Thermoelectric Materials

Subjects: Energy & Fuels

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Solid-state energy conversion has been established as one of the most promising solutions to address the issues related to conventional energy generation. Thermoelectric materials allow direct energy conversion without moving parts and being deprived of greenhouse gases emission, employing lightweight and quiet devices.

thermoelectricity bismuth telluride films

1. Introduction

The worldwide energy and pollution crisis is forcing the industry to innovate in sustainable directions: new ways to harvest and save energy are necessary [1][2][3]. Thermoelectric generators (TEGs) and coolers (TECs) are technological solutions which can address such issues. The operating principle of thermoelectric materials (TEMs) is based on the Seebeck effect, discovered as a thermomagnetic effect by Seebeck in 1821, and correctly addressed as a thermoelectric effect by Oersted in 1825 [4][5]. A thermoelectric (TE) generator is used to convert thermal energy into electrical energy. When a temperature gradient (ΔT) is applied to the opposite ends of a TE device, power is generated according to this temperature difference: the power generated therefore increases linearly with ΔT [6][7][8]. Oppositely, a thermoelectric cooler can generate a temperature gradient between two opposite ends when a current passes through the material from the appropriate pins of the thermoelements. In the first case, converted heat is referred to as the Seebeck effect. In the second case, the phenomenon is called the Peltier effect [1][2][9].

The disruptive impact of solid-state thermoelectric generators on the world is related to the possibility of directly converting waste heat into electrical energy; currently, research is therefore focusing on these materials thanks to the coupling of sustainable energy production and waste energy re-utilization. The lack of moving parts makes the devices relatively scalable, greenhouse gas emission-free, lightweight, and quiet; furthermore, thanks to these characteristics, thermoelectric devices are extremely reliable. Since these electricity generators do not depend on the nature of the consumable heat, the fields of application are quite numerous and diverse. The five main categories in which thermoelectric generators are used are: medical and wearable devices (e.g., wristband energy harvesters), microelectronics (e.g., wireless sensor networks nodes), electronics (e.g., reutilization of waste heat for energy harvesting), automotive (e.g., re-utilization of engine waste heat to power up devices installed on the vehicle), and aerospace (e.g., energy generation in extreme conditions, such as outer space) [10][11][12][13][14]. TEGs fit these applications because of their reliability, which is the main concern in such cases, not efficiency. Furthermore, in high tech applications such as aerospace and microelectronics, costs are of secondary concern, enabling even more TE material utilization [15][16][17][18]. The last 3 years of state-of-the-art, best performing TE materials (ZT) are summarized in **Figure 1**. Among the materials cited, those showing the best performance (ZT ≥ 2.4) are GeTe, PbTe, SbSe, and Cu_2Se; however, these values did not exhibit high reproducibility, remaining laboratory results never applied in in situ applications. The ZT_{max} values of similar materials of the years before 2021 are charted in the diagram in the work of Shin et al [18].

