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Review

Thermoelectric materials—Challenges, approaches and classes

N. Karthikeyan[1,*], **C. Prabhakaran**[1], **R. Akilan**[2]

[1] Department of Physics, Anna University, Chennai 600025, India
[2] Faculty of Science, Aksheyaa College of Arts and Science, Madhuranthagam 603314, India
*** Corresponding author:** N. Karthikeyan, karthin10@gmail.com

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Abstract: Thermoelectric (TE) materials have gained significant attention in recent days for their ability to convert waste heat energy into electrical energy. Numerous advances in new and a unique thermoelectric materials have been developed during the last decades due to their ease of device fabrication technique and technology. Thermoelectric research has become a hotspot in materials science over the recent years due to its promising global necessity in energy generation, energy conservation and subsequent utilization. Here this article seeks to highlight some of the recent advances in thermoelectric research such as criteria for ideal TE materials, various strategies that are in practice to improve TE performance and different methodologies adopted in the preparation of TE-based materials. This article also highlights some of the explored state-of-art materials in thermoelectric research to layout a grid for future purposes.

Keywords: thermoelectrics; figure of merit; power factor; waste heat; electricity

1. Introduction

The energy crisis was a universal concern due to many factors including the global campaign to reduce the emission of carbon and other related effects. In the early 2000s, the demand for fossil fuels contributed to show the renewed interest in the negative effects on climate change and it focused on reducing the emission of carbon [1]. Since much attention is gained on renewable energy i.e. it is derived from the sources that can be refilled, restored or reused [2]. One of the major advantages of renewable energy is that it does not release any harmful pollutants into the environment. The investment in renewable energy in our global market is considerably increased in our daily lives and the dropping investment in fossil fuels energy led to an energy shortage, which could not be filled by the emerging energy sources [3,4]. The major key factor influencing the growth of global energy demand is due to economic growth, urbanization, and industrialization. Solar and waste heat energy is the most attractive, abundant, renewable, clean and green energy sources.

Due to the rapid economic expansion and world's fastest-growing energy markets, severe energy demand was to be expected across the world, including in developing countries by 2035. It is projected that global energy demand will increase approximately by 128% in 2035, with an average annual growth rate of nearly 5%. Currently, about 65% of world's electricity is generated from thermal power plants utilizing fossil fuels such as coal, natural gas and petroleum. Nuclear sources contribute 20% of the electricity generation, while renewable sources account for 15%. It's worth noting that up to 50% of input energy is wasted as heat during the energy production process [5]. Thus, the major drawback associated with the above energy production sources are its environmental pollution and greenhouse gas emission. Hence, the future growth depends on the long-term and steady sources that are affordable, easily accessible, and environment-friendly. Also, there is a huge need in developing technologies that can utilize the wasted heat energy and convert it into an electrical energy [6]. **Figure 1** shows the schematic view that generates electrical energy from various sources. By making advancements in these areas, researchers aim to overcome the existing limitations by the usage of TE devices and unlock their full potential for practical applications in power generation, waste heat recovery, and refrigeration. These efforts are crucial for realizing the promise of thermoelectricity as a clean and sustainable energy technology.

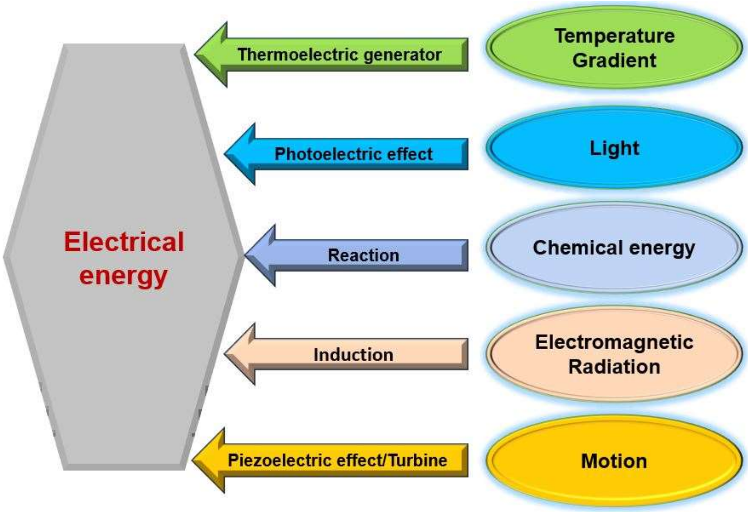

Figure 1. Schematic view of various sources that generates electrical energy.

