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Synthesis of bismuth telluride nanostructures by refluxing method

Srashti Gupta[1*], S. Neeleshwar[1*], Vinod Kumar[1], Y.Y. Chen[2]

[1]*University School of Basic and Applied Sciences, GGS Indraprastha University, Dwarka, Delhi 110075, India*
[2]*Institute of Physics, Academia Sinica, ROC, Taiwan,*

[*]Corresponding author. E-mail: srashti.3@gmail.com, sneeleshwar@gmail.com

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ABSTRACT

Bismuth telluride (Bi_2Te_3) nano particles were prepared by refluxing method in different conditions such as varying concentration of KOH and reaction timings. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements have been performed for structural and phase formation studies. The nanoparticles are showing the same structure of bulk except broadening of peak confirmed by XRD. The reaction time and KOH concentration are the key parameters to control the morphology and size of the particles. As the concentration of KOH increases, the particle size decreases from 23 to 15 nm and with increasing reaction time, nanorod like structures (~100 nm length and ~ 20 nm diameter) are formed. Copyright © 2011 VBRI press.

Keywords: Thermoelectric materials; bismuth telluride; nano tube; nano particle; refluxing method.

Srashti Gupta received her Master of Science in Physics from Ch. Charan Singh University, Meerut, India and Master of Technology in Engineering Physics from G.G.S. Indraprastha University, Delhi, India. She is pursuing her Ph.D. in Physics from G.G.S. Indraprastha University, Delhi, India and working on the project entitled "Synthesis and characterization of thermoelectric material by ion beam mixing", funded by Inter University Accelerator Centre (IUAC), New Delhi. Her field of interests are synthesis and characterization of thermoelectric materials using chemical method and ion beam technology.

S. Neeleshwar obtained Ph.D degree in Physics from Osmania University, India and Post Doctoral Fellow from Institute of Physics, Academia Sinica, Taiwan, ROC. He is presently working as a Assistant Professor, GGS Indraprastha University, Delhi, India. His research interest includes the fabrication and characterization of nano-materials. And study the quantum size effects in magnetic materials, thermoelectric material and superconductor. He has authored more than 25 publications in well-reputed international journals such as Advanced Materials, Chemistry of Materials, Applied Physics Letter and Physical Review B. He is also visiting Professor at Department of Physics, Sri Sathya Sai University, Prashanti Nilayam and visiting scientist at Institute of Physics, Academia Sinica, Taiwan, ROC.

Introduction

Bismuth telluride (Bi_2Te_3) is a narrow band gap (0.15eV) layered semiconductor material having trigonal structure with high melting pint (585 °C); also it is a heaviest stable binary compound. These interesting properties attracted the researchers for its wide range application in the field of thermoelectric material [**1-5**] used for power generation and refrigeration. Since last decades, efforts are in progress to enhance the properties of these materials using different approaches and one of the fruitful approaches is to synthesis it in nano scale [**6-13**]. Till today, many methods have been discussed to prepare nanostructure bismuth telluride with various sizes and shapes such as microwave assisted method [**14**], mechanical alloying [**15**], hot pressing [**16**], spark plasma sintering [**17**] and wet chemical method [**18**] etc.

Recently, nano structured bismuth telluride is synthesized using different chemical methods showing the enhanced thermoelectric properties due to its nanostructure properties [**16-18**]. Bulat et. al [**16**], have shown the enhancement of thermoelectric properties in nano structured Bi_2Te_3 by 20-40% on the basis of energy filtration of charge carrier. Enhancement in the thermoelectric and transport properties of nano structured n-type Bi_2Te_3 alloys is reported in light of the micro structural characteristics [**17**]. Zhang et al [**18**], has reported synthesis of nanoscale heterophase Bi_2Te_3–Te using surfactant-free, wet chemical, and easily up-scalable strategy and showed 40% enhancement of the figure of

merit over their lab-made material without nanoscale heterostructures.

