Odyssey of thermoelectric materials: foundation of the complex structure

Khalid Bin Masood¹, Pushpendra Kumar², R A Singh¹ and Jai Singh¹,³

¹ Department of Physics, Dr Hari Singh Gour University Sagar, M.P. India
² CSIR-National Chemical Laboratory, Homi Bhabha Road, Pune 411008, India
³ Author to whom any correspondence should be addressed.
E-mail: jai.bhu@gmail.com

Keywords: thermoelectric materials, figure of merit, complex structures

Abstract
Growing energy crises and pollution are the major issues of the modern world. The thermoelectric concept seems to be the promising solution to deal with these problems, because of the ability of thermoelectric materials to convert waste heat into electricity without adding more pollution to the atmosphere. The development of thermoelectric materials (TE) is driven by fundamental interest and their potential applications. To replace the conventional techniques, the figure of merit (zT) of the thermoelectric materials should be higher than 2 for power generation and greater than 3 for cooling. Recently, there have been significant advances in enhancing the figure of merit of thermoelectric materials and also to find new materials for the thermoelectric purpose. Low thermal conductivity is the key for a promising thermoelectric material that can be achieved through the complex structures. This review provides insights into the recent advancements in improving the efficiency of thermoelectric systems, complex nature of thermoelectric materials, with a concise introduction to preparative approaches for thermoelectric (TE) materials.

1. Introduction
Due to the increasing global energy crises, the hazardous impact on the environment and the limited supply of fossil fuels, the need for some alternative energy source is significant. The thermoelectric materials have come to rescue the world from the growing energy crisis. The waste heat coming out of motor vehicles and other electrical appliances can be put to good use by generating electricity from it without adding more pollution to the atmosphere which is only possible with the help of thermoelectric materials. Thermoelectric materials have a wide range of applications ranging from small-scale production of electricity to their use in missiles and spacecraft. Thermoelectric (TE) phenomenon involves three essential effects: Seebeck effect, Peltier effect and Thomson effect. Seebeck effect is the direct conversion of heat into electricity (power generation), and Peltier effect is just its opposite (cooling). For both the results, a junction needs to be formed between n-type and p-type semiconductors. Thomson effect, on the other hand, requires only one conductor carrying DC which when subjected to temperature gradient gives the absorption or evolution of heat. TE devices have the advantage over other conventional devices because of no moving parts, noise-free and exceptional service reliability. A TE module for both power generation and cooling is made of electrically connected thermocouples which include p-type and n-type semiconductors. For power generation, the thermocouples are connected thermally in parallel and electrically in series.

The efficiency of TE materials is governed by its dimensionless figure of merit \( zT = S^2\sigma T/K \) which depends on both electrical and thermal properties of the materials. \( S \) is the Seebeck coefficient which is given by the ratio of voltage output to the temperature gradient \( (V/ΔT) \), \( \sigma \) is the electrical conductivity, and \( K \) is the thermal conductivity \( (K = K_e + K_l; \text{electronic and lattice thermal conductivity}) \). The quantity \( S^2\sigma \) is called the power factor and is associated with the electric transport.
The thermodynamic efficiency of power generation is given by [39, 40] 
\[ \eta = \frac{\Delta T(\sqrt{1 + zT} - 1)}{T_h(\sqrt{1 + zT} + \frac{T_c}{T_h})} \]

\( T_c \) is the temperature of cold side, \( T_h \) is the temperature of hot side, \( zT \) is the figure of merit, and \( \Delta T/T_h \) is the Carnot efficiency. Thus large \( zT \) and substantial difference between \( T_c \) and \( T_h \) is the key to increase thermodynamic efficiency \( \eta \). Enhancing \( zT \) of any material requires the increment of \( \sigma \) and reduction of \( K \) simultaneously which contradicts with Weidmann-Franz law. According to Weidmann-Franz law, the ratio of \( \sigma \) to \( K \) remains constant which implies that these two quantities cannot be simultaneously increased and decreased respectively [41]. In order to enhance \( zT \), some special strategies have to be employed to reduce \( K \) and increase \( \sigma \) simultaneously. Searching for the materials that can be better thermoelectrics, it is found that degenerate semiconductors can be the potential thermoelectric materials as is clear from figure 1.

For degenerate semiconductors, \( S \) is given by [42] 
\[ S = \frac{8\pi^2 K_B^2}{3eh^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3} \]

\( K_B \) is the Boltzmann constant, \( e \) is electron charge, \( h \) is Planck constant, \( m^* \) is the effective mass of charge carriers. It is clear that \( S \) increases with the decrease in carrier concentration \( n \). Electrical conductivity on the other hand is given by \( \sigma = ne\mu \); where \( \mu \) is the mobility of charge carriers. To increase the power factor, it is necessary to decouple Seebeck coefficient and electrical conductivity because these two quantities depend on \( n \) in opposite manners. Also as total thermal conductivity \( K \) is the sum of electronic thermal conductivity \( K_e \) and lattice thermal conductivity \( K_l \), both these parts of thermal conductivity are to be looked at separately. \( K_e \) is given by \( L\sigma T = Lne\mu T \) where \( L \) is Lorentz number [41]. \( K_e \) is directly proportional to the number of charge carriers \( n \), and hence it becomes challenging to reduce this part of thermal conductivity.

Lattice thermal conductivity \( K_l \) is given by \( K_l = \frac{1}{3} C_v v l \) [43], where \( C_v \) is the specific heat per unit volume, \( v \) is the speed of sound, \( l \) is phonon mean free path (mfp) and has very little dependence on \( n \). Therefore to reduce thermal conductivity, strategies are to be made mainly to reduce \( K_e \). Altering \( C_v \) and \( v \) is very difficult because these quantities are constant in case of solids. So, the primary focus is to minimize mfp of phonons and that too of long wavelength phonons because heat is mainly carried by the long wavelength phonons [44, 45]. The mfp of phonons can be reduced by phonon scattering that can be induced by various approaches such as doping (also increases the carrier concentration) [40, 46], nanostructuring [45, 47], introducing fluid like characteristics in solid crystals [48-50] and by introducing rattling ions in cage like structures [51-53]. The phonon scattering mechanism can be understood from figure 2.

2. Ways to optimize thermoelectric properties

2.1. Phonon glass electron crystal (PGEC) and complex structures

The reduction in lattice thermal conductivity by scattering of phonons and not affecting the transport of electrons can be achieved in the materials favouring Phonon-Glass Electron-Crystal (PGEC) concept as is proposed by Slack [55]. Heat is mainly carried by a wide range of phonons with varying mean free paths [56].
Glasses have the lowest thermal conductivities because in glasses, thermal conductivity can be considered as the random walk of energy through the lattice and not by the transport of phonons while the crystalline materials favour electrical conductivity. PGEC behaviour in thermoelectric materials can be achieved by alloying. Alloying with isoelectronic elements (elements having same electronic configuration) increases the disorder and helps in the scattering of phonon on the sites and preserves the crystalline electronic structure. Complex crystal structures show better PGEC behaviour. Complexity may be due to disorder in the unit cells or due to the complex unit cell. More complex structures have less lattice thermal conductivity. The reduction in thermal conductivity through disorder in the unit cell is large in the species like clathrates and skutterudites. CsBi₄Te₆ (which is the complicated alternative of Bi₂Te₃) has low lattice thermal conductivity of 1.1 Wm⁻¹k⁻¹ due to complex unit cell and hence has improved zT of 0.8 below room temperature. A very low thermal conductivity of 0.42 to 0.20 Wm⁻¹k⁻¹ in the temperature range 300 to 837 K in K₂Bi₆Se₁₃ is due to its large unit cell and complex anisotropic structure which accounts for its high zT of 1.3 at 873 K. Recently, a new semiconductor Cs₄Cu₃Bi₉S₁₇ is found to have a low thermal conductivity of 0.71 Wm⁻¹k⁻¹ at room temperature and decreases to 0.46 Wm⁻¹k⁻¹ at 773 K. With such a small thermal conductivity, this material can be a promising thermoelectric material. The low thermal conductivity is due to its complex 3D structure consisting of interconnected Bi₂Te₃ and CdI₃ type fragments.

2.2. Phonon-phonon interaction and anharmonicity
Phonon-phonon interaction is the primary process for reducing the mean free path of phonons and inducing phonon scattering at high temperatures. There are two types of phonon-phonon interactions: a normal operation in which the total momentum is conserved and Umklapp process in which the whole momentum is not conserved. To attain low thermal conductivity, all the phonon scattering processes must be employed. Umklapp process is the dominating scattering process at high temperatures and at such temperatures lattice thermal conductivity takes the form

\[ K_\parallel \propto \frac{MV^3\theta_D^3}{T^5T} \]

Where M denotes average mass per atom, V is the average atomic volume, \( \theta_D \) is the Debye temperature, and \( \gamma \) is the Grüneisen parameter which is the measure of anharmonicity of lattice vibrations and is given by \( \gamma = \frac{\alpha_K\theta_D}{C_v\rho} \). Large \( \gamma \) is the condition for small \( K_\parallel \) and is observed in materials with large thermal expansion coefficient, isothermal bulk modulus and having low density. Also, significant anharmonicity (sizeable nonlinear dependence of restoring force on the atomic displacement) is the key for large \( \gamma \) which is generated by weak bonding and heavy elements. Large anharmonicities are observed in complex crystal structures with large primitive cells and thus lowering \( K_\parallel \).
Lattice thermal conductivity is proportional to specific heat $C_v$, which can be reduced in materials containing liquid like ions like in ionic conductors. Ionic conductors comprise molten sublattice (apart from the solid sublattice) in which atoms can move freely throughout. Specific heat $C_v$, in solid materials can be reduced to the liquid limit by introducing the unique structural characteristics of ionic conductors thereby increasing complexity in the crystal. This concept is called the Phonon-Liquid Electron-Crystal (PLEC) which is used to explain the low thermal conductivity and high thermoelectric performance of Cu based thermoelectric materials [48–50]. PLEC is discussed in detail in section 3.3.

2.3. Reduction of specific heat $C_v$

The position of $L$ and $\Xi$ conductivity of either of the bands. To maintain the large value of total Seebeck coefficient $S$, the two bands need to be aligned so that the Seebeck coefficient is same in the two bands while the total conductivity is higher than the specific conductivity of either of the bands.

2.4. Effective mass and band engineering

Carrier mobility $\mu$ is inversely proportional to the band effective mass $m_{\text{band}}^*$ of the charge carriers [62]. Seebeck coefficient, on the other hand, is directly proportional to the density of states effective mass $m_{\text{DOS}}^*$ [40, 42]. $m_{\text{band}}^*$ and $m_{\text{DOS}}^*$ are related by the equation $m_{\text{DOS}}^* = N_v^{2/3} m_{\text{band}}^*$ [63]. Moreover, $m_{\text{band}}^*$ and $m_{\text{DOS}}^*$ act in opposite manners when it comes to enhance $zT$ because large $m_{\text{band}}^*$ (for flat bands) lowers the carrier mobility which in turn reduces electrical conductivity while large $m_{\text{DOS}}^*$ increases power factor. Thus, low $m_{\text{band}}^*$ is required to increase the thermoelectric performance of materials. Such an effect of band effective mass $m_{\text{band}}^*$ on the electrical properties is observed by the doping of n-type PbTe [64, 65, 65a] as is shown in figure 3.

The maximum $zT$ of the thermoelectric material is determined by its quality factor given by $B \propto \frac{N_v}{m_{\text{band}}^*} \frac{\tilde{\sigma}}{\tilde{\sigma}_1}$ [46, 63, 66, 67], which can have greater value for considerable band degeneracy $N_v$, low lattice thermal conductivity, small band effective mass $m_{\text{band}}^*$ and small deformation potential coefficient $\Xi$. A low deformation potential coefficient $\Xi$ is required for the weak scattering of charge carriers dominated by acoustic phonons [68–70] which enables high carrier mobility without affecting the Seebeck coefficient.

In case of the system with two valence bands having the Seebeck coefficient and conductivity of $S_1$, $\sigma_1$, and $S_2$, $\sigma_2$, respectively, the total Seebeck coefficient is given by $S = (\sigma S_1 + \sigma_2 S_2) / (\sigma_1 + \sigma_2)$ and the overall conductivity is given by $\sigma = \sigma_1 + \sigma_2$. As is already mentioned that with the increase in the number of carriers (n), conductivity increases and the Seebeck coefficient decreases. The total Seebeck coefficient is closer to the smaller value of $S$ for the two bands. To maintain the large value of total Seebeck coefficient $S$, the two bands need to be aligned so that the Seebeck coefficient $S$ is same in the two bands while the total conductivity is higher than the specific conductivity of either of the bands.

Complex or multi-band systems show greater band degeneracy as compared to single-band systems. Lead chalcogenides and their alloys are the examples of complex band systems consisting of two bands in which apart from principal valence band $L$ there exists another secondary valence band $\Sigma$ [68, 69] as is shown in figure 4(a). Band convergence or overlapping of light valence band $L$ and heavy valence band $\Sigma$ can increase the band degeneracy in lead chalcogenides which can be achieved by higher doping concentration. The position of $L$ and $\Sigma$ bands is the function of temperature. $L$ band lowers its position with the increase in
temperature keeping the position of $\sum$ band almost constant [69, 71] resulting in the convergence of these bands as is shown in figure 4(a). By converging L and $\sum$ bands, $N_v$ of these two bands add up to increase the total band degeneracy and hence increasing $B$ which leads to the increment in $zT$ as is shown in figure 4(c). Apart from band convergence, the high degeneracy of $\sum$ band also significantly improves the quality factor [71]. Band convergence can also be achieved in specific materials by increasing the crystal symmetry of the materials towards a more cubic arrangement [72]. In some cases, resonant levels are formed by the dopants merged with the valence band which increase the Seebeck coefficient $S$ especially at room temperature leading to the improvement in thermoelectric properties [73, 74] as is shown in figure 4(b). The electron resonant states strongly scatter the charge carriers and hence reduce the electronic mobility thereby reducing electrical conductivity. To benefit from the resonant states, the Seebeck coefficient must be so increased to overpower the damage done by the reduction of electrical conductivity.

2.5. Nano-tailoring

Thermoelectric performance can be enhanced significantly by the nanostructuring of thermoelectric materials. Nanostructures like nanowires, nanotubes, nanoforks, quantum wells, quantum dots, and superlattices show improved power factor and reduced thermal conductivity than their bulk counterparts. Nanostructuring can increase the thermoelectric performance by taking into account the two approaches. One is by strengthening the DOS near Fermi level via quantum confinement, improving the power factor [77–79]. Other approach is by the efficient scattering of phonons at grain boundaries because of their large mfp than electrons, hence decreasing the lattice thermal conductivity [44, 45, 47]. In case of nanostructured thermoelectric materials, lattice thermal conductivity is mainly reduced by the phonon–electron scattering mechanism which promotes the scattering of long wavelength heat-carrying phonons. To achieve the peak $zT$, nanostructured thermoelectric materials require high doping concentration. At the grain boundaries, low energy minority carriers are scattered more strongly than the high energy majority charge carriers resulting in the more moderate bipolar transition [80, 81]. Due to this effect, nanostructured thermoelectrics show higher Seebeck coefficient than their bulk counterparts at similar doping concentrations.

In case of 1D thermoelectric materials (nanowires), quantum confinement greatly enhances the thermoelectric performance as compared to their 2D variants [82, 83]. Nanotubes show lower thermal conductivity than nanowires due to the additional phonon scattering on inner and outer surfaces [82, 84, 85]. In case of rough wires, the phonon drag can result in the increment of thermopower which in turn enhances the thermoelectric performance [86]. Nanocomposites show better thermoelectric properties because of their low lattice thermal conductivity due to scattering of phonons at the interfaces between neighbouring nanoparticles, and power factor is also larger than the constituent phases [87]. In case of the thermoelectrics with nano-inclusions, Seebeck coefficient $S$ can be increased by energy filtering [54, 88].

Combining all the above discussed mechanisms, there has been a significant reduction in lattice thermal conductivity of thermoelectric materials since the last decade. Recently developed thermoelectric

![Figure 4](https://example.com/figure4.png)

Figure 4. (a) The Relative energy of the valence bands in PbTe$_{0.85}$Se$_{0.15}$. At 500 K the two valence bands converge, resulting in transport contributions from both the L and $\sum$ bands. C, conduction band; L, low degeneracy hole band; $\sum$, high degeneracy hole band. Adapted from [75] with permission from Springer Nature. (b), Schematic representation of the density of states of the principle valence band in PbTe (dashed line) contrasted to that of multi bands and resonant doping. The resonant states and multiple bands increase the density of states and the Seebeck coefficient. Adapted from [69] with permission from John Wiley and Sons. (c), $zT$ in p-PbTe, which according to the model calculation can be enhanced by this band convergence effect (L + $\sum$) when adequately doped, as compared with each band alone (L and $\sum$). Adapted from [76] with permission from Elsevier.
nanocomposites, copper based thermoelectric materials and tin chalcogenides show significantly low lattice thermal conductivity apart from complex material systems as is clear from figure 5.

The groups of thermoelectric materials to be discussed in this review article are summarized in table 1.

