#### 1.1 History of Conducting Oxides

In this book, the term "oxides" is defined as an important part of ceramics. One oxide material contains at least one oxygen atom and one other nonoxygen element in its crystal structure. The widely accepted definition of a ceramic is given by Kingery: A ceramic is an inorganic, nonmetallic, solid material comprising metal, nonmetal, or metalloid atoms primarily held in ionic and covalent bonds.

Oxides possess the widest range of electrical properties. They could show good electrical insulation and the electrical resistivity,  $\rho > 10^{14} \Omega$  cm; meanwhile, they could also show extremely high electrical conduction, such as in high-temperature superconductors that have no resistance to the electrical current. The conductivity of oxides are usually found in two conditions: metal-like and semiconducting-like. Oxides with metal-like conduction such as ITO (indium tin oxides) are used as electrodes and transparent conducting oxides (TCOs) in portable electronics, displays, flexible electronics, and solar cells. Oxides in semiconductor condition such as TiO<sub>2</sub> are important for photocatalysis and solar cells. Besides the electrical conductor, some oxides are good ion conductors, such as lithium lanthanum titanate (La<sub>2/3-x</sub>Li<sub>3x</sub>TiO<sub>3</sub>), which exhibits high Li-ion conductivity. The electrical conductivities for ceramics are shown in Figure 1.1 [1].

It is difficult to simplify the history of conducting oxides due to the diversity of the oxides. As far as the application of TCOs is concerned, CdO was reported as the first TCO in 1907 by German physicist Karl Baedeker, who used thermal oxidation to yield it [2]. As far as the application of high-temperature superconductors is concerned, in the late 1980s, Ba–La–Cu–O and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7–x</sub> (YBCO) were the two first high-temperature superconductors discovered [3, 4]. In 1987, Bednorz and Müller were jointly awarded the Nobel Prize in Physics for discovery of the high-temperature superconductors. Recently, Hideo and coworkers discovered a new type of high-temperature superconductor, LaFeAsO, marking the new beginning of worldwide efforts to investigate high-temperature superconductor, especially in Japan and China (Figures 1.2-1.4) [5].

Thermoelectric (TE) materials can convert the temperature difference to voltage difference reversibly. As a result, TE materials have great potential application from solid-state cooling and thermal couples to power generation and waste heat recovery, as shown in Figure 1.5. The conversion efficiency is generally

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**Figure 1.1** Range of conductivities of ceramics. Source: Carter and Norton 2007 [1]. Reproduced with permission of Springer Nature.

characterized by the dimensionless figure of merit,  $ZT = S^2 \sigma T/(\kappa_1 + \kappa_e)$ , where T, S,  $\sigma$ , and  $\kappa_1$  ( $\kappa_e$ ) are the absolute temperature, Seebeck coefficient, electrical conductivity, and lattice thermal conductivity (electronic thermal conductivity), respectively. To date, state-of-the-art TE materials usually contain toxic, scarce, and expensive metal elements (e.g. Pb, Te, Sb). The practical application of these materials is restricted by the high-temperature instability and high cost (Figure 1.6).

After the discovery of NaCo<sub>2</sub>O<sub>4</sub> single crystals with high TE potential performance by Terasaki et al. [9], many oxides such as Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> [10], ZnO [11], and SrTiO<sub>3</sub> [12] were carefully investigated for oxide TE materials. These types of oxides have proven to be very promising for high-temperature TE application, which are thermally and chemically stable in air at high temperature. These oxides are easy to prepare, low-cost, and eco-friendly. Therefore, they have drawn considerable attention in the TE community. However, the TE performance of oxides, especially the polycrystallines, have relative low *ZT* values, which is ascribed to low electrical conductivity and high thermal conductivity caused by



**Figure 1.2** Temperature dependence of resistivity in  $Ba_x La_{5-x} Cu_5 O_{5(3-y)}$  for samples with x(Ba) = 1 (upper curves, left scale) and x(Ba) = 0.75 (lower curve, right scale). Source: Bednorz and Müller 1986 [3]. Reproduced with permission of Springer Nature.



**Figure 1.3** The transition temperature ( $T_c$ ) dependence of F<sup>-</sup> doping content. Source: Kamihara et al. 2008 [5]. Reproduced with permission of ACS.



**Figure 1.4** Superconducting transition temperatures versus year of discovery for various classes of superconductors. Source: Keimer et al. 2015 [6]. Reproduced with permission of Springer Nature.



**Figure 1.5** Overview of potential application of thermoelectric generators. Source: Nielsch et al. 2011 [7]. Reproduced with permission of John Wiley & Sons.



