## **Review of Recent Progresses in Thermoelectric Materials**



Jitendra Mohan Giri and Pawan Kumar Singh Nain

Abstract Thermoelectric (TE) technology facilitates the direct conversion of heat into electricity and vice versa. Thermoelectric materials attract researchers since they facilitate a promising green energy solution in the form of solid-state cooling and power generation. However, the low energy conversion efficiency restricts the use of TE materials in real-world applications. Developing highly efficient thermoelectric materials is necessary to benefit the environment as well as the economy. The performance of a particular TE material is generally evaluated by the dimensionless figure of merit (*ZT*). Recent years have witnessed progress with new techniques in maximizing the *ZT* values of various thermoelectric materials. In this review, we summarize recent development in thermoelectric materials for a specific temperature range, which has been developed to improve their maximum *ZT* value up to 95% at the same temperature.

**Keywords** Thermoelectric materials • Thermoelectric performance • Dimensionless figure of merit • Seebeck coefficient

### 1 Introduction

The environmental issues resulting from unsustainable consumption of fossil fuels are well known. Thermoelectric (TE) devices are compact, noiseless, and environmentally friendly and exhibit a leading potential for sustainable development. The thermoelectric module is a p-type and n-type semiconductor element-based solidstate device that converts the thermal energy with temperature difference into electric power (known as Seebeck effect) and also capable of converting electrical energy into temperature gradient (known as Peltier effect). Based on the directions of energy

J. M. Giri (🖂) · P. K. S. Nain

Galgotias University, Greater Noida 201312, India e-mail: jitendra.giri@galgotiasuniversity.edu.in

P. K. S. Nain e-mail: pawan.kumar@galgotiasuniversity.edu.in

<sup>©</sup> The Author(s), under exclusive license to Springer Nature Singapore Pte Ltd. 2021 B. P. Sharma et al. (eds.), *Advances in Engineering Materials*, Lecture Notes

in Mechanical Engineering, https://doi.org/10.1007/978-981-33-6029-7\_26

conversion, these devices are termed as thermoelectric coolers (TEC) and thermoelectric generator (TEG). Thermoelectric generators allow obtaining electricity from any heat source, which shows fantastic application potential. From micro-scale applications to large-scale applications, thermoelectric coolers offer a futuristic role in cooling systems as they work without any moving element involving working fluid.

#### 2 Background

Thermoelectricity is based on two primary thermoelectric effects; the Seebeck effect and the Peltier effect. According to the Seebeck effect, an electromotive force emerges through the electrical circuit consisting of p-type and n-type semiconductor materials and connected in series when contacts are maintained at different temperatures. According to the Peltier effect, if the electric current passes through the circuit of p-type and n-type semiconductor materials, interconnected in series, heat flows from one side to the other side. So, one side of the thermoelectric module is cooled while the other side gets heated.

The performance of any thermoelectric material is generally recognized by the figure of merit (*Z*). *Z* depends on three essential material parameters: Seebeck coefficient (*S*), electrical conductivity ( $\sigma$ ), and thermal conductivity ( $\kappa$ ) and usually expressed in the dimensionless form at an absolute temperature (*T*). The dimensionless figure of merit (*ZT*) is defined as  $ZT = S^2 \sigma T/\kappa$ . Alternatively, *ZT* is also defined as  $(S^2/\rho\kappa)T$ , where  $\rho$  is the electrical resistivity. A large power factor  $(S^2/\rho)$  is required to enhance thermoelectric performance. A good thermoelectric material should possess a large Seebeck coefficient (*S*), low thermal conductivity ( $\sigma$ ), and high electrical conductivity ( $\kappa$ ). The conversion efficiency of TE devices is directly related to the dimensionless figure of merit of their constituting materials. Thus, a high value of the figure of merit is highly desirable.

# **3** Recent Progresses to Enhance *ZT* of Thermoelectric Materials

In recent years, researchers applied new approaches and techniques in maximizing the *ZT* values of various thermoelectric materials. The available thermoelectric materials exhibit varying performance in the different temperature ranges. Improvement in each available thermoelectric material is a focused goal of researchers for a sustainable alternative of conventional energy converters. Earlier, the performance of the semiconductors used in TE applications was dependent on the available pure and perfect single crystals. However, these materials can be doped by adding small quantities of impurities. These impurities act as the electron donor for the parent materials. Most traditional semiconductors have cubic structures, whereas anisotropic crystals

are used for TE applications. The task of designing high-performance thermoelectric materials is to adjust the physical parameters of interconnected S,  $\sigma$ , and  $\kappa$  for a crystalline structure. Thermoelectric transport includes the flow of thermal energy and charge. The energy of phonons (vibrational waves of atoms) represents the thermal energy. Electron scattering on phonons creates electrical resistance. Through incorporating some new scattering mechanisms, nanostructures provide an opportunity to sever the connection between electric and thermal transport. The lattice thermal conductivity needs to be reduced for improvement in TE performance. Mass fluctuations increase through vacancies, and interstitial atoms result in higher phonon scattering that can lead to better TE performance. Sintering of bulk materials and melting production are the techniques used for research efforts to get improved TE materials. This work summarizes recent approaches to enhance the ZT of various thermoelectric materials. There is a wide variety of elements and compounds which can be categorized as thermoelectric materials. It is to be noted that every thermoelectric material exhibits different performance at different temperatures. Hence, it is not possible to recommend a single TE material that is suitable for all practical ranges of temperature in real-world applications. Thus in the present study, the authors have classified the TE materials based on their suitability for low-, medium-, and high-temperature applications.

