
THE SCIENCE AND ENGINEERING OF THERMOELECTRICS: A COMPREHENSIVE REVIEW

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ABSTRACT

The field of thermoelectrics lies at the interface of materials science and engineering, offering a solid state solution for direct heat-to-electricity conversion. This paper explores the science and engineering principles underpinning thermoelectric technology. Beginning with thermoelectric phenomena, it examines the Seebeck effect as the foundation for thermopower, which arises from carrier diffusion due to temperature gradients. The role of the electronic bandgap in optimizing carrier concentration and energy filtering is discussed, alongside Boltzmann-transport theory, which provides theoretical basis for evaluating electrical conductivity, thermal conductivity, and Seebeck coefficient. These parameters converge in the thermoelectric figure-of-merit (ZT), a critical performance metric. On the engineering front, the paper analyzes thermoelectric power generation systems, particularly the development of micro thermoelectric devices for portable electronics, segmented

generators for handling broad temperature gradients, and cascaded generators designed to maximize energy recovery across stages. The integration of materials design with system-level engineering solutions underscores the promise of thermoelectrics in waste heat recovery, renewable energy, and compact cooling systems.

KEYWORDS: Thermoelectrics, Seebeck effect, Badgap, Thermopower, Renewable energy.

INTRODUCTION

Thermoelectric (TE) phenomena refer to the direct conversion of a temperature into electrical voltage (Seebeck effect) or the absorption/emission of heat when electrical current flows across a junction of two materials (Peltier effect) (Zebarjadi et al 2012). According to Zebarjadi et al (2012), thermoelectric effects encompass three fundamental mechanisms: the Seebeck effect, the Peltier effect and the Thomson effect, which together describe how a temperature difference with a material can generate electric voltage and vice versa. These phenomena are governed by carrier transport and are strongly influenced by a material's electronic structure and thermal conductivity.

Since Seebeck's discovery in 1821 and Peltier's in 1834, thermoelectric materials have drawn interest for their potential to support energy harvesting and solid state cooling (Riffat & Ma, 2003). The fundamental appeal of thermoelectrics lies in their silent, maintenance free operation and reliability in harsh environments.

THE SCIENCE OF THERMOELECTRIC MATERIALS

1.1.The Seebeck Effect

The Seebeck effect is a fundamental TE phenomenon in which the voltage (electromotive force) is generated across two dissimilar conducting materials when their junctions are maintained at different temperatures (Seebeck, 1895). In a thermoelectric material or semiconductor, there are free electrons and holes which carry both charge and heat. These electrons and holes behave like a gas of charged particles.

When a normal (uncharged) gas is placed in a box within a temperature gradient, the gas molecules at the hot end moved faster than those at the cold end. As expected, the faster hot molecules diffuse further than the cold molecules, resulting in a net buildup of high density molecules results at the cold end. In reverse, as the molecules are charged, the buildup of charge at the cold end produced a repulsive electrostatic force (electric potential) which pushes the charges back to the hot end. This voltage (electric potential) produced (as shown

in Figure 1) by the temperature difference is known as the Seebeck effect, and the associated constant of proportionality is called the Seebeck coefficient, equation 1.

$$V = S\Delta T$$

.....1.0

Where; V is the voltage (electric potential), S is the Seebeck coefficient, and ΔT is the temperature difference.

If the free charges are positive, the material is a p-type material, hence the positive charge builds up on the cold end thereby having a positive potential. Conversely, negative free charges give rise to n-type materials which produce a negative potential at the cold end.

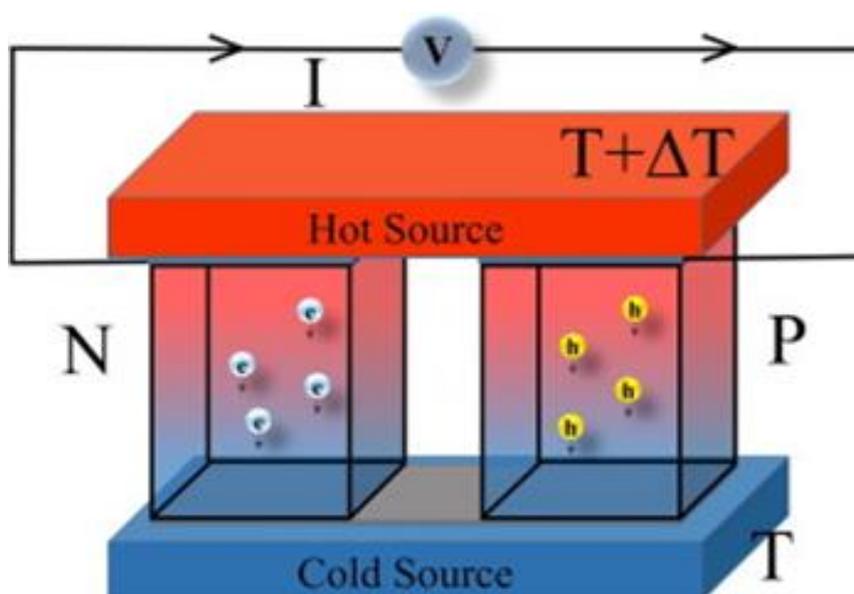


Figure 1. Generation of electric potential by a temperature difference. (Seebeck effect)

