Investigating Phase Transition and Morphology of Bi-Te Thermoelectric System

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Abstract

The optimization of secondary of secondary phase in a thermoelectric materials can help to improve the efficiency of the material. Being a potential candidate, Bismuth telluride (Bi\textsubscript{2}Te\textsubscript{3}) nanoparticles were synthesized via different routes and profiles to optimize its pure single phase. Systematic characterizations were performed with the help of X-ray diffraction, Rietveld refinement, Field effect-Scanning electron microscopy (FE-SEM) for structural and morphological behavior. Rietveld refinement in XRD-data of the samples revealed that only a small amount (∼1.6\%) of Bi\textsubscript{2}Te\textsubscript{3} was formed in co-precipitation method, while hydrothermal technique increases this phase with increment in synthesis duration. This work focussed on the phase evolution of Bi\textsubscript{2}Te\textsubscript{3} with increasing synthesis duration time at constant temperature. XRD Rietveld refinement revealed that 84\% pure phase was obtained when sample is synthesized at 150 °C for 48 hours by hydrothermal technique. FE-SEM and Energy Dispersive X-ray (EDX) analysis also indicated that impure phase is decreased along with atomic percentage of oxygen from 37\% to 11\% in hydrothermally synthesized sample. The detailed analysis has generalized the growth mechanism in Bi\textsubscript{2}Te\textsubscript{3} phase evolution by the diffusion of Bi into Te nanorods to fabricate hexagonal Bi\textsubscript{2}Te\textsubscript{3}.

Keywords: Thermoelectric(TE), Energy Harvesting, X-ray diffraction pattern, Rietveld refinement, Bi\textsubscript{2}Te\textsubscript{3}, Phase evolution

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1. Introduction

The world is currently facing environmental issues related to clean energy [1]. The consumption of fossil fuels induces worldwide energy exhaustion which lead to atmospheric pollution, ozone depletion, global warming etc [2]. This encouraged researchers to explore renewable and natural energy sources. A possible source of energy to meet the energy demand is the conversion of waste heat (household or industrial scale) into electricity. Researchers have recently attempted to make use of heat energy generated at garbage incinerator and for that they have installed a 60 W module at the boiler section where temperature variation was from 823 to 973 K and an efficiency of 4.4% was achieved with adequate cooling system [3]. The thermoelectric (TE) technology has been seen as the potential solution because of its ability to utilize waste heat into useful electric energy (by virtue of seebeck effect) without emission of any green house gases. Furthermore, the absence of any moving parts makes this technology vibration and noise free [4]. The thermoelectric performances of devices depend upon device design and selection of material [5]. The efficiency of thermoelectric device is further represented in terms of figure-of-merit given as

\[ ZT = \frac{\sigma S^2 T}{\kappa} \] (1)

where \( S, \kappa \sigma \) represents Seebeck coefficient, thermal conductivity and electrical conductivity, respectively [6]. These parameters are interdependent with each other which makes manipulation of high figure of merit a bit difficult to achieve. Generally, \( \sigma \) and \( S \) vary reciprocally, so the increment of TE power factor (\( \sigma S^2 \)) above the particular optimum value for bulk materials is not feasible.

The material’s total thermal conductivity(\( \kappa \)) is a combination of thermal conductivity due to charge carrier(\( \kappa_c \)) and phonons(\( \kappa_l \)) present in the material. The thermal conductivity due to charge carrier of a material is calculated from the equation \( \kappa_c = L_o \sigma T \), where \( L_o, \sigma \) and \( T \) be Lorenz number, electric conductivity and temperature, respectively. The value of \( \kappa_l \) can simply be calculated from the difference of total \( \kappa \) and \( \kappa_c \). To decrease the thermal conductivity one can either decrease the thermal conductivity due to charge carriers or phonons. But, decreasing the \( \kappa_c \) part will also lead to reduction in \( \sigma \), as \( \kappa_c \) is directly proportional to the \( \sigma \). So, one has to concentrate...
on reducing the $\kappa_l$ to obtain a high figure of merit [7]. Various strategies have been adopted to control these parameters such as phonon glass electron crystal (PGEC) [8], doping, energy filtering, multiple band conduction mechanism and convergence of electric bands [6, 9]. The idea behind these processes is the reduction of $\kappa_l$, either by scattering or blocking of phonons motions present in the material. Nanostructuring is a revolutionary step which made achievement of $ZT$ value up to 2 (two) possible as compare to $ZT < 1$ for bulk material, due to their enhancement of electrical and mechanical properties [10–13]. Nanostructuring also leads to the blocking of phonons, which results into the reduction of the $\kappa_l$ of the material. Nanotubes structures which are having low dimension and spacious cages, reduces the $\kappa_l$ by both blocking and strongly scattering the phonons through the cage like structures [14]. The nano thermoelectric materials with a a fine grain sizes and variety of morphologies such as nonorods, nanosheets, nanoparticles, sheet rods can be obtained by simple but effective synthesis method i.e. Solvothermal or Hydrothermal method. The variables reaction parameters such as temperature, pressure, reaction time, solvent used, concentration of reacting species etc. can be used to attain different size, morphology, to attain a desired thermoelectric properties of the materials.

