

Development of Bismuth Telluride Nanostructure Pellet for Thermoelectric Applications

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ABSTRACT

The bismuth telluride (Bi_2Te_3) nanostructure powders and pellet was successfully developed for thermoelectric applications by using a simple chemical process. Several characterization tools such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), atomic force microscopy (AFM) and Fourier transform infrared (FT-IR) spectrometry were carried out. The XRD, SEM, EDX, and FTIR analyses showed that the chemical structure of pellet is Bi_2Te_3 . The average crystalline size of the Bi_2Te_3 pellet is found to be 3.93 nm, as determined by the SEM. The AFM studies confirmed that the pellet is of nanostructure form and average surface roughness value is 68.06 nm. This is within the roughness range which can lead to an enhancement in thermoelectric properties of Bi_2Te_3 nanostructure. This could be evidenced by thermal conductivity which should be higher than the electrical conductivity.

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INTRODUCTION

The bismuth telluride (Bi_2Te_3) is an efficient thermoelectric (TE) semiconductor type material. When the post transition metal elements of bismuth (Bi) is alloyed with a metalloid non-metal elements of tellurium (Te) then it makes a compound semiconductor material, Bi_2Te_3 . An acceptable TE material is indicated by large density and mobility of charge carriers, at the coinciding by the low thermal conductivity and high electrical conductivity. Another attractive aspect is that the efficient energy conversion adaptability of a TE material is performed by the extensive dimensionless figure of merit: $ZT = (S^2\sigma T)/K$, where S is the Seebeck coefficient, σ is the electrical conductivity, K is the thermal conductivity and T is the temperature.

Nowadays, Bi_2Te_3 nanostructure has a great deal of interest in thermoelectric applications such as thermoelectric heating and cooling, thermoelectric generators and portable power supply [1-10]. Recent studies suggest that Bi_2Te_3 material usage in nanostructure form generates the higher ZT (from 0.62 to 1.13) values [11-17].

However, there are few studies about this [18,19]. For this reason it is a challenging task to develop the single crystal Bi_2Te_3 nanostructure materials. Development of the nanostructured thermoelectric material is firmly connected to the capability to find out the microstructural and optical characterization.

In this paper, a simple chemical method was tried to develop the Bi_2Te_3 nanostructure pellet for thermoelectric applications. In the studies presented previously [20-23], this method was compared with other electrochemical synthesis methods. Ultimately, the recommended method was suitable for the producing nanostructure material. Furthermore, the superiority of this method was demonstrated via comparing with other methods in two reviewed papers [24, 25]. In this paper handling a development of Bi_2Te_3 nanostructure pellet for TE applications, after the first introduction, experimental methods was presented in the second section. In the third section, the results and discussion section was given. Finally, the conclusion and future research section were clarified.

EXPERIMENTAL METHODS

Developed Bi₂Te₃ nanostructure pellet

The reagents of Bi(NO₃)₃·5H₂O (≥98%, Sigma Aldrich) and TeO₂ (≥97%, Sigma Aldrich) were purchased from Sigma Aldrich and used as starting materials for the co-precipitation of a simple chemical solution method. The solvents of HNO₃ (65%, Sigma Aldrich), NaOH (98-100%, Sigma Aldrich), NaBH₄ (98-100%, mark) and Ethanol (Analytical grade, Mark) were also supplied and used without any further purification. In advance of the synthesis of Bi₂Te₃ nanostructure, Bi(NO₃)₃·5H₂O and TeO₂ were employed as the starting materials in this method. The starting materials were taken with stoichiometric ratio of Bi:Te (2:3) for the co-precipitation. NaOH was utilized to precipitates of BiONO₃ and TeO₂ and regulated the pH value of the solution.

The NaBH₄ was used as a reducing agent for remove the oxidization. The chemicals were weighed according to their stoichiometry (Bi₂Te₃=2:3) and were prepared separate metal ion solutions by using 2 mmol (0.97 gm) Bi(NO₃)₃·5H₂O and 3 mmol (0.47 gm) TeO₂. Dissolving these materials was handled in concentrated (2 M = 31.86 ml) HNO₃. A stock solution of (3 M = 30 gm) NaOH was employed for pH value regulated. The two metallic solutions were reserved in one flux (sol. 1) and other flux has been fulfilled with NaOH solution (sol. 2). These two solutions was mixed together at room temperature with adjusted the hydro dynamic atmosphere and complete co-precipitation was developed by magnetic stirring for half an hour. After magnetic stirring, white precipitates were grown in a flux. 150 ml white precipitates were collected and reserved in a borosilicate flux (sol. 3) at 80°C by using the magnetic stirrer for several minutes.

