CHAPTER 2

THEORY AND LITERATURE REVIEWS

Thermoelectric Phenomena

Thermoelectrics have a long history of providing simple, reliable power generation solution.

The thermoelectric generator is made of semiconductor too which are direct conversion of temperature differences to electric voltage and vice versa (David Michael Rowe, 2005).

The thermoelectric refrigerator uses the Peltier effect to create a heat flux between the junctions of two different types of materials.

Thermoelectric phenomena has been described through various theories including the Seebeck effect, Peltier effect, and Thomson effect. These effects are all linked by way of the Kelvin relationship. Moreover, the Figure of Merit and Dimensionless Figure of Merit relating to thermoelectric materials, further describe the properties of these materials. (David Michael Rowe, 2005)

Seebeck Effect

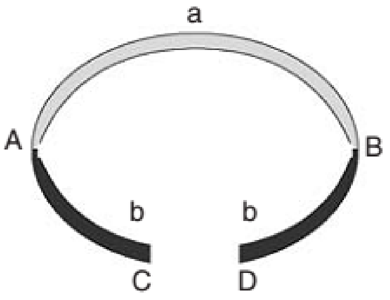

Figure 1 Schematic basic thermocouple (David Michael Rowe, 2005)

The thermometric phenomena which underlies thermoelectric energy conversion can be conveniently discussed, with reference to the schematic of a thermocouple, as shown in Figure 1. It can be considered as a circuit formed from two dissimilar conductors, a and b (referred to in thermoelectric terms as thermocouple legs, arms, thermoelements, or simply elements and sometimes as pellets by device manufacturers), which are connected electrically in series but thermally in parallel. If the junctions at A and B are maintained at different temperatures T_1 and T_2 and $T_1 > T_2$ an open circuit electromotive force (emf), V is voltage developed between C (V_1) and D(V_2) and given by $V_1 - V_2 = S(T_1 - T_2)$ or $S = -\Delta V / \Delta T$, which defines the differential Seebeck coefficient S_{ab} between the elements a and b. For small temperature differences the relationship is linear. The sign of a is positive if the emf causes a current to flow in a clockwise direction around the circuit and is measured in $\mathrm{V\,K^{-1}}$ or more often in $(\mathrm{\mu V\,K^{-1}})$. The semiconducting materials are the most promising materials for constructing the thermocouples used in the generator because they have Seebeck coefficients in excess of 100 $\mathrm{\mu V\,K^{-1}}$.

Peltier Effect

The Peltier effect is the presence of heating or cooling at an electrified junction of two different conductors and is named after French physicist Jean Charles Athanase Peltier, who discovered it in 1834. In Figure 1, the reverse situation is considered with an external emf source applied across C and D and a current I flows in a clockwise sense around the circuit. Then a rate of heating Q occurs at one junction between a and b and a rate of cooling $-Q$ occurs at the other. The ratio of I to Q defines the Peltier coefficient given by $\prod = I / Q$. This is positive if A is heated and B is cooled and is measured in watts per ampere or in volts. (David Michael Rowe, 2005)

Thomson Effect

The last of the thermoelectric effects, the Thomson effect was discovered by William Thomson (Lord Kelvin). The Thomson effect relates to the rate of generation of reversible heat Q , which results from the passage of a current along a portion of a single conductor, along which there is a temperature difference ΔT . Providing the temperature difference is small, $Q = \beta I \Delta T$ where β is the Thomson coefficient. The units of β are the same as those of the Seebeck coefficient $\mathrm{V\,K^{-1}}$. Although the Thomson effect is not of primary importance in thermoelectric devices it should not be neglected in detailed calculations.(David Michael Rowe, 2005)

The Kelvin Relationships

The above three thermoelectric coefficients are related by the following Kelvin relationships:

$$S_{\mathrm{ab}} = \frac{\Pi_{\mathrm{ab}}}{T} \tag{2.1}$$

$$\frac{\mathrm{d}S_{\mathrm{ab}}}{\mathrm{d}T} = \frac{\beta_{\mathrm{a}} - \beta_{\mathrm{b}}}{T} \tag{2.2}$$

These relationships can be derived using irreversible thermodynamics. Their validity has been demonstrated for many thermoelectric materials and it is assumed that they hold for all materials used in thermoelectric applications.

