JPhys Energy

PURPOSE-LED PUBLISHING™

ROADMAP • **OPEN ACCESS**

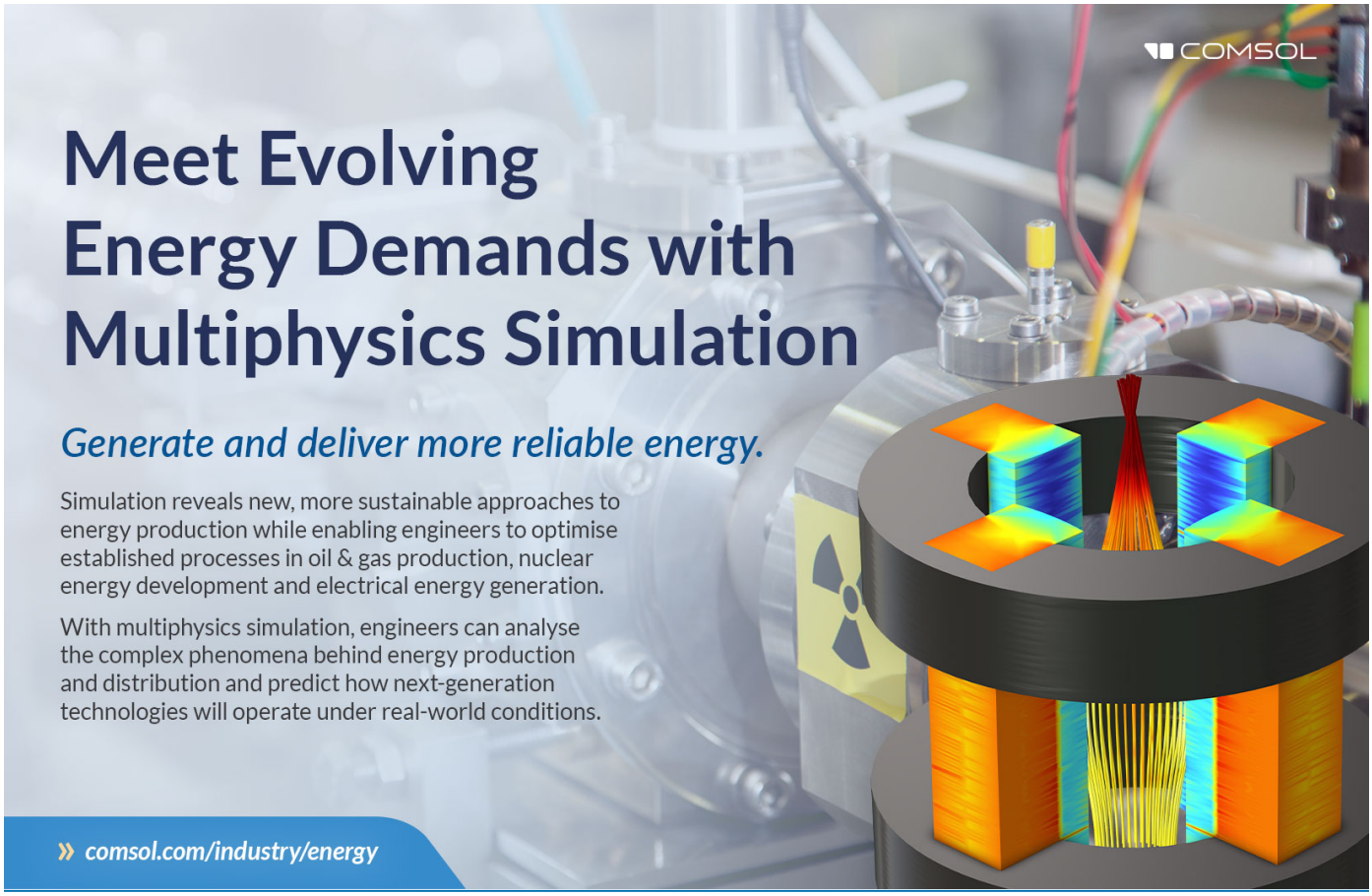
2026 roadmap toward sustainable thermoelectrics

To cite this article: Jan-Willem G Bos *et al* 2026 *J. Phys. Energy* **8** 011502

View the article online for updates and enhancements.

You may also like

- Anecdotes and guidance notes: surviving and thriving as a woman in science
B Gaggio, E H Driscoll, F C J Robinson et al.
- Process parameters' influence on integrated CO_2 capture and methanation: finding optimal conditions by Bayesian optimisation
Soudabeh Bahrami Gharamaleki, Michael Short, Tomas Ramirez Reina et al.
- Lead-free perovskites and derivatives for photogeneration: a roadmap to sustainable approaches for photovoltaics and photo(electro)catalysis
Isabella Poli, Teresa Gatti, Yan Li et al.



This content was downloaded from IP address 129.233.5.1 on 13/03/2026 at 11:06

Journal of Physics: Energy

Check for updates

OPEN ACCESS

RECEIVED
19 December 2024

REVISED
3 October 2025

ACCEPTED FOR PUBLICATION
16 December 2025

PUBLISHED
25 February 2026

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence.

Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

ROADMAP

2026 roadmap toward sustainable thermoelectrics

Jan-Willem G Bos[1,24,*], Trupti Mohanty[2], Taylor D Sparks[2], Wenjie Xie[3], Anke Weidenkaff[3], Salvatore Grasso[4], Ruizhi Zhang[4], Michael J Reece[4], Teng Wang[5,23], Jae Sung Son[5], Samina Akbar[6], Iris Nandhakumar[6], Richard Tuley[7], Cevriye Koz[7], Ran He[8], Pingjun Ying[8], Amin Bahrami[8], Vicente Pacheco[9], Kornelius Nielsch[8], Ricardo Grau-Crespo[10], Luis M Antunes[10], Keith T Butler[11], Neophytos Neophytou[12], Rajeev Dutt[12], Bhawna Sahni[12], Nagendra Singh Chauhan[13], Takao Mori[13,14], M Parzer[15], F Garmroudi[15], A Riss[15], E Bauer[15], Chongyang Zeng[16], Emiliano Bilotti[16], Chang You[4], Oliver Fenwick[4], Paz Vaqueiro[10], Emmanuel Guilmeau[17], Animesh Das[18], Kanishka Biswas[18], Yu Liu[19], Chenguang Fu[19], Tiejun Zhu[19], Gerda Rogl[20], Peter Rogl[20], Panagiotis Mangelis[21], Theodora Kyratsi[21] and Ryoji Funahashi[22]

[1] EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews KY16 9ST, United Kingdom
[2] Department of Materials Science & Engineering, University of Utah, Salt Lake City, UT-84112, United States of America
[3] Institute of Materials Science, Technische Universität Darmstadt, Peter-Grünberg-Str. 2, 64287 Darmstadt, Germany
[4] School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom
[5] Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea
[6] Department of Chemistry, University of Southampton, Southampton, United Kingdom
[7] European Thermodynamics Ltd, 8 Priory Business Park, Kibworth, Leicestershire LE8 0RX, United Kingdom
[8] Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research, Helmholtzstraße 20, 01069 Dresden, Germany
[9] Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Winterbergstraße 28, 01277 Dresden, Germany
[10] Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, United Kingdom
[11] Department of Chemistry, University College London, London WC1H 0AJ, United Kingdom
[12] School of Engineering, University of Warwick, Coventry CV4 7AL, United Kingdom
[13] Research Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan
[14] Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan
[15] Institute of Solid State Physics, TU Wien, A-1040 Wien, Austria
[16] Department of Aeronautics, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom
[17] Laboratoire de Cristallographie et Sciences des Matériaux, Université de Caen Normandie, ENSICAEN, CNRS, Normandie Univ, CRISMAT UMR6508, F-14000 Caen, France
[18] New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur PO, Bangalore 560064, India
[19] State Key Laboratory of Silicon and Advanced Semiconductor Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310058, People's Republic of China
[20] Institute for Materials Chemistry, University of Vienna, Waehringerstrasse 42, A-1090 Wien, Austria
[21] Department of Mechanical and Manufacturing Engineering, University of Cyprus, 1678 Nicosia, Cyprus
[22] Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka 563-8577, Japan
[23] Academy for Advanced Interdisciplinary Studies, Northeast Normal University, Changchun 130024, People's Republic of China
[24] Editor of the roadmap.
[*] Author to whom any correspondence should be addressed.

E-mail: j.w.g.bos@st-andrews.ac.uk

Keywords: sustainable, thermoelectrics, thermoelectric materials, sustainable materials

Abstract

Thermoelectric (TE) 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 TE energy conversion. Beyond using abundant elements, sustainability has so far not been a major consideration in the development of TE 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

© 2026 The Author(s). Published by IOP Publishing Ltd

TEs as well as guidance for future work. In terms of organization, the roadmap contains cross-cutting sections on aspects of sustainability and sections focused on the major TE 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 TE technology.

Contents

Introduction 4
1. Sustainability considerations 6
1.1. Raw materials supply for sustainable thermoelectrics 6
1.2. Life cycle assessment of thermoelectric materials 9
1.3. Efficient synthesis and processing 12
1.4. Novel routes—additive manufacturing 15
1.5. Novel routes—electrodeposition 19
1.6. Module fabrication 21
1.7. Upcycling waste for sustainable thermoelectrics 24
1.8. Data-driven design and discovery of thermoelectrics 28
1.9. Electronic transport modelling and simulations for thermoelectric materials 31
2. Materials 34
2.1. Bi_2Te_3—near ambient materials 34
2.2. Full-Heusler alloys 37
2.3. Polymer composites 40
2.4. Halide Perovskites 42
2.5. Sulfides: advances, issues and future challenges 45
2.6. Thermoelectrics based on metal tellurides/selenides 48
2.7. Insights into the challenges of half-Heusler materials and devices 52
2.8. Skutterudites 55
2.9. Silicides 58
2.10. Thermoelectric oxides 61
Data availability statement 63
References 63

Introduction

Jan-Willem G Bos

EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews KY16 9ST, United Kingdom

Introduction

Thermoelectric (TE) 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 Bi_2Te_3 and work well near room temperature. The TE figure of merit (zT) of these materials is near unity, enabling device conversion efficiencies of 5%–6%. Here, $zT = (S^2\sigma/\kappa)T$, 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 TE (power generation) 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 [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 TE devices. The first-generation materials include Bi_2Te_3, 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 TE 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 high-temperature 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, near room temperature materials including Mg_3Sb_2, MgAgSb and Ag_2Se have been developed, offering a potential replacement for Bi_2Te_3 [6]. In particular, the prospect of displacing commercial Bi_2Te_3 modules has led to an accelerated focus on building prototype devices, and developing stable electrical and thermal contacts [2, 3, 8, 11].

The aim of this roadmap 'towards sustainable TEs' is to start a discussion around sustainability aspects of TE 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 TE technology therefore relies on solving multiple issues, including green/ eco-friendly processing (defined as minimizing 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 TE technology but is needed to assess the sustainability of the technology over its lifetime.

Prior roadmaps on TEs have focused on technical aspects of technology development [13, 14], on activities in specific countries [15] 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 TE 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 TE materials that are currently considered.

Section 1.1 focuses on raw materials, including scarcity, geographic distribution and uses the Herfindahl–Hirschman index (HHI) to quantify market concentration. Section 1.2 is focused on life cycle analysis and provides a good overview of the challenges that need to be overcome before fully

quantitative life cycle assessment (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 TE materials, which offers advantages in terms of design flexibility, and minimization of materials wastage in device manufacturing. Section 1.5 covers advances in electrodeposition, which can be used for the fabrication of micro generators for Internet of Things (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 TE materials. Section 1.8 discusses the use of machine learning (ML) 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 (CRTA), 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 (fH) 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 (HPs) (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 TE 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 fH counterparts are amongst the most sustainable TEs 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 TEs, which potentially are highly sustainable TE 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 TEs. 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 TE technology, its reliability, scalability and lack of moving parts. With continued improvements in materials and module performance, TEs 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 TEs and will drive innovations in the future. We hope that this roadmap will help building in sustainability considerations from the outset.

1. Sustainability considerations

1.1. Raw materials supply for sustainable thermoelectrics

Trupti Mohanty and Taylor D Sparks

Department of Materials Science & Engineering, University of Utah, Salt Lake City, UT-84112, United States of America

Status

The advancement of 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 [18]. Currently, a significant challenge within the TE domain is the dependence on scarce materials such as bismuth and tellurium, utilized in high-efficiency TE materials like Bi_2Te_3 and PbTe [13, 19]. 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 TE, 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 [20]. Skutterudites, which utilize $CoSb_3$, rely on antimony, whose production is primarily concentrated in China and Tajikistan [21]. These materials also often incorporate rare earth elements or heavy metals to optimize their TE 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 [13, 19]. 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 TE.

Current and future challenges

Understanding market share and the 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 [18, 22]. 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) [21], 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 [23]. Figure 1(a) illustrates the production market share in the year 2023 for key TE 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 TE 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,

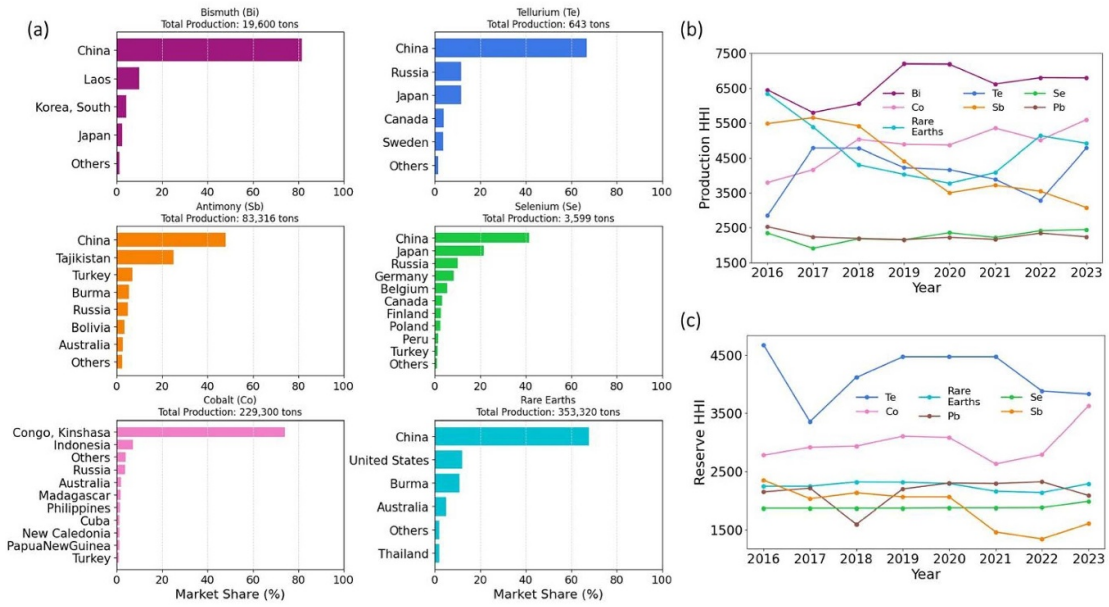


Figure 1. (a) Production market share in 2023 for key thermoelectric elements. (b) Production HHI; and (c) reserve HHI for these elements from 2016 to 2023, all based on USGS Mineral Commodity Summaries. *Note:* bismuth reserve data is not available in the USGS sources.

consistently maintains a high production HHI value (>5500), underscoring its persistent supply risk as a critical TE 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 TE 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 vulnerabilities, thereby ensuring the sustainability of the TE industry and facilitating the wider adoption of these technologies.

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 TE materials. These strategies aim to reduce dependency on scarce, expensive, or geopolitically sensitive materials, thereby enhancing TE technology's sustainability and economic feasibility. These strategies can be broadly categorized as:

Environmentally friendly material substitution: Recent trends in TE materials are shifting towards environmentally friendly substitutes that minimize ecological impact while maintaining high performance for sustainable energy applications. Alternative TE 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 fHs (e.g. Fe_2VAl), and half-Heuslers (e.g. TiNiSn) have gained attention due to their elemental abundance, non-toxicity, and lower environmental impacts [13, 19, 24–26]. The key constituent elements of these materials, like Cu, Fe, Mn, Ni, Sn, and Ti exhibit reserve HHIs below 2500 [23], 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 lists. Unlike traditional TE 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 TE generators (TEGs) [13, 19, 24–26].

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 [27]. 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 [28].

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 TE materials [29], design of TE 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 [18, 23]. Integrating advanced data analytics and AI, such as large language model (LLMs) querying capabilities, can enhance the management and accessibility of TE 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 TE materials for broad applications. While using scarce elements can drive high-impact innovations and deepen our understanding of material 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 TE technologies does not exceed the ecological and economic limits imposed by scarce resources.

Acknowledgements

The authors gratefully acknowledge funding from the Army Research Office Materials Design program under Contract Number #W911NF-23-1-0333.

1.2. Life cycle assessment of thermoelectric materials

Wenjie Xie and Anke Weidenkaff

Institute of Materials Science, Technische Universität Darmstadt, Peter-Grünberg-Str. 2, 64287 Darmstadt, Germany

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 TE 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 [24]. However, even the most abundant resources are finite and will eventually be used up. Thus, the concept of sustainable TE materials needs to be explored to offer a broader understanding of sustainability. By examining TEs 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, 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 2. In this general model, the proposed comprehensive process modelling framework is structured on a bottom–up representation of individual processes [30]. 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 LCA tool *GaBi* v4.4 to evaluate inorganic, organic, and hybrid TE materials [31]. 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 TE materials considered. In a related study, Kawajiri *et al* applied endpoint modelling (LIME2) to perform a cradle-to-grave LCA of an automotive TEG heat exchanger [32]. While both studies provide valuable insights, their reliance on specific models and system limits their general applicability. Despite these efforts, LCA analysis in the TE 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.

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 [33]. 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 analyse the results to identify areas of significant environmental impact and potential for improvement. Let us 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 3. 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.

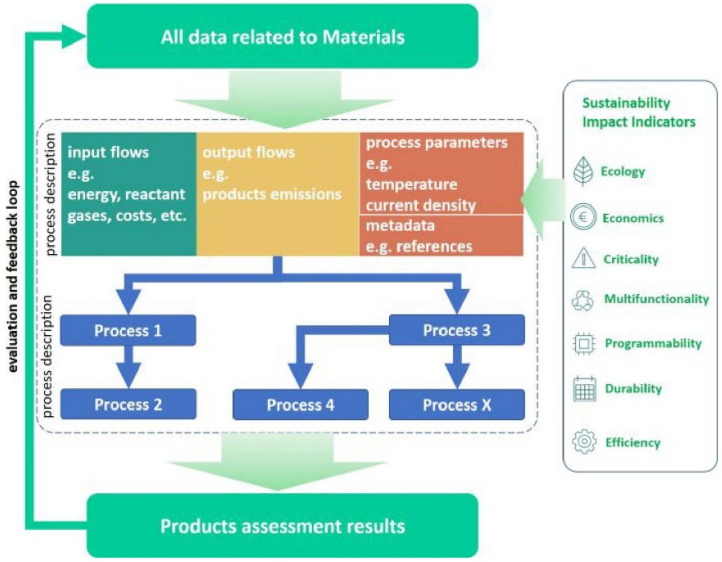


Figure 2. General model system structure for life cycle assessment (LCA). Reproduced with permission from [30]. © 2021 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH CC BY-NC 4.0.

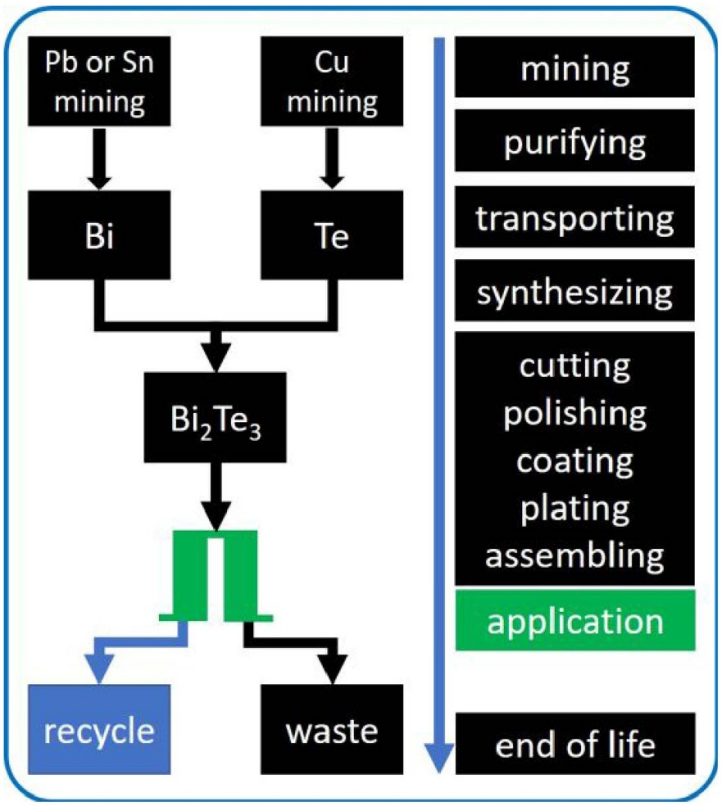


Figure 3. The sketch of the lifecycle of Bi_2Te_3 modules from the mining of raw materials to the end of life.

Advances in science and technology to meet challenges

To address the challenges associated with conducting reliable and comprehensive LCAs for TE 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 [34]. 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 modelling and simulation combined with ML and digital twin. Simulation-based process modelling 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 ML [35–37], 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 [38, 39]. 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 TE 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 TE materials has been measured by the zT. However, zT only considers TE performance without factoring in the overall environmental impact and sustainability of the materials. By incorporating LCA into the zT calculation, the sustainable aspect of TEs can be evaluated. Therefore, we would like to define a sustainable $zT_{sus} = S_{LCA} * zT$, where the S_{LCA} is the sustainable parameter obtained by the LCA analysis. In the ideal case, S_{LCA} can be normalized such that $\mathbf{S_{LCA} < 1, = 1, and > 1}$ 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 TE field will not only focus on improving material performance but also consider the sustainability factors behind that performance.

1.3. Efficient synthesis and processing

Salvatore Grasso, Ruizhi Zhang and Michael J Reece

School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

Status

Life cycle analysis establishes essential sustainability benchmarks for TEs, 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 TEs. However, only a limited number of these materials have found commercial application, those being mostly constituted by Bi–Sb–Te [40] based materials for applications up to 150 °C. Other TE 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 TEGs (RTGs) 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 [41], to MnSi with its spiral ladder structures with very large unit cells [42]. While most TE 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 TE 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 maximize their TE 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 [43], 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 composites with hard nano-inclusions, such as silicon carbide or boron carbide. Just small amounts of nano-inclusions (<1 mass%) can significantly increase their hardness and fracture toughness. This is achieved by limiting the grain size and thus increasing the grain boundary density of the materials, and the nano-inclusion acting as dispersion hardeners and crack deflectors. Another approach is the sintering of powders to make polycrystalline materials with higher fracture toughness because of the presence of grain boundaries deflecting cleavage. Additionally, there is growing interest to extrude *n*-type materials to produce bulks with highly preferred orientation to optimize their anisotropic properties [44].

Newer materials, investigated in small quantities in laboratories, are often prepared by melting in sealed quartz tubes. This is a good route for producing high-quality, single-phase materials for characterization. However, it is not a scalable processing route. With the increasing interest to develop materials that are ecofriendly and sustainable, and able to operate at higher temperatures, the favoured ways to prepare small quantities in laboratories is sintering. The method is versatile and the conditions for producing dense and single-phase materials can be quickly optimized. The precursor powders are first mixed by ball milling. In the case of materials with weaker bonding and lower melting temperatures, like sulfides [45], nearly single-phase materials can be produced by mechanochemistry. The powders can be highly amorphous, disordered and mechanically internally strained, all of which make the materials more sinter active. Following sintering, the secondary phases often disappear, and the main phase becomes highly ordered and crystalline. In the case of materials containing similar high melting temperature elements with low vapour pressure, arc melting and solidification can provide a suitable step to produce the target compound, which can then be ground down into a powder. In the case of high melting temperature materials like oxide ceramics, the oxide precursor powders can be mixed by ball milling.

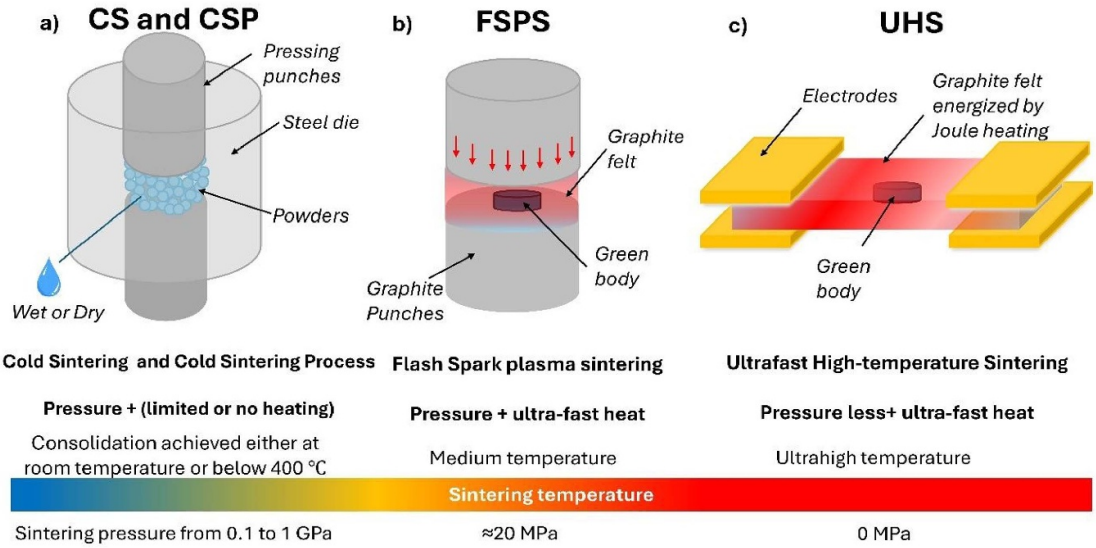


Figure 4. Emerging strategies for processing thermoelectric materials, including (a) cold sintering (CS), (b) flash spark plasma sintering (FSPS), and (c) ultrafast high-temperature sintering (UHS). These methods exhibit an inverse relationship between sintering temperature and applied uniaxial pressure. 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.

A further high temperature (<1000 °C) calcining step is required to form the target phase by solid state diffusion and reaction. A great advantage of the ball milling and sintering route is that it can then be easily scaled-up and commercialized.

The sintering can take place pressure-less in conventional furnaces after cold compaction of powders, with atmospheric control if needed. The use of hot-presses enables further densification. In the last twenty years there has been increasing use of field assisted or spark plasma sintering (SPS) furnaces that allow direct heating of conductive dies, usually made of graphite, to achieve high heating rates (>50 °C min^{-1}), combined with pressure, enabling rapid densification. Their use has been promoted by the desire to make fine grained and nanostructured materials to increase phonon scattering, thus reducing thermal conductivity. This is possible not only through the high heating and cooling rates that are achievable, but also the ability to monitor the compression ram displacement. This enables the optimum temperature for densification with minimal grain growth to be determined. The technique also has the advantage that the minimal times spent at high temperature reduces the loss of volatile elements. In materials with anisotropic crystal structures, particularly layered compounds, they can be sinter-forged to produced preferred orientation and anisotropic properties. The technique has been successfully used to produce textured bismuth tellurides, further demonstrating the versatility of the sintering route [46].

Advances in science and technology to meet challenges

More recently developed, emerging processing techniques, summarized in figures 4(a)–(c), are well-suited for processing TE materials. These methods prevent thermal decomposition by either employing ultrafast heating or, conversely, relying on low or minimal heating [47].

