State of the Art Review on Thermoelectric Materials

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Abstract: *Development of thermoelectric materials with high figure of merit has become the need of the hour for combating environmental problems such as global warming, climate change and for saving limited non renewable natural energy resources such as minerals and oil. The thermoelectric materials have ability to convert waste heat to electrical energy based on Seebeck and Peltier effects. Figure of merit (ZT) of a material is a performance indicator for assessing its ability to produce electricity when exposed to hot gases. Several researchers have reported thermoelectric materials exhibiting ZT greater than one. Greater the value of ZT greater is the generation of electricity. Researchers are striving to improve the value of ZT by adopting different technologies. ZT value approach to 2 or 3 is found to be difficult due to interdependence of thermo electric properties of materials which constitute the figure of merit. At present commercially available thermoelectric materials (Pb-Te, Bi-Te based etc) are toxic, denser and of high cost. Alternate materials such as Mg-based materials are cheaper but have low figure of merit, making these materials unsuitable for wide range of applications. Hence it has become inevitable to develop materials with high figure of merit. Nanotechnology aids to alter well as improve the thermoelectric properties of materials. This review focuses on state of the art on thermoelectric materials and different aspects in their design and development.*

Keywords: thermoelectric materials, figure of merit (ZT), nanotechnology, power factor, thermoelectric generators

1. Introduction

In the present day scenario, major problems such as limitation of energy sources, global warming and air pollution are affecting the planet earth and its inhabitants [1]. Approximately 70% of world's useful energy is entering into the earth's atmosphere as waste heat carried by dangerous and unwanted gases. This is resulting in wastage of fuel in manufacturing, transportation and service sectors [2]. There are demands for clean and sustainable energy sources. Use of energy converters and recovery of useful energy from waste heat helps in partly solving the above problems [3]. Thermoelectric technology and thermoelectric generators (TEGs) can be considered as a promising alternative for solution of the problems [1]. The TEGs are converting devices which use thermoelectric materials having energy conversion characteristics. The thermoelectric generators use heat (temperature gradient) energy as input and give electrical energy as output using thermoelectric technology principles such as Seebeck, Peltier and Thomson effects [4].

Thermoelectric materials having high figure of merit can be used as power generators, coolers, thermal sensors etc. They find uses in military applications, aerospace, electrical, manufacturing, power plant, chemical process, transportation industries where exhaust of hot gases takes place [5]. In recent years thermoelectric materials are finding application in increasing energy conversion of solar cells [6].The TEG's performance is measured in terms of conversion efficiency which depends on the thermoelectric materials' "Figure of Merit" denoted by ZT. High figure of merit materials (around ZT = 3 to 4) convert more than 40% of waste heat to useful electrical energy. The figure of merit (ZT) is a dimensionless quantity which is derived by combining properties such as Seebeck coefficient (S), electrical conductivity (σ) and thermal conductivity (k). The figure of merit $ZT = S^2\sigma T/k$ where S, σ, T and k are the Seebeck coefficient, the electrical conductivity, the absolute temperature and thermal conductivity respectively [7]. Enhancing of figure of merit (ZT) value is possible by optimizing the thermoelectric properties S, σ and k by either increasing power factor $S^2\sigma$ (PF) and/or decreasing the thermal conductivity (k). The thermoelectric properties vary with materials and their structure, dopants and fabrication methods. The overall effect of variation of material's properties should result in enhancement of figure of merit [8]. The figure of merit plays a key role in development of thermoelectric technology as well as TEGs for effective conversion of waste heat to electrical energy [9]. Optimizing the thermoelectric properties of materials for enhancing figure of merit (ZT) depends on material's electronic structure, the charge carrier concentration and phonon's behavior [10, 11, 12].

Enhancing ZT by optimizing thermoelectric properties is critical in bulk (micro level grains) thermoelectric materials because of the mutual interdependence of electrical and thermal properties. However researchers produced and developed some good bulk thermoelectric materials by alloying, controlling microstructure and doping with certain materials [13].Nanotechnology plays a key role in development of the figure of merit due to unique properties of nanoparticles and nanograins. Thermoelectric properties of materials at nano scale can be altered independently or separately, affecting the figure of merit. Researchers adopted approaches such as control of crystallographic texture, modulation by doping [14, 15], reduction of grain sizes to nano level, preparing nano-composites by incorporating nanoinclusions into the thermoelectric materials [16] etc. Nanostructuring of the material may cause increase in the figure of merit values relative to bulk materials with decrease in the thermal conductivity due to phonon scattering and/or increasing in the power factor due to quantum confinement [17]. Presently bismuth telluride and skutterudites are being used in the manufacture of TEGs due to their very high figure of merit values [18, 19].But these materials are toxic, of high cost, and high weight. Further these are not suitable for middle range temperature applications i.e. from 250-650   [20].

This paper discusses the development of thermoelectric technology in the last ten years, different approaches for altering the thermoelectric properties and also effect of nanotechnology on the thermoelectric properties. Further it addresses effect of different approaches on the thermoelectric properties considering a case study on Mg based thermoelectric materials. Materials which have ZT value more than 1.5, low weight and low cost are sufficient for middle range temperature applications like automotive exhaust, gas turbine exhaust, drying and baking ovens etc., where weight is an important factor [21, 22, 23]. Mg based compounds and their alloys are one of the alternate materials for toxic materials mentioned above (bismuth telluride and skutterudite families). The materials which are of light weight, low cost of constituent elements and ZT values 1 or more can be used in the thermoelectric applications instead of Tellurium Antimony Germanium and Silver (TAGS) and Te (telluride) based thermoelectric materials [24, 25, 20].

