

Dimensionality effects in high-performance thermoelectric materials: Computational and experimental progress in energy harvesting applications

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Funding information

Carl Tryggers Stiftelse för Vetenskaplig Forskning, Grant/Award Number: CTS: 18:4; Stiftelsen Olle Engkvist Byggmästare, Grant/Award Number: 198-0390; Swedish Research Council, Grant/Award Numbers: VR-2016-06014, VR-2020-04410

Edited by: Raghavan Sunoj, Associate Editor

Abstract

Thermoelectric (TE) materials can be used in the conversion of heat to electricity and vice versa, which can enhance the efficiency of the fuel, in addition to supplying solid alternative energy in several applications in accumulating waste heat and, as a result, help to find new energy sources. Considering the current environment as well as the energy crisis, the TE modules are a need of the future. The present review focuses on the new strategies and approaches to achieve high-performance TE materials including materials improvement, structures, and geometry improvement and their applications. Controlling the carrier concentration and the band structures of materials is an effective way to optimize the electrical transport properties, while engineered nanostructures and engineering defects can immensely decrease the thermal conductivity and significantly improved the power factor. The present review gives a better understanding of how the theory is affecting the TE field.

This article is categorized under:

Electronic Structure Theory > Density Functional Theory
Structure and Mechanism > Computational Materials Science

KEYWORDS

thermoelectric materials, dimensionality effect, performance improvement approaches, energy harvesting, power generation

1 | INTRODUCTION

Nowadays, there has been continuous development of thermoelectric (TE) technology which serves the growing demand for sustainable energy and various devices. The advantage of TE devices in the direct conversion achieved between thermal and electrical energy without emissions or moving parts gives various applications.^{1–4} At the latest, there have been significant efforts to develop new devices such as portable electronics, the Internet of things (IoTs) and the Internet of Nano Things (IoNTs).^{5–7} In these devices, a rechargeable lithium ion battery (LIB) is commonly used as the main power source. However, the process of LIB requires frequent charge/discharge mechanism, which are inconvenient for intelligent society based on IoT and IoNT. Since the IoT and IoNT are connected to the human body as

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portable devices (wearable),⁶ TE materials can be a best solution to power and, therefore, may replace LIB in IoT and IoNT devices. Especially, TE materials can generate electricity from the temperature difference between the human body and the environment.^{7–10} TE research advanced rapidly in the 1950s when the basic science of TE was well established. During this period, it was found that the compounds Bi_2Te_3 and its alloys had the highest ZT around the unity. Then there was a great improvement in the TE field, so $\text{ZT} \approx 1$ was considered the standard for advanced TEs.^{11,12} The turning point occurred in the early 1990s when Hicks and Dresselhaus^{13,14} said that “quantum mechanics could provide a new route for designing TE materials to the reduced dimensionality.” Later, different groups have made low-dimensional (LD) materials with an unusual high value of ZT.^{15–17} Eminently, the concept of the quantum confinement effect subsequently led to the notable development of TE materials in bulk through reasoned strategies of bands engineering^{12,18–21} and nanostructuring.²² Therefore, there is a new resurgence of TE research still being strengthened.¹²

Although fascinating results have been obtained by both theoretical investigations and experimental analyzes, a complete review of 2D TE materials is still lacking. To advance its development, it is essential to spread light on the developed of research in the same field. This review summarizes the theoretical and experimental progresses in the field of TE materials. Therefore, this work has as objective to accommodate better knowledge and undertake a comprehensive review of the strategies and progress to improve the efficiency of TE conversion and their performance. First, briefly describes the history and basic principles of TE, providing a theoretical basis for improving the TE performance. Next section discusses about the improvement of the TE module. Finally, TE materials combined with TE applications. A conclusion and future perspective of novel TE materials concludes this review.

2 | FUNDAMENTAL THEORY FOR IMPROVING TE PERFORMANCE

In 1821, Seebeck observed that “when two dissimilar metals are gathered which had different temperatures in the connection, an electromotive force was generated in the circuit connection was checked by changing the magnetic field.”²³ Furthermore, Peltier in 1834 stated that “two different metals joined together not only generate electricity from heat, but the reverse process can also happen and when the joints of two-different conductors absorb or reject the heat according to the direction of the current then there is an electric current.”²⁴ Based on the invention of this phenomenon, possibly a TE effect and TE materials develops.^{25,26} The TE module is typically a group of thermocouples made of n-type and p-type materials which are connected together. The representation of thermocouples pair used in TE module which operates as an electric generator and a heat pump²⁶ (see Figure 1a,b).

The charge carriers are transmitted through p-n junctions, and electrons/holes acts as a fluid in the TE module. The dT is known as temperature gradient which is used in TE module produces and the carrier gradient generates electrostatic potential difference (dV). This phenomena is caused by Seebeck effect and the TE parameter Seebeck coefficient (S) is described by dV/dT which provides the main concept of power generation mode. Also, the working mechanism of active refrigeration mode is the reverse process in which the current generates a heat flux at the junction of n- and p-

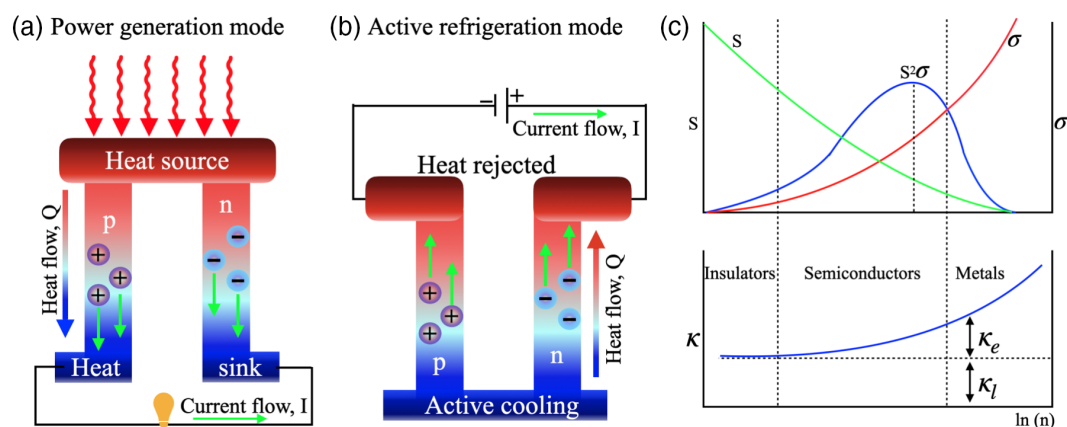


FIGURE 1 Schematic illustration of the TE devices in (a) power generation mode (Peltier effect) and (b) active refrigeration mode (Seebeck effect). (c) Representation of the variation of the S , σ , PF ($S^2\sigma$), κ_e , and κ_l as a function of n , for a material