The low-temperature consolidation approach, illustrated in figure 4(a), is known as cold sintering (CS) when performed under dry pressing conditions, or as the CS process (CSP) when moisture-assisted consolidation is used. This method enables the compaction of TE materials at temperatures well below 400 °C. In some cases, for layered Van der Waals bonded semiconductors [48], 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 of bismuth telluride [49]. Regarding CSP, the use of an appropriate solvent can effectively contribute to a grain boundary cleaning effect as reported in the case of Ag_2Se [50] where thiol-amine as a liquid medium was employed. The appropriate selection of solvent plays a dual role in the CSP: (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 CS for the green processing of TEs has recently been published [51]. 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 [52]. A more recent innovation in sintering has been flash sintering shown in figure 4(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^{-1}).

In 2010, Rishi Raj and colleagues introduced flash sintering [53], 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 TE 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 millimetres or dog-bone-shaped specimens. To overcome these limitations a further development of the technique is Flash-SPS [54], in which a standard SPS is used without a die as shown in figure 4(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 [55].

A recent development on ultrafast processing includes ultrafast high-temperature sintering (UHS) developed in May 2020 [56] (figure 4(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 Mg_2Si [57], and dense bulks with relative densities >95% were obtained in a firing cycle lasting less than 1 min. The ultra-short processing time contributes to minimal energy losses resulting in energy savings well above 90% [58] 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 TE 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 TE fabrication. This is especially true when considering industrially scaled up fabrication of TE devices. Indicatively, our recent work suggests energy consumption as low as 0.2 MJ kg^{-1} for cold-sintered bismuth telluride-like materials a reduction of 50–100 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.

1.4. Novel routes—additive manufacturing

Teng Wang[1] *and Jae Sung Son*[2]

[1] Academy for Advanced Interdisciplinary Studies, Northeast Normal University, Changchun 130024, People's Republic of China
[2] Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea

Status

TE 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 [59, 60]. TE 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 [61]. 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 TE materials and devices on a bulk scale [62]. This innovative method affords considerable versatility in the morphological and dimensional customization of TE 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 TE modules (TEMs) 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 TE materials and devices are briefly reviewed.

To date, various 3D printing methods have been employed in the fabrication of TE materials. These techniques include direct ink writing [63], fused deposition modelling [64], selective laser sintering [65], and aerosol jet printing [66]. 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 [63, 67–70], to intermediate temperature operable PbTe [71], $AgBiSe_2$ and $AgSbTe_2$ [72], and extending to high-temperature operable tin selenide [73] as shown in figure 5. Moreover, owing to the unique advantages of the 3D printing process, the feature size of a single TE leg can range from approximately 100 μm [63] to several centimetres [71–73]. Furthermore, the 3D printing process offer the potential for complex 3D geometrical configurations of TE legs within devices, thereby opening new avenues for the tailored design of TEM structures [74, 75]. 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.

Current and future challenges

In the context of material synthesis via 3D printing, the efficiencies of 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 TE 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 TE performance. Considering the enhancement of TE 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 6(a) [75]. 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 6(b)) [76].

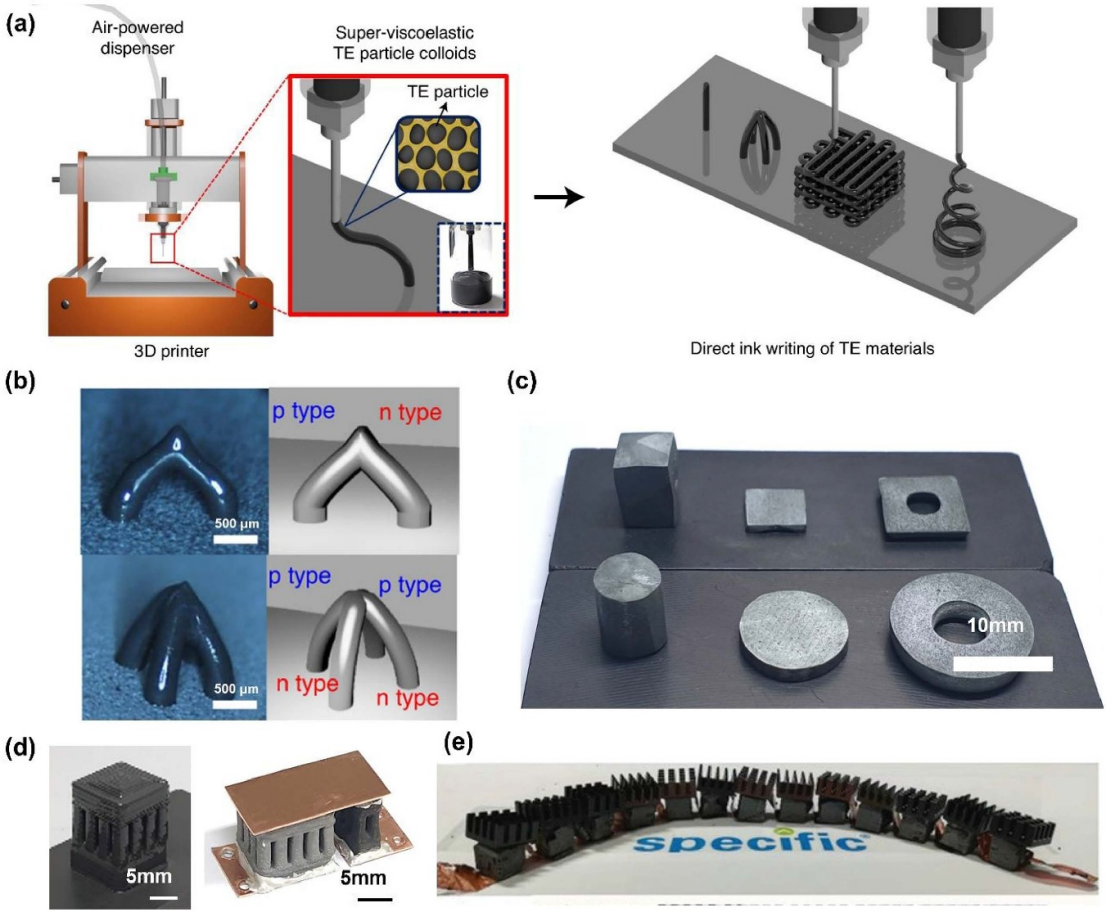


Figure 5. (a) Scheme of direct ink 3D writing for fabricating thermoelectric materials. (b) Bi_2Te_3-based. Reproduced from [63], with permission from Springer Nature, (c) PbTe-based [71] 3D-printed TE materials. [71] John Wiley & Sons. © 2021 Wiley-VCH GmbH. (d) Ternary silver chalcogenide-based. Reproduced from [72]. CC BY 4.0 and (e) SnSe-based 3D-printed TE devices. Reproduced from [73]. CC BY 4.0.

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 TE legs—geometries that are anticipated to yield superior energy conversion efficiencies than that of a cuboid—the 3D printing of TE materials presents an opportunity to fine-tune 3D architectures as shown in figure 6(c), thereby enhancing device efficiency (figures 6(d) and (e)) [75]. Nonetheless, this design paradigm has yet to be fully exploited in the optimization of TE 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 TE 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 TE materials exhibit porous nature, which significantly influences their thermal and electrical transport properties. Addressing this

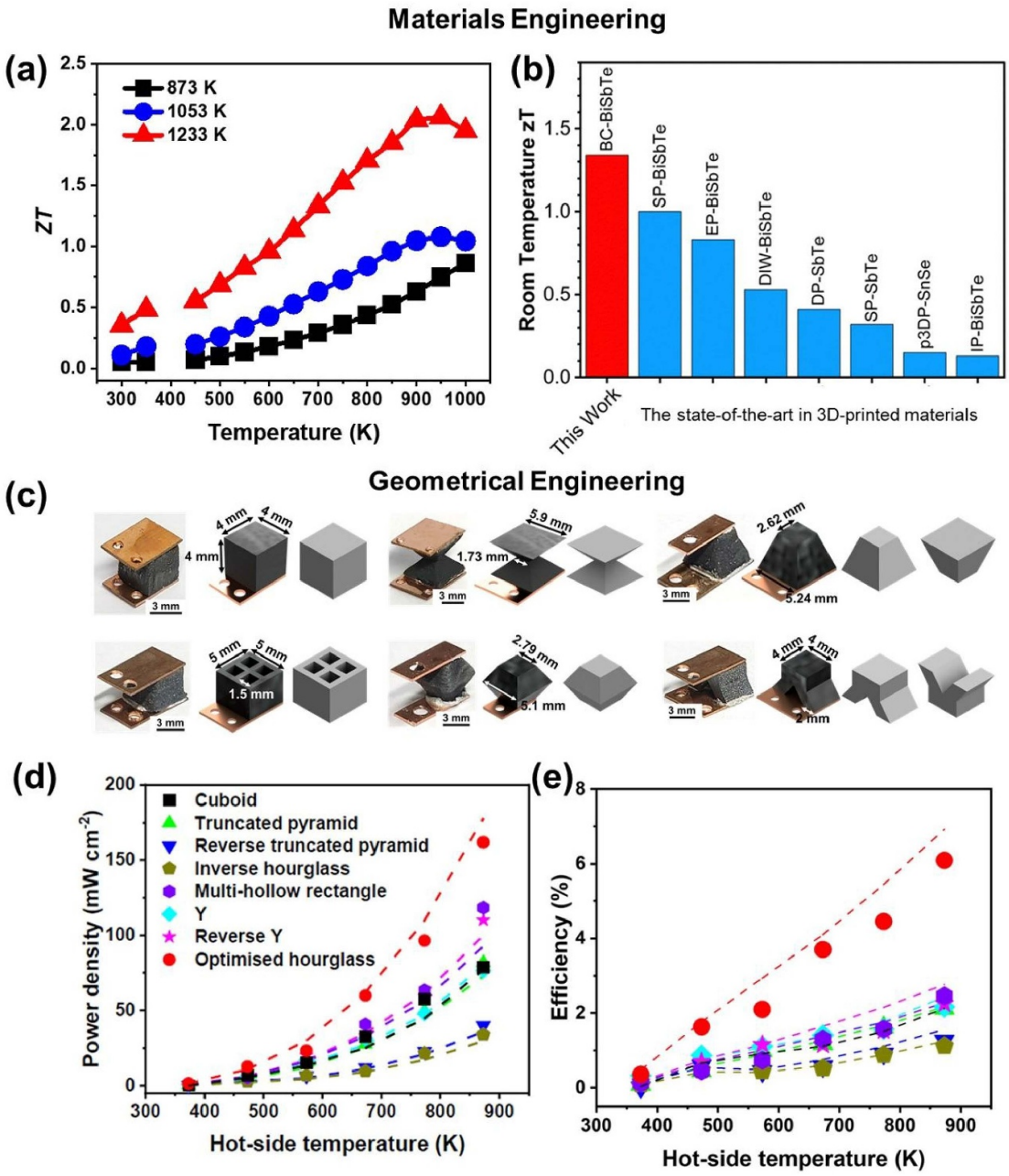


Figure 6. (a) *ZT* values of the 3D-printed Cu_2Se materials sintered at 873, 1053, and 1233 K [75]. (b) Comparison of room-temperature *zT* between the blade-coated BiSbTe-Te sample and other *p*-type thermoelectric materials made with different ink-based processes [76]. (c) Photographs and 3D illustrated models of single-leg devices chipped with the 3D-printed Cu_2Se legs with various geometries [76]. (d), (e) Power density and efficiency of the Cu_2Se-based single-leg devices shown in the panel (c). (a), (c), (d), (e) Reproduced from [75], with permission from Springer Nature. (b) Reproduced with permission from [76]. CC BY-NC 3.0.

issue can draw insights from the ceramic moulding industry, where ceramic slurries are cast and subsequently sintered under pressure-less conditions [77]. 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 TE materials, thereby enhancing their performance.

An alternative approach to elevating the TE performance beyond the intrinsic material efficiency is through the structural design of the TE legs within a device [72, 74, 75]. The Son group has recently reported several instances of 3D design and printing demonstrations for TE power generators [72, 74, 75]. 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 5(e)) within the TE legs can increase the temperature difference across the leg, resulting in improved power generation efficacy [72]. Furthermore, the geometric design and 3D printing of Cu_2Se TE materials with an hourglass shape have demonstrated superior power generation by optimizing thermal resistance and heat dissipation characteristics [75]. These advancements present a novel avenue for decoupling the interdependent relationship between thermal and electrical properties in TE 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 TE 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 TE materials (figure 6(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 TE ink technology.

Concluding remarks

The advent of 3D printing methodologies for TE materials and devices has unveiled expansive research opportunities in academia in terms of the printing process, 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 TE materials in the TE 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 TE materials and devices, but also accelerate the industrialization of 3D printing processes for manufacturing TE devices. I hope that this concise roadmap will contribute to charting the trajectory of future research in the 3D printing of TE materials and modules.

Acknowledgements

This research was supported by the Nano & Material Technology Development Program and the mid-career program through the National Research Foundation of Korea (NRF) funded by Ministry of Science and ICT (RS-2024-00449743 and RS-2022-NR070604).

1.5. Novel routes—electrodeposition

Samina Akbar and Iris Nandhakumar

Department of Chemistry, University of Southampton, Southampton, United Kingdom

Status

Electrodeposition has emerged as a promising technique for the fabrication of 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 [78]. A wide range of TE materials from thin films, nanostructures to 'bulk' materials and even miniaturized 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 compounds [79] which are TE materials that are known for their high zT 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 growth [80] and pulse deposition to grow thick and smooth films [81, 82] 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.

Current and future challenges

The ability to form materials into arbitrary 3D 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 [93]. To produce 3D geometries, the use of soft-templates has been reported [94]. To date, there are only very few studies which demonstrated the improvement of TE 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 and ionic liquids [95] (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 TE materials. Interestingly, ionic liquids such as trimethylamine hydrochloride also function as a structure directing agents, eliminating the need for templates [96].

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) [97], copper selenide (Cu_2Se), and silver selenide (Ag_2Se) [83]. Numerous studies have defined and investigated electroplating protocols, yet only a few have included the characterization of TE properties. In 2021 Manzano *et al* defined and investigated the electrodeposition of Ag_2Se and examined its TE properties. The chalcogenides of Sn, Cu, skutterudites, and clathrates have emerged as new high-performance TE materials for medium temperature range applications [79]. A recent study introduced CuNi alloys, with the highest zT, as a new inexpensive and scalable material, suitable for industrial applications [85]. 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 [98]. 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 [91].

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 ($\mu WK^{-2}m^{-1}$)	Measured temperature (K)	References
Ag_2Se	Thin film	—	−136	3421	RT	[83]
CuSbTe	Thin film	—	−382	2800	RT	[84]
$Cu_{0.65}Ni_{0.35}$	Nanocrystalline	6.1×10^{-2}	−76 −39	8248 1673	∼1000 RT	[85]
$CoSb_3$	Thick film		222.75	558.17	—	[86]
In doped $CoSb_3$	Thick film		−89.84	115.11	RT	[80]
Fe doped $CoSb_3$	Thin film		57	832	RT	[87]
Ce doped Fe_3CoSb_{12}	Thin film	0.6		>100	653	[88]
CuSe	Thin film		+106	5.3	—	[89]
SnSe	Thin film		1000	5.8	∼600	[90]
$Cu_3(HHTP)_2$	Thin film		−121.4	3.15×10^{-3}	—	[91]
$Ni_3(HITP)_2$	Nanostructured	1.19×10^{-3}	−11.9	0.833	RT	[92]

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 capitalizing 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 realize the full potential of electrochemical methods for the production of more sustainable TE materials for the next generation of TE devices.

1.6. Module fabrication

Richard Tuley and Cevriye Koz

European Thermodynamics Ltd, 8 Priory Business Park, Kibworth, Leicestershire LE8 0RX, United Kingdom

Status

The most common commercially available TEMs are fabricated using bismuth telluride materials, aluminium oxide substrates and conventional solder techniques. Many of the fabrication processes (figure 7) still used today were first established more than 50 years ago [99] and have led to bismuth telluride modules seeing commercial success in TE cooling applications. However their commercial success in TE generation, where the potential market is larger, >$1.5 billion [13], 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 utilize 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 TE legs to interconnects are commonly used [100], and more complex multi-layer metallization approaches on the ends of TE legs utilize sputtering or diffusion bonding [101] rather than electroplating.

It has been estimated that 30% of the global warming contribution and 20% of the resource depletion in a TE system is from manufacturing processes alone [102]. Module design also has a significant impact on the quantity of TE 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 TE materials [2].

Current and future challenges

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

1. Minimizing TE material usage in module fabrication
2. Maximizing performance and lifetime from the module, to maximize energy generation per unit of module production
3. Sustainability of module fabrication processes

Minimizing TE material in current module fabrication processes requires:

- maximizing the material yield by an often-neglected focus on the reproducibility of materials properties [103]
- minimization of losses in subtractive processes such as precision cutting which can be as high as 30% [104].

Material usage can also be reduced through module design. Neglecting thermal and electrical contact resistances, both the electrical and thermal resistances of TE legs scales with the aspect ratio of the leg alone. Therefore shorter, narrower legs can be used to give equivalent performance while utilizing less TE material. However to enable this approach, electrical and thermal contact resistances need to be very low [105], and the mechanical strength of the TE material must be sufficient to support both the same forces on a smaller total TE material cross-sectional area and the intrinsically higher thermal stresses from the shorter legs [106]. With the weaker research focus on the mechanical properties of TE materials, and the complex and application-specific loading conditions TEM 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 TE legs, where cutting losses only increase.

Approaches to maximize the TE material performance are the focuses of other sections. Maximizing the performance and lifetime of the module additionally requires highly thermally stable electrical contacts, with low contact resistances [105] e.g. <50 μOhm cm^2, good thermal conductance and mechanical robustness. Simultaneously achieving all of these while utilizing scalable, low-cost manufacturing processes is a difficult challenge, as great as producing the material itself. Long module lifetimes are required

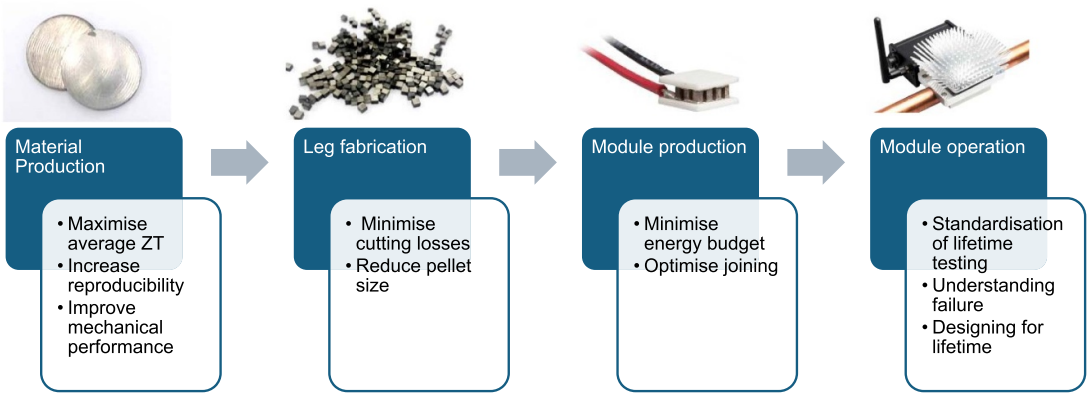


Figure 7. Module fabrication process and sustainability approaches at each stage.

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 (0.7 eV) would predict that 15 min 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 standardization of lifetime tests for high temperature modules makes comparisons more difficult, further complicating this task.

Sustainability of module fabrication processes requires minimizing 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 minimize material losses, as discussed further in sections 1.4 and 1.5 of this article. Further advances in subtractive processes are also possible by minimizing cut widths and maximizing leg yield. This typically requires more focus on improving the mechanical properties of high-performance TE materials to enable high quality, high speed cutting without chipping [107, 108], but this area has seen much less attention than TE 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 metallization layers, through calculating interfacial reaction energies and energy barriers to migration [109], charged point defect formation energies [110], multi-step screening strategies [61] and high throughput experimental tests of interfacial reactions [111]. 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 TE devices.

To minimize high temperature steps in fabrication requires us to break the link between joining temperatures and operating temperatures. Alternative joining approaches can be considered which utilize joining temperatures below the operating temperatures, for example solid-liquid interdiffusion bonding [112], also referred to as transient liquid phase bonding or sintering [113], which uses the rapid diffusion of a lower melting point material to form intermetallics with higher melting points. Sintering of Ag nanoparticles [114] 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 standardization 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 [115].

Concluding remarks

Module fabrication is a crucial step to enable sustainable TEs 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 optimization to minimize process temperatures and material use and wastage are promising areas. This requires improvements in the mechanical properties of TE materials. Increased understanding of the failure modes of TEMs alongside standardization 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 TE development, making an impact through real-world applications.

Acknowledgements

The author would like to thank the UKRI FLF scheme, Grant No MR/V026224/1 for funding.

1.7. Upcycling waste for sustainable thermoelectrics

Ran He[1], *Pingjun Ying*[1], *Amin Bahrami*[1], *Vicente Pacheco*[2] *and Kornelius Nielsch*[1]

[1] Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research, Helmholtzstraße 20, 01069 Dresden, Germany
[2] Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Winterbergstraße 28, 01277 Dresden, Germany

Status

Upcycling waste materials for 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 [104, 116] (figure 8). 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 [117]. 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 [118]. 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 sulphide 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 [119].

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.

Current and future challenges

The industrial adoption of waste materials and recycling of 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 (LCA) 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 strategies. These differences, which vary by manufacturer, demand tailored recycling approaches, making the process resource-intensive and technically demanding.

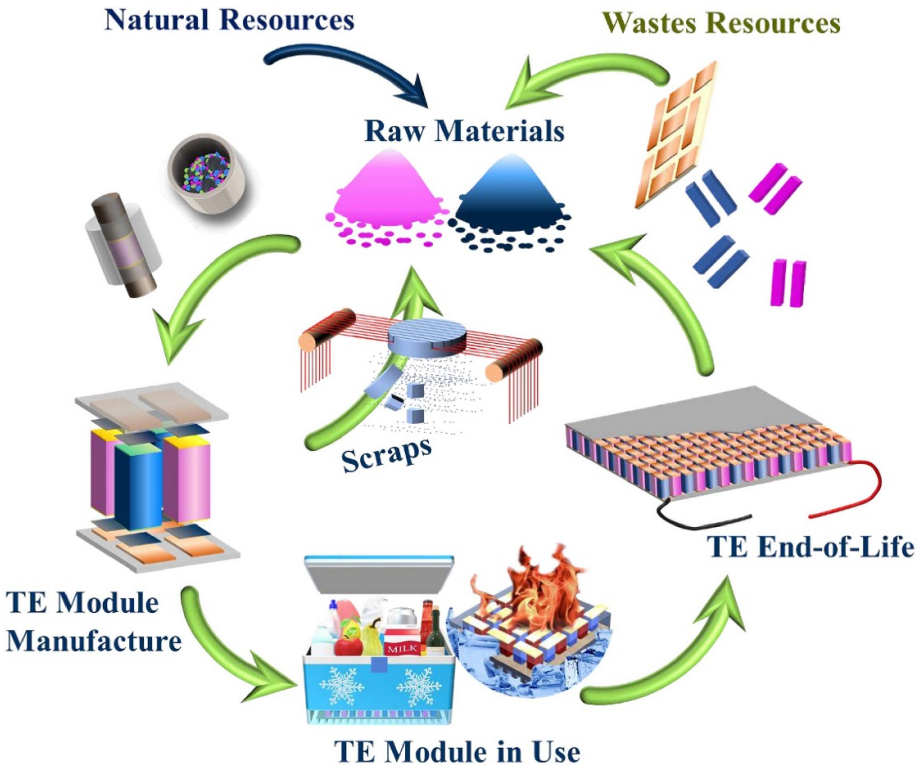


Figure 8. Schematic of the upcycling waste for sustainable thermoelectrics.

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

Moreover, most recycling research has focused on a limited range of materials, such as Bi_2Te_3, magnesium, and silicon. However, new high-performance TEMs have emerged in recent years such as $Mg_3(Sb, Bi)_2$, Ag_2Se, etc [120–123], and studies on their upcycling potential remain sparse, leaving a gap in the knowledge necessary to expand recycling efforts.

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

Advances in science and technology to meet challenges

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

The authors are currently involved in two ongoing projects, RecycleTEAM [124] and THERMOS [125], investigating the recycling of elements such as Bi, Se, Te, Sb, and Ag. One approach involves selective evaporation to separate elements from compounds (figure 9), enabling subsequent refinement through established processes. Another approach employs selective oxidation, producing MgO, Sb_2O_3, and metallic Ag from MgAgSb, followed by separation via soft chemistry methods. Both strategies prioritize avoiding hazardous chemicals and minimizing energy-intensive processes.

To enhance the adaptability of recycling technologies, advanced techniques such as high-resolution spectroscopy could be used for precise sorting of waste materials. This approach would allow for tailored

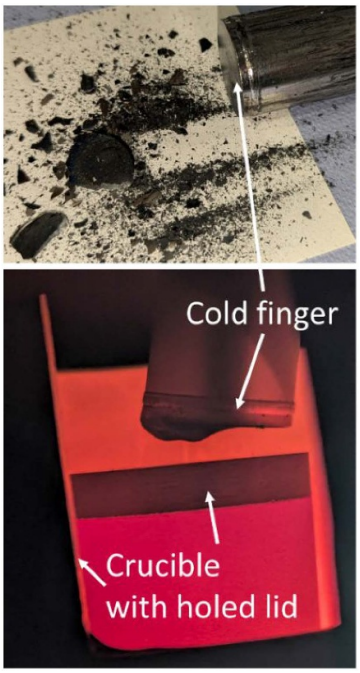


Figure 9. Tellurium-rich condensed phase (top) obtained by selective evaporation of a 50:50 mixture of *n*- and *p*-Bi_2Te_3 in a graphite crucible (bottom) and condensation in a cold finger (diameter 2.5 cm).

recycling processes that maximize the utility of specific waste streams. For example, variations in silicon kerf waste from different manufacturers could be managed, facilitating consistent TE material production from diverse, lower-purity sources.

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 Mg_2Si-based materials can mitigate impurity effects, enabling comparable zT values between samples derived from 100% solar-grade silicon and those from 100% reused silicon [126]. Such strategies highlight the potential of recycled materials to meet performance standards.

Integrating 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.

Concluding remarks

The future of TE materials is increasingly intertwined with the ability to upcycle waste into high-performing, sustainable devices. While significant strides have been made in recycling TE materials like Bi_2Te_3, 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

This work was supported by the state of Saxony via the M-ERA NET THERMOS project. R.H. acknowledges support from the European Union's Horizon Europe research and innovation programme (ERC Starting Grant, TENTATION, 101116340). The RecycleTEAM project is supported by the German Federal Ministry for Economic Affairs and Climate Action under the grant 03EN2056A.

1.8. Data-driven design and discovery of thermoelectrics

Ricardo Grau-Crespo[1], *Luis M Antunes*[1] *and Keith T Butler*[2]

[1] Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, United Kingdom
[2] Department of Chemistry, University College London, London WC1H 0AJ, United Kingdom

Status

TEs have proved to be a popular target for computer simulations and modelling, which can partly be attributed to the fact that the components of zT, namely the Seebeck coefficient, electrical conductivity and thermal conductivity, are all 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 ML has offered the promise of accelerating the prediction of these properties and hence facilitating computational discovery of new sustainable TEs.