Solid solution alloying is also process used to increase the $ZT$ of thermoelectric material. The idea behind the improvement of $ZT$ by solid solution alloying is to decrease the lattice thermal conductivity of the system, without altering its electric properties. Alloying in the materials, gives the short range distortions, which remarkably increases the phonons scattering. Since, the charge carriers have a longer wavelength than that of phonons, therefore these short range distortions does not affects the scattering of charge carriers [15]. But the disadvantage of this synthesis process over hydrothermal or solvothermal processes is that it is performed at a higher temperature ,while hydrothermal or solvothermal processes are relatively performed at a low synthesis temperatures.

With the generation of electricity by using thermoelectric generator(TEG), other energy sources like biomass, solar, geothermal, infrared radiation have gained increased utilization in thermoelectric based systems. Various attempts have been made to utilization TE generators in cogeneration systems to improve overall efficiency of the system [16–19]. In order to make advanced TE materials, the main challenge is to make a balance between the $ZT$ and power factor [4]. The commercial application of thermoelectric materials is very limited because of their low efficiency, which makes
TE materials incompetent with refrigeration and conventional power generation. To compete with conventional power sources, novel thermoelectric materials needs to increase in efficiency.

Various electronically conducting polymers consisting carbon nanomaterials and nanocomposites, has also being developed, in order to achieve high ZT value and lightweight thermoelectric devices \(^{20}\).

1.1. Bismuth Telluride as Thermoelectric material

The compound of Bismuth telluride (Bi$_2$Te$_3$) has been under intensive study due to its distinctive properties and TE application at room temperature. Bismuth telluride is one of the simplest and commonly available low-temperature thermoelectric material. It was first proposed in 1954 \(^{21}\). Both bismuth and tellurium have high atomic weight therefore it has high density at grain boundaries. This results in selective diffraction of phonons by highly dense grain boundaries and eventually leads to the reduction of $\kappa$ \(^{22}\). The crystal structure of Bi$_2$Te$_3$ consists of hexahedral-layered structure with 5 atomic layers stacked by van der walls interaction along with the c-axis of the unit cell. Bismuth telluride is a narrow band gap of 0.15 eV \(^{23}\) and low melting temperature at 585 °C \(^{24}\). In Bismuth telluride, the charged carriers may be holes or electrons, which gives the $p$- type or $n$- type characteristics to it. Charged carrier concentration in Bi$_2$Te$_3$ could be controlled generally by the doping of elements such as Cadmium, elements of Carbon & Nitrogen Families (Sn, Pb, As, Sb and Bi), etc. Doping of Bi, Pb, Sb$_2$Te$_3$, Te, Se results into $p$-type Bismuth telluride, as these are acceptor impurities that adds holes in the system, while the addition of compounds halides of Cu or Ag(CuBr, AgI, CuI etc.) as a donor impurities results into the $n$-type Bi$_2$Te$_3$ \(^{15}\).

1.2. Interdependence of Thermoelectric Properties of Bismuth Telluride

The relationship between Seebeck Coefficient and conductivity for Bi$_2$Te$_3$ is same as that of expected. At the higher conductivity, due to the Onset of degeneracy, the Seebeck Coefficient decreases, while at the lower conductivity range this decrease of Seebeck coefficient is more rapidly because of intrinsic conduction. At a particular value of conductivity, the Seebeck Coefficient for $n$-type Bi$_2$Te$_3$ is greater than for $p$-type Bi$_2$Te$_3$, mainly in the degeneracy region \(^{15}\).
The Seebeck Coefficient depends upon the density of state and the carrier mobility, and the carrier mobility of electrons is more than that of holes in the degeneracy region, while for electrons density of state is lesser than that of holes. So, the net value of Seebeck coefficient is almost same for both $n$-type and $p$-type, but, $p$-type Bi$_2$Te$_3$ shows lower electrical conductivity, that is because in some cases, excess of Bi present in the system adds degeneracy region, which decreases the mobility of holes, so the Seebeck coefficient and electric conductivity value is lesser for the $p$-type Bi$_2$Te$_3$ [15].

