A hot future for cool materials

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Abstract

The widespread need to pump heat provides an immediate imperative to pump heat better, i.e. in an environmentally friendly and energy efficient manner. As discussed at a recent conference, heat-pump devices based on caloric materials represent an intriguing alternative to gas combustion and vapour-compression.

The second law of thermodynamics dictates that energy is required to pump heat, which is rather unfortunate because human-engineered heating and cooling across the planet now constitute the largest global source of carbon emissions[1]. As things stand, heating is primarily achieved via the combustion of natural gas, while cooling is primarily achieved via the compression of gases that are in some way harmful[2]. Alternative methods of heating and cooling are highly desirable, and it has been suggested that caloric heat-pump devices could be energy efficient, environmentally friendly, or useful in some other way, e.g. small and quiet. Reflecting the upsurge of activity over the last several years (Fig. 1), progress on caloric materials, measurements and devices was discussed at a recent conference that kicked-off what is intended to be a new biennial series (Calorics 2022, Cambridge, UK, 12-14 September 2022).

Caloric effects are nominally reversible field-driven thermal changes that may be parameterized in the isothermal limit (as entropy change ΔS or heat Q) or the adiabatic limit (as temperature change ΔT), with $Q = T\Delta S \sim -c\Delta T$ (c denotes specific heat capacity)[8]. Caloric effects sub-divide into magnetocaloric, electrocaloric and mechanocaloric effects that arise in magnetically, electrically and mechanically responsive materials due to changes of magnetic, electric and mechanical field[3-14]. One may thus identify three main types of caloric effect, but most of the mechanocaloric effects that have been studied to date sub-divide into those driven by uniaxial stress (elastocaloric effects) and those driven by hydrostatic pressure (barocaloric efects), and caloric effects can be driven simultaneously or sequentially by more than one type of field (multicaloric effects)[7-9,16-18]. Caloric effects can be large at finite temperatures if they are driven near phase transitions, and so caloric materials could be exploited in various heating and cooling applications. However, further work on both materials and devices is required to improve device temperature span, cooling-power density and energy efficiency.

The majority of materials that display giant magnetocaloric effects exploit first-order magnetostructural phase transitions, whose magnetic-field hysteresis can be eliminated by transferring this hysteresis to the mechanical field (Vitalij Pecharsky, Ames Laboratory), and whose electron correlations and spin fluctuations influence the latent heat (Asaya Fujita, National Institute of Advanced Industrial Science and Technology). Analytical tools can be used to determine the order of magnetocaloric phase transitions, identify critical exponents, and evaluate tricritical compositions (Victorino Franco, University of Seville), while magnetocaloric effects in Ni-Mn-based thin films and disks appear to be promising (Simone Fabbrici, Institute of Materials for Electronics and Magnetism, Parma).

Over the last several decades, magnetocaloric materials have been used to pump heat in prototypes that operate near room temperature. For example, a cooling power of 1 kW can be achieved in a magnetocaloric heat pump that is based on either the second-order phase transition in gadolinium, or the first-order phase transition in La-Fe-Si-Mn-H (Christian Bahl, Technical University of Denmark). Thermal diodes, thermal switches and thermal modelling with new open-source software should all improve performance (Andrej Kitanovski, University of Ljubljana). Encouragingly, various challenges that arise when integrating magnetocaloric materials into cooling devices (heat transfer, corrosion, mechanical stability) have not precluded the development of a magnetocaloric wine cooler (Max Fries, MagnoTherm Solutions, Darmstadt).