The role of ML in modelling TEs is multi-faceted. As we outline in a more detailed perspective on the field [127], 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 TE properties. This is summarized in figure 10(a), 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 [18]. Since then there have been many studies that predict Seebeck coefficients [128], electrical conductivity [129] and thermal conductivity [130].

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 [131]. 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. [132]). 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 [133].

Current and future challenges

Comparing the uptake of ML for design of TEs to other applications, an interesting trend emerges. The data in figure 10(b) shows a comparison of ML usage in TEs and PVs (PV is chosen as a closely related materials field). The plot shows the percentage of publications in each field which mention ML (specific Web of Science search terms were 'TE ML' and 'PV ML' vs 'TE'/'PV'). Superficially, both fields appear to have similar uptake; however when we look for a specific type of ML, graph neural networks (GNNs)—the hatched areas—we see something different. GNNs are used in more than 25% of ML PVs studies in 2024 (59/230), but in TEs 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 TEs 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 [134]. This lack of uptake of GNNs for TEs signposts the biggest current challenge in ML discovery of TEs: lack of reliable training data.

There have been a series of efforts to develop datasets for TEs from both experiment and theory—see reference [127]'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 [127, 135], and there have been some attempts to learn predictive models from this data with GNNs [128] and transformers [129]. However, these theoretical databases are only as reliable as the approximations upon which they are built. A comparison of data from [135] with experiment found that, while Seebeck coefficients were relatively well reproduced, power factors calculated under the CRTA do not capture experimental trends well ($r^2 = 0.33$) [136].

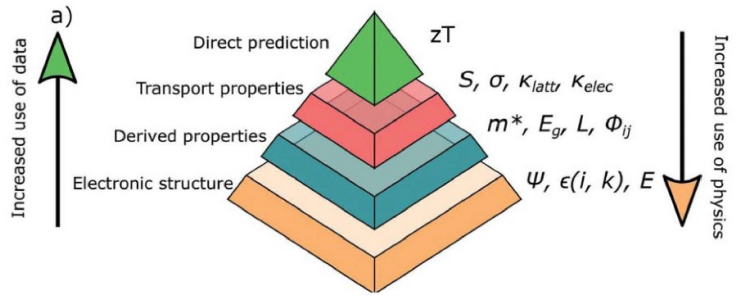


Figure 10. (a) The hierarchy of levels at which ML is being used for thermoelectrics with methods using more data and fewer physical biases at the top and vice versa; Reprinted with permission from [127]. Copyright (2022) American Chemical Society. (b) Publication data for ML in thermoelectrics and photovoltaics, normalized 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).

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 [137, 138].

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 [139], which should facilitate generation of more reliable theoretical data. There have also been recent efforts to develop databases and ML models for doping [140]. Experimentally, automated experiments have promise for generating highly uniform, well understood data [141], which can be of great value for training future ML models. However, we note that fully-automated materials synthesis and characterization is still far from realized [142], 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 [143]. 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 [144] set out a template of how research data should be shared; it is now imperative the sharing of data is incentivized 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 [145].

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 [146] and could be of use for both prediction of properties and for speeding up atomistic simulations. Another promising development is the advent of LLMs, which have recently found application in materials science [147]; of particular interest is the ability of LLMs to pre-train 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 TEs 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 TEs (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 TEs, critical assessment of these findings is essential. We would also like to re-iterate 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 recognized in future. Although we are only starting to explore the role of data-driven approaches in TEs, if we get things right in the coming years, there is potential to achieve highly significant advances.

Acknowledgements

KTB acknowledges funding from UKRI (EP/Y000552/1 & EP/Y014405/1).

1.9. Electronic transport modelling and simulations for thermoelectric materials

Neophytos Neophytou, Rajeev Dutt and Bhawna Sahni

School of Engineering, University of Warwick, Coventry CV4 7AL, United Kingdom

Status

The simulations for electronic transport properties of TE materials typically involve 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 TEs, 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 [148], the coherent phase approximation [149], or the special quasi-random structure using software such as ATAT [150] are used. Linear scaling DFT codes such as ONETEP [151] or BigDFT [152], and other specialized codes such as DFTB+ [153], can then provide the modified electronic structure. Then for first order understanding, quantities such as the weighted mobility [154], and simple parabolic band models [155], 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 [156]. It solves the Boltzmann transport equation (BTE) under the 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 ML 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 TEs 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 TE effects imperative to drive the field towards its next phase.

Current and future challenges

The imminent challenge in TE 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 TE 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 [156]. 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 [157]. 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) [139]. 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 [158]. Wannier interpolation to expedite the process has been implemented in the EPW [159], Perturbo [160], and Phoebe codes [161]. 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 is not clear how it can be used for transport calculations, or how scattering rates can be extracted reliably. Typically alloy scattering substantially affects electronic transport, but it is currently treated in a simplified manner, by considering the band edge variation of the

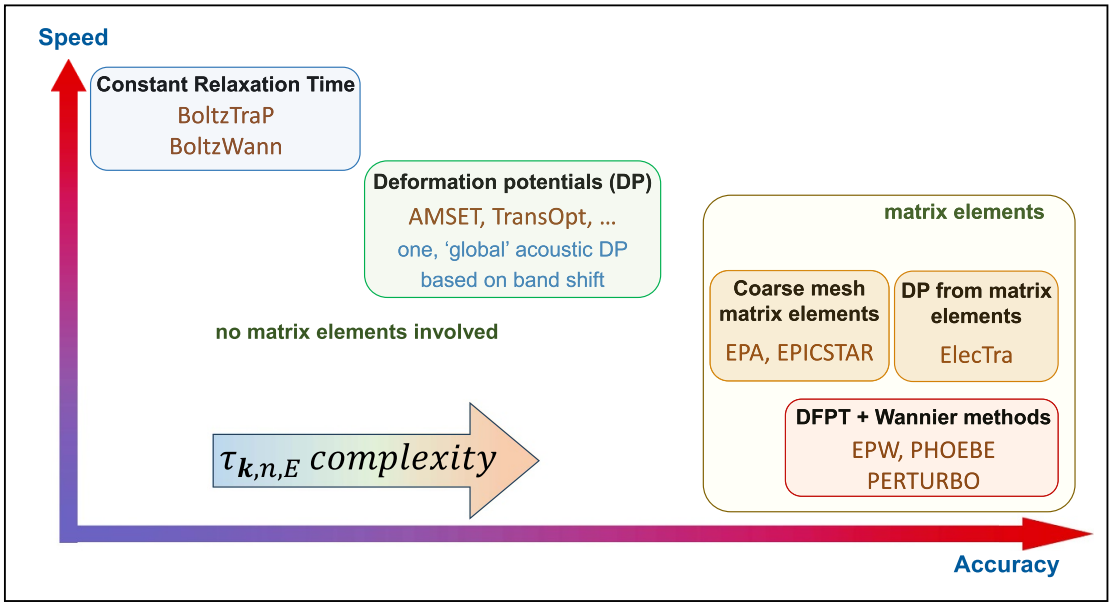


Figure 11. Hierarchy of existing electronic transport simulation methods and codes with respect to speed versus accuracy (with increasing relaxation time complexity).

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 TEs.

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 [162], EPICSTAR [163], and ElecTra [164]. The details of each differ, i.e. EPA and EPISTAR 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 figure 11 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 hierarchize 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 [165], thus the extraction of many matrix elements might deem unnecessary in some cases 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 able to drive the field should be 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 [166] and ShengBTE [167] widely adopted.

Concluding remarks

In conclusion, the large advances in the field of TEs, 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 TE 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 CRTA that drove the field until recently are not anymore adequate, especially in the era of materials screening and ML 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 still 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

This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Programme (Grant Agreement No. 678763) and from the UK Research and Innovation fund (project reference EP/X02346X/1).

2. Materials

2.1. Bi_2Te_3—near ambient materials

Nagendra Singh Chauhan[1] *and Takao Mori*[1,2]

[1] Research Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan
[2] Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba Ibaraki 305-8573, Japan

Status

Development of near-ambient 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 and wearable devices; and providing eco-friendly cooling options [11]. 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, Bi_2Te_3 and its solid solution alloys continues to remain the most widely used material in TE products, accounting for majority of the TE market share [11, 168]. At near, RT, they exhibit high electrical conductivity ($\sigma \approx 10^5$ S m^{-1}) and moderate Seebeck Coefficient ($S \approx 150$–200 μVK^{-1}), owing to high band degeneracy, low effective mass, and high carrier mobility ($\mu \approx 150$–500 cm^{2}V^{-1}s^{-1}), resulting in a significantly higher power factor (σ^2 $S > 2 \times 10^{-3}$ Wm^{-1}K^{-1}) for both n and p-type conduction [99, 169, 170]. Thus, leveraging the Seebeck and Peltier effects, $Bi_xSb_{2-x}Te_3$ (p-type) and $Bi_2Te_{3-x}Se_x$ (n-type) based compositions with inherently low thermal conductivity ($\kappa \approx 0.5$–1.5 Wm^{-1}K^{-1}) showing peak TE performance near room temperature, as quantified using TE 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 in refrigeration [99, 169, 170]. The longstanding limitation of inferior $zT \approx 0.5$ in n-type $Bi_2Te_{3-x}Se_x$ that resulted in inefficient TEMs, has now been overcome and outperformed by development of cost-effective and high performance ($zT > 1.5$@700 K) n-type $Mg_3(Sb, Bi_2)$-based Zintl compounds [26, 171–173], 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 [173, 174]. Thus, developing all-Mg–Sb-based modules or hybrid Mg_3Sb_2–Bi_2Te_3 devices, leverages both performance and material sustainability [173–176]. Alternatively, Bi_2Te_3 based superlattice/thin films are pioneering innovations in microTEGs and wearable electronics [177, 178]. Notably, Bi_2Te_3 based flexible films exhibiting power factors of 4.2 mWm^{-1}K^{-2} (p-type) and 4.6 mWm^{-1}K^{-2} (n-type) reported recently could accelerate flexible TE energy harvesting applications [174]. 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 synergize 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 [177, 179]. 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, as presented in figure 12.

- **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

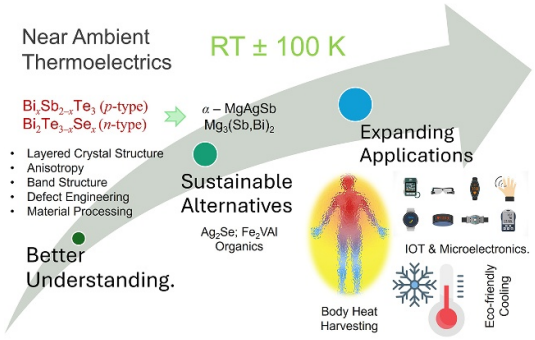


Figure 12. An overview of status of near ambient thermoelectrics.

TE performance, albeit being detrimental to mechanical properties [169, 179]. 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 TE performance [26, 171–173].

- **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 [99, 169], Mg_3Sb_2 can be susceptible to Mg-vacancies [26, 171, 172]. 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 [99, 169, 170]. In contrast, Mg_3Sb_2 and MgAgSb achieve high TE performance primarily in *n*-type and *p*-type forms, respectively, due to band degeneracy localized in either the conduction or valence bands [26, 171–173]. 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 optimizing 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_2VAl), 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 [180]. Self-powered skin electronics, capable of energy harvesting and health monitoring are being developed, based on Bi_2Te_3-based hybrid nanocomposites [181]. Alternatively, ductile inorganic semiconductors (such as Ag_2Se, InSe, Ag_2S) [182] and polymer nanocomposites (such as PEDOT:PSS, PANI) [183] 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 $Mg_3(Sb, Bi_2)$ based materials [169, 174]. To ensure long-term device stability above 473 K, low-resistivity barrier layers that meet the coefficient of thermal expansion criteria, such as Ti, Fe, Co–P, FeCrNi, and Ni-based alloys, are being studied [44, 174]. Simultaneously, in many cases integrating Mg-based materials as green alternatives into practical modules, have led to realization of higher efficiencies at relatively low temperature differences ($\Delta T \approx 250$ K) [173, 176]. Currently, *n*-type $Mg_3(Sb, Bi)_2$ and *p*-type α-MgAgSb are considered the most viable alternative for low-grade waste heat recovery ($\eta > 7\%$) using TEGs [173–176]. While inexpensive alternatives like *n*-type $Mg_3(Sb, Bi)_2$ 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 $Mg_3(Sb, Bi_2)$ 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 $Mg_3(Sb, Bi)_2$ and *p*-type α-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

Support from JST Mirai Program (JPMJMI19A1) is acknowledged.

2.2. Full-Heusler alloys

M Parzer[1] , *F Garmroudi*[1], *A Riss*[1], *T Mori*[2] *and E Bauer*[1]

[1] Institute of Solid State Physics, TU Wien, A-1040 Wien, Austria
[2] National Institute for Materials Science (NIMS), Tsukuba 305–0044, Japan

Status

Heusler materials are, in general, ternary alloys and compounds, where *d*-electrons dominate the electronic DOS (eDOS) near the Fermi energy. Thus, different ground states can emerge, attracting scientific and technological interest. Besides topological, magnetic, superconducting or heavy fermion properties, TE gained specific inquisitiveness. This is mostly due to the exceptional mechanical, thermal and chemical stability of these materials, as well as the high TE power factors, which, in best-performing systems, are significantly above archetypal Bi_2Te_3-based systems. There are several sub-groups of Heusler compounds, and several crystal structures have been identified [184]. With respect to TE, half-Heusler, *XYZ*, and fH, X_2YZ, 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 TE 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 fH alloys and compounds, crystallizing in the cubic Cu_2MnAl structure (space group Fm-3m, no. 225). FH materials with a valence electron count (VEC) $N_{vec} = 24$ (e.g. Fe_2VAl), are most promising with respect to TE, since such systems exhibit a gap in the eDOS near the Fermi energy and appear to be non-magnetic. Positive or negative deviations from $N_{vec} = 24$ 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 Cu_2MnAl structure, offering outstanding tunability. While TE power factors of fH systems can be superior, the often intrinsically large thermal conductivity prohibits competitive values of the TE *zT*. At present, the best TE performance of fHs reaches up to $zT_{max} = 0.3$–0.5 around 25 °C–100 °C, two to three times lower than archetypal Bi_2Te_3-based materials.

The quest for sustainability of products and raw materials (compare table 2) gains growing importance. The setup of a TEG, with several different components (active TE 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 [185]. Up to 50% of energy and up to 2/3 of CO_2 can be saved using scrap, in comparison to classical routes [186]. With respect to Bi_2Te_3, the US Geological Survey reports that there is no Te-based scrap available, from which secondary Te can be extracted, while about 5%–10% of the US consumption of Bi is re-extracted from Bi-containing alloy scrap [187].

Current and future challenges

Fe_2VAl-based fH compounds inherently meet several application-specific requirements, such as sustainability, stability, and cost-effectiveness. Moreover, as showcased in figure 13(a), both *n*- and *p*-type materials are available with similar stoichiometries, enabling matching thermal expansion coefficients. Primary challenges in fH TEs centre on enhancing the conversion efficiency of TEGs. Therefore, it is crucial to further optimize the dimensionless *zT*, especially for *p*-type compounds.

Figure 13(a) displays the doping-dependent Seebeck coefficient of *p*- and *n*-type Fe_2VAl TEs from various substitution studies in the literature [195]. The black solid line is a theoretical calculation using a two-parabolic band model, as also employed previously by Anand *et al* in [196]. The much larger density-of-states-effective mass and weighted mobilities of the conduction band electrons result in significantly higher TE performance for *n*-type Fe_2VAl TEs. Indeed, *p*-type Fe_2VAl rarely possess Seebeck coefficients exceeding 100 $\mu V \cdot K^{-1}$, 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 $\mu_W = 800$ $cm^2 \cdot V^{-1} \cdot s^{-1}$, being among the largest of any *n*-type semiconductor. This is highlighted in figure 13(b), which compares μ_W and the lattice thermal conductivity κ_L of Fe_2VAl-based materials with Bi_2Te_3 and other leading materials. As obvious from figure 13(b), the

Table 2. Raw material prices of relevant thermoelectric materials, their annual production and the estimated global reserves. Prices are collected on 15 July 2024, from various marketplaces. The annual production and global reserves refer to the year 2023 and are revealed from the U.S. Geological Survey [187].

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	$3.9 \cdot 10^{8}$[a]	$32 \cdot 10^{9}$[a]
V	~25	$1.0 \cdot 10^{5}$[b]	$19 \cdot 10^{6}$[b]
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	$9.2 \cdot 10^{6}$[c]	$75 \cdot 10^{7}$[c]
Mg	~2.5	$9.4 \cdot 10^5$	Sufficient for future use
Ge	~2800	$1.4 \cdot 10^2$	—

[a] …refers to bauxite.
[b] …refers to ferro-vanadium 80%.
[c] …refers to ilmenite and rutile.

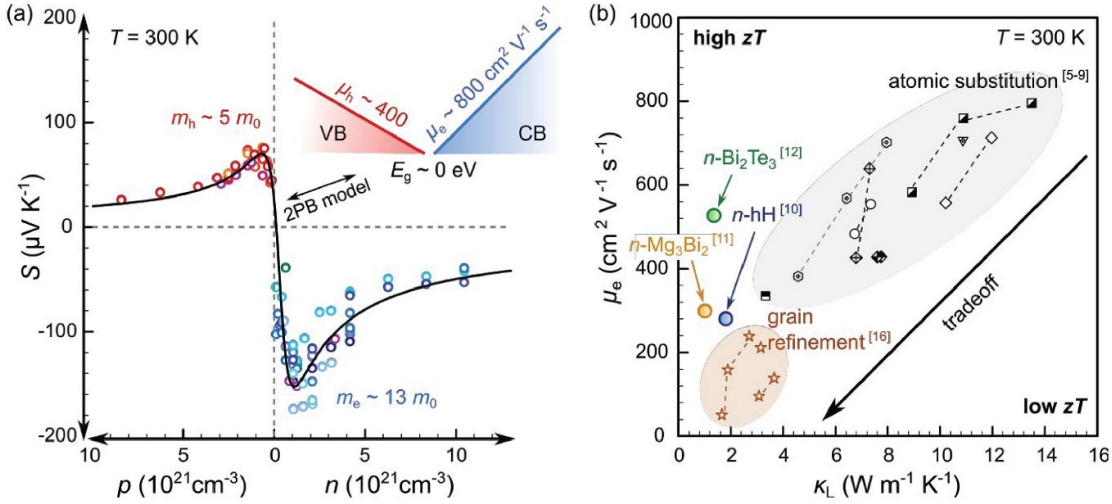


Figure 13. (a) Charge carrier density dependent Seebeck coefficient S of Fe_2VAl based alloys taken at $T = 300$ K. The open symbols are experimental data; the solid line is a theoretical prediction based on a two parabolic band model. The inset sketches the energy-dependent transport function near the 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 [99, 172, 188–194].

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 [197]. Reproducibility and large-scale production may, however, be an issue for such type of processing methods [194]. Thus, the crucial challenge remains: decreasing lattice thermal conductivity while maintaining favourable 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 TE performance, different strategies must be explored. As evidenced in figure 13(a), simple carrier concentration optimization by doping is not sufficient to increase zT in these materials. Instead, modifications of the electronic structure of p-type Fe_2VAl materials are necessary. To this aim, precise understanding of the band structure and chemical bonding within Heusler materials is necessary. DFT calculations are indispensable for this purpose, as they reliably predict the electronic structure and stability. Combining these calculations with efficient electronic transport modelling tools, can significantly advance our understanding of substitution and

alloying effects and will also be crucial for optimizing the electronic structure of *p*-type Fe_2VAl. While several studies in this direction have already found some success, vastly increasing the achievable values of the maximum Seebeck coefficient in *p*-type fH compounds [198–201], there seems to be still room for improvement.

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

The major challenge of reducing the large lattice thermal conductivity in Fe_2VAl has already been the focus of many studies [188, 190, 192, 197]. Achieving a breakthrough requires methods to decouple lattice-driven thermal transport from electronic transport in these materials. In half-Heuslers, using densification agents or phase-segregation of similar phases has stabilized electronic properties while reducing thermal conductivity through nanostructuring [172]. For fH compounds, similar or even more beneficial strategies must be explored, and methods to integrate nanostructuring optimally must be developed. Although high-pressure torsion has shown some success [197], it still leads to deteriorated electronic properties. In a recent work [194], we have shown that by forming composites with Bi–Sb alloys, which segregate at grain boundaries, charge and heat transport can be decoupled and zT can be improved dramatically above the values of the single components, i.e. Fe_2(V, Ta)Al and Bi–Sb, resulting in record-high zT up to $zT_{max} = 0.46$ at 300 K. Further overcoming the tradeoff between weighted mobility and lattice thermal conductivity in fH requires a systematic understanding of multi-phase materials and grain-boundary scattering, emerging as a hot topic in TE materials research. Tools to efficiently and reliably predict the effects of various micro- and nanostructuring strategies would significantly accelerate research and enable researchers to bypass this tradeoff.

Concluding remarks

Summarizing, fH compounds, specifically Fe_2VAl-based compounds, constitute a very promising material class for sustainable TE applications. The non-toxic, abundant and stable nature of the constituent elements, coupled with excellent recyclability and simpler device structures, are key advantages. First stability tests on basic fH devices have demonstrated the excellent long-term stability of the materials in practice, without any additional engineering [199]. Moreover, Fe_2VAl-based TE materials exhibit auspicious electronic properties, with the weighted mobility close to room temperature surpassing that of other state-of-the-art TE materials. If the lattice thermal conductivity could be decreased while retaining the excellent electronic properties, Fe_2VAl-based could become the best option for near-room-temperature TE applications.

Acknowledgements

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

2.3. Polymer composites

Chongyang Zeng and Emiliano Bilotti

Department of Aeronautics, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

Status

Polymers, polymer blends and polymer (nano)composites have attracted significant interest as sustainable TE materials due to their inherently low thermal conductivity, elemental abundance, high fracture toughness, low density and ease of processing [202], compared to traditional inorganic TE 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 TE 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 [203], 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 [204]. 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) [205] and polyaniline (PANi)/graphene-PEDOT:PSS/PANi/carbon nanotube (CNT)-PEDOT:PSS [206], with a zT value of 0.32 (at 20 wt% SnSe) and a power factor of 2710 μW m^{-1} K^{-2} at 300 K, compared with zT values of up to 1–2 for best inorganic TE materials (figure 14).

The combination of polymer matrices and TE fillers can not only tune the TE 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 TEGs. 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 [208], 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 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 TE 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 μV K^{-1} compared with 130–325 μV 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 TE power generation, yet significant challenges remain and will require a concerted and collaborative effort. Functionalizing the surface of conductive fillers can improve their dispersion in the polymer matrix and enhance interfacial compatibility. For example, the introduction of amino-terminated poly(3-hexylthiophene-2,5-diyl) (P3HT) on CNTs via covalent grafting [209]. For the combination of polymer matrix and fillers, strong interfacial interactions, including covalent bonding and ionic bonding, would be considered to provide good charge carrier transfer and improved mechanical properties. Advanced process techniques such as continuous melt extrusion or injection moulding can provide polymer composites with homogenous mixing and bulk structures for TE applications.

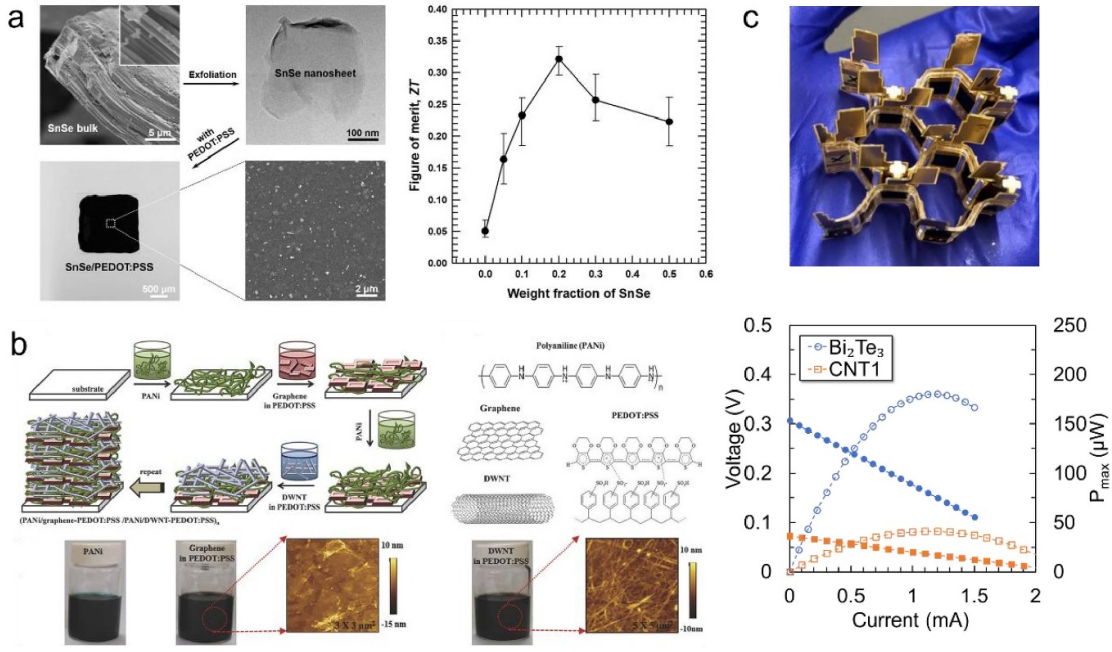


Figure 14. (a) Microstructures of SnSe and SnSe/PEDOT:PSS and *zT* values for PEDOT:PSS/SnSe composites. Reprinted with permission from [205]. Copyright (2016) American Chemical Society. (b) Schematic illustration of layer-by-layer deposition for polymer composites fabrication. [206] John Wiley & Sons. © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) A self-folded thermoelectric device and its thermoelectric performance. Reproduced from [207]. CC BY 4.0.

Numerous efforts have been made by researchers to process polymer composites, achieving high TE power factors (>100 μW m^{-1} K^{-2}) [210]. It has been reported that semiconducting CNT is a promising TE material with a high Seebeck coefficient, and that polymer-CNT composites with interconnected conductive percolated networks can reach good TE performance [211]. Controlling the order and orientation of conjugated polymer chains as well as their doping is another effective approach to improve their electrical conductivities and achieve high TE performance, particularly in combination with nanofillers [212]. Despite the limited working temperature of polymer composites (typically below 200 °C), this is sufficient for applications like energy harvesting from hot water pipes or the skin surface, for powering wearable electronics. From a different perspective, TE polymer composites could also work in tandem with inorganic materials, supplementing the poor low-temperature TE efficiency of typical inorganic materials.

For n-type polymer composites, one possible promising approach is to disperse good n-type (nano)fillers into polymer matrices, enhancing also the environmental stability of these fillers.

Some of the above challenges can also be met by designing new TE device architectures, enabled by mechanical flexibility, toughness and ease of manufacturing of polymers. For instance, a shape-programmed kirigami-inspired hexagonal honeycomb TE device, with built-in heat sink, has been recently demonstrated (figure 14(c)) [207]. Such a device architecture, applicable to both organic (e.g. CNT veils) and inorganic (e.g. Bi_2Te_3) TE thin films, achieved a maximum voltage of 0.53 V and a power output of at 406 μW at a ΔT of 47 K (in the case of Bi_2Te_3 with 76 p–n leg pairs) (figure 14).

Concluding remarks

Polymer composites have attracted significant interest as TE materials. While currently unsuitable for large-scale energy generation, due to the limited conversion efficiency, polymer composites show great promise for flexible, self-powered and wearable electronics. Researchers have demonstrated that good TE performance and mechanical flexibility can be achieved simultaneously by exploring new module geometries (e.g. sandwich or honeycomb structures). For a commercial breakthrough in wearable power electronics (with targets of ∼1.5 V voltage and ∼10 mA current [183]), it is paramount to extract high Seebeck coefficients from polymer composites.

