Thermoelectric Oxide Ceramics and Devices

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Thermoelectric materials have gained wide attention to realize multilevel efficient energy management to alleviate the increasingly severe energy crisis. Oxide ceramics were well-explored as potential thermoelectric candidates because of their outstanding merits, including abundance, eco-friendliness, high-temperature stability, and chemical stability. A comprehensive summary of the diversified state-of-the-art oxide ceramics and establish the links between composition designing, preparation process, structural characteristics, and properties to summarize the underlying chemistry and physics mechanism of band engineering, doping, composited with the second phase, defects engineering, and entropy engineering is provided. Furthermore, advanced device design and applications such as thermoelectric modules, miniature generators, sensors, and coolers were summarized. Ultimately, the challenges and future perspective of oxides ceramics for the device design and thermoelectric applications in the development of energy harvesting technology have been prospected.

ZT

thermoelectrics

oxides ceramics

electrical conductivity

phonon scattering

1. Introduction

Thermoelectric materials (TEs) have been used as a potential energy harvesting technology because they can convert heat into electricity and have no requirements for waste heat temperature [1][2][3]. Thermoelectric devices generally consist of *n*-type and *p*-type TEs wired electrically in series (or partly parallel) and thermally in parallel. Furthermore, there are also thermoelectric devices with single n-type and p-type TEs. They have the advantages of no moving parts, no noise, small size, etc., and have significant application merits in the military, aerospace, and high-tech energy fields [4][5].

It has been more than 200 years since the thermoelectric effect was discovered, and people have been constantly exploring and developing its industrial applications. In the early 1920s, Altenkirch, a German physicist, developed the fundamentals of thermoelectric power generation and refrigeration and summarized the performance evaluation parameters of TEs ^[6]: electrical conductivity (σ), Seebeck coefficient (*S*), and thermal conductivity (κ). Dimensionless thermoelectric merit ($ZT = S^2 \sigma T/\kappa$, *S* is Seebeck coefficient, σ is electrical conductivity, *T* is absolute temperature, κ is thermal conductivity) is usually used as an indicator to measure the thermoelectric performance ^[2]. TEs with large *ZT* values must meet the requirements of a high Seebeck coefficient to ensure the generation of the obvious thermoelectric effect—high electrical conductivity leading to small Joule heat, large output power, as well as low thermal conductivity, are required to generate a substantial temperature difference. The above three thermoelectric parameters have a strong coupled relationship because they are dependent on the carrier concentration in a conflicting manner that restricts and influences each other, making how to optimize

thermoelectric performance a huge challenge. Therefore, the coordinated regulation of *S*, σ , and κ to improve *ZT* has become the key point to realize the industrial application of thermoelectric materials.

2. Thermoelectric Fundamentals

Thermoelectric materials utilize the thermoelectric effect to achieve direct heat-to-electricity conversion. As shown in the schematic diagrams in **Figure 1**, the thermoelectric effect includes three effects: (i) the Seebeck effect, which transforms heat into electricity; (ii) the Peltier effect, absorption or release of heat at a junction in which there is an electric current; and (iii) the Thomson effect ^[1], the evolution or absorption of heat when an electric current passes through a circuit composed of a single material that has a temperature difference along its length. The most common application of the Seebeck effect is the widely existing thermocouple, which can be used in thermometers, thermoelectric power generation, and other thermal cycle fields. Static cooling is the major application of the Peltier effect. The Thomson effect establishes a connection between the previous two and reflects their differential influence.



Figure 1. Schematic diagram of thermoelectric effects. (**a**) Seebeck effect for power generation, (**b**) Peltier effect for refrigeration, (**c**) Thomson effect for reversible cooling or heating.