2. Thermoelectric Generators (TEGs)

Thermoelectric generators are solid state (no moving parts), reliable, noiseless and scalable devices which convert electricity directly from thermal energy by using the thermoelectric materials due to temperature gradient in the materials based on the Seebeck effect [1,26]. Thermoelectric generators contain both n-type and p-type semiconducting materials as legs or units and they are connected electrically in series and thermally in parallel [23, 27] as shown below.
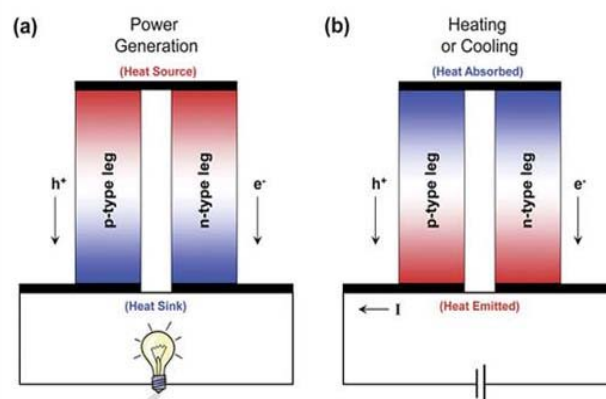

Figure 1: A schematic drawing of thermoelectric devices used for (a) power generation (b) heating and cooling applications [28].

2.1 Heat sources for TEGs

Large amounts of waste heat are generated from automobiles and industries. Different heat sources liberating the heat in different temperature ranges are listed in table 1. The thermoelectric materials selection for the TEGs depends on the temperature range. Some thermoelectric materials having good figure of merit at a particular temperature range may not be thermally stable in the same temperature range making them unfit to be used in the TEGs.

Table 1: Heat sources vs. temperature range [23,27]

Temperature range	Heat sources
Low temperature (<250˚C)	Air conditioning/refrigeration, condenser ovens, air compressors, furnace doors, electric circuit etc,
Middle temperature (250-650˚C)	Steam boilers exhaust, gas turbines exhaust, drying and baking ovens, automobiles exhaust etc
High temperature (>650˚C)	Metal refining furnace, steel heating furnace, hydrogen plants, satellite launching places, aerospace applications and natural decay of radio isotope (such as Pu^{238})

2.2 Advantages of TEGs

Nearly 70% of energy is wasted in different applications mentioned in table 1. The waste heat is released into atmosphere in the form of high temperature unwanted and harmful gases. It causes disturbance in environmental conditions like depletion of ozone layer, global warming etc. TEGs can be used as sustainable and green energy sources [1, 23] at the same time mitigating environmental problems. TEGs have the capability to enhance fuel efficiency. They reduce the CO_2 emissions from the automobiles and industries and thus reducing global warming and saving ozone layer from depletion [11, 29]. The TEGs help to improve the thermal efficiency of the fuel using equipment such as boiler, heaters and automobiles saving the fuel. These devices convert some part of waste heat into useful electrical energy. Thus TEGs play a key role in saving the energy of the world and solving environmental problems [1].

2.3 Applications of TEGs

TEGs find use in aerospace, military and automobiles applications [5]. Automobile industries are trying coupling of the TEGs with combustion engines for improving fuel efficiency of the vehicles and for generating of the electrical energy from the waste heat. The higher fuel efficiency gives good mileage for automobiles and the electrical energy produced can be used for vehicle lights [26]. Thermoelectric generators are also used to power space vehicles [27].

2.4 Problems associated with TEGs

Present thermoelectric generators are having problems like low conversion efficiencies, high costs and also high density. Because of these reasons the TEGs are unable to find uses in wide range applications [1, 27].

3. Thermoelectric Technology

3.1 Thermoelectricity

It is a phenomenon which converts thermal energy into electrical energy and vice versa by using thermoelectric materials having conversion characteristics based on Seebeck and Peltier effects [04].

3.1.1 Seebeck effect
This effect was discovered by Seebeck in 1821 [10]. According to Seebeck, temperature gradient in materials causes generation of voltage across the material. He explained this effect by taking two thermocouples (a, b) or dissimilar materials and connecting them electrically in series and thermally in parallel. The total set up was like an open circuit as shown in figure 2. At points A and B he applied two different temperatures (T1>T2) then there was voltage (V) or electromotive force (EMF) developed across two points C and D due to charge difference in the material. A linear relationship resulted between voltage (V) and temperature gradient (ΔT) for small ΔT ranges [10, 11, and 31]. $V\infty\Delta T$, $V=S(\Delta T)$ where S = Seebeck coefficient or thermopower between the thermocouples a and b, V = thermoelectric voltage and $\Delta T = T_1-T_2$, temperature difference. The sign of Seebeck coefficient gives the direction of flow of the charges in the circuit. Here voltage (V) is considered as Seebeck voltage [11, 30, 31].
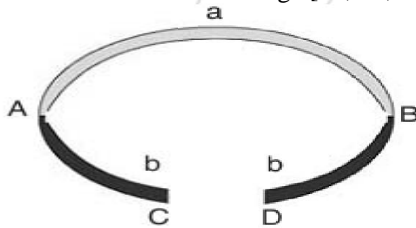

Figure 2: Schematic diagram of a basic thermocouple

3.1.2 Peltier effect
This effect was discovered by Peltier in 1834 [10]. 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). 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 [10, 30, 31]. Peltier effect is expressed in terms of an equation as $\Pi=I/q$ where, Π = the Peltier coefficient of the material, q = heat flow, I = electrical current.

