Thermomagnetic materials for harvesting low temperature waste heat

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Abstract

Thermomagnetic materials are an emerging type of magnetic energy materials, which enable the conversion of low temperature waste heat to electricity by three routes: Thermomagnetic motors, oscillators and generators. Here we analyse the material requirements for a more energy and economic efficient conversion. We describe the influence of magnetization change and heat capacity on thermodynamic efficiency, as well as the consequences of thermal conductivity on power density. Together with the raw materials cost this gives the price per watt as decisive value for an economic comparison with today’s power plants and thermoelectrics. We present a materials library which allows selecting the best available thermomagnetic materials in Ashby plots as figure of merit and gives guidelines for future development.

1 Introduction

Magnetic materials have an outstanding prominence among energy materials as the combination of hard and soft magnetic materials enables the efficient conversion between electrical and mechanical energy by electric motors and generators. Magnetocaloric materials expand the application range towards the
conversion from electric to thermal energy [1, 2]. In these materials, a steep change of magnetisation in the vicinity of room temperature yields a magnetically induced entropy change, which drives a magnetocaloric cooling cycle [3]. The high efficiency of this cycle has triggered intense research on magnetocaloric [4] and related multicaloric materials [5]. This enabled the development of several devices and prototypes [6], which address the urgent need for more energy efficient cooling in a world that heats up. The fast progress in magnetocaloric materials also allowed to reconsider the inverse energy conversion process: converting thermal to electrical energy in thermomagnetic systems, based on a steep change of magnetization. Though the first concepts for thermomagnetic energy harvesting had been already suggested by Tesla [7, 8], Stefan [9], and Edison [10, 11] more than 100 years ago, it required magnetocaloric materials to build the first thermomagnetic demonstrators [12]. This dual use of magnetocaloric materials happens at a tipping point for mankind, where the efficient use of primary energy becomes decisive [13]. This includes the need to recover waste heat, which is released during industrial and chemical processes. Recovering this waste heat is worth an effort, as it amounts up to 72 % of all electrical energy produced in the year 2016 [14]. 63 % of this heat is wasted at temperatures below 100 °C. The maximum of waste heat is just above room temperature [15], where hardly any technology exists for the conversion of heat to electricity. Only thermoelectric generators, which in particular use organic thermoelectric materials, are suitable in this temperature range. However, they suffer from a low thermodynamic efficiency below 0.6 % of the theoretical Carnot limit [16]. Thus, there is a strong need for the conversion of the low grade waste heat using suitable thermomagnetic materials.

In this paper we identify optimum intrinsic properties for thermomagnetic materials (TMM) and summarize which of today’s materials efficiently fulfill these conditions using Ashby type plots. As we emphasize the differences to optimum magnetocaloric materials, we can give guidelines for an independent improvement of TMMs. For this we first analyse the thermomagnetic harvesting cycle and describe
how this cycle is implemented within thermomagnetic motors, oscillators, and generators. From this we derive the magnetic and thermal properties required for optimum thermodynamic and economic efficiency by using two Ashby plots as figure of merit. For this we expand the pioneering work of Brillouin and Iskenderian [17] by a recent concept originally developed for magnetocaloric refrigeration. We identify the five TMMs with optimum intrinsic properties and compare them with thermoelectric materials with respect to their suitability to harvest low temperature waste heat.

2 Thermomagnetic cycle and device implementations

To understand the role of a thermomagnetic material (TMM) for the conversion of low temperature waste heat to electricity, we first describe a thermomagnetic cycle used within all thermomagnetic devices. As functional material TMM changes its magnetization $M$ at a transition temperature $T_t$. In a second order magnetic transition, a gradual decrease in magnetization is observed during heating, whereby the ferromagnetic material becomes paramagnetic. In a first order material this magnetic transition is coupled with a change in the crystal structure or volume. These materials are of particular interest because $M$ changes strongly from $M_{\text{cold}}$ to $M_{\text{hot}}$ during heating when temperature changes by a small $\Delta T$. This requires a certain amount of heat input $Q_{\text{in}}$. The TMM is used in a thermomagnetic cycle, which consists of four steps and is sketched in Figure 1a. Step I starts at ambient temperature, where the TMM is below its transition temperature and exhibits a high $M_{\text{cold}}$. At constant temperature a magnetic field $H$ is applied, which reduces the Gibbs energy $E_M$ of the TMM by the following term:

$$E_M = \mu_0 \Delta MH$$ (1)

where $\mu_0$ is the magnetic field constant [18]. In step II low temperature waste heat $Q_{\text{in}}$ is used to heat the TMM above $T_t$, which reduces magnetization to $M_{\text{hot}}$. When the magnetic field is removed in step III, just a low value of Gibbs energy term $+\mu_0 M_{\text{hot}}H$ is required. In step IV, the hot TMM is brought again into contact with
ambient temperature, which closes the thermomagnetic cycle and restores the high $M_{\text{cold}}$. Thus a thermomagnetic cycle requires $Q_{\text{in}}$ as input energy. The difference in Gibbs energy $-\mu_0 \Delta M H$ is used to create electricity, with $\Delta M = M_{\text{cold}} - M_{\text{hot}}$ being the decisive material property. As this contribution to Gibbs energy only contains magnetic properties, we call the positive counterpart, which can harvested by thermomagnetic systems, as magnetic energy (density) $E_M = +\mu_0 \Delta M H$ and drop the term density for better readability. During one cycle the TMM converts $E_M$, thus a thermomagnetic system can at best convert $E_M$ to electrical energy.

