

# Characterization of Nanocrystalline Bismuth Telluride (Bi<sub>2</sub>Te<sub>3</sub>) Synthesized by a Novel Approach Through Aqueous Precursor Method

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 $Bi_2Te_3$ -based alloys are currently best-known, technologically important thermoelectric materials near room temperature. In this paper, nanocrystalline  $Bi_2Te_3$  was synthesized by an aqueous solution technique based on the reaction between the aqueous solution of Bi-ethylenediamine tetraaceticacid (EDTA), TeO-EDTA, and NaBH<sub>4</sub> at room temperature. NaBH<sub>4</sub> was used as a reducing agent. TeO-EDTA was prepared from TeO<sub>2</sub> after satisfactory purification. The sample purity was examined by selected area energy dispersive X-ray analysis. The products were characterized by X-ray diffraction and high-resolution transmission electron microscopy by which the particle morphologies and size were studied. The particle size ranges from 60 to 90 nm.

#### I. Introduction

THE bismuth telluride (band gap:  $E_g = 0.15 \text{ eV}$ )-based alloys are known as the best currently available thermo-electric material for application near room temperature.<sup>1-5</sup> They have many important applications, for example, used as thermo-piles and thermal sensors, thermoelectric cooler for laser diodes, fiber optic, microelectrothermal systems, and so on.<sup>6-10</sup> Because of technological importance of Bi<sub>2</sub>Te<sub>3</sub>, a lot of processes have been developed to prepare bismuth telluride. Most of the processes use metallurgical methods like BMA,<sup>11</sup> Bridgman methods<sup>12,13</sup> for bulk preparation, and require elevated temperature and a relatively long duration under special protection against oxidation, and it is difficult to tailor their electrical and thermal transport properties independently. This is an important point to note that thermoelectric properties are greatly correlated with chemical homogeneity, shape, and size of nanoscale thermoelectric materials.

A simple approach is the coprecipitation of bismuth and telluride as oxides from aqueous solution, and the coprecipitated oxides are converted directly to fine Bi<sub>2</sub>Te<sub>3</sub> powder through hydrogen reduction.<sup>14</sup> Groshens *et al.*<sup>15</sup> have reported a different approach to the synthesis of Bi<sub>2</sub>Te<sub>3</sub> by means of reactions conducted in hexane at 230°C. Ritter<sup>14</sup> has reported a room-temperature process of coprecipitation of bismuth telluride precursor (Bi<sub>2</sub>O<sub>3</sub> 3TeO · *x*H<sub>2</sub>O) in aqueous media, then its hydrogen reduction to polycrystalline Bi<sub>2</sub>Te<sub>3</sub>. This group has also found an unusual metal-organo complex method to synthesize finely powdered Bi<sub>2</sub>Te<sub>3</sub>.<sup>16</sup> Yu *et al.*<sup>17</sup> and Deng *et al.*<sup>18–20</sup> have reported a low-temperature solvothermal method to synthesize Bi<sub>2</sub>Te<sub>3</sub> at room temperature.<sup>21,22</sup> Sapp *et al.*<sup>23</sup> and Foos *et al.*<sup>24</sup> have synthesized bismuth telluride nanowires by electro-deposition method in conjunction with template synthesis techniques

within the pores of alumina template membranes. All these process are to increase the Carnot efficiency, which is dependent on the improvement of the figure of merit, ZT of the thermoelectric material. Both theoretical and experimental results indicate that the ZT value of certain nanoscale materials increases several times compared with that of their bulk materials.<sup>25,26</sup> Therefore, the ZT value can be tailored through controlling the size and shape of nanoscale thermoelectric materials, which will have potential application in thermoelectric devices. New synthetic method for nanoscale bismuth telluride will be useful for both basic research and technological applications.<sup>26</sup>

In this report we present a low-energy cost and low-temperature route to get ultrafine  $Bi_2Te_3$  by aqueous precursor method using commercial tellurium metal after purification.