3.2 Thermoelectric properties

3.2.1 Seebeck coefficient (S or α):
It is a property of material which is derived from the Seebeck effect and is defined as "The amount of thermoelectric voltage (V) induced between the two thermocouples (Fig.2) per unit temperature difference (ΔT) [12, 32]. The Seebeck coefficient of the materials mainly depends on their electronic band structure [11] which depends on the 'density of states' (DOS) in the range of Fermi level. A high DOS and medium carrier concentration produces a large Seebeck coefficient. Understanding of the total Seebeck coefficient is critical due to incompleteness of the band theory [3, 9, 33]. It is measured in V/K or µV/K or µV/°C. The sign of Seebeck coefficient depends on the type of carriers conducting electricity. If electricity is produced by electrons then the coefficient sign is negative or by holes then the sign is positive [10].

3.2.2 Electrical conductivity (σ):
It is a property of material which measures the material's ability to conduct electricity by either electrons or holes and both. It can be expressed in the form of equation $\sigma = ne\mu$, where σ = electrical conductivity, n = carrier concentration per unit volume, e= charge on electron and µ= mobility of carriers. Both charge carriers (n) and mobility (µ) are functions of temperature and can be found from experiments through resistivity and Hall coefficient determination [3, 9]. The electrical conductivity values are finite numbers since there are no 100% pure materials on earth and each material is associated with some impurities which can act as barrier for flow of the electrons and scatter the electrons inside the materials [32]. Units for the electrical conductivity are $(\Omega\text{-m})^{-1}$ or mho/m. Based on the electrical conductivity values, the materials are divided into three categories such as metals $(10^7\ (\Omega\text{-m})^{-1})$, semiconductors $(10^{-6}$ to $10^4\ (\Omega\text{-m})^{-1})$ and insulators $(10^{-10}$ and $10^{-20}\ (\Omega\text{-m})^{-1})$ and the values may vary along with temperature and impurity amount present in that materials [34].

3.2.3 Thermal conductivity:
It is a property of material which measures the material's ability to conduct heat either by the charge carriers, phonons (vibrations of lattices), electromagnetic waves, spin waves or other excitations [10]. From Fourier's law equation the thermal conductivity can be expressed as $q = -k(dT/dx)$, and $k = -q/(dT/dx)$ where q = amount of heat flowing through the material, dT/dx = temperature gradient in the material, k = thermal conductivity of the material [11]. Sign indicates that direction of flow of heat through the materials. Here '–'signifies that the heat flows from hot place of the materials to cold place. Frequently total thermal conductivity of a crystalline material is summation of thermal conductivity due to electrons of the material and due to lattice vibrations of the material [10, 32]. It can be expressed as $k_{total} = k_e+k_l$.

3.2.3.1 Electronic thermal conductivity (k_e):
According to Weidemann- Franz law, there is a relationship between the thermal conductivity due to electron (k_e) and electrical conductivity (σ) [9, 32]. $k_e = L_0\sigma T$ where k_e = thermal conductivity due to electrons (electronic thermal conductivity), σ = electrical conductivity, T = Temperature, L_0 = Lorenz number, From above equation, electronic thermal conductivity (k_e) depends on the electrical conductivity (σ) of the material and also the temperature (T) so k_e varies with concentration of charge carriers (n) and their mobility (µ) [9]. From this it is concluded that the electrical conductivity (σ) and the thermal conductivity (k_l) are interdependent properties.

3.2.3.2 Lattice thermal conductivity (k_l): The lattice thermal conductivity (k_l) is different from electronic thermal conductivity (k_e). The lattice thermal conductivity depends on characteristics of phonons (vibrations of lattice) as shown by below equation which is derived from kinetic theory of gases [3, 28]. k_l= 1/3(Cvl), where k_l= lattice thermal conductivity of the materials, C = heat capacity of the material, v = phonon velocity (approximated by mean sound velocity), l = mean free path length between scattering events.

3.3 Figure of merit

Figure of merit or thermoelectric value (ZT) of the material is used to find the conversion efficiency of the TEGs from Carnot efficiency equation which is given by the equation **η = ((ΔT)/T$_{hot}$)(($\surd$(1+ZT)-1)/($\surd$(1+ZT)+T$_{cold}$/T$_{hot}$))** [16, 35]. The thermoelectric generators or device's working performance is measured by Carnot efficiency (η) equation which depends on the material's figure of merit expressed in terms of percentage (%). These two parameters are considered as thermodynamics related parameters because both parameters can vary with the temperature (T) [36]. From the above equation, it is concluded that the Carnot conversion efficiency ( ) of the TEGs enhances by increasing ZT and large temperature gradient (ΔT) across the material. Hence ZT and thermal stability of the thermoelectric material play a key role in development of TEGs with efficient conversion from waste heat to electricity [37].

4. Thermoelectric Materials

Thermoelectric materials are materials which are capable of converting thermal energy to electrical energy and vice versa. The thermoelectric materials are divided into three groups based on the temperature range applications. Low temperature range (< 177˚C) thermoelectric materials such as bismuth based alloys etc, intermediate or middle range (177˚C-577˚C) thermoelectric materials such as lead based alloys etc and high temperature range (>1027˚C) thermoelectric materials such as SiGe based alloys etc as shown in figure[1,31].
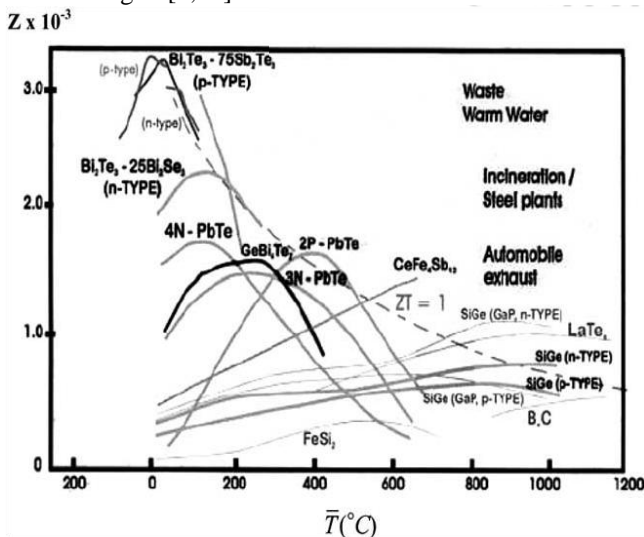

