

Thermoelectric Characterization of Nanostructures of Bismuth Prepared by Solvothermal Approach

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Nanostructured thermoelectric materials being an emerging area of research bismuth (Bi) nanostructures have been developed by solvothermal approach with a change of solvent. Structural characterization revealed that nanorods and nanospheres like structures were generated in the process when the solvent used were only ethylene glycol (EG) and ethylene glycol with absolute ethanol (AE) in the ratio of 1:1 respectively. Electrical properties viz. conductivity (σ) and thermoelectric power (S) have been measured in the temperature range 300K to 400K. From the observed value of σ and S power factor P has been calculated. The property improved for nanosphere like structures.

Keywords: Thermoelectric Materials, Nanostructures, Solvothermal, XRD, TEM, Power factor.

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1. INTRODUCTION

The search of alternative source of energy has been taken up by the researchers due to the limitation of the fossil fuel. Thermoelectric (TE) conversion can be one of the alternatives for converting waste heat into electrical power (Seebeck effect). Thermoelectric materials, which are very eco-friendly, serve for long time without any maintenance [1]. The effectiveness of a thermoelectric material is quantified by the dimensionless figure of merit defined as $ZT = \sigma S^2 / \kappa T = PT / \kappa$ where S is the Seebeck co-efficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the absolute temperature. P is the power factor.

Z (or P) can be improved by structuring low dimensional materials to modify the transport parameters independently. In recent years synthesis of nanostructured materials have played key role in the property enhancement which in turn depend on the morphology of the material [2,3]. The chemical and physical properties of these materials are different from those of their bulk phase. The high surface area to volume ratio plays an important role to improve properties of nanoscale materials. This parameter is not significant in macro or micro dimensions but it is significant when the materials become of nanometer size.

Bismuth is a semimetal with overlapping valence and conduction band at T point of the Brillouin zone. It is a potential thermoelectric materials [4] due to its low effective mass, high anisotropic electronic behavior, low conduction-band effective mass and high electronic mobility [5]. Different synthesis techniques for Bi nano particles have been proposed. Inverse micelles method [6], high temperature hydrothermal reduction [7], solventless methods [8, 9], electrochemical self-assembly techniques [10] were introduced to synthesize Bi nanostructures. Wang et al have reported the solution-based, one-pot syntheses of Bi dot, nanorods, nanoplates, and nanoribbons [11]. Ma et al. [12] reported an

aqueous reduction method to synthesize bismuth nanostructures of varied shapes at a temperature of 80°C. Different kinds of controlling agents and weight ratio of organic molecules to Bi cations in the aqueous solutions can change the shape and size of Bi nanostructures. From some theoretical and experimental investigations it has been observed that the enhancement of figure of merit (ZT) in nanostructured material is due to improved S and reduced κ [13]. The Bi nanowires show an enhanced ZT at temperature of 300K [14]. Among various methods solvothermal process is an important and promising technique to synthesize inorganic nano structures of controlled size and shape [15,16,17].

In the present work nano crystalline bismuth has been synthesized employing solvothermal technique to investigate the thermoelectric property of the material and draw a mapping between the structure and property modification. The synthesized materials have been characterized by XRD and TEM analysis to get the shape and size of the nano particles. Electrical characterizations have been undertaken to compare the dependence of the property on the morphology of the sample. It is observed that the property improves when the shape of the nanostructure changes from rod to sphere.

2. EXPERIMENTAL

2.1 Material Used

All the materials, namely, ethylene glycol (EG), absolute ethanol (AE), sodium bismuthate dihydrate ($\text{NaBiO}_3 \cdot 2\text{H}_2\text{O}$) and acetone were purchased from Merck specialties. All the reagents were analytically pure grade and were used without further purification.

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2.2 Synthesis Procedure

2.2.1 Synthesis of Bismuth Nanorods

In a typical procedure (Sample S₁) 2 gm of sodium bismuthate was added to 200 ml of ethylene glycol (EG) acting as solvent kept in a beaker at room temperature. The solution was mechanically stirred by magnetic stirrer (Remi) for 45 min for thorough dispersion. The resulting solution was then transferred into a container of 200 ml and was put into an autoclave which was then sealed and maintained at a constant temperature of 200 °C for 24 h. It was allowed to cool down to room temperature. The resultant product was taken out and centrifuged at 4000 rpm for about 30 minutes and the solid product was collected. The product thus obtained was rinsed with absolute ethanol for several times to remove all the impurities. It was then dried in vacuum at 60 °C for 4 hr and finally kept in a vacuum desiccator for further characterization.

2.2.2 Synthesis of Bismuth Nanospheres

In another process (sample S₂) the same procedure was followed as above. But the solvent used in this case was a mixture of ethylene glycol and absolute ethanol in the ratio 1:1.

2.3 Characterization

2.3.1 Structural Characterization

The prepared nanostructures of bismuth were structurally characterized by powder X-ray diffraction (XRD), Transmission electron microscopy (TEM). XRD measurement of bismuth nano particle powder samples were performed on a Ultima – III Rigaku (Japan) using Cu K α radiations operating system (Scan range 20-80 °C with a rate 5 °/min).

