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Study and Characterization of Thermoelectric Material (TE) Bismuth Antimony Telluride

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Abstract

Thermoelectric materials are used to convert the heat to electricity with no moving parts, in the present work an attempt has been made to prepare it for power generation function. Bismuth antimony telluride nanopowders were prepared by using mechanochemical method. Three different materials; Bismuth Telluride, $(Bi_{0.75}Sb_{0.25})_2Te_3$ and $(Bi_{0.5}Sb_{0.5})_2Te_3$ were synthesized. XRD and TEM analysis was carried out to confirm the results. The particle size of the material was determined by using FESEM analysis. The two alloys of Bismuth Telluride such prepared were converted in the pellet form using vacuum hydraulic pressure and their Seebeck coefficients were determined to test the material suitability for its use as a thermoelectric device. Their power factor measurement and Hall effect measurements were carried out at room temperature.

Keywords: Bismuth telluride; Mechanochemical method; Nanoparticals; Seebeck coefficients

Introduction

Thermoelectric (TE) is a branch of material science deals with study of the relationship between heat and electricity. Over the past 15 years, there has been a higher interest in the field of TE materials research. Among the other TE materials, Bismuth telluride and its alloys are used in many TE devices, power generation and due to their thermoelectric performance they are used in energy recycling system [1,2]. There are various applications of TE materials, most of the researchers have concentrated to improve the TE properties by managing their microstructures to get combination between electrical and thermal properties [3-6]. TE materials have good efficiency for generate the electricity, and it will play a powerful role as energy materials, for example materials for energy storage, conversion, recovery, and transfer [7]. However though better, TE properties have been investigated in the ternary system containing of Bi, Sb, and Te elements, many chemical path have only attained on synthesis of Bismuth Telluride nanoparticles [8]. In this study we synthesized Bismuth Telluride and its alloys by mechanochemical method. The mechanochemical synthetic technique required low cost mass production with controllable morphology, uniform particle size. Also this method has high purity, high yield and high crystallinity over the other synthetic technique. The thermo emf is important parameter for the thermoelectric devices. Bismuth telluride is used for construction of thermoelectric devices. The function of such devices is steadily improved by the several numbers of factors such as Figure of merit (ZT) [9]. Also investigated that thermoelectric generation and observe Seebeck coefficient change with the temperature. We synthesized Bi-Sb-Te (75-25%) and Bi-Sb-Te (50-50%) proportion and the synthesized nanopowders were characterized. The result which shows that, the nanopowder obtained from the materials which are used in high performance TE devices. Recently many novel process procedures have been developed to fabricate Bi_2Te_3 and its alloys with high value of ZT such as, ball milling of Bi-Sb-Te alloys and subsequent hot pressing technique is used for producing nanoparticles with average particle size 200 nm [10,11]. Another novel technique to obtained P-type Bismuth Telluride alloys is spinning technique followed by spark plasma sintering process which we get unique microstructures [12,13].

Thermoelectric materials are acts as transducers which converts energy in one form into another. Use of TE solid materials Applications in heat pump and refrigeration is well known [14] and it is now expanded such as cooled seats in luxury automobiles [15]. There has been renewed interest in TE materials for waste heat recovery, for boosting the efficiency microelectronics, use in the medical devices, sensors and wearable electronics [16].

Literature Review

Now days Nanotechnology is challenging field for research. The main challenging research is that surface to volume ratio of nanomaterials which improve different physical properties [17]. The nanoparticals are combinations of many organic and inorganic materials. The homogenous miscibility of such combinations has become another challenge in nanotechnology. Bi_2Te_3 is physically behaves like a semiconductor and when it is combined with the antimony or selenium then it is the most effective thermoelectric type material. For synthesis of thermoelectric materials various methods are used such as Hot Pressing, Hydrothermal Method, and Rapid Solidification Process. In the hot pressing method the powder is pressed into pellet by the applying the external heat source to the powder. The heat source has typically the lower temperature. The sample is subjected to the heat for longer period of time. There have been studies into the effect of each of type of powder compaction, including the effect of thermoelectric properties [18].

Rapid solidification is described as the removal of heat energy which includes superheat as well as latent heat during the transformation from a liquid state at high temperatures to solid state at ambient temperature. For a process the cooling rate should not be greater than 10^4 K/s while cooling rates of 10^3 K/s sometimes produce

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rapidly solidified microstructures [19]. The time of contact at high temperatures is finite to milli-seconds followed by rapid quenching to room temperature.

Hydrothermal techniques have the advantages of high yield, low synthesizing temperature, and the ability to control the size and shape of the material with the assistance of suitable surfactants capping agents compared to other synthesis method.

