Recently, various nanotechnological approaches have been incorporated to improve the thermoelectric properties of materials. In this review paper, the authors have performed a thorough literature survey of various kinds of TEG technology.

Keywords: thermoelectric, figure of merit (ZT), power generation, Seebeck effect, nanotechnology, energy

1. Introduction

The modern world is facing various energy crisis such as limitation of non-renewable resources, global warming, air and water pollution that are affecting the life of common people. According to one report, approximately seventy percent of energy into the planet earth is dissipated as heat due to dangerous gaseous emissions. A major fraction of the energy wastes comes from the fuel in production, transport and public sectors. The whole world is looking for the clean and sustainable sources of energy. The development in clean energy sources has various obstacles like abundance, cost, efficiency and climate. Though the well-known energy from the Sun is a better source clean energy yet it is constrained by the efficiency and availability of the sunlight. The conversion of waste heat using various energy converters and storing the energy for future use can be a possible solution to solve the above problem up to some extent. TEG technology can be considered as a powerful alternative to tackle the energy crisis all over the world.

The TEGs are generally the power devices which are used to convert the heat from waste to the useful electricity. These TEGs use temperature gradient as input and provide the electrical energy as output based on the thermoelectric principles like Seebeck and Peltier effects.

2. Thermoelectric Science and Technology

The thermoelectric science is based on the principle of energy conversion, from thermal energy to electricity or vice versa by thermoelectric materials based on various principles (Seebeck and Peltier effects) identified by Thomas Johann Seebeck in 1821 and Jean Charles Athanase Peltier in 1834.

2.1. Seebeck effect

The Seebeck effect tells us that if a thermal gradient is applied to a thermoelectric material, a voltage can be generated across the material. For example, if we connect two thermocouples or dissimilar metals A and B as shown in Fig. 1(a). The TEGs are generally the power devices which are used to convert the heat from waste to the useful electricity.
junctions can be expressed as.\(^5\sim7\)

\[ \Rightarrow V = S(T_A - T_B) \]  
\[ \Rightarrow V = S \Delta T \]  

Where \( S \) = Seebeck coefficient between the two metals, \( V \) = thermoelectric voltage and \( \Delta T = T_A - T_B \), temperature difference across the junction (Fig. 1(b)). The sign of Seebeck coefficient depends upon the direction of flow of the charge careers from one junction to other.

2.2. Peltier effect

The Peltier effect is just reverse of the Seebeck effect. For example, one junction is cooled and other one is heated after a potential difference is set up in a circuit of metals A and B as shown in figure 1. Suppose, in a circuit, two pieces of a metal plate are connected to a semiconducting wire joined by a battery. Then the junction gets heated where the current flows from metal to semiconductor, and cooling is noticed at the junction where the current flows from semiconductor to metal. The Peltier coefficient is expressed in terms of heating flow at one junction and a rate of cooling at the other junction. In other words, Peltier coefficient can be expressed as mathematically,\(^5\sim7\)

\[ \Rightarrow \Pi = I/Q, \]  

Where, \( Q \) = heat flow, \( I \) = electrical current generated.

3. Factors affecting Thermoelectricity

3.1. Seebeck coefficient

The Seebeck coefficient can be defined as a property of a material caused by Seebeck effect is the amount of voltage generated between the two thermocouples per unit temperature difference.\(^5\sim6\) Seebeck coefficient depends on the electronic band structure of the materials and the density of states (DOS) in the range of Fermi level. Higher DOS and moderate carrier concentration will produce a larger Seebeck coefficient. The type of the charge careers (holes or electrons) will determine the nature of the sign of Seebeck coefficient.\(^7\)

3.2. Electrical conductivity

The electrical conductivity of a material is expressed in the form of equation:

\[ \sigma = ne\mu, \]  

Where, \( \sigma \) is the electrical conductivity, \( n \) is the charge carrier concentration per unit volume, \( e \) is the electronic charge, and \( \mu \) is the mobility of the charge careers as determined from the Hall experiments. The charge careers and mobility are dependent on the temperature. The conductivity is further affected by various types of impurities in the material which act as a barrier to flow of the electrons and scatter them inside the crystal lattice. Metals are good conductors of electricity (10\(^7\) mho/m), semiconductors (10\(^{-6}\) to 10\(^4\) mho/m) and insulators (10\(^{-10}\) and 10\(^{-20}\) mho/m) and the values may vary along with temperature and impurity amount present in that materials.\(^5\sim8\)

