Printed ISSN 1330–0008
Online ISSN 1333–9125
CD ISSN 1333–8390
CODEN FIZAE4

MORPHOLOGY-CONTROLLED POWER FACTOR OF NANOSTRUCTURED BISMUTH TELLURIDE

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Received 31 October 2009; Revised manuscript received 27 October 2010
Accepted 24 November 2010 Online 6 April 2011

Bismuth telluride is a thermoelectric material with high figure of merit, used for cooling applications at room temperature. To investigate the effect of morphology and grain size on transport parameters, nanostructured bismuth telluride has been synthesized under different reaction conditions and characterized by X-ray diffraction, transmission electron microscopy and scanning electron microscopy. From the measurement of electrical conductivity and thermoelectric power, power factor for different samples has been obtained. The results show that the transport parameters are critically influenced by the morphology and dimension of the samples that in turn depend on the condition of synthesis. The experimentally observed variation of electrical conductivity with the change of dimensionality of the samples from 2D to 0D, which is in line with the theoretical prediction made by other workers, is discussed. There is a variation of the power factor of the samples prepared under different conditions of synthesis.

PACS numbers: 72.20.Dp, 72.20.Pa UDC 537.323

Keywords: nanostructures, semiconductors, X-ray dispersive analysis, thermoelectric effects

1. Introduction

Thermoelectric materials have recently attracted much attention for their ability of mutual conversion between temperature gradient and electricity [1, 2]. The

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advantages of using thermoelectric material for device applications are manyfold because of their reliability, miniaturized modules and environment-friendly nature [3]. The potential candidate for application in devices is usually selected by its dimensionless figure of merit $Z = S^2\sigma/k = P/k$, where S is the thermoelectric power, σ the electrical conductivity, k the thermal conductivity and P is the power factor. Among the various V-VI compounds, bismuth telluride (Bi_2Te_3) is the best known thermoelectric material at room temperature [4−6]. Work has been done on thermoelectric properties of Bi_2Te_3 based materials prepared by mechanical alloying and hot pressing [7], powder extrusion sintering [8, 9] etc. Recently, much attention has been given to bulk alloys [10], thin film super lattices [1, 11] nanowires [12, 13] of chalcogenides material for improving the Z value. This can be achieved by a decrease in thermal conductivity because of the selective diffraction of phonons by the high density of grain boundary. There are reports on synthesis of nanostructured bismuth telluride by chemical alloying [14], solvothermal synthesis [15, 16], hydrothermal method [17], wet chemistry technique [18] and laser ablation in solution [19]. Synthesis by different techniques yield nanoscale structure of various morphology and size which in turn influence the transport properties of the material. Even employing a particular technique for material synthesis, different morphology and grain size can be obtained if the reaction conditions like temperature or reagent are altered. Therefore, it is interesting to undertake the investigation on synthesis and characterization of structural and electrical transport properties of these materials under different conditions. Change in values of the transport parameter due to particle size and morphology may improve power factor of the material. To the best of our knowledge the investigation on transport properties of the nanostructured material with different morphology and sizes are scanty.

A very simple method for the synthesis of nanostructured Bi_2Te_3 from TeO_2 and $Bi(NO_3)_3$ by solvothermal method employed here is discussed elsewhere [20]. It is observed that depending on the reaction condition there is a variation in the morphology and size of grains of the prepared sample. In the present study we have attempted to map the variation in transport parameters with the system dimension/morphology of the prepared samples.

2. Experimental

2.1. Synthesis

Solvothermal preparation: For the synthesis of bismuth telluride, a reaction mixture was first prepared by mixing the aqueous solution of $Bi(NO_3)_3\,5H_2O$, TeO2 and $N_2H_4H_2O$. The reaction mixture was treated for 24 hours in an autoclave kept in an oven at different temperatures. In a typical synthesis, we took 1 gm of $Bi(NO_3)_3\,5H_2O$ in 20 ml water and added 0.4 gm of TeO_2 to the hydrolyzed bismuth solution. This solution was then subjected to soft sonication for thorough dispersion. The dispersed solution was transferred to a Teflon-lined 50 ml capacity autoclave and 5 ml $N_2H_4H_2O$ was added to that solution. After keeping the autoclave in an air oven at respective temperatures (130 °C, 170 °C and 200 °C) for 24 hours, we found a black precipitate which was filtered, washed with water several times and finally with ethanol and then dried in vacuum (10^{-5} Pa) at 60 °C for 24 hours. In another approach, Bi_2Te_3 was prepared in presence of TEA as a complexing agent. Addition of TEA to the hydrolyzed suspension of bismuth nitrate generated clear solution of TEA-Bi complex, which was then solvothermally treated at 170 °C in the same manner as described above. All samples (T_1-T_4) prepared in different reaction conditions are tabulated in Table 1.