2. Importance of thermoelectrics

The field of thermoelectric technology faces its limitations in widespread of application due to several factors such as low energy conversion efficiency, higher cost, and limited usage at higher temperature. Modern research efforts are primarily focused on addressing these limitations by improving the efficiency and power output of thermoelectric devices. A key parameter in this pursuit is the figure of merit (ZT), which quantifies the efficiency of thermoelectric materials [7]. The performance of TE materials can be analysed using figure of merit which can be calculated as ZT = $(S^2\sigma/\kappa)$ T, where S denotes the factor Seebeck coefficient, σ is electrical conductivity, T is an absolute temperature and κ is thermal conductivity. Researchers continually strive to enhance ZT values to maximize energy conversion efficiency. **Figure 2** illustrates the different steps involved in achieving the high ZT value. The barrier of the current TE materials is a low ZT, to be competitive with the today's power systems, TE devices must have a high ZT of 4. A secondary limitation of present technology is their unstability and poor performance at higher temperatures particularly their mechanical stability at elevated temperature is very low, the above are the main constraints to be taken into account while developing the materials for TE device [8]. Currently Bi_2Te_3 PbTe, CdO, Bi_2e_3 Sb_2Te_3 have appreciable ZT values and used in present commercial TE devices which are rare, toxicity, high cost, too hazardous to human health and environment. The present TE materials are too brittle which reduces the strength, hardness, and toughness during utilization, which might have to be considered for commercial viability. A material used in thermoelectric applications must possess a high stiffness (i.e. Young's modulus) to prevent defects during manufacturing, moderate hardness to resist surface damage during handling and significant thermal toughness to withstand thermal cycling without failure [9]. Improving materials with such mechanical properties by maintaining high ZT values possess a significant challenge due to the inverse relationships between mechanical, electrical and thermal behaviour. Enhancing one aspect often comes at the expense of others, complicating the search for an ideal thermoelectric material. Nevertheless, ongoing research and development efforts aim to overcome these challenges by exploring a new material, optimizing doping levels and employing advanced fabrication techniques. The ultimate goal is to identify materials with the highest potential for achieving a high figure of merit while also exhibiting desirable mechanical properties for commercial applications.

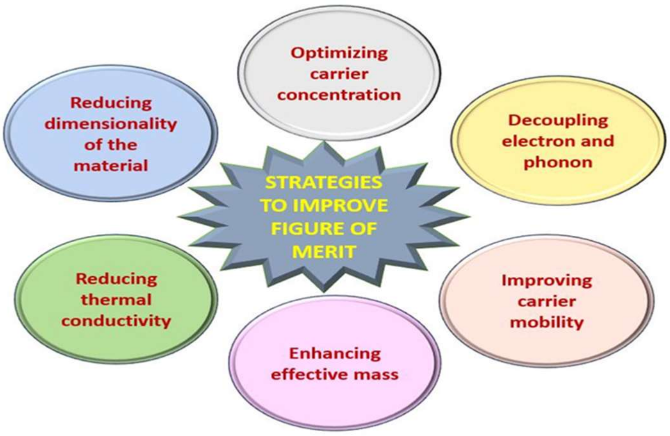

Figure 2. Strategies to improve the figure of merit.

Among vast field, this thermoelectrics presents a major challenge to physicists, as well as to materials scientists. Major challenge here is to develop a stable, efficient, less expensive, and an environment-friendly solid-state material. Further the research on developing new materials requires a combination of theoretical direction, intense chemical intuition, synthetic skill, materials processing, and a good expertise in measurement techniques. The combination on all of these led to a development of new and emerging thermoelectric materials.

