

A Brief Review on Thermoelectric Materials and their Applications

P.V. Sudharani

Ramaiah University of Applied Sciences, Bangalore, India

pvsudharani[at]gmail.com

Abstract: Waste heat recovery methods are the most promising technologies adopted to reduce the waste heat problem. The waste heat exploitation should be avoided and this can be done by moving towards the more efficient energy production methods, proper isolation of sources, by keeping the operations and the devices simple and flexible by optimization of energy and systematic control patterns. In such cases thermoelectric materials are very helpful as they are flexible, small in size and can be operated at less costs. The process of converting unwanted heat in to useful energy is the main advantage of thermoelectric materials. The disadvantage of these thermoelectric devices is their low efficiency. If the efficiency is improved, then the thermoelectric devices can act as a source for energy scarcity. The paper concentrates on discussing the factors that affect the thermoelectric efficiency and the means by which its figure of merit ZT can be improved. The main focus is to develop thermo electric material of good performance and to interplay between quantities like seebeck coefficient S , electrical conductivity σ and thermal coefficient κ . This paper briefs the various developments done in the field of thermoelectric materials and reviews the results that can be helpful.

Keywords: Efficiency, Figure of merit, Seebeck coefficient, Electrical conductivity, Thermal conductivity

1. Introduction

The process of conversion of heat in to electricity is called thermoelectricity which was first discovered by Seebeck in the year 1821. The efficiency of any thermo electric device can be given by a dimensionless quantity called as Figure of Merit (ZT). This gives an idea of alternate source of power generation and refrigeration. The process of converting unwanted heat in to useful energy is the main advantage of thermoelectric materials.

Hence, we need to develop a high efficiency thermoelectric material that can be used in many ways. Research is been going on to increase the Power factor (PF) and thus the Figure of merit of the thermo electric materials by reducing the thermal conductivity of the material, increasing their PF, or by enhancing some of their properties by nano structuring. It is a known fact that only 34% of world's total energy is utilized and the remaining 64% is wasted as heat or lost in any other energy form. There is a possibility of using this waste form of energy by retrieving it and converting it as useful energy with the help of thermo electric materials.

1.1 Applications of thermoelectric materials

Using the thermoelectric technology, the waste heat that has been emitted from the cars can be utilised for some useful purpose like charging a mobile or providing voltage for lights in the car. These are used to lift the performance of photovoltaic cells by taking some of Sun's heat and converting it to make electricity. Thermoelectric materials can also be used as refrigerators, called thermoelectric coolers. Some of the other applications include Air conditioning, Spot cooling of electronic chips in superconductors and also be used for Geo thermal power generation. They are used to prepare thermal suits for fire-fighting for soldiers for their safety.

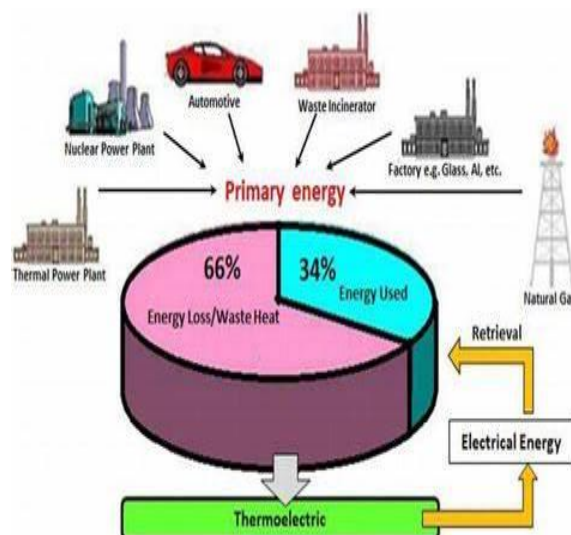


Figure (a): Pictorial representation of utilization of energy

FORD Company in 2011 has launched a vehicle called Ford Fusion which uses the waste heat recovery systems to deliver around 500W of power by using the materials Bi_2Te_3 and half- Heusler compounds. Volvo company has also undertaken a project with a €4.2 Million budget (partially funded by the French Government) to use this waste heat recovered from the vehicles in different ways.