There are several thermomagnetic systems, summarized by Kishore and Priya [19]. These different implementations of a thermomagnetic cycle can be classified by the type of mechanical movement involved. Mechanical rotation is employed within a thermomagnetic motor, also known as Curie wheel (Figure 1b). First proposals of such devices were made by Edison [10], Tesla [7] and Stefan [9] and later works predicted the efficiency of such a device to reach the thermodynamic limit [20, 21, 22]. A thermomagnetic motor uses a rotatable ring of TMM. Its rotation causes each part of the TMM to undergo the four stages of the thermodynamic cycle. In stage I the application of a magnetic field $H$ is realized by a permanent magnet. As the TMM exhibits a high $M_{\text{cold}}$, it is strongly attracted by the field gradient at the beginning of the permanent magnet. The integral gain of mechanical energy associated with this torque is identical to the gain of $\mu_0 M_{\text{cold}} H$. In stage II, the TMM is heated by the low temperature waste heat, which reduces the magnetization to $M_{\text{hot}}$. Thus, when the TMM leaves the permanent magnet region in stage III, only a low torque hinders the rotation of the TMM ring. In step IV the temperature of the TMM reduces to ambient and restores the high $M_{\text{cold}}$. Thus in a thermomagnetic motor the heat $Q_{\text{in}}$ is used to convert the magnetic energy $E_M = \mu_0 \Delta M H$ into mechanical energy, which can be converted to electrical energy by a conventional generator. While many miniature versions of a “Curie wheel” can be watched on Video-sharing websites, these motors can also reach a reasonable power, e.g. a prototype using gadolinium as TMM reached a power output of 1.4 kW [23].
Mechanical oscillation is used within thermomagnetic microsystems. In these systems the TMM is used in the shape of a thin film deposited on top of a vibrating cantilever (Figure 1c). In step I of the thermomagnetic cycle, the cold TMM film is attracted by a permanent magnet, which bends the cantilever. The permanent magnet is combined with the heat source, and thus in step II the temperature of the TMM increases, which reduces its magnetization. This decreases the attractive force of the TMM towards the permanent magnet. Accordingly in step III, the restoring force of the bent cantilever is sufficient to move the TMM away from the heat source. With the heat source also being the permanent magnet, $H$ is reduced. At sufficient distance the TMM cools to ambient (step IV). The mechanical energy of the vibrating cantilever is converted to electrical energy by an induction coil, which is located on top of the cantilever [24]. During vibration, this coil moves within the magnetic field gradient of the permanent magnet and thus according to Faraday’s law of induction the flux change induces an electric voltage. In a different design, as suggested by the group of Carman [25, 26, 27], a piezoelectric cantilever is used instead of the coil [28]. Though also bulk thermomagnetic oscillators have been demonstrated [29], the advantage of a microsystem is its fast heat exchange, which is possible due to the reduced size of the TMM. This results in a high frequency of the thermomagnetic cycle, which can reach up to 200 Hz when resonance frequency of the cantilever matches the thermal exchange frequency [24]. As the power of a thermomagnetic system is the energy per cycle times the frequency, an oscillating microsystem can reach a high power in relation to the small volume of the TMM required.

No mechanical movement of the TMM is required for a thermomagnetic generator. First concepts of TMG were invented by Edison and Tesla, and later Brillouin and Iskenderian calculated the relative efficiency to be up to 55 % [11, 8, 17]. Based on this work, other researcher treated such a device theoretically [30, 31, 32, 33]. In this implementation of a thermomagnetic cycle the TMM is used as a thermal switch for the magnetic flux $\Phi$, which is created by a permanent magnet, as illustrated in Figure 1d. At low temperatures the high $M_{\text{cold}}$ of the TMM guides $\Phi$ through a closed
magnetic circuit. At high temperatures the low $M_{\text{hot}}$ opens the magnetic circuit and reduces $\Phi$. Following Faraday’s law of induction, this flux change can induce an electric voltage. To harvest electric energy, an induction coil is wound around the soft magnetic yoke, connecting the permanent magnet and TMM. The flux change between step I and III converts a maximum of magnet energy $E_M$ into electrical energy. Opening and closing the magnetic circuit also changes the magnetic field $H$ that acts on the TMM, as illustrated by the different density of flux lines in figure 1d. The first proof-of-concept was published by Srivastava et al. in 2011 [12]. They used a Heusler alloy (Ni-Mn-Ga), developed for magnetic refrigeration at room temperature. The efficiency of this demonstrator was quite low mainly due to an unoptimized magnetic circuit. As a large difference in $H$ is beneficial to increase $E_M$, more complex magnetic field topologies have been used for thermomagnetic generators. A topology with two magnetic circuits avoids magnetic stray fields [34]. Recently we demonstrated that a topology with three circuits even allows a sign reversal of the magnetic flux, which increased both, output voltage and power, by orders of magnitude [35].

This paper focuses on the TMM, where $E_M$ and $Q_{\text{in}}$ are the key material properties. $E_M$ gives the upper limit for the electrical energy harvested, but most implementations today reach much lower values [34, 35]. Possible reasons for this are thermodynamic cycles, which are not consisting of strict adiabatic/isofield steps, losses by insufficient insulation or an incomplete use of the heat input to heat up the TMM. We will not address these engineering aspects here, as we expect a strong improvement from the very few prototypes existing. Instead we focus on the upper limits, defined by the TMM used.
Figure 1: The thermomagnetic cycle and three device implementations for thermomagnetic harvesting of low temperature waste heat. a) Within a thermomagnetic cycle a thermomagnetic material (TMM) is subjected to four steps. In step I a magnetic field $H$ is applied to the cold TMM (blue), having a high magnetisation $M_{\text{cold}}$. This reduces the Gibbs energy by $-\mu_0 M_{\text{cold}} H$, and in the following implementations this particular magnetic energy is converted to electric energy. In step II, low temperature waste heat $Q$ is used to increase the temperature of the TMM (red), which reduces its magnetisation $M_{\text{hot}}$ in the ideal case to zero. Thus when in step III the magnetic field is removed, there is no change in Gibbs energy. In step IV the TMM is cooled to ambient, which restores its high magnetisation $M_{\text{cold}}$ and closes the thermomagnetic cycle. b) Within a thermomagnetic motor a rotatable ring of TMM, depicted in a blue-red colour gradient according to its temperature, is subjected to
these four steps. c) Within a thermomagnetic oscillator a TMM film is mounted at the tip of a cantilever. An additional induction coil at the tip of the cantilever converts the mechanical oscillation within the gradient of the permanent magnet to electric energy.

d) Within a thermomagnetic generator the TMM is used to switch the magnetic flux \( \Phi \) (green arrows) within a magnetic circuit. In this circuit \( \Phi \) is created by a permanent magnet (green) and guided by a soft magnetic yoke (grey). As with the flux also the magnetic field acting on the TMM changes, a thermomagnetic generator is an implementation of a thermomagnetic cycle.

### 3 Efficiency of thermomagnetic materials

During each thermomagnetic cycle, the TMM uses the thermal input energy \( Q_{in} \) to make the magnetic energy \( E_M = \mu_0 \Delta MH \) available as output for the thermomagnetic system. Thus its thermodynamic efficiency of the material is given by the ratio of output and input energy:

\[
\eta = \frac{\mu_0 \Delta MH}{Q_{in}}
\]

Before using this key equation to compare different thermomagnetic materials, we shortly describe how the physical quantities used in eq. (2) are determined. This is specifically shown in Figure 2 for the La-Fe-Co-Si (Calorivac C\(^\circ\)) material, which exhibits a steep second order transition at 308 K, which is at the border to a first order transition. In addition, we discuss similarities and differences between thermomagnetic and magnetocaloric materials.

