



Review on Various Synthesis Methods of Bismuth Telluride Nanoparticles

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ABSTRACT

The investigations on the synthesis and various applications of the bismuth telluride (Bi_2Te_3) nanoparticle have gained great attention in the present era due to its wide range of applications. Continued efforts are made by researchers to develop devices based on nanostructured materials. In this review paper, different methods for the synthesis of nanostructured Bi_2Te_3 are presented. Dependence of properties based on the synthesis methods is reviewed as well. Both physical and chemical methods are applied to get different forms of nano compounds. The merits and demerits of both methods are also explained in this review. Briefly, the different synthesis methods of bismuth telluride nanoparticles and its unique properties are critically discussed in this overview.

Keywords: Bismuth telluride, Nanoparticles, Bulk materials, Synthesis methods

1. Introduction

Nanoscience primarily deals with the synthesis, characterization, exploration and exploitation of nanomaterials. The structural and other properties of the materials depend on the grain size of the same. In the last three decades, the researchers have been trying to confine the grain size of materials within the range of 10-100 nm, so as to modify their properties. Due to the recent progress and strong global demand for cost-effective, pollution-free energy conversion, research on thermoelectric materials is rising steadily. Bi_2Te_3 and Sb_2Te_3 alloys are by far the most commonly used thermoelectric materials. Bi_2Te_3 alloys have been shown to have the highest figure of merit for both n- and p-type thermoelectric systems in near-room-temperature applications, such as refrigeration and waste heat recovery up to 200 °C. In the 1950s, Bi_2Te_3 was first investigated as a substance with great

thermoelectric potential. It was quickly discovered that alloying Sb_2Te_3 and Bi_2Te_3 allowed for finer control of carrier concentration while lowering lattice thermal conductivity. Many researches are trying to explore the thermoelectric properties of the sulfur and selenium compounds or simply chalcogenides materials [1]. Because of the increased availability, reduced cost, and lower toxicity of the raw materials, these studies are becoming more beneficial. Sulfides and selenides possess almost all thermoelectric properties as the traditional material like tellurides.

Thermoelectric materials can convert waste heat energy into useful electrical energy. The dimensionless thermoelectric figure of merits of the materials determines the efficiency of these solid state thermoelectric energy converters. A good thermoelectric material must have a high Seebeck coefficient as well as low electrical and thermal

conductivity. The power factor is another important parameter to consider while defining the best thermoelectric materials. Because of the high value of the figure of merit, bismuth telluride compounds are widely used as thermoelectric materials. By improving their thermoelectric properties, they can be used in different areas of energy harvesting. They act as very good topological insulators, thermal sensors, thermoelectric coolers, etc [2]. One of the significances of the particular compound is that it can act as semiconductors as well as insulators. The behavioral diversity of a compound depends on the various conditions applied during the synthesis process. Synthesis methods and conditions play a crucial role in the physical properties of particular materials. Recently, the synthesis of bismuth telluride nanopowder, nano pellets, nanorods, and thin films has gained a considerable attention. The synthesis routes of nanoscale bismuth telluride include physical as well as chemical methods. The physical method includes sputtering techniques, evaporation techniques, pulsed laser ablation, lithographic processes, spray pyrolysis, etc. Electrolysis deposition, electrochemical deposition, solvothermal technique, sol-gel technique, hydrothermal technique, laser pyrolysis, etc. are the chemical methods widely used.

2. Synthesis methods

Due to their possible applications ranging from the thermoelectric generator to thermoelectric coolants and other fields of material science, nanostructure thermoelectric materials have attracted much interest. Nanostructure thermoelectric devices are used for transforming thermal energy to electrical energy in an energy conservation system. One of the best thermoelectric materials used for these applications is bismuth telluride as it has the potential to transform waste heat energy into useful electrical energy. Properties of the bismuth telluride are summarized in Table 1.

In this section, few important physical as well as chemical synthesis methods of nanoscale bismuth telluride and its properties are analyzed and reviewed.

2.1. Physical synthesis methods of bismuth telluride nanoparticle

In the past decades, the study on the synthesis of bulk materials and their properties are discussed by many researchers. But modern era of research demands the production of nano materials for the miniaturization of the devices. The energy crisis that we face today force researchers to work on the thermoelectric materials in detail. The relevance of the thermoelectric materials gained more attention in few years back. Now a days, more studies are going on the synthesis of thin films among the other forms of nanoparticles.