1.2. Thermopower Peak and Bandgap

From band theory, electrons in semiconductor at high temperature will possess a high energy to excite across the bandgap between the conduction and valence bands. When this occurs, there will be both n-type carriers and p-type carriers in the conduction band and valence band, respectively. As a result, the produced Thermopower is compensated or reduced because the two contributions subtract.

In a heavily doped thermoelectric material (i.e. introduction of carriers-p-type or n-type or both), the thermopower suffers reduction at high temperature due to the excitation of minority carriers. This therefore leads to a peak in the thermopower as a function of temperature (Gibbs et al, 2015) as shown in Figure 2. The temperature at which the thermopower

maximizes, T_{max} and the thermopower (absolute Seebeck coefficient), $|S|_{max}$ can be used to estimate the semiconducting bandgap, E_g (Gibbs et al, 2015).

$$E_g = 2e |S|_{max} T_{max}$$

.....2.0

Typical values of Seebeck coefficient required of a good TE materials are 150-250 $\mu\text{V/K}$ or greater with a corresponding electrical conductivity (σ) values of 500 -2000 S/cm (Dehkordi, 2015). For a large Seebeck coefficient to be obtained, only majority carriers devoid of bipolar contributions (i.e. mixture of majority and minority carriers) are required in the lattice (Bhattacharya et al, 2014). Mixed carrier system weakens the Seebeck voltage due to increase in the mixed charge carrier at the cold end. Hence, leading to opposing Seebeck effect and low Thermopower.

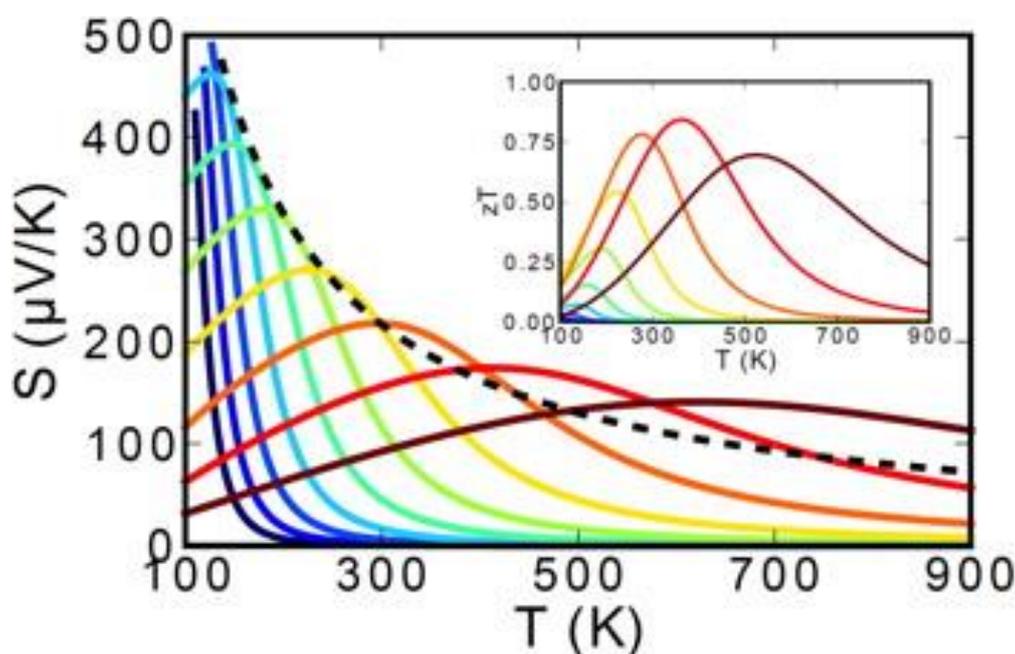


Figure 2. Change in Seebeck coefficient relative to temperature of a heavy doped TE materials.