3. Fabrication of Thermoelectric Oxide Ceramics

3.1. Lattice Structures of Thermoelectric Oxide Ceramics

3.1.1. n-Type Thermoelectric Oxides

As an *n*-type thermoelectric oxide, strontium titanate (SrTiO₃) has attracted widespread interest due to its high effective mass of carriers, chemical and thermal stability at high temperatures, and high structural tolerance. SrTiO₃ has a cubic perovskite structure and Pm3m space group at room temperature, and its lattice constant is a = b = c = 3.905 Å ^[8]. In a unit cell unit connected by solid lines in the figure, Ti⁴⁺ ions occupy the central position in the unit cell, Sr²⁺ ions occupy the eight vertex positions, O²⁻ ions form an oxygen octahedron at the center of six faces of the cubic unit cell, and Ti⁴⁺ ions occupied the octahedral gaps. Therefore, the coordination number of Sr²⁺ ions is 12, and the coordination number of Ti⁴⁺ ions is 6. From another perspective, there is a cubic unit cell structure composed of eight Ti-O octahedrons in strontium titanate. Eight Ti-O octahedrons are located at the eight top corners of the cubic structure, while Sr²⁺ ions occupy the center of the cubic structure. The direct band gap of SrTiO₃ is 3.2 eV, and its σ is very low. Its phase transitions from cubic to tetragonal will occur at temperatures below 105 K ^[9].

3.1.2. p-Type Thermoelectric Oxides

 $Ca_3Co_4O_9$ is a typical representative material in *p*-type thermoelectric oxides. A rock salt type Ca_2CoO_3 layer sublattice and CdI 2 type CoO_2 slabs alternated arrangement into the layered structure of $Ca_3Co_4O_9$ ^{[10][11]}. Along the c-axis, it can be seen as a sandwich construction (rock salt plate sandwiched between two plates). $Ca_3Co_4O_9$ belongs to the monoclinic system structure, which is a C2/m superspace group. The incommensurate structure consists of two layers with distinct lattice parameters, a = 4.8323 Å, b1 = 2.82 Å, b2 = 4.55 Å, c = 10.8428 Å, β = 98.13°, allocated to 2.82 Å cells of CoO_2 subsystem (b1) and 4.55 Å cells of Ca_2CoO_3 subsystem (b2).

BiCuSeO is a *p*-type oxide TE with excellent thermoelectric properties. It has a tetragonal crystal structure (a = b =3.9273 Å, c = 8.9293 Å, Z = 2) with symmetry of P4/nmm (No. 129) space group ^[12]. BiCuSeO possesses a layered "hybrid" crystal structure in which the conductive layer $(Cu_2Se_2)^{2-}$ alternates with the insulating layer $(Bi_2O_2)^{2+}$ ^{[13][14]}. The bond length of Bi-Se is 3.2 Å, which is larger than that of Bi-O of 2.33 Å, indicating that it has layer characteristics ^[12]. The $(Cu_2Se_2)^{2-}$ sublayer is the main conductive channel, called the conductive layer, which can be used to regulate electrical properties; the $(Bi_2O_2)^{2+}$ sublayer is a non-conductive layer (insulating layer), which can be effectively used for thermal conductivity suppression. Therefore, the layered structure of BiCuSeO-based compounds can achieve collaborative optimization of thermal and electrical conductivities (**Figure 2**).



Figure 2. Schematic of the crystal structure of thermoelectric oxides. (a) SrTiO₃, (b) ZnO ^[15], (c) CaMnO₃ ¹⁰, (d) Ca₃Co₄O₉ ¹¹⁷, (e) Na_xCoO₂ ¹¹⁸, (f) BiCuSeO ^[19].

3.2. Preparation Method

3.2.1. Bulk Crystal Growth

It is reported that for *p*-type layered oxide TEs, the thermoelectric properties of single crystals are much higher than those of polycrystalline samples for a given component. For example, the figure merit *ZT* of single crystal Na_xCoO₂ and Ca₃Co₄O₉ samples reach 1.2 and 0.87, respectively, and the performance of polycrystalline samples is generally only about half of that of single crystal samples. Fujita et al. used the flux technique to prepare Na_xCoO_{2- δ} single crystals and measured their high-temperature thermoelectric properties for the first time. At 800 K, the *PF* reaches 7.7 mWm⁻¹K⁻², and the *ZT* value reaches 1.2 ^[20].

