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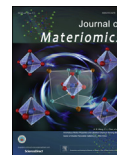


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Thermoelectric materials: Energy conversion between heat and electricity

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Abstract

Thermoelectric materials have drawn vast attentions for centuries, because thermoelectric effects enable direct conversion between thermal and electrical energy, thus providing an alternative for power generation and refrigeration. This review summarizes the thermoelectric phenomena, applications and parameter relationships. The approaches used for thermoelectric performance enhancement are outlined, including: modifications of electronic band structures and band convergence to enhance Seebeck coefficients; nanostructuring and all-scale hierarchical architecturing to reduce the lattice thermal conductivity. Several promising thermoelectric materials with intrinsically low thermal conductivities are introduced. The low thermal conductivities may arise from large molecular weights, complex crystal structures, liquid like transports or high anharmonicity of chemical bonds. At the end, a discussion of future possible strategies is proposed, aiming at further thermoelectric performance enhancements.

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Keywords: Thermoelectric; Electrical conductivity; Seebeck coefficient; Thermal conductivity

1. Introduction

Statistical results show that more than 60% of energy is lost in vain worldwide, most in the form of waste heat. High performance thermoelectric (TE) materials that can directly and reversibly convert heat to electrical energy have thus draw growing attentions of governments and research institutes [1]. Thermoelectric system is an environment-friendly energy conversion technology with the advantages of small size, high reliability, no pollutants and feasibility in a wide temperature range. However, the efficiency of thermoelectric devices is not high enough to rival the Carnot efficiency [2,3]. A dimensionless figure of merit (ZT) is defined as a symbol of the thermoelectric performance, $ZT = (\alpha^2 \sigma / \kappa) T$. Conceptually, to obtain a high ZT , both Seebeck coefficient (α) and electrical conductivity (σ) must be large, while thermal conductivity (κ) must be minimized so that the temperature

difference producing Seebeck coefficient (α) can be maintained [4,5].

Historically, in 1821, the German scientist Thomas Johann Seebeck (Fig. 1(a)) noticed an interesting experimental result that a compass needle was deflected by a nearby closed cycle jointed by two different metals, with a temperature difference between junctions. This phenomenon is called the Seebeck effect, which can be simply schematized by Fig. 1(b), where an applied temperature difference drives charge carriers in the material (electrons and/or holes) to diffuse from hot side to cold side, resulting in a current flow through the circuit [6]. Fig. 1(c) shows the power generation efficiency as a function of average ZT_{ave} , and the relationship can be given by Refs. [7,8]:

$$\eta_p = \frac{T_h - T_c}{T_h} \left[\frac{\sqrt{1 + ZT_{\text{ave}}} - 1}{\sqrt{1 + ZT_{\text{ave}}} + T_c/T_h} \right] \quad (1)$$

where ZT_{ave} is the average value of both n -type and p -type two legs, the ZT_{ave} per leg is averaged over the temperature dependent ZT curve between T_h and T_c , T_h and T_c are the hot and cold ends temperature, respectively [7,8]:

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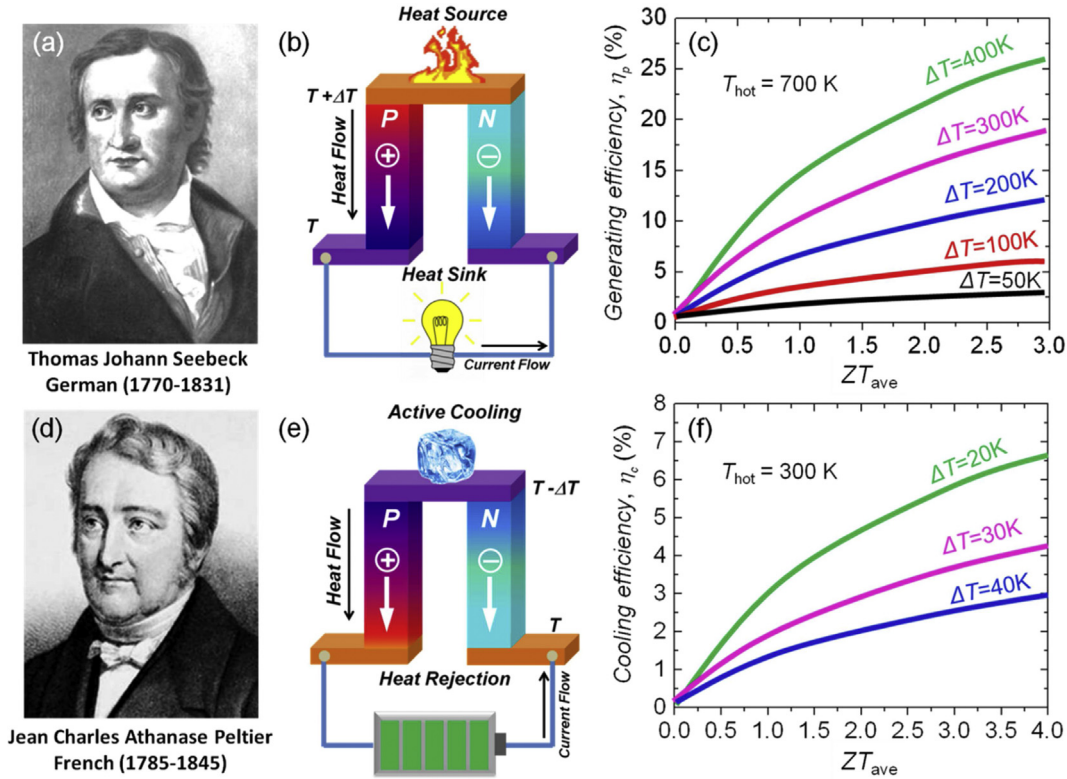


