CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Fossil fuel had been used as the main energy source to generate electricity for decades ago. Nowadays, as the main source is running out, researchers are trying to find an alternative source that can be used to generate electricity. They try to find more effective, clean, and sustainable energy resources for power generation. One alternative is to use thermoelectric materials that can be used to produce power and cooling based on thermoelectric phenomena (Mohsen, 2014). A thermoelectric phenomenon is related to the production of electrical potential produced from temperature difference or vice versa caused by three reversible thermoelectric effects which are known as the Seebeck effect, the Peltier effect, and the Thomson effect (Rowe, 1995)(Nadhrah Md. Yatim, 2012)(Bensebaa, 2013). It is a solid-state device that has no vibration and noise because there is no moving part. The device is a reliable energy converter, small in size and light in weight.

Another source of renewable energy that used temperature differences to produce electricity is known as Ocean Thermal Energy Conversion (OTEC). OTEC technology is not new because it was first proposed in 1881 by a French physicist, Jacques Arsene d'Arsonval. The first OTEC plant with low–pressure turbines was built in Cuba in 1930 by his student which produced 22 kilowatts. Later in 1935, another plant with 10-kilo ton pipe was secured away from the coast of Brazil. However, both plants were destroyed by waves before they were able to generate power. Therefore, another OTEC plant was designed in 1956 with a capacity of 3 megawatts in West Africa. The plant was never completed because it was too expensive. Later in 1974, the United State was involved in this research by establishing the Natural Energy Laboratory of Hawaii Authority which has become one of the test facilities in OTEC technology.

The electrical energy created by OTEC is produced from the temperature difference between the surface layer, the warmer part, and the lower layer, the deep cold water of the ocean. It is reported that OTEC would work best with a temperature difference is about 293 K (20^{o}C). To tap the heat energy from the ocean, the OTEC plant is immersed a mile or more into the deepness of the ocean. Therefore, a large diameter intake valve will be needed to bring up the cold water to the surface.

In contrast, a thermoelectric generator (TEG) has no moving part and no working inside it. This type of generator also has a long lifespan when working under a stable operation (W. He et al., 2015). The applications of TEG can be found either in daily uses or space applications.

2.2 Heat Transfer

Since the thermoelectric phenomenon is heat energy transformed into electrical energy, therefore it involves heat energy being transferred from one system to another system. Heat transfer is the process of heat is shift from a body of higher temperature to another body of low temperature. The shift causes the particle to move which produces kinetic energy. Therefore, heat is the measure of kinetic energy caused by the movement of particles. The temperature is proportional to the kinetic energy of particles. Heat transfer from one system to another system can be represented in equation 2.1:

$$Q = mc\Delta T \tag{2.1}$$

Where Q is the heat supplied to the system, m is the mass of the system, c is the specific heat capacity of the system and ΔT is the change of temperature in the system.

There are three main processes occurs involved in heat transfer which are conduction, convection and radiation. The differences in every process are shown in Table 2.1.

Table 2.1: Processes occur in heat transfer (S Surbhi, 2018)

	CONDUCTION	**CONVECTION**	**RADIATION**
Definition	A process where the heat of an object in direct contact is transferred.	Heat transfer within the fluid.	Heat is transferred without any physical contact between objects.
Concept	How does heat transfer from one object to another directly.	How heat flows through fluids.	How heat is emitted through empty spaces.
Causes	Caused by temperature differences.	Cause by density differences.	Occurs for all objects with a temperature greater than 0 K.
Place	Occurs in solids, through molecular collisions.	Occurs in fluids, by the actual flow of matter.	Occurs at a distance and does not heat the intervening substance.
Formula	$Q = \frac{kA\,(T_{Hot} - T_{Cold})t}{d}$ Q: Heat transferred K: Thermal conductivity t: Time A: Area of the surface d: thickness of the material	$Q = H_c A\,(T_{Hot} - T_{Cold})$ Q: Heat transferred H_c: Heat transfer coefficient A : area of the surface	$Q = \sigma(T^4_{Hot} - T^4_{Cold})A$ Q: Heat transferred σ: Stefan Bltzmann Constant A: area of the surface

2.3 Thermoelectric Effect

The mobile charge carriers in semiconductors and metals are free to move just like the gas molecules although when carrying charge as well as heat has caused the thermoelectric effect to rise. According to Synder (2008) (Kok S. Ong, 2018), when a material is applied by a temperature difference, the charge carriers at the hot end tend to move to the cold end. The build-up mobile charge carriers produce a net charge which is a positive charge for holes, h^+ and negative charge for electrons, e^- at the cold end, resulting in the production of an electrostatic potential known as voltage. However, as observed by Muto (2008) (Kok S. Ong, 2018) heat energy also moved when an electrical current flow through a material. The mentioned thermoelectric effect is firstlyknown as the Seebeck effect then the later effect is called as Peltier effect.

Two thermoelectric applications are shown in Figure 2.1. Figure 2.1 (a) shows that the thermoelectric module in power generation modes is based on the Seebeck Effect mode where a temperature gradient influences a voltage through a material. However, in Figure 2.1 (b) the thermoelectric module in refrigeration modes based on Peltier Effect is shown where a current flow influences heat flow through the material (D.M. Rowe, 2006) (Muto,2008).