**Figure 1.6** Schematic comparison of various thermoelectric (TE) materials, in terms of the temperature range of operation and environmental friendliness of constituent elements. Source: He et al. 2011 [8]. Reproduced with permission of Cambridge University Press.

the strong ionic bonding. So far, some layered structure oxides with outstanding performance have given some hope for further development. The p-type oxide TE materials, such as Co-based oxide material Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> has been intensively investigated due to low thermal conductivity originated from its misfitted structure and high Seebeck coefficient by the plus spin entropy. The highest *ZT* value of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> ~ 0.61 at 1118 K was achieved by heavy rare-earth doping and metallic nanoinclusion approach [13]. BiCuSeO oxyselenides have been reported to exhibit low intrinsic thermal conductivity and high *ZT* value [14]. Recently, high-performance TE oxyselenide BiCuSeO ceramics with *ZT* > 1.1 at 823 K and a high average *ZT* value (*ZT*<sub>ave</sub> ~ 0.8) that is comparable to the currently used alloy TEs (e.g. PbTe) are made by our group (Figures 1.7 and 1.8) [16].



Figure 1.7 ZT of the current bulk thermoelectric materials as a function of year. Source: Zhang and Zhao 2015 [15]. Reproduced with permission of Elsevier.



**Figure 1.8** *ZT* of the current bulk oxide thermoelectric materials as a function of temperature.

#### 1.2 Structural Characteristics of Oxides

Most of the oxides are ionically bonded due to their large electronegativity difference ( $\Delta x$ ) between transition metals and oxygen. When  $\Delta x > 1.7$ , the compound is considered to be ionic crystal, when  $\Delta x < 1.7$ , the covalent bonding is predominant. The fraction of ionic character (*I*) for binary system M<sub>a</sub>X<sub>b</sub> can be calculated by the following equation:

$$I = 1 - \exp(-0.25(X_{\rm M} - X_{\rm X})^2)$$
(1.1)

where  $X_{\rm M}$  and  $X_{\rm X}$  represent the electronegativities of M and X, respectively.

As mentioned earlier, oxide materials are ionically bonded. For most of the oxides, the volume of the oxygen anion is much larger than that of the cation in a crystal structure. The stabilization of the crystal structure is based on a balance between the attractive and repulsive forces in the crystal. Pauling's rules are regarded as a law in the scope of ceramics on most occasions, which are discussed in materials science–related textbooks in detail. In this chapter, we will show crystal structures of some typical oxides (ZnO, SrTiO<sub>3</sub>, and Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>).

Zinc oxide is a very promising material for semiconductor applications. ZnO crystallizes in three main phases: hexagonal wurtzite (B4), cubic zinc blende (B3), and rocksalt (or Rochelle salt) (B1). The wurtzite structure ZnO is very stable at ambient conditions. The zinc blende ZnO is not stable in the bulk, but it can be stabilized as the film grown on the cubic lattice structure substrates. The rocksalt (NaCl) structure can only be obtained under high pressure (Figure 1.9).

Strontium titanate (SrTiO<sub>3</sub>) has an ABO<sub>3</sub> cubic perovskite structure like calcium titanium oxide (CaTiO<sub>3</sub>) at room temperature. A perovskite refers to the materials with the same type of crystal structure as CaTiO<sub>3</sub>. The general chemical formula for perovskite compounds is ABO<sub>3</sub>, where "A" and "B" are two cations with large size difference. "A" is larger than "B", and O is an anion that bonds to both. The ideal cubic-symmetry structure has the B cation in sixfold coordination, surrounded by an octahedron of anions, and the A cation in 12-fold

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**Figure 1.9** Crystal structures of three forms of ZnO: (a) rocksalt (B1), (b) zinc blende (B3), and (c) wurtzite (B4). Source: Morkoç and Özgür 2009 [17]. Reproduced with permission of John Wiley & Sons.

**Figure 1.10** Crystal structure of perovskite structure in ABO<sub>3</sub> form.



cuboctahedral coordination. In SrTiO<sub>3</sub>, the Ti<sup>4+</sup> ions are sixfold coordinated by  $O^{2-}$  ions, the Sr<sup>2+</sup> ions are surrounded by four TiO<sub>6</sub> octahedra and are coordinated by 12  $O^{2-}$  ions (Figure 1.10).

