



Thermoelectric generators: Linking material properties and systems engineering for waste heat recovery applications



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ABSTRACT

Waste-heat recovery with thermoelectric power generators can improve energy efficiency and provide distributed electricity generation. New thermoelectric materials and material performance improvements motivate development of thermoelectric generators for numerous applications with excess exhaust and process heat. However, thermoelectric generator product development requires solving coupled challenges in materials development and systems engineering. This review discusses these challenges and indicates ways system-level performance relies on more factors than traditional thermoelectric material performance metrics alone. Relevant thermo-mechanical and chemical material properties, system components such as thermal interface materials and heat exchangers, and system form factors are examined. Manufacturing processes and total system cost components are evaluated to provide product development and commercial feasibility contexts.

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1. Introduction

Thermoelectric devices offer a unique power generation solution because they convert thermal energy into electricity without requiring moving components. Thermoelectric generators have been proposed for waste-heat recovery applications, and advancements in thermoelectric materials development have highlighted the technology's energy efficiency and commercial potential. To realize this potential and improve thermoelectric power generation feasibility, the gap between thermoelectric materials development and generator systems engineering must be closed. The thermoelectric generator materials characteristics are particularly important because it is a solid-state energy conversion device. Electron and thermal transport through multiple materials in the device is paramount and affects overall system performance. This review provides a systems-level perspective of thermoelectric generator development. It underscores the relationships between thermoelectric materials development goals and generator system requirements. Considerations for system components beyond the thermoelectric materials are discussed along with manufacturing and cost issues.

A thermoelectric (TE) module consists of units, or legs, of n- and p-type semiconducting materials connected electrically in series and thermally in parallel. The figure of merit ZT describes material performance. It depends on the thermoelectric material properties Seebeck coefficient S , electrical conductivity σ , and thermal conductivity k , and

$ZT = S^2 \sigma T / k$ where T is the temperature of the material. A TE couple is one pair of n- and p-type legs, and a module generally has several couples. These couples and their electrical interconnects are enclosed by an electrical insulator, typically a ceramic. A typical off-the-shelf module is shown in Fig. 1. As depicted in Fig. 2, a thermoelectric generator (TEG) is usually a more extensive system than the module. In a TEG, the modules are connected thermally in parallel with heat exchangers to facilitate the transfer of heat from the heat source to the module's hot side and away from its cold side. The modules are connected to an electrical load to close the circuit and enable electricity extraction.

Thermoelectric generators have been used to power space vehicles for several decades [1,2], so the research and development contributions and expertise from the space industry are invaluable in the development of terrestrial waste-heat recovery TEGs. Named radioisotope thermoelectric generators (RTGs), the heat source in spacecraft TEGs comes from the nuclear decay of radioactive isotopes. RTGs were selected to power space vehicles since they are highly reliable, robust, and compact. They are solid-state devices without the rotating machinery typical of other heat engines, so RTGs do not produce noise or vibration. These qualities made RTGs ideal for powering autonomous space vehicles with long life missions. RTGs for space power systems have unique characteristics which differentiate this application from the waste-heat recovery applications discussed here. The heat source temperature is typically higher ($\sim 1000^\circ\text{C}$) resulting in the use of thermoelectric materials such as silicon germanium which are suitable for high temperature power generation. The operating environments are outer space and other planetary surfaces. Moreover, the cost-performance considerations and constraints for space vehicle development are significantly different than for waste-heat recovery applications since significant

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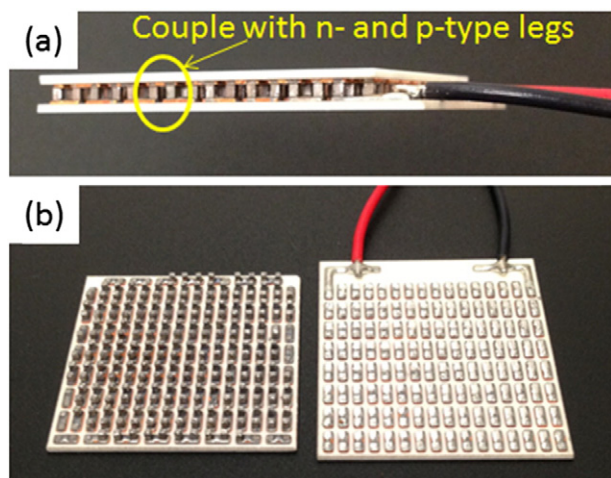


Fig. 1. Pictures of an off-the-shelf thermoelectric module. (a) Side view showing multiple thermoelectric leg couples. (b) Interior of module with one substrate removed to reveal the electrical interconnects and solder joints. The module pictured is approximately 1 in. by 1 in. and supplied by Marlow Industries, Inc.

value is placed on the RTG primary power generation capability and unique suitability for the requirements of space applications.

From electronics to industrial furnaces, numerous waste-heat sources at low- (<250 °C), mid- (~250–650 °C), and high- (>650 °C) temperatures exist. TEGs have mostly been proposed for waste-heat recovery in mid- and high-temperature applications such as automotive, engine, and industrial applications with untapped exhaust and process heat because of the potential for appreciable power generation [3–5]. The mid- to high-temperature exhaust and process heat types of applications are the focus of the discussion here, and sample heat source temperatures and applications are shown in Table 1. Vehicle applications include passenger vehicles and large trucks, and prototypes have already been demonstrated [5,6]. There are a myriad of industrial processes such as steel making and glass melting, and a comprehensive assessment of industrial waste-heat opportunities in the United States was conducted in 2008 [3]. The study notably indicated that thermoelectric generation had not been demonstrated in U.S. industrial applications. In Asia, particularly Japan, there have been multiple demonstrations of TEG waste-heat recovery [7,8] with a recently deployed TEG generating 250 W from a steel casting line [9].