TABLE 1. Preparative conditions and morphologies of the produced samples [20].

Sample	Reaction condition	Size XRD	Morphology and size
T_1	130 °C, 24h without TEA	12 nm	Small particle of dimensions 25 – 50 nm
T_2	170 °C, 24h without TEA	10 – 20 nm	1D network, diameter 30 – 40nm, length 200 – 500 nm
T_3	200 °C, 24h without TEA	15 – 20 nm	Chain like agglomeration of particles, diameters 50 – 70 nm
T_4	170 °C, 24h with TEA	9 nm	Thin wafer, irregularly shaped plate 100 nm × 100 nm, thickness < 10 nm

2.2. Characterization

The prepared samples were characterized by XRD, EDXA and TEM. The powder XRD patterns of the samples were recorded on a Rich, Seifert 3000P. The instrument was operated at 40 kV voltage and 35 mA current ($\lambda = 1.5406$ Å) and was calibrated with a standard silicon sample. The samples were scanned from $2\theta = 20°$ to 70° in the step scan mode (step size .01, preset time 1s). The morphology of the different samples was studied using a transmission electron microscope (TEM JEOL, 2010EX) operated at the acceleration voltage 200 kV. A drop of dilute solution of the product in ethanol dispersed by sonication on the carbon coated copper grid was dried finally in vacuum and was directly used for the TEM-experiments. For the field-emission scanning electron microscopy (FESEM), the samples were mounted on a double-sided carbon tape and were platinum coated by a fine coater, then the samples were observed using JEOL-JSM 6700F operated at 5 kV. The EDX profile was recorded on an OXFORD Inca analyzer attached to the TEM.

2.3. Transport properties

For measurements of the electrical conductivity and thermoelectric power, the synthesized Bi_2Te_3 powders were dried in a vacuum oven at 65 °C for 1 day and then disc shaped pellets were made by a hydraulic press by applying 5 ton pressure for 5 minutes. The rectangular samples of size $\sim 1\,\mathrm{cm} \times 0.4\,\mathrm{cm}$ of nanocrystalline bismuth telluride were cut in from disc-shaped pellets. Electrical conductivity was measured by the four-probe method. For the measurement of thermoelectric power, a small temperature difference was established at the two ends of the sample along its length by a controlled heating system. The temperatures and the voltage across the sample were measured by a HP data acquisition system (model number-34970A).

3. Results and discussion

To investigate the effect of temperature and complexing agents on the grain size and morphology of the nanostructured Bi_2Te_3, the samples were synthesized in different temperature regimes in the presence and absence of complexing agents TEA. The detailed description of the reaction conditions and the as prepared products are tabulated in Table 1.

A. XRD: It has been found that the XRD spectra of the prepared samples are identical with the hexagonal Bi_2Te_3 as reported by the JCPDF data sheet. Figure 1 shows the XRD spectra of different samples from which the size of the particles was calculated using Debye-Scherrer formula. The grain sizes are given in Table 1.

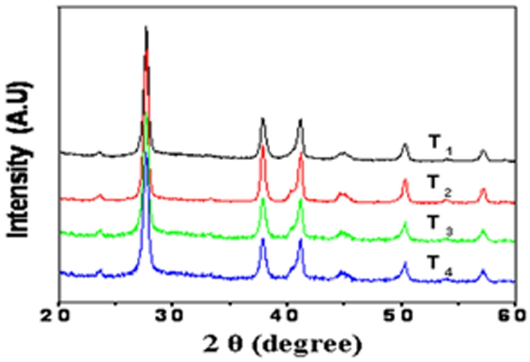

Fig. 1. XRD spectra of the samples T_1, T_2, T_3 and T_4.

B. EDXA: The purity and stoichometry of the product have been investigated by EDXA studies attached with TEM instrument. For all samples, there has been no impurity peak found in the EDXA spectra and the atomic ratio of Bi and Te, as calculated by the software from the spectra, was nearly equal to 2:3. One representative spectrum for the sample T_4 is given in Fig. 2.

