

# REVIEW OF THERMOELECTRIC MATERIALS AND ITS PROPERTIES WITH APPLICATIONS

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**Abstract:** From several decades, thermoelectric materials have been proved to be potential means of energy conversion due to its capability of directly converting heat energy in electricity form. However, due to its complication in construction & fabrication in addition with lower efficiency in performance, thermoelectric devices have limitations when it comes to their application in commercial sector. Electricity from heat or thermoelectricity has been accepted as the means of energy conversion technology which is eco-friendly since it does not harm the environment and carries out the conversion process for long period of time. The present paper depicts the studies and investigation performed in introducing the basic principles of thermoelectric materials including thermoelectric properties various applications of thermoelectric material and its construction process.

**Index Terms - Thermoelectric Materials, Thermoelectric Properties, Figure of merit (ZT), Applications**

## 1. Introduction

Thermoelectric materials can be used in direct conversion of heat to electricity and vice versa (Zhou *et al.*, 2018). Being a purely solid-state based technology, TE materials and devices have the advantage of small size, no moving parts, no noise, no pollutants and high reliability. The dimensionless figure of merit ZT is the most important parameter for evaluating the performance of the thermoelectric materials (Zeming, 2017). These characteristics give TE technology unique advantages in applications such as waste heat recovery and TE refrigeration. The efficiency of TE materials is determined by the dimensionless parameter, figure of merit (ZT) (Ohtaki, 2011) (Wang *et al.*, 2010), defined as

$$ZT = S^2 \sigma T / k = S^2 \sigma T / (k_e + k_l) \dots \dots \dots (1)$$

Where S is the Seebeck coefficient,  $\sigma$  is the electrical conductivity (Faghaninia and Lo, 2014), T is the absolute temperature and k is the thermal conductivity (Xie, Tang and Zhang, 2007) (Solanki, 2014) composed of electronic thermal conductivity  $K_e$  and lattice thermal conductivity  $K_l$ . According to the Seebeck and Peltier effect, the TE technology can be divided into two categories (Han, Li and Dou, 2014):

- (1) Thermoelectric generator (TEG) for power generation when the TE materials are exposed to different temperatures, as shown in Figure 1b;
- (2) Thermoelectric cooling (TEC) for refrigeration when the voltage is added onto the TE materials as indicated in Figure 1e (Yang, 2007) (Venugopal *et al.*, 2014).

Simple doping of impurities may also improve the Seebeck coefficient by changing the electron density of states (DOS) (Heremans JP, 2008). As shown in Equation (Chen *et al.*, 2012),

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

Where, the charge carriers ( $m^*$ ) which usually decreases with increasing carrier mobility.  $k_B$  and h are Boltzmann constant and Planck constant, respectively (Korotcenkov, Brinzari and Ham, 2018). Another way to enhance the Seebeck coefficient is by the use of external field effects (Liang WJ, 2009).

