ZINC OXIDE AS A PROMISING THERMOELECTRIC MATERIAL -REVIEW

[1]Karolinekersin. E, [2] AravindKumar.S, [3]Desigan.R

[1,2&3]Research Scholar

[1]Department of Physics and Nanotechnology,
[1]SRM institute of science and Technology ,Chengalpattu Dt, India

Abstract : The thermoelectric offers an interesting perspective for the direct conversion heat into electric power. The thermoelectric generator is capable of converting heat into electric power even with small temperature gradient. Thermoelectric applications gained lot of attention as it provides a potent way for energy recovery and harvesting by utilizing the wasted thermal energy to electrical power. The applications of thermoelectric generators are very inadequate because of the less efficiency in energy conversion. The efficiency of the thermoelectric generators confides on the materials having low thermal conductivity while maintaining good electrical conductivity. Many researchers are focusing on the development of thermoelectric materials with desired properties to enhance the efficiency. In this review, We Mainly focus on the Zinc oxide material for its thermoelectric applications. The basic principle of the thermoelectric behaviors, properties of the thermoelectric materials and the importance of ZnO as a thermoelectric material are discussed.

IndexTerms – **ZnO, Thermoelectric, Figure of merit, Nanostructure**

I. INTRODUCTION

The thermoelectric effect extends a captivating view for the direct conversion of heat into electrical energy from the 19th century, along the thermal gradient, a thermoelectric generator is well competent of translating heat into electrical power in contempt of small temperature differences(Shevelkov, 2010). This phenomenon was Thermoelectric devices works in the principle of conversion of thermal energy from a temperature gradient into electrical energy discovered by Thomas seebeck in 1821 named as "Seebeck effect," while the inverse of this phenomenon was discovered by Peltier in 1834 named as Peltier effects(Mahan, 2016). Thermoelectric generators (TEG) are simple, concise, potent and very reliable since they have no moving mechanical parts. Hence TEGs are gathering consideration for a several applications such as in the fields of energy recovery and green energy harvesting. For instance, TEGs can be used as a substitute to photovoltaic cells or collectively with advanced photovoltaic cells for the transformation of solar energy into electric power(Baranowski, Snyder and Toberer, 2012).

Many industrial proceedings require an enormous amount of heat which is wasted and dissipated in the atmosphere at the end of every manufacturing cycle hence it cannot be converted by current thermodynamics systems such as turbines or steam engines(Webb and Kramer, 2001). All the industrial processes could dexterously apply thermoelectric generators for recovering the wasted heat. Many studies are assigned to the development of modules, based on the thermoelectric generator for the exhaust heat reformation in cars(Petsagkourakis *et al.*, 2018a). Certain car designer companies afford an amplifying passion in these modules, to be executed for the generation of electrical power in hybrid cars and for the furnish of the onboard car sensors and electronics(Wang, Dai and Wang, 2013). Another important application area of TEG is energy harvesting. For instance, body temperature can be utilized for charging wearable sensor systems or ultimately for charging personnel such as mobile phones, tab(Su *et al.*, 2014).

It must be delivered that thermoelectric generators are also used as heat pumps and generator are also used as heat pumps and generators in domestic plants for air conditioning and heating. Anyhow, with the recent state of the art technology, operation of thermoelectric generators is restricted due to their less efficiency in converting thermal to electrical power. This is generally owing to the restraints of the materials presently accessible for the production of thermoelectric generators(Nolas, Poon and Kanatzidis, 2006). An immense research work is still required for the improvement of materials with thermoelectric properties desirable for conversion efficiencies greater than 10%(Tritt and Subramanian, 2020). In specific, one of the most significant factors that diminish the efficiency is the heat dissipation through the thermoelectric generators for thermal conduction. In many cases, a large amount of the heat passes through the generator and it is wasted on the cold side without being transformed into useful electrical power(Zoui *et al.*, 2020). Hence one of the ultimate purposes of the research work in thermoelectricity is to optimize the materials with a very low thermal conductivity, meantime, however, maintaining a high electrical conductivity. By this way, joule heating which is an irreversible process is decreased and moreover large number of electrical currents can be distributed to the external load(Petsagkourakis *et al.*, 2018a).