The applied magnetic field \( H \) is the only property in the equation, which depends on the device and not on the material. To compare material properties, we fix \( \mu_0 H = 1 \) T, since a field of 1 T can be easily obtained by today's permanent magnets. Indeed, also the related magnetocaloric materials are compared now at this value and not at 2 T, which requires much more effort \[36\]. Equivalent to magnetocaloric material, we consider the minimum field to be zero, which can be achieved by an appropriate magnetic shielding \[37\].
The difference in magnetization $\Delta M$ during cycling between $T_{\text{cold}}$ and $T_{\text{hot}}$ should be large in order to obtain a higher efficiency (Figure 2a). A higher value is also beneficial for magnetocaloric materials, since a high $\Delta M$ gives a high entropy change according to the Maxwell relation [38]. Thus, for both applications, materials exhibiting a first order phase transition are of particular interest, as they exhibit a steep change of magnetization over small $\Delta T$, compared to the gradual change in magnetization occurring during a second order transition. Throughout this paper we use the absolute value of $\Delta M$, as this allows also to encompass materials with an inverse transition like FeRh [39] and Ni-Mn-In(Sn) [40, 41], in which the magnetization increases with temperature. Though this uncommon dependency reverses the operation direction of a thermomagnetic system, neither the principle nor the thermodynamic properties change.

In addition to the temperature, magnetization also depends on the applied magnetic field. This is evaluated with the area within a $M$-$H$ loop to obtain $E_M$ [42]. As shown in supplementary figure S1, our approach is a good approximation of this precise treatment (0.87% difference). We use this approximation, since relevant materials values of $\Delta M$ are often available, but no complete $M$-$H$ loop.

The thermal input energy $Q_{\text{in}}$ should be low to obtain a high efficiency. When cycling between $T_{\text{cold}}$ and $T_{\text{hot}}$, the specific heat is always required to heat up the TMM and in case of a first order material the latent heat is required in addition. Both contributions are considered when integrating the specific heat capacity $c_p$: $Q_{\text{in}} = \int_{T_{\text{cold}}}^{T_{\text{hot}}} c_p(T) dT$, as depicted in Figure 2b. Within the methods section we describe how comparable values for the different TMM from literature were obtained. For magnetocaloric materials the equivalent property is the heat which can be transported from the cold to the hot reservoir during each cycle. This is determined by the entropy change $\Delta S$, which should be as high as possible. Thus the optimum thermomagnetic and magnetocaloric materials differ fundamentally with respect to heat capacity and latent heat: thermomagnetic materials require lower values than magnetocaloric materials.
The temperature difference $\Delta T = T_{\text{hot}} - T_{\text{cold}}$ between hot and cold reservoir is not directly part of eq. (2), but implicitly important as it affects both, $\Delta M$ and $Q_{\text{in}}$, as illustrated in Figure 2a) and b), respectively. Efficiency depends on $\Delta T$ due to different dependencies of $Q_{\text{in}}$ and $\Delta M$. At high $\Delta T$ the constant $c_p$ results in continuous increase of $Q_{\text{in}}$ whereas $\Delta M$ just increases slightly. For the particular material La-Fe-Co-Si, we discuss the efficiency in dependency of $\Delta T$ in more detail in section 7. Thus for the comparison of the different materials we select two particular temperature values: 10 and 30 K. It is worth to put these values in relation to the thermal hysteresis, which is a significant drawback occurring in materials exhibiting a first order transformation. This hysteresis can reach several Kelvin and hinders a complete reversible transformation when it exceeds $\Delta T$. We have marked all materials in the supplementary table S1, where hysteresis is larger than 10 K. The decisive property in magnetocalorics is the adiabatic temperature change, when applying a magnetic field. The typical adiabatic temperature change is small, e.g. 1.5 K for the specific La-Fe-Co-Si material analysed in Figure 2 [43]. When the thermal hysteresis approaches or even exceeds the adiabatic temperature change, magnetocaloric refrigeration becomes inefficient. As the $\Delta T$ used in thermomagnetic systems is much higher, hysteresis is less critical for thermomagnetic applications than for magnetocaloric materials.
Figure 2: Characterization of Thermomagnetic Materials (TMM) specifically for the La-Fe-Co-Si material. a) When increasing temperature $T$ the magnetization $M$ strongly decreases in vicinity of the transition temperature $T_t = 308$ K. The TMM is cycled by $\Delta T = 30$ K between $T_{hot}$ and $T_{cold}$, which results in a change of magnetisation $\Delta M$. To illustrate that the applied magnetic field $H$ only has a minor influence of 10 % on $\Delta M$, two curves are shown for 0.1 T (black) and 1 T (purple). Both measurements have been performed during heating and cooling, resulting in two hardly distinguishable curves. b) To determine the heat $Q_{in}$ required to cycle the TMM by $\Delta T$, the heat capacity $c_P$ is integrated in dependence of the temperature. Though the magnetic field changes the shape of the curve, this only has a negligible influence on the integral $Q_{in}$ of 1.3 %.
In order to identify the TMM with highest efficiency $\eta$ we evaluated the magnetization change $\Delta M$ and heat input $Q_{in}$ for several materials (figure 3). For our analysis we only select materials with a transition temperature between 273 K and 373 K, where water can be used as heat transfer fluid. The transition temperature can be tuned in many material systems by adjusting the composition, which can be used to adapt $T_t$ to the available waste heat. This is not possible for the pure magnetic elements (Fe, Ni, Co), which are only shown for comparison, as they also have $T_t$ far above the relevant temperature range. Details of the evaluation procedure are described within the methods. All values and references are given within supplementary table S1. To allow the selection of the most efficient TMM, the results are summarized in Ashby type plots within figure 3 for two different temperature changes, $\Delta T = 10$ K (a) and 30 K (b). The most efficient TMM are found in the top left corner of the plot, where a maximum of $\Delta M$ is obtained at a minimum $Q_{in}$. In these Ashby plots the grey diagonal guidelines represent lines of equal efficiency calculated with equation 2 ($H = 1$ T). The best TMM can reach an efficiency of about 2 %. The benchmark is the Carnot efficiency $\eta_{carnot} = \Delta T/T_{hot}$, which represents the upper theoretical limit according to thermodynamics. For $T_{hot} = 300$ K and $\Delta T = 10$ K the upper limit is $\eta_{carnot} = 3.3 \%$, and the best TMM reach about 60 % of this limit. This illustrates that already the existing TMM can make thermomagnetic harvesting quite efficient.
Figure 3: Selecting thermomagnetic materials with high thermodynamic efficiency $\eta$ by using an Ashby type plot. To reach high $\eta$, a large change of magnetization $\Delta M$ is beneficial, as well as a low heat input $Q_{in}$. The grey dashed lines represent a constant efficiency $\eta = \mu_0 \Delta M H Q_{in}^{-1}$. Accordingly the most efficient materials are located in the top left corner, where $\eta$ approaches 2 %. Material properties were evaluated for two different temperature spans, $\Delta T = 10 \text{ K}$ (a) and 30 K (b). For a low value of $\Delta T$ materials with the tendency of a first order transition (partially filled symbols) are best as they exhibit a sharp transition. For a large $\Delta T$ materials with a second order transition (full filled symbols) become competitive. In all Ashby plots metallic materials are displayed with reddish, ceramics with blue, metallic glasses with yellow colours, and elements with green colour.