The Bi and Te oxides were eliminated by using NaBH₄. Other flux was fulfilled with 15 mmol (1.134 gm) NaBH₄ solution of 100 ml distilled water at 80°C soluble by magnetic stirrer for 15 minute (sol. 4). The sol. 3 and sol. 4 was blended together at the 80°C temperature with adjusted the same conditions and black colour precipitate was developed by magnetic stirring for four hours to remove the oxidization. The developed black precipitates were collected, washed and separated by centrifuged in several times using ethanol and deionized water to remove the byproducts thereafter dried in an oven at 80°C for 18 hours. In the end, the product powder was put in a 1 cm diameter pellet base and was pressed 5 MPa pressure. Then the formed pellet was heated in a vacuum furnace at 180°C for two hours. Finally, the Bi₂Te₃ nanostructure pellet having 1 cm diameter and 1 mm thickness was made. The manufactured pellets are sequentially shown in Fig. 1.

Experimental techniques

The XRD patterns were recorded by using a X'Pert high score PANalytical diffractometer with Cu-K α radiation, operated at 45 kV and 40 mA, with angular range $05^\circ \leq 2\theta \leq 85^\circ$. The morphology and elemental atomic composition of the pellet was accomplished with a scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) of LEO 1430 VP system. 3D topographic surface were recorded in 0.01 nm discrimination using 10 MP CCD cameras by an atomic force microscopy. BRUKER TENSOR II spectrometry was used for FTIR measurements.

RESULTS AND DISCUSSION

The improvement of the TE materials into next generation devices crucially depends on the improvement of new characterization techniques and theoretical models for the initial understanding of the relationship between the structure and characteristics.

