HARNESSING HEAT: EXPLORING THE THERMOELECTRIC MARVELS OF STRONTIUM TITANATE

Abstract

The process relies on the Seebeck effect and utilizes specialized materials, referred to as thermoelectric materials, to efficiently convert temperature differences into electric voltage. Excess heat from diverse sources, including industrial processes and automotive systems, serves as a heat source for thermoelectric generators. Key thermoelectric components include modules composed of materials such as bismuth telluride, strategically connected to maximize temperature differentials. But due to its toxicity and high cost it is not mostly preferable. Strontium titanate (STO) is the material of choice for producing thermoelectric electricity. Excess heat from various sources becomes a valuable resource for thermoelectric generators, where STO modules play a pivotal role. This method offers a promising avenue for harnessing waste heat, contributing to improved energy efficiency. Although current thermoelectric generator efficiency may present challenges, ongoing research and advancements in STO-based technology aim to enhance performance for broader applications in the future.

Keywords: Seebeck effect, Peltier effect, Strontium titanate, Figure of merit, Thermoelectric materials, Greenhouse effect.

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I. INTRODUCTION

In this century, the need for effective energy harvesting technologies is paramount, considering the projected population growth to be around 11.8 billion by 2100. With the population doubling, the global energy supply has tripled. Presently, the world's electrical power and total energy are used by approximately 66% and 95%, respectively, enveloping heating, transport, and electric current generation, which are completely filled by fossil fuels. However, the combustion of fossil fuels is a major source of CO₂ emissions, making it the primary contributor to greenhouse gases, the greenhouse effect, and consequently, global warming. Transportation significantly contributes to CO_2 emissions. India has become the world's third-largest emitter of greenhouse gases (GHGs) after China and the United States. In the year 2009, CO₂ emissions from cars averaged 120 g of CO₂ per km, a figure set to be reduced to 113 g of CO₂ per km by 2021-22 due to regulations by Ministry of Power. Notably, only about 25% of the energy supplied by fuel is utilized for vehicle propulsion, with the rest lost as exhaust heat, unburnt fuel, and friction [1]. In 2021, India has emitted approximately 4 giga tons of CO₂ equivalent (GtCO₂e), accounting for roughly 7% of the total world. According to the international research carbon emissions in India are projected to increase by 8.2% in 2023 and by 4% in China. Cars and vans were the biggest source of transportation emissions in that year, accounting for approximately 48% of global transportation emissions. To address the inefficiency, the automotive sector is exploring the use of thermoelectric generators, leveraging waste heat from both radiator and exhaust gas systems. This technology has the potential to enhance fuel efficiency by up to 5% or more, depending on the vehicle size and the specific thermoelectric technology applied. Each year, automobiles generate considerable waste heat, primarily from fossil fuel combustion in their engines, and almost all of this heat is expelled into the environment. In the utilization of fossil fuels, electric energy, and solar energy, there is inevitably a generation of waste heat energy concurrently [2]. However, the non-renewable waste of fossil fuels is becoming global risk and endangers both human and natural systems. Conversely, heat is essentially renewable, being widespread and unavoidable [3]. Almost 90% of the energy used is produced by thermal processes, and the majority of that energy is discharged as heat [4]. Thermoelectric Generator stands out as a straightforward technology for converting heat into electricity [5-6]. The thermoelectric generators operated by leveraging the Seebeck effect, discovered in 1821. Since the 19th century, engineers have sought to create efficient and economically viable Thermoelectric Generators. In 1909, Engineer Edmund Altenkirch formulated a mathematical relationship connecting the physical properties of thermoelectric materials to the efficiency of simplified thermopiles or Thermoelectric Generators. Altenkirch's equation, which factors in electromotive force, thermal and electrical conductivity, laid the groundwork [7].

The thermoelectric (TE) phenomenon encompasses three effects: the Seebeck effect, the Peltier effect, and the Thomson effect. The term "ZT value" plays an important role in thermoelectric generators or thermoelectric piles. It was introduced by Thomas Seebeck in 1821 [8]. The charged particle at the hot end of a thermoelectric couple with n-type and ptype components naturally migrates towards the cold end when exposed to a temperature difference (ΔT), producing an electric potential (ΔV). This phenomenon is known as the Seebeck effect, and the Seebeck coefficient (S) is represented as S= $\Delta V/\Delta T$

The Seebeck effect-based electricity generators are versatile, operating independently of heat sources, making them applicable across various fields. The apparatus shown in Figure

1 is capable of both the forward and backward conversion of heat into electricity. When current is applied, it induces a temperature difference between its two dissimilar junctions, known as the Peltier effect. In 1834, Peltier discovered this effect. In this scenario, this device is referred to as a Thermo- Electric Cooler (TEC). TECs, designed as Peltier pastilles for compact applications with restricted space, find widespread use in temperature control and cooling of electronic components. Certainly! The Thomson effect is another thermoelectric phenomenon that connects the Seebeck coefficient and the Peltier effect through thermodynamics. It involves heat being absorbed or released when electric current flows through a conductor with a temperature gradient. Worldwide interest has grown in harnessing thermoelectric effects like the Seebeck coefficient, the Peltier effect, and the Thomson effect. This phenomenon, which involves the relationship between electric current and temperature gradient, finds applications in diverse fields such as recovering waste heat, utilizing solar energy, creating temperature controlling seats and portable coolers, and managing temperature in microprocessors [9]. These days, thermoelectric generators are simply stacks of two distinct materials paired together. A and B are two different materials that are connected in series by electrical conductors. The temperature difference across the thermoelectric generator prompts each pair to generate an electric potential. The combined potential of these pairs is termed the electromotive force of the stack. Adding more pairs of materials increases this force, and having materials A and B with different "n" (negative) and "p" (positive) electrical conductivity enhances the electromotive force.