#### 3.1 Low-Temperature Thermoelectric Materials (300–500 K)

 $Bi_2Te_3$  and its alloys with ZT values of around 0.9–1.0 are considered prominent TE materials at room temperature and widely used for practical thermoelectric applications [1, 2]. Hu et al. demonstrated that the porous structure affects thermoelectric performance [3]. As porosity increased, electrical and thermal conductivity decreased significantly. Reducing thermal conductivity compensates for the deterioration in electrical conductivity and improves the ZT value. A sample premixed with five wt percent  $NH_4HCO_3$  was reported with 1.1 value of maximum ZT at temperature 343 K. This was around 20% better than that of the entirely dense sample with 0.92 value of ZT. Bi-containing  $Sb_2Te_3$  and the related alloys with a high thermoelectric figure of merit can be futuristic options to use in thermoelectric devices.  $Sb_{2-x}Bi_xTe_3$ samples were milled, pressed, and annealed under vacuum for 3 h at 250 °C by Adam et al. [4]. Bi was added to the binary Sb<sub>2</sub>Te<sub>3</sub> system. An increased Seebeck coefficient and power factor were obtained for Sb<sub>1.65</sub>Bi<sub>0.35</sub>Te<sub>3</sub> with the reduced value of thermal conductivity. Subsequently, a high ZT of 1.14 at 400 K was achieved. The sample composition of  $(Bi_2Te_3)_{0.15} + (Sb_2Te_3)_{0.85}$  was prepared to shift maximum ZT to the high-temperature zone by Madavali et al. [5]. The maximum ZT values of 1.3 and 1.07 were reported at 400 K and 300 K, respectively.

Tellurium is the prevailing thermoelectric material utilized in low to medium range of temperature. However, it contains an inferior thermoelectric efficiency with a low value of ZT. An enhancement in the performance of amorphous silicon has

been reported by Banerjee et al. [6]. They applied the method of arsenic ion implantation. The low-temperature dopant activation was done. It was observed that the *ZT* value of amorphous silicon (a-Si) thin films could be enhanced by seven orders at room temperature. Arsenic doping at low-temperature results in the enhancement of electrical conductivity. Empowering a-Si as a conspicuous TE material may be useful for sustainable energy applications at room temperature with maximum *ZT* up to 0.77. The magneto-thermoelectric figure of merit (*ZT*) in 3-D Dirac semimetal Cd<sub>3</sub>As<sub>2</sub> crystal was reported by Wang et al. [7]. The magnetic field very effectively reduces electric conductivity and thermal conductivity. A maximum *ZT* value of 1.1 was obtained at 350 K temperature under 7 T of the magnetic field.

A hypothesis of thermoelectric transport properties in 2-D semiconducting quantum well structures is built up by Yelgel et al. [8]. Within the temperature range 50-600 K, computations are performed for n-type 0.1 wt% CuBr-doped Bi<sub>2</sub>Se<sub>3</sub>/Bi<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Se<sub>3</sub> and also for p-type 3 wt% Te-doped Sb<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> quantum well frameworks. It is discovered that diminishing the well thickness pronouncedly affects upgrading the ZT value. At 350 K temperature, the maximum ZT value of 0.97 is obtained for Bi<sub>2</sub>Se<sub>3</sub>/Bi<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Se<sub>3</sub>. At 440 K temperature, the maximum ZT value of 1.945 is obtained for Sb<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub>. CaMnO<sub>3</sub> has a generally high Seebeck coefficient; however, the electrical conductivity ( $\sigma$ ) is quite low (within the temperature range 300-1000 K). Hence, an un-doped material brings a low power factor ( $S^2\sigma$ ). The bismuth doping of Ca<sub>1-x</sub>Bi<sub>x</sub>MnO<sub>3</sub> has been reported by Paengson et al. [9]. With x range of 0-0.05, TE materials were setup. The solidstate reaction and hot pressing techniques were used. Bi doping increased carrier concentration for all samples with different x. The electrical resistivity diminished with expanding bismuth content. The maximum ZT value of 0.065 at 473 K was found for  $Ca_{0.97}Bi_{0.03}MnO_3$ . It is worth mentioning that the ZT value was increased by 95% at the same temperature compared to CaMnO<sub>3</sub>. Bi<sub>2</sub>Te<sub>3</sub> and the family of similar compounds potentially satisfy the thermoelectric efficiency levels at low temperatures. However, the dimensionless figure of merit values decreases severely at a temperature over 450 K. The bulk Bi<sub>1.9</sub>Lu<sub>0.1</sub>Te<sub>3</sub> samples with diverse micrograined particles were fabricated using cold isolated pressing (CIP) with annealing at high temperature and secondly by spark plasma sintering (at 653 and 683 K) by Yaprintsev et al. [10]. The maximum  $ZT \sim 0.9$  for 450–500 K range of temperature range is obtained.

