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ELUCIDATION OF MATERIAL AND MECHANICAL PROPERTIES ON BISMUTH TELLURIDE NANOCOMPOSITE FILM WITH GRAPHENE/NANOCELLULOSE INCLUSION

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DEDICATION

My beloved father, Abdul Rasyed bin Ab Rahman
My appreciated mother, Ezrine Oman
My adored sister and brother, Deenah Farhanah, Adam Harith, and Nurin Diyanah
for giving me moral support, money, cooperation, encouragement and also understandings
Thank You So Much & Love You All Forever

ABSTRACT

Thermoelectric (TE) is one of the interesting fields of study due to distinct characteristics on electrical energy generation from wasted heat retrieval. The focus on developing an improved TE-material especially in film condition has been crucial for enhanced applications in self-powered micro-devices. Bi_2Te_3 facing challenge in thermoelectric performance which not really fitted up and sustaining at its own micromechanical properties in film condition. Enhancement to improve the thermoelectric performance and increasing the micromechanical properties of the nanocomposite film with inclusions of graphene and CNF. The objective of this study is to enhance the micromechanical characteristics of Graphene-CNF/Bi_2Te_3 nanocomposite films. The process involves the addition of different amounts of carbon nanofibers (CNFs) into the nanocomposite using electrodeposition. The films are subsequently analysed to determine the surface morphology and composition. In the end, the micromechanical properties of the materials get evaluated to determine their mechanical performance. A succeed synthesis, effective diffused and coated in the film using -100mV pulsed deposition at ambient temperature determined by Cyclic Voltammetry analysis. The deposited carbon wt.% increased by approximately 10% comparing to the baseline reference of carbon wt.%. It determined that the deposition of CNFs increased as the weight percentage of carbon increased. Micromechanical properties are analysed using ultra-micro indentation device for evaluation of young's modulus and hardness. This study achieve 100% higher compared to pristine Bi_2Te_3 of hardness and 34% increment of young's modulus with inclusions of CNF. The advantage of CNFs has been verified through a comparison of Graphene-CNF/Bi_2Te_3 nanocomposite films containing different amounts of CNFs. In addition to the Hall-Petch effect, which restricts plastic deformation, the robust reinforcing impact of carbon nanofibers (CNFs) further enhances the mechanical properties.

ABSTRAK

Termoelektrik (TE) adalah salah satu bidang kajian yang menarik kerana ciri-ciri yang berbeza pada penjanaan tenaga elektrik daripada pengambilan haba terbuang. Tumpuan untuk membangunkan bahan TE yang dipertingkatkan terutamanya dalam keadaan filem adalah penting untuk aplikasi yang dipertingkatkan dalam peranti mikro berkuasa sendiri. Bi_2Te_3 menghadapi cabaran dalam prestasi termoelektrik yang tidak benar-benar dipasang dan mengekalkan sifat mikromekaniknya sendiri dalam keadaan filem. Peningkatan untuk meningkatkan prestasi termoelektrik dan meningkatkan sifat mikromekanik filem nanokomposit dengan kemasukan graphene dan CNF. Objektif kajian ini adalah untuk mempertingkatkan ciri-ciri mikromekanikal bagi filem komposit nano Graphene-CNF/ Bi_2Te_3. Proses ini melibatkan penambahan jumlah gentian nano karbon (CNF) yang berbeza ke dalam nanokomposit menggunakan elektrodeposisi. Filem-filem tersebut kemudiannya dianalisis untuk menentukan morfologi permukaan dan komposisi. Pada akhirnya, sifat mikromekanik bahan dinilai untuk menentukan prestasi mekanikalnya. Sintesis yang berjaya, tersebar dan disalut berkesan dalam filem menggunakan pemendapan denyutan -100mV pada suhu ambien yang ditentukan oleh analisis Voltammetri Kitaran. Berat karbon yang dimendapkan meningkat kira-kira 10% berbanding dengan rujukan asas berat karbon%. Ia menentukan bahawa pemendapan CNF meningkat apabila peratusan berat karbon meningkat. Sifat mikromekanikal dianalisis menggunakan peranti lekukan ultra-mikro untuk penilaian modulus dan kekerasan muda. Kajian ini mencapai 100% lebih tinggi berbanding dengan kekerasan Bi_2Te_3 murni dan peningkatan 34% modulus muda dengan kemasukan CNF. Kelebihan CNF telah disahkan melalui perbandingan filem nanokomposit Graphene-CNF/Bi_2Te_3 yang mengandungi jumlah CNF yang berbeza. Sebagai tambahan kepada kesan Hall-Petch, yang menyekat ubah bentuk plastik, kesan pengukuhan teguh serat nano karbon (CNF) meningkatkan lagi sifat mekanikal.