Misfit-layered cobaltite  $Ca_3Co_4O_9$  has received a special attention because of large power factor, strong electronic correlations, and natural misfit-layered structure.  $Ca_3Co_4O_9$  has two monoclinic layers: one is the triple rock salt-type  $Ca_2CoO_3$  layer and the other is  $CoO_2$  layer. These two layers alternately stack along *c* direction to build the structure. Two layers have the same lattice parameters except the length of *b*-axis, making  $Ca_3Co_4O_9$  possess more distorted structure, as shown in Figure 1.11.  $Ca_2CoO_3$  layer is charge-resistor layer, which can scatter phonon strongly due to the distorted substructure, while the  $CoO_2$  layer is a charge-conducting layer. Therefore,  $Ca_3Co_4O_9$  can be considered as naturally materials with decoupling electronic and thermal properties.



**Figure 1.11** Diagram of the crystal structure of  $Ca_3Co_4O_9$ , perpendicular to the *a*-axis (a) and the *b*-axis (b). The Co1 and Co2 sites refer to Co atoms from  $Ca_2CoO_3$  and  $CoO_2$  layers, respectively.



Figure 1.12 Band structures of typical n-type oxides (a) ZnO, (b) Ga<sub>2</sub>O<sub>3</sub>, (c) TiO<sub>2</sub>, and (d) In<sub>2</sub>O<sub>3</sub>.

## 1.3 Band Structure of Conventional Oxides

Most semiconducting oxides (e.g. ZnO, TiO<sub>2</sub>,  $In_2O_3$ ) are natural n-type oxides; a few oxides (e.g.  $Cu_2O$ ,  $Na_xCoO_2$ ) showed p-type conduction. This asymmetry can be understood based on fundamental principles of electronic structure. Furthermore, oxides always have wide band gaps due to the strong metal–oxide bond compared to the similar compounds, which are not favorable for high electrical conductivity. Figure 1.12 shows the typical band structures of ZnO,  $Ga_2O_3$ , TiO<sub>2</sub>, and  $In_2O_3$ . A density function theory (DFT) [18–20] calculation was performed in VASP code [21] to calculate the band structure of  $In_2O_3$ . The projector-augmented wave [22, 23] technique was used and the exchange-correlation energy is in the form of Perdew–Burke–Ernzerhof [24].

#### 1.4 Electrical Properties

The electrical properties have been fully summarized in some literature [25, 26]. In this chapter, we describe the electrical properties (Seebeck coefficient (S), electrical conductivity ( $\sigma$ ), and the electronic thermal conductivity ( $k_e$ )) derived from the Boltzmann transport equation (BTE).

The formal expression of BTE is

$$\left(\frac{\mathrm{d}f}{\mathrm{d}t}\right)_{\mathrm{sc}} = \frac{\mathrm{d}f}{\mathrm{d}t} + \frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t}\nabla_{\mathbf{k}}f + \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t}\nabla_{\mathbf{r}}f \tag{1.2}$$

where t is time, **k** and **r** are the wave and position vectors of electrons, and f is the nonequilibrium distribution function.

For electrons, the perturbations arise from the force exerted by an electric field ( $\epsilon$ ) or the temperature gradient (along the *x*-direction),

$$\frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t} = -\frac{e\varepsilon}{\hbar} \tag{1.3}$$

$$\nabla_{\mathbf{r}} f = (\partial f / \partial T) (\mathrm{d}T / \mathrm{d}x) \tag{1.4}$$

where -e is the unit charge of electrons.

The relaxation time  $(\tau)$  approximation usually is applied to resolve the BTE for *f*:

$$\left(\frac{\mathrm{d}f}{\mathrm{d}t}\right)_{\mathrm{sc}} = -(f - f_0)/\tau \tag{1.5}$$

At equilibrium, electron distribution follows the Fermi–Dirac statistics through:

$$f_0(E) = \frac{1}{\exp((E - E_F)/k_{\rm B}T) + 1}$$
(1.6)

where *E* is the electron's energy level,  $E_F$  is the "Fermi energy," and  $k_B$  is the Boltzmann constant.

Then, the first-order, steady-state ((df/dt) = 0) solution to the BTE may be written as

$$f(E) - f_0(E) = -\tau(E)\nu(E)\frac{\mathrm{d}f_0}{\mathrm{d}E} \left[\mp e\varepsilon - \left(\frac{E - E_F}{T}\right)\frac{\mathrm{d}T}{\mathrm{d}x}\right]$$
(1.7)

Subsequently, Eq. (1.7) is used to determine the magnitude of charge and heat current density (*J* and *Q*, respectively):

$$J \equiv \mp nev = \pm e \int_{-\infty}^{+\infty} g(E)v(E)[f(E) - f_0(E)]dE$$
(1.8)

$$Q \equiv n(E - E_F)v = \int_{-\infty}^{+\infty} g(E)(E - E_F)v(E)[f(E) - f_0(E)]dE$$
(1.9)

where *n* is the carrier concentration, *v* is the carrier velocity, and g(E) is the density of states (DOS).