4 Power density, specific cost and economic efficiency

In addition to thermodynamic efficiency, the economic efficiency is a decisive criterion for TMM. In this section we analyse power density and specific cost, which together determine the economic efficiency. The power density $P_d$ describes the power per unit volume, which can be harvested by a TMM. To obtain a high $P_d$, a high
energy per cycle $E_M$ (see section 4) is required, as well as a high cycle frequency $f$, represented by equation: $P_D = E_{mag} f$. For a high $f$, a fast heat exchange is needed. The key material properties for this are a high thermal conductivity $\lambda$, and a low volumetric specific heat $\rho c_p$, where $\rho$ is the density. As described in the methods section, we used a one dimensional lumped capacitance method to derive an analytical formula for $f$. In addition to the materials thermal properties, summarized within supplementary figure S2, only the thickness $d$ of the TMM is required. We selected $d = 0.5$ mm, since this thickness is reachable by most bulk processing routes. Indeed, for the La-Fe-Co-Si materials, plates with this thickness are already available commercially. In Figure 4 the $P_D$ of TMM are used as y-axis in an Ashby type plot. As x-axis we used the specific material cost $C$, which is the current raw material prices per volume. We did not include cost for processing and shaping in the present analysis, as this depends on production scale and is expected to decrease strongly once thermomagnetic harvesting is established. Furthermore, we consider only the TMM and not the periphery required for a complete thermomagnetic system (hard magnets, soft magnetic yoke, tubing etc.). A fair estimate of periphery is not possible at the present technology readiness level, but it is worth to note that the use of cheap ferrite hard magnets appears possible [35], whereas magnetocaloric refrigeration requires expensive Nd-Fe-B hard magnets. Thus the cost estimation within the following discussion represents the lower limit.

To evaluate the economic efficiency of TMM, we calculated the cost index $C/P_D$, which gives the price in Euros required for each Watt of output power (Figure 4). Lines of equal cost index are depicted as diagonal lines as they allow a comparison with common power generation like gas turbines or offshore wind plants. This is quantified by the Levelized Costs Of Electricity (LCOE), which considers construction, operation and financing of a power plant during life time. The LCOE of today's power plants range from 0.4 €/W for gas turbines to 4 €/W for offshore wind plants [44]. Thermoelectric power generation requires about 25 €/W, considering only the material, which is obviously worth for specific applications where no power grid is
available [45]. The lowest cost index of TMM is more than one order of magnitude lower compared to today’s power plants, which should leave enough budget for building a complete thermomagnetic system. As waste heat is available freely, this low cost index of TMM is a key advantage. We expect that the high economic efficiency will be more decisive for the success of thermomagnetic harvesting than thermodynamic efficiency, which only describes how much waste heat is required.

In addition to economic efficiency, one should also consider the criticality, which includes the geological availability, geopolitical situation, recyclability and sustainability of materials. Most of the interesting materials here had been analysed by Gottschall et al. [36] recently with respect to magnetocaloric refrigeration. Co, Ge, In and Rh were identified as critical elements, responsible for high cost of synthesis of thermomagnetic materials. Accordingly the materials in figure 4 with high cost index also exhibit a high criticality and are thus not suitable for thermomagnetic harvesting.
Figure 4: Identifying economically efficient thermomagnetic materials with high power density $P_D$ and low material cost per volume $C$ in an Ashby type chart. The ratio of both values $C/P_D$ gives the cost per power (diagonal grey lines), which allows for a comparison with the investment costs of today’s energy technologies in the order of 1 €/W (blue dotted lines). In particular, La-Fe-Si-H is a thermomagnetic material, which can be cheaper by more than one order of magnitude. Though $P_D$ considers only the cost of the active material and not the periphery (yoke, permanent magnets, processing, etc.), this illustrates that harvesting low temperature waste by thermomagnetic material can become competitive as no additional primary energy is needed. This data was evaluated for $\Delta T = 30$ K.

5 Identifying the most promising thermomagnetic materials

The libraries of thermomagnetic materials (Figure 3 and 4) are sorted by different criterions. Starting from the most general criterion and ending with the particular material, we identify the best TMM today and derive guidelines for a systematic search for even better TMM in future. When comparing materials with the tendency of a first order transition (half-filled symbols) and second order transition (full symbols), we observe that first order TMM reach higher efficiency at $\Delta T = 10$ K. At higher $\Delta T = 30$ K, materials with a second order transition become competitive. We attribute this to the steep change of magnetisation occurring in first order materials, whereas in second order materials a larger $\Delta T$ and $Q_{in}$ is required to reach a sufficiently high $\Delta M$. Accordingly, first order materials can also achieve a better cost index. Thus we suggest focussing on first order materials, however avoiding materials with a large hysteresis. Second order materials are interesting for harvest over a large temperature span.

Crystalline metallic materials (displayed in red) can reach higher values of $\Delta M$ compared to ceramics (blue) as they have a higher magnetization due to a higher density of ferromagnetic elements. Furthermore, ceramics have a low thermal conductivity compared to metals since they do not have free electrons which
contribute to conductivity, and thus their power density is low. Metallic glasses (yellow) typically have even lower $\Delta M$ due to their broad second order transition, but the equally reduced $Q_{in}$ results in a competitive thermodynamic efficiency. However, for glass forming, further additional alloying is required, which makes them expensive. Thus we propose to focus on crystalline metallic materials when searching for better TMM.