3. Criteria for good thermoelectric materials

The good TE materials should have large Seebeck coefficient and electrical conductivity at the same time low thermal conductivity. By rule of thumb, both Seebeck coefficient and electrical conductivity must be high, while thermal conductivity is minimized to obtain the maximum ZT. From the formula it is known, that by reducing the thermal conductivity as shown in **Figure 3**. one can create the more efficient thermoelectric device. The parameter $S^2\sigma$ also known as the power factor (PF), which means by having a large PF the device could output, a large voltage and current. Historically, most of TE materials and devices had ZT values around 2.0, and the energy conversion efficiency was approximately about 25% or less. Achieving a higher ZT value, ideally around 4 or higher, is considered a significant milestone in thermoelectric research [10]. With such a ZT value, the theoretical maximum energy conversion efficiency between heat and electricity could reach approximately 30%. This level of efficiency would represent a substantial improvement over current thermoelectric technologies and would open up a wide range of practical applications, including waste heat recovery in industrial processes, automotive exhaust systems, and power generation from renewable energy sources. Researchers are actively exploring various strategies to enhance the thermoelectric performance of materials and devices, including novel material synthesis techniques, nano structuring, and advanced characterization methods. By pushing the ZT value closer to the theoretical limit, thermoelectric technology holds the potential to become a more efficient and sustainable solution for energy harvesting and conversion in the future. By Slack, maximum ZT is referred as "Phonon Glass Electron Crystal" (PGEC). The PGEC material features the property as glass-like thermal conductivity by the coexistence of high mobility and charge carriers. However, those properties are interdependent to each other in a bulk material to increase the ZT, and it is hard to adjust one parameter individually [11]. Along with the concept of PGEC, a strategy named as Phonon-Liquid Electron-Crystal (PLEC)was also used to decrease the lattice thermal conductivity by using the liquid-like behaviour of superionic conductors for the transport of phonons. Both PGEC and PLEC strategies represent an innovative way to tailor the thermal and electronic properties of materials. By optimizing a balance between phonon scattering and electron transport mechanism, researchers aim to develop a material with an enhanced thermoelectric efficiency, ultimately enabling more efficient energy conversion in thermoelectric devices.

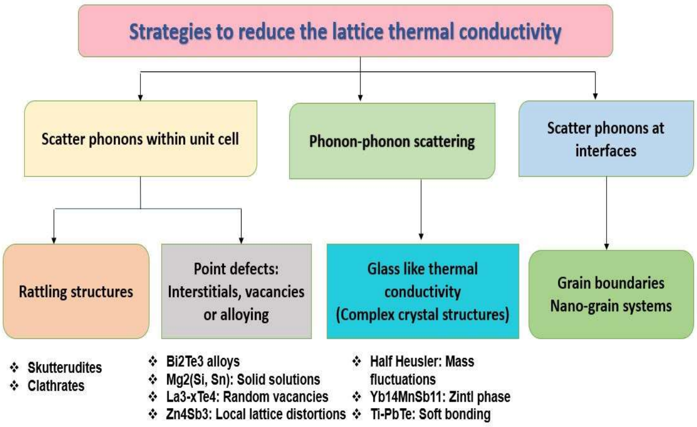

Figure 3. Strategies to achieve low thermal conductivity.

- Low temperature (up to 600 °C): Common application of TE are wearable and medical devices, here the device works near to room temperature and also used in the Microelectronics applications.
- Mid temperature (from 600 °C to 1000 °C): Commonly employed TE materials in this range are used in automotive and industries, where the heat waste is converted into an electricity.

- High temperature (from 1000 °C): Here the TE materials are mainly used in aerospace for energy harvesting, space missions and in exploration of outer space also [12].

4. Art of thermoelectric materials

In the past, many different techniques have been used to develop the thermoelectric materials. An overview about the recent most TE materials and its preparation methods are reported here. Hence, the below guidelines should be taken in to an account for best production and fabrication techniques in practical applications:

1) Employed technique needs to be adopted at low cost for the high crystallinity production and mass distribution.
2) For practical applications, the density of material should be 95% or above to that of theoretical density and the material must be normally stable during entire range of operation.

By the above-mentioned properties, various synthesis techniques have been progressed in the research such as single crystal growth, bulk technologies (Powder synthesis) and few of them are discussed below.

5. Preparation methods

5.1. Processing technologies: Single crystal growth

Currently, lot of studies have been reviewed on a modern technique called temperature gradient growth that enables the ease-fabrication of high-performing TE single crystals. Recently reported P and N-type SnSe shows the ZT values from 0.8–1.2 around 300–600K [13].

5.2. Bulk technologies: Powder synthesis

Bulk materials are fabricated from the route of powder processing technologies; among these few methods such as mechanical alloying, ball milling, magnetron sputtering, arc-melting and other are discussed below [14].

5.2.1. Hydrothermal method

Hydrothermal synthesis is a viable chemical process for material synthesis and it has been increased during the years. This method refers to the heterogeneous reactions for synthesizing inorganic materials in solution of aqueous as the reaction associated with high temperature and high-pressure systems. Hence, this method is associated to class of the liquid phase chemical solution synthesis and has numerous advantages such as quiet operation, simple and easy synthesis process, controlled particle size and morphology, high crystallization & homogeneity, and phase purity can be achieved. Here the **Table 1**. shows the different figure of merit values for different materials at different temperature, which was synthesized using the hydrothermal method.

