

New developments in caloric materials for cooling applications

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Caloric materials are in the spotlight as candidates for future environmentally friendly cooling technologies. We describe stimulating recent developments in the three caloric strands that are now being studied collectively, namely magnetocaloric, electrocaloric and mechanocaloric (elastocaloric or barocaloric) effects. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4922871>]

INTRODUCTION

From antiquity to early modern times, icehouses – first recorded in Mesopotamia nearly four millennia ago and still used by the Victorians – provided passive refrigeration for perishable food and delicacies. Active cooling via the cyclical compression and expansion of vapours was foreseen by Carnot in the early 19th Century, and commercialised in the 1910s as a luxury domestic product. Vapour-compression is now ubiquitous in both refrigerators and air conditioning units. These machines are essential for food and drinks, medicine, electronics and human comfort, but suffer several disadvantages: the volatile refrigerant fluids are harmful for the environment when released to the atmosphere; the potential for scale down is limited; and start-up times are slow. These deficiencies have stimulated research into new cooling technologies based on caloric materials that are driven by changes of external driving fields^{1–3} and named accordingly.

The present article is inspired by stimulating developments that have appeared since the publication of a review article¹ coauthored by X.M. and N.D.M. in 2014. This article described magnetocaloric (MC), electrocaloric (EC) and mechanocaloric (mC) materials together, providing insights into their history, methodology, performance and applications. Here we summarize these insights to introduce the topic, and present developments that update Ref. 1.

MC materials show nominally reversible thermal changes in response to changes of applied magnetic field H (Figure 1). The first demonstration of MC effects was performed⁴ by Weiss and Piccard in 1917, more than 50 years after the thermodynamic prediction provided by Lord Kelvin,⁵ using nickel near the ferromagnetic Curie temperature (changes in magnetic field of $\mu_0|\Delta H| \sim 1.4$ T produced adiabatic temperature changes of $|\Delta T| \sim 0.7$ K at ~ 627 K). MC cooling in paramagnetic salts was later employed in the 1930s to approach absolute zero,⁶ and is still exploited in research laboratories to achieve millikelvin temperatures over finite hold times. Continuous MC cooling near room temperature was first demonstrated in 1976 by exploiting the ferromagnetic phase transition in gadolinium⁷ (Curie point ~ 294 K). This seminal work stimulated MC research activity¹ and introduced regenerators in order to increase the temperature span that can be achieved in heat pumps based on caloric materials, thus achieving parity with vapour compression refrigerators.¹ MC research activity was further stimulated in the 1990s by the observation of giant MC effects near first-order magnetostructural phase transitions in $\text{Fe}_{49}\text{Rh}_{51}$ ($|\Delta T| \sim 8 - 13$ K in response to $\mu_0|\Delta H| = 2 - 2.5$ T at 308 K, Ref. 8 and 9), and most notably in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ ($|\Delta T| \sim 13$ K in response to $\mu_0|\Delta H| = 5$ T at 280 K, Ref. 10). $\text{Fe}_{49}\text{Rh}_{51}$ was initially misunderstood to show only one-shot magnetically driven thermal changes, but it has been now clarified that MC effects in this compound

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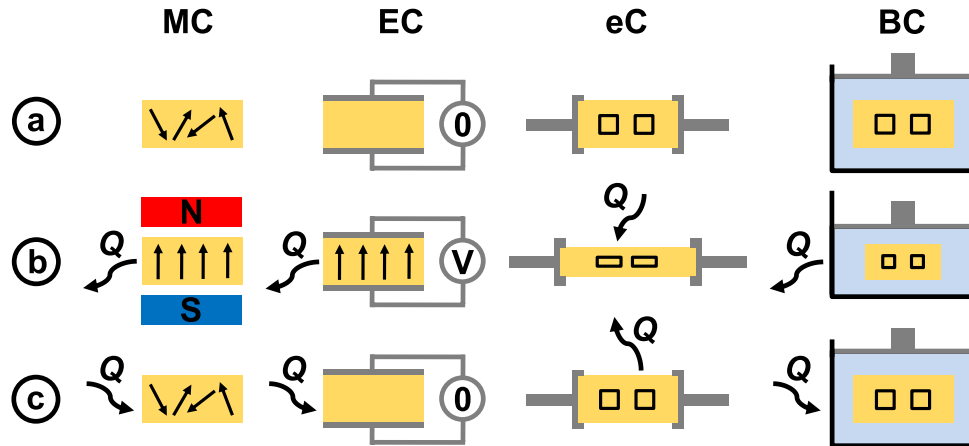