II. PRINCIPLES OF THERMOELECTRIC

2.1 Seebeck Effect

The Seebeck effect is a phenomenon in which a temperature difference between two dissimilar electrical conductors or semiconductors produces a voltage difference between the two substances. When heat is applied to one of the two conductors or semiconductors, heated electrons flow toward the cooler conductor or semiconductor. If the pair is connected through an electrical circuit, direct current (DC) flows through that circuit(Hogan, 2003).

Imagine a finite rod of a conducting material which is heated only at one end (Fig.1). The temperature gradient across the rod induces the charge carriers to move from the heated side to cooler side. In materials incepted superconductor below transition temperature entropy is transported along those charge carriers. Charge carriers will keep on moving to the cooler side of the material till an equilibrium state, which induce more charge carriers to move to the cooler side achieving a new potential difference. The maximum voltage is then reduced by the melting point of the material.
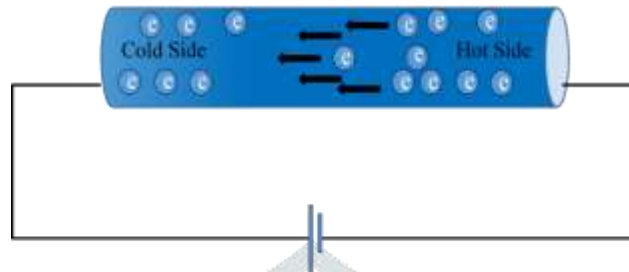

Figure 1. Schematic representation of Seebeck effect

The temperature gradient induces the charge carriers to move towards the cooler side till from on which an equilibrium state is achieved(Bellucci, Girolami and Trucchi, 2021). The Seebeck coefficient is the entropy transported along a charge carrier divided by the charge carriers charge. If a temperature gradient occurs at a junction of the two dissimilar conductors connected electrically in series and thermally in parallel, a voltage is generated. This potential drop resulted in the thermoelectric effect which was first reported by Thomas Seebeck 1921.

Seebeck concentrated exclusively on the power generating properties of a thermocouple known as the Seebeck effects. The voltage produced depends on the Seebeck coefficient S and the temperature difference between the two junctions in the thermocouple as shown in the equation. The Seebeck coefficient is the entropy moved along a charge carrier divided by the carrier's charge(Ong, Jiang and Lai, 2018).

2.2 Peltier Effect

Peltier effect describes that thermoelectric device can be used in the conversion of electricity into a temperature gradient. This effect was discovered by Peltier in 1834 and is known as the Peltier effect. This heat transfer is achieved when a direct current is passed through a pair of n-type and p- type semiconductor materials(Terasaki, 2005). The simple Peltier elements can be combined in series to develop complex Peltier modules, practically named as Thermoelectric cooler (TECs), which attributes greater cooling capabilities. Nevertheless, the highest temperature difference between the hot and the cold region for a Peltier device is on the order of 50°C. The most commonly utilized materials in the thermocouples based on Peltier effect (TECs) are the two semiconductors namely Bismuth and Telluride. In TEC, semiconductor-based cubes or pellets framed as an array, that are in contact with the radiators on both hot and cold region of the Peltier element(Terasaki, 2016). The extra impurities have been added to the cubes as a dopant to induce free electron for the improvement of conductivity. The Doped cubes with extra free electrons mainly carrying negative charge are said to be N-type semiconductors, whereas few free electrons mainly carrying positive charge are said to be P-type semiconductors. The pairs of P and N semiconductor cubes are arranged in such a way that series electrical connection and parallel thermal connection. When a current is applied to this system (the TEC), the way the current passes through the semiconductors generates a temperature difference, resulted in heating of the heat sink side and cooling of the cold side of the Peltier element and causes the heat-sink side of the Peltier element to heat up, and the cold side to cool (or cooling whatever is in thermal contact with that side)(Terasaki, 2005).
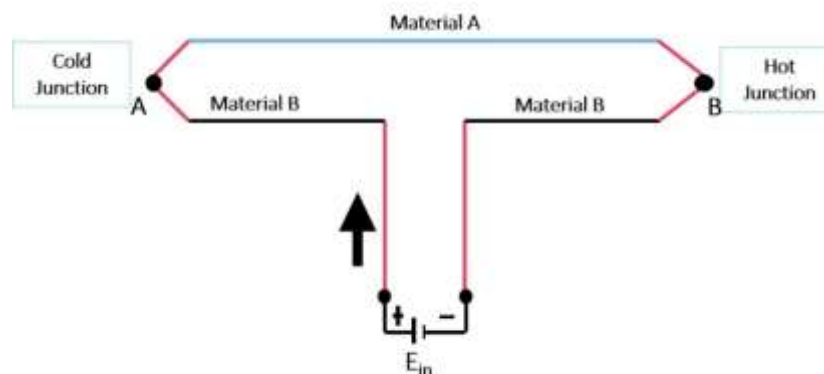