From Eqs. (1.8) and (1.9), we can obtain

$$\sigma \equiv \frac{J}{\varepsilon}|_{\mathrm{d}T/\mathrm{d}x=0} = e^2 X_0 \tag{1.10}$$

$$S \equiv \frac{\varepsilon}{\frac{dT}{dx}}|_{J=0} = \pm \frac{1}{eT} \left[ \frac{X_1}{X_0} - E_F \right]$$
(1.11)

$$\kappa_e \equiv \frac{Q}{\frac{\mathrm{d}T}{\mathrm{d}x}}|_{J=0} = \frac{1}{T} \left[ X_2 - \frac{(X_1)^2}{X_0} \right]$$
(1.12)

where  $X_i = -\int g(E)v^2(E)E^i(df_0/dE)dE$ . Now, assuming a single band/sub-band with parabolic energy dispersion, and a power law relaxation time ( $\tau(E) = \tau_0 E^r$ ), the integral  $X_i$  can be explicitly written as:

$$X_{i} = \frac{\tau_{0}}{2\pi^{2}m_{\sigma}} \left(\frac{2m_{d}}{\hbar^{2}}\right)^{3/2} (k_{\rm B}T)^{r+3/2+i} \left(\frac{3+2(r+i)}{3}\right) F_{1/2+r+i}$$
(1.13)

$$F_{j}(\eta) = \int_{0}^{+\infty} x^{j} / (\exp(x - \eta) + 1) \mathrm{d}x$$
(1.14)

$$\eta = E_F / k_{\rm B} T \tag{1.15}$$

where  $\eta = (E_F - E_0)/k_B T$  is the *reduced Fermi level*.

And then the parameters for TE materials can be written as:

$$n = \frac{1}{2\pi^2} \left(\frac{2k_{\rm B}Tm_{\rm d}}{\hbar^2}\right)^{3/2} F_{1/2}(\eta)$$
(1.16)

$$\mu = \frac{2r+3}{3} \frac{e\tau_0}{m_\sigma} (k_{\rm B}T)^r \frac{F_{1/2+r}(\eta)}{F_{1/2}(\eta)}$$
(1.17)

$$S = \pm \frac{k_{\rm B}}{e} \left( \frac{(r+5/2)F_{3/2+r}(\eta)}{(r+3/2)F_{1/2+r}(\eta)} - \eta \right)$$
(1.18)

$$L = \left(\frac{k_{\rm B}}{e}\right)^2 \left[\frac{(r+7/2)F_{5/2+r}(\eta)}{(r+3/2)F_{1/2+r}(\eta)} - \left(\frac{(r+5/2)F_{3/2+r}(\eta)}{(r+3/2)F_{1/2+r}(\eta)}\right)^2\right]$$
(1.19)



Using Eqs. (1.16) and (1.17), we can calculate the *n* and  $\mu$  for specific material with the parameter of *m* and *r*. In semiconductor technology, doping is the most common and effective method to alter the electrical conductivity. According to Figure 1.13a, the carrier concentration can be changed with 8 orders of magnitude by adjusting the  $\eta$ . The variation of the mobility as a function of  $\eta$  is different with the scattering constant *r*, as shown in Figure 1.13b. It is widely accepted that the parameter r = -1/2 is for acoustic scattering process, r = 0 for neutral impurity, r = 1/2 for optical-mode scattering, and r = 3/2 is for the ionized-impurity scattering. It is interesting to note that the mobility increases with the increase of  $\eta$  in the ionized-impurity scattering; in other words, high doping can lead to high mobility. However, most of the experiments show opposite results in the ionized-impurity samples.

When the Seebeck coefficient is plotted against  $\eta$ , as shown in Figure 1.14, a linear scale can be used when  $\eta \ll 0$ . For  $\eta \gg 0$ , the Seebeck coefficient becomes very small, ~0. At fixed  $\eta$ , the Seebeck coefficient exhibits larger value when r = 3/2. As seen in Figure 1.14b, for example, in order to obtain  $S = 200 \,\mu\text{V K}^{-1}$ , the doping concentration varies widely with different scattering mechanism.