FIG. 1. Schematic illustration of caloric effects. Straight arrows represent magnetic dipoles in MC materials addressed by a magnet, and electric dipoles in EC materials addressed by a voltage source. Black polygons represent unit cells in eC materials addressed by grips, and BC materials addressed via fluid. (a) With no field applied the order parameter is zero. Wavy arrows indicate subsequent heat flow when (b) driving and (c) undriving caloric materials isothermally. The wavy arrows are reversed for inverse caloric materials.¹

are repeatable when cycling a magnetic field at temperatures below the hysteretic regime of the transition.^{11,12}

EC materials show thermal changes analogous to those developed in MC materials, but in response to changes of applied electric field ΔE (Figure 1) that are more straightforward to generate than the large magnetic fields required to operate MC materials. EC effects were first reported¹³ in 1930 in Rochelle salt ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), the material in which ferroelectricity had been discovered ten years earlier.¹⁴ There was subsequently little EC research until the turn of the millennium when giant EC effects were found near ferroelectric transitions, first in thin films of the ceramic $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ ($|\Delta T| = 12$ K in response to $|\Delta E| = 480$ kV cm^{-1} at 499 K, Ref. 15), and then in thick films of two fluorinated polymers,¹⁶ [$|\Delta T| = 12.5$ K in response to $|\Delta E| = 2090$ kV cm^{-1} at 353 K in poly(vinylidene fluoride-trifluoroethylene) {P(VDF)}, $|\Delta T| = 12.5$ K in response to $|\Delta E| = 3070$ kV cm^{-1} at 328 K in poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) {P(VDF-TrFE-CFE)}]. Previous EC studies in bulk materials had been limited to $|\Delta T| < 3$ K at best¹⁷ in response to $|\Delta E| < 50$ kV cm^{-1} , as the breakdown field scales approximately inversely with sample thickness.

mC materials show reversible thermal changes in response to changes of applied stress field, and are subdivided into elastocaloric (eC) materials driven by uniaxial stress σ_u , and barocaloric (BC) materials driven by isotropic stress (hydrostatic pressure) p (Figure 1). Unlike BC effects, eC effects are limited by the onset of plastic flow, which typically occurs at hundreds of MPa for metals.

The first demonstration of eC effects was reported by John Gough in 1805, who found that Indian rubber heats slightly when stretched rapidly.¹⁸ More recently, giant eC effects near room temperature have been observed in shape-memory alloys based on copper ($|\Delta T| = 12$ -15 K for $|\Delta\sigma_u| \sim 0.1$ -0.2 GPa)¹⁹⁻²¹ and Ni-Ti ($|\Delta T| \sim 20$ -40 K for $|\Delta\sigma_u| \sim 0.6$ -0.8 GPa)²²⁻²⁴, which can be driven in a reversible manner well away from the hysteretic regime of the first-order structural phase transitions.²⁵

In 1998, Nobel laureate K. Alex Müller and co-workers first reported²⁶ small BC effects in the nickelate $\text{Pr}_{0.66}\text{La}_{0.34}\text{NiO}_3$ at 350 K. In 2010, Mañosa and co-workers first reported²⁷ giant BC effects in a superelastic magnetic alloy of $\text{Ni}_{49.26}\text{Mn}_{36.08}\text{In}_{14.66}$ ($|\Delta T| \sim 4.5$ K for $|\Delta p| = 0.26$ GPa). BC effects are only starting to attract levels of research interest comparable to the other caloric effects,¹ perhaps because their study generally requires the use of customised or bespoke equipment. However, BC materials show some of the most promising materials efficiencies, as seen later.

The discovery of giant thermal changes in MC, EC and mC materials has led to intense research activity in recent years,¹ motivated by the prospect of environmentally friendly cooling applications.