Acknowledgments

The authors would like to thank the support from UKRI Innovate UK (KiriTEG Project, Reference: 51868). C.Z. acknowledges Ph.D. scholarship funding from the China Scholarship Council.

2.4. Halide Perovskites

Chang You and Oliver Fenwick

School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

Status

Two major problems that limit the sustainability of widely-used bismuth telluride TE materials are tellurium scarcity and high energy consumption for production. 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 TE materials arises from the combination of good charge carrier mobilities and ultra-low thermal conductivities (typically $\sim$0.5 W mK^{-1}), putting them in the group of 'phonon glass electron crystals' with the potential for high values of the TE zT or power factor (figure 15).

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 TE 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 [213]. 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 [214], $MABI_3$ (MA = methylammonium CH_3NH_3, B = Pb^{2+} or Sn^{2+}) are predicted to have zT between 1 and 2 [215]. The mixed halide HP, $CsPb(I_{1-x}Br_x)_3$, is predicted to have zT = 1.7 [216], whilst the low-dimensional $Cs_3Cu_2I_5$ perovskite derivative is predicted to have zT = 2.6 at 600 K [217]. Therefore, HPs have significant potential to become next-generation TE materials which combine high TE performance with sustainable composition and processing routes.

Current and future challenges

Experimentally recorded zT values of most HPs remain far lower than predictions (figure 15), which is mainly ascribed to low electrical conductivities arising from insufficient carrier concentrations. Electronic structures of HPs are often tolerant to defects and ionic compensation of charged defects can also occur [218]. 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 [219], crystals of $MAPbBr_3$ were doped with up to 15% Bi at the B-site but the carrier concentration only increased $\sim10^{14}$ cm^{-3} with a doping efficiency of just $\sim10^{-5}$% (figure 16(a)).

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 TEs. Of these, organic cation-containing HPs, known as hybrid inorganic-organic perovskites 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 [220].

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 HPs, 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

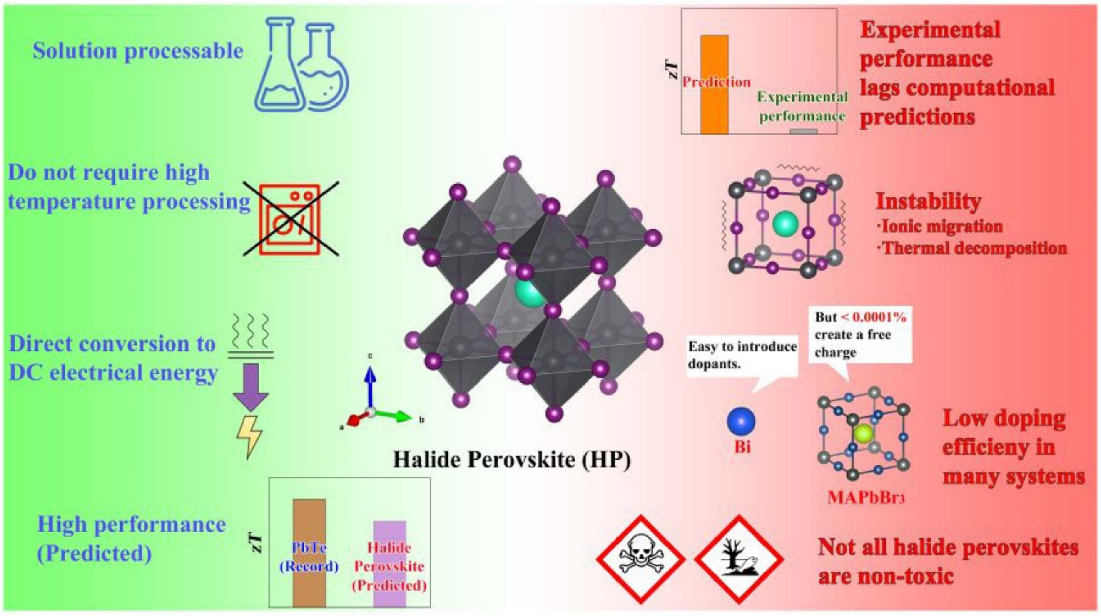


Figure 15. Advantages and challenges of halide perovskites.

[221], film morphology control [221, 222] and high entropy approaches using multiple anion and cation substitutions [223, 224]. However, these have barely been explored in HP TEs.

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, F_4-TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) has been used to treat $FASnI_3$ films [225], increasing the electrical conductivity from 0.06 $S{\cdot}cm^{-1}$ to 18 $S{\cdot}cm^{-1}$ and achieving $zT = 0.19$, which is a record for the HPs (figure 16(c)).

Compositional tuning is relatively easy in HPs and has several potential benefits. Increasing the ratio of MAI in $MAPbI_3$ or MABr in $MAPbBr_3$ can decrease trap density and increase carrier mobility by passivating ionic vacancy defects [226]. Compositional tuning by means of different precursor ratios during synthesis can also be used to tune HPs from *n*-type to *p*-type [227]. Only 1 at% of Cl^- dopant in $CsSnI_3$ can form a Cl-rich surface layer whilst enabling high zT (figure 16(b)) [228]. Ge^{2+} doping of $CsSnI_3$ at 20 at% Ge^{2+} increased lattice stability, reduce defect density and improved TE performance [229].

Thermal conductivity can also be tuned by diverse methods. Mixed halide $CsSnX_3$ with Br^- and I^- can decrease the thermal conductivity to 0.5 $W{\cdot}m^{-1}{\cdot}K^{-1}$ compared to the mono-halide at 0.8 $W{\cdot}m^{-1}{\cdot}K^{-1}$ [230]. 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 $CsPbI_3$ [231]. In $MASnI_3$ powders shear strain is more effective than normal strain (Figure 16(d)) [232], while ionic substitution can introduce internal strain with similar effects [233].

Concluding remarks

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

Stability is important for sustainability to ensure that energy pay-back times can be reached. This has been solved for HP 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 stabilization of the TE properties of HPs. One could expect that the operating

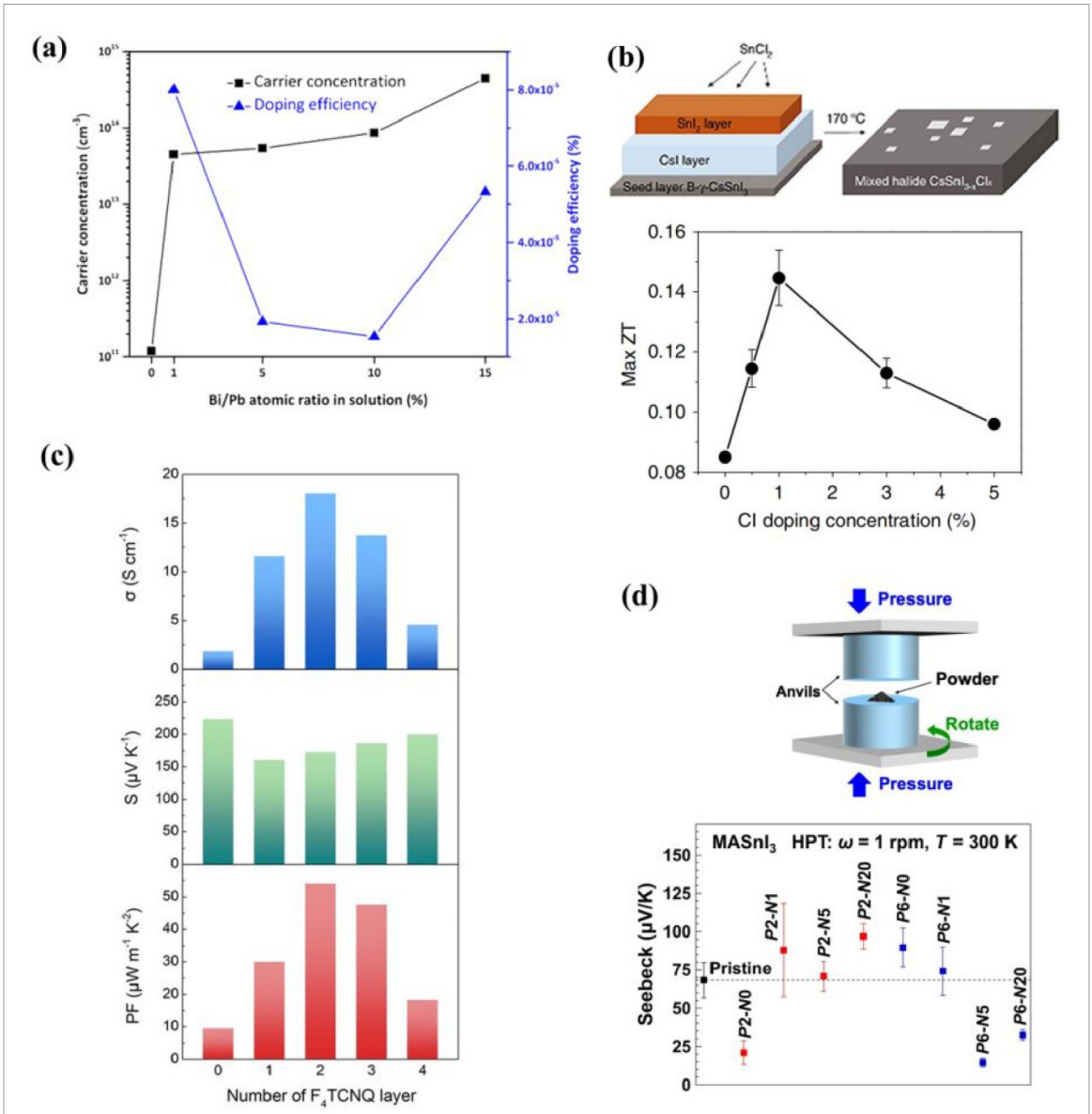


Figure 16. (a) The carrier concentration and doping efficiency of Bi-doped $MAPbI_3$ for various levels. Reproduced from [219]. CC BY 3.0. (b)The schematic graph of Cl-doped $CsSnI_3$ synthesis and the influence of introduced Cl on its *zT*. Reproduced from [228]. CC BY 4.0. (c) The electric conductivity, Seebeck coefficient and power factor (PF) of $FASnI_3$ after the treatment of different layers of F_4TCNQ. Reproduced from [225]. CC BY 4.0. (d) The schematic graph of applied stress and its influence on the Seebeck coefficient of $MASnI_3$. Reproduced from [232]. CC BY 4.0.

temperature range of future HP TEGs would be similar to solar cells, but there are uncertainties about how stabilization strategies might affect TE 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 HPs for TEs, but they nonetheless hold substantial potential as sustainable TE materials.

Acknowledgments

Oliver Fenwick is funded by a Royal Society University Research Fellowship [UF140372 and URF/R/201013] and the Engineering and Physical Sciences Research Council (Grant EP/Y008405/1). Chang You is funded by Queen Mary University of London and the Chinese Scholarship Council.

2.5. Sulfides: advances, issues and future challenges

Paz Vaqueiro[1] *and Emmanuel Guilmeau*[2]

[1] Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, United Kingdom
[2] Laboratoire de Cristallographie et Sciences des Matériaux, Université de Caen Normandie, ENSICAEN, CNRS, Normandie Univ, CRISMAT UMR6508, F-14000 Caen, France

Status

Large scale industrialization and mass adoption of TE devices require an easy manufacturing process of TE 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 TE performances. Bi_2Te_3 is commonly used in commercial Peltier modules and PbTe has been, for example, integrated in spacecraft and rover radioisotope TEGs. However, as discussed in section 1.1, the high HHI values and the toxicity of selenium and tellurium (table 3) 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 [13]. In this context, sulphide-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 sulphur (table 3) [234, 235]. The more iono-covalent nature of the chemical bonds and the higher atomic vibrational frequencies associated with the lighter sulphur 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.

Binary sulfides were first considered as potential TE materials in the 19th century, with A.C. Becquerel in 1866 describing the use of sulfides (Cu_2S) in 'TE batteries' [236]. In the 1980's, rare-earth-based sulfides were investigated as TE 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 $Cu_{12-x}TM_xSb_4S_{13}$ (TM = divalent transition metal) [237, 238], which is a sulphide mineral with intrinsically low thermal conductivity, aroused a renewed interest in sulfides as TE materials, and especially in p-type copper-rich sulfides [234, 239]. 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 17) [16, 240, 241]. The large diversity of crystal structures in sulfides offers a fantastic playground for the discovery of eco-friendly, non-toxic and low-cost TE compounds, and for their development in TE devices.

Current and future challenges

As highlighted by a recent compilation of properties of TE materials [16], 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 TE 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 ([242], and references therein). Fabrication of TE 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 SPS and hot pressing are often used for the consolidation of sulphide 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 sulphide materials, especially sintering at high temperatures, requires a precise control of the processing parameters to prevent sulphur 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 TE sulfides are 'liquid-like' superionic conductors, in which a mobile cation sublattice hinders phonon transport, resulting in ultralow thermal conductivity. However, the

Table 3. Abundance, toxicity, cost (adapted from [234]) and reserves HHI (section 1.1) of sulphur, 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

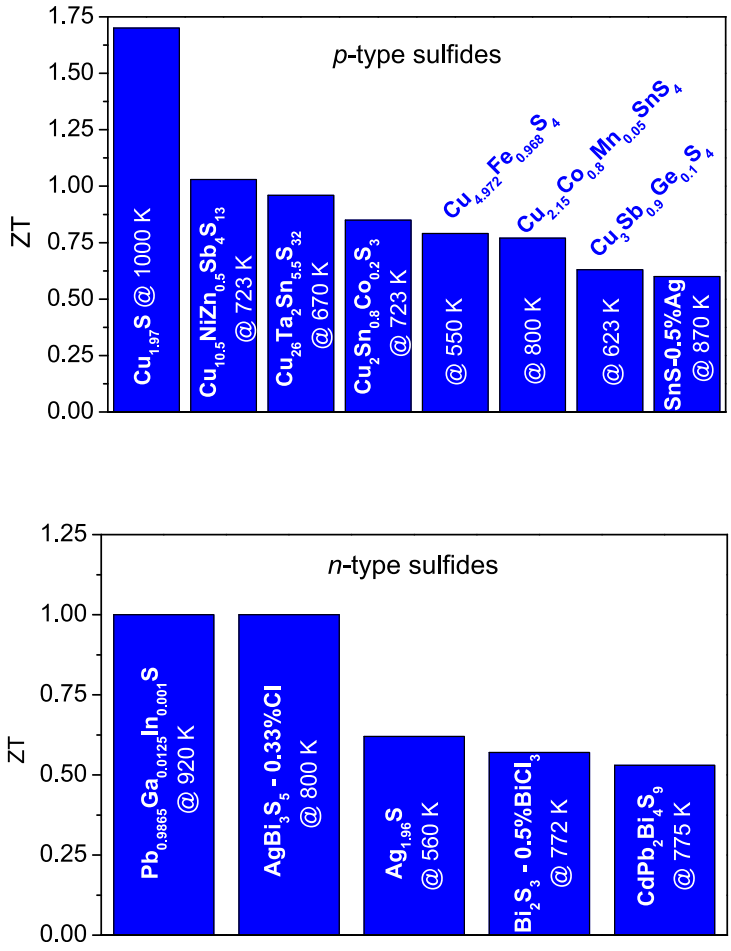


Figure 17. State-of-the-art figure of merit zT in n- and p-type bulk sulfides [16, 240, 241].

cation mobility that promotes 'liquid-like' behaviour also introduces instability into the materials when they are under operating conditions in a TE device. Copper-ion mobility leads to copper migration and deposition, which result in compositional changes that cause cracking and mechanical degradation [243]. Efforts aimed at overcoming these stability issues have resulted in a TEM design strategy, in which the leg geometry is tuned to ensure that the applied voltage remains below a critical threshold [244]. 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 [245, 246]. 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 TE devices based on sulfides. Examples include conventional TE devices consisting of p-type tetrahedrite and n-type magnesium silicide legs [247],

flexible thin film devices based on *p*-type PEDOT:PSS and *n*-type hybrid TiS_2 [248] or a single colusite element [249]. 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 TE legs. There is a need for systematic studies to identify stable barrier and electrical contact materials for TE 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 TE sulfides are also lacking. Moreover, there is also a need to discover stable protective coatings to avoid sulphur volatilization 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 [250, 251], but long-term stability studies have not been performed. Unless the coefficients of thermal expansion of the TE sulfides and the coatings are matched, cracking of the coating following thermal cycling may lead to the subsequent degradation of the sulphide leg.

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

Concluding remarks

Over the last decade, sulphide materials, based on Earth-abundant, cost-efficient, and sustainable elements, have emerged as serious candidates for TE 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.

2.6. Thermoelectrics based on metal tellurides/selenides

Animesh Das and Kanishka Biswas

New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur PO, Bangalore 560064, India

Status

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 TE performance of materials, driven by advanced material synthesis methods and a better understanding of electron and phonon transport mechanisms. One key advantage of TE 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 TE performance. Various modern approaches for improving TE 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 [10, 252]. Nevertheless, amongst Se and Te-based chalcogenides, $AgSbTe_2$ [253, 254], BiSbTe [255] and group IV–VI tellurides such as PbTe [256], GeTe, and SnTe [257] have garnered significant attention in development of high-performance TEs. At present, *p*-type TE materials based on GeTe and PbTe can attain a TE zT of 2.7 at 628 K and 2.8 at 850 K, respectively [258, 259], whereas, SnTe has so far reached a maximum zT of 1.85 at 823 K [260]. On the other hand, selenium (Se) is more abundant and significantly cheaper than tellurium (Te). However, the progress in Se-based TE 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 TE community since 1960 and 1970 [261]. However, ion migration of Cu ions limits its practical application. Only since the last decade, high-performance Se-based TE materials such as PbSe [262] and lead-free SnSe, GeSe, and BiSe gained prominence [263–265]. Furthermore, various ternary selenides, including $AgSbSe_2$, $AgBiSe_2$, and $TlBiSe_2$, as well as oxy-selenides like BiCuSeO, are gaining popularity in TE applications due to their inherent low lattice thermal conductivity [252, 266]. In figure 18, we have summarized the zT_{max} for a series of current metal telluride and selenide TE materials.

Current and future challenges

One of the major concerns in the field of metal telluride/selenide TEs 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 [271] and resonant level [272] 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 TEM requires both *p*-type and *n*-type materials which necessitates similarities in their chemical compositions. Achieving *n*-type TE material in SnTe or GeTe compounds is extremely challenging due to intrinsic Sn and Ge vacancies. Recently, TE transport in *n*-type SnTe is achieved through Pb and I alloying [257]. Certainly, TE transport is much more studied in *n*-type PbTe [256]. However, achieving high *n*-type TE 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 TE compounds incorporate elements such as Pb, Te etc, which raise sustainability concerns. The broader TE community must prioritize the design of sustainable, high-performance systems derived from earth-abundant, less toxic elements. In this regard, new TE materials like MnTe have recently emerged as promising candidates. For instance, Guodong Tang and

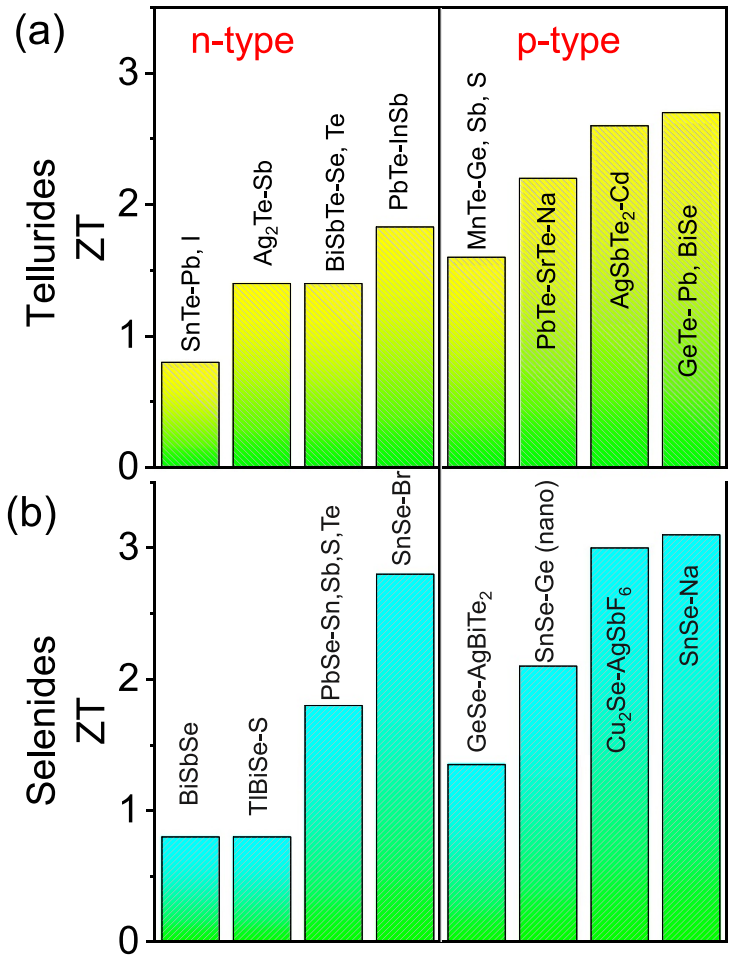


Figure 18. The zT_{max} of various tellurides and selenides: (a) *n*-type tellurides: SnTe–Pb, I [257]; Ag_2Te–Sb [254]; BiSbTe–Se, Te [255]; PbTe–InSb [256], *p*-type tellurides: MnTe–Ge, Sb, S [267]; PbTe–SrTe–Na [268]; $AgSbTe_2$–Cd [253]; GeTe–Pb, BiSe [258]. (b) *N*-type selenides: BiSbSe [265]; TlBiSe–S [266]; PbSe–Sn,Sb,S,Te [262]; SnSe–Br [263], *p*-type selenides: GeSe–$AgBiTe_2$ [264]; SnSe–Ge (nano) [269]; Cu_2Se–$AgSbF_6$ [245]; SnSe–Na [270].

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 [267].

Metal selenides face several challenges in TE 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 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 TE 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 TEs. 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 TE 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, ML has emerged as a powerful approach to accelerate the discovery of both *p*- and *n*-type TE candidates [273]. By training on existing

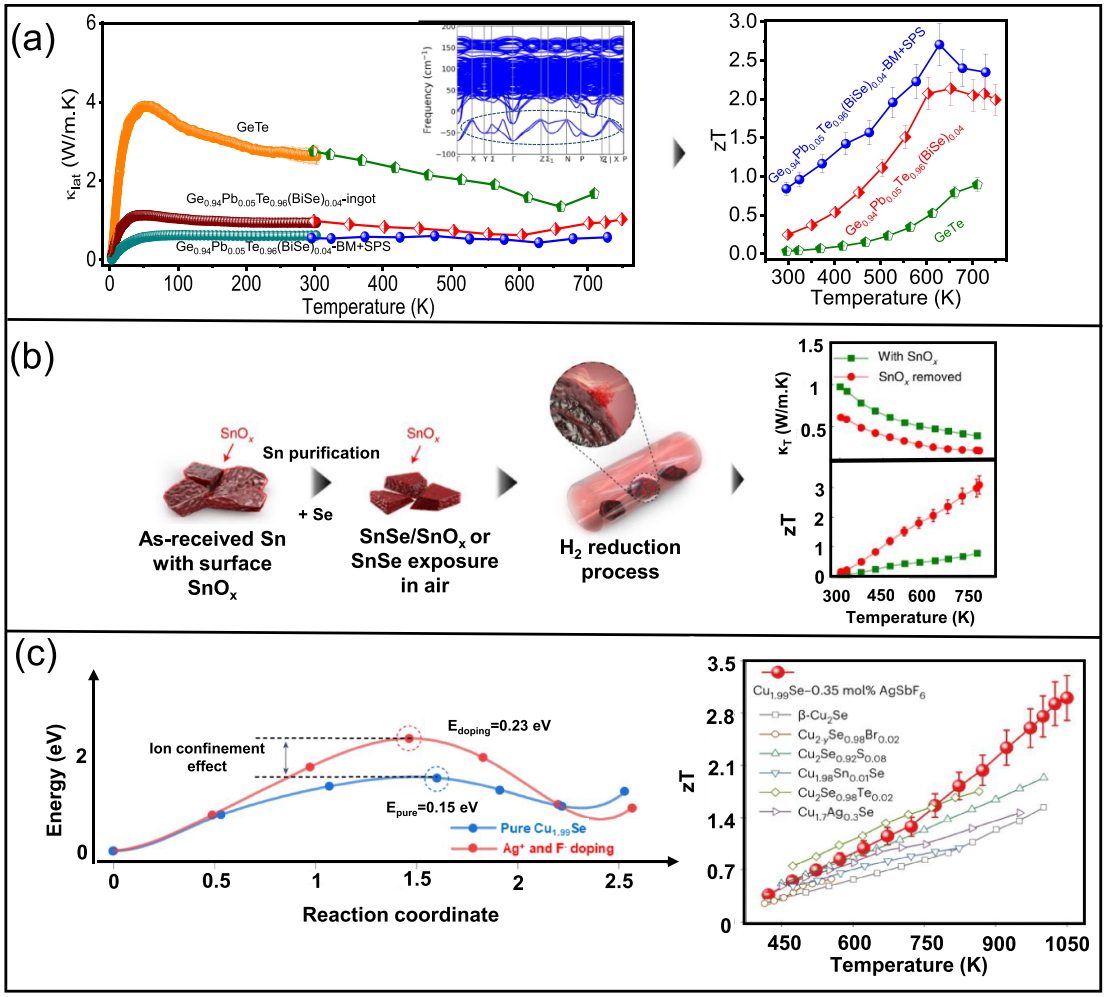


Figure 19. Recent advanced techniques utilized to obtain high zT of various metal tellurides and selenides. (a) Temperature dependence lattice thermal conductivity (κ_{lat}) and zT of $Ge_{0.94}Pb_{0.05}Te_{0.96}(BiSe)_{0.04}$ (BM + SPS). Inset: phonon dispersions of cubic $Ge_{0.92}Pb_{0.04}Te_{0.96}(BiSe)_{0.04}$ supercell. [258] John Wiley & Sons. © 2025 Wiley-VCH GmbH, (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_{tot}) 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. Reproduced from [270]. CC BY 4.0 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 $Cu_{1.99}Se$–$AgSbF_6$. Reproduced from [245], with permission from Springer Nature.

databases, ML algorithms can predict novel candidates with desirable electronic and thermal transport properties, substantially reducing reliance on conventional trial-and-error synthesis.

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 [268]. In figure 19, we have summarized some of the modern strategies that have been exploited on metal tellurides and selenides to enhance the TE zT.

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 SPS (BM + SPS) exhibits markedly improved zT owing to enhanced phonon scattering [274]. 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 $Ge_{0.94}Pb_{0.05}Te_{0.96}(BiSe)_{0.04}$ (figure 19(a)) [258]. Introducing Bi, Pb, and Se in pristine GeTe, splits the ferroelectric (Γ) instability into two components: a weaker Γ-centred mode (25i cm^{-1}) resembling pristine GeTe, and a stronger mode (69i cm^{-1}) localized on Ge–Se bonds

(Inset of figure 19(a)). The coupling of these instabilities drives complex acoustic-optic phonon interactions, giving rise to glass-like thermal transport [258].

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 [269]. At the same time, significant efforts should be directed toward improving the performance of polycrystalline SnSe. To mitigate surface oxidation issues discussed earlier [275], 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 [270] (figure 19(b)). Such findings highlight the potential for realizing high-performance practical TEs based on this material. However, contradictory findings suggest that SnO_2 may not significantly influence thermal conductivity [276], underscoring the need for further investigation and the exploration of alternative approaches to enhance the TE performance of polycrystalline SnSe.