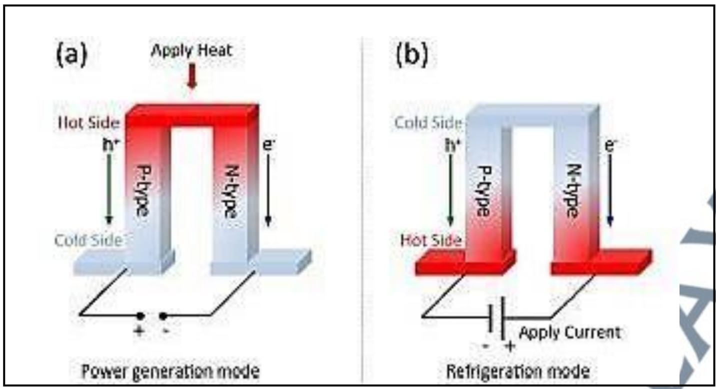

Figure 2.1: Thermoelectric Effect Module (Puneet,2013)

2.3.1 Seebeck Effect

Seebeck effect (α) also known as thermopower has been used in thermocouples in measuring the temperatures, for a long time. Traditionally thermocouples are made of metal alloys or metals. They produce small voltages that are proportional to the temperature differences. This is similar to the thermoelectric power conversion where it used the Seebeck coefficient (Terasaki, 2005)(Muto,2008). The Seebeck coefficient α is defined as the generation of an electric field at a given temperature difference in a material (Nilourfa Ghafouri,2012; Zuo et al., 2018). The thermoelectric *emf* (voltage), is produced by a temperature gradient between 2 different thermoelectric materials (1 and 2) such as semiconductors and metals as shown in Figure 2.2.

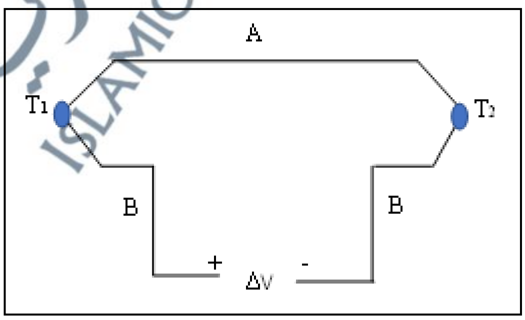

Figure 2.2: Seebeck Effect (Niloufar Ghafouri, 2012)

The mathematical relation of the Seebeck coefficient can be seen in equation 2.2:

$$\Delta V = (\alpha_1 - \alpha_2)\Delta T \quad (2.2)$$

where α_1 and α_2 are the relatively the Seebeck coefficients of materials 1 and 2 respectively in units of volts per degree temperature (V/K) or generally in ($\mu V/K$), ΔT is the temperature difference and ΔV is the voltage that is produced in the circuit. The Seebeck coefficient could be negative or positive depending on n-type and p-type material precisely (Nguyen and O'Leary, 2000)(Nadhrah Md. Yatim, 2012).

2.3.2 Peltier Effect

The complementary Seebeck phenomenon is known as the Peltier effect which describes that when an electric current passes through two different materials such as semiconductors or metals that are connected at two junctions, heat will be liberated at one junction and absorbed at the other junction. Thus, this causes one junction to heat-ups while the other cool off, relying on the current direction (Niloufar Ghafouri, 2012). Therefore, the Peltier effect is a measurement of the amount of heat (Q) carried by holes or electrons and it is proportional to the electric current (I) that is flowing through the circuit (Alam et al., 2013). The Peltier coefficient, π, is a measure of how much amount of heat current is rejected or absorbed at the junction of two dissimilar materials when one coulomb of electric charge flows through the junction. This can be observed in equation 2.3:

$$\pi_{ab} = QI \text{ (at } \Delta T = 0) \quad (2.3)$$

where π_{ab} is the Peltier coefficient of material a to material b which has a unit in Volts or Watt/A. On top of that, the p-type will produce a positive Peltier coefficient and the n-type will produce a negative Peltier coefficient (Nguyen and O'Leary, 2000)(Nadhrah Md. Yatim, 2012).

2.3.3 Thomson Effect

Another phenomenon occurs when current flows across the material with an external temperature difference applied to the material. The Seebeck Effect and Peltier Effect are connected through thermodynamics. The Peltier coefficient is straightforward, the Seebeck coefficient multiplies total temperature. Thus, the derivation of thermodynamics gives Thomson an ideal to produce the third thermoelectric effect which is familiar with the Thomson Effect. In this effect, when the current flows in a medium with a temperature gradient the heat is released or absorbed (Ghafouri et al., 2012). The heat is proportionate to both the temperature difference and electric current. The proportionality constant known as the Thomson coefficient is correlated to the Seebeck coefficient by thermodynamics.

Thus, the heat may be absorbed or rejected by the network heading to the third thermoelectric effect called the Thomson effect. In this effect, the rejected or absorbed heat is proportional to both the spatial temperature difference and the electric current as shown in equation 2.4 (Pooja Puneet, 2013):

$$\nabla Q = \sum . I . \Delta T \qquad (2.4)$$

where ∑ are the Thomson coefficient and this effect occurs in a special case which is in the absence of Joule heating.

2.4 Thermoelectric Materials

A good thermoelectric material has high electrical conductivity and low thermal conductivity which lead to a high value of ZT. Thermoelectric materials consist of semiconductors or metal. In an earlier era of thermoelectric, Bi_2Te_3, PbTe, and SiGe were known to be low medium and high-temperature thermoelectric materials shown in Figure 2.3. As time goes by, the study of thermoelectric materials thrived to produce more options for thermoelectric materials to be used in thermoelectric generators. Hence, there are oxides and organics thermoelectric materials which are used to replace harmful and expensive materials such as bismuth telluride (Bi_2Te_3) and lead telluride (PbTe) based materials.