There are several reports in the literature, studying the effect of solvents and reactants on the formation of nano structured bismuth telluride by sonochemical method [**19**], solvothermal method [**20**], refluxing method [**21**] and hydrothermal synthesis [**22, 23**]. Deng et al [**20**] have reported the synthesis of Bi_2Te_3 nanotubes by solvothermal method at 140 °C. They have suggested that the formation mechanism of Bi_2Te_3 depends on the starting materials fed, solvent and reaction temperature. Zhao et al [**23, 24**] have reported the synthesis of nanostructured bismuth telluride powder by hydrothermal method. They have prepared the powder with various morphologies like nanotubes, nano rods, thin sheets which all depends on the nucleation mechanism during synthesis. Sun et al [**25**] have reported Bi_2Te_3 nano wires by aquous chemical method and they have suggested that the directional effect of surfactant and dissolving of the amorphous tellurium colloids are responsible for the growth of nano wires. Bi_2Te_3 nano particles can also be formed by the same process without introduction of sodium dodecyl benzene sulfonate (SDBS) or using Na_2TeO_3 as Te precursor.

Among all these methods refluxing method has been accepted widely because it is one of the simple and low cost method and can achieve required product with precise control over reaction parameters [**21**]. Hu et al [**21**] reported the synthesis of bismuth telluride nanoparticles by refluxing method, and then prepared nanocomposites by hot pressing the mixture of nano and micro powders of Bi_2Te_3. To the best of our knowledge there is almost no report on the preparation of Bi_2Te_3 nano particles with control of size and shape using refluxing method by varying reaction time and concentration of KOH. To this endeavors, we presented a systematic study to observe the effect of reaction time & concentration of KOH on the size and shape of bismuth telluride nano particle by refluxing method.

Experimental

Chemicals/materials

All the chemicals used in the present synthesis were analytical grade and were purchased from Loba Chemicals. Bismuth chloride, ($BiCl_3$ with 97% purity), Tellurium powder, (Te with 99.9% purity), Ethylenediaminetetraacetic acid (EDTA), Potassium hydroxide (KOH), Sodium borohydride ($NaBH_4$ with 97% purity), Ar gas (99.9% purity). Some of these chemicals (Te and $BiCl_3$) are mildly toxic, so need to be handled carefully. All chemicals were used as received during the experiment.

Synthesis of bismuth telluride

Bismuth chloride ($BiCl_3$) and tellurium powder (Te) were taken as 2: 3 molar ratio and transfer into a 250 ml flask containing 200 ml water (as a solvent) and flask is attached with condenser, then EDTA was added as an organic surfactant [**21**]. The reaction was stirred for 10 min using magnetic stirrer at temperature 50 °C. Finally, KOH (act as a pH controller) and $NaBH_4$ (1 gm sufficient quantity, as a reducing agent) were added to reaction. Then reaction is carried out at the boiling point of solvent in presence of inert gas atmosphere (Ar gas) to avoid contamination. The schematic of reaction set up has shown in **Fig. 1**. As soon as the reaction is completed, precipitate was taken out and washed with acetone, ethanol and deionized water several times and then dried under Ar atmosphere.

Similarly, bismuth telluride nanoparticles were synthesized at different concentration of KOH (0.5 - 1.5 M) and for different reaction timings (2-24 hrs) in order to study the effect of these parameters on growth mechanism of Bi_2Te_3 nanoparticles.