For Cu_2Se-based superionic conductors, Jing-Feng Li group recently reported improved zT and stability via ion confinement [245]. Aided by DFT 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 ∼13.4% for a $\Delta T = 518$ K without any degradation after 120 cycles (figure 19(c)). 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 TE 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, TE 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 techniques, TE measurement methods, and commercially available instrumentation will contribute significantly to the expansion of the TE 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 TE transport parameters, progressively increasing zT values to well above 2. As discussed, achieving high-performance TEs 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 TE 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

K.B. acknowledges financial support from the SERB/CRG (CRG/2023/000826). A.D. would like to thank JNCASR for the fellowship.

2.7. Insights into the challenges of half-Heusler materials and devices

Yu Liu, Chenguang Fu and Tiejun Zhu

State Key Laboratory of Silicon and Advanced Semiconductor Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310058, People's Republic of China

Status

Half Heusler (HH) compounds, known for their excellent 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 20(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* [277] carried out systematic studies on the TE transport properties of *M*NiSn (*M* = Ti, Zr, Hf) HH compounds with 18 VEC. The bandgaps of HH compounds typically range from 0 eV to 1.2 eV, mainly depending on VEC and transition metals present [278]. Semiconducting HH compounds generally exhibit a large DOS 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 TEs (figure 20(b)), and have been endeavouring to advance fabrication techniques, investigate carrier and phonon transport mechanisms, and maximize TE properties of HH materials [279–281]. 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 [282]. Kang *et al* [283] 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* [284] achieved a record-high zT 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 $R_{1-\delta}$CoSb (*R* = V, Nb and Ta) 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 [285]. 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 TEM 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% [286].

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 TEs 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 TEs [287].

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 TiNiSn system, a proper excess of Ni occupies 4d vacancy sites, acting as scattering centres and forming in-gap state [288]. 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 [289]. The distribution and concentration of these defects significantly influence transport properties of HH-based compounds. Therefore, precise determination of crystal structure should be favourable for understanding the transport behaviour of HH compounds.

According to the equation [290]: $\eta = \frac{T_H}{T_C}\left(\frac{\sqrt{1+zT_{ave}}-1}{\sqrt{1+zT_{ave}}+T_C/T_H}\right)$, 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 TEG is related to zT_{ave}, rather than the peak. 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 21(a)), and those between segmented materials are crucial for transferring heat and electricity and withstanding stress

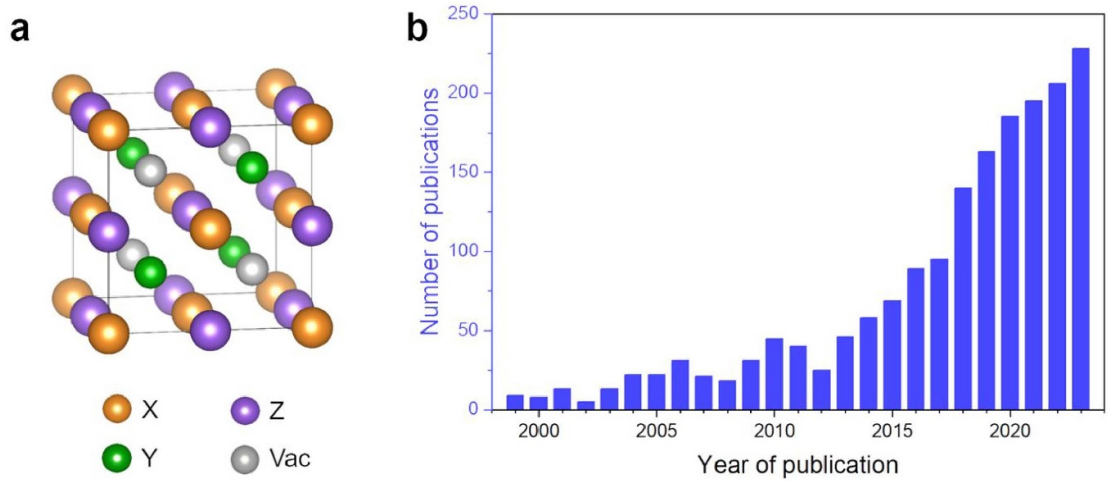


Figure 20. (a) Crystal structure of a HH compound. (b) The numbers of publications per year on HH thermoelectrics as reported by the Web of Science.

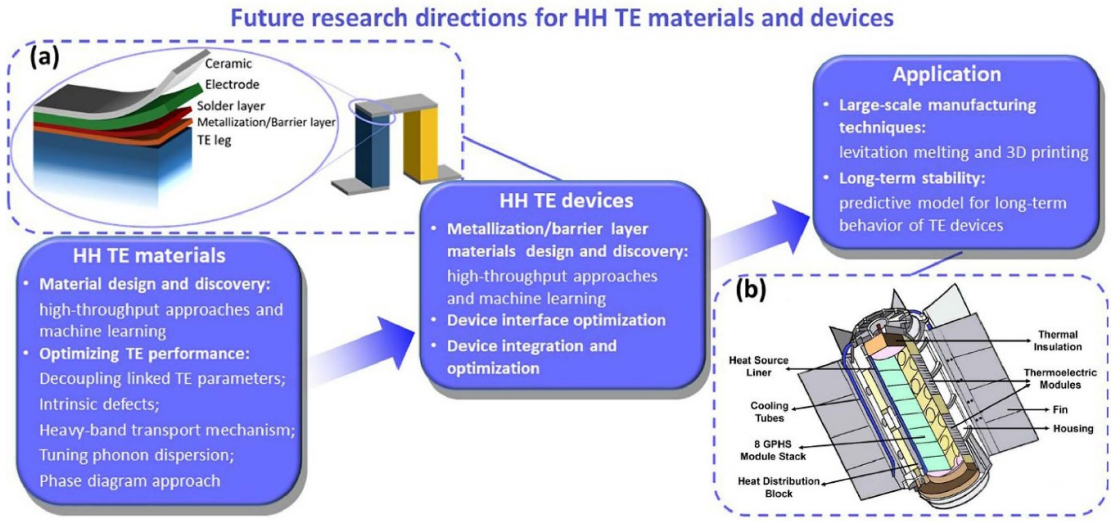


Figure 21. A summary of future research directions for HH TE materials and devices. (a) Schematic of the interface of a TE module. (b) Schematic of a multi-mission radioisotope thermoelectric generator (MMRTG). From [291]. Reprinted by permission of the American Institute of Aeronautics and Astronautics, Inc.

from various sources. As shown in figure 21(a), interface materials including metallization/barrier layers and soldering materials should have low electrical and thermal resistances, well-matched thermal expansion coefficients, and chemical and thermodynamical stability with TE legs and electrodes to minimize losses, mechanical stress, and atomic diffusion and reactions [286]. Given the wide range of compositions of HH family, selecting and designing appropriate interface materials is both important and challenging.

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

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

Advances in science and technology to meet challenges

The design and discovery of HH-based compounds can be realized under the guidance of phase diagram study. Li *et al* [292] determined the homogeneous region of $Nb_{1-x}CoSb$ compounds using ternary phase diagram calculated with CALculation PHAse Diagram, thereby simplifying traditional trial-and-error

methods. Meanwhile, high-throughput approaches are expected to further accelerate the calculation and screening process. He *et al* [293] discovered 99 new and stable quaternary Heusler compounds via high-throughput DFT screening combined with phase stability analysis.

Likewise, interface materials can be identified and designed based on the properties of electrodes and TE legs through a series of modelling work. Yin *et al* [294] have calculated the phase diagrams for specific TE leg and barrier layer materials and successfully identified Mg_2Ni as a promising barrier layer material for the Mg_3Sb_2 alloy. We could envision that it is feasible to effectively select appropriate interface materials for HH-based TE legs through predictive calculations integrated with a high-throughput approach. Furthermore, through training on high-throughput databases, ML could proficiently undertake discovery, design, analysis, and prediction tasks for HH-based compounds and interface materials, thereby significantly advancing research efficiency.

The levitation melting technique could be a suitable and promising approach for the large-scale fabrication of HH materials, taking into account its advantages such as the magnetic stirring, and time and energy efficiency. In practice, levitation melting has been applied to fabricate a wide range of high-quality HH-based compounds with excellent TE performance [284, 285]. Additionally, additive manufacturing, also known as 3D printing, offers advantages such as low waste, low cost, and design freedoms, and exhibits significant potential for large-scale production [295]. Malki *et al* [296] synthesized cation-deficient $Nb_{1-x}CoSb$ compound using 3D extrusion printing followed by sintering treatment, achieving a zT_{max} of 0.1 at 873 K. Despite issues with low density and the presence of secondary phases, the study demonstrated that additive manufacturing was applicable to HH compounds.

Traditionally, the lifetime of a TE device is assessed experimentally through thermal aging tests lasting a few hundred hours [297]. 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.

Concluding remarks

TEs 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 TEs, the following future directions are imperative (figure 21). 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 ML, 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

This work was supported by the National Key Research and Development Program of China (2023YFB3809400), the Fundamental Research Funds for the Central Universities, and the 111 Project (No. B16042).

2.8. Skutterudites

Gerda Rogl and Peter Rogl

Institute of Materials Chemistry, University of Vienna, Waehringerstrasse 42, A-1090 Wien, Austria

Status

As already a large variety of review articles about TE materials and skutterudites exist, e.g. [15, 298–300], 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 24*g* sites form a 3-dimensional and predominantly covalent framework enclosing Co-atoms in sites 8*c* at the centres of tilted non-regular As-octahedra: this framework provides two empty icosahedral spaces per unit cell (centres in sites 2*a*) for the incorporation of filler atoms (usually at partial occupation) thereby constituting the so-called filled skutterudites with general formula $E_yT_4X_{12}$ (figure 22).

Since the first TE activities in the early 1950s on unfilled $CoSb_3$, successful attempts were made to rise their TE 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 TE performance, among which $Co_4Sb_{11}Te_{0.7}Sn_{0.3}$ [301] and $Co_4Sb_{11.5}Te_{0.5}$ + 25 vol.% CNT [302], both achieved a $zT = 1.3$, whereas a nanostructured alloy $Co_{23.4}Sb_{69.1}Si_{1.5}Te_{6.0}$ (in at.%) still holds the record with $zT = 1.6$ by introducing nano- to micrometre-size irregularly shaped and randomly oriented pores [303].

Over the years *zTs* of Sb-based filled skutterudites, have reached *zTs* with the highest values for *p*- and *n*-type: $zT = 1.45$ at 800 K ($DD_{0.7}Fe_3CoSb_{12}$) [304] and $zT = 2.15$ at 823 K $(Sm,Mm)_{0.15}Co_4Sb_{12}$ [305], respectively (see figure 23; for details up to 2022 see [306]). Although the bulk number of investigations still dwells at $zT \leqslant 1$, more recent activities reached $zTs > 1.2$ for *p*-type and $zTs > 1.4$ for *n*-type materials with a trend towards a lower number of filler species (single-filled or double-filled).

Current and future challenges

A high *zT* demands a large $|S|$, >150 μV K^{-1}, but a low product $\rho(\kappa_e + \kappa_{ph})$. To fulfil this demand, it is necessary to find a compromise among the interleaved parameters $|S|$, ρ, κ by simultaneously (a) tuning the 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 [307, 308]. In addition, tunnelling of filler atoms may occur between equivalent off-centre sites in the icosahedral cage. Shi *et al* [309] published a guide to estimate the fraction of filler atoms on a correlation between the Pauling electronegativities ε of filler atom and antimony: $\varepsilon_{Sb} - \varepsilon_{FA} > 0.8$. 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 [306]. Double- and multi-filling, grain refinement via ball-milling and intrinsic precipitation such as Yb_2O_3, however, were efficient techniques to reach *zTs* 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 [306].

Nanostructuring theoretically promoted the idea on quantum confinement of electrons and phonons (Hicks and Dresselhaus [310]). High ZTs 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: $zT = 1.45$ ($DD_{0.7}Fe_3CoSb_{12}$) [304] and $zT = 2.15$ $(Sm, Mm)_{0.15}Co_4Sb_{12}$ [305], 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 $CeFe_3Cosb_{12}$ with 5 wt.% MoO_2 and $zT = 1.3$ for $DD_yFe_3CoSb_{12}$ with 0.5 wt.% $Ta_{0.8}Zr_{0.2}B$; *n*-type: composites, based on $Ba_yCo_4Sb_{12}$ and $Yb_yCo_4Sb_{12}$, reached *zTs* in the range of 1.3–1.5 with additions such as TiO_2, Ag, C_{60}, Yb_2O_3, CoSi, SiC, or Al (for details see [306]). Indeed, $(Sr, Ba, Yb)_yCo_4Sb_{12}$ with 9.1 wt.% $In_{0.4}Co_4Sb_{12}$ reached $zT = 1.8$ and $Al_{0.03}Yb_{0.25}Co_4Sb_{12}$ as well as $(Mm, Sm)_yCo_4Sb_{12}$ with 2 wt.% $La_{1.85}Sr_{0.15}CuO_4$ both yielded $zT = 1.7$ (see [306]). Substitutions at the Sb-site by Ga, Ge, Sn, Se, Te, In in combination with fillers generally helped to enhance *zT*.

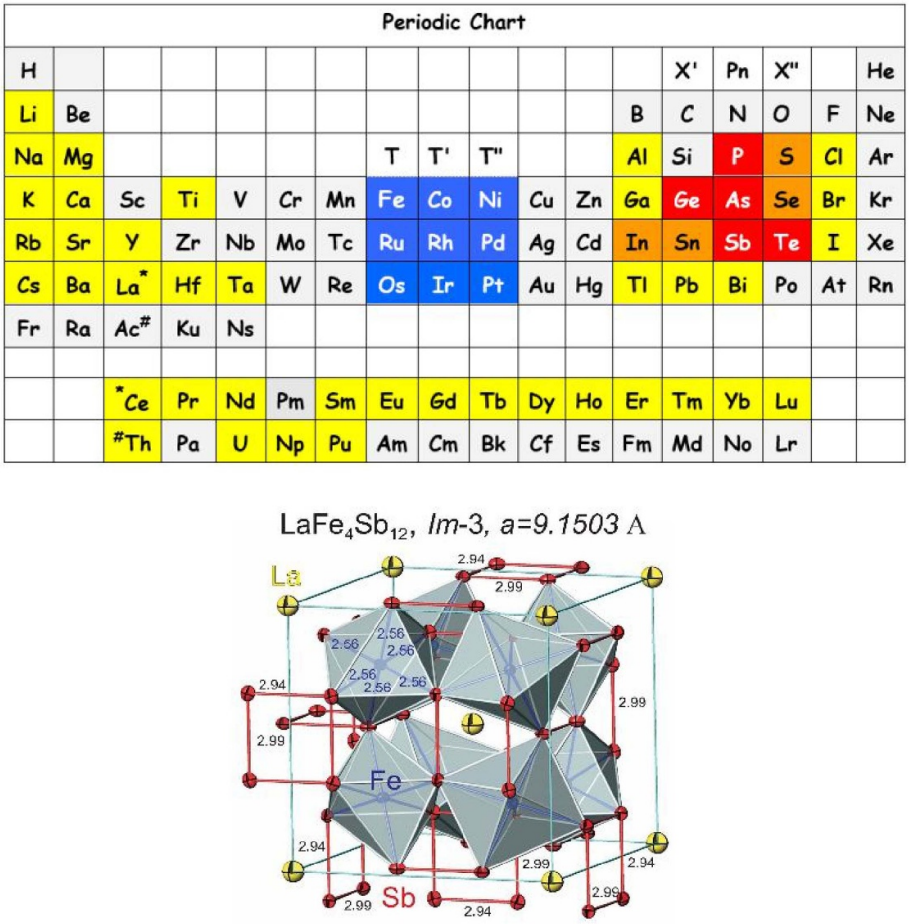


Figure 22. Top: distribution over the periodic chart of the various constituents forming skutterudite compounds, $E_yT_4X_{12}$: yellow stands for E, blue for T and red for X, orange for atoms acting as filler as well as framework atoms. Bottom: filled skutterudite $LaFe_4Sb_{12}$ with Sb in 24*g* (0, 0.160 60, 0.336 85), Fe in octahedron-centres 8*c* (¼, ¼, ¼) and La in icosahedral voids 2*a* (0, 0, 0). Sb-atoms form almost square rectangles (red).

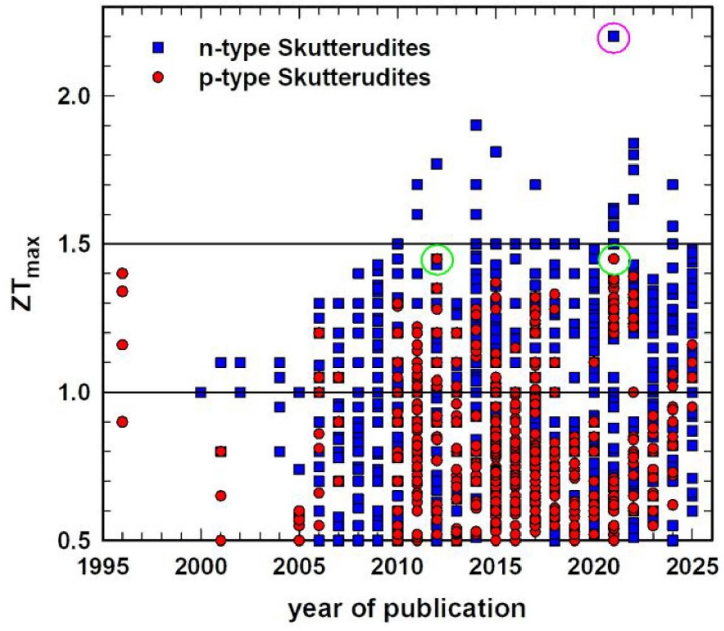


Figure 23. *ZTs* ⩾ 0.5 of Sb-based filled skutterudites vs publication year (red: *p*-type, blue: *n*-type). Maximum *zT* values for *p*- and *n*-type are indicated by large open circles; for details up to 2022 see [306].

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-$Ba_{0.15}DD_{0.28}Yb_{0.05}Fe_3NiSb_{12}$ + n-$Ba_{0.09}Sr_{0.02}DD_{0.22}Yb_{0.02}Fe_{2.4}Ni_{1.6}Sb_{12}$; $zT \sim 1.0$; see [306]). 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 TE conversion efficiencies of ∼10% (for an overview of module achievements, see [311]).

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.

As skutterudites react above ∼250 °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 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 TE properties in general. DFT techniques can thus define the proper parameter space for more efficient TE skutterudites.

ML and AI (artificial intelligence) gain increasing importance for finding new TE 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 yr^{-1} 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 TE 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 [312] and exhibit good mechanical properties [313].

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 TE behaviour [314]. DFT in combination with ML may be a tool with the potential to further define skutterudites, to optimize their zT and increase TE efficiencies [315]. As a promising result, high zT n-SKDs have been successfully combined with high zT *p*-type HHs to reach a module conversion efficiency of ∼12% [316].

2.9. Silicides

Panagiotis Mangelis and Theodora Kyratsi

Department of Mechanical and Manufacturing Engineering, University of Cyprus, 1678 Nicosia, Cyprus

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 TEs for intermediate-temperature applications. Some of the most promising silicide TEs are solid solutions of Mg_2X (X = Si, Ge, and Sn), $CrSi_2$, CoSi, $IrSi_3$, Ir_3Si_5 $FeSi_2$, $MnSi_{1.75}$, $ReSi_{1.75}$ and Ru_2Si_3 [317]. 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 TEGs 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 TEs for intermediate-temperature applications. First systematic investigations of Mg_2Si and its related solid solutions as TEs 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 24 [318–323]. 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 [319].

On the other hand, higher manganese silicides (HMSs) have attracted considerable attention as the most promising *p*-type thermoelctrics from the silicides family, as shown in figure 25 [324–328]. HMS are composed of environmentally-friendly and Earth-abundant elements, exhibiting also suitable mechanical and chemical stability for mid-temperature applications [329]. 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 [325].

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 TEMs in industrial level. Mg_2(Si, Sn) solid solutions exhibit relatively poor mechanical properties (low fracture toughness) which prevent their integration into TE applications [330]. Therefore, the enhancement of mechanical reliability is essential for these compounds before moving to the manufacturing of TEMs.

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) [329]. 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 n_e of ∼4%–7% [329], 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 SnO_2 are formed under air exposure [331]. HMS presents better chemical and mechanical stability. However, its oxidization is

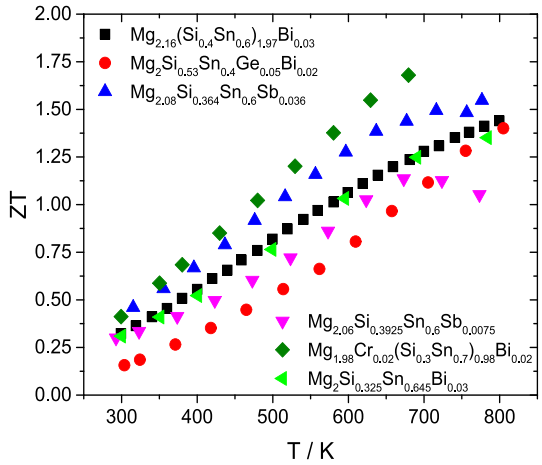


Figure 24. Best *n*-type silicide thermoelectrics based on Mg_2(Si, Sn) solid solutions.

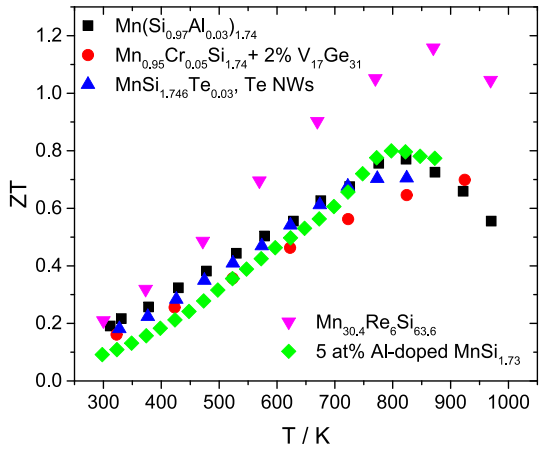


Figure 25. Best *p*-type silicide thermoelectrics based on HMS phases.

unavoidable for prolonged time in air, while the formation of MnSi leads to severe reductions of TE performance [329, 330].

Furthermore, new environmental issues arise, dictating more investigations of silicide TEs 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 TEMs with noteworthy efficiencies is a quite promising route for the utilization of vast amounts of silicon kerf from PV industry [332, 333]. 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 Mg_2Si-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 Mg_2(Si, Sn) solid solutions and the limitation of material degradation due to Mg losses at elevated temperatures [334]. New advances on the manufacturing and long-term stability of Mg_2(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 [329, 333].

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 Mg_2Si-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 [325], nano-additives or secondary nano-phases [326] 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 Mg_2Si-based solid solutions through hole doping with the best results ($zT_{max} \sim 0.4$–0.5) to be exhibited through Li substitution [317, 335], while recently a fully Mg_2(Si, Sn)-based TEM was fabricated [336]. Further efforts should concentrate in the zT improvement of *p*-type Mg_2Si-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 Mg_2Si-based compounds [335].

Concluding remarks

Silicide TEs 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 Mg_2Si-based solid solutions and $MnSi_x$ compounds stand out as the most promising *n*-and *p*-type TE materials respectively for intermediate-temperature applications. $Mg_2Si_{1-x}Sn_x$ 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-Mg_2(Si, Sn) alloys. Despite the progress and promising results on the construction of Mg_2(Si, Sn)/HMS TEMs, 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.

Acknowledgements

Funding from the European Union's Horizon 2020 research and innovation programme ICARUS Project under Grant Agreement No 958365.

2.10. Thermoelectric oxides

Ryoji Funahashi

National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka 563-8577, Japan

Status

The first report on 'TE' and 'oxide' in Web of Science, Clarivate Analytics is on the high electromotive force measured between −110 °C and 800 °C for CdO by Andrews in 1947 [337]. Other early investigations focused on binary oxides, including NiO with impurities and under several gas atmosphere [338], Cu_2O under different oxygen partial pressure [339]. After these initial reports, thermopower measurements were used to probe the electrical transport in the cuprate high-T_c superconductors [340]. In terms of technology development, gas sensors composed of oxide materials were developed [341, 342], and composites of superconductive $YBa_2Cu_3O_{7-X}$ and Ag_2O were tried for TE refrigeration instead of Bi_2Te_3 materials [343].

The first report discussing oxide materials aimed at power generation appeared from Ohtaki *et al* in 1994 [344] and got a lot of attention to the n-type $CaMnO_3$ in 1995 [345]. 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 TE oxides has been attempted based on this concept. The number of the publication on TE oxides grew up rapidly after 2000. The excellent TE properties of layered *p*-type Co-oxides originating the article from I. Terasaki in 1997 created a new researching field in TE technology [346–349]. These discoveries induced the inflow of many researchers in the research field of the TE oxides and led to the high temperature resistant modules in air [350, 351].

Current and future challenges

The research on TE 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 $Ca_{2.7}Bi_{0.3}Co_4O_9$ legs and *n*-type $CaMn_{0.98}Mo_{0.02}O_3$ legs were produced using silver paste with the powders of the *p*- and *n*-type oxides as the additives for each junction, respectively (figure 26) [351]. 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 TE 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 the zT values, preparation of the flexible devices, and the circuit integration [352]. It is proven that the two-dimensional structure is effective to realize the giant Seebeck coefficient [353]. It is 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 TEGs 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 [354]. Although TE 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 TE properties should be challenged by nano and microscopic structural control by the processing technologies.

Advances in science and technology to meet challenges

The electrical conductivity σ is more important than anything to develop good TE oxides. Of course, high thermal conductivity κ is other problem, but the σ values are several orders of magnitude higher than regular semiconducting TE 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,

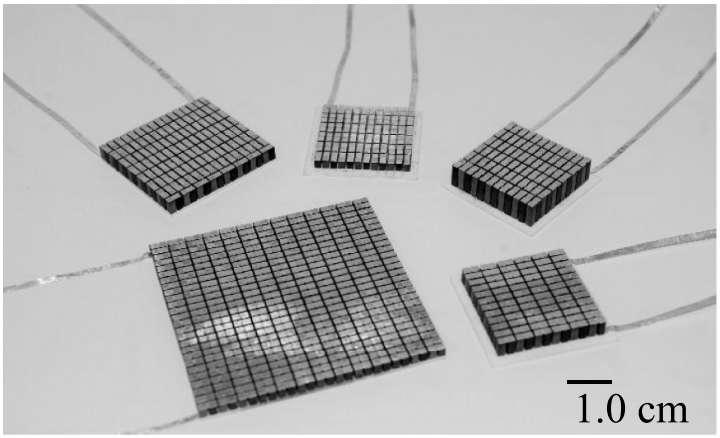


Figure 26. Thermoelectric modules composed of *p*-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ and *n*-type $CaMn_{0.98}Mo_{0.02}O_3$ [351].

