Review

Development of Perovskite-Type Materials for Thermoelectric Application

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Abstract: Oxide perovskite materials have a long history of being investigated for thermoelectric applications. Compared to the state-of-the-art tin and lead chalcogenides, these perovskite compounds have advantages of low toxicity, eco-friendliness, and high elemental abundance. However, because of low electrical conductivity and high thermal conductivity, the total thermoelectric performance of oxide perovskites is relatively poor. Variety of methods were used to enhance the TE properties of oxide perovskite materials, such as doping, inducing oxygen vacancy, embedding crystal imperfection, and so on. Recently, hybrid perovskite materials started to draw attention for thermoelectric application. Due to the low thermal conductivity and high Seebeck coefficient feature of hybrid perovskites materials, they can be promising thermoelectric materials and hold the potential for the application of wearable energy generators and cooling devices. This mini-review will build a bridge between oxide perovskites and burgeoning halide perovskites in the research of thermoelectric properties with an aim to further enhance the relevant performance of perovskite-type materials.

Keywords: perovskite; thermoelectric; generator; cooler

1. Introduction

1.1. Thermoelectrics (TE)

Thermoelectric effect includes Seebeck effect and Peltier effect. The Seebeck effect denotes the process that converts temperature gradient directly to electricity, which can be illustrated by the working principle of a thermoelectric generator (Figure 1A). In contrast, the Peltier effect can convert electrical energy to a temperature gradient, which leads to thermoelectric cooling device. Thermoelectric performance of a material is evaluated by the dimensionless thermoelectric figure of merit (ZT),

\[ ZT = \frac{S^2 \sigma}{\kappa T} \]  

where \( S \) (V·K\(^{-1}\)) is Seebeck coefficient, \( \sigma \) (S·m\(^{-1}\)) is electrical conductivity, \( \kappa \) (W·m\(^{-1}\)·K\(^{-1}\)) is thermal conductivity, and \( T \) (K) is absolute temperature. \( S^2 \sigma \) is defined as the thermoelectric power factor. The thermoelectric energy conversion efficiency and the maximum cooling temperature for Peltier devices are dependent on the value of ZT [1].
Figure 1. (A) Schematic of Seebeck effect; (B) schematic of interdependent relationship of Seebeck coefficient, electrical conductivity, and thermal conductivity, and the strategies to decouple their interdependency.

The maximum efficiency ($\eta$) of a thermoelectric device is defined as the quotient of the energy provided to the load ($W$) and the heat energy consumed at the hot junction ($Q$). It is a function of $ZT$ as well as the temperature of the hot and cold side ($T_H$, $T_C$), as shown in the equation

$$\eta = \frac{W}{Q} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_H}{T_C}} \quad (2)$$

Therefore, to enhance the thermoelectric properties of materials, namely increase the $ZT$ value, the materials should have high Seebeck coefficient, high electrical conductivity, and low thermal conductivity [1–4].

However, simply enhancing the $ZT$ value of TE materials is non-trivial, since the parameters are interrelated. One direct way to enhance the electrical conductivity of semiconductors is to increase the carrier concentration, as shown in the equation:

$$\sigma = e(n_e\mu_e + n_h\mu_h) \quad (3)$$

where $e$ is the elementary charge; $n_e$ and $n_h$ are the carrier concentrations of electrons and holes, respectively; $\mu_e$ and $\mu_h$ are the carrier mobility of electrons and holes, respectively.
However, the Seebeck coefficient for metal or degenerate semiconductor is defined by the equation:

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

(4)

where $k_B$ is Boltzmann constant, $h$ is Planck’s constant, $m^*$ is the effective mass of the charge carrier, $T$ is absolute temperature, and $n$ is the carrier concentration. According to Equation (4), $S$ would decrease when increasing the carrier concentration.

The thermal conductivity is linked to electron and phonon contributions. The electronic thermal conductivity (electron contributions, $\kappa_e$) can be expressed according to Wiedemann–Franz law:

$$\kappa_e = L \cdot \sigma \cdot T$$

(5)

where $L$ is the Lorentz number, and $T$ is absolute temperature. Thus, it is directly related to electrical conductivity. As a consequence, the TE materials have an optimum carrier concentration to improve ZT value. The interdependent relationship was of $\sigma$, $S$, and $\kappa$ shown in Figure 1B, the ZT value was determined by $\sigma$, $S$, and $\kappa$, which was interconnected shown as the inner circle. To further enhance the ZT value, it is inevitable to decouple the interrelationship between the parameters. In inorganic TE materials, multiple ways have been applied to enhance the ZT value. For example, a phonon scattering mechanism was introduced by processing of superlattices and by accessing thermodynamically stable phase separation to suppress the lattice thermal conductivity without the expense of electrical conductivity [5–7]. Additionally, mass fluctuation strategy, rattling strategy, and the panoscopic approach were also used to decouple the relationship between $\sigma$ and $\kappa$ [7–12]. Energy filtering effect is also normally used to decouple the electrical conductivity and Seebeck coefficient, in which an energy barrier was introduced in the TE materials by nanocomposites or grain boundaries. This energy barrier would filter out low energy carriers and let high energy carriers pass. As a result, the Seebeck coefficient can be improved without suppressing the electrical conductivity [13–16]. Additionally, the band engineering, which is used to decouple the Seebeck coefficient and electrical conductivity, also includes degeneration of multiple valleys, electronic resonance states, synergistic nanostructuring, and highly mismatched iso electronic doping. Furthermore, 2D superlattice can also be used to decouple $S$ and $\sigma$ [8–10,17,18]. These strategies were shown in the outer circle of Figure 1B.

TE devices can serve as generator and cooler and be used to recycle waste heat and manage temperature, respectively. Moreover, TE devices have advantages of no vibration, no noise, and highly reliable because they are solid-state devices without moving parts. In our previous studies, thick thermoelectric tellurium (Te) [19] and lead telluride (PbTe) [20] films were synthesized by electrodeposition with high film growth rate. The combination of electrochemical deposition of compound semiconductors with standard integrated circuit technique enables the fabrication of thermoelectric microdevices, which has a more compact size and a capability to handle a wider range of thermal and power management [21–23].

Materials, which are candidates for fabricating TE devices, can be classified as shown in Figure 2. Materials such as organic [5,6,24–32], hybrid perovskites [33–35] and the group V chalcogenides [3,7,10–12,36] are suitable for TE application at the near-room-temperature range. In addition, TE materials—such as the group IV chalcogenides [10,11,20,36], group III-V compounds [10,17,36], group IV-based materials [7,10,12,36], half-Heusler alloys [3,7,9,11], skutterudites [3,11,37], Zintl compounds [3,9,12,37], and clathrates [9,11]—are applicable at the middle temperature (about 400–900 K) range. Furthermore, materials—like rare earth chalcogenides [36], oxide perovskites [38–40], borides [36], and metal oxides [36]—can be used at a high temperature (>1000 K) range. However, normally there is no clear operation temperature boundary for each type of TE materials, for instance, rare earth chalcogenides, group III–V compounds, oxide perovskites materials, borides and metal oxides can be applied in a vast range of temperature depending on specific compounds [10,17,36,38–40]. The inorganic materials are the most well-studied TE
We have studied the thermoelectric properties of PbTe films [20] and silver telluride nanofibers [41]. Additionally, Te nanostructures including nanowire [42], nanotree [42], and nanorice [43] were synthesized, which can be used to be embedded into other TE materials as nanocomposite [44–46] or converted to metal tellurides through cation exchange reaction [47,48]. Metal oxide materials, other than oxide perovskite materials, were investigated for TE application. For example, NaCo$_2$O$_4$ was reported to have an in-plane S of 100 $\mu$V·K$^{-1}$ and $\sigma$ of 5000 S·cm$^{-1}$ at 300 K [49], Bi$_2$Se$_3$Co$_2$O$_4$ achieved a ZT value of 0.19 at 973 K with S of $\sim$150 $\mu$V·K$^{-1}$, $\sigma$ of $\sim$82 S·cm$^{-1}$ and $\kappa$ of $\sim$0.9 W·m$^{-1}$·K$^{-1}$ [50], Ca$_2$TeO$_4$ showed a S of $\sim$125 $\mu$V·K$^{-1}$ and $\sigma$ of $\sim$28 S·cm$^{-1}$ at 300 K [51], Zn$_{0.96}$Al$_{0.02}$Ga$_{0.02}$O reached a ZT value 0.65 at 1247 K with S of 230 $\mu$V·K$^{-1}$, $\sigma$ of $\sim$400 S·cm$^{-1}$ and $\kappa$ of 5 W·m$^{-1}$·K$^{-1}$ because of a bulk nanocomposite structure [52]. In the past decade, many efforts have been put into the investigation of organic thermoelectric materials [25–29]. Moreover, the hybrid perovskites started to draw attention for TE applications [35]. In this review, we are going to focus on oxide and hybrid perovskite materials.

Figure 2. Thermoelectric materials studied through experimentation or calculation.
1.2. Perovskite Materials

Perovskite materials are any materials that have the same type of crystal structure as calcium titanium oxide (CaTiO₃). The general chemical formula for perovskites compounds is ABX₃. A and B are two cations of very different sizes, and X is an anion that bonds to both [53]. Perovskite materials have a variety of applications, such as photovoltaics [53,54], light emitting diodes, thin film transistors, and so on [55]. Oxide perovskite materials have a long history of being applied for TE materials, while hybrid perovskite materials have just begun to be studied for TE applications in recent years.

The most common stable crystal phases of perovskite materials are orthorhombic, tetragonal, and cubic phases as shown in Figure 3 [56]. The stable phase of perovskites materials is determined by both ion size and temperature. For example, the orthorhombic phase of MAPbI₃ is the low-temperature state and can keep its structure stable up to 165 K. With increased temperature, MAPbI₃ undergoes a phase-transition to the tetragonal phase owing to the disordering of MA⁺. When temperature further reaches 327 K, highly disordered MA⁺ cations give rise to the high-symmetry state of MAPbI₃ which has the cubic phase. The packing densities of the three phases follow the trend: c-MAPbI₃ > o-MAPbI₃ > t-MAPbI₃, where the packing density of MAPbI₃ increases as the crystal symmetry and temperature increases [56].

![Figure 3](image_url)

**Figure 3.** Atomistic configurations of (a) orthorhombic; (b) tetragonal; and (c) cubic phases of perovskite materials. Reproduced with permission [56]. Copyright 2016, Advanced Functional Materials.