TABLE I. Selected giant caloric effects at phase transitions near room temperature. For materials not summarized previously,¹ we present field-driven isothermal entropy change $|\Delta S|$ and adiabatic temperature change $|\Delta T|$ at starting temperature T . All starting fields were zero. LC5CB = liquidcrystal 4-n-pentyl-4'-cyanobiphenyl.

EC material	$T(\text{K})$	$ \Delta S (\text{J K}^{-1}\text{kg}^{-1})$	$ \Delta S (\text{kJ K}^{-1}\text{m}^{-3})$	$\Delta T(\text{K})$	$ \Delta E (\text{kV cm}^{-1})$	Ref.
BaZr _{0.2} Ti _{0.8} O ₃	313	12.2	72.7	7.0	200	71
LC 5CB	312	23.6	23.8	4.3	900	72
eC material	$T(\text{K})$	$ \Delta S (\text{J K}^{-1}\text{kg}^{-1})$	$ \Delta S (\text{kJ K}^{-1}\text{m}^{-3})$	$\Delta T(\text{K})$	$ \Delta\sigma_{\text{ul}}(\text{GPa})$	Ref.
Ni _{45.7} Mn _{36.6} In _{13.3} Co _{5.1}	300	5.4	42.7	3.5	0.10	74
Ni ₄₆ Mn ₃₈ Sb ₁₂ Co ₄	296	21	170	15	0.10	75
BC material	$T(\text{K})$	$ \Delta S (\text{J K}^{-1}\text{kg}^{-1})$	$ \Delta S (\text{kJ K}^{-1}\text{m}^{-3})$	$\Delta T(\text{K})$	$ \Delta p (\text{GPa})$	Ref.
Fe ₄₉ Rh ₅₁	308	12.5	126.4	8.1	0.11	12
Mn ₃ GaN	285	21.6	151.4	4.8	0.09	76

Giant MC effects near room temperature have now been found in Fe₂P based compounds,^{28,29} La(Fe,Si)₁₃ based compounds,³⁰⁻³² manganites,³³ MnAs based compounds,³⁴ compounds made from manganese and transition metals,³⁵⁻³⁷ and Ni-Mn based Heusler alloys.³⁸⁻⁴⁴ Giant EC effects have now been found in Pb_{0.8}Ba_{0.2}ZrO₃ (Ref. 45), SrBi₂Ta₂O₉ (Ref. 46), and solid solutions of PbMg_{1/3}Nb_{2/3}O₃ (PMN) and PbTiO₃ (PT) (Ref. 47-49). Giant mC effects have been found also in^{9,50,51} Fe₄₉Rh₅₁ and Fe_{68.8}Pd_{31.2} (eC effects), and in^{52,53} LaFe_{11.33}Co_{0.47}Si_{1.2} and Gd₅Si₂Ge₂ (BC effects) [a selection of giant MC, EC and mC materials are described in Table I and Figure 2; a more detailed comparison can be found in Ref. 1]. The study of caloric phenomena near room temperature has also led to over 40 MC prototype cooling devices,⁵⁴ and a small number of EC and mC prototype cooling devices.⁵⁵⁻⁵⁷

MEASUREMENT METHODS

Caloric materials are parameterized via isothermal heat Q , isothermal entropy change ΔS , and adiabatic temperature change ΔT , which are related via $Q = T\Delta S \approx -c\Delta T$, using values of specific heat capacity c measured in zero field. Preferably, both Q and ΔT should be measured independently, and regarded as separate figures of merit for cooling, as Q determines the size of the load that can be cooled for a given amount of caloric material, and ΔT drives heat flow.

Values of the three caloric quantities can be obtained via indirect methods, quasi-direct methods and direct methods.¹ Direct measurements of heat⁵⁸⁻⁶⁰ can be performed using calorimeters that permit application of variable magnetic, electric or stress fields. Direct measurements of temperature change can be performed using contact or non-contact thermometry.^{19,23,24,52,61-63} Direct measurements are desirable but generally rare as they can be challenging, so it is common to use instead quasi-direct and indirect methods. Quasi-direct measurements of heat^{10,27,59,64,65} can be performed using calorimeters that permit application of constant field at variable temperature T , whereas indirect values of Q , ΔS and ΔT can be obtained via the thermodynamic analysis¹ of measurements of the temperature and field dependent local order parameter (magnetization M , polarization P , strain ϵ , or volume V).