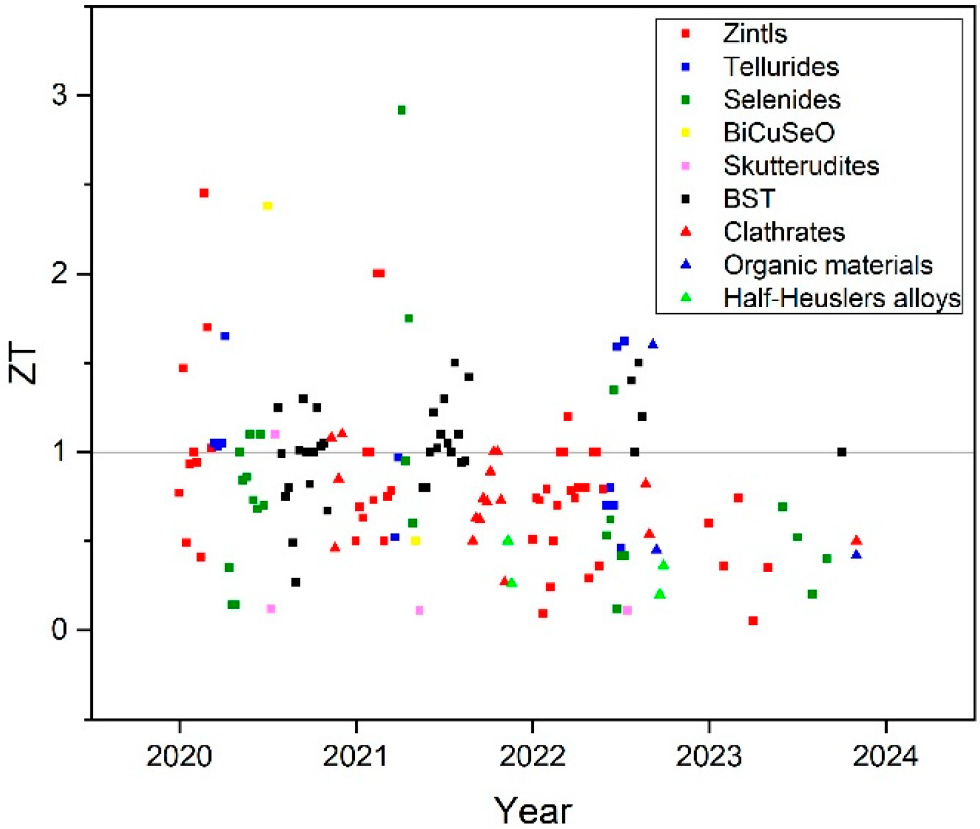

Figure 1. ZT values for state-of-the-art thermoelectric materials in the last 3 years. The image was created summarizing the ZT values at room temperature of the materials tested in the bibliography of thermoelectrics in the respective years.

Recent studies about the market of TEMs revealed that in 2019, bismuth telluride accounted for the 66% of the total thermoelectric market. This material is chosen by most companies because today's commercial applications are close to room temperature, where the highest figure of merit is claimed by Bi_2Te_3 and its alloys (it can function up to 600 K). Interestingly, the second material in this classification is lead telluride (PbTe) which is used at higher temperatures than bismuth telluride (up to 900 K). Furthermore, PbTe is a chalcogenide as well, indicating the potential of this material class.

Said studies also highlighted that the thermoelectric market is predicted to increase from the 51.9 million USD of 2019 to the 96.2 million USD of 2027, with a compound annual growth rate (CAGR) of 8.0% [20]. This demand derives from the increasing applications in industrial, automotive, healthcare, microelectronics, and aerospace. The advantages of using these materials are related to energy saving (e.g., in many applications conventional batteries could be substituted by these devices, for instance thermo-powered security systems in apartments), the reuse of waste heat (e.g., the heat dispersed by a vehicle engine can be used to power up different accessories of the car), and reducing greenhouse gases emissions, non-renewable sources, and fossil fuel utilization [15][16][18].

Up to 2027, different growth rates have been forecast for the application fields of TEMs (industrial, automotive, electric and electronics, healthcare, and others). Automotive and electric and electronics are the fields where the market is growing the fastest; the value of CAGR is around 9.7% for both, differently from the other fields where it is lower [20].

However, as can be seen from the prices summed up in **Figure 1**, the high production costs of these devices could lower TEMs' market growth. An example is in photovoltaic energy generation; a 1000 W photovoltaic panel currently costs less than 3000 USD, whereas a 125 W TEG (where the energy source is sun irradiation) costs 1200 USD. The use of TEMs for such an application has wide potential because when there is no sunlight, an in-house heat source can be used to re-charge the generator. However, the high production prices are not enabling this solution yet [21]. For example, relatively high efficiency values were reached using an n-type (Bi-Te-Se, PbTe) and a p-type (Bi-Te-Sb) for the TEG; however, as summed up in **Figure 1**, the ZT_{max}/cost effectiveness is low (0.9 for Bi-Te-Sb and Bi-Te-Se alloys and 1.2 for PbTe), slowing the unveiling on the market [18][21][22][23]. The main research goal is in fact to achieve relatively high efficiency values with scalable processes, delivering TE devices to markets where price is a main concern [21][22][24].

The achievement of high ZT values is related to high values of electrical conductivity and low values of thermal conductivity [14][25][26][27].