Figure of Merit

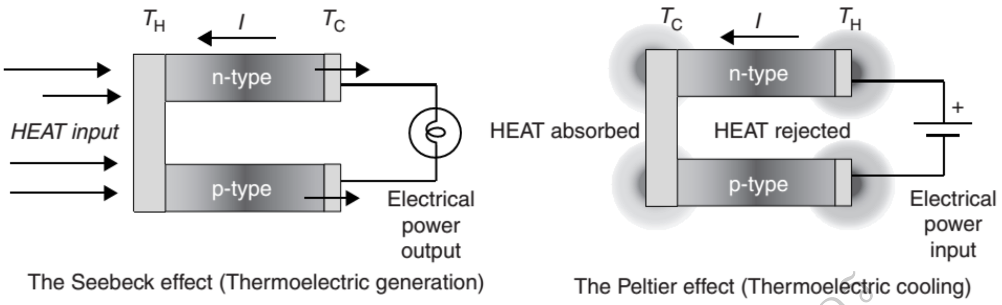

Figure 2 Thermoelectric generator (left); Thermoelectric refrigerator (right) (David Michael Rowe, 2005)

A thermoelectric converter is a heat engine and like all heat engines it obeys the laws of thermodynamics. If we first consider the converter operating as an ideal generator in which there are no heat losses, the efficiency is defined as the ratio of the electrical power delivered to the load, to the heat absorbed at the hot junction. Expressions for the important parameters in thermoelectric generation can readily be derived by considering the simplest generator, consisting of a single thermocouple with thermo-elements fabricated from *n*- and *p*-type semiconductors, as shown in Figure 2 (left). The efficiency of the generator is given by;

$$\eta = \frac{\text{energysupplied to the load}}{\text{heat energy absorbed at hot junction}} \tag{2.3}$$

If it is assumed that the electrical conductivities, thermal conductivities, and Seebeck coefficients of a and b are constant within an arm, and that the contact resistances at the hot and cold junctions are negligible compared with the sum of the arm resistance, then the efficiency can be expressed as;

$$\eta = \frac{I^2 R}{S_{\mathrm{ab}} I T_{\mathrm{H}}} = \frac{I^2 R}{\kappa'(T_{\mathrm{H}} - T_{\mathrm{C}}) - \frac{1}{2} I^2 R} \tag{2.4}$$

Where κ' is the thermal conductance of a and b in parallel and R is the series resistance of a and b. In thermoelectric materials σ, κ', and S change with temperature, and in both, generation and refrigeration should be taken into account. However, the simple expression obtained for the efficiency can still be employed with an acceptable degree of accuracy, if approximate averages of values are adopted for these parameters over the temperature range of interest. Appropriate allowances can also be made for contact resistance. Efficiency is clearly a function of the ratio of the load resistance to the sum of the generator arm resistances, and at maximum power output it can be shown that;

$$\eta_P = \frac{T_\mathrm{H} - T_\mathrm{C}}{\frac{3T_\mathrm{H}}{2} + \frac{T_\mathrm{C}}{2} + \frac{4}{Z_\mathrm{C}}} \tag{2.5}$$

while the maximum efficiency

$$\eta_\mathrm{max} = \eta_\mathrm{C}\gamma \tag{2.6}$$

where

$$\eta_\mathrm{C} = \frac{T_\mathrm{H} - T_\mathrm{C}}{T_\mathrm{H}} \tag{2.7}$$

$$\gamma = \frac{\sqrt{1 + \mathrm{Z_C}\overline{\mathrm{T}}} - 1}{\sqrt{1 + \mathrm{Z_C}\overline{\mathrm{T}}} + \frac{T_\mathrm{C}}{T_\mathrm{H}}} \tag{2.8}$$

$$\overline{\mathrm{T}} = \frac{T_\mathrm{H} + T_\mathrm{C}}{2} \tag{2.9}$$

$$\mathrm{Z_C}\ \text{(the Figure of Merit of the couple)} = \frac{S_\mathrm{ab}^2}{R\kappa'} \tag{2.10}$$

The maximum efficiency is thus the product of the Carnot efficiency, which is clearly less than unity, and γ, which embodies the parameters of the materials. If the geometries of a and b are matched to minimize heat absorption, then;

$$Z_C = \frac{S_{ab}^2}{\sqrt{\kappa_a / \sigma_a} + \sqrt{\kappa_b / \sigma_b})} \tag{2.11}$$

In practice, the two arms of the junction have similar material constants, in which case the concept of a Figure of Merit for a material is employed and given by;

$$Z = \frac{S^2\sigma}{\kappa} \tag{2.12}$$

where $S^2\sigma$ is referred to as the electrical power factor.

