Low-cost, abundant binary sulfides as promising thermoelectric materials

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In the past several years, metal sulfides have been the subject of extensive research as promising thermoelectric materials with high potential in future commercial applications due to their low cost, low toxicity, and abundance. This review summarizes recent developments and progress in the research of metal sulfides, particularly for binary metal sulfides such as Bi_2S_3, $Cu_{2-x}S$, and PbS. Methods for improving the thermoelectric properties of these binary sulfides are emphasized, and promising strategies are suggested to further enhance the thermoelectric figure of merit of these materials.

Introduction

In 1823, Thomas Johann Seebeck observed that the joining of two dissimilar metals held at different temperatures (T and $T + \Delta T$) induced a voltage difference (ΔV) that was proportional to the temperature difference (ΔT). The ratio of the induced voltage to the temperature difference ($\Delta V/\Delta T$) is denoted as the Seebeck coefficient (α), or the thermopower, and is strictly related to the materials involved. This effect can be understood in terms of Fig. 1a,b, where, in Fig. 1a, the temperature gradient induces the flow of charge carriers (in this example, negative charge carriers) from the hot side (T_h) to the cold side (T_c). This induced charge carrier flow naturally generates an electric field that impedes the resulting current, as shown in Fig. 1b [1–4]. The Seebeck effect is a common phenomenon observed in almost all materials. The Seebeck coefficient is very low in a metal (only a few microvolts per Kelvin), and is much higher in a semiconductor (typically hundreds of microvolts per Kelvin). Owing to this potential for direct energy transfer between heat and electricity, the thermoelectric (TE) effect has been utilized for industrial applications in accordance with the two typical models shown in Fig. 1c,d. Figure 1c illustrates the TE power generation model employing the Seebeck effect, whereas Fig. 1d illustrates the TE heat conduction model employing the Peltier effect. While the former depicts a current induced by a temperature gradient imposed on the two sides of a TE couple, the latter depicts a scenario where a voltage applied to a TE couple induces charge carriers to maintain electrical equilibrium by absorbing thermal energy at one end of the couple and releasing it at the other. Based on these two effects, materials with pronounced TE capabilities are of increasing interest. TE devices are silent, reliable, and scalable by connecting devices in series and parallel, and are therefore ideal for small and distributed power generation and rapid heating and cooling [4]. Due to these outstanding characteristics, TE materials have aroused worldwide interest in many applications such as waste heat recovery, solar heat utilization (power generation mode), and solid-state refrigeration and heating, which has been utilized in applications such as temperature-controlled seats and portable picnic warmers and coolers, as well as the thermal management of microprocessors [5,6].

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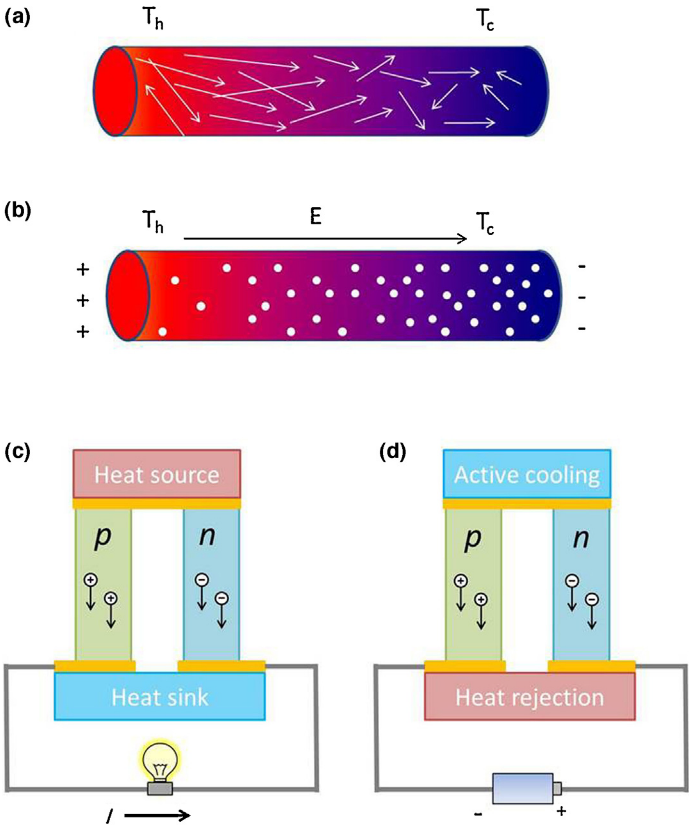

FIGURE 1

Schematic depictions of thermoelectric effects. (a) The more energetic electrons at the hot side (T_h) of the material have a longer mean free path compared with electrons at the cold side (T_c) of the material. (b) These more energetic electrons (denoted by white dots) then diffuse to the cold side, which induces the development of an electric field (E) to resist further diffusion. Schematic illustrations of thermoelectric modules for (c) power generation (the Seebeck effect) and (d) active refrigeration (the Peltier effect). In (c), an applied temperature difference causes charge carriers in the material (electrons or holes) to diffuse from the hot side to the cold side, resulting in a current flow through the circuit. In (d), heat is absorbed at the upper junction and released at the lower junction when a current is imposed in the circuit.