Source: Adopted from Ref. 27

type materials. The main parameter is figure of merit (ZT) which evaluate the performance of TE materials for TE devices. It should be large S for high ZT value in the materials which is generally found in the semiconductors or insulators but it contains low carrier concentration and it has been seen that the high carrier concentrations as well as high electrical conductivity (σ) in metals. Consequently, the maximum power factor (PF) is possible when the carrier concentrations lies between semiconductors and metals (see Figure 1c).²⁸ In particular, the connections between S and carrier concentration expressed as:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (1)$$

where k_B , e , h , m^* and n represent the Boltzmann constant, elementary charge, Plank's constant, effective mass of charge carrier and carrier concentration, respectively. Furthermore, the relationship between the electrical conductivity (σ) and n are as follows:

$$\sigma = ne\mu. \quad (2)$$

Here, μ represent the mobility of charge carrier. It was seen that the good TE materials for heavily doped semiconductors of n are found to be in the range of 10^{19} to 10^{21} cm^{-3} .²⁸ To confirm that the S is large, only one type of carriers (i.e., p-type or n-type) must be maintained. Apart from this, the thermopower will be less in case of mixed charge carriers (p-type/n-type). Therefore, it is very important to choice of the materials with single type of charge carriers and suitable band gap as well as appropriate doping (i.e., p-type and n-type should be well separated). Thus, strongly doped semiconductors with band gap <1 eV which have both a single carrier type and relatively high carrier mobility shows an efficient TE materials. It is clear from the dependencies of electronic and thermal terms which displayed the ZT value together with S and σ has been key approach to enhance the ZT.

The ZT for TE material is expressed as:

$$ZT = \frac{S^2 \sigma T}{\kappa} = \frac{S^2 \sigma T}{(\kappa_e + \kappa_l)}, \quad (3)$$

where the absolute temperature is represented by T , electronic thermal conductivity is represented by κ_e and lattice thermal conductivity is represented by κ_l . It was seen that from Equation (3), κ_e is inversely proportional to the ZT value. It means that, lower κ_e values for 3D materials, 2D sheet, 1D wire and molecules enhanced the ZT value for TE performance of TE materials. From Equation (3), the efficient TE materials needs to low thermal conductivity (κ) and high σ . The κ is made by two components: κ_l referred as heat transporting atomic vibrations (phonons) traveling via crystal lattice and κ_e which arises from the contribution to heat transfer/carrying by charge carriers, that is, electrons/holes moving via the crystal lattice. The relationship between the σ and κ_e can be represented by Wiedemann–Franz Law:

$$\kappa_e = L\sigma T, \quad (4)$$

where the Lorenz number is represented by L . According to Equation (4), κ_e is directly proportional to the σ and corresponding behavior as shown in Figure 1c. Hereby, the reduction of κ_e is not always the correct selection for TE materials because it directly affect on the σ and has little or no enhancement in ZT value. Additionally, the κ_l are as follows:

$$\kappa_l = \left(\frac{1}{3} \right) C_v \nu_s \lambda_{ph}, \quad (5)$$

where specific heat is represented by C_v , sound velocity is represented by ν_s and phonon mean free path (mfp) represented by λ_{ph} . From Equation (5), the κ_l is independent from electronic structure. According to that, minimizing of the κ_l can be significantly improving the ZT value.

There are two main methods for searching for TE materials with high ZT. (I) The first one is the “phononic glass electron crystal (PGEC)” method should be an ideal TE material with combination of crystal-like electronic properties

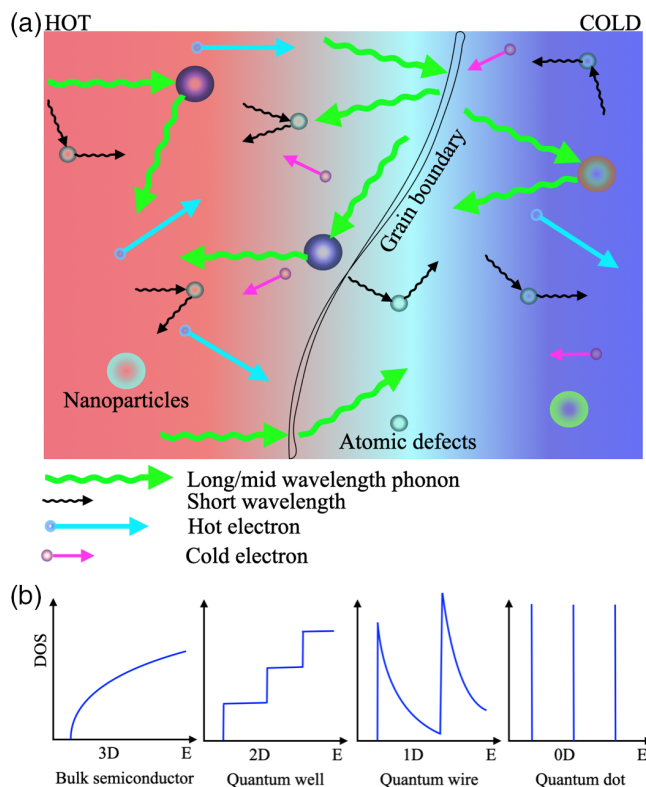


FIGURE 2 (a) Schematic illustration of the mechanisms of phonon scattering and electronic transport of cold and hot electrons inside the TE materials. (b) The significant variations in the electronic DOS with the reductions of dimensionality of the materials for a) 3D crystalline semiconductor, 2D quantum well, 1D nanowire/nanotube, and 0D quantum dot. The nanostructuring materials enhanced the electronic DOS near the Fermi level that may be useful for enhancing the performance of TE materials
Source: Adopted from Ref. 32

and glass-like thermal conductivity.²⁹ This is the best approach to significantly reduce κ via complex crystal structures in which the voids and heavy atoms located in the gaps acts as an effective phonon scattering centers. (II) Other one is nanostructured/nanoscale morphology's of the materials which improve the ZT.^{30–32} Due to the quantum confinement effect in case of nanostructures which enhance the electronic density of states (DOS) near the Fermi level as a results thermopower will increase and providing a way to decouple σ and S .^{30–32} Furthermore, in heavily doped semiconductors, due to the much shorter mfp of electrons than phonons, but in case of nanostructuring deliver a large density of interfaces in which phonons over an extensive mfp range can be effectively scatter more and better than electrons (see Figure 2a) thus κ_l reduced significantly as well as preserving electronic conduction and carrier mobility.³¹ The κ_l characterized the transport of thermal energy via phonons using lattice vibrations. In recent decades, the two main approaches to obtain a low κ_l : (I) strengthen the scattering of phonons by controlling nano-microstructures, and (II) to find materials with vibrational modes of unique lattice leading to intrinsically low κ_l .³³

It has been shown that normal approaches for reducing the κ succeed by suppressing mfp of phonon by controlling microstructures which is followed by,

$$\tau_p^{-1} = \tau_{PD}^{-1} + \tau_{DC}^{-1} + \tau_{DS}^{-1} + \tau_B^{-1} + \tau_U^{-1}, \quad (6)$$

where scattering rate depends on several processes with different frequency (ω) dependence such as, point-defect scattering ($\tau_{PD}^{-1} \sim \omega^4$), dislocation scattering for cores ($\tau_{DC}^{-1} \sim \omega^3$), dislocation scattering for strains ($\tau_{DS}^{-1} \sim \omega$), boundary scattering ($\tau_B^{-1} \sim \omega^0$) and phonon–phonon Umklapp scattering ($\tau_U^{-1} \sim \omega^2$) in which distributions of frequency of phonons varies with temperature.³³

