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2025 Roadmap Toward Sustainable Thermoelectrics

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2025 Roadmap Toward Sustainable Thermoelectrics

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Abstract

Thermoelectric technology uses the Seebeck effect to directly convert heat into electricity or vice versa. Amongst its advantages are the lack of moving parts, reliability, absence of refrigerant gasses and scalability. To date, commercial progress has been limited due to relatively low conversion efficiencies and high costs. However, with increasing energy costs, the advent of the Internet of Things and its needs to power many sensors, and the need for thermal management in electronics, there is plenty of reason to be optimistic about the future of thermoelectric energy conversion. Beyond using abundant elements, sustainability has so far not been a major consideration in the development of thermoelectric technology, with its understandable emphasis on improving performance. However, sustainability aspects, including eco-friendly processing, resource efficient module fabrication, ensuring a long working life and end of life recycling should all be major considerations from the outset. This roadmap aims to provide an overview of current efforts moving towards sustainable thermoelectrics as well as guidance for future work. In terms of organisation, the roadmap contains cross-cutting sections on aspects of sustainability and sections focused on the major thermoelectric materials. It can be read front to back or focusing on chapters of particular interest. We hope that this roadmap will stimulate new research, leading to the early adoption of sustainability concepts, beyond using abundant elements, in the development of large-scale thermoelectric technology.

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Introduction

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Introduction

Thermoelectric energy conversion offers great possibilities in power generation, harvesting and in thermal management, e.g. as heat pumps.^{1, 2} Commercially available modules use n- and p-type Bi₂Te₃ and work well near room temperature. The thermoelectric figure of merit of these materials is near unity, enabling device conversion efficiencies of 5-6%. Here, the thermoelectric figure of merit is defined as $zT = (S^2\sigma/\kappa)T$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the sum of the lattice and electronic thermal conductivity, and T is the absolute temperature. Taken together with the Carnot efficiency, zT determines the upper limit on the thermoelectric (power generation) conversion efficiency:²

$$\eta = \frac{T_H - T_C}{T_H} \left(\frac{\sqrt{1 + zT_{av}} - 1}{\sqrt{1 + zT_{av}} + T_C/T_H} \right)$$

From this expression and from the materials zT , it is clear that higher temperatures and larger temperature differences are favourable for power generation. Note that the zT in this expression is the average value over the temperature gradient.³ Waste heat recovery has been a major driver for the recent development of more efficient materials. However, thermal management near room temperature is the only current commercial market for thermoelectric devices. The first-generation materials include Bi₂Te₃, PbTe and SiGe, for near room temperature, mid- and high temperatures.⁴ All three use scarce, expensive and sometimes toxic components.⁵ Replacement of scarce and toxic elements like tellurium and lead has driven much of the recent thermoelectric materials research. In this roadmap, it is argued that a broader definition of sustainability needs to be used to guide further work.

The past 20-30 years has seen the development of many different strategies to improve zT and these are the topic of a large number of reviews.^{1, 2, 5-12} This development work has been tremendously successful with peak zT increasing towards 3 and temperature-averaged values >1 , enabling $>10\%$ efficiencies. These are highly promising developments, with performance now on the cusp of being commercially interesting for a wider range of applications. In addition, recently materials including Mg₃Sb₂, MgAgSb and Ag₂Se with good near room temperature performance have been developed, offering a potential replacement for Bi₂Te₃.⁶ In particular, the prospect of displacing Bi₂Te₃ for near room temperature applications has led to an increased focus on building prototype devices, and developing stable electrical and thermal contacts.^{2, 3, 8, 11}

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The aim of this roadmap “towards sustainable thermoelectrics” is to start a discussion around sustainability aspects of thermoelectric technology. The UN definition of sustainability is “meeting the needs of the present without compromising the ability of future generations to meet their own needs”. A major aspect of sustainability is doing little or no harm to the environment.

From this definition, it is clear that sustainability encompasses more than only using abundant elements, although that is clearly important. Other factors include the source of the raw materials, efficient synthesis and processing, module fabrication, operational life and end of life recycling. Achieving sustainable thermoelectric technology therefore relies on solving multiple issues, including green/ eco-friendly processing (defined as minimising environmental impact), stability of joints and materials, which are vital to the longevity of the device, more efficient materials design, reducing waste in manufacturing, etc. Attempts to quantify the energy and environmental cost using life cycle analysis are still in their infancy for thermoelectric technology but is needed to assess the sustainability of the technology over its lifetime.

Prior roadmaps on thermoelectrics have focused on technical aspects of technology development,^{13,14} on activities in specific countries¹⁵ or are a collation of tables of materials performance.¹⁶ The current roadmap has a different focus, aiming to embed sustainability considerations, beyond elemental abundance, into thermoelectric energy conversion and is similar in its ambition to a recent roadmap on sustainable batteries.¹⁷

The current roadmap is structured to have two major parts: the first is focused on cross-cutting aspects of sustainability; the second contains an overview of the major thermoelectric materials that are currently considered.

Section 1.1 focuses on raw materials, including scarcity, geographic distribution and uses the Herfindahl-Hirschman Index as to quantify market concentration. Section 1.2 is focused on life cycle analysis and provides a good overview of the diverse factors, beyond elemental abundance, and challenges that need to be overcome before fully quantitative LCA is possible. Section 1.3 gives an overview of processing methods and recent developments focused on making these eco-friendlier by reducing processing time and temperature. Section 1.4 is focused on additive manufacturing of thermoelectric materials, which offers advantages in terms of design flexibility, and minimisation of materials wastage in device manufacturing. Section 1.5 covers advances in electrodeposition, which can be used for the fabrication of micro generators for IoT applications. Section 1.6 focuses on traditional module fabrication and identifies ineffective use of materials, improving module performance and increasing operational lifetimes as key issues for improving sustainability. Section 1.7 gives an overview of efforts on upcycling waste, including of Bi_2Te_3 offcuts, silicon kerf, and mining waste, and research work on using recycled precursors in

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thermoelectric materials. Section 1.8 discusses the use of machine learning or artificial intelligence in speeding up materials discovery, reducing the resource impact of experimental work. Section 1.9 is focused on recent advances in electronic transport modelling, going beyond the constant relaxation time approximation, enabling more accurate prediction of targets for exploration.

The second part of this roadmap focuses on recent materials development. These are grouped by application area, starting from near room temperature materials suitable for thermal management, harvesting and power generation, followed by higher temperature materials.

Section 2.1 is focused on Bi_2Te_3 and near ambient materials, including Mg_3Sb_2 and MgAgSb that are currently heavily investigated as replacements for Bi_2Te_3 . Section 2.2 covers full-Heusler materials, which are potentially highly sustainable because they are based on widely mined metals, have high stability and durability, but their performance needs improving. The following two sections cover polymer composites (section 2.3) and halide perovskites (section 2.4) that are considered for harvesting and IoT applications. A major advantage of both systems is that they use solution-based processing, offering facile routes towards flexible and large area thermoelectric devices. The remaining sections are focused on higher temperature materials. Sulphur (section 2.5) is highly attractive because it is non-toxic and highly abundant, for example a by-product of fossil fuel production. Good p-type compositions are available, but a major challenge is the development of n-type materials with earth-abundant metals. Section 2.6 discusses metal selenides and tellurides. Metal tellurides have the highest zT values of materials currently available. However, replacement of scarce tellurium by selenium is not straightforward. Section 2.7 covers half-Heusler materials, which like their full-Heusler counterparts are amongst the most sustainable thermoelectrics in terms of precursors and stability at higher operating temperatures. Section 2.8 is focused on skutterudites, which are established materials with good performance and stability, but with issues surrounding the development of durable generators. Section 2.9 covers metal silicides, which are of great interest due to the high abundance of Si and metals such as Mg and Mn. The final section (2.10) covers metal oxide thermoelectrics, which potentially are highly sustainable thermoelectric materials due to ease of processing but are limited by lower performance.

As indicated by several authors of this roadmap, quantitative life cycle analysis is needed to make rational decisions about sustainability. At present this is usually not possible due to the lack of accurate input data. In addition, current fabrication of modules is small scale, involving manual assembly, and no mass-produced modules are on the market. Hence, the benefits of mass production have not been achieved for thermoelectrics. Large cost reductions and improved material and energy efficiencies are possible for industrial scale production of modules. For niche applications, use of scarce elements may still be a

sustainable option, as long as enough energy is generated over the lifetime of the module, and as long as the scarce elements can be recycled.

There is plenty of reason to be optimistic about the application of thermoelectric technology, its reliability, scalability and lack of moving parts. With continued improvements in materials and module performance, thermoelectrics will become more competitive with other renewable energy and harvesting technologies, whilst heat pumping over small temperature differences can already be highly efficient. Thermal management and reliable spot cooling, which is difficult to achieve with compression-based cooling, is a unique feature of thermoelectrics and will drive innovations in the future. We hope that this roadmap will help building in sustainability considerations from the outset.

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1. Sustainability Considerations

1.1 Raw Materials Supply for Sustainable Thermoelectrics

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Status

The advancement of thermoelectric (TE) technology, crucial in energy conversion systems, is profoundly influenced by the availability and sustainability of a diverse array of raw materials. These materials not only define the operational limits and efficiency of TE devices but also dictate their potential for energy conversion applications. Deep insights into material scarcity, cost implications, and geopolitical factors are essential for driving strategic innovations and development within the field [1]. Currently, a significant challenge within the TE domain is the dependence on scarce materials such as bismuth and tellurium, utilized in high-efficiency thermoelectric materials like Bi_2Te_3 and PbTe [2-3]. Bismuth and tellurium significantly enhance heat-to-electricity conversion efficiency; however, their supply chains pose concerns. Bismuth production is predominantly concentrated in China, while tellurium is exceedingly rare, primarily recovered as a byproduct of copper mining and sourced from limited geographic regions, posing significant risks to the scalability and global deployment of TE technologies.

Furthermore, elements like Cobalt, employed in oxide-based thermoelectric, along with rare earth elements essential for advanced materials, face similar scarcity and geopolitical challenges. These materials are not merely scarce; their supply is concentrated in regions with unstable political climates or restrictive export policies, intensifying supply risks. For instance, Cobalt mining in the Democratic Republic of the Congo has been associated with political instability, potentially disrupting supply chains and inflating costs [4]. Skutterudites, which utilize CoSb_3 , rely on antimony, whose production is primarily concentrated in China and Tajikistan [5]. These materials also often incorporate rare earth elements or heavy metals to optimize their thermoelectric performance, further compounding challenges related to material scarcity and geopolitical risk. Half-Heusler, like compounds of TiNiSn , although dependent on relatively more abundant elements like titanium and tin but often require precise doping with scarce elements like hafnium and antimony to optimize their properties, highlighting a complex balance between availability and performance [2-3]. Addressing these challenges demands a thorough evaluation of the life cycles, market availability, and geopolitical contexts that influence these materials. The global management of these resources affects their pricing and availability and impacts the economic feasibility and broader deployment of TE technologies. Therefore, assessing the raw material supply and global management of resources is an important aspect to consider for sustainable thermoelectric.

Current and Future Challenges

Understanding market share and the Herfindahl-Hirschman Index (HHI) is essential for industries reliant on critical raw materials. The HHI, a widely recognized metric for measuring market concentration, provides insights into the concentration of market power and underscores potential supply vulnerabilities [1, 6]. According to the U.S. Department of Justice and Federal Trade Commission, HHI classifies markets into three levels of concentration: an HHI below 1500 indicates a non-concentrated market, an HHI between 1500 and 2500 represents moderate concentration, and an HHI above 2500 signifies high concentration. This classification system was applied in our analysis to assess market risks associated with various elements.

Our study, leveraging data from the United States Geological Survey (USGS) [5], reveals important insights summarized in Figure 1. A more detailed market concentration study across the wide range of elements was conducted in our recent work [7]. Figure 1(a) illustrates the production market share in the year 2023 for key thermoelectric elements. Notably, elements such as Bi, Te, Sb, Se, and Rare Earths are predominantly produced by a few countries, particularly China, indicating high market concentration and increased risk of supply disruption. The HHI trends over time provide a better ability to estimate the risk and market volatility. Figure 1(b) shows the variation in production HHI, while Figure 1(c) shows reserve HHI trends from 2016 to 2023 of key thermoelectric elements. The production HHI for selenium and lead has remained relatively flat and below 2500, suggesting a stable and moderately concentrated market. In contrast, other elements exhibit fluctuations due to shifting production dynamics across countries, indicating greater market volatility. Antimony production HHI has shown notable fluctuation: initially dominated by China, the production HHI has decreased in recent years as countries like Tajikistan, Turkey, Burma, and Russia have expanded production, making antimony more accessible. Bismuth, however, consistently maintains a high production HHI value (>5500), underscoring its persistent supply risk as a critical thermoelectric element. The reserve HHI for elements such as Se, Sb, Pb, and Rare Earths remains below 2500, reflecting a more diversified supply base and moderate market concentration, which could help mitigate some risks associated with geopolitical instability.

As demand for thermoelectric materials rises with the growth of green technologies, raw material supply challenges are expected to intensify due to concentrated production and reserves. The absence of a dynamic platform for managing global supply data impedes strategic decision-making, limiting the industry's proactive response to market shifts. To address these challenges, a multifaceted approach is crucial, involving international collaborations, developing new mining sites, enhancing recycling techniques, and pursuing research into alternative materials. Strategic resource management and diversification of supply sources are vital to reduce risks linked to geopolitical instability and supply chain

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vulnerabilities, thereby ensuring the sustainability of the thermoelectric industry and facilitating the wider adoption of these technologies.

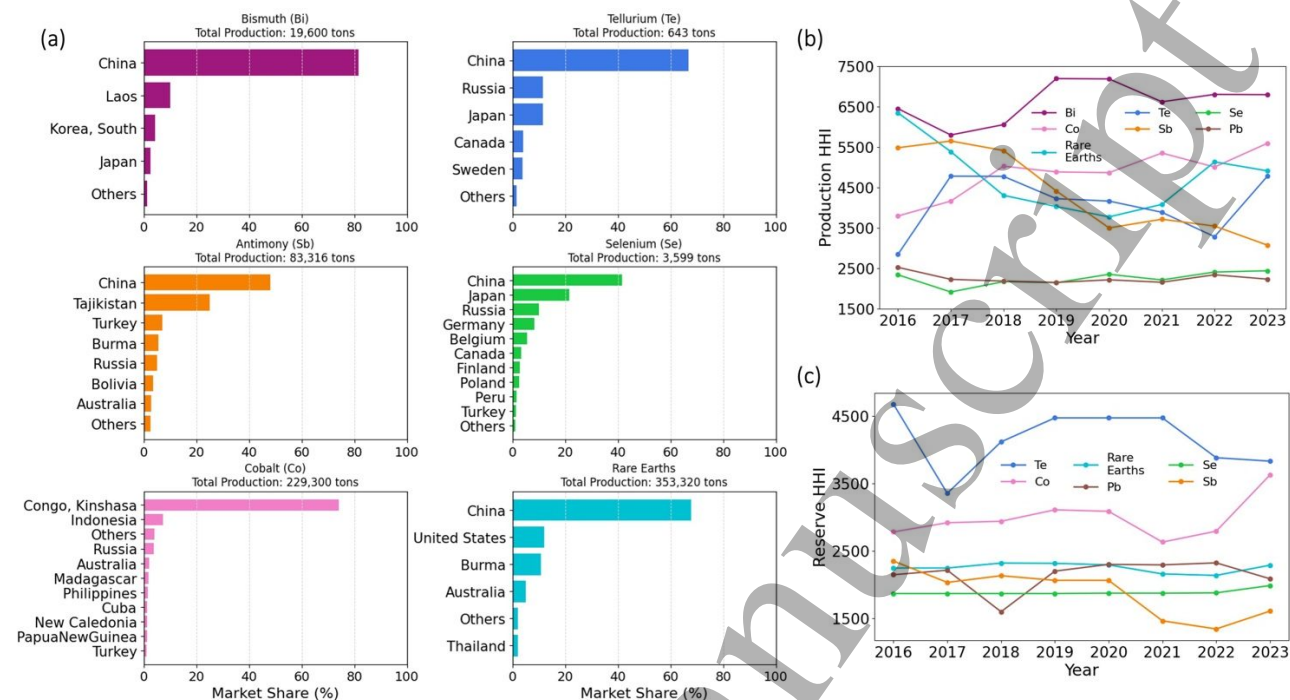


Figure 1(a) Production Market share in 2023 for key thermoelectric elements. (b) Production HHI; and (c) Reserve HHI for these elements from 2016 to 2023, all based on USGS Mineral Commodity Summaries. Note: Bismuth reserve data is not available in the USGS sources.

Advances in Science and Technology to Meet Challenges

Several strategies can be employed to address the resource issues associated with the production and use of thermoelectric materials. These strategies aim to reduce dependency on scarce, expensive, or geopolitically sensitive materials, thereby enhancing thermoelectric technology's sustainability and economic feasibility. These strategies can be broadly categorized as:

Environmentally Friendly Material Substitution: Recent trends in thermoelectric materials are shifting towards environmentally friendly substitutes that minimize ecological impact while maintaining high performance for sustainable energy applications. Alternative thermoelectric materials such as silicides (e.g., Mg_2Si , $MnSi$), sulfides (e.g., Cu_2S), tetrahedrites (e.g., $Cu_{12}Sb_4S_{13}$), Mg_3Sb_2 , Fe-based full-Heuslers (e.g., Fe_2VAl), and half-Heuslers (e.g., $TiNiSn$) have gained attention due to their elemental abundance, non-toxicity, and lower environmental impacts [2-3, 8-10]. The key constituent elements of these materials, like Cu, Fe, Mn, Ni, Sn, and Ti exhibit reserve HHIs below 2500 [7], indicating moderate market concentration and reduced supply risk. Moreover, elements like Mg, Al, S, and Si are abundant in the earth's crust, supporting the sustainability of these materials. However, these are not readily accessible in all locations, e.g. leading to Mg, Al and Si to appear in EU and UK critical materials

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lists. Unlike traditional thermoelectric materials that often rely on scarce and toxic elements like tellurium or bismuth, these alternatives provide a viable alternative for developing safe and widely applicable thermoelectric generators [2-3, 8-10].

Recycling and Recovery: Critical for sustainability, advanced recycling and recovery methodologies are especially important for elements like tellurium, antimony, and bismuth. Electrochemical recovery methods have been effective in extracting high-purity metals from by-products such as spent electrolytes [11]. Moreover, the potential of hydrometallurgical methods and innovative approaches like bioreduction for recovering tellurium from electronic waste highlights significant advancements in minimizing primary extraction and its ecological impacts, thereby fostering a circular economy within the sector [12].

Improved Material Efficiency: Enhancing the efficiency of how materials are used in devices can significantly lower the amount and cost of raw materials needed. Optimization of material usage through better manufacturing techniques that reduce waste during the production of thermoelectric materials [13], Design of thermoelectric devices that require less material by enhancing the material's intrinsic efficiency (zT), thereby lowering the total amount of material needed per unit of functionality.

Data-Driven Methodology: The lack of a comprehensive platform for visualizing the geographical distribution of resources complicates strategic decision-making. A data-driven approach is indispensable for identifying market concentration and trends in scarcity, informing strategic decisions in material selection and device design [1, 7]. Integrating advanced data analytics and AI, such as large language model querying capabilities, can enhance the management and accessibility of thermoelectric material databases, supporting more informed and agile responses to market and resource changes.

Geopolitical Diversification: Reducing risks from geopolitical concentration involves diversifying raw material sources across multiple countries to spread economic and supply risks and investing in domestic production to stabilize supply and mitigate international geopolitical risks.

Policy and Regulatory Support: Government policies and international agreements can support sustainable practices in material sourcing and use. Incentives for sustainable mining practices and the development of green technologies. Regulations that encourage recycling and the use of environmentally friendly materials in technological applications.

Concluding Remarks

A holistic analysis that integrates both performance metrics and resource considerations is crucial for selecting viable thermoelectric materials for broad applications. While using scarce elements can drive high-impact innovations and deepen our understanding of material

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trends, their integration becomes critical in the design phase for technologies intended for widespread deployment. Hence, careful consideration of material availability and sustainability must ensure that the development of thermoelectric technologies does not exceed the ecological and economic limits imposed by scarce resources.

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1.2 Life Cycle Assessment of Thermoelectric Materials

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Status

With the rapid development of human society and the accelerated consumption of Earth's resources, there is an increasing urgency for humanity to focus on sustainable development. In this circumstance, sustainability has become a cornerstone of material science, particularly in developing functional materials, including thermoelectric materials for energy recovery. In the past few decades, pursuing high performance and low cost has been the sole goal, but the environmental impact has not attracted much attention. Besides, the meaning of sustainability is not strictly defined. Sustainable materials are often understood as materials made from abundant elements, for instance Sulphur [1]. However, even the most abundant resources are finite and will eventually be used up. Thus, the concept of sustainable thermoelectric materials needs to be explored to offer a broader understanding of sustainability. By examining thermoelectrics as an example, we aim to present a more nuanced perspective that goes beyond resource abundance to include recyclability, durability, and overall environmental impact. In this regard, life cycle assessment (LCA) is a good measure to take for the implementation of sustainability since it can evaluate the environmental impact of a material (or product) through every phase of its lifetime – from the production of raw materials to waste and recycling of the final material (or product). A general model system structure for LCA is shown in Figure 1. In this general model, the proposed comprehensive process modelling framework is structured on a bottom-up representation of individual processes [2]. System inventory, boundaries, and process chain connectivity are consistently established through defined input and output flows. The inclusion of quantitative data within each process description enables the analysis and visualization of relationships among flow quantities, material properties, impact indicators, and technical process parameters. Soleimani et al. employed the life cycle assessment tool *GaBi* v4.4 to evaluate inorganic, organic, and hybrid thermoelectric materials [3]. Their analysis revealed that inorganic materials generally exhibited significantly greater environmental impacts compared to the other two types. However, Bi_2Te_3 showed by far the lowest environmental impact among all the thermoelectric materials considered. In a related study, Kawajiri et al. applied endpoint modelling (LIME2) to perform a cradle-to-grave LCA of an automotive thermoelectric generator (TEG) heat exchanger [4]. While both studies provide valuable insights, their reliance on specific models and system limits their general applicability. Despite these efforts, LCA analysis in the thermoelectric materials community remains limited. A more integrated use of LCA can yield valuable insights into material sustainability and inform more responsible design and selection strategies.

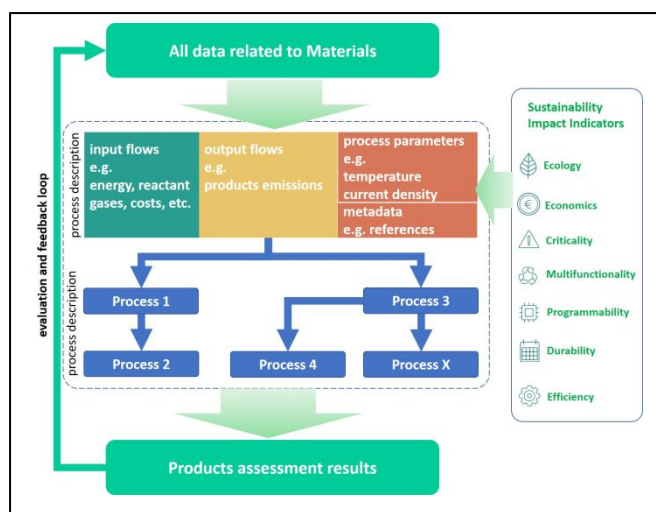


Figure 1. General model system structure for life cycle assessment (LCA).

Current and Future Challenges

LCA is a method for evaluating the environmental footprints of a product throughout its entire life cycle, in other words, from "cradle to grave". Generally, LCA includes four parts [5]. First, we need to define goal and scope, and to clearly outline the purpose of the assessment and define the boundaries of the analysis; second, we should have the Life Cycle Inventory (LCI), which means to collect data on all inputs (raw materials, energy, etc.) and outputs (emissions, waste, etc.) for each stage of the product's life; third, we need to carry out the Life Cycle Impact Assessment, in which we need to evaluate the environmental impacts of the LCI data; and last we need to interpret and analyze the results to identify areas of significant environmental impact and potential for improvement. Let's take commercial Bi_2Te_3 -based materials/modules as an example. A sketch of the lifecycle of Bi_2Te_3 -based materials/modules is shown in Figure 2. To carry out an LCA analysis on the Bi_2Te_3 -based modules, all information regarding mining, transporting, synthesizing, cutting, polishing, coating, plating, assembling, application, and end of life (waste or recycle) needs to be inputted into a certain model. One of the primary challenges of LCA analysis lies in collecting complete, accurate and reliable data that all processes involved. Data availability and quality significantly influence the credibility and resolution of the LCA outcomes. The system we are facing is highly dynamic. For instance, bismuth can be obtained from different mining resources; the energy consumed for mining processes can be obtained from traditional thermal power plants, nuclear power plants, solar power plants or mixed; the transportation of all resources can be in different or mixed ways; and there are several ways to deal with the end-of-life products. All those variables can change the LCA outcomes.

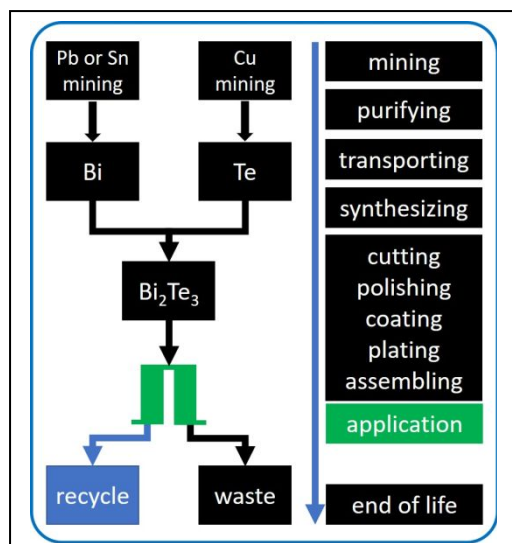


Figure 2. The sketch of the lifecycle of Bi₂Te₃ modules from the mining of raw materials to the end of life

Advances in Science and Technology to Meet Challenges

To address the challenges associated with conducting reliable and comprehensive LCAs for thermoelectric materials/modules, several approaches can be taken:

1) Building standardized databases. All data on energy use, emissions, synthesizing and industrial processes need to be collected and calculated in a uniform way. Several established databases, such as Ecoinvent and the U.S. LCI Database, already provide valuable resources, but broader and more harmonized data coverage is still needed. The European Union's implementation of the Digital Product Passport (DPP) in 2024 is a promising development. It aims to enhance transparency across product value chains by providing detailed information about each product's origin, material composition, environmental footprint, and end-of-life instructions [6]. Integrating DPP data into LCA databases may significantly improve data reliability and accessibility. Collecting DPP information can be a good approach for setting up the standardized database. Artificial intelligence tools can further support efficient data acquisition and maintenance.

2) Process modeling and simulation combined with machine learning and digital twin. Simulation-based process modeling can estimate energy and material flows when empirical data are scarce. Tools such as MATLAB allow for quantitative predictions of environmental burdens associated with various processing steps. When coupled with machine learning [7–9], these models can forecast impacts for novel materials or process conditions. Digital twins—virtual replicas of physical systems—enable real-time environmental monitoring and optimization [10,11]. Integrating digital twins into LCA frameworks allows for dynamic assessments that reflect real-world variability, thereby increasing accuracy and adaptability in environmental performance evaluation.

Concluding Remarks

LCA analysis is a necessary approach to be taken when sustainability needs to be considered for designing thermoelectric materials and modules. To carry out a reliable LCA, a large amount of detailed data is required, including information on material composition, energy consumption, emissions, and other factors that influence environmental performance. The accuracy and completeness of this data directly affect the quality and credibility of the assessment.