As shown in Figure 1.15, the Lorenz number is only weakly dependent on the Fermi energy when  $\eta \ll 0$ . When  $\eta \gg 0$ , the Lorenz number approaches  $2.45 \times 10^{-8} \text{ W } \Omega^{-1} \text{ K}^{-2}$  for metals.



**Figure 1.14** The Seebeck coefficient as a function of  $\eta$  (a) and carrier concentration (b). (Assuming  $m_{\sigma} = m_{d} = m_{0}$ , and  $m_{0}$  is the mass of free electron.)

**Figure 1.15** Plot of Lorenz number against  $\eta$ .

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When  $\eta \gg 1$  ( $\eta > 4$ ), the conductor can be treated as a metal and the degenerate approximation can be reasonably adopted. In this occasion, the Fermi–Dirac integrals can be written as:

$$F_n(\eta) = \frac{\eta^{n+1}}{n+1} + n\eta^{n-1}\frac{\pi^2}{6} + n(n-1)(n-2)\eta^{n-3}\frac{7\pi^4}{360} + \cdots$$
(1.20)

The first term of the expression can be used to obtain the electrical conductivity. Thus,

$$\sigma = \frac{\tau_0}{3\pi^2 m_\sigma} \left(\frac{2m_d}{\hbar^2}\right)^{3/2} e^2 (E_F)^{r+3/2}$$
(1.21)

$$n = \frac{1}{3\pi^2} \left( \frac{2E_{\rm F} m_{\rm d}}{\hbar^2} \right)^{3/2} \tag{1.22}$$

The Lorenz number is given by:

$$L = \frac{\pi^2}{3} \left(\frac{k_{\rm B}}{e}\right)^2 \tag{1.23}$$

But it requires the first two terms to calculate Seebeck coefficient.

$$S = \mp \frac{\pi^2 k_{\rm B}}{3e\eta} (r + 3/2) \tag{1.24}$$

For most of the semiconductors with not-so-high carrier concentration, the classical or nondegenerate approximation is acceptable. This assumption can be used when  $\eta < -2$ :

$$F_n(\eta) = \exp(\eta) \int_0^\infty \xi^n \exp(-\xi) d\xi = \exp(\eta) \Gamma(n+1)$$
(1.25)

where the gamma function is  $\Gamma(n + 1) = n\Gamma(n)$ ,  $\Gamma(1/2) = \pi^{1/2}$ , *n* is an integer,  $\Gamma(n + 1)$  is equal to *n*!. Thus,

$$S = \mp \frac{8\pi^2 k_{\rm B}^2 T}{3eh^2} m_{\rm d}^* \left(\frac{\pi}{3n}\right)^{2/3} (r+3/2)$$
(1.26)

$$n = \frac{1}{2\pi^{3/2}} \left(\frac{2k_{\rm B}Tm_{\rm d}}{\hbar^2}\right)^{3/2} \exp(\eta)$$
(1.27)

$$\mu = \frac{4}{3\pi^{1/2}} \frac{e\tau_0}{m_\sigma} (k_{\rm B}T)^r \Gamma(r+5/2)$$
(1.28)

$$S = \mp \frac{k_{\rm B}}{e} ((r+5/2) - \eta) \tag{1.29}$$

$$L = \left(\frac{k_{\rm B}}{e}\right)^2 (r + 5/2) \tag{1.30}$$

#### 1.5 Model for Thermoelectric Oxides

Generally, metal oxides are considered not suitable for TE application. Metal oxides are ionic in nature with smaller orbital overlap (narrow band) than those found in covalent intermetallic alloys. This leads to very low carrier mobility due to the strong localization.

The small polaron conduction model within 3d orbitals of transition-metal cations have been applied to investigate high-temperature Seebeck coefficient in transition-metal oxide (e.g.  $Ca_3Co_4O_9$ ,  $CaMnO_3$ ).

Assuming the energies of the Jahn–Teller ( $\Delta_{JT}$ ) effect and the Coulomb interaction (U) are smaller than the thermal energy  $k_{\rm B}T$ , the generalized Heikes formula for the Seebeck coefficient in the HT limit can be expressed as:

$$S = -\frac{k_{\rm B}}{e} \ln\left(\frac{2-\rho_{\rm e}}{\rho_{\rm e}}\right) \tag{1.31}$$

where  $\rho_e$  is the ratio of charge carriers to sites ( $\rho_e = n/N_v$ ; *n* is the number of charge carriers, and  $N_v$  is the number of available sites).