For comparison we considered the pure ferromagnetic elements (green). Fe, Ni, Co only reach a very low efficiency due to their high $T_c$, which results in a low $\eta$ compared to $\eta_{carnot}$. This illustrates that thermomagnetic harvesting is interesting for low temperature waste heat, but not for high temperatures (see also section 7). This hampers the application of Fe, though this TMM has the lowest raw material cost and cost index. Gd is the only element which exhibits a second order transformation in the vicinity of room temperature. Accordingly, it is still the benchmark for all magnetocaloric materials [36]. Also as TMM Gd is an interesting candidate, as it reaches a high efficiency of about 1 % for $\Delta T = 30$ K, as expected for a second order material. However, the high cost of Gd, the need to use ultra-pure material [46, 47, 48], and the tendency to oxidize makes Gd economically less competitive.

We now compare the particular material systems, starting with the most promising TMM. The key properties of the four most promising TMM with their particular compositions are summarized in Figure 5 within a radar chart, together with Gd as reference. Some aspects of the evaluation refers to thermal conductivity and diffusivity (supplementary figure S2) and particular material data (supplementary table S1).

LaFe-based TMM exhibit an itinerant metamagnetic transition accompanied by a favourable large $\Delta M$ [49]. The low transition temperature ($T_t$=198 K) of the ternary LaFe$_{11.4}$Si$_{1.6}$ compound can be increased above room temperature by adding Co [50] or hydrogen [51] which also allows tuning the transition between second and first order. The combination of high $\Delta M$ and moderate heat input results in a high thermodynamic efficiency of 0.62 % at $\Delta T = 30$ K. In addition, these alloys have a
reasonable thermal diffusivity and thus exhibit a higher power density. As these alloys contain mostly iron and a low fraction of the relatively inexpensive lanthanum, they are economically favourable. Though for each of these criteria there is at least one TMM which performs better, none of these competitors reach this optimum combination required for a low cost per power. This makes LaFe-based materials the benchmark for TMM till day. Furthermore, thin plates of these materials are available commercially. This is the favourable geometry for most thermomagnetic systems, as this allows both, a fast heat transfer perpendicular to the plate and an uninterrupted guidance of the magnetic flux within the plate.

MnFe-based TMM exhibit a structural transition from a low temperature hexagonal NiAs type to a high temperature orthorhombic MnP-type structure [52, 53, 54, 55]. These alloys reach slightly lower values for $\Delta M$ and slightly higher values for $Q_{in}$ compared to the benchmark, which reduces the thermodynamic efficiency. While these materials also have a favourable low cost of raw materials, the major drawback for MnFe-based materials is their lower thermal diffusivity, limiting the power density and thus increasing the cost per power compared to the benchmark material.

Heusler alloys have the generic formula $X_2YZ$. They are versatile, as their composition and functional properties can be varied broadly. Ni$_2$Mn-based Heusler alloys are of particular interest, which can be used in two ways. They can be applied at their Curie temperature, which is a Second Order Magnetic Transition (SOMT). Some of these alloys also exhibits a First Order Martensitic Transition (FOMT), which is associated with a sharp and large change of magnetization. With respect to thermodynamic efficiency, only FOMT can approach the benchmark material. A benefit of Heusler alloys is their high thermal diffusivity, resulting in a high power density. Bulk applications of Heusler alloys are hampered by large hysteresis (FOMT) and their high material cost, resulting in a high cost index. However, for microsystems the processing cost commonly dominates over the raw material cost. As there are many publications on Heusler thin films, but just very few on LaFe- and MnFe-based
films, we consider Heusler alloys as most promising for microsystems and indeed these alloys have been used for micro oscillators [24].

$\text{RE}_2\text{Fe}_{17}$ compounds with $\text{RE}=\text{Y}$ as the most promising representative [56] only reach a medium thermodynamic efficiency as $\Delta M$ is moderate due to the second order transformation. However, this alloy exhibits a high thermal diffusivity, which results in a high power density. Due to the high Fe-content, the cost of raw material is lower. This combination makes $\text{Y}_2\text{Fe}_{17}$ one of the most promising materials with second order transition.

Fe-based amorphous metals [57, 58] also exhibit a second order transition and their thermodynamic efficiency is similar to $\text{Y}_2\text{Fe}_{17}$. The addition of Co, required for glass forming, however results in a higher material price and thus higher cost per power.

Each of the remaining materials has its own drawback. Perovskites have significantly low thermal conductivity and metallic antiperovskites have a too low magnetization change. $\text{Gd}_5\text{Si}_2\text{Ge}_2$ as the first “giant” magnetocaloric material [1] reaches also a very high thermodynamic efficiency due to its first order transition. However, the high cost of Gd and Ge limits its economic competitiveness, which also holds for Gd-based metallic glasses. FeRh exhibits a high thermodynamic efficiency due to its sharp and high $\Delta M$ at a first order metamagnetic transition. Unfortunately, the extraordinary price of Rh hinders any practical application.
a) Direct and b) derived key properties of the most promising thermomagnetic materials displayed in two radar charts, where a large polygon area reflects the optimum material. For this graph the best composition for each material class is used. While the first order LaFe$_{11.8}$Si$_{1.8}$H$_1$ exhibits the optimum combination of all properties, Mn$_{1.25}$Fe$_{0.7}$P$_{0.5}$Si$_{0.5}$ has a substantially lower thermal diffusivity, which reduces frequency and accordingly power density. The first order Heusler alloys reach the highest power density, but exhibits a very high specific material cost. This will hinder bulk application, but not microsystems, where material cost is less important than processing cost. Y$_2$Fe$_{17}$ is the most promising thermomagnetic material with a second order transition. Gd is depicted as reference. This data was evaluated for $\Delta T = 30 \, K$. 

Figure 5:
6 Identifying the optimum temperature range

In this section we identify the temperature range $\Delta T$ of waste heat which can be harvested most efficiently. Therefore we focus on La-Fe-Co-Si (Calorivac C®) as most promising TMM available. As shown in Fig. 2, the efficiency is determined by the magnetization change $\Delta M$ and the heat input $Q_{in}$, both of which exhibit different dependencies on $\Delta T$. While $\Delta M$ has a favourable high value just at the transition temperature, $Q_{in}$ increases with $\Delta T$ continuously, making large temperature spans unfavourable. Thus thermomagnetic harvesting is most efficient at low $\Delta T$.