Figure 3: Figure of merit of number of thermoelectric materials and their potential applications [1]

The thermoelectric generator's performance depends on the material's electron and thermal transport characteristics [27]. Researchers are trying to develop materials which have high figure of merit values optimizing their thermoelectric properties using different approaches [1].

Ideal thermoelectric materials: In mid 1990s, Glen A.Slack presented the concept 'Phonon Glass Electron Crystal' (PGEC) related to thermoelectric materials. According to the concept, the ideal thermoelectric materials are materials which conduct electricity like crystal and conduct heat like glass at same time [38].

Commercial thermoelectric materials: The materials having ZT values above 2 or approach to 3 are considered as commercial thermoelectric materials and also the materials should be available at low price, high stability with respect to temperature and give sufficient output (good performance). 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 4 [5].
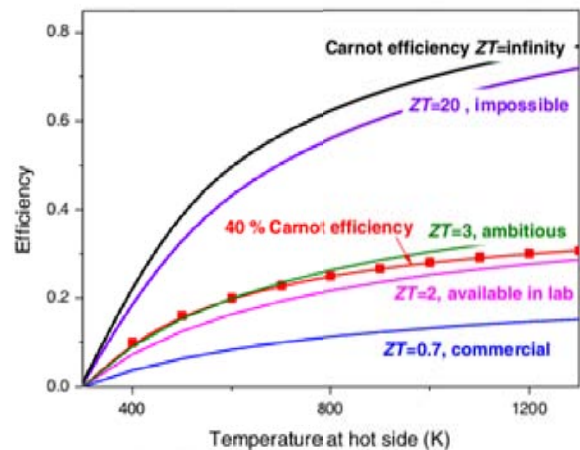

Figure 4: Conversion efficiency of TE materials with changing temperature difference and ZT, assuming that the cold side temperature is 300 K [5]

5. Enhancing ZT

For enhancing ZT, one should make proper material selection and analyze their thermoelectric properties, select suitable dopants for optimizing the properties. Sometimes fabrication methods also affect their thermoelectric properties.

5.1 Material Selection

Almost all metals (conductors) and semiconductor materials exhibit thermoelectricity. But till now the semiconductors are suitable thermoelectric materials for getting good ZT by optimizing their thermoelectric properties. Normally the semiconductor materials have high carrier mobility, medium range of carrier concentration and less number of electrons which signifies their ZT. Whereas the metals have high range carrier concentration, which causes high electrical conductivity but the Seebeck coefficient or thermopower is low. Electronic thermal conductivity of the metals increases with increasing temperature due to high electron carrier

concentration (for maximum power factor the carrier concentration (n) around 10^{25}/cm is sufficient, if more than this value then it is critical to create concentration gradient of carriers in the material with increasing temperature). So it

may totally degrade the figure of merit in metals as shown in figure 5. For this reason semiconductors and related materials are mostly used in thermoelectric applications [28, 31, 39, 40].
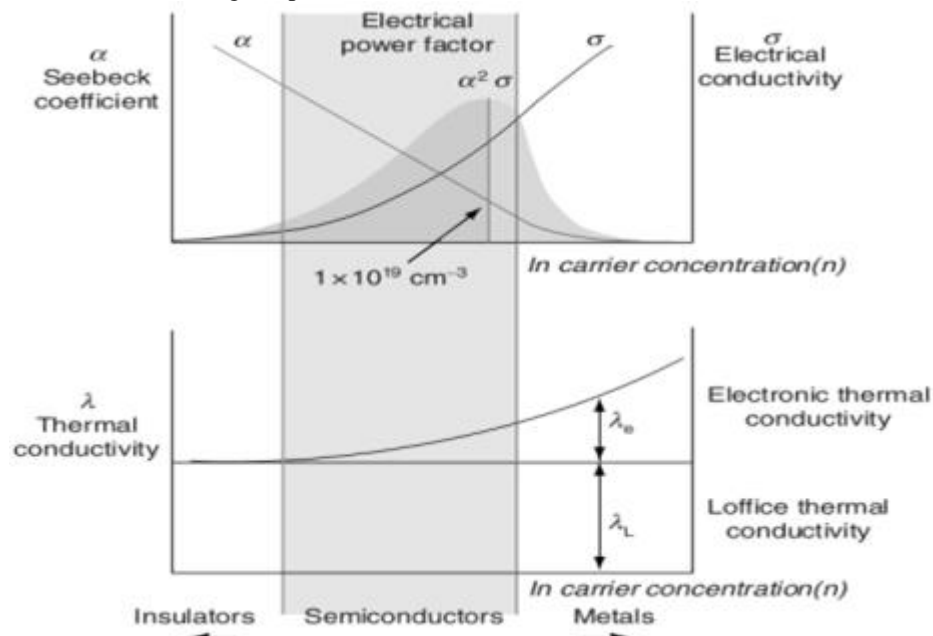

Figure 5: Schematic dependence of electrical conductivity, Seebeck coefficient, power factor, and thermal conductivity on concentration of free carriers. [31]

5.2 Optimization of thermoelectric properties

For optimizing thermoelectric characteristics or properties of the materials, till now there are two main approaches viz. development of bulk thermoelectric materials by alloying [41, 42], doping [43, 44], preparing nanostructured thermoelectric materials by reducing the grain size of the materials [8], nanocomposites preparation (addition or doping of nanomaterials in the form of nanoparticles, nanowires, nanoclusters, nanorods) [16, 45, 46, 47], and also preparing nano(thin) films [48,49] etc., based on nanotechnology. The nanotechnology plays a key role in development of the thermoelectric materials due to the unique properties displayed by nanosize materials. [17, 35, 50].