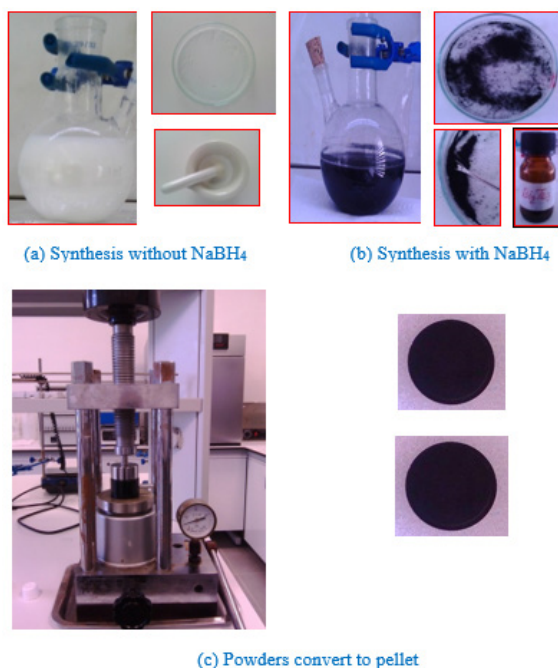
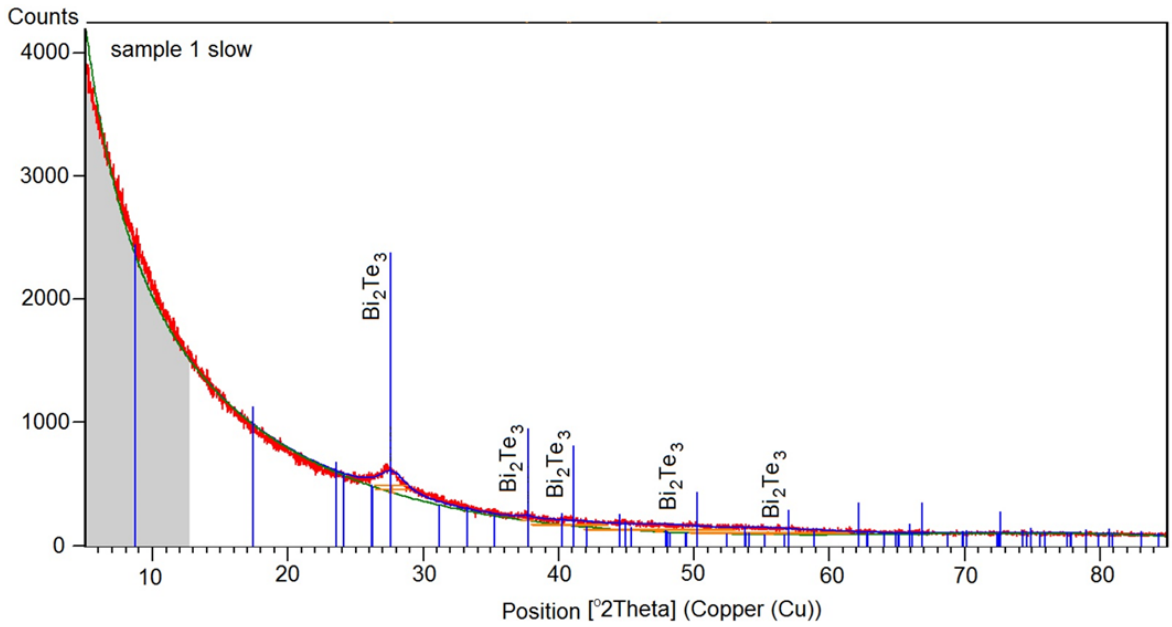
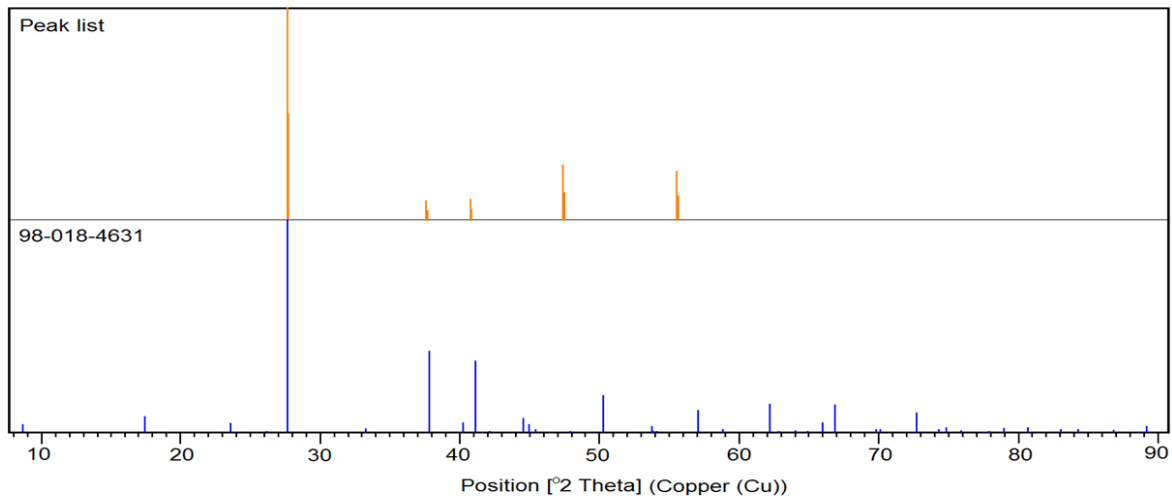


Figure 1. The manufacture of pellets is shown sequentially

The XRD provides complimentary information about the nanostructure materials by showing the average coherence length as a function of direction. Their results are averaged over a large volume giving an overall view of the nanostructure. A typical XRD spectrum of Bi₂Te₃ nanostructure pellet is shown in Fig. 2a. Fig. 2b shows the compare study of the spectrum with a standard reference code 98-018-4631 for Bi₂Te₃.



(a) XRD spectrum



(b) Spectrum is compared with a standard reference code 98-018-4631

Figure 2. XRD spectrum of Bi_2Te_3 nanostructure pellet.

