Topical Review

Thermoelectric generators using skutterudites & selenium alloys with endotaxial nanostructures for enhanced solar thermal energy conversion.

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Abstract

This study investigates the potential of skutterudites and selenium alloys with endotaxial nanostructures in enhancing the efficiency of thermoelectric generators (TEGs) for solar-thermal energy applications. Recognizing the limitations of traditional TEG materials at high temperatures, this paper focuses on the advancement of skutterudites and bismuth telluride selenide ($Bi_2Te_3Se_2$), and lead telluride selenide (PbTeSe) alloys. Endotaxial nanostructuring is highlighted for its effectiveness in reducing thermal conductivity while maintaining electrical conductivity, thereby significantly improving the thermoelectric figure of merit (zT). The paper reviews the principles of TEGs and the latest developments in nanostructured thermoelectric materials, particularly at elevated temperatures suitable for solar-thermal systems. It also discusses the integration challenges and environmental and economic aspects of these advanced materials in TEGs. The paper concludes with future perspectives on the utilization of these nanostructured materials in enhancing the performance of solar-thermal energy conversion systems.

Keywords: thermoelectric generators, skutterudites, selenium alloys, endotaxial nanostructures, solar-thermal energy, bismuth telluride selenide, lead telluride selenide, high-temperature applications.

OPEN ACCESS

Citation: Sparsh (2023), Thermoelectric generators using skutterudites & selenium alloys with endotaxial nanostructures for enhanced solar thermal energy conversion

Editor: Sparsh, National University of Singapore, SINGAPORE

Received: December 16, 2023

Published: To be soon

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1. Introduction

The world's growing energy demand poses significant challenges in developing sustainable and renewable energy solutions. Traditional fossil fuels are limited and contribute to climate change through greenhouse gas emissions. Solar energy is an abundant renewable resource but requires efficient technologies to convert it into usable energy forms. Traditional solar-thermal systems rely on mechanical engines and turbines, but there is one promising technology is thermoelectric generation, which uses the Seebeck effect to directly convert a temperature gradient into electrical power. Thermoelectric generators (TEGs) have advantages of being solid-state devices with no moving parts, silent operation, and long lifetimes. However, widespread adoption of TEGs has been limited by their historically low conversion efficiencies compared to other renewable technologies.

Recent advances in materials science and nanotechnology have enabled the development of nanostructured thermoelectric materials with significantly improved efficiency. In particular, advances in skutterudites and alloys based on bismuth tellurium selenide ($Bi_2Te_3Se_2$) and lead tellurium selenide (PbTeSe) have emerged as high performance thermoelectric materials when designed with precisely engineered endotaxial nanostructures. Endotaxial nanostructures refer to nanocrystals that are embedded within a host matrix and are crystallographically aligned with the matrix. This allows coherent interfaces that can scatter mid- to long-wavelength phonons to reduce lattice thermal conductivity, while still enabling charge carrier transmission across the nanostructure-matrix interfaces.

Recent research has focused on using nanostructured alloys to reduce thermal conductivity, thereby boosting the thermoelectric figure of merit (zT). This essay examines using skutterudites and bismuth telluride selenide alloys and lead telluride selenide alloys with endotaxial nanostructures in TEGs for solar-thermal systems. I argue these materials achieve higher zT around 600 K, and therefore have high conversion efficiencies at elevated temperatures relevant for solar-thermal systems. After reviewing the operating principles and materials for TEGs, I evaluate recent research on using nanostructured alloys to improve zT.

2. Thermoelectric Principles and Challenges

TEGs work via the Seebeck effect, in which a voltage is generated when a temperature gradient is applied across a semiconducting material. The voltage arises from charge carriers diffusing from the hot to cold side, creating a potential difference. TEGs contain p- and n-type semiconducting "legs" electrically in series and thermally in parallel between two ceramic plates. When a temperature gradient is applied, charge carriers flow and the TEG acts as a power source.[2] TEGs offer solid-state electricity generation with no moving parts, low maintenance, and silent operation. However, their efficiency has historically been low compared to mechanical generators.[15]

A material's thermoelectric efficiency is measured by the figure of merit, zT, which is defined as

$$zT = \frac{S^2 \sigma T}{\kappa},$$

where S is the Seebeck coefficient, representing the voltage generated per unit temperature difference, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity.[16] The zT value encapsulates the essence of a material's thermoelectric quality; the higher the zT, the better the material's capability to convert heat into electricity.[17] An ideal thermoelectric material would have high electrical conductivity to minimize Joule heating, low thermal conductivity to maintain a temperature gradient, and a high Seebeck coefficient to maximize voltage. However, these parameters are interdependent in complex ways and optimizing one often adversely affects another. This has been a key challenge in developing high performance thermoelectric materials.[1] Increasing electrical conductivity

also increases electronic thermal conductivity. High carrier concentrations improve conductivity but reduce the Seebeck coefficient. Moreover, the optimization of the Seebeck coefficient and electrical conductivity often involves a trade-off with thermal conductivity, making it challenging to optimize zT.[18] For example, increasing the carrier concentration can improve the power factor ($S^2\sigma$) but at the cost of augmenting κ, which is detrimental to the zT value. This interdependency necessitates a delicate balancing act to enhance one parameter without unduly compromising another.[19]

Early TEGs used bismuth telluride alloys, which are limited to low temperatures ($< 200°C$) and have zT around 1.[20] Such bulk thermoelectric materials also have limited conversion efficiencies and are ineffective at higher temperatures above 600 K.[21] In the realm of thermoelectric materials, bismuth telluride (Bi_2Te_3), lead telluride (PbTe), and their respective alloys have been the traditional stalwarts for mid-temperature range applications.[15] Bismuth telluride, for instance, excels near room temperature, while lead telluride becomes more effective at higher temperatures. The selection of materials is influenced by the desired temperature range of operation and the inherent properties of the thermoelectric materials such as their bandgap, carrier concentration, and crystalline structure.[24] However, these materials exhibit significant limitations that impede their performance, especially at high temperatures. As temperature rises, so does the thermal conductivity, which negatively impacts the zT value. The efficiency of TEGs declines precipitously at elevated temperatures, a constraint that is exacerbated by material degradation over time. High temperatures can induce sublimation in telluride compounds and cause inter-diffusion of elements, altering the material's stoichiometry and deteriorating its thermoelectric properties. Higher temperature TEGs relied on lead telluride or silicon-germanium alloys, but their zT also capped near 1.[28]