The efficiency of TE materials is determined by the dimensionless figure of merit (ZT), defined as $ZT = \alpha^2 T/\rho\kappa$, where T, ρ, and κ are the absolute temperature, electrical resistivity, and thermal conductivity, respectively [4]. Therefore, high TE performance requires both a high power factor (α^2/ρ) and a low thermal conductivity κ [5,7]. Although it is quite difficult to control the above parameters independently due to their complex interrelationships, TE performance records have been broken continuously in recent decades, which has been ascribed to the development of new concepts and/or mechanisms [8] such as synergistic nanostructuring [3], modification of the Fermi level close to the band-edges [1], degeneration of multiple valleys [9], electronic resonance states [10], electron energy barrier filtering [11], modulation doping [12], and depressing the bipolar effect at high temperature [13].

A typical TE couple consists of n-type and p-type TE legs, as shown in Fig. 1c,d, both of which demand high ZT values to achieve high device efficiency. Generally, only TE materials with ZT values above 1 are considered to be suitable for commercial applications. For example, Bi_2Te_3 and PbTe are two very important TE materials with high ZT values respectively near room temperature and in the intermediate temperature range, and have already been employed for TE cooling and power generation applications [3]. Other materials possessing ZT values greater than 1 include n-type materials: $AgPb_mSbTe_{m+2}$ [14,15], PbSnTe-PbS [16], In_4Se_3 [17], Cu-BiTeSe [18], PbSe [19,20], $Si_{80}Ge_{20}$ [21], and $Mg_2Si_{0.3}Sn_{0.7}$ [22]; and p-type materials: BiSbTe [23], Tl-PbTe [24], PbTe-PbS [25], $CoSb_3$-Sr, Ba, Y [26–28], BiCuSeO [29], Cu_2Se [30,31], and $Cu_{1.97}S$ [32]. However, despite the advantageous TE properties of the aforementioned materials, most of these contain high-toxicity and/or high-cost elements, which limits their large-scale application. Therefore, considerable incentive exists for researchers to develop alternative materials composed of environmentally benign, low-cost, and more abundant elements [33].

Binary metal sulfides as thermoelectric materials

The benefits of sulfides

Binary metal sulfides such as Bi_2S_3, $Cu_{2-x}S$ ($0 < x < 1$), PbS, CdS, TiS_2, and Ag_2S are a series of important semiconductors whose unique physical and chemical properties have facilitated their use in numerous applications such as photovoltaic devices, lithium batteries, photocatalysis, and photoluminescence [34–36]. Metal sulfides were intensively investigated as TE materials during the 1960s, although only the electrical transport properties were the focus of attention for a very long period [37]. Nonetheless, the low costs, low toxicity, and optimizable TE properties of these materials have attracted growing interest in recent years, which is clearly evident by the sudden increment of metal-sulfide-related publications, as shown in Fig. 2a.

Figure 2b shows the relative abundance of a number of elements typically employed in TE materials. A higher abundance value is indicative of larger reserves for a given element. For example, the abundance of Te is only 0.001 ppm, which is significantly lower than Ag, and even lower than those of the rare metals Au and Pt. Moreover, the price of Te is likely to rise sharply if Te-based materials reach mass markets. A broad search for more abundant materials is therefore necessary Oxides are also good TE materials in some respects, but their high thermal conductivity is a fatal drawback that interferes with their ability to retain a large temperature difference [38]. The abundance is one of the most important criteria that drives the price of basic elements. Figure 2c shows the prices of various high-purity elements, which are normalized with respect to the price of 99.99% Te. With the exception of Ag and In, nearly all other elements are less expensive than Te. For example, the price of S is less than one-tenth the price of Te.

In addition, environmental compatibility is crucial for determining the potential applications of a particular element. For example, wide-spread commercial use of highly toxic materials would not be possible due to the potential for damage to the environment and human health, even if they possess excellent TE properties. Figure 2d shows the median lethal dose (LD50) values as well as the globally harmonized system (GHS) classification codes (all LD50 and GHS data were obtained from materials safety data sheets) and related labeling for elements commonly employed in TE materials. The LD50 value of a chemical represents the dose administered per unit mass of the test subject that kills half of the test subjects within the following 14 days. Therefore,