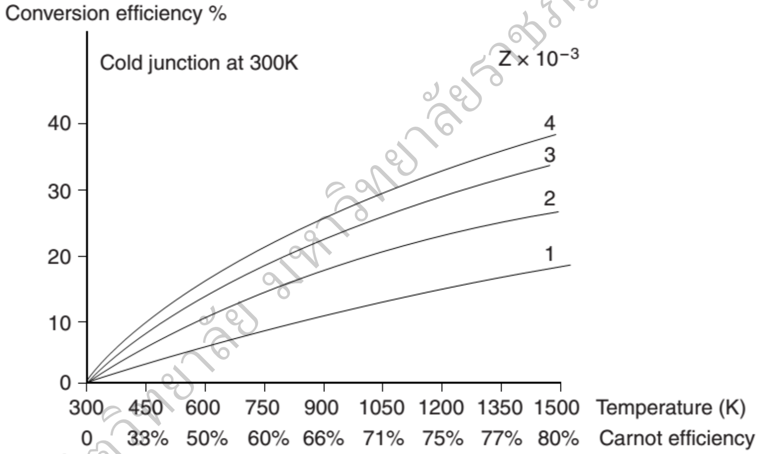

Figure 3 Generating efficiency as a function of temperature and thermocouple material Figure-of-merit (David Michael Rowe, 2005)

The above relationships have been derived assuming that the thermoelectric parameters which occur in the Figure of merit are independent to temperature. Although generally this is not the case, assuming an average value provides results which are within 10% of the true value. The conversion efficiency as a function of operating temperature difference across a range for values of the material's Figure of merit is displayed in Figure 3. Evidently an increase in temperature difference provides a corresponding increase in available heat for conversion as dictated by the Carnot efficiency. Consequently, large temperature differences are more desirable. As a ballpark figure, a thermocouple fabricated from a thermo-element with an average Figure of Merit of $3\times10^{-3}\,\mathrm{K}^{-1}$ would have an efficiency of 20%, when operated over a temperature difference of 500 K.

Dimensionless Figure of Merit

The figure of merit (Z) of a thermoelectric material is temperature dependent, it is more convenient to work with the dimensionless figure of merit (ZT) than the Z value. For thermoelectric materials, dimensionless figure of merit ZT is given by:

$$ZT = \frac{S^2T}{\kappa\rho} \tag{2.13}$$

Thermoelectric Materials

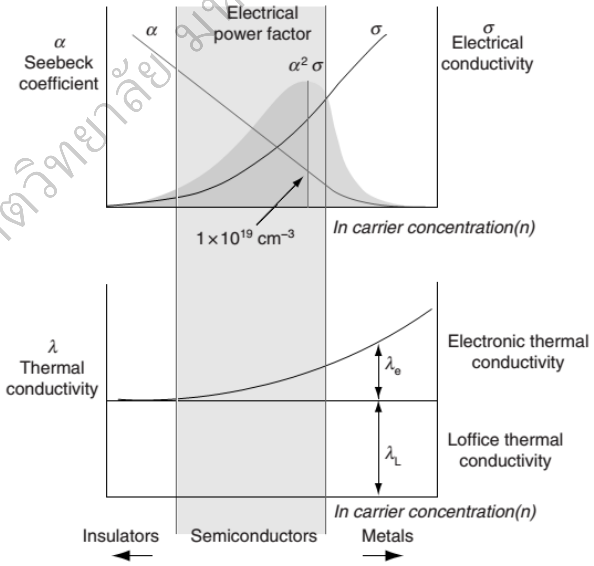

Figure 4 Schematic dependence of electrical conductivity, Seebeck coefficient, power factor, and thermal conductivity on concentration of free carriers (David Michael Rowe, 2005)

One of the parameters used in the classification of materials is electrical conductivity. Metals have high electrical conductivity, while insulators have very low conductivity which under normal conditions is taken as zero. Semiconductors occupy an intermediate position between the two. Electrical conductivity is a reflection of the charge carrier concentration. All three parameters which occur in the Figure of Merit are functions of carrier concentration. Electrical conductivity increases with an increase in carrier concentration as shown in Figure 4, while the Seebeck coefficient decreases and the electrical power factor maximizes at a carrier concentration of around 10^{25} cm^{-1}. The electronic contribution to the thermal conductivity κ_e , which in thermoelectric materials is generally around 1/3 of the total thermal conductivity, also increases with carrier concentration. Evidently the Figure of Merit optimizes at carrier concentrations which corresponds to semiconductor materials. Consequently, semiconductors are the materials most researched for thermoelectric applications.