The thermal conductivity and electric conductivity of a material depends directly upon the concentration of charge carriers, so, the minimization of charge carriers results into the decrease in the thermal as well as the electric conductivity. The only factor which can decrease the thermal conductivity without having any negative affect on the other parameters is the decrease in thermal conductivity due to the phonons by scattering of phonons. phonons are simply the lattice vibrations, which when couples with each other or with any structural defects leads to a term called “Scattering of phonons”. The lattice thermal conductivity of the material also alters by the presence of secondary phase. The $n$-type Bi$_2$Te$_3$ which contains halide impurities, exhibits a better coupling between halide impurity and Bi$_2$Te$_3$ lattice, which may leads to better dispersion of lattice vibrations, which in quantum terms called ‘more scattering of phonons’, and therefore leading to smaller thermal conductivity than $p$-type Bi$_2$Te$_3$ [15]. Their are many ways to decrease the lattice thermal conductivity of thermoelectric material, one of such way has been studied by Venkatasubramanian et al. [25] and Yim et al. [15] by studying the Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice structure which have lower lattice thermal conductivity because of more scattering of phonons in the supercrystal lattice system. Since both the parameters Seebeck Coefficient and thermal conductivity depends upon the electric conductivity, so electric conductivity must be closely controlled to get high ZT value. The investigation of ZT versus electric conductivity by Yim et al. [15],shows that maximum value of ZT for Bi$_2$Te$_3$ by is obtained at electric conductivity nearly 1000 ohm$^{-1}$cm$^{-1}$, With doping this value can be maximum value of ZT and electric conductivity can also be changed. For $p$-type Bi$_2$Te$_3$ (Bi or Pb in excess) maximum ZT value at lower conductivity ($Z_{\text{max}} = 2.2 \times 10^{-3}$ deg$^{-1}$ at 900 $\Omega^{-1}$cm$^{-1}$) than that at higher electric conductivity for $n$-type material (CuI doped Bi$_2$Te$_3$) ($Z_{\text{max}} = 2.6 \times 10^{-3}$ deg$^{-1}$ at 1100 $\Omega^{-1}$ cm$^{-1}$) [15].
1.2.1. *Morphology dependence*

The morphology (superlattices, nanowires, nanotubes etc.) of a system depends upon synthesis technique, route and reactions conditions followed [26, 27]. Bismuth telluride is prepared by various processes like mechanical alloying and hot pressing, powder extrusion sintering, chemical alloying, solvothermal synthesis, hydrothermal methods, wet chemical techniques and laser ablation in solution [28–33].

The morphology affects the transport property of the system and the increase in synthesis temperature may lead to agglomeration of the tiny particles and form a plate or wafer like structure. The value of $\sigma$ and $\kappa$ decreases as morphology of sample alters from small dimensional particle to higher dimensional plates [26].

Researchers have followed different routes to control the morphology and phase formation in Bi$_2$Te$_3$ system. Synthesis routes have been discussed in the section with main focus on hydrothermal method because of its ability to control the shape and size of synthesized materials. One of such attempts include formation of disc like structure with diameter 74.1 nm by Yokoyama *et al.* using hydrothermal method [28]. No impurity peak was observed in the system and hydrolyzed dehydroascorbic acid was proposed as an excellent oxidation resistant capping agent. On contrary to this, two groups Yang *et al.* [34] and Kim *et al.* [35] initially synthesized Te nanowires and used it as reagent template for further synthesis of Bi$_2$Te$_3$ nanowires. Zhang *et al.* [36] doped La-atoms into the lattice of Bi$_2$Te$_3$ by using bismuth chloride, lanthanum chloride and Te powder as initial precursors and sodium borohydride and sodium hydroxide as reducing agent and pH balance respectively. Y. Feutelais *et al.* [37] studied the different phases in the Bi – Te system. A new phase with Bi$_8$Te$_9$ composition was found platelet-like hexagonal crystals with parameters a = 4.41Å. The average distance between two consecutive atom's layer was 2Å. The Bi$_8$Te$_9$ can be considered to be made up from 51 layers of atoms i.e. 27 Te and 24 Bi. M. M. Rashad *et al.* [32] synthesized bismuth telluride via solvothermal process in the presence of different organic modifiers and sodium hydroxide was used as alkali modifier. Bismuth nitrate pentahydrate and ethylene glycol was used for making Bi precursor solution. Also tellurium oxide, ethylene glycol was used to synthesize Te nanopowders. Hydrazine hydrate was used as a reducing agent. No extra peaks in XRD pattern indicated the formation of pure rhombohedral of Bi$_2$Te$_3$ crystal structure.
(JCPDS 01-082-0358). Also it showed that crystallite size increased from 26.8 nm to 32.5 nm by the addition of NaOH. Bi$_2$Te$_3$ nanorods of 35-70 nm in diameter were observed in SEM images. The morphology of nanoparticles was converted to nano-circular sheets with a high homogeneity due to the presence of NaOH as it increases the alkalinity which further increased the solubility of TeO$_2$.