The XRD revealed that the structure was nanocrystalline with a (015) preferred orientation. By using the Scherrer equation [26], simplified by other researcher

$$B_{\text{crystalline}} = \frac{0.94 \lambda}{B \cos \theta} \quad (1)$$

where, λ is the wavelength of Cu-K α radiation, and B is the full-width half-maximum (FWHM) of high intensity peak. The unit of B should be converted into radian. Therefore the above equation takes the form:

$$B_{\text{crystalline}} = \frac{50.97 \lambda}{B \cos \theta} \quad (2)$$

The calculated value shows the crystalline size. The average crystalline size of the pellet was calculated to be 3.93 nm, which conformed reasonably well to the literature value [27]. The smallest crystallites materials have the lowest thermal conductivity but their high resistivity dominates and has a detrimental effect on the thermoelectric figure of merit, ZT. Recently, due to its capability of converting waste heat into electricity, thermoelectric applications have attracted increasing interest. In this overview, a thermoelectric material with size effect, specifically low dimensional materials is suitable for thermoelectric applications. In order to compare the spectrum with the Bi_2Te_3 nanostructure standard reference code, three peaks (015), (1010) and (110)

were similar. Other two peaks (205) and (2011) were slightly shifted to the reference code. The peaks did not match the Bi_2Te_3 nanostructure. The peaks matched with other oxides form of Bi_2Te_3 materials.

According to the XRD result, the pellets may be some oxidization form. When an atom is oxidized, its characteristics may be change. Every researcher wants to produce oxide free materials that the materials are pure form. In the literature [28], one report was issued that the pure H_2 gas was passed to synthesize Bi_2Te_3 nanostructure throughout the sample at 400°C for 2 hours. In order to overcome or minimize the oxidization and obtain pure Bi_2Te_3 nanostructure pellets, before construct the pellets, it has been recommended that the produced powder should be passed in 99% pure hydrogen (H_2) or nitrogen (N_2) gas at 250°C for 2 hours in a quartz crystal chamber atmosphere.

SEM provides the detailed high resolution images of the specimen by restoring a focused electron beam across the surface and detecting secondary or backscattered electron signals. The signals reveal the information about the specimen including external morphology, chemical composition, crystalline structure and orientation of materials. Fig. 3 shows the SEM image for the morphological and microstructural information about the prepared pellets. The homogeneity of the sample was arranged sequentially. A preliminary electron diffraction study indicated that the samples were quasi spherical granule shapes in agglomerated clusters with crystalline in nature. The results were quite in agreement with the previous report [29].

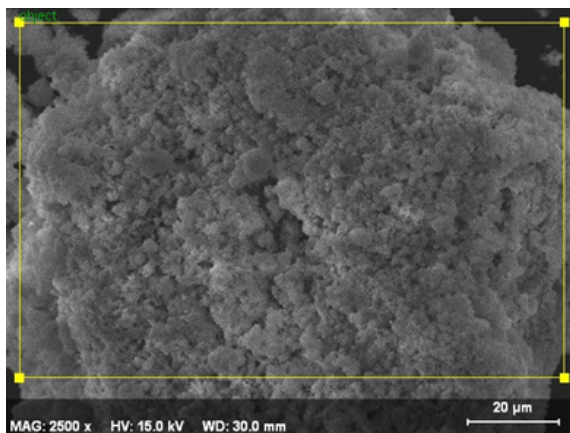


Figure 3. SEM image of Bi_2Te_3 nanostructure pellet

EDX is an x-ray technique used to identify the elemental composition of materials. The systems are attachments to SEM instruments where the image capability of the microscope identifies the specimen of interest. Table 1 shows the elemental atomic composition of the Bi_2Te_3 nanostructure. The materials of Bi and Te were arranged with their atomic stoichiometric ratio (34.62:51.52). From this table, it

was confirmed that ultra-fine device quality Bi_2Te_3 nanostructure pellet has been developed. It is also clear that the pellet contains stoichiometric form of Bi and Te.

Table 1. The atomic composition of the Bi_2Te_3 nanostructure.