The summary of recent ZT improvements of thermoelectric materials at low temperatures discussed in this study is presented in Table 1.

#### 3.2 Medium-Temperature Thermoelectric Materials (500–900 K)

CuAgSe exhibits excellent potential due to its fantastic carrier mobility. It also has low thermal conductivity. To prepare monodisperse CuAgSe nanocrystals, a scalable

Researchers	Year	Thermoelectric material	Method for properties enhancement	Impact on ZT performance
Hu et al.	2020	Bi <sub>0.4</sub> Sb <sub>1.6</sub> Te <sub>3</sub>	Pre-mixing with NH4HCO3	<ul> <li>Max. Dimensionless figure of merit (ZT<sub>max</sub>) of 1.11 at 343 K</li> <li>20% increment in ZT<sub>max</sub> as compared with fully dense material</li> </ul>
Adam et al.	2020	Sb <sub>2</sub> Te <sub>3</sub>	Bi-containing	$ZT_{\text{max}}$ value of 1.14 at 400 K for Sb <sub>2</sub> Te <sub>3</sub>
Madavali et al.	2018	$(Bi_2Te_3)_x + (Sb_2Te_3)_{1-x}$	Increasing $Sb_2Te_3$ content	<ul> <li><i>ZT</i> max value of 1.3 at 400 K</li> <li><i>ZT</i> max value of 1.07 at 300 K</li> </ul>
Banerjee et al.	2018	Amorphous silicon	Arsenic doping	$ZT$ around ~0.64 $\pm$ 0.13 at room temperature
Wang et al.	2018	Cd <sub>3</sub> As <sub>2</sub>	Enhancement by the magnetic field	$ZT_{\text{max}}$ value of 1.1 at 350 K
Yelgel and Srivastava	2014	$Bi_2Se_3/Bi_2Te_3/Bi_2Se_3$ and $Sb_2Te_3/Bi_2Te_3/Sb_2Te_3$	By varying the well thickness+	$ZT_{max} = 0.97$ at 350 K for Bi <sub>2</sub> Se <sub>3</sub> /Bi <sub>2</sub> Te <sub>3</sub> /Bi <sub>2</sub> Se <sub>3</sub> and $ZT_{max} = 1.945$ at 440 K for Sb <sub>2</sub> Te <sub>3</sub> /Bi <sub>2</sub> Te <sub>3</sub> /Sb <sub>2</sub> Te <sub>3</sub>
Paengson et al.	2017	CaMnO <sub>3</sub>	Bi doping and hot pressing of CaMnO <sub>3</sub>	<ul> <li>ZT<sub>max</sub> value of 0.065 at 473 K for Ca<sub>0.97</sub>Bi<sub>0.03</sub>MnO<sub>3</sub></li> <li>95% increment in ZT<sub>max</sub> as compared with un-doped material</li> </ul>
Yaprintsev et al.	2017	Bi <sub>1.9</sub> Lu <sub>0.1</sub> Te <sub>3</sub>	Fabrication by cold isostatic pressing and SPS	$ZT_{\text{max}}$ value ~0.9 for 450–500 K

 Table 1
 Summary of recent ZT improvements of TE materials at low temperatures

colloidal synthesis has been reported by Zuo et al. [11]. The gathered powder test was cleaned by a non-sulfur substance of NaNH<sub>2</sub>. It was done to expel the organic ligands from the surface. After that, annealing process was also done. A 0.68 value of maximum *ZT* at 566 K was obtained. The obtained material shows the potential of TE applications for mid-range temperatures. The material before annealing exhibits a temperature- controlled transition from n-type toward p-type. This makes it suitable for thermal control transistor applications. CoSb<sub>3</sub> skutterudite is considered potential TE material for power generation. La Filler atoms are used to minimize lattice thermal conductivity for the skutterudite to get better TE performance [12, 13]. Bashir et al. reported a high *ZT* value of 1.15 at 692 K with La and In as the In<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> skutterudite [14]. BiCuSeO contains low thermal conductivity and an average power

factor. BiCuSO was doped with Pb and effectively synthesized by high pressure by Zhu et al. [15]. BiCuSeO doped with Pb increases the carrier concentration. This Pb doping improves the power factor. The thermal conductivity is smothered by Pb doping. At 700 K temperature, the maximum ZT of 0.14 is achieved. Synthesization with feasible high-pressure and high-temperature techniques can increase the TE performance of Cu<sub>2</sub>Se bulk materials. At 723 K, a high ZT value of 1.19 was reported for Cu<sub>2</sub>Se synthesized at 3 GPa by Xue et al. [16]. Recently, GeTe and its derivatives have gained considerable attention as promising thermoelectric materials. Perumal et al. [17] reported a maximum ZT value of 2.1 for In and Bi co-doped GeTe at 723 K.