Figure 2: Schematic representation of Peltier effect

2.3 Variation of thermo emf with temperature

The thermo emf of the thermocouple increases, as the temperature difference increases between the two junction (A-cold, B-hot) and at a particular temperature thermo emf reaches maximum that is known as Neutral temperature θn which is expressed in Eq.1. The neutral temperature varies for different thermocouple(Enescu, 2019). If the temperature of hot junction B is increased

further, there is a fall in thermo emf and reaches zero, that is known as temperature of inversion θ(Camacho-Medina *et al.*, 2014)[i]. Neutral temperature is the mean of inversion temperature and cold junction temperature. The magnitude and direction of thermo emf generated in a thermocouple rely on the nature and characteristics of the two-metal forming the thermocouple.

$$\theta_n = \frac{\theta_i + \theta_c}{2} \qquad (1)$$

θ_n - Neutral temperature

θ_i - Inversion temperature

θ_c - Cold junction temperature

III THERMOELECTRIC PROPERTIES

Thermoelectric materials are responsible for the conversion of heat energy into electrical energy. These materials can be utilized in the conversion of wasted thermal energy into productive applications as efficient as possible. The efficiency of heat conversion is determined by the figure of merit (ZT) which is related to the Seebeck coefficient (S), thermal conductivity (k), electrical conductivity (σ) and absolute temperature (T) by the following relation

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

where S represents the Seebeck coefficient and T the absolute temperature. When ZT = 1, the device reveals 10% Carnot efficiency. The device attains the efficiency of a simple generator when ZT value is 4. The performance of a device thus can be enhanced by increasing the electrical conductivity and decreasing the thermal conductivity(Snyder and Toberer, 2008).

The material attributes high figure of merit owns the higher efficiency in conversion of thermal energy. Materials requires low thermal conductivity and high electrical conductivity to attain high ZT. Currently, among all the thermoelectric materials, Bi_2Te_3 and PdTe are the conventional thermoelectric materials with high figure of merit about 1. But these materials are less environment-friendly and poorly stable at high temperature. There are lot of researches are moving in the search of eco-friendly, economical, and high temperature stable thermoelectric materials(Zhang *et al.*, 2017). Thermoelectric materials can be applied in novel usage as biothermal batteries, automotive power generation, solid state, thermoelectric cooling, optoelectronic devices and space. In bulk material, increasing the thermoelectric power factor above the particular maximal value is difficult as electrical conductivity and seebeck coefficients are inversely related.