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By The Name of Allah The Most Merciful and Gracious

In the name of ALLAH, the most gracious, the most merciful, with the highest praise to Allah that I manage to complete this final year project successfully without difficulty.

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LIST OF ABBREVIATIONS

UTEM - Universiti Teknikal Malaysia Melaka

BiTe - Bismuth Telluride

CNF - Carbon Nano Fiber

SEM - Scanning Electron Microscope

EDX - Energy Dispersive X-Ray

TE - Thermoelectrics

IoT - Internet of Things

TEG - Thermoelectrics Generator

LIST OF SYMBOLS

S - Seebeck coefficient

σ - electrical conductivity

κ - thermal conductivity

μ - mu

CHAPTER 1

INTRODUCTION

CHAPTER 1

1.1 Background of Study

TE devices have drawn significant attention in recent years because of their unique features, including the ability to directly transform thermal energy into electrical energy. The ongoing progress of internet of things (IoT) technologies, energy harvesting, and self-powered micro-macro devices may contribute to an increased need for the TE industry. However, the progress of TE may be limited by limitations in manufacturing techniques and overall, TE efficiency, particularly in the creation of TE films. The assessment of TE materials often uses the TE material figure of merit, ZT, which takes into account the values of Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ). Nevertheless, thin films made of TE materials often demonstrate inadequate energy conversion efficiency, particularly when used in applications near to room temperature (300K). Consequently, the total performance of the TE material, as measured by ZT, degrades even more in low-temperature applications.

The enhancement needs for innovative materials that possess improved thermal and mechanical characteristics has resulted in a rise in scientific investigation centred on nanocomposite films. Out of these materials, Bismuth Telluride (Bi_2Te_3) is particularly notable due to its exceptional thermoelectric properties, which give it significant value in a wide range of applications, including energy harvesting and electrical devices. The integration of graphene and CNF into the Bi_2Te_3 matrix has emerged as a tempting approach to optimise these features.

The objective of this study is to thoroughly explain the characterization and micromechanical properties of Bismuth Telluride nanocomposite films that have been enhanced with graphene and CNF. Graphene, a carbon allotrope with two dimensions, is widely known for its remarkable mechanical strength and electrical conductivity. The particle is easy to be deposited using electrodeposition process with Bi_2Te_3. Carbon Nanofiber, obtained from sustainable sources, enhances the sustainability of the composite by providing favourable mechanical characteristics. Past researchers have conducted investigations to understand the combined effects of graphene and CNF on improving the thermal and mechanical properties of the Bismuth Telluride. It is expected that the complex interaction of these elements at the nanoscale will result in a nanocomposite film that has exceptional thermal conductivity, mechanical strength, and flexibility.

This investigation will utilise a range of characterisation techniques, such as Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX), and ultra micro-indentation device, to fully investigate the characterization and micromechanical of the nanocomposite films. The results of this work will not only enhance our knowledge of the interactions at the interface of the nanocomposite, but also offer essential knowledge for creating and manufacturing advanced materials with specific features for various technological uses. The study of the material and mechanical characteristics of this Bismuth Telluride nanocomposite film, which includes graphene and CNF, has the potential to open up new possibilities in the field of advanced materials. This could lead to creative solutions for energy conversion, electronics, and other related areas.

1.2 Problem Statement

The study of micromechanical properties of Bismuth Telluride (Bi_2Te_3) nanocomposites is still actively carried out by the researchers throughout the world. Bi_2Te_3 nanocomposites film only not at the best performance for thermal conductivity due to less electron mobility and electron scattering occur from high current, high voltage, and high heat. Film condition is weak in micromechanical properties due to thin layer of nanocomposite in micromechanical properties. Enhancement is needed to improve the thermoelectric properties and micromechanical properties. To improve the thermoelectric performance, graphene is deposited with Bi_2Te_3.