Traditionally, the efficiency of thermoelectric materials has been measured by the figure of merit (ZT). However, ZT only considers thermoelectric performance without factoring in the overall environmental impact and sustainability of the materials. By incorporating LCA into the ZT calculation, the sustainable aspect of thermoelectrics can be evaluated. Therefore, we would like to define a sustainable $ZT_{\text{sus}} = S_{\text{LCA}} * ZT$, where the S_{LCA} is the sustainable parameter obtained by the LCA analysis. In the ideal case, S_{LCA} can be normalized such that $S_{\text{LCA}} < 1$, $= 1$, and > 1 represent negative, neutral, and positive environmental impacts, respectively. We are aware that the S_{LCA} is affected by many parameters and is not yet well-defined. Our approach here is intended to spark further discussion, as we hope researchers in the thermoelectric field will not only focus on improving material performance but also consider the sustainability factors behind that performance.

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1.3 Efficient Synthesis and Processing

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Status

Life cycle analysis establishes essential sustainability benchmarks for thermoelectrics, yet material limitations remain a key barrier. Despite decades of research across diverse compounds, only select systems have achieved commercial viability. This gap between theoretical potential and practical application drives ongoing processing optimization while reducing its associated environmental impact. A very large number of materials, including intermetallics, ceramics and polymers, have been investigated as potential thermoelectrics. However, only a limited number of these materials have found commercial application, those being mostly constituted by Bi-Sb-Te[1] based materials for applications up to 150 °C. Other thermoelectric materials have found more limited applications where higher operating temperatures (>400°C) are required, such as PbTe based materials, and Si-Ge for more niche applications in radioactive thermoelectric generators (RTG) for space exploration. However, an ever increasing number of materials are being investigated based on compounds with a broad range of elements and diverse crystal structures, from very simple rock salt-based materials like SnSe [2], to MnSi with its spiral ladder structures with very large unit cells [3]. While most thermoelectric devices consist of n- and p- type legs in series, there is a growing interest in thick and thin film devices with different architectures, which are covered in other sections of this review. All of this means that a wide range of processing routes and conditions have been used to prepare thermoelectric materials and devices.

Current and Future Challenges

The commercial Bi-Sb-Te materials are largely produced using the Bridgman technique. The method is not versatile and does not lend itself to many materials of current interest, as it requires materials that melt congruently. The precursor elements are first melted and mixed in a rocking furnace. The solidified and granulated materials are then refined into large crystals with preferred orientation in vertical Bridgman furnaces in which a molten boule with a seed crystal is slowly solidified in a temperature gradient. The materials are then cut along favourable orientations to maximise their thermoelectric conversion efficiency along the direction of thermal gradient in application. A major downside of these materials and this processing route is the relatively poor mechanical properties. The reason for this is that their layered crystal structure contains tellurium layers held together by weak Van der Waal forces [4], and as a consequence they are easily cleaved. This not only leads to mechanical failure of devices, but also poor machineability, which can lead to high levels of rejection of machined legs and significant waste. To overcome these issues, there is increasing interest to form

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3 composites with hard nano-inclusions, such as silicon carbide or boron carbide. Just small
4 amounts of nano-inclusions (<1 mass%) can significantly increase their hardness and fracture
5 toughness. This is achieved by limiting the grain size and thus increasing the grain boundary
6 density of the materials, and the nano-inclusion acting as dispersion hardeners and crack
7 deflectors. Another approach is the sintering of powders to make polycrystalline materials
8 with higher fracture toughness because of the presence of grain boundaries deflecting
9 cleavage. Additionally, there is growing interest to extrude n-type materials to produce bulks
10 with highly preferred orientation to optimise their anisotropic properties [5].
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15 Newer materials, investigated in small quantities in laboratories, are often prepared by
16 melting in sealed quartz tubes. This is a good route for producing high-quality, single-phase
17 materials for characterisation. However, it is not a scalable processing route. With the
18 increasing interest to develop materials that are ecofriendly and sustainable, and able to
19 operate at higher temperatures, the favoured ways to prepare small quantities in laboratories
20 is sintering. The method is versatile and the conditions for producing dense and single-phase
21 materials can be quickly optimised. The precursor powders are first mixed by ball milling. In
22 the case of materials with weaker bonding and lower melting temperatures, like sulfides [6],
23 nearly single-phase materials can be produced by mechanochemistry. The powders can be
24 highly amorphous, disordered and mechanically internally strained, all of which make the
25 materials more sinter active. Following sintering, the secondary phases often disappear, and
26 the main phase becomes highly ordered and crystalline. In the case of materials containing
27 similar high melting temperature elements with low vapour pressure, arc melting and
28 solidification can provide a suitable step to produce the target compound, which can then be
29 ground down into a powder. In the case of high melting temperature materials like oxide
30 ceramics, the oxide precursor powders can be mixed by ball milling. A further high
31 temperature (<1000 °C) calcining step is required to form the target phase by solid state
32 diffusion and reaction. A great advantage of the ball milling and sintering route is that it can
33 then be easily scaled-up and commercialised.
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43 The sintering can take place pressure-less in conventional furnaces after cold compaction of
44 powders, with atmospheric control if needed. The use of hot-presses enables further
45 densification. In the last twenty years there has been increasing use of field assisted or Spark
46 Plasma Sintering (SPS) furnaces that allow direct heating of conductive dies, usually made of
47 graphite, to achieve high heating rates (>50 °C/min), combined with pressure, enabling rapid
48 densification. Their use has been promoted by the desire to make fine grained and
49 nanostructured materials to increase phonon scattering, thus reducing thermal conductivity.
50 This is possible not only through the high heating and cooling rates that are achievable, but
51 also the ability to monitor the compression ram displacement. This enables the optimum
52 temperature for densification with minimal grain growth to be determined. The technique
53 also has the advantage that the minimal times spent at high temperature reduces the loss of
54 volatile elements. In materials with anisotropic crystal structures, particularly layered
55 compounds, they can be sinter-forged to produced preferred orientation and anisotropic
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properties. The technique has been successfully used to produce textured bismuth tellurides, further demonstrating the versatility of the sintering route [7].

Advances in Science and Technology to Meet Challenges

More recently developed, emerging processing techniques, summarized in Figure 1(a-c), are well-suited for processing thermoelectric materials. These methods prevent thermal decomposition by either employing ultrafast heating or, conversely, relying on low or minimal heating[8].

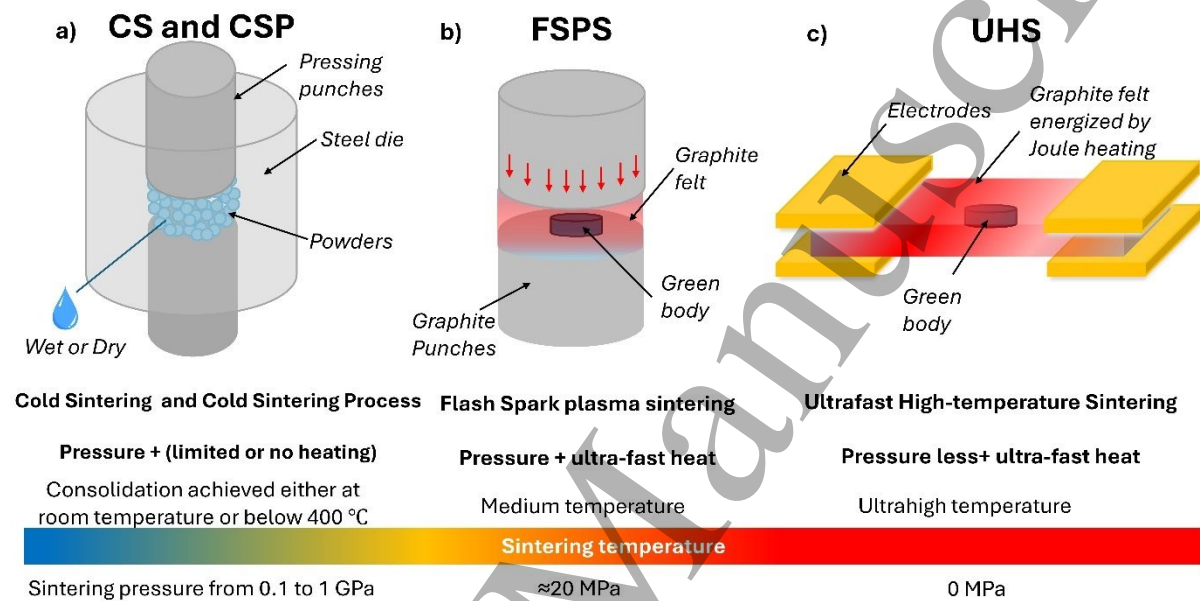


Figure 1: Emerging strategies for processing thermoelectric materials, including (a) Cold Sintering (CS), (b) Flash Spark Plasma Sintering (FSPS), and (c) Ultrafast High-Temperature Sintering (UHS). These methods exhibit an inverse relationship between sintering temperature and applied uniaxial pressure. A common feature among them is processing under far-from-equilibrium conditions: (i) ultralow temperatures in CS that inhibit thermally activated diffusion, and (ii) the ultrafast nature of FSPS and UHS, which prevents undesirable kinetic effects such as grain growth, thermal decomposition, volatilization, and defect annihilation typically observed in conventional sintering processes.

The low-temperature consolidation approach, illustrated in Figure 1(a), is known as Cold Sintering (CS) when performed under dry pressing conditions, or as the Cold Sintering Process (CSP) when moisture-assisted consolidation is used. This method enables the compaction of thermoelectric materials at temperatures well below 400°C. In some cases, for layered Van der Waals bonded semiconductors [9], complete densification is achieved through interplanar slipping even at room temperature under uniaxial pressure as low as 100 MPa. The room temperature processing has been demonstrated to induce a high density of defects contributing to ultra-low thermal conductivity, approaching the theoretical limit, in the case

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of bismuth telluride [10]. Regarding CSP, the use of an appropriate solvent can effectively contribute to a grain boundary cleaning effect as reported in the case of Ag₂Se [11] where thiol-amine (TA) as a liquid medium was employed. The appropriate selection of solvent plays a dual role in the cold sintering process: i) it facilitates surface particle cleaning, leading to the removal of undesired oxides; and ii) it enhances creep, supported by the role of the transient liquid phase. A useful review of the application of cold sintering for the green processing of thermoelectrics has recently been published [12]. On a wider perspective, CSP opens up new opportunities in design novel composition as it enables the integration of organic materials without incurring in thermal degradation [13]. A more recent innovation in sintering has been flash sintering shown in Figure 1 (b), in which electrically conductive materials, particularly semiconductors, can be directly Joule heated without the need for conductive dies, leading to increasing and rapid heating (>1000 °C/min).

In 2010, Rishi Raj and colleagues introduced flash sintering[14], a process well-suited for electrically conductive materials, particularly degenerate semiconductors. These materials can be directly heated through Joule heating without the need for conductive dies, enabling rapid temperature increases exceeding 1000°C per minute. The process can be difficult to control and reproduce because of the high heating rates, with the maximum temperature controlled by limiting the current. The size of the sample that can be prepared ultimately only being limited by the maximum power available assuming a difficult to achieve volumetric power dissipation across the sample. The technique lends itself well to thermoelectric materials because they are electrically conductive but also, the rapid heating rates can beneficially induce disorder, dislocation plasticity and internal stress, which further increase phonon scattering. The application of the technique has been limited to small samples, typically bars with volumes on the order of a few tens of cubic millimeters or dog-bone-shaped specimens. To overcome these limitations a further development of the technique is Flash-SPS[15], in which a standard SPS is used without a die as shown in Figure 1(b). The arrangement simplifies and speeds up the processing cycle, only requiring the pre-sintered ceramics to be partially sintered to achieve sufficient strength to allow minimal contact pressure from the rams through which the current flows. A further development of this, hybrid-Flash-SPS, uses thin metal walled dies to overcome the need for pre-sintering. The process is quick and easily scalable. The technique was demonstrated for TiNiCu_{0.05}Sn based compounds [16].

A recent development on ultrafast processing includes Ultrafast High-temperature Sintering (UHS) developed in May 2020[17] (Figure 1 c). The ultrafast sintering kinetics is aimed at accelerating densification while minimizing undesired effects associated with exposure at high temperature. These include grain growth, thermal decomposition, volatilization of elements with high vapour pressure and annihilation of defects that promote phonon scattering. The technique is well suited for n-doped Mg₂Si [18], and dense bulks with relative densities >95% were obtained in a firing cycle lasting less than one minute. The ultra-short processing time contributes to minimal energy losses resulting in energy savings well above 90%[19] compared with competitive sintering techniques. Since the technique is compatible

with a wide temperature range, up to 2000°C, it may be well-suited for fabricating a variety of thermoelectric compositions.

Despite significant research interest in novel processing techniques aimed at reducing energy consumption while enabling the fabrication of otherwise unattainable materials, limited data exists on the energy consumed during thermoelectric fabrication. This is especially true when considering industrially scaled up fabrication of thermoelectric devices. Indicatively, our recent work suggests energy consumption as low as 0.2 MJ/kg for cold-sintered bismuth telluride-like materials a reduction of 50 to 100 times compared to conventional furnace sintering requirements. A lesser reduction in consumed energy is also anticipated for consolidation using ultrafast firing techniques as result of the short exposure time contributing to reduced energy losses.

Concluding Remarks

There are a number of emerging new sintering techniques that could provide advantages and unique opportunities in terms of microstructure engineering compared to established methods. At the same time these techniques may also deliver reduced processing costs and energy consumption.

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1.4 Novel routes – Additive Manufacturing

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Status

Thermoelectric energy conversion has attracted significant interest across various fields due to its distinctive ability to directly convert heat into electricity and vice versa [1]. This functionality has led to diverse applications, such as generating power from waste heat in nature and multiple industries and Peltier cooling for active refrigeration [2,3]. Thermoelectric devices are constituted by p-type and n-type semiconductors, which are conjoined to form a thermocouple configuration. The traditional device fabrication process involves multiple steps including the synthesis of p-type and n-type materials, their subsequent dicing, metallization, and assembly on substrates [4]. This conventional methodology encounters limitations, especially with respect to form factor, as the production of complex geometries beyond cubic structures is not feasible via a top-down dicing approach in the context of mass production. In recent years, three-dimensional (3D) printing has been recognized as an alternative for the fabrication of thermoelectric materials and devices on a bulk scale [5]. This innovative method affords considerable versatility in the morphological and dimensional customization of thermoelectric materials, thereby enabling the creation of devices with customized designs. Furthermore, the printing process can offer potential to reduce the processing cost for the fabrication of thermoelectric modules owing to lower energy input and a simplified assembly process. Despite recent advances, this technology is still in the early stage of development, and further advancements in terms of material and device efficiency as well as manufacturability are required to industrialize this promising technology. In this roadmap the current status, future challenges, and perspective in the field of 3D printing for the thermoelectric materials and devices are briefly reviewed.

To date, various 3D printing methods have been employed in the fabrication of thermoelectric materials. These techniques include direct ink writing [6], fused deposition modelling [7], selective laser sintering [8], and aerosol jet printing [9]. Among these, direct ink 3D writing has undergone extensive investigation and has been utilized for a broad spectrum of materials, ranging from low-temperature operable Bi_2Te_3 and BiSbTe [6,10–13], to intermediate temperature operable PbTe [14], AgBiSe_2 and AgSbTe_2 [15], and extending to high-temperature operable tin selenide [16] as shown in Figure 1. Moreover, owing to the unique advantages of the 3D printing process, the feature size of a single thermoelectric leg can range from approximately $100\ \mu\text{m}$ [6] to several centimeters [14,15,16]. Furthermore, the 3D printing process offer the potential for complex 3D geometrical configurations of thermoelectric legs within devices, thereby opening new avenues for the tailored design of thermoelectric module structures [17,18]. Notably, this enhanced design capability, when

combined with computational thermal design, optimizes the energy conversion efficiency of the devices, overcomes the intrinsic efficiency of the materials under specific environmental conditions.

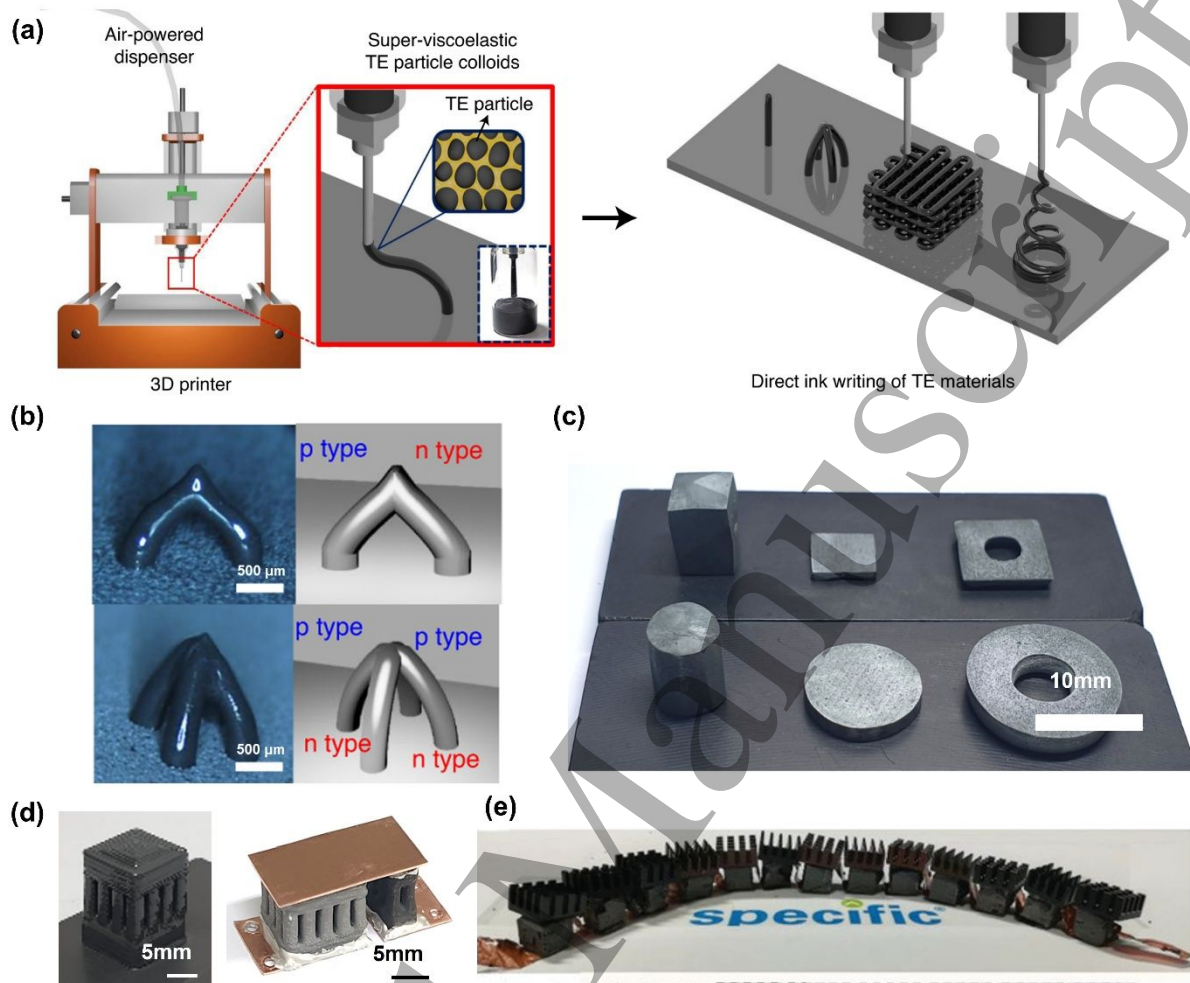


Figure 1. (a) Scheme of direct ink 3D writing for fabricating thermoelectric materials [6]. (b) Bi₂Te₃-based [6], (c) PbTe-based [14] 3D-printed TE materials. (d) ternary silver chalcogenide-based [15] and (e) SnSe-based 3D-printed TE devices [16].

Current and Future Challenges

In the context of material synthesis via 3D printing, the efficiencies of thermoelectric (TE) materials fabricated through this method, as denoted by their ZT values, have generally not reached the levels attained by conventional techniques such as hot pressing or melting. Typically, a long post-sintering process is imperative to obtain robust thermoelectric materials from the printed objects, necessitating specific sintering conditions that are pressure-less and below the melting point to preserve the integrity of the designed 3D structures. Furthermore, the integration of additives or alterations to the particulate composition of the inks is essential to ensure the 3D printability. Unfortunately, these alterations can detrimentally impact the microstructures of the materials, thereby degrading their thermoelectric performance. Considering the enhancement of thermoelectric properties of materials is

contingent upon the sophisticated engineering of atomic defects and microstructures during the fabrication stage, identifying an appropriate 3D printing-based synthesis approach remains a significant challenge. Recently, the Son group reported the enhancement of ZT values up to 2.0 for the 3D-printed Cu_2Se -based material as shown in Figure 2(a) [18]. In this material, the optimized sintering condition allowed to create numerous stacking fault defect that scatters phonons effectively and thereby reduce thermal conductivity significantly. Also, the Zhang group reported a room-temperature ZT value of 1.3 for the BiSbTe materials fabricated by the blade coating method (Figure 2(b)) [19].

The prominent function of 3D printing method could be unlimited design capability for the customization of component geometries. This capability is frequently harnessed in conjunction with various design tools aimed at refining structure-induced characteristics, encompassing mechanical, thermal, and optical properties. In light of the numerous efforts to computationally conceive non-cuboidal geometries of thermoelectric legs—geometries that are anticipated to yield superior energy conversion efficiencies than that of a cuboid—the 3D printing of thermoelectric materials presents an opportunity to fine-tune 3D architectures as shown in Figure 2(c), thereby enhancing device efficiency (Figure 2(d) and (e)) [18]. Nonetheless, this design paradigm has yet to be fully exploited in the optimization of thermoelectric devices. Further progress, integrated with 3D thermal design, is imperative to adapt it to diverse thermal environments. This stands in marked contrast to the mature domain of 3D printing within mechanical engineering, where diverse design tools have undergone rigorous exploration and have been applied to particularized applications over many years.

Another important challenge can be the manufacturing issue by 3D printing. Currently, the 3D printing process is utilized in the synthesis of thermoelectric materials, tailored to specific geometries. Consequently, the principal advantage of the printing process—its cost-efficiency in production—remains unrealized. To address this, the development of elementary processes, such as soldering, diffusion barrier deposition, and electrode patterning, is essential. These processes must be devised to seamlessly integrate with the 3D printing workflow, thereby actualizing the full potential of this manufacturing technique.

Advances in Science and Technology to Meet Challenges

To enhance the efficiency of 3D-printed materials, the development of an optimal sintering protocol to achieve material densification is paramount. The typical 3D-printed thermoelectric materials exhibit porous nature, which significantly influences their thermal and electrical transport properties. Addressing this issue can draw insights from the ceramic moulding industry, where ceramic slurries are cast and subsequently sintered under pressure-less conditions [20]. Within this perspective, the refinement of sintering promoters and the sintering process itself have been thoroughly established to yield fully dense ceramic components. These advancements serve as a foundational reference for implementing established strategies—such as nanostructuring and band convergence—into the field of 3D-printed thermoelectric materials, thereby enhancing their performance

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An alternative approach to elevating the thermoelectric performance beyond the intrinsic material efficiency is through the structural design of the thermoelectric legs within a device [15,17,18]. The Son group has recently reported several instances of 3D design and printing demonstrations for thermoelectric power generators [15,17, 18]. Their findings suggest that 3D structural designs of non-traditional, non-cuboid legs can amplify the temperature gradient across the legs, thereby enhancing the device's power generation performances. For instance, incorporating heat-dissipation design (Figure 1(e)) within the thermoelectric legs can increase the temperature difference across the leg, resulting in improved power generation efficacy [15]. Furthermore, the geometric design and 3D printing of Cu_2Se thermoelectric materials with an hourglass shape have demonstrated superior power generation by optimizing thermal resistance and heat dissipation characteristics [18]. These advancements present a novel avenue for decoupling the interdependent relationship between thermal and electrical properties in thermoelectric materials, ultimately boosting the overall energy conversion efficiency. Concurrently, the actualization of these design structures through 3D printing, in synergy with mechanical design principles, holds the potential to enhance the durability of thermoelectric devices against environmental vibrations and stresses.

The challenges inherent in module fabrication via 3D printing may be surmounted by employing existing technologies that involves the electrode patterning and connection. The effective integration of printing process into these processes could streamline the manufacturing workflow, thereby enhancing the cost-effectiveness of the production. Another way to solve these issues involves the advancement of the printing process for the creation of electrodes and diffusion barriers, which are integral to the 3D-printed thermoelectric materials (Figure 2(f)). Nonetheless, these are very challenging, as it necessitates the maintenance of printed layer stability against unwanted atomic diffusion or interlayer reactions during the high-temperature sintering stage. The progressive refinement of these foundational technologies is anticipated to boost the power conversion efficiency within the system and facilitate the commercialization of thermoelectric ink technology.

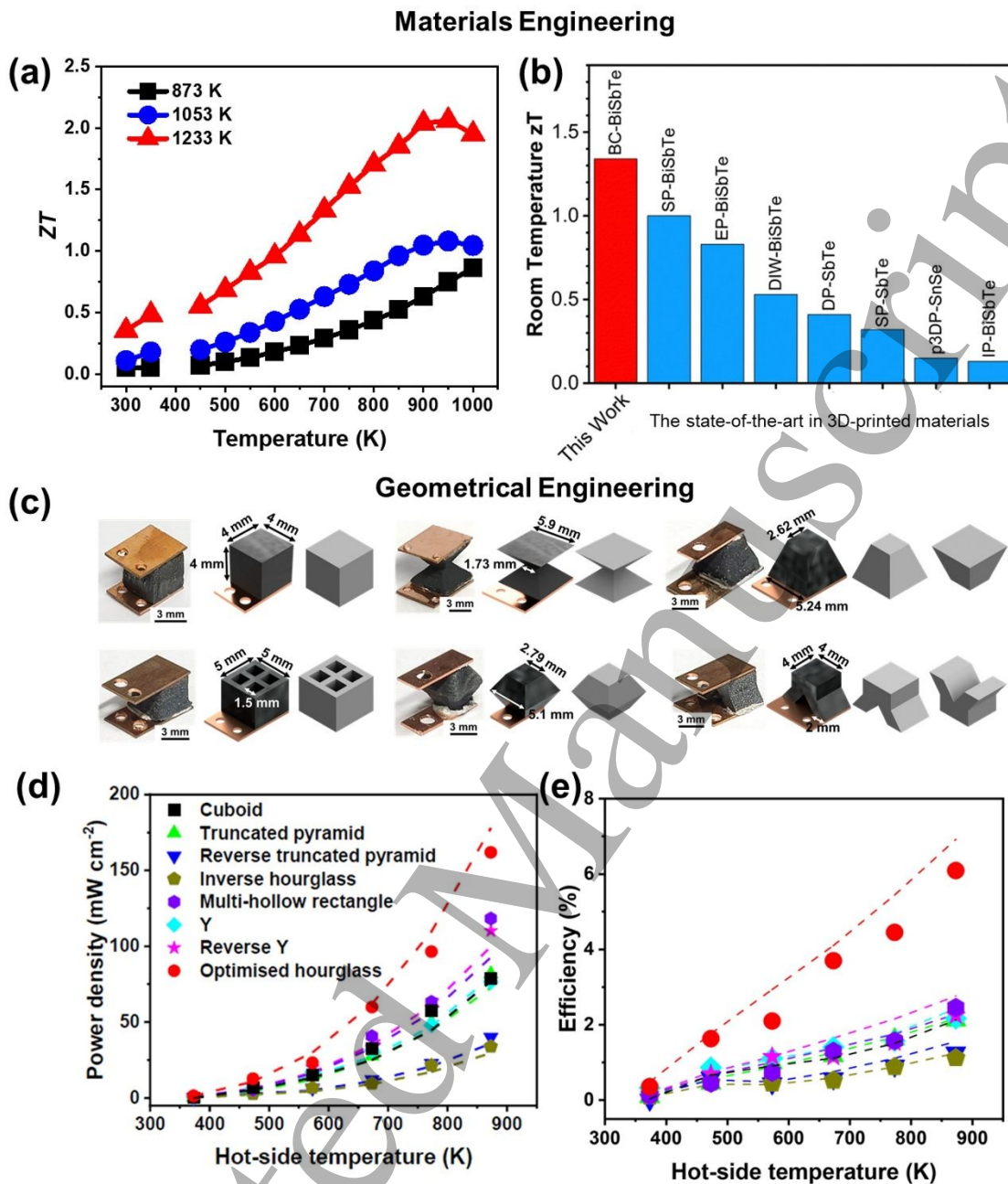


Figure 2. (a) ZT values of the 3D-printed Cu_2Se materials sintered at 873, 1053, and 1233 K [18]. (b) Comparison of room-temperature ZT between the blade-coated BiSbTe-Te sample and other p-type thermoelectric materials made with different ink-based processes [19]. (c) Photographs and 3D illustrated models of single-leg devices chipped with the 3D-printed Cu_2Se legs with various geometries [19]. (d, e) Power density and efficiency of the Cu_2Se -based single-leg devices shown in the panel (c).