3 | DIMENSIONALITY STRATEGY FOR TE PROPERTIES

For TE properties, there are various parameters affects the any materials in which dimensionality also plays a significant role in enhancing TE properties in many ways. Bulk materials have also given good TE performance through band engineering but in comparison LD material are found to be better candidate for TE applications. The TE parameters

such as σ , S , and κ for conventional 3D materials are dependent that why TE parameters cannot be control independently in order to ZT can be increased. As the S is directly proportional to the effective mass, that is, $S \propto m^*$ therefore an increase in m^* increases S and large effective mass decreases the σ value using $\sigma = ne\mu$ relationship, and a decrease in σ value result in a decrease in the electronic contribution to κ using Equation (4).^{32,34,35} Although, when the dimensionality of the material is reduced, then the new variable length scale can be used for controlling the properties of the materials. As the size of the system decreases around nanometer, then the electronic density of states change significantly (see Figure 2b) which allows the new possibilities to vary σ , S , and κ quasi-independently as the length scale is enough small to provide the effects of quantum confinement as the number of atoms in particular direction (i.e., x-, y-, z-directions) becomes small (e.g., $<10^2$).³² Additionally, when the dimensionality reduces of the materials from 3D to 2D to 1D and in last 0D, then new physical phenomena are entered and these phenomena can also create further chances for varying TE parameters S , σ and κ independently. Additionally, phonons scatter more effectively than electrons or used to filter low energy electrons at the interfacial energy barriers with the introduction of several interfaces which allows the development of LD materials with improved ZT value suitable for TE applications.³² These theoretical strategies/concepts were first tested on 2D quantum well system by experimentally^{36,37} after that on 1D quantum wire systems.^{38,39} Apart from this, energy filtering,^{40,41} carrier-pocket engineering^{37,42,43} and semimetal-semiconductor transition⁴⁴ these approaches further enhance the TE performance of nanostructured materials. Further to enhance the performance the TE materials, we have discussed details approaches such as enhancement of PF ($S^2\sigma$) and individual S , σ terms and reduction of κ .

3.1 | Approaches to enhance the PF ($S^2\sigma$)

There are several strategies to improve the PF quantity of materials for thermoelectricity. The PF can be maximizing through band engineering which include the optimization of present materials via exploration of nanoscale materials as well as doping in the materials.⁴⁵ The phenomena of quantum confinement can be used to improving S and also, we can control independently both TE quantity S and σ . In the recent developments, there are several strategies for modulating the electronic structures which shows the important role in the modern TE materials. The S and σ can be maximized by band engineering such as degeneration of multiple valleys has been used to modify the electronic band structure,¹⁹ states of electronic resonance,¹⁸ filtering of electron energy barrier,^{46,47} band gap tuning, effective mass optimization, anisotropic band mass engineering, layered structure, band flattening, band convergence, structural distortions, synergistic nanostructuring,⁴⁸ isoelectronic doping of highly mismatched,⁴⁹ modulation doping⁵⁰ and LD materials.⁵¹ Here, we have discussed in detail some of the approaches.

3.1.1 | Degeneration of multiple valleys bands

It was seen that the σ and the PF is improved from the convergence of several “valleys degenerate” within the band structure of PbTe material.⁵² The entropy per charge can pass via the materials increases when the number of valleys degeneracy increasing as a results it delivers higher S and σ . The presence of multiple bands is the good strategies to enhance the TE materials in bulk.⁵³

3.1.2 | Electronic resonance states

If dopant in the host materials can create new energy levels (resonant levels) which distort the electronic DOS near to the Fermi level and these levels are responsible for improving the thermopower. Because the resonant levels increase the effective mass of the carriers without affecting the carrier concentration as a results in an improvement of thermopower.^{21,45}

3.1.3 | Effective mass optimization

It was seen that the most TE performance materials are semiconductor and carrier concentration of heavily doped depends on temperature. While the optimal carrier concentration n_{opt} is depends on the temperature range as

$n_{opt} \sim (m^* T)^{3/2}$.⁵¹ Therefore, n_{opt} also be achieved by adjusting m^* . From Equation (1), the S is directly proportional to the m^* therefore we can enhance the TE performance of the materials.

3.1.4 | LD materials

At this time, the TE power of bulk materials is one of the fundamental interrupt which conflicting the relationship between σ , S and κ , therefore it is very complicated to enhance the performance of TE materials. Due to that, researchers try to control the TE parameters interdependently with the reduction of the dimensionality of the materials. Due to the quantum confinement effect of the system size reduces up to nanometer length then it is possible to quasi-independent control of σ , S and κ . When the dimensionality of the materials decreasing from 3D to 2D to 1D to 0D has displayed to significantly change the electronic properties and the electronic DOS near the Fermi level increased due to that S enhances significantly (see Figure 2b).⁵¹

3.2 | Methods to reduce the κ_l

There are several aspects to cover recent computational strategies to reduce the κ_l when we are reducing the dimensions of the materials then due to the presence of several interfaces for phonons scatters more influentially than electrons and the specially scatters phonons strongly which influences the κ .

1. Creating structural disorders: It was seen that the bonding nature between host atoms and guest atoms displayed weak which is the general reason to reduce the κ of the materials. The specific mechanism is still under debate for low κ . The first plausible mechanism is the resonant phonon dispersion appears via guest atoms which are weakly bound with the host atoms surrounding vibrations uncorrelated to the frequency ω_0 .^{54,55} Under the assumption of a constant group velocity, the relaxation time around ω_0 concludes a strong decrease in explaining the low κ .⁵⁶
2. Complex crystal structure: It is a good approach to obtain the thermal transport properties of the materials. The materials with zintl compounds are an eminent representation⁵⁷ such as Sr_3GaSb_3 , $\text{Ca}_5\text{M}_2\text{Sb}_6$ ($\text{M} = \text{Al, Ga, I}$), $\text{Al}_4\text{MgSb}_{11}$ ($\text{A} = \text{Ca, Yb}$), SrZnSb_2 , SrZnBi_2 , and so forth which exhibit exceptionally low κ_l , and a high TE performance. Generally, the zintl compounds belong to intermetallic compounds in which has different electronegativity of containing elements.⁵⁸ The electrostatic forces are formed between cations and anions while covalent bonds are formed between anions to maintain the charge naturality.⁵⁹ Such binding characteristic mixing results in a complex crystalline structure which makes a large number of atoms present in a primitive unit cell.⁵⁹ According to the Umklapp scattering's limit is given by Toberer et al. displayed the extremely low κ_l in zintl compounds when a large number of atoms presents in per unit cell.⁵⁶
3. LD materials: When the dimension of materials changes from 3D (conventional bulk materials) to 2D (thin films), 1D (nanowires) or 0D (quantum dots), the density of the electron energy state (DOS) could become noticeably different as shown in Figure 2b. In case of LD system, phonon transmission would be accompanied by dimensional confinement and diverse interface scattering/reflection, hierarchically blocking phonons at different frequencies and achieving more effective suppression of κ_l , as clearly presented in Figure 2a. Furthermore, the microstructure could also intentionally control the behavior of the carrier and κ_e , so that the total k can be reduced significantly.^{32,56,60}