3.2.2. Solid-State Method

The solid-state reaction method is the most widely employed method for preparing different oxide TEs $^{[21][22][23][24]}$ [^{25][26]}. Generally, two solid-state steps are required for the synthesis of polycrystalline oxide TEs, which mainly includes the preparation of pre-sintered powder, and then sintered compact bulk ceramic samples suitable for testing various properties. The high-purity solid precursor powders were mixed and calcined at high temperatures, such as TiO₂ and SrCO₃, required for the synthesis of strontium titanate $^{[27]}$. This approach possesses the advantage of simplicity and low cost, but generally, the synthetic product after a high-temperature calcination process is blocky and requires a secondary ball milling to obtain fine powders to maintain high reactivity to sinter ceramics.

Adopting sintering aids is a commonly used method to improve the bulk density of ceramics in the traditional solidstate sintering process. The sintering aids have the following functions: (1) Forming a liquid phase environment and increasing the diffusion driving force of particles; (2) increasing ceramic density and controlling grain size; (3) preventing the polycrystalline transformation of the matrix material; and (4) entering into the lattice of the matrix material to form solid solutions during the later stage of sintering. At present, the common sintering aids include Bi_2O_3 , CuO, V_2O_5 , and B_2O_3 , etc. [28][29][30][31][32].

3.2.3. Spark Plasma Sintering

Spark plasma sintering (SPS) technology is also commonly utilized to prepare bulk oxide TEs ^{[33][34][35][36][37][38]}. SPS is also known as Pulse Electric Current Sintering (PECS). During the sintering process, the discharge plasma generated at the moment when the electrode is connected to the DC pulse current makes each particle inside the powder produce Joule heat uniformly and activate the particle surface, which makes it easy to prepare uniform, dense, and high-quality ceramic samples.

3.2.4. Mechanical Alloying

Mechanical alloying is a method to obtain solid alloy or solid solution by high-speed ball milling or grinding. Mechanical alloying has gained widespread attention for its advantages of a short cycle, low energy consumption, and simple process. Liu et al. studied the synthesis of La-doped $SrTiO_3$ nanopowders using mechanical alloying in an air atmosphere. In comparison to the solid-phase reaction method, the mechanical alloying technique can eliminate the calcination stage and is more cost-effective and eco-friendly ^[39].

3.2.5. Liquid-Phase Synthesis

Colloidal Synthesis

Solid-phase reaction method has the disadvantages of low purity and high energy consumption. To overcome the shortcoming of the high-temperature solid-phase method, the hydrothermal synthesis and sol-gel method became aroused researchers' attention.

The materials synthesized by the sol-gel method generally use inorganic salt or organic alkoxide as the precursor and, through a chemical reaction such as hydrolysis polymerization, nucleation, and growth transform from liquid precursors to sol and then to a network structure known as a 'gel', and then after dried and heating treatment to obtain the target material.

Hydrothermal Synthesis

The hydrothermal method is a solution reaction-based approach and can synthesize nanomaterials, which have been successfully applied for the preparation of TEs ^[40]. Usually, hydrothermal synthesis may occur over a wide temperature range from ambient temperature to extremely high temperatures and requires high-pressure conditions to generate high vapor pressures to trigger the chemical reaction or to control the morphology.

Solvothermal Synthesis

The solvothermal synthesis is analogous to the hydrothermal method and is based on heating the precursors and a solvent in a closed system at a temperature above the boiling point of the solvent used ^[27]. The synthetic procedure usually requires high temperature and high pressure to create the supercritical circumstances to develop the peculiar behavior of the solvent, exerting different influences on the precursors resulting in the desired product. Park et al. synthesized Ag-SrTiO₃ nanocomposites by one-pot solvothermal method ^[41] using strontium nitrate (Sr(NO₃)₂), silver (I) nitrate (AgNO₃), and titanium tetraisopropoxide [(CH₃)₂CHO]₄Ti (TTIP) as starting ingredients. Furthermore, the loading quantity of Ag could be easily manipulated by adjusting the concentration of the AgNO₃ precursor. In addition, the thermoelectric properties of layered TEs can be effectively controlled by bottom-up wet chemical synthesis of two-dimensional nanosheets/nanoplates ^{[42][43][44]}.