For EC materials, interest continues to grow in developing direct means to measure temperature changes in films with small thermal mass, in order to reduce widespread reliance on the indirect method. Infra-red imaging has been used to confirm EC effects of $|\Delta T| \sim 5.2$ K in response to $|\Delta E| = 900$ kV cm⁻¹ in a free-standing 11- μm -thick film of P(VDF-TrFE-CFE).⁶⁶ Micro-thermometers integrated onto glass substrates have been used to measure EC temperature changes of $|\Delta T| \sim 8.5$ K for $|\Delta E| = 1100$ kV cm⁻¹ in similar fluorinated polymer films.⁶⁷ For ceramic thin films, an innovative optical technique has been recently introduced in order to perform direct measurements of EC temperature changes that are short lived in the presence of a substrate.⁶⁸ In this work, 150-nm-thick

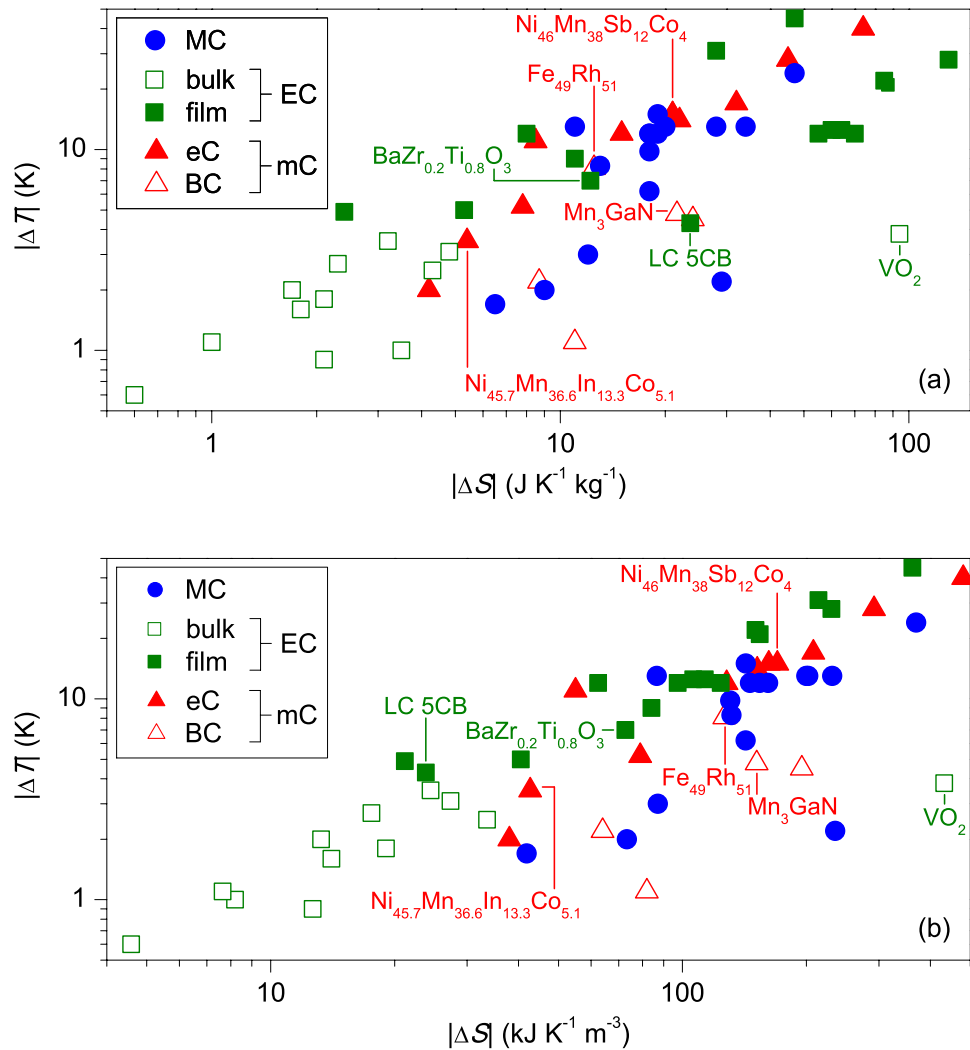


FIG. 2. Comparison of MC, EC and mC effects. Adiabatic temperature change $|\Delta T|$ versus isothermal entropy change $|\Delta S|$, normalised by (a) mass and (b) volume. The normalization of ΔS by mass favours low-density EC polymers and liquid crystals, which are roughly four times less dense than EC ceramics. Materials not summarized previously¹ are named here, and described in Table I. LC 5CB = liquid crystal 4-n-pentyl-4'-cyanobiphenyl.