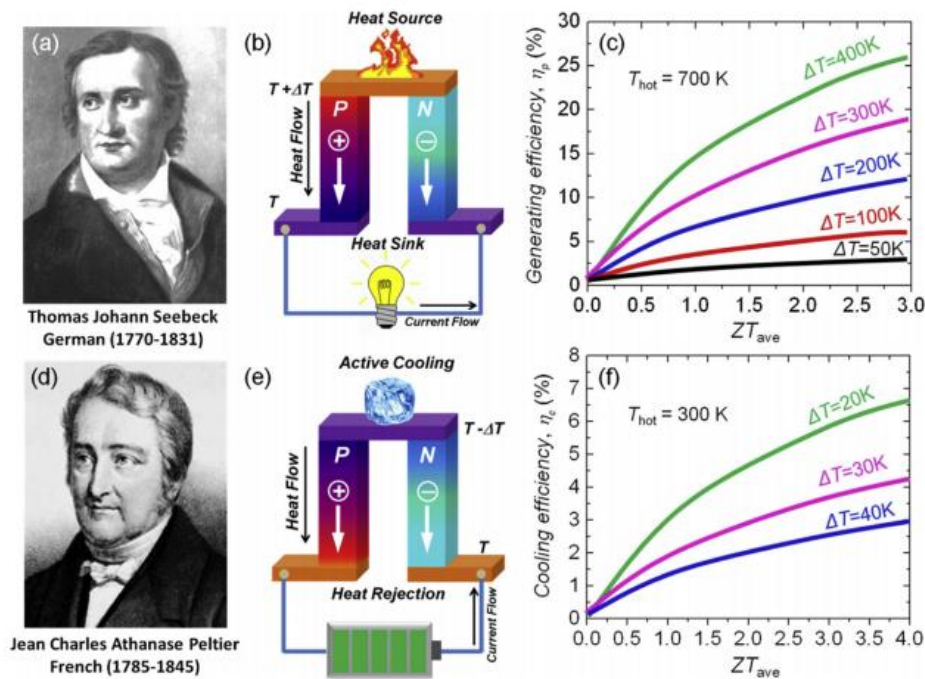


Figure 1(a-f) seebeck and peltier effect for the power generation

## 1.1 History of evolution

Although thermoelectric (TE) phenomena was discovered more than 150 years ago (Prof. N. B. Totala and Debarshi Gangopadhyay, 2014) The most efficient thermoelectrics have historically been heavily doped semiconductors because the Pauli principle restricts the heat carrying electrons to be close to the Fermi energy for metals (Boukai *et al.*, 2008). Thermoelectric (TE) phenomena were discovered at the beginning of the 19th century (Goupil *et al.*, 2011) first by Thomas J. Seebeck, who observed the deviation of a compass needle when keeping the two junctions of different metals at different temperatures (Seebeck T., 1821) (Seebeck, 1826). At the beginning of the 20th century both the theory and the application had been observed again (Kohlrausch, 1900) (Diesselhorst, 1900). In 1821, J. T. Seebeck (1770-1831) discovered that dissimilar metals that are connected at two different locations (junctions) will develop a micro-voltage if the two junctions are held at different temperatures. This effect is known as the "Seebeck effect" (Wango, 2016), (Huang, 2013). Although stagnant for most of the last 30 years, the search for advanced thermoelectric materials has undergone a remarkable rebirth over the last several years (Caillat, Fleurial and Snyder, 1999). The discovery (or development) of thermoelectric materials started from simple metal, conventional semiconductor The binary Zn-Sb system affords two semiconductor phases, ZnSb and  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub>, which have been known as thermoelectric materials since the 1960s (Fischer *et al.*, 2015). Especially  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> shows an excellent thermoelectric performance in the temperature range of 450 – 650 K and has been intensively studied during the past 15 years (E. S. Toberer, 2010). According to the primary criterion of figure of merit  $z = \frac{\alpha^2}{RK}$  a good thermoelectric material should have high Seebeck coefficient, high electrical conductivity, and low thermal conductivity. Commonly used thermoelectric materials are Bismuth Telluride (Bi<sub>2</sub>Te<sub>3</sub>), Lead Telluride (PbTe), Silicon Germanium (SiGe) and Cobalt Antimony (CoSb<sub>3</sub>), among which Bi<sub>2</sub>Te<sub>3</sub> is the most commonly used one. These materials usually process a ZT value (figure of merit at temperature) less than one. From 1960s to 1990s (Gaikwad *et al.*, 2016), developments in materials in the view of increasing ZT value was modest, but after the mid-1990s, by using nano structural engineering thermoelectric material efficiency is greatly improved. Thermoelectric materials such as primary bulk thermoelectric materials like skutterudites, clathrates and half-Heusler alloys, which are principally produced through doping method are developed but not exploited for commercial use (Zhao and Tan, 2014).

## 1.2 Classification of thermoelectric material

Thermoelectric materials are typically classified by material structure and composition. Some of the main classifications are chalcogenide, clathrate, skutterudite, half-Heusler, silicide, and oxide. Excellent reviews of thermoelectric materials have provided descriptions of both the material classifications and the relationship between material structure and thermoelectric properties (Sootsman, Chung and Kanatzidis, 2009) (Tritt, 2011) (Liu *et al.*, 2012), so comprehensive descriptions are not provided here. Chalcogenide materials have a long history of demonstrated thermoelectric use with bismuth telluride and lead telluride being the most prominent. Commercial, off-the-shelf thermoelectric modules for low temperature use are primarily made with bismuth telluride and its solid solutions with antimony or selenium. Lead telluride has better thermoelectric properties at higher temperatures (~500–600 °C). Materials engineering of clathrates and skutterudites has involved introduction of void-filling or guest atoms into a base structure. These additions can optimize electron concentration or act as phonon scattering sites. Such materials engineering to achieve a glass-like thermal conductivity combined with good charge carrier mobility has been termed the "phonon glass electron crystal" approach. With one vacant sublattice in the crystal structure, the properties of half-Heusler materials have also been improved through void-filling as well as doping of the filled sublattices. Silicides have generated interest due to the low cost of their abundant materials (i.e. silicon), and oxides are expected to have high temperature stability in air. Notable advancements have been made in both the types of materials synthesized and the reported properties. For low temperature thermoelectrics, nanostructured bismuth telluride (Poudel *et al.*, 2008), polymers and polymer-inorganic matrices (Sun *et al.*, 2012) (Bubnova and Crispin, 2012), and MgAgSb-based materials (Zhao *et al.*, 2014) have broadened the range of options. The reported material properties for high temperature thermoelectrics have demonstrated noteworthy gains resulting in

ZT values above 1. Hierarchical nano- to meso-scale structuring (Biswas *et al.*, 2012) and new materials such as tetrahedrites (Lu *et al.*, 2013) have contributed to the gains (LeBlanc, 2014).

### 1.3 Working principle and laws description.

To obtain a high ZT, both Seebeck coefficients ( $s$ ) must be large, while thermal conductivity ( $\kappa$ ) must be minimized; however, the laws of physics conspire against satisfying this requirement (Biswas, 2015). The Wiedemann-Franz law requires the electronic part of thermal conductivity ( $\kappa$ ) to be proportional to electrical conductivity ( $\sigma$ ) and the Pisarenko relation limits the simultaneous enlargement of  $s$  and  $\sigma$ . The complex relationships of these thermoelectric parameters can be summarized as: (Snyder and Toberer, 2008) (Zhang and Zhao, 2015)

$$s = \frac{8\pi^2 k_B^2}{3eh^2} mT \left(\frac{\pi}{3n}\right)^2$$

$$s = ne\vartheta = \frac{ne^2\tau}{m}$$

$$k_{tot} = k_{lat} + k_{ele} = k_{lat} + L\sigma T$$

According to the Seebeck and Peltier effect, the TE technology can be divided into two categories: (1) thermoelectric generator (TEG) for power generation when the TE materials are exposed to different temperatures (Chen *et al.*, 2012) (Korotcenkov, Brinzari and Ham, 2018). The TEG efficiency can be estimated by (Liu *et al.*, 2015) (Yu, Sun and Jena, 2016) (COTFAS *et al.*, 2016)

$$\eta_p = \frac{T_h - T_c}{T_c} \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h}$$

Where  $T_c$  and  $T_h$  are represent the temperature of the cold side and hot side respectively (Biswas, 2015). Obviously, when the ZT value is infinite, the efficiency of TEG approaches the Carnot efficiency.

