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Review Article

REVIEW OF THE BISMUTH TELLURIDE (Bi_2Te_3) NANOPARTICLE: GROWTH AND CHARACTERIZATION

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Abstract

In this paper, a review of Bismuth Telluride (Bi_2Te_3) nanoparticle growth and its characterization at nanoscale are discussed through a theoretical and analytical process. Nanotechnology research has become challenging task for modern science and technology. Material of Bi_2Te_3 is basically known for thermoelectric generation. Now in nanotechnology, all devices are migrating to the level of nanometer scale, the significant amount of experiments are being progressed to keep it up with the rapidly growing research field of nanotechnology. For these reasons, the characterization of Bi_2Te_3 at nanoscale is investigated and its application as a thermoelectric generator (TEG), thermoelectric cooling (TEC) and other field of material technology is presented. Finally, it is concluded that Bi_2Te_3 nanoparticles have many future aspect and applications.

Keywords- *Bismuth Telluride (Bi_2Te_3); Nanotechnology; Nanoparticle; Thermoelectric Generator*.

1. Introduction

This review paper presents an overview of the remarkable research progress on Bismuth Telluride (Bi_2Te_3) nanoparticle growth by solvothermal process. Bi_2Te_3 basically is a compound element of Bismuth (Bi) and Tellurium (Te). Bi physically behaves like a metal and when it is alloyed with Te then it behaves like an efficient thermoelectric type material which can be used for thermoelectric refrigeration, thermoelectric cooling (TEC) and other field of material science such as thermal sensor, thermoelectric generator (TEG) etc. [1-4].

Bi_2Te_3 and its alloys are most important semiconductor thermoelectric materials that used in state-of-the-art devices which temperature range between 200 and 400 K. The figure of merit, $ZT = (\alpha^2\sigma/\kappa)\,T$, of the best Bi_2Te_3 based alloys is about unit [5], where α is the Seebeck coefficient, σ and κ the electric and thermal conductivity, respectively.

Many works have been done in recent years to improve the thermoelectric properties of Bi_2Te_3 based alloys. It was reported that the figure of merit of thermoelectric materials could be significantly improved if the materials were nanostructured [6]. In the present work, we discussed the review of the Bi_2Te_3 nanoparticle has been growth by solvothermal process [6-15].

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2. Formation of Bismuth Telluride

There are two approaches for any nanostructure formation and fabrication. First is the top-down and second is the bottom-up approach [16]. The top-down approach includes the successive splitting of the bulk to nanostructure materials. However, in the bottom-up approach, the process to construct nanoparticles is started from building up from the atomic or molecular scale to until the nanoparticle is constructed.

Nowadays, although the top-down approach has been becoming out-dated rapidly, the bottom-up approach has been becoming appreciable in industrial applications over a decade. The bottom-up approach produces significantly best option of realizing nanostructures with very low record of defects in it and also provides more homogeneous chemical compositions.

Analysis on the characterization and growth of Bi_2Te_3 has already utilized both the top-down and the bottom-up approaches in the last three decades. In the growth process, these methods are generally categorized into two methods, first the physical and second the

chemical methods. In the growth of Bi_2Te_3, the physical methods basically involve evaporation, sputtering and spray pyrolysis techniques. In the chemical methods which involve electrochemical, chemical vapour, laser chemical vapour and electrolysis deposition, hydrothermal and solvothermal processes. The solvothermal process is the most common technique among the chemical methods.

3. Literature Review

Thermoelectric materials have attracted a great interest owing to their potential applications in TEGs, TECs and other field of material science.

A thermoelectric device is an energy conversion system that converts thermal energy to electrical energy. TEG occurs when the couple is put in a thermal gradient (i.e., the top is hotter than the bottom), in which case the device generates a current, thereby converting heat into electrical power by a phenomenon referred to as the Seebeck effect. Conversely, TEC occurs when current passes through the thermocouple, in which case the thermocouple cools on one side and heats on the other side by a phenomenon known as the Peltier effect.

Bi_2Te_3 is one of the best thermoelectric materials because they have the capability to convert waste heat energy into useful electric energy. In order to develop the solvothermal method, Bi_2Te_3 can be used to fabricate nanostructured form.

Recently, researchers have attempted to improve the efficiency of Bi_2Te_3 materials by creating the nanostructures where one or more dimensions are reduced, such as nanorod, nanowires, nanoplates, nanotubes, nanoflowers and nanosheets etc. [6, 8, 17-19]. The solvothermal method is found to be a simple way of preparing nanomaterials. In the preparation process, the size of crystal grain, formation of phase and growth of morphology can be well controlled. This method does not need organometallic precursors. In this section, solvothermal methods with reference to Bi_2Te_3 nanoparticles are reviewed.