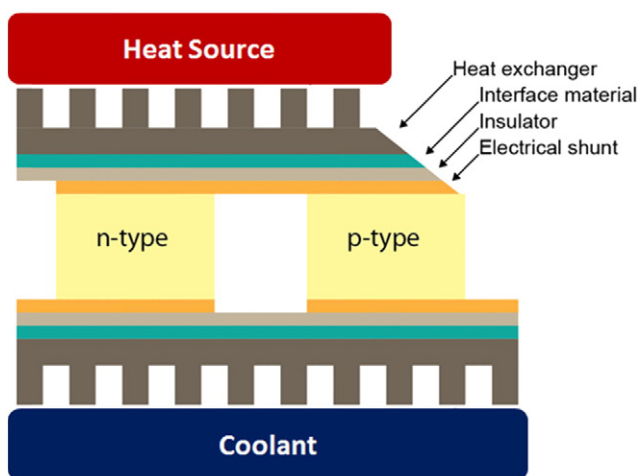


Fig. 2. Schematic of one thermoelectric couple in a thermoelectric generator system. A module consists of many couples between electrical insulators. The modules are connected to heat exchangers to interface with thermal reservoirs in the waste-heat recovery application.

Table 1

Approximate waste-heat source temperatures are provided for sample mid- and high-temperature TEG applications. Temperatures will vary based on TEG position in the system, and the temperature at the hot side of the thermoelectric will be lower than the heat source temperature.

Application	Heat source temperature	Reference
Automotive exhaust	400–700 °C	[10]
Diesel generator exhaust	~500 °C	[11]
Primary aluminum Hall–Heroult cells	700–900 °C	[3,4]
Glass melting regenerative furnace	~450 °C	[3,4]

As in space applications, key advantages of TEGs for waste-heat recovery are their simplicity, minimal maintenance requirements, and reliability since there is no rotating machinery in the system. Disadvantages include low efficiencies, high costs, and systems integration barriers. The assessment for TEG waste-heat recovery potential often focuses on the heat source temperature where high-temperature processes are favorable. Government-initiated studies and funding for TEGs reflect the interest in these promising, high-temperature industrial process applications. Additionally, a crucial consideration for TEG product development and commercial viability is identifying the appropriate fit between the product and potential markets [12]. The commercial drivers for product–market fit can lead to preference for mid-temperature applications over high-temperature applications. This product–market fit is closely related to practical materials development and systems engineering needs which do not necessarily correlate to obtaining higher material *ZT* values.

The following discussion provides key points about the link between TEG material properties and system performance. The target readers for this overview are those who are outside the thermoelectrics research and development community and/or want to understand overarching key issues with thermoelectric materials and systems development. Readers who are interested in the extensive literature on thermoelectric materials [13–16], systems design and development [11,17–20], and specific applications [21–23] are referred to more specialized books [16,24,25] and literature. In this review, an overview of thermoelectric materials considerations is followed by a description of system components and design factors and a comparison of material versus system performance metrics. Lastly, an overview of systems manufacturing and cost considerations is provided with particular attention paid to materials concerns.

2. Materials overview

Thermoelectric materials are typically classified by material structure and composition. Some of the main classifications are chalcogenide, clathrate, skutterudite, half-Heusler, silicide, and oxide. Excellent reviews of thermoelectric materials have provided descriptions of both the material classifications and the relationship between material structure and thermoelectric properties [13,14,26], so comprehensive descriptions are not provided here. Chalcogenide materials have a long history of demonstrated thermoelectric use with bismuth telluride and lead telluride being the most prominent. Commercial, off-the-shelf thermoelectric modules for low temperature use are primarily made with bismuth telluride and its solid solutions with antimony or selenium. Lead telluride has better thermoelectric properties at higher temperatures (~500–600 °C). Materials engineering of clathrates and skutterudites has involved introduction of void-filling or guest atoms into a base structure. These additions can optimize electron concentration or act as phonon scattering sites. Such materials engineering to achieve a glass-like thermal conductivity combined with good charge carrier mobility has been termed the “phonon glass electron crystal” approach. With one vacant sublattice in the crystal structure, the properties of half-Heusler materials have also been improved through void-filling as well as doping of the filled sublattices. Silicides have generated interest due to the low cost of their abundant materials (*i.e.*

silicon), and oxides are expected to have high temperature stability in air. Notable advancements have been made in both the types of materials synthesized and the reported properties. For low temperature thermoelectrics, nanostructured bismuth telluride [27], polymers and polymer–inorganic matrices [28–31], and MgAgSb-based materials [32] have broadened the range of options. The reported material properties for high temperature thermoelectrics have demonstrated noteworthy gains resulting in ZT values above 1. Hierarchical nano- to meso-scale structuring [33] and new materials such as tetrahedrites [34] have contributed to the gains.

While the materials development progress is promising, the increasing breadth of materials and the reports of ever-increasing ZT mask the underlying challenges of employing the materials in devices. Material properties are highly temperature-dependent, posing multiple challenges for application-specific materials selection. Few applications have heat sources at one single temperature, so matching an application temperature with the point of peak ZT in a thermoelectric material is unrealistic. Instead, most applications have some degree of thermal fluctuation or cycling. If the heat source is a fluid stream, the temperature of the fluid varies along the flow direction. The temperature decreases along the length of each thermoelectric leg, as well. Ways of combining different materials in one device through cascading, segmentation, and varying the material in the fluid flow direction have been developed [35–37]. Additionally, peak ZT values for high-temperature materials often occur at temperatures above 600 °C. However, the temperature at the hot side of the thermoelectric material itself is lower than the heat source temperature because there are system component thermal resistances between the heat source and the thermoelectric material. There are applications with heat sources above 600 °C such as industrial process furnaces and exhaust streams, and there are many opportunities for thermoelectric power generation in applications with heat sources in the 250–500 °C range [12]. In both cases, average ZT over the application temperature range is highly relevant to material selection and design. Fig. 3 presents ZT values for a high peak ZT material as well as materials which have generated commercial and product development interest and results [38–40].