3.3 | Designing the structure/geometry for TE module

It was seen that the formation of high performance TE module not only depends on the optimal length of TE module and materials but also depends on the geometric structure.²⁶ For that reason, except improved TE materials enhance the TE performance while TE performance also improved by improving the better arrangements of geometry/structure in the TE components^{26,61,62} depends on thermoelement length,⁶³ and number of thermocouples.⁶⁴ According to slenderness ratio, the relationship between cross-sectional area and thermocouple length is defined as $(X = (A_p L_n)/(A_n L_p))$ ^{65,66} and the thermoelement is defined with an area of special section.^{26,67,68}

4 | RESEARCH PROGRESS ON TE MATERIALS

Last few years, significant efforts have been made to enhance the TE performance of TE materials and have witnessed the rapid progress of TE research. It has been reported that the new approaches and examples are reported here for preferable materials and superior TE performance. Nowadays, researchers mainly focused on novel LD TE materials. Additionally, the physical/chemical properties of classical materials have been significantly enhanced as well as improvement of the properties of classical TE materials (such as chemical doping, vacancy creation, alloying, insertion of foreign species and nanostructuring), organic TE materials⁶⁹ and enhancing ZT values for high performance novel TE module shapes of TE materials using nanotechnology,⁷⁰ structure/geometry optimization of thermocouples.⁶¹

Nowadays, with the continuous development of engineering nanostructures, researchers are becoming more interested again in TE applications, which make researchers devote to exhibit nanostructured materials efficient as nano-system alloy, superlattices, nanowires and quantum dots. Figure 3 displayed some of TE materials acquired in recent years and enhanced TE properties with the reduction of dimension of the materials from 3D to 2D to 1D to 0D. In this section, we will discuss mainly focus on some methods that can significantly enhance the materials performance as the alloying/doping superlattices, and other nanostructures.²⁶

4.1 | TE materials for TE devices

The TE module has significantly influenced on their performance of materials used. Many researchers have worked hard to enhance the performance of the TE material and have made some significant progress to enhance its properties in recent years. They have enhanced the performance of many TE materials and have developed new materials (See Table 1). These materials range from semiconductors to ceramics,^{3,83–85} bulk to superlattices^{86,87} and nanoparticles to nanowires.^{19,83,84,86–92} Here, briefly mention advances in bulk materials and highlight advances in nanostructured TE materials.

4.1.1 | Bulk materials—alloying/doping approach for enhancing ZT

The key factor for designing superior-performance TE materials is to enhance the powerful relationship of σ , κ and S with n as shown in Equation (1). Generally, the S is directly related to the band gap, n and m^* of charge carrier's (i.e., flatness of the electronic band lines near the Fermi level). Also, from Equation (1), the S will vary linearly with the absolute temperature. Consequently, it was seen that the n is the key factor to set the peak temperature and maximum PF ($S^2\sigma$).²⁶

Change in the electronic band structures by the proper doping can enhance the carrier concentration of semiconducting materials. Thus, as we continue to grow the appropriate dopant atoms also increase the number of states at each level. States near the Fermi energy level can promote the transport of electron. According to the band theory, the

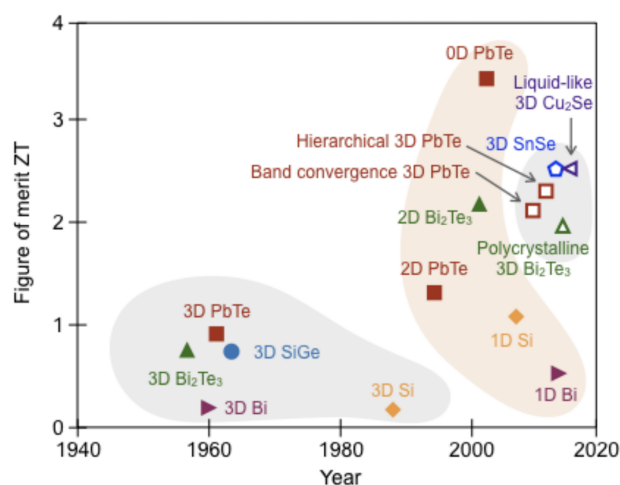


FIGURE 3 Recent developments of TE performance with the reducing the dimension of TE materials from 1940 till present
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TABLE 1 The status of current improvement in thermoelectric performance of thermoelectric materials in bulk and nanostructure in last few years

Materials	Carrier type	ZT	T (K)	References
<i>Bulk materials</i>				
Yb _{0.19} Co ₄ Sb ₁₂	n	1	600	71
In _{0.25} Co ₄ Sb ₁₂	n	1.2	575	72
CoSb _{2.75} Sn _{0.05} Te _{0.2}	n	1.1	823	73
Ba _{0.14} In _{0.23} Co ₄ Sb _{11.84}	n	1.34	850	74
Yb _{0.2} Co ₄ Sb _{12.3}	n	1.26	800	75
Na _{0.48} Co ₄ Sb ₁₂	n	1.25	850	76
Ba _{0.08} La _{0.05} Yb _{0.04} Co ₄ Sb ₁₂	n	1.7	850	77
<i>2D materials (quantum well and superlattices)</i>				
PbTe/Pb _{1-x} Eu _x Te	–	2	300	36
PbSeTe/PbTe	n	2	300	16
Bi ₂ Te ₃ /Sb ₂ Te ₃	p	2.4	300	15
Bi ₂ Te ₃ /Bi ₂ Te _{2.83} Se _{0.17}	n	1.4	300	15
<i>D materials (Nanowires)</i>				
Si	–	0.6	300	78
Si	p	1	200	79
<i>Nanocomposites materials</i>				
BiSbTe	p	1.4	373	22
(BiSb) ₂ Te ₃	p	1.5	390	80
Bi _{0.4} Sb _{1.6} Te ₃	p	1.8	316	81
AgPb ₁₈ SbTe ₂₀	n	2.2	800	82

valence band is made by the highest occupied energy levels of atomic lattice while the conduction band formed by lowest unoccupied electronic levels. It was seen that the band gap between the band lines is small enough to cause the electrons move from the valence band to conduction band under excitation then the conductivity occurs in the semiconductor.²⁶ As a result, the defect/doping in the semiconducting materials can introduce an additional energy levels between the valence and conduction band thus increasing the conductivity.^{4,26} It can be seen that the S and σ depends on n in which S decreases with increasing n and σ increases with increasing n (see Figure 1c). At certain values of n , the PF reaches maximum values. As a consequence, to enhance σ values by doping/defect is a powerful method to significantly enhance the performance of TE materials.