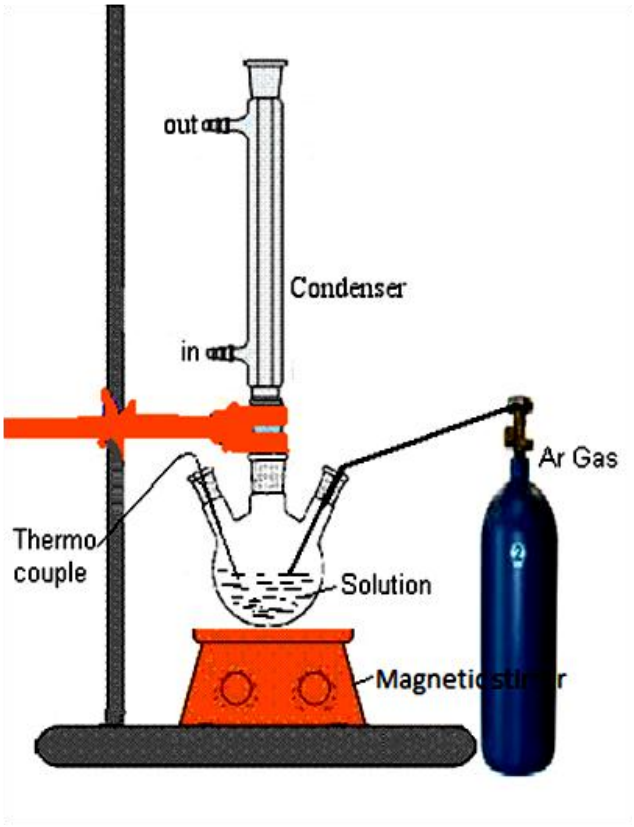

Fig. 1. Shows the schematic diagram of refluxing method for synthesis of Bi_2Te_3 nano particles.

Characterization Techniques

Structural studies and particle size estimations were carried out using table top X- ray diffraction (XRD) (Rikagu Mini Flex). Transmission electron microscopy (TEM) measurement was performed for understanding the changes in morphology of synthesized Bi_2Te_3, with field emission TEM, using JEOL JEM-2100 at 200 kV. The characterizations were repeated for synthesized nanopowder at different concentration of KOH and different reaction time.

Results and discussion

Fig. 2 shows the XRD patterns of Bi_2Te_3 nano particles with different concentration of KOH (**a**) 0.5 M, (**b**) 1.0 M and (**c**) 1.5 M. As the KOH concentration changes from 0.5 M to 1.5 M, all the samples show the same rhombohedral structure which is confirmed by JCPDS -

080027 data as shown in **Fig. 2**. The observed broadening of the peak at 2 Θ = 27.6 with (0 1 5) plane is due to the decrease in particle size as the concentration of KOH is increased.

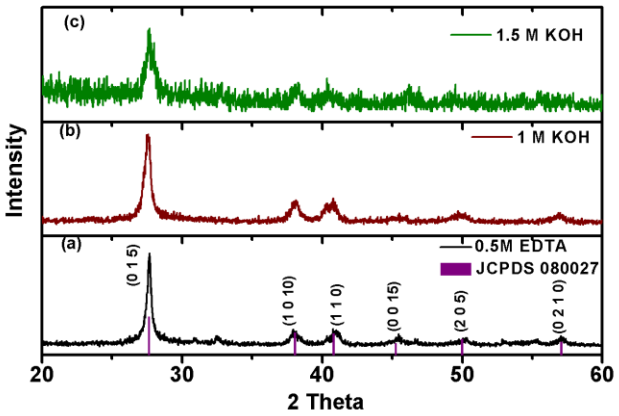

Fig. 2. X-ray diffraction (XRD) of bismuth telluride (Bi_2Te_3) nano particle for different concentration of KOH,(a) 0.5M, (b) 1.0M, and (c) 1.5M for 8 hr reaction time.