C. TEM: The morphology of the products obtained under different reaction condition was studied by an electron microscope. Figure 3 presents the TEM micrographs of samples the T_1, T_2, T_3 and T_4. From the TEM studies, it could be concluded that the morphology of the products depends on the reaction temperature. For the reaction temperature 130 °C, the obtained product T_1 consisted of very tiny particles (Fig. 3a) whose average size lies in the range of 25 nm to 50 nm. Sample T_2 (reaction temperature 170 °C) was agglomerated and consisted of agglomerated 1D particles. The product obtained at 200 °C (sample T_3) showed 1D chain-like agglomerated morphology with a few plate-like structures (Fig. 3c).

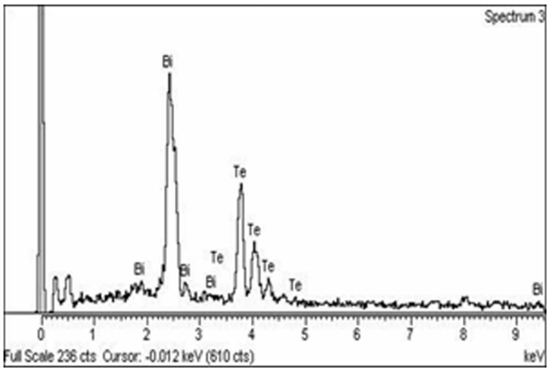

Fig. 2. EDXA spectrum of the sample T_2.

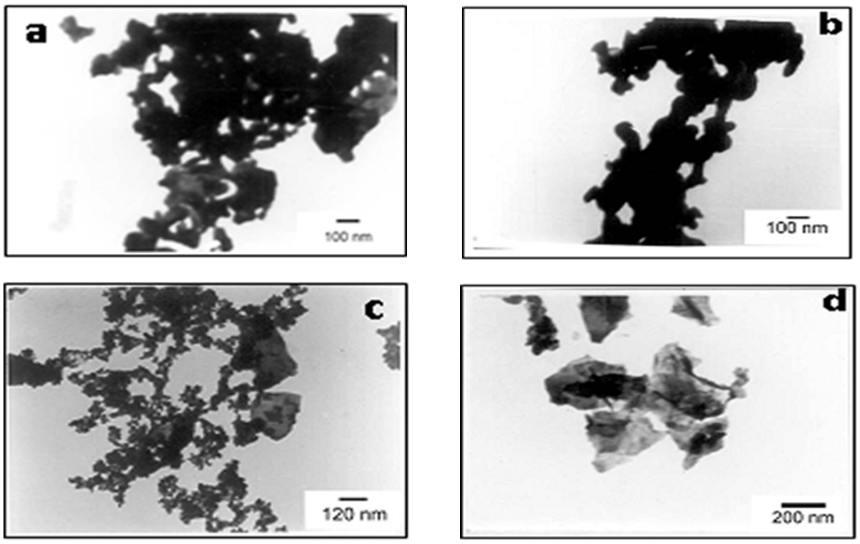

Fig. 3. TEM micrographs of the samples (a) T_1, *(b)* T_2, *(c)* T_3 *and (d)* T_4.

In the absence of any complexing agents for the reaction, it was found that the product (sample T_4) consisted of wafer-like structure, i.e thin plate-like structure. The thickness of these plates was of the order of a few nanometers and the width and length of these plates were in the range of 100 nm.

D. Electrical conductivity and thermoelectric power: From the measurement of thermoelectric power, it has been found that the sign of S is negative, so charge carriers are electrons. From the measured values of σ and S, the power factor P has been calculated. The values of electrical conductivity, thermoelectric power and power factor of different samples are tabulated in Table 2. Here it is seen that the value of electrical conductivity decreases as the morphology/dimension of the sample changes from small dimensional particles (0D) to irregular shaped plates (2D). Expression for transport coefficient is modified for low-dimensional system as compared to 3D system, so that there is a possibility of improving the electronic properties, i.e. to increase the power factor.

TABLE 2. Transport parameters of samples at room temperature. σ is the electrical conductivity, S thermoelectric power and P the power factor.