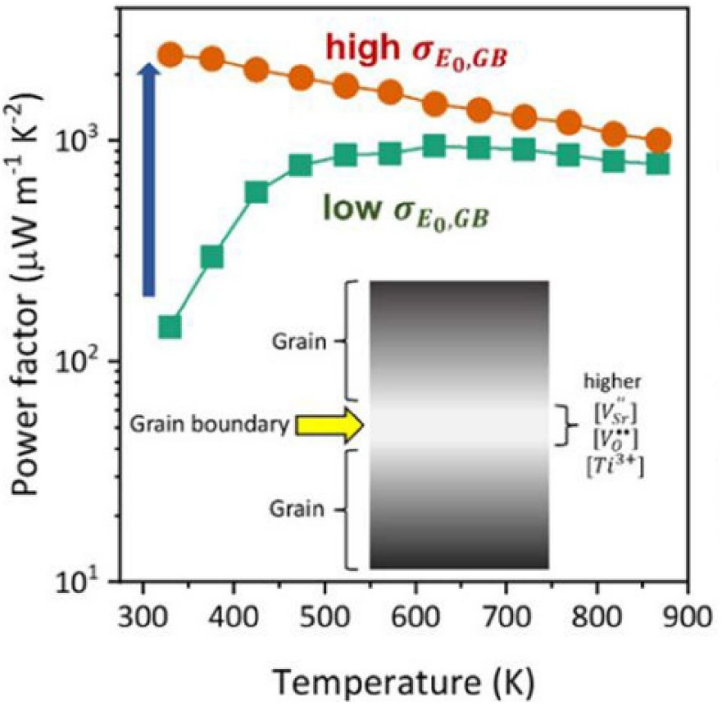


Figure 27. Improvement of power factor of La-doped $SrTiO_3$ by addition of graphene oxide. Reproduced from [362]. CC BY 4.0.

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 [355]. It is worthy of attention that the self-formation of core-shell structures by sintering is effective to reduce thermal conductivity [356]. Recently, nanocomposites of graphene or graphene oxide with the *n*-type ZnO and $SrTiO_3$ have been reported to improve electrical and thermal conduction at the grain boundaries, which is often one of the most serious problems (figure 27) [357–362]. ML is being attempted as a new approach to materials exploration [363–365]. Currently, the research is focused on thermal conductivity properties, but it is expected that exploration of other TE properties will also progress.

Concluding remarks

The TE 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 d. 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 TE materials. The application of TE oxides is limited to temperatures higher than 773 K. The development of new TE 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.

Data availability statement

No new data were created or analysed in this study.

ORCID iDs

Jan-Willem G Bos 0000-0003-3947-2024
Trupti Mohanty 0000-0003-4270-1430
Taylor D Sparks 0000-0001-8020-7711
Wenjie Xie 0000-0003-1826-7574
Salvatore Grasso 0000-0002-2753-4008
Ruizhi Zhang 0000-0001-7229-769X
Michael J Reece 0000-0002-2293-7123
Jae Sung Son 0000-0003-3498-9761
Iris Nandhakumar 0000-0002-9668-9126
Richard Tuley 0000-0002-2753-7639
Ran He 0000-0002-0295-6837
Amin Bahrami 0000-0001-8851-7351
Ricardo Grau-Crespo 0000-0001-8845-1719
Luis M Antunes 0000-0002-4867-5635
Keith T Butler 0000-0001-5432-5597
Neophytos Neophytou 0000-0001-6757-3733
Rajeev Dutt 0000-0001-8739-111X
Nagendra Singh Chauhan 0000-0003-2579-6642
Takao Mori 0000-0003-2682-1846
M Parzer 0000-0003-3509-7474
E Bauer 0000-0001-7376-5897
Paz Vaqueiro 0000-0001-7545-6262
Emmanuel Guilmeau 0000-0001-7439-088X
Kanishka Biswas 0000-0001-9119-2455
Chenguang Fu 0000-0002-9545-3277
Tiejun Zhu 0000-0002-3868-0633
Gerda Rogl 0000-0002-8056-5006
Peter Rogl 0000-0002-7733-1612
Panagiotis Mangelis 0000-0001-5948-1177
Ryoji Funahashi 0000-0002-1004-0204

References

[1] He J and Tritt T M 2017 Advances in thermoelectric materials research: looking back and moving forward *Science* **357** eaak9997
[2] Yan Q Y and Kanatzidis M G 2022 High-performance thermoelectrics and challenges for practical devices *Nat. Mater.* **21** 503–13
[3] Kim H S, Liu W and Ren Z 2017 The bridge between the materials and devices of thermoelectric power generators *Energy Environ. Sci.* **10** 69–85
[4] Snyder G J and Toberer E S 2008 Complex thermoelectric materials *Nat. Mater.* **7** 105–14
[5] Ming H, Luo Z-Z, Zou Z and Kanatzidis M G 2025 Strategies and prospects for high-performance Te-free thermoelectric materials *Chem. Rev.* **125** 3932–75
[6] Mao J, Chen G and Ren Z F 2021 Thermoelectric cooling materials *Nat. Mater.* **20** 454–61
[7] Zheng Y, Slade T J, Hu L, Tan X Y, Luo Y, Luo Z-Z, Xu J, Yan Q and Kanatzidis M G 2021 Defect engineering in thermoelectric materials: what have we learned? *Chem. Soc. Rev.* **50** 9022–54
[8] Shi X-L, Zou J and Chen Z-G 2020 Advanced thermoelectric design: from materials and structures to devices *Chem. Rev.* **120** 7399–515
[9] Zhu T J, Liu Y T, Fu C G, Heremans J P, Snyder J G and Zhao X B 2017 Compromise and synergy in high-efficiency thermoelectric materials *Adv. Mater.* **29** 1605884

[10] Zeier W G, Zevalkink A, Gibbs Z M, Hautier G, Kanatzidis M G and Snyder G J 2016 Thinking like a chemist: intuition in thermoelectric materials *Angew. Chem., Int. Ed.* **55** 6826–41
[11] Hendricks T, Caillat T and Mori T 2022 Keynote review of latest advances in thermoelectric generation materials, devices, and technologies 2022 *Energies* **15** 7307
[12] Mao J, Liu Z, Zhou J, Zhu H, Zhang Q, Chen G and Ren Z 2018 Advances in thermoelectrics *Adv. Phys.* **67** 69–147
[13] Freer R and Powell A V 2020 Realising the potential of thermoelectric technology: a roadmap *J. Mater. Chem. C* **8** 441–63
[14] Pecunia V *et al* 2023 Roadmap on energy harvesting materials *J. Phys. Mater.* **6** 042501
[15] Artini C *et al* 2023 Roadmap on thermoelectricity *Nanotechnology* **34** 292001
[16] Freer R *et al* 2022 Key properties of inorganic thermoelectric materials—tables (version 1) *J. Phys. Energy* **4** 022002
[17] Titirici M *et al* 2024 Roadmap for sustainable batteries *J. Phys. Energy* **6** 041502
[18] Gaultois M W, Sparks T D, Borg C K H, Seshadri R, Bonificio W D and Clarke D R 2013 Data-driven review of thermoelectric materials: performance and resource considerations *Chem. Mater.* **25** 2911–20
[19] Wolf M, Hinterding R and Feldhoff A 2019 High power factor vs. high zT—a review of thermoelectric materials for high-temperature application *Entropy* **21** 1058
[20] Sovacool B K 2019 The precarious political economy of cobalt: balancing prosperity, poverty, and brutality in artisanal and industrial mining in the Democratic Republic of the Congo *Extractive Ind. Soc.* **6** 915–39
[21] National Minerals Information Center, United States Geological Survey (USGS) minerals yearbook and mineral commodity summaries (available at: www.usgs.gov/centers/national-minerals-information-center/minerals-yearbook-metals-and-minerals)
[22] Theler B, Kauwe S K and Sparks T D 2020 Materials abundance, price, and availability data from the years 1998–2015 *Integr. Mater. Manuf. Innov.* **9** 144–50
[23] Mohanty T, Sayeed H M, Mohanty C and Sparks T D 2025 Comprehensive insights into global mineral commodities: analysis, visualization, and intelligent assistance *PRX Energy* **4** 023003
[24] Caballero-Calero O, Ares J R and Martín-González M 2021 Environmentally friendly thermoelectric materials: high performance from inorganic components with low toxicity and abundance in the earth *Adv. Sustain. Syst.* **5** 2100095
[25] Nozariasbmarz A, Agarwal A, Coutant Z A, Hall M J, Liu J, Liu R and Vashaee D 2017 Thermoelectric silicides: a review *Jpn. J. Appl. Phys.* **56** 05DA04
[26] Wang L, Zhang W, Back S Y, Kawamoto N, Nguyen D H and Mori T 2024 High-performance Mg_3Sb_2-based thermoelectrics with reduced structural disorder and microstructure evolution *Nat. Commun.* **15** 6800
[27] Thanu V R C and Jayakumar M 2020 Electrochemical recovery of antimony and bismuth from spent electrolytes *Sep. Purif. Technol.* **235** 116169
[28] Li Z, Qiu F, Tian Q, Yue X and Zhang T 2022 Production and recovery of tellurium from metallurgical intermediates and electronic waste-a comprehensive review *J. Clean. Prod.* **366** 132796
[29] Liu W, Hu J, Zhang S, Deng M, Han C-G and Liu Y 2017 New trends, strategies and opportunities in thermoelectric materials: a perspective *Mater. Today Phys.* **1** 50–60
[30] Klemenz S, Stegmüller A, Yoon S, Felser C, Tüysüz H and Weidenkaff A 2021 Holistic view on materials development: water electrolysis as a case study *Angew. Chem., Int. Ed.* **60** 20094–100
[31] Soleimani Z, Zoras S, Ceranic B, Shahzad S and Cui Y 2021 The cradle to gate life-cycle assessment of thermoelectric materials: a comparison of inorganic, organic and hybrid types *Sustain. Energy Technol. Assess.* **44** 101073
[32] Kawajiri K, Kishita Y and Shinohara Y 2021 Life cycle assessment of thermoelectric generators (TEGs) in an automobile application *Sustainability* **13** 13630
[33] ISO 14040 2006 Environmental management-life cycle assessment-principles and framework
[34] European Parliament, Council of the European Union, Regulation (EU) 2024/1781 of the European Parliament and of the Council (available at: http://data.europa.eu/eli/reg/2024/1781/oj)
[35] Sundaravaradan N, Patnaik D, Ramakrishnan N, Marwah M and Shah A, 2011 Discovering life cycle assessment trees from impact factor databases *Association for the Advancement of Artificial Intelligence Proc. AAAI Conf. on Artificial Intelligence* vol 25 pp 1415–20
[36] Romeiko X X, Zhang X, Pang Y, Gao F, Xu M, Lin S and Babbitt C 2024 A review of machine learning applications in life cycle assessment studies *Sci. Total Environ.* **912** 168969
[37] Algren M, Fisher W and Landis A E 2021 Machine learning in life cycle assessment *Data Science Applied to Sustainability Analysis* ed J Dunn and P Balaprakash (Elsevier) ch 8, pp 167–90
[38] Yang S, Yu Z, Ma W, Ma L, Li C, Fu L, Li M, Zhao Z and Yang Y 2023 Coupling the digital twin technology and life cycle assessment: carbon dioxide emissions from polysilicon production *Sustain. Prod. Consum.* **41** 156–66
[39] Riedelsheimer T, Seegrün A and Lindow K 2025 Digital twins for real-time life cycle assessment of products *EcoDesign for Circular Value Creation* vol I, ed S Fukushige, T Nonaka, H Kobayashi, C Tokoro and E Yamasue (Springer) 10.1007/978-981-97-9068-5_28
[40] George W R, Sharples R and Thompson J E 1959 The sintering of bismuth telluride *Proc. Phys. Soc.* **74** 768–70
[41] Wang D, He W, Chang C, Wang G, Wang J and Zhao L-D 2018 Thermoelectric transport properties of rock-salt SnSe: first-principles investigation *J. Mater. Chem. C* **6** 12016–22
[42] Chizhikov V A and Dmitrienko V E 2012 Frustrated magnetic helices in MnSi-type crystals *Phys. Rev. B* **85** 014421
[43] Han X 2020 Ductile van der Waals materials *Science* **369** 509
[44] Sun Y *et al* 2023 Performance boost for bismuth telluride thermoelectric generator via barrier layer based on low Young's modulus and particle sliding *Nat. Commun.* **14** 1–9
[45] Zhang R-Z, Gucci F, Zhu H, Chen K and Reece M J 2018 Data-driven design of ecofriendly thermoelectric high-entropy sulfides *Inorg. Chem.* **57** 13027–33
[46] Jiang Q, Yan H, Khaliq J, Ning H, Grasso S, Simpson K and Reece M J 2014 Large ZT enhancement in hot forged nanostructured p-type $Bi_{0.5}Sb_{1.5}Te_3$ bulk alloys *J. Mater. Chem. A* **2** 5785–90
[47] Grasso S, Biesuz M, Zoli L, Taveri G, Duff A I, Ke D, Jiang A and Reece M J 2020 A review of cold sintering processes *Adv. Appl. Ceram.* **119** 115–43
[48] Dai Z, Tyrpekl V, Boi F, Song J, Hu C and Grasso S 2022 Cold sintering of van der Waals layered compounds *Open Ceram.* **12** 100304
[49] Grasso S, Tsujii N, Jiang Q, Khaliq J, Maruyama S, Miranda M, Simpson K, Mori T and Reece M J 2013 Ultra low thermal conductivity of disordered layered p-type bismuth telluride *J. Mater. Chem. C* **1** 2362–7

[50] Palaporn D, Pinitsoontorn S, Kurosaki K and Snyder G J 2024 Porous Ag_2Se fabricated by a modified cold sintering process with the average zT around unity near room temperature *Adv. Mater. Technol.* **9** 2301242
[51] Ding J, Guo J, Yan R, Li W, Ma S, Fu Y, Xie W, Riedel R and Weidenkaffa A 2024 Cold sintering process: a green route to fabricate thermoelectrics *J. Adv. Ceram.* **13** 1697–712
[52] Zhao Y, Berbano S S, Gao L, Wang K, Guo J, Tsuji K, Wang J and Randall C A 2019 Cold-sintered V2O5-PEDOT:PSS nanocomposites for negative temperature coefficient materials *J. Eur. Ceram. Soc.* **39** 1257–62
[53] Cologna M, Rashkova B and Raj R 2010 Flash sintering of nanograin zirconia in <5 s at 850 °C *J. Am. Ceram. Soc.* **93** 3556–9
[54] Manière C, Lee G and Olevsky E A 2017 All-materials-inclusive flash spark plasma sintering *Sci. Rep.* **7** 15071
[55] Gucci F, Saunders T G, Srinivasan B, Cheviré F, Ferluccio D A, Bos J-W G and Reece M J 2020 Hybrid flash-SPS of $TiNiCu_{0.05}Sn$ with reduced thermal conductivity *J. Alloys Compd.* **837** 155058
[56] Wang C *et al* 2020 A general method to synthesize and sinter bulk ceramics in seconds *Science* **368** 521–6
[57] Boldrini S, Ferrario A, Fasolin S, Miozzo A and Barison S 2023 Ultrafast high-temperature sintering and thermoelectric properties of n-doped Mg_2Si *Nanotechnology* **34** 155601
[58] Ibn-Mohammed T, Randall C A, Mustapha K B, Guo J, Walker J, Berbano S, Koh S C L, Wang D, Sinclair D C and Reaney I M 2019 Decarbonising ceramic manufacturing: a techno-economic analysis of energy efficient sintering technologies in the functional materials sector *J. Eur. Ceram. Soc.* **39** 5213–35
[59] He R, Schierning G and Nielsch K 2018 Thermoelectric devices: a review of devices, architectures, and contact optimization *Adv. Mater. Technol.* **3** 1700256
[60] Qin Y, Qin B, Wang D, Chang C and Zhao L-D 2022 Solid-state cooling: thermoelectrics *Energy Environ. Sci.* **15** 4527–41
[61] Xie L J *et al* 2023 Screening strategy for developing thermoelectric interface materials *Science* **382** 921–8
[62] Yang S E, Han H and Son J S 2024 Recent progress in 3D printing of Bi_2Te_3-based thermoelectric materials and devices *J. Phys. Energy* **6** 022003
[63] Kim F *et al* 2021 Direct ink writing of three-dimensional thermoelectric microarchitectures *Nat. Electron.* **4** 579–87
[64] Oztan C, Ballikaya S, Ozgun U, Karkkainen R and Celik E 2019 Additive manufacturing of thermoelectric materials via fused filament fabrication *Appl. Mater. Today* **15** 77–82
[65] El-Desouky A, Carter M, Andre M A, Bardet P M and LeBlanc S 2016 Rapid processing and assembly of semiconductor thermoelectric materials for energy conversion devices *Mater. Lett.* **185** 598–602
[66] Ou C, Sangle A L, Datta A, Jing Q, Busolo T, Chalklen T, Narayan V and Kar-Narayan S 2018 Fully printed organic–inorganic nanocomposites for flexible thermoelectric applications *ACS Appl. Mater. Interfaces* **10** 19580–7
[67] He M, Zhao Y, Wang B, Xi Q, Zhou J and Liang Z 2015 3D printing fabrication of amorphous thermoelectric materials with ultralow thermal conductivity *Small* **11** 5889–94
[68] Zhang X, Chen J, Zhang H, Zhu P, Wang R, Li F and Li B 2023 Enhanced thermoelectric performance of 3D-printed Bi_2Te_3-based materials via adding Te/Se *J. Materiomics* **9** 328–37
[69] Peng J *et al* 2019 3D extruded composite thermoelectric threads for flexible energy harvesting *Nat. Commun.* **10** 5590
[70] Qiu J *et al* 2019 3D printing of highly textured bulk thermoelectric materials: mechanically robust BiSbTe alloys with superior performance *Energy Environ. Sci.* **12** 3106–17
[71] Lee J *et al* 2021 Doping-induced viscoelasticity in PbTe thermoelectric inks for 3D printing of power-generating tubes *Adv. Energy Mater.* **11** 2100190
[72] Kim K *et al* 2024 Heat-dissipation design and 3D printing of ternary silver chalcogenide-based thermoelectric legs for enhancing power generation performance *Adv. Sci.* **11** 2402934
[73] Burton M R, Mehraban S, Beynon D, McGettrick J, Watson T, Lavery N P and Carnie M J 2019 3D printed SnSe thermoelectric generators with high figure of merit *Adv. Energy Mater.* **9** 1900201
[74] Choo S *et al* 2021 Cu_2Se-based thermoelectric cellular architectures for efficient and durable power generation *Nat. Commun.* **12** 3550
[75] Choo S *et al* 2024 Geometric design of Cu2Se-based thermoelectric materials for enhancing power generation *Nat. Energy* **9** 1105–1116
[76] Tanvir A N M *et al* 2024 High-performance thermoelectric composites via scalable and low-cost ink processing *Energy Environ. Sci.* **17** 4560–8
[77] Zhou M, Liu W, Wu H, Song X, Chen Y, Cheng L, He F, Chen S and Wu S 2016 Preparation of a defect-free alumina cutting tool via additive manufacturing based on stereolithography-optimization of the drying and debinding processes *Ceram. Int.* **42** 11598–602
[78] Perry S C, Akbar S, Clarke R, Shah S Z H and Nandhakumar I 2025 Electrodeposition of thermoelectric materials *ChemElectroChem* **00** 1–12
[79] Hasan M N, Wahid H, Nayan N and Mohamed Ali M S 2020 Inorganic thermoelectric materials: a review *Int. J. Energy Res.* **44** 6170–222
[80] Sabran N S, Fadzallah I A, Mohd Sabri M F and Ono T 2023 Thermoelectric properties of Indium doped skutterudite thick film synthesized by a facile technique of electrochemical deposition *J. Mater.* **9** 899–909
[81] De Vos M, Zimmer A, Toledo M, Ghanbaja J, Haye E, Pernot G, Lacroix D and Stein N 2023 Tuning the physico-chemical properties of SnSe films by pulse electrodeposition *Appl. Surf. Sci.* **621** 156845
[82] Trahey L, Becker C R and Stacy A M 2007 Electrodeposited bismuth telluride nanowire arrays with uniform growth fronts *Nano Lett.* **7** 2535–9
[83] Manzano C V, Del Olmo C L, Caballero-Calero O and Martín-González M 2021 High thermoelectric efficiency in electrodeposited silver selenide films: from Pourbaix diagram to a flexible thermoelectric module *Sustain. Energy Fuels* **5** 4597–605
[84] Tanwar A, Kaur R, Padmanathan N and Razeeb K M 2023 Electrodeposited CuSbTe thin films with enhanced thermoelectric performance *Sustain. Energy Fuels* **7** 4160–71
[85] Manzano C V, Caballero-Calero O, Tranchant M, Bertero E, Cervino-Solana P, Martin-Gonzalez M and Philippe L 2021 Thermal conductivity reduction by nanostructuration in electrodeposited CuNi alloys *J. Mater. Chem. C* **9** 3447–54
[86] Sabran N S, Fadzallah I A, Sabri M F M, Ono T, Samat K F, Yusuf S N F and Saidur R 2021 Enhanced thermoelectric properties of skutterudite thick film polyvinyl alcohol assisted from the post-deposition annealing effect *J. Electrochem. Soc.* **168** 072508
[87] Yadav S, Chaudhary S and Pandya D K 2021 Enhancing thermoelectric properties of p-type $CoSb_3$ skutterudite by Fe doping *Mater. Sci. Semicond. Process.* **127** 105721
[88] Li D *et al* 2024 High-performance flexible p-type Ce-filled Fe_3CoSb_{12} skutterudite thin film for medium-to-high-temperature applications *Nat. Commun.* **15** 4242

[89] Qi Y, Li Y and Wang W 2022 Electrochemical reduction and preparation of Cu-Se thermoelectric thin film in solutions with PEG *Nanomaterials* **12** 3169
[90] Burton M R, Boyle C A, Liu T, McGettrick J, Nandhakumar I, Fenwick O and Carnie M J 2020 Full thermoelectric characterization of stoichiometric electrodeposited thin film tin selenide (SnSe) *ACS Appl. Mater. Interfaces* **12** 28232–8
[91] de Lourdes Gonzalez-juarez M, Flores E, Martin-Gonzalez M, Nandhakumar I and Bradshaw D 2020 Electrochemical deposition and thermoelectric characterisation of a semiconducting 2-D metal–organic framework thin film *J. Mater. Chem. A* **8** 13197–206
[92] Sun L *et al* 2017 A microporous and naturally nanostructured thermoelectric metal-organic framework with ultralow thermal conductivity *Joule* **1** 168–77
[93] Martín J, Martín-González M, Francisco Fernandez J and Caballero-Calero O 2014 Ordered three-dimensional interconnected nanoarchitectures in anodic porous alumina*Nat. Commun.* **5** 5130
Klösel K, Pané S, Mihailovic I A and Hierold C 2022 Template-assisted electrosynthesis of thick stoichiometric thermoelectric Bi_2Se_3 micropillars *Electrochimica Acta* **403** 139557
[94] Burton M, Selvam A, Lawrie-Ashton J, Squires A, Terrill N and Nandhakumar I 2018 Three-dimensional nanostructured palladium with single diamond architecture for enhanced catalytic activity *ACS Appl. Mater. Interfaces* **10** 37087–94
[95] Abellán M, Schrebler R and Gómez H 2015 Electrodeposition of Bi_2Te_3 thin
films onto FTO substrates from DMSO solution *Int. J. Electrochem. Sci.* **10** 7409–22
Golgovici F and Visan T 2012 Electrochemical deposition of BiTe films from choline chloride–malonic acid mixture as ionic liquid *Chalcogenide Lett.***10** 427–434
[96] Chen G, Chen Y, Guo Q, Wang H and Li B 2016 Template-free electrodeposition of AlFe alloy nanowires from a room-temperature ionic liquid as an anode material for Li-ion batteries *Faraday Discuss.* **190** 97–108
[97] Zhao L-D, Lo S-H, Zhang Y, Sun H, Tan G, Uher C, Wolverton C, Dravid V P and Kanatzidis M G 2014 Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals *Nature* **508** 373–7
[98] Abdy H, Heydari Z, Aletayeb A, Kolahdouz M and Asl-Soleimani E 2021 Electrodeposition, solvent engineering, and two-step solution deposition of the perovskite films: morphological and structural study *J. Mater. Sci., Mater. Electron.* **32** 12991–9
[99] Witting I T, Chasapis T C, Ricci F, Peters M, Heinz N A, Hautier G and Snyder G J 2019 The thermoelectric properties of bismuth telluride *Adv. Electron. Mater.* **5** 1800904
[100] Black D, Schoensee L, Richardson J, Vleisides T, Kempf N, Wang D, Ren Z and Zhang Y 2018 Power generation from nanostructured half-Heusler thermoelectrics for efficient and robust energy harvesting *ACS Appl. Energy Mater.* **1** 5986–92
[101] Fu Y, Ai X, Hu Z, Zhao S, Lu X, Huang J, Huang A, Wang L, Zhang Q and Jiang W 2024 Interface kinetic manipulation enabling efficient and reliable Mg_3Sb_2 thermoelectrics *Nat. Commun.* **15** 9355
[102] Kulkarni N, Tawade J V, Sampathi S, Hanumagowda B N, Abdelmohsen S A M, Khan M I, Saidani T and Batool N 2025 Sustainability and feasibility of low-grade heat utilization for thermoelectric systems in geothermal micro-seepages *Energy Rep.* **13** 4769–80
[103] Liu W, Len Y, Sui J, Liu Z and Ren Z 2018 *Advanced Thermoelectrics Materials, Contacts, Devices and Systems* ed Z Ren, Y Lan and Q Zhang (CRC Press) ch 3, p 83
[104] Bahrami A, Schierning G and Nielsch K 2020 Waste recycling in thermoelectric materials *Adv. Energy Mater.* **10** 1904159
[105] Min G 2006 Thermoelectric module design theories *Thermoelectrics Handbook: Macro to Nano* ed D M Rowe (CRC/Taylor & Francis)
[106] Kim H S, Wang T, Liu W and Ren Z 2016 Engineering thermal conductivity for balancing between reliability and performance of bulk thermoelectric generators *Adv. Funct. Mater.* **26** 3678–86
[107] Wu L, Feng X, Cao K and Li G 2023 Toughening thermoelectric materials: from mechanisms to applications *Int. J. Mol. Sci.* **24** 6325
[108] Zhang C *et al* 2023 Gibbs adsorption and Zener pinning enable mechanically robust high-performance Bi_2Te_3-based thermoelectric devices *Adv. Sci.* **10** 2302688
[109] Chu J *et al* 2020 Electrode interface optimization advances conversion efficiency and stability of thermoelectric devices *Nat. Commun.* **11** 2723
[110] Ayachi S, Park S, Ryu B, Park S, Mueller E and de Boor J 2023 High-performance thermoelectric devices made faster: interface design from first principles calculations *Adv. Phys. Res.* **3** 2300077
[111] Wu X, Han Z, Zhu Y, Deng B, Zhu K, Liu C, Jiang F and Liu W 2022 A general design strategy for thermoelectric interface materials in n-type $Mg_3Sb_{1.5}Bi_{0.5}$ single leg used in TEGs *Acta Mater.* **226** 117616
[112] Placha K, Tuley R S, Salvo M, Casalegno V and Simpson K 2018 Solid-liquid interdiffusion (SLID) bonding of p-type skutterudite thermoelectric material using Al-Ni interlayers *Materials* **11** 2483
[113] Li W *et al* 2023 High-performance skutterudite/half-Heusler cascaded thermoelectric module using the transient liquid phase sintering joining technique *ACS Appl. Mater. Interfaces* **15** 2961–70
[114] Yin L *et al* 2023 Low-temperature sintering of Ag nanoparticles for high-performance thermoelectric module design *Nat. Energy* **8** 665–74
[115] Funahashi R, Matsumura Y, Murakami H, Urata T, Ikenishi H and Sekine T 2025 Additives in silver paste improve the mechanical and thermal stability of thermoelectric modules composed of n-type half-Heusler and p-type oxide materials *Solid State Sci.* **159** 107780
[116] European Commission, Directorate-General for Environment 2026 *Circular Economy — Environment* (available at: https://environment.ec.europa.eu/strategy/circular-economy_en) (Accessed 04 February 2026)
[117] Zante G, Daskalopoulou E, Elgar C E, Rivera R M, Hartley J M, Simpson K, Tuley R, Kettle J and Abbott A P 2023 Targeted recovery of metals from thermoelectric generators (TEGs) using chloride brines and ultrasound *RSC Sustain.* **1** 1025–34
[118] Cao J *et al* 2022 Upcycling silicon photovoltaic waste into thermoelectrics *Adv. Mater.* **34** 2110518
[119] START Project 2025 Sustainable energy harvesting systems based on innovative mine waste recycling (START PROJECT – Official Website) (available at: https://www.start-heproject.com/) (Accessed 04 February 2026)
[120] Ying P, He R, Mao J, Zhang Q, Reith H, Sui J, Ren Z, Nielsch K and Schierning G 2021 Towards tellurium-free thermoelectric modules for power generation from low-grade heat *Nat. Commun.* **12** 1121
[121] Ying P, Wilkens L, Reith H, Rodriguez N, Hong X, Lu Q, Hess C, Nielsch K and He R 2022 A robust thermoelectric module based on $MgAgSb/Mg_3(Sb,Bi)_2$ with a conversion efficiency of 8.5% and a maximum cooling of 72 K *Energy Environ. Sci.* **15** 2557–66
[122] Ying P *et al* 2024 Performance degradation and protective effects of atomic layer deposition for Mg-based thermoelectric modules *Adv. Funct. Mater.* **34** 2406473