For fermions with large electron–electron repulsion (forbidden double occupancy) spins ( $k_{\rm B}T \ll U$ ), the Seebeck coefficient is expressed as:

$$S = -\frac{k_{\rm B}}{e} \ln\left(2\frac{1-\rho_{\rm e}}{\rho_{\rm e}}\right) \tag{1.32}$$

Koshibae et al. show that the spin state of the transition metallic ions (e.g.  $Co^{3+}$  and  $Co^{4+}$  ions) in the metal oxides is essential to the high Seebeck coefficient. The thermopower of the transition metal oxides at high temperature is given by:

$$S = -\frac{k_{\rm B}}{e} \ln\left(\frac{g_3}{g_4}\frac{x}{1-4}\right) \tag{1.33}$$

where  $g_3$  and  $g_4$  are the numbers of the configurations (low-, intermediate-, and high-spin states) of the Co<sup>3+</sup> and Co<sup>4+</sup> ions, respectively, and x is the concentration of Co<sup>4+</sup> ions. The above formula is applicable to most TE oxides, including Na<sub>x</sub>CoO<sub>2</sub> and its derivative structures La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub>, perovskites (e.g. CaMnO<sub>3</sub>), and double perovskites, and misfit-layered Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and its derivative structure Ca<sub>2</sub>Co<sub>2</sub>O<sub>5</sub> (Figure 1.16).



**Figure 1.16** Schematic representation of local states of cobalt ions,  $Co^{3+}$  and  $Co^{4+}$ . The lines indicate the energy levels of  $e_g$  and  $t_{2g}$  orbitals. The arrow represents a spin of an electron.

#### 1.6 Effect of Interface on Electron Transport

In this section, we can combine the BTE model and the rectangular potential barriers promoted by A. Popescu et al. [27]. The model has three parameters: an average height  $E_{\rm b}$ , width w, and distance between them L, as shown in Figure 1.17. In this chapter, we assumed the  $m_{\sigma} = m_{\rm d} = m_0$  and power law relaxation time  $(\tau(E) = \tau_0 E^r)$  is applicable. Then the total relaxation time is obtained according to the Mathiessen's rule:

$$\frac{1}{\tau(E)} = \sum_{i} \frac{1}{\tau_i(E)} \tag{1.34}$$

where  $\tau_i(E)$  is the relaxation time for each contributing mechanism. For TE bulk materials, the most carrier scattering may be due to acoustic phonons (r = -1/2), nonpolar optical phonons (r = 1/2), or ionized impurities (r = 3/2).

Then the relaxation time due to the barrier scattering is given by:

$$\tau_{\rm b} = \begin{pmatrix} L\sqrt{\frac{m}{2E}} \left( \frac{4\frac{E}{E_{\rm b}} \left(1 - \frac{E}{E_{\rm b}}\right)}{\sinh^2 \left(\sqrt{\frac{2mE_{\rm b}w^2}{\hbar^2}} \left(1 - \frac{E}{E_{\rm b}}\right)} \right), E < E_{\rm b} \\ L\sqrt{\frac{m}{2E}} \left( \frac{4\frac{E}{E_{\rm b}} \left(\frac{E}{E_{\rm b}} - 1\right)}{\sin^2 \left(\sqrt{\frac{2mE_{\rm b}w^2}{\hbar^2}} \left(\frac{E}{E_{\rm b}} - 1\right)} \right), E > E_{\rm b} \end{pmatrix}$$
(1.35)

Figure 1.18 shows the calculated values of normalized electrical conductivity as a function of the length *L*. The electrical conductivity increases with the increasing *L*. In this model, the volume fraction of nanoinclusions can be roughly evaluated by  $\varphi = (w/L)^3$ . For the neutral scattering samples, when the  $\varphi > 1\%$ , i.e. L > 43 nm, the electrical conductivity decreases to 80% of the pristine bulk sample. This result shows that the nanoparticle would strongly affect the electrical conductivity. In our calculation, we may overestimate the adverse effect of secondary nanoparticle on electrical conductivity due to the simplify of the scattering process. For the different scattering mechanism samples, the effect of nanoparticle on electrical conductivity is also different.

Figure 1.19 normalized Seebeck coefficient as a function of the length *L*. One can see that the Seebeck coefficient increases obviously by adding the nanoparticle, which is called energy-filtering effect due to a strongly energy-dependent

Figure 1.17 The model for the nanocomposite.





**Figure 1.18** The normalized electrical conductivity as the function of *L*. Parameters are  $E_b = 60$  meV and w = 20 nm.



**Figure 1.19** The normalized Seebeck coefficient as the function of *L*. Parameters are  $E_{\rm b} = 60$  meV and w = 20 nm.

electronic scattering time. For example, the 1% volume fraction nanoparticle in the acoustic scattering samples can bring up over 35% enhancement in Seebeck coefficient.