3. Thermoelectric materials

3.1. Caged compounds

The compounds with caged structures are better in showing the Phonon-Glass Electron-Crystal behaviour which focuses on conserving the electrical properties and reducing the lattice thermal conductivity. The typical caged compounds include Skutterudites and Clathrates. Both the families of caged compound possess cubic structure which favours good electronic transport. These compounds contain large voids in their framework. When these voids are filled with guest atoms, these act as independent oscillators. Due to the large size of the voids, these oscillators vibrate with the more substantial amplitudes than the atomic displacement of the structural atoms. This effect is called as rattling effect and due to this effect, the resonant modes of low frequency are formed. These resonant modes act as the traps for low-frequency phonons and hence decrease the lattice thermal conductivity. It is also believed that the resonant modes formed are high-frequency modes which actively interfere with the low-frequency phonon modes thereby diminishing the lattice thermal conductivity. The rattlers not only reduce the lattice thermal conductivity but also improve electrical conductivity due to their electro-positivity.

3.1.1. Skutterudites

These are the minerals with general formula TX₃ where T is the transition metal mainly Co, Rh or Ir and X is a pnictogen (group 15 element) primarily P, As or Sb. The structure of skutterudites is cubic with the space group Im3 which was first described by Oftedal in 1928. The binary skutterudite is filled by electropositive element A (rare-earth [91, 92], alkaline-earth [77, 93] or alkali metals [92, 94]) to form the ternary skutterudite A₂T₈X₂₄ which can also be described as the half of the unit cell AT₄X₁₂. The crystal structure of skutterudites is shown in figure 6(a). Skutterudites based on CoSb₃ are most studied because of the high mobility, low electrical resistivity, high atomic masses and good Seebeck coefficients [95, 96]. Despite having high power factor, CoSb₃ cannot achieve high zT due to its high lattice thermal conductivity [97, 98]. The lattice thermal conductivity is significantly reduced by filling the structural voids with appropriate filler elements. Filled antimonides have the smallest lattice thermal conductivity because of the more significant cage and due to these larger cages, the amplitude of vibration of a filled atom is stronger which in turn actively interferes with the acoustic phonons [99]. In case of CoSb₃ based skutterudites whether the atom or ion can serve as a filler or not, depends on the...
Table 1. Referenced table of families of thermoelectric compounds, including structures and information on Synthesis methods, Peak $zT$ with Temperature.

| Family of Thermoelectric compound | Structure | Synthesis method [Refs] | Example | Peak $zT$ (Range) | Temperature range (T) |
|-----------------------------------|-----------|-------------------------|---------|------------------|-----------------------|
| Skutterudites                     | TX, Cage type Structure | [1–12] | La$_{0.68}$Ce$_{0.22}$Fe$_{3.5}$Co$_{0.5}$Sb$_{12}$ (p-type), Li$_{0.08}$Ca$_{0.18}$Co$_{4}$Sb$_{12}$ (n-type), Ce$_{0.92}$Fe$_{4}$Sb$_{12}$ (p-type), La$_{0.29}$Co$_{4}$Sb$_{12}$ (n-type), Ca$_{0.31}$Co$_{4}$Sb$_{12}$ (n-type) etc. | 0.91–1.5 | 402–590 °C |
| Clathrates                        | [13–21] | K$_{6.5}$Ba$_{1.5}$Al$_{17}$ (type-I), (K,Sr)$_{24}$(Ga,Ge)$_{13.6}$ (type-II) Ba$_{8}$Cu$_{6}$Si$_{16}$Ge$_{24}$ (type-I), Ba$_{8}$Ni$_{0.1}$Zn$_{0.5}$Ga$_{13.8}$Ge$_{31.56}$ (type-II), Sr$_{7.92}$Ga$_{15.04}$Sn$_{0.35}$Ge$_{30.69}$ (type-I), Ba$_{8}$Cu$_{6}$Si$_{16}$Ge$_{24}$ (type-I), Ba$_{8}$Ga$_{16}$Ge$_{30}$ (type-I), etc. | 0.4–1.14 | 317–627 °C |
| Type I and Type II                |           |                         |         |                  |                       |
| Binary chalcogenides              | Layered Structure | [22 (a–f), 159 (c, d)] | Bi$_{2}$Se$_{3}$, Bi$_{2}$Te$_{2}$Se$_{0.3}$BiSbSe$_{3}$, Bi$_{0.5}$Sb$_{1.5}$Te$_{3}$ Bi$_{2}$Te$_{2}$(TeSe)$_{3}$, Bi$_{2}$Te$_{2}$S$_{0.15}$Bi$_{0.6}$Sb$_{1.6}$Te$_{3}$/ZnO etc. | 0.87–1.4 | 50–527 °C |
| Family of Thermoelectric compound | Structure | Synthesis method [Refs] | Example | Peak $zT$ (Range) | Temperature range (T) |
|-----------------------------------|-----------|-------------------------|---------|------------------|----------------------|
| Copper Based                      | [23]      | Cu$_{1.26}$Ni$_{0.01}$Se$_{1.15}$, Li$_{0.01}$Cu$_{1.3}$Se, Na$_{0.01}$Cu$_{0.9}$S, Cu$_{1.85}$Ag$_{0.15}$Sn$_{0.9}$In$_{0.1}$Se$_{3}$, Cu$_2$Se$_{0.98}$Te$_{0.02}$, Cu$_2$Se$_{0.95}$S$_{0.05}$, Cu$_2$Se/CNTs hybrid, Bi$_{0.95}$Sb$_{0.05}$Cu$_{0.9}$TeO etc. | 0.73–2.4 | 500–727 °C |
| Lead Chalcogenides                | [24–26]   | Pb$_{0.98}$Bi$_{0.02}$Te | Pb$_{0.94}$Se$_{0.06}$, Pb$_{0.95}$Bi$_{0.05}$, Mg$_{0.97}$Pb$_{0.02}$Te$_{0.98}$Se$_{0.02}$, Pb$_{0.98}$In$_{0.02}$Te$_{0.98}$Se$_{0.02}$, Na$_{0.02}$Bi$_{0.98}$Pb$_{0.02}$Te$_{0.98}$Se$_{0.02}$, Pb$_{0.95}$Sn$_{0.05}$Te$_{0.94}$Se$_{0.06}$, etc. | 0.83–2.2 | 352–547 °C |
| Family of Thermoelectric compound | Structure | Synthesis method [Refs] | Example | Peak zT (Range) | Temperature range (T) |
|-----------------------------------|-----------|-------------------------|---------|----------------|----------------------|
| Tin chalcogenides                 | [27–31 (a)] | Bi doped SnSe (single crystal), Na doped SnSe (Single crystal and polycrystalline), SnSe + 1% PbSe (polycrystalline), SnSe0.92Ge0.08Se (polycrystalline), Zn0.01Sn0.99Se (polycrystalline), SnSe0.9Te0.1 (polycrystalline), Sn0.96Ga0.04Te, SnCd0.03Te/Cds SnCd0.01Te/Zns etc. |         | 0.6–2.2 | 27–600 °C       |
| Oxides                            | [32, 33]  | Ca2.95Tb0.5Co4O9, Porous Ca3TiO3, Bi1.3Phb2.2Zr2Co4O10, SrTiO3, Cds0.98Ni0.02O, Zn0.99Cd0.01O, Sr1−3x/2La3TiO3+δ, etc. |         | 0.3–0.74 | 377–900 °C      |
| MgX compounds                     | [34, 35]  | MgSi3.8Si0.2Si0.2B1.03, Mg2.6Si1.4Sn0.29B1.03, Mg2Si0.8Sn0.29B1.02, Mg2Si0.8Sn0.4Ge0.06B1.02, Mg2Si1.37Sn0.6Ge0.3Sn0.125, MgSi0.7Si0.3B1.05Ge0.25 etc. |         | 1.0–1.4 | 400–600 °C      |
Table 1. (Continued.)

| Family of Thermoelectric compound | Structure | Synthesis method [Refs] | Example | Peak $zT$ (Range) | Temperature range (T) |
|-----------------------------------|-----------|-------------------------|---------|------------------|----------------------|
| Half-Heusler alloys              |           | [36–38]                 | FeNb$_{0.8}$Hf$_{0.2}$Sb, FeNb$_{0.8}$Hf$_{0.2}$Sb, FeNb$_{0.8}$Hf$_{0.2}$Sb, Zr$_{0.25}$Hf$_{0.25}$Ti$_{0.5}$NiSn$_{0.99}$Sb$_{0.006}$, FeNb$_{0.8}$Hf$_{0.2}$Sb, Zr$_{0.25}$Hf$_{0.25}$Ti$_{0.5}$NiSn$_{0.99}$Sb$_{0.006}$, FeNb$_{0.8}$Hf$_{0.2}$Sb, Zr$_{0.25}$Hf$_{0.25}$Ti$_{0.5}$NiSn$_{0.99}$Sb$_{0.006}$, FeNb$_{0.8}$Hf$_{0.2}$Sb, Zr$_{0.25}$Hf$_{0.25}$Ti$_{0.5}$NiSn$_{0.99}$Sb$_{0.006}$ | 0.83–1.5 | 500–927 °C |
The electronegativity difference between the filler and the Sb atom of the framework. Thermodynamically most stable filled skutterudites are the ones in which the electronegativity difference falls in the range $>0.8$ [100, 101]. $zT$ of CoSb$_3$ is enhanced from 0.5 for unfilled to 1.2 for partially filled CoSb$_3$ due to the reduction in lattice thermal conductivity and improved electrical conductivity [77, 102]. The lattice thermal conductivity is reduced in filled skutterudites by the formation of Einstein-like vibrational modes arising due to the weak bonding between fillers and Sb atoms of skutterudite framework, thereby scattering the normal phonon modes of the structure having similar energies [77, 103]. The vibrational frequencies depend on the type of fillers in the cages and it was found that the rare-earth metals possess weakest vibrational frequencies followed by the alkaline-earth metals which yield medium frequencies and the highest vibrational frequencies are maintained by alkali metals [104].

By introducing filler atoms in the cages, lattice thermal conductivity is reduced and this reduction can further be increased by adding two or more filler atoms of different vibrational frequencies which will help in the significant increase of $zT$ like in multi filled skutterudites Ba$_{0.08}$La$_{0.05}$Yb$_{0.04}$Co$_4$Sb$_{12}$ with the enhanced $zT$ of 1.7 at 577 $^\circ$C [105]. Recently it was found that $zT$ is improved in p-type skutterudites due to coherency strain fields arising from spinodal decomposition [107]. The lattice thermal conductivity is reduced due to phonon scattering through coherency strain field keeping the electrical conductivity unchanged. The Seebeck coefficient is increased due to increase in the density of states near Fermi level which is expected to happen because the coherency strain field is in the state of tension. Due to this, the enhanced $zT$ of 1.2 is obtained for multi-filled p-type La$_{0.8}$Ti$_{0.1}$Ga$_{0.1}$Fe$_5$CoSb$_{12}$ [107].
Table 2. Reported synthesis method and peak zT values of Skutterudites.

| Compound | zT   | T (°C) | Method of preparation |
|----------|------|--------|-----------------------|
| La0.08Ce0.24Fe3.5Co0.5Sb12 | 1.15 | 475 | Melting-quenching-annealing-ball milling-dc hot pressing method |
| Li0.08Ca0.18Co4Sb12 | 1.18 | 427 | High pressure synthesis method |
| Ce0.25Fe2CoSb12 (Co free) | 0.91 | 490 | High pressure synthesis method |
| La0.29Co4Sb12 | 1.06 | 590 | High pressure synthesis method |
| Ca0.31Co4Sb12 | 1.15 | 567 | High pressure synthesis method |
| Al0.15Yb0.25Co4Sb12 | 1.36 | 577 | Mechanical alloying, spark plasma sintering |
| Yb0.15Co4Sb12 (n-type) | 1.5 | 577 | Melting-quenching-annealing-sintering method |
| (Ga0.05In0.20)0.1Co4Sb12 | >1.1 | 402 | Direct reactions |
| Ce0.25Yb0.25Fe3.25Co0.75Sb12 (p-type) | 0.93 | 550 | Mechanical alloying |
| In0.5Co4Sb12 | 1.5 | 452 | Induction Melting process |
| Nd0.8Yb0.2Co4Sb12 (p-type) | 1.02 | 487 | Induction Melting process |
| Ce0.25Fe3.25Ni0.25Sb12 | 1.0 | 500 | Vacuum melting method |
| Te0.1 (Co free) |  (p-type) | | |

The lattice thermal conductivity is also reduced by the nano-inclusion in skutterudites forming skutterudite nanocomposites. This is another efficient way to enhance zT of skutterudites. Zong et al reported that in skutterudite/graphene nanocomposite, the lattice thermal conductivity is reduced due to increase in the grain boundaries [108]. zT of 1.5 was observed in n-type Yb0.25Co4Sb12, and zT of 1.06 was found in p-type Ce0.25Fe2CoSb12 by introducing multilayer graphene into grain boundaries of these skutterudites [108]. zT of 1.0 was achieved in In0.04Co4Sb12–(InSb)0.05 nanocomposite at 575 K which is highest for cobalt skutterudites at T ≤ 575 K containing single filler of In because of the reduced thermal conductivity and high electrical conductivity as compared to pristine Co4Sb12 [109]. Lattice thermal conductivity is reduced due to high phonon scattering at the InSb nano-inclusions, and electrical conductivity is increased due to the high mobility of InSb [109], Khan et al reported a porous architecture of skutterudites containing nano- to micro-sized, irregularly shaped and randomly oriented phonons to scatter a broad spectrum of phonons without employing the conventional rattling structure hence the zT of 1.6 was obtained in the nano-micro porous architecture Co23.4Sb69.1Si1.5Te6 alloy which is highest reported for any un-doped skutterudite [106]. Methods of preparation and peak zT of skutterudites is summarized in table 2.

3.1.2. Clathrates

Clathrate structure consists an open framework with voids similar to skutterudites filled by some guest fillers which act as rattlers and help in reducing lattice thermal conductivity [53]. Clathrates contain Al, Si, Ga, Ge, Sn, etc, atoms which are tetrahedrally coordinated with cages of different sizes. These cages are large polyhedrons having at least 12 faces and 20 vertices, hence making clathrates a unique class of compounds. The atoms are situated in the vertices of these polyhedra. There are various types of clathrates such as clathrate-I, clathrate-II, clathrate-III, clathrate-VII, clathrate-VIII, clathrate-XI and twisted clathrates out of which, only clathrate-I to clathrate-VII are true clathrates. The clathrates are classified according to the shape and number of cages. Clathrate-I and clathrate-II are the main types of clathrates having the crystal structures as shown in figures 7(a), (b). Clathrate-I consist of two polyhedra packed in a cubic arrangement and majority of these clathrates have the space group Pm3n. The clathrate-I structure is most accomplished for anionic and cationic clathrates and is represented by the formula 

\[ \text{U}_2\text{V}_6\text{E}_{136} \]

U and V being the guest atoms which can be of more than one type (like Na, K, Rb, Cs, Ba, Sr, Ca, Cl, Br, I, Eu, P, Te, Li, Mg), X can have the values between 0 to 24 and E represents Si, Ge, Sn, Al, Ga etc. X = 0 means no guest atom is present in the cage which is the unique property of the clathrate-II structure. This type of clathrate structure also allows partial filling of polyhedra, unlike Clathrate-I structure which favors only complete filling. Due to the partial filling, the electrical properties of clathrate-II can be readily adjusted [111]. Method of preparation and peak zT of clathrates is summarized in table 3.
3.2. Binary chalcogenides

Binary chalcogenides like bismuth telluride, bismuth selenide, antimony telluride and their alloys have the reputation of being the efficient thermoelectric materials at room temperature and are widely used for thermoelectric refrigeration. In the moderate temperature range of heat source, these materials can also be used in thermoelectric generators. Out of all the binary chalcogenides, Bi₂Te₃ and its alloys are mostly used for thermoelectric applications because of their efficiency over other binary chalcogenides. The crystal system of Bi₂Te₃ possesses layered hexagonal structure consisting of the quintuple layers of mostly covalently bonded Te(1)-Bi-Te(2)-Bi-Te(1) layer with adjacent layers connected by weak van der Waals bonds [77, 82] as is shown in Figure 7.

Figure 7. (a) Crystal structure of the type-I clathrates. The framework atoms are represented by the red spheres and guest atoms are represented by yellow spheres. Adapted from Ref.[111a] with permission from Elsevier. (b) Crystal structure of the type-II clathrates. The framework atoms are represented by the darker spheres and guest atoms are represented by the lighter spheres. Adapted from Ref.[111b] with permission from Elsevier. (c) Temperature dependence of zT for Ba₈Ga₁₆Ge₃₀ samples synthesized at a different pressure [19]. Adapted with permission from (Sun, B, Jia, X, Huo, D, Sun, H, Zhang, Liu, B, Y, Liu, H, Kong, I, Ma, H The Journal of Physical Chemistry C, 120(18), 10104–10110 (2016) American Chemical Society. (d) Temperature dependence of zT for recently developed efficient clathrate thermoelectric [15, 17–20].