Q. Zhao et al. [38] facilely synthesized low-dimensional structured Bi$_2$Te$_3$ nanocrystals with various morphologies by using Bismuth Chloride(BiCl$_3$), Tellurium(Te), Sodium-dodecyl-benzene-sulfonate (SDBS) or polyvinyl-pyrrolidone (PVP) as surfactants. The powder was synthesized at 373 K. NaBH$_4$ as a reductant and NaOH as a pH controller was used for the experiment. The XRD pattern was indexed using datasheet of hexagonal Bi$_2$Te$_3$ and indicated pure phase formation of Bi$_2$Te$_3$ nanoparticles. SEM images displayed irregular flakes with size ranging from 60-400 nm. TEM images showed that there was Bi$_2$Te$_3$ nanotubes of length 700 nm and diameter 45-64 nm. Also Bi$_2$Te$_3$ needle-shaped nanowires of length 2 µm and a diameter of 50 nm were in good agreement with SEM images. S. Gupta et al. [39] synthesized Bismuth Telluride nanostructures at different concentration of KOH (0.5 - 1.5 M) and for different reaction timings via refluxing method using Bismuth Chloride(BiCl$_3$), Tellurium powder, Ethylenediaminetetraacetic acid (EDTA), Potassium hydroxide (KOH), Sodium borohydrid (NaBH$_4$) in inert gas atmosphere (Ar gas). It was understood from XRD pattern that sizes of nanoparticles were inversely proportional to the concentration of KOH which is in well agreement with TEM images. It was also observed that increased reaction time leads to the rod-like formation of bismuth telluride nanoparticles which is a good result. B. Zhao et al. [14] has synthesized the rhombohedral Bi$_2$Te$_3$ nanotubes by hydrothermal method at 150°C from Bismuth chloride, Tellurium powder, EDTA, sodium borohydride and sodium hydroxide as reducing agent and pH balance respectively. These nanorods reduces the $\kappa_t$ by efficiently blocking the phonons, and gives higher ZT value as compared to the zone melted Bi$_2$Te$_3$ samples. The thermoelectric properties of quantum dots was inspected by E. E. Foos et al. [40] by synthesizing Bi$_2$Te$_3$ with particle size less than 10 nm using bismuth perchlorate oxide hydrate and sodium dioctylsulfosuccinate (AOT), trioctylphosphine (TOP) in the presence of nitrogen gas. Also deionized water, absolute ethanol, toluene and hexane were purged into N$_2$ gas. XRD pattern showed broad peaks at 27.80 °C which corresponds to
bismuth telluride peak. The average particle size measured from TEM images was 4.5 nm. This method minimized the need for special equipment, handling and reagents. Table 1 discusses the pure phase formation of Bi$_2$Te$_3$ nanoparticles using different reducing agents at different reaction temperature. Morphology and dimensions of the nanoparticles also have been mentioned for above discusses papers.

Table 1: Different reducing agents, reaction temperature, morphology and dimensions of the nanoparticles.

| Sample Code | Reducing agent | Reaction Temp. | Particles morphology | Particles dim. | Refs. |
|-------------|----------------|----------------|----------------------|----------------|-------|
| a.          | Ascorbic acid  | 30-70 °C       | Plates or wires      | L = 2.0µm, D=10 nm | [41]  |
| b.          | Hydrazine      | 160°C          | Rods                 | -              | [42]  |
| c.          | Hydrazine      | 160°C          | 1D nanowires         | L=3-5µm, D=200-300 nm | [38]  |
| d.          | Sodium         | 480 K          | Flowers and petals   | D = 30nm       | [43]  |
| e.          | Hydrazine      | Room temp. & annealed at 300°C | Irregular | D=30 nm | [44]  |
| f.          | Hydrazine      | 423 K          | Rods                 | L=1.0-2.0µm, D=80-150 nm | [28]  |
| g.          | Sodium         | 353 K          | Needle shaped nanowires | L=2-3µm | [45]  |
|             |                |                |                      | D=less than 100 nm |       |
|             |                | 373 K          | Flower               | L=2µm, D=50 nm |       |
|             |                | 473 K          | Flakes               | -              |       |