Thermoelectric phenomena are exhibited in almost all conducting materials (except for superconductors below T_C). Because the Figure of Merit varies with temperature, a more meaningful measure of performance is the Dimensionless Figure of Merit ZT , where T is absolute temperature. However, only those materials which possess a $ZT > 0.5$ are usually regarded as thermoelectric materials.

Germanium Antimony Telluride

Germanium antimony telluride (GST materials) discussed as high-performance thermoelectric properties, because of their good electrical properties and low thermal conductivity, a maximum ZT value of 0.75 at 710 K (Kosuga et al., 2015b). Thus, the search for a better material is still a premium in thermoelectric research (Sankar et al., 2015). GeSbTe (germanium-antimony-tellurium or GST) is a phase-change material from the group of chalcogenide. GeSbTe is a ternary compound of germanium, antimony, and tellurium, with composition GeTe–Sb_2Te_3 show in Figure 5. In the GeSbTe system, there is a pseudo-line as shown upon which most of the alloys lie. Moving down this pseudo-line, it can be seen that as we go from Sb_2Te_3 to GeTe, the melting point and glass transition temperature of the materials increase, crystallization speed decreases and data retention increases. Hence, in order to get high data transfer rate, we need to use material with fast crystallization speed such as Sb_2Te_3. This material is not stable because of its low activation energy. On the other hand, materials with good amorphous stability like GeTe has slow crystallization speed because of its high activation energy. In its stable state, crystalline GeSbTe has two possible configurations: hexagonal and a metastable face centered cubic (FCC) lattice (Yan, Zhu, Zhao, & Dong, 2007). When it is rapidly crystallized however, it was found to have a distorted rocksalt structure. GeSbTe has a glass transition temperature of around 373 K (Morales-Sanchez, Prokhorov, Mendoza-Galván, & González-Hernández, 2002). GeSbTe also has many vacancy defects in the lattice, of 20 to 25% depending on the specific GeSbTe compound (Matsunaga & Yamada, 2004). Hence, Te has an extra lone pair of electrons, which are important for many of the characteristics of GeSbTe. Crystal defects are also common in GeSbTe and due to these defects, an Urbach tail in the band structure is formed in these compounds. GeSbTe is generally p type and there are many electronic states in the band gap accounting for acceptor and donor like traps. GeSbTe has two stable states, crystalline and amorphous (Rosenthal, Schneider, Stiewe, Döblinger, & Oeckler, 2011). The phase change mechanism from high resistance amorphous phase to low resistance crystalline phase in nano-timescale and threshold switching are two of the most important characteristic of GeSbTe.

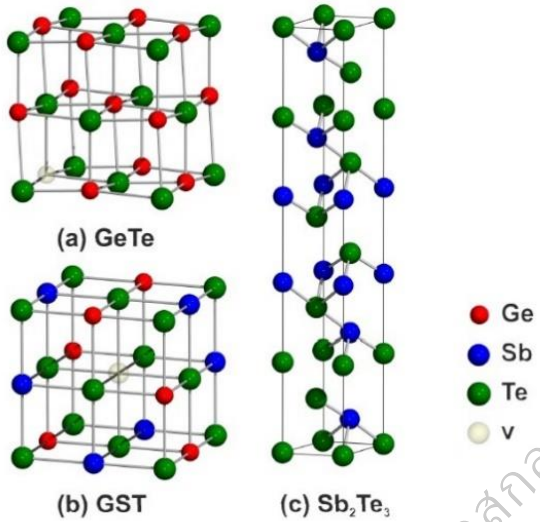

Figure 5 The GeSbTe system with composition GeTe–Sb_2Te_3 (Perumal, 2013)