2.1.1. Co-evaporation Technique

Co-evaporation technique of n-type and p-type Bi₂Te₃ and Sb₂Te₃ for thermopile sensor applications were reported by J. H. Kim et al. [3]. The crystallinity of the synthesized samples was found to depend on the substrate temperature. And the grain size of the samples was enlarged at an annealing temperature of 400°C. The substantial increase in the carrier mobility at 400°C was due to the enlarged grain size and reduction of point defects. E. M. F. Vieira et al. [4] studied the enhanced thermoelectric properties of Sb₂Te₃ and Bi₂Te₃ for flexible thermal sensors. These films were synthesized by using co-evaporation technique (Figure 1). Different types of substrates and various atomic percentages of the constituting elements determined the structure, morphology, electrical and thermoelectric properties. Co-evaporation technique of Bi₂Te₃ and Sb₂Te₃ thin films on polyimide substrate was discussed by many researchers [5,6]. This technique was relatively easy and inexpensive, yielding strong thermoelectric materials with a high figure of merit.

Table 1- Properties of Bi₂Te₃

Parameters	Properties	References
Crystal Structure	Rhombohedral	[6],[7],[13]
Lattice constant	a= 4.43Å, c=30.55 Å	[20]
Grain size	5-100 nm	[2],[6],[7]
Film thickness	100-342 nm	[4],[16],[20]
Band gap	0.15-0.38eV	[20],[32]
Seebeck Coefficient	-150- -189µV/°C	[8],[13],[16]
Electrical resistivity	7.7µΩm	[8]
Power factor	1.74*10 ⁻³ WK ⁻² m ⁻¹	[7],[10],[16]
Figure of Merit	0.43- 0.93	[5],[8]

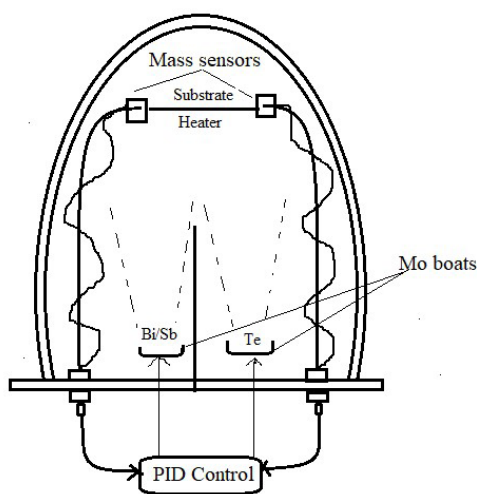


Fig. 1- Schematic sketch of Co-evaporation system.

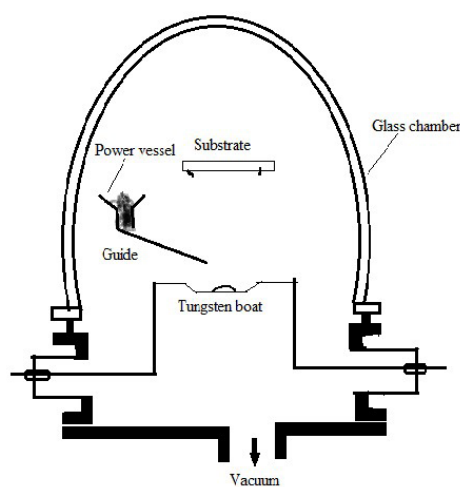


Fig. 2- Schematic diagram of flash evaporation reactor.

The low thermal conductivity of Kapton, strong adhesion and mechanical stability make it a good option for lateral Peltier device manufacturing.

2.1.2. Flash Evaporation Technique

Among the different physical synthesis methods, an easily available and low-cost production method was followed by M. Takashiri et al. [7]. In this flash evaporation method, they synthesized bismuth telluride based alloy thin films. These films showed relatively poor thermoelectric properties whereas annealed samples enhanced the same. In their study, the effect of annealing temperatures on grain size was discussed. The increase in annealing temperature enhanced the grain size; at a particular temperature (400°C) grain size reached the thickness of the film. XRD studies confirmed the rhombohedral structure of the compound and the effect of annealing temperature on that. Because of the porosity of the film, the intensity of the diffraction peaks was reduced at 400°C. A porous sample is indicated by low intensity of the characteristic peak and also determined by the broadness of the XRD peaks. Finally it was concluded that to get good thermoelectric films, one has to optimize the substrate temperature, distance between the substrate and tungsten boat, etc. Flash evaporation methods for the synthesis of thin films of bismuth antimony telluride were stated by M. Takashiri and J. Hamada [8]. For the development of the thin films, flash evaporation (Figure.2) accompanied by the corresponding two-step synthesis process of homogeneous

electron beam irradiation and thermal annealing is applied. Specific crystal orientation and strain were displayed in the films treated with the two-step process.