1.3. Boltzmann Transport Theory

This theory describes electronic and thermal transport of most solids. In this theory, the concept of Seebeck coefficient is expressed in the Mott equation (Sootsman et al, 2009; Jones & Mott, 1958).

$$S = \frac{\pi^2 K_B^2}{3e} \left. \frac{d \ln \sigma(E)}{dE} \right|_{E = E_f} \quad 3.0$$

Where e is the charge electron, and $\sigma(E)$ is the electrical conductivity determined as a function of the Fermi energy, E_f . The relationship between the Seebeck coefficient in the simple model of electron transport as stated below (Wilson, 1953):

$$s = \frac{9\pi^2 K_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}} \left[1 + \left(\frac{d \ln \lambda_s}{d \ln E} \right) E_f \right] \quad 4.0$$

Where h is the Planck's constant, n is the carrier concentration, m^* is the effective mass and λ_s is the scattering distance.

Studies have shown that large carrier effective mass materials correspond to high Seebeck coefficient, hence desirable for thermoelectric applications. On the other hand, large effective mass leads to low carrier mobility, μ , resulting to low electrical conductivity (Dehkordi, 2014). This implies that μ is inversely related to m^* as shown below:

$$\mu = \frac{e\tau}{m^*} \quad 5.0$$

Where τ is the scattering time or the mean scattering between collisions of carriers (carrier lifetime).

1.4. Thermoelectric Power Generation

In thermoelectric power generation, electrical energy is created by joining n-type and p-type materials at a heated junction while attaching an external load to their cooler extremities. This setup utilizes the **Seebeck effect**, where a temperature gradient generates a voltage that drives an electric current through the circuit. While the temperature spread determines the electrical potential, the continuous migration of heat through the materials is what actually facilitates the flow of current, allowing the system to produce usable power. This is attributed to the heat supplied at the hot junction and it is supported by the first law of thermodynamics (Ismail & Ahmed, 2009).

The produced usable (electrical) power is given by:

$$Q_H - Q_L = P_e \quad 6.0$$

Where, Q_H is the heat rate at the hot junction, Q_L is the heat rate at the cold junction and P_e is the electrical power. A typical diagram of thermoelectric generator modules operating across

a temperature gradient for power generation is shown in Figure 3 (US Energy Information Administration, 2013).

A thermoelectric generator (TEG) effectively functions as a voltage source paired with its own internal resistance, which stems from the properties of the semiconductor materials. When the system is under load, the actual output voltage is lower than the open-circuit voltage because some energy is lost to an internal voltage drop (calculated as $V = IR$). To optimize performance, engineers focus on the relationship between the generator and the load. According to the Maximum Power Transfer Theorem, the highest power output occurs when the load resistance matches the internal resistance.

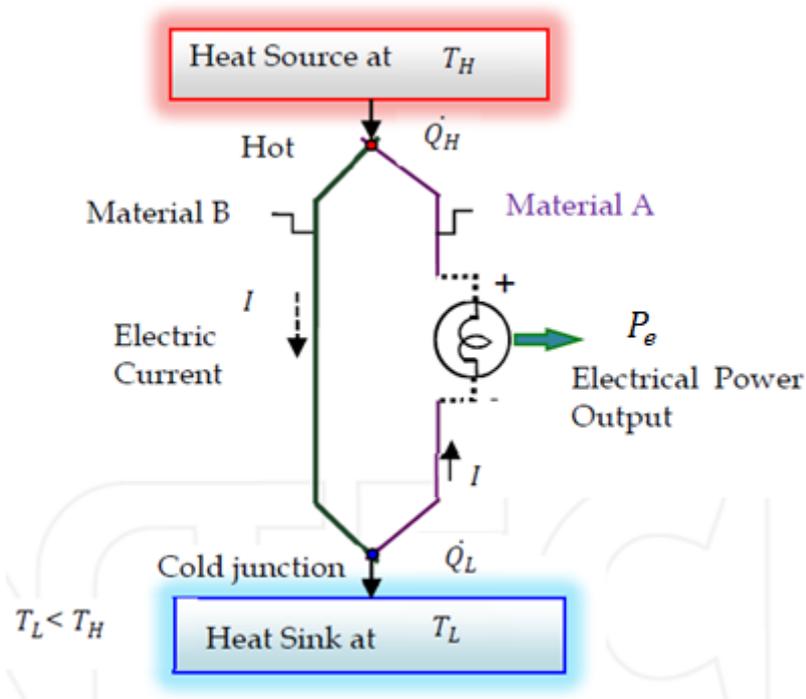


Figure 3. Schematic of the operating principle of Thermoelectric Power Generator (TEG) based on the Seebeck effect.

