

Research on the Basic Properties and Preparation Methods of Heat Conversion Materials

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Abstract. The purpose of this literature review is to discuss the research progress and application prospects of high-efficiency thermoelectric conversion materials. In recent years, high-efficiency thermoelectric materials have garnered extensive attention due to their significant applications in waste heat recovery and energy conversion. This paper reviews various types of thermoelectric materials, including metal chalcogenides, silicides, and skutterudite materials, and analyzes their synthesis methods, properties, and advantages and disadvantages. The findings indicate that chemical vapor deposition (CVD), hydrothermal synthesis, and hot pressing are the primary methods for preparing thermoelectric materials, each with distinct advantages and limitations. Nevertheless, by optimizing the preparation processes and material compositions, high-efficiency thermoelectric materials are poised to play a crucial role in the field of sustainable energy in the future. This review summarizes the key findings of current research and suggests potential directions and challenges for future studies.

Keywords: thermoelectric materials; energy conversion; ecofriendly; Hydrothermal.

1. Introduction

Thermoelectric conversion technology uses the Seebeck effect, discovered in the early 19th century, to directly convert thermal energy into electricity. This technology gained significant attention in the mid-20th century in the fields of space exploration and long-range power generation due to its solid-state nature and reliability [1]. Nowadays, thermoelectric technology shows great potential in a wide range of applications, such as industrial waste heat recovery, automotive exhaust heat recovery, portable power generation equipment, and thermoelectric coolers. These applications highlight the potential of thermoelectric technology to improve energy efficiency and reduce environmental impact by converting otherwise wasted heat energy into useful electricity. The performance of thermoelectric materials is typically measured by the dimensionless figure of merit, ZT , defined as

$$ZT = \frac{S^2 \sigma T}{\kappa} \quad (1)$$

Where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity [2]. A higher ZT value indicates better thermoelectric performance, which is critical for practical applications.

With the rise of nanotechnology, significant progress has been made in the development of high-quality thermoelectric materials. Nanostructuring improves thermoelectric performance by increasing phonon scattering without significantly affecting electrical conductivity. This approach involves the creation of quantum dots, superlattices, nanowires, and nanoparticle composites, which introduce interfaces that allow phonons to scatter more efficiently than electrons. With the advent of nanotechnology, there have been significant advancements in the development of high-performance thermoelectric materials. Nanostructuring can enhance thermoelectric properties by reducing thermal conductivity through increased phonon scattering without significantly affecting electrical conductivity. Materials such as bismuth telluride (Bi_2Te_3), lead telluride (PbTe), and tin selenide (SnSe) have shown substantial improvements in their thermoelectric properties when engineered at the nanoscale [3]. Despite these advancements, challenges still exist in synthesizing high-quality nanostructured materials, maintaining their stability, and scaling up the fabrication processes.

Given the potential of nanostructured materials to boost thermoelectric performance, this research aims to summary characteristics of various nanostructured thermoelectric materials to understand their properties and performance, focusing on optimizing the synthesis methods to achieve high purity and controlled nanostructures. By addressing these objectives, the study aims to contribute to the advancement of thermoelectric technology, making it a more viable solution for energy efficiency and sustainability.

2. Typical thermoelectric conversion Materials

According to relevant research, more than 60% of the world's energy is wasted, with most of it being lost as heat. Consequently, high-efficiency thermoelectric (TE) materials that can convert heat energy into electrical energy are increasingly attracting the attention of governments and research institutions worldwide. From the early discovery of metal chalcogenide thermoelectric materials in the last century, such as bismuth telluride (Bi_2Te_3), lead telluride (PbTe), and silicon germanium (SiGe), to the recent identification of new high-performance thermoelectric materials like galena and cage compounds, significant advancements have been made. Fig. 1 summarizes the various high-efficiency metallic thermoelectric materials discovered since the 1960s.

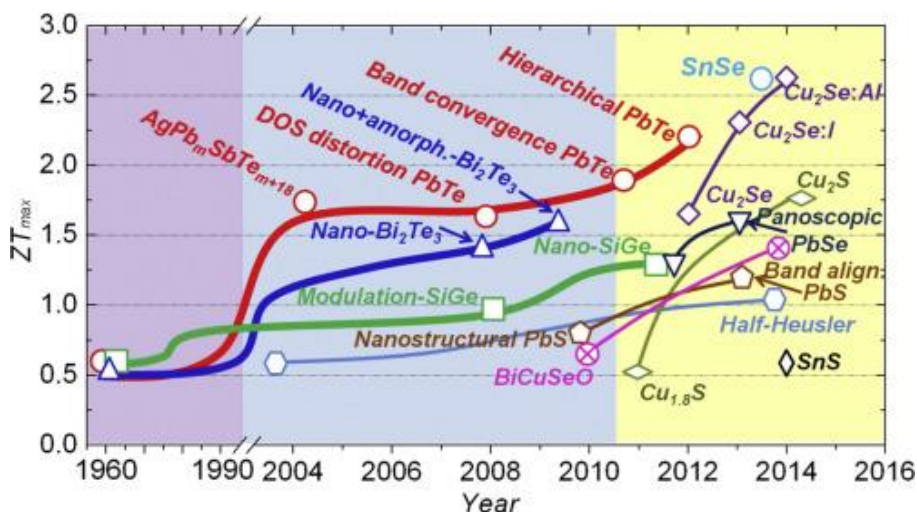


Fig 1. ZT of the current bulk thermoelectric materials as a function of year [4]