For comparison, the efficiency of thermoelectric materials is shown in figure 7 for the material $\text{Bi}_2\text{Te}_{2.79}\text{Se}_{0.21}$, reaching the highest values in vicinity of room temperature [59]. As for the thermomagnetic material, these values are the material efficiency and not the lower system efficiency. When a temperature difference of 10 K or lower is available, thermomagnetic materials reach a higher thermodynamic efficiency. In addition, values for an organic thermoelectric materials PEDOT:PSS [60] are shown, which are more suitable for this low temperature range as they are cheaper and more sustainable [16]. When taking organic thermoelectric materials as competitors, TMM are more efficient up to a temperature difference of 16 K.

To expand the temperature range for thermomagnetic energy harvesting one can use a series of TMMs with increasing transition temperatures. In this series each particular TMM just takes its optimum $\Delta T$ from the heat source and leaves a colder sink for its neighbouring TMM, having a lower transition temperature. This approach is equivalent to the “active regenerator” approach used for magnetocaloric refrigeration to reach a higher cooling span [61]. Though the application of this approach for energy harvesting had been proposed in the past [62], it had not yet been realized experimentally yet.
Figure 6: For harvesting low temperature waste heat, thermomagnetic materials reach a higher material efficiency relative to Carnot than thermoelectric materials. The temperature dependent relative efficiency of a commercial available thermomagnetic material La-Fe-Co-Si (Calorivac C®) is compared with two thermoelectric materials. Bi$_2$Te$_{2.79}$Se$_{0.21}$ [59] reaches the highest efficiency in vicinity of room temperature and the organic thermoelectric PEDOT:PSS [60] is cheaper and more sustainable. At low temperature differences thermomagnetic materials outperform thermoelectric materials.

7 Summary and Outlook

Thermomagnetic systems such as thermomagnetic motors, oscillators and generators convert waste heat to electricity. As all thermomagnetic systems are based on the same thermodynamic cycle, we can give a universal evaluation of thermomagnetic materials. We derive two Ashby charts, which serve as figures of merit for this emerging class of energy materials. The first figure of merit describes the thermodynamic efficiency, where high values are obtained when a large change of magnetization is obtained by a low heat input during each cycle. Some thermomagnetic materials outperform even the best thermoelectric materials for temperature differences below 10 K. This is a decisive advantage, since the largest
amount of waste heat is available at low temperatures. For high economic efficiency, in addition the thermodynamic cycle must be completed in a short time. Accordingly, for a high power density also a high thermal conductivity and low heat capacity are essential. Thus, in a second figure of merit, the economic efficiency is determined by the ratio of power density and materials cost. Our analysis reveals that the price per Watt of the best TMM is more than one order of magnitude lower compared to established power technologies and three orders lower compared to thermoelectrics. This leaves enough budget for realizing a complete thermomagnetic system. The combination of high thermodynamic and high economic efficiency of TMM drives the development of thermomagnetic energy harvesting.

Our Ashby type charts allow scientists and engineers selecting the optimum thermomagnetic material for their demand: Either a high thermodynamic efficiency or high output power at low materials costs. The La-Fa-Si-H system is the ideal compromise available today. However, this system was developed for the magnetocaloric cooling, which is the reverse thermodynamic process. For energy harvesting a new paradigm is necessary. While magnetocaloric materials must convert a large amount of heat during each cycle, TMM should consume a heat as low as possible and accordingly materials development must aim for low heat capacity and latent heat. From our materials library we predict that the next better TMM will be metallic, crystalline, contain a high amount of iron, and exhibit a transition at the border between first and second order.

Methods

Experimental methods: Temperature and magnetic field dependent magnetic properties of the La-Fe-Co-Si alloy (Calorivac C®) with $T_t = 308$ K were measured in a Quantum Design PPMS using a vibrating sample magnetometer insert. The heat capacity was measured in Quantum Design PPMS with heat capacity option. For all
temperature-dependent properties a heating and cooling rate of 0.5 K min\(^{-1}\) were used to avoid thermal lag between device and sample.

**Theoretical methods:** The material data were digitalized from their primary sources. The magnetization difference were derived from temperature-dependent measurements at sufficient magnetic fields or from field-dependent measurements at 1 T. The heat capacity data are from zero-field measurements. We calculated the heat capacity as mean value \(c_p = \frac{\int_{T_{\text{cold}}}^{T_{\text{hot}}} c_p \, dT}{\Delta T}\) for a temperature span of 30 K. To calculate the magnetic energy and the heat input we integrated the digitalized data. The temperature dependent heat conductivity and mass density were taken in vicinity of the transition temperature. We took raw material costs from different material market places in June 2018. All data are listed in Table S1 within the supplementary.

We calculated the power density of the TMM as product of magnetic energy per cycle and the cycle frequency. The cycle frequency is determined as the time to heat the material up and cool it respectively. To approximate the time in this transient conduction problem we used the one dimensional lumped capacitance method (LCM) [63]. Within this model the solid is spatially uniform and temperature gradients are negligible. When the temperature gradient approaches zero, the heat conductivity has to be infinitive following Fourier’s law. Accordingly, not heat equation but an overall energy balance is used to determine the transient temperature response. Thus the time \(t\) required for a solid to reach a given temperature \(T\) can be written as

\[
t = \frac{\rho c_p L^2}{\lambda Bi \ln \frac{T_i-T_\infty}{T-T_\infty}},
\]

whereby \(T_\infty\) is the end and \(T_i\) the start temperature. The Biot number \(Bi\) describes the ratio of thermal resistance of convection to conduction \(Bi = \frac{R_{\text{cond}}}{R_{\text{conv}}} = \frac{h L_c}{\lambda}\). So the Biot number is defined by heat transfer coefficient \(h\), the heat conductivity \(\lambda\) and the characteristic length \(L_c\) of the solid. This length could be either the half plate thickness or the volume to surface ratio. The LCM is only valid when the temperature gradient within the solid is negligible. This is the case when resistance to conduction within the solid is much less than the resistance to convection and thus with \(Bi \ll 1\). This is fulfilled for very small characteristic length or high thermal conductivities. For
the calculations of the heat transfer we set the Biot number to be 0.1. Additionally we set the term \( \ln \frac{T_1 - T_w}{T_f - T_w} = 1 \), which means that about 63% of the end temperature (270 K for cooling) is reached. In figure S6 of the supplementary we show that this value results in the maximal power output, although the magnetization change is slightly reduced. Accordingly the cycle frequency of heating and cooling is calculated as

\[
f = \frac{0.1 \lambda}{2 c_p \rho L^2}.
\]

The efficiency \( \eta \) of thermoelectric materials (Fig. 7) was calculated using

\[
\eta = \frac{T_h - T_c}{T_h} \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h},
\]

where \( ZT \) is the unitless figure of merit at the application temperature and \( \bar{T} \) is the average temperature of the hot \( T_h \) and cold temperature \( T_c \) [59].