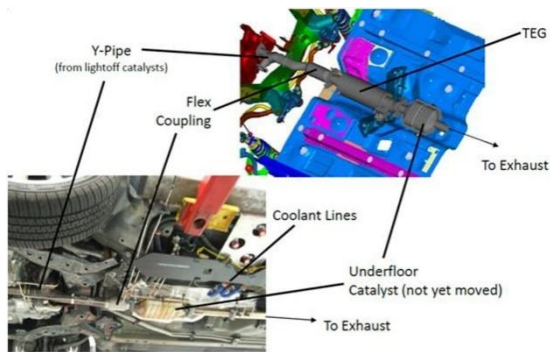


Figure (b): Representation of car exhaust system

It is expected that the energy consumption by the world increases by 40% by the end of 2040. The energy consumption that belonged to transportation sector occupies 33.3 percent of which most of the energy consumption is from road transport. Major dependence of the transportation sector is on petrol and there is much need to develop an alternate source that can reduce the consumption of petrol in the automobiles. Hence, the process of using the waste heat that is coming out from the exhaust gases and integrating the TEG module to the muffler of the engine can increase the performance of the engine thereby giving us a hope to sustainable green energy by reducing the fuel consumption. From the results it is clear that a thermoelectric material that is having high figure of merit can serve the purpose of utilizing the waste heat and thereby reducing the back pressure of the engine. [1]

The heat energy produced from the Sun is renewable and one can use it for alternate energy generation with the help of TEGs. The TEGs are small, durable, flexible, makes no noise and the experimental set up is also simple to use them for domestic applications. By mounting the TEGs to the solar panels 20 to 30 percent power of the total solar panel's power can be obtained.[2]

By establishing a thermo electric waste heat power plant, the insulation and hot water production problems are reduced. High profits can be obtained by lowering the unit cost and also payback time. These observations are based on the amount provided as incentive by the Turkish EMRA that is \$0.133 per kWh with a warranty of 5 years for the TEG modules. Since the power generation is completely dependent upon the temperature difference, a proper observation on the heat sources is to be made. The experimental results are compared with the simulation results at different temperatures. Then the pay back coefficient is calculated and it is found that $K > 1$. With a temperature difference of 100°C , a power of 150W is produced and the payback time is 6 years. The payback time decreases by 2 years when the ΔT is increased to 2 times. [3]

1.2 Figure of merit

Figure of merit tells us how good the material can exhibit the thermo electric power. It is dimensionless and given by,

$$ZT = \frac{\sigma S^2 T}{k} \quad (1.1)$$

which depends on the S seebeck coefficient, k thermal conductivity, σ electrical conductivity, temperature T , and the power factor is given by,

$$\text{Power factor} = S^2 \sigma \quad (1.2)$$

The thermal conductivity is a sum of electric and lattice thermal conductivities. So, the equation is rewritten as

$$ZT = \frac{\sigma S^2 T}{k_e + k_l} \quad (1.3)$$

According to Equation (1.1) if we have to increase the thermoelectric efficiency, we need to increase the Seebeck coefficient, electrical conductivity and decrease the thermal conductivity. But it is not that easy to do this task because σ , S , κ are all coupled with each other and are also very much dependent on the material's crystal structure, electronic structure and carrier concentration.

To be a good thermo electric material, it should have low thermal conductivity, high effective mass, large number of equivalent band edges and high carrier mobility.[4]

2. Literature Review

The first thermoelectric device was found around the 1950s and 1960s, with figure of merit equal to 1.0 and having an efficiency around 4 to 6 percent. [5]

Low dimensional materials are explored in the year 1990. And it is been observed that when the size is reduced there is an enormous change in the thermo electric properties of the material. These materials have shown promising results and are known to be used in waste heat utilization. Since then, the Figure of merit is calculated for various materials. Some materials even showed a Figure of merit 2.4 also. To find a good thermo electric material either we have to find a material that has complex structure and observe its thermo electric properties or study its properties in low dimensions.