Metal chalcogenides are a crucial material class characterized by their diverse compositions and structures, leading to a wide variety of chemical and physical properties. These conjugates, which contain at least one chalcogen atom (S, Se, Te), are not as ionic as metal oxides, resulting in smaller band gaps that make them highly suitable for thermoelectric applications [5]. For instance, Bi_2Te_3 and its alloys are the best materials for low-temperature cooling and have been utilized commercially since the 1950s [6]. Mid-temperature power generation (600-800 K) can be achieved with PbTe that is heavily doped and has been utilized in radioisotope thermoelectric generators for a period of time [7]. For applications above 1000 K, the superior thermal stability of rare-earth chalcogenides makes them the preferred choice.

Silicides fall under the broad category of binary or multinary compounds, where silicon can form stoichiometric or non-stoichiometric compounds with metals. While many silicides are known, only a few have been considered for thermoelectric applications. Among them, only two - Mg_2Si and the Higher Manganese Silicides (HMSs) with the general formula MnSi_x (where $1.71 \leq x \leq 1.75$) - have met all the necessary criteria for practical deployment. These criteria include not only achieving a high zT value but also the sustainability of the silicides, which depends on the abundance and toxicity of their metallic components [8].

Skutterudite is a thermoelectric conversion material known for its "phonon glass-electron crystal" transport characteristics. Among the various skutterudite materials, CoSb_3 has been extensively studied due to its excellent environmental friendliness, suitable band gap, and high carrier mobility

[9]. With a temperature difference of approximately 510°C between the hot and cold ends, the ZT value of N-type semiconductors can reach up to 1.8 [10], while that of P-type semiconductors can reach 1.3 [11]. In addition to inorganic thermoelectric conversion materials, many promising new materials have been developed recently, such as novel organic semiconductor materials and more complex composite materials. These will not be elaborated upon here

3. Common methods for the preparation of thermoelectric conversion materials

The preparation method of thermoelectric materials is critical, as it often determines the final properties of the material. Different preparation methods generally rely on powder processing and powder synthesis. However, other synthesis and crystal growth technologies must also be considered, such as the development of thin films and bulk materials with the desired nanostructures.

In the pursuit of high-performance thermoelectric conversion materials, achieving a high zT value is essential, making the preparation method particularly important. Currently, one approach is to reduce the lattice thermal conductivity (κ_L) to its limit through nanoengineering [12], without degrading electrical performance. Another approach is to enhance the power factor (PF, $S^2\sigma$) by optimizing n or band engineering, it is possible to decouple S and σ , allowing them to increase simultaneously [13].

3.1. Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition (CVD) is a technique that is versatile and widely used to produce solid materials of high quality and performance. In CVD, volatile precursor chemicals react or decompose on the surface of a substrate to form a solid material. This process is conducted in a controlled environment, typically at high temperatures, when one or more volatile precursors are exposed to the substrate. These precursors undergo a chemical reaction or decomposition to produce a thin film on the substrate. The ability to produce materials with excellent purity, uniformity, and reproducibility makes CVD an essential technique in various industries. It is used for depositing a vast array of materials, including metals, ceramics, and semiconductors. The flexibility of CVD allows for the fabrication of thin films, coatings, and complex nanostructures, making it crucial in the manufacturing of thermoelectric materials.

Kim J G and others invent a method that SiC films were deposited on a silicon nitride (Si_3N_4) substrate using a horizontal hot-wall tube furnace [14]. Methyltrichlorosilane (CH_3SiCl_3) served as the source material due to its ideal 1:1 silicon to carbon ratio. Hydrogen was the carrier gas, with argon or helium used as diluent gases. Each sample was deposited at 1400°C under the same conditions for comparison, with a total pressure of 50 torr and a gas ratio of 4:1 (diluent + carrier gas to MTS). The substrate was chosen to enhance adhesion and facilitate the measurement of the thermoelectric performance of SiC. The results show that the thermoelectric properties are related to the gas atmosphere and heating temperature. Those who deposit SiC in an Ar or He atmosphere have higher conductivity than those who deposit it in an H_2 atmosphere, and lower conductivity than those who deposit it in an N_2 atmosphere. This is mainly due to the fact that these samples have more carbon content than SiC deposited in H_2 atmosphere and have more open pores than SiC deposited in N_2 atmosphere. The effect of temperature on materials is mainly reflected in thermal conductivity and Seebeck coefficient [15].