**Availability of computer code and algorithm, data and material**

All data used for the comparison of TMM and the references to their origin is available within the supplementary material.

**Author contributions**

D.D. compared the different TMM and wrote the first version of this paper. A.W. contributed to the extrinsic properties and comparison with magnetocaloric materials. K.N. supervised the thesis of D.D. and contributed with the comparison with thermoelectric materials. S.F. suggested to make this analysis and wrote the second version of this paper. All authors contributed to the final version.

**Competing interests**

We declare no competing interests.

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References

[1] Pecharsky, V. K. and Gschneidner, Jr., K. A. Giant magnetocaloric effect in Gd$_5$(Si$_2$Ge$_2$). *Phys. Rev. Lett.* **78**, 4494–4497 (1997).

[2] Liu, J., Gottschall, T., Skokov, K. P., Moore, J. D., and Gutfleisch, O. Giant magnetocaloric effect driven by structural transitions. *Nat. Mater.* **11**, 620 (2012).

[3] Kitanovski, A. et al. *The Thermodynamics of Magnetocaloric Energy Conversion*, 1–21. Springer International Publishing, Cham (2015).

[4] Kitanovski, A. and Egolf, P. W. Innovative ideas for future research on magnetocaloric technologies. *Int. J. Refrig.* **33**(3), 449 – 464 (2010).

[5] Fähler, S. et al. Caloric effects in ferroic materials: New concepts for cooling. *Adv. Eng. Mater.* **14**(1-2), 10–19 (2012).

[6] Franco, V. et al. Magnetocaloric effect: From materials research to refrigeration devices. *Prog. Mater. Sci.* **93**, 112 – 232 (2018).

[7] Tesla, N. *US Patent* 396121A (1889).

[8] Tesla, N. *US Patent* 428057A (1890).

[9] Stefan, J. Ueber thermomagnetische Motoren. *Ann. Phys.* **274**(11), 427–440 (1889).

[10] Edison, T. A. *US Patent* 380100A (1888).

[11] Edison, T. A. *US Patent* 476983A (1892).

[12] Srivastava, V., Song, Y., Bhatti, K., and James, R. D. The direct conversion of heat to electricity using multiferroic alloys. *Adv. Energy Mater.* **1**, 97–104 (2011).

[13] Van Vuuren, D. P. et al. Integrated scenarios to support analysis of the food-energy-water nexus. *Nat. Sustain.* **2**(12), 1132–1141 (2019).

[14] Forman, C., Muritala, I. K., Pardemann, R., and Meyer, B. Estimating the global waste heat potential. *Renew. Sustain. Energy Rev.* **57**, 1568 – 1579 (2016).

[15] Schiering, G. Bring on the heat. *Nat. Energy* **3**(2), 92–93 (2018).
[16] Russ, B., Glaudell, A., Urban, J. J., Chabinyc, M. L., and Segalman, R. A. Organic thermoelectric materials for energy harvesting and temperature control. *Nat. Rev. Mater.* 1, 16050 (2016).

[17] Brillouin, L. and Iskenderian, H. Thermomagnetic generator, *Electrical Communication* 25(3) (1948).

[18] Bozorth, R. *Ferromagnetism*. John Wiley & Sons, Inc., Hoboken, (1993).

[19] Kishore, R. A. and Priya, S. A review on design and performance of thermomagnetic devices. *Renew. Sustain. Energy Rev.* 81, 33 – 44 (2018).

[20] Brailsford, F. Theory of a ferromagnetic heat engine, *Proc. Inst. Electr. Eng.* 111(9), 1602–1606 (1964).

[21] Steyert, W. A. Stirling-cycle rotating magnetic refrigerators and heat engines for use near room temperature. *J. Appl. Phys.* 49(3) (1978).

[22] Toftlund, H. A rotary curie point magnetic engine: A simple demonstration of a carnot-cycle device. *Am. J. Phys* 55(1), 48–49 (1987).

[23] Swiss Blue Energy AG: http://www.swiss-blue-energy.ch/en/index.htm, (2018).

[24] Gueltig, M. et al. High-performance thermomagnetic generators based on heusler alloy films. *Adv. Energy Mater.* 7(5), 1601879 (2017).

[25] Chung, T., Lee, D., Ujihara, M., and Carman, G. P. Design, simulation, and fabrication of a novel vibration-based magnetic energy harvesting device. *TRANSUDCERS 2007 - 2007 International Solid-State Sensors, Actuators and Microsystems Conference*, 867–870, (2007).

[26] Ujihara, M., Carman, G. P., and Lee, D. G. Thermal energy harvesting device using ferromagnetic materials. *Appl. Phys. Lett.* 91(9), 093508 (2007).

[27] Moss, S., Barry, A., Powlesland, I., Galea, S., and Carman, G. P. A low profile vibro-impacting energy harvester with symmetrical stops. *Appl. Phys. Lett.* 97(23), 234101 (2010).
[28] Chun, J. et al. Thermo-magneto-electric generator arrays for active heat recovery system. *Sci. Rep.* **7**(1), 41383 (2017).

[29] Deepak, K., Varma, V., Prasanna, G., and Ramanujan, R. Hybrid thermomagnetic oscillator for cooling and direct waste heat conversion to electricity. *Appl. Energy* **233-234**, 312 – 320 (2019).

[30] Elliott, J. F. Thermomagnetic generator. *J. Appl. Phys.* **30**(11), 1774–1777 (1959).

[31] Stauss, H. E. Efficiency of thermomagnetic generator. *J. Appl. Phys.* **30**(10), 1622–1623 (1959).

[32] Kirol, L. D. and Mills, J. I. Numerical analysis of thermomagnetic generators. *J. Appl. Phys.* **56**(3), 824–828 (1984).

[33] Solomon, D. J. Improving the performance of a thermomagnetic generator by cycling the magnetic field. *Appl. Phys.* **63**(3), 915–921 (1988).