Material stability over the full operating temperature range is relevant to device engineering. Thermoelectric materials must be stable within the filler medium. If the thermoelectric material is exposed to air, the material must not oxidize within the operating temperature range. Devices can be packaged in an inert gas to mediate this problem. In low temperature devices, a solid filler is sometimes used, but solid

filler media for high temperature applications – if they currently exist – must also be sufficiently stable and inactive with the TE material. For example, some materials undergo sublimation within the operating temperature range of high temperature applications. Even if the material properties are sufficient for most of the range or the nominal operating temperature, the risk associated with material sublimation during any temperature spikes is severe device performance degradation or even device failure [44]. Hence, reports of ever higher peak thermoelectric material ZT values deceptively allude to more power generation potential which may not be valid given realistic application parameters.

The translation of thermoelectric materials into devices also requires consideration of both n- and p-type thermoelectric materials. Although a thermoelectric unit, or couple is typically composed of n- and p-type legs, both are not strictly necessary. For instance, if ease of synthesis, material stability, and reliability are challenges for the n- or p-type variation of a new material, faster prototype/product development, demonstration, or commercialization could be achieved with one type (n or p) coupled with a metal shunt. Using both n- and p-types of materials significantly increases the thermopower and thus the open circuit voltage of the TEG since the total thermopower for a p–n leg couple, S_{pn} , equals the sum of the magnitude of each leg's thermopower. Again, advances in material ZT are thus deceptive. For instance, an increase in the ZT of an n-type (p-type) chalcogenide might be achieved, but a similar increase in the properties of a corresponding p-type (n-type) chalcogenide is not. Hence, the overall gain in ZT for the device is not proportionally as high as the gain in ZT for the individual material.

Although the topic receives far less attention than thermoelectric properties, mechanical properties of thermoelectric materials are critical for both device manufacturing and operation. Typical thermoelectric materials are brittle and behave mechanically like ceramics. Table 2 provides a perspective of measured parameters which reflect the brittle quality of these materials. However, it is challenging to characterize the brittleness as measured by hardness, fracture strength, and fracture toughness. Characterization results vary based on sample geometry and testing technique even when the material is held constant [45,46], and changes in composition during alloying of the same set of elements can lead to variations in microstructure and mechanical properties [47].

The coefficient of thermal expansion (CTE) is an important parameter due to the high operation temperatures and thermal cycling in potential TEG applications [44,53]. Because each thermoelectric leg is held rigidly in place by a solder joint to the electrical interconnect and substrate, significant stresses can build up in the material, particularly at the corners and edges. The CTE mismatch between the TE material, interface layers, interconnects, and substrates exacerbates the problem of stress concentration. Proposed solutions involve introduction of compliant interface materials. Examples include liquid metal layers [54] and novel structures such as carbon nanotube arrays [55].

3. System design and components

The power generation potential of a TEG depends largely on the system design, not only the TE material. In particular, the thermal and electrical impedance of the TE material relative to the impedances of the rest of the system components influence system output and performance [56–58]. For instance, the arrangement of the TE material within the TE module significantly affects thermal and electrical transport in the overall device. Although the typical uncouple formation is like the “pi” shaped structure, alternative structures like couples which optimize thermal and electrical transport have been proposed such as the “y” shaped connectors discussed in [54]. When considering material properties alone, the tradeoff between thermal conductivity and electrical resistivity is often discussed. However, at a device-level, the conflicting parameters become thermal conductance and electrical resistance which include the physical geometry of the material in addition to the intrinsic material properties. There is a tradeoff between the total

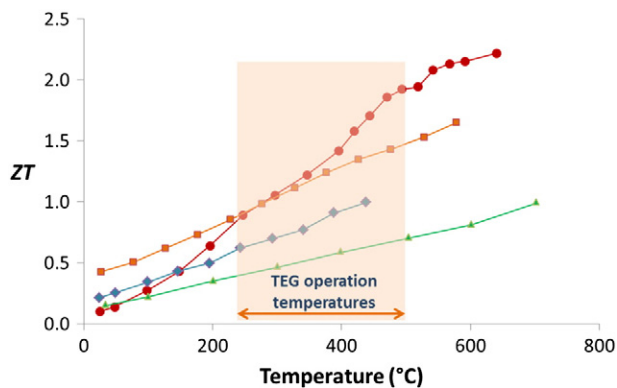


Fig. 3. The temperature range for typical waste-heat sources and TEG hot side operation values is overlaid on ZT versus temperature data for a top-performing thermoelectric material and ones which have generated commercial interest. High peak ZT values can mask the need for large average ZT values over the application temperature range. The data shown here for high ZT , p-type PbTe endotaxially nanostructured with SrTe (circles) are extracted from [33] and show a peak ZT of 2.2 at 642 °C. Skutterudite (squares, data depicted for $\text{Ba}_{0.08}\text{La}_{0.05}\text{Yb}_{0.04}\text{Co}_4\text{Sb}_{12}$) [41], tetrahedrite (diamonds, data depicted is for 0.5 natural mineral $\text{Cu}_{9.7}\text{Zn}_{1.9}\text{Fe}_{0.4}\text{As}_4\text{S}_{13}$ and 0.5 synthetic $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) [42], and half-Heusler (triangles, data depicted for $\text{Nb}_{0.6}\text{Ti}_{0.4}\text{FeSb}_{0.95}\text{Sn}_{0.05}$) [43] materials have generated commercial interests based in part on their average ZT values.

