 524 cm^{-1} or may arise due to the overtones of A_{1g}^1 and E_g^2 modes. The redox behavior was due to Bi^{3+} converted into Bi^{2+} and Bi metallic state. This redox peak was confined the formation of Bi_2Se_3 nanoparticles. The high temperature electrical conductivity studies were performed as-prepared and annealed sample using impedance spectroscopy.

1. Introduction

Bismuth selenide (Bi_2Se_3) is a gray powder that is a compound of bismuth and selenium also known as bismuth (III) selenide. It is a semiconductor and a thermoelectric material [1]. While perfect stoichiometric bismuth selenide should be a semiconductor (with a gap of 0.3 eV) naturally occurring selenium vacancies act as electron donors and it often acts as a semimetal [2]. Topologically protected surface states have been observed in Bismuth selenide [3] which is the subject of ongoing scientific research [4]. Studies on thin films of Bi_2Se_3 are attracting wide attention for various optoelectronic devices [5]. Semiconducting materials, which are based totally on sulfides, selenides and tellurides, have currently obtained a lot activity as materials for optoelectronics technology. Among these, bismuth selenide (Bi_2Se_3), a member of the family of $A^V B^VI$ semiconducting materials, has been significantly studied due to its achievable purposes in infrared photography [6], optical and photosensitive devices [7], present day thermo-electric cooling modules [8], photo electrochemical cells and electro-thermal devices [9, 15].

Bismuth selenide is a narrow direct band gap semiconductor ($E_g = 0.16\text{--}0.35\text{ eV}$) [16] and noticeable for its significant and motivating properties. It has attracted extensive interest due to its feature anisotropic layered structure as well as important applications in the field of optical recording systems and strain gauges [17]. Bismuth selenide crystallizes in the rhombohedral unit cell, where correspondent atoms are approved in two dimensional, layers perpendicular to the c-axis. Five such layers-in the sequence of $\text{Se}_1\text{--Bi--Se}_2\text{--Bi--Se}_1$, where the Se atoms occupy two different sites, form a tight bound unit, whereas these 'sandwiches' are held together by a much weaker $\text{Se}_1\text{--Se}_1$ interaction. The bonds interior these 'sandwiches' is usually regarded to be pre-dominantly covalent, and these between them, are due to van der Waals forces [18, 19].

Thus the structural arrangement leads to an easy cleavage perpendicular to the c-axis displaying a Se-terminated surface. Bismuth selenide has been the subject of a massive wide variety of investigations in the bulk structure [20]. Effect of Te doping and electron irradiation on thermal diffusivity of bismuth

selenide thin films have been studied via Augustine et al [21]. Observed a marked enlarge in thermo-electric performance. Synthesized rhombohedral bismuth selenide nano structures by using solvothermal technique [22]. The prepared bismuth selenide films by way of chemical deposition technique and synthesized hollow nano structured bismuth selenide particles by using chemical route [23, 24]. Thin films of bismuth selenide have been prepared by a variety of deposition methods, including thermal evaporation [25, 26], chemical vapour deposition [27], chemical bath deposition [28, 29], Electrodeposition and successive ionic layer absorption and reaction [30, 31].

2. Experimental Details

The Bi_2Se_3 nanoparticles were synthesized by the solvothermal method, in which Bi_2O_3 and SeO_2 were used as a precursor. The first step was preparing Bi_2Se_3 nanoparticles: Bi_2O_3

(2.6 g = 4 mmol), SeO_2 (1.9 g = 12 mmol), added polyvinylpyrrolidone (PVP) (0.2 g) (acts as surfactant), added NaOH solution (0.4g = 8 ml) were dissolved in ethylene glycol (72 ml). The solution was stirred for 2 hours. The solution was transferred to autoclave for $180^\circ\text{C}/6$ h. After the reaction was completed, the product solution was centrifuged, washed with distilled water, ethanol and acetone repeatedly to purify the product, and finally dried at $80^\circ\text{C}/30$ min under surrounding atmosphere. The samples were cooled under normal condition (room temperature) and collected gray color as-prepared Bi_2Se_3 nanoparticles. The As-prepared sample and 650°C annealed for 12 h in argon gas atmosphere sample was used for further analysis.