Table 3. Synthesis method and peak zT values of clathrates.

| Compound                  | zT  | T (°C) | Method of preparation                           | References       |
|---------------------------|-----|-------|------------------------------------------------|------------------|
| K₉Ba₂Al₅Se₂₂ (type-I)     | 0.4 | 600   | Solid state reactions at high temperature       | [13]             |
| (K,Sr)₂(Ga,Ge)₃₆ (type-II)| 0.43| 527   | Arc-melting, ball milling, spark plasma sintering| [14]             |
| Ba₇Y₁₄Se₁₀₃Ge₁₅₁₃.₅Ge₃₁₃₈ (type-II)| 0.91| 627 | High pressure synthesis method                   | [15]             |
| Ba₅Cu₃(Si,Ge,Sn)₁₈ (type-I)| 0.43| 500  | Melt spinning method                             | [16]             |
| Sr₇Ga₁₅₁₄Sn₉₀₅Ge₃₀₁₈ (type-I)| 1.0 | 477 | Sn-flux method                                   | [17]             |
| Ba₅Cu₃Si₁₈Ge₂₄ (type-I)   | 0.55| 400  | High pressure High temperature method            | [18]             |
| Ba₅Ga₃Ge₃₀ (type-I)       | 1.14| 500  | High pressure High temperature method            | [19]             |
| K₉Ba₂Al₆Sn₉₈ (type-II)    | 0.57| 317  | Direct melting, spark plasma sintering          | [20]             |
| K₉Ba₂Al₅Ge₉₇Se₇ (type-II) | 0.82| 367  | Direct melting, spark plasma sintering          | [20]             |
| Ba₅Cu₃Ge₁₈Si₁₈ (type-II)  | 0.43| 500  | High pressure High temperature method            | [21]             |
in Figure 8(a). Hence the intra-layer interactions are much stronger than inter-layer interactions. The electrical and thermal conductivities of bismuth telluride alloys are of anisotropic nature. Along the cleavage planes, lattice thermal conductivity is $1.5 \text{ Wm}^{-1}\text{K}^{-1}$ which is twice that of the lattice thermal conductivity in the perpendicular direction $^{[112, 113]}$ and resistivity along the cleavage plane is less than the resistivity along perpendicular direction by a factor of 3–4 at room temperature $^{[77]}$. In Bi$_2$Te$_3$, the minority charge carriers cannot be completely neglected because the energy gap of Bi$_2$Te$_3$ is only 5KT at 27°C and hence the minority carriers make a large contribution to thermal conductivity because of the bipolar effect $^{[114]}$. Moreover, the thermoelectric coefficients of minority and majority carriers are of opposite signs. This results in the reduction of Seebeck coefficient and hence for this reason, the minority carriers are unacceptable. Doping can minimize the effects of minority carriers in Bi$_2$Te$_3$ but the electronic thermal conductivity is also going to increase with the increase in doping concentration. Moreover, Bi$_2$Te$_3$ based alloys possess the excellent electronic transport properties despite being anisotropic because of the multi-valley nature of the band structure. On the other hand, tellurium is regarded as the high performance elemental thermoelectric due to the presence of the original band nesting which enables a large number of effective band valley degeneracy $^{[115]}$, which might be the possible reason for excellent thermoelectric performance of Bi$_2$Te$_3$ based thermoelectric materials. Ball milling and sintering techniques are commonly employed to produce Bi$_2$Te$_3$ based alloys with high efficiency. But during this process, oxygen inclusion takes place in the lattice, which results in the degradation of thermoelectric properties. To overcome this problem, Seo et al carried out annealing in hydrogen atmosphere to remove the dissolved oxygen due to which the hole concentration is increased thereby increasing the electrical conductivity.
and 18.2% increase in zT for hydrogen annealed samples of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ is reported as compared to the non-annealed sample [116]. Chiu et al. reported zT of Sb$_{1.5}$In$_{0.1}$Te$_3$ raised to 0.92 at 600 K showing up to 84% enhancement prepared via spark plasma sintering [117]. The enhancement in zT is based on the principle that the optimal sintering temperature coincided with the temperature at which the maximum Seebeck coefficient begins to degrade whereas the optimal sintering pressure coincided with the pressure at which the ratio of electrical conductivity to the total thermal conductivity reached the maximum value [117]. High ZT of 1.86 ± 0.15 was observed for Bi$_{0.5}$Sb$_{1.5}$Te$_3$ samples synthesized via meltspun process followed by spark plasma sintering [117a]. Such high zT is due to the formation of dense dislocation arrays at the grain boundaries which effectively scatter phonons in the mid-frequency range resulting in the drastic reduction of lattice thermal conductivity[117a], Zhang et al reported zT values of 1.59 ± 0.16 for p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ and 0.98 ± 0.07 for n-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ via liquid phase sintering[117b]. Excess Te enabled liquid phase sintering in spark plasma sintering process reduces the lattice and bipolar contribution to the thermal conductivity without affecting the power factor and hence resulting in the increment in zT value [117b].

Nanoinclusion in bulk materials also helps to scatter phonons and decreases the lattice thermal conductivity. Jiang et al. reported the nano-inclusion of n-type ZnO in p- and n-type Bi$_2$Te$_3$ [119]. ZnO is an intrinsic n-type semiconductor with low thermal conductivity. In case of n-type Bi$_2$Te$_3$, ZnO reduces carrier concentration, and hence resistivity is increased. In case of p-type Bi$_2$Sb$_{0.5}$Te$_3$, the lattice and total thermal conductivity is decreased and due to the decrease in thermal conductivity, zT reached the value of 1.3 [119]. Li et al. reported that the thermoelectric nanocomposite of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ incorporated with graphene nanosheets reached the zT value of 1.29 at 300 K and 1.54 at 440 K [118]. These values were obtained in Bi$_{0.4}$Sb$_{1.6}$Te$_3$ incorporated with only 0.3 vol% and 0.4 vol% graphene nanosheets. The Seebeck coefficient S increases with increase in temperature and after reaching a maximum value, it decreases with further increase in temperature. This behavior is due to the thermal excitation of minority carriers at high temperature. S also decreases with increase in the graphene nanosheet content [118]. Li et al. reported zT of 0.55 in Bi$_2$Te$_3$/GQDs (GQDs: Graphene Quantum Dots) hybrid nanosheets at 425 K [120]. This value of Bi$_2$Te$_3$/GQDs~20 nm is the higher than that of Bi$_2$Te$_3$ without hybrid nanostructures. Tang et al. reported that highest power factor of the MoS$_2$/Bi$_2$Te$_3$ nanocomposite of 18.3 μW cm$^{-1}$K$^{-1}$ which is about 30% higher than that of the pristine Bi$_2$Te$_3$ sample at 319 K achieved from a nanocomposite sample containing 6 wt% MoS$_2$ [121]. The MoS$_2$/Bi$_2$Te$_3$ composite sample has more compact microstructure than the pristine Bi$_2$Te$_3$ bulk sample. At a given temperature, the electrical conductivity of the composite increases first and then decreases as the MoS$_2$ content increases. This increase in electrical conductivity is due to more compact microstructure and well-grown grains. Out of all the MoS$_2$/Bi$_2$Te$_3$ nanocomposites, the nanocomposite in which the amount of added MoS$_2$ nanosheets is 17 wt% has the electrical conductivity lower than pristine Bi$_2$Te$_3$. It is because the MoS$_2$ grains form percolation networks in this sample which significantly lowers the electrical conductivity [121].

zT can also be increased up to 2–3 times in Bi$_{2}$Te$_{3}$-Sb$_{2}$Te$_{3}$ superlattices [122–124] and also in Bi$_2$Te$_3$ nanowires and nanoribbons [125]. Nano-particles based Bi$_{2}$Ge$_{1.2}$Te$_{1.8}$ thin films have the highest reported ZT of 2.75 [126]. Hong et al. reported ZT of 1.23 in n-type Bi$_{2}$Te$_{2.5}$Se$_{0.5}$ nanplates at 480 K synthesized via microwave assisted surfactant free solvothermal method [22]. Peak ZT and method of preparation of binary chalcogenides is summarized in table 4.

### 3.3. Copper-based thermoelectrics

Copper-based compounds are considered efficient thermoelectric materials and because of the abundance of copper in nature these have attracted considerable interests in thermoelectric applications [127]. The thermal conductivity of copper-based materials is low because of the liquid like behavior of copper ions. The heat conductivity of crystalline materials is usually very high because of the long mean free path of phonons in the periodic structure. The lattice heat conductivity can be reduced by introducing the scattering centres in the crystal structure as is already discussed. Due to this, lattice thermal conductivity is reduced to the glass limit only.

| Compound | zT | T     | Method of preparation                  | References |
|----------|----|-------|---------------------------------------|------------|
| Bi$_2$Te$_2$Se$_{0.5}$ | 1.23 | 207 °C | Microwave assisted surfactant-free solvothermal method | [22] |
| Bi$_2$Sb$_{1.5}$Te$_3$ | 1.48 | 102 °C | Solution chemical synthesis, liquid phase sintering | [22a] |
| Sb$_2$Te$_3$ | 1   | 250 °C | Solvothermal method                  | [22b] |
| BiSbTe$_3$ | 1   | 527 °C | Solid state reactions method         | [22c] |
| Bi$_2$Sb$_{1.5}$Te$_3$/ZnO | 1.21 | 100 °C | Mechanical alloying, plasma activated sintering | [22d] |
| Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ | 1.1  | 200 °C | Mechanical alloying, Spark plasma sintering | [22e] |
| Bi$_{0.4}$Sb$_{1.6}$Te$_3$ | 0.875 | 50 °C | Ball milling, Spark plasma sintering | [22f] |
| Bi$_2$Se$_3$ | 0.96 | 97 °C  | Vacuum melt method, hot pressing       | [22g] |

Table 4. Method of preparation and peak zT values of binary chalcogenides.
The lattice thermal conductivity can be reduced below the glass limit by eliminating some of the vibrational modes entirely which are responsible for the propagation of heat in crystalline solids. Transverse and shear vibrations are responsible for heat propagation in case of solid glass, but shear vibrations are not present in liquids\cite{128,129}. So by introducing fluid like behavior of some ionic conductors, the lattice thermal conductivity can be reduced below the glass limit. This concept is referred to as the phonon-liquid electron-crystal (PLEC) and can be considered as the extension of the concept phonon-glass electron-crystal (PGEC).

Also, the lattice thermal conductivity of solids is proportional to the specific heat as is mentioned earlier. Specific heat in the solid glass is usually constant and in liquids it is less than that of solids. By introducing the liquid-like behaviour in solids, the specific heat is reduced from $3NKB$ to $2-2.5NKB$ because the propagation of most transverse vibrational modes is hindered in liquids which in turn reduces the lattice thermal conductivity\cite{128–130}. As shown in figure 9(d). For a typical PLEC thermolectric Cu$_2$Se, the value of specific heat falls in the range between that of solid and a liquid because of the partial liquid behaviour due to the presence of liquid like copper ions which also gives the extra boost to scatter the lattice phonons to disrupt the further heat propagation\cite{50,131}. The crystal structure of Cu$_2$Se is shown in figure 9(a). Copper-based thermolectric are classified in various material systems termed as diamond-like compounds, superionic conductors, tetrahedrites, and oxyselenides. Copper-based diamond-like compounds are composed of tetrahedrally coordinated constituent elements which can be a ternary like Cu$_2$SnSe$_3$ or a quaternary like Cu$_2$ZnSn$_{0.9}$In$_{0.1}$Se$_4$. Cu$_2$SnSe$_3$ is a typical ternary copper based diamond-like compound, and its Indium doped variant is reported to have $zT$ of 1.14 at 850 K\cite{132}. The quarternary copper based diamond-like compound Cu$_2$ZnSn$_{0.9}$In$_{0.1}$Se$_4$ has $zT$ of 0.95 at 850 K\cite{133}. Most of the diamond-like compounds possess a large band gap and hence were not considered for the thermoelectric performance because usually, the efficient thermoelectric materials have narrow band gap\cite{134}. But high $zT$ of 0.95 in Cu$_2$ZnSn$_{0.9}$In$_{0.1}$Se$_4$ despite having large band gap opened a window to search for the lattice thermal conductivity of solids is proportional to the specific heat as is mentioned earlier. Specific heat in the solid glass is usually constant and in liquids it is less than that of solids. By introducing the liquid-like behaviour in solids, the specific heat is reduced from $3NKB$ to $2-2.5NKB$ because the propagation of most transverse vibrational modes is hindered in liquids which in turn reduces the lattice thermal conductivity\cite{128–130}. As shown in figure 9(d). For a typical PLEC thermolectric Cu$_2$Se, the value of specific heat falls in the range between that of solid and a liquid because of the partial liquid behaviour due to the presence of liquid like copper ions which also gives the extra boost to scatter the lattice phonons to disrupt the further heat propagation\cite{50,131}. The crystal structure of Cu$_2$Se is shown in figure 9(a). Copper-based thermolectric are classified in various material systems termed as diamond-like compounds, superionic conductors, tetrahedrites, and oxyselenides. Copper-based diamond-like compounds are composed of tetrahedrally coordinated constituent elements which can be a ternary like Cu$_2$SnSe$_3$ or a quaternary like Cu$_2$ZnSn$_{0.9}$In$_{0.1}$Se$_4$. Cu$_2$SnSe$_3$ is a typical ternary copper based diamond-like compound, and its Indium doped variant is reported to have $zT$ of 1.14 at 850 K\cite{132}. The quarternary copper based diamond-like compound Cu$_2$ZnSn$_{0.9}$In$_{0.1}$Se$_4$ has $zT$ of 0.95 at 850 K\cite{133}. Most of the diamond-like compounds possess a large band gap and hence were not considered for the thermoelectric performance because usually, the efficient thermoelectric materials have narrow band gap\cite{134}. But high $zT$ of 0.95 in Cu$_2$ZnSn$_{0.9}$In$_{0.1}$Se$_4$ despite having large band gap opened a window to search for

Figure 9. (a) The unit cell of cubic Cu$_2$Se β-phase where only the 8c and 32f interstitial positions are shown with Cu atoms. (b) Projected plane representation of the crystal structure along the cubic [100] direction. The arrows indicate that Cu ions can freely travel among the interstitial sites. Reprinted from [30] with permission from Springer Nature. (c), (d) show the diagram of phonon density of state and specific heat in liquid-like materials, respectively. The transverse phonons are softened and disappeared when the frequency is below the cut off frequency in liquid-like materials, leading to reduced $C_v$ values. Reprinted from [130] with permission from Elsevier. (e) Temperature dependence of $zT$ for Cu$_2$Se/x% wt. CNT’s ($x=0,0.25,0.5,0.75$). Adapted from [23f] with permission from The Royal Society of Chemistry. (f) Temperature dependence of $zT$ for recently developed efficient Cu-based thermolectric\cite{23,137a,23b,23e,23f,23g}.
high-performance thermoelectric materials in semiconductors possessing large band gaps [133]. Ma et al reported that $zT$ is enhanced in un-doped ternary $\text{Cu}_2\text{SnSe}_3$ with SnSe$_2$ secondary phase up to the value 0.84 at 773 K which is 50% more than that of single phase un-doped $\text{Cu}_2\text{SnSe}_3$ having $zT$ of 0.42 at 773 K [135]. Liu et al reported $zT$ of 1.24 in quarternary $\text{Cu}_{0.75}\text{Ag}_{0.2}\text{InTe}_2$ and such high $zT$ is due to the presence of multiple degenerate valence bands which influence the transport of electrons significantly. Moreover, a significant anharmonicity is brought up in the crystal structure due to Ag doping which further reduces the lattice thermal conductivity [136].

Superionic conductors are solids having ionic conductivities as high as found in molten salts [130]. Copper-based superionic compounds can be binary like $\text{Cu}_2\text{Se}$ and ternary like $\text{CuCrSe}_2$. $\text{Cu}_2\text{Se}$ consists of two different sub-lattices inside its crystal structure [50]. The Se atoms form a rigid sub-lattice favoring the electronic transport, and the copper sub-lattice exhibits liquid-like character which is responsible for the reduction of lattice thermal conductivity and thereby an increase in $zT$ up to 1.5 was reported at 1000 K [50]. The $zT$ value of 2.1 was reported in $\text{Cu}_2\text{Se}$ at 973 K prepared via ball milling method followed by spark plasma sintering and such high $zT$ is due to the record low thermal conductivity of 0.34 W/m$^\circ$K. Such low thermal conductivity is because of the enhancement in scattering of phonons of wide range of wavelengths by different kinds of defects generated during ball milling process [137]. Zhu et al reported $zT$ of 1.9 in $\text{Cu}_2\text{S}_0.5\text{Te}_{0.5}$ which is attributed to the formation of nanostructures in the crystal structures [138]. Enhancement in $zT$ of $\text{Cu}_2\cdots\text{Se}$ and its composites are reported by the inclusion of $\text{Cu}_2\text{S}$ nanosheets in $\text{Cu}_2\cdots\text{Se}$ matrix [139]. This enhancement is due to the simultaneous improvement of Seebeck coefficient because of the external strain induced by $\text{Cu}_2\text{S}$ nanoinclusion in $\text{Cu}_2\cdots\text{Se}$ matrix and decline of the total thermal conductivity by suppressing both electronic and lattice thermal conductivities. For the composite structure with 10 wt% nano inclusion of $\text{Cu}_2\text{S}$, the gain in Seebeck coefficient and the decline in thermal conductivity is largely resulting in the higher $zT$ value of 0.90 at 773 K [139]. This composite material is a promising material in the mid-temperature range energy harvesting applications. Tetrahedrite is a natural mineral having the base composition $\text{Cu}_1\_{12}\text{Sb}_4\text{S}_{13}$ having low thermal conductivity mainly due to the unique crystal structure. The maximum $zT$ reported in $\text{Cu}_1\_{12}\text{Sb}_4\text{S}_{13}$ tetrahedrite system so far is around 1 at 700 K [140, 141].