An enhancement in power factor can be observed in Figure 1.20. These results show that the rational design of nanocomposites can improve the TE properties.

In Figures 1.21–1.23, we discuss the influence of nanoparticle size w on the electrical properties. The electrical conductivity decreases with the increasing w because of the increasing volume fraction of nanoparticles.



**Figure 1.20** The normalized power factor as the function of *L*. Parameters are  $E_{\rm b} = 60$  meV and w = 20 nm.



**Figure 1.21** The normalized electrical conductivity as the function of *w*. Parameters are L = 100 nm and  $E_{b} = 60$  meV.

Figure 1.22 shows the relationship between Seebeck coefficient and *w*. It is interesting to note that a maximum value can be observed at around 5 nm. And the sharp increasing trend of *S* appears when w < 5 nm. These results demonstrate that the energy-filtering effect in nanocomposites depends on the size of nanoparticle. The smaller size of nanoparticles will cause larger enhancement in Seebeck coefficient.

Figure 1.23 demonstrates the enhancement on power factor with various *w*. A maximum peak can be observed at around 5 nm due to the moderate decrease in electrical conductivity and larger increase of Seebeck coefficient. It is clearly seen



Figure 1.22 The normalized Seebeck coefficient as the function of w. Parameters are L = 100 nm and  $E_{b} = 60 \text{ meV}$ .



Figure 1.23 The normalized power factor as the function of w. Parameters are L = 100 nm and  $E_{\rm b} = 60 \, {\rm meV}.$ 

that the acoustic scattering matrix has the highest enhancement on power factor, while the ionized-impurity scattering matrix does not have the obvious effect.

To get a more comprehensive understanding of the role of nanoinclusions in enhancing the TE properties, we plot the electrical conductivity, Seebeck coefficient, and power factor as functions of the interface potential  $E_{\rm b}$ , as shown in Figures 1.24–1.26. The interface potential plays an important role in tuning the electrical conductivity, as shown in Figure 1.24. When  $E_b > 0.1$  eV, the electrical conductivity becomes lesser than 30%, which indicates strong scattering of the



**Figure 1.24** The normalized electrical conductivity as the function of  $E_{\rm b}$ . Parameters are L = 100 nm and w = 20 nm.



**Figure 1.25** The normalized Seebeck coefficient as the function of  $E_b$ . Parameters are L = 100 nm and w = 20 nm.

electronic due to the high barrier. Therefore, the design of the interface is important in nanocomposites.

It is interesting to observe several maximum peaks of *S* in Figure 1.25. In Figure 1.25, four peaks appear when the  $E_{\rm b} < 0.2 \,\text{eV}$ . The results show that the barrier energy  $E_{\rm b}$  is the most critical factor that determines a successful nanocomposite design. The barrier energy  $E_{\rm b}$  is related not only to the intrinsic properties of matrix and nanofillers but also to the interface of the matrix and nanofillers.



**Figure 1.26** The normalized power factor as the function of  $E_{\rm b}$ . Parameters are L = 100 nm and w = 20 nm.

The relationship between power factor and the function of  $E_{\rm b}$  is depicted in Figure 1.26. The power factor can be greatly enhanced by more than fourfold in some specific interface potentials. For the interface potentials range from 0 to 0.2 eV, there are four maximum values and four worst peaks. So, the PF is very sensitive to the interface potential, which calls for an elaborate nanocomposite design.

### References

- 1 Carter, C.B. and Norton, M.G. (2007). *Ceramic Materials: Science and Engineering*, 546. Springer.
- 2 Bädeker, K. (1907). Über die elektrische Leitfähigkeit und die thermoelektrische Kraft einiger Schwermetallverbindungen. Annalen der Physik 327: 749–766. https://doi.org/10.1002/andp.19073270409.
- 3 Bednorz, J.G. and Müller, K.A. (1986). Possible high T<sub>c</sub> superconductivity in the Ba-La-Cu-O system. *Zeitschrift für Physik B Condensed Matter* 64: 189–193. https://doi.org/10.1007/BF01303701.
- 4 Wu, M.K., Ashburn, J.R., Torng, C.J. et al. (1987). Superconductivity at 93 K in a new mixed-phase Y–Ba–Cu–O compound system at ambient pressure. *Physical Review Letters* 58: 908–910. https://doi.org/10.1103/PhysRevLett.58 .908.
- **5** Kamihara, Y., Watanabe, T., Hirano, M., and Hosono, H. (2008). Iron-based layered superconductor  $La[O_{1-x}F_x]FeAs$  (x = 0.05-0.12) with  $T_c = 26$  K. *Journal of the American Chemical Society* 130: 3296–3297. https://doi.org/10.1021/ja800073m.