Table 2

Mechanical properties of selected thermoelectric materials. Measurement error and standard deviations are available in the original references.

Material type	Material	Young's modulus E (GPa)	Hardness H (GPa)	Fracture toughness K_{Ic} (MPa·m ^{1/2})	Fracture toughness K_{Ic} (MPa·m ^{1/2})	Fracture strength σ_f (MPa)	Reference
Skutterudite	CeFe ₃ RuSb ₃	133	–	1.1–2.8	–	37	[45]
	CoSb ₃	136	–	1.7	–	86	[45]
PbTe-based	Ag _{0.43} Pb ₁₈ Sb _{1.2} Te ₂₀	54.2	0.98	–	0.34	28.1	[48]
	Pb _{0.95} Sn _{0.05} Te–PbS 8%	54	1.28	–	0.31	–	[49]
Oxide	Ca ₃ Co ₄ O ₉	86	2.6	2.8	–	–	[50]
	Ca _{0.95} Sm _{0.05} MnO ₃	205.2	11.05	4.99	–	–	[51]
Antimonide	Zn ₄ Sb ₃	75	1.65	0.68	–	65	[52]

thermal conductance and the electrical resistance of the TE material at the module level, and two key features of module geometry, the fill factor and TE leg size, play a large part in this tradeoff. The fill factor is the ratio of the amount of module surface area occupied by TE material to the overall surface area. The total surface area is not necessarily covered by TE material (*i.e.* the fill factor is not 1) due to performance and/or cost optimization [58] and manufacturing constraints like minimum inter-leg spacing during assembly. Likewise, the tradeoff between thermal and electrical parameters necessitates an optimization of the TE leg height.

The materials needs for thermoelectric devices extend beyond the TE material alone. There are several other device components, some of which interact directly with the TE material, affecting overall device performance. For instance, there is a metallurgical bond between the TE leg and the metal interconnects. There are engineering considerations which influence the selection of the solder or braze material used to form this bond. The solder/braze material must not diffuse into the TE material; a diffusion barrier placed on the TE material surface is typically required [59–62]. The electrical contact resistance between the solder/braze material and TE material must be low. The reflow temperature of the solder/braze should be higher than the device operating temperature to prevent TE leg movement or changes in electrical resistance during operation. Additionally, the thermal contact resistance between the TE leg and the metal interconnect and between the metal interconnect and substrate will affect the temperature drop, and thus voltage, achieved across the thermoelectric leg.

There are challenging materials requirements for the module substrates and geometries. The substrates must be electrically insulating but thermally conducting. Since the substrate must withstand high temperatures, particularly on the hot side of the TE leg, the substrates are typically ceramic materials, and flexible substrates for high temperature TE devices have not been demonstrated. The TE legs are attached to the substrate, so the substrate must have the mechanical strength to support the legs and interconnects. Module design must incorporate the ability to shape ceramic to the desired design structure, so most

modules have a square or rectangular shape. If the application requires a different form factor, rectangular units are often positioned to accommodate this form factor. There have been limited demonstrations of cylindrical modules as shown in Fig. 4 [63,64].

The TE module is attached to the exterior system with thermal interface materials (TIMs) to improve the transfer of heat to and from the hot and cold sides of the TE device. The operating temperature, particularly on the TE system hot side, creates a critical constraint on the TIM used as these temperature can be above 200 °C. TIMs come in various forms including thermal greases or pastes, gap filler pads, and phase change materials [65–67]. However, the typical maximum operating temperature of most greases or pastes is approximately 150 °C. At high temperatures, greases and pastes dry out leaving air gaps which greatly increase the thermal resistance at the interface. Gap filler pads and phase change materials are more expensive but more reliable for hot side interfaces. Carbon-based TIMs are able to operate at higher temperatures with typical maximum operating temperatures near 300 °C, but the thermal conductivity is often anisotropic with the through-plane value being lower. Novel interface materials based on carbon nanotube arrays and composites have been proposed and experimentally demonstrated [55,68–70], and they have the potential to provide an appropriate TIM solution for mid- to high-temperature TEGs.

Thermoelectric systems for most applications require heat exchangers on both the hot and cold sides of the device. The heat exchangers enable sufficient heat transfer from the heat source to the TE module hot side as well as heat rejection or cooling on the cold side. Therefore, the effectiveness of the heat exchangers directly impacts the temperature drop (and thus voltage) across the TE material. The overall heat transfer capability of the heat exchanger, often denoted by an overall heat transfer coefficient U , depends on the exchanger design and material as well as the heat exchange fluid. The value of U is much higher when the fluid is a liquid, but use of a liquid adds complexity to the system as a closed-loop system must be implemented. In most waste-heat recovery applications, the heat source is a gas stream such as flue gas from a chimney or furnace, so a liquid working fluid on the hot

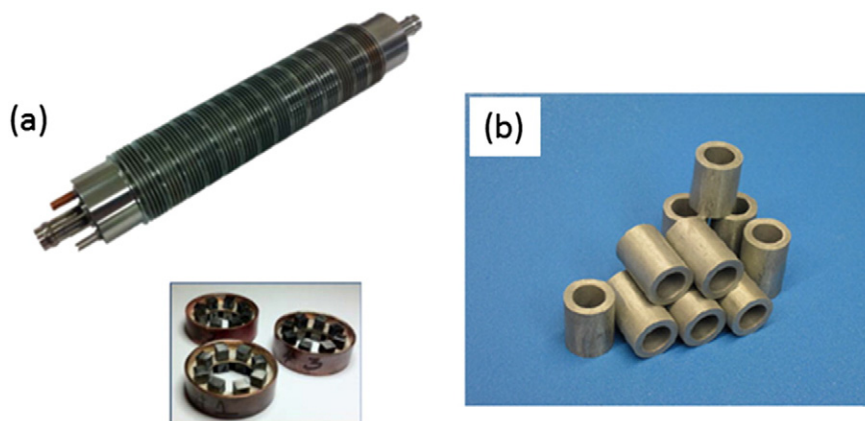


Fig. 4. Cylindrical TEG system produced by Gentherm (a) (figure reproduced from [63]) and cylindrical ingots of doped lead telluride (b) (figure reproduced from [64]).

side is unrealistic. The heat exchangers must also be integrated into the system with the TE module which adds system complexities such as increased weight and size and additional thermal interfaces.