Concluding Remarks

The advent of 3D printing methodologies for thermoelectric materials and devices has unveiled expansive research opportunities in academia in terms of the printing process,

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material synthesis, and device fabrication. Particularly, the research topics of the printing process combined with the ink development have actively been studied, successfully establishing the printing process as the new fabrication route for thermoelectric materials in the thermoelectric community. In contrast to traditional manufacturing techniques, 3D printing offers the distinct advantage of fabricating materials and devices with complex structures that are unattainable through conventional means. To further advance 3D printing processes to meet the standards of high-performance TE materials and devices, several critical research directions naturally emerge. First, enhancement of the ZT in 3D-printed materials is essential, as current state-of-the-art ZT values remain inferior to those achieved via traditional synthesis routes. Second, strategies aimed at improving device-level efficiency must be developed. This can be facilitated by leveraging the design freedom inherent to 3D printing, particularly through structural optimization for thermal management. Third, the demonstration of large-scale, manufacturable TE devices via 3D printing is necessary to validate its industrial feasibility. The research efforts to address these issues will not only enrich the fundamental understanding of thermoelectric materials and devices, but also accelerate the industrialization of 3D printing processes for manufacturing thermoelectric devices. I hope that this concise roadmap will contribute to charting the trajectory of future research in the 3D printing of thermoelectric materials and modules.

Acknowledgements

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1.5 Novel routes – Electrodeposition

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Status

Electrodeposition has emerged as a promising technique for the fabrication of thermoelectric (TE) materials as it offers several advantages over other methods: it operates at room temperature which minimizes interdiffusion and undesirable chemical reactions whilst providing precise control over morphology, composition, and crystallinity and enables the creation of shapes that are otherwise difficult or impossible to achieve. Its low equipment cost, lack of vacuum requirements, and material efficiency make it an economically viable option that can be scaled for industrial applications.¹ A wide range of TE materials from thin films, nanostructures to “bulk” materials and even miniaturised TE devices have been successfully fabricated using electrochemical approaches. To date a major thrust of research has been dedicated to the electrochemical fabrication of bismuth, antimony and lead chalcogenide compounds² which are TE materials that are known for their high zT figure of merit and have found application in commercial TE devices. Various strategies have been employed to enhance the TE performance in these materials which include the addition of additives such as surfactants and optical brighteners to the electroplating bath to regulate crystal growth³ and pulse deposition to grow thick and smooth films⁴⁻⁵ by controlling the deposition potential and pulse time. A summary of recent advancements in sustainable TE materials prepared by electrochemical techniques is presented in Table 1.

Table 1 provides a summary of current state-of-the-art sustainable TE materials that have been prepared by electrochemical methods.

Material	Nature of the material prepared	zT	Seebeck Coefficient (μVK^{-1})	Power factor ($\mu\text{WK}^{-2}\text{m}^{-1}$)	Measured temperature (K)	Ref
Ag ₂ Se	Thin film	-	-136	3421	RT	11
CuSbTe	Thin film	-	-382	2800	RT	15
Cu _{0.65} Ni _{0.35}	Nanocrystalline	6.1 x 10 ⁻²	-76 -39	8248 1673	~1000 RT	12
CoSb ₃	Thick film		222.75	558.17	-	16
In doped CoSb ₃	Thick film		-89.84	115.11	RT	3
Fe doped CoSb ₃	Thin film		57	832	RT	17
Ce doped Fe ₃ CoSb ₁₂	Thin film	0.6		>100	653	18

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CuSe	Thin film		+106	5.3	-	19
SnSe	Thin film		1000	5.8	~600	20
Cu ₃ (HHTP) ₂	Thin film		-121.4	3.15×10^{-3}	-	14
Ni ₃ (HITP) ₂	Nanostructured	1.19×10^{-3}	-11.9	0.833	RT	21

Current and Future Challenges

The ability to form materials into arbitrary three-dimensional geometries is a significant advantage of electrodeposition over other methods, contributing to its widespread adoption in nanotechnology. Due to its operation at low temperatures, electrodeposition is renowned for its ability to utilize templates to produce mechanically stable, high-density nanowires.⁶ To produce 3D geometries, the use of soft-templates has been reported.⁷ To date, there are only very few studies which demonstrated the improvement of thermoelectric efficiency of TE materials through dimension control and 3D conformality. The electrodeposition process is sensitive to the electrolyte composition, which must be chosen based on the material being fabricated. Compared to aqueous media, organic solvents (e.g., dimethylsulfoxide, DMSO) and ionic liquids⁸ (e.g., choline chloride–malonic acid mixture) have been employed displaying increased deposition rates due to improved solubility of metal ions, elimination of the need to coat the substrate to withstand aqueous acidic environments, and the ability to explore more negative overpotentials during electrodeposition without solvent reduction. Due to their non-flammability and high thermal stability, ionic liquids are emerging as one of the most promising green electrolytes for the electrodeposition of next-generation thermoelectric materials. Interestingly, ionic liquids such as trimethylamine hydrochloride (TMHC) also function as a structure directing agents, eliminating the need for templates⁹.

Advances in Science and Technology to Meet Challenges

Due to their toxicity and scarcity bismuth and lead chalcogenides need to be replaced with more sustainable TE materials that are composed of more abundant elements and recent efforts have therefore focussed on alternative materials. Selenides, in particular, are promising candidates due to their high power factor, low thermal conductivity, cost-effectiveness, and abundance compared to tellurides. Record-breaking figures of merit for TE performance have been achieved for materials such as tin selenide (SnSe),¹⁰ copper selenide (Cu₂Se), and silver selenide (Ag₂Se)¹¹. Numerous studies have defined and investigated electroplating protocols, yet only a few have included the characterization of thermoelectric properties. In 2021 Manzano *et al.* defined and investigated the electrodeposition of Ag₂Se and examined its thermoelectric properties. The chalcogenides of Sn, Cu, skutterudites, and clathrates have emerged as new high-performance TE materials for medium temperature range applications.² A recent study introduced CuNi alloys, with the highest figure of merit, as a new inexpensive and scalable material, suitable for industrial applications.¹² In 2015, the electrodeposition technique was adapted to fabricate perovskite films. Unlike other synthetic methods, electrodeposition successfully produced dense, uniform MAPbI₃ perovskite films with excellent coverage.¹³ The growing interest in thin film fabrication has led to extensive research on electrochemical deposition of thin film MOFs. Electrodeposition, capable of

producing multi-metallic MOF films, is emerging as a promising, economical, and reproducible method for developing MOFs in desired dimensions.¹⁴

Concluding Remarks

Electrodeposition studies have so far mainly focused on the fabrication of bismuth, antimony and lead chalcogenide compounds which are scarce and toxic whilst there are much fewer examples available that report the synthesis of more sustainable TE materials (cf. Table 1). Clearly there are a lot of opportunities available for using electrochemical approaches to fabricate these types of materials capitalising on the many unique benefits this technique offers. However, there are also many challenges ahead that need to be overcome such as e.g. adhesion to the underlying substrate to realise the full potential of electrochemical methods for the production of more sustainable TE materials for the next generation of TE devices.

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1.6 Module Fabrication

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Status

The most common commercially available thermoelectric modules are fabricated using bismuth telluride materials, aluminium oxide substrates and conventional solder techniques. Many of the fabrication processes (Fig. 1) still used today were first established more than 50 years ago [1] and have led to bismuth telluride modules seeing commercial success in thermoelectric cooling applications. However their commercial success in thermoelectric generation, where the potential market is larger, > \$1.5 Billion [2], has been more limited, restricted by their performance, cost and lifetime. While sustainability is often a later consideration, improvements in sustainability can enable cost reductions and more rapid scaling.

Newly developed bulk materials could unlock some of these new applications. However these new materials often require new fabrication processes, and so to enable a sustainable rapid scale up, it is crucial to consider sustainability in module production early in the development cycle. Current new bulk materials can utilise broadly similar fabrication steps to conventional bismuth telluride modules, although the process steps are often more complex. For example to enable higher temperatures, higher temperature silver based brazes for joining thermoelectric legs to interconnects are commonly used [3], and more complex multi-layer metallisation approaches on the ends of thermoelectric legs utilise sputtering or diffusion bonding [4] rather than electroplating.

It has been estimated that 30% of the global warming contribution and 20% of the resource depletion in a thermoelectric system is from manufacturing processes alone [5]. Module design also has a significant impact on the quantity of thermoelectric material used, with the material extraction step dominating with contributions of 60 and 70% respectively. However, little has been published focusing on improving the sustainability of module fabrication, likely due to the lower maturity and underdevelopment of research into module fabrication in comparison to thermoelectric materials [6].

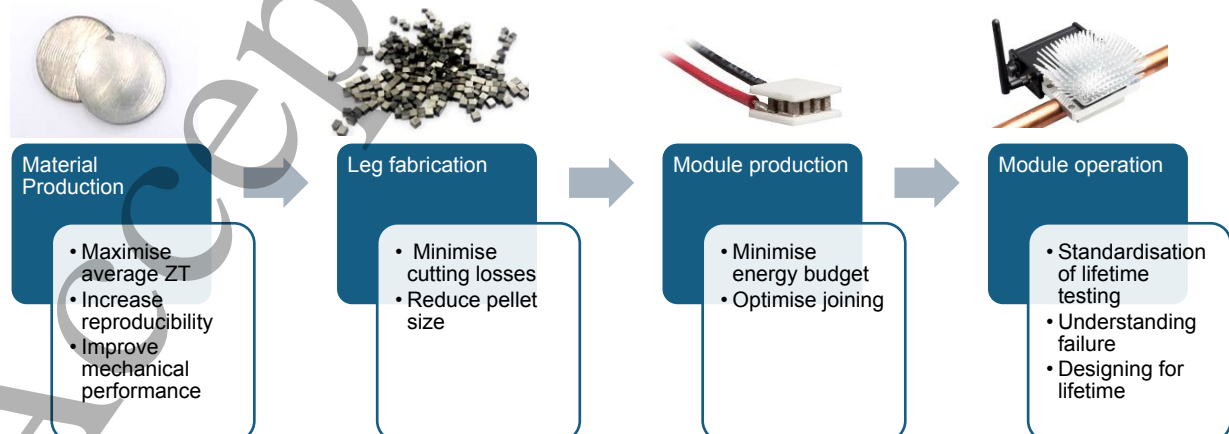


Figure 1. Module fabrication process and sustainability approaches at each stage.

Current and Future Challenges

To ensure more sustainable module fabrication, three aspects need to be considered:

1. Minimising thermoelectric material usage in module fabrication
2. Maximising performance and lifetime from the module, to maximise energy generation per unit of module production
3. Sustainability of module fabrication processes

Minimising thermoelectric material in current module fabrication processes requires:

- maximising the material yield by an often-neglected focus on the reproducibility of materials properties [7]
- minimisation of losses in subtractive processes such as precision cutting which can be as high as 30% [8].

Material usage can also be reduced through module design. Neglecting thermal and electrical contact resistances, both the electrical and thermal resistances of thermoelectric legs scales with the aspect ratio of the leg alone. Therefore shorter, narrower legs can be used to give equivalent performance while utilising less thermoelectric material. However to enable this approach, electrical and thermal contact resistances need to be very low [9], and the mechanical strength of the thermoelectric material must be sufficient to support both the same forces on a smaller total thermoelectric material cross-sectional area and the intrinsically higher thermal stresses from the shorter legs [10]. With the weaker research focus on the mechanical properties of TE materials, and the complex and application-specific loading conditions thermoelectric module experience in both fabrication and operation, it can be difficult to reliably predict the degree to which this approach can be successfully implemented. In addition, this requires moving to smaller thermoelectric legs, where cutting losses only increase.

Approaches to maximise the thermoelectric material performance are the focuses of other sections. Maximising the performance and lifetime of the module additionally requires highly thermally stable electrical contacts, with low contact resistances [9] e.g. $<50 \mu\text{Ohm}\cdot\text{cm}^2$, good thermal conductance and mechanical robustness. Simultaneously achieving all of these while utilising scalable, low-cost manufacturing processes is a difficult challenge, as great as producing the material itself. Long module lifetimes are required for both low levelized costs and high sustainability. The high potential temperatures of operation make this very challenging; for example a typical wear-out activation energy used for general electronic components (0.7eV) would predict that 15 minutes at 400 °C is equivalent to 100 years at room temperature. While actual activation energies will be different, for bismuth telluride modules an even higher temperature dependence of failure has been measured, so likely still gives an estimate of the scale of the challenge. There exists many failure mechanisms under a range of applications considerations, and limited standardisation of lifetime tests for high temperature modules makes comparisons more difficult, further complicating this task.

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Sustainability of module fabrication processes requires minimising high temperature steps and reducing additional materials usage. With potential application temperatures increasing, this can unfortunately require a corresponding increase in joining temperatures, for example moving from soldering to brazing processes, and thus reducing sustainability.

Advances in Science and Technology to Meet Challenges

Moving from subtractive to additive processes is one future approach to minimise material losses, as discussed further in Sections 1.4 and 1.5 of this article. Further advances in subtractive processes are also possible by minimising cut widths and maximising leg yield. This typically requires more focus on improving the mechanical properties of high-performance thermoelectric materials to enable high quality, high speed cutting without chipping [11, 12], but this area has seen much less attention than thermoelectric properties. The choice of which mechanical property metric to focus on can also be inconsistent (e.g. hardness, fracture strength, compressive/shear/flexural strength). Higher mechanical performance additionally enables a further push to smaller legs with the same aspect ratio, reducing material usage while maintaining performance.

Development of contacts has historically been largely empirical, as the underlying electrical and thermal stability mechanisms at the interfaces are complex. However, there is exciting initial work on approaches to select metallisation layers, through calculating interfacial reaction energies and energy barriers to migration [13], charged point defect formation energies [14], multi-step screening strategies [15] and high throughput experimental tests of interfacial reactions [16]. This may help accelerate contact development with its multiple difficult requirements. Development of suitable contact layers and scaling them into module demonstration remain a key future focus area to enable sustainable uptake of thermoelectric devices.

To minimise high temperature steps in fabrication requires us to break the link between joining temperatures and operating temperatures. Alternative joining approaches can be considered which utilise joining temperatures below the operating temperatures, for example solid-liquid interdiffusion bonding [17], also referred to as transient liquid phase bonding or sintering [18], which uses the rapid diffusion of a lower melting point material to form intermetallics with higher melting points. Sintering of Ag nanoparticles [19] can be used to make use of the size dependent melting point to form a joint at low temperature that is stable at higher temperatures, although often requires use of significant pressures during the sintering process.

Improvements in module lifetime require greater scale-up of module fabrication to produce sufficient modules to test, improved standardisation of testing to improve comparisons, and more investigation of options for rapid acceleration of these typically long terms tests, for example by initial testing through thermal shock [20].

Concluding Remarks

Module fabrication is a crucial step to enable sustainable thermoelectrics with the application reach to merit the sustainability focus. Electrical contacting and joining approaches remain as key bottlenecks, so new approaches for systematic investigation and methods to accelerate this work for future materials should be key areas of focus. In addition, process and design optimisation to minimise process temperatures and material use and wastage are promising areas. This requires improvements in the mechanical properties of thermoelectric materials. Increased understanding of the failure modes of thermoelectric modules alongside standardisation of lifetime testing are necessary to support and expand efforts to boost module lifetime. Such approaches when combined have the potential for significantly more sustainable thermoelectric development, making an impact through real-world applications.

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1.7 Upcycling waste for sustainable thermoelectrics

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Status

Upcycling waste materials for thermoelectric (TE) material synthesis is emerging as a sustainable solution to the rising demand for energy-efficient technologies and agrees with the circular economy action plan of the European Union [1, 2] (Figure 1). Over the past decade, significant advances in high-performance TE materials with zT values exceeding 1 or even 2 have largely relied on high-purity precursors, which are costly and resource-intensive. With global sustainability priorities intensifying, interest is shifting toward waste or recycled materials for TE synthesis, targeting three primary areas:

- **Recycling Bi_2Te_3 :** Widely used in ambient-temperature TE applications, Bi_2Te_3 production suffers from inefficient utilization, with less than 50% of feedstocks effectively used due to the material's poor mechanical properties. This results in substantial waste, including an estimated 48 tons of tellurium (Te) and 50 tons of bismuth (Bi) annually [3]. Both Bi, designated as a Critical Raw Material, and Te, one of Earth's rarest elements, face significant supply chain risks, as they are primarily by-products of other metal processing. Recycling Bi_2Te_3 waste is therefore essential for reducing environmental impact and costs.
- **Photovoltaic (PV) Silicon Waste:** The expanding PV technology generates considerable silicon waste. With PV modules' 30-year lifespan, global PV waste is projected to reach 8 million tons by 2030 and 80 million tons by 2050. Around 30% of the cost of PV modules is attributed to silicon wafer production, with 40% of silicon feedstock lost as kerf during cutting—an estimated 100,000 tons of silicon waste annually, valued at \$2 billion [4]. Repurposing these silicon particles for TE applications offers an effective means of value recovery.
- **Utilizing Mineral Waste for TE Synthesis:** Rather than relying on complex synthesis, naturally occurring minerals from waste sites are being explored for TE materials. P-type thermoelements using discarded sulfide minerals, such as those in the tetrahedrite-tennantite series found in copper mine tailings, offer a promising alternative to tellurium-based ones. These minerals, abundant in certain mining wastes, pose environmental risks but hold significant potential for TE applications [5].

While TE technology can tolerate some impurities, allowing the use of lower-purity materials like metallurgical-grade silicon, the industry still relies on high-purity precursors due to excessive impurities often found in waste materials, which exceed the tolerance levels for efficient TE performance. Bridging the gap between the potential of waste-based materials

and their practical applications is crucial to advancing sustainable TE material production and fully realizing the benefits of waste upcycling.



Figure 1. Schematic of the upcycling waste for sustainable thermoelectrics.

Current and Future Challenges

The industrial adoption of waste materials and recycling of thermoelectric (TE) materials face considerable present and future challenges. Although research in this area shows promise, scaling these practices beyond laboratory settings remains difficult due to several key obstacles.

Firstly, until recently, lax regulations allowed the disposal of industrial waste, such as silicon sludge and metallurgical slags, in landfills without requiring recycling. This regulatory gap limited incentives for companies to invest in recycling technologies. Additionally, TE technology remains a niche market with dispersed applications. Even for high-performance TE materials made from high-grade precursors, the limited demand for TE products has not driven large-scale upcycling efforts.

Another major challenge is related to conducting a comprehensive life-cycle analysis for TE materials and modules. Without clear data on degradation timelines, determining the appropriate time for recycling is challenging, creating uncertainty in end-of-life management and hindering recycling infrastructure development. Moreover, the variability in waste material properties, such as impurity levels in silicon kerf waste, complicates recycling

1
2
3 strategies. These differences, which vary by manufacturer, demand tailored recycling
4 approaches, making the process resource-intensive and technically demanding.

5
6 Ensuring consistent, high performance in TE materials synthesized from waste-based
7 precursors is another considerable challenge. Impurities in waste-derived materials often lead
8 to variable properties, affecting reliability and slowing commercial adoption. Recycling
9 valuable elements from TE modules also presents environmental challenges due to the
10 hazardous chemicals and high energy required. For instance, rare elements like Bi, Te, and Sb
11 are often purified with strong acids or bases, which can produce harmful waste by-products
12 and pose contamination risks. Additionally, energy-intensive recycling processes, which often
13 require high temperatures or specialized equipment, can result in a significant carbon
14 footprint, diminishing some of the environmental gains of recycling.

15
16 Moreover, most recycling research has focused on a limited range of materials, such as Bi_2Te_3 ,
17 magnesium, and silicon. However, new high-performance TE modules have emerged in recent
18 years such as $\text{Mg}_3(\text{Sb,Bi})_2$, Ag_2Se , *etc.* [6-9], and studies on their upcycling potential remain
19 sparse, leaving a gap in the knowledge necessary to expand recycling efforts.

20
21 Addressing these issues will require greener recycling technologies that reduce hazardous
22 chemical use and improve energy efficiency across a range of materials. This could involve
23 safer solvents, renewable energy integration, and optimized processes for lower
24 temperatures and increased material recovery. Such advancements would ensure that
25 reclaiming valuable elements from TE materials yields environmental benefits without a high
26 ecological cost.

27 **Advances in Science and Technology to Meet Challenges**

28
29 Addressing the challenges in upcycling waste materials for thermoelectric (TE) material
30 synthesis requires not only scientific and technological advancements but also a
31 multidisciplinary approach that integrates sustainable practices, innovative policy
32 frameworks, and cross-industry collaboration. To ensure scalability and minimize
33 environmental impact, several key areas of development are essential.

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35 The authors are currently involved in two ongoing projects, RecycleTEAM [10] and THERMOS
36 [11], investigating the recycling of elements such as Bi, Se, Te, Sb, and Ag. One approach
37 involves selective evaporation to separate elements from compounds (Figure 2), enabling
38 subsequent refinement through established processes. Another approach employs selective
39 oxidation, producing MgO , Sb_2O_3 , and metallic Ag from MgAgSb , followed by separation via
40 soft chemistry methods. Both strategies prioritize avoiding hazardous chemicals and
41 minimizing energy-intensive processes.

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43 To enhance the adaptability of recycling technologies, advanced techniques such as high-
44 resolution spectroscopy could be used for precise sorting of waste materials. This approach
45 would allow for tailored recycling processes that maximize the utility of specific waste streams.
46 For example, variations in silicon kerf waste from different manufacturers could be managed,
47 facilitating consistent TE material production from diverse, lower-purity sources.
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In materials science, innovations are necessary to ensure the reliability of TE materials synthesized from recycled precursors. A study by Honda *et al.* demonstrated that optimized doping in Mg₂Si-based materials can mitigate impurity effects, enabling comparable zT values between samples derived from 100% solar-grade silicon and those from 100% reused silicon [12]. Such strategies highlight the potential of recycled materials to meet performance standards.

Integrating life-cycle analysis (LCA) from the early stages of TE material and device development can offer insights into degradation patterns and support designs that are efficient and easier to recycle. This proactive use of LCA could inform material selection and process design, promoting sustainability and recyclability.

Additionally, expanding applications for TE materials with lower performance requirements could accelerate their industrial adoption. Applications that tolerate reduced performance, such as remote mini power generators for wireless sensors, could benefit from TE materials synthesized from recycled waste. These sensors, deployed in environmental monitoring, industrial automation, and agriculture, often prioritize longevity and low maintenance over high efficiency. By targeting applications that value durability and low maintenance, waste-derived TE materials can find viable uses, reducing costs and environmental impact while supporting sustainable technology integration.

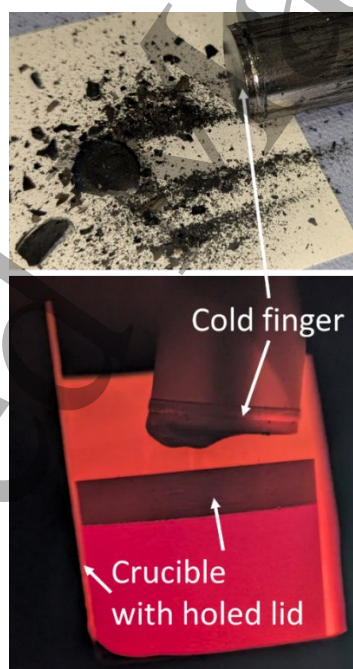


Figure 2. Tellurium-rich condensed phase (top) obtained by selective evaporation of a 50:50 mixture of n - and p -Bi₂Te₃ in a graphite crucible (bottom) and condensation in a cold finger (diameter 2.5 cm).

Concluding Remarks

The future of thermoelectric (TE) materials is increasingly intertwined with the ability to upcycle waste into high-performing, sustainable devices. While significant strides have been

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made in recycling TE materials like Bi₂Te₃, silicon kerf, and mining waste, these efforts are predominantly confined to the research stage. The transition to industrial-scale implementation faces substantial challenges, including the variability in waste material quality and the need for consistent performance in end products. To overcome these obstacles, advancements in adaptable recycling technologies, enhanced material science, and integrated life cycle analysis are essential.

Expanding the application of TE materials to scenarios that prioritize durability and low maintenance—such as distributed power generation for remote sensors—presents a clear pathway to broader adoption. These low-power applications can tolerate reduced efficiency, making them ideal candidates for materials derived from upcycled waste. As research continues to advance, these innovations hold the potential to significantly enhance the sustainability of TE technologies, driving the shift toward a more circular economy. In this emerging paradigm, waste is not merely discarded but transformed into valuable resources, heralding a new era of eco-friendly material science that balances performance with environmental responsibility.

Acknowledgements

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1.8 Data-driven design and discovery of thermoelectrics

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Status

Thermoelectrics have proved to be a popular target for computer simulations and modelling, this can partly be attributed to the fact that the components which contribute to the zT figure of merit, namely the Seebeck coefficient, electrical conductivity and thermal conductivity are all properties that are amenable to atomistic simulations. However, accurate determination of each of these components is computationally demanding, meaning that materials discovery from calculated properties on proposed materials remains a daunting task. In recent years machine learning (ML) has offered the promise of accelerating the prediction of these properties and hence facilitating computational discovery of new sustainable thermoelectrics.

The role of ML in modelling thermoelectrics is multi-faceted. As we outline in a more detailed perspective on the field [1], ML can contribute to speeding up electronic structure calculations, improving the accuracy of classical molecular dynamics, enhancing the efficiency of lattice dynamics, or by learning direct relations between composition, structure and thermoelectric properties. This is summarised in Figure 1a, which shows the different levels at which ML can participate in computational predictions.

ML has been applied to directly predict all components of zT , meaning that the ML model learns a direct mapping from the input (usually composition and sometimes structure) to the property of interest. Some of the earliest data-driven work developed a recommendation engine that provided confidence levels that different zT components fall within a desired range [2]. Since then there have been many studies that predict Seebeck coefficients [3], electrical conductivity [4] and thermal conductivity [5].