The synthesization of a group of TiNiSn-based alloys has been performed by Chen et al. [18]. It was done by way of an easy solid-state reaction followed by the SPS method. The amount and mixture of the heterogeneous phase were precisely managed, which results in a successful decrement of thermal conductivity (up to 2.3–3.0 Wm<sup>-1</sup>K<sup>-1</sup>). Besides, TE figure of merit was enhanced up to 0.49 at 750 K temperature. Silicon-germanium-based alloys are appealing. For radioisotope thermoelectric power generation at an excessive temperature (more than 1000 °C), they offer a good choice of TE material. On the other side, mesostructured  $In_{0.25}Co_4Sb_{12}$ and In<sub>0.25</sub>Yb<sub>0.05</sub>Co<sub>4</sub>Sb<sub>12</sub> samples have been synthesized by Benyahia et al. [19]. The samples were fabricated through melting and annealing. Then, the ball-milling procedure was applied to minimize size and sintered through the SPS method. With a mean grain size of 400 nm, a maximum dimensionless figure of merit of 1.4 at 750 K temperature is obtained. It was achieved in the BM  $In_{0.25}Co_4Sb_{12} + 0\%$  CeO<sub>2</sub>. TiNiSn-based half-Heusler (HH) alloys are widely studied. These thermoelectric materials show a high-temperature stabilization. However, the thermal conductivity is constantly enormously high, and hence, further ZT enhancement is difficult. SiC nanoparticles were brought into the matrix of Pb<sub>0.98</sub>Na<sub>0.02</sub>Te doped with SrTe by Ai et al. [20]. The increased Seebeck coefficient and decreased electrical conductivity resulted in a remarkable peak ZT of 1.73 at 750 K.

Copper selenide is a promising thermoelectric material because of its fantastic electrical properties. A hydrothermal technique to incorporate astounding β- $Cu_2Se_{1-x}I_x$  nanopowder with a cost-effective minimum consumption of energy is reported by Wang et al. [21]. The nanopowder with different levels of doped iodine was used. Utilizing this straightforward and modest methodology, an improved ZTof 1.13 is obtained at a temperature of 773 K in iodine-doped Cu<sub>2</sub>Se (x = 0.03) pellets after hot squeezing. Recently, the synthesis of p-type SiGe with boron using varied proportion is reported by Murugasami et al. [22]. The material was sintered through the spark plasma sintering technique. Doped with B<sub>1.5</sub> at.% synthesized SiGe alloy exhibits the enhanced ZT of 0.525 at 800 °C temperature. A considerable improvement of approximately 9.38% is obtained. Recently, the enhancement of skutterudite performance is reported by Yang et al. [23]. Tellurium-doped skutterudite has been shown to have promising TE properties using nano-micro-level pores. Cobalt, antimony, and tellurium powders were utterly blended with a nominal composition of Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub>. Then, the material was stacked into carbon cauldrons and kept inside quartz tubes below vacuum for heating. The acquired ingots were ground into powders utilizing two successive methods, first by a mortar and then

by ball milling below vacuum. The two powders (without ball milling and with ball milling) with different proportions were blended, and after that, sintered using spark plasma sintering technique. The annealing process below vacuum was also done on the obtained bulk material. The authors reported that annealed nanoparticles carry some randomly allotted nanopores with a range of sizes from 200 nm to 2  $\mu$ m. The development of these nanosized pores is due to strain during sintering. The thermal conductivity drops drastically which is a desired effect. A 1.2 value of the maximum dimensionless figure of merit is obtained for the annealed material at a temperature of 800 K. A significant increment of approx. 35% was reported. The thermoelectric properties of n-type-doped Mg<sub>2</sub> (Si<sub>0.4</sub>Sn<sub>0.6</sub>)<sub>1-y</sub> Bi<sub>y</sub> solid solutions are investigated theoretically by Yelgel [24]. From 300 to 800 K temperature range, the selected y range is 0.005–0.06 for doping Bi with available experimental data. It was found that an appropriate y can increase *ZT*. The maximum *ZT* is obtained with y = 0.03 at 800 K and values 1.82.