Yuan Deng *et al.* [15] were reported a solvothermal reaction of Bismuth (III) chloride dihydrate $BiCl_3.2H_2O$, Tellurium powder Te, Potassium hydroxide KOH, Potassium borohydride KBH_4 with the solvent of N, N-dimethyl formamide (DMF) at temperature between 100 and 180˚C to produce nanocrystalline Bi_2Te_3. They proposed the formation mechanism of Bi_2Te_3 nanoparticles could be a combination of two independent pathways. The first pathway, Te was reduced to Te^{2-} and then Te^{2-} reacts with Bi^{3+}. The second pathway was a direct combination of metal; Bismuth ions (Bi^{3+}) could be reduced to metal Bismuth readily by KBH_4 to form Bi_2Te_3 nanoparticles. The X-ray diffraction (XRD) pattern of the product revelled that the peaks in the patterns corresponded to the reflections of rhombohedral phase with cell constants a = 4.38 Å and c = 30.50Å. Morphology and size of synthesized nanoparticles were depended on the reaction temperature and time. When reaction temperature was low and also time was short, the first pathway was the dominant formation process; and it was easy to form rod-like nanoparticles. When the reaction temperature increased or the time was prolonged, the second pathway could be occurred; the morphology of Bi_2Te_3 nanocrystals tends to be sphere shaped.

X.B. Zhao *et al.* [14] were prepared by solvothermal synthesis to produce Bi_2Te_3 nanoparticles and nanowires by using Bismuth (III) chloride $BiCl_3$ and Te as a precursor with ethylene diamine (EN), dimethyl formamide (DMF), pyridine, acetone, ethanol and distilled water respectively as the reaction medium. A sufficient amount of $NaBH_4$ was put into the solution as the reductant and NaOH used to control the pH-value of the solution. According to the XRD results, the major by-products were metallic Bi, Te and Bismoclite (BiOCl). This means that in addition to the expected reaction for Bi^{3+} ions to combine with the reduced Te^{2-} ions to form Bi_2Te_3 during solvothermal synthesis. Distilled water was the best solvent for the solvothermal synthesis of Bi_2Te_3. The product synthesized in distilled water contained a large portion of nanowires with a diameter less than 100 nm and length of about 10 μm.

Yongbin Xu *et al.* [13] reported about the solvothermal methods by using the material Bi_2Cl_3, Te, Sodium hydroxide NaOH, Sodium borohydride $NaBH_4$ and the solvent of hexadecyltri methyl ammonium bromide (CTAB) mixed with distilled water & ethanol. The experimental results showed that CTAB played a vital role to the formation of the plate-like morphology and controlled the growth rates of different crystalline faces. XRD pattern indicated a pure rhombohedral phase with lattice constants a = 4.435 Å and c = 30.056 Å and produced pure Bi_2Te_3. In other experimental results the authors demonstrated single crystalline nanoparticles of Bi_2Te_3 were produced with 70 to 200 nm diagonal and 30 nm thickness.

S. H. Kim *et al.* [12] produced a Bi_2Te_3 alloy nanotubes with 1–D structure by interfusion at the interface of Bi and Te. The author's used the material Bismuth (III) oxide Bi_2O_3, Tellurium dioxide TeO_2 which dissolved in Hydrochloric acid HCl and employed as a solvent of Olic acid and Oleylamine at reaction temperature between 160 and 240˚C in a nitrogen atmosphere. Moreover, the author's synthesized the Te nanowire at a temperature of 200˚C with an average diameter of 150 to 200 nm and length of 10 to 15 μm. The Te nanowire was developed into Bi_2Te_3 nanotubes conformed by TEM images. Additionally, they observed the Bi and Te crystals in the XRD patterns.

Y. Liang *et al.* [11] employed a simple solvothermal process by using Bi_2O_3, Te that were added to the polyvinylpyrrolodone (PVP) with ethylene glycol solution in order to prepare Bi_2Te_3 hexagonal nanoplates in the absence of NaOH. According to the

author reports, the diffraction peaks in the XRD pattern could be indexed to Bi_2Te_3 rhombohedral lattice phase with the lattice constants a = 4.395 Å and c = 30.44 Å. Thus the XRD data indicated that Bi_2Te_3 nanoplates prepared this method was composed of Bi_2Te_3 rhombohedral lattice phase. Author's showed the transmission electron microscope (TEM) image of a single hexagonal Bi_2Te_3 nanoplate used to make a detailed investigation of crystallinity and microstructure. Corresponding spot pattern of selected area diffraction (SAED) and high-resolution transmission electron microscope (HRTEM) lattice demonstrated the single crystalline nature of the nanoplate. The SAED pattern was obtained by aligning the electron beam perpendicular to the face of this plate. The hexagonally symmetric spot pattern indicated the single crystallinity and could be indexed based on a rhombohedral phase. An HRTEM image revealed the expected hexagonal lattice fringes with a lattice spacing of 0.223 nm, indicating that the as-prepared nanoplates were highly crystallized. The Raman spectrum showed that infrared (IR) active mode, which must be odd parity and is Raman forbidden for bulk crystal due to its inversion symmetry, was greatly activated and shown up clearly in Raman scattering spectrum.