The maximum efficiency of the TEC is given by (Powell, 2013)

$$\eta_c = \frac{T_c}{T_h - T_c} \cdot \frac{\sqrt{1 + ZT} - T_h/T_c}{\sqrt{1 + ZT} + 1}$$

Thermoelectric technology is based on thermoelectric effects, including Seebeck effect, Peltier effect and Thomson effect (Solanki, 2014). It employs thermoelectric materials and transforms thermal energy to electricity (Zhou and Chu-ping, 2015)

#### 1.3.1 Seebeck effect

The Seebeck effect is predominant thermoelectric effects. The Seebeck effect is a phenomenon that voltage ( $V$ ) is induced in proportion to applied temperature gradient ( $\Delta T$ ), expressed as

$$V = S\Delta T$$

Where  $S$  is called the Seebeck coefficient (thermoelectric power, or thermopower) (Terasaki, 2005). The major activities in thermoelectric materials have been focussed on the increase of the Seebeck coefficient and the reduction of the thermal conductivity (Chen *et al.*, 2012).

As shown in Figure 1(g), for a circuit constituted of conductor (or semi-conductor) a or b in series, if there are two connectors 1 and 2 at temperature  $T_h$  and  $T_c$  respectively, there will produce a potential difference between  $y$  and  $z$  at the open-circuit position of  $b$ . Under the same material, the thermoelectricity potential is only related to the temperature difference of two connectors,  $\Delta T = T_h - T_c$  and it can be expressed by (Neeli, Behara and Kumar, 2013):

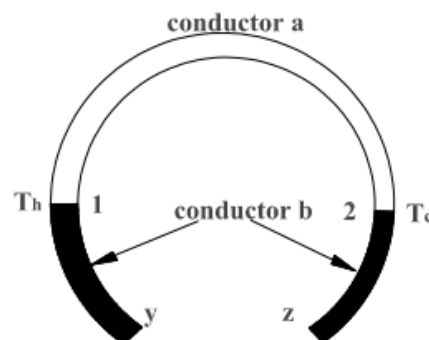


Figure 1(g) Seebeck effect

#### 1.3.2 Peltier effect

This effect was discovered by Peltier in 1834. It is opposite to the Seebeck effect. If EMF or voltage is applied across C and D points of the same material shown in figure 2, there will be flow of current through the material. The junctions of the materials (A and B) attain different temperatures. One junction attains maximum temperature and other junction attains minimum temperature (which is similar to heating at one point and cooling at other point) (Tritt and Subramanian, 2006). A rate of heating  $q$  takes place at one junction and a rate of cooling  $-q$  occurs at the other. This phenomenon depends on type of the material (Bashir, 2014), (Snyder, 2008), (Handbook, 2006) (Gonçalves and Godart, 2014). Peltier effect is expressed in terms of an equation as  $\Pi = I/q$  where,  $\Pi$  = the Peltier coefficient of the material,  $q$  = heat flow,  $I$  = electrical current (Neeli, Behara and Kumar, 2013).

**1.3.3 Thomson effect**

The Thomson effect describes the heating or cooling phenomenon along a material which an electric current is passing through and is subject to a temperature gradient, as shown in Figure 1(h). This effect was discovered by Thomson (Lord Kelvin) in 1851 (Goddard, 2011). The Thomson coefficient  $\tau$  is defined as

$$\frac{dQ}{dX} = \tau l \frac{dT}{dX}$$

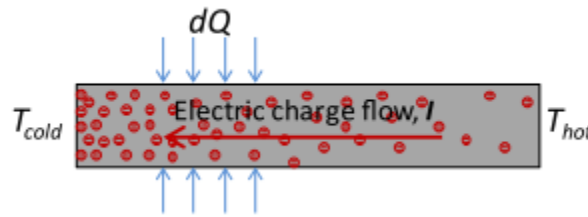


Figure 1(h) Thomson effect in a single material (Wang *et al.*, 2006).

A parabolic band model usually provides a good description of electron (hole) energy bands (Singh and Bhandari, 2004). An ideal thermoelectric material behaves like an electron crystal and phonon glass (Hippalgaonkar *et al.*, 2017). Thermoelectricity may be characterized by the simultaneous effects of both electrical and thermal currents. Using the conventional definitions for the transport coefficients, thermoelectric behavior is well approximated by

$$i = \sigma t(E - \alpha \nabla T) \dots \dots \dots (2)$$

$$q = Ts = \alpha T i - \alpha \nabla T$$

Or

$$\frac{i}{s} = L \begin{pmatrix} E \\ -\nabla T \end{pmatrix}$$

With the transport matrix L given by

$$\frac{i}{s} = \begin{pmatrix} \sigma t & \sigma T \alpha \\ \sigma T \alpha & \lambda E/T \end{pmatrix}$$

Here,  $i$  is the electric current density,  $E$  is the electric field,  $q$  is the heat current density,  $s$  is the entropy current,  $\nabla T$  is the temperature gradient at is the electrical conductivity and  $\alpha$  is the Seebeck coefficient (Dresselhaus *et al.*, 2005).

**2. Properties of thermoelectric material**

There is a great deal of ongoing research in the TE field to improve material and device efficiency (Snyder and Toberer, 2008). The efficiency of the n- and p-type semiconducting materials comprising TE devices can be directly measured or calculated from important material properties which are individually measured (Karri, 2011). Thermoelectric materials are rated by a dimensionless figure of merit,  $ZT$ , where a higher  $ZT$  translates to higher efficiency (Purohit, 2016).