5.3 Fabrication methods

There are many fabrication methods developed for synthesizing thermoelectric materials. The important and most used fabrication methods are mechanical alloying (MA) [51], melting process [52], microwave irradiation, hot pressing and spark plasma sintering (SPS) [10]. These fabrication techniques can be used based on the type of materials and their properties in different applications. The

fabrication methods affect thermoelectric properties of the materials and hence play a key role in optimizing thermoelectric properties of the materials.

5.4 Development of bulk-thermoelectric materials

Till now many thermoelectric materials have been developed by researchers. Still they are trying to approach the ideal thermoelectric materials. Thermoelectric materials are classified as chalcogenides, clathrates, skutterudites, Half- Heusler (HH) compounds, silicides, oxides and Zintl phase materials etc., based on the material's structure and their composition [27, 30]. There are many materials made from metals and ceramics based alloys and solid solutions and some of them have the figure of merit value (ZT) >1 as shown in table 2.

It is possible to alter the figure of merit in polymers by doping with suitable materials for enhancing electrical conductivity (see the last two rows of the table 3). The figures of merit (ZT) of materials seen so far are not sufficient enough for efficient conversion to electricity [53]. Hence it is imperative to improve the figure of merit values further by using latest technologies and different approaches.

Table 2: Figures of merit of developed bulk thermo electric materials [30]

S.No	Material class	Developed materials
1.	Skutterudites	$Yb_{0.19}Co_4Sb_{12}$ (ZT ≈1 at 387 deg C), $Ba_{0.30}Ni_{0.05}Co_{3.95}Sb_{12}$ (ZT≈1.25 at 627 deg C), $Ca_{0.18}Ni_{0.03}Co_{3.97}Sb_{1.24}$ (ZT≈1 at 527 deg C)
2.	Clathrates	$Ba_8In_{16}Sn_{30}$ (ZT≈1.7 at 527 deg C) $Ba_{24}Ga_{15}Ge_{85}$ (ZT≈1.25 at 670 deg C), $Ba_8Ga_{16}Ge_{30}$ (ZT≈1.35 at 627 deg C)
3.	HH Intermetallic compounds	n–type $Zr_{0.5}Hf_{0.5}Ni_{0.8}Pd_{0.2}Sn_{0.99}Sb_{0.01}$ (ZT≈0.7 at 527 deg C), $Hf_{0.75}Zr_{0.25}NiSn_{0.975}Sb_{0.025}$ (ZT≈0.81 at 752 deg C)
4.	Metal oxides	Bi doped $Ca_3Co_4O_9$ (ZT>1 at 727 deg C), $Bi_2Sr_2Co_2O_y$ (ZT≈1.15 at 677 deg C)
5.	Chalcogenide compounds	Tl_9BiTe_6 (ZT≈1.25 at 227 deg C), Tl_2SnTe_5 (ZT≈1 at 227 deg C), Ag_9TlTe_5 (ZT≈1.23 at 427 deg C)

Materials like Bi, Sb, and Te are being used for preparing above class of materials. These materials are expensive, toxic and unstable at high temperature [37]. Because of this the researchers are looking for alternate materials which can be used as commercial and green thermoelectric materials. Polymers (inorganic materials) are also playing key role in development of the thermoelectric materials and may be used as alternative for above categories due to light weight, flexible, ease of synthesis and their abundance (carbon sources). There are many polymer based thermoelectric materials developed but figure of merit values are low due to their very low electrical conductivity and Seebeck coefficient as shown in table 3 [5].

Table 3: Figures of merit of different polymer materials

S.No.	Polymer	ZT at 27degC
1	Polyacetylene	0.047 – 0.38
2	Polypyrrole	0.002
3	Polyaniline	0.051
4	Polythiophene	0.0066
5	Poly (3,4 ethylenedioxythiophene) (PEDOT)	0.25
6	Poly (styrenesulphonate) doping in PEDOT	0.42

6. Nano based Thermoelectric Materials

Nanoscience and nanotechnology is an emerging field which gives information about materials which having one or more of its dimensions less than 100 nm. Generally the nanomaterials are prepared or fabricated using nanopowders, nanowires, nanoclusters, nanorods and nanofilms (thin films) and also by reducing the grain size. These are synthesized by various methods such as chemical vapor and electrochemical deposition with use of X-ray laser and UV-irradiation, ultrasonic and microwave treatment, electron ion beam, arc discharge methods, sol-gel methods, combustion methods, reduction of salts and complexes [48]. Nanotechnology plays a key role in optimizing the thermoelectric properties of the materials. The thermoelectric materials which are prepared or fabricated using nanotechnology are considered as nanostructured thermoelectric materials. Properties of materials change when they are scaled down to nanosize. Similarly the nanostructured thermoelectric materials' properties change when compared with bulk structured thermoelectric materials due to unique characteristics of the nanomaterials [28]. Researchers have proposed many theoretical concepts for development of the nanoscale thermoelectric materials and since last decade they are successful in preparing good nanostructured thermoelectric materials. It is to be noted that the nanostructured materials have better ZT values compared to their bulk structured material. The nanostructured materials are synthesized in the form of nanocomposites, super lattices and nanostructures (grain size reduction). The superior values of figure of merit of nanomaterials are due to the phenomena such as quantum confinement, increased interfaces and surfaces. Efforts are on to prepare materials whose ZT values are greater than 3 - 4 by optimizing the thermoelectric properties using nanotechnology [9, 54].