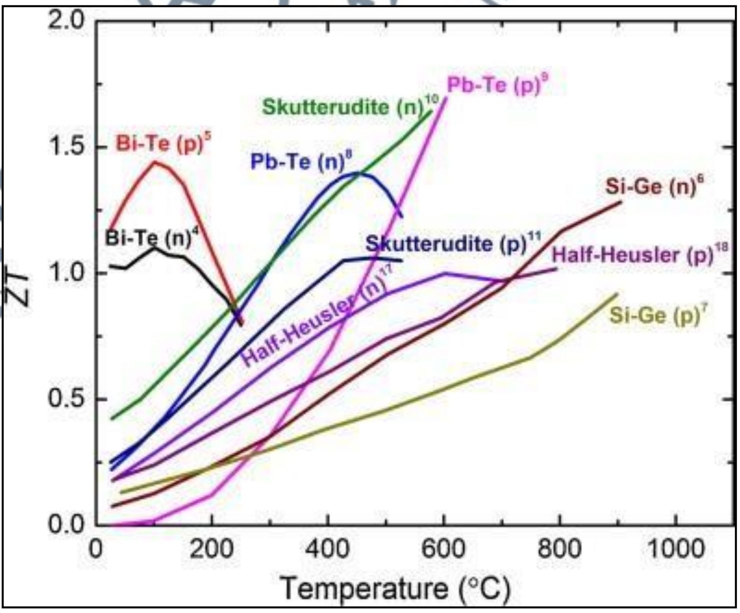

Figure 2.3: Overview of the performance of thermoelectric materials (Chen, 2013)

2.4.1 Inorganic Thermoelectric Materials

Inorganic thermoelectric materials are widely used as these materials have high performance and are also known to be classic thermoelectric materials as shown in Figure 2.4. Hasan et. al. reported that inorganic materials can be categorized into 3 temperature ranges which are near-room, medium, and high-temperature ranges. Examples of ZT value for high-performance inorganic thermoelectric materials are discussed in the next subtopic and shown in Table 2.2.

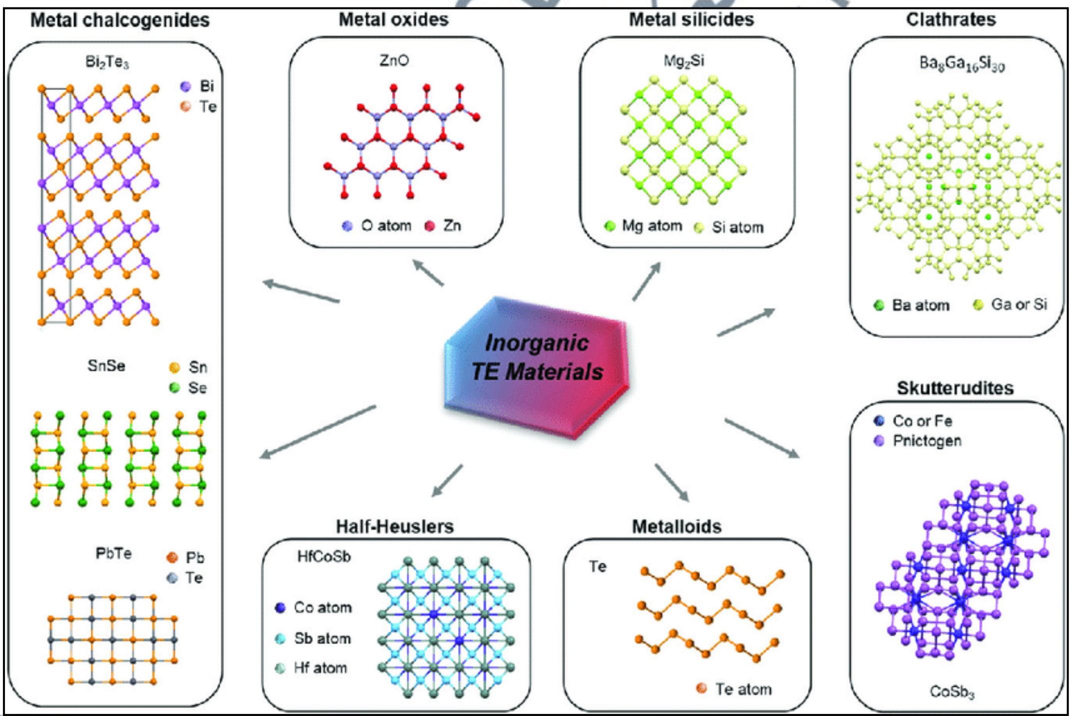

Figure 2.4: Types of inorganic thermoelectric materials (Minxiang Zeng et al., 2022)

2.4.1.1 Near-room Temperature Range

Since the 1960s bismuth telluride (Bi_2Te_3) based materials are most widely used in thermoelectric manufacturing. This material is known to have high performance at a temperature range of 300 – 500 K. Hasan et. al. mentioned that usually p-type Bi_2Te_3 based produce higher ZT value than n-type Bi_2Te_3 based. A value of 2.42 is the highest ZT value reported by Sharma et. al. for n-type Bi_2Te_3 based materials measured at 500 K. Meanwhile, for p-type Bi_2Te_3 based materials, at 320 K, an upgraded ZT value of around 1.86 can be achieved. In addition, silicon nanowires have been recently studied as part of near-room temperature range inorganic thermoelectric materials. Bulk Si is not efficient in thermoelectric manufacturing as the ZT value of 0.0004 at room temperature has been reported by Gayner et al. Si has been used as nanowires due to Boukai et. al research resulting in a high ZT value of nearly 1 at 200 K.

2.4.1.2 Medium Temperature Range

Moreover, the chalcogenides such as lead, copper, tin, clathrates, andskutterudites have been reviewed for application of thermoelectric at a medium temperature range (450 – 850 K). Since the 1960s, NASA has used the radioisotope thermoelectric generator which consists of lead. Furthermore, clathrates and skutterudites have been widely used in many commercial thermoelectric generators. PbTe-based thermoelectric materials have been widely used for nearly 50 years of thermoelectric generator application. According to Jood et. al, the combination of nanostructures PbTe and dopant resulting a high ZT value of ~1.9 for both n- and p- type thermoelectric materials at around 805 K. In addition, Xiao et. al reported that the

ZT value of 1.2 at 673 K for Se and Sn doped in PbTe. The enhancement of PbTe-based materials can improve the ZT value to more than 2.