ML techniques can also be used to accelerate physics-based simulations for predicting these quantities. For example, ML algorithms such as Recursive Feature Elimination can help extract second-, third- and higher-order force constants from density functional theory (DFT) simulations in a supercell with random atomic displacements, reducing, by orders of magnitude, the computational effort involved [6]. Using these force constants to solve Boltzmann's transport equation for phonons allows the fast and accurate evaluation of lattice thermal conductivities for large families of materials (e.g. [7]). For strongly anharmonic solids, where lattice dynamics based on small ion position perturbations is not adequate, ML forcefields allow the prediction of thermal conductivity, to all orders of anharmonicity, via molecular dynamics and the Green-Kubo approach [8].

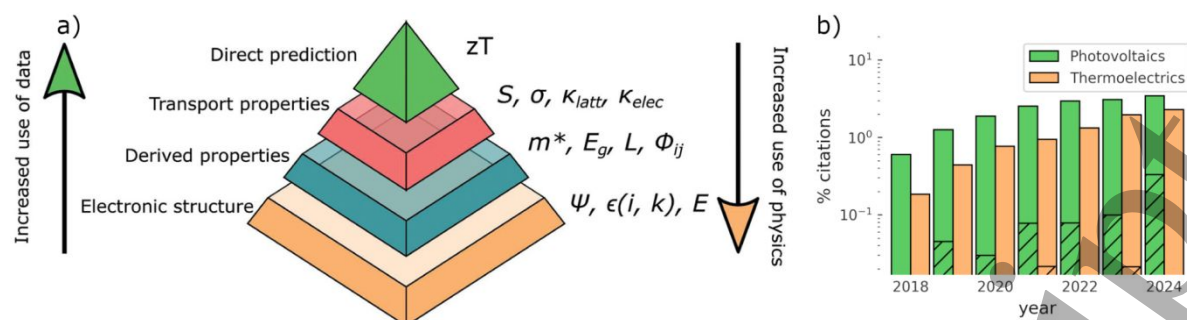
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Figure 1a) The hierarchy of levels at which ML is being used for thermoelectrics with methods using more data and fewer physical biases at the top and vice versa; reproduced from reference [1]. b) Publication data for ML in thermoelectrics and photovoltaics, normalised by the total numbers for each field, hatched areas denote number of publications using graph neural networks (note the abscissa is on a log scale).

Current and Future Challenges

Comparing the uptake of ML for design of thermoelectrics to other applications, an interesting trend emerges. The data in Figure 1b shows a comparison of ML usage in thermoelectrics and photovoltaics (PV is chosen as a closely related materials field). The plot shows the percentage of publications in each field which mention machine learning (specific Web of Science search terms were ‘thermoelectric machine learning’ and ‘photovoltaic machine learning’ vs ‘thermoelectric’/‘photovoltaic’). Superficially, both fields appear to have similar uptake; however when we look for a specific type of ML, graph neural networks (GNN) - the hatched areas - we see something different. GNNs are used in more than 25% of ML photovoltaics studies in 2024 (59/230), but in thermoelectrics they have negligible use. Why is this important? GNNs have become one of the standard ML approaches for materials modelling in recent years, because graphs are a natural way to encode materials’ structure. To some extent the availability of good materials descriptors for thermoelectrics might negate the need for GNNs, although the same might be said for PV. However, GNNs only outperform classical ML when large amounts ($\sim 10^3 - 10^4$) of labelled data with structures and properties are available [9]. This lack of uptake of GNNs for thermoelectrics signposts the biggest current challenge in ML discovery of thermoelectrics: lack of reliable training data.

There have been a series of efforts to develop datasets for thermoelectrics from both experiment and theory – see reference [1]’s Table 1. However, the experimental datasets are all significantly smaller than the sizes typically required for GNNs, or lack materials’ structure information. There are a number of theoretical databases [1], [10], and there have been some attempts to learn predictive models from this data with GNNs [3] and transformers [4]. However, these theoretical databases are only as reliable as the approximations upon which they are built. A comparison of data from [10] with experiment found that, while Seebeck coefficients were relatively well reproduced, power factors calculated under the constant relaxation time approximation (CRTA) do not capture experimental trends well ($r^2 = 0.33$) [11]. Another challenge is that most existing databases pertain to bulk properties and do not capture particle-size and interface effects, which are very important, since nano-structuring

is often employed to reduce thermal conductivity. Finally, doping effects are difficult to account for at DFT level, beyond the rigid band approximation, so theoretical databases provide only approximate data on doping. Some recent studies have demonstrated the potential of ML for predicting doping strategies [12], [13].

Advances in Science and Technology to Meet Challenges

The data scarcity problem can be addressed in two ways; (i) increasing the amount of high-quality labelled data available and (ii) increasing the data-efficiency of accurate predictive models.

Increasing data availability is a technical and a cultural challenge. Recent advances in high-throughput DFT workflows mean that carrier transport properties can now be calculated more accurately than under the CRTA [14], which should facilitate generation of more reliable theoretical data. There have also been recent efforts to develop databases and ML models for doping [15]. Experimentally, automated experiments have promise for generating highly uniform, well understood data [16], which can be of great value for training future ML models. However, we note that fully-automated materials synthesis and characterisation is still far from realised [17], and the role of human experts is critical in developing these processes. There is already a wealth of quality data published in the literature, but it is generally not easily available in a single location for training a model. Recent efforts in natural language processing mean that automated trawling of existing literature to generate structured scientific databases is now possible [18]. Arguably, more important than technological advances is a change in research culture to promote the sharing of data in easy-to-use formats. The FAIR data principles [19] set out a template of how research data should be shared; it is now imperative the sharing of data is incentivised and mandated, and that tools are developed to ensure good data practice is not a burden. To this end, efforts such as NOMAD offer immense promise [20].

There are several important developments that offer promise for training accurate prediction models on relatively small datasets. One promising approach is the inclusion of inductive biases in model construction, in such a way that the model must respect certain well-understood properties. A recent example of this in materials science is the development of equivariant neural networks, which enforce the symmetries of tensorial properties in predictions. These have been shown to drastically reduce the amount of training data required [21] and could be of use for both prediction of properties and for speeding up atomistic simulations. Another promising development is the advent of large language models (LLMs), which have recently found application in materials science [22]; of particular interest is the ability of LLMs to pretrain on large un-labelled datasets and then be fine-tuned for specific tasks on smaller datasets.

Concluding Remarks

Data-driven approaches are rapidly becoming an important complementary tool to the theory and experiments that have achieved so much progress in thermoelectrics in recent years.

Data-driven approaches promise to help discovery by speeding up simulations, guiding experiments and even predicting new, unexplored materials. However, we also preach some caution: it is unreasonable to expect that the ML-aided discovery of new thermoelectrics (or any material) is a solved problem. The role of expert researchers in the field is arguably more important than ever; as there are increasing numbers of newly-predicted efficient thermoelectrics, critical assessment of these findings is essential. We would also like to reiterate that the success of these data-driven approaches relies on the availability of open data and open software, none of this research would be possible without these resources. We would like to acknowledge those who generate this data and software and make it available; we hope that such crucial efforts will be more highly recognised in future. Although we are only starting to explore the role of data-driven approaches in thermoelectrics, if we get things right in the coming years, there is potential to achieve highly significant advances.

Acknowledgements

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1.9 Electronic transport modelling and simulations for thermoelectric materials

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Status

The simulations for electronic transport properties of thermoelectric materials typically involve density functional theory (DFT) to obtain a given material's electronic bandstructure. At first order, the number of bands and valleys, their effective masses and anisotropy, their symmetry and degeneracy, and the density of states (DOS) at the band extrema, provide an indication whether a material is promising for thermoelectrics, at least with regards to their Seebeck coefficient. In the case of alloys, for the prediction of their structure, especially under disorder, methods such as the virtual crystal approximation [1], the coherent phase approximation [2], or the special quasi-random structure (SQS) using software such as ATAT [3] are used. Linear scaling DFT codes such as ONETEP [4] or BigDFT [5], and other specialized codes such as DFTB+ [6], can then provide the modified electronic structure. Then for first order understanding, quantities such as the weighted mobility [7], and simple parabolic band models [8], are used due to their ease of use, assuming a reasonable value for the scattering relaxation times is provided. Traditionally, however, the main software that drives the evaluation of the transport properties is BoltzTraP [9]. It solves the Boltzmann transport equation (BTE) under the constant relaxation time approximation (CRTA), typically with relaxation time value $\tau_c=10$ fs. Due to the first-order independence of the Seebeck coefficient on the scattering details, this approach has driven the field for years. On the other hand, due to the arbitrary use of a τ_c value, quantitative results for the electronic conductivity and the power factor, or comparative performance studies between different materials, cannot be obtained accurately (for example materials screening or machine learning studies). With the remarkable advances in synthesis of myriad of new materials and their alloys, however, the importance of the simulation field has grown significantly for both electronic bandstructure calculations, and more importantly accurate transport evaluation. Transport simulations can identify promising directions for material investigations that guide experimental efforts effectively, but they can also provide deep understanding of the underlying processes that take place. The field of thermoelectrics has expanded even deeper into materials chemistry, band engineering, and areas of condensed matter and solid-state physics, with novel topological, spin, or magnon phenomena, being investigated. This makes further advances in theory and simulation of thermoelectric effects imperative to drive the field towards its next phase.

Current and Future Challenges

The imminent challenge in thermoelectric transport simulation research is to expand beyond the CRTA, by accurately and efficiently accounting for the different electron-phonon

scattering processes involved, to quantitatively and reliably access thermoelectric power factor performance. Unlike the carrier velocities and DOS (two of the inputs to BTE) which can be readily extracted from DFT, the scattering times (the other input to BTE) are much more complicated to obtain. They typically depend on different processes (electron-phonon, electron-impurity, electron-alloy, electron-boundary/defect scattering, etc.). Each process has its own energy, momentum, and temperature dependence as well. In general, they combine intra- and inter-valley/band processes with different strengths depending on the particular phonon, impurities or defects involved. Initial efforts to go beyond the CRTA included the energy dependence of the scattering rates, as in BoltzTraP2 [9]. Long-used models such as the Brooks-Herring for ionized impurity scattering, still find use and are considered accurate enough and computationally tractable. Electron-phonon scattering, on the other hand, is determined by interactions between electrons with phonons from the entire phonon spectrum of the material. An initial approach was to use deformation potential-based scattering rate expressions [10]. AMSET is a relatively new software which extracts approximate 'global' deformation potentials extracted from the band energy shift upon lattice deformation (as caused by phonons) [11]. However, the most accurate method for electron-phonon scattering involves the extraction of the matrix elements of the electron-phonon interaction. This is an extremely computationally expensive method which couples DFT with density functional perturbation theory [12]. Wannier interpolation to expediate the process has been implemented in the EPW [13], Perturbo [14], and Phoebe codes [15]. These computations are prohibitive for scaling to many material studies, because they require the extraction and post processing of an exceptionally large number of expensive matrix elements. An additional challenge is to expand such simulations for alloys. The alloy bandstructure is 'fragmented' and broadened, thus it's not clear how it can be used for transport calculations, or how scattering rates can be extracted reliably. Typically alloy scattering dominates electronic transport, but it is currently treated in a simplified manner, by considering the band edge variation of the constituent compounds. It is not clear how accurate this method is in general. Finally, a long-standing challenge is the treatment of boundaries and interfaces in transport simulations. These again affect transport strongly, especially for nanostructured materials, which is a main direction in thermoelectrics.

Advances in Science and Technology to Meet Challenges

To make the problem of accurate scattering rates tangible, still within fully ab initio considerations, a few methods have been developed recently that use fewer matrix elements and post process them in an efficient way. These are methods such as EPA [16], EPICSTAR [17], and ElecTra [18]. The details of each differ, i.e. EPA and EPICSTAR use a sparse matrix element grid in the Brillouin zone, whereas ElecTra uses very few matrix elements and extracts deformation potentials for all processes separately. Although these are computationally highly advantageous compared to full Wannier methods (see above), they are still very expensive for scaling or general use. (See Fig. 1 for a hierarchy of existing methods). An additional challenge is that the output still depends on the details of the DFT,

DFPT mesh discretization, as well as the matrix element number and choice, and convergence tests are typically computationally prohibitive. The computational cost is even amplified for materials with low symmetry and relatively large unit cells. Thus, in general, further advances are required in methods that make use of a limited, but highly relevant, number of matrix elements to extract electron-phonon scattering rates. Future methods should also hierarchise where possible the different scattering mechanisms based on their strength *a priori*, to direct the focus on more relevant computations. For example, the strength of electron-polar phonon scattering and ionized impurity scattering can overshadow the rest of the electron-phonon interactions [19], thus the extraction of many matrix elements might seem unnecessary and can be avoided. Then any methods and software could be advanced/modified to deliver deep insightful information that directly benefits experimental efforts (for example the relative strength between intra- versus inter-valley processes determines the efficiency of the band-alignment engineering). Typically, simulations hide this information and provide the overall 'result'. Any relevant software should be able to drive the field if it is automated at a degree that is user friendly to groups beyond the narrower computational ones. Beyond pristine material properties, methods to employ fully ab initio transport considerations with alloy bandstructures will be important in band-engineering optimization studies, as these exclusively involve alloys. Finally, real space transport methods such as non-equilibrium Green's functions could be advanced to provide interface transport details that would help understand transport in nanostructures. Note that a similar DFT+BTE process is followed in the case of thermal conductivity calculation, with codes such as Phono3py [20] and ShengBTE [21] been widely adopted.

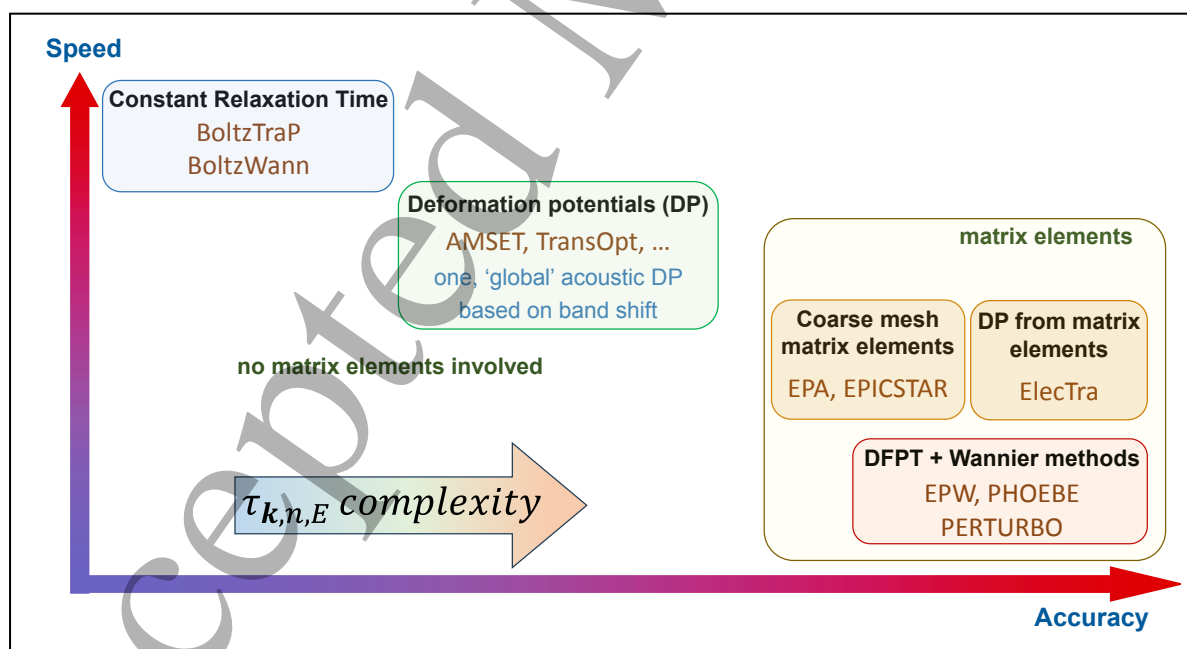


Figure 1: Hierarchy of existing electronic transport simulation methods and codes with respect to speed versus accuracy (with increasing relaxation time complexity)

Concluding Remarks

In conclusion, the large advances in the field of thermoelectrics, with the realization of a myriad of new materials and their alloys, dictate that robust and accurate computational approaches need to be readily available and easily used to drive the field into its next phase. The main difficulty in thermoelectric electronic transport simulations is the accurate evaluation of the scattering times of the many different processes, and especially the extraordinary computational challenges that the electron-phonon interaction involves. Approaches such as the constant relaxation time approximation that drove the field until recently are not anymore adequate, especially in the era of materials screening and machine learning studies which require accurate test sample results. The theoretical tools to extract scattering rates exist, but the computational complexity is tremendous. Methods are gradually emerging that reduce that complexity at different levels, which allow for the computation of transport from fully ab initio considerations. Nevertheless, for wider applicability, further computational simplifications are required to scale down the simulation time and scale up the number of material investigations, in addition to user-friendliness. Finally, more elaborate post-processing of computational outputs that will provide deep insight into the transport details and will allow for better materials engineering guidance.

Acknowledgements

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2. Materials

2.1 Bi₂Te₃ – near Ambient Materials

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Status

Development of near-ambient thermoelectric (TE) materials for operations near room temperature ($\approx RT \pm 100$ K) are playing a pivotal role in advancing sustainable thermal energy solutions, owing to their prospects for enabling waste heat recovery from low grade heat sources; reducing reliance on batteries for powering IoT (Internet of Things) and wearable devices; and providing eco-friendly cooling options.[1] For widespread adoption of TE technology, non-toxic and earth-abundant materials that exhibit a high thermal energy conversion efficiency (η), output power density, and long-term reliability is desirable. Interestingly, despite continuous advancements in materials design, and device fabrication for over several decades, Bi₂Te₃ and its solid solution alloys continues to remain the most widely used material in TE products, accounting for majority of the TE market share.[1, 2] At near ,RT, they exhibit high electrical conductivity ($\sigma \approx 10^5$ S/m) and moderate Seebeck Coefficient ($S \approx 150\text{--}200$ μVK^{-1}), owing to high band degeneracy, low effective mass, and high carrier mobility ($\mu \approx 150\text{--}500$ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$), resulting in a significantly higher power factor ($\sigma^2 S > 2 \times 10^{-3}$ $\text{Wm}^{-1}\text{K}^{-1}$) for both *n* and *p*-type conduction.[3–5] Thus, leveraging the Seebeck and Peltier effects, Bi_{*x*}Sb_{2–*x*}Te₃ (*p*-type) and Bi₂Te_{3–*x*}Se_{*x*} (*n*-type) based compositions with inherently low thermal conductivity ($\kappa \approx 0.5\text{--}1.5$ $\text{Wm}^{-1}\text{K}^{-1}$) showing peak TE performance near room temperature, as quantified using TE figure of merit(*zT*), i.e. $zT = \left(\frac{S^2\sigma}{\kappa}\right)T$.

Higher *zT* values > 1 in *n*-type and *p*-type compositions, respectively has led to an improved thermal efficiency (η) in power generation and higher Coefficient of Performance (COP) in refrigeration.[3–5] The longstanding limitation of inferior $zT \approx 0.5$ in *n*-type Bi₂Te_{3–*x*}Se_{*x*} that resulted in inefficient TE modules, has now been overcome and outperformed by development of cost-effective and high performance ($zT > 1.5@700\text{K}$) *n*-type Mg₃(Sb,Bi₂)-based Zintl compounds,[6–9] for near-RT applications, addressing sustainability concerns. Moreover, α -MgAgSb with minimized or replaced Ag content could serve as complementary or successor materials for *p*-type legs in modules, offering flexibility for performance, sustainability, and cost trade-offs.[9,10] Thus, developing all-Mg–Sb–based modules or hybrid Mg₃Sb₂–Bi₂Te₃ devices, leverages both performance and material sustainability.[9–12] Alternatively, Bi₂Te₃ based superlattice/thin films are pioneering innovations in microTEGs and wearable electronics.[13,14] Notably, Bi₂Te₃ based flexible films exhibiting power factors of 4.2 $\text{mWm}^{-1}\text{K}^{-2}$ (*p*-type) and 4.6 $\text{mWm}^{-1}\text{K}^{-2}$ (*n*-type) reported recently could accelerate

flexible TE energy harvesting applications.[10] Additionally, multilayer heterostructures of high performing Bi_2Te_3 , Ag_2Se , etc. or organic electrically conductive materials (i.e. conducting polymer and carbon materials) with inherent flexibility are being explored to synergise performance with stability and sustainability. Thus, integrated architectures with pairing for various surfaces and functionalities appear promising for sustainable TE adoption in the coming decade such as powering and regulating wearable electronics.

Current and Future Challenges

Mass deployment of sustainable TE systems requires exploration of earth-abundant materials and multi-scale application-specific modules architectures. Achieving high TE performance in Bi_2Te_3 and/or Mg-based analogues alongside mechanical flexibility (i.e. bending, folding, rolling, or stretching) is an ongoing challenge.[13,15] In the pursuit of modular optimization for sustainable TE, a key challenge remains in fully replacing both *n*- and *p*-type Bi_2Te_3 . Thus, extensive efforts adopt a transitional strategy that exploits material and process compatibility to attain functional convergence at both material and device levels. Here, we compare the high-performance Mg-based analogues with the commercially established benchmark Bi_2Te_3 to understand the applied and translational challenges.

- **Crystal Structure & Anisotropy.** Bi_2Te_3 crystallizes in a layered anisotropic structures, that can facilitate grain alignment, textured processing and directional tuning of thermal/electrical transport to optimize TE performance, albeit being detrimental to mechanical properties.[3,15] Decoupling nanostructuring approaches thus require precise control over the orientation or regulation of layered motifs. Moreover, anisotropy although enabling directional control in single crystals, poses challenges for scalability in sintered polycrystalline materials. Mg_3Sb_2 is not as anisotropic in nature and therefore has advantages for processing. The highly polarizable and weak van der Waals bonds within the structures has often led to strong lattice anharmonicity and consequently lower κ giving inherent advantages for high thermoelectric performance.[6–9]

- **Defect Chemistry & Stoichiometry Control and Scalability.** The Bi-Sb-Te and Mg-Sb system both require precise defect and composition control. While Bi_2Te_3 exhibits a narrow off-stoichiometric tolerance because of Te volatility and Bi/Te antisite defects,[3,4] Mg_3Sb_2 can be susceptible to Mg-vacancies.[6–8] In α -MgAgSb, phase transitions, Ag vacancies and disorder can strongly influence carrier type and mobility. Also, synthesis methods can introduce electrically active defects in polycrystals, potentially arising from charged defects at non-equilibrium grain boundaries or unknown impurities, further complicating the precise compositional control. Thus, defect-controlled doping strategies, scalable with optimized processing routes remains an innate challenge. Furthermore, adaptability challenges in flexible electronics are being explored through techniques such as bulk-thinning, deposition, paste casting, and template methods.

- **Complex Band Structure and Mixed Conduction Regime.** Bi_2Te_3 , a narrow-gap ($E_g \approx 0.15$ eV) indirect semiconductor and topological insulator with strong spin-orbit coupling and band inversion, displays high Seebeck coefficients and tunable *n*- and *p*-type transport owing

to its multivalley band structure at both conduction and valence band, which respond well to band engineering strategies.[3–5] In contrast, Mg_3Sb_2 and MgAgSb achieve high thermoelectric performance primarily in n -type and p -type forms, respectively, due to band degeneracy localized in either the conduction or valence bands.[6–9] Moreover, their wider band gaps effectively suppress bipolar conduction at elevated temperatures, favouring single-carrier transport. Thus, tuning complex band characteristics that regulates single-carrier regimes and exploring their interplay with topological states, remains an inherent challenge for optimising the electrical transport.

• **Sustainability and Cost-effective Alternatives.** Tellurium's scarcity raises concerns about long-term availability and cost in performance-dominant Bi_2Te_3 . As green alternatives, all-Mg–Sb–based modules are strategically robust sustaining supply-chain resilience and green electronics goals. Research is also underway to develop high-performance, cost-effective alternatives such as Zintl, Heusler (mostly Fe_2VAI), and chalcogenide compounds. Improving material efficiency, developing better recycling methods, and continuing research into alternative materials can thus address sustainability concerns. Deploying an all-earth-abundant TE systems for IoT, body heat, industrial waste, and autonomous electronics, thus remains a practical future challenge for sustainable TE adoption.

Advances in Science and Technology to Meet Challenges

Flexible and stretchable TE device designs with improved power density and thermal sensitivity, have garnered renewed attention for broader adoption of TE technology in low-grade heat harvesting. For instance, textile-based TEG using Bi_2Te_3 are enabling seamless integration into clothing.[16] Self-powered skin electronics, capable of energy harvesting and health monitoring are being developed, based on Bi_2Te_3 -based hybrid nanocomposites.[17] Alternatively, ductile inorganic semiconductors (such as Ag_2Se , InSe , Ag_2S)[18] and polymer nanocomposites (such as PEDOT:PSS, PANI)[19] are being explored for establishing functional and high-performance interfaces with the skin. Moreover, solution processing or printing methodologies have enabled reduction in cost of fabricating large-area TE devices. Recent advancements in entropy engineering, hierarchical architecture, doping, directional growth, texturing, nanocompositing, and defect engineering have significantly improved the regulation of electrical and thermal properties of both Bi_2Te_3 and $\text{Mg}_3(\text{Sb},\text{Bi})_2$ based materials.[3,10] To ensure long-term device stability above 473 K, low-resistivity barrier layers

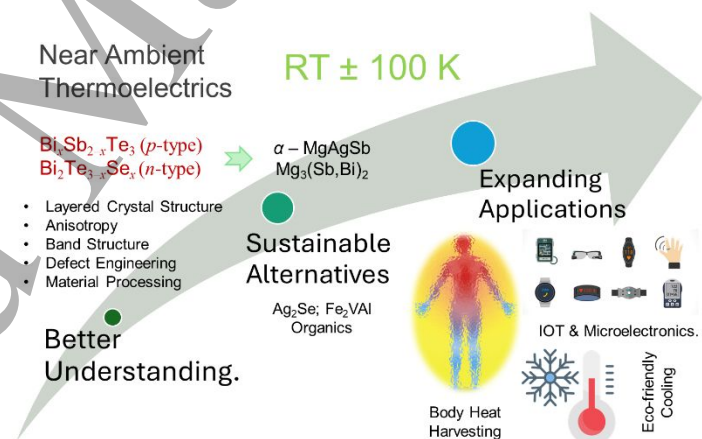


Figure 1. An overview of status of Near Ambient Thermoelectrics.

that meet the coefficient of thermal expansion (CTE) criteria, such as Ti, Fe, Co-P, FeCrNi, and Ni-based alloys, are being studied.[10,20] Simultaneously, in many cases integrating Mg-based materials as green alternatives into practical modules, have led to realisation of higher efficiencies at relatively low temperature differences ($\Delta T \approx 250$ K).[9,12] Currently, *n*-type $\text{Mg}_3(\text{Sb,Bi})_2$ and *p*-type $\alpha\text{-MgAgSb}$ are considered the most viable alternative for low-grade waste heat recovery ($\eta > 7\%$) using TE generators (TEG).[9–12] While inexpensive alternatives like *n*-type $\text{Mg}_3(\text{Sb,Bi})_2$ still face challenges in matching the scalability of Bi_2Te_3 -based materials, ongoing research continues to address concerns about the use of expensive elemental Te, structural instability above 523 K, and the relatively poor mechanical properties of Bi_2Te_3 -based devices.