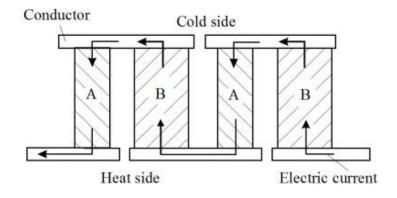


Figure 1: Thermoelectric Generator

The ZT value, which is well known for measureless figure of merit, is used to assess the efficiency of thermoelectric materials. To increase thermoelectric performance, the material's figure of merit should exceed 1. It offers additional benefits such as no moving parts, minimal noise, and outstanding reliability. The direct effect happens when electricity is generated between the cold and hot sections of TE materials. Its efficiency is connected to the figure of merit of the thermoelectric material ZT. To achieve effective thermoelectric energy conversion, thermoelectric materials need three essential physical properties, as follows:

- Low thermal conductivity (κ), it is necessary for the material to facilitate the generation of a substantial temperature difference between its ends.
- High electric conductivity (σ), it is essential for the material to minimize internal resistance in order to enhance its efficiency.

• To attain a large thermo- electro-motive force (Seebeck coefficient S), the materials must be able to produce a significant electrical potential difference.

The thermoelectric materials are commonly measured by certain characteristics given by $ZT{=}~S^2\sigma T/\kappa$ -----(1)

Where S, σ , T, and κ stand for Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively [10]. Recent advancements in bulk thermoelectric materials reveal how effectively they convert heat into electricity, as indicated by their efficiency, known as the ZT value, across varying temperatures [11,12]. Thermoelectrics have garnered global attention for their distinctive advantages, including compact design, reliable operation, and versatile applications. These applications involve harnessing energy from diverse heat sources, such as solar energy, utilizing the Seebeck effect, and achieving steady- state refrigeration through electricity input by leveraging the Peltier effect. Common thermoelectric materials, including alloys based on Bi₂Te₃[13], Si-Ge [14], and PbTe [15], have been created, showing high TE performance assessed through a measureless figure of merit. Among all these thermoelectric materials, oxides stand out because of their special interest due to their affordability, abundant availability, and remarkable resistance to high-temperature oxidation, surpassing conventional thermoelectric materials.

II. PRINCIPLES OF THERMOELECTRIC MATERIALS

This section explores the fundamental ideas that form the basis of the intriguing field of thermoelectric materials. To fully appreciate the significance and potential of minerals like strontium titanate in this study, one must have a solid understanding of these principles.

- 1. Seebeck Effect: The Seebeck effect is at the heart of thermoelectricity. When there's a temperature difference across a material, it induces an electric voltage. This phenomenon essentially allows us to convert a temperature gradient into usable electrical power. Strontium titanate's specific characteristics come into play in enhancing the Seebeck effect, making it a compelling material for thermoelectric applications.
- 2. Peltier Effect: Complementing the Seebeck effect is the Peltier effect. In this process, the application of an electric current at the ends of two dissimilar metals either absorbs or releases heat. Understanding this effect is essential for optimizing the efficiency of thermoelectric devices. The relationship between strontium titanate and the Peltier effect, as well as its consequences for energy conversion, will be investigated.
- **3.** Thomson Effect: The phenomenon known as the Thomson Effect occurs when there is a temperature gradient along a conductor or in thermoelectric materials, and this causes heat to be generated or absorbed at the junctions between various materials. In thermoelectric materials, this phenomenon happens in addition to the Seebeck effect, which produces an electric potential when temperatures vary.

- **4. Parameters Affecting Thermoelectric Performance:** The efficiency of a thermoelectric material is determined by a number of parameters. Important properties include a large Seebeck coefficient, poor thermal conductivity, and high electrical conductivity. This chapter explores the ways in which these elements enhance the overall performance of materials such as strontium titanate, which makes them the best possible choices for thermoelectric energy conversion.
- **5.** Figure of Merit (ZT): The Figure of merit (ZT) serves as a crucial measure when assessing the performance of thermoelectric materials. ZT is significant because it provides a comprehensive assessment of performance by combining many material qualities, such as electrical and thermal conductivity. The ZT value of strontium titanate and its importance are investigated.
- 6. Material Selection: Thermoelectric materials are often semiconductors, and choosing the material is critical. Thermoelectric materials should exhibit a high Seebeck coefficient and electrical conductivity, with low thermal conductivity.
- 7. Optimizing Temperature Gradient: To maximize efficiency, it's essential to create and maintain a significant temperature differences across the thermoelectric material. This involves careful engineering of the heat source and sink.

This section aims to demystify the principles that govern thermoelectric materials, setting the stage for a deeper understanding of how Strontium titanate contributes to this exciting field.