Element	Series	Atom.[at.%]
Carbon	K series	3.73
Oxygen	K series	10.13
Bismuth	M series	34.62
Tellurium	L series	51.52
Total: 100.00 %		

Fig. 4 shows the EDX spectrum of the Bi_2Te_3 nanostructure. The materials of Bi and Te were arranged with their stoichiometric (2:3) form. From these curve it was cleared that Bi_2Te_3 nanostructure were developed which was in good agreement with other researchers' report [30]. The spectrum shows the other peck that is carbon and oxygen which indicates the little amount of contamination of the pellet. H_2 gas passing throughout the pellet at $\sim 250^\circ\text{C}$ that the effects of post-depositional contamination. Contamination may be artificially caused, it occurs in the post-depositional environment. It is concerned with removing post-depositional contaminants by isolating the pellet fractions that containing a very small amount of carbon and oxygen.

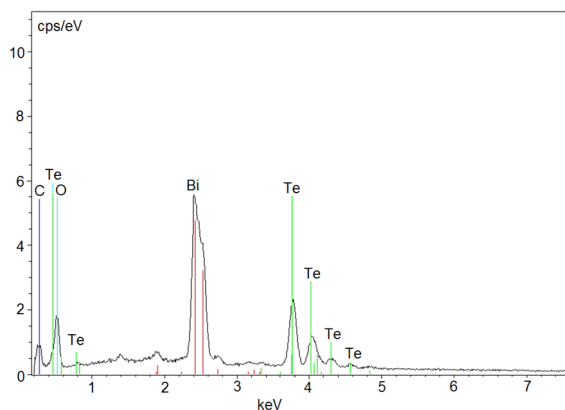


Figure 4. EDX spectrum of Bi_2Te_3 nanostructure pellet

It was also expressed that Bi_2Te_3 nanostructures consisted of Bi and Te. Moreover, same results were also found in the other researcher reports [31]. In this investigation, some other impurities such as carbon and oxygen were observed in this sample. In order to reduce the impurities and the obtained pure Bi_2Te_3 nanostructure pellet, while it is being mixed with the metal solution, the accurate hydro thermal condition was recommended. In here, the previous recommendation indicated the XRD investigation section was followed.

AFM demonstrates a 3D image of the produced pellet surface on a nano scale size by measuring forces between a sharp probe ($<10\text{ nm}$) and surface at very little distance

between 0.2-10 nm probe sample separation. The probe is supported on a flexible cantilever. The AFM tip gently touches the pellet surface and records the small force between the probe and the pellet surface. The sample in the study was prepared the topological surface and measurement the roughness value of the pellet surface. As shown Fig. 5, the AFM measurements were another confirmation that the technology set the standard for the lowest position noise. The surface roughness increases the efficiency of the heat to electricity conversion factor in nanostructure materials. The electronic parts of these conductivities are linearly connected. Therefore, only the phonon part of the thermal conductivity can be manipulated almost independently without effecting very much on the electrical counterpart. In nanostructure materials, the phonon scattering cross section of the rough surfaces dominates all other bulk scattering agents (point defects, dislocation, grain boundaries etc) due to the fact that it has higher weight factor in the sum of surface and bulk contributions. Therefore, ZT may show enhancement if one has rough surfaces in nano size materials. The surface roughness is important in evaluating the performance of a membrane as it may influence the transmembrane transport and fouling potential of nanostructure materials. Therefore, the surface roughness may also correlate with crystalline size.

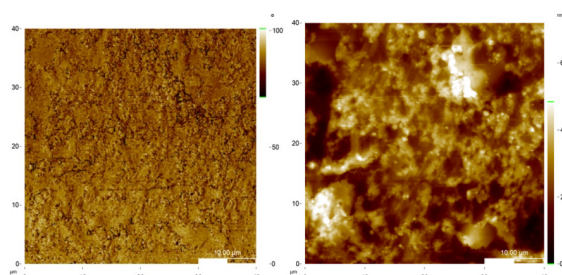


Figure 5. AFM images of Bi_2Te_3 nanostructure pellet

In addition, according to Fig. 5, the AFM studies revealed that the atom arrangement of the pellet was in homogeneous. Furthermore, in Fig. 5, it conformed to the structure in nano crystalline in form [32].