4. Development and Strategies to Improve the Thermoelectric Performance of Oxide Ceramics

Several of the selection rules are somewhat paradoxical as a result of the inherent trade-off effect between σ and *S*. Many optimized strategies may have a complicated correlated impact on S, σ , and κ . As an illustration, the increase of doping concentration will improve σ while decreasing *S*. Then, loffe's finding in doped semiconductors was the first effort to empirically determine the carrier concentration "sweet spot" of excellent thermoelectrics is $n = 10^{18} - 10^{20}$ cm⁻³ [45]. Consequently, an optimal power factor (*PF* = *S*² σ) versus doping concentration exists at a relatively high doping level. Furthermore, a further decrease of κ is necessary to produce a high *ZT*.

4.1. Band Engineering

Since *S*, σ , and κ of TEs are determined by the transport and interaction of carriers and phonons, adjusting one parameter often may sacrifice other physical parameters, making achieving collaborative optimization of thermoelectric performance a huge challenge. In bulk TEs, the band gap, the degeneracy of the conduction band, the extreme value of the valence band, and the effective mass in the band structure are fundamental parameters that determine the thermoelectric performance. According to the Mott formula ^[46], the parameter of *S* is in direct proportion to the slope of the energy band near the Fermi level. A greater slope means a greater S. Furthermore, the S is a function of the variation of σ near the Fermi surface, and increasing the complexity of the crystal structure can increase the complexity and the degeneracy of the band structure, leading to more extreme values in the conduction band and valence band, thus increasing *S*. In a word, factors of the band gap, energy band shape, effective mass of carriers, mobility, etc., determined by band structure are closely related and produce a trade-off effect on thermoelectric performa

4.2. Doping

Element doping is one of the widely used basic strategies to regulate carrier concentration for enhancing the thermoelectric performance of TEs. By properly doping elements with different valence states into different cationic lattice sites, a well-regulated *n* can be obtained, which leads to an optimized $S^2\sigma$. Doping will cause a change in cell parameters, induce point defects, and bring lattice distortion because of the position of atoms and the length of valence bonds changed, resulting in variations of *S*, κ , and σ . Furthermore, the length and strength of the valence bond is an important parameter that determines thermal conductivity.

In *n*-type SrTiO₃-based TEs, trivalent states of La ^{[32][34][39][40][46][47][48][49]}, Ce ^[49], Nd ^[49], Sm ^{[49][50]}, Gd ^[49], Dy ^[49], Pr ^[51], and Y ^[52] can be used to dope in Sr²⁺ site. The valence states of \geq 5⁺, such as Ta ^[53], Nb ^[54], and W ^[55], can be used to dope in the Ti⁴⁺ site. K. Singsoog et al. ^[56] investigated the influence of La doping amount on Sr_{1-x}La_xTiO₃ (x = 0, 0.06, 0.13, 0.25) through theoretical calculation; the results show that the parameters (*S*, σ , κ , *PF*, and *ZT*) increase first and then decrease. When the doping concentration of La = 0.13, it has the best thermoelectric performance of S_{900K} = -450 μ V/K, *PF*_{1200K} = 2.55 mW/m/K².