Approximately 90 % of the world's electricity is generated by heat energy which on average operates at 30-40 % efficiency thereby losing about of 1.5×10^{13} Watts of power in form of heat per year to the surroundings (Ginger & Brinker, 2020; Hochbaum et al, 2008). Thermoelectric generators convert some of this heat into useful electricity (Hochbaum et al, 2008). From laws of thermodynamics, the efficiency of a TEG is related to the properties of the TE materials. Therefore, the performance of TEG depends on the combined effects of efficiency of the Carnot process (η_C), efficiency of thermoelectric generator (η_T) and the

dimensionless figure of merit (ZT) resulting to a maximum conversion efficiency (η_{\max}) (Jarman et al, 2003; Sootsman et al, 2009; Kieslich et al, 2016);

$$\eta_{\max} = \frac{P}{Q_H} = \eta_C \cdot \eta_T = \eta_C \left[\frac{\sqrt{(1+ZT_{\text{avg}})^{-1}}}{\sqrt{(1+ZT_{\text{avg}}) + \left(\frac{T_C}{T_H}\right)}} \right] \quad 7.0$$

$$\eta_C = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H} \quad 8.0$$

where P is the power generated, Q_H is the net heat flow, T_H and T_C are the temperatures at the hot and cold sites, respectively, and T_{avg} is the average temperature $\left(\frac{T_H + T_C}{2}\right)$. Equation 8.0 shows that for an increased efficiency to be obtained, high ZT_{avg} values and large temperature gradients are required. ZT contains both electrical and thermal contributions to the properties of the TE materials and is given as:

$$ZT = \frac{S^2 \sigma T}{k} \quad 9.0$$

Where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature at which the properties are measured and $k = k_L + k_E$ (Tritt & Subramanian, 2006) is the total thermal conductivity. k_L and k_E are the lattice thermal conductivity and electronic thermal conductivity, respectively. ZT describes the material's performance, hence is a prerequisite for a good thermoelectric material. Dehkordi (2014) describes ZT as a measure of the competition between electronic transport (power factor) and thermal transport (total thermal conductivity) in a material. The higher the ZT, the better the efficiency of the TE materials to convert heat energy into useable electricity. In equation 9.0, $S^2 \sigma$ is known as the power factor (PF) and it is another important thermoelectric performance factor. Thus, PF is the determination of the capacity of electronic transport in a material for thermoelectric applications (Dehkordi et al, 2015). It is the electric power through which the heat flows between the hot and cold sides per unit temperature gradient, hence a measure of the power anticipated from a TEG (Carmo et al, 2011).

1.5. Thermoelectric Materials Development

A material with a large thermoelectric power factor is expected to have a large Seebeck coefficient as witnessed in semiconductors and insulators and a high electrical conductivity found in high carrier concentration metals.

Good thermoelectric materials are typically heavily doped semiconductors with carrier concentration, n of 10^{19} to 10^{21} Carriers/cm³ (Snyder & Toberer, 2008) and a Bandgap of $\sim 10k_B T$ (Nag & Shubha). By having a Bandgap large enough, n-type and p-type carriers can be separated, and doping will produce only a single Carrier type but small enough to sufficiently high doping and high mobility, leading to high electrical conductivity. For a high ZT to be achieved, the following parameter are essential (Tritt & Subramanian, 2006; Wood, 1988; Sales, 1998; Nolas & Poon, 2006):

- i. Large Seebeck coefficient, S to produce a required high voltage for a given temperature difference.
- ii. High electrical conductivity, σ to minimize losses through electrical heating (Joule heating), and
- iii. Low thermal conductivity, k to restrict diffusion of heat across the device by maintaining a large thermal gradient. k in such materials comes from two sources of heat transport viz; phonons and electrons (or holes) transports. Phonons travelling through the crystal lattice transport heat and lead to lattice thermal conductivity (k_L).

The electrons or holes transport heat and lead the electronic thermal conductivity, k_E . Thus, the electronic thermal conductivity is related to the electrical conductivity through the Wiedeman-Franz law (Snyder & Toberer, 2008; Doumerc et al, 2009):

$$k_E = L\sigma T \quad 10.0$$

Theoretically, the constant of proportionality, L is known as Lorentz number (factor) and is given by:

$$L = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.45 \times 10^{-8} \text{ W}\Omega\text{K}^{-2} \quad 11.0$$

The Wiedemann-Franz law exposes the impediment for a TE material to achieve high temperature efficiency by simultaneously increasing σ and decreasing k_E . An attempt to suppress k_E affects the electrical conductivity, leading to low ZT. Therefore, TE materials with k_L dominated are desirable since the σ will be preserved while k can be reduced through other techniques. The lattice contribution to the total thermal conductivity is given by a classical kinetic theory (Charles, 1996; Kieslich, 2016) as:

$$K_L = \frac{c_v \cdot l \cdot v_s}{3} \quad 12.0$$

where C is the specific heat capacity, l is the mean free path of the phonons and V_g is the group velocity of the phonons. Equation 12.0 shows that not only k_L depends on the electronic structure of the material. For a low k to be obtained, low C , short l and a low V_g are required (Kieslich, 2016). Thus, the greatest opportunity to enhance ZT is to minimize the k_L , and this can be achieved by increasing the phonon scattering via introducing heavy atoms, disorder, large unit cells, clusters and rattling atoms.