Experimental Procedure

For Bi-Sb-Te sources, Bismuth Nitrate, Antimony Trichloride, and Sodium Telluride were used as precursors which are converted into the Bi-Sb-Te alloys. We mixed all chemicals for $[Bi_{(1-x)}Sb_x]_2Te_3$ (75-25%), using 1:0.16:0.913 g of Bismuth Nitrate, Antimony Trichloride, and Sodium Telluride respectively. Similarly for $[Bi_{(1-x)}Sb_x]_2Te_3$ (50-50%) in the ratio of 1:0.47: 1.37 g. By using ball milling process, we mixed all Bi-Sb-Te chemicals into ball mill. Then added 2 ml of hydrazine hydrate in it. The revolutions of ball mill were 500 rpm. Kept that reaction for 24 h; the formed bismuth telluride alloy nanopowders were collected from the solution. After filtering, the nanopowders were dried at 70°C for 2 h. The nanopowders of Bi-Sb-Te were characterized by FE-SEM, TEM, X-Ray Diffraction (XRD) methods, then calculated Seebeck coefficient with different temperature. X-ray diffraction (XRD) technique was used to identify the phase of the nanocrystals and to get the information on the crystal structure. The XRD measurement was carried out using a Siemens D5000 diffractometer equipped with a Cu anode operated at 40 kV and 40 mA. The XRD patterns were collected with a step size of 0.01° and a scan rate of 1 sec/step. The X-ray peak intensity measure by an angle θ. The structural analysis of the nanostructures was identified by a transmission electron microscope. In TEM the electrons generated thermionically and accelerated with an accelerating voltage transmit through the sample and the transmitted beam is used to form the image. The images are of various types such as low and high magnification TEM, electron dispersive X-ray spectroscopy. FESEM is used for surface morphology of nanocrystals. To prepare a sample for SEM measurement, the powder sample was ultrasonicated in ethanol for 30 minutes. A very small drop of sample solution was dropped onto silicon substrate and the ethanol was allowed to evaporate.

Materials and Methods

To obtain an alloy powders, appropriate amount of elements powders of bismuth nitrate, antimony trichloride and sodium telluride were weighed according to composition of $(Bi_{0.75}Sb_{0.25})_2Te_3$ and $(Bi_{0.5}Sb_{0.5})_2Te_3$ loaded into the ball mill jar with ball then subjected to mechanical alloying for 24 h in 2 ml of hydrazine hydrate. The rotation speed of ball mill is 500 rpm and zirconium ball are used for this process. The formed bismuth antimony telluride nanopowders were dried after filtering and then consolidated into the pellet sample. The phases of ball milled powders were identified with X-ray diffraction (XRD). Microstructures of ball milled powders were analyzed by means of filed-emission scanning electron microscopy (FESEM). The structure size and shape of samples were identified by Transmission electron microscopy (TEM).The concentration; conductivity and mobility at room temperature were measured by the van der Pauw method using Hall- effect measurement system. The Seebeck coefficient was measured by dynamic method. The temperature difference (ΔT) between the both ends of sample pellets and output voltage (ΔV) were measured continually during the testing of every sample process. To take a ratio of output voltage (ΔV) and temperature difference (ΔT) and calculating the see beck coefficient.

Result and Discussion

The simplified mechanochemical process is used in this work for the reduction of Bi, Sb, and Te. It is expected that the reaction for making alloys of Bi-Sb-Te, the three reduced atoms took place together within a fast time to obtain a stable ternary mixture because here only metal salts were used instead of metal. Figure 1a XRD pattern shows that the pattern of nanopowder clarify that the formed phases mainly correspond to $(Bi_{0.75}Sb_{0.25})_2Te_3$ and $(Bi_{0.5}Sb_{0.5})_2Te_3$. Thus, it is confirmed that the ternary mixture of Bi-Sb-Te solid solution in nanopowder form was successfully synthesized by the mechanochemical process and good match with the $(Bi_{0.75}Sb_{0.25})_2Te_3$ and $(Bi_{0.5}Sb_{0.5})_2Te_3$ Standard patterns was clearly obtained. The diffraction peak shows that particles are small having particle size in between 45-50 nm. Figure 1b shows the synthesized nanopowder of $(Bi_{0.75}Sb_{0.25})_2Te_3$ material. All powders shows same morphology but it has a slight differences. The nanopowder reveals an average powder size is about 50nm which is agglomerated. The alloy shows rhombohedral lattice structure. The particles are small are also confirmed by these images. Some particles, agglomeration and crystal structure shown in Figure 1b. Similarly for the other composition $(Bi_{0.5}Sb_{0.5})_2Te_3$ nanopowder Lattice structure. The average particles size 200 nm. Figure 1c shows agglomerated particles and lattice structures and high magnification image. Form conformation of XRD results, EDS is used for elemental analysis of sample. In the EDS results Figure 1d of the nanopowder clearly states that the mechanochemical process produces alloying powders composed of three different elements that is Bi-Sb-Te.

