Doped Bi$_2$Te$_3$ nano-structured semiconductors obtained by ultrasonically assisted hydrothermal method

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Abstract: Nanocrystalline powders of doped Bi$_2$Te$_3$ with Ag (S1 sample), Sb (S2 sample), Sn (S3 sample) ions with different morphology and particle size 30-50 nm were prepared by a ultrasonically assisted hydrothermal method in alkaline aqueous solution with different concentration of NaBH$_4$ as reducing agent at 200°C for 3 hours and 80% fill degree of autoclave. The influence of dopants and hydrothermal treatment conditions on the formation features, phase composition, particle size, morphology and properties of the products were investigated by X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, atomic force microscopy and electrical measurements. This paper reports a comparative study regarding the dopants influence to the shape and size of nano-structured thermoelectric materials. It was found that hydrothermal processing results in formation of low dimensional dispersion of doped Bi$_2$Te$_3$ nanostructures with desired shape and size and high degree of crystallinity with typical semiconductor behavior.

Keywords: Semiconductors • X-ray diffraction • Atomic force microscopy • Chemical synthesis

1. Introduction

The efficiency of a thermoelectric device is determined by the materials used in making the device, and thus the current focus of research is on finding better materials. The materials with high electrical conductivity, high Seebeck coefficient and low thermal conductivity are needed to achieve good ZT values [1,2]. These are in general low cost materials that have sufficiently strong thermoelectric effects (and other required properties), and could be used for applications including power generation, refrigeration and a variety of other applications. In the power generation case, thermoelectric devices convert heat or in some cases waste heat into useful electricity [3]. Thermoelectric efficiency depends on the figure of merit, ZT. There is no theoretical upper limit for ZT, and as ZT approaches infinity, the thermoelectric efficiency approaches the Carnot limit. Materials with a large thermoelectric figure of merit, ZT, are needed to develop efficient solid-state thermoelectric devices [4]. Recent studies have reported that low-dimensional thermoelectric materials, such as superlattices and nanowires, have a higher ZT due to the quantum confinement effects of charge carriers, as well as the increase of phonon scattering at the nano-scale interfaces.

Currently the materials with the highest thermoelectric figure of merit Z are Bi$_2$Te$_3$ alloys [5]. Therefore these compounds are the best thermoelectric refrigeration...
elements. However, since the 1960s only slow progress has been made in enhancing Z, either in Bi$_2$Te$_3$ alloys or in other thermoelectric materials [6,7]. So far, the materials used in applications have all been in bulk form [8,9]. Also, many works have been done in the past years to improve their figure of merit by making the material nanostructured, by doping this with different ions and making this materials with different shape like nanowire arrays [10,11] and quantum dot super lattice thin films [12,13].

These materials are not suitable for large scale and economical TE applications, where bulk materials are used. In general a simple routine, like solvothermal routine are preferred to synthesize these materials [14,15]. This method enables mass synthesis of materials with designed chemical compositions at a relative low temperature, and with little contamination on the material. There have been some reports of the synthesis of nanostructured Bi$_2$Te$_3$ based TE materials through solvothermal methods [16-20] and hydrothermal methods with different morphology [21]. Metal–organic chemical vapor deposition (MOCVD), in the III–V and II–VI semiconductors industry, was used to elaborate Bi$_2$Te$_3$ thin films [22,23]. Sonochemical route for synthesized Bi$_2$Te$_3$ nanoflakes are also reported [24]. Several ultrasound-assisted synthetic routes have been explored in the production of nanstructured materials, including sonochemistry, ultrasound-induced deposition, sonoelectrochemistry, ultrasound-assisted laser ablation in liquid media, and USP [25-27]. Hydrothermal synthesis offers these facilities by controlling temperature and pressure in synthesis medium. Also, the extreme conditions during sonication can be exploited to prepare nanoscale materials. To improve the electrical properties of Bi$_2$Te$_3$-based materials, doping is a commonly used way to modulate the electrical properties. Researchers have achieved higher figure of merit by using various dopants, including the n-type dopants such as SbL, CuBr, and so on; and the p-type dopants such as Bi, Pb, Te, Sn, Ag and so on [28-30]. For example with an addition of 0.02 wt.% Ag ultra-fine particles, an increase of 20% for figure of merit was achieved for the p-type Bi$_2$Te$_3$-based materials [28].