It is observed that S , σ and k in ZT are tied to carrier concentration. Hence, increasing σ (which is desired) decreases S (which is undesirable). Thus, TE materials with high σ are essential for high performance but tend to have very low S and very high k which leads to low ZT and poor efficiency. As carrier concentration increases, σ and k simultaneously increase with a decrease in S thereby decreasing the overall ZT (Dehkordi et al, 2015)

A mutual correlation must be established amongst a large Seebeck coefficient, high electrical conductivity, and a low thermal conductivity to optimize the figure of merit. The balance lies on the carrier concentration, hence a good TE material requires a high carrier concentration, $10^{19} - 10^{21} \text{ cm}^{-3}$ (Snyder & Toberer, 2008). Figure 4 illustrates the dependence of ZT , σ , S and k on carrier concentration for a TE material. Maximizing the efficiency (ZT) of a thermoelectric material involves a compromise between thermal conductivity (k) and Seebeck coefficient (S) with electrical conductivity (σ) (Snyder & Toberer, 2008).

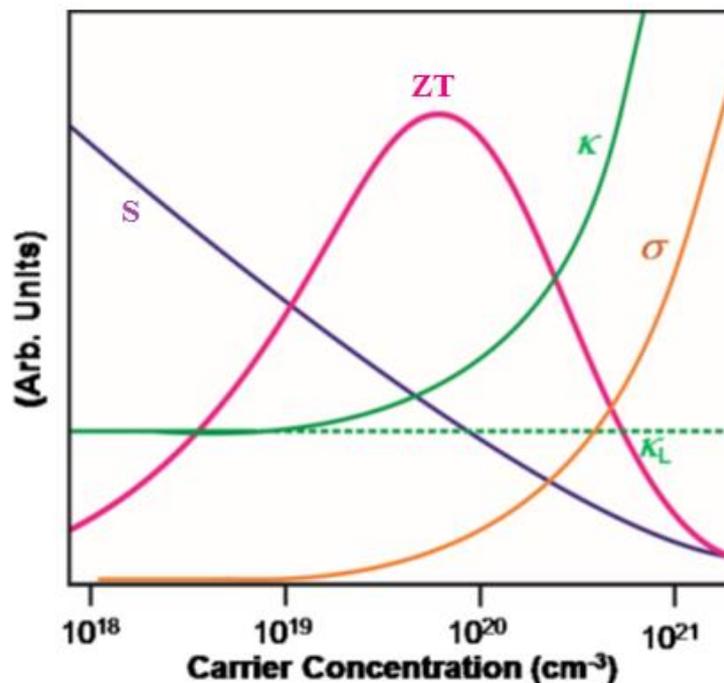


Figure 4. A schematic illustrating optimizing ZT through a carrier concentration tuning.

Using these principles as outlined above, a variety of high ZT materials have been developed (Figures 5 & 6).

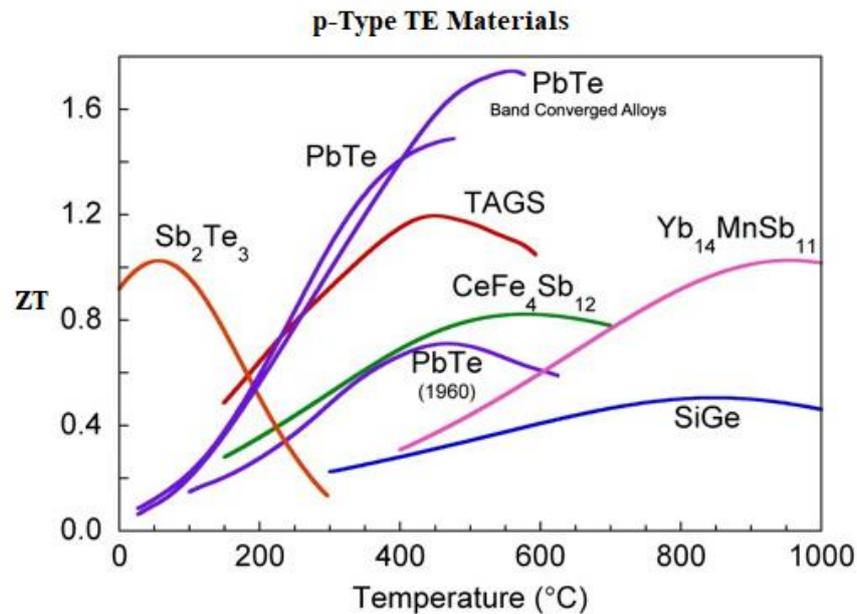


Figure 5. Thermoelectric figure of merit (ZT) as a function of temperature (K) for selected conventional p-type TE materials.