III.STRUCTURE AND COMPOSITION OF SRTIO3

The most important n-type thermoelectric oxides, like ZnO, CaMnO₃, and SrTiO₃ possess a perovskite ABO₃ structure [16]. Strontium titanate (SrTiO₃) possesses a naturally high Seebeck coefficient and maintains remarkable steadiness even at extreme temperatures, reaching up to 2080 degrees Celsius [17]. Strontium titanate (SrTiO₃) adopts a perovskite cubic crystal structure (Figure 2) within the unit cell of SrTiO₃ and its lattice parameters of 3.905Å and space group Pm-3m [18]. In this setup, Sr^{2+} ions occupy the cube corners (A site), Ti ions are at the cube center (B site), and O^2 ions are positioned at the cube faces. This specific arrangement forms the perovskite structure, and though appropriate doping, these materials can be modified to exhibit improved thermoelectric characteristics, making them noteworthy candidates for applications in thermoelectric devices. This arrangement is common among various oxide materials. At elevated temperatures, Strontium titanate exhibits a cubic crystal lattice. However, at lower temperatures, specifically below 110 degrees, it undergoes phase transitions involving octahedral rotation. The TiO₆ units are shared at the corners of octahedra [19], which are closely connected to the lattice structure. Transition metal oxide materials like alkaline earth metal titanates (ATiO₃, where A can be Ba, Sr, or Ca) with a perovskite structure were significant both in scientific understanding and practical applications. Their diverse chemical and physical properties make them crucial, especially in the field of thermoelectric applications. Between 1940 and 1960, researchers explored alloying and doping, particularly focusing on the microscopic effects facilitated by the introduction of semiconductors as thermoelectric materials [20]. SrTiO₃ displays a cubic perovskite structure under normal temperature and pressure conditions. However, when the

temperature drops to 105K or less, a phase transition can happen by shifting to a tetragonal structure (space group: P4mm) from a cubic structure (space group: Pm-3m) [18]. By the electrical properties a phase transition is accompanied. Typically, this type of phase transition would lead to the emergence of ferroelectric properties. SrTiO₃ does not undergo this phase transition down to 0 K, making it part of a category known as quantum para-electric or incipient ferroelectrics. At room temperature, pure strontium titanate acts as an electronic insulator. Free charge carriers or charged ionic species can be generated by introducing point defects into the lattice. In semiconducting SrTiO₃, electrons become the predominant charge carriers through donor in a reducing atmosphere by impurity doping or heating, creating an equivalent density of oxygen vacancies with significant lattice mobility, especially at higher temperatures. As a result, SrTiO₃ is recognized as a mixed electronic- ionic conductor. Moreover, SrTiO₃ serves as a promising photocatalyst for splitting water. Compared to TiO₂, SrTiO₃'s conduction-band edge is approximately 200 mV highly negative. Notably, SrTiO₃ exhibits high stability against thermal and chemical influences.

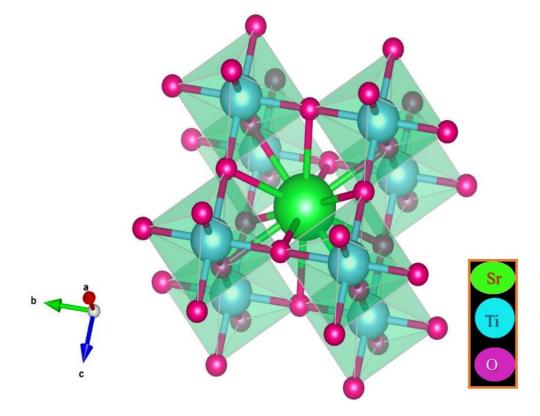


Figure 2: The lattice structure of SrTiO₃

Here, it is observed that Sr^{2+} within the structure can accept electrons in the conduction band, forming Sr. This Sr species can then transfer an electron to generate O for decomposing organic compounds, preventing the combination of photogenerated charge carriers. In earlier years, strontium titanate has garnered significant attention from researchers due to its notable photocatalytic properties [21]. Pure $SrTiO_3$ has a bandgap of 3.2 eV (indirect), meaning it can exhibits photocatalytic activity exclusively in the UV region. Its electrical conductivity can be flexibly tuned, allowing it to transition into a metallic phase based on the varying oxygen concentration [22]. Metal oxides like STO have recently

become a focal point of interest for high temperature thermoelectric power generation due to their enhanced chemical and thermal durability compared to heavy metal alloys. Among all other metal oxides, crystalline STO plays an important role in thermoelectric materials, certainly at higher temperatures. Moreover, the electrical conductivity of SrTiO₃ can be readily adjusted from insulator to metal by adding La³⁺ or Nb⁵⁺. At 1050K, the thermoelectric figure of merit (ZT value) reached 1.42 for Nb-doped SrTiO₃ (SrTi_{0.85}Nb_{0.15}O₃) [23], which is currently smaller than that of materials based on heavy metals. To enhance the ZT of STO, it's crucial to decrease its thermal conductivity (κ) without compromising its electrical conductivity (σ). Muta et al. suggested that substituting sites in SrTiO₃ with Ca²⁺ or Ba²⁺ might be an effective method to decrease the thermal conductivity. This is likely due to introducing defects, such as site substitution in the layered structure, which minimizes the thermal conductivity of SrTiO₃. Alternatively, the electrical conductivity of STO can be heightened, thereby improving its thermoelectric performance. This enhancement is achieved through a process known as donor-doping, involving the introduction of higher valence ions either on the site of A or B in the perovskite structure. Additionally, another approach involves reduction, leading to the creation of oxygen vacancies. These strategies aim to increase the availability of charge carriers in STO, positively influencing its electrical conductivity and, consequently, its thermoelectric efficiency. STO is intriguing for researchers due to its distinctive qualities. It functions as a quantum para-electric, exhibiting a constant increase in dielectric permittivity as it gets closer to 0k. Notably, ferroelectric anomalies are absent because of the impact of quantum fluctuation.