films of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ grown on DyScO_3 or GdScO_3 substrates were driven at high frequencies (kHz-MHz), and changes of temperature were inferred via the reflection of a laser beam from an overlying layer of vanadium, whose optical reflectance is strongly temperature sensitive. Direct studies of EC films may also benefit from new developments that arise in the other two caloric strands, e.g. a non-contact technique that uses thermopiles as temperature sensors, which has been recently employed to study thin MC samples.⁶⁹

RECENT DEVELOPMENTS

The development of caloric materials that perform better, in smaller applied fields, over wider ranges of temperature, holds the key to the commercial exploitation of caloric effects for cooling applications. The performance of materials described previously¹ and below is summarised in Figure 2.

Large EC effects have been recently reported⁷⁰ near room temperature in bulk ceramics of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ that were able to withstand relatively high electric fields ($|\Delta T| \sim 4.5$ K for $|\Delta E|$

$\sim 145 \text{ kV cm}^{-1}$). This value of ΔT represents the largest adiabatic temperature change observed in bulk EC materials, and changes of this magnitude were found over a large temperature range exceeding 30 K. Larger EC effects have been found⁷¹ in 12- μm -thick $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films ($|\Delta T| \sim 7 \text{ K}$ in response to $|\Delta E| \sim 200 \text{ kV cm}^{-1}$). Interestingly, large EC effects have been also found in two types of material that are not ferroelectric, namely dielectric liquid crystals⁷² that could be employed potentially as both refrigerant and heat exchanger ($|\Delta T| \sim 4.3 \text{ K}$ and $|\Delta S| \sim 23.6 \text{ J K}^{-1} \text{ kg}^{-1}$ for $|\Delta E| \sim 900 \text{ kV cm}^{-1}$), and VO_2 near its voltage-driven metal-insulator transition⁷³ ($|\Delta T| \sim 3.8 \text{ K}$ and $|\Delta S| \sim 94 \text{ J K}^{-1} \text{ kg}^{-1}$ in response to $|\Delta V| = 3 \text{ V}$ across 0.4-mm-thick samples).

Large eC effects have been found in ferromagnetic Ni-Mn based Heusler alloys, whose structural and magnetic properties are strongly coupled. Adiabatic changes in temperature of 3.5 K for $|\Delta\sigma_u| = 0.1 \text{ GPa}$ have been measured directly⁷⁴ in $\text{Ni}_{45.7}\text{Mn}_{36.6}\text{In}_{13.3}\text{Co}_{5.1}$, whereas values of $|\Delta T| \sim 15 \text{ K}$ for $|\Delta\sigma_u| \sim 0.1 \text{ GPa}$ have been obtained⁷⁵ from quasi-direct calorimetric methods in $\text{Ni}_{46}\text{Mn}_{38}\text{Sb}_{12}\text{Co}_4$.

Large BC effects have been found near magnetostructural phase transitions in Mn_3GaN ($|\Delta T| = 4.8 \text{ K}$ for $|\Delta p| = 0.09 \text{ GPa}$, Ref. 76) and $\text{Fe}_{49}\text{Rh}_{51}$ ($|\Delta T| = 8.1 \text{ K}$ for $|\Delta p| = 0.11 \text{ GPa}$, Ref. 12).