The graphene nanoplate incorporated into Cu<sub>2</sub>Se samples has been fabricated by Li et al. [25]. The ball-milling technique was applied. Then, sintering through the SPS method was done. The homogeneous dispersion of the carbon phase reduced the Cu<sub>2</sub>Se particles to form an excellent dense construction. Maximum *ZT* reached a high 1.7 value at 873 K. This gives an appropriate technique to use carbon engineering to maximize TE performance for Cu<sub>2</sub>Se and family compounds. The deliberate actuated dislocations and vacancies are compelling in diminishing the thermal conductivity of polycrystalline SnS, as reported by Asfandiyar et al. [26]. Low thermal conductivity and high electrical conductivity Sn<sub>0.99</sub>Ag<sub>0.005</sub>S sample were obtained at 877 K. Ag doping brings high power factor, and an enhanced *ZT* of 1.1 at 877 K was recorded for Sn<sub>0.99</sub>Ag<sub>0.005</sub>S. N-type half-Heusler NbCoSn performs well in TE performance, but p-type performs poorly. Replacing Sc at Nb site may change the n-type NbCoSn to a p-type semiconductor as reported by Yan et al. [27] by changing the Fermi level, indicating that Sc is a suitable p-type dopant. *ZT*<sub>max</sub> value of 0.13 at 879 K has been reported.

The summary of recent ZT improvements of thermoelectric materials at medium temperatures discussed in this study is presented in Table 2.

#### 3.3 High-Temperature Thermoelectric Materials (>900 K)

Lead selenide (PbSe) displays a temperature-dependent Seebeck coefficient, low thermal conductivity, and low electrical resistivity. Further, it has resolved the issue that emerges to get both n- and p-type legs. A simultaneous advancement of thermal and electrical properties of p-type PbSe has been reported by Zhao et al. [28]. The density hypothesis for estimations of valence band energy levels was used. Between lead selenide and nanostructures of  $CdS_{1-x}Se_x/ZnS_{1-x}Se_x$ , appropriate valence band alignments were introduced. A highly enhanced dimensionless figure of merit of 1.6 at 923 K was attained at Pb<sub>0.98</sub>Na<sub>0.02</sub>Se + 3%Cds. Due to its high TE efficiency, Si-Ge alloys are considered valuable TE materials operating at high temperatures. The effect

Table 2 Summary of	recent ZT	improvements of TE material	s at medium temperatures	
Researchers	Year	Thermoelectric material	Method for properties enhancement	Impact on ZT performance
Zuo et al.	2018	CuAgSe	Colloidal synthesis of monodisperse CuAgSe NCs	$ZT_{max}$ value of 0.68 at 566 K
Bashir et al.	2018	CoSb <sub>3</sub>	La and In filling	$ZT_{\text{max}}$ value of 1.15 at 692 K
Zhu et al.	2018	BiCuSO	Doping with Pb	$ZT_{\text{max}}$ value of 0.14 at 700 K
Xue et al.	2019	Cu <sub>2</sub> Se	Synthesis with high pressure	$ZT_{\text{max}}$ value of 1.1 at 723 K
Perumal et al.	2019	GeTe	In and Bi doping	$ZT_{\text{max}}$ value of 2.1 at 723 K
Chen et al.	2017	TiNiSn-based half-Heusler (HH) alloys	Synthesis with solid-state reaction	$ZT_{\rm max}$ value of 0.49 at 750 K
Benyahia et al.	2018	In <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>	Synthesis by a melting–ball-milling–SPS method	$ZT_{\rm max}$ value of 1.4 at 750 K
Ai et al.	2020	PbTe	SiC dispersing and SrTe doping	ZT <sub>max</sub> value of 1.73 at 750 K for Pb <sub>0.98</sub> Na <sub>0.02</sub> Te/4 mol%SrTe composite
Wang et al.	2019	Cu <sub>2</sub> Se	Synthesis of Cu <sub>2</sub> Se alloys doped with iodine	$ZT_{max}$ value of 1.13 at 773 K for Cu <sub>2</sub> Se <sub>1-x</sub> I <sub>x</sub> (x = 0.03)
Murugasami et al.	2019	SiGe	Synthesis of SiGe alloys doped with Boron	$ZT_{\rm max}$ value of 0.525 at 800 °C for doped with B $_{1.5}$
Yang et al.	2019	Te-doped skutterudite (Co4Sb <sub>11.5</sub> Te <sub>0.5</sub> )	Nanomicroporous structure in Co4Sb11.5Te0.5 materials via annealing the nano-Co4Sb11.5Te0.5/C04Sb11.5Te0.5 composites	<ul> <li>Max. Dimensionless figure of merit (ZT<sub>max</sub>) of 1.2 at 800 K for annealed sample (N10-A100)</li> <li>33.7% increment in ZT<sub>max</sub> as compared with dense material (N0)</li> </ul>
Yelgel	2016	$Mg_2Si_{0.4}Sn_{0.6}$	$Mg_2$ (Si <sub>0.4</sub> Sn <sub>0.6</sub> ) <sub>1-y</sub> Bi solid solutions	$ZT_{\rm max}$ value of 1.82 at 800 K
Li et al.	2018	Cu <sub>2</sub> Se	By graphene nanoplate incorporation	$ZT_{\text{max}}$ value of 1.7 at 873 K
Asfandiyar et al.	2020	SnS	Intentional-induced dislocations and vacancies and Ag doping	$ZT_{max}$ value of 1.1 at 877 K for Sn0.99 Ag0.005 S
Yan et al.	2020	NbCoSn	Sc substitution at the Nb site	$ZT_{max}$ value of 0.13 at 879 K