The oxyselenide $\text{BiCuSeO}$ is a copper-based oxide system which has gained considerable attention in recent years because it is considered a promising p-type thermoelectric material. The crystal structure of $\text{BiCuSeO}$ is shown in figure 10(a). Pristine $\text{BiCuSeO}$ has very low electrical conductivity of around $5 \times 10^2$ s m$^{-1}$ at 300 K [142]. To increase the electrical conductivity, $\text{BiCuSeO}$ is doped with various elements at Bi-sites. In doped samples, the electrical conductivities were enhanced up to two orders of magnitude as compared to pristine $\text{BiCuSeO}$ thereby improving $zT$ in doped samples. $zT$ of 1.4 was reported in Ba-doped $\text{BiCuSeO}$ at 923 K [143]. Lan et al reported the ultrafast and low-cost fabrication of $\text{BiCuSeO}$ in less than 20 min through self-propagating high-temperature synthesis combined with spark plasma sintering method [144]. They also reported high $zT$ up to 0.70 in $\text{Bi}_{0.85}\text{Na}_{0.15}\text{CuSeO}$ at 873 K which is about 100% higher than pristine $\text{BiCuSeO}$ [144]. Das et al reported $ZT$ of 1.09 in parent $\text{BiCuSeO}$ which is higher than its Sn doped variant $\text{Bi}_{0.96}\text{Sn}_{0.04}\text{CuSeO}$ [23]. This is due to the presence of thermally conducting $\text{SnO}_2$ secondary phase in the doped sample because of which the
3.4. Lead chalcogenides

Lead chalcogenides like (PbTe, PbSe, and PbS) and their derivatives are among the most promising thermoelectric materials in the mid-temperature range. The band gaps of PbTe, PbSe and PbS are 0.29, 0.27 and 0.37 eV respectively. Among these lead chalcogenides, PbTe is considered the best candidate for thermoelectric applications. The crystal structure of PbTe is shown in figure 11(a). PbTe based thermoelectric materials are the efficient thermoelectric materials in the temperature range of 500–900 K [76, 145] which is because of its two-valence band structure. A first light hole L band and a secondary lower-lying heavy hole $\Sigma$ band are present having the energy difference of 0.15–0.20 eV [68] as is shown in figure 11(b). PbTe is being used as thermoelectric material since 1960’s, and back then its figure of merit was believed to be 0.8 [76]. But according to recent studies, it is found that the intrinsic figure of merit of both n- and p-type PbTe materials is 1.4 [145]. PbTe has low thermal conductivity which may be due to many factors. In case of PbTe, the Umklapp process in overall thermal conductivity increases and thereby decreasing zT [23]. Method of preparation and peak zT values of Cu-based thermoelectric is summarized in table 5.

### Table 5. Peak ZT values of Cu-based thermoelectric and the synthesis methods.

| Compound                  | zT     | T (°C) | Method of preparation                                      | References |
|---------------------------|--------|--------|------------------------------------------------------------|------------|
| Cu$_{1.99}$Ni$_{0.01}$Se  | 1.51   | 550    | Conventional melting, ball milling and Spark plasma sintering | [23a]      |
| k$_{0.99}$Cu$_{0.01}$Se   | >1.4   | 727    | Ball milling, Mechanical alloying                           | [23b]      |
| Na$_{0.05}$Cu$_{0.95}$S   | 1.1    | 500    | Mechanical alloying                                        | [23c]      |
| Cu$_{0.95}$Nd$_{0.05}$Se  | 1.42   | 550    | Mechanical alloying, one step method of combustion synthesis | [23d]      |
| Cu$_{2}$Se$_{0.05}$Te$_{0.95}$ | 1.76 | 577    | Hydrothermal method, Spark plasma sintering                | [23e]      |
| Cu$_2$Se/CNTs hybrids     | 2.4    | 727    | Ball milling                                               | [23f]      |
| Bi$_{0.05}$Sb$_{0.95}$CuSeO | 0.73  | 600    | Mechanical alloying                                        | [23g]      |

Figure 11. (a) The Crystal structure of PbX ($X = \text{Te, Se and S}$). Adapted from [77] with permission from Taylor and Francis. (b) A schematic diagram of the near edge band structure in PbTe featuring two valence bands separated by an energy difference at room temperature. Adapted from [159] with permission from The Royal Society of Chemistry. (c) Temperature dependence of zT for $(\text{PbTe})_{1-x} \cdot (\text{PbSe})_x \cdot (\text{PbS})_x$. Adapted from Ref. [155] with permission from Elsevier. (d) Temperature dependence of zT for recently developed promising lead chalcogenides [24, 25, 155, 26a].
phonon scattering is the dominating process above 300 K which can be concluded because of the low speed of sound due to the harmonic lattice vibrations and relatively high anharmonicity. High anharmonicity is the key to large Gruneisen parameter. PbTe has weak bonding and contains heavy atoms which also result in large Gruneisen parameter. This large anharmonicity results in low lattice thermal conductivity which has already been discussed. The thermoelectric figure of merit of lead chalcogenides is continuously being increased by using different concepts of band engineering (band convergence \cite{146,147}, bands alignment \cite{148,149}, resonant levels \cite{150,151}, etc) and microstructure formation on all scale hierarchical architectures \cite{148,149,152}. P-type PbTe$_{0.9}$Se$_{0.1}$ shows a perfect example of band structure engineering to increase the band valley degeneracy where the small and controlled manipulation of band energies is allowed by alloying and the peak $zT$ of 1.8 was observed \cite{75}. Recently, $zT$ of 2.2 was reported in PbTe bulk materials by multifunctional alloying \cite{24}. PbTe$_{0.9}$Se$_{0.1}$ was taken as a base matrix because of its large $zT$ of 1.8. By alloying with Mg, $zT$ of 2.2 is obtained at 820k for Mg$_{0.01}$Pb$_{0.99}$Te$_{0.8}$Se$_{0.2}$ with 2% Na doping. Alloying with Mg affects the electrical conductivity as the carrier concentration and mobility are related to Mg content in the matrix PbTe$_{0.18}$Se$_{0.2}$ \cite{24}. Tan et al reported the high figure of merit up to 2.5 in PbTe-SrTe system \cite{153}. Hole doped PbTe was heavily alloyed with SrTe beyond its thermodynamic solubility limit of < 1 mol% which was predicted by previous studies using non-equilibrium processing. Such heavy alloying of SrTe produces an efficient thermoelectric material because the performance-enhancing mechanisms like valence band conduction and enhancement in the point defect phonon scattering work simultaneously in this material. As a result, the figure of merit as high as 2.5 is obtained in Na-doped PbTe-8%SrTe at 923 K \cite{153}. It is also reported that the average values of Na-doped PbTe-SrTe can be increased by the addition of small amount of Mn \cite{154}. Alloying of PbTe-SrTe with MnTe can greatly alter the band structure of PbTe-SrTe, enlarging the band gap and increasing the band degeneracy. Alloying with MnTe also introduces low angle grain boundaries and reduces the lattice thermal conductivity by dislocation scattering. As a result of these effects, $zT$ of 1.98 was observed \cite{154}. In another study, Bi is doped in PbTe nanocubes to develop high-performance n-type PbTe based thermoelectric material \cite{25}. The electronic transport properties of as-sintered PbTe nanocubes are improved by Bi addition and lattice thermal conductivity is reduced which is lower than its bulk counterparts. Such low thermal conductivity is due to the enhanced phonon scattering by high-density grain boundaries and dislocations. Hence the peak $zT$ of 1.35 at 675 K is observed for n-type Pb$_{0.99}$Bi$_{0.01}$Te which is the highest reported in n-type PbTe based thermoelectric materials \cite{25}. Ginting et al reported high $zT$ of 2.3 in (PbTe)$_{0.95-x}$(PbSe)$_x$(PbS)$_{0.05}$ for $x = 0.20$ at 800 K \cite{155}. With the increase in Se concentration, the energy band gap between conduction and valence L-band was decreased, and the energy difference between L- and $\Sigma$-bands was increased, and this band convergence enhances the power factor. Also, the PbS nanoscale precipitation in the matrix results in the reduction of lattice thermal conductivity. These two factors are responsible for such a huge $zT$ of (PbTe)$_{0.95-x}$(PbSe)$_x$(PbS)$_{0.05}$ \cite{155}. Now there is growing interest in tellurium free materials because of the growing expense and rarity of tellurium. PbSe can be considered as an alternative for PbTe but with lower performance because of its lower band gap at low temperatures \cite{156}. But Parker and Singh reported that the figure of merit of heavily doped PbSe might reach up to 2 at the temperatures near 1000 K \cite{157}. Wang et al reported $zT > 1.2$ at 850 K for Na doped polycrystalline P-type PbSe samples \cite{158}. Such high $zT$ is due to the sufficiently low thermal conductivity in PbSe particularly at high temperatures, which is mainly due to large Gruneisen parameter $\gamma$ and smaller lattice parameter \cite{158}. Qian et al reported that by introducing the mesostructures, the lattice thermal conductivity is reduced in n-type PbSe-PbS system and hence the increased $zT$ value of 1.3 to 1.5 is observed at 923 K \cite{26}. The development and large-scale applications of lead chalcogenides are restrained because of possible hazardous effects of lead present in these thermoelectric materials. Table 6 summarizes the methods of preparation and peak $zT$ of lead chalcogenides.

![Table 6. Enhanced $zT$ values and method of preparation of lead-based chalcogenide thermoelectrics.](image_url)
3.5. Lead-free tin chalcogenides

Tin chalcogenides like SnSe, SnTe, and SnS have emerged as the most promising thermoelectric materials in the last few years. The $zT$ value of 2.6 was reported in p-type SnSe single crystals in 2014 which attracted great interest in the thermoelectric properties of tin chalcogenides [90]. Among these tin chalcogenides, SnTe has rock salt crystal structure with isotropic crystal properties while SnSe and SnS have layered orthorhombic crystal structure and their thermoelectric properties are anisotropic which is mainly reflected in the thermal and electronic properties [159]. SnSe is a very stable compound containing abundant earth elements. The crystal structure of SnSe is shown in figures 12(a)–(d). It exhibits an intrinsically ultra-low thermal conductivity because of its complex, layered structure [90]. At the room temperature SnSe exhibits the space group Pnma, and at the higher temperature, there is a transition from Pnma phase to Cmcm space group [90, 160]. SnSe is known for its semiconducting properties having various applications like in solar cells and phase-change memory alloys [159, 161, 162]. Due to high resistivity and low $zT$ value of 0.15, SnSe compound did not get any attention as a thermoelectric material in the past years [163, 164]. But according to the recent investigation, ultra-high $zT$ of 2.6 was found along b axis, 2.3 along the c axis and 0.8 along a axis at 923 K for SnSe single crystals that is for the high-temperature Cmcm phase [90] as shown in figure 12(e). The difference in $zT$ along the three crystallographic axes is because the electrical conductivities along b and c axes are somewhat similar and higher than the electrical conductivity along a axis which is because of the higher carrier mobility along b and c directions [90]. The lattice thermal conductivity is significantly reduced in the high-temperature range, being lowest along a axis possibly because of the high anharmonicity while the Seebeck coefficient shows isotropic behavior [90]. Duong et al reported $zT$ of 2.2 along b axis 733 K for Bi-doped SnSe single crystals [27]. The addition of Bi increases the carrier concentration which has a significant influence on the thermoelectric properties. Even by having such a massive figure of merit, the application of SnSe compound is substantially limited because of the lower thermoelectric properties of low-temperature Pnma phase [27]. Peng et al reported that acceptor doping in SnSe single crystals increases the carrier concentration and enhances $zT$ in the Pnma phase. Na doped SnSe single crystals have average $zT$ of 1.17 in the temperature range 300K-800K and the peak

![Figure 12. SnSe crystal structure Pnma and ZT values.](image-url)
zT value exceeds 2 at 800 K along b axis in case of Sn$_{0.97}$Na$_{0.03}$Se. By Na doping, the Fermi level is shifted, the valence band edge is flattened, and the number of carrier pockets is increased which has the positive effect on the electronic transport properties of Na-doped SnSe single crystals [28]. Due to the more inferior mechanical properties of single crystals as compared to the polycrystalline materials, their use in the thermoelectric applications is hindered. But the problem with polycrystalline materials is that they don’t yield high zT values because of lower carrier mobility as compared to single crystals. Polycrystalline samples have lower thermal conductivity due to the presence of grain boundaries which scatter the phonons but also reducing the carrier mobility, and hence electrical conductivity is reduced [165]. The zT of undoped polycrystalline SnSe is reported to have the value 0.5 which is much lower than the undoped SnSe single crystals [166]. Various efforts have been made to enhance zT of polycrystalline SnSe for the use in thermoelectric applications. Fu et al reported zT as high as 0.92 at 873 K in p-type polycrystalline SnSe, and this enhancement is credited to the highly textured structure of SnSe crystals which is responsible for the increase in electrical conductivity. By introducing the grain boundaries, the peak zT value of 1.05 was obtained [167]. Chere et al reported the enhancement of zT in polycrystalline SnSe by Na doping [29]. The addition of Na increases the carrier concentration in polycrystalline SnSe which enhances the electrical conductivity and also because of the intrinsically low thermal conductivity, zT value as high as 0.8 at 773 K is obtained [29]. Zhang et al also reported zT of 0.8 in Iodine doped polycrystalline SnSe at 773 K and zT further attained to the value of 1 at 773 K by alloying the sample with 10at% SnS [168]. Tang et al demonstrated the simultaneous increment of power factor and the significant reduction in thermal conductivity in phase-separated Sn$_{1-x}$Pb$_x$Se samples [30]. The electrical conductivity and power factor are improved by the introduction of PbSe phase in SnSe compound. The lattice thermal conductivity is reduced because of the nanoscale precipitates and mesoscale grains in all-scale architecture structures. These two factors get the credit for the high zT of 1.7 at 873 K in polycrystalline (SnSe + 1% PbSe) samples [30].

SnTe is a highly degenerate p-type semiconductor but is considered a poor thermoelectric material. SnTe has high electrical conductivity but has very low zT of 0.5 at 900 K because of extremely low Seebeck coefficient and high thermal conductivity [159]. With the help of band structure engineering and nanostructure engineering, SnTe has the strong ability to become an efficient thermoelectric material [169–171]. In doping in SnTe creates resonant levels inside the valence band because of which the Seebeck coefficient around room temperature is enhanced [172]. The band structure engineering combined with nanostructure engineering leads to the maximum zT of 1.1 in In-doped SnTe [173]. Zhao et al reported zT of 0.9 at 823 K for Bi-doped Sn$_{0.95}$Bi$_{0.05}$Te because of the improved electrical transport properties and reduced thermal conductivity [174]. Doping resulted in the tuning of Fermi level and hence enhancing the electrical transport properties. zT is further increased by alloying with SrTe which created strained endotaxial nanostructures as phonon scattering centres to further reduce lattice thermal conductivity. The peak zT value of 1.2 at 823 K and the average zT value of 0.7 in the temperature range 300–823 K were obtained for Sn$_{0.97}$Bi$_{0.03}$Te-3%SrTe [174]. Doping of SnTe with Gd resulted in the drastic reduction of lattice thermal for Sn$_{0.95}$Gd$_{0.05}$Te, attributed to the formation of nanoprecipitates which strongly scatter phonons by mass fluctuation between a second phase and the matrix coupled with mesoscale scattering via grain boundaries [31]. The Seebeck coefficient is increased by the decrease in the carrier concentration due to further doping of Sn$_{0.96}$Gd$_{0.04}$Te with Ag. zT value of 1.1 at 823 K was obtained for Sn$_{0.95}$Gd$_{0.05}$Te containing 11at% Ag [31]. SnCd$_{0.03}$Te possesses zT of 0.96 at 823 K, and this increment is due to the valence band engineering [31a] as is shown in figure 13(a). SnCd$_{0.03}$Te entoxially nanostructured with CdS.
or ZnS possess zT values of 1.3 shown in figure 13(b) and 1.1 respectively. The introduction of endotaxial CdS or ZnS nanoprecipitates reduces the thermal conductivity in SnCd$_{0.03}$Te with no effect on power factor [31a].