Table 1. Figure of merit values for various materials prepared by hydrothermal method.

Materials	Methods	Figure of merit (ZT)	Temperature (K)	References
Ag/Cu_2S	Hydrothermal	1.4	773	Yue et al. [15]
Bi_2S_3/GO	Hydrothermal	0.17	300–650	Bai et al. [16]
Bi_2S_3 + 0.5Wt%f-$MWCNT_s$	Hydrothermal	0.33	589	Bai et al. [17]
$Bi_{1.985}Cu_{0.015}S_3$	Hydrothermal and SPS	0.3	573	Liu et al. [18]
$Zn_{0.3}BTS$	Hydrothermal	0.79	600	Yun et al. [19]

5.2.2. Mechanical alloying

Mechanical alloying and milling include two different ways of synthesizing thermoelectric materials. Mechanical alloying means individual elements are directly ground to form alloys while mechanical milling usually refers to grinding crystalline ingots into nanoparticles. The advantage of mechanical alloying and milling is that large quantity of nano powders can be produced through a relative convenient procedure and with a minimal requirement for equipment. Before high energy ball milling was introduced, mechanical alloying and milling was considered as a path to synthesize these TE materials directly and a wide variety of materials were produced, such as Si-Ge, rare-earth sulfides, Bi-Sb-Te, Pb-Te, Fe-Si and skutterudites. In conclusion, mechanical alloying has been developed into a very mature method of making different kinds of thermoelectric nanocomposites and significant improvement of ZT was observed in literature which was shown in the **Table 2**. The advantages of this method include simple procedure, minimal requirement on equipment, large yield, and surfactant-free environment. The disadvantages include energy intensive, time consuming and little morphology control. The oxide-based TE materials are earth abundant, non-toxic, and stable at higher temperature and also in oxidizing atmosphere. These oxide TE have low figure of merit due to their large thermal conductivity and lower mobilities compared to other TE materials like selenides, chalcogenides and pnictides.

Table 2. Figure of merit values for various materials prepared by mechanical alloying.

Materials	Methods	Figure of merit (ZT)	Temperature (K)	References
Bi_2O_2Se	Mechanical alloying	0.45	823	Zhou et al. [20]
$Bi_xSb_{2-x}Te_3$	Mechanical alloying	1.01–1.13	355	Ioannou et al. [21]
$Mg_2Si_{0.57}Sn_{0.4}Bi_{0.03}$ $Mg_2Si_{0.53}Sn_{0.4}Ge_{0.05}Bi_{0.02}$	Mechanical alloying	1.07 1.2	750	Symeou et al. [22]

5.2.3. Arc melting

Arc melting is one of the most primary and modern method which is used for melting metals to form an alloy. Here an arc is struck between the electrode, most commonly a tungsten is used and here the sample are placed over water-cooled copper hearth. Then electric arc generates a large amount of heat towards the sample, which melts the metal together in order to form an ingot. Evacuation chamber is mostly filled with an argon gas to prevent unwanted oxidation and reaction of the sample with the outer atmosphere. Then repeated melting of the sample is done to improve the homogeneity of alloy, but the small localized region in a melted sample is common.

And the different figure of merit for various materials prepared using an arc melting method was shown in **Table 3**.

Table 3. Figure of merit values for various materials prepared by arc melting.

Materials	**Methods**	**Figure of merit (ZT)**	**Temperature(K)**	**References**
$Ni_{0.07}Co_{0.93}Sb_3$	Arc melting	≈ 0.041	640	Bhardwaj et al. [23]
$TiNiFe_{0.03}Sn$	Arc melting/Melt spinning/SPS Method	0.54	900	He et al. [24]
$Ba_8Ga_xSi_{46-X}$	Arc melting and SPS	0.55	873	Anno et al. [25]
$Nb_{0.8}Ti_{0.2}Fe_{1.02}Sb$	Arc melting	0.73	390	Kihoi et al. [26]
Ru_2TiGe	Arc melting	0.025	1000	Mondal et al. [27]
P type-Ru_2TiSi &N type-$Ru_2Ti_{0.80}Ta_{0.20}Si$	Arc melting	0.42	900	Fujimoto et al. [28]