In the *n*-type CaMnO₃ system, three types of elements doped at the Ca position are rare earth elements (La, Y, Ce, Sm, Pu, Nd, Lu, etc.) ^{[57][58]}, main group elements such as Bi ^[59] and alkaline earth elements (Ba, Sr, Mg, etc.) ^[60]. Additionally, the doped elements in the Mn site mainly include Ta, V, Nb, Ru, etc. ^[61]. The doping cases such as Ca_{1-x}Bi_xMnO₃ ($0 \le x \le 0.10$) ^[59], CaMn_{1-x}Nb_xO₃ (x = 0.02, 0.05, 0.08) ^[62], Dy and Yb co-doping on Ca_{1-2x}Dy_xYb_xMnO₃ ($0 \le x \le 0.10$) ^[63], and Ca_{0.92-x}Pr_{0.08}Sr_xMnO₃ (x = 0.01, 0.02, 0.03, 0.04) ^[64] demonstrated that Bi, Nb, Dy, Yb, Pr doping at CaMnO₃ obtained the *ZT* values range of 0.18–0.27 which were much improved compared with the pure phase of CaMnO₃ (*ZT* = 0.04).

To improve the thermoelectric properties of ZnO, commonly used doping elements are C, Si, Fe, In, Ga, Al, Ni, and Sb ^{[21][65][66][67]}. Among them, Al-doped ZnO is the one widely studied and has the best TE performance at present. In the case of $Zn_{0.96}AI_{0.02}Ga_{0.02}O$ ^[65], ZT = 0.65 at 1247 K was obtained, which is one of the high levels of ZT values in n-type oxide thermoelectric materials. Additionally, this outstanding achievement can be attributed to the Al and Ga co-doping can significantly reduce the thermal conductivity from 40 W/m/K of $Zn_{0.98}AI_{0.02}O$ to 5 W/m/K of $Zn_{0.93}AI_{0.02}Ga_{0.05}O$.

In the p-type $Ca_3Co_4O_9$ -based TEs, much research focused on the partial substitution of cations on the Ca-site such as Na ^[68], Sr ^[69], Ba ^[70], La ^[71], Ag ^[71], Fe ^[72], Pb ^[73], Ag ^[74], Ga ^[75], Tb ^[76], and Yb ^[77], while Ni ^[78], Mn ^[79], Cu ^[79], and Ir ^[80] were introduced into the Co-site to optimize the thermoelectric properties in the $Ca_3Co_4O_9$ system. Specifically, as R³⁺ has a higher ox

4.3. Entropy Engineering

Due to its superior characteristics, such as low thermal conductivity [26][28][81][82][83], high-entropy ceramics (HECs) containing five or more cations have lately gained considerable interest in the TE field. High-entropy engineering has been confirmed to increase the *S* and reduce the κ_l in TE oxide ceramics, making it a promising strategy for

optimizing thermoelectric performance by broadening the composition design. High-throughput screening has been used to construct multi-component TEs with high entropy, as reported by Zhang et al. ^[84] and Liu et al. ^[85]. By decreasing the κ_l and/or increasing *S*, high-entropy engineering can become an efficient technique to considerably improve thermoelectric performance (**Figure 3**).



Figure 3. (a) XRD patterns, (b) κ , (c) TEM results of the high-entropy (Ca_{0.2}Sr_{0.2}Ba_{0.2}La_{0.2}Pb_{0.2})TiO₃ ceramics ^[86]. (d–h) *S*, σ , *PF*, κ_{total} , and *ZT* values of the high-entropy (Sr_{0.2}Ca_{0.255}Ba_{0.25}RE_{0.25})TiO₃ ceramics ^[87]. (i) Schematic diagram of the possible phonon scattering in reducing lattice thermal conductivity for high-entropy ceramic ^[88].

4.4. Defect Engineering

In ionic compounds, the heat transport mechanism is dominated by κ_l . Additionally, κ_l can be lowered due to phonon scattering. Based on Debye–Callaway's model and the relaxation-time approximation, the κ is a function of phonon scattering rates (1/ τ) or the relaxation time (τ) ^[89]. τ has contributions from grain boundary scattering (τ_B), point defect scattering (τ_{PD}), phonon-phonon Umklapp scattering (τ_U), and electron-phonon scattering (τ_{ep}) as represented by Equation (8) ^{[89][90]}.