In this review, we will focus on the application of perovskite materials in thermoelectrics, which has not been systematically reviewed. The perovskite materials used for TE application can be classified into oxide and hybrid perovskites materials. The elements used in perovskite materials are summarized in Figure 4. The elements in the red box were used for A-site, the ones in the pink box were used for A-site doping, and the ones in the brown box were used for both A-site and A-site doping materials. The elements in the blue box were used for B-site, the ones in green box were used for B-site doping, and the ones in the cyan box were used for both B-site and B-site doping. Compared to the traditional materials used for TE application, such as metal chalcogenide materials like Bi₂Te₃ and PbTe, perovskite materials are less capitaly expensive and can be processed by low energy cost methods, especially for hybrid perovskite materials, and can be used for flexible TE devices. The reported TE data about perovskite materials were shown in Table 1.
Table 1. Literature data about TE properties of perovskite material.

| Ref. | Materials | Seebeck (µV·K⁻¹) | Electrical Conductivity (S·cm⁻¹) | Thermal Conductivity (W·m⁻¹·K⁻¹) | Power Factor (µW·K⁻²·m⁻¹) | ZT | Measure Temp. (K) |
|------|-----------|------------------|---------------------------------|-----------------------------------|-----------------------------|----|-----------------|
| [38] | La-Doped SrTiO₃ | −260 | | | | | 298 |
| [57] | Sr₀.₈₂La₀.₁₈TiO₃ | 175 | 400 | 3 | 0.28 | 873 |
| [58] | SrTiO₃ | 210 | 250 | 200 | 0.09 | 760 |
| [59] | reduced graphene oxide—SrTiO₃ | −380 | 30 | | 0.4 | 323 |
| [60] | La-doped SrTiO₃ | 980 | | 0.39 | | 298 |
| [61] | Sr₀.₉La₀.₁TiO₃ | −250 | | | | 1000 |
| [62] | R = (La, Sm, Gd, Dy, Y) | −160 | 500 | 2.7 | 0.22 | 573 |
| [63] | Sr₀.₉₅La₀.₀₅TiO₃ | 250 | 150 | 4.2 | 0.15 | 780 |
| [64] | Sr₀.₉La₀.₁TiO₃ | −225 | 300 | 3.2 | 0.21 | 750 |
| [65] | La-doped SrTiO₃ | −300 | 80 | 3.1 | 0.27 | 1073 |
| [66] | Sr₀.₉₅Ce₀.₀₄TiO₃ | −65 | | | | |
| [67] | Sr₀.₉₆La₀.₀₂TiO₃ | −138 | | | | |
| [68] | Sr₀.₉₂CoTiO₆ | 60 | 10 | | | |
| [69] | Sr(Ti₀.₈Nb₀.₂)O₃ | −200 | | 3.5 | | 1000 |
| [70] | BaNb₀.₀₁Ti₀.₉₉O₃ | −640 | | | | |
| [71] | BaTiO₃ | −550 | | | | |
| [72] | Sr₀.₉₅Y₀.₀₅TiO₃ | −130 | 120 | 4.4 | 0.13 | 420 |
| [73] | Sr₀.₉₅Ca₀.₄₅La₀.₅TiO₃ | −195 | 250 | 3.7 | 0.22 | 850 |
| [74] | Sr₀.₉₆La₀.₀₄TiO₃ | −260 | 500 | 11 | 0.09 | 298 |
| [75] | SrTiO₃/SrTi₃O₈Nb₂O₇/SrTiO₃ | −850 | 1400 | 12 | 2.4 | 300 |
| [77] | Sr(Ti₀.₈Nb₀.₂)O₃ | −300 | 2.5 | | 0.35 | 1000 |
| [78] | Sr₀.₉₅Ta₀.₀₅O₃ | −175 | 300 | 4.4 | 0.17 | 752 |
| [79] | BaTiO₃ | −620 | 0.17 | | | |
| | PbTiO₃ | 110 | | | | |
| | BaTiO₃ | 110 | | | | |
| | SrTiO₃ | 100 | | | | |
| | SrO | −500 | | | | |
| [80] | Nb-doped SrTiO₃ | −540 | | | | |
| [81] | Sr₀.₉₅L₀.₀₅Ti₀.₉₈Mn₀.₀₂O₃ | −150 | 833 | | 0.15 | 300 |
| [82] | Sr₀.₹₅L₀.₀₅Ti₀.₉₈Mn₀.₀₂O₃ | 450 | | | | |
| [83] | Sr₀.₹₅L₀.₀₅Ti₀.₉₈Mn₀.₀₂O₃ | 300 | | | | |
| [84] | SrTiFeO₆ | 280 | 1.2 | | 10 | 1130 |
| | Sr₂TiCoO₆ | 60 | 20 | | 5.4 | 750 |
| [39] | Ba₀.₂₅Sr₁.₇₅Fe₂TiO₆ | 800 | | | | 1123 |
### Table 1. Cont.

| Ref. | Materials | Seebeck ($\mu$V·K$^{-1}$) | Electrical Conductivity (S·cm$^{-1}$) | Thermal Conductivity (W·m$^{-1}$·K$^{-1}$) | Power Factor ($\mu$W·K$^{-2}$·m$^{-1}$) | ZT | Measure Temp. (K) |
|------|-----------|-----------------|-----------------|----------------|-----------------|-----|-----------------|
| [87] | Sr$_2$TiMoO$_6$ | -10.8 | 960 | | 11 | | 1223 |
| [88] | SrTiO$_3$ | -150 | | | | | 1000 |
| [89] | (TB$_{0.1}$Ca$_{0.9}$)MnO$_3$ | -140 | -0.18 | 1.36 | 800 |
| [90] | (Ho$_{0.1}$Ca$_{0.9}$)MnO$_3$ | -110 | -0.18 | 0.13 | 950 |
| [91] | (Y$_{0.1}$Ca$_{0.9}$)MnO$_3$ | -130 | -0.2 | 0.08 | 950 |
| [92] | (Ca$_{0.9}$Bi$_{0.1}$)MnO$_3$ | 80 | 10 | 0.15 | 950 |
| [93] | CaMnO$_3$ | -520 | | | 0.095 | | 1173 |
| [94] | C$_{a0.85}$P$_{0.15}$MnO$_2$ | -130 | 111 | 1.5 | 0.17 | 1100 |
| [95] | C$_{a0.85}$P$_{0.15}$MnO$_2$ | -150 | 133 | 1.7 | 0.16 | 970 |
| [96] | C$_{a0.8}$Y$_{0.2}$MnO$_3$ | -135 | 270 | 510 | | 1073 |
| [97] | C$_{a0.8}$Y$_{0.2}$MnO$_3$ | -75 | 250 | 1.6 | 0.085 | | 1073 |
| [98] | Sm$_{0.25}$Ca$_{0.75}$MnO$_3$ | -380 | | | 65 | |
| [99] | CaMn$_{0.88}$Mn$_{0.12}$O$_3$ | -240 | 0.011 | | | | 100 |
| [100] | YNi$_2$MnO$_3$ | 90 | | | | | 357 |
| [101] | SrMnO$_3$ | -110 | 50 | | | | 300 |
| [102] | CaMn$_{0.85}$Mn$_{0.15}$O$_3$ | -270 | $10^{-4}$ | 0.6 | | | |
| [103] | Ca$_{0.96}$Bi$_{0.04}$MnO$_3$ | -170 | 66.7 | 3.6 | 0.866 | | 1000 |
| [104] | CaMn$_{0.96}$Mn$_{0.04}$O$_3$ | -90 | 3.4 | | 0.012 | | 270 |
| [105] | CaMn$_{0.96}$Mn$_{0.04}$O$_3$ | -140 | 5.4 | | 0.0085 | | 330 |
| [106] | CaMn$_{0.96}$Mn$_{0.04}$O$_3$ | -190 | 29 | | 0.05 | | 1000 |
| [107] | CaMn$_{0.96}$Mn$_{0.04}$O$_3$ | -205 | 50 | | | | 100 |
| [108] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -110 | 31 | | 0.32 | | 1050 |
| [109] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -255 | 31 | 1.8 | 0.32 | | 1050 |
| [110] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -40 | 50 | 1.8 | 0.01 | | 370 |
| [111] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -150 | 50 | | 0.01 | | 370 |
| [112] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -150 | 160 | 3.4 | | | 1123 |
| [113] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -120 | 0.13 | 5 | 0.003 | | 400 |
| [114] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -62 | 280 | 1.3 | 0.17 | | 873 |
| [115] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -340 | 2.25 | | | | 800 |
| [116] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -340 | 2.25 | | | | 800 |
| [117] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | -106 | 220 | 1.9 | 0.047 | | 358 |
| [118] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | 106 | 220 | 1.9 | 0.047 | | 358 |
| [119] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | 125 | 220 | 1.6 | 0.046 | | 450 |
| [120] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | 125 | 220 | 1.6 | 0.046 | | 450 |
| [121] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | 125 | 220 | 1.6 | 0.046 | | 450 |
| [122] | SrMn$_{0.7}$Ru$_{0.3}$O$_3$ | 125 | 220 | 1.6 | 0.046 | | 450 |
Table 1. Cont.