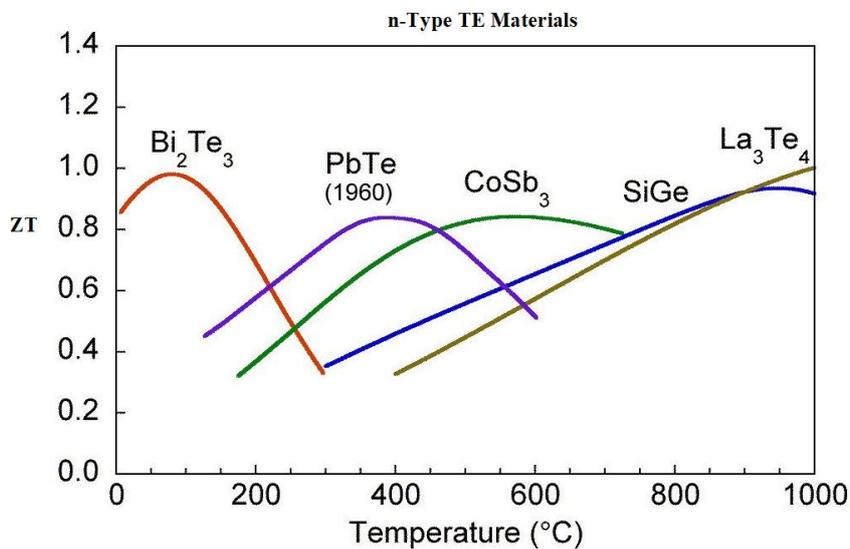


Figure 6. Thermoelectric figure of merit (ZT) as a function of temperature (K) for selected conventional n-type TE materials.

2. THE ENGINEERING OF THERMOELECTRIC DEVICES

Thermoelectric devices are made from thermoelectric modules (circuits). A thermoelectric module is an array of thermocouples (several doped p-type and n-type semiconductors) which

are configured within the thermoelectric module such that they are connected electrically in series and thermally in parallel. This arrangement forms the p-n junctions through which charge carriers (holes for p-type and electrons for n-type) are transported as shown in Figure 7.

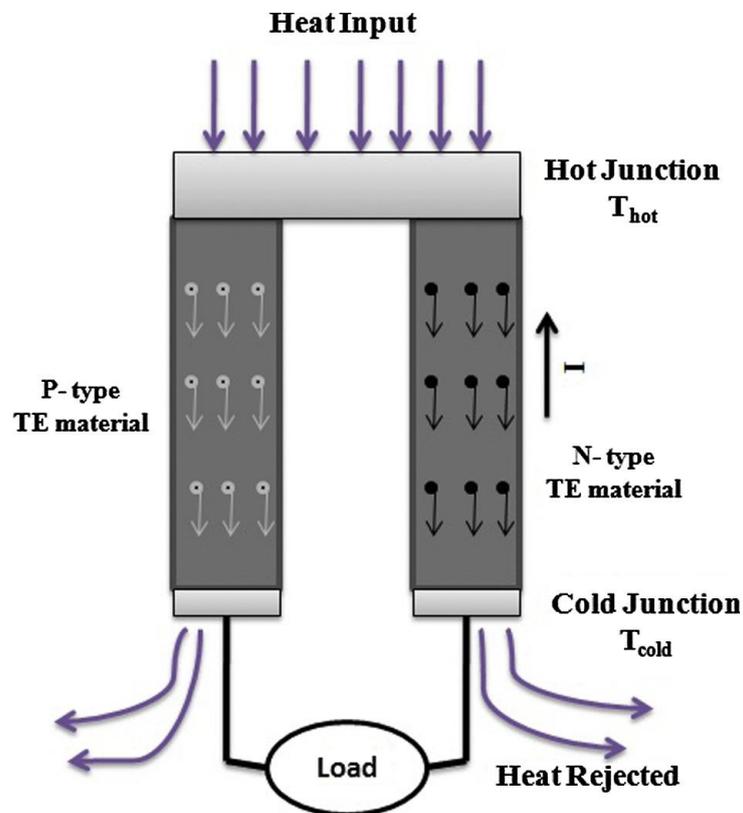


Figure 7. A schematic showing the thermoelectric modules operating across a temperature gradient for power generation (Cavallo, 2004).