A new class of materials called Multiphase composite materials are also considered to be good sources for thermo electric materials. [6] It is been predicted that the Figure of Merit for a two-dimensional system can never be greater than the Figure of Merit of their individual components. Again in 1999, Bergman and Fel proved that the power factor can be improved for composite materials also.[7] With the discovery of Bi_2Te_3 based alloys in 1960's, these thermo electric materials are highly in demand.

After this, many new materials have been discovered such as skutterudites, clathrates etc., whose k can be decreased while keeping the σ stable.

In 1993, a few other thermo electric materials have been proposed such as quantum wells, 1D conductors etc., by Hicks and Dresselhaus [8]. In 1996, multiple quantum structures in 2 Dimensions are found with high figure of merit 2.0. Experimentally the figure of merit is calculated for $\text{PbTe}/\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ systems and also in $\text{PbTe}/\text{PbSe}_{0.2}\text{Te}_{0.8}$. In 2001, Venkatasubramanian found the highest $ZT=2.4$ in $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ (p-type) quantum well superlattices.[9]

It is been observed that the nanostructured thermoelectric materials show better Figure of Merit than bulk materials due to the scattering of phonons by nano grains. InSb is also found to be a promising thermo electric material with high Figure of Merit.[10]

For more than five decades, the thermo electric materials like Bi-Sb-Te, Pb-Te, and Si-Ge based alloys have been the primary source with their ZT values nearly equal to 1. But we also need to consider how far we can use these materials and how efficiently we can use them. Therefore, Silicide alloys are made to use as attractive materials for thermoelectric applications as they have thermal stability, less density, availability of elements and low cost.[11] They are mainly used for waste heat recovery with in the temperature range of 400 K to 800 K where they show maximum Figure of Merit

2.1 Review of different thermoelectric materials SnS, SnSe, CuSnS, CuSnSe based materials

The figure of merit for a thermoelectric material is given by $ZT = TS^2\sigma/k$ where T is the absolute temperature, S is Seebeck coefficient, σ is the electrical conductivity and k is the thermal conductivity. The parameters S, σ and k are interdependent on each other which is the reason why there is a slow progress in finding the best thermoelectric material. Many thermo electric materials like Bi₂Te₃, PbTe etc., are developed in these two centuries which had applications in power generation and transmission. But there is always a quest for developing a thermoelectric material which is nontoxic, Earth- abundant, low in cost, simple and also having a high ZT. The Cu based materials, SnS and SnSe materials stand out for their excellent thermoelectric properties and satisfies the above criteria.

The Cu based thermo electric materials were first studied in 1827 by Becquerel. The next two decades, a lot of work is been done on Cu_{1.97}Ag_{0.03}Se- based radioisotope thermal generators (RTG's) but in 1979, the research activities are halted because of Selenium evaporation and Cu- ion migration. The Cu based thermo electric materials like, Cu – based diamond like compounds, Cu based superionic conductors, Tetrahydrites (Cu₁₂Sb₄S₁₃) and Oxyselenides (BiCuSeO) have proved to be promising materials for future applications. Materials like Cu₂SnSe₃, CuGaTe₂, CuInTe₂ etc. have shown ZT greater than 1. The binary superionic Cu -based materials show excellent thermo electric properties with high electric conductivity and excellent thermal transport properties. Currently, the ZT of Cu based materials is found to be greater than 2. They are widely used for their low cost and environmentally friendly nature that can be applied in many civil applications. But the two biggest challenges for using these Cu based thermo electric materials will be finding the ways to a.) to minimize the Cu ion migration and b.) developing n-type Cu based materials. Since the Cu ion migration will predict the reliability and life time of the thermo electric materials, one need to understand the process of Cu ion migration and find ways to suppress it. Hence if this is controlled, one can expect many promising and high performance thermo electric materials in near future.[12]

The Cu based chalcogenides like CuSnSe, CuSnS which are free from Te (not Earth abundant) and toxic Pb show decent values of ZT.[13] They are also of low cost when compared to Tellurium. In fact, Cu₄Sn₇S₁₆ with thermal conductivity $k=1\text{W/mK}$ at 300K with high Seebeck coefficient act as a promising n-type Cu based thermo electric material.