| Ref. | Materials                        | Seebeck (µV·K⁻¹) | Electrical Conductivity (S·cm⁻¹) | Thermal Conductivity (W·m⁻¹·K⁻¹) | Power Factor (µW·K⁻²·m⁻¹) | ZT   | Measure Temp. (K) |
|------|----------------------------------|------------------|----------------------------------|----------------------------------|--------------------------|------|------------------|
| [117]| Nd₀.₉₉Sr₀.₀₁CoO₃                  | 300              |                                  |                                  |                          |      | 290              |
| [118]| Pr₀.₉₉Sr₀.₀₁CoO₃                  | 450              |                                  |                                  |                          |      | 270              |
| [119]| LaCoO₃                           | 1200             |                                  |                                  |                          |      | 110              |
| [120]| La₀.₉₇₅Sr₀.₀₂₅CoO₃               | 720              | 100                              |                                  |                          |      | 300              |
| [121]| La₀.₉₉Sr₀.₀₁₅CoO₃                | 220              | 20                               | 0.75                             | 0.051                    | 573  | 300              |
| [122]| La₀.₉₇₅Sr₀.₁₂₅CoO₃               | 100              |                                  | 6                                | 0.035                    | 230  |                  |
| [123]| La₀.₉₉Sr₀.₁₅CoO₃                 | 720              | 20                               | 0.037                            | 0.18                      | 300  |                  |
| [124]| La₀.₉₉Sr₀.₁₉₅CoO₃                | 170              |                                  | 1.2                              | 0.033                    | 300  |                  |
| [125]| La₀.₉₉Sr₀.₁₅CoO₃                 | 120              |                                  | 1.5                              | 0.046                    | 300  |                  |
| [126]| La₀.₉₉Pb₀.₁CoO₃                  | 110              | 333                              | 0.8                              | 0.23                      | 575  |                  |
| [127]| Nd₀.₉₉₉Ca₀.₀₀₉CoO₃               | 500              | 1.1                              |                                  |                          |      | 300              |
| [128]| LaCo₀.₉₉₉Mn₀.₀₁₅CoO₃              | 80               | 40                               |                                  | 80                       | 0.08 | 420              |
| [129]| La₀.₉₉₉Ba₀.₀₁₉CoO₃               | 900              |                                  |                                  |                          |      | 300              |
| [130]| La₀.₉₉₉Ni₀.₀₂₅O₃                 | 600              | 0.067                            |                                  |                          |      | 300              |
| [131]| La₀.₉₉₉La₀.₀₁₅CoO₃               | 350              | 0.3                              |                                  |                          |      | 300              |
| [132]| La₀.₉₉₉Ce₀.₀₁₅CoO₃               | –300             | 0.03                             |                                  |                          |      | 300              |
| [133]| LaCo₀.₉₉₉Ga₀.₀₀₅O₃               | 480              |                                  |                                  |                          |      | 300              |
| [134]| LaCo₀.₉₉₉Ti₀.₀₁₅O₃               | –200             |                                  |                                  |                          |      | 300              |
| [135]| LaCo₀.₉₉₉Niₐ₀.₉₉₉O₂₉              | 220              | 33.3                             | 0.35                             | 0.2                      | 300  |                  |
| [136]| La₀.₉₉₉Sr₀.₁₆₅CoO₃               | 180              | 2                                | 0.048                            |                          |      | 300              |
| [137]| La₀.₉₉₉Sr₀.₁₆₅CoO₃               | 140              | 0.8                              | 0.024                            |                          |      | 850              |
| [138]| La₀.₉₉₉Sr₀.₁₆₅FeO₃               | 230              | 1.8                              | 0.076                            | 1.273                    | 1250 |                  |
| [139]| La₀.₉₉₉FeO₃                      | –108             | 300                              | 3.2                              | 0.14                     | 1250 |                  |
| [140]| La₀.₉₉₉FeO₃                      | –110             | 280                              | 3.2                              | 0.14                     | 1250 |                  |
| [141]| Sr₀.₉₉₉FeO₃                      | –100             | 260                              | 2.8                              | 0.14                     | 1250 |                  |
| [142]| Sr₀.₉₉₉FeO₃                      | –48              | 3.1                              | 0.24                             |                          |      | 1250             |
| [143]| Sr₀.₉₉₉FeO₃                      | –1350            |                                  | 0.995                            |                          |      | 300              |
| [144]| Ba₀.₉₉₉FeO₃                      | –26              | 600                              | 40                               | 600                      |      |                  |
| [145]| Ba₀.₉₉₉FeO₃                      | 1000             |                                  | 40                               | 600                      |      |                  |
| [146]| Sr₀.₉₉₉FeO₃                      | –80              | 0.03                             |                                  |                          |      | 300              |
| [147]| Sr₀.₉₉₉FeO₃                      | –170             | 150                              | 4                                | 0.1                      | 1073 |                  |
| [148]| Sr₀.₉₉₉FeO₃                      | –80              | 1.5                              | 3.6                              | 120                      | 0.05 | 1073             |
| [149]| Ba₀.₉₉₉FeO₃                      | –130             | 300                              | 3.4                              | 1400                     | 0.65 | 1200             |
| [150]| Ba₀.₉₉₉FeO₃                      | 125              | 250                              | 3.4                              | 1400                     | 0.65 | 1200             |
| [151]| Ba₀.₉₉₉FeO₃                      | –190             | 79                               | 1.8                              | 0.13                     | 680  |                  |
| Ref. | Materials | Seebeck ($\mu$V·K$^{-1}$) | Electrical Conductivity (S·cm$^{-1}$) | Thermal Conductivity (W·m$^{-1}$·K$^{-1}$) | Power Factor ($\mu$W·K$^{-2}$·m$^{-1}$) | ZT | Measure Temp. (K) |
|------|------------|-----------------------------|----------------------------------|---------------------------------|-----------------------------------|----|------------------|
| [148] | Sr$_{0.7}$Ba$_{0.3}$Pb$_{0.99}$Bi$_{0.01}$O$_3$ | $-70$ | | | 390 | 900 |
| [149] | Ba$_{0.7}$K$_{0.3}$BiO$_3$ | 3.2 | 10 | | | |
| [150] | BaBi$_{0.9}$Sb$_{0.1}$O$_3$ | 260 | 10 | | | 850 |
| [151] | BaMoO$_3$ | $-30$ | 316 | 83.2 | 0.015 | 1000 |
| [152] | Sr$_{1.4}$Ba$_{0.6}$Fe$_{0.8}$Mn$_{0.2}$V$_2$O$_6$ | $-58$ | | | | |
| [153] | SrRuO$_3$ | 5.3 | | | 0.03 | 1200 |
| [154] | Sr$_2$RuYO$_6$ | $-250$ | | | 1200 | |
| [155] | Sr$_2$RuErO$_6$ | $-160$ | | | 1200 | |
| [156] | Sr$_{1.4}$La$_{0.6}$La$_{0.1}$RuErO$_6$ | 700 | | | 0.001 | 800 |
| [157] | AgNbO$_3$ | $-500$ | 333 | | 0.03 | 300 |
| [158] | AgTaO$_3$ | 710 | | | 0.0002 | 880 |
| [159] | K$_{0.99}$Ba$_{0.009}$TaO$_3$ | 200 | | | 0.03 | 300 |
| [160] | BaTaO$_3$ | $-280$ | 0.1 | 0.8 | | 880 |
| [162] | Ba$_{0.9}$La$_{0.1}$RuErO$_6$ | $-220$ | 2950 | 3.25 | | 873 |
| [161] | BaCe$_{0.95}$Y$_{0.05}$O$_3$ | $-362$ | 89 | 0.145 | 10.5 | 1.61 | 600 |
| [163] | CH$_3$NH$_3$Sb$_{1-n}$Pb$_n$I$_3$-n-type | $-238$ | 160 | 8.4 | 0.61 | 300 |
| | | p-type | 181 | 94 | 0.06 | 3.1 | 0.25 | 300 |
| | | n-type | $-362$ | 89 | 0.145 | 10.5 | 1.61 | 600 |
| | | p-type | 295 | 41 | 0.06 | 3.6 | 0.71 | 600 |
| | | n-type | $-428$ | 68 | 0.151 | 11.3 | 2.56 | 800 |
| | | p-type | 358 | 25 | 0.04 | 3.3 | 1.08 | 800 |
| [164] | CH$_3$NH$_3$Sn$_3$I$_4$ | 720 | | 0.08 | 0.01 | 295 |
| [165] | CH$_3$NH$_3$Pb$_3$I$_4$ | 700 | $10^{-7}$ | 0.5 | 10$^{-7}$ | 295 |
| | (MA)PbI$_3$ | 200 | | | 0.44 | 298 |
| | (FA)PbI$_3$ | 200 | | | 0.44 | 298 |
| [166] | CsSnI$_3$ | 0.18 | | | 1.25 | 330 |
| | CsPbI$_3$ | 0.1 | | | 1.64 | 1000 |
2. Oxide Perovskites

Oxide perovskite materials have been used for the application of thermoelectrics. Usually, oxide perovskite materials have relatively high Seebeck coefficient, low electrical conductivity, and high thermal conductivity at a specific temperature. For example, polycrystalline SrTiO$_3$ has an S of $-410 \, \mu$V$\cdot$K$^{-1}$, a $\sigma$ of 0.18 S$\cdot$cm$^{-1}$ and a $\kappa$ of 7.5 W$\cdot$m$^{-1}\cdot$K$^{-1}$ at 375 K [59]. In general, two different approaches have been utilized to enhance ZT of thermoelectric materials. One approach is tuning the carrier concentration (n) to a suitable range since three interdependent thermoelectric parameters (i.e., S, $\sigma$, and $\kappa$) are functional to the carrier concentration [10]. The other approach is engineering of the material properties and structure of thermoelectric materials to decouple the parameters [16,163–165]. A variety of elements have been used for oxide perovskite materials, shown in Figure 4. In this review, the oxide perovskite materials were classified based on B-site elements, and their TE properties were discussed.

2.1. Titanium (Ti) as B-Site (ATiO$_3$)

The reported ZT as a function of temperature, when Ti was used as B-site, was presented in Figure 5. All the materials are n-type thermoelectric materials.

Figure 4. Elements that were used for perovskites in the A and B sites, which have been applied for thermoelectrics.

Figure 5. ZT value of ATiO$_3$ based oxide perovskite materials, all the materials are n-type semiconductors. The symbol “cal.” means the results come from the calculation.
2.1.1. Enhancing Electrical Conductivity