2. Commercial Thermoelectric Modules

TE modules are devices used to exploit thermoelectric phenomena for refrigeration or power generation. These objects consist of semiconductor couples electrically in series and thermally in parallel while being positioned between two ceramic substrates (usually made of alumina, Al_2O_3, silica, SiO_2, or beryllium oxide, BeO); the thermocouples are connected through metal contacts (commercially available products employ thick films of copper Cu between the leg ends and the substrate, which are called 'interconnects'). Furthermore, an anti-diffusion layer (often nickel, Ni, in one layer or silver, Ag, and tin, Sn, in two stacked layers) is soldered on every element to avoid the phenomenon when the module operates at high temperatures [15][16]. More specifically, thermoelectric couples are installed as alternating n- and p-doped semiconducting legs, where the electrons in the n-type legs move like the holes in the p-type legs with heat [14][15]. Doping a semiconductor corresponds to introducing impurities in the material to add an extra electron or a hole. In the conventional case of silicon, p-doping means introducing in the semiconductor 3-valent dopants (e.g., boron) which can catch an outer electron, generating a hole in the material. Oppositely, n-doping means inserting in the semiconductor 5-valent dopants (e.g., phosphorus) which can lose an outer electron, donating an extra electron to the material. Therefore, a p-dopant is an electron acceptor, and an n-dopant is an electron donor [27][28][29]. A single and generic thermoelectric couple is represented in **Figure 2**.

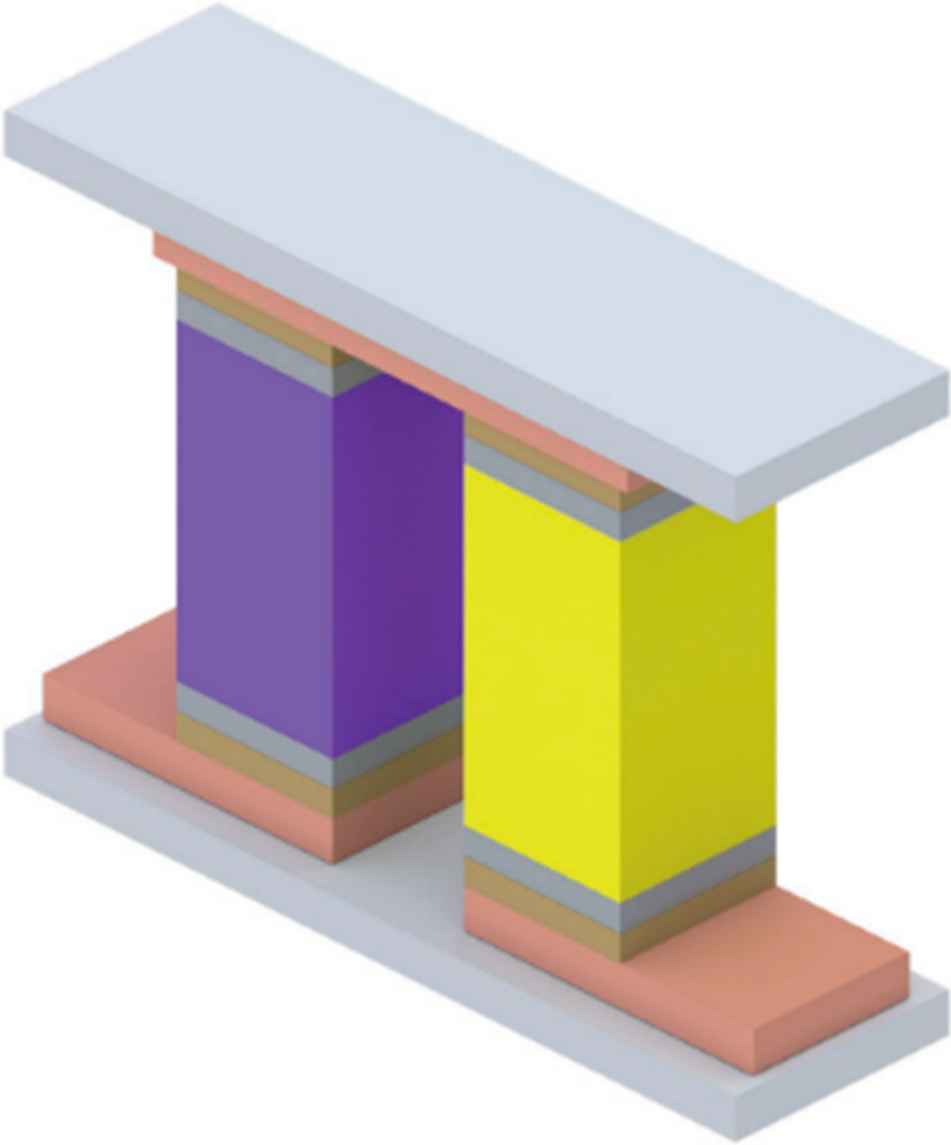

Figure 2 Representation of a single and generic thermoelectric couple. The blue and the yellow prisms are the p-type and n-type semiconductors, respectively. The light brown components are the contact metals, and the gray and brown elements are the soldered anti-diffusion layers. Finally, the upper plates are the ceramic substrates.

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