### 3.6. Oxide thermoelectric

Oxides have gained interest as thermoelectric materials in recent years but were neglected in the past because of low electrical conductivity and high thermal conductivity because the constituents of oxides are usually light elements [175]. The oxide thermoelectrics have various advantages like high thermal stability, high chemical stability in the oxidizing atmosphere, non-toxic nature and easy fabrication methods [176]. Among the p-type oxides, cobaltites like NaCo$_2$O$_4$, Ca$_3$Co$_4$O$_9$ and Bi$_2$Sr$_3$Co$_2$O$_9$ [175, 176] are the promising thermoelectric materials, showing a positive temperature dependence of electrical conductivity in the high-temperature range due to Jahn-Teller polarons [177, 178]. Out of these oxides, Ca$_3$Co$_4$O$_9$ is the most promising candidate for the use in thermoelectric applications because of the highly volatile character of Na and Bi in NaCo$_2$O$_4$ and Bi$_2$Sr$_3$Co$_2$O$_9$ respectively [179, 180]. These oxides have anisotropic thermoelectric properties with the in-plane electrical resistivity less than that of the out-of-plane resistivity [175]. NaCo$_2$O$_4$ single crystals have highly conducting CoO$_2$ block layer (CdI$_2$-type) which is an incomplete layer containing randomly oriented and highly disordered Na$^+$ ions resulting in low lattice thermal conductivity [77, 181]. The misfit layered single crystals of Ca$_3$Co$_4$O$_9$ show the better block-layer concept which is composed of two layers: the conducting layers of CoO$_2$ (CdI$_2$-type) which sandwich the rock salt-type Ca$_2$CoO$_3$ layer [182] as is shown in figure 14(a). The low thermal conductivity occurs because phonons get scattered at the interfaces of these two sublattices having different b parameters [181]. Electronic correlations and spin entropy can explain the enhanced thermopower in these oxides [180, 181]. zT of 0.74 was observed in Tb doped polycrystalline Ca$_3$Ca$_4$O$_9$ at 800 K which is the highest reported value for p-type oxides [32].

For n-type thermoelectric oxides, SrTiO$_3$, CaMn$_2$O$_4$, and ZnO based oxides have attracted a lot of attention. SrTiO$_3$-based oxides exhibit perovskite structures having a very high melting point of 2080 °C. These oxides are the promising n-type thermoelectrics because of the excellent electronic transport properties and greater stability at higher temperatures. zT of 0.33 at 900 K was reported by wang et al for Nb-doped SrTiO$_3$ ceramics doped with the surface modification of nanosized TiO$_2$ powder due to which the ratio of electrical to thermal conductivity is significantly increased without having much impact on the Seebeck coefficient [184]. zT of 0.41 at 973 K was reported in La-doped SrTiO$_3$ by Lu et al [183]. A record high zT > 0.6 at 1000–1100 K was observed in La-Nb-doped SrTiO$_3$ nanopowders [33]. Such high zT is due to the increase in carrier concentration and electrical conductivity by La and Nb doping. The thermal conductivity, on the other hand, is reduced through complex microstructures [33]. Gd/W double substitution in polycrystalline calcium magnetite Ca$_{89.90}$Gd$_{0.10}$Mn$_{0.99}$W$_{0.01}$O$_2$ resulted in the zT of 0.12 at 700 °C [185]. Due to Gd/W substitution, the electrical conductivity increases and thermal conductivity decreases [185]. zT of Ca$_{0.96}$Dy$_{0.02}$Yb$_{0.02}$MnO$_3$ reached the value of 0.27 at 800 °C as a result of the improved electrical properties by Dy and Yb co-doping and the reduced lattice thermal conductivity [186]. ZnO is reported to have zT of 0.44 at 1000 K due to low lattice thermal conductivity which is the result of enhanced phonon scattering by Al-induced grain refinement and the presence of ZnAl$_2$O$_4$ nanoprecipitates [187]. Method of preparation and peak zT of oxide thermoelectrics is summarized in table 8.

### 3.7. SiGe alloys

SiGe alloys are the promising thermoelectric materials used in RTGs and other high-temperature applications. SiGe has the band gap of 0.9 eV which is the reason for its significant Seebeck coefficient and low thermal

| Compound          | zT     | T     | Method of preparation                  | References |
|-------------------|--------|-------|---------------------------------------|------------|
| Bi doped SnSe (single crystal) | 2.2    | 460 °C | Temperature gradient growth method    | [27]       |
| Na doped SnSe (Single crystal) | 1.7    | 27 °C–527 °C | Bridgman method                       | [28]       |
| Na doped SnSe (polycrystalline) | 0.8    | 500 °C | Solid state reactions, ball milling    | [29]       |
| SnSe+1%PbSe (polycrystalline) | 1.7    | 600 °C | Hydrothermal method                    | [30]       |
| Zn$_{0.03}$Cd$_{0.07}$Te (polycrystalline) | 0.6    | 550 °C | Solid state reactions method           | [30a]      |
| Zn$_{0.03}$Sn$_{0.07}$Se (polycrystalline) | 1.1    | 600 °C | Solid state reactions method           | [30b]      |
| SnSe$_{0.9}$Te$_{0.1}$ (polycrystalline) | 2.8    | 527 °C | Microwave-assisted solvothermal method | [30c]      |
| Sn$_{0.96}$Ga$_{0.04}$Te | 1.3    | 550 °C | Solid state reactions method           | [30d]      |
| SnCd$_{0.03}$Te/CdS | 1.3    | 550 °C | Melting method, Spark plasma sintering | [31a]      |
| SnCd$_{0.03}$Te/ZnS | 1.1    |       |                                       |            |
SiGe alloys have potentially useful electronic properties because of their cubic structure \(^{188, 189}\). By only reducing the lattice thermal conductivity their thermoelectric properties can be optimized. The reduction in the thermal conductivity was reported by the addition of silicide nano-inclusions to SiGe alloy as compared to the single-phase SiGe alloy \(^{190}\). The power factor is maintained or increased by these nano-inclusions and by the reduction of thermal conductivity, \(zT\) value reached to 1.3 in Si\(_{0.88}\)Ge\(_{0.12}\)-Mg\(_2\)Si nanocomposite at 950 °C \(^{190}\). Peak \(zT\) of 0.73 was obtained in Boron-doped Si\(_{80}\)Ge\(_{20}\) with SiO\(_2\) nano-inclusions due to the reduction in thermal conductivity and high values of Seebeck coefficient \(^{191}\). Ahmad et al reported the enhanced \(zT\) value of 1.81 in the P-type SiGe alloys by the incorporation of metallic Yttrium silicide nanoparticles \(^{89}\). The thermal conductivity is reduced by YSi\(_2\) nano-inclusions due to the

| Compound | \(zT\) | \(T\) °C | Method of preparation | References |
|----------|--------|----------|-----------------------|------------|
| Ca\(_{2.95}\)Tb\(_{0.5}\)Co\(_4\)O\(_9\) | 0.74 | 527 | Solid state reactions method \(^{32}\) |
| Porous Ca\(_3\)Co\(_4\)O\(_9\) | 0.40 | 800 | Sol-gel method \(^{32a}\) |
| Bi\(_{1.4}\)Pb\(_{0.2}\)Ba\(_{0.4}\)Co\(_2\)O | 0.53 | 650 | Laser floating zone technique \(^{32b}\) |
| SrTiO\(_3\) (doped with 10 mol%La and 10 mol%Nb) | >0.60 | 727–827 | Hydrothermal method, high efficiency sintering \(^{33}\) |
| Ca\(_{0.98}\)Ni\(_{0.02}\)O | 0.43 | 727 | Solid state reactions method \(^{33a}\) |
| Zn\(_{0.95}\)Cd\(_{0.05}\)Sc\(_{0.01}\)O\(_{0.015}\) | 0.30 | 900 | Solid state reactions method \(^{33b}\) |
| Sr\(_{1−x}\)La\(_x\)TiO\(_3\) | 0.41 | 680 | Solid state reactions method \(^{183}\) |

Fig. 14. (a) Schematic of the crystal structure of Ca\(_3\)Co\(_4\)O\(_9\) (blue balls represent Ca, red balls represent O, and purple balls represent Co). Adapted from \(^{32c}\) with permission from The Royal Society of Chemistry. (b) Temperature dependence of \(zT\) for various Tb doped Ca\(_3\)Co\(_4\)O\(_9\) samples. Adapted from \(^{32}\) with permission from Springer Nature. (c) Temperature dependence of \(zT\) for recently developed promising oxide thermoelectric \(^{32, 32b, 183, 33a}\).
formation of coherent states with SiGe matrix and also due to the reduction of grain size [89]. The temperature dependence of $zT$ for various SiGe nanocomposites is shown in figure 15.

3.8. Mg$_2$X (X = Si, Ge, and Sn)

Mg$_2$X compounds are the efficient thermoelectric materials in mid-temperature range and have the composition of non-toxic, inexpensive and earth-abundant elements [77]. Superior thermoelectric properties are exhibited in p-type Mg$_2$X compounds originating from large density of states effective mass due to the large valley degeneracy of valence bands. Also like SiGe alloys, Mg$_2$X compounds have cubic structure as is shown in figure 16(a) and thus have good electronic properties. So to optimise the thermoelectric properties, main focus is the reduction of thermal conductivity. Due to the low lattice thermal conductivity, $zT$ value of 1.1 was observed in p-type Mg$_2$Sn at 800 K [192] which is more than Mg$_2$Si(0.8) and Mg$_2$Ge(1). The low lattice thermal conductivity is due to low velocity of optical modes caused by the large mass density [192]. $zT$ reached the value of 0.46 in Mg$_2$Si microstructure via Yb and Bi doping because Yb doping lowers the thermal conductivity and Bi doping adjusts the electronic transport properties [193]. $zT$ of 1.4 was obtained in Mg$_2$Sn$_{0.73}$Bi$_{0.02}$Ge$_{0.25}$ at 673 K which shows that the charge donors are much more effective at Sn-site than Mg site [34]. Li et al. reported HPHT synthesized Mg$_2$Si$_{0.995}$Sb$_{0.005}$ with $zT$ up to 0.62 at 800 K [194]. Due to high pressure and temperature, the electrical conductivity increased while changing the Seebeck coefficient slightly resulting in the significant increase in power factor [194]. Iida et al. reported that the thermal conductivity is reduced by the addition of small amount of Ge and this reduced thermal conductivity combined with the increased carrier concentration resulted in $zT$ of 0.47 for Mg$_2$Si$_{0.94}$Ge$_{0.05}$Sb$_{0.005}$ [35]. Table 9 summarizes the peak $zT$ and method of preparation of Mg$_2$X compounds.

3.9. Half-Heusler alloys

The general formula of half-Heusler alloys is XYZ, X being a noble or a transition metal, or a rare-earth element, Y being a noble or a transition metal and Z being the main group element. Half-Heusler compounds of the composition XNiSn and XCoSb (X = Ti, Zr or Hf) are the excellent candidates for thermoelectric applications because the half-Heusler structure (cubic structure) as is shown in figure 17(a) allows better electronic transport properties and also have an inexpensive elemental composition with low toxicity. The problem in employing half-Heusler alloys in thermoelectric applications lies in their high thermal conductivity and to optimise their thermoelectric properties, main focus is the reduction of the thermal conductivity rather than the increment of the electrical transport properties. The isoelectronic alloying in half-Heusler compounds XNiSn and XCoSb (X = Ti, Zr or Hf) reduces lattice thermal conductivity to the large extent but the electrical transport properties also get degraded. Recently $zT$ of 0.83 at 923 K was reported in Hf$_{0.25}$Zr$_{0.75}$NiSn$_{0.995}$Sb$_{0.005}$ which is 67% more than that of the undoped sample [36]. Sb is found to be an effective dopant for n-type ZrNiSn half-Heusler alloys which effectively increases the carrier concentration and also reduces thermal conductivity [36]. Chen et al. reported high $zT$ of 1.3 in n-typeHf$_{0.65}$Zr$_{0.25}$Ti$_{0.15}$NiSn$_{0.995}$Sb$_{0.005}$/ nano-ZrO$_2$ composition at 850 K [195]. Such high $zT$ resulted from

Figure 15. Temperature dependence of $zT$ for recently developed efficient SiGe alloy thermoelectric [190, 191, 89].
the elemental substitution of Ti in (Hf, Zr) sites and simultaneous embedment of ZrO₂ nanoparticles in (Hf, Zr)NiSn matrix. Due to Ti substitution, phonon scattering is enhanced which reduces lattice thermal conductivity. On the other hand, ZrO₂ nanoparticles act as potential barriers for carrier scattering that enhances the thermopower [195]. Among the prospective half-Heusler alloys are also p-type FeNbSb and α-MgAgSb based materials [196, 197]. The excellent thermoelectric performance was reported in Ti-doped FeNbSb and zT of 1.1 achieved in the composition FeNb₀.₈Ti₀.₂Sb at 1100 K which is twice that of ZrCoSb [196]. Lattice thermal conductivity is reduced due to the presence of high Ti content, and the electrical properties are optimized via band engineering [196]. Fu et al reported the enhanced thermoelectric

Figure 16. (a) Crystal structure of Mg₂Si. Reprinted from Ref. [77] with permission from Taylor and Francis (b) Temperature dependence of zT for Mg₂SiₓSn₀.₈₋ₓBi₀.₂ (x = 0.1, 0.2, 0.3) [35c]. Reprinted with permission from (Fan, W, Chen, S, Zeng, B, Zhang, Q, Meng, Q, Wang, W, and Mumir, Z. A. ACS Applied Materials & Interfaces, 9(34), 28635–28641) (2017) American Chemical Society (c) Temperature dependence of zT for recently developed promising Mg₂X compounds [34, 35a, 35c, 35d].

Table 9. Peak zT value and synthesis method of Mg₂X(X = Si, Ge, and Sn) thermoelectrics.

| Compound                  | zT  | T    | Method of preparation                              | References |
|---------------------------|-----|------|---------------------------------------------------|------------|
| Mg₁.₉₆Al₀.₀₄Si₀.₉₇Bi₀.₀₃ | 1.02| 600 °C| Solid state reaction, Spark plasma sintering       | [35a]      |
| Mg₁.₃₆Si₀.₄₀Sn₀.₂₀Bi₀.₁₃ | 1   | 452 °C| B₂O₃ flux method                                  | [35b]      |
| Mg₂Sn₀.₉₃Bi₀.₀₇         | 1.36| 502 °C| One step synthesis and consolidated method          | [35c]      |
| Mg₂Si₀.₆₆Sn₀.₃₈Bi₀.₂₀   | 1.4 | 527 °C| Solid state synthesis and hot pressing             | [35d]      |
| Mg₂Si₀.₅₃Sn₀.₄₆Ge₀.₀₅Bi₀.₁₂| 1.2| 547 °C| Low temperature reactions, ball milling, hot pressing consolidation | [35e]      |
| Mg₂Sn₀.₇₃Bi₀.₁₂Ge₀.₂₅   | 1.4 | 400 °C| Ball milling                                       | [34]       |
properties in Hf doped FeNbSb heavy band half-Heusler compound [37]. Hf doping at Nb sites induces more point defect scattering because of the larger mass and radius difference between Hf and Nb atoms. The heavy element Hf dopants optimize the electrical properties and suppress the thermal conductivity and hence $zT$ value reached 1.5 for FeNb$_{0.88}$Hf$_{0.12}$Sb and FeNb$_{0.86}$Hf$_{0.14}$Sb half-Heusler compound. Reprinted from [37] with permission from Springer Nature.

Figure 17. (a) Schematic representation of the half-Heusler structure. Half-Heusler compounds have the composition XYZ, consisting of a covalent, diamond-like (or ZnS) substructure of the (YZ)$_n$’ Zintl chemistry framework (purple tetrahedra) formed by the tetrahedral coordination of Y atoms (purple) and Z atoms (blue). The electropositive $X^+$ (red) fills the octahedral voids around the tetrahedral framework. Reprinted from [198] with permission from Springer Nature. (b) $zT$ versus temperature for FeNb$_{1-x}$Hf$_x$Sb half-Heusler compound. Reprinted from [37] with permission from Springer Nature. (c) Temperature dependence of $zT$ for recently developed efficient half-Heusler alloys [37, 37b, 37c, 37d].

Table 10. Reported $zT$ values and method of preparation of half-Heusler alloy thermoelectrics.

| Compound | $zT$ | $T$ (°C) | Method of preparation | References |
|----------|------|---------|-----------------------|------------|
| Hf$_{0.22}$Zr$_{0.78}$NiSn$_{0.985}$Sb$_{0.015}$ | 0.83 | 650 | Induction melting, plasma activated sintering | [36] |
| FeNb$_{0.84}$Hf$_{0.16}$Sb | 1.5 | 927 | Levitation melting, Spark plasma sintering | [37] |
| FeNb$_{0.84}$Hf$_{0.16}$Sb | 0.91 | 500 | Levitation melting, Spark plasma sintering | [37a] |
| Zr$_{0.22}$Hf$_{0.78}$Ti$_{0.02}$NiSn$_{0.996}$Sb$_{0.004}$ | 1.32 | 927 | Levitation melting, Spark plasma sintering | [37b] |
| Zr$_{0.3}$Hf$_{0.7}$Co$_{0.05}$Nb$_{0.15}$Sb | 1 | 800 | Arc melting, ball milling | [37c] |
| (Hf$_{0.6}$Zr$_{0.4}$)$_{0.99}$V$_{0.01}$Ni | 1.3 | 577 | Arc melting, Spark plasma sintering | [37d] |

Highly pure $\alpha$-MgAgSb is a promising thermoelectric material because of the intrinsically low thermal conductivity which can further be reduced by point defect scattering through doping. $zT$ of 1.1 was achieved in $\alpha$-MgAgSb$_{0.99}$In$_{0.1}$ at 525 K because of the enhancement of carrier concentration by In doping [38]. Methods of preparation and peak $zT$ of half-Heusler alloys is summarized in table 10.
The comparison of zT versus temperature of some efficient thermoelectric materials belonging to different groups is shown in figure 18.

