**Fundamentals of Thermoelectric materials**

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**Abstract:** Thermoelectric materials are having the capability to convert the waste heat energy to electrical energy and vice-versa. The conversion efficiency is measured by the dimensionless quantity i.e. figure of merit (ZT). For many researchers, exploring a material with a good ZT value is a big challenge. The electrical conductivity, Seebeck coefficient, power factor and thermal conductivity are the key factors which influences the ZT value. This chapter discuss about the measuring techniques and strategies towards enhanced electrical conductivity, improved Seebeck coefficient and reduced thermal conductivity and also written about the historical background and principles involving in development of thermoelectric materials. This chapter also explained the properties of various types of thermoelectric materials briefly such as Oxides, Skutterudites, Clathrates, Half-Heusler compounds and Zintl-phase materials.

**1. INTRODUCTION**

Now a days, thermal management and energy efficiency is a vital challenge as waste heat is ubiquitous from the advanced technologies and industries. To address these issues, one possible technology i.e. thermoelectric (TE) is to be employed, which can transform the waste heat into electricity. This technology makes use of materials that are referred to as TE materials because of their capacity to generate electrical potential based on the Seebeck effect with a temperature difference between both ends. The name of the device used to generate TE power is called TE generator (TEG). TEGs are quite beneficial, since no hazardous byproducts are created during operation, very small in size, simple structure, run with noiseless and environmentally friendly manner. In addition to having a long operating life, TEG may generate electricity from low-grade heat at low temperatures [1,2]

 Based on the range of operating temperatures, these materials can be categorized into three types[3].

1. low-temperature materials, where around 400 K is the typical operating temperature. In this temperature range, bismuth-based alloys are among the most commonly used materials.
2. Materials that operate at an intermediate temperature, or between 600 and 900 K. In this category, lead-based alloys are frequently utilized.
3. Materials with high operating temperatures—those with temperatures above 900 K. Typically, materials made up of silicon and germanium belong within this category.

**1.1 Historical background**:

Through systematic investigation, Volta unveiled the thermoelectric effect, establishing that the electromotive force originated from temperature disparities at the junctions of dissimilar conducting materials. This ground breaking work not only resolved the scientific debate but also laid the groundwork for understanding the direct conversion between thermal and electrical energy. Volta's discoveries marked the inception of thermoelectricity, electromagnetism, and electrochemistry, ultimately leading to the invention of the electrical battery. In 1821 Seebeck gave the perfect explanation for thermoelectricity[4] .

**1.2. Thermoelectric generator(TEG):**

Thermoelectric generator(TEG) is a solid semiconductor device designed to transform the temperature gradient across it to the electrical energy [5].A single thermoelectric can only generate a certain amount of output power and TE voltage.Therefore, a TEG module is made up of many P and N type semiconductors connected electrically in series and thermally in parallel[6]. A Thermoelectric device has the capability to transform the heat into electricity through the seebeck effect ,and conversely ,it can achieve the reverse process ,converting electricity into the heat through the peltier effect[7].

 

 Fig.1. Mechanism in Seebeck and Peltier effects.

**1.3. Various advantages of TEG**

Direct energy conversion, unlike many heat engines, which first transform thermal energy into mechanical energy and then use an alternator to turn mechanical energy into electricity. The TEG has no moving parts and no operating fluids, thus it requires no maintenance and doesn't cost extra. TEG can generate kilowatts or micro generation in extremely small places. Operation of TEG is noiseless.

**2. Principles of TEM:**

**2. 2. Seebeck coefficient:**The process of converting heat into the electricity and vice versa is known as thermoelectricity. Another name for this phenomena is Seebeck effect,named after German scientist ,Thomas Seebeck.In 1821Seebeck twisted two wires of different metals and heated one end of them.Thomas Seebeck noticed a tiny amount of current passing through the metal wires .The electrons' movement from one end to the other, which determines the direction of the current flow.[8]



Fig. 2. Schematic diagram of Seebeck effect

Seebeck came to the conclusion heat might produces the electricity.

∆E ∝∆T (1)

where E and T stand for the connections' temperature differences and emf output, respectively.The proportional constant of the Eq(1) is

 Sab= ∆E\∆T (2)

 Is called Seebeck cofficient .The material's Seebeck coefficient is the characteristic that establishes how well thermocouples work[9].

 **2.2. Peltier effect:** Seebeck failed to elucidate the true empirical hypothesis underlying this procedure and incorrectly concluded that flowing energy and flowing heat have the same outcome.In 1834 a French scientist discovered ,each side of the twisted wires showed signs of heating and cooling current passed through them[10].



Fig. 3. Schematic diagram of Peltier effect

It was revealed that

 Q∝I (3)

 Where Q is the rate of heating or cooling.The proportional constant for the above equation is called Peltier coefficient .

 Πab = (4)

In this case Πab = Πa\_Πbis the coefficient of the two different metals[11].

 **2.3. Thomson effect:** In 1854, William Thomson carry out a thorough analysis of the Seebeck and Peltier Effects and explained how they relate to one another.A thermodynamic relationship exists between the Seebeck and Peltier coefficients. William Thomson discovered that with a current carrying conductor,heat can be observed or released based on the material and flow of current direction when there is a temperature difference between the any two points of conductor .This effect is known as Thomson effect.

These three phenomena are called as thermoelectric effects[12].



***Fig. 4. Schematic diagram of Thomson effect***

The transfer derived by

 **=**ᴦI \_\_\_\_\_\_\_\_\_\_\_\_\_\_ (5)

ᴦ= \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(6)

Where ᴦ is the Thomson coefficient and is the transfer of thamson heat.

 The relation between Seebeck coefficient and Peltier coefficient are derived from first and second law of thermodynamics.

 Πab=Sab T \_\_\_\_\_\_\_\_\_\_\_(7)

 = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(8)

 From the equation (5) and (8) .We get

 Q=SabIT (9)

 If Sab is high,a big current will be needed to achieve the high Q value[9,13].

 **3. Power factor():**

The figure of merit depends upon the factors such as electrical conductivity,Seebeck coefficient and thermal conductivity. Several studies have been concentrated on the ways to increase in the ZT value of thermoelectric materials thay are: reducing the lattice component of thermal conductivity can be achieved through methods such as incorporating rattler atoms into cage-like structuring,embedding nano particles in the host matrix ,or nano structuring in conventional materials. improvement of power factor by doping impurities[14].