### **II. Experimental Procedure**

Materials used are Te metal (Hindustan Copper, Bihar, India, 98 at.%), HNO<sub>3</sub> (Merck, India), KOH (Merck),  $Bi_2O_3$  (Merck, Mumbai, India), ethylenediamine tetraaceticacid (EDTA) (Merck), 30% NH<sub>3</sub> solution (Merck), and NaBH<sub>4</sub> (Merck).

## (1) Purification and Preparation of Stock Solution of $Te^{4+}$

Tellurium metal was boiled with excess of concentrated HNO<sub>3</sub> for half an hour. After the completion of reaction, a white lump of tellurium oxide was formed. Boiling with excess nitric acid, the impurities (mainly iron and aluminum) were leached out as water-soluble nitrates. The white lumps of tellurium oxides were ground and dissolved in a 20% ammonia solution and filtered. The filtrate was re-precipitated with concentrated HNO<sub>3</sub>, and then washed with double distilled water to wash out the impurities. The lumps of oxides were ground to powders and dried at 150°C under vacuum. The powder was examined for impurities using selected area energy dispersive X-ray (SEDX-ray) analysis. This process was continued until the purity level reached to 99.9 at.%. Pure TeO<sub>2</sub> was then dissolved in ammonical EDTA (ED-TAH<sub>4</sub>) solution after warming on water bath for an hour. The strength of the prepared solution was determined by chemical assay through heating the known volume of solution at 500°C for 2 h and weighing the residual TeO<sub>2</sub>. The strength of the solution obtained was 0.02M.

## (2) Preparation of Solution of $Bi^{3+}$

Bismuth oxide was dissolved in dilute  $HNO_3$  solution and then complexed with EDTA solution in alkaline pH 11. The strength of the solution was determined from the weight of oxide and final volume of solution. The strength of the prepared solution was 0.25M.

## (3) Preparation of Nanoparticles of Bismuth Telluride

Required amount of TeO-EDTA complex solution (0.02M) was taken in a 500 mL beaker, maintained the pH at 11 with the help of KOH solution (30%). Proportionate amount of bismuth EDTA complex solution (0.25M) was poured with the simultaneous addition of KBH<sub>4</sub> aqueous solution (30%) resulting a vigorous reaction yielding the black colored Bi<sub>2</sub>Te<sub>3</sub> nanoparti-

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cles suspended into the solution. After the completion of the reaction, the suspended nanoparticles were collected by using a centrifuge and washed with double distilled water followed by 99.99% ethyl alcohol. Finally, the washed  $Bi_2Te_3$  nanoparticles were dried in vacuum at temperature 70°C.

Powder X-ray diffraction (XRD) was taken to characterize the samples using a Philips PW 1710 X-ray diffractometer (Eindhoven, the Netherlands) with CuK radiation ( $\lambda = 1.5406$ Å), equipped with a vertical goniometer. The XRD spectrum of Si crystal was used as a standard to calibrate the scanning angles. The step size of the scan was  $0.04^{\circ}2\theta$ , with a scanning speed of  $0.02^{\circ}2\theta$ /s. The particle morphology, size, and further structural and elemental analyses were performed by high-resolution transmission electron microscopy (HRTEM) in a JEOL 2010 microscope (Tokyo, Japan) with an ultra-high resolution polepiece using a LaB<sub>6</sub> filament operated at 200 kV, selected area electron diffraction (SAED), and SEDX in a JEOL JSM-5800.

#### III. Results and Discussion

The composition of the as-prepared product was determined by XRD (Fig. 1). All peaks in the patterns correspond to the reactions of rhombohedral phase R<sup>-</sup> 3m, Bi<sub>2</sub>Te<sub>3</sub>, with cell constants a = b = 4.38 Å and c = 30.50 Å, which are in agreement with the reported values a = 4.385 and c = 30.48 Å (JCPDS 15-0863). Information on crystallite size (*D*) and the effective strain ( $\eta$ ) was obtained from the full-width at half-maximum (FWHMs) of the diffraction peaks. After applying the correction for instrumental broadening with respect to standard silicon, the FWHMs can be expressed by the following equation assuming particle size and strain profiles are of Gaussian type:

$$(\beta_{i}^{Ob})^{2} = (\beta^{p})^{2} + (\beta^{s})^{2}$$
(1)

or

$$(\beta_{\rm i}\cos\theta/\lambda)^2 = (1/D)^2 + (\eta\sin\theta/\lambda)^2 \tag{2}$$

where  $\beta$  is the integral of FWHM;  $\beta^{p}$  the FWHM considering the particle size effect;  $\beta^{s}$  the FWHM because of strain;  $\theta$  the half incident angle of the X-ray, and  $\lambda$  the wave length of the target material.