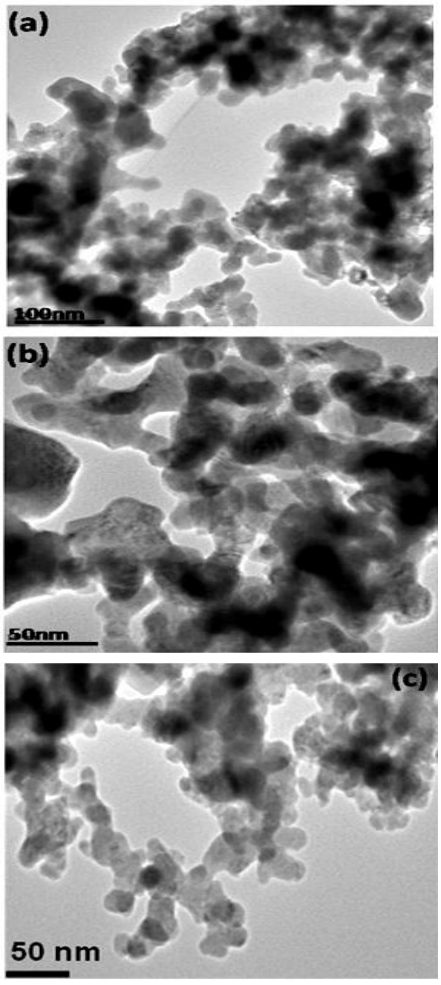

Fig. 3. TEM image of bismuth telluride (Bi_2Te_3) nano particles for reaction time 8 hr, at different concentration of KOH (a) 0.5M KOH (b) 1.0M KOH, (c) 1.5M KOH.

The particle size was estimated through the Debye – Scherrer formula ($d = k\lambda/\beta Cos\theta$), where k is 0.93, λ is CuKα wavelength (1.54 nm), β is the full width half maximum of the intense peak and θ is Bragg angle. The estimated particle size indicates, as the concentration of KOH increases, the particles size decreases as shown in the **Fig 2**. From this one can understand the size of the nanoparticles is dependent on the KOH concentration. In the present case, as the KOH concentration increases 0.5-1.5 M then particle size decreases 23-14 nm, these results strongly suggest that KOH is playing an important role on size of Bi_2Te_3 nanoparticles.

Fig. 3 shows the TEM images of Bi_2Te_3 powder prepared by varying concentrations of KOH: (**a**) 0.5 M, (**b**) 1 M and (**c**) 1.5 M. TEM images also show decrease in particle size with increasing KOH concentration and which is in well agreement with XRD results. From the **Fig. 2-3**, one can observe the variation of KOH concentration resulting in nanoparticles formation with reducing the particle size as well as negligible effect on the morphology of the particles. To understand noticeably the modification of morphology another parameter, variation of reaction time is studied.

In the present investigation, we also synthesized the bismuth telluride nanoparticles at different reaction time such as 2, 4, 8 and 24 hrs as shown in XRD pattern (**Fig. 4**). All these samples were fabricated at constant 1.0 M concentration of KOH. All the samples with varying reaction time from 2-24 hrs show the same rhombohedral structure of Bi_2Te_3. Particle size was estimated using the Debye-Scherrer formula. It is interesting to note that as the reaction time increases particle size decreases from ~26 (for 2 hrs) - ~18 nm (for 4 hrs) and on further increase in reaction time to 8 hrs no appreciable change in particle size was noticed. However, as the reaction time increases upto 24 hrs, further decrease in particle size to ~15 nm was observed.

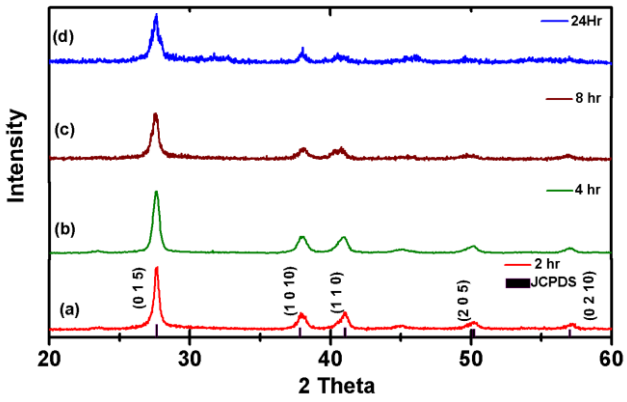

Fig. 4. XRD of bismuth telluride (Bi_2Te_3) nano particle with 1M KOH concentration at different reaction timings for (a) 2hr,(b) 4hr, (c) 8hr, (d) 24 hr.

To study the effect of reaction time on the growth of Bi_2Te_3 nanoparticles, TEM measurement was further performed as shown in **Fig. 5**. It shows the TEM images of bismuth telluride nanoparticles synthesized with 1.0 M KOH concentration at different reactions times for 8 and 24 hrs. TEM picture shows that, only nano particles were formed when the reaction time is 8 hrs and as the reaction

time increases to 24 hrs, the signature of the formation of rod like structure with ~100 nm length and ~ 20 nm diameter was observed as shown in **Fig. 5** (**b**).