 Power factor = (10)

 **3.1. Seebeck coefficient:** The ratio of an applied temperature gradient to an electric potential gradient is know as Seebeck coefficient. It is charaterised as

 S= - () (11)

Where is the electric potential and is the temperature difference at specific temperature T0 [15].According to the Pisarenko relationship the Seebeck coefficient is derived from the division of the temperature gradient by the TE voltage.

 Sab=Tm\* ( )2\3 (12)

Where m\* is density of states (DOS) effective mass,kB is the boltzman constant , h is planks constant,q is the carrier charge and p is the hole concentration .By adjusting the effective mass and carrier concentration ,the seebeck coefficient can be modified[16] .

**3.1.1. Measurement of Seebeck coefficient:**  Integral method is one of the most well known techniques to measure the Seebeck coefficient. Electric potential can be expressed as

 Vab(T1,T2) =(T)dT =b(T)-a(T)]dT (13)

Where a(T) refers the sample being measured the absolute Seebeck coefficient andb(T) refers the Seebeck coeffcient of the reference leads .For the thermoelectric material ,b has Ohmic and isothermal junctions with material a.Both exhibits uniform chemical and physical characteristics. In this method the temperature at one end of the specimen is held constant at T1,while the temperature at other end is adjusted within the range T2=T1+∆T ,where T represents the temperature variation of interest .A suitable analytical approximation is employed and extended to the entire Vab(T1,T2) dataset, followed by the computation of its derivative with respect to T2.The Eq(13) becomes [17].

(T2) =(T2) - (T2) = (14)

At high temperatures, the absolute Seebeck coefficient can be determined through a direct measurement of the Thomson coefficient µ, with subsequent application of the Kelvin relation to calculate the Seebeck coefficient i.e.

(T2) = (T1)+ dT (T1<T2) (15)

Where T1 and T2 denote the base temperature employed for calculating the initial term S(T1) with the superconductor reference material (which could be below Tc) and the target base temperature, respectively [18].

**3.1.2. Strategies to Enhance the Seebeck Coefficient:**

Quantum confinement is the one of technique to improve the seebeck coefficient.In 1993,Hicks and Dresselhaus demonstrated that the confinement of electrons or holes in low-dimensional materials enhances thermoelectricity. For the low-dimensional materials,the characteristic length of material in specific direction closely aligns with the effective de Brogile wavelength of carrier in the direction. Hence, the movement of carrier is confined in specific direction. Carriers are situated in potential wells enclosed by walls of unbounded height. In this special case, the electronic spectrum undergoes a notable transformation commonly referred to as the quantum size effect[19].

 In initial theoretical model, R&D addressed the thermoelectricity within 2D quantum well structures. The assumption made was that the electrons within the valance and conduction band exhibits a straight forward parabolic energy band structure and the electrons are exclusively inhabiting the lowest sub-band within quantum well. The electronic dispersion relation for a 2D system are follows

(kx,ky) = (16)

The width of the quantum well is denoted by dw,and the components of the effective mass tensor for constant energy surface are represented by mx,my,and mz.It is also assumed that the flow of current occur along the x-axis,while quantum confinement is present in the z-axis direction . The square 1D quantum wire is characterized by a specific connection

 Ԑ1D(kx) = (17)

Where the flow of current takes place in the x direction, while quantum confinement is experienced in the y and z direction. The solution for equation were subsquently derived for S, σ and ke for the 1D and 2D systems[20].

Exploring the Mott equation below provides the valuable insights into the origin of the observed S with enhancement in low-dimensional materials

 S = [ +]E=Ef (18)

Where kB is Boltzmann constant , is the carrier charge and Ef is fermi energy. If bands exhibits a parabolic relationship between energy and momentum ,formula can be expressed as follows.

 S = [ + ]E=Ef (19)

Where r refers the scattering parameter. From above formula ,improvement of S obtained from the increasing the and decreasing the [21].

NguyenT.Hung et al. reported the thermopower values exceeding 2000μV\K at room temparature can be achieved in certain single-walled carbon nanotubes (s-SWNTs) with the diameter smaller than 0.6nm. It is concluded that as the diameter of single-walled carbon nanotubes(s-SWNTs) decreases, their thermopower increases [22].

 **3.2. Electrical conductivity():** A material's electrical conductivity (σ) is a measurement of its capacity to carry an electrical current. The carrer mobility (μ) and electrical conductivity of a semiconductor are related by

 = neμ (20)

Regarding the charge carrier lattice scattering, it is expected that the free path's length is inversely proportional to the temperature.The mobility changes with temperature in accordance with the equation [23].

μ∝ (21)

**3.2.1. Measurement of electrical resistivity of TEM:** One of the method for measuring the electrical resistvity is the four-probe bipolar technique, described by

ρ= (22)

Where A is the averge cross -sectional area, is the effective distance between the centers of the two voltage contacts,V is the averaged bipolar voltage,I is the average current through the sample.The current value through the sample is determined by measuring the voltage across a high-precision resistor of known value, which is connected in series with the sample.The selection of the effective distance is based on the condition *l*−*l*0≥2*w* to guarantee uniform current distribution between the voltage contacts[24]

**3.2.2. Strategy to improve electrical conductivity:** The issue of ionized impurity scattering in 2D structures was resolved long ago by strategically spatially separating the conduction carriers from their parent atoms.The technique is referred to modulation -doping,remote-doping,or delta doping.Under this scheme,In a semiconductor device, all dopants are concentrated in a thin doping layer, a region that is strategically separated from the main transport channel by a spacer. Modulation-doping in the realm of 2D materials has played a crucial role in significantly advancing the semiconductor industry in the past.Optoelectronic devices and new efficient transistors have been developed by this technique[25].

**3.2.3. Electron Filtering:** loffe was introduced the concept of electron filtering(EF) in thermoelectric materials.In 1995 Rowe and Min developed the concept of EF[26]. They examined how various barriers impact the conductivity (σ) and the Seebeck coefficient (S) using the relaxation-time approximation technique. They suggested that the movement of minority charge carriers could be hindered by high-energy barriers, potentially reducing the occurrence of bipolar effects.This clearly demonstrates a reduction in conductivity (σ) through the facilitation of primary charge carrier transport. Nanostructures offer another avenue for boosting the power factor (PF) by employing energy filtering. Nano-sized precipitates serve as filters, selectively allowing carriers with higher energy levels to pass through, thereby elevating the Seebeck coefficient (S) and consequently enhancing the PF[27].