[123] Wu H, Shi X-L, Duan J, Liu Q and Chen Z-G 2023 Advances in Ag_2Se-based thermoelectrics from materials to applications *Energy Environ. Sci.* **16** 1870–906
[124] Fraunhofer-Gesellschaft 2024 Recycling and long-term stability of thermoelectric and magnetocaloric systems (RecycleTEAM) (available at: www.recycleteam.de/en.html) (Accessed 04 February 2026)
[125] M-ERA.NET. *Tellurium-Free Thermoelectric Modules by Interface Engineering (THERMOS)*. Materipedia — M-ERA.NET project database (available at: www.m-era.net/materipedia/2021/thermos (Accessed 4 November 2024)
[126] Honda Y *et al* 2009 Direct thermal-to-electric energy conversion material consisting of environmentally-benign Mg_2Si synthesized using waste Si sludge and recycled Mg alloy *MRS Online Proc. Library* **1218** 517
[127] Antunes L M *et al* 2022 Machine learning approaches for accelerating the discovery of thermoelectric materials *Machine Learning in Materials Informatics: Methods and Applications* vol 1416 (ACS Symposium Series; American Chemical Society) pp 1–32
[128] Vaitesswar S, Bash D, Huang T, Recatala-Gomez J, Deng T, Yang S-W, Wang X and Hippalgaonkar K 2024 Machine learning based feature engineering for thermoelectric materials by design *Digit. Discovery* **3** 210–20
[129] Antunes L M, Butler K T and Grau-Crespo R 2023 Predicting thermoelectric transport properties from composition with attention-based deep learning *Mach. Learn.: Sci. Technol.* **4** 015037
[130] Juneja R, Yumnam G, Satsangi S and Singh A K 2019 Coupling the high-throughput property map to machine learning for predicting lattice thermal conductivity *Chem. Mater.* **31** 5145–51
[131] Eriksson F, Fransson E and Erhart P 2019 The Hiphive package for the extraction of high-order force constants by machine learning *Adv. Theor. Simul.* **2** 1800184
[132] Plata J J, Posligua V, Márquez A M, Fernandez Sanz J and Grau-Crespo R 2022 Charting the lattice thermal conductivities of I–III–VI2 chalcopyrite semiconductors *Chem. Mater.* **34** 2833–41
[133] Langer M F, Knoop F, Carbogno C, Scheffler M and Rupp M 2023 Heat flux for semilocal machine-learning potentials *Phys. Rev. B* **108** L100302
[134] Chen C and Ong S P 2021 AtomSets as a hierarchical transfer learning framework for small and large materials datasets *npj Comput. Mater.* **7** 1–9
[135] Ricci F, Chen W, Aydemir U, Snyder G J, Rignanese G-M, Jain A and Hautier G 2017 An *ab initio* electronic transport database for inorganic materials *Sci. Data* **4** 170085
[136] Chen W *et al* 2016 Understanding thermoelectric properties from high-throughput calculations: trends, insights, and comparisons with experiment *J. Mater. Chem. C* **4** 4414–26
[137] Na G S, Jang S and Chang H 2021 Predicting thermoelectric properties from chemical formula with explicitly identifying dopant effects *npj Comput. Mater.* **7** 106
[138] Na G S and Chang H 2022 A public database of thermoelectric materials and system-identified material representation for data-driven discovery *npj Comput. Mater.* **8** 214
[139] Ganose A M, Park J, Faghaninia A, Woods-Robinson R, Persson K A and Jain A 2021 Efficient calculation of carrier scattering rates from first principles *Nat. Commun.* **12** 2222
[140] Miller S A, Dylla M, Anand S, Gordiz K, Snyder G J and Toberer E S 2018 Empirical modeling of dopability in diamond-like semiconductors *npj Comput. Mater.* **4** 1–8
[141] Abolhasani M and Kumacheva E 2023 The rise of self-driving labs in chemical and materials sciences *Nat. Synth.* **2** 483–92
[142] Leeman J, Liu Y, Stiles J, Lee S B, Bhatt P, Schoop L M and Palgrave R G 2024 Challenges in high-throughput inorganic materials prediction and autonomous synthesis *PRX Energy* **3** 011002
[143] Sierepeklis O and Cole J M 2022 A thermoelectric materials database auto-generated from the scientific literature using ChemDataExtractor *Sci. Data* **9** 648
[144] Wilkinson M D *et al* 2016 The FAIR guiding principles for scientific data management and stewardship *Sci. Data* **3** 160018
[145] Scheidgen M *et al* 2023 NOMAD: a distributed web-based platform for managing materials science research data *J. Open Source Softw.* **8** 5388
[146] Batatia I, Kovacs D P, Simm G and Ortner C 2022 MACE: higher order equivariant message passing neural networks for fast and accurate force fields *Advances in Neural Information Processing Systems* vol 35, ed S Koyejo *et al* (Curran Associates, Inc) pp 11423–36
[147] Antunes L M, Butler K T and Grau-Crespo R 2024 Crystal structure generation with autoregressive large language modeling Nature Communications **15** 10570
[148] Schoen J M 1969 Augmented plane-wave virtual crystal approximation *Phys. Rev.* **184** 858
[149] Velicky B 1969 Theory of electronic transport in disordered binary alloys *Phys. Rev.* **184** 614
[150] Van De Walle A, Tiwary P, de Jong M, Olmsted D L, Asta M, Dick A, Shin D, Wang Y, Chen L-Q and Liu Z-K 2013 Efficient stochastic generation of special quasirandom structures *Calphad* **42** 13
[151] Skylaris C-K, Haynes P D, Mostofi A A and Payne M C 2005 Introducing ONETEP: linear-scaling density functional simulations on parallel computers *J. Chem. Phys.* **122** 084119
[152] Mohr S, Ratcliff L, Genovese L, Caliste D, Boulanger P, Goedecker S and Deutsch T 2015 Accurrate and efficient linear scaling DFT calculations with universal applicability *Phys. Chem. Chem. Phys.* **17** 31360
[153] Hourahine B *et al* 2020 DFTB+ a software package for efficient approximate density functional theory based atomic simulations *J. Chem. Phys.* **152** 124101
[154] Slack G A 1995 New materials and performance limits for thermoelectric cooling *CRC Handbook of Thermoelectric* CRC Press, 1st Edition, 1995
[155] Graziosi P, Li Z and Neophytou N 2022 Bipolar conduction asymmetries lead to ultra-high thermoelectric power factor *Appl. Phys. Lett.* **120** 072102
[156] Madsen G K H, Carrete J and Verstraete M J 2018 BoltzTraP2, a program for interpolating band structures and calculating semi-classical transport coefficients *Comput. Phys. Commun.* **231** 140
[157] Neophytou N and Kosina H 2011 Effects of confinement and orientation on the thermoelectric power factor of silicon nanowires *Phys. Rev. B* **83** 245305
[158] Baroni S, Giannozzi P and Testa A 1987 Green's function approach to linear response in solids *Phys. Rev. Lett.* **58** 1861
[159] Lee H *et al* 2023 Electron–phonon physics from first principles using the EPW code *npj Comput. Mater.* **9** 156
[160] Zhou J, Park J, Lu I-T, Maliyov I, Tong X and Bernardi M 2021 Perturbo: a software package for *ab initio* electron-phonon interactions, charge transport and ultrafast dynamics *Comput. Phys. Commun.* **264** 107970
[161] Cepellotti A, Coulter J, Johansson A, Fedorova N S and Kozinsky B 2022 Phoebe, a high-performance framework for solving phonon and electron Boltzmann transport equations *J. Phys. Mater.* **5** 035003

[162] Samsonidze G and Kozinsky B 2018 Accelerated screening of thermoelectric materials by first-principles computations of electron–phonon scattering *Adv. Energy Mater.* **8** 1800246
[163] Deng T, Wu G, Sullivan M B, Wong Z M, Hippalgaonkar K, Wang J-S and Yang S-W 2020 EPIC STAR: a reliable and efficient approach for phonon- and impurity-limited charge transport calculations *npj Comput. Mater.* **6** 46
[164] Graziosi P, Li Z and Neophytou N 2023 ElecTra code: full-band electronic transport properties of materials *Comput. Phys. Commun.* **287** 108670
[165] Li Z, Graziosi P and Neophytou N 2024 Efficient first principles electronic transport approach to complex band structure materials: the case of n-type Mg_3Sb_2 *npj Comput. Mater.* **10** 8
[166] Togo A and Tanaka I 2015 First principles phonon calculations in materials science *Scr. Mater.* **108** 1
[167] Li W, Carrete J, Katcho N A and Mingo N 2014 ShengBTE: a solver of the Boltzmann transport equation for phonons *Comput. Phys. Commun.* **185** 1747
[168] Lee K-T, Lee D-S, Chen W-H, Lin Y-L, Luo D, Park Y-K and Bandala A 2023 An overview of commercialization and marketization of thermoelectric generators for low-temperature waste heat recovery *Iscience* **26** 107874
[169] Heremans J P and Wiendlocha B 2016 Tetradymites: Bi_2Te_3-related materials *Materials Aspect of Thermoelectricity* (CRC Press) pp 53–108
[170] Fang T, Li X, Hu C, Zhang Q, Yang J, Zhang W, Zhao X, Singh D J and Zhu T 2019 Complex band structures and lattice dynamics of Bi_2Te_3-based compounds and solid solutions *Adv. Funct. Mater.* **29** 1900677
[171] Tamaki H, Sato H K and Kanno T 2016 Isotropic conduction network and defect chemistry in $Mg_{3+\delta}Sb_2$-based layered zintl compounds with high thermoelectric performance *Adv. Mater.* **28** 10182–7
[172] Mao J, Zhu H, Ding Z, Liu Z, Gamage G A, Chen G and Ren Z 2019 High thermoelectric cooling performance of n-type Mg_3Bi_2-based materials *Science* **365** 495–8
[173] Liu Z *et al* 2021 Demonstration of ultrahigh thermoelectric efficiency of ∼7.3% in Mg_3Sb_2/MgAgSb module for low-temperature energy harvesting *Joule* **5** 1196–208
[174] Wu X, Huang J, Zhou Z, Han Z, Jiang F, Li H, Wang Y, Zhu K and Liu W 2023 Mg_3Sb_2-based thermoelectrics: materials, interfaces, and devices *Mater. Lab* **2** 230003
[175] Bano S, Chetty R, Babu J and Mori T 2024 $Mg_3(Sb,Bi)_2$-based materials and devices rivaling bismuth telluride for thermoelectric power generation and cooling *Device* **2** 100408
[176] Sun Y *et al* 2024 Rational design from materials to devices enables an efficiency of 10.5% based on thermoelectric $(Bi, Sb)_2Te_3$ and $Mg_3(Bi, Sb)_2$ for power generation *Energy Environ. Sci.* **17** 738–47
[177] Chauhan N S and Mori T 2024 Cooler, stronger, smaller: improving thermoelectric cooling *Natl Sci. Rev.* **12** nwae445
[178] Zheng Z-H *et al* 2023 Harvesting waste heat with flexible Bi_2Te_3 thermoelectric thin film *Nat. Sustain.* **6** 180–91
[179] Lu Y *et al* 2023 Staggered-layer-boosted flexible Bi_2Te_3 films with high thermoelectric performance *Nat. Nanotechnol.* **18** 1281–8
[180] Wang L and Zhang K 2020 Textile-based thermoelectric generators and their applications *Energy Environ. Mater.* **3** 67–79
[181] Tang W, Sun Q and Wang Z L 2023 Self-powered sensing in wearable electronics—a paradigm shift technology *Chem. Rev.* **123** 12105–34
[182] Yang Q, Yang S, Qiu P, Peng L, Wei T-R, Zhang Z, Shi X and Chen L 2022 Flexible thermoelectrics based on ductile semiconductors *Science* **377** 854–8
[183] Nandihalli N, Liu C-J and Mori T 2020 Polymer based thermoelectric nanocomposite materials and devices: fabrication and characteristics *Nano Energy* **78** 105186
[184] Graf T, Felser C and Parkin S 2011 Simple rules for the understanding of Heusler compounds *Prog. Solid State Chem.* **39** 1–50
[185] Katrakis E and Garcia E A 2020 Metal recycling factsheet by EuRIC (available at: https://circulareconomy.europa.eu/platform/en/knowledge/metal-recycling-factsheet-euric)
[186] Sustainability Indicators 2023 report (World Steel Association AISBL) (available at: https://worldsteel.org/steel-topics/sustainability/sustainability-indicators-2023-report/)
[187] U.S. Geological Survey 2024 Mineral commodity summaries 2024: U.S. Geological Survey p 212
[188] Mikami M, Kinemuchi Y, Ozaki K, Terazawa Y and Takeuchi T 2012 Thermoelectric properties of tungsten-substituted Heusler Fe_2VAl alloy *J. Appl. Phys.* **111** 093710
[189] Renard K, Mori A, Yamada Y, Tanaka S, Miyazaki H and Nishino Y 2014 Thermoelectric properties of the Heusler-type $Fe_2VTa_xAl_{1-x}$ alloys *J. Appl. Phys.* **115** 033707
[190] Nishino Y, Deguchi S and Mizutani U 2006 Thermal and transport properties of the Heusler-type $Fe_2VAl_{1-x}Ge_x$ ($0 \leqslant x \leqslant 0.20$) alloys: effect of doping on lattice thermal conductivity, electrical resistivity, and Seebeck coefficient *Phys. Rev. B* **74** 115115
[191] Miyazaki H, Tanaka S, Ide N, Soda K and Nishino Y 2013 Thermoelectric properties of Heusler-type off-stoichiometric $Fe_2V_{1+x}Al_{1-x}$ alloys *Mater. Res. Express* **1** 015901
[192] Takeuchi T, Terazawa Y, Furuta Y, Yamamoto A and Mikami M 2013 Effect of heavy element substitution and off-stoichiometric composition on thermoelectric properties of Fe_2VAl-based Heusler phase *J. Electron. Mater.* **42** 2084
[193] Rogl G, Sauerschnig P, Rykavets Z, Romaka V, Heinrich P, Hinterleitner B, Grytsiv A, Bauer E and Rogl P 2017 (V, Nb)-doped half Heusler alloys based on {Ti, Zr, Hf} NiSn with high ZT *Acta Mater.* **131** 336–48
[194] Garmroudi F *et al* 2025 Decoupled charge and heat transport in Fe_2VAl composite thermoelectric with topological-insulating grain boundary networks *Nat. Commun.* **16** 2976
[195] Garmroudi F, Parzer M, Riss A, Beyer S, Khmelevskyi S, Mori T, Reticcioli M and Bauer E 2022 Large thermoelectric power factors by opening the band gap in semimetallic Heusler alloys *Mater. Today Phys.* **27** 100742
[196] Anand S, Gurunathan R, Soldi T, Borgsmiller L, Orenstein R and Snyder G J 2020 Thermoelectric transport of semiconductor full-Heusler VFe_2Al *J. Mater. Chem. C* **8** 10174
[197] Fukuta K, Tsuchiya K, Miyazaki H and Nishino Y 2022 Improving thermoelectric performance of Fe_2VAl-based Heusler compounds via high-pressure torsion *Appl. Phys. A* **128** 184
[198] Parzer M, Garmroudi F, Riss A, Khmelevskyi S, Mori T and Bauer E 2022 High solubility of Al and enhanced thermoelectric performance due to resonant states in Fe_2VAl_x *Appl. Phys. Lett.* **120** 071901
[199] Parzer M 2024 Extending the phase space of thermoelectric full-Heusler compounds *Thesis* Technische Universität Wien
[200] Nishino Y, Kamizono S, Miyazaki H and Kimura K 2019 Effects of off-stoichiometry and Ti doping on thermoelectric performance of Fe_2VAl Heusler compound *AIP Adv.* **9** 125003
[201] Parzer M, Kositz A, Süß J, Garmroudi F, Mori T and Bauer E 2025 Enhanced thermopower by double-site substitution of Ti in $Fe_2(VAl)_{1-x}Ti_{2x}$ *Mater. Today Phys.* **54** 101712

[202] Li J, Huckleby A B and Zhang M 2022 Polymer-based thermoelectric materials: a review of power factor improving strategies *J. Materiomics* **8** 204–20
[203] Gayner C and Amouyal Y 2020 Energy filtering of charge carriers: current trends, challenges, and prospects for thermoelectric materials *Adv. Funct. Mater.* **30** 1901789
[204] Meng C Z, Liu C H and Fan S S 2010 A promising approach to enhanced thermoelectric properties using carbon nanotube networks *Adv. Mater.* **22** 535–9
[205] Ju H and Kim J 2016 Chemically exfoliated SnSe nanosheets and their SnSe/poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) composite films for polymer based thermoelectric applications *ACS Nano* **10** 5730–9
[206] Cho C, Wallace K L, Tzeng P, Hsu J-H, Yu C and Grunlan J C 2016 Outstanding low temperature thermoelectric power factor from completely organic thin films enabled by multidimensional conjugated nanomaterials *Adv. Energy Mater.* **6** 1502168
[207] Zeng C Y, Chen K, Koz C, Stefanaki E-C, Galindez E S S, Zhang H, Fenwick O, Tuley R and Bilotti E 2024 Kirigami-inspired organic and inorganic film-based flexible thermoelectric devices with built-in heat sink *Nano Energy* **121** 109213
[208] Wang L M, Zhang Z M, Liu Y C, Wang B R, Fang L, Qiu J J, Zhang K and Wang S R 2018 Exceptional thermoelectric properties of flexible organic−inorganic hybrids with monodispersed and periodic nanophase *Nat. Commun.* **9** 3817
[209] An C J, Lee Y C, Kang Y H and Cho S Y 2017 Improved interaction between semiconducting polymer and carbon nanotubes in thermoelectric composites through covalent grafting *Carbon* **124** 662–8
[210] Hao Y N, He X Y, Wang L M, Qin X H, Chen G M and Yu J Y 2022 Stretchable thermoelectrics: strategies, performances, and applications *Adv. Funct. Mater.* **32** 2109790
[211] Yusupov K and Vomiero A 2020 Polymer-based low-temperature thermoelectric composites *Adv. Funct. Mater.* **30** 2002015
[212] Yao Q, Wang Q, Wang L M and Chen L D 2014 Abnormally enhanced thermoelectric transport properties of SWNT/PANI hybrid films by the strengthened PANI molecular ordering *Energy Environ. Sci.* **7** 3801–7
[213] Akkerman Q A and Manna L 2020 What defines a halide perovskite? *ACS Energy Lett.* **5** 604–10
[214] Saad H, Alsobhi B O and Almeshal A 2024 Tuning of band gap and enhancing electronic properties of $CsSnBr_3$ under high pressure for optoelectronic applications *Comput. Condens. Matter* **38** e00870
[215] He Y P and Galli G 2014 Perovskites for solar thermoelectric applications: a first principle study of $CH_3NH_3Al_3$(A = Pb and Sn) *Chem. Mater.* **26** 5394–400
[216] Yan L F, Wang M C, Zhai C X, Zhao L L and Lin S C 2020 Symmetry breaking induced anisotropic carrier transport and remarkable thermoelectric performance in mixed halide perovskites $CsPb(I_{1-x}Br_x)_3$ *ACS Appl. Mater.* **12** 40453–64
[217] Jung Y-K, Han I T, Kim Y C and Walsh A 2021 Prediction of high thermoelectric performance in the low-dimensional metal halide $Cs_3Cu_2I_5$ *npj Comput. Mater.* **7** 51
[218] Walsh A, Scanlon D O, Chen S Y, Gong X G and Wei S-H 2014 Self-regulation mechanism for charged point defects in hybrid halide perovskites *Angew. Chem., Int. Ed.* **54** 1791–4
[219] Tang W *et al* 2020 Substitutional doping of hybrid organic-inorganic perovskite crystals for thermoelectrics *J. Mater. Chem. A* **8** 13594–9
[220] Shi W, Yao M, Wu X, Zhou T, Yong X, Deng T, Ma H and Xi J 2023 Atomistic insights into the origin of high-performance thermoelectric response in hybrid perovskites *Adv. Sci.* **10** 2300666
[221] Wang Y *et al* 2019 Thermodynamically stabilized β-$CsPbI_3$-based perovskite solar cells with efficiencies >18% *Science* **365** 591–5
[222] Tang W, Liu T and Fenwick O 2022 High thermoelectric performance based on $CsSnI_3$ thin films with improved stability *J. Mater. Chem. A* **10** 7020–8
[223] Wang T, Xu X, Li W, Li Y, Liu Q, Li C, Shan C, Li G, Shi T and Kyaw A K K 2022 Simultaneous enhancement of thermoelectric power factor and phase stability of tin-based perovskites by organic cation doping *ACS Appl. Energy Mater.* **5** 11191–9
[224] Yi C Y, Luo J, Meloni S, Boziki A, Ashari-Astani N, Grätzel C, Zakeeruddin S M, Röthlisberger U and Grätzel M 2016 Entropic stabilization of mixed a-cation ABX_3 metal halide perovskites for high performance perovskite solar cells *Energy Environ. Sci.* **9** 656–62
[225] Chen R, Yan Y, Tang J, Zeng H, Yao Q, Chen L and Liang Z 2022 Efficient p-type doping of tin halide perovskite via sequential diffusion for thermoelectrics *Small Sci.* **2** 2200004
[226] Haque F, Hoang N T T, Ji J and Mativenga M 2019 Effect of precursor composition on ion migration in hybrid perovskite $CH_3NH_3PbI_3$ *IEEE Electron. Device Lett.* **40** 1756–9
[227] Haque M A, Nugraha M I, Paleti S H K and Baran D 2019 Role of compositional tuning on thermoelectric parameters of hybrid halide perovskites *J. Phys. Chem. C* **123** 14928–33
[228] Liu T, Zhao X, Li J, Liu Z, Liscio F, Milita S, Schroeder B C and Fenwick O 2019 Enhanced control of self-doping in halide perovskites for improved thermoelectric performance *Nat. Commun.* **10** 5750
[229] Tang W, Zhang S, Liu T, Jung C, Kim S H, Scheu C, Yue S and Fenwick O 2025 Reduced thermal conductivity and improved stability by B-Site doping in tin halide perovskites *J. Phys. Chem. Lett.* **16** 525–36
[230] Xie H, Hao S, Bao J, Slade T J, Snyder G J, Wolverton C and Kanatzidis M G 2020 All-inorganic halide perovskites as potential thermoelectric materials: dynamic cation off-centering induces ultralow thermal conductivity *J. Am. Chem. Soc.* **142** 9553–63
[231] Shi Y-B, Li N, Dong H-K, Cao S, Song K-K, Shao Z-F and Qian P 2023 First-principles calculations of improving carrier mobility for β-$CsPbI_3$ *Mater. Sci. Semicond. Process.* **157** 107327
[232] Wang Q, Tang Y P, Horita Z J and Iikubo S 2022 Structural and thermoelectric properties of $CH_3NH_3SnI_3$ perovskites processed by applying high pressure with shear strain *Mater. Res. Lett.* **10** 521–9
[233] Lu X J *et al* 2020 Regulating off-centering distortion maximizes photoluminescence in halide perovskites *Natl Sci. Rev.* **8** nwaa288
[234] Powell A V 2019 Recent developments in Earth-abundant copper-sulfide thermoelectric materials *J. Appl. Phys.* **126** 100901
[235] Sun F-H, Li H, Tan J, Zhao L, Wang X, Hu H, Wang C and Mori T 2024 Review of current ZT > 1 thermoelectric sulfides *J. Mater.* **10** 218–233
[236] Becquerel A E 1866 Mémoire sur les pouvoirs thermos-électriques des corps et sur les piles thermos-électriques *Ann. Chim. Phys.* **48** 389
[237] Lu X, Morelli D T, Xia Y, Zhou F, Ozolins V, Chi H, Zhou X and Uher C 2013 High performance thermoelectricity in Earth-abundant compounds based on natural mineral tetrahedrite *Adv. Energy Mater.* **3** 342
[238] Suekuni K, Tsuruta K, Kunii M, Nishiate H, Nishibori E, Maki S, Ohta M, Yamamoto A and Koyano M 2013 High-performance thermoelectric mineral $Cu_{12-x}Ni_xSb_4S_{13}$ tetrahedrite *J. Appl. Phys.* **113** 043712
[239] Lemoine P, Guélou G, Raveau B and Guilmeau E 2022 Crystal structure classification of copper-based sulfides as a tool for the design of inorganic functional materials *Angew. Chem., Int. Ed.* **61** e202108686