Many couples are used in both power generation and cooling because the voltage drop across one couple is insignificant (in order of millivolts). Therefore, connecting many in series in order to bring the voltage closer to that of a typical DC power source. The Seebeck voltage, S of the couple is derived from the Seebeck coefficient of the thermoelements and the number of couples, n

$$S = n \int_{T_c}^{T_h} (\alpha_p - \alpha_n) dT$$

13.0

where, α is the thermal diffusivity.

The electrical resistance of the device depends not only on the electrical resistance of the thermoelectric materials but also the electrical resistance of the metal interconnects and the contact resistance between the interconnects and the thermoelectric materials. All of these contributions are temperature dependent making the exact computation of the resistance complex. The device resistance, R , can be approximated as:

$$R = n \left(\frac{\rho_n l}{A_n} + \frac{\rho_p l}{A_p} + R_l \right) \quad 14.0$$

assuming temperature independent properties.

Where; ρ is the electrical resistivity, R_l is the interconnect and contact resistance (loss) per couple, l is the length (height) and A is the cross-sectional area of the thermoelectric elements. Similar to the electrical resistance, the total thermal conductance of the device can be approximated by

$$K = n \left(\frac{\kappa_n A_n}{l} + \frac{\kappa_p A_p}{l} + K_l \right) \quad 15.0$$

where K_l is the parallel thermal loss per couples associated with gas conduction, radiation, or other losses. With these values the net heat absorbed or produced can be estimated from the sum of the Peltier, Fourier, and Joule heat terms.

$$Q = IST - K\Delta T - \frac{1}{2}I^2R \quad 16.0 \quad []$$

When operating as a cooler the best performance is achieved when then the current is approximately equal to I_{max} . When there is no heat load ($Q=0$) the temperature difference is ΔT_{max} . When there is no ΔT , the maximum heat pumping is Q_{max} .

$$I_{max} = \frac{ST_c}{R} \quad Q_{max} = \frac{S^2 T_c^2}{2R} \quad \Delta T_{max} = \frac{ZT_c}{2} \quad ZT = \frac{S^2 T}{KR} \quad 17.0$$

For these approximations, the device figure of merit for cooling, ZT is analogous to the materials figure of merit zT .

The performance of a TE cooler can then be written in the Generalized Cooling Equation which can be used for Q and COP vs I at constant ΔT .

$$\frac{Q}{Q_{\max}} = \frac{I}{I_{\max}} \left(2 - \frac{I}{I_{\max}} \right) - \frac{\Delta T}{\Delta T_{\max}} \quad 18.0$$

In a thermoelectric generator, the efficiency is often approximated with

$$\eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h} \quad 19.0$$

where ZT is thermoelectric figure of merit for the generator. Again ZT is related to and under certain approximations equal to the material figure of merit zT .

For the exact calculation of device ZT that accounts for temperature dependent thermoelectric properties including the compatibility effect (Heikes & Ure, 1961).

2.1.Types of Thermoelectric Devices

i. Micro Thermoelectric Devices

The ability to fabricate small semiconducting thermoelements has enabled the production of exceedingly small thermoelectric generators and Peltier coolers. The smaller devices operate with much higher heat fluxes (heat/area) which can benefit certain applications. Various thin and thick film techniques (Figure 20.0) have been utilized to produce small thermoelectric devices.

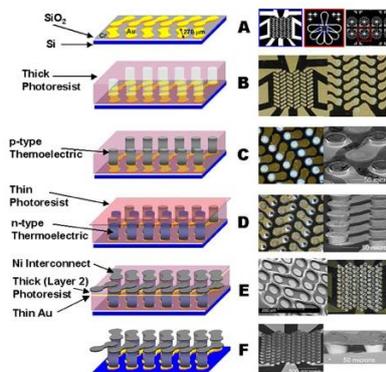


Figure 20. Various thick/thin film techniques for producing micro TE devices.

ii. Segmented Generators

Since the material thermoelectric properties viz Seebeck coefficient, electrical conductivity, thermal conductivity vary with temperature, it is not desirable to use the same material throughout an entire. Therefore, different materials can be segmented together such that a material with high efficiency at high temperature can be segmented with a different material with high efficiency at low temperature. Hence, both materials are operating only in their most efficient temperature range. This illustration is as shown in Figure 21.