 Quing Tan et al.,synthesized Ag doped SnS through mechanical alloying(MA) and spark plasma sintenring (SPS) processes. The addition of the p-type dopants Ag proved beneficial in enhancing the electrical conductivity (σ) of SnS by increasing the carrier concentration.They demonstrated a significant increase in σ from 0.001 to 3 Scm-1 at 323 K as the Ag doping concentrations increased. At a temperature of 873 K, a promising thermoelectric figure of merit (ZT) value of 0.6 was achieved. The results suggest that further improvements in ZT can be attained by optimized doping levels, microstructure, and composition to enhance carrier concentration. Overall, the synthesis of Ag-doped SnS through MA and SPS processes showed it's potential for thermoelectric applications with further optimization[28].

Wenyu Zhao et al., synthesized Ba and In double doped skutterudite compounds BarInsCa4Sb12 through the melting,quenching,annealing,and SPS methods and examine the thermal conductivity and electrical transport properties of BarInsCa4Sb12 with in the temperature range of 300-850k.They improved σ by modulation doping method and achieved high ZT values 1.33 and 1.34 at the temperature 850k for Ba0.15In0.16Ca4Sb11.83andBa0.14In0.23Co4Sb11.8respectively[29].

**4. Thermal conductivity ():**Thermal conductivity refers to a materials ability to conduct the heat in the direction of temperature gradient.

 q= -∇T (23)

 Where refers to thermal conductivity ,q refers to heat flux and ∇T refers to temperature gradient [30].There are two sources of thermal conductivity in thermoelectrics:heat is transported by electrons and holes(e) and phonons travelling via lattice(l).Through the Wiedemann-Franz law,the electronic term e is directly related to the electrical conductivity.

=e+l (24)

And e=LσT =neµLT

Where L referred to Lorenz factor,2.4\*10-8J2K-2C-2 with regard to free electrons.

**4.1. Measurement of thermal conductivity**: For a semiconductor where the heat transfer rate is comparable to that of surrounding environment. Heat exchange makes the measuring of thermal conductivity is difficult and time consuming[31].One of the best techniques to measure the thermal conductivity of thermoelectric material is steady state technique . According to the steady state condition,

**=**(Qs\A)(∆T\∆L) (25)

Where A is the cross section area,Qs is the amount of heat passing through the cross section area per unit time,∆T is the temperature difference and ∆L is the distance over the temperature difference .Qs\A is the heat flux responsible for the generation of the temperature gradient. ∆T\∆L Thus, temperature differential and heat flow measurements are necessary in order to determine thermal conductivity[32].

**4.2. Strategy to reduce the thermal conductivity:** Nanostructuring proved effectively in lowering thermal conductivity by incorporating nanoscale heterogeneities and nano dispersions. Energy filtering effects and quantum confinement are observed when the system size decreases and length scale becomes comparable to electron mean free path or wavelength . This leads to an increase in the density of states (DOS), ultimately boosting the Seebeck coefficient. Conversely, the introduction of nanostructured surfaces or interfaces results in a decrease in the thermal conductivity due to phonon scattering. This method has proven to be successful in enhancing the properties of superlattices, nanowires, quantum dots, and thin-film systems. When dealing with bulk materials such as PbTe, LAST, and LASTT, nanoscale impacts can be regulated by either reducing grain size to the nanometer scale or incorporating nanoparticles (NPs). Effectively manipulating nanoscale interfaces within nanostructured materials emerges as a crucial factor in diminishing lattice thermal conductivity. Consequently, leveraging these interfaces has the potential to substantially elevate the figure of merit (ZT), especially in the context of nanostructured materials[33].

Xiaoming Hu et,al. prepared the Bi0.4Sb1.6Te3 through the zone melting or Bridgeman method and reported an increase in porosity led to a notable decline in both thermal and electrical conductivities. Nevertheless, the decrease in electrical conductivity was counter balanced by the reduction in thermal conductivity, resulting in the achievement of a high ZT of approximately 1.1 at 343 K. This represents a significant improvement of about 20% compared to the original dense sample[34].

Yi Wu et al.,synthesized the n-type polycrystalline Bi2S3 doped with Lacl3 via solid state reaction and spark plasma sintering technique and reported the ZT value of 0.5 at 625k for the Bi2S3 sample with 2mole%LaCl3 which is higher than that of 0.11 observed for Pure Bi2S3 at same temperature. It is also reported that, at a temperature of 625k,Bi2S3 sample with 2mole%LaCl3 exhibited the maximum power factor(PF), approximately 483μWm-1K-2. The introduction of doping in the sample led to a reduction in its lattice thermal conductivity, which is attributed to the occurrence of multi-scale phonon scattering[35].

1. Alagar Nedunchezhian et al., frabricated the BixCo3-xO4 through the chemical precipitation method and reported a high power factor of 0.025μWm-1K-2at 530k observed in the Bi0.2Co2.8O4sample and showed that doping in Bi has a favorable impact on improving the thermoelectric properties of BixCo3-xO4 sample[36].

**5. Figure of merit (ZT):** In the earlier 19th century,engineers have been working to create an efficient and financial viability TEG. They believed that efficiency of the TEG depends upon the properties of thermoelectric material and construction of TEG. In 1909, a German scientist named Edmund Altenkirch described the mathematical relationship between the physical properties of TMs and the efficiency of TEG.The electromotive force, a thermopile's thermal resistance and electrical conductivity, and other factors are included in Altenkirch's equation .In 1949 to 1956, these characteristics were merged into the Z group (amount Z or parameter Z) by the renowned Russian scientist Abram F. Ioffe, who used the new parameter Z to determine the efficiency[37].The efficiency of TMs calculated by dimension less quantity

 ZT= = (26)

Where is called power factor ,S is the seebeck coefficient,expressed in units of VK-1; is the electrical conductivity,expressed in units of Scm-1;T is the absolute temperature ,expressed in units of K; is the thermal conductivity ,expressed in units of Wm-1K-1. The thermal conductivity with respect to the elctronic thermal conductivity and lattice thermal conductivity l A device with a huge power factor can produce high voltage and current[38]

**6. Maximum efficiency:** The expression for the thermoelectric efficiency ( Ԑ ) in power generation mode and coefficient of performance in refrigeration mode of a thermo electric couple are follows

Ԑ = [] (27)

And η = [] (28)

Where is the carnot efficiency as follows the

= (29)

Where is the hotside of TEG , is cold side of TEG ,and is average temperature of TEG[39].