As indicated earlier, the optimization of TEG power output and efficiency depends on TE material properties and dimensions as well as system-level electrical and thermal resistances. Hence, the selection of electrical and thermal contact/interface materials, substrates, and heat exchangers directly impact TEG performance, and the intricacies of this optimization have been explored through analytical and system modeling. The impact of asymmetric system-level thermal resistances on either side of the TE material has been investigated for idealized systems with constant temperature heat source, fill factor of 1, matched or averaged n- and p-type material properties, temperature-independent TE material performance, and negligible electrical contact and parasitic thermal resistance approximations [57,71]. The optimum ratio of electrical load to TE internal resistance was shown to take the form $\sqrt{1 + ZT}$. The optimum ratio between the hot and cold side system-level thermal resistances took on a value of 1 for maximum power output [57]. A recent study demonstrated the impact of a constant heat flux versus constant temperature boundary condition, and it included electrical contact resistances to the TE material [72]. A detailed TEG system model indicated the optimum hot to cold side thermal resistance ratio must be larger than 10–30 to achieve maximum TEG power output [73]. This model was quite extensive in that it incorporated TE material property temperature dependence, unmatched (real) n- and p-type material properties, electrical and thermal contact resistances, parasitic heat loss components, hot and cold side heat exchanger models, and TE device optimization models. Thus, TEG output and performance is highly dependent on the link between actual material and system-level parameters.

4. Material vs. system metrics

Typical metrics for TEGs are ZT , efficiency, and power output. While they are mostly reported in terms of intrinsic material properties, discussions about system-level performance point out alternative formulations which account for the contribution of other device and system components [16,58,74,75]. For instance, while ZT is often reported in terms of TE material properties S , σ , and k , a more relevant formulation for a module-level ZT parameter is $S_{pn}^2 T / (KR)$. The extrinsic parameters R and K indicate electrical resistance and thermal conductance of the TE material in a couple; these are dependent on the dimensions of the legs.

Thermoelectric efficiency is often reported on a materials basis; it is the electrical power generated divided by the thermal energy transferred into the TE material. However, the device- or system-level efficiency is actually lower since not all of the heat available to the system is transferred to the TE material. The effectiveness of heat exchange between the heat source and the TE device, primarily through the heat exchangers, determines the amount of heat transferred to the TE material. Fig. 5 shows the difference between thermoelectric material efficiency and TEG system-level efficiency for simulated TE waste-heat recovery systems in three combustion applications [4,76,77]. The TEG system efficiency can be considerably lower than the TE material efficiency which is often reported with material characterization results. Only the system parameters were changed in the simulation, and the selected thermoelectric material was held constant [76]. The difference between the material and system efficiencies can be reduced if the thermoelectric material selection is optimized for the application temperature.

Frequently, the TEG efficiency is less of a concern than the total power output since the power generated by the TEG is the valuable component to the end user. Sufficient understanding of the value of the power output depends on system-level parameters. There are system components which require power input, so the power generated by the TE device alone is less relevant than the net power, power generated less power required for system components, of the entire system.

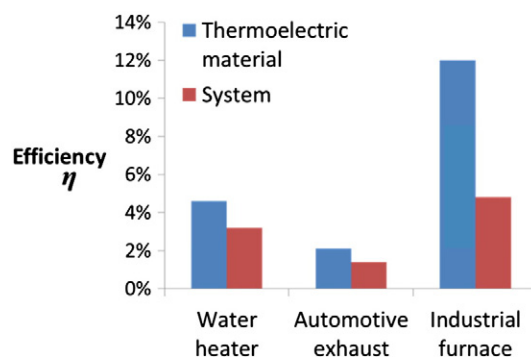


Fig. 5. Thermoelectric material efficiency compared to generator system efficiency simulated for three potential applications [76]. The system efficiency is 32%, 33%, and 59% lower than material conversion efficiency for the water heater, automotive exhaust, and industrial furnace applications, respectively. The variation can be reduced by selecting the thermoelectric materials based on each application's operating temperature range.

For instance, power is required to blow or pump a cooling fluid through the cold side heat exchanger. Although a higher mass flow rate of working fluid in the heat exchanger results in the benefit of more effective heat exchange, increased pumping power is required to achieve this benefit. Additionally, power electronics may be used in a TEG system or product. For example, these power electronics can be used for power conversion (e.g. converting DC TEG output to AC input for an electrical grid), and/or they can optimize the electrical load (e.g. matching a variable circuit load resistance to the fixed power source electrical resistance to maximize thermoelectric power generated). These power electronics can also have a power input requirement for operation. The net power delivered by the TEG, and thus the power generated for the end user, must account for these parasitic power requirements in the system. The end user may have requirements for the minimum net power which must be delivered for the investment in TEG power generation to be worthwhile. This is an important consideration to determine the feasibility of TEG power generation in various applications.