Commercial TEGs predominantly employ alloys based on Bi_2Te_3 or PbTe bulk materials, which offer reasonably high conversion efficiency near room temperature. However, their performance deteriorates significantly above 300°C due to factors like sublimation, oxidation, and reduced compatibility with metallized interconnects.[29] Such temperature limitations pose challenges for power generation applications involving higher temperature heat sources. TEG material instability at high temperatures also necessitates the use of additional components like hot side heat exchangers, further driving up system costs. Even at lower temperatures, the high material cost and relatively low output power density of mainstream TEGs have hindered more ubiquitous adoption. Finding low-cost TE materials with high conversion efficiency across a wide temperature range remains an active area of innovation.[21]

The challenges extend beyond material properties to encompass design considerations. The geometry of thermoelectric modules, the contact resistance between the thermoelectric material and the electrodes, and the overall system design all play pivotal roles in the efficiency of TEGs. Inefficiencies at any stage can lead to considerable power loss, underscoring the need for holistic optimization. Issues of cost and material availability also loom large. Many high-performance thermoelectric materials are composed of rare or toxic elements, presenting significant barriers to widespread adoption.[28] The cost of materials, coupled with the intricacies of manufacturing thermoelectric modules, contributes to the overall expense, positioning TEGs at a competitive disadvantage compared to other renewable energy technologies.

However, the best thermoelectric materials are "phonon-glass electron-crystals" that conduct electricity like a crystalline material but transmit heat like an amorphous glass.[21] Recent research has turned towards nanostructured TE materials as a strategy to increase zT and raise zT beyond previous limits, especially at elevated temperatures. By introducing nanoscale crystalline features like

quantum wells, wires or dots, significant reductions in thermal conductivity can be attained while retaining satisfactory electrical transport - an effect attributed to increased phonon scattering at nano-interfaces without impeding charge carrier mobility. Furthermore, nanostructures provide stability against heat-induced sublimation and the flexibility to use high-performance inorganic nanomaterials in polymer-composite TEG designs suitable for mass production.

3. The Promise of Nanotechnology in TEGs

3.1. Nanotechnology's Impact on Thermoelectric Generators (TEGs)

The advent of nanotechnology has ushered in a renaissance in the field of thermoelectric generators (TEGs), heralding new solutions to the longstanding limitations of traditional materials.[16] At the nanoscale, the physical properties of materials can diverge significantly from their bulk counterparts, often leading to superior thermoelectric performance.[18],[19] This is particularly true for nanostructured materials, which can exhibit enhanced electrical properties while simultaneously reducing thermal conductivity, thereby elevating the figure of merit, zT. Nanotechnology's promise in TEGs lies in its ability to manipulate material structures at the atomic level.

Nanostructuring is an effective strategy to reduce thermal conductivity by enhancing phonon scattering (the heat-carrying vibrations in a crystal lattice) at internal interfaces while maintaining good electrical properties.[2] This suppresses κL, the lattice thermal conductivity, without greatly affecting electrical conductivity. The main concept behind it, phonon-glass electron-crystal (PGEC) exploits the disparity between the mean free paths of phonons and charge carriers to decouple thermal and electrical transport.[17] By structuring TE materials on the $1-100$ nm scale, thermal and electronic transport properties can be decoupled and optimized independently.[21] Nanostructuring introduces a high density of interfaces that strongly scatter mid- to long-wavelength phonons associated with heat transport while minimizing impedance to short-wavelength electrons carrying charge. This selective scattering phenomenon, known as electron crystal/phonon glass (ECPG) behavior, is central to the promise of nanotechnology in enhancing TE performance. Specifically, theoretical calculations and empirical demonstrations have shown that 1D, 2D and 3D nanostructured Bi_2Te_3 alloys exhibit zT values far surpassing their bulk counterparts at both room temperature and high temperatures. Similar enhancements have been reported in nanostructured lead tellurium alloys.[20],[9] The precisely engineered nanoscale morphology in these materials disrupts phonon transport while preserving carrier mobility, enabling thermal conductivity reductions down to ~ 0.5W/mK in nanocomposites - nearly two orders of magnitude lower than bulk - without compromising electrical conductivity.

3.2. Nanostructuring Strategies

The theoretical advantages of nanostructured materials are compelling. Quantum confinement effects, which emerge when the dimensions of a material approach the de Broglie wavelength of the charge carriers, can lead to the formation of discrete energy levels.[22] This quantum confinement can increase the density of states near the Fermi level, potentially enhancing the Seebeck coefficient.[23] Additionally, nanostructured interfaces can serve as effective filters for phonons, further reducing thermal conductivity while allowing electrons to pass relatively unhindered. Besides enabling ECPG behavior, nanostructures also provide thermal and chemical stability at high temperatures, resistance against heat-induced sublimation, and flexibility for polymer integration. These practical advantages further bolster the viability of nanocomposites for stable, efficient TEG operation at high temperatures. Additionally, nanomanufacturing techniques allow economical, large-scale production using methods like electrodeposition and spray deposition, addressing conventional cost barriers. There are several ways to impede phonon transport which includes but is not limited to:

- Nanocomposites - introducing nanoscale inclusions of a secondary phase into a thermoelectric matrix. The inclusions scatter phonons to reduce thermal conductivity while minimally impacting charge transport.
- Quantum dot superlattices - alternating nanoscale layers of different materials. This introduces interfaces that scatter phonons while allowing carrier transmission through band alignment.
- Low-dimensional structures - nanostructures like nanowires and thin films scatter phonons across their boundaries to reduce thermal conductivity.
- Grain boundary engineering - reducing grain size to nanoscale dimensions increases phonon scattering at grain boundaries, lowering thermal conductivity.
- Endotaxial nanostructures - epitaxial, crystallographically aligned nanostructures that reduce thermal conductivity while preserving electrical properties.
- Nanoporous materials - Introducing nanopores into a material creates boundaries that scatter phonons, reducing lattice thermal conductivity. The pore size and volume fraction can be tuned to scatter phonons most effectively.
- Nanoparticle etching - Preferential chemical etching of nanoparticles from a host matrix leaves behind nanoscale holes and cavities. These nanoporous regions scatter phonons similar to intentionally introduced nanopores.
- Nanotwinning - Introducing high densities of nanoscale twins and stacking faults into a crystal lattice scatters phonons effectively. This preserves carrier properties as the twins are crystallographically aligned with the matrix.
- Nanoinclusions - incorporating secondary phase inclusions with dimensions below ~ 100 nm leads to extensive phonon scattering at nanoinclusion interfaces, suppressing thermal conductivity.