3. Characterization Techniques

The X-ray diffraction was used to identify the phase formation and crystallinity of the prepared sample. The Surface morphology of the Bi_2Se_3 nanoparticles was studied using HR-SEM and elemental composition analysis were made using EDS measurement. The redox nature of Bi_2Se_3 nanoparticles was carried out by cyclic voltammetry. The electrical properties were measured by Impedance Spectroscopy and the structural properties of Bi_2Se_3 nanoparticles were studied by using Raman Spectroscopy.

4. Results And Discussion

4.1 STRUCTURAL STUDIES

Figure 1 shows the X – ray diffraction pattern of nanocrystalline Bi_2Se_3 for as-prepared sample and samples annealed at 650°C for 12 h in argon gas atmosphere. The X- ray diffraction studies were carried out for 2θ angle ranges from 20° to 80° . The target Cu $K_{\alpha 1}$ radiation ($\lambda=1.5406 \text{ \AA}$) was used for this measurement. The XRD pattern of as-prepared nanocrystalline Bi_2Se_3 sample diffraction peaks and 650°C annealed for 12 h in argon gas atmosphere sample. The diffraction peaks for Bi_2Se_3 nanoparticles are $2\theta = 24.82^\circ, 27.79^\circ, 30.48^\circ, 32.99^\circ, 35.32^\circ, 37.55^\circ, 39.67^\circ, 41.69^\circ, 43.61^\circ, 45.51^\circ, 49.08^\circ, 52.47^\circ, 54.14^\circ$,

55.71°, 60.40°, 61.86°, 64.79°, 67.69°, 73.23° and 78.69° corresponding to identified to originate the diffraction hkl planes

(101), (104), (221), (107), (018), (332), (444), (1010), (110), (443), (555), (024), (200), (220), (655), (543), (442), (0213), (464) and (1211) respectively. The XRD analysis shows that the Bi₂Se₃ nanomaterials exhibit the rhombohedral structure of Bi₂Se₃ [space group: R3m with lattice constants a = 4.1396 Å and c = 28.636 Å (JCPDS = 33-0214 and 89-2008)]. From the X-ray diffraction measurement, a very high intensity peak obtained at 2θ = 27.84° (104) which correspond to Bi₂Se₃ nanoparticles.

The grain size of the prepared samples was calculated using Debye's Scherrer formula

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \longrightarrow (1)$$

Where **D** is a size of the nanoparticles, **θ** = diffraction angle, **λ** = wavelength of X-rays and **β** = line broadening at Full Width Half Maximum (FWHM). The average grain size was calculated above formula from diffraction pattern was found to be 25 nm for as-prepared sample and 37 nm for 650°C for 12 hours annealed sample.

4.2 HIGH RESOLUTION SCANNING ELECTRON MICROSCOPY WITH EDS STUDIES

Figure 2 (a-c) shows the high resolution SEM morphology of as-prepared Bi₂Se₃ nanocrystalline sample with EDS spectrum analysis. The images indicate that mostly well crystalline nature of as-prepared Bismuth Selenide (Bi₂Se₃) sample, which is confirmed through XRD analysis.

We found that most of the Bi₂Se₃ nanocrystalline have nano-rod and nano-flakes mixture with porous surface morphology nature as shown in Fig. 2.1 (a-b). Figure 2.1(c) shows the Energy dispersive spectroscopy (EDS) of Bi₂Se₃ as-prepared sample and confirms the presence of Bi and Se. Figures 2.2 (a-c) show the HRSEM images of Bi₂Se₃ nanocrystalline sample annealed at 650°C for 12 h in argon gas atmosphere with EDS spectrum analysis.

The images indicate that mostly Selenide (Se) nanoparticles well incorporated into the Bismuth materials as shown in Fig. 2.2 (a). The white crystalline of Se-nanoparticles is dispersed on the Bi materials at high magnification 500 nm. The evidences of that formation Bi₂Se₃ nanoparticle as shown in Fig. 2.2(b). Figure 2.2(c) shows the EDS spectrum of Bi₂Se₃ sample measurements confirms that Bi and Se elements are presented.