2.3.2 Electrical Characterization

The measurements of electrical conductivity (σ) as well as thermoelectric power (S) were performed in the temperature range 300 – 400 K. For the electrical characterization the samples were pressed into rectangular pellets by cold pressing under a pressure of 9 tons at room temperature. The resistances of the nanostructures were calculated from the I–V characteristics. Thus the conductivity of the nanorods and the nanospheres were calculated using the following formula

$$\text{Conductivity } \sigma = l / Rbt \quad (2.1)$$

where l is the length, R is the resistance, b is the breadth, and t is the thickness of the samples.

For the measurement of the thermoelectric power, an auxiliary heater at one end of the sample holder creates a temperature difference while the corresponding potential drop was measured by a Hewlett Packard data acquisition system (Model No. 34970A).

3. RESULTS AND DISCUSSIONS

3.1 Structural Characterization

3.1.1 XRD studies

The XRD spectrums of the prepared nanostructured bismuth are shown in fig 1. The formation of Bi is confirmed by the major peaks labelled in the XRD pattern that corresponds to the rhombohedral phase of Bi according to the reported values of JCPDS (No. 05-0519) data sheet.

The pattern reveals that the samples synthesized under the above stated conditions yielded pure bismuth with no impurity. Interestingly a higher (012) peak is observed in fig. 1 for Bi nanorod structure. Due to the presence of EG, the OH- functional group get adsorbed on other crystalline surfaces besides {012} planes resulting in anisotropic growth along certain direction thus producing nanorods [12]. The sizes of the nanostructures calculated by Debye Scherer formula are ~68 nm (for nanorods) and ~57 nm (for nanospheres).

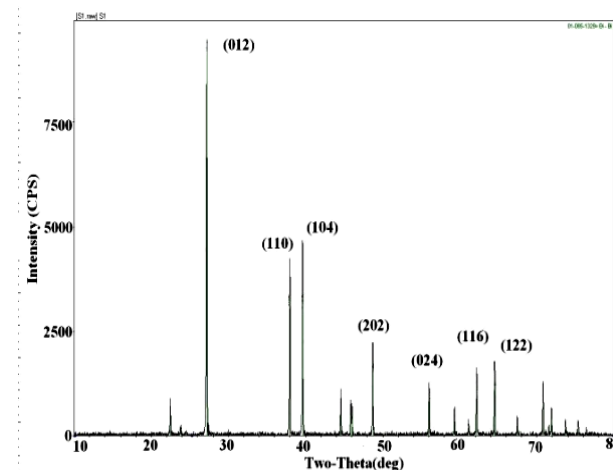


Fig. 1 – XRD of Bi nanostructures

3.1.2 TEM studies

The TEM images of the prepared bismuth nanocrystals are shown in Fig. 2 (nanorods and inset nanospheres).

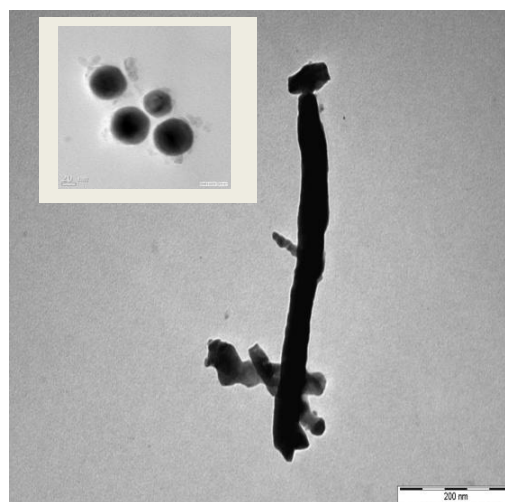
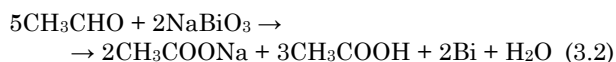


Fig. 2- TEM images of Bi nanorod (inset nanosphere)

Nanorod like structure of bismuth of diameter and length ranging from 30-60 nm and 450-500 nm respectively is observed for sample S₁ (EG as solvent). But for sample S₂ when AE was used along with EG as solvent in the ratio 1 : 1, well defined nanosphere like structure with smooth surface and of diameter ranging from 40-60 nm is observed

3.1.3 Synthesis of Bi Nanostructure (Nanorods and Nanospheres)

We now attempt to discuss the growth mechanism of the nanorods and nanospheres like structures of bismuth. As reported in literature, EG served both as solvent and reducing agent [18] in the synthesis process. The oxidation capability of sodium bismuthate (the electric potential for NaBiO₃/Bi is above 0.9 V) being strong, it is used in the process where reduction of sodium bismuthate with EG was carried out at the temperature of reaction (200°C). The chemical reaction involved in this process can be expressed as:



Bismuth nanorods and nanospheres are supposed to be formed on the basis of Ostwald ripening process [19]. Bi nanoparticles are formed in the solution according to the equations (3.1) and (3.2). These nanoparticles then grow into large crystals which serve as seed to grow into nanorod or nanosphere morphology. The EG molecules get adsorb on the surface of bismuth crystals forming O-Bi bonding thus decreasing growth rate in that direction. This leads to anisotropic growth of nanostructure [20,21] thereby generating nanorods as has been obtained in the present case. The addition of AE with EG in the ratio of 1:1 results in the formation of nanospheres like structures due to uniform and isotropic growth in all directions as the amount of EG in the solvent is decreased.