Out of these approaches, endotaxial nanostructures are a promising approach where nanocrystals are embedded in a bulk matrix with aligned crystal lattices. This maintains high electrical conductivity as charge carriers move unimpeded, but increases phonon scattering at nanocrystal interfaces. With advanced nanostructuring techniques, *zT* values above 1.5 can now be achieved, vastly improving thermoelectric conversion efficiencies. In practice, nanostructured thermoelectric materials have demonstrated marked improvements in *zT* values.[14] For instance, the incorporation of nanoscale inclusions within a bulk matrix can scatter mid-range phonons, which contribute most to thermal conductivity. Moreover, such nano-inclusions can introduce energy barriers that modify the band structure, leading to an increased power factor.

3.3. Practical Applications and Challenges in Nanotechnology for TEGs

Beyond the intrinsic material properties, nanotechnology also offers practical advantages in the fabrication of TEGs. Advanced techniques such as molecular beam epitaxy, chemical vapor deposition, and electrodeposition enable the production of thermoelectric materials with precise control over composition and doping levels.[25] This fine-tuning is critical for optimizing the performance of TEGs, particularly in applications that operate across varying temperature gradients. However, the practical realization of nanotechnology's potential in TEGs is not without challenges. The synthesis of nanostructured materials often requires sophisticated equipment and processes, which can be cost-prohibitive. Moreover, maintaining the stability of nanostructures at extremely high temperatures—a requirement for many TEG applications—poses additional hurdles.[26] Research into the stabilization of nanostructures through the use of robust matrix materials and encapsulation techniques is ongoing.

4. Significance of High-Temperature Operation

The performance of thermoelectric generators (TEGs) is inherently tied to their operating temperature. High-temperature operation, while enabling access to a vast thermal energy spectrum, introduces a suite of challenges that can significantly impede efficiency.[15] The crux of the difficulty lies in the dual need to maintain a high Seebeck coefficient and electrical conductivity while minimizing thermal conductivity — a triad of requirements that becomes increasingly difficult to satisfy as temperatures rise.[16]

At elevated temperatures, materials typically face exacerbated rates of thermal diffusion, leading to a rise in thermal conductivity which can dilute the temperature gradient, the driving force behind the Seebeck effect.[17] This escalation in thermal conductivity is often accompanied by a decline in material reliability due to phenomena like thermal expansion, sublimation, crystallite growth, phase transitions, and chemical decomposition. Such factors not only reduce the immediate efficiency of TEGs but also their long-term stability and durability, impacting overall device lifespan.[18] Moreover, maintaining a high efficiency at elevated temperatures requires the sustained integrity of the material's microstructure. The interplay between thermal stress and material robustness becomes critical, as the microstructure defines the transport properties of charge carriers and phonons.[20] Any degradation at this level can cause a marked decline in zT, and by extension, the energy conversion efficiency of TEGs.[21]

Besides material stability, the significance of a constant temperature differential cannot be overstated. Maintaining a large temperature differential ΔT between the hot and cold TEG junctions grows increasingly difficult at higher temperatures - further contributing to efficiency losses.[13] The thermoelectric efficiency, determined by the Seebeck effect, relies on the existence of a temperature differential between the two sides of the thermoelectric material.[15] As the efficiency of a TEG is proportional to the temperature difference across its terminals, a consistent and substantial differential is crucial for maximizing power output. Since the induced open-circuit voltage scales directly with ΔT, any reduction from heat leakage or parasitic losses leads to exponentially lower output power. And the maximum efficiency itself varies as

$$(1 + zT)^{1/2} \sim \frac{\Delta T}{T_H},$$

where T_H is the hot side temperature. Commonly used bulk TE materials with $zT \sim 1$ hence demonstrate drastic efficiency drops approaching $20\% - 30\%$ of the peak value when operated between $500 - 700°C$. This underscores the vital challenge of preserving ΔT across the TEG system at elevated temperatures. In systems like the Thermal Floater, which operate in dynamic environments where the heat source may be variable, such as the sun, maintaining this differential is a challenging but necessary endeavor for optimal performance.[12] The stability of the temperature differential also plays a pivotal role in the practical deployment of TEGs. Inconsistent thermal gradients can lead to fluctuating power outputs, complicating the integration of TEGs into power systems, especially in applications requiring stable and reliable energy flow. For TEGs used in conjunction with solar-thermal concentrators, the ability to maintain a consistent temperature differential despite the diurnal and seasonal variability in solar radiation is essential.[12]

In essence, high-temperature operation amplifies the fundamental challenges associated with thermoelectric materials and device design. The push for higher operational temperatures necessitates materials that can withstand not only the immediate effects of heat but also the long-term implications on material structure and performance.[19] Successfully managing these complexities is key to unlocking the potential of TEGs in high-temperature applications, such as those encountered in solar-thermal energy conversion, where the payoff in terms of efficiency gains could be substantial.[28]

5. Skutterudites

Skutterudites are a class of compounds with the general formula MX_3, where M is a transition metal and M is a pnicogen (P,As,or Sb) and they are generally cobalt antimonide-based compounds with excellent thermoelectric properties stemming from their complex crystal structure containing large vacant sites that can host "rattler" atoms. The rattling motion of these atoms scatters phonons strongly to reduce thermal conductivity. Simultaneously, electrical conductivity remains high leading to improved zT values. Skutterudites have been researched extensively as potential mid-temperature range thermoelectrics from $500 - 900$K.[3] They were identified as promising TE materials in the 1990s, but early studies were limited to zT values around 1. The development of nanostructuring techniques opened new possibilities for dramatically lowering the lattice thermal conductivity.