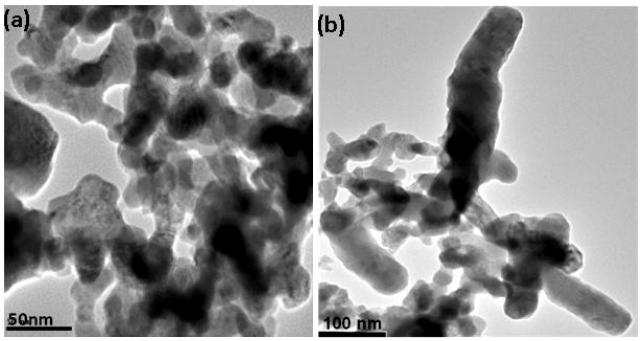

Fig. 5. TEM image of bismuth telluride (Bi_2Te_3) nano particles with 1M KOH concentration at different reaction timings for (**a**) 8 hr, (**b**) 24hr.

From these observations, one can conclude that increase in the reaction time plays key role in the morphology of nanostructure and particle size. Thus, it signifies the importance of refluxing method with reaction time of 24 hrs to form nano rod like structure of Bi_2Te_3.

However, there are many researchers, who have proposed the mechanism for the formation of Bi_2Te_3 of different size and shape prepared by different chemical routes [**19-25**]. In view of earlier proposed mechanism, the formation of Bi_2Te_3 particles with different size and morphology with varying KOH concentration and reaction time can also be proposed in the present case. The formation of bismuth telluride using the refluxing method can be explained as follows: bismuth telluride was formed due to the initially bismuth ions (Bi^{3+}) were formed in the solution where addition of EDTA plays an important role to stabilize Bi ions in the solution [**20**]. On the other hand, Te is reduced to tellurium ions (Te^{2-}) by $NaBH_4$/KOH acts as a reducing agent. Finally in the solution Bi ion and Te ion reacts to form bismuth telluride (Bi_2Te_3) as follows:

$$BiCl_3 \xrightarrow{aquous} Bi^{3+} + 3Cl^-$$

$$Te \xrightarrow{Reduction,KOH/\ NaBH_4} Te^{2-}$$

$$3Te^{2-} + 2Bi^{3+} \rightarrow Bi_2Te_3$$

Scheme 1. Reaction process for synthesis of Bi_2Te_3.

After the formation of bismuth telluride the surfactant EDTA acts as a structure directing agent, also can induce the growth manner and direction of nucleation to form different structure of the resulting product [**21**]. The surfactant EDTA also leads to different morphologies of the different nano structures [**19, 25**]. Hu et al [**21**] has also reported that using surfactant EDTA, $C_2H_8N_2$ and PVP, straight, branchy nano tubes and nano scale granules can be prepared respectively which also support the present case. However, the present investigation indicates that lower reaction time up to 8 hrs leads to the formation of nanoparticles and as the reaction time increases further to 24 hrs, rod like structure are observed. Finally, one can conclude that the growth and morphology of the bismuth telluride depends upon the surfactant, concentration of KOH and reaction timings.

Conclusion

Nanostructure bismuth telluride has been synthesized by refluxing method using EDTA as a surfactant, KOH (to make alkaline solution during reaction) and $NaBH_4$ taken as a reducing agent. It has been shown that increasing the reaction time upto 24 hr with 1.0 M KOH, signature of the formation of nanorod like structure of bismuth telluride with ~100 nm length and ~ 20 nm diamter have been found. Although, varying the concentration of KOH from 0.5-1.5 M, there is only decrease in the estimated particle size from 26-15 nm. These observations suggest that the sequence of introducing reactants into reaction, solvent, additives and reaction parameters (KOH concentration, reaction timings etc.) are playing a vital role in the synthesis of nanostructure bismuth telluride with different size and shape.

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