To improve the TE figure of merit ZT, the chemical doping is extensively used to modify the n .^{93–95} It was seen that the SnSe, Sn, Ag, and Cu generally behaves like p-type dopant^{53,96} while BiCl₃ act as n-type.⁹⁷ In the last 20 years, there has been tremendous advances in exploring TE materials^{62,98,99} and laboratory constantly records high values of ZT, for examples Bi₂Te₃-based compounds,^{100–102} hole doped crystals¹⁰³ and lead chalcogenides.¹⁰⁴ Additionally, it was found that the alloying,^{105–108} doping¹⁰⁹ and modulation of microstructuring^{110,111} in which polycrystalline samples displayed relatively higher ZT values ~ 1.05 is obtained at 873 K. According to Wei et al.,¹¹² reported that the doping of Li, K and Na on polycrystalline SnSe enhanced the TE performance and corresponding figure of merit ZT are found to be ~ 0.85 at 800 K. From these investigations, it was seen that the dopants enhanced the conductivity and carrier concentration of SnSe materials. The TE performance of doped SnSe samples with alkali ion was enhanced by 30% as compare to pristine SnSe samples. Another investigation found that the better TE properties by 3% Na doped in SnSe samples¹¹³ and corresponding TE performance ZT values was more than 2 at 800 K. Tan et al.¹¹⁴ reported that the p-type SnSe with the codoping of In/Cd displayed significantly enhanced TE properties. In this case, the values of ZT reached 1.4 at 923 K. According to Yang et al.,¹¹⁵ n-type PbTe-based materials shows excellent TE materials by doping of Bi in PbTe nanotubes and maximum values of ZT reached 1.35 at 675 K in case of Pb_{0.99}Bi_{0.01}Te samples. Wu et al.¹¹⁶ studied the excellent TE performance by K-doped PbTe_{0.7}S_{0.3} system which shows the ZT values of 2.2 at 923 K and it has first

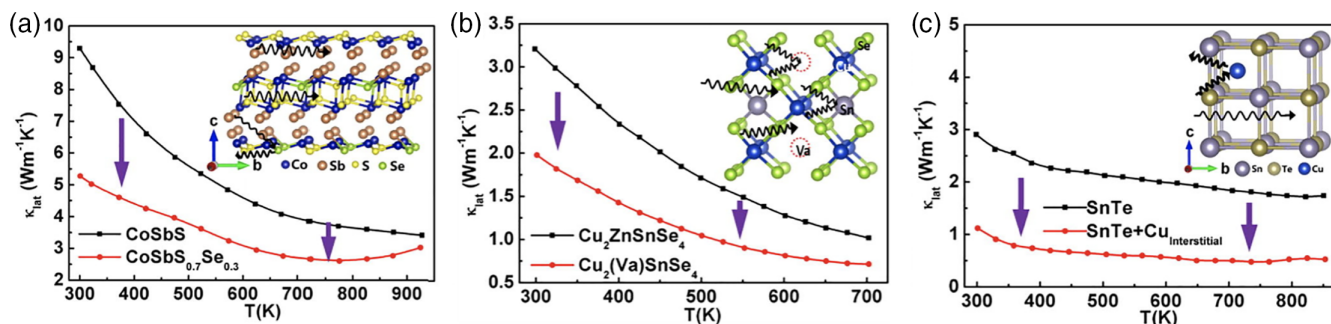


FIGURE 4 The significant changes in the κ_l and inserted crystal structure displayed the various types of structural defects such as (a) solid solutions, (b) vacancies, and (c) interstitials

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examples of widest created platform with ZT values larger than 2. And also, the 2.5% K-doped $\text{PbTe}_{0.7}\text{S}_{0.3}$ system has average values of ZT is 1.56. Zhao et al.¹⁰³ reported that the hole-doped single-crystal SnSe and acquired the high ZT_{dev} of 1.34. Apart from that, another group found that the $\text{Ge}_{0.92}\text{Cr}_{0.03}\text{Bi}_{0.05}\text{Te}$ by decreasing the formation energy of Ge vacancies by replacing Ge with Cr displayed the maximum ZT values of 2 at 600 K.¹¹⁷ Yu et al.,¹¹⁸ β -phase of copper selenide (Cu_2Se) made by ball milling and hot pressing displayed interesting TE material as compare to other conventional materials which shows the figure of merit of ~ 1.6 at 973 K. Recent study states that figure of merit ZT can be adapted by engineering defects in CoO.¹¹⁹ The spin-orbital states degenerate atomic vacancies neighboring sites make the spin-orbital degeneracy improve the thermopower in CoO. At certain percentage of vacancy (16.6%), the TE figure of merit is found to be 1.92 which is significantly larger than the pure CoO crystal (1.53). According to Zhao et al.,⁴ with the increasing improvement in TE performance, also accompanied by various defects in materials such as point defects, linear defects, the planar defects and volume defects are induced in TE materials to optimize the TE performance.

Among several mechanisms for phonon dispersion, the dispersion of point defects is the most powerful method for reducing κ_l for TE materials. Figure 4 displayed the structural defects significantly reduced the κ_l at room temperature as compared to pure form³³ which may be very beneficial for improving TE performance. It was seen that the CoSbS compound have relatively high κ due to the stiff chemical bonds between atoms. By forming solid solution with Se atom, the κ_l reduces significantly from $8.2 \text{ Wm}^{-1}\text{K}^{-1}$ to $4.7 \text{ Wm}^{-1}\text{K}^{-1}$ for CoSbS and $\text{CoSbS}_{0.7}\text{Se}_{0.3}$ near the room temperature presented in Figure 4a. The huge difference in the κ_l is appears due to the atomic mass and radius of Se and S atoms which can be described through the theory of strain and mass fluctuation.³³ Moreover, the vacancies and interstitial are also point-defects which are expected to effectually disperse phonons maximized due to fluctuations of strain and mass. The vacancies may occur in solids naturally or artificially. In case of $\text{Cu}_2\text{ZnSnSe}_4$, the κ_l is found to be $\sim 3.25 \text{ Wm}^{-1}\text{K}^{-1}$ while with the cation vacancy its values significantly reduce up to $\sim 2 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature. Consequently, gradually decreasing with the increased vacancy concentration of intrinsic cations also in the presence of vacancies the effectively scatter phonons in the crystal structure.¹²⁰ In addition, interstitial atoms also scattered phonon and has been proven successful in suppressing κ_l . When we are taking Cu atom as an interstitial site in the SnTe system then the κ_l suppresses as low as $\sim 1 \text{ Wm}^{-1}\text{K}^{-1}$ from $\sim 3 \text{ Wm}^{-1}\text{K}^{-1}$ in SnTe as shown in Figure 4c. Furthermore, the microstructure engineering significantly reduces the κ_l and improves the TE figure of merit¹²¹ of the TE materials.

4.1.2 | Superlattices

The κ is a vital parameter for enhancing the TE properties because κ is inversely proportional to the TE figure of merit. From this point of view, reducing κ can improve the TE performance of the materials. In the above section, it has been discussed that the alloying/doping in the materials is an effective approach to increasing the S by increasing the electronic DOS. It is observed that to achieve higher ZT value is to increase the σ without increasing κ . It was seen that the 90% of the κ normally comes from κ_l in the semiconducting materials. From this point of view, the reduction of κ_l is an important quantity to significantly enhance the TE performance of TE materials.¹²² The κ_l is mainly produced from the vibrations of lattice, that is, phonons and it is depending on the crystal structures and lattice parameters of the

materials.¹²³ Meanwhile, the drawback of the heavy doping required is that the values of S corresponding to the minimum values of conductivity in order to achieve optimal transport/TE properties.¹²⁴