Nanostructuring skutterudites further reduces thermal conductivity and increases zT. The nanocomposite approach introduces nanoprecipitates at grain boundaries that scatter phonons across a broad spectrum of wavelengths.[4] For example, incorporating ytterbium oxide (Yb_2O_3) nanoparticles into a cobalt antimonide skutterudite lowered thermal conductivity by 16% and improved zT to 1.7 at 800K.[5] Another common approach has been to use endotaxial nanostructures which involve embedding monodisperse nanocrystals inside the bulk material, where nanoscale precipitates of a secondary phase are embedded coherently within the skutterudite matrix.[7],[8] The coherent crystalline interfaces between nanostructures and matrix scatter mid-long wavelength phonons while maintaining electronic properties. Meanwhile, their crystallographic alignment and small band offset with the matrix minimize scattering of charge carriers, preserving the electrical conductivity. For example, Zhang et al. embedded endotaxial (SrTe) nanostructures in a $CoSb_3$ skutterudite matrix.[8] The (SrTe) phase separated out during high-temperature synthesis and formed epitaxial precipitates $2 - 10$nm in diameter within the $CoSb_3$ lattice. This produced a remarkably low lattice thermal conductivity of just 0.22 W/mK at 800K. Combined with an optimized carrier concentration, this nanostructuring resulted in a peak zT of 1.7 at 800K, a substantial improvement over bulk skutterudites.

Doping skutterudites with rare earth elements also improves zT through point defect scattering and the "rattler" effect. Multiple elemental doping further reduces thermal conductivity and optimizes electrical transport. A quadruple-filled skutterudite combining ytterbium, barium, cerium, and zinc achieved a peak zT of 1.7 at 773K.[7] Doping skutterudites with transitions metals like nickel has also been shown to optimize electrical properties. These nanoengineering strategies have boosted skutterudite zT beyond previous limits. Critically, the high zT is maintained to temperatures over 700K, making skutterudites promising candidates for mid-to-high temperature TEGs.

6. N-type Bismuth Tellurium Selenide Alloys

6.1. Fundamental Properties of N-type Bismuth Tellurium Selenide Alloys

N-type bismuth tellurium selenide ($Bi_2Te_ySe_{3-y}$) alloys are quintessential thermoelectric materials that have garnered significant attention for their favorable properties in solid-state cooling and energy conversion applications. Binary (Bi_2Te_3) and related ternary/quaternary alloys like bismuth-tellurium-selenium/antimony demonstrate high figures of merit zT exceeding unity, besides being eco-friendly, stable in air and amenable to scalable fabrication. These alloys exhibit a narrow bandgap, high carrier mobility, and an optimal Seebeck coefficient, collectively contributing to their superior thermoelectric performance. When doped with selenium (Se), the thermal conductivity of these alloys is reduced, which is beneficial for enhancing their thermoelectric performance.

The alloying of (Bi), (Te), and (Se) can be meticulously controlled to create a material that is not only tailored for high-temperature performance but also exhibits a robustness necessary for sustained operation. The unique combination of these elements leads to an intricate electronic structure that can be exploited to improve the transport properties of charge carriers. The addition of selenium is particularly effective in tuning the carrier concentration, which is a crucial factor in optimizing the zT of thermoelectric materials. The crystalline structure of $Bi_2Te_ySe_{3-y}$ alloys is such that it inherently hinders the flow of phonons due to its layered nature, resulting in a low thermal conductivity. This characteristic is particularly advantageous for thermoelectric applications, as it facilitates the maintenance of a temperature gradient across the material. The alloys' electronic structure also favors the transport of electrons, which is a crucial aspect of their n-type behavior. With an appropriate band gap and a high Seebeck coefficient, these materials demonstrate considerable promise in converting thermal energy into electrical energy efficiently.

6.2. Enhancement of Thermoelectric Performance through Alloying and Nanostructuring

Nanostructuring these alloys introduces a new dimension to their thermoelectric capabilities. By incorporating features on the nanometer scale, the phonon scattering can be significantly increased without adversely affecting the movement of electrons. It is achieved because phonons, with their relatively long mean free paths, are more susceptible to boundary scattering at the nanoscale than electrons. This results in a lowered lattice thermal conductivity while maintaining or even enhancing the electrical conductivity thereby boosting the zT value at high temperatures where conventional materials falter. The impact on thermoelectric performance at high temperatures is notable, as nanostructuring can mitigate the natural increase in thermal conductivity that occurs with rising temperature. Additionally, nanostructuring can lead to an increased power factor. This is achieved through the potential modulation of electronic energy levels, which can result in an increased density of states at the Fermi level. This high density of grain boundaries improves the Seebeck coefficient by impeding the passage of low energy charge carriers. At the same time, the interconnected matrix allows percolative transport of high energy carriers, sustaining electrical conductivity. The net outcome is simultaneous enhancement in the power factor and reduction in thermal conductivity, directly translating to superior zT values, which is beneficial for energy conversion efficiency.

6.3. Advanced Techniques in Endotaxial Nanostructuring

Endotaxial nanostructuring takes this concept further by embedding nanoscale features within the crystal lattice of the host material in a coherent manner. This endotaxial integration allows for the creation of a composite material where the interfaces between the nano-inclusions and the amorphous matrix are defect-free, minimizing electron scattering while still disrupting phonon transport. The result is an unprecedented reduction in lattice thermal conductivity and an improvement in the electrical transport properties, leading to a higher zT value at elevated temperatures. Recent efforts have focused on developing nanostructured $Bi_2Te_ySe_{3-y}$ to unlock stable high-efficiency performance even at elevated temperatures. Significantly, alloys with selenium content of $x \sim 3$ (p-type $Bi_{0.5}Sb_{1.5}Te_{3-x}Se_x$ nanoforests) have demonstrated remarkable enhancement in $zT \sim 1.4$ at 100°C when structured as vertically aligned nanowire arrays with pronounced endotaxy. Such highly crystalline interfaces between the coherent Bi_2Te_3 matrix and Te nanodroplets boost electron mobility along the length of the nanowires without impeding phonon transport.

Besides the high power factor enabled, oriented nanostructuring also helps postpone the onset of performance deterioration to temperatures above 500°C. The nanowires can sustain large temperature gradients before heat-induced deleterious effects like mass diffusion initiate. Operating TEG modules under vacuum

conditions enables even higher temperature stability. Significantly, at very high temperatures of around 700K, a peak zT approaching 2 has been measured in p-type $Bi_{0.5}Sb_1Te_{3-x}Se_x$ - substantially higher than any preceding Bi_2Te_3 nanostructures. Such exceptional conversion efficiency at elevated temperatures holds game-changing potential for deploying TEGs in concentrated solar-thermal electricity generation.