[240] Luo Z-Z *et al* 2019 Enhancement of thermoelectric performance for n-type PbS through synergy of gap state and Fermi level pinning *J. Am. Chem. Soc.* **141** 6403
[241] Tan G, Hao S, Zhao J, Wolverton C and Kanatzidis M G 2017 High thermoelectric performance in electron-doped $AgBi_3S_5$ with ultralow thermal conductivity *J. Am. Chem. Soc.* **139** 6467
[242] Baláž P 2004 Mechanochemistry of sulphides *J. Mater. Sci.* **39** 5097
[243] Dennler G, Chmielowski R, Jacob S, Capet F, Roussel P, Zastrow S, Nielsch K, Opahle I and Madsen G K H 2014 Are binary copper sulfides/selenides really new and promising thermoelectric materials? *Adv. Energy Mater.* **4** 1301581
[244] Qiu P *et al* 2019 High-efficiency and stable thermoelectric module based on liquid-like materials *Joule* **3** 1538
[245] Hu H *et al* 2024 Highly stabilized and efficient thermoelectric copper selenide *Nat. Mater.* **23** 527
[246] Mukherjee S, Voneshen D J, Duff A, Goddard P, Powell A V and Vaqueiro P 2023 Beyond rattling: tetrahedrites as incipient ionic conductors *Adv. Mater.* **35** 2306088
[247] Brito F P, Vieira R, Martins J, Goncalves L M, Goncalves A P, Coelho R, Lopes E B, Symeou E and Kyratsi T 2021 Analysis of thermoelectric generator incorporating n-magnesium silicide and p-tetrahedrite materials *Energy Convers. Manage.* **236** 114003
[248] Tian R, Wan C, Wang Y, Wei Q, Ishida T, Yamamoto A, Tsuruta A, Shin W, Li S and Koumoto K 2017 A solution-processed TiS_2/organic hybrid superlattice film towards flexible thermoelectric devices *J. Mater. Chem. A* **5** 564
[249] Chetty R, Kikuchi Y, Bouyrie Y, Jood P, Yamamoto A, Suekuni K and Ohta M 2019 Power generation from the $Cu_{26}Nb_2Ge_6S_{32}$-based single thermoelectric element with Au diffusion barrier *J. Mater. Chem. C* **7** 5184
[250] Gucci F, D'Isanto F, Zhang R, Reece M J, Smeacetto F and Salvo M 2019 Oxidation protective hybrid coating for thermoelectric materials *Materials* **12** 573
[251] Battiston S, Montagner F, Fiameni S, Famengo A, Boldrini S, Ferrario A, Fanciulli C, Agresti F and Fabrizio M 2019 AlTiN based thin films for degradation protection of tetrahedrite thermoelectric material *J. Alloys Compd.* **792** 953–959
[252] Tan G, Zhao L-D and Kanatzidis M G 2016 Rationally designing high-performance bulk thermoelectric materials *Chem. Rev.* **116** 12123–49
[253] Roychowdhury S, Ghosh T, Arora R, Samanta M, Xie L, Singh N K, Soni A, He J, Waghmare U V and Biswas K 2021 Enhanced atomic ordering leads to high thermoelectric performance in $AgSbTe_2$ *Science* **371** 722–7
[254] Zhu T, Bai H, Zhang J, Tan G, Yan Y, Liu W, Su X, Wu J, Zhang Q and Tang X 2020 Realizing high thermoelectric performance in Sb-doped Ag_2Te compounds with a low-temperature monoclinic structure *ACS Appl. Mater. Interfaces* **12** 39425–33
[255] Zhu B, Liu X, Wang Q, Qiu Y, Shu Z, Guo Z, Tong Y, Cui J, Gu M and He J 2020 Realizing record high performance in n-type Bi_2Te_3-based thermoelectric materials *Energy Environ. Sci.* **13** 2106–14
[256] Zhang J, Wu D, He D, Feng D, Yin M, Qin X and He J 2017 Extraordinary thermoelectric performance realized in n-type PbTe through multiphase nanostructure engineering *Adv. Math.* **29** 1703148
[257] Pang H, Qiu Y, Wang D, Qin Y, Huang R, Yang Z, Zhang X and Zhao L-D 2021 Realizing N-type SnTe thermoelectrics with competitive performance through suppressing Sn vacancies *J. Am. Chem. Soc.* **143** 8538–42
[258] Sarkar D *et al* 2025 Glassy thermal transport triggers ultra-high thermoelectric performance in GeTe *Adv. Mater.* **37** 2417561
[259] Jia B *et al* 2024 Pseudo-nanostructure and trapped-hole release induce high thermoelectric performance in PbTe *Science* **384** 81–86
[260] Hussain T, Li X, Danish M H, Rehman M U, Zhang J, Li D, Chen G and Tang G 2020 Realizing high thermoelectric performance in eco-friendly SnTe via synergistic resonance levels, band convergence and endotaxial nanostructuring with Cu_2Te *Nano Energy* **73** 104832
[261] Brown D R, Day T, Caillat T and Snyder G J 2013 Chemical stability of $(Ag,Cu)_2Se$: a historical overview *J. Electron. Mater.* **42** 2014–9
[262] Jiang B *et al* 2021 High-entropy-stabilized chalcogenides with high thermoelectric performance *Science* **371** 830–4
[263] Chang C *et al* 2018 3D charge and 2D phonon transports leading to high out-of-plane ZT in n-type SnSe crystals *Science* **360** 778–83
[264] Sarkar D, Roychowdhury S, Arora R, Ghosh T, Vasdev A, Joseph B, Sheet G, Waghmare U V and Biswas K 2021 Metavalent bonding in GeSe leads to high thermoelectric performance *Angew. Chem., Int. Ed.* **60** 10350–8
[265] Samanta M, Pal K, Pal P, Waghmare U V and Biswas K 2018 Localized vibrations of Bi bilayer leading to ultralow lattice thermal conductivity and high thermoelectric performance in weak topological insulator n-type BiSe *J. Am. Chem. Soc.* **140** 5866–72
[266] Maria I, Arora R, Dutta M, Roychowdhury S, Waghmare U V and Biswas K 2023 Metavalent bonding-mediated dual $6s^2$ lone pair expression leads to intrinsic lattice shearing in n-type $TlBiSe_2$ *J. Am. Chem. Soc.* **145** 9292–303
[267] Zulkifal S *et al* 2023 Multiple valence bands convergence and localized lattice engineering lead to superhigh thermoelectric figure of merit in MnTe *Adv. Sci.* **10** 2206342
[268] Biswas K, He J, Blum I D, Wu C-I, Hogan T P, Seidman D N, Dravid V P and Kanatzidis M G 2012 High-performance bulk thermoelectrics with all-scale hierarchical architectures *Nature* **489** 414–8
[269] Chandra S and Biswas K 2019 Realization of high thermoelectric figure of merit in solution synthesized 2D SnSe nanoplates via Ge alloying *J. Am. Chem. Soc.* **141** 6141–5
[270] Zhou C *et al* 2021 Polycrystalline SnSe with a thermoelectric figure of merit greater than the single crystal *Nat. Mater.* **20** 1378–84
[271] Pei Y, Shi X, LaLonde A, Wang H, Chen L and Snyder G J 2011 Convergence of electronic bands for high performance bulk thermoelectrics *Nature* **473** 66–69
[272] Heremans J P, Jovovic V, Toberer E S, Saramat A, Kurosaki K, Charoenphakdee A, Yamanaka S and Snyder G J 2008 Enhancement of thermoelectric efficiency in PbTe by distortion of the electronic density of states *Science* **321** 554–7
[273] Pal K, Xia Y, Shen J, He J, Luo Y, Kanatzidis M G and Wolverton C 2021 Accelerated discovery of a large family of quaternary chalcogenides with very low lattice thermal conductivity *npj Comput. Mater.* **7** 82
[274] Hong M, Lyv W, Li M, Xu S, Sun Q, Zou J and Chen Z-G 2020 Rashba effect maximizes thermoelectric performance of GeTe derivatives *Joule* **4** 2030–43
[275] Chen Y-X, Ge Z-H, Yin M, Feng D, Huang X-Q, Zhao W and He J 2016 Understanding of the extremely low thermal conductivity in high-performance polycrystalline SnSe through potassium doping *Adv. Funct. Mater.* **26** 6836–45
[276] Isotta E, Toriyama M Y, Adekoya A H, Shupp E, Snyder G J and Zevalkink A 2023 Effect of Sn oxides on the thermal conductivity of polycrystalline SnSe *Mater. Today Phys.* **31** 100967
[277] Uher C, Yang J, Hu S, Morelli D T and Meisner G P 1999 Transport properties of pure and doped MNiSn (M=Zr, Hf) *Phys. Rev. B* **59** 8615–21

[278] Yang J, Li H, Wu T, Zhang W, Chen L and Yang J 2008 Evaluation of half-Heusler compounds as thermoelectric materials based on the calculated electrical transport properties *Adv. Funct. Mater.* **18** 2880–8
[279] Chen R, Kang H, Min R, Chen Z, Guo E, Yang X and Wang T 2024 Thermoelectric properties of half-Heusler alloys *Int. Mater. Rev.* **69** 83–106
[280] Li W, Ghosh S, Liu N and Poudel B 2024 Half-Heusler thermoelectrics: advances from materials fundamental to device engineering *Joule* **8** 1274–311
[281] Han S *et al* 2023 Strong phonon softening and avoided crossing in aliovalence-doped heavy-band thermoelectrics *Nat. Phys.* **19** 1649–57
[282] Zhu T, Fu C, Xie H, Liu Y and Zhao X 2015 High efficiency half-Heusler thermoelectric materials for energy harvesting *Adv. Energy Mater.* **5** 1500588
[283] Kang H B, Poudel B, Li W, Lee H, Saparamadu U, Nozariasbmarz A, Kang M G, Gupta A, Heremans J J and Priya S 2020 Decoupled phononic-electronic transport in multi-phase n-type half-Heusler nanocomposites enabling efficient high temperature power generation *Mater. Today* **36** 63–72
[284] Fu C, Bai S, Liu Y, Tang Y, Chen L, Zhao X and Zhu T 2015 Realizing high figure of merit in heavy-band p-type half-Heusler thermoelectric materials *Nat. Commun.* **6** 8144
[285] Quinn R J and Bos J-W G 2021 Advances in half-Heusler alloys for thermoelectric power generation *Mater. Adv.* **2** 6246–66
[286] Liu R *et al* 2022 Thermal-inert and ohmic-contact interface for high performance half-Heusler based thermoelectric generator *Nat. Commun.* **13** 7738
[287] Zhang Q, Deng K, Wilkens L, Reith H and Nielsch K 2022 Micro-thermoelectric devices *Nat. Electron.* **5** 333–47
[288] Tang Y, Li X, Martin L H J, Cuervo Reyes E, Ivas T, Leinenbach C, Anand S, Peters M, Snyder G J and Battaglia C 2018 Impact of Ni content on the thermoelectric properties of half-Heusler TiNiSn *Energy Environ. Sci.* **11** 311–20
[289] Xia K, Hu C, Fu C, Zhao X and Zhu T 2021 Half-Heusler thermoelectric materials *Appl. Phys. Lett.* **118** 140503
[290] Snyder G J and Snyder A H 2017 Figure of merit ZT of a thermoelectric device defined from materials properties *Energy Environ. Sci.* **10** 2280–3
[291] Hammel T E, Bennett R, Otting W D and Fanale S M 2009 Multi-mission radioisotope thermoelectric generator (MMRTG) and performance prediction model *7th Int. Energy Conversion Engineering Conf.* (*Denver, Colorado*)
[292] Li X *et al* 2022 Thermodynamic approaches to determine the vacancy concentration in defective $Nb_{1-x}CoSb$ half-Heusler thermoelectric materials *Acta Mater.* **228** 117736
[293] He J, Naghavi S S, Hegde V I, Amsler M and Wolverton C 2018 Designing and discovering a new family of semiconducting quaternary Heusler compounds based on the 18-electron rule *Chem. Mater.* **30** 4978–85
[294] Yin L, Li X, Bao X, Cheng J, Chen C, Zhang Z, Liu X, Cao F, Mao J and Zhang Q 2024 CALPHAD accelerated design of advanced full-Zintl thermoelectric device *Nat. Commun.* **15** 1468
[295] Bi J, Liu Z, Li B, Li S, Yang Z, Starostenkov M D and Dong G 2023 Additive manufacturing of thermoelectric materials: materials, synthesis and manufacturing: a review *J. Mater. Sci.* **59** 359–81
[296] Malki M M A, Snyder G J and Dunand D C 2023 Ink casting and 3D-extrusion printing of the thermoelectric half-Heusler alloy $Nb_{1-x}CoSb$ *Addit. Manuf. Lett.* **4** 100113
[297] Xing Y, Liu R, Liao J, Wang C, Zhang Q, Song Q, Xia X, Zhu T, Bai S and Chen L 2020 A device-to-material strategy guiding the "double-high" thermoelectric module *Joule* **4** 2475–83
[298] Uher C 2001 Skutterudites: prospective novel thermoelectrics *Semicond. Semimet.* **69** 139–253
[299] Rull-Bravo M, Moure A, Fernández J F and Martín-González M 2015 Skutterudites as thermoelectric material: revisited *RSC Adv.* **5** 41653–67
[300] Liu Z Y, Zhu Y L, Tong X, Niu S and Zhao W Y 2020 A review of $CoSb_3$-based skutterudite thermoelectric materials *J. Adv. Ceram.* **9** 647–73
[301] Jiang Y, Na L and Ma H 2022 HPHT synthesis and enhanced thermoelectric transport properties of double-doped $Co_4Sb_{11}Te_xSn_{1-x}$ skutterudites *J. Alloys Compd.* **894** 162426–33
[302] Sun H, Jia X, Lv P, Deng L, Guo X, Zhang Y, Sun B, Liu B and Ma H 2015 Improved thermoelectric performance of Te-doped and CNT dispersed $CoSb_3$ skutterudite bulk materials via HTHP *RSC Adv.* **5** 1–6
[303] Khan A U *et al* 2017 Nano-micro-porous skutterudites with 100% enhancement in ZT for high performance thermoelectricity *Nano Energy* **31** 152–9
[304] Rogl G, Renk O, Ghosh S, Mallik R C, Grytsiv A, Bursik J, Schafler E, Tuomisto F, Bauer E and Rogl P F 2021 Properties of HPT-processed large bulks of p-type skutterudite $DD_{0.7}Fe_3CoSb_{12}$ with high ZT $>$ 1.3 *ACS Appl. Energy Mater.* **4** 4831–44
[305] Rogl G, Ghosh S, Renk O, Yubuta K, Grytsiv A, Schafler E, Zehetbauer M, Mallik R C, Bauer E and Rogl P F 2021 Influence of shear strain on HPT-processed n-type skutterudites yielding ZT$\sim$2.1 *J. Alloys Compd.* **855** 157409–19
[306] Rogl G and Rogl P 2022 Filled Sb-based skutterudites from 1996–2022 *Crystals* **12** 1843–73
[307] Koza M M, Johnson M R, Viennois R, Mutka H, Girard L and Ravot D 2008 Breakdown of phonon glass paradigm in La- and Ce-filled Fe_4Sb_{12} skutterudites *Nat. Mater.* **7** 806–10
[308] Feldman J L, Singh D J, Kendziora C, Mandrus D and Sales B C 2003 Lattice dynamics of filled skutterudites: $La(Fe,Co)_4Sb_{12}$ *Phys. Rev. B* **68** 094301–12
[309] Shi X, Zhang W, Chen L D, Yang J and Uher C 2007 Theoretical study of the filling fraction limits for impurities in $CoSb_3$ *Phys. Rev. B* **75** 1–9 see also: Acta Mater., vol. 56, pp. 1733–1740, 2008
[310] Hicks L D and Dresselhaus M S 1993 Effect of quantum well structures on the thermoelectric figure of merit *Phys. Rev. B* **47** 12727–32
[311] Li W, Stokes D, Poudel B, Saparamadu U, Nozariasbmarz A, Kang H B and Priya S 2019 High-efficiency skutterudite modules at a low temperature gradient *Energies* **12** 1–11
[312] Rogl G, Grytsiv A, Bauer E and Rogl P F 2018 Thermoelectric Sb-based skutterudites for medium temperature *Advanced Thermoelectrics: Materials, Contacts, Devices and Systems* ed Z Ren, Y Lan and Q Zhang (CRC Boca Raton) pp 193–230
[313] Rogl G R P and Rogl P 2011 Mechanical properties of skutterudites *Sci. Adv. Mater.* **3** 517–38
[314] Liu Z, Yang T, Wang Y, Xia A and Ma L 2022 Energy band and charge-carrier engineering in skutterudite thermoelectric materials *Chin. Phys. B* **31** 1–11
[315] Posligua V, Landivar K, Remesal E R, Rogl G, Rogl P, Sanz J F, Prado-Gonjal J, Marquez A M and Plata J J 2026 Deep learning framework for accurate prediction of the thermoelectric figure of merit in skutterudites J Mater Sci and Technology, in press
[316] Zhu X, Zuo Z, Wang W, Liu R and Jia B 2025 Design and single/multi-objective optimization of n-type Skutterudite/p-type half-Heusler-based thermoelectric modules based on an improved thermal resistance model *Renew. Energy* **250** 1–17

[317] Burkov A T 2018 Silicide thermoelectrics: materials for energy harvesting *Phys. Status Solidi a* **215** 1800105
[318] Khan A U, Vlachos N V, Hatzikraniotis E, Polymeris G S, Lioutas C B, Stefanaki E C, Paraskevopoulos K M, Giapintzakis I and Kyratsi T 2014 Thermoelectric properties of highly efficient Bi-doped $Mg_2Si_{1-x-y}Sn_xGe_y$ materials *Acta Mater.* **77** 43–53
[319] Goyal G K, Mukherjee S, Mallik R C, Vitta S, Samajdar I and Dasgupta T 2019 High thermoelectric performance in $Mg_2(Si_{0.3}Sn_{0.7})$ by enhanced phonon scattering *ACS Appl. Energy Mater.* **2** 2129–37
[320] Dasgupta T, Stiewe C, de Boor J and Müller E 2014 Influence of power factor enhancement on the thermoelectric figure of merit in $Mg_2Si_{0.4}Sn_{0.6}$ based materials *Phys. Status Solidi a* **211** 1250–4
[321] Macario L R, Cheng X, Ramirez D, Mori T and Kleinke H 2018 Thermoelectric properties of Bi-doped magnesium silicide stannides *ACS Appl. Mater. Interfaces* **10** 40585–91
[322] Liu W, Zhang Q, Yin K, Chi H, Zhou X, Tang X and Uher C 2013 High figure of merit and thermoelectric properties of Bi-doped $Mg_2Si_{0.4}Sn_{0.6}$ solid solutions *J. Solid State Chem.* **203** 333–9
[323] Gao P, Berkun I, Schmidt R D, Luzenski M F, Lu X, Sarac P B, Case E D and Hogan T P 2014 Transport and mechanical properties of high-ZT $Mg_{2.08}Si_{0.4-x}$ $Sn_{0.6}Sb_x$ thermoelectric materials *J. Electron. Mater.* **43** 1790–803
[324] Chauhan N S, Ono I, Hayashi K and Miyazaki Y 2022 Relevance of solidification kinetics for enhanced thermoelectric performance in Al-doped higher manganese silicides *ACS Appl. Mater. Interfaces* **14** 51983–93
[325] Ghodke S, Yamamoto A, Hu H-C, Nishino S, Matsunaga T, Byeon D, Ikuta H and Takeuchi T 2019 Improved thermoelectric properties of re-substituted higher manganese silicides by inducing phonon scattering and an energy-filtering effect at grain boundary interfaces *ACS Appl. Mater. Interfaces* **11** 31169–75
[326] Li Z, Dong J-F, Sun F-H, Hirono S and Li J-F 2017 Significant enhancement of the thermoelectric performance of higher manganese silicide by incorporating MnTe nanophase derived from Te nanowire *Chem. Mater.* **29** 7378–89
[327] Ponnambalam V and Morelli D T 2018 Effect of addition of the elements Cr, V, Mo, Ge, Re and Ru on the thermoelectric properties of higher manganese silicides MnSi ∼1.74 *Mater. Res. Express* **6** 025507
[328] Muthiah S, Singh R C, Pathak B D, Avasthi P K, Kumar R, Kumar A, Srivastava A K and Dhar A 2018 Significant enhancement in thermoelectric performance of nanostructured higher manganese silicides synthesized employing a melt spinning technique *Nanoscale* **10** 1970–7
[329] Liu W-D, Chen Z-G and Zou J 2018 Eco-friendly higher manganese silicide thermoelectric materials: progress and future challenges *Adv. Energy Mater.* **8** 1800056
[330] Kim G, Shin H, Lee J and Lee W 2021 A review on silicide-based materials: thermoelectric and mechanical properties *Met. Mater. Int.* **27** 2205–19
[331] Oulfarsi M, David N, Aranda L, Medjahdi G, Ihou-Mouko H and Dauscher A 2023 Thermal stability of Mg_2 $Si_{0.6}$ $Sn_{0.4}$ under oxidation conditions *ACS Appl. Mater. Interfaces* **15** 22616–25
[332] Mangelis P, Sousanis A, Mesaritis G, Ioannou P S, Søiland A-K, Xu Y and Kyratsi T 2024 High thermoelectric performance of Bi-doped Mg_2 $Si_{0.4}$ $Sn_{0.6}$ and Mg_2 $Si_{0.6}$ $Sn_{0.4}$ based on recyclable Si kerf derived from PV manufacturing *ACS Appl. Electron. Mater.* acsaelm.3c01802
[333] Ioannou P S, Mangelis P, Hadjipanteli S, Mina M, Søiland A K, Giapintzakis J and Kyratsi T 2025 Development of silicide thermoelectric modules based on high purity Si and recycled Si-kerf: a contact resistance investigation *Mater. Today Energy* **49** 101855
[334] Yasseri M, Mitra K, Sankhla A, De Boor J and Müller E 2021 Influence of Mg loss on the phase stability in Mg_2X (X = Si, Sn) and its correlation with coherency strain *Acta Mater.* **208** 116737
[335] De Boor J, Dasgupta T, Saparamadu U, Müller E and Ren Z F 2017 Recent progress in p-type thermoelectric magnesium silicide based solid solutions *Mater. Today Energy* **4** 105–21
[336] Camut J, Ziolkowski P, Ponnusamy P, Stiewe C, Mueller E and De Boor J 2023 Efficiency measurement and modeling of a high-performance Mg_2(Si,Sn)-based thermoelectric generator *Adv. Eng. Mater.* **25** 2200776
[337] Andrews J P 1947 Thermoelectric power of cadmium oxide *Proc. Phys. Soc.* **59** 990–8
[338] Parravano G 1955 Thermoelectric behavior of nickel oxide *J. Chem. Phys.* **23** 5–10
[339] Zirin M H and Trivich D 1963 Thermoelectric effect in single-crystal cuprous oxide at high temperatures *J. Chem. Phys.* **39** 870–5
[340] Cooper J R, Alavi B, Zhou L-W, Beyermann W P and Grüner G 1987 Thermoelectric power of some high-T_c oxides *Phys. Rev. B* **35** 8794–6
[341] Liessa M and Steffes H 2000 The modulation of thermoelectric power by chemisorption, a new detection principle for microchip chemical sensors *J. Electrochem. Soc.* **147** 3151–3
[342] Matsumiya M, Shin W, Izu N and Murayam N 2003 Nano-structured thin-film Pt catalyst for thermoelectric hydrogen gas sensor *Sens. Actuators B* **93** 309–15
[343] Fujishiro H, Kusaka K, Ikebe M, Ogasawara H and Noto K 1994 Possibility of Ag_2O+$YBa_2Cu_30_{7-x}$ ceramics for low temperature thermoelectric refrigeration *Cryogenics* **34** 231–4
[344] Ohtaki M, Ogura D, Eguchi K and Arai H 1994 High-temperature thermoelectric properties of In_2O_3-based mixed oxides and their applicability to thermoelectric-power generation *J. Mater. Chem.* **4** 653–6
[345] Ohtaki M, Koga H, Tokunaga T, Eguchi K and Arai H 1995 Electrical-transport properties and high-temperature thermoelectric performance of $(Ca_{0.9}M_{0.1})MnO_3$ (M=Y, La, Ce, Sm, In, Sn, Sb, Pb, Bi) *J. Solid State Chem.* **120** 105–11
[346] Terasaki I, Sasago Y and Uchinokura K 1997 Large thermoelectric power in $NaCo_2O_4$ single crystals *Phys. Rev. B* **56** R12685–R7
[347] Funahashi R, Matsubara I, Ikuta H, Takeuchi T, Mizutani U and Sodeoka S 2000 An oxide single crystal with high thermoelectric performance in air *Jpn. J. Appl. Phys.* **39** L1127–L9
[348] Masset A C, Michel C, Maignan A, Hervieu M, Toulemonde O, Studer F, Raveau B and Hejtmanek J 2000 Misfit-layered cobaltite with an anisotropic giant magnetoresistance: $Ca_3Co_4O_9$ *Phys. Rev. B* **62** 166–75
[349] Shin W and Murayama N 2000 Thermoelectric properties of (Bi,Pb)–Sr–Co–O oxide *J. Mater. Res.* **15** 382–6
[350] Matsubara I, Funahashi R, Takeuchi T, Sodeoka S, Shimizu T and Ueno K 2001 Fabrication of an all-oxide thermoelectric power generator *Appl. Phys. Lett.* **78** 3627–9
[351] Funahashi R, Matsumura Y, Urata T, Murakami H, Ikenishi H, Sasaki S and Sugiyama S 2021 Relationship between tensile strength and durability of oxide thermoelectric modules *J. Electron. Mater.* **50** 3996–4005
[352] Ohta H, Sugiura K and Koumoto K 2008 Recent progress in oxide thermoelectric materials: p-type $Ca_3Co_4O_9$ and n-type $SrTiO_3$ *Inorg. Chem.* **47** 8429–36
[353] Ohta H *et al* 2007 Giant thermoelectric Seebeck coefficient of a two-dimensional electron gas in $SrTiO_3$ *Nat. Mater.* **6** 129–34
[354] Funahashi S, Nakamura T, Kageyama K and Ieki H 2011 Monolithic oxide–metal composite thermoelectric generators for energy harvesting *J. Appl. Phys.* **109** 124509

[355] Kosuga A, Kurosaki K, Yubuta K, Charoenphakdee A, Yamanaka S and Funahashi R 2009 Thermal conductivity characterization in bulk Zn(Mn,Ga)O_4 with self-assembled nanocheckerboard structures *Jpn. J. Appl. Phys.* **48** 010201
[356] Srivastava D, Norman C, Azough F, Schäfer M C, Guilmeau E, Kepaptsoglou D, Ramasse Q M, Nicotrad G and Freer R 2016 Tuning the thermoelectric properties of A-site deficient $SrTiO_3$ ceramics by vacancies and carrier concentration *Phys. Chem. Chem. Phys.* **18** 26475–86
[357] Srivastava D, Norman C, Azough F, Ekren D, Chen K, Reece M J, Kinloch I A and Freer R 2019 Anisotropy and enhancement of thermoelectric performance of $Sr_{0.8}La_{0.067}Ti_{0.8}Nb_{0.2}O_{3-d}$ ceramics by graphene additions *J. Mater. Chem. A* **7** 24602–13
[358] Lin Y, Dylla M T, Kuo J J, Male J P, Kinloch I A, Freer R and Snyder G J 2020 Graphene/strontium titanate: approaching single crystal-like charge transport in polycrystalline oxide perovskite nanocomposites through grain boundary engineering *Adv. Funct. Mater.* **30** 1910079
[359] Ghosh S, Harish S, Ohtaki M and Saha B B 2020 Enhanced figure of merit of cement composites with graphene and ZnO nanoinclusions for efficient energy harvesting in buildings *Energy* **198** 117396
[360] Choi M *et al* 2024 High figure-of-merit for ZnO nanostructures by interfacing lowly-oxidized graphene quantum dots *Nat. Commun.* **15** 1996
[361] Biswas S, Singh S, Singh S, Chattopadhyay S, De Silva K K H, Yoshimura M, Mitra J and Kamble V B 2021 Selective enhancement in phonon scattering leads to a high thermoelectric figure-of-merit in graphene oxide-encapsulated ZnO nanocomposites *ACS Appl. Mater. Interfaces* **13** 23771–86
[362] Ekren D, Cao J, Azough F, Kepaptsoglou D, Ramasse Q, Kinloch I A and Freer R 2022 Controlling the thermoelectric behavior of La-doped $SrTiO_3$ through processing and addition of graphene oxide *ACS Appl. Mater. Interfaces* **14** 53711–23
[363] Collins C M *et al* 2021 Discovery of a low thermal conductivity oxide guided by probe structure prediction and machine learning *Angew. Chem., Int. Ed.* **60** 16457–65
[364] Wang Q, Zeng Z and Chen Y 2021 Revisiting phonon transport in perovskite $SrTiO_3$: anharmonic phonon renormalization and four-phonon scattering *Phys. Rev. B* **104** 235205
[365] He Z, Lei C, Shan D, Zhang Z, Luo H, Xie S and Liu Y 2025 Discovery of perovskite oxides with different thermal conductivities on demand by interpretable machine learning *Int. J. Heat Mass Transfer* **165** 109014