4.3 RAMAN STUDIES

Figure 3 shows Raman spectra of as prepared and annealed at 650 °C for 12 h in argon gas atmosphere sample. Raman spectroscopy has been an important investigation way as a high-resolution probe technology of crystal structure and vibrational properties of materials. The rhombohedral crystal structure

of Bi_2Se_3 corresponding to the [space group D_{3d}^5 (R3m)] symmetry and there are five atoms in a primitive unit cell and each unit cell consisting of three few-quintuple layers stacked together by weak van der Waals forces. The atomic arrangement of Bi_2Se_3 is distinctive (i.e., every repeating unit in the crystal is a quintuple layer of Se-Bi-Se-Bi-Se), which are held collectively through susceptible van der Waals forces. The Raman spectrum of Bi_2Se_3 with 785 nm excitation laser was also performed to investigate the four Raman active modes (E_{g1} , A_{1g1} , E_{g2} and A_{1g2}) of this sample. The letters “E” and “A” indicate the in-plane and out-of-plane (C- axis) lattice vibrations, and subscript “g” denote Raman active. Group theory predicts 12 zone center optical phonon modes in this crystal symmetry, out of 12 optical phonon modes only 4 modes are Raman active, they are E_{1g}^1 , A_{1g}^1 , E_g^2 and A_{1g}^2 verified polarization dependence, out-of-plane A_{1g}^1 and A_{1g}^2 , in-plane E_g^1 and E_g^2 modes. There are three optical phonon modes are clearly seen in the spectrum. They are $\sim 124\text{ cm}^{-1}$, 262 cm^{-1} and 524 cm^{-1} . The peak at 124 cm^{-1} corresponding to the well known E_g^2 mode indicate that good quality of the crystal structure.

The peak at 262 cm^{-1} due to combination of A_{1g}^1 and A_{1g}^2 modes indicate that well crystallinity of this sample. Raman spectrum appears in the higher frequency range, this is due to stronger bonding forces, i.e the peak at 524 cm^{-1} or may arise due to the overtones of A_{1g}^1 and E_g^2 modes. The observed frequencies are well compared with the previously reported experimental and calculated phonon vibration modes of Bi_2Se_3 . If the polarization of x-direction is present ($z(x\bar{x})z$ geometry), one will observe phonons denoted by A_{1g}^1 , A_{1g}^2 and E_g^2 . If one measures scattered light with a polarization in the y direction, only E_g^2 will appear in the Raman spectrum. This can be understood by considering the nature of the atomic displacements associated with the phonon modes.

4.4 CYCLIC VOLTAMMETRY STUDIES

The redox nature of Bi_2Se_3 nanoparticles was carried out by cyclic voltammetry. This process was done in a three electrode system, Glass Carbon Electrode (GCE) as a working electrode, Ag/AgCl electrode as a reference electrode and platinum wire as a counter electrode. The modified Bi_2Se_3 nanoparticles/GCE was carried out in TBPA (Tetra butyl ammonium perchlorate) used as a supporting electrolyte in acetonitrile (CH_3CN) condition at scan rate 50 mV/s . The modified Bi_2Se_3 nanoparticles/GCE obtained well define redox peak ($I_{pa} = 0.0114$ and $I_{pc} = -0.155$) as shown in Fig. 4. This redox behavior was due to Bi^{3+} converted into Bi^{2+} and Bi metallic state. This redox peak was confined the formation of Bi_2Se_3 nanoparticles. Bi_2Se_3 nanoparticles annealed at 650°C for 12 h sample. This is modified on the GCE (Bi_2Se_3 nanoparticles/GCE) was obtained well known the higher redox peak current with $I_{pa} = 0.021(\mu\text{A})$ and $I_{pc} = -0.144(\mu\text{A})$ as shown in Fig. 4.