5.2.4. Solid state reaction

Solid-state reaction is a decomposition of chemical reaction, where a reactant of solid is heated to form a composition of new solid material. This method is usually employed for the oxide preparation from the source of simple oxides, carbonates, nitrates, hydroxides, oxalates, alkoxides, and other metal salts. Normally, the procedure used in this reaction is employed with multiple steps of annealing and intermediate milling to increase the phase homogeneity, and to decrease particle size. Extra milling makes the powder more compact and to be active. This solid-state is one of the reactions which is most inexpensive routes and requires a simple apparatus. In this method a large volume of powder can be prepared by a simple and easy manner. Compared to other wet preparation routes, this solid-state reaction shows a higher agglomeration, large particle size as well as relative homogeneity. Here in the **Table 4** maximum figure of merit is 1.3 which was achieved at 680K in solid state reaction is reported by our research group [28].

Table 4. Figure of merit values for various materials prepared by solid state reaction.

Materials	**Methods**	**Figure of merit (ZT)/Power factor (PF)**	**Temperature (K)**	**References**
$Zn_{3.9}Cd_{0.1}Sb_3$	Solid state reaction	ZT = 1.3	680	Karthikeyan et al. [29]
Graphene/$CuAlo_2$	Solid state reaction	ZT = 0.0045	575	Daichakomphu et al. [30]
$Sn_{1-x}Sb_xO_2$	Solid state reaction	ZT = 0.06	1073	Macario et al.[31]
$Na_{1.2}Co_{1.8}Ag_{0.2}O_4$/rGO	Solid state reaction	PF (444 $\mu WCm^{-1}K^{-2)}$	859	Phochai et al. [32]
$Cu_{0.15}B_{0.15}Co_4Sb_{11.5}Te_{0.5}$	Solid state reaction	ZT = 0.66	814	Bai et al. [33]
$CuO_{0.75}ZnO_{0.25}$	Solid state reaction	PF (12.92 $\mu WCm^{-1}K^{-2}$)	575	Ghazi and Kadhim [34]
$La_{0.9}Ba_{0.1}FeO_3$	solid state reaction	PF (3.73 $\mu WCm^{-1}K^{-2}$)	650	Karthikeyan et al. [35]

5.2.5. Ball milling

Recently, ball milling was one of the popularly used method for preparing the nanostructured thermoelectric materials. During this process both mechanical alloying and nano structuring occurs simultaneously through a collision of events inside a high energy mill. This whole process was done inside an argon gas filled glove box to reduce the unwanted oxidation of precursor materials. Then the jar was placed in a high energy milling machine. Thus, the merit of ball milling includes high yield, with the potential to produce kilograms of material. Additionally, the resulting nanomaterials are conducive to sintering, facilitating the formation of high-density pellets with larger grain boundaries. This characteristic is advantageous for enhancing the Seebeck coefficient and reducing lattice thermal conductivity, thereby improving the figure of merit as illustrated in **Table 5** of relevant studies. However, a major significant drawback of milling is the challenge of controlling particle size distribution, particularly as materials may lose crystallinity over prolonged milling durations. This loss of crystallinity can impact the final properties of the material, necessitating careful monitoring and optimization of milling conditions to achieve desired outcomes.

Table 5. Figure of merit values for various materials prepared by ball milling.

Materials	Methods	Figure of merit (ZT)	Temperature (K)	References
P-type $(Bi, Sb)_2Te_3$	Ball milling	1.14	323	Son et al. [36]
Higher Manganese Silicide	Ball milling followed by SPS	0.39	770	Chen et al. [37]
ZnSb	Ball milling	0.76	600	Balasubramanian et al. [38]
$Bi_{0.9}Sn_{0.1}Se$	Ball milling	0.32	473	Lu et al. [39]

5.2.6. Magnetron sputtering

This magnetron sputtering is one of the techniques in vacuum coating process which allows material deposition, such as metals and ceramics, over a substrate material with the help of suitable magnetic field, which is applied into a sputtering target. Here the deposition rate is faster at lower pressure compared to other techniques by a strong adhesive coating on a substrate. Thus sputtering deposition does not require any high melting or evaporation of the source material, which lead to many advantages compared to other PVD technologies: first, all of the materials can be deposited with the help of magnetron sputtering regardless of their melting temperature; second, sources can be scaled up and positioned anywhere within the chamber based on our requirements; Then finally, a film of alloys and compounds can be deposited over the source material by maintaining the similar composition. Here **Table 6** shows the different power factor values for different materials using the magnetron sputtering method.