Copper selenide (Cu_2Se) and tin selenide (SnSe) are the rising materials as high-performance thermoelectric materials for medium temperature range applications. Similar to the mentioned thermoelectric-based materials above, the ZT value of Cu_2Se can be enhanced by nanostructuring and doping methods. Liu et. al reported that iodine-doped Cu_2Se has obtained a high ZT value of 2.3 at 400 K. Meanwhile, Hu et. al reported a ZT value of 2.14 at 973 K is obtained for doping alkaline metal Li in Cu_2Se. By using the nanostructuring method in Cu_2Se materials, Yang et.al obtained a ZT value of 1.82 at 850 K. Furthermore, the use of carbon-based material in Cu_2Se materials has been studied recently to improve thermoelectric performance. Hu et. al reported a ZT value of 1.98 for the use of carbon nanodots in Cu_2Se at 973 K. Moreover, Li et. al obtained a ZT value of nearly 2.23 at 1000 K by using carbon-coated-boron nanoparticles in Cu_2Se. The integrated graphene nanoplates into Cu_2Se resulted in a ZT value of nearly 2.44 at 873 K. Similar to Cu_2Se, SnSe produces remarkable properties such as a simple compound consisting of earth-abundant elements and has great stability. To enhance its performance, nanostructuring and doping are widely applied. Chandra et.al reported that SnSe doped with Ge ($Sn_{0.97}Ge_{0.03}Se$) has a high ZT value of 2.1 at 873 K. Moreover, Shi et.al reported that the research of $Sn_{0.948}Cd_{0.023}Se$ microplates resulted in a ZT value of nearly 1.7. Liu et. al. used both methods of nanostructuring and doping the polycrystalline SnSe with Zn and Pb dopant ($Sn_{0.98}Pb_{0.01}Zn_{0.01}Se$)which resulted in a high ZT value of 2.2 at a temperature of 873 K. Meanwhile Zhang et. al obtained a high ZT value of 2.6 at 923 K for the pure crystal of SnSe measured along the b-axis of the unit cell. High performance at a lower temperature can be obtained by increasing the *n* dopant. Peng et. al doped SnSe with Na dopant which produce a ZT value as high as 2 (at 800 K).

The origin of "Skutterudites" refers to the activity of CoAs3-based elements that were mined in huge quantities from a small mining city known as "Skutterud" located in Norway. The other compounds that exhibit a homogeneous structure similar to $CoAs_3$ are also known as Skutterudites. In 1928, Oftedal introduced the general formula of Skutterudites is MX_3 where M represents the transition elements such as Rh, Ir, or Co and X denotes pnictogen elements such as As, Sb, or P. A high value of ZT nearly 1.5 at a temperature of 725 K reported by Hu et. al by inducing the indium filler into Co_4Sb_{12}. According to Hasan et. al, almost all Skutterudites exhibit ZT more than or equal to 1 which indicates that it has high efficiency in thermoelectric applications.

In 1948, Powell and Palin was the first one who proposed the term "Clathrates". Similar to skutterudites, Clathrates are formed from the tetrahedral formation of the crystal structure of coordinated elements such as Si, Al, Ge, Sn, and Ga with voids. Various types of clathrates are classified according to their number of voids and shape. Type I and type II clathrates are widely used in the thermoelectric industry. Type I is represented by the formula of $X_2Y_6E_{46}$ while the general formula of type II is $X_8Y_{16}E_{136}$ where X and Y are elements from two different sites and E is the tetrahedrally coordinated elements. Similar to the other materials, the doping method has a high impact on adjusting the ZT value of clathrates. Chen et. al doped Yb into $Ba_{7.79}Yb_{0.21}Ni_{0.07}Zn_{0.38}Ga_{14.02}Ge_{30.25}$ which resulted in a ZT value of 0.91 at 900 K. Meanwhile, Shen et al obtained a ZT of 0.63 at 537 K for $Ba_8Ga_{16}Sn_{30}$ doped with Zn. Liu et. al reported a ZT value of 0.52 at 537 K for $Ba_8Ga_{16}In_xGe_{30-x}$ doped with Ge. In addition, Sun et. al reported that n-type $Yb_{0.5}Ba_{7.5}Ga_{16}Ge_{30}$ bulks fabricated using high temperature and high pressure (5 GPa) sintering produced a high ZT of 1.13 at 773 K. Hence, this concludes that general ZT values of clathrates are in the range of 0.5 – 1.3.

2.4.1.3 High-Temperature Range

The high-temperature range of thermoelectric materials is above 850 K. The silicon-germanium (SiGe), oxides based and Zintl phase alloy was recently reviewed for thermoelectric application at a high-temperature range. In 2013, NASA has been using the radioisotope thermoelectric generator consisting of SiGe alloys because it has a very high operating temperature range of 1073 – 1273 K. The n-type SiGe mostly has a higher ZT value of 1.3 at 1173 K, whereas ZT value of p-type SiGe is nearly 0.5. The nanostructuring method has a huge impact on enhancing the ZT value. For instance, Usenko et. al produced the n-type nanostructured SiGe bulk using the ball–milling and spark plasma sintering technique. At 1073 K, SiGe produced a ZT value of nearly 1.1. However, p-type nanostructured SiGe samples have a low value of ZT. Thus Usenko et al fabricated a nanostructured $Si_{80}Ge_{20}$ bulk sample doped with boron using the spark plasma sintering method. The sample produced a high ZT value of 0.72 at a temperature of 1073 K.

Earlier, oxide-based materials have been ignored in the thermoelectric application, however, after the studies done by Terasaki et. al in 1997 on single crystalline $NaCo_2O_4$ which resulted in a moderate power factor, the exploration of oxide-based materials started. Oxide-based materials can be divided into narrow and wide bandgap materials. Among the studied oxide-based materials, narrow bandgap materials such as $CaMnO_3$, $Ca_3Co_4O_9$, $NaCo_2O_4$, $SrTiO_3$, $SrTiO_4$, and BiCuSeO, whereas wide-bandgap oxide-based such as TiO, In2O3, SnO2, V2O5, and ZnO are the promising thermoelectric material. For instance, at a temperature of 773 K, BiCuSeO produced a ZT value of ~0.7.