**2.1 Physical properties**

Engineering of materials with specific physical properties has recently focused on the effect of nano-sized ‘guest domains’ in a ‘host matrix’ that enable tuning of electrical, mechanical, photo-optical or thermal properties. A low thermal conductivity is a prerequisite for obtaining effective thermoelectric materials, and the challenge is to limit the conduction of heat by phonons, without simultaneously reducing the charge transport (Christensen *et al.*, 2008). Many different compositions with these two structures are possible. They are of fundamental interest from the perspective of both bonding and their physical properties (Tritt, 2002). Altenkirch’s equation includes, among other parameters and variables, the electromotive force, thermal and electrical resistance/conductivity of a thermopile. Later, in 1949-1956, the famous Russian scientist, Abram F. Ioffe integrated these parameters into the  $Z$  group (quantity  $Z$  or parameter  $Z$ ) and used the new parameter  $Z$  to calculate the efficiency of thermoelectric devices. The Ioffe’s parameter  $Z$  is given by the formula (Polozine, Sirotinskaya and Schaeffer, 2014)

$$Z = \alpha^2 \frac{\sigma}{\lambda}$$

Where:

- $Z$  – Complex characteristic of the TM pair properties,
- [1/K];  $\alpha$  – electromotive force of the thermoelectric device;
- $\sigma$  – Electric conductivity of the TM pair;
- $\lambda$  – Thermal conductivity of the TM pair.

**2.2 Transport properties**

The Hall coefficient  $R_H$  was measured at room temperature to determine the electrical properties, and the carrier concentration  $n$ , and carrier mobility  $\mu_H$  were obtained from the measured  $R_H$  and  $\sigma$  at 300 K using the equations,  $n = 1/(e |R_H|)$  and  $\mu_H = |R_H| \times \sigma$  (Zhu *et al.*, 2004), respectively, where  $e$  is the electron charge (Liu *et al.*, 2017) (Dresselhaus *et al.*, 2007). thus hypothesize that improved p-type doping of ZnSb and  $Zn_4Sb_3$  – resulting in higher carrier concentrations and higher electrical conductivity – is achieved by using substitutional metal dopants that are more electropositive than Zn; thus, candidate dopants include Fe, Co, Ni, and Cu (Caillat, Fleurial and Borshchevsky, 1997). We presume that if the host material is only lightly doped, then any changes in carrier scattering would be slight enough to not affect the thermal conductivity, while still providing observable increases to the electrical transport properties (Faghaninia and Lo, 2014) (Tritt, 2011). New concepts for improving the  $ZT$  through reducing the thermal conductivity by anisotropic designing intrinsically low dimensional crystalline structures and enhancing the electron



transport abilities for achieving high PF will shed light on the feasible alternative paths to decouple the synergistic thermal conductivity and the electron transport properties (Zhou *et al.*, 2018). Considering the fact that low frequency acoustic phonons dominate phonon conduction, the size of the phonon scatterers plays an important role in lowering thermal conductivity (Twombly, 2016). It is worth mentioning that the knowledge of ballistic transport properties is a necessary starting point for investigating TE efficiency (Sevinçli *et al.*, 2013). The electrical conductivity is related to the density of charge carriers ( $n$ ) and their mobility ( $m$ ), typically given by

$$\sigma = ne\mu$$

The mobility is given by:

$$\mu = \frac{e\tau}{m_e}$$

Where  $m$  is the mobility of the carriers,  $m_e$  is the effective mass, and  $t$  is the mean scattering time between collisions for the carriers (Tritt, 2002)

### 2.3 Thermal Conductivity

The thermal conductivity,  $k$ , is related to the transfer of heat through a material (Singh and Bhandari, 2004), either by the electrons or via quantized vibrations of the lattice called phonons such that

$$k = k_L + k_E$$

Where  $k_L$  and  $k_E$  are the lattice and electronic contributions respectively. The electrical conductivity and the thermal conductivity are interrelated, in that  $s$  is tied to  $k_E$  through the Wiedemann–Franz relationship (Tritt, 2002).

### 3. Types of materials involved for thermoelectric effect.

Thermoelectric materials are normally classified into four categories depending on their temperature range of application (Gaikwad *et al.*, 2016): cryogenic temperature range: from 4 K to 250 K; near room-temperature range: from 250 K to 500 K; intermediate temperature range: from 500 K to 900 K; and high temperature range: beyond 900 K (Ohtaki, 2010) (Zou *et al.*, 2015). As intermediate temperature range is just the temperature range of most industrial waste heat sources, it is very important to research high intermediate thermo electrics. The ideal thermoelectric material should be a “phonon-glass and electron crystal” material (Zou *et al.*, 2015). Among the wide variety of intermediate temperature materials,  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> compounds with low thermal conductivity and made of relatively cheap and nontoxic elements are pointed out as one kind of most promising thermoelectric materials (S.-C. Ur, 2003)

#### 3.1 Construction of materials

Standard thermoelectric modules are constructed from P-type and N-type thermo-elements, often referred to as thermoelectric couples, connected electrically in series and thermally in parallel. Each couple is constructed from two ‘pellets’ of semiconductor material usually made from Bismuth Telluride. One of these pellets is doped to create a P-type pellet; the other is doped to produce an N-type pellet (Gould and Shamma, 2009). The two pellets are physically linked together on one side, usually with a small strip of copper, and placed between two ceramic plates. The ceramic plates perform two functions; they serve as a foundation on which to mount the thermo-element; and also electrically insulate the thermo-element (Riffat & Ma, 2003). A single couple of a thermoelectric module is shown below in Figure 3(a).