Apart from this, Morphology and inhomogeneities greatly affects the thermoelectric properties of a semiconductor. This inhomogeneities in the materials depends upon the particular growth
conditions during the synthesis process of material. Homogeneity in the crystal results into good carrier mobility, and a higher electrical conductivity. Slower the growth rate results into a greater homogeneity of the material. As the growth rate of formation of the $\text{Bi}_2\text{Te}_3$ increases, both $n$-type and $p$-type, the seebeck coefficient increases and total thermal conductivity and thermal conductivity due to phonons decreases. Variation in electric conductivity with growth rate doesn’t shows same trend for $n$-type and $p$-type $\text{Bi}_2\text{Te}_3$. As the growth time decreases the electric conductivity for $n$-type $\text{Bi}_2\text{Te}_3$ increases, while for $p$-type $\text{Bi}_2\text{Te}_3$ it decreases. The $n$-type $\text{Bi}_2\text{Te}_3$ is generally a single phase material, but in $p$-type alloy because of formation of a discontinuous phase, the electric conductivity is decreased. The exception of decrease in electric conductivity is reported by Cosgrove et al. [46] who showed that increase in the electric conductivity of $p$-type $(\text{Bi}_2\text{Te}_3)_{50}(\text{Sb}_2\text{Te}_3)_{48}(\text{Sb}_2\text{Se}_3)_{2}$ with decrease in growth rate. In this work, no discontinuous phase is detected but instead a $n$-type region in the $p$-type matrix had founded. $p$-type $\text{Bi}_2\text{Te}_3$ have phase boundaries due to the presence of the two phases, this results for the scattering of phonons from the phase boundaries, which increases the thermal conductivity. These is two phases exists in $p$-type, even after it is prepared under most ideal conditions. So, the thermal conductivity due to phonons is almost independent of the growth rate.

Thus, slower growth rate results into a higher figure of merit. Annealing of the sample results into the elimination of extra phases present in the sample, and gives a more homogeneous phases, which enhances the thermoelectric properties of the sample and increases the $ZT$ value.

### 1.2.2. Axial dependence of $ZT$

Bismuth Telluride exhibits anisotropic thermoelectric properties. The atoms of Bi and Te in the crystal structure of $\text{Bi}_2\text{Te}_3$, are arranged in a fixed alternating sequence in the parallel layers which is repeated continuously as shown in Fig. 1. Bi and Te layers are held together by covalent bond

![Figure 1: Bismuth Telluride structure along c-axis.](image)
along the c-axis, whereas the adjacent Te-layer are held together by weak van der wall bonds. In Bismuth telluride crystals, there are two axes inclined at 60° to each other which are perpendicular to the c-axis. The electrical and thermal conductivities are higher parallel to the cleavage planes than perpendicular to them [22]. The electric conductivity of Bi₂Te₃ along (111) plane is 3 or 4 times greater than plane perpendicular to it, at room temperature. Thermal conductivity due to phonons along (111) plane is two times larger than the plane perpendicular to it. In exception to this, Seebeck coefficient is generally isotropic throughout the material. This results into a higher ZT value along (111) plane of Bi₂Te₃ and its alloys because of the higher charge mobility along this plane [15]. In recent times, many experiments had been performed to improve the efficiency of thermoelectric materials through the development of bismuth telluride nanostructure.

Upadhyay et al. [47] had investigated the effect of change in the synthesis conditions on phase, morphology and electric properties of CoSb₃ system synthesized by solvothermal process and had successfully optimized the impure phase upto a greater extent with the increase in synthesis time. This lead us to study the effect of synthesis condition on formation of phases in Bi-Te system and morphology of Bi₂Te₃. The phase-evaluation of co-precipitation and hydrothermally synthesized samples have also been discussed.

2. Experimental Details

Bi₂Te₃ nanoparticles were synthesized by two different methods i.e. hydrothermal and co-precipitation using analytical grade precursors procured from Sigma Aldrich and Merck.

2.1. Chemicals/materials

For hydrothermal method: Bismuth chloride [BiCl₃], Tellurium dioxide [TeO₂], Hydrazine monohydrate [N₂H₄·H₂O], Sodium borohydride [Na(BH₄)], Ethanol [C₂H₅OH]. For Co-precipitation method: Bismuth nitrate pentahydrate [Bi(NO₃)₃·5H₂O], Nitric acid [HNO₃], Tellurium dioxide [TeO₂], Ammonia solution [NH₃], Hydrazine monohydrate [N₂H₄·H₂O], Sodium borohydride [Na(BH₄)] and Ethanol [C₂H₅OH]. Chemicals like [Bi(NO₃)₃·5H₂O], [TeO₂] and [N₂H₄·H₂O] are mildly toxic, so need to be handled carefully. All chemicals were used as received during the experiment.
2.2. Co-precipitation synthesis of Bi$_2$Te$_3$ nanocrystals