To enhance the electrical conductivity of ATiO$_3$, chemical doping is applied. Although the electrical conductivity, Seebeck coefficient, and thermal conductivity are interdependent, it is necessary to tune the carrier concentration to its optimum range. The electrical conductivity was modified by oxygen vacancy $[38,57–59]$, and chemical substitution in A-site $[40,60–67]$ and B-site $[65,68]$. Oxygen vacancy has been induced to enhance the electrical conductivity. The perovskite-type ATiO$_3$ is a wide gap band-insulator, where the valence band comes from the oxygen 2p state and the conduction band from the Ti 3d-t$_2g$ state with threefold orbital degeneracy $[38]$. Figure 6 shows the band structure and the density of states of SrTiO$_3$ (STO) $[80]$. The oxygen vacancy, which can be introduced into perovskite materials by controlling oxygen partial pressure, hydrogen reduction, and reduced graphene oxide, can generally add two electrons in the Ti site, providing charge carriers, therefore enhancing the electrical conductivity $[38,57–59]$. For example, Onoda et al. investigated the perovskite-type oxygen deficient system SrTiO$_3$-$\delta/2$ with 0.0046 $\leq \delta < 0.06$, the carrier concentration was enhanced from 2.5 $\times$ 10$^{18}$ to 1.0 $\times$ 10$^{21}$ cm$^{-3}$, when $\delta$ increased from 0.0046 to 0.06, resulting in the enhancement of electrical conductivity from about 5 to 1000 S cm$^{-1}$ $[38]$. The power factor 2000 $\mu$W m$^{-1}$ K$^{-2}$ was obtained with the carrier concentration of 2 $\times$ 10$^{20}$ cm$^{-3}$ $[58]$. Choi et al. investigated La-doped SrTiO$_3$ thin films with controlled elemental vacancies by varying the oxygen partial pressure P(O$_2$) during the film growth $[38]$. Decreasing P(O$_2$) would increase the cation (La and Sr) and oxygen vacancies $[38]$. The cation vacancies are known to compensate the generation of carriers by the oxygen vacancies $[38]$. Also, it also expands the lattice, thereby disturbing the carrier transport. The carrier concentration was tuned from $-0.43 \times 10^{21}$ to $1.15 \times 10^{21}$ cm$^{-3}$ when oxygen partial pressure decreased from $10^{-2}$ to $10^{-6}$ Torr $[38]$. Seebeck coefficient of the La-doped SrTiO$_3$ thin films can be modulated from $-120$ to $-260 \mu$V K$^{-1}$ $[38]$. Ravichandran et al. reported that the oxygen vacancy can tune the carrier concentration from $1 \times 10^{21}$ to $3 \times 10^{21}$ cm$^{-3}$ at La doping level of 15% in La-doped SrTiO$_3$, and a ZT value of 0.28 was achieved at 873 K at a carrier concentration of $2.5 \times 10^{21}$ cm$^{-3}$ $[57]$. Feng et al. induced the oxygen vacancy into undoped SrTiO$_3$ (STO) by hydrogen reduction (STO-H) and reduced graphene oxide (RGO). Their results showed that only 0.64 vol % of graphene content would enhance electrical properties of STO significantly, where the carrier concentration was $3.64 \times 10^{18}$, $4.54 \times 10^{19}$, and $1.59 \times 10^{20}$ cm$^{-3}$ for pure STO, STO-H, and RGO/STO, respectively. Additionally, the electrical conductivity increased from 2 to 14 to 30 S cm$^{-1}$ at 760 K, when the sample changed from pure STO to STO-H to RGO/STO. Electron energy loss spectrum confirmed high oxygen vacancy concentration in the RGO rich area in RGO/STO composite. The ZT value was increased to 0.09 at 760 K for RGO/STO composite, compared to 0.008 for pure STO $[59]$. Additionally, Lee et al. reported that electrical conductivity of BaTiO$_3$ can reach 11 S cm$^{-1}$ at 300 K with a carrier concentration of $-3 \times 10^{20}$ by inducing oxygen vacancy $[79]$, while the single crystal BaTiO$_3$ shows electrical conductivity of 0.05 S cm$^{-1}$ at 300 K $[70]$. However, the Seebeck coefficient decreased to $-280 \mu$V K$^{-1}$ $[79]$, compared to $-550 \mu$V K$^{-1}$ at 300 K for single crystal BaTiO$_3$ $[70]$. In short, the oxygen vacancy can increase the carrier concentration of the ATiO$_3$, thus improving the electrical conductivity. Additionally, oxygen vacancy can also reduce the lattice thermal conductivity because of phonon scattering $[79]$. However, the strategy of introducing oxygen vacancy needs to cooperate with other types of doping or strategies to achieve relatively high ZT value.

Additionally, chemical substitution (such as La $[60–67,74]$, Ce $[66]$, Ba $[39,72]$, Pr $[40]$, and Y $[71]$) in A-site is a widely-used method to enhance the electrical conductivity of ATiO$_3$. La is the most widely studied A-site doping element in SrTiO$_3$. The carrier concentration of Sr$_{1-x}$La$_x$TiO$_3$ increases from $2.0 \times 10^{18}$ to $9.0 \times 10^{21}$, when x increased from 0 to 0.5. As a result, the electrical conductivity is enhanced from 0.3 to 2000 S cm$^{-1}$ $[60–66,74]$. Since the electrical conductivity is interrelated with Seebeck coefficient, heavily La-doped STO also has a relatively low Seebeck coefficient. Additionally, La doping does not necessarily increase the thermal conductivity, which is probably attributed to the decrease of the mean free path of the phonons caused by lattice defects $[63]$. As a result, the ZT value achieved for Sr$_{0.95}$La$_{0.05}$TiO$_3$ (La-doped STO) was 0.14 at 773 K with n of about $8 \times 10^{20}$ cm$^{-3}$.
and $\sigma$ of 150 S cm$^{-1}$ [63]. Theoretical calculation by Boltzmann transport theory predicted that a ZT value of 0.7 at 1400 K could be achieved with an $n$ of $4 \times 10^{20}$ cm$^{-3}$ for La-doped STO [85]. However, such a high ZT value has not been obtained experimentally. Additionally, La was also used to dope STO together with Ba (i.e., Sr$_{0.9-x}$Ba$_x$La$_{0.1}$TiO$_3$) [72] and oxygen vacancy [57]. The electrical conductivity of Sr$_{0.9-x}$Ba$_x$La$_{0.1}$TiO$_3$ increased from 200 to 2500 S cm$^{-1}$, when $x$ increased from 0 to 0.9 at 420 K [72]. This is caused by the decrease of the Ti–Ti distance, which increases the overlap of Ti 3d orbital in the conduction band [72]. The highest ZT value achieved in the study is 0.13 at 420 K, with a formula of (Ba$_{0.3}$Sr$_{0.6}$La$_{0.1}$)TiO$_3$ [72]. Moreover, when the La content increased from 0 to 0.15, the carrier concentration of oxygen vacancy doped STO increased from $\sim$3 $\times$ 10$^{20}$ to 3 $\times$ 10$^{21}$ cm$^{-3}$, and electrical conductivity from $\sim$70 to 700 S cm$^{-1}$ [57]. The highest ZT value of 0.28 was achieved at 873 K at a carrier concentration of 2.5 $\times$ 10$^{21}$ cm$^{-3}$ [57]. Furthermore, Pr was also used as A-site dopant in Sr$_{1-x}$Pr$_x$TiO$_3$ (0 < $x$ < 0.125), in which, a linear increase in carrier concentration is observed with increasing Pr concentration [40]. The carrier concentration increased from 0.3 $\times$ 10$^{21}$ cm$^{-3}$ to 2.1 $\times$ 10$^{21}$, when $x$ changed from 0 to 0.125 [40], and the electrical conductivity was enhanced from 250 to 700 S cm$^{-1}$, when $x$ changed from 0.05 to 0.125 [40]. The mobility of STO was enhanced to about 12 cm$^2$ V$^{-1}$ s$^{-1}$ [40], compared to 4–6 cm$^2$ V$^{-1}$ s$^{-1}$ [166–169], in which the dramatic enhancement in carrier mobility was attributed to the formation of Pr-rich grain boundaries [40]. A ZT value of 0.4 at 773 K was achieved attributed to the high mobility [40]. In short, the combination of chemical doping and oxygen vacancy can lead to relatively high ZT value [57]. Furthermore, Pr doping with Pr-rich boundary can achieve high carrier concentration and mobility, which resulted in the highest ZT value obtained experimentally so far for ATiO$_3$ [40].

![Figure 6](image-url)  

**Figure 6.** The band structure and the density of states of SrTiO$_3$ [80]. Copyright 2010, Physical Review B.
theoretical analysis by advanced ab initio calculations showed that superlattice in Nb-doped STO could remarkably improve the Seebeck coefficient compared to the bulk at equivalent doping concentration, and the Seebeck coefficient in similar heterostructures would be improved more by weak, rather than tight, spatial confinement [82]. Moreover, the slight Mn substitution in B-site of Sr$_{1-x}$La$_x$TiO$_3$ can also enhance the effective mass of electrons, giving rise to an increase in |S| [83]. For example, the S was enhanced from $-120$ to $-180 \ \mu$V·K$^{-1}$, and the ZT value was changed from 0.07 to 0.15 at 300 K when the composition is tuned from Sr$_{0.95}$La$_{0.05}$TiO$_3$ to Sr$_{0.95}$La$_{0.05}$Ti$_{0.96}$Mn$_{0.04}$O$_3$ [83]. This phenomenon can be attributed to the coupling between itinerant electrons and localized spins or coupling between itinerant electrons and local lattice distortion around Mn$^{3+}$ ions [83]. Additionally, as Ta and Co-doped STO, the ZT value was 0.17 at 752 K and 0.135 at 300 K for SrTi$_{0.9}$Ta$_{0.1}$O$_3$ [78] and SrTi$_{0.875}$Co$_{0.125}$O$_3$ [89], respectively.

In short, the B-site doping cannot tune the carrier concentration as efficiently as A-site doping, but it can increase the effective mass of the materials, therefore enhancing the Seebeck coefficient at high carrier concentrations. In perspective, it can be promising to introduce both A-site and B-site doping into the materials, where A-site improves the electrical properties and B-site enhances the Seebeck coefficient.

2.1.2. Decoupling Electrical Conductivity and Seebeck Coefficient

The Seebeck coefficient is negatively interrelated with electrical conductivity (Equations (3) and (4)), where Seebeck coefficient decreases with increasing carrier concentration. However, there are some strategies that can enhance the Seebeck coefficient without reducing electrical conductivity. For example, the existence of oxygen vacancy can change the density of electronic states around the Fermi energy, which results in larger Seebeck coefficient [62–64]. The Seebeck coefficient of oxygen-deficient samples (e.g., S of $-300 \ \mu$V·K$^{-1}$ at 750 K for Sr$_{0.9}$La$_{0.1}$TiO$_3$) are larger than those with near-stoichiometric ones with the same La doping level (e.g., S of $-255 \ \mu$V·K$^{-1}$ at 750 K for Sr$_{0.9}$La$_{0.1}$TiO$_3$) [62,63]. This superiority leads to higher ZT value of 0.21 at 750 K [64]. Moreover, B-site substitution of Ti by Nb [65,68,76] and Mn [83] can also enhance the Seebeck coefficient by increasing the effective mass of electrons. A |S| of 160 $\mu$V·K$^{-1}$ is obtained from the 40% Nb-doped SrTiO$_3$ film despite a high carrier concentration of $7 \times 10^{21}$ cm$^{-3}$ [65,68,76]. A-site substitution of Sr by La in SrTiO$_3$ (i.e., Sr$_{1-x}$La$_x$TiO$_3$, 0.02 $\leq x \leq 0.1$) was also reported to have relatively large Seebeck coefficient compared to the materials in the same carrier concentration range of $10^{21}$ cm$^{-3}$, which is attributed to the orbital degeneracy of the Ti 3d-t2g conduction band, the relatively large electron effective mass, and large energy-dependent scattering rate [61,74]. Additionally, Sun et al. investigated the TE properties of La-doped SrTiO$_3$ and Ba doped KTaO$_3$ through the first-principles band calculation. Their results showed that the Seebeck coefficients are higher in multiple band systems than those with single-band [80], since the Fermi level tends to stay lower for systems with multiple bands given a fixed number of doped electrons [80]. Furthermore, quantum confinement effect can effectively enhance the Seebeck coefficient of SrTiO$_3$. Ohta et al. reported a high-density two-dimensional electron gas (2DEG) confined within 0.5 to 16 unit cell layer thickness in SrTiO$_3$ (i.e., SrTiO$_3$/SrTi$_{0.8}$Nb$_{0.2}$O$_3$/SrTiO$_3$ quantum-well, where $n_e = 10^{15}$ cm$^{-3}$ for SrTiO$_3$ and $n_e = 2.4 \times 10^{21}$ cm$^{-3}$ for SrTi$_{0.8}$Nb$_{0.2}$O$_3$) [75]. A dramatic increase in |S| at room temperature is observed when the thickness of the SrTi$_{0.8}$Nb$_{0.2}$O$_3$ layer becomes less than 1.56 nm (i.e., a four-unit cell layer thickness) [75]. For example, the one unit cell layer thickness of the SrTi$_{0.8}$Nb$_{0.2}$O$_3$ reached a large |S| of 480 $\mu$V·K$^{-1}$ at 300 K, approximately five times larger than that of SrTi$_{0.8}$Nb$_{0.2}$O$_3$ bulk (i.e., 108 $\mu$V·K$^{-1}$ at 300 K with $n_e$ of $2.4 \times 10^{21}$ cm$^{-3}$) [75]. This significant improvement of |S| suggests that strong electron confinement can be achieved by using strongly directive Ti 3d (t2g) orbitals; direct overlap between neighboring 3d orbitals is relatively small, and carrier electrons tend to localize in the Ti atoms [75]. They also claimed that with the measured |S| of 850 $\mu$V·K$^{-1}$, estimated $\sigma_{2DEG}$ of $1.4 \times 10^3$ S·cm$^{-1}$, and $\kappa$ of 12 W·m$^{-1}$·K$^{-1}$ from bulk single-crystal SrTiO$_3$, an estimated ZT of 2.4 was observed, corresponding to ZT=0.24 for a complete device having the 2DEG as the active region [75].
2.1.3. Reducing Thermal Conductivity