The thermo electric material tin sulfide (SnS) which is environmentally friendly and Earth abundant has gained lot of attention in recent years with ZT greater than 1 for SnS polycrystals. Although the crystal structure of SnS is similar to SnSe, the ZT values are rather disappointing for Na-doped SnS. Because of the low power factor and high thermal conductivity, the SnS materials show less performance than SnSe. Efficient methods like doping Ag or Na at Sn sites of polycrystalline SnS, have increased power factor, carrier mobility and reduced thermal conductivity [14]. However, for Sn_{0.99}Ag_{0.005}S, a maximum ZT of 1.1 is observed at 877K which is the highest so far observed in polycrystalline SnS samples.

It is clear that the development of a good thermo electric material with ZT greater than 1 is a slow process. But there is an exception to SnSe which is the most surprising thermo electric material with ZT above 2 and is Earth abundant, low cost and is a simple material [15]. The electronic band structure of SnSe is very unique which helps in increasing the Seebeck coefficient. The strength of anharmonicity is very high for SnSe which is responsible for the ultralow values of thermal conductivity k of around 0.4 to 0.5 W/Mk [14]. The main advantage of SnSe based TE materials are, they show high performance in both p-type and n-type crystals. By using advanced purifying technologies, one can reduce the effect of tin oxide impurities near the grain boundaries. If the internal oxygen in the starting materials is removed to get ultra-pure SnSe, a figure of merit of 3.1 can be reached giving an average ZT of 2.0 between the temperatures 400K and 700K [16]. If the figure of merit of SnSe is being compared to the other thermoelectric materials that has ZT=1, one can easily ensure that the overall performance can be increased by 50% if we use the thermo electric material SnSe. This gives a scope for future applications and a chance to explore new thermo electric materials.[17]

Reason for choosing composite silicides as thermo electric materials.

Reports suggests that the heat engines take on 80% world's total electric power. If we have such a large heat source like Sun or an automobile exhaust, it is very much desirable to use this unwanted heat in to electricity. By doing so, we can make a carbon free energy that is environmentfriendly. Many efforts are being made since early 1950's to develop such materials. Hopefully few thermoelectric materials are produced that are working efficiently. But even now the applications and the usage of these materials is very limited because, either they will be very costly to manufacture or they will not be environmentfriendly. So, an effort is certainly made to develop a material which is easily available, made at low cost and is non- toxic in nature. Hence, we can consider Nano powders of Earth abundant

materials like silicide-based materials such as Mg_2Si and its alloys.

Silicide based thermoelectric compounds/alloys show very good thermoelectric properties and are used for power generation applications. They have good thermal and chemical stability at high temperatures [18]. Hence alloying is a technique used to decrease the k of a material without changing its electrical properties through which very efficient thermo electric devices can be built. The properties of thermo electric materials are enhanced when a material is reduced in its dimensions.

The nanostructured thermo electric materials offer a method of tuning the energy conversion efficiency when compared to bulk materials. The way in which the thermoelectric efficiencies are enhanced, make them suitable for various applications such as waste heat recovery, power generation, reduction of global warming etc., For example, it has been estimated that we can save 500 million barrels of oil per year by using thermoelectric materials. But it seems that the strategies for the wide utilization of nanostructured thermoelectric materials is required and also experimental work is necessary.

Gaps/ issues to identify

Through the bottom-up approach, we cannot able to develop the nano structured thermo electric materials with $ZT > 1$. Even though the thermo electric generators (TEG's) are of great advantage, we cannot able to use all of them as they have some limitations like low efficiency, stability at high temperatures, toxicity and non-economic.

Hence there is need of developing inexpensive thermo electric materials that can be used in many applications.