In this study we report about doped bismuth telluride nanostructures synthesized through ultrasonically assisted hydrothermal method. The influences of precursors and hydrothermal treatment conditions on the formation features, phase composition, particle size, morphology and properties of the products are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM) and electrical measurements.

## 2. Experimental procedure

Analytically pure chemicals (Aldrich) and pure tellurium 5N (Merch) were used for the synthesis of the samples in the present work. Stoichiometric amounts of Bi(NO$_3$)$_3$ and Te powder with Ag NO$_3$ (S1), SbCl$_5$ (S2), SnO$_2$ (S3) as dopants of (99.99%) purity, was mixed in aqueous solution, using NaBH$_4$ as reductant and NaOH as pH regulator. This precursor was mixed and continuously stirred one hour for a better homogeneity and then introduced into a teflonized steel autoclave with an immersed sonotrode.

The synthesis is made under a fill degree of autoclave about 80%, under pH 11, for 3 hours at 200°C under continuous ultrasonication at 100W and 40 KHz (for all samples). Sonication was performed using a power high voltage amplifier (connected to computer via NI USB-6008 (National Instruments)) equipped with an immersion ultrasonic sonotrode, with the tip diameter of 7 mm and made of titanium alloy. The variable power output control allows the ultrasonic vibrations at the probe tip to be set to any desired amplitude and controlled by computer. After the reaction, the autoclave was cooled at room temperature, and the product was filtered, washed with bi-distilled water, and dried at 60°C for 4 hours.

Ultrasoundication process is an important factor in synthesis of Bi$_2$Te$_3$ materials by ultrasonically assisted hydrothermal method [31-33]. Ultrasound shows the main advantage shorter reaction/preparation time; reduction of the sample preparation time; usage of small amounts of materials, efficient and minimum expenditure on solvents, reagents, etc. [34,35]. Ultrasonic techniques when compared with the conventional methods like hydrothermal/solvothermal, co-precipitation, appears to be more effective. Because the efficiency of thermoelectric materials can be tailored by controlling the size and the shape of nanocrystals, the controllable synthesis of nanoscale thermoelectric materials is very important. Hydrothermal synthesis offers this facility by controlling temperature and pressure in synthesis medium. Also the extreme conditions during sonification can be exploited to prepare nanoscale materials.

The phase structures of the prepared samples were investigated by X-ray diffraction (XRD) using PANalytical X’PertPRO MPD Diffractometer with Cu Ka radiation $\lambda = 1.5406$ Å, 26-step of 0.01° from 10 to 100. Scherrer equation, $d = \frac{0.9\lambda}{B \cos \theta}$ was used to estimate grain average sizes of crystallites, where B is the half height width of the reflection peak at 2θ and $\lambda$ is the wavelength of the radiation. Powder morphology was observed using an Inspect S PANalytical model scanning electron microscopy (SEM) and a NanoSurf...
atomic force microscopy (AFM). The semiquantitative elemental analysis was analyzed through EDX facility of SEM. Electrical measurements were performed using an experimental setup for measuring electrical resistivity at different temperatures on pressed sample. To determine the temperature dependence of electrical resistance, both undoped and doped bismuth telluride were assessed using an ohmmeter (to measure electrical resistance) at temperatures between 30°C - 200°C.

3. Results and discussion

3.1. XRD analysis
X-ray diffraction (XRD) analysis (Fig. 1) indicates that sample S1 and S2 of hydrothermally synthesized have a single Bi$_2$Te$_3$ trigonal phase of R$_3$m rhombohedral lattice structure and S3 have a same lattice structure with a small quantity of unreacted tellurium [28]. The broadening of the diffraction peaks indicates that the samples are nanosized. The average grain crystallites sizes estimated with Scherrer equation using the (0 1 5), (1 0 10) and (1 1 0) reflection are about 40 nm for S1, 28 nm for S2 and 35 for S3.

The intensity of XRD patterns of compounds doped different dopants were influenced by the degree of crystallization and dopant type used. By doping materials based on Bi$_2$Te$_3$ with different transition metal ions, the crystal structure of the compounds did not change because the amount of dopant was low (x = 0.1 M).

3.2. SEM and EDX results
Figs. 2a, 2c and 2e present SEM images of the doped bismuth telluride with silver (S1), antimony (S2) and tin (S3), synthesized by ultrasonically assisted hydrothermal synthesis depending on the doping used. It can be seen from Fig. 2a that the hydrothermally synthesized powders show quasi-spherical granule shapes in agglomerated clusters. It can be seen in Fig. 2c that sample S2 contains irregular flakes of about couple of teen’s nm in thickness and a few hundred nanometers in width, randomly disposed. Fig. 2e shows the SEM images of the particles, which are irregular granule shapes and are agglomerated in spongiest structure. EDX analysis (Figs. 2b, 2d and 2f) provide semi-quantitative elemental analysis of the materials surface and confirm the dopants presence in the ratio pursued.