- 6 Keimer, B., Kivelson, S.A., Norman, M.R. et al. (2015). From quantum matter to high-temperature superconductivity in copper oxides. *Nature* 518: 179–186. https://doi.org/10.1038/nature14165.
- 7 Nielsch, K., Bachmann, J., Kimling, J., and Böttner, H. (2011). Thermoelectric nanostructures: from physical model systems towards nanograined composites. *Advanced Energy Materials* 1: 713–731.
- 8 He, J., Liu, Y., and Funahashi, R. (2011). Oxide thermoelectrics: the challenges, progress, and outlook. *Journal of Materials Research* 26: 1762–1772.
- **9** Terasaki, I., Sasago, Y., and Uchinokura, K. (1997). Large thermoelectric power in NaCo<sub>2</sub>O<sub>4</sub> single crystals. *Physical Review B* 56: R12685–R12687. https://doi.org/10.1103/PhysRevB.56.R12685.
- 10 Shikano, M. and Funahashi, R. (2003). Electrical and thermal properties of single-crystalline (Ca<sub>2</sub>CoO<sub>3</sub>)<sub>0.7</sub>CoO<sub>2</sub> with a Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> structure. *Applied Physics Letters* 82: 1851–1853.
- 11 Ohtaki, M., Tsubota, T., Eguchi, K., and Arai, H. (1996). High-temperature thermoelectric properties of (Zn<sub>1-x</sub>Al<sub>x</sub>)O. *Journal of Applied Physics* 79: 1816–1818.
- 12 Ohta, S., Nomura, T., Ohta, H., and Koumoto, K. (2005). High-temperature carrier transport and thermoelectric properties of heavily La- or Nb-doped SrTiO<sub>3</sub> single crystals. *Journal of Applied Physics* 97: 42.
- **13** Van, N.N., Pryds, N., Linderoth, S., and Ohtaki, M. (2011). Enhancement of the thermoelectric performance of p-type layered oxide  $Ca_3Co_4O_{(9+\delta)}$  through heavy doping and metallic nanoinclusions. *Advanced Materials* 23: 2484–2490.
- 14 Zhao, L.-D., He, J., Berardan, D. et al. (2014). BiCuSeO oxyselenides: new promising thermoelectric materials. *Energy & Environmental Science* 7: 2900–2924.
- 15 Zhang, X. and Zhao, L.-D. (2015). Thermoelectric materials: energy conversion between heat and electricity. *Journal of Materiomics* 1: 92–105.
- 16 Lan, J.-L., Liu, Y.-C., Zhan, B. et al. (2013). Enhanced thermoelectric properties of Pb-doped BiCuSeO ceramics. Advanced Materials 25: 5086–5090.
- 17 Morkoç, H. and Özgür, Ü. (2009). Zinc Oxide: Fundamentals, Materials and Device Technology. Wiley-VCH.
- 18 Kresse, G. and Hafner, J. (1993). Ab initio molecular dynamics for liquid metals. *Physical Review B* 47: 558.
- **19** Kresse, G. and Hafner, J. (1994). Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semi-conductor transition in germanium. *Physical Review B* 49: 14251.
- **20** Kresse, G. and Furthmüller, J. (1996). Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* 6: 15.
- **21** Kresse, G. and Furthmüller, J. (1996). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* 54: 11169.
- **22** Blöchl, P.E. (1994). Projector augmented-wave method. *Physical Review B* 50: 17953.

- **23** Kresse, G. and Joubert, D. (1999). From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* 59: 1758.
- 24 Perdew, J.P., Burke, K., and Ernzerhof, M. (1996). Generalized gradient approximation made simple. *Physical Review Letters* 77: 3865.
- **25** Mehdizadeh Dehkordi, A., Zebarjadi, M., He, J., and Tritt, T.M. (2015). Thermoelectric power factor: enhancement mechanisms and strategies for higher performance thermoelectric materials. *Materials Science and Engineering: R: Reports* 97: 1–22.
- 26 Pichanusakorn, P. and Bandaru, P. (2010). Nanostructured thermoelectrics. Materials Science and Engineering: R: Reports 67: 19–63.
- 27 Popescu, A., Woods, L.M., Martin, J., and Nolas, G.S. (2009). Model of transport properties of thermoelectric nanocomposite materials. *Physical Review B* 79 (20): 205302.