Table The electrochemical response of Bi_2Se_3 nanoparticles in $0.1\text{M H}_2\text{SO}_4$ at 50 mVs^{-1}

Material	Oxidation current (μA)	Oxidation potential (V)	Reduction Current (μA)	Reduction potential (V)
Bi ₂ Se ₃ - As prepared	0.0114	1.873×10 ⁻⁴	- 0.155	- 2.111×10 ⁻⁴
Bi ₂ Se ₃ -12 hours	0.021	1.852×10 ⁻⁴	- 0.144	- 2.804×10 ⁻⁴

From this data was clearly indicated that increasing the crystallinity of Bi₂Se₃ NPs. The crystalline further confirms the XRD data. It gives a broad peak, hence it shows that the three electron (3.4) transfer process was evident in this redox behavior. Here the electron calculating from below equation.

$$n = \frac{i_p \cdot 4RT}{FQv} \longrightarrow (2)$$

Where i_p is the current, R is the Gas Constant (8.314 J/mol K), T is the Temperature (298 K), F is the Faradays Constant (96,485.33 A/mol), Q is the Charge and v is the Scan Rate (50 mV/Sec).

4.5 IMPEDANCE SPECTROSCOPY STUDIES OF Bi₂Se₃ NANOPARTICLES

The complex impedance plots measured at different temperatures ranging from RT to 70 °C with the frequency range of 1 Hz – 1 X 10⁶ Hz are shown in Fig. 5. It should be noted from this plots most of the depressed semicircle are exists, whose center is slightly shifted below the real axis (this behavior is commonly considered to be an indication of a non-Debye relaxation process). At low temperatures as well as low measuring frequencies the curve slightly deviates from a perfect semicircle.

The impedance plots are fitted with complex non-linear least square fit (CNLLS) to acquire the resistance of the sample. With the geometry of the sample, this resistance value has been converted into conductivity using the relation,

$$\sigma = \frac{1}{\rho} = \frac{l}{R A} \longrightarrow (3)$$

Here R is the resistance of the sample, A is the area of the cross-section and l is the thickness of the pellet. The high temperature electrical conductivity studies were performed as-prepared and annealed sample using impedance spectroscopy. It shows that very high resistance as well as grain effect curve behavior.

5. Conclusions

In summary, Bi₂Se₃ nanoparticles were synthesized using the solvothermal method. The phase formation was confirmed through XRD measurement. The surface morphology and crystal structure of the nanoflakes were analyzed using HRSEM for Bi₂Se₃ nanomaterials. From the EDS spectrum analysis of Bi₂Se₃ (as-prepared and annealed) sample's measurements confirms that Bi and Se elements are presented. A Raman spectrum of the Bi₂Se₃ sample shows that four Raman active modes (E^1_g , A^1_{g1} , E^2_g and A^1_{g2}) were identified. From the Cyclic voltammetry measurement of Bi₂Se₃ nanoparticles, shows that the redox behavior was due to Bi³⁺ converted into Bi²⁺ and Bi metallic state. This redox peak was confined the formation of Bi₂Se₃ nanoparticles. It shows that very high resistance as well as grain effect curve behavior using impedance spectroscopy. This material has been a potential candidate in the area suited for thermo-electric and energy storage applications.

6. Declarations

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Figures

Figure 1: XRD pattern shown in Bi₂Se₃ nanoparticles: as-prepared and annealed 650 °C for 12 hours annealed sample.

Figure 1

See Image above for figure legend

Figure 2

See Image above for figure legend

Figure 3 Shows the Raman spectrum of the Bi_2Se_3 nanoparticles: right side as-prepared Bi_2Se_3 and left side Bi_2Se_3 annealed at 650°C for 12 h in argon gas atmosphere sample

Figure 3

See Image above for figure legend

Figure 4 Shows the C-V studies of Bi_2Se_3 nanoparticles (a) As-prepared sample and (b) Annealed sample

Figure 4

See Image above for figure legend

Figure 5 shows the impedance spectroscopy of Bi_2Se_3 nanoparticles (a) As-prepared sample (b) Annealed sample at 650 °C for 12h in argon gas atmosphere

Figure 5

See Image above for figure legend