Many of the electrocaloric materials under study are perovskite oxides, and multilayer capacitors of these materials combine many thin layers to which large electric fields can be applied without breakdown; we consider these multilayer capacitors as if they were materials, reserving the term devices to describe heat pumps. Electrocaloric multilayer capacitors of ferroelectric $PbScTaO_3$ and antiferroelectric $Pb(Mg,W)O_3$ both display conventional electrocaloric effects at higher temperatures (field application increases temperature), but the latter displays inverse electrocaloric effects at lower starting temperatures (field application decreases temperature) (Sakyo Hirose, Murata Manufacturing, Kyoto). Ceramic samples of ferroelectric $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ can be prepared by mechanochemical synthesis, and a mixture of ferroelectric $Pb(Fe_{0.5}Nb_{0.5})O_3$ and antiferromagnetic $BiFeO_3$ yields ceramic samples that display both electrocaloric and magnetocaloric effects (Hana Uršič, Jožef Stefan Institute). Electrocaloric materials have now been investigated via various theoretical methods, e.g. using molecular dynamic simulations to optimize the microstructure (Anna Grünebohm,Ruhr-University Bochum), and using phase-field (i.e. free-energy) modelling to understand local properties (Jiamian Hu, University of Wisconsin-Madison).

A growing number of electrocaloric heat pumps are currently being developed. The aforementioned multilayer capacitors of $PbScTaO_3$ (Sakyo Hirose, Murata Manufacturing, Kyoto) have now been used to demonstrate electrocaloric devices with fluid regeneration

(Alvar Torelló, Luxembourg Institute of Science and Technology) and fluid evaporation/condensation in alternate half cycles (Kilian Bartholomé, Fraunhofer Institute for Physical Measurement Techniques IPM, Freiburg im Breisgau). The same multilayer capacitors of $PbScTaO_3$ have also now been used to achieve improved performance in energy-harvesting (Alvar Torelló, Luxembourg Institute of Science and Technology). Returning to the theme of electrocaloric devices, good efficiency requires the electrical work done to be recovered as best as possible, and indeed up to 88% of the energy used to drive electrocaloric effects can now be recovered in demonstrations where this driving energy is not used to pump heat (Morgan Almanza, Université Paris-Saclay).

There are now many studies of elastocaloric polycrystals and single crystals. Novel dynamic methods can probe low-temperature elastocaloric effects in various quantum materials, revealing nematic fluctuations in $TmVO_4$ (Ian Fisher, Stanford University), and yielding detailed entropy-temperature-strain maps of superconducting Sr_2RuO_4 (Andreas Rost, University of St Andrews). For elastocaloric single crystals that operate near room temperature, the subject of microstructure remains fertile ground, as seen with oriented precipitates in Ni-Ti, and tweed-texture in Fe-Pd (Antoni Planes,University of Barcelona). Separately, it is now possible to determine the variable-stress latent heat in elastocaloric materials (Stefan Seelecke, Universität des Saarlandes).

Elastocaloric heat pumps typically exploit Ni-Ti under compressive or tensile stress, but copper-based alloys are also promising (Jun Cui, Ames Laboratory/Iowa State University). For example, tension can be used drive Ni-Ti wires (Stefan Seelecke, Universität des Saarlandes), and compression can be used to drive Ni-Ti tubes that exist either in bundles (Jun Cui, Ames Laboratory/Iowa State University) or a shell-and-tube-like configuration (Jaka Tušek, University of Ljubljana). If compressive stress can be applied without buckling then it permits much longer lifespans (e.g. 10^5 cycles) than tensile stress (Kurt Engelbrecht, Technical

University of Denmark). Impressively, a 60 kW elastocaloric heat pump based on Ni-Ti alloys has now been demonstrated (Mike Langan, Exergyn, Dublin).

Barocaloric effects arise in various types of material. For example, hybrid organic-inorganic perovskites display colossal barocaloric effects near room temperature (Pol Lloveras, Universitat Politècnica de Catalunya), plastic crystals display colossal barocaloric effects that can be modelled using Landau theory (Gian Guzmán-Verri, Universidad de Costa Rica), and manganese antiperovskites alloyed with multiple types of atom can significantly reduce hysteresis with no significant decrease in barocaloric performance (David Boldrin, University of Glasgow). Barocaloric devices are in their infancy, and a key issue in their development is heat transfer (Enric Stern-Taulats, University of Barcelona).