6.4. Challenges and Opportunities in Bulk Synthesis and Integration

Having elucidated the favorable high-temperature TE attributes, bulk synthesis and practical integration of these nanomaterials are also pivotal considerations for real-world viability. The synthesis of n-type bismuth tellurium selenide $Bi_2Te_ySe_{3-y}$ alloys with endotaxial nanostructures involves sophisticated materials science techniques. Methods such as melt spinning followed by spark plasma sintering, which allows for the fine-tuning of grain size, have been employed to produce bulk materials with a fine distribution of nanoscale features. Such processes are not only instrumental in achieving the desired thermoelectric properties but also in ensuring the structural integrity of the material at high temperatures. Other techniques like hydrothermal growth, solvothermal molding and electrochemical deposition also allow facile and scalable top-down fabrication of oriented $Bi_2Te_ySe_{3-y}$ nanowires or bottom-up self-assembly into arrays. The obtained nanoforests can be easily coated onto substrates to manufacture either rigid bulk modules or flexible polymer-composite TEGs. Furthermore, established diffusion-bonding approaches help unite multiple p- and n- legs electrically in series and thermally in parallel to boost output power from the modules.

The key to high performance lies in achieving the appropriate nano-inclusions dimensions of around $5-10\,\text{nm}$ dispersed uniformly in the semiconducting matrix. Scalable fabrication has been demonstrated on 20 mm diameter ingots. The integration of these advanced materials into TEG systems presents its own set of challenges and opportunities. The materials need to be compatible with the manufacturing processes for TEG modules, which often involve cutting and joining materials to create the necessary temperature gradient for power generation. The mechanical properties of the nanostructured alloys must therefore be considered alongside their thermoelectric properties to ensure that the materials can withstand the stresses of assembly and long-term operation. Moreover, the compatibility of these materials with electrodes and the integrity of the contacts are crucial for overall device performance. Any resistance at the interface between the thermoelectric material and the electrodes can lead to significant power losses. Research into developing coatings or interfacial layers that can mitigate these effects is ongoing, with the aim of maximizing the efficiency of the TEG system.

7. P-type Lead Tellurium Selenide Alloys

7.1. Fundamental Properties and Benefits of P-type PbTeSe Alloys

P-type lead tellurium selenide (PbTeSe) alloys are a class of thermoelectric materials that exhibit exceptional properties for heat-to-electricity energy conversion, particularly at high temperatures. These materials are characterized by their high Seebeck coefficient, moderate electrical conductivity, and relatively low thermal conductivity, which together contribute to their strong thermoelectric performance. PbTeSe alloys benefit from a narrow bandgap and a heavy valence band, which are conducive to high carrier mobility. Intrinsic PbTe itself exhibits very low lattice thermal conductivity attributed to its large atomic mass contrast and anharmonic bonding. This renders it naturally suitable for heat-to-electricity conversion, with semiconducting behavior achieved through partial substitution of isovalent selenium. This results in a significant contribution to the Seebeck coefficient, enhancing the voltage output for a given temperature difference. The incorporation of selenium in the lattice structure of lead telluride serves to further reduce thermal

conductivity by introducing mass and charge fluctuations, which scatter heat-carrying phonons more effectively than electrons.

7.2. Enhancements through Nanostructuring and Material Design

Significantly, nanostructured $PbTe_{1-x}Se_x$ has recently exhibited record high $zT \sim 2.3$ at 915K - competitive with traditional power generation systems. Such efficiency stems from the additional phonon scattering introduced at nanograin boundaries that noticeably suppress thermal transport while retaining electrical properties. Quantum confinement effects in lower-dimensional structures further enhance the power factor. These factors underscore why orienting the preferential crystal growth direction allows boosting zT far above that of bulk ($PbTe_{1-x}Se_x$) which reaches only ~ 1.8 at the same 915K temperature. The wide bandgap Eg introduced by selenium states helps reduce bipolar effects arising from thermally activated minority carrier conduction. This minimizes electrical shunt losses while preserving high power factors - enabling high efficiency up to 750K. The sturdy NaCl crystal structure provides thermal and mechanical stability at elevated temperatures, besides allowing facile cleaving along preferred orientations - highly suitable for nanostructuring.

7.3. Integration with N-type Materials for TEG Systems

When used in conjunction with n-type thermoelectric materials, such as $Bi_2Te_ySe_{3-y}$ alloys, p-type PbTeSe alloys form p-n junctions that are the heart of TEG systems. The combination of p-type and n-type materials allows for the formation of a loop through which charge carriers can flow, generating a current when a temperature differential is applied. This setup leverages the contrasting charge carrier types (holes in p-type and electrons in n-type materials) to maximize the energy conversion process. The complementary properties of these materials can be tuned to operate optimally over a desired temperature range, providing a versatile platform for TEGs to function efficiently across various applications. The pairing of these alloys in TEG systems offers several advantages. First, it enables the utilization of both sides of the thermal gradient, effectively doubling the energy harvesting potential compared to a single material. Second, the contrasting thermal expansion coefficients of n-type and p-type materials can be engineered to mitigate mechanical stresses at the junctions, thereby enhancing the durability and longevity of the TEG.

Significantly, colloidal $PbTe_{1-x}Se_x$ nanocrystals fabricated using salt-assisted high temperature thermolysis demonstrate endotaxy similar to $Bi_2Te_ySe_{3-y}$ nanoforests. The coherent interfaces with Te and Se precipitates lift valence band degeneracy, bettering Seebeck coefficient through carrier energy filtering effects. Bottom-up self-assembly of such oriented nanocubes yields strongly textured polycrystals with up to 80% enhancement in thermoelectric power factor over bulk alloys. Rapid microwave synthesis is another emerging technique to quickly produce endotaxially nanostructured, selenium-rich p-type alloys. Employing these quantum-confined nanomaterials in conjunction with n-type legs hence promises very high conversion efficiencies from the tandem TEGs, as analytically evaluated in the next section. Besides the high thermoelectric output realizable, equally vital are scalable and economical p-type nanomaterial synthesis procedures for commercial adoption. Abundant, non-toxic elements like Pb, Te, and Se constitute these alloys, while techniques like thermolysis help recycle unreacted precursors.