IV. FABRICATION TECHNIQUES FOR SRTIO3

Selecting the right starting materials for the creation of heterogenous catalysts, such as SrTiO3, affects how successful they are. Factors such as crystalline structure, particle size, surface area, and crystal phase play important roles in determining the catalyst's effectiveness. Put more simply, how the catalyst is made and assembled can have a big impact on how well it fulfills its function.

In the 2008-2023 research papers, the methodologies for producing $SrTiO_3$ nanomaterials were introduced. Before delving into various synthesis methods for $SrTiO_3$ nano materials, it's essential to note that the choice of method significantly influences the structural properties and particle size of the resulting nanoparticles. Every method employs distinct principles and conditions, offering researchers a range of options to tailor the characteristics of $SrTiO_3$ particles for specific applications. Whether utilizing sol-gel techniques, hydrothermal synthesis, solid-state reactions, or other approaches, researchers carefully control parameters to achieve desired outcomes. From the controlled growth in solvents to the high-energy processes like microwave-assisted synthesis, the methodologies aim to produce $SrTiO_3$ nanoparticles with finely tuned structures and sizes. Understanding these diverse synthesis techniques provides insights into optimizing the fabrication process and harnessing the unique properties of $SrTiO_3$ nano materials for various technological advancements.

Various methods have been employed for the preparation of nanomaterials with distinct structures and particle sizes. In sol-precipitation coupled with hydrothermal synthesis conducted in 2008 [24], nanocubes with a particle size range of 60 to 120 nm were successfully obtained. Another approach involved polymerized complex formation in 2008

[25], resulting in nanoparticles sized between 25 and 100 nm, while a solid- state reaction in the same year yielded nanoparticles with a size of 110-150 nm [25]. Ball milling-assisted solid-state reaction in 2008 [25] led to the production of nanoparticles with size range of 30 nm. Sol-gel combustion in 2008 [26] and the sol-gel method in 2009 [27] resulted in nanopowders with particle sizes of 20-30 nm and unspecified, respectively. In 2010, a molten salt reaction generated submicron crystallites ranging from 20 to 184nm [28], and solvothermal synthesis in the same year produced nanoparticles sized between 50 and 80nm [29]. Continuing into 2011 [30], a molten salt reaction gave rise to nanocubes with a particle size of 64-182 nm. Microwaving-assisted hydrothermal synthesis in 2012 [31] and 2012 [32] separately produced nanospheres and nanocubes. A sol-gel hydrothermal approach in 2012 [33] resulted in nanoparticles with a size range of 30-150 nm, while mesocrystals ranging from 100 to 200 nm were obtained in 2012 [34]. In 2013 [35], solvothermal and sol-gel combustion methods [36] produced nanocubes and nanoparticles with approximate sizes of 20 and 45-56 nm, respectively. Hydrothermal synthesis in 2014 [37] generated nanocubes with a size range of 20- 200 nm. Rapid Sol-precipitation, hydrothermal, in 2014 [38], [49], produced nanocubes and nanospheres with sizes ranging from 24-43 nm and 4-13 nm, respectively. In 2015, Hydrothermal produced microspheres with particle size from 30-46 nm [40], solid-state reaction (flux-based) [41] and electrospinning [42] led to nanocubes and nanotubes with sizes of 300 nm and approximately 100 nm, respectively. Ultrasound-assisted wet chemical synthesis in the same year resulted in nanocrystals with a size range of 7-17 nm [43]. Single crystals were obtained through an unspecified method in 2016 [44], while fluxmediated methods in the same year produced nanocubes with sizes ranging from 200 to 3000 nm [45]. Core-shell microspheres of approximately 700 nm were synthesized in 2017 [46] using a hydrothermal method. Additionally, ultrasound-assisted hydrothermal synthesis in 2017 [47] produced mesoporous microspheres with sizes between 8 and 18 nm. Finally, a hydrothermal approach in 2018 [48] resulted in nanocube particle sizes ranging from 30 to 56 nm.