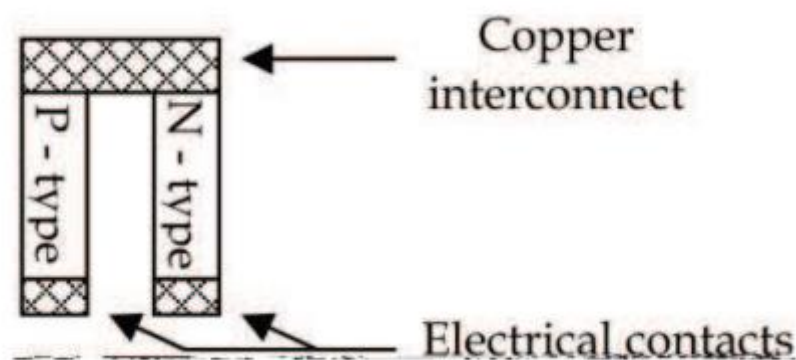


Figure 3(a) A single couple of a thermoelectric module

The thermo-element, or couple, is then connected electrically in series and thermally in parallel to other couples. Standard thermoelectric modules typically contain a minimum of 3 couples (Gould and Shamma, 2009), rising to 127 couples for larger devices. A schematic diagram of a thermoelectric module is shown in Figure 3(b) (Shamma, 2009).

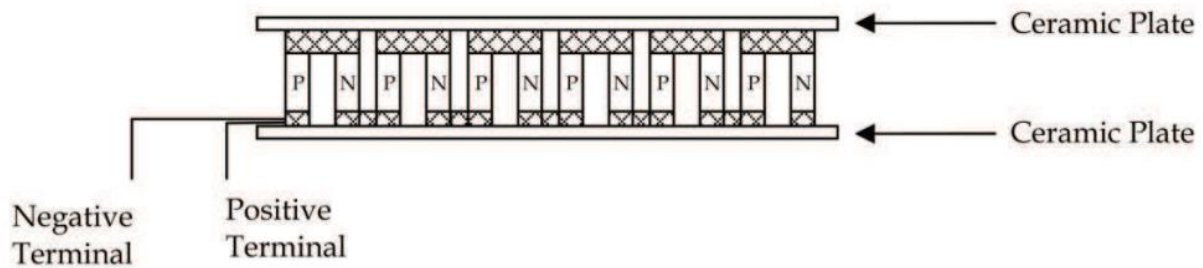


Figure 3(b) a schematic diagram of a thermoelectric module

### 3.2 Materials overview

Thermoelectric materials have attracted a renewed interest in recent years. The performance of a thermoelectric material is usually evaluated by the dimensionless figure of merit  $ZT = S^2\sigma T/\kappa$  (Effect and Background, 2014), where  $S$ ,  $\sigma$ ,  $T$  and  $\kappa$  are Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. A good thermoelectric material should possess high Seebeck coefficient, high electrical conductivity and low thermal conductivity (Biswas, 2015).

## 4. Factor effecting the thermoelectric effect

### 4.1 Effects of temperature

A temperature gradient across a solid (except superconducting materials) generates an electrical voltage between the hot and cold ends. While the voltage (thermo electromotive force, TMF) generated by metals is generally less than  $50 \mu\text{V}/\text{K}$  (Liu *et al.*, 2016), semiconductors can generate the TMF of several hundreds of  $\mu\text{V}/\text{K}$ . Since n- and p-type semiconductors generate the TMF of the opposite signs, and thereby double the voltage when combined, a semiconductor element (unicouple) as shown in Fig. 4(a) is fabricated as a unit component, and is connected in series to assemble thermoelectric modules in practical. This technology for direct conversion of heat to electricity is called thermoelectric conversion or thermoelectric power generation (Ohtaki, 2011). The overall performance depends on three key material properties that affect the device's ability to sustain the temperature difference and to effectively generate electrical power (Dresselhaus *et al.*, 2009). Improving thermoelectric efficiency hinges on: increasing the Seebeck coefficient  $S$  so that larger voltages can be obtained for each leg of the thermoelectric device (see Figure 4(a));

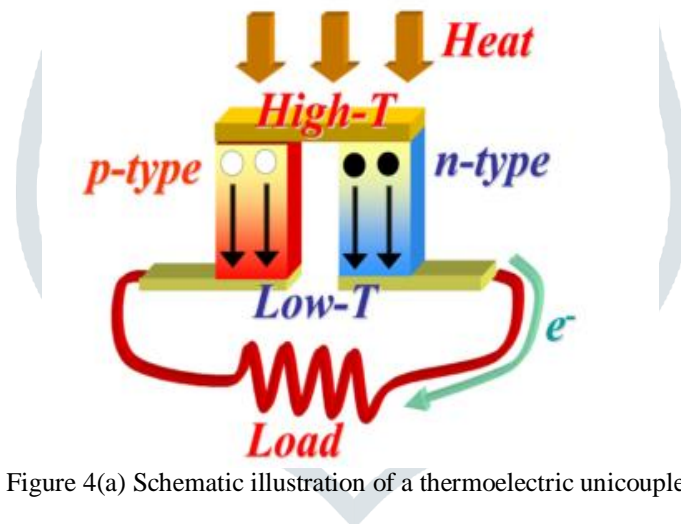


Figure 4(a) Schematic illustration of a thermoelectric unicouple.

According to (Levy, 2013) "During high temperature measurements, there is often a noticeable voltage offset, which can range from a few  $\mu\text{V}$  due to the electronics to almost  $1\text{mV}$ , which can sometimes be observed at high temperatures. The origin of the large offset and its effect on the accuracy of the measured Seebeck coefficient is unknown."

### 4.2 Effect of heat transfer

The heat transfer law represents the characteristic and regularity of the transfer. The characteristics of the thermoelectric device are influenced by the external heat transfer law. The external irreversibility is caused by the finite rate heat transfer between the thermoelectric generator and its heat reservoirs. When the heat transfer law is nonlinear then there are optimal working electrical currents and optimal ratio of thermal conductance allocations corresponding to the maximum power output and maximum efficiency. Since there are a variety of heat exchangers for thermoelectric device, the heat transfer laws are various and different from each other (Solanki, Deshmukh and Diware, 2016). By experiment or from empirical formula, one can find out the exponents  $n$  and  $m$ . The heat leakage through the lateral face can be neglected in a commercial thermoelectric generation module because they are thermal insulation packaged. At a steady work state, the temperature distribution of the air gap is the same with the thermoelectric elements, so the heat transfer of the whole device can be treated as one dimensional heat transfer approximately. The increment rate of inner energy of an infinitesimal is zero at steady-state (L. Chen, 2012).