3.3. Thermal conductivity

The ability of a material to conduct heat by lattice vibrations or phonons.\(^7\) Therefore, materials of high thermal conductivity are used for heat sink source whereas low thermal conducting materials are used for insulation. Thermal conductivity is also a function of temperature and can be expressed as:

\[ Q = -K \left( \frac{dT}{dx} \right) \]  

Where \( Q \) is the amount of heat flow through the mate-
The thermal conductivity of the material and $K_l$ is given by the region. The total thermal conductivity of a material is given by the

$$K_1 = K_{el} + K_l$$

Where, $K_{el}$ is the electronic contribution to thermal conductivity of the material and $K_l$ is due to the lattice vibrations.\(^7\)\(^8\)

The Weidemann Franz law tells us that electronic thermal conductivity is related to the Lorentz number according to the relation:

$$K_{el} = LσT, \quad (7)$$

Where $σ$ is the electronic conductivity, $T$ is the absolute temperature and $L$ is the Lorenz number. It can be concluded that $K_{el}$ is a function of $σ$ and $T$ and therefore, form equation (4), the $K_{el}$ also depends upon charge carrier density ($n$) and their mobility ($μ$).\(^9\)

The lattice contribution of thermal conductivity depends upon the phonon vibration characteristics. According to the kinetic theory of gases

$$K_1 = \frac{1}{3}C_v l \quad (8)$$

Where, $C_v$ is the heat capacity of the metal, $ν$ is the velocity of phonon vibrations and $l$ is the mean scattering free path.\(^7\)\(^10\)

### 3.4. Figure of merit

The conversion efficiency of the TEG device is measured in terms of the figure of merit ($ZT$). From Carnot equation, the maximum efficiency of TEG is given by:\(^11\)

$$n_{\text{max}} = \frac{ΔT}{T_{\text{hot}}} \sqrt{1 + \frac{ZT_{\text{mean}}}{T_{\text{mean}}} - 1} \quad (9)$$

Where $T_{\text{hot}}$ and $T_{\text{cold}}$ are the hot and cold junction temperatures, $ΔT$ is given by $T_{\text{hot}} - T_{\text{cold}}$, and $T_{\text{mean}}$ is given by $(T_{\text{hot}} + T_{\text{cold}})/2$, respectively. The Carnot efficiency is given by $ΔT/T_{\text{hot}}$ multiplied by a reduction factor:

$$Z = S^2 ρ^{-1}κ^{-1}, \quad (10)$$

Where $S$, $ρ$, and $κ$ are the Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively. The dimensionless figure of merit ($ZT$) has been utilized since 1950 as a design parameter to achieve highly efficient materials. High $ZT$ value ($ZT \approx 3-4$) materials convert a greater amount of waste heat to power.\(^12\) In the past various researchers have been discovered that exhibit $ZT > 1$ and still there is a need for increasing this $ZT$ value for realizing full potential of this technology. The conventional thermoelectric materials include Pb-Te or Bi-Te based compounds which are expensive, and pose a threat to our environment due to their toxicity. Other class of thermoelectric materials include Mg-based materials which are cheaper but they have a poor figure of merit which makes them unsuitable for electricity conversion in various applications. Figure of merit ($ZT$) can be enhanced by controlling various factors like materials electronic structure, charge carrier concentration and lattice vibrations characteristics.\(^11\)\(^-\)\(^13\) Now a days, nanotechnology have played a major role in enhancing the $ZT$ value to a larger extent due to the novel properties of nanoparticles by control of crystallographic texture, modulation by doping, creating nanograins, dispersion of nanoparticles into the thermoelectric materials.\(^14\)

### 4. Thermoelectric Materials

There are three categories of thermoelectric materials depending on the temperature range of applications.

1. Low temperature range (< 177°C): Bi based alloys
2. Moderate temperature range (177°C-577°C): Pb based alloys
3. High temperature range (>1027°C): Si-Ge based alloys etc.

#### 4.1. Conversion Efficiency

Commercial thermoelectric materials have $ZT≈1$. On laboratory scale, thermoelectric materials have $ZT≈2$ or approach to 3. Only the materials ($ZT$ values above 2 or approach to 3) have capability to convert into some useful electrical energy from waste heat with sufficient conversion efficiency as shown in figure 2.\(^15\)

#### 4.2. Material selection

Semiconductor materials are suitable for thermoelectric generators because of their high charge carrier mobility, moderate charge carrier concentration. A high conductivity of the metals causes lower Seebeck coefficient and hence the generated power is low. An increase in electronic thermal conductivity of metals when temperature rises due to high electron carrier concentration which may cross a threshold of $10^{25}$/cm and may degrade the $ZT$ value.\(^6\)\(^-\)\(^7\)\(^11\)\(^-\)\(^15\)
Various approaches have been tried to optimize the thermoelectric performance, for example, by alloying, doping, nanostructured thermoelectric, nanocomposites approach, nano thin films, segmented thermoelectric etc.