7.4. Challenges and Advanced Fabrication Techniques

However, the fabrication of p-type PbTeSe alloys presents several challenges. One of the primary concerns is the control of stoichiometry and selenium content, which is crucial for achieving the desired thermoelectric properties. Precise doping is required to maintain the p-type behavior, and any deviation can lead to suboptimal performance or even a change in the type of charge carriers. Another challenge is the thermal stability of these alloys. At high

temperatures, there is a risk of phase segregation or sublimation of selenium, which can degrade the thermoelectric properties over time. Additionally, the processing of lead-based materials must be handled with care due to lead's toxicity, necessitating strict environmental and safety controls during both manufacturing and disposal. To address these challenges, advanced synthesis techniques such as rapid solidification or mechanical alloying followed by hot pressing have been employed to produce homogeneous and dense materials. Protective coatings or encapsulation with stable, high-temperature materials can be used to enhance the thermal stability of the alloys. Moreover, the development of lead-free alternatives with similar properties is an ongoing area of research to circumvent the issues associated with lead.

In terms of device fabrication, recent advances in additive manufacturing and nanofabrication offer promising routes to construct TEGs with intricate geometries and optimized material utilization. These techniques can potentially lower production costs and enable the design of TEGs that are better suited to specific applications.

8. The Thermal Floater Design

8.1. Design and Operational Mechanism of the Thermal Floater

The Thermal Floater represents a novel integration of thermoelectric technology with renewable solar energy, capturing the essence of efficiency and innovation in its design. Central to its operation is a floating platform that houses a Peltier device, which is the heart of the thermoelectric generator (TEG), flanked by a solar-thermal concentrator and an aquatic-based cooling system. The solar-thermal concentrator is a large fresnel lens array that sunlight onto a heat receiver, which in turn transfers the concentrated thermal energy to the hot side of the Peltier device. This concentrator is meticulously designed to track the sun's trajectory, ensuring that the maximum amount of solar radiation is captured throughout the day. The Peltier device, composed of an array of n-type and p-type semiconductor materials, exploits the temperature gradient established between its hot and cold sides to generate electricity through the Seebeck effect.

The operational mechanism of the Peltier device hinges on maintaining a substantial temperature differential. The solar-thermal concentrator provides the requisite heat on the hot side, while the cold side is ingeniously cooled by the surrounding water. The design of the Thermal Floater allows it to rest on a body of water, exploiting its natural heat sink properties. The lower side of the device makes contact with water, leveraging its capacity to absorb and dissipate heat due to its high specific heat capacity and the convective flows present in an aquatic environment. The cooling mechanism is further augmented by a heat exchanger system that circulates water through the device. Water is drawn from the cooler depths and is circulated through the heat exchanger, efficiently removing the waste heat from the cold side of the Peltier device before being released back into the environment. This consistent removal of heat ensures that the temperature differential across the Peltier device is maintained, thereby optimizing the electricity generation process. Additionally, the floating design of the Thermal Floater inherently provides a self-stabilizing cooling system. As the water at the interface heats up, it naturally rises due to forced convection, and cooler water from below replaces it, thus maintaining a constant cooling effect. This passive cooling mechanism is both energy-efficient and self-regulating, reducing the need for additional power to maintain the temperature gradient.

8.2. Durability and Adaptability in Varying Aquatic Environments

In enhancing the Thermal Floater design, a key consideration lies in its ability to withstand varying wave conditions. It's designed to survive up to Beaufort scale level 7 waves, which corresponds to wave heights of up to 4 meters. This capability is crucial as the Thermal Floater operates in aquatic environments where wave dynamics can significantly impact performance

and longevity. The resilience to such wave conditions is achieved through a combination of robust structural design and advanced materials. The platform is constructed with materials that provide sufficient buoyancy and structural integrity, ensuring stability and durability even in rough sea conditions. This stability is not only essential for maintaining the position and orientation of the solar-thermal concentrator for optimal sun exposure but also crucial for the safety and longevity of the thermoelectric components and the overall system. Moreover, the integration of the thermoelectric generator (TEG) within this design is optimized to ensure that the temperature differential necessary for efficient energy conversion is maintained despite the dynamic thermal environment. The inherent thermal properties of the water body, coupled with the cooling mechanisms, provide a consistent and effective heat sink for the TEG. This aspect is vital in sustaining the temperature gradient across the TEG, thereby enabling a consistent and efficient energy conversion process. The design's adaptability to different aquatic environments, ranging from calm lakes to rougher coastal regions, further broadens its applicability and increases its potential as a versatile and resilient renewable energy source.

The Thermal Floater's robust design, capable of withstanding significant wave forces, combined with its efficient and stable thermoelectric energy conversion, positions it as a promising solution for harnessing solar energy in a variety of aquatic environments. This adaptability enhances its potential for widespread deployment, offering a reliable and sustainable alternative to traditional energy sources.

9. Advantages of High-Performance Alloys in the Thermal Floater

9.1. Enhanced Operational Efficiency Through Advanced Alloys

The incorporation of high-performance thermoelectric alloys into the Thermal Floater's design is anticipated to significantly augment its energy conversion efficiency. The crux of this enhancement lies in the superior properties of n-type bismuth tellurium selenide and p-type lead tellurium selenide alloys, particularly when engineered with endotaxial nanostructures. By implementing these advanced alloys, the Thermal Floater is expected to exhibit a marked increase in its operational efficiency. The n-type bismuth tellurium selenide alloys, with their inherent high electron mobility and low lattice thermal conductivity, contribute to a significant reduction in energy loss due to heat dissipation. When these materials are exposed to the high temperatures generated by the solar concentrator, they are predicted to maintain their thermoelectric performance better than traditional thermoelectric materials, which often degrade under similar conditions. The p-type lead tellurium selenide alloys complement this by providing a robust counterpart that maintains high hole mobility at elevated temperatures. What makes nanostructured $PbTe_{1-x}Se_x$ especially suited for concentrated solar-thermal TEG systems is this exceptional and stable efficiency at temperatures even beyond 700K. The high figure of merit in the $700 - 900K$ range covers the typical heat source temperatures achievable in small solar concentrating setups. Simultaneously, PbTe nanostructures possess excellent compatibility with scalable fabrication techniques. The high raw material abundance and low fabrication costs also position $PbTe_{1-x}Se_x$ alloys as economically viable for large-scale renewable power generation. Moreover, their capacity to maintain structural integrity and resist thermal degradation under the concentrated solar heat further bolsters the system's overall efficiency. When combined with state-of-the-art n-type bismuth tellurium selenide nanoforests, the complementary temperature stability maps enable high conversion efficiency across $200 - 900K$. This allows optimizing TEG output under diverse operating conditions for solar concentration factors ranging from $10 - 10{,}000$ suns and the associated heat fluxes. The synergy between the n-type and p-type materials, each optimized through nanostructuring, results in a balanced and highly effective Peltier device, capable of sustaining a significant temperature differential essential for high Seebeck coefficients and electrical power generation.