The work “Zintl phases” is derived from a subclass of intermetallic compounds that consist of electropositive cation usually alkali metal (group 1), alkaline earth metals (group 2), and metalloids or post-transition metals (group 13, 14, 15, and 16). Even though this material is new in the thermoelectric application, the study of the chemical bonding and structure started long ago in the 1920s which was introduced by Eduard Zintl. In 1941, Laves created the “Zintl phases” name in conjunction with the founder. Among n-type and p-type Zintl phases, the Zintl 1-2-2 compounds showed excellent properties in the low-medium temperature range. Meanwhile, at a high-temperature range of 975 – 1275 K, the Zintl 14-1-11 compounds have better performance than p-type Zintl phases.

Table 2.2: Examples of inorganic thermoelectric materials

Temperature Range	Materials	ZT Value	References
Near-Room (300-500 K)	n-type Bi_2Te_3	2.42	Sharma et al.
	p-type Bi_2Te_3	1.86	
	Bulk Si	0.0004	Gayner et al.
	Si nanowires	1	Boukai et al.
Medium (450-850 K)	n- and p-type PbTe	~1.9	Jood et al.
	Se & Sn doped in PbTe	1.2	Xiao et al.
	Iodine doped Cu_2Se	2.3	Liu et al.
	Li doped Cu_2Se	2.14	Hu et al.
	Nanostructuring Cu_2Se	1.82	Yang et al.
	Carbon nanodots in Cu_2Se	1.98	Hu et al.
	Carbon-coated-boron in Cu_2Se	2.23	Li et al.
	Integrated graphene nanoplates in Cu_2Se	2.44	Li et al.
	$Sn_{0.97}Ge_{0.03}Se$	2.1	Chandra et al.
	$Sn_{0.98}Pb_{0.01}Zn_{0.01}Se$	2.2	Liu et al.
	Pure SnSe	2.6	Zhang et al.
	Na doped SnSe	2	Peng et al.
	Indium filler in Co_4Sb_{12}	1.5	Hu et al.
	$Ba_{7.79}Yb_{0.21}Ni_{0.07}Zn_{0.38}Ga_{14.02}Ge_{30.25}$	0.91	Chen et al.
	$Ba_8Ga_{16}Sn_{30}$ doped with Zn	0.63	Shen et al.
	$Ba_8Ga_{16}In_xGe_{30-x}$	0.52	Liu et al.
	n-type $Yb_{0.5}Ba_{7.5}Ga_{16}Ge_{30}$	1.13	Sun et al.
High (>850 K)	n-type SiGe	1.3	NASA
	p-type SiGe	0.5	
	n-type SiGe	1.1	Usenko et al.
	$Si_{80}Ge_{20}$ doped with boron	0.72	

2.4.2 Organic Thermoelectric Materials

Alternatively, organic thermoelectric materials have been approached to replace inorganic and harmful materials used in conventional thermoelectric generators. Large–scale production methods, low cost and proposes unique mechanical adaptability are the properties for conducting polymers to be chosen to replace thermoelectric materialsin large-area applications. They have flexibility in geometrics which can integrate into complex 3D (three-dimensional) shape objects such as car roofs, wearables, and so on. The conductive polymer that has been studied nowadays is polyaniline (PANI) because it is easy to process and prepare from solution form. On top of that, it has good thermal and chemical stability with a high electrical conductivity which makes it suitable to be used as thermoelectric material. Next to PANI is PEDOT: PSS (poly(3,4-ethylene dioxythiophene): polystyrene sulfonate) which can be processed using water dispersions. In addition, it has good charge carrier properties such as electronic and ions carriers which results in high electrical conductivities. Nonetheless, PEDOT: PSS shows low resistance to humid surroundings during the PSS phase because the hygroscopic behaviour occurred. In addition, a complex basic unit of a compound made up of organic ligands and metal ions known as coordination polymers (CPs) has been considered by researchers since the 1960s. However, only a few studies have been done regarding CPs on thermoelectric properties. Campoy-Quiles M. reported that the temperature range of organic thermoelectric materials or organic thermoelectrics is 300 – 500 K. Kim et. al reported that p-type organic thermoelectric materials (PEDOT: PSS) produced a ZT value of 0.42 at 300 K while at a temperature of 440 K the n-type (coordination polymer poly [K_x(Ni-ett)]) produce ZT value of 0.20.

2.4.3 Hybrid Thermoelectric Materials

Hybrid thermoelectric materials are made up of a combination of organic-inorganic compounds which consists of organic semiconductors and inorganic thermoelectric materials. According to Huile J. et. al, inorganic thermoelectric materials that are mostly combined with PEDOT: PSS can be categorized into two types such as carbon-based nanostructure and metal-based materials (Bi_2Te_3, Te nanoparticle, Au nanoparticle, and $Ca_3Co_4O_9$). Most of the application of thermoelectric devices that consist of these materials has the advantages in the low surrounding application (room temperature). This is because the uses of organic materials that operate at a low-temperature range make them more suitable for room temperature power generators and cooling generators.

2.5 Thermoelectric Structure

2.5.1 Thermoelements

Thermoelectricity gives an important contribution to renewable energy because most of the energy produced will have a heat waste that can be converted into electricity. The common material used is according to their temperature range which for low-temperature system range such as Bi_2Te_3 (300 – 500 K), intermediate temperature range of PbTe (450 – 800 K), and high-temperature range of SiGe (600 – 900 K). However, this type of structure is only limited to a specific range.