Concluding Remarks

Despite challenges in material efficiency, scalability, cost, and power output, ongoing research and technological advancements hold promise for overcoming practical barriers and paving the way for broader adoption of TE devices in personalized cooling/heating, body heat energy harvesting, and powering wearable microelectronics. The inexpensive *p*-type alternative to match the performance of *n*-type $\text{Mg}_3(\text{Sb,Bi})_2$ counterpart will enable mass deployment of sustainable TE systems. Shifting the maximum *zT* to a higher temperature range (> 500 K) by suppressing bipolar conduction in *n*-type $\text{Mg}_3(\text{Sb,Bi})_2$ and *p*-type $\alpha\text{-MgAgSb}$ has enabled low-grade waste heat recovery, albeit material stability issues still need to be addressed. The underlying and coexisting topological nature along with the fascinating lattice dynamics, still makes Bi_2Te_3 an interesting material for both fundamental physics studies and potential applications in spintronics and quantum computing.

Acknowledgements

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2.2 Full-Heusler Alloys

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Status

Heusler materials are, in general, ternary alloys and compounds, where *d*-electrons dominate the electronic density of states (eDOS) near the Fermi energy. Thus, different ground states can emerge, attracting scientific and technological interest. Besides topological, magnetic, superconducting or heavy fermion properties, thermoelectricity gained specific inquisitiveness. This is mostly due to the exceptional mechanical, thermal and chemical stability of these materials, as well as the high thermoelectric power factors, which, in best-performing systems, are significantly above archetypal Bi₂Te₃-based systems. There are several sub-groups of Heusler compounds, and several crystal structures have been identified [1]. With respect to thermoelectricity, half-Heusler, XYZ, and full-Heusler, X₂YZ, alloys and compounds are the most important ones. Here, X and Y are transition metal elements, while Z represents a main group element. Properties and the thermoelectric performance of half-Heusler systems are discussed in a separate chapter of this topical review, while the focus of the present chapter is set on full-Heusler (fH) alloys and compounds, crystallizing in the cubic Cu₂MnAl structure (space group Fm-3m, no. 225). FH materials with a valence electron count $N_{\text{vec}} = 24$ (e.g., Fe₂VAl), are most promising with respect to thermoelectricity, since such systems exhibit a gap in the eDOS near the Fermi energy and appear to be non-magnetic. Positive or negative deviations from $N_{\text{vec}} = 24$ modify the electronic structure such that systems become either electron (for the former) or hole dominated (for the latter). Such modifications can be procured by substituting appropriate elements on all 3 sublattices of the Cu₂MnAl structure, offering outstanding tunability. While thermoelectric power factors of fH systems can be superior, the often intrinsically large thermal conductivity prohibits competitive values of the thermoelectric figure of merit. At present, the best thermoelectric performance of fHs reaches up to $ZT_{\text{max}} = 0.3 - 0.5$ around 25 – 100 °C, two to three times lower than archetypal Bi₂Te₃-based materials.

Table 1: Raw material prices of relevant thermoelectric materials, their annual production and the estimated global reserves. Prices are collected on July 15, 2024, from various marketplaces. The annual production and global reserves refer to the year 2023 and are revealed from the U.S. Geological Survey [2].

element	price/kg [US\$]	annual production [tons]	global reserves [tons]
Fe	~1.5	$1.5 \cdot 10^9$	$87 \cdot 10^9$
Al	~2.5	$3.9 \cdot 10^8$ *	$32 \cdot 10^9$ *
V	~25	$1.0 \cdot 10^5$ **	$19 \cdot 10^6$ **

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Sb	~22	$8.3 \cdot 10^4$	$>20 \cdot 10^5$
Bi	~10	$2.0 \cdot 10^4$	---
Te	~95	$6.4 \cdot 10^2$	$36 \cdot 10^2$
Sn	~34	$2.9 \cdot 10^5$	$43 \cdot 10^5$
Ni	~16	$3.6 \cdot 10^6$	$>13 \cdot 10^7$
Cu	~9.6	$2.7 \cdot 10^7$	$10 \cdot 10^8$
Ti	~6.5	$9.2 \cdot 10^6$ ***	$75 \cdot 10^7$ ***
Mg	~2.5	$9.4 \cdot 10^5$	sufficient for future use
Ge	~2800	$1.4 \cdot 10^2$	---

*...refers to bauxite; **...refers to ferro-vanadium 80%; ***...refers to ilmenite and rutile

The quest for sustainability of products and raw materials (compare Table 1) gains growing importance. The setup of a thermoelectric generator (TEG), with several different components (active thermoelectric alloys, diffusion barriers, contact layers, joining alloys, ceramic panels) requires sophisticated technologies and makes the recycling challenging. Much experience and knowledge already exist to reclaim pure elements from materials based on Fe, V or Al, which are - in part - base of high-performance steel. In 2017, about 35% of all raw steel produced worldwide, was fabricated by secondary feedstock [3]. Up to 50% of energy and up to 2/3 of CO₂ can be saved using scrap, in comparison to classical routes [4]. With respect to Bi₂Te₃, the US Geological Survey reports that there is no Te-based scrap available, from which secondary Te can be extracted, while about 5 to 10% of the US consumption of Bi is re-extracted from Bi-containing alloy scrap [2].

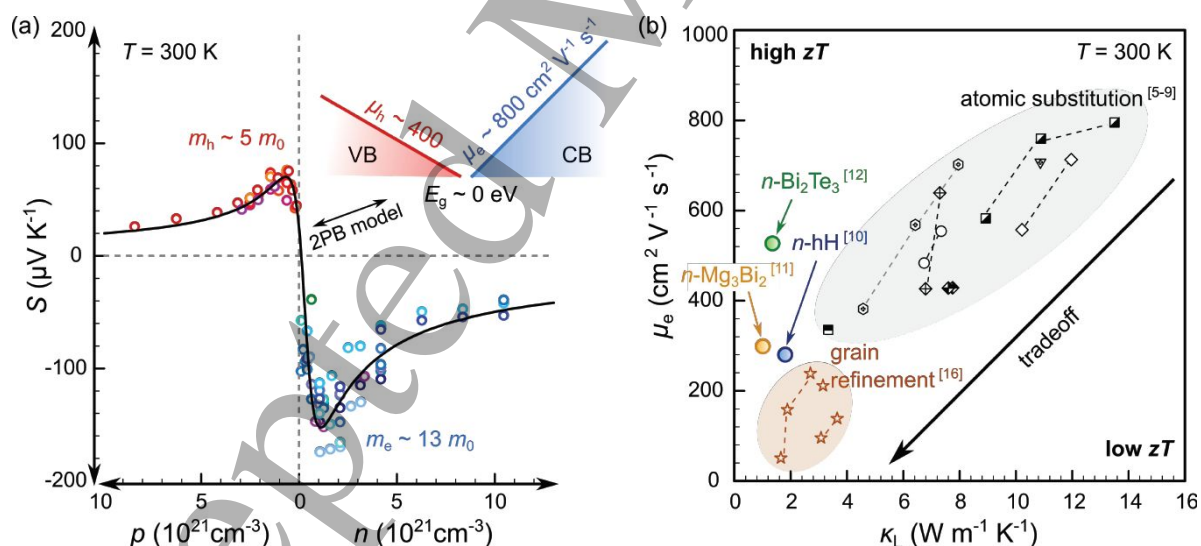


Figure 1: (a) Charge carrier density dependent Seebeck coefficient S of Fe₂VAI based alloys taken at $T = 300$ K. The open symbols are experimental data; the solid line is a theoretical prediction based on a two parabolic band model. The inset sketches the energy-dependent transport function near the Fermi energy for such full-Heusler alloys and indicates the respective weighted mobilities. (b) Weighted mobility of electrons as a function of the lattice

thermal conductivity for n -type Fe_2VAl -based alloys, together with other high-performance thermoelectrics at room temperature. Literature data were taken from Refs. [5-12,16].

Current and Future Challenges

Fe_2VAl -based full-Heusler compounds inherently meet several application-specific requirements, such as sustainability, stability, and cost-effectiveness. Moreover, as showcased in Fig. 1a, both n - and p -type materials are available with similar stoichiometries, enabling matching thermal expansion coefficients. Primary challenges in full-Heusler thermoelectrics center on enhancing the conversion efficiency of thermoelectric generators. Therefore, it is crucial to further optimize the dimensionless figure of merit ZT , especially for p -type compounds.

Fig. 1a displays the doping-dependent Seebeck coefficient of p - and n -type Fe_2VAl thermoelectrics from various substitution studies in the literature [13]. The black solid line is a theoretical calculation using a two-parabolic band model, as also employed previously by Anand et al. in Ref. [14]. The much larger density-of-states-effective mass and weighted mobilities of the conduction band electrons result in significantly higher thermoelectric performance for n -type Fe_2VAl thermoelectrics. Indeed, p -type Fe_2VAl rarely possess Seebeck coefficients exceeding $100 \mu\text{V}\cdot\text{K}^{-1}$, which implies that these materials cannot be competitive with state-of-the-art semiconductors, even in the unlikely case that the lattice thermal conductivity could be reduced to the amorphous limit, without deteriorating the weighted mobilities. Thus, it is essential to devise strategies which optimize the valence band electronic structure and enhance the Seebeck coefficient of p -type Fe_2VAl .

On the other hand, n -type Fe_2VAl -based materials already exhibit excellent electronic transport properties, with the weighted mobility $\mu W = 800 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$, being among the largest of any n -type semiconductor. This is highlighted in Fig. 1b, which compares μW and the lattice thermal conductivity κ_L of Fe_2VAl -based materials with Bi_2Te_3 and other leading materials. As obvious from Fig. 1b, the main challenge in Fe_2VAl -based materials lies in their large κ_L , attributed to their simple crystal structure and similar atomic masses of the constituents. Various strategies to reduce thermal conductivity have been explored, but they often result in a significant decrease in weighted mobility and ZT . Nonetheless, reasonably high ZT of up to 0.37 at 400 K have recently been reported for plastically deformed samples [15]. Reproducibility and large-scale production may, however, be an issue for such type of processing methods [16]. Thus, the crucial challenge remains: decreasing lattice thermal conductivity while maintaining favorable electronic properties, *i.e.* decoupling thermal and electronic transport.

Advances in Science and Technology to Meet Challenges

To bridge the gap between p - and n -type materials regarding thermoelectric performance, different strategies must be explored. As evidenced in Fig. 1a, simple carrier concentration

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3 optimization by doping is not sufficient to increase ZT in these materials. Instead,
4 modifications of the electronic structure of p -type Fe_2VAl materials are necessary. To this aim,
5 precise understanding of the band structure and chemical bonding within Heusler materials
6 is necessary. Density-functional theory (DFT) calculations are indispensable for this purpose,
7 as they reliably predict the electronic structure and stability. Combining these calculations
8 with efficient electronic transport modelling tools, can significantly advance our
9 understanding of substitution and alloying effects and will also be crucial for optimizing the
10 electronic structure of p -type Fe_2VAl . While several studies in this direction have already
11 found some success, vastly increasing the achievable values of the maximum Seebeck
12 coefficient in p -type full-Heusler compounds [17-20], there seems to be still room for
13 improvement.

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19 Significant progress in technology would involve enhancing the reliability and
20 efficiency of DFT calculations for disordered systems and materials with minor doping.
21 Currently, these calculations are time-consuming, hindering rapid progress. Additionally,
22 while extensive databases exist for stoichiometric compounds, there is a lack of
23 comprehensive databases for substituted or disordered materials. Compiling such data
24 systematically will be vital for understanding the effects of disorder and doping from a
25 theoretical perspective.

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29 The major challenge of reducing the large lattice thermal conductivity in Fe_2VAl has
30 already been the focus of many studies [5,7,9,15]. Achieving a breakthrough requires
31 methods to decouple lattice-driven thermal transport from electronic transport in these
32 materials. In half-Heuslers, using densification agents or phase-segregation of similar phases
33 has stabilized electronic properties while reducing thermal conductivity through
34 nanostructuring [11]. For full-Heusler compounds, similar or even more beneficial strategies
35 must be explored, and methods to integrate nanostructuring optimally must be developed.
36 Although high-pressure torsion has shown some success [15], it still leads to deteriorated
37 electronic properties. In a recent work [16], we have shown that by forming composites with
38 Bi-Sb alloys, which segregate at grain boundaries, charge and heat transport can be decoupled
39 and ZT can be improved dramatically above the values of the single components, i.e.
40 $\text{Fe}_2(\text{V,Ta})\text{Al}$ and Bi-Sb, resulting in record-high ZT up to $ZT_{\text{max}} = 0.46$ at 300 K. Further
41 overcoming the tradeoff between weighted mobility and lattice thermal conductivity in fH
42 requires a systematic understanding of multi-phase materials and grain-boundary scattering,
43 emerging as a hot topic in thermoelectric materials research. Tools to efficiently and reliably
44 predict the effects of various micro- and nanostructuring strategies would significantly
45 accelerate research and enable researchers to bypass this tradeoff.

Concluding Remarks

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55 Summarizing, full-Heusler compounds, specifically Fe_2VAl -based compounds, constitute a
56 very promising material class for sustainable thermoelectric applications. The non-toxic,
57 abundant and stable nature of the constituent elements, coupled with excellent recyclability
58 and simpler device structures, are key advantages. First stability tests on basic full-Heusler
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3 devices have demonstrated the excellent long-term stability of the materials in practice,
4 without any additional engineering [18]. Moreover, Fe₂VAl-based thermoelectric materials
5 exhibit auspicious electronic properties, with the weighted mobility close to room
6 temperature surpassing that of other state-of-the-art thermoelectric materials. If the lattice
7 thermal conductivity could be decreased while retaining the excellent electronic properties,
8 Fe₂VAl-based could become the best option for near-room-temperature thermoelectric
9 applications.
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15 **Acknowledgements**

16 The research in this paper was supported by the Japan Science and Technology Agency (JST)
17 programs MIRAI, No. JPMJMI19A1.
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2.3 Polymer composites

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Status

Polymers, polymer blends and polymer (nano)composites have attracted significant interest as sustainable thermoelectric (TE) materials due to their inherently low thermal conductivity, elemental abundance, high fracture toughness, low density and ease of processing [1], compared to traditional inorganic thermoelectric materials.

Despite these unique advantages, the generally low electrical conductivity and Seebeck coefficient of polymers can be fundamental limits to practical TE applications. To overcome these shortcomings, the use of conjugated polymers and/or suitable (nano)fillers (e.g. inorganic semiconductors like Te nanorods, Bi_2Te_3 , SnSe or nanocarbon) have shown potential in decoupling thermoelectric parameters (i.e. simultaneously increased Seebeck coefficient and electrical conductivity) and yielding improved power factors. The improved Seebeck coefficient in polymer composites has often been explained by the phenomenon of energy filtering [2], according to which an energy barrier can be created at the polymer/filler interface, allowing only high-energy charge carriers to cross the energy barrier while filtering out low-energy charge carriers [3]. The compatibility in the work function of constituents in polymer composites is important to achieve such energy filtering effect.

The best TE properties have been reported for poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/Tin Selenide(SnSe) [4] and polyaniline (PANI)/graphene-PEDOT:PSS/PANI/carbon nanotube (CNT)-PEDOT:PSS [5], with a ZT value of 0.32 (at 20 wt% SnSe) and a power factor of $2710 \mu\text{W m}^{-1} \text{K}^{-2}$ at 300 K, compared with ZT values of up to 1-2 for best inorganic TE materials (Figure 1).

The combination of polymer matrices and thermoelectric fillers can not only tune the thermoelectric properties but also regulate mechanical properties. Inorganic TE semiconductors are brittle and difficult to manufacture. It is a challenge to process them into flexible thin films or flexible thick thermoelectric generators. By dispersing inorganic TE materials as fillers into polymers, the resulting polymer composites exhibit enhanced mechanical properties (e.g. toughness), flexibility and ease of manufacture [6], particularly desirable features for broadening the TE application space to flexible and large area energy harvesting, with innovative TE device architectures.

Current and future challenges

Achieving a controlled dispersion of conductive fillers within a polymer matrix remains a challenge. Aggregation of fillers, particularly nanofillers, leads to poor electrical conductivity

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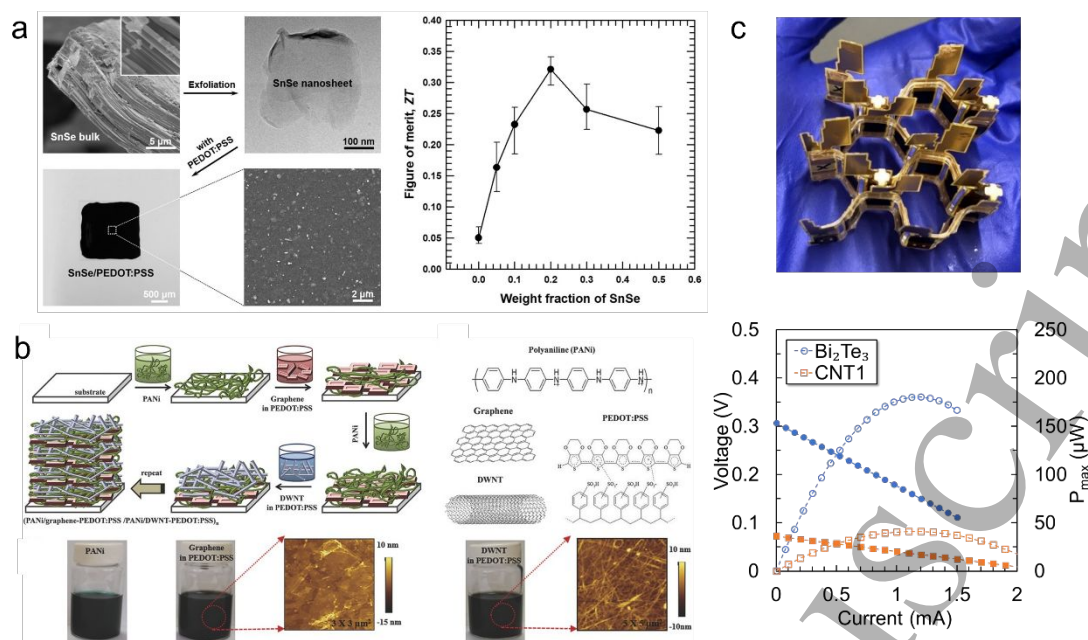


Figure 1 (a) Microstructures of SnSe and SnSe/PEDOT:PSS and ZT values for PEDOT:PSS/SnSe composites [4]. (b) Schematic illustration of layer-by-layer deposition for polymer composites fabrication [5]. (c) A self-folded thermoelectric device and its thermoelectric performance [7].

and mechanical properties. Furthermore, the interface between the polymer matrix and the filler plays a crucial role in the transport of charge carriers. Poor interfacial compatibility can result in high contact resistance and reduced thermoelectric performance. Moreover, the Seebeck coefficient of polymer/polymer or polymer/carbon nanostructure composites is still significantly lower than that of traditional inorganic materials (typically 35 - 120 $\mu\text{V K}^{-1}$ compared with 130 to 325 $\mu\text{V K}^{-1}$, for PbTe alloys, for instance), despite the significant recent improvements reported. Long-term stability and durability under high temperatures are essential for practical applications but remain challenging for polymer composites, since polymers are usually less resistant to high temperatures. It is also urgent to develop methods and techniques to accurately measure the thermal conductivity of, typically anisotropic, polymer composites along different directions (e.g. in-plane and through-thickness). Additional challenges are the difficulty of getting stable n-type polymer composites as well as the integration with components like heat sinks, which are bulky, rigid and heavy.

Advances in science and technology to meet challenges

Polymer composites have shown promise for thermoelectric power generation, yet significant challenges remain and will require a concerted and collaborative effort.

Functionalising the surface of conductive fillers can improve their dispersion in the polymer matrix and enhance interfacial compatibility. For example, the introduction of amino-

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3 terminated poly(3-hexylthiophene-2,5-diyl) (P3HT) on carbon nanotubes via covalent
4 grafting [8]. For the combination of polymer matrix and fillers, strong interfacial
5 interactions, including covalent bonding and ionic bonding, would be considered to provide
6 good charge carrier transfer and improved mechanical properties. Advanced process
7 techniques such as continuous melt extrusion or injection moulding can provide polymer
8 composites with homogenous mixing and bulk structures for thermoelectric applications.
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12 Numerous efforts have been made by researchers to process polymer composites, achieving
13 high thermoelectric power factors ($>100 \mu\text{W m}^{-1} \text{K}^{-2}$) [9]. It has been reported that
14 semiconducting carbon nanotube is a promising TE material with a high Seebeck coefficient,
15 and that polymer-carbon nanotube composites with interconnected conductive percolated
16 networks can reach good TE performance [10]. Controlling the order and orientation of
17 conjugated polymer chains as well as their doping is another effective approach to improve
18 their electrical conductivities and achieve high TE performance, particularly in combination
19 with nanofillers [11]. Despite the limited working temperature of polymer composites
20 (typically below $200 \text{ }^\circ\text{C}$), this is sufficient for applications like energy harvesting from hot
21 water pipes or the skin surface, for powering wearable electronics. From a different
22 perspective, TE polymer composites could also work in tandem with inorganic materials,
23 supplementing the poor low-temperature TE efficiency of typical inorganic materials.
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27 For n-type polymer composites, one possible promising approach is to disperse good n-type
28 (nano)fillers into polymer matrices, enhancing also the environmental stability of these
29 fillers.
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32 Some of the above challenges can also be met by designing new thermoelectric device
33 architectures, enabled by mechanical flexibility, toughness and ease of manufacturing of
34 polymers. For instance, a shape-programmed kirigami-inspired hexagonal honeycomb TE
35 device, with built-in heat sink, has been recently demonstrated (Figure 1.c) [7]. Such a
36 device architecture, applicable to both organic (e.g. CNT veils) and inorganic (e.g. Bi_2Te_3) TE
37 thin films, achieved a maximum voltage of 0.53 V and a power output of at $406 \mu\text{W}$ at a ΔT
38 of 47 K (in the case of Bi_2Te_3 with 76 p-n leg pairs) (Figure 1).
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45 **Concluding remarks**

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47 Polymer composites have attracted significant interest as thermoelectric materials. While
48 currently unsuitable for large-scale energy generation, due to the limited conversion
49 efficiency, polymer composites show great promise for flexible, self-powered and wearable
50 electronics. Researchers have demonstrated that good thermoelectric performance and
51 mechanical flexibility can be achieved simultaneously by exploring new module geometries
52 (e.g. sandwich or honeycomb structures). For a commercial breakthrough in wearable
53 power electronics (with targets of $\sim 1.5 \text{ V}$ voltage and $\sim 10 \text{ mA}$ current [12]), it is paramount
54 to extract high Seebeck coefficients from polymer composites.
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59 **Acknowledgments**

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2.4 Halide Perovskites

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Status

Two major problems that limit the sustainability of widely-used bismuth telluride thermoelectric materials are tellurium scarcity and high energy consumption for production. Halide perovskites (HPs) are a group of materials that with ABX_3 stoichiometry, where A is an organic or inorganic monovalent cation (e.g. $CH_3NH_3^+$, $NH_2CHNH_2^+$, Cs^+ , Rb^+ , K^+), B is a divalent metal cation (e.g. Sn^{2+} , Pb^{2+} , Ge^{2+}) and X is a halide anion (I⁻, Br⁻, F⁻, Cl⁻). Within this group of materials there are plenty of elementally abundant options with low toxicity. They can be prepared by low temperature methods from solution or by mechanochemistry, which limits their embodied energy. The potential of HPs as thermoelectric materials arises from the combination of good charge carrier mobilities and ultra-low thermal conductivities (typically ~ 0.5 W/mK), putting them in the group of “phonon glass electron crystals” with the potential for high values of the thermoelectric figure of merit (zT) or power factor.

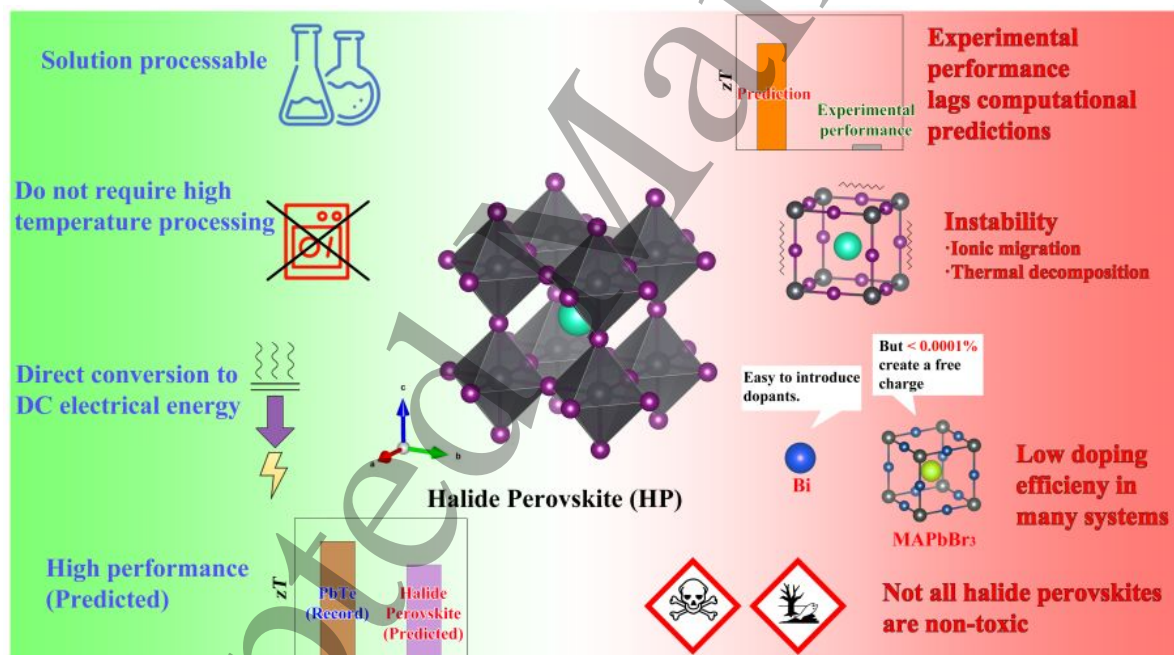


Fig. 1 Advantages and challenges of halide perovskites

The tolerance factor (t) determines which combination of anions and cations can form perovskites:

$$t = \frac{(r_A + r_B)}{\sqrt{2}(r_B + r_X)}$$

where r_A , r_B and r_X are the radii of ions located at A-, B- and X-sites for ABX_3 . Normally, t should be higher than 0.9 to ensure the perovskite structure is formed. Iodine at the X-site generally gives the best thermoelectric performances due to its ultra-low electric affinity, which provides highly delocalized electrons with high mobilities. Outside of this tolerance factor and stoichiometry, there are also more complex structural analogues, such as anti-perovskites, ordered and vacancy ordered perovskites [1]. Additionally, there are low dimensional analogues with 2D (layered), 1D (linear) and 0D (molecular cluster) features in their unit cells, giving opportunity for enhanced stability or lower thermal conductivity.

A series of theoretical calculations predict, for example, that $CsSnBr_3$ can have a zT of 1.0 [2], $MABl_3$ (MA = methylammonium CH_3NH_3 , B = Pb^{2+} or Sn^{2+}) are predicted to have zT between 1 and 2 [3]. The mixed halide HP, $CsPb(I_{1-x}Br_x)_3$, is predicted to have $zT = 1.7$ [4], whilst the low-dimensional $Cs_3Cu_2I_5$ perovskite derivative is predicted to have $zT = 2.6$ at 600 K [5]. Therefore, HPs have significant potential to become next-generation thermoelectric materials which combine high thermoelectric performance with sustainable composition and processing routes.

Current and future challenges

Experimentally recorded zT values of most HPs remain far lower than predictions, which is mainly ascribed to low electrical conductivities arising from insufficient carrier concentrations. Electronic structures of halide perovskites are often tolerant to defects and ionic compensation of charged defects can also occur [6]. Ionic compensation is a Schottky disorder with mobile ions that can neutralize the influence of configurational entropy of point defects and hinder charge carrier generation. In one example [7], crystals of $MAPbBr_3$ were doped with up to 15% Bi at the B-site but the carrier concentration only increased $\sim 10^{14} \text{ cm}^{-3}$ with a doping efficiency of just $\sim 10^{-5} \%$.