Controlling the shape and size of SrTiO₃ is crucial for creating effective photocatalysts with enhanced photo-reactive properties. Additionally, the external surface and morphological form of the photocatalyst impact the catalytic activity. Furthermore, variations in SrTiO3's Eg values were observed depending on the method of sample preparation and specific processing details. In simpler terms, shaping SrTiO₃ precisely is key for better photocatalysts, and variations in preparation methods can influence its performance characteristics. The bandgap of SrTiO₃ nanoparticles was nearly 3.10 eV by using Solid-State Reaction (SSR) [25] and hydrothermal synthesis [37]. SSR with ball milling assistance was used to synthesize SrTiO₃ nanoparticles. These nanoparticles exhibit a photoactive property under the irradiation of visible light, the bandgap of approximately 2.00eV [25]. Through coprecipitation synthesis, the SrTiO₃ nanoparticles were found to have an estimated bandgap of 3.35 eV [49], and other researchers synthesized SrTiO₃ nanoparticles using different methods, resulting in Eg values ranging from 3.40 to 3.60 eV [32]. Numerous scientists have employed various methods, including hydrothermal and solvothermal reactions, solid-state reaction, sonochemical and sol-gel processes, to produce SrTiO₃ nanoparticles. These diverse synthesis routes result in variations in the morphology, crystal structure, uniformity, size, and shape of the SrTiO₃ nanoparticles. Additional synthesis methods for SrTiO₃ nanoparticles include coprecipitation, chemical vapor deposition (CVD), and template-assisted approaches. Each method introduces distinct characteristics to the synthesized nanoparticles, influencing factors like particle size distribution, surface area, and overall structural properties.

Researchers select specific methods based on desired outcomes and application requirements in the fields of material science.

V. THERMOELECTRIC MATERIALS

Thermoelectric materials are evaluated based on their ZT value. Achieving optimal thermoelectric performance is challenging because these parameters are interdependent on the concentration carrier. Specifically, the decrease in Seebeck coefficient (S) tends to increase in carrier concentration, while electrical conductivity (σ) rises. This intricate relationship underscores the difficulty of simultaneously optimizing these crucial characteristics for efficient thermoelectric materials. The Seebeck effect (S) is linked to the logarithm of carrier concentration (n), while the electrical conductivity is directly proportional to the carrier concentration raised to power. This leads to an optimal carrier concentration range (10^{19} to 10^{20} cm⁻³) for maximizing the power factor (S² σ). Conventional metals have low Seebeck coefficients, while semiconductors often exhibit low conductivity. To enhance conductivity at the optimum carrier concentration, focus turns to maximizing mobility, explaining why high-mobility semiconductors are crucial in advanced thermoelectric materials. In degenerate semiconductors, lattice thermal conductivity takes precedence over electron thermal conductivity. The electron thermal conductivity can be easily calculated using the Wiedemann-Franz law, which is stated by a particular equation. In other words, heat is mostly conveyed by lattice vibrations in these materials rather than by electron mobility. The Wiedemann-Franz law offers a simple method for calculating the thermal conductivity of electrons based on the total conductivity. Thermoelectric materials typically exhibit a conductivity range of 500-1000 S/cm at room temperature, corresponding to a lattice thermal conductivity(κ_{el}) of 0.4-0.8 W/mK. High-performing of figure of merit in thermoelectric materials, however, aim for low total thermal conductivity, around 2-3 W/mK. The key challenge lies in minimizing the lattice thermal conductivity, making it a central concern in enhancing the efficiency of thermoelectric materials. Thermoelectric materials can be broadly categorized into seven types based on their properties and compositions. Some common types include:

1. Inorganic Semiconductors: Materials like Bismuth telluride (Bi₂Te₃) and Lead telluride (PbTe) are mostly used to get high thermoelectric efficiency. In the manufacturing sector, thermoelectric materials based on Bi₂Te₃, initially possessing a figure of merit (ZT) below 1.0, are crafted using techniques like zone melting and unidirectional solidification. Notably, over the past decades, there is a significant strides in the development of Bi₂Te₃based materials, now achieving ZT values surpassing 1.0. The highest ZT accomplishments (>1) for these materials, indicating the respective years and optimal temperature, give scope to both p-type materials and n-type materials [50, 51]. There are two prominent trends: p-type material routinely displays high ZT values, while n-type material exhibits ZT values at higher temperatures. Despite employing processes like polycrystalline fabrication for both types, the anticipated performance improvement observed in p-type materials had not been observed in n-type materials [52]. Nanocrystals played a crucial role in enhancing the peak ZT value of 1.4 by causing phonon scattering through the grain boundary and defect of the material [53]. The introduction of dispersed nano-SiC had a similar effect, partially uncoupling electrical conductivity (σ) and Seebeck coefficient due to the energy-filtering mechanism, resulting ZT of a peak is high as 1.33 at 373K [54]. In 2015, an outstanding ZT of peak 1.86 was observed through

liquid-phase Te extrusion by implementing dense dislocation arrays [55]. The concept of presenting dense dislocations captivated researchers, prompting recent studies focused on innovations in processing techniques [56]. The maximum ZT for n-type materials is found at temperatures ranging from 400 to 470K, which exceeds room temperature. The applications of cooling and refrigeration are commonly employed based on Bi_2Te_3 materials, with p-type materials performing optimally near room temperature. To enhance the overall performance of Bi_2Te_3 based thermoelectric devices, it is crucial to reduce the optimal temperature range for n-type materials, bringing them close to room temperature to align with the characteristics of p-type materials.