2.1.3. Thermal Evaporation Technique

Thermal evaporation technique of Bi_2Te_3 thin films on different substrate and its structural and optical properties were studied by F.S. Bahabri [9]. XRD studies confirmed the polycrystalline samples with hexagonal structure. SEM and TEM results also revealed the crystallinity of the synthesized films of different thicknesses. It was found from the optical studies that, the transition taking place in Bi_2Te_3 was indirect transition. P. P. Pradyumnan and Swathikrishnan [10] investigated the thermoelectric properties of the Bi_2Te_3 and Sb_2Te_3 bilayer thin films by vacuum thermal evaporation. The rhombohedral structure of the synthesized films was confirmed by the XRD. The temperature dependence of the samples by annealing was also discussed. The Bi_2Te_3 films showed high thermoelectric behavior at room temperature or relatively low temperature whereas Sb_2Te_3 films showed high thermoelectric behavior at high temperature. In the case bilayer, high thermoelectric behavior could be obtained in wide range of temperature. Thermal evaporation technique for the synthesis of Bi_2Te_3 nanoparticle was reported by S. M. Elahi et al. [11]. The thermoelectric power of the Bi_2Te_3 at the temperature of 300-380 K was studied. The higher value of Seebeck coefficient in nano Bi_2Te_3 films than the bulk was due to phonon scattering,

presence of interface between the crystals and low thermal conductivity. An investigation on electrical properties of thermal evaporated bismuth telluride thin films was carried out by J. K. Das and M. A. I. Nahid [12]. In their work, electrical studies were carried out in different range of thickness (50-300 nm). Electrical conductivity was found to be decrease with the thickness of the film and sheet resistance increased with the same. The negative temperature coefficient of resistance indicates that Bi_2Te_3 is a nonmetal. The positive Hall coefficient suggests that the synthesized films were semiconducting in nature. Many researchers have discussed the thermal evaporation technique for the synthesis of nanoscale Bi_2Te_3 compounds (12–14)]. The structural, electrical and thermoelectric properties of the same material are emphasized in these studies. The properties of the materials are determined by the various preparation conditions and the effect of annealing temperature. The method of annealing at unique temperatures improves the synthesized compound's thermoelectric properties.

2.1.4. Other Techniques

Y. Deng et al. [15] investigated the preferential growth of Bi_2Te_3 nano films by magnetron co-sputtering method. By adjusting the deposition temperature, the growth of the film constrained by (001) and (015) planes. Lower deposition temperature was beneficial for the growth of (001) plane and higher temperature for the (015) plane. The preferential growth of (001) plane was highly favorable to get two times higher electrical conductivity and Seebeck coefficient than those of films with growth of (015) plane. He concluded that the growth of (001) plane is advantageous for the enhancement of Bi_2Te_3 thermoelectric materials. D. Bourgault et al. [16] discussed the direct current magnetron sputtering process of thermoelectric devices based on bismuth telluride thin films. In this work, thermoelectric devices with 5 and 35 n-p junctions were fabricated. In plane configuration leads to high internal electrical resistance which is not compatible with cooling

or thermogeneration applications. So applications based on thermal sensors, flux meters and RF power detectors could be fabricated by using this in plane configuration. The unbalanced magnetron sputtering (UMBS) technique was employed by Q. Jin et al. [17] to synthesis in-plane and out-of-plane microstructures of bismuth telluride for thermoelectric applications. They could achieve good crystalline microstructures at low temperature. The researchers emphasized the advantages of UMBS for the fabrication of in-plane and out-of-plane well-ordered Bi_2Te_3 based alloys for enhanced thermoelectric performance. The Pb doping effect on the n-type bismuth telluride films fabricated by radiofrequency magnetron sputtering technique was investigated by Y. Zhou et al. [18]. The carrier concentration of the films could be controlled by the amount of dopant which strongly affects the transport properties of the same. From their findings, Pb doping enhances the Seebeck coefficient and hence the thermoelectric properties. So, Pb doped n-type bismuth telluride is a promising candidate for the fabrication of microdevices.