In this method, nanocrystals of Bi$_2$Te$_3$ were synthesized using [Bi(NO$_3$)$_3$·5H$_2$O] and [TeO$_2$]. For this synthesis technique, three solutions were prepared. In first solution, 0.1 mole of bismuth nitrate pentahydrate was dissolved in 30 ml water and 6-8 ml of HNO$_3$ was slowly added to it as the compound is insoluble in water. Then it was left for stirring at 200 rpm for 20 minutes until a clear solution was obtained. For second solution, 0.75 mole of TeO$_2$ was dissolved in 25 ml ammonia. 5 ml hydrazine hydrate was added to it as a reducing agent and was stirred at room temperature for 20 minutes. After that solution 1 was slowly added to solution 2 with continuous stirring at room temperature at 250 rpm for 1 hour. To prepare the third solution, 0.1 mole of sodium borohydrid i.e. Na(BH$_4$) was quickly dissolved in 50 ml water to obtain clear solution. Then it was transferred into a separators funnel and was slowly added to the initial mixture in the presence of N$_2$ gas. This lead to the formation of black precipitates and was stirred at 250 rpm for 1 hour. The obtained precipitates were washed three times with ethanol and three times with acetone to purify the product. The precipitates thus obtained were dried in two steps: (1). at room temperature for 16 hours (2). at 60°C for 24 hours in an oven. The dried precipitates were grinned in porcelain mortar to obtain fine powder.

Next step was to remove additional phases by reduction with hydrazine hydrate. For this, 2 grams of above obtained sample was transferred into the flask and were heated in the presence of N$_2$ gas. 30 ml of hydrazine hydrate was transferred into another flask and both flasks were connected to each other. Hydrazine temperature was 80°C and powder temperature was 300°C. After this the sample was reduced to 1.8 grams. The schematic drawing of the recommended co-precipitation process is shown in Fig. 2. The obtained sample was further annealed in N$_2$ atmosphere at 300°C. The as prepared sample and annealed samples were labeled as S1 and S4 respectively.

2.3. Hydrothermal synthesis of Bi$_2$Te$_3$ nanoparticles

This route for producing Bi$_2$Te$_3$ nanocrystals of pure phase using materials BiCl$_3$ and TeO$_2$ is simple, convenient and cost effective. In this method, 0.1 mol of BiCl$_3$ and 0.15 mol of TeO$_2$ were dissolved in 20 ml deionized water. Then NaBH$_4$ in deionized water was slowly added to

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Bi precursor solution. Also $\text{N}_2\text{H}_4$ was added to Te precursor solution. Both solutions were mixed and stirred for 10 minutes. It was then transferred to Teflon container and sonicated for half an hour. Furthermore, it was sealed in autoclave at 150 °C for 24 hours. It was allowed to cool down naturally at room temperature. Then it was filtered using filter paper to remove NaCl impurity and transferred into the crucible. The crucible was kept in oven for drying at 80 °C for 24 hours. The obtained sample was crushed using pastel and mortar and was stored in the storage tube and named as H1. Similarly two more samples were prepared by changing time from 24 hours to 36 hours and 48 hours. The schematic drawing of the recommended hydrothermal process is shown in Fig. 3. The samples were labeled as H1, H2 and H3 for 24, 36 and 48 hours, respectively hydrothermally synthesized.
2.4. **Characterization**

The X-ray diffraction (XRD) on the samples were performed using Rigaku equipped with Cu Kα radiation (1.5404 Å) from 10-80° with a rotation speed of 5°/min. Rietveld refinement technique was performed using X'pert HighScore Plus to overcome the constraint of overlapping reflections. The morphology and elemental analysis on the sample were accomplished employing field emission scanning electron microscope (FESEM) and energy dispersive spectroscopy (EDS) using HITACHI, SU8010. The data is handled and analyzed using different softwares like HighScore 3.0.5(Rietveld refinement), Origin 8.5(XRD), ImageJ(FE-SEM) etc.

3. **Results and Discussion**

3.1. **XRD and Rietveld Refinement**

Figure 4(a) represents the XRD of the samples synthesized through different methods and profiles. The XRD of S1 shows no peaks corresponding to Bi₂Te₃. This might be because the reaction has not attained the optimum conditions required for the formation of Bi₂Te₃ phase. On the other hand, S4, H1, H2 and H3 reveals peaks related to Bi₂Te₃ along with peaks of other impurity phases. The phases present in the sample are Bi₂Te₃, BiTe, Bi₄Te₃ and TeO₂ represented by *, #, $ and ♦ respectively. Some additional unidentified peaks are also obtained in the sample. The indexing of Bi₂Te₃ was performed with reference code 00-015-0863, BiTe by [01-083-1749], Bi₄Te₃ by [00-033-0216] and TeO₂ by [00-042-1365].