Graphene has a higher electrical conductivity, which makes it easier for charge carriers to move about and minimizes the amount of heat that is lost. Furthermore, the high thermal conductivity of graphene contributes to the effective dissipation of heat, which in turn helps to maintain a wide temperature gradient throughout the material. This significant temperature gradient is essential for maximizing the thermoelectric efficiency of the material. When CNF is dispersed throughout the matrix of the thermoelectric film, they perform the function of reinforcing agents. The micromechanical properties of the film are improved as a result of their providing structural support and their contribution in preventing the growth of cracks. As a result of their elongated form, CNF has a natural capacity for flexibility. They give flexibility to the material when they are included into thermoelectric films, which enables the material to bend and adapt to a variety of forms without compromising its thermoelectric performance. When it comes to applications that demand flexibility, such as wearable electronics, this is of utmost importance at the moment. As a result of the contribution that CNFs provide to the toughness of thermoelectric films, these films are more resistant to mechanical damage or deformation that may occur during operating, handling, or assembling.

Fabrication of Graphene-CNF/Bi_2Te_3 nanocomposite film has to ensure that the particles deposited completely by using electrodeposition process with 3-electrode cells. An improvement can increase the hardness also the young's modulus with inclusion of CNF as the outstanding interfacial bonding and the toughening mechanism and uncertainties weight percentage of CNF. Same to graphene to form better thermoelectric performance with uncertainties weight percentage (wt. %). This study is structuring to find the wt. % of graphene and CNF to improve the thermoelectric performance and micromechanical properties. Micromechanical properties will be tested using ultra-micro indentation device to perform the evaluation of young's modulus and hardness.

1.3 Objective

I. To formulate several amount CNF inclusions in the Graphene-CNF/Bi_2Te_3 nanocomposite film using electrodeposition process towards an improved micromechanical property.

II. To characterize the morphological surface and the compositional Graphene-CNF/Bi_2Te_3 nanocomposite film.

III. To evaluate the micromechanical properties of Bismuth Telluride (Bi_2Te_3) nanocomposite film using ultra micro-indentation device.

1.4 Scope of the study

I. Focussing on the formulating Bismuth Telluride with inclusion of graphene and CNF in film condition. Electrochemical deposition will be the method for the process. Multiple specimens will develop with same concentration amount of graphene but different concentration of CNF.

II. Properties morphology and crystalline structure examined using Scanning Electron Microscopic (SEM) to see the microstructure in micro size. For material composition, Energy Dispersive X-ray (EDX) for resulting the atomic percentage of Bismuth Telluride, Graphene, and CNF.

III. Evaluation of micromechanical testing undergoes using ultra-indentation device for young's modulus and hardness test result.

1.5 Significance of study

Bismuth Telluride is widely recognised for its exceptional thermoelectric performance, making it crucial for energy harvesting and conversion applications. The addition of graphene and CNF is anticipated to augment the thermoelectric efficiency of the composite material. Graphene, known for its remarkable mechanical strength, and CNF, recognised for enhancement of micromechanical properties, possess the capacity to greatly enhance characteristics of Bismuth Telluride nanocomposite films. The interactions among graphene, CNF, and Bismuth Telluride at the nanoscale are complex and can significantly influence the overall performance of the nanocomposite. The investigation entails the utilisation of sophisticated characterization methodologies, including Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX), and ultra micro-indentation device. The knowledge acquired from these procedures not only enhances the specific comprehension of the nanocomposite but also progresses the methodology for examining and characterising intricate nanomaterials. The results of this study have immediate consequences for the creation of advanced materials with customised characteristics. The optimised nanocomposite has potential uses in electronics devices that are intentionally positioned at room temperature (300K) with best characterization and best value of micromechanical properties.

This study as the evaluation and preparation to form a thermoelectric generator. Through the use of the thermoelectric effect, thermoelectric generators, also known as TEGs, are devices that are capable of converting heat energy directly into electrical energy. The thermoelectric materials that make up these devices are structured in such a manner that they make use of a temperature gradient in order to create an electric current. The thermoelectric effect is a phenomenon that occurs when there is a difference in temperature between two distinct materials, which then leads in the creation of an electric voltage. The Seebeck effect, which is characterised by the production of a voltage in the presence of a temperature gradient across a conductor, is responsible for cause of this phenomenon. This effect is used in a TEG in order to create energy with its help. Charge carriers, which include electrons and holes, go from the hot side to the cold side as a result of the temperature differential. In the external circuit that is coupled to the TEG, the movement of charge carriers ultimately results in the generation of an electric current. This energy conversion process is characterised by its efficiency, which is determined by the Seebeck coefficient, which is a material attribute. TEGs have a wide range of applications, including the recovery of waste heat in industrial processes, the improvement of exhaust systems in automobiles, the production of power in aircraft, and the development of portable energy harvesting devices. In addition, they are used in specialised applications such as the powering of distant sensors, wearable electronics, and military equipment.