276

Researchers	Year	Thermoelectric material	Method for properties enhancement	Impact on <i>ZT</i> performance
Zhao et al.	2013	PbSe	Integration of band structure with hierarchical structuring	ZT <sub>max</sub> value of 1.6 at 923 K
Muthusamy et al.	2020	Si–Ge–Au	Boron doping	$ZT_{\text{max}}$ value of 1.63 at 973 K
He et al.	2014	Cu <sub>2</sub> S	Cu deficiency	<i>ZT</i> <sub>max</sub> value of 1.7 at 1000 K
Fu et al.	2015	FeNbSb	Hf doping	$ZT_{\text{max}}$ value of 1.5 at 1200 K
Wille et al.	2019	Yb <sub>14</sub> ZnSb <sub>11</sub>	Containing RE	$ZT_{\text{max}}$ value of 0.7 at 1275 K

Table 3 Summary of recent ZT improvements of TE materials at high temperatures

on thermoelectric properties of B-doped Si-Ge-Au nanocomposites was investigated, taken as  $Si_{65-x}Ge_{31}Au_4B_x$  by Muthusamy et al. [29]. At 973 K, a maximum *ZT* value of 1.63 was reported at x = 3. The phonon-liquid electron-crystal concept for copper sulfide with reduced thermal conductivity and higher thermoelectric performance has been proposed by He et al. [30]. A high *ZT* value of 1.7 was reported at 1000 K by using copper deficiency as  $Cu_{2-x}S$  with x = 0.03.

Half-Heusler compounds are increasingly attracting attention because of their strong mechanical and electrical properties at high temperatures. At 1200 K, through heavier Hf doping the p-type FeNbSb heavy-band half-Heusler alloys with 1.5 value of high *ZT* was reported by Fu et al. [31]. Yb<sub>14</sub>ZnSb<sub>11</sub> is considered for intermediate valence interest. With rare earth (RE) solution as Yb<sub>14-x</sub>RE<sub>x</sub>ZnSb<sub>11</sub> was investigated by Wille et al. [32]. The dimensionless figure of merit was reported as high as 0.7 at 1275 K with x = 0.5.

The summary of recent ZT improvements of thermoelectric materials at high temperatures discussed in this study is presented in Table 3.

#### 4 Conclusion

Exploring advancement in thermoelectric materials for sustainable energy solutions is the contemporary area of interest. The *ZT* value of thermoelectric materials should be enhanced for a broad range of potential applications of thermoelectric devices. From this study, it can be highlighted that:

• In the recent past, material researchers are successfully applying new approaches to upgrade the performance of available materials for a particular temperature range.

- A promising new approach is to create nanolevel and macro-level pores in tellurium doped skutterudite to enhance *ZT* by approximately 35%.
- Another interesting approach is introducing a facile method for colloidal synthesis of copper-silver selenide. With  $ZT_{max}$  value of 0.68 at temperature 566 K, this resulted as a promising candidate for TE research in the intermediate temperature range.

The significant outcomes of researchers will boost the applicability of TE devices contribution to the present world's green energy solutions. For greater commercialization of thermoelectric applications, improved materials with high values of ZT are required at prevailing operating temperatures. This will boost the manufacture of better performing TE modules. These advancements in ZT values could close the gap in performance between conventional bismuth-tellurium-based materials and newer materials. The costs to invent newer thermoelectric materials are quite different from the production cost of those materials. The costs of candidate materials, costs to process those materials into TE elements, and cost to compensate the material loss are significant for the real commercial applications of newly researched materials. The non-availability of the requisite raw materials might result in holding the production of TE devices. More extensive work on that would be useful.