Table 6. Figure of merit values for various materials prepared by magneton sputtering.

Materials	Methods	Power factor (PF)	Temperature (K)	References
Mg_3Bi_2	Magnetron Sputtering	1.1 $\mu WCm^{-1}K^{-2}$	393	Fang et al. [40]
Cu_2Se	Magnetron Sputtering	15.6 $\mu WCm^{-1}K^{-2}$	723	Rapaka et al.[41]
Mg_2Sn	Magnetron Sputtering	1.45 $\mu WCm^{-1}K^{-2}$	623	Liu et al. [42]
Bi_2Te_3	Magnetron Sputtering	0.70 & 27.3$\mu WCm^{-1}K^{-2}$	573	Kurokawa et al. [43]

5.3. Role of physical methods

The physical method also plays a pivotal role in the performance and efficiency of a thermoelectric material by tuning their key parameters. These physical methods are employed to improve the figure of merit (ZT) by tailoring the various structural, electronic and phononic properties in a material. With the help of synthesis method and advanced computational tools one can yield a high thermoelectric performance material for practical applications [44]. There are several steps employed in the physical methods and some of them are discussed below

5.3.1. Precise control and sintering methods

Tuning of the key parameters offers an unmatched precision in a thermoelectric material. Spark Plasma Sintering (SPS) and Hot pressing is one of the sintering methods which consolidates a powder to bulk material with a controlled microstructural property [45,46].

5.3.2. Band engineering for enhancement of power factor

Through the bandgap engineering or doping strategies, we can able to modify the electronic structure to improve See-beck coefficient by maintaining electrical conductivity.

5.3.3. Reduction of thermal conductivity

Nano-structuring, alloying, interface engineering, enhancing electron transport across material junctions and increasing phonon scattering at the grain boundaries is one of the effective approaches used to reduce the lattice thermal conductivity by maintaining the electrical properties [47].

5.3.4. Minimization of material defects

Using the surface modification and controlled growth techniques such as CVD, PVD, ALD and defect engineering helps to minimize the unwanted defects in a material which can degrade their thermoelectric performance [48].

5.4. Categories of thermoelectric materials

The state-of-the-art; TE materials are broadly classified into eight main categories and detailed discussions on the different TE materials are reviewed below.

5.4.1. Half Heusler alloys

Mostly the Half-Heusler (HH) alloys are the primary focus on thermoelectric research for majority of high temperature applications. Due to its high mechanical strength, high thermal stability, high electrical conductivity, and also this HH have a moderate Seebeck coefficient when compared to other TE materials. Generally, HH alloys are known as a better TE material than full-Heusler because this HH have a small band gap, low electrical resistivity and high thermopower. Additionally, the natural vacancies are created in an unit cell either by doping or substitution in the parent elements, makes strengthening the Heusler alloys electronic properties. This HH alloys are mostly nontoxic, less expensive with the high and low melting elements. Synthesis of HH materials mostly requires a high temperature when compared to the other materials. The general procedure used for most of Half Heusler alloys is a melt technique, such as an arc melting or induction levitation melting, then it was followed by a secondary heat treatment known as the annealing, to produce a dense single-phase material. Densification using Hot Isotatic Press (HIP) or Spark Plasma Synthesis (SPS) is often implemented to reduce the porosity of material. Generally, the Half Heusler alloys prepared through various methods, and its different figure of merit values are reported in the **Table 7**.

Table 7. Figure of merit values for various Half Heusler alloys.

Materials	Methods	Figure of merit (ZT)	Temperature (K)	References
$FeNb_{0.8}Ti_{0.2}Sb$	Arc & Induction melting	0.20	800	El-khouly et al.[49]
CoTiP	Theoretical	0.95	300	Bouchrit et al. [50]
P type TiXSn (X = Ni, Pd, Pt)	Quantum ESPRESSO Packages	0.56–0.70	900	Xiong et al. [51]
NaYZ (Z = Si, Ge, Sn)	DFT	1.8–1.9	900–1200	Adeleye et al. [52]
PdMX (M = Sc, Y) & (X = P, As, Sb)	Theoretical	0.28–0.44	1000	Rani et al. [53]
$ZrNiCu_{0.05}Sn$	Arc melting	1.1	950	Yan et al. [54]
$Hf_{0.3}Zr_{0.7}Co\ (Sn_{0.3}Sb_{0.7})_{1-x}Al_x$	Arc melting followed by SPS	1.5	980	Mitra et al. [55]