Here, $v_{\rm m}$ is the mean acoustic velocity, *L* is the average grain size, $\Theta_{\rm D}$ is the Debye temperature, ω is the phonon frequency, and A, B, and C are parameters corresponding to the point defects. Umklapp process, and electron-phonon scattering, respectively. Phonons are more likely to be strongly scattered by lattice defects of considerable size. Therefore, during the defect regulation, attention should be paid to building a full-scale hierarchical structure containing defects of various forms and scales to achieve "total phonon scattering" in a broad frequency range. Specifically, the atomic scale point defects, such as vacancy, replacement atoms, etc., can realize effective phonon scattering by the high-frequency short wavelength ^{[81][83]} (**Figure 4** and **Figure 5**).



Figure 4. (a) Positron lifetime spectrum. (b) Schematic representation of trapped positrons for $Bi_{1-x}Cu_{1-y}SeO$ samples in (100) plane. (c) Schematic representation of phonon scattering with Bi/Cu vacancies. (d–f) σ , κ , and ZT values of the $Bi_{1-x}Cu_{1-y}SeO$ samples [91].



Figure 5. (a) HRTEM images of the $(Sr_{0.25}Ca_{0.25}Ba_{0.25}RE_{0.25})TiO_3$ sample ^[88], (b) HRTEM images and the corresponding FFT image and IFFT image (b-1) along the ^[92] zone axis of the $Sr_{0.9}La_{0.1}(Zr_{0.25}Sn_{0.25}Ti_{0.25}Hf_{0.25})O_3$ sample ^[93], (c) HRTEM images and the corresponding IFFT images (c1 and c2) and strain map (c3) by geometric phase analysis (GPA) method ^[94].

4.5. Grain Boundary and Nanostructure Engineering

Grain boundaries (GBs) form ubiquitous microstructures in polycrystalline oxide ceramics, which play a significant role in tuning their *ZT*. Different grain size has a varied impact on σ and κ . To ensure that the effect of GBs or/and the nanostructure on decreasing κ is larger than its deterioration in σ , the grain sizes should be appropriately tuned. The energy filtering mechanism was proposed, meaning that randomly distributed potential barriers can filter away low-energy carriers to cause a decrease in the actual carrier density to improve *S*. In the nanostructured polycrystalline ceramic TEs, low energy carrier filtering effects combined with the enhanced phonon scattering can effectively suppress κ_l ^{[32][40][95][96][97]}, confirmed by both computational and experimental results.

Optimized thermoelectric performance by grain boundary and nanostructure are mainly reflected in lowering κ ^[40] ^[98], or the formation of a conductive path at grain boundary to promote the carrier mobility; these two factors play a synergistic effect on the electron and phonon transport process contribute to a trade-off *ZT* values of 0.3–0.4. In the cases of the nanostructured Sr_{0.91}La_{0.09}TiO₃ sample, *ZT* = 0.37 was achieved at 973 K ^[99], a greatly improved

performance ZT = 0.35 in Pr-doped of SrTiO_{3- δ} because of the Pr-rich grain boundaries contributed to improving carrier mobility ^{[99][100]}, and the improving ZT = 0.38 obtained in Sr_{0.8}La_{0.067}Ti_{0.8}Nb_{0.2}O_{3- δ} system containing Cu or Fe inclusions ^[101].

4.6. Textured Engineering

Texture engineering offers a strategy for gaining better thermoelectric performance in bulk ceramics by creating crystallographic anisotropy. Especially in layered crystal structure TEs, the electron and phonon transport properties are highly anisotropic. Multi-scale parallel interfaces, including zigzag interfaces and "core-shell" interfaces inside the orientation of the stripe-like grains, the paralleled grain boundaries, and lattice stacking faults were observed in the "brick-wall" microstructure can contribute to suppressing the thermal conductivity ^{[71][102]}. The physical properties of this special crystallographic orientation in textured ceramics can approach 60–80% of the properties of single crystals of the same composition. Creating the textured structure helps to the decoupling of electrical and thermal properties (**Figure 6**).