However, ideal thermoelectric materials would have a high electrical conductivity for the conduction of electricity, which in turn induce a potential difference across the sample, and a low thermal conductivity to sustain the temperature gradient between the hot and cold side (Cai *et al.*, 2004). Earlier, thermoelectric based research resulted in lower values of Z, as the materials used did not own the ideal thermoelectric properties Most traditional materials demonstrates a correlation between electrical and thermal conductivity. A material (metals) that conducts electricity well, also conducts heat well, and a material (glass or ceramics) that insulates heat well has the ability to insulate electricity also (Cai *et al.*, 2004). Many years of effort to increase ZT have not yet led to a fundamental breakthrough. In fact, the history of thermoelectric materials can be determined by the progress in increasing ZT. Thus, for devices operating at room temperature (TE300 K), traditional thermoelectric materials, such as bismuth telluride (Bi_2Te_3) and lead telluride (PbTe), possess values of ZT 1(Bian and Shakouri, 2006). In recent years, superlattices and quantum dots-based materials at room temperature to increase ZT to 2–2.4. These improvements in performance are due to the reduction in lattice thermal and the thermoelectric power factor does not show huge change. The high-performance thermoelectric material employed for practical purposes should have ZT of 44, which is an unreachable goal that remained as a huge challenge(Urban, 2015)(Svilans, Leijnse and Linke, 2016).

3.1 Seebeck Coefficient

A temperature difference between two points in a conductor or semiconductor causes a voltage difference between these two points. This phenomenon is called the Seebeck effect or the thermoelectric effect (Brinks and Huijben, 2015). The Seebeck coefficient gauges the magnitude of this effect. The thermoelectric voltage developed per unit temperature difference in a conductor is called the Seebeck coefficient or thermopower. Only the net Seebeck voltage difference between different metals can be measured (Sootsman, Chung and Kanatzidis, 2009). The thermoelectric device can act as electrical power generators by the principle of seebeck effect (Zheng, 2008).

The Seebeck coefficient is expressed in units of V/K (or, more commonly, μV/K or μV/1C). It has been observed that only a combination of two different materials, a so-called thermocouple, resulting in the Seebeck effect. This effect cannot be observed in the two leads though both leads intrinsically has a Seebeck coefficient, for reasons of symmetry. The Seebeck effect is a bulk property and does not confide on specific arrangement or method of joining or material of the leads (Nolas, Poon and Kanatzidis, 2006). Metals have different thermoelectric sensitivities, or Seebeck coefficients. For example, iron has a Seebeck coefficient of 19 μV/1^0C at 1^0C, which means that for every 1^0C difference in temperature, a positive thermoelectric emf (or Seebeck voltage) of 19 μV is induced in iron at temperatures near 1^0C.

A negative thermoelectric electromotive force (emf) can also be generated in a metal, so Seebeck coefficients can also exhibit negative values. For example, constantan (a copper– nickel alloy) has a Seebeck coefficient of 35 μV/1^0C at 1^0C. Typically, most metals hold Seebeck coefficients of 10 μV/K or less, but semiconductor materials are promising for the development of thermocouples because they carry Seebeck coefficients in excess of 100 μV/K. It should be noted that the relation between the Seebeck voltage and the temperature is linear only for small changes in temperature and non-linear for larger temperature ranges. The temperature at which the seebeck coefficient attained plays a very important role.

3.2 Thermal Conductivity

A high-quality thermoelectric material should possess a high electrical conductivity, high thermopower and low thermal conductivity. Because the first two are determined only by the electronic properties of the material, they are often combined into the quantity referred to as the 'power factor.' In contrast, the thermal conductivity K¼KeþKL in thermoelectric is the sum of two contributions: (1) electrons and holes transporting heat (Ke) and (2) phonons travelling through the lattice (KL) (Camacho-Medina *et al.*, 2014). It then follows that the thermoelectric figure of merit can be enhanced by increasing the electrical conductivity and decreasing the thermal conductivity. However, there is a relation between the two: the Wiedemann–Franz law for electrons that obey degenerate and non-degenerate statistics (KB is the Boltzmann constant, and e is the electron charge)

$$\frac{k}{\sigma} = LT \text{ where } L=2.44 \times 10^{-8} W\Omega K^{-2} \qquad (3)$$