2.5.2 Segmented

To have a thermoelectric generator that can operate at a high-temperature range than a single structure, a segmented or cascaded structure has been introduced. A segmented structure is a combination of two or more thermoelectric materials as shown in Figure 2.5. The famous segmented leg was using bismuth telluride (Bi_2Te_3) and lead telluride (PbTe) based material segmentation. Bi_2Te_3-based material is usually used as the low-temperature part of the segmented leg because it is known to be the best thermoelectric material which can be performed at a temperature range from room temperature to around 500 K. For medium or higher temperature part of the segmented leg, many materials can be used such as skutterudite, Zintl phase materials, half-Heusler and lead telluride (PbTe) (D'angelo et al., 2011). PbTe-based materials are the perfect material for the high-temperature part of segmented thermoelectric generators because it has outstanding performance at a temperature range of 450 – 800 K. Therefore, the segmented leg will be able to perform at a temperature range of 300 K – 800 K.

Figure 2.5: Segmented thermoelectric structure.

2.5.3 Cascaded

A cascaded thermoelectric generator (CTEG) is known as a stacking structure of a thermoelectric generator. CTEG is made of more than one stage of thermoelectric module structure. Ferrotec has reported that the common shape of CTEG is a pyramid as shown in Figure 2.6 and Figure 2.7, but not all structure is a pyramid shape. Regardless of the structure shape, the lower part of CTEG should have a higher heat pumping capacity than the upper part. According to Ferrotec (USA) Corporation, a cascade structure can be constructed in up to six or seven stages. However, the common stages for cascaded structures are usually two or three stages. The more stages are added, the thermal analysis of the structure can become extremely complex as the value temperature in between the stages (interstage temperature) needs to be determined before the performance can be established. For example, the two-stages cascaded module must determine only one interstage temperature, if more stages are added then more interstage temperature needs to be determined (Ferrotec (USA) Corporation, 2001-2021).

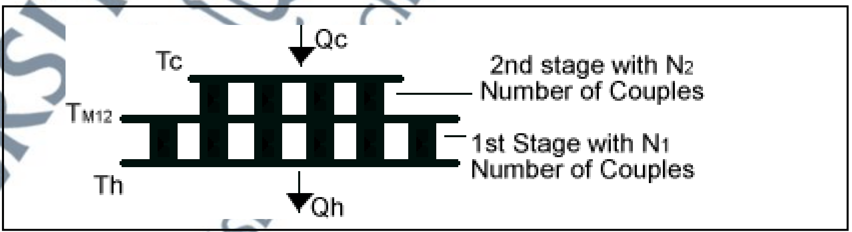

Figure 2.6: Two stages of CTEG structure (Ferrotec (USA) Corporation, 2001-2021).

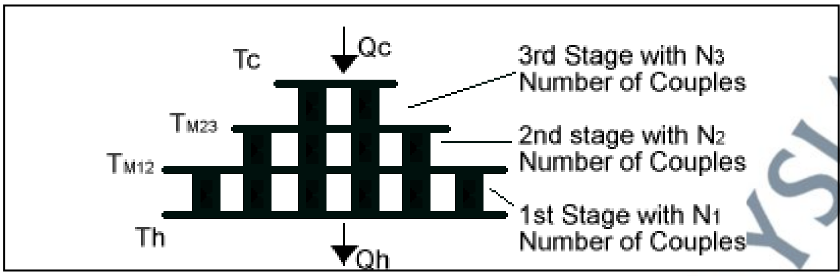

Figure 2.7: Three stages of CTEG structure (Ferrotec (USA) Corporation, 2001-2021).

2.5.4 Thin Film

Thin-film thermoelectric normally has the thickness of micrometre (μm) scale which can be developed using electrochemical deposited. There are two structures of a thermoelectric thin-film an in-plane device and an out-plane device. An out-plane TE, current moves vertically through the TE thin films, thus the temperature difference is between the top and bottom surface of the device (Yuendong Yu *et, al.*, 2019). However, for in-plane TE, the temperature difference is inside the plane because the current moves parallel with the plane. An illustrated figure of the out-plane device is shown in Figure 2.8 and the in-plane device is shown in Figure 2.9. Normally the thickness of the thin film is in microns, this results in current moving through the TE leg of an out-plane device with a large cross-sectional area and a relatively short path. Therefore, it gives a low internal resistance and large maximum cooling flux. However, it is the opposite for an in-plane structure. As the high cooling flux is crucial in a cooler, the out-plane device has been used for thermoelectric coolers (TECs).

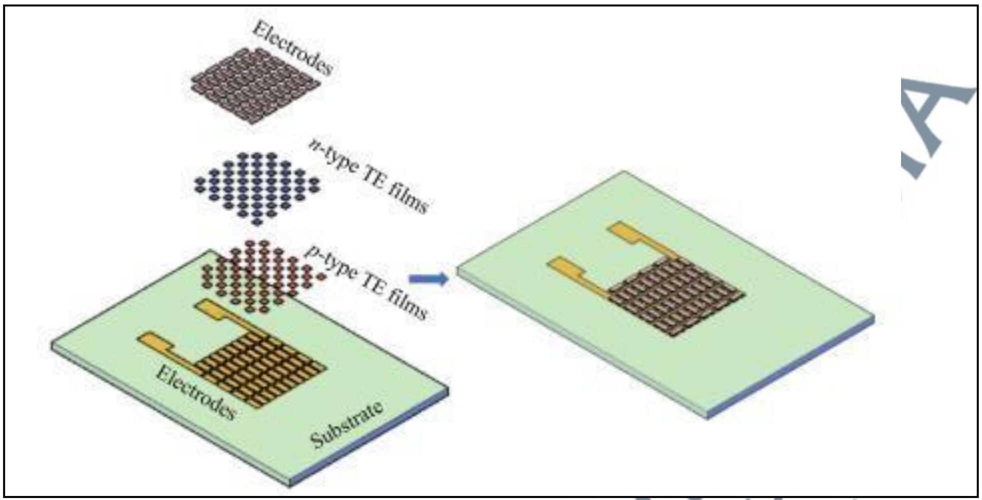

Figure 2.8: Schematic diagram of typical out-plane thin film TE structure.