Nano structured thermoelectric materials

The main focus is to develop thermo electric material of good performance and to interplay between quantities like S , σ , k . When a sample is nano structured, there will be a drastic change in the electric and thermal properties. Through quantum confinement, the power factor of the material will be increased as the density of states increases when the material is nano structured. This also effects the number of charge-carries thus increasing the electrical conductivity. Bulk materials fixed with nanoparticles are called Bulk nanostructured thermoelectric materials. There are 3 assumptions made when nano particles or nano inclusions are induced, the thermo electric properties of the materials will get enhanced. The possible assumptions made here are,

After adding these nano inclusions in the thermo electric material, they will add new interfaces due to which the phonons and the electrons gets scattered differently. If the mean free path between the phonons is less than the size of them, the thermal conductivity will be decreased. This will happen if we select the proper concentrations of these nano inclusions.

By using a method called as selective scattering, we can increase S which can be done by bending the electronbands

near the interfaces. If S is increased, the value of $(S^2\sigma)$ also increases and hence the value of ZT will be enhanced. With the addition of nano inclusions, the other possible effect will be a change in carrier concentration which is also beneficial.

3. Methodology and tools

Preparation of nanostructured Magnesium Silicide powders

Ball milling method is used by taking an excess of Mg that is oxidized. The size of the particles is measured by scanning electron microscope and the transmission electron microscope (TEM) helps to show the smaller grain sized particles of nano meter sizes. The powders are pressed by applying pressure and made in to pellets to measure the thermo electric properties.

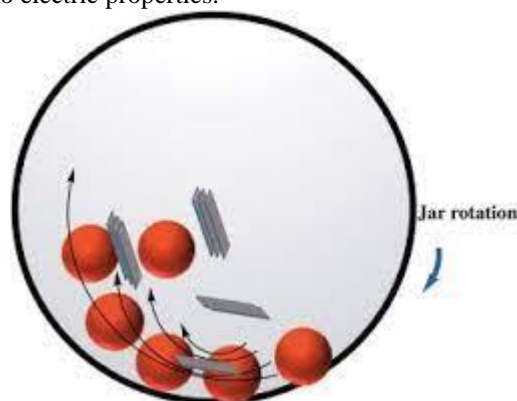


Figure 3: Picture representing the ball milling process of the nanoparticles.

Pure elements of Mg and Si were taken and are mixed in a glovebox. We need to take Mg composition by 2% extra as Mg gets evaporated during the reaction. A grounded mixture is to be made with all these powders with a time constraint of 2 x 20 minutes with a Mixer Miller. It is then annealed in a furnace at a temperature of around $600^\circ C$ for 24 hours. To Mg_2Si , a known amount of TiO_2 using the Mixer Miller for 2 x 15 minutes to prepare homogenous mixtures. Thus formed Mg_2Si/TiO_2 powders are pressed down by spark plasma sintering (SPS) at $725^\circ C$ for 5 min under a pressure of 75 MPa making disks of 12mm in diameter and 6 to 7 mm thickness and later the thermoelectric properties are measured. To check the homogeneity of the sample and its chemical composition, X-ray diffraction is performed on the sample. Thermal conductivity was measured using a Hot Disk instrument that works on the technique of transient plane source (TPS). The values of σ and S were measured. PPMS measures the mobility of charge carriers and the carrier concentration [19].

4. Results

From the results of XRD, titanium has played the role of dopant in the Mg_2Si structure. Hence it will donate some electrons to the structure so that the carrier concentration will increase. As the amount of Titanium is increased, there will be a decrease in the thermopower. Maximum absolute Seebeck values are obtained at the minimum value of added TiO_2 at $200^\circ C$. The 1% volume of added TiO_2 nano particles show lowest overall resistivity of $10\ m\ \Omega cm$ at all

temperatures. At a doping concentration of 1% TiO₂, we get maximum Figure of Merit value of 0.042 at 300°C which is 2.75 times greater than the value obtained for pure Mg₂Si. The possible reason for obtaining this is based on the fact that the electrical resistivity reduces quickly when compared to the Seebeck value.[19]

Comparison is done between the nano structures thermoelectric materials FeSi₂, Mg₂Si, and SiGe with their nanocomposites SiGe–Mg₂Si and SiGe–FeSi₂