Another challenge comes from the large size of iodine anions, which make it quite difficult to find compositions with a qualified tolerance factor. Some unsustainable cations with large radii (e.g. Pb^+ , Cs^+) can be used to obtain stable structures, but systems with sustainable cations at both A-site (e.g. Cu^+ , K^+ , MA^+ (methylammonium), FA^+) and B-site (e.g. Sn^{2+} , Ge^{2+} , Zn^{2+}) need more study in thermoelectrics. Of these, organic cation-containing HPs, known as hybrid inorganic-organic perovskites (HIOPs) show some particular advantages. The anharmonicity that the organic A-site cation introduces into the lattice can widen the frequency range of phonons being scattered and decrease the thermal conductivity [8].

Instability under high temperatures is a further challenge that is important for sustainability. Even the most efficient TEGs can only be deemed sustainable if their lifetime is long enough to offset the materials and energy consumed (and emissions released) during manufacture. The tolerance factor can be increased by using organic cations at the A-site, but

these are quite volatile, forming cationic vacancies, and anions can use these vacancies to migrate, decreasing stability.

This is partially mitigated by using all-inorganic halide perovskites, however, anion loss becomes more important in these materials, and this can cause phase separation and carrier-hindering defects. A number of stabilization strategies have been developed for perovskite solar cells, including grain boundary passivation [9], film morphology control [9, 10] and high entropy approaches using multiple anion and cation substitutions [11, 12]. However, these have barely been explored in halide perovskite thermoelectrics.

Advances in science and technology to meet challenges

Despite some significant challenges to overcome, progress is being made in this field. For example, novel methods to increase charge carrier concentration (other than atomic substitution) have been developed. The electron-accepting dopant, F₄-TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) has been used to treat FASnI₃ films [13], increasing the electrical conductivity from 0.06 S·cm⁻¹ to 18 S·cm⁻¹ and achieving $zT = 0.19$, which is a record for the halide perovskites.

Compositional tuning is relatively easy in HPs and has several potential benefits. Increasing the ratio of MAI in MAPbI₃ or MABr in MAPbBr₃ can decrease trap density and increase carrier mobility by passivating ionic vacancy defects [14]. Compositional tuning by means of different precursor ratios during synthesis can also be used to tune HPs from n-type to p-type [15]. Only 1 at% of Cl⁻ dopant in CsSnI₃ can form a Cl-rich surface layer whilst enabling high zT . Ge²⁺ doping of CsSnI₃ at 20 at% Ge²⁺ increased lattice stability, reduce defect density and improved thermoelectric performance [16].

Thermal conductivity can also be tuned by diverse methods. Mixed halide CsSnX₃ with Br⁻ and I⁻ can decrease the thermal conductivity to 0.5 W·m⁻¹·K⁻¹ compared to the mono-halide at 0.8 W·m⁻¹·K⁻¹ [17]. Lower dimensionality can also contribute to decreasing thermal conductivity because of low group velocities and localization of vibrational energy.

These are quite soft materials, and the mobility of holes and electrons are predicted to be increased substantially with strain on an orthogonal lattice in CsPbI₃ [18]. In MASnI₃ powders shear strain is more effective than normal strain [19], while ionic substitution can introduce internal strain with similar effects [20].

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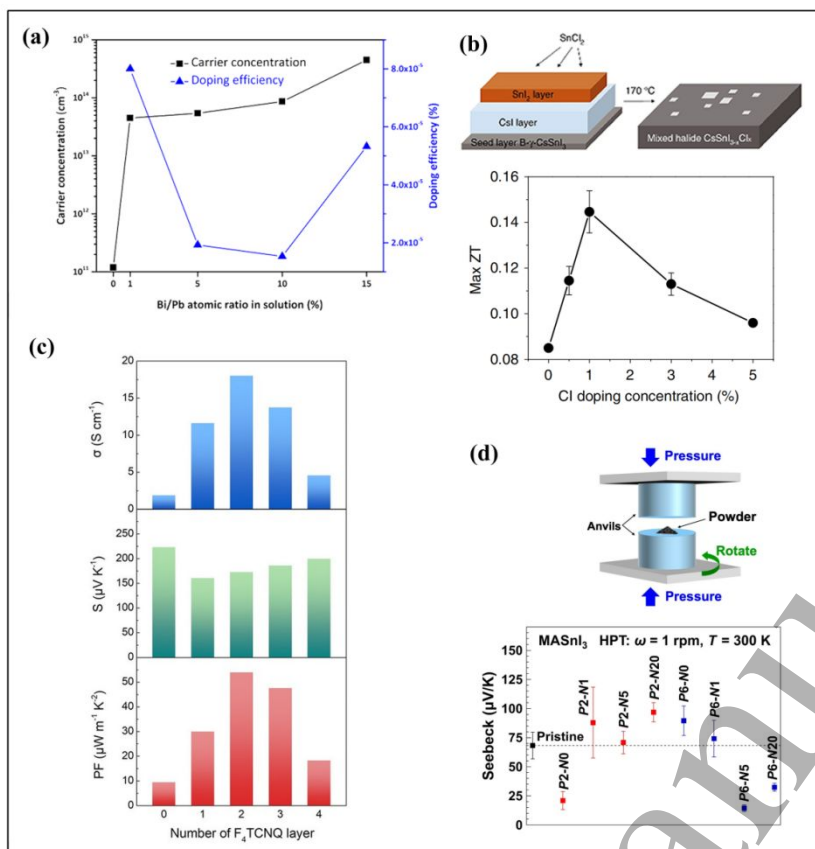


Fig.2 (a) The carrier concentration and doping efficiency of Bi-doped MAPbI₃ for various levels [7]. (b) The schematic graph of Cl-doped CsSnI₃ synthesis and the influence of introduced Cl on its zT [16]. (c) The electric conductivity, Seebeck coefficient and power factor (PF) of FASnI₃ after the treatment of different layers of F₄TCNQ [13]. (d) The schematic graph of applied stress and its influence on the Seebeck coefficient of MASnI₃ [19].

Concluding remarks

Halide perovskites and their analogues are interesting candidates for sustainable thermoelectrics, with options for sustainable composition and low-energy synthesis. Much research on tuning the properties of HP materials has been performed by the photovoltaic community, and translating these improvements to thermoelectric properties is important. However, performance is limited by difficulties of doping, which must remain the primary focus of research in their thermoelectric performance.

Stability is important for sustainability to ensure that energy pay-back times can be reached. This has been solved for halide perovskite solar cells, which operate in the temperature range -20 °C to 80 °C, by using multiple substitutions on the A, B and X-sites. Because of focus on improving zT, there has been limited research into temperature stabilisation of the thermoelectric properties of halide perovskites. One could expect that the operating temperature range of future halide perovskite TEGs would be similar to solar cells, but there are uncertainties about how stabilisation strategies might affect thermoelectric performance and if this can be done whilst avoiding toxic or scarce elements. It will certainly

be a long and uncertain path to develop high performance halide perovskites for thermoelectrics, but they nonetheless hold substantial potential as sustainable thermoelectric materials.

Acknowledgments

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2.5 Sulfides: Advances, issues and future challenges

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Status

Large scale industrialisation and mass adoption of thermoelectric devices requires an easy manufacturing process of thermoelectric materials composed of cheap, non-toxic and widely available elements, with a low market concentration. For several decades, tellurides and selenides have been deeply investigated due to their excellent thermoelectric performances. Bi₂Te₃ is commonly used in commercial Peltier modules and PbTe has been, for example, integrated in spacecraft and rover radioisotope thermoelectric generators. However, as discussed in section 1.1, the high HHI values and the toxicity of selenium and tellurium (**Table 1**) limit the adoption of the technology for large-scale applications, especially for the recovery of heat between room temperature and 700 K, the temperature window at which more than 80% of the waste heat in industry is lost [1]. In this context, sulfide-based materials are an attractive option for efficient energy conversion due to their specific characteristics, and the abundance, low HHI value and non-toxicity of sulfur (Table 1). [2-3]. The more ionic-covalent nature of the chemical bonds and the higher atomic vibrational frequencies associated with the lighter sulfur atom can present challenges in achieving low thermal conductivities, when compared to selenides and tellurides with higher atomic masses. However, the rich and unique crystal chemistry of sulfides can be exploited to create materials with exceptionally low thermal conductivities and high ZT values.

Table 1. Abundance, toxicity, cost (adapted from [2]) and reserves HHI (Section 1.1) of sulfur, selenium and tellurium.

Chalcogen	S	Se	Te
Terrestrial abundance (ppb)	3.50×10^5	50	1
Cost per kg (US\$)	0.15	44	82
HHI index	1000	1900	4900
Hazard classification	Skin irritation (Category 5)	Acute toxicity Inhalation (Category 3)	Acute toxicity Inhalation (Category 4)
Time-weighted average exposure limit (mg m ⁻³)	Not established	0.1	0.1

Binary sulfides were first considered as potential thermoelectric materials in the 19th century, with A.C. Becquerel in 1866 describing the use of sulfides (Cu_2S) in “thermoelectric batteries”. [4] In the 1980’s, rare-earth-based sulfides were investigated as thermoelectric compounds by NASA for high temperature applications ($T > 1000$ K). In 2013, the discovery of a ZT around unity at 700 K in synthetic tetrahedrite $\text{Cu}_{12-x}\text{TM}_x\text{Sb}_4\text{S}_{13}$ (TM = divalent transition metal), [5,6] which is a sulfide mineral with intrinsically low thermal conductivity, aroused a renewed interest in sulfides as thermoelectric materials, and especially in p -type copper-rich sulfides [2,7]. During the last decade, a wide variety of compounds and crystal structures have been studied and relatively large ZT values were, for example, obtained in p -type colusites, Cu-Sn-S compounds, and n -type PbS and AgBi_3S_5 (**Figure 1**). [8-10] The large diversity of crystal structures in sulfides offers a fantastic playground for the discovery of eco-friendly, non-toxic and low-cost thermoelectric compounds, and for their development in thermoelectric devices.

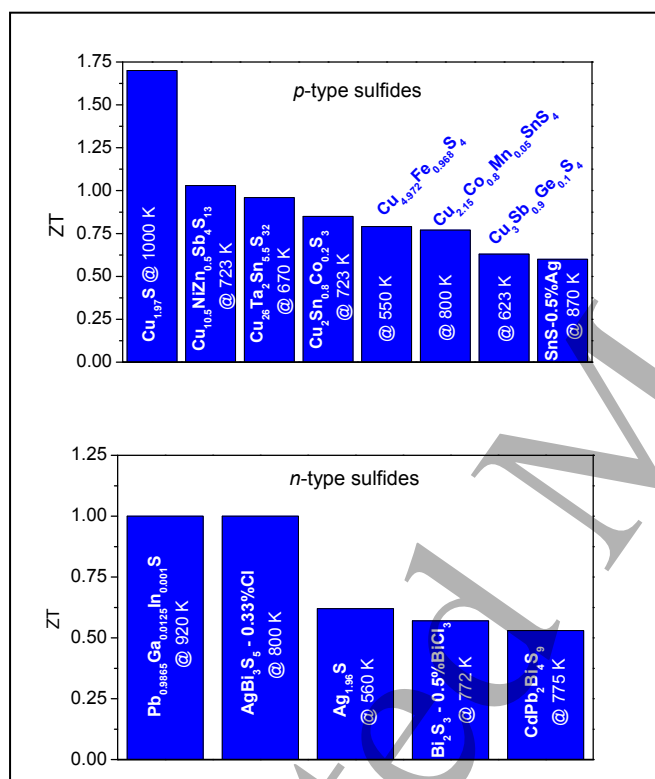


Figure 1. State-of-the-art figure of merit ZT in n - and p -type bulk sulfides. [8-10]

Current and Future Challenges

As highlighted by a recent compilation of properties of thermoelectric materials, [10] among the known families of sulfides with ZT values exceeding 0.5, more than two-thirds are p -type semiconductors. While there are several families of p -type sulfides containing Earth-abundant elements that exhibit figures of merit that approach or surpass unity (such as Cu_{2-x}S , tetrahedrites, and colusites), the thermoelectric performance of n -type sulfides generally lags behind. Additionally, the best-performing n -type sulfides (such as PbS, AgBi_3S_5 and Ag_{2-x}S) contain elements that are scarce and/or toxic. A significant challenge in this field is the discovery of Earth-abundant n -type sulfides with high ZT values.

Although the conventional high-temperature synthetic approach to sulfides, using sealed silica tubes, is not easily scalable, mechanochemistry has recently emerged as an alternative synthetic route that is amenable to scale-up and widely applicable, especially for Bi- and Cu-rich sulfides [11, and references therein]. Fabrication of thermoelectric devices requires dense ingots, and the melt-growth approach used for commercial Bi_2Te_3 alloys is not suitable for sulfides, since many of them do not melt congruently. Although Spark Plasma Sintering (SPS) and hot pressing are often used for the consolidation of sulfide powders into small ingots, suitable for research applications, work on producing larger sintered pieces of sulfides is necessary to increase production for industrial applications. However, the shaping of sulfide materials, especially sintering at high temperatures, requires a precise control of the processing parameters to prevent sulfur volatilization. This phenomenon usually leads to the material decomposition or, in the best scenario, to the formation of structural defects (disorder, stacking faults, precipitations), which can be either beneficial for transport properties (decrease of lattice thermal conductivity) or detrimental to the performances (reduction in charge carrier mobility).

Several of the best performing thermoelectric sulfides are “liquid-like” superionic conductors, in which a mobile cation sublattice hinders phonon transport, resulting in ultralow thermal conductivity. However, the cation mobility that promotes “liquid-like” behaviour also introduces instability into the materials when they are under operating conditions in a thermoelectric device. Copper-ion mobility leads to copper migration and deposition, which result in compositional changes that cause cracking and mechanical degradation.[12] Efforts aimed at overcoming these stability issues have resulted in a thermoelectric module design strategy, in which the leg geometry is tuned to ensure that the applied voltage remains below a critical threshold.[13] More recently, approaches in which copper-ion mobility is restricted have been proposed, either by increasing the energy barrier to ion diffusion, or by designing materials in which the diffusion path is blocked due to the trapping effect of the underlying crystal structure.[14, 15]. Given the outstanding performances of many of the “liquid-like” sulfides (and selenides), developing strategies that ensure the long-term stability of these materials under operating conditions is essential.

Advances in Science and Technology to Meet Challenges

There have been limited efforts in the construction of thermoelectric devices based on sulfides. Examples include conventional thermoelectric devices consisting of *p*-type tetrahedrite and *n*-type magnesium silicide legs,[16] flexible thin film devices based on *p*-type PEDOT:PSS and *n*-type hybrid TiS_2 [17] or a single colusite element [18]. However, for the construction of stable and practical power generation devices, it is important to achieve stable low-resistance electrical contacts (especially on the hot side) between the connecting electrodes and the thermoelectric legs. There is a need for systematic studies to identify stable barrier and electrical contact materials for thermoelectric sulfides, and development of high-throughput screening methods may assist on this task. Fundamental studies on the degradation processes at the interface between the electrodes and the thermoelectric

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sulfides are also lacking. Moreover, there is also a need to discover stable protective coatings to avoid sulphur volatilisation and oxidation at high temperatures. Inorganic protective coatings such as aluminium titanium nitride, as well as hybrid ceramic-polymer coatings have been successfully tested on tetrahedrites and Cu_2S over relatively short periods of time, [19, 20] but long-term stability studies have not been performed. Unless the coefficients of thermal expansion of the thermoelectric sulfides and the coatings are matched, cracking of the coating following thermal cycling may lead to the subsequent degradation of the sulfide leg.

Brittleness, also observed in bulk sulfide materials, can be a serious issue for the densification of large pieces and subsequent leg cutting. Powder metallurgy processing methods (i.e. powder synthesis, shaping and densification) must be deeply investigated and optimized to enhance mechanical properties and robustness, especially in working conditions.

Given that several of the thermoelectric sulfides are mineral ores (e.g. tetrahedrite, colusite, bornite), systematic studies into the extraction and purification of these minerals for the production of thermoelectric legs is highly desirable. This would require a cost analysis to evaluate whether using natural minerals, which will require compositional modification to optimise the level of doping, would be more cost effective than using synthetic materials.

Concluding Remarks

Over the last decade, sulfide materials, based on Earth-abundant, cost-efficient, and sustainable elements, have emerged as serious candidates for thermoelectric applications. Thanks to the rich and complex crystal chemistry of sulfides, originating mainly from natural minerals, an enormous variety of compounds with different crystal structures and microstructures can be synthesized, associated to fascinating electrical and thermal properties. Although ZT values near unity have been for example obtained in bulk Cu-rich sulfides, significant challenges must be still tackled to develop the use of sustainable sulfides in large-scale TE applications. This includes the discovery of large ZT in n -type non-toxic and abundant compounds, the processing at low cost of large and robust ingots with good thermal stability, coatings, contact engineering and device assembly.

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2.6 Thermoelectrics based on metal tellurides/selenides

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Status

Thermoelectric (TE) materials based on metal tellurides and selenides have been utilized in TE applications for a long time. Recently, there has been significant progress in the thermoelectric (TE) performance of materials, driven by advanced material synthesis methods and a better understanding of electron and phonon transport mechanisms. One key advantage of thermoelectric materials based on heavy metal chalcogenides is their inherently low lattice thermal conductivity, which results from the heavy atomic masses of their constituent elements. Additionally, the decline in electronegativity as one moves down the group-16, causes increasing potential of the anionic valence band orbitals. This results in a reduced bandgap (E_g), which ultimately enhances orbital overlap and broadens the bands, contributing to improved thermoelectric performance. Various modern approaches for improving thermoelectric performance, including tuning electronic band structure and phonon scattering manipulation, have been successfully demonstrated in these metal telluride and selenide materials e.g. band convergence, resonant levels, Rashba effect, quantum size effect, lone-pair induced anharmonicity, liquid-like ionic movements, ferroelectric instability, introduction of extrinsic point defects, nanostructuring, and all scale hierarchical architectures etc [1, 2]. Nevertheless, amongst Se and Te-based chalcogenides, AgSbTe_2 [3, 4], BiSbTe [5] and group IV-VI tellurides such as PbTe [6], GeTe , and SnTe [7] have garnered significant attention in development of high-performance thermoelectrics. At present, p-type thermoelectric materials based on GeTe and PbTe can attain a thermoelectric figure of merit (ZT) of 2.7 at 628 K and 2.8 at 850 K, respectively [8, 9], whereas, SnTe has so far reached a maximum ZT of 1.85 at 823 K [10]. On the other hand, selenium (Se) is more abundant and significantly cheaper than tellurium (Te). However, the progress in Se-based thermoelectric materials has been slower. A major challenge is the evaporation of Se at high temperatures due to its lower melting point (493 K) with respect to Te (723 K), which adversely affects the material's TE properties. Selenium compounds, like Cu_2Se , have been recognized in the thermoelectric community since 1960 and 1970 [11]. However, ion migration of Cu ions limits its practical application. Only since the last decade, high-performance Se-based thermoelectric materials such as PbSe [12] and lead-free SnSe , GeSe , and BiSe gained prominence [13-15]. Furthermore, various ternary selenides, including AgSbSe_2 , AgBiSe_2 , and TlBiSe_2 , as well as oxy-selenides like BiCuSeO , are gaining popularity in thermoelectric applications due to their inherent low lattice thermal conductivity. [1, 16]. In Figure 1, we have summarized the ZT_{max} for a series of current metal telluride and selenide TE materials.

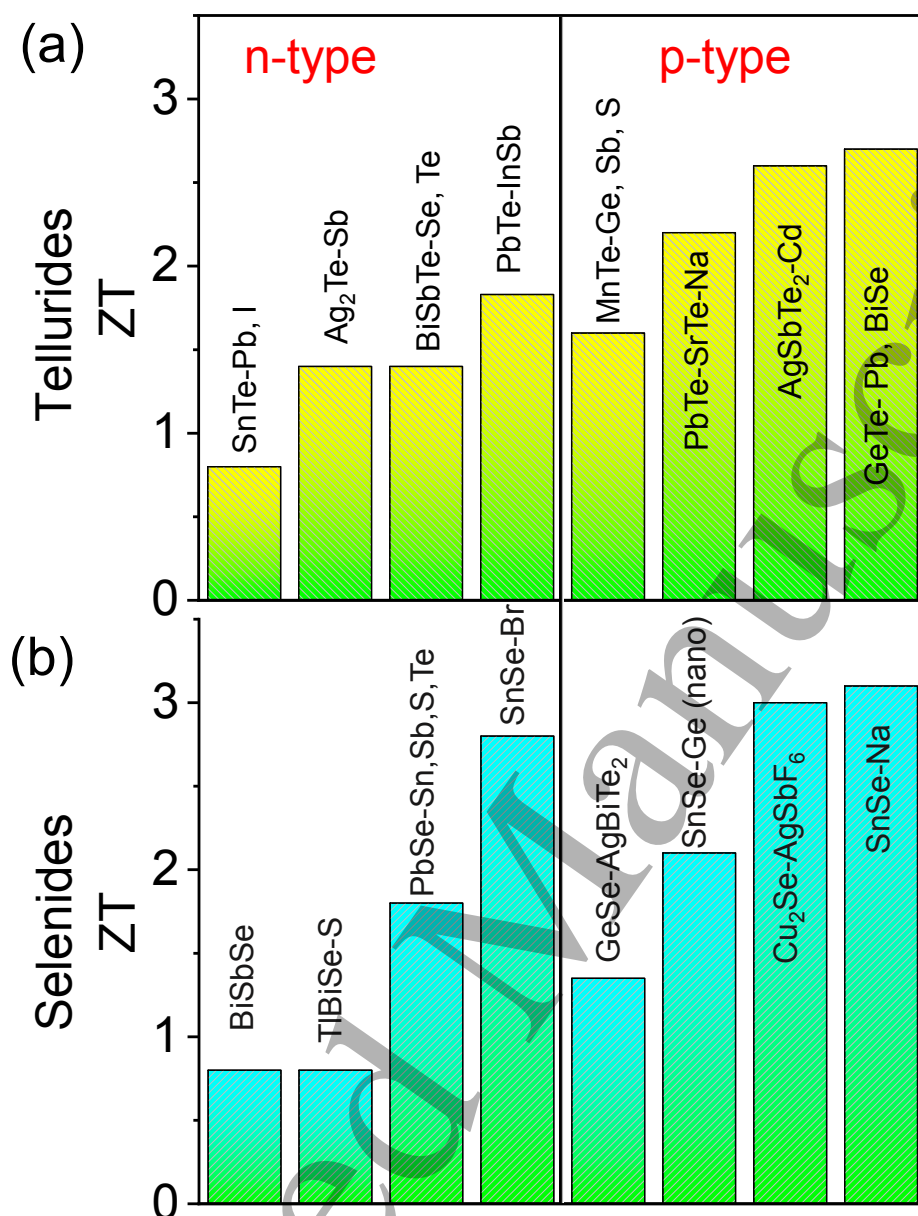


Figure 1. The ZT_{max} of various tellurides and selenides: (a) n-type tellurides: SnTe-Pb, I [7]; Ag₂Te-Sb[4]; ; BiSbTe-Se, Te [5]; PbTe-InSb [6], p-type tellurides: MnTe-Ge, Sb, S [19]; PbTe-SrTe-Na [21]; AgSbTe₂-Cd [3]; GeTe-Pb, BiSe [8]. (b) n-type selenides: BiSbSe [15]; TlBiSe-S [16]; PbSe-Sn,Sb,S,Te [12]; SnSe-Br [13], p-type selenides: GeSe-AgBiTe₂ [14]; SnSe-

Current and Future Challenges

One of the major concerns in the field of metal telluride/selenide thermoelectrics is the toxicity associated with lead-based materials like PbTe and PbSe. Despite PbTe being a benchmark TE material where strategies such as band convergence [17] and resonant level [18] were first illustrated, concerns about its potential environmental and health hazards limit its widespread use. This necessitates the development of less toxic alternatives like GeTe or SnTe. However, pristine SnTe and GeTe suffer from high p-type charge carrier density ($n_p \sim 10^{20}$ – 10^{21} cm⁻³) due to extensive cation vacancies, leading to inferior TE performance. Additionally, GeTe undergoes a structural phase transition from rhombohedral ($R3m$) to cubic

($Fm\bar{3}m$), degrading TE device performance. Thus, optimizing the phase transition temperature in GeTe is crucial for promising TE applications.

Besides, the ongoing challenge is to find a compatible n-type counterpart. Achieving better compatibility in a thermoelectric module requires both p-type and n-type materials which necessitates similarities in their chemical compositions. Achieving n-type thermoelectric material in SnTe or GeTe compounds is extremely challenging due to intrinsic Sn and Ge vacancies. Recently, thermoelectric transport in n-type SnTe is achieved through Pb and I alloying [7]. Certainly, thermoelectric transport is much more studied in n-type PbTe [6]. However, achieving high n-type thermoelectric transport in PbTe is challenging due to having a single L point conduction band, in contrast to degenerate multiple valence band at both the L and Σ points.

Notably, most of the state-of-the-art champion thermoelectric compounds incorporate elements such as Pb, Te etc., which raise sustainability concerns. The broader thermoelectric community must prioritize the design of sustainable, high-performance systems derived from earth-abundant, less toxic elements. In this regard, new thermoelectric materials like MnTe have recently emerged as promising candidates. For instance, Guodong Tang and co-workers demonstrated a ZT of 1.6 at 873 K in MnTe through the synergistic effects of valence band convergence and localized lattice modification induced by Ge, Sb, and S incorporation [19].

Metal selenides face several challenges in thermoelectric applications. The volatilization of selenium during synthesis can cause compositional variations and the formation of secondary phases. In certain cases, these interfaces can increase phonon scattering, thereby reducing thermal conductivity. Moreover, the use of single crystals in practical thermoelectric (TE) devices is often expensive and time intensive. For example, the highly anisotropic TE performance of SnSe single crystals presents a significant challenge for practical applications. Its layered structure easily cleaves along the (100) plane, making it susceptible to cracking. Consequently, there is an ongoing effort to improve the thermoelectric performance of polycrystalline SnSe. However, polycrystalline SnSe suffers from much poorer overall ZT compared to single crystalline SnSe, thwarting prospects for cost-effective lead-free thermoelectrics. The poor polycrystalline bulk TE performance in SnSe is attributed to traces of tin oxides covering the surface of SnSe powders, which increase thermal conductivity, reduce electrical conductivity, and thereby reduce ZT. Furthermore, although Cu_2Se is a typical superionic conductor with extraordinary ZT values, its superionic feature and directional segregation cause poor service stability and low mobility.

Advances in Science and Technology to Meet Challenges

Tailoring the electronic band structure of metal tellurides and selenides offers an effective pathway for enhancing thermoelectric efficiency. Controlled elemental doping or co-doping enables fine adjustment of the band gap and carrier concentration, thereby optimizing the Seebeck coefficient and electrical conductivity while concurrently suppressing thermal conductivity. In recent years, machine learning (ML) has emerged as a powerful approach to

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accelerate the discovery of both p- and n-type thermoelectric candidates [20]. By training on existing databases, ML algorithms can predict novel candidates with desirable electronic and thermal transport properties, substantially reducing reliance on conventional trial-and-error synthesis.