Figure 2 shows the plot of  $(\beta_i \cos \theta/\lambda)^2$  versus  $(\sin \theta/\lambda)^2$ . From the slope of the best fitted line and the intercept at x = 0, the crystallite size (D) and the effective strain ( $\eta$ ) were found to be 65.5 nm and 0.003675. Essentially the sample shows the absence of any significant strain.



Fig. 1. X-ray diffraction patterns of as prepared Bi<sub>2</sub>Te<sub>3</sub> powder.



Fig. 2.  $(\beta_i \cos \theta/\lambda)^2$  versus  $(\sin \theta/\lambda)^2$  for  $Bi_2Te_3$  whose  $\theta/2\theta$  scans are shown in Fig. 1.

TEM images of the samples taken onto a 300 mesh copper TEM grids coated with 50 nm carbon films after dispersing into acetone revealed that the products are mostly deformed spherical as well as some rod-like nanoparticle as shown in Fig. 3. The particle size was calculated with the help of UTHSCSA image tool (The University of Texas Health Science Center, San Antonio, TX) considering 50 particles. After statistic analysis the average particle size was found to be  $80\pm 2$  nm which is in close agreement obtained from XRD analysis. The dependency of the size of the nanocrystalline on the salt concentration has not been studied completely. This aspect is on the way of our investigation. Dilute solutions ( $\leq 0.2M$ ) of the salts do not find any significant change in their crystallite size on further dilution. The corresponding selected area diffraction (SAD) pattern in Fig. 4(d) shows a symmetrically dotted pattern, implying that these nanoparticles are well crystallized single crystals of Bi<sub>2</sub>Te<sub>3</sub>, which is consistent with the XRD measurements (Fig. 1). An HRTEM image of top-view of two attached particles is shown in Fig. 4(a), which is taken from the selected area shown in Fig. 3. Figure 4(b) is the HRTEM image of the area indicated by the bracket in Fig. 4(a). The details of lattice fringe indicate that there are very similar orientations in the attached particle, and only slightly angular mis-orientations are present in two attached particles. From the micrograph we have determined the lattice spacing in the particle to be 3.2 Å, which corresponds to (015) plane of rhombohedral phase of this material. The white line in Fig. 4(b), which is drawn parallel to the  $Bi_2Te_3$  (015) lattice fringes on the upper rod-like particle, is slightly inclined to the white line, which is also parallel to the (015) fringes on the lower particle. This slight misorientation suggests that defects are introduced into the particles during the process. The side-



Fig. 3. Bright field transmission electron microscopy image of  $Bi_2Te_3$  nanoparticle.



Fig.4. (a, b) High-resolution transmission electron microscopy (HRTEM) image of top view; (c) HRTEM image of side view; and (d) the corresponding electron diffraction pattern taken from the interval of particles; and (e) HRTEM image of the center between contiguous particles.

view is shown in Fig. 4(c), in which two particles are attached very closely.

All the lattice fringes in two continuous particles have almost the same spacing and direction where the singular fringe spacing is 9.8 Å, which is nearly consistent with the (003) reflection plane spacing of the rhombohedral  $Bi_2Te_3$  phase. The (003) direction was parallel to the long axis of the rods, indicating that the [003] direction is a common growth direction for the  $Bi_2Te_3$  particle. The SAED patterns of two adjoining particles and the joint in rods (Fig. 4(d)) are similar and confirm that it is a large single crystal.