The net power generated must also be understood relative to system sizing features. In most applications, there is limited space and capacity available in which to accommodate the TEG. The total surface area and weight of the TEG system influence the ability to integrate it into existing systems and architectures, so the power density (power generated normalized by surface area required or available) and specific power (power generated normalized by TEG system mass) are key metrics. For example, industrial furnaces have a finite surface area in which a TEG can be incorporated. Automotive exhaust systems have finite space to accommodate a TEG, and the additional weight of the TEG on the vehicle entails a consequential fuel use requirement [78,79].

5. Manufacturing

The manufacturing process for thermoelectric devices varies based on the type of thermoelectric material employed. The overview provided here applies to bulk materials and the most traditional manufacturing process. It is not comprehensive for all types of TE materials and devices but is provided as a reference to enhance understanding about engineering challenges commonly experienced with materials. A schematic of a TE device manufacturing process is shown in Fig. 6.

Process yield is a significant consideration for the manufacture of TE devices. As opposed to materials development and characterization where the primary yield concern corresponds to material synthesis and the number of samples which can be characterized, there are many more steps in the device manufacturing process. Thermoelectric material synthesis is commonly accomplished through ball milling powders of the constituent elements. While this can be a lengthy process, it is fairly repeatable with high yield once a processing recipe is

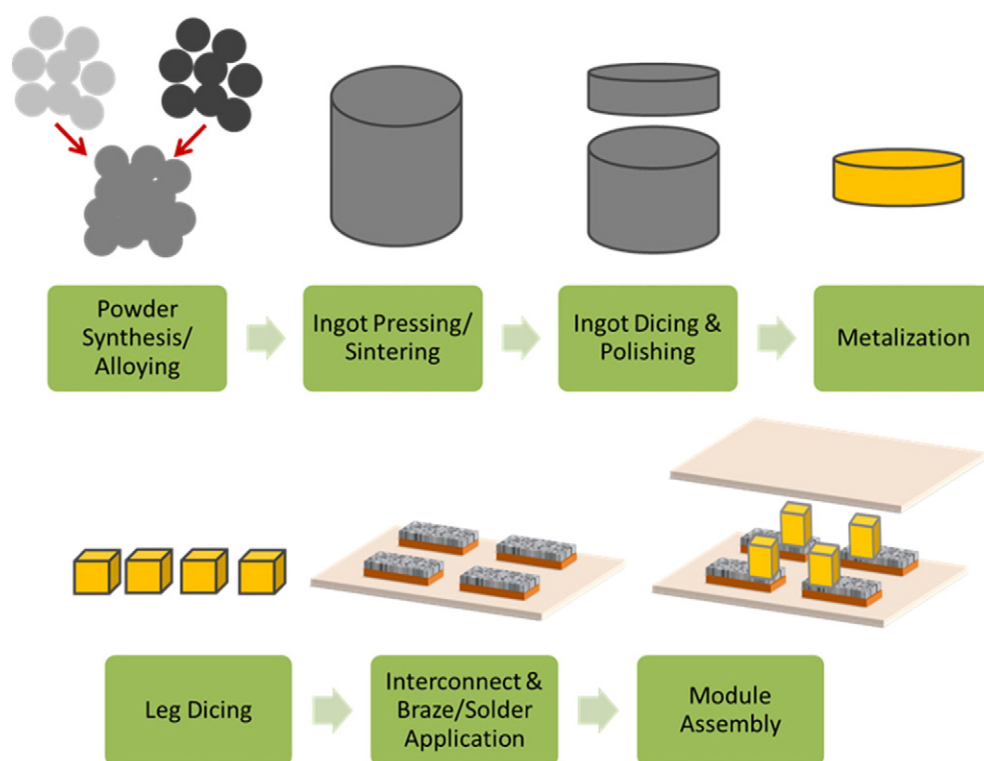


Fig. 6. Schematic showing typical steps for manufacturing of thermoelectric module.

established. However, establishing the process to repeatedly achieve a specific composition can be challenging. Complete mixing is required, and sufficient energy must be imparted to the powder particles. Thermoelectric materials can also be made through melting processes. Phase diagrams [80] of TE materials demonstrate the narrow process windows in which each phase is achieved, and the thermoelectric material properties depend on the phase. For instance, AgSbTe_2 is in PbTe-based materials such as TAGS and LAST thermoelectric materials in which microstructures reportedly improve thermoelectric performance [33,81]. The phase diagram for AgSbTe_2 (Fig. 7) demonstrates the complex variations in phase, and thus microstructures, which may arise due to process parameters [82]. Hence, process fluctuations can result in variations of phase, microstructure formation, repeatability of the synthesis process, and resulting material properties.

Once the TE material is synthesized in powder or particle form, it is consolidated into ingots, typically through hot pressing or spark plasma sintering. As discussed in the materials overview section, sublimation and stability/reactivity in the process gas environment must be considered. While a given TE material might be stable at the application's operating temperature, the consolidation process (or other manufacturing processes) may occur at a higher temperature in order to densify the material.

The ingots are then diced to form the thermoelectric legs, and the material brittleness is a primary concern in this process step. Any chipping of a thermoelectric leg changes the leg surface area and influences both the leg's thermal and electrical resistance. This in turn affects system performance, particularly when the geometry of each leg is not the same. Chipped legs would not be used in a device, reducing the manufacturing process yield. Moreover, dicing and subsequent chipping can lead to crack initiation. These cracks can propagate in subsequent process steps, or worse yet, during TE device operation. Even microcracks can affect thermal and electrical transport in the TE material. The dicing step also constrains the achievable leg dimensions since the post-dicing leg dimensions depend on the dicing equipment capabilities (e.g. saw blade width, dicing depth).