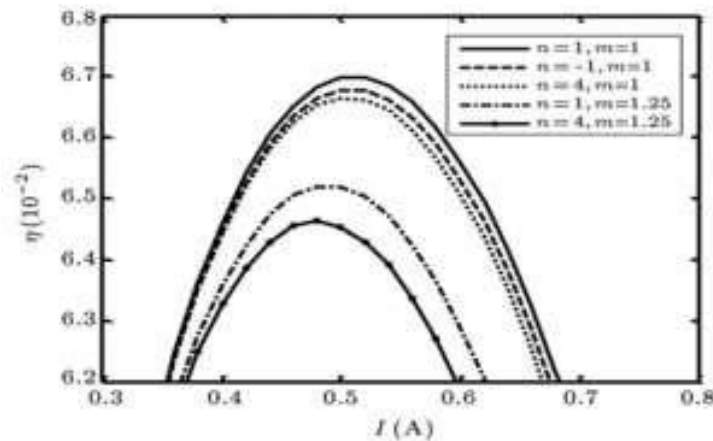


Figure 4(b) Effect of heat transfer law on efficiency versus working electrical current.

### 4.3 Effects of contact resistance and leg length

Good thermoelectric material properties are inevitable requirements for a thermoelectric module exhibiting high efficiency. (D.M. Rowe, 1996) Describe the impact of the module's contact resistance on the performance of thermoelectric generators. Even with very good thermoelectric material, the device performance can be rather poor, if the contact resistances of the module are too large. The figure of merit  $ZT$  of a thermoelectric generator is a measure of the performance and is closely related to the efficiency of a module (P. M. Solanki, 2000). It is strongly affected by the modules resistance and is given by:

$$ZT_{Module} = \frac{\alpha^2 T}{K_{Module} R_{Module}}$$

Where  $\alpha$  denotes the Seebeck coefficient of the thermoelectric material,  $T$  the average temperature of the module, and  $K$  and  $R$  are the heat conductance value and total resistance of the module, respectively (Solanki, Deshmukh and Diware, 2016). They are given by:

$$K_{Module} = \frac{\lambda_n A_n}{l} + \frac{\lambda_p A_p}{l}$$

$$R_{Module} = R_{legs} + R_c = \frac{\rho_n l}{A_n} + \frac{\rho_p l}{A_p} + R_c$$

Here,  $A$  and  $l$  denote the cross-section area and the lengths of the legs, and  $\lambda$  and  $\rho$  are the thermal conductivity and specific electric resistance, respectively.

### 5. Recent advancement in thermoelectric material

The discovery of new materials with  $ZT$  values over 2 combined with the rising concern on growing energy demand in our world have caused many new research project on how to utilize thermoelectricity as a new mean to produce and recover energy. Already thermoelectric energy conversion is finding its way into waste heat recovery for smaller systems where especially space and weight is of a concern. Almost all the challenges for further development are material related where some of the most important are:

- low efficiency materials
- too expensive materials and systems
- low durability at high temperatures
- toxic compounds
- low abundance of raw materials

It is obvious that all these aspects should be evaluated when deciding on materials for future mass production processes to get the most cost efficient and sustainable outcome. Only this way is it possible for thermoelectric energy conversion to be a part of the solution on waste heat recovery (Skomedal, 2013).

The search for new TE-materials can roughly be divided into two groups: increasing the powerfactor,  $S^2\sigma$ , or decrease the lattice thermal conductivity,  $\rho_{ph}$ . The first approach was the most frequently used in the early age of semiconductors while the second has gotten more and more attention the last decades. Some general rules to follow when looking for new thermoelectric materials where formulated by Slack (Biswas, 2012) and focuses on the increase of the  $ZT$  value.

- Reduction of the lattice thermal conductivity,  $\rho_{ph}$
- High carrier mobility,  $\mu$
- The density of state effective mass  $m^*$  should be equal to the free electron mass  $m^0$
- The band gap energy,  $E_g$ , should be equal or higher than 0.25 eV
- $\mu$ ,  $\rho_{ph}$  and  $m^*$  are independent of the charge carrier concentration  $n$ ,  $\rho_{ph}$  and  $m^*$  are independent of temperature

The characteristic these rules imply is often summarized as a Phonon Glass, Electron Crystal (PGEC) material. These are materials with very low lattice thermal conductivity similar to amorphous materials, but still have electric properties like a crystalline material (Skomedal, 2013).

## 6. Applications

Thermoelectric (TE) modules comprise arrays of thermoelectric (TE) junctions, which are connected electrically in series and thermally in parallel. The TE junctions, in turn, consist of p- and n-type thermoelectric materials, which are selected from the range of materials discussed so far in this review, based primarily on their physical thermoelectric performance. Auxiliary to the basic array of TE modules are components that contribute to the overall efficiency of the module, such as heat sinks, which absorb heat from the hot side, and cooling fins or cooling systems, which dissipate heat from the cool side. Typically, a single module may produce power in the range of 1–125W and may be modularly moving parts; they are durable and reliable, with over 100,000 h of operating lifetimes, and have a simple structure. They may operate in two modes: as thermoelectric generators (TEGs), generating electricity from a temperature gradient, or as thermoelectric coolers (TECs), converting a direct current into a temperature gradient (Riffat and Ma, 2003). Connected to produce power up to  $\leq 5$  kW. The maximum temperature gradient between the hot and cold side can be as high as 70 °C (Ahiska, Dislitas and Omer, 2012). The general TE module architecture is shown in Fig. 11. Given the nature of TE modules as solid-state devices with no moving parts, they are durable and reliable, with over 100,000 h of operating lifetimes, and have a simple structure. They may operate in two modes: as thermoelectric generators (TEGs), generating electricity from a temperature gradient, or as thermoelectric coolers (TECs), converting a direct current into a temperature gradient (Ahiska, Dislitas and Omer, 2012).