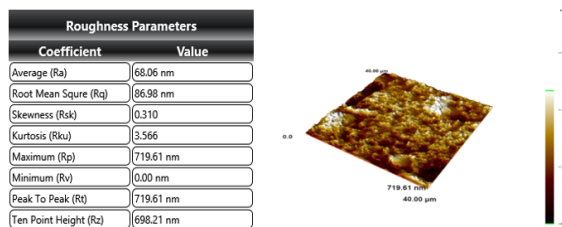


Figure 6. 3D AFM image and roughness parameters of Bi_2Te_3 nanostructure pellet

Fig. 6 gives the 3D view of the pellet. The roughness parameter was observed through Fig. 6. AFM image was not ideally sharp identification. As a consequence, an AFM ima-

ge does not reflect the accurate sample topography, but rather represents the interaction of the probe with the sample upper surface roughness value. The surface roughness at the nano scale plays an important role in determining of the functional performance of the TE devices.

Understanding and characterizing of nano scale roughness was a crucial data to continue the ability exploring and building TE devices at ever smaller length scales. In this observation, the average roughness value was about ~ 68 nm. The results of this investigation were significant because large position noise in a nano positioner could obscure an AFM surface roughness measurement. The nano meter size surface roughness value has been strongly influences the thermoelectric behaviour of nanostructure materials. AFM is especially recommended for the analyses of such nanostructure surfaces with nano meter size irregularities. It was found that variation in surface roughness influences the thermoelectric characteristics of the nanostructure materials even at low surface roughness values (~ 68 nm).

The FTIR spectroscopy is an analytical process used to clarification the organic, polymeric, and in some cases, inorganic materials. The FTIR analysis process uses infrared light to scan the test specimen and investigate the chemical behaviour of the materials. Fig. 7 illustrates the FT-IR spectrum of Bi_2Te_3 nanostructure pellet. Expected peak for the FTIR spectrum of the Bi_2Te_3 nanostructure were absorbed in the bands between 400 and 2366 cm^{-1} which correspond to C-S, C-H, C-O and O-H stretching vibrations. In this observation, the Bi_2Te_3 nanostructure pellet was adjusted the same stretching with the similar bands. In the developed pellet were conformed the nanostructure form according to other researcher reports [33].

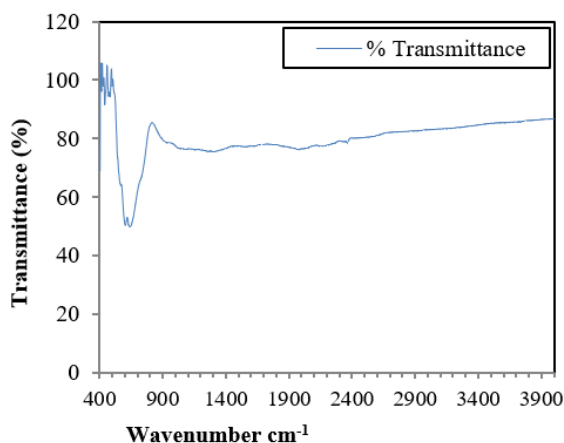


Figure 7. FT-IR spectrum of Bi_2Te_3 nanostructure pellet

On the other hand, the oxygen containing functional groups were almost reduced in the technique of reduction with NaBH_4 and thus the metal ions were transformed into Bi_2Te_3 nanostructure form. Eventually, nanostructure

of material was enhanced the thermoelectric power due to quantum confinement. Size effect was led to carrier confinement. Selective scattering and interface scattering was reduced. The thermal conductivity was improved more than the electrical conductivity; thus the figure of merit was increased.

CONCLUSION AND FUTURE RESEARCH

Current research activities on Bi₂Te₃ nanostructure are developed by using the several processes such as the thermal evaporation, sputtering, lithographic, pulsed laser ablation, simple chemical, electrochemical, grinding, solvothermal and hydrothermal. In this paper, the simple chemical process was employed in terms of financial aspect and potential for very large quantity of productions. The pellet was excited by some oxidization and impurity. In order to minimize the oxidization, a computer controlled pure H₂ or N₂ gas was passed throughout the pellet. It was concluded that by using this method, pure pellets would be produced. Further research recommended that the pellet to measure the electrical and thermal conductivity, Seebeck coefficient and figure of merit for proper utilization in thermoelectric applications.

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