The advent of thin film thermoelectrics has introduced manufacturing processes which are commonly associated with the semiconductor industry. Structures such as superlattices and nanowires have been proposed and are made with deposition, growth, and/or etching micro/nanofabrication processes including molecular beam epitaxy, chemical vapor deposition, vapor–liquid–solid growth, and electroless etching [83]. Additionally, recent demonstrations of thermoelectric materials

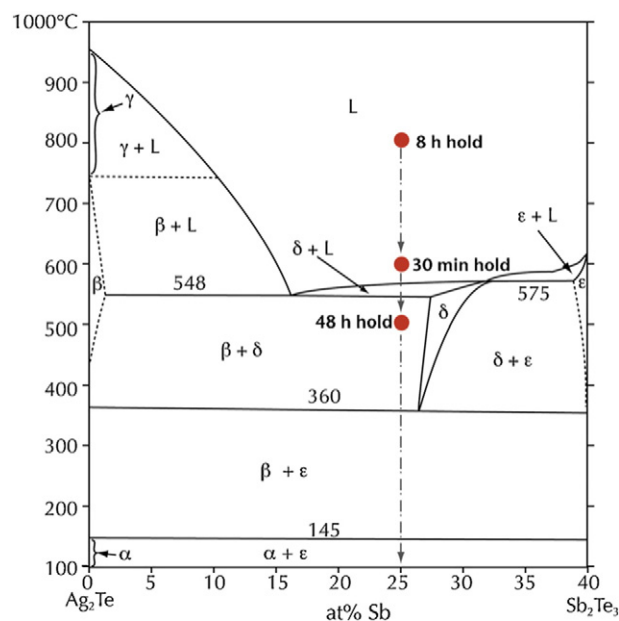


Fig. 7. Phase diagram of AgSbTe_2 , a common component in microstructured PbTe-based thermoelectric materials. The complexity and uncertainties about the bounds of the phase diagram demonstrates how small process fluctuations can affect thermoelectric material formation. The figure is reproduced from [82].

formed through solution processing techniques have been shown for both inorganic and organic materials. Since these approaches to making thin film thermoelectrics are quite varied, a generalizable, standard manufacturing process flow is not yet available.

Material characterization during manufacturing poses a unique challenge. Both standard and custom-built equipment exist to characterize thermoelectric properties of TE materials [84–87]. However, these are designed to accommodate individual samples of TE material (e.g. an ingot or one TE leg), and specialized contacts must be made to the sample. Hence, the techniques are destructive in that the characterization sample cannot subsequently be used for a TE device. The characterization process is also time-consuming, so it becomes a bottleneck in the overall manufacturing process stream. Standard, in-line characterization techniques which could be implemented within the manufacturing process would be valuable. They would enable characterization of the material as it is incorporated into the device as well as the effective properties of the material combined with its electrical and thermal contacts to other device components. In-line characterization could also increase process yield and reduce waste since defective devices would be detected earlier in the manufacturing process.

6. Cost considerations

The thermoelectric materials in established devices are based on bismuth telluride, lead telluride, and silicon germanium. The high cost of tellurium and germanium is touted as a reason to develop thermoelectric materials which do not use expensive elements [88]. The development of polymer, silicide, oxide, and tetrahedrite TE materials is motivated strongly by the need to lower costs and improve the commercial viability of TEGs. Fig. 8 demonstrates the raw materials costs associated with sample materials of the main types of TE material classifications. The materials cost depends heavily on material composition. Within a given classification of material, the cost can vary by a factor of two and sometimes even an order of magnitude, particularly when a

relatively inexpensive material is doped with an expensive element. The doping is done to achieve better performance (e.g. higher ZT), so it is particularly helpful to consider both cost and performance as discussed at the end of this section.

The standard practice is to synthesize thermoelectric compounds with high purity starting materials, and the purity of materials affects cost with higher purity resulting in higher costs. While the effect of material purity on TE material properties has not been widely established [90–93], and an up-to-date, systematic study would be useful, the presence of impurities in the TE material likely degrades the properties. The relative difference in material cost based on purity level is demonstrated in Table 3 for sample materials.

While thermoelectric material costs are non-negligible, the system component costs can overwhelm the material costs. Major contributions to system costs are due to the substrates and heat exchangers. Substrates are typically thin ceramic pieces, often alumina-based, with off-the-shelf costs of approximately \$0.10/cm². The cost of the hot and cold side heat exchangers is particularly significant. Heat exchangers have to be customized to the TEG in order to accommodate the form factor of the device and optimize system performance, so it is challenging to specify cost. However, cost estimates can be determined from off-the-shelf units. Heat exchanger cost generally scales with the overall heat transfer coefficient [58], or U -value, as shown in Fig. 9.

Both material and device manufacturing costs are relevant for TEG commercialization. Particularly with the advent of nanostructured thermoelectric materials, the cost of manufacturing techniques required to make thermoelectric materials can vary widely. The costs vary based on the complexity of the manufacturing process and the maturity of each process step's technology. In particular, the costs associated with lithographic or epitaxial deposition processes for thick/thin film materials are orders of magnitude larger than those associated with bulk material processing [75]. While there may be a tradeoff between increased material synthesis cost and assembly cost for thermoelectric thick/thin film materials, such comparisons are not readily available and remain