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2

2.1 Thermoelectric

Thermoelectric (TE) technology provides the immediate conversion of thermal and electrical energy by using the Seebeck coefficient and Peltier effect. A group of Chinese researchers who is Cai et al. (2019) saying that these phenomena was discovered around two centuries ago. In 1821, T. J. Seebeck discovered that when there is a difference in temperature between two separate conductors, a voltage drop occurs across the circuit. The phenomenon is known as the Seebeck effect and may be harnessed for the purpose of generating thermal power. In 1834, J. C. Peltier discovered that the passage of an electric current via a connection between two dissimilar conductors might result in the production or extraction of heat at the connection point. The phenomenon is referred to as the Peltier effect, which is the inverse of the Seebeck effect. In 1855, W. Thomson conducted an analysis of the relationship between the Seebeck effect and the Peltier effect. By applying thermodynamic theory, he proposed the existence of a third effect in a homogeneous conductor. This effect occurs when a current passes through a uniform conductor with a temperature gradient, resulting in the generation of reversible heat absorption or release, in addition to the irreversible Joule heat.

This technology has substantial promise for advancement in several domains of study and application, as researchers from Sweden who is Petsagkourakis et al. (2018) stated that it can be utilized in Internet of Things (IoT) systems which the widespread use of sensors may result in a significant need for power supply without the need of battery replacement. Thermoelectric materials are a favorable option in this regard, since they can harness the abundant heat in the environment to generate energy. In 2022, Guo et al. declared that thermoelectric are widespread use in wearable and flexible devices, and last not least it can be a cooling agent in devices. Zhou et al. (2023) explaining that thermoelectric (TE) materials were discovered as a possible alternative due to their unique ability to convert heat and electricity inside the same module, while also being compact in size and without moving components. Many researchers have been drawn to investigate high-performance thermoelectric materials. The evaluation of the effectiveness of TE materials is based on the dimensionless figure of merit ZT, which is mathematically represented as Equation 1.

$$ZT = \frac{S^2 \sigma \mathrm{T}}{\mathrm{k}} \tag{1}$$

The Seebeck coefficient, defined as S. The electrical conductivity, defined as σ. Temperature, defined as T, is measured in kelvin (K). The thermal conductivity, defined as k. The term Power Factor (PF) refers to the amount $S^2\sigma$, which indicates the ability of a device to produce high voltage and current. Ma et al. (2021).

2.1.1 Seebeck Coefficient

The Seebeck effect elucidates the formation of a potential difference (ΔV) across a semiconductor (or conductor) due to the migration of its charge carriers across a temperature gradient (ΔT=Thot – Tcold). If one side of a substance is heated or cooled, it undergoes an interaction.

Charge carriers migrate from the hot to the cold edge, leading to a change in the number of charge carriers. This effect is counteracted by the internal electrical field that is produced. The polarity of the potential difference is determined by the dominant charge carrier, with the cold side serving as the reference point for measuring the potential relative to the hot side as written in Ostroverkhova handbooks that published in 2018. The sign of the Seebeck coefficient determines whether the material is a p-type or n-type conductor. A positive sign indicates a p-type material, whereas a negative value indicates an n-type material. Seebeck Coefficient formula as Equation 2.

$$\text{The Seebeck coefficient (S): } S = -\frac{\Delta \mathrm{V}}{\Delta \mathrm{T}} \tag{2}$$

A temperature gradient (ΔT) needs to be established across the two sides of the sample, and the resulting voltage (ΔV) should be detected by making electrical connections to those two places (sides).

The primary difficulty in creating high ZT TE materials arises from the significant link between the Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ) due to the carrier concentration (n), as seen in the following Equation 3.

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m * T\left(\frac{\pi}{3n}\right)^{\frac{2}{3}} \tag{3}$$

The Boltzmann constant, represented as k_B, is the basic constant in physics that relates the average kinetic energy of particles in a system to its temperature. The electron charge, labeled as e, refers to the fundamental unit of electric charge. The Planck constant, represented as h, is a fundamental constant that relates the energy of a photon to its frequency. The charge carrier concentration, written as n, refers to the number of charge carriers per unit volume in a material. Lastly, the density of states effective mass of carriers, denoted as m∗, represents the effective mass of charge carriers in a material. Hence, materials with low values of n, such as semiconductors or insulators, often have large values of S. Conversely, as the value of n increases, S decreases fast, as seen in metals. (Nandihalli, 2022).