Increasing the electrical conductivity not only rise the electronic thermal conductivity but also reduces the thermopower; optimizing ZT thus turns out to be a challenge. While the power factor can in some cases be improved by altering the concentration of charge carriers in the material, decreasing K and KL is much more problematic, especially for KL, which is influenced by the structure, rigidity, atomic masses, and other characteristics of the lattice(Dmitriev and Zvyagin, 2010). As the ZT values of the currently available materials are too low for cost-effective applications, various approaches have been implied to improve them. The idea of reducing the KL of a compound by replacing the crystal lattice with an amorphous (glass-like) structure, and the phonon-glass electron-crystal (PGEC) concept has been proposed, which was first introduced by Slack which has become a general guideline for the development new thermoelectric materials, is at the heart of the investigation into the skutterudite material system for thermoelectric applications. A PGEC material would possess electronic properties similar to the good semiconductor single crystal but have thermal properties similar to an amorphous material(Nolas, Poon and Kanatzidis, 2006).

It is believed that the ideal thermoelectric material would have regions of its structure composed of a high-mobility semiconductor, which provides the electron-crystal electronic structure, interwoven with a phonon glass. The phonon-glass region would be ideal for hosting dopants and disordered structures without disrupting the carrier mobility in the electron-crystal region(Pei, Wang and Snyder, 2012). The thermal conductivity of a semiconductor material is associated to its position in the periodic table, i.e., larger mean atomic weight contributes lower thermal conductivity. This behavior has been attributed to the increase in density causing the velocity of sound in the crystal to decrease, leading to a subsequent decrease in thermal conductivity(Terasaki, 2016). The most widely used commercial thermoelectric material is bulk Bi2Te3 and its alloys with Sb, Se, and so on, which exhibit ZTE1. It is difficult to scale bulk Bi2Te3 to large-scale energy conversion, but fabricating synthetic nanostructures for this purpose is even more difficult and expensive. Conversely, the most common semiconductor, Silicon (Si), is abundant and extensively used in the electronics industry, and a large industrial infrastructure is available for the low-cost and high-yield processing of Si. Increasing ZT via the reduction of K, by reducing the lattice contribution to the thermal conductivity, is a powerful concept. The most important factors that can support in accomplishing this are (i) usage of compounds having complex crystal structures, (ii) the presence of heavy atoms weakly bonded to the structures, (iii) the presence of impurities, (iv) the formation of solid solutions and (v) occurrence of a large number of grain boundaries(Srivastava *et al.*, 2018). The introduction of nanostructure in thermoelectric devices has become a potential tool for lowering the thermal conductivity and and consequently increasing ZT. This concept has revolutionized the field of TE because, the utilization of nanostructures has led to the achievement of ZT values of approximately 1–2 compared to o1 for bulk materials. The nanostructured BixSb2xTe3 have been shown to exhibit significantly improved ZTE 1.4 at 100 1C, mostly because of the reduced KL (Srivastava *et al.*, 2018). Owing to demerits in heat transfer and cost, it is challenging scale up these super lattices for large volume energy-conversion applications. Joshi et al. investigated the enhanced thermoelectric figure of merit in nanostructured p-type silicon germanium bulk alloys and observed that ZT enhancement is facilitated by the increased phonon scattering at the grain boundaries and crystal defects caused by lattice distortion, with less contribution from the increased electron power factor at high temperatures(Joshi *et al.*, 2008).