SEDX analysis of sheet-rods showed that the atomic composition ratio of Bi/Te is always about 2:3, which is in good agreement with that of the stoichiometric composition of  $Bi_2Te_3$ . In addition, neither N nor C signals was detected in the SEDX spectrum, which means there exist no solvent or EDTA ligand in the sheet-rod crystals.

The structural details of the joint sheets shown in Figs. 4(c) and (e) show the lattice resolved HRTEM images taken near the edge and center between two continuous particles. Fig. 4(c) shows that the lattice planes in the joint of sheets have almost the same spacing and direction with the adjoining particles, and

no apparent boundary is present. It implies that the rod-particles are composed of consecutive particles. Figure 4(e) shows the attachment of the rod-particle is imperfect, which involve dislocations in the interface.

The exact mechanism has not been studied intensively. As known, tellurium, transition metals, and some donor solvents can form organometallic complexes.<sup>27,28</sup> The formation of  $Bi_2Te_3$  may be presented as follows:

Reactions:

 $\begin{array}{ccc} \text{Te}\,(\text{metal}) + \text{HNO}_3 & \stackrel{\text{boilfor3h}}{\longrightarrow} \text{TeO}_2(\text{ppt}) & \stackrel{\text{ammonia}}{\longrightarrow} (\text{NH}_4)_2 \text{TeO}_3 \\ & \stackrel{\text{HNO}_3}{\longrightarrow} \text{TeO}_2(\text{ppt}) \end{array}$ 

$$\label{eq:edge_eq} \begin{split} \text{TeO}_2 + \text{EDTA}^{4-} + \text{NH}_3 & \rightarrow \text{Ammonium salt of EDTA} \\ \text{complex of $Te^{4+}(\text{NH}_4)_2[\text{TeO EDTA}]$} \end{split}$$

$$3(NH_4)_2[TeO EDTA] + 2[Bi(EDTA)]^{1-} + NaBH_4$$
  
 $\stackrel{pH=11}{\longrightarrow}$  nano Bi<sub>2</sub> Te<sub>3</sub>.

The homogeneous mixture of anionic complexes of Bi<sup>3+</sup> ion and Te<sup>4+</sup> facilitate instantaneous formation and precipitation of Bi<sub>2</sub>Te<sub>3</sub>. The pH more than 11 is not beneficial because at that pH decomposition of  $BH_4^-$  to boric acid and  $H_2$  which is much faster than reduction of complexes.

As soon as the reducing agent (NaBH<sub>4</sub>) was added in the reaction system, bismuth ions  $(Bi^{3+})$  and  $Te^{4+}$  could be reduced to Bi<sub>2</sub>Te<sub>3</sub>, and then the pathway would take place in the following way to form the 2D structure (nanosheets or rags):

 $\left[Bi(EDTA)\right]^{1-} + \left[TeO - EDTA\right]^{2-} \overset{KBH_4}{\longrightarrow} Bi_2 \ Te_3 \ nano \ sheet$ 

EDTA acted as a structure directing agent in the formation of products. The present process proceeds through nucleation and growth steps. The crystalline seeds are formed in this solution process through a homogeneous nucleation. As bismuth telluride has a highly anisotropic structure, the growth direction is largely confined to one direction and the single crystalline seed tends to grow into the rod shape under the influence of soft capping agent EDTA which is a multidentate ligand with polyfunctional groups, which can serve as bridging ligand to form multinuclear complexes.<sup>19</sup> Then the chains of crystallite seeds would form in the next nucleation process, which finally yield sheet-rod-like products and thus control the particle size in nanometric range.

#### IV. Conclusion

In summary, the present study demonstrates a new approach for the synthesis of Bi<sub>2</sub>Te<sub>3</sub> nanoparticles. One of the advantages of the method is that the synthesized Bi<sub>2</sub>Te<sub>3</sub> nanoparticles are formed directly at room temperature using easily available reagents EDTA<sup>4-</sup> and NaBH<sub>4</sub>. EDTA plays a key role in this process for the formation of the nanoparticles of Bi<sub>2</sub>Te<sub>3</sub> as a capping agent. The particle sizes range from 60 to 90 nm in the present reaction conditions.

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