The thermal conductivity is correlated with electrical conductivity because of electron contributions (Equation (5)). To decouple to κ and σ, suppressing the phonon contribution (lattice thermal conductivity, κl) is usually applied, which was realized in ATiO3 by grain boundary phonon scattering [59], point defect phonon scattering [73], distortion of crystal lattice [62,77,83], and so on.

For instance, the lattice thermal conductivity of RGO/STO is 3.7 W·m⁻¹·K⁻¹ at 760 K, which is 37% lower than that of pure STO (i.e., 5.9 W·m⁻¹·K⁻¹ at 760 K) [59]. This can be ascribed to the highly restrained grain size in RGO/STO, which is 20 times smaller than that of pure STO [59].

Additionally, Ca and rare earth elements substitution in A-site can suppress the κl. Ca was used to substituted Sr in Sr₀.₉₋ₓCaₓLa₀.₁TiO₃ (0 < x < 0.6), and the resulted showed that the thermal conductivity decreased from 4.7 to 3.3 W·m⁻¹·K⁻¹ when x increased from 0 to 0.6, which is caused by the point defect scattering and the lowered symmetry [73]. As a result, Sr₀.₄₅Ca₀.₄₅La₀.₁TiO₃ has a ZT value of 0.22 at 873 K, compared to 0.2 for Sr₀.₉La₀.₁TiO₃ at 873 K [73]. Muta et al. studied the rare earth (e.g., Y, La, Sm, Gd, and Dy) doped SrTiO₃ [62]. The thermal conductivity of SrTiO₃ is dependent on the doping element, namely: the thermal conductivity decrease monotonically with the iconic rare earth radius, in which it decreased from 4.3 to 2.6 W·m⁻¹·K⁻¹ when the dopant changed from La to Dy [62]. This phenomenon is caused by lattice distortion with difference ionic radii, leading to phonon scattering [62]. The enhancement of ZT value in this work is owing to reducing the thermal conductivity without deteriorating the electrical conductivity of SrTiO₃, and (Sr₀.₉Dy₀.₁)TiO₃ showed a ZT value of 0.22 at 573 K [62]. Moreover, Eu⁺ substitution of SrTi₀.₈Nb₀.₂O₃ can reduce the thermal conductivity without reducing the thermo electric power factor [77]. The mean free path of the phonon was reduced about 12% at room temperature when half of the Sr⁺ was substituted by Eu⁺ [77]. As a result, the κ of the SrTi₀.₈Nb₀.₂O₃ ceramic at room temperature is 8.8 W·m⁻¹·K⁻¹, while it decreased to 7.7 W·m⁻¹·K⁻¹ with 50% of the Sr was substituted by Eu [77].

Also, the slight Mn substitution with some defects in B-site of Sr₁₋ₓLaxTiO₃ can enhance anharmonic lattice vibrations resulting in inelastic phonon-phonon scattering, which effectively suppresses thermal conductivity at high electrical conductivity [83]. The thermal conductivity was reduced from 7.1 to 3.8 W·m⁻¹·K⁻¹, when the composition changed from Sr₀.₉₅La₀.₀₅TiO₃ to Sr₀.₉₅La₀.₀₅Ti₀.₉₈Mn₀.₀₂O₃ [83]. The ZT value of Sr₀.₉₅La₀.₀₅Ti₀.₉₈Mn₀.₀₂O₃ reached 0.15 at 300 K compared to 0.07 for Sr₀.₉₅La₀.₀₅TiO₃ [83].

In short, among all the strategies (i.e., inducing grain boundary and chemical substitution in A-site and B-site), the most effective strategy to suppress lattice thermal conductivity is by rare earth substitution of A-site [62] and Mn substitution of B-site [83].

2.2. Manganese (Mn) as B-Site (AMnO₃)

The thermoelectric properties of AMnO₃ were summarized, and the ZT values as a function of temperature were shown in Figure 7, where all the materials are n-type semiconductors.

![Figure 7](image-url)
### 2.2.1. Enhancing Electrical Conductivity

Chemical doping in A-site was used as a strategy to enhance the electrical conductivity. Multiple elements have been used as A-site dopant in AMnO$_3$, including In [91], Sn [91], Sb [91], Pb [91], Bi [91,103], and rare earth element (e.g., Yb, Y, La, Ce, Sm, Dy, Tb, Ho, and Pr) [90–97]. In general, the electrical conductivity increases as the ionic radius ($r_A$) decreases [95]. The overlapping of Mn and O orbitals are substantially influenced by the $r_A$, which determines the Mn–O–Mn bond angles [95]. The decrease of $r_A$ enhances electrical conductivity owing to the strength of the bending of the Mn–O–Mn bond, which narrows the electron conduction bandwidth [95]. Additionally, a relatively high ZT value can be achieved not necessarily at the highest doping level, but sometimes at an optimum doping level. For example, the electrical conductivity of Ca$_{1-x}$Pr$_x$MnO$_{2.98}$ (0 < $x$ < 0.05, 0.1, 0.15) increased from 40 to 125 S·cm$^{-1}$ at 1100 K, when $x$ changed from 0 to 0.15, leading to a ZT value of 0.17 at 1100 K for Ca$_{0.85}$Pr$_{0.15}$MnO$_{2.98}$ [94]. The electrical conductivity increased from ~67 to 333 S·cm$^{-1}$ at 1073 K for Sr$_x$Pr$_{1-x}$MnO$_y$, when $x$ changed from 0 to 0.7 [97]. The electrical conductivity of (Ca$_{1-x}$R$_x$)MnO$_3$ (R: Tb, Ho, Y) increase with $x$ value (e.g., from 100 to 182 S·cm$^{-1}$ for (Ca$_{1-x}$Tb$_x$)MnO$_3$, from 91 to 250 S·cm$^{-1}$ for (Ca$_{1-x}$Ho$_x$)MnO$_3$ when $x$ increased from 0.1 to 0.3), and the highest ZT value was achieved at $x = 0.1$ for all three materials (e.g., 0.13, 0.08, 0.15, for (Tb$_{0.1}$Ca$_{0.9}$)MnO$_3$, (Ho$_{0.1}$Ca$_{0.9}$)MnO$_3$), and (Y$_{0.1}$Ca$_{0.9}$)MnO$_3$, respectively) [90]. The electrical conductivity of Ca$_{1-x}$Bi$_x$MnO$_3$ increased with Bi doping from 32 S·cm$^{-1}$ at $x = 0.02$ to 222 S·cm$^{-1}$ at $x = 0.2$, and a ZT value of 0.086 was achieved when $x = 0.04$ (i.e., Ca$_{0.96}$Bi$_{0.04}$MnO$_3$) at 1000 K [103]. A ZT value of 0.16 was obtained for Ca$_{0.9}$Yb$_{0.1}$MnO$_3$ with $\sigma$ of 167 S·cm$^{-1}$ at 1000 K [95].

On the other hand, chemical doping in the B-site was studied to enhance the electrical conductivity. Multiple elements have been used as a B-site dopant in AMnO$_3$, including Mo [104,107], Ru [104,108], Nb [105,107], Ta [105], and Ni [100]. The electrical conductivity of CaMn$_{0.96}$Mo$_{0.04}$O$_3$ was measured to be about 154 S·cm$^{-1}$, and the ZT value is 0.012 at 270 K [104]. The electrical conductivity was 67 S·cm$^{-1}$ for SrMn$_{0.7}$Ru$_{0.3}$O$_3$, and the ZT value reached 0.01 at 370 K [108]. CaMn$_{0.96}$Ta$_{0.04}$O$_3$ reached an electrical conductivity of 29 S·cm$^{-1}$ and a ZT value of 0.05 at 1000 K [105]. CaMn$_{0.98}$Nb$_{0.02}$O$_3$ have a $\sigma$ of −240 $\mu$V·K$^{-1}$, $\sigma$ of 31 S·cm$^{-1}$ and $\kappa$ of 0.8 W·m$^{-1}$K$^{-1}$ at 1070 K, leading a ZT values of 0.32 at 1070 K [107]. However, the significant enhancement of ZT value to 0.32 was mainly attributed to low thermal conductivity, caused by phonon scattering from the nanosized twinned domains or the porous morphology [107]. In short, the B-site doping can also serve the purpose of improving the electrical conductivity, but it is not as effective as A-site doping.

### 2.2.2. Reducing Thermal Conductivity

The thermal conductivity of AMnO$_3$ can be decoupled from electrical conductivity by introducing phonon scattering, which was realized by grain boundary [107], lattice distortion [94,95,102], and orbital fluctuation in the paramagnetic phase [110].