The crystal structure of GST-based material is the R3m space group and lattice shown by the a- and c-axis is represented by atomic layer units. The GeTe–Sb_2Te_3 pseudobinary and Sb–Te binary systems form various intermetallic compounds represented by the chemical formula $(GeTe)_n(Sb_2Te_3)_m$ and $(Sb_2)_n(Sb_2Te_3)_m$ (n, m: integer). All of these structures, which are called homologous phases (Kifune, Fujita, Kubota, Yamada, & Matsunaga, 2011). We was considerable interest in the layered compounds belonging to the homologous series nGeTe · mSb_2Te_3 (n = 1, m = 3). The homologous structure, consisting of two types of slab. This structure is based on the cubic ABC stacking structure with consists of five layers of Sb_2Te_3-type and seven layers of GST. The phase diagram of the $GeSb_6Te_{10}$¬ and Sb_2Te_3 pseudo binary systems were studied by Abrikosov and Danilova-Dobryakova (Kosyakov, Shestakov, Shelimova, Kuznetsov, & Zemskov, 2000).The result shows many-layered slabs are stacked along the c-axis in an ordered manner and are linked mainly by weak, van der Waals forces (Shelimova, Karpinskii, Zemskov, & Konstantinov, 2000). The GST exists in various compositions and crystal structures giving different physical properties that affect their functions. In which the composition changes along direction (Kosuga et al., 2015a) the crystal structure of GST-based material is the R3m space group and lattice shown by the a- and c-axis is represented by atomic layer units. (Namhongsa, Omoto, Fujii, Seetawan, & Kosuga, 2017) (Kosuga et al., 2015a), it has been report GST prepared using spark plasma sintering (SPS). SPS induced small amounts of Ge-rich precipitates with size of a few micrometers and SPS sample found the arrangement and distribution of some elements leads to change in the crystal structure.

Thermoelectric Cell and Module

The power generation from thermal of TE cell based on the Seebeck phenomenon. Thermoelectric cell are fabricated from two type of thermoelectric materials (p-type and n-type). The most of the semiconductor materials as the electrode connected serially called p-n junction. In other word, when heating at the p-n junction of thermoelectric cell. The heat that flows through it varies by the type of thermoelectric material, which results in temperature differences and potential voltages between the two electrodes. It is caused by the flow of electrons and holes. And at the same time, it absorbs heat from the other side of the thermoelectric material to cool it to the other end of the thermoelectric material. The hole flow of thermoelectric material is in the opposite direction to the flow of electrons, that is, when we heat it to the p-n junction. The flow of electrons and holes from the hot side to the cold side or the thermal absorption of the positive charge of the p-type material and then dissipate of the n-type material.

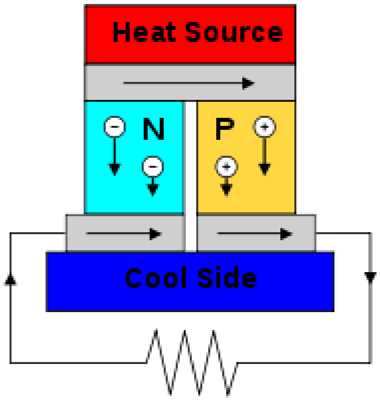

Figure 6 Schematic of thermoelectric cell. The power generation from thermal of thermoelectric cell. (https://en.wikipedia.org/wiki/Thermoelectric_effect)

The voltage output from semiconductor thermocouples remains relatively low, hundreds of microvolts per degree, and in practice a large number of thermocouples are connected electrically in series and thermally in parallel by sandwiching them between two high thermal conductivity but low electrical conductivity ceramic plates to form a module. The module is the building-block of a thermoelectric conversion system and its general construction is very similar for both generator and refrigerating applications. Ideally the geometry of the thermoelements should be wire-like (long and thin) for generation and squat (short and fat) for refrigeration (David Michael Rowe, 2005). A thermoelectric cell and modules are a solid-state energy converter consist of semiconductor material (p and n type), which are joined, thermally in parallel and electrically in series. The general design is shown in Figure 7.