A. Taylor et al. [19] synthesized Bi_2Te_3 thin films by post-processing technique and studied the carrier concentrations of the same. From this investigation, it is clear that carrier concentration can be controlled through the annealing in controlled vapour pressures of tellurium. Below certain temperatures, the mass transport of the tellurium through the gas phase occurs. And at higher temperature, mass transport of the tellurium through the solid happens. They also studied the connection between mobility and carrier concentration. A simplified mechanochemical process was employed by A. Mahajan et al. [20] to synthesize Bi-Sb-Te alloys nano powders. The structural and morphological studies on the synthesized compound were investigated in detail. The obtained nanopowders could be considered as the raw materials for the fabrication of nano devices. The physical synthesis methods presented in this review is summarized in Table 2.

Table 2- Different physical synthesis methods of Bi_2Te_3 nanostructures

Growth Technique	Precursors	Product	References
Co-evaporation	Bi pellets, Te lumps	N-type Bi_2Te_3 thin films	[3],[16],[17]
Vacuum thermal evaporation	Bi_2Te_3 powder	Bi_2Te_3 thin film	[4],[5],[6],[20],[21]
Co-sputtering	Bi_2Te_3 target	Bi_2Te_3 films with a nanolayer structure	[8]
DC-Sputtering	Hot pressed Bi_2Te_3 target	Bi_2Te_3 film	[18]
Ball milling process	Powder of bismuth nitrate, antimony trichloride and sodium telluride	Bi-Sb-Te alloy powder	[15]

2.2. Chemical synthesis methods of bismuth telluride nanoparticle

2.2.1. Solvothermal Technique

Nanostructured bismuth telluride synthesized by different chemical methods to enhance the thermoelectric properties has been reported by many scientists. Y. Deng et al. [21] studied the simple chemical method (solvothermal) which is an easily controllable and reproducible technique for the large scale synthesis of nanostructured Bi_2Te_3 . By using this technique, different morphologies such as sheet, rag, sheet-rod and rod-shaped were studied. In this work, the importance of the reducing agent and organic agent for the formation of the materials is emphasized. One of the important significance of the solvothermal synthesis is its ability to prepare a large variety of nanostructures. Solvothermal synthesis method was opted by R. R. Urkude et al. [22] for the investigation of the electrical properties of Bi_2Te_3 -PANI composite materials. In this study, Bi_2Te_3 was prepared by using a solvothermal process whereas the composite was prepared using the chemical oxidative method. Electrical conductivity was found to be high in composite material due to the effect of PANI generated molecular arrangement of Bi_2Te_3 . Many researchers [23,24] have reported the solvothermal synthesis of bismuth telluride and its alloys. XRD showed that the formed nanoparticle possesses a rhombohedral structure. TEM analysis explained about the different morphologies such as powders, rods, sheets, films and sheet-rod structures. The variety of the structure morphology was due to the reaction temperature and duration of the chemical reaction. This study revealed that according to the temperature variation large variety of the nanostructure of bismuth telluride and its alloys can be synthesized.

2.2.2. Sol-gel Technique

A very simple chemical wet method was exhibited by S. Tongpeng et al. [25] to develop Bi_2Te_3 nanorods. To get a better crystalline structure, the sample was annealed at 500°C for 2 hrs. in a nitrogen environment. Highest power factor also obtained from the sintered samples. This technique was one of the simple chemical methods by using the appropriate molar ratio. It is evident from these reviews that the general condition for fabricating high-quality nanostructures using chemical synthesis is to optimize the reaction temperature and chemical reaction time.

2.2.3. Electrodeposition Technique

The technique of electrodeposition for the synthesis of bismuth-tellurium-selenium ternary alloys was stated by S. Michel et al. [26]. It is possible to achieve a wide range of ternary compound composition by manipulating the chemical and electrochemical parameters. The XRD studies revealed the sample's polycrystalline nature. Thermoelectric properties of bismuth-antimony-telluride and antimony-telluride films fabricated by electrodeposition were investigated by S. K. Lim et al. [27]. In this study, Seebeck coefficients of the Bi-Sb-Te films were in the range of $21\text{-}71\ \mu\text{V/K}$ whereas that of Bi-Te films possessed high value ($250\ \mu\text{V/K}$). Because of the different electrodeposition rates of the three ions it was more difficult to optimize the thermoelectric properties than of two ions system. The value of the Bi-Sb-Te film was much lower than that of bulk samples because of the high carrier concentration. These amorphous films possessed a large power factor also. Thin films of bismuth telluride have been prepared by electroless method a new aqueous chemical method- by L. Scidone et al. [28]. This work suggested the advantage of the chemical synthesis methods as a cost-effective, simple technique, efficient and nonhazardous etc.