The fabrication route also affects the thermoelectric characteristics. Various routes like mechanical alloying (MA), melting and casting processes, microwave fabrication routes, hot pressing and spark plasma sintering (SPS) techniques.

4.3. Developments in thermoelectric materials

Various types of thermoelectric materials have been developed so far and still there is a need to approach ideal thermoelectric material. Thermoelectric materials according to their composition and structure are classified as chalcogenides, clathrates, skutterudites, Half-Heusler (HH) alloys, silicides, oxides and Zintl phase materials etc.\textsuperscript{31-33} Some examples of thermoelectric materials are shown in Table 1.

Most of these are based on Bi, Sb, and Te which are highly expensive, toxic and unstable at high temperature. Polymers have also been investigated as cheaper alternative due to their light weight and flexibility and abundance. However, the ZT value is rather lower due to their low electrical conductivity and Seebeck coefficient and their use is limited.

5. Nanotechnological approach to Thermoelectric Materials

With the emergence of nanotechnology which operates when the size of the material reaches at one or its dimensions < 100 nm. For example, the nanomaterials can be produced in the form of nanopowders, or nanotubesh/
nanowires, nano-rods and nanocoatings where the grain size falls in the nano-regime. The nanostructured thermoelectric materials have better figure of merit and conversion efficiencies as compared to the bulk counterparts.\textsuperscript{31-32} The reason why the ZT value is enhanced is due to the large decrement in the thermal conductivity as a consequence of the increased phonon scattering at the grain boundaries and higher power at higher temperatures.\textsuperscript{30-31}

Various kinds of nanostructured materials have been developed using nanotechnology, such as, nanocomposites, ultrafine grained materials and super lattices. In case of nanocomposites, the selection of the reinforcement and the dispersion process must be optimized before actually used in practice. In nanocomposites, at least one phase should be in the nanorange. The incorporation of nanoparticles can solve the problem due to the formation of new interface in the matrix. However, the nanoparticles are very high surface active entities. Their selection as a reinforcement is critical for avoiding the segregation and hence a depression in thermopower.\textsuperscript{10,14,31}

6. Thin Film thermoelectric Technology

Due to the miniaturization of the electronic circuits and systems, the amount of heat dissipation is large enough to cause thermal breakdown of the device and eventually failure of entire device. Traditional or bulk thermoelectric devices have been used for years to control the temperature of electronics where the cooling of the entire device is an efficient method for thermal management leading to the oversizing of the thermoelectric device. The modern thin film thermoelectric technology targets the heat flux source to provide thermal control. Such types of thermoelectric device incorporate nanostructured p and n type materials in the form of a coating, typically 5 to 20 μm thick, over 200 μm for traditional devices. This creates a huge heat flux around 20 times as compared to traditional ones. Gary et al synthesized Bi\textsubscript{2}Te\textsubscript{3} superlattice based thin thermoelectric device using metal organic chemical vapor deposition technique and obtained cooling fluxes of 200 W/cm\textsuperscript{2} over commercial 100 W/cm\textsuperscript{2}\textsuperscript{33-35}. However, there are various barriers in thin film technology which need to be sorted out for full potential of this technology. For example, electrical contact resistance between metal electrodes and the semiconductor layers can be comparable to that of the thermoelectric element itself, thus increasing the overall electric resistance of the thermoelectric device and reducing the cooling flux.\textsuperscript{34}

7. Magnesium based Thermoelectric

Magnesium based thermoelectric materials have attracted the researchers in the past to overcome the issue of cost, toxicity and light weight compared to the bulk traditional thermoelectric materials (Bi\textsubscript{2}Te\textsubscript{3}, PbTe and CoSb\textsubscript{3}). Mg is the light metal having density (1.73 g/cm\textsuperscript{3}) versus most popular aluminum (2.70 g/cm\textsuperscript{3}) and iron (7.86 g/cm\textsuperscript{3}). Mg based alloys are high strength and low weight, moderate melting points and their intermetallic compounds or alloys form Zintl phase with a large electronegativity gap.\textsuperscript{36} Zintl phases are the potential candidates for obtaining high ZT value in thermoelectric materials, e.g. (Eu\textsubscript{1} Yb\textsubscript{1/2})\textsubscript{1-x}Ca\textsubscript{x}Mg\textsubscript{1-x}Bi\textsubscript{2}, Mg\textsubscript{2}X (X=Si, Ge, Sn, Si-Sn, Si-Ge, etc) compounds have shown higher figure of merit as compared to the Si-Ge and β-FeSi\textsubscript{2} [37-41]. It is also noteworthy that band gap range of Mg based thermoelectric materials are close band gaps of semiconductor materials as shown in Table 2.