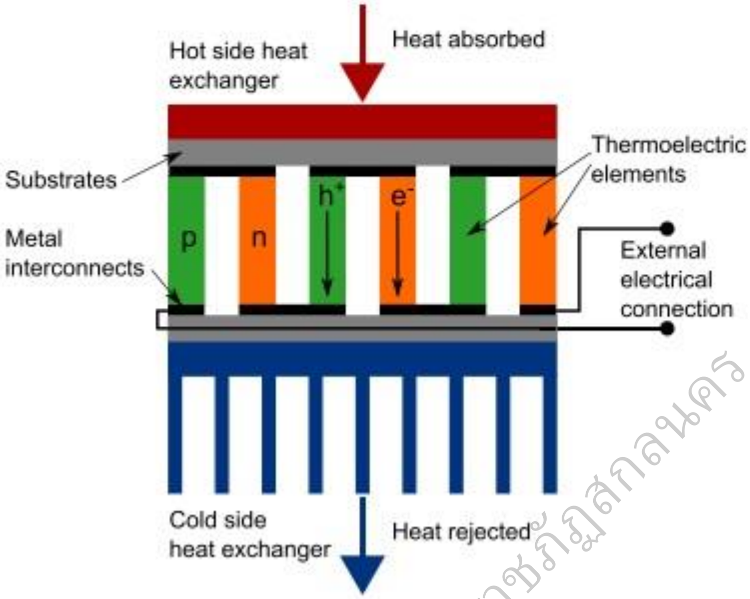

Figure 7 Schematic of thermoelectric module, many unicouples (n/p pairs) are connected electrically in series to form a module. Heat exchangers are used on either side of the module to enhance heat transfer into/out of the TE module.(Baranowski, Jeffrey Snyder, & Toberer, 2013)

Thermoelectric Applications

A thermoelectric generator is a unique heat engine in which charge carriers serve as the working fluid. It has no moving parts, is silent in operation and reliable. However, its relatively low efficiency (typically around 5%) has restricted its use to specialized medical, military and space applications, such as radioisotope power for deep space probes, and remote power, such as oil pipelines and sea buoys, where cost is not a main consideration. The use of a thermoelectric converter for electrical power generation has conventionally followed the basic arrangement shown in Figure 8. A thermoelectric module is sandwiched between a heat source and a heat sink. Heat from the source flows though the module and is rejected through the heat sink into the ambient. Provided a temperature difference can be maintained across the module, electrical power will be generated (Riffat & Ma, 2003).

Low power generation

Energy supply for small, independent and wireless system for remote sensing, control, safety surveillance and metering is mostly made with batteries. This presents a number of severe disadvantages: the lifetime of batteries is limited which implies that the system has to be maintained or replaced after a few years. Furthermore, batteries contain chemical substances that are harmful to the environment.

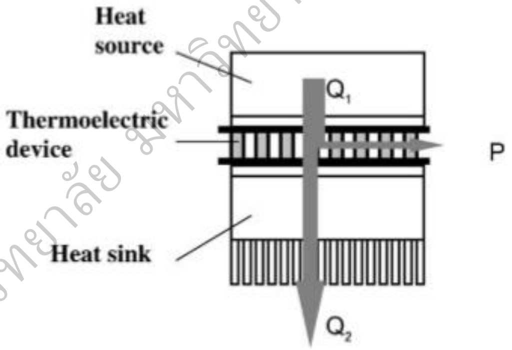

Figure 8 Conventional arrangement for thermoelectric power generation. Q_1 is the heat supplied by the heat source. P is the electrical power generated. Q_2 is the heat dissipated to the heat sink, which is the thermal energy wasted. (Riffat & Ma, 2003)

For this reason, the disposal of battery operated systems has to be controlled, which is a very expensive procedure. Another common solution is the solar cell as it is used for small calculators or watches. If no light is available the small temperature differences which are present could be used to operate a small thermoelectric generator. Therefore, small, inexpensive and efficient thermoelectric generators are gaining importance as a replacement for batteries in many systems (Glosch, Ashauer, Pfeiffer, & Lang, 1999). One of the examples is to operate a small preamplifier and a sensor control system with a thermoelectric generator generating an electrical power of 1.5 μW with a temperature difference of 283 K. A large number of studies have been reported on the (Bi,Sb)$_2$(Te,Se)$_3$–based thermoelectric materials and devices because of their excellent performance in thermoelectric refrigeration and power generation at room temperature. Thermoelements have been usually fabricated from sintered blocks of these materials. There are, however, certain difficulties and limitation in making highly miniaturized modules because of the fragile nature of these materials. Moreover, the number of P/N couples fitting in a limited space available makes it impossible to obtain relatively high output voltage (order of volt) for power generation. To overcome these drawbacks, thermoelectric modules based on thin film technology for both refrigeration and power generation have been studied (Kim, 2000). Microwatt or mill watt power level could be obtained by thin film thermoelectric generators. At present, the thin film thermoelectric generators for electronic applications have be commercially available from <www.dts-generator.com>. Any available heat source such as the surface of a water pipe would provide sufficient heat flux to these low power applications.