3.3 Electrical resistivity (ρ)

Electrical resistivity is an integral material-property that responds to the temperature. The value of ρ at room temperature is indicative of whether a material is an insulator (ρ is on the order of 106 Ω m or more) or a metal (ρ is on the order of 106 Ω m or less). In the latter case, if the lattice was perfect, the electron would travel infinitely through it, and the material would only exhibit finite conductivity because of the thermal motion of the lattice and the effect of impurities(Bulusu and Walker, 2008). The resistivity of a semiconductor material falls between the metal and insulator regimes. It has been found that the optimum range of electrical resistivity for a thermoelectric material is from 103 to 102 Ω m (Brinks and Huijben, 2015). Variations in the electrical resistivity of a semiconductor depend on changes in the carrier concentration and the mean free path of the charge carriers. The charge carriers are reflected/scattered by the surface of the material when they reach it(Camacho-Medina *et al.*, 2014). To attain low electrical resistivity in semiconductors, the lattice should possess nearly infinite conductance at low temperatures, but in reality, the conductivity of semiconductors is significantly low at low temperatures due to the restricted number of free electrons (Brinks and Huijben, 2015).The intrinsic properties of the materials can be obtained from analyzing the temperature dependence of the electrical resistivity . The temperature range depends on the scattering of electrons on the thermal excitation of the lattice(Sootsman, Chung and Kanatzidis, 2009).

3.4 The figure of merit

The energy conversion efficiency of a material is a behavior of its thermometric figure of merit ZT 3-5 which is defined,

$$ZT = S^2\rho^{-1}K^{-1}T \qquad (4)$$

Where S is the Seebeck coefficient/thermopower (TEP), σ is the electrical conductivity, T is the absolute temperature, and K is the thermal conductivity, which has a contribution from lattice thermal conductivity. K_1 and Ke are the electronic thermal conductivity. Equation reveals that a good thermoelectric material should have a high Seebeck coefficient, a good electrical conductivity, and low thermal conductivity. Heavily doped semiconductors form the best thermoelectric materials as an insulator that have very poor electrical conductivity and metals show low Seebeck coefficient. Phonon contribution controls the thermal conductivity in semiconductors with the negligible contribution from electrons, Ke(Petsagkourakis *et al.*, 2018b) (Wang, Dai and Wang, 2013).

IV THERMOELECTRIC MATERIALS

For a thermoelectric generator with maximum efficiency, the material employed should have a large thermoelectric power. High thermoelectric power is acquired from large electrical conductivity and large Seebeck coefficients. This power factor is optimized between a metal and a semiconductor. Heavily doped semiconductors are generally good thermoelectric materials, exclusively those with about 1019 to 1021 carriers per cubic centimeter. Doping is a process in which tiny impurities and irregularities are combined to a material to improve or adjust its properties. In thermoelectric semiconductors, materials are doped in order that they have as innumerable majority carriers as possible, which confirms that the Seebeck coefficient is as large as possible (Petsagkourakis *et al.*, 2018b).

Semiconductors are determined in thermal power generation as they can have large bandgaps, so that n-type and p-type carriers are detached. Nevertheless, a good material will always have sufficient bandgaps to achieve high doing and high electron mobility (Zheng, 2008). A good thermoelectric material need not to be highly conductive of heat, but it should be highly conductive of electricity. This determines that the electrons cannot be agitated since then the material will not be electrically conductive. Nevertheless, by agitating collective excitations of electrons, thermal conductivity can be decreased without compromising electrical conductivity. These collective excitations of assembly of articles are called phonons. The foremost way to reduce thermal conductivity is due to the materials so that the phonons are agitated or collapsed(Wanarattikan *et al.*, 2019)

The excellent thermoelectric material would be an 'electron crystal- phonon glass; in which electrons are mobile and freely transfer charge and heat but phonons are agitated so they cannot transfer heat (Webb and Kramer, 2001). These two necessary properties, high mobility and high thermopower, a balance should be achieved in dominant charge carriers between the two characteristics .materials having high electro negatively differences usually have high effective masses and low mobility (such as oxides or chalcogenides) or low effect masses and high mobility (such as SiGe and GaAs)

Based on these aspects, many materials have been developed. When temperature increases, the materials become more active at electricity generation. Nevertheless, and many materials have a maximum temperature of operation, shown in figure. This shows that no individual material is excellent for all temperature ranges, so the perfect material for a generator is completely based on the expected temperature range.