Parallel to the development of new caloric materials, strategies to improve the caloric performance of existing materials have been also explored recently. Grading of chemical composition in 300-nm-thick $(\text{Ba,Sr})\text{TiO}_3$ films⁷⁷ yielded adiabatic changes in temperature $|\Delta T| \sim 3 \text{ K}$ for $|\Delta E| \sim 350 \text{ kV cm}^{-1}$ over a large temperature span of $>100 \text{ K}$, dramatically improving the performance of films with a single composition. Ion bombardment of thin MnAs films⁷⁸ suppressed thermal hysteresis without significantly degrading the MC effect. Ceramic sintering from nano-sized powders reduced electrical fatigue in BaTiO_3 ceramics.⁷⁹ Last, careful selection of chemical composition in MC compounds of $\text{MnFe}(\text{P,Si,B})$ enhanced resistance to mechanical fatigue associated with the large volume changes at the magnetostructural phase transition.⁸⁰

Multiferroic materials that can develop thermal changes in response to more than one species of driving field are increasingly being considered for multicaloric cooling. A general thermodynamic framework for multicaloric materials is now available,⁸¹ and both MC and EC effects have been found in multiferroic Y_2CoMnO_6 (Ref. 82). Application of a tuning field can be exploited in order to modify the operating temperature of caloric materials,¹ as recently demonstrated for $\text{Ni}_{44}\text{Co}_{5.2}\text{Mn}_{36.7}\text{In}_{14.1}$ films in PMN-PT substrates,⁸³ where MC operating temperatures in the film were tuned via piezoelectric strain arising in the substrate under electric field. Similar phenomena were earlier predicted in all-oxide multiferroic heterostructures,⁸⁴ in which strain coupling can also create phase transitions leading to large extrinsic caloric effects.⁸⁵

EC heat pumps are under active development, and several recent publications have addressed different aspects related to the engineering of cooling devices. In a novel design for a practical EC heat pump,⁸⁶ a series of rotating EC discs achieve regeneration⁷ by transferring heat between themselves at intermediate stages of rotation. Numerical simulations suggest that the temperature difference between sink and load is an order of magnitude larger than the value of $|\Delta T|$ for the EC discs alone. In a separate study, numerical simulations have shown how mechanical stress could be used to control domain-wall density and therefore the thermal conductivity of twinned ferroelastic thin films,⁸⁷ for thermal switches in caloric devices. Also, the two existing EC prototypes^{55,56} have now been joined by a third prototype,⁸⁸ where regenerator fluid flows in alternate directions across thirty 200- μm -thick 0.9PMN-0.1PT ceramic plates to establish a 3.3 K temperature span, exceeding by several times the value of $|\Delta T|$ for each plate (a larger 14 K temperature span may be achieved after device optimisation, as revealed by numerical simulations⁸⁸).

The performance of heat pumps based on caloric materials will ultimately be affected by the efficiency^{89,90} $\eta = |Q/W|$ of the caloric material at its core, where W is the work done to drive isothermal caloric heat Q . This quantity was initially introduced for comparing EC ceramics and polymers,⁸⁹ and has been recently used to compare the energy efficiency of MC, EC and eC materials.⁹⁰ This latter comparison revealed that MC materials driven using the magnetic fields from a permanent magnet are more energy efficient than EC materials driven using an electric field generated by charging capacitor plates.⁹⁰ However, this discrepancy disappears if the electrical energy used to drive EC effects is artificially recovered using simple circuitry (E. Defay, G. Despesse, S. Crossley, D. Sette, X. Moya and N. D. Mathur, manuscript in preparation). BC materials

TABLE II. The efficiency of giant BC materials. For giant BC materials operating at temperature T near first-order phase transitions, we present heat $|Q|$ (obtained via $|Q| = T\Delta S$ from Ref. 1 and Table I), work $|W| = |\Delta p\Delta V_0/2V_0|$, and efficiency $\eta = |Q/W|$, for changes of applied pressure $|\Delta p|$. $|\Delta V_0|/V_0$ is the relative volume change across the first-order phase transition.