Fig. 1. Schematic illustrations of thermoelectric modules for power generation (Seebeck effect) and active refrigeration (Peltier effect): (a) the German physicist, Thomas Johann Seebeck, (b) Seebeck effect for the power generation, an applied temperature difference causes charge carriers in the material (electrons or holes) to diffuse from the hot side to the cold side, resulting in current flow through the circuit, (c) power generation efficiency as a function of average ZT_{ave} ; (d) the French physicist, Jean Charles Athanase Peltier, (e) Peltier effect for the active refrigeration, heat evolves at the upper junction and is absorbed at the lower junction when a current is made to flow through the circuit, (f) cooling efficiency as a function of average ZT_{ave} . Higher ZT_{ave} projects higher thermoelectric power generation and cooling efficiency.

$$ZT_{ave} = \frac{1}{T_h - T_c} \int_{T_c}^{T_h} ZT dT \quad (2)$$

Fig. 1(c) shows that a higher ZT_{ave} and a larger temperature difference will produce the higher conversion efficiency. One can see that if $ZT_{ave} = 3.0$ and $\Delta T = 400$ K the power generation efficiency η_p can reach 25%, comparable to that of traditional heat engines [7,8]. The Seebeck effect is the thermoelectric power generation model. And in some extreme situations or special occasions, the thermoelectric technology plays an irreplaceable role. The radioisotope thermoelectric generators (RTGs) have long been used as power sources in satellites and space probes, such as Apollo 12, Voyager 1 and Voyager 2, *etc.* Nowadays, thermoelectric power generation gets increasing application in advanced scientific fields, and the thermal source could be fuels, waste-heat, geothermal energy, solar energy and radioisotope [7,8].

Opposite to the Seebeck effect, the Peltier effect is the presence of heating or cooling at an electrified junction of two different conductors and was named after the French physicist Jean Charles Athanase Peltier (Fig. 1(d)), who discovered it in 1834. As shown in Fig. 1(e), heat is absorbed at the upper junction and rejected at the lower junction when a current is made to flow through the circuit, and the upper end is active

cooling [6]. The thermoelectric cooling efficiency η_c can be given by Refs. [7,8]:

$$\eta_c = \frac{T_h}{T_h - T_c} \left[\frac{\sqrt{1 + ZT_{ave}} - T_h/T_c}{\sqrt{1 + ZT_{ave}} + 1} \right] \quad (3)$$

As illustrated in Fig. 1(f), similar with the thermoelectric power generation, a higher ZT_{ave} value will produce a larger thermoelectric cooling efficiency η_c . For example, When $ZT_{ave} = 3.0$, $\Delta T = 20$ K, η_c could reach 6%. The Peltier effect is the thermoelectric cooling power refrigeration model, which have already been used in some electronic equipments intended for military use. Thermoelectric coolers can also be used to cool computer components to keep temperatures within design limits, or to maintain stable functioning when over-clocking. For optical fiber communication applications, where the wavelength of a laser or a component is highly dependent on temperature, Peltier coolers are used along with a thermistor in a feedback loop to maintain a constant temperature and thereby stabilize the wavelength of the device.

2. Current thermoelectric materials and advanced approaches

To obtain a high ZT , both Seebeck coefficient (α) and electrical conductivity (σ) must be large, while thermal

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