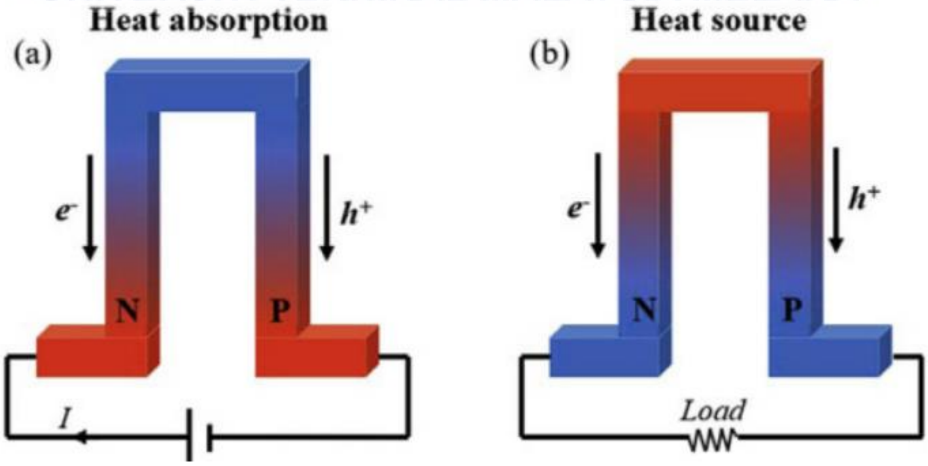

Figure 2.1.1 (a) the standard arrangement of thermoelectric cooling, and (b) Power generating modules. Ma et al. (2021)

Researchers from Figure 2.1.1 (a) and (b) also say that subjecting the n-type and p-type materials to an electrical current, a thermal gradient may be generated across the p-n junctions. If there is a temperature disparity between the two ends of p-n junctions, a voltage potential will be seen across the p-n junction.

2.1.2 Peltier Effect

During the year 1821, a German scientist named Thomas Seebeck conducted a number of experiments on electricity. During these experiments, he discovered that electricity may function across a circuit that consists of two independent conductors. Seebeck failed to elucidate the true empirical hypothesis underlying this process and erroneously inferred that the flow of heat produces the same outcome as the movement of energy. In 1834, French scientist Gene Peltier made the discovery that heat may be absorbed at a single junction of different metals and released at a different connection of the exact same circuit while studying the effects of Seebeck. The Peltier effect arises due to the disparity in the mean power of the electrons participating in the conduction of electric current across different conductors. Figure 2.1.2 shows the thermoelectric module’s ability to generate power and provide electronic refrigeration through the Peltier effect. Jouhara et al. (2021).

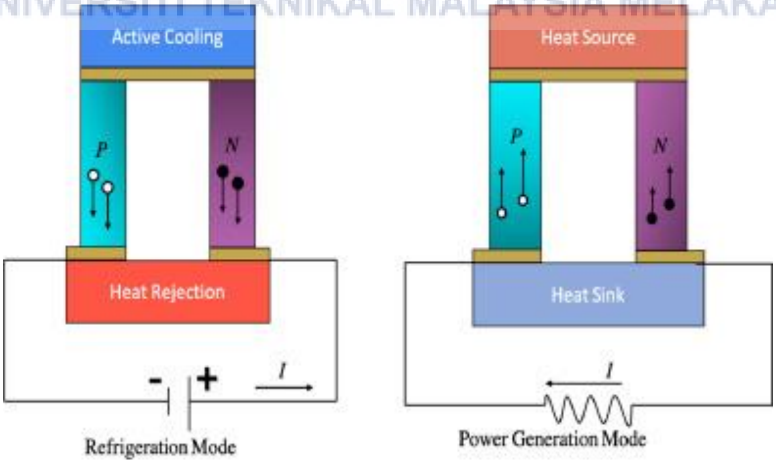

Figure 2.1.2 Peltier Effect on Electricity Production and Thermoelectric Cooling from Tritt (2002)

According to research conducted by Memon and Tahir (2018), the most significant benefit of the Peltier effect is that it is feasible to develop devices for heating and cooling temperatures that do not need any mechanical components to function. As a result, these devices are significantly less susceptible to malfunction compared to conventional coolers and heaters, and consequently require minimal maintenance.