Giant BC material	T K	$ \Delta p $ (GPa)	$ \Delta V_0 /V_0$ %	$ Q $ J cm^{-3}	$ W $ J cm^{-3}	η	Ref.
$\text{Ni}_{49.26}\text{Mn}_{36.08}\text{In}_{14.66}$	293	0.26	0.4	57.8	0.52	111	27
$\text{LaFe}_{11.33}\text{Co}_{0.47}\text{Si}_{1.2}$	237	0.20	1.2	14.8	1.20	12.3	52
$\text{Gd}_5\text{Si}_2\text{Ge}_2$	270	0.20	0.5	21.7	0.50	43.4	53
$\text{Fe}_{49}\text{Rh}_{51}$	308	0.11	1.2 ⁹	38.9	0.66	58.9	12
Mn_3GaN	285	0.09	1.2 ⁹³	43.2	0.56	77.4	76

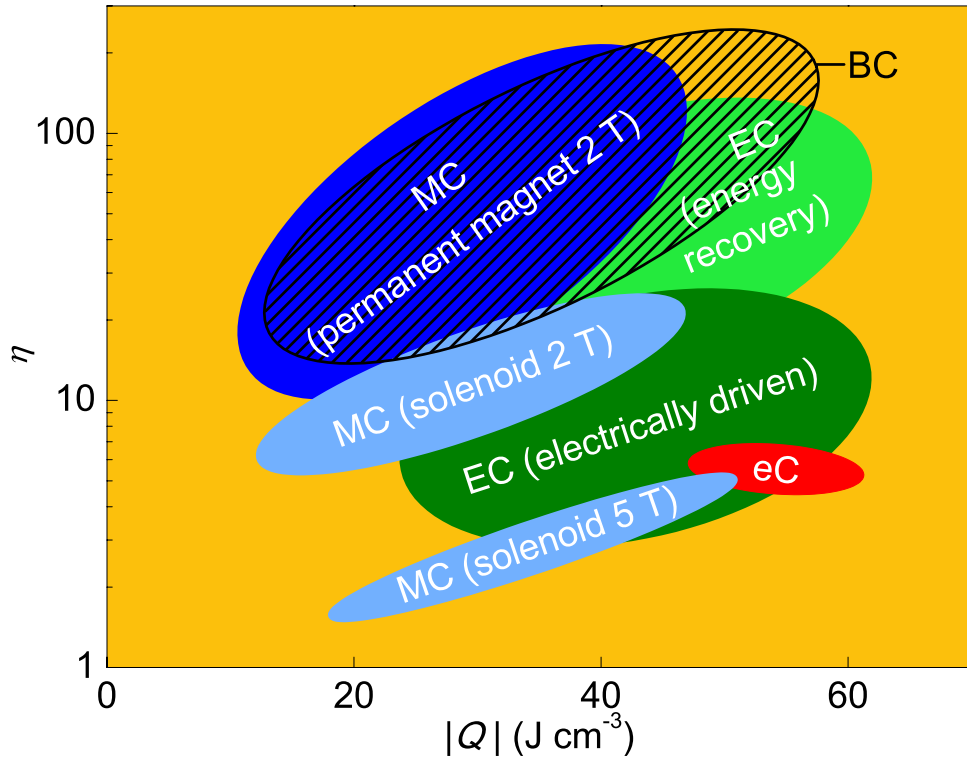


FIG. 3. Comparison of materials efficiency for different caloric materials. Energy efficiency η describes the heat Q divided by the work W done to drive the different caloric effects. Efficiency map is adapted from Ref. 90 with permission from Macmillan Publishers Ltd, to include barocaloric (BC) materials driven by hydrostatic pressure (black hashed ellipse). MC = magnetocaloric, EC = electrocaloric, eC = elastocaloric. BC, EC and eC effects in each material are driven by fields of different magnitude.

were not included in this comparison because there were no pressure-volume data from which to calculate work done. However, the missing values of W can be estimated near structural phase transitions because volume change is approximately proportional to applied pressure (Table II). This reveals that BC materials are as efficient as the best MC materials driven with permanent magnets (Figure 3).

OUTLOOK

The primary challenge in developing caloric materials is to increase the isothermal heat and adiabatic temperature change, achieved using relatively small fields, over a wide range of temperatures. Applications will also likely require materials to show better resistance to fatigue, reduced

thermal and field hysteresis, enhanced thermal conductivity (e.g. by subdividing caloric materials using metallic phases⁹¹ or metallic layers⁹²), and reduced cost. Also important is the development of heat switches or thermal diodes for fast and efficient heat transfer.¹ Overcoming these challenges could lead to technologically useful cooling devices. Therefore research activity into MC, EC and mC materials is growing in size and ambition, and prototype heat pumps based on all three caloric effects are under development.

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