2.2.4. Electrochemical Atomic Layer Epitaxy Technique

Optimization of the bismuth telluride thin film on different substrates by using ECALE (Electrochemical Atomic Layer Epitaxy) [29,30] was reported by many researchers. This growth technique was cost-effective and can be done at low temperature. ECALE growth exhibits the significance of both electrochemical deposition and atomic layer epitaxy.

2.2.5. Metal Organic Chemical Vapour Deposition Technique

A chemical treatment of the c-plane of sapphire substrates using MOCVD [31] could be used to manufacture BiSbTe_3 films with good surface morphology. Nanostructured Bi-Te based films were fabricated by modified MOCVD by H. You et al. [32]. They discussed the two different nucleation site, morphology and crystalline size of the film. This method can be applied to other thermoelectric materials that can be used as power generation devices and coolers. The diagram of experimental set up of MOCVD is given in the Figure 3.

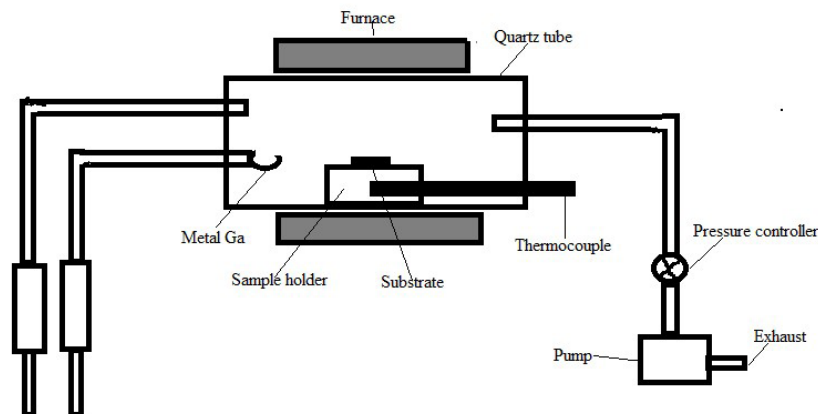


Fig. 3- Experimental set up of MOCVD.

2.2.6. Hydrothermal Synthesis

The hydrothermal synthesis of Bi_2Te_3 nanostructure was reported by H. J. Kim et al. [33]. They investigated different morphologies such as nanoplates, nanorods and nanotubes of the same. The temperature and stabilizing agent play an inevitable role to control the morphology of the synthesized powders. As the morphology/dimension of the sample varies from small dimensional particles (0D) to irregularly formed plates (2D), electrical conductivity decreases. On comparing a low-dimensional system to a three-dimensional system, it was observed that the transport coefficient can be modified so that the electronic properties, i.e. the power factor, can be increased. From the XRD studies, it was confirmed that all of the samples possessed the rhombohedral structure. Hydrothermal synthesis [34] has been commonly used for the large-scale synthesis of nanorods alloyed with bismuth telluride. The structure of the particular compound was verified by XRD and chemical composition was determined by ICP and EDX.

To consolidate the synthesized powder into bulk pellets for the future applications two sintering technologies were employed. One of them was the HPHT (High-Pressure High Temperature) technique and other was SPS (Spark Plasma Sintering) method. They concluded with the result of the optimized value of ZT (0.47-HPHT and 0.42-SPS) at 430 K. S. M. Elahi et al. [14] obtained the nanoparticle of Bi_2Te_3 by sonochemical method. By using these nanoparticles, thin films were deposited on a glass substrate by the method of thermal evaporation. By varying some preparation conditions such as film thickness and annealing

temperatures, they studied the structural and optical properties. Finally, it was concluded that the band gap decreases with thickness and annealing temperature.

By changing the reaction temperature, hydrothermal synthesis produces a number of sample morphologies. In thermoelectric applications, different morphologies have different advantages. Layered nanoplates are good materials for photoelectrochemical (PEC) photodetectors, while Nanowires oriented horizontally have an electric and thermal insulating surface, resulting in high performance TE devices like topological insulators. Nanorods can be used to create a wide variety of nanodevices. For versatile thermoelectric system applications, thin films on a Kapton (Polyimide) substrate are used.