As in the enlarged image of XRD from Fig. 4(b to d), the major Bi₂Te₃ planes formed are (101), (015), (1 0 10), (110), (311), (412), (654). Among those, the highest intensity peak of (015) plane is present in H1, H2 and H3 samples at 2θ = 27.66°, indicates the presence of Bi₂Te₃ phase. This peak is absent in S1 and S4 sample which are prepared by co-precipitation method.

Although, the peak of (101), (1 0 10) and (110) plane of Bi₂Te₃ phase at 2θ = 23.68°, 2θ = 37.834° and ,2θ = 41.148°, respectively are missing in S4 sample and there intensities are increases from H1 to H3. This implies, Bi₂Te₃ phase is formed maximum in case of H3 sample.

The impurity peaks of Bi₄Te₃, are majorally formed at 2θ values of 23.460°, 27.516°, 40.491°, representing (0 1 2), (1 0 7) and (1 1 0) planes, respectively. The intensity of the peak representing
(0 1 2) plane of Bi$_4$Te$_3$ increasing from S4 to H2 system, and than decreases for H3 sample. Similarly, the peak of [1 0 7] plane of Bi$_4$Te$_3$ at 27.516° is more intense for H2 then S4 system, and is absent in H1 and H3 samples. For H3 system the other intense peaks of Bi$_4$Te$_3$ (1 1 0) and (1 0 28) planes are at 40.491° and 67.061°.

The peaks of Bi$_4$Te$_3$ impurity phase is most intense for H2 sample among all the samples prepared. Bi$_4$Te$_3$ structure consists of Bi$_2$ blocks stacked by Bi$_2$Te$_3$ blocks and due to the presence of excess of Bi in the form of Bi$_2$ blocks along with Bi$_2$Te$_3$, this makes it a $p$-type material [48].

The BiTe phase is another impurity found in the XRD data of the samples. BiTe impurity peaks are found at 2θ = 27.594°, 32.305°, 38.022°, 43.580°, 51.418°, 65.980° and 67.612° 2θ values representing (1 0 4), (1 0 6), (0 1 8), (1 1 4), (1 0 12), (0 0 17) planes, respectively. Among all these different phases, the peak representing (1 0 4) plane is most intense peak and is found for H1, H2 and H3 samples. At 2θ = 38.022°, the (0 1 8) plane of BiTe is present in all the samples with H2 having most intense peak. At 32.305° only the H2 sample is having BiTe peak.

This impurity is mostly found in S4 samples with impurity peaks at 2θ = 65.980° and 67.612°.

Apart Bi-Te phases, some of the TeO$_2$ has also been found possibly during the drying stage. The XRD peaks at 39.263°, 64.104°, 74.823° and 75.448° are representing TeO$_2$ phases. These peaks are generally of low intensity. The only peak of TeO$_2$ phases at 2θ = 39.263° is having appreciable intensity and represents the (201) plane of TeO$_2$ phase.

To get a better picture of the amount of distant phases present, we performed Rietveld refinement on the synthesized samples. Fig. 4 represents the Rietveld refinement of the samples. It can be seen from Fig. 5(a) pie chart, that only 1.6% of Bi$_2$Te$_3$ was formed with 67% of TeO$_2$ as impurity. On contrary to co-precipitation synthesized sample, the hydrothermally synthesized samples H1, H2 and H3 showed an drastic increase in the amount of Bi$_2$Te$_3$ phase from 44.7%, 75.8% to 84% respectively. The amount of TeO$_2$ decreased from 7.4%, 0.3% to 0.1% for H1, H2 and H3 respectively, can be referred form Figs. 4(b), (c) and (d). It can be concluded from the Table 3.1 that by switching the synthesis route and with incrementing the synthesis duration, the lattice parameter is decreased and amount of Bi$_2$Te$_3$ is increased. Also, the variation in TeO$_2$ phase indicates that increasing the synthesis duration might have decreased the amount Te impurity which eventually led to the formation of TeO$_2$ during the drying process. Thus we predict
that if we further increases the synthesis duration, a pure phase of Bi$_2$Te$_3$ sample can be attained.

Table 3.1 and 3.1 lists the refinement parameters, refined cell parameters and amount percentage of different phases. Table 3.1 reveals that the refinement parameters and GOF for different samples were satisfactory in regards to refinement criteria.