Figure 6. (a) BSE image, (b–d) TEM images, and (e) the sketch diagram of phonon scattering at the grain boundary and zigzag edge of the $(Ca_{0.87}Ag_{0.1}La_{0.03})_3Co_4O_9$ textured ceramics, and temperature dependence of the thermoelectric properties of the samples in parallel and perpendicular to the tape-casting direction. (f,g) Electrical resistivity, (h,i) thermal conductivity, (j,k) *ZT* values ^[103]. (I) BSE image, (m) Total thermal conductivity, and (n) *ZT* values of the Sr_{0.9}La_{0.1}TiO₃-based textured ceramic ^[104].

4.7. Composites

For the ionic compound of oxide ceramics, their resistivity after doping modification, nanostructuring, or entropy engineering is still relatively high. To further reduce the resistivity of oxide ceramics, some compounds with excellent electrical conductivity, such as metal particles, graphene, and its derivatives, are added to the matrix to improve the thermoelectric properties.

In addition, it has been confirmed that the 2D graphene can be introduced into $SrTiO_3$ -based ceramics for grain refinement and promoting more oxygen vacancy formation to enhance carrier mobility ^[105]. Therefore, $SrTiO_3$ -based ceramics containing graphite or its derivatives achieve single-crystal-like electron mobility ^[105][106][107][108] because the delocalization of Anderson localized electrons aided by graphite leads to a manifold improvement in weighted mobility and further the enhanced electron transport properties.

5. Device Applications

5.1. Power Generation

In recent years, thermoelectric modules have attracted wide attention due to their great potential for power generation and electronic refrigeration. At present, oxide thermoelectric devices can be used in a wide temperature range, especially in high temperatures, but there are few types of research focused on oxide thermoelectric devices, and the efficiency and power of thermoelectric conversion still need to be further improved. Most of these modules are made of $Ca_3Co_4O_9$ as *p*-type materials, and the most common thermoelectric *n*-type oxides are CaMnO₃, SrTiO₃, ZnO, etc. ^[109]. TE modules usually adopt the silver bar and silver paste ^[110], Cu, Ni, etc., as electrode contacts.

5.2. Sensor Devices

One of the primary applications of TEs is the temperature sensors, namely thermocouples, in which the temperature measurement of thin film thermocouples belongs to the contact in situ temperature measurement technology. For example, indium tin oxide (ITO) $-\ln_2O_3$ film thermocouple ^[111] have a limit measuring temperature reaching 1300 °C and the Seebeck coefficient reaches 160 μ V/°C, the MoSi₂-Al₂O₃ and TaSi₂-Al₂O₃ thin film thermocouple ^[112] prepared by screen printing technology presented the thermoelectric output of 16 mV at the high-temperature stage.

5.3. Flexibility and Wearable Devices

Flexible thermoelectric materials with excellent plastic deformation, light, inconspicuous, and other characteristics have a widespread application in portable electronic devices and wearable devices. Due to the ductility of inorganic semiconductors and ceramic insulators rarely observed, the application of inorganic oxides in flexible TEs field is rarely reported.

5.4. Other Application

Other applications of thermoelectric modules include aerospace, automotive waste heat recovery systems, refrigeration, etc. At present, the application of alloy thermoelectric has been well-researched, while oxide needs to be further studied.

Recently, organic-inorganic composites and hybrid materials have promoted a flexible TE devices' design and exploration, which can be used in wearable electronic devices, and sensors to apply to the "Internet of Things" (IoT) field ^[113] with the spring-up and development of novel two-dimensional (2D) materials growth, superlattice growth, and inorganic-organic composites. Furthermore, using of high-performance nanostructured TEs combined with spectrally selective solar absorbers to develop solar thermoelectric generators (STEGs) obtained a peak efficiency of 4.6% ^[114], opening up the door to the comprehensive application of TEs for energy conversion.

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