4.1 ZnO Based thermoelectric material

ZnO is a familiar wide direct bandgap semiconductor. Research on ZnO has extended for many with advantage for its potential applications in many fields. On account of its direct wide band gap (Eg~3.3eV at 300K), ZnO is most prominent in its expectancy for optoelectronics application (Ohtaki, Araki and Yamamoto, 2009). Other uses, such as fabrication of transparent thin film –transistors, and spintronic applications area also effectively scrutinized and described (Zimmler *et al.*, 2009). ZnO can also be doped with donor impurities and transformed from an insulator to an n-type semiconductor and then to a material along metal-like conductivity whereas maintaining optical transparency. That brings it useful for transparent electrodes in flat panel displays and solar cells (Ohtaki, Araki and Yamamoto, 2009). The doping caused n-type electrical conductivity and carrier mobility also leads to its potential as an n-type oxide thermoelectric. The most general crystal structure of ZnO is the hexagonal wurtzite structure .it is most strong at ambient conditions. The zinc oxide structure is an exceptional form of ZnO which only remain at relatively high pressures of about 10Gpa.

Due to the simple crystal structure and light element composition as mentioned above, ZnO would results from the high thermal conductivity.

4.2 Nano structuring of ZnO thermoelectric and the issues

From 2010, the synthesis of Nano structuring to the ZnO based thermoelectric has become an attractive topic. kinemuchi et al integrated nano grained ZnO using a pressure induced deformation method. Bulk samples along grain size up to 20nmwere achieved(Kinemuchi *et al.*, 2010). even though the thermal conductivity was favorably decreased down to at 8000C, the electrical conductivity was also significantly determined by the strong interface scattering which led to a 10 times higher electrical resistivity as the Seebeck coefficient remained almost the same. The overall ZT was not enhanced at all while comparing the nano grained samples to the ordinary bulk samples. In 2011, Jood et all stated on the al doped ZnO nanocomposites sintered by nano precursors prepared by a microwave aided hydrothermal method(Jood *et al.*, 2011). The thermal conductivity calculated at room temperature was decreased down to 28 Wm-1k-1 compared to 49 Wm-1k-1 for bulk ZnO. Even though the electrical conductivity was also decreased 10 times. In comparison with other bulk samples (Yang *et al.*, 2021), the Seebeck coefficient was improved very much due to the boundary scattering. anticipating the thermal conductivity up to 1000K the authors stated a peak ZT of 0.44. Nam et al. later scrutinized he charge transport properties of Al-doped ZnO owing to the boundary scattering. the hall carrier mobility keep on enlarging with the rising temperatures as the grain boundaries behave as a potential barrier to the electrons, as the carrier contraction remained the same(Nam *et al.*, 2012).As a consequence, the Nano structuring changed out to be very advantages to high-temperature ZT of Al-doped ZnO, but at room temperature ZT is generally lower than the bulk samples owing to less electrical conductivity. Generally, for ZnO nanocomposites, the high-temperature thermoelectric properties are much better than those at room temperature, as the reduction of the thermal conductivity by boundary and interface scattering may be passivated by the loss of electrical conductivity.

This remains an affair for ZnO nanocomposites for its controversial overall improvement of average ZT values. The different morphology of the ZnO based thermoelectric material are summarized in **Table 1**. ZnO based thermoelectric properties are summarized in **Table 2** .

Table 1. ZnO based thermoelectric material preparation method and their morphologies.