6.1 Effect of nanotechnology on the thermoelectric properties

Using nanoscale approach, there are many nanostructured thermoelectric materials developed in the form of the nanocomposites, nanograins formation in bulk materials and super lattices. It is to be noted that the optimization of the thermoelectric properties for the mentioned nanostructured thermoelectric materials is very different. For instance, in nanocomposites by incorporating suitable nanoparticles into bulk thermoelectric materials thermoelectric properties of host material may be optimized at a time. But in the nanograined thermoelectric materials there is reduction in both electrical and thermal conductivities. This is due to large number of nanograins, which act as barrier for flow of charges as well as phonon. So selection of the methods

(either incorporating the nanoparticles or reducing grain size and both) for optimizing thermoelectric properties of materials mainly depend on the material's internal properties like carrier concentration, mobility (electrical properties) and phonons (thermal properties) [8, 50 and 38].

6.2 Nanocomposites and their thermoelectric properties

Nanocomposites are composites which having one of its phases in nanometer range [45]. The nanocomposites thermoelectric materials are synthesized by the addition/doping of suitable or appropriate and limited amount of the nanoparticles called nanoinclusions in bulk thermoelectric material's host. The nanoparticles can be distributed in the host material in many possible ways as shown in figures 6(a), 6(b) and 6(c) [35, 45].
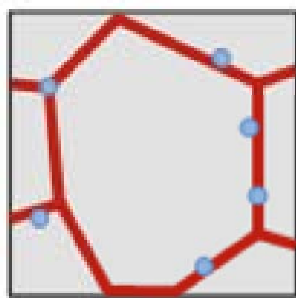

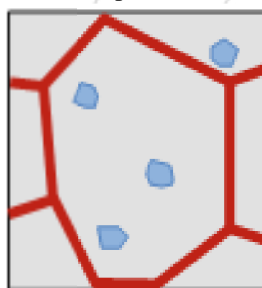**Figure 6:** (a) co-compaction of physical mixture of the two components

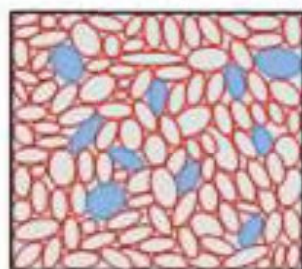**Figure 6:** (b) in situ formation of nanosized precipitates within the bulk matrix

Figure 6: (c) mixture of nanoparticles with different compositions

The optimization of the thermoelectric properties in bulk structured thermoelectric material is very difficult (Wiedemann-Franz law). But incorporation of the nanoparticles may overcome the difficulty due to the formation of new interfaces in the host materials. The nanoparticles exhibit enhanced electrical conductivity because of the splitting of energy levels in the materials (quantum confinement phenomenon) due to the variation in the conduction and valence band edges created by the interfaces [55]. The nanoparticles behave as energy filters for electrons i.e. they have capability to separate charge

carriers as high energy charge carriers and low energy charge carriers. This is due to the electron band bending between the host material and the nanoparticles. This increases the Seebeck coefficient. The nanoparticles can act as point defects in the materials which can be considered as scattering centers for phonons which have capability to scatter short wavelength phonons (normal point defects can scatter high wavelength phonons). This can cause a significant reduction in thermal conductivity when compared with that of the bulk structured materials [28, 37, 38, 56].

All above mentioned results mainly depends on concentration of the nanoparticles, their sizes and distribution in the host material [43, 57]. Also nanoparticles are having some disadvantages like unstableness and tendency for aggregation at higher temperatures [48]. Hence selection of the suitable nanoparticles for the host material is critical for avoiding depression in thermoelectric properties [35].

6.3 Nano grained materials (Size reduction) and their thermoelectric properties

In this method, more interfaces per unit volume are created in the thermoelectric material by reducing the grain size to nano-range using metallurgical methods. The enhancement of the figure of merit of the materials is also possible either by significant reduction in the thermal conductivity or by increasing the power factor ($S^2\sigma$). Here the materials are having more grain boundaries (interface boundaries) which act as barrier or scattering centers for both electrons and phonons.
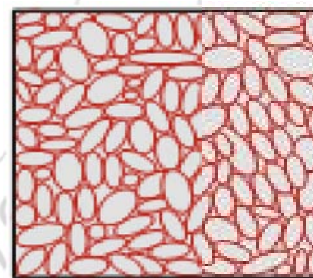

Figure 7: Schematic representation of nanograins [35]