Figure 2a TEM image shows that the nanoparticles have particle size ranging up to 50 nm. The high resolution TEM image confirms the outstandisng crystallinity of nanoparticles. Figure 2b also shows that some nanoparticles are even smaller than the 5 nm. The electrical properties of Bi-Sb-Te nanopowders such as concentration, mobility, and resistivity were obtained by using Hall Effect measurement system. Before measurement of samples pressed into small pellet with the

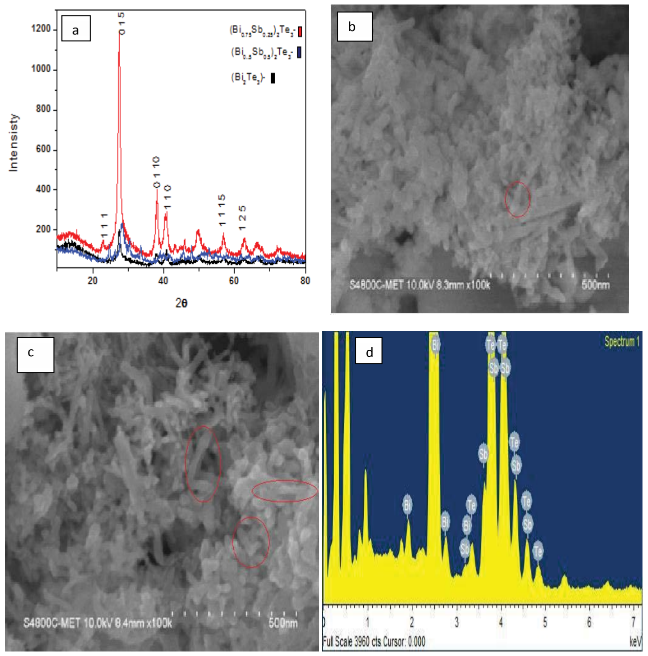

Figure 1: (a) XRD pattern Bi-Sb-Te alloys. (b) FE-SEM of $(Bi_{0.75}Sb_{0.25})_2Te_3$. (c) FE-SEM of $(Bi_{0.5}Sb_{0.5})_2Te_3$. (d) EDS result.

Sample	Temperature	Current	Concentration	Mobility	Resistivity
1.$(Bi_{.75}Sb_{0.25})_2Te_3$	294 K	4 × 10^{-4} A	-2.59 × 10^{15} g/mL	-4.35 × 10^{3} $m^2/V.s$	18.1 Ωm
	294 K	7 × 10^{-6} A	2.38 × 10^{15} g/mL	-6.89 × 10^{-2} $m^2/V.s$	17.4 Ωm
2. $(Bi_{0.5}Sb_{0.5})_2Te_3$	294 K	4 × 10^{-4} A	-4.39 × 10^{16} g/mL	-3.05 × 10^{1} $m^2/V.s$	4.07 Ωm
	294 K	7 × 10^{6} A	3.77 × 10^{15} g/mL	-8.99 × 10^{2} $m^2/V.s$	3.41 Ωm

Table 1: Hall effect measurements at Room temperature.

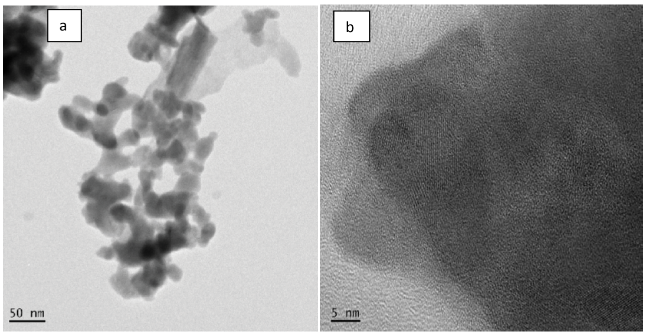

Figure 2: TEM of $(Bi_{.75}Sb_{0.25})_2Te_3$ a) low magnification TEM b) high magnification TEM.