High power generation

Waste heat thermoelectric generator

In general, a thermoelectric generator exhibits low efficiency due to the relatively small dimensionless figure of merit ($ZT \leq 1$) of currently available thermoelectric materials. For low power generation, the low efficiency of the thermoelectric generators is not a main drawback. But for high power generation, low efficiency is a disadvantage and has limited its application to specialized areas. In the case of waste heat, efficiency of the thermoelectric generation system is not an overriding consideration. The use of waste heat as an energy source particularly at temperatures below 413 K substantially increases the commercial competitiveness of this method of generating electrical power (David M Rowe, 1999). In general, the cost of thermoelectrically producing electricity mainly consists of the running cost and module cost but in this case, the running cost is negligible compared with the module cost because the fuels cost very little or nothing. Consequently, an important objective in thermoelectric power generation using waste heat is to reduce the cost-per-watt of the devices. A figure of about £4/W can readily be obtained using commercially available thermoelectric device with an appropriate thermoelement length. Furthermore, cost-per-watt can be reduced by optimizing the device geometry, improving the manufacture quality and simply by operating the device at a larger temperature difference. The power-per-area can also be significantly improved by reducing the inter-thermoelement separation. Although the inter-thermoelement separation may not affect most cooling applications, its reduction will significantly increase the power-per-area of a device when it is used in generating mode. One investigation of the performance of thermoelectric generating systems powered by waste hot water indicates that, over a three year operating period, electrical power can be produced by this method and at a price which matches that of conventional utilities. Another study carried out by Yodovard et al. (Yodovard, Khedari, & Hirunlabh, 2001). Assesses the potential of waste heat thermoelectric power generation for diesel cycle and gas turbine cogeneration in the manufacturing industrial sector in Thailand. The data from more than 27,000 factories from different sectors, namely, chemical product, food processing, oil refining, palm oil mills petrochemical, pulp and paper rice mills, sugar mills, and textiles, were used. It is shown that gas turbine and diesel cycle cogeneration systems produced electricity estimated at 33% and 40% of fuel input, respectively. The useful waste heat from stack exhaust of cogeneration systems was estimated at 20% for a gas turbine and 10% for the diesel cycle. The corresponding net power generation is about 100 MW. Although a reciprocating piston engine (automobile) efficiently converts the chemical energy in fossil fuels into mechanical work, a considerable amount of energy is dissipated to the environment through exhaust gas, cooling water, lubricating oils and radiation. Typical exhaust output at normal running speed for a family car is 20–30 kW. A comprehensive theoretical study concluded that a thermoelectric generator powered by exhaust heat could meet the electrical requirements of a medium sized automobile (David M Rowe, 1999). Wide-scale applications of thermoelectric in the automobile industry would lead to some reductions in fuel consumption but this technology is not yet proven. In Japan the solid waste per capita is around 1 kg per day and the total amount of energy in equivalent oil estimated at 18 million kiloliter by the beginning of the 21st century. The possibility of utilizing the heat from incinerating municipal waste has been considered. A small-scale on-site experiment using a 60 W thermoelectric module was installed near the boiler section of an incinerator plant. The gas temperature varied between 823 and 973 K and with forced air cooling an estimated conversion efficiency of 4.4% was achieved. An analysis of a conceptual large scale system burning 200 ton a day indicated that around 2000 kW could be recovered. Vast amounts of heat are rejected from industry, manufacturing plants and power utilities as gases or liquids at temperature which are too low for use in conventional generating units (<450 K). Thermoelectric generators offer an alternative and a series of prototype systems, powered by low temperature waste heat, have been constructed at University of Wales, Cardiff and operated for several years. Small prototype generating systems powered by waste warm water are economically competitive at present and their competitiveness will increase further as the technology develops (David M Rowe, 1999). The use of the waste heat would totally change the economic competitiveness of thermoelectric generating systems. Using available technology a thermoelectric generating system if operated over a three year period will produce electrical power at a cost which matches the major utilities.

Thermoelectric technology has been used practically in wide areas recently. The thermoelectric devices can act as coolers, power generators, or thermal energy sensors and are used in almost all the fields such as military, aerospace, instrument, biology, medicine and industrial or commercial products. In recent years it has been realized that in situations where the supply of heat is cheap or free, as in the case of waste heat or solar energy, efficiency of the thermoelectric generation system is not an overriding consideration. Efficient, clean energy conversion for high value-added applications such as space, defense is needed in the future. Thermoelectric power plant should be a good candidate. The development of new thermoelectric materials with large ZT could make a breakthrough on applications of the thermoelectric devices in various fields.

References

Baranowski, L. L., Jeffrey Snyder, G., & Toberer, E. S. (2013). Effective thermal conductivity in thermoelectric materials. *Journal of applied physics, 113*(20), 204904.