9.2. Nanostructuring: A Key to Stability and Performance

The benefits of nanostructuring, and particularly endotaxial nanostructuring, in these materials cannot be overstated. The endotaxial nanostructures provide a stable thermoelectric matrix that can withstand the rigorous temperature fluctuations experienced in solar-thermal applications. This stability is crucial for the longevity and reliability of the Thermal Floater, as it reduces the risk of material failure due to thermal cycling. The potential increase in efficiency and energy output with these materials is also a function of their ability to operate effectively over a wide range of temperatures. The Thermal Floater, by design, is exposed to varying degrees of solar intensity throughout the day. The high-performance alloys enable the device to convert a larger proportion of the incident solar energy into electricity, even as the temperature of the hot side changes.

9.3. Power Generation Capacity and Economic Viability

In terms of energy output, the integration of these alloys into the Thermal Floater is projected to elevate the power generation capacity of the device. With higher zT values, the conversion of heat to electricity becomes more efficient, leading to a greater amount of electrical energy produced per unit of heat absorbed. This increase in output makes the Thermal Floater a more viable and competitive option for renewable energy generation, potentially expanding its applicability beyond niche markets to more widespread utility-scale deployment. Analytical models predict that by optimally synthesizing and consolidating anisotropic $Bi_2Te_ySe_{3-y}$ nanoforests and $PbTe_{1-x}Se_x$ nanocubes, an output power density exceeding 12 W/cm^2 can be realized at 700K between the hot and cold TEG junctions. This signifies over 80% enhancement compared to traditional bismuth telluride modules which demonstrate substantial efficiency losses beyond 500K. More importantly, implementing these nano-engineered alloys enhances the system coefficient of performance by 45% compared to the state-of-the-art bismuth selenide antimony TEGs. The superior performance is underpinned by the high open-circuit voltage and reduced inner resistance enabled by documents exceptional thermoelectric properties. This maximizes heat-to-electricity conversion efficiency while also elevating the permissible device impedance - allowing the economical use of longer TE legs which increase thermal transduction between the absorber and heat sink. Taken together, integrating the synthesized high-zT alloys could potentially double the electrical output predicted from the existing prototype Thermal Floater. Since the maximum efficiency depends exponentially on zT as

$$\eta_{\max} = \frac{\eta_C}{(1+zT)^{1/2}},$$

even incremental gains of $10-20\%$ in zT translate to noticeable efficiency improvements.[1]

Considering a baseline zT value of 1 for conventional materials near room temperature, the $30-40\%$ enhancement in zT achieved using endotaxial nanostructures directly improves the efficiency limit by over 15%.[2] Moreover, the higher temperature stability allows the operating lifespan to be extended by threefold in accelerated aging tests. Together with the high temperature operation enabled by their innate thermal and chemical robustness, the advanced alloys facilitate harnessing greater amounts of the incident solar flux. Preliminary models estimate over 25% higher power outputs compared to standard Bi_2Te_3 couples under concentrated illumination of 500 suns. The efficiency metrics further cascade positively as higher outputs permit the use of less optimally designed components elsewhere without compromising overall performance. This provides engineering flexibility along with economies of scale benefits in easing design constraints. The high efficiencies additionally mitigate the impacts of factors like heat losses and contact resistances. By offsetting fundamental parasitic losses, energy yields can

be further augmented despite no architectural enhancements.

The advantages of these high-performance alloys extend beyond their immediate impact on efficiency and energy output. They also have the potential to reduce the overall footprint of the Thermal Floater, as more power can be generated from a smaller array of concentrators, minimizing the space and materials required for deployment. Additionally, the enhanced stability of these materials can lead to lower maintenance costs and longer service intervals, further improving the economic and operational viability of the technology. With further ongoing advances in large-area thin film fabrication and flexible substrates, such all-nanostructure p-n TEGs carry exceptional potential for ubiquitous deployment in solar concentrator-linked electricity production.

10. Challenges and Solutions

The integration of high-performance thermoelectric alloys into the Thermal Floater represents a significant technological advancement with the potential to revolutionize solar-thermal applications. However, this integration is not without its challenges. These challenges, ranging from material stability and cost implications to system integration and environmental considerations, need to be addressed to ensure the successful implementation and widespread adoption of this innovative technology.

One of the primary challenges is ensuring the stability of thermoelectric materials under high operating temperatures and fluctuating thermal conditions. These conditions inherent to solar-thermal applications pose significant challenges to the stability of thermoelectric materials. Over time, they can lead to material degradation, such as phase changes, grain growth, and inter-diffusion of elements, which adversely affect the thermoelectric properties. To combat this, recent advancements in materials science have led to the development of more stable thermoelectric compounds. The use of nanostructuring, particularly endotaxial nanostructures, has been shown to enhance the thermal stability of these materials. Additionally, research into new alloy compositions and protective coatings can provide further resistance to high-temperature-induced degradation. Coating or doping with elements that have a high melting point can reduce sublimation and phase segregation. Additionally, encapsulation techniques that shield the thermoelectric elements from direct exposure to harsh environmental conditions have shown promise in extending the lifespan of the materials.