2.1.3 Electrical conductivity

The electrical conductivity, σ, may be determined based on the resistivity, ρ, of the material. As resistivity and electrical conductivity are inversely related, the fundamental equation may be stated as follows Equation 4.

$$\Sigma = \frac{1}{\rho} \tag{4}$$

Electrical resistivity is a measure of a material's ability to impede the flow of electricity. Thus, it is closely associated with numerical values that describe the movement of electrons and holes inside a substance. The electrical conductivity of a material is primarily determined by two factors, the mobility of electrons and the mobility of holes. These factors are mathematically related to the conductivity through the following Equation 5.

$$\sigma = e(\mu e\ .\ n + \mu h.\ p) \tag{5}$$

The symbols μe, n, μh, and p represent the electron mobility, electron carrier density, hole mobility, and hole carrier density, respectively. The link between lattice vibration and electron mobility may be described by the following Equation 6, where μI and μL are the mobility numbers resulting from ionized impurity and lattice vibration effects, respectively.

$$\frac{1}{\mathrm{\mu e}} = \frac{1}{\mathrm{\mu}_I} + \frac{1}{\mathrm{\mu}_L} \tag{6}$$

Equation 6 provides a more straightforward explanation of the impact of lattice vibration when considering the influence of temperature variation in a material. The lattice vibration scattering in a material will be enhanced with the application of higher temperatures. The scattering effect causes a disruption in the flow of electrons, leading to a decrease in electron mobility due to the influence of lattice vibrations (μL). Conversely, the material will exhibit reduced dispersion of ionized impurity as a result of elevated temperature. The presence of a small number of ionized impurities leads to a significant increase in electron mobility, as shown in the ionized impurity effect (μI). Muchuweni and Mombeshora (2023).

2.1.4 Thermal conductivity

The thermal conductivity κ and the lattice thermal conductivity (κl, the inner component) fluctuate with temperature for various doping amounts and orientations. The κl values are derived from the given Equation 7.

$$K_{\mathrm{lattice}} = \kappa - \kappa_{\mathrm{e}} \tag{7}$$

*K*e represents electronic thermal conductivity. The calculation of the electronic thermal conductivity is performed using this Equation 8,

$$\kappa_{\mathrm{e}} = L\sigma T \tag{8}$$

Regarding the equation for lattice thermal conductivity, it may be expressed as the following Equation 9, where D, Cp, and ρ represent thermal diffusivity, specific heat, and material density.

$$K_{lattice} = DC_p\rho \tag{9}$$

The overall thermal conductivity of a metal increases when its electrical conductivity is high, since there is a direct proportional relationship between electrical conductivity and the thermal conductivity carried by charge carriers. Hence, the only approach to diminish thermal conductivity is by examining the magnitude of lattice thermal conductivity. A decrease in lattice thermal conductivity results in a corresponding decrease in the overall thermal conductivity. The inclusion of nanoparticles into the metal might decrease the lattice thermal conductivity by impeding the transmission of lattice vibrations, which are often referred to as phonons. Interrupting the flow of phonons leads to an increase in phonon scattering and causes the phonon wavelength to become longer. Consequently, the duration required for the heat to transfer will be extended as writtened by Li et al. (2018).

2.2 Thermoelectric performance of Pristine Bismuth Telluride

Pure Bismuth Telluride (Bi_2Te_3) is widely used by researchers because of the thermoelectric performance and sustain efficiency that operates in room temperature as stated in Table 2.2. Room temperature is classified around 300K or 27^{o}C. In 2019, the experiment conducted by Wang et al. which they were using pure Bismuth Telluride and resulting the thermoelectric performance. ZT showing 0.33 at room temperature which does not indicate best performance since it is below half by using ball milling and spark plasma sintering method. The Seebeck coefficient is -105μV/K and electrical conductivity also has a large value which is 1600S/cm, but the thermal conductivity is just at 1.65W/mk. But then, another researcher who is Wang et al. (2018) managed to achieve a higher ZT value which is 0.4 with same Seebeck coefficient and a bit higher for electrical conductivity value. On the other hand, in 2019, Kong et al. are using magnetron sputtering method which resulting different value of Seebeck coefficient which is -177.2μV/K but showing low electrical conductivity with only 690S/cm. But not too far from Samat et al. (2022) journals which show the Seebeck coefficient close to the previous journal which is 618.6μV/K and they are using electrodeposition method.