3.2. Hot pressing

Hot pressing is a commonly used method for preparing high-density thermoelectric materials. In this process, powder material is placed in a mold and subjected to both high temperature and uniaxial pressure in a vacuum or inert gas atmosphere to prevent oxidation and contamination. The simultaneous application of heat and pressure enhances atomic diffusion, promoting the densification of the powder to form a homogeneous solid. This method is particularly advantageous for producing

thermoelectric materials, as it allows for precise control over the microstructure, grain size, and density, all of which are critical factors affecting thermoelectric properties.

K. Ueno and others invented a method that the initial powders of Zn_4Sb_3 were made by directly reacting high-purity Zn and Sb powders, then pulverizing and sieving through a #140 mesh screen [16, 17]. Vacuum hot pressing was conducted at 738, 743, 748, and 753 K under a uniaxial pressure of 49 MPa for 5 hours. Based on preliminary experiments, it was revealed that 5 hours was sufficient for complete densification, as determined by the shrinkage measurements of the powder briquettes. Specimens hot-pressed under both vacuum and inert gas conditions were free of cracks. The sintered bodies were then polished and cut into parallelepipeds approximately $3\text{ mm} \times 3\text{ mm} \times 20\text{ mm}$ in size. The density of the specimens was measured using the method of water immersion. The electrical resistance and Seebeck coefficients were evaluated using the DC four-probe method and the Seebeck coefficient/resistance measurement system ZEM-1 (ULVAC-RIKO Inc.) in a temperature range that is between 323 and 674 K, with helium as the medium. $\epsilon\text{-Zn}_4\text{Sb}_3$ material was hot-pressed under different circumstances, and its physical and transport attributes were assessed. The sample prepared by vacuum hot pressing at 748 K and 49 MPa for five hours exhibited the combination of low resistance and low thermal conductivity Zn_4Sb_3 [18]. The material that has the greatest thermoelectricity properties demonstrated a ZT value that exceeds 1. The performance of Zn_4Sb_3 was not affected by the fabrication process in an inert gas atmosphere at different pressures.

3.3. Hydrothermal

The hydrothermal method of thermoelectric materials usually involves dissolving the precursor in water or organic solvent, reacting in a hydrothermal reactor at high temperature and high pressure, and then obtaining nano-scale thermoelectric material powder through steps such as cooling, filtration, washing and drying, and finally preparing the formed thermoelectric material through pressing and sintering processes.

Chen, Z invented a method that Hydrothermal synthesis was employed to prepare nano-Bi-Sb-Te thermoelectric materials [19]. The starting reagents included analytically pure BiCl_3 , SbCl_3 , NaBH_4 , and NaOH , with TeO_2 being 99.99% pure. Based on the molecular formula $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, adequate amounts of BiCl_3 , TeO_2 , SbCl_3 , NaBH_4 , and NaOH (as a reducing agent) were placed in an autoclave. The autoclave was filled with distilled water until it was 80% full. After sealing and maintaining the autoclave at 200°C for 20 hours, it was allowed to naturally cool to room temperature. The pellet was obtained by centrifugation and washed multiple times with distilled water, ethanol, and acetone. Finally, the product was vacuum dried at 353K for 6 hours. Subsequently, the synthesized powder was hot-pressed in a graphite mold (15 cm in diameter) at 50 MPa and 673K in a vacuum for 20 minutes. The maximum ZT value of the prepared nanosample was achieved at 398 K, reaching 1.26, which surpasses that of the alloy ingot. The primary cause of this significant improvement in ZT is the substantial decrease in thermal conductivity. In nanostructured materials, phonon scattering increases, which is the main cause of low thermal conductivity. Therefore, hydrothermal synthesis of nanomaterials can achieve the best thermoelectric properties, demonstrating thermoelectric energy conversion has a high potential application.

4. Conclusion

Due to its high efficiency and environmental friendliness, the thermoelectric conversion effect has a very broad application prospect for waste heat treatment in the future. Among the various methods of synthesizing thermoelectric materials, the products produced by the chemical vapor deposition (CVD) method have excellent uniformity and are suitable for large-scale production and the manufacture of complex geometries. However, the equipment cost is high and the operation is more complex. The hydrothermal method can produce a variety of materials with different nanostructures and has a lower temperature requirement, but it needs to be carried out in a high-pressure environment, requiring a professional autoclave and pressure control system, and is only suitable for small-scale

production. The hot-pressing method can produce high-quality products without cracks by precisely controlling the microstructure, grain size, and density, but it requires high temperature and pressure control and takes a long time. Advances in equipment and process control are expected to enhance the quality and efficiency of materials produced by hydrothermal processes, playing an important role as the search for nanotechnology and sustainable materials continues. Meanwhile, CVD is likely to be widely used in energy conversion and coating applications in the future. Thermoelectric materials with different morphologies and structures have a significant impact on their performance, making the choice of synthesis method crucial for preparing thermoelectric materials for various applications.

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