### 6.1 Applications of thermoelectric devices as coolers Thermoelectric

Thermoelectric coolers, which are commonly known as Peltier coolers, have been successfully commercialized for high-performance, niche cooling systems that require high heat-flux dissipation to a very low temperature at a precise rate (Zhao and Tan, 2014). These Peltier coolers are well suited for such applications, for which a conventional air-cooling system is no longer adequate to remove the heat fluxes at a sufficiently high rate. The general design criteria for these TECs include high reliability, flexibility in packaging and integration and low weight (Ahiska, Dislitas and Omer, 2012) (Chen and Huang, 2004). The schematic of the thermoelectric cooler is shown in Figure 6(a). (Huang, Chin and Duang, 2000) developed a system design method of TE cooler in their study which utilizes the performance curve of the TE module.

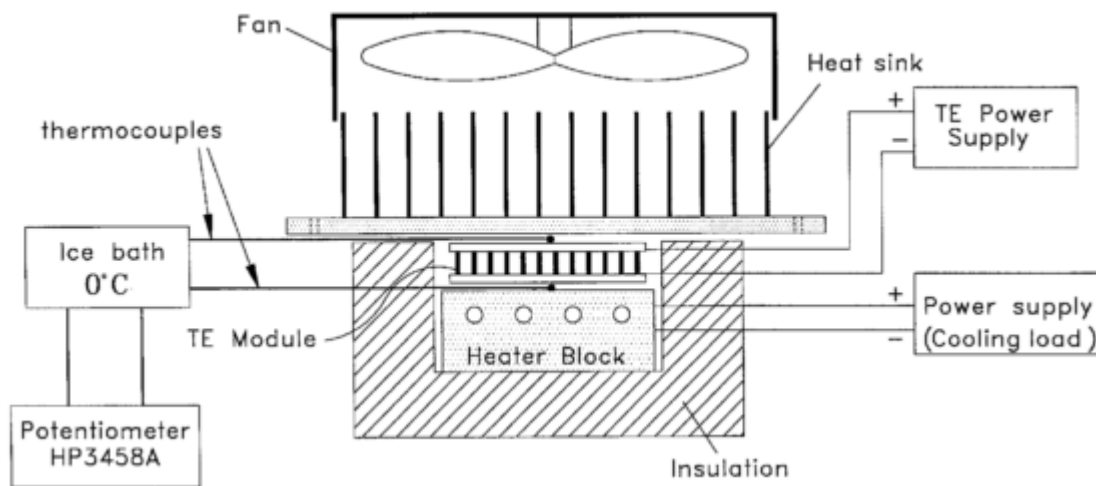


Figure 6(a) Schematic of Thermoelectric Cooler (Gaikwad *et al.*, 2016)

(Jiajitsawat and Clean, 2012) investigated theoretically & experimentally the effect of combination of TER system & DEAC system. For this he had fabricate a portable hybrid thermoelectric-direct evaporative air cooling system and tested. The schematic of the prototype is shown in Figure 6 (b). (Jiajitsawat and Clean, 2012) The operating principle of the prototype is the conversion of sensible heat of the hot air to the latent heat of water vaporization. Installation of thermoelectric refrigeration system is to remove the sensible heat from the water in the container for further improvement of the air cooling capacity.

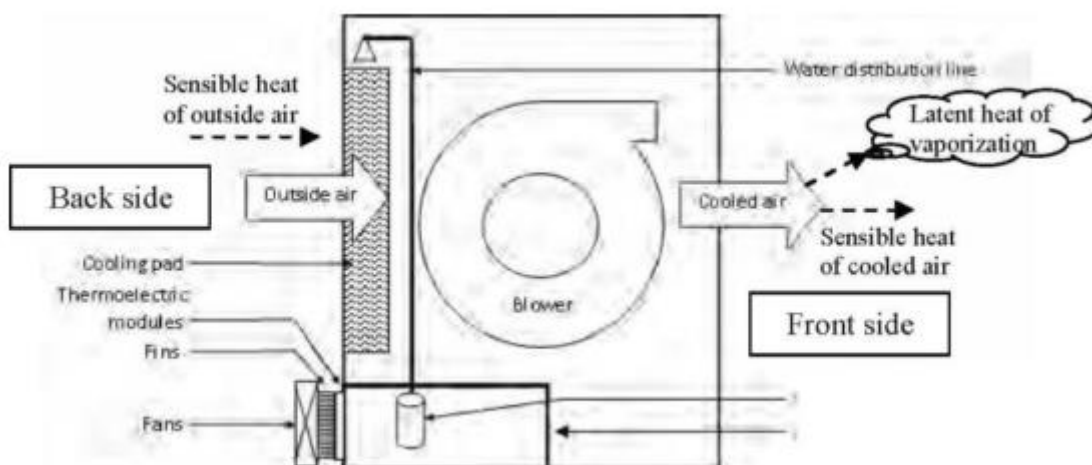


Figure 6 (b) The Combined TE-Direct Evaporative Air Cooler



## 6.2 Application of thermoelectric devices for power generation Thermoelectric

Thermoelectric generators (TEG), in principle, may offer many advantages over conventional electric-power generators, such as being highly reliable, silent in operation, and environmentally friendly and containing no moving parts (Niu, Yu and Wang, 2009). Because of these advantages, considerable emphasis has been placed on the development of TEGs as a standalone power-generation technology for a variety of aerospace, biomedical, remote power and military applications (Riffat and Ma, 2003).