Glosch, H., Ashauer, M., Pfeiffer, U., & Lang, W. (1999). A thermoelectric converter for energy supply. *Sensors and Actuators A: Physical, 74*(1), 246-250.

Kifune, K., Fujita, T., Kubota, Y., Yamada, N., & Matsunaga, T. (2011). Crystallization of the chalcogenide compound Sb8Te3. *Acta Crystallographica Section B, 67*(5), 381-385. doi: doi:10.1107/S0108768111033738

Kim, I.-H. (2000). (Bi, Sb) 2 (Te, Se) 3-based thin film thermoelectric generators. *Materials letters, 43*(5), 221-224.

Kosuga, A., Nakai, K., Matsuzawa, M., Fujii, Y., Funahashi, R., Tachizawa, T., . . . Kifune, K. (2015a). Crystal structure, microstructure, and thermoelectric properties of GeSb6Te10 prepared by spark plasma sintering. *Journal of Alloys and Compounds, 618*, 463-468. doi: http://dx.doi.org/10.1016/j.jallcom.2014.08.183

Kosuga, A., Nakai, K., Matsuzawa, M., Fujii, Y., Funahashi, R., Tachizawa, T., . . . Kifune, K. (2015b). Crystal structure, microstructure, and thermoelectric properties of GeSb 6 Te 10 prepared by spark plasma sintering. *Journal of Alloys and Compounds, 618*, 463-468.

Kosyakov, V. I., Shestakov, V. A., Shelimova, L. E., Kuznetsov, F. A., & Zemskov, V. S. (2000). Topological characterization of the Ge-Sb-Te phase diagram. *Inorganic Materials, 36*(10), 1004-1017. doi: 10.1007/BF02757976

Matsunaga, T., & Yamada, N. (2004). Structural investigation of GeSb 2 Te 4: A high-speed phase-change material. *Physical Review B, 69*(10), 104111.

Morales-Sanchez, E., Prokhorov, E., Mendoza-Galván, A., & González-Hernández, J. (2002). Determination of the glass transition and nucleation temperatures in Ge 2 Sb 2 Te 5 sputtered films. *Journal of applied physics, 91*(2), 697-702.

Namhongsa, W., Omoto, T., Fujii, Y., Seetawan, T., & Kosuga, A. (2017). Effect of the crystal structure on the electronic structure and electrical properties of thermoelectric GeSb 6 Te 10 prepared by hot pressing. *Scripta Materialia, 133*, 96-100.

Perumal, K. (2013). *Epitaxial growth of Ge-Sb-Te based phase change materials.* Humboldt-Universität zu Berlin, Mathematisch-Naturwissenschaftliche Fakultät I.

Riffat, S. B., & Ma, X. (2003). Thermoelectrics: a review of present and potential applications. *Applied thermal engineering, 23*(8), 913-935.

Rosenthal, T., Schneider, M. N., Stiewe, C., Döblinger, M., & Oeckler, O. (2011). Real Structure and Thermoelectric Properties of GeTe-Rich Germanium Antimony Tellurides. *Chemistry of Materials, 23*(19), 4349-4356. doi: 10.1021/cm201717z

Rowe, D. M. (1999). Thermoelectrics, an environmentally-friendly source of electrical power. *Renewable Energy, 16*(1-4), 1251-1256.

Rowe, D. M. (2005). *Thermoelectrics handbook: macro to nano*: CRC press.

Sankar, R., Wong, D. P., Chi, C.-S., Chien, W.-L., Hwang, J.-S., Chou, F.-C., . . . Chen, K.-H. (2015). Enhanced thermoelectric performance of GeTe-rich germanium antimony tellurides through the control of composition and structure. *CrystEngComm, 17*(18), 3440-3445. doi: 10.1039/C5CE00228A

Shelimova, L. E., Karpinskii, O. G., Zemskov, V. S., & Konstantinov, P. P. (2000). Structural and electrical properties of layered tetradymite-like compounds in the GeTe—Bi2Te3 and GeTe—Sb2Te3 systems. *Inorganic Materials, 36*(3), 235-242. doi: 10.1007/BF02757928

Yan, F., Zhu, T., Zhao, X., & Dong, S. (2007). Microstructures and thermoelectric properties of GeSbTe based layered compounds. *Applied Physics A: Materials Science & Processing, 88*(2), 425-428.

Yodovard, P., Khedari, J., & Hirunlabh, J. (2001). The potential of waste heat thermoelectric power generation from diesel cycle and gas turbine cogeneration plants. *Energy sources, 23*(3), 213-224.