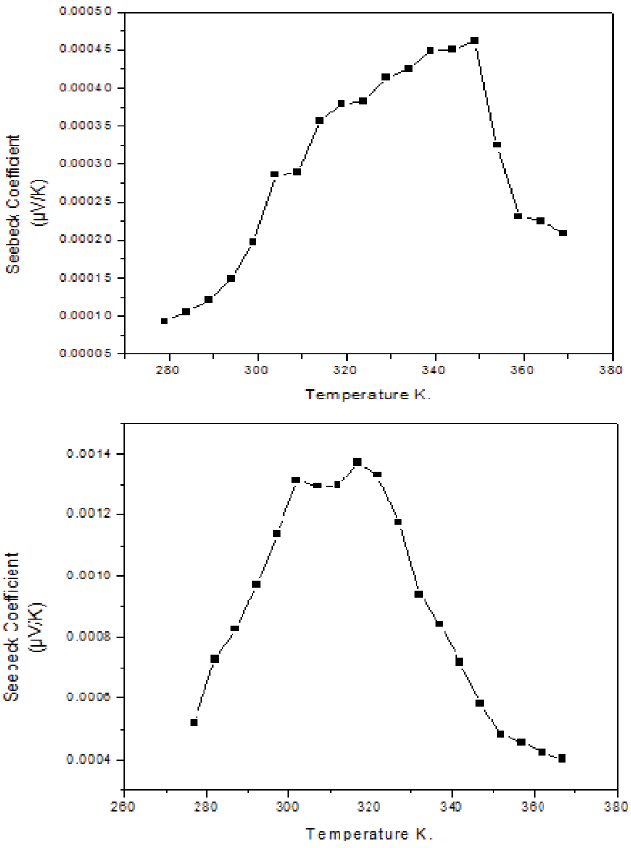

Figure 3: Seebeck coefficients.

5 mm in diameter and 0.5 mm thickness using a vacuum hydraulic presser under pressure 400 kpa for 5 min. In this article we study the current, mobility, and resistivity, concentration of $(Bi_{0.75}Sb_{0.25})_2Te_3$ and $(Bi_{0.5}Sb_{0.5})_2Te_3$ (Table 1).

Seebeck coefficient measurements, the value shows that a direct relationship with the temperature as shown in Figure 3. Figure 3 shows temperature increase from 280 K to 380 K. The value of see-beck coefficients are firstly increases from 279 K to 349 K and then reduces rapidly further increasing to 380 K. Figure 3 shows temperature dependent Seebeck coefficient of sample $(Bi_{0.75}Sb_{0.25})_2Te_3$ which give all positive Seebeck value which indicates that p-type semiconductor. The highest Seebeck coefficient detected is about 4.62 × 10^{-4} (μV/K) at 349 K. Similarly in Figure 3 temperature dependent Seebeck coefficient of sample $(Bi_{0.5}Sb_{0.5})_2Te_3$. The highest Seebeck value is 1.36 × 10^{-3} (μV/K) at 318 K.

Sample	Current (A)	Power Factor $\mu W/mK^2$
1. $(Bi_{0.75}Sb_{0.25})_2Te_3$	1 × 10^{-6} A	2.8824 × 10^{-8} $\mu W/mK^2$
	4 × 10^{-6} A	1.8075 × 10^{-9} $\mu W/mK^2$
	7 × 10^{-6} A	1.9690 × 10^{-9} $\mu W/mK^2$
2. $(Bi_{0.5}Sb_{0.5})_2Te_3$	1 × 10^{-6} A	5.9512 × 10^{-6} $\mu W/mK^2$
	4 × 10^{-6} A	1.3585 × 10^{-7} $\mu W/mK^2$
	7 × 10^{-6} A	1.5727 × 10^{-6} $\mu W/mK^2$

Table 2: Power factor of the samples at different current.

Table 2 shows that temperature dependence of the power factor ($S^2\sigma$) of the $(Bi_{0.75}Sb_{0.25})_2Te_3$ and $(Bi_{.50}Sb_{0.50})_2Te_3$. The obtained power factor of sample $(Bi_{0.75}Sb_{0.25})_2Te_3$ is 2.8824 × 10^{-8} $\mu W/mK^2$ at 295 K and on the other hand the maximum power factor of $(Bi_{.50}Sb_{0.50})_2Te_3$ is 5.9512 × 10^{-6} $\mu W/mK^2$ at 295 K, which is higher than the $(Bi_{0.75}Sb_{0.25})_2Te_3$ nanopowder which is synthesized by the mechanochemical method.

Conclusion

In summary, the simplified mechanochemical process is used to synthesize Bi-Sb-Te alloys nanopowder with using three different metal salts. The developed process is produced Bi-Sb-Te nanopowder consisting of $(Bi_{0.75}Sb_{0.25})_2Te_3$ and $(Bi_{.50}Sb_{0.50})_2Te_{3.}$ The study revealed that the morphological study and the effect of temperature on nanomaterials were investigated in detail. The synthesized nanopowder showed a clear crystalline microstructure with few nm-sizes. The $(Bi_{.50}Sb_{0.50})_2Te_3$ exhibits the highest Seebeck value 1.36 × 10^{-3} (μV/K) at 318 K and for $(Bi_{0.75}Sb_{0.25})_2Te_3$ 4.62 × 10^{-4} (μV/K) at 349 K. The results show that the mechanochemical process results in Bi-Sb-Te nanopowder that can be used as raw materials for high performance thermoelectric devices.

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