Generally phonons with short mean free paths can be affected by normal grain boundaries of the materials but not longer free mean paths [2]. But the nanostructured materials having nano grain sizes can affect phonons with long free paths. Then there is high reduction in the lattice thermal conductivity due to scattering of the phonons and also there is reduction in the electrical conductivity as the boundaries resist flow of the charges. This phenomenon is shown in figure 8. Reduction in the thermal conductivity can be dominant over the reduction in the electrical conductivity in certain materials only.
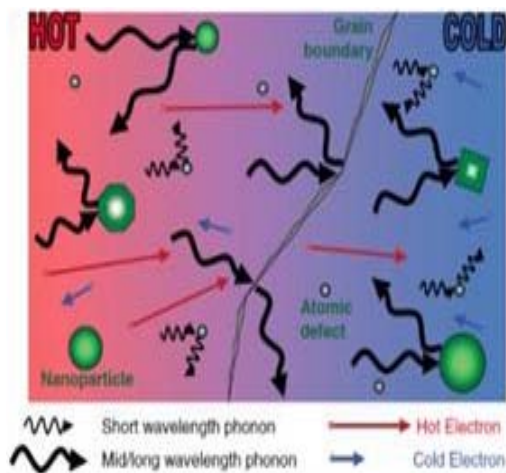
Figure 8: Schematic diagram representing various scatterings in nanograined thermoelectric materials [4]

This method is suitable for materials having higher charge carrier concentration (n) and mobility (μ). For such materials the effect of reduction in the electrical conductivity (σ) on the figure of merit is not significant. So this method is also a possible approach to enhance figure of merit value of materials [4, 6, 58, and 59].

6.4 Thin films and their thermoelectric properties

Optimization of the thermoelectric properties of the thin films is different from above mentioned nanostructured materials because in the nanostructured material optimization of the carrier concentration or chemical potential depends on the doping element's properties where as in two dimensional (2D) materials such as thin films, it can be optimized by varying the material's layer thickness. The layers' interfaces can act as scatter centers for phonons causing reduction in the thermal conductivity of the material. But the thicknesses of the layers should be less than the phonon free path [4, 7]. Other nanomaterials like superlattice and nanowires and carbon nanotubes etc are having good thermoelectric properties and current research is on all these materials. But synthesis of the materials is very expensive and time consuming process and hence difficult to produce in large amounts.

7. A Case Study on 'Mg based thermoelectric materials'

Mg based thermoelectric materials are the thermoelectric material which has magnesium (Mg) as the main constituent element. Mg is a structural material having low density (1.73 g/cc) when compared to other structural elements such as aluminum (2.70 g/cc) and iron (7.86 g/cc). Even though pure Mg is having disadvantages like high chemical reactivity, high vapor pressure and low melting point (650˚C) [7] but alloys of Mg have high melting point, high mechanical strength and also high chemical strength [10].Mg based intermetallic compounds and their alloys or solid solutions consist of two or more metals or semimetals and form Zintl phase with large electro negativity difference [60]. Since 1950 many experiments are being carried out on electrical, optical and thermal properties of the Mg compounds and their solid solutions. In 1961 E.N. Nikitin et al showed that

the compounds and alloys of Mg have good physical and chemical properties for possible use as thermoelectric materials [61].The constituent elements of Mg based thermoelectric materials (Mg, Si, Sn, and Ge) are low cost, eco-friendly and also have lower densities than developed and commercial thermoelectric materials such as Bi_2Te_3, PbTe and $CoSb_3$ [22]. C.B.Vining noticed that figure of merit (ZT_{max}) is proportional to the parameter A= ( ) ( ) $^{2/3}($ where m* is carrier effective mass, μ is the mobility in cm^2.V/s and k_L is the lattice thermal conductivity [52]. In Mg_2X compounds parameter A value ranges between 3.7 and 14 which is higher than that of conventional thermoelectric materials such as SiGe (1.2-2.6) and β-$FeSi_2$ (0.05-0.8) so the Mg_2X compounds may have capability to get high figure of merit and may be better thermoelectric materials for use in different thermoelectric applications [52, 62]. Some Mg based thermoelectric materials are having advantages like ZT values are one and above. For instance $MgSi_{0.4}Sn_{0.6}$ has ZT_{max} 1.1 [14] which is almost comparable to current commercial and conventional thermoelectric materials such as bismuth telluride based and skutterudite family [18, 19]. Also it is of low cost when compared to bismuth telluride [8]. So researchers are focusing on further development of figure of merit values of the Mg based thermoelectric materials by using different approaches and technologies.

7.1 Development in the figure of merit of the Mg based materials with optimization of the thermoelectric properties

Thermoelectric technology of Mg based thermoelectric materials: Many Mg based thermoelectric materials are fabricated as Mg_2X (X=Si, Sn, Ge) compounds, Mg_2 (Si-Sn), Mg_2 (Si-Ge) based materials and their solid solutions.

Bandgap of Mg based thermoelectric materials: For good thermoelectric materials, the materials should approach to PGEC (phonon glass electron crystal) concept as discussed earlier. According to this concept semiconductor and some metal based materials are suitable for fabrication of the thermoelectric materials. Mg based thermoelectric materials showed semiconductor properties because of their band gap range is very close to semiconductor's band gaps as shown by table 4 [10]:

Table 4: Band gaps for different Mg based thermoelectric materials

S.No	Material	Band Gap (eV)
1	Mg_2Si	0.78
2	Mg_2Ge	0.69
3	Mg_2Sn	0.36
4	$Mg_2Si_{0.6}Sn_{0.7}$	0.51
5	$Mg_2Si_{1-x}Ge_x$	0.05-0.23

So Mg based materials almost belong to semiconductor category which is suitable for the thermoelectric material fabrication. Many researchers developed Mg based

thermoelectric materials and determined their thermoelectric properties (table 5).