The desire to address multicaloric materials has inspired advanced experimental set-ups that permit the application of more than one type of driving field. Both magnetic field and uniaxial stress can be applied either in a calorimeter (Lluís Mañosa, University of Barcelona), or at a facility where the magnetic field is pulsed and therefore large (Tino Gottschall, Helmholtz-Zentrum Dresden-Rossendorf). Various multicaloric magnetic shape memory alloys have now been investigated (Lluís Mañosa, University of Barcelona), e.g. with different microstructures, chemical compositions and processing protocols (Franziska Scheibel, Technical University Darmstadt). Multicaloric materials with strong magnetostructural coupling have also inspired ab-initio modelling (Eduardo Mendive-Tapia, Forschungszentrum Jülich).

The different caloric effects discussed above offer alternative device implementations at potentially different temperature ranges of operation. However, it is too early to tell which type of caloric effect is the most promising for applications; each has its own idiosyncratic merits and demerits, and further development is required. Any product coming to market would provide a huge stimulus for the field of calorics, and perhaps the magnetocaloric wine cooler will lead the way (Max Fries, MagnoTherm Solutions, Darmstadt). If so, we will drink to that at Calorics 2024.

Acknowledgements

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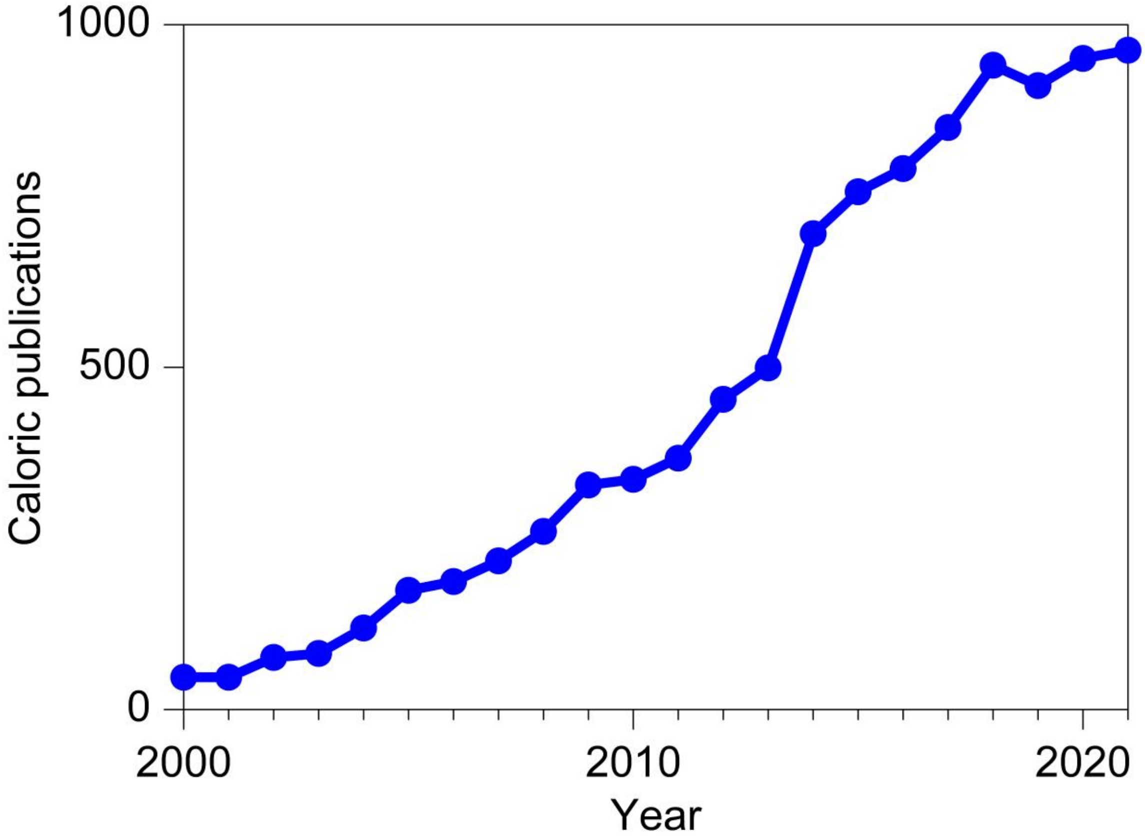

Figure 1. Caloric publications per year in 2000-2021.