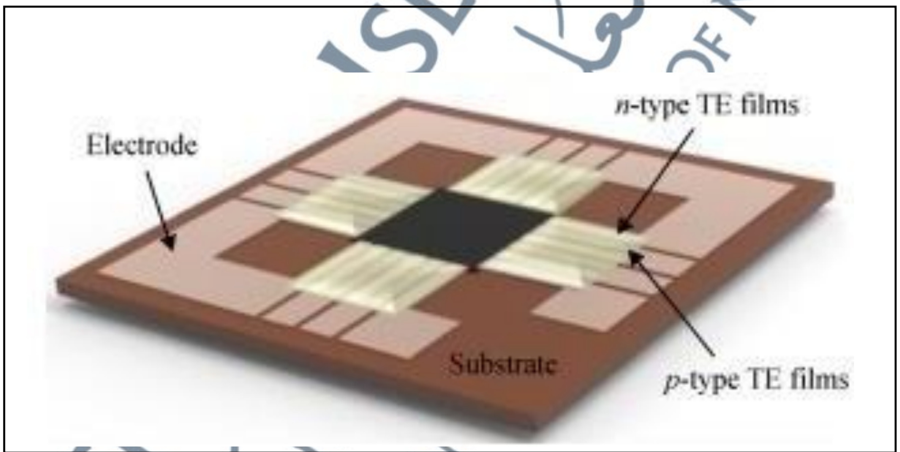

Figure 2.9: Schematic diagram of typical in-plane thin film TE structure.

2.6 Fabrication Method

Fabrication techniques for thermoelectric materials had been carried out years ago. Thermoelectric materials have been fabricated in various ways. The materials were synthesized using a wet chemical method of undergoing energy-efficient routes before the sintering process in some approaches. The energy-efficient routes involved in the fabrication of thermoelectric materials such as microwave-assisted, solvothermal-reduction, and electrodeposition (Liu Chia-Jyi, 2021). The microwave-assisted synthesis has the advantage of providing a higher reaction rate, faster volumetric reaction, and shorter reaction compared to conventional heating techniques (Yao et. al., 2009)(Pradhan et. al., 2017). Meanwhile, solvothermal-reduction synthesis requires a long reaction rate and high pressure (Yao et. al., 2009). Electrodeposition is a simple process with high deposition rates which can achieve up to tens of μm, but resultant films present low ZT. In addition, the product structure of this technique needs an expensive template with a special structure to depend on. However, this material has to undergo the sintering process before its thermoelectric properties of the material can be studied (Sakamoto et.al.,2012).

Nevertheless, the most common methods in the sintering technique were spark plasma sintering (SPS) and hot press (HP). The difference between SPS and HP techniques is the existence of electric current flow during the sintering process. Anselmi-Tamburini, 2019 reported that the SPS process starts with a fine powder pressed using uniaxial pressure within low vacuum surroundings. The use of low vacuum is to prevent the graphite tools from oxidizing and thermal reduction. Usually, inert gas is used in the machine to prevent explosive samples from evaporating. The graphite dies as casting is used due to its high thermal conductivity but it has the limitation pressure of 60 MPa. Therefore, the process conducted undergoes a pressure process of 20 MPa to 50 MPa at a high-temperature range of 773 K to 1373 K. This sintering process started with a heating rate of 50 – 200 degrees Celsius per min. Thus, it will take only a few minutes to achieve a high temperature for fabrication. In addition, it is conducted under an argon (Ar) atmosphere to avoid oxidation during the process. After the sintering process is finished, the samples need to be cooled at room temperature before they can be discharged from SPS.

Meanwhile, for the HP technique, the mixed powder thermoelectric materials were loaded into a mould before the sintering process take place. Previously, the HP techniques only used conventional hydraulic pressing machines without Ar atmosphere. Nowadays, to avoid oxidation occurring during the process, the HP techniques were carried out under the Ar atmosphere (Nguyen et al, 2018). As for pressure in HP, the limitation depends on the type of mould and machine used. Using graphite mould, the pressure will be limited to the same pressure as SPS, while for other moulds the pressure can be up to 56 MPa (Yan et al., 2016). In addition, the HP method can reach up to 96 MPa with a suitable mould used in graphite furnace HP machine (Achraf Kallel, 2013). Furthermore, according to Achraf Kallel (2013), the heating rate of HP was 10 degrees Celcius per min (283 K/min) to achieve the high vacuum of 10^{-5} mbar at 1373 K. Thus, HP took a longer time to acquire high temperature than SPS method.

A lead-free thermoelectric generator that used oxide-based material was fabricated in 2001 using the sintering technique (Matsubara, 2001). They reported that the p-type thermoelectric material $Ca_{2.75}Gd_{0.25}Co_4O_9$ was constructed using SPS under the pressure of 50 MPa at 1073 K for 5 min while the n-type material $Ca_{0.92}La_{0.08}MnO_3$

was constructed using conventional sintering technique. After that, the sintered samples undergo annealed under O_2 condition at 1173 K for 20 hours to eliminate carbon on the surface. The resistivity obtained for n- and p-type thermoelectric material was 7.8 μΩ and 6.6 μΩ respectively. In 2012, fabrication of the material of Mg_2Si by a Plasma-activated Sintering (PAS) using monobloc sintered under the pressure of 30 MPa at 1113 K for 11 min. The Ni electrode is sintered simultaneously with the thermoelectric material providing 6 mΩ of contact resistivity. The overall resistance of sintered sample was about 10.5 mΩ (Sakamoto et. al., 2012).