The results of bulk nanostructured SiGe, FeSi₂, and Mg₂Si are compared with nanocomposites of SiGe with embedded Mg₂Si and FeSi₂ nano inclusions. It has been observed that the power factor increased and value of k is decreased when nano inclusions are added to SiGe. The materials Mg₂Si–SiGe and FeSi₂–SiGe nanocomposites have shown higher figure of merit values and lower thermal conductivity.[20]

Bergman and Levy in 1991 claimed theoretically that the value of ZT when two components are mixed may not be greater than the value of the single component [21]. After in 1999 it was proved that the Figure of merit of composite material structures increases as they have considered the wavelength relaxation times which effects the lattice thermal conductivity

5. Methodology and Tools

The Ball milling method is used to prepare the silicide alloys of Si_{0.88}Ge_{0.12}, FeSi₂, and Mg₂Si. The n-type dopants used are P, Cu, and Bi in In the powders, SiGe, FeSi₂, and Mg₂Si the n-type dopants P, Cu, Bi are used. The Ball milling time for each material is measured and then the nano composites SiGe–FeSi₂ and SiGe–Mg₂Si are prepared. Then they are pressed and sintered with a diameter of 12,7mm. SEM is used to know the distribution of charge carriers. It is fitted with energy dispersive spectrometer and TEM. The σ and S of the prepared samples are measured using the Ulvac instrument, at room temperature to 950 °C. The thermal diffusivities (α) were measured by laser flash, with in the range of 25 to 950°C. The value of k is measured using the expression $\kappa = \alpha\rho C_p$, where ρ - mass density, measured by Archimedes method, and C_p - specific heat.[20]

In SiGe–FeSi₂ sample, the thermal conductivity will be reduced since the nano particles will scatter the phonons. In SiGe–Mg₂Si sample, both crystal defects and grain boundaries can be observed which points out that there is an increase in the phonon scattering centers which will reduce the value of thermal conductivity. Up to the temperature of 550°C, the σ of the sample Mg₂Si rises and then it falls if the temperature is further increased. Due to the electron -phonon scattering, there will decrease in the carrier mobility, with temperature till 750°C for SiGe. Both the samples of SiGe and FeSi₂ show decrease in k values as the phonon scattering increases after 750°C.

The value of S of the nanocomposite sample is greater than that of the Radio isotope Thermo electric Generators (RTG) SiGe sample, which concludes that the carrier concentration might be low. When a dopant is added to SiGe, the carrier concentration increases and one should need to take care of

the concentration of the dopants that are precipitated. It has been observed that the k values of nanostructured SiGe and RTG SiGe are greater than that of the nanocomposites SiGe–FeSi₂ and SiGe–Mg₂Si. Results show that the nano inclusions of Mg₂Si work very effectively in decreasing the thermal conductivity.

When these silicide nano inclusions are added to SiGe, either the power factor of the thermo electric material increased or it remained same.

For a wide temperature range the figure of merit values of both the samples that have nano inclusions is greater than the RTG sample and the nano structured SiGe. For Si_{0.88}Ge_{0.12}–Mg₂Si nanocomposite the figure of merit value is observed to be 1.3 and for Si_{0.88}Ge_{0.12}–FeSi₂ the figure of merit shows higher values than 1 above 670 °C and reaches a maximum value of 1.2 with in the temperature range 800–950°C [20].

Enhancing the thermo electric properties of Bulk Nano structured Magnesium Silicide Mg₂Si.

The reason for choosing Magnesium Silicide is, even though Magnesium Silicide does not possess good thermo electric properties, we can enhance its thermo electric properties by doping nano or metal inclusions. Even though its ZT is lesser than 1, we can enhance the properties by various methods using nano structuring (Please refer the table (b)Comparative table below). The other reason for choosing this material is, we need a thermo electric material that is widely used, naturally abundant, nontoxic and should be made at low cost so that it is available to every usage.