Superlattice includes periodic layers of two or more materials having a thickness of ~ 1 nm. Where an alternate layers of different materials can inhibit transmission of phonons via scattering by the scattering of the internal interface and electronic properties can remain substantially inefficient as long as the periodicity of the superlattice are correctly set so that the κ value in the superlattice is reduced considerably led to many theoretical studies in this field.²⁶ In the field of nanostructured materials, the first demonstration was for a 2D superlattice consisting of PbTe quantum walls and $Pb_{1-x}Eu_xTe$ barriers which significantly enhance the TE performance.³⁶ Initially, n-type PbTe³⁶ was demonstrated after that its p-type with quantum well¹²⁵ and below 4 nm width that increased S^2n (n is the carrier density) as compare to bulk PbTe. After that several studied demonstrated that the significant enhancement in ZT with the introduction of nanostructuring materials. Yang et al.¹²⁶ reported that the κ of nanostructures is significantly lower than that of the bulk materials. The influence of superlattice structure in the κ_l has been assigned to various effects, such as localization of phonons and modifying the phonon spectrum, diffuse scattering or specular interfaces phonon mismatch due to acoustic phonons and scattering defects.¹²⁷ The considered approaches have been investigated via various superlattice in which the composition of the materials starts with good TE properties for examples Bi_2Te_3/Sb_3Te_3 ,^{15,128} PbTe/PbSe,^{16,128} PbTe/Te,¹²⁹ Ge/SiGe,¹³⁰ Si/Ge,^{131,132} Bi/Sb¹³³ and inorganic/organic.¹³⁴ These superlattices remarkably reduces the κ of the materials and enhanced the ZT values.¹³⁵

First time, idea of superlattice was given by Venkatasubramanian¹³⁶ to improve the value of ZT by reducing the κ_l . Further this approaches continuously explored by other researchers. In case of p-type Bi_2Te_3/Sb_3Te_3 superlattice by controlling the phonons transmission and electrons in superlattices and corresponding high ZT obtained 2.4 by Venkatasubramanian et al.¹⁵ Further many experimental researchers have been investigated that the κ of several superlattice is considerably decreased.¹³⁷ This approach leads to a great enhancement in ZT of the TE of superlattices. Another work reported that the superlattice structures PbTe/PeSe_{0.98}Te_{0.02} on the BaF₂ surface shows improved TE performance and corresponding ZT values reached ~ 1.6 at 300 K and ~ 3.5 at 570 K.^{16,17,133} Park et al.¹³⁸ prepared p-type of superlattice structure $Bi_2Te_3/Bi_{0.5}Sb_{1.5}Te_3$ displayed impressive TE ZT values of 1.44 at 400 K which is 43% higher than the original structure. Priyadarshi et al.¹³⁹ analyzed various designs of superlattices and concluded that a Gaussian distribution with superlattices thick barrier provides very high ZT values. In such cases where it has been found that the thermal conductivity of the lattice is much lower than the limit of the alloy and sometimes close to the values of the amorphous phases, the high ZT value ($ZT = 6$) can be obtained. The drawback of superlattices is complexity of synthesis, due to the temperature difference of the materials cannot be supported and the cost is high. It is observed that some of the superlattices may not be attractive for conventional TE applications. Due to unfavorable properties such as high κ can be tailored by introducing the 2D nanofeatures across the atomic-thick materials such as 2D monolayer, 1D nanoribbons or periodic nanopores and 0D quantum dots. The below section covering the major advancement for enhancing the performance of TE materials for TE applications.

4.1.3 | Nanostructures

The TE performance of superlattices is a 2D nanomaterials which is discussed in the above section. With the reduction of the grain size to nanoscale then the TE materials performance can be enhanced, it maintained the electrical performance with the phonon scattering can be increased and corresponding κ_l can be reduced.¹⁴⁰ But due to the cost limitations and heat transfer, it is very difficult to make TE devices for large energy conversion applications. Furthermore, application of high temperatures is also limited. For that reason, the development of new nano approaches to enhance the performance of TE materials is necessary.^{7,141,142}

Hicks et al.¹⁴ reported in 1992, displayed the LD structures modify the properties of materials. In theory, they showed that using 2D, 1D or even 0D structures can significantly enhances the electronic properties. Furthermore, other researchers^{32,136,143} displayed that the nanostructures could significantly reduce the κ_l . Later in 1993, Hicks and Dresselhaus¹⁴ used the nanostructure concept as an enhancement tool to improve material properties. Moreover, nanostructured materials such as 2D TE nanomaterials (i.e., quantum wells),¹³³ 1D TE nanomaterials (i.e., nanowires/nanotubes/nanoribbons/nanomeses)^{79,144–146} have been used in the manufacture of new TE devices.¹⁴⁷ This reveals that enhanced TE ZT can be acquired in the form of nanostructures. Above all, the nanostructuring can enhance the electronic DOS near the Fermi level via quantum confinement thus a way to decouple conductivity and thermoelectricity.^{148–150} This can lead to a ZT value in some nanostructures over and above three.¹⁵¹

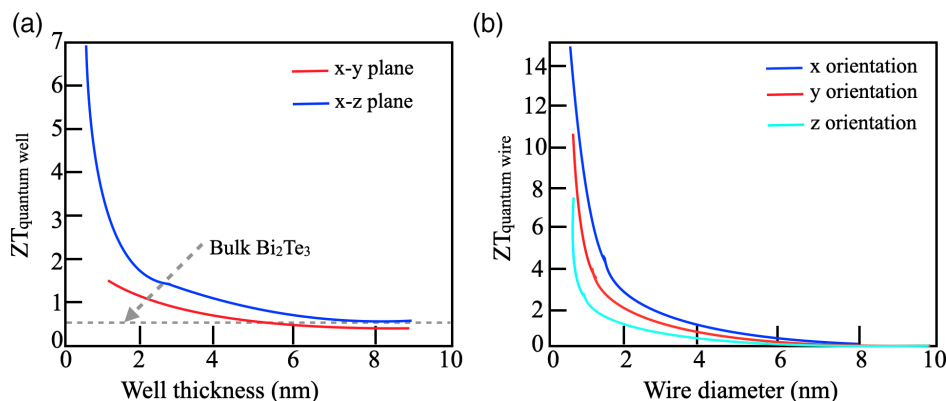


FIGURE 5 The change in ZT values of (a) 2D, that is, quantum well depends on layer thickness (nm), (b) 1D, that is, quantum wire depend on diameter (nm)

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A very interesting result was found by Biswas et al.¹⁵² in which they observed the maximum reduction of κ_l by adjusting the mesoscale arrangement of nanostructured TE materials. A nanostructure demonstrates a maximum value of ZT of ~ 2.2 at 915 K. Tan et al.⁸⁸ synthesized the n-type $\text{Bi}_2(\text{Te,Se})_3$ compound in the form of nanowire arrangement using simple thermal co-evaporation method. The value of TE ZT of nanowire with n-type $\text{Bi}_2(\text{Te,Se})_3$ system was found to be 1.01 at 300 K.⁸⁸ Moreover, another work displayed that the natural electronic properties of graphene band can be fully preserved and TE properties of it can be significantly enhanced. The ZT values can be improved from 0.26 to 2.5 at 300 K but enhancement of this TE performance is found a very expansive nanomaterial growth method.¹⁴⁹ Such type of very expansive TE materials is not useful in commercial area. The TE materials should be inexpensive for practical applications. From this point of view, the TE materials of nanostructured composite provide the possibility to resolve this problem. TE materials doped with impurities refers as a nanocomposite TE material.⁸⁴ As compared to the quantum well, the quantum wire can enhance the DOS. It was seen that the nanowires may have good TE performance than superlattice.⁹⁵ Figure 5 represents that the reduction of wall thickness and wire diameter less than 10 nm significantly enhanced the TE performance of TE materials.^{13,14} The values of ZT of TE materials may be greater than 7 in quantum well and more than 10 in quantum wire. Additionally, PbS-Ag nanocomposites (semiconductor with metal nanocrystals) form ohmic contact with bulk semiconductors and it enhances the TE properties with enhanced ZT values up to 1.7 at 850 K.¹⁵³