To clarify, enhancing the temperature differential across the legs results in an elevation of the conversion efficiency of Thermoelectric Generators (TEGs). To optimize the Carnot efficiency (ηC), a highly effective strategy involves adjusting the structural configuration of the Thermoelectric (TE) legs in accordance with the ideal proportion of the cross-sectional area of the p-type (Ap) and n-type (An) legs. Determining the optimal ratio can be achieved by evaluating the respective measurements of these cross-sectional areas.

 [ ] = (30))

Where and represents the electrical conductivity and , are represents the thermal conductivity[40].

**7. Output power of TEG:** The output power (P) is derived as below:

 P = (31)

Where is the internal electrical resistance and is external electrical resistance .The TEG maximum power occurs when the internal electrical resistance () is equivalent to the external electrical resistance . The output power density measured by the equation

 E = = (32)

Where S is the surface area of the TEG,W is the width of the TEG and L is the length of the TEG[41].

**8. Applications:** Mainly the thermoelectric devices are classified into the two types, one is thermoelectric generator (TEG) is used to generate the electricity from the heat. Another one is the thermoelectric cooler (TEC) which is used to convert the electricity to heat. TEG and TEC are using in many areas including space ,automobiles ,electronic devices and buildings etc.,

For many missions exploring different planets, relying on solar power to generate electricity isn't feasible due to the diminishing solar brightness. This is especially true on Mars, where it's only about 45% as bright as in Earth's orbit, less than 4% on Jupiter, and virtually nonexistent farther out. Instead, over the past forty years, missions have utilized radioisotope thermoelectric generators to convert the thermal energy from a radioactive heat source into electricity for power[42]. Since 1961, the United States has utilized Radioisotope Thermoelectric Generators (RTGs) to supply electrical power for spacecraft missions. These generators achieve the necessary electrical output by incorporating General-Purpose Heat-Source (GPHS) modules. These modules consist of a composite carbon structure housing four fuel pellets, primarily containing plutonium dioxide (238PuO2) at around 80% density. The RTG system employs thermoelectric junctions, like SiGe junctions, for power conversion[43].

Bombardier submitted a patent outlining a Thermoelectric Generator (TEG) coupled with a latent heat storage unit linked to the TEG's high-temperature end. This storage mechanism aims to reduce the temperature fluctuations commonly experienced in applications like diesel-electric locomotives[44].

**9. Thermoelectric materials:**

 There are several types of materials that have been exhibiting the thermoelectric properties such as polymers, carbon nano materials,inorganic materials etc. Due to the superior thermoelectric properties of inorganic compunds compared to organic made them to use widely .The inorganic compunds are divided into oxides , clathrates , skutterudites, HH alloys, Zinc-phase materials ,intermatallics, and nitrides each with their own unique physical properties,thermoelectric perfomance,and crystal structure

**9.1. Oxides:**

 Oxides are the well known inorganic materials for the preparation of thermoelectric materials. The oxides are gaining much interest towards high temperature applications as they are potentially stable and chemically inert. Yakabeet al.[45] discovered the potential for utilizing them as thermoelements when they observed a significant figure of merit in NaCo2O4, a material they prepared through sintering, employing both hot and cold pressing methods. The hot pressing material maintained a figure of merit above 0.510-3K-1 across the 100-400C temperature range. The Seebeck coefficient ranged from 100to140 V/K, falling short of the optimal value. Doping agents like Ba, Cu, and Mn were found to enhance the seebeck coefficient, especially the material Na(Co0.95Cu0.05)2O4 displaying the highest figure of merit 0.810-3K-1 due to its remarkably low thermal conductivity of about 1.0W/m k from 100to400C. The peak value of zT reached approximately 0.54 at 400°C, marking a promising starting point for further exploration of oxide systems.

Ohtaki et al. [46] revealed an enhancement in the thermoelectric properties of NaCo2O4 through a crucial double-sintering method. This process resulted in highest Seebeck coefficient and electrical conductivity, doubling the power factor, albeit starting from a relatively modest level. At 780 °C, the p-type conductor exhibited a ZT value of 0.78, a performance similar to another p-type oxide, Ca3Co4O9 [47]. This underscores that NaCo2O4 is not the sole oxide manifesting noteworthy thermoelectric characteristics.

The first compounds belonging to Ruddlesden- Popper phase (Sr3Ti2O7) were reported in 1958[48] whose parent peroviskite is SrTiO3. It shows the large thermopower value because of the large effective mass of the carriers resulting from its d band structure. SrTiO3 is one of the best p-type oxide[49].Despite its low mobility, SrTiO3 boasts a high effective mass, and its power factor at room temperature competes favorably with materials like Bi2Te3. Nevertheless, the material's thermal conductivity is relatively high at around 8 W/m K, yielding a modest ZT value of about 0.08 at room temperature. Notably, Muta et al.[50] successfully reduced the thermal conductivity to 3.4 W/m K at 300 K by incorporating Dy in partial substitution for Sr. Additionally, a promising zT value of 0.37 at 1000 K has been achieved for SrTiO3 with a notable concentration of Nb[51]. Despite this progress, further advancements are necessary to establish a satisfactory n-type oxide at 1000 K. Importantly, SrTiO3's high melting temperature of 2080 °C suggests potential applications in environments not suitable for other thermoelectric materials. Enhancing the power factor of the pure SrTiO3 involves doping with Nb, but reaching the optimal Seebeck coefficient is hindered by limitations in the amount of dopant that can be added. Alternatively, adjusting for reduction or oxygen-deficiency doping helps bring the Seebeck coefficient closer to the desired value[52]. At 1000 K, the Nb-doped and reduced material exhibited a zT value of 0.25. Other oxides, such as co-doped n-type SrTiO3 with La and Y on one site and Nb on another, surpass this with a zT above 0.3. Additionally, incorporating TiB2 as a second phase or utilizing n-type materials based on Ti2O3 yields comparable, albeit slightly inferior, properties.