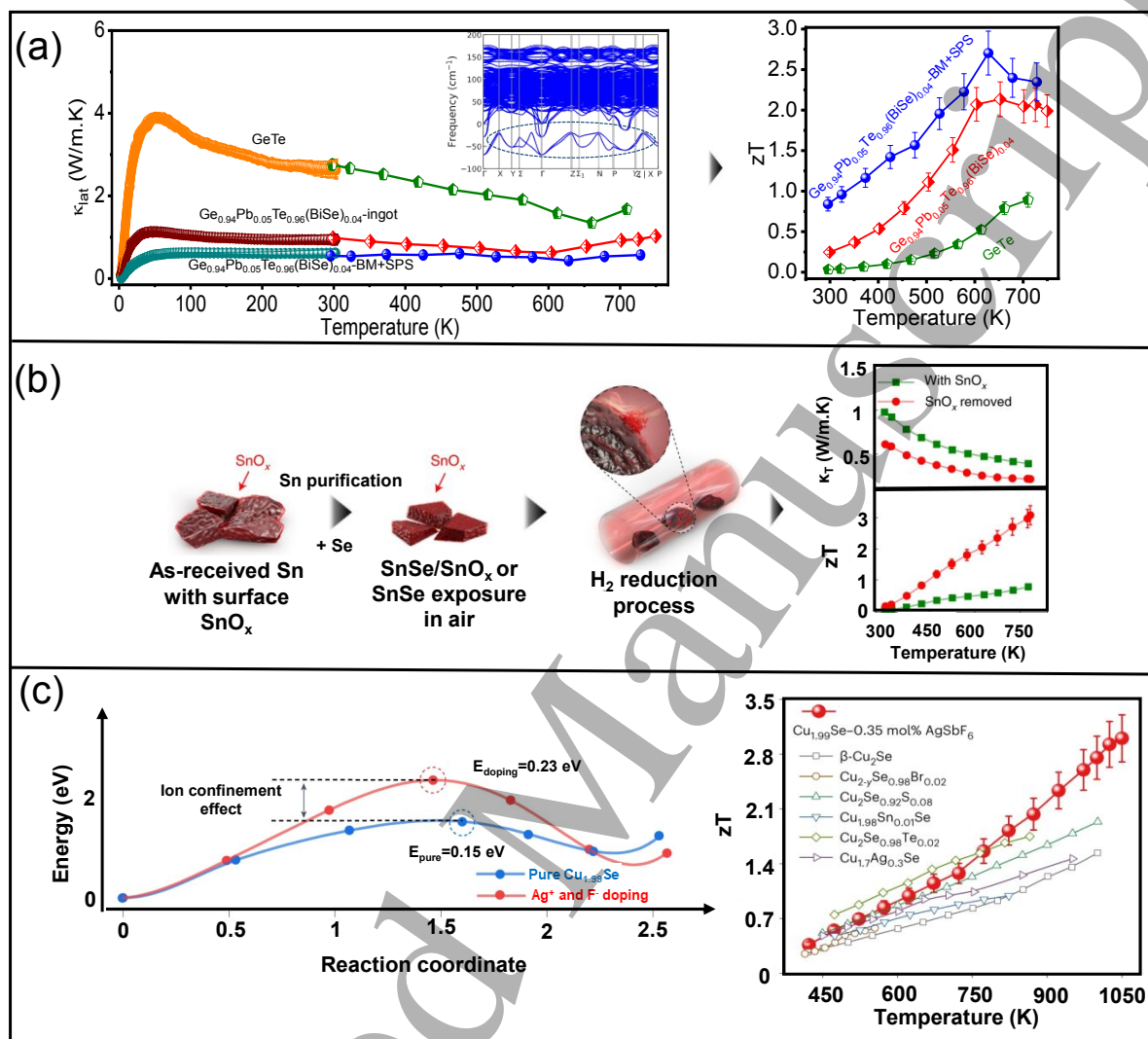


Figure 2. Recent advanced techniques utilized to obtain high zT of various metal tellurides and selenides. (a) Temperature dependence lattice thermal conductivity (κ_{lat}) and zT of $\text{Ge}_{0.94}\text{Pb}_{0.05}\text{Te}_{0.96}(\text{BiSe})_{0.04}$ (BM+SPS). Inset: phonon dispersions of cubic $\text{Ge}_{0.92}\text{Pb}_{0.04}\text{Te}_{0.96}(\text{BiSe})_{0.04}$ supercell [8]. (b) the two-step process includes purifying the tin starting reagent and the synthesized SnSe samples. This minimizes SnO_x in SPS-processed pellets, revealing ultralow thermal conductivity (κ_{lat}) in the purified sample (green squares), compared to high values in the untreated sample (red circles). This results in a record-high ZT of approximately 3.1 [25] and, (c) energy landscapes of the system, before and after doping, during Cu ion migration and the energy difference is due to ion confinement effects. As a result, a high ZT of 3.1 is achieved in $\text{Cu}_{1.99}\text{Se}-\text{AgSbF}_6$ [27]. Figure 2a is reproduced with permissions from ref. 8. Copyright, 2025, Wiley-VCH. Figure 2c is adapted with permissions from ref. 27. Copyright, 2024 Springer Nature.

Innovative synthesis strategies can also be exploited in advancing TE performance of a material by significantly reducing lattice thermal conductivity through novel phonon scattering centres like introducing stacking faults, superlattice precipitates or via introducing ferroelectric instability. For example, the phonon scattering mechanism in a hierarchical variable-scale architecture was first illustrated in PbTe, resulting in an ultrahigh $ZT \sim$ of 2.2 at 915 K [21]. In Figure 2, we have summarized some of the modern strategies that have been exploited on metal tellurides and selenides to enhance the TE figure of merit.

Careful dopant selection combined with effective processing routes has also yielded significant performance gains in GeTe-based systems. For instance, Sn doping induces Rashba-driven band splitting, while Sn, Sb-co-doped GeTe prepared via ball milling and spark plasma sintering (BM+SPS) exhibits markedly improved ZT owing to enhanced phonon scattering[22]. An intriguing strategy involves exploiting glass-like ultralow lattice thermal conductivity (κ_{lat}) in crystalline TE materials that retain high electrical transport, a rare but highly advantageous combination. We demonstrated that GeTe exhibits spatially inhomogeneous ferroelectric instability, enabling suppressed thermal conduction and resulting in an ultrahigh ZT of 2.7 at 628 K in BM+SPS-processed $\text{Ge}_{0.94}\text{Pb}_{0.05}\text{Te}_{0.96}(\text{BiSe})_{0.04}$ (Figure 2a) [8]. Introducing Bi, Pb, and Se in pristine GeTe, splits the ferroelectric (Γ) instability into two components: a weaker Γ -centered mode (25i cm^{-1}) resembling pristine GeTe, and a stronger mode (69i cm^{-1}) localized on Ge-Se bonds (Inset of Figure 2a). The coupling of these instabilities drives complex acoustic-optic phonon interactions, giving rise to glass-like thermal transport [8].

In the context of metal selenides, synthesis innovations are crucial for minimizing selenium volatility during fabrication. For example, bottom-up solution-phase synthesis has been demonstrated as an effective strategy to address volatilization issues, while also enabling precise control over crystallite size and morphology, as shown in the SnSe system [23]. At the same time, significant efforts should be directed toward improving the performance of polycrystalline SnSe. To mitigate surface oxidation issues discussed earlier [24], In Chung's group demonstrated that hole-doped polycrystalline SnSe samples achieved a ZT of about 3.1 at 783 K by efficiently removing thermally conductive surface oxides from SnSe grains [25] (Figure 2b). Such findings highlight the potential for realizing high-performance practical thermoelectrics based on this material. However, contradictory findings suggest that SnO_2 may not significantly influence thermal conductivity [26], underscoring the need for further investigation and the exploration of alternative approaches to enhance the thermoelectric performance of polycrystalline SnSe.

For Cu_2Se -based superionic conductors, Jing-Feng Li group recently reported improved ZT and stability via ion confinement [27]. Aided by density functional theory and elastic band simulations, they demonstrated an increase in activation energy to limit ion migration, through cation-anion co-doping and showed conversion efficiency of $\sim 13.4\%$ for a $\Delta T=518\text{ K}$ without any degradation after 120 cycles (Figure 2c). This novel approach could be optimized further to develop robust materials with ionic migration characteristics. In conclusion, advancements in theoretical modelling and experimental techniques will aid in the discovery of new thermoelectric materials and provide insights into the structures and mechanisms that govern properties from the microscopic to the macroscopic level.

Concluding Remarks

Although over the past two decades, thermoelectric research based on metal tellurides and selenides has experienced rapid growth with numerous exciting breakthroughs in both concepts and performance, the development of improved physical property measurement

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techniques, thermoelectric measurement methods, and commercially available instrumentation will contribute significantly to the expansion of the thermoelectric community. Moreover, solid-state chemistry has played a key role in the development of new materials and processing techniques, advancing this progress. Innovative concepts have led to the creation of strategies that decouple the strong interdependence of thermoelectric transport parameters, progressively increasing ZT values to well above 2. As discussed, achieving high-performance thermoelectrics generally follows two main directions: (1) optimizing already established materials through electronic as well as phonon band structure manipulation, and (2) discovering new compounds with novel TE properties that may lead to exceptionally high ZT values, aided by theoretical calculations. The currently poor performance of n-type thermoelectric materials is a significant drawback that needs to be addressed to obtain high efficiency in TE devices. At the same time, many state-of-the-art compounds rely on scarce or toxic elements, further underscoring the urgency of discovering alternatives based on earth-abundant constituents. Finally, application of tellurides/selenides needs to be assessed over the entire lifecycle, balancing efficient power generation against the use of scarce elements, to establish their overall sustainability. With continued efforts, these materials would hold the promise of playing a pivotal role in the development of efficient and sustainable energy solutions.

Acknowledgements

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2.7 Insights into the Challenges of Half-Heusler Materials and Devices

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Status

Half Heusler (HH) compounds, known for their excellent thermoelectric (TE) performance in medium- and high-temperature ranges, are promising candidates for sustainably harvesting waste heat. The formula for a conventional HH unit cell is XYZ (Figure 1(a)), where X , Y and Z represent strongly electropositive atoms, late transition metals and main group atoms, respectively. In the late 20th century, Uher *et al.* [1] carried out systematic studies on the TE transport properties of $MNiSn$ ($M = Ti, Zr, Hf$) HH compounds with 18 valence electron count (VEC). The bandgaps of HH compounds typically range from 0 eV to 1.2 eV, mainly depending on VEC and transition metals present [2]. Semiconducting HH compounds generally exhibit a large density of states effective mass (m_{DOS}^*). Despite the excellent electrical transport properties, good stability and mechanical properties, a notable limitation of HH compounds is their large lattice thermal conductivity κ_L , restricting the achievement of higher zT values. Researchers have paid increasing attention to HH-based thermoelectrics (Figure 1(b)), and have been endeavouring to advance fabrication techniques, investigate carrier and phonon transport mechanisms, and maximize TE properties of HH materials [3-5]. As HH compounds comprises elements with significantly different melting points and specific gravity, levitation melting has been adopted to rapidly fabricate high-quality HH samples, offering advantages such as eliminating container contamination and increasing time efficiency [6]. Kang *et al.* [7] boosted the peak zT to ~ 1.4 for n -type $(Hf_{0.6}Zr_{0.4})NiSn_{0.99}Sb_{0.01}$ through incorporating tungsten nano-inclusions. Fu *et al.* [8] achieved a record-high zT_{max} of ~ 1.5 for p -type $FeNbSb$ heavy-band HH compounds through Hf doping and band engineering. Moreover, cation-deficient 19-VEC HH compounds such as $R_{1-8}CoSb$ ($R = V, Nb$ and Ti) systems with X -site vacancies arranged in a short-range ordered (SRO) manner have been found to exhibit much lower κ_L than 18-VEC HH compounds [9]. Inspired by the outstanding TE performance and mechanical robustness of HH materials, HH-based modules have been prepared to motivate practical applications by joining HH-based TE legs with electrodes. A HH-based segmented TE module containing 8 pairs of $Zr_{0.5}Hf_{0.5}NiSn_{0.99}Sb_{0.01}/Bi_2Te_3$ (n -type) and $Zr_{0.5}Hf_{0.5}CoSb_{0.8}Sn_{0.2}/Bi_2Te_3$ (p -type) achieved a conversion efficiency of 13.3% [10]. HH materials also exhibit high thermal and radiation stabilities, making them suitable for long-term operation in harsh environments, while promoting environmental and resource sustainability. HH-based thermoelectrics show significant potential for deep space exploration, where traditional energy sources like fuel combustion and solar energy are inadequate, encouraging further efforts to improve the performance of HH-based thermoelectrics [11].

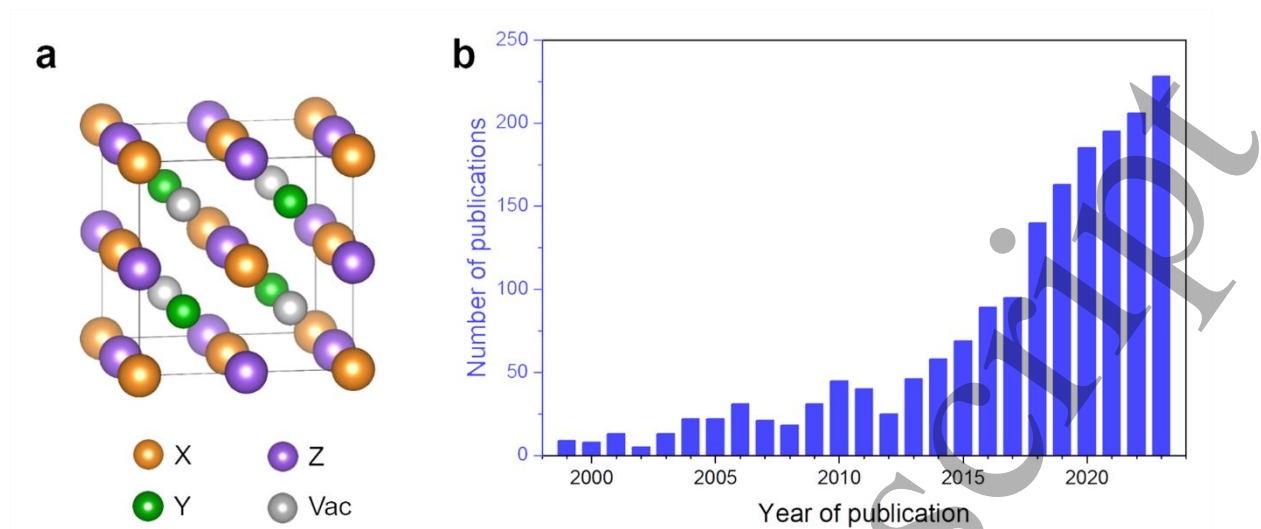


Figure 1. (a) Crystal structure of a HH compound. (b) The numbers of publications per year on HH thermoelectrics as reported by the Web of Science.

Current and Future Challenges

Considering the sensitivity of TE transport properties to phases constituents and stoichiometry, controlling compositions is a key strategy for enhancing TE performance of multi-element HH-based materials. Phase diagram approach enabling precise determination of off-stoichiometry and equilibrium phase, should be employed. In ZrNiSn system, a proper excess of Ni occupies 4d vacancy sites, acting as scattering centres and forming in-gap state [12]. But the occupation of Ni is still disputed and elusive. Cation-defective 19-VEC HH compounds possesses intrinsically low κ_L originating from cation-vacancies [13]. The distribution and concentration of these defects significantly influence transport properties of HH-based compounds. Therefore, precise determination of crystal structure should be favorable for understanding the transport behavior of HH compounds.

According to the equation [14]: $\eta = \frac{T_H}{T_C} \left(\frac{\sqrt{1+zT_{ave}}-1}{\sqrt{1+zT_{ave}+T_C/T_H}} \right)$, where T_H and T_C represent temperatures of hot side and cold side respectively, and zT_{ave} is the average zT , the efficiency (η) of a TE generator is related to zT_{ave} , rather than the peak zT . However, the TE performance of HH-based compounds near room temperature is not ideal, suppressing zT_{ave} and thereby conceivably delaying the advancement of TE devices. While boosting the low-temperature TE properties of existing HH compounds is important, discovering new low- and mid-temperature HH compounds represents a promising avenue. Additionally, segmenting with low-temperature TE materials holds promise for maintaining a high efficiency of HH-based modules.

In TE devices, the interfaces joining between electrodes and TE legs (Figure 2(a)), and those between segmented materials are crucial for transferring heat and electricity and withstanding stress from various sources. As shown in Figure 2(a), interface materials including metallization/barrier layers and soldering materials should have low electrical and

1
2
3 thermal resistances, well-matched thermal expansion coefficients, and chemical and
4 thermodynamical stability with TE legs and electrodes to minimize losses, mechanical stress,
5 and atomic diffusion and reactions [10]. Given the wide range of compositions of HH family,
6 selecting and designing appropriate interface materials is both important and challenging.

7
8 The realization of upscaling HH TE materials and devices from laboratory- to industry-scale
9 requires mass production technology. Ensuring reliability, reproducibility, and uniformity
10 while maintaining high productivity is the main concern. However, the upscale fabrication of
11 HH compound is challenging.

12
13 In practical application scenarios such as extended unmanned voyages, HH-based devices
14 should also possess long-term stability. Thus, a standardized and effective method for
15 evaluating the behaviour of TE devices after long-term service in extreme environments is
16 necessary.

21 **Advances in Science and Technology to Meet Challenges**

22
23 The design and discovery of HH-based compounds can be realized under the guidance of
24 phase diagram study. Li *et al.* [15] determined the homogeneous region of $Nb_{1-x}CoSb$
25 compounds using ternary phase diagram calculated with CALculation PHase Diagram
26 (CALPHAD), thereby simplifying traditional trial-and-error methods. Meanwhile, high-
27 throughput approaches are expected to further accelerate the calculation and screening
28 process. He *et al.* [16] discovered 99 new and stable quaternary Heusler compounds via high-
29 throughput density functional theory (DFT) screening combined with phase stability analysis.
30 Likewise, interface materials can be identified and designed based on the properties of
31 electrodes and TE legs through a series of modelling work. Yin *et al.* [17] have calculated the
32 phase diagrams for specific TE leg and barrier layer materials and successfully identified Mg_2Ni
33 as a promising barrier layer material for the Mg_3Sb_2 alloy. We could envision that it is feasible
34 to effectively select appropriate interface materials for HH-based TE legs through predictive
35 calculations integrated with a high-throughput approach. Furthermore, through training on
36 high-throughput databases, machine learning could proficiently undertake discovery, design,
37 analysis, and prediction tasks for HH-based compounds and interface materials, thereby
38 significantly advancing research efficiency.

39
40 The levitation melting technique could be a suitable and promising approach for the large-
41 scale fabrication of HH materials, taking into account its advantages such as the magnetic
42 stirring, and time and energy efficiency. In practice, levitation melting has been applied to
43 fabricate a wide range of high-quality HH-based compounds with excellent TE performance
44 [8, 9]. Additionally, additive manufacturing, also known as 3D printing, offers advantages such
45 as low waste, low cost, and design freedoms, and exhibits significant potential for large-scale
46 production [18]. Malki *et al.* [19] synthesized cation-deficient $Nb_{1-x}CoSb$ compound using 3D
47 extrusion printing followed by sintering treatment, achieving a zT_{max} of 0.1 at 873 K. Despite
48 issues with low density and the presence of secondary phases, the study demonstrated that
49 additive manufacturing was applicable to HH compounds.

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Traditionally, the lifetime of a TE device is assessed experimentally through thermal aging tests lasting a few hundred hours [20]. However, extending these tests to longer durations would require several months or years for each batch of TE devices. Hence, developing a reliable and authoritative approach to predict the lifetime of HH-based TE devices is both time-saving and economically beneficial. This could be potentially achieved by building a prediction model or fitting the degradation rate of TE devices based on experimental long-term test data.

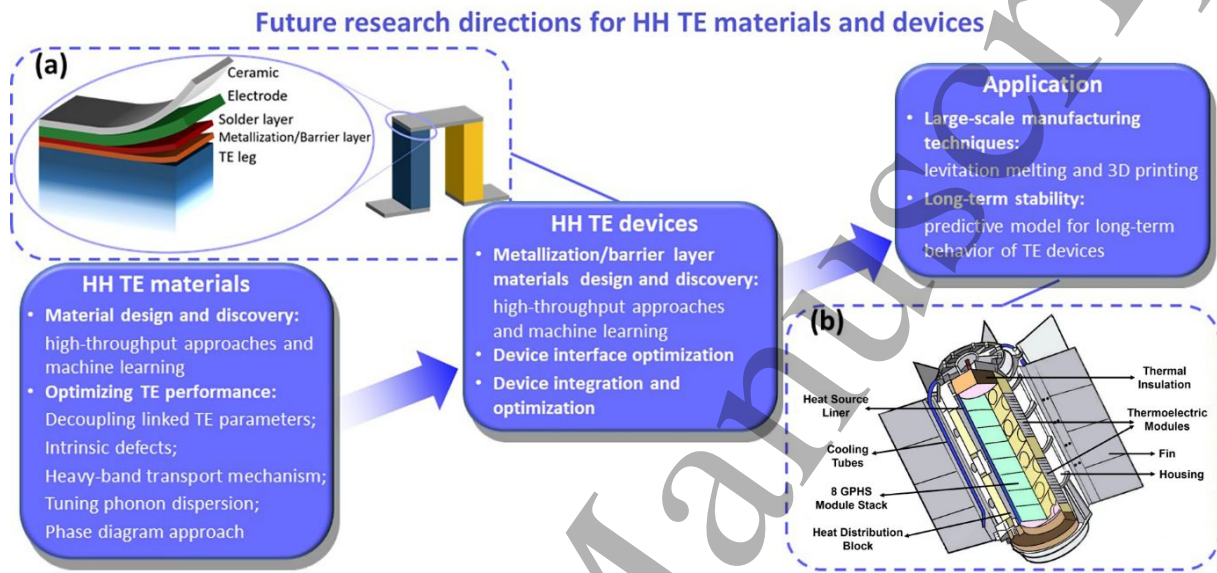


Figure 2. A summary of future research directions for HH TE materials and devices. (a) Schematic of the interface of a TE module. (b) Schematic of a multi-mission radioisotope thermoelectric generator (MMRTG).

Concluding Remarks

Thermoelectrics provide a promising and reliable solution for sustainable energy generation. Due to their outstanding comprehensive performance including TE properties, mechanical properties and stability, HH-based compounds can be regarded as the most promising novel TE materials for practical applications in recent years. To further accelerate the development of HH-based thermoelectrics, the following future directions are imperative (Figure 2). Enhancing TE properties of HH materials remains a crucial focus, potentially achievable through decoupling linked TE parameters, tuning phonon dispersion, exploiting intrinsic defects, heavy-band transport mechanisms, and phase diagram approaches. High-throughput methods and machine learning, as emerging data-driven sciences, possess capability to discover and design new high-performance HH-based compounds and select appropriate interface materials for HH-based modules. The design and optimization of the integration of HH-based TE devices are essential for practical applications. To catalyse commercial applications, large-scale manufacturing techniques such as levitation melting and 3D printing deserve more attention and promotion. Additionally, developing a reliable approach to

predict the long-term behaviour of HH-based TE devices is one of the most important foundations for applications, requiring further efforts.

There remains significant potential for HH-based TE materials and devices, and a promising future can be anticipated.

Acknowledgements

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2.8 Skutterudites

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Status

As already a large variety of review articles about thermoelectric materials and skutterudites exist, e.g. [1-4], only an intense short overview will be given here.

Skutterudites (SKDs) crystallize with cubic CoAs_3 -type (S.G. $Im-3$, No. 204) in which As-atoms in $24g$ sites form a 3-dimensional and predominantly covalent framework enclosing Co-atoms in sites $8c$ at the centers of tilted non-regular As-octahedra: this framework provides two empty icosahedral spaces per unit cell (centers in sites $2a$) for the incorporation of filler atoms (usually at partial occupation) thereby constituting the so-called filled skutterudites with general formula $\text{E}_y\text{T}_4\text{X}_{12}$ (Fig. 1).

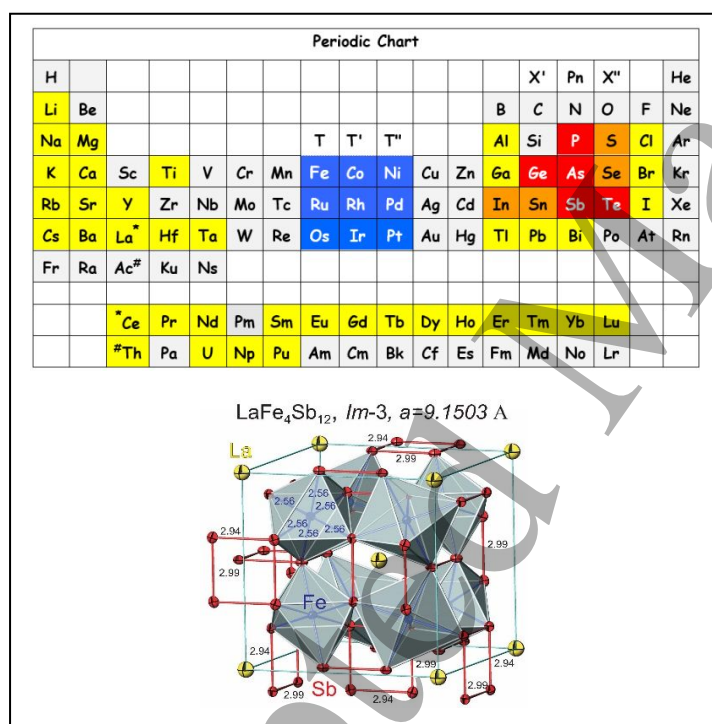


Fig. 1. Top: Distribution over the Periodic Chart of the various constituents forming skutterudite compounds, $\text{E}_y\text{T}_4\text{X}_{12}$: yellow stands for E, blue for T and red for X, orange for atoms acting as filler as well as framework atoms. Bottom: Filled skutterudite $\text{LaFe}_4\text{Sb}_{12}$ with Sb in $24g$ ($0, 0.16060, 0.33685$), Fe in octahedron-centers $8c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) and La in icosahedral voids $2a$ ($0,0,0$). Sb-atoms form almost square rectangles (red).

Since the first thermoelectric activities in the early 1950ies on unfilled CoSb_3 , successful attempts were made to rise their thermoelectric performance, tuning the electronic structure via chemical substitution in the T and X sublattices and choosing a proper type of filler atoms E (single-, double- and multi-filling) as well optimizing the overall filling level, whereby

skutterudites may switch from n-type to p-type semiconductor. A slowly rising number of reports refers to unfilled skutterudites with good thermoelectric performance, among which $\text{Co}_4\text{Sb}_{11}\text{Te}_{0.7}\text{Sn}_{0.3}$ [5] and $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5} + 25 \text{ vol.}\% \text{ CNT}$ [6], both achieved a $ZT = 1.3$, whereas a nanostructured alloy $\text{Co}_{23.4}\text{Sb}_{69.1}\text{Si}_{1.5}\text{Te}_{6.0}$ (in at.%) still holds the record with $ZT = 1.6$ by introducing nano- to micrometer-size irregularly shaped and randomly oriented pores [7]. Over the years ZT s of Sb-based filled skutterudites, have reached ZT s with the highest values for p- and n-type: $ZT = 1.45$ at 800 K ($\text{DD}_{0.7}\text{Fe}_3\text{CoSb}_{12}$) [8] and $ZT = 2.15$ at 823 K ($(\text{Sm},\text{Mm})_{0.15}\text{Co}_4\text{Sb}_{12}$) [9], respectively (see Figure 2; for details up to 2022 see Ref. [10]). Although the bulk number of investigations still dwells at ZT s ≤ 1 , more recent activities reached ZT s > 1.2 for p-type and $ZT > 1.4$ for n-type materials with a trend towards a lower number of filler species (single-filled or double-filled).