In the recent times, thermoelectric research has been shifted to towards producing an economic way for making thermoelectric nanostructures. And new bulk-nano structuring approaches have attained a great success. Hence research is being continued to make such thermo electric materials which can be made economically and are less toxic in nature. Their thermo electric properties can be enhanced in many ways such as nano structuring, doping or adding new metal elements or nano inclusions. One needs to consider the fact that the phonons need to get scattered without effecting the electrical parameters. This is achieved by carefully selecting the that have high density grain boundaries. The point to be noted here is that, there is no particular rule like if the nano particles are added then the thermo electric properties will be enhanced always. In this case, the thermo electric properties are enhanced only at 1% of TiO₂ particles added to Mg₂Si. [19]

And for all the values even if we increase or decrease the composition of TiO₂, the thermo electric properties showed no effect. So, if we can adjust the ratio of Seebeck coefficient and electrical resistivity, the thermo electric properties can be enhanced.

It can be done by either exploring other titanium containing nano inclusions or by still adding TiO₂ The amount of scattering done by the nano particles if usually small when compared to the scattering of the other dopants. Both σ and k get reduced but the amount of reduction of σ should be

less than the amount of reduction of k in order to increase the efficiency of the thermo electric material.

The future work of points out that we can increase the values of ZT by 10% by just changing the electrical properties. We

can explore new ideas by using different dopants such as In, Se etc. and hence increase the power factor. The hole density can be controlled carefully with the post annealing treatments. If the annealing temperature is carefully modified, it can even increase the power factor.

Table a: The results of the different samples are listed below.[19]

S. No	Name	Sintering Temperature (°C)	Soak time (min)	Density (g/cm ³)	Temperature at max ZT (°C)	Thermal conductivity at max ZT (W/mK)	Max ZT
1.	FeSi ₂	1100	6	4.43	665	3.7	0.2
2.	Mg ₂ Si	800	10	2.00	655	3.1	0.6
3.	SiGe	1100	6	2.59	860	3.1	0.9
4.	SiGe-FeSi ₂	1000	15	2.62	800	2.8	1.2
5.	SiGe-Mg ₂ Si	1250	15	2.55	850	2.7	1.3

On other hand Oxide impurities can be present in Silicide based materials after making them as nano structures which can be removed spark plasma sintering SPS process and compacting them in the inert atmosphere. This will definitely increase the thermo electric efficiency of the material. Such well performed efficient materials can be used in thermo electric power generation applications.

Design rules: The design rules for any thermo electric material are as follows,

The material should possess low thermal conductivity that can be obtained by appropriate phonon scattering, by taking materials that has complicated crystal structures with increased grain boundaries and by managing the scattering. By increasing the density of states to enhance the Seebeck coefficient which can be done by manipulating the band structures, having carriers with high effective mass or by correlated electrons. By enhancing the electrical conductivity with increasing the carrier concentration and mobility. This can be done by minimizing the electron scattering and using a semiconductor that has narrow band gap. The expressions for Seebeck coefficient, Electrical conductivity and total thermal conductivity are given by [22],

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}$$

$$\sigma = ne\mu = \frac{ne^2 T}{m^*}$$

$$k_{tot} = k_{ph} + k_{el} = k_{ph} + L\sigma T$$

Where, k_B is the Boltzmann constant, m^* is the density of states effective mass, h is the Planck's constant, n is the carrier concentration, μ is the carrier mobility k_{tot} is the total thermal conductivity, k_{ph} is the lattice or phonon thermal conductivity, k_{el} is electronic thermal conductivity and L is the Lorentz number.

By manipulating the phonon scattering, the value of k_{ph} can be decreased which can affect in lowering the overall

thermal conductivity. The value of phonon thermal conductivity is given by,

$$k_{ph} \propto C v_s l_{ph}$$

Where, l_{ph} is the mean free path of the phonon, v_s is the phonon velocity and C is the heat capacity per unit volume.

Hence to increase the phonon scattering, the grain boundaries and defects should be reduced which decreases the phonon mean free path, by using crystal structures that are complex or "misfit" and by using the elements that have high atomic weight which reduces the phonon velocity. In these cases, "phonon-glass electron-crystal" model can be a solution to design a good thermoelectric material with enhanced properties.