#### References

- Witting, I. T., Chasapis, T. C., Ricci, F., Peters, M., Heinz, N. A., Hautier, G., & Snyder, G. J. (2019). The thermoelectric properties of bismuth telluride. *Advanced Electronic Materials*, *5*, 1800904. https://doi.org/10.1002/aelm.201800904.
- Goldsmid, H. J. (2014). Bismuth telluride and its alloys as materials for thermoelectric generation. https://doi.org/10.3390/ma7042577.
- Hu, X., Hu, J., Fan, X., Feng, B., Pan, Z., Liu, P., Zhang, Y., Li, R., He, Z., Li, G., & Li, Y. (2020). Artificial porous structure: An effective method to improve thermoelectric performance of Bi<sub>2</sub>Te<sub>3</sub> based alloys. *Journal of Solid State Chemistry*, 282. https://doi.org/10.1016/j.jssc. 2019.121060.
- Adam, A. M., El-Khouly, A., Novitskii, A. P., Ibrahim, E. M. M., Kalugina, A. V., Pankratova, D. S., Taranova, A. I., Sakr, A. A., Trukhanov, A. V., Salem, M. M., & Khovaylo, V. (2020). Enhanced thermoelectric figure of merit in Bi-containing Sb<sub>2</sub>Te<sub>3</sub> bulk crystalline alloys. *Journal of Physics and Chemistry of Solids*, *138*, 109262. https://doi.org/10.1016/j.jpcs.2019. 109262.
- Madavali, B., Kim, H. S., Lee, C. H., Kim, D.-S., & Hong, S. J. (2019). High thermoelectric figure of merit in p-type (Bi<sub>2</sub>Te<sub>3</sub>)<sub>x</sub>-(Sb<sub>2</sub>Te<sub>3</sub>)<sub>1-x</sub> alloys made from element-mechanical alloying and spark plasma sintering. *Journal of Electronic Materials*, 48, 416–424. https://doi.org/10.1007/s11664-018-6706-7.
- Banerjee, D., Vallin, Ö., Samani, K. M., Majee, S., Zhang, S. L., Liu, J., & Zhang, Z. B.: Elevated thermoelectric figure of merit of n-type amorphous silicon by efficient electrical doping process. *Nano Energy*, 44, 89–94.
- Wang, H., Luo, X., Chen, W., Wang, N., Lei, B., Meng, F., Shang, C., Ma, L., Wu, T., Dai, X., Wang, Z., & Chen, X. (2018). Magnetic-field enhanced high-thermoelectric performance in topological Dirac semimetal Cd<sub>3</sub>As<sub>2</sub> crystal. *Science Bulletin*, 63, 411–418.

- Yelgel, Ö. C., & Srivastava, G. P. (2014) Thermoelectric properties of Bi<sub>2</sub>Se<sub>3</sub>/Bi<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Se<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> quantum well systems. *Philosophical Magazine*, *94*, 2072–2099. https://doi.org/10.1080/14786435.2014.903340.
- Paengson, S., Pilasuta, P., Singsoog, K., Namhongsa, W., Impho, W., & Seetawan, T. (2017). Improvement in thermoelectric properties of CaMnO<sub>3</sub> by Bi doping and hot pressing. In: *Materials today: Proceedings* (pp. 6289–6295). https://doi.org/10.1016/j.matpr.2017.06.129.
- Yaprintsev, M., Lyubushkin, R., Soklakova, O., & Ivanov, O. (2018). Microstructure and thermoelectric properties of Bi<sub>1.9</sub>Lu<sub>0.1</sub>Te<sub>3</sub> compound. *Rare Metals*, 37, 642–649.
- Zuo, Y., Liu, Y., He, Q. P., Song, J. M., Niu, H. L., & Mao, C. J. (2018). CuAgSe nanocrystals: Colloidal synthesis, characterization and their thermoelectric performance. *Journal of Materials Science*, 53, 14998–15008. http://doi.org/10.1007/s10853-018-2676-7.
- Bao, S., Yang, J., Zhu, W., Fan, X., Duan, X., & Peng, J. (2006). Preparation and thermoelectric properties of La filled skutterudites by mechanical alloying and hot pressing. *Materials Letters*, 60, 2029–2032. https://doi.org/10.1016/j.matlet.2005.12.074.
- 13. Liu, K., Dong, X., & Jiuxing, Z. (2006). The effects of La on thermoelectric properties of La<sub>x</sub>Co <sub>4</sub>Sb<sub>12</sub> prepared by MA-SPS. *Materials Chemistry and Physics*, *96*, 371–375.
- Bashir, M. B. A., Said, S. M., Sabri, M. F. M., Miyazaki, Y., Shnawah, D. A., Shimada, M., Salleh, M. F. M., Mahmood, M. S., Salih, E. Y., Fitriani, F., & Elsheikh, M. H. (2018). Infilled La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> Skutterudite system with high thermoelectric figure of merit. *Journal of Electronic Materials*, 47, 2429–2438.
- Zhu, H., Su, T., Li, H., Hu, Q., Li, S., & Hu, M. (2018). Thermoelectric properties of BiCuSO doped with Pb. Solid State Communications. https://doi.org/10.1016/j.ssc.2018.04.013.
- Xue, L., Zhang, Z., Shen, W., Ma, H., Zhang, Y., Fang, C., Jia, X. (2019). Thermoelectric performance of Cu<sub>2</sub>Se bulk materials by high-temperature and high-pressure synthesis. *Journal* of Materiomics, 5, 103–110. http://doi.org/10.1016/j.jmat.2018.12.002.
- Perumal, S., Samanta, M., Ghosh, T., Shenoy, U. S., Bohra, A. K., Bhattacharya, S., Singh, A., Waghmare, U. V., & Biswas, K. (2019). Realization of high thermoelectric figure of merit in gete by complementary co-doping of Bi and In. *Joule*, *3*, 2565–2580. https://doi.org/10.1016/ j.joule.2019.08.017.
- Chen, J. L., Liu, C., Miao, L., Gao, J., Zheng, Y. Y., Wang, X., Lu, J., & Shu, M. (2018). Improved thermoelectric performance achieved by regulating heterogeneous phase in halfheusler TiNiSn-based materials. *Journal of Electronic Materials* (2018).
- Benyahia, M., Ohorodniichuk, V., Leroy, E., Dauscher, A., Lenoir, B., & Alleno, E. (2018). High thermoelectric figure of merit in mesostructured In<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> n-type skutterudite. *Journal of Alloys and Compounds*. http://doi.org/10.1016/j.jallcom.2017.11.195.
- Ai, X., Hou, D., Liu, X., Gu, S., Wang, L., & Jiang, W. (2020). Enhanced thermoelectric performance of PbTe-based nanocomposites through element doping and SiC nanoparticles dispersion. *Scripta Materialia*, 179, 86–91.
- Wang, J., Liu, B., Miao, N., Zhou, J., & Sun, Z. (2019). I-doped Cu<sub>2</sub>Se nanocrystals for highperformance thermoelectric applications. *Journal of Alloys and Compounds* (2019). https:// doi.org/10.1016/j.jallcom.2018.08.291.
- Murugasami, R., Vivekanandhan, P., Kumaran, S., Suresh Kumar, R., & John Tharakan, T. (2019). Simultaneous enhancement in thermoelectric performance and mechanical stability of p-type SiGe alloy doped with Boron prepared by mechanical alloying and spark plasma sintering. *Journal of Alloys and Compounds* (2019). https://doi.org/10.1016/j.jallcom.2018. 09.029.
- Yang, H., Wen, P., Zhou, X., Li, Y., Duan, B., Zhai, P., & Zhang, Q. (2019). Enhanced thermoelectric performance of Te-doped skutterudite with nano-micro-porous architecture. *Scripta Materialia*. http://doi.org/10.1016/j.scriptamat.2018.09.015.
- Yelgel, Ö. C. (2016). Theoretical study of thermoelectric properties of n-type doped Mg<sub>2</sub>Si<sub>0.4</sub>Sn<sub>0.6</sub> solid solutions. *Philosophical Magazine*. https://doi.org/10.1080/14786435. 2016.1143128.
- Li, M., Kazi Nazrul Islam, S. M., Dou, S., & Wang, X. (2018). Significantly enhanced figure-ofmerit in graphene nanoplate incorporated Cu<sub>2</sub>Se fabricated by spark plasma sintering. *Journal* of Alloys and Compounds (2018). https://doi.org/10.1016/j.jallcom.2018.07.353.