Sample	σ (ohm^{-1}cm^{-1})	S (μV/K)	P (μW/(mK)^2)
T_1	15.5	−55	4.69
T_2	6	−110	7.26
T_3	8.25	−78	5.02
T_4	3.75	−160	9.6

For the two-dimensional quantum well of width a in the z direction, the expression for σ for a constant relaxation time is given by [21]

$$\sigma_{2\mathrm{D}} = \frac{1}{2\pi a}\left(\frac{2kT}{\hbar^2}\right)\left(m_x m_y\right)^{1/2} F_0 e\mu_x \,. \tag{1}$$

For a one-dimensional system or quantum wires with square cross-section of side a, the expression for σ becomes [22]

$$\sigma_{1\mathrm{D}} = \frac{1}{\pi a^2}\left(\frac{2kT}{\hbar^2}\right)^{1/2}\left(m_x\right)^{1/2} F_{-1/2} e\mu_x \,, \tag{2}$$

where F_0 and $F_{-1/2}$ are Fermi-Dirac integrals. Since $\sigma_{1\mathrm{D}}$ depends on a^2 and $\sigma_{2\mathrm{D}}$ depends on a, it is obvious that $\sigma_{1\mathrm{D}}$ should rise much more rapidly as a decreases.

In the present investigation, the measured σ value increases as the nanoscale pattern changes from 2D for the sample T_4 to 0D for sample T_1 through fractal D for T_3 and 1D for T_2. This observation is in conformity with the theoretical calculations made by Hicks and Dresselhaus for low-dimensional system [21, 22]. However, for the samples prepared with and without TEA, the dependence of S on the dimension of the material shows that it is maximum for T_4 (2D) having size 9 nm of thickness, as shown in Table 2. Among all materials prepared under different conditions, sample T_4 has the maximum power factor as shown in Fig. 4. The power factor for thermoelectric materials depends on the carrier mobility and density of states. The carrier mobility is assumed to be the same for nanostructures and bulk materials. Therefore, it seems that there is an increase in density of states in the low-dimensional configuration which may be attributed to an enhancement of the power factor [23].

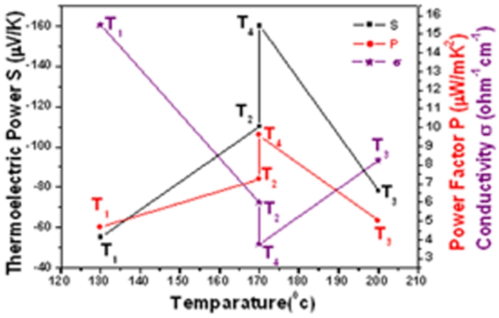

Fig. 4. Thermoelectric power, conductivity, power factor of the samples prepared under different temperatures and conditions.

4. Conclusion

Synthesis of nanostructure Bi_2Te_3 with varying morphologies prepared by employing different reaction conditions is reported. Electrical characterizations of the prepared materials exhibit that transport parameters are influenced by the reaction conditions. The sign of the thermoelectric power is negative suggesting that the majority carriers taking part in the transport process are electrons. As has been prompted by theoretical work, there is an increase in the value of σ as the dimensionality of the prepared samples is reduced, from 2D to 0D. Interestingly, even by using the same temperature of synthesis, the sample T_4 (2D) of the size 9 nm thickness, prepared by adding TEA during the process of synthesis, shows the highest value of thermoelectric power. As a result, this sample has the maximum power factor.

Acknowledgements

D. Banerjee. and K. Chatterjee acknowledge Department of Science and Technology, India for the financial support.

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FAKTOR SNAGE NANOSTRUKTURIRANOG BIZMUT TELURIDA ODREĐEN OBLICIMA

Bizmut telurid je termoelektrična tvar s visokom učinkovitošću koja se rabi za hlađenje na sobnim temperaturama. Radi istraživanja učinka oblika i veličine zrna na transportne parametre, sintetizirali smo nanostrukturirani bizmut telurid u različitim uvjetima i ispitivali rentgenskom difrakcijom, te propusnom i pretražnom elektronskom mikroskopijom. Mjerenjem električne vodljivosti i termoelektrične snage niza uzoraka odredili smo faktore snage. Ishodi analize pokazuju da transportni parametri jako ovise o obliku i veličini uzoraka, koji pak ovise o uvjetima njihove sinteze. Raspravljamo o opaženim promjenama električne vodljivosti ovisnim o dimenzionalnosti uzoraka od 2D do 0D i nalazimo sklad s teorijskim predviđanjima drugih autora. Nalazimo promjene faktora snage uzoraka pripremljenih uz različite uvjete sinteze.