4. Conclusion

The constant high demand for energy, thermal management, and increasing pollution are the major issues of the world. Thermoelectric concept ties a knot between these major problems and can solve these problems simultaneously. The basic concepts are related to various challenges to find the suitable materials for thermoelectricity. These materials should follow phonon-glass electron-crystal behavior. Attaining phonon-glass electron-crystal behavior by decoupling electrical and thermal transport properties of materials has haunted researchers for many years. The discovery of materials with complex unit cells like the complex variants of chalcogenides and disordered large unit cells like skutterudites and clathrates have managed to decouple these properties. Band engineering strategies in materials like lead chalcogenides have demonstrated highly efficient thermoelectric materials. By reducing the specific heat in case of thermoelectrics with liquid-like behavior, the increased performance can be guaranteed. Nanostructure engineering also has the reputation of delivering efficient thermoelectric materials. The development of nanocomposite materials provides a new route to develop efficient thermoelectric materials because of their ability to scatter phonons randomly. The efficiency of bulk materials can be improved to a large extent with the inclusion of nanocomposites. This review insights the complex structures and have highlighted the strategies to increase zT of TE materials. The recent advances in the field of thermoelectricity have also been discussed. Still, a lot of work has to be done to deliver the thermoelectric materials with superior efficiency so that the energy crisis and pollution could be eliminated. It is anticipated that the further progress in TE materials with improved zT values and device fabrication shall lead to practical applications in the future so that living in the cleaner and greener world would be possible.

Acknowledgments

One of the authors (Khalid) acknowledges Central University Research Fellowship provided by University Grants Commission (UGC), Govt. of India. Jai Singh would like to acknowledge DST for providing project under DST Fast track Grant no. SR/FTP/PS [HYPHEN] 144/2012.

ORCID iDs

Pushpendra Kumar  https://orcid.org/0000-0001-6712-5834
Jai Singh  https://orcid.org/0000-0001-5314-9288
References

[1] Dahal T, Kim H S, Ghalawat S, Dahal K, Jie Q, Liu W, Yan Y, White K and Ren Z 2016 Transport and mechanical properties of the double-filled p-type skutterudites La$_{0.6}$Co$_{0.95}$Fe$_{0.05}$Si$_{12}$ Acta Mater. 117 13–22

[2] Li X, Kang Y, Chen C, Li J, Zhang L, Yu F, Yu D, Tian Y and Xu B 2017 Thermoelectric properties of high pressure synthesized lithium and calcium double-filled Co$_2$Sb$_3$, AIP Adv. 7 015204

[3] Liu Y, Li X, Zhang Q, Zhang L, Yu D, Xu B and Tian Y 2016 High pressure synthesis of p-type Ce$_5$Fe$_{14}$–Co$_8$Sb$_3$ skutterudites Materials 9 257

[4] Chen C, Zhang L, Li J, Yu F, Yu D, Tian Y and Xu B 2017 Enhanced thermoelectric performance of lanthanum filled Co$_2$Sb$_3$ synthesized under high pressure J. Alloys Compd. 699 751–5

[5] Park K and Kim I 2010 Thermoelectric properties of Ca-filled Co$_2$Sb$_3$-based skutterudites synthesized by mechanical alloying J. Electron. Mater. 40 193–8

[6] Elsheikh M H, Sabri M F, Said S M, Miyazaki M, Masjuki H A, Masjuki H and Burkov A T 2017 Rapid preparation of In$_x$Co$_4$Sb$_{12}$ with a record-breaking ZT = 1.5; the role of the In overfilling fraction limit and Sb overstoichiometry J. Mater. Chem. A 5 3541–5

[7] Guo L, Wang G, Peng K, Yan Y, Yang X, Zeng M, Dai I, Wang G and Zhou X 2016 Melt spinning synthesis of p-type skutterudites: drastically speed up the process of high performance thermoelectrics Sci. Technol. 116 26–30

[8] Fu L, Jiang Q, Yang J, Peng J, Xiao Y, Luo Y, Zhou Z and Zhang D 2016 Enhancement of thermoelectric performance of Ca$_{0.25}$Fe$_{1.5}$Sb$_{12}$ p-type skutterudite by tellurium addition J. Mater. Chem. A 4 16499–506

[9] Sui F and Kauzlarich S M 2016 Tuning thermoelectric properties of Type I clathrate K$_{0.9}$Ba$_{0.1}$Al$_{8}$Si$_{38}$ through Barium substitution Chem. Mater. 28 1099–107

[10] Kishimoto K, Utsumiomya S, Akai K, Kudo H and Koyanagi T 2017 Synthesis and thermoelectric properties of semiconducting germanium-based Type-II clathrate (K,Sr)$_x$Co$_4$Ge$_{12}$J. Alloys Compd. 695 1016–10

[11] Chen C, Zhang L, Dong J and Xu B 2016 Thermoelectric performance of Yb-doped Ba$_{0.9}$Sb$_{1.1}$Ga$_{1.3}$Ge$_{32.3}$ Type-I clathrate synthesized by high-pressure technique J. Electron. Mater. 46 2860–8

[12] Tometi P, Yan X, Kastner R, Svagera R, Waas M, Eitertsen J, Weidenkaff A and Paschen S 2016 Thermoelectric properties of melt spun Ba$_2$Cu$_4$Si$_6$Ge$_3$H$_4$ clathrates J. Alloys Compd. 654 300–7

[13] Deng S, Liu H, Li D, Wang J, Cheng F, Shen L and Deng S 2016 Thermoelectric properties of Sr-filled Ge-based type I single-crystal clathrate grown by Sn-flux method J. Electron. Mater. 46 2662–7

[14] Sun B, Jia X, Huo D, Sun H, Zhang Y, Liu B, Liu H, Kong L and Ma H 2016 Rapid synthesis and effect of high temperature and high pressure processing on the structure and thermoelectric properties of clathrate Ba$_{0.9}$Co$_4$Si$_{33}$J. Alloys Compd. 658 19–22

[15] Sun B, Jia X, Huo D, Sun H, Zhang Y, Liu B, Liu H, Kong L and Ma H 2016 Effect of high-temperature and high pressure processing on the structure and thermoelectric properties of clathrate Ba$_{0.9}$Ga$_4$Ge$_3$ The Journal of Physical Chemistry C 120 10104–10

[16] Utsumiomya S, Kishimoto K, Koda S, Akai K, Fujita R, Asada H and Koyanagi T 2017 Preparation and thermoelectric properties of sintered type-II clathrates (K,Ba)$_x$Al$_{8}$Si$_{38}$J. Alloys Compd. 693 1039–44

[17] Sun B, Jia X, Huo D, Sun H, Zhang Y, Liu B, Liu H, Kong L and Ma H 2016 Rapid synthesis and thermoelectric properties of clathrate Ba$_{0.9}$Cu$_4$Ge$_3$Sb$_3$, by high temperature and high pressure Modern Physics Letters B 30 1500587

[18] Hong M, Chasapis T C, Chen Z, Yang L, Kanatzidis M G, Snyder G J and Zou J 2016 N-Type Bi$_{2}$Te$_{3}$–Se$_{x}$ nanoparticles with enhanced thermoelectric efficiency driven by wide-frequency phonon scatterings and synergistic carrier scatterings ACS Nano 10 4719–27

[19] Zhang C, Ng H, Li Z, Khor K and Xiong Q 2017 Minority carrier blocking to enhance the thermoelectric performance of Bi$_2$Te$_3$ nanocomposites via a liquid-phase sintering process ACS Applied Materials & Interfaces 9 12501–10

[20] Yan X, Zheng W, Liu F, Yang S and Wang Z 2016 Thickness effects for thermoelectric property of antimony telluride nanoplatelets via solvothermal method Sci. Rep. 6 37772

[21] Wang S, Sun Y, Zhang J, Duan B, Wu L, Zhang W and Yang J 2016 High thermoelectric performance in Te-free (Bi$_2$Sb)$_3$Se$_2$via structural transition induced band convergence and chemical bond softening Energy Environ. Sci. 9 3436–47

[22] Xiao Y, Yang J, Jiang Q, Pu L, Luo Y, Zhang D and Zhou J 2015 Improvement of thermoelectric properties of Bi$_{0.9}$Sb$_{1.1}$Te$_3$ with addition of nanoscale zinc oxide particles J. Electron. Mater. 45 1266–70

[23] Pan Y and Li J 2016 Thermoelectric performance enhancement in n-type Bi$_2$(TeSe)$_3$ alloys owing to nanoscale inhomogeneity combined with a spark plasma-textured microstructure NPG Asia Mater. 8 e275

[24] Han S T, Rimal P, Lee C H, Kim H, Sohn Y and Hong S 2016 Enhanced thermoelectric cooling properties of Bi$_2$Te$_3$–Se$_x$ alloys fabricated by combining casting, milling and spark plasma sintering International Metals Reviews 78 42–9

[25] Bobra A K, Bhart R, Singh A, Basu R, Bhattacharya S and Meshram K 2017 Tellurium-free thermoelectrics: improved thermoelectric performance of n-type Bi$_2$Se$_2$ having multiscale hierarchical architecture Energy Convers. Manage. 145 415–24

[26] Das S, Chetty R, Wojciechowski K, Suswas S and Mallik R C 2017 Thermoelectric properties of Sn doped BiCu$_2$SeO$_6$ Appl. Surf. Sci. 418 238–45

[27] Peng P, Gong Z, Liu F, Huang M, Ao W, Li Y and Li J 2016 Structure and thermoelectric performance of β-Cu$_2$Se doped with Fe, Ni, Mn, In, Zn or Sn Materials 9 72

[28] Kang S D, Pößl J, Aydemir U, Qi P, Stoumpos C C, Hanus R and Snyder G J 2017 Enhanced stability and thermoelectric figure-of-merit in copper selenide by lithium doping Materials Today Physics 7 17–13

[29] Ge Z, Liu X, Feng D, Lin J and He J 2016 High-performance thermoelectricity in nanocrystalline earth-abundant copper sulfides bulk materials Adv. Energy Mater. 6 1600607

[30] Li Y, Liu G, Cao T, Liu L, Li J, Chen K and Zhou M 2016 Enhanced thermoelectric properties of Cu$_x$Sn$_{2}$Se$_2$ by (Ag,In)-Co-Doping Adv. Funct. Mater. 26 6025–32

[31] Yang L, Chen Z, Han G, Hong M, Huang L and Zou J 2016 Te-Doped Cu$_2$Se nanopololites with a high average thermoelectric figure of merit J. Mater. Chem. A 4 9213–9.
f. Nunna B, Qiu P, Yin M, Chen H, Hanus R, Song Q and Chen L 2017 Ultrahigh thermoelectric performance in Ca$_9$Se$_x$-based hybrid materials with highly dispersed molecular CNFs Energy Environ. Sci. 10 1928–35

g. Feng B, Li G, Hou Y, Zhang C, Jiang C, Hu J and Fan X 2017 Enhanced thermoelectric properties of Sn$_2$-doped Bi$_2$Se$_3$ due to decreased band gap J. Alloys Compd. 712 386–93

[24] Fu T, Yue X, Wu H, Fu C, Zhu T, Liu X, Hu L, Ying P, He J and Zhao X 2016 Enhanced thermoelectric performance of Pb$_2$Te bulk materials with figure of merit $zT > 2$ by multi-functional alloying Journal of Materials Science 2 141–9

[25] Yang L, Chen Z, Hong M, Wang L, Kong D, Huang L, Han G, Zou Y, Dargusch M and Zou J 2017 N-type Bi$_2$-doped Pb$_2$Te nanocubes with enhanced thermoelectric performance Nano Energy 31 105–12

[26] Qian X, Zheng L, Xiao Y, Chang C and Zhao L 2017 Enhancing thermoelectric performance of n-type PbSe via additional meso-scale phonon scattering Inorg. Chem. Front. 4 719–26

a. Zhang Q, Chere E, Wang Y, Kim L, He R, Cao F and Ren Z 2016 High thermoelectric performance of n-type Pb$_2$Te$_{0.5}$Sn$_{0.5}$S$_x$ due to deep lying states induced by indium doping and spinodal decomposition Nano Energy 22 527–82

b. Zhang K, Zhang Q, Wang L, Jiang W and Chen L 2017 Enhanced thermoelectric performance of Se$_2$-doped Pb$_2$Te bulk materials via nanostructuring and multi-scale hierarchical architecture J. Alloys Compd. 725 563–72

c. Du X, Shi R, Gou Y, Wang Y, Ma Y and Yuan Z 2017 Enhanced thermoelectric properties of Pb$_n$-$\text{Bi$_2$S}_x$ prepared with hydrothermal synthesis and microwave sintering Dalton Trans. 46 2129–36

d. Wu C, Wei T and Li J 2016 Enhancing average $zT$ in pristine PbSe by over-stoichiometric Pb addition APL Materials 4 104801

e. Xiao Y, Li W, Chang C, Chen Y, Huang L, He J and Zhao L 2017 Synergistically optimizing thermoelectric transport properties of n-type PbTe via Se and Sn co-alloying J. Alloys Compd. 724 208–21

[27] Duong AT et al 2016 Achieving $zT = 2.2$ with Bi$_2$-doped n-type SnSe single crystals Nat. Commun. 7 13713

[28] Peng K, Lu X, Zhan H, Hui S, Tang X, Wang G, Dai J, Uher C and Zuo X 2016 Broad temperature plateau for high ZTs in heavily doped p-type SnSe single crystals Energy Environ. Sci. 9 454–60

[29] Chere E K, Zhang Q, Dahal K, Cao F, Mao J and Ren Z 2016 Studies on thermoelectric figure of merit of Na-doped p-type polycrystalline SnSe J. Mater. Chem. A 4 18418–54

[30] Tang G, Wei W, Zhang J, Li Y, Wang X, Xu G, Chang C, Wang Z, Du Y and Zhao L 2016 Realizing high figure of merit in phase-separated polycrystalline Sn$_{0.5}$-Pb$_{0.5}$Se J. Am. Chem. Soc. 138 16347–54

d. Fu Y, Xu J, Liu G, Tian F, Song S, Liu W and Ren Z 2017 The effect of charge carrier and doping site on thermoelectric performance in SnTe:Ga materials Chem. Mater. 29 612–20

[31] Zhang L, Wang J, Cheng Z, Sun Q, Li Z and Dou S 2016 Lead-free SnTe-based thermoelectrics: enhancement of thermoelectric performance by doping with Gd J. Electron. Mater. 46 3182–6

b. Li J, Li D, Qin X and Zhao L 2017 Enhanced thermoelectric performance of p-type SnSe doped with Zn Sc. Mater. 126 6–10

[32] Chere E K, Zhang Q, Dahal K, Cao F, Mao J and Ren Z 2016 Studies on thermoelectric figure of merit of Na-doped p-type polycrystalline SnSe J. Mater. Chem. A 4 18418–54

[33] Saini S, Yaddanapudi H S, Tian K, Yin Y, Maggipinto D and Tiwari A 2017 Terbium ion doping in Ca$_3$Co$_4$O$_9$: a step towards high-performance thermoelectric materials Sci. Rep. 7 44621

b. Bittner M, Helmich L, Nietschke F, Geppert B, Oeckler O and Feldhoff A 2017 Porous Ca$_3$Co$_4$O$_9$ with enhanced thermoelectric performance by directional growth and annealing J. Electron. Mater. 46 3182–6

c. Bittner M, Helmich L, Nietschke F, Geppert B, Oeckler O and Feldhoff A 2017 Porous Ca$_3$Co$_4$O$_9$ with enhanced thermoelectric properties derived from Sol–Gel synthesis J. Eur. Ceram. Soc. 37 3909–15

d. Madre M, Costa F, Ferrari N, Costa S, Rasekh S, Torres M and Soto A 2016 High thermoelectric performance in Bi$_{2}$-Pb$_{0.2}$Ca$_{0.8}$O$_{2}$ promoted by directional growth and annealing J. Eur. Ceram. Soc. 36 67–74

e. Wu T, Tyson T A, Bai J, Pandya K, Jaye C and Fischer D 2013 On the origin of enhanced thermoelectricity in Fe doped Ca$_3$Co$_4$O$_9$ J. Mater. Chem. C 1 1114–21

[34] Wang J et al 2017 Record high thermoelectric performance in bulk SrTiO$_3$ via nano-scale modulation doping Nano Energy 35 385–97

a. Gao L, Wang S, Liu R, Zhai S, Zhang H, Wang J and Fu G 2016 The effect of Ni doping on the thermoelectric transport properties of CdO ceramics J. Alloys Compd. 662 213–9

b. Han L, Christensen D V, Bhowmik A, Simonsen S B, Hung L T, Abdellahi E and Pryds N 2016 Scandium-doped zinc cadmium oxide as a new stable n-type oxide thermoelectric material J. Eur. Ceram. Soc. 36 3961–5

e. Khan A, Vlachos N, Hatzikraniotis E, Polymeris G, Lioutas C, Stefanaki E and Kyratsi T 2014 Thermoelectric properties of highly doped p-type Bi$_2$-doped Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ materials Adv. Energy Mater. 4 104211–21