Later, a study on manipulating 0 – 4 percentage mol concentration of SrTe for PbTe-SrTe thermoelectric material was done by doping with 2 per cent mol of Na. The samples were fabricated in the form of ingots by melting for over 10h at 1323 K and quenching to room temperature at 297 K. The ingots undergo powder processing and sintered with Spark Plasma Sintering at 823 K for 10 min under the pressure of 60 MPa in argon atmosphere (Biswas et. al., 2012). The maximum ZT value that can be achieved when using the above steps was nearly 2.2 at 915 K compared to the ZT value of nearly 1.7 at 800 K of the ingot sample. This proved that the uses of SPS can increase the performance of thermoelectric samples produced. Other than that, a SnSe sample was first synthesized in the form of ingot at 1223 K for over 9.5 hours then soak for 6 hours followed by furnace-cooling at room temperature before being heated up to 1223 K over 9.5 hours by vertical Bridgman crystal and cooled to room temperature with moving sample at a rate of 2 mm h^{-1} (Zhao et. al., 2014). The ZT value reported was 2.62 at 923 K with a lower lattice thermal conductivity of 0.23 $Wm^{-1}K^{-1}$. It is a high ZT value for a low thermal conductivity material. Therefore, most of the research has been done by using SPS because this method is known to be a short time and effective method in fabricating thermoelectrics.

Nevertheless, Yan et al. (2016) studies the properties of bulk material of type-I clathrate $Ba_8Cu_{4.8}Si_{41.2}$ which were fabricated using both SPS and HP techniques. The study found that the sintered sample using HP with a temperature of 1073 K shows the highest ZT of 0.3 at 870 K as compared to SPS sintered sample. This might be due to the formation of a simulated Cu-rich phase during the SPS process. Meanwhile, Achraf Kallel's research on SiGe alloy was fabricated using the HP method with various pressure, temperature, and holding times. The study found that thermoelectric properties of the dense sintered material have the closest value to the alloy sample fromthe previous study (Achraf Kallel, 2013).

All of the mentioned above are basically for single thermoelectric material. Generally, fabrications of a segmented thermoelectric material are the same as single thermoelectric material. This is because to form a segmented thermoelectric leg, the single legs will be formed first followed by joining the legs together.

2.7 Thermoelectric Performance

Thermoelectric material offers a direct energy conversion of heat to electricity. The material used is usually a doped semiconductor that carries holes for p-type and electrons for n-type material. Each thermoelectric material has its working temperature range where it can perform energy conversion. The performance of the material is shown by the value of dimensionless figure-of-merit (ZT). Generally, a ZT can be determined by

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} \tag{2.5}$$

where α is the Seebeck coefficient, σ is the electrical conductivity of the material, mean temperature, *T* and thermal conductivity, *κ*.

Seebeck coefficient, *α*, electrical conductivity, *σ*, and *λ* depend on temperature, *T*. A good thermoelectric material should have a high Seebeck coefficient and electrical conductivity but low thermal conductivity which is not easily obtained. The higher the *ZT* value, the better efficiency could be provided. Many ways to enhance the efficiency of thermoelectric material have been introduced from fabrication to designing the generators.

Each thermoelectric material poses a high *ZT* value at its perspective temperature range. Therefore, the operation temperature period of a thermoelectric generator built by a single material is limited as the material used can only have a maximum *ZT* value at a certain temperature range. The innovation of combining the materials has captured the attention of researchers because the combined material will operate in a wide temperature range than a single material. This combined material is known as segmented thermoelectric material. Conversion efficiency is proportional to the value of *ZT*. Thus, to achieve high conversion efficiency, it is necessary to use combined thermoelectric materials that excel in the different temperature ranges.

This can be seen from the introduction of designing the segmented generators by using computational analysis in 2013 (Hadjistassou et. al., 2013), followed by the experimental work of segmenting the material in 2015 by (Hung L. T., 2015), where the way of fabrication also being manipulated by researchers where they used different fabrication technique to find the best technique to fabricate the materials. Determining the *ZT* value of each material is the main objective in every research to know the efficiency of the material. The technique to measure *ZT* value has become one of the challenges that need to be faced by researchers. The *ZT* value can be obtained analytically or experimentally where it can be the direct or indirect measurement.

Recently, most of the experimental approaches to gaining the *ZT* value is involving 2 different sets up where the Seebeck and electrical resistivity commonly being measured simultaneously by one apparatus set up while the thermal conductivity is measured by another setup. Then those values will be inserted into the *ZT* equation, $ZT = \alpha^2\sigma/\kappa$ to get the *ZT* value. For example, Zhao et al. have measured the thermoelectric properties of *SnSe* crystals by using two apparatus where the Seebeck coefficient and electrical resistivity were measured simultaneously using the ULVAC-RIKO ZEM-3 instrument system while the thermal diffusivity was directly measured by using another instrument that is laser flash diffusivity to calculate the thermal conductivity of the crystals (Zhao, et al., 2014). This technique is also being used by Zhang et al., but they do some measurements on the specific heat of the material using an apparatus which is a differential scanning calorimetry thermal analyzer instead of directly deriving it from a representative sample (Zhang, et al., 2015). In addition, there are also studies involving a single measurement of electrical resistivity, Seebeck coefficient, and thermal conductivity where those measurements were using a 4-point probe, hot-probe setup, and laser flash respectively. Then, the *ZT* value can be obtained by calculating those measurements together.

2.8 Conclusion

All in all, most fabrications of bulk thermoelectric material either for thermoelements or segmented legs are using the Spark Plasma Sintering (SPS) method due to its ability in high temperature and high pressure under a short time. SPS technique is the best method for the time being due to its ability to produce good thermoelectric sample performance. However, using SPS techniques required an SPS machine which is not available in Malaysia. Therefore, despite using SPS in fabricating the sample feasibility of using the HP technique has been investigated in this study.

As for the materials, the traditional thermoelectric materials which are inorganic thermoelectric materials have been chosen in this study. Both p-type and n-type low and intermediate thermoelectric materials such as Bi_2Te_3 and PbTe-based alloys were used in this research. Despite the physical characteristics of the materials, these materials have been studied a lot and they have also been used in commercial thermoelectric generators.