## 6.3 Applications of thermoelectric devices as thermal-energy sensors

Many new types of thermal-energy sensors based on the Peltier effect or Seebeck effect of thermoelectric modules have been developed in the last two decades, such as sensors for power ultrasound effects (Faïd *et al.*, 1998), cryogenic heat-flux sensors (Faïd *et al.*, 1998), (Ahamat and Tierney, 2011), water-condensation detectors (Vancauwenberghe *et al.*, 1996)(Sawaguchi *et al.*, 2005), fluid-flow sensors, and infrared sensors (Müller *et al.*, 1996). These sensors generally rely on the conversion of heat into electrical signals or vice versa. Infrared (IR) sensors, which operate on the principle that any mass radiates heat, allow the detection of heat using the Seebeck effect; the absorption of heat causes a specific temperature rise, which subsequently produces a Seebeck voltage. The main sensor parameters are the responsivity, which is given by the ratio of the sensor voltage to the incoming radiation power; the time constant; and the noise voltage (Müller *et al.*, 1996). (Hirota *et al.*, 2007) developed a low-cost thermoelectric infrared sensor (thermopile) using polysilicon with a precisely patterned Au-black absorber that provides a high responsivity of 3900 V/W and a low cost potential. However, most thermoelectric IR sensors are able to operate in the range of 7–14  $\mu\text{m}$ .

## 6.4 Aerospace applications

Advanced autonomous power systems that can be operated continuously and independently of the sun and are capable of providing electric power from a few watts to hundreds of kilo-watts for 7–10 years are required for extraterrestrial exploration vehicles. For example, the solar brightness on Mars and Jupiter is as weak as 45% and 4%, respectively, and it is negligible on other planets. As a result, the solar option is suitable only for robotic and spacecraft missions that are limited in their time scope of operation and require only a few watts of electrical power ( $\leq 10\text{W}$ ) (El-Genk and Saber, 2005). Radioisotope thermoelectric generators (RTGs) have been used by the United States to provide electrical power for spacecraft since 1961. The required electrical output power levels can be achieved by the appropriate selection of a number of general-purpose heat-source (GPHS) modules incorporated in an RTG system. A GPHS module is a composite carbon body that houses a total of four fuel pellets and acts as an aero-impact shell. The isotope fuel for the GPHS-RTG is in the form of plutonium dioxide ( $^{238}\text{PuO}_2$ ) at approximately 80% density. For power conversion by the GPHS-RTG, thermoelectric junctions have been used, such as SiGe junctions (O'Brien *et al.*, 2008).

## 7. Summary of new thermoelectric properties

Currently, there are no theoretical or thermodynamic limits to the possible values of  $ZT$ . Given the current need for alternative energy technologies and materials to replace the shrinking supply of fossil fuels, the effort is becoming more urgent. Energy-related research will grow rapidly over the next few years, and higher-performance thermoelectric materials and devices are direly needed. Slack estimated that an optimized phonon glass/ electron-crystal material could possibly exhibit values of  $ZT$  4. This gives encouragement that such materials may be possible and could address many of our energy-related problems. Thus, a systematic search and subsequent thorough investigation may eventually yield these much-needed materials for the next generation of TE devices. Although many strategies are being employed in hopes of identifying novel TE materials, the PGEC approach appears to be the best, as will become apparent in the following articles. One has to decide whether “holey” semiconductors (materials with cages, such as skutterudites or clathrates) or “unholey” semiconductors (such as SiGe or PbTe) are the best to pursue, and which tuning parameters are available to improve these materials. To date, none of the new materials has displaced the current state-of-the-art materials ( $\text{Bi}_2\text{Te}_3$ , PbTe, or SiGe) in a commercial TE device. These materials have held that distinction for more than 30 years. However, given the many materials yet to be investigated, there is certainly much more work ahead and promise for developing higher-efficiency thermoelectric materials and devices. While the results are very exciting, thin films may be most appropriate for small-scale electronic and optoelectronics applications where small heat loads or low levels of power generation are more appropriate. To address large-scale refrigeration (home refrigerators) or power-generation (automotive or industrial) requirements, higher-performance bulk materials will have to be developed. Certainly, theoretical guidance, in terms of band structure calculations and modeling, will be essential to identifying the most promising TE materials. In addition, rapid yet accurate characterization of materials and verification of results are also essential in order to effectively advance this field of research. A multidisciplinary approach will be required to develop higher-efficiency thermoelectric materials and devices. The techniques used to develop “designer materials” needed for thermoelectrics will most likely prove important in other areas of materials research as well.

## 8. Conclusion

The value of figure-of-merit (ZT) is importance in determining which segmented thermoelectric materials are the best materials to be used in order to design a good thermoelectric generator with high efficiency conversion. The performance of the segmented thermoelectric materials need to be predicted before producing the segmented thermoelectric. However a direct ZT measurement of segmented thermoelectric is yet to be studied. In order to know the performance of segmented materials in real life application which under condition of large temperature difference, the measurement of figure-of-merit for the materials need to be carried out under large temperature difference. Therefore, it is necessary to do some studies on what apparatus set up or technique that is suitable and easiest way to examine the performance of segmented materials under large temperature difference. Lacks of developed techniques to evaluate the performances of thermoelectric materials under large temperature difference need to be overcome. The technique used to measure the ZT need to be simple and capable to measure ZT under large temperature difference. Most of those mentioned techniques used to measure ZT value of a single homogeneous material. The “open-short circuit” technique was proved to be able to measure ZT not only in different condition (small and large temperature difference) but also for both single and segmented material. All in all, this method has the ability to measure ZT value of single and segmented material under both small and large temperature difference.

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