H. He *et al.* [10] were prepared the Bi_2Te_3 nanosheets by the solvothermal method. The raw materials were Bi_2O_3, TeO_2, glycol, NaOH and PVPK-30. The samples were a hexagonal lattice with an average crystal size of 42 nm. Scanning electron microscope (SEM) revealed the samples excellent hexagonal nanosheets, which was in accordance with the results obtained by XRD. The diameter and thickness of the nanosheets could be estimated to be 400 to 600 and 40 to 50 nm, respectively.

On the other hand, the authors report indicated that the absorption spectrum which exist two absorption peaks around 362 nm (with energy of 3.43 eV) and 663 nm (with energy of 1.87 eV). The electron affinity of Te was 1.97 eV. Taking the chemically combined Te atoms in Bi_2Te_3 nanosheets into consideration, the value of the electron affinity might be changed. The absorption peak around 663 nm corresponds to the electron affinity of Te. In order to confirm the conclusion, the emission spectrum of the Bi_2Te_3 nanosheets was obtained. The theoretical value of the electron affinity (1.97 eV) was slightly different from the experimental value (1.87 eV).

Y. Zhang *et al.* [9] were reported the hexagonal nanosheet of Bi_2Te_3 single crystals with uniform morphology through a high yield solvothermal route at low temperature. The author's used the raw materials such as $BiCl_3$, Sodium telluride Na_2TeO_3, NaOH, and the kind of surfactants that PVP-K30, ethylene diamine tetra acetic acid (EDTA), CTAB, sodium dodecyl benzene sulfonates (SDBS), ethylene glycol (EG). The author's obtained the nanosheets by solvothermal route display a pure rhombohedral phase of Bi_2Te_3. The calculated lattice constants were a = 4.386 Å and c = 30.482 Å. The experimental results clearly explained that high-yield hexagon nanosheets were obtained, which have a thickness of 40 to 60 nm and a distance of 400 to 600 nm between the opposite edges. These nanosheets exhibited a flat surface and sharp edges, which indicated an excellent crystallinity. Reaction time and temperature, concentration of NaOH, and kinds of surfactants played important roles in the growth of Bi_2Te_3 nanocrystals.

R. Jin *et al.* [8] synthesized a hierarchical flower-like Bi_2Te_3 through a facile solvothermal method. Author's were employed the Bismuth (III) nitrate pentahydrate $Bi(NO_3)_3.5H_2O$ and Na_2TeO_3 which dissolved in the water and EG solution. Glucose, NaOH and hydrazine hydrate $N_2H_4{\cdot}H_2O$ were added into the solution. The XRD pattern of the obtained products demonstrated a rhombohedral phase of Bi_2Te_3. No other crystalline impurities were detected, indicating the phase purity of the Bi_2Te_3 product. The SEM images displayed that the Bi_2Te_3 had a flower-like morphology with the width of 300 to 2000 nm. Closer observation demonstrated that the flowers were composed of smaller nanoplates with the average thickness of 30 nm. The concentration of glucose played a crucial role in the formation mechanism on structure and morphology. The results showed that the maximum ZT value of 0.6 could be achieved at 600 K.

Lei Yang *et al.* [7] inspected an N-type Bi_2Te_3 nanostructure by using a solvothermal method and enhanced thermoelectric performance. They were used the Bi_2O_3, TeO_2, NaOH, EG and PVP in order to product the Bi_2Te_3 nanostructures. Author's indexed exclusively the XRD as a rhombohedra phase with lattice parameters were a = 4.386 Å and c = 30.478 Å. The SEM images displayed that the Bi_2Te_3 had a hexagonal plate-like nanostructures. The lateral size distributions of these nanostructures were varied from 100 to several 100 of nanometres. Their typical thickness could be observed in the high magnification SEM, which was around 20 nm. These structural features reduced the overall thermal conductivity and in turn led to an enhanced ZT of 0.88 at 400 K.