For example, CaMn$_{0.96}$Nb$_{0.04}$O$_3$ has a $\kappa$ of 0.8 W·m$^{-1}$K$^{-1}$ at 1070 K, caused by higher phonon scattering from the nanosized twinned domains or the porous morphology, in which a ZT value of 0.32 at 1070 K was obtained [107]. Additionally, chemical substitution can result in local lattice distortions linked with quasi-static Mn$^{2+}$ ions, therefore suppressing the lattice thermal conductivity [94,95,102]. For instance, $\kappa$ of Ca$_{1-x}$Pr$_x$MnO$_{2.98}$ decreased from 2.1 to 1.5 W·m$^{-1}$K$^{-1}$ at ~1100 K, when $x$ varied from 0 to 0.15 [94]; $\kappa$ of CaMn$_{1-x}$Mo$_x$O$_3$ decreased from 2.7 to 1.3 W·m$^{-1}$K$^{-1}$ at 300 K, when $x$ increased from 0.07 to 0.15 [102]; $\kappa$ of CaMnO$_3$ decreased from 3.6 to ~1.7 W·m$^{-1}$K$^{-1}$ at 300 K, when Ca was substituted with Yb [95] and Ho [95]. Moreover, Mo in Sr(Mn$_{1-x}$Mo$_x$)$_3$O$_7$ introduces orbital fluctuation in the paramagnetic phase, leading to scattering the acoustic phonons, which results in a reduction of the $\kappa$ from 6.1 to 5 W·m$^{-1}$K$^{-1}$ at 390 K, when $x$ increased from 0 to 0.025 [110].

In short, thermal conductivity is dominated by lattice thermal conductivity for AMnO$_3$ [107,110], and the results showed that phonon scattering by nano-engineering is relatively more effective at suppressing the lattice thermal conductivity [107].
2.3. Cobalt (Co) as B-Site (ACoO₃)

The reported ZT as a function of temperature when Co was used as B-site (ACoO₃) was presented in Figure 8. Normally, the rare earth elements (i.e., Pr [113–115], Ho [114,121], Nd [113–115], Tb [115], Sm [113,114], Gd [113,114], Dy [114,115], and La [122–129]) were used as A-site elements. The electrical conductivity increased with increasing ionic radii of the rare earth cations. The degree of distortion of the structure determines the onset of the electronic localization-delocalization transition. With a given R³⁺ size, the CoO₆ octahedron is tilted in order to optimize R-O bond distances, resulting in a deviation of the Co-O-Co angles from 180°, which determines the degree of overlapping of the cobalt 3d and oxygen 2p orbitals. Large rare-earth ions cause the Co-O-Co bonds to straighten out and become closer to 180°. The Co 3d and O 2p orbital overlap increases as the Co-O-Co angles become closer to 180°, and this structural change leads to the observed rare-earth element dependence of the electronic behavior of RCoO₃ [113–115].

![Figure 8. ZT value of ACoO₃ based oxide perovskite materials, all the materials are p-type semiconductors. The symbol “cal.” means the results come from the calculation.](image-url)

For example, Hashimoto et al. reported Pr, Nd, Tb, and Dy as A-site in cobalt oxide RCoO₃ (R = Pr, Nd, Tb, Dy) ceramics [115]. The electrical conductivity increased with increasing ionic radii of the rare earth cations (ionic radii: Pr³⁺ > Nd³⁺ > Tb³⁺ > Dy³⁺), where the electrical conductivity increased from 180 to 400 S cm⁻¹ at 873 K, when A-site changed from Dy (DyCoO₃) to Pr (PrCoO₃) [115]. However, the highest ZT value of 0.05 was obtained for DyCoO₃ at 873 K with S of about 80 µV K⁻¹ and k of 1.6 W m⁻¹ K⁻¹ [115]. Moon et al. presented the TE properties of (R₀.₉Ca₀.₁)CoO₃ (R = Gd, Sm, Nd, Pr) [113]. The results showed that electrical conductivity of samples increased sharply with increasing the ionic radius of the rare-earth element (Pr > Nd > Sm > Gd). The σ changed from 23 to 210 S cm⁻¹, when the samples changed from (Gd₀.₉Ca₀.₁)CoO₃ to (Pr₀.₉Ca₀.₁)CoO₃ [113]. A ZT value of 0.047 was achieved at 358 K for (Pr₀.₉Ca₀.₁)CoO₃ with σ of 210 S cm⁻¹ and S of about 108 µV K⁻¹ [113].

In addition, similar phenomenon were observed when the ionic radius of dopants (Ca²⁺ < Sr²⁺ < Ba²⁺) increased for (Pr₀.₉M₀.₁)CoO₃ (M = Ca, Sr, Ba). The electrical conductivity increased from 350 to 420 S cm⁻¹, when varied from (Pr₀.₉Ca₀.₁)CoO₃ to (Pr₀.₉Ba₀.₁)CoO₃ [114].

Furthermore, the electrical conductivity of LaCoO₃ normally increases with increasing temperature. For instance, σ increased from 14 to 1230 S cm⁻¹ for La₀.₉₅Sr₀.₀₅CoO₃, when temperature increased from 300 to 750 K [124]. This temperature dependent conduction behaviors of La₀.₉₅Sr₀.₀₅CoO₃ were explained regarding small polaron hopping mechanism with positive polarons (Co⁴⁺Co⁴⁺⁻) as transport carriers [124]. Increase of σ with increasing temperature was attributed to the increase of the (Co⁴⁺Co⁴⁺⁻) concentration on the Co sites [124].
2.3.1. Chemical Doping in A-Site

The strategy of A-site doping was applied to tune the electrical conductivity further. LaCoO$_3$ was investigated with Sr [122-125], Pb [126], Na [126], and Ba [128] used as A-site dopant. Sr-doped LaCoO$_3$ (i.e., La$_{1-x}$Sr$_x$CoO$_3$, 0 ≤ x ≤ 0.2) was investigated. The electrical conductivity enhanced from ~2 to 296 S·cm$^{-1}$ when x changed from 0 to 0.2 at 300 K [123-125]. A ZT value of La$_{0.9}$Sr$_{0.1}$CoO$_3$ obtained was 0.046 at 300 K with σ of ~180 S·cm$^{-1}$, S of ~120 μV·K$^{-1}$, and κ of 1.45 W·m$^{-1}$·K$^{-1}$ [125]; and a ZT value of 0.18 was achieved for La$_{0.95}$Sr$_{0.05}$CoO$_3$ with S of ~710 μV·K$^{-1}$ and κ of 3.7 W·m$^{-1}$·K$^{-1}$ [123]. Pb and Na were used as A-site dopant for LaCoO$_3$ with composition La$_{0.9}$R$_{0.1}$CoO$_3$ (R = Pb, Na). The electrical conductivity for undoped polycrystalline LaCoO$_3$ was 25 S·cm$^{-1}$, and was enhanced to 250 and 33 S·cm$^{-1}$ at 575 K, when doped with Pb (i.e., La$_{0.9}$Pb$_{0.1}$CoO$_3$) and Na (i.e., La$_{0.9}$Na$_{0.1}$CoO$_3$), respectively [126]. The thermal conductivity of LaCoO$_3$, La$_{0.9}$Pb$_{0.1}$CoO$_3$, and La$_{0.9}$Na$_{0.1}$CoO$_3$ were 1.83, 1.55, and 0.9 W·m$^{-1}$·K$^{-1}$, respectively [126]. A ZT value of 0.23 was achieved at 575 K for La$_{0.9}$Pb$_{0.1}$CoO$_3$ with S of ~110 μV·K$^{-1}$, which was attributed to both increasing the electrical conductivity and suppressing the lattice thermal conductivity [126]. The electronic part of the thermal conductivity contribution was estimated using the Wiedemann–Franz law in La$_{1-x}$R$_x$CoO$_3$ to be about 1% in LaCoO$_3$, 3% in La$_{0.9}$Na$_{0.1}$CoO$_3$, and 31% in La$_{0.9}$Pb$_{0.1}$CoO$_3$ of the total thermal conductivity at 575 K, which shows that lattice thermal conductivity plays a major role in these samples [126]. The overall suppression of the total thermal conductivity upon Pb and Na substitution mainly comes from the reduction of the lattice thermal conductivity, possibly through the lattice strain induced by the atomic disorder at the A-site of the perovskite structure and the mixed valency at the Co-site [126].

Additionally, Moon et al. investigated TE properties of (Ho$_{1-x}$Ca$_x$)CoO$_3$. The electrical conductivity was enhanced from 1 × 10$^{-4}$ S·cm$^{-1}$ to 2 S·cm$^{-1}$ when x changed from 0 to 0.1 at 573 K. The highest ZT value obtained was 0.051 at 573 K for Ho$_{0.9}$Ca$_{0.1}$CoO$_3$ with S of about 210 μV·K$^{-1}$ and κ of 0.75 W·m$^{-1}$·K$^{-1}$ [121].

2.3.2. Chemical Doping in B-Site

Mn [127] and Ni [129] were used as a B-site dopant in LaCoO$_3$. For example, the electrical conductivity reached 5 S·cm$^{-1}$ at 400 K for LaCo$_{0.99}$Mn$_{0.01}$O$_3$ [127]. The carrier concentration increases from 6.1 × 10$^{14}$ to 2.6 × 10$^{17}$ cm$^{-3}$ for YCo$_{1-x}$Ni$_x$O$_3$, leading to increasing in electrical conductivity from 0.0015 to 0.011 S·cm$^{-1}$ at room temperature, when x changes from 0 to 0.07 [129].

2.3.3. Reducing Thermal Conductivity

Suppressing the lattice thermal conductivity was applied to decouple σ and κ, which was realized by chemical substitution. The chemical substitution can induce lattice disorder, lattice strain, or mass disorder, leading to phonon scattering [122,126,128]. In the reported studies, the effect of A-site doping (e.g., Sr [122], Pb [126], Na [126], Ba [128]) on lattice thermal conductivity of ACoO$_3$ was investigated, while the B-site doping was barely discussed.

For instance, single crystal La$_{0.82}$Sr$_{0.18}$CoO$_3$ has a lower κ of 1 W·m$^{-1}$·K$^{-1}$ compared to ~5 W·m$^{-1}$·K$^{-1}$ for LaCoO$_3$ at 60 K, due to lattice disorder caused by temperature and/or doping-induced spin-state transitions of the Co ions [122]. Moreover, the thermal conductivity of LaCoO$_3$ can be tuned by Na and Pb substitution of La. The thermal conductivity of LaCoO$_3$, La$_{0.9}$Pb$_{0.1}$CoO$_3$, and La$_{0.9}$Na$_{0.1}$CoO$_3$ were 1.83, 1.55, and 0.9 W·m$^{-1}$·K$^{-1}$, respectively, which may be attributed to the lattice strain induced by the atomic disorder at the A-site of the perovskite structure and the mixed valency at the Co-site [126]. The thermal conductivity of LaCoO$_3$ can also be suppressed by Ba substitution. The thermal conductivity of La$_{1-x}$Ba$_x$CoO$_3$ (x = 0.01, 0.03, 0.05) was about 0.5–0.6 W·m$^{-1}$·K$^{-1}$ at 320 K [128], while the thermal conductivity of LaCoO$_3$ is about 2.5 W·m$^{-1}$·K$^{-1}$ in the same temperature range [126]. This phenomenon can be explained by mass disorder scattering of phonons, reducing the lattice part of the thermal conductivity, resulting in a ZT value of 0.08 in the 400 K range for La$_{0.97}$Ba$_{0.03}$CoO$_3$ with σ of 350 S·cm$^{-1}$ and S of ~220 μV·K$^{-1}$ [128].
In short, the A-site dopant is more effective than B-site dopant in improving the carrier concentration and electrical conductivity. However, high ZT of 0.23 was achieved with the combination of high electrical conductivity and low thermal conductivity [126].