3.3. AFM results
Figs. 3 show the AFM images of surface morphology for S1 (3a), S2 (3b) and S3 (3c). The AFM studies reveal non-uniform surface for the samples. The average grain size for Bi$_2$Te$_3$ results from the analysis of AFM image with Scion Image and fitted with TableCurve software have the maximum at 38 nm for S1, 24 nm for S2 and at 36 nm for S3 in good agreement with dimension results from the XRD pattern. The analysis was performed for about 200 particles. It was found that the dimensional distribution function is LogNormal. The roughness of the bismuth telluride can be quantitatively identified by the root mean-squared roughness (rms) ($R_{rms}$). Roughness is given by the standard deviation of the data from the AFM image, and determined using the standard definition:

$$R_{rms} = \sqrt{\frac{1}{N-1} \sum_{n=1}^{N} (z_n - \bar{z})^2}$$  \hspace{1cm} (1)

Where $z_n$ represents the height of the n-th data, $\bar{z}$ is equal to the mean height of $Z_n$ in AFM topography, and N is the number of the data. For area 1.25 μm$^2$ the average roughness is about 2.1 nm for S1, 1.3 nm for S2 and about 1.9 nm for S3.

Figure 1. XRD patterns for doped Bi$_2$Te$_3$ with S1, S2, and S3, synthesized by ultrasonically assisted hydrothermal method.
3.4. Electrical measurements

Temperature dependence of the electrical resistivity of undoped Bi$_2$Te$_3$ and doped Bi$_2$Te$_3$ with Ag (S1), Sb (S2), Sn (S3) is shown in Fig. 4. It can be seen that electrical resistivity of the investigated samples present an exponential dependence, which indicates that undoped and doped bismuth telluride obtained by ultrasonic assisted hydrothermal method have a typical semiconductor behavior.

In order to determine the band gap, we have measured the temperature dependence (in the range 300-480 K) of the electrical resistivity, which in the case of semiconductor materials is given by the equation (linear form):

$$\ln \rho = \ln \rho_0 + \frac{E_G}{2kT}$$  \hspace{1cm} (2)
Figure 3. AFM image with scan area of 1.13×1.12 µm, dimensional distribution of particle for S1 (3a), S2 (3b), and S3 (3c) synthesized by ultrasonically assisted hydrothermal method.
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The plot of Eq. 2 in $\ln \rho$ and $1/T$ coordinates is a straight line. By fitting the plot of Eq. 2 with the general equation of a straight line, $y = A + Bx$, one obtains the parameters A and B. The band gap $E_g$ of the investigated sample can be computed from the value of the slope, B, resulting in

$$E_g = 2k \times B$$

(3)

The experimental results for the sample S1, S2 and S3 confirm a typical semiconductor behavior with the band gap slightly less than undoped Bi$_2$Te$_3$ (0.150 eV) [36], and 0.135 eV for S1, 0.146 eV for S2 and 0.142 eV for S3 respectively.

4. Conclusions

Materials based on bismuth telluride have been successfully synthesized through ultrasonically assisted hydrothermal method with different dopants (Ag, Sb, Sn). It was found that hydrothermal processing resulted in formation of low dimensional dispersion of Bi$_2$Te$_3$ nanostructures with desirable form and size and high degree of crystallinity.

XRD pattern showed that the particles are crystallized in a single phase, the crystallite sizes being 40 nm (S1), 28 nm (S2) and 35 nm (S3).

The SEM morphology showed various topographies (depending on the doping used) of the powders prepared by ultrasonically assisted hydrothermal synthesis. The SEM analysis shows that the particles have different shape and is strongly agglomerated. EDX analysis confirms the material purity and the dopant presence in pursed ratio.

The average grain size for Bi$_2$Te$_3$ obtained from the AFM analysis was 38 nm for S1, 24 nm for S2 and at 36 nm for S3; the dimensional dispersion had LogNormal distribution and was in good agreement with XRD results.

The electrical measurements results suggest that the materials synthesized through ultrasonic assisted hydrothermal method exhibit typical semiconductor behavior.

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