2. Organic Semiconductors: Certain organic materials exhibit thermoelectric properties, and research in this area explores the potential of organic semiconductors for flexible and lightweight applications. A high ZT value is crucial for capable in power generation and Peltier cooling, especially in applications like wearable electronic devices and the Internet of Things (IoT), where energy supply at room temperature is essential. Currently, commercially available materials typically have a ZT value ranging from 0.6 to 1 [57]. However, only some organic thermoelectric materials are reported to have ZT values exceeding 0.1. This is mainly due to limitations in material categories and unsatisfactory doping methods. In this context, more p-type and n-type organic thermoelectric materials with having ZT values exceeding 0.1, offering potential advantages for applications were discussed. Earlier investigations into organic thermoelectric materials focused primarily on p-type conducting polymers like Poly (3,4-ethylenedioxythiophene) (PEDOT) [58]. Due to its poor solvent solubility, PEDOT is typically emulsified with polyelectrolytes like polystyrene sulfonate (PSS) and Tosylate (Tos) in water. The thermoelectric properties of PEDOT can be fine-tuned by doping it with organic solvents or vapors [59]. Crispin et al. [60] in 2011 introduced a method for precise control of the oxidation level of PEDOT Tos. They achieved this by reducing films using the vapor tetrakis (dimethylamino) ethylene. The power factor of these thin films reached 324 μ W/(m/K²), at 22% oxidation level, with a maximum ZT value of 0.25 at room temperature. Additionally, PEDOT: PSS, when mixed with DMSO, has been reported to exhibit a ZT value at room temperature of up to 0.42 [61]. An additional class of organic thermoelectric materials is represented by doped organic semiconductors (OSCs), such as (3-hexylthiophene) (P3HT), poly (2,5-bis(3-dodecyl-2-thienyl) thieno[3,2-b] polv thiophene) (PBTTT), and diketopyrrolopyrrole polymer (PDPPs) [62]. Despite numerous high-mobility organic semiconductors reported, only a few have been explored as organic thermoelectric materials Notably, when exposed to chemical doping treatments, derivatives based on diketopyrrolopyrrole (DPP) and DPP-like structures have demonstrated potential as organic semiconductor materials. The Selenium-substituted DPP derivative, PDPPSe-12 had shown high performance [63]. Liu et al. recently showcased a highly thermoelectrically efficient, molecularly n-doped fullerene derivative using the "phonon-glass electron-crystal" concept. By carefully designing the molecular structure of the fullerene derivative, the researchers achieved thermal stability in N-DMBI by doping and induced a disorder to order transition through annealing. This process involved using fullerene molecules with double-triethylene-glycol-type side chains. Consequently, they formed an organic electron cryatalline film with an electrical conductivity exceeding 10 S/cm and a thermal conductivity below 0.1 W/m-K. This innovative approach resulted in highest achieved ZT value of 0.34 [64].

3. Intermetallic Compounds: Intermetallic compounds, such as Half-Heusler alloys like NiMnSb, clathrates, lead chalcogenides, magnesium antimonides, copper selenides, and Skutterudites, which are intermetallic and remove oxygen impurities, have shown promising thermoelectric properties. Clathrates, categorized as Potential Green Energy Conversion (PGEC) materials, represent a novel class of promising thermoelectric materials [65]. Inorganic clathrates exhibit an "open-structured" composition, forming a 3D network framework primarily composed of group 14 atoms like Si, Ge, or Sn that are connected through bonds like covalent tetrahedral bonds. This framework creates cavities, or cages, where metal atoms can be embedded [66]. A growing interest in Clathrates stems from their favorable transport properties and wide band-gap range, making them attractive for both TE and optical applications.

Half-Heusler alloys consisting of metal elements exhibit a combination of high electrical conductivity and Seebeck coefficient. Due to their robust mechanical and thermal stability, Half-Heusler alloys are considered promising thermoelectric materials suitable for power generation at moderate to high temperatures, thanks to their strong mechanical and thermal stability. Theoretical studies have pinpointed the compound LaPtSb as a promising Half-Heusler alloy with optimized TE properties. Specifically, at room temperature, LaPtSb demonstrated a thermal conductivity of 1.72 Wm⁻¹K⁻¹, resulting in a calculated ZT value of 2.2 at 300K [67]. These intermetallic compounds are all performing well as thermoelectric generators.

4. Complex Oxides: Materials like perovskite oxides, including $SrTiO_3$, have been investigated for their thermoelectric capabilities. Complex oxides refer to compounds that contain oxygen combined with two or more metal elements, often forming intricate crystal structures. These materials exhibit a wide range of physical and chemical properties. Here are some key aspects of complex oxides: crystal structure, electronic properties, magnetic properties, optical properties, and catalytic activity. Additionally, topological insulators, hybrid materials, and nanostructured materials are alternative forms of thermoelectric materials.

VI. THERMOELECTRIC MATERIALS APPLICATIONS

Thermoelectric materials have gained importance due to increasing demand for efficiency and added functionalities in various customer-driven applications. These applications can be broadly categorized into two segments: one utilizing the Peltier effect for heating or cooling applications, and the other employing the Seebeck effect for power generation, particularly from waste heat [68]. Since some of these are already being made, let's start with the heating and cooling applications. Research on thermoelectric materials is concentrated on determining the ideal crystal structure. This ideal structure would yield a thermoelectric material with an average efficiency of 20%. Achieving this efficiency will greatly enhance its practicality and feasibility. Generally, thermoelectric applications span various fields, from powering small devices like sensors, wearables, and medical implants to larger-scale uses in automotive waste heat recovery, aerospace systems, and even potentially in renewable energy conversion systems [69]. Some of the applications are discussed below.