[34] Christiaanse, T. and Brück, E. Proof-of-concept static thermomagnetic generator experimental device. *Metall. Mater. Trans E* **1**(1) 12 (2013).

[35] Waske, A. et al. Energy harvesting near room temperature using a thermomagnetic generator with a pretzel-like magnetic flux topology. *Nat. Energy* **4**(68-74) (2019).

[36] Gottschall, T. et al. Making a cool choice: The materials library of magnetic refrigeration. *Adv. Energy Mater.* **9**(34), 1901322 (2019).

[37] Czernuszewicz, A. et al. A test stand to study the possibility of using magnetocaloric materials for refrigerators. *Int. J. Refrig.* **37**, 72 – 77 (2014).

[38] Gómez, J. R., Garcia, R. F., Catoira, A. D. M., and Gómez, M. R. Magnetocaloric effect: A review of the thermodynamic cycles in magnetic refrigeration. *Renew. Sustain. Energy Rev.* **17**, 74–82 (2013).
[39] Kouvel, J. S. and Hartelius, C. C. Anomalous magnetic moments and transformations in the ordered alloy FeRh. *J. Appl. Phys.* **33**(3), 1343–1344 (1962).

[40] Krenke, T. et al. Inverse magnetocaloric effect in ferromagnetic Ni-Mn-Sn alloys. *Nat. Mater.* **4**, 450 (2005).

[41] Krenke, T. et al. Magnetic superelasticity and inverse magnetocaloric effect in Ni-Mn-In. *Phys. Rev. B* **75**, 104414 (2007).

[42] Hsu, C.-J., Sandoval, S. M., Wetzlar, K. P., and Carman, G. P. Thermomagnetic conversion efficiencies for ferromagnetic materials. *J. Appl. Phys.* **110**(12), 123923 (2011).

[43] Advanced materials - The key to Progress VACUUMSCHMELZE
https://vacuumschmelze.com/Assets-Web/CALORIVAC-PCV-001_2015.pdf, (2015).

[44] Stromentstehungskosten Erneuerbare Energien
https://www.ise.fraunhofer.de/content/dam/ise/de/documents/publications/studies/DE2018_ISE_Studie_Stromgestehungskosten_Erneuerbare_Energien.pdf, (2018).

[45] LeBlanc, S., Yee, S. K., Scullin, M. L., Dames, C., and Goodson, K. E. Material and manufacturing cost considerations for thermoelectrics. *Renew. Sustain. Energy Rev.* **32**, 313–327 (2014).

[46] Dan’kov, S., Spichkin, Y., and Tishin, A. Magnetic entropy and phase transitions in Gd, Tb, Dy and Ho. *J. Magn. Magn. Mater.* **152**(1), 208 – 212 (1996).

[47] Dan’kov, S. Y., Tishin, A. M., Pecharsky, V. K., and Gschneidner, K. A. Magnetic phase transitions and the magnetothermal properties of gadolinium. *Phys. Rev. B* **57**, 3478–3490 (1998).

[48] Nikitin, S., Andreyenko, A., Tishin, A., Arkharov, A., and Zherdev, A. Magnetocaloric effect in heavy rare-earth metals. *Phys. Met. Metallogr.* **60**, 56–61 01 (1985).
[49] Fujita, A., Akamatsu, Y., and Fukamichi, K. J. Itinerant electron metamagnetic transition in $\text{La(Fe}_x\text{Si}_{1-x})_{13}$ intermetallic compounds. *Appl. Phys.* **85**(8), 4756–4758 (1999).

[50] Hu, F.-x., Shen, B.-g., Sun, J.-r., and Zhang, X.-x. Great magnetic entropy change in $\text{La(Fe,M)}_{13}$ ( $M = \text{Si, Al}$) with Co doping. *Chin. Phys.* **9**(7), 550 (2000).

[51] Fujita, A., Fujieda, S., Fukamichi, K., Yamazaki, Y., and Iijima, Y. Giant magnetic entropy change in hydrogenated $\text{La(Fe}_{0.88}\text{Si}_{0.12})_{13}$H$_y$ compounds. *Mater. Trans.* **43**(5), 1202 – 1204 (2002).

[52] Haneda, S., Kazama, N., Yamaguchi, Y., and Watanabe, H. J. Electronic state of high spin MnAs. *Phys. Soc. Jpn.* **42**(4), 1201–1211 (1977).

[53] Wada, H. and Tanabe, Y. Giant magnetocaloric effect of MnAs$_{1-x}$Sb. *Appl. Phys. Lett.* **79**(20), 3302–3304 (2001).

[54] Tegus, O. et al. Magnetic-phase transitions and magnetocaloric effects. *Physica B* **319**(1), 174 – 192 (2002).

[55] Cam Thanh, D. T. et al. Structure, magnetism, and magnetocaloric properties of $\text{MnFeP}_{1-x}\text{Si}_x$ compounds. *J. Appl. Phys.* **103**(7), 07B318 (2008).

[56] Mandal, K. et al. The study of magnetocaloric effect in $\text{R}_2\text{Fe}_{17}$ ( $\text{R} = \text{Y, Pr}$) alloys. *J. Phys. D: Appl. Phys.* **37**(19), 2628 (2004).

[57] Skorvanek, I. and Kovac, J. Magnetocaloric behaviour in amorphus and nanocrystalline FeNbB soft magnetic alloys. *J. Phys.* **54** (2004).

[58] Waske, A. et al. Magnetocaloric effect of a Fe-based metallic glass compared to benchmark gadolinium. *J. Appl. Phys.* **112**(12), 123918 (2012).

[59] Yang, L., Chen, Z.-G., Dargusch, M. S., and Zou, J. High performance thermoelectric materials: Progress and their applications. *Adv. Energy Mater.* **8**(6), 1701797 (2018).
[60] Kim, G.-H., Shao, L., Zhang, K. and Pipe, K. P. Engineered doping of organic semiconductors for enhanced thermoelectric efficiency. *Nat. Mater.* **12**(8), 719–723 (2013).

[61] Rowe, A. and Tura, A. Experimental investigation of a three-material layered active magnetic regenerator. *Int. J. Refrig.* **29**(8), 1286–1293 (2006).

[62] Russberg, G. and Thorburn, S. Patent WO 2010/139538 A1 (2010).

[63] Incropera, F. P., Dewitt, D. P., Bergman, T. L., and Lavine, A. S. *Fundamentals of Heat and Mass Transfer*. John Wiley & Sons, Inc., Hoboken, 6th edition, (2007).