

Recent advances in oxide thermoelectric materials and modules



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ABSTRACT

Due to the growing concern on depletion of non-renewable resources, waste heat harvesting has become one of the effective approaches for solving the energy shortage issue. Oxide thermoelectric materials have the advantages of low cost, environment-friendly manufacturing and chemical stability at high temperatures. However, compared to traditional thermoelectric materials, they exhibit only modest thermoelectric properties due to their low electrical- and high thermal conductivity. Numerous studies have been done to improve their thermoelectric response by doping. These oxide materials mainly include the p-type $\text{Ca}_3\text{Co}_4\text{O}_9$ and n-type ZnO , SrTiO_3 , and CaMnO_3 . By connecting these both types of thermoelectric oxides in series, a module which is capable of generating considerable power can be obtained. In this review, we present the progress made on p-type and n-type thermoelectric oxides in recent years. We discuss the electronic structure of these oxides as it plays an important role in determining the thermoelectric properties. We also discuss the advanced modules which have been fabricated using these thermoelectric oxide couples.

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1. Introduction

Energy demand is one of the major concerns to the whole world. Depletion of natural energy resources, as well as negative environmental impacts of pollution and global warming, has stimulated researchers to look for alternative and sustainable energy harvesting methods. One of the eco-friendly though straightforward approach is the conversion of waste heat or environmental heat into energy. The basis of this approach is the Seebeck effect, a phenomenon where a voltage is generated across a solid when maintained under a temperature difference [1,2]. Thermoelectric materials are thus promising candidates for solid-state energy generators for converting the huge amount of industry and automobile exhausted waste heat into electricity.

For thermal power generation, the energy conversion efficiency or the thermoelectric efficiency, η can be expressed in terms of the temperatures of the hot side (T_h), cold side (T_c) and their average (T_m) as [3]

$$\eta = \frac{T_h - T_c}{T_h} \left[\frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + \frac{T_c}{T_h}} \right], \quad (1)$$

where ZT is the dimensionless figure of merit which is further related to the Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ) by Refs. [3,4]

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

where T is the absolute temperature, κ_e is the thermal conductivity contribution from the electrons and the holes, and κ_l is the corresponding contribution from the phonons moving through the lattice. The term $S^2 \sigma$ represents the power factor which gives a measure of the amount of energy generated at a particular temperature. ZT plays an important role in the overall conversion efficiency. The dependence of conversion efficiency on the temperature difference ($T_h - T_c$) for different ZT values is shown in Fig. 1a [3]. This indicates that the value of ZT for any thermoelectric material should be at least 1 for its practical application [3]. As evident from equation (2), the value of ZT can be improved by either increasing the Seebeck coefficient and electrical conductivity or lowering the thermal conductivity of the material. However, increasing electrical conductivity is accompanied by an increase in the heat transport by electrons and holes according to the

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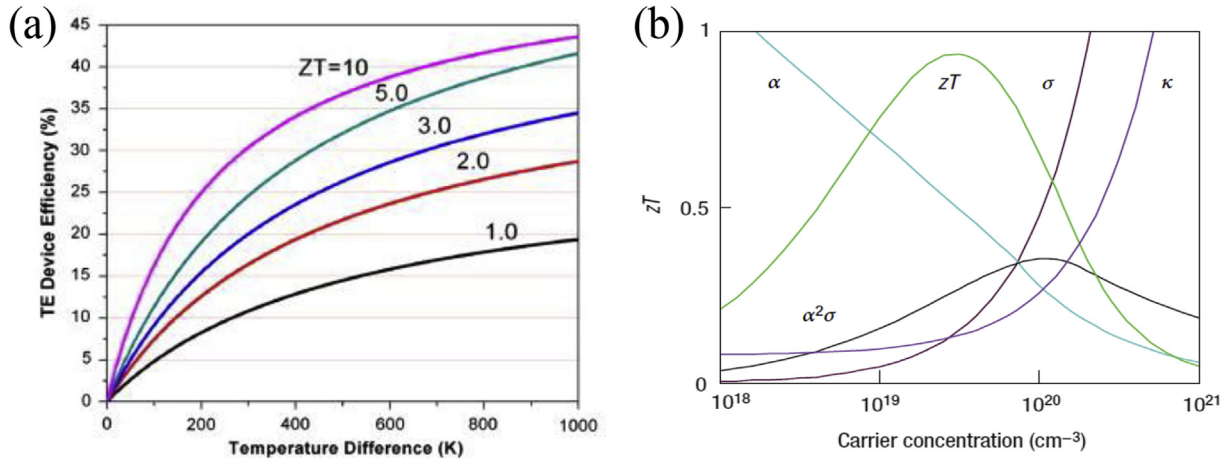


Fig. 1. (a) Thermoelectric conversion efficiency as a function of temperature difference for different ZT values corresponding to the cold side temperature of 300 K. Reprinted from Z. G. Chen, G. Han, L. Yang, L. Cheng and J. Zou, Nanostructured thermoelectric materials: Current research and future challenge, Chinese Materials Research Society, 22 (2012) 535–549, copyright (2012), with permission from Elsevier; (b) Carrier concentration dependence of Seebeck coefficient α , electrical conductivity σ , thermal conductivity κ and ZT. Reprinted by permission from Macmillan Publishers Ltd: [NATURE] (G. J. Snyder and E. S. Toberer, Complex thermoelectric materials, Nat. Mater. 7 (2008) 105–114), copyright (2008).