S.No	Various forms	Method	Structure
1.	Amorphous ZnO Thin Film	PLD (pulsed laser deposition)	Amorphous structure with random hexagonal network
2.	AI-doped ZnO ceramics	Hot pressing Method	Single phase of wurtzite-type

3.	zinc oxide (ZnO)	Chemical co- precipitation	Hexagonal wurtzite structure
4.	Al-doped ZnO (AZO)	Chemical vapor synthesis (CVS)	Hexagonal wurtzite structure and are single phase
5.	Al-Doped Mesoporous ZnO Thin Films	Sol-gel process and an evaporation- induced self-assembly	Hexagonal wurtzite structure
6.	Al-doped ZnO nanoparticles	Forced- hydrolysis method	Single crystal in the wurtzite structure,
7.	Al-Doped Zinc Oxide Nanocomposites	Microwave- stimulated Solvo thermal synthesis	Single-crystal with the wurtzite structure
8.	ZnO-P2O5	Classical quenching technique	Amorphous
9.	Transparent aluminum zinc oxide thin films	Radio frequency (RF) and pulsed Direct Current (DC) magnetron	Hexagonal wurtzite structure of ZnO
10.	Bi Doped Nanostructured Zinc Oxide	Microwave synthesis method	Wurtzite structure
11.	In Doped Nanostructured Zinc Oxide	Microwave synthesis method	Wurtzite structure
12.	ZnO Nanofibers	Electrospinning	wurtzite-lattice structure

Table 2. ZnO based thermoelectric material and thermoelectric properties

Where S – Seebeck Coefficient, σ- Electrical conductivity, K- Thermal conductivity, PF- Power Factor, ZT- Figure of Merit, T-

S.No	Sample	S (μV/K)	σ (Ωm)$^{-1}$	K (Wm^{-1}K^{-1})	PF (Wm^{-1}K^{-2})	ZT	T(K)
1.	Zinc oxide nanofibers	44.6	0.18	-	0.46	-	823
2.	Non-doped amorphous zinc oxide (ZnO) thin film	135	1.01×10^{-4}	-	1.79×10^{-4}	-	RT to 67
3	Nano crystalline Al-doped ZnO	-50	10^5	-	1.0	-	973
4.	Co-Doped ZnO	-	2.68×10^3	3.31	3×10^{-4}	0.04 at 680 K	680
5.	ZnO−P$_2$O$_5$/Ni	-	~1	-	2×10^{-3}	-	407
6.	Aluminum Zinc Oxide (AZO) thin films	98	4×10^4	<1.19	3.9×10^{-4}	>0.1 at RT	near RT
7	Al-doped mesoporous ZnO thin films	−63.58	15.37	-	-	-	383
8	ZnO: Al$_2$O$_3$	120	10^4	5.15	8×10^{-4}	0.17	1173
9	ZnO: Al$_2$O$_3$	88	10^4	2	3.2×10^{-4}	0.085	675
10	ZnO: Al$_2$O$_3$	200	10^{-4}	14	5×10^{-4}	~0.02	373
11	ZnO: Al$_2$O$_3$	37	10^{-4}	28	1.3×10^{-4}	2×10^{-3}	RT
12	ZnO: Al$_2$O$_3$	100	10^4 to 10^5	40.2	8×10^{-3}	6×10^{-3}	RT

Measurement temperature and RT- Room Temperature

5 CONCLUSION AND OUTLOOK

ZnO based thermoelectric materials shows perfect electrical properties in comparison with other n-type oxide materials. Anyway, its highest ZT may need not only Nano structuring, however also other strategies like alloying and band structure engineering. The new Scandium (sc) –doped zinc oxide material is a byproduct of oxide alloying methods which rectifies the problems of high thermal conductivity, low accuracy and declined electrical conductivity by reducing the size as nanostructure for decorous ZnO materials .Nevertheless, the employing Cd is a hazard for its toxicity issues ,.The hazardous appraisal and absolute high temperature long term stability analysis must be observed .Concurrently, substitute of cd for other elements must also be studied in the future.

However, the knowledge attained in the research for ZnO based oxide thermoelectric materials is also suitable to several other oxide or non-oxide systems The continual investigation of new materials as thermoelectric applicants is the solution to improve overall thermoelectric efficiencies

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