Moreover, there are some theoretical investigations displayed that the peak n-type value of ZT increases by a factor of 6–8 over the bulk value for transition metal dichalcogenides (TMDs) materials. All these four TMDs materials with different thicknesses of the structures, bilayer MoSe_2 gives the maximum n-type ZT value of 2.4. The ZT values is increased by 5–12 in case of p-type as compared to the bulk materials¹⁵⁴ (see Figure 6a–d). Huang et al.¹⁵⁵ investigated the bulk and monolayer material of n-type Mg_3Sb_2 which is also shows the high performance of TE materials when it is reducing at monolayer. Apart from this, doping in polycrystalline Mg_3Sb_2 materials enhancing the TE ZT values (see Figure 6e).

Harman et al. reported that the quantum dot superlattice (QDSL) of $\text{PbTe}/\text{PbSe}_{0.98}\text{Te}_{0.02}$ on the substrate of BaF_2 . It is observed that QDSL system have the ZT value of ~ 1.6 at room temperature while the Bi doping on it enhanced the value from ~ 1.6 at room temperature to 3.5 at ~ 570 K for n-type of the material. Also, Na doping has high ZT value for p-type doping.^{16,17,133} The significantly enhanced TE performance of QDSL can be controlled by independent quantity, σ , S and κ which can simultaneously enhance by increases PF (σS^2) and decrease κ values. Apart from this, Bi quantum wires and $\text{Bi}_{1-x}\text{Sb}_x$ alloys also displayed promising TE performance.³² Some other investigations also suggest that the LD materials improved the TE performance.^{108,156–166} The lists of novel LD TE materials for high TE performance are summarized in Table 2. From these results, the nanostructures significantly improved the performance of TE materials.

5 | APPLICATIONS AND DEVICES OF TE MATERIALS

TE devices have been implemented long as they can get solid state power generation or cooling without noise or vibration, showing several advantages in the form of high sensitivity for temperature changes and operation emissions.

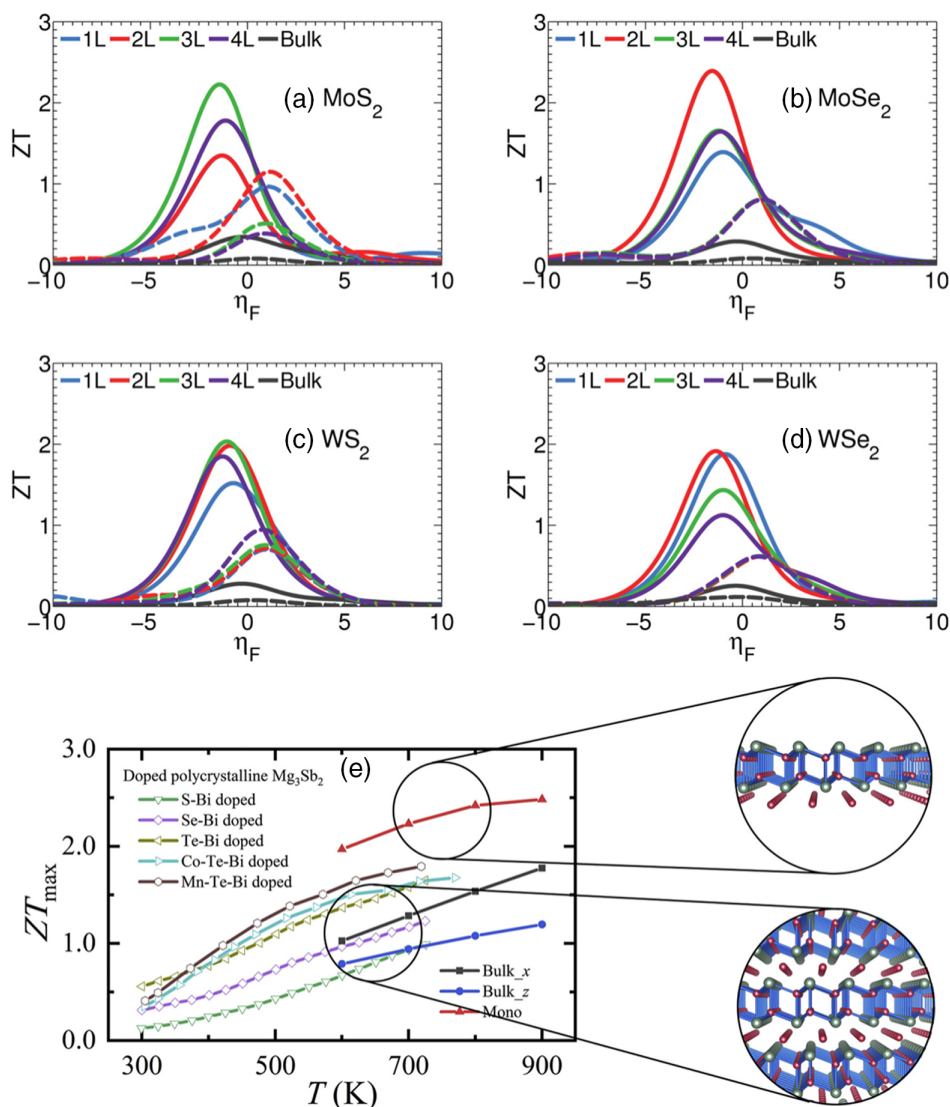


FIGURE 6 The variation of ZT at room temperature for (a) MoS_2 , (b) MoSe_2 , (c) WS_2 , and (d) WSe_2 for bulk and its monolayer structures. The dotted line and solid line represent the p-type and n-type as a function of the reduced Fermi energy η_F . Reproduced from Ref. 154. Copyright 2014, American Institute of Physics. (e) The TE ZT values of n-type Mg_3Sb_2 of bulk and its monolayer form as a function of temperature and also including the certain defect inside the polycrystalline Mg_3Sb_2 materials. Reproduced from Ref. 155. Copyright 2019, Elsevier

These characteristics become enormous benefits such as TE materials are used in several fields as the TE generators radioisotopes, temperature sensors, automotive, condensation, control devices, aerospace, industrial utilities, medical services, transportation tools, electronic and implantable/wearable devices. So far, significant improvement has been made in progressing high-performance TE devices, in which some of the applications presented in details.