Terasaki [53] conducted a study on the power factor of transition metal oxides, projecting a broad temperature range with a predicted power factor of 9 μW/cm K2. The associated Seebeck coefficient magnitude would be around 300 μV/K. When considering a realistic thermal conductivity of 10 W/m K, the resulting zT is estimated to reach 0.9 at 1000 K.

Zinc oxide (ZnO) stands out as a promising n-type oxide thermoelectric material due to its abundant and cost-effective nature, coupled with a high power factor of approximately 80 μW/mK² at room temperature. However, its elevated thermal conductivity around room temperature (about 40 W/mK) and structural symmetry from the wurtzite-like arrangement make it more suitable for high-temperature applications. The substantial reduction in thermal conductivity to around 5 W/mK at 1000 K is attributed to the pronounced anisotropic thermal expansion.

Efforts to enhance the thermoelectric performance of ZnO have been focused on reducing thermal conductivity while preserving electronic properties, aiming to improve the dimensionless figure of merit (zT). One effective strategy involves the controlled introduction of a secondary phase, forming nano-precipitates through precise thermal treatment. Despite the complexity of this approach, promising results have been achieved, particularly with Al nanocomposites[54]. The creation of defects and interfaces in these composites led to a significant reduction in thermal conductivity to approximately 2 W/mK at 1000 K, while electronic properties remained largely unaffected, resulting in a final zT of 0.44 at 1000 K.

Similarly, the incorporation of polyparaphenylene (PPP) nanoparticles into the Zn1-xNiₓO matrix yielded a zT of 0.54 at 1173 K[55]. This success was attributed to an increased power factor and reduced thermal conductivity. Nanostructuring of undoped or doped ZnO has consistently demonstrated the ability to lower the thermal conductivity values as low as 3 Wm⁻¹ K⁻¹ at room temperature for nanograined ZnO[56]. However, challenges persist, such as the limitation in electrical conductivity (σ), hindering substantial improvements in zT. By combining nanostructure with selective dopiant or co-dopants enabled the achievement of enhanced zT values up to 0.65 at 1247 K[57].

**9.2. Skutterudites:**

 Skutterudite, a mineral initially discovered in Skutterud, Norway, possesses a cubic structure with 32 atoms per unit cell and showcases a distorted AB3-type perovskite structure [58]. CoSb3, a notable skutterudite, undergoes transformation into a heavily doped semiconductor, particularly in the Co-rich phase, making it viable for high-temperature thermoelectric applications [59]. The void-filling atoms play a crucial role by altering electron concentration and acting as potent phonon-scattering centers, thereby reducing the lattice thermal conductivity [58]. Through substitutions of foreign atoms at Co and Sb sites, such as Fe, Ni, Sn, or Te, can alter the properties of CoSb3 for specific applications [60,61].

Studies have revealed that the YbxCo4Sb12 system with incorporating fillers significantly enhances the thermoelectric response, resulting in improved ZT values, indicating its suitability for thermoelectric devices [62,63,64,and 65]. The decrease in lattice thermal conductivity without affecting electrical conductivity, as seen in materials like PGEC (Phonon-glass electron-crystal), is caused by the phenomenon known as the 'rattling effect', where guest atoms establish feeble bonds with the host lattice. [66]. Moreover, nanostructuring and reducing grain size have been identified as effective strategies to enhance the thermoelectric properties of CoSb3 [67,68]. A thermal conductivity of 1.61 W/m K has been attained for bulk CoSb3, which was fabricated from nanopowder synthesized hydrothermally, employing either spark plasma sintering or hot pressing techniques.[67,69].

CoSb3 stands out as a promising candidate for medium-temperature thermoelectric devices due to its well-balanced mechanical and thermal properties, as supported by various studies [67,61,70].

 PGEC materials exhibit a structured, cage-like arrangement at regular intervals, enabling unrestricted electron mobility akin to that of a perfect crystal. However, the incorporation of a sizable, heavier guest atom with weak bonding, referred to as a "rattler," disturbs the oscillations caused by lattice vibrations. This disruption results in a material resembling glass, characterized by diminished thermal conductivity.[71]. Shi et al. conducted research wherein they decreased lattice thermal conductivity by introducing Ba and Yb atoms into the voids of a skutterudite structure. This incorporation led to a broad spectrum of resonant phonon scattering. [72].Shi et al. achieved a ZT value of 1.36 at 527°C with an n-type BaxYbyCo4Sb12 material, while the skutterudite Ba0.08La0.05Yb0.04Co4Sb12, featuring multiple-filled voids, exhibited an even higher ZT of 1.7 at 577°C. The importance of reducing lattice thermal conductivity is underscored, particularly in cases like Ba0.08La0.05Yb0.04Co4Sb12, where the efficacy of multiple filling of filler atoms is demonstrated to be more efficient. The notable increase in the ZT value can be attributed to the Spark Plasma Sintering (SPS) process, which not only enhances the material's microstructure but also ensures a uniform and homogeneous filling of atoms within the voids. Yang and colleagues introduced a filled-skutterudite system denoted by the formula GyM4X12, where G represents a rare earth element, M signifies Co, Rh, or Ir, and X stands for Sb, P, or As. Remarkably, multiple-filled skutterudite systems, such as Ba0.08Yb0.04La0.05Co4Sb12, demonstrated an outstanding ZT value of 1.8 at 900 K, marking the highest reported value for skutterudites.[73].

**9.3. Clathrates:**

 As discussed above, the interaction between structure and chemical composition plays a crucial role in determining the electrical and thermal transport properties, ultimately influencing the thermoelectric performance of materials. This observation is particularly pertinent in the case of intermetallic clathrates, where the distinct geometric arrangement of atoms directly correlates with unconventional thermal transport characteristics. Additionally, the chemical flexibility of these materials results in a diverse range of electrical transport behaviors. The term "clathrate" broadly refers to a diverse set of inclusion compounds sharing a common structural feature: a host framework of one species capable of encapsulating atomic or molecular guests of another [74].