5.4.2. Chalcogenides

A chalcogenide is a class of compound which has atleast one chalcogen anion (group 16 element, such as Te, Se and S) and an electropositive element (such as Bi, Pb and Sn). Mostly widely used chalcogenide in the applications of TE are based on group IV-VI compounds such as (PbTe, SnSe, GeTe, etc.) and V-VI compounds (Bi_2Te_3, Sb_2Te_3, Bi_2Se_3, etc.); these compounds are generally rock-salt structure in nature. These chalcogenides are the commonly employed materials for TE applications, almost 75% of the global market is occupied by the bismuth telluride and lead tellurides. Among the other TE materials, the above two tellurides have the high ZT reported so far. Currently Bi_2Te_3, PbTe have enhanced ZT values and used in the TE modules, but one major drawback is they are rare, toxic, high cost, too hazardous to human health and environment and brittle in nature. Recently Duong et al. developed a Bi-doped SnSe single crystal with a maximum ZT of 2.2 around 773 K; currently this was only the material which shows highest ZT value, reported so far in Bulk materials as shown in **Table 8**.

Table 8. Figure of merit values for various chalcogenides.

Materials	Methods	Figure of merit (ZT)/Power factor (PF)	Temperature (K)	References
$BaErCuS_3$, $BaGdCuS_3$	Theoretical	ZT = 0.4–0.5, ZT = 0.3-0.45	400, 800	Khan et al. [56]
Sr_2GeX_4 (X = S, Se)	Theoretical	ZT = 0.001–0.006	800	Jawad et al. [57]
Bi doped n type Sn,Se single crystals	Temperature gradient growth method	ZT = 2.2	773	Duong et al. [58]
$FeIn_2Se_4$	Conventional solid state reaction method	PF (3.5μWCm^{-1}K^{-2})	643	Karthikeyan et al. [59]

5.4.3. Skutterudites

Skutterudites (SKUs) are a trending class of materials that gained a lot of attention within the research community since 1990s. Here by incorporating a smaller ion into the voids of skutterudite results in lowering the Thermal conductivity. Skutterudite exhibit a semiconductor like property and they have common formula AB_3, where (A = Co, Rh, Ir and B = P, As, Sb). The skutterudite materials mostly used for energy conversion are based on $CoSb_3$. Both the P and N type $CoSb_3$ shows a large power factor values compared to others. These SKU generally have a high thermal conductivity, but it can be lowered by heavy doping or alloying. Then an alternate way to reduce the thermal conductivity is by the introduction of Rare-earth elements or Lanthanides into the voids of crystal structure, by the substitution of Fe or Ni instead of Co. Currently the La-Fe-Co-Sb and Ba-Ni-Co-Sb system yielded a figure of merit above one, at or above 600 °C. The temperature range for SKUs is nearly from RT to 900K and these SKUs based materials are used in various applications such as waste heat recovery, thermophiles and high temperature energy harvesting and used in aerospace also. The highest ZT value reached in the literature is so far around 1.9 at 823K which was shown in the **Table 9**.

Table 9. Figure of merit values for various skutterudites.

Materials	Methods	Figure of merit (ZT)/Power factor (PF)	Temperature (K)	References
Double doped CO_4Sb	High temperature vacuum melting	0.65–0.7	673	Karthikeyan et al. [60]
N-type$(R_{0.33}Ba_{0.33}Yb_{0.33})_{0.35}Co_4Sb_{12.3}$	Ball milling	1.9	823	Rogl et al. [61]
Co_4Sb_{12} & $Co_4Sb_{10.8}Se_{0.6}Te_{0.6}$	Fast SHS-PPS route	PF (0.46-2.16$\mu WCm^{-1}K^{-2}$)	598-673	Kruszewski et al. [62]

5.4.4. Zintls

Zintls are a class of P-type material, which demonstrates a large potential to the field of TE community. Currently Sb, Zn, Cd based Zintls yields the high TE performance via band engineering. So far, the highest ZT in Zintls is 2.5 which was achieved around 700K through the first principle method with the Generalised Gradient Approximation (GGA) was shown in the **Table 10**.

Table 10. Figure of merit values for various Zintls.