5.1 | TE nanogenerator applications

Depending on the style of the application, parasitic application and host application are the main categories. In case of host applications, the total amount of heat sources is used for energy conversion while the heat is partially converted into electricity without influencing main functions. For these applications, the heat sources are available with a wide range of temperatures because low quality waste heat at 325–350 K, residual heat to high quality 850–1100 K has been used.¹⁰⁸

TABLE 2 The recent theoretically reported high-performance of LD TE materials

Materials	ZT	T (K)	References
<i>2D monolayer</i>			
GeAsSe and SnSbTe	~4 and 6	300	167
RbAgSe and RbAgTe	2.2 and 4.1	700	168
As ₂ S ₃	2.75	300	156
NiCl ₃	0.44	300	169
SnP ₃	2.01	700	170
<i>Nanoribbons</i>			
GNR	2–6	300	149,171–174
Graphane	~2	300	175
Silicene	~2.5	300	176
MoS ₂	2.7	300	177
WSe ₂	2.2	300	178
Phosphorene	6.4	300	179
Si, Ge and hybrid	2.5	300	180
Graphene/h-BN hybrid	0.8	300	181
MoS ₂ /WS ₂	5.5	600	182
TMDC hybrid	2–3 (7.4)	300 (800)	183
<i>Porous 2D materials</i>			
GAL	~1	300	184
HG	1.13	300	163
Silicene	3.5	300	185

Abbreviations: GAL, graphene antidot lattices; GNR, graphene nanoribbon; HG, Holey graphene; TMDC, transition metal dichalcogenides.

5.2 | Heat engine applications

In case of conventional cooling system, it has four main parts named as condenser, evaporator, compression and expansion value. In which evaporator part is used to expand and evaporates of pressurized refrigerant. During this change of state, the energy is absorbed. The compressor work as a coolant pump. The condenser destroys the heat absorbed in the evaporation as well as the heat generated during compression in the atmosphere. For TE cooler based on the same basic laws of thermodynamics that conventional heat pumps which are solid state with no moving parts, and without using gases or fluids. Their structure is compact, simple along with operation that is quiet and maintenance free. The TE energy conversion for heating and cooling applications is known as “Peltier effect” in which the temperature difference is created across the two different legs of semiconducting materials by giving an electric current via legs (see Figure 1a). The electrons absorb heat at cold junction as they supply via low to high energy level in the p-type semiconductor to the n-type semiconductor. The power supply energy to move the electrons via system. An energy is expelled to heat sink when electrons move from high to lower energy level of an element.^{107,108}

5.3 | Temperature sensing and control

Temperature based sensors on the simple “Seebeck effect”^{186,187} and thermocouples^{188–190} consist of traditional metal, bulk semiconductor and thin film¹⁸⁶ has been extensively used which is characterized as a voltage difference produced by temperature difference in an electrical circuit of two different electrical conductors. Measured and change temperature can be examined by finding the output voltage given for thermocouples. Recent years, thin film and bulk semiconductor thermocouples are widely investigated and applied in many advanced fields because of lack of vibration, energy efficiency, temperature range that has wide applications and high sensitivity value.^{107,187,190–197} So far, the cooling

devices TE^{107,198} have been examined and used in systems microclimate cooling that have been developed for military missions, medical devices, refrigerators powered by solar cells, interior air coolers and temperature controllers for microelectronic devices.¹⁰⁷

5.4 | TE materials requirements for IoTs applications

To achieve high performance for IoTs technologies, integrated TEG must be optimized in various levels. The material should have a high ZT and a low κ to increase the temperature gradient ($\Delta T = T_{hot} - T_{cold}$) through the TEG.¹⁹⁹ This requirement is primarily due to the thermal resistance of the skin and the limitations for using a large heat diffuser in a wearable electronic device.⁹ To use TEG in a wearable electronic device, the material with a high S is required.²⁰⁰ It was reported that the bismuth-telluride-based alloys are the most favorable candidates among the known TE materials for room-temperature applications. They have been widely developed in recent decades. Till date several researchers reported the room temperature S , κ , and ZT on p-type $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ ^{22,201} and n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ alloys.^{202–204} But some of these alloys have ZT > 1 which are more appropriate for IoTs applications. Nanostructured materials as compared to commercial alloys,^{22,203} primarily displayed a smaller value of κ and a higher ZT value.^{22,201–204} Thus, nanostructured alloys $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ and $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ are the most favorable candidate for applications for heat harvesting in body. It was seen that the semiconductor microfabrication techniques is used for manufacturing of micro TE nano-generators which is very useful for IoTs applications.^{205,206} Continuously developments obtained in IoTs with various devices will be involved such as wireless sensor networks (WSN) are used for controlling processes, medical treatment, security and surveillance.

6 | SUMMARY AND FUTURE PERSPECTIVES

In the present review, the effect of dimensionality on TE materials is discussed. Also, we have discussed recent developments in various strategies for modulation of electronic structures and vital role in modern TE materials. From these discussions, it is clear that the extrinsic doping/alloying plays a key role in achieving the modulations of the electronic structure. The two strategies for modulation of the electronic structure, that is, the convergence of the valence band and the resonance level, are being implemented in a broader category of materials. With the reducing of dimensionality of the materials, the significant variation in the electronic DOS due to the quantum confinement effect has been discussed. Additionally, the confinement effect and phonon scattering interface on reducing the κ_l are also included. Especially, researchers more focus on layered and LD materials which can be used to improve the TE performance. This review focuses thoroughly on the methods used to enhance the TE properties, improvement in the performance of TE materials and their applications in various fields.

The summaries of the present review collectively are as follows: (I) The performance of TE devices is examined by their material performance and thermal structure design which is related to the Z and temperature T. To solve this problem, we need to achieve high performance TE materials and flexible TE modules design and optimization. (II) Although we have obtained a high ZT TE materials in some LD systems. The highest ZT TE materials ever found at 300 K is higher than 2.4 in laboratory but a lot of them are not feasible for commercial use in large-scale today because of its complex processes and expensive materials. Therefore, developing novel ways of TE modules on demand or a flexible TE module is the need to solve this problem. (III) The performance of LD TE materials is still much smaller than the conventional bulk TE materials. There must be an accurate chemical doping during synthesis of these systems to achieve a high ZT value. (IV) By integrating physical effects caused by multiple dimensional induced defects in materials, it has made significant progress in TE materials, and also opens a new space for the optimization of the TE performance in future research. (V) The embodiment of the fabrication and characterization of thin films based on LD materials remain a challenge. With increasing demand for portable and flexible portable devices, thin film TE materials have received great attention. In spite of their very short time study as compared to bulk TE materials, still for practical applications they are considered as the future of TE materials. Because of their better mechanical and electronic properties, the production of thin film TE materials using layered nanomaterials and their composites is focused area of research but measuring the thermal conductivity of thin films remain a challenge.

ACKNOWLEDGMENT

SNIC and HPC2N are gratefully acknowledge for computational resources.

CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

AUTHOR CONTRIBUTIONS

Deobrat Singh: Formal analysis; writing-original draft; writing-review & editing. **Rajeev Ahuja:** Funding acquisition; resources; software; supervision; writing-original draft; writing-review & editing.

DATA AVAILABILITY STATEMENT

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

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How to cite this article: Singh D, Ahuja R. Dimensionality effects in high-performance thermoelectric materials: Computational and experimental progress in energy harvesting applications. WIREs Comput Mol Sci. 2022;12:e1547. <https://doi.org/10.1002/wcms.1547>