While the term encompasses a wide range of crystalline guest-host solids, the clathrate materials relevant to thermoelectric applications represent a more specific subset within this extensive category. The terms "inorganic" and "intermetallic" clathrates are often used interchangeably, albeit somewhat imprecisely, to describe compounds where covalently bonded atoms typically tetrahedrally coordinated form rigid frameworks consisting of face-sharing coordination polyhedra that can host various guest atoms. The crystallization of clathrate compositions can occur in various structure types, each characterized by distinctive polyhedral cages that geometrically constitute the framework [75,76,77, and 78].

Clathrates possess a unique crystal structure resembling a cage, created by guest atoms housed within the lattice, thereby leading to reduced thermal conductivity. These clathrate families tetrahedrally coordinate with elements such as Al, Si, Ga, Ge, or Sn, constructing an open framework. They are categorized into type I (A8E46), type II (A24E136), and type III systems, differentiated by their coordination arrangements. [79,80, and 81]. Type III clathrates, exemplified by Ba8Ga15Ge85, are characterized by covalently bonded Ga–Ge pairs within their structure, with cages housing rattling cations. These cations bond to the anion frameworks of tetrakaidecahedral and dodecahedral polyhedra, resulting in polyatomic compounds where one component forms a cage structure enveloping another. [79, and 81].

Certainly:

Although clathrates often exhibit complex structures with multiple phases, the presence of a semiconducting phase is desirable for thermoelectric applications [79]. Clathrates display characteristics reminiscent of glasses, and their electronic properties can be adjusted through doping [79, 81, and 82]. Guest atoms within the clathrate structure act as "rattlers" confined within the host matrix, effectively dispersing lattice phonons and thereby reducing thermal conductivity [83]. Nevertheless, the concept of "rattling" is under scrutiny, given the presence of lattice irregularities and point defects, which also contribute to diminishing lattice thermal conductivity.

The crystal Ba8Ga16Ge30, synthesized using the Czochralski method, exhibited a ZT of 1.35 at 627 °C, with a projected ZT of 1.63 at 827 °C [84]. Similarly, for type III clathrates like Ba8Ga15Ge85, a ZT of roughly 1.25 at 627 °C and a lowered thermal conductivity of around 0.8 W/m K were reported.[85]. YbxBa8-xGa16Ge30, synthesized by Tang et al. through a combination of melting and Spark Plasma Sintering (SPS), showcased a ZT value of 1.1. The incorporation of Yb atoms filled the voids within Ga and Ge, resulting in an enhanced electrical conductivity. However, this enhancement came at the expense of a reduced Seebeck coefficient and lattice thermal conductivity.[82].

Zhang et al. examined the influence of synthesis techniques, particularly Spark Plasma Sintering (SPS), on the thermoelectric performance of a single crystal of Ba8Au5.3Ge40.7, fabricated using the Bridgman method . This crystal, demonstrating p-type characteristics alongside low thermal conductivity and high Seebeck coefficient, exhibited an increase in ZT from 0.3 at 227 °C to 0.9 at 407 °C following SPS treatment [80]. Toberer et al. noted an exceptionally low lattice thermal conductivity of 0.14 W/m K at 727 °C in Ba8Ga16Ge30, albeit with a relatively modest ZT value of 0.8.[79].

In the case of type I Ba8Ga16Ge30, formed through the cross-substitution of framework elements, a power factor of 15 μW/cm K² was attained, credited to the modification in carrier scattering mechanisms. Additionally, a ZT value of around 1.2 at 727 °C was documented for a polycrystalline material system composed of Ba8Ni0.31Zn0.52Ga13.06Ge32.2. The substitution of framework elements introduced ionized impurities and lattice defects, leading to phonon scattering [86]. Additionally, for Ba8Ni0.22Zn7.22Ge37.12Sn1.44 prepared through Ni substitution, a ZT value of 0.87 at 557 °C was reported [87].Sr8Ga16-xGe30-y, synthesized via a solid-state reaction and subsequent Spark Plasma Sintering (SPS), demonstrated a thermal conductivity of less than 1 W/m K at 27 °C, coupled with an elevated power factor of 12 μW/cm K². Moreover, it was observed that the power factor increased as the Ga/Ge ratio decreased.[88].

**9.4. Half-Heusler compounds:**

The Cu2MnAl Heusler alloy, in its basic form exhibits ferromagnetic properties and with a structure where copper atoms arrange in a primitive cubic lattice and in alternate cells, manganese (Mn) and aluminum (Al) atoms are present. The half-Heusler variant of this alloy retains the same structure, but with a notable difference — half of the copper sites lack atoms. Taking the example of the half-Heusler compound AgAsMg, it adopts a rock salt structure with magnesium (Mg) and silver (Ag) atoms. Additionally, the arsenic (As) atoms, along with either Mg or Ag atoms, form a zinc blende structure. A distinct group of half-Heusler (HH) compounds, characterized by the formula MNiSn, where M can be hydrogen (H), zirconium (Zr), or titanium (Ti), is recognized for its commendable n-type thermoelectric properties. Notably, despite a relatively high lattice thermal conductivity, these compounds demonstrate good thermoelectric behavior.

 The cubic structure currently under investigation involves 18 valence electrons and displays a complex band structure. The electronic characteristics of this structure are predominantly influenced by the covalent bonding between two elements. These bonding configurations are pivotal in determining phase stability and the formation of a bandgap, as detailed in a prior investigation [89]. Within an HH alloy, the presence of vacant atomic sites can facilitate the emergence of narrow bands, which in turn induce d-orbital hybridization, imparting a semiconducting nature. [90]. Notably, HH alloys typically demonstrate narrow bandgaps falling within the range of 0.1 to 0.3 eV [89,90]. These alloys also showed the elevated Seebeck coefficients, reaching up to 300 μV/K, and high electrical conductivity in the order of 103–104 S/cm at room temperature. Nonetheless, their practical applicability is hindered by their relatively elevated thermal conductivity, typically around 10 W/m K. Despite this, HH alloys demonstrate exceptional material characteristics, such as a high melting point (1100–1300 °C) and outstanding thermal stability up to 1000 °C, as evidenced in prior research [59, 89, and 91]. The atomic disorder which is present at transition metal sites contributing to a reduced lattice thermal conductivity, attributed to induced mass fluctuations and strain field effects within HH alloys [92, and 93].