- 1. Harnessing Thermoelectric Generators (TEG) to Recover Heat from Vehicles: Thermoelectric technology offers a solution for reusing energy in vehicles with internal combustion engines, particularly by capturing waste heat from the exhaust pipe and the radiator. Placing thermoelectric generators (TEGs) at strategic points in the vehicle allows the generation of energy from this waste heat. Efficient utilization of this energy reduces the need for diesel fuel consumption, as it eliminates the requirement for a generator used in battery charging and other low-energy functions [70]. The optimal position for TEGs is often after the catalyst in the exhaust pipe, where the highest temperatures are present. With advancements in TE technology, there's potential for significant future reductions in fuel consumption [71].
- 2. Utilizing Thermoelectric Devices for Efficient Electric Power Generation: While thermoelectric technology finds applications in diverse heat energy conversion areas, this section especially focuses on electric power generation using thermoelectric generators. The primary emphasis lies in converting recovered heat into electrical energy across various applications. Recent advancements in TEGs primarily center on standalone power generation for biomedical, aerospace, military, and remote power scenarios [72]. Electricity generation applications are typically classified into two main groups based on power output: low and high-power generation applications.
 - Low Power Generation: Low-power generation involves the development of thermoelectric generators (TEGs) as self-sustaining power alternatives to batteries. These TEGs aim to be complete with batteries in applications such as body-mounted devices, operating within the range of 5 microwatts to 1 W with a lifespan of around 5 years. Notably, companies like Citizen and Seiko are manufacturing wristwatches equipped with TEGs, with Seiko's version achieving an efficiency of approximately 0.1%, an open voltage of 300mV, and operating at 1.5 K temperature gradient [73].
 - **High Power Generation:** In high-power generation, major automotive manufacturers like BMW and Volkswagen are actively working on thermoelectric generator systems capable of producing around 1 kW of power. Utilizing a thermoelectric generator with a ZT value (figure of merit) of 1.25 and an efficiency of approximately 10%, it becomes feasible to recover 35-40% of the exhaust manifold. This recovery occurs at an average temperature of 250 ^oC, potentially increasing it by up to 16% [74].
- **3.** Fuel-Powered Transportation: In the end of the 20th century, researcher Birkholz revealed findings of a thermoelectric generator installed in collaboration with Porche within the exhaust system of the 944 model. In 1987, Hi-Z Technology initiated a program aiming to create a thermoelectric generator is capable of producing 200 watts of electrical power from heat conversion, which was published in 1991. In the subsequent phase of the program, they aimed for a 1-kilowatt electric energy generation capability and tested a thermoelectric generator in a truck by mid-1993. Initially, the generator produced only about 400 watts, but through optimizations, it reached 1068 watts. During durability testing using new HZ-14 converters in vehicles, some mechanical issues were identified. In the following years, the thermoelectric generator was adjusted for a hybrid SUV to produce 180 watts of electricity, capable of charging 300-volt batteries. Hi-Z

Technology started exploring a similar generator in 1999, aiming for 300-330 watts and the ability to charge both 12 V and 24 V batteries, but achieved 150 watts by 2004 [75].

In 2005, BSST, BMW, Visteon, and Marlow Industries shared their research findings at the DEER conference about implementing a thermoelectric generator in a BMW 5 series with an internal combustion engine 3000 cc, capable of producing 500 watts of power from a temperature difference of 207 °C. A group of companies aims to enhance this technology to generate 1 kilowatt of electric power. They intend to bring this improved thermoelectric generator to market in the coming years. Indeed, utilizing heat recovery methods, such as harnessing energy from the car's exhaust and cooling system losses through thermoelectric converters, can potentially enhance electric energy generation in hybrid cars. Studies suggest that with converters operating at around 5% efficiency, it could increase energy in a hybrid vehicle by approximately 6% (1% from the cooling system and 5% from the exhaust) [69]. This method taps into otherwise wasted heat to generate additional electric power, contributing to more efficient energy utilization in automobiles. Around the catalyst of the generator, there are three sections where thermoelectric modules are affixed. These sections contribute to a notable boost in the generation's output power when connected. The battery gets charged using thermoelectric modules placed in the hotter exhaust section of the engine, resulting in high power output due to the increased temperature in that area. A temperature difference is created, leading to the production of a small amount of power through micro-generation [76].