6. Conclusion

The new thermoelectric should be designed to have good thermal stability and efficiency. The design parameters are based on size, band gap and controlling the defects by using new and innovative synthesis processes. They should be scalable and eco-friendly produced from low-cost materials. By using the material combinations on nano structuring, one can observe thermo electric conversion above 700°C with enhanced thermo electric properties at high temperatures. The challenge in designing a good thermo electric material lies in increasing the phonon scattering while keeping the electrical conductivity least affected. The material must be scalable, non-toxic, abundant in nature and available at low cost. This paper briefly reviews the various thermoelectric materials and compares the results in terms of their efficiencies. The requirements of a good thermoelectric material and its design rules are discussed which gives a scope for future developments in the field of thermoelectric material engineering. For the thermo electric efficiency to increase, there should be effective developments taking place in the matter of its sustainability and stability. New methods of synthesis and analysis can together help to enhance the thermo electric properties of the materials. It is assumed that the materials that maintain high temperature difference are expected to show good thermo electric properties.

Table b: Comparative tabular form depicting the performance of the nano structured thermo electric materials

S. No	Sample	Dopant	Milling time In hours	Sintering Temperature	Carrier concentration in cm^{-3}	Thermal conductivity In W/mK	Temperature at Maximum ZT in $^{\circ}\text{C}$	Maximum ZT
1.	Mg_2Si	Pure	24		2.9×10^{17}		600	0.026
2.	Mg_2Si	1% vol TiO_2		725	1.3×10^{18}		300	0.042
3.	Mg_2Si	3% vol TiO_2		725	1.7×10^{18}		Same as Pure Mg_2Si	Same as Pure Mg_2Si
4.	Fe_2Si	Cu, 1%	50	1100		3.7	665	0.2
5.	Mg_2Si	Bi, 2%	23	800		3.1	655	0.6
6.	SiGe	P, 2%	65	1100		3.1	860	0.9
7.	SiGe-FeSi_2	P, 2% - Cu, 1%	50	1000		2.8	800	1.2
8.	$\text{SiGe-Mg}_2\text{Si}$	P, 2% - Bi, 5%	20	1250		2.7	950	1.3
9.	Mg_2Si	Sn					700	1.2
10.	Mg_2Si	Bi, Al					720	0.55
11.	Mg_2Si	Bi co doped poly crystalline Bulk					873	0.82
12.	$\text{Mg}_{1.96}\text{Al}_{0.04}\text{Si}_{0.97}\text{Bi}_{0.03}$	Metal Nano particles with dual nano inclusions.					873	0.57
13.	Mg_2Si					7.9		
14.	Mg_2Sn					5.9		
15.	$\text{Mg}_2\text{Si}_{0.4-x}\text{Sn}_{0.6}\text{Sb}_x$	$x = 0.05, 0.075, 1.010$	2	973	7.1×10^{17} for $x = 0$	1.5 to 2.1 at 300 k	773	1, 1.1, 0.83.
16.	Mg_2Si Alloys		10	860		2.5		0.6
17.	$\text{Mg}_2(\text{Si}, \text{Sn})$					1.2	800	1.1

Symbols and notations used in the report

1. SS - Solid State Synthesis
2. MA - Mechanical Alloying
3. MC- Microstructure Characterization
4. TC- Thermal Characterization
5. TGA- Thermal gravimetric analysis
6. MS - Melt Spinning
7. K - thermal conductivity
8. S -Seebeck coefficient,
9. σ - Electrical conductivity
10. m^* -Effective mass
11. N_V -Number of equivalent band edges
12. μ - High carrier mobility.
13. ZM – Zone Melting process
14. α - Thermal diffusivities
15. SEM- Scanning electron microscope
16. TEM- Transmission electron microscope
17. PF- Power Factor
18. FM- Figure of merit
19. PPMS- Physical Property Measurement System
20. ZT – Figure of Merit.

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