Materials	Methods	Figure of merit (ZT)	Temperature (K)	References
Sc doped Mg_3X_2 (X = Sb, Bi)	First principle calculations	1.53	703	Yu et al. [63]
P type-Mg_3Sb_2	Ball mill & SPS	0.85	723	Zhang et al. [64]
$YbMg_2X_2$ (X = P, As, Sb, Bi)	Theoretical	0.72–0.74	950	Khan et al. [65]
P type-Mg_3sb_2	Theoretical	2.5	700	Ning et al. [66]

5.4.5. Oxyselenides

Oxyselenides are a group of compounds which contains both the oxygen and selenium atoms. This Oxyselenides are a class of compound which contains various transition metal elements, and they show a wide range of structure and properties. Recently this BiCuSeO gained a much more increased attention and they have been extensively studied and widely used as a promising material, due to its low electrical conductivity and carrier concentration by comparing to other materials, here the doping is the main strategy to improve its properties and to enhance its figure of merit of a material. The low lattice thermal conductivity due to slow transport of phonons which means less stiffness makes the Oxyselenides an attractive material. Currently there is a major demand on BiCuSeO based TE materials in the market, but many papers reviewed that by doping this BiCuSeO material with Mg, Cd or Pb and Ba shows the higher performance. The different Oxyselenide materials with different ZT values was reported in **Table 11**.

Table 11. Figure of merit values for various Oxyselenides.

Materials	Methods	Figure of merit (ZT)	Temperature(K)	References
Sm doped BiCuSeO	Two step solid state method	0.74	873	Feng et al. [67]
Sm doped BiCuSeO	Two step solid state method	0.65	823	Kang et al. [68]
I doped Bi_2O_2Se	Solid state reaction	0.32-0.35	790	Kim et al. [69]
Pb doped BiCuSeO	Microwave synthesis combined with SPS Sintering	0.76	773	Lei et al. [70]

5.4.6. Organic-inorganic and hybrid materials

Hybrid organic-inorganic materials are a emerging new material in the Te field, due to its great potential by utilizing a lower thermal conductivity in organic materials, and high Seebeck coefficient and electrical conductivity in inorganic materials. Here the Metal-organic coordination polymers belong to a class of metal compounds where each metal tends to bind with more than a ligand to create an array of metal centres. Linearly coordinated polymers with transition-metal ions and Ethylenetetrathiolate are expected to be an attractive and highly efficient material for achieving the good electrical conductivity. Recently these hybrid perovskites, such as $CH_3NH_3PbI_3$ and $CH_3NH_3SnI_3$ have been known as an effective TE material compared to other material due to its high seebeck coefficient and low thermal conductivity. So far, Iron phthalocyanine polymer achieved the highest figure of merit 1.02 at 300K was reported by M. Bashi et al. shown in the **Table 12** using the theoretical FP-Law method.

The different ways implied for improving the TE Performance in the Hybrid Organic–Inorganic Nanocomposites.

1) By controlling a major factor, such as size, shape, morphology and dimension led to improvement of high figure of merit in a inorganic nanostructure material.
2) Modifying their properties literally improves the electrical conductivity of organic materials either through doping or by controlling the oxidation state
3) Tuning and modifying the interfaces of material led to an increased power factor by improving the Seebeck coefficient on the hybrids.

Table 12. Figure of merit values for various organic-inorganic & hybrid materials.

Materials	Methods	Figure of merit (ZT)	Temperature (K)	References
Iron phthalocyanine polymer	Theoretical	1.02	300	Bashi et al. [71]
PE DOT: PSS-Bi_2Te_3	Solution mixing	0.58	Room temperature (RT)	Wang et al. [72]
WSe_2	Electrochemical-intercalation	0.245	340	Liang et al. [73]
2AL-PR-X (X = 2H, Ni, Pt, Zn)	Theoretical	0.32,0.9	RT,800	Wu et al. [74]

6. Conclusion

Development of new and modification in existing materials have been considerably increased in thermoelectric research over the past decades. It has been perceived that due to interdependence between the key parameters such as electrical conductivity, Seebeck coefficient and thermal conductivity, various criterions and strategies are adopted to achieve high ZT values and still yet to develop. Several mechanisms are been in trend to increase the power factor (σS^2) and to diminish the thermal conductivity (κ) to pull off high figure of merit values. Both theoretical and experimental approaches were been in a practise to move the field forward. Based on the current advances numerous TE materials were already developed and achieved reasonable ZT values of ≈ 2 with thermoelectric efficiency of ≈ 25% as potential barrier. It is anticipated that for the futuristic TE materials development various strategies has to be made to improve the ZT values to ≈ 4 with thermoelectric efficiency of ≈ 45%.

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