The thermoelectric properties of several half-Heusler alloys have been extensively studied to enhance their performance, with particularly focused on ZnNiSn as the most intensively investigated member[94-97]. Notably, Sb-doped TiNiSn alloys have demonstrated impressive power factors, reaching up to 70 μW/cmK2 at 377°C. However, their high thermal conductivity of approximately 10 W/mK limits their overall thermoelectric efficiency, resulting in a modest ZT value of only 0.45 at 377°C[96,98]. In addressing the thermal conductivity challenges, researchers have explored alternative alloy compositions. For example, Shutoh and Sakurada synthesized a Ti0.5(Zr0.5Hf0.5)0.5NiSn1-ySby alloy, achieving a ZT of 1.5 at 527°C [91]. The substitution of Ti with Zr and Hf in this alloy significantly reduced the thermal conductivity to 3.1 W/m K at 527°C, leading to an increased Seebeck coefficient [91, 99]. Additionally, Hf0.6Zr0.4NiSn0.98Sb0.02 and Hf0.75Zr0.25NiSn0.99Sb0.01 alloys were developed and demonstrated ZT values of 1.0 at 727°C and approximately 1 at 600–700°C, respectively [100]. Moreover, Zr0.25Hf0.75NiSn alloys prepared through high-energy ball milling and spark plasma sintering (SPS) exhibited improved ZT values compared to their bulk forms synthesized by arc melting. These alloys offer simultaneous reductions in thermal conductivity and enhancements in the Seebeck coefficient. Recent studies have revealed that the irregular micro- and nanostructures in arc-melted solid solutions, such as Ti0.37Zr0.37Hf0.26NiSn, led to ZT values of 1 at 452°C and 1.5 at 352°C, due to phonon scattering effects caused by mass and strain fluctuations [101]. In a different context, the lattice thermal conductivity of FeVSb alloys increased with higher Nb content. For example, FeV0.6Nb0.4Sb exhibited a lower lattice thermal conductivity (5.6 W/m K) compared to FeVSb (12.2 W/m K) at room temperature [102]. These findings underscore the importance of alloy composition and processing techniques in tailoring thermoelectric properties for optimal performance.

In accordance with Makongo et al., the sensitivity of electrical conductivity, thermal conductivity, and carrier mobility in materials is intricately linked to crucial parameters like synthesis routes, processing conditions, and microstructures. [103]. In mechanically alloyed samples, a notable finding was that a decrease in grain size resulted in a significant reduction in carrier mobility and lattice thermal conductivity. Conversely, in samples processed through a Spark Plasma Sintering (SPS), grain growth was observed, leading to low lattice thermal conductivity and moderate carrier mobility [103]. Effective nanostructuring techniques, including ball milling and High-Pressure (HP) methods, demonstrated their ability to enhance the ZT value up to 1 at 600–700 °C for n-type Hf0.75Zr0.25NiSn0.99Sb0.01 half-Heusler alloys, with grain sizes below 100 nm contributing to further improvements [104].Yan et al. documented a significant 60% rise in ZT for p-type half-Heusler (HH) nanopowder fabricated via ball milling and high pressing [105]. Additionally, the incorporation of excess Ni in TiNi1+xSn (x = 0–0.15) through microwave-assisted methods followed by Spark Plasma Sintering (SPS) processes led to reduced thermal conductivity and an augmented power factor. [106].

Chen et al. successfully prepared a nanocomposite through spark plasma sintering (SPS), wherein nanophase inclusions of ZrO2 were dispersed into the matrix of Zr0.5Hf0.5Ni0.8Pd0.2Sn0.99Sb0.01 [107]. This nanocomposite exhibited a decreased thermal conductivity attributed to the phonon scattering effect induced by ZrO2 nanoparticle aggregates at the grain boundaries, serving as effective scattering centers for phonons [107]. On the contrary, the Seebeck coefficient and electrical resistivity were observed to escalate as a result of potential barrier scattering. Another study has been involved in the grain refinement and the incorporation of nanoparticles in n-type Hf0.6Zr0.4NiSn0.995Sb0.005 and p-type Hf0.3Zr0.7CoSn0.3Sb0.7/nano-ZrO2 composites and resulting materials displayed the enhanced ZT values of 1.05 and 0.8 at temperatures of 627 and 727 °C, respectively [108]. By employing the atomic-scale structural engineering of thermoelectric (ASSET) approach, simultaneous enhancements in thermopower and electrical conductivity were achieved in bulk half-Heusler (HH) alloys integrated with Hf inclusions.The successful application of this approach was evident in (1-x)ZrzHf1-zNiSn1-ySby+xZrzHf1-zNi2Sn1-yBiy nanocomposites, where x is from 0 to 0.1. This strategy increased the power factor from 10 to 47 µW/K2, observed in the temperature range of 454 to 527 °C [109]. Sahoo et al. synthesized a bulk HH matrix of Ti0.5Hf0.5CoSb0.9Sn0.1 embedded with varying mole fractions of Hf through solid-state reactions and this study highlighted the effectiveness of this method in increasing the thermopower while minimizing the reduction in electrical conductivity. The hole-culling effect observed in heavily doped HH alloys tuned the mobility without affecting thermal conductivity, leading to an increase in the Seebeck coefficient [110]. Multiatom substitution in half-Heusler (HH) alloys has been recognized as a more effective strategy for enhancing thermoelectric properties. The highest power factors at 427°C were attained for multiatom-filled HH alloys, where multiatom filling and high-temperature annealing notably reduced thermal conductivity while enhancing electrical properties, leading to elevated ZT values [111]. Moving forward, future advancements such as nanostructuring and bandgap engineering are expected to further optimize the thermoelectric properties of HH alloys, potentially yielding ZT values exceeding 2.