2.4. Other Elements, Including Iron (Fe), Nickel (Ni), Tin (Sn), Lead (Pb), Bismuth (Bi), Molybdenum (Mo), Ruthenium (Ru), and Uranium (U) as B-Site (ABO$_3$)

2.4.1. Fe as B-Site (AFeO$_3$)

The reported ZT when Fe was used as B-site was presented in Figure 9. LaFeO$_3$ was investigated for TE application. To improve the electrical conductivity, Sr [134,136] and Pr [135] were used as A-site dopant or substitution. The electrical conductivity was increased from 21 to 158 S·cm$^{-1}$ for La$_{1-x}$Sr$_x$FeO$_3$, when $x$ changed from 0.05 to 0.25, and a ZT value of 0.076 at 1273 K was achieved when $x = 0.05$ (La$_{0.95}$Sr$_{0.05}$FeO$_3$) with S of 228 $\mu$V·K$^{-1}$, $\sigma$ of 21 S·cm$^{-1}$, and $\kappa$ of 1.85 W·m$^{-1}$·K$^{-1}$ [136].

Double perovskite A$_2$FeMoO$_6$ was also studied for thermoelectric application. For example, Sugahara et al. reported a ZT value of 0.14 at 1250 K for Ca$_2$FeMoO$_6$ with S of $-108$ $\mu$V·K$^{-1}$, $\sigma$ of 270 S·cm$^{-1}$, and $\kappa$ of 3.1 W·m$^{-1}$·K$^{-1}$ [137]. Additionally, they also presented a ZT value of 0.24 at 1250 K for Sr$_{1.6}$FeMoO$_6$ with S of 48 $\mu$V·K$^{-1}$, $\sigma$ of 600 S·cm$^{-1}$, and $\kappa$ of 3.1 W·m$^{-1}$·K$^{-1}$ [138]. Sahnoun et al. investigated electrical and TE properties of Ba$_2$FeMoO$_6$ by Wien2K calculations and Boltzmann transport theory in the temperature range of 200 to 1100 K [139]. Their results revealed that Ba$_2$FeMoO$_6$ could achieve a ZT value of 0.98 at 1000 K with enhanced electrical conductivity [139].

![Figure 9. ZT value of AFeO$_3$ based oxide perovskite materials, the majority carrier types (n or p) were marked in the legend. The symbol “cal.” means the results come from the calculation.](image)

2.4.2. Ni as B-Site (ANiO$_3$)

The TE properties of LaNi$_{1-x}$Cu$_x$O$_3$ (0.2 < $x$ < 0.5) was investigated. Electrical conductivity of 790 S·cm$^{-1}$ was obtained at $x = 0.3$. Additionally, Cu doping into Ni sites in LaNi$_{1-x}$Cu$_x$O$_3$ solid solutions can suppress the formation of intermediate secondary phases (the deoxidized La$_4$Ni$_3$O$_{10}$ and La$_3$Ni$_2$O$_7$ phases) using donor doping effects. Since the increase in the charge valence of a metal ion can be counterbalanced by an equivalent decrease in the formation of oxygen vacancies, Cu doping into Ni ion sites can prohibit the formation of oxygen vacancies. A power factor of 40 $\mu$W·K$^{-2}$·m$^{-1}$ was achieved for LaNi$_{0.9}$Cu$_{0.2}$O$_3$ at 600 K [140].

2.4.3. Sn as B-Site (ASnO$_3$)

The reported ZT when Sn was used as B-site was presented in Figure 10. So far, there are several studies that have reported the A-site chemical substitution (e.g., Ba [143] and Sr [144]) to enhance $\sigma$. For examples, La was used as A-site dopant in Ba$_{1-x}$La$_x$SnO$_3$ with $x = 0.002, 0.005, 0.008$, and 0.010 [143]. The electrical conductivity increased from 120 to 350 S·cm$^{-1}$, when $x$ changed from 0.002 to 0.010.
The electrical conductivity increased from 20 to 1585 S cm\(^{-1}\) when \(x\) changed from 0.01 to 0.03 [144]. A ZT value of 0.05 was achieved at 1073 K for \(\text{Sr}_0.99\text{La}_{0.01}\text{SnO}_3\) [144].

![ZT value of oxide perovskite materials](image1)

**Figure 10.** ZT value of A\text{SnO}_3\ based oxide perovskite materials, all the materials are n-type semiconductors. The symbol “cal.” means the results come from the calculation.

Additionally, the thermoelectric transport properties of Ba\text{SnO}_3 were calculated using density functional theory combined with Boltzmann transport theory, where the electrical conductivity of Ba\text{SnO}_3 is improved dramatically after doping, owing to small effective mass and high mobility [145]. The power factor can reach 1.5 \(\times\) 10\(^{-3}\) W m\(^{-1}\) K\(^{-2}\) at 1200 K with a carrier concentration of 1.6 \(\times\) 10\(^{19}\) cm\(^{-3}\), giving rise to a ZT value of 0.65 at 1200 K by calculation [145].

2.4.4. Pb as B-site (APbO\(_3\))

The ZT values as a function of temperature for oxide perovskite materials, when Pb was used as B-site, were showed in Figure 11A. Ba has been used as A-site dopant for Sr\(_{1−x}\)Ba\(_x\)PbO\(_3\) (0 < \(x\) < 1). The electrical conductivity increased from 20 to 1585 S cm\(^{-1}\), when \(x\) changed from 0 to 1, a ZT of 0.13 was achieved at 673 K when \(x = 0.4\) (Sr\(_{0.6}\)Ba\(_{0.4}\)PbO\(_3\)) [146,147]. Additionally, Bi was used as B-site dopant for Sr\(_{1-x}\)Ba\(_x\)Pb\(_{1-x}\)BiO\(_3\) with 0.00 \(\leq\) \(x\) \(\leq\) 0.25, where the electrical conductivity increased from 250 to 400 S cm\(^{-1}\), when \(x\) changed from 0 to 0.05 [148].

![ZT value of APbO\(_3\) and AUO\(_3\) based oxide perovskite materials](image2)

**Figure 11.** ZT value of (A) APbO\(_3\) and (B) AUO\(_3\) based oxide perovskite materials, all the materials are n-type semiconductors.
2.4.5. Bi as B-Site (ABiO₃)

The TE properties of p-type BaBi₁₋ₓSbₓO₃ (0.0 ≤ x ≤ 0.5) was investigated at temperatures between 423 K and 973 K. The electrical conduction mechanism is explained by hopping of small polaronic holes localized on the pentavalent cations, and substitution of Bi with Sb would decrease the electrical conductivity but improve the Seebeck coefficient. The electrical conduction in the BaBiO₃ is due to hopping of small polaronic 6s holes from Bi⁵⁺ (6s⁰) to Bi³⁺ (6s²) with the aid of electron–phonon coupling. Substitution of Bi⁵⁺ with Sb⁵⁺ causes the 6s holes to decrease, leading to smaller electrical conductivity and a larger Seebeck coefficient as the Sb content increases. As a result, Sb doping does not enhance the TE properties of BaBiO₃, a power factor of 30 μW·m⁻¹·K⁻² was obtained for Sb-undoped BaBiO₃ at 773 K [150].

2.4.6. Mo as B-Site (AMoO₃)

Kurosaki et al. prepared a polycrystalline sample of perovskite-type barium molybdate (BaMoO₃), and a ZT value of 0.015 was obtained at 470 K with S of ~−30 μV·K⁻¹ [151]. Oba et al. investigated thermoelectric properties of V, Sr, and Mn substituted Sr₂FeMoO₆ systems. For Sr₁₋ₓBaₓFe₁₋ₓMo₂O₆ samples, the Seebeck coefficient increased with increasing Mn substitution. The power factor reached 83.2 μW·m⁻¹·K⁻² in the composition of Sr₁₋ₓBaₓFe₁₋ₓMo₂O₆ at 773 K [152].

2.4.7. Ru as B-Site (ARuO₃)

Several studies reported the TE properties of ARuO₃ based materials. For example, polycrystalline SrRuO₃ was studied, and a ZT value of 0.03 was obtained at 670 K with S of 36 μV·K⁻¹ and κ of 5.3 W·m⁻¹·K⁻¹ [153]. Sr₂RuYO₃ and Sr₂RuErO₆ were reported to have a S of −475 and −400 μV·K⁻¹ at room temperature, respectively [154]. Additionally, La was used as A-site dopant for (Sr₁₋ₓLaₓ)₂ErRuO₆ (0 < x < 0.3). The carrier concentration was enhanced from 9.7 × 10²⁰ to 2.2 × 10²¹ cm⁻³, when x changed from 0.1 to 0.3, resulting in the electrical conductivity increased from 0.1 to 1.7 S·cm⁻¹ at 800 K. A ZT value of ~0.001 was obtained with S of −160 μV·K⁻¹ and κ of 7 mW·cm⁻¹·K⁻¹ for (Sr₀.₉La₀.₁)₂ErRuO₆ at 800 K [155].

2.4.8. U as B-Site (AUO₃)

The TE properties of BaUO₃ in the temperature range from room temperature to 1000 K was investigated. A ZT value of 0.0002 was obtained at 880 K (Figure 11B) with S of −270 μV·K⁻¹, σ of 0.1 S·cm⁻¹ and κ of 0.9 W·m⁻¹·K⁻¹. The low κ was attributed to its phonon glass property [158].

3. Hybrid Perovskites

The ZT values of hybrid perovskite materials reported by different groups were summarized in Figure 12. Hybrid perovskite materials have a relatively high Seebeck coefficient (700 μV·K⁻¹ for CH₂NH₃PbI₃ at 295 K) [160] and low thermal conductivity (0.5 W·m⁻¹·K⁻¹ for CH₂NH₃PbI₃ at 295 K) [160], but the electrical conductivity is relatively low compared to traditional thermoelectric materials. Studies so far have all focused on how to improve the electrical conductivity through photo-induced or chemical doping strategies. Several hybrid perovskite materials—such as ABl₃ (A = CH₃NH₃ (MA), NH₂CHNH₂ (FA) and B = Sn, Pb) [33,34,160,161], CsMI₃ [162], and CsH₂NH₂CuBr₂I [35]—were studied theoretically or experimentally for TE application.