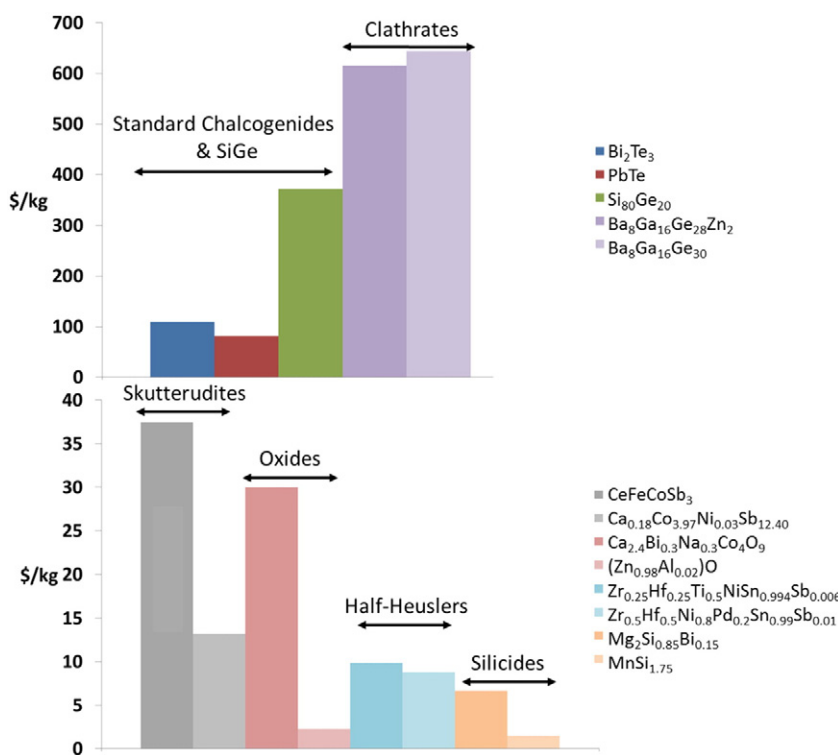


Fig. 8. Cost of various thermoelectric materials based on the raw material costs [89] of the constituent elements. The exact cost values and calculations are provided in [75].

Table 3

Comparison of raw [89] and pure [94] material costs for select thermoelectric materials. Representative materials from each main type of thermoelectric material are shown. Values are rounded to the nearest dollar. The table is adapted from [75].

Material type	Material name	Material composition	Material cost (\$/kg)	
			Reference	Raw Pure
Chalcogenide	Bi ₂ Te ₃	[95]	110	806
	AgPb ₁₈ SbTe ₂₀	[96]	84	581
SiGe	Si _{0.8} Ge _{0.2}	[97]	371	7081
Clathrate	Ba ₈ Ga ₁₆ Ge ₂₈ Zn ₁₂	[98]	615	3973
Skutterudite	Yb _{0.2} In _{0.2} Co ₄ Sb ₁₂	[99]	24	204
Half-Heusler	Ti _{0.8} Hf _{0.2} NiSn	[100]	11	530
Silicide	Mg ₂ Si _{0.85} Bi _{0.15}	[101]	7	191
Oxide	(Zn _{0.98} Al _{0.02})O	[102]	2	50

largely unspecified. The cost of assembly is a significant consideration. Assembling the thermoelectric legs into the typical uncouple formation can be performed manually or automated through pick-and-place or shaker machines, and the cost depends on the assembly technique. Since exact cost values for assembly steps are not publicly available, the impact of this cost is difficult to project.

Various cost analyses for thermoelectric devices have been developed and use different approaches. An early cost calculation used fuel cost and module construction costs for given leg thicknesses [74]. The tradeoff between cost and efficiency was investigated by first determining optimum device geometry followed by calculating material cost for that geometry [104]. A recent analysis created a cost–performance metric which coupled materials, manufacturing, and system costs with TEG performance [58], and the cost in \$/W for TEGs made with various TE materials was calculated [75]. The analysis concluded that bulk thermoelectric materials can achieve costs below \$1/W for applications where the thermoelectric material temperature is higher than 275 °C, and the high costs of heat exchanger and ceramic substrate system components present a barrier to achieving low-cost thermoelectric generators. Particularly for high-temperature applications, it is relevant to determine whether alternative heat recovery technologies are more cost-effective than TEGs. For instance, the higher conversion efficiencies of organic Rankine cycle systems could outweigh the impact of their capital cost and maintenance requirements.

7. Conclusion

The abundance of waste-heat sources and increasing energy efficiency goals make waste-heat recovery with thermoelectric power generation a promising technology. The realization of commercial thermoelectric generators hinges on solving the intimately coupled

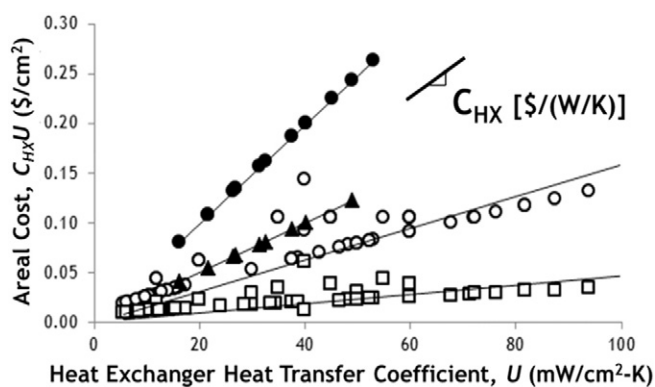


Fig. 9. The cost of heat exchangers related to their overall heat transfer coefficient, or U -value [103]. The slope is the heat exchanger cost per thermal conductance. The figure is reproduced from [58].

challenges with materials development and systems engineering. Measuring system performance with thermoelectric material ZT alone is insufficient for determining generator performance, and other thermo-mechanical/chemical material properties and components strongly impact product development. Major issues to resolve for TEG commercialization are material selection based on average (not peak) ZT , material thermal and chemical stability, engineering of interfaces and interface materials, and optimization of hot and cold side thermal resistances (e.g. heat exchangers). Moreover, the manufacturability of thermoelectric devices combined with the total system cost will influence the technology's time-to-market, readiness of product supply, and cost competitiveness. Active research and development efforts along with the emergence of new prototypes and pilot systems indicate solutions to the linked materials and systems challenges are well underway, and thermoelectric generators can contribute to sustainable development.

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