**9.5. Zintl-phase materials:** Zintl phases, a specific category of intermetallic compounds consisting of electropositive cations primarily from group 1 alkali metals, group 2 alkaline earth metals, and post-transition metals or metalloids from groups 13, 14, 15, or 16, have gained attention in the field of thermoelectrics. Although the exploration of their structure and chemical bonding commenced in the 1920s, credit for their discovery goes to German chemist Eduard Zintl, with the term "Zintl phases" coined by Laves in 1941 [112]. These compounds exhibited the promising thermoelectric properties, including high thermopower (S). Notably, Yb2-xEuxCdSb2 boasts the highest S value of 269 μVK−1 [113], while Mg3Pb0.2Sb1.8 and Yb14MgSb11 have also demonstrated S values of approximately 280 μVK−1 [114][115]. A significant advantage of Zintl phases lies in their adaptability to a broad temperature range. In the low-to-middle temperature range, Zintl 1-2-2 compounds stand out as having superior properties among both p-type and n-type Zintl phases. Conversely, in the high-temperature range, typically between (975-1275) K, the Zintl 14-1-11 compounds outperform other p-type Zintl families [116]. This versatility makes Zintl phases a promising class of materials for thermoelectric applications.

To achieve high thermoelectric figure of merit (zT), the required materials are characterized by light carrier effective mass, high band degeneracy [117], small deformation potentials (resulting in reduced electron-phonon scattering) [118], and low phonon/lattice contribution to the thermal conductivity(κph) resembling that of glass. As mentioned earlier, many Zintl compounds have explored due to their intrinsically low κph and exceptional stability at high temperatures, capitalizing on the temperature component (T) in the zT equation. The commonly observed low κph in Zintl phases is often attributed to their large unit cells [119], leading to a complex phonon dispersions, low average group velocity, and abundant channels for phonon-phonon scattering. However, recent instances of low κph (1.5 W m−1 K−1) in relatively simple compounds like Mg3Sb2 [120], adopting the CaAl2Si2 structure type with only 5 atoms per unit cell, challenge this simple explanation. Despite their lower density [121], Mg3Sb2 and Mg3Bi2 exhibit much lower κph than other compounds with the same structure type. This anomalous behavior is linked to strongly anharmonic bonding resulting from the undersized Mg cations in the octahedral site, leading to weak and unstable interlayer bonding [120,121].

In the realm of Zintl phases, the primary impediment to achieving elevated thermoelectric figure of merit (zT) typically arises from electronic considerations. The majority of thermoelectric Zintl phases reported thus far are of p-type, and enhancing the optimization of p-type carrier concentration is commonly straightforward. P-type doping can be accomplished through either aliovalent doping, such as incorporating Mn2+ on the Al3+ site in Yb14MnSb11 or Zn2+ on the In3+ site in Ca5In2Sb6 [122], or by leveraging intrinsic acceptor-type defects [123]. For instance, optimizing zT has been achieved by alloying with isoelectronic elements on the A site in A1-xZn2Sb2 compounds, thereby controlling vacancy concentration [124]. Regrettably, low mobility is a prevalent characteristic of p-type Zintl phases, a quality that can be partially ascribed to their salt-like, ionic nature. To gauge the extent of the salt-like nature of a specific AaMmXx compound, the ratio of cations to anions, denoted by a/(m + x), and the polarity of the bonds in the polyanion, measured by the difference in electronegativity (χX - χM) between the anions M and X, are considered. Utilizing these straightforward indicators, it has been observed that the intrinsic mobility of Zintl thermoelectrics assessed through high-temperature Hall mobility data within a single-band model, tends to be diminished in the more salt-like, ionic compounds.

The electronic mobility of compounds, particularly at lower temperatures, is influenced by the factors such as air sensitivity and the propensity to form resistive phases at grain boundaries. This phenomenon results in low mobility and conductivity (σ) at room temperature and observed to be increase as temperature rises. A comparative study between large-grained (5–20 μm) and small-grained (0.5–2 μm) Mg3Sb2 samples [125] revealed the similar behavior. Comparable trends have also been documented in various other Zintl phases, including Ca3AlSb3, Sr3GaSb3, and YbZn2Sb2 [126, and 127]. It is noteworthy that the challenge of low mobility attributed to grain boundary resistance is not necessarily inherent, but rather a challenge that can often be mitigated through processing modifications. Such modifications can lead to substantial enhancements in the average thermoelectric figure of merit (zT) [126,and 127].

In a recent high-throughput study conducted by Ortiz et al., the findings indicate a prevalent preference for electron transport over hole transport in the majority of known Zintl phases, primarily attributed to the lighter band mass in the conduction bands [128,129]. Despite the intrinsic tendency of Zintl phases to form acceptor-type defects, as demonstrated by Lasse et al. [130], the achievement of n-type doping has been limited to a specific set of compounds [131]. Tamaki et al. emphasized the significance of controlling defect formation enthalpies through synthesis condition modifications. Specifically, they compared the formation energies of Mg interstitials (Mgi), Mg vacancies (VMg(1) and VMg(2)), and Te on the Sb site (TeSb) under both Mg-excess and Mg-deficient synthesis conditions. The use of excess Mg during synthesis was found to facilitate n-type doping with Te on the Sb site, resulting in the highest reported zT values within any Zintl phase. Notably, Te-doped Mg3Sb1.5Bi0.5 demonstrated a remarkable zT value of 1.6, κph of 0.8, and PF of 12 μW cm−1 K-1 [132]. This successful strategy of excess Mg during synthesis holds promise for enhancing the thermoelectric performance of other Zintl phases. Consequently, while Zintl phases have traditionally been recognized for their p-type, high-temperature thermoelectric capabilities, recent results challenge these expectations and underscore the potential for significant advances in n-type doping [132].

**Conclusion:** This book chapter presents the overall review on historical background , principles involving in thermoelectric materials,enhancing techniques of ZT and properties of some thermoelectric materials .In a late 18th century volta reviled the concept of thermoelectricity . In 1821 Seebeck discovered phenomena of thermoelectricity is due to the temperature difference in material.In 1834, Peltier discovered the reverse phenomena of Seebeck effect .In 1854 ,Thomson gives the relation between the Seebeck and Peltier coefficients.Ioffe used the parameter ZT to determine the efficiency of TEM. There are some parameters which are contributing to ZT such as electrical conductivity,thermal conductivity and Seebeck coefficient.In this book chapter successfully explained measuring techniques of electrical conductivity by bipolar technique,thermal conductivity by Steady state technique and Seebeck coefficient by Integral method and explained improving strategies of electrical conductivity by Modulation-doping and electron filtering , Seebeck coefficient by Quantum confinement and explained the reduction strategy of thermal conductivity by nano structuring. This chapter reveled some other parameters maximum efficiency of TEG , output power of TEG as well as applications.

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