[35] Saparamadu U, Mao J, Dahal K, Zhang H, Tian F, Song S, Liu W and Ren Z 2017 The effect of charge carrier and doping site on thermoelectric properties of Mg$_{5}$Sn$_{0.5}$Ge$_{0.5}$ Acta Mater. 124 528–35

[36] Iida M, Nakamura T, Fujimoto K, Yamaguchi Y, Tamura K, Iida T and Nishio K 2016 Thermoelectric properties of Mg$_{5}$Sn$_{0.5}$Ge$_{0.5}$ prepared by spark plasma sintering Scr. Mater. 116 11–5

d. Liu X, Zhu T, Wang H, Hu L, Xie H, Jiang G and Zhang X 2013 Low electron scattering potentials in high performance Mg$_{5}$Sn$_{0.5}$Ge$_{0.5}$ based thermoelectric solid solutions with band convergence Adv. Energy Mater. 3 1238–44

c. Fan W, Chen S, Zeng B, Zhang Q, Meng Q, Wang W and Munir Z A 2017 Enhancing the $zT$ value of Bi-doped Mg$_{5}$Sn$_{0.5}$Ge$_{0.5}$ through reduction of bipolar thermal conductivity ACS Applied Materials & Interfaces 9 28635–41

d. Khan A, Vlachos N, Hatzikraniotis E, Polymeris G, Lioutas C, Stefanaki E and Kyrtasi T 2014 Thermoelectric properties of highly efficient Bi-doped Mg$_{5}$Sn$_{0.5}$Ge$_{0.5}$ materials Acta Mater. 77 43–53

e. Khan A U, Vlachos N and Kyrtasi T 2013 High thermoelectric figure of merit of Mg$_{5}$Sn$_{0.5}$Ge$_{0.5}$ materials doped with Bi and Sn Scr. Mater. 69 609–66

[37] Akram R, Yan Y, Yang D, She X, Zheng G, Su X and Tang X 2016 Microstructure and thermoelectric properties of Sn$_2$-doped Hf$_{0.25}$Zr$_{0.75}$NiSn half-Heusler compounds with improved carrier mobility Internmetallics 74 1–7

[38] Fu C, Bai S, Liu Y, Tang Y, Chen L, Zhao X and Zhu T 2015 Realizing high figure of merit in heavy-band p-type half-Heusler thermoelectric materials Nat. Commun. 6 6144

a. Visconti A, Bernard-Granger G, Navone C, Lefebre J and Mingo N 2016 Microstructure investigations and thermoelectric properties of an N-type Half-Heusler alloy sintered by spark plasma sintering Scr. Mater. 123 100–4

b. Shen J, Fu C, Liu Y, Zhao X and Zhu T 2018 Enhancing thermoelectric performance of FeNbSn half-Heusler compound by Hf-Ti doping Energy Storage Materials 10 69–74
Zeier W G, Zevalkink A, Gibbs Z M, Hautier G, Kanatzidis M G and Snyder G J 2016 Thinking like a chemist: intuition in
Pei Y, LaLonde A D, Wang H and Snyder G J 2012 Low effective mass leading to high thermoelectric performance
Goldsmid H J 1986
Pei Y, Shi X, Lalonde A, Wang H, Chen L and Snyder G J 2011 Convergence of electronic bands for high performance bulk
Zhao J, Islam S M, Tan G, Hao S, Wolverton C, Li R K and Kanatzidis M G 2017 The new semiconductor Cs4Cu3Bi9S17
Ravich Y I, E
Vineis C J, Shakouri A, Majumdar A and Kanatzidis M G 2010 Nanostructured thermoelectrics: big ef
He Y, Day T, Zhang T, Liu H, Shi X, Chen L and Snyder G J 2014 High thermoelectric performance in non-toxic earth-abundant
copper sulfide Adv. Mater. 26.3974–8
Liu H, Shi X, Xu F, Zhang L, Zhang W, Chen L and Snyder G J 2012 Copper ion liquid-like thermoelectrics Nat. Mater. 11 422
Nolas G S, Cohn J L, Slack G A and Schuiman S B 1998 Semiconducting Ge clathrates: promising candidates for thermoelectric applications Appl. Phys. Lett. 73.178
Uber C 2001 Thermoelectric Materials Research I ed T Tritt (Semiconductors and Semimetals Series 69) (Amsterdam: Elsevier) pp 139–253
Nolas G S, Morelli D T and Tritt T M 1999 Skutterudites: a phonon-glass-electron crystal approach to advanced thermoelectric energy conversion applications Annual Review of Materials Science 29 89–116
Vineis C J, Shahkouri A, Majumdar A and Kanatzidis M G 2010 Nanostructured thermoelectrics: big efficiency gains from small features Adv. Mater. 22 3970–80
Rowe D M (ed) 1995 CRC Handbook of Thermoelectrics (Boca Raton: CRC press)
Dames C and Chen G 2006 Thermoelectrics Handbook Macro to Nano ed D M Rowe ch. 42 (Boca Raton: CRC)
Wood C 1988 Materials for thermoelectric energy conversion Rep. Prog. Phys. 51 459
Snyder G J and Toberer E S 2008 Complex thermoelectric materials Nat. Mater. 7 105–14
Pei Y et al 2016 Multiple converged conduction bands in K4Cu6Se12: a promising thermoelectric material with extremely low thermal conductivity J. Am. Chem. Soc. 138 16364–71
Zhao J, Islam S M, Tan G, Hao S, Wolverton C, Li R K and Kanatzidis M G 2017 The new semiconductor Cu2Cu,Bi6Se17 Chem. Mater. 29 1744–51
Goldsmid H J 1986 Electronic Refrigeration (London: Pion limited)
Pei Y, LaLonde A D, Wang H and Snyder G J 2012 Low effective mass leading to high thermoelectric performance Energy & Environmental Science 5 7963–9
Zeier W G, Zevalkink A, Gibbs Z M, Hautier G, Kanatzidis M G and Snyder G J 2016 Thinking like a chemist: intuition in thermoelectric materials Angewandte Chemie International Edition 55 6826–41
Pei Y, Gibbs Z M, Gloskovskii A, Balke B, Zeier W G and Snyder G J 2014 Optimum carrier concentration in n-type PbTe thermoelectrics Adv. Energy Mater. 4 1400086
Takagiwa Y, Pei Y, Pomrehn G and Snyder G J 2012 Dopsant effect on the band structure of PbTe thermoelectric material Appl. Phys. Lett. 101 092102
Pei Y, LaLonde A D, Wang H and Snyder G J 2012 Low effective mass leading to high thermoelectric performance Energy & Environmental Science 5 7963–9
Wang H, Pei Y, LaLonde A D and Snyder G J 2013 Material design considerations based on thermoelectric quality factor Thermoelectric Nanomaterials (Berlin: Heidelberg: Springer) pp 3–32
Mahan G D 1988 Solid State Phys. vol 51 ed H Ehrenreich and F Spaepen (San Diego: Academic Press Inc) p 81
Pei Y, Wang H and Snyder G J 2012 Band engineering of thermoelectric materials Adv. Mater. 24 6125–35
Ravich Y L, Efi mova B A and Smirnov I A 1970 Semiconducting Lead Chalcogenides (New York: Plenum Press)
Ravich Y L, Efimova B A and Tamarchenko V I 1971 Scattering of current carriers and transport phenomena in lead chalcogenides ii. experiment Phys. Status Solidi (b) 43 453–69
Pei Y, Shi X, LaLonde A, Wang H, Chen L and Snyder G J 2011 Convergence of electronic bands for high performance bulk thermoelectrics Nature 473 66
Zeier W G, Zhu H, Gibbs Z M, Ceder G, Tremel W and Snyder G J 2014 Band convergence in the non-cubic chalcopyrite compounds Cu9MgSe4S2, J. Mater. Chem. C 2 10189–94
Zhang Q, Wang H, Liu W, Wang H, Yu B, Zhang Q and Chen G 2012 Enhancement of thermoelectric figure of-merit by resonant states of lead selenide Energy & Environmental Science 5 5246–51
Jaworski C M, Wiendlocha B, Jovovic V and Heremans J P 2011 Combining alloy scattering of phonons and resonant electronic levels to reach a high thermoelectric figure of merit in PbTeSe and PbTeS alloys Energy & Environmental Science 4 4155–62
Pei Y, Shi X, Lalonde A, Wang H, Chen L and Snyder G J 2011 Convergence of electronic bands for high performance bulk thermoelectrics Nature 473 66–9
LaLonde A D, Pei Y, Wang H and Snyder G J 2011 Lead telluride alloy thermoelectrics Materials Today 14 5326–32
Shi X, Chen L and Uher C 2016 Recent advances in high-performance bulk thermoelectric materials Int. Mater. Rev. 61 379–415
Dresselhaus M S, Chen G, Tang M Y, Yang R G, Lee L, Wang D Z, Ren Z F, Fluerau J P and Gognaec P 2007 New directions for low-dimensional thermoelectric materials Adv. Mater. 19 1043–53
Hicks I D and Dresselhaus M S 1993 Effect of quantum-well structures on the thermoelectric figure of merit Phys. Rev. B 47 12727
Lan Y, Minnich A J, Chen G and Ren Z 2010 Enhancement of thermoelectric figure-of-merit by a bulk nanostructuring approach Adv. Funct. Mater. 20 357–76
[81] Zamanipour Z, Shi X, Dehkordi A M, Krasinski J S and Vashaei D 2012 The effect of synthesis parameters on transport properties of nanostructured bulk thermoelectric p-type silicon germanium alloy Phys. Status Solidi (a) 209 2049–58

[82] Chen Z G, Han G, Yang L, Cheng L and Zou J 2012 Nanostructured thermoelectric material: current research and future challenge Progress in Natural Science: Materials International 22 535–49

[83] Hicks L D and Dresselhaus M S 1993 Thermoelectric figure of merit of a one-dimensional conductor Phys. Rev. B 47 16631

[84] Zhao X B, Li X H, Zhang Y H, Zhu T J, Tu J P and Zhang X B 2005 Bismuth telluride nanotubes and the effects on the thermoelectric properties of nanotube-containing nanostructures Appl. Phys. Lett. 86 062111

[85] Zhang G, Yu Q, Wang W and Li X 2010 Nanostructures for thermoelectric applications: synthesis, growth mechanism, and property studies Adv. Mater. 22 1595–62

[86] Boukai A, Buninovich Y, Tahir-Kheli J, Yu K, Goddard IIi W A and Heath J R 2008 Silicon nanowires as efficient thermoelectric materials Nature 451 168

[87] Zide J M O, Vashaei D, Bian Z X, Zeng G, Bowers J E, Shakouri A and Gossard A C 2006 Demonstration of electron filtering to increase the seebeck coefficient in In 0.53 Ga 0.47 As In 0.5 Ga 0.5 Al 0.19 As superlattices Phys. Rev. B 74 205335

[88] Faleev S V and Léonard F 2008 Theory of enhancement of thermoelectric properties of materials with nanoinsertions Phys. Rev. B 77 214304

[89] Ahmad S et al 2016 Boosting thermoelectric performance of p-type SiGe alloys through in situ metallic YS2 nanoinsertions Nano Energy 27 282–97

[90] Zhao L D, Lo S H, Zhang Y, Sun H, Tan G, Uher C and Kanatzidis M G 2014 Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals Nature 508 373

[91] Tang Y, Hanus R, Chen S W and Snyder G J 2015 Solubility design leading to high figure of merit in low-cost Ce–CoSb, skutterudites Nat. Commun. 6 7584

[92] Nolas G S, Kaezer M, Littleton R T IV and Tritt T M 2000 High figure of merit in partially filled yterbium skutterudite materials Appl. Phys. Lett. 77 1855–7

[93] Zhao X Y, Shi X, Chen L D, Zhang W Q, Zhang W B and Pei Y Z 2006 Synthesis and thermoelectric properties of Sr–filled skutterudite Sr12Co8Sb12 J. Appl. Phys. 99 053711

[94] Pei Y Z, Yang J, Chen L D, Zhang W, Salvador J R and Yang J 2009 Improving thermoelectric performance of caged compounds through light-element filling Appl. Phys. Lett. 95 042101

[95] Uher C 2000 Recent trends in thermoelectric materials research II Semicond. Semimet. vol 69 (San Diego: Academic) pp 139–253

[96] Caillat T, Fleurial J P and Borshchevsky A 1996 Bridgman–solution crystal growth and characterization of the skutterudite compounds CoSb3 and RhSb3 J. Cryst. Growth 166 722–6

[97] Morelli D T, Caillat T, Fleurial J P, Borshchevsky A, Vandensande J, Chen B and Uher C 1995 Low-temperature transport properties of p-type CoSb3 Phys. Rev. B 51 9622

[98] Sales B C, Mandrus D and Williams R K 1996 Filled skutterudite antimonides: a new class of thermoelectric materials Science 272 1325

[99] Fleurial J P, Caillat T and Borshchevsky A 1997 Skutterudites: an update 16th Int. Conf. on Thermoelectrics (Dresden, Germany) pp 1–11

[100] Shi X, Zhang W, Chen L D, Yang J and Uher C 2007 Theoretical study of the filling fraction limits for impurities in CoSb3 Phys. Rev. B 75 235208

[101] Shi X, Zhang W, Chen L and Yang J 2005 Filling fraction limit for intrinsic voids in crystals: doping in skutterudites Phys. Rev. Lett. 95 205503

[102] Shi X, Bai S, Xu, Yang J, Zhang W, Chen L and Yang J 2011 Realization of high thermoelectric performance in n-type partially filled skutterudites J. Mater. Res. 26 1745–54

[103] Hermann R P, Jin R, Schweika W, Grandjean F, Mandrus D, Sales B C and Long G J 2003 Einstein oscillators in thallium filled antimony skutterudites Phys. Rev. Lett. 90 135505

[104] Shi X, Salvador J R, Yang J and Wang H 2009 Thermoelectric properties of n-type multiple-filled skutterudites J. Electron. Mater. 38 930–3

[105] Shi X, Yang J, Salvador J R, Chi M, Cho J Y, Wang H and Chen L 2011 Multiple-filled skutterudites: high thermoelectric figure of merit through separately optimizing electrical and thermal transports J. Am. Chem. Soc. 133 7837–46

[106] Khan A U et al 2017 Nano-micro-porous skutterudites with 100% enhancement in ZT for high performance thermoelectricity Nano Energy 31 152–9

[107] Meng X, Cai W, Liu Z, Li J, Geng H and Sai J 2015 Enhanced thermoelectric performance of p-type filled skutterudites via the coherence strain fields from spinodal decomposition Acta Mater. 98 405–15

[108] Zong P, Hanus R, Dylla M, Tang Y, Liao J, Zhang Q, Synder G J and Chen L 2017 Skutterudite with graphene-modified grain-boundary complexion enhancements ZT enabling high-efficiency thermoelectric device Energy Environ. Sci. 10 183–91

[109] Gharleghi A, Huang P, Lin F and Liu C 2016 Enhanced ZT of In0.53Ga0.47As by InSb nanocomposites fabricated by hydrothermal synthesis combined with solid–vapor reaction: a signature of phonon-glass and electron-crystal materials ACS Applied Materials & Interfaces 8 35123–31

[110] Chakoumakos B C, Sales B C, Mandrus D G and Nolas G S 2000 Structural disorder and thermal conductivity of the semiconducting clathrate Sr3Ga5Ge12 J. Alloys Compd. 296 80–6

[111] Nolas G S, Poon J and Kanatzidis M 2006 Recent developments in bulk thermoelectric materials MRS Bull. 31 199–205

[a] Li Z, Tang J, Nishino T, Sato K, Wang Y and Tanigaki K 2010 Carrier control in Ba8Ga16Ge30 single crystals Phys. Rev. B 81 155312

[b] Beekman M van d and Nolas G S 2006 Synthesis and thermal conductivity of type II silicon clathrates Physica C: Superconductivity and its applications 470 5616–8

[c] Nolas G S 2006Synthesis of bulk thermoelectric devices Proc. Phys. Society. Section B 89 203

[d] Goldsmid H J 2014 Bismuth telluride and its alloys as materials for thermoelectric generation Materials 7 2577–92

[e] Goldsmid H J 1956 The thermal conductivity of bismuth telluride Proceedings of the Physical Society. Section B 69 203

[f] Goldsmid H J, Gopinathan K K, Matthews D N, Taylor K N R and Baird C A 1988 High-Tc superconductors as passive thermoelectrics J. Phys. D: Appl. Phys. 21 344

[g] Lin S, Li W, Chen Z, Shen J, Ge B and Pei Y 2016 Tellurium as a high-performance elemental thermoelectric Nat. Commun. 7 10287

[h] Seo S, Jeong Y, Oh M and Yoo B 2017 Effect of hydrogen annealing of ball-milled Bi2S3Te3 powders on thermoelectric properties J. Alloys Compd. 706 576–83