Wiedemann–Franz law

$$\kappa_e = LT\sigma, \quad (3)$$

where L is the Lorenz number, which is equal to $2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ (neglecting the bipolar effect). This means that reducing the value of κ_e worsens the electrical conductivity which is not desired, so the lattice thermal conductivity has to be reduced to get a lower thermal conductivity [4]. One of the most important approaches for reducing the value κ_l is to use the Phonon-Glass Electron-Crystal (PGEC) approach [2,5,6]. PGEC is a concept where the material should have a lower thermal conductivity like the amorphous materials such as glass, while good electronic properties similar to the semiconductor crystals [1,6–8]. Typical PGEC materials are skutterudites and clathrates, where oversized voids can be filled with foreign atoms i.e. rattlers which have slower vibrations and loose bonding energy [9–11]. The reduction of κ_l in these materials was known to be a result of the resonant phonon scattering by vibrations of the rattlers which consequently decrease the average phonon relaxation time [11,12]. However, recent studies on the clathrate, $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ show that the main mechanism for reduction of κ_l can be either a decrease in average sound velocity or due to the non-resonant phonon scattering [13,14].

It has been discussed earlier that ZT can be improved by increasing the electrical conductivity and Seebeck coefficient. In broad-band materials such as metals, the Seebeck coefficient in the parabolic band model and energy-independent scattering approximation can be expressed as [4,9]:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m_b^* T \left(\frac{\pi}{3n}\right)^{2/3}, \quad (4)$$

where e is the electron charge, h is the Planck's constant, k_B is the Boltzmann constant, n is the carrier concentration and $m_b^* = N_V^{2/3} m_b^*$ is the density-of-state effective mass (N_V and m_b^* are valley degeneracy and band effective mass respectively) [15]. Thus, low carrier concentration, flat bands and symmetric crystal structure with high degeneracy can contribute to the improvement of Seebeck coefficient. However, flat bands with heavy band effective mass and low carrier concentration are not advantageous for electrical transport properties. The dependence of Seebeck coefficient, electrical conductivity and power factor on the carrier

concentration of typical broad-band materials is presented in Fig. 1b [4]. It can be inferred that in order to obtain optimum thermoelectric property, a band gap of less than $10 k_B T$ and a carrier concentration of $\sim 10^{19} - 10^{21} / \text{cm}^3$ are desired [3,16]. However, for the non-parabolic band, the band effective mass becomes dependent on band gap and temperature, which consequently can influence the temperature dependence of the Seebeck coefficient [9,17]. In the case of narrow-band materials such as transition metal oxides, the carriers are no longer itinerant and hopping conduction occurs. In ionic compounds, polarons (quasiparticles consisting of charged carriers together with its surrounding lattice distortion) are formed due to the strong interaction between carriers and lattices. When small polarons hop between the energetically inequivalent lattice sites with different vibrational energies, the Seebeck coefficient is given as [18]:

$$S = \frac{\Delta S^*}{e} + \frac{E_T}{eT}, \quad (5)$$

where ΔS^* is the average change of the material's entropy with the injection of charge carriers, and E_T is the average vibrational energy. The Seebeck coefficient consists of two parts: temperature-independent (first term) and temperature-dependent (second term). The first term is related to the entropy of materials, which means a disordered crystal structure contribute to high ZT. When the energies of crystal lattice are broadly distributed, the second term becomes directly proportional to temperature, which means the Seebeck coefficient increases linearly with temperature. It indicates that the value of Z can be improved at higher temperatures [18].

Recently, a number of studies have been conducted on the skutterudites, clathrates, Heusler alloys and bismuth/lead chalcogenides, most of which reported ZT value reaching 1 [6,9,10,19–23]. With the development of nanostructure engineering, low-dimensional thermoelectric materials have been explored which show better thermoelectric performance compared to their corresponding bulk materials due to their enhanced density of states and decreased thermal conductivity [3,23,24]. For instance, $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices have an extraordinary ZT of 2.4 at 300 K [24]. However, most of these thermoelectric materials are toxic and/or unstable at high temperatures [25]. In this context, metal oxides have good chemical stability and environment friendliness, which

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