The theoretical analysis showed that the ZT value of hybrid perovskite materials could achieve 0.9 for n-type [33,34,161,162] and 1.25 for p-type [161,162] through chemical doping strategies. For example, the thermoelectric behavior of CH₂NH₃PbI₃ for a wide range of temperatures and carrier concentrations was theoretically analyzed. The results showed optimal carrier concentration of about 10¹⁹ cm⁻³, leading to an electrical conductivity of 160 S·cm⁻¹ and a calculated Seebeck coefficient of ~238 μV·K⁻¹. In combination with a thermal conductivity ~0.3–0.5 W·m⁻¹·K⁻¹, this delivers
ZT of 0.3–0.9 (Figure 13) [33]. Additionally, the TE properties for CH$_3$NH$_3$PbI$_3$ were theoretically investigated as a function of carrier concentration based on first-principles calculations. The results showed that ZT values of 0.9 and 1.25 could be achieved for n-type and p-type tetragonal CH$_3$NH$_3$PbI$_3$, respectively, with a carrier concentration of 10$^{19}$ cm$^{-3}$ at 330 K [161]. The effect of doping on TE properties of organic–inorganic perovskite iodides ABI$_3$ (A = CH$_3$NH$_3$ (MA), NH$_2$CHNH$_2$ (FA); B = Sn, Pb) at 300 K were analyzed through calculation. The results indicated that ZT value of 0.44, 0.45, 0.42 and 0.35 can be achieved for n-type (MA)PbI$_3$, (MA)SnI$_3$, (FA)PbI$_3$, and (FA)SnI$_3$ at carrier concentrations of 2.3 × 10$^{19}$, 3.3 × 10$^{19}$, 1.2 × 10$^{19}$, and 5.0 × 10$^{19}$ cm$^{-3}$, respectively [34]. Moreover, TE properties of halide perovskite CsMI$_3$ (M = Sn and Pb) was investigated by a combination of first-principles calculations and semiclassical Boltzmann transport theory by taking into account both the electron and phonon transport. The calculation showed that the ZT values are up to 0.63 and 0.64 for n-type CsSnI$_3$ and CsPbI$_3$ at 1000 K with the carrier concentration of 4.2 × 10$^{19}$ and 0.53 × 10$^{19}$ cm$^{-3}$, respectively [162].

![Figure 12](image.png)

**Figure 12.** ZT value of hybrid perovskite materials. The majority carrier types (n or p) were marked in the legend. The symbol “cal.” means the results come from the calculation.

![Figure 13](image.png)

**Figure 13.** ZT vs. charge concentration for electron-doped CH$_3$NH$_3$PbI$_3$, calculated at 300 K. Black dots and red squares correspond to single crystal and polycrystal CH$_3$NH$_3$PbI$_3$, respectively; the other symbols are for mimicking ZT value in 2D wells of thickness L = 40 nm (green diamonds), 20 nm (blue circles), and 10 nm (orange squares). Reproduced with permission [33]. Copyright 2016, American Chemical Society.

Experimentally, the electrical conductivity of hybrid perovskite material was improved by photo or chemical induced doping [35,160].

The effect of light (photoelectron) and impurity doping on thermoelectric properties of CH$_3$NH$_3$MI$_3$ (M = Pb, Sn) samples were investigated. The electrical conductivity of CH$_3$NH$_3$PbI$_3$
increased from $10^{-7}$ to $10^{-5}$ S·cm$^{-1}$ with a carrier concentration of about $10^{14}$ cm$^{-3}$ from light doping, when changed from dark to light intensities of 220 mW·cm$^{-2}$. The $S$ at room temperature (295 K) decreased upon illumination, from $S_{\text{dark}} = 820$ μV·K$^{-1}$ to $S_{\text{light}} = 540$ μV·K$^{-1}$. Additionally, the electrical conductivity of $10^{-3}$ S·cm$^{-1}$ was achieved for CH$_3$NH$_3$SnI$_3$ through impurity doping. The largest ZT values obtained was 0.008 at 295 K for CH$_3$NH$_3$SnI$_3$ (Figure 14) [160]. Additionally, the TE properties of n-type organic/inorganic hybrid C$_6$H$_4$NH$_2$CuBr$_2$I were investigated. The materials achieved a carrier concentration of $8.7 \times 10^{20}$ cm$^{-3}$. This high charge carrier concentration could be attributed to the self-doping effect caused by the reduction of Cu$^{2+}$ in the C$_6$H$_4$NH$_2$CuBr$_2$I film. A part of the Cu$^{2+}$ sites in the film could be replaced by Cu$^+$, which can be reduced during the annealing process and affected by the presence of Br$^-$. When a part of the Cu$^{2+}$ sites was replaced by Cu$^+$, the negatively charged Cu($+)^{\text{Cu}}_{(2+)}$ defects would be formed in C$_6$H$_4$NH$_2$CuBr$_2$I. Furthermore, the former composition becomes C$_6$H$_4$NH$_2$Cu$_{1-x}^{2+}$Cu$_x^{\text{+}}$X$_{3-x}^{-}$ ($X = \text{I}^-$ or Br$^-$), resulting in vacancies of $X^{-}$ ($V'_X$). The formation of negatively charged defects, such as Cu($+)^{\text{Cu}}_{(2+)}$ and $V'_X$, induce electron doping. The film has an electrical conductivity of $\sim 3.6 \times 10^3$ S·cm$^{-1}$ and a Seebeck coefficient of $\sim -70$ μV·K$^{-1}$ at room temperature, resulting in a power factor of 1740 μW·m$^{-1}$·K$^{-2}$. The details about the TE properties were shown in Figure 15. The highest estimated ZT value using calculated thermal conductivity was 0.21 at 363 K [35].

**Figure 14.** ZT of CH$_3$NH$_2$PbI$_3$ and CH$_3$NH$_3$SnI$_3$ at 295 K, with doping, monitored through the conductivity increase with photo and impurity doping. Red, orange, and yellow correspond to light intensities of 80, 165, and 220 mW·cm$^{-2}$. The dashed line marks ZT = 3. Adapted with permission [160]. Copyright 2015, American Chemical Society.

**Figure 15.** Electrical conductivity, Seebeck coefficient, power factor, calculated thermal conductivity, and ZT at different temperatures for the C$_6$H$_4$NH$_2$CuBr$_2$I. Reproduced with permission [35]. Copyright 2017, Royal Society of Chemistry.
In short, chemical doping is more effective than light doping strategy in hybrid perovskite materials [35,160]. The investigation of hybrid perovskite materials for TE application is just started, but it shows great potential with a power factor reaching 1740 µW·m⁻¹·K⁻² by self-doping strategies [35]. Hybrid perovskites can be promising TE materials with further modification by strategies, such as band-engineering, nano-engineering, doping/substitution, and self-doping (Figure 16).

**Figure 16.** Possible strategies to enhance the thermoelectric ZT value of perovskite materials.

### 4. Conclusions and Outlook

The ZT values of the oxide and hybrid perovskite materials from reported experimental data were summarized in Figure 17. The ZT in Figure 17 was read from the literature at its optimum working temperature. Compared to the ZT value of the conventional thermoelectric materials (e.g., BiSbTe [163], AgPb₁₈SbTe₂₀ (LAST) [171], and SiGe [172]), the ZT values of perovskite materials still need to be further improved.

**Figure 17.** Summary of thermoelectric ZT values of oxide and hybrid perovskite materials by year. The three dashed lines are the ZT value of BiSbTe [163], AgPb₁₈SbTe₂₀ (LAST) [171], and SiGe [172], which have a different optimum working temperature. The thermoelectric ZT values of all materials were extracted from literature at its optimum working temperature.
Oxide perovskites were applied as TE materials in a wide range of temperature (from 100 K–1400 K). The highest ZT value of oxide perovskite materials obtained experimentally so far is ~0.4. The reason for the low ZT value is that oxide perovskite materials have low electrical conductivity and high thermal conductivity. Doping is usually used as a strategy to improve the TE properties, which would normally increase the carrier concentration of materials, thus enhancing the electrical conductivity. In general, A-site doping (e.g., La doping in SrTiO$_3$) [40,60–67] is more effective than B-site doping [65,68,69,76] in enhancing the electrical conductivity through increasing the carrier concentration, in some cases when lattice thermal conductivity is dominant, A-site doping can also reduce the thermal conductivity [62,73]. On the other hand, B-site doping [83,107] and grain boundary [59] are typically more effective in introducing phonon scattering, thus suppressing the lattice thermal conductivity (e.g., Pb substitution of La in LaCoO$_3$) [83,94,95,102,107,126]. Additionally, the B-site doping can improve the ZT because of increase the effective mass (e.g., Nb substitution of Ti in SrTiO$_3$) [65,68]. Moreover, quantum confinement effect can also enhance the Seebeck coefficient of perovskite materials dramatically [75]. Furthermore, a small amount of oxygen vacancy in the crystal can have a positive effect on electrical conductivity [38,57–59], enhance the Seebeck coefficient [62–64], or even suppress the thermal conductivity [79], but it needs to cooperate with other strategies (e.g., A-site or B-site doping) to have a dramatic effect on TE properties. Also, the Pr doping in STO can create Pr rich grain boundaries, which enhances the mobility of the charge carrier significantly [40].

Hybrid perovskite materials started to draw attention for TE application in recent years. It can be a promising TE because of high Seebeck coefficient (700 µV K$^{-1}$ for CH$_3$NH$_3$PbI$_3$ at 295 K) [160] and low thermal conductivity (0.5 W m$^{-1}$K$^{-1}$ for CH$_3$NH$_3$PbI$_3$ at 295 K) [160]. To improve the electrical conductivity, photo-induced and/or chemical-induced doping was applied. Chemical doping has experimentally proven to be more effective than light doping strategy [35,160]. For instance, in the film of C$_6$H$_4$NH$_2$CuBr$_2$I, a part of the Cu$^{2+}$ sites could be replaced by Cu$^+$, then the negatively charged Cu(+)’Cu(2+) defects would form in C$_6$H$_4$NH$_2$CuBr$_2$I, resulting in a carrier concentration of ~8.7 × 10$^{20}$ cm$^{-3}$ [35]. The TE properties of hybrid perovskite materials were simulated at high temperature (T > 600 K) [33], but they can be decomposed at about 373 K based on their stability limitations [173]. According to the self-doping mechanism, Pb can be replaced by elements that have multiple valence states, which is a potential choice for self-doping elements in hybrid perovskites. Other strategies to improve TE properties of materials, such as band-engineering and nanoengineering, can be applied to hybrid perovskite materials (Figure 16). The theoretical calculation results claimed that hybrid perovskite materials could achieve a ZT value of 0.9 for n-type [33,34,161,162] and 1.25 for p-type [161,162]. Hybrid perovskite materials, which have low capital cost and can be quickly processed by energy cost methods, can be a promising candidate for TE application near room temperature range. Hybrid perovskite materials have the potential for flexible/wearable thermoelectric generator/cooling devices.

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