Table 5: Thermoelectric properties of different Mg based thermoelectric materials

Material	Dopants	ZT(Temp deg C)	σ(S/cm) (approx)	S or α (μV/K)	k (W/m K)	k_L(W/mK)	Ref.
Mg_2Sn	——	0.025(427)	400	–100	4.75	—	[7]
Mg_2Sn	Ag (3mol %)	0.18(327)	850	125	4	2.57	[7]
Mg_2Si	——	0.41(327)	400	–250	3.8	——	[42]
Mg_2Si	Ca (1mol %)	0.34(387)	790	–140	3.3	——	[42]
$Mg_2Si_{0.4}Sn_{0.6}$	Bi (3 mol%)	1.4 (527)	1000	–220	2.25	1.00	[13]
$Mg_2Si_{0.6}Ge_{0.4}$	Bi (2 mol %)	0.75(647)	——	175	2.5	——	[63]
$Mg_2Si_{0.7}Sn_{0.3}$	Sb (1 mol %)	0.64(450)	——	–270	——	——	[10]
$Mg_2Si_{0.3}Sn_{0.7}$	Sb (2 mol %)	1.3 (477)	625	–225	2.5	1.5	[64]
$Mg_2Si_{0.5}Sn_{0.5}$	Sb (1.3 mol %)	0.9 (467)	800	–180	2.6	1.55	[22]

Among all developed Mg based thermoelectric materials, $Mg_2(Si,Sn)$ based materials are most focused presently due to their constituents elements are abundant, nontoxic and these material's figure of merit (ZT) value is very close to 1 and more. Also output power is higher than the developed thermoelectric materials in middle range temperatures [64, 70]. But synthesis or processing of these $Mg_2(Si, Sn)$ based materials, getting single phase of these materials is difficult and time consuming due to high vapor pressure and chemical reactivity of Mg and large difference in melting points between the constituent elements [71]. Processing or preparation of $Mg_2Si_{1-x}Ge_x$ compounds and their alloys and their stability at high temperatures is better than $Mg_2(Si, Sn)$ but the cost of Ge is high [29,65]. However presently numerous methods have been developed for synthesizing and processing of Mg based thermoelectric materials such as mechanical alloying, hot pressing, melt spinning, self propagating high temperature synthesis, co-melting, solid state reaction and spark plasma sintering [52,71].

7.2 Role of nanotechnology in the development of Mg based thermoelectric materials

Interested by the unique properties of Mg based thermoelectric materials researchers are applying principles of nanotechnology for the development of Mg based thermoelectric materials. Tables 6 give information about application of nanotechnology in the development of different Mg based thermoelectric materials and the resulting ZT values.

It is understood from above discussion that the performance of thermoelectric materials is largely dependent on thermal conductivity. Low thermal conductivity is always observed in amorphous materials. Development of materials with amorphous nature is challenging. Further, it is essential to understand the mechanism of grain boundary movements in these materials which gives rise to low thermal conductivity and helps to design/develop materials with thermal conductivity as low as possible. Additionally, continued research is needed in this direction to gain a more quantitative understanding of materials for wide range of power generation and cooling applications.

Table 6: Application of nanoscience and technology in the development of Mg based thermoelectric materials

S.No	Developed Material	ZT (Temp)	Nanotechnology Used[Ref.]
1	$Mg_2Si_{0.3875}Sn_{0.6}Sb_{0.0125}$	0.85 (773K)	Mg/Sn nanoinclusions dispersed. When compared with developed material using bulk materials having same alloy composition, the material has capability to maintain lower thermal conductivity at higher temperature (473K) due to the scattering of the lattice vibrations by nanoinclusions higher than that in bulk material [66].
2	$Mg_2(Si_{0.38}Sb_{0.02}Sn_{0.6})$	1.30 (773K)	$Mg_2Si_{0.4}Sn_{0.6}$ nanoscale precipitates are formed. The precipitates can scatter the phonons with mid range mean free paths. So, it effects on the phonon transport of the material [67].
3	Mg_2Si	——	Si nanoparticles are introduced. There is reduction in lattice thermal conductivity (2.0 W/m K) of the developed material due to the phonon scattering when compare with undoped Mg_2Si (2.7 W/m K) [68].
4	$Mg_{0.9925}Na_{0.0075}Ag_{0.97}Sb_{0.99}$	1.26 (523K)	Na was doped in the developed nanostructured material. Here undoped materials are having low thermal conductivity and lower power factor due to nanostructuring (grain size reduction). When Na is doped in the material then there is increase in carrier concentration as well as power factor which lead to higher ZT value [44].
5	$MgAg_{0.963}Cu_{0.007}Sb_{0.99}$	1.30 (523K)	Cu was doped in the developed nanostructured material. Here substitution of Cu reduced the thermal conductivity and also increased the power factor of the materials which lead to increased ZT values of the material compared to the bulk materials [69].

8. Conclusion

Semiconductor materials are one of the good choices for thermoelectric material preparation due to medium range of carrier concentration, high carrier mobility, and low electrons that are contributing to the thermal conductivity. The materials with high figure of merit can be classified as metals, polymers, chalcogenides, clathrates, skutterudites, Half-heusler (HH) compounds, and silicides. It is desirable to develop materials with high figure of merit by combining their doped forms in suitable proportions. However it is highly challenging to develop materials with high figure of merit as the constituent elements are toxic, non-abundant and have high densities which are not better choice. Polymers are also a good choice as thermoelectric materials due to light weight, flexible, abundance (carbon sources), and easy way to synthesize, if their thermoelectric properties can be altered by doping process so as to make them suitable for desirable applications. Nanocomposites, nanograined materials and thin films are also major forms of materials for enhancing figure of merit. In nanocomposites, either addition or doping of nanoinclusions affects the thermoelectric properties. In nanograined materials, the number of interfaces affects the thermoelectric properties. In thin films the layer's thickness affects the thermoelectric properties. But 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). The issues addressed in this review article will be helpful for better design of thermoelectric materials with high figure of merit.

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