2.2.7. Other Techniques

H. J. Kim et al. [35] established a new approach to vary the reaction temperature and synthesized the nanopowders of Bi_2Te_3 and Sb_2Te_3 . The reaction temperature determines the crystallinity of the materials. To produce the nanostructured thermoelectric materials commercially, this simple cost-effective and large scale production method is suitable. A round-shaped Te-rich Bi_2Te_3 nanoparticles were synthesized by using Polyol technique [36]. Because of the nanostructure formed by the chemical route method, the thermal conductivity was very low and hence the enhanced ZT value. To ensure thermoelectric properties and system manufacture, a smooth surface morphology of thermoelectric films is a prerequisite. The synthesis of nanostructured bismuth telluride by introducing reactants into the solvent, additives,

Table 3- Different chemical synthesis method of Bi₂Te₃ nanostructures

Growth techniques	Precursors	Products	References
Solvothermal synthesis	BiCl ₃ , Te powder, KOH	Bi ₂ Te ₃ powder	[21], [24]
Electroless method	Bismuth nitrate pentahydrate, Te powder	Bi ₂ Te ₃ film	[28]
Electrochemical atomic layer epitaxy (ECALE)	Bismuth and Tellurium solutions	Bi ₂ Te ₃ film	[29], [30]
Electrodeposition	Bi ₂ O ₃ , Sb ₂ O ₃ , TeO ₂ , HNO ₃	Bi-Sb-Te film	[27]
Facile synthesis	Bismuth acetate, Te powder, Oleic acid	Bi ₂ Te ₃ nanoparticle	[35]
Polyol Process	Bi(III) chloride, Te(IV) chloride, oleyl amine, tri octyl phosphine, ethylene glycol	Bi ₂ Te ₃ nanoparticle	[36]
Metal organic chemical vapour deposition (MOCVD)	Trimethyl bismuth, Di-isopropyl telluride	Bi ₂ Te ₃ film	[32]
Refluxing method	BiCl ₃ , Te powder, EDTA, KOH, NaBH ₄	Bi ₂ Te ₃ nanoparticles	[37]
Hydrothermal method	BiCl ₃ , Te powder, EDTA, NaOH, NaBH ₄	Bi ₂ Te ₃ nanoparticles	[33], [34]
Liquid phase Sintering method	Bismuth acetate, potassium tellurite monohydrate, antimony acetate, KOH, PVP, ethylene glycol	Bi-Sb-Te nanocomposite	[38]
Sol-gel method	Bismuth acetate, TeO ₂ , ethylene glycol, diethanolamine	Bi ₂ Te ₃ nanopowder	[25]

reaction parameters etc. were investigated by S. Gupta et al. [37] in refluxing method. This result suggested that the above parameters play a crucial role to determine the size and shape of the nanostructured bismuth telluride.

A liquid phase sintering technique was introduced by C. Zhang et al. [38] to develop bismuth telluride based nanocomposites. The high value of ZT was achieved due to the nanosized grains and boundaries derived from this technique. So this technique was considered to be the cost-effective, facile and scalable chemical bottom-up approach. They concluded that if the chemical bottom-up approach is effectively used, it helps to improve the thermoelectric performance of the materials. The chemical synthesis of the bismuth telluride nanostructures presented here is listed in the Table.3

3. Summary

In this review, the different methods for the synthesis of nanostructured Bi₂Te₃ are presented. Dependence of properties based on the synthesis methods is reviewed as well. Both physical and chemical methods are applied to get different forms of nano compounds. These two synthesis methods have their own merits and demerits. Among the other physical methods, thermal evaporation technique is more advantageous because it has good deposition rate, controls film deposition and possess

comparatively high ZT etc. Nowadays, although the top-down strategy has increasingly become obsolete, over a decade the bottom-up strategy has become appreciable in technical applications. The bottom-up method dramatically produces the best alternative to construct nanostructures with a very low record of defects and also provides a possibility of uniform chemical compositions. Due to the need for alternate materials to be produced, the solvothermal reactions were primarily used to prepare nanostructure types with different morphologies. This approach is considered to be a basic way of preparing a nanostructured thermoelectric material. By using the arrangement procedure, the dimension of crystalline grain, phase formation and morphology production can be easily inspected.

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