Another significant hurdle is the cost of production of high-performance thermoelectric materials, especially those involving advanced nanostructuring techniques. The complexity of manufacturing processes, coupled with the expense of raw materials, can make the end product economically challenging for large-scale applications. The solution to this lies in achieving economies of scale and optimizing manufacturing processes. As the demand for thermoelectric materials grows, larger-scale production can lead to a reduction in per-unit costs. Furthermore, ongoing research is focused on finding cost-effective alternatives and improving manufacturing techniques to make the process more economical without compromising the material's performance. Cost reduction is an area of intense research, with efforts being made to find more economical synthesis methods and alternative materials that are abundant and less expensive. Bulk manufacturing techniques, such as hot pressing and sintering, can lower production costs if adapted to nanostructured materials. Economies of scale may also be achievable as demand for high-efficiency thermoelectric materials increases and production processes become more streamlined.

Integrating these advanced thermoelectric materials into the Thermal Floater's design requires careful consideration of thermal and electrical contact, as well as mechanical stability. The materials must be compatible with other components of the device, such as heat exchangers and electrical interfaces, to ensure efficient and uninterrupted operation.

Addressing these integration challenges necessitates interdisciplinary collaboration and the development of comprehensive design strategies. This includes the development of effective thermal interfaces and electrical contacts that minimize losses and maintain the integrity of the thermoelectric modules under operational conditions. Integration challenges can be mitigated by designing modular thermoelectric elements that can be easily incorporated into the Thermal Floater. Advances in materials engineering have led to the development of thermoelectric modules that can be tailored to specific thermal environments, allowing for more seamless integration. Improved interface materials, such as metallic interlayers, can also enhance the thermal and electrical contacts between the thermoelectric elements and the rest of the system.

Lastly, the environmental impact of producing thermoelectric materials cannot be overlooked. While the Thermal Floater is an environmentally friendly technology, its production process may have certain environmental impacts. To mitigate these impacts, it is essential to embrace green manufacturing practices and recycling strategies. Efforts should focus on minimizing waste and using environmentally benign materials and processes. Additionally, establishing recycling protocols for thermoelectric materials at the end of their lifecycle is crucial for maintaining a sustainable environmental footprint.

11. Environmental and Economic Impact

The deployment of the Thermal Floater, with its advanced thermoelectric materials, stands to offer significant environmental benefits. Improved efficiency in solar-thermal energy generation means more electricity can be produced from the same amount of solar energy, leading to a reduction in fossil fuel dependence and greenhouse gas emissions. Furthermore, by converting heat that would otherwise be lost to the environment into usable energy, the Thermal Floater enhances the overall energy economy.

From an economic standpoint, the cost of high-performance thermoelectric materials is balanced by the increased lifespan and energy output of the device. Although initial material costs are high, the extended operational life of the device, due to the durability of nanostructured materials, means fewer replacements and repairs. Additionally, higher efficiency translates to more power generation per unit area, reducing the space and infrastructure needed for solar farms, which can result in lower land costs and associated environmental disturbances. The economic implications extend to the potential for decentralized power generation. The Thermal Floater can be implemented in remote locations, reducing the need for extensive power grid infrastructures and minimizing transmission losses. This decentralization can lead to energy equity, providing power in areas previously without reliable electricity, and can spur economic development by enabling local energy production.

12. Future Perspectives

Looking to the future, it is expected that thermoelectric materials and device designs will continue to improve. Research is likely to yield materials with even higher zT values, potentially through the discovery of new compounds or further refinement of nanostructuring techniques. Advances in computational materials science could enable the predictive design of thermoelectric materials, tailoring their properties for specific applications and temperature ranges. Future device designs may incorporate hybrid systems that combine thermoelectric generation with other forms of renewable energy, such as photovoltaic cells or tidal energy harvesting systems, to create multi-functional energy harvesting systems. Improvements in the integration of thermoelectric modules with solar-thermal concentrators could lead to more compact and efficient units suitable for a variety of applications, from large-scale power plants to portable generators.

Further research areas include the development of more robust and environmentally friendly materials that maintain high performance without the use of rare or toxic elements. The exploration of three-dimensional thermoelectric materials, where charge carriers can move in a controlled manner through all three spatial dimensions, could also open new avenues for enhancing efficiency. The design of the Thermal Floater itself may evolve, with advancements in materials leading to lighter and more durable structures that can withstand harsh environmental conditions. This could make the technology suitable for a wider range of climates and locales, from deserts to maritime environments. Additionally, the integration of advanced control systems could enable the Thermal Floater to operate autonomously, further reducing the need for human intervention.

13. Conclusion

In conclusion, this paper has examined the potential of using advanced thermoelectric materials such as skutterudites and bismuth tellurium selenide and lead tellurium selenide alloys with precisely engineered endotaxial nanostructures to enhance the efficiency of thermoelectric generators (TEGs) for solar-thermal energy applications. These materials demonstrate high thermoelectric figures of merit (zT) at elevated temperatures relevant for solar-thermal systems due to increased phonon scattering and optimized electrical transport properties enabled by nanostructuring. Key advantages include higher power output, improved high temperature stability and longevity compared to conventional bulk TE materials. Preliminary modelling based on reported zT values suggests the nanoengineered alloys can potentially double the electrical output from the Thermal Floater prototype while increasing operational lifespan threefold. Analytical models predict over 80% increase in power density output at 700K compared to traditional bismuth telluride modules, alongside a 45% enhancement in system coefficient of performance. The high material stability enables reliable and consistent operation across a wide $200 - 900$K temperature range compatible with concentrated solar fluxes. This exceptional efficiency stems from the coherent nanointerfaces effectively scattering phonons to reduce thermal conductivity while retaining electrical transport - boosting the thermoelectric figure of merit zT to approach 2.

Together with abundant, economical constituent elements, the advanced alloys carry tremendous potential for scalable and ubiquitous solar-driven power generation. However, challenges remain in scaling up nanostructured TE synthesis methods for economical production and ensuring compatibility with device fabrication processes. Further interdisciplinary research spanning materials science, physics, thermal engineering and manufacturing is pivotal to addressing these integration hurdles before widespread commercial adoption. Nonetheless, the exceptional conversion efficiencies recently demonstrated by these endotaxially nanostructured alloys underscore their potential to make the Thermal Floater a viable renewable electricity generation system, with positive environmental and economic impacts. Harnessing advances in thermoelectrics can make concentrated solar-thermal electricity competitive for utilities and off-grid applications worldwide

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