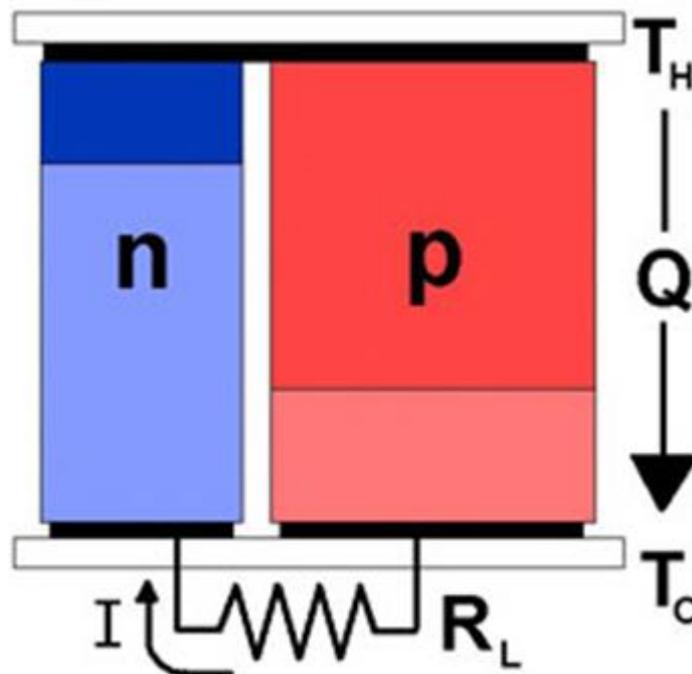


Figure 21. Thermoelectric Segmented Generator with two different n-type materials and two different p-type materials.

It is important to note that only compatible materials are suitable for segmented generators. Therefore, it is advisable to select materials with high ZT and similar compatibility factors (Snyder & Ursell, 2003). The compatibility factors should not differ by a factor more than two. This is to avoid the relative current density u for the materials not being suitable, leading to inefficiency of the segmentation.

iii. Cascaded Generator

In a cascaded generating system, there are in principle independent electrical circuits for each stage. Independent electrical current allows independent values of the relative current density

in each stage. Hence, the optimal relative current density can be used for each stage. Shown below is a typical diagram of Cascaded TE generator (Figure 22).

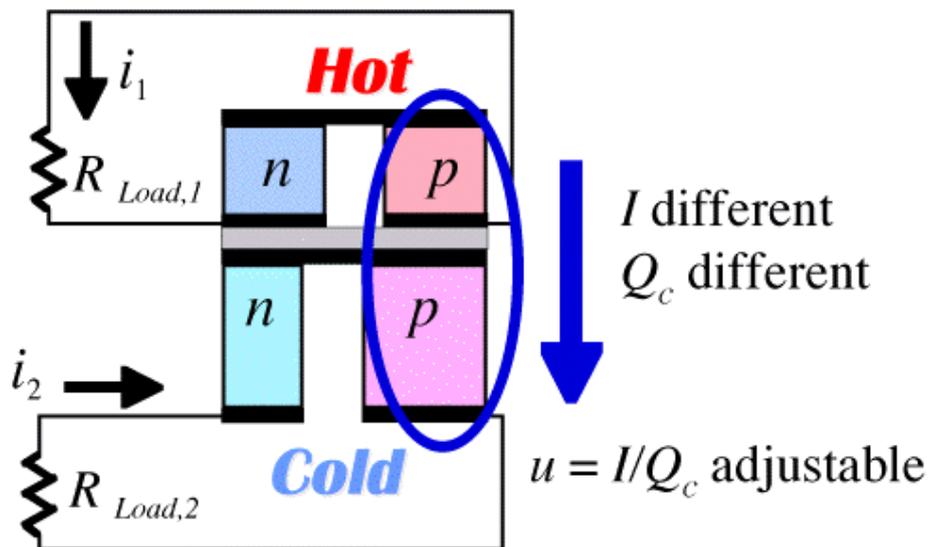


Figure 22. A typical schematic of Cascaded TE Generator.

In practice, it is not advisable to connect the high temperature stages directly to the load. This kind of connection has two-way effects. One, if the connectors have low electrical resistance, they will conduct heat away from the hot side due to Wiedeman-Franz law. Two, if they have high electrical resistance, additional Joule losses will occur.

As a remedy, the electrical current should pass from the high temperature stage to the load by going through the thermoelectric elements of the low temperature stage.

CONCLUSION

The science and engineering of thermoelectrics offer immense potential for transforming how we harvest and utilize thermal energy. Through a deep understanding of thermoelectric principles such as Seebeck effect, Thermopower, transport theory and continued innovation in materials development, significant strides are being made to enhance device efficiency. In addition, engineering breakthroughs in micro, segmented and cascaded devices reflect the practical realization of these scientific principles.

With current global emphasis on clean and renewable energy, thermoelectric systems represent a promising path way for waste heat recovery and sustainable power generation. The future of thermoelectrics lies in the successful integration of advanced materials with smart engineering designs and robust processing techniques.

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