- 4. Enhancing Cooling System with Thermoelectric Device Innovations: Thermoelectric coolers, often known as Peltier coolers, prove ideal for applications where conventional air-cooling systems are struggling to manage high heat fluxes effectively. Key design considerations for these TECs include prioritizing reliability, offering flexible packing and integration, and minimizing weights for enhanced performance [73]. Thermoelectric devices are primarily used for cooling in three main areas: thermos-electric air conditioners (TEACs), refrigeration and air conditioning systems, and cooling electronic devices [77].
 - **Thermoelectric Air Conditioner:** TEACs are eco-friendly, uncomplicated, and dependable. They are providing easy installation and can seamlessly switch between cooling and heating modes by doing input current reverse. These systems are currently quite costly, but they have the advantage that their power consumption is relatively low [73].
 - **Cooling Electronics:** In this cooling electronic device, a thermoelectric cooler acts as a heat transporter, pulling heat away from a surface that's warmer than the surrounding environment. Its primary objective is to ensure that the electronic device's junction temperature stays below a designated limit by effectively dissipating heat from the device [77].
 - **Refrigerators:** Peltier cooling devices, like solar-powered refrigerators, can quickly cool from 27 ^oC to 5 ^oC in approximately 44 minutes. Thermoelectric refrigeration systems are advantageous due to their lightweight, durability, reliability, and lack of

noise. Mass-producing TE refrigeration devices become cost-effective when utilizing charge carriers in the thermoelectric material instead of traditional refrigerants for removing heat [73].

5. Industrial

- Impact on Aerospace Industry: In space exploration, where resources are • insufficient but crucial for research and technology advancement, organizations like JPL are creating innovative high-temperature materials like skutterudites. These developments will not only benefit space missions but also lead to advancements in power generation on Earth. An MMRTG (Multi-Mission Radioisotope Thermoelectric Generator) driven by PbTe/TAGS TE materials was used by the Mars Science Laboratory. This generator produced 120W of power when fueled and operated with an efficiency of 6.0%. The RTG (Radioisotope Thermoelectric Generator) was located on the moon. Additionally, in space missions, Peltier cooling systems are employed to regulate the temperature of electronics [78].
- Electricity Generation from Terrestrial Sources: Global thermoelectric was the most advanced company in developing and selling thermoelectric generators. In 1971, it was founded by two individuals who had previously worked at 3M. In 1970, 3M decided to close its thermoelectric research and provided its expertise to these two individuals, who established Global Thermoelectric in Canada. This company designed units using individual thermoelectric elements secured by separate springs, all contained within a sealed environment made of lead Tin-Telluride (PbSnTe) [75]. The particular design by Global Thermoelectric has proven to be extremely good, with units functioning continuously in the field. The term "energy" now commonly refers to freely available and accessible power resources [78].

VII. THE GAS SENSING CAPABILITIES OF SRTIO₃

In 2004, Meyer and Weser introduced a framework describing the swift sensor reactivity of a resistive donor-doped variant of SrTiO₃ within the temperature range of 850 to 950 °C [79]. In the same year, Hu and colleagues introduced a groundbreaking approach by creating a low-temperature nanostructured SrTiO₃ thick-film oxygen sensor. They utilized high-energy ball milling and screen-printing techniques to achieve this innovation. Notably, the sensor demonstrated remarkable performance at an operating temperature as low as 40 $^{\circ}$ C, a significant achievement even by today's standards. The experiments involved testing the sensors with 2-20% oxygen exposure. Furthermore, results indicated that SrTiO₃ sensors synthesized with a 400 ^oC annealing temperature exhibited superior sensing properties compared to both commercially available milled and non-milled SrTiO₃ sensors [80]. The same research team examined and reported on the effects of different annealing temperatures on the sensing properties of SrTiO₃ oxygen gas sensors that were nanosized in 2005 [81]. The used a range of methods, such as differential thermal analysis researchers (DTA)/thermogravimetric analysis (TGA), X-ray diffraction (XRD), and transmission electron microscopy (TEM), to confirm and assess the effect of annealing temperature on the performance of nano-sized SrTiO₃ oxygen gas sensors [80]. Ozone gas (O₃) is also detected by using the SrTiO₃-based gas sensors. In 2013, Mastelaro and colleagues introduced a nanocrystalline material known as SrT1-Fe₂O₃ (STF), designed for detecting ozone gas [82]. Kajale et al. demonstrated noteworthy findings with SrTiO₃-based gas sensors. The sensors, based on SrTiO₃, displayed significant sensitivity to carbon monoxide (CO) while showing no response to hydrogen sulfide (H₂S). Conversely, sensors incorporating Cu-doped SrTiO₃ exhibited the opposite behavior, attributed to the conversion of copper (Cu) into copper sulfide (CuS) [83]. Using a sol-gel hydrothermal technique, researchers successfully crafted the SrTiO₃ nanomaterial, showing an exceptional gas sensor response (S) exceeding 500 at a mere 150 $^{\circ}$ C for 80 ppm of H₂S [84]. In 2015, Zaza et al. further explored the sensor's capabilities, confirming its efficacy in detecting carbon dioxide (CO₂) under room-operating conditions in their study involving SrTiO₃-based sensors [85].

VIII. CONCLUSIONS

Thermoelectric generators convert heat into electricity. The principles related to thermoelectric phenomena like the Seebeck effect, Peltier effect, and Thomson effect were discussed. And parameters that affect the thermoelectric performance, like the figure of merit, the selection of materials, and optimizing the temperature gradient were also briefed. The earlier reports on different fabrication techniques were mentioned. Different thermoelectric materials based on their ZT values were also discussed. In this chapter, SrTiO₃ material properties related to thermoelectric phenomenon were highlighted. SrTiO₃ has a cubic perovskite structure with Pm-3m space group. A Wide range of thermoelectric materials applications and gas sensing capabilities were also discussed in this chapter.

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