[i] Chiu W, Chen C and Chen Y 2016 A strategy to optimize the thermoelectric performance in a spark plasma sintering process Sci. Rep. 6 23143

[a] Kim S, Lee J H, Youn H A, Kim H S, Hwang S W, Roh J W and Snyder G J 2015 Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics Science 348 109–14
Zhao L D, Berardan D, Pei Y L, Byl C, Pinsard-Gaudart L and Dragoe N 2010 Bi1-
Tang G, Cai K, Cai K, Cui J, Yin J and Shen S 2016 Preparation and thermoelectric properties of MoS2/Bi2Te3 nanocomposites Ceram. Int. 42 17927–92
Venkatasubramanian R 2000 Lattice thermal conductivity reduction and phonon localization like behavior in superlattice structures Phys. Rev. B 61 3091–7
Böttner H, Chen G and Venkatasubramanian R 2006 Aspects of thin-ﬁlm superlattice thermoelectric materials, devices, and applications MRS Bull. 31 211–7
Venkatasubramanian R, Siivola E, Colpitts T and Oquinn B 2001 Thin-ﬁlm thermoelectric devices with high room-temperature ﬁgures of merit Nature 413 597–602
Park D, Park S, Jeong K, Jeong H, Song I Y and Cho M 2016 Thermal and electrical conduction of single-crystal Bi2Te3 nanostructures grown using a one step process Sci. Rep. 6 19132
Adam A, Lilov E and Petkov F 2017 Optical and thermoelectric properties of nano-particles based Bi2(Se0.135Te0.865) thin ﬁlms Superlattices Microstruct. 101 609–24
Amaty R and Ram R J 2012 Trend for thermoelectric materials and their earth abundance J. Electron. Mater. 41 1011–9
Pilgrim W C and Morkel C 2006 State dependent particle dynamics in liquid alkali metals J. Phys. Condens. Matter 18 S5855–633
Trachenko K 2008 Heat capacity of liquids: an approach from the solid phase Phys. Rev. B 78 104201
Qiu P, Shi X and Chen L 2016 Cu-based thermoelectric materials Energy Storage Mater. 3 85–97
Frenkel I 1947 Kinetic Theory of Liquids ed R H Fowler et al. (Oxford: Oxford Univ Press) pp 188–249
Shi X, Li X, Fan J, Zhang W and Chen L 2010 Cu–Se bond network and thermoelectric compounds with complex diamond like structure Chem. Mater. 22 6029–31
Shi X Y, Huang F Q, Liu M L and Chen L D 2009 Thermoelectric properties of tetrahedrally bonded wide-gap stannite compounds Cu2ZnSnS4_InSe Appl. Phys. Lett. 94 121103
Slack G A 1995 CRC Handbook of Thermoelectricity (Boca Raton: CRC Press)
Ma R, Liu G, Li J, Li Y, Chen K, Han Y, Zhou M and Li L 2017 Effect of secondary phases on thermoelectric properties of Cu2SnSe3 Ceram. Int. 43 7002–10
Liu R, Qin Y, Cheng N, Zhang J, Shi X, Grin Y and Chen L 2016 Thermoelectric performance of Cu1–x−δAgInTe2 diamond-like materials with a pseudocubic crystal structure Inorg. Chem. Front. 3 1167–77
Gahtori B, Bathula S, Tyagi K, Jayasimhandri M, Srivastava A K, Singh S and Dhar A 2015 Giant enhancement in thermoelectric performance of copper selenide by incorporation of different nanoscale dimensional defect features Nano Energy 13 36–46
Zhu C, He Y, Liu P, Fu Z, Xu F, Yao H, Zhang L, Shi F and Chen L 2017 Multiple nanostructures in high performance Cu2Sn0.5Te0.5 thermoelectric materials Ceram. Int. 43 7866–9
Farooq M, Butt S, Gao K, Sun X, Pang X, Khan S U, Xu W, Mohmed F, Mahmood A and Mahmood N 2016 Enhanced thermoelectric efficiency of Cu2−δSe−Cu2S composite by incorporating Cu2S nanoparticles Ceram. Int. 42 8395–401
Heo J, Laurita G, Mui M, Subramanian A M and Keszer D A 2014 Enhanced thermoelectric performance of synthetic tetrahedrites Chem. Mater. 26 2047–51
Lu X, Morelli D T, Xia Y and Ozolins V 2015 Increasing the thermoelectric ﬁgure of merit of tetrahedrites by Co-doping with nickel and zinc Chem. Mater. 27 408–15
Zhao I D, Berardan D, Pei Y L, Byl C, Pimsard-Gaudart I and Dragoe N 2010 Bi1–xSrxCuSeO oxyselenides as promising thermoelectric materials Appl. Phys. Lett. 97 092118
Sui J, Li J, He J, Pei Y L, Berardan D, Wu H and Zhao I D 2013 Texturization boosts the thermoelectric performance of Bi2CuSeO4 Energy & Environmental Science 6 2916–20
Lan J L, Deng C, Ma W, Ren G K, Lin Y H and Yang X 2017 Ultra-fast synthesis and high thermoelectric properties of heavy sodium doped Bi2CuSeO4 J. Alloys Compd. 708 955–60
LaLonde A D, Pei Y and Snyder G J 2011 Reevaluation of PbTe1−xIn as high performance n-type thermoelectric material Energy & Environmental Science 4 2090–9
Zhao I D, Wu H J, Hao S Q, Wu C I, Zhou X Y, Biswas K and Dravid V P 2013 All-scale hierarchical thermoelectrics: MgTe in PbTe facilitates valence band convergence and suppresses bipolar thermal transport for high performance Energy & Environmental Science 6 3399–405
Ye P, LaLonde A D, Heyn N A and Snyder G J 2012 High thermoelectric ﬁgure of merit in PbTe alloys demonstrated in PbTe–CdTe Adv. Energy Mater. 2 670–5
Biswas K, He J, Zhang Q, Wang G, Uher C, Dravid V P and Kanatzidis M G 2011 Strained endotaxial nanostructures with high thermoelectric ﬁgure of merit Nat. Chem. 3 160–6
He J, Girard S N, Kanatzidis M G and Dravid V P 2010 Microstructure-lattice thermal conductivity correlation in nanostructured PbTeSn0.5 thermoelectric materials Adv. Funct. Mater. 20 764–72
Heremans J P, Wiendlocha B and Chamoire A M 2012 Resonant levels in bulk thermoelectric semiconductors Energy & Environmental Science 5 5510–30
Ahn K, Han M K, He J, Androulakis I, Ballikaya S, Uher C and Kanatzidis M G 2010 Exploring resonance levels and nanostructuring in the PbTe–CdTe system and enhancement of the thermoelectric ﬁgure of merit J. Am. Chem. Soc. 132 5227–35
Johnsen S, He J, Androulakis I, Dravid V P, Todorov I, Chung D Y and Kanatzidis M G 2011 Nanostructures boost the thermoelectric performance of PbS I, J. Am. Chem. Soc. 133 3460–70
Tang G, Shi F, Hao S, Zhao L, Chi H, Zhang X, Uher C, Wolverton C, Dravid V P and Kanatzidis M G 2016 Non-equilibrium processing leads to record high thermoelectric ﬁgure of merit in PbTe–SrTe Nat. Commun. 7 12167
Luo J, You L, Zhang J, Guo K, Zhu H, Gui L, Yang Z, Li X, Yang J and Zhang W 2017 Enhanced average thermoelectric ﬁgure of merit of the PbTe–SrTe–MnTe alloy ACS Applied Materials & Interfaces 9 8729–36
[155] Ginting D, Lin C, Lydia R, So H S, Lee H, Hwang J, Kim W, Orabi R and Rhee J 2017 High thermoelectric performance in pseudo quaternary compounds of (PbTe)_{1-x} (PbSe)_{x} (PbS)_{y} by simultaneous band convergence and nano precipitation Acta Mater. 131 98–109

[156] Ravich Y L, Efimova B A and Smirnov I A 1970 Semiconducting Lead Chalcogenides (New York: Plenum Press) p 1970

[157] Parker D and Singh D J 2010 High-temperature thermoelectric performance of heavily doped PbSe Phys. Rev. B 82 035204

[158] Wang H, Pei Y, Lalonde A D and Snyder G J 2011 Heavily doped p-type PbSe with high thermoelectric performance: an alternative for PbTe Adv. Mater. 23 1366–70

[159] Zhou M, Snyder G, Li J and Zhao L D 2016 Lead-free tin chalcogenide thermoelectric materials Inorganic Chemistry Frontiers 3 1449–63

[160] Sun B Z, Ma Z, He C and Wu K 2015 Enhanced thermoelectric performance of layered SnS crystals: the synergetic effect of temperature and carrier concentration Rsc Advances 5 56382–90

[161] Guillen C, Montero J and Herrero J 2011 Characteristics of SnSe and SnSe2 thin films grown onto polycrystalline SnO2-coated glass substrates Phys. Status Solidi (a) 208 679–83

[162] Chang K M, Wamwangi D, Woda M, Wuttig M and Bensch W 2008 Investigation of SnSe, SnSe2, and SnSe3 alloys for phase change memory applications J. Appl. Phys. 103 083523

[163] Yu J G, Yue A S and Stafsudd O M 1981 Growth and electronic properties of the SnSe semiconductor J. Cryst. Growth 54 248–52

[164] Wasscher JD, Albers W and Haas C 1963 Simple evaluation of the maximum thermoelectric figure of merit, with application to mixed crystals SnS, SnSe, Solid-State Electron. 6 261–4

[165] Chen C L, Wang H, Chen Y Y, Day T and Snyder G J 2014 Thermoelectric properties of p-type polycrystalline SnSe doped with Ag J. Mater. Chem. A 2 11171–6

[166] Sassi S, Candolfi C, Vaney J B, Ohorodniuchuk V, Masschelein P, Daascher A and Lenoir B 2014 Assessment of the thermoelectric performance of polycrystalline p-type SnSe Appl. Phys. Lett. 104 212105

[167] Fu Y et al 2014 Enhanced thermoelectric performance in p-type polycrystalline SnSe benefiting from texture modulation J. Mater. Chem. C 2 14201–7

[168] Zhang Q, Chen H Y, Qian J, Cao F, Dhalak K, Chen S, Gang C and Ren Z 2015 Studies on Thermoelectric properties of n-type polycrystalline SnSe1−x Sx by iodine doping Adv. Energy Mater. 5 1500360

[169] Tan G, Shi F, Doak J W, Sun H, Zhao L D, Wang P and Kanatzidis M G 2015 Extraordinary role of Hg in enhancing the thermoelectric performance of p-type SnTe Energy & Environmental Science 8 267–77

[170] Zhao L D, Zhang X, Wu H, Tan G, Pei Y, Xiao Y and Gong S 2016 Enhanced thermoelectric properties in the counter-doped SnTe system with strained endotaxial SrTe J. Am. Chem. Soc. 138 2366–73

[171] He J, Tan X, Xu J, Liu G G, Shao H, Fu Y and Jiang J 2015 Valence band engineering and thermoelectric performance optimization in SnTe by Mn−alloying via a zone-melting method J. Mater. Chem. A 3 19974–9

[172] Tan G, Shi F, Hao S, Chi H, Zhao L D, Uhler C and Kanatzidis M G 2015 Codoping in SnTe: enhancement of thermoelectric performance through synergy of resonance levels and band convergence J. Am. Chem. Soc. 137 51100–12

[173] Zhang Q, Liao B, Lan Y, Lukas J, Liu W, Esfarjani K and Ren Z 2013 High thermoelectric performance by resonant dopant indium in nanostructured SnTe Proc. Natl. Acad. Sci. 110 13261–6

[174] Zhao L et al 2016 Enhanced thermoelectric properties in the counter-doped SnTe system with strained endotaxial SrTe J. Am. Chem. Soc. 138 2366–73

[175] Ohtaki M 2011 Recent aspects of oxide thermoelectric materials for power generation from mid-to-high temperature heat source J. Ceram. Soc. Japan 119 770–5

[176] He J, Liu Y and Fanahashi R 2011 Oxide thermoelectrics: the challenges, progress, and outlook J. Mater. Res. 26 1762–72

[177] Khan W, Nasqi A H, Gupta M, Husain S and Kumar R 2011 Small polaron hopping conduction mechanism in Fe doped LaMnO3, The Journal of Chemical Physics 135 054501

[178] Lin Y H, Nan C W, Liu Y, Li J, Mizokawa T and Shen Z 2007 High-temperature electrical transport and thermoelectric power of partially substituted Ca0.5Co0.5O2-based ceramics J. Am. Ceram. Soc. 90 132–6

[179] Liu Y, Lin Y, Shi Z, Nan C W and Shen Z 2005 Preparation of Ca0.4Co0.6O2 and improvement of its thermoelectric properties by spark plasma sintering J. Am. Ceram. Soc. 88 1337–40

[180] Altim S, Aksan M A and Bayri A 2014 High temperature spin state transitions in misfit-layered Ca0.4Co0.6O2 J. Alloys Compd. 587 40–4

[181] Koshihara W and Maekawa S 2001 Effects of spin and orbital degeneracy on the thermopower of strongly correlated systems Phys. Rev. Lett. 87 236603

[182] Masset A C, Michel C, Maigrau A, Hervieu M, Toulemonde O, Studer F and Hejtmanek J 2000 Misfit-layered cobaltite with an anisotropic giant magnetoaristance: Ca0.5Co0.5O2 Phys. Rev. B 62 166

[183] Lu Z, Zhang H, Lei W, Sinclair D C and Reaney I M 2016 High-figure-of-Merit thermoelectric La-doped A-site-deficient SrTiO3 ceramics Chem. Mater. 28 925–35

[184] Li E, Wang N, He H and Chen H 2016 Improved thermoelectric performances of SrTiO3 ceramic doped with Nb by surface modification of nanosized titanata Nanoscale Res. Lett. 11 1188

[185] Reimann T and Topfer J 2017 Thermoelectric properties of Ge/W double substituted calcium manganite J. Alloys Compd. 699 788–95

[186] Zha Y, Su W, Liu J, Zhou Y, Li J, Zhang X, Du Y and Wang C 2015 Effects of Dy and Yb co-doping on the thermoelectric performance of CaMnO3 ceramics Ceram. Int. 41 1535–9

[187] Jood P, Mehta R J, Zhang Y, Peleckis G, Wang X, Siegel R W and Ramanath G 2011 Al-doped zinc oxide nanocomposites with enhanced thermoelectric properties Nano Lett. 11 4337–42

[188] Slack G A and Hussain M A 1991 The maximum possible conversion efficiency of silicon-germanium thermoelectric generators J. Appl. Phys. 70 7694–718

[189] Vining C B 1991 A model for the high-temperature transport properties of heavily doped n-type silicon-germanium alloys J. Appl. Phys. 69 331–41

[190] Nozariashvare A, Roy P, Zamanipur Z, Dycus J H, Cabral M J, Lebeau J M, Krasiski J and Vashaeie D 2016 Comparison of thermoelectric properties of nanostructured Mg2Si, Fe5Si3, SiGe, and nanocomposites of SiGe–MgSi, SiGe–Fe5Si3 APL Materials 4.0 104814

[191] Usenko A, Moskovskikh D, Gorshenkov M, Voronin A, Stepashkin A, Kaloshkin S, Arkhipov D and Khovaylo V 2017 Enhanced thermoelectric figure of merit of p-type SnGe2 nanostructured spark plasma sintered alloys with embedded SiOx nanoinclusions Scr. Mater. 127 65–7

[192] Jin Y R, Feng Z Z, Ye L Y, Yan Y L and Wang Y X 2016 Mg2Sn: a potential mid-temperature thermoelectric material RSC Adv. 6 48728–36
[193] Janka O, Zaikina J V, Tabatabaifar H, Yang H, Browning N D and Kauzlarich S M 2017 Microstructure investigations of Yb- and Bi-doped Mg$_2$Si prepared from metal hydrides for thermoelectric applications J. Solid State Chem. 245 152–9

[194] Li J, Chen G, Duan B, Zhu Y, Hu X, Zhai P and Li P 2016 Thermoelectric properties of Mg$_2$Si$_{0.995}$Sb$_{0.005}$ prepared by the high-pressure high-temperature method J. Electron. Mater. 46 2570–5

[195] Chen L, Zeng X, Tritt T M and Poon S J 2016 Half-Heusler alloys for efficient thermoelectric power conversion J. Electron. Mater. 45 5554–60

[196] Fu C, Zhu T, Liu Y, Xie H and Zhao X 2012 Band engineering of high performance p-type FeNbSb based half-Heusler thermoelectric materials for figure of merit $zT > 1$ Energy & Environmental Science 5 216–20

[197] Zhao H, Sui J, Tang Z, Lan Y, Jie Q, Kraemer D and Ren Z 2014 High thermoelectric performance of MgAgSb-based materials Nano Energy 7 97–103

[198] Zeier W G, Schmitt J, Hautier G, Aydemir U, Gibbs Z M, Felser C and Snyder G J 2016 Engineering half-Heusler thermoelectric materials using Zintl chemistry Nature Reviews Materials 1 16032