### 3.2. FE-SEM and EDX

Figure 6 shows the FESEM micrographs and EDX of the prepared samples. Figure 5(a) reveals that most of the particles are formed in 200 to 250 nm range. The nanorods of TeO$_2$ was found to be $663 \times 138$ nm, calculated from ImageJ software. Similarly, H1 showed presence of nanorods with $0.9 \times 1.9 \mu$m dimensions. This is due to the formation of TeO$_2$ during drying stage as predicted in the previous section, no such rods were observed in H2 and H3 micrographs as the amount of TeO$_2$ was only 0.3% and 0.1% respectively. It can be seen in the micrographs of H2 and H3 that the
samples consists of irregular hexagonal nanocrystals also that the bigger flakes become larger and thicker with increase in reaction time while smaller flakes disappears. This can be explained by Gibbs-Thompson effect, the small crystals reduce in size, ions and atoms combines to form large crystal with low free energy to form a stable system. The dimensions of the hexagonal crystals are labeled in the figures. The EDX of the samples supports the observation from XRD, Rietveld refinement and FE-SEM about the formation of impure phase. It can be seen from Figs. (e),(f), (g) and (h) that amount of oxygen decreased from 37% (in S4 sample) to 11% (in H3 sample). In
Table 3: Value of lattice parameter and percentage of each phase obtained from Rietveld refinement.

| Sample/phase | S4      | H1      | H2      | H3      |
|--------------|---------|---------|---------|---------|
| Bi₂Te₃       | a       | 4.3867  | 4.3836  | 3.383   | 4.382   |
|              | c       | 30.491  | 30.462  | 30.457  | 30.474  |
|              | %       | 1.6     | 44.7    | 75.8    | 84.0    |
| Bi₄Te₃       | a       | 4.4590  | 4.4574  | 4.455   | 4.454   |
|              | c       | 41.40   | 41.496  | 41.465  | 41.458  |
|              | %       | 30.8    | 47.2    | 23.6    | 6.8     |
| BiTe         | a       | 4.423   | 4.4222  | 4.4252  | 4.458   |
|              | c       | 24.02   | 23.980  | 24.07   | 23.81   |
|              | %       | 0.4     | 0.7     | 0.3     | 9.1     |
| TeO₂         | a       | 5.08    | 4.918   | 5.504   | 8.26    |
|              | b       | 8.38    | 8.777   | 11.77   | 4.87    |
|              | c       | 4.19    | 4.295   | 5.585   | 3.38    |
|              | %       | 67.1    | 7.4     | 0.3     | 0.1     |

Figure 6: FE-SEM and EDX image of (a)S4; (b)H1; (c)H2 and (d)H3

In our experiment, when hydrazine is added to mixed solution of Tellurium dioxide and de-ionized water, under the condition that the thermodynamic energy is appropriately supplied, homogeneous
Te nanorods can be obtained through the following reaction process:

\[
TeO_2 + 2N_2H_2 \cdot H_2O \rightarrow Te + 4H_2O + 2N_2
\]  

(2)

The net reaction involved in this process can be presented as follows:

**Co-precipitation**

\[
Bi(NO_3)_3 + NaBH_4 \rightarrow Bi^{3+} + NaNO_3 + BH_3 + H_2
\]  

(3)

**Hydrothermal**

\[
BiCl_3 + H_2O \rightarrow BiOCl + 2HCl
\]  

(4)

\[
3NaBH_4 + 4HCl + 8BiOCl \rightarrow 8Bi + 8H_2O + 4HCl + 3NaCl + 3BCl_3
\]  

(5)

\[
2Bi + 3Te \rightarrow Bi_2Te_3
\]  

(6)

(7)

BiCl\(_3\) selected as the Bi source is immediately hydrolyzed to form BiOCl and HCl when distilled water is added to it. NaOH is added to neutralize the acidic environment because the generation of HCl induces an acidic liquid system. In the transformation process from Te nanorods to Bi\(_2\)Te\(_3\) nanorods, Bi\(^{3+}\) ions are reduced to Bi atoms by NaBH\(_4\) and then diffused into the lattice of Te nanorods to generate hexagonal Bi\(_2\)Te\(_3\). The study to obtain a pure phase TE material is important as presence of impurity phases may introduce two type of types of conduction (i.e. electrons and holes). This will eventually lead to uncertainty in \(\kappa_e\) (electronic thermal conductivity) introduced by bipolar effect and also the seebeck voltage developed across the ends will decrease \([24, 38]\).

4. Conclusion

In summary, alternate methods are adopted for synthesis of pure phase of bismuth telluride as presence of impure phase deteriorate the thermoelectric performance of the material. In our hydrothermally synthesized sample case, we have observed that increasing the synthesis duration resulted in less impure Bi\(_2\)Te\(_3\) phase along with change in morphology of the system. The hydrothermal method is more rapid and efficient for preparation of bismuth telluride than co-precipitation methods. Pure phase of Bi\(_2\)Te\(_3\) has been formed by preparing the sample through this
method which may exhibit enhanced thermoelectric properties whereas additional phases such as BiTe, Bi$_4$Te$_3$, TeO$_2$ were formed in co-precipitation method along with Bi$_2$Te$_3$.

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