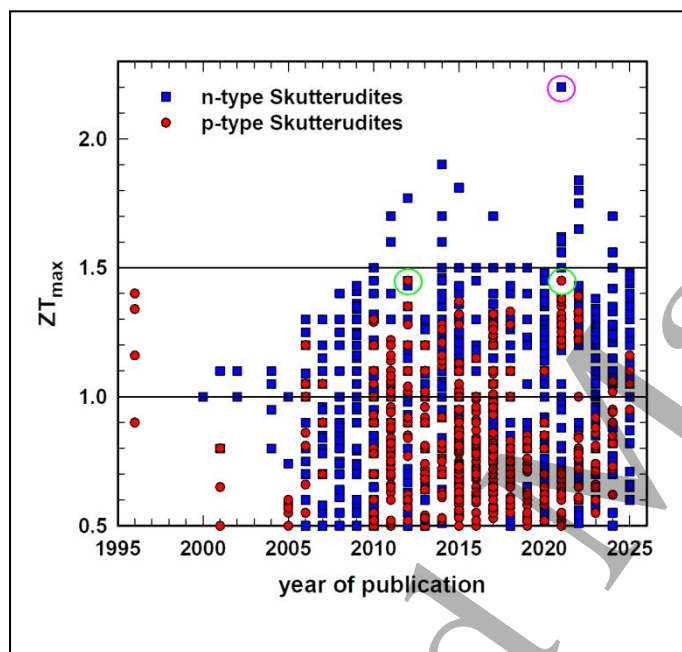


Figure 2. ZT s ≥ 0.5 of Sb-based filled skutterudites vs. publication year (red: p-type, blue: n-type). Maximum ZT values for p- and n-type are indicated by large open circles; for details up to 2022 see Ref. [10].

Current and Future Challenges

A high ZT demands a large $|S|$, $>150 \mu\text{V}/\text{K}$, but a low product $\rho(\kappa_e + \kappa_{ph})$. To fulfill this demand, it is necessary to find a compromise among the interleaved parameters $|S|$, ρ , κ by simultaneously (a) tuning the electronic density of states (eDOS), (b) band engineering and (c) grain boundary engineering. Skutterudites provide an open crystallographic structure with framework atoms exhibiting excellent electronic properties and “rattlers” filling the voids. Consequently, the strong reduction of the lattice thermal conductivity, κ_{ph} , was claimed to result from the interaction between the vibrational dynamics of the filler atoms with acoustic phonons of the T_4Sb_{12} matrix [11, 12]. In addition, tunneling of filler atoms may occur between equivalent off-center sites in the icosahedral cage. Shi et al. [13] published a guide to estimate

the fraction of filler atoms on a correlation between the Pauling electronegativities ϵ of filler atom and antimony: $\epsilon_{\text{Sb}} - \epsilon_{\text{FA}} > 0.8$. Although a variety of single fillers has been employed, only few of them managed to surpass a $ZT > 1.2$ (p-type: Ce) or a $ZT > 1.4$ (n-type: Yb, In); for details see Ref. [10]. Double- and multi-filling, grain refinement via ball-milling and intrinsic precipitation such as Yb_2O_3 , however, were efficient techniques to reach ZT s of about 1.3 for p-type and $ZT \sim 1.7$ -1.8 for n-type skutterudites. Didymium, DD, a natural double-filler (Pr~5%, Nd~95%), and mischmetal, Mm (Ce~51%, La~28%, Nd~16%, Pr~5%) proved to be exceptionally good fillers [10].

Nanostructuring theoretically promoted the idea on quantum confinement of electrons and phonons (Hicks and Dresselhaus [14]). High ZT s could be derived from nano-sized microstructures achieved via ball-milling and/or severe plastic deformation (e.g. high-pressure-torsion) in combination with intrinsic or extrinsic nano-precipitates: highest values at 823 K for p- and n-type: $ZT=1.45$ ($\text{DD}_{0.7}\text{Fe}_3\text{CoSb}_{12}$) [8] and $ZT=2.15$ ($\text{Sm,Mm}_{0.15}\text{Co}_4\text{Sb}_{12}$) [9], respectively. Although additions of various finely dispersed secondary phases were said to significantly enhance ZT , only a few composites reached high values (p-type: $ZT=1.25$ for $\text{CeFe}_3\text{CoSb}_{12}$ with 5 wt.% MoO_2 and $ZT=1.3$ for $\text{DD}_y\text{Fe}_3\text{CoSb}_{12}$ with 0.5 wt.% $\text{Ta}_{0.8}\text{Zr}_{0.2}\text{B}$; n-type: composites, based on $\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ and $\text{Yb}_y\text{Co}_4\text{Sb}_{12}$, reached ZT s in the range of 1.3 to 1.5 with additions such as TiO_2 , Ag, C_{60} , Yb_2O_3 , CoSi , SiC , or Al (for details see Ref. [10]). Indeed, $(\text{Sr,Ba,Yb})_y\text{Co}_4\text{Sb}_{12}$ with 9.1 wt.% $\text{In}_{0.4}\text{Co}_4\text{Sb}_{12}$ reached $ZT=1.8$ and $\text{Al}_{0.03}\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}$ as well as $(\text{Mm,Sm})_y\text{Co}_4\text{Sb}_{12}$ with 2 wt.% $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ both yielded $ZT=1.7$ (see Ref. [10]). Substitutions at the Sb-site by Ga, Ge, Sn, Se, Te, In in combination with fillers generally helped to enhance ZT .

Advances in Science and Technology to Meet Challenges

While advanced n-, p-type skutterudite materials are available, module engineering still poses challenges in respect to long-term stability i.e. proper bonding to efficient diffusion barriers and contact electrodes all within tolerable thermal expansion coefficients at the hot side. Proper flexible electrodes are still an issue. In this context skutterudites can provide system-inherent p-, n-type materials with matching thermal expansion coefficients (p- $\text{Ba}_{0.15}\text{DD}_{0.28}\text{Yb}_{0.05}\text{Fe}_3\text{NiSb}_{12}$ +n- $\text{Ba}_{0.09}\text{Sr}_{0.02}\text{DD}_{0.22}\text{Yb}_{0.02}\text{Fe}_{2.4}\text{Ni}_{1.6}\text{Sb}_{12}$; $ZT \sim 1.0$; see [10]). Recent advances in laboratory-scale SKD-module production (development of innovative diffusion barriers and metallization layers) have demonstrated significant enhancements in power density and robust mechanical performance reaching thermoelectric conversion efficiencies of ~10 % (for an overview of module achievements, see Ref. [15]).

Ball-milling proved efficient to gain nano-scaled SKD-powders: Further tuning of the ball-milling parameters may provide even smaller particles, and properly selected densification aids that get liquid at the maximum hot-press or SPS process temperature (for instance excess Sb) provide clean grain boundaries. Technologies, like severe plastic deformation, need to be extended towards wide die-diameters at carefully defined sample thickness, particularly in view of a fast large-scale leg production.

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As skutterudites react above $\sim 250^{\circ}\text{C}$ with oxygen and moisture, corresponding protection is a must. The problem of oxidation appears solved via glassy surface protection or by complete module-encapsulation, but awaits further improvement.

Removing toxic elements (Se, Te) and particularly non-sustainable Co from skutterudites may not warrant the high TE-efficiencies already achieved, but proper replacements (Mn, Fe, Ni, etc. for Co) need to be engineered in view of a large-scale production.

The well-developed DFT (Density Functional Theory) calculation techniques can explain, modify and improve strategies not only for energy-band and charge-carrier engineering but also for phonon and grain boundary engineering such as low dimensionalization, introduction of secondary nano phases, nanointerfaces or nanopores, phonon resonance scattering of filler atoms i.e. for thermoelectric properties in general. DFT techniques can thus define the proper parameter space for more efficient thermoelectric skutterudites.

ML (machine learning) and AI (artificial intelligence) gain increasing importance for finding new thermoelectric candidates and for optimizing properties and this way helps to reduce practical work in the labs. Current interdisciplinary science and technology are certainly apt to solve all the aforementioned problems once commercial large-scale module-producers are found. In this respect large-scale production of high-ZT p-, n-type skutterudite materials needs to be resumed from a stage already reached around 2010, when a production capacity of 1 ton/year of SKD-powders (ZT of p-type ~ 1 - 1.2 ; n-type ~ 1.2 - 1.4) was claimed (<https://treibacher.com>).

Concluding Remarks

Skutterudites are good candidates for environment friendly thermoelectric devices because they have high ZTs and besides that, their starting material is relatively cheap and abundant, they can be used in a wide temperature range, once protected against oxidation they reveal long-term stability [16] and exhibit good mechanical properties [17].

Strategies for (a) energy band engineering (band convergence or resonant energy levels via doping/filling), for (b) simultaneous charge-carrier engineering (optimization of carrier concentration and mobility via doping/filling, forming modulation doped structures or introducing nano-sized secondary phases) and (c) for phonon and grain boundary engineering have been outlined to improve skutterudite thermoelectric behavior [18]. DFT in combination with machine learning may be a tool with the potential to further define skutterudites, to optimize their figure of merit and increase thermoelectric efficiencies [19]. As a promising result, high ZT n-SKDs have been successfully combined with high ZT p-type half Heuslers to reach a module conversion efficiency of $\sim 12\%$ [20].

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2.9 Silicides

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Status

There are several compounds from the group of silicides which have attracted particular interest since these materials combine a range of promising properties and sustainable features which make them possible candidate thermoelectrics for intermediate-temperature applications. Some of the most promising silicide thermoelectrics are solid solutions of Mg_2X ($X = Si, Ge, \text{ and } Sn$), $CrSi_2$, $CoSi$, $IrSi_3$, Ir_3Si_5 , $FeSi_2$, $MnSi_{1.75}$, $ReSi_{1.75}$ and Ru_2Si_3 . [1] Si-Ge alloys were firstly investigated and developed in 1960s by NASA for space applications. Although these materials present high cost and moderate efficiencies, their superior mechanical and thermal stability enabled the manufacturing of radio-isotope thermoelectric generators with high operational temperatures above 1300 °C, powering several space missions.

Recently intensive efforts are focused on the development of low-cost, non-toxic, earth-abundant and eco-friendly TE materials with high efficiencies ($ZT > 1$). Combining the aforementioned critical parameters, Mg_2Si -based compounds are considered the most attractive n -type silicide thermoelectrics for intermediate-temperature applications. First systematic investigations of Mg_2Si and its related solid solutions as thermoelectrics were carried out in 1990s. Many studies have focused on the development of $Mg_2Si_{1-x}Sn_x$ alloys since they exhibit the highest TE efficiencies among silicide phases with maximum ZT values between 1.1 and 1.7 as presented in Figure 1. [2], [3], [4], [5], [6], [7] Electron doping with Bi or Sb has been proved to be the most efficient method to tune the electrical transport properties and achieve high improvements in ZT . A record high ZT of 1.7 has been obtained by double substitution with Bi and Cr at the Si and Mg sites respectively. [3]

On the other hand, higher manganese silicides (HMS) have attracted considerable attention as the most promising p -type thermoelectrics from the silicides family, as shown in Figure 2. [8], [9], [10], [11], [12] HMS are composed of environmentally-friendly and earth-abundant elements, exhibiting also suitable mechanical and chemical stability for mid-temperature applications. [13] HMS compounds are developed mostly by melting methods or mechanical alloying, presenting diverse stoichiometry. They belong to the Nowotny Chimney ladder phases where Mn and Si atoms form the chimney and helical (ladder) sublattices respectively in tetragonal superstructures. Implementing hole doping with dopants such as Al and Cr, the electrical transport properties and power factor can be enhanced effectively, leading to ZT increases with maximum values 0.6 - 0.8. However, isoelectronic doping with Re results in high reductions in lattice thermal conductivity, accomplishing remarkable TE efficiency improvements and reaching a record high ZT of 1.15. [9]

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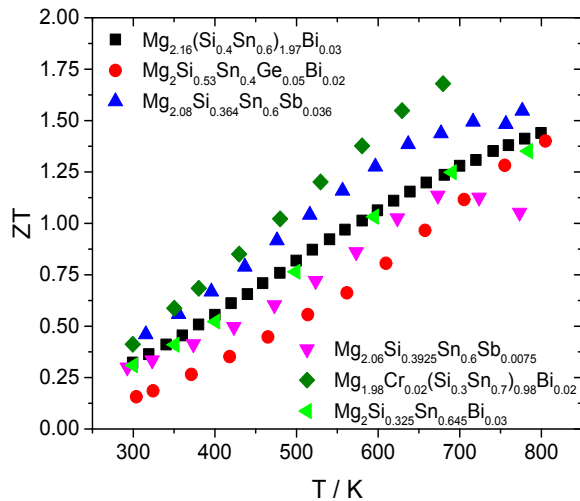


Figure 1. Best *n*-type silicide thermoelectrics based on $Mg_2(Si, Sn)$ solid solutions.

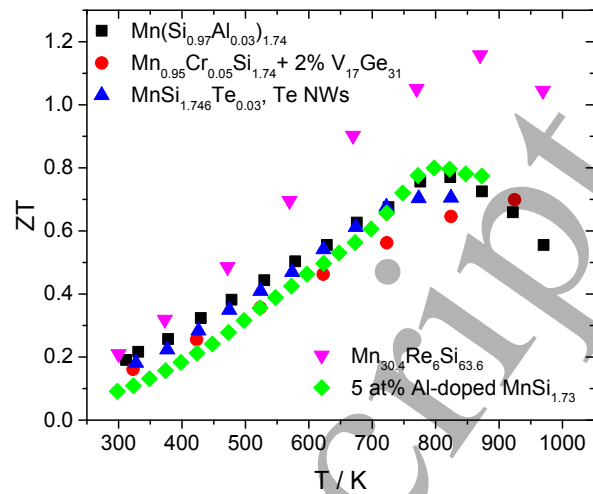


Figure 2. Best *p*-type silicide thermoelectrics based on HMS phases.

Current and Future Challenges

Despite the advancements in the TE performance of Mg_2Si -based compounds, there are still research issues and challenges which must be overcome in order to enable their integration in practical applications and the manufacturing of silicide TE modules in industrial level. $Mg_2(Si, Sn)$ solid solutions exhibit relatively poor mechanical properties (low fracture toughness) which prevent their integration into TE applications.[14] Therefore, the enhancement of mechanical reliability is essential for these compounds before moving to the manufacturing of TE modules (TEM).

Although recent studies have demonstrated notable improvements of TE properties of HMS phases, they still present lower ZT values compared with those of *n*-type Mg_2Si -based materials. Research efforts have been focused on co-doping of HMS phases, implementing multiple substitution with various dopants (Al/Ge, Cr/Ru, Fe/W).[13] However, it has not discovered yet an effective combination of dopants which will induce a strong decrease in lattice thermal conductivity and improve in parallel the power factor of the material.

Despite the progress on the construction of an all-silicide-based TEM consisted of $Mg_2Si_{1-x}Sn_x$ and HMS legs and the promising results with efficiencies η_e of $\sim 4 - 7\%$, [13] the performance mismatch due to the limitation of *p*-type ZT is a critical issue for the overall efficiency of the device. The difference in thermal expansion coefficients is also a major challenge which should be addressed since it often causes breakages in the metal contacts and the modules. Another important issue is the long-term chemical stability of $Mg_2Si_{1-x}Sn_x$ solid solutions and HMS phases in their operational temperature range (700 - 850 K). A recent study showed that *n*-type $Mg_2Si_{0.6}Sn_{0.4}$ legs present a reliable thermal stability only up to 400 °C, while above 500 °C, oxidation products such as MgO and SnO₂ are formed under air exposure.[15] HMS presents better chemical and mechanical stability. However, its oxidation is unavoidable for

prolonged time in air, while the formation of MnSi leads to severe reductions of TE performance.[13], [14]

Furthermore, new environmental issues arise, dictating more investigations of silicide thermoelectrics to a more sustainable direction which will provide a potential solution for the recycling of silicon. Our recent studies showed that using recyclable Si for the development of silicide materials and TE modules with noteworthy efficiencies is a quite promising route for the utilization of vast amounts of silicon kerf from PV industry.[16], [17] This is a new, emerging challenge which must be taken into consideration the following years.

Advances in Science and Technology to Meet Challenges

The reliability and applicability of a TEM is directly dependent on the long-term stability of materials evolved in terms of electrical, thermal and mechanical properties. This implies that more research efforts need to focus on the improvement of thermal and mechanical stability of Mg₂Si-based solutions. For instance, as recent studies have shown, by controlling the Mg vapour pressure is a crucial parameter for the long-term chemical stability of Mg₂(Si,Sn) solid solutions and the limitation of material degradation due to Mg losses at elevated temperatures.[18] New advances on the manufacturing and long-term stability of Mg₂(Si,Sn)/HMS TEMs are also focused on the fabrication of metal contacts and the development of protective coatings. Research efforts are performed to develop new electrode and contact materials with robust thermal and chemical stability at high temperatures, durable to high mechanical stress and thermal cycling. The optimization of interface material deposition, compatible with Mg- and Mn-based silicide legs, is also of high importance for the mechanical stability as well as the reduction of contact resistance which affects strongly the performance of TEMs.[13], [17]

Regarding the TE properties of *p*-type HMS phases, more efforts must be undertaken to enhance further the ZT and reduce the gap with that of *n*-type Mg₂Si-based solid solutions. Various strategies need to be explored for the optimization of electrical transport properties and the simultaneous reduction of lattice thermal conductivity. Investigations should focus on new co-doping attempts, including heavy elements which work as point defects in the lattice and combined with appropriate nano-structuring,[9] nano-additives or secondary nano-phases[10] can lead to the accomplishment of a panoscopic approach with hierarchical phonon scattering and notable ZT improvements.

In order to avoid the discrepancy of thermal expansion coefficients in a TEM, it is more convenient to use the same material for the *n*- and *p*-type legs. According to this concept, several studies have focused on the development of *p*-type Mg₂Si-based solid solutions through hole doping with the best results ($ZT_{\max} \sim 0.4 - 0.5$) to be exhibited through Li substitution[1], [19], while recently a fully Mg₂(Si,Sn)-based TEM was fabricated.[20] Further efforts should concentrate in the ZT improvement of *p*-type Mg₂Si-based solutions investigating multiple substitution strategies with new dopant combinations, new synthesis methods to increase the solubility limits of atomic defects as well as the suppression of bipolar

thermal conduction which is a severe issue for the limitation of *p*-type TE efficiency of Mg₂Si-based compounds.[19]

Concluding Remarks

Silicide thermoelectrics have attracted considerable attention the last years due to a range of advantageous characteristics. Some of these compounds are composed of low-cost, earth-abundant, non-toxic and eco-friendly elements, demonstrating in parallel quite promising TE properties. From the family of silicides, the Mg₂Si-based solid solutions and MnSi_x compounds stand out as the most promising *n*- and *p*-type TE materials respectively for intermediate-temperature applications. Mg₂Si_{1-x}Sn_x alloys doped with electron dopants such as Bi and Sb have demonstrated high ZT enhancements (1.1 - 1.7), comparable with those of other state-of-the-art materials, while the *p*-type HMS phases reach efficiencies with maximum ZT values of 0.6 – 1.1. Therefore, in order to reduce this performance mismatch and enable the fabrication of more efficient all-silicide-based TE devices, further investigations must be carried out to improve the *p*-type ZT either of HMS phases or alternatively of the hole doped-Mg₂(Si,Sn) alloys. Despite the progress and promising results on the construction of Mg₂(Si,Sn)/HMS TE modules, more research efforts are necessary to address issues related with the mechanical, thermal and chemical stability of TE legs, interface materials and electrodes in order to ensure the manufacturing of robust and durable silicide-based modules, providing reliability and applicability for potential commercialization in the future.

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2.10 Thermoelectric oxides

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Status

The first report on “thermoelectric” and “oxide” in Web of Science, Clarivate Analytics is on the high electromotive force measured between $-110 \sim 800$ °C for CdO by J. P. Andrews in 1947 [1]. Other early investigations focused on binary oxides, including NiO with impurities and under several gas atmosphere [2], Cu₂O under different oxygen partial pressure [3]. After these initial reports, thermopower measurements were used to probe the electrical transport in the cuprate high- T_c superconductors [4]. In terms of technology development, gas sensors composed of oxide materials were developed [5, 6], and composites of superconductive YBa₂Cu₃O_{7-x} and Ag₂O were tried for thermoelectric refrigeration instead of Bi₂Te₃ materials [7].

The first report discussing oxide materials aimed at power generation appeared from M. Ohtaki in 1994 [8] and got a lot of attention to the n-type CaMnO₃ in 1995 [9]. Here, an increase in the electrical conductivity σ to enhance the zT values is achieved by substitution with higher valence elements at the Ca-site. Larger ionic radii on the perovskite A-site were found to be favourable for improving the carrier mobility in this hopping conduction system. Since many conductive oxides belong to the hopping conduction system, the exploration of new thermoelectric oxides has been attempted based on this concept. The number of the publication on thermoelectric oxides grew up rapidly after 2000. The excellent thermoelectric properties of layered p-type Co-oxides originating the article from I. Terasaki in 1997 created a new researching field in thermoelectric technology [10-13]. These discoveries induced the inflow of many researchers in the research field of the thermoelectric oxides and led to the high temperature resistant modules in air [14, 15].

Current and Future Challenges

The research on thermoelectric oxides moved forward to the development of modules. New joining technology different from conventional metallurgical technology was developed using silver paste. Modules composed of p-type Ca_{2.7}Bi_{0.3}Co₄O₉ legs and n-type CaMn_{0.98}Mo_{0.02}O₃ legs were produced using silver paste with the powders of the p- and n-type oxides as the additives for each junction, respectively (Fig. 1) [15]. Basically, the vacuum system is not necessary to from synthesis of the oxide materials to production of the modules. The entry barriers are not high for even the developing countries where the provision of infrastructure is not satisfactory. The low production cost can be also expected. Although the number of the publications about thermoelectric oxide materials decreased at one point, the development of the processing of materials and production of the modules would be continued. Metal oxide film deposition technology has been progressed for the purpose of the improvement of

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the zT values, preparation of the flexible devices, and the circuit integration [16]. It is proven that the two-dimensional structure is effective to realize the giant Seebeck coefficient [17]. It's not always necessary to cool the high temperature resistant modules by water circulation, which decreases the net power output, to avoid the damages. The heated effluent can be generated as the new cogeneration systems. The non-water-cooled thermoelectric generators have the advantage for widely scattered power sources for the IoT sensors. Since the oxides can be heat treated in the atmosphere, the thick film devices, which are prepared from the precursors of the oxide powders mixed with organic binders, can be produced by printing or tape casting methods [18]. Although thermoelectric oxides have many advantages, especially in the processing, the generation efficiency is at most 1-2 %. Needless to say, the exploration of the high zT materials is very important. Moreover, the improvement of the thermoelectric properties should be challenged by nano and microscopic structural control by the processing technologies.

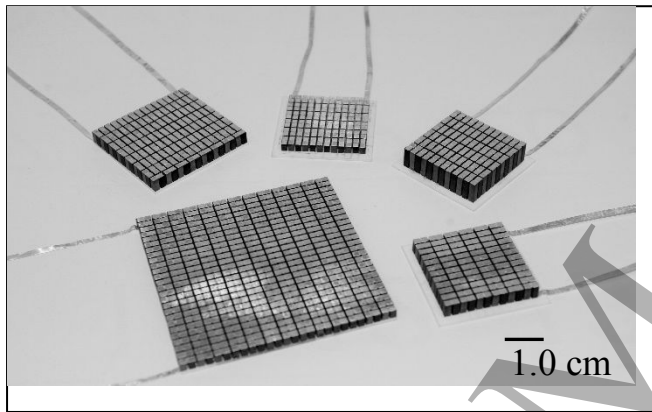


Figure 1. Thermoelectric modules composed of p-type $\text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_4\text{O}_9$ and n-type $\text{CaMn}_{0.98}\text{Mo}_{0.02}\text{O}_3$ [15]

Advances in Science and Technology to Meet Challenges

The electrical conductivity σ is more important than anything to develop good thermoelectric oxides. Of course, high thermal conductivity κ is other problem, but the σ values are several orders of magnitude higher than regular semiconducting thermoelectric materials. Generally, oxides have ionic bonding character, therefore the electrons tend to be localized. It looks a good strategy to pay attention to more covalent high mobility oxide compounds based on main group elements. In addition, grain boundaries induce serious scattering of electrical carriers in the polycrystalline oxides. Single crystalline devices are ideal from electrical conductivity point of view. But it is impractical to the mass production and the cost. The densification, preferable grain orientation in the case of anisotropic electrical conductivity, desirable grain size, and composition control near the grain boundaries are effective to obtain the high σ values in the polycrystalline oxides. The κ for the oxides is rather high because of the low atomic mass of the oxide ions and strong ionic bonds. It needs to be careful to refine the grains to scatter the phonons at the grain boundaries. The decrease in σ often exceeds

the decrease in κ . It seems like the phonons can be scattered selectively at the secondary phases formed by the precipitation of phases through peritectic or eutectic reactions [19]. It is worthy of attention that the self-formation of core-shell structures by sintering is effective to reduce thermal conductivity [20]. Recently, nanocomposites of graphene or graphene oxide with the n-type ZnO and SrTiO₃ have been reported to improve electrical and thermal conduction at the grain boundaries, which is often one of the most serious problems [21-25]. Machine learning is being attempted as a new approach to materials exploration [26-28]. Currently, the research is focused on thermal conductivity properties, but it is expected that exploration of other thermoelectric properties will also progress.

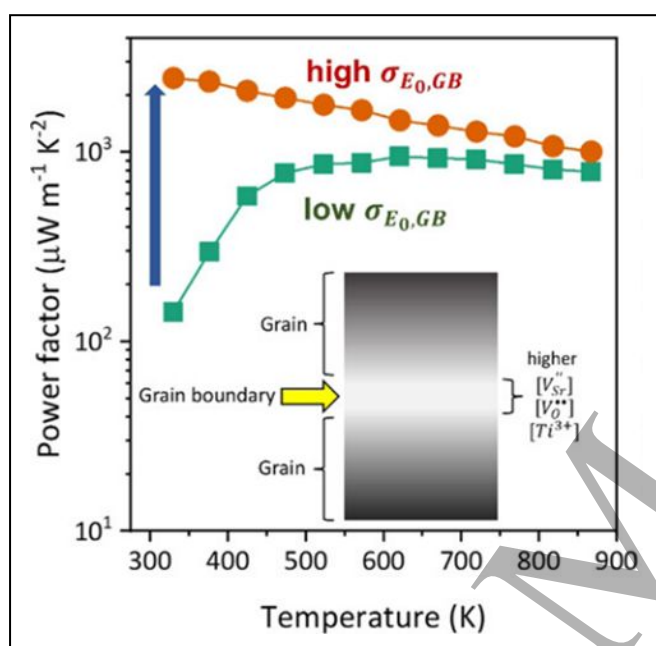


Figure 2. Improvement of power factor of La-doped SrTiO₃ by addition of graphene oxide [26]

Concluding Remarks

The thermoelectric oxides have clear advantages in durability, production cost, non-toxicity, are lightweight etc. The energy payback period against the production of the oxide module is estimated to be about 40-50 days. Since the processing is similar to the traditional ceramic manufacturing, the research can be relatively easily promoted in developing countries. However, currently, the zT values are not particularly better than other thermoelectric materials. The application of thermoelectric oxides is limited to temperatures higher than 773 K. The development of new thermoelectric oxides with high zT at lower temperatures (373-773 K) using some of the grain boundary engineering concepts discussed above is of great interest and would enable wider application.

Acknowledgements

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