- Asfandiyar, Cai, B., Zhao, L. D., & Li, J. F. (2020). High thermoelectric figure of merit ZT > 1 in SnS polycrystals. *Journal of Materiomics*, 6, 77–85.
- Yan, R., Xie, W., Balke, B., Chen, G., & Weidenkaff, A. (2020) Realizing p-type NbCoSn half-Heusler compounds with enhanced thermoelectric performance via Sc substitution. *Science* and Technology of Advanced Materials, 21, 122–130.
- Zhao, L. D., Hao, S., Lo, S. H., Wu, C. I., Zhou, X., Lee, Y., Li, H., Biswas, K., Hogan, T. P., Uher, C., Wolverton, C., Dravid, V. P., & Kanatzidis, M. G.: High thermoelectric performance via hierarchical compositionally alloyed nanostructures. *Journal of the American Chemical Society*. https://doi.org/10.1021/ja403134b.
- Muthusamy, O., Ghodke, S., Singh, S., Delime-Codrin, K., Nishino, S., Adachi, M., Yamamoto, Y., Matsunami, M., Harish, S., Shimomura, M., & Takeuchi, T.: Enhancement of the thermoelectric performance of Si-Ge nanocomposites containing a small amount of Au and optimization of boron doping. *Journal of Electronic Materials*, 49, 2813–2824. https://doi.org/10.1007/ s11664-019-07857-5.
- He, Y., Day, T., Zhang, T., Liu, H., Shi, X., Chen, L., & Snyder, G. J. (2014). High thermoelectric performance in non-toxic earth-abundant copper sulfide. *Advanced Materials*, 26, 3974–3978. https://doi.org/10.1002/adma.201400515.
- Fu, C., Bai, S., Liu, Y., Tang, Y., Chen, L., Zhao, X., & Zhu, T.: Realizing high figure of merit in heavy-band p-type half-Heusler thermoelectric materials. *Nature Communications*, 6, 1–7. https://doi.org/10.1038/ncomms9144.
- 32. Kunz Wille, E., Grewal, N., Bux, S., & Kauzlarich, S.: Seebeck and figure of merit enhancement by rare earth doping in  $Yb_{14-x}RE_xZnSb_{11}$  (x = 0.5). *Materials*, *12*, 731. https://doi.org/10. 3390/ma12050731.