3.2 Electrical Characterization

3.2.1 Electrical conductivity (σ)

The temperature variation of electrical conductivity (σ) of the two prepared sample were measured as shown in the Fig. 3.

σ for both the sample S₁ and S₂ decreased with increase in temperature. But the decrease was nonlinear in both the cases. There was no remarkable difference in the value of σ for the two samples (17.8 Scm⁻¹ for S₁ and 18.25 Scm⁻¹ for S₂) at room temperature. In comparison to bulk bismuth, the conductivity values of both the prepared samples are relatively low. Interestingly, the room temperature conductivity values in the present case are found to be more than that reported for microstructure and nanostructure of bismuth [22]. The nonlinear decrease in σ with temperature is indicative of metallic type of conduction with hopping mechanism operative between the grain boundaries of the crystallites.

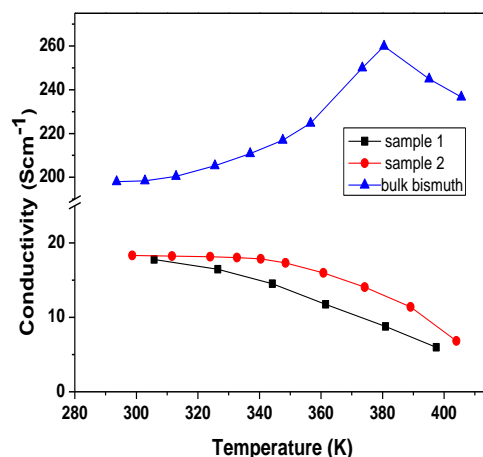


Fig. 3- Temperature variation of σ of Bi nanostructures

3.2.2 Thermoelectric Power (S)

Temperature variations of thermoelectric power (S) for nanorods and nanospheres of Bi are as shown in Fig. 4.

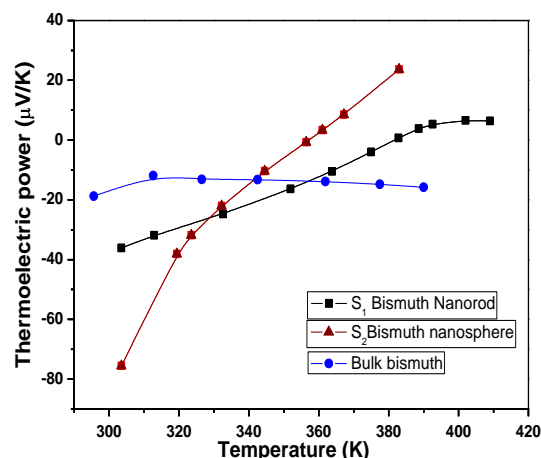


Fig. 4- Temperature variation of S of Bi nanostructures

For both the samples the value of S was negative at room temperature suggesting the presence of electrons as majority carriers. Room temperature value of thermoelectric power for sample 2 ($-76.2 \mu\text{V/K}$) was higher than that of sample 1 ($-36.5 \mu\text{V/K}$) and both the values are higher than bulk bismuth in the present case. Further for both the samples there was decrease in the negative value of S with temperature which ultimately became positive above ~ 370 K and increased with temperature. This indicated that at higher temperature (above 382.03 K for rod like structure and 357.65 K for sphere like structure) majority carriers were holes. Within the temperature range 300 – 400 K the variation of S for sample 2 was more than that of sample 1. For bulk bismuth the value of S was negative throughout and showed a weak dependence on temperature.

3.2.3 Power Factor (P)

The variation of Power factor ($P = S^2\sigma$) of the both the sample S_1 and S_2 with temperature is as shown in fig 5. In both the cases power factor decreased with temperature. The value of power factor of sample S_2 ($9.8\mu\text{W}/\text{mK}^2$) is higher than sample S_1 ($2.7\mu\text{W}/\text{mK}^2$) at temperature 300 K whereas for bulk material the value is $8.8\mu\text{W}/\text{mK}^2$ at the same temperature. So comparing the power factor, it is found that among three sample S_2 shows the maximum P at room temperature.

4. CONCLUSIONS

Solvothermal method was employed for synthesis of nanostructured bismuth. The prepared samples were characterised by XRD and TEM analysis. Two different morphologies were obtained by changing the solvent of the reaction. Nanorods (30-60 nm diameter and 450-500 nm length) and nanospheres (40-60 nm diameter)

like structures were obtained. Investigation on electrical transport properties of the two samples have been carried out in the temperature range 300-400K. Electrical conductivity σ is found to be almost same for the two samples at room temperature. The variation of σ with temperature is found to be nonlinear suggesting a metallic type of conduction with hopping mechanism operative between the nanocrystals. Variation of S with temperature point towards a change of majority carriers from electrons at room temperature to holes at high temperature. A comparison of power factor of the samples reveals that it is maximum for nanosphere structure.

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