However, the synthesis of these Mg\textsubscript{2}(Si, Sn) single phase is difficult due to the high vapor pressure and chemical

| Table 1. Figures of merit of developed bulk thermoelectric materials\textsuperscript{33,30} |
|-----------------|----------|------------------|
| Materials       | Examples | ZT at Temperature |
| Metal Oxides    | Bi doped Ca\textsubscript{2}Co\textsubscript{3}O\textsubscript{6} | >1 at 727°C |
| Chalcogenides   | T\textsubscript{0}BiT\textsubscript{0} | 1.25 at 226°C |
| Clathrates      | Ba\textsubscript{4}Ga\textsubscript{12}Ge\textsubscript{30} | 1.35 at 627°C |
| Half Heuslers   | H\textsubscript{3}25Zn\textsubscript{25}NiS\textsubscript{0}S\textsubscript{25}Sb\textsubscript{0}S\textsubscript{25} | 0.81 at 752°C |
| Skutterudites   | Ba\textsubscript{0.3}Ni\textsubscript{0.5}Co\textsubscript{0.2}S\textsubscript{2} | 1.25 at 627°C |
| Polyacetylene   | 0.047-0.38 at 27°C |
| Polyaniline     | 0.002 at 27°C |
| PEDOT           | 0.051 at 27°C |
| Polymers        | 0.25 at 27°C |

| Table 2. Band gaps for different Mg based thermoelectric materials\textsuperscript{70} |
|-----------------|----------|
| Material        | Band Gap (eV) |
| Mg\textsubscript{2}Si | 0.78 |
| Mg\textsubscript{2}Ge | 0.69 |
| Mg\textsubscript{2}Sn | 0.36 |
| Mg\textsubscript{2}Si\textsubscript{0.5}Sn\textsubscript{0.5} | 0.51 |
| Mg\textsubscript{2}Si\textsubscript{0.5}Ge\textsubscript{0.5} | 0.05-0.23 |
| SiGe            | 0.7 |
| PbTe            | 0.3 |
| Bi\textsubscript{2}Te\textsubscript{3} | 0.1 |
| Ge              | 0.67 |
| Si              | 1.14 |
activity of Mg as well as large gap in melting points of the constituents. The stability and performance of Mg(Si,Ge) is better than Mg(Si,Sn) but is highly expensive due to cost of Ge. Application of nanotechnology has been also found to increase the figure of merit of these alloys via nanoparticles inclusion in the matrix.

8. Conclusion

Thermoelectric materials are the backbone of energy sector to avoid the energy crisis in the coming years worldwide. Materials with high figure of merit categorized as metals, polymers, chalcogenides, clathrates, skutterudites, half-Heusler alloys, and silicides. The task to develop the Mg based thermoelectric is challenging in view of the purity, melting point, light weight, cost, abundance, ecofreindly nature etc. Polymers have also gained importance in thermoelectric as a portable, light weight and flexible options and further investigations are needed to bring them into market. Nanostuctured materials and thin films are also attractive ways to enhance the figure of merit of these materials. However, these approaches depend on the material’s internal properties such as carrier concentration, their mobility and phonon’s behavior (like mean free path of the phonons). It is to be noted that further research is needed in this direction to gain a more quantitative understanding of thermoelectric materials for wide range of power applications.

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• Ashutosh Sharma  
  Department of Materials Science and Engineering University of Seoul, Seoul-02504, Korea  
  Research Interests: Pulse Electroplating, Lead Free Soldering, Brazing, Metal Matrix Nanocomposites  
  Email: stannum.ashu@gmail.com

• Jun-Hyeong Lee  
  Duksan Himetal Co. Ltd., 66, Muryong 1-ro, Buk-gu, Ulsan, Korea  
  Research Interests: Electroplating, Thermoelectric module  
  Email: leewnsgud@naver.com

• Kyung-Heum Kim  
  Duksan Himetal Co. Ltd., 66, Muryong 1-ro, Buk-gu, Ulsan, Korea  
  Research Interests: Soldering, Thermoelectric module  
  Email: khkim@oneduksan.com

• Jae Pil Jung  
  Department of Materials Science and Engineering University of Seoul, Seoul-02504, Korea  
  Research Interests: Microjoining, Electroplating, Brazing Fillers, Solder-Joint Reliability, Metal Matrix Nanocomposites, Lead Free Soldering  
  Email: jppjung@uos.ac.kr