W. Guo *et al.* [6] prepared the hierarchical Bi_2Te_3 nanoflowers assembled by 2–D thin nanosheets with defects by using a facile solvothermal method. They used the materials of $Bi(NO_3)_3.5H_2O$, Na_2TeO_3, PVP K30, EG, hydrazine monohydrate N_2H_4, formic acid, ethanol and acetone. The peaks in the XRD pattern were well indexed to the rhombohedral Bi_2Te_3. The low-magnification FE-SEM image shows that Bi_2Te_3 sample was composed of hierarchical nanoflowers assembled by curved and inter crossed nanosheets. The high magnification FE-SEM image further showed that of Bi_2Te_3 nanosheets had a diameter ranging from 500 to 600 nm and a thickness of about 16 nm. Authors were achieved the controllable self-assembly of nanoflowers consisted of 2–D thin nanosheets. The results showed that the maximum ZT value of 0.68 at 475 K.

The Bi_2Te_3 nanostructures have unique properties, which is summarized in the Table 1. Table 2. shows the growth and characterization parameters of Bi_2Te_3 nanostructure:

Table 1. Properties of bismuth telluride nanostructure.

Parameter	Properties	Ref.
ZT Value	0.60 to 0.88	6, 7, 8
Crystal Structure	Hexagonal-Rhombohedral Phase	7, 9, 11, 13, 15
Lattice Constant	a = 4.396 Å and c = 30.391 Å	7, 9, 11, 13, 15
Crystalline Size	42 nm	10
Width	300 to 2000 nm	8
Diameter	400 to 600 nm	6, 9, 10
Thickness	16 to 60 nm	6, 8-10
Electron Affinity	3.7 to 4.2 eV	10
Band Gap	~0.15 eV	7

Table 2. Growth and characterization parameters.

Growth	Main Chemicals	Characterization	Ref.
Nanoflower	$Bi(NO_3)_3.5H_2O$, Na_2TeO_3	XRD, SEM, TEM, EDS, TE Properties	6
Nanostructure	Bi_2O_3, TeO2	XRD, SEM, TEM, TE Properties	7
Nanoflower	$Bi(NO_3)_3.5H_2O$, Na_2TeO_3	XRD, SEM, TEM, TE Properties	8
Nanosheet	BiCl3, Na_2TeO_3	XRD, SEM, TEM	9
Nanosheet	Bi_2O_3, TeO2	XRD, SEM, TEM, Optical Properties	10
Nanoplate	Bi_2O_3, Te	XRD, TEM, Raman Spectroscopy	11
Nanotube	Bi_2O_3, TeO2	XRD, SEM, TEM	12
Nanoplate	$BiCl_3$, Te	XRD, SEM, TEM, FT-IR	13
Nanowire	$BiCl_3$, Te	XRD, TEM	14
Nanorod	$BiCl_3$, Te	XRD, TEM	15

Bi_2Te_3 is one of the best thermoelectric materials with a relatively high electrical conductivity and lower thermal conductivity. Already a lot of works has been done in Bi_2Te_3. Recent advances in theories and experiments have proved that defects can break the sub lattice symmetry and are thought to play a key role in the electronic scattering processes in the nanosheets. Thus, to enhance the transport and electronic properties of Bi_2Te_3 crystals, the ability to manipulate hierarchical Bi_2Te_3 nanostructures with defects is highly desirable. In this communication, the controllable Bi_2Te_3 single crystal nanostructure to improve the thermoelectric performance, which governed by the dimensionless figure-of merit ZT.

4. Conclusion and Future Research

Eventually, the use of main materials of $Bi(NO_3)_3.5H_2O$ and TeO_2 in solvothermal growth has been proposed in the review paper. Since it's are ecological behaviour with low toxicity, low cost, stability in air, commercial availability and easy of handling properties. Many researchers use the KOH and other materials to prepare the solution. Here, in order to prepare the solution, Nitric Acid HNO_3 instead of these materials has also been recommended. TeO_2 powder has been dissolved in HNO_3. Thereafter $Bi(NO_3)_3.5H_2O$ material is added at 80°C and dissolved accompanied by magnetic stirring and complete the other treatments to produce Bi_2Te_3 nanostructure. Possible chemical reaction under as follows:

$$TeO_2+2HNO_3 \rightarrow H_2TeO_4+NO_2$$

$$Bi\ (NO_3)_3.5H_2O \rightarrow BiONO_3+2HNO_3+4H_2O$$

$$3HTeO_2^+ + 9H^+ + 18e^- + 2Bi^{3+} \rightarrow Bi_2Te_3 + 6H_2O$$

Further research is required to improve the Seebeck coefficient while still keeping the thermal conductivity low and electrical conductivity high.

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